Photocyclodehydrofluorination (PCDHF) –
A synthetic method for fluorinated polynuclear aromatic hydrocarbons

A dissertation submitted
to Kent State University in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy

by
Zhe LI

December 2015
Dissertation written by

Zhe Li

B.S., Nanjing University, P.R.China, 2009

Ph.D., Kent State University, 2015

Approved by

Dr. Robert J. Twieg, Department of Chemistry, Kent State University, Doctoral Advisor

Dr. Scott Bunge, Department of Chemistry, Kent State University

Dr. Paul Sampson, Department of Chemistry, Kent State University

Dr. Liang-Chy Chien, Liquid Crystal Institute, Kent State University

Dr. Brett Ellman, Department of Physics, Kent State University

Accepted by

Dr. Michael Tubergen, Chair, Department of Chemistry, Kent State University

Dr. James L. Blank, Dean, College of Arts and Sciences
Contents
List of Figures ........................................................................................................................... viii
List of Schemes ........................................................................................................................... xiv
List of Tables ............................................................................................................................. xvii
Dedication and Acknowledgements ........................................................................................... xix
1. Chapter One – Background and Introduction ........................................................................ 1
   1.1. Introduction of fluorine .................................................................................................. 1
   1.2. Non-bonded interactions .............................................................................................. 2
   1.3. Non-bonding interactions in fluorinated compounds ....................................................... 4
      1.3.1. Phenyl – perfluorophenyl interaction ......................................................................... 5
      1.3.2. C-F···H interactions ................................................................................................ 9
      1.3.3. F···F interactions ..................................................................................................... 12
      1.3.4. C-F···πF interactions .............................................................................................. 15
   1.4. A brief introduction about semiconductors ..................................................................... 17
   1.5. Organic Semiconductors ................................................................................................. 19
   1.6. Experimental Procedures ............................................................................................. 25
   1.7. Summary ........................................................................................................................ 27
   1.8. References ...................................................................................................................... 28
2. Chapter Two - The investigation on the crystal packing of 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives .............................................................................. 34
2.1. Introduction ........................................................................................................................................ 34

2.2. Synthesis of fluorinate tolanes and 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives ................................................................. 35

2.3. X-ray crystallography analysis of fluorinated tolanes .................................................................. 38

2.4. X-ray crystallography analysis of 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives ........................................................................... 54

2.5. Summary and discussion ................................................................................................................. 67

2.6. Experiment procedures .................................................................................................................... 70

2.6.1. The synthesis of fluorinated tolanes ......................................................................................... 70

2.6.2. The synthesis of 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives ........................................................................................................... 75

2.6.3. Compounds that failed to obtain crystal structure ..................................................................... 84

2.7. References ......................................................................................................................................... 91

3. Chapter Three - Photocyclodehydrofluorination (PCDHF) .................................................................. 93

3.1. Background ......................................................................................................................................... 93

3.2. Mallory photocyclization .................................................................................................................. 94

3.2.1. Oxidative Mallory photocyclization .............................................................................................. 94

3.2.2. Mallory photocyclization involving leaving group ........................................................................ 96

3.3. Mallory photocyclization involving the losing of HF - Photocyclodehydrofluorination (PCDHF) .................................................................................................................. 99

3.3.1. PCDHF in 2,3,4,5,6-pentafluorostilbene type precursors ........................................................... 101
3.3.2. PCDHF in 2,3,4,5,6-pentafluoro-1,1':2',1"-terphenyl type precursors .................. 103
3.3.3. PCDHF involving heterocycles ........................................................................... 106
3.3.4. PCDHF of 2,3,5,6-tetrafluoro precursors .............................................................. 107
3.3.5. PCDHF of difluoro precursors - two fluorine atoms located at the two reactive ortho-sites 110
3.3.6. Competition between PCDHF and oxidative cyclization ......................................... 111
3.3.7. PCDHF with possible isomer production ................................................................. 115
3.3.8. PCDHF involving competition with other halogens (Cl, Br) ....................................... 117
3.3.9. Circumstances under which PCDHF is unsuccessful ............................................... 119
3.3.10. The extension for PCDHF to other halogens – Chlorine (PCDHCl) ...................... 124
3.4. Summary for PCDHF ................................................................................................. 126
3.5. Experimental procedures .......................................................................................... 127
3.5.1. Synthesis of precursors for photocyclodehydrofluorination ..................................... 127
3.5.2. Procedure for photocyclodehydrofluorination ......................................................... 195
3.6. References .................................................................................................................. 255

4. Chapter Four - The synthesis of the 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene backbone and its derivatives .................................................................................................................. 258
4.1. Synthesis of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene ...................... 258
4.2. Derivatives of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene with alkoxy groups 269
4.3. Derivatives of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene with thiophene rings 277

4.4. Summary ................................................................................................................. 282

4.5. Experimental procedures.......................................................................................... 283

4.6. References.................................................................................................................. 321

5. Chapter Five – The synthesis of some smaller polycyclic aromatic hydrocarbons (PAHs) via PCDHF ............................................................................................................ 322

  5.1. Fluorinated 1,2,3,4-tetrafluorodibenzo[g,p]chrysene ........................................ 322

  5.2. Fluorinated dibenzo[fg,op]tetracene derivatives ..................................................... 328

  5.3. Summary ................................................................................................................ 335

  5.4. Experimental procedures.......................................................................................... 336

  5.5. References................................................................................................................ 365


  6.1. Introduction ............................................................................................................. 366

  6.2. The synthesis of non-fluorinated [5][helicene - naphtho[1,2-g]chrysene ............ 371

  6.3. The synthesis of fluorinated [5]-helicene - 7,8,9,10-tetrafluoronaphtho[1,2-g]chrysene and 7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene ........................................... 372

  6.4. The crystal structure of [5]-helicenes .................................................................... 376

  6.5. Summary ................................................................................................................ 385

  6.6. Experimental procedures.......................................................................................... 386
6.7. References ................................................................................................................................. 421

7. Chapter Seven - The synthesis of fluorinated triphenylene discotic liquid crystals via a sequential SnAr reactions and PCDHF ......................................................................................... 424

7.1. Introduction to discotic liquid crystals ........................................................................................ 424

7.2. Fluorinated triphenylene discotic liquid crystals ......................................................................... 424

7.3. SnAr nucleophilic aromatic substitution of 1,2,3,4-tetrafluoro compounds ............................ 426

7.4. Hexakisalkoxytriphenylene discotic LCs via PCDHF and SnAr approach ................................. 429

7.5. Pentakisalkoxytriphenylene discotic LCs via PCDHF and SnAr approach ............................... 431

7.6. Phase behavior ............................................................................................................................ 432

7.7. Summary ...................................................................................................................................... 434

7.8. Experimental procedures ........................................................................................................... 435

7.9. References .................................................................................................................................... 467

8. Chapter Eight - Low absorption liquid crystals for infrared applications ................................. 469

8.1. Optical anisotropy, birefringence and liquid crystals ................................................................. 469

8.2. The introduction of infrared transparent liquid crystals ............................................................. 470

8.3. Further investigation on chlorinated liquid crystals ................................................................. 481

8.3.1. Synthesis of 4,2’-dichlorinated cyclohexylterphenyls .............................................................. 482

8.3.2. 2,2’,4-Trichlorinated terphenyls .............................................................................................. 490

8.3.3. 2’,3,4-Trichlorinated terphenyls ............................................................................................. 491

8.3.4. 2’,3,5-Trichlorinated terphenyls ............................................................................................. 494
8.3.5. 2',3,4,5-Tetrachloro terphenyls ................................................................. 496

8.3.6. Summary for the chlorinated liquid crystal project. .................................. 498

8.4. Aromatic ring deuterated cyanobiphenyl .................................................... 498

8.5. Experimental procedures .......................................................................... 505

8.6. Reference.................................................................................................... 546
List of Figures

**Figure 1.1** Phenyl – perfluorophenyl interaction, C-F···H interaction, F···F interaction and C-F···π interaction .......................................................... 4

**Figure 1.2** The “T shaped” crystal packing of benzene (Top left) and hexafluorobenzene (Top right) and the alternative sequence packing of 1:1 benzene:hexafluorobenzene complex (Bottom). The cif data files were obtained from CCDC crystal database and the figures were generated by Mercury 3.6 software. .......................................................... 6

**Figure 1.3** The crystal packing of trans-2,3,4,5,6-pentafluorostilbene (Left), 1:1 complex of trans-stilbene and trans-decafluorostilbene (Right). The cif data files were obtained from CCDC crystal database and the figures were generated by Mercury 3.6 software. ........................................................................ 7

**Figure 1.4** The [2+2] photocyclization product of trans-2,3,4,5,6-pentafluorostilbene. The cif data files were obtained from CCDC crystal database and the figures were generated by Mercury 3.6 software............................................................................................................................... 8

**Figure 1.5** The crystal packing of 1,2,3,5-tetrafluorobenzene (Top) and 1,3,5-trifluorobenzene (Bottom). The cif data files were obtained from CCDC crystal database and the figures were generated by Mercury 3.6 software. ............................................................................................................................... 11

**Figure 1.6** Classification of halogen–halogen interactions .............................. 12

**Figure 1.7** The crystal structure of 4,5-(2,2'-difluoropropylendifthio)-1,3-dithiol-2-one (Top) and 2,3,5,6-tetrafluoro-trans-1,4-diethylnylcylohexan-2,5-diene-1,4-diol (Bottom). The F···F contacts are showed in a separate figure. ........................................................................................................ 14

**Figure 1.8** “T Shaped” packing of perfluoronaphthalene (Top) and perfluoropentacene (Bottom). Figures were generated by Mercury 3.6 software. ............................................................................................................................... 16

**Figure 1.9** Examples of organic semiconductors (Top left: Pentacene; Top right: DH-6T
(dihexylsexithiophene); Bottom left: C_{60}; Bottom right: Poly(trans-acetylene)). .................................. 19

**Figure 1.10** Molecular orbital diagram of C=C double bond in ethylene\(^83\). ........................................ 21

**Figure 1.11** Molecular orbital diagram of C=C double bond in benzene\(^83\). ........................................ 21

**Figure 1.12** The crystal packing of Pentacene. Viewed from a axis (left) and c axis (right)\(^92\). ... 24

**Figure 2.1** 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives .......................... 34

**Figure 2.2** Crystal packing of diphenylacetylene (DPHACT), showing C-H···π interactions (Bottom figure). .................................................................................................................. 41

**Figure 2.3** Crystal structure of 1-fluoro-4-(phenylethynyl)benzene, shows the H···F intermolecular interactions (top) and C\(_{sp2}\)-H···π interactions (bottom right). ............................................. 43

**Figure 2.4** Crystal packing of 1,3-difluoro-2-(phenylethynyl)benzene (top), C\(_{sp2}\)-H···F–C\(_{sp2}\) interactions and F···F contacts (middle), C\(_{sp2}\)-H···π interaction (bottom). .................................................. 45

**Figure 2.5** Crystal structures of 1,3,5-trifluoro-2-(phenylethynyl)benzene (top), C\(_{sp2}\)-H···F–C\(_{sp2}\) interactions(middle) and C\(_{sp2}\)-F···πF interactions (bottom). ................................................................................. 47

**Figure 2.6** Crystal structures 1,2,3-trifluoro-5-(phenylethynyl)benzene - 8 molecules in the lattice are paralleled to axis a (top), 8 parallel to axis b (middle). F involved interactions are shown in the bottom figure............................................................................................................................................. 49

**Figure 2.7** Crystal structure of 1,2,4,5-tetrafluoro-3-(phenylethynyl)benzene, shows the C\(_{sp2}\)-H···F–C\(_{sp2}\) interaction matrix (bottom left) and the torsion angle of two aromatic rings(bottom right). .............................................................................................................. 51

**Figure 2.8** Crystal packing of AISJIV, shows the C\(_{sp2}\)-H···F–C\(_{sp2}\) interaction and aryl-perfluoroaryl stacking (bottom). .............................................................................................................................................. 52

**Figure 2.9** Crystal structure of perfluoro diphenylacetylene (PFDRAV). Viewed from a axis (top), viewed from c axis (middle) and C-F···πF interactions (bottom). ................................................................................. 53
Figure 2.10 Crystal packing of 1,2,4,5-tetrakis(phenylethynyl)benzene, shows the interactions that lead to the T shaped stacking (bottom). Two rings in each molecule (para- position) show disorder in the crystal.

Figure 2.11 1,4-bis(p-fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (top), shows the C$_{sp2}$−H⋯F−C$_{sp2}$ interactions and C$_{sp2}$−H⋯π interactions (bottom).

Figure 2.12 Crystal packing of 1,4-bis(2,3,5,6-tetrafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (top) and various intermolecular interactions (bottom).

Figure 2.13 Crystal packing of 1,4-bis(pentafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (top), shows the torsion angle of side chain aromatic ring (middle) and fluorine involved intermolecular interactions (bottom).

Figure 2.14 Crystal structure of 1,4-bis(3',5'-bistrifluoromethylphenylethynyl)-2,5-bis(phenylethynyl)benzene, shows the torsion of CF$_3$ equipped aromatic ring (middle) and the bent of C-C triple bond (bottom).

Figure 2.15 Intermolecular interactions of 1,4-bis(pentafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene.

Figure 2.16 Potential repulsions between H and F atoms due to over too near distances.

Figure 4.1 The structure of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene.

Figure 4.2 Crystal packing of 2',5'-bis(perfluorophenyl)-1,1':4',1''-terphenyl (4.4).

Figure 4.3 $^{19}$F-NMR analysis of single ring closure product 1,2,3,4-tetrafluoro-6-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)triphenylene (4.10). The four smaller peaks (integration area ratio about 1:1:1:1) are the fluorine atoms on the tetrafluorobenzene ring where PCDHF occurred; the three larger peaks (integration area ratio about 2:1:2) are the fluorine atoms on the pentafluorobenzene ring where PCDHF did not occur.
Figure 4.4 HRMS of 2',5'-bis(perfluorophenyl)-1,1':4',1''-terphenyl (4.4) and 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene (4.5). The peak at 525.0525 might come from the possible compound C_{29}H_{30}OF_{8} during the ionization process. .......................................................... 268

Figure 4.5 The crystal packing of 1,2,3,4,10,11,12,13-octafluoro-6,15-dimethoxytribenzo[f,k,m]tetraphene, the aryl – perfluoroaryl stacking distance is about 3.3 Å. ....................................................................................................................................................... 273

Figure 4.6 Phase transition temperature of 1,2,4,10,11,13-hexafluoro-3,6,12,15-tetrakis(hexyloxy)tribenzo[f,k,m]tetraphene (4.18). .............................................................................................................................................. 275

Figure 4.7 1,2,4,10,11,13-Hexafluoro-3,6,12,15-tetrakis(hexyloxy)tribenzo[f,k,m]tetraphene (4.18) at 180 °C. ......................................................................................................................................................... 275

Figure 4.8 Crystal packing of 2,2'-(2,2''-3,3'',4,4'',5,5'',6,6''-decafluoro-[1,1':4',1''-terphenyl]-2',5'-diyl)dithiophene (4.24) ...................................................................................................................................................... 280

Figure 4.9 HRMS of 2,2'-(2,2''-3,3'',4,4'',5,5'',6,6''-decafluoro-[1,1':4',1''-terphenyl]-2',5'-diyl)dithiophene (4.24) and 4,5,6,7,12,13,14,15-octafluorobenzo[8,9]tetrathieno[6,5-b:11,10-b']dithiophene (4.25) .............................................................................................................................................. 281

Figure 5.1 Crystal packing of 1,2,3,4-tetrafluorodibenzo[g,p]chrysene. ................................................. 326

Figure 5.2 Crystal packing of dibenzo[g,p]chrysene². ............................................................................... 327

Figure 5.3 ^19F-NMR of single PCDHF product 1,2,3,4-tetrafluoro-7-phenyltriphenylene (5.11). ......................................................................................................................................................... 329

Figure 5.4 X-ray crystallography demonstrated the PCDHF product is 1,2,3,4-tetrafluoro-7-phenyltriphenylene (5.11). .............................................................................................................................................. 330

Figure 5.5 ^1H-NMR and ^19F-NMR of 4,5,6,7,11,12,13,14-octafluorodibenzo[fg,op]tetracene. 334

Figure 6.1 The structure of molecule and the crystal packing of dibenzo[c,g]phenanthrene – the
smallest helicene molecule. It is clear to see the twisted molecular structure (H-H distance is 2.603 Å). The T-shaped intermolecular stacking is supported by the C–H···Cπ interactions (2.663 Å, 2.809 Å).

**Figure 6.2** The synthesis and crystal packing of 7:8,9:10-dibenzo-1,2,3,4-tetrafluorotriphenylene. C–F···CπF interaction (3.136 Å) plays an important role in the molecule stacking along with b axis.

**Figure 6.3** PCDHF of α-(pentaurorostyryl)naphthalenes.

**Figure 6.4** Crystal structure of naphtho[1,2-g]chrysene, shows the torsion of C(1)-C(26)-C(25)-C(24) and intermolecular interactions.

**Figure 6.5** Crystal structure of 7,8,9,10-tetrafluoronaphtho[1,2-g]chrysene, shows the torsion of C(6)-C(7)-C(8)-C(9) and intermolecular interactions.

**Figure 6.6** Crystal structure of 7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene, shows the torsion of C(6)-C(7)-C(11)-C(12) and intermolecular interactions.

**Figure 7.1** X-ray crystallography of 1,4-difluoro-2,3-dimethoxytriphenylene. C–H···F interactions (2.617 Å) and C–H···O interactions (2.522 Å, 2.537 Å) are able to be observed in the crystal packing.

**Figure 8.1** Regions of IR spectrum (Source: http://www.lotusgemology.com/index.php/library/articles/294-ftir-in-gem-testing-ftir-intrigue-lotus-gemology).

**Figure 8.2** Temperature dependence of refractive (Source: http://www.personal.kent.edu/~bisenyuk/liquidcrystals/maintypes3.html).

**Figure 8.3** Measured absorption coefficient spectrum of 5CB (measurement was conducted in anisotropic phase, two cells with 100 and 50 μm gaps were employed) (Courtesy Prof.
Figure 8.4 The infrared spectra of 5CB (top) and D5CB (bottom).

Figure 8.5 Measured transmission spectra of 5CB (Red), 1CB (Blue), FB (Green) and F7CB (Violet) in MWIR region.

Figure 8.6 Measured transmission spectra of 5CB (red line) and FT (blue line) in MWIR region.

Figure 8.7 (color line) Measured absorption coefficient spectrum of 5CB and Mix I.

Figure 8.8 Measured absorption coefficient of 5CB (Black) and Mix II (Red).

Figure 8.9 Temperature dependent birefringence of IR-M2 at $\lambda = 633$nm. The black dots are measured data and the red line is a fitting curve with Haller’s semi-empirical equation.

Figure 8.10 Birefringence dispersion of IR-M2 at room temperature.

Figure 8.11 Temperature dependent visco-elastic coefficients of IR-M2.

Figure 8.12 Measured transmittance spectrum of IR-M2 in the IR region with cell gap $d = 21$ $\mu$m.

Figure 8.13 New D5CB and 5CB at NIR region.

Figure 8.14 New D5CB and 5CB at 8~12$\mu$m region.

Figure 8.15 Temperature dependent birefringence of NEW D5CB.

Figure 8.16 GC-MS of final product 4'-pentyl-[1,1'-biphenyl]-4-carbonitrile-2,2',3,3',5,5',6,6'-d$_8$ (8.34). The major peak at $t=20.60$ min is the desired product, whereas the peaks at $t=19.82$ min and $t=19.90$ min might be the ortho- and meta- isomers of desired product.

Figure 8.17 $^1$H-NMR of final product 4'-pentyl-[1,1'-biphenyl]-4-carbonitrile-2,2',3,3',5,5',6,6'-d$_8$ (8.34).
List of Schemes

Scheme 2.1 The synthesis of fluorinated diphenylacetylene............................................................................. 36

Scheme 2.2 Synthesis of 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzenes (the CF₃ derivative 2.9a was synthesized by Dr. Twieg). .............................................................................................................. 37

Scheme 3.1 Retrosynthesis of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene series compound........................................................................................................................................... 93

Scheme 3.2 Mechanism of Mallory photocyclization................................................................................................. 95

Scheme 3.3 Diphenyldiselenide or Cu(II) salts are able to work as the oxidizing agent in oxidative Mallory photocyclizations. .............................................................................................................................................. 95

Scheme 3.4 Synthesis of granulatimid from didemnimide A²⁰ ...................................................................................... 96

Scheme 3.5 The first photosynthesis of helicene via oxidative Mallory photocyclization¹⁵ ...................................... 96

Scheme 3.6 Examples of photocyclodehydrohalogenation involving Cl, Br and I as leaving group²¹,²³,²⁶ .............................................................................................................................................. 97

Scheme 3.7 Early examples of photocyclization involving the loss of HF²⁷,²⁸ ........................................................................ 99

Scheme 3.8 Photocyclization processes .................................................................................................................. 100

Scheme 3.9 Preparation methods for 3,4,5,6-pentafluorostilbene type precursors. ................................................. 102

Scheme 3.10 Preparation methods of 2,3,4,5,6-pentafluoro-1,1':2',1''-terphenyl type precursors. .............................................................................................................................................. 104

Scheme 3.11 Preparation of precursors with a 2,3,5,6-tetrafluoro substituted benzene ring. .... 108

Scheme 3.12 Preparation of precursors by using Suzuki coupling and condensation reaction. 110

Scheme 4.1 The synthesis of 2',5'-bis(perfluorophenyl)-1,1':4',1''-terphenyl............................................................... 259

Scheme 4.2 The PCDHF of 2',5'-bis(perfluorophenyl)-1,1':4',1''-terphenyl failed when using toluene as solvent.............................................................................................................................................. 261

Scheme 4.3 Alternative route to get access to 1,2,3,4,10,11,12,13-
octafluorotribenzo[f,k,m]tetrathrene. ................................................................. 262

Scheme 4.4 Synthesis of 2,3,4,5,6,2''''''',3''''''',4''''''',5''''''',6'''''''-decafluoro-1,l':2',1''':4',1''''':2'',1''''''-quinquephenyl ................................................................. 263

Scheme 4.5 The PCDHF of 2,3,4,5,6,2''''''',3''''''',4''''''',5''''''',6'''''''-octafluoro-1,l':2',1''':4',1''''':2'',1''''''-quinquephenyl when using THF:Acetonitrile = 1:1 mixture as solvent ........................................ 266

Scheme 4.6 PCDHF of 2',5'-bis(perfluorophenyl)-1',1':4',1'''-terphenyl ................................................ 266

Scheme 4.7 The synthesis of 1,2,3,4,10,11,12,13-octafluoro-6,15-dimethoxytribenzo[f,k,m]tetrathrene ................................................................. 271

Scheme 4.8 Synthesis of 1,2,3,4,10,11,12,13-octafluoro-6,15-bis(hexyloxy)tribenzo[f,k,m]tetrathrene (4.16) and 1,2,4,10,11,13-hexafluoro-3,6,12,15-tetrakis(hexyloxy)tribenzo[f,k,m]tetrathrene (4.18) ................................................ 274

Scheme 4.9 Synthesis of 6,15-di-tert-butyl-1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetrathrene (4.20) ................................................................................ 276

Scheme 4.10 The attempt to prepare the dimethoxy bis-trifluoromethoxy compound ........... 276

Scheme 4.11 Synthesis of 2,2''-(2,2'''',3,3''''',4,4''''',5,5'''''',6,6'''''''-decafluoro-[1,1':4',1'''-terphenyl]-2',5'-diyl)dithiophene (4.24) and 4,5,6,7,12,13,14,15-octafluorobenz0[8,9]tetrathieno[6,5-b:11,10-b']dithiophene (4.25) ................................................................................ 277

Scheme 5.1 9-(perfluorophenyl)-10-phenylphenanthrene (5.2) failed to undergo PCDHF ..... 323

Scheme 5.2 Oxidative photocyclization is much faster than PCDHF for (2-(perfluorophenyl)ethene-1,1,2-triyl)tribenzene (5.4) ................................................................................ 324

Scheme 5.3 Synthesis of 1,2,3,4-tetrafluorodibenzo[g,p]chrysene .............................................. 324

Scheme 5.4 Proposed synthesis of 1,2,3-trifluorodibenzo[fg,op]tetracene ........................................ 328

Scheme 5.5 Formation of 1,2,3,4-tetrafluoro-7-phenyltriphenylene ........................................... 331
Scheme 5.6 Synthesis of 4,5,6,7,11,12,13,14-octafluorodibenzo[fg,op]tetracene. 333

Scheme 6.1 Synthesis of [7] helicene\textsuperscript{16,17} 367

Scheme 6.2 The synthesis of helicenes via the Diels-Alder reaction \textsuperscript{19-21}, Friedel-Crafts reaction \textsuperscript{22,23} and metal-mediated cyclizations \textsuperscript{24-26} 368

Scheme 6.3 Synthesis of naphtho[1,2-g]chrysene (6.6). 372

Scheme 6.4 The synthesis of 7,8,9,10-tetrafluoronaphtho[1,2-g]chrysene. 374

Scheme 6.5 The synthesis of 7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene. 375

Scheme 7.1 Literature fluorinated triphenylene synthesis 425

Scheme 7.2 Retrosynthetic route involving PCDHF 426

Scheme 7.3 SnAr reaction (i) PCDHF/Acetonitrile 94%; (ii) R-OH/t-BuOK (8 eq)/Heating R=CH\textsubscript{3} 60%; R=C\textsubscript{2}H\textsubscript{5} 55%; R=n-C\textsubscript{6}H\textsubscript{13} 25% 426

Scheme 7.4 The synthesis of a terphenyl intermediate 7.6. 429

Scheme 7.5 The synthesis of hexakisalkoxytriphenylene discotic liquid crystals. 430

Scheme 7.6 The synthesis of pentakisalkoxytriphenylene discotic liquid crystals. 431

Scheme 8.1 Synthesis of 4,2'-chlorinated cyclohexylterphenyls 482

Scheme 8.2 Preparation of corresponding boronic acids 483

Scheme 8.3 Synthesis of 2,2',4-trichlorinated terphenyls. 490

Scheme 8.4 Synthesis of 2',3,4-trichlorinated terphenyls. 492

Scheme 8.5 Failed approach to obtain 4-bromo-2,3',5'-trichloro-1,1'-biphenyl 494

Scheme 8.6 The synthesis of 2',3,5-trichlorinated terphenyls. 495

Scheme 8.7 The synthesis of 2',3,4,5-tetrachlorinated terphenyls. 496

Scheme 8.8 Synthesis of aromatic deuterated 5CB 499
List of Tables

Table 2.1 Summary of crystallographic and refinement data for tolanes 2.2a – 2.2e. .................. 38

Table 2.2 Summary of crystallographic and refinement data for Compound 2.5, 2.9a-2.9d........ 55

Table 3.1 PCDHF in 2,3,4,5,6-pentafluorostilbene type precursors ........................................... 102

Table 3.2 PCDHF in 2,3,4,5,6-pentafluoro-1,1':2',1"-terphenyl type precursors ..................... 104

Table 3.3 PCDHF involving heterocycles.................................................................................. 107

Table 3.4 PCDHF of 2,3,5,6-tetrafluoro precursors .................................................................. 109

Table 3.5 PCDHF of precursors with two fluorine atoms (at the two ortho sites). ...................... 111

Table 3.6 Competition between PCDHF and oxidative cyclization.......................................... 112

Table 3.7 PCDHF involving steric control.................................................................................. 116

Table 3.8 PCDHF involving competition with other halogens (Cl, Br).................................. 118

Table 3.9 Precursors that do not provide good results for PCDHF. .................................... 120

Table 3.10 The extension for PCDHF to other halogens – Chlorine (PCDHCl) ....................... 125

Table 6.1 Summary of crystallographic and refinement data for [5] helicenes. ...................... 376

Table 7.1 Phase behavior of the fluorinated triphenylene discotic liquid crystals prepared in this study. .................................................................................................................. 432

Table 8.1 Corresponding absorption mechanisms for Zones A–D shown in the figure above. 472

Table 8.2 Chemical structures, abbreviations and phase transition temperatures of compounds studied. 476

Table 8.3 Chemical structures and properties of the seven compounds. 479

Table 8.4 Phase transition temperatures for 4,2’-chlorinated terphenyls. 485

Table 8.5 Phase transition temperature of 2,2’,4-trichlorinated terphenyls. 491

Table 8.6 Phase transition temperature of 2’,3,4-trichlorinated terphenyls. 493

Table 8.7 Phase transition behavior of 2’,3,4,5-tetrachlorinated terphenyls (The figures are the
DSC for compound 3 (8.28c). ................................................................. 497
Dedication and Acknowledgements

At here, I dedicate my work to all the people who have helped me in the past years.

With deepest appreciation, I would like to say thanks to my research advisor, Prof. Robert J. Twieg. He is really a kind gentleman and helped me overcome countless of difficulties in the past six and half years. Without his support and suggestions, it is impossible for me to accomplish my research.

I would like to say thanks to all of my dissertation committee members - Dr. Brett Ellman, Dr. Paul Sampson, Dr. Scott Bunge and Dr. Liang-Chy Chien for their guidance on the correction and improvement of my thesis.

Thanks Dr. Robert J. Twieg, Dr. Paul Sampson, Dr. Alexander Seed, Dr. Ruth Leslie, Dr. Nicola E Brasch and Dr. Simon M. Mwongela for the excellent courses they have offered. All the knowledge I learnt from these classes have given great help in my own research.

Thanks Dr. Mahinda Gangoda for his effort on the maintenance of instrument facility in our whole department. Thanks Dr. Brett Ellman’s group helping me setup the photo reactor and determination for the electrical properties for some of my materials. Also, thanks Dr. Scott Bunge’s group on the X-ray crystallography analysis and Dr. Jacob Shelley’s group on the HRMS work. Of course, very thanks to our cooperator Dr. Shintson Wu in University of Central Florida. Their group help me determined the IR transparency and birefringence for some of my materials.
I would also like to thank and acknowledge all other members in our research group once and now - Dr. Prabin Pai, Dr. Jarrod Williams, Dr. Suvagata Tripathi, David Davis, Kunlun Wang and Tawfik Khattab. We used to be working together happily and all of these memories will be engraved in my brain for my whole life.

Of course, I would like to thank my parents and countless of friends who have given their encouragement in the past years. At here, a special thank will be given to my girlfriend Shenyue Jia who is still chasing her dream in University of California, Los Angeles. Her love is just like beautiful sunshine and helped me passed the toughest era of my graduate study.

Finally, I must say thanks to Dr. Arne Gericke who offered me the opportunity to come and study at Kent State University. Without this, all the stories I mentioned before would never happen!

Zhe Li
Nov.29.2015
1. Chapter One – Background and Introduction

1.1. Introduction of fluorine

Fluorine (symbol F) is a very common element existing in the crust of the earth (approximately 0.08 % and ranks 13th in the abundance of elements in earth's crust)\(^1\) in many common natural minerals such as fluorite (CaF\(_2\)), fluorapatite (Ca\(_5\)(PO\(_4\))\(_3\)F) and cryolite (Na\(_3\)AlF\(_6\))^2. The element fluorine got this name during the initial application of fluorite which was used to lower melting points in metal smelting\(^3\). Because the natural compounds of fluorine are usually very stable and due to its extraordinary reactivity, it took an extremely long time between its initial discovery and final isolation as pure elemental fluorine (F\(_2\)). After countless failures, French chemist Henri Moissan^4 successfully isolated it by using electrolysis on a mixture of potassium hydrogen difluoride (KHF\(_2\)) and liquid hydrogen fluoride (HF) (pure hydrogen fluoride is a kind of insulator). Because of this achievement, he was awarded the Nobel Prize in Chemistry in 1906^5.

Fluorinated compounds are closely associated with our daily lives. Polytetrafluoroethylene (Teflon) is a very successful perfluorinated polymer material\(^6\). Its high resistance to heat and many chemicals leads to applications as a non-stick coating of cookware such as pans and spatula, insulating materials\(^7\), construction blocks and as a container for chemical reactions that withstand harsh conditions\(^8,9\). Freon-12 (CCl\(_2\)F\(_2\)) had been used as refrigerant for a long time before its replacement by other fluorinated alkanes such as R-134a (1,1,1,2-tetrafluoroethane) and HFO-1234yf (2,3,3,3-tetrafluoropropene) with the consideration of their ozone depletion potential (ODP)^10,11. In the nuclear industry, the fluorinated compound of uranium UF\(_6\) is a very important intermediate that using in the uranium enrichment process. Due to its easy sublimation physical property\(^12\), isotopes of uranium will be slowly separated via a diffusion process\(^13\). Trace amounts
of fluoride such as sodium fluoride can be used as an additive in toothpaste to prevent the decay of teeth\textsuperscript{14}. Furthermore, in the area of photography, a large piece of ultra-pure fluorite single crystal can be used as lens element, which can enhance the quality of images by controlling chromatic aberration (caused by light dispersion)\textsuperscript{15} at a relatively low level\textsuperscript{16}.

As the first halogen, the fluorine atom is characterized with the $1s^22s^22p^5$ electron configuration and has an extreme affinity for an additional electron to form the “eight-electron” octet stable structure. Because of this, fluorine features the highest electronegativity (EN = 4.0) in the periodic table\textsuperscript{17}. This particular property makes fluorine a “magical” element and thus it has attracted numerous researchers. In organic chemistry, the replacement of hydrogen atoms with fluorine atoms may dramatically perturb the electron density distribution in the whole molecule. Because of this, fluorinated compounds usually show some special chemical and physical properties, leading to significant attention in a field called fluorine chemistry. The effects of fluorination on a range of physical properties and on chemical reactivity become particularly evident in perfluorinated compounds in which all hydrogens are replaced by fluorine.

1.2. Non-bonded interactions

In the field of material science, the patterns of molecular packing are crucial as they deeply determine the functionality and reactivity of a particular material\textsuperscript{18-22}. For this reason, it is necessary to seek insight and understand the factors that can control the molecular packing style. The great challenge behind this mission is how we can adjust and modulate the molecular interactions via molecular design - especially the non-covalent weak interactions\textsuperscript{23,24}. 
As is common knowledge for chemists, the non-covalent interactions include van der Waals force and hydrogen bonds. For some molecules with special structures (e.g. various interactions involving fluorine will be discussed in subsequent sections), some other types of special contacts may also be observed.

The van der Waals force, which is considered as a kind of weak interactions between molecules, got its name from the Dutch scientist Johannes Diderik van der Waals. Generally speaking, the van der Waals force is a combination of dipole-dipole interactions and London dispersion. The difference between them is that dipole–dipole interaction comes from two permanent dipoles or a permanent dipole with a corresponding induced dipole whereas London dispersion force comes from the instantaneously induced dipoles of otherwise non-polar molecules. Based on the mechanism of their origin, the dipole-dipole interaction is much stronger than the dispersion force. However, these kinds of interactions usually work in concert rather than individually.

Hydrogen bonds are the electrostatic interactions that exist between sites equipped with at least a hydrogen (H) atom and another highly electronegativity atom such as nitrogen (N), oxygen (O) and fluorine (F). Under this circumstance, the hydrogen atom will experience attraction to the nearby highly electronegative atom. The interacting atoms may be in different molecules (an intermolecular hydrogen bond) or in the same molecule (an intramolecular hydrogen bond). The hydrogen bond is typically much stronger than the van der Waals force. It exists in both inorganic and organic components and plays an important role in influencing their physical properties. For example, due to the contribution of hydrogen bonds, water is liquid at room temperature and has
a boiling point as high as 100 °C (The H-bond energy for bulk water is 7.9 kJ/mol\textsuperscript{28}) at 1 atm whereas the higher molecular weight H\textsubscript{2}S is just a gas at room temperature and standard atmosphere pressure (the M.P. of H\textsubscript{2}S is -83.5 °C\textsuperscript{29} and the B.P. is -60.3 °C\textsuperscript{30}. The H-bond energy in H\textsubscript{2}S at semi-empirical level is 3.0 kJ/mol\textsuperscript{31,32}).

### 1.3. Non-bonding interactions in fluorinated compounds

One of our group’s research focus areas involves investigation of materials with novel electrical and optical properties. One of the projects involves research on organic semiconducting materials that involves the control of arene–perfluoroarene solid-state packing and perfluorinated aromatic compounds seem to be a good choice that fit this criterion\textsuperscript{33}. As already mentioned before, fluorine is a special halogen element. Due to its extraordinary electronegativity, the presence of fluorine atoms in organic molecules will dramatically change the distribution of electrons and lead to some special intramolecular and intermolecular interactions that ordinary compounds do not feature. In the review made by Juerg Hulliger\textsuperscript{34}, the interactions in organic compounds involving fluorine can be classified as phenyl-perfluorophenyl interactions; C-F···H interactions, F···F interactions and C-F···π\textsubscript{F} interactions.

![Figure 0.1 Phenyl – perfluorophenyl interaction, C-F···H interaction, F···F interaction and C-F···π\textsubscript{F} interaction.](image)

\textsuperscript{31}T. S. A. V. G., \textit{Nature} \textbf{4}, 28
\textsuperscript{32}F. R. D. H., \textit{Science} \textbf{5}, 50
\textsuperscript{33}P. A. B. C., \textit{Advanced Materials} \textbf{6}, 60
\textsuperscript{34}J. H. M. J., \textit{Chemical Reviews} \textbf{7}, 70
1.3.1. Phenyl – perfluorophenyl interaction

The phenyl – perfluorophenyl interaction is probably the most widely known interaction type for fluorinated compounds and the simplest circumstance of this interaction is in the 1:1 mixture of benzene/hexafluorobenzene initially reported by Patrice and Prosser in 1960\textsuperscript{35}. They describe it as “it was observed that a solid was formed on mixing these two substances although this frequently disappeared before the mixing process was complete”. Their experimental freezing-point diagram showed the maximum melting point as high as 23.7 °C “corresponding to a mixture containing equimolar quantities of the two substances”. As both benzene and hexafluorobenzene individually possess lower melting points (5.4 °C and 5.0 °C), this phenomenon clearly demonstrated the formation of a 1:1 complex during the process of mixing. X-ray crystal analysis confirmed this assumption. Both benzene\textsuperscript{36} and hexafluorobenzene\textsuperscript{37} have an edge to edge (T-shaped) structure whereas their 1:1 complex features a stacked structure with an alternative sequence of non-fluoro/perfluoro molecules\textsuperscript{38}. The similar stacking pattern can also be observed in other phenyl-perfluorophenyl complexes such as the 1:1 complexes of hexafluorobenzene with naphthalene, anthracene, phenanthrene, pyrene and even triphenylene\textsuperscript{39}.

Any kind of particular interaction seldom exists alone and the phenyl – perfluorophenyl system also fits this rule. When the aryl – perfluoroaryl interaction occurs, it is usually supported by the C-F⋯H interactions from nearby aromatic rings.
Figure 0.2 The “T shaped” crystal packing of benzene (Top left) and hexafluorobenzene (Top right) and the alternative sequence packing of 1:1 benzene:hexafluorobenzene complex (Bottom). The cif data files were obtained from CCDC crystal database and the figures were generated by Mercury 3.6 software.
Of course, this kind of interaction is not limited to the phenyl-perfluorophenyl complexes with two kinds of components, but also exists in single compound that contains both phenyl and perfluorophenyl ring structures\textsuperscript{40}. For example, G. W. Coates et al.\textsuperscript{40} have confirmed that trans-2,3,4,5,6-pentafluorostilbene itself can make phenyl – perfluorophenyl stacking just as the 1:1 complex of trans-stilbene and trans-decafluorostilbene.

\textbf{Figure 0.3} The crystal packing of trans-2,3,4,5,6-pentafluorostilbene (Left), 1:1 complex of trans-stilbene and trans-decafluorostilbene (Right). The cif data files were obtained from CCDC crystal database and the figures were generated by Mercury 3.6 software.
The more interesting outcome worthy of mention here is that the coplannar stilbenes have center-to-center distances from 3.5 – 4.2 Å. The nearby stilbene molecules in the solid state with this packing distance\textsuperscript{41} are able to undergo [2+2] photocyclization\textsuperscript{42} to form the 4-membered cyclobutane ring in the solid state under appropriate irradiation.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure04.png}
\caption{The [2+2] photocyclization product of trans-2,3,4,5,6-pentafluorostilbene. The cif data files were obtained from CCDC crystal database and the figures were generated by Mercury 3.6 software.}
\end{figure}
1.3.2. C-F···H interactions

C-H and C-F bonds usually exist altogether in fluorinated organic compounds. Because of this, the electrostatic C-F···H interactions will almost invariably accompany the previously discussed phenyl–perfluorophenyl interactions. In fact, C-F···H interactions can be observed much more frequently than phenyl–perfluorophenyl interactions. The phenyl–perfluorophenyl interactions require the existence of both highly fluorinated and non-fluorinated aromatic compounds (or highly fluorinated and non-fluorinated parts within the same compound) and they need to have a short distance parallel stacking. On the other hand, C-F···H interactions are able to occur in lower fluorinated aromatic compounds and the necessary condition for C-F···H interactions is just the distance of fluorine atom and hydrogen atom should be less than a particular value (usually the sum of their van der Waals radii 2.9 Å).

What is emphasized here is that the organic C-F···H interaction should not be confused with the previously discussed hydrogen bond H···F. For hydrogen bonds, their strength is associated with the EN value of the acceptor atom. For this reason, fluorine features the highest EN = 4 value and it should form the strongest hydrogen bonds. In fact, the results exactly fit this rule for ionic fluorine compounds. For example, in the H-bond of FH···F−, the energy can be as high as 155 kJ/mol, which has nearly reached the value of some covalent bonds.

In contrast to inorganic fluorine compounds, organic fluorine atoms (F-atom connected to a C-atom) only will form relatively weak interactions with protons. Jack D. Dunitz and Robin Taylor described them as “hardly ever accepts hydrogen bonds”. They did a thorough search in
CSD (Cambridge Structural Database) and got a result that showed “out of 5947 C-F bonds (in 1218 crystal structures), only 37 (0.6 %) are involved in possible C-F ⋅⋅⋅H-X hydrogen bonds”, which is totally in contrast with what ionic fluorine atoms typically do. They conclude the reason for this as “the energies of the relevant orbitals can be modified by the effect of electron delocalization with molecules and of cooperativity in extended systems”.

Although the C-F⋅⋅⋅H interactions are usually relatively weak, they can still play important roles in stabilizing the crystal packing pattern. Just consider some very simple examples, in the crystal of 1,2,3,5-tetrafluorobenzene, the C-F⋅⋅⋅H interactions make the molecules align in a straight line and in 1,3,5-trichlorobenzene, each fluorine atom and proton can form two C-F⋅⋅⋅H interactions with each other to form a network structure.
Figure 0.5 The crystal packing of 1,2,3,5-tetrafluorobenzene (Top) and 1,3,5-trifluorobenzene (Bottom). The cif data files were obtained from CCDC crystal database and the figures were generated by Mercury 3.6 software.
1.3.3. F···F interactions

The early research of interactions between halogen atoms can be traced back to 1963. Sakurai et al.\textsuperscript{48} observed an extremely short intermolecular Cl-Cl distance 3.37 Å in the crystal of 2,5-dichloroaniline, which was much shorter than the 3.6 Å van der Waals distance. In 1986, Parthasarathy et al.\textsuperscript{49,50} performed searches on existing compounds that involved this kind of interaction and classified them into two species – type I ($\theta_1 = \theta_2$) and type II ($\theta_1 = 180^\circ / \theta_2 = 90^\circ$). The difference between them is that the type II interaction is usually believed to come from the polarization of nearby halogen atoms whereas type I interaction is caused by continuously crystal-packing and is just a kind of crystallographic symmetry.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{classification_of_halogen-halogen_interactions.png}
\caption{Classification of halogen–halogen interactions\textsuperscript{50}}
\end{figure}

However, according to Pauling’s rule\textsuperscript{43}, fluorine features the lowest polarizability compared to the other halogens. For this reason, fluorine atoms are much more prone to form C-F···H contacts which come from the electrostatic and the F···F contacts that require polarization might be an impossible task.

Here, we can take the experiment results to verify the previous suspicion - according to the review of Juerg Hulliger, after a review of fluorinated materials in the database “788 compounds could be
found in the CSD with F⋯F distances up to 3.0 Å of which only 13 show F⋯F contacts of type II”. Among these 13 candidates, only the 4,5-(2,2′-difluoropropylenedithio)-1,3-dithiol-2-one (2.769 Å)\textsuperscript{51} and 2,3,5,6-tetrafluoro-trans-1,4-diethynylcylohexan-2,5-diene-1,4-diol (2.865 Å)\textsuperscript{52} would like to form short distance type II F⋯F interactions (both of these two distances are shorter than sum of van der Waals radii 2.94 Å). However, both of the two F⋯F contacts are just the result of close crystal packing rather than involving the polarization of the fluorine atoms.

At this point, it is already clear that although F⋯F contacts are able to form two kinds of stacking pattern similar as other halogens, however, both of them are just the result of crystal packing rather than real interactions that require polarization.
The crystal structure of 4,5-(2,2’-difluoropropylenedithio)-1,3-dithiol-2-one (Top) and 2,3,5,6-tetrafluoro-trans-1,4-diethynylcylohexan-2,5-diene-1,4-diol (Bottom) The F···F contacts are showed in a separate figure.
1.3.4. C-F⋯πₖ interactions

The C-F⋯πₖ interactions can be regarded as a reversed version of C-H⋯π interactions which have been observed in non-fluorinated aromatic compounds. In perfluorinated aromatic rings, due to the highly electronegative fluorine atoms, the electron density distribution will be completely reversed. Because of this, the δ⁺ perfluorinated aromatic center would like to form interactions with δ⁻ fluorine atoms. This phenomenon can be observed in many perfluorinated aromatic compounds. For example, in the very beginning of our discussion, it has already mentioned that hexafluorobenzene would like to perform “T shaped” stacking in crystalline systems. This is due to the C-F⋯πₖ interactions of nearby molecules. Other perfluorinated polycyclic aromatic hydrocarbons (PAHs) such as perfluoronaphthalene and perfluoropentacene are also able to stack in the same way\textsuperscript{53,54}.

In this section, a short introduction was provided about short distance non-bonding interactions that involve fluorine atoms. When we design some fluorinated molecules, we need to thoroughly consider all kinds of interactions that might occur in the crystal packing. Our target is to obtain some nonpolar, high symmetric compounds that would like to perform short distance cofacial stacking by modulating the number and positions of fluorine atoms in the molecule(s). This class of compounds may be good candidates for organic semiconductors.
Figure 0.8 "T Shaped" packing of perfluoronaphthalene (Top) and perfluorpentacene (Bottom)\textsuperscript{53,54}. Figures were generated by Mercury 3.6 software.
1.4. A brief introduction about semiconductors

These days semiconductor is not a strange term for most people. They are a series of materials with electrical conductivity between conductors and insulators. Semiconductors have usually been applied in the manufacture of semiconductor devices, which are the electronic components that rely on the special electronic properties of semiconductors. These devices have deeply influenced and changed our world in the 20th century. After the first transistor was invented at Bell Labs in 1947, the whole world entered a new era. From then on, the rapid development of semiconductor devices contributed to the rapid flourishing of electronic technology and science, especially computer science.

For inorganic semiconductors, most of them are constituted from the elements in IIIA, IVA, VA and VIA groups of the periodic table. The most commonly used material is silicon (Si) for its abundance and affordable cost (2nd most abundant element in the earth). Electronic equipment is absolutely the area that consumes most monocrystalline silicon, which can be applied as the base material for chips. Aside of that, in the area of solar energy, monocrystalline silicon is used in photovoltaics as light absorbing materials.

In physics, insulators should have infinite resistance but metals have particular resistance (some of them feature superconductivity) at absolute zero temperature. At room temperature, electrical conductivities of metals are usually higher than $10^3$ S/cm (eg. Copper: $5.96 \times 10^5$ S/cm; Silver: $6.30 \times 10^5$ S/cm), much lower than $10^{-8}$ S/cm for insulators (eg. Glass $10^{-17}$ – $10^{-13}$ S/cm) and between $10^{-8}$ S/cm and $10^3$ S/cm for semiconductors (eg. Silicon $1.56 \times 10^{-5}$ S/cm).
formation mechanism of conductor, insulator and semiconductor can be explained by using the “bandgap” theory. The electrons in individual atoms have their own orbitals. When they are combined together and form a molecule, the atomic orbitals of each atom will intact with each other and their energy levels will be redistributed to form the so-called molecular orbital. If the molecule size expands, the density of orbitals in each energy levels will become much higher and higher due to larger numbers of orbitals. Eventually, if countless numbers of atoms gather and form a solid, the amount of atomic orbitals rise accordingly and a particular orbital will suffer the influence from all nearby orbitals. The result of this is that the density of orbitals in each energy levels will be extremely high and form “bands” and these “bands” will be very near to each other but without any overlapping.

The valence band and the conduction band are two crucial bands that determine the conductivity of a solid. The valence band is the “highest range of electron energies that electrons are able to reach at absolute zero temperature”; on the other hand, the conduction band is the lowest energy level of vacant electronic band. For typical metals, the valence band is not fully filled by the electrons. In this “half full” circumstance, the valance band itself is also the conduction band and the electrons are able to move freely without the hinder of energy gap. On the contrary, in both semiconductors and insulators, there is an energy gap between the valence band and conduction band. The difference is that in semiconductors this energy gap is relatively small (Si = 1.11 eV, Ge = 0.67 eV) and the electrons in the valence band are able to jump into the conduction band under appropriate excitation. However, this task is impossible to accomplish in insulators as their energy gaps are over too large (SiO₂ = 9 eV).
1.5. Organic Semiconductors

Compared with the widely known inorganic materials with semiconducting properties, organic semiconductors might be less known word. Just like its name, organic semiconductors are organic materials with semiconductor properties and their study is a very hot topic in recent decades. Compared with the traditional inorganic semiconductor materials, such as silicon already mentioned above, the organic semiconductors have their own advantages such as lower cost and easy processing. Different from their inorganic counterparts, appropriate organic semiconducting materials are able to be processed in the form of a solution at relatively low temperature, which can avoid using expensive processing instruments.

Organic semiconductors can have a very wide range of structures - they can be single molecules (such as anthracene, pentacene, rubrene and various compounds with heterocycles), oligomers (short chains), C_{60}, and even polymers (the most famous example of a conductive polymer is the polyacetylene; the Nobel Prize in Chemistry in 2010 was awarded to Alan G. MacDiarmid, Alan J. Heeger, and Hideki Shirakawa due to their contribution in this area).

Figure 0.9 Examples of organic semiconductors (Top left: Pentacene; Top right: DH-6T (dihexylsexithiophene); Bottom left: C_{60}; Bottom right: Poly(trans-acetylene)).
The figure above just listed several species of organic semiconductors. By carefully examining their molecular structures, it is not hard to observe all of these examples feature one special structure – the conjugation systems building up by the sp² hybridized carbon atoms, which is the key factor that leads to the charge mobility in organic semiconductors\textsuperscript{81}.

The electronic configuration of C is 1s\(^2\)2s\(^2\)2p\(^2\), this means that two out of four valence electrons, the two p electrons are available to form chemical bonds as their p orbitals are not full. However, the hybridization will change everything. In sp\(^2\) hybridization, the 2s orbital and two 2p orbitals (p\(_x\), p\(_y\)) of carbon atom are hybridized and form three energy equivalent sp\(^2\) orbitals, leaving the third p orbital p\(_z\) without any hybridization. In the C=C double bond formation, two sp\(^2\) hybridized orbitals from adjacent carbon atoms make a head-to-head overlapping to form a so-called \(\sigma\) bond. The result of this is energy difference between the occupied bonding orbitals and the unoccupied anti-binding orbitals is very large and at least 6 eV of energy is required to promote an electron from bonding orbital \(\sigma\) to the anti-bonding orbital \(\sigma^*\)\textsuperscript{82}. However, the two unhybridized p\(_z\) orbitals will perform a shoulder-to-shoulder overlap to form a second covalent bond - the \(\pi\) bond. Compared with a \(\sigma\) bond, the orbital interaction in the \(\pi\) bond is much weaker and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is not very large. Appropriate excitation is able to make the electrons jump into the LUMO orbital and lead the material to show some kind of semiconducting properties\textsuperscript{83}.
In much larger conjugated aromatic systems, which often consist of benzene rings as basic units, all of the unhybridized p-orbitals become delocalized and form a huge \( \pi \)-system along with the whole molecule. In this circumstance, any particular orbital will get the influence from others in the p-system and the energy gap between HOMO and LUMO orbitals becomes smaller with the increasing level of delocalization. Finally, the huge amount of HOMO and LUMO orbitals will gather into two bands, just like the valence band and conduction band in previous discussed inorganic semiconductors.

---

**Figure 0.10** Molecular orbital diagram of C=C double bond in ethylene
(http://www.iapp.de/orgworld/?Basics:What_are_organic_semiconductors)

---

**Figure 0.11** Molecular orbital diagram of C=C double bond in benzene
(http://www.iapp.de/orgworld/?Basics:What_are_organic_semiconductors)
After learning the formation mechanism of organic semiconductors as above, it is possible for us to define some of the criteria necessary to obtain a good organic semiconductor compound:

First, a conjugated system is mandatory for organic semiconductors.
Second, the π electron clouds are preferred to overlap as much as possible.
Third, high purity compounds are always preferred.
Fourth, the compound should have relatively good stability.

The first factor has already been explained above – the conjugation system is the fundamental condition for charge transfer. The second factor is an extension of the first one, as the more overlapped electron clouds will provide much better charge transport. Furthermore, high purity components usually show neat and uniform crystal packing, which might be a great help for charge transfer (some impurities might serve as traps and reduce charge mobility). Finally, in actual applications such as photovoltaic materials, organic semiconductor materials might suffer from severe environment conditions such as exposure to atmosphere and sunlight. Because of this, the ideal organic semiconducting material should be stable and able to bear the test of time.

In the design of organic semiconductors, what we can do is try to control the crystal packing by modulating their intermolecular interactions deriving from a characteristic molecular structure. Among the crystal packing patterns, there is always a contradiction between the edge-to-face herringbone packing and cofacial π-stacking. Cofacial π-stacking is believed to be the most desirable pattern as it could maximize the interaction of π orbitals between molecules and yield to the highest theoretical predicted charge carrier mobilities. However, the ideal completely cofacial
π-stacking is really hard to locate in the database. Even for some high mobility polynuclear aromatic compounds that have already been thoroughly investigated, such as pentacene (which has a hole mobility $\mu$ as high as $\sim 35 \text{ cm}^2/\text{Vs}$ at room temperature\textsuperscript{98}) and naphthalene (offers a hole mobility $\mu = 1.4 \text{ cm}^2/\text{Vs}$ at room temperature and as high as $300 \text{ cm}^2/\text{Vs}$ at 10 K\textsuperscript{91}), they just show cofacial stackings viewed from one direction but herringbone stackings from the other direction (Figure 1.12).
Figure 0.12 The crystal packing of Pentacene. Viewed from a axis (left) and c axis (right)\textsuperscript{92}. 
1.6. Experimental Procedures

The chemical reagents used in this study were purchased from major chemical vendors including Sigma Aldrich, Fischer Scientific, Acros Organic, Alfa Aesar, TCI America, Matrix Scientific, Oakwoods and Combi-Blocks.

A Mettler Toledo FP82HT Hot Stage controlled by a Mettler Toledo FP90 Central Processor (Mettler Toledo, P.O. Box 71, USA-Hightstown, NJ) was used to determine melting points. The melting process was observed using a Nikon Eclipse E600 POL microscope.

IR analysis was accomplished by using a Bruker Vector 33 FTIR spectrometer (Bruker Optics Inc, Billerica, MA, USA). The data obtained was processed and plotted by OPUS software.

A Bruker 400 NMR was used for NMR data acquisition (Frequency: 400 MHz for $^1$H-NMR; 100 MHz for $^{13}$C-NMR and 376 MHz for $^{19}$F-NMR) and the plots were generated by TOPSPIN 2 software. In the data, $^1J$, $^2J$, $^3J$ represent the 1st, 2nd and 3rd coupling constant.

A Thermo Finnigan Trace - GC 2000 (Thermo Scientific, Austin, TX, USA) and Polaris Q Mass Spectrometer (Thermo Scientific, Austin, TX, USA) were used to follow the photochemical reactions and assay product purity. The GC-MS data was collected and processed via Xcalibur software (Ver. 1.4, Thermo Scientific, San Jose, CA, USA).

The HRMS analysis was performed by Dr. Jacob Shelley et al. Here the high resolution mass
spectra of created ions were recorded on an Exactive Plus mass spectrometer (Thermo Scientific, Bremen, Germany). Mass spectra were recorded in the positive ionization mode with a scan range of 50–700 m/z, a mass resolving power setting of 140,000, and an automatic gain control (AGC) target value of $1 \times 10^6$ ions. To ensure very high mass accuracy (found to be better than 1 ppm) the instrument was mass calibrated daily and a lock mass of m/z 371.10124, due to polysiloxane, was used throughout. The Xcalibur software (ver. 3.0, Thermo Scientific, San Jose, CA, USA) was used to collect and process mass spectral data as well as determine elemental compositions based on the high mass accuracy measurements.

X-ray crystallography was done by Dr. Scott Bunge et al. It was performed by mounting each crystal onto a thin glass fiber from a pool of Fluorolube™ and immediately placing it under a liquid N$_2$ cooled N$_2$ stream, on a Bruker AXS diffractometer. The radiation used was graphite monochromatized Mo K$_\alpha$ radiation ($\lambda = 0.7107$ Å). The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination, data collection, structure refinement, scaling, and data reduction were carried out using APEX2 version 2014.11-0 software package. Each structure was solved using direct methods. This procedure yielded a number of the C atoms. Subsequent Fourier synthesis yielded the remaining atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined within the XSHELL software. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic U of the C atoms to which they were bonded. The final refinement of each compound included anisotropic thermal parameters on all non-hydrogen atoms.

For the photocyclization reactions, two types of photochemical reactors can be selected: 1) The
Rayonet photochemical reactor can be fitted with up to $16 \times 254$ nm lamps or $16 \times 300$ nm lamps.

2) The Hanovia photochemical reactor has a single 450 W lamp. The output of this lamp was not used directly. Instead, either a Pyrex or Vycor cutoff filter was employed to eliminate short wavelength UV. In either case, the solutions of the materials were charged in quartz tubes (approximately 40 cm $\times$ 25 mm with a 24/40ST joint) for irradiation.

For liquid crystal samples, differential scanning calorimetry (DSC) analysis is required to determine their phase transition temperatures and this task was done by a 2920 Modulated DSC from TA instruments (TA Instruments Inc., New Castle, DE, USA). Experimental data was analyzed and exported by using the Thermal Advantage software (Version 1.1A, TA Instruments Inc., New Castle, DE, USA).

1.7. Summary

In this chapter, we made a brief introduction about the intermolecular interactions involving fluorine substances and the background of organic semiconductors. The concepts mentioned here will be discussed again in the following chapters with actual examples.

Aside from this, the common instruments for the whole research were listed above. For some circumstances that require special techniques, the details will be discussed individually in the experimental procedure sections.
1.8. References

http://www.daviddarling.info/encyclopedia/E/elterr.html


(7) Division, M. E. P., 3M 60 Tape PTFE Film With Silicone Adhesive, 1998,
http://multimedia.3m.com/mws/media/37395O/tape-60.pdf


(14) Mullen, J. *Br Dent J*.


(17) Pauling, L. *The nature of the chemical bond and the structure of molecules and crystals* :

(31) Sabin, J. R. Journal of the American Chemical Society 1971, 93, 3613.
(33) Liu, N., Kent State University, 2008.


(42) Ciamician, G.; Silber, P. *Berichte der deutschen chemischen Gesellschaft* 1908, 41, 1928.

(43) *Journal of the American Pharmaceutical Association* 1941, 30, 30.


(49) Desiraju, G. R.; Parthasarathy, R. *Journal of the American Chemical Society* 1989, 111, 8725.


Crystallographica Section B 2000, 56, 1063.


(64) Forrest, S. R.; Thompson, M. E. Chemical Reviews 2007, 107, 923.


Chemistry of Materials 2005, 17, 1261.


(84) Stella, M., Universitat de Barcelona, 2009.


2. Chapter Two - The investigation on the crystal packing of 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives

2.1. Introduction

As mentioned before, our research group focuses on the research of organic semiconducting materials\(^1\) involving the control of arene–perfluoroarene solid-state structure interactions\(^2\). The 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzenes derivatives might be good candidates that fit our plans. This series of compounds features a non-polar and possible C\(_2\) symmetric structure. By controlling the fluorination level in the terminal rings of the side chains, some of them might exhibit arene–perfluoroarene interactions that lead close contact packing.

![Figure 2.1 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives](image)

However, we came to realize that 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzenes derivatives themselves are, in fact, quite a complicated structure to start out with. We did not appreciate the full set of important factors potentially influencing the packing of these molecules when this project was initiated. To get a better understanding of crystal packing and the fluorine related non-bonding intermolecular interactions, their parent compounds - fluorinated tolans\(^3\) were investigated initially. The crystal structure of diphenylacetylene (DPHACT) (the known
crystal structure will be presented with CCDC database reference code) with no fluorinated ring, 1-pentafluorophenyl-2-phenylacetylene (ASIJIV) with one perfluorinated ring and perfluorodiphenylacetylene (PFDPAY) have all already been characterized\textsuperscript{3-6}.

In contrast, no other tolanes with one partially-fluorinated aromatic ring and one non-fluorinated aromatic ring have yet been documented in the CCDC database. It is worthwhile to see how the crystal structure will perform as the fluorination level changes, which could give a better understanding for the non-covalent bond weak interactions involving fluorine. In other words, we are trying to find if is there some threshold for fluorine content (number and location of fluorine atoms) at which time the desired cofacial interactions turn on and off.

2.2. Synthesis of fluorinate tolanes and 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives

All of our starting materials and reagents used in these experiments were purchased directly from major chemical distributors without any purification unless otherwise explicitly stated in the experimental details section. The partially fluorinated tolanes (\textbf{2.2a} – \textbf{2.2e}), were all easily obtained by the coupling of phenylacetylene with the respective fluorinated aromatic bromide/iodide (depends on the availability and prices) via the traditional Sonogashira approach\textsuperscript{7}. 

35
In contrast, the 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives are more complicated to obtain. Commercially available 1,4-dibromobenzene (2.3) was heated with iodine and concentrated sulfuric acid to afford 1,4-dibromo-2,5-diiodobenzene (2.4) as product. At this point, the non-fluorinated 1,2,4,5-tetrakis(phenylethynyl)benzene (2.5) could be easily accessed via the Sonogashira coupling of 1,4-dibromo-2,5-diiodobenzene (2.4) with an excess (more than 4.0 eq) of phenylacetylene. On the other hand, by carefully controlling the amount of phenylacetylene (~2.0 eq), only the two iodine atoms (with higher reactivity than the bromine atoms) will be coupled to give 1,4-dibromo-2,5-bis(phenylethynyl)benzene (2.6) which can be isolated in good yield and in a high state of purity. After coupling with trimethylsilylacetylene (more than 2.0 eq was required due to its highly volatility) followed by the removal of TMS protecting groups with potassium carbonate in a mixture methanol and dichloromethane, the compound (2.8) with two terminal acetylenes was isolated. The free acetylenes in compound 2.8 were finally coupled with the respective fluorinated aromatic bromides or iodides to give compounds (2.9a – 2.9d) as final products. It is worth mentioning here that is that warm toluene
is required to elute compound 2.9d in column chromatography. All the details for synthetic procedures and data are provided in the experimental section.

All the crude mixtures from Sonogashira reactions showed a dark yellow color and therefore tolanes and 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzenes derivatives were purified via silica gel column chromatography followed by recrystallization from appropriate solvents. Single crystals suitable for X-ray crystallography were acquired by slow evaporation of their saturated solutions. Details about individual crystal structures of selected compounds will be

Scheme 2.2 Synthesis of 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzenes (the CF₃ derivative 2.9a was synthesized by Dr. Twieg).
discussed in the section below.

2.3. X-ray crystallography analysis of fluorinated tolanes

Table 2.1 Summary of crystallographic and refinement data for tolanes 2.2a – 2.2e.

<table>
<thead>
<tr>
<th>Compound</th>
<th>2.2a</th>
<th>2.2b</th>
<th>2.2c</th>
<th>2.2d</th>
<th>2.2e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{14}H_{9}F</td>
<td>C_{14}H_{8}F_{2}</td>
<td>C_{14}H_{7}F_{3}</td>
<td>C_{14}H_{7}F_{3}</td>
<td>C_{14}H_{6}F_{4}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>196.21</td>
<td>214.20</td>
<td>232.20</td>
<td>232.20</td>
<td>250.19</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2\textsubscript{1}/n</td>
<td>P2\textsubscript{1}/n</td>
<td>P2\textsubscript{1}/n</td>
<td>C2/c</td>
<td>Fdd2</td>
</tr>
<tr>
<td>a, Å</td>
<td>9.926(2)</td>
<td>5.9073(4)</td>
<td>10.7853(9)</td>
<td>14.2113(18)</td>
<td>8.425(3)</td>
</tr>
<tr>
<td>b, Å</td>
<td>10.356(3)</td>
<td>9.4881(6)</td>
<td>9.2702(7)</td>
<td>14.2274(18)</td>
<td>10.828(4)</td>
</tr>
<tr>
<td>c, Å</td>
<td>10.801(3)</td>
<td>18.6761(11)</td>
<td>11.5227(9)</td>
<td>22.082(3)</td>
<td>23.884(7)</td>
</tr>
<tr>
<td>α, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>117.012(3)</td>
<td>91.6770(10)</td>
<td>113.8560(10)</td>
<td>108.344(2)</td>
<td>90</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>Volume, Å³</td>
<td>989.1(4)</td>
<td>1046.33(11)</td>
<td>1053.63(14)</td>
<td>4237.9(9)</td>
</tr>
<tr>
<td>------------------------</td>
<td>-------------</td>
<td>----------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Z</td>
<td></td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>Density, mg/m³</td>
<td></td>
<td>1.318</td>
<td>1.360</td>
<td>1.464</td>
<td>1.456</td>
</tr>
<tr>
<td>F(000)</td>
<td></td>
<td>408</td>
<td>440</td>
<td>472</td>
<td>1888</td>
</tr>
<tr>
<td>Theta range, deg</td>
<td></td>
<td>2.31 – 25.05</td>
<td>2.41 – 25.05</td>
<td>2.93 – 25.05</td>
<td>1.94 – 25.05</td>
</tr>
<tr>
<td>Index ranges</td>
<td>±11 ±12 ±12</td>
<td>±7 ±11 ±22</td>
<td>±12 ±10 – 13</td>
<td>±16 ±16 ±26</td>
<td>±10 ±12 ±28</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td></td>
<td>0.9912 and 0.9678 and 0.9645 and 0.9751 and 0.9892 and 0.9826 and 0.9552 and 0.9530 and 0.9510 and 0.9799</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GOF</td>
<td></td>
<td>1.888</td>
<td>1.114</td>
<td>0.805</td>
<td>1.876</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td></td>
<td>R₁ = 0.0965, wR₂ = 0.2804</td>
<td>R₁ = 0.0322, wR₂ = 0.1231</td>
<td>R₁ = 0.0359, wR₂ = 0.1096</td>
<td>R₁ = 0.0634, wR₂ = 0.1733</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td></td>
<td>R₁ = 0.1233, wR₂ = 0.2942</td>
<td>R₁ = 0.0362, wR₂ = 0.1292</td>
<td>R₁ = 0.0443, wR₂ = 0.1209</td>
<td>R₁ = 0.0766, wR₂ = 0.1776</td>
</tr>
</tbody>
</table>
The summary of crystallographic data for tolanes 2.2a – 2.2e are listed below in Table 2.1 and the crystal structure for each will be discussed individually in detail. By gradually changing the fluorination level of one aromatic ring in the tolanes, a change of crystal structure can be observed from mono-fluorinated tolane 2.2a through to the tetra-fluorinated compound 2.2e. This phenomenon might be attributed to an increase in fluorine-involving intermolecular interactions such as $C_{sp2}−H⋯F–C_{sp2}$ and $C_{sp2}−F⋯π^{18}$ from more fluorine atoms. All the cif data files in this section are provided by Prof. Bunge et al. and the figures are generated by Mercury 3.6 software. In the figures, blue lines represent the interactions between the molecules shown in the figure and red lines represent the expand interactions that formed with nearby molecules which are not shown in the figures.

Before the discussion of newly prepared samples, it is worthwhile to obtain some insight about the structure of the parent non-fluorinated tolane diphenylacetylene (DPHACT). Overall, the tolane molecules perform a herringbone stacking in the lattice and this kind of packing is attributed by C-H⋯π interactions (with π electrons of aromatic ring and C-C triple bonds). Also, all the atoms in the tolane molecule are located in the same plane and no obvious twisting angle can be observed between the two benzene rings.
Figure 2.2 Crystal packing of diphenylacetylene (DPHACT), showing C-H···π interactions (Bottom figure).
With one proton substituted by fluorine atom at the 4-position, the crystal structure of 1-fluoro-4-(phenylethynyl)benzene (2.2a) is shown in Figure 2.3. The structure consists of four non-equivalent molecules, which shows some similarity as the parent non-fluorinated diphenylacetylene (DPHACT). The four non-equivalent tolane molecules can be grouped into two categories and the tolane molecules in each category are “head tail” aligned via the H···F intermolecular interactions (2.504 Å) and perform a partial cofacial stacking between neighborhood layers. Furthermore, two series of molecules form a T-shaped configuration with each other by C\textsubscript{sp2}-H···π interactions (2.876 Å, 2.894 Å).

There are two more monofluorotolane isomers but neither of them were examined in this study.
**Figure 2.3** Crystal structure of 1-fluoro-4-(phenylethynyl)benzene, shows the H···F intermolecular interactions (top) and C(sp²)-H···π interactions (bottom right).
With one more fluorine atom than 2.2a, the crystal lattice of 1,3-difluoro-2-(phenylethynyl)benzene (2.2b) also consists four non-equivalent molecules and the packing of molecules is also quite similar to 2.2a (Figure 2.4) - parallel molecules are aligned “head to tail” by the effect of $\text{C}_{\text{sp}2}-\text{H}\cdots\text{F} - \text{C}_{\text{sp}2}$ (2.637 Å, 2.551 Å). Also, the non-parallel molecules also bear the $\text{C}_{\text{sp}2}-\text{H}\cdots\pi - \text{C}_{\text{sp}}$ (2.878 Å) T-shaped interactions which stabilize the whole crystal structure. Also, there are $\text{C}_{\text{sp}2}-\text{F}\cdots\text{F} - \text{C}_{\text{sp}2}$ (2.926 Å) contacts that exist in this packing and according to the rule discussed before, this should just be a result of continuous crystal packing.

There are also five additional difluoro tolane isomers with both fluorines in the same ring but none of these were examined in this study.
Figure 2.4 Crystal packing of 1,3-difluoro-2-(phenylethynyl)benzene (top), C\(_{sp2}\)−H⋯F−C\(_{sp2}\) interactions and F⋯F contacts (middle), C\(_{sp2}\)−H⋯π interaction (bottom).
For the trifluorinated tolanes, two different isomeric molecules were investigated - 1,3,5-trifluoro-2-(phenylethynyl)benzene (2.2c) and 1,2,3-trifluoro-5-(phenylethynyl)benzene (2.2d). In 1,3,5-trifluoro-2-(phenylethynyl)benzene (2.2c) (Figure 2.5), the intermolecular interactions are similar but much more complicated than 2b resulting from the presence of one additional fluorine atom. The parallel molecules are still fixed by C_sp2−H···F−C_sp2 (2.500 Å) interactions head to tail. For the non-parallel molecules, C_sp2−H···F−C_sp2 (2.654 Å) and C_sp2−F···πF (~ 3 Å) effects were observed.
Figure 2.5 Crystal structures of 1,3,5-trifluoro-2-(phenylethynyl)benzene (top), \( C_{sp^2}-H \cdots F-C_{sp^2} \) interactions (middle) and \( C_{sp^2}-F \cdots \pi F \) interactions (bottom).
Similar to **2.2c**, compound 1,2,3-trifluoro-5-(phenylethynyl)benzene (**2.2d**) is also tri-fluorinated, but it gave a much more complicated crystal lattice containing 16 non-equivalent molecules (**Figure 2.6**). The tolane molecules in **2.2d** could also be separated into two categories – 8 molecules in the lattice are roughly parallel to axis *a* and another 8 of them are roughly parallel to axis *b*. The parallel molecules are still connected head-to-tail via C_{sp2}−H···F−C_{sp2} (2.438 Å, 2.385 Å) interactions. Also, C_{sp2}−F···π (~3.1 Å, 2.885 Å) interactions play an important role between non-parallel molecules and hold them together.

There are four additional trifluoro tolane isomers with both fluorine atoms in the same ring but these were not examined in this study.
Figure 2.6 Crystal structures 1,2,3-trifluoro-5-(phenylethynyl)benzene - 8 molecules in the lattice are paralleled to axis $a$ (top), 8 parallel to axis $b$ (middle). F involved interactions are shown in the bottom figure.
The crystal structure of 1,2,4,5-tetrafluoro-3-(phenylethynyl)benzene (2e) (Figure 2.7) is dramatically different than the crystal structures described before as all the 8 non-equivalent molecules in the lattice are perfectly parallel to axis c through $\text{C}_\text{sp}^2\text{H} \cdots \text{F} \cdots \text{C}_\text{sp}^2$ (2.623 Å) interactions in the lattice. Furthermore, this kind of intermolecular interaction in the matrix also provides another special property for the crystal structure of 2e – the non-fluorinated ring and tetra-fluorinated ring has a torsion angle as high as 60 degrees, which in comparison is negligible in compounds 2a to 2d and even the previous reported diphenylacetylene (DPHACT) and fully-fluorinated 1-pentafluorophenyl-2-phenylacetylene (ASIJIV).
Figure 2.7 Crystal structure of 1,2,4,5-tetrafluoro-3-(phenylethynyl)benzene, shows the C\(_{sp2}\)−H···F−C\(_{sp2}\) interaction matrix (bottom left) and the torsion angle of two aromatic rings (bottom right).
To make much a more thorough comparison, the structures of 1-pentafluorophenyl-2-phenylacetylene (ASIIV) (Figure 2.8) and perfluorodiphenylacetylene (PFDPAY) (Figure 2.9) are also shown here. The 1-pentafluorophenyl-2-phenylacetylene (ASIIV) molecules give a cofacial stacking with the aryl-perfluoroaryl interaction distance at 3.370 Å and the molecules in the same layer are parallel with each other with C_{sp2}−H···F−C_{sp2} interactions (2.545 Å). The torsion angle of two aromatic rings looks very small, which is very difference comparing to tetrafluoro compound 2e features a huge torsion angle as high as 60 degrees.
Finally, we also considered the crystal structure of perfluorodiphenylacetylene (PFDPAY). In the lattice, all the molecules are parallel with the $c$ axis. However, if we look from the $c$ axis, it obviously shows a T shaped stacking which is similar to hexafluorobenzene. Furthermore, the formation mechanism of this is also the same as hexafluorobenzene – the $C$-$F\cdots\pi$F interactions ($3.104$ Å, $3.097$ Å, $3.056$ Å).

*Figure 2.9* Crystal structure of perfluoro diphenylacetylene (PFDRAY). Viewed from $a$ axis (top), viewed from $c$ axis (middle) and $C$-$F\cdots\pi$F interactions (bottom).
2.4. X-ray crystallography analysis of 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives

The crystallographic data for the parent 1,2,4,5-tetra(phenylethynyl)benzene 2.5, 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives 2.9a, 2.9b, 2.9c) and 1,4-bis(3’,5’-bistrifluoromethylphenylethynyl)-2,5-bis(phenylethynyl)benzene (2.9d) are summarized in Table 2.2. As all of them formally include four tolane backbones (with the center ring the site of superposition) and more intramolecular interactions, still more complicated crystal structures might be anticipated. What is worthy of emphasis here is that four of the 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives (2.5, 2.9a, 2.9b, 2.9c) give T shaped crystal packing while the most fluorinated 1,4-bis(pentafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (2.9d), is a maverick that has a distinctly different arene–perfluoroarene stacking.
Table 2.2 Summary of crystallographic and refinement data for Compound 2.5, 2.9a-2.9d.

<table>
<thead>
<tr>
<th>Compound</th>
<th>2.5</th>
<th>2.9a</th>
<th>2.9b</th>
<th>2.9c</th>
<th>2.9d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{38}H_{22}</td>
<td>C_{38}H_{20}F_{2}</td>
<td>C_{38}H_{14}F_{8}</td>
<td>C_{38}H_{12}F_{10}</td>
<td>C_{42}H_{18}F_{12}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>478.56</td>
<td>514.54</td>
<td>622.49</td>
<td>658.48</td>
<td>750.56</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>P21/n</td>
<td>P</td>
<td>P-1</td>
<td>P21/c</td>
</tr>
<tr>
<td>a, Å</td>
<td>30.719(10)</td>
<td>6.559(3)</td>
<td>12.399(12)</td>
<td>7.6837(7)</td>
<td>19.158(3)</td>
</tr>
<tr>
<td>b, Å</td>
<td>4.9071(15)</td>
<td>19.693(9)</td>
<td>5.177(5)</td>
<td>11.4649(10)</td>
<td>4.6466(8)</td>
</tr>
<tr>
<td>c, Å</td>
<td>18.732(6)</td>
<td>10.247(5)</td>
<td>22.337(19)</td>
<td>16.8125(15)</td>
<td>19.033(3)</td>
</tr>
<tr>
<td>α, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>106.800(2)</td>
<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>111.528(6)</td>
<td>96.169(7)</td>
<td>106.154(14)</td>
<td>97.005(2)</td>
<td>107.913(3)</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>95.825(2)</td>
<td>90</td>
</tr>
<tr>
<td>Volume, Å³</td>
<td>2626.7(14)</td>
<td>1315.9(10)</td>
<td>1377(2)</td>
<td>1392.6(2)</td>
<td>1612.2(5)</td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
<td>------------</td>
<td>----------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Density, mg/m³</td>
<td>1.210</td>
<td>1.299</td>
<td>1.501</td>
<td>1.570</td>
<td>1.546</td>
</tr>
<tr>
<td>F(000)</td>
<td>1000</td>
<td>532</td>
<td>628</td>
<td>660</td>
<td>756</td>
</tr>
<tr>
<td>Theta range, deg</td>
<td>1.43 – 25.05</td>
<td>2.07 – 25.05</td>
<td>1.71 – 25.05</td>
<td>1.28 – 25.05</td>
<td>1.12 – 25.05</td>
</tr>
<tr>
<td>Index ranges</td>
<td>±36 ±5 ±22</td>
<td>±7 ±23 ±12</td>
<td>±14 ±6 ±26</td>
<td>±9 ±13 ±20</td>
<td>±22 ±5 ±22</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9932 and 0.9797</td>
<td>0.9834 and 0.9672</td>
<td>0.9901 and 0.9816</td>
<td>0.9864 and 0.9534</td>
<td>0.9890 and 0.9663</td>
</tr>
<tr>
<td>GOF</td>
<td>1.090</td>
<td>0.738</td>
<td>0.909</td>
<td>0.803</td>
<td>0.987</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁ = 0.0670, wR₂ = 0.1711</td>
<td>R₁ = 0.0526, wR₂ = 0.1300</td>
<td>R₁ = 0.0635, wR₂ = 0.1403</td>
<td>R₁ = 0.0408, wR₂ = 0.1149</td>
<td>R₁ = 0.0501, wR₂ = 0.1317</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1121, wR₂ = 0.1978</td>
<td>R₁ = 0.1392, wR₂ = 0.1706</td>
<td>R₁ = 0.2267, wR₂ = 0.2372</td>
<td>R₁ = 0.0689, wR₂ = 0.1446</td>
<td>R₁ = 0.0932, wR₂ = 0.1690</td>
</tr>
</tbody>
</table>
The crystal structure of the non-fluorinated parent 1,2,4,5-tetrakis(phenylethynyl)benzene (Figure 2.10) is much more complicated than that of the tolanes already discussed. Overall, two series of 1,2,4,5-tetrakis(phenylethynyl)benzene molecules are aligned inside the crystal lattice and form a T-shaped configuration with each other. Similar to benzene, this T-shaped packing is also the result of C-H···π interactions. In fact, the real crystal structure is much more complicated than this, as some of the phenylethynyl chains have some rotational freedom and thus the crystal is partially disordered.
Figure 2.10 Crystal packing of 1,2,4,5-tetrakis(phenylethynyl)benzene, shows the interactions that lead to the T shaped stacking (bottom). Two rings in each molecule (para-position) show disorder in the crystal.
In compound 1,4-bis(\(\rho\)-fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene \(2.9a\) (Figure 2.11), the crystal structure is similar as the previous non-fluorinated counterpart \(2.5\). \(\text{C}_{\text{sp}2}\cdot\cdot\cdot\text{H}\cdots\text{F} = \text{C}_{\text{sp}2}\) (2.574 Å) interactions keeps one series of molecules parallel with each other side by side and the \(\text{C}_{\text{sp}2}\cdot\cdot\cdot\text{H}\cdots\pi\) (2.872 Å, 2.857 Å) interactions make a different series of molecules form the T-shaped structure. Compared with the non-fluorinated parent compound \(2.5\), compound \(2.9a\) does not have any disordered packing, which might due to the influence of H\cdots F interactions.
Figure 2.11 1,4-bis(p-fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (top), shows the C(sp²)−H···F−C(sp²) interactions and C(sp²)−H···π interactions (bottom).
In 1,4-bis(2,3,5,6-tetrafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (2.9b) (Figure 2.12), with a much higher level of fluorination, the carbon atoms on the fluorinated aromatic rings become electron deficient and now close contact with the electron rich carbon atoms in the C-C triple bonds (~ 3.3 Å). Aside of this, all other types of previous discussed interactions such as C\textsubscript{sp2}−H···F− C\textsubscript{sp2} (2.628 Å), C\textsubscript{sp2}−H···π (2.895 Å) and C\textsubscript{sp2}−F···F− C\textsubscript{sp2} (2.790 Å, 2.930 Å) can also be found in this crystal structure.
Figure 2.12 Crystal packing of 1,4-bis(2,3,5,6-tetrafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (top) and various intermolecular interactions (bottom).
The presence of the perfluorinated aromatic rings in 1,4-bis(pentafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (2.9d) dramatically changed the crystal packing pattern (Figure 2.13). Molecules no longer align in two different directions to form the T-shaped packing. Instead, all of the molecules are tightly aligned with the interval stacking of nonfluoro and pentafluoro side-chains, which might be attributed to π-interactions that was found in the crystal structure of the 1:1 benzene:hexafluorobenzene mixture\textsuperscript{19,20} and 1-pentafluorophenyl-2-phenylacetylene (ASIJIV)\textsuperscript{3}. Aside of this major effect, other kinds of interactions as $\text{C}_{\text{sp2}}$−$\text{H}$···$\text{F}$−$\text{C}_{\text{sp2}}$ (2.531 Å), $\text{C}_{\text{sp2}}$−$\text{F}$···π (3.113 Å, 3.130 Å, 3.061 Å, 3.111 Å), $\text{C}_{\text{sp2}}$−$\text{F}$···$\text{F}$−$\text{C}_{\text{sp2}}$ (2.780 Å, 2.800 Å) are also extremely complicated, which make the perfluorinated rings form a torsion angle as large as approximately 30 degrees relative to the central ring.
Figure 2.13 Crystal packing of 1,4-bis(pentafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (top), shows the torsion
For the special compound **2.9d**, two protons (3,5-positions) in two opposite sidechains are substituted by trifluoromethyl groups. In spite of these large groups, the packing of 1,4-bis(3’,5’-bistrifluoromethylphenylethynyl)-2,5-bis(phenylethynyl)benzene is quite similar to the non-fluorinated compound **2.5** discussed previously. However, the presence of the CF₃- groups is manifested in the structure. Because of the steric demand of the large CF₃- groups, the four aromatic rings on the side chains are now impossible to locate in the same plane (torsion angle as high as 41°). Aside of the Cₛᵖ₂−H⋯π (2.836 Å) attractions make the non-fluorinated side chains form a T-shaped structure, Cₛᵖ₂−H⋯π (3.135 Å) interactions made the crystal structure more complicated. Furthermore, in this case, the four carbon atoms connecting the fluorinated side chain and the center benzene ring (including the two carbon atoms in C-C triple bond) are not in a straight line but have a large bend as high as 8 degrees.
Figure 2.14 Crystal structure of 1,4-bis(3',5'-bistrifluoromethylphenylethynyl)-2,5-bis(phenylethynyl)benzene, shows the torsion of CF₃ equipped aromatic ring (middle) and the bent of C-C triple bond (bottom).
2.5. Summary and discussion

After significant effort, we finally obtained the single crystal structure of some 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives. Although it was impossible to obtain a single crystal structure for all of them, the most important compound 1,4-bis(pentafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene was finally well documented. In the crystal packing, we indeed observed that the molecules possess an arene-perfluoroarene interval stacking just as its parent compound 2,3,4,5,6-pentafluorodiphenylacetylene (AISJIV). However, this substance is not the perfect molecule that all the atoms are located in the same plane – two of the side chain aromatic ring (50% of non-fluorinated aromatic rings and 50% of perfluorinated ones) will form a torsion angle as large as 30 degrees out of the main plane of the molecules.

After some simple considerations, there may be at least two reasons that lead to this torsion. The first reason has already been mentioned above, the fluorine atom located on the twisted perfluorinated rings would like to form $C_{sp^2}$−$F\cdots p$ interactions with the adjacent electron rich acetylenes and these interactions might pull the perfluorinated ring out of the main plane of the molecule (Figure 2.15). These torsions will also influence the non-fluorinated aromatic rings that have arene-perfluoroarene attractions with them.
The second reason for the torsion looks much simpler: if all the atoms in 1,4-bis(pentafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene can locate in the same plane, the distance of closest H and F atoms will be as near as approximately 1.76 Å. This distance is much shorter than the common C-F···H interactions in organic compounds and just 21nm longer than the distance of adjacent H and F atoms in HF orthorhombic crystals. Under this circumstance, a repulsion might occur between the nearby H and F (see Fig 2.16) atoms and push the rings to which they are attached to form a torsion angle. The torsion may be accommodated in one bistolane linkage (as in the case of what is show in Fig 2.16) or could be accommodated with torsions in both of the crossed terphenyls.
To solve this problem and obtain a “flat” molecule to perform the arene-perfluoroarene stacking, the best solution might be use some technique to form a new stable covalent bond between the side chains of nonfluorinated and perfluorinated aromatic rings and thus force them in the same plane. This inspiration promoted us to discover and develope a new derivative of Mallory photocyclization – the photocyclodehydrofluorination (PCDHF).
2.6. Experiment procedures

2.6.1. The synthesis of fluorinated tolanes

1-(4-fluorophenyl)phenylacetylene (2.2a)

![Chemical structure](image)

Chemical Formula: $C_{14}H_9F$
Molecular Weight: 196.22

A 100 mL two-necked flask with magnetic stir bar was flushed by nitrogen, and then PdCl$_2$ (0.03542 g, 0.20 mmol), PPh$_3$ (0.2110 g, 0.80 mmol) and anhydrous diethylamine (5 mL) were added in sequence. After being stirred at 45 °C for half an hour, CuI (0.01942 g, 0.10 mmol) was also added to give a dark-yellow colored mixture. Next, more anhydrous diethylamine (15 mL) was added and then followed by $p$-fluoriodobenzene (4.445 g, 20.0 mmol) and phenylacetylene (2.052 g, 20.0 mmol). During the whole reaction, the temperature was kept at 45 °C for 15h (overnight). After that, the solvent was removed by rotary evaporation, diethyl ether (100 mL) was added into the brown colored residue and the insoluble salts were filtered off. The solution was then washed with water (3 x 50 mL) and dried over anhydrous MgSO$_4$. MgSO$_4$ was removed by gravity filtration and the solvent was removed by rotary evaporation. The dark-yellow colored residue was subjected to chromatography (hexane eluent) and a white solid (3.540 g, 18.0 mmol, 90% yield) was obtained.

**MP:** 102.5-104.8 °C (Lit: 105.5 – 106.5 °C).

$^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ 7.58 (m, 4H), 7.39 (m, 3H), 7.09 (t, $J = 8.4$ Hz, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, TMS): $\delta$ 163.57 (d, $J = 240$ Hz), 133.50 (d, $J = 8.0$ Hz), 131.59, 128.38 (d, $J = 4.2$ Hz), 123.14, 119.43, 115.66 (d, $J = 22.0$ Hz), 89.10, 88.35.
1-(2,6-difluorophenyl)phenylacetylene (2.2b)

\[
\begin{array}{c}
\text{Chemical Formula: } C_{14}H_9F_2 \\
\text{Molecular Weight: 214.21}
\end{array}
\]

A 100mL two-necked flask with magnetic stir bar was flushed thoroughly with nitrogen. And then, PdCl\(_2\) (0.01836 g, ~ 0.10 mmol), PPh\(_3\) (0.1139 g, ~ 0.40 mmol), CuI (0.01003 g, ~ 0.05 mmol) and diisopropylamine (15 mL) were added in sequence. After stirring under nitrogen at 70 °C for one hour, a yellow colored suspension was obtained. After that, 2,6-difluoroiodobenzene (2.396 g, 10 mmol) and phenylacetylene (1.088 g, ~ 10 mmol) were added inside in sequence. After being stirring under nitrogen at 75 °C for 20h, TLC indicated that there was no starting material. The mixture was cooled down and the solvent was removed by rotary evaporation to give a yellow residue. The yellow residue was subjected to column chromatography (Eluent: Hexane) directly, giving 2.025g (9.4 mmol, 94 % yield) of white crystals as product.

**MP:** 36.0 – 42.0 °C (No Lit M.P. data).

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS): 7.647-7.623 (m, 2H), 7.423-7.398 (m, 3H), 7.336-7.262 (m, 1H), 6.972 (dd, \(^1\)J = 8.4 Hz, \(^2\)J = 7.2 Hz, 2H).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\), TMS): 163.019 (dd, \(^1\)J = 252 Hz, \(^2\)J = 5.2 Hz), 131.813, 129.631 (t, \(J = 9.8 \) Hz), 128.941, 128.401, 122.609, 111.209 (dd, \(^1\)J = 18.6 Hz, \(^2\)J = 5.5 Hz), 102.496, 99.218, 76.210.
$^{19}$F-NMR (376 MHz, CDCl$_3$, TMS): -107.43.

**Reference:** Feuerstein, Marie; Berthiol, Florian; Doucet, Henri; Santelli, Maurice *Synthesis, 2004*, 1281 - 1289

**1-(2,4,6-trifluorophenyl)phenylacetylele (2.2c)**

![Chemical Structure](image)

Chemical Formula: C$_{14}$H$_7$F$_3$

Molecular Weight: 232.21

A 100mL two-necked flask with magnetic stir bar was flushed with nitrogen, and then PdCl$_2$ (0.01814 g, 0.10 mmol), PPh$_3$ (0.1087 g, 0.40 mmol), CuI (0.01076 g, 0.05 mmol) and diisopropylamine (15 mL) were added in sequence. After stirring under nitrogen at 75 °C for one hour, a yellow colored mixture was obtained. Next, 1-bromo-2,4,6-trifluorobenzene (2.117 g, 10.0 mmol) and phenylacetylene (1.042 g, ~10.0 mmol) were also added in sequence. After stirring under nitrogen at 75 °C for 24h the TLC indicated that there was no starting material. The mixture was cooled down and the solvent was removed by rotary evaporation to give a light-yellow solid. Ethyl acetate (100 mL) was added and the insoluble salt was isolated via filtration. The filtrate was concentrated and subjected to column chromatography (Hexane:EtOAc = 20:1) to give the product as a white solid (1.419 g, 61% yield).

**MP:** 69.0 – 71.5 °C.

$^1$H NMR (400 MHz, CDCl$_3$, TMS): 7.61-7.59 (m, 2H), 7.41-7.38 (m, 3H), 6.75 (dd, $^1J$ = 8.6 Hz, $^2J$ = 7 Hz, 2H)

$^{13}$C-NMR (100 MHz, CDCl$_3$, TMS): 163.226 (ddd, $^1J$ = 253 Hz, $^2J$ = 8 Hz, $^3J$ = 8 Hz), 162.230
(dt, \( J = 251 \text{ Hz} \), \( J = 15 \text{ Hz} \)), 131.749, 130.86 (d, \( J = 330 \text{ Hz} \)), 128.987, 128.405, 122.411, 101.69, 100.490 (m), 87.335.

\(^{19}\text{F-NMR (376 MHz, CDCl}_3, \text{TMS)}: -104.37, -105.26.

1-(3,4,5-trifluorophenyl)phenylacetylene (2.2d)

\[
\begin{array}{c}
\text{F} \\
\cdot \\
\text{F} \\
\cdot \\
\text{F}
\end{array}
\]

Chemical Formula: \( \text{C}_{14}\text{H}_7\text{F}_3 \)
Molecular Weight: 232.21

A 100mL two-necked flask and magnetic stir bar were flushed with nitrogen, and then \( \text{PdCl}_2 \) (0.01802 g, 0.10 mmol, 1 %), \( \text{PPh}_3 \) (0.1056 g, 0.40 mmol, 4 %) and anhydrous diethylamine (4 mL) were added in sequence. The mixture was stirred at 45 °C for half an hour, then \( \text{CuI} \) (0.009954 g, 0.05 mmol, 0.5 %) was added to give a dark-yellow colored mixture. Next, more anhydrous diethylamine (8 mL) and then followed by 3,4,5-triflorobromobenzene (2.111 g, 10.0 mmol) and phenylacetylene (1.131 g, 11.0 mmol). The temperature was kept at 45 °C for 6h until no starting material can be observed by TLC. After that, solvent was removed by rotary evaporation, diethyl ether (50 mL) was added into the yellow residue and the insoluble white salt was filtrated off. The solution was washed with water (3 x 25 mL) and dried over anhydrous MgSO\(_4\). After removing MgSO\(_4\) by filtration, solvent was removed by rotary evaporation. The dark yellow colored residue was subjected to chromatography (Hexane:EtOAc = 20:1 eluent) to give the product as a white solid (1.745 g, 7.5 mmol, 75% yield).

**MP:** 95.0 - 98.0 °C (Lit. 95.5 – 96.5 °C).
\[ ^1\text{H NMR (400 MHz, CDCl}_3, \text{TMS):} \delta 7.54 \text{ (m, 2H), 7.40 (m, 3H), 7.17(dd, } ^1J = 8 \text{ Hz, } ^2J = 6.4 \text{ Hz, 2H).} \]

\[ ^{13}\text{C-NMR (100 MHz, CDCl}_3, \text{TMS):} \delta 151.02 \text{ (ddd, } ^1J = 250 \text{ Hz, } ^2J = 10 \text{ Hz, } ^3J = 5.3 \text{ Hz), 140.25 (dt, } ^1J = 250 \text{ Hz, } ^2J = 15 \text{ Hz), 131.68, 128.97, 128.47, 122.17, 119.25 (t, } J = 5 \text{ Hz), 115.82 (dd, } ^1J = 16 \text{ Hz, } ^2J = 6.3 \text{ Hz), 90.90, 86.25.} \]

Reference: Sakaguchi, Toshikazu; Shiotsuki, Masashi; Sanda, Fumio; Freeman, Benny D.; Masuda, Toshio *Macromolecules*, 2005, Vol. 38, 8327 - 8332

**1-(2,3,5,6-tetrafluorophenyl)phenylacetylene (2.2e)**

![Chemical Structure](image)

Chemical Formula: C\(_{14}\)H\(_6\)F\(_4\)
Molecular Weight: 250.20

A 100mL two-necked flask with magnetic stir bar was flushed with nitrogen, and then PdCl\(_2\) (0.01768 g, 0.10 mmol), PPh\(_3\) (0.1080 g, 0.40 mmol), CuI (0.01018 g, 0.05 mmol) and diisopropylamine (15 mL) were added in sequence. After stirring under nitrogen at 75 °C for one hour, a yellow colored mixture was obtained. Next, 1-bromo-2,3,5,6-tetrafluorobenzene (1.150 g, 5.0 mmol) and phenylacetylene (0.536 g, ~ 5.0 mmol) were added in sequence. Stirring under nitrogen at 75 °C was continued for 20h and TLC indicated that there was no starting material. After that, the mixture was cooled down and the solvent was removed by rotary evaporation to give a dark-brown residue. Ethyl acetate (50 mL) was added and the insoluble salts were isolated via filtration. The filtrate was concentrated and subjected to column chromatography (hexane) to give a white crystals (1.139 g, 91 % yield).
**MP:** 90.0 – 92.0 °C (Lit. 82 – 88 °C).

$^1$H NMR (400 MHz, CDCl$_3$, TMS): 7.641-7.617 (m, 2H), 7.451-7.407 (m, 3H), 7.071 (tt, $^1J = 9.6$ Hz, $^2J = 7.2$ Hz, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, TMS): 146,650 (dd, $^1J = 250$ Hz, $^2J = 15$ Hz), 145.806 (dm, $^1J = 246$ Hz), 131.962, 129.600, 128.504, 121.6918, 106.048 (t, $^1J = 23$ Hz), 101.822, 74.380.

$^{19}$F-NMR (376 MHz, CDCl$_3$, TMS): -136.750, -139.057

**Reference:** Wiles; Massey Tetrahedron Letters, 1967, p. 5137

### 2.6.2. The synthesis of 1,4-bis(fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene derivatives

**1,4-dibromo-2,5-diiodobenzene (2.4)**

![Chemical structure of 1,4-dibromo-2,5-diiodobenzene](image)

**Chemical Formula:** C$_8$H$_2$Br$_2$I$_2$

**Molecular Weight:** 487.70

1,4-Dibromobenzene (5.816 g, 25.0 mmol) and iodine (23.9 g, 95.0 mmol) and concentrated sulfuric acid (80 mL) were charged into a 250 mL flask. The resulting mixture was heated to 140 °C for 12 hours. After that, the mixture was cooled to room temperature and poured into a mixture of ice and water. Na$_2$SO$_3$ powder (~ 30 g) was added to remove excess iodine. After that, the crude product was isolated by suction filtration and recrystallized from 2-butanol to provide pure final product (3.677 g, 7.0 mmol, 28 % yield).

**MP:** 158.0 – 160.0 °C (Lit: 160 – 162 °C).
\[^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3, \text{TMS}): \delta 8.075 \text{ (s, 2H).} \]

\[^{13}\text{C-NMR} \ (100 \text{ MHz, CDCl}_3, \text{TMS}): \delta 142.299, 133.156, 121.089. \]

**Reference:** Modjewski, Matthew; Lindeman, Sergey V.; Rathore, Rajendra Organic Letters, 2009, *Vol. 11*, 4656 - 4659

\[1,2,4,5\text{-tetra(phenylethynyl)benzene} \ (2.5)\]

![Chemical structure of 1,2,4,5-tetra(phenylethynyl)benzene](image)

Chemical Formula: \(\text{C}_{38}\text{H}_{22}\)
Molecular Weight: 478.59

A 50 mL round bottom flask was charged with \(\text{PdCl}_2\) (0.0167 g, \(1.0 \times 10^{-4}\) mol), \(\text{CuI}\) (0.0086 g, \(4.5 \times 10^{-5}\) mol) and triphenylphosphine (0.097 g, \(3.7 \times 10^{-4}\) mol) in diethylamine (2 mL). The mixture was mixed well and then 1,4-dibromo-2,5-diiodobenzene (2.01 g, \(4.1 \times 10^{-3}\) mol), phenylacetylene (1.95 g, 0.019 mol) and more diethylamine (20 mL) were added and the mixture was stirred under nitrogen at 75 °C for 6 hours. After that, the resulting mixture was cooled and concentrated. After purification by column chromatography (Hexane), the final product (1.634 g, \(3.4 \times 10^{-3}\) mol, 82 % yield) was obtained as white crystals.

**MP:** 187.5-191.7 °C (Lit. 193 – 194 °C).

\[^1\text{H NMR} \ (400 \text{ MHz, Tetrachloroethane-d}_2, \text{TMS}): \delta 7.880 \text{ (s, 2H), 7.706 – 7.683 (m, 8H), 7.487 – 7.455 (m, 12H).} \]

\[^{13}\text{C-NMR} \ (100 \text{ MHz, Tetrachloroethane-d}_2, \text{TMS}): \delta 135.109, 131.972, 129.108, 128.726, \]
A 50 mL round bottom flask was charged with PdCl₂ (0.00879 g, 0.50 x 10⁻⁴ mol), CuI (0.0044 g, 2.2 x 10⁻⁵ mol) and triphenylphosphine (0.042 g, 1.6 x 10⁻⁴ mol) in diethylamine (2 mL). The obtained mixture was well mixed to achieve a yellow mixture. Then 1,4-dibromo-2,5-diiodobenzene (2.010 g, 4.1 x 10⁻³ mol), phenylacetylene (0.985 g, 9.6 x 10⁻³ mol) and more diethylamine (10 mL) were added inside and the mixture was stirring under nitrogen at 75 °C for 6 hours. After that, the resulting mixture was cooled and concentrated. After purified by column chromatography (Hexane), a white crystal (1.120 g, 2.56 mmol, 62 % yield) was obtained as final product.

**MP:** 156.5 – 158.0 °C (Lit: 165 – 167 °C).

**¹H NMR (400 MHz, CDCl₃, TMS):** 7.784 (s, 2H), 7.589 – 7.565 (m, 4H), 7.389 – 7.372 (m, 6H).

**¹³C NMR (100 MHz, CDCl₃, TMS):** 136.029, 131.814, 129.144, 128.477, 126.423, 123.732, 122.314, 96.668, 86.815.
Palladium chloride (17.91 mg 0.10 mmol), triphenylphosphine (54.30 mg 0.20 mmol), copper(I) iodide (50.07 mg 0.26 mmol) and diisopropylamine (5mL) were added successively. Stir until a yellow colored mixture was obtained. Then, the temperature was heated up to 50 °C and 1,4-dibromo-2,5-bis(phenylethynyl)benzene (2.189 g 5 mmol), diisopropylamine (50 mL), toluene (50 mL) and trimethylsilylacetylene (1.103g 11mmol) were also added successively. The reaction was run at this temperature under nitrogen protection for 10h, then all the solvent was removed at reduced pressure. The residue was dissolved by dichloromethane (100 mL) and washed by water (3 x 100 mL). The organic phase was dried (MgSO₄) and all the solvent was removed under reduced pressure. The residue was purified via chromatography (Hexane:EtOAc=10:1) to give a yellow solid, which was recrystallized from toluene to give the product as light-yellow crystals (1.467 g 3.1 mmol, 62% yield).

**MP:** 206.0 – 208.0 °C.

**¹H NMR (400 MHz, CDCl₃, TMS):** 7.775 (s, 2H), 7.584 – 7.529 (m, 4H), 7.399 – 7.335 (m,6H),
0.273 (s, 18H)

$^{13}$C NMR (100 MHz, CDCl$_3$, TMS): 135.400, 131.778, 128.723, 128.380, 125.442, 125.313, 122.967, 102.349, 100.965, 95.382, 87.339, 0.068.

1,4- bis(phenylethynyl) -2,5- bis(trimethylsilylthynyl) benzene (2.8)

![Chemical Structure of 1,4- bis(phenylethynyl) -2,5- bis(trimethylsilylthynyl) benzene](image)

Chemical Formula: C$_{26}$H$_{14}$
Molecular Weight: 326.40

Bis(phenylethynyl)-2,5-bis(trimethylsilylthynyl) benzene (1.412 g 3.00 mmol) was dissolve in a mixture of methanol (100 mL) and dichloromethane (100 mL). Potassium carbonate (4.155g, 30 mmol) was added to the solution and the mixture was stirred overnight at room temperature. The reaction was then subjected to an aqueous workup (200mL brine) and the aqueous phase was extracted by dichloromethane (3 x 100 mL). After drying the combined organic layers (anhydrous MgSO$_4$), the solvent was removed under reduced pressure to give a light-yellow solid (0.965 g 2.96 mmol, 98.6% yield).

**MP:** 184.0 – 185.0 °C.

$^1$H NMR (400 MHz, CDCl$_3$, TMS): 7.695 (s, 2H), 7.573 – 7.549 (m, 4H), 7.380 – 7.350 (m, 6H), 3.450 (s, 2H)

$^{13}$C NMR (400 MHz, CDCl$_3$, TMS): 135.650, 131.863, 128.890, 128.423, 125.786, 124.794, 122.734, 95.701, 86.899, 83.098, 81.068.
1,4-Bis(3',5'-bistrifluoromethylphenylethynyl)-2,5-bis(phenylethynyl)benzene (2.9a)

This compound was synthesized by Prof. R. Twieg. Experimental details are not available.

\[
\text{Chemical Formula: } C_{42}H_{38}F_{12} \\
\text{Molecular Weight: } 750.59
\]

**MP:** 219.0 – 224.0 °C.

**\(^1\)H NMR (400 MHz, Tetrachloroethane-d\(_2\), TMS):** 8.000-7.996 (br, 4H), 7.851 (s, 2H), 7.806 (s, 2H), 7.580-7.556 (m, 4H), 7.401-7.381 (m, 6H).

**\(^{13}\)C-NMR (100 MHz, Tetrachloroethane-d\(_2\), TMS):** 134.988, 132.198 (q, \(J = 33.6 \text{ Hz}\)), 131.598, 131.549 (m), 129.251, 128.651, 126.003, 125.157, 124.913, 122.870 (q, \(J = 271.3 \text{ Hz}\)), 122.391, 122.139 (m), 96.478, 92.421, 90.558, 86.783.

**\(^{19}\)F-NMR (376 MHz, Tetrachloroethane-d\(_2\):** -63.170.
1,4-Bis(p-fluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (2.9b)

A two-necked flask (100mL) with magnetic stir bar was flushed by nitrogen, and then PdCl₂ (0.00117 g, 0.0066 mmol), PPh₃ (0.00500 g, 0.019 mmol), CuI (0.00128 g, 0.0067 mmol) and diethylamine (1 mL) were added in sequence to obtain a yellow colored mixture. After that, 4-fluorobromobenzene (0.248 g, 1.1 mmol), 1,4-diethynyl-2,5-bis(phenylethynyl)benzene (0.163 g, 0.5 mmol) and more diethylamine (4 mL) were added in sequence. The mixture was stirred at 50 °C for 3 hours, giving a dark brown suspension. The mixture was cooled and water (20 mL) was added to precipitate the crude product. It was filtered off, washed with cold water:acetone = 4:1 solution and air dried, giving yellow powder (0.229 g, 0.44 mmol, 88% yield) as final product.

**MP:** 215.5 – 219.0 °C.

**¹H NMR (400 MHz, Tetrachloroethane-d₂, TMS):** 7.849 – 7.841 (s, 2H), 7.673 – 7.632 (m, 8H), 7.475 – 7.461 (m, 6H), 7.179 – 7.128 (m, 4H)

**¹³C-NMR (100 MHz, Tetrachloroethane-d₂, TMS):** 162.932 (d, J = 249 Hz), 134.988, 133.875 (d, J = 7.8 Hz), 131.893, 129.067, 128.674, 125.290 (d, J = 10.5 Hz), 122.966, 119.164, 115.947, 115.727, 95.879, 94.767, 87.785, 87.544.

**¹⁹F-NMR (376 MHz, Tetrachloroethane-d₂):** -109.19
1,4-Bis(2',3',5',6'-tetrafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (2.9c)

![Chemical structure image]

Chemical Formula: $C_{38}H_{14}F_8$
Molecular Weight: 622.52

A two-necked flask (100mL) with magnetic stir bar was flushed by nitrogen, and then PdCl$_2$ (0.007286 g, 0.04 mmol), PPh$_3$ (0.04254 g, 0.16 mmol), CuI (0.004844 g, 0.02 mmol) and diisopropylamine (20 mL) were added into the mixture in sequence to obtain a yellow colored mixture. After that, 2,3,5,6-tetrafluorobromobenzene (1.017 g, 4 mmol), 1,4-diethynyl-2,5-bis(phenylethynyl)benzene (0.652 g, 2 mmol) were added in sequence. Toluene (20 mL) was added as co-solvent to dissolve the solid. The mixture was stirred at 70 °C for 24 hours, giving a dark brown suspension. After that time, the mixture was cooled down and the solvent was removed under vacuum. The residue was subjected to column chromatography (Hexane:DCM = 10:1), giving 0.125g (0.20 mmol, 10 % yield) yellow solid as product. The product can be recrystallized from toluene to give a fiber-like crystal.

Note: Maybe this compound is also a highly crystalline stuff and chromatography by hot toluene might give higher yield.

**MP:** 268.0 – 271.5 °C

**$^1$H NMR (400 MHz, Tetrachloroethane-D$_2$, TMS):** 7.938 (s, 2H), 7.702-7.697 (br, 4H), 7.473-
7.469 (br, 6H), 7.227-7.142 (m, 2H).

$^{13}$C-NMR (100 MHz, Tetrachloroethane-D$_2$, TMS): 147.022 (d, $J = 251$ Hz), 146.080 (d, $J = 249$ Hz), 135.991, 132.119, 129.084, 128.479, 125.937, 125.006, 122.810, 106.826 (t, $J = 22.6$ Hz), 99.600, 97.161, 86.701, 80.544.

$^{19}$F-NMR (376 MHz, Tetrachloroethane-D$_2$): -135.17, -138.09.

1,4-Bis(2’,3’,4’,5’,6’-pentafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (2.9d)

A flask (100mL) with a magnetic stir bar was flushed with nitrogen and PdCl$_2$ (0.003509 g, 0.02 mmol), PPh$_3$ (0.022625 g, $\sim$ 0.08 mmol), CuI (0.002670 g, 0.014 mmol) and diisopropylamine (60 mL) were added in sequence. After being stirred for about half an hour, a yellow colored mixture was obtained. After that, pentafluoroiodobenzene (0.888 g, 3.0 mmol) (150 %) and 1,4-diethynyl-2,5-bis(phenylethynyl)benzene (0.326 g, 1.0 mmol) were added and the mixture was stirred at 80 $^\circ$C for 24 hours, giving a yellow suspension. The resulting mixture was cooled down and well mixed with silica gel ($\sim$ 5g). Toluene was heated up (around 90-100 Celsius) to give a rapid column chromatography (avoid it from cooling down) and red colored eluent was obtained. The solvent was removed by rotary evaporation to give a brown colored residue, which was washed with cold acetone to give a white powder (0.518g 0.79 mmol, 79% yield).
Due to its bad solubility in common organic solvents, the NMR analysis was done at 100 °C and only \(^1\)H NMR and \(^{19}\)F-NMR are able to obtain good data.

\(^1\)H NMR (400 MHz, Tetrachloroethane-\(\text{D}_2\), TMS): 7.924 (s, 2H), 7.688 (s, 4H), 7.478 (br, 6H).

\(^{19}\)F-NMR (376 MHz, Tetrachloroethane-\(\text{D}_2\)): -134.55 (d, \(J = 19.2\) Hz), -151.03, -161.03.

2.6.3. Compounds that failed to obtain crystal structure

1-Phenyl-2-(3,5-difluorophenyl)acetylene

\[
\text{F} \quad \text{F}
\]

Chemical Formula: C\(_{14}\)H\(_8\)F\(_2\)
Molecular Weight: 214.21

A 250mL two-necked flask and magnetic stir bar were flushed by nitrogen. Then, PdCl\(_2\) (0.03587 g, 0.20 mmol), PPh\(_3\) (0.2130 g, 0.81 mmol) and anhydrous diethylamine (5 mL) were added in sequence. After being stirred at 45 °C for half an hour, CuI(0.02079 g, 0.10 mmol) was added to obtain a dark-yellow colored mixture. After that, more anhydrous diethylamine (15 mL), 1-bromo-3,5-difluorobenzene(3.875 g, 20 mmol) and phenylacetylene(2.256 g, 22 mmol) were added in sequence. The temperature was kept at 45 °C for 20h. After that, the solvent was removed via rotation evaporation, diethyl ether (100 mL) was added into the residue and the insoluble salt was filtrated off. The solution was washed by water (3 * 50 mL) and dried by anhydrous MgSO\(_4\). Remove solvent via rotation evaporation and the brown colored raw material was purified via chromatography (Hexane) to give colorless oil. The oil was cooled down and white crystal (2.746
g, 12.8 mmol, 64% yield) was obtained.

**MP:** 42.5-43.3°C.

**$^1$H NMR (CDCl$_3$,ppm):** 7.566 – 7.481 (m, 2H), 7.377 – 7.345 (m, 3H), 7.047 – 7.022 (m, 2H), 6.820 – 6.764 (m, 1H).

**$^{13}$C-NMR (CDCl$_3$,ppm):** 162.713 (dd, $^1J = 250$ Hz, $^2J = 13$ Hz), 131.759, 128.935, 128.467, 126.002 (d, $J = 11.8$ Hz), 122.319, 114.526 (dd, $^1J = 19$ Hz, $^2J = 7.4$ Hz), 104.395 (t, $J = 25.2$ Hz), 91.305, 87.111.

**1-(3,4-difluorophenyl)phenylacetylene**

![Chemical structure](image)

Chemical Formula: C$_{14}$H$_8$F$_2$
Molecular Weight: 214.21

A 100mL two-necked flask equipped with magnetic stir bar were flushed with nitrogen. PdCl$_2$ (0.01766 g, 0.10 mmol, 1 %), PPh$_3$ (0.1065 g, 0.41 mmol, ~4 %) and diethylamine (4 mL) were added in sequence. The mixture was stirred at 45 °C for half an hour, then CuI (0.009908 g, 0.05 mmol, 0.5 %) was added to give a dark-yellow colored mixture. Next, more anhydrous diethylamine (8 mL), 3,4-diflorobromobenzene (1.940 g, 10 mmol) and phenylacetylene (1.131 g, 10 mmol) were added in sequence. This orange colored mixture was stirred at 45 °C for 6h until no starting material can be observed by TLC. After that, solvent was removed by rotary evaporation, diethyl ether (50 mL) was added into the yellow residue and the insoluble white salt was removed via filtration. The solution was washed with water (3 x 25 mL) and dried over anhydrous MgSO$_4$. After filtrated the residue of MgSO$_4$, solvent was removed by rotary
evaporation. The dark yellow colored residue was subjected to chromatography (Hex: EtOAc = 20:1 eluent) to give a white solid (1.282 g, 6.0 mmol, 60% yield) as final product.

**MP:** 82.0 - 84.5 °C.

**1H-NMR (400 MHz, CDCl$_3$, TMS):** $\delta$ 7.576 – 7.541 (m, 2H), 7.406 – 7.362 (m, 4H), 7.290 – 7.285 (m, 1H), 7.197 – 7.130 (m, 1H).

**13C-NMR (100 MHz, CDCl$_3$, TMS):** $\delta$ 150.510 (dd, $^1J = 250$ Hz, $^2J = 12.5$ Hz), 149.022 (dd, $^1J = 250$ Hz, $^2J = 13$ Hz), 132.508, 131.628, 129.204, 128.656, 128.429, 122.636, 120.488 (d, J = 18 Hz), 117.482 (d, J = 18 Hz), 89.846, 87.209.

**1,4-bis(3,4-difluorophenylethynyl)-2,5-bis(phenylethynyl)benzene**

![Chemical Structure Image]

Chemical Formula: C$_{38}$H$_{18}$F$_4$

Molecular Weight: 550.56

A two-necked flask (100mL) and magnetic stir bar were flushed by nitrogen, and then PdCl$_2$ (0.007288 g, 0.04 mmol), PPh$_3$ (0.04267 g, 0.16 mmol) and diethylamine (5 mL) were added in sequence. After being stirred at 50 °C for half an hour, CuI (0.004187 g, 0.02 mmol) was also added into the mixture to obtain a yellow colored mixture. After that, 1,2-difluoro-4-iodobenzene (0.963 g, ~ 4 mmol), 1,4-diethynyl-2,5-bis(phenylethynyl)benzene (0.653 g, ~ 2 mmol) were
added in sequence and diethylamine (15 mL) was added to dissolve the solid. The mixture was stirred at 50 °C for 6 hours to obtain a yellow suspension. The solvent was removed and the residue was subjected to column chromatography (Hexane:DCM = 10:1), given 0.698g (1.27 mmol, 63.5 % yield) of a yellow product.

Obtained data:

**MP:** 215.0-217.5 °C

**^1H NMR (400 MHz, CDCl₃, TMS):** 7.738 (s, 2H), 7.557 – 7.549 (m, 4H), 7.383 (s, 6H), 7.333 – 7.255 (m, 4H), 7.174 – 7.110 (m, 2H).

**^13C-NMR (100 MHz, CDCl₃, TMS):** 150.984 (d, J = 247 Hz), 147.654 (d, J = 245 Hz), 134.932, 131.667, 128.999, 128.569, 128.419, 125.510, 125.061, 122.732, 120.617 (d, J = 18.4 Hz), 117.710 (d, J = 17.7 Hz), 110.003, 95.795, 93.311, 857.850, 87.183.
1,4-Bis(2,5-difluorophenylethynyl)-2,5-bis(phenylethynyl)benzene

![Chemical Structure](Image)

**Chemical Formula:** C$_{38}$H$_{18}$F$_4$

**Molecular Weight:** 550.56

A flask (100mL) with magnetic stir bar was flushed thoroughly with nitrogen, and then PdCl$_2$ (0.007325 g, 0.04 mmol), PPh$_3$ (0.044651 g, ~ 0.16 mmol), CuI (0.004179 g, 0.02 mmol) and diisopropylamine (60 mL) were added into the mixture in sequence. After being stirred for 30min, a yellow colored mixture was obtained. After that, 2,5-difluorobromobenzene (1.158 g, 6.0 mmol) (150 %), 1,4-diethynyl-2,5-bis(phenylethynyl)benzene (0.652 g, 2.0 mmol) were added. The mixture was stirred at 80 °C for 24 hours, giving a yellow suspension. The resulting mixture was cooled down. The solvent was removed under vacuum and the residue was subjected to column chromatography (Hexane:DCM = 10:1), giving 0.415 g (0.75 mmol, 38 % yield) of product as a bright-yellow solid. The product was recrystallized from toluene to give needle-like bright-yellow crystals.

**MP:** 203.0 – 206.0 °C

$^1$H NMR (400 MHz, Tetrachloroethane-d$_2$, TMS): $\delta$ 7.815 (s, 2H), 7.623 – 7.600 (m, 4H), 7.434 – 7.418 (m, 6H), 7.133 (d, 4H, $J = 6.5$ Hz), 6.897 – 6.877 (m, 2H)
$^{13}$C-NMR (100 MHz, Tetrachloroethane-d$_2$, TMS): $\delta$ 162.652 (dd, $^1J = 248$ Hz, $^2J = 13.2$ Hz), 134.970, 131.586, 128.981, 128.452, 125.539, 125.290 (t, $J = 11.7$ Hz), 124.822, 122.399, 114.557 (dd, $^1J = 19.0$ Hz, $^2J = 7.6$ Hz), 104.865 (t, $J = 25.2$ Hz), 96.086, 93.134, 89.143, 87.035.

$^{19}$F-NMR (376 MHz, Tetrachloroethane-d$_2$): $\delta$ -108.68.

1,4-bis(3,4,5-trifluorophenylethynyl)-2,5-bis(phenylethynyl)benzene

![Chemical Structure](image)

Chemical Formula: C$_{38}$H$_{16}$F$_6$
Molecular Weight: 586.54

A two-necked flask (100mL) with magnetic stir bar was flushed by nitrogen, and then PdCl$_2$ (0.007291 g, 0.04 mmol), PPh$_3$ (0.04339 g, 0.16 mmol), CuI (0.004705 g, 0.02 mmol) and diisopropylamine (20 mL) were added into the mixture in sequence to obtain a yellow colored mixture. After that, 3,4,5-trifluorobromobenzene (0.936 g, 4 mmol), 1,4-diethynyl-2,5-bis(phenylethynyl)benzene (0.652 g, 2 mmol) were added in sequence and toluene (20 mL) was added as a cosolvent to dissolve the solid. The mixture was stirred at 75 °C for 24 hours to obtain a dark brown suspension. After that, the mixture was cooled and the solvent was removed by rotary evaporation. The residue was subjected to column chromatography (Hexane:DCM = 10:1) which gave 0.269g (0.46 mmol, 23 % yield) of a yellow solid as product. The product can be
recrystallized from toluene.

**MP:** 229.0-230.5 °C.

**$^1$H NMR (400 MHz, Tetrachloroethane-D$_2$, TMS):** 7.832 (s, 2H), 7.667-7.643 (m, 4H), 7.484-7.448 (s, 6H), 7.286-7.237 (m, 4H).

**$^{13}$C-NMR (100 MHz, Tetrachloroethane-D$_2$, TMS):** 151.302 (d, $^1J = 250$ Hz), 140.803 (dt, $^1J = 255$ Hz, $^2J = 15$ Hz), 135.117, 131.794, 129.194, 128.657, 125.978, 125.138, 122.813, 119.035 (m), 116.179 (dd, $^1J = 16$ Hz, $^2J = 6.7$ Hz), 96.493, 92.621, 89.198, 87.317.

**$^{19}$F-NMR (376 MHz, Tetrachloroethane-D$_2$, TMS):** -133.165 - -133.253 (m), -157.313 - -157.420 (m).
2.7. References


(2) Liu, N., Kent State University, 2008.


3. Chapter Three - Photocyclodehydrofluorination (PCDHF)

A communication about this new photoreaction has been published in *Chem. Eur. J*¹.

3.1. Background

![Scheme 3.1 Retrosynthesis of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene series compound.](image)

Having observed that due to steric issues all atoms cannot located in the same plane in 1,2,4,5-tetra(phenylethynyl)benzene compounds (Chapter 2), we recognized that we needed some design changes that could include new covalent bonds between the perfluorinated ring and non-fluorinated ring. This action might lead to new polycyclic aromatic hydrocarbons (PAHs) in which all the atoms are located in the same plane. Thus, a first step in the design was to omit the acetylenes entirely on a simple steric basis. However, and in addition to the steric issues, it is worthy to note that acetylene groups may be inherently unsuitable because they are electrostatically prone to orthogonal vs. parallel alignment.
Taking 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene as an example, this ideal compound is a C2h symmetric flat molecule and has pairs of perfluorinated and perprotio benzene rings on the corners. These non-polar molecules can stack with each layer rotated 180° and might deliver our desired short distance phenyl – perfluorophenyl interactions. From the structural retrosynthesis listed above, by using the same starting material 1,4-dibromo-2,5-diiodobenzene as in the last chapter, the two iodine atoms are able to undergo during copper-catalyzed decarboxylative coupling with potassium pentafluorobenzoate to provide 2',5'-dibromo-2,2",3,3",4,4",5,5",6,6"-decafluoro-1,1':4',1"-terphenyl. Then, the remaining two bromine atoms can undergo a Suzuki coupling reaction with phenyl boronic acid and yield 2',5'-bis(perfluorophenyl)-1,1':4',1"-terphenyl. Everything seems to be very simple up to this point; however, the challenge in front of us is how to eliminate the adjacent H and F atoms to form new C-C covalent bonds in the desired heptacyclic compound.

3.2. Mallory photocyclization

3.2.1. Oxidative Mallory photocyclization

The photochemical conversion of stilbene to phenanthrene is a very commonly used photoreaction that was initially discovered in the 1930s and then subsequently extended to numerous analogues. This reaction initiates by the excitation of stilbenes under irradiation and proceeds via a trans-cis isomerization followed by a symmetry allowed Woodward–Hoffmann electrocyclic ring closure to deliver trans-4a,4b-dihydrophenanthrene as intermediate, which is eventually converted to phenanthrene by a formal loss of H2 facilitated by the presence of atmospheric oxygen.
In 1964, Mallory’s introduction of iodine as oxidant significantly enhanced the utility of the reaction and this widely used method bears Mallory’s name. As the pioneer of this research area, Mallory compiled a huge review chapter named “Photocyclization of Stilbenes and Related Molecules” in the book *Organic Reactions* that includes nearly all the “early age” reactions in this field no later than 1984. However the development of photocyclization did not stop but greatly proceeded after that. The neutralization of the highly reactive HI byproduct produced during the Mallory reaction by trapping with epoxides or THF were important subsequent improvements in methodology. Other milder oxidants such as diphenyldiselenide or copper salts have also been employed.

Scheme 3.3 Diphenyldiselenide or Cu(II) salts are able to work as the oxidizing agent in oxidative Mallory photocyclizations.
The conversion of ortho-terphenyls to triphenylenes follows a comparable pathway except the initial cis-trans equilibration step is not involved. Along with the development of these reliable experimental photochemical techniques have come a multitude of applications for the creation of materials of use in medicine\textsuperscript{12,13} and materials science (the synthesis of helicenes might be the best example\textsuperscript{14-19}).

\begin{center}
\textbf{Scheme 3.4} Synthesis of granulatimide from didemnimide A\textsuperscript{20}
\end{center}

\begin{center}
\textbf{Scheme 3.5} The first photosynthesis of helicene via oxidative Mallory photocyclization\textsuperscript{15}.
\end{center}

3.2.2. Mallory photocyclization involving leaving group

A lesser known and lesser used variant of this process involves an eliminative mechanism involving the loss of HX from a 4a-H,4b-X-dihydropenanthenrene (or comparable triphenylene derived precursor). In this case, an X-functional group (halogen, ether, etc.) is almost invariably present in the stilbene on an ortho- position of one ring, along with at least one hydrogen atom on
a complementary *ortho*- position of the other ring (for *ortho*-terphenyls, the same applies for the *ortho*-positions on the two rings attached *ortho-* on the common central ring of the terphenyl).

Upon photocyclization, the H atom and the X- group become situated on adjacent carbons of the 4a-H,4b-X-dihydrophenanthrene (dihydrotriphenylene for *ortho*-terphenyls), and are easily lost (driving force is rearomitization) as HX as they are *trans* as is established by the symmetry controlled electrocyclic process. Amongst the halogens, chlorine, bromine and iodine are usually employed as the X-group and in these cases the overall process is often described as a photocyclodehydrohalogenation reaction. In the case of HF elimination the process is called photocyclodehydrofluorination (PCDHF as abbreviation). Other suitable leaving groups are known and, in fact, can be located in the molecule elsewhere than the ring closure sites. While the PCDHF reaction resembles these other photocyclodehydrohalogenations it also has its own unique features which we have begun to unravel here.

**Scheme 3.6** Examples of photocyclodehydrohalogenation involving Cl, Br and I as leaving group.
Unlike the previously discussed use of chlorine, bromine and iodine in photocyclodehydrohalogenation, fluorine has rarely been reported as an X-group in such eliminative photochemical ring closure reactions and its efficacy as a participant in such photoprocesses was unclear since these photoreactions were run with intentionally added oxidants (or uncontrolled vicarious oxidants)\textsuperscript{27,28}. The irradiation of \textit{trans}-1-(1-fluoro-2-naphthyl)-2-phenylethylene gave only \textit{cis-trans} isomerization without any evidence for HF loss and the desired product was ultimately made from another precursor via loss of HI\textsuperscript{29}. In another study, fluorinated precursors capable of losing HF in ring closing reactions were examined and defluorinated products were noted but not clearly identified\textsuperscript{30}. The efficient loss of HF has been observed in azatriene-azacyclohexadiene photochemistry\textsuperscript{27}. In the photocyclization of 1-fluoro[5]helicenes a fluorine migration was found in addition to eliminative loss of HF\textsuperscript{28}. In another study of helicene photochemistry it was found that fluorine atoms potentially available for PCDHF reacted by other mechanisms\textsuperscript{31}. No products resulting from loss of HF were reported from irradiation of a series of 1-phenyl-2-(2-naphthyl)ethenes with appropriately disposed ortho fluorine and ortho hydrogen atoms\textsuperscript{32}. Likewise, only difluorinated products were observed from oxidative cyclization of 2,5-difluorophenynaphthylethenes\textsuperscript{33}. In a related process, it has been demonstrated that monofluoro phenanthrenes can be prepared by irradiation of difluoroethylene precursors followed by an additional base mediated dehydrofluorination step\textsuperscript{34}. 
3.3. **Mallory photocyclization involving the losing of HF - Photocyclodehydrofluorination (PCDHF)**

In the study we present here the elimination of hydrogen fluoride has been found to be both general and efficient in the process of photocyclodehydrofluorination (PCDHF). The experimental methods we employ are designed to suppress the oxidative route by exclusion of vicarious oxidants (such as oxygen) and abandon the use of intentional oxidants (such as iodine). We have found that the loss of HF, especially in multiply fluorinated substrates, is just as facile as the loss of HX seen in the more thoroughly studied cases involving the other halogens. Here we will demonstrate that the PCDHF method permits the preparation of a wide range of selectively fluorinated polynuclear aromatic materials which contain a phenanthrene substructure.
For the UV irradiation, two types of photochemical reactors were applied in our experiments: 1) The Rayonet photochemical reactor can be fitted with up to $16 \times 254$ nm lamps or $16 \times 300$ nm lamps. 2) The Hanovia photochemical reactor has a single 450 W lamp. The output of this lamp was not used directly. Instead, either a Pyrex or Vycor cutoff filter was employed to eliminate short wavelength UV. In either case the solutions of the materials were placed in quartz tubes for its transparency in the near UV region (approximately $40 \text{ cm} \times 25 \text{ mm}$ with a 24/40ST joint).

For the solvent, acetonitrile was selected as our first choice as it could dissolve the majority of the precursors studied and provided good to excellent yields in most cases. Other solvents, such as toluene and THF were also selected if the precursor had poor solubility in acetonitrile. In our studies, we also found that the solvent could be a crucial factor and could have huge influence on the final product distribution in the reactions that have a competition between PCDHF and traditional oxidative cyclization. All of these issues will be discussed later.

Thus far, we have explored the scope of the PCDHF process predominantly in the structural regime.
and the reactions described here are sorted into the following categories and tables by their general structural features. Other important experimental variables required for ultimate optimization of individual reactions (such as the irradiation wavelength, solvent and concentration) have been examined less thoroughly and will require further future attention and elaboration. Details for the reactions found in the following tables are provided in the experimental procedure section.

3.3.1. PCDHF in 2,3,4,5,6-pentafluorostilbene type precursors

The table below summarizes the results of PCDHF of stilbenes with a perfluorinated terminal ring. Simple stilbene type precursors such as 3.1a and 3.1b gave modest yields of phenanthrenes. The larger phenylnapthylethenes gave various results depending on the particular isomer involved. For α-styrylnaphthalenes, the chrysene products were obtained in excellent yields (Entries 3 & 5). For β-styrylnaphthalene, only one PCDHF product 3.2f was formed although two ring closure sites are available (Entry 6). The PCDHF regioselectivity found here matches the results for oxidative cyclizations of comparable non-fluorinated β-styrylnaphthalene\(^8,35\). The double ring closure (Entry 7) led to an interesting highly nonplanar [5]helicene adduct 3.2g\(^36\). Note that if bromine is found in a precursor it can be lost in a photochemical side reaction atom independent of the PCDHF process (Entries 2 & 4). The pentafluorostilbene type precursors used here were typically prepared from pentafluorostyrene and corresponding aromatic halides via a Jeffery type modification of the Heck reaction\(^37\) or a Wittig reaction of pentafluorobenzaldehyde with phosphonium salt.
**Scheme 3.9** Preparation methods for 3,4,5,6-pentafluorostilbene type precursors.

**Table 3.1** PCDHF in 2,3,4,5,6-pentafluorostilbene type precursors

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Substrate 1" /></td>
<td><img src="image2" alt="Product 1" /></td>
<td>49%</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="Substrate 2" /></td>
<td><img src="image4" alt="Product 2" /></td>
<td>46%</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5" alt="Substrate 3" /></td>
<td><img src="image6" alt="Product 3" /></td>
<td>75%</td>
</tr>
</tbody>
</table>
3.3.2. PCDHF in 2,3,4,5,6-pentafluoro-1,1':2',1''-terphenyl type precursors

The PCDHF of ortho-terphenyls with a perfluorinated terminal ring are generally more facile and give higher yields than their stilbene counterparts. This difference may be in part attributable to the presence of the ortho-terphenyl structure itself as trans-cis photoequilibration is not required. The ortho-terphenyl type precursors with one terminal ring perfluorinated were easily accessed by
copper mediated decarboxylative coupling of potassium pentafluorobenzoate$^2$ with 2-iodobiphenyl (3.3a) or with 1-bromo-2-iodobenzene, in the latter cases followed by Suzuki coupling reactions (3.3b – 3.3h).

Scheme 3.10 Preparation methods of 2,3,4,5,6-pentafluoro-1,1':2',1''-terphenyl type precursors.

Table 3.2 PCDHF in 2,3,4,5,6-pentafluoro-1,1':2',1''-terphenyl type precursors

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.3a</td>
<td>3.4a</td>
<td>94 %</td>
</tr>
</tbody>
</table>
3.3.3. PCDHF involving heterocycles

A few fluorinated polynuclear materials containing heterocycles have also been prepared and the results are summarized below. It is noteworthy that some heterocycles can be accommodated in PCDHF. For thiophene derivatives, both 3.5a (Entry 1) and 3.5b (Entry 2) underwent PCDHF and excellent yields of the respective cyclized products were obtained. Likewise, irradiation of the pyridine derivative 3.5c also gave an efficient conversion to an azatriphenylene (Entry 3).
### Table 3.3 PCDHF involving heterocycles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="Substrate 3.5a" /></td>
<td><img src="image" alt="Product 3.6a" /></td>
<td>71%</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Substrate 3.5b" /></td>
<td><img src="image" alt="Product 3.6b" /></td>
<td>78%</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Substrate 3.5c" /></td>
<td><img src="image" alt="Product 3.6c" /></td>
<td>77%</td>
</tr>
</tbody>
</table>

### 3.3.4. PCDHF of 2,3,5,6-tetrafluoro precursors

All the precursors mentioned in the tables above contain a pentafluorophenyl ring and necessarily give photoproducts containing a perfluorinated ring. The presence of a pentafluorinated benzene ring is not a prerequisite for successful PCDHF and the following precursors will be ortho-terphenyls with a 2,3,5,6-tetrafluoro terminal ring. Here, the 2,3,5,6-tetrafluoro-1,1′:2′,1″-terphenyl was obtained from copper catalyzed decarboxylation of 2-iodobiphenyl and potassium 2,3,5,6-tetrafluorobenzoate. The 4-alkoxy-2,3,5,6-tetrafluoro-1,1′:2′,1″-terphenyls and hexyl(2,3,5,6-tetrafluoro-[1,1′:2′,1″-terphenyl]-4-yl)sulfane were obtained from the nucleophilic SNAr reaction of 2,3,4,5,6-pentafluoro-1,1′:2′,1″-terphenyl with various of alcohols in the presence...
of t-BuOK. The SnAr chemistry on perfluoroaromatic compounds utilized here will be discussed in more details later.

The PCDHF results are shown in the table below. All of the 4-protio substituted and 4-alkoxy substituted 2,3,5,6-tetrafluoro-1,1':2',1"-terphenyls gave acceptable (55 %) to good (76 %) yield. The sulfane compound (3.7e) showed some difficulty for PCDHF – although it could still undergo the reaction successfully, a much lower yield (24 %) was obtained compared with previous discussed examples. The C-S bond is much weaker than the C-O bond (the bond energy of C-O is 360 kJ/mol whereas that of C-S is 272 kJ/mol respectively), which might be destroyed under UV irradiation under the conditions of the PCDHF reaction.

![Chemical diagram]

**Scheme 3.11** Preparation of precursors with a 2,3,5,6-tetrafluoro substituted benzene ring.
Table 3.4 PCDHF of 2,3,5,6-tetrafluoro precursors

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="" /></td>
<td><img src="image2" alt="" /></td>
<td>60%</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="" /></td>
<td><img src="image4" alt="" /></td>
<td>56%</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5" alt="" /></td>
<td><img src="image6" alt="" /></td>
<td>76%</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7" alt="" /></td>
<td><img src="image8" alt="" /></td>
<td>55%</td>
</tr>
<tr>
<td>5</td>
<td><img src="image9" alt="" /></td>
<td><img src="image10" alt="" /></td>
<td>24%</td>
</tr>
</tbody>
</table>
3.3.5. PCDHF of difluoro precursors - two fluorine atoms located at the two reactive ortho-sites

While the PCDHF reaction outcome is influenced by the exact number and locations of fluorine atoms, it turns out that all that is absolutely required for successful PCDHF is a substrate with at least one $o$-fluoro substituent and a partner site in another ring bearing an $o$-hydrogen atom. The examples found in the table below are $ortho$-terphenyls and stilbenes that contain a single ring with at least two fluorine atoms located at the two ring closure $ortho$-sites.

In this set of compounds, 2,6-difluoro-1,1':2',1''-terphenyl (3.9a) was prepared via Suzuki reaction. Other 2,6-difluorostilbenes used here were obtained by Wittig reaction (3.9b, 3.9e) and cyano styryl type derivatives (3.9c, 3.9d) were accessed easily by the Knoevenegel condensation of the respective aldehydes with cyanomethylene aromatics. All of these substrates underwent PCDHF with yields not significantly different than those obtained for similar but more highly fluorinated substrates.

Scheme 3.12 Preparation of precursors by using Suzuki coupling and condensation reaction.
Table 3.5 PCDHF of precursors with two fluorine atoms (at the two ortho sites).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="3.9a" alt="Substrate Image" /></td>
<td><img src="3.10a" alt="Product Image" /></td>
<td>79 %</td>
</tr>
<tr>
<td>2</td>
<td><img src="3.9b" alt="Substrate Image" /></td>
<td><img src="3.10b" alt="Product Image" /></td>
<td>62 %</td>
</tr>
<tr>
<td>3</td>
<td><img src="3.9c" alt="Substrate Image" /></td>
<td><img src="3.10c" alt="Product Image" /></td>
<td>71 %</td>
</tr>
<tr>
<td>4</td>
<td><img src="3.9d" alt="Substrate Image" /></td>
<td><img src="3.10d" alt="Product Image" /></td>
<td>74 %</td>
</tr>
<tr>
<td>5</td>
<td><img src="3.9e" alt="Substrate Image" /></td>
<td><img src="3.10e" alt="Product Image" /></td>
<td>43 %</td>
</tr>
</tbody>
</table>

3.3.6. Competition between PCDHF and oxidative cyclization

An extra degree of complication occurs if one ortho-position on a ring is occupied by fluorine and
the other *ortho*-position on the ring by hydrogen. In such cases loss of HF may occur by PCDHF and/or the loss of H₂ may occur competitively by the classical oxidative photoprocess. In cases examined thus far we find that both processes usually proceed simultaneously (even if the system is carefully degassed to remove vicarious oxygen in an attempt to suppress the oxidative process). The most interesting discovery is in entry 8. Here 2,3-difluoro-1,1':2',1"-terphenyl was selected as the precursor, the reaction went almost exclusively through the PCDHF process and yielded the same compound as 3.10a. Only a trace of oxidative cyclization product 1,2-difluorotriphenylene was observed from the irradiation. This phenomenon might be caused by the second fluorine atom located next to fluorine atom was lost, which leading to lower electron density on the ring closure position carbon atom and thus facilitated the PCDHF process.

*Table 3.6 Competition between PCDHF and oxidative cyclization*

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="3.11a" /></td>
<td><img src="image" alt="3.12.1a" /> &amp; <img src="image" alt="3.12.2a" /></td>
<td>16 % (acetonitrile) &amp; 28 % (THF)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>47 % (acetonitrile) &amp; 9 % (THF)</td>
</tr>
</tbody>
</table>
2

3.11b

44 % (acetonitrile)

52 % (THF)

29 % (acetonitrile)

9 % (THF)

3

3.11c

14 %

3.11c

14 %

3.12.1c

46 %

3.12.2c

46 %

3.12.1c

18 %

18 %

3.12.2d

3.11d

3.11d

16 %

16 %

3.12.2d

3.11e

3.11e

32 %

3.12.1e

32 %
Note 1: For Entries 1 & 2, GC yields are provided.

Note 2: Unless mentioned, the solvent used in these reactions is acetonitrile.
As has been mentioned briefly before, in these preliminary studies, the solvent had also been identified as a factor that influences competition between PCDHF and the classical oxidative photoprocess. In both **Entries 1 & 2**, when acetonitrile was employed as the solvent, the photoreaction proceeds quickly but the selectivity between the PCDHF/oxidative photoprocesses is relatively low. In contrast, use of THF minimized the oxidative process and the PCDHF reaction was preferred (but with lower overall yield). Obviously more studies about solvent effects are required to better understand the mechanistic implications and also further optimize the reaction as a reliable preparative method.

The stilbene type precursors in this series were easily prepared by the same methods as in the previous section but using different fluorinated benzaldehydes. The 2,3-difluoro-1,1':2',1"-terphenyl precursor in entry 8 was prepared via the Suzuki reaction of 2-biphenylboronic acid and 2,3-difluoriodobenzene.

**3.3.7. PCDHF with possible isomer production**

Using the same procedure, we also prepared some precursors that equiped with a pentafluorobenzene ring and a non “symmetric” ring to perform the PCDHF reaction. Here, we placed groups at the *meta*- position to see if it they would influence some kind of regioselectivity for the PCDHF reaction.

The results are listed in **Table 3.7**. For the two compounds including a methoxy group (**3.13a**, **3.13b**), both of them provided good selectivity and would preferred to undergo the ring closure at
the *para-* position relative to the methoxy group. The compound with a nitrile group (3.13c) showed similar result in that the PCDHF preferred to occur at the *para-* position relative to the nitrile group. However, the regioselectivity is not as good as in the previous two cases. The good news at here is that the product 5,6,7,8-tetrafluorophenanthrene-2-carbonitrile (3.14.1c) and 5,6,7,8-tetrafluorophenanthrene-4-carbonitrile (3.14.2c) can be easily separated by silica gel column chromatography due to their large difference of polarity. Clearly more substituents need to be examined in this fashion.

*Table 3.7* PCDHF involving regioselectivity control.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="3.13a" /></td>
<td><img src="image" alt="3.14.1a" /></td>
<td>49 %</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="3.13b" /></td>
<td><img src="image" alt="3.14.1b" /></td>
<td>Trace</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="3.14.1c" /></td>
<td><img src="image" alt="3.14.2c" /></td>
<td>Trace</td>
</tr>
</tbody>
</table>
3.3.8. PCDHF involving competition with other halogens (Cl, Br)

An additional question that arises is how HF and HX elimination may compete. To evaluate such cases, substrates were designed which contain F and Cl or F and Br in the two o- positions of one of the rings. From previous experimental experience, the highly fluorinated α-styrylnaphthalenes and o-terphenyls were found to be excellent precursors for PCDHF. In fact, good yields of photoproducts were obtained from the mixed halogen systems but from our preliminary results all that can be said is that there is no clear preference for photocyclization leading to HF elimination vs. HCl or HBr elimination.
Table 3.8 PCDHF involving competition with other halogens (Cl, Br)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield (GC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Substrate 1" /></td>
<td><img src="image2" alt="Product 1a" /></td>
<td>27 %</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="Substrate 2" /></td>
<td><img src="image4" alt="Product 1b" /></td>
<td>27 %</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5" alt="Substrate 3" /></td>
<td><img src="image6" alt="Product 1c" /></td>
<td>52 %</td>
</tr>
<tr>
<td></td>
<td><img src="image7" alt="Substrate 4" /></td>
<td><img src="image8" alt="Product 2c" /></td>
<td>23 %</td>
</tr>
</tbody>
</table>

3.15a  
3.15b  
3.15c  
3.16.1a  
3.16.1b  
3.16.1c  
3.16.2a  
3.16.2b  
3.16.2c
3.3.9. Circumstances under which PCDHF is unsuccessful

All the precursors discussed above underwent PCDHF successfully regardless of the yield of the final products. However, for some of the precursors we have tried, although they have similar structures as the previous examples, they only provide a trace amount of product that was impossible to isolate or just gave cis-trans isomerization without any signs of the desired cyclized product at all. In many cases, small amounts of products were evident from GC-MS used to follow the reaction but it proved impossible to finally isolate the compound. Examples we have encountered in which the PCDHF process does not work well or at all are summarized in Table 3.9.

Note: GC yields are provided in this table.
### Table 3.9 Precursors that do not provide good results for PCDHF.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Condition</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="3.17a" /></td>
<td><img src="image" alt="3.17a" /></td>
<td>Solvent: toluene Hanovia Hardware Irradiated with UV lamps with pyrex filter. Conc = 0.01 mol/L</td>
<td>Only trans – cis isomerization was observed. No ring closure was observed.</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="3.17b" /></td>
<td><img src="image" alt="3.17b" /></td>
<td>Solvent: Acetonitrile Hanovia Hardware Irradiated with UV lamps in quartz probe. Vycor filter. Conc = 0.01 mol/L</td>
<td>The height of the two product peaks on GC-MS had a ratio about 3:2 (tiny amount). Just gave a black residue and impossible to separate them.</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="3.17c" /></td>
<td><img src="image" alt="3.17c" /></td>
<td>Solvent: toluene Hanovia Hardware Irradiated with UV lamps in quartz probe. Vycor filter Conc = 0.01 mol/L</td>
<td>Reaction proceeded slowly. Desired product can be observed in tiny amount via GC-MS. Impossible to separate the product.</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="3.17d" /></td>
<td><img src="image" alt="3.17d" /></td>
<td>Solvent: Acetonitrile Rayonet Hardware Irradiated with 254 nm UV lamps Conc = 0.01 mol/L</td>
<td>Tiny amount of product observed. Longer reaction time gave more impurities. Impossible to separate the product.</td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="3.17e" /></td>
<td><img src="image" alt="3.17e" /></td>
<td>Solvent: acetonitrile Hanovia Hardware Irradiated with UV lamps with pyrex filter. Conc = 0.01 mol/L</td>
<td>Only trans – cis isomerization was observed. Ring closure could be observed after a long time of irradiation. (After about 40 hours, the starting material, cis-isomer and product ratio was about 2:1:1)</td>
</tr>
</tbody>
</table>
Solvent: acetonitrile/THF=4:1
Hanovia Hardware
Irradiated with UV lamps with pyrex filter.
Conc = 0.01 mol/L
Gave many peaks in GC-MS (contains many impurities). No hope to isolate the desired product.

Solvent: acetonitrile/THF=4:1
Hanovia Hardware
Irradiated with UV lamps with pyrex filter.
Conc = 0.01 mol/L
Gave a mixture (contain many impurities).
Tiny amount of desired product can be observed in GC-MS. No hope to isolate the desired product.

Solvent: toluene
Hanovia Hardware
Irradiated with UV lamps with pyrex filter.
Conc = 0.01 mol/L
Only trans – cis isomerization was observed. No ring closure was observed.
Solvent: Acetonitrile
Hanovia Hardware
Irradiated with UV lamps in quartz probe for 8 hours.
Vycor filter.
Conc = 0.01 mol/L
Desired PCDHF reaction can be observed by GC-MS (M-40 peaks)
However, there are numerous impurities, impossible to separate out the product.

Solvent: Toluene
Rayonet Hardware
Irradiated with 254 nm UV lamps.
Conc = 0.01 mol/L
Reaction is slow, only a trace amount of desired product can be observed by using GC-MS, impossible to isolate.

Solvent: Toluene
Rayonet Hardware
Irradiated with 254 nm UV lamps.
Conc = 0.01 mol/L
After 18 hours of irradiation, a mixture of peaks was observed via GC-MS.

Solvent: Toluene
Hanovia Hardware
Irradiated with UV lamps in quartz probe.
Vycor filter
Conc = 0.01 mol/L
During the reaction, the loss of two H is observed.
The loss of H₂ was much faster than loss of HF.
From all of the examples listed above, we can arrive at several conclusions here and they might be good lessons for the design of PCDHF reactions in future.

Firstly, it appears that a bromine atom in the substrate is not always tolerated in PCDHF. For the two precursors (3.1b and 3.1d) discussed before, regardless of extremely long irradiation time and the Br atom was also lost via some unknown mechanism, they could still slowly perform PCDHF and the products (3.2b and 3.2d) could be isolated. However, the two precursors 3.17c and 3.17d here just provided trace of product (observed by using GC-MS) and did not have any hope to be isolated.

Secondly, precursors that have a complicated structure (some functional groups) might not good for PCDHF such as esters. They would like to perform some side reactions (observed plenty of peaks on GC-MS, which means that the molecule might fragment under UV irradiation) and obviously enhance the difficulty to isolate the product.

Third, it might be not a good choice to use PCDHF to build a five membered ring as both attempts here just ended in failure.

Fourth, the pentafluorostilbene type precursors containing heterocycles examined here (thiophene or pyridine ring instead of a second benzene ring) do not work well. This is in strong contrast to the ortho-terphenyls equipped with the same heterocycles discussed before. This phenomenon again shows that ortho-terphenyl type structures usually undergo PCDHF better than the corresponding stilbenes.
Fifth, the dual PCDHF appears to be very difficult. The 1,4-\textit{bis}(\textit{E})-2-pentafluorostyryl)naphthalene did undergo dual PCDHF and this might be attributed to the highly reactivity of $\alpha$-styrylnaphthalenes. However, the ordinary \textit{bis}-stilbenes such as 1,4-\textit{bis}(\textit{E})-2-(perfluorophenyl)vinyl)benzene and 1,3-\textit{bis}(\textit{E})-2-(perfluorophenyl)vinyl)benzene just provided \textit{cis}-\textit{trans} isomerization or trace product that was impossible to isolate. Literature search found that the irradiation of \textit{m}-distyrylbenzene could give benzo[e]chrysene in about 70 % yield\textsuperscript{41} and the irradiation of \textit{p}-distyrylbenzene would yield 1,12-benzperylen in 11.5 %\textsuperscript{42}. Maybe the optimization of reaction conditions for perfluorinated precursors could provide a much better result.

Sixth, the outcomes of the reactions collected here that failed might be different if alternative wavelengths or solvents were employed.

\textbf{3.3.10. The extension for PCDHF to other halogens – Chlorine (PCDHCl)}

In the introduction, it was already mentioned that chlorine\textsuperscript{21}, bromine\textsuperscript{22} and iodine\textsuperscript{23} have all been documented as the X- leaving group and in these cases the overall process is often described as a photocyclodehydrohalogenation reaction. In these studies we are describing we have extended the photocyclodehydrohalogenation into a new area – photocyclodehydrofluorination (PCDHF) involving fluorine as leaving group.

In PCDHF, perfluorinated compounds were shown to be excellent precursors, which usually underwent the reaction smoothly and from which good yields were obtained. This fact prompted
us to inquire if this pattern also existed with other perhalogenated compounds. To answer this
question, we designed a set of precursors and irradiated them under the same condition as PCDHF.
The results are summarized in Table 3.10 below. Due to the limitation of time, we just tested
chlorinated compounds. Here, we acknowledge the contributions of Michael Schmidt who
undertook part of this work during the summer of 2012 as an REU student (Entries 1-4).

*Table 3.10* The extension for PCDHF to other halogens – Chlorine (PCDHCl)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Condition</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="Substrate 3.19a" /></td>
<td><img src="image" alt="Product 3.19a" /></td>
<td>Solvent: Acetonitrile Rayonet Hardware Irradiated with 254 nm UV lamps</td>
<td>Only cis-trans isomerization observed. Longer reaction time just give side reactions.</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Substrate 3.19b" /></td>
<td><img src="image" alt="Product 3.19b" /></td>
<td>Solvent: Toluene Rayonet Hardware Irradiated with 254 nm UV lamps</td>
<td>Only cis-trans isomerization observed. No sign of product.</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Substrate 3.19c" /></td>
<td><img src="image" alt="Product 3.19c" /></td>
<td>Solvent: Acetonitrile Rayonet Hardware Irradiated with 254 nm UV lamps</td>
<td>Only cis-trans isomerization observed. After 24h, very small amount of product, majority is still starting material. Reaction ceased at this point and no hope to isolate the product.</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Substrate 3.19d" /></td>
<td><img src="image" alt="Product 3.19d" /></td>
<td>Solvent: Acetonitrile Rayonet Hardware Irradiated with 254 nm UV lamps</td>
<td>Only cis-trans isomerization observed. No sign of product.</td>
</tr>
</tbody>
</table>
3.4. Summary for PCDHF

Based on this study we can conclude that photocyclodehydrofluorination (PCDHF) is a versatile and often efficient means to prepare selectively fluorinated polynuclear aromatic compounds with a phenanthrene substructure. This photochemical route is tolerant of a range of functional groups and will prove valuable for the preparation of compounds with carefully controlled fluorine content which may otherwise be difficult or even impossible to prepare. This method compliments other techniques available to prepare fluorine containing polynuclear aromatics (PAHs). Refinements of the PCDHF reaction including systematic examination of the influence of solvent, wavelength and
compatibility with other functional groups still need further investigation.

3.5. Experimental procedures

3.5.1. Synthesis of precursors for photocyclodehydrofluorination

3.5.1.1. Pentafluorostilbene type precursors

The pentafluorostilbene type precursors (3.1a, 3.1b, 3.1c, 3.1e, 3.1f, 3.1g) were generally prepared from the corresponding aromatic halides using a Jeffery modification of the Heck reaction. The 1-bromo-4-(2-(perfluorophenyl)vinyl)naphthalene (3.1d) was prepared via Wittig reaction.

(E)-pentafluorostilbene (3.1a)

A 100 mL round bottom flask equipped with magnetic stirbar was flushed thoroughly with nitrogen and then charged with anhydrous DMF (20 mL), iodobenzene (1.025 g, 5.0 mmol), pentafluorostyrene (0.978 g, 5.0 mmol), Pd(OAc)$_2$ (11.365 mg, 0.05 mmol), potassium carbonate (0.699 g, 5.0 mmol) and 2-(2-methoxyethoxy)-N,N-bis[2-(2-methoxyethoxy)ethyl]ethanamine (0.13 mL). The mixture was stirred at 110 °C for 3 hours under a nitrogen atmosphere and TLC indicated that no starting materials remained. The mixture was then cooled and water (~ 80 mL) was added dropwise to precipitate the solid. The solid was isolated by suction filtration, washed with water and air-dried, giving a grey powder as crude product. The powder was then dissolved in ethyl acetate (~ 50 mL) and mixed with silica gel (~ 5 g). After the solvent was removed, the mixture was placed on the top of column to perform a silica gel chromatography (eluent: hexanes: DCM = 4:1), giving white crystals (0.981 g, 3.6 mmol, 73 %) as final product.


**M.P.:** 136.0 – 138.0 °C (Lit.: 137 °C).

**$^1$H-NMR (400 MHz, CDCl$_3$) δ:** 7.537 – 7.513 (m, 2H), 7.448 – 7.372 (m, 3H), 7.352 – 7.331 (m, 1H), 6.975 (d, $J$ = 16.8 Hz, 1H).

**$^{13}$C-NMR (100 MHz, CDCl$_3$) δ:** 144.888 (d, $J$ = 245.6 Hz), 139.747 (d, $J$ = 250.6 Hz), 137.880
(d, $J = 235.3$ Hz), 137.249 (t, $J = 7.2$ Hz), 136.504, 129.009, 128.886, 126.923, 112.707.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -142.763 (dd, $^1J = 21.6$ Hz, $^2J = 7.7$ Hz, 2F), -156.571 (t, $J = 20.7$ Hz, 1F), -162.909 $-$ -163.054 (m, 2F).

UV/Vis (Acetonitrile): $\lambda_{\text{max}}(e) = 220$ (14900), 292 (27100) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 270.93.

**(E)-4'-bromopentafluorostilbene (3.1b)**

A 100 ml pear flask equipped with magnetic stirbar was charged with 1-bromo-4-iodobenzene (2.83 g, 10.0 mmol), pentafluorostyrene (1.94 g, 10.0 mmol), anhydrous DMF (5 mL), K$_2$CO$_3$ (1.75 g, 12.5 mmol) and 2-(2-methoxyethoxy)-N,N-bis[2-(2-methoxyethoxy)ethyl]ethanamine (0.08 g, 0.25 mmol). After being degassed thoroughly with nitrogen, the resulting mixture was placed in 60 °C oil bath and then Pd(OAc)$_2$ (11 mg, 0.05 mmol) was added. The reaction was gradually warmed to 110 °C under a nitrogen atmosphere and followed by TLC over the next 6 hours. After this time, TLC indicated that only a trace of the starting material 1-bromo-4-iodobenzene remained (and only a trace of diaduct had formed). The mixture was cooled to room temperature and water was added dropwise with stirring to 100 mL. The resulting suspension was stirred and then the solid was isolated by suction filtration, washed well with water and air-dried. The solid crude product was transferred to an Erlenmeyer flask and dissolved in boiling isooctane to which some Montmorillonite clay and silica gel were added. The resulting suspension was
boiled, poured through a fluted filter and the solvent was boiled into the filter to remove any residual product. Upon cooling the product was obtained as a white solid (1.587 g, 4.5 mmol, 45 % yield), which was isolated by suction filtration and air-dried.


M.P.: 101.0 – 103.0 °C.

\(^{1}\text{H-NMR (400 MHz, CDCl}_3\text{)} \delta: 7.502 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.372 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.346 (d, J = 16.8 \text{ Hz}, 1\text{H}), 6.948 (d, J = 16.8 \text{ Hz}, 1\text{H}).

\(^{13}\text{C-NMR (100 MHz, CDCl}_3\text{)} \delta: 144.878 (d, J = 249.5 \text{ Hz}), 139.955 (d, J = 252.8 \text{ Hz}), 137.852 (d, J = 249.4 \text{ Hz}), 135.863 (t, J = 8.4 \text{ Hz}), 135.417, 132.060, 128.341, 123.036, 113.388, 112.106.

\(^{19}\text{F-NMR (376 MHz, CDCl}_3\text{)} \delta: -142.521 – -142.600 (m, 2\text{F}), -155.880 (t, J = 20.7 \text{ Hz}, 1\text{F}), -162.629 – -162.775 (m, 2\text{F}).

UV/Vis (Acetonitrile): \(\lambda_{\text{max}}(\varepsilon) = 296 \text{ (15800) nm (M}^{-1}\text{cm}^{-1}).

GCMS (m/z): 347.88, 349.88.

\((E)-1\text{-pentafluorophenyl-2-(1’-naphthyl)ethane (3.1c)}\)

\[
\begin{align*}
\text{Chemical Formula: } & C_{18}H_{9}F_5 \\
\text{Molecular Weight: } & 320.26
\end{align*}
\]

A 100 mL round bottom flask equipped with a magnetic stirbar was flushed thoroughly with nitrogen and charged with 1-iodonaphthalene (1.271 g, 5.0 mmol), pentafluorostyrene (0.981 g,
5.0 mmol), Pd(OAc)$_2$ (11.378 mg, 0.05 mmol), potassium carbonate (0.703 g, 5.0 mmol), anhydrous DMF (20 mL) and 2-(2-methoxyethoxy)-$N,N$-bis[2-(2-methoxyethoxy)ethyl]ethanamine (0.13 mL). The mixture was stirred at 110 °C under nitrogen atmosphere for 3 hours and TLC indicated that no starting materials remained.

The mixture was cooled to room temperature and water (~ 80 mL) was added to give a grey precipitate, which was isolated by suction filtration, washed with water and air-dried. The crude product was dissolved in ethyl acetate (~ 50 mL) and mixed with silica gel (~ 5 g). The solvent was removed and the grey powder was placed on the top of column for silica gel chromatography (eluent: hexanes: DCM = 4:1) to give a white powder (microscopic needles) (0.909 g, 2.8 mmol, 57 % yield) as final product.

**M.P.:** 185.0 – 187.5 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 8.208 (d, $J = 16.4$ Hz, 1H), 8.123 (d, $J = 8$ Hz, 1H), 7.865 (t, $J = 8.2$ Hz, 2H), 7.748 (d, $J = 7.2$ Hz, 1H), 7.579 – 7.487 (m, 3H), 7.006 (d, $J = 16.4$ Hz, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 144.918 (d, $J = 248.5$ Hz), 139.854 (d, $J = 257.0$ Hz), 137.836 (d, $J = 246.7$ Hz), 134.634 (t, $J = 7.8$ Hz), 134.305, 133.685, 131.224, 129.318, 128.726, 126.626, 126.146, 125.653, 123.944, 123.415, 115.489, 112.564.

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -142.711 (dd, $^1J = 21.6$ Hz, $^2J = 7.7$ Hz, 2F), -156.252 (t, $J = 20.9$ Hz, 1F), -162.729 – -162.864 (m, 2F).

**UV/Vis (Acetonitrile):** $\lambda_{\text{max}}(\varepsilon) = 203$ (40200), 226 (34600), 324 (17200) nm (M$^{-1}$cm$^{-1}$).

**GCMS (m/z):** 320.96.

**HRMS:** M$^+$ = 300.06189 (Calc = 300.06189).
1-bromo-4-(2-(perfluorophenyl)vinyl)naphthalene (3.1d)

![Chemical structure](image)

Chemical Formula: $C_{18}H_8BrF_5$
Molecular Weight: 399.15

A solution of $t$-BuOK (1.176 g, 10.5 mmol) in EtOH (50 mL) was added dropwise to a suspension of ((4-bromonaphthalen-1-yl)methyl)triphenylphosphonium bromide (5.625 g, 10.0 mmol) and pentafluorobenzaldehyde (1.967 g, 10.0 mmol) in ethanol (50 mL) in a 250 mL flask. The mixture was stirred under room temperature overnight after which time no starting materials were observed by TLC. Silica gel (~ 5 g) was added and after removal of solvent by rotary evaporation, the powder obtained was placed on the top of a silica gel column and chromatographed (eluent: hexanes). Fractions containing the isomeric products were combined and concentrated. The white solid that came out of the early fractions was demonstrated to be the $E$-isomer (0.287 g, 0.72 mmol, 7.2 % yield). The remaining product was obtained as a mixture of $E/Z$-isomers (1.982 g, 5.0 mmol, 50 % yield).

Reference1: Cammidge, Andrew N.; Crepy, Karen V.; Fugier, Matthieu, Synthetic Communications, 1997, Vol.27, 4159 – 4162


$(E)$-1-bromo-4-(2-(perfluorophenyl)vinyl)naphthalene

M.P.: 203.0 – 205.0 °C.
$^1\text{H}-\text{NMR (400 MHz, CDCl}_3\text{)} \delta$: 8.320 – 8.297 (m, 1H), 8.120 (d, $J = 16.4$ Hz, 1H), 8.108 (d, $J = 7.4$ Hz, 1H), 7.807 (d, $J = 7.4$ Hz, 1H), 7.649 – 7.576 (m, 2H), 7.551 (d, $J = 8.0$ Hz, 1H), 6.987 (d, $J = 16.4$ Hz, 1H).

$^{13}\text{C}-\text{NMR (100 MHz, CDCl}_3\text{)} \delta$: 145.119 (d, $J = 244.6$ Hz), 140.336 (d, $J = 240.0$ Hz), 137.987 (d, $J = 229.8$ Hz), 134.621, 134.232 (t, $J = 8.2$ Hz), 132.508, 132.274, 129.929, 128.080, 127.604, 127.446, 124.341, 124.186, 124.072, 116.298, 112.565.

$^{19}\text{F}-\text{NMR (376 MHz, CDCl}_3\text{)} \delta$: -143.050 (dd, $^1J = 21.4$ Hz, $^2J = 7.5$ Hz, 2F), -156.138 (t, $J = 20.9$ Hz, 1F), -163.007 – -163.140 (m, 2F).

UV/Vis (Acetonitrile): $\lambda_{\text{max}}(\varepsilon)$ = 207 (22400), 235 (34200), 330 (23450) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 397.83, 399.84.
In a 100 ml pear flask with magnetic stirbar was placed 1-cyano-4-iodonaphthalene (0.70 g, 5.0 mmol), pentafluorostyrene (1.07 g, 5.5 mmol), anhydrous DMF (10 mL), K$_2$CO$_3$ (1.75 g, 12.5 mmol) and 2-(2-methoxyethoxy)-N,N-bis[2-(2-methoxyethoxy)ethyl]ethanamine (40 mg, 0.125 mmol). The resulting mixture was placed in 60 °C oil bath, degassed thoroughly with nitrogen and then Pd(OAc)$_2$ (5.0 mg, 1%) was added. The reaction was then warmed to 120 °C and left stirring for another 2 hours under a nitrogen atmosphere. After this time TLC indicated virtually all the 1-cyano-4-iodonaphthalene was consumed so the mixture was cooled to room temperature and water was added dropwise with stirring to 100 mL. The resulting suspension was stirred and then the solid was isolated by suction filtration, washed well with water and air-dried. The solid crude product was transferred to an Erlenmeyer and dissolved in boiling 2-methoxyethanol. The dark suspension was boiled and poured through two fluted filters and the solvent was boiled into the filters to remove any residual product. Some 1-propanol was added to the hot filtrate. Upon cooling the product was obtained as yellow needles by suction filtration (1.19 g, 3.4 mmol, 69 % yield).

**M.P.:** Slowly sublimed above 180 °C, melted at 201.5 – 203.0 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$) δ:** 8.310 – 8.285 (m, 1H), 8.207 – 8.166 (m, 2H), 7.940 (d, $J$ = 7.6 Hz, 1H), 7.773 (d, $J$ = 7.6 Hz, 1H), 7.767 – 7.679 (m, 2H), 7.102 (d, $J$ = 16.4 Hz, 1H).

**$^{13}$C-NMR (100 MHz, CDCl$_3$) δ:** 145.090 (d, $J$ = 253.3 Hz), 140.538 (d, $J$ = 249.1 Hz), 139.613,
137.908 (d, $J = 250.8$ Hz), 132.979 (t, $J = 7.8$ Hz), 132.659, 132.249, 130.815, 128.772, 128.149, 126.000, 124.267, 122.880, 118.563, 117.779, 111.780, 110.695.

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -142.475 – -142.568 (m, 2F), -154.765 (t, $J = 20.8$ Hz, 1F), -162.522 – -162.656.

UV/Vis (Acetonitrile): $\lambda_{\text{max}}(\varepsilon)$ = 202 (37500), 234 (24300), 338 (18900) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 345.97.

(E)-1-pentafluorophenyl-2-(2'-naphthyl)ethane (3.1f)

A 100 mL round bottom flask equipped with magnetic stirbar was degassed thoroughly with nitrogen and charged with 2-bromonaphthalene (1.035 g, 5.0 mmol), pentafluorostyrene (0.975 g, 5.0 mmol), potassium carbonate (0.701 g, 5.0 mmol), anhydrous DMF (20 mL), Pd(OAc)$_2$ (11.396 mg, 0.05 mmol) and 2-(2-methoxyethoxy)-$N,N$-bis[2-(2-methoxyethoxy)ethyl]ethanamine (0.13 mL). The resulting mixture was stirred at 110 °C for 12 hours under a nitrogen atmosphere and TLC indicated that all the 2-bromonaphthalene was consumed.

The resulting mixture was cooled to room temperature, poured into water (~ 200 mL) and extracted with EtOAc (3 x 100 mL). The organic phases were combined and dried with anhydrous MgSO$_4$. After removing the drying agent via filtration, silica gel (~ 5 g) was added to absorb the product. The solvent was removed by rotary evaporation and the yellow powder was placed on the top of
silica gel column for chromatography (eluent: hexanes: DCM = 6:1), giving the final product as a white powder (microscopic needles) (0.579 g, 1.8 mmol, 36 % yield).

**M.P.:** 165.0 – 167.0 °C.

**\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\):** 7.870 – 7.808 (m, 4H), 7.716 (dd, \(^1J = 8.6\) Hz, \(^2J = 1.8\) Hz, 1H), 7.579 (d, \(J = 16.8\) Hz, 1H), 7.513 – 7.463 (m, 2H), 7.077 (d, \(J = 16.8\) Hz, 1H).

**\(^13\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\):** 144.892 (d, \(J = 245\) Hz), 139.754 (d, \(J = 254\) Hz), 137.843 (d, \(J = 250\) Hz), 137.210 (t, \(J = 7.3\) Hz), 133.941, 133.634, 133.519, 128.620, 128.279, 128.014, 127.757, 126.664, 126.636, 122.942, 112.900, 112.478.

**\(^19\)F-NMR (376 MHz, CDCl\(_3\)) \(\delta\):** -142.704 (dd, \(^1J = 21.6\) Hz, \(^2J = 7.7\) Hz, 2F), -156.526 (t, \(J = 20.7\) Hz, 1F), -162.859 – -163.004 (m, 2F).

**UV/Vis (Acetonitrile):** \(\lambda_{\text{max}}(\varepsilon) = 270\) (39360), 280 (36750), 314 (41550) nm (M\(^{-1}\)cm\(^{-1}\))

**GCMS (m/z):** 320.96.

**1,4-bis((E)-2-(perfluorophenyl)vinyl)naphthalene (3.1g)**

![Chemical Structure](image)

**Chemical Formula:** C\(_{26}\)H\(_{10}\)F\(_{10}\)

**Molecular Weight:** 512.34

In a 100 ml pear flask equipped with magnetic stirbar was placed 1,4-diiodonaphthalene (1.90 g, 5.0 mmol), pentafluorostyrene (2.15 g, 11.0 mmol), K\(_2\)CO\(_3\) (1.75 g, 12.7 mmol), anhydrous DMF (10 ml) and 2-(2-methoxyethoxy)-\(N,N\)-bis[2-(2-methoxyethoxy)ethyl]ethanamine (0.080 g, 0.24 mmol). The resulting mixture was degassed thoroughly with nitrogen, placed in a 80 °C oil bath,
and then Pd(OAc)$_2$ (11 mg, 1%) was added. The reaction was warmed to 110 °C and left stirring for 8 hours under nitrogen atmosphere. After this time, TLC indicated all the diiodide starting material was consumed and a small amount of mono adduct was present in addition to the desired diadduct. The mixture was cooled to room temperature and water was added dropwise with stirring to 100 ml. The resulting suspension was stirred and then the solid was isolated by suction filtration, washed well with water and air-dried. The crude product was transferred to an Erlenmeyer and dissolved in boiling toluene to which some Montmorillonite clay and silica gel were added. The resulting suspension was boiled and poured into a fluted filter and the solvent was boiled into the filter to remove any residual product. Upon cooling the product obtained was contaminated by palladium metal. Two more cycles of clay treatment and filtration were needed to remove the palladium residue. Finally, a pure product of fine yellow crystals (1.50 g, 2.9 mmol, 59 % yield) was obtained from a mixture of toluene and iso-octane and isolated by suction filtration.

**M.P.:** 236.5 – 240.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 8.220 (d, $J$ = 16.8 Hz, 2H), 8.197 – 8.172 (m, 2H), 7.788 (s, 2H), 7.623 – 7.599 (m, 2H), 7.054 (d, $J$ = 16.8 Hz, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 145.106 (d, $J$ = 246.8 Hz), 140.298 (d, $J$ = 251.6 Hz), 138.084 (d, $J$ = 249.3 Hz), 135.505, 134.527 (t, $J$ = 7.4Hz), 131.582, 126.875, 124.252, 123.897, 116.055, 112.671.

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -143.251 (dd, $^1J = 21.2$ Hz, $^2J = 7.7$ Hz, 2F), -156.605 (t, $J$ = 20.3 Hz, 1F), -163.330 – -163.459 (m, 2F).

**UV/Vis (DCM):** $\lambda_{\text{max}}(\varepsilon) = 230$ (23750), 262 (20750), 367 (22840) nm (M$^{-1}$cm$^{-1}$).

**GCMS (m/z):** 511.91.
3.5.1.2. **Pentafluoro-ortho-triphenyl type precursors**

The parent 2-(pentafluorophenyl)biphenyl (3a) could be obtained directly from 2-iodobiphenyl and potassium pentafluorobenzoate mediated by CuI. The other ortho-terphenyl type precursors (3b–3h) were obtained by Suzuki coupling of 1-bromo-2-pentafluorophenylbenzene with the respective boronic acids. The 1-bromo-2-pentafluorophenylbenzene itself can be easily synthesized from 1-bromo-2-iodobenzene and potassium pentafluorobenzoate with the catalysis of CuI.


2-(pentafluorophenyl)biphenyl (3.3a)
A 50 mL flask with magnetic stirbar was flushed thoroughly with nitrogen and charged with CuI (0.076 g, 0.40 mmol, 20 %), 2-iodobiphenyl (0.562 g, 2.01 mmol), potassium pentafluorobenzoate (0.758 g, 3.02 mmol, 150%) and diglyme (1.0 mL). The mixture was kept at 130 °C for 24 hours under nitrogen atmosphere. The mixture was cooled and the brown-colored residue was diluted with ethyl acetate (25 mL) and mixed with some silica gel (~ 2 g). The volatile solvents were removed by rotary evaporation and the adsorbed material was placed at the top of a silica gel column and eluted (eluent: hexanes). The product was obtained as white crystals (0.428 g, 1.33 mmol, 66.9 % yield).

**Reference:** Lafrance, Marc; Shore, Daniel; Fagnou, Keith *Organic Letters, 2006, Vol.8, 5097 – 5100.*

**M.P.:** 86.5 – 88.0 °C (Lit.: 89 – 91 °C).

**1H-NMR (400 MHz, CDCl₃) δ:** 7.555 – 7.436 (m, 3H), 7.342 – 7.320 (m, 1H), 7.272 – 7.234 (m, 3H), 7.145 – 7.121 (m, 2H).

**13C-NMR (100 MHz, CDCl₃) δ:** 144.060 (d, \(J = 246\) Hz), 143.040, 140.532 (d, \(J = 252\) Hz), 140.350, 137.386 (d, \(J = 251\) Hz), 131.112, 130.385, 129.788, 128.508, 128.165, 127.485, 127.446, 124.918, 115.941 (t, \(J = 18.9\) Hz).

**19F-NMR (376 MHz, CDCl₃) δ:** -140.147 (dd, \(^1J = 23.3\) Hz, \(^2J = 8.3\) Hz, 2F), -153.360 (t, \(J =
21.0 Hz, 1F), -162.414 – -162.554 (m, 2F).

**UV/Vis (Acetonitrile):** $\lambda_{\text{max}}(e) = 196 \text{ (54600) nm (M}^{-1}\text{cm}^{-1})$.

**GCMS (m/z):** 320.96.

2'-bromo-2,3,4,5,6-pentafluorobiphenyl

![Chemical Structure](image)

Chemical Formula: $C_{12}H_4BrF_5$

Molecular Weight: 323.06

A 250 mL flask equipped with magnetic stirbar was flushed thoroughly with nitrogen and charged with potassium pentafluorobenzoate (13.779 g, 55 mmol), CuI (1.917 g, 10 mmol), 1-bromo-2-iodobenzene (14.176 g, 50 mmol) and diglyme (50 mL). The mixture was stirred at 130 °C overnight (~ 12 hours) under a nitrogen atmosphere.

The resulting mixture was cooled and diluted with ethyl acetate (150 mL). After gravity filtration, the filtrate was washed with water (200 mL x 4) and brine (200 mL) to remove diglyme. The organic phase was then separated and dried over anhydrous MgSO$_4$. Silica gel (~ 10 g) was added and the solvent was removed by rotary evaporation. The yellow powder obtained was placed at the top of a silica column and eluted (eluent: hexanes). After removing the solvent by rotary evaporation, a colorless oil was obtained which crystallized after cooling (11.519 g, 36 mmol, 72 % yield).

**M.P.:** 40.0 – 42.5 °C (Lit.: 39.5 – 41.0 °C).

**$^1$H-NMR (400 MHz, CDCl$_3$)** δ: 7.721 (dd, $^1J = 7.6$ Hz, $^2J = 1.0$ Hz, 1H), 7.424 (dd, $^1J = 7.6$ Hz, $^2J = 1.3$ Hz, 1H), 7.342 (dd, $^1J = 7.7$ Hz, $^2J = 1.3$ Hz, 1H), 7.283 (dd, $^1J = 7.7$ Hz, $^2J = 1.8$ Hz, 1H).

**$^{13}$C-NMR (100 MHz, CDCl$_3$)** δ: 144.245 (d, $J = 247$ Hz), 141.346 (d, $J = 252$ Hz), 137.759 (d, $J = 251$ Hz), 133.244, 132.070, 131.202, 128.103, 127.647, 124.387, 115.320 (dd, $^1J = 19$ Hz, $^2J = 3.9$ Hz).

**$^{19}$F-NMR (376 MHz, CDCl$_3$)** δ: -139.698 – -139.798 (m, 2F), -154.148 (tt, $^1J = 21$ Hz, $^2J = 1.5$ Hz, 1F), -162.023 – -162.175 (m, 2F).

**2,3,4,5,6-pentafluoro-4''-methoxy-1,1':2',1''-terphenyl (3.3b)**

![Chemical Structure](image)

**Chemical Formula:** C$_{19}$H$_{11}$F$_5$O  
**Molecular Weight:** 350.28

A 100 mL flask with magnetic stir bar was charged with 2'-bromo-2,3,4,5,6-pentafluorobiphenyl (0.646 g, 2.0 mmol), 4-methoxyphenyl boronic acid (0.455 g, 3.0 mmol, 1.5 eq), K$_2$CO$_3$ (0.552 g, 4.0 mmol, 2.0 eq), toluene (10 mL) and EtOH (2.5 mL). The system heated up to 90 °C under nitrogen protection. Finally, Pd(PPh$_3$)$_4$ (24.105 mg, 0.020 mmol, 1%) was added and the mixture was gently refluxed overnight (12 hours) under nitrogen atmosphere.
The mixture was cooled, silica gel (~ 2 g) was added to absorb the product and the solvents were
removed by rotary evaporation. The yellow powder obtained was placed at the top of a silica
column and eluted (eluent: hexanes) to give a colorless oil which eventually crystallized (0.486g,
1.4 mmol, 70 % yield).

**M.P.:** 84.5 – 87.5 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.536 – 7.495 (m, 1H), 7.463 – 7.405 (m, 2H), 7.306 (d, $J = 7.6$
Hz, 1H), 7.051(d, $J = 8.8$ Hz, 2H), 6.809 – 6.781 (m, 2H), 3.786 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 158.949, 144.052 (d, $J = 245$ Hz), 142.696, 140.488 (d, $J = 251$
Hz), 137.408 (d, $J = 251$ Hz), 132.767, 131.074, 130.399, 129.743, 129.613, 127.123, 124.942,
116.113 (t, $J = 21$ Hz), 113.621, 55.174.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -140.237 (dd, $^1J = 23.3$ Hz, $^2J = 8.3$ Hz, 2F), -155.549 (t, $J =$
21.0 Hz, 1F), -162.402 – -162.542 (m, 2F).

UV/Vis (Acetonitrile): $\lambda_{\text{max}}(\varepsilon) = 197$ (59800), 259 (13900) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 350.96.
2,3,4,5,6-pentafluoro-4''-(hexyloxy)-1,1':2',1''-terphenyl (3.3c)

In a 100 mL flask was placed 2'-bromo-2,3,4,5,6-pentafluorobiphenyl (1.635 g, 5.0 mmol), 4-(n-hexyloxy)phenylboronic acid (2.221 g, 10.0 mmol), K₂CO₃ (1.390 g, 10.0 mmol), toluene (40 mL) and EtOH (10 mL). After being flushed thoroughly with nitrogen, the mixture was heated up to approximately 90 °C to achieve reflux. Finally, Pd(PPh₃)₄ (56.312 mg, 0.05 mmol, 1 %) was added and the resulting mixture was gently refluxed overnight (~ 12 hours) under nitrogen.

After this time, the mixture was cooled to room temperature. Silica gel (~ 5g) was added and the mixture was concentrated to dryness by rotary evaporation. The tan powder obtained was placed on the top of a silica gel column and eluted (eluent: hexanes: EtOAc = 20:1). Fractions containing the product were combined and concentrated to dryness, giving the final product as a sticky colorless oil (1.976 g, 4.7 mmol, 94 % yield).

\[ \text{Chemical Formula: } C_{24}H_{21}F_5O \]

Molecular Weight: 420.41

1H-NMR (400 MHz, CDCl₃) δ: 7.514 – 7.399 (m, 3H), 7.328 – 7.292 (m, 1H), 7.043 – 7.021 (m, 2H), 6.790 – 6.768 (m, 2H), 3.925 (t, \( J = 6.6 \) Hz, 2H), 1.786 – 1.748 (m, 2H), 1.471 – 1.454 (m, 2H), 1.358 – 1.313 (m, 4H), 0.903 (t, \( J = 7.2 \) Hz, 3H).
\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\): 158.551, 144.063 (d, \(J = 246\) Hz), 142.785, 140.478 (d, \(J = 251\) Hz), 137.403 (d, \(J = 251\) Hz), 132.540, 131.084, 130.418, 129.751, 129.590, 127.084, 124.989, 116.140, 114.162, 67.995, 31.643, 29.277, 25.771, 22.636, 14.058.

\(^{19}\)F-NMR (376 MHz, CDCl\(_3\)) \(\delta\): -140.828 (dd, \(^1J = 23.3\) Hz, \(^2J = 8.3\) Hz, 2F), -156.140 (t, \(J = 21.0\) Hz, 1F), -162.993 – -163.133 (m, 2F).

UV/Vis (Acetonitrile): \(\lambda_{\text{max}}(e) = 195\) (54800), 260 (10180) nm (M\(^{-1}\)cm\(^{-1}\)).

GCMS (m/z): 420.89.

2,3,4,5,6-pentafluoro-4''-(trifluoromethoxy)-1,1':2',1''-terphenyl (3.3d)

![Chemical structure](image)

Chemical Formula: C\(_{19}\)H\(_6\)F\(_8\)O  
Molecular Weight: 404.25

A 100 mL 2-neck flask with magnetic stir bar was charged with 2'-bromo-2,3,4,5,6-pentafluorobiphenyl (0.646 g, 2.0 mmol), 4-(trifluoromethoxy) phenyl boronic acid (0.620 g, 3.0 mmol, 1.5 eq), K\(_2\)CO\(_3\) (0.553 g, 4.0 mmol, 2.0 eq), toluene (10 mL) and EtOH (2.5 mL). The system was flushed thoroughly with nitrogen and heated in a 90 °C oil bath. Finally, Pd(PPh\(_3\))\(_4\) (24.331 mg, 0.020 mmol, 1%) was added and the mixture was gently refluxed overnight (12 hours) under nitrogen.

After this time the mixture was then cooled, silica gel (~ 2 g) was added and the solvent was
removed by rotary evaporation. The resulting yellow powder was placed at the top of a silica column and eluted (eluent: hexanes: EtOAc = 20:1). Fractions containing the product were combined and concentrated to give the final product as white crystals (0.592g, 1.47 mmol, 73% yield).

**M.P.:** 72.5 – 74.0 °C.

**1H-NMR (400 MHz, CDCl₃) δ:** 7.556 (td, \(^1J = 7.4\) Hz, \(^2J = 1.6\) Hz, 1H), 7.480 (qd, \(^1J = 7.7\) Hz, \(^2J = 1.2\) Hz, 2H), 7.347 (dd, \(^1J = 7.6\) Hz, \(^2J = 0.4\) Hz, 1H), 7.173 – 7.105 (m, 4H).

**13C-NMR (100 MHz, CDCl₃) δ:** 148.685, 143.996 (d, \(J = 245\) Hz), 141.608, 140.709 (d, \(J = 253\) Hz), 139.010, 137.484 (d, \(J = 251\) Hz), 131.303, 130.342, 129.977, 129.941, 127.979, 124.960, 120.566, 120.465 (q, \(J = 256\) Hz, CF₃), 115.504 (t, \(J = 18\) Hz).

**19F-NMR (376 MHz, CDCl₃) δ:** -57.835 (s, 3F), -140.202 (dd, \(^1J = 23.3\) Hz, \(^2J = 8.3\) Hz, 2F), -154.687 (t, \(J = 21.0\) Hz, 1F), -162.039 – -162.178 (m, 2F).

**UV/Vis (Acetonitrile):** No maximum absorption, the absorption coefficient at 254nm is provided. 
\(\varepsilon = 10100 \text{ M}^{-1}\text{cm}^{-1} \) (254 nm).

**GCMS (m/z):** 404.81.
2,3,3‴,4,5,5‴,6-heptafluoro-1,1′:2′,1‴-terphenyl (3.3e)

A 100 mL 2-neck flask with magnetic stir bar was charged with 2′-bromo-2,3,4,5,6-pentafluorobiphenyl (0.970 g, 3.0 mmol), 3,5-difluorophenyl boronic acid (0.714 g, 4.5 mmol, 1.5 eq), K$_2$CO$_3$ (0.830 g, 6.0 mmol, 2.0 eq), toluene (15 mL) and EtOH (3 mL). After being flushed via nitrogen, the mixture was heated in a 90 °C oil bath. Finally, Pd(PPh$_3$)$_4$ (34.707 mg, 0.030 mmol, 1%) was added and the mixture was gently refluxed overnight (12 hours) under nitrogen.

After this time the mixture was cooled, silica gel (~ 2 g) was added to absorb the product and the solvent was removed under vacuum. The yellow powder obtained was placed at the top of a silica column and eluted (eluent: hexanes) to give a colorless oil, which eventually was converted to white crystals (0.968g, 2.72 mmol, 91 % yield) after cooling.

**M.P.:** 65.0 – 68.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.574 – 7.481 (m, 2H), 7.459 – 7.437 (m, 1H), 7.362 – 7.328 (m, 1H), 6.742 – 6.646 (m, 3H)

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 162.579 (dd, $^1J = 248$ Hz, $^2J = 13$ Hz), 143.989 (d, $J = 246$ Hz), 143.601 (t, $J = 9.5$ Hz), 140.830 (d, $J = 253$ Hz), 140.677, 137.526 (d, $J = 252$ Hz), 131.452,
In a 100 mL flask with magnetic stir bar was placed 2′-bromo-2,3,4,5,6-pentafluoro-1,1′-biphenyl (0.651 g, 2.0 mmol), 3,5-bis(trifluoromethyl)phenyl boronic acid (0.774 g, 3.0 mmol, 150%), K$_2$CO$_3$ (0.414 g, 3.0 mmol, 150%), toluene (40 mL) and EtOH (10 mL). The flask was flushed thoroughly with nitrogen and the mixture was heated up to 90 °C in an oil bath under nitrogen. Finally, Pd(PPh$_3$)$_4$ (23.944 mg, 0.02 mmol, 1%) was added. After the mixture was refluxed for 12 hours. TLC indicated that the biphenyl starting material was completely consumed.

The mixture was then cooled to room temperature and silica gel (~ 2 g) was added. After the
solvent was removed by rotary evaporation, the tan powder was placed on the top of a silica gel
column and eluted (eluent: hexanes). The fractions containing the product were combined and
concentrated to dryness, giving a colorless oil which eventually crystallized (0.638 g, 1.4 mmol,
70% yield).

M.P.: 70.0 – 74.5 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.800 (t, $J = 0.8$ Hz), 7.651 – 7.518 (m, 5H), 7.432 – 7.411 (m,
1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 143.884 (d, $J = 245.5$ Hz), 142.297, 141.006 (d, $J = 258.1$ Hz),
139.716, 137.582 (d, $J = 252.5$ Hz), 131.473, 131.714, 130.369, 130.104, 129.521, 129.082,
128.760 (d, $J = 1.8$ Hz), 123.050 (q, $J = 271.1$ Hz), 121.319 (t, $J = 3.7$ Hz), 114.659 (t, $J = 19.2$
Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -63.557 (t, $J = 80.1$ Hz, 6F), -140.648 – -140.732 (m, 2F), -
154.112 – -154.226 (m, 1F), -161.895 – -162.027 (m, 2F).

UV/Vis (Acetonitrile): No maximum absorption, the absorption coefficient at 254 nm is provided.
ε = 9485 M$^{-1}$cm$^{-1}$ (254 nm).

GCMS (m/z): 455.86.
2,3,4,5,6-pentafluoro-1,1':2',1''':4'',1'''-quaterphenyl (3.3g)

A 100 mL flask with magnetic stir bar was charged with 2'-bromo-2,3,4,5,6-pentafluoro-1,1'-biphenyl (1.617 g, 5.0 mmol), 4-biphenyl boronic acid (1.986g, 10.0 mmol, 200%), K₂CO₃ (1.397 g, 10.0 mmol, 200%), toluene (40 mL) and EtOH (10 ml). After being flushed thoroughly with nitrogen, the mixture was heated up to 90 °C in an oil bath and Pd(PPh₃)₄ (58.037 mg, 0.050mmol, 1%) was finally added. After 10 hours of reflux TLC indicated that starting material biphenyl was completely consumed.

The mixture was then cooled to room temperature and silica gel (~ 5g) was added. After the solvent was removed by rotary evaporation, the tan powder obtained was placed on the top of a silica gel column and eluted (eluent: hexanes). The fractions containing the product were combined together and concentrated to dryness, giving white crystals (1.495 g, 3.7 mmol, 74% yield) as final product.

M.P.: 169.5 – 170.5 °C.

¹H-NMR (400 MHz, CDCl₃) δ: 7.603 – 7.410 (m, 9H), 7.359 – 7.319 (m, 2H), 7.220 – 7.199 (m, 2H).

¹³C-NMR (100 MHz, CDCl₃) δ: 144.096 (d, J = 245 Hz), 142.609, 140.874 (d, J = 252 Hz),

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -140.664 (dd, $^1J = 23$ Hz, $^2J = 8.3$ Hz, 2F), -155.694 (t, $J = 21$ Hz, 1F), -162.706 -- -162.851 (m, 2F).

UV/Vis (Acetonitrile): $\lambda_{\text{max}}(\varepsilon) = 203$ (64880), 271 (27200) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 396.06.

2''',3''',4''',5''',6'''-pentafluoro-[1,1':2',1''-terphenyl]-4-carbonitrile (3.3h)

Chemical Formula: C$_{19}$H$_8$F$_{15}$N  
Molecular Weight: 345.27

A 100 mL flask with magnetic stir bar was charged with 2'-bromo-2,3,4,5,6-pentafluoro-1,1’-biphenyl (1.620 g, 5.0 mmol), 4-cyanophenyl boronic acid (1.472g, 10.0 mmol), K$_2$CO$_3$ (1.398 g, 10.0 mmol), toluene (40 mL) and EtOH (10 ml). This mixture was degassed thoroughly with nitrogen and warmed up, at 90 °C Pd(PPh$_3$)$_4$ (58.037 mg, 0.050mmol, 1%) was eventually added. After being refluxed for 10 hours, TLC indicated that starting material biphenyl was completely consumed.

The mixture was then cooled and silica gel (~ 5g) was added. After the solvent was removed via rotary evaporation, the tan powder obtained was placed on the top of a silica gel column and eluted.
(eluent: hexanes: EtOAc = 10:1). Fractions containing the product were combined and concentrated to dryness, giving white crystals (1.386 g, 4.0 mmol, 80% yield) as final product.

**M.P.:** 130.0 – 130.5 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.615 – 7.520 (m, 4H), 7.462 (dd, $^1J = 7.2$ Hz, $^2J = 1.6$ Hz, 1H), 7.383 (dd, $^1J = 7.2$ Hz, $^2J = 0.8$ Hz, 1H), 7.258 (dt, $^1J = 8.4$ Hz, $^2J = 1.6$ Hz, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 145.087, 143.870 (d, $J = 243$ Hz), 141.032, 140.838 (d, $J = 253$ Hz), 137.502 (d, $J = 252$ Hz), 132.083, 131.558, 130.115, 129.320, 128.658, 124.733, 118.560, 115.017 (t, $J = 18.7$ Hz), 111.514.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -140.718 (dd, $^1J = 23$ Hz, $^2J = 8.1$ Hz, 2F), -154.397 (t, $J = 21$ Hz, 1F), -161.917 – -162.064 (m, 2F).

**UV/Vis (Acetonitrile):** $\lambda_{\text{max}}(\varepsilon) = 258$ (17400) nm (M$^{-1}$cm$^{-1}$).

**GCMS (m/z):** 345.00.
3.5.1.3. **Precursors involving heterocycles**

2-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)thiophene (3.5a)

Chemical Formula: 
C_{16}H_{7}F_{6}S  
Molecular Weight: 326.28

A 100 ml flask with magnetic stirbar was placed with 2'-bromo-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3.23 g, 10.0 mmol), 2-thiopheneboronic acid (1.929 g, 15.0 mmol), toluene (10 ml), 1-propanol (25 ml) and sodium carbonate (1.53 g, 15.0 mmol). This mixture was degassed thoroughly with nitrogen and warmed up to 70 °C and Pd(PPh\textsubscript{3})\textsubscript{4} (110 mg, 1%) was added. The resulting mixture was heated to 120 °C for six hours. After this time the mixture was cooled and most of the volatile components were removed under vacuum overnight. Silica gel (~ 10 g) and THF (25 ml) were added and the resulting slurry was stirred and the solvent was removed by rotary evaporation. This material was placed at the top of a silica gel column and eluted (eluent: hexanes). A small amount of starting bromide eluted first followed by the product and then an unidentified byproduct. Fractions containing pure product were combined and concentrated to give an oil, which crystallized on standing overnight. The crystals (2.65 g, 8.7 mmol, 87% yield) were collected and air-dried.

**MP:** 52.0 – 54.0 °C.

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) δ: 7.626 – 7.622 (m, 1H), 7.518 (ddd, \textsuperscript{1}J = 7.6 Hz, \textsuperscript{2}J = 7.6 Hz, \textsuperscript{3}J =
2.4 Hz, 1H), 7.440 (dd, \( ^1J = 7.6\) Hz, \( ^2J = 7.6\) Hz, \( ^3J = 2.4\) Hz, 1H), 7.310 (dd, \( ^1J = 7.6\) Hz, \( ^2J = 0.8\) Hz, 1H), 7.253 – 7.234 (m, 1H), 6.934 (dd, \( ^1J = 4.8\) Hz, \( ^2J = 3.6\) Hz, 1H), 6.814 (dd, \( ^1J = 3.6\) Hz, \( ^2J = 0.8\) Hz, 1H).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\): 144.478 (d, \( J = 249\) Hz), 141.374, 140.916 (d, \( J = 253\) Hz), 137.580 (d, \( J = 251\) Hz), 135.353, 131.432, 130.672, 129.934, 127.900, 127.209, 126.251, 124.876, 115.565.

\(^{19}\)F-NMR (376 MHz, CDCl\(_3\)) \(\delta\): -140.647 (dd, \( ^1J = 23\) Hz, \( ^2J = 8\) Hz, 2F), -155.428 (t, \( J = 21\) Hz, 1F), -162.683 – -162.835 (m, 2F).

UV/Vis (Acetonitrile): \(\lambda_{max}(\varepsilon) = 274\) (10060) nm (M\(^{-1}\)cm\(^{-1}\)).

GCMS (m/z): 327.00.

HRMS: M\(^+\) = 326.01855 (Calc = 326.01831).

\((E)-2-(2-\text{(Perfluorophenyl)vinyl})\text{benzo[b]thiophene (3.5b)}\)

![Chemical Structure](image)

Chemical Formula: C\(_{16}\)H\(_7\)F\(_5\)S
Molecular Weight: 326.28

A 100 mL round bottom flask was charged with 2-iodobenzothiophene (1.300 g, 5.0 mmol), pentafluorostyrene (1.068 g, 5.5 mmol), anhydrous DMF (5 mL), potassium carbonate (0.770 g, 5.5 mmol), 2-(2-methoxyethoxy)-\(N,N\)-bis[2-(2-methoxyethoxy)ethyl]ethanamine (0.2 mL) and Pd(OAc)\(_2\) (12 mg, 1%). The mixture was heated under a nitrogen atmosphere to 120 °C and after 20 hours TLC showed the starting material was completely consumed.
After the mixture was cooled, water was added to a total volume of 100 mL to precipitate the product. The product was separated by suction filtration, washed with water and air-dried (0.978 g, 3.0 mmol, 60 % yield). This product was recrystallized from isooctane, to yellow crystals (0.617 g, 2.0 mmol, 40 % yield) as final product.

**M.P.:** Slowly sublimed above 169 °C

**$^1H$-NMR (400 MHz, CDCl$_3$) $\delta$:** 7.820 – 7.722 (m, 2H), 7.644 (d, $J = 16.4$ Hz, 1H), 7.357 – 7.334 (m, 3H), 7.852 (d, $J = 16.4$ Hz, 1H).

**$^{19}F$-NMR (376 MHz, CDCl$_3$) $\delta$:** -142.780 – -142.858 (m, 2F), -156.251 (d, $J = 20.1$ Hz, 1F), -163.101 – -163.234 (m, 2F).

**UV/Vis (Acetonitrile):** $\lambda_{\text{max}}(\varepsilon) = 220$ (24420), 263 (8400), 333 (39630) nm (M$^{-1}$cm$^{-1}$).

**GCMS (m/z):** 326.05.

**4-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)pyridine (3.5c)**

![Chemical Structure](image)

Chemical Formula: C$_{17}$H$_8$F$_5$N  
Molecular Weight: 321.24

A 100 mL flask with magnetic stir bar was charged with 2'-bromo-2,3,4,5,6-pentafluoro-1,1'-biphenyl (1.621 g, 5.0 mmol), 4-pyridineboronic acid (1.227g, 10.0 mmol), K$_2$CO$_3$ (1.393 g, 10.0
mmol), toluene (40 mL) and 1-PrOH (10 ml). Under a nitrogen atmosphere, the mixture was warmed up to gently reflux and then Pd(PPh₃)₄ (58.109 mg, 0.050mmol, 1%) was added. After 12 hours, TLC indicated that the biphenyl starting material was consumed and a new product was observed.

The mixture was cooled to room temperature and silica gel (~ 5g) was added. After the solvent was removed by rotary evaporation, the tan powder was placed on the top of a silica gel column and eluted (eluent: hexanes: EtOAc = 3:1). The fractions containing the product were combined and concentrated to dryness, giving white crystals (0.783 g, 2.5 mmol, 50% yield) as final product.

**M.P.:** Slowly sublimed above 75 °C, melted at 108.5 – 111.5 °C.

**¹H-NMR (400 MHz, CDCl₃) δ:** 8.534 (d, J = 6.0 Hz, 2H), 7.619 – 7.525 (m, 2H), 7.490 – 7.466 (m, 1H), 7.396 – 7.373 (m, 1H), 7.073 (dd, ¹J = 4.8 Hz, ²J = 1.6 Hz, 2H).

**¹³C-NMR (100 MHz, CDCl₃) δ:** 149.802, 148.204, 143.990 (d, J = 245.5 Hz), 140.894 (d, J = 253.2 Hz), 140.194, 137.514 (d, J = 252.1 Hz), 131.552, 130.137, 129.941, 128.781, 124.667, 123.359, 114.970 (td, ¹J = 19.1 Hz, ²J = 3.8 Hz).

**¹⁹F-NMR (376 MHz, CDCl₃) δ:** -140.717 (dd, ¹J = 22.6 Hz, ²J = 8.2 Hz, 2F), -154.551 (t, J = 20.9 Hz, 1F), -162.010 – -162.150 (m, 2F).

**UV/Vis (Acetonitrile):** No maximum absorption, the absorption coefficient at 254 nm is provided. ε = 9560 M⁻¹cm⁻¹ (254 nm).

**GCMS (m/z):** 320.97.
3.5.1.4. 2,3,5,6-tetrafluoro precursors

2,3,5,6-tetrafluorobenzonic acid

\[
\begin{array}{c}
\text{COOH} \\
\text{F} & \text{F} \\
\text{F} & \text{F} \\
\text{H}
\end{array}
\]

Chemical Formula: C₇H₂F₄O₂
Molecular Weight: 194.08

In a 1 L round bottom flask with magnetic stir bar was placed pentafluorobenzoic acid (53.093 g, 0.25 mol), water (180 mL) and ammonium hydroxide (425 mL). This mixture was stirred to obtain a clear solution and then zinc powder (81.829 g 1.25 mol) was added all at once. The resulting mixture was stirred at room temperature for four days. After this time the remaining zinc powder residue was filtered off with a sintered glass funnel and the filtrate was acidified with concentrated HCl (approximately 400 mL) with cooling in an ice bath.

The precipitate obtained was isolated by suction filtration, washed with water and air-dried, giving the final product as a white powder (33.360 g, 0.17 mol, 68 % yield).

References:


M.P.: 148.0 – 148.5 °C (Lit.: 150 – 152 °C).

\(^1\)H-NMR (400 MHz, DMSO) δ: 7.925 (tt, \(^1\)J = 10.4 Hz, \(^2\)J = 7.6 Hz).

\(^1^3\)C-NMR (100 MHz, DMSO) δ: 160.881, 146.049 (dddd, \(^1\)J = 245.0 Hz, \(^2\)J = 13.4 Hz, \(^3\)J = 10.5 Hz, \(^4\)J = 3.8 Hz), 144.056 (ddddd, \(^1\)J = 250.5 Hz, \(^2\)J = 14.9 Hz, \(^3\)J = 4.4 Hz, \(^4\)J = 4.3 Hz), 115.101 (t, \(J = 17.4\) Hz), 109.124 (t, \(J = 23.2\) Hz).
$^{19}$F-NMR (376 MHz, DMSO) $\delta$: -138.728 – -138.860 (m, 2F), -141.536 – -141.660 (m, 2F).

**potassium 2,3,5,6-tetrafluorobenzoate**

\[
\begin{array}{c}
\text{COOK} \\
\text{F} \quad \text{F} \\
\text{F} \quad \text{H} \\
\text{F} \quad \text{F}
\end{array}
\]

Chemical Formula: C$_7$H$_4$KO$_2$

Molecular Weight: 232.17

A solution of $t$-BuOK (4.719 g, 42.0 mmol) in EtOH (50 mL) was added dropwise into a 500 mL round bottom flask containing a solution of 2,3,5,6-tetrafluorobenzoic acid (7.769 g, 40.0 mmol) in EtOH (50 mL). A white precipitate formed during addition.

After the addition was complete, the resulting mixture was stirred overnight. The white precipitate was filtered by suction filtration and air-dried, giving the desired product as a white powder (9.120 g, 39.0 mmol, 98% yield).

**Reference:** Shang, Rui; Fu, Yao; Wang, Yan; Xu, Qing; Yu, Hai-Zhu; Liu, Lei *Angewandte Chemie, International Edition*, 2009, vol.48, #49, p.9350 - 9354.
2,3,5,6-tetrafluoro-1,1':2',1''-terphenyl (3.7a)

Chemical Formula: C_{18}H_{10}F_{4}
Molecular Weight: 302.27

A 100 mL 2-necked round-bottomed flask was charged with 2-iodobiphenyl (2.811 g, 10.0 mmol), potassium 2,3,5,6-tetrafluorobenzoate (3.499 g, 15.0 mmol), CuI (0.382 g, 2.0 mmol), 1,10-phenanthroline (0.365 g, 2.0 mmol) and DMA (15 mL). The mixture was then heated and stirred 150 °C for 24 hours under nitrogen.

The mixture was cooled to room temperature and the brown residue was diluted to a total volume of 100 mL with ethyl acetate. After gravity filtration, the solid residue was washed with ethyl acetate (50 mL x 2) and the filtrates were combined, washed with water (200 mL x 2), brine (200 mL x 1), and then dried over anhydrous MgSO₄.

The drying agent was removed by filtration, silica gel (~ 5 g) was added and the solvent was removed via rotary evaporation. The brown powder was placed on the top of a silica gel column and chromatographed (eluent: hexanes). The major band was collected and concentrated, giving white crystals (0.670 g, 2.2 mmol, 22% yield) as final product.

M.P.: 64.0 – 68.0 °C.
\[ \text{H-NMR (400 MHz, CDCl}_3 \text{)} \delta: 7.534 - 7.418 (m, 3H), 7.344 (dd, \text{ }^1J = 7.6 \text{ Hz, } \text{ }^2J = 0.8 \text{ Hz}), 7.244 - 7.202 (m, 3H), 7.168 - 7.138 (m, 2H), 6.907 (tt, \text{ }^1J = 9.6 \text{ Hz, } \text{ }^2J = 7.2 \text{ Hz, 1H}). \]

\[ \text{C-NMR (100 MHz, CDCl}_3 \text{)} \delta: 145.740 (dddd, \text{ }^1J = 246 \text{ Hz, } \text{ }^2J = 14.5 \text{ Hz, } \text{ }^3J = 10.6 \text{ Hz, } \text{ }^4J = 3.9 \text{ Hz}), 143.725 (ddt, \text{ }^1J = 244 \text{ Hz, } \text{ }^2J = 13.5 \text{ Hz, } \text{ }^3J = 4.3 \text{ Hz}), 142.881, 140.485, 139.533, 130.947, 130.311, 129.629, 128.605, 128.073, 127.362 (d, \text{ } J = 4.2 \text{ Hz}), 126.029, 121.708 (t, \text{ } J = 18.6 \text{ Hz}), 105.035 (t, \text{ } J = 22.5 \text{ Hz}). \]

\[ \text{F-NMR (376 MHz, CDCl}_3 \text{)} \delta: -139.397 - -139.518 (m, 2F), -140.812 - -140.926 (m, 2F). \]

\[ \text{UV/Vis (Acetonitrile): } \lambda_{\text{max}}(\varepsilon) = 194 (48760), 227 (21760) \text{ nm (M}^{-1}\text{cm}^{-1}). \]

\[ \text{GCMS (m/z): 303.01.} \]

2,3,5,6-tetrafluoro-4-methoxy-1,1':2',1''-terphenyl (3.7b)

![Chemical Structure]

Chemical Formula: C\textsubscript{19}H\textsubscript{12}F\textsubscript{4}O  
Molecular Weight: 332.30

A 100 mL flask was charged with 2,3,4,5,6-pentafluoro-1,1':2',1''-terphenyl (0.643 g, 2.0 mmol), methanol (20 mL) and potassium \textit{t}-butoxide (1.173 g, 10 mmol, 5 eq). The obtained solution was stirred continuously under room temperature.

After 48 hours, TLC indicated that the starting material was completely consumed. Silica gel (~5g) was then added into the flask and the mixture was concentrated to dryness. The obtained white powder was placed on the top of silica gel column and eluted (Hexanes). The fractions containing
the product was collected and condensed, giving colorless oil (0.640 g, 1.9 mmol, 95% yield) as final product.

¹H-NMR (400 MHz, CDCl₃)δ: 7.517 - 7.443 (m, 3H), 7.340 (d, J = 7.6 Hz, 1H), 7.255 - 7.235 (m, 3H), 7.157 - 7.149 (m, 2H), 4.035 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃)δ: 144.202 (d, J = 243 Hz), 143.046, 140.794 (d, J = 246 Hz), 140.637, 140.636 (d, J = 246 Hz), 137.605, 131.308, 130.298, 129.442, 128.577, 128.055, 127.349, 127.246, 125.731, 114.205 (t, J = 19.2 Hz), 62.102 (t, J = 3.4 Hz).

¹⁹F-NMR (376 MHz, CDCl₃)δ: -142.666 (dd, ¹J = 22.5 Hz, ²J = 8.8 Hz, 2F), -159.081(dd, ¹J = 22.5 Hz, ²J = 8.8 Hz, 2F).

4-ethoxy-2,3,5,6-tetrafluoro-1,1':2',1''-terphenyl (3.7c)

![Chemical Structure](image)

Chemical Formula: C₂₀H₁₄F₄O  
Molecular Weight: 346.32

A 100 mL flask was charged with 2,3,4,5,6-pentafluoro-1,1':2',1''-terphenyl (0.645 g, 2.0 mmol), ethanol (20 mL) and potassium t-butoxide (1.126 g, 10 mmol, 5 eq). The mixture was well stirred to a colorless solution and then being stirred continuously under room temperature.

After 48 hours, TLC indicated that the starting material no longer existed. Silica gel (~5g) was
then added into the solution and concentrated to dryness. The obtained white powder was placed on the top of silica gel column and eluted (Hexanes). The fractions containing the product was collected and condensed, giving colorless oil (0.648 g, 1.9 mmol, 95 % yield) as final product.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.527 – 7.413 (m, 3H), 7.356 – 7.334 (m, 1H), 7.241 – 7.224 (m, 3H), 7.156 – 7.132 (m, 2H), 4.247 (q, $J = 7.2$ Hz, 2H), 1.370 (t, $J = 7.2$ Hz, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 144.177 (d, $J = 243$ Hz), 143.046, 141.222 (d, $J = 245$ Hz), 141.069 (d, $J = 245$ Hz), 140.647, 136.568, 131.300, 130.265, 129.431, 128.587, 128.027, 17.347, 127.238, 125.827, 114.329 (t, $J = 19.2$ Hz), 70.816 (t, $J = 2.5$ Hz), 15.316.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: 142.786 – 142.875 (m, 2F), 158.340 (dd, $^1J = 22.6$ Hz, $^2J = 8.3$ Hz, 2F).

2,3,5,6-tetrafluoro-4-propoxy-1,1’:2’,1”-terphenyl (3.7d)

Chemical Formula: C$_{21}$H$_{18}$F$_4$O
Molecular Weight: 360.35

In a 100 mL flask was placed with 2,3,4,5,6-pentafluoro-1,1’:2’,1”-terphenyl (0.645 g, 2.0 mmol), 1-propanol (20 mL) and potassium t-butoxide (1.152 g, 10 mmol, 5 eq). The mixture was well stirred to give a colorless solution and the obtained solution was then being stirred continuously under room temperature.
After 72 hours, TLC indicated that the starting material no longer existed. Silica gel (~ 5g) was then charged inside and the mixture was concentrated to dryness. The obtained white powder was placed on the top of silica gel column and eluted (Hexanes). The fractions containing the product was collected and condensed, giving colorless oil (0.712 g, 1.9 mmol, 95 % yield) as desired product.

\[ ^1H\text{-}NMR \ (400 \text{ MHz, CDCl}_3)\delta: \ 7.536 -7.423 \ (m, 3H), \ 7.350 \ (d, J = 7.6 \text{ Hz, 1H}), \ 7.248 - 7.233 \ (m, 3H), \ 7.156 - 7.139 \ (m, 2H), \ 4.146 \ (t, J = 6.4 \text{ Hz, 2H}), \ 1.815 - 1.727 \ (m, 2H), \ 1.023 \ (t, J = 7.4 \text{ Hz, 3H}). \]

\[ ^{13}\text{C}\text{-}NMR \ (100 \text{ MHz, CDCl}_3)\delta: \ 144.160 \ (d, J = 243 \text{ Hz}), \ 143.027, \ 141.146 \ (d, J = 246 \text{ Hz}), \ 140.992 \ (d, J = 246 \text{ Hz}), \ 140.632, \ 136.921, \ 131.303, \ 130.259, \ 129.409, \ 128.577, \ 128.020, \ 127.331, \ 127.219, \ 125.823, \ 114.178 \ (t, J = 19.4 \text{ Hz}), \ 76.725, \ 23.217, \ 10.095. \]

\[ ^{19}\text{F}\text{-}NMR \ (376 \text{ MHz, CDCl}_3): \ -142.892 \ (dd, J^1 = 22.6 \text{ Hz, J^2 = 8.8 Hz, 2F}), \ -158.362(dd, J^1 = 22.6 \text{ Hz, J^2 = 8.8 Hz, 2F}). \]

**Hexyl(2,3,5,6-tetrafluoro-[1,1':2',1''-terphenyl]-4-yl)sulfane (3.7e)**

A 100 mL flask was charged with 2,3,4,5,6-pentafluoro-1,1':2',1''-terphenyl (1.602 g, 5.0 mmol), 1-hexanethiol (0.653 g, 5.5 mmol), DME (25 mL) and t-BuOK (1.128 g, 10 mmol). The obtained
mixture was well stirred and heated up to gently reflux in 86 °C oil bath.

After 12 hours, TLC indicated that the starting material was consumed. Silica gel (~ 5g) was then added into the mixture and concentrated to dryness. The obtained tan powder was placed on the top of silica gel column and eluted (eluent: hexanes). The fractions containing the product was collected and condensed, giving colorless oil (1.885 g, 4.5 mmol, 90 % yield) as final product.

\( ^1\text{H-NMR (400 MHz, CDCl}_3\): \) 7.556 – 7.441 (m, 3H), 7.366 (d, \( J = 7.6 \) Hz, 1H), 7.245 – 7.227 (m, 3H), 7.156 – 7.135 (m, 2H), 2.883 (t, \( J = 7.2 \) Hz, 2H), 1.542 – 1.470 (m, 2H), 1.420 – 1.349 (m, 2H), 1.321 – 1.238 (m, 4H), 0.891 (t, \( J = 6.6 \) Hz, 2H).

\( ^13\text{C-NMR (100 MHz, CDCl}_3\): \) 146.824 (dd, \( ^1J = 243.6 \) Hz, \( ^2J = 14.6 \) Hz), 143.774 (dd, \( ^1J = 246.5 \) Hz, \( ^2J = 15.3 \) Hz), 142.865, 140.438, 130.923, 130.284, 129.659, 128.573, 128.048, 127.367, 127.343, 125.845, 120.694 (t, \( J = 18.9 \) Hz), 113.479 (t, \( J = 20.2 \) Hz), 34.571 (t, \( J = 2.5 \) Hz), 31.292, 29.637, 28.020, 22.486, 13.997.

\( ^19\text{F-NMR (376 MHz, CDCl}_3\): \) -135.332 (dd, \( ^1J = 24.82 \) Hz, \( ^2J = 12.03 \) Hz), -141.100 (dd, \( ^1J = 24.82 \) Hz, \( ^2J = 12.03 \) Hz).
3.5.1.5. 2,6-Difluoro precursors - two fluorine atoms located at the two reactive ortho-sites

biphenyl-2-boronic acid

Chemical Formula: C_{12}H_{11}BO_{2}
Molecular Weight: 198.03

An oven dried 250 mL flask equipped with magnetic stir bar was charged with 2-iodobiphenyl (5.603 g, 20.0 mmol) and anhydrous THF (30 mL). Under a nitrogen atmosphere, the solution was cooled to -78 °C and n-BuLi solution (16 mL, 2.5M in hexane, 40 mmol) was added dropwise. After the addition was complete, the mixture was stirred for approximately 30 min at -78 °C. Next, B(OiPr)_3 (7.568 g, 40.0 mmol) was added to the previous mixture to give a white suspension.

The mixture obtained was stirred overnight (~ 12 h) during which time the temperature was allowed to warm from -78 °C to room temperature. This mixture was treated with hydrochloric acid (1M, 100 mL) to form two layers. The aqueous phase was extracted with diethyl ether (100 mL x 3) and the organic phases were combined. After being dried over with anhydrous MgSO₄, the solution was concentrated to dryness. The brown crude product was recrystallized from water, giving the final product as white needle-like crystals (1.892 g, 9.6 mmol, 48 % yield).

Reference: Bettinger, Holger F.; Filthaus, Matthias; Oppel, Iris M. Organic and Biomolecular
M.P.: 190.0 – 194.0 °C (Lit.: 194 – 196 °C).

$^1$H-NMR (400 MHz, DMSO) $\delta$: 7.923 (s, 2H), 7.462 – 7.290 (m, 9H).

$^{13}$C-NMR (100 MHz, DMSO) $\delta$: 144.468, 143.577, 137.873, 132.552, 128.589, 128.540, 127.077, 126.361.

2,6-difluoro-1,1':2',1''-terphenyl (3.9a)

A nitrogen flushed 100 mL flask with magnetic stir bar was charged with 2,6-difluoriodobenzene (1.209 g, 5.0 mmol), biphenyl-2-boronic acid (1.502g, 7.5 mmol), potassium carbonate (1.403 g, 10.0 mmol), 1,4-dioxane (10 mL) and water (4 mL). The solution was heated to a gentle reflux and Pd(PPh$_3$)$_4$ (118.3 mg, 0.10 mmol, 2%) was finally added.

After 24 hours of reflux, TLC indicated that the starting material 2,6-difluoriodobenzene was completely consumed. After cooling, the mixture was diluted to 100 mL with ethyl acetate and washed with water (100 mL x 3). The organic phase was then isolated and dried with anhydrous MgSO$_4$. After removal of the drying reagent via gravity filtration, the filtrate was mixed with silica gel (~ 2 g). This mixture was concentrated to dryness via rotary evaporation and the tan powder was placed on the top of a silica gel column and eluted (eluent: hexanes). The product (1.197 g,
4.5 mmol, 90% yield) was obtained as a colorless oil.


$^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.486 – 7.364 (m, 4H), 7.222 – 7.130 (m, 6H), 6.787 – 6.750 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 160.132 (dd, $^1J = 246.0$ Hz, $^2J = 7.2$ Hz), 142.737, 141.109, 131.243, 129.992, 129.027 (t, $J = 10.0$ Hz), 128.790, 128.713, 127.755, 127.091, 126.833, 118.447 (t, $J = 20.6$ Hz), 111.010 (dd, $^1J = 19.1$ Hz, $^2J = 6.6$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -112.601 – -112.644 (m, 2F).

UV/Vis (Acetonitrile): $\lambda_{\text{max}}(\epsilon) = 223$ (24770) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 266.04.

2,6-difluorostilbene (3.9b)

![Chemical structure of 2,6-difluorostilbene]

Chemical Formula: C$_{14}$H$_{10}$F$_2$ Chemical Formula: C$_{14}$H$_{10}$F$_2$
Molecular Weight: 216.23 Molecular Weight: 216.23

A 250 mL flask with magnetic stir bar was charged with benzyltriphenylphosphonium chloride (3.907 g, 10.0 mmol), 2,6-difluorobenzaldehyde (1.426 g, 10.0 mmol) and ethanol (50 mL). A solution of t-BuOK (1.184 g, 10.5 mmol) in ethanol (50 mL) was added dropwise and the resulting mixture was stirred at room temperature overnight (~ 12h). Silica gel (~ 5 g) was then added into the mixture and after removal of the solvent by rotary evaporation the white powder was placed
on the top of a silica gel column and eluted (eluent: hexanes). The fractions containing the isomeric products were combined and concentrated to dryness. The obtained colorless oil was cooled, giving colorless crystals (1.377 g, 6.4 mmol, 64 % yield) as E-isomer and the remaining colorless oil (0.424 g, 2.0 mmol, 20 % yield) as Z-isomer.

References: Fan, Shilu; He, Chun-Yang; Jiang, Zhong-Xing; Min, Qiao-Qiao; Wan, Xiaolong; Yang, Jie; Zhang, Xingang Journal of the American Chemical Society, 2010, Vol.132, 4506 – 4507. 

(E)-2,6-difluorostilbene

M.P.: 66.0 – 67.5 °C (Lit.: 66 °C).

$^1$H-NMR (400 MHz, CDCl$_3$): 7.547 – 7.525 (m, 2H), 7.443 (d, $J$ = 16.8 Hz, 1H), 7.385 – 7.347 (m, 2H), 7.304 – 7.261 (m, 1H), 7.161 – 7.104 (m, 2H), 6.901 (t, $J$ = 8.4 Hz, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): 161.052 (dd, $^1J$ = 249.9 Hz, $^2J$ = 7.6Hz), 137.528, 135.170 (t, $J$ = 8.2 Hz), 128.708, 128.182, 127.873 (t, $J$ = 10.8 Hz), 126.706, 115.231, 114.831 (t, $J$ = 15.1 Hz), 111.574 (dd, $^1J$ = 19.4 Hz, $^2J$ = 6.5Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$): -113.445 – -113.485 (m, 2F).

UV/Vis (Acetonitrile): $\lambda_{max}(e) = 201$ (26620), 221 (15500), 291 (31110) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 216.05.

(Z)-2,6-difluorostilbene

(The sample of the Z-isomer was not pure and included some E-isomer. Thus the NMR for the Z-isomer was obtained by comparison NMRs for the mixture and the pure E-isomer).

$^1$H-NMR (400 MHz, CDCl$_3$): 7.215 – 7.108 (m, 6H), 6.913 – 6.804 (m, 3H), 6.357 (d, $J$ = 12 Hz, 1H).
$^{13}$C-NMR (100 MHz, CDCl$_3$): 160.388 (dd, $^1J = 248.2$ Hz, $^2J = 7.8$Hz), 137.171, 135.353, 128.892, 128.791, 128.176, 128.048, 127.700, 115.704, 114.888 (t, $J = 20.1$ Hz), 111.352 (dd, $^1J = 19.2$ Hz, $^2J = 6.0$Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$): -110.622 – -110.639 (m, 2F).

(Z)-3-(2,6-difluorophenyl)-2-phenylacrylonitrile (3.9c)

\[
\text{Chemical Formula: C}_{15}\text{H}_{9}\text{F}_{2}\text{N} \\
\text{Molecular Weight: 241.24}
\]

In a 250mL Erlenmeyer flask with magnetic stir bar was placed 2,6-difluorobenzaldehyde (2.851 g, 20.0 mmol), phenylacetonitrile (2.352 g, 20.1 mmol) and EtOH (80 mL). This mixture was stirred and then K$_3$PO$_4$ (1.705 g, 8.0 mmol) was added.

The resulting suspension was stirred at room temperature overnight and then water was added dropwise with stirring to a total volume of 200 mL. This suspension was transferred to a 600 mL beaker and water was added to 400 mL in total. The solid was isolated by suction filtration, washed well with water and air-dried. The crude product was obtained as a white powder (3.886 g, 16.1 mmol, 80.5 % yield) which was recrystallized from iso-propanol to give white crystals (3.652 g, 15.1 mmol, 75.5 % yield) as pure product.

M.P.: 104.0 – 105.5°C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.694 – 7.673 (m, 2H), 7.461 – 7.320 (m, 5H), 6.981 (t, $J = 8.2$ Hz, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 160.304 (dd, $^1J = 251.5$ Hz, $^2J = 6.4$ Hz), 133.242, 131.546 (t, $J = 10.4$ Hz), 129.978, 129.132, 128.846, 126.222, 120.457, 116.325, 112.415 (t, $J = 18.1$ Hz), 111.834 (dd, $^1J = 19.6$ Hz, $^2J = 5.3$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -107.879 (t, $J = 7.0$ Hz, 2F).

UV/Vis (Acetonitrile): $\lambda_{\text{max}}(\varepsilon)$ = 223 (10600), 293 (20080) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 241.01.

(Z)-2-([1,1'-biphenyl]-4-yl)-3-(2,6-difluorophenyl)acrylonitrile (3.9d)

![Chemical structure](image_url)

Chemical Formula: C$_{21}$H$_{13}$F$_2$N
Molecular Weight: 317.33

In a 200 ml pear flask with magnetic stirbar was placed 2,6-difluorobenzaldehyde (1.42 g, 10.0 mmol), 4-biphenylacetonitrile (1.93 g, 10.0 mmol) and EtOH (40 ml). This mixture was warmed to dissolve the biphenyl derivative and after cooling K$_3$PO$_4$ (0.84 g, 4.0 mmol) was added. The resulting mixture was stirred and soon the crystallization of product began. The slurry was stirred overnight at room temperature and then water was added dropwise with stirring to 200 mL. The solid was isolated by suction filtration, washed well with water and air-dried. The crude product was taken up in boiling 1-propanol and upon cooling the product appeared as white crystals which were collected by suction filtration, washed with methanol and air-dried (2.52 g, 7.9 mmol, 79 %
yield).

**M.P.:** 145.5 – 147.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.787 (d, $J = 8.8$ Hz, 2H), 7.693 (d, $J = 8.8$ Hz, 2H), 7.642 – 7.618 (m, 2H), 7.497 – 7.456 (m, 3H), 7.418 – 7.374 (m, 2H), 7.027 (t, $J = 8.0$ Hz, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 160.366 (dd, $^1J = 251.6$ Hz, $^2J = 6.3$ Hz), 142.831, 139.851, 132.180, 131.505 (t, $J = 10.4$ Hz), 128.972, 128.461, 127.994, 127.743, 127.100, 126.706, 120.095, 116.304, 112.501 (t, $J = 10.4$ Hz), 111.874 (dd, $^1J = 19.7$ Hz, $^2J = 5.2$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -108.376 (t, $J = 7.0$ Hz, 2F).

UV/Vis (Acetonitrile): $\lambda_{\text{max}}(\varepsilon) = 198$ (60860), 243 (14540), 315 (32860) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 317.09.

### 1-(2,6-difluorostyryl)naphthalene (3.9e)

![Chemical Structure](image)

Chemical Formula: C$_{18}$H$_{12}$F$_2$

Molecular Weight: 266.28

A solution of $t$-BuOK (2.263 g, 20.2 mmol) dissolved in EtOH (100 mL) was added dropwise into the suspension of (1-naphthylmethyl)triphenylphosphonium bromide (9.666 g, 20.0 mmol) and 2,6-difluorobenzaldehyde (2.861 g, 20.1 mmol) in EtOH (100 mL) in a 250 mL flask.
This mixture was stirred at room temperature overnight after which time no starting materials could be observed by TLC. Silica gel was added and after removal of the solvent by rotary evaporation, the powder obtained was placed on the top of a silica gel column and chromatographed (eluent: hexanes), giving light yellow crystals (0.302 g $E$-isomer was isolated pure and 3.101 g as a mixture of $Z/E$-isomers, 12.8 mmol in total, 64% yield).

$(E)$-1-(2,6-difluorostyryl)naphthalene

**M.P.:** 47.0 – 49.5 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.200 (d, $J = 16.6$ Hz, 1H), 8.161 (dd, $^1J = 8.4$ Hz, $^2J = 1.2$ Hz, 1H), 7.815 – 7.791 (m, 1H), 7.765 – 7.709 (m, 2H), 7.510 – 7.413 (m, 3H), 7.138 (d, $J = 16.6$ Hz, 1H), 7.110 – 7.037 (m, 1H), 6.888 – 6.845 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 161.083 (dd, $^1J = 250.0$ Hz, $^2J = 7.6$ Hz), 153.300, 133.678, 132.477 (t, $J = 8.4$ Hz), 131.344, 128.534 (d, $J = 5.7$ Hz), 127.998 (t, $J = 10.8$ Hz), 126.235, 125.867, 125.658, 123.662 (d, $J = 10.6$ Hz), 117.999, 115.025 (t, $J = 15.0$ Hz), 111.580 (dd, $^1J = 19.4$ Hz, $^2J = 6.4$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -112-741 – -112.810 (m, 2F).

UV/Vis (Acetonitrile): $\lambda_{\text{max}(\epsilon)}$ = 202 (55500), 227 (38100), 319 (18460) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 266.07.
3.5.1.6. Non-perfluorinated precursors for competition of PCDHF vs oxidative photocyclization

2-fluorostilbene (3.11a)

![Chemical Structure](image)

Chemical Formula: C\textsubscript{14}H\textsubscript{11}F  
Molecular Weight: 198.24

A 500 mL flask with magnetic stir bar was charged with 2-fluorobenzyltriphenylphosphonium chloride (8.127 g, 20 mmol), benzaldehyde (2.125 g, 20 mmol) and ethanol (100 mL). Then, a solution of t-BuOK (2.307 g, 21.0 mmol) in ethanol (50 mL) was added dropwise. The mixture was stirred at room temperature overnight (~ 12h) and then silica gel (~5 g) was added to the mixture. After removal of the solvent via rotary evaporation, the white powder obtained was placed on the top of a silica gel column and eluted (eluent: hexanes: EtOAc = 20:1). The fractions containing the product were combined and concentrated to dryness, giving a mixture of colorless oil and crystals (3.828 g, 19 mmol, 95 % yield). The mixture was cooled, giving colorless crystals as E-isomer (1.413 g, 7.1 mmol, 35.5 % yield) and colorless oil (1.751 g, 8.8 mmol, 44 % yield) as Z-isomer.

References: Byrne, Peter A.; Gilheany, Declan G.; Muldoon, Jimmy; Rajendran, Kamalraj V.  

Data:

**(E)-2-fluorostilbene**

\[^{1}\text{H-}NMR\ (400\ \text{MHz, CDCl\textsubscript{3}})\ \delta:\ septet, ^{1}J = 7.6\ \text{Hz}, ^{2}J = 7.6\ \text{Hz}, ^{3}J = 1.6\ \text{Hz}, 1\text{H}), 7.520\ (\text{app. d, } J = 7.6\ \text{Hz, 2H}), 7.352\ (\text{app. t, } J = 7.6\ \text{Hz, 2H}), 7.293 – 7.029\ (m, 6\text{H}).\n
\[^{13}\text{C-}NMR\ (100\ \text{MHz, CDCl\textsubscript{3}})\ \delta:\ 160.420\ (d, J = 248.3\ \text{Hz}), 137.200, 130.875\ (d, J = 4.6\ \text{Hz}), 128.804, 128.695, 127.922, 126.998\ (d, J = 3.5\ \text{Hz}), 126.656, 125.179\ (d, J = 12.0\ \text{Hz}), 124.171\ (d, J = 3.4\ \text{Hz}), 120.875\ (d, J = 3.6\ \text{Hz}), 115.785\ (d, J = 22\ \text{Hz}).\n
\[^{19}\text{F-}NMR\ (376\ \text{MHz, CDCl\textsubscript{3}})\ \delta:\ -118.417\ – -118.480\ (m, 1\text{F}).\n
\text{UV/Vis (Acetonitrile): } \lambda_{\text{max}}(\varepsilon) = 201\ (19220), 225(10690), 299\ (18470)\ \text{nm (M}^{-1}\text{cm}^{-1}).\n
\text{GCMS (m/z): 198.09.}\n
(Z)-2-fluorostilbene

\[^{1}\text{H-}NMR\ (400\ \text{MHz, CDCl\textsubscript{3}})\ \delta:\ 7.229 – 7.146\ (m, 7\text{H}), 7.048 – 6.999\ (m, 1\text{H}), 6.930 – 6.889\ (m, 1\text{H}), 6.710\ (d, J = 12.4\ \text{Hz, 1H}), 6.610\ (d, J = 12.4\ \text{Hz, 1H}).\n
\[^{13}\text{C-}NMR\ (100\ \text{MHz, CDCl\textsubscript{3}})\ \delta:\ 160.340\ (d, J = 246.1\ \text{Hz}), 136.869, 132.259, 130.538\ (d, J = 3.5\ \text{Hz}), 128.974\ (d, J = 8.1\ \text{Hz}), 128.782, 128.275, 127.418, 125.060\ (d, J = 14.5\ \text{Hz}), 123.646\ (d, J = 3.3\ \text{Hz}), 122.637\ (d, J = 3.2\ \text{Hz}), 115.632\ (d, J = 21.9\ \text{Hz}).\n
\[^{19}\text{F-}NMR\ (376\ \text{MHz, CDCl\textsubscript{3}})\ \delta:\ -115.340\ – -115.404\ (m, 1\text{F}).\n
2,2’-difluorostilbene (3.11b)

\[
\begin{align*}
\text{Chemical Formula: } & \ C_{14}H_{10}F_{2} \ & \text{Chemical Formula: } \ C_{14}H_{10}F_{2} \\
\text{Molecular Weight: } & \ 216.23 \ & \text{Molecular Weight: } \ 216.23
\end{align*}
\]

A 250 mL round bottom flask was charged with 2-fluorobenzoyltriphosphonium chloride (8.154
g, 20 mmol), 2-fluorobenzaldehyde (2.484 g, 20 mmol) and ethanol (100 mL). Then, a solution of t-BuOK (2.355 g, 21 mmol) in ethanol (100 mL) was added dropwise to the suspension over one hour.

The resulting mixture was stirred overnight (~12 hours) and TLC indicated no starting material remained. Silica gel was added and the solvent was removed under vacuum. The powder obtained was placed on the top of a silica gel column and chromatographed (eluent: hexanes). The fractions were combined and concentrated. After cooling, colorless crystals of the E-isomer were filtered off (0.880 g, 4 mmol, 20 % yield) and the filtrate was concentrated to give the second product (3.161 g, 15 mmol, 75 % yield) which was the Z-isomer as colorless oil.


(E)- 2,2’-difluorostilbene


$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.634 (ddd, $^1J = 7.6$ Hz, $^2J = 7.6$ Hz, $^3J = 2.0$ Hz, 2H), 7.343 (s, 2H), 7.268 – 7.212 (m, 2H), 7.142 (ddd, $^1J = 7.6$ Hz, $^2J = 7.6$ Hz, $^3J = 1.2$ Hz, 2H), 7.070 (ddd, $^1J = 10.8$ Hz, $^2J = 8.4$ Hz, $^3J = 1.2$ Hz, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 160.571 (d, $J = 248.4$ Hz), 129.225 (d, $J = 8.4$ Hz), 127.148 (d, $J = 3.3$ Hz), 125.199 (d, $J = 11.8$ Hz), 124.319 (d, $J = 3.4$ Hz), 123.071 (t, $J = 4.2$ Hz), 115.898 (d, $J = 21.9$ Hz).

$^{19}$F-NMR (100 MHz, CDCl$_3$) $\delta$: -118.424 – -118.487 (m, 2F).
UV/Vis (Acetonitrile): $\lambda_{\text{max}}(\varepsilon) = 200 (28750), 220 (14890), 293 (25450), 305 (25310)$ nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 216.08.

(Z)-2,2'-difluorostilbene

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.218 – 7.129 (m, 4H), 7.026 (ddd, $^J = 10.8$ Hz, $^2J = 8.4$ Hz, $^3J = 1.2$ Hz, 2H), 6.910 (ddd, $^J = 7.6$ Hz, $^2J = 7.6$ Hz, $^3J = 1.2$ Hz, 2H), 6.758 (s, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 160.334 (d, $J = 246.7$ Hz), 130.132 (d, $J = 3.3$ Hz), 129.182 (d, $J = 8.1$ Hz), 124.704 (d, $J = 12.9$ Hz), 124.652 (d, $J = 2.6$ Hz), 123.624 (d, $J = 3.5$ Hz), 115.584 (d, $J = 21.8$ Hz).

$^{19}$F-NMR (100 MHz, CDCl$_3$) $\delta$: -115.497 – -115.558 (m, 2F).

(Z)-3-(2,4-difluorophenyl)-2-phenylacrylonitrile (3.11c)

![Chemical Structure](image)

Chemical Formula: C$_{15}$H$_9$F$_2$N
Molecular Weight: 241.24

In a 250mL Erlenmeyer flask with magnetic stir bar was placed 2,4-difluorobenzaldehyde (2.873 g, 20.0 mmol), phenylacetonitrile (2.353 g, 20.1 mmol) and EtOH (80 mL). This mixture was stirred and then K$_3$PO$_4$ (2.126 g, 10.0 mmol) was added.

The resulting slurry was stirred overnight at room temperature and then water was added dropwise with stirring to 200 mL. This suspension was then transferred to a 600 mL beaker and water was
added to give a total volume 400 mL. The solid was isolated by suction filtration, washed well with water and air-dried. The crude product was obtained as a white powder (4.541 g, 18.8 mmol, 94% yield), which was recrystallized from 1-propanol as white crystals (4.290 g, 17.8 mmol, 89% yield).

**M.P.:** 115.5 – 117.0 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$) δ:** 8.279 (td, $^1J = 8.8$ Hz, $^2J = 6.4$ Hz), 7.682 – 7.651 (m, 3H), 7.468 – 7.384 (m, 3H), 7.021 – 6.971 (m, 1H), 6.889 (td, $^1J = 9.4$ Hz, $^2J = 2.4$ Hz).

**$^{13}$C-NMR (100 MHz, CDCl$_3$) δ:** 164.086 (dd, $^1J = 253.5$ Hz, $^2J = 12.4$ Hz), 161.368 (dd, $^1J = 253.7$ Hz, $^2J = 11.9$ Hz), 133.930, 132.373 (d, $J = 5.6$ Hz), 129.750 (d, $J = 2.9$ Hz), 129.637, 129.163, 126.095, 118.504 (dd, $^1J = 11.6$ Hz, $^2J = 3.9$ Hz), 117.556, 113.537, 112.180 (dd, $^1J = 21.5$ Hz, $^2J = 3.4$ Hz), 104.334 (t, $J = 25.5$ Hz).

**$^{19}$F-NMR (376 MHz, CDCl$_3$) δ:** -104.338 – -104.423 (m, 1F), -109.871 (dd, $^1J = 18.8$ Hz, $^2J = 9.4$ Hz, 1F).

**UV/Vis (Acetonitrile):** $\lambda_{max}(\varepsilon) = 226$ (10180), 310 (17180) nm (M$^{-1}$cm$^{-1}$).

**GCMS (m/z):** 239.05.
(Z)-2-[[1,1′-biphenyl]-4-yl]-3-(2,4-difluorophenyl)acrylonitrile (3.11d)

\[
\begin{array}{c}
\text{Chemical Formula: } \text{C}_{21}\text{H}_{13}\text{F}_{2}\text{N} \\
\text{Molecular Weight: } 317.34
\end{array}
\]

In a 200 ml pear flask with stirbar was placed 2,4-difluorobenzaldehyde (1.42 g, 10.0 mmol), 4-biphenylacetanitrile (1.93 gm, 10.0 mmol) and EtOH (40 ml). This mixture was warmed to dissolve the biphenyl derivative and after cooling K$_3$PO$_4$ (0.84 gm, 4.0 mmol) was added. The resulting mixture was stirred and soon the crystallization of product began. The slurry was stirred overnight at room temperature and then water was added dropwise with stirring to 200 ml. The solid was isolated by suction filtration, washed well with water and air dried. The crude product was taken up in boiling 1-propanol (with the assistance of some tetrahydrofuran which was eventually boiled out). Upon cooling to room temperature the product appeared as white crystals which were collected by suction filtration, washed with methanol and air dried. Yield 2.74 gm (86%)

**M.P.** 162.0 – 163.0 °C

\[\text{1H-NMR (400 MHz, CDCl}_3\text{)}\delta: 8.336 – 8.277 \text{ (m, 1H), 7.765 – 7.731 \text{ (m, 3H), 7.690 – 7.668 \text{ (m, 2H), 7.632 – 7.608 \text{ (m, 2H), 7.488 – 7.447 \text{ (m, 2H), 7.406 – 7.366 \text{ (m, 1H), 7.040 – 6.992 \text{ (m, 1H), 6.937 – 6.904 \text{ (m, 1H).}}}}\]

\[\text{13C-NMR (100 MHz, CDCl}_3\text{)}\delta: 164.092 \text{ (dd, }^1J = 253.4 \text{ Hz, }^2J = 12.3 \text{ Hz), 161.381 \text{ (dd, }^1J = 253.7 \text{ Hz, }^2J = 11.9 \text{ Hz), 142.471, 139.843, 132.799, 131.982 \text{ (d, } J = 5.5 \text{ Hz), 129.669 \text{ (dd, }^1J = 9.8 \text{ Hz, }^2J = 2.8 \text{ Hz), 128.967, 127.954, 127.752, 127.058, 126.505, 118.540 \text{ (dd, }^1J = 11.6 \text{ Hz, }^2J = 3.9 \text{ Hz).}}\]

177
Hz), 117.551, 113.107, 122.213 (dd, $^1J = 21.5$ Hz, $^2J = 3.5$ Hz), 104.357 (t, $J = 25.5$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$): -104.832- -104.910 (m, 1F), -110.380 (dd, $^1J = 18.8$ Hz, $^2J = 9.4$ Hz, 1F).

(Z)-2-((1,1'-biphenyl)-4-yl)-3-(2,4,5-trifluorophenyl)acrylonitrile (3.11e)

\[\text{Chemical Formula: C}_{21}\text{H}_{12}\text{F}_3\text{N} \]
\[\text{Molecular Weight: 335.32} \]

In a 200 ml pear flask with stirbar was placed 2,4,5-trifluorobenzaldehyde (1.60 g, 10.0 mmol), 4-biphenylacetonitrile (1.93 g, 10.0 mmol) and EtOH (40 mL). This mixture was warmed to dissolve the biphenyl derivative and after cooling K$_3$PO$_4$ (0.84 g, 4.0 mmol) was added. The resulting mixture was stirred and soon the crystallization of product began. The slurry was stirred overnight at room temperature and then water was added dropwise with stirring to 200 mL. The solid was isolated by suction filtration, washed well with water and air-dried. The crude product was taken up in boiling 1-propanol (with the assistance of some tetrahydrofuran which was eventually boiled out). Upon cooling to room temperature the product appeared as yellow fluorescent crystals which were collected by suction filtration, washed with methanol and air-dried (2.91 g, 8.7 mmol, 87 % yield).

M.P.: 178.0 – 179.5 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.177 (ddd, $^1J = 10.8$ Hz, $^2J = 8.6$ Hz, $^3J = 6.8$ Hz, 1H), 7.754 (d, $J = 8.8$ Hz, 2H), 7.687 (d, $J = 8.8$ Hz, 2H), 7.632 – 7.608 (m, 2H), 7.489 – 7.451 (m, 2H), 7.412 –
7.373 (m, 1H), 7.034 (td, \( ^1J = 9.6\) Hz, \( ^2J = 6.4\) Hz, 1H).

\(^{13}\text{C-NMR (100 MHz, CDCl}_3\) δ: 142.825, 139.741, 132.416, 130.572 (d, \( J = 5.7\) Hz), 128.996, 128.052, 127.821, 127.072, 126.593, 118.470, 117.074, 116.168 (d, \( J = 20.7\) Hz), 114.199, 106.018 (dd, \( ^1J = 28\) Hz, \( ^2J = 21\) Hz).

\(^{19}\text{F-NMR (376 MHz, CDCl}_3\) δ: -115.727 – -115.823 (m, 1F), -128.144 – -128.264 (m, 1F), -140.400 – -140.542 (m, 1F).

UV/Vis (Acetonitrile): \( \lambda_{\text{max}}(\varepsilon) = 198 \) (53390), 246 (12990), 330 (29120) nm (M\(^{-1}\)cm\(^{-1}\)).

GCMS (m/z): 335.10.

1-(2,4-difluorostyryl)naphthalene (3.11f)

![Chemical Structure](image)

Chemical Formula: \( \text{C}_{18}\text{H}_{12}\text{F}_2 \)
Molecular Weight: 266.29

A solution of \( \text{t-BuOK} \) (2.362 g, 21.0 mmol) dissolved in EtOH (100 mL) was added dropwise to a suspension of (1-naphthylmethyl)triphenylphosphonium bromide (9.682 g, 20.0 mmol) and 2,4-difluorobenzaldehyde (2.846 g, 20.0 mmol) in ethanol (100 mL) in a 250 mL flask.

The resulting mixture was stirred at room temperature overnight and TLC indicated no starting materials remained. Silica gel was then added and after removal of the solvent by rotary evaporation the powder obtained was placed on the top of a silica gel column and chromatographed (eluent: hexanes). After removal of the solvent, a sticky yellow oil was obtained which eventually partially crystallized.
A sample of the pure $E$-isomer was obtained as yellow crystals (1.309 g, 4.9 mmol, 24 % yield) along with a $Z/E$-isomers mixture (3.647g, 13.7 mmol, 68 % yield) as a yellow oil.

$(E)$-1-(2,4-difluorostyryl)naphthalene

M.P.: 56.0 – 59.5 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.079 (d, $J = 8.0$ Hz, 1H), 7.767 – 7.726 (m, 2H), 7.679 (d, $J = 8.0$ Hz, 1H), 7.596 (d, $J = 7.2$ Hz, 1H), 7.447 – 7.324 (m, 4H), 7.090 (d, $J = 16.4$ Hz, 1H), 6.778 – 6.716 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 162.278 (dd, $^1J = 248.3$ Hz, $^2J = 12.0$ Hz), 160.532 (dd, $^1J = 250.9$ Hz, $^2J = 11.6$ Hz), 134.780, 133.838, 131.439, 128.659. 128.363, 128.271 (t, $J = 4.8$ Hz), 127.972 (dd, $^1J = 5.2$ Hz, $^2J = 2.1$ Hz), 126.161, 125.838, 125.631, 123.725, 123.629, 123.076, 121.974 (dd, $^1J = 12.2$ Hz, $^2J = 3.9$ Hz), 111.521 (dd, $^1J = 21.3$ Hz, $^2J = 3.8$ Hz), 104.122 (t, $J = 25.6$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -110.479 (q, $J = 7.5$ Hz, 1F), -113.066 – -113.140 (m, 1F).

UV/Vis (Acetonitrile): $\lambda_{\text{max}}(c) = 202$ (54740), 229 (34070), 323 (19270) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 267.99.
1-(2,4,5-trifluorostyryl)naphthalene (3.11g)

A solution of t-BuOK (2.352 g, 21.0 mmol) in EtOH (100 mL) was added dropwise to a suspension of (1-naphthylmethyl)triphenylphosphonium bromide (9.686 g, 20.0 mmol) and 2,4,5-trifluorobenzaldehyde (3.216 g, 20.0 mmol) in ethanol (100 mL) in a 250 mL flask. The mixture was stirred at room temperature overnight after which time no starting materials were observed by TLC. Silica gel was added and after removal of solvent by rotary evaporation, the powder obtained was placed on the top of a silica gel column and chromatographed (eluent: hexanes). Fractions containing the isomeric products were combined and concentrated. Yellow crystals were obtained as product after removing the solvent from which the less soluble E-isomer was isolated by recrystallization from hexanes (1.051 g, 3.7 mmol, 18 % yield) along with a Z/E-isomers mixture (3.060 g, 10.8 mmol, 51 % yield).

(E)-1-(2,4,5-trifluorostyryl)naphthalene

**M.P.:** 133.5 – 134.5 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$)** δ: 8.133 (d, $J = 8.0$ Hz, 1H), 7.851 – 7.782 (m, 3H), 7.690 (d, $J = 7.2$ Hz, 1H), 7.538 – 7.401 (m, 4H), 7.124 (d, $J = 16.0$ Hz, 1H), 6.961 – 6.895 (m, 1H).

**$^{13}$C-NMR (100 MHz, CDCl$_3$)** δ: 155.598 (d, $J = 246.9$ Hz), 149.455 (d, $J = 253.2$ Hz), 147.312
(d, J = 243.0 Hz), 134.408, 133.928, 131.491, 129.324 (d, J = 2.3 Hz), 128.792 (d, J = 1.9 Hz), 126.417, 126.031, 125.677, 124.015, 123.602, 122.401 (t, J = 5.1 Hz), 122.211, 121.428 (d, J = 11.6 Hz), 114.721 (dd, \( J_1 = 19.6 \) Hz, \( J_2 = 5.0 \) Hz), 105.928 (dd, \( J_1 = 28.3 \) Hz, \( J_2 = 20.9 \) Hz).

\(^{19}\text{F-NMR (376 MHz, CDCl}_3\) \( \delta \): -119.262 – -119.355 (m, 1F), -134.131 – -134.247 (m, 1F), -142.469 – -142.572 (m, 1F).

UV/Vis (Acetonitrile): \( \lambda_{\text{max}}(\varepsilon) = 202 (46620), 231 (31800), 327 (20050) \text{ nm (M}^{-1}\text{cm}^{-1}).

GCMS (m/z): 284.05.

2,3-difluoro-1,1':2',1''-terphenyl (3.11h)

\[ \text{Chemical Formula: C}_{18}\text{H}_{12}\text{F}_{2} \]
\[ \text{Molecular Weight: 266.29} \]

A 250 mL two-necked flask was charged with 2-biphenyl boronic acid (1.659 g, 8.4 mmol), 1-bromo-2,3-difluorobenzene (1.454 g, 7.5 mmol), sodium carbonate (1.601 g, 15.0 mmol), 1,4-dioxnae (25 mL) and water (10 mL). \( \text{Pd(PPh}_3\text{)}_4 \) (0.090 g, 0.077 mmol) was added at last and the mixture was heated to gently reflux under nitrogen atmosphere overnight (~12 hours). Meanwhile, TLC indicated that 1-bromo-2,3-difluorobenzene was completely consumed, the mixture was then cooled to room temperature and mixed with silica gel (~5g). After the removal of organic solvent and water residue by rotary evaporation, the obtained powder was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were
combined and concentrated to dryness, giving colorless crystals (1.893 g, 7.1 mmol, 94% yield) as final product.

**M.P.:** 95.0-97.0 °C.

**H-NMR (400 MHz, CDCl\textsubscript{3}) δ:** 7.466 – 7.385 (m, 4H), 7.257 – 7.129 (m, 5H), 7.030 – 6.842 (m, 3H).

**C-NMR (100 MHz, CDCl\textsubscript{3}) δ:** 150.692 (dd, \textsuperscript{1}J = 246.2 Hz, \textsuperscript{2}J = 13.1 Hz), 147.822 (dd, \textsuperscript{1}J = 246.7 Hz, \textsuperscript{2}J = 12.5 Hz), 141.806, 140.977, 133.263, 131.552 (d, \textit{J} = 12.5 Hz), 130.833, 130.300, 129.184, 128.577, 127.919, 127.240, 126.892, 126.837, 123.446 (t, \textit{J} = 5.8 Hz), 115.880 (d, \textit{J} = 17.1 Hz).

### 3.5.1.7. Precursors for PCDHF reactions involving regioselectivity

**2,3,4,5,6-pentafluoro-3''-methoxy-1,1':2',1''-terphenyl (3.13b)**

![Chemical structure](https://example.com/structure.png)

- Chemical Formula: C\textsubscript{19}H\textsubscript{11}F\textsubscript{5}O
- Molecular Weight: 350.29

A nitrogen flushed 100 mL flask with magnetic stir bar was charged with 1-bromo-2-pentafluorophenyl benzene (1.605 g, 5.0 mmol), 3-methoxyphenylboronic acid (1.813 g, 10.0 mmol), potassium carbonate (1.462 g, 10.0 mmol), toluene (40 mL) and \textit{i}-propanol (10 mL). The obtained solution was heated to gently reflux and tetrakis(triphenylphosphine)palladium(0) (58.9
mg, 0.05 mmol, 1%) was finally added inside.

After being refluxed for 12 hours, TLC indicated that a new compound was formed and the mixture was then cooled to room temperature. The solid inside was filtered with gravity filtration and the filtrate was well mixed with silica gel (~ 5g). The volatile solvent was removed by rotary evaporation and the adsorbed material was placed at the top of a silica gel column to elute (eluent: hexane: EtOAc = 20:1), affording sticky colorless oil (1.348 g, 3.9 mmol, 78 % yield) as final product.

\[ ^1H-\text{NMR (400 MHz, CDCl}_3\] \( \delta \): 7.558 – 7.443 (m, 3H), 7.323 (d, \( J = 7.6 \) Hz, 1H), 7.160 (t, \( J = 7.6 \) Hz, 1H), 6.803 (dd, \( ^1J = 8.4 \) Hz, \( ^2J = 2.0 \) Hz, 1H), 6.713 – 6.681 (m, 2H), 3.738 (s, 3H).

\[ ^13C-\text{NMR (100 MHz, CDCl}_3\] \( \delta \): 159.255, 144.103 (d, \( J = 244.6 \) Hz), 142.880, 141.719, 139.999 (d, \( J = 243.9 \) Hz), 137.371 (d, \( J = 251.2 \) Hz), 131.089, 130.311, 129.767, 129.150, 127.563, 124.886, 120.955, 115.937, 114.157, 113.064, 55.170.

\[ ^19F-\text{NMR (376 MHz, CDCl}_3\] \( \delta \): -140.614 (dd, \( ^1J = 23.3 \) Hz, \( ^2J = 8.3 \) Hz, 2F), -155.835 (t, \( J = 21.0 \) Hz, 1F), -162.943 – -163.083 (m, 2F).
(E)-3-(2-(perfluorophenyl)vinyl)benzonitrile (3.13c)

In a 100 ml pear flask with magnetic stirbar was placed 3-iodobenzonitrile (3.470 g, 15.1 mmol), pentafluorostyrene (3.688 g, 19.0 mmol), anhydrous DMF (10 mL), K$_2$CO$_3$ (4.224 g, 30.6 mmol) and 2-(2-methoxyethoxy)-N,N-bis[2-(2-methoxyethoxy)ethyl]ethanamine (0.4 mL). The resulting mixture was placed in 60 °C oil bath, degassed thoroughly with nitrogen and then Pd(OAc)$_2$ (40 mg, 1%) was added. The reaction was then warmed to 120 °C and left stirring for another 6 hours under a nitrogen atmosphere. After this time TLC indicated virtually all the 1-cyano-4-iodonaphthalene was consumed so the mixture was cooled to room temperature and water was added dropwise with stirring to 100 mL. The resulting suspension was stirred and then the solid was isolated by suction filtration, washed well with water and air-dried. The solid crude product was transferred to an Erlenmeyer and dissolved in boiling iso-octane. The dark suspension was boiled and poured through two fluted filters and the solvent was boiled into the filters to remove any residual product. Upon cooling the product was obtained as white powder (3.330 g, 11.3 mmol, 75 % yield).

M.P.: 98.5 – 100.0 °C

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.804 – 7.795 (m, 2H), 7.771 – 7.743 (m, 1H), 7.619 (ddd, $^1$J = 8.0 Hz, $^2$J = 1.4 Hz, $^3$J = 1.4 Hz, 1H), 7.520 (dd, $^1$J = 8.0 Hz, $^2$J = 8.0 Hz, 1H), 7.407 (d, J = 16.8 Hz, 1H), 7.041 (d, J = 16.8 Hz, 1H).
$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 144.974 (d, $J = 246.2$ Hz), 140.322 (d, $J = 254.2$ Hz), 137.814 (d, $J = 247.5$ Hz), 137.704, 134.588 (t, $J = 7.4$ Hz), 132.013, 130.838, 130.315, 129.738, 118.399, 115.385, 113.273, 111.542.

3.5.1.8. Precursors with differing halogens for competitive reactions

1-(2-chloro-6-fluorostyryl)naphthalene (3.15a)

![Chemical Structure](image)

Chemical Formula: C$_{18}$H$_{12}$ClF
Molecular Weight: 282.74

A solution of t-BuOK (2.357 g, 21.0 mmol) in ethanol (50 mL) was added dropwise to a suspension of (1-naphthylmethyl)triphenylphosphonium bromide (9.669 g, 20.0 mmol) and 2-chloro-6-fluorobenzaldehyde (2.861 g, 20.1 mmol) in ethanol (50 mL).

The mixture was stirred at room temperature overnight after which time no starting materials were observed by TLC. Silica gel was then added to absorb the product and after the removal of solvent by rotary evaporation the powder obtained was placed on the top of a silica gel column and chromatographed (eluent: hexanes). In this case the two isomeric compounds were completely separated. The first product which was the E-isomer was collected as needle crystals (4.235 g, 15.0 mmol, 75 % yield), which can be recrystallized in isooctane (4.046 g, 14.3 mmol, 71.5 % yield). The second product which was the Z-isomer was obtained as a wax (1.178 g, 4.2 mmol, 21 % yield), which can be recrystallized in hexanes (1.101 g, 3.9 mmol, 19 % yield).
(E)-1-(2-chloro-6-fluorostyryl)naphthalene

M.P.: 88.0 – 89.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$): 8.153 (s, 1H), 8.142 (d, $J = 23.6$ Hz, 1H), 7.838 – 7.748 (m, 3H), 7.526 – 7.449 (m, 3H), 7.236 (d, $J = 16.4$ Hz, 1H), 7.205 – 7.161 (m, 1H), 7.106 – 6.990 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): 161.266 (d, $J = 250.8$ Hz), 135.211, 134.628 (d, $J = 5.5$ Hz), 133.643, 133.542 (d, $J = 12.9$ Hz), 131.338, 128.564, 128.550, 128.138, 128.037, 126.260, 125.882, 125.662, 124.370 (d, $J = 14.5$ Hz), 123.842, 123.776, 122.176 (d, $J = 11.9$ Hz), 114.674 (d, $J = 23.5$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$): -110.764 (dd, $^1J = 10.9$ Hz, $^2J = 6.0$ Hz, 1F).

UV/Vis (Acetonitrile): $\lambda_{\text{max}}(\varepsilon) = 204 (62780), 229 (39150), 322 (21100)$ nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 282.04.

(Z)-1-(2-chloro-6-fluorostyryl)naphthalene

M.P.: 65.0 – 66.5 °C.

$^1$H-NMR (400 MHz, CDCl$_3$): 8.061 – 8.040 (m, 1H), 7.779 – 7.755 (m, 1H), 7.659 – 7.637 (m, 1H), 7.482 – 7.392 (m, 3H), 7.165 – 7.127 (m, 1H), 7.101 – 7.053 (m, 2H), 7.001 – 6.965 (m, 1H), 6.671 – 6.626 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): 159.775 (d, $J = 249.6$ Hz), 134.847 (d, $J = 5.2$ Hz), 134.487, 133.599 (d, $J = 1.2$ Hz), 133.429, 131.375, 128.620, 128.526, 128.339, 127.974, 125.956, 125.760, 125.508, 125.097, 124.922 (d, $J = 3.5$ Hz), 124.429, 122.013, 113.953 (d, $J = 22.8$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$): -108.068 (dd, $^1J = 9.0$ Hz, $^2J = 5.8$ Hz, 1F).
(E)-1-(2-bromo-6-fluoro styryl)naphthalene (3.15b)

In a 500 ml pear flask with magnetic stirbar was charged with 2-bromo-6-fluorobenzaldehyde (2.03 g, 10.0 mmol), 1-naphthylmethyltriphenylphosphonium bromide (4.83 g, 10.0 mmol) and EtOH (100 mL). This mixture was stirred and t-BuOK (1.23 g, 11.0 mmol) was added all at once. The reaction was allowed to proceed at room temperature for two days at which time the aldehyde appeared to be consumed by TLC analysis. Most of the solvent was removed under vacuum and THF (25 mL) was added along with silica gel (10 g). Solvent was removed again and the product adsorbed on silica gel was placed at the top of a silica gel column and eluted (eluent: hexanes). Fractions containing the product were combined and concentrated to a white solid, which was recrystallized from methanol. The product was isolated in two crops (2.23 g, 68% yield).

M.P.: 81.0 – 83.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.184 (d, $J = 8.4$ Hz, 1H), 8.086 (d, $J = 16.4$ Hz, 1H), 7.875 – 7.782 (m, 3H), 7.559 – 7.480 (m, 3H), 7.444 – 7.422 (m, 1H), 7.202 (d, $J = 16.4$ Hz, 1H), 7.140 – 7.046 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 160.990 (d, $J = 251.7$ Hz), 135.157, 133.682 (d, $J = 12.7$ Hz), 133.661, 131.344, 128.934 (d, $J = 3.3$ Hz), 128.690, 128.593, 128.567, 126.296, 126.066, 125.922,
125.705, 124.960 (d, $J = 4.5$ Hz), 124.818 (d, $J = 2.5$ Hz), 123.936, 123.840, 115.399 (d, $J = 23.6$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -110.626 (dd, $^1J = 10.5$ Hz, $^2J = 6.0$ Hz, 1F).

UV/Vis (Acetonitrile): $\lambda_{\text{max}}(\varepsilon) = 204$ (63790), 229 (39290), 321 (20430) nm (M$^{-1}$cm$^{-1}$).

GCMS (m/z): 326.94.

1-chloro-3-fluoro-2-iodobenzene

\[
\begin{array}{c}
\text{F} \\
\text{Cl} \\
\end{array}
\]

Chemical Formula: C$_8$H$_3$ClFI
Molecular Weight: 256.44

Under a nitrogen atmosphere, an oven dried 250 mL round bottom flask equipped with magnetic stir bar was charged with diisopropylamine (6.2 mL, 4.4 g, 44.0 mmol) and anhydrous THF (60 mL). The obtained mixture was cooled to -78 °C and n-BuLi solution (2.5M in hexanes, 18 mL, 44.0 mmol) was added dropwise via syringe. The solution obtained was stirred for 0.5 h and then 1-fluoro-3-chlorobenzene (5.212 g, 40.0 mmol) was added and the mixture was stirred at -78 °C for another 2 hours. Next, a solution of iodine (11.261 g, 44.0 mmol) dissolved in THF (40 mL) was added into the previous mixture in 10 min. The solution obtained was stirred overnight and the temperature of the reaction was allowed to gradually warm to room temperature (~12 h).

The resulting brown solution was treated with Na$_2$SO$_3$ solution (5.0 g in 100 mL water) to remove the remaining iodine and the aqueous phase was extracted with diethyl ether (50 mL x 3). The organic phases were combined and dried with anhydrous MgSO$_4$. After removal of the drying agent
by gravity filtration, solvent was removed by rotary evaporation to give a yellow oil (13.345 g) as crude product. Kugelrohr distillation (1 millibar, 110 °C) was used to provide the product as colorless oil (8.796 g, 34 mmol, 85 % yield).


$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.294 – 7.229 (m, 2H), 6.978 – 6.911 (m, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 162.740 (d, $J = 245.9$ Hz), 139.975, 130.212 (d, $J = 9.0$ Hz), 125.068 (d, $J = 3.1$ Hz), 113.492 (d, $J = 24.6$ Hz), 87.439 (d, $J = 27.8$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -85.841 – -85.869 (m, 1F).

2-chloro-6-fluoro-1,1':2',1''-terphenyl (3.15c)

A nitrogen flushed 100 mL flask equipped with magnetic stir bar was charged with 1-chloro-3-fluoro-2-iodobenzene (1.282 g, 5.0 mmol), biphenyl-2-boronic acid (1.478 g, 7.5 mmol), potassium carbonate (1.396 g, 10.0 mmol), 1,4-dioxane (10 mL) and water (4 mL). This solution was heated to a gentle reflux and Pd(PPh$_3$)$_4$ (119.6 mg, 0.10 mmol, 2%) was finally added into the flask.

After being refluxed for approximately 6 hours under nitrogen atmosphere, TLC indicated that
starting material was nearly consumed. The solution was cooled and diluted to a total of 100 mL with ethyl acetate. This solution was washed with water (100 mL x3) and then the organic phase was isolated and dried with anhydrous MgSO₄. After removal the drying agent via gravity filtration, the filtrate was mixed with silica gel (~ 2g). This mixture was concentrated by rotary evaporation and the tan powder obtained was placed on the top of a silica gel column and chromatographed (eluent: hexanes). Colorless oil (0.323 g, 1.1 mmol, 22% yield) was obtained as final product.

\(^1\text{H-NMR (400 MHz, CDCl}_3\) \(\delta\): 7.500 – 7.422 (m, 3H), 7.320 – 7.300 (m, 1H), 7.189 – 7.172 (m, 5H), 7.148 – 7.123 (m, 2H), 6.885 – 6.840 (m, 1H).

\(^{13}\text{C-NMR (100 MHz, CDCl}_3\) \(\delta\): 160.214 (d, \(J = 246.1\) Hz), 142.376, 140.923, 134.966, 132.605, 130.782, 129.920, 129.160, 129.068, 128.749, 127.689, 127.109, 126.849, 124.900 (d, \(J = 3.2\) Hz), 124.351, 113.688 (d, \(J = 22.9\) Hz).

\(^{19}\text{F-NMR (376 MHz, CDCl}_3\) \(\delta\): -109.700 – -109.773 (m, 1F).

UV/Vis (Acetonitrile): No maximum absorption, the absorption coefficient at 254 nm is provided. \(\varepsilon = 9980\ M^{-1}\text{cm}^{-1}\) (254 nm).

GCMS (m/z): 281.97.
1-bromo-3-fluoro-2-iodobenzene

Chemical Formula: C₆H₃BrF₁
Molecular Weight: 300.89

Under a nitrogen atmosphere, an oven dried 250 mL round bottom flask equipped with magnetic stir bar was charged with diisopropylamine (6.1 mL, 4.4 g, 44.0 mmol) and anhydrous THF (60 mL). The obtained mixture was cooled to -78 °C and n-BuLi (2.5M in hexanes, 18 mL, 44.0 mmol) solution was added dropwise via syringe. After being stirred for 30 min, 3-bromofluorobenzene (7.060 g, 40.0 mmol) was added and the resulting mixture was stirred at -78 °C for 2 hours. After that, a solution of iodine (11.182 g, 44.0 mmol) in THF (40 mL) was added in 10 min. The obtained solution was stirred overnight and the temperature of the reaction was allowed to gradually warm to room temperature (~12 h).

The brown solution was then treated with Na₂SO₃ solution (5.0 g in 100 mL water) to remove the remaining iodine and the aqueous phase was extracted with diethyl ether (50 mL x 3). The organic phases were combined and dried with anhydrous MgSO₄. After removal of the solvent by rotary evaporation, the remaining liquid was purified by Kugelrohr distillation (1 millibar, 110 °C), giving a colorless oil (11.138 g, 37 mmol, 92 % yield) as final product.


¹H-NMR (400 MHz, CDCl₃) δ: 7.289 (dd, ¹J = 8.0 Hz, ²J = 1.0 Hz, 1H), 7.259 – 7.176 (m, 1H),
6.985 (tt, $^1J = 8.0$ Hz, $^2J = 1.0$ Hz, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 162.552 (d, $J = 247.3$ Hz), 130.891, 130.603 (d, $J = 8.6$ Hz), 128.365 (d, $J = 3.1$ Hz), 113.890 (d, $J = 24.7$ Hz), 90.500 (d, $J = 27.0$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -82.948 – -82.996 (m, 1F).

2-bromo-6-fluoro-1,1':2',1''-terphenyl (3.15d)

A nitrogen flushed 100 mL flask with magnetic stir bar was charged with 1-bromo-3-fluoro-2-iodobenzene (0.752 g, 2.5 mmol), biphenyl-2-boronic acid (0.499g, 2.5 mmol), potassium carbonate (0.367 g, 2.5 mmol), toluene (16 mL) and ethanol (4 mL). The mixture was heated to 90 °C and Pd(PPh$_3$)$_4$ (28.890 mg, 0.025mmol, 1%) was added into the mixture.

After being refluxed for approximately 48 hours under nitrogen atmosphere, TLC indicated that starting material was nearly consumed. The mixture was cooled and silica gel (~ 2g) was added. After the solvent was removed by rotary evaporation, the tan powder obtained was placed on the top of a silica gel column and eluted (eluent: hexanes). The fractions containing the product were combined together and concentrated to dryness, giving a colorless oil (0.333 g, 1.0 mmol, 50 % yield) as final product.
\[ ^1\text{H-NMR (400 MHz, CDCl}_3\) \delta: 7.518 – 7.416 (m, 3H), 7.332 – 7.276 (m, 2H), 7.191 – 7.180 (m, 5H), 7.059 (td, \text{ } ^1J = 8.0 \text{ Hz}, \text{ } ^2J = 5.6 \text{ Hz, 1H}), 6.890 (td, \text{ } ^1J = 8.4 \text{ Hz, } ^2J = 1.2 \text{ Hz, 1H}). \]

\[ ^{13}\text{C-NMR (100 MHz, CDCl}_3\) \delta: 159.988 (d, \text{ } ^1J = 247.0 \text{ Hz}), 142.083, 140.820, 133.234, 130.702, 129.913, 129.578 (d, \text{ } ^1J = 8.9 \text{ Hz}), 128.810, 128.741, 128.048, 128.012, 127.655, 127.092, 126.837, 125.117 (d, \text{ } ^1J = 3.3 \text{ Hz}), 114.244 (d, \text{ } ^1J = 22.9 \text{ Hz}). \]

\[ ^{19}\text{F-NMR (376 MHz, CDCl}_3\) \delta: -107.582 (d, \text{ } ^1J = 5.6 \text{ Hz}). \]

**UV/Vis (Acetonitrile):** No maximum absorption, the absorption coefficient at 254 nm is provided. 
\[ \varepsilon = 10630 \text{ M}^{-1}\text{cm}^{-1} (254 \text{ nm}) \]

**GCMS (m/z):** 326.85.
3.5.2. Procedure for photocyclodehydrofluorination

A quartz vessel (approximately 40 cm x 25 mm with a 24/40ST joint) was charged with starting material and solvent (acetonitrile, THF, toluene, etc.). The resulting solution (typically the concentration is 0.01 mol/L) was flushed thoroughly with nitrogen and irradiated in a photochemical reactor.

Typically, the progress of the photochemistry was followed by GC-MS. After the starting material was completely (or nearly completely) consumed, the solution was transferred to a flask and the solvent was removed by rotary evaporation to give the crude product. This crude material was dissolved in EtOAc (~ 10 – 25 mL) and mixed with silica gel (~ 2 – 5 g). After removal of the solvent by using rotary evaporation, the powder obtained was placed on the top of a silica gel column and chromatographed, affording a purified product (recrystallization was applied if necessary).

In some cases, the photoproduct would precipitate out of the solution in the quartz tube. In these cases at least a portion of the product could often be separated easily by suction filtration at this stage prior to any column chromatography.
3.5.2.1. Photocyclodehydrofluorination of pentafluorostilbenes

1,2,3,4-tetrafluorophenanthrene (3.2a)

In a quartz vessel, \((E)\)-pentafluorostilbene (0.272 g, 1.0 mmol) was dissolved in acetonitrile (100 mL). The mixture was flushed with nitrogen and irradiated for 120 hours (5 days) in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After column chromatography (eluent: hexanes: DCM = 6:1), white fiber-like crystals (0.122g, 0.49mmol, 49 % overall yield) were obtained as final product.


M.P.: 164.0 – 167.5 °C (Lit.: 163 – 164 °C).

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.959 – 8.935 (m, 1H), 7.920 – 7.871 (m, 2H), 7.791 (d, \(J = 9.2\) Hz, 1H), 7.722 – 7.655 (m, 2H).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\): 145.967 (d, \(J = 252.2\) Hz), 142.436 (d, \(J = 246.6\) Hz), 139.378 (d, \(J = 251.7\) Hz), 137.879 (d, \(J = 251.6\) Hz), 132.294, 128.994, 128.958, 128.060, 127.860, 127.108, 126.867, 118.242 (d, \(J = 14.6\) Hz), 116.803 (d, \(J = 2.0\) Hz), 115.823.

\(^{19}\)F-NMR (376 MHz, CDCl\(_3\)) \(\delta\): -139.586 – -139.678 (m, 1F), -148.914 (dd, \(^1\)J = 20.5 Hz, \(^2\)J = 14.1 Hz, 1F), -158.163 (d, \(J = 19.2\) Hz, 1F), -158.503 (td, \(^1\)J = 20.5 Hz, \(^2\)J = 3.8 Hz, 1F).
GCMS (m/z): 250.98.

1,2,3,4-tetrafluorophenanthrene (3.2b)

![Chemical Structure]

Chemical Formula: C_{14}H_{6}F_{4}
Molecular Weight: 250.19

In a quartz vessel, a solution of (E)-1-(4-bromostyryl)-2,3,4,5,6-pentafluorobenzene (0.349g, 1.0 mmol) in acetonitrile (100 mL) was degassed with nitrogen and irradiated for 150 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After column chromatography (eluent: hexanes), white crystals (0.115 g, 0.46 mmol, 46 % yield) were obtained as final product.

The characterization data obtained is the same for 3.2a, which demonstrates that they are the same compound.
1,2,3,4-tetrafluorochrysene (3.2c)

![Chemical structure of 1,2,3,4-tetrafluorochrysene](image)

Chemical Formula: C$_{18}$H$_{8}$F$_{4}$
Molecular Weight: 300.25

In a quartz vessel, (E)-1-(2-(perfluorophenyl)vinyl)naphthalene (0.321 g, 1.0 mmol) was dissolved in acetonitrile (100 mL). The solution was degassed with nitrogen and irradiated for 48 hours in a Rayonette photochemical reactor equipped with 16 x 300 nm ultraviolet lamps. During the irradiation, white needle-like crystals precipitated out of the solution.

The white solid was filtered off directly by suction filtration and air-dried, giving milk-white crystals (0.226 g, 0.75 mmol, 75 % yield as product) as final product.

**M.P.:** Sublimed around 220 – 225 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$:** 8.998 (dd, $^1J = 9.2$ Hz, $^2J = 2.4$ Hz, 1H), 8.832 (d, $J = 9.2$ Hz, 1H), 8.766(d, $J = 8.4$ Hz, 1H), 8.188 (dd, $^1J = 9.2$ Hz, $^2J = 1.6$ Hz, 1H), 8.058 – 7.999 (m, 2H), 7.766 – 7.677 (m, 2H).

**$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$:** -139.365 (t, $J = 16.2$ Hz, 1F), -149.224 (dd, $^1J = 19.9$ Hz, $^2J = 14.7$ Hz, 1F), -157.792 (t, $J = 18.8$ Hz, 1F), -158.495 (t, $J = 20.1$ Hz, 1F).

**GCMS (m/z):** 300.97.

**HRMS:** M$^+$ = 300.05566 (Calc = 300.05566).
1,2,3,4-tetrafluorochrysene (3.2d)

![Chemical Structure](image)

Chemical Formula: C_{18}H_{8}F_{4}
Molecular Weight: 300.25

In a quartz vessel, 1-bromo-4-(2-(perfluorophenyl)vinyl)naphthalene (0.200 g, 0.5 mmol) was dissolved in acetonitrile (100 mL). The solution was degassed with nitrogen and irradiated for 48 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After column chromatography (eluent: hexanes), white crystals (0.061 g, 0.20 mmol, 41 % yield) were obtained as final product.

Data obtained is the same as 3.2c.

The result was similar to 3.2b, the product without bromine was obtained. We also tried two other solvents such as THF and toluene. For THF, the same product 1,2,3,4-tetrafluorochrysene without bromine was obtained. On the other hand when toluene was selected as solvent, a compound with molecular weight 379/381 was observed (which might be 6-bromo-1,2,3,4-tetrafluorochrysene) in the half way. However, this reaction proceeded very slowly and lots of side reaction impurities came out after a long time of irradiation, which made it impossible to purify the product.
1,2,3,4-tetrafluorochrysene-6-carbonitrile (3.2e)

In a quartz vessel, (E)-4-(2-(perfluorophenyl)vinyl)-1-naphthonitrile (0.346 g, 1.0 mmol) was dissolved in acetonitrile (100 mL). The solution was degassed with nitrogen and irradiated for 6 hours with a 450W Hanovia lamp equipped with a Pyrex filter. During the process of reaction, yellow fiber-like crystals precipitated out of the solution.

The mixture was cooled down and the yellow precipitate was filtrated off directly by suction filtration, washed with cold acetone and air-dried. Pale yellow fibers (0.226 g, 0.69 mmol, 69 % yield) were obtained as the final product.

**M.P.:** Sublimed above 200 °C, melted completely at 225.0 – 227.0 °C.

**$^1$H-NMR (400 MHz, 1,1,2,2-Tetrachloroethane-d$_2$) $\delta$:** 9.348 (d, $J = 4.8$ Hz, 1H), 8.775 – 8.756 (m, 2H), 8.364 – 8.348 (m, 1H), 8.291 (dd, $^1J = 9.2$ Hz, $^2J = 1.6$ Hz, 1H), 7.886 – 7.853 (m, 2H).

**$^{13}$C-NMR (100 MHz, 1,1,2,2-Tetrachloroethane-d$_2$) $\delta$:** 145.450 (d, $J = 251.3$ Hz), 142.466 (d, $J = 242.4$ Hz), 140.176 (d, $J = 255.9$ Hz), 138.224 (d, $J = 255.8$ Hz), 131.838, 131.577, 129.593 (d, $J = 9.8$ Hz), 129.276, 128.770, 125.820, 123.749, 122.635, 121.155, 118.557 (d, $J = 13.2$ Hz), 118.062, 117.749, 115.591, 113.859, 110.755.

**$^{19}$F-NMR (376 MHz, 1,1,2,2-Tetrachloroethane-d$_2$) $\delta$:** -138.783 (t, $J = 15.4$ Hz, 1F), -147.088
In a quartz vessel, \((E)-2-(2-(\text{perfluorophenyl})\text{vinyl})\text{naphthalene}\) (0.160 g, 0.5 mmol) was dissolved in acetonitrile (50 mL). The solution was degassed with nitrogen and irradiated for 15 hours with a 450W Hanovia lamp equipped with a Pyrex filter.

After column chromatography (eluent: hexanes), white crystals (0.049g, 0.16mmol, 33 % yield) were obtained as final product.


M.P.: Sublimed around 156.0 – 157.5 °C (Lit.: 153.1 – 153.2 °C).

\[^1\text{H-NMR (400 MHz, CDCI}_3\)]\(\delta\): 8.209 – 8.145 (m, 1H), 8.078 (ddd, \(^1J = 8.8\) Hz, \(^2J = 1.6\) Hz, \(^3J = 0.8\) Hz, 1H), 8.018 – 7.972 (m, 2H), 7.866 (d, \(J = 8.8\) Hz, 1H), 7.802 (d, \(J = 8.4\) Hz, 1H), 7.660 – 7.614 (m, 2H).
$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 143.960 (d, $J = 253$ Hz), 142.499 (d, $J = 243$ Hz), 139.304 (d, $J = 249$ Hz), 138.026 (d, $J = 249$ Hz), 133.096, 132.025, 129.550, 129.410, 128.980 (d, $J = 17.3$ Hz), 128.493, 127.598, 126.683, 125.757, 125.544 (d, $J = 2.6$ Hz), 123.671, 119.334 (d, $J = 12.9$ Hz), 117.984, 115.150 (d, $J = 11.3$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -127.206 – -127.349 (m, 1F), -149.017 (dd, $^1J = 20.2$ Hz, $^2J = 13.1$ Hz, 1F), -157.528 (d, $J = 20.2$ Hz, 1F), -158.544 (td, $^1J = 20.2$ Hz, $^2J = 3.8$ Hz, 1F).

GCMS (m/z): 301.00.

7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene (3.2g)

![Chemical structure of 7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene]

Chemical Formula: C$_{26}$H$_6$F$_8$
Molecular Weight: 472.33

In a quartz vessel, 1,4-bis((E)-2-(perfluorophenyl)vinyl)naphthalene (0.512 g, 1.0 mmol) was dissolved in toluene (100 mL). The solution was flushed with nitrogen and irradiated for 30 hours with a 450W Hanovia lamp equipped with a Vycor filter.

After column chromatography (eluent: hexanes: EtOAc = 4:1), yellow crystals (0.109 g, 0.23 mmol, 23 % yield) were obtained as final product.

M.P.: 270.0 – 275.0 °C.
\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.808 (d, \(J = 9.2\) Hz, 2H), 8.772 (q, \(J = 2.8\) Hz, 2H), 8.332 (dd, \(^1J = 9.2\) Hz, \(^2J = 1.4\) Hz, 2H), 7.862 – 7.838 (m, 2H).

\(^{19}\)F-NMR (376 MHz, CDCl\(_3\)) \(\delta\): -134.593 (t, \(J = 16.4\) Hz, 2F), -149.282 (dd, \(^1J = 19.6\) Hz, \(^2J = 13.9\) Hz, 2F), -158.048 (t, \(J = 19.4\) Hz, 2F), -158.381 (td, \(^1J = 19.6\) Hz, \(^2J = 2.6\) Hz, 2F).

HRMS: \(M^+ = 472.04929\) (Calc = 472.04928).

3.5.2.2. Photocyclodehydrofluorination of pentafluoro-ortho-triphenyls

1,2,3,4-tetrafluorotriphenylene (3.4a)

Chemical Formula: C\(_{18}\)H\(_6\)F\(_4\)
Molecular Weight: 300.25

In a quartz vessel, 2-(pentafluorophenyl)biphenyl (0.486 g, 1.5 mmol) was dissolved in acetonitrile (80 mL). The solution was degassed with nitrogen and irradiated for 12 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After chromatography (eluent: hexanes: DCM = 10:1), a pale tan powder (0.423 g, 1.4 mmol, 94 % yield) was obtained as final product.

M.P.: 197.0 – 203.5 °C (Lit.: 229 °C).

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 8.922 (d, $J = 8.0$ Hz, 2H), 8.627 (d, $J = 8.0$ Hz, 2H), 7.722 – 7.630 (m, 4H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 146.268 (d, $J = 247$ Hz), 139.600 (d, $J = 243$ Hz), 130.563, 128.575, 127.968, 127.709, 126.085, 123.334, 116.509.

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -138.034 (d, $J = 13.7$ Hz, 2F), -157.478 (d, $J = 13.7$ Hz, 2F).

GCMS (m/z): 301.02.

1,2,3,4-tetrafluoro-6-methoxytriphenylene (3.4b)

![Chemical structure](image)

Chemical Formula: C$_{19}$H$_{10}$F$_4$O  
Molecular Weight: 330.28

In a quartz vessel, 2,3,4,5,6-pentafluoro-4"-methoxy-1,1':2',1"-terphenyl (0.175 g, 0.5 mmol) was dissolved in acetonitrile (40 mL). The solution was irradiated for 10 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After purification by column chromatography (eluent: hexanes: EtOAc = 1:1), a pale tan powder (0.109 g, 0.33 mmol, 66 % yield) was obtained as product.

M.P.: 157.5 – 162.0 °C.
\[^1\text{H}-\text{NMR (400 MHz, CDCl}_3\text{) \delta:}\] 8.845 (ddd, \(^1J = 8.8\ \text{Hz}, \ ^2J = 2.8\ \text{Hz}, \ ^3J = 1.2\ \text{Hz}, \ 1\text{H}),\ 8.502 – 8.473 (m, 2H), 8.321 (dd, \(^1J = 2.4\ \text{Hz},\ ^2J = 2.4\ \text{Hz},\ 1\text{H}),\ 7.678 – 7.636 (m, 1H),\ 7.592 – 7.546 (m, 1H),\ 7.292 (dd, \(^1J = 8.8\ \text{Hz},\ ^2J = 2.4\ \text{Hz},\ 1\text{H}),\ 3.976 (s, 3H).

\[^{13}\text{C}-\text{NMR (100 MHz, CDCl}_3\text{) \delta:}\] 158.926, 146.068 (d, \(^J = 248\ \text{Hz}),\ 145.965 (d, \(^J = 250\ \text{Hz}),\ 139.321 (d, \(^J = 252\ \text{Hz}),\ 139.204 (d, \(^J = 246\ \text{Hz}),\ 130.365,\ 128.466,\ 127.660 (d, \(^J = 29\ \text{Hz}),\ 127.098,\ 126.831 (d, \(^J = 4.1\ \text{Hz}),\ 124.845,\ 124.554,\ 124.063,\ 122.560,\ 117.109,\ 116.636,\ 115.974,\ 110.094 (d, \(^J = 30\ \text{Hz}),\ 55.380.

\[^{19}\text{F}-\text{NMR (376 MHz, CDCl}_3\text{) \delta:}\] -137.681 – -137.767 (m, 1F), \(^{-1}38.185 – -138.269 (m, 1F),\ -157.128 (td, \(^J = 20.7\ \text{Hz},\ ^2J = 4.51\ \text{Hz},\ 1\text{F}),\ -157.596 (td, \(^J = 20.7\ \text{Hz},\ ^2J = 4.51\ \text{Hz},\ 1\text{F}).

GCMS (m/z): 330.99.

\[1,2,3,4\text{-tetrafluoro-6-(hexyloxy)triphenylene(3.4c)}\]

\[
\begin{align*}
\text{Chemical Formula: } & C_{24}H_{20}F_4O \\
\text{Molecular Weight: } & 400.41
\end{align*}
\]

In a quartz vessel, 2,3,4,5,6-pentafluoro-4"-(hexyloxy)-1,1':2',1"-terphenyl (0.420 g, 1.0 mmol) was dissolved in acetonitrile (100 mL), degassed with nitrogen and irradiated for 18 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After column chromatography (eluent: hexanes: EtOAc = 10:1), fractions containing the product
were combined and concentrated, giving white crystals (0.238 g, 0.6 mmol, 60% yield) as final product.

**M.P.:** 108.5 – 110.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.717 – 8.689 (m, 1H), 8.366 – 8.314 (m, 2H), 8.142 – 8.123 (m, 1H), 7.599 – 7.561 (m, 1H), 7.507 – 7.468 (m, 1H), 7.202 – 7.173 (m, 1H), 4.072 – 4.039 (m, 2H), 1.903 – 1.832 (m, 2H), 1.556 – 1.518 (m, 2H), 1.411 – 1.385 (m, 4H), 0.948 (t, $J = 7.2$ Hz, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 158.465, 145.958 (d, $J = 249$ Hz), 145.864 (d, $J = 250$ Hz), 139.165 (d, $J = 251$ Hz), 139.012 (d, $J = 254$ Hz), 130.300, 128.322, 127.542 (d, $J = 29.4$ Hz), 126.901, 126.634, 124.643, 124.330, 123.719, 122.409, 117.429, 116.481, 115.853, 110.577 (d, $J = 30$ Hz), 68.164, 31.682, 29.282, 25.809, 22.673, 14.077.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -137.789 – -137.874 (m, 1F), -138.193 – -138.278 (m, 1F), -157.794 (t, $J = 19.9$ Hz, 1F).

GCMS (m/z): 399.99.

**1,2,3,4-tetrafluoro-6-(trifluoromethoxy)triphenylene (3.4d)**

![1,2,3,4-tetrafluoro-6-(trifluoromethoxy)triphenylene (3.4d)](image)

Chemical Formula: C$_{19}$H$_7$F$_7$O  
Molecular Weight: 384.25

In a quartz vessel, 2,3,4,5,6-pentafluoro-4"-trifluoromethoxy-1,1':2',1"-terphenyl (0.202 g, 0.5
mmol) was dissolved in acetonitrile (40 mL). The solution was degassed with nitrogen and irradiated for 10 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After column chromatography (eluent: hexanes: EtOAc = 1:1), a pale tan powder (0.149g, 0.39 mmol, 78% yield) was obtained as final product.

**M.P.:** 127.5 – 131.0 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$:** 8.844 – 8.816 (m, 1H), 8.684 (dd, $^1J = 5.2$ Hz, $^2J = 1.6$ Hz, 1H), 8.567 (d, $J = 8.8$ Hz, 1H), 8.509 – 8.486 (m, 1H), 7.717 – 7.623 (m, 2H), 7.540 (d, $J = 8.8$ Hz, 1H).

**$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$:** 148.378, 146.106 (d, $J = 247$ Hz), 145.987 (d, $J = 248$ Hz), 139.920 (d, $J = 251$ Hz), 139.394 (d, $J = 251$ Hz), 129.373, 128.824, 128.314 (d, $J = 2$ Hz), 127.773 (d, $J = 29.4$ Hz), 126.836, 125.773, 124.950, 123.218, 121.260, 120.628 (q, $J = 256$ Hz), 119.614 (d, $J = 30.4$ Hz), 116.594, 115.241.

**$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$:** -57.654 (s, CF$_3$, 3F), -155.486 (td, $^1J = 20.5$ Hz, $^2J = 5.26$ Hz, 1F), -156.376 (td, $^1J = 20.7$ Hz, $^2J = 4.89$ Hz, 1F), -137.171 – -137.275 (m, 1F), -137.604 – -137.718 (m, 1F).

**GCMS (m/z):** 384.91.
1,2,3,4,5,7-hexafluorotriphenylene (3.4e)

In a quartz vessel, 2,3,3",4,5,5",6-heptafluoro-1,1':2',1"-terphenyl (0.178 g, 0.5 mmol) was dissolved in acetonitrile (40 mL). The solution was degassed with nitrogen and irradiated for 18 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After column chromatography (eluent: hexanes: DCM = 3:1), fractions containing the product were combined and concentrated to give the desired product as a pale tan powder (0.145g, 0.43 mmol, 86% yield).

**M.P.:** 163.5 – 166.0 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$:** 8.841 – 8.810 (m, 1H), 8.392 – 8.368 (m, 1H), 7.959 (dt, $^1J = 9.2$ Hz, $^2J = 1.0$ Hz, 1H), 7.702 – 7.678 (m, 2H), 7.125 – 7.069 (m, 1H).

**$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$:** 162.837 (dd, $^1J = 199$ Hz, $^2J = 14$ Hz), 160.304 (dd, $^1J = 208$ Hz, $^2J = 14$ Hz), 145.725 (d, $J = 253$ Hz), 144.432 (d, $J = 253$ Hz), 140.236 (d, $J = 238$ Hz), 139.788 (d, $J = 248$ Hz), 134.309, 129.350, 129.083, 128.940, 127.667 (d, $J = 27$ Hz), 126.750, 123.574, 115.936, 111.994, 110.280, 104.998 (dd, $^1J = 23$ Hz, $^2J = 3$ Hz), 103.766 (t, $J = 27$ Hz).

**$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$:** -97.162 (dt, $J = 149.3$ Hz, $^2J = 11.3$ Hz, 1F), -108.458 (q, $J = 9.8$ Hz).
Hz, 1F), -130.138 – -130.639 (m, 1F), -139.079 – -139.162 (m, 1F), -156.174 – -156.296 (m, 1F), -156.632 – -156.756 (m, 1F).

**GCMS (m/z):** 336.96.

1,2,3,4-tetrafluoro-5,7-bis(trifluoromethyl)triphenylene (3.4f)

[Chemical structure image]

Chemical Formula: C_{20}H_{16}F_{10}
Molecular Weight: 436.25

A quartz reaction vessel was charged with 2,3,4,5,6-pentafluoro-3",5"-bis(trifluoromethyl)-1,1':2',1"-terphenyl (0.457 g, 1.0 mmol) and acetonitrile (100 mL). The solution was degassed with nitrogen and irradiated for 48 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After column chromatography (eluent: hexanes: EtOAc = 20:1), fractions containing the pure product were combined and concentrated to give the final product as a yellow powder (0.365g, 0.84 mmol, 84 %).

**M.P.:** 158.0 – 161.5 °C.

**^1H-NMR (400 MHz, CDCl₃) δ:** 8.905 (s, 1H), 8.802 – 8.778 (m, 1H), 8.526 – 8.502 (m, 1H), 8.101 (s, 1H), 7.799 – 7.728 (m, 2H).


$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 145.176 (d, $J = 248$ Hz), 141.258 (d, $J = 253$ Hz), 138.732 (d, $J = 252$ Hz), 132.770, 131.012 (d, $J = 32$ Hz), 130.273 (d, $J = 34$ Hz), 129.531, 128.883, 128.066, 127.823, 126.046, 124.070 (t, $J = 3.6$ Hz), 123.956 (q, $J = 274$ Hz), 123.400, 123.391 (q, $J = 271$ Hz), 123.005, 122.084 (d, $J = 3.2$ Hz), 117.313, 113.657 (d, $J = 11.4$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -58.300 (d, $J = 30.4$ Hz, CF$_3$, 3F), -62.602 (s, CF$_3$, 3F), -135.735 – -135.966 (m, 1F), -139.665 – -139.760 (m, 1F), -152.668 (td, $^1J = 20.5$ Hz, $^2J = 5.3$ Hz, 1F), -156.918 (td, $^1J = 21.0$ Hz, $^2J = 4.5$ Hz, 1F).

GCMS (m/z): 435.97.

1,2,3,4-tetrafluoro-6-phenyltriphenylene (3.4g)

![Chemical Structure](image)

Chemical Formula: C$_{24}$H$_{12}$F$_4$
Molecular Weight: 376.35

Two quartz tubes were charged with 2,3,4,5,6-pentafluoro-1,1':2',1"':4",1""'-quaterphenyl (0.398 g x 2, 1.0 mmol x 2) and acetonitrile (100 mL x 2). The solutions were irradiated for 10 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

The contents of the tubes were combined and after column chromatography (eluent: hexanes: EtOAc=10:1), fractions containing the pure product were combined and concentrated to give yellow powder (0.448g, 1.2 mmol, 60 %) as final product.
M.P.: 199.0 – 201.5 °C.

$^1$H-NMR (400 MHz, 1,1,2,2-Tetrachloroethane-d$_2$) δ: 9.046 – 9.034 (m, 1H), 8.818 – 8.794 (m, $J$ = 1H), 8.548 (t, $J$ = 8.8 Hz, 2H), 7.882 (dd, $J$ = 8.8 Hz, $^2J$ = 1.8 Hz, 1H), 7.734 – 7.580 (m, 4H), 7.475 (t, $J$ = 7.6 Hz, 2H), 7.421 – 7.381 (m, 1H).

$^{13}$C-NMR (100 MHz, 1,1,2,2-Tetrachloroethane-d$_2$) δ: 146.162 (d, $J$ = 251.4 Hz), 140.493, 140.448, 139.549 ($J$ = 247.2 Hz), 130.237, 129.447, 129.154, 128.747, 128.044, 127.960, 127.665, 127.486, 127.360, 126.193, 125.908, 123.867, 123.363, 116.681, 116.434.

$^{19}$F-NMR (376 MHz, 1,1,2,2-Tetrachloroethane-d$_2$) δ: -138.168 – -138.345 (m, 2F), -157.547 – -157.806 (m, 2F).

9,10,11,12-tetrafluorotriphenylene-2-carbonitrile (3.4h)

![Chemical Structure](image)

Chemical Formula: C$_{19}$H$_7$F$_4$N
Molecular Weight: 325.26

Two quartz tubes were charged with 2",3",4",5",6"-pentafluoro-[1,1':2',1"-terphenyl]-4-carbonitrile (0.346 g x 2, 1.0 mmol x 2) and acetonitrile (100 mL x 2). The solutions were irradiated for 6 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

The contents of the tubes were combined and after column chromatography (eluent: hexanes:
EtOAc = 10:1), fractions containing the pure product were combined and concentrated to give orange crystals (0.368 g, 1.1 mmol, 55%) as final product.

**M.P.:** Slowly sublimed above ~ 210 °C.

$^1$H-NMR (400 MHz, 1,1,2,2-Tetrachloroethane-d$_2$) $\delta$: 9.001 (dd, $^1J = 5.6$ Hz, $^2J = 1.6$ Hz, 1H), 8.794 – 8.762 (m, 1H), 8.575 (d, $J = 8.8$ Hz, 1H), 8.516 - 8.491 (m, 1H), 7.847 (dd, $^1J = 8.8$ Hz, $^2J = 1.6$ Hz, 1H), 7.769 – 7.701 (m, 2H).

$^{13}$C-NMR (100 MHz, 1,1,2,2-Tetrachloroethane-d$_2$) $\delta$: 145.802 (d, $J = 251.1$ Hz), 145.694 (d, $J = 251.0$ Hz), 139.816 (d, $J = 252.6$ Hz), 139.228 (d, $J = 252.3$ Hz), 133.119, 131.962 (d, $J = 30.6$ Hz), 130.175, 129.637, 129.046, 128.362, 127.580 (d, $J = 29.5$ Hz), 126.269, 125.380, 124.055, 123.713, 118.835, 116.162, 114.164, 110.998.

$^{19}$F-NMR (376 MHz, 1,1,2,2-Tetrachloroethane-d$_2$) $\delta$: -136.980 – -137.065 (m, 1F), -137.502 – -137.617 (m, 1F), -154.506 – -154.627 (m, 1F), -155.495 – -155.605 (m, 1F).

### 3.5.2.3. Photocyclodehydrofluorination involving heterocycles

**Phenanthro[9,10-b]thiophene (3.6a)**

![Chemical Structure]

**Chemical Formula:** C$_{16}$H$_8$F$_4$S  
**Molecular Weight:** 306.28

The 2-([1,1'-biphenyl]-2-yl)thiophene (0.323 g, 1.0 mmol) was dissolved in acetonitrile (100 mL) in a quartz reaction vessel. The solution was thoroughly degassed with nitrogen and irradiated for
3 hours in a Rayonet photochemical reactor equipped with 16 x 254 nm UV lamps under nitrogen atmosphere. Meanwhile, tan crystals precipitated directly out of the solution.

The resulting suspension was filtered and the solid obtained (0.341 g) was recrystallized from toluene, giving tan needles (0.218 g, 71 % yield) as final product.

**M.P:** Slowly sublimed at ~ 195 °C and melted completely at 217.0 – 220.0 °C.

**$^1$H-NMR (400 MHz, 1,1,2,2-Tetrachloroethane-d$_2$)** $\delta$: 8.878 (d, $J = 8.4$ Hz, 1H), 8.118 – 8.048 (m, 2H), 7.648 – 7.551 (m, 3H).

**$^{13}$C-NMR (100 MHz, 1,1,2,2-Tetrachloroethane-d$_2$)** $\delta$: 146.358 (d, $J = 249.3$ Hz), 143.506 (d, $J = 245.3$ Hz), 139.426, 138.800 (d, $J = 249.3$ Hz), 138.610 (d, $J = 247.3$ Hz), 128.391, 127.787, 127.510, 127.276, 126.425, 126.234, 125.382, 124.697, 124.040, 115.133, 114.943.

**$^{19}$F-NMR (376 MHz, 1,1,2,2-Tetrachloroethane-d$_2$)** $\delta$: -137.562 (t, $J = 15.8$ Hz, 1F), -140.857 (dddd, $^1J = 20.3$ Hz, $^2J = 12.4$ Hz, $^3J = 3.0$ Hz, $^4J = 2.2$ Hz, 1F), -157.340 (td, $^1J = 20.5$ Hz, $^2J = 4.5$ Hz, 1F), -158.605 – -158.714 (m, 1F).

**GCMS (m/z):** 307.03.

**HRMS:** M$^+$ = 306.01212 (Calc = 306.01209).

**1,2,3,4-tetrafluorobenzo[b]naphtho[1,2-d]thiophene (3.6b)**

![Chemical Structure](image)

**Chemical Formula:** C$_{16}$H$_8$F$_4$S

**Molecular Weight:** 306.28
(E)-2-(2-(Perfluorophenyl)vinyl)benzo[b]thiophene (0.164 g, 0.5 mmol) was dissolved in acetonitrile (100 mL) in a quartz reaction vessel. The solution was thoroughly degassed with nitrogen and then irradiated in a Rayonet photochemical reactor equipped with 16 x 300 nm UV lamps.

After 18 hours, the starting material was nearly consumed (via GC-MS). The solution was transferred into a pear flask, and the solvent was removed and a yellow residue (0.156 g, 0.51 mmol, not very dry) was obtained. This material was dissolved in ethyl acetate, silica gel was added and the solvent was removed by rotary evaporation. Column chromatography (eluent: hexanes: DCM = 5:1) was used to purify the product which was obtained as a slightly pink powder (0.140 g, 0.46 mmol, 92% yield). This product was recrystallized from isooctane, to give tan crystals (0.120 g, 0.39 mmol, 78 % yield) as final product.

**M.P:** 191.0 – 194.0 °C.

**1H-NMR (400 MHz, CDCl₃):** 8.770 – 8.746 (m, 1H), 8.083 – 8.056 (m, 1H), 7.970 – 7.944 (m, 1H), 7.791 – 7.743 (m, 1H), 7.558 – 7.515 (m, 1H), 7.359 – 7.321 (m, 1H).

**19F-NMR (376 MHz, CDCl₃):** -133.331 – -133.416 (m, 1F), -147.637 (dd, ¹J = 20.1 Hz, ²J = 13.3 Hz, 1F), -157.568 (t, ³J = 19.5 Hz, 1F), -160.490 – -160.602 (m, 1F).

**GCMS (m/z):** 306.11.
9,10,11,12-tetrafluorodibenzo[f,h]isoquinoline (3.6c)

![Chemical Structure](image)

Chemical Formula: C_{17}H_{7}F_{4}N  
Molecular Weight: 301.24

The 4-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)pyridine (0.322 g, 1.0 mmol) was dissolved in acetonitrile (100 mL) in a quartz reaction vessel, thoroughly degassed with nitrogen and irradiated for 4 hours in a Rayonet photochemical reactor equipped with 16 x 254 nm UV lamps under the protection of nitrogen. During this time, a gray-colored powder precipitated directly out of the solution.

The resulting suspension was filtered directly by suction filtration and air-dried. The final product was obtained as a powder (0.232 g, 0.77 mmol, 77 % yield).

**M.P:** Slowly sublimed above 180 °C.

**^1^H-NMR (400 MHz, CDCl₃) δ:** 10.176 (s, 1H), 8.964 (d, J = 6.4 Hz, 1H), 8.839 (d, J = 5.4 Hz, 1H), 8.648 – 8.626 (m, 1H), 8.360 (d, J = 5.4 Hz, 1H), 7.784 – 7.748 (m, 2H).

**^1^9^F-NMR (376 MHz, CDCl₃) δ:** -135.783 (t, J = 15.8 Hz), -137.565 (t, J = 15.2 Hz), -155.956 – -156.061 (m), -156.190 – -156.299 (m).

**GCMS (m/z):** 301.04.
3.5.2.4. Photocyclodehydrofluorination of 2,3,5,6-tetrafluoro precursors

1,2,4-trifluorotriphenylene (3.8a)

![Chemical Structure]

Chemical Formula: C_{18}H_{9}F_{3}
Molecular Weight: 282.27

The 2,3,5,6-tetrafluoro-1,1':2',1''-terphenyl (0.303 g, 1.0 mmol) was dissolved in acetonitrile (100 mL) in a quartz reaction vessel, degassed thoroughly with nitrogen and irradiated for 12 hours in a Rayonet photochemical reactor equipped with 16 x 254 nm UV lamps under the protection of nitrogen. Analysis of reaction progress by GC-MS demonstrated the starting material was nearly consumed.

After purification by column chromatography (eluent: hexanes), a white powder (0.317 g) was obtained. This powder was recrystallized from iso-octane, giving white needle like crystals as final product (0.169 g, 60 % yield).

**M.P.:** Slowly sublimed above 130 °C melted completely at 151.0 – 152.0 °C.

**1H-NMR (400 MHz, CDCl₃):** 8.850 (ddd, ¹J = 8.4 Hz, ²J = 3.6 Hz, ³J = 1.2 Hz, 1H), 8.816 – 8.783 (m, 1H), 8.501 – 8.466 (m, 2H), 7.636 – 7.537 (m, 4H), 7.129 (ddd, ¹J = 9.6 Hz, ²J = 6.8 Hz, ³J = 6.8 Hz, 1H).

**13C-NMR (100 MHz, CDCl₃):** 156.187 (ddd, ¹J = 250 Hz, ²J = 10.8 Hz, ³J = 3.2 Hz), 148.460 (dt,
\( J = 247 \text{ Hz}, 2J = 16.2 \text{ Hz} \), 145.674 (ddd, 1\( J = 248 \text{ Hz}, 3J = 13.3 \text{ Hz}, 2J = 4.0 \text{ Hz} \)), 130.701, 129.991, 128.506 (d, 1\( J = 1.7 \text{ Hz} \)), 128.156, 127.861, 127.794, 127.671, 127.644, 127.550, 127.521, 126.410, 122.998 (d, 1\( J = 6.7 \text{ Hz} \)), 121.856 (t, 1\( J = 4.9 \text{ Hz} \)), 116.436 (d, 1\( J = 7.2 \text{ Hz} \)), 104.202 (dd, 1\( J = 32.3 \text{ Hz}, 2J = 21.6 \text{ Hz} \)).

\(^{19}F\)-NMR (376 MHz, CDCl\(_3\)): -108.738 – -108.842 (m), -135.749 – -135.841 (m), -140.970 – -141.076 (m).

GCMS (m/z): 283.06.

1,2,4-trifluoro-3-methoxytriphenylene (3.8b)

![Chemical Structure](image)

Chemical Formula: C\(_{19}\)H\(_{11}\)F\(_{3}\)O  
Molecular Weight: 312.29

A quartz vessel (approximately 40 cm x 25 mm) were charged with 2,3,5,6-tetrafluoro-4-methoxy-1,1':2',1''-terphenyl (\( \lambda_{\text{max}} = 233\text{nm} \)) (0.333 g, 1.0 mmol) and acetonitrile (100 mL). The obtained solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

The solutions were irradiated for 9 hours and GC-MS showed that nearly no starting material remained. The solvent was then removed with rotary evaporation, giving tan residue (0.338 g) as crude product. Then the residue was dissolved in ethyl acetate (approximately 15 mL) again and charged with silica gel (approximately 2 g). After concentrate the mixture to dryness again, the tan
powder obtained was placed at the top of a silica gel column and eluted (Hexanes). Fractions containing the pure product were combined and concentrated to give white crystals (0.176g, 0.56mmol, 56 % yield) as final product.

M.P. 106.0 – 107.0°C

$^1$H-NMR (400 MHz, CDCl$_3$): 8.846– 8.786 (m, 2H), 8.495– 8.476 (m, 2H), 7.618 - 7.232 (m, 4H), 4.152 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): 150.282(d, $J = 249$ Hz), 146.208 (d, $J = 249$ Hz), 143.478 (d, $J = 247$ Hz), 136.321, 130.142 (d, $J = 12.6$ Hz), 127.929, 127.908, 127.696, 127.634, 127.599, 127.558, 127.406, 126.264, 123.040 (d, $J = 2.9$ Hz), 115.832 (d, $J = 44.9$ Hz), 62.391 (t, $J = 3.3$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$): -131.754 - -131.806 (m), -139.961 - -140.055 (m), -152.783 (ddd, $^1J = 18.8$ Hz, $^2J = 7.1$ Hz, $^2J = 1.1$ Hz).

2-ethoxy-1,3,4-trifluorotriphenylene (3.8c)

A quartz vessel(approximately 40 cm x 25 mm) was charged with 4-ethoxy-2,3,5,6-tetrafluoro-1,1';2',1"-terphenyl($\lambda_{max}$ = 233nm) (0.346 g, 1.0 mmol) and acetonitrile (100 mL). The obtained solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.
The solutions were irradiated for 12 hours and GC-MS showed that no starting material remained. The solvent was then removed with rotary evaporation, giving tan residue (0.405 g) as crude product. Then the residue was dissolved in ethyl acetate (approximately 15 mL) again and charged with silica gel (approximately 2 g). After concentrate the mixture to dryness again, the tan powder obtained was placed at the top of a silica gel column and eluted (Hexanes). Fractions containing the pure product were combined and concentrated to give light yellow powder (0.248 g, 0.76 mmol, 76 % yield) as final product.

**M.P.** 114.0 – 115.5 °C

$^1$H-NMR (400 MHz, CDCl$_3$): 8.944 – 8.889 (m, 2H), 8.596 – 8.568 (m, 2H), 7.670 - 7.592 (m, 4H), 4.394 (q, $J$ = 7.2 Hz, 2H), 1.503 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): 150.797 (d, $J$ = 249 Hz), 146.280 (d, $J$ = 250 Hz), 143.962 (d, $J$ = 247 Hz), 130.271 (d, $J$ = 10.2 Hz), 128.065, 128.013, 127.998, 127.969, 127.816, 127.764, 127.728, 127.701, 127.675, 127.648, 127.527, 126.461, 123.160 (d, $J$ = 1.1Hz), 115.938 (d, $J$ = 25.4 Hz), 71.092, 15.564.

$^{19}$F-NMR (376 MHz, CDCl$_3$): -130.984 - -131.044 (m), -140.082 - -140.174 (m), -152.115 (dd, $^1J$ = 18.8 Hz, $^2J$ = 7.1 Hz).
A quartz vessel (approximately 40 cm x 25 mm) were charged with 2,3,5,6-tetrafluoro-4-propoxy-1,1':2,1''-terphenyl ($\lambda_{\text{max}} = 233 \text{nm}$) (0.361 g, 1.0 mmol) and acetonitrile (100 mL). The obtained solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps. The solutions were irradiated for 12 hours and GC-MS showed that no starting material remained. The solvent was then removed with rotary evaporation, giving tan residue (0.332 g) as crude product. Then the residue was dissolved in ethyl acetate (approximately 15 mL) again and charged with silica gel (approximately 2 g). After concentrate the mixture to dryness again, the tan powder obtained was placed at the top of a silica gel column and eluted (Hexanes). Fractions containing the pure product were combined and concentrated to give white crystals (0.188 g, 0.55 mmol, 55 % yield) as final product.

**M.P.** 101.0 – 102.0°C

**$^1$H-NMR (400 MHz, CDCl$_3$):** 8.950 – 8.897 (m, 2H), 8.605 – 8.576 (m, 2H), 7.675 - 7.601 (m, 4H), 4.286 (t, $J = 6.8$ Hz, 2H), 1.941 – 1.853 (m, 2H), 1.122 (t, $J = 7.2$ Hz, 3H).
\[ ^{13}C-\text{NMR (100 MHz, CDCl}_3\]: 150.732 (d, \(J = 249\) Hz), 146.301 (d, \(J = 249\) Hz), 143.931 (d, \(J = 248\) Hz), 130.274(d, \(J = 11.8\) Hz), 128.085, 127.998, 127.973, 127.950, 127.815, 127.787, 127.730, 127.705, 127.668, 127.642, 127.528, 126.494, 123.164, 115.932 (d, \(J = 43.7\) Hz), 77.069, 23.429, 10.260.

\[ ^{19}F-\text{NMR (376 MHz, CDCl}_3\]: -131.048 - -131.092 (m), -140.126 - -140.215 (m), -152.114 (dd, \(J = 18.8\) Hz, \(J = 7.1\) Hz).

**hexyl(1,3,4-trifluorotriphenyl-2-yl)sulfane (3.8e)**

The hexyl(2,3,5,6-tetrafluoro-[1,1':2',1"-terphenyl]-4-yl)sulfane (0.422 g, 1.0 mmol) was dissolved in THF (100 mL) in a quartz reaction vessel, thoroughly degassed with nitrogen and irradiated in a Rayonet photochemical reactor equipped with 16x 254 mn UV lamps under the protection of nitrogen.

After 18 hours of irradiation, GC-MS demonstrated that the starting material was nearly consumed. The solution was transferred to a pear flask and the solvent was removed with rotary evaporation to give crude product as brown oil (0.454 g). The crude material was dissolved with EtOAc (~ 10 mL) and mixed with silica gel (~ 2 g). After the solvent was removed again in vacuo, the tan powder obtained was placed on the top of a silica gel column and carefully chromatographed (Eluent: hexanes), affording desired pure product as white crystals (0.095 g, 2.4 mmol, 24 % yield).
M.P.: 78.5 – 83.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 8.944 – 8.914 (m, 2H), 8.589 – 8.568 (m, 2H), 7.704 – 7.601 (m, 4H), 3.028 (t, $J = 7.2$ Hz, 2H), 1.641 – 1.584 (m, 2H), 1.458 – 1.421 (m, 2H), 1.286 – 1.258 (m, 4H), 0.860 (t, $J = 7.2$ Hz, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 157.924, 155.443, 149.401 (ddd, $^1J = 243.7$ Hz, $^2J = 16.6$ Hz, $^3J = 6.8$ Hz), 145.738 (ddd, $^1J = 250.0$ Hz, $^2J = 15.3$ Hz, $^3J = 3.8$ Hz), 130.813, 130.350, 128.708, 128.696, 128.179 (d, $J = 9.4$ Hz), 128.035, 127.935, 127.827, 127.742 (d, $J = 2.3$ Hz), 126.304 (t, $J = 7.2$ Hz), 123.167, 121.127, 116.216 (d, $J = 8.5$ Hz), 112.122 (dd, $^1J = 28.4$ Hz, $^2J = 19.2$ Hz), 34.916, 31.297, 29.895, 28.179, 22.494, 13.975.

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -104.588 (d, $J = 14.7$ Hz, 1F), -130.820 (dd, $^1J = 21.0$ Hz, $^2J = 4.5$ Hz, 1F), -140.156 – -140.258 (m, 1F).

3.5.2.5. Photocyclodehydrofluorination of 2,6-difluoro precursors

1-fluorotriphenylene (3.10a)

![Chemical Structure](image)

Chemical Formula: C$_{18}$H$_{11}$F
Molecular Weight: 246.28

A quartz tube (approximately 40 cm x 25 mm) was charged with 2,6-fluoro-1,1':2',1"-terphenyl (0.267 g, 1.0 mmol) and acetonitrile (100 mL). The solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps and the reaction progress was
followed by GC-MS.

After 6 hours, GC-MS indicated that the starting material was nearly completely consumed. After purification by column chromatography (eluent: hexanes), white crystals (0.195 g, 0.79 mmol, 79 % yield) were obtained as final product.


M.P.: 166.0 – 167.0 °C (Lit.: 167 – 168 °C).

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 9.117 – 9.082 (m, 1H), 8.676 – 8.580 (m, 3H), 8.459 (dt, $^1J$ = 8.0 Hz, $^2J$ = 0.6 Hz, 1H), 7.679 – 7.632 (m, 4H), 7.597 – 7.544 (m, 1H), 7.364 (ddd, $^1J$ = 14.4 Hz, $^2J$ = 8.0 Hz, $^3J$ = 1.2 Hz, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 161.823 (d, $J$ = 250.7 Hz), 132.783 (d, $J$ = 3.7 Hz), 130.208 (d, $J$ = 3.0 Hz), 129.125 (d, $J$ = 2.6 Hz), 128.516, 128.234, 127.823, 127.716, 127.664, 127.432, 127.260, 127.154, 123.835, 123.356, 122.998, 119.128 (d, $J$ = 3.2 Hz), 114.685, 114.427.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -108.859 (dt, $^1J$ = 14.3 Hz, $^2J$ = 4.7 Hz, 1F).

GCMS (m/z): 246.12.
In a quartz tube (approximately 40 cm x 25 mm) was placed 2,6-difluorostilbene (0.218 g, 1.0 mmol) and acetonitrile (100 mL). The solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps for 144 hours.

After purification by column chromatography (eluent: hexanes), white crystals (0.121g, 0.62 mmol, 62 %) were obtained as final product.

**Reference:** Bavin; Dewar *Journal of the Chemical Society*, 1955, p.4486.

**M.P.:** 93.0 – 96.0 °C (Lit.: 100 °C).

**$^1$H-NMR (400 MHz, CDCl$_3$):** 8.667 – 8.642 (m, 1H), 8.453 (d, $J = 8.4$ Hz, 1H), 8.031 (d, $J = 9.2$ Hz, 1H), 7.992 – 7.899 (m, 1H), 7.796 (d, $J = 9.2$ Hz, 1H), 7.694 – 7.545 (m, 3H), 7.303 – 7.256 (m, 1H).

**$^{13}$C-NMR (100 MHz, CDCl$_3$):** 159.324 (d, $J = 248.5$ Hz), 132.185 (d, $J = 3.8$ Hz), 132.113, 129.672 (d, $J = 2.4$ Hz), 128.811, 127.406 (d, $J = 1.3$ Hz), 127.135, 127.029, 126.499 (d, $J = 8.8$ Hz), 123.044, 121.598 (d, $J = 15.4$ Hz), 118.542 (d, $J = 7.0$ Hz), 118.422 (d, $J = 3.7$ Hz), 111.035 (d, $J = 20.2$ Hz).

**$^{19}$F-NMR (376 MHz, CDCl$_3$):** 122.794 (dd, $^1J = 10.0$ Hz, $^2J = 5.8$ Hz).

**GCMS (m/z):** 196.06.
1-fluorophenanthrene-9-carbonitrile (3.10c)

The (Z)-3-(2,6-difluorophenyl)-2-phenylacrylonitrile (0.243 g, 1.0 mmol) was dissolved in acetonitrile (100 mL) in a quartz reaction vessel, degassed with nitrogen and irradiated for 36 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After purification by column chromatography (eluent: hexanes: DCM = 2:1), white crystals (0.158 g, 0.71 mmol, 71 % yield) were obtained as final product.

**M.P.:** 147.5 – 148.5 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$:** 8.621 – 8.598 (m, 1H), 8.426 (s, 1H), 8.386 (d, $J = 8.4$ Hz, 1H), 8.268 – 8.243 (m, 1H), 7.779 – 7.679 (m, 3H), 7.320 (ddd, $^1J = 10.0$ Hz, $^2J = 8.0$ Hz, $^3J = 0.8$ Hz).

**$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$:** 159.149 (d, $J = 253.0$ Hz), 133.160 (d, $J = 2.7$ Hz), 130.120 (d, $J = 8.8$ Hz), 129.310 (d, $J = 2.1$ Hz), 128.68, 128.658 (d, $J = 2.7$ Hz), 127.472 (d, $J = 7.1$ Hz), 126.245, 123.457, 119.665 (d, $J = 21.2$ Hz), 118.600 (d, $J = 3.9$ Hz), 117.586, 112.084 (d, $J = 19.9$ Hz), 109.898.

**$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$:** -119.611 (dd, $^1J = 9.6$ Hz, $^2J = 5.8$ Hz, 1F).

**GCMS (m/z):** 221.08.
1-fluoro-6-phenylphenanthrene-9-carbonitrile (3.10d)

The (Z)-2-([1,1'-biphenyl]-4-yl)-3-(2,6-difluorophenyl)acrylonitrile (0.317 g, 1.0 mmol) was dissolved in acetonitrile (100 mL). The solution was thoroughly degassed with nitrogen and then irradiated for 24 hours in a Rayonet photochemical reactor equipped with 16x 300 nm UV lamps.

After column chromatography (eluent: hexanes: EtOAc: DCM = 10:1:1) a white powder (0.220g, 0.74 mmol, 74% yield) was obtained as final product.

**M.P.:** 209.0 – 210.5 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$:** 8.791 (d, $J = 1.6$ Hz, 1H), 8.486 (d, $J = 8.4$ Hz, 1H), 8.458 (s, 1H), 8.328 (dd, $^1J = 8.4$ Hz,$^2J = 0.4$ Hz, 1H), 7.981 (dd, $^1J = 8.4$ Hz, $^2J = 2.0$ Hz, 1H), 7.767 – 7.703 (m, 3H), 7.566 – 7.518 (m, 2H), 7.477 – 7.434 (m, 1H), 7.349 (ddd, $^1J = 9.6$ Hz, $^2J = 8.0$ Hz, $^3J = 0.8$ Hz, 1H).

**$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$:** 159.250 (d, $J = 253.1$ Hz), 141.597, 140.275, 133.253 (d, $J = 2.8$ Hz), 130.136 (d, $J = 8.8$ Hz), 129.692, 129.137, 128.873, 128.114 (d, $J = 12.1$ Hz), 127.618, 127.276 (d, $J = 7.1$ Hz), 126.997, 126.783, 121.708, 119.986 (d, $J = 15.2$ Hz), 118.655 (d, $J = 3.8$ Hz), 117.607, 112.237 (d, $J = 19.8$ Hz), 109.740.
$^{19}$F-NMR (100 MHz, CDCl$_3$) $\delta$: -119.828 (dd, $^1J = 9.6$ Hz, $^2J = 5.8$ Hz, 1F).

**GCMS (m/z):** 297.15.

1-fluorochrysene (3.10e)

![Chemical Structure of 1-fluorochrysene]

**Chemical Formula:** C$_{18}$H$_{11}$F  
**Molecular Weight:** 246.28

The 1-(2,6-difluorostyryl)naphthalene (0.265 g, a mixture of Z/E-isomers, 1.0 mmol) was dissolved in acetonitrile (100 mL). This solution was charged in to a quartz reaction vessel, degassed with nitrogen and irradiated for 18 hours with a 450W Hanovia lamp equipped with a Vycor filter.

After purification by silica gel column chromatography (eluent: hexanes: DCM = 10:1), the product was obtained as white crystals (0.107 g, 0.43 mmol, 43 % yield).


**M.P.:** Slowly sublimed above 200 °C, and then melted completely at 246 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.760 (dd, $^1J = 8.4$ Hz, $^2J = 0.4$ Hz, 1H), 8.748 (d, $J = 9.2$ Hz, 1H), 8.634 (d, $J = 9.2$ Hz, 1H), 8.512 (d, $J = 8.4$ Hz, 1H), 8.268 (d, $J = 9.2$ Hz, 1H), 8.001 – 7.960 (m, 2H), 7.719 – 7.677 (m, 1H), 7.649 – 7.563 (m, 2H), 7.281 (ddd, $^1J = 10.0$ Hz, $^2J = 7.6$ Hz, $^3J = 0.8$ Hz, 1H).
$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 159.502 (d, $J = 249.3$ Hz), 132.588 (d, $J = 4.5$ Hz), 132.496, 130.637, 128.758, 128.653, 127.898, 126.947, 126.760, 126.512 (d, $J = 8.6$ Hz), 123.322, 122.187 (d, $J = 15.8$ Hz), 121.725, 121.364, 119.238 (d, $J = 6.6$ Hz), 119.020 (d, $J = 3.8$ Hz), 110.489 (d, $J = 10.0$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -122.355 (q, $J = 4.1$ Hz, 1F).

GCMS (m/z): 247.06.

3.5.2.6. Photocyclodehydrofluorination involving competition of PCDHF vs oxidative photocyclization

phenanthrene (3.12.1a) & 1-fluorophenenthrene (3.12.2a)

![Chemical structures](image)

Chemical Formula: C$_{14}$H$_{10}$  Chemical Formula: C$_{14}$H$_9$F
Molecular Weight: 178.23  Molecular Weight: 196.22

Two quartz tubes (approximately 40 cm x 25 mm) were charged with 2-fluorostilbene (0.199 g, 1.0 mmol each) and solvents (one tube with 100 ml acetonitrile and the other tube with 100 ml THF). These solutions were irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps side by side and the reaction progress was followed by GC-MS.

The solutions were irradiated until GC-MS showed that no starting material remained (48 h for acetonitrile sample; 168 hours for the THF sample). After purification by column chromatography (eluent: hexanes), fractions containing the respective individual pure products were combined and concentrated to give white crystals (0.121 g for the reaction in acetonitrile; 0.068 g for the reaction in THF) as final product.
The phenanthrene (GCMS (m/z): 178.01) and 1-fluorophenanthrene (GCMS (m/z): 196.03) products cannot be separated by column chromatography. The final yields were calculated using compositions found by GC-MS.

**Results:**

When acetonitrile was used as solvent, the integrated areas of phenanthrene: 1-fluorophenanthrene on GC-MS were about 1:3. The average MW is about 191.72. Yields - phenanthrene: 16 %; 1-fluorophenanthrene: 47 %.

When THF was used as solvent, the integrated area of phenanthrene: 1-fluorophenanthrene on GC-MS were about 3:1. The average MW is about 182.73. Yields - phenanthrene: 28 %; 1-fluorophenanthrene: 9 %.

In this case the solvent had a dramatic effect on the product composition (resulting from competitive loss of H₂ or HF)

1-fluorophenanthrene (3.12.1b) & 1,8-difluorophenanthrene(3.12.2b)

![Chemical structures of 1-fluorophenanthrene and 1,8-difluorophenanthrene](image)

Chemical Formula: C₁₄H₉F²  
Molecular Weight: 196.22  

Chemical Formula: C₁₄H₈F₂  
Molecular Weight: 214.21

A quartz tube (approximately 40 cm x 25 mm) was charged with 2,2'-difluorostilbene (0.216 g,
1.0 mmol) and acetonitrile (100 mL). A second quartz tube was charged with 2,2’-difluorostilbene (0.216 g, 1.0 mmol) and THF (100 mL). Both tubes were degassed thoroughly and irradiated in a Rayonet photochemical reactor equipped with 16 x 254 nm UV lamps side by side. The reaction was followed by using GC-MS.

The solutions were irradiated for 96 hours and GC-MS showed that no starting material remained (in either tube). After purification by column chromatography (eluent: hexanes), fractions containing the products were combined and concentrated to give white crystals (0.149 g for the acetonitrile tube; 0.122 g for THF tube)

The monofluoro (GCMS (m/z): 196.09) and difluoro (GCMS (m/z): 214.10) products cannot be separated by column chromatography. The final yields were calculated using compositions found by GC-MS.

**Result:**

When acetonitrile was used as solvent, the integrated area of 1-fluorophenanthrene: 1,8-difluorophenanthrene on GC-MS were about 1.5:1. The average MW is about 203.42. Yields - 1-fluorophenanthrene: 44 %; 1,8-difluorophenanthrene: 29 %

When THF was used as solvent, the integration area of 1-fluorophenanthrene: 1,8-difluorophenanthrene on GC-MS were about 6:1. The average MW is about 198.79. Yields - 1-fluorophenanthrene: 52 %; 1,8-difluorophenanthrene:9 %.
3-fluorophenanthrene-9-carbonitrile (3.12.1c) & 1,3-difluorophenanthrene-9-carbonitrile (3.12.2c)

\[
\text{Chemical Formula: } C_{15}H_8FN \quad \text{Chemical Formula: } C_{15}H_7F_2N \\
\text{Molecular Weight: } 221.23 \quad \text{Molecular Weight: } 239.22
\]

(Z)-3-(2,4-difluorophenyl)-2-phenylacrylonitrile (0.241 g, 1.0 mmol) was dissolved in acetonitrile (100 mL), degassed with nitrogen and irradiated for 84 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After column chromatography (eluent: hexanes: EtOAc = 10:1), two products were obtained. The first product was obtained as white crystals (0.034 g, 0.14 mmol, 14 % yield), demonstrated to be 1,3-difluorophenanthrene-9-carbonitrile. The second product was obtained as white fibers (0.030 g, 0.14 mmol, 14 % yield), demonstrated to be 3-fluorophenanthrene-9-carbonitrile.

3-fluorophenanthrene-9-carbonitrile

M.P.: sublimation began at 160 °C, quickly sublimed at 169 – 170 °C.

\(^1\text{H-NMR (400 MHz, CDCl}_3\): 8.561 – 8.537 (m, 1H), 8.305 – 8.242 (m, 2H), 7.926 (dd, \(^1J = 8.6\) Hz, \(^2J = 5.8\) Hz, 1H), 7.789 – 7.763 (m, 2H), 7.424 (ddd, \(^1J = 8.8\) Hz, \(^2J = 8.0\) Hz, \(^3J = 2.4\) Hz, 1H).

\(^19\text{F-NMR (376 MHz, CDCl}_3\): -107.370 – -107.435 (m, 1F).

GCMS (m/z): 221.09.
1,3-difluorophenanthrene-9-carbonitrile

**M.P.:** sublimation began at 170 °C, quickly sublimed at 183 – 185 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$)** δ: 8.556 – 8.533 (m, 1H), 8.459 (s, 1H), 8.340 – 8.316 (m, 1H), 8.114 – 8.083 (m, 1H), 7.851 – 7.783 (m, 2H), 7.172 (ddd, $^1J = 9.6$ Hz, $^2J = 8.4$ Hz, $^3J = 2.4$ Hz, 1H).

**$^{19}$F-NMR (376 MHz, CDCl$_3$)** δ: -104.363 – -104.437 (m, 1F), -114.722 (td, $^1J = 9.4$ Hz, $^2J = 1.1$ Hz, 1F).

**GCMS (m/z):** 239.07.

3-Fluoro-6-phenylphenanthrene-9-carbonitrile (3.12.1d) & 1,3-difluoro-6-phenylphenanthrene-9-carbonitrile (3.12.2d)

![Chemical结构](image)

Chemical Formula: C$_{21}$H$_{12}$FN  
Molecular Weight: 297.33

![Chemical结构](image)

Chemical Formula: C$_{21}$H$_{11}$F$_2$N  
Molecular Weight: 315.32

(Z)-2-([1,1'-biphenyl]-4-yl)-3-(2,4-difluorophenyl)acrylonitrile (0.318 g, 1.0 mmol) was dissolved in acetonitrile (100 mL) (conc = 0.01 mol/L), degassed with nitrogen thoroughly overnight and then irradiated in a Rayonet photochemical reactor equipped with 16 x 300 nm UV lamps for 42 hours.
After column chromatography (Eluent: hexane: EtOAc= 20:1), two kinds of white powder were obtained as final products. The first product (0.050 g, 0.18 mmol, 18% yield) was demonstrated to be 1,3-difluoro-6-phenylphenanthrene-9-carbonitrile and the second product (0.069 g, 0.23 mmol, 23 % yield) was demonstrated to be 3-fluoro-6-phenylphenanthrene-9-carbonitrile.

3-fluoro-6-phenylphenanthrene-9-carbonitrile

M.P.: 205.0 – 207.0 °C.

\(^{1}\)H-NMR (400 MHz, CDCl\(_3\)): 8.690 (d, \(J = 1.2\) Hz, 1H), 8.334 (d, \(J = 8.4\) Hz, 1H), 8.320 (dd, \(^{1}J = 10.8\) Hz, \(^{2}J = 2.4\) Hz, 1H), 8.178 (s, 1H), 7.992 (dd, \(^{1}J = 8.4\) Hz, \(^{2}J = 1.6\) Hz, 1H), 7.926 (dd, \(^{1}J = 8.8\) Hz, \(^{2}J = 6.0\) Hz, 1H), 7.762 – 7.741 (m, 2H), 7.555 – 7.517 (m, 2H), 7.466 – 7.400 (m, 2H).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): 163.544 (d, \(J = 250\) Hz), 141.436, 140.379, 134.600, 133.901 (d, \(J = 8.6\) Hz), 132.006 (d, \(J = 9.3\) Hz), 129.844 (d, \(J = 4.1\) Hz), 129.185, 128.836, 128.358, 128.210, 127.657, 126.989 (d, \(J = 4.8\) Hz), 126.769, 121.564, 117.668, 117.106 (d, \(J = 24.1\) Hz), 108.810, 108.442 (d, \(J = 22.8\) Hz).

\(^{19}\)F-NMR (100 MHz, CDCl\(_3\)): -107.913 - -107.978 (m).

1,3-difluoro-6-phenylphenanthrene-9-carbonitrile

M.P.: 211.0 – 213.0 °C.

\(^{1}\)H-NMR (400 MHz, CDCl\(_3\)): 8.680 (d, \(J = 1.6\) Hz, 1H), 8.437 (s, 1H), 8.374 (d, \(J = 8.4\) Hz, 1H), 8.160 (d, \(J = 10.4\) Hz, 1H), 8.380 (dd, \(^{1}J = 8.4\) Hz, \(^{2}J = 1.6\) Hz, 1H), 7.761 – 7.732 (m, 2H), 7.563 – 7.519 (m, 2H), 7.478 – 7.435 (m, 2H), 7.170 (ddd, \(^{1}J = 9.6\) Hz, \(^{2}J = 8.4\) Hz, \(^{3}J = 2.4\) Hz, 1H)

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): 163.131 (dd, \(^{1}J = 250.8\) Hz, \(^{2}J = 13.0\) Hz), 160.116 (dd, \(^{1}J = 256.0\) Hz, \(^{2}J = 10.4\) Hz).
Hz, $^2J = 13.3$ Hz), 141.976, 140.147, 134.319 (d, $J = 4.6$ Hz), 134.266 (d, $J = 4.6$ Hz), 129.239, 128.866, 128.647, 128.368, 127.670, 127.043, 126.887 (d, $J = 3.3$ Hz), 121.851, 117.384, 117.168 (d, $J = 14.8$ Hz), 109.382, 104.525 (dd, $^1J = 22.8$ Hz, $^2J = 4.2$ Hz), 103.140 (dd, $^1J = 27.8$ Hz, $^2J = 24.0$ Hz)

$^{19}$F-NMR (100 MHz, CDCl$_3$): -104.990 (dt, $^1J = 9.7$ Hz, $^2J = 8.8$ Hz), -115.111 (td, $^1J = 9.6$ Hz, $^2J = 1.0$ Hz).

2,3-difluoro-6-phenylphenanthrene-9-carbonitrile (3.12.1e) & 1,3,4-trifluoro-6-phenylphenanthrene-9-carbonitrile (3.12.2e)

![Chemical Structure](image)

**Chemical Formula:** C$_{21}$H$_{12}$F$_2$N  **Chemical Formula:** C$_{21}$H$_{10}$F$_3$N

**Molecular Weight:** 315.32  **Molecular Weight:** 333.31

The (Z)-2-([1,1'-biphenyl]-4-yl)-3-(2,4,5-trifluorophenyl)acrylonitrile (0.336 g, 1.0 mmol) was dissolved in acetonitrile (100 mL), degassed thoroughly with nitrogen and then irradiated for 42 hours in a Rayonet photochemical reactor equipped with 16 x 300 nm UV lamps.

Two products were separated by column chromatography. The first product was eluted (eluent: hexanes: EtOAc = 50:1), giving white crystals (0.105g, 31.5 % yield) that were found to be 1,3,4-trifluoro-6-phenylphenanthrene-9-carbonitrile. The second product was eluted (eluent: hexanes: EtOAc = 25:1) to give white crystals (0.052g, 16.5 % yield) that were found to be 2,3-difluoro-6-
phenylphenanthrene-9-carbonitrile.

2,3-difluoro-6-phenylphenanthrene-9-carbonitrile

*M.P.*: 233.0 – 236.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.646 (s, 1H), 8.473 (dd, $^1J = 10.8$ Hz, $^2J = 7.6$ Hz, 1H), 8.364 (d, $J = 8.4$ Hz, 1H), 8.128 (s, 1H), 8.006 (d, $J = 7.6$ Hz, 1H), 7.761 – 7.683 (m, 3H), 7.544 – 7.457 (m, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 152.143 (dd, $^1J = 252.1$ Hz, $^2J = 14.0$ Hz), 150.618 (dd, $^1J = 252.0$ Hz, $^2J = 14.4$ Hz), 141.946, 140.268, 133.499, 129.695, 129.439, 129.226, 128.330, 128.107, 127.899, 127.684, 127.235, 126.966, 121.432, 117.310, 116.208 (d, $J = 17$ Hz), 111.044 (d, $J = 18.7$ Hz), 110.309.

$^{19}$F-NMR (100 MHz, CDCl$_3$) $\delta$: -131.148 – -131.259 (m, 1F), -135.692 – -135.792 (m, 1F).

GCMS (m/z): 315.19.

1,3,4-trifluoro-6-phenylphenanthrene-9-carbonitrile

*M.P.*: 206.0 – 208.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 9.263 (dd, $^1J = 4.0$ Hz, $^2J = 2.0$ Hz, 1H), 8.379 (d, $J = 6.4$ Hz, 1H), 8.366 (s, 1H), 8.062 (dd, $^1J = 8.4$ Hz, $^2J = 1.6$ Hz, 1H), 7.754 – 7.725 (m, 2H), 7.548 – 7.503 (m, 2H), 7.464 – 7.421 (m, 1H), 7.282 (ddd, $^1J = 9.2$ Hz, $^2J = 9.2$ Hz, $^3J = 6.0$ Hz, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 154.494 (ddd, $^1J = 252.0$ Hz, $^2J = 11.8$ Hz, $^3J = 3.5$ Hz), 150.490 (ddd, $^1J = 252.3$ Hz, $^2J = 16.3$ Hz, $^3J = 13.6$ Hz), 145.534 (ddd, $^1J = 250.5$ Hz, $^2J = 14.0$ Hz, $^3J = 4.8$ Hz), 142.305, 140.029, 129.236, 128.822, 128.703, 128.366, 127.623, 126.825, 126.319 (d, $J = 7.4$ Hz), 126.229, 125.973, 122.439, 117.340 (d, $J = 15.7$ Hz), 116.989, 110.757, 103.679 (dd,
$^1J = 25.9$ Hz, $^2J = 23.7$ Hz).

$^{19}$F-NMR (100 MHz, CDCl$_3$) δ: -119.904 – -119.985 (m, 1F), -130.194 – -130.278 (m, 1F), -141.867 – -141.990 (m, 1F).

GCMS (m/z): 333.17.

3-fluorochrysene (3.12.1f) & 1,3-difluorochrysene (3.12.2f)

![Chemical structures of 3-fluorochrysene and 1,3-difluorochrysene](image)

Chemical Formula: C$_{18}$H$_{11}$F  Chemical Formula: C$_{18}$H$_{10}$F$_2$

Molecular Weight: 246.28  Molecular Weight: 264.27

The 1-(2,4-difluorostyril)naphthalene ($E/Z$ isomer mixture) (0.267 g, 1.0 mmol) was dissolved in acetonitrile (100 mL). This solution was transferred in to a quartz reaction vessel, degassed with nitrogen and irradiated with a 450W Hanovia lamp equipped with a quartz probe and Vycor filter for 40 hours under the protection of nitrogen.

After careful column chromatography (eluent: hexanes), the first product 1,3-difluorochrysene (0.035 g, 0.14 mmol, 14 % yield) was obtained as white crystals. The second product 3-fluorochrysene (0.125 g, 0.51 mmol, 51 % yield) was also obtained as white crystals.

3-fluorochrysene

M.P.: 221.0 – 222.0 °C (Lit.: 218 - 219 °C).

\(^1\)H-NMR (400 MHz, 1,1,2,2-Tetrachloroethane-D\(_2\)) δ: 8.726 (d, \(J = 8.0\) Hz, 1H), 8.616 (d, \(J = 9.2\) Hz, 1H), 8.490 (d, \(J = 9.2\) Hz, 1H), 8.328 (dd, \(^1J = 11.6\) Hz, \(^2J = 2.4\) Hz, 1H), 7.981 – 7.932 (m, 4H), 7.724 – 7.626 (m, 2H), 7.387 (td, \(^1J = 8.4\) Hz, \(^2J = 2.4\) Hz, 1H).

\(^13\)C-NMR (100 MHz, 1,1,2,2-Tetrachloroethane-D\(_2\)) δ: 161.381 (d, \(J = 243.8\) Hz), 132.093, 131.618 (d, \(J = 8.5\) Hz), 130.673 (d, \(J = 9.0\) Hz), 130.109, 128.711, 128.537, 128.457, 127.391, 126.834, 126.731, 123.153, 120.991, 120.382 (d, \(J = 1.9\) Hz), 115.785 (d, \(J = 24.2\) Hz), 107.735 (d, \(J = 22.0\) Hz), 103.805 (d, \(J = 22.2\) Hz), 101.544 (dd, \(^1J = 28.1\) Hz, \(^2J = 24.1\) Hz).

\(^19\)F-NMR (376 MHz, 1,1,2,2-Tetrachloroethane-D\(_2\)) δ: -111.044 – -111.112 (m, 1F).

GCMS (m/z): 247.19.

1,3-difluorochrysene

M.P.: 211.0 – 214.5 °C.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) δ: 8.733 – 8.710 (m, 1H), 8.652 (d, \(J = 9.2\) Hz, 1H), 8.424 (d, \(J = 9.2\) Hz, 1H), 8.160 (d, \(J = 9.2\) Hz, 1H), 8.131 – 8.098 (m, 1H), 7.978 – 7.950 (m, 2H), 7.725 – 7.628 (m, 2H), 7.093 (ddd, \(^1J = 10.8\) Hz, \(^2J = 8.4\) Hz, \(^3J = 2.0\) Hz, 1H)

\(^13\)C-NMR (100 MHz, CDCl\(_3\)) δ: 160.738 (dd, \(^1J = 244.6\) Hz, \(^2J = 12.9\) Hz), 159.694 (dd, \(^1J = 252.1\) Hz, \(^2J = 13.3\) Hz), 132.491, 130.644 (d, \(J = 8.9\) Hz), 130.293, 129.291, 128.624, 127.890, 127.011, 126.792, 123.317, 121.049, 120.842, 118.920 (d, \(J = 5.2\) Hz), 115.804 (d, \(J = 24.3\) Hz), 107.856 (d, \(J = 22.2\) Hz), 103.878 (dd, \(^1J = 22.1\) Hz, \(^2J = 4.2\) Hz), 101.550 (dd, \(^1J = 28.3\) Hz, \(^2J = 24.0\) Hz).

\(^19\)F-NMR (376 MHz, CDCl\(_3\)) δ: -110.710 – -110.782 (m, 1F), -117.827 – -117.876 (m, 1F).

GCMS (m/z): 265.19.
2,3-difluorochrysene (3.12.1g) & 1,3,4-trifluorochrysene (3.12.2g)

The 1-(2,4,5-trifluorostyryl)naphthalene (E/Z isomer mixture) (0.285 g, 1.0 mmol) was dissolved in acetonitrile (100 mL). This solution was transferred to a quartz reaction vessel (25mm diameter x 40cm length), degassed with nitrogen thoroughly and irradiated for 45 hours with a 450W Hanovia lamp equipped with a quartz probe and Vycor filter under the protection of nitrogen.

After careful column chromatography (eluent: hexanes), the first product 1,3,4-trifluorochrysene was obtained as white crystals (0.050 g, 0.18 mmol, 18 % yield). The second product 2,3-difluorochrysene was also obtained as white crystals (0.068 g, 0.26 mmol, 26 % yield).

1,3,4-trifluorochrysene

M.P.: 189.5 – 193.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 9.015 (dd, $^1J = 9.6$ Hz, $^2J = 3.0$ Hz, 1H), 8.736 (d, $J = 6.4$ Hz, 1H), 8.717 (d, $J = 8.8$ Hz, 1H), 8.132 (dd, $^1J = 9.2$ Hz, $^2J = 2.0$ Hz, 1H), 8.003 – 7.974 (m, 2H), 7.739 – 7.659 (m, 2H), 7.231 – 7.168 (m, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 154.042 (d, $J = 247.6$ Hz), 147.880 (d, $J = 263.3$ Hz), 145.456 (d, $J = 252.9$ Hz), 132.324, 129.913 (d, $J = 6.6$ Hz), 128.418, 128.147, 127.295, 126.906, 126.165,
124.715, 124.460, 123.345, 122.044, 121.502, 119.374 (d, $J = 16.1$ Hz), 118.532 (d, $J = 6.8$ Hz), 102.009 (dd, $^1J = 26.0$ Hz, $^2J = 24.0$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -122.914 (ddd, $^1J = 17.3$ Hz, $^2J = 9.0$ Hz, $^3J = 2.6$ Hz, 1F), -136.468 (ddd, $^1J = 17.3$ Hz, $^2J = 9.8$ Hz, $^3J = 2.6$ Hz, 1F), -143.288 – -143.388 (m, 1F).

GCMS (m/z): 283.03.

2,3-difluorochrysene

M.P.: 213.0 – 215.0 °C.

$^1$H-NMR (400 MHz, 1,1,2,2-Tetrachloroethane-D$_2$) δ: 8.668 (d, $J = 8.4$ Hz, 1H), 8.616 (d, $J = 9.2$ Hz, 1H), 8.409 – 8.359 (m, 2H), 7.934 (d, $J = 8.8$ Hz, 2H), 7.818 (d, $J = 9.2$ Hz, 1H), 7.686 – 7.587 (m, 3H).

$^{19}$F-NMR (376 MHz, 1,1,2,2-Tetrachloroethane-D$_2$) δ: -135.727 (ddd, $^1J = 21.0$ Hz, $^2J = 12.8$ Hz, $^3J = 8.3$ Hz, 1F), -137.360 (ddd, $^1J = 20.7$ Hz, $^2J = 10.5$ Hz, $^3J = 7.5$ Hz, 1F).

GCMS (m/z): 265.07.
3.5.2.7. Steric controlled PCDHF reactions

1,2,3,4-tetrafluoro-7-methoxyphenanthrene (3.14.1a) and 1,2,3,4-tetrafluoro-5-methoxyphenanthrene (3.14.2a)

In a quartz vessel, (E)-1,2,3,4,5-pentafluoro-6-(3-methoxystyryl)benzene (0.299 g, 1.0 mmol) was dissolved in acetonitrile (100 mL). The solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps for 18 hours and both TLC and GC-MS showed two different products (one was the majority one and the other only had trace amount). The obtained solution was well mixed with silica gel and the solvent was removed by rotary evaporation. The obtained yellow powder was placed on the top of silica gel column and eluted (eluent: hexanes: EtOAc = 20:1) and the fractions containing the pure product were combined and condensed, giving white crystals (0.137 g, 0.49 mmol, 49% yield) as product. Only the main product can be isolated and characterized.

One proton features a high chemical shift at 8.829 indicated the major product is 1,2,3,4-tetrafluoro-7-methoxyphenanthrene (deshielded by the nearby fluorine atom).

\(^1\text{H-NMR (400 MHz, CDCl}_3\) \(\delta\): 8.829 (dd, \(^1J = 9.2\) Hz, \(^2J = 2.0\) Hz, 1H), 7.855 (dd, \(^1J = 9.2\) Hz, 1H),
$^{2}J = 2.0$ Hz, 1H), 7.708 (d, $J = 9.2$ Hz, 1H), 7.303 (ddd, $^{1}J = 9.2$ Hz, $^{2}J = 2.8$ Hz, $^{3}J = 2.0$ Hz, 1H), 7.258 (d, $J = 2.8$ Hz, 1H), 3.971 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 158.769, 145.406 (d, $J = 251.9$ Hz), 142.498(d, $J = 255.9$ Hz), 139.452 (d, $J = 243.2$ Hz), 137.158 (d, $J = 249.7$ Hz), 134.161, 128.662, 128.507, 128.424, 118.146, 117.440, 109.211, 55.413.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -140.832 (t, $J = 14.9$ Hz, 1F), -149.100 (dd, $^{1}J = 20.3$ Hz, $^{2}J = 14.0$ Hz, 1F), -158.265 (t, $J = 19.4$ Hz, 1F), -160.156 - -160.272 (m, 1F).
A quartz vessel (approx. 40cm x 25mm) was charged with 2,3,4,5,6-pentafluoro-3''-methoxy-1,1':2',1''-terphenyl (0.352 g, 1.0 mmol), which was dissolved in acetonitrile (100 mL). The resulting solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After 9 hours, GC-MS indicated the starting material was completely consumed and two new products were observed. The solvent was removed and crude product (0.353 g) was obtained as tan solid. The solid was dissolved again in EtOAc (~10 mL) and mixed with silica gel (~2 g). After the removal of solvent under reduced pressure, the obtained powder was placed on a silica gel column to elute (eluent: hexane: EtOAc = 20:1), affording white solid (0.232 g, 0.75 mmol, 75% yield) as final product.

The two products were impossible to be isolated by column chromatography.
Similar as before, one proton features a high chemical shift at 8.990 – 8.868 indicated the major product is 1,2,3,4-tetrafluoro-7-methoxytriphenylene.

**M.P.:** 158.0 – 1562.0 °C.

**Only H NMR Obtained:**

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.990 – 8.868 (m, 1H), 8.810 (dd, $^1J = 9.6$ Hz, $^2J = 3.6$ Hz, 1H), 8.519 (dd, $^1J = 8.0$ Hz, $^2J = 1.6$ Hz, 1H), 7.982 (d, $J = 2.8$ Hz, 1H), 7.705 – 7.620 (m, 2H), 7.249 – 7.215 (m, 1H), 4.024 (s, 3H).
In a quartz vessel, (E)-3-(2-(perfluorophenyl)vinyl)benzonitrile (0.592 g, 2.0 mmol) was dissolved in acetonitrile (100 mL). The solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps for 48 hours and both TLC and GC-MS showed two different products. The obtained solution was well mixed with silica gel and the solvent was removed by rotary evaporation. The obtained yellow powder was placed on the top of silica gel column and eluted (eluent: hexanes : EtOAc = 20:1) and the fractions containing the pure product were combined and condensed, giving two kinds of white crystals as product. The first fraction was demonstrated to be 5,6,7,8-tetrafluorophenanthrene-2-carbonitrile (0.225 g, 0.82 mmol, 41 % yield) and the second fraction was shown to be 5,6,7,8-tetrafluorophenanthrene-4-carbonitrile (0.155 g, 0.56 mmol, 28 % yield).

The very deshielded proton at 9.088 indicated the major product is 5,6,7,8-tetrafluorophenanthrene-2-carbonitrile.
5,6,7,8-tetrafluorophenanthrene-2-carbonitrile

**M.P.:** 208 – 210 °C.

**\(^1\)H-NMR (400 MHz, CDCl\(_3\))** \(\delta\): 9.088 (dd, \(^1J = 8.8\) Hz, \(^2J = 3.2\) Hz, 1H), 8.285 (d, \(^J = 2.0\) Hz, 1H), 8.073 (dd, \(^1J = 8.8\) Hz, \(^2J = 1.6\) Hz, 1H), 7.907 (ddd, \(^1J = 8.8\) Hz, \(^2J = 1.6\) Hz, \(^3J = 1.6\) Hz, 1H), 7.856 (d, \(^J = 8.8\) Hz, 1H).

**\(^19\)F-NMR (376 MHz, CDCl\(_3\))** \(\delta\): -138.093 (t, \(^J = 15.4\) Hz, 1F), -147.199 (dd, \(^1J = 20.3\) Hz, \(^2J = 14.3\) Hz, 1F), -154.656 - -154.778 (m, 1F), -155.615 (t, \(^J = 19.3\) Hz, 1F).

5,6,7,8-tetrafluorophenanthrene-2-carbonitrile

**M.P.:** 174 – 176 °C.

**\(^1\)H-NMR (400 MHz, CDCl\(_3\))** \(\delta\): 8.167 – 8.130 (m, 2H), 8.033 (dd, \(^1J = 8.8\) Hz, \(^2J = 1.6\) Hz, 1H), 7.822 (d, \(^J = 8.8\) Hz, 1H), 7.778 (dd, \(^1J = 7.6\) Hz, \(^2J = 7.6\) Hz, 1H).

**\(^19\)F-NMR (376 MHz, CDCl\(_3\))** \(\delta\): -125.861 - -125.945 (m, 1F), -148.003 (dd, \(^1J = 20.3\) Hz, \(^2J = 13.5\) Hz, 1F), -154.268 - -154.390 (m, 1F), -155.514 (t, \(^J = 20.1\) Hz, 1F).
3.5.2.8. Photocyclodehydrofluorination involving competition with other halogens

1-fluorochrysene (3.16.1a) & 1-chlorochrysene (3.16.2a)

![Chemical Structure of 1-fluorochrysene](image1)  ![Chemical Structure of 1-chlorochrysene](image2)

Chemical Formula: \( \text{C}_{18}\text{H}_{11}\text{F} \)  Molecular Weight: 246.28
Chemical Formula: \( \text{C}_{18}\text{H}_{11}\text{Cl} \)  Molecular Weight: 262.73

The \((E)-1\)-(2-chloro-6-fluorostyryl)naphthalene (0.285 g, 1.0 mmol) was dissolve in acetonitrile (100 mL) in a quartz reaction vessel (25mm diameter x 40cm length), degassed with nitrogen and irradiated with a 450W Hanovia lamp equipped with Vycor filter and quartz cooling probe. After 35 hours, GC-MS showed that the starting material was consumed.

Column chromatography (eluent: hexanes), cannot separate the two products. White crystals of a mixture (0.163 g) were obtained as final product. By GC-MS, the integration area ratio of 1-fluorochrysene (GCMS \( \text{m/z}: 246.14 \): 1-chlorochrysene (GCMS \( \text{m/z}: 262.07 \) is approximately 1:1.4. The average MW is about 255.88. Yields: 1-fluorochrysene: 27 %; 1-chlorochrysene: 37 %.
1-fluorochrysene (3.16.1b) & 1-bromochrysene (3.16.2b)

The \((E)-1-(2\text{-bromo-6-fluorostyryl})\text{naphthalene (0.329 g, 1.0 mmol) was dissolved in acetonitrile (100 mL in a quartz reaction vessel (25mm diameter x 40cm length), degassed with nitrogen and then irradiated with a Hanovia UV lamps in a quartz probe with Vycor filter. After 40 hours, GC-MS showed that the starting material was consumed.}

Column chromatography (eluent: hexanes), cannot separate the two products. White crystals (0.116 g) of a mixture were obtained as final product. Composition of the mixture was determined by GC-MS; the integration area ratio of 1-fluorochrysene (GCMS (m/z): 247.13): 1-bromochrysene (GCMS (m/z): 306.03) is about 1.7:1. The average MW is about 268.84. Yields: 1-fluorochrysene: 27 %; 1-bromochrysene 16 %.
A quartz tube (25mm diameter x 40cm length) was charged with 2-chloro-6-fluoro-1,1':2',1'-terphenyl (0.296 g, 1.0 mmol) and acetonitrile (100 mL). The solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps and the reaction progress was followed by GC-MS. After 6 hours, GC-MS indicated that the starting material was nearly completely consumed. The solvent was removed by rotary evaporation, giving a tan residue (0.236 g) as crude product. The residue was then dissolved in ethyl acetate (approximately 25 mL) and mixed with silica gel (approximately 2 g). After concentration to dryness, the tan powder was placed at the top of a silica gel column and eluted (eluent: hexanes). Fractions containing the product were combined and concentrated to give white crystals of a mixture (0.187g) as final product.

According to the result of GC-MS, the integration area ratio of 1-fluorotriphenylene (GCMS (m/z): 246.13): 1-chlorotriphenylene (GCMS (m/z): 262.09) is about 2.3:1. The average MW is about 251.26. Yields: 1-fluorotriphenylene 52 %, 1-chlorotriphenylene 23 %.
A quartz tube (approximately 40 cm x 25 mm) was charged with 2-bromo-6-fluoro-1,1':2',1""-terphenyl (0.258 g, 0.8 mmol) and acetonitrile (80 mL). The solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps and the reaction progress was followed by GC-MS. After 6 hours, GC-MS indicated that the starting material was nearly completely consumed. The solvent was removed by rotary evaporation, giving a tan residue (0.208 g) as crude product. The residue was then dissolved in ethyl acetate (approximately 25 mL) again and charged with silica gel (approximately 2 g). After concentration to dryness, the tan powder was placed at the top of a silica gel column and eluted (eluent: hexanes). Fractions containing the product were combined and concentrated to give white crystals (0.171g) as final product.

According to GC-MS, the integration ratio of 1-fluorotriphenylene (GCMS (m/z): 246.03): 1-bromotriphenylene (GCMS (m/z): 305.99) is about 5.5:1. The average MW is about 255.65. Yields: 1-fluorotriphenylene 55 %, 1-bromotriphenylene 10%.
3.6. References


(38) Bond Lengths and Energies, http://www.science.uwaterloo.ca/~cchieh/cact/c120/bondel.html

(39) Knoevenagel, E. Berichte der deutschen chemischen Gesellschaft 1898, 31, 2596.


Chapter Four - The synthesis of the 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene backbone and its derivatives

4.1. Synthesis of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene

With the photocyclodehydrofluorination (PCDHF) technique in hand, it should be possible to prepare the ideal 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene compound which might give us the desirable phenyl-perfluorophenyl cofacial stacking.

![Figure 4.1 The structure of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene.](image)

The total synthesis resembles that of 1,4-bis(pentafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene already described. With the treatment of iodine in concentrated sulfuric acid and heating, 1,4-dibromobenzene (4.1) is easily converted to 1,4-dibromo-2,5-diiodobenzene (4.2). Initially, we attempted to react 1,4-dibromo-2,5-diiodobenzene (4.2) with phenylboronic acid under Suzuki conditions, hoping to obtain 2',5'-dibromo-1,1':4',1''-terphenyl as product. However, even after multiple attempts, this reaction did not proceed at all. We then switched to another route and performed the copper mediated decarboxylative coupling of potassium pentafluorobenzoate first. By using an excess amount (more than 2 eq.) of potassium
pentafluorobenzoate, both iodine atoms could be substituted to give 2',5'-dibromo-2,2",3,3",4,4",5,5",6,6"-decafluoro-1,1':4',1"-terphenyl (4.3) in 67 % yield. At this stage, the two remaining bromine atoms were able to undergo Suzuki coupling with phenylboronic acid to yield 2',5'-is(perfluorophenyl)-1,1':4',1"-terphenyl (4.4) in as high as 70 % yield.

Although 2',5'-bis(perfluorophenyl)-1,1':4',1"-terphenyl was not the final product which we are interested in, we still obtained an X-ray crystallography analysis on it. In its crystal packing, we were able to observe C-F···H interactions, Cπ···CπF interactions and also F···F interactions. Here, according to the discussion in Chapter One, the F···F interactions in this crystal packing is just a kind of result of continuously crystal packing.
Figure 4.2 Crystal packing of 2',5'-bis(perfluorophenyl)-1,1':4',1''-terphenyl (4.4).
With 2',5'-bis(perfluorophenyl)-1,1':4',1''-terphenyl (4.4) in hand it was only two sequential
photochemical (PCDHF) steps to our desired final product 1,2,3,4,10,11,12,13-
octafluorotribenzo[\textit{f,k,m}]tetraphene. Unfortunately, another crucial problem emerged at this point
- 2',5'-bis(perfluorophenyl)-1,1':4',1''-terphenyl (4.4) had very poor solubility in our commonly
used irradiation solvent acetonitrile (this might occur if the molecule of the precursor has a large
and symmetric structure). To overcome this issue, we tried toluene as the solvent as it offered good
result in the dual PCDHF of 1,4-bis((E)-2-(perfluorophenyl)vinyl)naphthalene (3.1g – 2.2g).
However, the miracle did not repeat this time. Only a sticky tan residue was obtained after
removing the solvent from irradiation of 2',5'-bis(perfluorophenyl)-1,1':4',1''-terphenyl and the
efforts to isolate the desired product via silica gel column chromatography also ended in failure.

![Scheme 4.2 The PCDHF of 2',5'-bis(perfluorophenyl)-1,1':4',1''-terphenyl failed when using toluene as solvent.](image)

To overcome the solubility issue, we temporarily gave up testing different solvents and instead
switched to another synthetic route. This time, we tried to obtain a new precursor
2,3,4,5,6,2''',3''',4''',5''',6'''-octafluoro-1,1':2',1'':4'',1'''':2''',1'''''-quinquephenyl for PCDHF, hoping
it might have a much better solubility.
Scheme 4.3 Alternative route to get access to 1,2,3,4,10,11,12,13-octafluorotribenzo[\(f,k,m\)]tetraphene.

Starting from the readily available 1,4-dibromobenzene (4.1), treatment with an excess amount of magnesium powder in anhydrous THF provides the double Grignard reagent, which could be trapped with trimethylborate followed by acid workup to yield benzene-1,4-diboronic acid (4.6). The other component needed was prepared by carefully controlling the amount of potassium pentafluorobenzoate and reaction temperature in reaction with 1-bromo-2-iodobenzene (4.7). Under the right conditions 2'-bromo-2,3,4,5,6-pentafluoro-1,1'-biphenyl (4.8) could be prepared in good yield. Finally, this 2'-bromo-2,3,4,5,6-pentafluoro-1,1'-biphenyl (4.8) was reacted with benzene-1,4-diboronic acid (4.6) in a 2:1 ratio (double Suzuki coupling reaction) to provide the intermediate 2,3,4,5,6,2'''',3''''',4''''',5''''',6'''''-decafluoro-1,1':2',1''':4'',1'''':2''',1'''''-quinquephenyl (4.9).
Scheme 4.4 Synthesis of 2,3,4,5,6,2'''',3'''',4'''',5'''',6''''-octafluoro-1,1':2',1''':4'',1'''':2''',1''''-quinquephenyl

The 2,3,4,5,6,2'''',3'''',4'''',5'''',6''''-octafluoro-1,1':2',1''':4'',1'''':2''',1''''-quinquephenyl (4.9) obtained indeed was more soluble and dissolved well in acetonitrile. During irradiation, some white powder precipitated out of the solution due to its lower solubility in acetonitrile. It was then filtered directly and air-dried. $^{19}$F-NMR analysis of this sample (refer to the figure below) showed that the PCDHF reaction did occur this time, however, seven peaks with total integration of 9 on $^{19}$F-NMR spectra gave us a hint that only one ring was closed. As the dual ring closure was a step by step process, after the first single ring closure was done, the product 1,2,3,4-tetrafluoro-6-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)triphenylene (4.10) precipitates out of the solution due to poor solubility, which hindered the further process of PCDHF.
Figure 4.3 $^{19}$F-NMR analysis of single ring closure product 1,2,3,4-tetrafluoro-6-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)triphenylene (4.10). The four smaller peaks (integration area ratio about 1:1:1:1) are the fluorine atoms on the tetrafluorobenzene ring where PCDHF occurred; the three larger peaks (integration area ratio about 2:1:2) are the fluorine atoms on the pentafluorobenzene ring where PCDHF did not occur.
For a long time, we were unable to find an appropriate single solvent to dissolve 1,2,3,4-tetrafluoro-6-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)triphenylene (4.10) and finish the second PCDHF ring closure. Because of this, a co-solvent became a reasonable consideration at this point – THF is a very popular solvent in various organic syntheses and it often has acceptable solvent power for polycyclic aromatic hydrocarbons, however, it seemed not to be a good choice for PCDHF as it might extend the reaction time and give lower the yield (Refer to the PCDHF chapter). With the consideration of both factors, we mixed THF and acetonitrile in a 1:1 ratio and this solvent mixture successfully dissolved the single ring closure intermediate 1,2,3,4-tetrafluoro-6-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)triphenylene (4.10). The irradiation of this solution led to another white precipitate out of this solution. This phenomenon hinted that we should have already obtained our desired product 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene (4.5) as the lower solubility compared to 1,2,3,4-tetrafluoro-6-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)triphenylene (4.10) implied an ever larger polycyclic aromatic hydrocarbon had been formed.

The 1:1 mixture of THF and acetonitrile could dissolve the single ring closure intermediate and precipitate the dual ring closure final product. For this reason, we also dissolved 2,3,4,5,6,2'''',3'''',4'''',5'''',6''''-octafluoro-1,1':2',1''':4'',1':2'',1''''-quinquephenyl (4.9) to try a one pot photochemical reaction. This action did proceed smoothly and led to a much higher yield than the previous two-step irradiation.
By using the same mixture of solvents (THF:Acetonitrile = 1:1), we backtracked and used it for the PCDHF of 2',5'-bis(perfluorophenyl)-1,1':4',1''-terphenyl (4.4) again. This time, the precursor successfully dissolved and precipitated a white powder after irradiation. Further investigation demonstrated that it was also 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene (4.5).

The characterization of this compound was also a challenge – the bad solubility made it impossible to find an appropriate solvent to perform regular NMR analysis. Finally, thanks to the HRMS analysis from Prof. Shelley et al., we were able to know the molecular weight of this compound is 522.06539, which was nearly identical as the calculation result (the highest MS peak of compound
4.5 is 522.06539.

ZL02009-C30F10H12 #28 RT: 0.24  AV: 1  NL: 1.27E8
T: FTMS + p ESI Full ms [50.00-750.00]

\[
\begin{align*}
\text{ZL02009} & \\
\text{C}_{30}H_{12}F_{10} & \\
M^+_{\text{calc}} & = 562.07738 \\
M^+_{\text{meas}} & = 562.07782 \\
\Delta & = 0.436 \text{ mmu}
\end{align*}
\]
Finally, we have to face a frustrating fact - although it can be concluded that we already obtained 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetrabene (4.5), its large polycyclic aromatic structure (and anticipated cofacial molecular packing) lead to extremely poor solubility. This did not only give difficulty in NMR characterization, but also make it hard to find an appropriate
solvent to perform a recrystallization. Up to now, we have not obtained the crystal structure of this compound as all the solvents (eg. THF, benzene, toluene, xylene, nitrobenzene and chlorobenzene) we tried for recrystallization just provided white powder instead of X-ray quality crystals.

4.2. Derivatives of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene with alkoxy groups

In the last section, we discovered that 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene (4.5) has a very poor solubility in variety of solvents, which was caused by its large polycyclic aromatic structure. This led to the failure to obtain single crystals for X-ray crystallography using traditional recrystallization techniques. Although 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene (4.5) might exactly exhibit the short distance aryl – perfluoroaryl stacking we expect, it has been impossible for us to (so far) prove this hypothesis with a single crystal structure.

So, at least to skirt this problem, we designed some derivatives of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene (4.5) in which some alkoxy groups were installed on the rings, hoping this modification would enhance the solubility of these compounds.

In order to accomplish this we were able to use the intermediate 2',5'-dibromo-2,2'',3,3'',4,4'',5,5'',6,6''-decafluoro-1,1':4',1''-terphenyl (4.3) obtained previously. Here, a simple switch from phenylboronic acid was made to p-methoxyphenyl boronic acid, leading to the 2,3,4,5,6-pentafluoro-4''-methoxy-5'-(4-methoxyphenyl)-4'-(perfluorophenyl)-1,1':2',1''-terphenyl (4.11) after Suzuki coupling. As before, this compound was dissolved into the 1:1 mixture of THF
and acetonitrile and irradiated, yielding 30% of the dual cyclization product 1,2,3,4,10,11,12,13-octafluoro-6,15-dimethoxytribenzo[f,k,m]tetraphene (4.12).

Also, a S_{\text{NAr}} reaction of 2,3,4,5,6-pentafluoro-4''-methoxy-5'-(4-methoxyphenyl)-4'- (perfluorophenyl)-1,1':2',1''-terphenyl (4.11) was tried in methanol in the presence of potassium tert-butoxide. This reaction substitutes the para- position fluorine atoms with methoxy groups to give another precursor 2,3,5,6-tetrafluoro-4,4''-dimethoxy-5'- (4-methoxyphenyl)-4'-(2,3,5,6-tetrafluoro-4-methoxyphenyl)-1,1':2',1''-terphenyl (4.13) for PCDHF. Still using the same conditions to perform the PCDHF process on (4.13), an 11% yield of the final product 1,2,4,10,11,13-hexafluoro-3,6,12,15-tetramethoxytribenzo[f,k,m]tetraphene (4.14) was obtained.

The methoxy substituted compounds (4.12) and (4.14) provided better solubility than the parent system 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene (4.5). Thanks to the help of Prof. Ellman from the Physics Department, by using a nonconventional solvent 1-methoxynaphthalene, some single crystals of 1,2,3,4,10,11,12,13-octafluoro-6,15-dimethoxytribenzo[f,k,m]tetraphene (4.12) were successfully obtained and the crystal packing was finally determined.
Scheme 4.7 The synthesis of 1,2,3,4,10,11,12,13-octafluoro-6,15-dimethoxytribenzo[f,k,m]tetraphene.

In fact, in this series of compounds, 1,2,3,4,10,11,12,13-octafluoro-6,15-dimethoxytribenzo[f,k,m]tetraphene (4.12) is the only compound that has a successfully crystal structure determination thus far. The flat molecule performs the desired aryl – perfluoroaryl stacking in a distance at about 3.3 Å (Figure 4.5).
Figure 4.5: The crystal packing of 1,2,3,4,10,11,12,13-octafluoro-6,15-dimethoxytribenzo[f,k,m]tetr phen e, the aryl–per fluoroaryl stacking distance is about 3.3 Å.

Given the initial success with compound series with methoxy substituents we again started from 2',5'-dibromo-2,2",3,3",4,4",5,5",6,6"-decafluoro-1,1':4',1"'-terphenyl (4.3), but this time did the Suzuki coupling with 4-n-hexyloxyphenylboronic acid. As intended, we were able to obtain 2,3,4,5,6-pentafluoro-4"-(hexyloxy)-5'-(4-(hexyloxy)phenyl)-4'-(perfluorophenyl)-1,1':2',1"'-terphenyl (4.15). Direct PCDHF of this compound in a 1:1 mixture of THF/acetonitrile led to 1,2,3,4,10,11,12,13-octafluoro-6,15-bis(hexyloxy)tribenzo[f,k,m]tetr phen e (4.16) with a yield as high as 76%. As in the case of the methoxy substituted compounds, reaction this time in n-hexanol with t-BuOK now substitutes two n-hexyloxy groups at the position of the para-fluorine atoms to yield 2,3,5,6-tetrafluoro-4,4"-bis(hexyloxy)-5'-(4-(hexyloxy)phenyl)-4'-(2,3,5,6-tetrafluoro-4-(hexyloxy)phenyl)-1,1':2',1"'-terphenyl (4.17). A subsequent PCDHF process also eliminates 2 HF as expected to yield 1,2,4,10,11,13-hexafluoro-3,6,12,15-tetrakis(hexyloxy)tribenzo[f,k,m]tetr phen e (4.18). In the case of these hexyloxy derivatives unfortunately no crystal structures have been obtained thus far for these two compounds. However, it is worth noting that 1,2,4,10,11,13-hexafluoro-3,6,12,15-tetrakis(hexyloxy)tribenzo[f,k,m]tetr phen e (4.18) appears to be a discotic liquid crystal as the
appropriate texture could be observed by polarized optical microscopy (POM) (Figure 4.6 and 4.7).

Scheme 4.8 Synthesis of 1,2,3,4,10,11,12,13-octafluoro-6,15-bis(hexyloxy)tribenzo[f,k,m]tetraphene (4.16) and 1,2,4,10,11,13-hexafluoro-3,6,12,15-tetrakis(hexyloxy)tribenzo[f,k,m]tetraphene (4.18).
Aside of the simple methoxy and long carbon chain hexyloxy derivatives, we also obtained the tert-butyl derivative 6,15-di-tert-butyl-1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene (4.20) just by changing the boronic acid to 4-tert-butylphenylboronic acid in the Suzuki reaction step.
Another attempt here is that we designed a molecule 1,2,4,10,11,13-hexafluoro-3,12-dimethoxy-6,15-bis(trifluoromethoxy)tribenzo[f,k,m]tetraphene. The S_N_Ar reaction of 2',5'-dibromo-2',3',4',5',6',6'-decafluoro-1,1':4',1''-terphenyl (4.3) could efficiently put two methoxy groups on the positions of the para-fluorine atoms. The Suzuki coupling was also able to deliver compound 4.22 in a 90% yield. However, the final PCDHF did not work well and only gave a trace amount of product 4.23 which was not enough for further investigation.

**Scheme 4.9** Synthesis of 6,15-di-tert-butyl-1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene (4.20).

**Scheme 4.10** The attempt to prepare the dimethoxy bis-trifluoromethoxy compound.
4.3. Derivatives of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene with thiophene rings

All the examples discussed above are compounds only constituted with benzene rings while the next example contains two thiophene rings. The plan of this design is similar as before – the thiophene ring is much more electron rich than an ordinary benzene ring, which might promote closer aryl-perfluoroaryl molecule stacking (however, the sulfur atom is larger which may inhibit closer packing).

Still using the same starting material as before, the Suzuki coupling with 1-thiopheneboronic acid gave 2,2'-(2,2",3,3",4,4",5,5",6,6"-decafluoro-[1,1':4',1"-terphenyl]-2',5'-diyl)dithiophene (4.24) and the following PCDHF proceeded smoothly in the mixed solvent (THF/acetonitrile = 1:1) to precipitate out 4,5,6,7,12,13,14,15-octafluorobenzo[8,9]tetrapheno[6,5-b:11,10-b']dithiophene (4.25) as product (Scheme 4.11).

![Scheme 4.11](image)

Here, we were able to get the crystal structure of compound 4.24. Although the chemical structure of 4.24 is just a modified version of 4.4 (by changing the non-fluorinated benzene side rings to thiophene rings), it shows a much more complicated crystal packing compared to 4.4. The crystal system is orthorhombic and the space group is Pbca. Each crystal lattice contains 4 molecules of
4.24 (instead of 2 units in 4.4) and they feature C-F···πF and H···F interactions.

The recrystallization of compound 4.25 from toluene did provide tiny yellow needles. However, they are still way too small to subject to an X-ray crystallography and thus a structure is not available yet.
Figure 4.8 Crystal packing of 2,2'-{2,2'',3,3'',4,4'',5,5'',6,6''-decafluoro-[1,1':4',1''-terphenyl]-2',5'-diyl)dithiophene (4.24)
Figure 4.9 HRMS of 2,2''-(2,2'',3,3'',4,4'',5,5'',6,6''-decafluoro-[1,1'-4',1''-terphenyl]-2',5'-diyl)dithiophene (4.24) and 4,5,6,7,12,13,14,15-octafluorobenzo[8,9][tetrapheno[6,5-b:11,10-b']dithiophene (4.25).
4.4. Summary

In this chapter, we described the successful synthesis of a series of compounds with the core structure of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene as well as the thiophene analogue 4,5,6,7,12,13,14,15-octafluorobenzo[8,9]tetrathieno[6,5-b:11,10-b']dithiophene. Amongst all of these compounds, two of them might be highlighted - the dimethoxy derivative 1,2,3,4,10,11,12,13-octafluoro-6,15-dimethoxytribenzo[f,k,m]tetraphene (4.12) is the only compound that has a crystal structure determination and the tetrahexyloxy compound 1,2,4,10,11,13-hexafluoro-3,6,12,15-tetrakis(hexyloxy)tribenzo[f,k,m]tetraphene (4.18) shows discotic liquid crystal properties. Obviously, the PCDHF reaction has found some utility here in the preparation of materials of interest as organic semiconductors and/or discotic liquid crystals.
4.5. Experimental procedures

**Synthesis of 1,4-dibromo-2,5-bis(pentafluorophenyl)benzene (4.3)**

![Chemical structure of 1,4-dibromo-2,5-bis(pentafluorophenyl)benzene](image)

Chemical Formula: $\text{C}_{18}\text{H}_2\text{Br}_2\text{F}_{10}$  
Molecular Weight: 568.01

A 50 mL flask with magnetic stir bar was charged with 1,4-dibromo-2,5-diiodobenzene (0.976 g, 2.00 mmol), potassium pentafluorobenzoate (1.513 g, 6.05 mmol, 150 %) and copper (I) iodide (0.152 g, 0.800 mmol). The system was thoroughly flushed with nitrogen and diglyme (2 mL) was added via a syringe. The mixture obtained was stirring under room temperature for about 10 min and then gradually warmed and maintained at $130^\circ$ C for 24 hours. During this time, the color of the mixture changed from white to dark gray. Next, the mixture was cooled to room temperature and the dark brown residue was diluted with ethyl acetate (25 mL) and absorbed on silica gel. The solvent was removed by rotary evaporation and the absorbed material was subjected to column chromatography (eluent: Hexane). The final pure product was obtained as white crystals (0.707 g, 1.24 mmol, 62 % yield).

**M.P.:** 209.0 – 211.0 °C

$^1\text{H-NMR (400 MHz, CDCl}_3\text{):}$ 7.676 (s, 2H).

$^{13}\text{C-NMR (100 MHz, CDCl}_3\text{):}$ 144.201 (d, $J = 248$ Hz), 141.980 (d, $J = 255$ Hz), 137.948 (d, $J = 253$ Hz), 136.198, 131.265, 123.476, 113.359 (t, $J = 14.5$ Hz).

$^{19}\text{F-NMR (376 MHz, CDCl}_3\text{):}$ -138.88 (dd, $^1J = 24.0$ Hz, $^2J = 9.4$ Hz, 2F), -152.01 (t, $J = 20.7$ Hz, 1F), -160.87- -161.02 (m, 2F).
Synthesis of 1,4-bis(pentafluorophenyl)-2,5-diphenylbenzene (4.4)

![Chemical structure of the compound](image)

Chemical Formula: C$_{30}$H$_{12}$F$_{10}$
Molecular Weight: 562.41

A 100 mL flask with a stir bar, condenser and nitrogen inlet was charged with 1,4-dibromo-2,5-bis(pentafluorophenyl)benzene (0.566 g, 1.00 mmol), phenylboronic acid (0.488 g, 4.00 mmol, 200%), toluene (16 mL) and ethanol (4 mL). After this, potassium carbonate (0.555 g, 4.01 mmol, 200%) was added and the flask was thoroughly flushed with nitrogen. The flask was placed in a 90 °C oil bath and tetrakis(triphenylphosphine)palladium(0) (23.016 mg, 0.020 mmol, 1%) was added and the mixture was gently refluxed overnight. The next day the mixture was cooled down and the solvent was removed under vacuum. The residue was diluted with EtOAc (100 mL) and extracted by water (3 x 50 mL). The organic phase was dried with anhydrous MgSO$_4$ and silica gel was added to absorb the product. After the solvent was removed, the yellow powder placed at the top of a chromatography column and the compound was eluted with hot toluene. Fractions containing pure product were combined and concentrate to give the produce as white crystals (0.105 g, 0.187 mmol, 18.7% yield) as product.

The same reaction was repeated again for a much higher yield.
A 100 mL flask with a stir bar, condenser and nitrogen inlet was charged with 1,4-dibromo-2,5-bis(pentafluorophenyl)benzene (1.137 g, 2.00 mmol), phenylboronic acid (0.978 g, 8.00 mmol, 200%), toluene (32 mL) and ethanol (8 mL). After this, potassium carbonate (1.111 g, 8.04 mmol, 200%) was added and the flask was thoroughly flushed with nitrogen. The flask was placed in a 90 °C oil bath and tetrakis(triphenylphosphine)palladium(0) (46.750 mg, 0.040 mmol, 1%) was added at last and the mixture was gently refluxed overnight. The next day the mixture was cooled to room temperature and silica gel was added inside directly to absorb the product. After the solvent was removed by rotary evaporation, the resulting yellow powder was placed at the top of a chromatography column and the compound was eluted with hot toluene. Fractions containing pure product were combined and concentrate to give the produce as white crystals (0.790 g, 1.40 mmol, 70 % yield) as product.

Tried this reaction for a second time, every steps were nearly the same as before. The only dif the resulting mixture of Suzuki coupling was given a column chromatography directly via hot toluene (the old trick in the synthesis of 1,4-bis(2’,3’,4’,5’,6’-pentafluorophenylethynyl)-2,5-bis(phenylethynyl)benzene (2.9d)).

**Obtained data for the product:**

**MP:** Sublimated (possibly decomposed – yellow residue was observed on the slide after the test) at around 245-255 °C.

**$^1$H-NMR (400 MHz, 1,1,2,2-Tetrachloroethane-d$_2$):** 7.542 (br, 2H), 7.347 (br, 6H), 7.277 (br, 4H).

**$^{13}$C-NMR (100 MHz, 1,1,2,2-Tetrachloroethane-d$_2$):** 144.040 (d, $J = 246$ Hz), 142.159, 140.762
(d, J = 255 Hz), 138.990, 137.438 (d, J = 251 Hz), 132.752, 128.241, 128.087, 127.689, 126.426, 115.063 (t, J = 15.6 Hz).

$^{19}$F-NMR (376 MHz, 1,1,2,2-Tetrachloroethane-d$_2$): -139.02 (d, J = 18.8 Hz, 2F), -154.31 (t, J = 18.8 Hz, 1F), -161.88 (br, 2F).

1,4-benzenediboronic acid (4.6)

$\begin{array}{c}
\text{B(OH)}_2 \\
\text{B(OH)}_2 \\
\end{array}$

Chemical Formula: C$_6$H$_8$B$_2$O$_4$

Molecular Weight: 165.75

In an oven dried 250 mL flask, under the protection of nitrogen, a solution of 1,4-dibromobenzene (11.800 g, 50.0 mmol) in THF (75 mL) was added to magnesium turnings (2.512 g, ~ 0.1 mol) in THF (25 mL). Once initiation happens, the exothermic reaction heated the mixture to reflux itself. As the reaction proceeded, the mixture would become cloudy. After the spontaneous reflux subsided, the mixture was refluxed again for another 12 hours while heating in an oil bath.

This Grignard Reagent solution was added dropwise to a solution of trimethyl borate (10.507 g, ~ 0.1 mmol) in THF (20 mL) at –78 °C. The mixture was stirred for 2 hours, then the temperature was gradually raised up to room temperature and stirred at this temperature for 2 days.

The mixture was poured into a stirred mixture of crushed ice (~ 250 g) and concentrated HCl (~
10 mL). After all the ice was melted, diethyl ether (3 x 150 mL) was used for extraction. The organic layers were combined and dried by MgSO₄. The solvent was removed under vacuum to give the product as a tan powder (6.137 g, 37 mmol, 74 % yield).

No characterization data for this compound, the obtained boronic acid was just used directly in the next step.

2,3,4,5,6,2'''',3'''',4'''',5'''',6''''-octafluoro-1,1':2',1''':4'',1'''':2'',1''''-quinquephenyl (4.9)

A 100 mL 2-neck flask fitted with magnetic stir bar, condenser and nitrogen inlet was charged with 2’-bromo-2,3,4,5,6-pentafluorobiphenyl (2.433 g, 7.5 mmol) and 1,4-benzenediboronic acid (0.500 g, 3.0 mmol). Toluene (24 mL) and ethanol (6 mL) were the added and under the protection of nitrogen, the mixture was stirred to achieve a solution. After that, potassium carbonate (0.831 g, 6.0 mmol) was added and the mixture was placed in a 90°C oil bath. Tetrakis(triphenylphosphine)palladium(0) (69.194 mg, 0.040 mmol, 1%) was added. And the mixture was heated at gently reflux for 24 hours

After this time the mixture was cooled down. Silica gel (~ 10 g) was added to absorb the product
and the solvent was removed via rotary evaporation. The gray powder obtained was placed on the top of silica gel column and eluted first with hexane to remove the unreacted 2’-bromo-2,3,4,5,6-pentafluorobiphenyl, then used hexane : DCM = 2:1 mixture to wash off the product). The second band was collected and gave the product as tiny white crystals (1.185 g, 2.1 mmol, 70 % yield)

Data:

M.P. 226.5 – 229.5 °C

$^1$H-NMR (400 MHz, CDCl$_3$): 7.563 – 7.522 (m, 2H), 7.495-7.442 (m, 4H), 7.338 – 7.317 (m, 2H), 7.046 (s, 4H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): 143.998 (d, $J = 245$ Hz), 142.286, 140.578 (d, $J = 251$ Hz), 139.485, 137.410 (d, $J = 251$ Hz), 131.245, 130.351, 129.822, 128.330, 127.641, 124.843, 115.719 (t, $J = 18$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$): -140.390 (dd, $^1J = 23.1$ Hz, $^2J = 8.5$ Hz, 4F), -155.310 (t, $J = 19.0$ Hz, 2F), -162.503 - -162.626 (m, 4F)

1,4-bis(pentafluorophenyl)-2,5-bis(p-methoxyphenyl)benzene (4.11)

![Chemical Structure](image)

Chemical Formula: C$_{32}$H$_{18}$F$_{10}$O$_2$

Molecular Weight: 622.46

A 100 mL 2-neck flask, was charged with1,4-dibromo-2,5-bis(pentafluorophenyl)benzene (1.136
g, 2.0 mmol), 4-methoxyphenylboronic acid (1.220 g, 8.0 mmol, 2.0 eq) and solvent (toluene 16 mL/ EtOH 4mL). Stirring was performed to help dissolve the solid. Potassium carbonate (1.115 g, 8.0 mmol, 2.0 eq) was added and the mixture was heated up to 90 °C with oil bath and tetrakis(triphenylphosphine)palladium(0) (46.283 mg, 0.040 mmol, 1%) was added. The mixture was stirred at 90 °C under N₂ protection for 12 hours and TLC indicated that no starting materials were left. The mixture was cooled to room temperature and silica gel was added to absorb the product and the solvent was removed under vacuum. The yellow powder obtained was placed at the top of a column and eluted (first to wash off some impurities via hexane and then to wash off the product with hot toluene). The product was isolated as a snow-white powder (1.090 g, 1.75 mmol, 88% yield).

**MP:** 264.5 – 269.0 °C.

**¹H-NMR (400 MHz, 1,1,2,2-Tetrachloroethane-D₂):** 7.456 (s, 2H), 7.130 (d, J = 8.8 Hz, 4H), 6.841 (d, J = 8.8 Hz, 4H), 3.808 (s, 6H).

**¹³C-NMR (100 MHz, 1,1,2,2-Tetrachloroethane-D₂):** 158.931, 143.830 (d, J = 252.9 Hz), 141.105, 140.520 (d, J = 252.4 Hz), 137.281 (d, J = 260.2 Hz), 132.916, 131.255, 129.521, 126.112, 115.048, 113.751, 55.240.

**¹⁹F-NMR (376 MHz, 1,1,2,2-Tetrachloroethane-D₂):** -139.172 (dd, ¹J = 22.6 Hz, ²J = 7.9 Hz, 2F), -154.416 (t, J = 18.4 Hz, 1F), -161.727 (br, 2F).
A quartz vessel (approx. 40cm x 25mm) was charged with 2,3,4,5,6-pentafluoro-4''-methoxy-5'- (4-methoxyphenyl)-4'-(perfluorophenyl)-1,1':2',1"-terphenyl (0.310 g, 0.5 mmol), acetonitrile (50 mL) and THF (50 mL). The colorless solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps. After 9 hours of irradiation a yellow solid precipitated out of solution. The suspension was cooled and the solid was filtered and air-dried (0.085 g, 0.15 mmol, 30 % yield).

Due to its bad solubility in common deuterated solvents, only X-ray crystallography was accomplished as the characterization.
**Table 1.** Crystal data and structure refinement for compound 4.12.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>4.12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C\textsubscript{32}H\textsubscript{14}F\textsubscript{8}O\textsubscript{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>582.43</td>
</tr>
<tr>
<td>Temperature</td>
<td>105(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, P-1</td>
</tr>
</tbody>
</table>
| Unit cell dimensions| a = 4.545(3) Å, alpha = 100.98(2) deg.  
b = 7.979(7) Å, beta = 93.248(18) deg.  
c = 16.030(13) Å, gamma = 100.53(2) deg. |
| Volume              | 558.5(8) Å\textsuperscript{3} |
Z, Calculated density                                    1, 1.732 Mg/m^3
Absorption coefficient                                    0.153 mm^-1
F(000)                                                     294
Crystal size                                               0.200 x 0.050 x 0.050 mm
Theta range for data collection                          1.300 to 25.047 deg.
Limiting indices                                          -5<=h<=5, -9<=k<=9, -19<=l<=19
Reflections collected / unique                           8260 / 1980 [R(int) = 0.1322]
Completeness to theta = 25.047                            100.0 %
Absorption correction                                     Semi-empirical from equivalents
Refinement method                                         Full-matrix least-squares on F^2
Data / restraints / parameters                            1980 / 0 / 190
Goodness-of-fit on F^2                                    0.948
Final R indices [I>2sigma(I)]                            R1 = 0.0699, wR2 = 0.1535
R indices (all data)                                      R1 = 0.1663, wR2 = 0.2131
Extinction coefficient                                    n/a
Largest diff. peak and hole                               0.287 and -0.370 e.A^-3
Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for 4.12.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>3049(7)</td>
<td>6115(4)</td>
<td>9720(2)</td>
<td>32(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>-398(7)</td>
<td>3804(4)</td>
<td>8528(2)</td>
<td>32(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>631(7)</td>
<td>3573(4)</td>
<td>6857(2)</td>
<td>36(1)</td>
</tr>
<tr>
<td>F(4)</td>
<td>5157(7)</td>
<td>5546(4)</td>
<td>6404(2)</td>
<td>37(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>13244(9)</td>
<td>9281(5)</td>
<td>5725(2)</td>
<td>41(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>12279(12)</td>
<td>11130(7)</td>
<td>9750(3)</td>
<td>27(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>10508(12)</td>
<td>9795(7)</td>
<td>9128(3)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>8160(12)</td>
<td>8639(7)</td>
<td>9381(3)</td>
<td>21(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>6245(12)</td>
<td>7263(7)</td>
<td>8723(3)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>3836(12)</td>
<td>6100(7)</td>
<td>8909(3)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>1949(12)</td>
<td>4855(7)</td>
<td>8316(3)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>2504(12)</td>
<td>4732(7)</td>
<td>7468(3)</td>
<td>28(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>4865(13)</td>
<td>5819(7)</td>
<td>7257(3)</td>
<td>29(2)</td>
</tr>
<tr>
<td>C(9)</td>
<td>6841(12)</td>
<td>7116(7)</td>
<td>7840(3)</td>
<td>26(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>9352(12)</td>
<td>8311(7)</td>
<td>7594(3)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>10063(12)</td>
<td>8210(7)</td>
<td>6742(3)</td>
<td>29(2)</td>
</tr>
<tr>
<td>C(12)</td>
<td>12419(12)</td>
<td>9328(7)</td>
<td>6544(3)</td>
<td>27(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>14215(13)</td>
<td>10587(7)</td>
<td>7161(3)</td>
<td>30(2)</td>
</tr>
<tr>
<td>C(14)</td>
<td>13566(12)</td>
<td>10740(7)</td>
<td>7989(3)</td>
<td>28(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>11153(12)</td>
<td>9617(7)</td>
<td>8235(3)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>11505(15)</td>
<td>8001(9)</td>
<td>5051(3)</td>
<td>51(2)</td>
</tr>
</tbody>
</table>
Table 3. Bond lengths [Å] and angles [deg] for 4.12.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)-C(5)</td>
<td>1.366(5)</td>
</tr>
<tr>
<td>F(2)-C(6)</td>
<td>1.334(6)</td>
</tr>
<tr>
<td>F(3)-C(7)</td>
<td>1.346(6)</td>
</tr>
<tr>
<td>F(4)-C(8)</td>
<td>1.361(6)</td>
</tr>
<tr>
<td>O(1)-C(12)</td>
<td>1.381(6)</td>
</tr>
<tr>
<td>O(1)-C(16)</td>
<td>1.422(7)</td>
</tr>
<tr>
<td>C(1)-C(3)#1</td>
<td>1.399(7)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.403(7)</td>
</tr>
<tr>
<td>C(1)-H(1)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.409(7)</td>
</tr>
<tr>
<td>C(2)-C(15)</td>
<td>1.463(7)</td>
</tr>
<tr>
<td>C(3)-C(1)#1</td>
<td>1.399(7)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.477(7)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.385(7)</td>
</tr>
<tr>
<td>C(4)-C(9)</td>
<td>1.444(7)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.364(7)</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.385(7)</td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td>1.353(7)</td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td>1.396(7)</td>
</tr>
<tr>
<td>C(9)-C(10)</td>
<td>1.471(7)</td>
</tr>
<tr>
<td>C(10)-C(11)</td>
<td>1.411(7)</td>
</tr>
<tr>
<td>C(10)-C(15)</td>
<td>1.414(7)</td>
</tr>
<tr>
<td>C(11)-C(12)</td>
<td>1.357(7)</td>
</tr>
<tr>
<td>C(11)-H(11)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(12)-C(13)</td>
<td>1.373(7)</td>
</tr>
<tr>
<td>C(13)-C(14)</td>
<td>1.364(7)</td>
</tr>
<tr>
<td>C(13)-H(13)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(14)-C(15)</td>
<td>1.409(7)</td>
</tr>
<tr>
<td>C(14)-H(14)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(16)-H(16C)</td>
<td>0.9800</td>
</tr>
<tr>
<td>C(16)-H(16A)</td>
<td>0.9800</td>
</tr>
<tr>
<td>C(16)-H(16B)</td>
<td>0.9800</td>
</tr>
<tr>
<td>C(12)-O(1)-C(16)</td>
<td>118.1(4)</td>
</tr>
<tr>
<td>C(3)#1-C(1)-C(2)</td>
<td>122.9(5)</td>
</tr>
<tr>
<td>C(3)#1-C(1)-H(1)</td>
<td>118.6</td>
</tr>
<tr>
<td>C(2)-C(1)-H(1)</td>
<td>118.6</td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>119.0(5)</td>
</tr>
<tr>
<td>C(1)-C(2)-C(15)</td>
<td>119.6(5)</td>
</tr>
<tr>
<td>C(3)-C(2)-C(15)</td>
<td>121.4(5)</td>
</tr>
<tr>
<td>C(1)#1-C(3)-C(2)</td>
<td>118.1(5)</td>
</tr>
<tr>
<td>C(1)#1-C(3)-C(4)</td>
<td>122.9(5)</td>
</tr>
<tr>
<td>Bond</td>
<td>Length (Å)</td>
</tr>
<tr>
<td>----------------------</td>
<td>------------</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)</td>
<td>119.0(5)</td>
</tr>
<tr>
<td>C(5)-C(4)-C(9)</td>
<td>117.5(5)</td>
</tr>
<tr>
<td>C(5)-C(4)-C(3)</td>
<td>123.0(5)</td>
</tr>
<tr>
<td>C(9)-C(4)-C(3)</td>
<td>119.5(5)</td>
</tr>
<tr>
<td>C(6)-C(5)-F(1)</td>
<td>112.4(4)</td>
</tr>
<tr>
<td>C(5)-C(6)-C(7)</td>
<td>117.6(5)</td>
</tr>
<tr>
<td>C(7)-C(8)-F(4)</td>
<td>113.6(5)</td>
</tr>
<tr>
<td>C(7)-C(8)-C(9)</td>
<td>124.6(5)</td>
</tr>
<tr>
<td>C(5)-C(6)-C(7)</td>
<td>120.1(5)</td>
</tr>
<tr>
<td>F(1)-C(5)-C(4)</td>
<td>122.8(5)</td>
</tr>
<tr>
<td>F(2)-C(6)-C(5)</td>
<td>122.3(5)</td>
</tr>
<tr>
<td>F(2)-C(6)-C(7)</td>
<td>124.8(5)</td>
</tr>
<tr>
<td>F(1)-C(5)-C(4)</td>
<td>122.8(5)</td>
</tr>
<tr>
<td>F(2)-C(6)-C(7)</td>
<td>120.1(5)</td>
</tr>
<tr>
<td>C(5)-C(6)-C(7)</td>
<td>117.6(5)</td>
</tr>
<tr>
<td>F(4)-C(8)-C(9)</td>
<td>121.9(5)</td>
</tr>
<tr>
<td>C(8)-C(9)-C(4)</td>
<td>115.8(5)</td>
</tr>
<tr>
<td>C(8)-C(9)-C(10)</td>
<td>123.7(5)</td>
</tr>
<tr>
<td>C(4)-C(9)-C(10)</td>
<td>120.5(5)</td>
</tr>
<tr>
<td>C(11)-C(10)-C(15)</td>
<td>118.2(5)</td>
</tr>
<tr>
<td>C(11)-C(10)-C(9)</td>
<td>122.9(5)</td>
</tr>
<tr>
<td>C(15)-C(10)-C(9)</td>
<td>118.9(5)</td>
</tr>
<tr>
<td>C(12)-C(11)-C(10)</td>
<td>121.0(5)</td>
</tr>
<tr>
<td>C(12)-C(11)-H(11)</td>
<td>119.5</td>
</tr>
<tr>
<td>C(10)-C(11)-H(11)</td>
<td>119.5</td>
</tr>
<tr>
<td>C(11)-C(12)-C(13)</td>
<td>121.5(5)</td>
</tr>
<tr>
<td>C(11)-C(12)-O(1)</td>
<td>123.7(5)</td>
</tr>
<tr>
<td>C(13)-C(12)-O(1)</td>
<td>114.8(5)</td>
</tr>
<tr>
<td>C(14)-C(13)-C(12)</td>
<td>119.0(5)</td>
</tr>
<tr>
<td>C(14)-C(13)-H(13)</td>
<td>120.5</td>
</tr>
<tr>
<td>C(12)-C(13)-H(13)</td>
<td>120.5</td>
</tr>
<tr>
<td>C(13)-C(14)-C(15)</td>
<td>122.1(5)</td>
</tr>
<tr>
<td>C(13)-C(14)-H(14)</td>
<td>119.0</td>
</tr>
<tr>
<td>C(15)-C(14)-H(14)</td>
<td>119.0</td>
</tr>
<tr>
<td>C(14)-C(15)-C(10)</td>
<td>118.2(5)</td>
</tr>
<tr>
<td>C(14)-C(15)-C(2)</td>
<td>121.2(5)</td>
</tr>
<tr>
<td>C(10)-C(15)-C(2)</td>
<td>120.6(5)</td>
</tr>
<tr>
<td>O(1)-C(16)-H(16C)</td>
<td>109.5</td>
</tr>
<tr>
<td>O(1)-C(16)-H(16A)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(16C)-C(16)-H(16A)</td>
<td>109.5</td>
</tr>
<tr>
<td>O(1)-C(16)-H(16B)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(16C)-C(16)-H(16B)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(16A)-C(16)-H(16B)</td>
<td>109.5</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:
Table 4. Anisotropic displacement parameters (Å^2 x 10^3) for 4.12.
The anisotropic displacement factor exponent takes the form:
\[-2 \pi^2 [ h^2 a^*^2 U11 + ... + 2 h k a^* b^* U12 ]\]

<table>
<thead>
<tr>
<th></th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>38(2)</td>
<td>43(2)</td>
<td>11(2)</td>
<td>3(2)</td>
<td>7(1)</td>
<td>-4(2)</td>
</tr>
<tr>
<td>F(2)</td>
<td>33(2)</td>
<td>38(2)</td>
<td>20(2)</td>
<td>3(2)</td>
<td>4(1)</td>
<td>-8(2)</td>
</tr>
<tr>
<td>F(3)</td>
<td>40(2)</td>
<td>45(2)</td>
<td>12(2)</td>
<td>-3(2)</td>
<td>-2(2)</td>
<td>-10(2)</td>
</tr>
<tr>
<td>F(4)</td>
<td>46(2)</td>
<td>50(2)</td>
<td>6(2)</td>
<td>-4(2)</td>
<td>1(1)</td>
<td>-7(2)</td>
</tr>
<tr>
<td>O(1)</td>
<td>52(3)</td>
<td>55(3)</td>
<td>3(2)</td>
<td>0(2)</td>
<td>4(2)</td>
<td>-14(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>33(3)</td>
<td>32(4)</td>
<td>16(3)</td>
<td>8(3)</td>
<td>8(3)</td>
<td>5(3)</td>
</tr>
<tr>
<td>C(2)</td>
<td>30(3)</td>
<td>24(3)</td>
<td>13(3)</td>
<td>0(3)</td>
<td>1(2)</td>
<td>5(3)</td>
</tr>
<tr>
<td>C(3)</td>
<td>27(3)</td>
<td>23(3)</td>
<td>13(3)</td>
<td>3(2)</td>
<td>2(2)</td>
<td>2(3)</td>
</tr>
<tr>
<td>C(4)</td>
<td>31(3)</td>
<td>25(3)</td>
<td>16(3)</td>
<td>4(3)</td>
<td>0(3)</td>
<td>4(3)</td>
</tr>
<tr>
<td>C(5)</td>
<td>29(3)</td>
<td>28(3)</td>
<td>16(3)</td>
<td>6(3)</td>
<td>6(3)</td>
<td>2(3)</td>
</tr>
<tr>
<td>C(6)</td>
<td>28(3)</td>
<td>32(3)</td>
<td>17(3)</td>
<td>9(3)</td>
<td>5(3)</td>
<td>4(3)</td>
</tr>
<tr>
<td>C(7)</td>
<td>30(3)</td>
<td>30(4)</td>
<td>18(3)</td>
<td>-1(3)</td>
<td>-4(3)</td>
<td>-5(3)</td>
</tr>
<tr>
<td>C(8)</td>
<td>38(4)</td>
<td>38(4)</td>
<td>8(3)</td>
<td>2(3)</td>
<td>4(3)</td>
<td>2(3)</td>
</tr>
<tr>
<td>C(9)</td>
<td>29(3)</td>
<td>28(3)</td>
<td>16(3)</td>
<td>-1(3)</td>
<td>2(3)</td>
<td>3(3)</td>
</tr>
<tr>
<td>C(10)</td>
<td>28(3)</td>
<td>30(4)</td>
<td>15(3)</td>
<td>6(3)</td>
<td>5(3)</td>
<td>6(3)</td>
</tr>
<tr>
<td>C(11)</td>
<td>33(4)</td>
<td>41(4)</td>
<td>13(3)</td>
<td>5(3)</td>
<td>2(3)</td>
<td>7(3)</td>
</tr>
<tr>
<td>C(12)</td>
<td>34(3)</td>
<td>39(4)</td>
<td>8(3)</td>
<td>6(3)</td>
<td>7(3)</td>
<td>2(3)</td>
</tr>
<tr>
<td>C(13)</td>
<td>30(3)</td>
<td>32(4)</td>
<td>22(3)</td>
<td>2(3)</td>
<td>1(3)</td>
<td>-6(3)</td>
</tr>
<tr>
<td>C(14)</td>
<td>33(3)</td>
<td>33(4)</td>
<td>15(3)</td>
<td>3(3)</td>
<td>6(3)</td>
<td>2(3)</td>
</tr>
<tr>
<td>C(15)</td>
<td>28(3)</td>
<td>32(4)</td>
<td>16(3)</td>
<td>4(3)</td>
<td>3(3)</td>
<td>11(3)</td>
</tr>
<tr>
<td>C(16)</td>
<td>64(5)</td>
<td>67(5)</td>
<td>4(3)</td>
<td>-6(3)</td>
<td>4(3)</td>
<td>-21(4)</td>
</tr>
</tbody>
</table>
Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 4.12.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>13844</td>
<td>11912</td>
<td>9575</td>
<td>32</td>
</tr>
<tr>
<td>H(11)</td>
<td>8874</td>
<td>7345</td>
<td>6301</td>
<td>35</td>
</tr>
<tr>
<td>H(13)</td>
<td>15886</td>
<td>11341</td>
<td>7013</td>
<td>36</td>
</tr>
<tr>
<td>H(14)</td>
<td>14778</td>
<td>11632</td>
<td>8413</td>
<td>33</td>
</tr>
<tr>
<td>H(16C)</td>
<td>12334</td>
<td>8115</td>
<td>4509</td>
<td>77</td>
</tr>
<tr>
<td>H(16A)</td>
<td>11560</td>
<td>6838</td>
<td>5159</td>
<td>77</td>
</tr>
<tr>
<td>H(16B)</td>
<td>9421</td>
<td>8168</td>
<td>5022</td>
<td>77</td>
</tr>
</tbody>
</table>
2,3,5,6-tetrafluoro-4,4''-dimethoxy-5'-(4-methoxyphenyl)-4'-(2,3,5,6-tetrafluoro-4-methoxyphenyl)-1,1':2',1''-terphenyl (4.13)

![Molecular Structure](image)

Molecular Weight: 646.52

A 250 mL flask with magnetic stir bar was placed with 2,3,4,5,6-pentafluoro-4''-(methoxy)-5'-(4-(methoxy)phenyl)-4'-(perfluorophenyl)-1,1':2',1''-terphenyl (1.225 g, 2.0 mmol), methanol (50 mL) and t-BuOK (0.890 g, 8.0 mmol). The mixture was heated to gently reflux for 5 hours. However, some of the solid still did not dissolved at this moment and toluene (50 mL) was added inside as a co-solvent. After another 5 hours, TLC indicated the starting material was completely consumed and a new product with higher polarity was formed. The resulting solution was cooled to room temperature and all the solvent was removed under reduced pressure. Water (100 mL) was added and ultrasonic cleaning was applied to dissolve the inorganic salt inside the solid. The insoluble solid was filtered and air-dried, which was finally recrystallized from toluene to give white crystals (1,193 g, 1.8 mmol, 90 % yield) as final product.

Data:

**M.P.:** 246.0 – 250.0 °C.

**¹H-NMR (400 MHz, CDCl₃) δ:** 7.415 (s, 2H), 7.125 (d, J = 8.8 Hz, 4H), 6.809 (d, J = 8.8 Hz, 4H), 4.074 (t, J = 1.2 Hz, 6H), 3.801 (s, 6H).

**¹³C-NMR (100 MHz, CDCl₃) δ:** 159.030, 144.229 (d, J = 244.2 Hz), 141.216, 140.785 (dd, J =
246.0 Hz, $^2J = 15.4$ Hz), 137.805, 1330196, 132.019, 129.713, 126.808, 113.683, 113.562, 62.144, 55.219.

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -141.707 (dd, $^1J = 21.4$ Hz, $^2J = 7.9$ Hz, 4F), -158.072 - -158.154 (m, 4F).

1,2,4,10,11,13-hexafluoro-3,6,12,15-tetramethoxytribenzo[f,k,m]tetraphene (4.14)

In a quartz vessel (appx. 40cm x 25mm), 1,4-bis(p-methoxyphenyl)-2,5-bis(p-methoxytetrafluorophenyl)benzene (0.651 g, 1.0 mmol) was dissolved in a mixing solvent of acetonitrile (90 mL) and THF (10 mL). The solution was then irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps for 24 hours. After that time, the solution was cooled to room temperature and suction filtration was applied to isolate the solid as final product (0.066 g, 0.11 mmol, 11% yield).

M.P.: 316.2 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 9.902 (d, $J = 4.8$ Hz, 2H), 8.596 (d, $J = 8.8$ Hz, 2H), 8.406 (dd, $^1J = 4.8$ Hz, $^2J = 2.4$ Hz, 2H), 7.321 (dd, $^1J = 8.8$ Hz, $^2J = 2.4$ Hz, 2H), 4.224 (s, 6H), 4.011 (s, 6H).

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -131.104 (m, 2F), -139.482 (m, 2F), -152.017 (m, 2F).
A 100 mL flask with magnetic stir bar was charged with 1,4-dibromo-2,5-bis(pentafluorophenyl)benzene (2.843 g, 5.0 mmol), [4-(n-hexyloxy)phenyl]boronic acid (4.451 g, 20 mmol, 200%), toluene (40 mL) and 1-propanol (40 mL). After that, potassium carbonate (2.767 g, 20 mmol, 200%) was added into the flask and the flask was thoroughly flushed with nitrogen. The flask was sit inside a 90 °C oil bath and tetrakis(triphenylphosphine)palladium(0) (0.116 g, 0.1 mmol) was added into the mixture at last. A condenser was attached on the top of the flask to give the mixture a gently reflux overnight.

The materials in the flask was then gravity filtered and the solid was well washed with diethyl ether (50 mL x 3). The filtrates were combined and mixed with silica gel (~ 5 g). After the removal of solvent by using rotary evaporation, the resulting yellow powder was placed on the top of silica gel column and subjected to column chromatography (eluent: hexanes: EtOAc = 50:1). The fractions containing the product were combined and concentrated, giving white fiber (2.585 g, 3.4 mmol, 68 % yield) as product.
M.P.: 152.0 – 155.0 ºC

\(^1\text{H}-\text{NMR} (400 MHz, CDCl}_3\) δ: 7.417 (s, 2H), 7.086 (d, \(J = 8.8\) Hz, 4H), 6.805 (d, \(J = 8.8\) Hz, 4H), 3.938 (t, \(J = 6.6\) Hz, 4H), 1.810 – 1.739 (m, 4H), 1.482 – 1.421 (m, 4H), 1.367 – 1.317 (m, 8H), 0.905 (t, \(J = 7.2\) Hz, 6H)

\(^13\text{C}-\text{NMR} (100 MHz, CDCl}_3\) δ: 158.852, 144.098 (d, \(J = 244.4\) Hz), 140.744 (d, \(J = 252.7\) Hz), 141.462, 137.526 (d, \(J = 251.7\) Hz), 133.078, 131.294, 129.621, 126.397, 115.291 (t, \(J = 18.9\) Hz), 114.365, 68.046, 31.628, 29.246, 25.751, 22.623, 14.045.
1,2,3,4,10,11,12,13-octafluoro-6,15-bis(hexyloxy)tribenzo[f,k,m]tetraphene (4.16)

A quartz vessel (appx. 40cm x 25mm) was charged with 2,3,4,5,6-pentafluoro-4''-(hexyloxy)-5'- (4-(hexyloxy)phenyl)-4'-perfluorophenyl)-1,1'2',1'-terphenyl (0.385 g, 0.50 mmol), acetonitrile (90 mL) and THF (10 mL). The obtained colorless solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After 12 hours of irradiation, yellow solid precipitate out of solution. The solvent was removed and gave a yellow powder (0.413 g) as crude product, which was recrystallized from toluene to give yellow solid (0.178 g, 0.25 mmol, 50 % yield) as product.

**M.P.**: 245.0 – 250.0 °C.
2,3,5,6-tetrafluoro-4,4''-bis(hexyloxy)-5'-4-(hexyloxy)phenyl)-4'-2,3,5,6-tetrafluoro-4-(hexyloxy)phenyl)-1,1':2',1''-terphenyl (4.17)

![Chemical Structure]

Chemical Formula: C₅₄H₆₂F₈O₄
Molecular Weight: 927.07

A 50 mL flask with magnetic stir bar was placed with 2,3,4,5,6-pentafluoro-4''-(n-hexyloxy)-5'-4-(n-hexyloxy)phenyl)-4'-(perfluorophenyl)-1,1':2',1''-terphenyl (0.573 g, 0.75 mmol), n-hexanol (7.5 mL) and t-BuOK (0.255 g, 2.28 mmol). The mixture was heated up to approximately 100 °C to make all the solid dissolve. After 10 hour, the resulting mixture was cooled and diluted with diethyl ether to a total volume of 100 mL followed by water washing (3 x 100 mL). The organic phase was then dried with anhydrous MgSO₄. After the removal of solvent by rotary evaporation, the excess amount of 1-hexanol was removed by Kugelrohr distillation (75 °C, 0.8 millibar). The remaining residue was dissolved in ethyl acetate (~ 50 mL) and well mixed with silica gel (~ 2g). Yellow powder was obtained after the removal solvent and it was placed at the top of a silica column to elute (eluent: hexane). Fractions containing the product were combined and concentrated to dryness, giving white solid as final product (0.685 g, 0.74 mmol, 98 % yield).

M.P.: 75.0 – 79.0 °C.

¹H-NMR (400 MHz, CDCl₃) δ: 7.417 (s, 2H), 7.102 (d, J = 8.8 Hz, 4H), 6.784 (d, J = 8.8 Hz, 4H), 4.208 (t, J = 6.6 Hz, 4H), 3.929 (t, J = 6.6 Hz, 4H), 1.788 – 1.744 (m, 8H), 1.480 – 1.433 (m,
In a quartz vessel, 2,3,5,6-tetrafluoro-4,4''-bis(hexyloxy)-5′-(4-(hexyloxy)phenyl)-4′-(2,3,5,6-tetrafluoro-4-(hexyloxy)phenyl)-1,1′:2′,1\text{''}-terphenyl (0.231 g, 0.25 mmol) was dissolved in a mixture of acetonitrile (90 mL) and THF (10 mL). The solution was degassed with nitrogen and irradiated for 24 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps. Meanwhile, yellow fibers precipitated out of the solution itself. After that, the solution was cooled to room temperature and the solid was suction filtrated and air-dried, giving yellow crystals (0.121 g, 0.14 mmol, 56 % yield) as final product.
$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.867 (d, $J = 6.4$ Hz, 2H), 73898 – 7.868 (m, 4H), 6.950 (dd, $^1J = 8.8$ Hz, $^2J = 2.4$ Hz, 2H), 4.241 (t, $J = 6.6$ Hz, 4H), 4.005 (t, $J = 6.6$ Hz, 4H), 1.907 – 1.869 (m, 8H), 1.593 – 1.555 (m, 8H), 1.471 – 1.417 (m, 16H), 1.015 – 0.973 (m, 12H)

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 158.051, 150.302 (d, $J = 248.3$ Hz), 146.016 (d, $J = 249.0$ Hz), 143.320 (d, $J = 247.1$ Hz), 135.418 (dd, $^1J = 19.4$ Hz, $^2J = 11.3$ Hz), 127.312, 126.838, 123.824, 123.292, 120.319, 120.017, 116.167, 115.522, 114.804, 111.005, 110.690, 75.328, 67.966, 31.845, 31.698, 30.249, 25.884, 25.471, 22.747, 22.697, 14.145, 14.125.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: $-131.146$ (t, $J = 5.5$ Hz, 2F), $-140.012$ - $-140.095$ (m, 2F), $-152.408$ (dd, $^1J = 19.4$ Hz, $^2J = 7.0$ Hz, 2F).

**UV/Vis (DCM):** $\lambda_{\text{max}}(\varepsilon) = 266$ (18820), 313 (40120), 330 (21000) nm (M$^{-1}$cm$^{-1}$).

1,4-Bis(p-(t-butyl)phenyl)-2,5-bis(pentafluorophenyl)benzene (4.19)

![Chemical Structure](image)

Chemical Formula: C$_{38}$H$_{28}$F$_{10}$  
Molecular Weight: 674.63

A 100 mL flask with magnetic stir bar was charged with 1,4-dibromo-2,5-bis(pentafluorophenyl)benzene (0.569 g, 1.00 mmol), p-(t-butyl)phenyl boronic acid (0.718 g, 4.00 mmol, 200%), potassium carbonate (0.562 g, 4.00 mmol, 200%), toluene (40 mL) and ethanol (10 mL). Then the flask was flushed thoroughly with nitrogen.
The flask was heated in a 90 °C oil bath and tetrakis(triphenylphosphine)palladium(0) (23.930 mg, 0.020 mmol, 1%) was added at last. The obtained mixture was heated to reflux overnight (12 h) under nitrogen atmosphere.

After this, the mixture was cooled to room temperature. Silica gel (~ 5 g) was added into the mixture and the solvent was removed under vacuum. The yellow powder obtained was placed on a silica gel column and eluted (Hexanes: EtOAc = 10:1). Fractions containing the product was combined and concentrated to dryness, giving light yellow powder (0.516 g, 0.76 mmol, 76% yield). This powder could be recrystallized (isooctane : toluene=1:1 mixture) and gave white powder (0.387 g, 0.57 mmol, 57% yield) as final product.

**M.P.** Sublimation can be observed above approximately 255.0 °C and melted at 273.0 – 275.0 °C.

**$^{19}$F-NMR (376 MHz, CDCl$_3$):** $-140.130$ (dd, $^1J =$23.0 Hz, $^2J =$ 8.1 Hz), $-155.126$ (t, $J =$21.0 Hz), $-162.589$ - $-162.729$ (m).

**$^1$H-NMR (400 MHz, CDCl$_3$):** 7.452 (s, 2H), 7.306 (d, $J =$8.4 Hz, 4H), 7.112 (d, $J =$8.4 Hz, 4H), 1.306 (s, 18H).

**$^{13}$C-NMR (100 MHz, CDCl$_3$):** 150.834, 144.118 (d, $J =$246.1 Hz), 141.777, 140.732 (d, $J =$252.3 Hz), 137.494 (d, $J =$251.1 Hz), 136.107, 133.259, 128.127, 126.310, 125.303, 115.205 (t, $J =$19.2 Hz), 34.571, 31.253.
6,15-di-tert-butyl-1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene (4.20)

A quartz vessel (appr. 40cm x 25mm) was charged with 4''-(tert-butyl)-5'-((4-(tert-butyl)phenyl)-2,3,4,5,6-pentafluoro-4'-(perfluorophenyl)-1,1':2',1''-terphenyl (0.166 g, 0.25 mmol), acetonitrile (50 mL) and THF (50 mL). The obtained colorless solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After 12 hours of irradiation, yellow solid precipitate out of solution. The suspension was cooled and the solid was filtered followed by air-drying (0.115 g, 0.17 mmol, 68 % yield).

\(^1\text{H-NMR (400 MHz, CDCl}_3\text{):}\) 10.159 (d, J =9.6 Hz, 2H), 9.001, 8.726 (d, J =8.8 Hz, 2H), 7.860 (d, J = 6.8 Hz, 2H), 1.508 (s, 18H).

Only melting \(^1\text{H-NMR was obtained for this compound. However, from the experience of previous compound, this solid obtained should be the double PCDHF product.}
A 250 mL flask with magnetic stir bar was placed with 1,4-\textit{bis}(pentafluorophenyl)-2,5-dibromobenzene (1.722 g, 3.0 mmol), methanol (100 mL) and \textit{t}-BuOK (1.030 g, 9.0 mmol). The mixture was heated to gently reflux. The initially clear solution turned into a white suspension after a while. After 3 hours, the mixture was cooled and solvent was removed under reduced pressure. Water (100 mL) was added and followed by ultrasound cleaning to dissolve the salt inside the solid. The insoluble solid was then filtered and air dried, which was recrystallized from toluene to give white crystals (1.507 g, 2.5 mmol, 83 % yield) as final product.

**Data:**

\textbf{M.P.}: 190.0 – 195.0 °C.

\textbf{\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3})} δ: 7.660 (s, 2H), 4.173 (t, \textit{J} = 1.6 Hz, 6H).

\textbf{\textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3})} δ: 144.199 (d, \textit{J} = 246.2 Hz), 142.257, 140.921 (dd, \textit{J} = 247.1 Hz, \textit{J} = 14.9 Hz), 139.127, 136.142, 135.281, 131.575, 123.424, 111.422 (t, \textit{J} = 18.6 Hz).

\textbf{\textsuperscript{19}F-NMR (376 MHz, CDCl\textsubscript{3})} δ: -140.950 (dd, \textit{J} = 20.3 Hz, \textit{J} = 6.8 Hz, 4F), -157.432 - -157.524 (m, 4F)
A 250 mL flask with magnetic stir bar was placed with 2',5'-dibromo-2,2",3,3",5,5",6,6"-octafluoro-4,4"-dimethoxy-1,1':4',1"-terphenyl (1.186 g, 2.0 mmol), 4-trifluoromethoxyphenyl boronic acid (1.240 g, 6.0 mmol), potassium carbonate (0.851 g, 6.0 mmol), 1,4-dioxane (30 mL) and water (13 mL). The obtained mixture was flushed thoroughly with nitrogen and heated in oil bath. After the addition of Pd(PPh₃)₄ (0.056 g, 2%) at last, the solution was gently refluxed overnight (~ 8h) and TLC indicated that the starting material terphenyl was completely consumed.

The obtained solution was then cooled to room temperature. After mixing with silica gel (~ 5g), the solvent was removed by rotary evaporation. The resulting yellow powder was placed on the top of silica gel column to eluted (eluent: hexanes:EtOAc = 20:1) and the fractions containing the pure product were combined and condensed, giving white crystals (1.384 g, 1.8 mmol, 90 % yield) as final product.

**M.P.:** 244.0 – 246.0 °C.

**¹H-NMR (400 MHz, CDCl₃) δ:** 7.463 (s, 2H), 7.242 (d, J = 8.0 Hz, 4H), 7.148 (d, J = 8.0 Hz,
4H), 4.084 (s, 6H).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -57.785 (s, 6F), -141.670 (d, $J = 13.5$ Hz, 4F), -157.740 (s, 4F).

1,2,4,10,11,13-hexafluoro-3,12-dimethoxy-6,15-bis(trifluoromethoxy)tribenko[f,k,m]tetraphene (4.23)

In a quartz vessel, 1,4-bis(p-trifluoromethoxyphenyl)-2,5-bis(p-methoxyltetrafluorophenyl)benzene (0.378 g, 0.5 mmol) was dissolved in acetonitrile (90 mL) and THF (10 mL). The solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps for 24 hours.

The solution was then cooled to room temperature and filtered, only give trace amount of yellow solid as product (NMR demonstrated that was the desired product, however, the yield is over too low).

A column chromatography was applied and another 0.031 g of yellow solid was obtained. However, NMR demonstrated that it is a mixture of mono- and double-ring closure product.
\(^{19}\text{F-NMR (376 MHz, CDCl}_3\) \(\delta\): -57.445 (s, 6F), -130.618 (m, 2F), -137.991 - -138.085 (m, 2F), -149.941 - -149.984 (m, 2F), -156.490 - -156.554 (m, 2F).

\[2,2'-(2,2'',3,3'',4,4'',5,5'',6,6''-\text{decafluoro}-[1,1':4',1''-\text{terphenyl}]-2',5'-\text{diyl})\text{dithiophene (4.24)}\]

\[
\text{Chemical Formula: } C_{26}H_{8}F_{10}S_{2} \\
\text{Molecular Weight: } 574.45
\]

A 100 mL flask with magnetic stir bar was charged with 1,4-dibromo-2,5-bis(pentafluorophenyl)benzene (1.141 g, 2 mmol), thiophene-2-boronic acid (1.026 g, 8 mmol, 200%) and potassium carbonate (1.105 g, 8 mmol, 200%). After this, toluene (40 mL) and ethanol (10 mL) were added in sequence and the flask was thoroughly flushed with nitrogen.

The flask was heated to 90 °C and tetrakis(triphenylphosphine)palladium(0) (46.091 mg, 0.040 mmol, 1%) was added into the mixture at last. A condenser was fitted on the flask and gently refluxed overnight under nitrogen.

After approximately 12 hours, TLC indicated that starting material was complete consumed and a new product showed purple fluorescent under UV lamp. The mixture was cooled to room temperature, diluted to a total of 100 mL with EtOAc and silica gel (about 5g) was added inside. After the solvent was removed by rotary evaporation, the obtained tan powder obtained was placed
on the top of a silica gel column and eluted (hot hexane:toluene=1:1). The fractions containing the product were combined together and concentrated to dryness, giving tan crystal (1.155 g, 2 mmol, 100% yield) as crude product. It was recrystallized from chlorobenzene and gave white crystal (0.950 g, 1.6 mmol, 80% yield) as final product.

Due to its bad solubility in common deuterated solvents, only X-ray crystallography was successfully accomplished as the characterization.

Table 1. Crystal data and structure refinement for 4.24.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>4.24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C26 H8 F10 S2</td>
</tr>
</tbody>
</table>
Formula weight 574.44
Temperature 180(2) K
Wavelength 0.71073 Å

Crystal system, space group Orthorhombic, Pbca

Unit cell dimensions:
\[ a = 11.2142(6) \text{ Å} \quad \alpha = 90 \text{ deg.} \]
\[ b = 11.4552(6) \text{ Å} \quad \beta = 90 \text{ deg.} \]
\[ c = 17.3597(9) \text{ Å} \quad \gamma = 90 \text{ deg.} \]

Volume 2230.0(2) Å³

Z, Calculated density 4, 1.711 Mg/m³

Absorption coefficient 0.338 mm⁻¹

F(000) 1144

Crystal size 0.15 x 0.15 x 0.07 mm

Theta range for data collection 2.35 to 25.05 deg.

Limiting indices \(-13 \leq h \leq 13, -13 \leq k \leq 13, -20 \leq l \leq 20\)

Reflections collected / unique 16792 / 1972 [R(int) = 0.0249]

Completeness to theta = 25.05 100.0 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.9767 and 0.9511

Refinement method Full-matrix least-squares on F²

Data / restraints / parameters 1972 / 0 / 172

Goodness-of-fit on F² 1.203

Final R indices [I>2σ(I)] R1 = 0.0357, wR2 = 0.1300

R indices (all data) R1 = 0.0419, wR2 = 0.1402

Largest diff. peak and hole 0.349 and -0.404 eÅ⁻³
Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 4.24.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)</td>
<td>-5(1)</td>
<td>1756(1)</td>
<td>4082(1)</td>
<td>39(1)</td>
</tr>
<tr>
<td>F(1)</td>
<td>-540(1)</td>
<td>2217(1)</td>
<td>6106(1)</td>
<td>30(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>296(1)</td>
<td>962(1)</td>
<td>7297(1)</td>
<td>39(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>2296(1)</td>
<td>1645(1)</td>
<td>8046(1)</td>
<td>45(1)</td>
</tr>
<tr>
<td>F(4)</td>
<td>3402(1)</td>
<td>3678(1)</td>
<td>7639(1)</td>
<td>45(1)</td>
</tr>
<tr>
<td>F(5)</td>
<td>2548(1)</td>
<td>4959(1)</td>
<td>6468(1)</td>
<td>38(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>439(2)</td>
<td>2594(2)</td>
<td>6476(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>859(2)</td>
<td>1940(2)</td>
<td>7079(1)</td>
<td>27(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>1874(2)</td>
<td>2297(2)</td>
<td>7472(1)</td>
<td>32(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>2422(2)</td>
<td>3320(2)</td>
<td>7268(1)</td>
<td>31(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>1974(2)</td>
<td>3974(2)</td>
<td>6662(1)</td>
<td>27(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>982(2)</td>
<td>3626(2)</td>
<td>6241(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>505(1)</td>
<td>4323(2)</td>
<td>5586(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>397(2)</td>
<td>3847(2)</td>
<td>4842(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>-117(2)</td>
<td>4545(2)</td>
<td>4270(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>836(2)</td>
<td>2676(2)</td>
<td>4646(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>1929(2)</td>
<td>2145(2)</td>
<td>4844(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>2022(2)</td>
<td>1024(2)</td>
<td>4505(2)</td>
<td>43(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>1062(2)</td>
<td>702(2)</td>
<td>4096(2)</td>
<td>44(1)</td>
</tr>
</tbody>
</table>
Table 3. Bond lengths [Å] and angles [deg] for 4.24.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)-C(13)</td>
<td>1.700(2)</td>
</tr>
<tr>
<td>S(1)-C(10)</td>
<td>1.7204(19)</td>
</tr>
<tr>
<td>F(1)-C(1)</td>
<td>1.344(2)</td>
</tr>
<tr>
<td>F(2)-C(2)</td>
<td>1.341(2)</td>
</tr>
<tr>
<td>F(3)-C(3)</td>
<td>1.332(2)</td>
</tr>
<tr>
<td>F(4)-C(4)</td>
<td>1.338(2)</td>
</tr>
<tr>
<td>F(5)-C(5)</td>
<td>1.342(2)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.370(3)</td>
</tr>
<tr>
<td>C(1)-C(6)</td>
<td>1.391(3)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.389(3)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.371(3)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.386(3)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.389(3)</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.489(3)</td>
</tr>
<tr>
<td>C(7)-C(9)#1</td>
<td>1.391(3)</td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td>1.406(3)</td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td>1.400(3)</td>
</tr>
<tr>
<td>C(8)-C(10)</td>
<td>1.469(3)</td>
</tr>
<tr>
<td>C(9)-C(7)#1</td>
<td>1.391(3)</td>
</tr>
<tr>
<td>C(9)-H(9)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(10)-C(11)</td>
<td>1.410(3)</td>
</tr>
<tr>
<td>C(11)-C(12)</td>
<td>1.416(3)</td>
</tr>
<tr>
<td>C(11)-H(11)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(12)-C(13)</td>
<td>1.341(4)</td>
</tr>
<tr>
<td>C(12)-H(12)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(13)-H(13)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(13)-S(1)-C(10)</td>
<td>92.35(10)</td>
</tr>
<tr>
<td>F(1)-C(1)-C(2)</td>
<td>118.03(17)</td>
</tr>
<tr>
<td>F(1)-C(1)-C(6)</td>
<td>119.38(17)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(6)</td>
<td>122.59(18)</td>
</tr>
<tr>
<td>F(2)-C(2)-C(1)</td>
<td>120.72(18)</td>
</tr>
<tr>
<td>F(2)-C(2)-C(3)</td>
<td>119.53(18)</td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>119.74(18)</td>
</tr>
<tr>
<td>F(3)-C(3)-C(4)</td>
<td>120.88(19)</td>
</tr>
<tr>
<td>F(3)-C(3)-C(2)</td>
<td>119.64(18)</td>
</tr>
<tr>
<td>C(4)-C(3)-C(2)</td>
<td>119.48(18)</td>
</tr>
<tr>
<td>F(4)-C(4)-C(3)</td>
<td>120.37(19)</td>
</tr>
<tr>
<td>F(4)-C(4)-C(5)</td>
<td>119.88(19)</td>
</tr>
<tr>
<td>C(3)-C(4)-C(5)</td>
<td>119.73(19)</td>
</tr>
<tr>
<td>F(5)-C(5)-C(4)</td>
<td>118.10(17)</td>
</tr>
<tr>
<td>F(5)-C(5)-C(6)</td>
<td>119.56(17)</td>
</tr>
</tbody>
</table>
C(4)-C(5)-C(6)     122.31(17)
C(5)-C(6)-C(1)     116.11(17)
C(5)-C(6)-C(7)     122.35(16)
C(1)-C(6)-C(7)     121.53(16)
C(9)#1-C(7)-C(8)   120.01(17)
C(9)#1-C(7)-C(6)   118.33(17)
C(8)-C(7)-C(6)     121.61(17)
C(9)-C(8)-C(7)     117.78(18)
C(9)-C(8)-C(10)    119.66(17)
C(7)-C(8)-C(10)    122.53(17)
C(7)#1-C(9)-C(8)   122.21(18)
C(7)#1-C(9)-H(9)   118.9
C(8)-C(9)-H(9)     118.9
C(11)-C(10)-C(8)   128.94(17)
C(11)-C(10)-S(1)   110.54(14)
C(8)-C(10)-S(1)    120.50(14)
C(10)-C(11)-C(12)  110.71(18)
C(10)-C(11)-H(11)  124.6
C(12)-C(11)-H(11)  124.6
C(13)-C(12)-C(11)  114.24(19)
C(13)-C(12)-H(12)  122.9
C(11)-C(12)-H(12)  122.9
C(12)-C(13)-S(1)   112.13(17)
C(12)-C(13)-H(13)  123.9
S(1)-C(13)-H(13)   123.9

Symmetry transformations used to generate equivalent atoms:
#1  -x,-y+1,-z+1
Table 4. Anisotropic displacement parameters (Å² x 10³) for 4.24.

The anisotropic displacement factor exponent takes the form:
\[-2 \pi^2 \{ h^2 a^*^2 U11 + \ldots + 2 h k a^* b^* U12 \} \]

<table>
<thead>
<tr>
<th></th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)</td>
<td>39(1)</td>
<td>30(1)</td>
<td>48(1)</td>
<td>-12(1)</td>
<td>-9(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>F(1)</td>
<td>28(1)</td>
<td>33(1)</td>
<td>30(1)</td>
<td>3(1)</td>
<td>-4(1)</td>
<td>-6(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>50(1)</td>
<td>32(1)</td>
<td>34(1)</td>
<td>12(1)</td>
<td>-1(1)</td>
<td>-7(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>53(1)</td>
<td>48(1)</td>
<td>35(1)</td>
<td>18(1)</td>
<td>-14(1)</td>
<td>4(1)</td>
</tr>
<tr>
<td>F(4)</td>
<td>40(1)</td>
<td>56(1)</td>
<td>40(1)</td>
<td>7(1)</td>
<td>-20(1)</td>
<td>-7(1)</td>
</tr>
<tr>
<td>F(5)</td>
<td>40(1)</td>
<td>32(1)</td>
<td>40(1)</td>
<td>6(1)</td>
<td>-12(1)</td>
<td>-12(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>24(1)</td>
<td>25(1)</td>
<td>25(1)</td>
<td>-3(1)</td>
<td>0(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>31(1)</td>
<td>26(1)</td>
<td>24(1)</td>
<td>3(1)</td>
<td>5(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>38(1)</td>
<td>36(1)</td>
<td>21(1)</td>
<td>5(1)</td>
<td>-2(1)</td>
<td>8(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>29(1)</td>
<td>37(1)</td>
<td>27(1)</td>
<td>-1(1)</td>
<td>-8(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>29(1)</td>
<td>27(1)</td>
<td>26(1)</td>
<td>2(1)</td>
<td>0(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>25(1)</td>
<td>22(1)</td>
<td>20(1)</td>
<td>-1(1)</td>
<td>1(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>21(1)</td>
<td>22(1)</td>
<td>22(1)</td>
<td>0(1)</td>
<td>1(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>21(1)</td>
<td>20(1)</td>
<td>24(1)</td>
<td>0(1)</td>
<td>-1(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>25(1)</td>
<td>24(1)</td>
<td>19(1)</td>
<td>-1(1)</td>
<td>-1(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>25(1)</td>
<td>22(1)</td>
<td>22(1)</td>
<td>-1(1)</td>
<td>0(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>30(1)</td>
<td>27(1)</td>
<td>31(1)</td>
<td>-9(1)</td>
<td>2(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>49(1)</td>
<td>35(1)</td>
<td>45(1)</td>
<td>-3(1)</td>
<td>-2(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>60(2)</td>
<td>24(1)</td>
<td>49(1)</td>
<td>-11(1)</td>
<td>0(1)</td>
<td>4(1)</td>
</tr>
</tbody>
</table>
Table 5. Hydrogen coordinates \((x \times 10^4)\) and isotropic displacement parameters \((A^2 \times 10^3)\) for 4.24.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(9)</td>
<td>-203</td>
<td>4235</td>
<td>3765</td>
<td>27</td>
</tr>
<tr>
<td>H(11)</td>
<td>2521</td>
<td>2491</td>
<td>5162</td>
<td>35</td>
</tr>
<tr>
<td>H(12)</td>
<td>2705</td>
<td>541</td>
<td>4563</td>
<td>51</td>
</tr>
<tr>
<td>H(13)</td>
<td>988</td>
<td>-30</td>
<td>3842</td>
<td>53</td>
</tr>
</tbody>
</table>
4,5,6,7,12,13,14,15-octafluorobenzo[8,9]tetrapheno[6,5-b:11,10-b']dithiophene (4.25)

![Chemical Structure](image)

**Chemical Formula:** C_{26}H_{6}F_{8}S_{2}

**Molecular Weight:** 534.44

In a quartz vessel (appx. 40cm x 25mm), 2,2'-(2,2'',3,3'',4,4'',5,5'',6,6''-decafluoro-[1,1':4',1"-terphenyl]-2',5'-diyl)dithiophene (0.150 g, 0.25 mmol) was dissolved in a mixture of acetonitrile (50 mL) and THF (50 mL). The obtained colorless solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.

After 9 hours, yellow solid precipitate out of solution, which was filtered directly and air-dried (0.079 g, 0.15 mmol, 60 % yield).

**M.P.:** Slowly sublimated above 350 °C

Due to its bad solubility in common deuterated solvents, only melting point and HRMS was successfully accomplished as the characterization.
4.6. References.


5. Chapter Five – The synthesis of some smaller polycyclic aromatic hydrocarbons (PAHs) via PCDHF

Based on the previous discussions, it can be seen that the PCDHF reaction provides a new arsenal to build a variety of fluorinated polycyclic aromatic hydrocarbons (PAHs)\(^1\). The successful synthesis of 1,2,3,4,10,11,12,13-octafluorotribenzo[f,k,m]tetraphene and its derivatives was really a breakthrough. However, we also need to face some issues about the structures themselves – the large polycyclic aromatic hydrocarbons (PAHs) molecules sometimes have challenging solubility issues that have impeded their processing and characterization. The fact of the matter is that we have intentionally designed molecules that we want to have strong intermolecular interactions. Therefore, we should hardly complain if we succeed and we just need to accept the collateral properties.

In this section, we focus on some smaller but still interesting polycyclic aromatic hydrocarbons (PAHs). In these cases, at least the solubility problems will not be so much of a concern.

5.1. Fluorinated 1,2,3,4-tetrafluorodibenzo[g,p]chrysene

The first candidate amongst the relatively small PAH molecules we selected to prepare is the tetrafluorinated 1,2,3,4-tetrafluorodibenzo[g,p]chrysene as it appeared to be readily accessed from the precursor 9-(perfluorophenyl)-10-phenylphenanthrene. Starting from 9-iodo-10-phenylphenanthrene (5.1 prepared by Dr. Twieg), the iodine could be easily substituted by the copper mediated decarboxylative coupling of potassium pentafluorobenzoate at 145 °C. However, the crucial PCDHF cyclization of 9-(perfluorophenyl)-10-phenylphenanthrene (5.2) ended with an
unexpected failure (Scheme 5.1). This was a surprise since our previous experience was that ortho-terphenyl type precursors were usually excellent for PCDHF cyclization. This maverick might result from a simple steric effect – the nearby atoms (H···F and H···H) on the two rings made it difficult to achieve sufficient coplanarity to finish the cyclization process.

![Scheme 5.1 9-(perfluorophenyl)-10-phenylenanthrene (5.2) failed to undergo PCDHF.]

Dr. Prabin Rai successfully prepared some (2-(perfluorophenyl)ethene-1,1,2-triyl)tribenzene (5.4). Our plan was that the more freely rotating rings in 5.4 should reduce the steric issue mentioned before. During the irradiation of this compound, we followed the reaction progress by using GC. Although both PCDHF and traditional oxidative approaches were possible here, the oxidative approach proceeded much faster than PCDHF, yielding only 9-(perfluorophenyl)-10-phenylenanthrene (5.2) (Scheme 5.2).
Scheme 5.2 Oxidative photocyclization is much faster than PCDHF for (2-(perfluorophenyl)ethene-1,1,2-triyl)tribenzene (5.4).

It seemed that we had trapped ourselves at a dead end and that the whole synthetic route required a complete redesign. After considering other alternative pathways and searching for commercially available reagents, we selected 9-phenanthreneboronic acid and reacted it with the previously prepared 2'-bromo-2,3,4,5,6-pentafluoro-1,1'-biphenyl (5.5) under Suzuki conditions. The 9-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)phenanthrene (5.6) obtained appeared like a sticky oil and was difficult to purify. Therefore, we proceeded with the PCDHF directly with the expectation that the final desired product 1,2,3,4-tetrafluorodibenzo[g,p]chrysene (5.3) would be easier to be purify (Scheme 5.3). This time we were successful, and as expected – 1,2,3,4-tetrafluorodibenzo[g,p]chrysene (5.3) was obtained as white crystals which were good enough for X-ray crystallography analysis.

Scheme 5.3 Synthesis of 1,2,3,4-tetrafluorodibenzo[g,p]chrysene.
The molecule 1,2,3,4-tetrafluorodibenzo[g,p]chrysene (5.3) has a twisted structure due to steric effect of nearby atoms (H···F and H···H) in the two fjord regions. The twisting angle was as large as 42°. The bulk crystal structure is created by C−F···H−C and C−F···Cπ by C−F···H−C and C−F···Cπ interactions. Compared to the non-fluorinated parent compound dibenzo[g,p]chrysene\(^2\), the tetrafluoro compound 5.3 has a similar crystal packing (both of them feature the P2\(_1\)/n spacegroup). The only difference between them is that compound 5.3 contains more complicated intermolecular interactions due to the presence of fluorine atoms (only C−H···π interactions play important roles in dibenzo[g,p]chrysene).
Figure 5.1 Crystal packing of 1,2,3,4-tetrafluorodibenzo[g,p]chrysene.
Figure 5.2 Crystal packing of dibenzo[g,p]chrysene².
5.2. Fluorinated dibenzo[fg,op]tetracene derivatives

Aside from 1,2,3,4-tetrafluorodibenzo[g,p]chrysene, we also tried to use the PCDHF technique to synthesize some dibenzo[fg,op]tetracene derivatives (Scheme 5.4). The first one we tried to access was 1,2,3-trifluorodibenzo[fg,op]tetracene. The commercially available 3-bromobiphenyl (5.7) could be easily converted to corresponding boronic acid (5.8) and underwent Suzuki coupling with the previously prepared 2'-bromo-2,3,4,5,6-pentafluoro-1,1'-biphenyl (5.5) to provide 2,3,4,5,6-pentafluoro-1,1':2',1":3",1"'-quaterphenyl (5.9).

![Scheme 5.4 Proposed synthesis of 1,2,3-trifluorodibenzo[fg,op]tetracene.]

The next step was the crucial part – the PCDHF reaction. The progress of this reaction was followed by GC-MS and appeared to be very slow (three days were required to make sure all the starting materials completely consumed). From GC-MS spectra, only a M-20 peak was observed rather than the desired M-40 peak, which meant only one HF was lost during PCDHF process.
This also matched the result of $^{19}$F-NMR spectra (total integration area of 4)

![Figure 5.3 $^{19}$F-NMR of single PCDHF product 1,2,3,4-tetrafluoro-7-phenyltriphenylene (5.11).](image)

The good news at here is that this single ring closure product was easy to recrystallize. We thus submitted the obtained recrystallized single crystals for an X-ray crystallography and the result showed us why only one PCDHF cyclization was accomplished rather than two.

Also worth mentioning here is that in the crystal packing of 1,2,3,4-tetrafluoro-7-phenyltriphenylene (5.11), the tetrafluorotriphenylene parts are able to perform aryl-perfluoroaryl stacking. Also, the protons on the freely rotating benzene rings can form $\text{C–F} \cdots \text{H–C}$ interactions with the fluorine atoms in tetrafluorotriphenylene.
Figure 5.4 X-ray crystallography demonstrated the PCDHF product is 1,2,3,4-tetrafluoro-7-phenyltriphenylene (5.11).
As shown in Figure 5.4, this single ring closure product was revealed to be 1,2,3,4-tetrafluoro-7-phenyltriphenylene, which meant the reaction did not proceed as hoped (it was a long shot). The C-C single bonds linking the aromatic rings can freely rotate and the terminal rings preferred to stay away from each other due to steric reasons. As a result, PCDHF proceeded only through a preferred route to yield 1,2,3,4-tetrafluoro-7-phenyltriphenylene (5.11) rather than the 1,2,3,4-tetrafluoro-5-phenyltriphenylene intermediate which could make a second PCDHF to provide our desired product 1,2,3-trifluorodibenzo[fg,op]tetracene (5.10). In the future it would appear that a derivative of 1,2,3-triphenylbenzene (with a pentafluorophenyl group at the 2-position) might be a better precursor.

Taking a lesson from the previous steric issues, we designed a route for the synthesis of 4,5,6,7,11,12,13,14-octafluorodibenzo[fg,op]tetracene which is shown below (Scheme 5.6). In
this case, 1,2-dibromobenzene was treated with approximately a half equivalent of $n$-BuLi at -78 °C to provide 2,2'-dibromo-1,1'-biphenyl as product in 88 % yield$^{3-5}$. Next, there were two possible routes – convert dibromobiphenyl to diiodobiphenyl followed by copper mediated decarboxylative coupling of potassium pentafluorobenzoate (left) or convert the dibromobiphenyl to a diboronic acid followed by Suzuki coupling with pentafluoriodobenzene (right). After considering the relative difficulty of diboronic acid preparation, we selected the route on the left. Treatment with 2.2 eq $n$-BuLi followed by 2.0 eq of iodine led to the conversion of 2,2'-dibromo-1,1'-biphenyl (5.13) to 2,2'-diiodo-1,1'-biphenyl (5.14) in a 71 % yield.$^{4,6,7}$ In the copper mediated decarboxylative coupling, 4.0 eq of potassium pentafluorobenzoate ($C_6F_5COOK$) was added and much higher reaction temperature 165 °C was applied (usually 145 °C suffices) to make sure the reaction was complete and provided 2,2",3,3",4,4",5,5",6,6"-decafluoro-1',2',1"',2"',1""-quaterphenyl (5.15) in 74 % yield. Finally, the PCDHF step gave the desired product in a 22 % yield. Considering this is a double ring closure, this was an acceptable yield.
Both $^1$H-NMR and $^{19}$F-NMR verified that the resulting yellow powder was our desired product 4,5,6,7,11,12,13,14-octafluorodibenzo[fg,op]tetracene – the $^1$H-NMR showed a doublet and a triplet with an integration ratio of 2:1 (4H:2H) and the $^{19}$F-NMR showed two doublets with an integration ratio of approximately 1:1 (4F:4F) (Figure 5.5).

The sample of 4,5,6,7,11,12,13,14-octafluorodibenzo[fg,op]tetracene (5.16) from the PCDHF reaction seems to be not completely pure (some minor peaks observed in $^1$H-NMR). We have tried various solvents to perform the recrystallization, hoping to get single crystals for X-ray crystallography. However, multiple attempts thus far have only ended in failure.
Figure 5.5 $^1$H-NMR and $^{19}$F-NMR of 4,5,6,7,11,12,13,14-octafluorodibenzo[fg,op]tetracene.
5.3. Summary

In this chapter, by using the PCDHF technique, we successfully synthesized several new fluorinated polycyclic aromatic hydrocarbons (PAHs) such as 1,2,3,4-tetrafluorodibenzo\[g,p\]chrysene and 4,5,6,7,11,12,13,14-octafluorodibenzo\[fg,op\]tetracene. On the contrary, the synthesis of 1,2,3-trifluorodibenzo\[fg,op\]tetracene ended in failure and 1,2,3,4-tetrafluoro-7-phenyltriphenylene was obtained instead. This result told us that it is necessary to consider about the steric issue during the PCDHF cyclization.
5.4. Experimental procedures

9-(perfluorophenyl)-10-phenylphenanthrene (5.2)

A 50 mL pear flask was charged with 9-iodo-10-phenylphenanthrene (0.382 g, 1.0 mmol), PhF3COOK (0.378 g, 1.5 mmol), CuI (0.041 g, 0.2 mmol) and diglyme (2 mL). The mixture was flushed thoroughly with nitrogen and kept in a 145 °C oil bath for 24 hours.

After that, TLC showed that nearly no starting material remained and so the resulting mixture was cooled to room temperature. Silica gel (~ 2 g) was added and the solvent was removed in vacuo. The brown powder obtained was placed at the top of a silica gel column and eluted (Eluent: hexanes). Fractions containing the product were combined and concentrated to give white crystals (0.286g, 0.68 mmol, 68 % yield) as final product.

M.P.: 161.0 – 164.0 °C

\[^1\text{H-NMR (400 MHz, CDCl}_3\text{)}\]: 8.836 – 8.803 (m, 2H), 7.736 – 7.692 (m, 2H), 7.586 – 7.509 (m, 3H), 7.399 – 7.329 (m, 4H), 7.268 – 7.245 (m, 2H).

\[^13\text{C-NMR (100 MHz, CDCl}_3\text{)}\]: 144.196 (d, \(J = 240.8\) Hz), 140.756, 140.722 (d, \(J = 252.0\) Hz),
138.638, 137.370 (d, \(J = 253.5\) Hz), 131.464, 130.904, 130.257, 130.172, 129.160, 128.195, 128.095, 127.822, 127.652, 127.512, 127.163, 126.986, 125.518, 123.072, 122.720, 121.679, 144.186 (td, \(^1J = 20.3\) Hz, \(^2J = 3.8\) Hz).

\(^{19}\text{F-NMR (376 MHz, CDCl}_3\)) \(\delta\): -138.444 (dd, \(^1J = 23.3\) Hz, \(^2J = 8.5\) Hz, 2F), -154.894 (t, \(J = 20.9\) Hz, 1F), -162.728 – -162.867 (m, 2F).

9-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)phenanthrene (5.6)

![Chemical structure of 9-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)phenanthrene](image)

Chemical Formula: C\(_{26}\)H\(_{13}\)F\(_5\)
Molecular Weight: 420.38

A 250 mL flask with magnetic stir bar was placed with 1-bromo-2-pentafluorophenyl benzene (0.814 g, 2.5 mmol), 9-phenanthrene boronic acid (0.695 g, 3.1 mmol), potassium carbonate (0.501 g, 3.5 mmol), 1,4-dioxane (30 mL) and water (13 mL). The obtained mixture was flushed thoroughly with nitrogen and heated up in oil bath. After the addition of Pd(PPh\(_3\))\(_4\) (0.030 g, 1%), the resulting solution was gently refluxed overnight (~ 12h) and TLC indicated that the starting material 1-bromo-2-pentafluorophenyl benzene was completely consumed.

The resulting solution was cooled to room temperature and well mixed with silica gel (~ 5g). After the removal of solvent, the powder was placed at the top of silica gel column to elute (eluent:
hexanes). The fractions containing the main product were combined and condensed, giving a sticky oil. Kugelrohr distillation was applied to remove more solvent, giving sticky solid (0.333 g) as product. It was not pure and was used in the PCDHF step directly.

$^{1}$H-NMR (400 MHz, CDCl$_3$) δ: 8.642 – 8.601 (m, 2H), 7.803 (dd, $^1J$ = 8.0 Hz, $^2J$ = 1.6 Hz, 1H), 7.596 – 7.546 (m, 8H), 7.473 – 7.396 (m, 2H).

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -139.148 (dd, $^1J$ = 24.1 Hz, $^2J$ = 7.9 Hz, 1F), -139.977 (dd, $^1J$ = 23.7 Hz, $^2J$ = 8.3 Hz, 1F), -155.114 (t, $J$ = 21.0 Hz, 1F), -162.193 - -162.337 (m, 1F), - 162.454 - -162.599 (m, 1F).

1,2,3,4-tetrafluorodibenzo[g,p]chrysene (5.3)

![Chemical Structure]

Chemical Formula: $\text{C}_{26}\text{H}_{12}\text{F}_4$
Molecular Weight: 400.38

A quartz vessel was charged with 9-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)phenanthrene (1.002 g, 2.5 mmol), which was dissolved in acetonitrile (100 mL). The solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps for 24 hours. At that time, the solution was mixed again with silica gel (~ 2g) and the solvent was removed by
rotary evaporation. The yellow powder obtained was placed on the top of silica gel column and eluted (eluent: hexanes: EtOAc = 20:1). Fractions containing the pure product were combined and condensed, giving white crystals (0.212 g, 0.53 mmol, 21 % overall yield) as final product.

**M.P.:** 225.0 – 229.5 °C.

**1H-NMR (400 MHz, DMSO-D6) δ:** 8.847 – 8.726 (m, 3H), 8.572 – 8.506 (m, 2H), 7.868 – 7.583 (m, 6H), 7.601 (t, J = 7.4 Hz, 1H).

**19F-NMR (376 MHz, DMSO-D6) δ:** -127.877 - -128.008 (m, 1F), -140.698 (ddd, 1J = 21.8 Hz, 2J = 12.0 Hz, 2J = 2.6 Hz, 1F), -125.329 (ddd, 1J = 22.9 Hz, 2J = 22.9 Hz, 2J = 3.0 Hz, 1F), -157.737 (ddd, 1J = 22.2 Hz, 2J = 22.2 Hz, 2J = 3.0 Hz, 1F).
Table 1. Crystal data and structure refinement for compound 5.3.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>5.3</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{26}H_{12}F_{4}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>400.36</td>
</tr>
<tr>
<td>Temperature</td>
<td>105(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2(1)/n</td>
</tr>
</tbody>
</table>
Unit cell dimensions

\[ a = 7.4838(5) \text{ Å} \quad \text{alpha} = 90 \text{ deg.} \]
\[ b = 19.2635(13) \text{ Å} \quad \text{beta} = 91.304(2) \text{ deg.} \]
\[ c = 11.8041(8) \text{ Å} \quad \text{gamma} = 90 \text{ deg.} \]

Volume \hfill 1701.3(2) \text{ Å}^3

Z, Calculated density \hfill 4, 1.563 \text{ Mg/m}^3

Absorption coefficient \hfill 0.120 \text{ mm}^{-1}

F(000) \hfill 816

Crystal size \hfill 0.350 \times 0.300 \times 0.250 \text{ mm}

Theta range for data collection \hfill 2.024 \text{ to } 25.048 \text{ deg.}

Limiting indices \hfill -8 \leq h \leq 8, -22 \leq k \leq 22, -14 \leq l \leq 14

Reflections collected / unique \hfill 27243 / 3002 [R(int) = 0.0356]

Completeness to theta = 25.048 \hfill 99.8 \%

Absorption correction \hfill \text{Semi-empirical from equivalents}

Max. and min. transmission \hfill 0.971 \text{ and } 0.910

Refinement method \hfill \text{Full-matrix least-squares on } F^2

Data / restraints / parameters \hfill 3002 / 0 / 271

Goodness-of-fit on \text{F}^2 \hfill 0.966

Final R indices [I>2\text{sigma(I)}] \hfill R1 = 0.0361, wR2 = 0.1216

R indices (all data) \hfill R1 = 0.0446, wR2 = 0.1337

Extinction coefficient \hfill \text{n/a}

Largest diff. peak and hole \hfill 0.255 \text{ and } -0.191 \text{ e.Å}^{-3}
Table 2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for compound 53. U(eq) is defined as one third of the trace of the orthogonalized \( U_{ij} \) tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>4696</td>
<td>1183</td>
<td>5753</td>
<td>28</td>
</tr>
<tr>
<td>F(2)</td>
<td>4444</td>
<td>568</td>
<td>3746</td>
<td>35</td>
</tr>
<tr>
<td>F(3)</td>
<td>5469</td>
<td>1245</td>
<td>1847</td>
<td>37</td>
</tr>
<tr>
<td>F(4)</td>
<td>6615</td>
<td>2534</td>
<td>1948</td>
<td>36</td>
</tr>
<tr>
<td>C(1)</td>
<td>5383</td>
<td>1521</td>
<td>4864</td>
<td>23</td>
</tr>
<tr>
<td>C(2)</td>
<td>5173</td>
<td>1202</td>
<td>3828</td>
<td>26</td>
</tr>
<tr>
<td>C(3)</td>
<td>5669</td>
<td>1551</td>
<td>2866</td>
<td>27</td>
</tr>
<tr>
<td>C(4)</td>
<td>6297</td>
<td>2215</td>
<td>2946</td>
<td>25</td>
</tr>
<tr>
<td>C(5)</td>
<td>6557</td>
<td>2560</td>
<td>3988</td>
<td>21</td>
</tr>
<tr>
<td>C(6)</td>
<td>7126</td>
<td>3281</td>
<td>4088</td>
<td>21</td>
</tr>
<tr>
<td>C(7)</td>
<td>7897</td>
<td>3648</td>
<td>3188</td>
<td>24</td>
</tr>
<tr>
<td>C(8)</td>
<td>8400</td>
<td>4331</td>
<td>3299</td>
<td>27</td>
</tr>
<tr>
<td>C(9)</td>
<td>8185</td>
<td>4673</td>
<td>4327</td>
<td>26</td>
</tr>
<tr>
<td>C(10)</td>
<td>7468</td>
<td>4323</td>
<td>5232</td>
<td>23</td>
</tr>
<tr>
<td>C(11)</td>
<td>6892</td>
<td>3628</td>
<td>5140</td>
<td>19</td>
</tr>
<tr>
<td>C(12)</td>
<td>6326</td>
<td>3235</td>
<td>6133</td>
<td>18</td>
</tr>
<tr>
<td>C(13)</td>
<td>5812</td>
<td>3563</td>
<td>7195</td>
<td>18</td>
</tr>
<tr>
<td>C(14)</td>
<td>5035</td>
<td>4232</td>
<td>7224</td>
<td>20</td>
</tr>
<tr>
<td>C(15)</td>
<td>4509</td>
<td>4530</td>
<td>8220</td>
<td>23</td>
</tr>
<tr>
<td>C(16)</td>
<td>4720</td>
<td>4166</td>
<td>9238</td>
<td>23</td>
</tr>
<tr>
<td>C(17)</td>
<td>5374</td>
<td>3499</td>
<td>9233</td>
<td>21</td>
</tr>
<tr>
<td>C(18)</td>
<td>5909</td>
<td>3178</td>
<td>8223</td>
<td>17</td>
</tr>
<tr>
<td>C(19)</td>
<td>6552</td>
<td>2464</td>
<td>8199</td>
<td>18</td>
</tr>
<tr>
<td>C(20)</td>
<td>6977</td>
<td>2096</td>
<td>9198</td>
<td>21</td>
</tr>
<tr>
<td>C(21)</td>
<td>7638</td>
<td>1432</td>
<td>9161</td>
<td>23</td>
</tr>
<tr>
<td>C(22)</td>
<td>7955</td>
<td>1121</td>
<td>8118</td>
<td>24</td>
</tr>
<tr>
<td>C(23)</td>
<td>7508</td>
<td>1464</td>
<td>7129</td>
<td>22</td>
</tr>
<tr>
<td>C(24)</td>
<td>6743</td>
<td>2132</td>
<td>7140</td>
<td>18</td>
</tr>
<tr>
<td>C(25)</td>
<td>6382</td>
<td>2517</td>
<td>6095</td>
<td>18</td>
</tr>
<tr>
<td>C(26)</td>
<td>6167</td>
<td>2181</td>
<td>4990</td>
<td>19</td>
</tr>
<tr>
<td>Bond</td>
<td>Length [Å]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(1)-C(1)</td>
<td>1.3474(19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(2)-C(2)</td>
<td>1.341(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(3)-C(3)</td>
<td>1.3452(18)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(4)-C(4)</td>
<td>1.3537(19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.374(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1)-C(26)</td>
<td>1.405(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.377(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.366(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.408(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5)-C(26)</td>
<td>1.426(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.458(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.410(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6)-C(11)</td>
<td>1.423(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td>1.374(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-H(7)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td>1.394(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(8)-H(8)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9)-C(10)</td>
<td>1.382(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9)-H(9)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(10)-C(11)</td>
<td>1.411(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(10)-H(10)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(11)-C(12)</td>
<td>1.466(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(12)-C(25)</td>
<td>1.385(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(12)-C(13)</td>
<td>1.463(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(13)-C(14)</td>
<td>1.414(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(13)-C(18)</td>
<td>1.422(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(14)-C(15)</td>
<td>1.375(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(14)-H(14)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(15)-C(16)</td>
<td>1.397(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(15)-H(15)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(16)-C(17)</td>
<td>1.375(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(16)-H(16)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(17)-C(18)</td>
<td>1.410(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(17)-H(17)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(18)-C(19)</td>
<td>1.457(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(19)-C(20)</td>
<td>1.407(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(19)-C(24)</td>
<td>1.414(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(20)-C(21)</td>
<td>1.372(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(20)-H(20)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(21)-C(22)</td>
<td>1.395(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(21)-H(21)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(22)-C(23)</td>
<td>1.376(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bond</td>
<td>Length (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
<td>------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(22)-H(22)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(23)-C(24)</td>
<td>1.410(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(23)-H(23)</td>
<td>0.9500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(24)-C(25)</td>
<td>1.459(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(25)-C(26)</td>
<td>1.461(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(1)-C(1)-C(2)</td>
<td>115.97(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(1)-C(1)-C(26)</td>
<td>121.36(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2)-C(1)-C(26)</td>
<td>122.56(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(2)-C(2)-C(1)</td>
<td>120.69(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(2)-C(2)-C(3)</td>
<td>120.12(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>119.16(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(3)-C(3)-C(4)</td>
<td>120.19(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(3)-C(3)-C(2)</td>
<td>119.81(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4)-C(3)-C(2)</td>
<td>119.95(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(4)-C(4)-C(3)</td>
<td>115.60(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(4)-C(4)-C(5)</td>
<td>121.54(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3)-C(4)-C(5)</td>
<td>122.84(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4)-C(5)-C(26)</td>
<td>117.17(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4)-C(5)-C(6)</td>
<td>123.72(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(26)-C(5)-C(6)</td>
<td>119.07(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-C(6)-C(11)</td>
<td>118.87(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-C(6)-C(5)</td>
<td>122.69(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(11)-C(6)-C(5)</td>
<td>118.44(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(8)-C(7)-C(6)</td>
<td>121.61(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(8)-C(7)-H(7)</td>
<td>119.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6)-C(7)-H(7)</td>
<td>119.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-C(8)-C(9)</td>
<td>119.88(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-C(8)-H(8)</td>
<td>120.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9)-C(8)-H(8)</td>
<td>120.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(10)-C(9)-C(8)</td>
<td>119.81(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(10)-C(9)-H(9)</td>
<td>120.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(8)-C(9)-H(9)</td>
<td>120.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9)-C(10)-C(11)</td>
<td>121.81(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9)-C(10)-H(10)</td>
<td>119.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(11)-C(10)-H(10)</td>
<td>119.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(10)-C(11)-C(6)</td>
<td>117.98(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(10)-C(11)-C(12)</td>
<td>121.41(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6)-C(11)-C(12)</td>
<td>119.96(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(25)-C(12)-C(13)</td>
<td>117.87(13)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(25)-C(12)-C(11)</td>
<td>118.65(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(13)-C(12)-C(11)</td>
<td>123.35(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(14)-C(13)-C(18)</td>
<td>117.85(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(14)-C(13)-C(12)</td>
<td>121.99(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(18)-C(13)-C(12)</td>
<td>119.83(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(15)-C(14)-C(13)</td>
<td>121.84(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
C(15)-C(14)-H(14)   119.1
C(13)-C(14)-H(14)   119.1
C(14)-C(15)-C(16)   119.79(15)
C(14)-C(15)-H(15)   120.1
C(16)-C(15)-H(15)   120.1
C(17)-C(16)-C(15)   119.89(14)
C(17)-C(16)-H(16)   120.1
C(15)-C(16)-H(16)   120.1
C(16)-C(17)-C(18)   121.46(14)
C(16)-C(17)-H(17)   119.3
C(18)-C(17)-H(17)   119.3
C(17)-C(18)-C(13)   118.91(14)
C(17)-C(18)-C(19)   122.06(14)
C(13)-C(18)-C(19)   119.03(14)
C(20)-C(19)-C(24)   119.19(14)
C(20)-C(19)-C(18)   121.87(14)
C(24)-C(19)-C(18)   118.94(14)
C(21)-C(20)-C(19)   121.19(15)
C(21)-C(20)-H(20)   119.4
C(19)-C(20)-H(20)   119.4
C(20)-C(21)-C(22)   119.85(15)
C(20)-C(21)-H(21)   120.1
C(22)-C(21)-H(21)   120.1
C(23)-C(22)-C(21)   119.95(15)
C(23)-C(22)-H(22)   120.0
C(21)-C(22)-H(22)   120.0
C(22)-C(23)-C(24)   121.49(15)
C(22)-C(23)-H(23)   119.3
C(24)-C(23)-H(23)   119.3
C(23)-C(24)-C(19)   118.04(14)
C(23)-C(24)-C(25)   121.60(14)
C(19)-C(24)-C(25)   119.81(14)
C(12)-C(25)-C(24)   119.01(13)
C(12)-C(25)-C(26)   117.98(14)
C(24)-C(25)-C(26)   122.92(14)
C(1)-C(26)-C(5)     117.87(14)
C(1)-C(26)-C(25)    122.18(14)
C(5)-C(26)-C(25)    119.50(15)

Symmetry transformations used to generate equivalent atoms:
Table 4. Anisotropic displacement parameters (A^2 x 10^3) for compound 5.3.
The anisotropic displacement factor exponent takes the form:
\[-2 \pi^2 \left[ h^2 a^{*2} U_{11} + \ldots + 2 h k a^* b^* U_{12} \right] \]

<table>
<thead>
<tr>
<th></th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>35(1)</td>
<td>26(1)</td>
<td>24(1)</td>
<td>-4(1)</td>
<td>6(1)</td>
<td>-6(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>37(1)</td>
<td>32(1)</td>
<td>36(1)</td>
<td>-15(1)</td>
<td>-1(1)</td>
<td>-3(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>21(1)</td>
<td>-17(1)</td>
<td>-5(1)</td>
<td>6(1)</td>
</tr>
<tr>
<td>F(4)</td>
<td>46(1)</td>
<td>50(1)</td>
<td>12(1)</td>
<td>0(1)</td>
<td>2(1)</td>
<td>3(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>21(1)</td>
<td>28(1)</td>
<td>20(1)</td>
<td>-3(1)</td>
<td>3(1)</td>
<td>4(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>20(1)</td>
<td>26(1)</td>
<td>31(1)</td>
<td>-9(1)</td>
<td>-2(1)</td>
<td>3(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>24(1)</td>
<td>40(1)</td>
<td>17(1)</td>
<td>-12(1)</td>
<td>-4(1)</td>
<td>8(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>24(1)</td>
<td>37(1)</td>
<td>15(1)</td>
<td>-1(1)</td>
<td>0(1)</td>
<td>8(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>16(1)</td>
<td>32(1)</td>
<td>16(1)</td>
<td>-1(1)</td>
<td>1(1)</td>
<td>6(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>15(1)</td>
<td>30(1)</td>
<td>17(1)</td>
<td>3(1)</td>
<td>1(1)</td>
<td>6(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>20(1)</td>
<td>37(1)</td>
<td>17(1)</td>
<td>5(1)</td>
<td>3(1)</td>
<td>8(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>21(1)</td>
<td>38(1)</td>
<td>23(1)</td>
<td>13(1)</td>
<td>4(1)</td>
<td>5(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>20(1)</td>
<td>27(1)</td>
<td>31(1)</td>
<td>8(1)</td>
<td>0(1)</td>
<td>4(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>20(1)</td>
<td>27(1)</td>
<td>21(1)</td>
<td>3(1)</td>
<td>1(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>15(1)</td>
<td>27(1)</td>
<td>16(1)</td>
<td>3(1)</td>
<td>-1(1)</td>
<td>4(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>15(1)</td>
<td>23(1)</td>
<td>15(1)</td>
<td>1(1)</td>
<td>-1(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>16(1)</td>
<td>21(1)</td>
<td>16(1)</td>
<td>-1(1)</td>
<td>0(1)</td>
<td>-4(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>19(1)</td>
<td>22(1)</td>
<td>20(1)</td>
<td>2(1)</td>
<td>-1(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>22(1)</td>
<td>21(1)</td>
<td>26(1)</td>
<td>-3(1)</td>
<td>2(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>26(1)</td>
<td>24(1)</td>
<td>19(1)</td>
<td>-6(1)</td>
<td>5(1)</td>
<td>-5(1)</td>
</tr>
<tr>
<td>C(17)</td>
<td>24(1)</td>
<td>23(1)</td>
<td>16(1)</td>
<td>0(1)</td>
<td>0(1)</td>
<td>-6(1)</td>
</tr>
<tr>
<td>C(18)</td>
<td>14(1)</td>
<td>21(1)</td>
<td>17(1)</td>
<td>-1(1)</td>
<td>-1(1)</td>
<td>-5(1)</td>
</tr>
<tr>
<td>C(19)</td>
<td>14(1)</td>
<td>22(1)</td>
<td>17(1)</td>
<td>1(1)</td>
<td>1(1)</td>
<td>-4(1)</td>
</tr>
<tr>
<td>C(20)</td>
<td>20(1)</td>
<td>26(1)</td>
<td>18(1)</td>
<td>1(1)</td>
<td>1(1)</td>
<td>-5(1)</td>
</tr>
<tr>
<td>C(21)</td>
<td>20(1)</td>
<td>26(1)</td>
<td>22(1)</td>
<td>7(1)</td>
<td>-3(1)</td>
<td>-4(1)</td>
</tr>
<tr>
<td>C(22)</td>
<td>20(1)</td>
<td>21(1)</td>
<td>32(1)</td>
<td>5(1)</td>
<td>3(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(23)</td>
<td>20(1)</td>
<td>24(1)</td>
<td>22(1)</td>
<td>-2(1)</td>
<td>4(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(24)</td>
<td>15(1)</td>
<td>22(1)</td>
<td>18(1)</td>
<td>0(1)</td>
<td>2(1)</td>
<td>-4(1)</td>
</tr>
<tr>
<td>C(25)</td>
<td>14(1)</td>
<td>25(1)</td>
<td>16(1)</td>
<td>-1(1)</td>
<td>3(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(26)</td>
<td>16(1)</td>
<td>23(1)</td>
<td>18(1)</td>
<td>-2(1)</td>
<td>0(1)</td>
<td>5(1)</td>
</tr>
</tbody>
</table>
Biphenyl-3-boronic acid (5.8)

\[
\begin{align*}
\text{Chemical Formula: C}_{12}\text{H}_{11}\text{BO}_2 \\
\text{Molecular Weight: 198.03}
\end{align*}
\]

An oven dried 250 mL flask equipped with magnetic stir bar was flushed with nitrogen and charged with 3-bromo-1,1'-biphenyl (3.990 g, 17 mmol) and THF (50 mL). The solution was cooled down to -78 °C and \( n \)-BuLi solution (7.5 mL, 2.5M in hexane, 18.8 mmol) was added dropwise. After being stirred for approximately 30 min, B(OiPr)\(_3\) (4.854 g, 25.8 mmol) was added to the solution to give a white suspension.

The resulting mixture was stirred overnight (about 12h) and the temperature was raised up gradually from -78 °C to room temperature. The resulting mixture was treated with hydrochloric acid (1M, 50 mL) to form two layers. The aqueous phase was extracted with diethyl ether (100 mL x 3) and organic phases were combined together. After drying with anhydrous MgSO\(_4\), the filtrate was concentrated to dryness and a white powder (5.212 g) was obtained as crude product. The crude product was recrystallized from water, giving white crystals (3.017 g, 15 mmol, 88% yield) as final product.

**M.P.** 202.0 – 204.0 °C

**\(^1\)H-NMR (400 MHz, DMSO):** 8.123 (app t, \( J = 1.2 \) Hz, 1H), 7.788 (app dt, \( ^1J = 7.2 \) Hz, \( ^2J = 1.2 \) Hz, 1H), 7.709 – 7.651 (m, 3H), 7.495 – 7.421 (m, 3H), 7.362 (app tt, \( ^1J = 7.2 \) Hz, \( ^2J = 1.2 \) Hz, 1H).
\(^{13}\text{C}-\text{NMR (100 MHz, DMSO)}\): 140.482, 139.043, 133.103, 132.402, 128.780, 128.212, 127.921, 127.143, 126.579.


\(2,3,4,5,6\)-pentafluoro-1,1':2',1''':3'',1'''''-quaterphenyl (5.9)

![Chemical structure](image)

**Chemical Formula:** C\(_{24}\)H\(_{13}\)F\(_5\)

**Molecular Weight:** 396.36

A 100 mL flask with magnetic stir bar was charged with 2'-bromo-2,3,4,5,6-pentafluoro-1,1'-biphenyl (1.633 g, 5 mmol), biphenyl-3-boronic acid (1.500 g, 7.5 mmol, 1.5 eq), potassium carbonate (1.055 g, 7.5 mmol, 1.5 eq), toluene (40 mL) and ethanol (10 mL). The obtained mixture was heated to 90 °C under nitrogen atmosphere and a condenser was attached at the top to give a gentle reflux. Tetrakis(triphenylphosphine)palladium(0) (58.620 mg, 0.05 mmol, 1%) was added at last.

After being stirred for approximately 12 hours, TLC indicated that starting material (1-bromo-2-(pentafluorophenyl)benzene) was completely consumed. Then the reaction mixture was cooled down and mixed together with silica gel (~5 g). After the solvent was removed under vacuum, the resulting yellow powder was placed on a silica gel column to elute (Hexanes). Fractions containing the product was combined and concentrated, giving colorless oil (1.178 g, 3 mmol, 60% yield) as
final product.

$^1$H-NMR (400 MHz, CDCl$_3$): 7.659 – 7.314 (m, 12H), 6.080 (d, $J = 7.2$ Hz, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): 145.491 (d, $J = 230$ Hz), 144.342, 141.133, 140.833, 140.678, 140.566 (d, $J = 251.6$ Hz), 137.694 (d, $J = 250.8$ Hz), 131.130, 130.392, 129.836, 129.202, 128.838, 128.530, 127.621, 127.486, 127.391, 127.317, 127.046, 126.258, 125.000, 115.954.

1,2,3,4-tetrafluoro-7-phenyltriphenylene (5.11)

A quartz vessel (approximately 40 cm x 25 mm) was charged with 2,3,4,5,6-pentafluoro-1,1';2',1";3",1"'-quaterphenyl ($\lambda_{\text{max}} = 237$ - 247 nm) (0.396 g, 1.0 mmol) and THF (100 mL). The resulting solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps for 3 days (72 hours) and then GC-MS indicated no starting material remained.

The solvent was slowly evaporated and yellow crystals were formed (0.136 g, 0.36 mmol, 36 % yield). Some large crystals was picked out and turned over to Dr. Bunge’s group to determine the structure via X-ray crystallography.
M.P. Slowly sublimated above 180 °C, melted completely at 189.5 – 191.5 °C.

\( ^1H\)-NMR (400 MHz, CDCl\(_3\)): 8.909 – 8.861 (m, 2H), 8.746 (s, 1H), 8.647 (d, \( J = 8.0 \) Hz, 1H), 7.834 (d, \( J = 8.8 \) Hz, 1H), 7.768 – 7.747 (m, 2H), 7.699 – 7.606 (m, 2H), 7.543 – 7.498 (m, 2H), 7.450 – 7.407 (m, 1H).

\( ^{13}C\)-NMR (100 MHz, CDCl\(_3\)): 146.168 (d, \( J = 250 \) Hz), 141.147, 140.539, 139.558 (d, \( J = 252 \) Hz), 130.836, 130.483, 129.078, 128.549, 128.381, 128.091, 128.006, 127.723, 127.432, 126.893, 126.877, 126.252, 124.963, 123.309, 121.567, 116.288.

\( ^{19}F\)-NMR (376 MHz, CDCl\(_3\)): -138.287 - -138.501 (m, 2F), -157.584 - -157.806 (m, 2F).

Table 1. Crystal data and structure refinement for compound 5.11.

Identification code 5.11
Empirical formula          \( \text{C}_2\text{H}_12\text{F}_4 \)

Formula weight             376.34

Temperature               296(2) K

Wavelength                0.71073 \( \text{\AA} \)

Crystal system, space group Monoclinic, \( \text{P } 21/\text{n} \)

Unit cell dimensions 
\( a = 15.0409(11) \text{\AA} \)  \( \alpha = 90 \text{ deg.} \)
\( b = 6.7993(5) \text{\AA} \)  \( \beta = 113.666(3) \text{ deg.} \)
\( c = 17.0437(11) \text{\AA} \)  \( \gamma = 90 \text{ deg.} \)

Volume                      1596.4(2) \( \text{\AA}^3 \)

Z, Calculated density   4, 1.566 \( \text{Mg/m}^3 \)

Absorption coefficient  0.123 \( \text{mm}^{-1} \)

\( F(000) \)                  768

Crystal size                0.250 x 0.200 x 0.150 mm

Theta range for data collection 1.529 to 25.050 deg.

Limiting indices 
\(-17 \leq h \leq 17, -8 \leq k \leq 8, -17 \leq l \leq 20\)

Reflections collected / unique 13753 / 2817 \( [R(\text{int}) = 0.0350] \)

Completeness to theta = 25.242 97.5 %

Absorption correction Semi-empirical from equivalents

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 2817 / 80 / 253

Goodness-of-fit on \( F^2 \) 0.841

Final R indices \([I>2\sigma(I)]\)  \( R1 = 0.0349, wR2 = 0.1037 \)

R indices (all data)  \( R1 = 0.0499, wR2 = 0.1289 \)

Extinction coefficient n/a
Largest diff. peak and hole 0.306 and -0.355 e.A^-3
Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for compound **5.11**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>-1776(1)</td>
<td>9214(2)</td>
<td>9097(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>-3632(1)</td>
<td>9326(2)</td>
<td>8730(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>-4948(1)</td>
<td>9579(2)</td>
<td>7074(1)</td>
<td>28(1)</td>
</tr>
<tr>
<td>F(4)</td>
<td>-4389(1)</td>
<td>9632(2)</td>
<td>5814(1)</td>
<td>33(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>-2360(1)</td>
<td>9368(3)</td>
<td>8256(1)</td>
<td>16(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>-3332(1)</td>
<td>9409(3)</td>
<td>8088(1)</td>
<td>18(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>-3995(1)</td>
<td>9517(3)</td>
<td>7253(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>-3673(1)</td>
<td>9548(3)</td>
<td>6606(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>-2685(1)</td>
<td>9500(2)</td>
<td>6747(1)</td>
<td>14(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>-2349(1)</td>
<td>9454(2)</td>
<td>6043(1)</td>
<td>14(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>-2997(1)</td>
<td>9449(3)</td>
<td>5168(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>-2665(1)</td>
<td>9293(3)</td>
<td>4529(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>-1678(1)</td>
<td>9126(3)</td>
<td>4726(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>-1032(1)</td>
<td>9177(2)</td>
<td>5568(1)</td>
<td>17(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>-1341(1)</td>
<td>9363(2)</td>
<td>6243(1)</td>
<td>14(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>-633(1)</td>
<td>9477(2)</td>
<td>7138(1)</td>
<td>13(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>368(1)</td>
<td>9606(2)</td>
<td>7330(1)</td>
<td>14(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>1068(1)</td>
<td>9730(2)</td>
<td>8160(1)</td>
<td>15(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>745(1)</td>
<td>9736(3)</td>
<td>8825(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>-227(1)</td>
<td>9627(3)</td>
<td>8658(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(17)</td>
<td>-947(1)</td>
<td>9502(2)</td>
<td>7814(1)</td>
<td>14(1)</td>
</tr>
<tr>
<td>C(18)</td>
<td>-1996(1)</td>
<td>9443(2)</td>
<td>7618(1)</td>
<td>14(1)</td>
</tr>
<tr>
<td>C(19)</td>
<td>2121(1)</td>
<td>9870(3)</td>
<td>8342(1)</td>
<td>14(1)</td>
</tr>
<tr>
<td>C(20)</td>
<td>2497(1)</td>
<td>9037(3)</td>
<td>7788(1)</td>
<td>16(1)</td>
</tr>
<tr>
<td>C(21)</td>
<td>3478(1)</td>
<td>9175(2)</td>
<td>7960(1)</td>
<td>17(1)</td>
</tr>
<tr>
<td>C(22)</td>
<td>4108(1)</td>
<td>10135(3)</td>
<td>8694(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(23)</td>
<td>3748(1)</td>
<td>10952(3)</td>
<td>9251(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(24)</td>
<td>2765(1)</td>
<td>10829(3)</td>
<td>9078(1)</td>
<td>17(1)</td>
</tr>
</tbody>
</table>
Table 3. Bond lengths [Å] and angles [deg] for compound 5.11.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)-C(1)</td>
<td>1.352(2)</td>
</tr>
<tr>
<td>F(2)-C(2)</td>
<td>1.3427(19)</td>
</tr>
<tr>
<td>F(3)-C(3)</td>
<td>1.3420(19)</td>
</tr>
<tr>
<td>F(4)-C(4)</td>
<td>1.349(2)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.371(2)</td>
</tr>
<tr>
<td>C(1)-C(18)</td>
<td>1.401(2)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.373(3)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.371(3)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.407(2)</td>
</tr>
<tr>
<td>C(5)-C(18)</td>
<td>1.430(2)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.477(2)</td>
</tr>
<tr>
<td>C(6)-C(11)</td>
<td>1.416(2)</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.416(2)</td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td>1.374(2)</td>
</tr>
<tr>
<td>C(7)-H(7)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td>1.388(2)</td>
</tr>
<tr>
<td>C(8)-H(8)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(9)-C(10)</td>
<td>1.374(2)</td>
</tr>
<tr>
<td>C(9)-H(9)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(10)-C(11)</td>
<td>1.409(2)</td>
</tr>
<tr>
<td>C(10)-H(10)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(11)-C(12)</td>
<td>1.470(2)</td>
</tr>
<tr>
<td>C(12)-C(13)</td>
<td>1.409(2)</td>
</tr>
<tr>
<td>C(12)-C(17)</td>
<td>1.411(2)</td>
</tr>
<tr>
<td>C(13)-C(14)</td>
<td>1.386(2)</td>
</tr>
<tr>
<td>C(13)-H(13)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(14)-C(15)</td>
<td>1.401(2)</td>
</tr>
<tr>
<td>C(14)-C(19)</td>
<td>1.490(2)</td>
</tr>
<tr>
<td>C(15)-C(16)</td>
<td>1.374(2)</td>
</tr>
<tr>
<td>C(15)-H(15)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(16)-C(17)</td>
<td>1.414(2)</td>
</tr>
<tr>
<td>C(16)-H(16)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(17)-C(18)</td>
<td>1.475(2)</td>
</tr>
<tr>
<td>C(19)-C(24)</td>
<td>1.400(2)</td>
</tr>
<tr>
<td>C(19)-C(20)</td>
<td>1.401(2)</td>
</tr>
<tr>
<td>C(20)-C(21)</td>
<td>1.388(2)</td>
</tr>
<tr>
<td>C(20)-H(20)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(21)-C(22)</td>
<td>1.391(3)</td>
</tr>
<tr>
<td>C(21)-H(21)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(22)-C(23)</td>
<td>1.385(3)</td>
</tr>
<tr>
<td>C(22)-H(22)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(23)-C(24)</td>
<td>1.389(2)</td>
</tr>
<tr>
<td>Bond</td>
<td>Distance</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------</td>
</tr>
<tr>
<td>C(23)-H(23)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(24)-H(24)</td>
<td>0.9300</td>
</tr>
<tr>
<td>F(1)-C(1)-C(2)</td>
<td>114.09(14)</td>
</tr>
<tr>
<td>F(1)-C(1)-C(18)</td>
<td>122.29(15)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(18)</td>
<td>123.61(16)</td>
</tr>
<tr>
<td>F(2)-C(2)-C(1)</td>
<td>120.53(15)</td>
</tr>
<tr>
<td>F(2)-C(2)-C(3)</td>
<td>120.30(15)</td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>119.17(16)</td>
</tr>
<tr>
<td>F(3)-C(3)-C(4)</td>
<td>120.46(16)</td>
</tr>
<tr>
<td>F(3)-C(3)-C(2)</td>
<td>120.20(15)</td>
</tr>
<tr>
<td>C(4)-C(3)-C(2)</td>
<td>119.34(16)</td>
</tr>
<tr>
<td>F(4)-C(4)-C(3)</td>
<td>114.08(15)</td>
</tr>
<tr>
<td>F(4)-C(4)-C(5)</td>
<td>122.42(15)</td>
</tr>
<tr>
<td>C(3)-C(4)-C(5)</td>
<td>123.50(16)</td>
</tr>
<tr>
<td>C(4)-C(5)-C(18)</td>
<td>117.00(15)</td>
</tr>
<tr>
<td>C(4)-C(5)-C(6)</td>
<td>122.96(15)</td>
</tr>
<tr>
<td>C(18)-C(5)-C(6)</td>
<td>120.02(15)</td>
</tr>
<tr>
<td>C(11)-C(6)-C(7)</td>
<td>118.08(15)</td>
</tr>
<tr>
<td>C(11)-C(6)-C(5)</td>
<td>119.23(15)</td>
</tr>
<tr>
<td>C(7)-C(6)-C(5)</td>
<td>122.68(15)</td>
</tr>
<tr>
<td>C(8)-C(7)-C(6)</td>
<td>121.35(16)</td>
</tr>
<tr>
<td>C(8)-C(7)-H(7)</td>
<td>119.3</td>
</tr>
<tr>
<td>C(6)-C(7)-H(7)</td>
<td>119.3</td>
</tr>
<tr>
<td>C(7)-C(8)-C(9)</td>
<td>120.53(16)</td>
</tr>
<tr>
<td>C(7)-C(8)-H(8)</td>
<td>119.7</td>
</tr>
<tr>
<td>C(9)-C(8)-H(8)</td>
<td>119.7</td>
</tr>
<tr>
<td>C(10)-C(9)-C(8)</td>
<td>119.38(16)</td>
</tr>
<tr>
<td>C(10)-C(9)-H(9)</td>
<td>120.3</td>
</tr>
<tr>
<td>C(8)-C(9)-H(9)</td>
<td>120.3</td>
</tr>
<tr>
<td>C(9)-C(10)-C(11)</td>
<td>121.88(16)</td>
</tr>
<tr>
<td>C(9)-C(10)-H(10)</td>
<td>119.1</td>
</tr>
<tr>
<td>C(11)-C(10)-H(10)</td>
<td>119.1</td>
</tr>
<tr>
<td>C(10)-C(11)-C(6)</td>
<td>118.70(15)</td>
</tr>
<tr>
<td>C(10)-C(11)-C(12)</td>
<td>120.82(15)</td>
</tr>
<tr>
<td>C(6)-C(11)-C(12)</td>
<td>120.47(15)</td>
</tr>
<tr>
<td>C(13)-C(12)-C(17)</td>
<td>119.10(15)</td>
</tr>
<tr>
<td>C(13)-C(12)-C(11)</td>
<td>120.42(15)</td>
</tr>
<tr>
<td>C(17)-C(12)-C(11)</td>
<td>120.47(15)</td>
</tr>
<tr>
<td>C(14)-C(13)-C(12)</td>
<td>122.98(15)</td>
</tr>
<tr>
<td>C(14)-C(13)-H(13)</td>
<td>118.5</td>
</tr>
<tr>
<td>C(12)-C(13)-H(13)</td>
<td>118.5</td>
</tr>
<tr>
<td>C(13)-C(14)-C(15)</td>
<td>117.25(16)</td>
</tr>
<tr>
<td>C(13)-C(14)-C(19)</td>
<td>121.65(15)</td>
</tr>
<tr>
<td>C(15)-C(14)-C(19)</td>
<td>121.09(15)</td>
</tr>
<tr>
<td>C(16)-C(15)-C(14)</td>
<td>121.15(16)</td>
</tr>
</tbody>
</table>
C(16)-C(15)-H(15)    119.4  
C(14)-C(15)-H(15)    119.4  
C(15)-C(16)-C(17)    122.12(16)  
C(15)-C(16)-H(16)    118.9  
C(17)-C(16)-H(16)    118.9  
C(12)-C(17)-C(16)    117.39(15)  
C(12)-C(17)-C(18)    119.55(15)  
C(16)-C(17)-C(18)    123.04(15)  
C(1)-C(18)-C(5)      117.34(16)  
C(1)-C(18)-C(17)     122.77(15)  
C(5)-C(18)-C(17)     119.88(15)  
C(24)-C(19)-C(20)    118.10(15)  
C(24)-C(19)-C(14)    120.78(15)  
C(20)-C(19)-C(14)    121.13(15)  
C(21)-C(20)-C(19)    120.88(15)  
C(21)-C(20)-H(20)    119.6  
C(19)-C(20)-H(20)    119.6  
C(20)-C(21)-C(22)    120.27(16)  
C(20)-C(21)-H(21)    119.9  
C(22)-C(21)-H(21)    119.9  
C(23)-C(22)-C(21)    119.47(16)  
C(23)-C(22)-H(22)    120.3  
C(21)-C(22)-H(22)    120.3  
C(22)-C(23)-C(24)    120.45(16)  
C(22)-C(23)-H(23)    119.8  
C(24)-C(23)-H(23)    119.8  
C(23)-C(24)-C(19)    120.84(16)  
C(23)-C(24)-H(24)    119.6  
C(19)-C(24)-H(24)    119.6

Symmetry transformations used to generate equivalent atoms:
Table 4. Anisotropic displacement parameters (A^2 x 10^3) for compound 5.11. The anisotropic displacement factor exponent takes the form:

\[-2 \pi^2 \left( h^2 a^*^2 U_{11} + \ldots + 2h k a^* b^* U_{12} \right)\]

<table>
<thead>
<tr>
<th></th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>17(1)</td>
<td>44(1)</td>
<td>14(1)</td>
<td>-1(1)</td>
<td>8(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>21(1)</td>
<td>31(1)</td>
<td>26(1)</td>
<td>0(1)</td>
<td>17(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>11(1)</td>
<td>44(1)</td>
<td>33(1)</td>
<td>5(1)</td>
<td>11(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>F(4)</td>
<td>10(1)</td>
<td>66(1)</td>
<td>21(1)</td>
<td>7(1)</td>
<td>2(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>16(1)</td>
<td>16(1)</td>
<td>17(1)</td>
<td>-1(1)</td>
<td>6(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>19(1)</td>
<td>16(1)</td>
<td>22(1)</td>
<td>0(1)</td>
<td>13(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>11(1)</td>
<td>19(1)</td>
<td>30(1)</td>
<td>1(1)</td>
<td>10(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>12(1)</td>
<td>22(1)</td>
<td>18(1)</td>
<td>2(1)</td>
<td>3(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>14(1)</td>
<td>10(1)</td>
<td>19(1)</td>
<td>-1(1)</td>
<td>7(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>14(1)</td>
<td>11(1)</td>
<td>17(1)</td>
<td>-1(1)</td>
<td>6(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>13(1)</td>
<td>24(1)</td>
<td>20(1)</td>
<td>-1(1)</td>
<td>5(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>19(1)</td>
<td>22(1)</td>
<td>14(1)</td>
<td>-2(1)</td>
<td>2(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>22(1)</td>
<td>20(1)</td>
<td>16(1)</td>
<td>-2(1)</td>
<td>10(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>13(1)</td>
<td>20(1)</td>
<td>19(1)</td>
<td>-1(1)</td>
<td>7(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>14(1)</td>
<td>10(1)</td>
<td>16(1)</td>
<td>0(1)</td>
<td>5(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>14(1)</td>
<td>11(1)</td>
<td>16(1)</td>
<td>1(1)</td>
<td>6(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>14(1)</td>
<td>17(1)</td>
<td>15(1)</td>
<td>-1(1)</td>
<td>8(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>14(1)</td>
<td>14(1)</td>
<td>19(1)</td>
<td>1(1)</td>
<td>7(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>14(1)</td>
<td>32(1)</td>
<td>12(1)</td>
<td>-1(1)</td>
<td>3(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>16(1)</td>
<td>31(1)</td>
<td>15(1)</td>
<td>-1(1)</td>
<td>8(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(17)</td>
<td>14(1)</td>
<td>13(1)</td>
<td>16(1)</td>
<td>0(1)</td>
<td>7(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(18)</td>
<td>13(1)</td>
<td>12(1)</td>
<td>19(1)</td>
<td>-1(1)</td>
<td>7(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(19)</td>
<td>12(1)</td>
<td>15(1)</td>
<td>15(1)</td>
<td>4(1)</td>
<td>4(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(20)</td>
<td>15(1)</td>
<td>17(1)</td>
<td>16(1)</td>
<td>1(1)</td>
<td>6(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(21)</td>
<td>16(1)</td>
<td>17(1)</td>
<td>21(1)</td>
<td>2(1)</td>
<td>10(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(22)</td>
<td>10(1)</td>
<td>20(1)</td>
<td>25(1)</td>
<td>6(1)</td>
<td>7(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(23)</td>
<td>15(1)</td>
<td>20(1)</td>
<td>16(1)</td>
<td>1(1)</td>
<td>1(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(24)</td>
<td>16(1)</td>
<td>18(1)</td>
<td>17(1)</td>
<td>1(1)</td>
<td>7(1)</td>
<td>2(1)</td>
</tr>
</tbody>
</table>
Table 5. Hydrogen coordinates \((x \times 10^4)\) and isotropic displacement parameters \((A^2 \times 10^3)\) for compound 5.11.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(7)</td>
<td>-3661</td>
<td>9552</td>
<td>5024</td>
<td>23</td>
</tr>
<tr>
<td>H(8)</td>
<td>-3104</td>
<td>9300</td>
<td>3959</td>
<td>24</td>
</tr>
<tr>
<td>H(9)</td>
<td>-1457</td>
<td>8981</td>
<td>4292</td>
<td>23</td>
</tr>
<tr>
<td>H(10)</td>
<td>-371</td>
<td>9086</td>
<td>5696</td>
<td>21</td>
</tr>
<tr>
<td>H(13)</td>
<td>568</td>
<td>9609</td>
<td>6880</td>
<td>17</td>
</tr>
<tr>
<td>H(15)</td>
<td>1196</td>
<td>9814</td>
<td>9390</td>
<td>25</td>
</tr>
<tr>
<td>H(16)</td>
<td>-416</td>
<td>9636</td>
<td>9114</td>
<td>24</td>
</tr>
<tr>
<td>H(20)</td>
<td>2083</td>
<td>8382</td>
<td>7298</td>
<td>19</td>
</tr>
<tr>
<td>H(21)</td>
<td>3716</td>
<td>8625</td>
<td>7583</td>
<td>21</td>
</tr>
<tr>
<td>H(22)</td>
<td>4766</td>
<td>10226</td>
<td>8809</td>
<td>23</td>
</tr>
<tr>
<td>H(23)</td>
<td>4166</td>
<td>11588</td>
<td>9744</td>
<td>22</td>
</tr>
<tr>
<td>H(24)</td>
<td>2531</td>
<td>11391</td>
<td>9456</td>
<td>20</td>
</tr>
</tbody>
</table>
An oven dried 250 mL flask was charged with 1,2-dibromobenzene (17.744 g, 75 mmol) and distilled dry THF (100 mL). Then $n$-BuLi solution (2.5M, 16 mL, 40 mmol) was added dropwise inside at -78°C under nitrogen atmosphere. The mixture was stirred overnight and the temperature was gradually allowed to rise up to room temperature.

Then the reaction was quenched with water (100 mL). After the organic phase was separated, the aqueous phase was extracted with diethyl ether (50 mL x 3) and combined together with the previous organic phase. The organic phase was dried over with anhydrous MgSO4. After the drying agent was removed by gravity filtration, the filtrate was mixed together with silica gel (~10g). Solvent was removed under vacuum and the yellow powder obtained was placed on a silica gel column to elute (hexanes). Fractions containing the product was combined and concentrated, giving white crystals (10.244 g, 33 mmol, 88% yield) as final product.

**M.P.** 72.0 – 75.0 °C

$^1$H-NMR (400 MHz, CDCl$_3$): 7.674 – 7.647 (m, 1H), 7.381 – 7.341 (m, 1H), 7.266 – 7.223 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): 142.012, 132.543, 130.942, 129.350, 127.081, 123.477.
References:
Chan, Khai Leok; Watkins, Scott E.; Mak, Chris S. K.; McKiernan, Mary J.; Towns, Carl R.; Pascu, Sofia I.; Holmes, Andrew B. *Chemical Communications*, 2005, *5766 – 5768*.
Cui, Jian-Fang; Huang, Hui; Wong, Henry N. C. *Synlett*, 2011, 1018 – 1022.
Ma, Jun; Li, Gaoqiang; Qiao, Yan; Tu, Jingxuan; Liu, Sha; Xu, Feng *Synlett*, 2015, Vol.26, 1991 - 1996

2,2’-Diodobiphenyl (5.14)

![2,2’-Diodobiphenyl](image)

Chemical Formula: C_{12}H_{8}I_{2}
Molecular Weight: 406.00

An oven dried 250 mL flask was charged with 2,2’-dibromobiphenyl (9.242 g, 30 mmol) and distillated dry THF (100 mL). Then n-BuLi solution (2.5M, 27 mL, 67 mmol, 110%) was added dropwise at -78 °C under a nitrogen atmosphere. After being stirred for 1h, a solution of iodine (15.247 g, 60 mmol) in THF (60 mL) was added slowly into the previous solution. The mixture was stirred overnight and the temperature was gradually raised up to room temperature.

The reaction solution was washed with saturated Na_{2}SO_{3} solution (100 mL) to remove the remaining iodine. After the organic phase was separated, the aqueous phase was extracted with diethyl ether (50 mL x 3) and combined together with the previous organic phase. The organic
phase was dried over with anhydrous MgSO$_4$. After the drying agent was removed with gravity filtration, the filtrate was mixed together with silica gel (~ 10g). Solvent was then removed under vacuum and the yellow powder obtained was placed on a silica gel column to elute (hexanes). Fractions containing the product were combined and concentrated, giving white crystals (8.659 g, 21 mmol, 71% yield) as final product.

**M.P.** 106.0 – 108.5 °C

$^1$H-NMR (400 MHz, CDCl$_3$): 7.934 (ddd, $^1$$J$=8.0 Hz, $^2$$J$=1.2 Hz, $^3$$J$=0.4 Hz, 1H), 7.407 (ddd, $^1$$J$=7.6 Hz, $^2$$J$=7.6 Hz, $^3$$J$=1.2 Hz, 1H), 7.185 (ddd, $^1$$J$=7.6 Hz, $^2$$J$=1.6 Hz, $^3$$J$=0.4 Hz, 1H), 7.078 (ddd, $^1$$J$=8.0 Hz, $^2$$J$=7.6 Hz, $^3$$J$=1.6 Hz, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): 148.876, 138.840, 129.861, 129.326, 127.988, 99.598.

**References:**


Cui, Jian-Fang; Huang, Hui; Wong, Henry N. C. *Synlett*, 2011, p.1018 – 1022.

A 50 mL flask with magnetic stir bar was filled with 2,2'-diiodobiphenyl (2.031 g, 5.0 mmol), potassium pentafluorobenzonate (5.023 g, 20.0 mmol), Copper(I) iodide (0.391 g, 2.0 mmol) and diglyme (10 mL). Under nitrogen atmosphere, the mixture obtained was stirred at room temperature for approximately 10 min and then heated up to 165 °C for 24 hours.

After that, the mixture was cooled to room temperature, giving a dark-brown residue. The residue was diluted with ethyl acetate to a total volume of 50 mL. Gravity filtration was applied and the solids on the filtration paper were washed thoroughly with additional ethyl acetate (50 mL). The combined filtrates were washed with water (50 mL x 5) to remove diglyme. The organic phase was dried with anhydrous MgSO₄ and mixed together with silica gel (~ 5g). Solvent was then removed under vacuum and the resulting yellow powder was placed on the top of a silica gel column to elute (eluent: hexanes). Fractions containing the product were combined and concentrated, giving white crystals (1.807g, 3.7 mmol, 74 % yield) as final product.

**M.P.:** 140.0 – 143.5 °C

**1H-NMR (400 MHz, CDCl₃):** 7.528 (d, J = 4.8 Hz, 2H), 7.526 (d, J = 4.8 Hz, 2H), 7.446 – 7.384
(m, 2H), 7.110 (d, $J = 7.6$ Hz, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): 144.013 (d, $J = 241$ Hz), 143.406 (d, $J = 254$ Hz), 141.026, 140.736 (d, $J = 253$ Hz), 137.586 (d, $J = 250$ Hz), 137.422 (d, $J = 250$ Hz), 131.852 (d, $J = 2.2$ Hz), 130.798, 129.562, 128.119, 124.952, 114.694 (td, $^1J = 18.6$ Hz, $^2J = 3.3$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$): -137.000 (dd, $^1J = 23.3$ Hz, $^2J = 7.9$ Hz, 2F), -144.188 (dd, $^1J = 20.9$ Hz, $^2J = 5.4$ Hz, 2F), -154.784 (t, $J = 20.9$ Hz, 2F), -162.167 - -162.304 (m, 2F), -162.395 - -162.527 (m, 2F).

4,5,6,7,11,12,13,14-Octafluorodibenzo[fg,op]tetracene (5.16)

A quartz tube (approximately 40 cm x 25 mm) was charged with 2,2''',3,3''',4,4''',5,5''',6,6'''-decafluoro-1,1':2',1'''-quaterphenyl ($\lambda_{\text{max}} = 231$ nm) (0.483 g, 1.0 mmol) and THF (100 mL). The obtained solution was degased thoroughly and irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps for 48 hours and Hanovia lamp with Vycor filter for 6 hours.

After that, the solvent was removed and a brown residue (0.777 g) was obtained. The residue was dissolved in ethyl acetate (~ 25mL) and mixed well with silica gel (~2 g). After removing the solvent under vacuum, the tan powder obtained was placed on the top of a silica gel column to
elute (hexanes:EtOAc=3:1). Fractions containing the product were collected and concentrated, giving pale yellow fibers (0.092 g, 0.22 mmol, 22 % yield) as final product.

**M.P.** Slowly sublimated above 305 °C.

**H-NMR (400 MHz, 1,1,2,2-Tetrachloroethane):** 9.106 (d, $J = 8.4$ Hz, 4H), 8.000 (t, 8.4 Hz, 2H).

**F-NMR (376 MHz, 1,1,2,2-Tetrachloroethane):** -139.097 (d, $J = 15$ Hz, 4F), -156.550 (d, $J = 15$ Hz, 4F).
5.5. References.


6.1. Introduction

Helicenes are polycyclic aromatic hydrocarbons with screw-shaped structures usually constructed from *ortho*-fused benzene rings and/or other heterocyclic aromatic rings. Their screw-like structures can provide left- (M helicenes) or right-handed (P helicenes) chiral molecules with unusual physical and optical properties\(^1,2\). Due to these novel properties, helicenes have found applications in many fields such as asymmetric catalysis, molecular machines\(^3-5\), dye materials\(^6,7\), molecular recognition\(^8\), liquid crystal materials\(^9,10\) and even biological applications\(^11,12\). It is believed that the first helicene [f]naphtho[2,1-c]cinnoline was obtained during the reduction of 2-nitronaphthalene by Meisenheimer and Witte in 1903\(^13\). Subsequently, in order to create different types of helicenes, a variety of new synthetic routes were optimized and utilized. Photocyclization is generally recognized to be the most common approach for helicene synthesis and has received the most frequent investigation (Scheme 6.1)\(^14-18\). Photocyclization is believed to be the most straightforward synthetic route, as it does not require the involvement of complicated functional groups. However, low yields are sometimes observed in photocyclizations and optimization may be needed. Also, photocyclizations are usually performed in dilute solutions, which could hinder applications in large-scale synthesis.
Other approaches such as the Diels-Alder reaction (Scheme 6.2 top)\textsuperscript{19-21}, Friedel-Crafts reaction (Scheme 6.2 middle)\textsuperscript{22,23} and metal-mediated cyclizations (Scheme 6.2 bottom)\textsuperscript{24-26} have also been reported. These methodologies might enable the large-scale synthesis compared with the previous discussed photochemistry. However, nearly all of these techniques need the existence of some functional groups to facilitate the reaction. Because of this, sometimes extra steps are needed to remove the “assistant” functional groups and reveal the desired helicenes.
As more synthetic methodologies for the helicenes were developed, more new helicenes were produced and the number of X-ray analyses on their crystal structures also gradually increased. The [5]helicenes are the smallest molecules in the helicene family and the simplest member – dibenzo[c,g]phenanthrene – was characterized by Kudora in 1982. 

\[ \text{Scheme 6.2 The synthesis of helicenes via the Diels-Alder reaction}^{19-21}, \text{Friedel-Crafts reaction}^{22,23} \text{and metal-mediated cyclizations}^{24-26}. \]
Figure 6.1 The structure of molecule and the crystal packing of dibenzo[c,g]phenanthrene – the smallest helicene molecule. It is clear to see the twisted molecular structure (H-H distance is 2.603 Å). The T-shaped intermolecular stacking is supported by the C−H···Cπ interactions (2.663 Å, 2.809 Å).
The 5,6:9,10-dianhydride of dibenzo[c,g]phenanthrene was reported in 1995\textsuperscript{28}, 9,12-diphosphine derivative in 1997\textsuperscript{29,30} and cyano- methyl- substituted derivatives (2,13-dicyano[5]helicene, 1,4-dicyano-13-methyl[5]helicene, 11,14-dicyano-1,3-dimethyl[5]helicene) in 1999\textsuperscript{15}. Subsequently, 7:8,9:10-dibenzo-1,2,3,4-tetrafluorotriphenylene was characterized in 2005 (Figure 6.2)\textsuperscript{31}, diaza[5]helicenes in 2008\textsuperscript{32}, azoxydichinyl helicene (pyrido[3,2-f]quinolino[6,5-c]cinnoline 5-oxide monohydrate)\textsuperscript{33} and oxa[5]helicenes\textsuperscript{34} in 2011, 5,10-diaza[5]helicene in 2012\textsuperscript{35} and N-containing pentacyclic helicene in 2013\textsuperscript{36}.

\textbf{Figure 6.2} The synthesis and crystal packing of 7:8,9:10-dibenzo-1,2,3,4-tetrafluorotriphenylene. C–F···CnF interaction (3.136 Å) plays an important role in the molecule stacking along with b axis.
6.2. The synthesis of non-fluorinated [5][helicene - naphtho[1,2-g]chrysene

Although the preparation of helicenes by photocyclization sometimes proceeds in low yields, it is still the most straightforward and widely used synthetic approach \(^3^7\). By application of this methodology, we have synthesized the non-fluorinated [5]helicene - naphtho[1,2-g]chrysene in order to obtain a single crystal sample for determination of its molecular packing (Scheme 6.3). The structure of this perprotio compound was not in the literature and we needed the structure for comparison with fluorinated derivatives. In this synthesis, commercially available 1-methylnaphthalene (6.1) underwent highly regioselective electrophilic bromination para- to the methyl group under mild conditions to yield bromo-4-methylnaphthalene (6.2)\(^3^8\). From this common precursor, one of the styryl units was installed by reacting with styrene via the traditional Heck reaction and the other one was installed via a three step Wittig-type process to give the precursor 1,4-distyrylnaphthalene (6.5). For the final step, 1,4-distyrylnaphthalene was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps for 24 hours. During this process, iodine was added as oxidant to facilitate the oxidative Mallory photocyclization. From TLC analysis, a tiny spot showed purple fluorescence under 254 nm UV lamp, which might be the desired product. After chromatography with hexanes, the yield of this photocyclization step was very poor and provided only a trace amount of desired product (6.6). This low yield might due to the terminal rings were able to turn off further photochemical reactions. Fortunately, even with the very limited amount of sample, we were able to successfully determine the crystal structure.
6.3. The synthesis of fluorinated [5]-helicene - 7,8,9,10-tetrafluoronaphtho[1,2-g]chrysene and 7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene

In the last chapter, we introduced the photocyclodehydrofluorination (PCDHF) reaction - wherein HF is eliminated after a stilbene or o-terphenyl photocyclization. Application of this PCDHF technique enables the preparation of a wide range of selectively fluorinated polynuclear aromatic hydrocarbons (PAHs), which contain a phenanthrene substructure (and thus, potentially includes many fluorinated helicenes).

From the preliminary results of our PCDHF research in the last chapter, \(\alpha\)-styrylnaphthalenes were shown to be excellent precursors that went through the photocyclization process rapidly with high yields (Figure 6.3). In the case of \((E)-1\)-(pentafluorostyryl)naphthalene, an acetonitrile solution was irradiated in a Rayonette photochemical reactor and the pure product 1,2,3,4-
tetrafluorochrysene precipitated out of solution directly (75 % isolated yield) without the need for any further purification. The related cyano-precursor (E)-1-cyano-substituted 4-(pentafluorostyryl)naphthalene also underwent PCDHF\textsuperscript{39} efficiently and gave the corresponding cyclized product 1,2,3,4-tetrafluorochrysene-6-carbonitrile (69 % isolated yield).

![Figure 6.3 PCDHF of α-(pentafluorostyryl)naphthalenes.](image)

Since high yields of PCDHF on simple α-styrylnaphthalenes were observed, we decided to combine this new technique with the traditional oxidative Mallory approach (Scheme 6.4). This dual cyclization should yield new [5]helicene 7,8,9,10-tetrafluoronaphtho[1,2-g]chrysene (6.8) equipped with both perfluorinated terminal ring and a nonfluorinated terminal ring. Starting from the phosphonium salt (6.4) described previously for the synthesis of naphtho[1,2-g]chrysene, a Wittig reaction with pentafluorobenzaldehyde was run to yield 1-(E)-perfluorostyryl-4-(E)-styrylnaphthalene (6.7). Iodine was also added as an oxidant to facilitate the reaction as both PCDHF and traditional oxidative Mallory photocyclization were involved in this final cyclization step. The overall yield was only 10%. Similar to the case with the parent hydrocarbon, further photochemical reactions might occur and lead to a low yield.
Finally, we also synthesized 7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene with two perfluorinated terminal rings (Scheme 6.5). Compared to the other two syntheses, this preparation was overall much simpler. The symmetrical precursor (E)-1,4-bis(pentafluorostyryl)naphthalene (6.10) was prepared from 1,4-diiodonaphthalene (6.9) and pentafluorostyrene via a Jeffery modified Heck reaction \(^{40}\) and it cyclized via PCDHF approach under UV irradiation as expected, giving the desired final product 7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene (6.11). Only PCDHF was involved in the final cyclization step and it proceeded smoothly without the need for addition of any external oxidant. The yield of the double PCDHF reaction was low (21%) but better than the other previous two cases that involved the standard Mallory process.
Scheme 6.5 The synthesis of 7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene.


### Table 6.1 Summary of crystallographic and refinement data for [5] helicenes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>naphtho[1,2-g]chrysene (6.6)</th>
<th>7,8,9,10-tetrafluoronaphtho[1,2-g]chrysene (6.8)</th>
<th>7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene (6.11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{26}H_{16}</td>
<td>C_{26}H_{12}F_4</td>
<td>C_{26}H_{8}F_8</td>
</tr>
<tr>
<td>Formula weight</td>
<td>328.39</td>
<td>400.36</td>
<td>472.32</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P_{21}/n</td>
<td>P_{21}2_{1}2_{1}</td>
<td>P_{21}2_{1}2_{1}</td>
</tr>
<tr>
<td>a, Å</td>
<td>5.8441(11)</td>
<td>5.097(3)</td>
<td>5.1723(4)</td>
</tr>
<tr>
<td>b, Å</td>
<td>13.161(3)</td>
<td>12.568(8)</td>
<td>12.5875(9)</td>
</tr>
<tr>
<td>c, Å</td>
<td>21.012(4)</td>
<td>26.022(17)</td>
<td>27.3127(19)</td>
</tr>
<tr>
<td>α, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>93.482(4)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume, Å³</td>
<td>1613.1(5)</td>
<td>1666.8(19)</td>
<td>1778.2(2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Density, mg/m³</td>
<td>1.352</td>
<td>1.595</td>
<td>1.764</td>
</tr>
<tr>
<td>F(000)</td>
<td>688</td>
<td>816</td>
<td>944</td>
</tr>
<tr>
<td>Theta range, deg</td>
<td>1.827 – 25.046</td>
<td>1.565 – 25.044</td>
<td>1.49 – 25.05</td>
</tr>
<tr>
<td>Index ranges</td>
<td>±6 ±15 ±24</td>
<td>-6&lt;=h&lt;=4, -14&lt;=k&lt;=10, -31&lt;=l&lt;=29</td>
<td>±6 ±14 ±32</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.994 and 0.839</td>
<td>0.998 and 0.652</td>
<td>0.9841 and 0.9384</td>
</tr>
<tr>
<td>GOF</td>
<td>1.745</td>
<td>1.037</td>
<td>0.774</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁ = 0.0918, wR₂ = 0.2682</td>
<td>R₁ = 0.1032, wR₂ = 0.2034</td>
<td>R₁ = 0.0248, wR₂ = 0.0789</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1140, wR₂ = 0.2754</td>
<td>R₁ = 0.2413, wR₂ = 0.2713</td>
<td>R₁ = 0.0292, wR₂ = 0.0951</td>
</tr>
</tbody>
</table>

Our discussion of the three helicenes starts with the parent perprotio substance. The crystal lattice of naphtho[1,2-g]chrysene contains four helicene molecules aligning in P_{21}2_{1}2_{1} space group. As
there are no interactions involving fluorine in this structure, the C−H⋯Cπ interactions (C(6)⋯H(18′), 2.892 Å; C(7)⋯H(18′), 2.808 Å; C(11)⋯H(20′), 2.891 Å; C(22)⋯H(12′), 2.835 Å) play the most important role in the crystal packing. The torsion of C(1)-C(26)-C(25)-C(24) in the middle of the molecule is 31.40°. The longest C-C bonds are located at the “shoulder” positions (about 1.46 Å).
**Figure 6.4** Crystal structure of naphtho[1,2-g]chrysene, shows the torsion of C(1)-C(26)-C(25)-C(24) and intermolecular interactions.
On the other hand, the 7,8,9,10-tetrafluoronaphtho[1,2-g]chrysene with a single perfluorinated ring gives a similar packing to the non-fluorinated parent compound which also forms a P2₁2₁2₁ space group in the crystal lattice. The torsion angle of C(6)-C(7)-C(8)-C(9) is 35.52° and C(7)-C(8) is the most stretched C-C bond (1.467 Å). Intermolecular contacts are a bit more complicated due to the presence of fluorine atoms. The C–F···H–C contacts can be found (2.484 Å, 2.465 Å). C–F···Cπ–F contacts (3.105 Å; 3.125 Å) play an important role in the molecule slipped face-to-face stacking. On the other hand, the C–H···Cπ (2.695 Å) interactions help the T-shaped aligned molecules interact.
Figure 6.5 Crystal structure of 7,8,9,10-tetrafluoronaphtho[1,2-g]chrysene, shows the torsion of C(6)-C(7)-C(8)-C(9) and intermolecular interactions.
For 7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene with two terminal perfluorinated rings, the crystal lattice still contains four helicene molecules that align in a space group $P2_12_12_1$. A large torsion angle was found in C(6)-C(7)-C(11)-C(12) as high as \(35.37^\circ\) and the most stretched C(7)-C(11) bond is 1.469 Å long. Various types of fluorine-involving intermolecular contacts can be found in the crystal. The most obvious one is the C−F⋯F−C contact between two slipped face-to-face molecules (F(1)⋯F(5′), 2.736 Å). Aside of this, C−F⋯Cπ−F contacts can be found between slipped face-to-face molecules (F(6)⋯C(16′), 3.096 Å) and and T-shaped aligned molecules (F(6)⋯C(14′), 2.968 Å; F(6)⋯C(15′), 3.102 Å; F(7)⋯C(2′), 3.127 Å). Of course, the very common C−F⋯H−C interactions in fluorinated organic compounds also could be found here (F(4)⋯H(9′), 2.502 Å; F(4)⋯H(23′), 2.515 Å).
Figure 6.6 Crystal structure of 7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene, shows the torsion of C(6)-C(7)-C(11)-C(12) and intermolecular interactions.
6.5. Summary

In this section, by using the traditional oxidative Mallory photocyclization, we successfully prepared naphtho[1,2-g]chrysene and determined its crystal structure which had not been documented before. Using photocyclodehydrofluorination (PCDHF), we also successfully synthesized two new derivatives of this hydrocarbon that differ in the presence of perfluorination in the terminal rings of the helix - the 7,8,9,10-tetrafluoronaphtho[1,2-g]chrysene has one single perfluorinated ring and 7,8,9,10,11,12,13,14-octafluoronaphtho[1,2-g]chrysene has a two perfluorinated rings.
6.6. Experimental procedures

1-bromo-4-methylnaphthalene (6.2)

A 250 mL round bottom flask was charged with 1-methylnaphthalene (5.697 g, 40.1 mmol), N-bromosuccinimide (7.416 g, 41.7 mmol) and acetonitrile (60 mL). The mixture was stirred at room temperature for 24h and then the solvent was removed by rotary evaporation. The residue was dissolved in diethyl ether (150 mL) and washed with water (100 mL x 3). The organic phase was separated and dried with anhydrous MgSO\(_4\). The drying agent was removed by filtration and after removal of solvent by rotary evaporation, the brown sticky residue was purified by Kugelrohr distillation (145 °C, 150 torr) to give a colorless oil (8.230 g, 37 mmol, 92 % yield) as final product.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.264 – 8.241 (m, 1H), 7.957 (dd, \(^1J = 7.6\) Hz, \(^2J = 2.0\) Hz, 1H), 7.646 (d, \(J = 7.6\) Hz, 1H), 7.600 – 7.523 (m, 2H), 7.135 (d, \(J = 7.6\) Hz, 1H), 2.630 (s, 3H).

\(^13\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\): 134.373, 133.791, 131.787, 129.516, 127.696, 126.959, 126.904, 126.487, 124.557, 120.670, 19.296.

A 250 mL round bottom flask was charged with 1-bromo-4-methylnaphthalene (16.805 g, 75.0 mmol), styrene (8.601 g, 83.0 mmol), potassium carbonate (13.915 g, 100.0 mmol), anhydrous DMF (50 mL), palladium acetate (0.171 g, 0.75 mmol) and TDA -1 (tris[2-(2-methoxyethoxy)ethyl]amine) (0.8 mL).

The resulting mixture was stirred under nitrogen atmosphere at 110 °C overnight (~ 12h) and TLC indicated a new product. Some starting material remained but longer reaction time was not of any benefit. The mixture was cooled, filtered and the liquid component was Kugelrohr distilled to remove DMF and unreacted starting material. The yellow oil obtained was diluted with ethyl acetate (~ 50 mL) and mixed with silica gel (~ 10g). After the removal of solvent, the yellow powder obtained was placed on the top of silica gel column to elute (eluent: hexanes). The fractions containing the desired product were combined and concentrated, giving light yellow crystals (13.928 g, 57 mmol, 76 % yield) after cooling.

**M.P.:** 55.0 – 59.0 °C (Lit. 69.0 – 70.0 °C).

**¹H-NMR (400 MHz, CDCl₃) δ:** 8.249 – 8.224 (m, 1H), 8.043 – 8.017 (m, 1H), 7.873 (d, J = 16.0 Hz, 1H), 7.640 (d, J = 7.6 Hz, 1H), 7.607 – 7.583 (m, 2H), 7.557 – 7.532 (m, 2H), 7.410 – 7.372 (m, 2H), 7.333 (d, J = 7.2 Hz, 1H), 7.306 – 7.266 (m, 1H), 7.106 (d, J = 16.0 Hz, 1H), 2.709 (s,
$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 137.783, 134.375, 133.430, 132.745, 131.475, 131.078, 128.726, 127.617, 126.611, 126.076, 125.729, 125.675, 124.705, 124.344, 123.398, 19.645.


*(E)-triphenyl((4-styrylnaphthalen-1-yl)methyl)phosphonium bromide (6.4)*

![Chemical Structure](image)

Chemical Formula: C$_{37}$H$_{30}$BrP
Molecular Weight: 585.51

A 250 mL flask was charged with *trans*-1-styryl-4-methylnaphthalene (7.308 g, 30.0 mmol), NBS (5.348 g, 30.0 mmol), benzoyl peroxide (0.221 g, 0.91 mmol, 3%) and chlorobenzene (50 mL). The resulting mixture was heated to 120 °C to obtain a clear solution.

After 6 hours of heating, the formation of the benzyl bromide was complete. Triphenylphosphine (7.902 g, 30.2 mmol) was added during reflux and a white precipitate gradually formed. After six additional hours of heating, the mixture was cooled to room temperature and the white powder was isolated by suction filtration, washed with hexanes (25 mL) and air-dried to give final product (17.158 g, 29.3 mmol, 97 % yield).

M.P.: 301.0 – 305.0 °C (Lit: 268 – 271 °C).

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.020 (d, $J = 8.4$ Hz, 1H), 7.747 – 7.653 (m, 10H), 7.550 – 7.490
(m, 9H), 7.455 (d, J = 8.8 Hz, 1H), 7.397 – 7.361 (m, 3H), 7.317 – 7.253 (m, 3H), 7.045 – 6.995 (m, 2H), 5.890 (d, J = 14.0 Hz, 2H).


1, 4-bisstyrylnaphthalene (6.5)

A solution of t-BuOK (0.925 g, 8.2 mmol) in ethanol (50 mL) was added dropwise to a suspension of (E)-triphenyl((4-styrylnaphthalen-1-yl)methyl)phosphonium bromide (4.401 g, 7.5 mmol) and benzaldehyde (0.801 g, 7.5 mmol) in ethanol (50 mL) in a 250 mL flask.

The resulting mixture was stirred at room temperature overnight (~ 12h) to ensure the reaction was complete. After this time, silica gel (~ 10g) was added into the mixture and the solvent was removed by rotary evaporation to give a bright yellow powder. The yellow powder was placed on the top of silica gel column and eluted (solvent: hexanes). The yellow fractions were combined and condensed, giving bright yellow crystals (1.857 g, 5.6 mmol, 75 % yield) as final product.

M.P.: 182.0 – 186.0 °C (Lit: 186 – 187 °C).

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 8.272 (dd, $^1J$ = 6.8 Hz, $^2J$ = 3.2 Hz, 2H), 7.910 (d, J = 16.0 Hz, 2H), 7.782 (s, 2H), 7.636 – 7.612 (m, 4H), 7.573 (dd, $^1J$ = 6.4 Hz, $^2J$ = 3.2 Hz, 2H), 7.431 – 7.393
(m, 4H), 7.308 (dt, \( \text{J} = 7.2 \, \text{Hz} \), \( \text{J} = 2.0 \, \text{Hz} \)), 7.183 (d, \( \text{J} = 16.0 \, \text{Hz} \)).

\(^{13}\text{C-NMR} \, (100 \, \text{MHz, CDCl}_3)\) \( \delta: 137.637, 134.860, 131.643, 131.584, 128.782, 127.820, 126.713, 126.038, 125.754, 124.355, 123.562, \ldots \)

**UV/Vis (DCM):** \( \lambda_{\text{max}}(\varepsilon) = 238 \, (27660), 253 \, (28250), 372 \, (38320) \, \text{nm (M}^{-1}\text{cm}^{-1}) \).  


naphtho[1,2-g]chrysene (6.6)

![Chemical Structure](image)

**Chemical Formula:** \( \text{C}_{26}\text{H}_{16} \)  
**Molecular Weight:** 328.41

In a quartz vessel was placed 1,4-bisstyrylnaphthalene (0.335 g, 1.0 mmol), iodine (0.525 g, 2.0 mmol) and toluene (100 mL). The resulting solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps for 24 hours and TLC indicated a new product was formed. The resulting solution was then washed with saturated Na\(_2\)SO\(_3\) solution (50 mL) to remove remaining iodine and dried over with anhydrous MgSO\(_4\). After the removal of drying agent, the solution was mixed with silica gel (\(~10\)g) and the solvent was removed by using rotatory evaporation. The brown power obtained was placed on the top of silica gel column and eluted (eluent: hexanes). The fraction containing the product was collected and concentrated to dryness to give pale yellow crystals as final product (0.008 g, 0.024 mmol, 2.4 \% yield). The crystals
suitable for X-ray crystallography were obtained by slowly evaporating a chlorobenzene solution.


**Table 1.** Crystal data and structure refinement for compound 6.6.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>6.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{26}H_{16}</td>
</tr>
</tbody>
</table>
Formula weight                    328.39
Temperature                       105(2) K
Wavelength                        0.71073 A
Crystal system, space group       Monoclinic,  P2(1)/n
Unit cell dimensions
a = 5.8441(11) A   alpha = 90 deg.
b = 13.161(3) A    beta = 93.482(4) deg.
c = 21.012(4) A   gamma = 90 deg.
Volume                            1613.1(5) A^3
Z, Calculated density             4,  1.352 Mg/m^3
Absorption coefficient            0.077 mm^-1
F(000)                            688
Crystal size                      0.150 x 0.080 x 0.080 mm
Theta range for data collection   1.827 to 25.046 deg.
Limiting indices                  -6<=h<=6, -15<=k<=15, -24<=l<=24
Reflections collected / unique    21763 / 2835 [R(int) = 0.0746]
Completeness to theta = 25.046    99.9 %
Absorption correction             Semi-empirical from equivalents
Max. and min. transmission        0.994 and 0.839
Refinement method                 Full-matrix least-squares on F^2
Data / restraints / parameters    2835 / 0 / 235
Goodness-of-fit on F^2            1.745
Final R indices [I>2sigma(I)]    R1 = 0.0918, wR2 = 0.2682
R indices (all data)              R1 = 0.1140, wR2 = 0.2754
Extinction coefficient            n/a
Largest diff. peak and hole \( 0.352 \text{ and } -0.319 \text{ e.A}^{-3} \)
Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for compound 6.6. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>3659(7)</td>
<td>8455(3)</td>
<td>8134(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>5199(7)</td>
<td>8608(3)</td>
<td>8677(2)</td>
</tr>
<tr>
<td>C(3)</td>
<td>4676(8)</td>
<td>9245(3)</td>
<td>9161(2)</td>
</tr>
<tr>
<td>C(4)</td>
<td>2563(8)</td>
<td>9749(3)</td>
<td>9143(2)</td>
</tr>
<tr>
<td>C(5)</td>
<td>1068(8)</td>
<td>9642(3)</td>
<td>8620(2)</td>
</tr>
<tr>
<td>C(6)</td>
<td>1610(7)</td>
<td>9032(3)</td>
<td>8103(2)</td>
</tr>
<tr>
<td>C(7)</td>
<td>236(7)</td>
<td>9044(3)</td>
<td>7518(2)</td>
</tr>
<tr>
<td>C(8)</td>
<td>1005(7)</td>
<td>8625(3)</td>
<td>6985(2)</td>
</tr>
<tr>
<td>C(9)</td>
<td>3040(7)</td>
<td>8031(3)</td>
<td>7001(2)</td>
</tr>
<tr>
<td>C(10)</td>
<td>4027(7)</td>
<td>7661(3)</td>
<td>6420(2)</td>
</tr>
<tr>
<td>C(11)</td>
<td>2985(9)</td>
<td>7870(3)</td>
<td>5808(2)</td>
</tr>
<tr>
<td>C(12)</td>
<td>4037(9)</td>
<td>7617(3)</td>
<td>5266(2)</td>
</tr>
<tr>
<td>C(13)</td>
<td>6182(9)</td>
<td>7156(3)</td>
<td>5309(2)</td>
</tr>
<tr>
<td>C(14)</td>
<td>7218(8)</td>
<td>6920(3)</td>
<td>5898(2)</td>
</tr>
<tr>
<td>C(15)</td>
<td>6156(8)</td>
<td>7155(3)</td>
<td>6466(2)</td>
</tr>
<tr>
<td>C(16)</td>
<td>7119(7)</td>
<td>6810(3)</td>
<td>7086(2)</td>
</tr>
<tr>
<td>C(17)</td>
<td>9130(7)</td>
<td>6206(3)</td>
<td>7146(2)</td>
</tr>
<tr>
<td>C(18)</td>
<td>9897(7)</td>
<td>5790(3)</td>
<td>7710(2)</td>
</tr>
<tr>
<td>C(19)</td>
<td>8558(7)</td>
<td>5857(3)</td>
<td>8249(2)</td>
</tr>
<tr>
<td>C(20)</td>
<td>9078(8)</td>
<td>5260(3)</td>
<td>8798(2)</td>
</tr>
<tr>
<td>C(21)</td>
<td>7628(8)</td>
<td>5205(3)</td>
<td>9280(2)</td>
</tr>
<tr>
<td>C(22)</td>
<td>5547(8)</td>
<td>5739(3)</td>
<td>9226(2)</td>
</tr>
<tr>
<td>C(23)</td>
<td>5039(7)</td>
<td>6357(3)</td>
<td>8710(2)</td>
</tr>
<tr>
<td>C(24)</td>
<td>6528(7)</td>
<td>6459(3)</td>
<td>8211(2)</td>
</tr>
<tr>
<td>C(25)</td>
<td>5970(7)</td>
<td>7047(3)</td>
<td>7635(2)</td>
</tr>
<tr>
<td>C(26)</td>
<td>4226(7)</td>
<td>7828(3)</td>
<td>7595(2)</td>
</tr>
</tbody>
</table>
Table 3. Bond lengths [Å] and angles [deg] for compound 6.6.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-C(6)</td>
<td>1.416(6)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.424(5)</td>
</tr>
<tr>
<td>C(1)-C(26)</td>
<td>1.456(6)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.366(6)</td>
</tr>
<tr>
<td>C(2)-H(2)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.400(6)</td>
</tr>
<tr>
<td>C(3)-H(3)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.369(6)</td>
</tr>
<tr>
<td>C(4)-H(4)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.401(6)</td>
</tr>
<tr>
<td>C(5)-H(5)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.428(5)</td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td>1.349(6)</td>
</tr>
<tr>
<td>C(7)-H(7)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td>1.422(6)</td>
</tr>
<tr>
<td>C(8)-H(8)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(9)-C(26)</td>
<td>1.416(5)</td>
</tr>
<tr>
<td>C(9)-C(10)</td>
<td>1.465(6)</td>
</tr>
<tr>
<td>C(10)-C(15)</td>
<td>1.409(6)</td>
</tr>
<tr>
<td>C(10)-C(11)</td>
<td>1.417(5)</td>
</tr>
<tr>
<td>C(11)-C(12)</td>
<td>1.367(6)</td>
</tr>
<tr>
<td>C(11)-H(11)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(12)-C(13)</td>
<td>1.391(7)</td>
</tr>
<tr>
<td>C(12)-H(12)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(13)-C(14)</td>
<td>1.379(6)</td>
</tr>
<tr>
<td>C(13)-H(13)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(14)-C(15)</td>
<td>1.413(6)</td>
</tr>
<tr>
<td>C(14)-H(14)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(15)-C(16)</td>
<td>1.460(5)</td>
</tr>
<tr>
<td>C(16)-C(25)</td>
<td>1.405(6)</td>
</tr>
<tr>
<td>C(16)-C(17)</td>
<td>1.418(6)</td>
</tr>
<tr>
<td>C(17)-C(18)</td>
<td>1.356(6)</td>
</tr>
<tr>
<td>C(17)-H(17)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(18)-C(19)</td>
<td>1.418(6)</td>
</tr>
<tr>
<td>C(18)-H(18)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(19)-C(20)</td>
<td>1.414(6)</td>
</tr>
<tr>
<td>C(19)-C(24)</td>
<td>1.425(6)</td>
</tr>
<tr>
<td>C(20)-C(21)</td>
<td>1.361(6)</td>
</tr>
<tr>
<td>C(20)-H(20)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(21)-C(22)</td>
<td>1.403(6)</td>
</tr>
<tr>
<td>C(21)-H(21)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(22)-C(23)</td>
<td>1.373(6)</td>
</tr>
<tr>
<td>Bond</td>
<td>Distance (Å)</td>
</tr>
<tr>
<td>----------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>C(22)-H(22)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(23)-C(24)</td>
<td>1.409(6)</td>
</tr>
<tr>
<td>C(23)-H(23)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(24)-C(25)</td>
<td>1.456(5)</td>
</tr>
<tr>
<td>C(25)-C(26)</td>
<td>1.446(6)</td>
</tr>
<tr>
<td>C(6)-C(1)-C(2)</td>
<td>116.9(4)</td>
</tr>
<tr>
<td>C(6)-C(1)-C(26)</td>
<td>120.0(4)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(26)</td>
<td>122.7(4)</td>
</tr>
<tr>
<td>C(3)-C(2)-C(1)</td>
<td>121.6(4)</td>
</tr>
<tr>
<td>C(3)-C(2)-H(2)</td>
<td>119.2</td>
</tr>
<tr>
<td>C(1)-C(2)-H(2)</td>
<td>119.2</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)</td>
<td>120.5(4)</td>
</tr>
<tr>
<td>C(2)-C(3)-H(3)</td>
<td>119.8</td>
</tr>
<tr>
<td>C(4)-C(3)-H(3)</td>
<td>119.8</td>
</tr>
<tr>
<td>C(5)-C(4)-C(3)</td>
<td>119.4(4)</td>
</tr>
<tr>
<td>C(5)-C(4)-H(4)</td>
<td>120.3</td>
</tr>
<tr>
<td>C(3)-C(4)-H(4)</td>
<td>120.3</td>
</tr>
<tr>
<td>C(4)-C(5)-C(6)</td>
<td>121.2(4)</td>
</tr>
<tr>
<td>C(4)-C(5)-H(5)</td>
<td>119.4</td>
</tr>
<tr>
<td>C(6)-C(5)-H(5)</td>
<td>119.4</td>
</tr>
<tr>
<td>C(5)-C(6)-C(1)</td>
<td>120.2(4)</td>
</tr>
<tr>
<td>C(5)-C(6)-C(7)</td>
<td>121.3(4)</td>
</tr>
<tr>
<td>C(1)-C(6)-C(7)</td>
<td>118.4(4)</td>
</tr>
<tr>
<td>C(8)-C(7)-C(6)</td>
<td>120.8(4)</td>
</tr>
<tr>
<td>C(8)-C(7)-H(7)</td>
<td>119.6</td>
</tr>
<tr>
<td>C(6)-C(7)-H(7)</td>
<td>119.6</td>
</tr>
<tr>
<td>C(7)-C(8)-C(9)</td>
<td>121.7(4)</td>
</tr>
<tr>
<td>C(7)-C(8)-H(8)</td>
<td>119.1</td>
</tr>
<tr>
<td>C(9)-C(8)-H(8)</td>
<td>119.1</td>
</tr>
<tr>
<td>C(26)-C(9)-C(8)</td>
<td>119.2(4)</td>
</tr>
<tr>
<td>C(26)-C(9)-C(10)</td>
<td>118.4(4)</td>
</tr>
<tr>
<td>C(8)-C(9)-C(10)</td>
<td>122.3(4)</td>
</tr>
<tr>
<td>C(15)-C(10)-C(11)</td>
<td>118.9(4)</td>
</tr>
<tr>
<td>C(15)-C(10)-C(9)</td>
<td>119.4(4)</td>
</tr>
<tr>
<td>C(11)-C(10)-C(9)</td>
<td>121.5(4)</td>
</tr>
<tr>
<td>C(12)-C(11)-C(10)</td>
<td>121.2(5)</td>
</tr>
<tr>
<td>C(12)-C(11)-H(11)</td>
<td>119.4</td>
</tr>
<tr>
<td>C(10)-C(11)-H(11)</td>
<td>119.4</td>
</tr>
<tr>
<td>C(11)-C(12)-C(13)</td>
<td>120.1(4)</td>
</tr>
<tr>
<td>C(11)-C(12)-H(12)</td>
<td>120.0</td>
</tr>
<tr>
<td>C(13)-C(12)-H(12)</td>
<td>120.0</td>
</tr>
<tr>
<td>C(14)-C(13)-C(12)</td>
<td>120.1(4)</td>
</tr>
<tr>
<td>C(14)-C(13)-H(13)</td>
<td>119.9</td>
</tr>
<tr>
<td>C(12)-C(13)-H(13)</td>
<td>119.9</td>
</tr>
<tr>
<td>C(13)-C(14)-C(15)</td>
<td>121.1(4)</td>
</tr>
</tbody>
</table>
C(13)-C(14)-H(14)  119.4
C(15)-C(14)-H(14)  119.4
C(10)-C(15)-C(14)  118.5(4)
C(10)-C(15)-C(16)  119.9(4)
C(14)-C(15)-C(16)  121.4(4)
C(25)-C(16)-C(17)  119.1(4)
C(25)-C(16)-C(15)  119.1(4)
C(17)-C(16)-C(15)  121.8(4)
C(18)-C(17)-C(16)  122.2(4)
C(18)-C(17)-H(17)  118.9
C(16)-C(17)-H(17)  118.9
C(17)-C(18)-C(19)  120.2(4)
C(17)-C(18)-H(18)  119.9
C(19)-C(18)-H(18)  119.9
C(20)-C(19)-C(18)  121.1(4)
C(20)-C(19)-C(24)  119.4(4)
C(18)-C(19)-C(24)  119.2(4)
C(21)-C(20)-C(19)  121.6(4)
C(21)-C(20)-H(20)  119.2
C(19)-C(20)-H(20)  119.2
C(20)-C(21)-C(22)  119.2(4)
C(20)-C(21)-H(21)  120.4
C(22)-C(21)-H(21)  120.4
C(23)-C(22)-C(21)  120.4(4)
C(23)-C(22)-H(22)  119.8
C(21)-C(22)-H(22)  119.8
C(22)-C(23)-C(24)  122.0(4)
C(22)-C(23)-H(23)  119.0
C(24)-C(23)-H(23)  119.0
C(23)-C(24)-C(19)  117.1(4)
C(23)-C(24)-C(25)  123.5(4)
C(19)-C(24)-C(25)  119.1(4)
C(16)-C(25)-C(26)  118.7(4)
C(16)-C(25)-C(24)  118.0(4)
C(26)-C(25)-C(24)  123.2(4)
C(9)-C(26)-C(25)   119.4(4)
C(9)-C(26)-C(1)    117.2(4)
C(25)-C(26)-C(1)   123.4(3)

Symmetry transformations used to generate equivalent atoms:
Table 4. Anisotropic displacement parameters (Å^2 x 10^3) for compound 6.6. The anisotropic displacement factor exponent takes the form:

\[-2 \pi^2 \left[ h^2 a^* U11 + \ldots + 2hk a^* b^* U12 \right] \]

<table>
<thead>
<tr>
<th></th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>19(2)</td>
<td>14(2)</td>
<td>26(2)</td>
<td>1(2)</td>
<td>6(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>21(2)</td>
<td>18(2)</td>
<td>28(2)</td>
<td>3(2)</td>
<td>2(2)</td>
<td>2(2)</td>
</tr>
<tr>
<td>C(3)</td>
<td>31(3)</td>
<td>21(2)</td>
<td>27(2)</td>
<td>-3(2)</td>
<td>6(2)</td>
<td>-5(2)</td>
</tr>
<tr>
<td>C(4)</td>
<td>37(3)</td>
<td>20(2)</td>
<td>28(2)</td>
<td>-2(2)</td>
<td>10(2)</td>
<td>0(2)</td>
</tr>
<tr>
<td>C(5)</td>
<td>24(3)</td>
<td>19(2)</td>
<td>35(3)</td>
<td>4(2)</td>
<td>12(2)</td>
<td>4(2)</td>
</tr>
<tr>
<td>C(6)</td>
<td>14(2)</td>
<td>15(2)</td>
<td>32(2)</td>
<td>5(2)</td>
<td>3(2)</td>
<td>-3(2)</td>
</tr>
<tr>
<td>C(7)</td>
<td>14(2)</td>
<td>20(2)</td>
<td>38(3)</td>
<td>4(2)</td>
<td>-3(2)</td>
<td>0(2)</td>
</tr>
<tr>
<td>C(8)</td>
<td>20(2)</td>
<td>17(2)</td>
<td>34(3)</td>
<td>4(2)</td>
<td>-5(2)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>C(9)</td>
<td>16(2)</td>
<td>15(2)</td>
<td>27(2)</td>
<td>1(2)</td>
<td>-2(2)</td>
<td>-4(2)</td>
</tr>
<tr>
<td>C(10)</td>
<td>24(2)</td>
<td>12(2)</td>
<td>27(2)</td>
<td>2(2)</td>
<td>-2(2)</td>
<td>-7(2)</td>
</tr>
<tr>
<td>C(11)</td>
<td>36(3)</td>
<td>18(2)</td>
<td>29(2)</td>
<td>2(2)</td>
<td>-8(2)</td>
<td>-7(2)</td>
</tr>
<tr>
<td>C(12)</td>
<td>48(3)</td>
<td>23(2)</td>
<td>26(2)</td>
<td>1(2)</td>
<td>-4(2)</td>
<td>-5(2)</td>
</tr>
<tr>
<td>C(13)</td>
<td>51(3)</td>
<td>22(2)</td>
<td>25(2)</td>
<td>0(2)</td>
<td>9(2)</td>
<td>-4(2)</td>
</tr>
<tr>
<td>C(14)</td>
<td>31(3)</td>
<td>21(2)</td>
<td>34(3)</td>
<td>1(2)</td>
<td>4(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>C(15)</td>
<td>27(2)</td>
<td>13(2)</td>
<td>25(2)</td>
<td>1(2)</td>
<td>1(2)</td>
<td>-7(2)</td>
</tr>
<tr>
<td>C(16)</td>
<td>17(2)</td>
<td>12(2)</td>
<td>28(2)</td>
<td>-2(2)</td>
<td>5(2)</td>
<td>-6(2)</td>
</tr>
<tr>
<td>C(17)</td>
<td>22(2)</td>
<td>17(2)</td>
<td>30(2)</td>
<td>-5(2)</td>
<td>5(2)</td>
<td>-5(2)</td>
</tr>
<tr>
<td>C(18)</td>
<td>17(2)</td>
<td>15(2)</td>
<td>35(2)</td>
<td>-7(2)</td>
<td>2(2)</td>
<td>-3(2)</td>
</tr>
<tr>
<td>C(19)</td>
<td>18(2)</td>
<td>15(2)</td>
<td>27(2)</td>
<td>-4(2)</td>
<td>-3(2)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>C(20)</td>
<td>21(2)</td>
<td>18(2)</td>
<td>33(2)</td>
<td>-1(2)</td>
<td>-4(2)</td>
<td>2(2)</td>
</tr>
<tr>
<td>C(21)</td>
<td>31(3)</td>
<td>21(2)</td>
<td>30(3)</td>
<td>4(2)</td>
<td>-4(2)</td>
<td>0(2)</td>
</tr>
<tr>
<td>C(22)</td>
<td>27(2)</td>
<td>21(2)</td>
<td>25(2)</td>
<td>4(2)</td>
<td>-1(2)</td>
<td>-4(2)</td>
</tr>
<tr>
<td>C(23)</td>
<td>19(2)</td>
<td>16(2)</td>
<td>31(2)</td>
<td>-4(2)</td>
<td>-1(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>C(24)</td>
<td>16(2)</td>
<td>16(2)</td>
<td>23(2)</td>
<td>-1(2)</td>
<td>-3(2)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>C(25)</td>
<td>17(2)</td>
<td>14(2)</td>
<td>25(2)</td>
<td>0(2)</td>
<td>-1(2)</td>
<td>-4(2)</td>
</tr>
<tr>
<td>C(26)</td>
<td>14(2)</td>
<td>18(2)</td>
<td>24(2)</td>
<td>0(2)</td>
<td>1(2)</td>
<td>-4(2)</td>
</tr>
</tbody>
</table>
Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å$^2$ x $10^3$) for compound 6.6.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(2)</td>
<td>6625</td>
<td>8260</td>
<td>8703</td>
<td>27</td>
</tr>
<tr>
<td>H(3)</td>
<td>5754</td>
<td>9347</td>
<td>9512</td>
<td>31</td>
</tr>
<tr>
<td>H(4)</td>
<td>2170</td>
<td>10162</td>
<td>9491</td>
<td>33</td>
</tr>
<tr>
<td>H(5)</td>
<td>-361</td>
<td>9987</td>
<td>8606</td>
<td>31</td>
</tr>
<tr>
<td>H(7)</td>
<td>-1237</td>
<td>9351</td>
<td>7504</td>
<td>29</td>
</tr>
<tr>
<td>H(8)</td>
<td>165</td>
<td>8729</td>
<td>6589</td>
<td>29</td>
</tr>
<tr>
<td>H(11)</td>
<td>1529</td>
<td>8193</td>
<td>5773</td>
<td>34</td>
</tr>
<tr>
<td>H(12)</td>
<td>3301</td>
<td>7755</td>
<td>4860</td>
<td>39</td>
</tr>
<tr>
<td>H(13)</td>
<td>6935</td>
<td>7003</td>
<td>4933</td>
<td>39</td>
</tr>
<tr>
<td>H(14)</td>
<td>8671</td>
<td>6594</td>
<td>5922</td>
<td>34</td>
</tr>
<tr>
<td>H(17)</td>
<td>9968</td>
<td>6090</td>
<td>6780</td>
<td>27</td>
</tr>
<tr>
<td>H(18)</td>
<td>11336</td>
<td>5452</td>
<td>7744</td>
<td>27</td>
</tr>
<tr>
<td>H(20)</td>
<td>10473</td>
<td>4888</td>
<td>8832</td>
<td>29</td>
</tr>
<tr>
<td>H(21)</td>
<td>8021</td>
<td>4811</td>
<td>9649</td>
<td>33</td>
</tr>
<tr>
<td>H(22)</td>
<td>4483</td>
<td>5672</td>
<td>9548</td>
<td>29</td>
</tr>
<tr>
<td>H(23)</td>
<td>3641</td>
<td>6727</td>
<td>8689</td>
<td>26</td>
</tr>
</tbody>
</table>
1-((E)-pentafluorostyryl)-4-((E)-styryl)naphthalene (6.7)

A 250 mL flask was charged with (E)-triphenyl((4-styrylnaphthalen-1-yl)methyl)phosphonium bromide (9.701 g, 16.6 mmol), pentafluorobenzaldehyde (2.952 g, 15.1 mmol) and ethanol (100 mL). To the resulting suspension a solution of t-BuOK (1.865 g, 16.6 mmol) in ethanol (50 mL) was added dropwise.

The resulting mixture was stirred at room temperature overnight (~ 12h) to make sure the reaction was complete. After that, silica gel (~ 10g) was added to the mixture and the solvent was removed by rotary evaporation to give a bright yellow powder. The yellow powder was placed on the top of silica gel column and eluted with warm solvent (hexanes: toluene = 4:1). The yellow fractions were combined and condensed, giving bright yellow crystals (3.993 g, 9.5 mmol, 57 % yield) as final product.

M.P.: 200.0 – 203.5 °C

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.286 – 8.267 (m, 1H), 8.240 (d, $J = 16.4$ Hz, 1H), 8.186 – 8.162 (m, 1H), 7.897 (d, $J = 16.0$ Hz, 1H), 7.786 (s, 2H), 7.636 – 7.582 (m, 4H), 7.435 – 7.397 (m, 2H), 7.399 – 7.300 (m, 1H), 7.193 (d, $J = 16.0$ Hz, 1H), 7.042 (d, $J = 16.4$ Hz, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 144.920 (d, $J = 246.3$ Hz), 139.844 (d, $J = 253.0$ Hz), 137.864
(d, $J = 252.5$ Hz), 137.451, 136.227, 134.484 (t, $J = 8.2$ Hz), 133.986, 132.309, 131.530, 131.445, 128.812, 128.009, 126.780, 126.544, 126.299, 125.480, 124.478, 123.990, 123.872, 123.462, 115.243, 112.803.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -142.639 - -142.718 (m, 2F), -156.251 (t, $J = 20.7$ Hz, 1F), -162.715 - -162.855 (m, 2F).

UV/Vis (DCM): $\lambda_{\text{max}}(\varepsilon) = 257$ (24000), 374 (32560) nm (M$^{-1}$cm$^{-1}$).

HRMS: M$^+$ = 422.10884 (Calc: 422.10939).

7,8,9,10-tetrafluoronaphtho[1,2-g]chrysene (6.8)

![Chemical Structure]

Chemical Formula: C$_{28}$H$_{12}$F$_4$
Molecular Weight: 400.37

In a quartz vessel was placed trans,trans-1-pentafluorostyryl-4-styryl-naphthalene (0.215 g, 0.51 mmol), iodine (0.128 g, 0.50 mmol) and toluene (100 mL). The resulting solution was irradiated in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps for 48 hours and TLC indicated a new product was formed. The resulting solution was then washed with saturated Na$_2$SO$_3$ solution (50 mL) to remove remaining iodine and dried over with anhydrous MgSO$_4$. After the removal of drying agent, the solution was mixed with silica gel (~ 10g) and filtered. Recrystallization from chlorobenzene provided light yellow crystals (0.021 g, 0.05 mmol, 10 % yield) as product. The crystals suitable for X-ray crystallography were obtained by slowly
evaporating a chlorobenzene solution.

**M.P.:** 314.0 – 315.5 °C

**\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\):** 8.844 (d, \(J = 9.2\) Hz, 1H), 8.809 – 8.785 (m, 1H), 8.732 – 8.693 (m, 2H), 8.312 (dd, \(^1J = 8.8\) Hz, \(^2J = 0.8\) Hz, 1H), 8.134 (d, \(J = 8.8\) Hz, 1H), 8.010 (ddd, \(^1J = 8.0\) Hz, \(^2J = 0.8\) Hz, \(^3J = 0.8\) Hz, 1H), 7.858 – 7.769 (m, 3H), 7.539 (ddd, \(^1J = 8.0\) Hz, \(^2J = 8.0\) Hz, \(^3J = 1.2\) Hz, 1H), 7.313 (ddd, \(^1J = 8.0\) Hz, \(^2J = 8.0\) Hz, \(^3J = 1.2\) Hz, 1H).

**\(^19\)F-NMR (376 MHz, CDCl\(_3\)) \(\delta\):** -128.641 (dd, \(^1J = 16.0\) Hz, \(^2J = 16.0\) Hz, 1F), -150.020 (dd, \(^1J = 19.6\) Hz, \(^2J = 13.9\) Hz, 1F), -158.644 (dd, \(^1J = 19.6\) Hz, \(^2J = 19.6\) Hz, 1F), -158.916 (ddd, \(^1J = 19.9\) Hz, \(^2J = 19.9\) Hz, \(^3J = 3.4\) Hz, 1F).

**HRMS:** MH\(^+\) = 401.08479 (Calc: 400.08751).
Table 1. Crystal data and structure refinement for compound 6.8.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>6.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂₆H₁₂F₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>400.36</td>
</tr>
<tr>
<td>Temperature</td>
<td>105(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Orthorhombic, P2(1)2(1)2(1)</td>
</tr>
</tbody>
</table>
Unit cell dimensions

\[ a = 5.097(3) \text{ Å} \quad \alpha = 90 \text{ deg.} \]
\[ b = 12.568(8) \text{ Å} \quad \beta = 90 \text{ deg.} \]
\[ c = 26.022(17) \text{ Å} \quad \gamma = 90 \text{ deg.} \]

Volume: \( 1666.8(19) \text{ Å}^3 \)

\[ Z, \text{ Calculated density} \quad 4, \quad 1.595 \text{ Mg/m}^3 \]

Absorption coefficient: \( 0.123 \text{ mm}^{-1} \)

\[ F(000) \quad 816 \]

Crystal size: \( 0.200 \times 0.050 \times 0.020 \text{ mm} \)

Theta range for data collection: \( 1.565 \text{ to } 25.044 \text{ deg.} \)

Limiting indices: \(-6 \leq h \leq 4, -14 \leq k \leq 10, -31 \leq l \leq 29\)

Reflections collected / unique: \( 7772 / 2920 \) \( [R(int) = 0.1718] \)

Completeness to theta = \( 25.044 \text{ deg.} \quad 100.0 \% \)

Absorption correction: Semi-empirical from equivalents

Max. and min. transmission: \( 0.998 \text{ and } 0.652 \)

Refinement method: Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters: \( 2920 / 0 / 271 \)

Goodness-of-fit on \( F^2 \): \( 1.037 \)

Final R indices [I>2\sigma(I)]: \( R1 = 0.1032, \text{ wR2 = 0.2034} \)

R indices (all data): \( R1 = 0.2413, \text{ wR2 = 0.2713} \)

Extinction coefficient: n/a

Largest diff. peak and hole: \( 0.451 \text{ and } -0.390 \text{ e.Å}^{-3} \)
Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for compound 6.8. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>1706(15)</td>
<td>6457(6)</td>
<td>3934(3)</td>
<td>37(2)</td>
</tr>
<tr>
<td>F(2)</td>
<td>3054(16)</td>
<td>8309(6)</td>
<td>3538(3)</td>
<td>43(2)</td>
</tr>
<tr>
<td>F(3)</td>
<td>7326(16)</td>
<td>8517(6)</td>
<td>2925(3)</td>
<td>47(2)</td>
</tr>
<tr>
<td>F(4)</td>
<td>10144(16)</td>
<td>6770(6)</td>
<td>2667(3)</td>
<td>41(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>3920(30)</td>
<td>6505(14)</td>
<td>3642(6)</td>
<td>36(4)</td>
</tr>
<tr>
<td>C(2)</td>
<td>4560(30)</td>
<td>7437(12)</td>
<td>3435(6)</td>
<td>35(4)</td>
</tr>
<tr>
<td>C(3)</td>
<td>6700(30)</td>
<td>7572(11)</td>
<td>3125(5)</td>
<td>28(4)</td>
</tr>
<tr>
<td>C(4)</td>
<td>8000(30)</td>
<td>6656(13)</td>
<td>2992(5)</td>
<td>31(4)</td>
</tr>
<tr>
<td>C(5)</td>
<td>7430(30)</td>
<td>5675(11)</td>
<td>3181(5)</td>
<td>25(3)</td>
</tr>
<tr>
<td>C(6)</td>
<td>5330(30)</td>
<td>5570(10)</td>
<td>3545(5)</td>
<td>23(3)</td>
</tr>
<tr>
<td>C(7)</td>
<td>4720(30)</td>
<td>4502(12)</td>
<td>3734(5)</td>
<td>29(4)</td>
</tr>
<tr>
<td>C(8)</td>
<td>3150(30)</td>
<td>4319(11)</td>
<td>4198(6)</td>
<td>34(4)</td>
</tr>
<tr>
<td>C(9)</td>
<td>3290(30)</td>
<td>5011(11)</td>
<td>4645(5)</td>
<td>30(4)</td>
</tr>
<tr>
<td>C(10)</td>
<td>5290(30)</td>
<td>5823(11)</td>
<td>4724(5)</td>
<td>30(4)</td>
</tr>
<tr>
<td>C(11)</td>
<td>5350(30)</td>
<td>6393(11)</td>
<td>5148(5)</td>
<td>33(4)</td>
</tr>
<tr>
<td>C(12)</td>
<td>3470(30)</td>
<td>6303(11)</td>
<td>5543(6)</td>
<td>37(4)</td>
</tr>
<tr>
<td>C(13)</td>
<td>1590(30)</td>
<td>5500(11)</td>
<td>5486(5)</td>
<td>35(4)</td>
</tr>
<tr>
<td>C(14)</td>
<td>1490(30)</td>
<td>4881(12)</td>
<td>5060(5)</td>
<td>30(4)</td>
</tr>
<tr>
<td>C(15)</td>
<td>-280(30)</td>
<td>3965(11)</td>
<td>5026(6)</td>
<td>33(4)</td>
</tr>
<tr>
<td>C(16)</td>
<td>-110(30)</td>
<td>3284(12)</td>
<td>4648(5)</td>
<td>32(4)</td>
</tr>
<tr>
<td>C(17)</td>
<td>1680(30)</td>
<td>3412(11)</td>
<td>4229(6)</td>
<td>32(4)</td>
</tr>
<tr>
<td>C(18)</td>
<td>2110(30)</td>
<td>2544(11)</td>
<td>3865(5)</td>
<td>29(4)</td>
</tr>
<tr>
<td>C(19)</td>
<td>640(30)</td>
<td>1615(12)</td>
<td>3866(5)</td>
<td>32(4)</td>
</tr>
<tr>
<td>C(20)</td>
<td>1260(30)</td>
<td>741(12)</td>
<td>3560(6)</td>
<td>36(4)</td>
</tr>
<tr>
<td>C(21)</td>
<td>3420(30)</td>
<td>820(12)</td>
<td>3239(6)</td>
<td>40(4)</td>
</tr>
<tr>
<td>C(22)</td>
<td>4860(30)</td>
<td>1728(11)</td>
<td>3216(5)</td>
<td>35(4)</td>
</tr>
<tr>
<td>C(23)</td>
<td>4250(30)</td>
<td>2625(11)</td>
<td>3519(5)</td>
<td>31(4)</td>
</tr>
<tr>
<td>C(24)</td>
<td>5520(30)</td>
<td>3637(12)</td>
<td>3454(5)</td>
<td>30(4)</td>
</tr>
<tr>
<td>C(25)</td>
<td>7670(30)</td>
<td>3766(11)</td>
<td>3099(5)</td>
<td>34(4)</td>
</tr>
<tr>
<td>C(26)</td>
<td>8650(30)</td>
<td>4739(12)</td>
<td>2985(5)</td>
<td>38(4)</td>
</tr>
</tbody>
</table>
Table 3. Bond lengths [Å] and angles [deg] for compound 6.8.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)-C(1)</td>
<td>1.362(15)</td>
</tr>
<tr>
<td>F(2)-C(2)</td>
<td>1.364(16)</td>
</tr>
<tr>
<td>F(3)-C(3)</td>
<td>1.336(15)</td>
</tr>
<tr>
<td>F(4)-C(4)</td>
<td>1.388(15)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.33(2)</td>
</tr>
<tr>
<td>C(1)-C(6)</td>
<td>1.400(19)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.37(2)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.37(2)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.358(19)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.425(18)</td>
</tr>
<tr>
<td>C(5)-C(26)</td>
<td>1.436(19)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.463(17)</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.372(18)</td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td>1.466(19)</td>
</tr>
<tr>
<td>C(8)-C(17)</td>
<td>1.366(19)</td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td>1.453(18)</td>
</tr>
<tr>
<td>C(9)-C(14)</td>
<td>1.428(18)</td>
</tr>
<tr>
<td>C(9)-C(10)</td>
<td>1.458(19)</td>
</tr>
<tr>
<td>C(10)-C(11)</td>
<td>1.317(18)</td>
</tr>
<tr>
<td>C(10)-H(10)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(11)-C(12)</td>
<td>1.41(2)</td>
</tr>
<tr>
<td>C(11)-H(11)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(12)-C(13)</td>
<td>1.399(19)</td>
</tr>
<tr>
<td>C(12)-H(12)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(13)-C(14)</td>
<td>1.355(18)</td>
</tr>
<tr>
<td>C(13)-H(13)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(14)-C(15)</td>
<td>1.465(19)</td>
</tr>
<tr>
<td>C(15)-C(16)</td>
<td>1.307(18)</td>
</tr>
<tr>
<td>C(15)-H(15)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(16)-C(17)</td>
<td>1.431(19)</td>
</tr>
<tr>
<td>C(16)-H(16)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(17)-C(18)</td>
<td>1.462(19)</td>
</tr>
<tr>
<td>C(18)-C(19)</td>
<td>1.388(19)</td>
</tr>
<tr>
<td>C(18)-C(23)</td>
<td>1.42(2)</td>
</tr>
<tr>
<td>C(19)-C(20)</td>
<td>1.394(19)</td>
</tr>
<tr>
<td>C(19)-H(19)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(20)-C(21)</td>
<td>1.38(2)</td>
</tr>
<tr>
<td>C(20)-H(20)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(21)-C(22)</td>
<td>1.36(2)</td>
</tr>
<tr>
<td>C(21)-H(21)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(22)-C(23)</td>
<td>1.411(19)</td>
</tr>
<tr>
<td>C(22)-H(22)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(23)-C(24)</td>
<td>1.438(18)</td>
</tr>
<tr>
<td>C(24)-C(25)</td>
<td>1.442(19)</td>
</tr>
<tr>
<td>C(25)-C(26)</td>
<td>1.354(19)</td>
</tr>
<tr>
<td>C(25)-H(25)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(26)-H(26)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(2)-C(1)-F(1)</td>
<td>117.9(14)</td>
</tr>
</tbody>
</table>
C(2)-C(1)-C(6) 122.7(14)
F(1)-C(1)-C(6) 119.2(14)
C(1)-C(2)-F(2) 119.3(14)
C(1)-C(2)-C(3) 123.0(15)
F(2)-C(2)-C(3) 117.7(14)
F(3)-C(3)-C(2) 122.1(14)
F(3)-C(3)-C(4) 122.1(14)
C(2)-C(3)-C(4) 115.5(13)
C(5)-C(4)-C(3) 124.4(13)
C(5)-C(4)-F(4) 118.9(13)
C(3)-C(4)-F(4) 116.5(13)
F(3)-C(3)-C(2) 122.1(14)
C(2)-C(3)-C(4) 115.5(13)
C(2)-C(3)-C(4) 115.5(13)
F(4)-C(4)-C(3) 124.4(13)
F(4)-C(4)-C(3) 124.4(13)
C(2)-C(3)-C(4) 115.5(13)
C(18)-C(19)-C(20)  122.6(14)
C(18)-C(19)-H(19)  118.7
C(20)-C(19)-H(19)  118.7
C(21)-C(20)-C(19)  118.0(15)
C(21)-C(20)-H(20)  121.0
C(19)-C(20)-H(20)  121.0
C(22)-C(21)-C(20)  121.1(15)
C(22)-C(21)-H(21)  119.5
C(20)-C(21)-H(21)  119.5
C(21)-C(22)-C(23)  121.8(15)
C(21)-C(22)-H(22)  119.1
C(23)-C(22)-H(22)  119.1
C(22)-C(23)-C(18)  117.9(14)
C(22)-C(23)-C(24)  122.8(14)
C(18)-C(23)-C(24)  119.0(13)
C(7)-C(24)-C(23)   120.3(13)
C(7)-C(24)-C(25)   118.6(13)
C(23)-C(24)-C(25)  121.1(13)
C(26)-C(25)-C(24)  121.5(14)
C(26)-C(25)-H(25)  119.3
C(24)-C(25)-H(25)  119.3
C(25)-C(26)-C(5)   120.5(14)
C(25)-C(26)-H(26)  119.8
C(5)-C(26)-H(26)   119.8

Symmetry transformations used to generate equivalent atoms:
Table 4. Anisotropic displacement parameters (Å² x 10³) for compound 6.8.

The anisotropic displacement factor exponent takes the form:
\[-2 \pi^2 [ h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12 ] \]

<table>
<thead>
<tr>
<th></th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>16(5)</td>
<td>46(6)</td>
<td>50(5)</td>
<td>0(4)</td>
<td>3(4)</td>
<td>5(4)</td>
</tr>
<tr>
<td>F(2)</td>
<td>27(5)</td>
<td>40(5)</td>
<td>63(6)</td>
<td>3(4)</td>
<td>2(5)</td>
<td>0(5)</td>
</tr>
<tr>
<td>F(3)</td>
<td>25(5)</td>
<td>44(6)</td>
<td>72(6)</td>
<td>13(5)</td>
<td>1(5)</td>
<td>-4(5)</td>
</tr>
<tr>
<td>F(4)</td>
<td>21(5)</td>
<td>49(5)</td>
<td>52(5)</td>
<td>9(4)</td>
<td>6(5)</td>
<td>-4(5)</td>
</tr>
<tr>
<td>C(1)</td>
<td>10(9)</td>
<td>60(13)</td>
<td>40(10)</td>
<td>-11(9)</td>
<td>5(7)</td>
<td>3(8)</td>
</tr>
<tr>
<td>C(2)</td>
<td>28(10)</td>
<td>32(9)</td>
<td>45(10)</td>
<td>-4(8)</td>
<td>9(9)</td>
<td>4(9)</td>
</tr>
<tr>
<td>C(3)</td>
<td>38(11)</td>
<td>33(9)</td>
<td>15(7)</td>
<td>4(6)</td>
<td>-3(8)</td>
<td>-10(8)</td>
</tr>
<tr>
<td>C(4)</td>
<td>18(9)</td>
<td>56(11)</td>
<td>18(8)</td>
<td>-5(7)</td>
<td>12(7)</td>
<td>-4(8)</td>
</tr>
<tr>
<td>C(5)</td>
<td>21(10)</td>
<td>33(9)</td>
<td>22(8)</td>
<td>11(7)</td>
<td>-1(7)</td>
<td>0(7)</td>
</tr>
<tr>
<td>C(6)</td>
<td>27(9)</td>
<td>24(8)</td>
<td>19(7)</td>
<td>-1(6)</td>
<td>6(7)</td>
<td>-3(7)</td>
</tr>
<tr>
<td>C(7)</td>
<td>11(9)</td>
<td>43(10)</td>
<td>34(9)</td>
<td>6(7)</td>
<td>0(7)</td>
<td>2(8)</td>
</tr>
<tr>
<td>C(8)</td>
<td>20(10)</td>
<td>33(10)</td>
<td>47(10)</td>
<td>6(8)</td>
<td>-4(8)</td>
<td>1(8)</td>
</tr>
<tr>
<td>C(9)</td>
<td>17(8)</td>
<td>37(9)</td>
<td>37(9)</td>
<td>-6(7)</td>
<td>8(8)</td>
<td>-8(8)</td>
</tr>
<tr>
<td>C(10)</td>
<td>22(9)</td>
<td>36(9)</td>
<td>33(9)</td>
<td>4(7)</td>
<td>7(8)</td>
<td>3(8)</td>
</tr>
<tr>
<td>C(11)</td>
<td>29(9)</td>
<td>46(10)</td>
<td>23(8)</td>
<td>-1(7)</td>
<td>-2(8)</td>
<td>-4(8)</td>
</tr>
<tr>
<td>C(12)</td>
<td>34(10)</td>
<td>38(10)</td>
<td>39(9)</td>
<td>-5(7)</td>
<td>3(9)</td>
<td>-9(9)</td>
</tr>
<tr>
<td>C(13)</td>
<td>30(10)</td>
<td>56(11)</td>
<td>20(8)</td>
<td>7(8)</td>
<td>3(8)</td>
<td>22(9)</td>
</tr>
<tr>
<td>C(14)</td>
<td>15(9)</td>
<td>49(10)</td>
<td>27(9)</td>
<td>-1(7)</td>
<td>0(7)</td>
<td>-7(8)</td>
</tr>
<tr>
<td>C(15)</td>
<td>19(9)</td>
<td>41(10)</td>
<td>39(10)</td>
<td>-5(7)</td>
<td>0(8)</td>
<td>1(8)</td>
</tr>
<tr>
<td>C(16)</td>
<td>18(9)</td>
<td>42(9)</td>
<td>36(9)</td>
<td>7(8)</td>
<td>6(8)</td>
<td>-2(8)</td>
</tr>
<tr>
<td>C(17)</td>
<td>24(9)</td>
<td>26(9)</td>
<td>47(10)</td>
<td>6(8)</td>
<td>-6(8)</td>
<td>5(8)</td>
</tr>
<tr>
<td>C(18)</td>
<td>24(10)</td>
<td>40(10)</td>
<td>24(8)</td>
<td>4(7)</td>
<td>0(8)</td>
<td>13(8)</td>
</tr>
<tr>
<td>C(19)</td>
<td>12(8)</td>
<td>38(10)</td>
<td>45(10)</td>
<td>-1(8)</td>
<td>3(7)</td>
<td>5(8)</td>
</tr>
<tr>
<td>C(20)</td>
<td>23(10)</td>
<td>49(11)</td>
<td>35(9)</td>
<td>12(8)</td>
<td>0(8)</td>
<td>0(8)</td>
</tr>
<tr>
<td>C(21)</td>
<td>41(11)</td>
<td>43(10)</td>
<td>37(9)</td>
<td>17(8)</td>
<td>6(9)</td>
<td>2(9)</td>
</tr>
<tr>
<td>C(22)</td>
<td>21(9)</td>
<td>40(9)</td>
<td>43(9)</td>
<td>9(8)</td>
<td>6(8)</td>
<td>-4(9)</td>
</tr>
<tr>
<td>C(23)</td>
<td>18(9)</td>
<td>40(10)</td>
<td>34(9)</td>
<td>3(8)</td>
<td>-2(8)</td>
<td>8(7)</td>
</tr>
<tr>
<td>C(24)</td>
<td>15(9)</td>
<td>48(10)</td>
<td>28(9)</td>
<td>2(7)</td>
<td>4(7)</td>
<td>-6(8)</td>
</tr>
<tr>
<td>C(25)</td>
<td>23(10)</td>
<td>31(9)</td>
<td>49(11)</td>
<td>7(7)</td>
<td>3(8)</td>
<td>-2(8)</td>
</tr>
<tr>
<td>C(26)</td>
<td>10(9)</td>
<td>57(12)</td>
<td>45(11)</td>
<td>5(8)</td>
<td>-2(8)</td>
<td>0(8)</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>y</td>
<td>z</td>
<td>U(eq)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(10)</td>
<td>6577</td>
<td>5943</td>
<td>4466</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(11)</td>
<td>6729</td>
<td>6893</td>
<td>5191</td>
<td>39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(12)</td>
<td>3477</td>
<td>6763</td>
<td>5833</td>
<td>44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(13)</td>
<td>352</td>
<td>5385</td>
<td>5753</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(15)</td>
<td>-1578</td>
<td>3863</td>
<td>5284</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(16)</td>
<td>-1226</td>
<td>2678</td>
<td>4651</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(19)</td>
<td>-856</td>
<td>1574</td>
<td>4083</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(20)</td>
<td>242</td>
<td>109</td>
<td>3572</td>
<td>43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(21)</td>
<td>3900</td>
<td>229</td>
<td>3032</td>
<td>48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(22)</td>
<td>6317</td>
<td>1761</td>
<td>2989</td>
<td>41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(25)</td>
<td>8409</td>
<td>3155</td>
<td>2941</td>
<td>41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(26)</td>
<td>10159</td>
<td>4798</td>
<td>2773</td>
<td>45</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1,4-bis(\(E\))-2-(perfluorophenyl)vinyl)naphthalene (6.10)

![Chemical structure](image)

Chemical Formula: \(C_{26}H_{10}F_{10}\)
Molecular Weight: 512.34

In a 100 ml pear flask equipped with magnetic stirbar was placed 1,4-diiodonaphthalene (1.90 g, 5.0 mmol), pentafluorostyrene (2.15 g, 11.0 mmol), \(K_2CO_3\) (1.75 g, 12.7 mmol), anhydrous DMF (10 ml) and 2-(2-methoxyethoxy)-\(N, N\)-bis[2-(2-methoxyethoxy)ethyl]ethanamine (0.080 g, 0.24 mmol). The resulting mixture was degassed thoroughly with nitrogen, placed in a 80 °C oil bath, and then \(Pd(OAc)_{2}\) (11 mg, 1%) was added. The reaction was warmed to 110 °C and left stirring for 8 hours under a nitrogen atmosphere. After this time, TLC indicated all the diiodide starting material was consumed and a small amount of mono adduct was present in addition to the desired diadduct. The mixture was cooled to room temperature and water was added dropwise with stirring to 100 ml. The resulting suspension was stirred and then the solid was isolated by suction filtration, washed well with water and air-dried. The crude product was transferred to an Erlenmeyer flask and dissolved in boiling toluene to which some Montmorillonite clay and silica gel were added. The resulting suspension was boiled and poured into a fluted filter and the solvent was boiled into the filter to remove any residual product. Upon cooling the product obtained was contaminated by palladium metal. Two more cycles of clay treatment and filtration were needed to remove the residual palladium. Finally, a pure product of fine yellow crystals (1.50 g, 2.9 mmol, 59 % yield) was obtained from a mixture of toluene and iso-octane and isolated by suction filtration.

**M.P.:** 236.5 – 240.0 °C.
1H-NMR (400 MHz, CDCl3) δ: 8.220 (d, J = 16.8 Hz, 2H), 8.197 – 8.172 (m, 2H), 7.788 (s, 2H), 7.623 – 7.599 (m, 2H), 7.054 (d, J = 16.8 Hz, 2H).

13C-NMR (100 MHz, CDCl3) δ: 145.106 (d, J = 246.8 Hz), 140.298 (d, J = 251.6 Hz), 138.084 (d, J = 249.3 Hz), 135.505, 134.527 (t, J = 7.4 Hz), 131.582, 126.875, 124.252, 123.897, 116.055, 112.671.

19F-NMR (376 MHz, CDCl3) δ: -143.251 (dd, J1 = 21.2 Hz, J2 = 7.7 Hz, 2F), -156.605 (t, J = 20.3 Hz, 1F), -163.330 – -163.459 (m, 2F).

UV/Vis (DCM): λmax(ε) = 230 (23750), 262 (20750), 367 (22840) nm (M⁻¹cm⁻¹).

GCMS (m/z): 511.91.

HRMS: M⁺ = 512.06158 (Calc: 512.06228).

7,8,9,10,11,12,13,14-Octafluoronaphtho[1,2-g]chrysene (6.11)

Chemical Formula: C26H8F8
Molecular Weight: 472.33

In a quartz vessel, 1,4-bis((E)-2-(perfluorophenyl)vinyl)naphthalene (0.512 g, 1.0 mmol) was dissolved in toluene (100 mL). The solution was flushed with nitrogen and irradiated for 30 hours with a 450W Hanovia lamp equipped with a Vycor filter.
After column chromatography (eluent: hexanes: EtOAc = 4:1), yellow crystals (0.109 g, 0.23 mmol, 23 % yield) were obtained as final product. The crystals suitable for X-ray crystallography were obtained by slowly evaporating a chlorobenzene solution.

**M.P.:** 284.0 – 286.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.808 (d, $J = 9.2$ Hz, 2H), 8.772 (dd, $^1J = 2.8$ Hz, $^2J = 2.8$ Hz, 2H), 8.332 (dd, $^1J = 9.2$ Hz, $^2J = 1.4$ Hz, 2H), 7.862 – 7.838 (m, 2H).

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -134.593 (t, $J = 16.4$ Hz, 2F), -149.282 (dd, $^1J = 19.6$ Hz, $^2J = 13.9$ Hz, 2F), -158.048 (t, $J = 19.4$ Hz, 2F), -158.381 (td, $^1J = 19.6$ Hz, $^2J = 2.6$ Hz, 2F).

**HRMS:** M$^+$ = 472.04929 (Calc: 472.04982).

**Table 1.** Crystal data and structure refinement for compound 6.11.
Identification code  

6.11

Empirical formula  

C_{26}H_{8}F_{8}

Formula weight  

472.32

Temperature  

188(2) K

Wavelength  

0.71073 Å

Crystal system, space group  

Orthorhombic, p_21_21_21

Unit cell dimensions  

a = 5.1723(4) Å  alpha = 90 deg.
b = 12.5875(9) Å  beta = 90 deg.
c = 27.3127(19) Å  gamma = 90 deg.

Volume  

1778.2(2) Å^3

Z, Calculated density  

4, 1.764 Mg/m^3

Absorption coefficient  

0.161 mm^-1

F(000)  

944

Crystal size  

0.40 x 0.15 x 0.10 mm

Theta range for data collection  

1.49 to 25.05 deg.

Limiting indices  

-6<=h<=6, -14<=k<=14, -32<=l<=32

Reflections collected / unique  

14365 / 1865 [R(int) = 0.0261]

Completeness to theta = 25.05  

99.9 %

Absorption correction  

Semi-empirical from equivalents

Max. and min. transmission  

0.9841 and 0.9384

Refinement method  

Full-matrix least-squares on F^2

Data / restraints / parameters  

1865 / 0 / 307

Goodness-of-fit on F^2  

0.774

Final R indices [I>2sigma(I)]  

R1 = 0.0248, wR2 = 0.0789

R indices (all data)  

R1 = 0.0292, wR2 = 0.0951

Largest diff. peak and hole  

0.244 and -0.261 e.A^-3
Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for compound 6.11.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>-2938(3)</td>
<td>-1292(1)</td>
<td>1090(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>-1552(4)</td>
<td>-3143(1)</td>
<td>1474(1)</td>
<td>40(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>2606(4)</td>
<td>-3312(1)</td>
<td>2068(1)</td>
<td>46(1)</td>
</tr>
<tr>
<td>F(4)</td>
<td>5298(4)</td>
<td>-1544(1)</td>
<td>2324(1)</td>
<td>39(1)</td>
</tr>
<tr>
<td>F(5)</td>
<td>2592(3)</td>
<td>-698(1)</td>
<td>630(1)</td>
<td>28(1)</td>
</tr>
<tr>
<td>F(6)</td>
<td>2528(3)</td>
<td>-190(1)</td>
<td>-157(1)</td>
<td>34(1)</td>
</tr>
<tr>
<td>F(7)</td>
<td>-1195(4)</td>
<td>-1704(1)</td>
<td>-847(1)</td>
<td>40(1)</td>
</tr>
<tr>
<td>F(8)</td>
<td>-4828(3)</td>
<td>-168(1)</td>
<td>-753(1)</td>
<td>39(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>-818(5)</td>
<td>-1310(2)</td>
<td>1379(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>-157(6)</td>
<td>-2273(2)</td>
<td>1572(1)</td>
<td>28(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>1969(6)</td>
<td>-2356(2)</td>
<td>1889(1)</td>
<td>32(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>3273(5)</td>
<td>-1465(2)</td>
<td>2012(1)</td>
<td>28(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>2573(5)</td>
<td>-457(2)</td>
<td>1838(1)</td>
<td>26(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>544(5)</td>
<td>-372(2)</td>
<td>1486(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>-108(5)</td>
<td>669(2)</td>
<td>1295(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>636(5)</td>
<td>1552(2)</td>
<td>1572(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>2686(6)</td>
<td>1441(2)</td>
<td>1920(1)</td>
<td>30(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>3738(6)</td>
<td>480(2)</td>
<td>2024(1)</td>
<td>30(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>-1584(5)</td>
<td>850(2)</td>
<td>843(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>-1383(5)</td>
<td>182(2)</td>
<td>412(1)</td>
<td>21(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>581(5)</td>
<td>-571(2)</td>
<td>321(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>630(5)</td>
<td>-1190(2)</td>
<td>-92(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>-1256(6)</td>
<td>-1080(2)</td>
<td>-452(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>-3079(5)</td>
<td>-313(2)</td>
<td>-397(1)</td>
<td>26(1)</td>
</tr>
<tr>
<td>C(17)</td>
<td>-3179(5)</td>
<td>341(2)</td>
<td>21(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(18)</td>
<td>-4983(5)</td>
<td>1191(2)</td>
<td>44(1)</td>
<td>27(1)</td>
</tr>
<tr>
<td>C(19)</td>
<td>-4865(5)</td>
<td>1887(2)</td>
<td>418(1)</td>
<td>27(1)</td>
</tr>
<tr>
<td>C(20)</td>
<td>-3109(5)</td>
<td>1769(2)</td>
<td>815(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(21)</td>
<td>-2797(5)</td>
<td>2613(2)</td>
<td>1178(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(22)</td>
<td>-717(5)</td>
<td>2557(2)</td>
<td>1512(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(23)</td>
<td>-208(6)</td>
<td>3441(2)</td>
<td>1815(1)</td>
<td>31(1)</td>
</tr>
<tr>
<td>C(24)</td>
<td>-1727(6)</td>
<td>4335(2)</td>
<td>1798(1)</td>
<td>34(1)</td>
</tr>
<tr>
<td>C(25)</td>
<td>-3860(6)</td>
<td>4366(2)</td>
<td>1486(1)</td>
<td>34(1)</td>
</tr>
<tr>
<td>C(26)</td>
<td>-4384(6)</td>
<td>3529(2)</td>
<td>1182(1)</td>
<td>29(1)</td>
</tr>
</tbody>
</table>
Table 3. Bond lengths [Å] and angles [deg] for compound 6.11.

<table>
<thead>
<tr>
<th>Bond 1</th>
<th>Bond 2</th>
<th>Length/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)-C(1)</td>
<td></td>
<td>1.351(3)</td>
</tr>
<tr>
<td>F(2)-C(2)</td>
<td></td>
<td>1.339(3)</td>
</tr>
<tr>
<td>F(3)-C(3)</td>
<td></td>
<td>1.340(3)</td>
</tr>
<tr>
<td>F(4)-C(4)</td>
<td></td>
<td>1.353(3)</td>
</tr>
<tr>
<td>F(5)-C(13)</td>
<td></td>
<td>1.349(3)</td>
</tr>
<tr>
<td>F(6)-C(14)</td>
<td></td>
<td>1.340(3)</td>
</tr>
<tr>
<td>F(7)-C(15)</td>
<td></td>
<td>1.335(3)</td>
</tr>
<tr>
<td>F(8)-C(16)</td>
<td></td>
<td>1.341(3)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td></td>
<td>1.365(3)</td>
</tr>
<tr>
<td>C(1)-C(6)</td>
<td></td>
<td>1.406(4)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td></td>
<td>1.403(4)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td></td>
<td>1.352(4)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td></td>
<td>1.402(4)</td>
</tr>
<tr>
<td>C(5)-C(10)</td>
<td></td>
<td>1.420(4)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td></td>
<td>1.428(4)</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td></td>
<td>1.450(3)</td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td></td>
<td>1.399(3)</td>
</tr>
<tr>
<td>C(7)-C(11)</td>
<td></td>
<td>1.469(3)</td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td></td>
<td>1.430(4)</td>
</tr>
<tr>
<td>C(8)-C(22)</td>
<td></td>
<td>1.455(4)</td>
</tr>
<tr>
<td>C(9)-C(10)</td>
<td></td>
<td>1.357(4)</td>
</tr>
<tr>
<td>C(9)-H(9)</td>
<td></td>
<td>0.9500</td>
</tr>
<tr>
<td>C(10)-H(10)</td>
<td></td>
<td>0.9500</td>
</tr>
<tr>
<td>C(11)-C(20)</td>
<td></td>
<td>1.403(3)</td>
</tr>
<tr>
<td>C(11)-C(12)</td>
<td></td>
<td>1.450(3)</td>
</tr>
<tr>
<td>C(12)-C(13)</td>
<td></td>
<td>1.412(3)</td>
</tr>
<tr>
<td>C(12)-C(17)</td>
<td></td>
<td>1.430(3)</td>
</tr>
<tr>
<td>C(13)-C(14)</td>
<td></td>
<td>1.370(4)</td>
</tr>
<tr>
<td>C(14)-C(15)</td>
<td></td>
<td>1.393(4)</td>
</tr>
<tr>
<td>C(15)-C(16)</td>
<td></td>
<td>1.358(4)</td>
</tr>
<tr>
<td>C(16)-C(17)</td>
<td></td>
<td>1.407(4)</td>
</tr>
<tr>
<td>C(17)-C(18)</td>
<td></td>
<td>1.422(4)</td>
</tr>
<tr>
<td>C(18)-C(19)</td>
<td></td>
<td>1.347(4)</td>
</tr>
<tr>
<td>C(18)-H(18)</td>
<td></td>
<td>0.9500</td>
</tr>
<tr>
<td>C(19)-C(20)</td>
<td></td>
<td>1.421(3)</td>
</tr>
<tr>
<td>C(19)-H(19)</td>
<td></td>
<td>0.9500</td>
</tr>
<tr>
<td>C(20)-C(21)</td>
<td></td>
<td>1.462(3)</td>
</tr>
<tr>
<td>C(21)-C(22)</td>
<td></td>
<td>1.412(4)</td>
</tr>
<tr>
<td>C(21)-C(26)</td>
<td></td>
<td>1.415(4)</td>
</tr>
<tr>
<td>C(22)-C(23)</td>
<td></td>
<td>1.412(4)</td>
</tr>
<tr>
<td>C(23)-C(24)</td>
<td></td>
<td>1.373(4)</td>
</tr>
<tr>
<td>C(23)-H(23)</td>
<td></td>
<td>0.9500</td>
</tr>
<tr>
<td>C(24)-C(25)</td>
<td></td>
<td>1.394(4)</td>
</tr>
<tr>
<td>C(24)-H(24)</td>
<td></td>
<td>0.9500</td>
</tr>
<tr>
<td>C(25)-C(26)</td>
<td></td>
<td>1.369(4)</td>
</tr>
<tr>
<td>C(25)-H(25)</td>
<td></td>
<td>0.9500</td>
</tr>
<tr>
<td>C(26)-H(26)</td>
<td></td>
<td>0.9500</td>
</tr>
<tr>
<td>F(1)-C(1)-C(2)</td>
<td></td>
<td>116.3(2)</td>
</tr>
<tr>
<td>F(1)-C(1)-C(6)</td>
<td></td>
<td>120.9(2)</td>
</tr>
<tr>
<td>Bond</td>
<td>Angle (°)</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>C(2)-C(1)-C(6)</td>
<td>122.7(2)</td>
<td></td>
</tr>
<tr>
<td>F(2)-C(2)-C(1)</td>
<td>121.0(2)</td>
<td></td>
</tr>
<tr>
<td>F(2)-C(2)-C(3)</td>
<td>119.0(2)</td>
<td></td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>120.0(2)</td>
<td></td>
</tr>
<tr>
<td>F(3)-C(3)-C(4)</td>
<td>122.1(3)</td>
<td></td>
</tr>
<tr>
<td>F(3)-C(3)-C(2)</td>
<td>119.0(3)</td>
<td></td>
</tr>
<tr>
<td>C(4)-C(3)-C(2)</td>
<td>118.9(2)</td>
<td></td>
</tr>
<tr>
<td>C(3)-C(4)-F(4)</td>
<td>118.8(2)</td>
<td></td>
</tr>
<tr>
<td>C(3)-C(4)-C(5)</td>
<td>122.5(2)</td>
<td></td>
</tr>
<tr>
<td>F(4)-C(4)-C(5)</td>
<td>118.7(2)</td>
<td></td>
</tr>
<tr>
<td>C(4)-C(5)-C(10)</td>
<td>121.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(4)-C(5)-C(6)</td>
<td>119.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(10)-C(5)-C(6)</td>
<td>119.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(1)-C(6)-C(5)</td>
<td>116.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(1)-C(6)-C(7)</td>
<td>124.6(2)</td>
<td></td>
</tr>
<tr>
<td>C(5)-C(6)-C(7)</td>
<td>118.8(2)</td>
<td></td>
</tr>
<tr>
<td>C(8)-C(7)-C(6)</td>
<td>117.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(8)-C(7)-C(11)</td>
<td>118.3(2)</td>
<td></td>
</tr>
<tr>
<td>C(6)-C(7)-C(11)</td>
<td>124.2(2)</td>
<td></td>
</tr>
<tr>
<td>C(7)-C(8)-C(9)</td>
<td>119.0(2)</td>
<td></td>
</tr>
<tr>
<td>C(7)-C(8)-C(22)</td>
<td>119.8(2)</td>
<td></td>
</tr>
<tr>
<td>C(9)-C(8)-C(22)</td>
<td>121.2(2)</td>
<td></td>
</tr>
<tr>
<td>C(10)-C(9)-C(8)</td>
<td>121.7(2)</td>
<td></td>
</tr>
<tr>
<td>C(10)-C(9)-H(9)</td>
<td>119.2</td>
<td></td>
</tr>
<tr>
<td>C(9)-C(10)-C(5)</td>
<td>119.7(2)</td>
<td></td>
</tr>
<tr>
<td>C(9)-C(10)-H(10)</td>
<td>120.2</td>
<td></td>
</tr>
<tr>
<td>C(5)-C(10)-H(10)</td>
<td>120.2</td>
<td></td>
</tr>
<tr>
<td>C(20)-C(11)-C(12)</td>
<td>118.3(2)</td>
<td></td>
</tr>
<tr>
<td>C(20)-C(11)-C(7)</td>
<td>117.8(2)</td>
<td></td>
</tr>
<tr>
<td>C(12)-C(11)-C(7)</td>
<td>123.7(2)</td>
<td></td>
</tr>
<tr>
<td>C(13)-C(12)-C(17)</td>
<td>115.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(13)-C(12)-C(11)</td>
<td>125.7(2)</td>
<td></td>
</tr>
<tr>
<td>C(17)-C(12)-C(11)</td>
<td>118.6(2)</td>
<td></td>
</tr>
<tr>
<td>F(5)-C(13)-C(14)</td>
<td>115.6(2)</td>
<td></td>
</tr>
<tr>
<td>F(5)-C(13)-C(12)</td>
<td>121.6(2)</td>
<td></td>
</tr>
<tr>
<td>C(14)-C(13)-C(12)</td>
<td>122.7(2)</td>
<td></td>
</tr>
<tr>
<td>F(6)-C(14)-C(13)</td>
<td>120.2(2)</td>
<td></td>
</tr>
<tr>
<td>F(6)-C(14)-C(15)</td>
<td>119.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(13)-C(14)-C(15)</td>
<td>120.8(2)</td>
<td></td>
</tr>
<tr>
<td>F(7)-C(15)-C(16)</td>
<td>121.7(2)</td>
<td></td>
</tr>
<tr>
<td>F(7)-C(15)-C(14)</td>
<td>119.8(3)</td>
<td></td>
</tr>
<tr>
<td>C(16)-C(15)-C(14)</td>
<td>118.5(2)</td>
<td></td>
</tr>
<tr>
<td>F(8)-C(16)-C(15)</td>
<td>118.9(2)</td>
<td></td>
</tr>
<tr>
<td>F(8)-C(16)-C(17)</td>
<td>118.9(2)</td>
<td></td>
</tr>
<tr>
<td>C(15)-C(16)-C(17)</td>
<td>122.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(16)-C(17)-C(18)</td>
<td>120.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(16)-C(17)-C(12)</td>
<td>120.0(2)</td>
<td></td>
</tr>
<tr>
<td>C(18)-C(17)-C(12)</td>
<td>119.9(2)</td>
<td></td>
</tr>
<tr>
<td>C(19)-C(18)-C(17)</td>
<td>119.6(2)</td>
<td></td>
</tr>
<tr>
<td>C(19)-C(18)-H(18)</td>
<td>120.2</td>
<td></td>
</tr>
<tr>
<td>C(17)-C(18)-H(18)</td>
<td>120.2</td>
<td></td>
</tr>
<tr>
<td>C(18)-C(19)-C(20)</td>
<td>122.6(2)</td>
<td></td>
</tr>
</tbody>
</table>
C(18)-C(19)-H(19)  118.7
C(20)-C(19)-H(19)  118.7
C(11)-C(20)-C(19)  119.2(2)
C(11)-C(20)-C(21)  120.0(2)
C(19)-C(20)-C(21)  120.8(2)
C(22)-C(21)-C(26)  118.5(2)
C(22)-C(21)-C(20)  119.1(2)
C(26)-C(21)-C(20)  122.2(2)
C(21)-C(22)-C(23)  118.8(2)
C(21)-C(22)-C(8)   118.9(2)
C(23)-C(22)-C(8)   121.9(2)
C(24)-C(23)-C(22)  121.3(3)
C(24)-C(23)-H(23)  119.4
C(22)-C(23)-H(23)  119.4
C(23)-C(24)-C(25)  119.8(3)
C(23)-C(24)-H(24)  120.1
C(25)-C(24)-H(24)  120.1
C(26)-C(25)-C(24)  120.4(3)
C(26)-C(25)-H(25)  119.8
C(24)-C(25)-H(25)  119.8
C(25)-C(26)-C(21)  121.1(3)
C(25)-C(26)-H(26)  119.4
C(21)-C(26)-H(26)  119.4

Symmetry transformations used to generate equivalent atoms:
Table 4. Anisotropic displacement parameters (Å² x 10³) for compound 6.11.
The anisotropic displacement factor exponent takes the form:
\[-2\pi^2 \left[ h^2 a^*^2 U_{11} + \ldots + 2hk a^* b^* U_{12} \right]\]

<table>
<thead>
<tr>
<th></th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>27(1)</td>
<td>27(1)</td>
<td>34(1)</td>
<td>6(1)</td>
<td>-8(1)</td>
<td>-3(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>50(1)</td>
<td>22(1)</td>
<td>49(1)</td>
<td>4(1)</td>
<td>-6(1)</td>
<td>-5(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>60(1)</td>
<td>29(1)</td>
<td>50(1)</td>
<td>13(1)</td>
<td>-10(1)</td>
<td>14(1)</td>
</tr>
<tr>
<td>F(4)</td>
<td>38(1)</td>
<td>47(1)</td>
<td>32(1)</td>
<td>6(1)</td>
<td>-11(1)</td>
<td>12(1)</td>
</tr>
<tr>
<td>F(5)</td>
<td>24(1)</td>
<td>35(1)</td>
<td>26(1)</td>
<td>2(1)</td>
<td>-5(1)</td>
<td>7(1)</td>
</tr>
<tr>
<td>F(6)</td>
<td>36(1)</td>
<td>33(1)</td>
<td>35(1)</td>
<td>-2(1)</td>
<td>1(1)</td>
<td>9(1)</td>
</tr>
<tr>
<td>F(7)</td>
<td>49(1)</td>
<td>40(1)</td>
<td>31(1)</td>
<td>-12(1)</td>
<td>-4(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>F(8)</td>
<td>41(1)</td>
<td>45(1)</td>
<td>29(1)</td>
<td>-1(1)</td>
<td>-16(1)</td>
<td>4(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>24(1)</td>
<td>25(1)</td>
<td>22(1)</td>
<td>2(1)</td>
<td>0(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>32(2)</td>
<td>22(1)</td>
<td>31(1)</td>
<td>1(1)</td>
<td>2(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>39(2)</td>
<td>28(1)</td>
<td>27(1)</td>
<td>8(1)</td>
<td>3(1)</td>
<td>11(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>28(1)</td>
<td>38(2)</td>
<td>19(1)</td>
<td>4(1)</td>
<td>-3(1)</td>
<td>11(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>26(1)</td>
<td>30(1)</td>
<td>21(1)</td>
<td>1(1)</td>
<td>2(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>24(1)</td>
<td>24(1)</td>
<td>18(1)</td>
<td>1(1)</td>
<td>1(1)</td>
<td>3(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>20(1)</td>
<td>24(1)</td>
<td>21(1)</td>
<td>1(1)</td>
<td>0(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>26(1)</td>
<td>25(1)</td>
<td>22(1)</td>
<td>2(1)</td>
<td>1(1)</td>
<td>-3(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>32(1)</td>
<td>30(1)</td>
<td>26(1)</td>
<td>-2(1)</td>
<td>-5(1)</td>
<td>-4(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>28(1)</td>
<td>36(1)</td>
<td>24(1)</td>
<td>0(1)</td>
<td>-6(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>21(1)</td>
<td>20(1)</td>
<td>25(1)</td>
<td>5(1)</td>
<td>0(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>21(1)</td>
<td>19(1)</td>
<td>23(1)</td>
<td>5(1)</td>
<td>-2(1)</td>
<td>-3(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>22(1)</td>
<td>24(1)</td>
<td>24(1)</td>
<td>6(1)</td>
<td>-2(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>25(1)</td>
<td>22(1)</td>
<td>29(1)</td>
<td>3(1)</td>
<td>3(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>34(2)</td>
<td>28(1)</td>
<td>23(1)</td>
<td>-1(1)</td>
<td>2(1)</td>
<td>-6(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>28(1)</td>
<td>27(1)</td>
<td>23(1)</td>
<td>4(1)</td>
<td>-6(1)</td>
<td>-5(1)</td>
</tr>
<tr>
<td>C(17)</td>
<td>22(1)</td>
<td>24(1)</td>
<td>24(1)</td>
<td>8(1)</td>
<td>-1(1)</td>
<td>-5(1)</td>
</tr>
<tr>
<td>C(18)</td>
<td>24(1)</td>
<td>27(1)</td>
<td>30(1)</td>
<td>8(1)</td>
<td>-6(1)</td>
<td>-3(1)</td>
</tr>
<tr>
<td>C(19)</td>
<td>23(1)</td>
<td>22(1)</td>
<td>36(1)</td>
<td>8(1)</td>
<td>-2(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(20)</td>
<td>20(1)</td>
<td>22(1)</td>
<td>29(1)</td>
<td>4(1)</td>
<td>2(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(21)</td>
<td>27(1)</td>
<td>21(1)</td>
<td>25(1)</td>
<td>4(1)</td>
<td>5(1)</td>
<td>-3(1)</td>
</tr>
<tr>
<td>C(22)</td>
<td>27(1)</td>
<td>22(1)</td>
<td>24(1)</td>
<td>2(1)</td>
<td>5(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(23)</td>
<td>37(2)</td>
<td>29(1)</td>
<td>27(1)</td>
<td>-1(1)</td>
<td>5(1)</td>
<td>-5(1)</td>
</tr>
<tr>
<td>C(24)</td>
<td>49(2)</td>
<td>23(1)</td>
<td>31(1)</td>
<td>-2(1)</td>
<td>10(1)</td>
<td>-5(1)</td>
</tr>
<tr>
<td>C(25)</td>
<td>42(2)</td>
<td>24(1)</td>
<td>36(1)</td>
<td>3(1)</td>
<td>13(1)</td>
<td>5(1)</td>
</tr>
<tr>
<td>C(26)</td>
<td>31(1)</td>
<td>25(1)</td>
<td>32(1)</td>
<td>6(1)</td>
<td>5(1)</td>
<td>2(1)</td>
</tr>
</tbody>
</table>
Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å$^2 x 10^3$) for compound 6.11.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(9)</td>
<td>3327</td>
<td>2055</td>
<td>2081</td>
<td>36</td>
</tr>
<tr>
<td>H(10)</td>
<td>5248</td>
<td>435</td>
<td>2221</td>
<td>35</td>
</tr>
<tr>
<td>H(18)</td>
<td>-6264</td>
<td>1269</td>
<td>-202</td>
<td>32</td>
</tr>
<tr>
<td>H(19)</td>
<td>-6001</td>
<td>2480</td>
<td>417</td>
<td>32</td>
</tr>
<tr>
<td>H(23)</td>
<td>1212</td>
<td>3417</td>
<td>2035</td>
<td>37</td>
</tr>
<tr>
<td>H(24)</td>
<td>-1326</td>
<td>4931</td>
<td>1997</td>
<td>41</td>
</tr>
<tr>
<td>H(25)</td>
<td>-4956</td>
<td>4972</td>
<td>1484</td>
<td>41</td>
</tr>
<tr>
<td>H(26)</td>
<td>-5839</td>
<td>3563</td>
<td>970</td>
<td>35</td>
</tr>
</tbody>
</table>
6.7. References

(1) Gingras, M. *Chemical Society Reviews* **2013**, *42*, 968.


(13) Meisenheimer, J.; Witte, K. Berichte der deutschen chemischen Gesellschaft 1903, 36, 4153.


7. Chapter Seven - The synthesis of fluorinated triphenylene discotic liquid crystals via a sequential SNAr reactions and PCDHF

7.1. Introduction to discotic liquid crystals

Discotic liquid crystals have attracted the attention of researchers over the last few decades\(^1\),\(^2\) because of their spontaneously aligned “stacked-disc-like” mesogenic structures – which can allow charge transfer along the stacking direction through the \(\pi-\pi\) interactions of their conjugation systems. This kind of charge transfer ability has motivated the study of discotic liquid crystals as a valuable class of organic semiconductors\(^3\),\(^4\) which may be applied in photovoltaic devices\(^5\), organic light emitting diodes (OLED)\(^6\), nano wires\(^7\) and in other areas. Among the many different types of discotic liquid crystals, the triphenylene derivatives are currently perhaps the most widely investigated do to their relative ease of synthesis. However, none of the simple triphenylene derivatives could provide a broad temperature columnar phase as low as room temperature\(^8\),\(^9\).

7.2. Fluorinated triphenylene discotic liquid crystals

The investigations and applications of these materials would be simplified if the discotic phases manifested themselves at ambient temperatures. The systems initially examined usually had no mesogenic behavior at room temperature. However, O.R. Lolman et al.\(^8\) found a solution involving introduction of two fluorine atoms in the triphenylene core such as in 1,4-difluoro-2,3,6,7,10,11-hexakishexyloxytriphenylene (2F-HAT6). This design feature introduces a dipole into the aryl core as it is believed that the columnar phase can be stabilized “through antiferroelectric alignment of molecular dipoles”\(^10\). The 2F-HAT is able to show a Col\(_h\) phase as low as room temperature and
its 1:1 mixture with 2,3,6,7,10,11-hexakis(4-nonylphenyl)triphenylene (PTP9) provides a higher clearing point. The total synthetic route (Scheme 7.1) of Lolman et al. is shown below and includes seven steps to obtain the final product 1,4-difluoro-2,3,6,7,10,11-hexakis(hexyloxy)triphenylene (2F-HAT6). In this case the triphenylene is formed by an oxidative cyclization of an appropriate difluorinated terphenyl precursor.

Here we describe a new synthetic route to such 1,4-difluorinated triphenylene derivatives by using a combination of the newly reported PCDHF\textsuperscript{11} and SNAr methodologies we have finessed. The PCDHF reaction is used to create a fluorinated triphenylene and the SNAr reaction is used to introduce alkoxy tails into the fluorine containing ring(s). Examination of the proposed retrosynthetic route clearly indicates that the 1,2,3,4-tetrafluoro-triphenylene core can be easily accessed via the PCDHF approach\textsuperscript{11}. The only issue at here is how to introduce another two alkoxy tails into the fluorinated aromatic ring in order to prepare the final compound equipped with six
alkoxy tails.

Scheme 7.2 Retrosynthetic route involving PCDHF.

7.3. $\text{S}_{\text{N}}\text{Ar}$ nucleophilic aromatic substitution of 1,2,3,4-tetrafluoro compounds

It is well known that in most pentafluorinated benzene derivatives that the $\text{para}$-fluorine atom is the most active site for nucleophilic aromatic substitution ($\text{S}_{\text{N}}\text{Ar}$)$^{12,13}$. Such perfluorinated rings are particularly prone to substitutions due to the mutual activation influence of all five fluorines. However, the location of multiple substitution on 1,2,3,4-tetrafluoro compounds appears to be much less clearly documented$^{14,15}$. In order to clarify this situation, several simple substrates and test reactions were designed as below. Here, 1,2,3,4-tetrafluorotriphenylene was selected as a test precursor as it can be obtained in high yield from the corresponding precursor 2,3,4,5,6-pentafluoro-1,1':2',1"-terphenyl via the PCDHF approach shown.

Scheme 7.3 $\text{S}_{\text{N}}\text{Ar}$ reaction (i) PCDHF/Acetonitrile 94%; (ii) R-OH/t-BuOK (8 eq)/Heating R= CH$_3$ 60%; R= C$_2$H$_5$ 55%; R= n-C$_6$H$_{13}$ 25%

To accomplish the $\text{S}_{\text{N}}\text{Ar}$ alkoxylation, different alcohols were deprotonated with potassium tert-butoxide. Of course potassium $t$-butoxide has special properties that make it useful here (enhanced basicity relative to most primary and secondary alcohols and very poor nuceophilic activity). When
low boiling alcohols such as methanol and ethanol were used, toluene was added in a 1:1 ratio as co-solvent to increase the solubility of 1,2,3,4-tetrafluorotriphenylene. In the case of methanol, after three hours of refluxing, the di-substituted product 1,4-difluoro-2,3-dimethoxytriphenylene was obtained in 60 % yield. Ethanol was less reactive and after 5 hours of refluxing, only the mono-substituted product 2-ethoxy-1,3,4-trifluorotriphenylene was obtained in 75 % yield. In order to push the second S_N2Ar reaction a Dean-Stark apparatus was utilized. After the removal of the low boiling point excess ethanol, the reaction temperature was increased and a mixture of mono-substituted product 2-ethoxy-1,3,4-trifluorotriphenylene (33 % yield) and di-substituted product 2,3-diethoxy-1,4-difluorotriphenylene (55 % yield) were obtained (we have not investigated these reactions under conditions other than atmospheric pressure). Higher boiling point primary alcohols (e.g. n-hexanol) with potassium tert-butoxide were also able to react with 1,2,3,4-tetrafluorotriphenylene to give di-alkoxylation (1,4-difluoro-2,3-bis(hexyloxy)triphenylene, 25 % yield). These S_N2Ar processes are liable to further improvement. Here, we acknowledge S_N2Ar exploratory research on related substrates accomplished by Kayla Ivey.

X-ray crystallography analysis of the product from reaction of 1,4-difluoro-2,3-dimethoxytriphenylene with potassium methoxide clearly showed that the fluorine atoms on 2,3-positions in the 1,2,3,4-tetrafluoro substrate are significantly more active than the 1,4-positions in the S_N2Ar reaction (Figure 7.1). This outcome exactly fits our needs – which require the conversion of a 1,2,3,4-tetrafluoro-6,7,10,11-tetraalkoxy triphenylene intermediate into the desired 2,3,6,7,10,11-hexaalkoxy discotic liquid crystal product.
Figure 7.1 X-ray crystallography of 1,4-difluoro-2,3-dimethoxytriphenylene. C–H···F interactions (2.617 Å) and C–H···O interactions (2.522 Å, 2.537 Å) are able to be observed in the crystal packing.
7.4. Hexakisalkoxytriphenylene discotic LCs via PCDHF and SNAr approach

Scheme 7.4 The synthesis of a terphenyl intermediate 7.6.

(i) I\(_2\)/Periodic Acid/Methanol, 89%; (ii) PhF\(_5\)COOK/CuI (0.1 eq)/Diglyme/150\(^{\circ}\)C, 55%; (iii) NBS/Silica Gel/CHCl\(_3\)/rt, 92%; (iv) (1) \(n\)-BuLi/\(-78\)^\(\circ\)C, (2) Triisopropyl borate/\(-78\)^\(\circ\)C, (3) HCl, rt, 51%; (v) Suzuki Coupling, 73%.

As a first fluorinated and alkoxy substituted triphenylene target we set out to prepare the known 1,4-difluoro-2,3,6,7,10,11-hexakishexyloxytriphenylene via a new route. The central synthetic target in the whole synthesis is the \(o\)-terphenyl (7.6). Veratrol (7.1) is a readily available starting material which when treated with iodine and periodic acid in methanol easily provides 4,5-diiodoveratrol (7.2) in high yield\(^{16}\). By using copper mediated decarboxylative coupling of potassium pentafluorobenzoate in diglyme\(^{17}\), one of the two iodine atoms in compound (7.2) could be selectively substituted to provide 2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (7.3). This biphenyl is then coupled with boronic acid 5 which itself is also synthesized starting from veratrol. Here, mono bromination occurs on veratrol under mild conditions at room temperature \(^{18}\) to provide 4-bromoveratrol (7.4). This 4-bromoveratrol was then converted to the corresponding boronic acid (7.5) to react with biphenyl (7.3) via a Suzuki coupling reaction, yielding the desired terphenyl (7.6).
The synthesis of hexakisalkoxytriphenylene discotic liquid crystals

(i) PCDHF, 89%; (ii) BBr$_3$/DCM, 98%; (iii) R$_1$-I/K$_2$CO$_3$/DMF, 87%; (iv) R$_2$-OH/t-BuOK, 55%

The o-terphenyl (7.6) underwent the PCDHF reaction (irradiation at 254 nm in acetonitrile) efficiently to yield 1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (7.7), which conveniently precipitated out of solution directly without the need for any further purification. After the deprotection of the four methoxy groups using BBr$_3$ in dichloromethane$^{19}$, 9,10,11,12-tetrafluorotriphenylene-2,3,6,7-tetraol (7.8) was obtained and subsequently treated with an alkyl halide and potassium carbonate in DMF to yield 1,2,3,4-tetrafluoro-6,7,10,11-tetraalkoxyphenylene (7.9). Finally, the previously discussed SNAr technique was applied here and the fluorine atoms at the 2,3-positions were selectively substituted by alkoxy chains to give the desired 1,4-difluoro-2,3,6,7,10,11-hexakishexyloxytriphenylene discotic liquid crystals (7.10) as final product. Note this approach also provides the opportunity to introduce different alkoxy groups between the 1,2,3,4- and 5,6-positions.
7.5. Pentakisalkoxytriphenylene discotic LCs via PCDHF and S\textsubscript{N}Ar approach

With a simple modification of this synthetic route involving changing the order of steps, pentakisalkoxytriphenylenes could also be obtained. Firstly, rather than PCDHF, the terphenyl 7.6 was treated with BBr\textsubscript{3} in dichloromethane to cleave the methyl ethers. Similar to the case as was already mentioned above, 2\textquoteright\textquoteright,3\textquoteright\textquoteright,4\textquoteright\textquoteright,5\textquoteright\textquoteright,6\textquoteright\textquoteright-pentafluoro-[1,1\textprime;:2\prime;:1\prime\prime-terphenyl]-3,4,4\prime;,5\prime\prime-tetraol 7.11 now reacted with an alkyl halide to give the tetraalkoxy terphenyl 7.12. As the para-fluorine atom in the pentafluoro compound 7.12 is most active, the S\textsubscript{N}Ar substitution occurs at that position and gave 7.13. Finally, triphenylene synthesis was accomplished by PCDHF under UV irradiation to give 14 as final product. Compared with 7.10, compound 7.14 differs only in having one fewer alkoxy tails present. Note again that this approach also provides the opportunity to introduce different alkoxy groups between the 1,2,3,4- and 5- positions. Furthermore (and this remains to be demonstrated) yet another different alkoxy tail might be introduced to provide a hexaalkoxy product with as many as three different tails.

Scheme 7.6 The synthesis of pentakisalkoxytriphenylene discotic liquid crystals.
(i) BBr3/DCM, ~100%; (ii) R1-I/K2CO3/DMF, 68%; (iii) R2-OH/t-BuOK, 70%; (iv) PCDHF, 55%

7.6. Phase behavior

By using the methodology mentioned above, we have successfully synthesized several fluorinated triphenylene discotic liquid crystal compounds with different length of alkoxy tails. All of these compounds are able to show mesogenic behavior at room temperature.

Table 7.1. Phase behavior of the fluorinated triphenylene discotic liquid crystals prepared in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Phase behavior °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAT5</td>
<td>Cr 64.2 Colh 121.4 I</td>
</tr>
<tr>
<td>HAT6</td>
<td>Cr 69.5 Colh 99.5 I</td>
</tr>
<tr>
<td>7.10 R1=R2=C5H11</td>
<td>Colh 144.8 I 139.9 Colh</td>
</tr>
<tr>
<td>7.10 R1=R2=C6H13</td>
<td>Colh 117.4 I 114.5 Colh</td>
</tr>
<tr>
<td>7.10 R1=C5H13 R2=C12H25</td>
<td>Cr 39.5 I 35.7 Colh 15.4 Cr</td>
</tr>
<tr>
<td>7.14 R1=R2=C5H11</td>
<td>Colh 171.8 I 168.0 Colh</td>
</tr>
<tr>
<td>7.14 R1=R2=C6H13</td>
<td>Colh 156.3 I 154.2 Colh</td>
</tr>
</tbody>
</table>

HAT5 80 °C  
7.10 R1=R2=C5H11  
Room temperature
7.10 $R_1 = R_2 = C_6H_{13}$
Room temperature

7.10 $R_1 = C_6H_{13}$ $R_2 = C_{12}H_{25}$
Room temperature during cooling

7.14 $R_1 = R_2 = C_5H_{11}$
Room temperature

7.14 $R_1 = R_2 = C_6H_{13}$
Room temperature
7.7. Summary

Compared with the synthetic route of O.R. Lolman et al., the combination of PCDHF and $S_N$Ar approach does not provide a much shorter synthetic route (both have seven steps in total). However, this new route is somewhat more “flexible” – the alkoxy chains were installed very late in the synthesis and a wide variety of hexakisalkoxytriphenylene derivatives can be easily obtained. Also, from the same intermediate terphenyl 7.6, this new methodology can also provide pentakisalkoxytriphenylenes, which the earlier route is incapable of delivering.

Their electronic properties are under investigation by Prof. Brett Ellman and will be reported elsewhere in future.
7.8. Experimental procedures

1,4-Difluoro-2,3-dimethoxytriphenylene

![Chemical Structure]

Chemical Formula: C_{20}H_{14}F_{2}O_{2}
Molecular Weight: 324.33

A 100 mL round bottom flask was charged with 1,2,3,4-tetrafluorotriphenylene (0.603 g, 2.0 mmol), methanol (25 mL), toluene (25 mL) and t-BuOK (1.798 g, 16 mmol, 8 eq). The mixture was heated up in an oil bath to give a clear solution and refluxed for 3 hours.

After that, TLC showed that no starting material remained and the mixture was cooled down to room temperature. Silica gel (approximately 2 g) was charged inside and the remaining solvent was removed by rotary evaporation. The brown powder obtained was then placed at the top of a silica gel column and eluted (Hexanes). Fractions containing the product were combined together and concentrated to give white fiber crystal (0.398 g, 0.12 mmol, 60 % yield) as final product.

**MP:** 127.0 – 128.5 °C

**\(^1H\)-NMR (400 MHz, CDCl\(_3\)) \(\delta\):** 8.989 – 8.957 (m, 2H), 8.628 – 8.604 (m, 2H), 7.678 - 7.606 (m, 4H), 4.131 (m, 6H).

**\(^13C\)-NMR (100 MHz, CDCl\(_3\)) \(\delta\):** 151.002 (dd, \(^1J = 248\) Hz, \(^2J = 4\) Hz), 140.933 (dd, \(^1J = 13.5\) Hz, \(^2J = 7.8\) Hz), 130.240, 127.842 (t, \(J = 19.7\) Hz), 127.838 (d, \(J = 31.3\) Hz), 127.592 (d, \(J =
11.1 Hz), 126.831, 123.113, 116.122 (t, J = 5.5 Hz), 62.239.

$^{19}\text{F-NMR (376 MHz, }\text{CDCl}_3\text{) }\delta: -132.770 \text{ (s).}$

**Table 1.** Crystal data and structure refinement for 1,4-Difluoro-2,3-dimethoxytriphenylene.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>1,4-Difluoro-2,3-dimethoxytriphenylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{20}$H$</em>{14}$F$_2$O$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>324.31</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
</tbody>
</table>
Wavelength                        0.71073 Å
Crystal system, space group       Monoclinic, P 21/c
Unit cell dimensions              a = 9.680(3) Å   alpha = 90 deg.
b = 3.9219(10) Å    beta = 91.613(8) deg.
c = 37.508(10) Å   gamma = 90 deg.
Volume                            1423.4(7) Å³
Z, Calculated density             4,  1.513 Mg/m³
Absorption coefficient            0.114 mm⁻¹
F(000)                            672
Crystal size                      0.120 x 0.070 x 0.050 mm
Theta range for data collection   1.086 to 25.723 deg.
Limiting indices                  -6<=h<=11, -4<=k<=4, -40<=l<=45
Reflections collected / unique    5570 / 2451 [R(int) = 0.0730]
Completeness to theta = 25.242    92.1 %
Absorption correction             Semi-empirical from equivalents
Max. and min. transmission        0.994 and 0.746
Refinement method                 Full-matrix least-squares on F²
Data / restraints / parameters    2451 / 0 / 219
Goodness-of-fit on F²             0.904
Final R indices [I>2sigma(I)]     R1 = 0.0658, wR2 = 0.1491
R indices (all data)              R1 = 0.1540, wR2 = 0.2046
Extinction coefficient            n/a
Largest diff. peak and hole       0.270 and -0.283 e.A⁻³
Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 1,4-Difluoro-2,3-dimethoxytriphenylene. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>9524(2)</td>
<td>-1513(7)</td>
<td>1273(1)</td>
<td>30(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>4407(2)</td>
<td>-1669(7)</td>
<td>658(1)</td>
<td>31(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>9128(3)</td>
<td>-4242(8)</td>
<td>628(1)</td>
<td>31(1)</td>
</tr>
<tr>
<td>O(2)</td>
<td>6469(3)</td>
<td>-4376(8)</td>
<td>320(1)</td>
<td>32(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>3709(4)</td>
<td>4499(11)</td>
<td>1872(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>2429(5)</td>
<td>4815(12)</td>
<td>1706(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>2229(5)</td>
<td>3705(11)</td>
<td>1358(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>3313(4)</td>
<td>2239(12)</td>
<td>1179(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>4640(4)</td>
<td>1826(11)</td>
<td>1343(1)</td>
<td>18(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>5813(4)</td>
<td>257(11)</td>
<td>1158(1)</td>
<td>17(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>5670(4)</td>
<td>-1338(11)</td>
<td>825(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>6740(5)</td>
<td>-2735(11)</td>
<td>638(1)</td>
<td>21(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>8052(5)</td>
<td>-2643(11)</td>
<td>799(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>8221(4)</td>
<td>-1233(12)</td>
<td>1132(1)</td>
<td>21(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>7151(4)</td>
<td>286(11)</td>
<td>1322(1)</td>
<td>17(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>7376(4)</td>
<td>1811(11)</td>
<td>1680(1)</td>
<td>17(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>8707(4)</td>
<td>2176(11)</td>
<td>1849(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>8882(5)</td>
<td>3476(12)</td>
<td>2184(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>7739(5)</td>
<td>4509(12)</td>
<td>2374(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>6454(4)</td>
<td>4293(12)</td>
<td>2215(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(17)</td>
<td>6221(4)</td>
<td>3001(11)</td>
<td>1867(1)</td>
<td>16(1)</td>
</tr>
<tr>
<td>C(18)</td>
<td>4843(4)</td>
<td>3076(11)</td>
<td>1696(1)</td>
<td>16(1)</td>
</tr>
<tr>
<td>C(19)</td>
<td>10249(5)</td>
<td>-2061(12)</td>
<td>527(1)</td>
<td>34(1)</td>
</tr>
<tr>
<td>C(20)</td>
<td>6776(6)</td>
<td>-2469(13)</td>
<td>12(1)</td>
<td>40(2)</td>
</tr>
</tbody>
</table>
Table 3. Bond lengths [Å] and angles [deg] for 1,4-Difluoro-2,3-dimethoxytriphenylene.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)-C(10)</td>
<td>1.359(5)</td>
</tr>
<tr>
<td>F(2)-C(7)</td>
<td>1.365(5)</td>
</tr>
<tr>
<td>O(1)-C(9)</td>
<td>1.387(5)</td>
</tr>
<tr>
<td>O(1)-C(19)</td>
<td>1.441(5)</td>
</tr>
<tr>
<td>O(2)-C(8)</td>
<td>1.375(5)</td>
</tr>
<tr>
<td>O(2)-C(20)</td>
<td>1.414(5)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.376(6)</td>
</tr>
<tr>
<td>C(1)-C(18)</td>
<td>1.412(6)</td>
</tr>
<tr>
<td>C(1)-H(1)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.386(6)</td>
</tr>
<tr>
<td>C(2)-H(2)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.385(6)</td>
</tr>
<tr>
<td>C(3)-H(3)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.418(6)</td>
</tr>
<tr>
<td>C(4)-H(4)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(5)-C(18)</td>
<td>1.420(6)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.482(6)</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.397(6)</td>
</tr>
<tr>
<td>C(6)-C(11)</td>
<td>1.419(6)</td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td>1.382(6)</td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td>1.390(6)</td>
</tr>
<tr>
<td>C(9)-C(10)</td>
<td>1.372(6)</td>
</tr>
<tr>
<td>C(10)-C(11)</td>
<td>1.408(6)</td>
</tr>
<tr>
<td>C(11)-C(12)</td>
<td>1.480(6)</td>
</tr>
<tr>
<td>C(12)-C(17)</td>
<td>1.416(6)</td>
</tr>
<tr>
<td>C(12)-C(13)</td>
<td>1.426(6)</td>
</tr>
<tr>
<td>C(13)-C(14)</td>
<td>1.363(6)</td>
</tr>
<tr>
<td>C(13)-H(13)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(14)-C(15)</td>
<td>1.394(6)</td>
</tr>
<tr>
<td>C(14)-H(14)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(15)-C(16)</td>
<td>1.367(6)</td>
</tr>
<tr>
<td>C(15)-H(15)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(16)-C(17)</td>
<td>1.413(6)</td>
</tr>
<tr>
<td>C(16)-H(16)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(17)-C(18)</td>
<td>1.464(6)</td>
</tr>
<tr>
<td>C(19)-H(19A)</td>
<td>0.9800</td>
</tr>
<tr>
<td>C(19)-H(19B)</td>
<td>0.9800</td>
</tr>
<tr>
<td>C(19)-H(19C)</td>
<td>0.9800</td>
</tr>
<tr>
<td>C(20)-H(20A)</td>
<td>0.9800</td>
</tr>
<tr>
<td>C(20)-H(20B)</td>
<td>0.9800</td>
</tr>
<tr>
<td>C(20)-H(20C)</td>
<td>0.9800</td>
</tr>
<tr>
<td>Bond</td>
<td>Angle</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>C(9)-O(1)-C(19)</td>
<td>115.7(3)</td>
</tr>
<tr>
<td>C(8)-O(2)-C(20)</td>
<td>114.9(4)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(18)</td>
<td>121.9(4)</td>
</tr>
<tr>
<td>C(2)-C(1)-H(1)</td>
<td>119.1</td>
</tr>
<tr>
<td>C(18)-C(1)-H(1)</td>
<td>119.1</td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>119.8(4)</td>
</tr>
<tr>
<td>C(1)-C(2)-H(2)</td>
<td>120.1</td>
</tr>
<tr>
<td>C(3)-C(2)-H(2)</td>
<td>120.1</td>
</tr>
<tr>
<td>C(4)-C(3)-C(2)</td>
<td>119.9(4)</td>
</tr>
<tr>
<td>C(4)-C(3)-H(3)</td>
<td>120.1</td>
</tr>
<tr>
<td>C(2)-C(3)-H(3)</td>
<td>120.1</td>
</tr>
<tr>
<td>C(3)-C(4)-C(5)</td>
<td>121.9(4)</td>
</tr>
<tr>
<td>C(3)-C(4)-H(4)</td>
<td>119.1</td>
</tr>
<tr>
<td>C(5)-C(4)-H(4)</td>
<td>119.1</td>
</tr>
<tr>
<td>C(4)-C(5)-C(18)</td>
<td>117.7(4)</td>
</tr>
<tr>
<td>C(4)-C(5)-C(6)</td>
<td>122.8(4)</td>
</tr>
<tr>
<td>C(18)-C(5)-C(6)</td>
<td>119.5(4)</td>
</tr>
<tr>
<td>C(7)-C(6)-C(11)</td>
<td>117.3(4)</td>
</tr>
<tr>
<td>C(7)-C(6)-C(5)</td>
<td>123.1(4)</td>
</tr>
<tr>
<td>C(11)-C(6)-C(5)</td>
<td>119.6(4)</td>
</tr>
<tr>
<td>F(2)-C(7)-C(8)</td>
<td>113.7(4)</td>
</tr>
<tr>
<td>F(2)-C(7)-C(6)</td>
<td>121.2(4)</td>
</tr>
<tr>
<td>C(8)-C(7)-C(6)</td>
<td>125.1(4)</td>
</tr>
<tr>
<td>O(2)-C(8)-C(7)</td>
<td>120.0(4)</td>
</tr>
<tr>
<td>O(2)-C(8)-C(9)</td>
<td>122.6(4)</td>
</tr>
<tr>
<td>C(7)-C(8)-C(9)</td>
<td>117.2(4)</td>
</tr>
<tr>
<td>C(10)-C(9)-O(1)</td>
<td>122.0(4)</td>
</tr>
<tr>
<td>C(10)-C(9)-C(8)</td>
<td>119.3(4)</td>
</tr>
<tr>
<td>O(1)-C(9)-C(8)</td>
<td>118.5(4)</td>
</tr>
<tr>
<td>F(1)-C(10)-C(9)</td>
<td>114.2(4)</td>
</tr>
<tr>
<td>F(1)-C(10)-C(11)</td>
<td>121.5(4)</td>
</tr>
<tr>
<td>C(9)-C(10)-C(11)</td>
<td>124.3(4)</td>
</tr>
<tr>
<td>C(10)-C(11)-C(6)</td>
<td>116.8(4)</td>
</tr>
<tr>
<td>C(10)-C(11)-C(12)</td>
<td>122.7(4)</td>
</tr>
<tr>
<td>C(6)-C(11)-C(12)</td>
<td>120.5(4)</td>
</tr>
<tr>
<td>C(17)-C(12)-C(13)</td>
<td>117.6(4)</td>
</tr>
<tr>
<td>C(17)-C(12)-C(11)</td>
<td>119.0(4)</td>
</tr>
<tr>
<td>C(13)-C(12)-C(11)</td>
<td>123.4(4)</td>
</tr>
<tr>
<td>C(14)-C(13)-C(12)</td>
<td>122.2(4)</td>
</tr>
<tr>
<td>C(14)-C(13)-H(13)</td>
<td>118.9</td>
</tr>
<tr>
<td>C(12)-C(13)-H(13)</td>
<td>118.9</td>
</tr>
<tr>
<td>C(13)-C(14)-C(15)</td>
<td>120.1(4)</td>
</tr>
<tr>
<td>C(13)-C(14)-H(14)</td>
<td>119.9</td>
</tr>
<tr>
<td>C(15)-C(14)-H(14)</td>
<td>119.9</td>
</tr>
<tr>
<td>C(16)-C(15)-C(14)</td>
<td>118.9(4)</td>
</tr>
<tr>
<td>C(16)-C(15)-H(15)</td>
<td>120.5</td>
</tr>
<tr>
<td>Bond</td>
<td>Angle (°)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>C(14)-C(15)-H(15)</td>
<td>120.5</td>
</tr>
<tr>
<td>C(15)-C(16)-C(17)</td>
<td>123.1(4)</td>
</tr>
<tr>
<td>C(15)-C(16)-H(16)</td>
<td>118.5</td>
</tr>
<tr>
<td>C(17)-C(16)-H(16)</td>
<td>118.5</td>
</tr>
<tr>
<td>C(16)-C(17)-C(12)</td>
<td>117.9(4)</td>
</tr>
<tr>
<td>C(16)-C(17)-C(18)</td>
<td>121.2(4)</td>
</tr>
<tr>
<td>C(12)-C(17)-C(18)</td>
<td>120.7(4)</td>
</tr>
<tr>
<td>C(1)-C(18)-C(5)</td>
<td>118.8(4)</td>
</tr>
<tr>
<td>C(1)-C(18)-C(17)</td>
<td>120.9(4)</td>
</tr>
<tr>
<td>C(5)-C(18)-C(17)</td>
<td>120.2(4)</td>
</tr>
<tr>
<td>O(1)-C(19)-H(19A)</td>
<td>109.5</td>
</tr>
<tr>
<td>O(1)-C(19)-H(19B)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(19A)-C(19)-H(19B)</td>
<td>109.5</td>
</tr>
<tr>
<td>O(1)-C(19)-H(19C)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(19A)-C(19)-H(19C)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(19B)-C(19)-H(19C)</td>
<td>109.5</td>
</tr>
<tr>
<td>O(2)-C(20)-H(20A)</td>
<td>109.5</td>
</tr>
<tr>
<td>O(2)-C(20)-H(20B)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(20A)-C(20)-H(20B)</td>
<td>109.5</td>
</tr>
<tr>
<td>O(2)-C(20)-H(20C)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(20A)-C(20)-H(20C)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(20B)-C(20)-H(20C)</td>
<td>109.5</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:
Table 4. Anisotropic displacement parameters ($A^2 \times 10^3$) for 1,4-Difluoro-2,3-dimethoxytriphenylene.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 \left[ h^2 a^* U_{11} + ... + 2hk a^* b^* U_{12} \right]$$

<table>
<thead>
<tr>
<th></th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>25(2)</td>
<td>33(2)</td>
<td>32(2)</td>
<td>-6(1)</td>
<td>4(1)</td>
<td>9(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>30(2)</td>
<td>33(2)</td>
<td>29(2)</td>
<td>-6(1)</td>
<td>-4(1)</td>
<td>-5(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>37(2)</td>
<td>15(2)</td>
<td>41(2)</td>
<td>-4(2)</td>
<td>19(2)</td>
<td>2(2)</td>
</tr>
<tr>
<td>O(2)</td>
<td>57(2)</td>
<td>20(2)</td>
<td>20(2)</td>
<td>-4(2)</td>
<td>6(2)</td>
<td>-9(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>23(2)</td>
<td>10(3)</td>
<td>27(3)</td>
<td>2(2)</td>
<td>8(2)</td>
<td>4(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>22(3)</td>
<td>18(3)</td>
<td>32(3)</td>
<td>1(2)</td>
<td>5(2)</td>
<td>0(2)</td>
</tr>
<tr>
<td>C(3)</td>
<td>19(2)</td>
<td>21(3)</td>
<td>36(3)</td>
<td>5(2)</td>
<td>0(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>C(4)</td>
<td>24(3)</td>
<td>19(3)</td>
<td>25(3)</td>
<td>3(2)</td>
<td>1(2)</td>
<td>1(2)</td>
</tr>
<tr>
<td>C(5)</td>
<td>19(2)</td>
<td>14(3)</td>
<td>20(3)</td>
<td>5(2)</td>
<td>0(2)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>C(6)</td>
<td>24(2)</td>
<td>10(3)</td>
<td>16(3)</td>
<td>2(2)</td>
<td>2(2)</td>
<td>1(2)</td>
</tr>
<tr>
<td>C(7)</td>
<td>24(2)</td>
<td>15(3)</td>
<td>20(3)</td>
<td>1(2)</td>
<td>-6(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>C(8)</td>
<td>39(3)</td>
<td>7(3)</td>
<td>18(3)</td>
<td>0(2)</td>
<td>6(2)</td>
<td>-4(2)</td>
</tr>
<tr>
<td>C(9)</td>
<td>34(3)</td>
<td>6(3)</td>
<td>30(3)</td>
<td>0(2)</td>
<td>12(2)</td>
<td>3(2)</td>
</tr>
<tr>
<td>C(10)</td>
<td>23(3)</td>
<td>16(3)</td>
<td>24(3)</td>
<td>2(2)</td>
<td>-2(2)</td>
<td>1(2)</td>
</tr>
<tr>
<td>C(11)</td>
<td>24(2)</td>
<td>10(3)</td>
<td>16(3)</td>
<td>4(2)</td>
<td>8(2)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>C(12)</td>
<td>23(2)</td>
<td>12(3)</td>
<td>16(3)</td>
<td>6(2)</td>
<td>4(2)</td>
<td>-3(2)</td>
</tr>
<tr>
<td>C(13)</td>
<td>20(2)</td>
<td>18(3)</td>
<td>28(3)</td>
<td>0(2)</td>
<td>4(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>C(14)</td>
<td>23(2)</td>
<td>28(3)</td>
<td>21(3)</td>
<td>0(2)</td>
<td>-8(2)</td>
<td>0(2)</td>
</tr>
<tr>
<td>C(15)</td>
<td>30(3)</td>
<td>20(3)</td>
<td>19(3)</td>
<td>-3(2)</td>
<td>1(2)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>C(16)</td>
<td>25(3)</td>
<td>15(3)</td>
<td>18(3)</td>
<td>1(2)</td>
<td>5(2)</td>
<td>0(2)</td>
</tr>
<tr>
<td>C(17)</td>
<td>20(2)</td>
<td>8(3)</td>
<td>20(3)</td>
<td>3(2)</td>
<td>4(2)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>C(18)</td>
<td>22(2)</td>
<td>11(3)</td>
<td>17(3)</td>
<td>5(2)</td>
<td>5(2)</td>
<td>0(2)</td>
</tr>
<tr>
<td>C(19)</td>
<td>32(3)</td>
<td>31(3)</td>
<td>42(3)</td>
<td>1(3)</td>
<td>19(2)</td>
<td>7(3)</td>
</tr>
<tr>
<td>C(20)</td>
<td>68(4)</td>
<td>33(3)</td>
<td>21(3)</td>
<td>2(3)</td>
<td>2(3)</td>
<td>-4(3)</td>
</tr>
</tbody>
</table>
Table 5. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for 1,4-Difluoro-2,3-dimethoxytriphenylene.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>3833</td>
<td>5260</td>
<td>2111</td>
<td>24</td>
</tr>
<tr>
<td>H(2)</td>
<td>1684</td>
<td>5792</td>
<td>1830</td>
<td>29</td>
</tr>
<tr>
<td>H(3)</td>
<td>1350</td>
<td>3950</td>
<td>1241</td>
<td>30</td>
</tr>
<tr>
<td>H(4)</td>
<td>3163</td>
<td>1489</td>
<td>941</td>
<td>27</td>
</tr>
<tr>
<td>H(13)</td>
<td>9499</td>
<td>1489</td>
<td>1723</td>
<td>26</td>
</tr>
<tr>
<td>H(14)</td>
<td>9784</td>
<td>3678</td>
<td>2288</td>
<td>29</td>
</tr>
<tr>
<td>H(15)</td>
<td>7851</td>
<td>5349</td>
<td>2611</td>
<td>28</td>
</tr>
<tr>
<td>H(16)</td>
<td>5682</td>
<td>5048</td>
<td>2345</td>
<td>23</td>
</tr>
<tr>
<td>H(19A)</td>
<td>9875</td>
<td>-16</td>
<td>409</td>
<td>52</td>
</tr>
<tr>
<td>H(19B)</td>
<td>10843</td>
<td>-3287</td>
<td>363</td>
<td>52</td>
</tr>
<tr>
<td>H(19C)</td>
<td>10792</td>
<td>-1396</td>
<td>740</td>
<td>52</td>
</tr>
<tr>
<td>H(20A)</td>
<td>6353</td>
<td>-206</td>
<td>27</td>
<td>61</td>
</tr>
<tr>
<td>H(20B)</td>
<td>6409</td>
<td>-3652</td>
<td>-201</td>
<td>61</td>
</tr>
<tr>
<td>H(20C)</td>
<td>7780</td>
<td>-2228</td>
<td>-4</td>
<td>61</td>
</tr>
</tbody>
</table>
2-ethoxy-1,3,4-trifluorotriphenylene and 2,3-diethoxy-1,4-difluorotriphenylene

![Chemical structures of 2-ethoxy-1,3,4-trifluorotriphenylene and 2,3-diethoxy-1,4-difluorotriphenylene](image)

Chemical Formula: C_{20}H_{13}F_{3}O  
Molecular Weight: 326.32

Chemical Formula: C_{22}H_{18}F_{2}O_{2}  
Molecular Weight: 352.38

A 100 mL round bottom flask was charged with 1,2,3,4-tetrafluorotriphenylene (0.601 g, 2.0 mmol), ethanol (25 mL), toluene (25 mL) and t-BuOK (1.804 g, 16 mmol, 8 eq). The mixture was heated up in an oil bath to give a clear solution and refluxed overnight (approximately 12 hours).

After this time, TLC showed that no starting material remained and only the mono-substituted product was formed. Then, a Dean-Stark apparatus was applied to remove approximately half the amount of solvent and the remaining solution was refluxed for another 5 hours. TLC showed that a new product with higher polarity was obtained.

Then the mixture was cooled down to room temperature. Silica gel (approximately 2 g) was charged inside and the remaining solvent was removed by rotary evaporation. The brown powder obtained was then placed at the top of a silica gel column and eluted (Hexanes). Fractions containing the product were combined together and concentrated to give white fiber crystal (0.218 g, 6.7 mmol, 33 % yield) as first product, colorless needle like crystal (0.386 g, 1.1 mmol, 55% yield) as second product.

**The first product was demonstrated to be 2-ethoxy-1,3,4-trifluorotriphenylene.**
The second product was demonstrated to be 2,3-diethoxy-1,4-difluorotriphenylene.

M.P.: 96.0 – 102.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.991 – 8.959 (m, 2H), 8.617 – 8.593 (m, 2H), 7.664 - 7.591 (m, 4H), 4.341 (q, $J$ = 7.2 Hz, 4H), 1.490 (t, $J$ = 7.2 Hz, 4H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 151.351 (dd, $^1J$ = 248 Hz, $^2J$ = 4 Hz), 140.280 (dd, $^1J$ = 13.5 Hz, $^2J$ = 7.5 Hz), 130.253, 127.883 (t, $J$ = 19.8 Hz), 127.883 (d, $J$ = 30.5 Hz), 127.559 (d, $J$ = 6.2 Hz), 126.975, 123.124, 116.050 (t, $J$ = 5.8 Hz), 70.594, 15.703.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -132.240 (s).

1,4-Difluoro-2,3-dimethoxytriphenylene

![Chemical structure](image)

Chemical Formula: C$_{22}$H$_{18}$F$_2$O$_2$
Molecular Weight: 352.38

A 100 mL round bottom flask was charged with 2-ethoxy-1,3,4-trifluorotriphenylene (0.328 g, 1.0 mmol), ethanol (15 mL), toluene (25 mL) and $t$-BuOK (1.119 g, 10.0 mmol). The mixture was refluxed in a 90 °C oil bath for half an hour, then a Dean-Stark apparatus was applied to remove the ethanol and the remaining solution was refluxed at 110 °C for another 12 hours.

After this time, TLC showed that the starting material was nearly consumed and the mixture was cooled to room temperature. Silica gel (approximately 2 g) was charged inside and the remaining
solvent was removed by rotary evaporation. The brown powder obtained was then placed at the top of a silica gel column and eluted (Eluent: hexanes). Fractions containing the product were combined together and concentrated to give white crystals (0.275 g, 0.78 mmol, 78 % yield) as final product.

1,4-Difluoro-2,3-dihexyloxytriphenylene

![Chemical Structure]

Chemical Formula: C\textsubscript{30}H\textsubscript{34}F\textsubscript{2}O\textsubscript{2}
Molecular Weight: 464.60

A 100 mL round bottom flask was charged with 1,2,3,4-tetrafluorotriphenylene (0.301 g, 1.0 mmol), 1-hexanol (0.809 g, 8.0 mmol), p-xylene (10 mL) and t-BuOK (0.901 g, 8.0 mmol). The obtained mixture was refluxed for 24 hours and TLC showed that the starting material was nearly consumed.

Then the mixture was cooled to room temperature, the solvent was removed by Kugelrohr distillation. The residue was dissolve in ethyl acetate (~ 10 mL) and silica gel (approximately 2 g) was charged inside. After removing the solvent by rotary evaporation, the brown powder obtained was then placed at the top of a silica gel column and eluted (Eluent: hexanes). Fractions containing the product were combined together and concentrated to give sticky yellow oil, which was cooled to give yellow crystals (0.112 g, 0.24 mmol, 24 % yield) as final product.
M.P.: 46.0 – 49.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.990 – 8.967 (m, 2H), 8.620 – 8.596 (m, 2H), 7.664 - 7.595 (m, 4H), 4.245 (q, $J = 6.6$ Hz, 4H), 1.895 – 1.823 (m, 4H), 1.589 -1.514 (m, 4H), 1.400 – 1.355 (m, 8H), 0.929 (q, $J = 7.0$ Hz, 6H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 151.326 (dd, $^1J = 248$ Hz, $^2J = 4$ Hz), 140.610 (dd, $^1J = 13.5$ Hz, $^2J = 7.7$ Hz), 130.243, 127.898 (d, $J = 30.5$ Hz), 127.899 (t, $J = 19.7$ Hz), 127.538 (d, $J = 3.4$ Hz), 123.121, 122.980, 115.987 (t, $J = 5.3$ Hz), 75.188, 31.653, 30.229, 25.592, 22.655, 14.070.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -132.240 (s).

1,2-diiodo-4,5-dimethoxybenzene (7.2)

![Chemical structure of 1,2-diiodo-4,5-dimethoxybenzene](image)

Chemical Formula: C$_8$H$_8$I$_2$O$_2$
Molecular Weight: 389.96

In a 100 mL flask, periodic acid (4.560 g, 20.0 mmol) was dissolved in methanol (30 mL). Iodine (10.356 g, 40.8 mmol) was then added and the mixture obtained was stirred for 15 min. Veratrol (6.944 g, 50.3 mmol) was added and the mixture was gently refluxed at 70 °C for 4 hours. During this time, a white precipitate formed.

The mixture was then cooled to room temperature and poured into a solution of Na$_2$SO$_3$ (20g in 200 mL water). The white solid formed was isolated via suction filtration, washed with cold methanol (20 mL) and air-dried, giving white powder (17.296 g, 44.4 mmol, 89 % yield) as final product.
Obtained data:

**M.P.:** 132.0 – 133.0 °C (Lit: 133 °C).

\(^1\text{H}-\text{NMR} (400 \text{ MHz, CDCl}_3) \delta: 7.235 (s, 2H), 3.836 (d, J = 0.4 \text{ Hz, } 6H).\)

\(^{13}\text{C}-\text{NMR} (100 \text{ MHz, CDCl}_3) \delta: 149.548, 121.577, 96.045, 56.147.\)


2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (7.3)

![Chemical structure of 2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl](image)

Chemical Formula: \(C_{14}H_8F_5IO_2\)
Molecular Weight: 430.11

A 100 mL flask equipped with magnetic stirbar was flushed thoroughly with nitrogen and charged with potassium pentafluorobenzoate (5.002 g, 20.0 mmol), CuI (0.765 g, 4.0 mmol), 4,5-diiodoveratrol (7.809 g, 20.0 mmol) and diglyme (20 mL). The mixture was stirred at 145 °C and TLC was used to follow the reaction progress. After 6 hours, TLC indicated some of 4,5-diiodoveratrol still persisted and more potassium pentafluorobenzoate (2.511 g, 10.0 mmol) was added to complete the reaction in 2 hours.

The resulting mixture was cooled and diluted with ethyl acetate (100 mL). After being filtered via gravity, the filtrate was washed with water (150 mL x 5) to remove diglyme. The organic phase
was dried over with anhydrous MgSO₄ and mixed with silica gel (~ 10g). After the removal of solvent, the yellow powder obtained was placed at the top of a silica column and eluted (eluent: hexanes). After removing the solvent by rotary evaporation, a colorless oil was obtained which crystallized after cooling (4.725 g, 11.0 mmol, 55 % yield).

**M.P.:** 88 – 93 °C.

**¹H-NMR (400 MHz, CDCl₃)** δ: 7.356 (s, 1H), 6.726 (s, 1H), 3.923 (s, 3H), 3.855 (s, 3H).

**¹³C-NMR (100 MHz, CDCl₃)** δ: 150.336, 149.455, 144.203 (d, J = 245.3 Hz), 141.200 (d, J = 252.9 Hz), 137.700 (d, J = 251.5 Hz), 124.412, 121.599, 113.923, 113.632, 88.058, 56.257, 56.109.

**¹⁹F-NMR (376 MHz, CDCl₃)** δ: 139.998 (dd, ¹J = 23.5 Hz, ²J = 8.1 Hz, 2F), -154.783 (t, J = 20.9 Hz, 1F), -162.419 – -162.560 (m, 2F).

**4-Bromoveratol (7.4)**

![Chemical structure of 4-Bromoveratol](image)

Chemical Formula: C₈H₉BrO₂
Molecular Weight: 217.06

A 250 mL flask was charged with CHCl₃ (50 mL), veratrol (6.902 g, 50.0 mmol), NBS (8.975 g, 50.4 mmol) and silica gel (~ 5g). The mixture obtained was stirred under room temperature overnight (~ 12h). After that, the solid was filtered and the filtrate was washed with Na₂SO₃ solution (10 g in 100 mL water, 50 mL x 2). The organic phase was dried over anhydrous MgSO₄, the drying agent was removed by filtration and the solvent was removed via rotary evaporation. The obtained crude product was purified by Kugelrohr distillation, giving colorless oil (9.971 g,
45.9 mmol, 92 % yield) as final product.

**Obained data:**

**1H-NMR (400 MHz, CDCl₃) δ:** 7.006 (dd, 1J = 8.4 Hz, 2J = 2.4 Hz, 1H), 6.961 (d, J = 2.4 Hz, 1H), 6.710 (d, J = 8.4 Hz, 1H), 3.843 (s, 3H), 3.831 (s, 3H).

**13C-NMR (100 MHz, CDCl₃) δ:** 149.676, 148.262, 123.317, 114.689, 112.644, 112.440, 56.010, 55.949.


**3,4-dimethoxyphenylboronic acid (7.5)**

```
MeO
OMe
B(OH)₂
```

Chemical Formula: C₈H₁₁BO₄
Molecular Weight: 181.98

An oven dried 250 mL flask equipped with magnetic stir bar was charged with 4-bromoveratrol (8.683 g, 40.0 mmol) and freshly distilled anhydrous THF (40 mL). The resulting solution was cooled to -78 °C under a nitrogen atmosphere and n-BuLi solution (32 mL, 1.6 M in hexane, 51.2 mmol) was added dropwise. After being stirred for approximately 1 hour, B(Oi-Pr)₃ (11.316 g, 60.2 mmol) was added to the previous solution to give a pale yellow suspension.

The mixture obtained was stirred overnight (~ 12h) and the temperature was permitted to rise to
room temperature. It was then treated with hydrochloric acid (1M, 100 mL) to form two layers. The aqueous phase was extracted with diethyl ether (100 mL x 3) and the organic phases were combined together. After drying with anhydrous MgSO\(_4\), the solution was concentrated to give yellow sticky oil. Hexane (~ 10 mL) was added to precipitate white solid (3.713 g, 20.4 mmol, 51 % yield) as final product.

**M.P.:** 247.0 – 250.5 °C.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.864 (s, 2H), 7.384 (s, 1H), 7.378 (d, \(J = 6.8\) Hz, 1H), 6.912 (d, \(J = 8.4\) Hz, 1H), 3.752 (s, 3H), 3.744 (s, 3H).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\): 150.581, 147.894, 127.651, 125.725, 117.158, 110.867, 55.310, 55.249.

A nitrogen flushed 50 mL flask with magnetic stir bar was charged with 2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (1.491 g, 3.5 mmol), 3,4-dimethoxyphenylboronic acid (0.882 g, 4.85 mmol), potassium carbonate (0.675 g, 4.89 mmol), toluene (20 mL) and ethanol (5 mL). The resulting mixture was heated to a gentle reflux and tetrakis(triphenylphosphine)palladium(0) (40.812 mg, 0.035 mmol, 1%) was added.

After being refluxed for 12 hours, TLC indicated that a new compound was formed and the mixture was cooled to room temperature. The solid was filtered off with gravity filtration and the filtrate was well mixed with silica gel (~ 5g). The volatile solvent was removed by rotary evaporation and the adsorbed material was placed at the top of a silica gel column to elute (eluent: hexane: EtOAc = 10:1), affording white crystals (1.319 g, 3.0 mmol, 86 % yield) as final product.

**M.P.:** 152.0 – 154.5 °C.

**1H-NMR (400 MHz, CDCl3)** \( \delta \): 6.968 (s, 1H), 6.781 (s, 1H), 6.764 (d, \( J = 8.4 \) Hz, 1H), 6.697 – 6.651 (m, 2H), 3.957 (s, 3H), 3.917 (s, 3H), 3.865 (s, 3H), 3.758 (s, 3H).

**19F-NMR (376 MHz, CDCl3)** \( \delta \): -140.538 (dd, \( ^1J = 23.7 \) Hz, \( ^2J = 8.3 \) Hz, 2F), -156.112 (t, \( J =
20.7 Hz, 1F), -163.067 – -163.208 (m, 2F).

1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (7.7)

![Chemical Structure](image)

Chemical Formula: C_{22}H_{18}F_{4}O_{4}
Molecular Weight: 420.36

In a quartz vessel, 2,3,4,5,6-pentafluoro-3",4",4",5"-tetramethoxy-1,1':2',1"'-terphenyl (0.444 g, 1.0 mmol) was dissolved in acetonitrile (100 mL). The solution was degassed with nitrogen and irradiated for 2 hours in a Rayonette photochemical reactor equipped with 16 x 254nm ultraviolet lamps. After that time, TLC indicated the starting material was completely consumed and white needle-like crystals precipitated out of the solution.

About half of the solvent was removed by rotary evaporation and the remaining slurry was cooled in an ice bath. The suspended solid was isolated by suction filtration and air dried, giving grey crystals (0.357 g, 0.85 mmol, 85 % yield as product) as final product.

\[ ^1H-NMR\ (400\ MHz,\ CDCl_3)\ \delta:\ 8.218\ (dd,\ ^1J = 4.0\ Hz,\ ^2J = 2.4\ Hz,\ 2H),\ 7.618\ (s,\ 2H),\ 4.110\ (s,\ 6H),\ 4.036\ (s,\ 6H).\]

\[ ^13C-NMR\ (100\ MHz,\ CDCl_3)\ \delta:\ 149.164\ (d,\ J = 111.8\ Hz),\ 145.362\ (d,\ J = 248.1\ Hz),\ 138.476\ (d,\ J = 249.4\ Hz),\ 124.774,\ 119.389,\ 115.172,\ 108.742,\ 108.741\ (d,\ J = 31.4\ Hz),\ 103.572,\ 55.835,\]
\(^{19}\text{F-NMR (376 MHz, CDCl}_3\) \(\delta\): -140.359 – - 140.418 (m, 2F), -159.900 (d, \(J = 16.2\) Hz, 2F).

**9,10,11,12-tetrafluorotriphenylene-2,3,6,7-tetraol (7.8)**

[Chemical structure image]

Chemical Formula: \(\text{C}_{18}\text{H}_8\text{F}_4\text{O}_4\)
Molecular Weight: 364.25

A 100 mL flask equipped with magnetic stirbar was charged with 1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (0.631 g, 1.5 mmol) and pyridine hydrochloride (6.905 g, 60 mmol). The mixture was heated in oil bath up to approximately 170 °C and the pyridine hydrochloride melted. The mixture was heated while stirring for approximately 4 hours and it was then cooled to room temperature.

The black solid obtained was dissolved in water (100 mL) and extracted with ethyl acetate (50 mL x5). The organic phases were combined and dried over with anhydrous MgSO\(_4\). After being mixed with silica gel (~5 g). The solvent was removed under reduced pressure. The resulting yellow powder was placed at the top of a silica column and eluted (eluent: hexanes: EtOAc = 3:1). Fractions containing the pure product were combined and concentrated to tan solid (0.537 g, 1.47 mmol, 98 %) as final product.
M.P.: > 375 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 9.776 – 9.775 (br, 4H), 8.230 (s, 2H), 7.758 (s, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 147.507, 145.602, 144.636 (d, $J = 242.5$ Hz), 137.471 (d, $J = 244.8$ Hz), 124.162, 117.092, 114.818, 112.605 (t, $J = 14.7$ Hz), 107.938.

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -139.893 (d, $J = 16.5$ Hz, 2F), -160.386 (d, $J = 17.3$ Hz, 2F).

1,2,3,4-tetrafluoro-6,7,10,11-tetrakis(hexyloxy)triphenylene (7.9-C6)

A 100 mL flask equipped with magnetic stirbar was charged with 9,10,11,12-tetrafluorotriphenylene-2,3,6,7-tetraol (0.365 g, 1.0 mmol), 1-iodohexane (1.701 g, 8.0 mmol) potassium carbonate (2.223 g, 16 mmol) and anhydrous DMF (5 mL). The mixture was heated at 100 °C for 24 hours and TLC indicated a new product was formed and the starting material tetraol is completely consumed.

The mixture was then cooled to room temperature and diluted with water to a volume of 100 mL and stirred for 2 hours. The solid was filtered and air-dried, giving a grey powder (0.607 g, 0.87 mmol, 87 % yield) as product.
$^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.718 (s, 2H), 7.261 (s, 2H), 4.228 (t, J = 6.4 Hz, 4H), 4.152 (t, J = 6.4 Hz, 4H), 1.953 – 1.904 (m, 8H), 1.634 – 1.559 (m, 8H), 1.419 – 1.381 (m, 16H), 0.960 – 0.920 (m, 12H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 149.784, 148.716, 145.423 (d, J = 248.8 Hz), 138.430 (d, J = 241.5 Hz), 125.009, 119.510, 115.413, 110.830 (t, J = 15.5 Hz), 106.252, 69.379, 69.054, 31.688, 31.672, 29.307, 29.215, 25.836, 25.803, 22.670, 14.058.

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -140.408 (d, J = 11.6 Hz, 2F), -160.202 (d, J = 16.2 Hz, 2F).

6,7,10,11-tetrakis(dodecyloxy)-1,4-difluoro-2,3-bis(hexyloxy)triphenylene (7.10-C6-C12)

A 100 mL round bottom flask with magnetic stir bar was charged with 6,7,10,11-tetrakis(dodecyloxy)-1,2,3,4-tetrafluorotriphenylene (0.207 g, 0.2 mmol), 1-hexanol (0.082 g, 0.8 mmol), toluene (10 mL) and NaH (60 % in mineral oil, 0.049 g, 2.0 mmol). The mixture was heated until all the solid dissolved. After being gently refluxed for 2 days and TLC indicated the starting material completely consumed. It was cooled and diluted with ethyl acetate to a total volume of 100 mL followed by washing with water (100 mL x 3). The organic phase was then dried over with anhydrous MgSO$_4$ and mixed with silica gel (~2 g). After the removal of solvent,
the yellow powder obtained was placed at the top of a silica column and eluted (eluent: hexanes:EtOAc = 20:1). Fractions containing the product were combined and concentrated to give white solid (0.203 g) as final product. The product was demonstrated to be impure – which is a mixture of starting material and mono-substitute product.

The impure product was transferred into a 100 mL round bottom flask again and charged with 1-hexanol (10 mL), t-BuOK (0.178 g, 1.6 mmol). The mixture was heated up to a gentle reflux. After 24 hours, the same workup procedure was applied and the desired product was isolated as tan solid (0.135 g, 0.11 mmol, 55 % yield).

**¹H-NMR (400 MHz, CDCl₃) δ:** 8.469 (t, J = 2.6 Hz, 2H), 7.812 (s, 2H), 4.237 (t, J = 6.4 Hz, 4H), 4.224 (t, J = 6.4 Hz, 4H), 4.187 (t, J = 6.4 Hz, 4H), 1.936 – 1.859 (m, 12H), 1.563 – 1.526 (m, 12H), 1.399 – 1.268 (m, 72H), 0.928 (t, J = 7.0 Hz, 6H), 0.878 (t, J = 6.8 Hz, 12H).

**¹³C-NMR (100 MHz, CDCl₃) δ:** 150.765 (d, J = 242.6 Hz), 149.211, 148.605, 139.480 (t, J = 10.6 Hz), 124.901, 120.730, 115.511 (t, J = 5.4 Hz), 111.591 (t, J = 16.0 Hz), 106.866, 75.141, 69.573, 69.133, 31.951, 31.674, 30.232, 29.748, 29.697, 29.548, 29.513, 29.399, 29.314, 26.189, 26.160, 25.597, 22.710, 22.659, 14.123, 14.066.

**¹⁹F-NMR (376 MHz, CDCl₃) δ:** -134.064 (s, 2F).
2''',3''',4''',5''',6'''-pentafluoro-[1,1':2',1''-terphenyl]-3,4,4',5'-tetraol (7.11)

![Chemical structure](image)

Chemical Formula: C₁₈H₉F₆O₄  
Molecular Weight: 384.26

A 250 mL flask with magnetic stir bar was charged with 2,3,4,5,6-pentafluoro-3''',4''',5'''-tetramethoxy-1,1':2',1''-terphenyl (1.106 g, 2.5 mmol) which was dissolved in DCM (50 mL). The resulting solution was chilled in an ice bath and a solution of BBr₃ (3.698 g, 15.0 mmol, 6 eq) in DCM (15 mL) was added dropwise. The mixture obtained was stirred overnight and the temperature was allowed to reach room temperature. Water (100 mL) was added into the solution to form a cloudy mixture. Diethyl ether (50 mL) was added to make the mixture become clear. The organic phase was isolated and dried over with anhydrous MgSO₄. After the removal of drying agent via filtration, the solvent was removed under reduced pressure and gave grey crystals (1.131 g) as final product.

The yield of crude product was higher than theoretical, but was used directly for the next step.

**M.P.:** 59.0 – 65.0 °C.

**¹H-NMR (400 MHz, DMSO) δ:** 6.815 (s, H), 6.731 (s, H), 6.589 (d, J = 8.0 Hz, 1H), 6.410 (d, J = 2.0 Hz, 1H), 6.290 (dd, ¹J = 8.0 Hz, ²J = 2.0 Hz, 1H).

**¹³C-NMR (100 MHz, DMSO) δ:** 146.585, 144.576, 144.197, 144.142, 143.755 (d, J = 240.4 Hz),
139.258 (d, J = 248.7 Hz), 136.762 (d, J = 250.7 Hz), 133.881, 131.248, 119.060, 117.911, 116.903, 116.312 (t, J = 19.5 Hz), 115.517, 115.400, 113.728.

$^1$F-NMR (376 MHz, DMSO) δ: -140.854 (dd, $^1J = 25.6$ Hz, $^2J = 7.5$ Hz, 2F), -157.494 (t, J = 22.2 Hz, 1F), -163.293 – -163.439 (m, 2F).

2,3,4,5,6-pentafluoro-3''',4''',5'''-terakis(hexyloxy)-1,1':2',1'''-terphenyl (7.12-C6)

A 50 mL flask with magnetic stir bar was charged with 2''',3''',4''',5''',6''-pentafluoro-[1,1':2',1''-terphenyl]-3,4,4',5'-tetraol (0.969 g, 2.5 mmol), 1-iodohexane (3.196 g, 15 mmol), potassium carbonate (2.868 g, 20 mmol) and DMF (10 mL). The obtained mixture was well stirred at 100 °C for 24 hours and after that it was cooled to room temperature. The mixture was diluted with diethyl ether to a total volume of 100 mL and washed with water (3 x 100 mL). Organic phase was then separated and dried over anhydrous MgSO₄. Drying agent was removed by filtration and silica gel (~ 2 g) was charged inside before the removal of solvent. The powder obtained was placed on a silica gel column (Eluent: Hexanes). The fractions containing the product was combined and concentrated to dryness, giving a colorless oil (1.198 g, 1.7 mmol, 68 % yield) as final product.

$^1$H-NMR (400 MHz, CDCl₃) δ: 6.974 (s, H), 6.801 (s, H), 6.750 (d, J = 8.0 Hz, 1H), 6.671 –
6.638 (m, 2H), 4.069 (t, J = 6.6 Hz, 2H), 4.024 (t, J = 6.6 Hz, 2H), 3.959 (t, J = 6.6 Hz, 2H), 3.841 (t, J = 6.6 Hz, 2H), 1.894 – 1.708 (m, 8H), 1.526 – 1.440 (m, 8H), 1.367 – 1.328 (m, 16H), 0.920 – 0.895 (m, 12H).


$^{19}$F-NMR (376 MHz, CDCl$_3$) δ: -140.025 – -140.133 (m, 2F), -156.285 (t, J = 20.9 Hz, 1F), -162.924 – -163.065 (m, 2F).

2,3,5,6-tetrafluoro-3"',4,4',4'',5'-pentakis(hexyloxy)-1,1':2',1''-terphenyl (7.13-C6)

A 50 mL flask with magnetic stir bar was charged with 2,3,4,5,6-pentafluoro-3"',4',4'',5'-tetrakis(hexyloxy)-1,1':2',1''-terphenyl (0.901 g, 1.25 mmol), 1-hexanol (10 mL) and $\tau$-BuOK (0.282 g, 2.5 mmol). The mixture was heated up to approximately 100 °C to make all the solids dissolve. After 24 hours, TLC indicated the starting material was completely consumed. It was cooled to room temperature and diluted with diethyl ether to a total volume of 100 mL followed washing with water (3 x 100 mL). The organic phase was dried over anhydrous MgSO$_4$ and drying
agent was then filtered with gravity filtration. After the removal of solvent, the excess amount of 1-hexanol was removed by Kugelrohr distillation (75 °C, 0.8 millibar). The remaining residue was dissolved in ethyl acetate (~ 50 mL) and mixed with silica gel (~ 2g). The yellow powder obtained after removing the solvent and was placed at the top of a silica column (eluent: hexane). Fractions containing the product were combined and concentrated to give sticky oil as final product (0.700 g, 0.87 mmol, 70 % yield).

\[ \text{1H-NMR (400 MHz, CDCl}_3 \text{)} \delta: 6.950 (s, 1 H), 6.790 (s, 1 H), 6.745 (d, J = 8.0 Hz, 1H), 6.670 (dd, \text{ }^1J = 8.0 Hz, \text{ }^2J = 2.0 Hz, 1H), 6.628 (d, J = 2.0 Hz, 1H), 4.164 (t, J = 6.6 Hz, 2H), 4.057 (t, J = 6.6 Hz, 2H), 4.015 (t, J = 6.6 Hz, 2H), 3.953 (t, J = 6.6 Hz, 2H), 3.802 (t, J = 6.6 Hz, 2H), 1.884 – 1.690 (m, 10H), 1.510 – 1.399 (m, 10H), 1.355 – 1.321 (m, 20H), 0.922 – 0.882 (m, 15H).
\]

\[ \text{13C-NMR (100 MHz, CDCl}_3 \text{)} \delta: \text{Need to do again.} \]

\[ \text{19F-NMR (376 MHz, CDCl}_3 \text{)} \delta: -142.198 (dd, \text{ }^1J = 22.9 Hz, \text{ }^2J = 8.3 Hz, 2F), -158.075 (dd, \text{ }^1J = 22.9 Hz, \text{ }^2J = 8.3 Hz, 2F). \]

1,2,4-trifluoro-3,6,7,10,11-pentakis(hexyloxy)triphenylene (7.14-C6)

![Chemical structure of 1,2,4-trifluoro-3,6,7,10,11-pentakis(hexyloxy)triphenylene](image)

Chemical Formula: C\textsubscript{48}H\textsubscript{69}F\textsubscript{3}O\textsubscript{5}

Molecular Weight: 783.07

In a quartz vessel, 2,3,5,6-tetrafluoro-3",4,4",5"-pentakis(hexyloxy)-1,1";2',1"-terphenyl (0.680
g, 0.85 mmol) was dissolved in acetonitrile (100 mL). The solution was degassed with nitrogen and irradiated for 8 hours in a Rayonette photochemical reactor equipped with 16 x 254nm ultraviolet lamps.

After this time, the solvent was removed to give a brown residue (0.673 g) as crude product. The solid was dissolved again in ethyl acetate (~ 5 mL) and mixed with silica gel (~ 2 g). After concentrate to dryness, the tan powder obtained was placed on the top of silica gel column and eluted (eluent: hexanes). Fractions containing the product were combined and concentrated, giving a sticky solid (0.368 g, 0.47 mmol, 55 % yield) as final product.

$^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.412 (d, $J = 6.0$ Hz, 1H), 8.376 (d, $J = 6.0$ Hz, 1H), 7.768 (d, $J = 2.4$ Hz, 2H), 4.287 (d, $J = 6.6$ Hz, 2H), 4.234 (d, $J = 6.6$ Hz, 2H), 4.180 (d, $J = 6.6$ Hz, 2H), 4.171 (d, $J = 6.6$ Hz, 2H), 1.963 – 1.846 (m, 10H), 1.597 – 1.541 (m, 10H), 1.413 – 1.363 (m, 20H), 0.954 – 0.919 (m, 15H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 151.402, 149.466, 149.428, 148.939, 148.647, 145.664 (dd, $^1J = 247.0$ Hz, $^2J = 11.7$ Hz), 143.178 (dd, $^1J = 245.2$ Hz, $^2J = 6.3$ Hz), 143.006 (dd, $^1J = 245.4$ Hz, $^2J = 6.3$ Hz), 134.605 (d, $J = 12.2$ Hz), 134.430 (d, $J = 9.6$ Hz), 124.987, 124.882, 120.146, 115.434, 115.155, 111.399 (d, $J = 30.8$ Hz), 110.996 (d, $J = 29.7$ Hz), 106.567 (d, $J = 4.0$ Hz), 75.561, 69.455, 69.083, 69.051, 31.693, 31.673, 31.574, 30.083, 29.339, 29.256, 29.226, 25.837, 25.815, 25.394, 22.669, 22.622, 14.056.

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -132.421 – -132.486 (m, 1F), -141.400 – -141.499 (m, 1F), -153.682 (dd, $^1J = 18.8$ Hz, $^2J = 5.6$ Hz, 1F).
2,3,4,5,6-pentafluoro-3'',4'',4'',5''-tetrakis(pentyloxy)-1,1':2',1''-terphenyl (7.12-C5)

A 50 mL flask with magnetic stir bar was charged with 2'',3'',4'',5'',6''-pentafluoro-[1,1':2',1''-terphenyl]-3,4,4',5'-tetraol (0.463 g, 1.2 mmol), 1-iodopentane (1.922 g, 9.7 mmol), potassium carbonate (1.351 g, 9.8 mmol) and DMF (10 mL). The mixture was well stirred at 100 °C for 24 hours and after that it was cooled to room temperature. The mixture was diluted with diethyl ether to a total volume of 100 mL and washed with water (3 x 100 mL) to remove DMF. Organic phase was then separated and dried over anhydrous MgSO₄. After the drying agent was removed by gravity filtration, silica gel (~ 2 g) was added before the removal of solvent. The powder obtained was placed on a silica gel column (Eluent: Hexanes). The fractions containing the product was combined and concentrated to dryness, giving a colorless oil (0.480 g, 0.72 mmol, 60 % yield) as final product.

**1H-NMR (400 MHz, CDCl₃)  δ:** 6.948 (s, 1 H), 6.767 (s, H), 6.744 (d, J = 8.4 Hz, 1H), 6.650 – 6.619 (m, 2H), 4.059 (t, J = 6.6 Hz, 2H), 4.014 (t, J = 6.6 Hz, 2H), 3.957 (t, J = 6.6 Hz, 2H), 3.828 (t, J = 6.6 Hz, 2H), 1.879 – 1.724 (m, 8H), 1.481 – 1.369 (m, 16H), 0.955 – 0.901 (m, 12H).

**13C-NMR (100 MHz, CDCl₃)  δ:** 150.030, 148.397, 148.337, 148.030, 144.323 (d, J = 244.5 Hz), 140.277 (d, J = 251.0 Hz), 137.318 (d, J = 256.6 Hz), 136.035, 133.239, 121.119, 116.404, 116.132,

$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -140.042 (dd, $^1J = 23.7$ Hz, $^2J = 8.3$ Hz, 2F), -156.142 (t, $^1J = 20.9$ Hz, 1F), -162.802 – -162.943 (m, 2H).

2,3,5,6-tetrafluoro-3",4,4',4",5'-pentakis(pentyloxy)-1,1':2',1"-terphenyl (7.13-C5)

A 50 mL flask with magnetic stir bar was charged with 2,3,4,5,6-pentafluoro-3",4',4",5'-tetrakis(pentyloxy)-1,1':2',1"-terphenyl (0.340 g, 0.51 mmol), 1-pentanol (5 mL) and t-BuOK (0.089 g, 0.8 mmol). The mixture was heated up to approximately 100 °C to make all the solid dissolve. After 24 hours, it was cooled to room temperature and diluted with diethyl ether to a total volume of 100 mL followed by water washing (3 x 100 mL). The organic phase was dried over with anhydrous MgSO$_4$. After the removal of solvent, the excess amount of 1-pentanol was removed by Kugelrohr distillation (75 °C, 0.8 millibar). The residue was dissolved in ethyl acetate (~ 50 mL) and mixed with silica gel (~ 2g). A yellow powder was obtained after the removal of solvent and it was placed at the top of a silica column (eluent: hexane). Fractions containing the product were combined and concentrated to give sticky oil as final product (0.361 g, 0.49 mmol, 96 % yield).
$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 6.955 (s, 1 H), 6.796 (s, H), 6.748 (d, $J = 8.4$ Hz, 1H), 6.674 (dd, $^1J = 8.4$ Hz, $^2J = 2.0$ Hz, 1H), 6.632 (d, $J = 2.0$ Hz, 1H), 4.168 (t, $J = 6.6$ Hz, 2H), 4.061 (t, $J = 6.6$ Hz, 2H), 4.019 (t, $J = 6.6$ Hz, 2H), 3.957 (t, $J = 6.6$ Hz, 2H), 3.806 (t, $J = 6.6$ Hz, 2H), 1.897 – 1.705 (m, 10H), 1.508 – 1.336 (m, 20H), 0.956 – 0.902 (m, 15H).


$^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: -142.714 (dd, $^1J = 26.7$ Hz, $^2J = 8.6$ Hz, 2F), -158.596 (dd, $^1J = 22.9$ Hz, $^2J = 8.6$ Hz, 2F).

1,2,4-trifluoro-3,6,7,10,11-pentakis(pentyloxy)triphenylene (7.14-C5)

In a quartz vessel, 2,3,5,6-tetrafluoro-3",4,4',5"-pentakis(pentyloxy)-1,1':2',1"-terphenyl (0.550 g, 0.75 mmol) was dissolved in acetonitrile (100 mL). The solution was degassed with nitrogen and irradiated for 6 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps.
After this time, the solvent was removed and gave brown residue (0.605 g) as crude product. The solid was dissolved in ethyl acetate (~ 5 mL) and mixed with silica gel (~ 2 g). After concentration to dryness, the tan powder obtained was placed on the top of a silica gel column and eluted (eluent: hexanes), giving sticky solid (0.288 g, 0.40 mmol, 53 % yield) as final product.

**$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$:** 8.388 (d, $J = 6.0$ Hz, 1H), 8.347 (d, $J = 6.0$ Hz, 1H), 7.740 (d, $J = 2.4$ Hz, 2H), 4.282 (d, $J = 6.6$ Hz, 2H), 4.231 (d, $J = 6.6$ Hz, 2H), 4.227 (d, $J = 6.6$ Hz, 2H), 4.177 (d, $J = 6.6$ Hz, 2H), 4.163 (d, $J = 6.6$ Hz, 2H), 1.976 – 1.911 (m, 10H), 1.586 – 1.418 (m, 20H), 1.000 – 0.947 (m, 15H).

**$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$:** 151.377, 149.424, 149.145, 148.918, 148.603, 145.621 (d, $J = 238.0$ Hz), 143.149 (d, $J = 240.0$ Hz), 143.062 (d, $J = 238.0$ Hz), 134.668, 124.959, 124.846, 120.097, 115.405, 115.115, 115.071, 111.352 (d, $J = 31.4$ Hz), 110.932 (d, $J = 29.6$ Hz), 106.677, 106.447 (d, $J = 4.2$ Hz), 75.554, 75.530, 69.390, 69.062, 69.018, 29.822, 29.055, 28.986, 28.960, 28.380, 28.359, 28.314, 27.884, 22.591, 22.562, 22.471, 14.126, 14.108.
7.9. References


(2) Kumar, S. *NPG Asia Mater* **2014**, *6*, e82.


8. Chapter Eight - Low absorption liquid crystals for infrared applications

8.1. Optical anisotropy, birefringence and liquid crystals

Liquid crystals are materials that possess some certain states between the ordinary liquid and solid crystal under specific conditions. Thermotropic liquid crystals are the most common type and their liquid crystal phases (called mesogen such as nematic, smetic phase or previously discussed discotic phase) only occur in an appropriate temperature range. Usually, too high of a temperature will destroy the ordering of LC phase, pushing it into an ordinary liquid (isotropic liquid phase). On the contrary, too low a temperature will slow down the molecule thermal motion and “freeze” it into a crystal 1,2.

In the temperature interval(s) in which materials show a mesogenic phase(s), the molecules are aligned in a relatively ordered pattern(s) and this most often leads to an anisotropy in many physical properties such as refractive index, viscosity, conductivity, etc.

Consider the situation of multiple refractive indices; it will lead to a special property called birefringence (double refraction) in liquid crystals. When a beam of non-polarized light enters an anisotropic material (such as a nematic liquid crystal sample), the light beam will be broken up into two slightly different pathways and each of them will become polarized. This separation of non-polarized light into two pathways is due to the different indices of refraction leading to different travel velocities of light. The faster light beam is called the ordinary ray (refractive index \(n_0 = c/V_0\)) at here the electrical vector of the polarized light is perpendicular to the liquid crystal director. On the other hand, the relatively slower beam is named extraordinary ray (refractive index \(n_e = c/V_e\)) and its electrical vector is parallel to the director. The intensity of birefringence can be
determined by $\Delta n = n_e - n_o$. Here, we just consider about uniaxial materials ($n_e > n_o$) and nematic liquid crystals belong to this type. Typically the $n_o$ value of nematic liquid crystals is approximately 1.5 and the $\Delta n$ value range from 0.05 to 0.5$^3$ (the commonly known room temperature liquid crystal 5-CB has $\Delta n = 0.179$ at 589.3 nm and 25°C$^4$). In addition to the range of visible light, it has also been demonstrated that liquid crystals are able to show high birefringence in the infrared range as well$^5$.

8.2. The introduction of infrared transparent liquid crystals


Because of the previously discussed special birefringence property, aside of well-known amplitude modulation application such as LCD display$^6$, liquid crystals can also be used for phase modulation$^7$ such as light modulators for laser beam steering$^8$ and adaptive optics in the mid-wave IR (3-5 µm) and long-wave IR (8-12 µm) regions. For IR applications, high birefringence is absolutely the desired property. However, light absorption of the liquid crystal media is another very important criterion need to concern. There are various molecular band vibrations associated
with IR absorption. The IR absorption of the liquid crystal should be minimized as the adsorbed light is lost and the device function will be diminished accordingly. Any light absorption in the media will finally be converted into thermal energy. The accumulated thermal energy will likely to increase the temperature of liquid crystal samples and influence the birefringence $\Delta n$ of the media. Even worse, if the temperature finally exceeds the clearing point ($T_c$) of liquid crystals, the LC sample will just turn into an ordinary isotropic liquid and the capability of any light modulation will completely vanish (Figure 8.2). Because of this, ideal LCs employed for IR applications must be designed to have a low IR absorption, wide nematic range and high clearing point ($T_c$).

![Figure 8.2 Temperature dependence of refractive index](http://www.personal.kent.edu/~bisenyuk/liquidcrystals/maintypes3.html)

The IR absorption of a well-known room temperature nematic liquid crystal – 5CB (4-cyano-4′-pentylbiphenyl) is shown as below from 4000 cm$^{-1}$ (2.5 µm) to 650 cm$^{-1}$ (15.4 µm) (Figure 8.3). Near 3000 cm$^{-1}$, very sharp and strong absorptions of C-H stretching (including aromatic C-H and alkane -CH$_2$ and CH$_3$) can be observed. As long as most of organic compounds contains C-H bonds, this absorption is nearly impossible to avoid. The C≡N stretching shows a narrow but strong absorption in the middle position of MWIR (Zone B, approximately 2250 cm$^{-1}$, 4.45 µm). This hints that the C≡N group should be avoided in MWIR transparent liquid crystal design, although it is an excellent polar group and electron acceptor that could lead to highly dielectric anisotropy and birefringence. In Zone B, the overtones (doubled frequency of a given band or sum
frequency of two separated bands) of C-H and C-C from Zone D also add to the baseline absorption. The absorptions in zone C are usually from the C–H deformation (in alkyl chain) and C–C skeletal stretching, the overtone of these absorptions will also have influence in Zone A. Finally, the C–C skeletal stretching (in the alkyl chain) and the in-plane deformation of C–H in the phenyl rings lead to the absorptions in Zone D. All of these absorptions are well organized and listed in Table 8.1 below.

![Figure 8.3 Measured absorption coefficient spectrum of 5CB (measurement was conducted in anisotropic phase, two cells with 100 and 50 μm gaps were employed) (Courtesy Prof. Shin-Tson Wu, University of Central Florida)](image)

<table>
<thead>
<tr>
<th>Zone</th>
<th>Absorption mechanism</th>
<th>Frequency (cm⁻¹)</th>
<th>Wavelength (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>C–H (in CH₂, CH₃) deformation overtone</td>
<td>2790 – 2500</td>
<td>3.6 – 4.0</td>
</tr>
<tr>
<td></td>
<td>C–C skeletal stretching overtone</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C≡N stretching</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>C–H (in phenyl ring) in plane deformation overtone</td>
<td>2500 – 2000</td>
<td>4.0 – 5.0</td>
</tr>
<tr>
<td></td>
<td>C–C (in alkyl chain) skeletal stretch overtone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>C–H in CH₂, CH₃ deformation</td>
<td>1485 – 1250</td>
<td>6.7 – 8.0</td>
</tr>
<tr>
<td></td>
<td>C–C skeletal stretch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>C–H (in phenyl ring) in-plane deformation</td>
<td>1250 – 1000</td>
<td>8.0 – 10.0</td>
</tr>
<tr>
<td></td>
<td>C–C (in alkyl chain) skeletal stretching</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8.1 Corresponding absorption mechanisms for Zones A–D shown in the figure above.
If we just simplify the atoms and chemical bonds as a spring–mass system, the molecular vibration bands can be described as the equation below. Here, \( k \) is the spring constant and \( \mu \) is the reduced mass.

\[
\lambda = 2\pi\sqrt{\frac{\mu}{k}}
\]

From this equation, it is clear that if the reduced mass \( \mu \) increases, the absorption will move to a much longer wavelength. In the region of MWIR, the C-H bonds usually have very strong absorption that covers in the range of 3-5 \( \mu \)m. Up to now, to shift the absorption out of the interested MWIR region, several methods have been investigated – deuteration, fluorination and chlorination.

The deuteration approach has already been investigated by Prof. Wu and Prof. Kornfield et al. more than 10 years ago \(^{10}\). The fully deuterated D5CB liquid crystal was time consuming and the synthetic route was described below. By using Pt as catalyst under a temperature of between 150 and 200 °C, in a pressurized reaction vessel, the hydrogen atoms on 4-\( n \)-pentyl-biphenyl (5B) were exchanged with deuterium using excess amount of D\(_2\)O as deuterium source. After three days of reaction and analysis showed that the deuteration level could be as high as 95 %. After treating the fully deuterated 4-pentyl-biphenyl (D5B) with bromine, the bromine atom on 4'-bromo-4-pentylbiphenyl was finally substituted with a nitrile group by using KCN under the existence of tetrakis(triphenylphosphine)palladium(0) catalyst and 18-crown-6-ether. Finally, multiple silica gel chromatographies were applied to purify the desired fully deuterated product 5CB (D5CB) and the analysis of \(^1\)H-NMR showed that the deuteration level of alkyl chain hydrogens were in the range of 89 % – 97 % and aromatic hydrogens could be as high as 95 %.

The IR absorption of perdeuterated pentylicyanobiphenyl (D5CB) is shown below (Figure 8.4).
Compared with the IR absorption of ordinary 5CB, D5CB has a much cleaner absorption spectrum and lower absorption coefficient. The most obvious C-H stretching absorption at 3.2 – 3.6 µm range was nearly completely depressed (as long as it was not a 100% deuterated sample, some C-H absorption still persisted) and the overtones of the aromatic C-H bonds in the 5.0 – 6.3 µm range also completely vanished. However, according to the equation mentioned above, the exchange of C-H to C-D will shift the vibration bands to a longer wavelength by $\sqrt{2}$ and the C-D vibration now just showed up as an absorption at 4.8 µm as calculated.
The infrared spectra of 5CB (top) and D5CB (bottom) illustrate the absorption bands of CH and CN.

Figure 8.4 The infrared spectra of 5CB (top) and D5CB (bottom)\textsuperscript{10}

The result of perdeuteration is that the IR absorption of C-D is very close to C≡N (4.8 \( \mu \text{m} \) vs 4.45 \( \mu \text{m} \)), which unfortunately is still in the MWIR region. To ensure the absorption band will be shifted out of the desired MWIR slot, some still heavier atom such as fluorine is required to replace the protons.
An investigation of fluorination methodology as already been accomplished about four years ago by our lab’s former Ph.D. student Suvagata Tripathi with the guidance of Prof. Twieg and in cooperation of Prof. Wu et al. To accomplish this task, several fluorinated compounds (Table 8.2) were prepared to test the function of fluorine atoms in IR absorption.

### Table 8.2 Chemical structures, abbreviations and phase transition temperatures of compounds studied.

<table>
<thead>
<tr>
<th>Compound No</th>
<th>Structure</th>
<th>Abbreviation</th>
<th>PTT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="1CB" /></td>
<td>1CB</td>
<td>Cr 109 N (45) I</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2" alt="5CB" /></td>
<td>5CB</td>
<td>Cr 24 N 35.3 I</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="FB" /></td>
<td>FB</td>
<td>Cr 88 I</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4" alt="F7CB" /></td>
<td>F7CB</td>
<td>Cr 120.4 I</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5" alt="FT" /></td>
<td>FT</td>
<td>Cr 85.8 N 87.6 I</td>
</tr>
</tbody>
</table>

Note: Compound 5 was prepared in Poland by Przemyslaw Kula and Roman Dabrowski.

The IR absorptions of different compounds were tested at the same concentration and the results in the MWIR range are shown in Figure 8.5. The 1CB (Blue line) and 5CB (Red line) have similar structures and thus their absorptions are nearly the same except the 5CB compounds showed much stronger absorption at 3.2 – 3.6 µm due to longer alkyl carbon chain and corresponding CH bonds. The 4,4'-difluorobiphenyl (FB) (Green line) is just a reference compound to demonstrate that the absorption of CH bonds in aromatic rings is much weaker (and shorter wavelength) than those in alkyl tails. The 4'-perfluoroheptylbiphenyl-4-carbonitrile (F7CB) (Purple line) compound has a
strong C≡N absorption at 4.48 μm that is the same as 1CB and 5CB. It also features weak aromatic CH absorption that similar as FB. Aside of this, the interesting phenomenon is that F7CB has a characteristic absorption at ~4.25μm due to the overtone of the strong C-F vibration at ~8.5 μm. The lesson learned from the F7CB compound is that the perfluorinated alkyl chain cannot be too long, as it will eliminate any nematic phase. Furthermore, it would absolutely lead to the C-F overtone absorptions at ~4.25μm which is still in the MWIR range.

![Figure 8.5 Measured transmission spectra of 5CB (Red), 1CB (Blue), FB (Green) and F7CB (Violet) in MWIR region.](image)

According to the table above, both of FB and F7CB do not possess any mesogenic phase. To overcome this issue, a new fluorinated compound FT was also prepared to test its IR transparency (Figure 8.6). In this compound, trifluoromethoxy group –OCF₃ was selected as the polar group for a substitution of nitrile group C≡N. Aside of this, three phenyl rings were enclosed to ensure its relatively high birefringence. Compare to the spectra of 5CB, the IR absorption of FT from 3 μm to 5 μm is relatively clean (absence of alkyl chain and nitrile group). Very weak absorptions
could be observed at 3.3 – 3.5 μm due to aromatic CH bonds; another weak absorption at ~ 4 μm is from the overtone of C-F stretching vibration at higher than 8 μm (outside of the spectra).

![Transmission spectra of 5CB (red line) and FT (blue line) in MWIR region.](image)

**Figure 8.6** Measured transmission spectra of 5CB (red line) and FT (blue line) in MWIR region.12

The neat FT compound only features an extremely narrow nematic phase range within about 2 °C (Cr 85.8 N 87.6 I) thus further optimization was made by Tripathi, Twieg and Wu et al.9. The fluorinated compounds being studied are listed in **Table 8.3** and the first three of them are able to show nematic phase. To widen the range of nematic phase, two additional fluorinated compounds 4 and 5 were utilized to design a eutectic mixture called Mix I. According to the result of DSC, the Mix I was possessed a nematic phase from 42 to 51.5 °C during heating and the crystallization can be as low as -10 °C due to supercooling.
### Table 8.3: Chemical structures and properties of the seven compounds

<table>
<thead>
<tr>
<th>No.</th>
<th>Structure</th>
<th>PPT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Structure 1" /></td>
<td>Cr 86 N 88 I</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2" alt="Structure 2" /></td>
<td>Cr 86 N (84) I&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="Structure 3" /></td>
<td>Cr 55 N (40) I</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4" alt="Structure 4" /></td>
<td>Cr 113 I</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5" alt="Structure 5" /></td>
<td>Cr 66 I</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6" alt="Structure 6" /></td>
<td>Cr 71 N (65) I</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7" alt="Structure 7" /></td>
<td>Cr 95 N (68) I</td>
</tr>
</tbody>
</table>

**Note1:**<sup>a</sup>(<sup>a</sup>) indicates a monotropic phase.

**Note2:** Suvagata Tripathi prepared compounds 6-7. Compounds 1-5 were prepared in Poland.

The IR absorption of Mix I (Red line) is shown in Figure 8.7 and the result is nearly the same as before – compared with the strong alkyl CH stretching absorption in 5CB, the aromatic CH stretching in Mix I only has moderate absorption in the region of 3.3 – 3.6 μm. However, the C-O and C-F stretching peaks are located in the range at about 7.5 – 8.5 μm (1300 – 1100 cm<sup>-1</sup>, outside of the figure) and unfortunately their overtones cause an obvious bump up in the baseline at ~ 4 μm.
To shift such overtone peaks to much lower wavenumbers, chlorine atoms were then selected to replace fluorine atoms. Different from fluorinated liquid crystal compounds, the alkyl tail in chlorinated liquid crystal compound is more important to keep the flexibility and aspect ratio. In consideration of this, two chlorinated compounds 6 and 7 were synthesized. As before, 60 wt% of compound 6 and 40 wt% of compound 7 were used to prepare Mix II which featured a thermodynamically stable nematic range from 48.3 to 69.2 °C. Furthermore, a supercooling effect also moved its range to 0 °C.

The IR absorptions of both Mix II and 5CB are seen in Figure 8.8 for a much better comparison. Clearly, Mix II features a much weaker absorption from about 3.6 μm to 5.0 μm. Since the C≡N group does not exist in any of the two chlorinated compounds of Mix II, the absorption at 4.45 μm is completely absent. Also, the peaks of C-Cl bond vibration is in the very right fingerprint region of IR spectra (~ 12.5 μm) and its overtones will not show up in the MWIR region.
However, it has already mentioned before – the alkyl tail seems to be mandatory in chlorinated liquid crystal compounds in keeping the flexibility altogether with aspect ratio. As a result of this, the strong CH stretching vibration absorption at \( \sim 3.3 \text{ \( \mu \)m} \) is unavoidable for Mix II.

Both fluorinated and chlorinated liquid crystals have their own pros and cons. For fluorinated liquid crystal compounds Mix I, the CF overtone absorption at \( \sim 4 \text{ \( \mu \)m} \) is an annoying issue, however, it shows very low absorption coefficient at \( \sim 3 \text{ \( \mu \)m} \) thus it is suitable for operations within that range. On the other hand, chlorinated systems Mix II is suitable for 4 – 5 \( \mu \)m operations.

### 8.3. Further investigation on chlorinated liquid crystals

The chlorinated compounds in Mix II have already been investigated before\(^9\) and the next
challenge for us was to optimize the liquid crystal compounds’ properties (e.g. still wider nematic range, higher birefringence and lower IR absorption in desired regions) by additional structure changes (e.g. number and positions of chlorine atoms and the length of alkyl tails and type of alkyl content).

### 8.3.1. Synthesis of 4,2’-dichlorinated cyclohexylterphenyls

The first series of compounds we synthesized were the 4,2’-chlorinated terphenyls as they had already been verified to possess nematic phases. Their synthesis was relatively simple as only two sequential Suzuki coupling reactions were involved (Scheme 8.1). First, commercially available 4-bromo-2-chloro-1-iodobenzene was coupled with 4-chlorophenyl boronic acid to yield 4-bromo-2,4’-dichloro-1,1’-biphenyl. Then, the bromine atom was substituted with various length alkyl tail phenyl boronic acids to yield the desired 4,2’-chlorinated terphenyl.

![Scheme 8.1 Synthesis of 4,2’-chlorinated cyclohexylterphenyls](image)

Fortunately, the 4-(n-propyl)phenyl boronic acid and 4-(n-pentyl)phenyl boronic acid could be
purchased directly from chemical vendors due to their relatively affordable prices. The 4-(n-heptyl)phenyl boronic acid and the boronic acids involving cyclohexane rings were prepared from their corresponding bromide precursors (Scheme 8.2). One observation worthy of mention at here is that the bromination of n-pentyl benzene with bromine\textsuperscript{13} absolutely leads to a mixture of para- and ortho- products (about 4:1 ratio followed by GC-MS) and this ortho- impurity would also be passed onto the boronic acid stages. However, the mixture of para- and ortho- (n-heptyl)phenyl boronic acids could be used directly and only one product 2',4-dichloro-4"-heptyl-1,1':4',1"-terphenyl was obtained.

Scheme 8.2 Preparation of corresponding boronic acids

The samples were sent to Dr. Wu at the University of Central Florida for further characterization including DSC, birefringence, visco elastic constants and IR absorption. The results have already been published online\textsuperscript{14}.

The phase transition temperatures of all five compounds obtained via DSC are shown in Table 8.4.
Compounds 1 to 3 only have a monotropic nematic phase and their melting points are a bit high. Here, a eutectic mixture IR-M1 was prepared by mixing these three compounds in an appropriate ratio. Compound 4 and 5 show a wide nematic range more than 110 °C, however, their melting points are very high (more than 125 °C). To overcome this issue, about 10 wt% of compound 5 was added into the previously prepared mixture IR-M1 which led to a new mixture IR-M2. The newly prepared mixture IR-M2 features a very wide nematic range - the melting point is less than −40 °C (the melting point may be much lower, however, the due to the limitations of our DSC hardware, it cannot be verified) and clearing point climbed up to 85 °C. According to the analysis of Dr. Wu, compounds 4 was not selected here due to its “poor solubility, high melting point and large heat of fusion”.
Table 8.4 Phase transition temperatures for 4,2'-chlorinated terphenyls.\textsuperscript{14}

<table>
<thead>
<tr>
<th>Compound #.</th>
<th>Chemical structure</th>
<th>T\textsubscript{m} (°C)</th>
<th>T\textsubscript{c} (°C)</th>
</tr>
</thead>
</table>
| 1           | \( \text{C}_3\text{H}_7 \)
|             | \( \text{Cl} \)
|             | \( \text{Cl} \)
|             | \( \text{Cl} \) |
|             | \( \text{Cl} \) |
| 2           | \( \text{C}_9\text{H}_{11} \)
|             | \( \text{Cl} \)
|             | \( \text{Cl} \)
|             | \( \text{Cl} \) |
| 3           | \( \text{C}_7\text{H}_{15} \)
|             | \( \text{Cl} \)
|             | \( \text{Cl} \)
|             | \( \text{Cl} \) |
| 4           | \( \text{C}_3\text{H}_{11}^{\text{mm}} \)
|             | \( \text{Cl} \)
|             | \( \text{Cl} \)
|             | \( \text{Cl} \) |
| 5           | \( \text{C}_9\text{H}_{11}^{\text{mm}} \)
|             | \( \text{Cl} \)
|             | \( \text{Cl} \)
|             | \( \text{Cl} \) |

Note: Compound 4 was prepared by Andrew Bostwick.

By using a He-Ne laser source (\( \lambda = 633\text{nm} \)), the temperature dependent birefringence test was done from 25 °C to 80 °C (black dot) and Haller’s semi-empirical equation\textsuperscript{15} was used to fit the curve (red line).

\[
\Delta n = \Delta n_0 (1 - \frac{T}{T_c})^\beta
\]

where \( \Delta n_0 \) is the extrapolated birefringence at \( T = 0 \), \( T \) is the temperature, \( T_c \) is the clearing point, and \( \beta \) is a material parameter. According to the result of fitting, \( \Delta n_0 = 0.29 \) and \( \beta = 0.15 \).

The birefringence of IR-M2 at \( \lambda = 633\text{nm} \) was measured. In fact, we need to apply this material
for MWIR application and the determination of birefringence at that range is required. To accomplish this task, different $\Delta n$ data were measured at different wavelength and the dispersion curve was fit with single-band birefringence dispersion model$^{5,16}$.

$$\Delta n = G \frac{\lambda^2 \lambda^*}{\lambda^2 - \lambda^*}$$

Where $G$ a constant and $\lambda^*$ is the mean resonance wavelength. According to the result of fitting, $G = 3.37 \mu m^{-2}$ and $\lambda^* = 0.240 \mu m$ were obtained (Figure 8.9). The dispersion curve (Figure 8.10) features an extremely decrease within the range of visible light to short wave IR region and then becomes smooth after it enter the range of MWIR ($\Delta n \approx 0.194$).

*Figure 8.9* Temperature dependent birefringence of IR-M2 at $\lambda = 633$nm. The black dots are measured data and the red line is a fitting curve with Haller’s semi-empirical equation (Prof. Shin-Tson Wu, University of Central Florida).$^{14}$
From this result, according to the following phase retardation equation\textsuperscript{17}:

\[ \delta = 2\pi d\Delta n/\lambda \]

Where \( d \) is the cell gap. In an operation of IR phase modulation, in order to achieve \( 2\pi \) phase change at \( \lambda = 4.0 \) \( \mu \)m, the desired cell gap would be 20.62 \( \mu \)m.

For the visco-elastic constant, it was tested at different temperatures from room temperature to 80 °C. All the data were plotted (black dots) and the curve (red line) was fitted with this equation:

\[ \frac{\gamma_1}{K_{11}} = A \exp \left( \frac{E_a/k_B T}{T} \right) \left( 1 - \frac{T}{T_c} \right)^\beta \]
Where $A$ is a constant number, $k_B$ is the Boltzmann constant number, $E_a$ is the activation energy and $\beta$ is a material parameter (which had already been obtained in birefringence test). The fitting result showed that the activation energy $E_a = 525$ meV.

The visco-elastic coefficient of IR-M2 is about 135 ms/μm² at room temperature and this number is much higher than that of previous discussed fluorinated mixture Mix I (Only about 25 ms/μm²). This phenomenon might due to the relatively heavier chlorine atom and the long alkyl chains in chlorinated compounds. When the temperature increases, the visco-elastic coefficient drops dramatically (Figure 8.11).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure811.png}
\caption{Temperature dependent visco-elastic coefficients of IR-M2 (Prof. Shin-Tson Wu, University of Central Florida).}
\end{figure}
Since a 20.62 μm cell gap is required to obtain a phase $2\pi$ phase change at MWIR region ($\lambda = 4.0$ μm). The IR transmittance spectrum (Figure 8.12) was just obtained by using a 21μm cell gap at room temperature. Within the region of 3.8 μm to 5 μm, the transmittance can be up as high as 98 %. This is because the C-Cl vibration peak is in the very low energy fingerprint region (~ 12.5 μm) and its overtone is still outside of the MWIR region. To make sure the chlorinated compounds have a mesogenic phase, an alkyl chain is necessary and it will introduce a huge stretching absorption at ~ 3.4 μm. Furthermore, the C-C vibration will cause some strong absorption at 6 – 8 μm and C-H in-plane deformation vibration will lead to some a series of continuous peaks at 8 – 10 μm.

![Figure 8.12](image)
8.3.2. 2,2’,4-Trichlorinated terphenyls

Aside of the 4,2’-chlorinated terphenyls, the second series of compounds we synthesized are 2,2’,4-trichlorinated terphenyls. The whole synthesis was still accomplished by two sequential Suzuki coupling reactions just by switching the boronic acid to 2,4-dichlorophenyl boronic acid in the first step (Scheme 8.3).

![Scheme 8.3 Synthesis of 2,2’,4-trichlorinated terphenyls.](image)

The DSC results are shown in Table 8.5. Compared with previous 4,2’-dichlorinated derivatives, 2,2’,4-trichlorinated terphenyls show compounds show a lower transition temperature but the nematic phase range is also much narrower.
Table 8.5 Phase transition temperature of 2,2′,4-trichlorinated terphenyls.

<table>
<thead>
<tr>
<th>Compound #.</th>
<th>Chemical structure</th>
<th>DSC (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Chemical structure 1" /></td>
<td>Cr 126 N 134 I 130 N 74 Cr</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2" alt="Chemical structure 2" /></td>
<td>Cr 120 N 127 I 125 N 60 Cr</td>
</tr>
</tbody>
</table>

8.3.3. 2′,3,4-Trichlorinated terphenyls

The 2’,3,4-Trichlorinated terphenyl liquid crystal compounds were synthesized by using the same technique as before but substituting 3,4-dichlorophenylboronic acid (Scheme 8.4).
These 2',3,4 chlorinated compounds are particularly interesting as they provide relatively low melting points (only about 40 – 60 °C above ambient) and high clear points (more than 160 °C), and thus offer a very wide (~ 100 °C) nematic phase range (Table 8.6).
Table 8.6 Phase transition temperature of 2',3,4-trichlorinated terphenyls.

<table>
<thead>
<tr>
<th>Compound #.</th>
<th>Chemical structure</th>
<th>DSC (˚C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZL06100</td>
<td>Cr 63 N 162 I 160 N</td>
</tr>
<tr>
<td>2</td>
<td>ZL06097</td>
<td>Cr 85 N 173 I 170 N</td>
</tr>
</tbody>
</table>
8.3.4. 2’,3,5-Trichlorinated terphenyls

Previously we have successfully prepared dichlorinated terphenyls with chlorine atoms at the 4,2’-positions and trichlorinated terphenyls with chlorine atoms at the 2,2’,4- positions and 2’,3,4-positions. All of these compounds show nematic phases although their transition temperatures and mesogenic phase ranges varied amongst them.

We considered if other positions of chlorine atoms might be helpful to maintain a relatively low and wide nematic phase range. To answer this question, we also synthesized some 2’,3,5-trichlorinated terphenyls.

The synthesis in this case began with 4-bromo-2-chloro-1-iodobenzene. However, the synthesis proved to be more difficult than previous discussions. It proved to be very hard to control the reaction of 3,5-dichlorophenylboronic acid to only undergo Suzuki coupling with the iodine without involving the bromine atom. Because of this, we failed to obtain the crucial intermediate 4-bromo-2,3’,5’-trichloro-1,1’-biphenyl (Scheme 8.5).

![Scheme 8.5 Failed approach to obtain 4-bromo-2,3’,5’-trichloro-1,1’-biphenyl.]

To overcome this problem, we decided to switch the starting material to 1-bromo-2-chloro-4-
iodobenzene and synthesize the whole molecule from the left side. There is a disadvantage with this route in that there is no common intermediate that can be shared and different alkyl tails must be installed at the very beginning. Due to the limitations of time, only three compounds with \( n \)-propyl, \( n \)-pentyl and trans-4-propylcyclohexyl tails were prepared (Scheme 8.6).

In any case, the final results were disappointing—these compounds just showed monotropic nematic phases. This demonstrates that the chlorine at the 4-position may be crucial to maintain the mesogenic nematic phase in this class of compounds.

Scheme 8.6 The synthesis of 2',3,5-trichlorinated terphenyls.
8.3.5. 2',3,4,5-Tetrachloro terphenyls

Using the remaining intermediates left over from the last section, we tried to react them with 3,4,5-trichlorophenylboronic acid to yield 2',3,4,5-tetrachloro terphenyls (Scheme 8.7). The DSC results here were disappointing (Table 8.7). Here, all of 8.28a – 8.28c have chlorine atoms on the 4-position, however, it seemed that none of them was able to possess nematic phase. Another interesting phenomenon involves the DSC of compound 8.28c. In the first cycle of DSC, compound 8.28c just gives an endothermic peak at 115.7 °C (Crystal to isotropic). However, the second cycle of DSC gives another endothermic peak at about 99.5 °C along with the old 115.5 °C peak. In the third cycle, the 115.5 °C endothermic peak is completely vanished and only the peak at 99.3 °C can be observed. Aside of this, another phenomenon here is that as the time passed by, the areas of all the peaks are shrinking in DSC (by comparing the DSC of the same compound in cycle 1, 2 and 3). Possibly this compound is not stable at high temperature.

Scheme 8.7 The synthesis of 2',3,4,5-tetrachlorinated terphenyls.
Table 8.7 Phase transition behavior of 2',3,4,5-tetrachlorinated terphenyls (The figures are the DSC for compound 3 (8.28c)).

<table>
<thead>
<tr>
<th>Compound #.</th>
<th>Chemical structure</th>
<th>DSC (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>![Chemical Structure 1]</td>
<td>Cr 133.2 I</td>
</tr>
<tr>
<td>2</td>
<td>![Chemical Structure 2]</td>
<td>Cr 48.8 I</td>
</tr>
<tr>
<td>3</td>
<td>![Chemical Structure 3]</td>
<td>Cr 115.7 I</td>
</tr>
</tbody>
</table>
8.3.6. Summary for the chlorinated liquid crystal project.

In this project, we have successfully prepared a number of terphenyl compounds with various locations of chlorine atoms. The 4,2’-dichlorinated compounds have been demonstrated to have excellent electrical and optical properties. The investigation of other trichlorinated compounds is still in progress. In fact, aside of the examples mentioned above, we still have plans for the investigation of other related compounds. However, some of the syntheses are more challenging (e.g. the perchloro compound). In addition, due to the limitation of time and absence of continuing grant support, this project was suspended at this point.

8.4. Aromatic ring deuterated cyanobiphenyl

Aside of the chlorinated terphenyls, another project we briefly pursued during this period was the synthesis of deuterated cyanobiphenyl as it might be a potential compound for LWIR application. The final target we pursued is the 4-cyano-4’-pentyl biphenyl with full deuterium substitution on all aromatic hydrogens and an ordinary alkyl tail (regular protio substitution). The rationale of this approach is to try to shift the C-H (aromatic ring) in-plane deformation vibration absorption out of the LWIR region (ordinarily it is located at $\sim$1250 – 1000 cm$^{-1}$, $\sim$8.0 – 10.0 $\mu$m). We only want the aromatic hydrogens to be deuterated because deuteration on alkyl chain would shift the strong 3.4 $\mu$m C-H stretching to the C-D stretching at 4.6 $\mu$m$^{10}$.

Due to the limitation of time, we just purchased the starting material perdeuteriobiphenyl from Cambridge Isotope Laboratories, Inc. It underwent Friedel-Crafts acetylation$^{18}$ smoothly with
valeryl chloride and an excess amount of anhydrous aluminum chloride in dichloromethane. The Huang modification of the traditional Wolff-Kishner reduction\textsuperscript{19} was applied to reduce the ketone to the \textit{n}-pentyl carbon chain. The bromination procedure required a relatively long time\textsuperscript{18} to accomplish and finally the bromine atom was replaced with nitrile group by using potassium cyanide catalyzed by Pd(PPh\textsubscript{3})\textsubscript{4} in dimethylacetamide\textsuperscript{20}. All the steps just described were practiced using cheap ordinary biphenyl before the deuterated series was pursued (Scheme 8.8).

\textbf{Scheme 8.8} Synthesis of aromatic deuterated 5CB

Starting from ~7.5 g of perdeuteriobiphenyl, we were able to obtain ~ 0.5 g aromatic deuterated 5CB after Kugelrohr distillation and multiple column chromatographies (Named as NEW D5CB).

The analysis done by Prof. Wu \textit{et al.} in University of Central Florida showed the transition temperature of our sample was much lower (Cr 14.96 N 22.84 I) compared with literature data\textsuperscript{21}. The MWIR shows alkyl CH stretching at ~ 3.4 μm, aromatic CD stretching at ~ 4.4 μm and C≡N stretching at ~ 4.5 μm. Although there are still about 10% of hydrogen atoms on aromatic rings
are ordinary protons, it still shows a tiny aromatic CH stretching overtone at \( \sim 5.8 \, \mu m \) (Figure 8.13).

In the LWIR range (Figure 8.14), the aromatic CD stretching overtone occurs at \( \sim 8.3 \, \mu m \). The overtone of CD out-of-plane deformation and the CH in-plane deformation absorptions are crowded at \( \sim 9.0 \, \mu m \). Compared with ordinary 5CB, the CD in-plane deformation absorption was
shifted from 7.76 μm to 10.94 μm.

Finally, NEW 5CB shows a relatively low birefringence (Figure 8.15) related to the low clearing point (according to the explanation in Dr. Wu’s PPT). The reason for the lower transition temperatures in this sample appear to be due to problems with the bromination step. The bromination of the 4-pentylbiphenyl does not occur 100% at the para- position and two minor isomers (ortho- and meta-) can also be formed (GC – MS showed that the desired para- isomer is about 90%). This mixture was carried through the final cyanation step they will yield the corresponding small amount of ortho- and meta- cyanobiphenyls, which are still impossible to be separated from our desired product. Any future synthesis in this series will have to take into account and eliminate the presence of any isomer content.
Aside of this, $^1$H-NMR shows the deuteration level of the aromatic rings is about ~90 % (by comparing the integration of aromatic region and alkyl tail) although we started from 98 % deuterated biphenyl. After examination of the $^1$H-NMR, we found that the proton content in the aromatic region had a noticeable increase after Wolff-Kishner-Huang reduction and this might due to the harsh conditions of the reduction and resulted in some C-D exchange.

![Figure 8.15](image)

*Figure 8.15* Temperature dependent birefringence of NEW D5CB (Prof. Shin-Tson Wu, University of Central Florida).
Figure 8.16 GC-MS of final product 4'-pentylyl-[1,1'-biphenyl]-4-carbonitrile-2,2',3,3',5,5',6,6'-d₈ (8.34). The major peak at t=20.60 min is the desired product, whereas the peaks at t=19.82 min and t=19.90 min might be the ortho- and meta- isomers of desired product.
As in the case of the chlorinated terphenyl project, this study of deuterated cyanobiphenyl also stopped due to time limitations and the absence of continuing grant support. If the project is resumed in the future, we need to find a better way to do the bromination and reduction in order to increase the isotopic and isomeric purities delivered by these reactions, respectively.
8.5. Experimental procedures

4-bromo-2,4’-dichloro-1,1’-biphenyl (8.3)

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-2-chloroiodobenzene (4.787 g, 15.1 mmol), 4-chlorophenylboronic acid (2.330 g, 15.0 mmol), potassium carbonate (3.103 g, 22.5 mmol), water (24 mL) and 1,4-dioxane (60 mL). The mixture was carefully degassed with nitrogen and heated up in a 100 °C oil bath. Pd(PPh₃)₄ (0.179 g, 0.15 mmol) was added and the mixture was refluxed for 12 hours under nitrogen atmosphere. After this time TLC indicated the starting material 4-bromo-2-chloroiodobenzene was still present. More 4-chlorophenylboronic acid (0.458 g, 3.0 mmol) was added and another 6 hours was given to consume the remaining 4-bromo-2-chloroiodobenzene. At this point, the mixture was cooled to room temperature and adsorbed on silica gel (~5g). After the removal of solvent, the resulting powder was placed on the top of a silica gel column to elute (eluent: hexane). Fractions containing the product were combined and concentrated to dryness, giving the final product as a white solid as (3.520 g, 11.6 mmol, 77 % yield).

Data:

$^1$H-NMR (400 MHz, CDCl₃) δ: 7.640 (d, $J = 2.0$ Hz, 1H), 7.445 (dd, $^1J = 8.0$ Hz, $^2J = 2.0$ Hz, 1H), 7.414 – 7.387 (m, 2H), 7.350 – 7.322 (m, 2H), 7.171 (d, $J = 8.0$ Hz, 1H).

$^{13}$C-NMR (100 MHz, CDCl₃) δ: 138.304, 136.656, 134.098, 133.385, 132.591, 132.192, 130.609, 130.196, 128.441, 121.775.
A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-2-chloro-1-(4-chlorophenyl)benzene (2.278 g, 7.5 mmol), 4-pentylphenylboronic acid (2.182 g, 11.3 mmol), potassium carbonate (2.102 g, 15.2 mmol), water (24 mL) and 1,4-dioxane (60 mL). The mixture was carefully degassed with nitrogen and after the mixture was warmed up in a 100 °C oil bath, Pd(PPh₃)₄ (0.179 g, 0.15 mmol) was added. This mixture was refluxed for 12 hours under nitrogen atmosphere and TLC indicated the starting material 4-bromo-2-chloro-1-(4-chlorophenyl)benzene was completely consumed. At this stage, the mixture was cooled to room temperature and mixed with silica gel (~ 5g). After the removal of solvent, the resulting powder was placed on the top of a silica gel column to elute (eluent: hexane). Fractions containing the product were combined and concentrated to dryness, giving the final product as white crystals (2.154 g, 5.8 mmol, 77 % yield).

Data:

¹H-NMR (400 MHz, CDCl₃) δ: 7.695 (d, J = 2.0 Hz, 1H), 7.526 (d, J = 8.0 Hz, 1H), 7.521 (d, J = 8.0 Hz, 2H), 7.421 (s, 4H), 7.359 (d, J = 8.0 Hz, 1H), 7.278 (d, J = 8.0 Hz, 2H), 2.656 (t, J = 8.0 Hz, 2H), 1.697 – 1.622 (m, 2H), 1.371 – 1.336 (m, 4H), 0.911 (t, J = 7.0 Hz, 3H).

¹³C-NMR (100 MHz, CDCl₃) δ: 137.583, 137.481, 136.503, 133.686, 132.674, 131.415, 130.808, 129.014, 128.328, 128.288, 126.833, 125.407, 35.575, 31.511, 31.119, 22.533, 14.019.
A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-2-chloro-1-(4-chlorophenyl)benzene (3.036 g, 10.0 mmol), 4-propylphenylboronic acid (2.468 g, 15.0 mmol), potassium carbonate (2.806 g, 20.3 mmol), water (36 mL) and 1,4-dioxane (90 mL). The flask with the mixture was carefully degassed with nitrogen. After the mixture was warmed up in a 100 °C oil bath, Pd(PPh₃)₄ (0.117 g, 0.10 mmol) was added inside the mixture at last. This mixture was refluxed for 12 hours under nitrogen atmosphere and TLC indicated the starting material 4-bromo-2-chloro-1-(4-chlorophenyl)benzene was completely consumed. At this point, the mixture was cooled to room temperature and mixed well with silica gel (~ 5g). After the removal of solvent, the resulting powder was placed on the top of a silica gel column to elute (eluent: hexane). Fractions containing the product were combined and concentrated to dryness, giving white crystals as final product (2.274 g, 6.7 mmol, 67 % yield).

Data:

\[ ^1H\text{-NMR (400 MHz, CDCl}_3) \delta: 7.695 (d, J = 2.0 Hz, 1H), 7.533 – 7.506 (m, 3H), 7.418 (s, 4H), 7.356 (d, J = 8.0 Hz, 1H), 7.275 (d, J = 8.0 Hz, 2H), 2.641 (t, J = 7.6 Hz, 2H), 1.734 – 1.641 (m, 2H), 0.979 (t, J = 7.2 Hz, 3H). \]

\[ ^13C\text{-NMR (100 MHz, CDCl}_3) \delta: 142.634, 141.965, 137.499, 137.389, 136.455, 133.597, 132.588, 131.327, 130.718, 128.985, 128.239, 128.198, 126.730, 125.317, 37.586, 24.411, 13.756. \]
1-bromo-4-heptylbenzene (8.11)

\[
\begin{align*}
C_7H_{15} & - & \text{Br} \\
\text{Chemical Formula: } & C_{13}H_{19}Br \\
\text{Molecular Weight: } & 255.20
\end{align*}
\]

In a 250 ml beaker \(n\)-heptylbenzene (5.286 gm, 30.0 mmol) was adsorbed on neutral alumina (15 gm). In another 250 ml beaker bromine (1.6 mL, 30.0 mmol) was also adsorbed on neutral alumina (15 gm). The two components were mixed together and stirred with magnetic star for 1 minute then the color of bromine disappeared. The powder placed inside a sintered glass funnel and the product was eluted with DCM. The filtrate was collected and the solvent was removed under reduced pressure to obtain a light yellow oil as final product (6.274 g, 82 % yield).

According to GC –MS, the ratio of \(para:ortho\)-isomers is about 4:1.
(4-n-heptylphenyl)boronic acid (8.12)

\[
\text{C}_7\text{H}_{15} - \text{B(OH)}_2
\]

Chemical Formula: \(\text{C}_{13}\text{H}_{21}\text{BO}_2\)
Molecular Weight: 220.12

A 250 ml two-necked round bottom flask was charged with 1-bromo-4-n-heptylbenzene (6.274 g, 24.6 mmol, a mixture of \textit{para}- and \textit{ortho}- isomers). Then dry THF (90 ml) was added under a nitrogen atmosphere and the temperature of the mixture was cooled to -78 °C. In this mixture \(n\)-BuLi (20 ml, 1.6 M in hexanes) was added dropwise and the mixture was stirred for another one hour after the addition was complete. Then triisopropyl borate (6.918 g, 36.8 mmol) was added inside and the mixture was allowed to warm up to room temperature. At last, hydrochloric acid (3 M, 50 mL) was added to do the hydrolysis. The mixture was then extracted with diethyl ether (100 mL x 3) and the organic layers were combined any dried with anhydrous MgSO\(_4\). The solvent was removed under reduced pressure and small amount of hexanes (~ 5 mL) was added to precipitate the white solid, which was suction filtrated and air-dried (2.862 g, 13.0 mmol, 52 % yield).

\textbf{Note:} The NMR indicated that this product is a mixture of \textit{para}- and \textit{ortho}- isomers. However, it was used directly and the product of next step seems to be pure.

\(^1\text{H-NMR (400 MHz, DMSO)} \delta:\ 7.690 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, 7.140 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, 2.556 \text{ (t, } J = 7.6 \text{ Hz, 2H)}, 1.570 – 1.535 \text{ (m, 2H)}, 1.281 – 1.242 \text{ (m, 8H)}, 0.856 \text{ (t, } J = 7.0 \text{ Hz, 3H)}
A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-2-chloro-1-(4-chlorophenyl)benzene (2.270 g, 7.5 mmol), 4-heptylphenylboronic acid (2.211 g, 10.0 mmol), potassium carbonate (1.402 g, 10.0 mmol), water (25 mL) and 1,4-dioxane (60 mL). The mixture was carefully degassed with nitrogen and after the mixture was warmed up in a 100 °C oil bath, Pd(PPh₃)₄ (0.088 g, 0.075 mmol) was added. This mixture was refluxed for 6 hours under a nitrogen atmosphere and TLC indicated the starting material 4-bromo-2-chloro-1-(4-chlorophenyl)benzene was completely consumed. At this stage, the mixture was cooled to room temperature and silica gel (~ 5g) was added. After the removal of solvent, the resulting powder was placed on the top of a silica gel column to elute (eluent: hexane). Fractions containing the product were combined and concentrated to dryness, giving white crystals as final product (2.154 g, 6.1 mmol, 81 % yield).

Data:

¹H-NMR (400 MHz, CDCl₃) δ: 7.692 (d, J = 2.0 Hz, 1H), 7.531 – 7.506 (m, 3H), 7.417 (s, 4H), 7.353 (d, J = 8.0 Hz, 1H), 7.272 (d, J = 8.0 Hz, 2H), 2.653 (t, J = 8.0 Hz, 2H), 1.688 – 1.614 (m, 2H), 1.357 – 1.277 (m, 8H), 0.889 (t, J = 7.0 Hz, 3H).

(4-((1S,4R)-4-pentylcyclohexyl)phenyl)boronic acid (8.9)

\[
\text{C}_5\text{H}_{11}\text{B} (\text{OH})_2
\]

Chemical Formula: C_{17}H_{27}BO_2  
Molecular Weight: 274.21

A 250 ml two-necked round bottom flask was charged with 1-bromo-4-(trans-4-pentylcyclohexyl)benzene (4.659 g, 15.0 mmol). Then dry THF (100 ml) was added inside under a nitrogen atmosphere and the temperature of the mixture was cooled to -78 °C. In this mixture, n-BuLi (15 ml, 1.6 M in hexanes) was added dropwise and the mixture was stirred for another one
hour after the addition was complete. Then triisopropyl borate (5.702 g, 30 mmol) was added inside and the mixture was allowed to warm up to room temperature. Next, pre-diluted hydrochloric acid (3 M, 50 mL) was added to perform the hydrolysis. The mixture was then extracted with ethyl ether (100 mL x 3) and the organic layers were combined. After drying with anhydrous MgSO₄, the solvent was removed under reduced pressure and a small amount of hexanes (~ 5 mL) was added to precipitate the white solid, which was suction filtrated and air-dried (3.181 g, 11.6 mmol, 77 % yield).

Data:

**M.P.:** 128.0 – 132.0 °C.

**¹H-NMR (400 MHz, DMSO) δ:** 7.691 (d, J = 8.0 Hz, 2H), 7.165 (d, J = 8.0 Hz, 2H), 2.435 (t, J = 12.0 Hz, 1H), 1.794 (t, J = 12.0 Hz, 4H), 1.471 – 1.377 (m, 2H), 1.296 – 1.202 (m, 9H), 1.062 – 1.004 (m, 2H), 0.869 (t, J = 6.8 Hz, 3H).

**¹³C-NMR (100 MHz, DMSO) δ:** 149.152, 134.111, 131.284, 125.648, 43.681, 36.789, 36.567, 33.640, 32.995, 31.544, 25.964, 22.053, 13.870.

**2',4-dichloro-4''-((Is,4r)-4-pentylcyclohexyl)-1,1':4',1''-terphenyl (8.5e)**

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-2-chloro-1-(4-chlorophenyl)benzene (2.263 g, 7.5 mmol), 4-(trans-4-pentylcyclohexyl)phenylboronic acid (2.751 g, 10.0 mmol), potassium carbonate (1.401 g, 10.0 mmol), water (25 mL) and 1,4-dioxane
(60 mL). The mixture was carefully degassed with nitrogen and after the mixture was warmed up in a 100 °C oil bath, Pd(PPh₃)₄ (0.090 g, 0.075 mmol) was added. This mixture was refluxed for 6 hours under nitrogen atmosphere and TLC indicated the starting material 4-bromo-2-chloro-1-(4-chlorophenyl)benzene was completely consumed. At this stage, the mixture was cooled to room temperature and mixed with silica gel (~ 5g). After the removal of solvent, the resulting powder was placed on the top of a silica gel column to elute (eluent: hexane). Fractions containing the product were combined and concentrated to dryness, giving white crystals as final product (2.865 g, 6.3 mmol, 84 % yield).

Data:

¹H-NMR (400 MHz, CDCl₃) δ: 7.690 (d, J = 1.6 Hz, 1H), 7.542 – 7.509 (m, 3H), 7.421 (br, 4H), 7.357 (d, J = 8.0 Hz, 1H), 7.309 (d, J = 8.0 Hz, 2H), 2.524 (t, J = 12.0 Hz, 1H), 1.914 (t, J = 12.0 Hz, 4H), 1.543 – 1.448 (m, 2H), 1.335 – 1.244 (m, 9H), 1.115 – 1.057 (m, 2H), 0.903 (t, J = 7.0 Hz, 3H).

¹³C-NMR (100 MHz, CDCl₃) δ: 147.972, 142.100, 137.611, 137.528, 136.733, 133.721, 132.702, 131.446, 130.848, 128.385, 128.323, 127.494, 126.923, 125.460, 44.351, 37.391, 37.324, 34.332, 33.592, 32.232, 26.675, 22.742, 14.145.
4-bromo-2,2',4'-trichloro-1,1'-biphenyl (8.14)

Chemical Formula: C_{12}H_6BrCl_3
Molecular Weight: 336.43

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-2-chloroiodobenzene (6.404 g, 20.0 mmol), 2,4-dichlorophenylboronic acid (4.583 g, 24.0 mmol), potassium carbonate (4.142 g, 30.0 mmol) water (20 mL) and 1,4-dioxane (50 mL). The mixture
was flushed with nitrogen and warmed up in a 100 °C oil bath and Pd(PPh₃)₄ (0.233 g, 0.20 mmol) was added. This mixture was then refluxed for 12 hours under nitrogen atmosphere and at that time TLC indicated the starting material 4-bromo-2-chloroiodobenzene was completely consumed. At this stage, the mixture was cooled to room temperature and mixed with silica gel (~ 10g). After the removal of solvent, the obtained powder was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and concentrated to dryness, giving the product as a colorless oil (4.117 g, 12.2 mmol, 61 % yield).

Data:

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.655 (d, \(J = 2.0\) Hz, 1H), 7.501 (d, \(J = 2.0\) Hz, 1H), 7.463 (dd, \(J = 8.4\) Hz, \(J = 2.0\) Hz, 1H), 7.312 (dd, \(J = 8.4\) Hz, \(J = 2.0\) Hz, 1H), 7.172 (d, \(J = 8.4\) Hz, 1H), 7.110 (d, \(J = 8.4\) Hz, 1H).

\(^13\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\): 136.247, 135.794, 134.871, 134.553, 134.272, 132.271, 132.230, 131.864, 129.976, 129.505, 127.066, 122.596.

2,2',4-trichloro-4''-((1s,4r)-4-propylcyclohexyl)-1,1':4',1''-terphenyl (8.15)

\[\text{C}_3\text{H}_7\text{Cl}_{11}\]

Chemical Formula: C\(_{27}\)H\(_{27}\)Cl\(_3\)
Molecular Weight: 457.86

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-2,2',4'-trichloro-1,1'-biphenyl (1.708 g, 5.1 mmol), 4-(trans-4-propylcyclohexyl)phenylboronic acid (1.853 g, 7.5 mmol), potassium carbonate (1.382 g, 10.0 mmol), 1,4-dioxane and water (50:20
mL). The flask with the mixture was flushed with nitrogen and after the mixture was warmed up in a 100 °C oil bath, Pd(PPh₃)₄ (0.059 g, 0.05 mmol) was added inside to catalyze the reaction. This mixture was refluxed for 6 hours under nitrogen protection and TLC analysis showed the starting material 4-bromo-2,2',4'-trichloro-1,1'-biphenyl was completely consumed. At this stage, the mixture was cooled and mixed with silica gel (~ 5g) at room temperature. After the removal of solvent, the resulting powder was placed on the top of a silica gel column to elute (eluent: hexane). Fractions containing the product were combined and concentrated to dryness, giving white crystals (2.199 g, 4.8 mmol, 94 % yield), which was purified via recrystallized from iso-octane (1.856 g).

Data:

$^{1}H$-NMR (400 MHz, CDCl₃) δ: 7.692 (d, $J = 1.6$ Hz, 1H), 7.547 – 7.510 (m, 4H), 7.337 – 7.250 (m, 5H), 2.523 (tt, $^{1}J = 12.0$ Hz, $^{2}J = 3.2$ Hz, 1H), 1.913 (t, $J = 12.0$ Hz, 4H), 1.528 – 1.473 (m, 2H), 1.375 – 1.336 (m, 2H), 1.257 – 1.092 (m, 4H), 0.913 (t, $J = 7.4$ Hz, 3H).

2,2',4-trichloro-4''-((Is,4r)-4-pentylecyclohexyl)-1,1':4',1''-terphenyl (8.16)

\[ \text{Chemical Formula: } \text{C}_{29}\text{H}_{31}\text{Cl}_3 \]

\[ \text{Molecular Weight: 485.92} \]

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-2,2',4'-trichloro-1,1'-biphenyl (1.725 g, 5.1 mmol), 4-(trans-4-pentylecyclohexyl)phenylboronic acid (2.075 g, 7.5 mmol), potassium carbonate (1.405 g, 10.0 mmol), water (20 mL) and 1,4-dioxane
(50 mL). The flask with the mixture was flushed with nitrogen and after the mixture was warmed up to 100 °C, Pd(PPh₃)₄ (0.061 g, 0.05 mmol) was added. This mixture was refluxed for 6 hours under nitrogen atmosphere and TLC indicated the starting material 4-bromo-2,2',4'-trichloro-1,1'-biphenyl was completely consumed. At this stage, the mixture was cooled to room temperature and mixed with silica gel (~ 5g). After the removal of solvent by rotary evaporation, the resulting powder was placed on the top of a silica gel column to elute (eluent: hexane). Fractions containing the product were combined and concentrated to dryness, giving white crystals (1.936 g, 4.0 mmol, 78 % yield), which were further purified by recrystallization from iso-octane (1.889 g).

Data:

\(^1\)H-NMR (400 MHz, CDCl₃) δ: 7.693 (d, \(J = 2.0\) Hz, 1H), 7.550 – 7.513 (m, 4H), 7.340 – 7.239 (m, 5H), 2.517 (tt, \(^1\)J = 12.0 Hz, \(^2\)J = 3.2 Hz, 1H), 1.916 (t, \(J = 12.0\) Hz, 4H), 1.536 – 1.473 (m, 2H), 1.335 – 1.244 (m, 8H), 1.117 – 1.057 (m, 2H), 0.903 (t, \(J = 7.0\) Hz, 3H).

4-bromo-2,3',4'-trichloro-1,1'-biphenyl (8.18)

\[
\text{Chemical Formula: } C_{12}H_8BrCl_3 \\
\text{Molecular Weight: } 336.43
\]

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-2-chloroiodobenzene (11.163 g, 35 mmol), 2,4-dichlorophenylboronic acid (8.303 g, 43 mmol), potassium carbonate (9.671 g, 70 mmol) 1,4-dioxane and water (100:40 mL). The mixture was then flushed with nitrogen and warmed up in a 100 °C and Pd(PPh₃)₂Cl₂ (0.131 g, 0.18 mmol,
0.5 \%) was added. This mixture was gently refluxed for 12 hours under nitrogen atmosphere and at that time TLC indicated the starting material 4-bromo-2-chloroiodobenzene was nearly completely consumed. At this stage, the mixture was cooled to room temperature and mixed with silica gel. After the removal of solvent by rotary evaporation, the powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and concentrated to dryness, giving the product as white crystals (7.116 g, 21.2 mmol, 61 \% yield).

Data:

\textbf{M.P.:} 121.0 – 123.0 °C.

\textbf{\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\):} 7.654 (d, \(J = 2.0\) Hz, 1H), 7.508 (d, \(J = 5.2\) Hz, 1H), 7.495 (d, \(J = 0.8\) Hz, 1H), 7.464 (d, \(J = 8.0\) Hz, \(J = 2.0\) Hz, 1H), 7.250 (d, \(J = 8.0\) Hz, \(J = 2.0\) Hz, 1H), 7.172 (d, \(J = 8.4\) Hz, 1H).

\textbf{\textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\):} 138.113, 137.122, 133.351, 132.736, 132.428, 132.360, 132.062, 131.164, 130.340, 130.220, 128.694, 122.337.

\textbf{2',3,4-trichloro-4''-((1s,4r)-4-pentyloxyhexyl)-1,1':4',1''-terphenyl (8.20)}

![Chemical structure of 2',3,4-trichloro-4''-((1s,4r)-4-pentyloxyhexyl)-1,1':4',1''-terphenyl]

Chemical Formula: \(C_{29}H_{31}Cl_3\)

Molecular Weight: 485.92

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-2,3',4'-trichloro-1,1'-biphenyl (2.022 g, 6.0 mmol), 4-(\textit{trans}-4-pentyloxyhexyl)phenylboronic acid (2.062 g, 7.5 mmol), potassium carbonate (1.701 g, 12.3 mmol), water (20 mL) and 1,4-dioxane
(50 mL). The flask with the mixture was flushed with nitrogen. After the mixture was warmed up in a 100 °C oil bath, Pd(PPh3)2Cl2 (0.045 g, 0.064 mmol) was added inside at last. This mixture was refluxed for 6 hours under nitrogen atmosphere and TLC indicated the starting material 4-bromo-2,3',4'-trichloro-1,1'-biphenyl was completely consumed. At this stage, the mixture was cooled to room temperature and mixed with silica gel (~ 5g). After the removal of solvent, the resulting powder was placed on the top of a silica gel column to elute (eluent: hexane). Fractions containing the product were combined and concentrated to dryness, giving white crystals (2.395 g, 4.9 mmol, 82 % yield), which was recrystallized from iso-octane (2.174 g).

Data:

\[ ^1H\text{-NMR (400 MHz, CDCl}_3\text{)}\ \delta: 7.692 (d, J = 2.0 Hz, 1H), 7.580 (d, J = 2.0 Hz, 1H), 7.357 – 7.500 (m, 4H), 7.354 – 7.299 (m, 4H), 2.525 (tt, J = 12.4 Hz, J = 3.0 Hz, 1H), 1.913 (t, J = 12.4 Hz, 4H), 1.524 – 1.447 (m, 2H), 1.352 – 1.227 (m, 9H), 1.116 – 1.060 (m, 2H), 0.906 (t, J = 6.6 Hz, 3H). \]

\[ ^13C\text{-NMR (100 MHz, CDCl}_3\text{)}\ \delta: 148.109, 142.556, 139.000, 136.552, 136.378, 132.636, 132.234, 131.903, 131.378, 131.310, 130.064, 128.930, 128.449, 127.516, 126.926, 125.530, 44.354, 37.383, 37.325, 34.325, 33.585, 32.228, 26.667, 22.733, 14.130. \]
A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-2,3',4'-trichloro-1,1'-biphenyl (2.018 g, 6.0 mmol), 4-(trans-4-propylcyclohexyl)phenylboronic acid (1.824 g, 7.5 mmol), potassium carbonate (1.703 g, 12.3 mmol), water (20 mL) and 1,4-dioxane (50 mL). The flask with the mixture was flushed with nitrogen. After the mixture was warmed up
in a 100 °C oil bath, Pd(PPh₃)₂Cl₂ (0.046 g, 0.066 mmol) was added at last. This mixture was gently refluxed for 6 hours under nitrogen atmosphere and TLC indicated the starting material 4-bromo-2,3',4'-trichloro-1,1'-biphenyl was completely consumed. At this stage, the mixture was cooled to room temperature and mixed with silica gel (~ 5g). After the removal of solvent, the resulting powder was placed on the top of a silica gel column to elute (eluent: hexane). Fractions containing the product were combined and concentrated to dryness, giving white crystals (2.658 g, 5.8 mmol, 97 % yield), which was recrystallized from iso-octane (2.456 g).

Data:

¹H-NMR (400 MHz, CDCl₃) δ: 7.690 (d, J = 2.0 Hz, 1H), 7.578 (d, J = 2.0 Hz, 1H), 7.535 – 7.498 (m, 4H), 7.352 – 7.298 (m, 4H), 2.523 (tt, ³J = 12.2 Hz, ²J = 3.0 Hz, 1H), 1.911 (t, J = 13.6 Hz, 4H), 1.522 – 1.472 (m, 2H), 1.374 – 1.335 (m, 3H), 1.257 – 1.217 (m, 2H), 1.091 – 1.062 (m, 2H), 0.913 (t, J = 7.4 Hz, 3H).

4-bromo-3-chloro-4'-propyl-1,1'-biphenyl (8.25a)

\[
\begin{align*}
\text{C}_3\text{H}_7 & \quad \begin{array}{c}
\text{Cl} \\
\text{Br}
\end{array} \\
\text{Chemical Formula: } & \ C_{15}H_{14}BrCl \\
\text{Molecular Weight: } & \ 309.63
\end{align*}
\]

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 1-bromo-2-chloro-4-iodobenzene (2.401 g, 7.5 mmol), 4-propylphenylboronic acid (1.401 g, 8.5 mmol), potassium carbonate (2.079 g, 15.0 mmol) 1,4-dioxane and water (50:20 mL). The flask with the mixture was
well flushed with nitrogen and then warmed up in a 100 °C. Pd(PPh$_3$)$_2$Cl$_2$ (0.059 g, 0.08 mmol, 1 %) was added at this moment. This mixture was gently refluxed for 6 hours under nitrogen atmosphere and at that time TLC indicated the starting material 1-bromo-2-chloro-4-iodobenzene was nearly completely consumed. At this stage, the mixture was cooled to room temperature and mixed with silica gel (~ 5g). After the removal of organic solvent and water residue by rotary evaporation, the powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and concentrated to dryness, giving colorless oil (1.917 g, 6.2 mmol, 83 % yield) as final product.

Data:

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.653 (d, $J = 2.0$ Hz, 1H), 7.633 (d, $J = 8.4$ Hz, 1H), 7.456 – 7.431 (m, 2H), 7.310 (dd, $^1J = 8.4$ Hz, $^2J = 2.0$ Hz, 1H), 7.251 (d, $J = 8.0$ Hz, 2H), 2.623 (t, $J = 7.6$ Hz, 2H), 1.716 – 1.623 (m, 2H), 0.964 (t, $J = 7.4$ Hz, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 142.932, 141.925, 136.108, 134.728, 133.875, 129.139, 128.669, 126.728, 126.370, 120.831, 37.682, 24.488, 13.836.

4-bromo-3-chloro-4'-penty1-1,1'-biphenyl (8.25b)

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 1-bromo-2-chloro-4-iodobenzene (2.405 g, 7.5 mmol), 4-propylphenylboronic acid (1.451 g, 7.5 mmol), potassium carbonate (2.107 g, 15.0 mmol) 1,4-dioxane and water (50:20 mL). The flask with the mixture was
well flushed with nitrogen and then warmed up in a 100 °C. Pd(PPh)\textsubscript{3}\textsubscript{2}Cl\textsubscript{2} (0.055 g, 0.08 mmol, 1 \%) was added at this moment. This mixture was gently refluxed for 6 hours under nitrogen atmosphere and at that time TLC indicated the starting material 1-bromo-2-chloro-4-iodobenzene was nearly completely consumed. At this stage, the mixture was cooled to room temperature and mixed with silica gel (∼ 5g). After the removal of organic solvent and water residue by rotary evaporation, the powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and concentrated to dryness, giving colorless oil (2.153 g, 6.4 mmol, 85 \% yield) as final product.

Data:

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) δ: 7.646 (d, \textit{J} = 2.0 Hz, 1H), 7.622 (d, \textit{J} = 8.4 Hz, 1H), 7.446 – 7.425 (m, 2H), 7.250 (dd, \textit{J} = 8.4 Hz, \textit{J} = 2.0 Hz, 1H), 2.630 (t, \textit{J} = 7.6 Hz, 2H), 1.675 – 1.599 (m, 2H), 1.354 – 1.318 (m, 4H), 0.900 (t, \textit{J} = 7.0 Hz, 3H).

\textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}) δ: 143.196, 141.921, 136.054, 134.722, 133.865, 129.074, 128.658, 126.733, 126.359, 120.819, 35.578, 31.506, 31.095, 22.545, 14.030.

2',3,5-trichloro-4''-propyl-1,1':4',1''-terphenyl (8.26a)

![Chemical Structure](image)

Chemical Formula: C\textsubscript{21}H\textsubscript{17}Cl\textsubscript{3}
Molecular Weight: 375.72

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-3-chloro-4'-propyl-1,1'-biphenyl (1.795 g, 5.8 mmol), 3,5-dichlorophenylboronic acid (1.389 g, 7.3 mmol),
potassium carbonate (1.609 g, 11.6 mmol) 1,4-dioxane and water (50:20 mL). The flask with the mixture was well flushed with nitrogen and then warmed up in a 100 °C. Pd(PPh$_3$)$_2$Cl$_2$ (0.041 g, 0.06 mmol, 1 %) was added at this moment. This mixture was kept at 100 °C to make gently refluxed for 6 hours under nitrogen atmosphere. At that time, TLC indicated the starting material biphenyl was nearly completely consumed. The mixture was then cooled to room temperature and mixed with silica gel (~ 5g). After the removal of organic solvent and water residue by rotary evaporation, the powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and concentrated to dryness, giving colorless oil (1.937 g, 5.2 mmol, 89 % yield) as final product.

Data:

$^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.697 (d, $J = 1.6$ Hz, 1H), 7.543 – 7.508 (m, 3H), 7.391 – 7.369 (m, 3H), 7.343 (d, $J = 8.0$ Hz, 1H), 7.280 (d, $J = 8.4$ Hz, 1H), 2.645 (t, $J = 7.6$ Hz, 2H), 1.736 – 1.642 (m, 2H), 0.979 (t, $J = 7.2$ Hz, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 142.963, 142.774, 141.892, 136.362, 136.173, 134.609, 132.608, 131.292, 129.149, 128.451, 128.038, 127.705, 126.881, 125.523, 37.711, 24.516, 13.859.
A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-3-chloro-4'-pentyl-1,1'-biphenyl (2.003 g, 5.9 mmol), 3,5-dichlorophenylboronic acid (1.415 g, 7.4 mmol), potassium carbonate (1.706 g, 12.4 mmol) 1,4-dioxane and water (50:20 mL). The flask with the mixture was well flushed with nitrogen and then warmed up in a 100 °C. Pd(PPh$_3$)$_2$Cl$_2$ (0.043 g,
0.06 mmol, 1 %) was added at this moment. This mixture was kept at 100 °C to make gently refluxed for 6 hours under nitrogen atmosphere. At that time, TLC indicated the starting material biphenyl was nearly completely consumed. The mixture was then cooled to room temperature and mixed with silica gel (~ 5 g). After the removal of organic solvent and water residue by rotary evaporation, the powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and concentrated to dryness, giving colorless oil (1.881 g, 4.7 mmol, 80 % yield).

Data:

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.697 (d, \(J = 1.6 \text{ Hz}, 1\)H), 7.543 – 7.502 (m, 3H), 7.392 – 7.369 (m, 3H), 7.343 (d, \(J = 8.0 \text{ Hz}, 1\)H), 7.280 (d, \(J = 8.4 \text{ Hz}, 1\)H), 2.658 (t, \(J = 7.8 \text{ Hz}, 2\)H), 1.697 – 1.622 (m, 2H), 1.372 – 1.336 (m, 4H), 0.919 (t, \(J = 7.2 \text{ Hz}, 3\)H).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\): 142.781, 141.897, 136.320, 136.170, 134.612, 132.608, 131.294, 129.093, 128.451, 128.042, 127.707, 126.898, 125.524, 35.613, 31.537, 31.133, 22.563, 14.044.
4-bromo-3-chloro-4'-(1s,4r)-4-propylcyclohexyl)-1,1'-biphenyl (8.25c)

Chemical Formula: C_{21}H_{24}BrCl
Molecular Weight: 391.78

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 1-bromo-2-chloro-4-iodobenzene (2.401 g, 7.5 mmol), 4-(trans-4-propylcyclohexyl)phenylboronic acid (1.901 g, 7.7 mmol), potassium carbonate (2.091 g, 15.0 mmol) 1,4-dioxane and water (50:20 mL). The flask with the mixture was well flushed with nitrogen and then warmed up in a 100 °C. Pd(PPh$_3$)$_2$Cl$_2$
(0.055 g, 0.08 mmol, 1 %) was added inside at this moment. This mixture was gently refluxed for 6 hours under nitrogen atmosphere and at that time TLC indicated the starting material 1-bromo-2-chloro-4-iodobenzene was nearly completely consumed. At this stage, the mixture was cooled to room temperature and mixed with silica gel (~ 5g). After the removal of organic solvent and water residue by rotary evaporation, the powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and concentrated to dryness, giving colorless crystals after cooling (2.660 g, 6.8 mmol, 90 % yield) as product.

Data:

M.P.: 75.5 – 78.5 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.650 (d, $J = 1.6$ Hz, 1H), 7.630 (d, $J = 8.4$ Hz, 1H), 7.454 (d, $J = 8.0$ Hz, 1H), 7.320 – 7.267 (m, 3H), 2.502 (tt, $^1J = 12.0$ Hz, $^2J = 3.2$ Hz, 1H), 1.924 – 1.857 (m, 4H), 1.522 – 1.451 (m, 2H), 1.367 – 1.328 (m, 3H), 1.248 – 1.208 (m, 2H), 1.079 – 1.049 (m, 2H), 0.907 (t, $J = 7.2$ Hz, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 148.135, 141.915, 136.232, 134.712, 133.863, 128.669, 127.514, 126.784, 126.370, 120.818, 44.322, 39.701, 37.709, 34.283, 33.521, 20.034, 14.413.

$^{2',3,5}$-trichloro-4''-((1s,4r)-4-propylcyclohexyl)-1,1':4',1''-terphenyl (8.26c)

![Chemical Structure](image)

Chemical Formula: C$_{27}$H$_{27}$Cl$_3$
Molecular Weight: 457.86
A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-3-chloro-4'-(1s,4r)-4-propylcyclohexyl)-1,1'-biphenyl (1.961 g, 5.0 mmol), 3,5-dichlorophenylboronic acid (1.436 g, 7.5 mmol), potassium carbonate (1.392 g, 10.0 mmol) 1,4-dioxane and water (50:20 mL). The flask with the mixture was well flushed with nitrogen and then warmed up in a 100 °C. Pd(PPh$_3$)$_2$Cl$_2$ (0.035 g, 0.05 mmol, 1 %) was added inside at this moment. This mixture was kept at 100 °C to make gently refluxed for 6 hours under nitrogen atmosphere. At that time, TLC indicated the starting material biphenyl was nearly completely consumed. The mixture was then cooled to room temperature and mixed with silica gel (~ 5g). After the removal of organic solvent and water residue by rotary evaporation, the powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and concentrated to dryness, giving white crystals (2.033 g, 4.4 mmol, 88 % yield) as final product.

**Data:**

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.692 (d, $J = 1.6$ Hz, 1H), 7.527 (d, $J = 8.0$ Hz, 3H), 7.391 – 7.369 (m, 3H), 7.339 (d, $J = 8.0$ Hz, 1H), 7.311 (d, $J = 8.0$ Hz, 2H), 2.525 (tt, $^1J = 12.0$ Hz, $^2J = 3.0$ Hz, 1H), 1.953 – 1.871 (m, 4H), 1.528 – 1.473 (m, 2H), 1.375 – 1.336 (m, 3H), 1.258 – 1.218 (m, 2H), 1.093 – 1.085 (m, 2H), 0.913 (t, $J = 7.2$ Hz, 3H).

2',3,4,5-tetrachloro-4''-propyl-1,1':4',1''-terphenyl (8.28a)

\[
\begin{align*}
\text{C}_3\text{H}_7 & - \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array} & - \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\end{align*}
\]

Chemical Formula: C\text{21}H\text{16}Cl\text{4}

Molecular Weight: 410.16

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-3-chloro-4'-propyl-1,1'-biphenyl (2.342 g, 7.5 mmol), 3,4,5-trichlorophenylboronic acid (1.691 g, 7.5 mmol), potassium carbonate (2.065 g, 15 mmol), 1,4-dioxane and water (25:10 mL). The flask
with the mixture was well flushed with nitrogen and then warmed up in a 100 °C. Pd(PPh$_3$)$_2$Cl$_2$ (0.051 g, 0.07 mmol, 1 %) was added inside at this moment. This mixture was kept at 100 °C to make gently refluxed for 12 hours under nitrogen atmosphere. At that time, TLC indicated the starting material biphenyl was nearly consumed. The mixture was cooled to room temperature and then mixed with silica gel (~ 10 g). After the removal of organic solvent and water residue by rotary evaporation, the powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and concentrated to dryness, giving colorless oil (1.891 g, 4.6 mmol, 61 % yield). This colorless oil took a long time (~ 3-5 days) to crystallize and form the final product.

Data:

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.697 (d, $J$ = 1.6 Hz, 1H), 7.544 – 7.503 (m, 5H), 7.335 (d, $J$ = 8.0 Hz, 1H), 7.280 (d, $J$ = 8.0 Hz, 2H), 2.643 (t, $J$ = 7.8 Hz, 2H), 1.733 – 1.640 (m, 2H), 0.978 (t, $J$ = 7.4 Hz, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 143.040, 142.961, 138.958, 136.225, 135.322, 133.829, 132.566, 131.193, 130.735, 129.676, 129.161, 128.498, 127.075, 126.866, 125.599, 37.700, 24.518, 13.858.
A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-3-chloro-4'-pentyl-1,1'-biphenyl (1.359 g, 4.0 mmol), 3,4,5-trichlorophenylboronic acid (0.898 g, 4.0 mmol), potassium carbonate (1.112 g, 8.0 mmol) 1,4-dioxane and water (25:10 mL). The flask with the mixture was well flushed with nitrogen and then warmed up in a 100 °C. Pd(PPh₃)₄ (0.049 g, 0.04
mmol, 1 %) was added inside at this moment. This mixture was kept at 100 °C to make gently refluxed for 12 hours under nitrogen atmosphere. At that time, TLC indicated the starting material biphenyl was nearly consumed. The mixture was then cooled to room temperature and mixed with silica gel (~ 5g). After the removal of organic solvent and water residue by rotary evaporation, the powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and concentrated to dryness, giving colorless oil (1.253 g, 2.9 mmol, 72 % yield), which took a long time (~ 3-5 days) to crystallize.

Data:

\(^1\text{H-NMR (400 MHz, CDCl}_3\) \(\delta\): 7.699 (d, \(J = 1.6\) Hz, 1H), 7.548 – 7.503 (m, 5H), 7.340 (d, \(J = 8.0\) Hz, 1H), 7.282 (d, \(J = 8.0\) Hz, 2H), 2.658 (t, \(J = 5.6\) Hz, 2H), 1.397 – 1.622 (m, 2H), 1.371 – 1.335 (m, 4H), 0.911 (t, \(J = 7.0\) Hz, 3H).

\(^{13}\text{C-NMR (100 MHz, CDCl}_3\) \(\delta\): 143.325, 142.990, 138.983, 136.214, 135.343, 133.847, 132.585, 131.199, 130.751, 129.690, 129.111, 128.512, 126.892, 126.750, 125.610, 35.610, 31.531, 31.127, 22.559, 14.040.
2',3,4,5-tetrachloro-4''-((1s,4r)-4-propylcyclohexyl)-1,1'-4',1''-terphenyl (8.28c)

\[
\text{C}_3\text{H}_7\text{C}_9\text{H}_6\text{Cl}_4
\]

Chemical Formula: \(\text{C}_{27}\text{H}_{26}\text{Cl}_4\)
Molecular Weight: 492.31

A 250 mL two-neck round bottom flask with magnetic stir bar was charged with 4-bromo-3-chloro-4'-(1s,4r)-4-propylcyclohexyl)-1,1'-biphenyl (1.567 g, 4.0 mmol), 3,4,5-trichlorophenylboronic acid (0.901 g, 4.0 mmol), potassium carbonate (1.109 g, 8.0 mmol) 1,4-dioxane and water (25:10
mL). The flask with the mixture was well flushed with nitrogen and then warmed up in a 100 °C. Pd(PPh₃)₄ (0.049 g, 0.04 mmol, 1 %) was added inside at this moment. This mixture was kept at 100 °C to make gently refluxed for 12 hours under nitrogen atmosphere. At that time, TLC indicated the starting material biphenyl was nearly completely consumed. The mixture was then cooled to room temperature and mixed with silica gel (~5g). After the removal of organic solvent and water residue by rotary evaporation, the powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and concentrated to dryness, giving white crystals (1.435 g, 2.9 mmol, 73 % yield) as final product.

**Data:**

**¹H-NMR (400 MHz, CDCl₃) δ:** 7.693 (d, J = 2.0 Hz, 1H), 7.542 – 7.514 (m, 5H), 7.344 – 7.301 (m, 3H), 2.525 (tt, ¹J = 12.0 Hz, ²J = 3.0 Hz, 1H), 1.945 – 1.877 (m, 4H), 1.544 – 1.446 (m, 2H), 1.371 – 1.335 (m, 3H), 1.256 – 1.217 (m, 2H), 1.125 – 1.031 (m, 2H), 0.913 (t, J = 7.2 Hz, 3H).

**¹³C-NMR (100 MHz, CDCl₃) δ:** 148.262, 142.988, 138.994, 136.399, 135.336, 133.851, 132.580, 131.199, 130.752, 129.696, 128.528, 127.557, 126.948, 125.625.
In a 250 mL flask, a solution of valeryl chloride (0.950 g, 7.9 mmol) in dichloromethane (10 mL) was added dropwise into a suspension of biphenyl-D_{10} (1.230 g, 7.5 mmol) and anhydrous AlCl_{3} (1.251 g, 9.4 mmol) in dichloromethane (10 mL) under nitrogen protection at 0 °C. After the addition was accomplished, the mixture obtained was stirred at 0 °C and then allowed to gradually...
rise up to room temperature overnight. After that time, the mixture was chilled in an ice bath and HCl (6 M, 25 mL) was added dropwise. After all the solids inside were dissolved, the organic solvent was removed by using rotary evaporation. The resulting mixture was cooled to room temperature and the crude product was isolated by suction filtration and air-dried (1.933 g). After recrystallization from methanol, the pure product was obtained as pale yellow powder (1.812 g, 7.3 mmol, 97 % yield).

From 1H-NMR, the deuteration level on the aromatic ring is about 95%.

**M.P.:** 76.0 – 78.0 °C.

1H-NMR (400 MHz, CDCl3) δ: 3.000 (t, J = 7.2 Hz, 2H), 1.771 – 1.714 (m, 2H), 1.482 – 1.389 (m, 2H), 0.971 (t, J = 7.2 Hz, 3H).

13C-NMR (100 MHz, CDCl3) δ: 200.221, 38.414, 26.580, 22.530, 13.975.

4-pentyl-1,1'-biphenyl-2,2',3,3',4',5,5',6,6'-d9 (8.32)

Chemical Formula: C17H11D9
Molecular Weight: 233.40

A 100 mL pear flask was charged 1-[(1,1'-biphenyl-D9]-4-yI)pentan-1-one (1.498 g, 6.0 mmol), hydrazine monohydrate (1.501 g, 30 mmol), potassium hydroxide (1.008 g, 18 mmol) and diethylene glycol (10 mL). The mixture was stirred and heated up to 130 °C. After that temperature
was maintained overnight, the bath was heated up to 200 °C to distill out the excess amount of water and hydrazine by using a Dean-Stark apparatus. The heating was stopped when there is no nitrogen evolution.

After cooling to room temperature, toluene (15 mL) and water (15 mL) were added. The organic layer was separated and the aqueous layer was extracted with toluene (15 mL x 3). The organic layers were combined and dried over with anhydrous MgSO₄. After the removal of solvent by rotary evaporation, the brown sticky residue was purified with Kugelrohr distillation (170 °C, 0.7 millibar) to give the product as a colorless oil (0.865 g, 3.7 mmol, 62 % yield).

From $^1$H-NMR, the deuteriation level on the aromatic ring is about 90%.

$^1$H-NMR (400 MHz, CDCl₃) δ: 2.643 (t, $J = 7.8$ Hz, 2H), 1.673 – 1.617 (m, 2H), 1.368 – 1.332 (m, 4H), 0.906 (t, $J = 6.8$ Hz, 3H).

$^{13}$C-NMR (100 MHz, CDCl₃) δ: 35.476, 31.572, 31.182, 22.574, 14.053.

4-bromo-4'-pentyl-1,1'-biphenyl-2,2',3,3',5,5',6,6'-d₈ (8.33)

![Chemical structure of 4-bromo-4'-pentyl-1,1'-biphenyl-2,2',3,3',5,5',6,6'-d₈](image)

Chemical Formula: C₁₇H₁₁D₈Br
Molecular Weight: 311.29

In an ice bath, a solution of bromine (0.658 g, 4.11 mmol) in CCl₄ was added dropwise into a 100 mL flask containing 4-$n$-pentanoylbiphenyl-D₉ (0.870 g, 3.75 mmol), iron powder (0.021 g, 0.37
mmol) and CCl₄ (10 mL). The mixture was stirred at 0 °C and then the temperature was allowed to gradually rise to room temperature. After 24 hours, TLC indicated a new product was formed and most of the starting material was consumed. At this point, saturated Na₂SO₃ solution (25 mL) was added to remove the excess bromine and the organic phase was separated and dried with anhydrous MgSO₄. After the removal of drying agent, silica gel (~ 5g) was mixed with the filtrate and the organic solvent was removed by rotary evaporation. The powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes). Fractions containing the product were combined and condensed, giving white crystal (0.661 g, 2.8 mmol) as product. At the same time, unreacted starting material 4-n-pentanoylbiphenyl-D₉ (0.165 g, 0.7 mmol) was successfully recovered.

From ¹H-NMR, the deuteration level on the aromatic ring is about 90%.

**M.P.:** 91.0 – 92.5 °C.

**¹H-NMR (400 MHz, CDCl₃)** δ: 2.635 (t, J = 7.8 Hz, 2H), 1.681 – 1.607 (m, 2H), 1.366 – 1.324 (m, 4H), 0.902 (t, J = 7.0 Hz, 3H).

**¹³C-NMR (100 MHz, CDCl₃)** δ: 35.466, 31.533, 31.135, 22.557, 14.040.
A 50 mL flask was well flushed with nitrogen and charged with 4-bromo-4’-n-pentyl-1,1’-biphenyl-D$_8$ (0.637 g, 2.0 mmol), potassium cyanide (0.268 g, 4.0 mmol), Pd(PPh$_3$)$_4$ (0.120 g, 0.1 mmol) and DMA (10 mL). The mixture was stirred at 130 °C under nitrogen protection overnight and after that time TLC indicated partial of starting material still existed. More potassium cyanide (0.068 g, 1.0 mmol) was added and another 2 hours of reaction time was applied to make sure no starting material biphenyl remained.

At this point, the mixture was cooled and water (50 mL) was added into the resulting mixture. After being extracted with ethyl acetate (25 mL x 5), the organic layers were combined and dried with anhydrous MgSO$_4$. After the removal of drying agent, silica gel (~ 5g) was well mixed the filtrate and organic solvent was removed by rotary evaporation. The powder obtained was placed on the top of silica gel column to afford chromatography (eluent = hexanes:EtOAc=50:1). Fractions containing the product were combined and condensed, giving colorless cloudy oil as product. However, TLC indicated there was still tiny amount of impurities at this stage and Kugelrohr distillation (190 °C, 0.7 millibar) was applied to obtain the final product (0.187 g, 0.65 mmol, 37 % yield).

The aqueous phase containing remaining potassium cyanide was treated with hydrogen peroxide
in the presence of Cu$^{2+}$ before dumping into the waste container.

From $^1$H-NMR, the deuteration level on the aromatic ring is about 90%.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 2.653 (t, $J = 7.8$ Hz, 2H), 1.688 – 1.613 (m, 2H), 1.362 – 1.325 (m, 4H), 0.903 (t, $J = 6.8$ Hz, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 35.528, 31.538, 31.096, 22.579, 14.067.
8.6. Reference


(19) Huang, M. *Journal of the American Chemical Society* **1949**, *71*, 3301.
