CYCLOPENTADIENONE CONVERSIONS TO TEREPTHALATES AND CYCLOADDITIONS OF ALKynes AND AZIDES

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

By

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B.S. Chemistry, United States Air Force Academy, 2001

2011
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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Sarah E. Bragg ENTITLED Cyclopentadienone Conversions to Terephthalates and Cycloadditions of Alkynes and Azides BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.
ABSTRACT

Bragg, Sarah E. M.S., Department of Chemistry, Wright State University, 2011. Cyclopentadienone Conversions to Terephthalates and Cycloadditions of Alkynes and Azides.

Cyclopentadienone derivatives can be converted via a Diels-Alder reaction to multifunctional terephthalate derivatives, which can then be converted to poly(phenylene vinylene) derivatives. It was demonstrated that terephthalate derivatives can be simply and reproducibly synthesized from 2,5-diethoxycarbonyl-3,4-diphenylcyclopentadienone with a variety of acetylenes, having yields ranging from 63% to quantitative yields. The terephthalate derivatives synthesized varied from oils to crystalline solids, but were readily isolated and generally had high rates of completion despite expected steric factors. Terephthalate derivatives with pendent acetylenes were formed in reactions with as low as a 3:1 ratio of diacetylene to cyclopentadienone. A terephthalate derivative with a pendent carbohydrate function was also synthesized using the same method.

Characterization of the terephthalate derivatives was accomplished by $^1$H NMR, $^{13}$C and related DEPT 135 NMR, IR, and elemental analysis with overall conclusive results. Melting points of the terephthalate derivatives varied widely and were not useful in characterization. A one-pot procedure for Huisgen 1,3-dipolar cycloaddition was developed for “clicking” the alkynyl terephthalates with azides in situ to yield 1,4-disubstituted 1,2,3-triazoles. The dipolar cycloaddition reactions had yields ranging from 32% to 75% and purification of these products was difficult.
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DEDICATION

I would like to dedicate this work to my family, friends, supervisors and coworkers, whose encouragement and support made this undertaking possible. I would also like to dedicate this to Mr. Glenn Bell, who sparked my interest in chemistry, and to Dr. Gary Balaich, whose enthusiasm for chemistry was permanently contagious.
ACKNOWLEDGEMENTS

I would like to acknowledge my advisor, Dr. William Feld, for his guidance, patience, and encouragement throughout the entire program. His assistance in planning my coursework and tutelage during this project were critical in my timely completion of this degree. I would also like to acknowledge the Wright State University Chemistry Department faculty and my fellow graduate students, especially Rachel Sayers and Jeffrey Fogle. Rachel’s foundational work with the cyclopentadienones and Jeff’s vast laboratory expertise were invaluable to the success of this research.
INTRODUCTION

The conversion of 2,5-diethoxycarbonyl-3,4-diphenylcyclopentadienone 1 to poly[(2,3-diphenyl-p-phenylene) vinylene] (DP-PPV) 2 takes five steps. The first of these steps is a Diels-Alder addition of an acetylene to form an arene like 3. The newly formed arene may be further functionalized, depending on the alkyne used.

PPV derivatives 2 have been shown to exhibit electroluminescence which has applications in light-emitting diodes and light-emitting electrochemical cells. Functionalizing PPV has been shown to alter the luminescence properties of light-emitting efficiency and color control, and may allow applications such as chemical detection. The current focus is to create a derivative of 2 with a pendent ethynyl group available for later functionalization of the polymer. An alternate approach considered is to create a functionalized terephthalate 3, then continue with polymerization.

The goals of the current research were 1) to efficiently synthesize a series of terephthalates with pendent acetylene groups, 2) to characterize each by melting point, $^1$H and $^{13}$C NMR, IR, and elemental analysis, 3) to use them in cycloaddition reactions with azides, and 4) to explore the synthesis of a terephthalate with a pendent carbohydrate function, such as glucose 4.
HISTORICAL

Cyclopentadienones: History and Synthesis

Research on cyclopentadienones 5 began in the early 1900s, however, there were great difficulties with isolating the unsubstituted compound in its monomeric form. Dimeric products 6, even of simply substituted cyclopentadienones, were the most common products found.

Monomeric cyclopentadienones with aryl substituents 7 and 8 were successfully synthesized in 1905 by Ruhemann and Merriman and in 1927 by Diels, Buddenberg and Wang, respectively. Ruhemann and Merriman also noted an array of color changes for the cyclopentadienone derivative in a variety of solvents and solutions. Although successful, the preparations were complex and required synthesis of multiple precursors, which after combining, could be reduced to yield the desired cyclopentadienones.
A parallel progression of research was occurring at the same time, ultimately yielding di-, tri-, and tetra-substituted cyclopentadienones. Starting in 1887 with Japp and coworkers, the condensation reaction of benzil with acetone was performed, although initially thought to result in only single bond formation as shown in the cyclobutanone structure 9.\(^5\)

![Chemical structures](image1)

In 1897, they discovered that the proposed structure of 9 was incorrect and they had successfully conducted a condensation that resulted in a five-membered cyclic compound, dehydrating one side of the ring to yield a cyclopentenone 10.\(^6\) Although they proposed a second dehydration could yield a cyclopentadienone, further work on this hypothesis was not published by Japp’s group and, in 1933, Allen and Spanagel completed the second dehydration to 3,4-diphenylcyclopentadienone 11, which confirmed a method of synthesis that required only one intermediate and had only sodium hydroxide and water as by-products.\(^7\) Monomeric isolation was not possible in these experiments as shown in the dimeric form of 3,4-diphenylcyclopentadienone 12.\(^{2,3}\)
Later experimentation, however, resulted in many cyclopentadienones being isolated as unimolecular species at room temperature, especially when the 2 and 5 positions had sterically large substituents as exhibited by 2,5-di(carboxymethyl)-3,4-diphenylcyclopentadienone 13.\textsuperscript{2,3} Cyclopentadienones have since been synthesized with a wide array of substituents, particularly in the 2 and 5 positions through condensation of 1,3-disubstituted acetones and $\alpha$-diketones like benzil.\textsuperscript{3} Further research has determined that an ethyl group in the 2 and 5 position, as in 2,5-diethyl-3,4-diphenylcyclopentadienone 14, is the minimum size substituent in the 2 and 5 positions necessary for monomer formation, since 2,5-dimethyl-3,4-diphenylcyclopentadienone 15 is a dissociating dimer 16.\textsuperscript{3} It is a colorless crystalline solid when isolated, but is red when in solution even under standard conditions.\textsuperscript{3}
Cyclopentadienone Conversion to Arenes

Monomeric cyclopentadienones like 17 were shown to react with alkenes such as 18 and 21 to form dihydrobenzenes 20 and 24 through the elimination of carbon monoxide from intermediates such as 19 and 22.\(^3\)

In some instances, following carbon monoxide elimination, oxidation of two substituents on the dihydrobenzene resulted in substituted benzenes like 24.\(^3\) The majority of the reactions between monomeric cyclopentadienones and alkenes required either high temperatures (over 150°C) or metal catalysts such as palladium or potassium permanganate to form arenes such as 24.\(^3\)

Reactions with acetylenes, however, directly form arenes in a Diels-Alder cycloaddition, and do so under milder conditions.\(^2,3\) An example of this is the reaction of
2,5-methyl-3,4-diphenylcyclopentadienone 15 with acetylene 25 to form 1,4-dimethyl-2,3-diphenyl benzene 26.³

\[
\begin{align*}
\text{15} & \quad \text{HC≡CH} \quad \text{25} \quad \text{26}
\end{align*}
\]

The reaction of 1,4-diethynyl benzene 27 with 2,5-methyl-3,4-diphenyl-cyclopentadienone 15, when mixed in a 1:2 ratio, also forms arenes such as 28.³ This general reaction applies to a wide variety of diacetylenes and cyclopentadienones.³

\[
\begin{align*}
\text{15} & \quad \text{27} \quad \text{28}
\end{align*}
\]

Additionally, reactions of cyclopentadienones with nitriles also resulted in aromatics, specifically pyridines.³ A good example of this reaction is that of

\[
\begin{align*}
\text{29} & \quad \text{30} \quad \text{31}
\end{align*}
\]
3,4-di(4-methoxyphenyl)-2,5-diphenylicyclopentadienone 29 with benzonitrile 30 to form 3,4-di(4-methoxyphenyl)-2,5,6-triphenylpyridine 31.3

The size of the 2 and 5 substituents affects the conditions under which cycloaddition must be conducted, with higher temperatures necessary for reactions with cyclopentadienones bearing large substituents in the 2 and 5 positions.2 For example, reactions of acetylenes and cyclopentadienones with phenyl groups in the 2 and 5 positions require a temperature approximately 50°C above those with alkyl esters in the 2 and 5 positions.2 Correspondingly, the reactions of acetylenes and cyclopentadienones with methyl groups in the 2 and 5 positions have reaction temperatures 50°C lower than the cyclopentadienones with alkyl ester substituents in the 2 and 5 positions.2

**Polymerization of Cyclopentadienone-Derived Arenes**

Conjugated polymers are well-known for their properties as organic semiconductors, and have been used as sensory materials in detecting water, explosives and organic vapors.9 Poly (p-phenylene vinylene) (PPV) 32 was the first conjugated polymer identified for use in light-emitting diodes by Friend and coworkers in 1990, and along with some derivatives continues to be widely used for that and other similar purposes.1,8,9 PPV is most frequently produced as a thin film by a number of methods, including the use of precursors, side chain derivatives and in situ polymerization.1,8 Using precursors requires
the polymer to be made, cast into a thin film, then converted to the final conjugated form. The side-chain method allows the desired polymer to be made in solution, due to the solubilizing side chains, then be cast into a thin film with no conversion necessary. This method is not always an option due to polymer gelation during polymerization, thus preventing casting into a thin film.

There are three common methods of PPV preparation through precursors: 1) through sulfonium precursors, 2) through xanthate precursors, and 3) through halomethyl precursors. The substituents of the starting material drive which method is most successful.

Sulfonium precursors are used primarily for simple PPV synthesis, as other methods are better for substituted PPV synthesis, especially where a quality thin film is desired. The reaction of 2,5-di(trimethylsilyl)-1,4-di(bromomethyl) benzene 33

\[
\begin{align*}
\text{Br} & \quad \text{Si} & \quad \text{Br} \\
\text{Si} & \quad \text{Br} & \quad \text{Si} \\
\text{Si} & \quad \text{Si} & \quad \text{Br} \\
\text{Si} & \quad \text{Si} & \quad \text{Si}
\end{align*}
\]

33

\[
\begin{align*}
\text{Br} & \quad \text{Si} & \quad \text{Br} \\
\text{Si} & \quad \text{Br} & \quad \text{Si} \\
\text{Si} & \quad \text{Si} & \quad \text{Br} \\
\text{Si} & \quad \text{Si} & \quad \text{Si}
\end{align*}
\]

34

\[
\begin{align*}
\text{NaOH} & \quad \text{H}_2\text{O} & \quad \text{dialysis} & \quad 3\text{ days} \\
\text{vacuum} & \quad 230^\circ\text{C}
\end{align*}
\]

35

36

33 34 35 36
with tetrahydrothiophene yields 2,5-di(trimethylsilyl)-1,4-phenylenedimethylene di(tetrahydrothiophenium) dibromide 34 as the sulfonium monomer.\textsuperscript{22} The monomer 34 is polymerized to yield 35, which undergoes thermal elimination to form poly [2,5-bis(trimethylsilyl)-1,4-phenylenevinylene] 36.\textsuperscript{22}

Xanthate precursors are most useful in the syntheses of derivatives with small substituents, such as methoxy groups.\textsuperscript{1} One example is the reaction of 1,4-di(chloromethyl)-2,5-dimethoxybenzene 37 with potassium O-ethylxanthate, to yield 1,4-di[S-(O-ethylxanthato)]methyl-2,5-dimethoxybenzene 38, which can be polymerized in t-butoxide to form poly[(2,5-dimethoxy-p-phenylene) (2-S-(O-ethylxanthato)ethylene)] 39.\textsuperscript{20} The polymer 39 then undergoes elimination by heating to yield poly[(2,5-di(methoxy)-p-phenylene)vinylene] 40.\textsuperscript{20}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\textbf{37}}; \node at (2,0) {\textbf{38}}; \node at (4,0) {\textbf{39}}; \node at (6,0) {\textbf{40}};
\end{tikzpicture}
\end{center}

Bis-halomethyl precursors have shown great success for derivatives with large substituents including phenyl groups.\textsuperscript{1} This route has been successfully used to synthesize DP-PPV 46 from 2,5-diethoxycarbonyl-3,4-diphenylcyclopentadienone 1.\textsuperscript{1} The first step is a Diels-Alder reaction with 1 and norbornadiene 41 to form diethyl 2,3-diphenylterephthalate 42. Reduction with lithium aluminum hydride forms 2,3-diphenyl-
1,4-dihydroxymethyl benzene 43, and subsequent halogenation with thionyl chloride yields 2,3-diphenyl-1,4-dichloromethyl benzene 44. Polymerization is conducted with potassium t-butoxide to form the precursor polymer 45, which subsequently undergoes thermal elimination to yield DP-PPV 46.

The properties of PPV are affected, as most polymers are, by its molecular weight and the substituents. The substituents on the phenylene may be those from

![Diagram](image_url)
3 and 4 positions on a cyclopentadienone precursor or those introduced by the acetylene during the Diels-Alder reaction during formation of the arene (Figure 1).8,10

Click Chemistry: Reactions with Acetylenes and Azides

Huisgen 1,3-dipolar cycloadditions are irreversible reactions in which two unsaturated reactants form a five-membered heterocycle.11 Although a wide variety of products have been formed from this fusion, the most useful reaction is that of an alkyne 47 and an azide 48 to form triazoles 49 and 50, as the azide is very rarely involved in side reactions.11

\[
\begin{align*}
&\text{47} & \text{48} & \text{heat} & \text{49} & \text{50} \\
&\text{R}_2 & \text{N} & \text{N} & \text{N} & \text{R}_2 \\
&\text{N} & \text{N} & \text{N} & \text{N} & \text{R}_1 \\
&\text{R}_1 & \text{R}_1 & \text{R}_1 & \text{R}_1
\end{align*}
\]

Contrary to fears about azides, their stability in the presence of water, oxygen, and most organic synthesis conditions makes them valuable for click reactions.11 Due to safety concerns with isolating small azides, an in situ procedure was developed to conduct the cycloaddition resulting in disubstituted 1,2,3-triazoles.11 The entire reaction is conducted in a solution which is at least half water to provide a constant heat-sink for the exothermic reaction.16 Since two regioisomers 49 and 50 were formed in nearly equal quantities under standard conditions, Sharpless and coworkers considered catalyzed reactions to control regioselectivity.11 They discovered that using Cu(I) as a catalyst resulted in 91% of the 1,4 isomer 49 being produced under a variety of conditions and with a wide variety of functional groups in the \( R_1 \) and \( R_2 \) positions.11
A mechanism was proposed (Figure 2) for the catalyzed cycloaddition, in which the acetylene is converted to a cuprous acetylide with copper(I) sulfate (Step A). The copper is coordinated by the nitrogen in the azide immediately adjacent to \( R_2 \) (Step B), thereby ensuring 1,4-disubstitution. The acetylene then attacks the terminal nitrogen (Step C) to form a six-membered ring. A subsequent rearrangement (Step D) forms the five-membered ring, with copper(I) as a substituent in the 5 position. The five-membered ring undergoes proteolysis, leaving hydrogen at the 5 position. The copper (I) is then able to continue catalyzing the reaction and the 1,4-disubstituted 1,2,3-triazole is formed (Step E).

Figure 2. Mechanism of Copper-Catalyzed Dipolar Cycloaddition.
Click Chemistry: Polymer Applications

Click chemistry has become popular for a variety of syntheses hinging on 1,2,3-triazole formation.\textsuperscript{12} Triazoles have been noted in industrial applications such as fluorophores, chemosensors, charge-transfer compounds, herbicides, fungicides and dyes.\textsuperscript{12,18} Additionally, click chemistry has been demonstrated as an effective method of functionalizing polymer surfaces, and triazole formation has been used in the creation of strong adhesives.\textsuperscript{14}

Click chemistry has become important to the formation of block copolymers (\textbf{Figure 3}) and dendrimers like 53.\textsuperscript{12,13} Use of click chemistry has broadened the variety of block copolymers that can be formed.\textsuperscript{15} Polymer blocks can now be made independently, allowing for different polymerization techniques, and joined rapidly under conditions that preserve each block’s functional groups.\textsuperscript{15} \textbf{Figure 3} demonstrates how two different polymers, illustrated by the blue and green lines, can be formed with azide and acetylene end groups.\textsuperscript{15} These polymers can be made under different conditions, as long as they can both exist under the same conditions during the 1,3-dipolar cycloaddition.\textsuperscript{15} As shown, the two polymers can be joined by triazole formation.\textsuperscript{15}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Formation of Copolymers with Click Chemistry.}
\end{figure}

Click chemistry is favored as a method of dendrimer synthesis because it leads to the formation of unidisperse and highly branched dendrimers.\textsuperscript{13} In the example shown
below, the alkyne 51 and azide 52 can be clicked under mild conditions to form a first generation dendrimer 53.\textsuperscript{13}

The carboxylic acid in 53 can undergo esterification with propargyl alcohol and the chloroethyl groups can be converted to organoazides by nucleophilic substitution of
the chlorides with sodium azide.\textsuperscript{13} The modified trimer 53 is thus able to react to form larger oligomers 54 and so on.\textsuperscript{13}
Click Chemistry: Biological Applications

Click chemistry has most recently become known for creating 1,2,3-triazoles with biological and pharmacological applications.\textsuperscript{12,16,17}

Communication between cells is controlled by three classes of biopolymers: nucleic acids, proteins and carbohydrates.\textsuperscript{19} Altering these can result in changes in cell adhesion, reproduction, growth, and differentiation.\textsuperscript{19} Carbohydrates, found on the surface of cells, are at the beginning of the communications and metabolic processes, thus making them pivotal to research.\textsuperscript{16,19}

In 2005, Chaikof and coworkers attached carbohydrates and proteins to a polymer surface for use on implantable medical devices and solid-phase-based assays.\textsuperscript{15} Most important for these applications were the mild reaction conditions, which include room temperature and organic solvents, which prevent denaturing the proteins or decomposition of the carbohydrates.\textsuperscript{15}

![Figure 4. Functionalizing Surfaces Through Click Chemistry.](image_url)
In 2007, Ju and coworkers further advanced this area of research by using click chemistry to create oligomers with carbohydrate 55 and nucleic acid derivative 56.\textsuperscript{18}

\begin{center}
\includegraphics[width=0.8\textwidth]{image}
\end{center}

The oligomers were formed by the reaction of 1,3-propanediamine 57 with propargyl bromide to form N,N,N',N'-tetrapropargyl-1,3-propanediamine 58, which was then clicked with 1-azido-1-deoxy-2,3,4,6-tetra-O-acetyl-\beta-D-glucopyranose 55 to form 1,3-diamino[N,N,N',N'-tetra[(1-deoxy-2,3,4,6-tetra-O-acetylglucopyranosyl)-4-(1,2,3-triazo)methyl]propane 59.\textsuperscript{18} The reactions were also conducted with the nucleic acid derivative, the oligomer of which demonstrated antibiotic activity against \textit{E.coli}.\textsuperscript{18}
In 2010, Iyer and coworkers identified the methods by which multiple pathogens bind to the carbohydrates on the surface of mammalian cells (Figure 3). They proposed that these binding methods could be used against the pathogens if the area around the cells were flooded with analogs (Figure 6). If the pathogens bound to the analogs instead of the cells, the cells would be spared.

**Figure 5. Pathogen Binding to Cell-Surface Carbohydrates.**

**Figure 6. Pathogen Binding to Carbohydrate Analogs.**
Furthermore, the analogs could inhibit the pathogens’ activity if bound to an appropriate compound, for example a galactose-linked sialic acid derivative 60.\textsuperscript{19} In particular, inhibition of influenza viruses and Shiga toxin were demonstrated by a variety of compounds.\textsuperscript{19}

\[
\text{\includegraphics[width=\textwidth]{60.png}}\]

In addition to creating analogs to keep pathogens away from cells and inhibit their activities, Iyer proposed that carbohydrate analogs could be developed to intentionally bind with pathogens in order to detect them.\textsuperscript{21} Since PPV derivatives are known for their light-emitting properties, he proposed that PPV derivatives with specific carbohydrate functional groups could be developed using click chemistry (\textbf{Figure 7}) to indicate the presence of a particular pathogen or group of pathogens.\textsuperscript{21}
To expand on over 100 years of history in this field, this research sought to efficiently synthesize and characterize terephthalates with pendent ethynyl groups, to use them in cycloaddition reactions with azides, and to explore the synthesis of a terephthalate with a pendent carbohydrate function.
EXPERIMENTAL

Chemicals and Instrumentation

Melting points were obtained with a DigiMelt MPA-160 or Electrothermal MP Apparatus. Nuclear magnetic resonance (NMR) \( ^1H \) and \( ^{13}C \) spectra were obtained using a Bruker Avance 300 MHz NMR Spectrometer. Solvents for NMR were CDCl\(_3\), DMSO-d\(_6\), and Acetone-d\(_6\). Infrared (IR) spectra were recorded as thin films (NaCl) with a Nicolet 6700 FT-IR spectrometer. Elemental analyses were obtained through Midwest Microlab, LLC, Indianapolis, IN. A 35 mL Q-Tube™ (pressure tube reactor) was purchased from Sigma-Aldrich Labware. Chemicals were purchased from Aldrich and GFS, and used as received.

2,5-di(ethoxycarbonyl)-3,4-diphenylcyclopentadienone 1

In a round-bottomed flask was placed 10.5 g (0.05 mol) of benzil 61 and 12.1 g (0.06 mol) of diethyl 1,3-acetonedicarboxylate 62 in 40 mL of absolute ethanol. The mixture was heated in an oil bath at 95° until a clear, yellow solution formed, and sodium ethoxide, prepared from 1.38 g of sodium in ethanol (40 mL) no more than 0.4 g at a time, was added. The mixture was stirred and refluxed for 20 min until a precipitate formed and the mixture became cloudy. The solution was refluxed and stirred for 15 min more, until precipitation was complete and a thick, yellow-orange mixture resulted. The solution was cooled for 10 min and the precipitate was filtered, resulting in a yellow powder 63. The yellow powder was slurried (40 mL of acetic anhydride) in a beaker.
with a stir bar, thermometer, and watch glass. Concentrated sulfuric acid (approximately 3 mL) was added dropwise until the powder was completely dissolved. Deionized water was added dropwise 3-4 drops at a time alternatively with 3 drops of sulfuric acid until the temperature rose to 70-80°. Deionized water continued to be added dropwise, keeping the temperature between 70-80°, until water could be added without a rise in temperature. Another 150 mL of deionized water was added slowly until a precipitate was formed. The mixture was stirred for 15 min and the orange product was filtered and air-dried overnight. The resulting bright orange, crystalline solid was recrystallized from high boiling (60-80°) petroleum ether (100 mL per gram of product) to yield 14.1 g (75%) of bright orange crystals: m.p. 114.6-118.4°; ¹H NMR (300 MHz, CDCl₃, δ) 7.40-7.03 (m, 10H, Ar-H), 4.25-4.27 (q, 4H, -CH₂), 1.21-1.16 (t, 6H, -CH₃); ¹³C-NMR (300 MHz, CDCl₃, ppm) 191.0, 162.1, 131.0, 130.1, 128.9, 127.7, 119.8, 61.2, 13.9; IR (NaCl salt plate) cm⁻¹ 2993 (m, C-H), 1730 (s, C=O), 1714 (s, C=O), 1601 (m, C=C), 1444 (m, C-H), 1371 (m, C-H), 1213 (m, C(=O)-O), 700 (m, C=C). Anal. Calc. for C₂₃H₂₀O₅ (376.40): C, 73.39; H, 5.35. Found: C, 73.24; H, 5.26.

Tris[(2,5-di(ethoxycarbonyl)-3,4-diphenyl)phenylmethyl] amine 67

To a 35 mL Q-tube was added 0.5646 g (1.5 mmol) of 1 and 0.0656 g (0.5 mmol) of tripropargyl amine 66 (a 3:1 ratio of 1 to 66) and 9 mL of toluene. The Q-tube was heated to 170° (in a heating mantle with sand) overnight. On cooling, the contents of the tube were poured into a beaker and evaporated overnight, resulting in a dark, amber solid 67. (TLC did not result in a separation of 67 from 1 and 66, despite using varying concentrations and combinations of hexane, ethyl acetate, dichloromethane, and toluene.)
The solid was recrystallized from 100 mL of ethanol. The resulting crystals were filtered and vacuum-dried (250 millitorr) overnight to yield 0.4 g (63%) of light yellow crystals: m.p. 118.5-125.9°; \(^1\)H NMR (300 MHz, CDCl\(_3\), \(\delta\)) 8.12 (s, 3H, Ar-H), 7.12-7.00 (m, 30H, Ar-H), 4.06-3.99 (q, 12H, -CH\(_2\)), 3.86 (s, 6H, -CH\(_2\)), 0.95-0.83 (m, 18H, -CH\(_3\)); \(^{13}\)C-NMR (300 MHz, CDCl\(_3\), ppm) 168.1, 139.7, 138.9, 138.1, 137.1, 135.2, 133.8, 130.3, 129.8, 129.3, 127.2, 127.1, 126.8, 126.5, 61.1, 61.0, 57.1, 13.54, 13.48; IR (NaCl salt plate) cm\(^{-1}\) 2981 (m, C-H), 1724 (s, C=O), 1603 (m, C=C), 1444 (m, C-H), 1365 (m, C-H), 1298 (s, C-N), 1246 (s, C(=O)-O), 1174 (s, C-O-C), 700 (s, C=C). Anal. Calc. for C\(_{75}\)H\(_{69}\)NO\(_{12}\) (1176.37): C, 76.58; H, 5.91. Found: C, 76.58; H, 5.99.

5-(5-hexynyl)-2,3-diphenyterephthalate 69

To a 35 mL Q-tube was added 0.3772 g (1 mmol) of 1, 0.40 mL (3 mmol) of 1,7-octadiyne 68, and 8 mL of toluene. The mixture was stirred and heated to 170° (in a heating mantle with sand) overnight. On cooling, the contents of the tube were poured into a round-bottomed flask and evaporated, then vacuum-dried (250 millitorr) overnight to yield 0.47 g (100%) of amber viscous liquid: \(^1\)H NMR (300 MHz, CDCl\(_3\), \(\delta\)) 7.59 (s, 1H, Ar-H), 7.03-6.88 (m, 10H, Ar-H), 3.91-3.84 (m, 4H, -CH\(_2\)), 2.68-1.76 (m, 8H/1H, -CH\(_2\) / CH), 0.82-0.77 (m, 6H, -CH\(_3\)); \(^{13}\)C-NMR (300 MHz, CDCl\(_3\), ppm) 168.7, 168.6, 139.7, 139.0, 138.7, 138.2, 138.1, 137.2, 133.7, 130.2, 129.8, 128.9, 127.22, 127.19, 126.8, 126.5, 84.2, 68.5, 61.0, 32.9, 30.1, 28.2, 18.3, 13.6, 13.5; IR (NaCl salt plate) cm\(^{-1}\) 3296, (m, C-H), 2937 (m, C-H), 2116 (m, C≡C), 1724 (s, C=O), 1603 (w, C≡C), 1444 (m, C-H), 1367 (m, C-H), 1254 (s, C-H), 1174 (s, C(=O)-O), 700 (s, C=C). Anal. Calc. for C\(_{30}\)H\(_{30}\)O\(_{4}\) (454.56): C, 79.27; H, 6.65. Found: C, 77.34; H, 6.46.
5-(propargyloxymethyl)-2,3-diphenylterephthalate 70

To a 35 mL Q-tube was added 0.3764 g (1 mmol) of 1, 0.31 mL (3 mmol) of propargyl ether 64, and 8 mL of toluene. The Q-tube was heated to 170° (in a heating mantle with sand) overnight. On cooling, the contents of the tube were poured into a round-bottomed flask and evaporated, then vacuum-dried (250 millitorr) overnight to yield 0.4 g (91%) of amber viscous liquid: $^1$H NMR (300 MHz, CDCl$_3$, δ) 7.89 (s, 1H, Ar-H), 7.13-6.99 (m, 10H, Ar-H), 4.77 (s, 2H, -CH$_2$), 4.24-4.23 (d, 2H, -CH$_2$), 4.04-3.97 (m, 4H, -CH$_3$), 4.25-2.37 (m, 1H, CH), 0.93-0.81 (m, 6H, -CH$_3$); $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm) 168.1, 140.9, 140.2, 138.7, 137.9, 136.3, 134.0, 133.8, 130.1, 129.7, 128.3, 127.3, 127.2, 126.9, 126.7, 79.3, 74.9, 69.0, 61.2, 61.1, 57.8, 13.54, 13.49; IR (NaCl salt plate) cm$^{-1}$ 3290, (m, C-H), 2982 (m, C-H), 2116 (m, C=O), 1724 (s, C=O), 1444 (m, C=O), 1366 (m, C-H), 1252 (s, C-O-C), 1252 (s, C-O-C), 700 (s, C=O). Anal. Calc. for C$_{28}$H$_{26}$O$_5$ (442.51): C, 76.00; H, 5.92. Found: C, 76.01; H, 6.01.

5-(3-butynyl)-2,3-diphenylterephthalate 72

To a 35 mL Q-tube was added 0.3772 g (1 mmol) of 1, 0.6 mL of 1,5-hexadiyne 71, 50% by weight in pentane (3 mmol of hexadiyne), and 8 mL of toluene. The mixture was stirred and heated to 170° (in a heating mantle with sand) overnight. On cooling, the contents of the tube were poured into a round-bottomed flask and evaporated, then vacuum-dried (250 millitorr) overnight to yield 0.5 g (100%) of brown crystals: m.p. >260°C; $^1$H NMR (300 MHz, CDCl$_3$, δ) 7.76 (s, 1H, Ar-H), 7.12-6.98 (m, 10H, Ar-H), 4.01-3.98 (m, 4H, -CH$_2$), 3.11-2.62 (m, 4H, -CH$_3$), 2.06 (s, 1H, CH), 0.92-0.88 (m, 6H, -CH$_3$); $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm) 168.5, 168.3, 140.0, 139.4, 138.8, 138.1,
137.2, 136.2, 133.7, 130.1, 129.8, 129.2, 127.3, 127.2, 126.9, 126.6, 83.2, 69.4, 61.2, 61.1, 32.6, 20.2, 13.5; IR (NaCl salt plate) cm\(^{-1}\) 3294, (m, C-H), 2981 (m, C-H), 2117 (w, C≡C), 1722 (s, C=O), 1603 (w, C≡C), 1443 (m, C-H), 1365 (m, C-H), 1252 (s, C-H), 1176 (s, C(=O)-O), 700 (s, C≡C). Anal. Calc. for C\(_{28}H_{26}O_4\) (426.511): C, 78.85; H, 6.14. Found: C, 80.10; H, 6.38.

5-[O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)]methyl-2,3-diphenylterephthalate 74

To a 35 mL Q-tube was added 0.1870 g (0.5 mmol) of 1, 0.1956 g (0.5 mmol) of 2-propynyl-tetra-O-acetyl-β-D-glucopyranoside 73, and 8 mL of toluene. The mixture was stirred and heated to 170° (in a heating mantle with sand) overnight. On cooling, the contents of the tube were poured into a round-bottomed flask and evaporated, then vacuum-dried (250 millitorr) overnight to yield 0.3 g (80%) of tan crystals: m.p. 122.3-127.1°C; \(^1\)H NMR (300 MHz, CDCl\(_3\), δ) 7.86 (s, 1H, Ar-H), 7.20-6.97 (m, 10H, Ar-H), 5.24-5.11 (m, 3H, -CH), 5.01-4.96 (d, 1H, -CH), 4.79-4.63 (m, 2H, -CH\(_2\)), 4.39-4.15 (m, 2H, -CH\(_2\)), 4.00-3.93 (m, 4H, -CH\(_2\)), 3.79-3.74 (m, 1H, -CH), 2.12-2.02 (m, 12H, -CH\(_3\)), 0.89-0.86 (m, 6H, -CH\(_3\)); \(^13\)C-NMR (300 MHz, CDCl\(_3\), ppm) 170.7, 170.3, 169.5, 169.4, 168.1, 167.9, 140.8, 140.1, 138.5, 137.8, 136.2, 134.2, 133.2, 130.1, 130.0, 129.7, 128.1, 127.4, 127.3, 127.0, 126.8, 99.2, 73.0, 71.8, 71.2, 68.3, 67.3, 61.8, 61.3, 61.1, 20.7, 20.6, 13.51, 13.48; IR (NaCl salt plate) cm\(^{-1}\) 2980 (m, C-H), 1755 (s, C=O), 1724 (s, C=O), 1603 (w, C≡C), 1443 (m, C-H), 1367 (m, C-H), 1174 (s, C(=O)-O), 1039 (s, C-O-C), 702 (s, C≡C). Anal. Calc. for C\(_{39}H_{42}O_{14}\) (734.7524): C, 63.75; H, 5.76. Found: C, 63.61; H, 5.76.
1-benzyl-4-phenoxy methyl-1,2,3-triazole 79

In a round-bottomed flask was placed 0.18 mL (1.5 mmol) of benzyl bromide 75 and 3.3 mL of 0.5 M NaN₃ (DMSO) 76 (1.7 mmol). The mixture was stirred at room temperature for 1 h. To the mixture was added 8 mL of water, 4 mL of tert-butyl alcohol, 0.19 mL (1.5 mmol) of phenyl propargyl ether 78, 0.3 mL of 1 M sodium ascorbate (0.3 mmol) in water, and 0.1 mL of 0.5 M copper(II) sulfate (0.05 mmol). The mixture was stirred at room temperature for 24 h and the reaction was quenched with 50 mL of ice cold water. The mixture was stirred for another 10 min. The white precipitate was filtered over a vacuum, washed twice with 25 mL of ice cold water and once with 50 mL of NH₄OH. The precipitate was vacuum-dried (250 millitorr) overnight to yield 0.3 g (75%) of off-white solid: m.p. 119.0-130.3°C; ¹H NMR (300 MHz, CDCl₃, δ) 7.68 (s, 1H, =C-H), 7.38-6.98 (m, 10H, Ar-H), 5.54 (s, 2H, -CH₂), 5.20 (s, 2H, -CH₂); ¹³C-NMR (300 MHz, CDCl₃, ppm) 158.2, 134.5, 129.5, 129.1, 128.9, 128.8, 128.2, 121.4, 121.3, 114.8, 114.4, 61.9, 54.6; IR (NaCl salt plate) cm⁻¹ 3134 (m, C-H), 2923 (m, C-H), 1599 (m, C=C), 1495 (s, C=C), 1331 (m, C-N), 1225 (s, C-O-C), 1053 (s, C-O-C), 756 (s, C-H). Anal. Calc. for C₁₆H₁₅N₃ (265.314): C, 72.43; H, 5.70. Found: C, 72.21; H, 5.84.

1-benzyl-4-hexyl-1,2,3-triazole 81

In a round-bottomed flask was placed 0.18 mL (1.5 mmol) of benzyl bromide 75 and 3.3 mL of 0.5 M NaN₃ (DMSO) 76 (1.7 mmol). The mixture was stirred at room temperature for 1 h. To the mixture was added 8 mL of water, 4 mL of tert-butyl alcohol, 0.22 mL (1.5 mmol) of 1-octyne 80, 0.3 mL of 1 M sodium ascorbate (0.3 mmol) in water, and 0.1 mL of 0.5 M copper(II) sulfate (0.05 mmol). The mixture was stirred at
room temperature for 24 h and the reaction was quenched with 50 mL of ice cold water. The mixture was stirred for another 10 min. The white precipitate was filtered over a vacuum, washed twice with 25 mL of ice cold water and once with 50 mL of NH₄OH, and recrystallized from ethanol/water (3:1). The precipitate was vacuum-dried (250 millitorr) for 2 days to yield 0.1 g (32%) of off-white solid: m.p. 52.2-54.2°C; ¹H NMR (300 MHz, CDCl₃, δ) 7.38-7.26 (m, 5H/1H, Ar-H/=CH), 5.54 (s, 2H, -CH₂), 2.70 (s, 2H, -CH₂), 1.75 (s, 6H, -CH₃), 1.33 (m, 2H, -CH₂), 0.89 (m, 3H, -CH₃); ¹³C-NMR (300 MHz, CDCl₃, ppm) 134.8, 129.0, 128.7, 128.1, 31.5, 28.9, 25.7, 22.5, 14.0; IR (NaCl salt plate) cm⁻¹ 3113 (m, =C-H), 2927 (s, -C-H), 1552 (m, C=C), 1456 (s, C=C), 1327 (m, C-N), 704 (s, C-H). Anal. Calc. for C₁₅H₂₁N₃ (243.351): C, 74.04; H, 8.70. Found: C, 72.46; H, 8.59.
RESULTS AND DISCUSSION

“Orange”

The synthesis of 2,5-di(ethoxycarbonyl)-3,4-diphenylcyclopentadienone 1 was critical to all other syntheses in this research. The condensation of benzil 61 with diethyl 1,3-acetonedicarboxylate 62 the intermediate yields a bright yellow salt 63. Dehydration of 63 yielded a bright orange crystalline compound 1.

Characterization of 1 was accomplished using $^1$H NMR, $^{13}$C and related DEPT 135 NMR, IR, and elemental analysis. In the $^1$H NMR spectrum (Figure 15), the multiplets at 7.40-7.03 ppm correspond to the aromatic ring protons (10), the quartet at 4.25-4.27 ppm corresponds to the protons (4) in the CH$_2$ of the ethyl ester groups, and the triplet at 1.21-1.16 ppm corresponds to the protons (6) of the CH$_3$ of the ethyl ester groups. The integrations of the $^1$H NMR peaks matched those expected at the respective absorption positions. The $^{13}$C NMR spectrum (Figure 16) exhibited the expected peaks, with key identifying absorptions being the cyclopentadienone carbonyl carbon at 191.0 ppm, the ester carbonyl carbons at 162.1 ppm, and the ethyl carbons at 61.2 ppm and 13.9
Additional peaks were present in the aromatic region as expected, but were not easily assigned to specific carbons in the aromatic rings. In the IR spectrum (Figure 17), absorptions were observed at 2993 cm\(^{-1}\) for the alkyl C-H, 1730 cm\(^{-1}\) for the ester C=O, 1714 cm\(^{-1}\) for the ketone C=O, and 1601 cm\(^{-1}\) for the aromatic ring C=C. Elemental analysis was expected to show carbon at 73.39\% and hydrogen at 5.35\%. The analysis results showed carbon content of 73.24\% and hydrogen content of 5.26\%, which is within acceptable limits.

**Diels-Alder Synthesis of Terephthalate Derivatives**

A series of terephthalates were synthesized by a known Diels-Alder reaction starting with 1. The acetylenes used in the Diels-Alder reactions generally had low boiling points and low molecular weights, which generally allowed the terephthalates, particularly those that were liquids, to be purified by vacuum evaporation of any excess reagents. Exceptions to this general procedure are delineated in the experimental section. The three terephthalate derivatives with pendent acetylene groups were generated to determine the effect of functionality and distance between the terephthalic nucleus and the pendant acetylene on the success of subsequent click reactions.

Previous work by our group had developed a simple and reproducible method for the Diels-Alder process, especially those involving volatile reactants. Previous work had also established that a diacetylene 64 could be reacted with 2 equivalents of 1 to yield bis-terephthalates 65 with no pendent acetylene groups. These reactions proceeded in excellent yields and gave pure, isolatable products.
**Diels-Alder with Tripropargyl Amine**

As an extension of the use of diacetylenes in the Diels-Alder reaction, tripropargyl amine 66 was used as a Diels-Alder substrate. Because of the expected steric crowding in this reaction, three different products (mono-, di-, and trisubstituted amines) were expected. A Diels-Alder reaction of 3 equivalents of 1 with 1 equivalent of tripropargyl amine 66 provided tris[(2,5-di(ethoxycarbonyl)-3,4-diphenyl)phenylmethyl]amine 67 in 63% isolated yield. Interestingly, the purified product exhibited no mono- or disubstituted products.
Characterization of 67 was accomplished using $^1$H NMR, $^{13}$C and related DEPT 135 NMR, IR, and elemental analysis. Figure 8 gives reference labels to particular carbons (or their attached hydrogens) for clarifying the peak assignments.

![Figure 8. Compound 67 with Labeled Atoms.](image)

In the $^1$H NMR spectrum (Figure 18), the singlet at 8.12 ppm corresponds to the newly formed aromatic ring protons (a, 3), the multiplet at 7.12-7.00 ppm corresponds to the pendent aromatic ring protons (30), the quartet at 4.06-3.99 ppm corresponds to the protons (d, 12) in the CH$_2$ of the ethyl ester groups, the singlet at 3.86 ppm corresponds to the protons (b, 6) in the CH$_2$ attached to the amine nitrogen, and the multiplet at 0.95-0.83 ppm corresponds to the protons (e, 18) of the CH$_3$ of the ethyl ester groups. The integrations of the $^1$H NMR peaks matched those expected at the respective absorptions.

The $^{13}$C NMR spectrum (Figure 19) exhibited the expected peaks, with key identifying absorptions being the ester carbonyl carbons (c) at 168.1 ppm, the newly formed aromatic ring carbons at 139.7 ppm and 138.9 ppm, the methylenes attached to nitrogen (b) at 57.1 ppm, and ethyl ester carbons (d, e) at 61.1 ppm, 61.0 ppm, 13.54 ppm, and 13.48 ppm. Additional peaks were present in the aromatic region as expected, but were not easily
assigned to specific carbons in the aromatic rings. In the IR spectrum (Figure 20), absorptions were observed at 2981 cm$^{-1}$ for the alkyl C-H, 1724 cm$^{-1}$ for the ester C=O, 1603 cm$^{-1}$ for the aromatic ring C=C, and 1298 cm$^{-1}$ for the amine, and. Elemental analysis was expected to show carbon content at 76.58% and hydrogen at 5.91%. The analysis results showed carbon content of 76.58% and hydrogen content of 5.99%, which is within acceptable limits.

**Diels-Alder with 1,7-Octadiyne**

Because a pendent acetylene is required for cycloaddition reactions with azides, a Diels-Alder reaction was originally attempted employing an equivalent amount of 1 and a diacetylene.$^{24}$ The first attempt at the 1:1 reaction was unsuccessful at yielding a pendent acetylene. A second attempt was successful or unsuccessful, depending on your point of view, because it was discovered that the reaction was actually conducted in a ratio of 10 equivalents of diacetylene to each equivalent of 1.$^{24}$

Thus, the Diels-Alder reaction employing 10 equivalents of 1,7-octadiyne 68 and 1 equivalent of 1 to yield 5-(5-hexynyl)-2,3-diphenylterephthalate 69 was conducted. Due to the expense of the diacetylenes, reactions were also conducted in 5:1 and 3:1 ratios of 1,7-octadiyne to 1 to reduce the amount of starting material. These reactions proved as reliable as a 10:1 ratio based on the $^1$H NMR comparison (Figures 21, 22 and 23). Each occurred in quantitative yield.
Characterization of 69 was accomplished using $^1$H NMR, $^{13}$C and related DEPT 135 NMR, IR, and elemental analysis. Figure 9 gives reference labels to particular carbons (or their attached hydrogens) for clarifying the peak assignments.

Figure 9. Compound 69 with Labeled Atoms.

In the $^1$H NMR spectrum (Figure 23) of the 3:1 synthesis, the singlet at 7.59 ppm corresponds to the newly formed aromatic ring proton (a, 1), the multiplet at 7.03-6.88 ppm corresponds to the pendent aromatic ring protons (10), the multiplet at 3.91-3.84 ppm corresponds to the protons (i, 4) in the CH$_2$ of the ethyl ester groups, the multiplet at 2.68-1.76 ppm corresponds to the protons (b, c, d, e, 8) in the CH$_2$ of the pendent alkyl chain and to the acetylenic CH proton (g, 1), and the multiplet at 0.82-0.77 ppm corresponds to the protons (j, 6) of the CH$_3$ of the ethyl ester groups. The integrations of the $^1$H NMR peaks matched those expected at the respective absorptions. The $^{13}$C NMR spectrum (Figure 24) exhibited the expected peaks, with key identifying absorptions being the ester carbonyl carbons (h) at 168.7 ppm and 168.6 ppm, the newly formed
aromatic ring carbons at 139.7 ppm and 139.0 ppm, the acetylene carbons (f, g) at 84.2 ppm and 68.5 ppm, the ethyl ester carbons (i, j) at 61.0 ppm, 13.6 ppm, and 13.5 ppm, and the alkyl carbons (d, b, c, e) of the pendant chain at 32.9 ppm, 30.1 ppm, 28.2 ppm, and 18.3 ppm. Additional peaks were present in the aromatic region as expected, but were not easily assigned to specific carbons on the aromatic rings. In the IR spectrum (Figure 25), absorptions were observed at 3296 cm$^{-1}$ and 2116 cm$^{-1}$ for the acetylene, 2937 cm$^{-1}$ for the alkyl C-H, 1724 cm$^{-1}$ for the ester C=O, and 1603 cm$^{-1}$ for the aromatic ring C=C. Elemental analysis was expected to show carbon content at 79.27% and hydrogen at 6.65%. Three separate analyses yielded carbon contents of 72.52%, 69.46% and 77.34% for an average of 73.11%. Two samples were specifically labeled as difficult to burn. The inconsistency points to the need for a better sample handling and/or purification procedure. The hydrogen contents of the analyses were 5.97%, 5.77%, and 6.46%, for an average of 6.07%, which is outside acceptable limits.

**Diels-Alder with Propargyl Ether**

Using the same procedure, 5-(propargyloxymethyl)-2,3-diphenyterephthalate 70 was formed by a Diels-Alder reaction of 1 with propargyl ether 64, in a 91% yield. This reaction was conducted originally in the ratio of 10 equivalents of 64 to 1 equivalent of 1. A second run of this reaction was carried out in a 3:1 ratio, which proved equally successful based on the $^1$H NMR comparison (Figures 26 and 27). Successive Diels-Alder reactions were only conducted in the 3:1 ratio to conserve materials.
Characterization of 70 was accomplished using $^1$H NMR, $^{13}$C and related DEPT 135 NMR, IR, and elemental analysis. Figure 10 gives reference labels to particular carbons (or their attached hydrogens) for clarifying the peak assignments.

Figure 10. Compound 70 with Labeled Atoms.

In the $^1$H NMR spectrum (Figure 27) of the 3:1 synthesis, the singlet at 7.89 ppm corresponds to the newly formed aromatic ring proton (a, 1), the multiplet at 7.13-6.99 ppm corresponds to the pendent aromatic ring protons (10), the singlet at 4.77 ppm corresponds to the protons (b, 2) in the CH$_2$ of the benzylic methylene group, the doublet at 4.24-4.23 ppm corresponds to the protons (c, 2) in the CH$_2$ of the propargyl group, the multiplet at 4.04-3.97 ppm corresponds to the protons (g, 4) in the CH$_2$ of the ethyl ester groups, the multiplet at 2.50-2.37 ppm corresponds to the acetylenic CH proton (e, 1), and the multiplet at 0.93-0.81 ppm corresponds to the protons (h, 6) of the CH$_3$ of the ethyl ester groups. The integrations of the $^1$H NMR peaks matched those expected at the respective absorptions. The $^{13}$C NMR spectrum (Figure 28) exhibited the expected peaks, with key identifying absorptions being the ester carbonyl carbons (f) at 168.1 ppm,
the newly formed aromatic ring carbons at 140.9 ppm and 140.2 ppm, the acetylene carbons (e, d) at 79.3 ppm and 74.9 ppm, the alkyl carbon (c) of the propargyl group at 69.0 ppm, the ethyl ester carbons (g, h) at 61.2 ppm, 61.1 ppm, 13.54 ppm, and 13.49 ppm, and the benzylic methylene carbon (b) at 57.8 ppm. Additional peaks were present in the aromatic region as expected, but were not easily assigned to specific carbons on the aromatic rings. In the IR spectrum (Figure 29), absorptions were observed at 3290 cm\(^{-1}\) and 2116 cm\(^{-1}\) for the acetylene, 2982 cm\(^{-1}\) for the alkyl C-H, 1724 cm\(^{-1}\) for the ester C=O, and 1603 cm\(^{-1}\) for the aromatic ring C=C. Elemental analysis was expected to show carbon content at 76.00% and hydrogen at 5.92%. The analysis results showed carbon content of 76.01% and hydrogen content of 6.01%, which is within acceptable limits.

Diels-Alder with 1,5-Hexadiyne

A fourth terephthalate derivative was synthesized with a shorter alkyl chain between the terephthalate and the acetylene group. A short chain was used to provide a substrate to be used to determine if there exist steric effects during cycloaddition with an azide. A Diels-Alder reaction employing 3 equivalents of 1,5-hexadiyne 71 and 1 equivalent of 1 provided 5-(3-butynyl)-2,3-diphenyterephthalate 72 in quantitative yield.
Characterization of 72 was accomplished using $^1$H NMR, $^{13}$C and related DEPT 135 NMR, IR, and elemental analysis. Figure 11 gives reference labels to particular carbons (or their attached hydrogens) for clarifying the peak assignments.

![Figure 11. Compound 72 with Labeled Atoms.](image)

In the $^1$H NMR spectrum (Figure 30) of 72, the singlet at 7.76 ppm corresponds to the newly formed aromatic ring proton (a, 1), the multiplet at 7.12-6.98 ppm corresponds to the pendent aromatic ring protons (10), the multiplet at 4.01-3.98 ppm corresponds to the protons (g, 4) in the CH$_2$ of the ethyl ester groups, the multiplet at 3.11-2.62 ppm corresponds to the protons (b, c, 4) in the CH$_2$ groups of the pendent alkyl chain, the singlet at 2.06 ppm corresponds to the acetylenic CH proton (e, 1), and the multiplet at 0.92-0.88 ppm corresponds to the protons (h, 6) of the CH$_3$ of the ethyl ester groups. The integrations of the $^1$H NMR peaks matched those expected at the respective absorptions. The $^{13}$C NMR spectrum (Figure 31) exhibited the expected peaks, with key identifying absorptions being the ester carbonyl carbons (f) at 168.5 ppm and 168.3 ppm, the newly formed aromatic ring carbons at 140.0 ppm and 139.4 ppm, the acetylene carbons (d, e) at 83.2 ppm and 69.4 ppm, the ethyl ester carbons (g, h) at 61.2 ppm, 61.1 ppm, and 13.5 ppm, and the alkyl carbons (b, c) of the pendent chain at 32.6 ppm and 20.2 ppm. Additional peaks were present in the aromatic region as expected, but were not easily assigned to specific carbons on the aromatic rings. In the IR spectrum (Figure
absorptions were observed at 3294 cm\(^{-1}\) and 2117 cm\(^{-1}\) for the acetylene, 2981 cm\(^{-1}\) for the alkyl C-H, 1722 cm\(^{-1}\) for the ester C=O, and 1603 cm\(^{-1}\) for the aromatic ring C=C. Elemental analysis was expected to show carbon content at 78.85\% and hydrogen at 6.14\%. Two separate analyses yielded carbon contents of 77.94\% and 80.10\% for an average of 79.02\%. One sample was specifically labeled as difficult to burn. The inconsistency points to the need for a better sample handling and/or purification procedure. The hydrogen contents of the analyses were 6.26\% and 6.38\%, both of which are within acceptable limits.

### Diels-Alder with Glucose Derivative

A terephthalate derivative having a protected glucose unit attached was also synthesized, by way of a Diels-Alder reaction. Although it is uncertain if the glucose unit could withstand the conversions necessary to generate a monomer or a subsequent polymer, this reaction may represent a more efficient method of generating a PPV precursor derivative with glucose-derivative functionalization.

A Diels-Alder reaction was used to synthesize 5-[O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)]methyl-2,3-diphenylterephthalate 74 in 80\% yield from equivalent amounts of 1 and 2-propynyl-tetra-O-acetyl-β-D-glucopyranoside 73.
Characterization of 74 was accomplished using $^1$H NMR, $^{13}$C and related DEPT 135 NMR, IR, and elemental analysis. For the $^1$H and $^{13}$C NMR, a correspondence was drawn between calculated values for the expected carbon and hydrogen absorptions and the spectra. A comparison was also done with the $^1$H NMR of the starting material 73 (Figure 33), from which was observed the glucose derivative remained intact and the acetylene was no longer present. Figure 12 gives reference labels to particular carbons (or their attached hydrogens) for clarifying the peak assignments.

Figure 12. Compound 74 with Labeled Atoms.

In the $^1$H NMR spectrum (Figure 34), the singlet at 7.86 ppm corresponds to the newly formed aromatic ring proton (a, 1), the multiplet at 7.20-6.97 ppm corresponds to the pendent aromatic ring protons (10), the multiplet at 5.24-5.11 ppm corresponds to the protons (d, e, f, 3) in the CH of the glucose ring, the doublet at 5.01-4.96 ppm corresponds to the proton (c, 1) in the CH between the glucose and ether oxygens, the multiplet at 4.79-4.63 ppm corresponds to the protons (b, 2) in the CH$_2$ of the benzylic methylene, the multiplet at 4.39-4.15 ppm corresponds to the protons (h, 2) in the CH$_2$ attached to the glucose ring, the multiplet at 4.00-3.93 ppm corresponds to the protons (r, 4) in the CH$_2$ of the ethyl ester groups, the multiplet at 3.79-3.74 ppm corresponds to the proton (g, 1) in the CH of the glucose ring adjacent to the methylene, the multiplet at
2.12-2.02 ppm corresponds to the protons (j, l, n, p, 12) in the CH₃ of the acetyl groups, and the multiplet at 0.89-0.86 ppm corresponds to the protons (s, 6) of the CH₃ of the ethyl ester groups. The integrations of the ¹H NMR peaks matched those expected at the respective absorptions. The ¹³C NMR spectrum (Figure 35) exhibited the expected peaks, with key identifying absorptions being the acetyl carbons (i, k, m, o) at 170.7 ppm, 170.3 ppm, 169.5 ppm and 169.4 ppm, the ester carbonyl carbons (q) at 168.1 ppm and 167.9 ppm, the newly formed aromatic ring carbons at 140.8 ppm and 140.1 ppm, the glucose ring carbons (c, d, e, f, g) at 99.2 ppm, 73.0 ppm, 71.8 ppm, 71.2 ppm and 68.3 ppm, the carbon of the methylene group (h) off the glucose ring at 67.3 ppm, the benzylic methylene (b) at 61.8 ppm, the ethyl ester carbons (r, s) at 61.3 ppm, 61.1 ppm, 13.51 ppm, and 13.48 ppm, and the terminal carbons (j, l, n, p) of the acetyl groups at 20.7 ppm and 20.6 ppm. Additional peaks were present in the aromatic region as expected, but were not easily assigned to specific carbons on the aromatic rings. In the IR spectrum (Figure 36), absorptions were observed at 2980 cm⁻¹ for the alkyl C-H, 1755 cm⁻¹ for the glucopyranosyl acetyl carbonyl C=O, 1724 cm⁻¹ for the terephthalic ethyl ester C=O, 1603 cm⁻¹ for the aromatic ring C=C, and 1039 cm⁻¹ for the ether in the glucose and bridge C-O. Elemental analysis was expected to show carbon content at 63.75% and hydrogen at 5.76%. The analysis results showed carbon content of 63.61% and hydrogen content of 5.76%, which is within acceptable limits.

Elemental analysis was performed on all samples in the series, to establish their composition. The agreement between calculated and found values for carbon and hydrogen for all compounds except 69 and 72 are well within acceptable limits. All analyses for 69 and 72 are out of range of publishable results.
Table 1. Elemental Analysis of Terephthalate Derivatives and Precursor.

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<th>Found</th>
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<td>C: 73.24%</td>
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<tr>
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<td>C: 76.58%</td>
<td>C: 75.19%</td>
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<td>69</td>
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“Click” Cycloaddition Reactions

A series of 1,2,3-triazoles were synthesized by a Huisgen 1,3-dipolar cycloaddition. The initial reaction used relatively inexpensive compounds to establish an efficient method of synthesis. After four variations on published procedures, it was determined that the most pure product at the highest yield was obtained from the one-pot reaction of a halogenated compound with sodium azide, followed by addition of the acetylene with sodium ascorbate and copper (II) sulfate in a 2:1 water/t-butyl alcohol solvent. Purification methods varied and are delineated in the experimental section. The reactions were initially conducted with some common click reactants, then proceeded to reactants with similar properties of the synthesized terephthalate derivatives to allow for solvent and purification adjustments if needed.
The first triazole synthesized was 1-benzyl-4-phenoxyethyl-1,2,3-triazole 79, and was done entirely under standard conditions. The synthesis consisted of nucleophilic substitution of the azide for the halogen followed by 1,3-dipolar cycloaddition. Equal parts of benzyl bromide 75 and sodium azide 76 yielded benzyl azide 77 in situ, which then reacted with phenyl propargyl ether 78 to yield 79. The reaction was catalyzed by copper(I) resulting from the reduction of copper (II) sulfate, with sodium ascorbate as the reductant. Purification (no recrystallization) resulted in a white powder in 75% yield.

Characterization of 79 was accomplished using $^1$H NMR, $^{13}$C and related DEPT 135 NMR, IR, and elemental analysis. Figure 13 gives reference labels to particular carbons (or their attached hydrogens) for clarifying the peak assignments.

Figure 13. Compound 79 with Labeled Atoms.

In the $^1$H NMR spectrum (Figure 37), the singlet at 7.68 ppm corresponds to the triazole ring proton (a, 1), the multiplet at 7.38-6.98 ppm corresponds to the aromatic ring protons (10), the singlet at 5.54 ppm corresponds to the protons (j, 2) in the benzylic CH$_2$, and the singlet at 5.20 ppm corresponds to the protons (c, 2) of the CH$_2$ of the ether. The integrations of the $^1$H NMR peaks matched those expected at the respective absorptions.
The $^{13}$C NMR spectrum (Figure 38) exhibited the expected peaks, with key identifying absorptions being the aromatic carbon (d) attached to the oxygen at 158.2 ppm, the triazole carbons (b, a) at 134.5 ppm and 129.5 ppm, the benzylic CH$_2$ carbon (j) at 61.9 ppm, and the methylene carbon (c) attached to the oxygen at 54.6 ppm. Additional peaks were present in the aromatic region as expected, but were not easily assigned to specific carbons on the aromatic rings. Additional peaks at 60.8 ppm and 52.7 ppm were likely a result of the carbons (j, c) in the 1,5-disubstituted isomer. In the IR spectrum (Figure 39), absorptions were observed at 3134 cm$^{-1}$ for the triazole C-H, 2923 cm$^{-1}$ for the alkyl C-H, 1599 cm$^{-1}$ for the aromatic ring C=C, 1495 cm$^{-1}$ for the triazole C=C, 1331 cm$^{-1}$ for the triazole C-N, and 1225 cm$^{-1}$ for the ether C-O-C. Elemental analysis was expected to show carbon content at 72.43% and hydrogen at 5.70%. The analysis results showed carbon content of 72.21% and hydrogen content of 5.84%, which is within acceptable limits.

The synthesis of 1-benzyl-4-hexyl-1,2,3-triazole 81 involved a nucleophilic substitution by azide 76 on benzyl bromide 75, yielding benzyl azide 77 in situ, which then reacted with 1-octyne 80 to yield 81. The reaction was catalyzed by copper(I) resulting from the reduction of copper (II) sulfate, with sodium ascorbate as the reductant. Recrystallization from ethanol/water yielded a white powder in 32% yield; however the product still showed evidence of solvents after drying under a vacuum.
Characterization of 81 was accomplished using $^1$H NMR, $^{13}$C and related DEPT 135 NMR, IR, and elemental analysis. Figure 14 gives reference labels to particular carbons (or their attached hydrogens) for clarifying the peak assignments.

**Figure 14. Compound 81 with Labeled Atoms.**

In the $^1$H NMR spectrum (Figure 40), the multiplet at 7.38-7.26 ppm corresponds to the triazole ring proton (a, 1) and the aromatic ring protons (5), the singlet at 5.54 ppm corresponds to the protons (i, 2) in the benzylic CH$_2$, the singlet at 2.70 ppm corresponds to the protons (c, 2) of the CH$_2$ of the alkyl chain adjacent to the triazole, the singlet at 1.75 ppm corresponds to the protons (d, e, f, 6) of the CH$_2$ of the alkyl chain, the multiplet at 1.33 ppm corresponds to the protons (g, 2) of the CH$_2$ of the alkyl chain.
adjacent to the CH₃, and the multiplet at 0.89 ppm corresponds to the protons (h, 3) of the CH₃ of the alkyl chain. The peak resolutions were not well defined and integrations of the £H NMR peaks did not match those expected at the absorptions in the range of 2.70-0.89 ppm, likely due to remaining solvent. The £3C NMR spectrum (Figure 41) exhibited the expected peaks, with key identifying absorptions being the aromatic carbons (j, m) at 134.8 ppm and 129.0 ppm, the aromatic carbons (l, n) at 128.7 ppm, the aromatic carbons (k, o) at 128.1 ppm, the alkyl CH₂ carbons (c, d, g) at 31.5 ppm, 25.7 ppm, and 22.5 ppm, the alkyl CH₂ carbons (e, f) at 28.9 ppm, and the methyl carbon (h) at 14.0 ppm. The carbons of the triazole and the benzylic CH₂ were not observed in the expected ranges (approximately 130 ppm and 62 ppm, respectively), possibly due to extended relaxation times. A £3C NMR was conducted, monitoring the spectrum as it progressed through the scans to determine if those expected peaks were subtracted out, but they were not visible between 60 and 450 scans either. In the IR spectrum (Figure 42), absorptions were observed at 3113 cm⁻¹ for the triazole C-H, 2927 cm⁻¹ for the alkyl C-H, 1552 cm⁻¹ for the aromatic ring C=C, 1456 cm⁻¹ for the triazole C=C, and 1327 cm⁻¹ for the triazole C-N. Elemental analysis was expected to show carbon content at 74.04% and hydrogen at 8.70%. The analysis results showed carbon content of 72.46% and hydrogen content of 8.59%, which is not within acceptable limits. This disparity is likely due to purification difficulties which are also evident in some of the other characterization methods.
Conclusions

1. Multifunctional terephthalates could be synthesized by Diels-Alder reactions between cyclopentadienone derivatives and moieties with multiple acetylene groups,
2. Diels-Alder reactions could be used to synthesize terephthalate derivatives with a pendent acetylene with as little as 3 equivalents of diacetylene to 1 equivalent of cyclopentadienones,
3. Glucose can be incorporated into the terephthalate derivatives through the established Diels-Alder method, and
4. A method for Huisgen 1,3-dipolar cycloaddition with terminal acetylenes and terminal azides.

Future Research

From these findings, several avenues exist for further research in this field. The Diels-Alder method may be used to incorporate unprotected glucose into terephthalate derivatives. Reduction or hydrolysis of the terephthalate ethyl esters may be used to convert multifunctional terephthalate derivatives, such as 67, to fluorenone derivatives with more spherical shape to the overall molecule. Also, the cycloaddition method may be useful in attaching desired functional groups to a PPV backbone by polymerizing terephthalate derivatives with pendent acetylene groups 82 or pendent azide groups 83, then clicking with the functional groups.
The acetylene or azide pendent group, however, must be able to withstand the polymerization conditions to be useful, and functionalizing reactions cannot damage the polymer. Another possibility is conducting a cycloaddition with the terephthalate derivatives and desired functional groups prior to polymerization through the terephthalate group, if the desired functional group and triazole can withstand polymerization conditions.
Figure 15. $^1$H NMR Spectrum of 2,5-di(ethoxycarbonyl)-3,4-diphenylcyclopentadienone 1.

Figure 16. $^{13}$C and DEPT 135 NMR Spectrum of 2,5-di(ethoxycarbonyl)-3,4-diphenylcyclopentadienone 1.
Figure 17. IR Spectrum of 2,5-di(ethoxycarbonyl)-3,4-diphenylcyclopentadienone 1.
Figure 18. $^1$H NMR Spectrum of Tris[(2,5-di(ethoxycarbonyl)-3,4-diphenyl)phenylmethyl] amine 67.
Figure 19. $^{13}$C and DEPT 135 NMR Spectrum of Tris[(2,5-di(ethoxycarbonyl)-3,4-diphenyl) phenylmethyl] amine 67.
Figure 20. IR Spectrum of Tris[(2,5-di(ethoxycarbonyl)-3,4-diphenyl) phenylmethyl] amine 67.
Figure 21. $^1$H NMR Spectrum of 5-(5-hexynyl)-2,3-diphenylterephthalate 69 (10:1 ratio).

Figure 22. $^1$H NMR Spectrum of 5-(5-hexynyl)-2,3-diphenylterephthalate 69 (5:1 ratio).
Figure 23. $^1$H NMR Spectrum of 5-(5-hexynyl)-2,3-diphenylterephthalate 69 (3:1 ratio).

Figure 24. $^{13}$C and DEPT 135 NMR Spectrum of 5-(5-hexynyl)-2,3-diphenylterephthalate 69 (3:1 ratio).
Figure 25. IR Spectrum of 5-(5-hexynyl)-2,3-diphenylterephthalate 69 (3:1 ratio).

Figure 26. $^1$H NMR Spectrum of 5-(propargyloxymethyl)-2,3-diphenylterephthalate 70 (10:1 ratio).
Figure 27. $^1$H NMR Spectrum of 5-(propargyloxymethyl)-2,3-diphenylterephthalate 70 (3:1 ratio).

Figure 28. $^{13}$C and DEPT 135 NMR Spectrum of 5-(propargyloxymethyl)-2,3-diphenylterephthalate 70 (3:1 ratio).
Figure 29. IR Spectrum of 5-(propargyloxymethyl)-2,3-diphenylterephthalate 70 (3:1 ratio).

Figure 30. $^1$H NMR Spectrum of 5-(3-butynyl)-2,3-diphenylterephthalate 72 (3:1 ratio).
Figure 31. $^{13}$C and DEPT 135 NMR Spectrum of 5-(3-butynyl)-2,3-diphenylterephthalate 72 (3:1 ratio).

Figure 32. IR Spectrum of 5-(3-butynyl)-2,3-diphenylterephthalate 72 (3:1 ratio).
Figure 33. $^1$H NMR Spectrum of 2-propynyl-tetra-O-acetyl-$\beta$-D-glucopyranoside 73.
Figure 34. $^1$H NMR Spectrum of 5-$[O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)]$methyl-2,3-diphenylterephthalate 74.
Figure 35. $^{13}$C and DEPT 135 NMR Spectrum of 5-[O-(2,3,4,6-tetra-O-acetyl-$\beta$-D-glucopyranosyl)]methyl-2,3-diphenylterephthalate 74.
Figure 36. IR Spectrum of 5-[O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)]methyl-2,3-diphenylterephthalate 74.
Figure 37. $^1$H NMR Spectrum of 1-benzyl-4-phenoxy methyl-1,2,3-triazole 79.

Figure 38. $^{13}$C and DEPT 135 NMR Spectrum of 1-benzyl-4-phenoxy methyl-1,2,3- triazole 79.
Figure 39. IR Spectrum of 1-benzyl-4-phenoxyethyl-1,2,3-triazole 79.

Figure 40. $^1$H NMR Spectrum of 1-benzyl-4-hexyl-1,2,3-triazole 81.
Figure 41. $^{13}$C and DEPT 135 NMR Spectrum of 1-benzyl-4-hexyl-1,2,3-triazole 81.

Figure 42. IR Spectrum of 1-benzyl-4-hexyl-1,2,3-triazole 81.
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VITA

Sarah Bragg was born in Pennsylvania on December 7, 1979. She attended the Governor’s School for Government and International Studies in Richmond, Virginia, for high school and graduated in 1997. She attended the United States Air Force Academy and received her Bachelor of Science in Chemistry in 2001. In 2008, she was admitted to Wright State University to earn her Master of Science in Chemistry.