PALLADIUM-CATALYZED SILYLSTANNYLATION-CYCLIZATION OF 1,6-DIYNES; AXIAL CHIRALITY IN (Z,Z)-1,3-DIENES.

DISSERTATION

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ABSTRACT

The silylstannane-mediated cyclization of mono-substituted α,ω-diynes is readily catalyzed by palladium in the presence of a weakly coordinating phosphine. The products of the reaction are highly functionalized carbo- or heterocycles. The reaction displays wide functional group compatibility, tolerating groups like carboxylic esters, amines and amides. The reaction is not sensitive to moisture or air, and the isolation of the products is operationally simple.

The 1,2-bis-alkylidenecycloalkane products display very interesting stereochemical features. First, the silyl and stannyl groups are pointing toward each other, despite the apparent steric hindrance thus generated. Second, this stereochemistry of the individual double-bonds can lead to axial chirality in the diene system. It has been shown that the 1,2-bis-alkylidenecycloalkanes are indeed axially chiral at low temperatures, but they display a fluxional behaviour at room temperature. The coalescence temperatures have been determined for several compounds, ranging from –70°C to + 20°C, giving insight into the exchange process and the influence of various substituents. Also, the energies of activation of the exchange process have been determined via NMR Line Shape Analysis for a selected set of compounds. These energies appear to depend not
only on the groups on the silicon and the tin, but also on the cyclopentane ring substituents. Free energies of activations in the range of 52.3 to 56.9 kJ.mol\(^{-1}\) were observed.

The synthetic applications of these compounds have been the object of preliminary studies. Although many reactions did not yield the desired products, tin-lithium and tin-halogen exchange and epoxidation of the alkenes seem to offer some promise. Diels-Alder reactions of the destannylated products can be carried out in quantitative yield. The first example of a Stille coupling with a vinyl iodide is also described.
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Figure 4.1. Possible dynamic kinetic resolution pathway.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-BBN</td>
<td>9-Bora-bicyclo[3.3.1] nonyl</td>
</tr>
<tr>
<td>Å</td>
<td>Ångstrom</td>
</tr>
<tr>
<td>AM1</td>
<td>Austin Model 1</td>
</tr>
<tr>
<td>ACN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>AcO</td>
<td>Acetate</td>
</tr>
<tr>
<td>BICP</td>
<td>2(R),2′(R)-Bis-(diphenylphosphine)-1(R),1′(R)-dicyclopentane</td>
</tr>
<tr>
<td>Bu</td>
<td>Butyl</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>calcd</td>
<td>Calculated</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>COD</td>
<td>Cyclooctadiene</td>
</tr>
<tr>
<td>COSY</td>
<td>H-H correlational spectroscopy (NMR)</td>
</tr>
<tr>
<td>Cp</td>
<td>Cyclopentadienyl</td>
</tr>
<tr>
<td>Cp*</td>
<td>Pentamethylocyclopentadienyl</td>
</tr>
<tr>
<td>Cy</td>
<td>Cyclohexyl</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical shift in parts per million (ppm)</td>
</tr>
</tbody>
</table>
d Doublet (spectral)
dba Dibenzylideneacetone
DCC $N,N'$-Dicyclohexylcarbodiimide
DEPT Distortionless Enhancement by Polarization Transfer
DMAP 4-Dimethylaminopyridine
DME Dimethoxyethane
DMF Dimethylformamide
DMSO Dimethylsulfoxide
DUPHOS 1,2-\(\text{Bis-}(2R,5R)-2,5\text{-dimethylphospholano)benzene}\)
equiv. Equivalent
Et Ethyl
etpo 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane
FID Free Induction Decay (NMR)
GC Gas Chromatography
h Hour
hfbc 3-Heptafluorobutyryl-\(d\)-camphorato
HMOC Heteronuclear Multiple Quantum Coherence (NMR)
HPLC High Pressure Liquid Chromatography
Hz Hertz
i. d. Internal Diameter
m Multiplet (spectral)
M Molar

xxvi
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>m-CPBA</td>
<td><em>Meta</em>-chloroperbenzoic acid</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>min.</td>
<td>Minute</td>
</tr>
<tr>
<td>µL</td>
<td>Microliter</td>
</tr>
<tr>
<td>mL</td>
<td>Milliliter</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>mmol</td>
<td>Millimole</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>N</td>
<td>Normal</td>
</tr>
<tr>
<td>NBS</td>
<td><em>N</em>-Bromosuccinimide</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NOE</td>
<td>Nuclear Overhauser Effect (NMR)</td>
</tr>
<tr>
<td>NOESY</td>
<td>Nuclear Overhauser and Exchange Spectroscopy (NMR)</td>
</tr>
<tr>
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</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>ppm</td>
<td>Part Per Million (NMR)</td>
</tr>
<tr>
<td>Pr</td>
<td>Propyl</td>
</tr>
<tr>
<td>q</td>
<td>Quartet (spectral)</td>
</tr>
<tr>
<td>rt</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>t</td>
<td>Triplet (spectral)</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetrabutylammonium fluoride</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>TBSCI</td>
<td>Tert-butyldimethylsilylchloride</td>
</tr>
<tr>
<td>Temp.</td>
<td>Temperature</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
<tr>
<td>TMEDA</td>
<td>Tetramethylethylenediamine</td>
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</table>
CHAPTER 1

INTRODUCTION

In the past, 1,2-bis-alkylidenecycloalkane derivatives have been shown to be extremely useful intermediates in organic synthesis.\textsuperscript{1} They have been used for the synthesis of complex polycyclic molecules, such as steroids (Scheme 1.1) or stereopolide (Scheme 1.2),\textsuperscript{2} and macrocycles.

Those 1,2-bis-alkylidenecycloalkanes are easily prepared from $\alpha,\omega$-diynes or eneynes. Several methodologies have been reported for the cyclization of $\alpha,\omega$-diynes. This reaction can be promoted by low-valent titanium\textsuperscript{3} or zirconium\textsuperscript{4} reagents and proceeds with very high stereoselectivity. The stereoselectivity is easily understood in terms of the mechanism, which involves a metallacycle as an intermediate (Scheme 1.3). The drawbacks of this reaction are the low functional group compatibility of the reaction and the need for a stoichiometric amount of the metal.
Scheme 1.1. Steroid synthesis from a diyne via a 1,2-bis-alkylidene cycloalkane.

Scheme 1.2. Synthesis of Sterepolide via a 1,2-bis-alkylidene cycloalkane.
Catalytic methods have been developed for similar cyclizations as well. For example, one can use a catalytic amount of zirconium in the presence of several equivalents of Grignard reagent (Scheme 1.4). Very good yields have been achieved using this method. The Grignard reagents can also be substituted by trimethylaluminium (Scheme 1.5).

Scheme 1.3. Cyclization of α,ω-diynes promoted by low-valent titanium or zirconium reagents.

Scheme 1.4. Cyclization of a diene catalyzed by zirconium in the presence of a Grignard reagent.
These cyclizations have also been reported to occur in the presence of catalytic amounts of various other metals, such as titanium\(^7\) (Scheme 1.6), yttrium\(^8\) (Scheme 1.7), rhodium\(^9\) (Scheme 1.8) and ruthenium\(^10\) (Scheme 1.9). Asymmetric versions have even been achieved, using rhodium as a catalyst\(^11\) (Scheme 1.10).

Scheme 1.5. Cyclization of a diene catalyzed by zirconium in the presence of trimethylaluminium.

Scheme 1.6. Titanium-catalyzed cyclization of an eneyne.
Scheme 1.7. Yttrium-catalyzed cyclization of a diene.

Scheme 1.8. Rhodium-catalyzed cyclization of an enyne.

Scheme 1.9. Ruthenium-catalyzed cyclization of an enyne.
Nickel$^{12}$ (Scheme 1.11) and palladium$^{12-13}$ (Schemes 1.12 and 1.13) have also been used to catalyze the formation of carbocycles. Nickel can even effect the cyclization of $\omega$-formyl-1,3-dienes$^{14}$ (Scheme 1.14).

![Scheme 1.10. Enantioselective cyclization of an eneyne catalyzed by rhodium.](image1)

![Scheme 1.11. Nickel-catalyzed cyclization of a diene.](image2)

Scheme 1.13. Palladium-catalyzed cyclization of an eneyne.

Another reaction that has enjoyed spectacular success for the synthesis of carbocycles is the olefin metathesis, usually catalyzed by ruthenium or molybdenum\textsuperscript{15} (Scheme 1.15). Recently, advances have been made in the asymmetric version of this reaction\textsuperscript{16} (Scheme 1.16).

Scheme 1.15. Molybdenum-catalyzed olefin metathesis.
Scheme 1.16. Example of enantioselective olefin metathesis.

An important limitation of many of these cyclization reactions is the lack of functional handles in the end-product (often a methylene or an alkyl residue). The utility of such cyclizations could be improved if a protocol can be developed in which a functionalized alkylidene can be generated at the end of the reaction. In this connection, we became interested in trialkylsilyltrialkylstannanes, a set of reagents described by Chenard and Mitchell independently.\textsuperscript{17} This reaction, which is catalytic in palladium, allows the functionalization of an alkyne with very high regio- and stereoselectivities (Scheme 1.17). The silyl and stannyl groups in the final product are always syn, with the silyl group at the terminal end of the alkene. The resulting alkene presents a number of
options for further functionalization thanks to the vinylsilyl and the vinylstannane moieties, which can take part in a variety of cross-coupling and anionic coupling reactions.

\[
\begin{align*}
\text{Ph} & \quad \text{Bu}_3\text{SnSiMe}_2\text{t-Bu} \quad \text{Ph} \\
\text{H} & \quad \text{H} \\
38 & \quad 39
\end{align*}
\]

Scheme 1.17. Silylstannylation of alkynes.

We wondered whether the silylstannylation and cyclization could be carried out in one step, using a catalytic amount of metal, thus yielding a highly functionalized bis-alkylidene cycloalkane. This thesis will describe the development of this reaction and the unusual stereochemical features associated with the 1,3-(Z,Z)-diene products that are formed.

The one-step cyclization and functionalization of \(\alpha,\omega\)-diynes had already been reported, even before our work, using different X-Y groups for the functionalization of bis-acetylenes (Scheme 1.18). Some examples, using silanes as the functionalizing group, are shown in Schemes 1.19 to 1.21.\textsuperscript{18} Carbon monoxide can even be incorporated and polycyclization can be induced, all in one step.
Scheme 1.18. One-step cyclization and functionalization of diynes.

Scheme 1.19. Hydrosilylation and cyclization of diynes.

Scheme 1.20. Hydrosilylation and cyclization of diynes with incorporation of carbon monoxide.
Scheme 1.21. Polycyclization of an enediyne.

Other functionalizing groups have also been used, such as stannanes (Scheme 1.22)\textsuperscript{19}, silylboranes (Scheme 1.23)\textsuperscript{20} and borostannanes (Scheme 1.24).\textsuperscript{21}

Scheme 1.22. Hydrostannylation and cyclization of diynes.
Many of these reactions give products with two functionalized alkene groups, which give rise to a number of derivatization opportunities. Unfortunately, several of these reactions proceed at high temperature, which can be a problem for sensitive substrates. Also, the separation of the side-product can be extremely difficult. Milder
conditions are used for some of the reactions (Scheme 1.24). However, the products are quite unstable and difficult to purify. In addition, in no case has the synthetic potential of the (Z,Z) stereochemical outcome been explicitly discussed.

Dr. Radetich in our group showed that silylstannanes could be used as functionalizing groups for similar reactions (Schemes 1.25 and 1.26). The compounds are extremely stable and can be purified by standard silica gel chromatography. Some of the reaction could even be performed at room temperature. However, very different conditions had to be used for each substrate.

Scheme 1.25. Silylstannylation-cyclization of $N$-tosyl-$N$, $N$-dipropargyl amine 54.

Since we first reported the discovery of the silylstannane-mediated diyne cyclization\textsuperscript{23}, Kang et al. have reported that diallenes can also be used as the starting material, yielding highly functionalized molecules as shown in Scheme 1.27.\textsuperscript{24}

Scheme 1.27. Silylstannylation-cyclization of diallenes.

In addition, Seunghoon Shin in our group has shown that alleneynes can be cyclized in the same fashion (Scheme 1.28, unpublished results).

As mentioned before, the placement of the silyl and stannyl groups ‘inside’ the diene system provides an unusual opportunity for the creation and observation of uncommon helical chirality in these molecules (Scheme 1.29).

In the only related example in the literature, Kiefer et al. showed that the presence of methyl groups in compound 61 leads to helical chirality below –46°C (Scheme 1.30). Since silyl and stannyl groups are much bulkier, we expected helical chirality in our
system as well, although one has to keep in mind that the carbon-silicon and carbon-tin bonds are also longer than carbon-carbon bonds. Can we tune the rate of equilibration by modifying the size of the silyl and stannyl substituents?

This system is ideally suited for a kinetic study using NMR line shape analysis, as described by Kaplan and Fraenkel. This is the most accurate method to determine the enthalpies and entropies of activation of a fast reaction at equilibrium. Line Shape Analysis starts with the density matrix equation in operator form (equation 1.1), which is derived from physics and physical chemistry principles.

\[
i[H]\rho - \frac{\rho}{T} + E\rho = 0 \tag{1.1}
\]

The commutator \([\rho, H]\) describes the NMR properties of the static system studied. The relaxation term \((\rho/T)\) describes the intrinsic line widths of the different peaks. These are largely due to field inhomogeneity. At last, term, \((E\rho)\), accounts for the mechanism and dynamics of the exchange process. One takes all the elements of the density matrix equation whose states correspond to the transitions in the NMR spectrum, which are perturbed by the dynamic process. This generates a coupled set of unhomogeneous equations, first order in elements of the density matrix. These are conveniently expressed and manipulated as a matrix equation. Several of these are shown in Section 3.3. Some of the parameters in the matrix equation (shifts, coupling constants and frequency points) are known. The rate constants are chosen in many trial calculations. The equations are solved for the elements of the density matrix \((\langle \phi_i | \rho | \phi_j \rangle \equiv \rho_{i,j})\) as a function of the frequency. Equation 1.2 provides the NMR lineshape.
Many calculations are done varying the rate constant. Comparison of calculated and observed spectra provides the rate constants. The thermodynamic activation parameters are obtained from the Eyring plot (Equation 1.3) where $k$ is the rate constant and $K$ the temperature in Kelvin.

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} + \ln\left(\frac{k_b}{h}\right)$$

The success of the method depends on the identification of the proper well-behaved spin system to investigate. At the outset we had no knowledge of what would be appropriate, and hence the synthetic chemistry had to be sufficiently general to prepare various derivatives.

This thesis will describe (a) the development of general reaction conditions for the silylstannylation-cyclization of $\alpha,\omega$-diynes, (b) an exploration of the scope, limitations and applications of the resulting products and (c) a dynamic NMR study of the unusual 1,3-($Z, Z$)-dienes generated in the cyclization.
2.1. OPTIMIZATION

As explained earlier, at the outset, there was no uniform set of conditions to effect the silylstannylation-cyclization reaction on different substrates, such as \( N,N \)-dipropargyl-\( N \)-tosylamine 54 and di-\( O \)-methyldipropargylmalonate 42. Further, the scope and limitations of the reaction were not known. This posed a number of problems for the future development and use of the reaction. From early experiments, it became apparent that the reaction could easily be followed by \( ^1 \)H NMR spectroscopy. Therefore, we decided to run the optimization reactions in NMR tubes and follow those reactions by \( ^1 \)H NMR. The different reagents and products had very distinctive peaks in the spectra and this allowed us to run a large number of reactions in a relatively short period. The yields reported in this section were all determined by NMR. When the products could be easily purified, NMR yields and isolated yields were compared. In all cases, good correlations were observed.
2.1.1. STUDY OF THE ROLE OF ANISOLE AS AN INTERNAL STANDARD

The first task was to find an internal standard with no overlapping signal, so that we could reliably assess the yield of each reaction. In $^1$H NMR, the silyl and stannyl groups appeared between 0 and 2.5 ppm. The olefinic peaks of the cyclized product appeared between 5 and 6 ppm and those of the mono- and di-addition products...
appeared between 6 and 7 ppm (very distinct from each other). Some of the ligands used could be found in the aromatic region (see Figure 2.1). Therefore, we concluded that the internal standard should have reliable peaks between 2.5 and 5 ppm. Anisole, which has absorptions around 3.1 ppm \((OCH_3)\), appeared to be a perfect choice, provided it did not interfere with the reaction.

\[
\begin{align*}
\text{Bu}_3\text{SnSiMe}_3, \text{Pd}_2(\text{dba})_3 \\
\text{Tris}(o\text{-tolyl})\text{phosphine} \\
\text{Pd} : \text{Ligand} = 1 : 2 \\
\text{C}_6\text{D}_6, \text{anisole, 0.5 M}
\end{align*}
\]

\[
\begin{align*}
\text{Bu}_3\text{SnSiMe}_3 + \text{SnBu}_3 + \text{Me}_3\text{Si} + \text{Me}_3\text{Si} \rightarrow \text{Bu}_3\text{SnSiMe}_3, \text{Pd}_2(\text{dba})_3 \\
\text{Tris}(o\text{-tolyl})\text{phosphine}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry number</th>
<th>Notebook page number</th>
<th>Anisole (equiv.)</th>
<th>Conditions</th>
<th>Conversion (%)</th>
<th>Ratio (63 : 64 : 65)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SG-II-098</td>
<td>0.15</td>
<td>rt, 17.5 h</td>
<td>44</td>
<td>1.6 : 1 : 0.1</td>
</tr>
<tr>
<td>2</td>
<td>SG-II-099</td>
<td>0.29</td>
<td>rt, 17.5 h</td>
<td>36</td>
<td>1.8 : 1 : 0.1</td>
</tr>
<tr>
<td>3</td>
<td>SG-II-100</td>
<td>0.58</td>
<td>rt, 17.5 h</td>
<td>38</td>
<td>2.6 : 1 : 0.1</td>
</tr>
<tr>
<td>4</td>
<td>SG-II-098</td>
<td>0.15</td>
<td>rt, 17.5 h; 58°C, 3 h</td>
<td>47</td>
<td>1.8 : 1 : 0.1</td>
</tr>
<tr>
<td>5</td>
<td>SG-II-099</td>
<td>0.29</td>
<td>rt, 17.5 h; 58°C, 3 h</td>
<td>41</td>
<td>2.1 : 1 : 0.1</td>
</tr>
<tr>
<td>6</td>
<td>SG-II-100</td>
<td>0.58</td>
<td>rt, 17.5 h; 58°C, 3 h</td>
<td>45</td>
<td>3.1 : 1 : 0.1</td>
</tr>
<tr>
<td>7</td>
<td>SG-II-119</td>
<td>0.58</td>
<td>rt, 17 h</td>
<td>60</td>
<td>1.8 : 1 : 0.1</td>
</tr>
<tr>
<td>8</td>
<td>SG-II-120</td>
<td>9.9</td>
<td>rt, 17 h</td>
<td>49</td>
<td>1.8 : 1 : 0</td>
</tr>
</tbody>
</table>

**Table 2.1. Effect of anisole on the silylstannylation-cyclization of 1,6-heptadiyne 62.**

The results shown in Table 2.1 suggested that anisole slightly favored the cyclized product over the addition products (Entries 1-3), up to a certain concentration of
anisole, after which this effect leveled out (Entries 7 and 8). However, it also decreased the yield of the reaction if used in large amounts. Similar results were obtained when the influence of anisole on the reaction was tested at 58°C (Entries 4-6). Therefore, we concluded that anisole could be used as an internal standard, as long as the same amount of anisole was used in all cases.

![Reaction Scheme]

<table>
<thead>
<tr>
<th>Time</th>
<th>Yield of 63 (%)</th>
<th>Conversion (%)</th>
<th>Ratio 63 : 64 : 65</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 h</td>
<td>7</td>
<td>11</td>
<td>2.2 : 1 : 0</td>
</tr>
<tr>
<td>4.5 h</td>
<td>25</td>
<td>43</td>
<td>1.7 : 1 : 0.1</td>
</tr>
<tr>
<td>6.5 h</td>
<td>28</td>
<td>47</td>
<td>1.5 : 1 : 0.1</td>
</tr>
<tr>
<td>8.5 h</td>
<td>32</td>
<td>55</td>
<td>1.6 : 1 : 0.1</td>
</tr>
<tr>
<td>23.5 h</td>
<td>43</td>
<td>75</td>
<td>1.6 : 1 : 0.1</td>
</tr>
<tr>
<td>47 h</td>
<td>50</td>
<td>89</td>
<td>1.5 : 1 : 0.2</td>
</tr>
<tr>
<td>74 h</td>
<td>52</td>
<td>86</td>
<td>1.9 : 1 : 0.2</td>
</tr>
<tr>
<td>5 days</td>
<td>49</td>
<td>81</td>
<td>2.0 : 1 : 0.3</td>
</tr>
</tbody>
</table>

Table 2.2. Kinetic study of the silylstannylation-cyclization reaction.

2.1.2. KINETIC STUDIES

Following the reaction by taking the $^1$H NMR spectrum of the same sample at various times showed the results listed in Table 2.2. As seen from the data, the reaction was slow at room temperature. Similar kinetic studies at 60°C showed that the rate...
of the reaction was not dramatically increased at higher temperatures. However, in general, after 24 h at room temperature, the yield was near the optimum value. After three days, decomposition of the products started to occur. Most of the reactions run after this observation were checked by NMR after 16-18 h.

2.1.3. CONCENTRATION STUDIES

The effect of the concentration on the reaction was also studied. Not surprisingly, the results showed (Table 2.3) that the more dilute the solution, the higher the proportion of cyclized product. However, the yield also decreased dramatically, making the reaction unusable at high dilutions (Entry 12). Therefore, most reactions were run at a concentration of 0.5 M.

![Chemical structure](image)

Table 2.3. Effect of the concentration on the silylstannylation-cyclization reaction.

<table>
<thead>
<tr>
<th>Entry number</th>
<th>Notebook page number</th>
<th>Concentration</th>
<th>Time</th>
<th>Conversion (%)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>SG-II-094</td>
<td>1 M</td>
<td>16 h</td>
<td>61</td>
<td>0.5 : 1 : 0.3</td>
</tr>
<tr>
<td>11</td>
<td>SG-II-095</td>
<td>0.5 M</td>
<td>16 h</td>
<td>45</td>
<td>1.4 : 1 : 0.1</td>
</tr>
<tr>
<td>12</td>
<td>SG-II-096</td>
<td>0.1 M</td>
<td>16 h</td>
<td>8</td>
<td>3.0 : 1 : 0</td>
</tr>
</tbody>
</table>
2.1.4. SOLVENT STUDIES

Since the polarity of the reaction medium is known to have quite an impact on the outcome of several reactions, various solvents were tested (not all of these were run in NMR tubes). It was obvious from the results shown in Table 2.4 that polar solvents strongly favored the undesired acyclic products (Entries 14-15). So did the absence of any solvent (Entry 16). Another problem encountered in the absence of a solvent was that the catalyst would not dissolve in the silylstannane, thus creating heterogeneous reaction conditions. An apolar solvent such as benzene seemed to be the best solution (Entry 13).

![Chemical diagram](image-url)

<table>
<thead>
<tr>
<th>Entry number</th>
<th>Notebook page number</th>
<th>Solvent</th>
<th>Conversion (%)</th>
<th>Ratio $63 : 64 : 65$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>SG-II-119</td>
<td>C$_6$D$_6$</td>
<td>60</td>
<td>1.8 : 1 : 0.1</td>
</tr>
<tr>
<td>14</td>
<td>SG-II-121</td>
<td>DME</td>
<td>41</td>
<td>0.8 : 1 : 0.2</td>
</tr>
<tr>
<td>15</td>
<td>SG-II-122</td>
<td>THF</td>
<td>45</td>
<td>1.1 : 1 : 0.2</td>
</tr>
<tr>
<td>16</td>
<td>SG-II-123</td>
<td>None</td>
<td>77</td>
<td>0.4 : 1 : 0.6</td>
</tr>
</tbody>
</table>

Table 2.4. Influence of the solvent on the silylstannylation-cyclization reaction.
2.1.5. STUDY OF THE EFFECT OF THE RATIO OF DIYNE TO SILYLSTANNA NANE

The effect of the relative stoichiometries of the diyne and the silylstannane was also studied (Table 2.5). As could be expected, a larger amount of silylstannane resulted in much higher conversions of the diyne. However, it also decreased the proportion of the desired cyclization product formed. So, increasing the amount of silylstannane in the reaction medium is not a solution to improve the yield of the cyclization product.

2.1.6. CATALYST STUDIES

Different palladium sources were tested as catalysts. The results (Table 2.6) showed that the ligands present around the palladium had a large effect on the reaction. Among the catalysts tested, Pd$_2$(dba)$_3$ was the one giving the best ratio of cyclized to acyclic products at room temperature (entry 20). Although Pd(PPh$_3$)$_4$ gave higher conversions, the selectivity was poor (entry 22). Interestingly, Cl$_2$Pd(PPh$_3$)$_2$ and

Table 2.5. Effect of the ratio of diyne to silylstannane on the silylstannylation-cyclization reaction.

<table>
<thead>
<tr>
<th>Entry number</th>
<th>Notebook page number</th>
<th>Ratio of diyne to Bu$_3$SnSiMe$_3$</th>
<th>Conversion (%)</th>
<th>Ratio 63 : 64 : 65</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>SG-II-101</td>
<td>1 : 1</td>
<td>47</td>
<td>2.2 : 1 : 0.1</td>
</tr>
<tr>
<td>18</td>
<td>SG-II-102</td>
<td>1 : 3.1</td>
<td>99</td>
<td>1.8 : 1 : 1.1</td>
</tr>
<tr>
<td>19</td>
<td>SG-II-103</td>
<td>1 : 6.2</td>
<td>96</td>
<td>1.9 : 1 : 0.9</td>
</tr>
</tbody>
</table>
Pd(OAc)$_2$ were much more active at 65ºC than at room temperature (Entries 20 and 25). Pd(OAc)$_2$ even gave excellent selectivity at higher temperatures (4.5:1:0), unfortunately with a lower conversion (50 %).

Table 2.6. Effect of the catalyst precursor on the silylstannylation-cyclization reaction.

<table>
<thead>
<tr>
<th>Entry number</th>
<th>Notebook page number</th>
<th>Catalyst</th>
<th>Conversion after 16 h (%)</th>
<th>Ratio 63 : 64 : 65 after 16 h</th>
<th>Conversion after 45 h (%)</th>
<th>Ratio 63 : 64 : 65 after 45 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>SG-II-124</td>
<td>Pd$_2$(dba)$_3$</td>
<td>52</td>
<td>2.1 : 1 : 0.1</td>
<td>63</td>
<td>2.5 : 1 : 0.2</td>
</tr>
<tr>
<td>21</td>
<td>SG-II-125</td>
<td>Cl$_2$Pd(PPh$_3$)$_2$</td>
<td>5</td>
<td>0 : 1 : 0</td>
<td>69</td>
<td>0.5 : 1 : 0.4</td>
</tr>
<tr>
<td>22</td>
<td>SG-II-126</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>73</td>
<td>0.1 : 1 : 0.3</td>
<td>70</td>
<td>0.3 : 1 : 0.5</td>
</tr>
<tr>
<td>23</td>
<td>SG-II-127</td>
<td>Cl$_2$Pd(ACN)$_2$</td>
<td>26</td>
<td>1.2 : 1 : 0</td>
<td>58</td>
<td>1.5 : 1 : 0.2</td>
</tr>
<tr>
<td>24</td>
<td>SG-II-128</td>
<td>[ClPd(allyl)]$_2$</td>
<td>47</td>
<td>1.3 : 1 : 0.1</td>
<td>54</td>
<td>1.4 : 1 : 0.3</td>
</tr>
<tr>
<td>25</td>
<td>SG-II-129</td>
<td>Pd(OAc)$_2$</td>
<td>3</td>
<td>0.6 : 1 : 0</td>
<td>50</td>
<td>4.5 : 1 : 0</td>
</tr>
<tr>
<td>26</td>
<td>SG-II-130</td>
<td>Cl$_2$Pd(PhCN)$_2$</td>
<td>48</td>
<td>1.5 : 1 : 0</td>
<td>74</td>
<td>2.1 : 1 : 0</td>
</tr>
</tbody>
</table>

2.1.7. PHOSPHINE STUDIES

Since the ligands on the palladium seemed to have a very important role on the outcome of the reaction, the effect of the phosphine added to the reaction mixture was also studied (Table 2.7). Very electron-rich phosphines, such as tris-(4-methoxyphenyl)-phosphine, completely stopped the reaction (Entry 28). On the other hand, an electron-poor phosphine, such as tris- (pentafluorophenyl)phosphine, gave
extremely good selectivities, since none of the addition products were observed (entry 29). Given how difficult it was to separate the cyclized product from the addition side-products, this was an extremely important observation, although the yield was only 44 % for this substrate (vide infra for other diynes).

Table 2.7. Phosphine effect on the silylstannylation-cyclization of 1,6-heptadiyne 62.

<table>
<thead>
<tr>
<th>Entry number</th>
<th>Notebook page number</th>
<th>Phosphine</th>
<th>Conversion (%)</th>
<th>Ratio 63 : 64 : 65</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>SG-II-132</td>
<td>Tris-(2-methylphenyl)phosphine</td>
<td>54</td>
<td>1 : 0.7 : 0.1</td>
</tr>
<tr>
<td>28</td>
<td>SG-II-133</td>
<td>Tris-(4-methoxyphenyl)phosphine</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>29</td>
<td>SG-II-134</td>
<td>Tris-(pentafluorophenyl)phosphine</td>
<td>44</td>
<td>1 : \ : \</td>
</tr>
<tr>
<td>30</td>
<td>SG-II-135</td>
<td>Tris-(2-furyl)phosphine</td>
<td>13</td>
<td>1 : 3.1 : \</td>
</tr>
</tbody>
</table>

To test if this ligand effect was general, another phosphine study was carried on di-O-methyldipropargylmalonate 42 (Table 2.8). No internal standard was used in this study. The yields were estimated by relative integration of the trimethylsilyl peaks for the silylstannane and of the cyclized product in the $^1$H NMR spectrum. There again, tris-(pentafluorophenyl)phosphine, along with tris-(2,4,6-trimethylphenyl)phosphine, were the best phosphines, giving the desired product in 65 % yield, with none of the addition products being detected (Entries 31-32). If the phosphines used were more electron-rich
((2-methoxyphenyl)diphenylphosphine (Entry 36); tris-(4-methoxyphenyl)phosphine (Entry 38)) or less hindered tris-(o-tolyl)phosphine (Entry 33); triphenylphosphine (Entry 39)), the yields went down dramatically. Therefore, we concluded that an electron-poor or a bulky phosphine, which are less coordinating, were necessary for good selectivities and yields of the reaction. Finally, the reaction was carried out without using any phosphine at all. This reaction was tried on 1,6-heptadiyne. Unfortunately, the yields were highly variable (8-38 %), possibly due to catalyst decomposition.

\[
\begin{align*}
\text{Bu}_3\text{SnSiMe}_3, \text{Pd}_2(\text{dba})_3 & \quad \text{C}_6\text{D}_6, \text{rt}, 16 \text{ h}, 0.5 \text{ M} \\
\text{Pd} : \text{Ligand} & = 1 : 2 \\
\text{Entry Notebook page number Phosphine Yield of 57} \\
31 & \text{SG-III-34} & \text{Tris-(pentafluorophenyl)phosphine} & 65 \% \\
32 & \text{SG-III-41} & \text{Tris-(2,4,6-trimethylphenyl)phosphine} & 65 \% \\
33 & \text{SG-III-38} & \text{Tris-(o-tolyl)phosphine} & 50 \% \\
34 & \text{SG-III-39} & \text{Tris-(2,6-dimethoxyphenyl)phosphine} & 44 \% \\
35 & \text{SG-III-37} & \text{Tricyclohexylphosphine} & 28 \% \\
36 & \text{SG-III-40} & \text{(2-methoxyphenyl)diphenylphosphine} & 20 \% \\
37 & \text{SG-III-35} & \text{Tris-(2-furyl)phosphine} & 14 \% \\
38 & \text{SG-III-36} & \text{Tris-(4-methoxyphenyl)phosphine) } & 11 \% \\
39 & \text{SG-III-42} & \text{Triphenylphosphine} & 0 \% \\
40 & \text{SG-III-43} & \text{Triethylphosphine} & 0 \% \\
41 & \text{SG-III-44} & \text{Triethylphosphite} & 0 \%
\end{align*}
\]

Table 2.8. Phosphine effect on the silylstannylation-cyclization of di-O-methyl-dipropargylmalonate 42.
2.1.8. OPTIMIZATION OF THE REACTION CONDITIONS USING TRIS-(PENTAFLUOROPHENYL)PHOSPHINE

The results summarized in Table 2.9 showed that the concentration of the reaction mixture (Entries 42 and 43) and the amount of anisole (Entries 42 and 44) used did not influence the yield of the reaction as much as with tris-(o-tolyl)phosphine. The ratio of diyne to silylstannane had a minor effect on the yield (Entries 42, 45 and 46). A study of the kinetics of the reaction at 63°C led to the conclusion that, again, the optimum reaction time was 15 h (after that, decomposition began to set in). None of the acyclic addition products were observed under these conditions.

Table 2.9. Silylstannylation-cyclization of 1,6-heptadiyne in the presence of tris-(pentafluorophenyl)phosphine.

<table>
<thead>
<tr>
<th>Entry number</th>
<th>Notebook page number</th>
<th>diyne : Bu₃SnSiMe₃</th>
<th>Concentration</th>
<th>Anisole (equiv.)</th>
<th>Yield of 63 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>SG-II-141</td>
<td>1 : 1</td>
<td>0.5 M</td>
<td>0.58</td>
<td>27</td>
</tr>
<tr>
<td>43</td>
<td>SG-II-142</td>
<td>1 : 1</td>
<td>1 M</td>
<td>0.58</td>
<td>26</td>
</tr>
<tr>
<td>44</td>
<td>SG-II-143</td>
<td>1 : 1</td>
<td>0.5 M</td>
<td>1.16</td>
<td>26</td>
</tr>
<tr>
<td>45</td>
<td>SG-II-144</td>
<td>1 : 2</td>
<td>0.5 M</td>
<td>0.58</td>
<td>33</td>
</tr>
<tr>
<td>46</td>
<td>SG-II-145</td>
<td>1 : 3</td>
<td>0.5 M</td>
<td>0.58</td>
<td>34</td>
</tr>
</tbody>
</table>
### Table 2.10. Optimization of the silylstannylation-cyclization reaction in the presence of tris-(pentafluorophenyl)phosphine.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Pd : P ratio</th>
<th>Pd (mol %)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>SG-II-167</td>
<td>1 : 1</td>
<td>1.7</td>
<td>38 % a</td>
</tr>
<tr>
<td>48</td>
<td>SG-II-168</td>
<td>1 : 1</td>
<td>5.2</td>
<td>27 % a</td>
</tr>
<tr>
<td>49</td>
<td>SG-II-166</td>
<td>1 : 2.2</td>
<td>1.7</td>
<td>28 %</td>
</tr>
<tr>
<td>50</td>
<td>SG-II-169</td>
<td>1 : 2</td>
<td>5.2</td>
<td>31 %</td>
</tr>
</tbody>
</table>

a: some unidentified impurities could be observed in the $^1$H NMR spectrum.

2.1.9. STUDY OF THE ROLE OF THE AMOUNT AND RATIO OF PALLADIUM TO PHOSPHINE.

Reducing the amount of palladium and phosphine used can be economically and environmentally important, especially in large-scale processes. However, the results shown in Table 2.10 suggested that the most efficient conditions involved the use of a ratio of palladium to phosphine of 1 : 2 (Entries 49 and 50). A ratio of 1 : 1 gave rise to side-reactions, making the purification process more difficult (Entries 47 and 48). The catalyst loading seemed to have only a minor effect, since the yields for 1.7 and 5.2 % loadings were similar (Entries 49 and 50). In the absence of catalyst there was very little reaction: stirring the diyne with silylstannane and anisole for 19 h at 70$^\circ$C yielded only 1 % of the cyclized product, the rest of the starting material being unconverted.
2.2. SCOPE AND LIMITATIONS

2.2.1. SYNTHESIS OF THE SUBSTRATES

Scheme 2.1. Synthesis of di-\(\text{O}\)-methyldipropargylmalonate \(42\).\(^{22,27}\)

\[
\text{H}_3\text{COOC} \xrightarrow{\text{H}_3\text{COOC}} \text{COOCH}_3 + \text{NaH} + \text{Br} \xrightarrow{\text{rt, 17 h}} \text{99 \%} \xrightarrow{\text{Entry 51, SG-II-267}} \text{COOCH}_3
\]

\(42\)

Scheme 2.2. Synthesis of \(\text{O}\)-methyl-2-(2-propynyl)-4-pentynoate \(66\).\(^{28}\)

\[
\text{H}_3\text{COOC} \xrightarrow{\text{H}_3\text{COOC}} \text{COOCH}_3 + \text{LiCl} + \text{H}_2\text{O} \xrightarrow{\text{DMSO, 170-200°C, 1.5 h}} \text{49 \%} \xrightarrow{\text{Entry 52, SG-II-296}} \text{H}_3\text{COOC}
\]

\(66\)
Scheme 2.3. Synthesis of 2-(2-propynyl)-4-pentynoic acid 67.²⁹

Scheme 2.4. Synthesis of \([(S)-\alpha\text{-carboxymethoxyphenylmethyl}]-2-(2\text{-propynyl})-4\text{-pentynoate} 68.³⁰

Scheme 2.5. Synthesis of \((R)-[(\alpha\text{-methyl})\text{benzyl}]\text{-}N,N\text{-dipropargylamine} 69.³¹
Scheme 2.6. Synthesis of $(S)$-[(α-methyl)benzyl]-\(N,N\)-dipropargylamine 70.$^{31}$

Scheme 2.7. Synthesis of oct-7-ene-2-yne-4-ol 71.$^{32}$

Scheme 2.8. Synthesis of 4-(\textit{tert}-butyldimethylsiloxy)-oct-7-ene-2-yne 72.$^{33}$
2.2.2. FUNCTIONAL GROUP COMPATIBILITY

The next step in the development of the silylstannylation-cyclization reaction was to test its functional group compatibility. Di-O-methyl dipropargylmalonate 42 was tested first (Table 2.11). Using the conditions found earlier [Pd₂(dba)₃, tris-(pentafluorophenyl)-phosphine, at room temperature overnight], we were able to get a very acceptable yield of 71 % of the cyclized product (Entry 60). None of the addition products were observed. Dr. Radetich had been able to obtain 79 % yield of this product using different conditions²² (Entry 59).

![Chemical Structure](image)

Table 2.11. Optimization of the silylstannylation-cyclization of di-O-methyl dipropargylmalonate 42.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Phosphine</th>
<th>Time</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>59</td>
<td>RB-412-112 ²</td>
<td>Tris-(o-tolyl)phosphine</td>
<td>2 h</td>
<td>65-70</td>
<td>79</td>
</tr>
<tr>
<td>60</td>
<td>SG-II-194</td>
<td>Tris-(pentafluorophenyl)phosphine</td>
<td>22 h</td>
<td>rt</td>
<td>71</td>
</tr>
<tr>
<td>61</td>
<td>SG-II-206</td>
<td>Tris-(pentafluorophenyl)phosphine</td>
<td>18 h</td>
<td>61</td>
<td>69</td>
</tr>
</tbody>
</table>

²: result obtained by Dr. Radetich²².
When the monoester O-methyl-2-(2-propynyl)-4-pentynoate 66 was reacted under the “standard” set of conditions, 66 % yield of the clean cyclized product was obtained (Scheme 2.9). This reaction was performed both inside a glove-box (oxygen- and water-free atmosphere) and outside the glove-box using pipet techniques. Both gave the same results, showing that this reaction is NOT sensitive to water or oxygen.

Scheme 2.9. Silylstannylation-cyclization of O-methyl-2-(2-propynyl)-4-pentynoate 66.

The mandelate ester 68 was also reacted under the same set of conditions to give 75 % of product (Scheme 2.10). Again, no side product was observed.
Scheme 2.10. Silylstannylation-cyclization of \([(S)-\alpha\text{-carboxymethoxyphenylmethyl}]-2\text{-}(2\text{-propynyl})\text{-4-pynoate} 68.

Table 2.12. Silylstannylation-cyclization of \(N, N\text{-dipropargyl-N-tosylamine} 54.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Catalyst</th>
<th>Phosphine</th>
<th>Time</th>
<th>Temp.</th>
<th>Yield of 55</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>RB-437-138-3*</td>
<td>(ACN)\text{PdCl}_2</td>
<td>none</td>
<td>1 day</td>
<td>rt</td>
<td>45%</td>
</tr>
<tr>
<td>65</td>
<td>SG-II-175</td>
<td>(ACN)\text{PdCl}_2</td>
<td>\text{Tris-(pentafluorophenyl)-phosphine}</td>
<td>24 h</td>
<td>rt</td>
<td>27%</td>
</tr>
<tr>
<td>66</td>
<td>SG-II-181</td>
<td>(ACN)\text{PdCl}_2</td>
<td>\text{Tris-(pentafluorophenyl)-phosphine}</td>
<td>17 h</td>
<td>63º C</td>
<td>61%</td>
</tr>
<tr>
<td>67</td>
<td>SG-II-183</td>
<td>\text{Pd}_2\text{(dba)}_3</td>
<td>\text{Tris-(pentafluorophenyl)-phosphine}</td>
<td>17 h</td>
<td>63º C</td>
<td>58%</td>
</tr>
<tr>
<td>68</td>
<td>SG-II-189</td>
<td>\text{Pd}_2\text{(dba)}_3</td>
<td>\text{Tris-(pentafluorophenyl)-phosphine}</td>
<td>18 h</td>
<td>rt</td>
<td>77%</td>
</tr>
</tbody>
</table>

*: result obtained by Dr. Radetich\textsuperscript{22}.
The compatibility of the reaction with nitrogen moieties was then addressed. Using the standard conditions, \(N,N\)-dipropargyl-\(N\)-tosylamine 54 was cyclized in 77 % yield with absolutely no addition side-products (Table 2.12, Entry 68). When the reaction was performed at 63ºC overnight, the product was obtained in lower yield (Entry 67). Dr. Radetich had been able to get 45 % yield using a different set of conditions 22 (Entry 64).

\((R)\)-[(\(\alpha\)-Methyl)benzyl]-\(N,N\)-dipropargylamine 70 was also cyclized, using the same conditions, in 79 % yield (Table 2.13, Entry 69). At 61ºC for 18 h, the yield was 72 % (Entry 71). In the absence of the phosphine at room temperature, the product was obtained in only 54 % yield (Entry 70).

![Chemical structure](image.png)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Phosphine</th>
<th>Time</th>
<th>Temperature</th>
<th>Yield of 75</th>
</tr>
</thead>
<tbody>
<tr>
<td>69</td>
<td>SG-II-196</td>
<td>(Tris)-(pentafluorophenyl)phosphine</td>
<td>24 h</td>
<td>rt</td>
<td>79 %</td>
</tr>
<tr>
<td>70</td>
<td>SG-II-202</td>
<td>None</td>
<td>23 h</td>
<td>rt</td>
<td>54 %</td>
</tr>
<tr>
<td>71</td>
<td>SG-II-204</td>
<td>(Tris)-(pentafluorophenyl)phosphine</td>
<td>18 h</td>
<td>61ºC</td>
<td>72 %</td>
</tr>
</tbody>
</table>

Table 2.13. Silylstannylation-cyclization of \((R)\)-[(\(\alpha\)-methyl)benzyl]-\(N,N\)-dipropargylamine 69.
Scheme 2.11. Silylstannylation-cyclization of (S)-[(α-methyl)benzyl]-N,N-dipropargylamine 70.

The (S) isomer of the substrate was also cyclized under standard conditions in 85 \% yield (Scheme 2.11).

2.2.3. SCOPE OF THE SILYlstANNANES USED
2.2.3.1. SYNTHESIS OF THE SILYlstANNANES

All the silylstannanes used were synthesized in the same fashion, reacting the tin hydride with lithium di-iso-propylamine and then quenching the tin anion with the desired chlorosilane\textsuperscript{22, 34}. When successful, the silylstannanes were produced in excellent yield, requiring very little purification. For reasons we do not yet understand, trimethylsilyltriphenylstannane and triethylsilyltriphenylstannane could not be obtained clean, using the same procedure (and reagents!) as for the other silylstannanes (Table 2.14, Entries 77 and 78).
HN\((i-Pr)_3\) + BuLi + R_3SnH + ClSiR'\_3 \rightarrow R_3SnSiR'_3

\[77-84\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Molecule number</th>
<th>Silylstannane</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>73</td>
<td>SG-II-081</td>
<td>77</td>
<td>Bu_3SnSiMe_3</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>74</td>
<td>SG-II-281</td>
<td>78</td>
<td>Bu_3SnSiMe_2-t-Bu</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>75</td>
<td>SG-III-073</td>
<td>79</td>
<td>Bu_3SnSiEt_3</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>76</td>
<td>SG-III-074</td>
<td>80</td>
<td>Bu_3SnSi((i-Pr)_3)</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>77</td>
<td>SG-III-094</td>
<td>81</td>
<td>Ph_3SnSiMe_3</td>
<td>Failed</td>
</tr>
<tr>
<td>78</td>
<td>SG-III-095</td>
<td>82</td>
<td>Ph_3SnSiEt_3</td>
<td>Failed</td>
</tr>
<tr>
<td>79</td>
<td>SG-III-081</td>
<td>83</td>
<td>Ph_3SnSi((i-Pr)_3)</td>
<td>68 %</td>
</tr>
<tr>
<td>80</td>
<td>SG-III-082</td>
<td>84</td>
<td>Ph_3SnSiMe_2-t-Bu</td>
<td>&gt; 99 %</td>
</tr>
</tbody>
</table>

**Table 2.14. Synthesis of the various silylstannanes.**

**2.2.3.2. USE OF THE SILYLSTANNANES**

The reactions of the various silylstannanes with di-\(O\)-methyldipropargylmalonate 42 gave very interesting results (Table 2.15). The reactions with tert-butyldimethylsilyltrimethylstannane did not work (presumably, the product is unstable to isolation, Entry 81). For the various tri-\(n\)-butylstannanes, an increase in the bulk of the silyl group decreased the yield dramatically even with higher reaction temperatures, as could be expected (Entries 82-88). The most dramatic example was obtained by using tris-(iso-propyl)silyltri-\(n\)-butylstannane, where no product could be isolated, even at 68°C for 16 h (Entry 88). Interestingly, the triphenylstannanes behaved quite differently, as a very good yield could be obtained for tert-butyldimethylsilyltriphenylstannane, presumably more for electronic than for steric reasons (Entry 89). Indeed, highest yields of silylstannylation-cyclization products were obtained for this reagent. Even tris-(iso-propyl)silyltriphenylstannane reacted to give 27 % yield of the desired product at 68°C for 16 h (entry 92).
The same observations were made in the reactions of \( O \)-methyl-2-(2-propynyl)-4-pentynoate 66 with the various silylstannanes (Table 2.16). With tert-butylidimethylsilyltri-\( n \)-butylstannane, the product was obtained in only 4 % yield at 52°C for 17 h (entry 94), whereas the triphenylstannane equivalent yields the desired product in 89 % at room temperature (entry 96)!

Reaction of (\( tert \)-butylidimethylsilyl)triphenylstannane with \([S]-\alpha\text{-carbomethoxyphenylmethyl}]\)-2-(2-propargyl)-4-pentynoate 68 also proceeded in very good yield at room temperature (Scheme 2.12).
Table 2.16. Reactions of \(O\)-methyl-2-(2-propynyl)-4-pentynoate 66 with various silylstannanes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>(R_3)</th>
<th>(R'_3)</th>
<th>Molecule number</th>
<th>Temperature</th>
<th>Time</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>93</td>
<td>SG-II-284</td>
<td>Bu3</td>
<td>Me2-t-Bu</td>
<td>91</td>
<td>rt</td>
<td>23 h</td>
<td>0</td>
</tr>
<tr>
<td>94</td>
<td>SG-III-064</td>
<td>Bu3</td>
<td>Me2-t-Bu</td>
<td>91</td>
<td>52°C</td>
<td>17 h</td>
<td>4</td>
</tr>
<tr>
<td>95</td>
<td>SG-III-008</td>
<td>Bu3</td>
<td>Me2-t-Bu</td>
<td>91</td>
<td>115°C</td>
<td>15 h</td>
<td>0</td>
</tr>
<tr>
<td>96</td>
<td>SG-III-136</td>
<td>Ph3</td>
<td>Me2-t-Bu</td>
<td>92</td>
<td>rt</td>
<td>15 h</td>
<td>89</td>
</tr>
</tbody>
</table>

Scheme 2.12. Reaction of (tert-butyldimethylsilyl)triphenylstannane with \([(S)\-\alpha\-carbomethoxyphenylmethyl]-2-(2-propargyl)-4-pentynoate 68.
Table 2.17. Reactions of (R)-[(α-methyl)benzyl]dipropargylamine 69 with various silylstannanes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>R₃SnSiR’₃</th>
<th>R’₃</th>
<th>Molecule number</th>
<th>Time</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>98</td>
<td>SG-II-203</td>
<td>Me₃</td>
<td>Me₂-t-Bu</td>
<td>94</td>
<td>14 h</td>
<td>16 %</td>
</tr>
<tr>
<td>99</td>
<td>SG-III-115</td>
<td>Bu₃</td>
<td>Me₂-t-Bu</td>
<td>95</td>
<td>15 h</td>
<td>25 %</td>
</tr>
<tr>
<td>100</td>
<td>SG-III-190</td>
<td>Ph₃</td>
<td>Me₂-t-Bu</td>
<td>96</td>
<td>15 h</td>
<td>58 %</td>
</tr>
</tbody>
</table>

Scheme 2.13. Reaction of (S)-[(α-methyl)benzyl]dipropargylamine 70 with (dimethyl-tert-butylsilyl)trimethylstannane.

Similar results were obtained with the nitrogen-containing substrates, although the yield of the reaction of (R)-[(α-methyl)benzyl]-N,N-dipropargylamine 69 with
(tert-butyldimethylsilyl)triphenylstannane was much lower than for the substrates mentioned earlier (Table 2.17, Entry 100). It should also be mentioned that the product of the reaction of (tert-butyldimethylsilyl)trimethylstannane with [(α-methyl)benzyl]-N,N-dipropargylamine 69 is quite unstable (Entry 98).

Scheme 2.14. Reaction of N-tosyl-N,N-dipropargylamine 54 with (tert-butyldimethylsilyl)triphenylstannane.

2.2.4. LIMITATIONS

2.2.4.1. RING SIZES

We tried to cyclized 4- through 8-membered rings. Only the 5-membered rings could be obtained. All the other substrates led exclusively to mono- and di-addition products (Tables 2.18 to 2.21). However, extensive optimization was done only for 5-membered rings. It is possible that, by placing more effort on the optimization of a different ring size, cyclization could be achieved, especially if substituents were present on the alkyl chain connecting the two alkynes in the starting diyne (thus taking
advantage of the Thorpe-Ingold effect\textsuperscript{35}). Indeed, the studies done on the 5-membered rings showed that the plain unsubstituted substrates were the most difficult ones to cyclize.

\[
\text{Entry} & \quad \text{Notebook page number} & \quad \text{Phosphine} & \quad \text{Temperature} & \quad \text{Time} & \quad \text{Yield} \\
103 & SG-II-109 & \text{Tris-}(\text{o-tolyl})\text{phosphine} & \text{rt} & 40 \text{ h} & 26 \% \\
104 & SG-II-170 & \text{Tris-}(\text{pentafluorophenyl})\text{phosphine} & 68^\circ \text{C} & 16 \text{ h} & 7 \% \\

\textbf{Table 2.18. Attempted silylstannylation-cyclization of 1,5-hexadiyne 99.}

\[
\text{Entry} & \quad \text{Notebook page number} & \quad \text{Phosphine} & \quad \text{Anisole} & \quad \text{Conditions} & \quad \text{Yield} \\
105 & SG-II-054 & \text{Tris-}(\text{o-tolyl})\text{phosphine} & 0 & 58^\circ \text{C}, 2 \text{ h}; \text{rt, 40 h} & 30 \\
106 & SG-II-154 & \text{Tris-}(\text{pentafluorophenyl})\text{phosphine} & 0.58 & 70^\circ \text{C}, 18 \text{ h} & 6 \text{ (NMR)} \\
107 & SG-II-155 & \text{None} & 0.58 & 70^\circ \text{C}, 18 \text{ h} & 4 \text{ (NMR)} \\

\textbf{Table 2.19. Attempted silylstannylation-cyclization of 1,7-octadiyne 101.}
Table 2.20. Attempted silylstannylation-cyclization of 1,8-nonadiyne 103.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Phosphine</th>
<th>Anisole (equiv.)</th>
<th>Conditions</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
<td>SG-II-078</td>
<td>Tris-(o-tolyl)phosphine</td>
<td>0</td>
<td>64°C, 2 h</td>
<td>30</td>
</tr>
<tr>
<td>109</td>
<td>SG-II-173</td>
<td>Tris-(pentafluorophenyl)phosphine</td>
<td>0.58</td>
<td>68°C, 16 h</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 2.21. Attempted silylstannylation-cyclization of 1,9-decadiyne 105.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Phosphine</th>
<th>Conditions</th>
<th>Yield of 106</th>
<th>Yield of 107</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>SG-II-110</td>
<td>Tris-(o-tolyl)phosphine</td>
<td>rt, 40 h</td>
<td>46 %</td>
<td>24 %</td>
</tr>
<tr>
<td>111</td>
<td>SG-II-174</td>
<td>Tris-(pentafluorophenyl)phosphine</td>
<td>68°C, 16 h</td>
<td>4 %</td>
<td>0 %</td>
</tr>
</tbody>
</table>

2.2.4.2. OTHER FUNCTIONALITIES

The only unsubstituted diyne which failed to cyclize was 2-(2-propynyl)-4-pentynoic acid 67. The starting material apparently decomposed under the reaction conditions, suggesting that the reaction is not compatible with unprotected carboxylic acids (Scheme 2.15).
Scheme 2.15. Attempted silylstannylation-cyclization of 2-(2-propynyl)-4-pentynoic acid 67.

Silylstannylation-cyclization of substituted diynes could provide a route to tri- and tetrasubstituted bis-alkylidene cycloalkanes. Therefore, (R)-[(α-methyl)benzyl]-N,N-di(2-butynyl)amine 108 was subjected to the usual reaction conditions. Unfortunately, the starting material decomposed again. No desired product could be isolated (Scheme 2.16).

Scheme 2.16. Attempted silylstannylation-cyclization of (R)-[(α-methyl)benzyl]-N,N-di(2-butynyl)amine 108.
The cyclization of enynes was also attempted. The cyclization of di-O-methylallylpropargylmalonate 109 could be achieved in 49% yield using \textit{tris-} (pentafluorophenyl)phosphine (Table 2.22, Entry 116). Although this yield was still rather low, this was a good improvement on the maximum yield of 35% obtained by Dr. Radetich\textsuperscript{22} (Entry 114). So, \textit{tris-} (pentafluorophenyl)phosphine seems to be a good choice of ligand for the silylstannylation-cyclization of enynes also, although more optimization is required to make this process practical.

When a substituted enyne such as 4-\textit{(}\textit{tert}-butyldimethylsiloxy)\textit{-}oct-7-ene-2-yne 72 was subjected to the standard reaction conditions, no product could be obtained. In this case, some starting material could be recovered (Table 2.23). This together with other observations confirm one of the limitations of the silylstannylation-cyclization reaction, namely it works best with terminal alkynes.

![Diagram](https://example.com/diagram.png)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Catalyst</th>
<th>phosphine</th>
<th>Conditions</th>
<th>Yield of 110</th>
</tr>
</thead>
<tbody>
<tr>
<td>114</td>
<td>RB-452-153-3\textsuperscript{a}</td>
<td>PdCl\textsubscript{2}</td>
<td>None</td>
<td>rt, 5 days</td>
<td>35%</td>
</tr>
<tr>
<td>115</td>
<td>SG-II-195</td>
<td>Pd\textsubscript{2}(dba)\textsubscript{3}</td>
<td>\textit{tris-}(pentafluorophenyl)phosphine</td>
<td>rt, 24 h</td>
<td>43%</td>
</tr>
<tr>
<td>116</td>
<td>SG-II-207</td>
<td>Pd\textsubscript{2}(dba)\textsubscript{3}</td>
<td>\textit{tris-}(pentafluorophenyl)phosphine</td>
<td>62\textdegree C, 20 h</td>
<td>49%</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: result obtained by Dr. Radetich\textsuperscript{22}.

\textbf{Table 2.22. Silylstannylation-cyclization of di-O-methylallylpropargylmalonate 109.}
Table 2.23. Attempted silylstannylation-cyclization of 4-(*tert*-butyldimethylsiloxy)-oct-7-ene-2-yne 72.

The cyclization of hept-6-eneyne oxide 111 was also attempted. However, the substrate decomposed under the reaction conditions and no product could be isolated (Scheme 2.17).

Scheme 2.17. Attempted silylstannylation-cyclization of hept-6-eneyne oxide 111.
2.2.5. ASYMMETRIC INDUCTION IN SILYLSTANNYLATION-CYCLIZATION

When meso $O$-methyl-2-(2-propynyl)-4-pentynoate 66 is cyclized, the C-1 carbon becomes chiral. In theory, by using a chiral ligand, enantioselectivity could be obtained at this carbon. We tried to use of bis-carbenes, bis-phosphines, hemilabile ligands and monodentate phosphines as chiral inductors (Figure 2.2). Unfortunately, none of these gave any indication of enantioselectivity in the cyclization. Many of those ligands even significantly slowed down the reaction (Table 2.24). The enantioselectivity of each reaction was determined by chiral HPLC on OD column. A typical HPLC trace is shown in Figure 2.3. The two enantiomers are easily separated with times of retention of 10.32 s and 11.48 s.
Table 2.24. Attempts at asymmetric induction in the silylstannylation-cyclization of O-methyl-2-(2-propynyl)-4-pentyne-60ate 66.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>L</th>
<th>Pd (mol%)</th>
<th>L (mol%)</th>
<th>Conditions</th>
<th>73 (%)</th>
<th>112 (%)</th>
<th>113 (%)</th>
<th>ee of 73 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>SG-III-143</td>
<td>L1</td>
<td>3.3</td>
<td>10.2</td>
<td>rt, 19.5 h</td>
<td>44</td>
<td>/</td>
<td>/</td>
<td>NA</td>
</tr>
<tr>
<td>121</td>
<td>SG-III-144</td>
<td>L2</td>
<td>3.3</td>
<td>11.1</td>
<td>rt, 19.5 h</td>
<td>35</td>
<td>15</td>
<td>/</td>
<td>0</td>
</tr>
<tr>
<td>122</td>
<td>SG-III-145</td>
<td>L3</td>
<td>3.3</td>
<td>9.4</td>
<td>rt, 19.5 h</td>
<td>18</td>
<td>6</td>
<td>/</td>
<td>0</td>
</tr>
<tr>
<td>123</td>
<td>SG-III-146</td>
<td>L4</td>
<td>3.3</td>
<td>8.9</td>
<td>rt, 19.5 h</td>
<td>29</td>
<td>/</td>
<td>/</td>
<td>0</td>
</tr>
<tr>
<td>124</td>
<td>SG-III-162</td>
<td>L5</td>
<td>3.3</td>
<td>10.7</td>
<td>rt, 16 h</td>
<td>15</td>
<td>/</td>
<td>/</td>
<td>0</td>
</tr>
<tr>
<td>125</td>
<td>SG-III-163</td>
<td>L6</td>
<td>3.3</td>
<td>8.8</td>
<td>rt, 16 h</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>NA</td>
</tr>
<tr>
<td>126</td>
<td>SG-III-164</td>
<td>L7</td>
<td>3.3</td>
<td>10.0</td>
<td>rt, 16 h</td>
<td>41</td>
<td>/</td>
<td>/</td>
<td>0</td>
</tr>
<tr>
<td>127</td>
<td>SG-III-165</td>
<td>L8</td>
<td>3.3</td>
<td>9.6</td>
<td>rt, 16 h</td>
<td>18</td>
<td>26</td>
<td>/</td>
<td>4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>128</td>
<td>SG-III-166</td>
<td>L9</td>
<td>3.3</td>
<td>9.0</td>
<td>rt, 16 h</td>
<td>29</td>
<td>29</td>
<td>5</td>
<td>4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>129</td>
<td>SG-III-167</td>
<td>L10</td>
<td>1.6</td>
<td>4.6</td>
<td>rt, 16 h</td>
<td>32</td>
<td>/</td>
<td>/</td>
<td>0</td>
</tr>
<tr>
<td>130</td>
<td>SG-III-168</td>
<td>L11</td>
<td>9.3</td>
<td></td>
<td>rt, 16 h</td>
<td>50</td>
<td>/</td>
<td>/</td>
<td>0</td>
</tr>
<tr>
<td>131</td>
<td>SG-III-176</td>
<td>L12</td>
<td>3.3</td>
<td>11.5</td>
<td>rt, 4 days</td>
<td>71</td>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>132</td>
<td>SG-III-177</td>
<td>L13</td>
<td>3.3</td>
<td>11.5</td>
<td>rt, 4 days</td>
<td>76</td>
<td>&lt;3</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

<sup>a</sup>: The limits of detection and the error of the measurements were not established.
Figure 2.2. Ligands tested for asymmetric induction in the silylstannylation-cyclization of O-methyl-2-(2-propynyl)-4-pentyoate 66.
Figure 2.3. Determination of the enantiomeric excess for SG-III-166 (Entry 128, for conditions, see Chapter 5).
2.3. PROPOSED MECHANISM

The mechanism we propose for the silylstannylation–cyclization reaction is a traditional Pd(0) to Pd(II) mechanism (Figure 2.4). At first, the silylstannane oxidatively adds to Pd(0). The first triple-bond coordinates to the metal and the palladium and the silicon add stereoselectively syn to this alkyne. This is followed by coordination of the second triple-bond and a stereoselective syn insertion of this bond into the Pd-C$_{sp2}$ bond. Reductive elimination of Pd(0) with concomitant formation of the C-Sn bond proceeds with retention of configuration to complete the catalytic cycle.

This mechanism allows us to explain a number of observations made...
earlier, especially the unusual stereochemistry of the dienes formed during the reaction. Interestingly, none of the diastereomers of the product has ever been observed at the end of the reaction. The phosphine effect can also be explained in light of this mechanism. After the first syn addition, there is competition between step 4 and step 5. Either reductive elimination occurs, yielding the undesired acyclic addition product, or there is coordination of the second triple-bond, yielding the desired cyclization product. If an electron-rich phosphine is present in the reaction medium (strongly coordinating ligand), it is unlikely that a coordination site will be opened for the triple-bond to coordinate to the metal, preventing step 4 and yielding the addition product. If the phosphine is very electron-rich, it can even prevent coordination of the first alkyne (step 2), thus shutting down the reaction. On the other hand, if we have a poorly coordinating phosphine (electron-poor or large cone angle), this problem is less prevalent and cyclization is more likely to happen. The influence of the catalyst on the outcome of the reaction can be explained similarly. The presence of the coordinating triphenylphosphine in the precatalyst favors the addition products. Complexes like Pd$_2$(dba)$_3$ or salts like Pd(OAc)$_2$ do not have any strongly coordinating ligands, thus favoring the cyclization product. It has also been observed that bidentate phosphines stop the reaction (presumably, they prevent the alkynes from coordinating to the palladium in step 2). Along the same line, part of the negative effect of using a polar solvent may be that it coordinates to the palladium, preventing the desired coordination of the alkynes.

It is also clear from the substrate scope study that the 5-membered rings are formed more effectively when there are substituents at the 4-position of the 1,6-diyne. Indeed, these substituents bring the two alkynes closer together, through Thorpe-
Ingold effect, entropically favoring the cyclization. Also, it is well known that 5-membered rings are entropically more favored than 4- and 6- to 8- membered rings.

2.4. SUMMARY

Through careful examination of the reaction parameters and ligands effects, we found suitable conditions for the silylstannylation-cyclization of \( \alpha, \omega \)-diynes. These are among the most difficult substrates to cyclized and these optimized conditions seem to be quite general for a wide variety of other substrates. The most important factor appears to be the use of a poorly coordinating phosphine. This is required to get high yields and, especially, high selectivities. Indeed, the addition products have never been observed for any substrate when \( \text{tris-(pentafluorophenyl)} \)phosphine was being used. The functional group compatibility with amine, amide and ester groups is excellent. The major limitation of the reaction appears to be that it is limited to 5-membered ring-formation from unsubstituted diynes. Substituted alkynes do not take part in the reaction. Eneynes do work, although in lower yields. It might be possible to expand the scope of the reaction by systematic optimization of the metal, ligand and reaction conditions.
3.1. STEREOCHEMISTRY OF THE DOUBLE-BONDS

The stereochemistry of the double-bonds in the final cyclization products is unusual, if not unexpected on mechanistic grounds. From the point of view of steric hindrance, one would have expected the silyl and stannyl groups to be pointing away from each other. However, the reaction proceeds through stereoselective syn additions on both triple-bonds and a reductive elimination, which is known to occur with retention of stereochemistry. Therefore, we should have expected both groups to be pointing toward each other (Figure 2.4). Most of the compounds synthesized in the course of this study were subjected to Nuclear Overhauser Effect (NOE) experiments (for details, see NMR data in chapter 5). NOE is an NMR experiment that gives insight into the through-space interactions of nuclei, and therefore into their relative positions. A typical example of these NOE experiments is shown in Figure 3.1. All of the NOE experiments carried on the silylstannylation-cyclization products showed that each olefinic proton was close in space to one of the methylene groups (however, each olefinic proton was interacting with a different methylene group). The olefinic protons did not show any interactions with
each other. This demonstrated that the olefins protons were indeed pointing away from each other. Therefore, the silyl and stannyl groups were pointing toward each other. Interestingly, none of the less sterically hindered stereoisomers have ever been observed in the course of this study.

Figure 3.1. Nuclear Overhauser Experiment on (3E,4E)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]-1-tosyl-pyrrolidine 55.
3.2. HELICAL CHIRALITY OF THE DIENE SYSTEM

The second stereochemical issue that needs to be addressed is the chirality of the diene system as a whole. With the two bulky silyl and stannyl groups pointing toward each other, it is difficult to imagine them being in the same plane. If they are not in the same plane, then the diene system must be puckered, creating helical chirality. The two helices could be exchanging with each other rapidly at room temperature, or they could be very distinct from each other, with the possibility of separation of right- and left-handed helices. This would be a case of atropoisomerism (chirality created by steric hindrance preventing rotation around a single-bond).

Observation of the $^1$H, $^{13}$C and $^{119}$Sn NMR spectra of all the compounds made in the course of this study suggested that the diene system underwent fast exchange and there was no possibility of separating the atropisomers. Unfortunately, all of those compounds were oils, which meant that no X-ray structure could be obtained for them. Such data could have given some insight into the chirality of this diene system. Hence we decided to make salt derivatives of some of the nitrogen-containing products, hoping to get X-ray structures of those salts.

3.2.1. SYNTHESIS AND NMR ANALYSIS OF THE SALTS.

The salts (Figure 3.2) were synthesized by simple mixing of the precursors with methyl triflate, methyl iodide, oxalic acid, camphorsulfonic acid or picric acid in dichloromethane overnight. All those compounds had one fixed chiral center ($\alpha$ to the nitrogen) and up to two other chiral centers each existing as a mixture of both enantiomers (at the quaternary nitrogen atom and the atropoisomeric diene system).
Therefore, we could expect four stereoisomers for each salt if the diene system was not inverting. For example, the expected isomers for a salt of the \((3E,4E)-3-[(\text{tri-}n\text{-butylstannyl})\text{methylene}]-1-[(S)-\alpha\text{-methylbenzyl}]-4-[(\text{trimethylsilyl})\text{methylene}]\text{pyrrolidine}\) are depicted in Figure 3.3.

The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectrum of all these salts were taken. All of them showed the presence of only two diastereomers in a 1 : 1 ratio (the oxalic acid salts behaved differently, displaying only one set of peaks. However, after reprecipitation from diethyl ether and hexanes, two diastereomers could be observed, suggesting that the stoichiometry of these salts is not 1 : 1. Interestingly, in the case of the camphorsulfonic acid salts, the presence of a chiral anion did not influence the ratio of the diastereomers, suggesting a rather lose ion pair. Also, salts 121 and 122 displayed the same NMR spectra, in spite of the fact that they are diastereomers. The presence of only two diastereomers suggested that the diene helical chirality might be inverting fast. All of the salts were also oils, except for the oxalic acid salts, which were oily solids. After many attempts, crystals of these were obtained by diffusion of hexanes into a diethyl ether solution of the salt. One of these crystals was of good enough quality to get an X-ray structure.
Figure 3.2. Salts of the $N$-[(R)-α-methylbenzyl]pyrrolidines.
Figure 3.3. Expected isomers for a salt of (3\textit{E}, 4\textit{E})-3-[(tri-\textit{n}-butylstannyl)methylene]-1-[(\textit{R})-\alpha\alpha\alpha\alpha\alpha -methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidine 75.

3.2.2. X-RAY STRUCTURES

As explained earlier, compound 75 can have four diastereoisomers (Figure 3.4.). The X-ray structure (Figure 3.5) obtained showed that each unit cell of the crystal contained four molecules (2 of configuration B and 2 of configuration D). The other two diastereoisomers were not observed. Presumably, these two were not solids, but oils, which explained why the crystallization proved difficult.
Figure 3.4. Diastereomers possibly observable in the X-ray structure.

Figure 3.5. X-ray structures showing diastereomers B and D.
The X-ray structures obtained presented three interesting features. First, they confirmed the assignment of the chirality of the double-bonds determined by NOE (the silyl and stannyl groups were indeed pointing toward each other in both structures). Second, both diastereomers present in the crystal had a very puckered diene system (in both cases, the dihedral angle is close to 60°). This meant that the diene system could indeed be chiral. Finally, the first structure was a right-handed helix, whereas the second one was a left-handed helix. Therefore, we did have helical chirality in the solid state.

In both cases, the carbon-tin and carbon-silicon bond lengths are quite close to the average published values (2.143 Å and 1.865 Å respectively). The bond length in the diene system itself also presents interesting features, since the carbon-carbon bonds are quite typical for carbon-carbon single- and double-bonds (1.541 Å and 1.337 Å respectively). This suggests very low conjugation of the diene system (we seem to have two alkene, more than a conjugated diene).

3.2.3. HPLC STUDIES

Given the previous results, it was known that the diene system was indeed chiral, at least in the solid state. To find out if that was also the case in solution, the compounds were subjected to HPLC methods. They were tested both on reverse-phase (C_{18} column) and normal-phase HPLC (Silica, OD and OJ columns). Unfortunately, no reproducible results could be obtained by reverse-phase HPLC. However, both normal and chiral phase HPLC methods gave very reproducible results. Unfortunately, all compounds behaved as if the diene system was NOT chiral, suggesting again that it was inverting fast (the results are shown in Table 3.1).
Table 3.1. HPLC results (for conditions and retention times, see chapter 5).
Running compound 73 on GC/MS (60°C for 5 minutes, followed by an increase in
temperature of 10°C.min\(^{-1}\) until 250°C, temperature that was maintained for 30 min)
showed that it decomposes under these conditions.

2.2.4. NMR CHIRAL SHIFT REAGENTS

Chiral NMR shift reagents were also used to test the chirality of the diene
system\(^{36}\). These chiral reagents were expected to coordinate to the ester groups of O-
methyl (3Z,4Z)-3-[(tri-\(n\)-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73, thus inducing separation of the peaks of the different diastereomers
by \(^1\)H NMR. When Eu(hfbc)\(_3\) and Yb(hfbc)\(_3\) were used, no separation could be observed.
Those compounds induced only broadening of the NMR signal. However, with Pr(hfbc)\(_3\)
as the NMR shift reagent, splitting occurred (Figure 3.6). Unfortunately, only two
stereoisomers could be observed, instead of the four expected. The chirality that was thus
proven is most likely the chirality at the C-1 center, rather than the possible helical
chirality of the diene system, since this compound also gave a 1:1 ratio of peaks in chiral
HPLC (see Table 3.1).
Figure 3.6. Olefinic region of the $^1$H NMR spectrum of $O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyI)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73 in the presence of increasing amounts of the NMR chiral shift reagent Pr(hfbc)$_3$. 
3.2.5. DYNAMIC NMR

At this point, it became apparent that the diene system was rapidly exchanging at room temperature. However, according to results published by Kiefer et al.\textsuperscript{25}, it was possible that this exchange process could be slowed down or even frozen at lower temperatures. Therefore, these compounds were subjected to Variable Temperature NMR, in order to check whether or not there was a dynamic process going on. All of the silylstannylation-cyclization products described in chapter 2 were studied at different temperatures by $^1$H NMR (every 5 or 10°C), $^{13}$C and $^{119}$Sn NMR (50 to 100°C, 27°C and –40 to -90°C). A typical example is shown in Figure 3.7 (for more examples, see appendix). In Figure 3.8 are depicted the two options at hand. Either the diene system is not inverting, in which case the NMR should prove the presence of two isomers (only one set of peaks, but diastereotopic groups), or it is indeed inverting, in which case the NMR should show the presence of only one apparently achiral molecule (enantiotopic groups). Figure 3.7 shows that, at low temperature, we really have diastereotopic methylene groups (2 AB groups), proving the chirality of the diene system. However, at higher temperatures, the peaks coalesce, leaving two singlets showing that the chirality of the diene system vanished. The other possibly diastereotopic groups display the same behaviour (see appendix). This is the first tangible evidence that the diene system is inverting at room temperature (this supports all the data previously described in this chapter). All of the dynamic NMR spectra taken agreed on this point: the right-handed and the left-handed helices of the diene system are exchanging very fast at room temperature. The exchange process has a rather wide range of coalescence temperatures of –70°C to +20°C (Table 3.2).
Figure 3.7. A typical example of Dynamic $^1$H NMR.

If the diene system is NOT inverting

MeOOC COOMe | MeOOC COOMe

$t$-BuMe$_2$Si SnPh$_3$ | Ph$_3$Sn $\text{Si-t-BuMe}_2$

1 compound expected by NMR
CH$_3$ and CH$_2$ groups should be diastereotopic

If the diene system IS inverting

MeOOC COOMe

$t$-BuMe$_2$Si SnPh$_3$

1 compound expected by NMR
CH$_3$ and CH$_2$ groups should be enantiotopic

Figure 3.8. Explanation of the Dynamic NMR data.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>$R_3$</th>
<th>$R'_3$</th>
<th>Coalescence temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$COOC$_2$COOCH$_3$</td>
<td>Bu$_3$</td>
<td>Me$_3$</td>
<td>+ 10°C</td>
</tr>
<tr>
<td></td>
<td>Bu$_3$</td>
<td>Et$_3$</td>
<td>+ 20°C</td>
</tr>
<tr>
<td></td>
<td>Bu$_3$</td>
<td>$t$-BuMe$_2$</td>
<td>+ 20°C</td>
</tr>
<tr>
<td></td>
<td>Ph$_3$</td>
<td>$t$-BuMe$_2$</td>
<td>+ 20°C</td>
</tr>
<tr>
<td></td>
<td>Ph$_3$</td>
<td>$i$-Pr$_3$</td>
<td>-10°C</td>
</tr>
<tr>
<td>COOCH$_3$</td>
<td>Bu$_3$</td>
<td>Me$_3$</td>
<td>- 20°C</td>
</tr>
<tr>
<td></td>
<td>Bu$_3$</td>
<td>$t$-BuMe$_2$</td>
<td>- 5°C</td>
</tr>
<tr>
<td></td>
<td>Ph$_3$</td>
<td>$t$-BuMe$_2$</td>
<td>+ 0°C</td>
</tr>
<tr>
<td>O</td>
<td>Bu$_3$</td>
<td>Me$_3$</td>
<td>- 20°C</td>
</tr>
<tr>
<td></td>
<td>Ph$_3$</td>
<td>$t$-BuMe$_2$</td>
<td>+ 0°C</td>
</tr>
<tr>
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<td>Me$_3$</td>
<td>$t$-BuMe$_2$</td>
<td>- 50°C</td>
</tr>
<tr>
<td></td>
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<td>Me$_3$</td>
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</tr>
<tr>
<td></td>
<td>Ph$_3$</td>
<td>$t$-BuMe$_2$</td>
<td>- 20°C</td>
</tr>
</tbody>
</table>

Table 3.2. Coalescence temperatures of the silylstannylation–cyclization products.
As could have been expected, an increase in the bulk of the silyl group leads to an increase in the coalescence temperature. More surprisingly, an increase in the bulk present at the 1-position (i.e., the bis-homoallylic carbon) also means an increase in the coalescence temperature, which seems to imply that the ring is involved in the inversion process as well.

3.2.6. COMPUTATIONAL STUDIES

Some computational studies were run using semi-empirical methods (AM1) on a closely related compound. The relative energy values obtained for each of the diastereomers are depicted in Figure 3.9. The relative thermodynamic values are quite close to each other, which implies that none of the diastereomers are drastically favored over the other ones (this agrees with the previous experiments, which all suggested equimolar ratios of diastereomers). In order to mimic the transition state of the inversion process, the three dihedral angles of the diene system (indicated in bold in Figure 3.10) were constrained at 0°. This led to an activation energy of about 115 kJ.mol⁻¹ for the inversion process. This would suggest that the diene system would not invert at room temperature through a transition state in which the silicon and tin atoms are in the same plane, and in which there is no change in the bond distances and angles. A more rigorous calculation with further relaxed geometrical parameters needs to be carried out before any meaningful conclusions can be made about the activation energy of the isomerization process.
This suggested that major structural changes have to occur in the molecule for the inversion process to occur. This is in agreement with our suggestion (vide infra) that the pyrrolidine ring might be strongly involved in this process. Also, it was observed that the ring methylene peaks showed unexpected behavior by $^1$H and $^{13}$C NMR spectroscopy. For example, it was noticed that, around coalescence temperature, these methylene carbons were more difficult to observe than the quaternary sp$^2$ carbons of the diene.
system, which suggested that the C-2 and C-5 positions also played a large role in the exchange process. This means that all of the positions in the ring are largely involved in the exchange process; a factor that was not taken into account in the calculation.

![Chemical structure](image)

116 kJ/mol

Figure 3.10. Energy (relative to conformation D) of the proposed transition state for the inversion of the diene system in (3E,4E)-3-[(trimethylsilyl)methylene]-1-[(S)-α-methylbenzyl]-4-[(trimethylstannyl)methylene]pyrrolidine 124 calculated using Cerius.

3.3. LINE-SHAPE ANALYSIS

As explained earlier, the density matrix theory for NMR line shapes (described by Kaplan and Fraenkel\(^\text{26}\)) can be used to calculate the rates of fast exchange processes at equilibrium. The system at hand was ideally suited for such a study. Three different kinds of systems were studied. The first one involved the averaging of two singlets to one singlet. The second one consisted of the sum of two such systems. Since the latter were overlapped, they had to be treated together. The third system had two AB systems
lines) averaging to two singlets with coupling between A and B. A problem we encountered in the course of this study was that the chemical shifts of the peaks observed shifted as a function of temperature, independently of the exchange process. For four molecules, a linear relationship between the shift and the temperature was found. Therefore, we could correct for this shift and still obtain meaningful results. In another case, however, the relationship did not seem to be linear. No reliable result could be obtained in this case.

3.3.1. TWO SINGLETS AVERAGING TO ONE SINGLET

![Diagram of two singlets averaging to one singlet](image)

**Figure 3.11. Example of a case where two singlets exchange to one singlet.**

In the system depicted in Figure 3.11, at low temperature, the molecule has one source of chirality (the diene system). Therefore, the methyl groups on the silicon are magnetically non-equivalent, hence the presence of two singlets for the methylsilyl...
groups at low temperature. With increasing temperature, the shift between the methyls progressively averages to a single line. Since group theory allows us to treat each methyl group as a pseudo-half spin, this system can be depicted as in equation 3.1.

\[ AB \leftrightarrow BA \]  

(3.1)

Equation 3.2 is the density matrix equation used to calculate the NMR line shape of this system, where \( T^{-1} \) is the line width at fast exchange, \( k \) is the exchange rate, \( C \) is an arbitrary proportionality constant and \( (\Delta\nu_i) \) are the chemical shifts in Hertz, as defined in Equation 3.3.

\[
\begin{bmatrix}
  i2\pi(\Delta\nu_a) - T^{-1} - k \\
  k \\
  i2\pi(\Delta\nu_b) - T^{-1} - k
\end{bmatrix}
\begin{bmatrix}
  \rho_1 \\
  \rho_2
\end{bmatrix} = iC
\begin{bmatrix}
  1 \\
  1
\end{bmatrix}
\]

(3.2)

\[ \Delta\nu_i = \nu - \nu_i \]  

(3.3)

The term \( \nu_i \) is the observed chemical shift of the peak corresponding to transition \( i \). The term \( \nu \) is the frequency on the x-axis of the calculated spectrum. Terms \( \rho_1 \) and \( \rho_2 \) are the elements of the density matrix (Equations 3.4 and 3.5) needed to calculate the intensity of the spectrum (equation 3.6).

\[ \rho_1 = \langle \alpha | \rho^A | \beta \rangle \]  

(3.4)

\[ \rho_2 = \langle \alpha | \rho^B | \beta \rangle \]  

(3.5)

\[ Abs(\nu) = -\text{Im}(\rho_1 + \rho_2) \]  

(3.6)

Thus, the rate is determined by comparison of observed and trial calculated spectra: input a rate, calculate \( \rho_1 \) and \( \rho_2 \) (therefore the absorption Abs) for all frequencies.
v in the desired range, plot the results in a calculated spectrum, compare with the experimental spectrum, input a new rate if needed, etc, and the iteration is continued until a suitable match between the experimental and calculated spectra is found.

For the system described above, \((\nu_b - \nu_a)\) was plotted against the temperature to give the relationship shown in equation 3.7 (Figure 3.12).

\[
(\nu_b - \nu_a) = -1.6616T + 805.54
\]  

(3.7)

The line width used was \(T^{-1} = 1.5\) s\(^{-1}\). Figure 3.13 shows the calculated and experimental spectra for each temperature. As can be seen, very good fits could be obtained at all temperatures. Rates and temperatures were then used to construct an Eyring plot using Equation 3.8 (Figure 3.14). This led to an enthalpy of activation of 55.4 kJ.mol\(^{-1}\) and an entropy of activation of \(-4.3\) J.K\(^{-1}\).mol\(^{-1}\).

\[
\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^\neq}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^\neq}{R} + \ln\left(\frac{k_b}{h}\right)
\]  

(3.8)
Figure 3.12. Temperature-dependence of the chemical shift between the methylsilyl groups of di-O-methyl-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(triphenylstanny1)methylene]cyclopentanedicarboxylate 89 in $^1$H NMR spectroscopy.
Figure 3.13. Calculated and experimental $^1$H NMR spectra of the methylsilyl groups of di-$O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89.
\[ y = -6660.7x + 23.238 \]
\[ R^2 = 0.9876 \]

Figure 3.14. Eyring plot for di-\(O\)-methyl-(3\(Z\),4\(Z\))-3-[(tert-butyldimethylsilyl)-methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89, using the methylsilyl resonances in \(^1\)H NMR spectroscopy.
3.3.2. FOUR SINGLETS AVERAGING TO TWO SINGLETS

![Chemical Structures](image)

Figure 3.15. Example of a case where four singlets exchange to two singlets.

In the situation depicted in Figure 3.15, there is a permanent chiral center at C-1. At low temperature, there is a second source of chirality (the diene system), creating two diastereomers with each two magnetically non-equivalent methyl groups (four singlets). With increasing temperature, one of the non-equivalences averages due to fast exchange of the diene system. At high temperature, though, there are only two enantiomers (same NMR spectrum), with two magnetically non-equivalent methyl groups (two peaks). Basically, this is the sum of two systems in similar fashion to the one described in the previous section. This system can be depicted as in Equation 3.9.

$$2 \text{ (AB} \leftrightarrow \text{BA)}$$

(3.9)

The density matrix equation for this system is depicted in Equation 3.10.
The results are obtained the same way as before. Note that in this case, there are two options: -the first and third peaks averaging together; the second and fourth peaks averaging together.

- the first and fourth peaks averaging together; the second and third peaks averaging together.

Both sets of calculations were done and yielded the exact same results. The temperature dependence of the shifts is depicted in Figure 3.16. The line width used in this case was 3.4 Hz. The calculated and experimental spectra are depicted in Figure 3.17. Again, excellent fits were obtained. The rates and temperatures were then entered in an Eyring plot (Figure 3.18), which led to an enthalpy of activation of 48.8 k.mol⁻¹ and an entropy of activation of −11.6 J.K⁻¹.mol⁻¹.
Figure 3.16. Temperature-dependence of the chemical shift of the methylsilyl groups of O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 92 in $^1$H NMR spectroscopy.
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<tr>
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<th>Experimental Rate</th>
<th>Calculated Rate</th>
</tr>
</thead>
<tbody>
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<td>50000</td>
</tr>
<tr>
<td>329 K</td>
<td></td>
<td>30000</td>
</tr>
<tr>
<td>323 K</td>
<td></td>
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<tr>
<td>202 K</td>
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<td>0</td>
</tr>
</tbody>
</table>

Figure 3.17. Calculated and experimental $^1$H NMR spectra of the methylsilyl groups of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstanny) methylene]cyclopentanecarboxylate 92.
Figure 3.18. Eyring plot for $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentane carboxylate 92, using the methylsilyl resonances in $^1$H NMR spectroscopy.
3.3.3. TWO AB SYSTEMS AVERAGING TO TWO SINGLETS

Figure 3.19. Example of a case where two AB systems exchange to two singlets.

In this situation, we have one source of chirality at low temperature (diene system), resulting in the methylene groups to appear as one AB system each. At higher temperature, there is no apparent chirality and each methylene group appears as a singlet. This system can be described as in Equation 3.16 (two independent AB systems).

\[
2 \text{(AB} \xleftrightarrow{} \text{BA)} \quad (3.16)
\]

The difference with the previous cases is that we have tight coupling between A and B, and A’ and B’. The density matrix for this system is described in Equation 3.17, where J and J’ are the coupling constants of the two AB systems and \( \rho_i \) are defined as described in Equations 3.18 to 2.15.
\[
\begin{bmatrix}
    i2\pi \left( v_a - \frac{J}{2} \right) & 0 & i2\pi \frac{J}{2} + k & 0 & 0 & 0 & 0 & 0 \\
    -T^{-1} - k & 0 & i2\pi \left( v_a + \frac{J'}{2} \right) & 0 & -i2\pi \frac{J}{2} + k & 0 & 0 & 0 \\
    -T^{-1} - k & -i2\pi \left( v_a + \frac{J}{2} \right) & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & -i2\pi \frac{J}{2} + k & 0 & i2\pi \left( v_a - \frac{J'}{2} \right) & 0 & 0 & 0 & 0 \\
    -T^{-1} - k & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & i2\pi \left( v_a + \frac{J'}{2} \right) & 0 & -i2\pi \frac{J}{2} + k \\
    -T^{-1} - k & -i2\pi \left( v_a + \frac{J}{2} \right) & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & i2\pi \frac{J}{2} + k & 0 & i2\pi \left( v_a - \frac{J'}{2} \right) \\
    -T^{-1} - k & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & -i2\pi \frac{J}{2} + k & 0 & i2\pi \left( v_a + \frac{J'}{2} \right) \\
    -T^{-1} - k & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{bmatrix}
\begin{bmatrix}
    \rho_1 \\
    \rho_2 \\
    \rho_3 \\
    \rho_4 \\
    \rho_5 \\
    \rho_6 \\
    \rho_7 \\
    \rho_8 \\
\end{bmatrix} = iC
\]

(3.17)
\[ \rho_1 = \langle \alpha \alpha | \rho^{\alpha \beta} | \beta \alpha \rangle \] (3.18)

\[ \rho_2 = \langle \alpha \beta | \rho^{\alpha \beta} | \beta \beta \rangle \] (3.19)

\[ \rho_3 = \langle \alpha \alpha | \rho^{\alpha \beta} | \alpha \beta \rangle \] (3.20)

\[ \rho_4 = \langle \beta \alpha | \rho^{\alpha \beta} | \beta \beta \rangle \] (3.21)

\[ \rho_5 = \langle \alpha \alpha | \rho^{\alpha \beta} | \beta \alpha \rangle \] (3.22)

\[ \rho_6 = \langle \alpha \beta | \rho^{\alpha \beta} | \beta \beta \rangle \] (3.23)

\[ \rho_7 = \langle \alpha \alpha | \rho^{\alpha \beta} | \alpha \beta \rangle \] (3.24)

\[ \rho_8 = \langle \beta \alpha | \rho^{\alpha \beta} | \beta \beta \rangle \] (3.25)

\[ \text{Abs}(\nu) = - \text{Im}(\rho_1 + \rho_2 + \rho_3 + \rho_4 + \rho_5 + \rho_6 + \rho_7 + \rho_8) \] (3.26)

In this case, the two AB systems are overlapping such that the peaks can be exchanging only one way. The temperature dependence of the shifts is depicted in Figure 3.20. The line width used for the right-most system is 1.8 Hz, the one for the left-most system is 2.0 Hz. The value of the coupling constant for the left-most system is \( J = 14.84 \) Hz, for the right-most system, it is \( J' = 15.11 \) Hz. The calculated and experimental spectra are depicted in Figure 3.21. Excellent fits were obtained, in spite of the complexity of this system. The rates and temperatures were then incorporated in an Eyring plot (Figure 3.22), which led to an enthalpy of activation of 54.8 kJ.mol\(^{-1}\) and an entropy of activation of 0.4 J.K\(^{-1}\).mol\(^{-1}\).
Figure 3.20. Temperature-dependence of the chemical shift of the methylene groups of di-$O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 in $^1$H NMR spectroscopy.
Figure 3.21. Calculated and experimental $^1$H NMR spectra of the methylene groups of di-O-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56.
Figure 3.22. Eyring plot for di-O-methyl-(3Z,4Z)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56, using the methylene resonances in $^1$H NMR spectroscopy.
The last system we studied via line shape analysis is depicted in Figure 3.23. This is a system similar to the previous one, having two AB systems exchanging to two singlets. In this case though, the AB systems are not overlapping as much and we have two options to explore: - the two outers doublets exchanging together and the two inner ones exchanging with each other.

- the first and third doublets exchanging together; the second and fourth doublets exchanging together.

Both possibilities were explored. However, only the first possibility led to reasonable results (the second one led to an enthalpy of activation of 73.6 kJ.mol\(^{-1}\) and an entropy of activation of 60.1 J.K\(^{-1}\).mol\(^{-1}\), which did not seem likely).

The same matrix as for the previous example was used (Equation 3.17). The temperature dependence of the shifts is depicted in Figure 3.24. The line width used for the two inner doublets is 3 Hz, the one for the outer doublets is 3.5 Hz. The value of both geminal coupling constants are \(J = J' = 15\) Hz. The calculated and experimental spectra are
depicted in Figure 3.25. Excellent fits were obtained again. The rates and temperatures were then entered in an Eyring plot (Figure 3.26), which led to an enthalpy of activation of 63.2 kJ.mol\(^{-1}\) and an entropy of activation of 21.0 J.K\(^{-1}\).mol\(^{-1}\).

Figure 3.24. Temperature-dependence of the chemical shift of the methylene groups of di-O-methyl-(3Z,4Z)-3-[(tri-\(n\)-butylstannyl)methylene]-4-[(triethylsilyl)methylene]cyclopentanedicarboxylate 86 in \(^1\)H NMR spectroscopy.
Figure 3.25. Calculated and experimental $^1$H NMR spectra of the methylene groups of di-$O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(triethylsilyl)methylene]cyclopentanedicarboxylate 86.
Figure 3.26. Eyring plot for di-O-methyl-(3Z,4Z)-3-[(tri-\text{-}n\text{-}butylstannyl)methylene]-4-[(triethylsilyl)methylene]cyclopentanedicarboxylate 86, using the methylene resonances in $^1\text{H}$ NMR spectroscopy.

The results are summarized in Table 3.3. For all the molecules studied, the enthalpies of activation are remarkably similar. However, the smallest one is observed for the compound presenting the least hindrance at the C-1 carbon, which agrees with previous
results. As the bulk on the silyl group increases (56 to 86), the enthalpy of activation also increases (this observation was also made earlier). The most striking result about the entropies of activation is that, for the triphenylstannanes, it is negative, whereas it is positive for the tributylstannanes. That means that the transition state is more organized than the ground state for the triphenylstannanes (it is possible that the phenyl groups organize themselves as a cogwheel for the inversion). The opposite holds for the tributylstannanes, probably because butyl groups have many more degrees of freedom than the phenyl groups.

3.4. SUMMARY

By the results described in this chapter, we have been able to demonstrate the stereochemistry of the individual double-bonds by two different methods (NOE and X-ray structure). Although the stereochemistry obtained at the double-bonds is not likely to be the thermodynamically favored one, it makes perfect sense in light of the reaction mechanism. The X-ray structure obtained proves the helical chirality of the diene system in the solid state. Dynamic NMR experiments show that the two enantiomers undergo fast equilibration in solution at room temperature due to fast inversion, that is, the diene system is fluxional at room temperature. The inversion process displays a coalescence temperature of –70°C to +20°C, depending on the structure. Line shape analysis could be performed on these systems to determine the energy of activation of this inversion process.
Table 3.3. Summary of the results obtained via line shape analysis.
CHAPTER 4

SYNTHETIC APPLICATIONS OF THE PRODUCTS OF THE
SILYLSTANNYLATION–CYCLIZATION REACTION

4.1. HYDRODESILYLATION AND HYDRODESTANNYLATION

Hydrodestannylation of the silylstannylation-cyclization products was attempted using two different acids: camphorsulfonic acid and p-toluenesulfonic acid (Schemes 4.1-4.2, Tables 4.1-4.2).

\[
\text{COOCH}_3
\]

\[
\text{Si SnPh}_3 t-Bu\text{-dimethylsilyl)methylene]} 4-[(\text{tri phenylstannyl)methylene]cyclopentanecarboxylate} 92.
\]

Unfortunately, the yields obtained were low, when any product was formed at all. As can be seen from the results in Table 4.2, there seems to be decomposition of the product over time under the reaction conditions. The addition of potassium fluoride, tested with both camphorsulfonic acid and \(p\)-toluenesulfonic acid, significantly slowed the reaction down, although no decomposition was observed. However, after 20 h of reaction, the yield of the product was still too low to be of any practical use. It is possible that longer reaction times and/or higher temperatures may result in more acceptable yields of the product. However, direct hydrostannylation-cyclization of the starting diyne as described in Chapter 1 of this thesis (page 12) could yield the same product in only one step in similar or higher yields. The lack of reactivity of the amine derivative in Scheme 4.2 can be explained by formation of the ammonium salt preventing the hydrodestannylation from taking place.

\[
\begin{align*}
\text{CH}_3\text{OOC} & \quad \text{COOCH}_3 \\
\text{Me}_3\text{Si} & \quad \text{SnBu}_3 \\
\text{Camphorsulfonic acid} & \\
\text{CH}_2\text{Cl}_2, \text{rt}, 21 \text{ h} & \\
\text{Me}_3\text{Si} & \quad \text{COOCH}_3
\end{align*}
\]

![Diagram](image)

<table>
<thead>
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<th>Notebook page number</th>
<th>Additive</th>
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<th>Recovery of 56 (%)</th>
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<td>44</td>
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<td>SG-III-248</td>
<td>KF</td>
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Table 4.1. Hydrodestannylation of (3Z,4Z)-di-\(O\)-methyl-3-[(tri-\(n\)-butylstanny)\(n\)-methylen]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 using camphorsulfonic acid.
Table 4.2. Hydrodestannylation of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstanny1)-methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 using p-toluenesulfonic acid.

<table>
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<td>65</td>
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<td>KF</td>
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Scheme 4.2. Hydrodestannylation of (3E,4E)-3-[(tri-n-butylstanny1)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 75 by p-toluenesulfonic acid.
Hydrodesilylation can be performed in the presence of tetrabutylammonium fluoride, although this reaction also proceeded in low yields (Scheme 4.3). In this case, decomposition was also a major problem.

Scheme 4.3. Hydrodesilylation of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstanny1)-methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56.
4.2. REACTIONS ON THE VINYL TIN MOIETY

4.2.1. TIN-HALOGEN EXCHANGE

Scheme 4.4. Tin-iodine exchange in $O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)-methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73.

Scheme 4.5. Tin-iodine exchange in (3Z,4Z)-di-$O$-methyl-3-[(tri-$n$-butylstannyl)-methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56.
Scheme 4.6. Tin-iodine exchange in (3E,4E)-3-[(tri-n-butylstannyl)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 75.

Tin-iodide exchange on the vinyl stannane moiety can easily be performed by titration of the proper substrate with iodine in dichloromethane at 0ºC (Scheme 4.4-4.6)\textsuperscript{38}. The reaction is instantaneous and proceeds in high yields. However, reaction and purification must be performed in the dark, as the products are extremely light sensitive. Even when they are stored under nitrogen in a fridge, away from light, they decompose in a few weeks.

Tin-bromine exchange can also be effected. A reaction similar to the tin-iodine exchange described above, using bromine in place of the iodine, does not yield the desired product (Scheme 4.7). However, reaction with N-bromosuccinimide (Scheme 4.8) allows for the quantitative formation of the product (the \textsuperscript{1}H NMR spectrum of the crude mixture shows the presence of only the product and the succinimide). Unfortunately, this compound seems to decompose on silica gel and could not be purified.

4.2.2. TIN-LITHIUM EXCHANGE

\[
\begin{align*}
\text{Ph} & \quad \text{Me}_3\text{Si} \quad \text{SnBu}_3 \\
\text{N} & \quad \text{Ph} \\
\text{Me}_3\text{Si} & \quad \text{131} \\
\end{align*}
\]

1. RLi, THF, -78ºC
2. NH₄Cl

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<th>Entry</th>
<th>Notebook page number</th>
<th>RLi</th>
<th>Yield of 131 (%)</th>
<th>Recovery of 76 (%)</th>
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<td>BuLi</td>
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<td>46</td>
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<td>147</td>
<td>SG-IV-015</td>
<td>MeLi</td>
<td>46</td>
<td>14</td>
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Table 4.3. Attempted tin-lithium exchange in \((3E,4E)-3\text{-}[\text{tri-}n\text{-butylstannyl}]\text{-methylene}]\text{-}1\text{-}[\text{\(\alpha\text{-}\text{methylbenzyl}\}]\text{-}4\text{-}[\text{trimethylsilyl}]\text{methylene}]\text{pyrrolidine} 76 followed by quenching with ammonium chloride.

\[
\begin{align*}
\text{Ts} & \quad \text{Me}_3\text{Si} \quad \text{SnBu}_3 \\
\text{N} & \quad \text{Ts} \\
\text{Me}_3\text{Si} & \quad \text{132} \\
\end{align*}
\]

1. MeLi, THF
2. NH₄Cl

<table>
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<th>Entry</th>
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<th>Temperature</th>
<th>Yield of 132 (%)</th>
<th>Recovery of 55 (%)</th>
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<td>149</td>
<td>SG-III-301</td>
<td>-78ºC</td>
<td>71</td>
<td>0</td>
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Table 4.4. Attempted tin-lithium exchange in \((3E,4E)-3\text{-}[\text{tri-}n\text{-butylstannyl}]\text{-methylene}]\text{-}4\text{-}[\text{trimethylsilyl}]\text{methylene}]\text{1-tosylpyrrolidine} 55 followed by quenching with ammonium chloride.
Table 4.5. Attempted tin-lithium exchange in (3E,4E)-3-[(tri-\(n\)-butylstannyl)methylene]-1-[(\(\alpha\)-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 75 and 76 followed by quenching with benzaldehyde.

<table>
<thead>
<tr>
<th>Entry</th>
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<th>Configuration</th>
<th>Additive</th>
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<td>151</td>
<td>SG-III-215</td>
<td>(R)</td>
<td>TMEDA</td>
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Table 4.6. Attempted tin-lithium exchange in (3E,4E)-3-[(tri-\(n\)-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]-1-tosylpyrrolidine 55 followed by quenching with benzaldehyde.

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<td>0(^\circ)C</td>
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<td>153</td>
<td>SG-III-302</td>
<td>-78(^\circ)C</td>
<td>0</td>
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Tin-lithium exchange\textsuperscript{39} was also investigated, but seemed to be difficult to perform. However, it was observed that methyllithium effected the exchange with tin more readily than butyllithium (71 % yield of the desired product could be obtained, Tables 4.3-4.4). When the mixture was quenched with benzaldehyde, no product could be obtained (Tables 4.5-4.6). However, when quenching with ammonium chloride, it was observed that the temperature at each stage of the reaction was of the utmost importance. It is possible that a careful study of the effect of the temperature on the outcome of the reaction would yield positive results (see Table 4.4).

4.2.3. PALLADIUM-CATALYZED CROSS-COUPLING REACTIONS AND ALUMINIUM CHLORIDE-MEDIATED ACYLATION REACTIONS

Many attempts were made at cross-coupling the vinyl stannane moiety with various partners (Tables 4.7-4.13). Those included Stille or Lewis acid (AlCl\textsubscript{3})-catalyzed couplings with vinyliodides or bromides, acylchlorides or aryltriflates and Suzuki couplings with arylboronic acid\textsuperscript{40}. Only one of those attempts met with moderate success: the Stille coupling with \textit{trans}-1-iododec-1-ene. After extensive optimization, the desired product could be obtained in very moderate yields (Table 4.7, Entry 173). However, the results could not be repeated. It should also be mentioned that the purification process was quite difficult to perform and the stereochemistry of the triene system could not be unambiguously confirmed.
Table 4.7. Attempted cross-coupling of the vinylstannane moiety of (3E,4E)-3-[(tri-
\textit{n}-butyl-stannyl)methylene]-1-[(\textit{R})-(\textit{\alpha\alpha\alpha\alpha}-methylbenzyl)]-4-[(trimethylsilyl)methylene]-pyrrolidine 75 with \textit{trans}-1-iododec-1-ene.

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<th>Pd (mol%)</th>
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<th>Temp.</th>
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<th>Recovery of 75 (%)</th>
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<td>L1 (16)</td>
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\(^a\) L1 is tris(\textit{o}-furyl)phosphine and L2 is triphenylarsine.
**Entry** | **Notebook page number** | **Conditions** | **Yield of 132 (%)** | **Recovery of 55 (%)**
--- | --- | --- | --- | ---
180 | SG-III-242 | AlCl₃, 0º, 1 h; rt, 19.5 h | 31 | 0
181 | SG-III-243 | Pd₂(dba)₃, tris-(o-furyl)phosphine, rt, 20 h | 80 | 18

**Table 4.8. Attempted coupling of the vinylstannane moiety of (3E,4E)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]-1-tosyl-pyrrolidine 55 with benzoyl chloride.**

**Entry** | **Notebook page number** | **Conditions** | **Yield of 125 (%)** | **Recovery of 56 (%)**
--- | --- | --- | --- | ---
182 | SG-III-172 | AlCl₃, 0ºC, 20 min, rt, 20 min; rt, 19 h | 41 | 14
183 | SG-III-173 | Pd₂(dba)₃, tris-(o-furyl)phosphine | 21 | 45

**Table 4.9. Attempted coupling of the vinylstannane moiety of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 with (S)-2-(6-methoxy-2-naphtyl)-propanoyl chloride (naproxen chloride).**
Table 4.10. Attempted Stille coupling of the vinylstannane moiety of (3Z,4Z)-di-O-methyl-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89 with naproxen chloride.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Conditions</th>
<th>Recovery of 89 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>184</td>
<td>SG-III-217</td>
<td>AlCl₃, rt, 3 days</td>
<td>42</td>
</tr>
<tr>
<td>185</td>
<td>SG-III-226</td>
<td>AlCl₃, rt, 2 h</td>
<td>19</td>
</tr>
</tbody>
</table>

Table 4.11. Attempted Stille coupling of the vinylstannane moiety of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 with phenyltriflate.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Conditions</th>
<th>Recovery of 56 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>186</td>
<td>SG-III-296</td>
<td>Pd₂(dba)₃, LiCl</td>
<td>15</td>
</tr>
<tr>
<td>187</td>
<td>SG-III-297</td>
<td>Cl₂Pd(PhCN)₂, CuI</td>
<td>0</td>
</tr>
</tbody>
</table>
Entry | Notebook page number | X | Conditions | Recovery of 128 or 130 (%) |
---|---|---|---|---|
188 | SG-III-279 | Br | Pd₂dba₃, Na₂CO₃ | 55 |
189 | SG-III-280 | Br | Ag₂O, Cl₂Pd(CH₃CN)₂, *tris*-(*-furyl)phosphine | 15 |
190 | SG-III-281 | Br | Pd₂dba₃, Cs₂CO₃, P(t-Bu)₃ | 83 |
191 | SG-III-303 | I | Pd₂dba₃, Cs₂CO₃, P(t-Bu)₃ | 0 |

Table 4.12. Attempted Suzuki coupling of the vinylstannane moiety of (3Z,4Z)-di-O-methyl-3-[(halo)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 128 or 130 with phenylboronic acid.

Entry | Notebook page number | Conditions | Recovery of 130 (%) |
---|---|---|---|
192 | SG-III-298 | Cl₂Pd(CH₃CN)₂, Cul, *tris*-(*-furyl)phosphine | 10 |
193 | SG-III-299 | Cl₂Pd(CH₃CN)₂ | 0 |

Various attempts were made to accomplish the coupling of the vinylstannane moiety with isocyanates to yield conjugated amides\(^1\). Unfortunately, although the starting material did react, no identifiable product could be isolated (Table 4.14).

4.3. REACTIONS OF THE ALKENES

4.3.1. DIELS-ALDER REACTIONS

Scheme 4.9. Diels-Alder reaction on (3Z,4Z)-di-O-methyl-3-methylene-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 125 (the stereochemistry of the product was determined by NOE experiments, see chapter 5).

Scheme 4.10. Diels-Alder reaction on (3E,4E)-3-methylene-4-[(trimethylsilyl)methylene]-1-tosyl-pyrrolidine 132 (the stereochemistry was assigned by comparison with 134).
Scheme 4.11. Attempted Diels-Alder reaction on \( O \)-methyl-(3Z,4Z)-3-[(tri-\( n \)-butyl-stannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73.

Diels-Alder reactions with maleic anhydride were tested on the hydrodestannylated products (Schemes 4.9-4.10). In the case of the tosylamine derivative, the reaction was very slow due to high dilution. Polycyclic molecules could easily be obtained in one quantitative step. However, while Diels-Alder reactions of the hydrodestannylated products proceeded very readily, the parent compounds failed to react under similar conditions (Scheme 4.11). This confirmed the fact that the diene system was extremely puckered and thus really behaved as two independent alkenes, rather than a conjugated diene.

4.3.2. HYDROBORATION

Various hydroboration reactions were attempted on different substrates (Tables 4.15, Schemes 4.12-4.13).\(^{42}\) In no case could any of the desired alcoholic products be observed.
Table 4.15. Attempted hydroboration of (3E,4E)-3-[(tri-n-butylstannyl)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrroldine 75.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Borane</th>
<th>Conditions</th>
<th>Yield of 136 (%)</th>
<th>Recovery of 75 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>199</td>
<td>SG-III-223</td>
<td>BH₃,THF</td>
<td>rt, 46.5 h</td>
<td>31</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>SG-III-254</td>
<td>BH₃,THF</td>
<td>rt, 3 h</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>201</td>
<td>SG-III-255</td>
<td>9-BBN</td>
<td>rt, 19 h</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>


Table 4.16. Attempts at the epoxidation of (3\textit{Z},4\textit{Z})-di-\textit{O}-methyl-3-[(tri-\textit{n}-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 57 with oxaziridines.
4.3.3. EPOXIDATION

Epoxidation of the diene system was attempted using various well-known procedures, such as oxaziridines\textsuperscript{43}, m-CPBA\textsuperscript{44}, dioxiranes\textsuperscript{45} and Jacobsen’s epoxidation\textsuperscript{46}. Epoxidation with oxaziridines, dioxiranes and Jacobsen’s conditions, along with dihydroxylations (see next section) have been reported to proceed enantioselectively on many substrates. We were hoping to get dynamic kinetic resolution of the diene system during the reaction. Figure 4.1 describes such a system. The two configurations of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 have been shown to be in fast exchange at room temperature. In the presence of a chiral reagent, these two enantiomers can give rise to diastereomeric transition states. If these have significantly different energies, one of the enantiomers might react faster than the other (\(k_1>k_2\) or \(k_1<k_2\)). Since the starting enantiomers are rapidly exchanging, one of the enantiomers of the chiral product might be obtained in excess over the other. Since the enantiomers of the product are not undergoing any exchange, chirality can be created this way.

The reactions with oxaziridines described in Table 4.16 were followed by \(^1\)H NMR over time. This led to the observation that the oxaziridine steadily disappears from the reaction medium, without forming the desired epoxide. Instead, only small yields of the hydrodestannylation product could be observed.

When \(m\)-CPBA was used, the desired epoxide could be observed and isolated, although in low yields (Table 4.17). Interestingly, the only product that was observed is
the one resulting from epoxidation of the vinylstannane moiety. Unfortunately, in spite of the low yields, very little starting material could be recovered, suggesting that decomposition occurred. Furthermore, some hydrodestannylated product could be observed in some cases, suggesting that acid-mediated reactions occurred (see section 4.1). This prompted the use of a buffer in the reaction. Using potassium fluoride as a buffer stopped decomposition, but also the epoxidation. Buffering with sodium bicarbonate gave more promising results. Unfortunately, the yields were still low, although large amounts of starting material could be recovered in some cases. It is possible that a different peracid would yield better results.

Figure 4.1. Possible dynamic kinetic resolution pathway.
Table 4.17. Attempted epoxidation reaction of \((3Z,4Z)-\text{di-}O\text{-methyl-3-}[\text{tri-}n\text{-butylstannyl}]\text{methylene}-4-\text{[trimethylsilyl]methylene}\text{cyclopentanedicarboxylate} \ 56\) with \(m\text{-CPBA}\

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Equivalents of (m\text{-CPBA} )</th>
<th>Additives</th>
<th>Conditions</th>
<th>Yield of (137 ) (%)</th>
<th>Yield of (125 ) (%)</th>
<th>Recovery of (56 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>206</td>
<td>SG-III-222</td>
<td>1.5+1.1</td>
<td>None</td>
<td>rt, 24 h</td>
<td>19</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>207</td>
<td>SG-III-244</td>
<td>4.9</td>
<td>None</td>
<td>rt, 21 h</td>
<td>13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>208</td>
<td>SG-III-258</td>
<td>1.1</td>
<td>None</td>
<td>45°C, 3 h</td>
<td>29</td>
<td>24</td>
<td>14</td>
</tr>
<tr>
<td>209</td>
<td>SG-III-270</td>
<td>3*1.0</td>
<td>None</td>
<td>rt, 3 h</td>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>210</td>
<td>SG-III-256</td>
<td>1.1</td>
<td>KF (solid)</td>
<td>rt, 18 h</td>
<td>0</td>
<td>0</td>
<td>98</td>
</tr>
<tr>
<td>211</td>
<td>SG-III-257</td>
<td>0.9</td>
<td>NaHCO(_3) (aqueous)</td>
<td>rt, 19 h</td>
<td>15</td>
<td>0</td>
<td>64</td>
</tr>
<tr>
<td>212</td>
<td>SG-III-269</td>
<td>4*1.0</td>
<td>NaHCO(_3) (aqueous)</td>
<td>rt, 4 days</td>
<td>12</td>
<td>0</td>
<td>16</td>
</tr>
</tbody>
</table>

Table 4.18. Attempts at the epoxidation of \((3Z,4Z)-\text{di-}O\text{-methyl-3-}[\text{tri-}n\text{-butylstannyl}]\text{methylene}-4-\text{[trimethylsilyl]methylene}\text{cyclopentanedicarboxylate} \ 56\) with dimethyldioxirane.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>213</td>
<td>SG-III-266</td>
<td>0°C, 3 h; rt, 43 h</td>
<td>No conversion</td>
</tr>
<tr>
<td>214</td>
<td>SG-III-273</td>
<td>rt, 10 days, 4*0.6 equiv. of dimethyldioxirane</td>
<td>No conversion</td>
</tr>
</tbody>
</table>

117
Dioxiranes are known to epoxidize alkenes. There have even been reports of asymmetric epoxidation using chiral dioxiranes. However, the products of the silylstannylation-cyclization reaction did not react with several equivalents of dimethyl-dioxirane for 10 days. All of the starting material could be recovered (Table 4.18).

![Chemical structure](image)

**Table 4.19. Attempted Jacobsen epoxidation of (3Z,4Z)-di-O-methyl-3-[(tri-\textit{n}-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Notebook page number</th>
<th>Equivalents of NaOCl</th>
<th>Conditions</th>
<th>Yield of 138 (%)</th>
<th>Recovery of 56 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>215</td>
<td>SG-III-267</td>
<td>2.2</td>
<td>rt, 42.5 h</td>
<td>18</td>
<td>51</td>
</tr>
<tr>
<td>216</td>
<td>SG-III-278</td>
<td>7.7</td>
<td>rt, 6.5 h</td>
<td>15</td>
<td>7</td>
</tr>
</tbody>
</table>

Jacobsen’s epoxidation was also tested. Unfortunately, no epoxide could be isolated. Instead, small amounts of a chlorinated product 138 could be isolated (Table 4.19). This product could come for an electrophilic cleavage of the carbon-tin bond with a source of Cl\(^+\) in the oxidation medium.
4.3.3. DIHYDROXYLATION

Several dihydroxylation methods were tested, including Sharpless catalytic dihydroxylation\(^{47}\) (Schemes 4.14 and 4.15) and stoichiometric osmium tetroxide dihydroxylation\(^{48}\) (Scheme 4.16).

Scheme 4.14. Attempted Sharpless catalytic dihydroxylation on (3\(E\),4\(E\))-3-[(tri-\(n\)-butylstannyl)methylene]-1-[(\(R\)-(\(\alpha\α\α\α\)-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 75.

Scheme 4.15. Attempted Sharpless catalytic dihydroxylation on (3Z,4Z)-di-O-methyl-3-[(tri-\(n\)-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentane-dicarboxylate 56.

4.4. SUMMARY

From these experiments, the silylstannylation-cyclization products seem to be very difficult substrates for several typical electrophilic reactions, which seems to limit their utility. However, other reactions present hope for the future. Bromine- and iodine-tin exchange can be performed very easily. The product may then be used in further reactions. Tin-lithium exchange is also a reaction that should work, given the proper optimization. Temperature control seems to be important. Among the reactions to be tested are dipolar cycloadditions, Diels-Alder reactions (as dienophiles) and optimized conditions from cross-coupling reactions. Some success in these areas has since been achieved (unpublished results of Seunghoon Shin).
CHAPTER 5

EXPERIMENTAL PROCEDURES

*General methods.* Tetrahydrofuran (THF), benzene and diethylether were distilled under nitrogen from sodium/benzophenone. Dimethylformamide (DMF) was distilled under reduced pressure from magnesium sulfate. Methylene chloride was distilled under nitrogen from calcium hydride. All solvents were freshly distilled or stored over 3 Å molecular sieves. The unsubstituted diynes were purchased from Aldrich, filtered through magnesium sulfate and kept at -30 °C under nitrogen. Tri-\textit{n}-butyltinhydride\textsuperscript{49} and Pd\textsubscript{2}(dba)\textsubscript{3}\textsuperscript{50} were synthesized according to published procedures. All other reagents were purified using procedures described in *Purification of Laboratory Chemicals*\textsuperscript{51}.

NMR spectra were obtained in CDCl\textsubscript{3} solutions using Brucker DPX-400 and DRX-500 spectrometers. Chemical shifts are reported in parts per million (ppm, \(\delta\)) relative to CHCl\textsubscript{3} (\(\delta = 7.24\)) as an internal standard for proton. Coupling constants are reported in Hz. Analytical TLC was performed on E. Merck precoated (0.25 mm) silica gel 60 F\textsubscript{254} plates. Column chromatography was conducted by using silica gel 40 (Doz
Inc.). HPLC analyses were performed on Chiralsel OD-H and Chiralsel OJ columns (25 cm length x 4.6 mm i. d.). Elemental analyses were done by Atlantic Microlab Inc., Norcross, GA.

The NMR spectra recorded for the line shape analysis required special precautions. The NMR probe temperature was calibrated using methanol\(^\text{52}\). The shims and tuning were maintained as good as possible at all temperatures. At each temperature, the spectra were recorded 2 to 3 minutes after the shims had stabilized. The FID’s of the spectra were submitted to Fourier transform and phasing only. No other treatments such as line broadening were performed, as these would affect the shape of the peaks obtained. The calculations for line shape simulations were then performed using Mathematica 3.0. Printing of these calculated spectra was performed by importing the spectra into Microsoft Excel 2000. The experimental spectra were printed on transparencies, allowing for easy comparison.

Entry 1, SG-II-098

**Optimization of the silylstannylation-cyclization of 1,6-heptadiyne 62.** A solution of 29 µL of hepta-1,6-diyne 62 (0.253 mmol), 87 µL of trimethylsilyltri-\(n\)-butylstannane (0.251 mmol), 4 µL of anisole (0.037 mmol), 2.1 mg of Pd\(_2\)(dba), (0.002 mmol), 3 mg of tris-(\(o\)-tolyl)phosphine (0.010 mmol) in 0.5 mL of deuterated benzene was prepared in an NMR tube. The NMR spectrum of the reaction mixture after 17.5 h showed the formation of monoaddition (17 %) and cyclization (20 %) products.
(1Z,2Z)-1-[(Tri-\textit{n}-butylstannyl)methylene]-2-[(trimethylsilyl)methylene]cyclopentane 63.

![Diagram of 63]

This product was purified by distilling off the trimethylsilyltri-\textit{n}-butylstannane (55°C, 0.2 mm Hg), but could not be obtained more than 61% pure (determined by GC). It was still contaminated with trimethylsilyltri-\textit{n}-butylstannane. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.06 (9 H, s, SiCH$_3$), 0.86-0.90 (15 H, m, CH$_3$CH$_2$), 1.26-1.44 (12 H, m, SnCH$_2$CH$_2$), 1.68 (2 H, quintet, $J_{HH}$=7.7 Hz, H$_4$), 2.29 (2 H, t, $J_{HH}$=7.4 Hz, H$_5$), 2.33 (2 H, t, $J_{HH}$=7.3 Hz, H$_5$), 5.17 (1 H, s, H$_2'$), 5.57 (1 H, s, J$_{H}$Sn= 55; 57 Hz, H$_1'$). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 0.7 (q, SiCH$_3$), 10.7 (t, CH$_3$CH$_2$), 13.8 (q, CH$_2$CH$_3$), 20.4 (t, C$_3$), 27.4 (t, Bu), 29.1 (t, Bu), 36.1 (t), 36.3 (t), 122.7 (d, J$_{C}$Sn= 381, 399 Hz, C$_7$), 122.8 (d, C$_5$), 160.6 (s), 161.1 (s). Assignments were confirmed by HMQC and DEPT 135.

(Z)-2-(Tri-\textit{n}-butylstannyl)-1-(trimethylsilyl)hept-1-ene-6-yne 64.

![Diagram of 64]

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 0.07 (s, 9H, SiCH$_3$), 0.86-0.93 (m, 15 H, CH$_3$CH$_2$), 1.27-1.52 (m, 14 H, SnCH$_2$CH$_4$, H$_4$), 1.93 (t, 1 H, J$_{HH}$ = 2.6 Hz, H$_7$), 2.13 (dt, 2 H, J$_{HH}$ = 2.6, 7.1 Hz, H$_5$), 2.34 (t, 2 H, J$_{HH}$ = 7.5 Hz, H$_5$), 6.35 (s, 1 H, J$_{H}$Sn = 172, 180 Hz, H$_7$); $^{13}$C NMR
(CDCl₃, 100 MHz): δ 0.18 (q), 11.18 (t), 13.64 (q), 17.75 (t), 27.48 (t), 28.50 (t), 29.22 (t), 46.21 (t), 68.36 (d), 84.47 (q), 144.62 (d), 164.19 (q).

(1Z,6Z)-2,6-Bis-(tri-n-butylstannyl)-1,7-bis-(trimethylsilyl)hepta-1,6-diene 65.

\[
\text{Me}_3\text{Si}\begin{array}{c}
\text{Bu}_3\text{Sn} \\
\text{CH}_2
\end{array}\begin{array}{c}
\text{SiMe}_3 \\
\text{SnBu}_3
\end{array}
\]

1H NMR (CDCl₃, 500 MHz): δ 0.06 (18 H, s, SiCH₃), 0.79-0.90 (30 H, m, Bu), 1.25 (12 H, quintet, J_HH= 4.4 Hz, Bu), 1.32-1.46 (14 H, m, Bu, H₃), 2.15 (4 H, t, J_HH= 7.4 Hz, H₃, H₄), 6.24 (2 H, s, J_HSn= 175, 178 Hz, H₁, H₇).

Entries 2-30, see Entry 1.

Entry 31, SG-III-34.

Phosphine study for the cyclization of di-O-methylidipropargylmalonate 42. Di-O-methylidipropargylmalonate 42 (20 mg, 0.096 mmol), tris-(pentafluorophenyl)phosphine (5 mg, 0.009 mmol) and Pd₂(dbach)₃ (2 mg, 0.002 mmol) were placed in a vial. Using 0.5 mL of C₆D₆, the mixture was transferred into an NMR tube. (Trimethylsilyl)tri-n-butylstannane (33 µL, 0.095 mmol) was then added to the solution. After 16 h at room temperature, the NMR spectrum of the solution was taken. Relative integration of the TMS peaks showed a yield of 65 % of the desired cyclic product.

For NMR data, see Entry 60.
A suspension of 2.1 g (87.5 mmol) of sodium hydride in 100 mL of THF was cooled to 0° C. Di-O-methylmalonate (5 mL, 43.7 mmol) in 25 mL of THF was added dropwise over 30 minutes. The temperature was maintained between 0 and 4 ° C. The addition funnel was rinsed with 25 mL of THF. After 5 minutes, the solution was brought back to room temperature. Propargyl bromide (9.2 mL, 82.6 mmol) was added over 1 h. The addition funnel was then rinsed with 10 mL of THF. The solution was stirred at room temperature overnight. The solution was then poured into 100 mL of a cold saturated solution of ammonium chloride. This mixture was extracted with four times 200 mL of diethyl ether. The organic solution was dried on magnesium sulfate, filtered and evaporated. The residue was then run on a silica gel column (petroleum ether/diethylether: 4/1) to yield 9.0 g of product (99 %).
$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 2.01 (2 H, t, $J_{HH}=2.5$ Hz, $H_5$), 2.98 (4 H, d, $J_{HH}=2.6$ Hz, $H_3$), 3.74 (6 H, s, CH$_3$); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 22.6 (C$_3$), 53.1 (CH$_3$), 56.4 (C$_5$), 71.7 (C$_4$), 78.3 (C$_2$), 169.0 (C$_1$).

Entry 52, SG-II-296.

$O$-Methyl-2-(2-propynyl)-4-pentynoate 66.

A flask equipped with a condenser was charged with di-$O$-methyl dipropargyImalonate 42 (4.38 g, 21.1 mmol) and lithium chloride (2.31 g, 54.4 mmol). The flask was purged with nitrogen. Water (0.4 mL, 22.2 mmol) and DMSO (100 mL) were added. The solution was brought to 170-200°C under nitrogen for 35 minutes. Gas evolution and darkening of the solution could be observed. After cooling of the solution, water (200 mL) was added to the dark mixture. The solution was extracted with four times 150 mL of hexanes. The solution was dried on magnesium sulfate, filtered and evaporated. The residue was finally distilled (47-50°C under 1.1 mm Hg) to yield 1.54 g (49 %) of the desired product.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.98 (2 H, t, $J_{HH}=2.7$ Hz, $H_5$), 2.58 (2 H, ddd (ABX), $J_{HH}=2.7$, 7.1, 16.9 Hz, $H_3$), 2.61 (2 H, ddd (ABX), $J_{HH}=2.7$, 5.9, 16.9 Hz, $H_3$), 2.74 (1 H, quintet, $J_{HH}=6.5$ Hz, $H_2$), 3.70 (3 H, s, CH$_3$). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 19.8 (t, C$_3$), 42.9 (d, C$_2$), 52.1 (q, CH$_3$), 70.5 (d, C$_3$), 80.3 (s, C$_9$), 172.7 (s, C$_7$).
A flask was charged with 504 mg (3.36 mmol) of 2-(2-propynyl)-4-pentynoate, 1.5 ml (9.00 mmol) of a 6 N aqueous sodium hydroxide solution and 30 mL of methanol. The solution was stirred at room temperature overnight. The solvent was then evaporated. After the addition of 20 mL of water, the solution was brought to pH 1 with 6 N HCl. It was then extracted three times with 20 mL of dichloromethane. The organic phase was dried on sodium sulfate, filtered and evaporated. The residue was then run on silica gel (ethyl acetate/hexanes: 1/3) to yield 380 mg (83 %) of product.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 2.01 (2 H, t, $J_{HH} = 2.6$ Hz, $H_3$), 2.60 (2 H, ddd (ABX), $J_{HH} = 2.6$, 7.1, 17.0 Hz, $H_3$), 2.61 (2 H, ddd (ABX), $J_{HH} = 2.6$, 6.0, 17.0 Hz, $H_3$), 2.76 (1 H, quintet, $J_{HH} = 6.5$ Hz, $H_2$), 12.13 (1 H, s, COOH). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 19.4 (t, $C_3$), 42.7 (d, $C_2$), 70.8 (d, $C_5$), 80.0 (s, $C_4$), 178.8 (s, $C_1$).

Entry 54, SG-III-62.

(S)-$\alpha$-Carboxymethoxyphenylmethyl]-2-(2-propynyl)-4-pentynoate 68.

$\begin{align*}
\text{H} & \quad \text{O} \\
\text{O} & \quad \text{COOCH}_3 \\
\text{Ph} & \quad \text{68}
\end{align*}$
2-(2-propynyl)-4-pentynoic acid 67 (100 mg, 0.735 mmol) was dissolved in 8 mL of dichloromethane. The solution was cooled to −10 °C. DMAP (5 mg, 0.063 mmol), methyl mandelate (124 mg, 0.746 mmol) and DCC (152 mg, 0.737 mmol) were added to the reaction mixture. After 30 minutes, the solution was brought back to room temperature and stirred overnight. After 17.5 h, the reaction mixture was filtered and evaporated. The residue was run on silica gel (hexanes/diethylether: 4/1) to afford 116 mg of product (56%).

$^1$H NMR (CDCl$_3$, 500 MHz): δ 1.97 (1 H, t, $J_{HH} = 2.5$ Hz, $H_5$), 2.03 (1 H, t, $J_{HH} = 2.5$ Hz, $H_5$), 2.66-2.71 (3 H, m, $H_3$), 2.76 (1 H, ddd, $J_{HH} = 2.7$, 5.6, 17.0 Hz, $H_3$), 2.92 (1 H, quintet, $J_{HH} = 6.5$ Hz, $H_2$), 3.70 (3 H, s, CH$_3$), 5.97 (1 H, s, CHPh), 7.36-7.46 (5 H, m, Ph). $^{13}$C NMR (CDCl$_3$, 125 MHz): δ 19.6 (t, $C_3$), 19.9 (t, $C_3$), 42.7 (d, $C_2$), 52.6 (q, CH$_3$), 70.6 (d, $C_5$), 70.8 (d, $C_5$), 74.8 (d, COOCHCOO), 80.1 (s, $C_4$), 127.6 (d, Ph), 128.8 (d, Ph), 129.3 (d, Ph), 133.5 (s, Ph), 168.8 (s, CO), 171.6 (s, CO). Assignments were confirmed by COSY, HMQC and DEPT 135.

Entry 55, SG-II-190.

(R)-[(α-Methyl)benzyl]-N,N-dipropargylamine 69.

To a solution of 2.30 g (16.7 mmol) of potassium carbonate in 4 mL of diethylether, were added 1.1 mL (8.5 mmol) of (R)-[α-methylbenzyl]amine and 2.3 mL (25.8 mmol) of diethylether.
mmol) of 80\% propargyl bromide in toluene. The vial was sealed and placed in an oil bath at 35°C for 22 h. The solvent was then evaporated and the residue was run on a silica gel column (dichloromethane) to yield 1.18 g (70 \% ) of the desired product.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.31 (3 H, d, J$_{HH}$= 6.6 Hz, CH$_3$), 2.14 (2 H, t, J$_{HH}$= 2.2 Hz, $H_d$), 3.42 (4 H, d, J$_{HH}$= 2.2 Hz, $H_2$), 3.58 (1 H, q, J$_{HH}$= 6.6 Hz, NCH), 7.17-7.29 (5 H, m, Ph). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 21.6 (q, CH$_3$), 39.8 (t, CH), 60.7 (d, NCH), 72.8 (d, CH), 79.1 (s, C), 127.3 (d, Ph), 128.6 (d, Ph), 144.3 (s, Ph).

Entry 56, SG-II-209.

(S)-[(α-Methyl)benzyl]-N,N-dipropargylamine 70.

To a solution of 230 mg (1.67 mmol) of potassium carbonate in 0.4 mL of diethylether, were added 110 µL (0.85 mmol) of (S)-[α-methylbenzyl]amine and 230 µL (2.06 mmol) of 80\% propargyl bromide in toluene. The vial was sealed and placed in an oil bath at 38°C for 16 h. The solvent was then evaporated and the residue was run on a silica gel column (dichloromethane) to yield 107 mg (64 \% ) of the desired product.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.31 (3 H, d, J$_{HH}$= 6.6 Hz, CH$_3$), 2.15 (2 H, t, J$_{HH}$= 2.2 Hz, $H_d$), 3.42 (4 H, d, J$_{HH}$= 2.2 Hz, $H_2$), 3.58 (1 H, q, J$_{HH}$= 6.6 Hz, NCH), 7.17-7.30 (5 H, m, Ph).
A solution of 87 mg of pent-4-enal (1.03 mmol) in 1 mL of diethyl ether was cooled to 0°C. Propynyl magnesium bromide (0.5 M, 2.5 mL, 1.25 mmol) was added to the solution. The cooling bath was removed and the reaction mixture was stirred at room temperature for 6.5 h. Aqueous ammonium chloride was then added and the mixture was extracted three times with diethyl ether. The organic phases were combined and dried on magnesium sulfate. After filtration and evaporation, the residue was purified by column chromatography on silica gel (ethyl acetate/hexanes: 1/4) to yield 62 mg (48 %) of the desired product.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.70-1.76 (m, 2H, $H_5$), 1.81 (s, 3 H, $H_1$), 1.91 (brd s, D$_2$O exchangeable, 1 H, OH), 2.18 (qt, 2 H, $J_{HH} = 7.2$, 1.2 Hz, $H_6$), 4.32 (brd s, 1 H, $H_4$), 4.95 (dt, 1 H, $J_{HH} = 10.2$, 1.5 Hz, $H_8$ cis), 5.02 (dt, 1 H, $J_{HH} = 17.1$, 1.6 Hz, $H_8$ trans), 5.80 (ddt, 1 H, $J_{HH} = 17.1$, 10.2, 6.7 Hz, $H_7$). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 3.5 (q, $C_1$), 29.4 (t, $C_6$), 37.1 (t, $C_5$), 62.0 (d, $C_4$), 80.1 (q), 81.2 (q), 115.1 (t, $C_8$), 137.8 (d, $C_7$).

Entry 58, SG-II-192.

$4$-($Tert$-butyldimethylsiloxy)$-oct-7$-ene-2$-yne$ 72.
Oct-7-ene-2-yne-4-ol 71 (59 mg, 0.48 mmol) was freeze-dried 3 times with 2 mL of benzene. DMF (0.6 mL), imidazole (82 mg, 1.20 mmol) and tert-butyldimethylsilyl-chloride (125 mg, 0.83 mmol) were added. The vial was sealed and placed in an oil bath at 65°C for 14 h. The mixture was then chromatographed on silica gel (petroleum ether/diethylether: 9/1) to afford 97 mg (86 %) of the product as a colorless oil.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.08 (s, 3H, $CH_3$), 0.10 (s, 3H, Si$CH_3$), 0.88 (s, 9 H, SiCC$CH_3$), 1.67-1.73 (m, 2 H, $H_5$), 1.80 (d, 3 H, $J_{HH} = 1.9$ Hz, $H_1$), 2.16 (q, 2 H, $J_{HH} = 7.7$ Hz, $H_6$), 4.31 (tq, 1 H, $J_{HH} = 6.4$, 1.9 Hz, $H_4$), 4.94 (dd, 1 H, $J_{HH} = 10.3$, 1.0 Hz, $H_8$ cis), 5.01 (dd, 1 H, $J_{HH} = 17.2$, 1.5 Hz, $H_8$ trans), 5.80 (ddt, 1 H, $J_{HH} = 17.0$, 10.3, 6.6 Hz, $H_7$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ -5.0 (q, Si$CH_3$), -4.5 (q, Si$CH_3$), 3.5 (q, $C_i$), 18.2 (s, t-Bu), 25.8 (q, t-Bu), 29.5 (t, $C_9$), 38.1 (t, $C_5$), 62.5 (d, $C_4$), 80.1 (s), 80.8 (s), 114.7 (t, $C_8$), 138.2 (q, $C_3$).

Entry 59, see Reference 22.

Entry 60, SG-II-194.

(3Z,4Z)-Di-O-methyl-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)-methylene]cyclopentanedicarboxylate 56.

![Structure of 56](image-url)
A solution of 50 mg of di-O-methyl dipropargylmalonate 42 (0.240 mmol), 83 µL of trimethylsilyltri-n-butylstannane (0.239 mmol), 4 mg of Pd₂(dba)₃ (0.004 mmol), 13 mg of tris-(pentafluorophenyl)phosphine (0.024 mmol) in 0.2 mL of benzene was prepared. The solution was stirred at room temperature for 22 h. The reaction was then run on silica gel (hexanes/diethylether: 9/1) to yield 97 mg (71 %) of the desired product.

1H NMR (CDCl₃, 500 MHz): δ 0.05 (9 H, s, SiCH₃), 0.85-0.88 (15 H, m, Bu), 1.24-1.44 (12 H, m, Bu), 2.66-3.20 (4 H, brd s, H₂, H₅), 3.69 (6 H, s, CH₃), 5.23 (1 H, s, SiCH), 5.65 (1 H, s, J_HSn= 50.0 Hz, SnCH). 13C NMR (CDCl₃, 125 MHz): δ 0.4 (q, SiCH₃), 10.7 (t, Bu), 13.6 (q, Bu), 27.3 (t, Bu), 28.9 (t, Bu), 44.1 (t), 44.10 (t), 52.7 (q, CH₃), 55.0 (s, C₁), 125.6 (d, SnCH), 126.2 (d, SiCH), 155.3 (s), 155.9 (s), 172.1 (s, CO). The assignment of the 13C NMR peaks was confirmed by HMQC. NOE: SnCH→H₂: 4.2 %; SnCH→SnBu₃: 4.0 %; SiCH→H₅: 4.2 %; SiCH→SiMe₃: 2.3 %. The retention times on HPLC were: 34.22 minutes on Chiralsel OJ (100 % hexanes, flow of 0.1 mL/min) and 51.92 minutes on Chiralsel OD (100 % hexanes, flow of 0.1 mL/min).

Entry 61, see entry 60.

Entry 62, SG-II-270.

O-Methyl-(3Z,4Z)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]-cyclopentanecarboxylate 73.

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*O*-Methyl-2-(2-propynyl)-4-pentyneate 66 (100 µL, 0.633 mmol), (trimethylsilyl)tri-\textit{n}-butylstannane (220 µL, 0.635 mmol), Pd$_2$(dba)$_3$ (12 mg, 0.013 mmol) and \textit{tri}s-(pentafluorophenyl)phosphine (36 mg, 0.068 mmol) were mixed in 0.2 mL of benzene. After 22 h of stirring at room temperature, the solvent was evaporated and the residue was chromatographed on silica gel (petroleum ether/diethylether: 99/1) to yield 215 mg (66 %) of the desired product.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.05 (9 H, s, SiCH$_3$), 0.84-0.88 (15 H, m, Bu), 1.24-1.44 (12 H, m, Bu), 2.56 (2 H, d, J$_{HH}=8.0$ Hz, $H_3$), 2.59 (2 H, d, J$_{HH}=7.9$ Hz, $H_5$), 2.83 (1 H, quintet, J$_{HH}=8.4$ Hz, $H_4$), 3.64 (3 H, s, CH$_3$), 5.21 (1 H, s, SiCH), 5.62 (1 H, s, J$_{HSn}$= 51.1, 53.2 Hz, SnCH). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 0.5 (SiCH$_3$), 10.7 (Bu), 13.6 (Bu), 27.3 (Bu), 29.0 (Bu), 38.5 ($C_4$), 39.5 (CH$_2$), 39.8 (CH$_2$), 51.7 (CH$_3$), 124.5 (SiCH), 124.8 (SnCH), 157.5, 157.9, 175.9 (CO). $^{119}$Sn NMR (CDCl$_3$, 185 MHz): $\delta$ -56.8 Reduce spectrum too. The assignments were confirmed by COSY and HMQC. NOE: SnCH→$H_2$: 6.6 %; SnCH→SnBu$_3$: 5.7 %; SnCH→SiMe$_3$: 2.1 %; SiCH→$H_5$: 5.8 %; SiCH→SiMe$_3$: 2.3 % %. The retention times on HPLC were: 31.31 minutes on Chiralsel OJ (100 % hexanes, flow of 0.1 mL/min), 13.26 and 15.13 minutes on Chiralsel OD (100 % hexanes, flow of 0.4 mL/min) and 15.53 minutes on silica (100 % hexanes, flow of 0.5 mL/min).
Entry 63, SG-III-063

\[ \{(S)-\alpha\text{-Carbomethoxyphenylmethyl}\}-\{(3Z,4Z)-3\text{-}[\text{tri-}n\text{-butylstannyl}]\text{methylene}\}-4\text{-}\{(\text{trimethylsilyl})\text{methylene}\}\text{cyclopentanecarboxylate 74.} \]

\[
\begin{align*}
&\text{O} \quad \text{O} \\
&\text{COOCH}_3 \\
&\text{Me}_3\text{Si} \quad \text{SnBu}_3 \\
&\text{Ph} \\
&\text{74}
\end{align*}
\]

\[ \{(S)-\alpha\text{-Carboxymethoxyphenylmethyl}\}-\{(2\text{-propynyl})\text{-4-pentynoate 68 (32 mg, 0.113 mmol), (trimethylsilyl)tri-}n\text{-butylstannane (43 \mu L, 0.124 mmol), Pd}_2(\text{dba})_3 (8 mg, 0.009 mmol) and tris\text{-}(\text{pentafluorophenyl})\text{phosphine (7 mg, 0.014 mmol) were mixed in 0.4 mL of benzene. After 18 h of stirring at room temperature, the solvent was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 9/1) to yield 55 mg (75 \%) of the desired product.} \]

\^H NMR (CDCl\textsubscript{3}, 500 MHz): \(\delta\) 0.06 (9 H, s, SiCH\textsubscript{3}), 0.85-0.89 (15 H, m, Bu), 1.25-1.46 (12 H, m, Bu), 2.62-2.77 (4 H, m, CH\textsubscript{2}), 3.01 (1 H, quintet, \(J\textsubscript{HH}= 8.4\) Hz, \(H_1\)), 3.70 (3 H, s, COOCH\textsubscript{3}), 5.23 (0.5 H, s, SiCH), 5.26 (0.5 H, s, SiCH), 5.64 (0.5 H, s, \(J\textsubscript{HSn}= 51.0, 52.8\) Hz, SnCH), 5.67 (0.5 H, s, \(J\textsubscript{HSn}= 52.0, 52.9\) Hz, SnCH), 5.92 (1 H, s, COOCHCOO), 7.36-7.45 (5 H, m, Ph). \(^{13}\)C NMR (CDCl\textsubscript{3}, 125 MHz): \(\delta\) 0.5 (SiCH\textsubscript{3}), 10.7 (Bu), 13.7 (Bu), 27.3 (Bu), 29.0 (Bu), 38.3 (\(C_1\)), 39.6 (CH\textsubscript{2}), 52.5 (COOCH\textsubscript{3}), 74.3 (COOCHCOO), 124.7 (SiCH), 125.0 (SnCH), 127.5 (Ph), 128.8 (Ph), 129.2 (Ph), 133.9 (Ph), 157.2, 157.6, 169.3 (CO), 174.8 (CO), 174.9 (CO). \(^{119}\)Sn NMR (CDCl\textsubscript{3}, 185 MHz): \(\delta\) -56.9, -56.8. Assignments were confirmed by COSY and HMQC. NOE: SnCH\textsubscript{4}→H\textsubscript{2}: 5.3
%; SnCH→SnBu3: 3.4 %; SiCH→H5: 3.7 %; SiCH→SiMe3: 1.8 %. The retention times on HPLC were: 7.02 minutes on Chiralsel OJ (100 % hexanes, flow of 0.5 mL/min), 34.22 minutes on Chiralsel OD (99 % hexanes, flow of 0.1 mL/min) and 13.42 minutes on silica (99 % hexanes, flow of 0.1 mL/min).

Entry 64, see Reference 22.

Entry 65-67, see Entry 68.

Entry 68, SG-II-189

(3E,4E)-3-[(Tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]-1-tosylpyrrolidine 55.

A solution of 97 mg of dipropargyltosylamine 54 (0.393 mmol), 140 µL of trimethylsilyltri-n-butylstannane (0.404 mmol), 8 mg of Pd2(dba)3 (0.009 mmol), 20 mg of tris-(pentfluorophenyl)phosphine (0.038 mmol) in 0.4 mL of benzene was prepared. The solution was stirred for 18 h. The reaction mixture was then chromatographed on silica gel (hexanes/diethylether: 4/1) to yield 184 mg (77 %) of the desired product.

1H NMR (CDCl3, 500 MHz): δ -0.02 (9 H, s, SiCH3), 0.80-0.87 (15 H, m, Bu), 1.19-1.38 (12 H, m, Bu), 2.39 (3 H, s, CH3), 3.82 (2 H, brd s, H5), 3.87 (2 H, brd s, H2), 5.28 (1
H, s, SiCH), 5.75 (1 H, s, J_{SnH}= 42.9 Hz, SnCH), 7.27 (2 H, d, J_{HH}= 8.1 Hz, Ph), 7.66 (2 H, d, J_{HH}= 8.3 Hz, Ph). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 0.1 (q, SiCH$_3$), 10.7 (t, Bu), 13.6 (q, Bu), 21.5 (q, CH$_3$), 27.2 (t, Bu), 28.8 (t, Bu), 56.4 (t, C$_2$), 56.6 (t, C$_2$), 127.3 (d, SiCH), 127.5 (d, Ph), 128.7 (d, SnCH), 129.6 (d, Ph), 134.2 (s, Ph), 143.3 (s, Ph), 150.5 (s), 150.9 (s). Assignments were confirmed by HMQC. NOE: SnCH→H$_2$: 5.9 %; SnCH→SnBu$_3$: 4.5 %; SiCH→H$_5$: 3.7 %; SiCH→SiMe$_3$: 1.6 %. The retention times on HPLC were: 13.50 minutes on Chiralsel OJ (99 % hexanes, flow of 0.3 mL/min) and 19.02 minutes on Chiralsel OD (99 % hexanes, flow of 0.3 mL/min).

Entry 69, SG-II-196.

(3E,4E)-3-[(Tri-n-butylstannylmethylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilylmethylene]pyrrolidine 75.

![Structure of compound 75](image)

A solution of 107 mg of (R)-[(α-methylbenzyl)-N,N-dipropargylamine 69 (0.543 mmol), 188 µL of trimethylsilyltri-n-butylstannane (0.542 mmol), 10 mg of Pd$_3$(dba)$_2$ (0.011 mmol), 29 mg of tris-(pentafluorophenyl)phosphine (0.055 mmol) in 0.2 mL of benzene was prepared. The solution was stirred for 24 h. The residue was then chromatographed on silica gel (hexanes/diethylether: 9/1) to yield 240 mg (79 %) of the desired product.
$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.08 (9 H, s, SiCH$_3$), 0.85-0.91 (15 H, m, Bu), 1.25-1.47 (12 H, m, Bu), 1.32 (3 H, d, $J_{HH}=6.6$ Hz, CH$_3$), 3.18 (1 H, d (AB), $J_{HH}=11.8$ Hz, $H_3$), 3.24 (2 H, d (AB), $J_{HH}=13.8$ Hz, $H_2$, $H_5'$), 3.35 (1 H, d (AB), $J_{HH}=11.8$ Hz, $H_2$), 3.36 (1 H, q, $J_{HH}=6.5$ Hz, NCH), 5.22 (1 H, s, SiCH), 5.67 (1 H, s, $J_{HSn}=47.5$ Hz, SnCH), 7.19-7.33 (5 H, m, Ph). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 0.5 (q, SiCH$_3$), 10.8 (t, Bu), 13.7 (q, Bu), 22.7 (q, CH$_3$), 27.3 (t, Bu), 29.0 (t, Bu), 62.1 (t, C$_2$), 62.5 (t, C$_3$), 66.3 (d, NCH), 123.5 (d, SiCH), 124.8 (d, SnCH), 126.9 (d, Ph), 127.4 (d, Ph), 128.3 (d, Ph), 145.1 (s), 155.7 (s), 156.2 (s). Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SnCH$\rightarrow$H$_2$: 6.4 %; SnCH$\rightarrow$SnBu$_3$: 4.3 %; SiCH$\rightarrow$H$_5$: 8.6 %. The retention times on HPLC were: 10.33 minutes on Chiralsel OJ (99 % hexanes, flow of 1.0 mL/min) and 8.80 minutes on Chiralsel OD (99.5 % hexanes, flow of 0.4 mL/min).

Entries 70-71, see entry 69.

Entry 72, SG-II-211.

(3$E$,4$E$)-3-[(Tri-$n$-butylstannyl)methylene]-1-[(S)-(α-methylbenzyl)]-4-[(trimethyl-silyl)methylene]pyrrolidine 76.
A solution of 107 mg of (S)-[(α-methyl)benzyl]-N,N-dipropargylamine 70 (0.543 mmol), 197 µL of trimethylsilyltrini-<i>n</i>-butylstannane (0.568 mmol), 14 mg of Pd<sub>2</sub>(dba), (0.015 mmol), 32 mg of tris-(pentafluorophenyl)phosphine (0.060 mmol) in 0.2 mL of benzene was prepared. The solution was stirred for 18 h. The residue was then chromatographed on silica gel (hexanes/diethylether: 9/1) to yield 257 mg (85 %) of the desired product.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 0.08 (9 H, s, SiC<sub>H</sub><sub>3</sub>), 0.85-0.91 (15 H, m, Bu), 1.25-1.47 (12 H, m, Bu), 1.32 (3 H, d, J<sub>H</sub>H<sub>3</sub>= 6.6 Hz, CH<sub>3</sub>), 3.18 (1 H, d (AB), J<sub>H</sub>H<sub>3</sub>= 11.8 Hz, H<sub>3</sub>), 3.24 (2 H, d (AB), J<sub>H</sub>H<sub>3</sub>= 13.8 Hz, H<sub>2</sub>, H<sub>5</sub>'), 3.35 (1 H, d (AB), J<sub>H</sub>H<sub>3</sub>= 11.8 Hz, H<sub>2</sub>'), 3.36 (1 H, q, J<sub>H</sub>H<sub>3</sub>= 6.5 Hz, NCH), 5.22 (1 H, s, SiCH), 5.67 (1 H, s, J<sub>H</sub>Sn= 47.5 Hz, SnCH), 7.19-7.33 (5 H, m, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 0.5 (q, SiCH<sub>3</sub>), 10.8 (t, Bu), 13.7 (q, Bu), 22.7 (q, CH<sub>3</sub>), 27.3 (t, Bu), 29.0 (t, Bu), 62.1 (t, C<sub>2</sub>), 62.4 (t, C<sub>3</sub>), 66.3 (d, NCH), 123.5 (d, SiCH), 124.8 (d, SnCH), 126.8 (d, Ph), 127.4 (d, Ph), 128.3 (d, Ph), 145.1 (s), 155.6 (s), 156.2 (s). Assignments were confirmed by DEPT 135.

Entry 73, SG-II-81.

(Trimethylsilyl)tri-<i>n</i>-butylstannane 77.

Me<sub>3</sub>SiSnBu<sub>3</sub> 77

A solution of 0.8 mL (5.71 mmol) of di-<i>iso</i>-propylamine in 10 mL of THF was cooled to −78°C. After 10 minutes, 2.1 mL ( 5.00 mmol) of 2.38 M <i>n</i>-butyl lithium was added over 5 minutes. After 5 minutes, the cooling bath was removed and the solution was brought back to room temperature. Tri-<i>n</i>-butyltinhydride (1 mL, 3.72 mmol) was then added over 5 minutes. The reaction mixture was stirred at room temperature for 20 minutes.
Trimethylsilylchloride (0.75 mL, 5.91 mmol) was then added to the solution over 5 minutes. After about 5 minutes, the solution became cloudy (formation of lithium chloride). The solution was stirred at room temperature for 10 more minutes, evaporated and chromatographed on silica gel (hexanes). The product was obtained in quantitative yield. Alternatively, the product could be distilled at 85°C under 2 mm Hg.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 0.22 (s, 9 H, SiCH$_3$), 0.81-0.89 (m, 15 H, CH$_2$CH$_3$), 1.24-1.51 (m, 12 H, SnCH$_2$CH$_3$). $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 1.49 (q), 7.86 (t), 13.74 (q), 27.61 (t), 30.34 (t).

Entry 74, SG-II-281.

**(Tert-butyldimethylsilyl)tri-n-butylstannane 78.**

$t$-BuMe$_2$SiSnBu$_3$

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A solution of 1 mL (7.14 mmol) of di-*iso*-propylamine in 10 mL of THF was cooled to $-78^\circ$C. After 10 minutes, 4.4 mL (6.25 mmol) of 1.42 M $n$-butyl lithium was added over 5 minutes. After 10 minutes, the cooling bath was removed and the solution was brought back to room temperature. Tri-$n$-butyltinhydride (1.3 mL, 4.83 mmol) was then added over 5 minutes. The reaction mixture was stirred at room temperature for 30 minutes. *Tert*-butyldimethylsilylchloride (2.13 g, 14.13 mmol) was then added to the solution. After about 5 minutes, the solution became cloudy (formation of lithium chloride). The solution was stirred at room temperature for 1.5 h, evaporated and chromatographed on silica gel (hexanes). The product was obtained in quantitative yield.
\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 0.16 (6 H, s, SiCH\(_3\)), 0.84-0.93 (15 H, m, Bu), 0.92 (9 H, s, t-Bu), 1.30 (6 H, sextuplet, J\(_{HH}\)= 7.3 Hz, Bu), 1.43-1.50 (6 H, m, Bu). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) -2.8 (SiCH\(_3\)), 8.2 (Bu), 13.7 (Bu), 18.5 (CSi), 27.4 (CH\(_3\)), 27.7 (Bu), 30.2 (Bu). \(^{119}\)Sn NMR (CDCl\(_3\), 185 MHz): \(\delta\) -123.0.

Entry 75, SG-III-73.

(Triethylsilyl)tri-\(n\)-butylstannane 79.

\[\text{Et}_3\text{SiSnBu}_3\]

A solution of 0.5 mL (3.57 mmol) of di-\(iso\)-propylamine in 5 mL of THF was cooled to \(-78^\circ\)C. After 10 minutes, 2.5mL (3.00 mmol) of 1.20 M \(n\)-butyl lithium was added over 5 minutes. After 15 minutes, the cooling bath was removed and the solution was brought back to room temperature. Tri-\(n\)-butyltinhydride (0.6 mL, 2.23 mmol) was then added over 5 minutes. The reaction mixture was stirred at room temperature for 30 minutes. Triethylsilylchloride (0.5 mL, 2.98 mmol) was then added to the solution. After about 5 minutes, the solution became cloudy (formation of lithium chloride). The solution was stirred at room temperature for 3 h, evaporated and chromatographed on silica gel (hexanes). The product was obtained in quantitative yield.

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 0.72 (6 H, q, J\(_{HH}\)= 7.9 Hz, SiCH\(_2\)), 0.84-0.89 (15 H, m, Bu), 0.97 (9 H, t, J\(_{HH}\)= 7.9 Hz, SiCH\(_2\)CH\(_3\)), 1.29 (6 H, sextuplet, J\(_{HH}\)= 7.4 Hz, Bu), 1.43-1.49 (6 H, m, Bu). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 5.9 (t, SiCH\(_2\)), 8.3 (t, Bu), 8.7 (q, SiCH\(_2\)).
Si\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 13.7 (q, Bu), 27.7 (t, Bu), 30.3 (t, Bu). \textsuperscript{119}Sn NMR (CDCl\textsubscript{3}, 185 MHz): \(\delta -122.8\).

Entry 76, SG-III-74.

(Tri-iso-propylsilyl)tri-\textit{n}-butylstannane 80.

(i-Pr\textsubscript{3})SiSnBu\textsubscript{3} 80

A solution of 0.5 mL (3.57 mmol) of di-\textit{iso}-propylamine in 5 mL of THF was cooled to –78°C. After 10 minutes, 2.5mL (3.00 mmol) of 1.20 M \textit{n}-butyl lithium was added over 5 minutes. After 10 minutes, the cooling bath was removed and the solution was brought back to room temperature. Tri-\textit{n}-butyltinhydride (0.6 mL, 2.23 mmol) was then added over 5 minutes. The reaction mixture was stirred at room temperature for 30 minutes. Tri-\textit{iso}-propylsilylchloride (0.6 mL, 2.80 mmol) was then added to the solution. After about 5 minutes, the solution became cloudy (formation of lithium chloride). The solution was stirred at room temperature for 4 h, evaporated and chromatographed on silica gel (hexanes). The product was obtained in quantitative yield.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz): \(\delta 0.86-0.89\) (15 H, m, Bu), 1.07 (18 H, d, J\textsubscript{HH}= 7.2 Hz, CHCH\textsubscript{3}), 1.15-1.22 (3 H, m, SiCH), 1.30 (6 H, sextuplet, J\textsubscript{HH}= 7.3 Hz, Bu), 1.43-1.49 (6 H, m, Bu). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz): \(\delta 9.2\) (t, Bu), 13.5 (q, Bu), 13.6 (d, CH), 20.2 (q, SiCHCH\textsubscript{3}), 27.8 (t, Bu), 30.1 (t, Bu). \textsuperscript{119}Sn NMR (CDCl\textsubscript{3}, 185 MHz): \(\delta -125.2\).

Entry 77-78, see Entry 79.
Entry 79, SG-III-81.

(Tri-iso-propylsilyl)triphenylstannane 83.

\[(i-Pr)_3SiSnPh_3 \]

A solution of 0.5 mL (3.57 mmol) of di-iso-propylamine in 5 mL of THF was cooled to –78°C. After 10 minutes, 2.5mL (3.00 mmol) of 1.20 M n-butyl lithium was added over 5 minutes. After 10 minutes, the cooling bath was removed and the solution was brought back to room temperature. Triphenyltinhydride (0.57 mL, 2.23 mmol) was then added over 5 minutes. The reaction mixture was stirred at room temperature for 0.5 h. Tri-iso-propylsilylchloride (0.5 mL, 2.34 mmol) was then added to the solution. The solution was stirred at room temperature overnight. The reaction mixture was then evaporated and chromatographed on silica gel (hexanes). The product was obtained 68 % yield (767 mg).

\(^1\)H NMR (CDCl₃, 500 MHz): \(\delta\) 1.12 (18 H, t, JHH= 7.4 Hz, CH₃), 1.42 (3 H, quintet, JHH= 7.4 Hz, CH), 7.27-7.29 (9 H, m, Ph), 7.49-7.51 (6 H, m, Ph). \(^{13}\)C NMR (CDCl₃, 125 MHz): \(\delta\) 13.5 (CH), 20.2 (CH₃), 128.0 (Ph), 128.3 (Ph), 137.5 (Ph), 141.6 (Ph). \(^{119}\)Sn NMR (CDCl₃, 185 MHz): \(\delta\) -166.9.

Entry 80, SG-III-82.

(Tert-butyldimethylsilyl)triphenylstannane 84.

\[t-BuMe_2SiSnPh_3 \]

A solution of 0.5 mL (3.57 mmol) of di-iso-propylamine in 5 mL of THF was cooled to –78°C. After 10 minutes, 2.5mL (3.00 mmol) of 1.20 M n-butyl lithium was added over 5
minutes. After 10 minutes, the cooling bath was removed and the solution was brought back to room temperature. Triphenyltinhydride (0.57 mL, 2.23 mmol) was then added over 5 minutes. The reaction mixture was stirred at room temperature for 0.5 h. Tert-butyldimethylsilylchloride (600 mg, 3.98 mmol) was then added to the solution. The solution was stirred at room temperature overnight. The reaction mixture was then evaporated and chromatographed on silica gel (hexanes). The product was obtained 99 % yield (1.033 g).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta 0.40 (6 \text{ H, s, SiCH}_3), 0.96 (9 \text{ H, s, CCH}_3), 7.30-7.31 (9 \text{ H, m, Ph}), 7.50-7.51 (6 \text{ H, m, Ph})\). \(^13\)C NMR (CDCl\(_3\), 125 MHz): \(\delta -2.5 (\text{SiCH}_3), 19.0 (\text{CCH}_3), 27.5 (\text{CCH}_3), 128.1 \text{ (Ph), 128.3 \text{ (Ph), 137.5 \text{ (Ph), 140.6 \text{ (Ph)})}\). \(^{119}\)Sn NMR (CDCl\(_3\), 185 MHz): \(\delta -170.8\).

Entries 81-82, see Entry 83.

Entry 83, SG-III-122.

**Di-O-methyl-(3Z,4Z)-3-[(tri-\(n\)-butylstannyl)methylene]-4-[(triethylsilyl)methylene]-cyclopentanedicarboxylate 86.**
Di-O-methylpropargylmalonate 42 (51 mg, 0.245 mmol), (triethylsilyl)tri-n-butylstannane (99 mg, 0.244 mmol), Pd$_2$(dba)$_3$ (7 mg, 0.008 mmol) and tris-(pentafluorophenyl)phosphine (22 mg, 0.041 mmol) were mixed in 0.5 mL of benzene. The vial was sealed and placed in an oil bath at 68ºC. After 16 h, the solvent was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 95/5; 80/20) to yield 51 mg (34 %) of the desired product and 17 mg of di-O-methylpropargylmalonate.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.58 (6 H, q, $J_{HH}=7.8$ Hz, SiCH$_2$), 0.85-0.90 (24 H, m, Bu, SiCH$_2$CH$_3$), 1.27 (6 H, hex, $J_{HH}=7.3$ Hz, Bu), 1.37-1.44 (6 H, m, Bu), 2.94 (4 H, brd s, $H_3$, $H_5$), 3.69 (6 H, s, CH$_3$), 5.23 (1 H, s, SiCH), 5.63 (1 H, s, $J_{H_{119}Sn}=49.5$ Hz, SnCH).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 4.5 (t, SiCH$_2$), 7.4 (q, SiCH$_2$CH$_3$), 10.6 (t, Bu), 13.7 (q, Bu), 27.3 (t, Bu), 29.0 (t, Bu), 44.3 (CH$_2$), 44.4 (CH$_2$), 52.7 (q, CH$_3$), 54.9 (s, C$_1$), 122.3 (d, SiCH), 125.9 (d, SnCH), 155.6 (s), 156.9 (s), 172.2 (s, CO). $^{119}$Sn NMR (CDCl$_3$, 185 MHz): $\delta$ -55.0. Assignments were confirmed by COSY, HETCOR and DEPT 135. NOE: SnCH$\rightarrow$H$_2$: 8.8 %; SnCH$\rightarrow$SnBu$_3$: 5.5 %; SiCH$\rightarrow$H$_5$: 7.7 %; SiCH$\rightarrow$SiEt$_3$: 5.7 %.

Entry 84, see Entry 85.

Entry 85, SG-II-295.

A vial was charged with 103 mg (0.495 mmol) of di-O-methyldipropargylmalonate, 207 mg (0.511 mmol) of (tert-butyldimethylsilyl)tri-n-butylstannane, 11 mg (0.012 mmol) of Pd₂(dba)₃ and 28 mg (0.053 mmol) of tris-(pentafluorophenyl)phosphine in 0.4 mL of benzene. The vial was sealed and placed in an oil bath at 58°C for 13 h. The solvent was then evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 95/5) to yield 50 mg (17 %) of the desired product.

¹H NMR (CDCl₃, 500 MHz): δ 0.04 (6 H, s, Si CH₃), 0.82-0.90 (24 H, m, t-Bu, Bu), 1.23-1.45 (12 H, m, Bu), 2.87-3.00 (4 H, brd peak, H₂, H₃), 3.70 (6 H, s, CH₃), 5.29 (1 H, s, Si CH), 5.65 (1 H, s, J_HSn = 50 Hz, Sn CH). ¹³C NMR (CDCl₃, 125 MHz): δ -4.4 (Si CH₃), 10.8 (Bu), 13.7 (Bu), 17.2 (C CH₃), 26.4 (C CH₃), 27.3 (Bu), 29.0 (Bu), 44.1 (CH₂), 44.5 (CH₂), 52.8 (CH₃), 54.7 (C₁), 122.4 (Si CH), 126.3 (Sn CH), 155.3, 157.6, 172.2. ¹¹⁹Sn NMR (CDCl₃, 185 MHz): δ -55.6. Assignments were confirmed by COSY and HMQC. NOE: Sn CH→H₅: 6.4 %; Sn CH→Sn Bu₃: 3.7 %; Si CH→H₂: 6.8 %; Si CH→Si Me₂: 1.4 %; Si CH→t-Bu: 5.2 %. The retention time on HPLC was: 53.36 minutes on Chiralsel OJ (100 % hexanes, flow of 0.1 mL/min) and 21.34 minutes on Chiralsel OD (100 % hexanes, flow of 0.3 mL/min).

Entries 86-88, see Entry 85.
Entry 89, SG-III-121.

Di-O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyln)-methylene]cyclopentanedicarboxylate 89.

\[
\begin{align*}
&\text{H}_3\text{COOC} \quad \text{COOCH}_3 \\
&\text{t-BuMe}_2\text{Si} \quad \text{SnPh}_3 \\
\end{align*}
\]

Di-O-methylidipropargylmalonate 42 (51 mg, 0.245 mmol), (tert-butyldimethylsilyl)-triphenylstannane (115 mg, 0.247 mmol), Pd\(_2\)(dba)\(_3\) (7 mg, 0.008 mmol) and tris-(pentafluorophenyl)phosphine (25 mg, 0.047 mmol) were mixed in 0.5 mL of benzene. After 16 h of stirring at room temperature, the solvent was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 95/5; 80/20) to yield 151 mg (91 %) of the desired product.

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) -0.7-0.2 (6 H, brd lump, SiCH\(_3\)), 0.78 (9 H, s, SiCCH\(_3\)), 3.01 (2 H, brd s, \(H_2\)), 3.20 (2 H, brd s, \(H_2\)), 3.77 (6 H, s, CH\(_3\)), 5.23 (1 H, s, SiCH), 6.13 (1 H, s, \(J_{\text{HSn}} = 66.4 \text{ Hz}, \text{SnCH}\)), 7.39-7.40 (9 H, m, Ph), 7.47-7.70 (6 H, m, Ph). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) -5.5—3.5 (lump, SiCH\(_3\)), 17.4 (s, SiCCH\(_3\)), 26.3 (q, SiCCH\(_3\)), 43.8 (t, CH\(_2\)), 44.4 (t, CH\(_2\)), 52.9 (q, CH\(_3\)), 54.7 (s, C\(_1\)), 122.4 (d, SnCH), 125.4 (d, SiCH), 128.3 (d, Ph), 128.7 (d, Ph), 137.2 (d, Ph), 139.8 (s, Ph), 155.9 (s), 159.2 (s), 172.0 (s, CO). \(^{119}\)Sn NMR (CDCl\(_3\), 185 MHz): \(\delta\) -154.5. Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SnCH→\(H_5\): 5.5 %; SnCH→SnPh\(_3\): 3.8 %; SiCH→\(H_2\): 4.5 %; SiCH→t-Bu: 3.8 %.
Entry 90, see Entry 89.

Entry 91, see Entry 92.

Entry 92, SG-III-124.

**Di-O-methyl-(3Z,4Z)-3-[(triphenylstannyl)methylene]-4-[(tri-iso-propylsilyl)-methylene]cyclopentanedicarboxylate 90.**

![Structure](image)

Di-O-methylpropargyldimaleate 42 (50 mg, 0.240 mmol), (tri-iso-propylsilyl)triphenyl-stannane (117 mg, 0.231 mmol), Pd$_2$(dba)$_3$ (9 mg, 0.010 mmol) and tris-(pentafluorophenyl)phosphine (30 mg, 0.056 mmol) were mixed in 0.5 mL of benzene. After 16 h of stirring at 68°C, the solvent was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 80/20) to yield 44 mg (27 %) of the desired product.

$^1$H NMR (CDCl$_3$, 500 MHz): δ 0.75 (18 H, d, $J_{HH}=7.1$ Hz, SiCH$_2$H$_3$), 0.88 (3 H, q, $J_{HH}=7.3$ Hz, SiCH$_3$), 3.02 (2 H, brd s, $H_5$), 3.15 (2 H, brd s, $H_2$), 3.70 (6 H, s, CH$_3$), 5.24 (1 H, s, SiCH), 5.96 (1 H, s, $J_{HSSn}=58.0$, 60.1 Hz, SnCH), 7.29-7.36 (9 H, m, Ph), 7.47-7.58 (6 H, m, Ph). $^{13}$C NMR (CDCl$_3$, 125 MHz): δ 13.0 (d, SiCHCH$_3$), 19.3 (q, SiCHCH$_3$), 44.9 (t, CH$_2$), 45.2 (t, CH$_2$), 52.9 (q, CH$_3$), 54.7 (s, $C_7$), 121.9 (d, SnCH), 125.3 (d, SiCH), 128.3 (d, Ph), 128.7 (d, Ph), 137.0 (d, Ph), 139.7 (s, Ph), 154.9 (s), 159.4 (s), 172.0 (s, CO). $^{119}$Sn NMR (CDCl$_3$, 185 MHz): δ -162.6. Assignments were
confirmed by COSY, HMQC and DEPT 135. The retention times on HPLC were: 30.91 minutes on Chiralsel OJ (100 % hexanes, flow of 0.1 mL/min) and 37.90 minutes on Chiralsel OD (100 % hexanes, flow of 0.1 mL/min).

Entry 93, see Entry 94.

Entry 94, SG-III-64.

\[ O\text{-Methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-n-butylstannyl)-methylene]cyclopentanecarboxylate 91.} \]

\[
\begin{align*}
&\text{COOCH}_3 \\
&\text{t-BuMe}_2\text{Si SnBu}_3 \\
&\text{91}
\end{align*}
\]

A vial was charged with 200 mg (1.333 mmol) of \( O\text{-methyl-2-(2-propynyl)-4-pentynoate 66} \), 540 mg (1.333 mmol) of \((\text{tert-butyldimethylsilyl)tri-n-butylstannane}, 30 \text{ mg (0.033 mmol) of Pd}_2(\text{dba})_3 \) and 71 mg (0.133 mmol) of \text{tris-(pentafluorophenyl)phosphine} \text{ in 0.4 mL of benzene. The vial was sealed and placed in an oil bath at 52°C for 17.5 h. The solvent was then evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 99/1) to yield 32 mg (4 %) of the desired product.}

\( ^1\)H NMR (CDCl\textsubscript{3}, 500 MHz): \( \delta 0.11 (3 \text{ H, s, SiCH}_3), 0.12 (3 \text{ H, s, SiCH}_3), 0.90-0.99 (24 \text{ H, m, Bu, t-Bu}), 1.30-1.51 (12 \text{ H, m, Bu}), 2.66 (4 \text{ H, brd s, CH}_2), 2.91 (1 \text{ H, quintet, J}_{HH} = 8.3 \text{ Hz, } H_1), 2.72 (3 \text{ H, s, CH}_3), 5.34 (1 \text{ H, s, SiCH}), 5.70 (1 \text{ H, s, J}_{H\text{Sn}} = 54.3 \text{ Hz, SnCH}). \)

\( ^1\)C NMR (CDCl\textsubscript{3}, 125 MHz): \( \delta -4.4 \text{ (q, SiCH}_3), -4.3 \text{ (q, SiCH}_3), 10.8 \text{ (t, Bu), 13.7} \)
(q, Bu), 17.3 (s, SiC), 26.5 (q, SiC\textsubscript{3}H\textsubscript{3}), 27.3 (t, Bu), 29.1 (t, Bu), 38.4 (d, C\textsubscript{1}), 39.9 (Broad, CH\textsubscript{2}), 51.8 (q, COOCH\textsubscript{3}), 121.5 (SiCH), 125.1 (SnCH), 176.0 (COO). \textsuperscript{119}Sn NMR (CDCl\textsubscript{3}, 185 MHz): δ –56.5. Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SnCH→H\textsubscript{3}: 4.8 %; SnCH→SnBu\textsubscript{3}: 4.0 %; SiCH→H\textsubscript{2}: 3.6 %; SiCH→t-Bu: 4.0 %; SiCH→SiMe\textsubscript{2}: 1.0%.

Entry 95, see Entry 94.

Entry 96, SG-III-136.

\textit{O-Methyl-(3Z,4Z)-3-[(\textit{tert}-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)-methylene]cyclopentanecarboxylate 92.}

\begin{center}
\begin{tikzpicture}
\node[draw] (c) at (0,0) {COOCH\textsubscript{3}};
\node[draw] (s) at (-0.5,0) {t-BuMe\textsubscript{2}Si SnPh\textsubscript{3}};
\end{tikzpicture}
\end{center}

\textit{O-methyl-2-(2-propynyl)-4-pentynoate 66} (62 mg, 0.413 mmol), (\textit{tert}-butyldimethylsilyl)triphenylstannane (154 mg, 0.331 mmol), Pd\textsubscript{2}(dba)\textsubscript{3} (14 mg, 0.015 mmol) and \textit{tris-}(pentafluorophenyl)phosphine (50 mg, 0.094 mmol) were mixed in 1 mL of benzene. After 15 h of stirring at room temperature, the solvent was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 95/5; 90/10) to yield 181 mg (89 %) of the desired product.
\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) -0.19 (6 H, brd s, SiCH\(_3\)), 0.83 (9 H, s, SiCCH\(_3\)), 2.68-2.74 (2 H, m, H\(_2\)), 2.90 (2 H, d, J\(_{HH}\)=7.6 Hz, H\(_3\)), 3.06 (1 H, quintet, H\(_1\)), 3.77 (3 H, s, CH\(_3\)), 5.27 (1 H, s, SiCH), 6.15 (1 H, s, J\(_{H_{Sn}}=69.5\) Hz, SnCH), 7.41-7.43 (9 H, m, Ph), 7.59-7.68 (6 H, m, Ph). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) -4.6 (SiCH\(_3\)), 17.4 (SiCCH\(_3\)), 26.4 (SiCCH\(_3\)), 38.3 (C\(_i\)), 39.5 (CH\(_2\)), 51.8 (CH\(_3\)), 121.2 (SnCH), 124.5 (SiCH), 128.3 (Ph), 128.7 (Ph), 137.2 (Ph), 140.0 (Ph), 158.1, 161.2, 175.7 (CO). \(^{119}\)Sn NMR (CDCl\(_3\), 185 MHz): \(\delta\) -154.5. Assignments were confirmed by COSY and HMQC. NOE: SnCH\(_2\)→H\(_5\): 5.4 %; SnCH\(_2\)→SnPh\(_3\): 3.4 %; SiCH\(_2\)→H\(_2\): 4.4 %; SiCH\(_2\)→t-Bu: 4.0.

Entry 97, SG-III-142.

\([\text{(S)-}\alpha\text{-Carbomethoxyphenylmethyl}][-\text{(3Z,4Z)-3-}[\text{(t} \text{ert-} \text{butyldimethylsilyl)}\text{methylen}e][-\text{4-}[\text{triphenylstanny}l]\text{methylen}e]\text{cyclopentanecarboxylate 93.}\]

\([\text{(S)-}\alpha\text{-carbomethoxyphenylmethyl}]-2-(2\text{-propynyl})-4\text{-penty}noate 68\) (52 mg, 0.183 mmol), (t\text{ert-butyldimethyl}si\ell)\text{triphenylstannane} (82 mg, 0.176 mmol), Pd\(_2\)(dba)\(_3\) (4 mg, 0.004 mmol) and tris-(\text{pentafluorophenyl}) phosphate (9 mg, 0.017 mmol) were mixed in 0.5 mL of benzene. After 15 h of stirring at room temperature, the solvent was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 90/10) to yield 101 mg (74 %) of the desired product.
\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) -0.22 (12 H, s, SiC\(_6\)H\(_3\)), 0.78 (9 H, s, SiC\(_6\)H\(_3\)), 0.79 (9 H, s, SiC\(_6\)H\(_3\)), 2.73-3.01 (8 H, m, CH\(_2\)), 3.19 (2 H, quintet, \(J_{HH}=8.2\) Hz, \(H_1\)), 3.76 (3 H, s, CH\(_3\)), 3.77 (3 H, s, CH\(_3\)), 5.24 (1 H, s, SiCH), 5.27 (1 H, s, SiCH), 6.02 (1 H, s, COOCH\(_2\)COO), 6.03 (1 H, s, COOCH\(_2\)COO), 6.12 (1 H, s, \(J_{HH}=69.2\) Hz, SnCH), 6.15 (1 H, s, \(J_{HH}=69.4\) Hz, SnCH), 7.39-7.62 (40 H, m, Ph). \(^1^3\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) -4.0 (SiC\(_6\)H\(_3\)), 17.9 (SiC\(_6\)H\(_3\)), 26.9 (SiC\(_6\)H\(_3\)), 38.6 (C\(_i\)), 39.8 (CH\(_2\)), 53.0 (COOCH\(_3\)), 74.9 (COOCH\(_2\)COO), 121.8 (CH), 125.3 (CH), 128.1 (Ph), 128.8 (Ph), 129.2 (Ph), 129.2 (Ph), 129.7 (Ph), 137.7 (Ph), 140.5 (Ph), 158.4, 161.5, 169.7 (CO), 175.0 (CO). \(^{119}\)Sn NMR (CDCl\(_3\), 185 MHz): \(\delta\) -154.6, -154.7. Assignments were confirmed by COSY and HMQC. NOE: SnCH→\(H_5\): 3.6 %; SnCH→SnPh\(_3\): 3.5 %; SnCH→CH\(_3\): 1.0 %; SiCH→\(H_2\): 3.7 %; SiCH→t-Bu: 2.3 %.

Entry 98, SG-II-203.

\((3E,4E)-3-[(\text{Tert-butyldimethylsilyl})\text{methylene}]\text{-1-}[\text{(R)-(a-methylbenzyl)}]-4-[(\text{trimethylstannyl})\text{methylene}]\text{pyrrolidine} 94.\)

\[
\text{Ph} \\
\begin{array}{c}
|\
\end{array} \\
\begin{array}{c}
|\
\end{array} \\
\begin{array}{c}
t-\text{BuMe}_2\text{Si} \\
\end{array} \\
\begin{array}{c}
\text{SnMe}_3 \\
94 \\
\end{array}

A solution of 100 mg of \((R)-[(\alpha\text{-methyl})\text{benzyl}]\text{-N,N-propargylamine} 69\) (0.508 mmol), 147 mg of tert-butyldimethylsilyltrimethylstannane (0.527 mmol), 10 mg of Pd\(_2\)(dba),
(0.011 mmol), 29 mg of tris-(pentafluorophenyl)phosphine (0.055 mmol) in 0.5 mL of benzene was prepared. The solution was stirred for 14 h. The reaction was then chromatographed on silica gel (hexanes/diethylether: 95/5) to yield 38 mg (16 %) of the desired product.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.05 (3 H, s, SiCH$_3$), 0.06 (3 H, s, SiCH$_3$), 0.13 (9 H, s, SnCH$_3$), 0.84 (9 H, s, t-Bu), 1.32 (3 H, d, $J_{HH}$= 6.6 Hz, CH$_3$), 3.16 (1 H, d (AB), $J_{HH}$= 10.6 Hz, $H_5$), 3.27 (1 H, d (AB), $J_{HH}$= 10.6 Hz, $H_5'$), 3.28 (1 H, d (AB), $J_{HH}$= 13.1 Hz, $H_2$), 3.34 (1 H, q, $J_{HH}$= 6.7 Hz, NCH), 3.35 (1 H, d (AB), $J_{HH}$= 13.0 Hz, $H_2'$), 5.28 (1 H, s, SiCH), 5.68 (1 H, s, $J_{HSn}$= 56.9 Hz, SnCH), 7.21-7.33 (5 H, m, Ph). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ -7.1 (q, SnCH$_3$), -4.7 (q, SiCH$_3$), -4.6 (q, SiCH$_3$), 17.4 (s, t-Bu), 22.6 (q, CH$_3$), 26.5 (q, t-Bu), 61.9 (d, $C_2$), 62.5 (d, $C_5$), 66.4 (d, NCH), 120.8 (d, SiCH), 125.6 (d, SnCH), 126.9 (d, Ph), 127.4 (d, Ph), 128.3 (d, Ph), 144.9 (s), 155.6 (s), 157.3 (s). Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SnCH→$H_2$: 3.4 %; SnCH→SnMe$_3$: 1.8 %; SiCH→$H_5$: 4.9 %; SiCH→t-Bu: 3.6 %; SiCH→SiMe$_2$: 1.8 %.


$(3E,4E)$-3-[(Tert-butyldimethylsilyl)methylene]-1-[(R)-$\alpha$-methylbenzyl]-4-[(tri-$n$-butylstannyl)methylene]pyrrolidine 95.
A solution of 50 mg of \((R)-[(\alpha\text{-methyl})\text{benzyl}]\text{-}N,N\text{-dipropargylamine}\) 69 (0.254 mmol), 103 mg of \((\text{tert}-\text{butyldimethylsilyl})\text{tri-}n\text{-butylstannane}\) (0.254 mmol), 6 mg of \(\text{Pd}_2\text{(dba)}_3\) (0.007 mmol), 14 mg of \(\text{tris-(pentafluorophenyl)}\text{phosphine}\) (0.026 mmol) in 0.5 mL of benzene was prepared. The solution was stirred for 15 h. The reaction was then chromatographed on silica gel (hexanes/diethylether: 95/5) to yield 38 mg (25 %) of the desired product.

\(^1\text{H NMR (CDCl}_3, 500\text{ MHz): } \delta 0.06 (3\text{ H, s, SiC}_3\text{H}_3), 0.07 (3\text{ H, s, SiC}_3\text{H}_3), 0.85-0.91 (24\text{ H, m, Bu, SiCCH}_3), 1.24-1.46 (15\text{ H, m, Bu, CHCH}_3), 3.20 (1\text{ H, d (AB), }J_{HH}=10.9\text{ Hz, H}_5), 3.26 (2\text{ H, s, H}_2), 3.29 (1\text{ H, d (AB), }J_{HH}=11.3\text{ Hz, }H'_5), 3.36 (1\text{ H, q, }J_{HH}=6.4\text{ Hz, NCH}), 5.24 (1\text{ H, s, SiCH}), 5.68 (1\text{ H, s, }J_{HSn}= 49.0\text{ Hz, SnCH}), 7.21-7.32 (5\text{ H, m, Ph}).

\(^{13}\text{C NMR (CDCl}_3, 125\text{ MHz): } \delta -4.4 (q, \text{SiCH}_3), 11.0 (t, \text{Bu}), 13.7 (q, \text{Bu}), 17.5 (s, \text{SiCCH}_3), 22.8 (q, \text{CHCH}_3), 26.5 (q, \text{SiCCH}_3), 27.3 (t, \text{Bu}), 29.0 (t, \text{Bu}), 62.0 (t, \text{CH}_2), 62.2 (t, \text{CH}_2), 66.0 (d, \text{NCH}), 120.5 (d, \text{SiCH}), 124.9 (d, \text{SnCH}), 126.8 (d, \text{Ph}), 127.4 (d, \text{Ph}), 128.3 (d, \text{Ph}), 145.4 (s, \text{Ph}), 156.1 (s), 158.2 (s). \(^{119}\text{Sn NMR (CDCl}_3, 185\text{ MHz): } \delta -55.0.\text{ Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SnCH→H}_5: 5.2\%; \text{SnCH→SnBu}_3: 5.8\%; \text{SiCH→H}_5: 5.1\%; \text{SiCH→t-Bu: 5.1\%}; \text{SiCH→SiMe}_2: 1.6\%.

Entry 100, SG-III-190.

\((3E,4E)-3-[\text{(Tert-butyl)dimethylsilyl)}\text{methylene]}-1-[(R)-\alpha\text{-methylbenzyl}]\text{-4-}\[(\text{triphenylstannyl)}\text{methylene]}\text{pyrrolidine}\) 96.
A solution of 49 mg of (R)-[(α-methyl)benzyl]dipropargylamine 69 (0.249 mmol), 123 mg of (tert-butyldimethylsilyl)triphenylstannane (0.265 mmol), 5 mg of Pd$_2$(dba)$_3$ (0.005 mmol), 26 mg of tris-(pentafluorophenyl)phosphine (0.049 mmol) in 1 mL of benzene was prepared AWAY FROM LIGHT. The solution was stirred for 15 h. The reaction was then chromatographed on silica gel (hexanes/diethylether: 95/5; 90/10) in the dark to yield 95 mg (58 %) of the desired product. This compound was light sensitive.

$^1$H NMR (CDCl$_3$, 500 MHz): δ -0.25 (3 H, s, SiC$_3$H$_3$), -0.17 (3 H, s, SiC$_3$H$_3$), 0.84 (9 H, s, SiCCH$_3$), 1.45 (3 H, d, J$_{HH}$=6.3 Hz, CHCH$_3$), 3.42 (2 H, s, H$_2$), 3.47-3.60 (3 H, m, NC$_H$, H$_5$), 5.28 (1 H, s, SiC), 6.16 (1 H, s, J$_{H_{Sn}}$=64.7 Hz, SnC$_H$), 7.33-7.47 (14 H, m, Ph), 7.65-7.66 (5 H, m, Ph).

$^{13}$C NMR (CDCl$_3$, 125 MHz): δ -4.1 (q, SiC$_3$H$_3$), -3.8 (q, SiC$_3$H$_3$), 18.3 (s, SiCCH$_3$), 23.3 (q, NCHCH$_3$), 27.0 (q, SiCCH$_3$), 62.0 (t, CH$_2$), 62.4 (t, CH$_2$), 66.3 (d, NCH), 121.1 (d, SnC), 124.4 (d, SiC), 127.4 (d, Ph), 127.8 (d, Ph), 128.8 (d, Ph), 129.2 (d, Ph), 137.7 (d, Ph), 140.7 (s, Ph), 145.7 (s, Ph), 157.3 (s), 160.3 (s).

$^{119}$Sn NMR (CDCl$_3$, 185 MHz): δ -154.6. Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SnC$H$$\rightarrow$H$_5$: 5.4 %; SnC$H$$\rightarrow$SnC$_H$: 6.6 %; SnC$H$$\rightarrow$-Bu: 1.7 %; SiC$H$$\rightarrow$H$_2$: 4.8 %; SiC$H$$\rightarrow$t-Bu: 4.0 %; SiC$H$$\rightarrow$SiMe$_2$: 1.9 %; SiC$H$$\rightarrow$Ph: 3.1 %.
Entry 101, SG-II-225.

(3E,4E)-3-[(Tert-butyldimethylsilyl)methylene]-1-[(S)-α-methylbenzyl]-4-
[(trimethylstannyl)methylene]pyrrolidine 97.

A vial was charged with 96 mg (0.487 mmol) of (S)-[(α-methyl)benzyl]-N,N-dipropargyl-
amine 70, 147 mg (0.527 mmol) of (tert-butyldimethylsilyl)trimethylstannane, 10 mg
(0.011 mmol) of Pd2(dba)3 and 29 mg (0.055 mmol) of tris-(pentafluorophenyl)phosphine
in 0.5 mL of benzene. This mixture was stirred at room temperature for 22 h. The solvent
was then evaporated and the residue was chromatographed on silica gel
(hexanes/diethylether: 95/5). Although the product probably decomposes on the column,
58 mg (25 %) of almost clean product was obtained, along with 20 mg (21 %) of
recovered starting material.

1H NMR (CDCl3, 500 MHz): δ 0.05 (3 H, s, SiC\textsubscript{H}3), 0.06 (3 H, s, SiC\textsubscript{H}3), 0.13 (9 H, s,
SnC\textsubscript{H}3), 0.84 (9 H, s, t-Bu), 1.32 (3 H, d, J\textsubscript{HH}= 6.6 Hz, CH\textsubscript{2}), 3.16 (1 H, d (AB), J\textsubscript{HH}= 10.6 Hz, H\textsubscript{3}), 3.27 (1 H, d (AB), J\textsubscript{HH}= 10.6 Hz, H\textsubscript{5}), 3.28 (1 H, d (AB), J\textsubscript{HH}= 13.1 Hz, H\textsubscript{2}), 3.34 (1 H, q, J\textsubscript{HH}= 6.7 Hz, CHCH\textsubscript{3}), 3.35 (1 H, d (AB), J\textsubscript{HH}= 13.0 Hz, CH\textsubscript{2}), 5.28 (1
H, s, SiCH), 5.68 (1 H, s, J\textsubscript{HSn}= 56.9 Hz, SnCH\textsubscript{2}), 7.21-7.33 (5 H, m, Ph). 13C NMR
(CDC\textsubscript{13}, 125 MHz): δ -7.1 (SnC\textsubscript{H}3), -4.7 (SiC\textsubscript{H}3), -4.6 (SiC\textsubscript{H}3), 17.4 (s, CCH\textsubscript{3}), 22.6 (q,
CHCH\textsubscript{3}), 26.5 (q, CCH\textsubscript{3}), 61.9 (d, C\textsubscript{2}), 62.5 (d, C\textsubscript{3}), 66.4 (d, CHCH\textsubscript{3}), 120.8 (d, SiCH),
125.6 (d, SnCH), 126.9 (d, Ph), 127.4 (d, Ph), 128.3 (d, Ph), 144.9 (s), 155.6 (s), 157.3 (s). The retention times on HPLC were: 7.55 minutes on Chiralsel OJ (99 % hexanes, flow of 0.5 mL/min) and 10.72 minutes on Chiralsel OD (99 % hexanes, flow of 0.3 mL/min).

Entry 102, SG-III-140.

(3E,4E)-3-[(Tert-butyldimethylsilyl)methylene]-1-[tosyl]-4-[(triphenylstanny1)methylene]pyrrolidine 98.

A solution of 49 mg of N-tosyl-N,N-dipropargylamine 54 (0.198 mmol), 139 mg of (tert-butyldimethylsilyl)triphenylstannane (0.299 mmol), 5 mg of Pd3(dba)3 (0.005 mmol), 11 mg of tris-(pentafluorophenyl)phosphine (0.021 mmol) in 0.5 mL of benzene was prepared. The solution was stirred for 15 h. The reaction was then chromatographed on silica gel (hexanes/diethylether: 4/1) to yield 109 mg (77 %) of the desired product.

1H NMR (CDCl3, 500 MHz): δ -0.30 (6 H, brd s, SiC(CH3)), 0.59 (9 H, s, SiC(CH3)), 2.43 (3 H, s, CH3), 3.87 (2 H, s, H2), 4.06 (2 H, s, H5), 5.23 (1 H, s, SiCH), 6.27 (1 H, s, JH5Sn=58.0 Hz, SnCH), 7.30-7.76 (19 H, m, Ph). 13C NMR (CDCl3, 125 MHz): δ -4.8 (q, SiCH3), 17.3 (s, SiCCH3), 21.5 (q, PhCH3), 26.1 (q, SiCCH3), 56.1 (t, C2), 56.5 (t, C3), 125.5 (d, SnCH), 127.5 (d, Ts), 127.6 (d, SiCH), 128.5 (d, Ph), 129.0 (d, Ph), 129.8 (d,
$\delta -154.4$. Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SnCH→$H_5$: 4.8 %; SnCH→SnPh$_3$: 3.2 %; SiCH→$H_2$: 4.7 %; SiCH→t-Bu: 4.0 %.

Entry 103, SG-II-109.

(Z)-2-(Tri-n-butylstannyl)-1-(trimethylsilyl)hex-1-ene-5-yne 100.

![Chemical Structure of 100]

A solution of 39 mg of hexa-1,5-diyne 99 (50% weight in pentane, 0.250 mmol), 87 µL of trimethylsilyltri-n-butylstannane (0.251 mmol), 16 µL of anisole (0.147 mmol), 2.0 mg of Pd$_2$(dba)$_3$ (0.002 mmol), 3 mg of tris-(o-tolyl)phosphate (0.010 mmol) in 0.5 mL of deuterated benzene was prepared in an NMR tube. The NMR spectrum of the reaction mixture was taken after 16 h and 40 h. No major difference was noted between the two spectra. Using anisole as an internal standard, it was determined that the yield of monoaddition product was 29%, whereas very little (2%) cyclized product could be detected. After column chromatography on silica gel (hexanes), 23 mg (21%) of monoaddition product were isolated. The cyclized product was either lost or decomposed.

$^1$H NMR (CDCl$_3$, 500 MHz): δ 0.08 (s, 9H, CH$_3$), 0.86-0.94 (m, 15 H, CH$_3$CH$_2$), 1.28-1.46 (m, 12 H, SnCH$_2$CH$_2$), 1.92 (t, 1 H, $J_{HH} = 2.4$ Hz, $H_6$), 2.17 (dt, 2 H, $J_{HH} = 2.4$, 7.7 Hz, $H_8$).
$H_3$, 2.46 (t, 2 H, $J_{HH} = 7.7$ Hz, $H_3$), 6.38 (s, 1 H, $J_{HSS} = 169$, 177 Hz, $H_1$). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 0.1 (q), 11.2 (t), 13.7 (q), 19.0 (t), 27.5 (t), 29.2 (t), 45.2 (t), 68.4 (d), 84.1 (q), 144.9 (d), 162.5 (q).

Entry 104, see Entry 103.

Entry 105, SG-II-054.

(Z)-2-(Tri-$n$-butylstannyl)-1-(trimethylsilyloct-1-ene-7-yne 102.

\[ \text{CH}_2\text{SnBu}_3\text{SiMe}_3 \]

A solution of 66 µL of octa-1,7-diyne 101 (0.50 mmol), 180 mg of trimethylsilyltri-$n$-butylstannane (0.50 mmol), 4.3 mg of Pd$_2$(dba)$_3$ (0.005 mmol), 5 mg of tris-(o-tolyl)-phosphine (0.015 mmol) in 5 drops of benzene was heated at 58°C for two hours and stirred at room temperature for 40 h. The solution was then evaporated. After column chromatography on silica gel (hexanes), 70 mg (30%) of monoaddition product were isolated.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 0.07 (s, 9H, $CH_3$), 0.86-0.93 (m, 15 H, $CH_2CH_3$), 1.27-1.48 (m, 16 H, $SnCH_2CH_2$, $H_\alpha$, $H_\beta$), 1.92 (t, 1 H, $J_{HH} = 2.6$ Hz, $H_8$), 2.17 (dt, 2 H, $J_{HH} = 2.6$, 6.8 Hz, $H_6$), 2.26 (td, 2 H, $J_{HH} = 6.9$, 0.9 Hz, $H_7$), 6.32 (d, 1 H, $J_{HH} = 1.1$ Hz, $J_{HSS} = 173$, 181 Hz, $H_1$). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 0.2 (q), 11.2 (t), 13.7 (q), 18.3 (t), 27.5 (t), 28.0 (t), 29.0 (t), 29.2 (t), 46.9 (t), 68.2 (d), 84.6 (q), 143.6 (d), 165.1 (q).
Entries 106-107, see Entry 105.

Entry 108, SG-II-078.

(Z)-2-(Tri-\(n\)-butylstannyl)-1-(trimethylsilyl)non-1-ene-8-yne 104.

\[
\text{CH}_2\text{SnBu}_3\text{SiMe}_3
\]

A solution of 75 µL of nona-1,8-diyne 103 (0.499 mmol), 181 mg of trimethylsilyltri-\(n\)-butylstannane (0.499 mmol), 4 mg of Pd\(_2\)(dba)_3 (0.004 mmol), 5 mg of tris-(o-tolyl)-phosphine (0.016 mmol) in 0.2 mL of benzene was prepared in a vial. The vial was sealed and placed in an oil bath at 64ºC for two hours. After column chromatography on silica gel (hexanes), 72 mg (30%) of monoaddition product were isolated.

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 0.07 (s, 9H, CH\(_3\)), 0.86-0.93 (m, 15 H, CH\(_2\)CH\(_3\)), 1.28-1.48 (m, 18 H, SnCH\(_2\)CH\(_2\)), 1.91 (t, 1 H, J\(\text{HH}\) = 2.6 Hz, \(H_9\)), 2.16 (dt, 2 H, J\(\text{HH}\) = 2.6, 7.1 Hz, \(H_7\)), 2.25 (dt, 2 H, J\(\text{HH}\) = 0.7, 7.0 Hz, \(H_3\)), 6.31 (d, 1 H, J\(\text{HH}\) = 0.7 Hz, J\(\text{HSn}\) = 174, 182 Hz, \(H_1\)). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 0.2 (q), 11.2 (t), 13.7 (q), 18.4 (t), 27.5 (t), 28.3 (t), 28.4 (t), 29.2 (t), 29.4 (t), 47.4 (t), 68.1 (d), 84.6 (q), 143.4 (d), 165.4 (q).

Entry 109, see Entry 108.

Entry 110, SG-II-110.

(Z)-2-(Tri-\(n\)-butylstannyl)-1-(trimethylsilyl)deca-1-ene-9-yne 106.
A solution of 35 mg of deca-1,9-diyn-105 (0.261 mmol), 87 µL of trimethylsilyltri-n-butyldistannane (0.251 mmol), 16 µL of anisole (0.147 mmol), 2.0 mg of Pd₂(dba)₃ (0.002 mmol), 3 mg of tris-(o-tolyl)phosphine (0.010 mmol) in 0.5 mL of deuterated benzene was prepared in an NMR tube. The NMR spectrum of the reaction mixture after 16 h and 40 h showed the formation of monoaddition and diaddition products. No cyclized product could be observed. After column chromatography on silica gel (hexanes), 48 mg (37%) of monoaddition product and 29 mg (22%) of the diaddition product were isolated. The diaddition product 107 could not be separated from the trimethylsilyltri-n-butyldistannane.

\[
\text{\textsuperscript{1}H NMR (CDCl}_3, 500 \text{ MHz}): \delta 0.08 (s, 9H, CH}_3), 0.88-0.93 (m, 15 H, CH}_2CH}_3), 1.30-1.49 (m, 20 H, SnCH}_2CH}_2, H_\alpha, H_\beta, H_\gamma, H_\delta), 1.93 (t, 1 H, J_\text{HH} = 2.7 \text{ Hz}, H_\eta), 2.18 (dt, 2 H, J_\text{HH} = 2.6, 7.1 \text{ Hz}, H_\delta), 2.25 (t, 2 H, J_\text{HH} = 7.1 \text{ Hz}, H_\gamma), 6.32 (s, 1 H, J_\text{HH} = 175, 183 \text{ Hz}, H_\eta).
\]

\[
\text{\textsuperscript{13}C NMR (CDCl}_3, 125 \text{ MHz}): \delta 0.2 (q), 11.2 (t), 13.6 (q), 18.4 (t), 27.5 (t), 28.5 (t), 28.6 (t), 28.7 (t), 29.3 (t), 29.8 (t), 47.5 (t), 68.1 (d), 84.7 (q), 143.3 (d), 165.6 (q).
\]

Entry 111, see Entry 110.

Entry 112, SG-II-289.

**Attempted cyclization of 2-(2-propynyl)-4-pentynoic acid 67.** A vial was charged with 33 mg (0.243 mmol) of 2-(2-propynyl)-4-pentynoic acid 67, 91 mg (0.251 mmol) of (trimethylsilyl)tri-n-butyldistannane, 6 mg (0.007 mmol) of Pd₂(dba)₃, 14 mg (0.026 mmol)
of tris-(pentafluorophenyl)phosphine and 0.2 mL of benzene. After 16 h of stirring at room temperature, the solvent was evaporated and the NMR spectrum was taken. However, no characteristic peaks of the product could be detected.


Attempted cyclization of (R)-[(α-methyl)benzyl]di(2-butynyl)amine 108. A solution of 10 mg of (R)-[(α-methyl)benzyl]di(2-butynyl)amine 108 (0.044 mmol), 16 mg of (trimethylsilyl)tri-n-butylstannane (0.043 mmol), 1 mg of Pd(db)3 (0.001 mmol), 4 mg of tris-(pentafluorophenyl)phosphine (0.008 mmol) in 0.8 mL of deuterated benzene was prepared in an NMR tube. The solution was stirred at room temperature for 14 h. The NMR spectrum of the reaction mixture was then taken. It showed the disparition of the starting material, but no product. The crude product was chromatographed on silica gel (hexanes/diethylether: 10/1), but nothing could be isolated nor identified.

Entry 114, see Reference 22.

Entry 115, see Entry 116

Entry 116, SG-II-207.

(Z)-Di-O-methyl-3-[(tributyl-n-stannyl)methyl]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 110.
A solution of 101 mg of di-\textit{O}-methylallylpropargylmalonate 109 (0.481 mmol), 165 µL of trimethylsilyltri-\textit{n}-butylstannane (0.476 mmol), 8 mg of Pd\textsubscript{d}(dba\textsubscript{3}) (0.009 mmol), 25 mg of \textit{tris}-(pentafluorophenyl)phosphine (0.047 mmol) in 0.2 mL of benzene was prepared. The solution was heated at 62°C for 20 h. The reaction mixture was then chromatographed on silica gel (hexanes/diethylether: 95/5, 90/10) to yield 136 mg (49 %) of the desired product.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz): δ 0.60 (9 H, s, SiC\textsubscript{H\textsubscript{3}}), 0.81-0.91 (15 H, m, Bu), 0.94 (1 H, d, J\textsubscript{HH}= 13.1 Hz, SnCH\textsubscript{2}), 1.04 (1 H, dd, J\textsubscript{HH}= 13.0, 2.7 Hz, SnCH\textsubscript{2}), 1.25-1.49 (12 H, m, Bu), 1.74 (1 H, dd, J\textsubscript{HH}= 13.1, 5.2 Hz, H\textsubscript{2}), 2.67 (1 H, dd, J\textsubscript{HH}= 13.3, 8.3 Hz, H\textsubscript{2'}), 2.72 (1 H, d, J\textsubscript{HH}= 16.3 Hz, H\textsubscript{5}), 2.79-2.83 (1 H, m, H\textsubscript{5}), 3.29 (1 H, dt, J\textsubscript{HH}= 16.0, 1.9 Hz, H\textsubscript{5'}), 3.68 (3 H, s, CH\textsubscript{3}), 3.70 (3 H, s, CH\textsubscript{3}), 5.25 (1 H, s, SiCH). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz): δ 0.2 (q, SiCH\textsubscript{3}), 9.3 (t, Bu), 13.6 (q, Bu), 19.1 (t, SnCH\textsubscript{2}), 27.4 (t, Bu), 29.2 (t, Bu), 40.3 (d, C\textsubscript{3}), 42.6 (t, C\textsubscript{2}), 44.3 (t, C\textsubscript{5}), 52.7 (q, CH\textsubscript{3}), 58.4 (s, C\textsubscript{1}), 119.9 (d, SiCH), 165.1 (s, C\textsubscript{4}), 172.2 (s, CO), 172.5 (s, CO). Assignments were confirmed by HMQC.

Attempted cyclization of 4-(\textit{tert}-butyldimethylsiloxy)-oct-7-ene-2-yne 72. A solution of 4-(\textit{tert}-butyldimethylsiloxy)-oct-7-ene-2-yne 72 (40 mg, 0.168 mmol), 58 µL of
trimethylsilyltri-\textit{n}-butylstannane (0.167 mmol), 3 mg of \text{Pd}_2(\text{dba})_3, (0.003 mmol), 9 mg of \textit{tris}-\text{(pentafluorophenyl)}\textit{phosphine} (0.017 mmol) in 0.2 mL of benzene was prepared. After 3.5 h, the solution was chromatographed on silica gel (hexanes/diethylether: 9/1). The starting material (25 mg, 62\%) was recovered. No product was obtained.

Entry 118, see Entry 117.

Entry 119, SG-II-176.

Attempted cyclization of hept-6-eneyne oxide 111. A solution of hept-6-eneyne oxide 111 (30 mg, 0.273 mmol), 63 \(\mu\text{L}\) of trimethylsilyltri-\textit{n}-butylstannane (0.182 mmol), 3 mg of \text{Pd}_2(\text{dba})_3, (0.003 mmol) in 0.4 mL of benzene was prepared. After 21 h, the solution was chromatographed on silica gel (hexanes/diethylether: 4/1). However, nothing of interest could be isolated.

Entry 120, SG-III-143.

Attempted chiral induction in the cyclization of \textit{O}-methyl-2-(2-propynyl)-4-pentynoate 66. A solution of 13 mg of \textit{O}-methyl-2-(2-propynyl)-4-pentynoate 66 (0.087 mmol), 24 mg of (trimethylsilyl)tri-\textit{n}-butylstannane (0.066 mmol), 1 mg of \text{Pd}_2(\text{dba})_3, (0.001 mmol), 5 mg of ligand (0.007 mmol) in 0.5 mL of deuterated benzene was prepared in an NMR tube. After 19.5 h at room temperature, the NMR spectrum of the reaction mixture was taken. It showed the formation of the desired product. The crude product was chromatographed on silica gel (hexanes/diethylether: 99/1) to yield 15 mg.
(44 %) of product 73. When applicable, the enantiomeric excess of the product was checked by HPLC on Chiralsel OD column with 100 % hexanes and a flow of 0.4 mL/min (the enantiomers had retention times of 13.26 and 15.13 minutes). For related results, see Table 2.24.

Entries 121-132, see Entry 120.

**Typical synthesis of a salt.** To a solution of 201 mg (0.360 mmol) of (3\textit{E},4\textit{E})-3-[(tri-\textit{n}-butylstannyl)methylene]-1-[(\textit{S})-\alpha-\textit{methylbenzyl}]-4-[(trimethylsilyl)methylene]pyrrolidine 76 in 0.5 mL of ethyl acetate, was added 83 mg (0.358 mmol) of camphorsulfonic acid. After stirring at room temperature overnight and evaporation of the solvent, a quantitative yield of product was obtained.

NMR data for the salts.

\textbf{A, B, C, D, E and F} represent groups of peaks that have been shown to belong to the same molecule.

$^1$H NMR (CDCl$_3$, 500 MHz): δ 0.11 (9 H, s, SiCH$_3$), 0.13 (9 H, s, SiCH$_3$), 0.84-0.95 (30 H, m, Bu), 1.24-1.42 (24 H, m, Bu), 1.82 (6 H, d, CHCH$_3$), 3.17 (3 H, s, NCH$_3$), 3.18 (3 H, s, NCH$_3$), 3.72 (1 H, d, J$_{HH}$= 13.4 Hz, A $H_2$), 3.77 (1 H, d, J$_{HH}$= 13.7 Hz, B $H_5$), 3.99 (2 H, d, J$_{HH}$= 13.2 Hz, C $H_2$, D $H_5$), 4.67 (1 H, d, J$_{HH}$= 13.1 Hz, C $H_2$), 4.69 (1 H, d, J$_{HH}$= 13.7 Hz, D $H_5$), 4.70 (1 H, d, J$_{HH}$= 13.7 Hz, A $H_5$), 4.78 (1 H, d, J$_{HH}$= 13.3 Hz, B $H_2$), 5.66 (1 H, s, A SiCH), 5.72 (1 H, s, C SiCH), 5.91 (1 H, q, J$_{HH}$= 6.9 Hz, CHCH$_3$), 5.93 (1 H, q, J$_{HH}$= 7.0 Hz, CHCH$_3$), 6.13 (1 H, s, J$_{HSn}$ = 34.3 Hz, B SnCH), 6.21 (1 H, s, J$_{HSn}$ = 34.0 Hz, D SnCH), 7.19-7.71 (10 H, m, Ph). $^{13}$C NMR (CDCl$_3$, 125 MHz): δ 0.1 (q, SiCH$_3$), 0.2 (q, SiCH$_3$), 11.0 (t, Bu), 11.1 (t, Bu), 13.6 (q, Bu), 13.7 (q, Bu), 15.8 (CHCH$_3$), 15.9 (CHCH$_3$), 27.2 (t, Bu), 28.9 (t, Bu), 49.1 (NCH$_3$), 49.4 (NCH$_3$), 68.8 (t, C C$_2$), 69.0 (t, D C$_5$), 70.1 (t, B C$_5$), 70.4 (t, A C$_2$), 71.8 (d, CHCH$_3$), 71.9 (d, CHCH$_3$), 123.5 (d, Ph), 124.8 (d, Ph), 127.4 (d, Ph), 128.3 (d, Ph), 129.4 (d, Ph), 130.4 (d, Ph), 130.8 (d, Ph), 132.9 (Ph), 132.9 (Ph), 133.7 (d, A SiCH), 134.0 (d, C SiCH), 136.9 (d, B SnCH), 137.2 (d, D SnCH), 144.7, 144.8, 145.0, 145.1, 155.7. Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SnCH→$H_2$: 5.4 %; SnCH→Bu$_3$: 1.8 %; SiCH→$H_5$: 1.8 %; SiCH→SiCH$_3$: 2.9 %.
(3E,4E)-3-[(Tri-n-butylstannyl)methylene]-1-methyl-1-[(S)-α-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium trifluoromethanesulfonate 115.

$\text{Me}_3\text{Si} \quad \text{SnBu}_3$

$\text{Ph}$

$\text{OTf}$

1H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.09 (9 H, s, SiCH$_3$), 0.10 (9 H, s, SiCH$_3$), 0.82-0.94 (30 H, m, Bu), 1.22-1.44 (24 H, m, Bu), 1.79 (3 H, d, J$_{HH}$ = 6.8 Hz, CHCH$_3$), 1.81 (3 H, d, J$_{HH}$ = 6.8 Hz, CHCH$_3$), 3.00 (6 H, s, NCH$_3$), 3.49 (1 H, d, J$_{HH}$ = 13.1 Hz, A $H_2$), 3.54 (1 H, d, J$_{HH}$ = 13.6 Hz, B $H_3$), 3.92 (1 H, d, J$_{HH}$ = 13.2 Hz, C $H_2$), 3.93 (1 H, d, J$_{HH}$ = 13.6 Hz, D $H_3$), 4.42 (1 H, d, J$_{HH}$ = 13.7 Hz, B $H_3$), 4.43 (1 H, d, J$_{HH}$ = 14.2 Hz, D $H_3$), 4.47 (2 H, d, J$_{HH}$ = 13.3 Hz, C $H_2$, A $H_2$), 5.04 (1 H, q, J$_{HH}$ = 6.8 Hz, CHCH$_3$), 5.05 (1 H, q, J$_{HH}$ = 6.8 Hz, CHCH$_3$), 5.61 (1 H, s, B SiCH), 5.67 (1 H, s, D SiCH), 6.10 (1 H, s, J$_{HSn}$ = 33.9 Hz, A SnCH), 6.18 (1 H, s, J$_{HSn}$ = 33.8 Hz, C SnCH), 7.20-7.59 (10 H, m, Ph). 13C NMR (CDCl$_3$, 125 MHz): $\delta$ -0.1 (q, SiCH$_3$), 10.9 (t, Bu), 13.5 (q, Bu), 15.3 (q, CHCH$_3$), 15.4 (q, CHCH$_3$), 27.1 (t, Bu), 28.8 (t, Bu), 47.7 (NCH$_3$), 48.0 (NCH$_3$), 69.2 (t, CH$_2$), 69.3 (t, CH$_2$), 70.0 (t, CH$_2$), 70.3 (t, CH$_2$), 73.2 (d, CHCH$_3$), 73.2 (d, CHCH$_3$), 119.3 (OTf), 121.8 (OTf), 127.3 (d, Ph), 128.5 (d, Ph), 129.4 (d, Ph), 130.3 (d, Ph), 130.7 (d, Ph), 132.6 (s, Ph), 132.7 (s, Ph), 133.5 (d, SiCH), 133.5 (d, SiCH), 137.0 (d, SnCH), 144.7 (s), 144.9 (s), 145.0 (s). Assignments were confirmed by COSY, HMQC and DEPT 135.
(3E,4E)-3-[(Tri-n-butylstannyl)methylene]-1-methyl-1-[(R)-α-methylbenzyl]-4-

\[
\begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{Me}_3\text{Si} \quad \text{SnBu}_3 \\
\text{OTf} \\
\end{array}
\]

\(^1\)H NMR (CDCl\textsubscript{3}, 500 MHz): \(\delta\) 0.09 (9 H, s, SiCH\textsubscript{3}), 0.10 (9 H, s, SiCH\textsubscript{3}), 0.83-0.94 (30 H, m, Bu), 1.23-1.44 (24 H, m, Bu), 1.80 (3 H, d, J\textsubscript{HH} = 6.7 Hz, CHCH\textsubscript{3}), 1.80 (3 H, d, J\textsubscript{HH} = 6.7 Hz, CHCH\textsubscript{3}), 3.01 (6 H, s, NCH\textsubscript{3}), 3.52 (1 H, d, J\textsubscript{HH} = 13.2 Hz, A H\textsubscript{2}), 3.56 (1 H, d, J\textsubscript{HH} = 13.8 Hz, B H\textsubscript{5}), 3.92 (1 H, d, J\textsubscript{HH} = 13.0 Hz, C H\textsubscript{2}), 3.93 (1 H, d, J\textsubscript{HH} = 13.6 Hz, D H\textsubscript{5}), 4.44 (1 H, d, J\textsubscript{HH} = 13.7 Hz, B H\textsubscript{5}'), 4.45 (1 H, d, J\textsubscript{HH} = 14.2 Hz, D H\textsubscript{5}'), 4.49 (2 H, d, J\textsubscript{HH} = 13.3 Hz, C H\textsubscript{2}, A H\textsubscript{2}), 5.08 (1 H, q, J\textsubscript{HH} = 6.8 Hz, CHCH\textsubscript{3}), 5.09 (1 H, q, J\textsubscript{HH} = 6.8 Hz, CHCH\textsubscript{3}) 5.62 (1 H, s, B SiCH), 5.67 (1 H, s, D SiCH), 6.10 (1 H, s, J\textsubscript{HSn} = 33.9 Hz, A SnCH), 6.18 (1 H, s, J\textsubscript{HSn} = 34.0 Hz, C SnCH), 7.42-7.56 (10 H, m, Ph). \(^{13}\)C NMR (CDCl\textsubscript{3}, 125 MHz): \(\delta\) -0.1 (q, SiCH\textsubscript{3}), 10.9 (t, Bu), 13.5 (q, Bu), 15.4 (q, CHCH\textsubscript{3}), 15.4 (q, CHCH\textsubscript{3}), 27.9 (t, Bu), 28.9 (t, Bu), 47.9 (NCH\textsubscript{3}), 48.2 (NCH\textsubscript{3}), 69.1 (t, CH\textsubscript{2}), 69.3 (t, CH\textsubscript{2}), 70.0 (t, CH\textsubscript{2}), 70.3 (t, CH\textsubscript{2}), 73.2 (d, CHCH\textsubscript{3}), 73.2 (d, CHCH\textsubscript{3}), 119.5 (OTf), 122.1 (OTf), 129.4 (d, Ph), 130.4 (d, Ph), 130.7 (d, Ph), 132.7 (s, Ph), 132.8 (s, Ph), 133.5 (d, SiCH), 136.9 (d, SiCH), 136.9 (d, SnCH), 144.8 (s), 144.9 (s), 145.0 (s), 145.1 (s). Assignments were confirmed by COSY, HMQC and DEPT 135.
(3E,4E)-3-[Iodomethylene]-1-methyl-1-[(R)-α-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium trifluoromethanesulfonate 117.

\[
\text{Ph} \begin{array}{c}
\text{N} \\
\text{Me}_3\text{Si} \\
117
\end{array} \text{OTf}
\]

^1H NMR (CDCl₃, 500 MHz): δ 0.23 (9 H, s, SiCH₃), 0.24 (9 H, s, SiCH₃), 1.83 (3 H, d, J₃H= 6.3 Hz, E CHCH₃), 1.84 (3 H, d, J₃H= 6.0 Hz, F CHCH₃), 2.96 (3 H, s, NCH₃), 2.98 (3 H, s, NCH₃), 3.46 (1 H, d, J₃H= 14.1 Hz, A H₅), 3.64 (1 H, d, J₃H= 12.8 Hz, B H₂), 4.10 (1 H, d, J₃H= 14.1 Hz, C H₅), 4.41 (1 H, d, J₃H= 13.0 Hz, D H₂), 4.58 (1 H, d, J₃H= 14.0 Hz, A H₅), 4.63 (1 H, d, J₃H= 17.0 Hz, D H₂), 4.66 (2 H, d, J₃H= 13.5 Hz, B H₂'), C H₅), 5.07 (1 H, q, J₃H= 6.9 Hz, F CHCH₃), 5.15 (1 H, q, J₃H= 7.0 Hz, E CHCH₃), 5.76 (1 H, s, A SiCH), 5.89 (1 H, s, C SiCH), 6.77 (1 H, s, B ICH), 6.92 (1 H, s, D ICH), 7.46-7.57 (10 H, m, Ph). Assignments were confirmed by COSY.

(3E,4E)-3-[(Tert-butyldimethylsilyl)methylene]-1-methyl-1-[(R)-α-methylbenzyl]-4-[(trimethylstannyl)methylene]pyrrolidinium trifluoromethanesulfonate 118.

\[
\text{Ph} \begin{array}{c}
\text{N} \\
\text{t-BuMe}_2\text{Si} \\
118
\end{array} \text{SnMe}_3 \text{OTf}
\]
Note: This compound was not the cleanest. This is a tentative interpretation of the NMR.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.07 (3 H, s, SiCH$_3$), 0.08 (3 H, s, SiCH$_3$), 0.08 (3 H, s, SiCH$_3$), 0.09 (3 H, s, SiCH$_3$), 0.20 (18 H, s, SnCH$_3$), 0.81 (9 H, s, CCH$_3$), 0.84 (9 H, s, CCH$_3$), 1.81 (3 H, d, J$_{HH}$= 6.7 Hz, CHCH$_3$), 1.81 (3 H, d, J$_{HH}$= 6.7 Hz, CHCH$_3$), 3.02 (3 H, s, NCH$_3$), 3.03 (3 H, s, NCH$_3$), 3.53 (1 H, d, J$_{HH}$= 13.4 Hz, A H$_2$), 3.63 (1 H, d, J$_{HH}$= 13.6 Hz, B H$_3$), 3.96 (2 H, d, J$_{HH}$= 17.2 Hz, C H$_2$, D H$_3$), 4.46-4.51 (4 H, m, A H$_2$, B H$_5$, C H$_2$, D H$_3$), 5.06-5.16 (2 H, m, CHCH$_3$), 5.69 (1 H, s, SiCH), 5.79 (1 H, s, SiCH), 6.13 (1 H, s, J$_{HSn}$= 38.8 Hz, SnCH), 6.18 (1 H, s, J$_{HSn}$= 38.4 Hz, SnCH), 7.44-7.57 (10 H, m, Ph). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ -7.3 (q, SnCH$_3$), -5.4 (q, SiCH$_3$), -5.2 (q, SiCH$_3$), -4.9 (q, SiCH$_3$), -4.8 (q, SiCH$_3$), 15.4 (q, CHCH$_3$), 17.2 (s, CCH$_3$), 26.1 (q, CCH$_3$), 26.3 (q, CCH$_3$), 48.2 (q, NCH$_3$), 68.9 (t, CH$_2$), 69.4 (t, CH$_2$), 69.9 (t, CH$_2$), 70.5 (t, CH$_2$), 73.2 (d, CHCH$_3$), 73.2 (d, CHCH$_3$), 119.3 (s, OTf), 121.8 (s, OTf), 129.5 (d, Ph), 130.3 (d, Ph), 130.3 (d, Ph), 130.9 (d, Ph), 131.3 (d, SiCH), 131.6 (d, SiCH), 132.6 (s, Ph), 132.6 (s, Ph), 137.0 (d, SnCH), 137.2 (d, SnCH), 144.2 (s), 144.4 (s), 146.4 (s), 146.6 (s). $^{119}$Sn NMR (CDCl$_3$, 185 MHz): $\delta$ -36.6, -36.4. Assignments were confirmed by COSY, HMQC and DEPT 135.

$(3E,4E)-3-[(Tri-n-butylstannyl)methylene]-1-[(R)-\alpha\text{-methylbenzyl}]-4-[(trimethylsilyl)methylene]pyrrolidinium oxalate 119.$
To a solution of 50 mg (0.089 mmol) of (3E,4E)-3-[(tri-n-butylstannyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrroolidine 76 in 0.5 mL of dichloromethane, was added 9 mg (0.100 mmol) of oxalic acid. After stirring at room temperature for 4 hours and evaporation of the solvent, a quantitative yield of product was obtained. The $^1$H and $^{13}$C NMR spectra showed the presence of only one diastereomers (one set of peaks). However, after many attempts, the product could be recrystallized by diffusion of hexanes in a diethylether solution of the salt. The NMR spectra of the recrystallized product showed the presence of two diastereomers.

**CRUDE NMR, BEFORE RECRYSTALLIZATION.** $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.06 (9 H, s, SiCH$_3$), 0.83-0.96 (15 H, m, Bu), 1.23-1.45 (12 H, m, Bu), 1.66 (3 H, d, $J_{HH}= 6.7$ Hz, CHCH$_3$), 3.65 (1 H, d, $J_{HH}= 12.5$ Hz, $H_5$), 3.76 (1 H, d, $J_{HH}= 12.8$ Hz, $H_2$), 3.80 (1 H, d, $J_{HH}= 12.5$ Hz, $H_5$), 3.86 (1 H, d, $J_{HH}= 12.0$ Hz, $H_2$), 3.96 (1 H, q, $J_{HH}= 6.6$ Hz, CHCH$_3$), 5.46 (1 H, s, SiCH), 5.91 (1 H, s, $J_{HH}= 39.3$ Hz, SnCH), 7.24-7.42 (5 H, m, Ph), 10.91 (1.4 H, brd s). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 0.1 (q, SiCH$_3$), 10.8 (t, Bu), 13.6 (q, Bu), 19.2 (q, CHCH$_3$), 27.2 (t, Bu), 28.9 (t, Bu), 59.6 (t, $C_2$), 60.1 (t, $C_5$), 66.6 (d, CHCH$_3$), 128.1 (d, Ph), 129.2 (d, Ph), 129.2 (d, Ph), 130.2 (d, SiCH), 131.8 (d, SnCH), 137.2 (s, Ph), 148.1 (s), 148.4 (s), 163.0 (s, CO).
(3E,4E)-3-[(Tri-n-butylstannyl)methylene]-1-[(S)-α-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium oxalate 120.

\[
\text{HOOC\text{COOH}}
\]

CRUDE NMR, BEFORE RECRYSTALLIZATION. \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 0.04 (9 H, s, Si\(\text{CH}_3\)), 0.82-0.89 (15 H, m, Bu), 1.22-1.42 (12 H, m, Bu), 1.64 (3 H, d, J\(_{HH}\)= 6.7 Hz, \(\text{CHCH}_3\)), 3.64 (1 H, d, J\(_{HH}\)= 12.7 Hz, \(H_3\)), 3.78 (1 H, d, J\(_{HH}\)= 12.9 Hz, \(H_2\)), 3.8 (1 H, d, J\(_{HH}\)= 12.6 Hz, \(H_5\)), 3.85 (1 H, d, J\(_{HH}\)= 12.7 Hz, \(H_2\)), 3.97 (1 H, q, J\(_{HH}\)= 6.7 Hz, \(\text{CHCH}_3\)), 11.74 (1.6 H, brd s). \(^13\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) –0.0 (q, Si\(\text{CH}_3\)), 10.7 (t, Bu), 13.5 (q, Bu), 19.1 (q, CH\(\text{CH}_3\)), 27.1 (t, Bu), 28.8 (t, Bu), 59.5 (t, \(C_2\)), 59.9 (t, \(C_5\)), 66.4 (d, CH\(\text{CH}_3\)), 128.1 (d, Ph), 129.1 (d, Ph), 129.1 (d, Ph), 130.0 (d, Si\(\text{CH}\)), 131.6 (d, Sn\(\text{CH}\)), 137.0 (s, Ph), 148.0 (s), 148.4 (s), 163.3 (s, CO).

(3E,4E)-3-[(Tri-n-butylstannyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium camphorsulfonate 121.
$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.04 (9 H, s, SiCH$_3$), 0.05 (9 H, s, SiCH$_3$), 0.78-0.89 (36 H, m, Bu, CSA $H_5$, CSA $H_6$), 1.07 (6 H, s, CSA $H_5$, CSA $H_9$), 1.19-1.39 (26 H, m, Bu, CSA $H_5$, CSA $H_6$), 1.67 (2 H, ddd, $J_{HH}$= 14.2, 9.5, 4.8 Hz, CSA $H_5$, CSA $H_6$), 1.73 (3 H, d, $J_{HH}$= 7.4 Hz, CHCH$_3$), 1.75 (3 H, d, $J_{HH}$= 7.3 Hz, CHCH$_3$), 1.80 (2 H, d, $J_{HH}$= 18.2 Hz, CSA $H_3$), 1.91-1.97 (4 H, m, CSA $H_5$, CSA $H_6$, CSA $H_9$), 2.24 (2 H, dt, $J_{HH}$= 18.1, 4.0 Hz, CSA $H_3$), 2.71 (2 H, t, $J_{HH}$= 11.0 Hz, CSA $H_5$, CSA $H_6$), 2.78 (2 H, d, $J_{HH}$= 14.6 Hz, CSA $H_3$), 3.27 (3 H, d, $J_{HH}$= 14.7 Hz, A CH$_2$, CSA $H_{10}$), 3.32 (1 H, dd, $J_{HH}$= 13.5, 2.6 Hz, B CH$_2$), 3.58 (1 H, dd, $J_{HH}$= 13.0, 2.8 Hz, C CH$_2$), 3.63 (1 H, d, $J_{HH}$= 13.4 Hz, D CH$_2$), 3.75 (1 H, dd, $J_{HH}$= 13.0, 5.8 Hz, A CH$_2$), 3.94-4.04 (3 H, m, CHCH$_3$, B CH$_2$), 4.60 (1 H, dd, $J_{HH}$= 13.1, 5.8 Hz, C CH$_2$), 4.72 (1 H, dd, $J_{HH}$= 13.2, 6.0 Hz, D CH$_2$), 5.42 (1 H, s, SiCH), 5.64 (1 H, s, SiCH), 5.87 (1 H, s, $J_{HH}$= 38.2 Hz, SnCH), 6.03 (1 H, s, $J_{HH}$= 38.2 Hz, SnCH), 7.30-7.46 (10 H, m, Ph), 11.47 (1 H, s, NH), 11.51 (1 H, s, NH). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ -0.1 (q, SiCH$_3$), -0.1 (q, SiCH$_3$), 10.7 (t, Bu), 13.5 (t, Bu), 18.2 (q, CHCH$_3$), 18.6 (q, CHCH$_3$), 19.7 (q, CSA), 19.9 (q, CSA), 24.4 (t, CSA), 26.9 (t, CSA), 27.1 (t, Bu), 28.8 (t, Bu), 42.6 (d, CSA $C_4$), 42.7 (t, CSA $C_3$), 47.1 (t, CSA $C_{10}$), 47.6 (s, CSA $C_7$), 58.1 (t, B CH$_2$), 58.3 (s, CSA $C_5$), 58.8 (t, A CH$_2$), 59.4 (t, D CH$_2$), 59.6 (t, C CH$_2$), 66.3 (d, CHCH$_3$), 66.5 (d, CHCH$_3$), 128.3 (d, Ph), 129.4 (d, Ph), 129.5 (d, Ph), 172
131.4 (d, SiCH), 131.7 (d, SiCH), 133.2 (d, SnCH), 133.4 (d, SnCH), 135.3 (s), 135.4 (s), 146.2 (s), 146.2 (s), 146.4 (s), 146.4 (s), 216.4 (s, CSA C₂). Assignments were confirmed by COSY, HMQC and DEPT 135.

(3E,4E)-3-[(Tri-n-butylstannyl)methylene]-1-[(S)-α-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium camphorsulfonate 122.

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\text{\includegraphics[width=0.2\textwidth]{122.png}}
\]

\[^{1}\text{H NMR (CDCl}_3, 500 MHz): \delta 0.09 (9 \text{ H, s, SiCH}_3), 0.10 (9 \text{ H, s, SiCH}_3), 0.83-0.95 (36 \text{ H, m, Bu, CSA H}_8, \text{CSA H}_9), 1.12 (6 \text{ H, s, CSA H}_8, \text{CSA H}_9), 1.23-1.46 (24 \text{ H, m, Bu), 1.69-1.75 (4 \text{ H, m, CSA), 1.79 (3 \text{ H, d, J}_{HH}= 6.6 \text{ Hz, CHCH}_3), 1.80 (3 \text{ H, d, J}_{HH}= 6.6 \text{ Hz, CHCH}_3), 1.85 (2 \text{ H, d, J}_{HH}= 18.1 \text{ Hz, CSA H}_3), 1.97-2.02 (4 \text{ H, m, CSA), 2.29 (2 \text{ H, dt, J}_{HH}= 18.1, 4.0 \text{ Hz, CSA H}_3), 2.76 (2 \text{ H, t, J}_{HH}= 15.4 \text{ Hz, CSA), 2.84 (2 \text{ H, d, J}_{HH}= 14.7 \text{ Hz, CSA H}_{10}), 3.33 (2 \text{ H, d, J}_{HH}= 14.7 \text{ Hz, CSA H}_{10}), 3.33-3.36 (2 \text{ H, m, A CH}_2, B CH}_2), 3.62 (1 \text{ H, d, J}_{HH}= 14.9 \text{ Hz, C CH}_2), 3.67 (1 \text{ H, d, J}_{HH}= 15.1 \text{ Hz, D CH}_2), 3.86 (1 \text{ H, dd, J}_{HH}= 12.9, 5.6 \text{ Hz, A CH}_2), 4.00-4.06 (3 \text{ H, m, CHCH}_3, B CH}_2), 4.60 (1 \text{ H, dd, J}_{HH}= 13.0, 5.7 \text{ Hz, C CH}_2), 4.74 (1 \text{ H, dd, J}_{HH}= 12.7, 5.8 \text{ Hz, D CH}_2), 5.50 (1 \text{ H, s, SiCH), 5.63 (1 \text{ H, s, SiCH), 5.89 (1 \text{ H, s, J}_{HH}= 38.0 \text{ Hz, SnCH), 6.04 (1 \text{ H, s, J}_{HH}= 37.9 \text{ Hz, SnCH), 7.36-7.50 (10 \text{ H, m, Ph), 11.57 (1 \text{ H, s, NH), 11.61 (1 \text{ H, s, NH).}^{13}\text{C NMR (CDCl}_3, 125 MHz): \delta -0.0 (q, SiCH}_3), 10.8 (t, Bu), 13.6 (t, Bu), 18.4 (q, CHCH}_3), 18.7 (q, CHCH}_3),
\]

173
19.9 (q, CSA), 20.1 (q, CSA), 24.6 (t, CSA), 27.1 (t, CSA), 27.3 (t, Bu), 28.9 (t, Bu), 42.7 (d, CSA $C_4$), 42.9 (t, CSA $C_3$), 47.3 (t, CSA $C_{10}$), 47.8 (s, CSA $C_7$), 58.4 (t, $B$ CH$_2$), 58.5 (s, CSA $C_7$), 58.9 (t, CH$_2$), 59.5 (t, CH$_2$), 59.8 (t, CH$_2$), 66.4 (d, CHCH$_3$), 66.6 (d, CHCH$_3$), 128.5 (d, Ph), 129.5 (d, Ph), 129.5 (d, Ph), 129.7 (d, Ph), 131.6 (d, SiCH), 131.8 (d, SiCH), 133.4 (d, SnCH), 133.6 (d, SnCH), 135.5 (s), 135.6 (s), 146.4 (s), 146.5 (s), 216.6 (s, CSA $C_2$). $^{119}$Sn NMR (CDCl$_3$, 185 MHz): $\delta$ -52.6, -52.3.

Assignments were confirmed by COSY, HMQC and DEPT 135.

(3E,4E)-3-[(Tri-$n$-butylstannyl)methylene]-1-[(R)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium picrate 123.

![Structure 123](image)

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ -0.02 (4.5 H, s, SiCH$_3$), 0.02 (4.5 H, s, SiCH$_3$), 0.80-0.89 (15 H, m, Bu), 1.18-1.43 (12 H, m, Bu), 1.81 (1.5 H, d, $J_{HH}$= 6.8 Hz, CHCH$_3$), 1.81 (1.5 H, d, $J_{HH}$= 6.8 Hz, CHCH$_3$), 3.43 (0.5 H, dd, $J_{HH}$= 4.7, 13.3 Hz, $A$ $H_2$), 3.47 (0.5 H, dd, $J_{HH}$= 4.9, 13.3 Hz, $B$ $H_2$), 3.69 (0.5 H, dd, $J_{HH}$= 5.2, 12.6 Hz, C $H_3$), 3.74 (0.5 H, dd, $J_{HH}$= 4.7, 12.5 Hz, D $H_2$), 4.04 (0.5 H, dd, $J_{HH}$= 5.1, 12.4 Hz, A $H_5$'), 4.11-4.17 (1.5 H, m, CHCH$_3$, B $H_2$'), 4.49 (0.5 H, dd, $J_{HH}$= 5.5, 12.4 Hz, C $H_3$'), 4.54 (0.5 H, dd, $J_{HH}$= 5.5, 12.4 Hz, D $H_2$'), 5.47 (0.5 H, s, A SiCH), 5.57 (0.5 H, s, C SiCH), 5.97 (0.5 H, s, J$_{HH}$= 37.0 Hz, B SnCH), 6.08 (0.5 H, s, J$_{HH}$= 36.6 Hz, D SnCH), 7.39-7.50 (5 H, m, Ph), 8.86
(2 H, s, COOH), 11.17 (1 H, brd s, NH). $^{13}$C NMR (CDCl$_3$, 125 MHz): δ -0.2 (q, SiCH$_3$), -0.1 (q, SiCH$_3$), 10.7 (t, Bu), 10.7 (t, Bu), 13.5 (q, CHCH$_3$), 18.5 (q, Bu), 18.5 (q, Bu), 27.0 (t, Bu), 28.7 (t, Bu), 59.6 (t, CH$_2$), 59.8 (t, CH$_2$), 60.5 (t, CH$_2$), 60.7 (t, CH$_2$), 67.6 (d, CHCH$_3$), 113.3, 126.3 (d), 128.1 (d), 128.1 (d), 129.4 (d), 129.5 (d), 130.0 (d), 130.1 (d), 131.5 (SiCH), 131.9 (SiCH), 134.0 (SnCH), 134.6 (SnCH), 134.8, 135.1, 141.8, 145.8, 145.9, 146.3, 146.3, 161.1. $^{119}$Sn NMR (CDCl$_3$, 185 MHz): δ -51.9, -52.2. Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SnCH→H$_2$: 13.7 %; SnCH→Bu$_3$: 8.3 %; SiCH→H$_3$: 11.8 %; SiCH→SiCH$_3$: 6.4 %.

Entry 133, SG-III-148.

**Attempted hydrodestannylation of O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 92.** O-Methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 92 (7 mg, 0.011 mmol) was dissolved in 1 mL CDCl$_3$ and transferred to an NMR tube. Camphorsulfonic acid (6 mg, 0.026 mmol) was added and the reaction was followed by $^1$H NMR. After 20 h at room temperature, the starting material was gone, but no product could be observed.

Entry 134, see Entry 135.
Entry 135, SG-III-248.

(4Z)-Di-O-methyl-3-(methylene)-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 125.

![Chemical structure of 125](image)

(3Z,4Z)-Di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (51 mg, 0.089 mmol), camphorsulfonic acid (4 mg, 0.017 mmol) and potassium fluoride (6 mg, 0.103 mmol) were dissolved in 1 mL of chloroform. The reaction was followed by TLC. After 19 h at room temperature, the solution was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 9/1) to yield 4 mg of the desired product (16 %) and 44 mg of starting material.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.11 (9 H, s, SiCH$_3$), 3.02 (2 H, s, $H_2$), 3.05 (2 H, s, $H_5$), 3.70 (6 H, s, $CH_3$), 5.05 (1 H, s, $H_{3\text{out}}$), 5.28 (1 H, s, $H_{3\text{in}}$), 5.50 (1 H, s, $H_4$). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ -0.4 (q, SiCH$_3$), 42.1 (t, $C_2$), 45.1 (t, $C_3$), 52.8 (q, COOCH$_3$), 56.9 (s, $C_7$), 110.8 (t, $C_7$), 124.1 (d, $C_6$), 145.0 (s), 152.9 (s), 171.8 (s, COO). Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SiCH→$H_5$: 2.6 %; SiCH→SiMe$_3$: 1.7 %; CH(in)→CH(out): 10.3 %; CH(in)→SiMe$_3$: 2.5 %; CH(out)→CH(in): 10.9 %; CH(out)→$H_2$: 2.1 %. HRMS calcd for C$_{14}$H$_{22}$O$_4$SiNa: M$^+$ = 305.1185, found 305.1181.
Entries 136-137, see Entry 138.


**Hydrodestannylation of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56.** (3Z,4Z)-Di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (49 mg, 0.086 mmol), p-toluenesulfonic acid (4 mg, 0.021 mmol) and potassium fluoride (5 mg, 0.086 mmol) were dissolved in 2 mL of acetonitrile. Water (40 µL, 2.222 mmol) was added. The reaction mixture was refluxed for 19 h. The solution was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 95/5, 9/1) to yield 3 mg of the desired product (12 %) and 43 mg of starting material.

For NMR data, see Entry 135.

Entry 139, SG-III-240.

**Attempted hydrodestannylation of (3E,4E)-3-[(tri-n-butylstannyl)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 75.** (3E,4E)-3-[(tri-n-butylstannyl)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 75 (49 mg, 0.087 mmol) and p-toluenesulfonic acid (4 mg, 0.021 mmol) were dissolved in 2 mL of acetonitrile. Water (20 µL, 1.111 mmol) was added. The reaction mixture was refluxed for 19 h. The solution was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 9/1) to yield 36 mg of starting material.
Entry 140, SG-III-277.

(4Z)-Di-O-methyl-3-(methylenes)-4-[(tri-\textit{n}-butylstannyl)methylene]cyclopentanedicarboxylate 126.

![Chemical structure of 126](image)

(3Z,4Z)-Di-O-methyl-3-[(tri-\textit{n}-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (29 mg, 0.051 mmol) was dissolved in 1 mL of THF. Tetra-\textit{n}-butylammonium fluoride (1 M, 150 \(\mu\)L, 0.150 mmol) was added and the reaction was followed by TLC. After 22 h at room temperature, the reaction mixture was poured in 5 mL of water and extracted three times with 5 mL of dichloromethane. The organic phases were dried on MgSO\(_4\), filtered and evaporated. The residue was then chromatographed on silica gel (hexanes/ diethylether: 95/5; 9/1; 1/1) to yield 6 mg (24 \%) of the desired product and 3 mg of starting material.

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 0.84-0.92 (15 H, m, Bu), 1.23-1.29 (6 H, m, Bu), 1.43-1.52 (6 H, m, Bu), 3.04 (2 H, s, \(H_2\)), 3.10 (2 H, s, \(H_5\)), 3.70 (6 H, s, COOC\(_3\)H\(_3\)), 4.87 (1 H, s, \(H_{3\text{out}}\)), 5.18 (1 H, s, \(H_{3\text{in}}\)), 5.81 (1 H, s, \(J_{H_{Sn}=47.4}\text{ Hz, }H_4\)). \(^13\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 10.3 (t, Bu), 13.7 (q, Bu), 27.3 (t, Bu), 29.1 (t, Bu), 42.0 (t, \(C_2\)), 45.2 (t, \(C_5\)), 52.7 (q, CH\(_3\)), 57.1 (s, \(C_1\)), 106.6 (t, \(C_3\)), 122.6 (d, \(C_4\)), 146.6 (s), 153.0 (s), 171.8 (s, CO).

\(^{119}\)Sn NMR (CDCl\(_3\), 185 MHz): \(\delta\) -56.7. Assignments were confirmed by COSY. 

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Entry 141, SG-III-48.

O-Methyl-(3Z,4Z)-3-(iodomethylene)-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 127.

A solution of 57 mg (0.111 mmol) of O-methyl-(3Z,4Z)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73 in 0.4 mL of dichloromethane was cooled to 0°C. In another vial, a solution of 72 mg (0.283 mmol) of iodine in 3 mL of dichloromethane was prepared. About 1 mL of the iodine solution was added dropwise to the stannane solution until the red color of the iodine persisted. After stirring at 0 °C for 35 minutes, the solution was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 95/5) in the dark, yielding 28 mg (72 %) of the desired product.

¹H NMR (CDCl₃, 500 MHz): δ 0.17 (9 H, s, Si(CH₃)), 2.65-2.78 (4 H, m, CH₂), 2.88 (1 H, quintet, JHH= 8.0 Hz, CH), 3.67 (3 H, s, COOCH₃), 5.47 (1 H, s, SiCH), 6.07 (1 H, s, ICH). ¹³C NMR (CDCl₃, 125 MHz): δ -0.4 (q, SiCH₃), 38.1 (t, CH₂), 38.6 (d, CH), 39.5
(t, CH₂), 52.0 (q, OCH₃), 71.3 (d, ICH), 128.2 (d, SiCH), 150.5 (s), 152.9 (s), 175.3 (s, CO). Assignments were confirmed by COSY and DEPT 135. NOE: ICH→H₂: 0.8 %; SiCH→H₅: 5.1 %; SiCH→SiCH₃: 2.6 %.

Entry 142, SG-IV-002.

(3Z,4Z)-Di-O-Methyl3-(iodomethylene)-4-[(trimethylsilyl)methylene]cyclopentane dicarboxylate 128.

A solution of 57 mg (0.100 mmol) of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)-methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 in 1 mL of dichloromethane was cooled to 0°C. In another vial, a solution of 81 mg (0.319 mmol) of iodine in 3 mL of dichloromethane was prepared. About 1 mL of the iodine solution was added dropwise to the stannane solution until the red color of the iodine persisted. After stirring at 0 °C for 10 minutes, the solution was evaporated and the residue was chromatography on silica gel (hexanes/diethylether: 9/1; 85/15) in the dark, yielding 35 mg (85 %) of the desired product.

¹H NMR (CDCl₃, 500 MHz): δ 0.16 (9 H, s, SiCH₃), 3.01 (2 H, d, JHH= 1.3 Hz, H₂), 3.05 (2 H, d, JHH= 1.3 Hz, H₂), 3.71 (6 H, s, COOC₃H), 5.49 (1 H, s, SiCH), 6.11 (1 H, s, ICH). ¹³C NMR (CDCl₃, 125 MHz): δ -0.5 (q, SiCH₃), 42.3 (t, C₂), 43.9 (t, C₃), 53.0 (q, COOC₃H), 55.2 (s, C₁), 72.3 (d, ICH), 129.2 (d, SiCH), 148.7 (s), 151.1 (s), 171.5
(s, CO). Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: ICH→H₂: 2.5 %; ICH→SiCH₃: 1.0 %; SiCH→H₅: 2.8 %; SiCH→SiCH₃: 1.7 %.

Entry 143, SG-II-259.

(3E,4E)-3-(Iodomethylene)-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]-pyrrolidine 129.

A solution of 201 mg (0.359 mmol) of (3E,4E)-3-[(tri-n-butylstannyl)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 75 in 1 mL of dichloromethane was cooled to 0°C. A solution of 155 mg (1.700) mg of iodine in 10 mL of dichloromethane was added dropwise until the red color remained. After 15 minutes of stirring at 0°C, the solvent was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 95/5, 90/10) to yield 105 mg (73 %) of the desired product.

¹H NMR (CDCl₃, 500 MHz): δ 0.20 (9 H, s, SiCH₃), 1.33 (3 H, d, JHH= 6.6 Hz, CH₃), 3.28 (1 H, d (AB), JHH= 11.1 Hz, H₂), 3.30 (1 H, dd, JHH= 12.6, 1.3 Hz, H₅), 3.33 (1 H, q, JHH= 6.6 Hz, NCH), 3.39 (1 H, d (AB), JHH= 11.2 Hz, H₂'), 3.44 (1 H, dd, JHH= 12.6, 1.2 Hz, H₅'), 5.46 (1 H, s, SiCH), 6.17 (1 H, s, ICH), 7.24-7.30 (5 H, m, Ph). ¹³C NMR (CDCl₃, 500 MHz): δ -0.3 (q, SiCH₃), 22.5 (q, CH₃), 61.1 (t, C₂), 62.0 (t, C₅), 66.0 (d, 181
NCH, 72.1 (d, ICH), 127.1 (d), 127.1 (d), 127.3 (d, Ph), 128.4 (d, Ph), 144.4 (s), 148.7 (s), 151.2 (s). Assignments were confirmed by COSY, HETCOR and DEPT 135. NOE: ICH→H₂: 3.9 %; SiCH→H₅: 4.5 %; SiCH→SiCH₃: 2.3 %.

Entry 144, SG-III-229.

Attempted tin-bromine exchange in (3Z,4Z)-di-O-methyl-3-[(tri-\textit{n}-butylstannyl)-methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56. A solution of 49 mg (0.086 mmol) of (3Z,4Z)-di-O-methyl-3-[(tri-\textit{n}-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 in 1 mL of dichloromethane was cooled to -78°C. In another vial, a solution of 50 µL (0.976 mmol) of bromine in 10 mL of dichloromethane was prepared and also cooled to –78°C. About 1 mL of the bromine solution was added dropwise to the stannane solution until the orange color of the bromine persisted. After stirring at -78 °C for 10 minutes, the solution was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 9/1). Nothing could be isolated and characterized.

Entry 145, SG-III-241.

(3Z,4Z)-Di-O-methyl-3-[bromomethylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 130.
(3Z,4Z)-Di-\textit{O}-methyl-3-[(\textit{tri}-n\textit{-butylstannyl})methylene]-4-[(\textit{trimethylsilyl})methylene]cyclopentanedicarboxylate 56 (51 mg, 0.089 mmol) was dissolved in 1 mL of dichloromethane. N-Bromosuccinimide (16 mg, 0.090 mmol) was added and the reaction mixture was stirred at room temperature overnight. After 15.5 h, the solvent was evaporated. A crude NMR showed the presence of the desired product and succinimide and tin residues, suggesting a quantitative transformation. Purification attempts by chromatography on silica gel or by simple extraction all failed.

\begin{align*}
1^H \text{NMR (CDCl}_3, 500 \text{ MHz): } & \delta 0.10 (9 \text{ H, s, SiC}_3H_3), 2.96 (2 \text{ H, d, J}_{HH}= 1.6 \text{ Hz, } H_2), 3.01 (2 \text{ H, d, J}_{HH}= 1.8 \text{ Hz, } H_5), 3.69 (6 \text{ H, s, CH}_3), 5.58 (1 \text{ H, t, J}_{HH}= 1.8 \text{ Hz, SiCH}), 6.01 (1 \text{ H, t, J}_{HH}= 1.8 \text{ Hz, BrCH}). \\
13^C \text{NMR (CDCl}_3, 125 \text{ MHz): } & \delta -0.9 (q, \text{ SiCH}_3), 41.5 (t, C_2), 44.0 (t, C_5), 52.9 (q, \text{ CH}_3), 55.2 (s, C_7), 100.1 (d, BrCH), 129.9 (d, SiCH), 142.3 (s), 148.4 (s), 171.5 (s, CO). \text{ Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: BrCH} \rightarrow H_2: 2.6 \text{ %; BrCH} \rightarrow \text{SiCH}_3: 1.0 \text{ %; SiCH} \rightarrow H_5: 3.0 \text{ %; SiCH} \rightarrow \text{SiCH}_3: 2.0 \text{ %.}
\end{align*}

Entry 146, see Entry 147.

Entry 147, SG-IV-015.

\begin{align*}
(4E)-3-(\text{Methylene})-1-[(S)-(\text{\alpha-methylbenzyl})]-4-[(\text{trimethylsilyl})methylene]pyrroliidine 131.
\end{align*}
(3E,4E)-3-[(Tri-\(n\)-butylstannyl)methylene]-1-[(S)-(\(\alpha\)-methylbenzyl)]-4-[(trimethylsilyl)-methylenepyrrrolidine 76 (50 mg. 0.089 mmol) was dissolved in 1 mL of THF and cooled to \(-78^\circ\)C. Methylithium (1.4 M, 0.3 mL, 0.420 mmol) was added dropwise. The solution turned red. A saturated aqueous solution of ammonium chloride was added 30 minutes later and the cooling bath was removed quickly to prevent freezing of the aqueous solution. The mixture was then stirred at room temperature overnight. After 19 h, the reaction mixture was poured into 5 mL of water and was extracted three times with 5 mL of diethyl ether. The organic phases were dried on MgSO\(_4\), filtered and evaporated. The residue was then chromatographed on silica gel (hexanes/diethylether: 9/1) to yield 11 mg (46 %) of the desired product.

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 0.20 (9 H, s, SiC\(\text{H}_3\)), 3.22-3.29 (3 H, m), 3.40 (1 H, d (AB), \(J_{HH} = 12.2\) Hz), 3.42 (1 H, d (AB), \(J_{HH} = 12.1\) Hz), 5.07 (1 H, s), 5.36 (1 H, s), 5.53 (1 H, s), 7.29-7.40 (5 H, m, Ph).

Entry 148, see Entry 149.
Entry 149, SG-III-301.

*(3E,4E)-3-[Methylene]-4-[(trimethylsilyl)methylene]-1-tosyl-pyrrolidine 132.*

![Chemical structure](image)

*(3E,4E)-3-[(Tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]-1-tosyl-pyrrolidine 55 (45 mg, 0.074 mmol) was dissolved in 1 mL of THF and cooled to –78ºC. Methyllithium (1.4 M, 0.3 mL, 0.420 mmol) was added dropwise. The solution turned orange immediately. After 10 minutes, the solution was dark red. A saturated aqueous solution of ammonium chloride was added 30 minutes later and the cooling bath was removed quickly to prevent freezing of the aqueous solution. The mixture was then stirred at room temperature overnight. After 17 h, the reaction mixture was poured into 5 mL of water and was extracted three times with 5 mL of diethylether. The organic phases were dried on MgSO₄, filtered and evaporated. The residue was then chromatographed on silica gel (hexanes/diethylether: 8/2) to yield 17 mg (71 %) of the desired product.

¹H NMR (CDCl₃, 500 MHz): δ 0.09 (9 H, s, SiC₃H₃), 2.41 (3 H, s, PhC₃H₃), 3.91 (2 H, d, JHH= 1.8 Hz, H₂), 3.96 (2 H, t, H₅), 5.05 (1 H, s, H₄'out), 5.31 (1 H, t, JHH= 2.0 Hz, H₄'in), 5.49 (1 H, s, H₃'), 7.30 (2 H, d, JHH= 8.0 Hz), 7.68 (2 H, d, JHH= 8.2 Hz). ¹³C NMR (CDCl₃, 125 MHz): δ -0.8 (q, SiC₃H₃), 22.3 (q, PhC₃H₃), 54.1 (t, C₅), 56.4 (t, C₂), 110.6 (t, C₄), 124.6 (d, C₃'), 128.0 (d, Ph), 129.7 (d, Ph), 132.8 (s, Ph), 141.6 (s, Ph), 143.7 (s), 148.7 (s). Assignments were confirmed by COSY, HMQC and DEPT 135. NOE:
SiCH→H5: 2.9 %; SiCH→SiCH3: 1.6 %; CH(in)→CH(out): 8.6 %; CH(in)→SiCH3: 2.3 %; CH(out)→CH(in): 11.4 %; CH(out)→H2: 3.8 %. HRMS calcd for C16H23NO2SSiNa: M⁺ = 344.1116, found 344.1112.

Entries 150-153, see Entry 149.

Entries 154-172, see Entry 173.

Entry 173, SG-III-85.

(3E,4E)-3-[(n-Dec-1-ene)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 133.

The reaction was carried in the dark. Copper (I) iodide (3 mg, 0.016 mmol) and Pd₂(dba)₃ (3 mg, 0.003 mmol) were dissolved in 1 mL of NMP. Trans-1-iododec-1-ene (15 µL, 0.076 mmol) was added. After 15 minutes of stirring at room temperature, (3E,4E)-3-[(tri-n-butylstannyl)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]-pyrrolidine 75 (49 mg, 0.087 mmol) was added in 1 mL of NMP. After 16 h at room temperature, 1 mL of 1 M aqueous potassium fluoride was added. After 30 minutes at
room temperature, the mixture was filtered into 5 mL of water. The solution was extracted three times with 5 mL of hexanes. The organic phases were then dried on Na₂SO₄, filtered and evaporated. The residue was chromatographed on silica gel (hexanes/diethylether: 9/1) to yield 13 mg (42%) of the desired product.

¹H NMR (CDCl₃, 500 MHz): δ 0.15 (9 H, s, SiCH₃), 0.93 (3 H, t, J_HH= 7.0 Hz, chain-CH₃), 1.41 (3 H, d, J_HH= 6.5 Hz, NCHCH₃), 1.31-1.48 (12 H, m, alkyl chain), 2.16 (2 H, q, J_HH= 7.0 Hz, chain-CH₂), 3.24 (1 H, d (AB), J_HH= 11.7 Hz, CH₂), 3.26 (1 H, d (AB), J_HH= 12.5 Hz, CH₂), 3.34 (1 H, q, J_HH= 6.2 Hz, NCH), 3.40 (2 H, d (AB), J_HH= 12.7 Hz, CH₂), 5.53 (1 H, s, SiCH), 5.72 (1 H, dt, J_HH= 15.0, 7.1 Hz, CH₂CH), 5.98 (1 H, d, J_HH= 11.0 Hz, CH), 6.45 (1 H, dd, J_HH= 15.0, 11.3 Hz, CHCHCH), 7.33-7.39 (5 H, m, Ph). ¹³C NMR (CDCl₃, 125 MHz): δ -0.2 (SiCH₃), 14.1 (octyl), 22.7 (NCHCH₃), 29.2 (octyl), 29.3 (octyl), 29.5 (octyl), 29.6 (octyl), 31.9 (octyl), 32.7 (octyl), 60.4 (NCH₂), 63.4 (NCH₂), 66.3 (CHCH₃), 125.4, 127.4, 128.3, 128.4 (Ph), 129.0 (Ph), 130.5, 134.8, 135.9, 143.3. Assignments were confirmed by COSY.

Entries 174-179, see Entry 173.

Entry 180, see Entry 181.

Entry 181, SG-III-243.

Attempts at coupling the vinylstannane moiety of (3E,4E)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilylmethylene]-1-tosyl-pyrrolidine 55 with benzoyl chloride. Tris-(2-furyl)phosphine (21 mg, 0.091 mmol) and Pd₂dba₃ (15 mg, 0.016 187
mmol) were dissolved in 1 mL of NMP. Benzoyl chloride (10 µL, 0.087 mmol) was added. After 15 minutes, (3E,4E)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)-methylene]-1-tosyl-pyrrolidine 55 (50 mg, 0.082 mmol) was added in 3 mL of NMP. After 20 h at room temperature, 1 mL of a 1 M aqueous solution of potassium fluoride was added. After 1h, the mixture was filtered into 5 mL of water. The mixture was extracted three times with 5 mL of dichloromethane. The organic phases were dried on MgSO₄, filtered and evaporated. The residue was then chromatographed on silica gel (hexanes/diethylether: 9/1) to yield 23 mg (80 %) of undesired product 132 and 9 mg of starting material.

For NMR data, see Entry 149.

Entry 182, SG-III-172.

Attempts at coupling the vinylstannane moiety of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 with naproxen chloride. Naproxen (20 mg, 0.087 mmol) was dissolved in 1 mL of dichloromethane and cooled to 0°C under nitrogen. Oxalyl chloride (8 µL, 0.092 mmol) was added and the solution was kept at 0°C for 20 h. The solution was then evaporated. NMR confirmed the quantitative transformation of naproxen into naproxen chloride. Aluminum chloride (6 mg, 0.045 mmol) was added, along with 1 mL of dichloromethane. The solution was then cooled to 0°C and (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (49 mg, 0.086 mmol) was added. After 20 minutes, the solution was warmed back up to room temperature. After 19 h, the mixture was poured into 5 mL of water. The solution
was extracted three times with 5 mL of dichloromethane. The organic phases were dried on sodium sulfate, filtered and evaporated. The residue was then chromatographed on silica gel (hexanes/diethylether: 95/5) to yield 10 mg (41%) of the undesired product 125 and 7 mg of starting material.

Entry 183, see Entry 182.

Entry 184, SG-III-217.

Attempts at coupling the vinylstannane moiety of (3Z,4Z)-di-O-methyl-3-[(tert-butyl-dimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89 with naproxen chloride. Naproxen chloride was prepared as described in Entry 182. Naproxen chloride (20 mg, 0.080 mmol) and aluminum chloride (20 mg, 0.150 mmol) were dissolved in 0.5 mL of dichloromethane. This solution was cooled to 0ºC. Simultaneously, a solution of (3Z,4Z)-di-O-methyl-3-[(tert-butyl(dimethyl)silyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89 (50 mg, 0.074 mmol) in 1 mL of dichloromethane was also cooled to 0ºC. The first solution was added to the second one. After 1.5 h at 0ºC, the solution was brought back to room temperature. After stirring for 3 days, the mixture was poured in 10 mL of water and extracted three times with 5 mL of dichloromethane. The organic phases were dried on magnesium sulfate, filtered and evaporated. The residue was chromatographed on silica gel (hexanes/diethylether: 95/5; 80/20) to yield 21 mg of starting material back.
Attempts at coupling the vinylstannane moiety of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 with phenyltriflate. Phenyltriflate (16 mg, 0.099 mmol), copper (I) iodide (2 mg, 0.010 mmol), tris-(2-furyl)phosphine (3 mg, 0.013 mmol) and Cl₂Pd(PhCN)₂ (2 mg, 0.005 mmol) were mixed in 1 mL of NMP. After 15 minutes, (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (53 mg, 0.093 mmol) was added in 2 mL of NMP. The solution was stirred at room temperature for 22 h. An aqueous solution of potassium fluoride (1 M, 1 mL) was then added. After 45 minutes, the solution was filtered into 15 mL of water. The mixture was extracted three times with 10 mL hexanes. The organic phase was then dried on magnesium sulfate, filtered and evaporated. The residue was chromatographed on silica gel (hexanes/diethylether: 9/1; 65/35; 1/1), but nothing could be isolated and characterized.

Entries 188-189, see Entry 190.
Attempts at coupling the vinylstannane moiety of (3Z,4Z)-di-O-methyl-3-[(bromo)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 128 with phenylboronic acid. (3Z,4Z)-Di-O-methyl-3-[(bromo)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 128 (0.081 mmol), phenylboronic acid (34 mg, 0.279 mmol), Pd\textsubscript{2}(dba)\textsubscript{3} (9 mg, 0.010 mmol), cesium carbonate (64 mg, 0.196 mmol) and tris-( tert-butyl)phosphine (6 mg, 0.030 mmol) were mixed in 1 mL of dioxane and placed in an oil bath at 80°C for 2 days. The solvent was then evaporated. The residue was poured in 5 mL of water and extracted three times with 5 mL of dichloromethane. The organic solution was dried on magnesium sulfate, filtered and evaporated. The residue was chromatographed on silica gel (hexanes/diethylether: 95/5; 8/2), but no product could be isolated.

Entry 191, see Entry 190.

Attempts at coupling the vinylstannane moiety of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstanny1)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 with (3Z,4Z)-di-O-methyl-3-[(bromo)methylene]-4-[(trimethylsilyl)methylene]cyclopentane dicarboxylate 130. (3Z,4Z)-Di-O-methyl-3-[(bromo)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 130 (0.110 mmol), Cl\textsubscript{2}Pd(CH\textsubscript{3}CN)\textsubscript{2} (3 mg, 0.008 mmol), copper (I) iodide (2 mg, 0.010 mmol) and tris-(2-furyl)phosphine (5 mg, 0.022 mmol) were dissolved in 1 mL of NMP. (3Z,4Z)-di-O-methyl-3-[(tri-n-butyl-
stannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 57 (50 mg, 0.088 mmol) was added and the reaction mixture was stirred at room temperature for 2 days. The solution was poured in 10 mL of water and extracted three times with 5 mL of hexanes. The organic phases were dried on magnesium sulfate, filtered and evaporated. The residue was chromatographed (hexanes/diethylether: 9/1; 1/1), but nothing could be isolated and characterized.

Entry 193, see Entry 192.

Entry 194, SG-III-245.

Attempts at coupling the vinylstannane moiety of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 with isocyanate. (3Z,4Z)-Di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (50 mg, 0.088 mmol) was dissolved in 1 mL of dichloromethane and was cooled to 0°C. ClSO₂NCO (10 µL, 0.115 mmol) was added. The solution was stirred at 0°C for 45 minutes. The cold bath was then removed and the reaction mixture was stirred at room temperature for 18 h. The mixture was poured in 5 mL of water and extracted three times with 5 mL of dichloromethane. The organic phases were dried on magnesium sulfate, filtered and evaporated. A crude NMR showed the absence of any olefinic peaks in the mixture.

Entry 195, see Entry 194.
Diels-Alder adduct of (3Z,4Z)-di-O-methyl-3-methylene-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate.

(3Z,4Z)-Di-O-methyl-3-methylene-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 125 (19 mg, 0.067 mmol) was dissolved in 0.5 mL of CDCl₃. This solution was transferred into an NMR tube. Maleic anhydride (9 mg, 0.092 mmol) was added and the reaction was followed by ¹H NMR. After 24 h, the starting material could not be observed any more. The solution was evaporated and the residue was chromatographed on silica gel (hexanes/diethyl ether: 1/1) to yield 24 mg (96 %) of Diels-Alder adduct.

¹H NMR (CDCl₃, 500 MHz): δ 0.09 (9 H, s, SiCH₃), 2.19 (1 H, s, SiCH), 2.32-2.38 (1 H, m, C=CH₂), 2.50 (1 H, d, J₃,₄ = 17.2 Hz, C=CH₂), 2.88-3.02 (4 H, m, CH₂), 3.29 (1 H, dd, J₃,₄ = 9.6, 1.5 Hz, CH₂), 3.40 (1 H, dt, J₄,₅ = 2.3, 9.6 Hz, C=CH₂), 3.70 (6 H, s, CH₃). ¹³C NMR (CDCl₃, 125 MHz): δ -1.9 (q, CH₃), 24.2 (t, CH₂), 27.8 (d, CH₂), 39.9 (d, C=CH₂), 41.0 (d, CH₂), 43.5 (t, CH₂), 44.3 (t, CH₂), 52.8 (q, CH₃), 52.9 (q, CH₃), 57.7 (q, CCOO), 127.1 (s), 133.7 (s), 171.7 (s), 172.4 (s), 174.0 (s), 174.8 (s). Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SiCH₃→SiCH: 2.9 %; SiCH₃→C=CH₂: 4.1 %; SiCH₃→CH₂: 4.0 %; SiCH₃→SiCHCH: 3.2 %; SiCH₃→C=CH₂: 2.4 %. HRMS calcd for C₁₈H₂₄O₇SiNa: M⁺ = 403.1189, found 403.1198.
(3E,4E)-3-Methylene-4-[(trimethylsilyl)methylene]-1-tosyl-pyrrolidine 132 (5 mg, 0.016 mmol) was dissolved in 0.5 mL of CDCl$_3$. This solution was transferred into an NMR tube. Maleic anhydride (3 mg, 0.031 mmol) was added and the reaction was followed by $^1$H NMR. After 11 days, the starting material could not be observed any more. The solution was evaporated to yield the Diels-Alder adduct.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.07 (9 H, s, SiC$_3$H$_3$), 2.11 (1 H, brd s, SiCH), 2.30 (1 H, m, C=CCH$_2$), 2.41 (3 H, s, PhCH$_3$), 2.4 (1 H, m, C=CCH$_2$), 3.27 (1 H, dd, $J_{HH}$= 9.8, 1.5 HZ, SiCHCH), 3.39 (1 H, td, $J_{HH}$= 9.6, 2.2 Hz, C=CCH$_2$CH), 3.91-3.94 (2 H, m, C$_2$H), 4.08-4.17 (2 H, m, CH$_2$), 7.30 (2 H, d, $J_{HH}$= 8.0 Hz, Ph), 7.64 (2 H, d, $J_{HH}$= 8.3 Hz, Ph).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 1.0 (q, SiCH$_3$), 21.5 (q, PhCH$_3$), 22.1 (t, C=CCH), 25.9 (d, SiCH), 39.3 (d, C=CCH$_2$CH), 40.5 (d, SiCHCH), 56.9 (t, CH$_2$), 57.4 (t, CH$_2$), 125.0 (s), 127.2 (d, Ph), 129.9 (d, Ph), 132.0 (s), 133.7 (s), 136.5 (s), 143.9 (s), 173.3 (s), 174.1 (s). Assignments were confirmed by COSY, HMQC and DEPT 135. HRMS calcd for C$_{18}$H$_{24}$O$_7$SiNa: $M^+$ = 442.1120, found 442.1117. NOE experiments did not give any insight into the configuration of the product.
Entry 198, SG-III-111.

**Attempted Diels-Alder reaction on O-methyl-(3Z,4Z)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73.** O-Methyl-(3Z,4Z)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentane-carboxylate 73 (44 mg, 0.086 mmol) was dissolved in 5 mL of chloroform. Maleic anhydride (9 mg, 0.092 mmol) was added and the reaction was stirred at room temperature for 15.5 h. The solution was evaporated and a crude $^1$H NMR showed that the starting material was untouched.

Entries 199-200, see Entry 201.

Entry 201, SG-III-255.

**Attempted hydroboration of (3E,4E)-3-[(tri-n-butylstannyl)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 75.** (3E,4E)-3-[(Tri-n-butylstannyl)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 75 (53 mg, 0.095 mmol) was dissolved in 1 mL of THF. 9-BBN (0.5 M, 200 μL, 0.100 mmol) was added and the reaction mixture was stirred at room temperature for 19 h. More 9-BBN (0.5 M, 200 μL, 0.100 mmol) was then added. After 3 more hours, water (1 mL), sodium hydroxide (6 N, 0.5 mL) and hydrogen peroxide (1 mL) were added and stirred at room temperature for 1 h. The solution was then extracted three times with 5
mL of diethylether. The organic phases were dried on magnesium sulfate, filtered and evaporated. The residue was then chromatographed on silica gel (hexanes/diethylether: 8/2; 1/1), but nothing could be isolated.

Entries 202-203, see Entry 201

Entry 204, see Entry 205.

Entry 205, SG-III-263

Attempts at the epoxidation of (3\(Z\),4\(Z\))-di-O-methyl-3-[(tri-\(n\)-butylstannyl)-methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 with oxaziridine. (3\(Z\),4\(Z\))-Di-O-methyl-3-[(tri-\(n\)-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (21 mg, 0.037 mmol) was dissolved in 0.5 mL of C\(_6\)D\(_6\) and the solution was transferred to an NMR tube. The oxaziridine (24 mg, 0.070 mmol) was added and the NMR tube was placed in an oil bath at 62°C. The reaction was followed by NMR, but little change was observed. After 28 h, the oxaziridine had almost disappeared. The solution was evaporated and the residue was chromatographed on silica gel (hexanes/diethylether: 9/1) to yield 2 mg (20 %) of undesired product 125 and 9 mg of the starting material.

Entries 206-207, see Entry 208.
Entry 208, SG-III-258.

(3Z,4Z)-Di-O-methyl-3-[(tri-n-butylstannyl)methylene]oxo-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 137.

(3Z,4Z)-Di-O-methyl-3-[(tri-n-butylstannyl)methylene]oxo-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (50 mg, 0.088 mmol) was dissolved in 2 mL of dichloromethane. M-CPBA (23 mg, 0.095 mmol) was added. The reaction mixture was placed in an oil bath at 45ºC. After 3 h of reflux, the solution was cooled down. It was then filtered into a saturated sodium bicarbonate solution. The mixture was extracted three times with 5 mL of dichloromethane. The organic phases were dried on magnesium sulfate, filtered and evaporated. The residue was then chromatographed on silica gel (hexanes/diethylether: 95/5; 9/1) to yield 15 mg (29 %) of desired product 137, 6 mg (24 %) of undesired product 125 and 7 mg of starting material.

1H NMR (CDCl3, 500 MHz): δ 0.09 (9 H, s, SiCH3), 0.86-0.93 (15 H, m, Bu), 1.24-1.33 (6 H, m, Bu), 1.44-1.52 (6 H, m, Bu), 2.20 (1 H, d (AB), JHH= 13.1 Hz, H2), 2.64 (1 H, d (AB), JHH= 13.1 Hz, H2), 2.71 (1 H, s, SnCH), 2.87 (1 H, d (AB), JHH= 16.4 Hz, H3), 3.16 (1 H, dd (AB), JHH= 2.3, 16.2 Hz, H3), 3.72 (6 H, s, CH3), 5.31 (1 H, s, SiCH). 13C NMR (CDCl3, 125 MHz): δ 1.2 (q, SiCH3), 9.9 (t, Bu), 13.6 (q, Bu), 27.3 (t, Bu), 29.0 (t, Bu), 39.9 (t, CH2), 40.4 (t, CH2), 52.9 (q, CH3), 54.1 (s, C1), 64.9 (d, SnCH), 66.8 (s, SnCHC), 123.7 (d, SiCH), 153.7 (s, SiCHC), 171.8 (s, CO), 172.2 (s, CO). 119Sn NMR
(CDCl₃, 185 MHz): δ -41.6. Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SiCH→SiCH₃: 2.2 %; SiCH→CH₂: 2.8 %. HRMS calcd for C₂₆H₄₈O₅SiSnNa: M⁺ = 611.2191, found 611.2188.

Entries 209–212, see Entry 208.

Entry 213, SG-III-266.

Attempts at the epoxidation of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 with dimethyldioxirane. (3Z,4Z)-Di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (29 mg, 0.051 mmol) was dissolved in 1 mL of dichloromethane. Potassium carbonate (129 mg, 0.935 mmol) was added and the reaction mixture was cooled to 0°C. Cold dimethyl dioxirane⁴⁴ (0.085 M, 0.6 mL, 0.051 mmol) was then added. The solution was brought back to room temperature. After 43 h at room temperature, the solution was poured into 5 mL of water and extracted three times with 5 mL of dichloromethane. The organic phases were dried on sodium sulfate, filtered and evaporated. The residue was chromatographed on silica gel to yield 21 mg of the starting material back.

Entry 214, see Entry 213.


\[
\begin{align*}
\text{H}_3\text{COOC} & \quad \text{COOCCH}_3 \\
\text{Me}_3\text{Si} & \quad \text{Cl} \\
\end{align*}
\]

(3Z,4Z)-Di-O-methyl-3-[[tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (51 mg, 0.089 mmol) was dissolved in 1 mL of dichloromethane. The manganese complex (4 mg, 0.006 mmol) and 4-phenylpyridine-N-oxide (6 mg, 0.035 mmol) were added, along with 0.2 mL of commercial bleach. The reaction mixture was stirred at room temperature for 43 h. It was then poured in 5 mL of water and extracted three times with 5 mL of dichloromethane. The organic phases were dried on sodium sulfate, filtered and evaporated. The residue was chromatographed on silica gel (hexanes/diethylether: 95/5; 9/1) to yield 5 mg (18 %) of an unexpected compound 138 and 26 mg of starting material back.

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta 0.16\) (9 H, s, SiCH\(_3\)), \(3.05\) (2 H, d, \(J_{HH}= 1.7\) Hz, CH\(_2\)), \(3.12\) (2 H, d, \(J_{HH}= 1.9\) Hz, CH\(_2\)), \(3.78\) (6 H, s, CH\(_3\)), \(5.73\) (1 H, s, SiCH), \(5.97\) (1 H, s, ClCH). \(^13\)C NMR (CDCl\(_3\), 125 MHz): \(\delta -1.0\) (q, SiCH\(_3\)), \(40.7\) (t, CH\(_2\)), \(44.3\) (t, CH\(_2\)), \(53.0\) (q, CH\(_3\)), \(55.5\) (s, C\(_t\)), \(111.7\) (d, CH), \(130.2\) (d, CH), \(139.3\) (s, CCH), \(147.2\) (s, CCH),
171.6 (s, CO). Assignments were confirmed by COSY, HMQC and DEPT 135. NOE: SiCH$\rightarrow$SiCH$_3$: 1.1 %; SiCH$\rightarrow$CH$_2$: 3.1 %; ClCH$\rightarrow$CH$_2$: 2.1 %. HRMS calcd for C$_{14}$H$_{21}$ClO$_4$SiNa: M$^+$ = 339.0795, found 339.0793.

Entry 216, see Entry 215.

Entry 217, see Entry 218.

Entry 218, SG-IV-011.

**Attempted Sharpless dihydroxylation on (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56.** AD Mix β (125 mg) was dissolved in 0.4 mL of water and 0.4 mL of tert-butanol. Methanesulfonamide (9 mg, 0.095 mmol) was added. After 5 minutes, (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (53 mg, 0.093 mmol) in 0.4 mL of tert-butanol was added. The reaction mixture was stirred at room temperature for 5 days. It was then poured in 10 mL of water and extracted three times with 10 mL of dichloromethane. The organic phases were then dried on magnesium sulfate, filtered and evaporated. A crude $^1$H NMR was then taken and showed the presence of only the starting material.
Attempted osmium tetroxide dihydroxylation on (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56. (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 (61 mg, 0.107 mmol) was dissolved in 0.2 mL of diethyl-ether. In another flask, osmium tetroxide (26 mg, 0.102 mmol) was dissolved in 0.7 mL of diethyl ether and 100 µL of pyridine (0.951 mmol). The osmium tetroxide solution was then added to the stannane. The reaction was followed by TLC. After 17.5 h, sodium bisulfite (50 mg) in 0.9 mL of water and 0.6 mL of pyridine was added. After 3 h of stirring at room temperature, the mixture was poured into 5 mL of water and extracted three times with 5 mL of dichloromethane. The organic phases were dried on sodium sulfate, filtered and evaporated. The residue was chromatographed on silica gel (hexanes/diethylether: 9/1; 1/1; diethyl ether; methanol) to yield 34 mg (56 %) of the starting material back. No desired product could be identified.


(32) Brandsma, L. *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, New York, **1971**.


APPENDIX A

SELECTED NMR SPECTRA
$^1$H NMR spectrum of (3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]-1-tosyl-pyrrolidine 55 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]-1-tosyl-pyrrolidine 55 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (3Z,4Z)-di-O-methyl-3-[(tri-n-butylstannyl)methylene]-4-[(tri-methylsilyl)methylene]cyclopentanedicarboxylate 56 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-di-\(O\)-methyl-3-[(tri-\(n\)-butylstannyl)methylene]-4-[(tri-methylsilyl)methylene]cyclopentanedicarboxylate 56 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (1Z,2Z)-1-[(tri-$n$-butylstannyl)methylene]-2-[(trimethylsilyl)methylene]cyclopentane 63 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (1Z,2Z)-1-[(tri-$n$-butylstannyl)methylene]-2-[(trimethylsilyl)methylene]cyclopentane 63 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (Z)-2-(tri-$n$-butylstannyl)-1-(trimethylsilyl)hept-1-ene-6-yne 64 (CDCl$_3$, 400 MHz).
$^{13}\text{C}$ NMR spectrum of (Z)-2-(tri-$n$-butylstannyl)-1-(trimethylsilyl)hept-1-ene-6-yné 64 (CDCl$_3$, 100 MHz).
$^1$H NMR spectrum of (1Z,6Z)-2,6-bis-(tri-$n$-butylstannyl)-1,7-bis-(trimethylsilyl)hepta-1,6-diene 65 (CDCl$_3$, 500 MHz).
$^1$H NMR spectrum of $O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of $O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73 (CDCl$_3$, 125 MHz).
$^{119}\text{Sn}$ NMR spectrum of $O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73 (CDCl$_3$, 185 MHz).
$^1$H NMR spectrum of [(S)-$\alpha$-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 74 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of [(S)-α-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-\(n\)-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 74 (CDCl$_3$, 125 MHz).
$^{119}\text{Sn}$ NMR spectrum of $[(S)-\alpha$-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 74 (CDCl$_3$, 185 MHz).
$^1$H NMR spectrum of (3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrroldidine 75 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 75 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-1-[(S)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 76 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-1-[(S)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 76 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of di-$O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(triethylsilyl)methylene]cyclopentanedicarboxylate 86 (CDCl₃, 500 MHz).
$^{13}$C NMR spectrum of di-O-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(tri-ethlysilyl)methylene]cyclopentanedicarboxylate 86 (CDCl$_3$, 125 MHz).
$^{119}$Sn NMR spectrum of di-O-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(tri-ethylsilyl)methylene]cyclopentanedicarboxylate 86 (CDCl$_3$, 185 MHz).
$^1$H NMR spectrum of di-O-methyl-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(tri-$n$-butylstannyl)methylene]cyclopentanedicarboxylate 87 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of di-O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-$n$-butylstannyl)methylene]cyclopentanedicarboxylate 87 (CDCl$_3$, 125 MHz).
\[ ^{119}\text{Sn} \text{ NMR spectrum of di-O-methyl-(3Z,4Z)-3-[(\text{tert-butyl}dime\text{thylsilyl})\text{methylene}]\text{-4-[(tri-\text{n-bu}}
\text{tylstannyl)methylene]cyclopentanedicarboxylate 87 (CDCl}_3, 185 MHz). \]
$^1$H NMR spectrum of di-O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstanny)l)methylene]cyclopentanedicarboxylate 89 (CDCl$_3$, 500 MHz).
COSY spectrum of di-O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89 (CDCl₃, 500 MHz).
NOE spectrum of di-O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89 (CDCl₃, 500 MHz).
$^{13}$C NMR spectrum of di-$O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89 (CDCl$_3$, 125 MHz).
DEPT 135 spectrum of di-O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89 (CDCl₃, 125 MHz).
HMOC spectrum of di-$O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-phenylstannyI)methylene]cyclopentanedicarboxylate 89 (CDCl3, 500 MHz).
$^{119}$Sn NMR spectrum of di-\(O\)-methyl-(3Z,4Z)-3-[(\textit{tert}-butyldimethylsilyl)methylene]-4-[(triphenylstanny1)methylene]cyclopentanedicarboxylate 89 (CDCl\(_3\), 185 MHz).
$^1$H NMR spectrum of di-\(O\)-methyl-(3Z,4Z)-3-[(triphenylstannylyl)methylene]-4-[(tri-\textit{iso}-
propylsilyl)methylene]cyclopentanedicarboxylate \textbf{90} (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of di-$O$-methyl-(3Z,4Z)-3-[(triphenylstannyl)methylene]-4-[(tri-$iso$-propylsilyl)methylene]cyclopentanedicarboxylate 90 (CDCl$_3$, 125 MHz).
$^{119}$Sn NMR spectrum of di-$O$-methyl-(3Z,4Z)-3-[(triphenylstannyI)methylene]-4-[(tri-$iso$-propylsilyl)methylene]cyclopentanedicarboxylate 90 (CDCl$_3$, 185 MHz).
$^1$H NMR spectrum of O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-n-butylstannyl)methylene]cyclopentanecarboxylate 91 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-$n$-butylstannyl)methylene]cyclopentanecarboxylate 91 (CDCl$_3$, 125 MHz).
$^{119}$Sn NMR spectrum of $O$-methyl-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(tri-$n$-butylstanny)lmethylene]cyclopentanecarboxylate 91 (CDCl$_3$, 185 MHz).
$^1$H NMR spectrum of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 92 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of $O$-methyl-(3Z,4Z)-3-[(tert-butyl dimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 92 (CDCl$_3$, 125 MHz).
\[^{119}\text{Sn}\] NMR spectrum of O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 92 (CDCl\textsubscript{3}, 185 MHz).
\(^{1}\)H NMR spectrum of [(S)-α-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 93 (CDCl\(_3\), 500 MHz).
$^{13}$C NMR spectrum of [(S)-α-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)-methylene]cyclopentanecarboxylate (CDCl$_3$, 125 MHz).
$^{119}$Sn NMR spectrum of $[(S)\-\alpha\-\text{carboxethoxyphenylmethyl}]\-(3Z,4Z)-3\-[(\text{tert\-butyldimethylsilyl})\text{methylene}]\-4\-[(\text{triphenylstanny})\-\text{methylene}]\text{cyclopentanecarboxylate}$ (CDCl$_3$, 185 MHz).
$^1$H NMR spectrum of (3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-(α-methyl-benzyl)]-4-[(trimethylstannyl)methylene]pyrrolidine 94 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylstannyl)methylene]pyrrolidine 94 (CDCl₃, 125 MHz).
$^1$H NMR spectrum of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(tri-$n$-butylstannyl)methylene]pyrroolidine 95 (CDCl$_3$, 500 MHz).
NOE spectrum of \((3E,4E)-3-[(\text{tert-butyl}d\text{imethyl}silyl)methylene]-1-[(R)-\alpha\text{-methylbenzyl}]-4-[(\text{tri-}n\text{-butylstannyl})\text{methylen}]\text{pyrrolidine} 95 \text{ (CDCl}_3, 500 \text{ MHz)}.
COSY spectrum of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(tri-n-butylstanny)l)methylene]pyrrolidine 95 (CDCl₃, 500 MHz).
$^{13}$C NMR spectrum of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(tri-$n$-butylstannyl)methylene]pyrrolidine 95 (CDCl$_3$, 125 MHz).
DEPT 135 spectrum of (3E,4E)-3-[(tert-butyl(dimethyl)silyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(tri-n-butylstannyl)methylene]pyrrolidine 95 (CDCl₃, 125 MHz).
HMOC spectrum of \((3E,4E)-3-[(\text{tert-butyl}dimehtylsilyl)\text{methylene}]\)-1-\(\text{(R)}\)-\(\alpha\)-methylbenzyl]-4-\(\text{[(tri-}n\text{-butylstanny}l)]\text{methylene}]\)pyrrolidine 95 (CDCl\textsubscript{3}, 500 MHz).
$^{119}\text{Sn NMR spectrum of (3E,4E)-3-[(}t\text{ert-}b\text{utyldimethylsilyl)methylene]-1-[(}R\text{-}\alpha\text{-methyl-}
\text{benzyl]-4-[(tri-}n\text{-butylstannyl)methylene]pyrrolidine 95 (CDCl}_3\text{, 185 MHz).}$
$^1$H NMR spectrum of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(triphenylstanny)l)methylene]pyrrolidine 96 (CDCl₃, 500 MHz).
$^{13}$C NMR spectrum of (3E,4E)-3-[[tert-butyldimethylsilyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(triphenylstanny)lmethylene]pyrroolidine 96 (CDCl$_3$, 125 MHz).
$^{119}$Sn NMR spectrum of (3\(E\),4\(E\))-3-\([\text{tert-butyldimethylsilyl}]\text{methylene}\)-1-\([\text{(R)}-\alpha\text{-methyl-benzyl}]\)-4-\([\text{triphenylstanny}]\text{lmethylene}\)pyrrolidine 96 (CDCl$_3$, 185 MHz).
$^1$H NMR spectrum of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[tosyl]-4-[(triphenylstannyl)methylene]pyrrolidine 98 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[tosyl]-4-[(tri-phenylstanny]methylene]pyrrolidine 98 (CDCl$_3$, 125 MHz).
$^{119}$Sn NMR spectrum of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[tosyl]-4-[(triphenylstannyl)methylene]pyrrolidine 98 (CDCl₃, 185 MHz).
\(^1\)H NMR spectrum of (Z)-2-(tri-\(n\)-butylstannyl)-1-(trimethylsilyl)hex-1-ene-5-yne 100 (CDCl\(_3\), 500 MHz).
$^{13}$C NMR spectrum of (Z)-2-(tri-$n$-butylstannyl)-1-(trimethylsilyl)hex-1-ene-5-yne (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (Z)-2-(tri-$n$-butylstannyl)-1-(trimethylsilyl)oct-1-ene-7-yne 102 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (Z)-2-(tri-$n$-butylstannyl)-1-(trimethylsilyl)oct-1-ene-7-yne (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (Z)-2-(tri-n-butylstannyl)-1-(trimethylsilyl)non-1-ene-8-yne 104 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (Z)-2-(tri-$n$-butylstannyl)-1-(trimethylsilyl)non-1-ene-8-yne (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (Z)-2-(tri-$n$-butylstannyl)-1-(trimethylsilyl)deca-1-ene-9-yne 106 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (Z)-2-(tri-n-butyllstannyl)-1-(trimethylsilyl)deca-1-ene-9-yne 106

(CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (Z)-di-$O$-methyl-3-[(tri-$n$-butylstannyl)methyl]-4-[(trimethylsilyl)-methylene]cyclopentanedicarboxylate 110 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (Z)-di-\(O\)-methyl-3-[(tri-n-butylstannyl)methyl]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 110 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (3E,4E)-3-[(tri-$n$-butylstannyl)methylene]-1-methyl-1-[(S)-$\alpha$-methylenbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium iodide 114 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of $(3E,4E)-3-[(\text{tri-}n\text{-butylstannyl})\text{methylene}]-1\text{-methyl}-1-[(S)-\alpha\text{-methylnbenzyl}]-4-[(\text{trimethylsilyl})\text{methylene}]\text{pyrrolidinium iodide 114 (CDCl}_3, 125 \text{ MHz).}$
$^1$H NMR spectrum of (3E,4E)-3-[(tri-$n$-butylstannyl)methylene]-1-methyl-1-[(S)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium trifluoromethanesulfonate (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3E,4E)-3-[(tri-$n$-butylstannyl)methylene]-1-methyl-1-[(S)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium trifluoromethanesulfonate (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (3E,4E)-3-[(tri-$n$-butylstannyl)methylene]-1-methyl-1-[(R)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium trifluoromethanesulfonate (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3E,4E)-3-[(tri-$n$-butylstannyl)methylene]-1-methyl-1-[(R)-$\alpha$-methylnaphthylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium trifluoromethanesulfonate (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (3E,4E)-3-[iodomethylene]-1-methyl-1-[(R)-α-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium trifluoromethanesulfonate 117 (CDCl$_3$, 500 MHz).
$^1$H NMR spectrum of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-methyl-1-[(R)-α-methylbenzyl]-4-[(trimethylstannyl)methylene]pyrrolidinium trifluoromethanesulfonate 118 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-methyl-1-[(R)-α-methylbenzyl]-4-[(trimethylstannyl)methylene]pyrrolidinium trifluoromethanesulfonate 118 (CDCl$_3$, 125 MHz).
$^{119}$Sn NMR spectrum of $(3E, 4E)$-3-[(tert-butyldimethylsilyl)methylene]-1-methyl-1-[(R)-$\alpha$-methylbenzyl]-4-[(trimethylstannyl)methylene]pyrrolidinium trifluoromethanesulfonate 118 (CDCl$_3$, 185 MHz).
\(^1\)H NMR spectrum of (3E,4E)-3-[(tri-\(n\)-butylstannyl)methylene]-1-[(\(R\)-\(\alpha\)-methylbenzyl)-4-[(trimethylsilyl)methylene]pyrrolidinium oxalate 119 (CDCl\(_3\), 500 MHz).
\(^{13}\)C NMR spectrum of (3E,4E)-3-[(tri-\(n\)-butylstannyl)methylene]-1-[(\(R\)-\(\alpha\)-methylbenzyl)-4-[(trimethylsilyl)methylene]pyrrolidinium oxalate 119 (CDCl\(_3\), 125 MHz).
$^1$H NMR spectrum of (3E,4E)-3-[(tri-$n$-butylstannyl)methylene]-1-[(R)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium oxalate 119 after reprecipitation (CDCl$_3$, 500 MHz).
$^1$H NMR spectrum of (3E,4E)-3-[(tri-n-butylstannyl)methylene]-1-[(S)-α-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium oxalate 120 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of $\left(3E,4E\right)$-3-[(tri-$n$-butylstannyl)methylene]-1-[(S)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium oxalate 120 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (3E,4E)-3-[(tri-$n$-butylstannyl)methylene]-1-[(R)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium camphorsulfonate 121 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3\textit{E},4\textit{E})-3-[(tri-\textit{n}-butylstannyl)methylene]-1-[(\textit{R})-\textalpha-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium camphorsulfonate 121 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (3\textit{E},4\textit{E})-3-[(tri-\textit{n}-butylstannyl)methylene]-1-[(\textit{S}-\alpha\text{-methylbenzyl}]-4-[(trimethylsilyl)methylene]pyrrolidinium camphorsulfonate 122 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3$E$,4$E$)-3-[(tri-$n$-butylstannyl)methylene]-1-[(S)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium camphorsulfonate 122 (CDCl$_3$, 125 MHz).
$^{119}$Sn NMR spectrum of (3\textit{E},4\textit{E})-3-[(tri-\textit{n}-butylstannyl)methylene]-1-[(\textit{S})-\alpha\text{-methyl-benzyl}]-4-[(trimethylsilyl)methylene]pyrrolidinium camphorsulfonate 122 (CDCl$_3$, 185 MHz).
$^1$H NMR spectrum of (3E,4E)-3-[(tri-$n$-butylstannyl)methylene]-1-[(R)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium picrate 123 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3$E$,4$E$)-3-[(tri-$n$-butylstannyl)methylene]-1-[(R)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium picrate 123 (CDCl$_3$, 125 MHz).
$^{119}$Sn NMR spectrum of (3\textit{E},4\textit{E})-3-[(\textit{tri}-\textit{n}-butylstannyl)methylene]-1-[(\textit{R})-\textit{\alpha}-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium picrate 123 (CDCl$_3$, 185 MHz).
$^1$H NMR spectrum of (4Z)-di-O-methyl-3-(methylene)-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 125 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (4Z)-di-$O$-methyl-3-((methylene)-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 125 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (4Z)-di-O-methyl-3-(methylene)-4-[(tri-$n$-butylstannyl)methylene]-cyclopentanedicarboxylate 126 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (4Z)-di-O-methyl-3-(methylene)-4-[(tri-$n$-butylstannyl)methylene]cyclopentanedicarboxylate 126 (CDCl$_3$, 125 MHz).
$^{119}\text{Sn}$ NMR spectrum of (4Z)-di-$O$-methyl-3-(methylene)-4-[(tri-$n$-butylstanny)l)methyl-}
-ene]cyclopentanedicarboxylate 126 (CDCl$_3$, 185 MHz).
$^1$H NMR spectrum of $O$-methyl-(3Z,4Z)-3-(iodomethylene)-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 127 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of $O$-methyl-(3Z,4Z)-3-(iodomethylene)-4-[(trimethylsilyl)methyl-}
linecyclopentanecarboxylate 127 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (3Z,4Z)-di-O-methyl-3-(iodomethylene)-4-[(trimethylsilyl)methyl-128lene]cyclopentanedicarboxylate 128 (CDCl$_3$, 500 MHz).
COSY spectrum of (3Z,4Z)-di-\textit{O}-methyl-3-(iodomethylene)-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 128 (CDCl$_3$, 500 MHz).
NOE spectrum of (3Z,4Z)-di-O-methyl-3-(iodomethylene)-4-[(trimethylsilyl)methylene]-cyclopentanedicarboxylate 128 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-di-O-methyl-3-(iodomethylene)-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate **128** (CDCl$_3$, 125 MHz).
DEPT spectrum of (3Z,4Z)-di-O-methyl-3-(iodomethylene)-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 128 (CDCl₃, 125 MHz).
HMOC spectrum of (3Z,4Z)-di-\(O\)-methyl-3-(iodomethylene)-4-[(trimethylsilyl)methyl-\(l\)ene]cyclopentanedicarboxylate 128 (CDCl\(_3\), 500 MHz).
\(^1\)H NMR spectrum of (3Z,4Z)-3-(iodomethylene)-1-[(R)-(\(\alpha\)-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 129 (CDCl\(_3\), 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-3-(iodomethylene)-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 129 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (3Z,4Z)-di-O-methyl-3-[bromomethylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 130 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-di-O-methyl-3-[bromomethylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 130 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (4Z)-3-(methylene)-1-[(S)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 131 (CDCl₃, 500 MHz).
$^1$H NMR spectrum of (3Z,4Z)-3-[methylene]-4-[(trimethylsilyl)methylene]-1-tosyl-pyrroolidine 132 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-3-[methylene]-4-[(trimethylsilyl)methylene]-1-tosyl-pyrrolidine 132 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (3Z,4Z)-3-[(n-dec-1-ene)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 133 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-3-[(n-dec-1-ene)methylene]-1-[(R)-(α-methylbenzyl)]-4-[(trimethylsilyl)methylene]pyrrolidine 133 (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of the Diels-Alder adduct of (3Z,4Z)-di-O-methyl-3-methylene-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of the Diels-Alder adduct of (3Z,4Z)-di-O-methyl-3-methylene-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate (CDCl$_3$, 125 MHz).
\(^1\)H NMR spectrum of the Diels-Alder adduct of (3Z,4Z)-3-methylene-4-[(trimethylsilyl)-methylene]-1-tosylpyrroloidine (CDCl\(_3\), 500 MHz).
$^{13}$C NMR spectrum of the Diels-Alder adduct of (3Z,4Z)-3-methylene-4-[(trimethylsilyl)-methylene]-1-tosylpyrrolidine (CDCl$_3$, 125 MHz).
$^1$H NMR spectrum of (3Z,4Z)-di-O-methyl-3-[(tri-$n$-butylstannyl)methyleneoxide]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 137 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-di-O-methyl-3-[(tri-$n$-butylstannyl)methyleneoxide]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 137 (CDCl$_3$, 125 MHz).
$^{119}\text{Sn}$ NMR spectrum of (3Z,4Z)-di-O-methyl-3-[(tri-$n$-butylstannyl)methyleneoxide]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 137 (CDCl$_3$, 185 MHz).
$^1$H NMR spectrum of (3Z,4Z)-di-0-methyl-3-(chloromethylene)-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 138 (CDCl$_3$, 500 MHz).
$^{13}$C NMR spectrum of (3Z,4Z)-di-\(O\)-methyl-3-(chloromethylene)-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 138 (CDCl$_3$, 125 MHz).
APPENDIX B

SELECTED DYNAMIC NMR SPECTRA
Dynamic $^1$H NMR of (3Z,4Z)-3-[(tri-$n$-butylstanny) methylene]-4-[(trimethylsilyl) methylene]-1-tosyl-pyrrolidine 55 in CD$_2$Cl$_2$ (full spectrum, 500 MHz).

-17°C
-5°C
-27°C
-32°C
-38°C
-43°C
-49°C
-71°C
-76°C
-82°C
-93°C
Dynamic $^1$H NMR of (3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]-1-tosyl-pyrrolidine 55 in CD$_2$Cl$_2$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of (3Z,4Z)-di-O-methyl-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 in CD$_2$Cl$_2$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of (3Z,4Z)-di-O-methyl-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 in CD$_2$Cl$_2$ (carbomethoxy region, 500 MHz).
Dynamic $^1$H NMR of (3Z,4Z)-di-O-methyl-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 in CD$_2$Cl$_2$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of (3Z,4Z)-di-O-methyl-3-[(tr-i-n-butylstanny]methylene]-4-[(trime-thylsirel)methylene]cyclopentanedicarboxylate 56 in CDCl$_3$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of (3Z,4Z)-di-O-methyl-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 in CDCl$_3$ (carbomethoxy region, 500 MHz).
Dynamic $^1$H NMR of (3Z,4Z)-di-O-methyl-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 in CDCl$_3$ (methylene region, 500 MHz).
Dynamic $^{13}\text{C}$ NMR of (3Z,4Z)-di-O-methyl-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 in CDCl$_3$ (full spectrum, 125 MHz).
Dynamic $^{13}$C NMR of (3Z,4Z)-di-O-methyl-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 in CDCl$_3$ (carbonyl region, 125 MHz).
Dynamic $^{13}$C NMR of (3Z,4Z)-di-$O$-methyl-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanedicarboxylate 56 in CDCl$_3$ (40-60 ppm, 125 MHz).
Dynamic $^1$H NMR of $O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73 in CD$_2$Cl$_2$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of $O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73 in CD$_2$Cl$_2$ (methylene region, 500 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tri-\textit{n}-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73 (full spectrum, 125 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73 (olefinic region, 125 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 73 (methylene region, 125 MHz).
Dynamic $^1$H NMR of [(S)-α-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilylmethylene]cyclopentanecarboxylate 74 in CD$_2$Cl$_2$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of $[(S)$-$\alpha$-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 74 in CD$_2$Cl$_2$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of [(S)-$\alpha$-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 74 in CDCl$_3$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of [(S)-α-carbethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 74 in CDCl$_3$ (olefinic region, 500 MHz).
Dynamic $^1$H NMR of [(S)-α-carbethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilylmethylene]cyclopentanecarboxylate 74 in CDCl$_3$ (methylene region, 500 MHz).
Dynamic $^{13}$C NMR of [(S)-α-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 74 (full spectrum, 125 MHz).
Dynamic $^{13}$C NMR of [(S)-α-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-n-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 74 (carbonyl region, 125 MHz).

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**Diagram:**

- **67°C, C$_6$D$_6$:**
  - Peaks at specific chemical shifts.
- **25°C, CDCl$_3$:**
  - Peaks at specific chemical shifts.
- **-60°C, CD$_2$Cl$_2$:**
  - Peaks at specific chemical shifts.
Dynamic $^{13}$C NMR of [(S)-$\alpha$-carbomethoxyphenylmethyl]-$(3Z,4Z)$-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 74 (olefinic region, 125 MHz).
Dynamic $^{13}$C NMR of [(S)-α-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 74 (methylene region, 125 MHz).
Dynamic $^{13}$C NMR of [(S)-$\alpha$-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(trimethylsilyl)methylene]cyclopentanecarboxylate 74 (trimethylsilyl region, 125 MHz).
Dynamic $^1$H NMR of (3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-1-[(R)-($\alpha$-methylbenzy)]-4-[(trimethylsilyl)methylene]pyrrolidine 75 in CD$_3$OD (full spectrum, 500 MHz).
Dynamic $^1$H NMR of (3Z,4Z)-3-[(tri-$n$-butylstanny]methylen]e-1-[(R)-(α-methylbenzy1)]-4-[(trimethylsilyl)methylen]pyrrolidine 75 in CD$_3$OD (olefinic region, 500 MHz).
Dynamic $^1$H NMR of di-O-methyl-(3Z,4Z)-3-[(tri-n-butylstanny]methylen]e-4-[(triethylsilyl)methylen]cyclopentanedicarboxylate 86 in CDCl$_3$ (full spectrum, 500 MHz).
Dynamic $^{1}$H NMR of di-O-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(triethyl-silyl)methylene]cyclopentanedicarboxylate 86 in CDCl$_3$ (methylen region, 500 MHz).
Dynamic $^{13}$C NMR of di-$O$-methyl-(3\(Z\),4\(Z\))-3-[(tri-$n$-butylstanny)l)methylene]-4-[(tri-ethylsilyl)methylene]cyclopentanedicarboxylate 86 in CDCl$_3$ (full spectrum, 125 MHz).
Dynamic $^{13}$C NMR of di-O-methyl-(3Z,4Z)-3-[(tri-$n$-butylstannyl)methylene]-4-[(tri-ethylsilyl)methylene]cyclopentanedicarboxylate 86 in CDCl$_3$ (carbonyl region, 125 MHz).
Dynamic $^{13}$C NMR of di-\textit{O}-methyl-(3Z,4Z)-3-[(tri-\textit{n}-butylstannyl)methylene]-4-[(tri-\textit{ethyl}silyl)methylene]cyclopentanedicarboxylate 86 in CDCl$_3$ (carbomethoxy region, 125 MHz).
Dynamic $^1$H NMR of di-O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-n-butylstanny)l]methylenecyclopentanedicarboxylate 87 in CDCl$_3$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of di-\textit{O}-methyl-(3Z,4Z)-3-[(\textit{tert}-butyldimethylsilyl)methylene]-4-[(\textit{tri}-\textit{n}-butylstannyl)methylene]cyclopentanedicarboxylate \textbf{87} in CDCl$_3$ (carbomethoxy region, 500 MHz).

![NMR spectrum showing signals at various temperatures from -38°C to 50°C.](image-url)
Dynamic $^1$H NMR of di-O-methyl-(3Z,4Z)-3-[(tert-butyl(dimethyl)silyl)methylene]-4-[(tri-$n$-butylstannyl)methylene]cyclopentanedicarboxylate 87 in CDCl$_3$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of di-O-methyl-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(tri-n-butylstanny]methylene]cyclopentanedicarboxylate 87 in CDCl$_3$ (methylsilyl region, 500 MHz).
Dynamic $^{13}$C NMR of di-O-methyl-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(tri-n-butylstannyl)methylene]cyclopentanedicarboxylate 87 in CDCl$_3$ (full spectrum, 125 MHz).
Dynamic $^{13}\text{C}$ NMR of di-$O$-methyl-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(tri-$n$-butylstannyl)methylene]cyclopentanedicarboxylate 87 in CDCl$_3$ (40-60 ppm, 125 MHz).
Dynamic $^{13}\text{C}$ NMR of di-O-methyl-(3Z,4Z)-3-[(tert-butyl(dimethyl)silyl)methylene]-4-[(tri-n-butylstannyl)methylene]cyclopentanedicarboxylate 87 in CDCl$_3$ (methylsilyl region, 125 MHz).
Dynamic $^1$H NMR of di-$O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89 in CDCl$_3$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of di-\(\text{O}\)-methyl-(3Z,4Z)-3-[(\text{tert}-\text{butyldimethylsilyl})\text{methylen}]4-[(\text{triphenylstannyl})\text{methylen}]\text{cyclopentanedicarboxylate 89} \) in CDCl$_3$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of di-\text{-}O\text{-}methyl\text{-}(3Z,4Z)-3\text{\text{"{}}\text{-}(\text{tert}\text{-}butyldimethylsilyl)methylene\text{-}4\text{\text{"{}}\text{-}(\text{triphenylstannyl)}methylene\text{-}cyclopentanedicarboxylate 89 in CDCl}_3$ (carbomethoxy region, 500 MHz).
Dynamic $^1$H NMR of di-$O$-methyl-$(3Z,4Z)$-$3$-[(tert-butyldimethylsilyl)methylene]-$4$-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89 in CDCl$_3$ (methylsilyl region, 500 MHz).
Dynamic $^{13}$C NMR of di-O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstanny]methylene)cyclopentanedicarboxylate 89 in CDCl$_3$ (full spectrum, 125 MHz).
Dynamic $^{13}\text{C}$ NMR of di-$O$-methyl-(3Z,4Z)-3-$[(\text{tert-butyl}d$imethylsilyl)$methylene]-4-[(\text{triphenylstanny})methylene]cyclopentanedicarboxylate 89 in CDCl$_3$ (methylsilyl region, 125 MHz).
Dynamic $^{13}$C NMR of di-O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89 in CDCl$_3$ (carbomethoxy region, 125 MHz).
Dynamic $^{13}$C NMR of di-$O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanedicarboxylate 89 in CDCl$_3$ (carbonyl region, 125 MHz).
Dynamic $^1$H NMR of di-$O$-methyl-(3Z,4Z)-3-[(triphenylstannyl)methylene]-4-[(tri-$iso$-propylsilyl)methylene]cyclopentanedicarboxylate 90 in CD$_2$Cl$_2$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of di-\textit{O}-methyl-(3\textit{Z},4\textit{Z})-3-[(triphenylstannyln)methylene]-4-[(tri-\textit{iso}-propylsilyl)methylene]cyclopentanedicarboxylate 90 in CD$_2$Cl$_2$ (carbomethoxy region, 500 MHz).
Dynamic $^1$H NMR of di-O-methyl-(3Z,4Z)-3-[(triphenylstanny]methylene]-4-[(tri-iso-propylsilyl)methylene]cyclopentanedicarboxylate 90 in CD$_2$Cl$_2$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of di-\textit{O}-methyl-(3Z,4Z)-3-[(tri-phenylstannyl)methylene]-4-[(tri-\textit{iso}-propylsilyl)methylene]cyclopentanedicarboxylate 90 in CD$_2$Cl$_2$ (\textit{iso}-propylsilyl region, 500 MHz).
Dynamic $^1$H NMR of di-O-methyl-(3Z,4Z)-3-[(triphenylstanny)methylene]-4-[(tri-iso-propylsilyl)methylene]cyclopentanedicarboxylate 90 in CDCl$_3$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of di-$O$-methyl-(3Z,4Z)-3-[(triphenylstannylmethylene]-4-[(tri-iso-propylsilylmethylene]cyclopentanedicarboxylate 90 in CDCl$_3$ (carbomethoxy region, 500 MHz).
Dynamic $^1$H NMR of di-O-methyl-(3Z,4Z)-3-[(triphenylstannyl)methylene]-4-[(tri-isopropylsilyl)methylene]cyclopentanedicarboxylate 90 in CDCl$_3$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of di-O-methyl-(3Z,4Z)-3-[(triphenylstannyl)methylene]-4-[(tri-iso-propylsilyl)methylene]cyclopentanedicarboxylate 90 in CDCl$_3$ (iso-propylsilyl region, 500 MHz).
Dynamic $^{13}$C NMR of di-$O$-methyl-(3Z,4Z)-3-[(triphenylstanny)methylene]-4-[(tri-iso-propylsilyl)methylene]cyclopentanedicarboxylate 90 in CDCl$_3$ (full spectrum, 125 MHz).
Dynamic $^{13}\text{C}$ NMR of di-$O$-methyl-($3Z,4Z$)-3-[(triphenylstannyI)methylene]-4-[(tri-$iso$-propylsilyl)methylene]cyclopentanedicarboxylate 90 in CDCl$_3$ (carbonyl region, 125 MHz).
Dynamic $^{13}$C NMR of di-$O$-methyl-(3$Z$,4$Z$)-3-[(triphenylstanny1)methylene]-4-[(tri-$iso$-propylsilyl)methylene]cyclopentanedicarboxylate 90 in CDCl$_3$ ($iso$-propylsilyl region, 125 MHz).

![Diagram of molecule 90 with labeled atoms a to k and chemical shifts at 25°C and -71°C.]}
Dynamic $^{13}$C NMR of di-$O$-methyl-(3Z,4Z)-3-[(triphenylstanny)l]methylen]-4-[(tri-iso-propylsilyl)methylene]cyclopentanedicarboxylate 90 in CDCl$_3$ (carbomethoxy region, 125 MHz).
Dynamic $^1$H NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-n-butylstanny)lmethylene]cyclopentanecarboxylate 91 in CD$_2$Cl$_2$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of O-methyl-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(tri-$n$-butylstanny)lmethylene]cyclopentanecarboxylate 91 in CD$_2$Cl$_2$ (carbomethoxy region, 500 MHz).
Dynamic $^1$H NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-$n$-butylstannyl)methylene]cyclopentanecarboxylate 91 in CD$_2$Cl$_2$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-\textit{n}-butylstanny]methylene]cyclopentanecarboxylate 91 in CD$_2$Cl$_2$ (methylsilyl region, 500 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-$n$-butylstannyl)methylene]cyclopentanecarboxylate 91 (full spectrum, 125 MHz).
Dynamic $^{13}$C NMR of O-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-$n$-butylstannyl)methylene]cyclopentanecarboxylate 91 (carbonyl region, 125 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butylimethyldimethylsilyl)methylene]-4-[(tri-$n$-butylstannyl)methylene]cyclopentanecarboxylate 91 (olefinic region, 125 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-$n$-butylstannyl)methylene]cyclopentanecarboxylate 91 (methylene region, 125 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-$\{\text{(tert-butyl} \text{dimethyl}silyl)\text{methylene}\}$-4-$\{\text{(tri-n-butyl} \text{stanny}l)\text{methylene}\}$cyclopentanecarboxylate 91 (methylsilyl region, 125 MHz).
Dynamic $^1$H NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 92 in CDCl$_3$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(triphenylstanny1)methylene]cyclopentanecarboxylate 92 in CDCl₃ (5-5.5 ppm, 500 MHz).
Dynamic $^1$H NMR of $O$-methyl-$(3Z,4Z)$-3-[(tert-butyl(dimethyl)silyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate $92$ in CDCl$_3$ (carbomethoxy region, 500 MHz).
Dynamic $^1$H NMR of $O$-methyl-$(3Z,4Z)$-3-[$(t$-b$er$-butyldimethyl$silyl)methylene$]4-[$(tr$-phenylstannyl)methylene$]cyclopentanecarboxylate 92 in CDCl$_3$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphénylstannyl)methylene]cyclopentanecarboxylate 92 in CDCl$_3$ (tert-butylsilyl region, 500 MHz).
Dynamic $^1$H NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-phenylstannyl)methylene]cyclopentanecarboxylate 92 in CDCl$_3$ (methylsilyl region, 500 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-phenylstanny)methylene]cyclopentanecarboxylate 92 in CDCl$_3$ (full spectrum, 125 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 92 in CDCl$_3$ (methylsilyl region, 125 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-phenylstannyl)methylene]cyclopentanecarboxylate 92 in CDCl$_3$ (methylene region, 125 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 92 in CDCl$_3$ ( tert-butylsilyl region, 125 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 92 in CDCl$_3$ (olefinic region, 125 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-$(3Z,4Z)-3-[(\text{tert-butyldimethylsilyl})\text{methylene}]-4-[(\text{triphenylstannyl})\text{methylene}]\text{cyclopentanecarboxylate}$ 92 in CDCl$_3$ (150-180 ppm, 125 MHz).
Dynamic $^{13}$C NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-phenylstannyl)methylene]cyclopentanecarboxylate 92 in CDCl$_3$ (aromatic region, 125 MHz).
Dynamic $^{119}$Sn NMR of $O$-methyl-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(tri-phenylstannyldimethylsilyl)methylene]cyclopentane carboxylate 92 in CDCl$_3$ (185 MHz).
Dynamic $^1$H NMR of $[(S)-\alpha$-carbomethoxyphenylmethyl]-(3Z,4Z)-3-([tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 93 in CDCl$_3$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of [(S)-α-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 93 in CDCl$_3$ (olefinic region, 500 MHz).
Dynamic $^1$H NMR of [(S)-$\alpha$-carbethoxyphenylmethyl]-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstanny)methylene]cyclopentanecarboxylate 93 in CDCl$_3$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of $[(S)$-α-carbomethoxyphenylmethyl$]-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]$cyclopentanecarboxylate 93 in CDCl$_3$ (methylsilyl region, 500 MHz).
Dynamic $^{13}$C NMR of [(S)-α-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tert-butylidimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 93 in CDCl₃ (full spectrum, 125 MHz).
Dynamic $^{13}$C NMR of [(S)-α-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 93 in CDCl$_3$ (methylsilyl region, 125 MHz).
Dynamic $^{13}$C NMR of [($S$-α-carbomethoxyphenylmethyl)-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyln)methylene]cyclopentanecarboxylate 93 in CDCl$_3$ (carbonyl region, 125 MHz).
Dynamic $^{119}$Sn NMR of [(S)-α-carbomethoxyphenylmethyl]-(3Z,4Z)-3-[(tert-butyldimethylsilyl)methylene]-4-[(triphenylstannyl)methylene]cyclopentanecarboxylate 93 in CDCl$_3$ (185 MHz).
Dynamic $^1$H NMR of $(3E,4E)-3-[\text{((tert-butyl)methylsilyl)methylene}]\cdot1-[\text{(R-$\alpha$-methylbenzyl)}\cdot4-[\text{((tri-$n$-butylstannyl)methylene}]\text{pyrrolidine 95 in CD}_2\text{Cl}_2$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(tri-$n$-butylstannyl)methylene]pyrroolidine 95 in CD$_2$Cl$_2$ (olefinic region, 500 MHz).
Dynamic $^1$H NMR of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(tri-$n$-butylstannyl)methylene]pyrrolidine 95 in CD$_2$Cl$_2$ (methylene region, 500 MHz).
Dynamic $^{13}\text{C}$ NMR of $\text{(3E,4E)-3-[(\text{tert-butyldimethylsilyl})\text{methylene}-1-[(\text{R-}\alpha\text{-methylbenzyl})-4-[(\text{tri-}\text{n-butyllstannyl})\text{methylene}]\text{pyrroline}} \, 95 \) (full spectrum, 125 MHz).
Dynamic $^{13}$C NMR of $(3E,4E)$-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-$\alpha$-methylbenzyl]-4-[(tri-$n$-butylstannyl)methylene]pyrrolidine 95 (olefinic region, 125 MHz).
Dynamic $^{13}$C NMR of ($3E,4E$)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-$\alpha$-methylbenzyl]-4-[(tri-$n$-butylstannyl)methylene]pyrrolidine 95 (methylsilyl region, 125 MHz).
Dynamic $^1$H NMR of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(triphenylstannyl)methylene]pyrrolidine 96 in CD$_2$Cl$_2$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of (3$E$,4$E$)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-$\alpha$-methylbenzyl]-4-[(triphenylstannyl)methylene]pyrrolidine 96 in CD$_2$Cl$_2$ (olefinic region, 500 MHz).
Dynamic $^1$H NMR of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(triphenylstanny]methylene]pyrrolidine 96 in CD$_2$Cl$_2$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of $(3E,4E)$-3-[(tert-butyldimethylsilyl)methylene]-1-[(R)-α-methylbenzyl]-4-[(triphenylstanny)methylene]pyrrolidine 96 in CD$_2$Cl$_2$ (methylsilyl region, 500 MHz).
Dynamic $^1$H NMR of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[(S)-α-methylbenzyl]-4-[(trimethylstannyl)methylene]pyrrolidine 97 in CD$_3$OD (full spectrum, 500 MHz).
Dynamic $^1$H NMR of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[(S)-$\alpha$-methylbenzyl]-4-[(trimethylstannyl)methylene]pyrrolidine 97 in CD$_3$OD (methylene region, 500 MHz).
Dynamic $^1$H NMR of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[tosyl]-4-[(triphenylstannyl)methylene]pyrrolidine 98 in CD$_2$Cl$_2$ (full spectrum, 500 MHz).
Dynamic $^1$H NMR of (3\textit{E},4\textit{E})-3-[(\textit{tert}-butyldimethylsilyl)methylene]-1-[tosyl]-4-[(triphenylstannyl)methylene]pyrrolidine 98 in CD$_2$Cl$_2$ (methylene region, 500 MHz).
Dynamic $^1$H NMR of $(3E,4E)$-3-[(tert-butyldimethylsilyl)methylene]-1-[tosyl]-4-[(triphenylstannyl)methylene]pyrrolidine $98$ in CD$_2$Cl$_2$ (methylsilyl region, 500 MHz).
Dynamic $^{13}$C NMR of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[tosyl]-4-[(triphenylstannyln)methylene]pyrrolidine 98 (full spectrum, 125 MHz).
Dynamic $^{13}$C NMR of (3E,4E)-3-[(tert-butyldimethylsilyl)methylene]-1-[tosyl]-4-[(triphenylstannylo)methylene]pyrrolidine 98 (methylsilyl region, 125 MHz).
Dynamic $^1$H NMR of (3$E,4E$)-3-{[(tri-$n$-butylstannyl)methylene]-1-methyl-1-[(R)-$\alpha$-methylbenzyl]-4-{[(trimethylsilyl)methylene]pyrrolidinium trifluoromethanesulfonate 116 in CD$_3$OD (full spectrum, 500 MHz).
Dynamic $^1$H NMR of (3E,4E)-3-[(tri-$n$-butylstannyl)methylene]-1-methyl-1-[(R)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium trifluoromethanesulfonate 116 in CD$_3$OD (olefinic region, 500 MHz).
Dynamic $^1$H NMR of $\text{3(E,E)-3-[(tri-n-butylstannyl)methylene]-1-methyl-1-[(R)-\alpha\text{-methylbenzyl}]-4-[(trimethylsilyl)methylene]pyrrolidinium trifluoromethanesulfonate}$ 116 in CD$_3$OD (methylene region, 500 MHz).
Dynamic $^{119}\text{Sn}$ NMR of $(3E,4E)$-3-[(tri-$n$-butylstannyl)methylene]-1-methyl-1-[(R)-$\alpha$-methylbenzyl]-4-[(trimethylsilyl)methylene]pyrrolidinium trifluoromethanesulfonate 116 in CD$_3$OD (185 MHz).