December 2015

Ruthenium-Catalyzed Transformations for the Synthesis of Conjugated Dienes

Lauren Kaminsky
Syracuse University

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Abstract

A general description of transition metal catalysis of alkynes and alkenes for the formation of conjugated dienes is briefly discussed. Specifically, a synopsis of ruthenium-hydride catalysis for the formation of 1,3-dienes is presented.

The development of the trans-silylvinylation of internal alkynes with acrylates and vinyl boronates to form conjugated dienes is discussed. This transformation was accomplished via a recently developed tandem silylative coupling using RuHCl(CO)(PCy3)2. The reaction optimization, mechanistic hypothesis and substrate scope for the coupling with acrylates and vinyl boronates is described. The vinyl boronate scope and alkyne scope is presented, in addition to the selective derivatization of the boronate moiety. The synthesis of a chiral silicon-tethered alkyne is described and its application toward a stereo- and enantioselective chiral conjugated diene utilizing the aforementioned methodology was accomplished and is discussed herein.

The development of an intramolecular trans-silylvinylation of internal alkynes catalyzed by RuHCl(CO)(H2IMes)(PPh3) with methyl vinyl ketone (MVK) additive is discussed. The substrate scope of the reaction provided five-, six-, and seven-membered oxasilacycles. The ruthenium-hydride catalyzed trans-silylvinylation of internal alkynes under an atmosphere of ethylene gas is discussed. This methodology improved upon the reactivity of the starting alkynes and upon the selectivity of the diene products formed from the previous transformations with MVK additive. Reversal of Z/E selectivity can be obtained with increased pressures of ethylene gas. Further functionalization of the diene products to form more diverse scaffolds is described.
Lastly, the cycloisomerization of silicon-tethered 1,7-enynes to form 1,3-dienes utilizing catalytic Cp’Ru(COD)Cl is described herein. The reaction optimization, mechanistic hypothesis, substrate tolerance and synthetic utility is discussed. The question of whether a silicon atom is required in the tether of the starting enyne for the reaction to proceed is addressed.
Ruthenium-Catalyzed Transformations for the Synthesis of Conjugated Dienes

by

Lauren Kaminsky

B.S. Chemistry, York College of Pennsylvania, 2010

Dissertation

Submitted in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy in Chemistry

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<td>chemical shift in parts per million</td>
<td>conv</td>
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<td>µ</td>
<td>micro</td>
<td>COSY</td>
<td>correlated spectroscopy</td>
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<td>Ts</td>
<td>p-toluenesulfonyl</td>
</tr>
<tr>
<td>Xyl</td>
<td>xylyl</td>
</tr>
</tbody>
</table>
PREFACE

This thesis has been adapted from the following published articles co-written by the author:


1.0 INTRODUCTION

Transition metal-catalyzed coupling reactions between alkynes and alkenes are useful synthetic protocols for the formation of conjugated dienes. Conjugated dienes are of great importance due to their prevalence in a variety of natural products that possess a wide array of biological activity, including those shown in Figure 1.

![Figure 1. Select diene-containing natural products](image_url)

However, one of the drawbacks of utilizing transition metals to form dienes is the need for one or both of the coupling partners to be activated before the coupling can occur (Scheme 1).
Scheme 1. Classic cross-couplings for formation of dienes

Generally, one coupling partner is functionalized with a metal or metalloid species (i.e. boron, tin, silicon; compound 1) and the other (compound 2) a halogen (bromine, chlorine) or pseudo-halogen (triflate, tosylate). In many cases one or both of the activated olefin coupling partners are derived from alkynes. The use of a metal-hydride catalyst to facilitate the formation of conjugated dienes is of particular interest as it could potentially eliminate the need for intermediate activated cross-coupling partners shown in Scheme 1. Development of a methodology that does not require functionalization of the olefin and/or alkyne is of great importance because it increases efficiency and eliminates the need for intermediates that can generate toxic by-products.

The use of ruthenium catalysts to couple alkenes and alkynes is a reliable method for carbon-carbon bond formation. Such methods can lead to the formation of complex diene systems and furthermore, polyketide synthesis. An advantage of utilizing ruthenium is that there is no need for pre-activation of the alkyne and olefin coupling partner. Such ruthenium-catalyzed reactions can be classified as four major groups based on mechanistic identity: metallocycles (Alder-Ene/cycloisomerization), C-H activation, vinyl carbenes and the least explored, ruthenium hydrides.

The first reported use of ruthenium to form diene systems via a ruthenium hydride intermediate was by Watanabe et al. These researchers coupled acetylenes (4) and alkenes (5)
to give dienes (6) with high levels of regioselectivity in good yields (Scheme 2, eq. 1). This methodology worked well with internal alkynes but gave poor yields when terminal alkynes (7) were used (Scheme 2, eq. 2). In addition, high catalyst loadings (25 mol%) were required for complete conversion of the starting alkynes.

Scheme 2. Ru(cod)(cot)-catalyzed intermolecular coupling of alkynes and olefins

The researchers proposed that the coupling of acetylenes with electron withdrawing olefins proceeded via a ruthenacyclopentene intermediate (Scheme 3).

Scheme 3. Mechanistic rationale
Coordination of alkyne 10 and alkene 11 with a zero-valent ruthenium complex yields ruthenacyclopentene 13, which undergoes β-hydride elimination to give vinyl ruthenium hydride 14. Reductive elimination of 14 yields the product diene 12.

The hydrovinylation of alkynes (15) catalyzed by a cationic-alkylidene ruthenium complex is known to give diene scaffolds (17) in good yields (Scheme 4). These conditions tolerate a variety of substituents on the alkyne terminus, including aryl, alkyl and alcohol functionality.

Scheme 4. Hydrovinylation of alkynes with ethylene

Yi et al. proposed the hydrovinylation of alkynes as follows (Scheme 5): Deprotonation of the δ-methyl group of the initial cationic ruthenium complex and elimination of Cy3PH+BF4- and the triene, followed by coordination of alkyne 15 generated ruthenium intermediate 18. Alkyne insertion and olefin coordination gave intermediate 19. Subsequent olefin (ethylene) insertion (20) yielded ruthenium hydride 21, which underwent β-hydride elimination to yield the diene product 17.
Scheme 5. Mechanistic hypothesis for the hydrovinylation of alkynes

The first intramolecular cyclization of enynes (22) to give 1,3-dienes (23) using catalytic RuHCl(CO)(PPh3)3 was accomplished by Mori's group (Scheme 6).1 The cyclization proceeded in one hour and gave fair to good yields of the cyclopentene derivatives. However, the scope of investigation was somewhat limited because only aromatic groups on the alkyne terminus were investigated.
Mori et al. envisioned the reaction mechanism as follows (Scheme 7): Hydoruthenation (cis addition) of enyne 22 generates vinyl ruthenium 24, which isomerizes to vinyl ruthenium complex 26 via the dipolar intermediate 25. Subsequent intramolecular olefin insertion yields cyclopentene 27, which subsequently undergoes trans β-hydride elimination to yield diene product 23.
Scheme 7. Mechanistic proposal for the intramolecular cyclization of enynes

The Mori group later extended the methodology using Murai’s catalyst to include the preparation of heterocycles and utilized it for the synthesis of Carbapenam skeletons (Scheme 8). This process was useful in the fact that they obtained the desired products, but complete conversion of the starting enynes was not achieved resulting in poor to average yields.

Scheme 8. Intramolecular cyclization to afford Carbapenam skeletons
Alternatively, intermolecular couplings of alkynes with vinyl boronates in the presence of ruthenium hydride RuHCl(CO)(PCy₃)₂ (32) has been explored by Marciniec (Table 1).²⁰ Although one regioisomer was generated, stereocontrol was problematic with only isomers A and B isolated. In addition, only terminal alkynes were utilized, providing minimal functionality on the diene scaffold.

![Chemical reaction](image)

Table 1. Coupling of terminal alkynes with vinyl boronates

<table>
<thead>
<tr>
<th>R</th>
<th>A:B</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cy</td>
<td>83:15</td>
<td>74</td>
</tr>
<tr>
<td>SiEt₃</td>
<td>80:13</td>
<td>78</td>
</tr>
<tr>
<td>EtOTMS</td>
<td>84:16</td>
<td>66</td>
</tr>
<tr>
<td>TMSO</td>
<td>81:19</td>
<td>70</td>
</tr>
<tr>
<td>Hexyl</td>
<td>60:40</td>
<td>nd</td>
</tr>
</tbody>
</table>

This group believed the coupling to proceed as follows (Scheme 9): Dissociation of a phosphine ligand from ruthenium hydride 32 generates a highly reactive 14-electron complex 33.
Scheme 9. Mechanistic proposal for the coupling of alkynes with vinyl boronates

Subsequent cis-hydoruthenation of alkyne 30 generates vinyl ruthenium intermediate 34. Coordination (intermediate 35) and subsequent insertion of vinyl boronate 31 yields the boro-ruthenate species 36. β-Hydride elimination produces the dienyl boronate product and regenerates the active catalytic species.

More recently, Plietker’s group reported an intermolecular ruthenium-catalyzed hydrovinylation of alkynes to give 1,3-dienes (Scheme 10). The active catalytic species, RuH₂(CO)(PPh₃)₃, is generated in situ by treatment of catalytic sodium methoxide with DMF.
This methodology was tolerable to a wide variety of substrates, including terminal and internal alkynes with aromatic and alkyl functionality. In addition, acrylates and acrylamides proved to be superior olefin coupling partners. Despite the diverse substrate scope of the reaction, when unsymmetrical internal alkynes (such as 37) were used a mixture of stereo- and regioisomers (38A, 38B) was obtained (Scheme 11).

Further, the substitution patterns of the dienes formed are somewhat limited because the products must incorporate a hydrogen atom. In some cases, the regioselectivity of products could be controlled. For example, when a benzyl ether moiety was on the alkyne terminus (alkyne 39),
solely regioisomer 40A was observed (Scheme 12). It was proposed that the benzyl ether coordinates to the ruthenium, therefore preventing formation of regioisomer 40B.

![Scheme 12. Plietker's control of regioselectivity](image)

In conclusion, several groups have utilized catalytic ruthenium to couple alkynes with alkenes for the synthesis of conjugated dienes. Despite the synthetic utility, stereo- and regiocontrol of the diene products was problematic. In addition, mandatory incorporation of a hydrogen atom on the diene scaffold was required, hence limiting the diversity on the diene backbone. In one case reported by Plietker, a benzyl ether moiety at the propargylic position of the alkyne controlled the regioselectivity of the reaction.

### 1.1 INTRAMOLECULAR APPROACH: USE OF A VINYL SILICON TETHER

Typically, hydrometallations to form diene scaffolds require mandatory hydrogen incorporation into the product and also give a mixture of stereo- and regioisomers. To alleviate
mandatory hydrogen incorporation and regioselectivity issues that arose from such methods, the Clark group envisioned utilizing an intramolecular approach that relied on the use of a vinyl silicon tether (Scheme 13). Replacing a hydrogen atom with a silicon atom would provide for a more diverse diene scaffold and hence, would eliminate the need for mandatory incorporation of hydrogen.

![Scheme 13. Vinyl silicon tether approach](image)

To initiate these studies, it was envisioned that the silicon-tethered alkyne 41 could be used to direct the ruthenium species towards the pendent alkyne 42 to obtain the desired regioisomer 43. At the time, the 43-cis addition isomer was expected to be favored due to the literature precedence of cis-hydroruthenations of alkynes (as discussed in Chapter 1), but we did not ignore the possibility for the formation of the 43-trans isomer.

The use of a vinyl silicon tether to control regioselectivity has been reported by Tomooka, as shown in Scheme 14. The researchers utilized a dimethylvinylsilicon "directing group" to obtain regiocontrol of a platinum-catalyzed hydrosilylation of unsymmetrical alkynes.
As depicted in Scheme 14, the platinum complex coordinates to the dimethylvinylsilicon group (A and B), which allows for the favorable formation of the proximal hydrosilylated product 45a. The substrate scope of the directing group controlled hydrosilylation included propargyl, homopropargyl, and bis-homopropargylic silanes. This methodology is somewhat different to the Clark group's reaction design due to the fact that they utilized the directing group for sole formation of silyl-alkenes. In addition, a mandatory hydrogen atom was incorporated. The Clark group's directing group strategy allowed for the regioselective formation of a tetra-substituted double bond and an oxasilacycle is formed in the process.
1.2 **TRANS-SILYL VINYLATION OF ALKYNES WITH ACRYLATES**

1.2.1 Previous work from the Clark group\(^{26}\)

Studies began with alkyne \(^{41}\)\(^{26}\) and L-menthyl acrylate in refluxing DCE with catalytic RuHCl(CO)(PC\(_3\))\(_2\).\(^{27}\) L-menthyl acrylate was chosen as the olefinic coupling partner because of its ease to synthesize in the laboratory in addition to its visibility by thin layer chromatography. A single diene isomer \(^{47}\) was observed in 56% yield by \(^1\)H NMR (Scheme 15). Ethylene and a small amount of the acrylate dimer \(^{48}\) were the only visible by-products of the reaction observed by \(^1\)H NMR.

![Scheme 15. Initial studies of the intermolecular coupling\(^a\)](image)

\(^a\) Reaction run by Shasha Liu.

Further analysis of the product by 1D and 2D NMR allowed Dr. Liu to determine the stereochemical outcome. Using NOESY NMR experiments, a strong correlation between the proton β to the acrylate moiety and the diastereotopic protons of the five-membered oxasilacycle allowed them to conclude the stereochemical outcome of the transformation (Figure 2, \(^{47A}\)). Dr.
Liu did not observe an nOe correlation between the β-proton and methyl protons attached to the silicon (47B).

![Figure 2. Stereochemical outcome](image)

Dr. Liu did not expect to observe the *trans*-addition isomer 47A due to the literature precedence of ruthenium-catalyzed diene formation occurring via a *cis*-metallation pathway. However, the researchers were intrigued by the unexpected product outcome. A discussion of *trans*-functionalization of alkynes will follow after the mechanistic hypothesis is explained.

### 1.2.2 Mechanistic hypothesis

It is believed by the researchers that the transformation proceeds as follows (Scheme 16): Dissociation of a phosphine ligand from 32 gives a highly reactive 14-electron ruthenium complex 33, which upon reaction with the silicon-tethered alkyne 41, adds at the sterically most accessible (terminal) position of the vinyl moiety to give intermediate 49.
β-Silyl transfer and subsequent loss of ethylene results in formation of silyl-ruthenium intermediate 42. The transformation from 42 to 43 can proceed via direct trans silyl-ruthenation (see section 2.2.3 for literature precedence) or by a cis silyl-ruthenation pathway to give intermediate 43-cis followed by isomerization to generate 43-trans. The isomerization is proposed to proceed via a vinylidene-type intermediate 43A (favorable due to the charge stability by the silicon atom). Intermolecular olefin insertion (acrylate 46) at the most sterically accessible
position of the alkene yields 50, which subsequently undergoes β-hydride elimination to give the desired diene 47A. Upon formation of 47A, ruthenium hydride complex 33 is regenerated.

1.2.3 Trans-functionalization of alkynes

Metal catalyzed trans-functionalization of alkynes is known in the literature but is quite rare. Fu and Tanaka reported on the trans-hydroacylation of alkynes to give cyclopentenones using cationic rhodium (Scheme 17). Oxidative addition of the aldehyde 51 carbon-hydrogen bond to a rhodium (I) complex yields a rhodium (III) acyl hydride 52. Next, the rhodium hydride adds in a trans fashion to the coordinated alkyne to generate a rhodium metalacyclohexene 53. Reductive elimination of 53 yields the cyclopentenone 54 and regenerates the active rhodium (I) species.

Scheme 17. Fu's hydroacylation of alkynes
Yamamoto and co-workers reported on the Lewis acid-catalyzed intramolecular *trans*-hydrosilylation, *trans*-vinylsilylation and *trans*-arylsilylation of unactivated alkynes (Scheme 18). Intramolecular *trans*-silylvinylation is observed with catalytic AlCl₃ via coordination of the aluminum to the alkyne and intramolecular attack of a hydride from the hydrosilane on the electron-deficient sp carbon opposite of the Lewis acid (aluminum). This pathway is also observed by the Yamamoto group with the aluminum-catalyzed *trans*-silylvinylation of alkynes. The intramolecular attack by the silane moiety on the electron deficient alkyne occurs on the opposite side to the Lewis acid.

![Scheme 18. Yamamoto's trans-functionalization of alkynes](image)

Trost and co-workers have reported on the inter- (Scheme 19, eq. 1) and intramolecular (Scheme 19, eq. 2) ruthenium catalyzed *trans*-hydrosilylation of alkynes. They also conducted a deuterium labeling experiment to verify the *trans*-addition pathway (Scheme 19, eq. 3). Reaction of the alkyne with triethylsilane-\(d\) and a cationic ruthenium complex gave a single
product with 100% deuterium incorporation at the *trans* vinyl position. They noted that they were able to assign this by $^1$H NMR because the *trans* and *cis* vinyl protons relative to silicon are quite distinct in chemical shift (*trans* $\delta$ 5.65-5.75, *cis* $\delta$ 5.28-5.37).

\[
\text{Scheme 19. Trost's ruthenium catalyzed *trans*-hydrosilylation of alkynes}
\]

Lastly, Denmark utilized catalytic $[\text{RuCl}_2(\text{benzene})]_2$ for an intramolecular *trans*-hydrosilylation of alkynes (Scheme 20).\(^{38}\) Denmark was able to isolate exo-type products, whereas typically endo-type products are observed in *trans*-hydrosilylation protocols (as seen by Yamamoto).

\[
\text{Scheme 20. Denmark's conditions for formation of oxasilacycles}
\]
After examination of the few examples in the literature of direct trans-addition/functionalization of alkynes, it is important to recall that the Clark group's observation of trans-addition products is believed to originate from a different mechanistic pathway. The formation of the unique trans-addition products is postulated to occur from a cis-addition of the ruthenium metal to the alkyne followed by isomerization.

1.2.4 Previous work from the Clark group: reaction optimization and scope

With a promising result from the initial studies (Scheme 15), a solvent screen was conducted and DCE at 85°C proved to be superior reaction conditions. Additional metal hydride complexes were examined and RuHCl(CO)(PCy$_3$)$_2$ proved the most effective. After those conditions were established, the olefin coupling partner was examined (Table 2).

![Scheme 15](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>55%</td>
</tr>
<tr>
<td>2</td>
<td>Et</td>
<td>54%</td>
</tr>
<tr>
<td>3</td>
<td>nBu</td>
<td>51%</td>
</tr>
<tr>
<td>4</td>
<td>tBu</td>
<td>58%</td>
</tr>
<tr>
<td>5</td>
<td>isobornyl</td>
<td>73%</td>
</tr>
<tr>
<td>6</td>
<td>CH$_2$-biphenyl</td>
<td>79%</td>
</tr>
<tr>
<td>7</td>
<td>L-menthol</td>
<td>70%</td>
</tr>
</tbody>
</table>

Table 2. Olefin coupling partner scope$^a$

$^a$ All reactions performed by Shasha Liu and/or Jinbo Zhao.
Alkyl-substituted acrylates (entries 1-4) gave the desired diene products in modest yields of 51%-58%. Bulkier acrylates proved to work best in the reaction (entries 5-7) and a significant improvement in product yield was obtained with 70%-79% isolated yields, respectively. The authors were pleased to discover that biphenyl acrylate (entry 6) gave the desired diene as a crystalline solid. The chemical structure of the diene product observed from this transformation was further verified with X-Ray Crystallography.

L-Menthyl acrylate was chosen as the olefin coupling partner to explore the alkyne scope. With a phenyl group at the alkyne terminus, substitution at R₁ and R₂ was examined (Table 3). Alkyl substitution (entries 1-3), including an n-heptyl chain and the bulky cyclohexane ring, was well tolerated, giving the desired products in good yields of 72%-77%. Aromatic substitution was also tolerated (entries 4-7) and worked best in refluxing toluene, resulting in 65%-69% yields of the products. Use of a chiral alkyne worked well to give the product as one isomer with no racemization (entry 5).
Table 3. Phenyl-substituted alkyne scope\textsuperscript{a}

\textsuperscript{a} All reactions performed by Shasha Liu and/or Jinbo Zhao.\textsuperscript{b} Reaction conducted in toluene at 110°C.\textsuperscript{c} Biphenyl acrylate was used as the olefinic coupling partner.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne</th>
<th>(R_1)</th>
<th>(R_2)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55</td>
<td>H</td>
<td>(\text{C}_7\text{H}_5)</td>
<td>77%</td>
</tr>
<tr>
<td>2</td>
<td>56</td>
<td>H</td>
<td>((\text{CH}_2)_2\text{Ph})</td>
<td>72%</td>
</tr>
<tr>
<td>3</td>
<td>57</td>
<td>H</td>
<td>(\text{Cy})</td>
<td>75%</td>
</tr>
<tr>
<td>4\textsuperscript{a}</td>
<td>58</td>
<td>H</td>
<td>(\text{Ph})</td>
<td>69%</td>
</tr>
<tr>
<td>5\textsuperscript{b}</td>
<td>59</td>
<td>H</td>
<td>((R)_\text{Ph})</td>
<td>65%</td>
</tr>
<tr>
<td>6\textsuperscript{b,c}</td>
<td>60</td>
<td>H</td>
<td>4-\text{NO}_2\text{Ph}</td>
<td>68%</td>
</tr>
<tr>
<td>7\textsuperscript{c}</td>
<td>61</td>
<td>H</td>
<td>4-\text{Ph-Ph}</td>
<td>68%</td>
</tr>
<tr>
<td>8</td>
<td>62</td>
<td>\text{Ph}</td>
<td>\text{Me}</td>
<td>83%</td>
</tr>
<tr>
<td>9</td>
<td>63</td>
<td>(R_2) = ((\text{CH}_2)_3)</td>
<td>92%</td>
<td></td>
</tr>
</tbody>
</table>

Other aromatic substituents, such as 4-nitrophenyl and \(p\)-biphenyl (entries 6 and 7), worked best with the biphenyl acrylate coupling partner in refluxing toluene and gave the dienes in 68% yield. Increasing the Thorpe-Ingold effect\textsuperscript{39} at the homo-propargylic position (entries 8 and 9) gave excellent product yields of 83% and 92%, respectively.

Varying the aromatic substituent at the alkyne terminus, additional alkyne substrates were examined (Table 4). The inductively withdrawing 4-fluorophenyl alkyne (entry 1) gave the resulting diene in 60% yield. The electron-donating 4-methoxyphenyl substituent (entry 2) was well tolerated in the reaction and gave the product in 73% yield. Lastly, tolyl and 3,5-xylyl substitution (entries 3 and 4) performed well and gave good yields of the products.
The use of alkyl-substituents at the alkyne terminus initially seemed problematic. Dr. Liu and Dr. Zhao focused on utilizing methyl-substituted alkynes due to the resulting diene products being more common in natural product scaffolds. The standard reaction conditions used for aromatic alkyne substitution (5 mol% \( \text{RuHCl(CO)(PCy}_3 \text{)}_2 \) and 2 equivalents of menthyl acrylate) resulted in poor yields of the desired products. Increasing the catalyst loading of \( \text{RuHCl(CO)(PCy}_3 \text{)}_2 \) to 10 mol% improved upon the product yield. However, it was also hypothesized that poor product yields could be derived from β-hydride elimination of intermediate 43. They envisioned that increasing the amount of acrylate concentration in the reaction mixture could circumvent β-hydride elimination and favor acrylate incorporation to give the product. Using methyl-substituted alkyne 68, an easy to handle and non-volatile starting material, subjection with 10 mol% of \( \text{RuHCl(CO)(PCy}_3 \text{)}_2 \) and 5 equivalents of alkyl-substituted acrylates proved to be most effective (Table 5). A benefit for the use of lower-boiling acrylates is the ease of removal from the reaction mixture prior to product isolation. Subjection of alkyne 68

\[
\text{Entry} \quad \text{Alkyne} \quad \text{Ar} \quad \text{Yield}
\begin{array}{ccc}
1 & 64 & 4-F & 60 \\
2 & 65 & 4-MeO & 73 \\
3 & 66 & 4-Me & 74 \\
4 & 67 & 3,5-Xyl & 74 \\
\end{array}
\]
to the conditions shown in Table 5 gave the desired diene in 61% yield (entry 1). However, formation of the inseparable Z isomer was also observed.

![Chemical Reaction Diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Yield % (E:Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>61 (7.4:1)</td>
</tr>
<tr>
<td>2</td>
<td>Et</td>
<td>75 (7.5:1)</td>
</tr>
<tr>
<td>3</td>
<td>tBu</td>
<td>64 (6.3:1)</td>
</tr>
</tbody>
</table>

Table 5. Methyl-substituted alkyne scope\(^a\)

\(^a\) All reactions performed by Shasha Liu and/or Jinbo Zhao

Switching from methyl acrylate to the slightly less volatile ethyl acrylate improved the product yield to 75% with the E:Z ratio remaining the same (entry 2). The bulkier t-butyl acrylate also allowed for 64% isolated yield of the diene product but with a slightly diminished E:Z ratio of 6.3:1 (entry 3).

In conclusion, a novel ruthenium hydride-catalyzed trans-silylvinylation of silicon-tethered alkynes with acrylates protocol was demonstrated by Dr. Clark and co-workers. The diene products possessed a tetra-substituted double bond and a silicon atom, which allowed for further diversity in the backbone. A variety of silicon-tethered alkynes were demonstrated, including aryl and alkyl substitution at the alkyne terminus and homopropargylic position. In addition, numerous acrylate coupling partners performed well, including the bulky L-menthol acrylate and the lower boiling methyl acrylate.
2.0 THE TRANS-SILYLVINYLATION OF INTERNAL ALKYNES WITH ACRYLATES AND VINYL BORONATES

2.1 TRANS-SILYLVINYLATION OF ALKYNES WITH ACRYLATES

2.1.1 Results: synthesis of chiral, methyl-substituted alkyne 77

It was desired to extend the aforementioned methodology by expanding the alkyne scope to further mimic such backbones present in diene-containing natural products. This extension would include introduction of chirality, functionality at the propargylic position (Figure 3, position 2) and further tolerance of alkyl functionality on the alkyne terminus. At the outset of this project, the focus was synthesizing an alkyne that would include such characteristics and where product volatility would not be an issue. Inclusion of an aromatic-type moiety in the target molecule was desired in hopes of eliminating the possibility of volatility and therefore allowing for ease of handling and purification (Figure 3, target).
To begin the synthesis (Scheme 21), commercially available L-phenylalanine was reduced via an iodine-mediated sodium borohydride reduction to give L-phenylalanol 69 in 61% yield. This reaction was performed on 605 mmol (100 g) of the starting amino acid. Protection of 69 via the literature protocol using diethyl carbonate and potassium carbonate afforded oxazolidinone 70 in 85% yield. Subsequent acylation with nBuLi and propionyl chloride via the known literature protocol afforded acylated oxazolidinone 71 in an excellent yield of 94%. Originally, use of the Evans’ syn aldol protocol was planned as a means of obtaining our desired substrate 72. However, after freshly preparing dibutylboron triflate and subjecting oxazolidinone 71 to the Evans’ aldol conditions, the aldol adduct 72 was difficult to isolate due to poor conversion of the starting material. Poor yields of 72 (39%-56%) were obtained (in comparison to 93% reported in the literature). Numerous attempts were made to circumvent those issues, including: multiple distillations of benzaldehyde, multiple distillations of the freshly prepared dibutylboron triflate, use of commercial dibutylboron triflate and and use of freshly distilled reaction solvent. Those methods did not alleviate the reaction conversion and poor yields of 72 were still observed. A yield of 62% was obtained only once and occurred when the reaction was performed on a small scale (4 mmol of 71). However, such a small scale was not practical at such an early stage of our synthetic route.
At a later date the method developed by Crimmins\textsuperscript{45} (TiCl\textsubscript{4}, DIPEA, NMP) was employed to improve reaction conversion and yield of 72. Full conversion of the starting material was observed and 72 was obtained in 89% yield (d.r. 33:1). Synthesis of Weinreb amide 73 was accomplished using a modified literature protocol\textsuperscript{46} in an excellent yield of 88% (over two steps). Initially, Grignard addition into amide 73 using a solution of ethyl magnesium bromide (prepared from reagent grade magnesium turnings) was sluggish and required large amounts (3-5 equivalents) of the Grignard reagent. To resolve this issue, a fresh solution of ethyl magnesium bromide was made by mechanical activation of magnesium turnings following the procedure of Brown \textit{et al.}\textsuperscript{47} The protocol of mechanically activating the magnesium turnings via vigorous
stirring for 1-2 days provided finely dispersed/ground magnesium, which in turn formed a highly reactive Grignard reagent. Using this "super activated" Grignard reagent resulted in much shorter reaction times and full consumption of the starting material. Furthermore, ethyl ketone 74 was obtained in 85% yield. Formation of enol triflate 75 was attempted with LDA and McMurry’s reagent 48 (Figure 4) but gave poor reaction conversion and very low yields of product (14%-18%).

![McMurry's reagent and Comins' reagent](image)

**Figure 4. Triflating reagents**

Use of triflic anhydride resulted in decomposition of starting material. A third triflating reagent, Comins’ reagent (Figure 4), prepared by the literature procedure 49 and in combination with KHMD gave enol triflate 75 in improved yields. It was further discovered that slow addition of the base 50 resulted in full conversion and gave the product in 60% isolated yield. NOESY data was used to confirm the isomer formed during triflation (Figure 5).

![NOESY correlations observed for enol triflate 75](image)

**Figure 5. NOESY correlations observed for enol triflate 75**
Correlation between protons H\(_1\) (1.76 ppm), H\(_2\) (5.39 ppm) and H\(_3\) (0.94 ppm) (as indicated by NOESY crosspeaks) suggest the formation of isomer 75. Elimination of the triflate and removal of the TBS group to form alkyne 76 was accomplished in one pot using solid TBAF at 60°C in DMF.\(^{51}\) Lastly, silylation with dimethylvinylchlorosilane gave the desired silicon-tethered alkyne 77 in 92% yield. The synthesis of an enantiopure methyl substituted silicon-tethered alkyne possessing substitution at the propargylic position was accomplished in 10 linear steps with an overall yield of 19% from L-phenylalanine.

### 2.1.2 Exploration of alkyne 77 with the coupling of acrylates

The reactivity of alkyne 77 was explored with the Clark group’s previously established trans-silylvinylation methodology. Initially, conditions that worked well for alkyl substituted alkyne 77 were utilized (Table 5, entry 2): 10 mol% of RuHCl(CO)(PCy\(_3\))\(_2\) with 5 equivalents of ethyl acrylate in refluxing DCE (Scheme 22).

![Scheme 22. Initial reactivity of alkyne 77](image)

\(^{a}\) Determined by \(^1\)H NMR using mesitylene as an internal standard.
After 15 hours, 87% conversion of 77 was observed by $^1$H NMR. Three product isomers was also observed in the crude $^1$H NMR spectrum in a ratio of 4:3:1. The major isomer was believed to be the desired product 78A but verification of its identity was needed (as well as the two minor isomers). After purification of the crude material via column chromatography, 45% was isolated as a mixture of two isomers. None of the isomer believed to be 78C was obtained. These isomers were identical in chemical shift to the two major isomers in the crude $^1$H NMR spectrum. In hopes of determining the identity of these compounds, the diene mixture was subjected to desilylation conditions using TBAF·3H$_2$O (Scheme 23). If 78A and 78B were the two major isomers isolated from the mixture, two distinct doublets (compounds 79A and 79B) in the $^1$H NMR spectrum after desilylation were expected to be observed. If a quartet was observed (compound 79C), formation of 78C would be expected.

![Scheme 23. Desilylation of diene mixture](image-url)
Once the mixture was subjected to desilylation, two distinct doublets were observed by $^1$H NMR accounting for the formation of 79A and 79B. Even though 79C was not observed after desilylation, the possibility of 78C being the minor isomer formed in the acrylate coupling was acknowledged. At a later date, preparative thin layer chromatography was used to obtain a clean sample of 78A for NOESY analysis (Figure 6). A clean sample of 78B was not obtained after preparative thin layer chromatography. NOESY data confirmed 78A as the major isomer because of strong correlation between H$_1$-H$_2$ and H$_3$-H$_4$.

![Figure 6. NOESY data obtained from major isomer 78A](image)

Subsequently, additional ruthenium hydrides were screened in hopes of observing improved reaction conversion and product ratio (Table 6). Exchange of RuHCl(CO)(PCy$_3$)$_2$ for the di-tert-butylmethylphosphine complex RuHCl(CO)(PrBu$_2$Me)$_2$ resulted in a shorter reaction time and improved product ratio; however, the crude yield of 78A was poor (entry 1). An increase of catalyst loading of RuHCl(CO)(PrBu$_2$Me)$_2$ to 20 mol% (entry 2) allowed for rapid conversion of the starting material and slightly improved crude yield (36%). Substituting complex RuHCl(CO)(PrBu$_2$Me)$_2$ for the triisopropylphosphine ruthenium complex RuHCl(CO)(PrPr$_3$)$_2$ proved to be less effective (entry 3) and resulted in a longer reaction time with a poor crude yield of 12%.
Lastly, ruthenium complex RuHCl(CO)(H$_2$IMes)(PPh$_3$)$_2$,$^{54}$ bearing a N-heterocyclic carbene (NHC) ligand, proved to be most successful in the transformation (entry 4). Despite only 84% conversion of the starting material after 7 hours, improvement of the isomeric ratio was observed and a 56% crude yield of 78A was obtained.

With these results in hand, a solvent screen was pursued with RuHCl(CO)(H$_2$IMes)(PPh$_3$)$_2$ as the catalyst for the transformation (Table 7). Refluxing in toluene gave a shorter reaction time of two hours but a decreased crude yield of product was observed (entry 1). It was concluded that a minimum temperature of 80°C was necessary for conversion of starting material (entries 2 and 3), with an isolated yield of 55% obtained in toluene at 80°C. Decreasing the temperature to 50°C resulted in poor conversion (14%) after 22 hours (entry 3). More polar solvents, such as

### Table 6. Catalyst screen

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conversion$^a$</th>
<th>Ratio$^a$</th>
<th>Crude Yield$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RuHCl(CO)(PrBu$_2$Me)$_2$</td>
<td>3.5</td>
<td>91%</td>
<td>9:1:1</td>
<td>27%</td>
</tr>
<tr>
<td>2$^b$</td>
<td>RuHCl(CO)(PrBu$_2$Me)$_2$</td>
<td>2.5</td>
<td>97%</td>
<td>7:1:6:1</td>
<td>36%</td>
</tr>
<tr>
<td>3</td>
<td>RuHCl(CO)(Pr$_3$)$_2$</td>
<td>18</td>
<td>89%</td>
<td>6:0:1</td>
<td>12%</td>
</tr>
<tr>
<td>4</td>
<td>RuHCl(CO)(H$_2$IMes)(PPh$_3$)$_2$</td>
<td>7</td>
<td>84%</td>
<td>11:2:1</td>
<td>56%</td>
</tr>
</tbody>
</table>

$^a$ Determined by $^1$H NMR using mesitylene as an internal standard. $^b$ Reaction performed with 20 mol% catalyst.
α,α,α-trifluorotoluene, gave a comparable result to toluene (entry 4) albeit at slightly longer reaction times.

![Chemical structure](image)

Table 7. Solvent screen

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Conversion(^a)</th>
<th>Ratio(^a)</th>
<th>Crude Yield(^{a,b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>toluene</td>
<td>110</td>
<td>30</td>
<td>92%</td>
<td>N/D</td>
<td>45%</td>
</tr>
<tr>
<td>2</td>
<td>toluene</td>
<td>80</td>
<td>45</td>
<td>91%</td>
<td>4:1:1</td>
<td>62% (55%)</td>
</tr>
<tr>
<td>3</td>
<td>toluene</td>
<td>50</td>
<td>22</td>
<td>14%</td>
<td>3:1:0</td>
<td>10%</td>
</tr>
<tr>
<td>4</td>
<td>CF₃Ph</td>
<td>80</td>
<td>2</td>
<td>87%</td>
<td>4:1:1</td>
<td>62% (56%)</td>
</tr>
<tr>
<td>5</td>
<td>hexanes</td>
<td>70</td>
<td>5.5</td>
<td>86%</td>
<td>2.5:1:0</td>
<td>45%</td>
</tr>
</tbody>
</table>

\(^a\) Determined by \(^1\)H NMR using mesitylene as an internal standard. \(^b\) Isolated yield reported in parentheses.

Non-polar solvents, such as hexanes, were suited to the coupling but gave a longer reaction time with decreased product yield (entry 5). Therefore, five equivalents of ethyl acrylate with 10 mol% RuHCl(CO)(H₂IMes)(PPh₃) in toluene at 80°C was established as the optimal conditions for this transformation.

In conclusion, reaction conditions were optimized for the ruthenium-hydride catalyzed trans-silylvinylation of alkyne 77 with ethyl acrylate. The newly formed diene was isolated in 56% yield (5.4:1 \textbf{78A:78B} ratio) and the resulting diene geometry was verified by NOESY NMR.
analysis. With these optimized conditions in hand, broadening of the substrate scope by introduction of aryl functionality at the alkyne terminus was desired.

2.1.3 Synthesis of chiral, aryl-substituted alkyne 80

Given that multi-gram quantities of alkyne 77 was secured with relative ease, the synthesis was extended to include aromatic substitution on the alkyne terminus, such as alkyne 80 (Figure 7).

![Figure 7. Target: phenyl-substituted alkyne 80](image)

The synthetic route towards alkyne 80 began with Grignard addition into Weinreb amide 73 to give methyl ketone 81 in 82% yield (Scheme 24). Formation of enol triflate 82 proceeded uneventfully in a good yield of 81% and elimination with TBAF·3H₂O gave the terminal alkyne, which was subjected crude to a Sonogashira coupling with iodobenzene to give phenyl-substituted alkyne 83 in 72% yield over two steps. Lastly, silylation with vinyldimethylchlorosilane gave silicon-tethered alkyne 80 in 83% yield. Multi-gram quantities of an enantiopure phenyl-substituted silicon-tethered alkyne possessing substitution at the propargylic position was synthesized in 11 linear steps from L-phenylalanine with an overall yield of 15%.
2.1.4 Exploration of alkyne 80 with the coupling of acrylates

Initially, investigations began with the conditions for aryl-substituted alkynes that were previously established by the Clark group: 5 mol% RuHCl(CO)(PCy3)2, 2 equivalents of L-menthyl acrylate, toluene, reflux (Scheme 25); however, these conditions gave 62% conversion of alkyne 80 with low crude yield (18%) of diene 84 after 9.5 hours.

Scheme 25. Initial studies of alkyne 80

* Determined by 1H NMR using mesitylene as an internal standard.
Displeased with this result, it was questioned whether propargylic substitution was a hindrance to product formation. Since the previously developed methodology for phenyl-substituted alkynes was not successful in this case, the conditions that gave success with propargylic substituted methyl alkyne 77 were utilized (Scheme 26).

![Scheme 26. Unexpected product formation](image_url)

\* Determined by $^1$H NMR using mesitylene as an internal standard.

Alkyne 80 was subjected to 10 mol% RuHCl(CO)(H$_2$IMes)(PPh$_3$) with 5 equivalents of ethyl acrylate in refluxing toluene. After 30 minutes, 100% conversion was achieved; unexpectedly diene 85 was the major product formed in the transformation. The formation of diene 85 was attributed from the loss and subsequent re-insertion of ethylene instead of acrylate incorporation. However, the acrylate incorporated diene 84 was obtained as a minor component in the reaction. Despite being able to isolate 22% of 84 as one isomer, we chose not to pursue further avenues for the coupling of alkyne 80 with acrylates.
2.1.5 Conclusion

Synthetic routes were designed and optimized for chiral alkynes 77 and 80 in 10 and 11 linear steps, respectively. Such alkynes possess propargylic functionality and contain methyl and phenyl substitution at the alkyne terminus. Their synthetic applicability was demonstrated with the Clark group's previously established ruthenium hydride catalyzed trans-silylvinylation conditions.

2.2 TRANS-SILYLVINYLATION OF ALKYNES WITH VINYL BORONATES

2.2.1 Introduction

Vinyl boronates\textsuperscript{55-58} have played an important role as intermediates in coupling reactions that are utilized in the syntheses of highly functionalized scaffolds and complex natural products.\textsuperscript{20, 22, 59} Specifically, silyl-dienyl boronates are of particular interest due to silicon and boron being versatile functional handles for selective functional group manipulation. Well-known methods of doing so include Suzuki-Miyaura coupling,\textsuperscript{60, 61} Heck reaction,\textsuperscript{62, 63} Hiyama-Denmark reaction\textsuperscript{64} and Tamao oxidation.\textsuperscript{65}

The use of vinyl boronates for the synthesis of dienyl boronates has been reported, one example being via cross metathesis (Table 8). Grubbs \textit{et al.} coupled various dienes with an excess of vinyl pinacol boronate and 5 mol\% Grubbs Gen. II catalyst.\textsuperscript{66} The resulting substituted dienyl boronates were isolated in fair to good yields of 40\%-80\%. 
Table 8. Synthesis of dienyl boronates via cross metathesis

The utility of the dienyl boronates reported by this process was demonstrated via a one-pot cross metathesis/Suzuki coupling (Scheme 27).

Despite the synthetic utility of the dienyl boronates, one drawback to the cross metathesis methodology is the requirement of synthesizing the diene precursor prior to the
coupling/installment of the boronate moiety. In addition, some of the diene precursors are volatile, hence resulting in difficulty of handling.

As mentioned in chapter 1 (see Table 1), Marciniec reported on the synthesis of silyl-dienyl boronates via the ruthenium catalyzed coupling of silyl-acetylenes with vinyl boronates.\textsuperscript{20} Despite the fact that bi-functional dienes were formed from this transformation, stereocontrol was problematic and alkyne dimerization was observed. In addition, the study was limited to use of terminal alkynes, limiting the substitution of the silyl-dienyl boronates.

With that being said, extension of the Clark group’s previous methodology\textsuperscript{26} to include vinyl boronate coupling partners was sought after. Such an extension of the olefin coupling partner would allow for the formation of a more diverse and synthetically useful silyl-dienyl boronate scaffold. Also, the approach produces $Z,E$-diene systems, which pose as a challenge to obtain despite their prevalence in nature.\textsuperscript{67-69}

### 2.2.2 Initial investigations

We began our studies using alkyne 41\textsuperscript{26} and vinyl boronate 86 with the conditions previously established for our acrylate coupling (Scheme 28). Full conversion of the starting alkyne 41 was achieved after 9 hours. Upon $^1$H NMR analysis, an 87\% crude yield of desired silyl-dienyl boronate 87 was observed. The only observable by-product of the reaction was the boronate dimer 88. A substantial loss of product yield was observed after isolation of 87 via column chromatography. This was believed to be due to hydrolysis of the product upon exposure to silica gel.
Scheme 28. Initial studies of the vinyl boronate coupling

a Determined by 1H NMR using mesitylene as an internal standard.

Deactivation of the silica gel by treatment with triethylamine, trimethylchlorosilane and boric acid\textsuperscript{70} gave no improvement of isolated yield. Another minor setback was the difficulty of separating the boronate dimer from the product.

2.2.3 Mechanistic hypothesis\textsuperscript{71}

The aforementioned transformation is believed to proceed as follows (Scheme 29):

Dissociation of a phosphine ligand from RuHCl(CO)(PCy\textsubscript{3})\textsubscript{2} gives a highly reactive 14-electron ruthenium complex \textbf{33}, which upon reaction with the silicon-tethered alkyne \textbf{41}, adds at the sterically most accessible (terminal) position of the vinyl moiety to give intermediate \textbf{49}. β-Silyl transfer and subsequent loss of ethylene\textsuperscript{28} results in formation of silyl-ruthenium intermediate \textbf{42}. The transformation from \textbf{42} to \textbf{43} can proceed via direct \textit{trans} silyl-ruthenation (see section 1.2.3 for literature precedence) or by a \textit{cis} silyl-ruthenation pathway to give intermediate \textbf{43-cis} followed by isomerization to generate \textbf{43-trans}. The isomerization is proposed to proceed via a vinylidene-type intermediate \textbf{43A} (favorable due to the charge stability by the silicon atom).
Intermolecular olefin insertion (vinyl boronate) at the most sterically accessible position of the alkene yields 89, which subsequently undergoes β-hydride elimination to give the desired silyl-dienyl boronate. Upon formation of the product, ruthenium hydride complex 33 is regenerated.

Scheme 29. Mechanistic hypothesis

Boronate dimer formation can be attributed as follows (Scheme 30): Dissociation of a phosphine ligand from RuHCl(CO)(PCy₃)₂ generates a highly reactive 14-electron ruthenium complex 33, which upon introduction with the vinyl boronate, adds at the most sterically accessible (terminal) position to give intermediate 90. β-Boron transfer and the resulting loss of
ethylene generates boro-ruthenium intermediate 91. Upon introduction of another molecule of vinyl boronate, boro-ruthenation of 91 occurs to generate bis-borylated species 92. Subsequent β-hydride elimination of 92 yields the vinyl boronate dimer, upon which ruthenium intermediate 33 is regenerated.

Scheme 30. Mechanistic hypothesis for vinyl boronate dimer formation

2.2.4 Reaction optimization

Further optimization of the reaction was performed to increase the crude yield of product and suppress the boronate dimer formation. A catalyst screen was conducted (Table 9), beginning with some of the previously explored ruthenium hydrides. Ruthenium complex RuHCl(CO)(PrBu₂Me)₂ gave only 55% crude yield of product after 9 hours with a substantially
higher amount of dimer (entry 1). Switching to the tri-isopropylphosphine complex RuHCl(CO)(PiPr)\textsubscript{3} resulted in 69\% crude yield of product and only 4\% crude yield of dimer (entry 2), however, the crude yield was not comparable to what was initially observed with RuHCl(CO)(PCy\textsubscript{3}).

![Chemical reaction diagram](attachment:reaction_diagram.png)

**Table 9. Catalyst screen with vinyl boronate 86**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Crude Yield\textsuperscript{a} of 87</th>
<th>Crude Yield\textsuperscript{a} of 88</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{b}</td>
<td>RuHCl(CO)(PfBu\textsubscript{2}Me)\textsubscript{2}</td>
<td>55%</td>
<td>14%</td>
</tr>
<tr>
<td>2\textsuperscript{b}</td>
<td>RuHCl(CO)(PPr\textsubscript{3})\textsubscript{2}</td>
<td>69%</td>
<td>4%</td>
</tr>
<tr>
<td>3\textsuperscript{c}</td>
<td>RuHCl(CO)(H\textsubscript{2}Mes)(PPh\textsubscript{3})</td>
<td>23%</td>
<td>12%</td>
</tr>
<tr>
<td>4</td>
<td>RuHCl(CO)(PAd\textsubscript{2}nBu)\textsubscript{2}</td>
<td>N/D</td>
<td>32%</td>
</tr>
<tr>
<td>5\textsuperscript{b,d}</td>
<td>RuH(OSiPh\textsubscript{3})(CO)(PfBu\textsubscript{2}Me)\textsubscript{2}</td>
<td>17%</td>
<td>0%</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Determined by \textsuperscript{1}H NMR using mesitylene as an internal standard. \textsuperscript{b} Starting material observed after 9 hours. \textsuperscript{c} Reaction complete after 2 hours. \textsuperscript{d} Reaction run by Robert Wilson.

The NHC-complex RuHCl(CO)(H\textsubscript{2}IMes)(PPh\textsubscript{3}) gave rapid conversion of the alkyne in 2 hours but poor product yield was observed (entry 3). The bulkier bis-adamantyl-\textit{n}-butylphosphine complex RuHCl(CO)(PAd\textsubscript{2}nBu)\textsubscript{2}\textsuperscript{72} gave a large amount of boronate dimer (entry 4); poor conversion and poor product yield (17\%) was observed with RuH(OSiPh\textsubscript{3})(CO)(PrBu\textsubscript{2}Me)\textsubscript{2}\textsuperscript{73} (entry 5).
With ruthenium hydride RuHCl(CO)(PCy$_3$)$_2$ being the optimal catalyst for the transformation, a solvent screen was conducted (Table 10). The use of DCE at decreased reaction temperatures was envisioned to circumvent dimer formation (entries 1 and 2); indeed, a decreased amount of dimer was observed but reaction conversion and product yield were sacrificed. Toluene at 85°C gave a shorter reaction time and less dimer was observed but the product yield was reduced (entry 3). Refluxing trifluorotoluene resulted in poor conversion and product yield after 9 hours (entry 4). Exchange for 1,4-dioxane gave similar results to toluene (entry 5) and refluxing THF resulted in no dimer formation albeit decreased product yield (64%) after 9 hours (entry 6).

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Crude Yield$^a$ of 87</th>
<th>Crude Yield$^a$ of 88</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^{b,c}$</td>
<td>DCE</td>
<td>70</td>
<td>15</td>
<td>65%</td>
<td>2%</td>
</tr>
<tr>
<td>2$^{b,c}$</td>
<td>DCE</td>
<td>60</td>
<td>15</td>
<td>53%</td>
<td>1%</td>
</tr>
<tr>
<td>3</td>
<td>toluene</td>
<td>85</td>
<td>5.5</td>
<td>72% (53%)</td>
<td>1%</td>
</tr>
<tr>
<td>4$^{b,c}$</td>
<td>CF$_3$Ph</td>
<td>105</td>
<td>9</td>
<td>45%</td>
<td>0</td>
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<tr>
<td>5</td>
<td>1,4-dioxane</td>
<td>85</td>
<td>5.5</td>
<td>78% (59%)</td>
<td>3%</td>
</tr>
<tr>
<td>6$^b$</td>
<td>THF</td>
<td>70</td>
<td>9</td>
<td>64%</td>
<td>0</td>
</tr>
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<td>7$^{b,c}$</td>
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<td>7</td>
<td>27%</td>
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</tr>
<tr>
<td>8</td>
<td>MeCN</td>
<td>70</td>
<td>9</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>9$^c$</td>
<td>DMF</td>
<td>105</td>
<td>9</td>
<td>NR</td>
<td>NR</td>
</tr>
</tbody>
</table>

Table 10. Solvent screen with vinyl boronate 86

$^a$ Determined by $^1$H NMR using mesitylene as an internal standard. $^b$ Starting material observed after designated reaction time. $^c$ Reaction run by Robert Wilson. $^d$ Isolated yield reported in parenthesis.
The lower boiling solvent DCM proved detrimental to reaction conversion and product yield (entry 7). No reactivity was observed with acetonitrile, possibly due to solvent coordination to the metal (entry 8). Additionally, no reaction occurred in DMF at 105°C (entry 9).

With these results in hand, complex RuHCl(CO)(PCy₃)₂ in DCE at 85°C was chosen as the optimal catalyst, solvent and temperature for the coupling with vinyl boronate 86. Lastly, the equivalents of the vinyl boronate was varied to observe the effect on dimer formation (Table 11). Decreasing the amount of vinyl boronate from 2 equivalents (entry 3) to 1.5 equivalents (entry 2) had a significant effect on the reaction. Full conversion of the starting material was not achieved after 9 hours and the crude product yield decreased by 20%. However, as expected, the amount of dimer decreased from 9% to 3%. Further decrease of boronate to 1.2 equivalents (entry 1) gave similar results as entry 2.

![Reaction Diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Equiv of 86</th>
<th>Crude Yield* of 87</th>
<th>Crude Yield* of 88</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ᵇ</td>
<td>1.2</td>
<td>63%</td>
<td>2%</td>
</tr>
<tr>
<td>2ᵇ</td>
<td>1.5</td>
<td>66%</td>
<td>3%</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>87%</td>
<td>9%</td>
</tr>
</tbody>
</table>

Table 11. Variation of equivalents of 86

ᵇ Determined by ¹H NMR using mesitylene as an internal standard. ᶦ Starting material observed after 9 hours.
After numerous attempts to improve the crude yield of 87 and decrease the amount of dimer 88, new vinyl boronate coupling partners were explored (Table 12). Beginning with vinyl boronate 93, which was easily prepared on multi-gram scale according to the literature protocol,74 a 75\% crude yield of product 97 and 5\% boronate dimer was observed under standard reaction conditions (entry 1). We were surprised to discover that there was no observable impact on characterization (by \(^1\)H NMR and \(^{13}\)C NMR) of 97 despite a total of four stereoisomers being present. However, substantial loss of 97 was observed upon exposure to silica gel and only 55\% isolated material was obtained. Despite this minor setback, the boronate dimer was easier to visualize by thin layer chromatography and therefore less of a challenge to separate compared to dimer 88. Pinacol boronate 94, an easy to prepare but highly volatile and readily polymerizable compound, gave a slightly lower crude yield of product 98 but with comparable isolated yield (entry 2).74 The MIDA boronate 9575 and potassium trifluoroborate salt 96,76 both air stable solids, were unreactive in the chemistry (entries 3 and 4). Based on these results, vinyl boronate 93 was the most successful.
For the purpose of minimizing dimer formation, a solvent screen was conducted (Table 13). Reactions run in DCE, toluene and 1,4-dioxane worked well at 85°C (entries 1-3). Raising the temperature resulted in a shorter reaction time albeit increase in dimer formation (entry 3). Lowering the temperature to 70°C resulted in longer reaction times and decreased the amount of both product and dimer (entry 4). Refluxing THF compromised reaction conversion and yield of product (entry 6), and a poor crude yield of product was observed in refluxing DCM (entry 7). No reactivity was observed in acetonitrile (entry 8). Toluene at 85°C proved optimal for the reaction (entry 2) due to a shorter reaction time and minimal formation of dimer.
The boronate dimer 101 was independently synthesized using the optimized conditions to verify its formation (Scheme 31). One equivalent of vinyl boronate 93 with 5 mol% RuHCl(CO)(PCy₃)₂ in refluxing DCE gave a pale brown air stable solid 101 upon purification via column chromatography.

Table 13. Solvent screen with boronate 93

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Crude Yield of 97</th>
<th>Crude Yield of 101</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCE</td>
<td>85</td>
<td>5</td>
<td>75%</td>
<td>5%</td>
</tr>
<tr>
<td>2</td>
<td>toluene</td>
<td>85</td>
<td>3.5</td>
<td>75%</td>
<td>3%</td>
</tr>
<tr>
<td>3ᵇ</td>
<td>toluene</td>
<td>100</td>
<td>3</td>
<td>78%</td>
<td>5%</td>
</tr>
<tr>
<td>4ᵇˣᵉ</td>
<td>toluene</td>
<td>70</td>
<td>7</td>
<td>63%</td>
<td>1%</td>
</tr>
<tr>
<td>5</td>
<td>1,4-dioxane</td>
<td>85</td>
<td>4</td>
<td>67%</td>
<td>3%</td>
</tr>
<tr>
<td>6ᵇ</td>
<td>THF</td>
<td>70</td>
<td>7</td>
<td>58%</td>
<td>0</td>
</tr>
<tr>
<td>7ᵇ</td>
<td>DCM</td>
<td>45</td>
<td>7</td>
<td>27%</td>
<td>0</td>
</tr>
<tr>
<td>8ᵇ</td>
<td>MeCN</td>
<td>70</td>
<td>7</td>
<td>N/R</td>
<td>N/R</td>
</tr>
</tbody>
</table>

*a* Determined by ¹H NMR using mesitylene as an internal standard. *ᵇ* Reaction run by Robert Wilson. *ˣᵉ* Starting material observed after designated reaction time.

Scheme 31. Synthesis of boronate dimer
Additional ruthenium hydrides were also examined (Table 14). Ruthenium complex RuHCl(CO)(PCy$_3$)$_2$ proved to be most suitable for the coupling with vinyl boronate 93, allowing for a short reaction time, good yield of product and minimal dimer formation (entry 1).

![Chemical reaction diagram]

**Table 14. Catalyst screen with boronate 93**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Crude Yield$^a$ of 97</th>
<th>Crude Yield$^a$ of 101</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RuHCl(CO)(PCy$_3$)$_2$</td>
<td>3.5</td>
<td>75%</td>
<td>3%</td>
</tr>
<tr>
<td>2$^b$</td>
<td>RuHCl(CO)(PrBu$_2$Me)$_2$</td>
<td>5</td>
<td>67%</td>
<td>10%</td>
</tr>
<tr>
<td>3$^c$</td>
<td>RuHCl(CO)(Pr$_3$)$_2$</td>
<td>8</td>
<td>72%</td>
<td>4%</td>
</tr>
<tr>
<td>4</td>
<td>RuHCl(CO)(PrBu$_2$Cy)$_2$</td>
<td>2</td>
<td>61%</td>
<td>11%</td>
</tr>
<tr>
<td>5$^c$</td>
<td>RuHCl(CO)(PCy$_2$Bu)$_2$</td>
<td>8</td>
<td>60%</td>
<td>6%</td>
</tr>
<tr>
<td>6$^{b,c}$</td>
<td>RuHCl(CO)(Pr$_2$[3,5-CF$_3$C$_6$H$_3$])$_2$</td>
<td>8</td>
<td>15%</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ Determined by $^1$H NMR using mesitylene as an internal standard. $^b$ Reaction run by Robert Wilson. $^c$ Starting material observed after 8 hours.

Electron-rich ruthenium hydride complex RuHCl(CO)(PrBu$_2$Me)$_2$ catalyzed the transformation in a reasonable time (5 hours) but product yield was compromised and the amount of dimer increased (entry 2). Complex RuHCl(CO)(Pr$_3$)$_2$ gave good product yield but required a longer reaction time of 8 hours (entry 3). Ruthenium complexes RuHCl(CO)(PrBu$_2$Cy)$_2$ and RuHCl(CO)(PCy$_2$Bu)$_2$, developed by the Clark group, catalyzed the transformation but yield was compromised and increased dimer formation was observed (entries 4 and 5). Lastly, complex RuHCl(CO)(Pr$_2$[3,5-CF$_3$C$_6$H$_3$])$_2$, bearing electron-deficient phosphine ligands,
exhibited poor reactivity and only 15% product was observed after 8 hours. After significant optimization, 5 mol% RuHCl(CO)(PCy$_3$)$_2$ with 2 equivalents of vinyl boronate 93 in toluene (0.5M in alkyne) at 85°C was adopted as the standard conditions for the reaction.

2.2.5 Substrate scope for vinyl boronate 93

The substrate scope was explored using the aforementioned optimized conditions for vinyl boronate 93. We began by varying the substitution at the homopropargylic position (Table 15). Alkyl substitution at R$_1$ was well tolerated (entries 1-4) with isolated yields of 55%-60%. A biphenyl moiety worked well (entry 5) in the coupling with a 60% isolated yield obtained. A substrate bearing geminal substitution also worked well (entry 6), presumably due to the Thorpe-Ingold effect.$^{39}$ NOESY NMR analysis of dienyl-silyl boronates 97 and 104 verified the Z,E olefin geometry.
Aryl groups at the alkyne terminus also worked well in the reaction (Table 16). Toluene-bearing and the 3,5-xylyl moiety gave the desired products 107 and 108 in good yields (entries 1 and 2).
In hopes of extending the substrate scope to include alkyl functionality on the alkyne terminus, the reactivity of alkyne 68 was explored (Table 17). Initially, the standard reaction conditions were used (entry 1), resulting in 100% conversion of starting material but only 38% crude yield (30% isolated yield) of product 109. The catalyst loading was doubled to 20 mol% (entry 2), which in turn shortened the reaction time to 3 hours with no improvement in product yield. In hopes of increasing the crude yield of product, changes in the equivalents of vinyl boronate were explored. Three equivalents of vinyl boronate significantly improved the crude yield to 50%, however, a significant amount of boronate dimer was formed (entry 3). Further increase of the vinyl boronate to 5 equivalents did not improve product yield, but the amount of dimer doubled to 25% (entry 4). This development was problematic due to the difficulty of separating the product from the boronate dimer.
Decreasing the catalyst loading to 5 mol% with 5 equivalents of vinyl boronate significantly reduced the amount of dimer formation (13%), but the reaction was not complete after 24 hours (entry 5). Decrease of the vinyl boronate to 1.5 equivalents resulted in only 2% dimer albeit compromised product yield was observed (entry 6). Based on the preliminary solvent screen in Table 12, THF was examined for the transformation. During the initial solvent screen, THF was sluggish for the coupling but gave the product without any formation of boronate dimer (Table 13, entry 6). In the case for alkyl-substituted alkyne 68, THF allowed for minimal dimer formation (2%) and only 30% crude yield of 109 was observed after 22 hours (entry 7). Despite minimal dimer formation, a low crude yield was a setback due to the instability of the product on

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Equiv of 93</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Crude Yield&lt;sup&gt;a&lt;/sup&gt; of 109</th>
<th>Crude Yield&lt;sup&gt;b&lt;/sup&gt; of 101</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RuHCl(CO)(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; (10)</td>
<td>2</td>
<td>toluene</td>
<td>85</td>
<td>5</td>
<td>38% (30%)</td>
<td>4%</td>
</tr>
<tr>
<td>2</td>
<td>RuHCl(CO)(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; (20)</td>
<td>2</td>
<td>toluene</td>
<td>85</td>
<td>3</td>
<td>34%</td>
<td>5%</td>
</tr>
<tr>
<td>3</td>
<td>RuHCl(CO)(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; (10)</td>
<td>3</td>
<td>toluene</td>
<td>85</td>
<td>5</td>
<td>50%</td>
<td>12%</td>
</tr>
<tr>
<td>4</td>
<td>RuHCl(CO)(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; (10)</td>
<td>5</td>
<td>toluene</td>
<td>85</td>
<td>6</td>
<td>47%</td>
<td>25%</td>
</tr>
<tr>
<td>5</td>
<td>RuHCl(CO)(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; (6)</td>
<td>5</td>
<td>toluene</td>
<td>85</td>
<td>24</td>
<td>40%</td>
<td>13%</td>
</tr>
<tr>
<td>6</td>
<td>RuHCl(CO)(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; (10)</td>
<td>1.5</td>
<td>toluene</td>
<td>85</td>
<td>8</td>
<td>27%</td>
<td>2%</td>
</tr>
<tr>
<td>7</td>
<td>RuHCl(CO)(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; (10)</td>
<td>2</td>
<td>THF</td>
<td>70</td>
<td>22</td>
<td>30%</td>
<td>2%</td>
</tr>
<tr>
<td>8</td>
<td>RuHCl(CO)(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; (20)</td>
<td>2</td>
<td>THF</td>
<td>70</td>
<td>20</td>
<td>22%</td>
<td>3%</td>
</tr>
<tr>
<td>9&lt;sup&gt;c&lt;/sup&gt;</td>
<td>RuHCl(CO)(P&lt;sub&gt;2&lt;/sub&gt;Bu&lt;sub&gt;2&lt;/sub&gt;Me)&lt;sub&gt;2&lt;/sub&gt; (6)</td>
<td>2</td>
<td>THF</td>
<td>70</td>
<td>18</td>
<td>9%</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>RuHCl(CO)(P&lt;sub&gt;2&lt;/sub&gt;Bu&lt;sub&gt;2&lt;/sub&gt;Me)&lt;sub&gt;2&lt;/sub&gt; (5)</td>
<td>2</td>
<td>THF</td>
<td>70</td>
<td>3</td>
<td>20%</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>RuHCl(CO)(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; (10)</td>
<td>2</td>
<td>1,4-Dioxane</td>
<td>85</td>
<td>7</td>
<td>32%</td>
<td>3%</td>
</tr>
<tr>
<td>12</td>
<td>RuHCl(CO)(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; (20)</td>
<td>2</td>
<td>1,4-Dioxane</td>
<td>85</td>
<td>3</td>
<td>34%</td>
<td>4%</td>
</tr>
</tbody>
</table>

Table 17. Alkyl substrate reaction optimization

<sup>a</sup> Determined by <sup>1</sup>H NMR using mesitylene as an internal standard. <sup>b</sup> Isolated yield reported in parentheses. <sup>c</sup> Starting material observed after 18 hours.
silica gel. Increasing the catalyst loading to 20 mol% slightly improved reaction conversion after 22 hours but was detrimental to product yield (entry 8). Additional ruthenium catalysts were explored with THF but poor reactivity was observed (entries 9 and 10). Also, based on results from the preliminary solvent screen, 1,4-dioxane was briefly examined. Only a small amount of dimer (3%-4%) was observed in 1,4-dioxane at 85°C but poor crude yields of product (32%-34%) were obtained (entries 11 and 12). After considerable optimization, 10 mol% RuHCl(CO)(PCy3)2 with 3 equivalents of vinyl boronate 93 in toluene at 85°C was found to be superior for the transformation with alkyne 68 (entry 3) giving a 50% crude yield of 109 after 5 hours.

Additional alkyl-substituted alkynes were next examined in the coupling (Table 18). Poor reactivity and crude yield of product were observed with methyl- and ethyl-substituted alkynes 110 and 111 bearing a phenyl group at the homopropargylic position.

![Chemical diagram]

### Table 18. Other alkyl-substituted alkyne substrates

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne</th>
<th>R</th>
<th>Catalyst Mol%</th>
<th>Equiv of 93</th>
<th>Time (h)</th>
<th>Crude Yield* of Product</th>
<th>Crude Yield* of 101</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>110</td>
<td>Me</td>
<td>10</td>
<td>2</td>
<td>8</td>
<td>31% (4:1)</td>
<td>2%</td>
</tr>
<tr>
<td>2b</td>
<td>110</td>
<td>Me</td>
<td>5</td>
<td>2.5</td>
<td>24</td>
<td>15%</td>
<td>4%</td>
</tr>
<tr>
<td>3</td>
<td>111</td>
<td>Et</td>
<td>10</td>
<td>2</td>
<td>5</td>
<td>18% (5:1)</td>
<td>2%</td>
</tr>
<tr>
<td>4</td>
<td>111</td>
<td>Et</td>
<td>5</td>
<td>2.5</td>
<td>7</td>
<td>23%</td>
<td>3%</td>
</tr>
</tbody>
</table>

* Determined by 1H NMR using mesitylene as an internal standard. *b Starting material observed after 24 hours.
Varying the catalyst loading improved reaction time but product yield varied by substrate. Increasing the catalyst loading for the methyl-substituted alkyne significantly improved the crude product yield from 15% to 31% (entries 1 and 2), however, a Z:E isomeric mixture of products was observed. In regards to the ethyl-substituted alkyne (entries 3 and 4), increase of the catalyst loading was detrimental to product yield and an Z:E isomeric mixture was also observed. No further optimization of these substrates was performed.

The substrate scope tolerance for propargylic substitution was also investigated. Previously synthesized alkyl-substituted alkyne 77 was subjected to 10 mol% RuHCl(CO)(PCy3)2 with 2 equivalents of vinyl boronate 93 in toluene at 85°C (Scheme 32).

![Scheme 32. Reactivity of alkyne 3 with vinyl boronate 93](image)

After 3 hours 100% conversion of alkyne 77 was observed and a 76% isolated yield of 112 (3:1 E:Z) was obtained. It was concluded that further optimization was not necessary for alkyne 77 in the transformation. The resulting silyl-dienyl boronate 112 was subjected to iodo-deboration77 to verify that the isomers observed from the coupling were stereoisomers and not diastereomers stemming from the vinyl boronate moiety (Scheme 33).
Scheme 33. Confirmation of isomeric mixture by iodo-deboration

The resulting silyl-dienyl iodide 113 was isolated in 72% yield and two isomers were observed by $^1$H NMR in a 3:1 ratio, therefore confirming stereochemical relationship of isomers from the vinyl boronate coupling.

2.2.6 Substrate scope for vinyl boronate 94

Since isolated yields of below 70% were observed for all but one substrate with vinyl boronate 93, a few substrates were inspected using pinacol boronate 94 (Table 19). These substrates did not give as high a crude yield as when vinyl boronate 93 was used but a majority of the dienes were more stable to isolation with little product loss. In entry 1, the isolated yield of 114 was identical to that of 97 despite a different vinyl boronate used. A significant increase in isolated yield (17%) was observed with alkyne 62 (entry 2); however, a few substrates that were scrutinized gave conflicting results. The cyclohexane-substituted diene 116 (entry 3) gave a poor crude yield of 46% (in comparison to a 60% isolated yield of 104) so no attempts were made for isolation of 116. In addition, the para-nitro phenyl-substituted diene 117 was isolated in only 49% yield (entry 4). To conclude, the vinyl pinacol boronate 94 was utilized with some of the previously screened alkyne substrates to obtain improved isolated yields of products.
2.2.7 Synthetic elaboration of silyl-dienyl boronates

Once coupling conditions were optimized and substrate scope determined for vinyl boronates 93 and 94, demonstration of the synthetic utility of the silyl-dienyl boronates was desired. Initially, a variety of Suzuki coupling conditions were explored to selectively functionalize the boronate moiety (Table 20). 4-Iodotoluene was chosen as the aryl halide due to ease of handling and storage in the glovebox. Since the aryl halide was readily available, conditions were sought after where that compound could be used in excess instead of the diene substrate. At the outset, conditions used by Whiting using vinyl boronate 93 (entries 1-3) were examined. The reaction of Pd(PPh3)4 and KOtBu in refluxing THF with slight excess (1.2 equivalents) of halide resulted in only 22% crude yield of product 118 (entry 1).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne</th>
<th>Product</th>
<th>Yield*</th>
<th>Entry</th>
<th>Alkyne</th>
<th>Product</th>
<th>Yield*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1°</td>
<td>41</td>
<td>114</td>
<td>(55%)</td>
<td>3</td>
<td>57</td>
<td>116</td>
<td>46%</td>
</tr>
<tr>
<td>2°</td>
<td>62</td>
<td>115</td>
<td>76% (72%)</td>
<td>4</td>
<td>60</td>
<td>117</td>
<td>65% (49%)</td>
</tr>
</tbody>
</table>

Table 19. Vinyl pinacol boronate 94 substrate scope

*a* Isolated yield reported in parentheses. Crude yield determined by 1H NMR using mesitylene as an internal standard. b Reaction run by Robert Wilson.
Table 20. Suzuki coupling reaction optimization

<table>
<thead>
<tr>
<th>Entry</th>
<th>Equiv. of Halide</th>
<th>Catalyst/Ligand (mol%)</th>
<th>Base (Equiv.)</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Crude Yield (Z:E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2</td>
<td>Pd(PPh₃)₄ (5)</td>
<td>KOtBu (1.2)</td>
<td>THF</td>
<td>70</td>
<td>22</td>
<td>22% (5:1)</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>Pd(PPh₃)₄ (5)</td>
<td>Ag₂O (1.2)</td>
<td>THF</td>
<td>70</td>
<td>22</td>
<td>43% (10:1)</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>Pd(PPh₃)₄ (5)</td>
<td>Ag₂O (1.2)</td>
<td>1,4-Dioxane</td>
<td>105</td>
<td>5</td>
<td>23% (1:1)</td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>Pd(PPh₃)₄ (5)</td>
<td>1M K₂CO₃ (1.2)</td>
<td>THF</td>
<td>50</td>
<td>21</td>
<td>26%</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>PdCl₂(PPh₃)₂ (5)</td>
<td>2M Na₂CO₃ (1.5)</td>
<td>THF</td>
<td>70</td>
<td>22</td>
<td>68% (1:1)</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>PdCl₂(PPh₃)₂ (5)</td>
<td>2M Na₂CO₃ (1.5)</td>
<td>THF</td>
<td>70</td>
<td>22</td>
<td>61% (2:1)</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>Pd(PPh₃)₄ (5)</td>
<td>1M K₂PO₄ (1.5)</td>
<td>Toluene</td>
<td>105</td>
<td>19</td>
<td>38% (1:1)</td>
</tr>
<tr>
<td>8</td>
<td>1.2</td>
<td>Pd(PPh₃)₄ (5)</td>
<td>K₂PO₄ (1.5)</td>
<td>DME</td>
<td>85</td>
<td>18</td>
<td>64% (1:1)</td>
</tr>
<tr>
<td>9</td>
<td>1.2</td>
<td>Pd(PPh₃)₄ (5)</td>
<td>K₂PO₄ (1.5)</td>
<td>1,4-Dioxane</td>
<td>85</td>
<td>18</td>
<td>57% (1:1)</td>
</tr>
<tr>
<td>10</td>
<td>1.5</td>
<td>Pd(OAc)₂ (5)</td>
<td>55M K₂PO₄ (3)</td>
<td>THF</td>
<td>50</td>
<td>24</td>
<td>63%</td>
</tr>
</tbody>
</table>

a Determined by crude ¹H NMR using mesitylene as an internal standard. b Starting material observed after designated reaction time.

A 5:1 ratio of Z:E isomers was also observed from the transformation. In hopes of improving the crude yield and minimizing additional isomer formation, the base was exchanged to silver oxide. In refluxing THF, starting material was present after 22 hours; however, the crude yield significantly increased to 43% and the isomeric ratio improved to 10:1 (entry 2). Refluxing these components in 1,4-dioxane resulted in rapid consumption of the starting material but a poor isomeric ratio of 1:1 was obtained (entry 3). After perusing several reviews, additional conditions were screened (entries 4-9). Aqueous K₂CO₃ in THF at 50°C proved detrimental to reaction conversion but only one product isomer was observed (entry 4). A considerable crude yield of 118 (61% and 68%) was obtained with aqueous Na₂CO₃ in the presence of catalytic
Pd(PPh$_3$)$_4$ (entry 5) and PdCl$_2$(PPh$_3$)$_2$ (entry 6) albeit poor isomeric ratios resulted. Aqueous K$_3$PO$_4$ in refluxing toluene gave only a 38% crude yield and a poor isomeric ratio after 19 hours (entry 7). Exchange of toluene to the more polar solvents DME and 1,4-dioxane improved product yield (64% and 57%, respectively) but the isomeric ratios remained unchanged (entries 8 and 9). When the conditions reported by Suginome et al.$^{82}$ (5 mol% Pd(OAc)$_2$, 10 mol% S-Phos, 3 equivalents K$_3$PO$_4$, 3 equivalents of H$_2$O and 1.5 equivalents of 4-iodotoluene in THF at 50°C) were used, a 63% crude yield of 118 was obtained as a single isomer (entry 10).

Repetition of entry 10 resulted in a 45% isolated yield of diene 118 (Scheme 34).

![Scheme 34. Suzuki coupling of 97 with 4-iodotoluene](image)

In hopes of improving overall product yield, a tandem silyl-boration of alkyne 41 and subsequent Suzuki coupling of 97 was performed (Scheme 35). This protocol provided diene 118 in 54% isolated yield over two steps. When these conditions were utilized with alkyne 41 and vinyl pinacol boronate 94, diene 118 was obtained in a comparable yield of 55% over two steps (Scheme 35).
With regards to problematic alkyl-substituted alkyne 68, the isolation difficulty of silyldienyl boronate 109 was circumvented by utilizing the tandem coupling/Suzuki protocol. Using the optimized vinyl boronate coupling conditions (Table 17, entry 3) and Suzuki conditions (Table 20, entry 10), diene 119 was easily separated from the boronate dimer and isolated in 39% yield over two steps (Scheme 36, E:Z 6:1).

Additional aryl halide coupling partners were explored with various substrates for the Suzuki coupling. Switching to a more activated aryl halide, 4'-bromoacetophenone, was also
tolerable and gave the desired product 120 in 59% yield after 4 hours (Scheme 37).

Scheme 37. Suzuki coupling with 4'-bromoacetophenone

Improved isolated yields were obtained when iodobenzene was used as the coupling partner (Scheme 38). Upon subjection of silyl-dienyl boronates 121\textsuperscript{71} and 122\textsuperscript{71} to the Suzuki conditions with iodobenzene, the resulting phenyl substituted diene 123 was isolated in 70% and 73% yields, respectively.

Scheme 38. Suzuki coupling with iodobenzene
In addition to Suzuki couplings, selective functionalization of the boronate moiety was accomplished in other ways. Iodo-deboration\textsuperscript{77} of silyl-dienyl boronates \textit{97, 105, 121}\textsuperscript{71} and \textit{122}\textsuperscript{71} proceeded smoothly to give silyl-dienyl iodides \textit{124-126} in good yields ranging from 60\%-74\% with complete retention of stereochemistry (Scheme 39).

\textbf{Scheme 39. Iodo-deboration of silyl-dienyl boronates}

\textsuperscript{a} Reaction run by Robert Wilson.

Formation of silyl-dienyl iodide \textit{124} was confirmed by subjecting it in a Suzuki coupling using Fu's conditions\textsuperscript{83} with 4-methoxyphenylboronic acid (Scheme 40). This gave the desired diene \textit{127} in satisfactory yield as one isomer. The reaction would not proceed to yield \textit{127} if \textit{124} did not possess an iodide moiety.
Bromo-deboration of silyl-dienyl boronate 97 following the conditions reported by Morken\textsuperscript{84} and Hartwig\textsuperscript{85} gave silyl-dienyl bromide 128 as one isomer in 58\% yield (Scheme 41). In addition, suitable conditions were discovered for a tandem silyl-boration/bromo-deboration of alkyne 41 to give silyl-dienyl bromide 128 in 57\% over two steps (Scheme 41). Attempts to form the Z,Z-dienyl bromide\textsuperscript{77} using Br\textsubscript{2}/NaOMe were not successful and gave unidentifiable complex mixtures.
Another means of derivatization was conversion of silyl-dienyl boronate 97 into triene 129 via Oxidative Heck reaction (Scheme 42). The resulting triene was stable to isolation via column chromatography and was obtained in 45% yield. Several attempts to improve the yield of this transformation gave no success. Surprisingly, the pinacol silyl-dienyl boronate 114 was unreactive under Oxidative Heck reaction conditions.

![Scheme 42. Formation of triene 129](image)

Lastly, boronate substrate 97 was subjected to Chan-Lam type conditions using stoichiometric copper. This transformation gave allyl ether 130 in a modest 40% yield (Scheme 43). Additional attempts to improve the yield were unsuccessful.

![Scheme 43. Copper-promoted etherification](image)
2.2.8 Conclusion

In conclusion, the formation of silyl-dienyl boronates via a trans-silylvinylation of internal alkynes has been demonstrated. This one step regio- and stereoselective method affords bi-functional diene scaffolds in good yields. The highly substituted olefins can be transformed into more complex products by iodo- and bromo-deboration and various metal-catalyzed coupling methods. In addition, the formation of a triene was demonstrated.

Future directions for this project would be to utilize the silyl-dienyl boronates towards the synthesis of a diene-containing natural product, an example being one from the myxalamide family. Synthesizing a natural product would further demonstrate the synthetic applicability of the newly formed silyl-dienyl boronates.
3.0 RUTHENIUM-HYDRIDE CATALYZED TRANS-SILYLVINYLATION OF INTERNAL ALKYNES: EXAMINATION OF MVK ADDITIVE AND ETHYLENE ATMOSPHERE

3.1 MVK ADDITIVE

3.1.1 Introduction and Reaction Discovery

While conducting a catalyst screen for the trans-silylvinylation of internal alkynes with acrylates (see chapter 1), an interesting discovery was made. In addition to the expected acrylate product 47A, a significant amount (42%) of vinylation product 131 was observed in the presence of RuHCl(CO)(H2IMes)(PPh3) (Scheme 44). NOE experiments later confirmed the formation and structure of 131.
Scheme 44. Reaction discovery: unexpected formation of vinylated product$^a$

$^a$ Reaction run by Shasha Liu and/or Jinbo Zhao.

Shortly thereafter, alkyne 41 was subjected solely to 5 mol% RuHCl(CO)(H$_2$IMes)(PPh$_3$) in refluxing DCE. After 24 hours, 70% conversion of the starting material and a 53% crude yield of diene 131 was observed. In addition, a minor by-product (17%) was also observed via $^1$H NMR analysis of the crude reaction mixture. The minor product was assigned as cycloisomerization adduct 132 (Scheme 45).

Scheme 45. Initial investigations$^a$

$^a$ Reaction run by Shasha Liu and/or Jinbo Zhao.
3.1.2 Reaction Optimization

Based on these initial results, it was hypothesized that the acrylate source played an important role in the reaction. Additional electron-deficient olefinic "additives" were screened and methyl vinyl ketone (MVK) proved to be superior because it provided the highest ratio of 131:132 and was easily removed from the reaction mixture (due to its volatility). Treating alkyne 41 with 5 mol% RuHCl(CO)(H$_2$IMes)(PPh$_3$) and 10 mol% MVK in refluxing DCE in a sealed tube resulted in consumption of the starting material after 5 hours. An 85% crude yield of vinylation product 131 was observed in addition to 15% of cycloisomerization product 132 (Scheme 46).

![Scheme 46. Trans-silylvinylation of 41 with MVK additive$^a$](image)

$^a$ Reaction run by Shasha Liu and/or Jinbo Zhao.

The reaction was further optimized by screening the amount of RuHCl(CO)(H$_2$IMes)(PPh$_3$) in relation to MVK (Table 21). With 5 mol% RuHCl(CO)(H$_2$IMes)(PPh$_3$), decreasing the amount of MVK from 10 mol% to 5 mol% (entry 2, 1:1 ratio) gave 55% crude yield of 131 after 5 hours with 83% conversion of the starting material. Increasing the amount of MVK to 20 mol% (entry 4, 1:4 ratio) resulted in 98% conversion of the starting material after 5 hours but the yield of 131 decreased to 68% (in comparison to entry 3 with 10 mol% MVK).
Lowering the catalyst loading to 2.5 mol% in the presence of 5 mol% MVK resulted in only 46% conversion of starting material after 24 hours with a poor crude yield (22%) of 131 (entry 5); however, drastically increasing the amount of MVK to 25 mol% (1:10 ratio) resulted in 100% conversion after 24 hours and 131 was observed in 88% crude yield (entry 6). When the amount of RuHCl(CO)(H$_2$IMes)(PPh$_3$) was further decreased to 1 mol% with 2 mol% MVK, the cycloisomerization product 132 was favored albeit in poor yield after 48 hours (13%, entry 7). Lastly, a significant increase of MVK to 25 mol% with 1 mol% RuHCl(CO)(H$_2$IMes)(PPh$_3$) (1:25 ratio) resulted in an improved ratio of 131:132, however, the crude yield of 131 decreased (in comparison to entry 3) and a longer reaction time was required (48 hours) to achieve 91% conversion. It was gathered from the results of Table 21 that use of 10 mol% MVK allowed for a short reaction time and superior ratio/yield of 131:132. Additionally, it was concluded that lower loadings of RuHCl(CO)(H$_2$IMes)(PPh$_3$) were tolerated in the presence of high concentrations of

---

**Table 21. Optimization of RuHCl(CO)(H$_2$IMes)(PPh$_3$) and MVK additive**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>MVK (mol%)</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Ratio 1V:1C$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^a$</td>
<td>5</td>
<td>0</td>
<td>24</td>
<td>70</td>
<td>53:17</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>83</td>
<td>55:9</td>
</tr>
<tr>
<td>3$^a$</td>
<td>5</td>
<td>10</td>
<td>5</td>
<td>100</td>
<td>85:15</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>20</td>
<td>5</td>
<td>98</td>
<td>68:11</td>
</tr>
<tr>
<td>5$^a$</td>
<td>2.5</td>
<td>5</td>
<td>24</td>
<td>46</td>
<td>22:10</td>
</tr>
<tr>
<td>6$^a$</td>
<td>2.5</td>
<td>25</td>
<td>24</td>
<td>100</td>
<td>88:12</td>
</tr>
<tr>
<td>7$^a$</td>
<td>1</td>
<td>2</td>
<td>48</td>
<td>27</td>
<td>6:13</td>
</tr>
<tr>
<td>8$^a$</td>
<td>1</td>
<td>25</td>
<td>48</td>
<td>91</td>
<td>76:8</td>
</tr>
</tbody>
</table>

$^a$ Reaction run by Shasha Liu/Jinbo Zhao. $^b$ Crude yield determined by $^1$H NMR using mesitylene as an internal standard.
MVK but with sacrificed (longer) reaction time. Use of 5 mol% RuHCl(CO)(H$_2$IMes)(PPh$_3$) and 10 mol% MVK (entry 3, results from Scheme 46), was chosen as the optimized conditions for the transformation.

### 3.1.3 Alkyne Substrate Tolerance

It was also discovered that a wide variety of silicon-tethered alkynes were tolerated in the trans-silylvinylation conditions with MVK additive (Scheme 47).$^{88}$

![Scheme 47. Substrate scope with MVK additive$^c$](image)

$^a$ Isolated yields of vinylated product V. $^b$ Ratio of crude reaction mixture (determined by $^1$H NMR using mesitylene as an internal standard). $^c$ All reactions run by Shasha Liu and Jinbo Zhao.

Alkyl and aryl substitution at the homo-propargylic position was well tolerated, in addition to various aromatic substitution at the alkyne terminus. The isolated yields of the vinylation products V were obtained in 55%-80% after column chromatography. In some cases, separation of the cycloisomerization product C from the desired product V was difficult; preparative thin layer chromatography was used in these cases.
The substrate scope was broadened to include alkyl substitution at the alkyne terminus. However, the expected trans-silylvinylation products (type V) were not observed; only cycloisomerization-type products were obtained from the reaction (Scheme 48).

![Scheme 48. Alkyl substituted alkynes with MVK additive\(^a\)](image)

\(^a\) All reactions run by Shasha Liu and/or Jinbo Zhao.

It was initially hypothesized that sterics resulting from the bulky tert-butyl group on the alkyne played a role in this unexpected observation, but exchange for the less hindered methyl group also gave solely the cycloisomerization product. The cycloisomerization of enynes in the presence of ruthenium is known but was not initially sought after by the Clark group.

With this prior body of work, it was wanted to explore the reactivity of substrates possessing substitution at the propargylic position, i.e. alkynes 77 and 80 (Scheme 49). When the previously-synthesized methyl-substituted alkyne 77 was subjected to the optimized conditions, it was expected to observe formation of cycloisomerization product 133.
However, we were perplexed to discover alkyne 77 did not react under these conditions even after 24 hours (eq. 1). It was hypothesized that propargylic substitution was the reasoning behind this discovery but confirmation was desired by examining other propargylic-substituted alkyne substrates. Subjection of phenyl-substituted alkyne 80 resulted in 100% conversion and gave solely the vinylation product 134 in 54% yield. In addition to alkynes 77 and 80, the effect of a racemic-syn and racemic-anti relationship was also examined with propargylic-substituted alkynes 135 and 137 (Scheme 50). The racemic-syn alkyne 135 worked well under the optimized conditions to give vinylation product 136 in 58% isolated yield (eq. 1). A trace amount of the cycloisomerization product (~2%) was observed in the crude reaction mixture but was not obtained after purification. The reaction of racemic-trans alkyne 137 was comparable to syn alkyne 135 and the resulting product 138 was isolated in 61% yield (eq. 2). The cycloisomerization product 139 was observed in the crude reaction ratio but was separated from 138 during purification.
Scheme 50. *Trans*-silylvinylation of propargylic substituted alkynes with MVK additive

\[ \text{Scheme 50} \]

- Isolated ratio of Z/E isomers as determined by \(^1\)H NMR.
- Ratio of 138:139 as determined by crude \(^1\)H NMR using mesitylene as an internal standard.
- Reaction run by Robert Wilson.

3.2 ETHYLENE ATMOSPHERE

3.2.1 Introduction and Reaction Discovery

Ethylene, the simplest of all alkenes, is produced in massive quantities (approximately 150 million pounds each day).\(^{89}\) It is an ideal source in vinylation chemistry because it possesses a high atom economy, having only one hydrogen lost during the vinylation process.\(^{90}\) Ethylene has been utilized in numerous transformations (Scheme 51), including hydrovinylation (eq. 1),\(^{18,91-93}\) Mizoroki-Heck (eq. 2),\(^{94,95}\) and enyne metathesis (eq. 3);\(^{96}\) however, its use for alkyne silylvinylation has not been thoroughly explored.
Since the presence of ethylene in silylvinylation chemistry had not been well explored, investigations and a comparison of the outcome of the silylvinylation protocol in an atmosphere of ethylene versus the previously reported MVK methodology was desired. The study began by treating alkyne 41 with RuHCl(CO)(H2IMes)(PPh3) in DCE at 80°C under a balloon of ethylene (Scheme 52).
With only 1 mol% catalyst, 100% conversion of the starting alkyne was observed after 1 h. Analysis of the crude $^1$H NMR spectrum revealed the expected major vinylation product 131 and two minor by-products, cycloisomerization adduct 132 and E isomer 140. Isolation of the product 131 by column chromatography resulted in an 80% yield as a 10:1 mixture of Z/E isomers (131:140).

### 3.2.2 Reaction Optimization

With this promising initial result in hand a catalyst screen was conducted to determine what role, if any, the ligand environment around the metal would have in the transformation (Table 22). Exchange for RuHCl(CO)(PCy$_3$)$_2$, the catalyst proven optimal in the acrylate and boronate coupling methodology, resulted in only 89% conversion after a 7 hour reaction time, but an improved product ratio of 55:4:1 was observed (entry 2).

![Reaction scheme](image)

**Table 22. Catalyst screen**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conv.</th>
<th>131:132:140</th>
<th>Crude Yield$^a$ of 131</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RuHCl(CO)(H$_2$Mes)(PPh$_3$)</td>
<td>1</td>
<td>100%</td>
<td>18:1:2</td>
<td>91%</td>
</tr>
<tr>
<td>2$^b$</td>
<td>RuHCl(CO)(PCy$_3$)$_2$</td>
<td>7</td>
<td>89%</td>
<td>55:4:1</td>
<td>55%</td>
</tr>
<tr>
<td>3$^b$</td>
<td>RuHCl(CO)(P'Bu$_2$Cy)$_2$</td>
<td>7</td>
<td>43%</td>
<td>1:0:0</td>
<td>23%</td>
</tr>
<tr>
<td>4$^b$</td>
<td>RuHCl(CO)(P'Bu$_2$Me)$_2$</td>
<td>7</td>
<td>33%</td>
<td>6:1:0</td>
<td>18%</td>
</tr>
<tr>
<td>5$^b$</td>
<td>RuHCl(CO)(P'Py$_2$(5,5-CF$_3$C$_6$H$_3$)$_2$</td>
<td>7</td>
<td>29%</td>
<td>1:0:0</td>
<td>11%</td>
</tr>
</tbody>
</table>

$^a$ Determined by crude $^1$H NMR using mesitylene as an internal standard. $^b$ 5 mol% catalyst used.
The bulky RuHCl(CO)(PrBu₂Cy)₂ complex gave only 23% crude yield of 131 after 7 hours (entry 3). The RuHCl(CO)(PrBu₂Me)₂ performed poorly, with 33% conversion of starting material and 18% crude yield of product observed after 7 hours (entry 4). Only 29% conversion and 11% crude yield of product was obtained with the electron-deficient phosphine complex RuHCl(CO)(PiPr₂[3,5-CF₃C₆H₃])₂ (entry 5). It was concluded that the NHC-bearing complex RuHCl(CO)(H₂IMes)(PPh₃) (entry 1) proved to be the optimal ruthenium catalyst for the trans-silylvinylation under ethylene atmosphere.

A brief solvent screen was also conducted for the transformation (Table 23). In addition to DCE (entry 1), the reaction was complete in 1 hour in toluene and α,α,α-trifluorotoluene at 85°C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Ratio of 131:132:140</th>
<th>Crude Yield of 131</th>
<th>Isolated Yield of 131</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCE</td>
<td>80</td>
<td>18:1:2</td>
<td>91%</td>
<td>80% (11:0:1)</td>
</tr>
<tr>
<td>2</td>
<td>toluene</td>
<td>85</td>
<td>12:1:1</td>
<td>71%</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>CF₃Ph</td>
<td>85</td>
<td>26:3:1</td>
<td>83%</td>
<td>74% (18:2:1)</td>
</tr>
</tbody>
</table>

Table 23. Brief solvent screen

*Ratio of the crude reaction mixture (determined by ¹H NMR using mesitylene as an internal standard).

b Determined by crude ¹H NMR using mesitylene as an internal standard.

In toluene (entry 2), a slightly decreased product ratio (12:1:1) and crude yield of 131 (71%) was obtained, so isolation was not deemed necessary. α,α,α-Trifluorotoluene gave an excellent product ratio of 26:3:1 but the crude (83%) and isolated yield of 131 were not as high as was
obtained with DCE (entry 3). It was concluded that 1 mol% RuHCl(CO)(H$_2$IMes)(PPh$_3$) in DCE at 80°C proved optimal for the trans-silylvinylation of internal alkynes under ethylene atmosphere.

3.2.3 Mechanistic Hypothesis

A mechanism that accounts for the trans-silylvinylation protocol is proposed in Scheme 53: dissociation of a triphenylphosphine ligand from RuHCl(CO)(H$_2$IMes)(PPh$_3$) gives 141 (possessing an open coordination site). Introduction of alkyne 41 allows for the ruthenium complex to add to the most sterically accessible position on the vinyl moiety, giving 49. Subsequent β-silyl transfer (with loss of ethylene) gives silyl-ruthenium species 42. Cis silyl-ruthenation (43-cis) followed by isomerization (43-trans) and subsequent ethylene insertion results in the formation of intermediate 142. (Although direct trans-metallation is known in the literature$^{30, 37, 38, 97-99}$ [see section 1.2.3 in this thesis], it is believed that a cis-metallation followed by isomerization has occurred due to minor isomer 140 appearing in the crude reaction mixture and isolated material.) The product 131 is generated upon β-hydride elimination and the active catalytic species 141 is regenerated.
3.2.4 Substrate Scope

Once the conditions were optimized, the alkyne substrate scope was evaluated. Initially alkynes bearing a phenyl group at the terminus were scrutinized (Table 24). It is important to note that the cycloisomerization by-product was observed with each alkyne substrate examined but it was separated from the desired vinylation product. However, separation of the Z/E stereoisomers was not successful. In some cases the ratio was improved after isolation. To begin,
the previously synthesized alkyne 80, possessing propargylic substitution, performed well in the transformation and gave the desired product 134 in 68% yield (14:1).

![Chemical structure diagram]

Table 24. Phenyl-substituted alkyne scope

<table>
<thead>
<tr>
<th>Alkyne</th>
<th>Product</th>
<th>Ratio&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Isolated Yield&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Alkyne</th>
<th>Product</th>
<th>Ratio&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Isolated Yield&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>131</td>
<td>18:1:2</td>
<td>80% (9:1)</td>
<td>57</td>
<td>143&lt;sup&gt;d&lt;/sup&gt;</td>
<td>17:2:1</td>
<td>70% (17:1)</td>
</tr>
<tr>
<td>80&lt;sup&gt;d&lt;/sup&gt;</td>
<td>134&lt;sup&gt;d&lt;/sup&gt;</td>
<td>8:1:1</td>
<td>68% (14:1)</td>
<td>144</td>
<td>145&lt;sup&gt;e&lt;/sup&gt;</td>
<td>34:1:3</td>
<td>78% (11:1)</td>
</tr>
</tbody>
</table>

<sup>a</sup> The synthesis of the alkyne substrates can be found in the experimental chapter of this thesis. <sup>b</sup> Ratio of the crude reaction mixture as determined by <sup>1</sup>H NMR using mesitylene as an internal standard. <sup>c</sup> Isolated yields are reported as a ratio of Z/E isomers. <sup>d</sup> Reaction run with 2 mol% catalyst. <sup>e</sup> Reaction run with 5 mol% catalyst.

The yield of 134 (68%) was substantially better under an ethylene atmosphere than in the presence of the MVK additive (54%). Additional alkyl substitution was tolerated, with the cyclohexyl-substituted 143 isolated in 70% yield (17:1). An improvement in yield compared to MVK additive was also observed (64%). Lastly, a cis 6,5-fused ring system was also tolerated and gave vinylation product 145 in 78% yield (11:1).

Various aryl functionality on the alkyne terminus was also examined (Table 25). Para-substitution was well tolerated and the 4-fluorophenyl moiety 146 was isolated in 64% yield.
The bulky napthyl group was also tolerated in the reaction and provided 148 in 73% yield (13:1). Additionally, a 3,5-xylyl group worked well and 149 was essentially isolated as one isomer (26:1) in 74% yield.

![Chemical structure diagram]

Table 25. Aryl-substituted alkyne scope

<table>
<thead>
<tr>
<th>Alkyne*</th>
<th>Product</th>
<th>Ratio&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Isolated Yield&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Alkyne*</th>
<th>Product</th>
<th>Ratio&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Isolated Yield&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>64 146</td>
<td>O-Si- 4-F</td>
<td>23:3:1</td>
<td>64% (20:1)</td>
<td>67 149d</td>
<td>O-Si- 3,5-Xyl</td>
<td>32:3:1</td>
<td>74% (26:1)</td>
</tr>
<tr>
<td>147 148d</td>
<td>O-Si- 1-Nap</td>
<td>24:1:2</td>
<td>73% (13:1)</td>
<td>150 151e</td>
<td>O-Si- 4-NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4:1:2</td>
<td>30% (2:1)</td>
</tr>
</tbody>
</table>

<sup>a</sup> The synthesis of the alkyne substrates can be found in the experimental chapter of this thesis.  
<sup>b</sup> Ratio of the crude reaction mixture as determined by <sup>1</sup>H NMR using mesitylene as an internal standard.  
<sup>c</sup> Isolated yields are reported as a ratio of Z:E.  
<sup>d</sup> Reaction run with 5 mol% catalyst.  
<sup>e</sup> Reaction run with 2 mol% catalyst.

The electron-withdrawing para-nitro moiety was also examined, but the resulting diene 151 was isolated in only 30% yield with a poor isomeric ratio of 2:1.

It was also desired to examine the reactivity of the previously synthesized methyl-substituted alkyne 77, which proved unreactive in the trans-silylvinylation protocol with MVK additive (see Scheme 49, eq. 1). It was discovered that under an atmosphere of ethylene a 90%
conversion of the alkyne 77 was observed after 7 hours in the presence of 5 mol% RuHCl(CO)(H₂IMes)(PPh₃) (Scheme 54).

Scheme 54. Reactivity of alkyne 77 under ethylene atmosphere

a Ratio of the isolated material determined by ¹H NMR. b Determined by ¹H NMR using mesitylene as an internal standard.

When alkyl-substituted alkynes were subjected to the silylvinylation conditions with MVK additive, the cycloisomerization-type product was the only product observed (see Scheme 48). Formation of the cycloisomerization product 133 was expected under an atmosphere of ethylene but surprising vinylation products 152 and 153 were observed. Additionally, no presence of 133 was detected in the crude reaction mixture by ¹H NMR. Despite not having an explanation to the aforementioned result, vinylation product 152 was isolated in 56% yield as a 4:1 isomeric mixture.
3.2.5  Increase of Ethylene Pressure

The substrates explored under an ethylene of atmosphere gave an improved ratio of vinylation to cycloisomerization (V:C) in comparison to MVK additive. With that in mind, the possibility of eliminating isomer C was desired. Based on the mechanistic hypothesis (see Scheme 53), it was envisioned that increasing the pressure of ethylene in the system would increase the production of vinylation isomer V and thwart production of isomer C due to the affinity of ethylene adding to the ruthenium. Additionally, it was predicted that an increased pressure of ethylene could trap intermediate 43-cis prior to isomerization to 43-trans, thus decreasing or possibly eliminating the Z vinylation isomer altogether.

Under a balloon of ethylene a 9:1 ratio of \textbf{131:140} was observed (Table 26, entry 1). Increasing the pressure of ethylene to 20 psi increased the amount of \textbf{140} (entry 2). At 40 psi, an additional increase in formation of \textbf{140} was observed (entry 3).

![Scheme 53](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pressure</th>
<th>Ratio* 131:140</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>balloon</td>
<td>9:1</td>
</tr>
<tr>
<td>2\textsuperscript{b}</td>
<td>20 psi</td>
<td>6:1</td>
</tr>
<tr>
<td>3\textsuperscript{b}</td>
<td>40 psi</td>
<td>2.5:1</td>
</tr>
<tr>
<td>4</td>
<td>60 psi</td>
<td>1:1.4</td>
</tr>
<tr>
<td>5</td>
<td>80 psi</td>
<td>1.2</td>
</tr>
<tr>
<td>6\textsuperscript{b,c}</td>
<td>80 psi $\Delta_{(q)}$</td>
<td>1.0</td>
</tr>
</tbody>
</table>

\textit{Table 26. Increase of ethylene pressure}

\textsuperscript{a} Ratio determined by crude $^1$H NMR using mesitylene as an internal standard. \textsuperscript{b} Reaction run by Robert Wilson.

\textsuperscript{c} 23% conversion and 11% of \textbf{131} was observed.
At 60 psi and 80 psi a reversal in product ratio was observed, with 140 being the major isomer formed in the reaction (entries 4 and 5). In addition, no cycloisomerization product was observed under increased pressures of ethylene. Lastly, to determine if ethylene pressure or ethylene concentration influenced the selectivity outcome, an experiment with increased pressure of argon was conducted (entry 6). Under 80 psi of argon, 23% conversion of alkyne 41 was observed with an 11% crude yield of isomer 131 only. This supports the idea that increased ethylene concentration thwarts isomerization (promotes formation of 140), thus favoring syn-silylvinylation.

It was also desired to examine the effect of increased ethylene pressure on substrates that solely formed the cycloisomerization product, as reported in the previous methodology with MVK additive (Scheme 55). Subjection of methyl-substituted alkyne 68 to 80 psi of ethylene resulted in an 80% isolated yield of a 1:1 mixture of 154; the cycloisomerization product 155 was not observed.

Scheme 55. Increased ethylene pressure with alkyl-substituted alkyne 68

* Isolated yield as a 1:1 ratio of Z/E isomers. * Reaction with MVK additive run by Shasha Liu.
The effects of increased ethylene pressure on the previously synthesized methyl substituted alkyne 77 was also examined (Scheme 56). A reversal in selectivity in comparison to balloon pressure of ethylene was observed. After 4 hours at 80 psi, the ratio of 152:153 was 1:1.1, which supports the aforementioned hypothesis. To the best of our knowledge, the use of increased pressures of ethylene to alter the stereoselectivity of a reaction has not been shown previously.

Scheme 56. Increased ethylene pressure with alkyne 77

*a Determined by $^1$H NMR using mesitylene as an internal standard.

3.2.6 Synthetic Elaboration

The synthetic utility of the vinylation products by various transformations was demonstrated (Scheme 57). Fleming-Tamao oxidation$^{100, 101}$ of diene 154 (1:1 mixture of Z/E isomers) under acidic conditions 18V gave the desired diene 156 as one double-bond isomer in 73% yield.

Scheme 57. Synthetic elaboration
3.3 CONCLUSION

In conclusion, a ruthenium-catalyzed trans-silylvinylation of internal alkynes with MVK as an additive was demonstrated. This regiospecific 5-exo-dig process provided 1,3-dienes in good yields. In addition to formation of the expected vinylation products, cycloisomerization minor by-products was observed. The substrate scope of the silylvinylation included aryl-substituted alkynes and was tolerable to substitution at the propargylic substitution, however, methyl-substituted alkyne 77 was unreactive.

The ruthenium-hydride catalyzed trans-silylvinylation of silicon-tethered alkynes under an atmosphere of ethylene was also demonstrated. With substantially shorter reaction times, lower catalyst loadings and improved product ratio and yields, this methodology significantly improved upon the previous methodology that utilized MVK as an additive. Increased pressures of ethylene altered the Z/E product ratio and prevented formation of cycloisomerization isomer C. Use of alkyl-substituted alkynes with increased ethylene pressure allowed for isolation of only vinylation-type products. The synthetic utility of the dienes was demonstrated via a Fleming-Tamao oxidation.

Future directions for this project would be for the development of reaction conditions tolerable to terminal alkyne substrates. Conditions for tolerance of various substitution on the vinyl silicon tether (i.e. phenyl, alkyl) should also be examined to allow for greater diversity on the silicon atom. Lastly, greater pressures of ethylene (up to 1000 psi) should be examined to further evaluate the Z/E product ratio of the vinylation products.
4.0 RUTHENIUM CATALYZED CYCLOISOMERIZATION OF SILICON-TETHERED 1,7-ENYNES

4.1 INTRODUCTION

One of the most common methods for acquiring dienes is via the cycloisomerization of enynes. This method is greatly beneficial because the reactions require the use of few reagents and generate minimal by-products. Another advantage is the relative ease of synthesis of the starting enynes. Additionally, transition metal-catalyzed cycloisomerization reactions are an atom-economical route to achieve molecular complexity and access diene scaffolds. A plethora of transition metals have been used to catalyze the cycloisomerization of enynes to form dienes: palladium (pioneered by Trost), rhodium, iridium, platinum, gold, titanium, chromium, iron, cobalt, nickel, silver, gallium, indium and lastly, ruthenium (which will be discussed in detail in this chapter).

4.1.1 Ruthenium-catalyzed cycloisomerization of enynes to form dienes

The first reported use of ruthenium to catalyze the cycloisomerization of enynes was by Chatani and Murai in 1994. A catalytic amount of a ruthenium complex [RuCl₂(CO)₃]₂ was
utilized under an atmosphere of CO with 1,6-enynes to form 1,3-dienes selectively (Scheme 58). After exploring other ruthenium complexes, it was deemed the presence of a halide and CO ligands on ruthenium necessary for the reaction to proceed.

The conditions were tolerable for a substrate bearing no substitution on the alkyne terminus or on the olefinic terminus (eq. 1) and gave the product in 96% yield. Regardless of the geometry of the starting enyne, the $E$ geometry was observed in the products (eq. 2). This methodology was also demonstrated with a 1,7-enyne and gave the six-membered ring product in 86% yield (eq. 3). At the time, Trost's palladium conditions in the presence of 1,7-enynes resulted solely in the formation of bicyclo[4.2.0]octene derivatives.$^{194}$

In 1995, Trost published on the intermolecular coupling of alkynes and alkenes (Alder-Ene) to give linear and branched 1,4-dienes catalyzed by CpRu(COD)Cl.$^{195}$ A few years later, Trost
and Toste were able to develop conditions for an intramolecular version utilizing 1,6-enynoates and catalyzed by the cationic ruthenium complex \([\text{CpRu(MeCN)}_3]\text{PF}_6\) (Scheme 59).

Interestingly, the ring size of the product varied when the number of substituents at the propargylic position of the starting 1,6-enynoate substrate was altered. Substrate 163, bearing a single-substituent (silyl ether) at the propargylic position, yielded a cyclopentene 164 (eq. 1); however, when a quaternary center was introduced at the propargylic position of the enynoate (165), cycloheptene 166 was obtained in 67% yield (eq. 2). It was determined that two different mechanistic pathways accounted for this change in selectivity. They proposed the formation of 164 as follows (Scheme 60): coordination of the cationic ruthenium species to the olefin and alkyne moieties of enynoate 163 (167) and oxidative cyclization resulted in the formation of ruthenacyclopentene 168. Subsequent β-hydride elimination gave vinyl ruthenium hydride 169, which yielded diene 164 upon reductive elimination and regeneration of the active catalytic species.

Scheme 59. Formation of cyclopentene vs. cycloheptene derivatives
Scheme 60. Cycloisomerization via a ruthenacyclopentene intermediate

The formation of 166 is believed to proceed via an allylic C-H activation pathway (Scheme 61). Activation of the allylic position of enynoate 165 (170) generated π-allyl intermediate 171. A 7-exo-dig carboruthenation of 171 gave vinyl ruthenium hydride 172 which subsequently underwent reductive elimination to yield cycloheptene 166. The rationale for 165 proceeding via a C-H activation pathway is due to the avoidance of a possible steric congestion that would arise during the formation of a ruthenacyclopentene intermediate (A₁,₃-type strain that would occur between the quaternary center and the methyl ester). With understanding of the reaction selectivity, Trost was able to isolate a variety of cycloheptenes by varying the substituents of the quaternary center located at the propargylic position of the 1,6-enynoates.
Shortly thereafter, Trost and Toste extended the methodology to include enynes not containing an ester moiety on the alkyne terminus (Scheme 62). With 10 mol% of cationic \([\text{CpRu(MeCN)}_3]\text{PF}_6\), the formation of 1,4-dienes was demonstrated (five- and six-membered ring products) from 1,6-enynes (eq. 1) and from 1,7-enynes (eq. 2).

Scheme 62. Examples of Trost's Ru-catalyzed cycloisomerization of 1,6- and 1,7-enynes
In addition, it was demonstrated the first example where the regioselectivity of the reaction is dependent upon the geometry of the olefin in the enyne substrate (Scheme 63).\textsuperscript{197}

The reaction of enyne 177, possessing an \textit{E} olefin, with 10 mol\% [CpRu(MeCN)\textsubscript{3}]PF\textsubscript{6} in DMF favored formation of the more substituted 1,4-diene 178\textsubscript{A} (8:1). Whereas the reaction of enyne 179, possessing a \textit{Z} olefin, with the aforementioned conditions resulted in a complete reversal of selectivity, with 1,4-diene 178\textsubscript{B} being favored (17:1). The regioselectivity of these transformations can be explained via examination of the ruthenacyclopentene intermediates (Figure 8). In both cases, the substituents on the ruthenacyle oriented in a pseudoequatorial manner place a hydrogen proximal to the ruthenium, which in turn allows for the overlap needed for β-hydride elimination to occur. With enyne 177, the long alkyl chain is oriented pseudoequatorially, allowing for β-hydride elimination of H\textsubscript{a} to give diene 178\textsubscript{A}. With enyne 179, the methyl group is oriented pseudoequatorially, allowing for β-hydride elimination to give the less substituted diene 178\textsubscript{B}.
Up to this point, all cases reported by Trost et al. utilizing 1,6- and 1,7-enynes/enynoates result in the formation of 1,4 dienes, respectively. Shortly thereafter (in 2000), Dixneuf et al. synthesized 1,3-dienes using Cp*Ru(COD)Cl as a "pre-catalyst" (Scheme 64).  

Scheme 64. Cycloisomerization of 1,6-enynes via Cp*Ru(COD)Cl "pre-catalyst"

Various enynes were transformed into tetrahydrofurans containing a 1,3-diene moiety (one example shown in eq. 1) under catalytic amounts of Cp*Ru(COD)Cl in the presence of ethanol or acetic acid. Polymerization was observed when a terminal alkyne was reacted in ethanol; acetic acid at 65°C was used to circumvent polymerization. To account for the reaction...
mechanism and active catalytic species (Scheme 65), treatment of Cp*Ru(COD)Cl in ethanol or acetic acid causes decoordination of the COD ligand and generates Cp*RuH(OAc/OEt)Cl \textit{in situ}. Coordination of the ruthenium hydride to the alkyne moiety of enyne 184 (185) and cis addition to the alkyne generates vinyl ruthenium 186, which undergoes insertion into the olefinic moiety to give the tetrahydrofuran 187. Subsequent $\beta$-hydride elimination of H$_a$ yields the product diene 188 and regenerates the active ruthenium hydride species.

\begin{center}
\textbf{Scheme 65. Mechanistic pathway for Cp*RuH(OAc)Cl-catalyzed cycloisomerization}
\end{center}

A deuterium label study was conducted to evaluate the mechanism (Scheme 64, eq. 2). The cycloisomerization was conducted in deuterated acetic acid and the resulting deuterated diene
was obtained. The orientation of the deuterium atom confirmed that the addition of Ru-D occurred in a cis manner to the alkyne.

In 2002, Trost and Toste reported on further mechanistic investigations into their ruthenium-catalyzed cycloisomerization protocol. As previously mentioned, their conditions afford 1,4-dienes, respectively. However, it was mentioned a special case in which a mixture of 1,4- and 1,3-dienes was obtained (Scheme 66).

![Scheme 66. Special case of Trost's conditions](image)

The 1,6-enyne 189 bearing a cyclobutane on the olefin terminus gave a 2:1 mixture of 1,4-diene 190 and 1,3-diene 191 when subjected to their standard ruthenium conditions. The reasoning for the formation of 191 can be attributed via examination of the reaction pathway (Scheme 67). Upon oxidative cyclization of 192, ruthenacyclopentene 193 is formed. Exocyclic β-hydride elimination of H_a to form 1,4-diene 195 is challenging (but feasible) because of the strain resulting in the formation of an alkylidenecyclobutane. The reasoning to why 1,3-diene formation occurred is due to the competition for endocyclic β-hydride elimination of H_b (194). After reductive elimination of the vinyl ruthenium hydride species (194, 195), the mixture of dienes 190 and 191 is accounted.
Scheme 67. Mechanistic explanation for 1,3-diene formation

In 2004, Trost et al. demonstrated the effects of an allylic silyl ether moiety on the stereoselectivity of ruthenium-catalyzed enyne cycloisomerizations (Scheme 68). It was discovered that the E/Z product selectivity was reversed when exchanging the Cp ligand for the Cp* ligand on the ruthenium catalyst. When the starting enyne 196 was subjected to 10 mol% [CpRu(MeCN)_3]PF_6, the trans silyl enol ether (E)-197 was favored 2.4:1. Exchange for [Cp*Ru(MeCN)_3]PF_6 resulted in reversal of selectivity, with the cis silyl enol ether (Z)-197 being favored 5:1.
Examination of the ruthenacyclopentene intermediates formed from this transformation can account for the reversal in selectivity (Figure 9). Formation of the $E$ olefin geometry resulted from $\beta$-hydride elimination of $H_b$. When the $Cp$ ligand was exchanged for the $Cp^*$ ligand, the steric repulsion between the silyl ether and the $Cp^*$ ligand disfavored $\beta$-hydride elimination of $H_b$.

When the silyl ether is orientated away from the ligand, the steric strain is relieved and $H_a$ is placed proximally to the metal. Subsequent elimination of $H_a$ resulted in formation of the $Z$ olefin geometry.
In addition, the possible effects of the Cp and Cp\(^*\) ligands on the diastereoselectivity of a cycloisomerization was examined (Scheme 69).\(^{199}\)

\[\text{Scheme 69. Cp vs. Cp}^*\text{ stereoselectivity outcome}\]

It was observed that the diastereomeric ratio (d.r.) of the resulting diene 199 was greatly enhanced from 2.2:1 to 32:1 when the Cp ligand was exchanged for the Cp\(^*\) ligand. The rationale behind the enhancement in selectivity can be explained from examination of the ruthenacyclopentene intermediate formed (Figure 10).

\[\text{Figure 10. Comparison of intermediates to account for diastereoselectivity}\]

In regards to the selectivity with the Cp ligand, the \textit{trans} isomer is somewhat favored due to only a slight steric interaction being observed between the methyl group and the Cp ligand present in the \textit{cis} intermediate. When the Cp ligand is exchanged for the Cp\(^*\) ligand, the dr is dramatically
improved because the steric interaction is significantly enhanced between the ligand and methyl group.

In 2008, Trost et al. extended their ruthenium-catalyzed methodology to include formation of trans-fused decalin scaffolds (Scheme 57).\textsuperscript{104}

\begin{center}
\textbf{Scheme 70. Synthesis of trans-fused decalin system}
\end{center}

In the presence of 10 mol\% $\text{[CpRu(MeCN)$_3$]PF$_6}$, the starting 1,7-enynoate 200 gave a 90\% yield of the trans-decalin system 201 as a single diastereomer. A variety of 1,7-enynes were scrutinized but it was deemed necessary to have an electron withdrawing group (ester, aldehyde, amide) at the quaternary center of the enyne substrate. In addition, the enynes investigated contained an ester or amide moiety on the alkyne terminus. It was initially hypothesized by the group that a cis-fused decalin system would arise from the reaction conditions. It was thought that the electron withdrawing group on the alkyne would act as a directing group for allylic C-H activation. However, it was determined that since the carbon-carbon bond formation occurred syn to the ester, the C-H insertion must have occurred from the same face. Therefore, the
carbonyl moiety on the quaternary center acted as a directing group and allowed for the stereoselective formation of the allyl ruthenium species (Scheme 70). Subsequent ligand exchange, carboruthenation and reductive elimination generated the trans-fused decalin product as a single diastereomer.

Recently, Chatani et al. reported the cycloisomerization of 1,6-enynes catalyzed by a mixed valence Ru(II)-Ru(III) complex to give endocyclic 1,3-dienes in excellent yields (example shown in Scheme 71).\textsuperscript{200} The group previously investigated the cycloisomerization of enynes catalyzed by a similar complex, Rh\textsubscript{2}(O\textsubscript{2}CCF\textsubscript{3})\textsubscript{2}\textsuperscript{149}. More recently they have investigated the catalytic activity of a Ru\textsubscript{2}(OAc)\textsubscript{4}X complex due to its structural similarity with the rhodium species and its minimal use in organic synthesis.

\textbf{Scheme 71. Cycloisomerization catalyzed by a mixed valence Ru(II)-Ru(III) complex}

The reaction with [Ru\textsubscript{2}(O\textsubscript{2}CPh)\textsubscript{4}(THF)]BF\textsubscript{4} tolerated a variety of 1,6-enynes bearing alkyl and aromatic functionality. In addition, it was observed that the yields of the dienes were dramatically improved when the reactions were carried out under an atmosphere of CO (or O\textsubscript{2}). It was believed that a CO atmosphere increased the electrophilicity of the catalyst by coordinating to the ruthenium, which in turn greater facilitated the interaction between the metal and the alkyne moiety due to its $\pi$-acidity.\textsuperscript{201}
4.2 REACTION DISCOVERY

Initially, we were intrigued by methodology reported by Mori et al. that gave unique 1,3-diene systems (Scheme 72). Subjection of 1,6-enyne 157 to 5 mol% Cp*Ru(COD)Cl under an atmosphere of ethylene produced 1,3-diene 204 in 85% yield. The methodology was intriguing because the expected reductive elimination pathway did not occur (typically observed with ruthenacyclopentene intermediates).

Mori proposed that once oxidative cyclization of the starting enyne (ruthenacyclopentene formation) occurred, insertion of ethylene (A in Scheme 72) generated a ruthenacycloheptene intermediate B. Subsequent β-hydride elimination gave a ruthenium hydride complex C which underwent reductive elimination to form the 1,3-diene product 204. We sought to apply this novel methodology to our silicon-tethered alkyne substrates (Scheme 73).
The investigation began by reacting silicon-tethered alkyne 41 with 10 mol% Cp*Ru(COD)Cl under an atmosphere of ethylene in toluene at room temperature (Scheme 74, eq. 1). After 4 hours, analysis of the reaction by TLC indicated a new spot (possibly product) but starting material remained. After 17 hours, 30% conversion of 41 was obtained and the only product observed was diene 132, which was believed to result from a cycloisomerization pathway.

Increasing the reaction temperature to 70°C (Scheme 74, eq. 2) resulted in 100% conversion of 41 in only 3 hours. A 94% crude yield of 132 was obtained. This type of product was seen with the silylvinylation methodology discussed in chapter 3, but only as a minor isomer. This result
was intriguing because this chemistry provided a potential route for selectively obtaining these products.

Based on the prediction of 132 resulting from a cycloisomerization pathway, it was desired to determine if an atmosphere of ethylene was necessary for the reaction to proceed (Scheme 75). The reaction of alkyne 41 with 10 mol% Cp*Ru(COD)Cl in toluene at 70°C under Ar(g) shortened the reaction time to 1 hour and a quantitative crude yield of 132 (82% isolated) was obtained. Based on this result, it was determined that ethylene was not needed in the reaction.

![Reaction Scheme](attachment:image.png)

**Scheme 75. Reaction discovery: argon atmosphere**

* Determined by ¹H NMR using mesitylene as an internal standard.

Typically when a 1,7-enyne is subjected to ruthenium-catalyzed cycloisomerization conditions, a 1,4-diene is formed (as discussed in 4.1.1 of this thesis). It was pleasing to discover that our new methodology extended the utility of such ruthenium-catalyzed cyclization reactions to selectively give a 1,3-diene from a 1,7-enyne.
4.3 MECHANISTIC HYPOTHESIS

Mechanistically, the transformation is believed to proceed as follows (Scheme 76): dissociation of the COD ligand (206) and coordination to the 1,7-ene 41 gives 207, which undergoes oxidative cyclization to form ruthenacyclopentene 208. To selectively obtain the exocyclic diene that was observed (132), it is believed that an endocyclic β-hydride elimination of H_a must occur to form the vinyl ruthenium hydride 209. Subsequent reductive elimination produces the 1,3-diene 132 and regenerates the active catalytic species.

Scheme 76. Mechanistic hypothesis
The ruthenium complex Cp*Ru(COD)Cl has been previously shown to undergo ruthenacyclopentene formation (Scheme 77). Sato et al. used Cp*Ru(COD)Cl to catalyze the regio- and stereoselective formation of 2-amino-1,3-dienes.\textsuperscript{203}

Scheme 77. Example of Cp*Ru(COD)Cl forming a ruthenacyclopentene intermediate

It was proposed that Cp*Ru(COD)Cl catalyzed the oxidative cyclization of ynamide 210 and ethylene to generate a ruthenacyclopentene A, which subsequently underwent β-hydride elimination to afford B and reductive elimination to give the 2-amino-1,3-diene product 211.

4.4 REACTION OPTIMIZATION\textsuperscript{204}

4.4.1 Catalyst Screen

It was sought to design a route to selectively obtain 132 by moving away from ruthenium hydride complexes (typically known to form dienes via hydrometallation).\textsuperscript{1, 19} The investigation
began by treating 10 mol% of the ruthenium $p$-cymene dimer [RuCl$_2$(p-cymene)]$_2$ with alkyne 41 in toluene at 70°C (Table 27, entry 1). After 8 hours no reaction was observed. Complexes bearing the chelating dppm ligand (entries 2 and 3) also were ineffective for the cyclization. The cationic ruthenium complex [CpRu(MeCN)$_3$]PF$_6$ (favored by Trost) was also unreactive (entry 4). The indenyl bis-triphenylphosphine complex in entry 5 gave only a 13% crude yield of 132 after 17 hours.

![Reaction diagram](image)

**Table 27. Catalyst screen**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[RuCl$_2$(p-cymene)]$_2$</td>
<td>70</td>
<td>8</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>RuCl(Ind)(dppm)</td>
<td>70</td>
<td>18</td>
<td>NR</td>
</tr>
<tr>
<td>3</td>
<td>CpRuCl(dppm)</td>
<td>70</td>
<td>17</td>
<td>NR</td>
</tr>
<tr>
<td>4</td>
<td>[CpRu(MeCN)$_3$]PF$_6$</td>
<td>70</td>
<td>6</td>
<td>NR</td>
</tr>
<tr>
<td>5</td>
<td>RuCl(Ind)(PPh$_3$)$_2$</td>
<td>70</td>
<td>17</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>CpRuCl(PPh$_3$)$_2$</td>
<td>70</td>
<td>18</td>
<td>86</td>
</tr>
<tr>
<td>7</td>
<td>Cp*RuCl(PPh$_3$)$_2$</td>
<td>70</td>
<td>2</td>
<td>&gt;98</td>
</tr>
<tr>
<td>8</td>
<td>Cp*Ru(COD)Cl</td>
<td>70</td>
<td>1</td>
<td>&gt;98</td>
</tr>
<tr>
<td>9$^b$</td>
<td>Cp*Ru(COD)Cl</td>
<td>70</td>
<td>20</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>Cp*Ru(COD)Cl</td>
<td>50</td>
<td>16</td>
<td>&gt;98</td>
</tr>
<tr>
<td>11</td>
<td>Cp*Ru(COD)Cl</td>
<td>23</td>
<td>16</td>
<td>11</td>
</tr>
</tbody>
</table>

$^a$ Crude yield determined by $^1$H NMR using mesitylene as an internal standard. $^b$ Reaction run with 5 mol% catalyst.

Full conversion of alkyne 41 was achieved after 18 hours with the Cp bis-triphenylphosphine complex in entry 6 and 132 was obtained in 86% yield. Exchange for the Cp* ligand proved more effective and gave full conversion of 41 with a quantitative yield of 132 after 2 hours (entry 7). We hypothesize that the bulky Cp* ligand increases the rate of β-hydride elimination. Exchange of the triphenylphosphine ligand for the COD ligand (Cp*Ru(COD)Cl, as previously
noted in Scheme 75), resulted in consumption of the starting material after 1 hour and gave quantitative crude yield of 132. With these results in hand, it was concluded that Cp*Ru(COD)Cl proved to be optimal for the cyclization because of quantitative crude yield of 132 being obtained in a reduced reaction time of 1 hour (Table 27, entry 8). Reduction of the loading of Cp*Ru(COD)Cl to 5 mol% gave 90% crude yield of the product after 20 hours (entry 9), so 10 mol% was deemed necessary for the cyclization. Having found Cp*Ru(COD)Cl the most apt for the transformation, additional reaction temperatures were examined. Decreasing the reaction temperature to 50°C (entry 10) resulted in quantitative yield of 132 however, a much longer reaction time was required; room temperature (entry 11) proved futile with only 11% yield of 132 observed after 16 hours. Entry 8, 10 mol% Cp*Ru(COD)Cl at 70°C, proved to be optimal for the cyclization.

4.4.2 Solvent Screen

Additional solvents were examined with 10 mol% Cp*Ru(COD)Cl (Table 28). Methanol at 70°C consumed the starting material rapidly (30 minutes) however, the major product observed was the desilylated starting alkyne (entry 2).
Table 2. Solvent screen

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Conversion</th>
<th>Yield*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>70</td>
<td>1</td>
<td>100%</td>
<td>&gt;98%</td>
</tr>
<tr>
<td>2</td>
<td>Methanol</td>
<td>70</td>
<td>0.5</td>
<td>100%</td>
<td>15%</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>70</td>
<td>1.5</td>
<td>100%</td>
<td>&gt;98%</td>
</tr>
<tr>
<td>4</td>
<td>DCE</td>
<td>70</td>
<td>1.5</td>
<td>100%</td>
<td>&gt;98%</td>
</tr>
<tr>
<td>5</td>
<td>DCM</td>
<td>45</td>
<td>8</td>
<td>77%</td>
<td>77%</td>
</tr>
<tr>
<td>6</td>
<td>Acetone</td>
<td>60</td>
<td>6</td>
<td>100%</td>
<td>&gt;98%</td>
</tr>
</tbody>
</table>

* Determined by crude $^1$H NMR using mesitylene as an internal standard.

DMF, one of the solvents of choice for Trost in cycloisomerization reactions, gave 100% conversion of 41 and quantitative crude yield of 132 after 1.5 hours (entry 3); DCE gave identical results (entry 4). Only 77% conversion of the starting enyne was observed after 8 hours with DCM at reflux (entry 5). Lastly, acetone (another solvent of choice for Trost) was sluggish in the transformation but gave quantitative crude yield of 132 after 6 hours (entry 6). Based on the results from the solvent screen, it was concluded that toluene proved superior due to quantitative crude yield of product observed after 1 hour (entry 1).

4.4.3 Variation of Silicon Tether

Variations to the substituents on silicon were explored utilizing the optimized conditions (Table 29). Both methyl-phenyl (entry 2) and diphenyl (entry 3) substituted silanes (212 and 213) gave shorter reaction times compared to the dimethyl in entry 1, presumably due to an increased Thorpe-Ingold effect.\textsuperscript{39,207} Having bulky isopropyl groups on the silane hampered the
reaction and only 26% conversion of the starting alkyne 214 was observed after 45 hours. It is believed the steric bulk on the silicon hindered the formation of the ruthenacyclopentene. Although the reaction times of alkynes 212 and 213 were shorter, the dimethylvinyl silicon tether (entry 1, alkyne 41) was chosen due the availability and low cost of the starting vinylidimethylchlorosilane (<$1 per gram from Gelest).

![Reaction diagram]

Table 29. Variation of silicon tether

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne</th>
<th>R₁</th>
<th>R₂</th>
<th>Time (h)</th>
<th>Conversion</th>
<th>Product</th>
<th>Yield[a, c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41</td>
<td>Me</td>
<td>Me</td>
<td>1</td>
<td>100%</td>
<td>132</td>
<td>&gt;98% (82%)</td>
</tr>
<tr>
<td>2</td>
<td>212</td>
<td>Me</td>
<td>Ph</td>
<td>0.5</td>
<td>100%</td>
<td>215</td>
<td>&gt;98% (83%)</td>
</tr>
<tr>
<td>3</td>
<td>213</td>
<td>Ph</td>
<td>Ph</td>
<td>0.5</td>
<td>100%</td>
<td>216</td>
<td>&gt;98% (85%)</td>
</tr>
<tr>
<td>4</td>
<td>214</td>
<td>iPr</td>
<td>iPr</td>
<td>45</td>
<td>26%</td>
<td>217</td>
<td>26%</td>
</tr>
</tbody>
</table>

*a The preparations for the silicon-tethered alkynes can be found in the experimental chapter of this thesis.

*b Determined by crude ¹H NMR using mesitylene as an internal standard. *c Isolated yield reported in parentheses.

### 4.5 SUBSTRATE SCOPE

With optimized reaction conditions in hand, the alkyne substrate tolerance for the cycloisomerization was examined. It began by exploring substrates bearing a phenyl group on the alkyne terminus (Table 30). Alkyl functionality (methyl and n-heptyl) at R₁ was well tolerated and gave 132 and 220 in good yields of 82% and 80% (entries 1 and 2). Hydrogen at R₁
was also tolerated (entry 3) and gave 221 in 77% yield. Cyclohexyl and phenyl groups performed well and gave dienes 222 and 223 in good yields of 88% and 75%, respectively (entries 4 and 5). A nitro group was tolerated on the phenyl ring and 224 was isolated in 71% yield (entry 6). The biphenyl moiety (entry 7) performed well and gave an excellent yield (93%) of 225. An increase of the Thorpe-Ingold effect in the starting alkynes (entries 8 and 9) resulted in an excellent isolated yield of 94% of both 226 and 227. Lastly, a trans-fused bicyclic system 228 was achieved in 73% yield (entry 10).
Next various aryl substitution at the alkyne terminus was examined (Table 31). The electron-donating methoxy group was well tolerated and 232 was isolated in 89% yield (entry 1). Additionally, the electron-withdrawing acetyl and nitro moieties were well tolerated and gave good yields of the desired dienes 233 and 234 (76% and 85%, entries 2 and 3). Substrates bearing tolyl and xylyl substituents (entries 4 and 5) gave the products 235 and 236 in 80% yield,
respectively. The para-fluoro and ortho-chloro moieties gave good and excellent yields of 237 and 238 (81% and 95%, entries 6 and 7). Lastly, the potentially chelating and basic pyridine moiety was tolerated in the reaction and a 52% isolated yield of 239 was obtained (entry 8).

![Chemical Reaction](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Product</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Entry</th>
<th>Alkyne&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Product</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65</td>
<td>232</td>
<td>89</td>
<td>5</td>
<td>67</td>
<td>236</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-MeOPh</td>
<td></td>
<td></td>
<td></td>
<td>3,5-xy/</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>229</td>
<td>233</td>
<td>76</td>
<td>6</td>
<td>64</td>
<td>237</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-AcPh</td>
<td></td>
<td></td>
<td></td>
<td>4-FPh</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>234</td>
<td>85</td>
<td>7</td>
<td>230</td>
<td>238</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-NO₂Ph</td>
<td></td>
<td></td>
<td></td>
<td>2-ClPh</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>66</td>
<td>235</td>
<td>80</td>
<td>8&lt;sup&gt;c&lt;/sup&gt;</td>
<td>231</td>
<td>239</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-tol</td>
<td></td>
<td></td>
<td></td>
<td>3-pyr</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Aryl-substituted alkyne substrate scope

<sup>a</sup>The preparations for the silicon-tethered alkynes can be found in the experimental chapter of this thesis. <sup>b</sup>Isolated yield after purification by column chromatography. <sup>c</sup>Reaction run with 12 mol% catalyst.

The substrate scope was expanded to include alkyl functionality on the alkyne terminus (Table 32). Methyl-substituted alkyne 68 gave the desired diene 155 in 64% yield. A 5% increase in isolated yield of 155 was achieved compared to our previous methodology utilizing
MVK (chapter 3). It was pleasing to discover the reaction tolerance to cyclopropyl-substituted alkyne 240, allowing for isolation of diene 241 in 74% yield.

![Cycloisomerization Reaction](image)

**Table 32. Alkyl substrate scope**

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph(CH₂)₂Me</td>
<td>68</td>
<td>64%</td>
</tr>
<tr>
<td>C₆H₁₃</td>
<td>240</td>
<td>74%</td>
</tr>
<tr>
<td>C₆H₁₃</td>
<td>242</td>
<td>61%</td>
</tr>
</tbody>
</table>

a Isolated yields after purification by column chromatography. b Reaction run with 15 mol% catalyst. c The preparations for the silicon-tethered alkynes can be found in the experimental chapter of this thesis.

Lastly, olefinic substitution on the alkyne terminus was utilized and a 61% yield of triene 243 was obtained.

To finish the substrate scope, it was desired to know if silicon was needed in the tether for the cycloisomerization to proceed. This was answered by synthesizing allyl-tethered alkyne 244 and subjecting it to the standard reaction conditions (Scheme 78).

![Scheme 78. Non-silicon tether variation](image)

a The preparation of alkyne 244 can be found in the experimental chapter of this thesis.
The reaction proceeded smoothly and gave diene 245 in 61% isolated yield after 2.5 hours. With this result it was concluded that silicon is not needed in the tether of the substrates.

It is important to note that several alkyne substrates proved difficult with the reaction conditions (Figure 11). An alkyne bearing a bulky 1-naphthyl moiety resulted in only 56% conversion and a 34% crude yield of diene 246 was observed after 7 hours. The bulkiness of the naphthyl group can be attributed to the poor reactivity. A terminal alkyne possessing a biphenyl moiety at the homopropargylic position (to avoid volatility) was also examined. With 10 mol% catalyst, 40% conversion and 40% crude yield of 247 was observed. Increase of the catalyst loading to 13 mol% did not change reactivity or product yield. An attempt at forming a seven-membered ring substrate 248 was unsuccessful and only 5% conversion and 5% crude yield was observed. The addition of a methyl group alpha to the oxygen atom improved the crude yield and conversion of expected diene 249 to 20% but no further improvements were observed.

![Figure 11. Difficult substrates](image)

*Conversions and crude yields were determined by $^1$H NMR using mesitylene as an internal standard.*
Several alkyne substrates were unreactive in the cycloisomerization (Figure 12). Alkyne 250, bearing a bulky mesityl moiety on the alkyne terminus proved unreactive. Attempts to form a five-membered ring product from alkyne 251 and an eight-membered ring from alkyne 252 were unsuccessful. Exchange of the vinyl silicon tether for Z and E styryl tethered alkyynes 253 and 254 resulted in no product formation. Lastly, acrylate-tethered alkyne 255 proved unreactive to the conditions.

![Figure 12. Unreactive alkyne substrates](image)

*a Only starting material observed in crude $^1$H NMR after subjection of alkyne with 10 mol% Cp*Ru(COD)Cl.

### 4.6 PRODUCT DERIVATIZATION

The synthetic utility of the cycloisomerization products was demonstrated utilizing various transformations. The Diels-Alder reaction of diene 227 and N-methylmaleimide in toluene in a sealed tube at 130°C gave the highly substituted tetracyclic system 256 as the endo
isomer (confirmed by NOESY and COSY NMR) in 89% yield (Scheme 79). It was then discovered that the reaction could be performed at room temperature with an improved isolated yield of 94%.

![Scheme 79. Diels-Alder reaction of 227](image)

Protodesilylation of 132 using TFAF gave known alcohol 257 in an excellent yield of 90% (Scheme 80, eq. 1). Addition of methyllithium gave hydroxy silane 258 in 87% yield and required no purification (eq. 2).

![Scheme 80. Synthetic elaboration of 132](image)

Attempts to form the vinyl iodides 259 and 260 were unsuccessful with ICl and NIS (Scheme 81). In both cases decomposition of the starting materials 132 and 227 was observed after the designated reaction time.
Numerous attempts were made to facilitate the Fleming-Tamao oxidation of 227 (Scheme 82). Conditions reported by Marshall\textsuperscript{209} (eq. 1) resulted in 90% recovery of starting material and conditions reported by Woerpel\textsuperscript{210} (eq. 2) gave starting material decomposition in 1 hour.

Later, conditions (potassium hydrogen fluoride, acetic anhydride, peroxide, DMF) were discovered to effect the Tamao oxidation\textsuperscript{211} however, the expected product 263 was not obtained (Scheme 83, eq. 1). Instead, keto ester 262 was isolated in 40% yield.
The formation of 262 is attributed as follows (Scheme 84): Oxidation of 132 resulted in formation of enol silane A, which underwent Baeyer-Villiger oxidation to generate the hydroxy enol-acetate C (with loss of silicon). *Trans*-esterification and tautomerization formed the keto-ester 262. To prove the mechanistic hypothesis, the oxidation was conducted with propionic anhydride (Scheme 83, eq. 2). With delight, keto ester 262 was obtained in an improved isolated yield of 56% (Scheme 83, eq. 2).
4.7 CONCLUSION

In conclusion, the formation of 1,3-dienes by a ruthenium-catalyzed cycloisomerization of silicon-tethered 1,7-enynes was demonstrated. The transformation is believed to proceed via a ruthenacyclopentene followed by a rare endocyclic β-hydride elimination to generate the diene product. A wide variety of substitution on the starting enynes was tolerated, including both aryl and alkyl functionality in good to excellent yields. Variation of the substituents on the silicon atom was also accomplished and well tolerated. In addition, it was determined silicon is not required in the starting enyne for the reaction to proceed.

The synthetic utility of the 1,3-dienes was demonstrated via various organic transformations. A Diels-Alder reaction with N-methylmaleimide selectively formed the endo isomer product in excellent yield. The unexpected formation of a keto-ester was accomplished via a Fleming-Tamao oxidation. The highly functionalized cyclic and acyclic substrates obtained from the derivatization of the cycloisomerization adducts can be utilized for further elaboration into more complex molecular structures.

A future direction for this project is the development of reaction conditions that will tolerate styryl silicon tethers and various alkyl substituted olefinic silicon tethers. This would allow for further product diversity on the diene scaffold.
5.0 BIBLIOGRAPHY


6.0 EXPERIMENTALS

**General Procedures:** Unless otherwise indicated, all reactions were conducted in oven-(140°C) or flame-dried glassware using distilled and degassed solvents under positive pressure of dry argon with standard Schlenk techniques. All air-sensitive reagents were stored in an MBraun labmaster glovebox containing dry argon gas. Dry dichloromethane (DCM), toluene, diethyl ether (Et₂O) and tetrahydrofuran (THF) was obtained by passing commercially available pre-dried, oxygen-free formulations through two activated alumina columns using an MBraun MB-SPS solvent purification system. Stainless steel syringes or cannulae that had been oven-dried (140°C) and cooled under argon atmosphere or in a desiccator were used to transfer air- and moisture-sensitive liquids. Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on precoated glass plates of silica gel (0.25 mm) 60 F₂₅₄ from EMD Chemicals Inc. using the indicated solvent system. Visualization was accomplished with ultraviolet light (UV 254 nm). Alternatively, plates were treated with one of the following solutions (this was accomplished by holding the edge of the TLC plate with forceps or tweezers and immersing the plate into a wide-mouth jar containing the desired staining solution) and carefully heating with a hot-air gun (450°C) for approximately 1-2 min: anisaldehyde in ethanol with 10% sulfuric acid. Flash column chromatography was performed using Silia Flash P60
silica gel (40-63 µm) from Silicycle. All work-up and purification procedures were carried out with reagent grade solvents (purchased from VWR) in air.

**Instrumentation:** Infrared (IR) spectra were recorded on a Thermo Nicolet IR-100 spectrometer, \( \nu_{\text{max}} \) in cm\(^{-1}\), and were obtained from samples prepared as thin films between NaCl plates for samples. \(^1\)H NMR spectra were recorded on a Bruker Avance DPX-300 (300 MHz) spectrometer or a Bruker Avance DPX-400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) and are calibrated using residual undeuterated solvent as an internal reference (CDCl\(_3\): 7.26 ppm). Data are reported as follows: chemical shift, multiplicity, coupling constants (Hz) and integration. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, dq = doublet of quartets. \(^{13}\)C NMR spectra were recorded on a Bruker Avance DPX-300 (75 MHz) spectrometer or a Bruker Avance DPX-400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm and are calibrated using residual undeuterated solvent as an internal reference (CDCl\(_3\): \( \delta \) 77.23 ppm). 2D NMR spectra were recorded on a Bruker Avance DPX-600 spectrometer. Melting points (m.p.) are uncorrected and were recorded using an Electrothermal Mel-Temp melting point apparatus. Elemental analyses were performed on a Costech Instruments ECS 4010 elemental analyzer with a 2 meter GC column maintained at 65°C and thermal conductivity detector.
**Reagents and Catalysts**: Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated.

Compounds 55, 56, 57, 61, 62, 63, 66, SI-3, SI-8, SI-11 were prepared by co-workers according to the literature procedure.\textsuperscript{26}

Compounds 218, 230, SI-16 were prepared by co-workers according to the literature protocol.\textsuperscript{88}

Compounds 86, 93, 121, 122 were prepared by Robert Wilson according to the literature protocol.\textsuperscript{71}

RuHCl(CO)(H\textsubscript{2}IMes)(PPh\textsubscript{3}) was prepared by Robert Wilson according to the literature protocol.\textsuperscript{54}
Alcohol SI-1

To a flame-dried 3-neck 500 mL RBF equipped with magnetic stir bar and pressure equalizing addition funnel under Ar(g) was added phenylacetylene (16.5 mL, 150 mmol, 1 equiv) and THF (160 mL). The solution was cooled to -78°C (dry ice/acetone bath) and nBuLi (72 mL, 180 mmol, 1.2 equiv) was added dropwise over 45 min. After stirring for 1 h at -78°C, a solution of propylene oxide (34 mL, 480 mmol, 3.2 equiv) in HMPA (40 mL) was added dropwise over 25 min. Once addition was complete, the resulting green/brown solution stirred at rt for 3 h. The reaction mixture was poured into H₂O (475 mL) and extracted with hexanes (3 x 120 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated in vacuo to give a yellow oil. The oil was dissolved in ether (100 mL) and washed with 10% HCl (3 x 50 mL). The organic layer was refluxed over activated carbon for 30 min, dried over MgSO₄, filtered through Celite and concentrated in vacuo to give alcohol SI-1 as off-white crystals (22.6 g, 94%). Spectroscopic data corresponded to what was reported in the literature.²¹²

\[ R_f \ (50\% \ EtOAc/hexanes) = 0.54 \]

\[ ^1H \ NMR \ (300 \ MHz, CDCl₃) \ \delta = 7.43-7.40 \ (m, 2H), \ 7.31-7.28 \ (m, 3H), \ 4.10-4.00 \ (m, 1H), \ 2.59 \ (d \ ABq, 2H, J_{AB} = 16.7 \ Hz, J_{AX} = 5.1 \ Hz, J_{BX} = 6.6 \ Hz), \ 2.06 \ (br \ s, 1H), \ 1.33 \ (d, 3H, J = 6.2 \ Hz) \]
Silicon-Tethered Alkyne 41

To an oven-dried 250 mL RBF equipped with magnetic stir bar under Ar\textsuperscript(g) was added alcohol SI-1 (2.4 g, 15 mmol, 1 equiv) and DCM (100 mL). To the resulting pale yellow solution was added imidazole (2.04 g, 30 mmol, 2 equiv) and DMAP (367 mg, 3.0 mmol, 0.2 equiv). The solution was cooled to 0°C (ice/H\textsubscript{2}O bath) and vinyldimethylchlorosilane (3.1 mL, 22.5 mmol, 1.5 equiv) was added. The suspension stirred at rt for 5 h and was quenched by sat. NH\textsubscript{4}Cl\textsubscript{(aq)} (100 mL). The aqueous layer was extracted with DCM (3 x 50 mL) then the combined organic layers were washed with brine (2 x 100 mL), dried over MgSO\textsubscript{4}, filtered and concentrated \textit{in vacuo} to give a yellow oil. Purification via column chromatography (silica gel 4.5 x 12 cm; gradient elution with 2%-6% ether/hexanes) gave alkyne 41 as a clear oil (3.39 g, 92\%). Spectroscopic data corresponded to what was reported in the literature.\textsuperscript{26}

\textbf{R\textsubscript{f}} (20\% ether/hexanes) = 0.70

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta = 7.43\text{-}7.40\) (m, 2H), 7.31\text{-}7.27 (m, 3H), 6.21 (dd, 1H, \(J = 26.6, 19.8\) Hz), 6.04 (dd, 1H, \(J = 19.8, 5.6\) Hz), 5.83 (dd, 1H, \(J = 19.9, 4.3\) Hz), 4.12\text{-}4.01 (m, 1H), 2.55 (d ABq, 2H, \(J_{AB} = 16.5\) Hz, \(J_{AX} = 6.0\) Hz, \(J_{BX} = 7.0\) Hz), 1.32 (d, 3H, \(J = 6.03\) Hz), 0.25 (d, 6H, \(J = 1.02\) Hz)
Alcohol SI-2

To a flame-dried 3-neck 500 mL RBF equipped with magnetic stir bar and pressure equalizing addition funnel under Ar\(_g\) was added phenylacetylene (20 mL, 180 mmol, 1.2 equiv) and THF (160 mL). The solution was cooled to -78°C (dry ice/acetone bath) and nBuLi (72 mL, 180 mmol, 1.2 equiv) was added dropwise over 15 min. After stirring for 1 h at -78°C, a solution of styrene oxide (17 mL, 150 mmol, 1 equiv) in HMPA (39 mL) was added dropwise over 20 min. Once addition was complete, the resulting brown solution stirred at rt overnight. The reaction mixture was poured into H\(_2\)O (450 mL) then the layers were separated. The organic layer was washed with H\(_2\)O (200 mL), dried over MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give a dark red oil. Hexanes (190 mL) was added to the oil, the flask was capped and the solution was shaken vigorously (with periodic venting) to induce precipitation. The resulting suspension was then opened to the air and stirred vigorously at rt for 1.5 h. Filtration of the suspension yielded alcohol SI-2 as a cream-colored power (19.7 g). A second (3.56 g) and third crop (2.45 g) were obtained from the mother liquor (25.7 g total, 75%). Spectroscopic data corresponded to what was reported in the literature.\(^{26}\)

\[\text{R}_f (20\% \text{ EtOAc/hexanes}) = 0.36\]

\(^1\text{H NMR}\ (400 \text{ MHz, CDCl}_3) \delta = 7.46-7.44 (m, 2H), 7.40-7.37 (m, 4H), 7.34-7.28 (m, 4H), 4.99-4.95 (m, 1H), 2.92-2.82 (app m, 2H), 2.42 (d, 1H, J = 3.5 \text{ Hz})\]
**Silicon-Tethered Alkyne 58**

To a 250 mL RBF equipped with a magnetic stir bar under Ar\(_{(g)}\) was added **SI-2** (4.56 g, 20 mmol, 1 equiv), DCM (130 mL), imidazole (2.72 g, 40 mmol, 2 equiv) and DMAP (488 mg, 4 mmol, 0.2 equiv). The pale yellow solution was cooled to 0°C (ice/H\(_2\)O bath) then vinyltrimethylchlorosilane (3.3 mL, 24 mmol, 1.2 equiv) was added via syringe. The resulting yellow suspension stirred at rt for 6 h, was quenched with sat. NH\(_4\)Cl\(_{aq}\) (100 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 50 mL) then the combined organic layers were dried over MgSO\(_4\), filtered and concentrated *in vacuo* to give an orange residue. Hexanes (50 mL) was added to the residue and the resulting cloudy orange suspension stirred vigorously at rt for 15 min. The solid was filtered away and the resulting hexanes filtrate was treated with activated carbon, stirred at rt for 30 min then filtered through a pad of silica gel (eluted with ether). Concentration *in vacuo* afforded alkyne **58** as a yellow oil (5.8 g, 95%). Spectroscopic data corresponded to what was reported in the literature.\(^{26}\)

\[R_f\] (10% ether/hexanes) = 0.72

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta = 7.41\text{-}7.25 \text{ (m, 10H)}, 6.10 \text{ (dd, 1H, } J = 20.3, 14.7 \text{ Hz)}, 5.97 \text{ (dd, 1H, } J = 14.7, 4.1 \text{ Hz)}, 5.75 \text{ (dd, 1H, } J = 19.9, 4.1 \text{ Hz)}, 4.93\text{-}4.90 \text{ (m, 1H)}, 2.77 \text{ (d ABq, 2H, } J_{AB} = 16.6 \text{ Hz), } J_{AX} = 7.4 \text{ Hz, } J_{BX} = 5.5 \text{ Hz)}, 0.19 \text{ (s, 3H), 0.14 (s, 3H)}\]
Alcohol SI-4

To an oven-dried 3-neck 100 mL RBF equipped with a magnetic stir bar under Ar\(_{(g)}\) was added PdCl\(_2\)(PPh\(_3\))\(_2\) (70 mg, 0.10 mmol, 0.02 equiv), CuI (40 mg, 0.21 mmol, 0.04 equiv), alkyne SI-3\(^{26}\) (1 g, 5.2 mmol, 1 equiv), THF (30 mL), NEt\(_3\) (15 mL) and iodobenzene (0.7 mL, 6.2 mmol, 1.2 equiv). The resulting dark red solution was subjected to three cycles of freeze/pump/thaw then placed under Ar\(_{(g)}\). Once warmed to rt the red/orange suspension stirred at 55°C. After 1 h, the resulting orange suspension was cooled to rt then filtered through celite. The filtrate was washed with brine (2 x 75 mL), dried over MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give a dark red oil. Purification by column chromatography (silica gel 2.5 x 12 cm; gradient elution with 20%-50% EtOAc/hexanes) gave alcohol SI-4 as a red/orange solid (1.07 g, 77%). Spectroscopic data corresponded to what was reported in the literature.\(^{26}\)

\(R_f\) (30% EtOAc/hexanes) = 0.29

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 8.24\) (d, 2H, \(J = 9.8\) Hz), 7.63 (d, 2H, \(J = 9.8\) Hz), 7.39-7.29 (m, 5H), 5.07 (t, 1H, \(J = 5.8\) Hz), 2.97-2.81 (app m, 2H), 2.59 (br s, 1H)
Silicon-Tethered Alkyne 60

To an oven-dried 100 mL RBF equipped with a magnetic stir bar under Ar\(_{(g)}\) was added SI-4 (1.09 g, 4.1 mmol, 1 equiv), DCM (27 mL), imidazole (556 mg, 8.2 mmol, 2 equiv) and DMAP (100 mg, 0.82 mmol, 0.2 equiv). The orange solution was cooled to 0°C (ice/H\(_2\)O bath) then vinyl dimethylchlorosilane (0.85 mL, 6.1 mmol, 1.5 equiv) was added via syringe. The resulting yellow suspension stirred at rt overnight, was quenched with sat. NH\(_4\)Cl\(_{(aq)}\) (25 mL) then the layers were separated. The aqueous layer was extracted with DCM (2 x 25 mL) then the combined organic layers were dried over MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give an orange oil. Purification by column chromatography (silica gel 2.5 x 13 cm; gradient elution with 3%-4% EtOAc/hexanes) gave alkyne 60 as a bright yellow oil (1.31 g, 92%). Spectroscopic data corresponded to what was reported in the literature.\(^{26}\)

\(R_f\) (10% EtOAc/hexanes) = 0.63

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 8.21\) (d, 2H, \(J = 8.5\) Hz), 7.59 (d, 2H, \(J = 8.5\) Hz), 7.35-7.27 (m, 5H), 6.08 (dd, 1H, \(J = 18.4, 14.7\) Hz), 5.99 (dd, 1H, \(J = 14.7, 5.5\) Hz), 5.77 (dd, 1H, \(J = 18.6, 5.7\) Hz), 4.99 (t, 1H, \(J = 6.6\) Hz), 2.80 (d ABq, 2H, \(J_{AB} = 16.6\) Hz, \(J_{AX} = 6.6\) Hz, \(J_{BX} = 6.6\) Hz), 0.23 (s, 3H), 0.17 (s, 3H)
Alcohol SI-5

To an oven-dried 3-neck 100 mL RBF equipped with a magnetic stir bar and reflux condenser under Ar\(_{(g)}\) was added PdCl\(_2\)(PPh\(_3\))\(_2\) (351 mg, 0.5 mmol, 0.05 equiv), CuI (190 mg, 0.10 mmol, 0.10 equiv), THF (20 mL), NEt\(_3\) (10 mL), 4-pentyn-2-ol (0.9 mL, 10 mmol, 1 equiv) and 4-fluoriodobenzene (1.4 mL, 12 mmol, 1.2 equiv). The resulting dark brown solution was subjected to three cycles of freeze/pump/thaw then placed under Ar\(_{(g)}\). Once warmed to rt the dark brown suspension stirred at 65°C. After 2 h, the resulting red/orange suspension was cooled to rt and sat. NH\(_4\)Cl\(_{(aq)}\) (30 mL) was added. The reaction was extracted with ether (3 x 30 mL) then the combined organics were washed with brine (2 x 75 mL), dried over MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give red/orange oil. Purification by column chromatography (silica gel 4.5 x 12 cm; gradient elution with 20%-40% EtOAc/hexanes) gave SI-5 as a red/brown solid (1.28 g, 72%). Spectroscopic data corresponded to what was reported in the literature.\(^{26}\)

\(\text{R}_f\) (20% EtOAc/hexanes; developed 2x) = 0.43

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.41-7.36\) (m, 2H), 7.02-6.96 (m, 2H), 4.06-4.01 (m, 1H), 2.57 (d ABq, 2H, \(J_{AB} = 16.6\) Hz, \(J_{AX} = 5.4\) Hz, \(J_{BX} = 6.4\) Hz), 1.94 (br s, 1H), 1.32 (d, 3H, \(J = 6.2\) Hz)
Silicon Tethered Alkyne 64

To an oven-dried 100 mL RBF equipped with a magnetic stir bar under Ar(g) was added SI-5 (1.28 g, 7.2 mmol, 1 equiv), DCM (40 mL), imidazole (981 mg, 14.4 mmol, 2 equiv) and DMAP (176 mg, 1.44 mmol, 0.2 equiv) sequentially. The yellow solution was cooled to 0°C (ice/H₂O bath) and vinyldimethylchlorosilane (1.5 mL, 10.8 mmol, 1.5 equiv) was added via syringe. The yellow suspension stirred at rt overnight then was quenched by sat. NH₄Cl(aq) (40 mL). The aqueous layer was extracted with DCM (2 x 25 mL) then the combined organics were washed with brine (2 x 50 mL), dried over MgSO₄, filtered and concentrated in vacuo to give an orange oil. Purification by column chromatography (silica gel 2.5 x 11.5 cm; gradient elution with 1%-2% ether/hexanes) gave 64 as a pale yellow oil (1.53 g, 81%). Spectroscopic data corresponded to what was reported in the literature.²⁶

Rᵣ (10% EtOAc/hexanes) = 0.63

¹H NMR (300 MHz, CDCl₃) δ = 7.39-7.34 (m, 2H), 7.00-6.94 (m, 2H), 6.18 (dd, 1H, J = 19.9, 14.7 Hz), 6.02 (dd, 1H, J = 14.7, 4.3 Hz), 5.80 (dd, 1H, J = 19.9, 4.3 Hz), 4.09-3.98 (m, 1H), 2.52 (d ABq, 2H, J_AB = 16.6 Hz, J_AX = 5.7 Hz, J_BX = 7.1 Hz), 1.29 (d, 3H, J = 6.2 Hz), 0.22 (s, 6H)
**Alcohol SI-6**

To an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar and reflux condenser under Ar\(_{(g)}\) was added PdCl\(_2\)(PPh\(_3\))\(_2\) (526 mg, 0.75 mmol, 0.05 equiv), CuI (286 mg, 1.5 mmol, 0.10 equiv), piperidine (15 mL), 4-pentyn-2-ol (1.4 mL, 15 mmol, 1 equiv) and 4-bromoanisole (2.3 mL, 18 mmol, 1.2 equiv) in THF (15 mL). The resulting brown solution was subjected to three cycles of freeze/pump/thaw, placed under Ar\(_{(g)}\) then stirred at 65°C for 48 h. The resulting black solution was cooled to rt then sat. NH\(_4\)Cl\(_{(aq)}\) (30 mL) was added. The aqueous layer was extracted with ether (3 x 50 mL) then the combined organics were washed with brine (2 x 75 mL), dried over MgSO\(_4\), filtered and concentrated in vacuo to give a brown oil. Purification via column chromatography (silica gel 4.5 x 13.5 cm; gradient elution with 25%-35% EtOAc/hexanes) gave SI-6 as an orange solid (1.33 g, 47%). Spectroscopic data corresponded to what was reported in the literature.\(^{26}\)

\(R_f\) (25% EtOAc/hexanes) = 0.34

\(^1\)H NMR (300 MHz, CDCl\(_3\) \(\delta = 7.37-7.33\) (app m, 2H), 6.85-6.80 (app m, 2H), 4.08-4.00 (m, 1H), 3.81 (s, 3H), 2.57 (d ABq, 2H, \(J_{AB} = 16.6\) Hz, \(J_{AX} = 5.1\) Hz, \(J_{BX} = 6.7\) Hz), 1.79 (br s, 1H), 1.32 (d, 3H, \(J = 6.3\) Hz)
Silicon-Tethered Alkyne 65

To a 250 mL RBF equipped with a magnetic stir bar under Ar(g) was added SI-6 (1.33 g, 7 mmol, 1 equiv), DCM (47 mL), imidazole (953 mg, 14 mmol, 2 equiv) and DMAP (171 mg, 1.4 mmol, 0.2 equiv). The pale yellow solution was cooled to 0°C (ice/H₂O bath) then vinyldimethylchlorosilane (1.5 mL, 10.5 mmol, 1.5 equiv) was added dropwise via syringe. The resulting yellow suspension stirred at rt overnight, was quenched with sat. NH₄Cl(aq) (50 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 35 mL) then the combined organic layers were dried over MgSO₄, filtered and concentrated in vacuo to give an orange oil. Purification by column chromatography (silica gel 2.5 x 13 cm; gradient elution with 2%-3% ether/hexanes) gave alkyne 65 as a clear oil (1.69 g, 88%). Spectroscopic data corresponded to what was reported in the literature.²⁶

Rᵣ (25% EtOAc/hexanes) = 0.58

¹H NMR (300 MHz, CDCl₃) δ = 7.32 (d, 2H, J = 8.5 Hz), 6.82 (d, 2H, J = 8.5 Hz), 6.18 (ddd, 1H, J = 20.0, 14.9, 0.5 Hz), 5.99 (ddd, 1H, J = 14.7, 4.2, 0.5 Hz), 5.80 (ddd, 1H, J = 20.0, 4.2, 0.4 Hz), 4.08-3.98 (m, 1H), 3.80 (s, 3H), 2.51 (d ABq, 2H, Jᴬᴮ = 16.6 Hz, Jᴬₓ = 5.9 Hz, Jᴮₓ = 7.2 Hz), 1.29 (d, 3H, J = 6.2), 0.23 (s, 6H)
Alcohol SI-7

To an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar under Ar\textsubscript{(g)} was added PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (175 mg, 0.025 mmol, 0.05 equiv), CuI (95.2 mg, 0.5 mmol, 0.10 equiv), THF (5 mL), piperidine (5 mL), 4-pentyn-2-ol (0.47 mL, 5 mmol, 1 equiv) and 1-bromo-3,5-dimethylbenzene (0.82 mL, 6 mmol, 1.2 equiv). The resulting green suspension was subjected to three cycles of freeze/pump/thaw then placed under Ar\textsubscript{(g)}. Once warmed to rt, a cold-finger was quickly attached and the orange solution stirred at 70°C. After 1 h, the resulting black solution was cooled to rt then diluted with ether (10 mL) and sat. NH\textsubscript{4}Cl\textsubscript{(aq)} (10 mL). The organic layer was washed with brine (2 x 25 mL), dried over MgSO\textsubscript{4}, filtered and concentrated \textit{in vacuo} to give a brown oil. Purification via column chromatography (silica gel 2.5 x 12 cm; eluted with 15% EtOAc/hexanes) gave SI-7 as an orange oil (605 mg, 64%). Spectroscopic data corresponded to what was reported in the literature.\textsuperscript{26}

\[ R_f (30\% \text{ EtOAc/hexanes}) = 0.41 \]

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \textit{\delta} = 7.05 (s, 2H), 6.93 (s, 1H), 4.08-3.98 (m, 1H), 2.57 (d ABq, 2H, \( J_{AB} = 16.1 \) Hz, \( J_{AX} = 5.2 \) Hz, \( J_{BX} = 6.5 \) Hz), 2.28 (s, 6H), 1.81 (br s, 1H), 1.32 (d, 3H, \( J = 6.1 \) Hz)
Silicon Tethered Alkyne 67

To an oven-dried 50 mL RBF equipped with magnetic stir bar under Ar\textsubscript{(g)} was added alcohol SI-7 (469 mg, 2.5 mmol, 1 equiv) and DCM (15 mL). To the resulting yellow solution was added imidazole (339 mg, 5 mmol, 2 equiv) and DMAP (61 mg, 0.5 mmol, 0.2 equiv). The solution was cooled to 0°C (ice/H\textsubscript{2}O bath) and vinyldimethylchlorosilane (0.52 mL, 3.7 mmol, 1.5 equiv) was added. The suspension stirred at rt overnight then was quenched by sat. NH\textsubscript{4}Cl\textsubscript{(aq)} (20 mL). The aqueous layer was extracted with DCM (3 x 15 mL) then the combined organic layers were washed with brine (2 x 50 mL), dried over MgSO\textsubscript{4}, filtered and concentrated \textit{in vacuo} to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 12.5 cm; gradient elution with 1%-2% ether/hexanes) gave alkyne 67 as a clear oil (559 mg, 82%). Spectroscopic data corresponded to what was reported in the literature.\textsuperscript{26}

R\textsubscript{f} (20% EtOAc/hexanes) = 0.72

\textbf{\textsuperscript{1}H NMR} (300 MHz, CDCl\textsubscript{3}) \(\delta = 7.03\) (s, 2H), 6.91 (s, 1H), 6.18 (dd, 1H, \(J = 20.0, 15.2\) Hz), 6.02 (dd, 1H, \(J = 14.9, 4.2\) Hz), 5.81 (dd, 1H, \(J = 19.9, 4.2\) Hz), 4.08-3.98 (m, 1H), 2.52 (d ABq, 2H, \(J_{AB} = 16.5\) Hz, \(J_{AX} = 5.8\) Hz, \(J_{BX} = 7.2\) Hz), 2.27 (s, 6H), 1.29 (d, 3H, \(J = 6.0\) Hz), 0.22 (d, \(J = 0.9\) Hz)
Alcohol SI-9

To an oven-dried 100 mL RBF equipped with a magnetic stir bar under Ar\(_{(g)}\) was added SI-8\(^{26}\) (2.50 g, 14.4 mmol, 1 equiv), DCM (40 mL) and PPTS (362 mg, 1.44 mmol, 0.10 equiv). The pale yellow solution was cooled to 0°C (ice/H\(_2\)O bath) and DHP (2.6 mL, 28.8 mmol, 2 equiv) was added via syringe. The resulting solution stirred at rt for 5.5 h then was quenched by sat. NaHCO\(_3\)(aq) (40 mL). The organic layer was washed with brine (2 x 50 mL), dried over MgSO\(_4\), filtered and concentrated in vacuo to give a red/orange oil, 3.34 g. The oil was dissolved in THF (65 mL) and added to an oven-dried 3-neck 250 mL RBF equipped with a magnetic stir bar under Ar\(_{(g)}\). The solution was cooled to -78°C (dry ice/acetone bath) and nBuLi (7.7 mL, 15.5 mmol, 1.2 equiv) was added dropwise over 10 min. The resulting brown solution stirred at -78°C for 1 h then MeI (1.2 mL, 19.4 mmol, 1.5 equiv) was added. The orange solution stirred at rt for 5 h then was quenched by sat. NH\(_4\)Cl(aq) (60 mL). The aqueous layer was extracted with ether (2 x 50 mL) and the combined organic layers were washed with brine (2 x 75 mL), dried over Na\(_2\)SO\(_4\), filtered and concentrated in vacuo to give a dark red oil, 2.50 g. The oil was dissolved in EtOH (25 mL) and added to an oven-dried 100 mL RBF equipped with a magnetic stir bar under Ar\(_{(g)}\). PPTS (694 mg, 2.76 mmol, 0.30 equiv) was subsequently added and the light orange solution stirred at 50°C for 4 h. The solution was then cooled to rt and concentrated in vacuo to give an orange oil. The oil was dissolved in DCM, washed with brine (2 x 25 mL), dried over MgSO\(_4\), filtered and concentrated in vacuo to give a dark orange oil.
Purification via column chromatography (silica gel 2.5 x 12 cm; gradient elution with 10%-13% EtOAc/hexanes) gave alcohol SI-9 as a yellow oil (900 mg, 33% over 3 steps). Spectroscopic data corresponded to what was reported in the literature.²⁶

$$R_f(20\% \text{ EtOAc/hexanes}) = 0.45$$

\(^1\text{H NMR}\) (300 MHz, CDCl₃) δ = 7.33-7.16 (m, 5H), 3.75-3.67 (m, 1H), 2.86-2.64 (m, 2H), 2.45-2.31 (m, 2H), 1.88-1.80 (m, 6H)
Silicon-Tethered Alkyne 68

To an oven-dried 100 mL RBF equipped with magnetic stir bar under Ar\(_{(g)}\) was added **SI-9** (900 mg, 4.8 mmol, 1 equiv), DCM (30 mL), imidazole (654 mg, 9.6 mmol, 2 equiv) and DMAP (117 mg, 0.96 mmol, 0.20 equiv). The solution was cooled to 0°C (ice/H\(_2\)O bath) and vinyldimethylchlorosilane (0.9 mL, 6.2 mmol, 1.3 equiv) was added. The white suspension stirred at rt overnight then was quenched by sat. NH\(_4\)Cl\(_{(aq)}\) (35 mL). The aqueous layer was extracted with DCM (3 x 25 mL) then the combined organic layers were dried over MgSO\(_4\), filtered and concentrated in vacuo to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 13 cm; gradient elution with 2%-3% ether/hexanes) gave alkyne **68** as a clear oil (1.05 g, 80%). Spectroscopic data corresponded to what was reported in the literature.\(^{26}\)

**R\(_f\)** (10% ether/hexanes) = 0.45

**\(^1\)H NMR** (300 MHz, CDCl\(_3\)) \(\delta = 7.31\text{-}7.26\) (m, 2H), 7.21\text{-}7.15 (m, 3H), 6.18 (dd, 1H, \(J = 20.0, 14.9\) Hz), 6.02 (dd, 1H, \(J = 14.9, 4.2\) Hz), 5.79 (dd, 1H, \(J = 19.9, 4.2\) Hz), 3.85\text{-}3.77 (m, 1H), 2.76 (ddd, 1H, \(J = 16.4, 10.9, 5.6\) Hz), 2.58 (ddd, 1H, \(J = 16.6, 10.9, 5.9\) Hz), 2.39\text{-}2.23 (m, 2H), 2.00\text{-}1.88 (m, 1H), 1.87\text{-}1.74 (m, 1H), 1.78 (t, 3H, \(J = 2.5\) Hz), 0.22 (d, 6H, \(J = 1.2\) Hz)
(S)-Phenylalanol (69)

To an oven-dried 3-neck 3 L RBF equipped with overhead mechanical stirrer, pressure equalizing addition funnel and reflux condenser under Ar (g) was added L-phenylalanine (100 g, 605 mmol, 1 equiv), THF (1 L) and sodium borohydride (55 g, 1.45 mol, 2.4 equiv). The white suspension was cooled to 0°C (ice/H₂O bath) and a solution of iodine (154 g, 605 mmol, 1 equiv) in THF (400 mL) was added dropwise over 4 h. (Caution: Vigorous gas evolution!) Once the addition was complete, the cloudy reaction mixture was slowly warmed to rt then stirred at reflux overnight. The reaction mixture was cooled to rt and quenched by dropwise addition of MeOH (200 mL over 1.5 h) until the solution turned clear. (Caution: Vigorous gas evolution!) The solution stirred at rt for 30 min then concentrated in vacuo to give a white paste. The paste was dissolved in 20% KOH (aq) (650 mL) and stirred at rt for 4 h. The mixture was extracted with DCM (3 x 600 mL) [note: DCM is top layer], dried over Na₂SO₄, filtered and concentrated in vacuo to give a yellow oil. To the oil was added EtOAc (100 mL) and the solution stirred vigorously until precipitation occurred. The resulting suspension was concentrated in vacuo to yield a white pasty solid, which was recrystallized from EtOAc (350 mL) to give 69 as a white powder (36.7 g). A second (17.9 g) and third crop (1.22 g) were obtained for a total yield of 55.8 g (61%). Spectroscopic data corresponded to what was reported in the literature.⁴⁰

mp = 89-92°C
**Oxazolidinone 70**

To a flame-dried 3-neck 100 mL RBF equipped with a magnetic stir bar and 12 inch Vigreux column fitted with a distillation head and 25 mL collection flask under Ar (g) was added 69 (9.72 g, 64 mmol, 1 equiv), diethyl carbonate (16 mL, 132 mmol, 2.1 equiv) and K$_2$CO$_3$ (885 mg, 6.4 mmol, 0.10 equiv). The white suspension was heated to 135°C. The collection flask was cooled in an ice-bath and ethanol was collected over a 4 h period. Upon cessation of ethanol distillation, the reaction mixture was cooled to rt, diluted with DCM (50 mL) and washed with H$_2$O (50 mL). The organic layer was dried over MgSO$_4$, filtered and concentrated *in vacuo* to give an off-white solid. Recrystallization from 2:1 EtOAc/hexanes (60 mL) gave 70 as white needles (9.5 g, 85%). Spectroscopic data corresponded to what was reported in the literature.$^{41}$

**mp = 86-89°C**

$^1$H NMR (300 MHz, CDCl$_3$) δ = 7.34-7.18 (m, 5H), 3.64 (dd, 1H, $J = 10.5$, 3.9 Hz), 3.38 (dd, 1H, $J = 10.5$, 7.2 Hz), 3.17-3.08 (m, 1H), 2.80 (dd, 1H, $J = 13.5$, 5.1 Hz), 2.53 (dd, 1H, $J = 13.5$, 8.7 Hz), 1.93 (s, 3H)
Acylated Oxazolidinone 71

To an oven-dried 2-neck 2L flask equipped with a magnetic stir bar and pressure equalizing addition funnel under Ar (g) was added 70 (51 g, 288 mmol, 1 equiv) and THF (870 mL). The solution was cooled to -78°C (dry ice/acetone bath) and nBuLi (116 mL, 291 mmol, 1.01 equiv) was added dropwise over 30 min, followed by addition of propionyl chloride (28 mL, 317 mmol, 1.1 equiv) in one portion. The reaction stirred at -78°C for 30 min then was warmed to rt over 1 h. Upon warming, the orange solution was quenched by sat. NH₄Cl(aq) (175 mL) and concentrated in vacuo to give an orange suspension. The suspension was extracted with DCM (3 x 225 mL) and the combined organic layers were washed with 1M NaOH(aq) (400 mL) and brine (400 mL), dried over Na₂SO₄, filtered and concentrated in vacuo to give a yellow oil. The oil was placed in the freezer overnight to yield a yellow solid, which was pulverized and tritutrated with cold hexanes to give 71 as a white powder (59 g). A second crop (4.3 g) was obtained to give a total yield of 63.3 g (94%). Spectroscopic data corresponded to what was reported in the literature.⁴²

\[
R_f (25\% \text{ EtOAc/hexanes}) = 0.59
\]

\[
\text{mp} = 42-44^\circ\text{C}
\]

\[
^1\text{H NMR} \ (300 \text{ MHz, CDCl}_3) \ \delta = 7.37-7.20 \ (m, 5H), \ 4.72-4.64 \ (m, 1H), \ 4.24-4.15 \ (m, 2H), \ 3.31 \ (dd, 1H, J = 13.3, 3.3 \text{ Hz}), \ 3.07-2.86 \ (m, 2H), \ 2.77 \ (dd, 1H, J = 13.4, 9.6 \text{ Hz}), \ 1.21 \ (t, 3H, J = 7.3 \text{ Hz})
\]
**Aldol Adduct 72**

*Evans method:* To an oven-dried 100 mL 3-neck RBF equipped with a magnetic stir bar and internal thermometer under Ar\(_{(g)}\) was added 71 (1.0 g, 4.3 mmol, 1 equiv) and DCM (8.5 mL). The solution was cooled to 0°C and Bu\(_2\)BOTf (1.4 mL, 6.5 mL, 1.5 equiv) was added dropwise at such a rate to maintain the internal temperature below 3°C. Once the addition was complete, NEt\(_3\) (0.8 mL, 5.7 mmol, 1.32 equiv) was added dropwise at such a rate to maintain the internal temperature below 3°C. Once the addition was complete, the resulting light yellow solution was cooled to -78°C (dry ice/acetone bath) and benzaldehyde (0.5 mL, 4.7 mmol, 1.1 equiv) was added dropwise. The solution stirred at -78°C for 2 h then stirred at rt overnight. The reaction mixture was quenched with pH 7 phosphate buffer (5 mL), cold methanol (15 mL) then dropwise addition of a 2:1 MeOH/30% H\(_2\)O\(_2\) solution (15 mL) at such a rate to maintain the internal temperature below 10°C. After stirring in an ice bath for 1 h, the reaction mixture was concentrated *in vacuo* to give a white slurry, which was then extracted with ether (25 mL). The organics were washed with 5% NaHCO\(_3\) (25 mL) and brine (25 mL), dried over MgSO\(_4\), filtered and concentrated *in vacuo* to give a pale yellow solid. Recrystallization from 1:2 EtOAc/hexanes (2 mL) gave 72 as a white solid (911 mg, 62%). Spectroscopic data corresponded to what was reported in the literature.\(^{42}\)

*Crimmins method:* To a flame-dried 50 mL RBF equipped with a magnetic stir bar under Ar\(_{(g)}\) was added 71 (233 mg, 1.0 mmol, 1 equiv) and DCM (10 mL). The solution was cooled to 0°C (ice/H\(_2\)O bath) and TiCl\(_4\) (0.12 mL, 1.05 mmol, 1.05 equiv) was added dropwise. The resulting yellow suspension stirred at 0°C for 15 min then DIPEA (0.14 mL, 1.10 mmol, 1.1 equiv) was
added dropwise. The dark-colored solution stirred at 0°C for 40 min then NMP (0.10 mL, 1.0 mmol, 1 equiv) was added dropwise. After stirring at 0°C for 10 min, benzaldehyde (0.11 mL, 1.10 mmol, 1.1 equiv) was added in one portion. After stirring at 0°C for 1 h, the reaction mixture was quenched by sat. NH₄Cl(aq) (25 mL). The aqueous layer was extracted with DCM (3 x 20 mL) and the combined organic layers were dried over Na₂SO₄, filtered and concentrated in vacuo to give an orange oil. Purification via column chromatography (silica gel 2.5 x 11 cm; eluted with 25% EtOAc/Hexanes) gave 72 as a pale yellow solid (33:2:1, 301 mg, 89%). Spectroscopic data corresponded to what was reported in the literature.⁴⁵

\[ R_f (20\% \text{ EtOAc/hexanes}) = 0.12 \]

\[ \text{mp} = 92-94°C \]

\[ ^1\text{H NMR} (300 \text{ MHz, CDCl}_3) \delta = 7.42-7.19 \text{ (m, 10H), 5.11-5.09 \text{ (m, 1H), 4.64-4.57 \text{ (m, 1H), 4.17-4.05 \text{ (m, 3H), 3.25 (dd, 1H, } J = 13.2, 3.3 \text{ Hz), 3.06 (d, 1H, } J = 2.4 \text{ Hz), 2.78 (dd, 1H, } J = 13.5, 9.6 \text{ Hz), 1.23 (d, 3H, } J = 6.9 \text{ Hz) } \]
Weinreb Amide 73

To an oven-dried 3-neck 500 mL RBF equipped with magnetic stir bar and pressure equalizing addition funnel under Ar\(_\text{g}\) was added Weinreb salt (10.4 g, 106 mmol, 3 equiv) and THF (55 mL). The suspension was cooled to 0°C (ice/H\(_2\)O bath) and AlMe\(_3\) (54 mL, 107 mmol, 3.02 equiv) was added dropwise over 30 min. (Caution: Vigorous gas evolution!) Once the addition was complete the cooling bath was removed and the cloudy solution stirred at rt for 30 min. The solution was re-cooled to -15°C (salt/ice/H\(_2\)O bath) and a solution of aldol adduct 72 (12.0 g, 35.4 mmol, 1 equiv) in THF (55 mL) was added dropwise. (Caution: Vigorous gas evolution!) The reaction mixture stirred for 45 min then was quenched by cannula transfer into a 2 L RBF cooled at 0°C (ice/H\(_2\)O bath) containing 1:2 DCM/1N HCl\(_{\text{aq}}\) (780 mL). (Caution: Vigorous gas evolution!) After stirring for 30 min the layers were separated and the aqueous was extracted with DCM (3 x 250 mL). The combined organic layers were washed with brine, dried over Na\(_2\)SO\(_4\), filtered and concentrated \textit{in vacuo} to give a yellow oil. To the oil was added DMF (55 mL), imidazole (4.8 g, 71 mmol, 2 equiv) and TBSCl (5.9 g, 39 mmol, 1.1 equiv). The yellow solution stirred at rt overnight then poured into H\(_2\)O (200 mL) and extracted with EtOAc (3 x 200 mL). The organic layers were washed with brine, dried over Na\(_2\)SO\(_4\), filtered and concentrated \textit{in vacuo} to give a yellow oil. Purification via column chromatography (silica gel 4.5 x 10 cm; gradient elution with 10%-30% EtOAc/hexanes) gave 73 as a clear oil (10.5g, 88% over two steps).

\(R_f\) (30% EtOAc/hexanes) = 0.56

\([\alpha]_D^{24} = -2.1^\circ (c = 1.030 \text{ in CHCl}_3)\)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.34$-$7.17$ (m, 5H), 4.80 (d, 1H, $J = 8.6$ Hz), 3.26 (s, 3H), 3.16 (bs, 1H), 2.95 (s, 3H), 1.27 (d, 3H, $J = 6.8$ Hz), 0.87 (s, 9H), 0.04 (s, 3H), -0.22 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 175.6$, 144.3, 128.0, 127.4, 127.0, 76.6, 61.3, 45.5, 31.9, 26.0, 18.4, 15.0, -4.4, -4.8

FT-IR (NaCl, thin film) $\nu = 3499$, 3032, 2959, 1660, 1462, 1256 cm$^{-1}$

Anal. calcd for C$_{18}$H$_{31}$NO$_3$Si: C 64.05, H 9.26, N 4.15; found: C 63.99, H 9.33, N 4.07
**Ethyl Ketone 74**

To a flame-dried 50 mL 3-neck RBF equipped with a magnetic stir bar and pressure equalizing addition funnel under Ar$_{(g)}$ was added a solution of Weinreb amide 73 (2.2 g, 6.5 mmol, 1 equiv) in THF (13 mL). The reaction mixture was cooled to 0°C (ice/water bath) and ethyl magnesium bromide (13.3 mL, 19.5 mmol, 3 equiv) was added dropwise. The dark grey solution stirred at 0°C for 5 min then was warmed to rt and stirred for 5 h. The reaction mixture was poured into 1M HCl and the layers were separated. The aqueous phase was extracted with ether (3 x 40 mL) then the combined organic extracts were dried over MgSO$_4$, filtered and concentrated in vacuo to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 15 cm; gradient elution with 2%-6% EtOAc/hexanes) gave 74 as a clear oil (1.70 g, 85%).

\[ R_f (5\% \text{ EtOAc/hexanes}) = 0.26 \]

\[ [\alpha]_D^{24} = -3.9^\circ \ (c = 2.428 \text{ in EtOAc}) \]

$^1$H NMR (300 MHz, CDCl$_3$) $\delta = 7.30$-7.18 (m, 5H), 4.75 (d, 1H, $J = 7.5$ Hz), 2.87-2.30 (m, 1H), 2.24 (dq, 1H, $J = 18.3$, 7.2 Hz), 1.90 (dq, 1H, $J = 18.0$, 7.2 Hz), 1.17 (d, 3H, $J = 6.9$ Hz), 0.86 (s, 9H), 0.79 (t, 3H, $J = 7.2$ Hz), 0.01 (s, 3H), -0.24 (s, 3H)

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta = 213.3$, 143.5, 128.0, 127.3, 126.5, 76.6, 55.4, 36.5, 25.8, 18.0, 13.3, 7.1, -4.6, -4.8

FT-IR (NaCl, thin film) $\nu = 3032$, 2933, 1714, 1454, 1361, 1256 cm$^{-1}$

HRMS (ESI) calcd for (C$_{18}$H$_{30}$O$_2$Si)Na$: 329.1907$; found 329.1911.
Enol Triflate 75

To a flame-dried 250 mL RBF equipped with a magnetic stir bar under Ar(g) was added ethyl ketone 74 (3.73 g, 12.2 mmol, 1 equiv) and THF (100 mL). Comins’ reagent 49 (9.6 g, 24.4 mmol, 2 equiv) was added in one portion. The clear solution was cooled to -78°C (dry ice/acetone bath) and freshly prepared KHMDS (0.90M in THF, 15 mL, 13.4 mmol, 1.1 equiv) was added dropwise over 15 min. The orange solution stirred at -78°C for 30 min then an additional portion of KHMDS (0.90M in THF, 7.4 mL, 6.7 mmol, 0.55 equiv) was added dropwise over 10 min. The red/orange solution continued stirring at -78°C for 30 min then an additional portion of KHMDS (0.90M in THF, 3.4 mL, 3.1 mmol, 0.25 equiv) was added dropwise over 5 min. After stirring an additional 15 min, the reaction mixture was warmed slightly and then quenched by addition of sat. NaHCO₃(aq) (100 mL). The layers were separated and the aqueous phase was extracted with DCM (3 x 50 mL). The combined organics were washed with brine (2 x 100 mL), dried over Na₂SO₄, filtered and concentrated in vacuo to give a brown oil. Purification via column chromatography (silica gel 4.5 x 12 cm; gradient elution with hexanes-10% EtOAc/hexanes) gave 75 as a clear oil (3.2 g, 60%).

R_f (10% EtOAc/hexanes) = 0.62

[α]_D^24 = +9.1° (c = 0.610 in CHCl₃)

^1H NMR (400 MHz, CDCl₃) δ = 7.33-7.21 (m, 5H), 5.38 (dq, 1H, J = 6.9, 0.9 Hz), 4.99 (d, 1H, J = 2.6 Hz), 2.68-2.63 (m, 1H), 1.76 (dd, 3H, J = 7.0, 1.4 Hz), 0.94 (d, 3H, J = 6.9 Hz), 0.90 (s, 9H), -0.03 (s, 3H), -0.18 (s, 3H)
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 151.9, 143.0, 128.2, 127.3, 126.2, 118.7\) (q, \(J_{C-F} = 317.5\) Hz),
117.0, 73.1, 46.8, 26.0, 18.4, 11.5, 10.5, -4.6, -5.5

**FT-IR** (NaCl, thin film) \(\nu = 3499, 2957, 2860, 1645, 1414, 1244, 1211, 1135\) cm\(^{-1}\)

**HRMS** (ESI) calcd for (C\(_{19}\)H\(_{29}\)F\(_3\)O\(_4\)Si)Na\(^+\): 461.1400; found 461.1411.
Alcohol 76

To a 100 mL RBF equipped with a magnetic stir bar was added a solution of enol triflate 75 (3.0 g, 6.84 mmol, 1 equiv) in DMF (18 mL). To the clear solution was added TBAF∙3H$_2$O (8.9 g, 34.2 mmol, 5 equiv) then the solution stirred at 60°C for 1 h. The reaction mixture was cooled to rt, quenched with water (60 mL) and the layers were separated. The aqueous phase was extracted with DCM (3 x 30 mL) then the combined organic extracts were washed with brine (60 mL), dried over MgSO$_4$, filtered and concentrated \textit{in vacuo} to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 13 cm; gradient elution with 3%-4% EtOAc/hexanes) gave 76 as a clear oil (997 mg, 84%).

$R_f$ (10% EtOAc/hexanes) = 0.14

$[\alpha]^D_{24} = -41.1^\circ$ (c = 0.50 in CHCl$_3$)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.39-7.26 (m, 5H), 4.70 (d, 1H, $J = 5.1$ Hz), 2.87-2.77 (m, 1H), 2.31 (bs, 1H), 1.79 (d, 3H, $J = 2.4$ Hz), 1.05 (d, 3H, $J = 7.2$ Hz)

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 141.7, 128.2, 127.7, 126.6, 80.7, 78.8, 76.5, 34.4, 15.8, 3.7

FT-IR (NaCl, thin film) $\nu$ = 3401, 3030, 2974, 1593, 1513, 1452, 1022 cm$^{-1}$

Anal. calcd for C$_{12}$H$_{14}$O: C 82.72, H 8.10; found: C 82.56, H 8.07.
Silicon Tethered Alkyne 77

To a flame-dried 50 mL RBF equipped with a magnetic stir bar under Ar\(_{(g)}\) was added a solution of alcohol 76 (450 mg, 2.6 mmol, 1 equiv) in DCM (17 mL). To the clear solution was added imidazole (354 mg, 5.2 mmol, 2 equiv) and DMAP (64 mg, 0.52 mmol, 0.2 equiv). The solution was cooled to 0°C (ice/water bath) and vinyl(dimethylchlorosilane) (0.54 mL, 3.9 mmol, 1.5 equiv) was added in one portion via syringe. The white suspension stirred at 0°C for 5 min then was warmed to rt and stirred for 1 h. The reaction was quenched by addition of sat. NH\(_4\)Cl\(_{(aq)}\) (20 mL) and extracted with DCM (3 x 25 mL). The combined organics were dried over MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give a yellow oil. Purification via column chromatography (silica gel; gradient elution with hexanes-3% EtOAc/hexanes) gave 77 as a clear oil (616 mg, 92%).

\(R_f\) (10% EtOAc/hexanes) = 0.53

\([\alpha]D^{24} = -30.5^\circ\text{ (c = 0.934 in CHCl}_3\text{)}\)

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\)) \(\delta = 7.35 - 7.21\) (m, 5H), 6.07 (dd, 1H, \(J = 19.5, 14.9\) Hz), 5.95 (dd, 1H, \(J = 14.8, 4.8\) Hz), 5.72 (dd, 1H, \(J = 19.5, 4.8\) Hz), 4.59 (d, 1H, \(J = 6.5\) Hz), 2.68-2.58 (m, 1H), 1.72 (d, 3H, \(J = 2.4\) Hz), 1.12 (d, 3H, \(J = 6.9\) Hz), 0.13 (s, 3H), 0.09 (s, 3H)

\(^{13}\text{C NMR}\) (75 MHz, CDCl\(_3\)) \(\delta = 143.4, 137.9, 133.1, 127.8, 127.3, 126.9, 81.7, 78.4, 77.6, 35.5, 16.9, 3.7, -1.3, -1.5

\textbf{FT-IR\textit{ (NaCl, thin film)}} \(\nu = 3051, 2968, 1595, 1494, 1453, 1253, 1086\) cm\(^{-1}\)

\textbf{HRMS\textit{ (ESI)}} calcd for (C\(_{16}\)H\(_{22}\)OSi)Na\(^+\): 281.1332; found: 281.1338.
Diene 78A

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar in an Ar\(_{(g)}\) filled glovebox was added RuHCl(CO)(H\text{IMes})(PPh\text{3}) (15 mg, 0.021 mmol, 0.10 equiv) and a solution of alkyne 77 (55 mg, 0.21 mmol, 1 equiv) and ethyl acrylate (114 µL, 1.05 mmol, 5 equiv) in toluene (0.42 mL). The Schlenk tube was sealed with a rubber septum, removed from the glovebox and stirred under Ar\(_{(g)}\) at 80°C. After 45 min, the brown solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a brown oil. Purification via column chromatography (silica gel 1.5 x 8.5 cm; eluted with 3% ether/hexanes) gave diene 78A as a clear oil (38 mg, 55%, 5.4:1 78A:78B). Further purification via preparative thin layer chromatography (gradient elution with 3%-5% ether/hexanes) provided 78A in a 10:1 ratio (78A:78B).

\[^{13}C\text{ NMR}\] (75 MHz, CDCl\(_{3}\)) \(\delta = 167.9, 157.4, 142.2, 141.5, 137.3, 128.5, 127.3, 126.0, 119.4, 80.5, 60.8, 44.0, 20.8, 16.6, 14.7, 0.6, -0.1\)

\[^{1}H\text{ NMR}\] (300 MHz, CDCl\(_{3}\)) \(\delta = 7.65\ (d, 1H, J = 15.6\ Hz), 7.36\-7.22\ (m, 5H), 5.96\ (d, 1H, J = 15.6\ Hz), 5.13\ (d, 1H, J = 4.2\ Hz), 4.24\ (q, 2H, J = 11.4, 4.2\ Hz), 3.33\-3.29\ (m, 1H), 1.96\ (s, 3H), 1.32\ (t, 3H, J = 5.1\ Hz), 0.61\ (d, 3H, J = 7.2\ Hz), 0.46\ (s, 3H), 0.40\ (s, 3H)\)

\[^{31}P\text{ NMR}\] (162 MHz, CDCl\(_{3}\)) \(\delta = 31.2, 22.5, -3.3, -13.1\)

\[^{13}P\text{ NMR}\] (162 MHz, CDCl\(_{3}\)) \(\delta = 31.2, 22.5, -3.3, -13.1\)

FT-IR (NaCl, thin film) \(v = 2965, 1713, 1620, 1597, 1451, 1367, 1293, 1253, 1177\ cm\(^{-1}\))
**Diene Mixture 79A & 79B**

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under Ar\(_{(g)}\) was added diene mixture (1.5:1 78A:78B, 52 mg, 0.16 mmol, 1 equiv) and THF (0.8 mL). To the pale yellow solution was added TBAF (1M in THF, 0.32 mL, 0.32 mmol, 2 equiv). After stirring at rt for 1 h the reaction mixture was concentrated *in vacuo* to give an orange oil. Purification via column chromatography (silica gel; eluted with 30% ether/hexanes) gave the alcohol mixture as a clear oil (2:1 79A:79B, 13 mg, 30%).

\[R_f (40\% \text{ ether/hexanes}) = 0.26\]

\[^1\text{H NMR} (300 \text{ MHz, CDCl}_3) \delta = \text{isomer 79A:} \]

\[7.63 (d, 1H, J = 15.9 \text{ Hz}), 7.32-7.24 (m, 5H), 5.81 (d, 1H, J = 15.5 \text{ Hz}), 5.56 (d, 1H, J = 9.8 \text{ Hz}), 4.59 (d, 1H, J = 6.0 \text{ Hz}), 4.21 (q, 1H, J = 14.3, 7.2 Hz), 3.20-3.08 (m, 1H), 1.86 (br s, 1H), 1.79 (d, 3H, J = 1.3 Hz), 1.31 (t, 3H, J = 7.1 Hz), 1.05 (d, 3H, J = 6.8 Hz); \text{isomer 79B diagnostic peaks:} \]

\[5.72 (d, 1H, J = 15.6 \text{ Hz}), 5.69 (d, 1H, J = 9.7 \text{ Hz}), 4.55 (d, 1H, J = 6.8 \text{ Hz}), 4.18 (q, 1H, J = 13.5, 7.5 \text{ Hz}), 2.99-2.86 (m, 1H), 1.86 (br s, 1H), 1.59 (d, 1H, J = 1.2 Hz), 1.28 (t, 3H, J = 7.1 Hz), 1.09 (d, 3H, J = 6.8 Hz)\]
Silicon Tethered Alkyne 80

To a flame-dried 50 mL RBF equipped with a magnetic stir bar under Ar\textsubscript{(g)} was added a solution of alcohol 83 (296 mg, 1.3 mmol, 1 equiv) in DCM (9 mL). To the yellow solution was added imidazole (177 mg, 2.6 mmol, 2 equiv) and DMAP (32 mg, 0.26 mmol, 0.2 equiv). The solution was cooled to 0°C (ice/water bath) and vinyltrimethylchlorosilane (0.27 mL, 2.0 mmol, 1.5 equiv) was added in one portion via syringe. The yellow suspension stirred at 0°C for 5 min then was warmed to rt and stirred overnight. The reaction was quenched by addition of sat. NH\textsubscript{4}Cl\textsubscript{(aq)} (10 mL) and extracted with DCM (3 x 10 mL). The combined organics were dried over MgSO\textsubscript{4}, filtered and concentrated \textit{in vacuo} to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 10 cm; gradient elution with hexanes-3% EtOAc/hexanes) gave silicon-tethered alkyne 80 as a clear oil (348 mg, 83%).

R\textsubscript{f} (10\% EtOAc/hexanes) = 0.53

\([\alpha]D^{24} = +25.4^\circ \ (c = 0.956 \ \text{in CHCl}_3)\)

\(^1\text{H} \text{ NMR} \ (300 \ \text{MHz, CDCl}_3) \delta = 7.47-7.30 \ (m, 10H), 6.18 \ (dd, 1H, J = 19.7, 4.9 \text{ Hz}), 6.04 \ (dd, 1H, J = 14.9, 10.3 \text{ Hz}), 5.82 \ (dd, 1H, J = 19.7, 15.2 \text{ Hz}), 4.79 \ (d, 1H, J = 6.8 \text{ Hz}), 3.04-2.95 \ (m, 1H), 1.36 \ (d, 3H, J = 6.9 \text{ Hz}), 0.24 \ (s, 3H), 0.20 \ (s, 3H)

\(^{13}\text{C} \text{ NMR} \ (75 \ \text{MHz, CDCl}_3) \delta = 143.6, 138.0, 133.6, 131.9, 128.6, 128.2, 128.0, 127.8, 127.3, 124.3, 92.8, 82.9, 78.6, 36.6, 17.1, -1.0, -1.1

\textbf{FT-IR} \ (\text{NaCl, thin film}) \nu = 3053, 2967, 2887, 1597, 1491, 1452, 1407, 1253, 1086, 1070 \text{ cm}^{-1}

\textbf{Anal.} calcd for C\textsubscript{21}H\textsubscript{24}OSi: C 78.70, H 7.55; found: C 78.58, H 7.81.
**Methyl Ketone 81**

To a flame-dried 25 mL RBF equipped with a magnetic stir bar under Ar\(_{(g)}\) was added a solution of Weinreb amide 73 (1.0 g, 3.0 mmol, 1 equiv) in THF (6 mL). The reaction mixture was cooled to 0°C (ice/water bath) and methylmagnesium chloride (2 mL, 6.0 mmol, 2 equiv) was added dropwise. The reaction stirred at 0°C for 5 min then was warmed to rt and stirred for 3 h. The white suspension was poured into 1M HCl (10 mL) and the layers were separated. The aqueous phase was extracted with ether (3 x 10 mL) then the combined organic extracts were dried over MgSO\(_4\), filtered and concentrated *in vacuo* to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 15 cm; gradient elution with 1%-4% EtOAc/hexanes) gave 81 as a clear oil (718 mg, 82%).

\(R_f\) (15% EtOAc/hexanes) = 0.59

\([\alpha]_D^{24} = -16.9^\circ \ (c = 0.946\text{ in CHCl}_3)\)

\(^1H\text{ NMR} (300\text{ MHz, CDCl}_3)\ \delta = 7.33-7.21 \text{ (m, 5H), 4.83 (d, 1H, } J = 6.8 \text{ Hz), 2.86-2.77 (m, 1H), 1.91 (s, 3H), 1.16 (d, 3H, } J = 6.9 \text{ Hz), 0.88 (s, 9H), 0.03 (s, 3H), -0.22 (s, 3H)}\)

\(^13C\text{ NMR} (75\text{ MHz, CDCl}_3)\ \delta = 211.2, 143.4, 128.1, 127.5, 126.3, 76.3, 56.0, 30.5, 25.9, 18.2, 12.6, -4.5, -5.1\)

\text{FT-IR (NaCl, thin film)} \ \nu = 2959, 1715, 1454, 1360, 1256 \text{ cm}^{-1}\)

\text{Anal. calcd for C}_{17}\text{H}_{28}\text{O}_2\text{Si: C 69.81, H 9.65; found C 69.65, H 9.52.}
Enol Triflate 82

To a oven-dried 100 mL RBF equipped with a magnetic stir bar under Ar\(_{g}\) was added freshly prepared KHMD (1M in THF, 7.5 mmol, 1.1 equiv). The pale yellow solution was cooled to -78°C (dry ice/acetone bath) and methyl ketone 81 (2.0 g, 6.8 mmol, 1 equiv) in THF (6.8 mL) was added dropwise. Comins' reagent\(^{49}\) (5.3 g, 13.6 mmol, 2 equiv) in THF (6.8 mL) was subsequently added in one portion. The yellow solution stirred at -78°C for 2 h. The reaction mixture was warmed slightly and quenched with H\(_2\)O (15 mL). The layers were separated and the aqueous phase was extracted with DCM (3 x 10 mL). The combined organics were dried over MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give a yellow oil. The residue was purified by column chromatography (silica gel; gradient elution with 1%-2% EtOAc/hexanes) to give 82 as a clear oil (2.35 g, 81%).

\(R_f\) (10% EtOAc/hexanes) = 0.68

\([\alpha]_D^{24} = +1.4^\circ\ (c = 0.946 \text{ in CHCl}_3)\)

\(^1\text{H NMR\ (300 MHz, CDCl}_3\) \(\delta = 7.34-7.21 \text{ (m, 5H), 5.17 \text{ (d, 1H, } J = 3.8 \text{ Hz), 4.95-4.93 \text{ (m, 2H), 2.67-2.59 \text{ (m, 1H), 1.05 \text{ (d, 3H, } J = 6.9 \text{ Hz), 0.91 \text{ (s, 9H), 0.02 \text{ (s, 3H), -0.18 \text{ (s, 3H))}}}}\)

\(^{13}\text{C NMR\ (75 MHz, CDCl}_3\) \(\delta = 158.6, 142.8, 128.2, 127.6, 126.4, 118.8 \text{ (q, } J_{C,F} = 316.4 \text{ Hz), 105.5, 74.0, 47.7, 26.0, 18.5, 11.3, -4.5, -5.3}}\)

\text{Anal. calcd for } C_{18}H_{27}F_3O_4Si: \text{ C 50.92, H 6.41; found C 50.47, H 6.38.}
**Alcohol 83**

To an oven-dried 100 mL RBF equipped with a magnetic stir bar was added a solution of enol triflate 82 (2.56 g, 6.0 mmol, 1 equiv) in DMF (25 mL). To the clear solution was added TBAF·3H₂O (7.8 g, 30 mmol, 5 equiv) then the solution stirred at 60°C for 1 h. The reaction mixture was cooled to rt, quenched with water (50 mL) and the layers were separated. The aqueous phase was extracted with DCM (3 x 30 mL) then the combined organic extracts were washed with brine (2 x 60 mL), dried over MgSO₄, filtered and concentrated *in vacuo* to give a yellow oil, 875 mg. The oil was dissolved in THF (22 mL) and added to an oven-dried 100 mL Schlenk tube under Ar(g) containing PdCl₂(PPh₃)₂ (197 mg, 0.28 mmol, 0.05 equiv), CuI (105 mg, 0.55 mmol, 0.10 equiv), NEt₃ (2.3 mL, 16.5 mmol, 3 equiv) and iodobenzene (0.92 mL, 8.3 mmol, 1.5 equiv). The orange solution was subjected to three cycles of freeze/pump/thaw then stirred at rt under Ar(g). After 30 min, the brown suspension was diluted with ether (20 mL), washed with sat. NH₄Cl(aq) (2 x 35 mL) and brine (2 x 35 mL), dried over MgSO₄, filtered and concentrated *in vacuo* to give a red/orange oil. Purification via column chromatography (silica gel 2.5 x 15 cm; gradient elution with 10%-20% EtOAc/hexanes) gave 83 as an orange oil (1.02 g, 72% over two steps).

*R*<sub>f</sub> (20% EtOAc/hexanes) = 0.33

[α]_<sub>D</sub><sup>24</sup> = -14.9° (c = 0.728 in CHCl₃)

**1H NMR** (300 MHz, CDCl₃) δ = 7.50-7.30 (m, 10H), 4.80 (d, 1H, *J* = 3.7 Hz), 3.17-3.08 (m, 1H), 2.67 (s, 1H), 1.30 (d, 3H, *J* = 7.0 Hz)
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta =$ 141.7, 131.7, 128.3, 128.2, 128.0, 127.9, 126.8, 123.5, 91.3, 83.3, 76.8, 35.1, 16.3

Anal. calcd for C$_{17}$H$_{16}$O: C 86.40, H 6.82; found C 86.46, H 6.64.
To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar in an Ar\textsubscript{(g)} filled glovebox was added RuHCl(CO)(H\textsubscript{2}IMes)(PPh\textsubscript{3}) (12 mg, 0.016 mmol, 0.10 equiv) and a solution of alkyne 80 (50 mg, 0.16 mmol, 1 equiv) and ethyl acrylate (87 µL, 0.80 mmol, 5 equiv) in toluene (0.5 mL). The vessel was sealed with a rubber septum, removed from the glovebox and placed under Ar\textsubscript{(g)}. The septum was removed, a cold-finger was quickly attached then the solution stirred at 110°C. After 30 min the brown solution was cooled to rt, filtered through a plug of silica gel (eluted with DCM) and concentrated \textit{in vacuo} to give a brown oil. Purification via column chromatography (silica gel 1.5 x 8.5 cm; gradient elution with 1\%-4\% ether/hexanes) gave diene 84 as a clear oil (14 mg, 22%).

\textit{R}_f (1:15 ether/hexanes) = 0.22

\textbf{\textit{1H NMR}} (300 MHz, CDCl\textsubscript{3}) \(\delta = 7.85 \) (d, 1H, \(J = 15.8\) Hz), 7.40-7.24 (m, 8H), 7.18-7.14 (m, 2H), 5.57 (d, 1H, \(J = 15.4\) Hz), 5.18 (d, 1H, \(J = 4.1\) Hz), 4.20 (q, 1H, \(J = 14.4, 7.2\) Hz), 3.51-3.42 (m, 1H), 1.27 (t, 3H, \(J = 7.1\) Hz), 0.75 (d, 3H, \(J = 7.2\) Hz), 0.30 (s, 3H), -0.30 (s, 3H)
Silyl-Dienyl Boronate 87

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar in an argon filled glovebox was added RuHCl(CO)(PCy$_3$)$_2$ (9.4 mg, 0.013 mmol, 0.05 equiv), alkyne 41 (62.9 mg, 0.26 mmol, 1 equiv) in DCE (0.52 mL) and vinyl boronate 86 (82 µL, 0.52 mmol, 2 equiv). The vessel was sealed with a rubber septum, removed from the glovebox and placed under Ar$_{(g)}$. A cold-finger was quickly attached then the reaction stirred at 85°C for 3.5 h. The brown solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a brown oil. Purification via column chromatography (silica gel 1.5 x 11 cm; gradient elution with 5%-40% ether/hexanes) gave 87 as a light brown oil (58.6 mg, 63%).

R$_f$(10% ether/hexanes) = 0.10

$^1$H NMR (300 MHz, CDCl$_3$) δ = 7.45 (d, 1H, J = 17.8 Hz), 7.29-7.23 (m, 3H), 7.09-7.05 (m, 2H), 5.20 (d, 1H, J = 17.8 Hz), 4.24-4.14 (m, 1H), 3.62 (s, 4H), 3.08 (dd, 1H, J = 16.2, 5.3 Hz), 2.40 (dd, 1H, J = 16.2, 8.2 Hz), 1.31 (d, 3H, J = 6.1 Hz), 0.95 (s, 6H), -0.09 (s, 3H), -0.23 (s, 3H)
**General Procedure A: Vinyl Boronate Coupling**

**Silyl-Dienyl Boronate 97**

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar in an argon filled glovebox was added RuHCl(CO)(PCy$_3$)$_2$ (9.4 mg, 0.013 mmol, 0.05 equiv), alkyne 41 (62.9 mg, 0.26 mmol, 1 equiv) in toluene (0.52 mL) and vinyl boronate 93 (90 µL, 0.52 mmol, 2 equiv). The vessel was sealed with a rubber septum, removed from the glovebox, placed under Ar$_{(g)}$, then stirred at 85°C for 3.5 h. The orange/brown solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give an amber-colored oil. Purification via column chromatography (silica gel 2.5 x 12 cm; eluted with 10% ether/hexanes) gave 97 as a light brown oil (53.2 mg, 55%).

$R_f$ (10% ether/hexanes) = 0.14

$^1$H NMR (300 MHz, CDCl$_3$) δ = 7.43 (dd, 1H, $J = 18.0$, 1.5 Hz), 7.29-7.22 (m, 3H), 7.08-7.05 (m, 2H), 5.20 (d, 1H, $J = 17.7$ Hz), 4.23-4.16 (m, 1H), 3.07 (ddd, 1H, $J = 16.5$, 5.1, 3.9 Hz), 2.40 (ddd, 1H, $J = 16.5$, 8.1, 4.2 Hz), 1.77 (dd, 1H, $J = 14.1$, 3.0 Hz), 1.47 (dd, 1H, $J = 13.8$, 11.7 Hz), 1.33-1.24 (m, 12H), -0.09 (s, 1.5H), -0.11 (s, 1.5H), -0.24 (s, 1.5H), -0.26 (s, 1.5H)

$^{13}$C NMR (75 MHz, CDCl$_3$) δ = 148.4, 145.9, 144.7, 141.9, 129.9, 127.9, 127.2, 72.7, 71.0, 65.0, 46.1, 40.8, 31.4, 28.3, 24.2, 23.3, 0.7, 0.6, -0.3, -0.4

$^{11}$B NMR (96 MHz, CDCl$_3$) δ = 28.7

FT-IR (NaCl, thin film) ν = 2976, 1629, 1384, 1306, 1260, 1209, 1170, 1090, 807 cm$^{-1}$

Anal. calcd for C$_{21}$H$_{31}$BO$_3$Si: C 68.10, H 8.44; found C 67.91, H 8.73.
**Boronate Dimer 101**

To an oven-dried 25 mL Schlenk tube with stir bar under Ar\(_g\) was added RuHCl(CO)(PCy\(_3\))\(_2\) (36 mg, 0.05 mmol, 0.05 equiv), vinyl boronate 93 (0.17 mL, 1.0 mmol, 1 equiv) and DCE (1 mL). A cold-finger was quickly attached and the orange suspension stirred at 85°C overnight. The resulting red/brown solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a brown oil. Purification via column chromatography (silica gel 2.5 x 15 cm; gradient elution with 10%-20% ether/hexanes) gave 101 as a light brown solid (60 mg, 43%).

\[ R_f (20\% \text{ ether/hexanes}) = 0.12 \]

\[ mp = 57-59^\circ C \]

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta = 6.50 \text{ (s, 2H), } 4.23-4.15 \text{ (m, 2H), } 1.76 \text{ (dd, 2H, } J = 13.6, 2.8 \text{ Hz), } 1.44 \text{ (dd, 2H, } J = 13.6, 11.6 \text{ Hz), } 1.26 \text{ (s, 12H), } 1.23 \text{ (d, 6H, } J = 6.4 \text{ Hz) }\]

**\(^13\)C NMR** (100 MHz, CDCl\(_3\)) \(\delta = 70.8, 64.8, 46.1, 31.4, 28.2, 23.3 \]

**\(^11\)B NMR** (128 MHz, CDCl\(_3\)) \(\delta = 25.4 \]

**FT-IR** (NaCl, thin film) \(\nu = 2976, 2910, 2362, 1945, 1394, 1266, 1208, 1178, 1031 \text{ cm}^{-1}\)

**Anal.** calcd for C\(_{14}H_{26}B_2O_4\): C 60.06, H 9.36; found C 60.14, H 9.36.
Silyl-Dienyl Boronate 102

Following general procedure A: RuHCl(CO)(PCy₃)₂ (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne 55²⁶ (82.0 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate 93 (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 3 h. The residue was purified by column chromatography (silica gel 2.5 x 12 cm; eluted with 10% ether/hexanes) to give 102 as a pale brown oil (68.3 mg, 60%).

Rf (10% ether/hexanes) = 0.19

¹H NMR (300 MHz, CDCl₃) δ = 7.43 (dd, 1H, J = 17.7, 1.5 Hz), 7.27-7.23 (m, 3H), 7.07-7.04 (m, 2H), 5.20 (d, 1H, J = 17.7 Hz), 4.23-4.19 (m, 1H), 4.07-4.03 (m, 1H), 3.04 (dt, 1H, J = 15.9, 4.8 Hz), 2.45 (ddd, 1H, J = 16.2, 7.5, 3.6 Hz), 1.77 (dd, 1H, J = 13.8, 2.7 Hz), 1.48 (t, 1H, J = 11.7 Hz), 1.95-0.99 (m, 24H), -0.12 (s, 1.5H), -0.14 (s, 1.5H), -0.22 (s, 1.5H), -0.24 (s, 1.5H)

¹³C NMR (75 MHz, CDCl₃) δ = 148.4, 145.8, 144.8, 142.0, 129.9, 127.9, 127.1, 76.7, 71.0, 65.0, 46.1, 38.9, 38.6, 32.0, 31.4, 29.9, 29.5, 28.3, 25.9, 23.3, 22.9, 14.3, 0.7, 0.6, -0.2, -0.3

¹¹B NMR (96 MHz, CDCl₃) δ = 27.5

FT-IR (NaCl, thin film) ν = 2930, 2858, 1597, 1583, 1417, 1390, 1324, 1291, 1272, 1200 cm⁻¹

HRMS (ESI) calcd for (C₂₇H₄₃BO₃Si)Na⁺: 477.2967; found: 477.2966.
Silyl-Dienyl Boronate 103

Following general procedure A: RuHCl(CO)(PCy$_3$)$_2$ (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne 56$^{26}$ (82.7 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate 93 (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 6 h. The residue was purified by column chromatography (silica gel 2.5 x 12.5 cm; eluted with 10% ether/hexanes) to give 103 as a pale brown oil (67 mg, 58%).

$\textbf{R}_f$ (10% ether/hexanes) = 0.16

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.45 (dd, 1H, $J$ = 17.7, 1.5 Hz), 7.33-7.07 (m, 10H), 5.24 (d, 1H, $J$ = 17.7 Hz), 4.26-4.20 (m, 1H), 4.16-4.07 (m, 1H), 3.07 (dt, 1H, $J$ = 15.9, 5.1 Hz), 2.90-2.69 (m, 2H), 2.53 (ddd, 1H, $J$ = 16.2, 7.2, 4.2 Hz), 1.91 (m, 2H), 1.79 (dd, 1H, $J$ = 13.8, 3.0 Hz), 1.50 (t, 1H, $J$ = 11.7 Hz), 1.30-1.27 (m, 9H), -0.06 (s, 1.5H), -0.08 (s, 1.5H), -0.16 (s, 1.5H), -0.18 (s, 1.5H)

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 148.5, 145.4, 144.7, 142.5, 142.0, 129.9, 128.6, 128.5, 127.9, 127.2, 125.9, 75.9, 71.0, 65.0, 46.1, 40.2, 38.9, 32.3, 31.4, 28.3, 23.3, 0.7, 0.6, -0.2, -0.3

$^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ = 27.6

FT-IR (NaCl, thin film) $\nu$ = 3029, 2977, 2933, 1583, 1390, 1303, 1290, 1272, 1252, 1200 cm$^{-1}$

HRMS (ESI) calc. for (C$_{28}$H$_{37}$BO$_3$Si)Na$^+$: 483.2497; found 483.2496.
Silyl-Dienyl Boronate 104

Following general procedure A: \( \text{RuHCl(CO)(PCy}_3)_2 \) (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne 57\(^{26} \) (78.9 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate 93 (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 4.5 h. The residue was purified by column chromatography (silica gel 2.5 x 12 cm; eluted with 5% ether/hexanes) to give 104 as a pale brown oil (66.3 mg, 60%).

\( R_f \) (10% ether/hexanes) = 0.37

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta = 7.43 \) (dd, 1H, \( J = 18.0, 2.1 \) Hz), 7.28-7.24 (m, 3H), 7.07-7.04 (m, 2H), 5.20 (d, 1H, \( J = 17.7 \) Hz), 4.23-4.20 (m, 1H), 3.77 (q, 1H, \( J = 6.5 \) Hz), 2.99 (ddd, 1H, \( J = 16.5, 5.7, 3.6 \) Hz), 2.51 (ddd, 1H, \( J = 16.5, 8.4, 1.5 \) Hz), 1.95-1.09 (m, 1H), 1.80-1.00 (m, 21H), -0.10 (s, 1.5H), -0.12 (s, 1.5H), -0.26 (s, 1.5H), -0.28 (s, 1.5H)

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta = 148.1, 146.0, 144.7, 142.1, 129.9, 127.9, 127.1, 80.9, 71.0, 65.0, 46.1, 44.8, 36.0, 31.4, 29.2, 28.8, 28.3, 26.8, 26.4, 26.3, 23.3, 0.5, 0.4, -0.3, -0.4

\(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \( \delta = 28.0 \)

FT-IR (NaCl, thin film) \( \nu = 2974, 2927, 2854, 1597, 1583, 1416, 1390, 1291, 1250, 1206, 1163, 1030 \) cm\(^{-1}\)

HRMS (ESI) calc. for \((C_{26}H_{39}BO_3)Na^+\): 461.2654; found: 461.2651.
Silyl-Dienyl Boronate 105

Following general procedure A: RuHCl(CO)(PCy₃)₂ (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne 61²⁶ (94.8 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate 93 (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 3.5 h. The residue was purified by column chromatography (silica gel 2.5 x 13.5 cm; eluted with 5% ether/hexanes) to give 105 as a pale yellow solid (72.2 mg, 57%).

R_f (10% ether/hexanes) = 0.31

mp = 51-54°C

^1H NMR (300 MHz, CDCl₃) δ = 7.64-7.13 (m, 15H), 5.28 (d, 1H, J = 17.7 Hz), 5.11 (dd, 1H, J = 9.6, 5.4 Hz), 4.24-4.19 (m, 1H), 3.46 (ddd, 1H, J = 16.5, 5.4, 2.7 Hz), 2.72 (dd, 1H, J = 16.2, 9.6 Hz), 1.78 (dd, 1H, J = 14.1, 3.0 Hz), 1.49 (t, 1H, J = 11.7 Hz), 1.29-1.25 (m, 9H), 0.12 (s, 1.5H), 0.11 (s, 1.5H), -0.15 (s, 1.5H), -0.17 (s, 1.5H)

^13C NMR (75 MHz, CDCl₃) δ = 148.6, 145.1, 144.6, 143.9, 143.8, 141.9, 141.3, 140.5, 129.9, 128.9, 128.0, 127.4, 127.3, 126.2, 77.9, 71.1, 65.0, 46.1, 42.2, 42.1, 31.4, 28.3, 23.3, 0.6, 0.5, -0.5, -0.6

^11B NMR (96 MHz, CDCl₃) δ = 28.1

FT-IR (NaCl, thin film) ν = 3057, 2793, 1598, 1583, 1417, 1346, 1251, 1207 cm⁻¹

Anal. calcd for C₃₂H₃₇BO₃Si: C 75.58, H 7.33; found C 75.98, H 7.62.
Silyl-Dienyl Boronate 106

Following general procedure A: RuHCl(CO)(PCy)_3 (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne 62 (79.2 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate 93 (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 2 h. The residue was purified by column chromatography (silica gel 2.5 x 13 cm; gradient elution with 5%-10% ether/hexanes) to give 106 as a pale brown oil (61.7 mg, 55%).

R_f (10% ether/hexanes) = 0.35

^1H NMR (300 MHz, CDCl_3) δ = 7.53-7.06 (m, 11H), 5.24 (d, 1H, J = 17.7 Hz), 4.29-4.18 (m, 1H), 3.25 (d, 1H, J = 16.2 Hz), 3.04 (d, 1H, J = 16.2 Hz), 1.79 (dd, 1H, J = 13.8, 2.7 Hz), 1.58 (s, 3H), 1.54-1.46 (m, 1H), 1.30-1.27 (m, 9H), -0.06 (s, 3H), -0.17 (d, 3H, J = 2.1 Hz)

^13C NMR (75 MHz, CDCl_3) δ = 149.5, 148.9, 145.4, 144.5, 142.0, 129.9, 128.2, 128.0, 127.2, 126.6, 124.9, 81.7, 71.1, 65.0, 46.5, 46.1, 31.9, 31.4, 28.3, 23.4, 0.92, 0.90, 0.85, 0.83

^11B NMR (96 MHz, CDCl_3) δ = 27.6

FT-IR (NaCl, thin film) ν = 3060, 3028, 2975, 1584, 1493, 1418, 1391, 1324, 1291, 1252, 1207, 1162 cm⁻¹

HRMS (ESI) calc. for (C_{27}H_{35}BO_{3}Si)Na⁺: 469.2341; found 469.2339.
Silyl-Dienyl Boronate 107

Following general procedure A: RuHCl(CO)(PCy$_3$)$_2$ (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne 66$^{26}$ (64.4 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate 93 (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 4.5 h. The residue was purified by column chromatography (silica gel 2.5 x 12 cm; eluted with 10% ether/hexanes) to give 107 as a pale brown oil (53 mg, 55%).

\[ R_f (10\%\ ether/hexanes) = 0.20 \]

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.42 (dd, 1H, $J = 17.7$, 1.5 Hz), 7.08-7.05 (m, 2H), 6.96-6.93 (m, 2H), 5.21 (d, 1H, $J = 18.0$ Hz), 4.23-4.16 (m, 2H), 3.06 (ddd, 1H, $J = 16.2$, 5.1, 3.9 Hz), 2.39 (ddd, 1H, $J = 16.2$, 8.1, 3.9 Hz), 2.32 (s, 3H), 1.77 (dd, 1H, $J = 13.8$, 3.0 Hz), 1.47 (dd, 1H, $J = 13.8$, 11.7 Hz), 1.33-1.24 (m, 12H), -0.08 (s, 1.5H), -0.10 (s, 1.5H), -0.22 (s, 1.5H), -0.24 (s, 1.5H)

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 148.4, 145.6, 144.9, 138.9, 136.7, 129.8, 128.6, 72.7, 71.0, 65.0, 46.1, 40.8, 31.4, 28.3, 24.2, 23.4, 21.4, 0.8, 0.7, -0.2, -0.3

$^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ = 28.6

FT-IR (NaCl, thin film) $\nu$ = 2973, 1583, 1510, 1390, 1346, 1291, 1206, 1123, 1060 cm$^{-1}$

HRMS (ESI) calc. for (C$_{22}$H$_{33}$BO$_3$Si)Na$^+$: 407.2184; found 407.2183.
Silyl-Dienyl Boronate 108

Following general procedure A: RuHCl(CO)(PCy₃)₂ (8.7 mg, 0.012 mmol, 0.05 equiv), alkyne 67 (65.2 mg, 0.24 mmol, 1 equiv) in toluene (0.48 mL) and vinyl boronate 93 (83 µL, 0.48 mmol, 2 equiv) were combined and stirred at 85°C for 5 h. The residue was purified by column chromatography (silica gel 2.5 x 12 cm; eluted with 10% ether/hexanes) to give 108 as a pale brown oil (54.5 mg, 57%).

R<sub>f</sub> (10% ether/hexanes) = 0.20

<sup>1</sup>H NMR (300 MHz, CDCl₃) δ = 7.41 (dd, 1H, J = 17.7, 1.8 Hz), 6.86 (s, 1H), 6.66 (s, 2H), 5.26 (d, 1H, J = 17.7 Hz), 4.24-4.15 (m, 2H), 3.05 (dt, 1H, J = 15.9, 5.1 Hz), 2.37 (ddd, 1H, J = 16.2, 8.1, 5.1 Hz), 2.25 (s, 6H), 1.77 (dd, 1H, J = 13.8, 3.0 Hz), 1.48 (dd, 1H, J = 13.8, 11.7 Hz), 1.37-1.29 (m, 12H), -0.04 (s, 1.5H), -0.08 (s, 1.5H), -0.18 (s, 1.5H), -0.21 (s, 1.5H)

<sup>13</sup>C NMR (75 MHz, CDCl₃) δ = 148.7, 145.4, 144.8, 141.8, 137.1, 128.6, 127.6, 72.7, 71.0, 65.0, 46.1, 40.7, 31.4, 28.3, 24.2, 23.4, 21.4, 0.7, 0.6, -0.3, -0.4

<sup>11</sup>B NMR (96 MHz, CDCl₃) δ = 27.6

FT-IR (NaCl, thin film) ν = 2973, 2927, 1598, 1417, 1346, 1230, 1207, 1162, 1124 cm⁻¹

HRMS (ESI) calc. for (C<sub>23</sub>H<sub>35</sub>BO<sub>3</sub>Si)Na⁺: 421.2341; found 421.2340.
Silyl-Dienyl Boronate 109

Following general procedure A: RuHCl(CO)(PCy$_3$)$_2$ (20 mg, 0.027 mmol, 0.10 equiv), alkyne 68 (73.1 mg, 0.27 mmol, 1 equiv) in toluene (0.54 mL) and vinyl boronate 93 (94 µL, 0.54 mmol, 2 equiv) were combined and stirred at 85°C for 5 h. The residue was purified by column chromatography (silica gel 1.5 x 15 cm; gradient elution with 4%-8% ether/hexanes) to give 109 as a pale brown oil (32.4 mg, 30%, 16:3:1).

R$_f$ (10% ether/hexanes) = 0.26

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.21-7.07 (m, 6H), 5.51 (d, 1H, $J$ = 18.0 Hz), 4.21-4.11 (m, 1H), 4.01-3.94 (m, 1H), 2.87-2.81 (m, 1H), 2.77-2.59 (m, 3H), 2.32-2.25 (m, 1H), 1.81 (s, 3H), 1.72 (dd, 2H, $J$ = 13.9, 2.8 Hz), 1.44 (dd, 1H, $J$ = 13.7, 11.8 Hz), 1.24 (d, 6H, $J$ = 2.8 Hz), 1.21 (d, 3H, $J$ = 6.3 Hz), 0.25 (s, 3H), 0.21 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 145.1, 142.6, 142.5, 140.5, 128.6, 128.5, 125.9, 76.2, 71.0, 65.0, 46.2, 40.2, 38.6, 32.3, 31.4, 28.3, 23.4, 20.4, 0.5, 0.0

FT-IR (NaCl, thin film) $\nu$ = 3062, 2973, 2933, 1590, 1418, 1391, 1298, 1201, 1163 cm$^{-1}$

Anal. calcd for C$_{32}$H$_{37}$BO$_3$Si: C 69.34, H 8.85; found C 69.39, H 9.05.
Silyl-Dienyl Boronate 112

Following general procedure A: RuHCl(CO)(PCy$_3$)$_2$ (28 mg, 0.039 mmol, 0.10 equiv), alkyne 77 (101 mg, 0.39 mmol, 1 equiv) in toluene (0.8 mL) and vinyl boronate 93 (0.14 mL, 0.78 mmol, 2 equiv) were combined and stirred at 85°C for 3 h. The residue was purified by column chromatography (silica gel 2.5 x 15 cm; gradient elution with 3%-6% ether/hexanes) to give 112 as a brown oil (114 mg, 76%, 3:1 E:Z).

$R_f$ (10% ether/hexanes) = 0.32

$[\alpha]_D^{24} = -36.0^\circ$ ($c = 0.464$ in DCM)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta =$ major isomer: 7.31-7.16 (m, 6H), 5.58 (d, 1H, $J = 17.9$ Hz), 5.04 (d, 1H, $J = 4.3$ Hz), 4.24-4.13 (m, 1H), 3.28-3.23 (m, 1H), 1.87 (s, 3H), 1.74 (dd, 1H, $J = 13.9$, 2.9 Hz), 1.46 (dd, 1H, $J = 13.6$, 11.7 Hz), 1.26-1.20 (m, 12H), 0.39 (s, 3H), 0.31 (s, 3H); minor isomer diagnostic peaks: 6.97 (d, 1H, $J = 17.5$ Hz), 5.49 (d, 1H, $J = 17.5$ Hz), 5.07 (d, 1H, $J = 4.3$ Hz), 3.02-2.93 (m, 1H), 1.84 (s, 3H), 0.50 (d, 3H, $J = 6.9$ Hz), 0.42 (s, 3H), 0.37 (s, 3H)

$^1$C NMR (75 MHz, CDCl$_3$) $\delta =$ major isomer: 149.2, 144.3, 141.9, 140.3, 128.1, 126.9, 126.0, 80.6, 71.0, 65.0, 46.2, 43.1, 31.4, 28.30, 23.4, 20.7, 16.1, 0.6, -0.2; minor isomer diagnostic peaks: 152.8, 151.0, 142.6, 125.9, 80.3, 70.9, 64.9, 46.1, 44.5, 28.34, 14.6, 1.0, 0.4

$^{11}$B NMR (96 MHz, CDCl$_3$) $\delta = 26.7$

FT-IR (NaCl, thin film) $\nu =$ 2972, 2929, 2869, 1589, 1496, 1391, 1297 cm$^{-1}$

Anal. calcd for C$_{22}$H$_{33}$BO$_3$Si: C 68.74, H 8.65; found C 68.97, H 8.72.
Silyl-Dienyl Iodide 113

To an oven-dried 25 mL Schlenk tube with stir bar was added silyl dienyl boronate 112 (113 mg, 0.29 mmol, 1 equiv) and THF (0.6 mL). A solution of 5M NaOH (0.17 mL, 0.87 mmol, 3 equiv) was added dropwise and the tan-colored reaction mixture stirred at rt. After 15 min, I₂ (147 mg, 0.58 mmol, 2 equiv) in THF (0.6 mL) was added. The reaction stirred in the dark at rt for 20 min then was quenched by sat. Na₂S₂O₃(aq) (3 mL). After extraction with DCM (3 x 3 mL), the combined organics were dried over MgSO₄, filtered and concentrated in vacuo. The orange residue was purified by column chromatography (silica gel 1.5 x 7 cm; eluted with 3% ether/hexanes) to give 113 as a yellow oil (80.2 mg, 72%, 3:1 E:Z).

Rₓ (10% ether/hexanes) = 0.56

[α]D²⁴ = -22.0° (c = 1.538 in CDCl₃)

¹H NMR (400 MHz, CDCl₃) δ = major isomer: 7.35 (d, 1H, J = 14.6 Hz), 7.24-7.13 (m, 5H), 6.21 (d, 1H, J = 14.6 Hz), 5.02 (d, 1H, J = 4.4 Hz), 3.08-3.01 (m, 1H), 1.81 (s, 3H), 0.51 (d, 3H, J = 7.3 Hz), 0.37 (s, 3H), 0.30 (s, 3H); minor isomer diagnostic peaks: 6.94 (d, 1H, J = 14.3 Hz), 6.29 (d, 1H, J = 14.4 Hz), 5.03 (d, 1H, J = 4.3 Hz), 2.95-2.88 (m, 1H), 1.79 (s, 3H), 0.48 (d, 3H, J = 7.2 Hz), 0.39 (s, 3H), 0.32 (s, 3H)

¹³C NMR (100 MHz, CDCl₃) δ = major isomer: 149.0, 148.1, 144.2, 141.43, 138.7, 128.2, 125.8, 80.2, 79.7, 43.4, 20.3, 16.0, 0.5, -0.2; minor isomer diagnostic peaks: 151.2, 141.41, 141.4, 127.0, 80.1, 76.5, 44.4, 15.0, 14.5, 1.1, 0.4

FT-IR (NaCl, thin film) ν = 3027, 2962, 2924, 1603, 1494, 1251, 1093, 1064, 993 cm⁻¹

Anal. calcd for C₁₆H₂₁IOSi: C 50.00, H 5.51; found C 49.84, H 5.43.
Silyl-Dienyl Boronate 117

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar in an Ar\(_{(g)}\) filled glovebox was added RuHCl(CO)(PCy\(_{3}\))\(_2\) (11 mg, 0.015 mmol, 0.05 equiv), alkyne 60 (102.7 mg, 0.29 mmol, 1 equiv), vinyl boronate 94 (89.3 mg, 0.58 mmol, 2 equiv) and DCE (0.58 mL). The vessel was sealed with a rubber septum, removed from the glovebox then placed under Ar\(_{(g)}\). The septum was removed, a cold-finger was quickly attached and the orange solution stirred at 85°C. After 2 h, the resulting brown solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated to give a brown oil. Purification via column chromatography (silica gel 2.5 x 15 cm; gradient elution with 5%-15% ether/hexanes) gave 117 as a pale brown solid (68 mg, 49%, 11:1 Z:E).

R\(_f\) (10% ether/hexanes) = 0.14

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = \text{major isomer:}\) 8.18 (d, 2H, \(J = 8.8\) Hz), 7.53 (d, 2H, \(J = 8.4\) Hz), 7.43 (d, 1H, \(J = 18.5\) Hz), 7.30-7.23 (m, 3H), 7.07-7.05 (m, 2H), 5.28 (d, 1H, \(J = 18.5\) Hz), 5.12-5.08 (m, 1H), 3.45 (dd, 1H, \(J = 16.4, 5.6\) Hz), 2.52 (dd, 1H, \(J = 16.4, 9.6\) Hz), 1.20 (s, 12H), 0.05 (s, 3H), -0.20 (s, 3H); \textit{minor isomer diagnostic peaks:} 5.60 (d, 1H, \(J = 14.5\) Hz), 3.21 (dd, 1H, \(J = 16.2, 5.4\) Hz), 0.13 (s, 3H), -0.17 (s, 3H)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = \text{major isomer:}\) 152.3, 148.9, 147.3, 146.8, 145.2, 141.1, 129.8, 128.1, 127.6, 126.2, 123.9, 83.6, 77.0, 41.8, 24.9, 0.4, -0.6; \textit{minor isomer diagnostic peaks:} 152.6, 149.1, 148.1, 143.7, 142.7, 137.2, 129.2, 128.3, 127.8, 126.1, 83.3, 76.7, 43.2, 25.1, 0.8, -0.6
Anal. calcd for $\text{C}_{26}\text{H}_{32}\text{BNO}_5\text{Si}$: C 65.41, H 6.76, N 2.93; found C 65.48, H 6.89, N 2.81.
Diene 118

Following general procedure A: RuHCl(CO)(PCy$_3$)$_2$ (10.2 mg, 0.014 mmol, 0.05 equiv), alkyne 41 (67.7 mg, 0.28 mmol, 1 equiv) in THF (0.6 mL) and vinyl boronate 93 (97 µL, 0.56 mmol, 2 equiv) were combined and stirred at 70°C overnight. In a separate oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under Ar$_{(g)}$ was added Pd(OAc)$_2$ (3.1 mg, 0.014 mmol, 0.05 equiv), S-Phos (11.5 mg, 0.028 mmol, 0.10 equiv), 4-iodotoluene (91.6 mg, 0.42 mmol, 1.5 equiv), K$_3$PO$_4$ (2M, freshly prepared and degassed prior, 0.84 mmol, 0.42 mL, 3 equiv) and THF (2.2 mL, degassed). To the resulting orange solution was added the crude diene reaction mixture then the dark brown mixture stirred at 50°C overnight. The solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a brown oil. The residue was purified by column chromatography (silica gel 1.5 x 13 cm; gradient elution with 5%-10% ether/hexanes) to give 118 as an orange oil (50.4 mg, 54% over two steps).

R$_f$ (10% ether/hexanes) = 0.18

$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.39-7.08 (m, 10H), 6.16 (d, 1H, $J$ = 15.9 Hz), 4.30-4.20 (m, 1H), 3.07 (dd, 1H, $J$ = 16.2, 5.1 Hz), 2.43 (dd, 1H, $J$ = 16.2, 8.4 Hz), 2.32 (s, 3H), 1.36 (d, 3H, $J$ = 6.0 Hz), -0.07 (s, 3H), -0.19 (s, 3H)

FT-IR (NaCl, thin film) ν = 3078, 3026, 2966, 2866, 2241, 1603, 1584, 1510, 1491, 1376, 1249, 1124, 1095 cm$^{-1}$

Anal. calcd for C$_{22}$H$_{26}$OSi: C 78.99, H 7.83; found C 78.77, H 7.44.
Diene 119

Following general procedure A: RuHCl(CO)(PCy₃)₂ (17.4 mg, 0.024 mmol, 0.10 equiv), alkyne 68 (66.2 mg, 0.24 mmol, 1 equiv) in toluene (0.48 mL) and vinyl boronate 93 (125 µL, 0.72 mmol, 3 equiv) were combined and stirred at 85°C for 3 h. In a separate oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under Ar(g) was added Pd(OAc)₂ (3 mg, 0.012 mmol, 0.05 equiv), S-Phos (10 mg, 0.024 mmol, 0.10 equiv) and 4-iodotoluene (239 mg, 1.2 mmol, 5 equiv). The crude silyl-dienyl boronate was dissolved in THF (2.4 mL) and degassed for 30 min then added to the solids, followed by K₃PO₄ (2M, freshly prepared and degassed prior, 2.4 mmol, 1.2 mL, 10 equiv). The brown reaction mixture stirred at 50°C overnight. The solution was cooled to rt, dried over MgSO₄ while stirring, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a brown oil. The residue was purified by column chromatography (silica gel 2.5 x 17 cm; gradient elution with 3%-5% ether/hexanes) to give 119 as an orange oil (3 isomers, 34 mg, 39% over two steps, 6:1 E:Z).

Rᶠ (10% ether/hexanes) = 0.53

¹H NMR (300 MHz, CDCl₃) δ = major isomer (E): 7.16-6.93 (m, 9H), 6.85 (d, 1H, J = 16.2 Hz), 6.40 (d, 1H, J = 16.1 Hz), 3.94-3.85 (m, 1H), 2.74-2.48 (m, 3H), 2.21-2.08 (m, 1H), 2.15 (s, 3H), 1.81 (s, 3H), 1.74-1.60 (m, 2H), 0.17 (s, 3H), 0.13 (s, 3H); minor isomer diagnostic peaks (Z): 6.52 (d, 1H, J = 15.8 Hz), 6.34 (d, 1H, J = 16.1 Hz)

¹³C NMR (75 MHz, CDCl₃) δ = major isomer: 142.5, 140.5, 139.4, 137.7, 135.1, 129.6, 128.7, 128.5, 127.3, 126.8, 126.4, 125.9, 76.2, 40.2, 38.8, 32.3, 21.4, 20.9, 0.6, 0.2
FT-IR (NaCl, thin film) $\nu = 3026, 2925, 2860, 1602, 1510, 1452, 1377, 1253, 1052$ cm$^{-1}$

Anal. calcd for $C_{24}H_{30}OSi$: C 79.50, H 8.34; found C 79.49, H 8.59.
Diene 120

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar under Ar(g) was added Pd(OAc)$_2$ (2.2 mg, 0.01 mmol, 0.05 equiv), S-Phos (8.2 mg, 0.02 mmol, 0.10 equiv), K$_3$PO$_4$ (127 mg, 0.60 mmol, 3 equiv) and 4'-bromoacetophenone (60 mg, 0.30 mmol, 1.5 equiv). The solids were purged with vacuum then placed under Ar(g). To the solids was then added silyl dienyl boronate 97 (1M in THF, 0.20 mL, 0.20 mmol, 1 equiv) and H$_2$O (degassed 30 min, 0.3 mL). The orange mixture stirred at 50°C for 4 h then was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated \textit{in vacuo} to give a dark red oil. Purification via column chromatography (silica gel 1.5 x 10.5 cm; gradient elution with 10%-30% ether/hexanes) gave 120 as a bright yellow oil (42.6 mg, 59%).


R$_t$ (40% EtOAc/hexanes) = 0.62

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.88 (d, 2H, $J = 8.4$ Hz), 7.45-7.36 (m, 6H), 7.20-7.17 (m, 2H), 6.20 (d, 1H, $J = 15.9$ Hz), 4.32-4.21 (m, 1H), 3.10 (dd, 1H, $J = 16.2$, 5.4 Hz), 2.58 (s, 3H), 2.46 (dd, 1H, $J = 16.5$, 8.4 Hz), 1.37 (d, 3H, $J = 6.0$ Hz), -0.06 (s, 3H), -0.18 (s, 3H)

FT-IR (NaCl, thin film) $\nu$ = 2965, 2926, 1681, 1599, 1264, 828 cm$^{-1}$

Anal. calcd for C$_{23}$H$_{26}$O$_2$Si: C 76.20, H 7.23; found C 75.92, H 7.24.
Diene 123

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar under \( \text{Ar}(g) \) was added silyl dienyl boronate 121 \(^{71} \) (64.8 mg, 0.15 mmol, 1 equiv), \( \text{Pd(OAc)}_2 \) (1.7 mg, 0.008 mmol, 0.05 equiv), S-Phos (6.2 mg, 0.015 mmol, 0.10 equiv) and \( \text{K}_3\text{PO}_4 \) (96 mg, 0.45 mmol, 3 equiv). The vessel was evacuated then placed under \( \text{Ar}(g) \). To the solids was added degassed \( \text{H}_2\text{O} \) (8.1 µL, 0.45 mmol, 3 equiv), degassed \( \text{THF} \) (1.5 mL) and iodobenzene (25 µL, 0.23 mmol, 1.5 equiv). The resulting light brown suspension stirred at 50°C overnight. The brown suspension was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated \textit{in vacuo} to give an orange oil. Purification via column chromatography (silica gel 1.5 x 13 cm; gradient elution with 2%-4% ether/hexanes) gave 123 as a yellow solid (40.4 mg, 70%)

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar under \( \text{Ar}(g) \) was added silyl dienyl boronate 122 \(^{71} \) (50.4 mg, 0.12 mmol, 1 equiv), \( \text{Pd(OAc)}_2 \) (1.3 mg, 0.006 mmol, 0.05 equiv), S-Phos (5.0 mg, 0.012 mmol, 0.10 equiv) and \( \text{K}_3\text{PO}_4 \) (76.4 mg, 0.36 mmol, 3 equiv). The vessel was evacuated then placed under \( \text{Ar}(g) \). To the solids was added degassed \( \text{H}_2\text{O} \) (6.5 µL, 0.36 mmol, 3 equiv), degassed \( \text{THF} \) (1.2 mL) and iodobenzene (20 µL, 0.18 mmol, 1.5 equiv). The resulting orange suspension stirred at 50°C overnight. The orange suspension was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated \textit{in vacuo} to give an orange oil. Purification via column chromatography (silica gel 1.5 x 15 cm; gradient elution with 2%-4% ether/hexanes) gave 123 as a yellow solid (33.3 mg, 73%).
$R_f$ (10% ether/hexanes) = 0.35

$\text{mp} = 117-118^\circ\text{C}$

$^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta = 7.37-7.09$ (m, 16H), 6.13 (d, 1H, $J = 16.0$ Hz), 5.02 (m, 1H), 3.30 (dd, 1H, $J = 16.0, 6.0$ Hz), 2.61 (dd, 1H, $J = 16.0, 9.3$ Hz), 0.00 (s, 3H), -0.22 (s, 3H)

$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) $\delta = 147.3, 144.9, 143.6, 142.1, 137.5, 133.5, 129.9, 128.8, 128.6, 128.2, 128.1, 128.0, 127.6, 127.5, 126.9, 125.6, 78.0, 42.4, 0.6, -0.3

$\text{FT-IR}$ (NaCl, thin film) $\nu = 3059, 3030, 2927, 1599, 1492, 1447, 1249, 1031$ cm$^{-1}$

$\text{Anal. calcd for C}_{26}\text{H}_{28}\text{OSi}: \text{C} 81.63, \text{H} 6.85; \text{found C} 81.57, \text{H} 6.66.
Diene 124

To an oven-dried 50 mL Schlenk tube with stir bar was added silyl dienyl boronate 97 (0.805M in benzene, 163 mg, 0.44 mmol, 1 equiv) and THF (3 mL). A solution of 5M NaOH (1.32 mmol, 3.0 equiv) was added dropwise and the reaction mixture stirred at rt. After 10 min, I$_2$ (168 mg, 0.66 mmol, 1.5 equiv) in THF (1.8 mL) was added dropwise. The reaction stirred in the dark at rt for 2 h then was quenched by sat. Na$_2$S$_2$O$_3$(aq) (5 mL). After extraction with DCM (3 x 5 mL), the combined organics were dried over MgSO$_4$, filtered and concentrated in vacuo to give an orange oil. Purification via column chromatography (1.5 x 13 cm; eluted with 5% ether/hexanes) gave 124 as a yellow oil (99.9 mg, 61%).

$R_f$ (10% ether/hexanes) = 0.45

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.56 (d, 1H, $J$ = 14.4 Hz), 7.34-7.30 (m, 3H), 7.13-7.10 (m, 2H), 6.03 (d, 1H, $J$ = 14.1 Hz), 4.26-4.15 (m, 1H), 2.92 (dd, 1H, $J$ = 16.2, 5.4 Hz), 2.28 (dd, 1H, $J$ = 16.2, 8.1 Hz), 1.32 (d, 3H, $J$ = 6.3 Hz), -0.08 (s, 3H), -0.21 (s, 3H)

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 146.7, 144.57, 144.55, 140.5, 129.7, 128.3, 127.8, 83.8, 72.5, 41.1, 24.1, 0.6, -0.4

FT-IR (NaCl, thin film) $\nu$ = 3058, 2965, 2924, 1591, 1491, 1249 cm$^{-1}$

Anal. calcd for C$_{15}$H$_{19}$OSi: C 48.65, H 5.17; found C 48.92, H 5.49.
Diene 126

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under Ar\(_(g)\) was added silyl dienyl boronate 105 (183 mg, 0.36 mmol, 1 equiv) and THF (0.85 mL). To the pale yellow solution was added NaOH (5M in H\(_2\)O, 1.08 mmol, 3 equiv). After stirring for 10 min, a solution of I\(_2\) (183 mg, 0.72 mmol, 1.5 equiv) in THF (0.8 mL) was added dropwise. The dark red solution stirred at rt for 1 h then was quenched by addition of sat. Na\(_2\)S\(_2\)O\(_3\) (aq) (3 mL). The aqueous layer was extracted with DCM (3 x 3 mL) and the combined organic layers were dried over MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give an orange oil. Purification via column chromatography (silica gel 1.5 x 12 cm; eluted with 5% ether/hexanes) gave 126 as a pale yellow solid (132 mg, 74%).

\( R_f \) (10% ether/hexanes) = 0.53

\textbf{mp} = 51-53°C

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta = 7.60-7.15 \) (m, 15H), 6.09 (d, 1H, \( J = 14.8 \) Hz), 5.12 (dd, 1H, \( J = 9.6, 5.6 \) Hz), 3.27 (dd, 1H, \( J = 16.4, 5.6 \) Hz), 2.60 (dd, 1H, \( J = 16.4, 9.2 \) Hz), 0.08 (s, 3H), -0.15 (s, 3H)

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta = 146.9, 144.5, 143.8, 143.6, 141.3, 140.6, 140.5, 129.7, 129.0, 128.8, 128.5, 128.0, 127.4, 127.3, 126.0, 84.3, 42.3, 0.4, -0.5

\textbf{Anal.} calcd for C\(_{26}\)H\(_{25}\)IOSi: C 61.42, H 4.96; found C 61.10, H 5.04.
Diene 127

To an oven-dried 25 mL Schlenk tube with equipped with a magnetic stir bar in an Ar\textsuperscript{(g)}-filled glovebox was added Pd(PrBu\textsubscript{3})\textsubscript{2} (4 mg, 0.0075 mmol, 0.05 equiv), 4-methoxyphenylboronic acid (34 mg, 0.23 mmol, 1.5 equiv), K\textsubscript{3}PO\textsubscript{4} (64 mg, 0.30 mmol, 2 equiv), silyl dienyl iodide 124 (1.05M in benzene, 55.5 mg, 0.15 mmol, 1 equiv) and 1,4-dioxane (0.6 mL). The vessel was sealed with a rubber septum, removed from the glovebox and placed under Ar\textsuperscript{(g)}. The dark brown reaction stirred at 80°C for 2 h then was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated \textit{in vacuo}. Purification via column chromatography (silica gel 1.5 x 11.5 cm; eluted with 5% ether/hexanes) gave 127 as an orange oil (27.4 mg, 52%).

\textbf{R}_f (10\% ether/hexanes) = 0.23

\textit{\textsuperscript{1}H NMR} (300 MHz, CDCl\textsubscript{3}) \(\delta = 7.38-7.29\) (m, 5H), 7.20-7.13 (m, 3H), 6.83 (d, 2H, \(J = 8.8\) Hz), 6.14 (d, 1H, \(J = 16.0\) Hz), 4.30-4.19 (m, 1H), 3.80 (s, 3H), 3.06 (dd, 1H, \(J = 16.0, 5.3\) Hz), 2.42 (dd, 1H, \(J = 16.0, 8.4\) Hz), 1.36 (d, 3H, \(J = 6.1\) Hz), -0.07 (s, 3H), -0.20 (s, 3H)

\textbf{Anal.} calcd for C\textsubscript{22}H\textsubscript{26}O\textsubscript{2}Si: C 75.38, H 7.48; found C 75.20, H 7.93.
Diene 128

Following general procedure A: RuHCl(CO)(PCy$_3$)$_2$ (9.8 mg, 0.0135 mmol, 0.05 equiv), alkyne 41 (66.6 mg, 0.27 mmol, 1 equiv) in toluene (0.54 mL) and vinyl boronate 93 (94 µL, 0.54 mmol, 2 equiv) were combined and stirred at 85°C for 3 h. After plug filtering and concentration in vacuo, the crude oil was dissolved in 1:1 MeOH/H$_2$O (7 mL) and CuBr$_2$ (181 mg, 0.81 mmol, 3 equiv) was added in one portion. The aqua solution stirred at 45°C overnight. Upon cooling to rt, the reaction was diluted with H$_2$O (13 mL) and extracted with DCM (3 x 20 mL). The combined organics were dried over MgSO$_4$, filtered and concentrated in vacuo to give a brown oil. Purification via column chromatography (silica gel 1.5 x 13 cm; gradient elution with 2%-4% ether/hexanes) gave 128 as a yellow oil (46.4 mg, 57% over two steps).

R$_f$ (10% ether/hexanes) = 0.47

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.34-7.29 (m, 3H), 7.22 (d, 1H, $J = 13.8$ Hz), 7.13-7.10 (m, 2H), 5.97 (d, 1H, $J = 13.8$ Hz), 4.26-4.15 (m, 1H), 2.90 (dd, 1H, $J = 16.2$, 5.3 Hz), 2.28 (dd, 1H, $J = 16.3$, 8.2 Hz), 1.32 (d, 3H, $J = 6.1$ Hz), -0.09 (s, 3H), -0.21 (s, 3H)

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 144.9, 144.8, 140.7, 140.0, 129.6, 128.4, 127.9, 112.5, 72.5, 41.1, 24.2, 0.6, -0.3
Triene 129

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar open to the air was added tert-butyl acrylate (66 µL, 0.45 mmol, 3 equiv) and DMA (0.75 mL). To the clear solution was added silyl dienyl boronate 97 (0.58M in benzene, 0.15 mmol, 1 equiv), Pd(OAc)$_2$ (3.4 mg, 0.015 mmol, 0.10 equiv) and Na$_2$CO$_3$ (31.8 mg, 0.30 mmol, 2 equiv). The pale brown suspension was purged with O$_2$(g) for 1 min then placed under a positive stream of O$_2$(g) (balloon) and stirred at rt for 25 h. The reaction was diluted with EtOAc (6 mL) and washed with H$_2$O (3 x 3 mL). The organic layer was dried over Na$_2$SO$_4$, filtered and concentrated in vacuo to give a brown oil. Purification by column chromatography (silica gel 1.5 x 12 cm; gradient elution with 10%-15% ether/hexanes) gave 129 as a yellow oil (25.2 mg, 45%).

$R_f$ (10% ether/hexanes) = 0.20

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.35-7.23 (m, 4H), 7.12-7.09 (m, 2H), 6.99 (d, 1H, $J$ = 15.0 Hz), 5.91 (dd, 1H, $J$ = 15.0, 11.4 Hz), 5.70 (d, 1H, $J$ = 15.3 Hz), 4.27-4.17 (m, 1H), 2.79 (s, 3H), 2.37 (dd, 1H, $J$ = 16.5, 8.4 Hz), 1.34 (s, 3H) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 166.5, 148.9, 146.6, 143.6, 141.4, 138.4, 130.6, 129.7, 128.2, 127.7, 124.2, 80.4, 72.6, 41.2, 28.4, 24.2, 0.6, -0.3 ppm.

FT-IR (NaCl, thin film) $\nu$ = 2974, 2930, 1705, 1620, 1454, 1368, 1248, 1165, 1135 cm$^{-1}$

Anal. calcd for C$_{22}$H$_{30}$O$_3$Si: C 71.31, H 8.16; found C 71.27, H 7.80.
Diene 131

To an oven-dried 50 mL Schlenk tube equipped with magnetic stir bar in an Argon-filled glovebox was added RuHCl(CO)(H2IMes)(PPh3)3 (2.2 mg, 0.003 mmol, 0.01 equiv) and a solution of alkyne 41 (74 mg, 0.30 mmol, 1 equiv) in DCE (1.2 mL). The vessel was sealed with a rubber septum, removed from the glovebox and placed under a positive stream of Ar(g). The yellow reaction mixture was degassed with ethylene (balloon) for ~2 minutes, then placed under an atmosphere of ethylene (balloon) and stirred at 70°C. After 1 h the yellow solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a light brown oil. Purification by column chromatography (silica gel 1.5 x 10 cm; gradient elution with 2%-3% ether/hexanes) gave 131 as a clear oil (59.5 mg, 80%, 11:1 Z:E).

Rf (10% ether/hexanes) = 0.36

1H NMR (300 MHz, CDCl3) major isomer 131: δ = 7.34-7.26 (m, 3H), 7.14-7.11 (m, 2H), 6.86 (dd, 1H, J = 17.1, 10.6 Hz), 5.24 (d, 1H, J = 10.6 Hz), 4.87 (d, 1H, J = 17.3 Hz), 4.26-4.15 (m, 1H), 2.96 (dd, 1H, J = 16.1, 5.4 Hz), 2.32 (dd, 1H, J = 16.1, 8.1 Hz), 1.32 (d, 3H, J = 6.0 Hz), -0.07 (s, 3H), -0.20 (s, 3H); minor isomer 140 diagnostic peaks: δ = 6.52 (dd, 1H, J = 16.7, 10.2 Hz), 5.09 (d, 1H, J = 10.5 Hz), 4.76 (d, 1H, J = 16.9 Hz), 4.13-4.02 (m, 1H), 2.04 (dd, 1H, J = 16.7, 8.4 Hz), 1.20 (d, 3H, J = 6.2 Hz), 0.43 (s, 3H), 0.40 (s, 3H)
**General procedure for the ruthenium-catalyzed cycloisomerization:**

To a 25 mL Schlenk tube equipped with a magnetic stir bar in an argon filled glovebox was added Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 41 (61.0 mg, 0.25 mmol, 1 equiv) in toluene (1 mL). The sealed reaction vessel was removed from the glovebox, placed under a positive stream of argon and stirred at 70°C for 1 h. TLC analysis indicated complete consumption of the starting material. The dark green suspension was cooled to rt, filtered through a plug of silica gel eluted with ether then concentrated *in vacuo* to give a dark green oil. Purification by column chromatography (silica gel 1.5 x 4 cm; eluted with 3% ether/hexanes) gave 132 as a clear oil (49.9 mg, 82%). Spectroscopic data corresponded to what was reported in the literature.\(^8\)

\[ R_f (5\% \text{ ether/hexanes}) = 0.45 \]

\[ ^1H \text{ NMR} \ (300 \text{ MHz, CDCl}_3) \delta = 7.39-7.21 \text{ (m, 5H), 6.62 (s, 1H), 5.92 (d, 1H, J = 3.0 Hz), 5.26 (d, 1H, J = 3.0 Hz), 4.14-4.04 (m, 1H), 2.90 (dd, 1H, J = 14.7, 1.8 Hz), 2.30 (ddd, 1H, J = 14.4, 9.9, 1.8 Hz), 1.26 (d, 3H, J = 6.3 Hz), 0.34 (s, 3H), 0.27 (s, 3H) } \]

\[ ^{13}C \text{ NMR} \ (75 \text{ MHz, CDCl}_3) \delta = 151.4, 142.7, 137.8, 129.2, 128.2, 126.4, 123.3, 121.5, 70.0, 39.9, 24.3, -0.4, -1.0 \]
Diene 134

**MVK procedure:** To an oven-dried 15 mL glass tube equipped with a magnetic stir bar was added alkyne 80 (50.0 mg, 0.16 mmol, 1 equiv). The vessel was transferred to an argon-filled glovebox then RuHCl(CO)(H$_2$IMes)(PPh$_3$) (6.0 mg, 0.008 mmol, 0.05 equiv) was added, followed by MVK (1.3 µL, 0.016 mmol, 0.10 equiv) and DCE (0.32 mL). The vessel was sealed with a teflon screw cap, removed from the glovebox then stirred at 85°C for 24 h. Upon cooling to rt, the dark orange solution was filtered through a plug of silica gel (eluted with DCM) and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 1.5 x 9 cm; eluted with 1% ether/hexanes) gave 134 as a white oil (27 mg, 54%).

**Ethylene procedure:** To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H$_2$IMes)(PPh$_3$) (3.7 mg, 0.005 mmol, 0.02 equiv) and a solution of alkyne 80 (79.6 mg, 0.25 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The dark orange solution stirred at 80°C for 2.5 h, cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a pale brown oil. Purification by preparative thin layer chromatography (eluted with 2% ether/hexanes) gave 134 as a pale yellow oil (53.8 mg, 68%, 14:1 Z/E).

$R_f$ (10% ether/hexanes) = 0.34
$^1$H NMR (300 MHz, CDCl$_3$) $\delta =$ 7.39-7.18 (m, 10H), 6.95 (dd, 1H, $J = 17.2$, 10.6 Hz), 5.29 (dd, 1H, $J = 10.6$, 1.6 Hz), 5.18 (d, 1H, $J = 4.4$ Hz), 4.79 (dd, 1H, $J = 17.2$, 1.6 Hz), 3.38-3.29 (m, 1H), 0.73 (d, 3H, $J = 7.2$ Hz), 0.29 (s, 3H), -0.30 (s, 3H)

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta =$ 150.1, 147.4, 142.1, 141.8, 135.5, 130.1, 128.4, 128.3, 127.7, 127.1, 126.1, 119.2, 80.5, 43.7, 15.8, -0.9, -2.1

Anal. calcd for C$_{21}$H$_{24}$OSi: C 78.70, H 7.55; found C 78.53, H 7.21.
Racemic Alcohol SI-10

To a flame-dried 3-neck 250 mL RBF equipped with a magnetic stir bar and a pressure-equalizing addition funnel under Ar\textsubscript{(g)} was added phenylacetylene (2.6 mL, 24 mmol, 1.2 equiv) and ether (100 mL). The solution was cooled to -78°C (dry ice/acetone bath) and nBuLi (2.5M in hexane, 9.6 mL, 24 mmol, 1.2 equiv) was added dropwise over 20 min. After stirring at -78°C for 20 min, AlMe\textsubscript{3} (2M in hexane, 12 mL, 24 mmol, 1.2 equiv) was added dropwise over 35 min. The reaction stirred at -78°C for 30 min and -45°C for 30 min, then was cooled to -78°C, whereupon trans-2,3-epoxybutane (1.8 mL, 20 mmol, 1 equiv) in ether (11 mL) was added dropwise over 10 min. After stirring at -78°C for 15 min, BF\textsubscript{3}·OEt\textsubscript{2} (2.8 mL, 22 mmol, 1.1 equiv) in ether (11 mL) was added dropwise over 10 min. After stirring at -78°C for 1 h, methanol (36 mL) was added dropwise over 10 min, then the reaction mixture was allowed to warm to rt over 25 min. Upon warming, sat. NH\textsubscript{4}Cl\textsubscript{(aq)} (36 mL) was added then the reaction stirred at rt for an additional 30 min. The mixture was then diluted with H\textsubscript{2}O (150 mL) and extracted with ether (3 x 100 mL). The organics were dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated in vacuo to give a yellow oil. Purification by column chromatography (silica gel 4.5 x 14 cm; gradient elution with 10%-50% ether/pentane) gave SI-10 as a pale yellow oil (1.54 g, 44%). Spectroscopic data corresponded to what was reported in the literature.\textsuperscript{213}

R\textsubscript{f} (25% EtOAc/hexanes) = 0.21
$^1\text{H NMR}$ (300 MHz, CDCl$_3$) $\delta = 7.43$-7.39 (m, 2H), 7.30-7.28 (m, 3H), 3.87-3.77 (m, 1H), 2.86-2.77 (m, 1H), 1.68 (br s, 1H), 1.32 (d, 3H, $J = 6.3$ Hz), 1.26 (d, 3H, $J = 7.0$ Hz)
**Silicon Tethered Alkyne 135**

To an oven dried 50 mL RBF equipped with magnetic stir bar under Ar(g) was added alcohol SI-10 (508 mg, 2.9 mmol, 1 equiv), DCM (20 mL), imidazole (395 mg, 5.8 mmol, 2 equiv) and DMAP (71 mg, 0.58 mmol, 0.2 equiv). The clear solution was cooled to 0°C (ice/H₂O bath) and vinyldimethylchlorosilane (0.6 mL, 4.35 mmol, 1.5 equiv) was added dropwise. The resulting white suspension stirred at rt for 2 h then was quenched by sat. NH₄Cl(aq) (20 mL). The aqueous layer was extracted with DCM (2 x 10 mL) then the combined organics were dried over MgSO₄, filtered and concentrated *in vacuo* to give a clear oil. Purification by column chromatography (silica gel 2.5 x 12.5 cm; gradient elution with 1%-3% ether/hexanes) gave 135 as a clear oil (672 mg, 90%).

\[ R_f (10\% \text{ ether/hexanes}) = 0.71 \]

\(^1\text{H NMR}\) (300 MHz, CDCl₃) \(\delta = 7.40-7.37 \text{ (m, 2H)}, 7.28-7.26 \text{ (m, 3H)}, 6.18 \text{ (dd, 1H, } J = 20.1, 15.0 \text{ Hz)}, 6.02 \text{ (dd, 1H, } J = 14.7, 4.2 \text{ Hz)}, 5.80 \text{ (dd, 1H, } J = 20.1, 4.5 \text{ Hz)}, 3.79-3.70 \text{ (m, 1H), 2.64-2.55 \text{ (m, 1H), 1.33 \text{ (d, 3H, } J = 6.0 \text{ Hz)}, 1.25 \text{ (d, 3H, } J = 6.9 \text{ Hz)}, 0.22 \text{ (s, 6H)}}\]

\(^13\text{C NMR}\) (75 MHz, CDCl₃) \(\delta = 138.1, 133.3, 131.7, 128.3, 127.7, 124.0, 92.6, 82.2, 72.4, 35.4, 22.3, 17.8, -1.2, -1.3\)

\textbf{FT-IR} (NaCl, thin film) \(\nu = 3054, 2973, 2879, 1597, 1491, 1372, 1252, 1099, 838 \text{ cm}^{-1}\)

**Anal.** calcd for C₁₆H₂₂OSi: C 74.36, H 8.58; found: C 74.63, H 8.80.
Diene 136

To an oven-dried 15 mL glass tube equipped with a magnetic stir bar was added alkyne 135 (66.7 mg, 0.26 mmol, 1 equiv). The vessel was transferred to an argon-filled glovebox then RuHCl(CO)(H₂IMes)(PPh₃) (9.5 mg, 0.013 mmol, 0.05 equiv) was added, followed by MVK (2.1 µL, 0.016 mmol, 0.10 equiv) and DCE (0.52 mL). The vessel was sealed with a teflon screw cap, removed from the glovebox then stirred at 85°C for 22 h. Upon cooling to rt, the dark orange solution was filtered through a plug of silica gel (eluted with DCM) and concentrated in vacuo to give an orange oil. Purification by column chromatography (silica gel 1.5 x 12.5 cm; gradient elution with 2%-3% ether/hexanes) gave 136 as a clear oil (38.4 mg, 58%, 33:1 Z:E).

\[ R_f (10\% \text{ ether/hexanes}) = 0.27 \]

\(^1\)H NMR (300 MHz, CDCl₃) major isomer: \( \delta = 7.33-7.27 \) (m, 3H), 7.13-7.10 (m, 2H), 6.88 (dd, 1H, \( J = 17.4, 10.8 \) Hz), 5.23 (dd, 1H, \( J = 10.8, 1.8 \) Hz), 4.86 (dd, 1H, \( J = 17.4, 1.8 \) Hz), 4.12-4.08 (m, 1H), 2.98-2.93 (m, 1H), 1.27 (d, 3H, \( J = 6.3 \) Hz), 1.17 (d, 3H, \( J = 7.2 \) Hz), 0.13 (s, 3H), -0.41 (s, 3H); minor isomer diagnostic peaks: \( \delta = 6.48 \) (dd, 1H, \( J = 17.0, 10.5 \) Hz), 5.09 (dd, 1H, \( J = 10.4, 1.4 \) Hz), 4.68 (dd, 1H, \( J = 16.9, 1.2 \) Hz)

\(^{13}\)C NMR (75 MHz, CDCl₃) \( \delta = 150.5, 146.6, 141.5, 135.3, 129.8, 127.9, 127.2, 118.6, 74.5, 42.0, 19.1, 14.3, 1.7, -1.2 \)

FT-IR (NaCl, thin film) \( \nu = 3082, 2967, 2869, 1598, 1491, 1141, 743 \)

Anal. calcd for C₁₆H₂₂OSi: C 74.36, H 8.58; found C 74.44, H 8.98.
Diene 143

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H$_2$IMes)(PPh$_3$) (3.7 mg, 0.005 mmol, 0.02 equiv) and a solution of alkyne 57$^{26}$ (77.7 mg, 0.25 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 1 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a pale brown oil. Purification by preparative thin layer chromatography (eluted with 1:150 ether/hexanes) gave 143 as a pale yellow oil (54.6 mg, 70%, 17:1 Z/E).

R$_f$ (10% ether/hexanes) = 0.44

$^1$H NMR (300 MHz, CDCl$_3$) major isomer: δ = 7.32-7.28 (m, 3H), 7.14-7.11 (m, 2H), 6.89 (dd, 1H, $J$ = 17.1, 10.3 Hz), 5.23 (d, 1H, $J$ = 11.1 Hz), 4.87 (dd, 1H, $J$ = 17.0, 1.1 Hz), 3.82-3.75 (m, 1H), 2.87 (dd, 1H, $J$ = 16.0, 5.3 Hz), 2.44 (dd, 1H, $J$ = 16.2, 8.4 Hz), 1.96-1.92 (m, 1H), 1.80-1.65 (m, 4H), 1.45-0.98 (m, 6H), -0.09 (s, 3H), -0.22 (s, 3H); minor isomer diagnostic peaks: δ = 6.53 (dd, 1H, $J$ = 17.1, 10.3 Hz), 5.23 (d, 1H, $J$ = 11.1 Hz), 5.08 (d, 1H, $J$ = 10.1 Hz), 4.74 (d, 1H, $J$ = 17.0 Hz), 3.69-3.62 (m, 1H), 0.40 (s, 3H), 0.39 (s, 3H)
Ester SI-12

To an oven-dried 100 mL RBF equipped with a magnetic stir bar under Ar<sub>(g)</sub> was added SI-11<sup>26</sup> (408 mg, 2.04 mmol, 1 equiv) and toluene (20 mL). The clear solution was cooled to 0°C (ice/H<sub>2</sub>O bath) and the acid (682 mg, 4.08 mmol, 2 equiv) and phosphine (1.1 g, 4.08 mmol, 2 equiv) were added sequentially. DIAD (0.8 mL, 4.08 mmol, 2 equiv) in toluene (6 mL) was added dropwise and the resulting yellow solution warmed to rt slowly. After 26 h, the reaction mixture was quenched with sat. NaHCO<sub>3</sub>(aq) (20 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL) then the combined organics were washed with brine (2 x 30 mL), dried over MgSO<sub>4</sub>, filtered and concentrated <i>in vacuo</i> to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 17 cm; gradient elution with 7%-17% ether/hexanes) gave SI-12 as a yellow oil (502 mg, 70%). Spectroscopic data corresponded to what was reported in the literature.<sup>26</sup>

<sup>R</sup><sub>f</sub> (20% EtOAc/hexanes) = 0.49

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.94 (t, 1H, J = 1.7 Hz), 8.43-8.40 (m, 2H), 7.65 (t, 1H, J = 7.9 Hz), 7.42-7.39 (m, 2H), 7.30-7.27 (m, 3H), 5.23-5.19 (m, 1H), 3.29-3.27 (m, 1H), 2.11-2.01 (m, 2H), 1.88-1.75 (m, 4H), 1.59-1.46 (m, 2H)
Alcohol SI-13

To a 100 mL RBF equipped with magnetic stir bar was added SI-12 (640 mg, 1.8 mmol, 1 equiv), MeOH (35 mL) and K$_2$CO$_3$ (995 mg, 7.2 mmol, 4 equiv). The white suspension stirred at rt for 4 h then H$_2$O (10 mL) was added to dissolve the excess K$_2$CO$_3$. The solution was extracted with DCM (3 x 30 mL) then the combined organics were dried over MgSO$_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 17 cm; eluted with 10% EtOAc/hexanes) gave SI-13 as a clear oil (226 mg, 63%). Spectroscopic data corresponded to what was reported in the literature.$^{26}$

$^\text{R}_f$ (20% EtOAc/hexanes) = 0.34

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.45-7.41 (m, 2H), 7.31-7.28 (m, 3H), 3.78-3.73 (m, 1H), 3.07-3.03 (m, 1H), 1.98-1.90 (m, 1H), 1.78-1.34 (m, 8H)
Silicon Tethered Alkyne 144

To an oven-dried 25 mL RBF equipped with a magnetic stir bar under Ar (g) was added SI-13 (278 mg, 1.39 mmol, 1 equiv), DCM (10 mL), imidazole (189 mg, 2.78 mmol, 2 equiv) and DMAP (34 mg, 0.28 mmol, 0.2 equiv) sequentially. The clear solution was cooled to 0°C (ice/H₂O bath) and vinyldimethylchlorosilane (0.23 mL, 1.67 mmol, 1.2 equiv) was added via syringe. The white suspension stirred at rt for 2 h then was quenched by sat. NH₄Cl (aq) (10 mL). The aqueous layer was extracted with DCM (3 x 5 mL) then the combined organics were dried over MgSO₄, filtered and concentrated in vacuo to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 10 cm; gradient elution with 2%-3% ether/hexanes) gave 144 as a clear oil (301 mg, 76%). Spectroscopic data corresponded to what was reported in the literature.²⁶

R_f (10% ether/hexanes) = 0.67

¹H NMR (400 MHz, CDCl₃) δ = 7.43-7.40 (m, 2H), 7.29-7.25 (m, 3H), 6.20 (dd, 1H, J = 20.6, 15.1 Hz), 5.99 (dd, 1H, J = 15.1, 4.0 Hz), 5.81 (dd, 1H, J = 20.2, 4.0 Hz), 3.88-3.85 (m, 1H), 2.86-2.82 (m, 1H), 1.96-1.88 (m, 1H), 1.82-1.57 (m, 5H), 1.40-1.26 (m, 2H), 0.23 (s, 3H), 0.22 (s, 3H)
Diene 145

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H$_2$IMes)(PPh$_3$) (9.0 mg, 0.0125 mmol, 0.05 equiv) and a solution of alkyne 144 (71.1 mg, 0.25 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 1 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a pale brown oil. Purification by column chromatography (silica gel 1.5 x 11 cm; eluted with 2% ether/hexanes) gave 145 as a clear oil (55.5 mg, 78%, 11:1 Z/E).

$R_f$ = 0.34 (10% diethyl ether/hexanes)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.34-7.26 (m, 3H), 7.14-7.10 (m, 2H), 6.89 (dd, $J$ = 17.1, 10.5 Hz, H), 5.20 (dd, $J$ = 10.5, 1.5 Hz, 1H), 4.85 (dd, $J$ = 17.1, 1.5 Hz, 1H), 4.07-4.06 (m, 1H), 2.89-2.82 (m, 1H), 2.08-2.03 (m, 1H), 1.74-1.72 (m, 1H), 1.65-1.50 (m, 4H), 1.40-1.26 (m, 2H), 0.17 (s, H), -0.39 (s, 3H); minor isomer diagnostic peaks: $\delta$ = 6.47 (dd, $J$ = 16.8, 10.5 Hz, 1H), 5.07 (dd, $J$ = 10.8, 1.2 Hz, 1H), 4.65 (dd, $J$ = 16.8, 1.5 Hz, 1H), 0.48 (s, 3H), 0.39 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 150.0, 146.3, 141.6, 135.5, 129.9, 128.0, 127.3, 118.3, 74.1, 44.3, 31.3, 28.4, 25.6, 19.7, 1.7, -1.1

IR (film): $\nu$ = 3054, 2931, 2851, 1582, 1491, 1441, 1249 cm$^{-1}$

Anal. calcd. for C$_{18}$H$_{24}$OSi: C 76.00, H 8.56; found: C 75.94, H 8.79
Diene 146

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H₂IMes)(PPh₃) (2.1 mg, 0.0028 mmol, 0.01 equiv) and a solution of alkyne 64 (73.9 mg, 0.28 mmol, 1 equiv) in DCE (1.1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 1 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a pale brown oil. Purification by column chromatography (silica gel 1.5 x 11 cm; gradient elution with 3%-5% ether/hexanes) gave 146 as a pale yellow oil (47.3 mg, 64%, 20:1 Z/E).

$R_f$ (10% ether/hexanes) = 0.26

$^1$H NMR (300 MHz, CDCl₃) major isomer: δ = 7.11-6.98 (m, 4H), 6.84 (dd, 1H, $J = 17.3, 10.6$ Hz), 5.22 (d, 1H, $J = 10.7$ Hz), 4.80 (d, 1H, $J = 17.0$ Hz), 4.25-4.14 (m, 1H), 2.94 (dd, 1H, $J = 16.2, 5.3$ Hz), 2.30 (dd, 1H, $J = 16.3, 8.1$ Hz), 1.32 (d, 3H, $J = 6.1$ Hz), -0.07 (s, 3H), -0.19 (s, 3H); minor isomer diagnostic peaks: δ = 6.50 (dd, 1H, $J = 17.3, 10.6$ Hz), 5.09 (d, 1H, $J = 10.7$ Hz), 4.73 (d, 1H, $J = 17.0$ Hz), 2.02 (dd, 1H, $J = 16.8, 8.4$ Hz), 1.20 (d, 3H, $J = 5.9$ Hz), 0.41 (s, 3H), 0.38 (s, 3H)
Alcohol SI-14

To an oven-dried 3-neck 250 mL RBF equipped with a magnetic stir bar and reflux condenser under Ar\((g)\) was added \(\text{PdCl}_2(\text{PPh}_3)_2\) (526 mg, 0.75 mmol, 0.05 equiv), CuI (286 mg, 0.15 mmol, 0.10 equiv), THF (60 mL), piperidine (3 mL, 30 mmol, 2 equiv), 4-pentyn-2-ol (1.4 mL, 15 mmol, 1 equiv) and 1-bromonapthalene (2.3 mL, 16.5 mmol, 1.1 equiv). The resulting green solution was subjected to three cycles of freeze/pump/thaw then placed under Ar\((g)\). Once warmed to rt the lime green solution stirred at 65°C. After 6 h, the resulting black suspension was cooled to rt, diluted with ether (50 mL) then washed with sat. NH\(_4\)Cl\((aq)\) (2 x 50 mL) and brine (2 x 50 mL). The organics were dried over Na\(_2\)SO\(_4\), filtered and concentrated \textit{in vacuo} to give a dark brown oil. Purification by column chromatography (silica gel 4.5 x 12 cm; gradient elution with 25%-30% EtOAc/hexanes) gave SI-14 as an orange oil (1.32 g, 42%). Spectroscopic data corresponded to what was reported in the literature.\(^{88}\)

\(R_f\) (25% EtOAc/hexanes) = 0.33

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\)) \(\delta = 8.33\) (d, 1H, \(J = 8.7\) Hz), 7.87-7.81 (m, 2H), 7.66 (d, 1H, \(J = 6.9\) Hz), 7.60-7.50 (m, 2H), 7.42 (dd, 1H, \(J = 8.3, 7.4\) Hz), 4.21-4.10 (m, 1H), 2.77 (d ABq, 2H, \(J_{AB} = 16.6\) Hz, \(J_{AX} = 5.3\) Hz, \(J_{BX} = 6.3\) Hz), 2.03 (s, 1H), 1.42 (d, 3H, \(J = 6.4\) Hz)
Silicon Tethered Alkyne 147

To an oven-dried 100 mL RBF equipped with a magnetic stir bar under Ar\(_{(g)}\) was added SI-14 (1.27 g, 6 mmol, 1 equiv), DCM (40 mL), imidazole (817 mg, 12 mmol, 2 equiv) and DMAP (147 mg, 1.2 mmol, 0.2 equiv) sequentially. The yellow solution was cooled to 0°C (ice/H\(_2\)O bath) and vinylidimethylchlorosilane (1.24 mL, 9 mmol, 1.5 equiv) was added via syringe. The yellow suspension stirred at rt overnight then was quenched by sat. NH\(_4\)Cl\(_{(aq)}\) (50 mL). The aqueous layer was extracted with DCM (3 x 25 mL) then the combined organics were washed with brine (2 x 50 mL), dried over MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give an orange oil. Purification by column chromatography (silica gel 2.5 x 10 cm; eluted with 5% EtOAc/hexanes) gave 147 as an orange oil (1.33 g, 75%). Spectroscopic data corresponded to what was reported in the literature.\(^8^8\)

\[ R_f (10\% \text{ EtOAc/hexanes}) = 0.55 \]

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\)) \(\delta = \) 8.34 (d, 1H, \(J = 8.2\) Hz), 7.85-7.77 (m, 2H), 7.62 (d, 1H, \(J = 7.4\) Hz), 7.58-7.47 (m, 2H), 7.40 (app t, 1H, \(J = 7.6\) Hz), 6.21 (dd, 1H, \(J = 20.3, 15.0\) Hz), 6.03 (ddd, 1H, \(J = 14.8, 4.2, 0.4\) Hz), 5.83 (dd, 1H, \(J = 20.1, 4.2\) Hz), 4.20-4.08 (m, 1H), 2.70 (d ABq, 2H, \(J_{AB} = 16.5\) Hz, \(J_{AX} = 5.9\) Hz, \(J_{BX} = 6.9\) Hz), 1.38 (d, 3H, \(J = 6.0\) Hz), 0.25 (s, 6H)
Diene 148

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H$_2$IMes)(PPh$_3$)$_2$ (9.2 mg, 0.0125 mmol, 0.05 equiv) and a solution of alkyne 147 (74.3 mg, 0.25 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 3 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a brown/black oil. Purification by column chromatography (silica gel 1.5 x 11.5 cm; gradient elution with 2%-3% ether/hexanes) gave 148 as a pale yellow oil (54.4 mg, 73%, 13:1 Z/E).

$R_f$ = 0.44 (10% diethyl ether/hexanes)

$^1$H NMR (300 MHz, CDCl$_3$) (mixture of rotamers): $\delta$ = 7.85-7.76 (m, 3H), 7.51-7.38 (m, 3H), 7.25 (d, $J$ = 6.7 Hz, 1H), 7.01 (ddd, $J$ = 17.2, 10.4, 2.4 Hz, 1H), 5.18 (d, $J$ = 10.4 Hz, 1H), 4.67 (d, $J$ = 17.2 Hz, 1H), 4.39-4.30 (m, 0.5H), 4.28-4.19 (m, 0.5H), 3.16 (dd, $J$ = 16.1, 5.1 Hz, 0.5H), 2.42 (dd, $J$ = 16.5, 5.7 Hz, 0.5H), 1.39 (d, $J$ = 6.1 Hz, 1.5H), 1.36 (d, $J$ = 6.1 Hz, 0.5H), 0.00 (s, 1.5H), -0.1 (s, 1.5H), -0.7 (s, 1.5H), -0.8 (1.5H); minor isomer diagnostic peaks: $\delta$ = 6.70 (ddd, $J$ = 16.6, 10.4, 2.4 Hz, 1H), 5.28 (d, $J$ = 10.2 Hz, 1H), 4.90 (d, $J$ = 17.2 Hz, 1H), 1.16 (d, $J$ = 6.1 Hz, 3H), 1.13 (d, $J$ = 6.1 Hz, 3H), -0.1 (s, 3H), -0.2 (s, 3H)

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 145.8, 145.6, 145.1, 144.7, 139.2, 139.0, 135.9, 135.8, 133.6, 133.5, 132.7, 132.7, 128.2, 127.9, 127.9, 127.8, 126.8, 126.7, 125.9, 125.9, 125.3, 125.2, 118.6, 118.6, 72.8, 72.6, 40.9, 40.5, 24.3, 24.2, 1.1, 0.4, -1.1, -1.8
IR (film): $v = 3046, 2966, 2927, 1585, 1507, 1395, 1376, 1249, 1104, 1037, 944, 781$ cm$^{-1}$

Anal. calcd. for C$_{19}$H$_{22}$OSi: C 77.50, H 7.53; found: C 77.48, H 7.48.
Diene 149

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H$_2$IMes)(PPh$_3$) (2 mg, 0.0027 mmol, 0.01 equiv) and a solution of alkyne 67 (73.1 mg, 0.27 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 1 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a pale brown oil. Purification by column chromatography (silica gel 1.5 x 11 cm; gradient elution with 2%-3% ether/hexanes) gave 149 as a clear oil (54.1 mg, 74%, 26:1 Z/E).

R$_f$ (10% ether/hexanes) = 0.34

$^1$H NMR (300 MHz, CDCl$_3$) major isomer: $\delta$ = 6.92 (s, 1H), 6.84 (dd, 1H, $J$ = 17.2, 10.7 Hz), 6.75 (s, 2H), 5.22 (d, 1H, $J$ = 10.6 Hz), 4.95 (dd, 1H, $J$ = 17.3, 1.6 Hz), 4.25-4.14 (m, 1H), 2.93 (dd, 1H, $J$ = 16.1, 5.3 Hz), 2.34-2.26 (m, 7H), 1.32 (d, 3H, $J$ = 6.1 Hz), -0.07 (s, 3H), -0.20 (s, 3H); minor isomer diagnostic peaks: $\delta$ = 5.07 (d, 1H, $J$ = 10.4 Hz), 4.78 (d, 1H, $J$ = 17.0 Hz), 1.21 (d, 3H, $J$ = 6.1 Hz), 0.42 (s, 3H), 0.39 (s, 3H)
Alcohol SI-15

To an oven-dried 3-neck 250 mL RBF equipped with a magnetic stir bar under Ar(g) was added PdCl$_2$(PPh$_3$)$_2$ (211 mg, 0.30 mmol, 0.02 equiv), CuI (114 mg, 0.60 mmol, 0.04 equiv), THF (60 mL), NEt$_3$ (3 mL), 4-pentyn-2-ol (1.4 mL, 15 mmol, 1 equiv) and 1-bromo-4-nitrobenzene (3.64 g, 18 mmol, 1.2 equiv). The resulting red/brown suspension was subjected to three cycles of freeze/pump/thaw then placed under Ar(g). Once warmed to rt the dark brown solution stirred at 55°C. After 2 h, the resulting black suspension was cooled to rt and sat. NH$_4$Cl(aq) (60 mL) was added. The aqueous layer was extracted with DCM (2 x 50 mL) then the combined organics were washed with brine (2 x 80 mL). The organics were dried over MgSO$_4$, filtered and concentrated in vacuo to give a dark brown oil. Purification by column chromatography (silica gel 4.5 x 12.5 cm; gradient elution with 20%-50% EtOAc/hexanes) gave SI-15 as a dark red oil (2.60 g, 84%). Spectroscopic data corresponded to what was reported in the literature.$^{88}$

$^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ = 8.16 (d, 1H, $J = 9.0$ Hz), 7.54 (d, 1H, $J = 9.0$ Hz), 4.14-4.04 (m, 1H), 2.64 (d ABq, 2H, $J_{AB} = 16.9$ Hz, $J_{AX} = 5.5$ Hz, $J_{BX} = 6.3$ Hz), 1.84 (br s, 1H), 1.35 (d, 3H, $J = 6.1$ Hz)

$R_f$ (30% EtOAc/hexanes) = 0.17
Silicon-Tethered Alkyne 150

To an oven-dried 50 mL RBF equipped with a magnetic stir bar under Ar\textsubscript{(g)} was added SI-15 (455 mg, 2.2 mmol, 1 equiv), DCM (15 mL), imidazole (300 mg, 4.4 mmol, 2 equiv) and DMAP (54 mg, 0.44 mmol, 0.2 equiv) sequentially. The yellow/orange solution was cooled to 0°C (ice/H\textsubscript{2}O bath) and vinylidimethylchlorosilane (0.46 mL, 3.3 mmol, 1.5 equiv) was added via syringe. The yellow suspension stirred at rt for 3 h then was quenched by sat. NH\textsubscript{4}Cl\textsubscript{(aq)} (15 mL). The aqueous layer was extracted with DCM (3 x 10 mL) then the combined organics were dried over MgSO\textsubscript{4}, filtered and concentrated \textit{in vacuo} to give an orange oil. Purification by column chromatography (silica gel 2.5 x 12 cm; gradient elution with 3%-5% EtOAc/hexanes) gave 150 as a pale yellow oil (538 mg, 84%). Spectroscopic data corresponded to what was reported in the literature.\textsuperscript{88}

\[ \text{R}_\text{f} (20\% \text{ EtOAc/hexanes}) = 0.70 \]

\textbf{\textsuperscript{1}H NMR} (300 MHz, CDCl\textsubscript{3}) \( \delta = 8.16 \) (d, 1H, \( J = 8.8 \) Hz), 7.52 (d, 1H, \( J = 8.8 \) Hz), 6.17 (dd, 1H, \( J = 19.8, 14.8 \) Hz), 6.03 (dd, 1H, \( J = 14.8, 4.3 \) Hz), 5.80 (dd, 1H, \( J = 19.9, 4.3 \) Hz), 4.12-4.02 (m, 1H), 2.57 (d ABq, 2H, \( J_{\text{AB}} = 16.7 \) Hz, \( J_{\text{AX}} = 5.9 \) Hz, \( J_{\text{BX}} = 6.6 \) Hz), 1.30 (d, 3H, \( J = 6.2 \) Hz), 0.23 (s, 6H)

\textbf{Anal.} calcd for C\textsubscript{15}H\textsubscript{19}NO\textsubscript{3}Si: C 62.25, H 6.62, N 4.84; found C 62.64, H 6.64, N 5.13.
Diene 151

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H$_2$IMes)(PPh$_3$) (3.8 mg, 0.0052 mmol, 0.02 equiv) and a solution of alkyne 150 (75.2 mg, 0.26 mmol, 1 equiv) in DCE (1.04 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 5 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a dark brown oil. Purification by column chromatography (silica gel 1.5 x 12 cm; gradient elution with 3%-10% ether/hexanes) then preparative thin layer chromatography (eluted with 5% ether/hexanes) gave 151 as a yellow oil (22.9 mg, 30%, 2:1 Z/E).

R$_f$(30% EtOAc/hexanes) = 0.35

$^1$H NMR (300 MHz, CDCl$_3$) **major isomer:** δ = 8.26-8.19 (m, 2H), 7.33-7.29 (m, 2H), 6.85 (dd, 1H, $J = 17.3$, 10.8 Hz), 5.28 (d, 1H, $J = 10.8$ Hz), 4.75 (d, 1H, $J = 17.3$ Hz), 4.24-4.16 (m, 1H), 2.98 (dd, 1H, $J = 16.3$, 5.2 Hz), 2.35 (dd, 1H, $J = 16.0$, 8.5 Hz), 1.33 (d, 3H, $J = 6.3$ Hz), -0.06 (s, 3H), -0.18 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.51 (dd, 1H, $J = 17.0$, 10.5 Hz), 5.13 (d, 1H, $J = 10.5$ Hz), 4.67 (d, 1H, $J = 17.0$ Hz), 4.12-4.05 (m, 1H), 2.00 (ddd, 1H, $J = 16.8$, 8.3, 0.5 Hz), 1.20 (d, 3H, $J = 6.3$ Hz), 0.43 (s, 3H), 0.40 (s, 3H)
To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H$_2$IMes)(PPh$_3$) (9.2 mg, 0.0125 mmol, 0.05 equiv) and a solution of alkyne 77 (64.7 mg, 0.25 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 7 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated in vacuo to give a dark brown oil. Purification by preparative thin layer chromatography (eluted with 1% ether/hexanes) gave 152 as a yellow oil (36.4 mg, 56%, 4:1 Z/E).

$R_f$ (10% ether/hexanes) = 0.38

$^1$H NMR (300 MHz, CDCl$_3$) major isomer: $\delta$ = 7.36-7.34 (m, 3H), 7.26-7.22 (m, 2H), 6.75 (dd, 1H, $J$ = 17.5, 11.1 Hz), 5.33 (dd, 1H, $J$ = 17.5, 1.3 Hz), 5.18 (dd, 1H, $J$ = 10.9, 1.3 Hz), 5.12 (d, 1H, $J$ = 4.4 Hz) 3.22-3.14 (m, 1H), 1.94 (s, 3H), 0.59 (d, 3H, $J$ = 7.2 Hz), 0.46 (s, 3H), 0.39 (s, 3H); minor isomer (153) diagnostic peaks: $\delta$ = 6.37 (dd, 1H, $J$ = 16.9, 10.6 Hz), 5.26 (d, 1H, $J$ = 17.3 Hz), 3.09-3.00 (m, 1H), 1.92 (s, 3H), 0.58 (d, 3H, $J$ = 7.1 Hz), 0.41 (s, 3H)

$^{13}$C NMR (75 MHz, CDCl$_3$) major isomer: $\delta$ = 147.2, 142.1, 139.5, 135.7, 128.4, 127.1, 126.1, 115.2, 80.7, 43.3, 20.4, 16.0, 0.8, 0.1; minor isomer (153) diagnostic peaks: $\delta$ = 141.7, 140.9, 126.1, 113.4, 80.4, 44.6, 14.9, 1.2, 0.6
**Diene 154**

An oven dried Fischer Porter bottle equipped with a magnetic stir bar was brought into an argon filled glove box. To the Fischer Porter bottle was added RuHCl(CO)(H$_2$IMes)(PPh$_3$) (15 mg, 0.02 mmol, 0.02 equiv) and a solution of alkyne 68 (275 mg, 1.01 mmol, 1 equiv) in toluene. The bottle was plugged with a septum and removed from the glove box. The septum was replaced with a Swagelok regulator and the system was purged with ethylene (80 psi) and vented three times, then refilled to 80 psi and heated to 80°C for 24 h. The reaction was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a brown oil. Purification by column chromatography (gradient elution with hexanes-4% ether/hexanes) gave 154 as a bright yellow oil (239 mg, 80%, 1:1 Z/E).

$R_f$ (10% ether/hexanes) = 0.45  

$^1$H NMR (300 MHz, CDCl$_3$) *Z/E mixture*: δ = 7.11-6.95 (m, 10H), 6.48 (dd, 1H, $J = 17.4$, 10.9 Hz), 6.13 (dd, 1H, $J = 16.7$, 10.9 Hz), 5.10-4.82 (m, 4H), 3.91-3.81 (m, 2H), 2.64-2.45 (m, 7H), 2.12-2.03 (m, 2H), 1.75-1.54 (m, 9H), 0.15 (s, 6H), 0.11 (s, 6H)
**Diene 155**

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.9 mg, 0.026 mmol, 0.10 equiv) and alkyne 68 (70.2 mg, 0.26 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified by column chromatography (silica gel 1.5 x 7 cm; eluted with 3% ether/hexanes) to give 155 as a clear oil (45.1 mg, 64%). Spectroscopic data correlated with what was reported in the literature.  

R\text{f} (5\% \text{ ether/hexanes}) = 0.54

\begin{align*}
^1H \text{ NMR} \ (300 \text{ MHz, CDCl}_3) \ & \delta = 7.31-7.18 \ (m, 5H), 5.68 \ (d, 1H, J = 2.7 \text{ Hz}), 5.61 \ (app \ q, 1H, J = 7.2 \text{ Hz}), 5.08 \ (d, 1H, J = 3.0 \text{ Hz}), 3.89-3.81 \ (m, 1H), 2.86-2.64 \ (m, 2H), 2.52 \ (dd, 1H, J = 14.7, 1.8 \text{ Hz}), 2.16 \ (app \ dd, 1H, J = 14.7, 9.3 \text{ Hz}), 1.96-1.71 \ (m, 2H), 1.63 \ (d, 3H, J = 6.9 \text{ Hz}), 0.26 \ (s, 3H), 0.19 \ (s, 3H) \\
^13C \text{ NMR} \ (75 \text{ MHz, CDCl}_3) \ & \delta = 151.5, 142.3, 140.3, 128.6, 128.3, 125.7, 119.8, 117.9, 72.5, 39.5, 36.7, 31.9, 13.4, -0.2, -0.9
\end{align*}
Hydroxy Ketone 156

To a flame dried 50 mL round bottom flask equipped with a magnetic stir bar under Ar(g) was added diene 154 (105 mg, 0.39 mmol, 1 equiv, 1:1 Z/E), DMF (15 mL), KHF$_2$ (91.3 mg, 1.17 mmol, 3 equiv), propionic anhydride (1.6 mL, 9.75 mmol, 25 equiv) and H$_2$O$_2$ (1.1 mL, 9.75 mmol, 25 equiv) sequentially. The reaction was stirred at rt overnight then poured into water (25 mL), extracted with ether (3 x 25 mL), washed with brine (25 mL), dried over MgSO$_4$, filtered and concentrated in vacuo. The crude oil was purified by column chromatography (silica gel 2.5 x 15 cm, gradient elution with 15%-30% ether/hexanes) to afford ketone 156 as a clear oil (66 mg, 73%).

$R_f$ (20% ether/hexanes) = 0.12

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.30$-$7.16$ (m, 5H), 6.75 (dq, $J = 6.8$, 1.6 Hz, 1H), 4.11-4.05 (m, 1H), 3.47 (br s, 1H), 2.88-2.81 (m, 2H), 2.75-2.67 (m, 2H), 1.91-1.82 (m, 4H), 1.77 (t, $J = 1.2$ Hz, 3H), 1.75-1.71 (m, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 202.5$, 142.3, 139.0, 138.7, 128.7, 128.6, 126.0, 67.5, 43.6, 38.4, 32.1, 15.1, 11.0

IR (film): $\nu = 3496$, 3061, 3026, 2927, 2860, 1655, 1496, 1451, 1073, 700 cm$^{-1}$

Anal. calcd. for C$_{15}$H$_{20}$O$_2$: C 77.55, H 8.68; found: C 77.71, H 8.54.
Silicon-Tethered Alkyne 212

To a 100 mL round bottom flask equipped with a magnetic stir bar under Ar\textsubscript{(g)} was added SI-1 (801 mg, 5 mmol, 1 equiv), DCM (30 mL), imidazole (681 mg, 10 mmol, 2 equiv) and DMAP (122 mg, 1 mmol, 0.2 equiv). The pale yellow solution was cooled to 0°C (ice/H\textsubscript{2}O bath) then vinylphenylmethylchlorosilane (1.3 mL, 7.5 mmol, 1.5 equiv) was added dropwise via syringe. The resulting white suspension stirred at rt overnight. The reaction was quenched with sat. NH\textsubscript{4}Cl\textsubscript{(aq)} (35 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 30 mL) then the combined organic layers were washed with brine (2 x 50 mL), dried over MgSO\textsubscript{4}, filtered and concentrated\textit{ in vacuo} to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 13 cm; eluted with 1% ether/hexanes) gave alkyne 212 as a clear oil (1:1 dr, 790 mg, 52%).

\textit{R}_f (10% ether/hexanes) = 0.72

\textbf{\textit{H NMR}} (400 MHz, CDCl\textsubscript{3}) \(\delta = 7.68-7.66\) (m, 2H), \(7.43-7.40\) (m, 5H), \(7.31-7.29\) (m, 3H), 6.37 (2 dd, 1H, \(J = 20.0, 14.8\) Hz), 6.19 (2 dd, 1H, \(J = 14.8, 4.0\) Hz), 5.94 (2 dd, 1H, \(J = 20.0, 3.6\) Hz), 4.21-4.13 (2 m, 1H), 2.61 (2 d ABq, 2H, \(J_{AB} = 16.8\) Hz, \(J_{AX} = 6.0\) Hz, \(J_{BX} = 7.2\) Hz), 1.35 (2 d, 3H, \(J = 6.0\) Hz), 0.54 (s, 3H)

\textbf{\textit{C NMR}} (100 MHz, CDCl\textsubscript{3}) \(\delta = 136.6, 136.1, 135.2, 134.3, 131.8, 130.0, 128.4, 128.0, 127.8, 124.0, 87.6, 82.3, 68.5, 30.4, 23.6, -2.7

\textbf{FT-IR} (NaCl, thin film) \(\nu = 3052, 2972, 1595, 1490, 1429, 1378, 1254, 1118, 1007, 973\) cm\textsuperscript{-1}

\textbf{Anal.} calcd for C\textsubscript{20}H\textsubscript{22}OSi: C 78.38, H 7.24; found: C 78.07, H 7.02.
Silicon-Tethered Alkyne 213

To a 100 mL round bottom flask equipped with a magnetic stir bar under Ar\(_{g}\) was added SI-1 (400 mg, 2.5 mmol, 1 equiv), DCM (20 mL), imidazole (341 mg, 5 mmol, 2 equiv) and DMAP (61 mg, 0.5 mmol, 0.2 equiv). The pale yellow solution was cooled to 0°C (ice/H\(_2\)O bath) then vinyl diphenylchlorosilane (0.83 mL, 3.8 mmol, 1.5 equiv) was added dropwise via syringe. The resulting white suspension stirred at rt overnight. The reaction was quenched with sat. NH\(_4\)Cl\(_{aq}\) (10 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 10 mL) then the combined organic layers were dried over MgSO\(_4\), filtered and concentrated in vacuo to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 15 cm; eluted with hexanes) gave alkyne 213 as a clear oil (621 mg, 67%).

\[ R_f (10\% \text{ ether/hexanes}) = 0.68 \]

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\)) \(\delta = 7.68-7.64 \text{ (m, 4H)}, 7.46-7.31 \text{ (m, 8H)}, 7.29-7.26 \text{ (m, 3H)}, 6.54 \text{ (dd, 1H, } J = 20.4, 15.0 \text{ Hz)}, 6.29 \text{ (dd, 1H, } J = 15.0, 3.9 \text{ Hz}), 5.92 \text{ (dd, 1H, } J = 20.4, 3.9 \text{ Hz)}, 4.28-4.18 \text{ (m, 1H)}, 2.63 \text{ (d ABq, 2H, } J_{\text{AB}} = 16.8 \text{ Hz}, J_{\text{AX}} = 5.7 \text{ Hz}, J_{\text{BX}} = 6.8 \text{ Hz}), 1.35 \text{ (d, 3H, } J = 6.0 \text{ Hz})

\(^{13}\text{C NMR}\) (75 MHz, CDCl\(_3\)) \(\delta = 137.2, 135.1, 134.7, 134.6, 134.5, 133.9, 131.6, 129.9, 128.1, 127.8, 127.7, 127.6, 123.8, 87.3, 82.2, 68.7, 30.1, 23.3

\text{FT-IR (NaCl, thin film)} \nu = 1591, 1489 \text{ cm}^{-1}

\text{HRMS (ESI) calcd. for (C}_{25}\text{H}_{24}\text{OSi})_{2}\text{Na}^+: 391.1499; found: 391.1496. 
Diene 215

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 212 (76.3 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified by column chromatography (silica gel 2.5 x 7 cm; eluted with 2% ether/hexanes) to give 215 as a clear oil (53.3 mg, 70%).

\[ \text{Rf (5\% ether/hexanes) = 0.34} \]

**\(^1\)H NMR** (300 MHz, CDCl\(_3\)) \(\delta = 7.73\)-7.65 (m, 4H), 7.44-7.26 (m, 16H), 6.73 (d, 2H, \(J = 6.9\) Hz.), 6.10 (dd, 2H, \(J = 5.1, 2.7\) Hz), 5.43 (d, 1H, \(J = 2.7\) Hz), 5.32 (d, 1H, \(J = 2.7\) Hz), 4.31-4.23 (m, 1H), 4.17-4.10 (m, 1H), 2.99 (d, 1H, \(J = 14.7\) Hz), 2.47 (dd, 1H, \(J = 15.0, 9.6\) Hz), 2.37 (dd, 1H, \(J = 14.4, 10.2\) Hz), 1.32 (d, 3H, \(J = 3.3\) Hz), 1.30 (d, 3H, \(J = 3.0\) Hz), 0.56 (s, 3H), 0.54 (s, 3H).

**\(^{13}\)C NMR** (75 MHz, CDCl\(_3\)) \(\delta = 149.5, 149.4, 143.3, 142.4, 138.0, 137.9, 136.8, 136.8, 134.2, 134.0, 130.2, 130.1, 129.4, 129.3, 128.4, 128.4, 128.1, 128.1, 126.7, 70.7, 70.6, 40.1, 39.9, 24.6, 24.6, -1.6, -2.0.

**FT-IR** (NaCl, thin film) \(\nu = 2969, 1597, 1428, 1252, 1114\) cm\(^{-1}\)

**Anal.** calcd for C\(_{20}\)H\(_{22}\)OSi: C 78.38, H 7.24; found: C 78.78, H 7.00.
Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (8.0 mg, 0.021 mmol, 0.10 equiv) and alkyne 213 (77.7 mg, 0.21 mmol, 1 equiv) in toluene (0.84 mL) were combined and stirred at 70°C for 1 h. The residue was purified by column chromatography (silica gel 2.5 x 7 cm; eluted with 3% ether/hexanes) to give 216 a clear oil (56.2 mg, 72%).

\[ R_f \ (5\% \ ether/hexanes) = 0.31 \]

\[ ^1\text{H NMR} \ (300 \text{ MHz, CDCl}_3) \ \delta = 7.68-7.59 \ (m, \ 4\text{H}), \ 7.41-7.26 \ (m, \ 10\text{H}), \ 7.25-7.18 \ (m, \ 2\text{H}), \ 6.79 \ (s, \ 1\text{H}), \ 6.09 \ (dd, \ 1\text{H}, \ J = 14.7 \text{ Hz, } 0.6 \text{ Hz}), \ 4.53-4.43 \ (m, \ 1\text{H}), \ 2.88 \ (dd, \ 1\text{H}, \ J = 15.3 \text{ Hz, } 1.5 \text{ Hz}), \ 2.73 \ (dd, \ 1\text{H}, \ J = 15.3 \text{ Hz, } 8.1 \text{ Hz}), \ 1.29 \ (d, \ 3\text{H}, \ J = 6.6 \text{ Hz}) \]

\[ ^{13}\text{C NMR} \ (75 \text{ MHz, CDCl}_3) \ \delta = 153.9, \ 140.6, \ 137.2, \ 137.0, \ 136.7, \ 136.4, \ 134.7, \ 134.5, \ 134.3, \ 129.80, \ 129.75, \ 128.9, \ 128.3, \ 127.9, \ 127.1, \ 126.4, \ 72.2, \ 38.9, \ 24.2 \]

\[ \text{FT-IR} \ (\text{NaCl, thin film}): \ 2925, \ 1597, \ 1562, \ 1490 \text{ cm}^{-1} \]

\[ \text{HRMS} \ (\text{ESI}): \ \text{calcd for } C_{25}H_{24}OSiNa^+: \ 391.1489; \ \text{found: } 391.1499. \]
Silicon-Tethered Alkyne 219

To a 50 mL RBF equipped with a magnetic stir bar was added SI-11\textsuperscript{26} (502 mg, 2.5 mmol, 1 equiv), DCM (10 mL), imidazole (341 mg, 5 mmol, 2 equiv) and DMAP (61 mg, 0.5 mmol, 0.2 equiv). The solution was cooled to 0°C (ice/H\textsubscript{2}O bath) then vinlyldimethylchlorosilane (0.52 mL, 3.8 mmol, 1.5 equiv) was added dropwise via syringe. The resulting white suspension stirred at rt overnight. The reaction was quenched with sat. NH\textsubscript{4}Cl\textsubscript{(aq)} (10 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 10 mL) then the combined organic layers were dried over MgSO\textsubscript{4}, filtered and concentrated \textit{in vacuo} to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 15 cm; eluted with 2% EtOAc/hexanes) gave alkyne 219 as a pale yellow oil (471 mg, 66%).

R\textsubscript{f} (5% ether/hexanes) = 0.50

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) δ = 7.33-7.31 (m, 2H), 7.21-7.16 (m, 3H), 6.13 (dd, 1H, J = 20.4, 14.8 Hz), 5.91 (dd, 1H, J = 14.8, 4.0 Hz), 5.72 (dd, 1H, J = 20.4, 4.0 Hz), 3.59-3.54 (m, 1H), 2.43 (ddd, 1H, J = 12.4, 8.4, 4.0 Hz), 2.01-1.96 (m, 1H), 1.86-1.81 (m, 1H), 1.66-1.57 (m, 2H), 1.45-1.35 (m, 1H), 1.32-1.11 (m, 3H), 0.16 (s, 3H), 0.15 (s, 3H)

\textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}) δ = 138.4, 133.0, 131.7, 128.3, 127.6, 124.3, 93.0, 81.7, 74.0, 38.8, 34.9, 31.1, 24.6, 24.0, -1.0, -1.2

\textbf{FT-IR} (NaCl, thin film) ν = 2937, 2860, 1491, 1252, 1102 cm\textsuperscript{-1}

\textbf{Anal.} calcd for C\textsubscript{18}H\textsubscript{24}OSi: C 76.00, H 8.50; found: C 76.29, H 8.22.
Diene 220

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 55 (81.1 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4.5 cm; eluted with 3% ether/hexanes) to give 220 as a pale yellow oil (64.9 mg, 80%).

Rf (5% ether/hexanes) = 0.63

^1H NMR (300 MHz, CDCl₃) δ = 7.36-7.21 (m, 5H), 6.58 (s, 1H), 5.89 (d, 1H, J = 3.0 Hz), 5.22 (d, 1H, J = 3.0 Hz), 3.88-3.83 (m, 1H), 2.86 (app d, 1H, J = 15.0 Hz), 2.31 (app dd, 1H, J = 14.7, 9.9 Hz), 1.42-1.23 (m, 12H), 0.89-0.84 (m, 3H), 0.30 (s, 3H), 0.23 (s, 3H)

^13C NMR (75 MHz, CDCl₃) δ = 152.1, 143.1, 138.1, 129.3, 128.4, 126.6, 123.5, 121.5, 74.0, 38.3, 38.3, 32.0, 29.7, 29.5, 25.8, 22.9, 14.3, -0.1, -0.7

FT-IR (NaCl, thin film) ν = 3079, 2956, 2927, 2856, 1599, 1493, 1402, 1252, 1111, 1045 cm⁻¹

Anal. calcd for C₂₁H₃₂OSi: C 76.77, H 9.82; found: C 76.95, H 9.47.
Diene 221

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 218 (58.1 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via flash column chromatography (silica gel 1.5 x 5 cm; eluted with 3% ether/hexanes) to give 221 as a clear oil (45 mg, 77%).

R_f (5% ether/hexanes) = 0.33

^1H NMR (300 MHz, CDCl_3) δ = 7.36-7.21 (m, 5H), 6.58 (s, 1H), 5.90 (d, 1H, J = 2.7 Hz), 5.24 (d, 1H, J = 2.7 Hz), 3.95 (t, 2H, J = 5.4 Hz), 2.73-2.69 (app t, 2H, J = 5.1 Hz), 0.28 (s, 6H)

^13C NMR (75 MHz, CDCl_3) δ = 152.0, 143.7, 138.0, 129.4, 128.4, 126.7, 123.4, 122.0, 64.3, 33.7, -0.9

FT-IR (NaCl, thin film) ν = 3079, 3048, 2958, 2858, 1599, 1401, 1253, 1083, 1045 cm^{-1}

Anal. calcd for C_{14}H_{18}OSi: C 72.99, H 7.88; found: C 73.11, H 8.21.
Diene 222

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 57 (78.4 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 5 cm; eluted with 3% ether/hexanes) to give 222 as a yellow oil (69.0 mg, 88%).

\[ \text{R}_f \text{ (hexanes)} = 0.28 \]

\[ ^1H \text{ NMR} \ (300 \text{ MHz, CDCl}_3) \delta = 7.36-7.21 \text{ (m, 5H)}, 6.58 \text{ (s, 1H)}, 5.88 \text{ (d, 1H, } J = 2.7 \text{ Hz)}, 5.21 \text{ (d, 1H, } J = 2.7 \text{ Hz)}, 3.63 \text{ (ddd, 1H, } J = 9.9, 6.0, 2.1 \text{ Hz)}, 2.87 \text{ (app d, 1H, } J = 13.5 \text{ Hz)}, 2.29 \text{ (app dd, 1H, } J = 14.4, 10.2 \text{ Hz)}, 1.89-1.85 \text{ (m, 1H)}, 1.75-0.93 \text{ (m, 10H)}, 0.28 \text{ (s, 3H)}, 0.22 \text{ (s, 3H)} \]

\[ ^13C \text{ NMR} \ (75 \text{ MHz, CDCl}_3) \delta = 152.5, 143.5, 138.2, 129.3, 128.4, 126.5, 123.4, 121.2, 78.3, 44.4, 35.2, 28.9, 28.7, 26.7, 26.4, 26.4, -0.1, -0.7 \]

\[ \text{FT-IR} \ (\text{NaCl, thin film}) \nu = 3079, 2949, 2861, 1707, 1599, 1493, 1449, 1251, 1064 \text{ cm}^{-1} \]

\[ \text{Anal. calcd for C}_{20}H_{28}OSi: C \ 76.86, \ H \ 9.03; \ found: C \ 76.76, \ H \ 8.71. \]
Diene 223

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 58 (75.1 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 1 h. The residue was purified via column chromatography (silica gel 2.5 x 6 cm; eluted with 2% ether/hexanes) to give 223 as a clear oil (56.7 mg, 80%).

\[ \text{R}_f (5\% \text{ ether/hexanes}) = 0.40 \]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta = 7.29-7.12 \text{ (m, 10H)}, 6.58 \text{ (s, 1H)}, 5.89 \text{ (d, 1H, } J = 2.4 \text{ Hz)}, 5.24 \text{ (d, 1H, } J = 2.8 \text{ Hz)}, 4.91 \text{ (dd, 1H, } J = 10.8, 2.0 \text{ Hz)}, 3.05 \text{ (dd, 1H, } J = 14.8, 2.0 \text{ Hz)}, 2.43 \text{ (ddd, 1H, } J = 14.8, 10.8, 2.0 \text{ Hz)}, 0.34 \text{ (s, 3H)}, 0.25 \text{ (s, 3H)}

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta = 151.6, 144.5, 142.7, 137.8, 129.3, 128.6, 128.5, 127.5, 126.7, 125.7, 124.1, 122.0, 76.1, 41.5, -0.2, -0.7

\text{FT-IR (NaCl, thin film)} \nu = 3061, 3028, 2958, 2897, 1601, 1493, 1452, 1253 \text{ cm}^{-1}

\text{Anal. calcd for } C_{20}H_{22}OSi: C 78.38, H 7.24; \text{ found: } C 78.61, H 7.34.
Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (5.7 mg, 0.015 mmol, 0.10 equiv) and alkyne 117 (54.3 mg, 0.15 mmol, 1 equiv) in toluene (0.6 mL) were combined and stirred at 70°C for 2 h. The residue was purified via column chromatography (silica gel 2.5 x 5 cm; gradient elution with 3%-4% ether/hexanes) to give 224 as a yellow oil (43.2 mg, 80%).

\[
\begin{align*}
R_f (5\% \text{ ether/hexanes}) & = 0.22 \\
^{1}H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta = & 8.07 \ (d, \ 2H, \ J = 8.8 \text{ Hz}), \ 7.38 \ (d, \ 2H, \ J = 8.4 \text{ Hz}), \ 7.24-7.22 \ (m, \ 2H), \ 7.16-7.12 \ (m, \ 3H), \ 6.60 \ (s, \ 1H), \ 5.89 \ (d, \ 1H, \ J = 2.4 \text{ Hz}), \ 5.25 \ (d, \ 1H, \ J = 2.4 \text{ Hz}), \ 4.99 \ (dd, \ 1H, \ J = 10.4, \ 2.0 \text{ Hz}), \ 3.03 \ (dd, \ 1H, \ J = 14.8, \ 2.0 \text{ Hz}), \ 2.38 \ (ddd, \ 1H, \ J = 14.8, \ 10.8, \ 2.0 \text{ Hz}), \ 0.35 \ (s, \ 3H), \ 0.25 \ (s, \ 3H) \\
^{13}C \text{ NMR} \ (100 \text{ MHz, CDCl}_3) \delta = & 151.7, \ 150.8, \ 147.3, \ 141.5, \ 137.5, \ 129.2, \ 128.5, \ 127.0, \ 126.4, \ 124.7, \ 123.8, \ 122.6, \ 75.1, \ 41.1, \ -0.3, \ -0.6 \\
\text{FT-IR} \ (\text{NaCl, thin film}) \nu = & 3056, \ 2956, \ 2897, \ 1602, \ 1520, \ 1492, \ 1347, \ 1253 \text{ cm}^{-1} \\
\text{Anal. calcd for C}_{20}\text{H}_{21}\text{NO}_3\text{Si}: \ C \ 68.35, \ H \ 6.02, \ N \ 3.99; \ \text{found:} \ C \ 68.11, \ H \ 6.11, \ N \ 3.90.
\end{align*}
\]
Diene 225

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (5.3 mg, 0.014 mmol, 0.10 equiv) and alkyne 61\textsuperscript{26} (51.9 mg, 0.14 mmol, 1 equiv) in toluene (0.6 mL) were combined and stirred at 70 °C for 30 min. The residue was purified via column chromatography (silica gel 2.5 x 7 cm; gradient elution with 1%-4% ether/hexanes) to give 225 as a white oil (40.4 mg, 78%).

\[ R_f (5\% \text{ ether/hexanes}) = 0.39 \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta = 7.61-7.57 (m, 4H), 7.47-7.43 (m, 4H), 7.33-7.22 (m, 6H), 6.70 (s, 1H), 6.00 (d, 1H, } J = 2.7 \text{ Hz), 5.36 (d, 1H, } J = 2.7 \text{ Hz), 5.06 (dd, 1H, } J = 10.8, 2.0 \text{ Hz), 3.19 (dd, 1H, } J = 14.8, 2.0 \text{ Hz), 2.59 (ddd, 1H, } J = 14.7, 10.8, 1.8 \text{ Hz), 0.46 (s, 3H), 0.37 (s, 3H) \]

\[ ^13C \text{ NMR (100 MHz, CDCl}_3) \delta = 151.6, 143.5, 142.7, 141.2, 140.5, 137.8, 129.3, 128.9, 128.5, 127.4, 127.3, 126.8, 126.2, 124.2, 122.1, 75.8, 41.4, -0.2, -0.7 \]

\[ \text{FT-IR (NaCl, thin film)} v = 3028, 2956, 1600, 1487, 1252, 1067 \text{ cm}^{-1} \]

\[ \text{Anal. calcd for C}_{26}H_{26}OSi: C 81.63, H 6.85; found: C 81.31, H 6.52. \]
Diene 226

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 62\textsuperscript{26} (81.2 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 5 cm; eluted with 3% ether/hexanes) to give 226 as a pale yellow oil (76.2 mg, 94%). Spectroscopic data corresponded to what was reported in the literature.\textsuperscript{88}

\( R_f \) (hexanes) = 0.67

**\textsuperscript{1}H NMR** (300 MHz, CDCl\textsubscript{3}) \( \delta = 7.42-7.23 \) (m, 10H), 6.84 (s, 1H), 6.04 (d, 1H, \( J = 2.1 \) Hz), 5.32 (d, 1H, \( J = 2.1 \) Hz), 3.11 (d, 1H, \( J = 14.4 \) Hz), 2.92 (d, 1H, \( J = 14.4 \) Hz), 1.55 (s, 3H), 0.43 (s, 3H), 0.42 (s, 3H)

**\textsuperscript{13}C NMR** (75 MHz, CDCl\textsubscript{3}) \( \delta = 150.4, 148.5, 140.0, 137.8, 129.1, 128.2, 127.8, 126.5, 126.3, 124.7, 124.5, 121.4, 78.0, 43.5, 30.4, 1.9, 1.0 \)
Diene 227

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (114 mg, 0.30 mmol, 0.10 equiv) and alkyne 63 (896 mg, 3.0 mmol, 1 equiv) in toluene (12 mL) were combined and stirred at 70°C for 1 h. The residue was purified by column chromatography (silica gel 2.5 x 6 cm; eluted with 2% ether/hexanes) to give 227 as a pale yellow solid (840 mg, 94%). Spectroscopic data corresponded to what was reported in the literature.88

Rf (hexanes) = 0.38

1H NMR (300 MHz, CDCl3) δ = 7.38-7.22 (m, 5H), 6.78 (s, 1H), 5.97 (d, 1H, J = 2.7 Hz), 5.25 (d, 1H, J = 2.7 Hz), 2.63 (s, 2H), 1.67-1.20 (m, 10H), 0.31 (s, 6H)

13C NMR (75 MHz, CDCl3) δ = 151.5, 141.0, 138.1, 129.2, 128.1, 126.3, 124.0, 121.0, 75.3, 41.9, 38.5, 25.7, 22.0, 1.5
Diene 228

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 219 (72.0 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 20 h. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; eluted with 3% ether/hexanes) to give 228 as a clear oil (52.3 mg, 73%).

Rf (5% ether/hexanes) = 0.33

1H NMR (300 MHz, CDCl3): δ = 7.40-7.20 (m, 5H), 6.36 (s, 1H), 5.85 (d, 1H, J = 3.0 Hz), 5.28 (d, 1H, J = 3.3 Hz), 3.52 (td, 1H, J = 10.2, 3.9 Hz), 2.97 (app t, 1H, J = 9.9 Hz), 2.05-2.01 (m, 1H), 1.86-1.78 (m, 2H), 1.60-1.19 (m, 4H), 1.04-0.99 (m, 1H), 0.24 (s, 3H), 0.23 (s, 3H)

13C NMR (75 MHz, CDCl3) δ = 153.7, 148.4, 138.1, 128.7, 128.5, 126.5, 125.5, 122.7, 75.5, 48.1, 35.2, 29.4, 25.8, 25.4, -0.9, -2.0

FT-IR (NaCl, thin film) ν = 3048, 2932, 2858, 1598, 1493, 1446, 1251, 1057 cm⁻¹

Anal. calcd for C₁₈H₂₄O₅Si: C 76.00, H 8.50; found: C 76.09, H 8.87.
Silicon-Tethered Alkyne 229

To a flame-dried 50 mL RBF equipped with a magnetic stir bar under Ar (g) was added SI-1688 (555 mg, 2.74 mmol, 1 equiv), DCM (18 mL), imidazole (373 mg, 5.48 mmol, 2 equiv) and DMAP (67 mg, 0.55 mmol, 0.2 equiv). The yellow solution was cooled to 0°C (ice/H2O bath) then vinyldimethylchlorosilane (0.57 mL, 4.11 mmol, 1.5 equiv) was added via syringe. The resulting yellow suspension stirred at rt for 3 h, was quenched with sat. NH4Cl (aq) (20 mL) then the layers were separated. The organic layer was washed with brine (2 x 20 mL), dried over MgSO4, filtered and concentrated in vacuo to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 12.5 cm; gradient elution with 7%-13% ether/hexanes) gave alkyne 229 as a pale yellow oil (632 mg, 81%). Spectroscopic data corresponded to what was reported in the literature.88

Rf (25% EtOAc/hexanes) = 0.52

1H NMR (300 MHz, CDCl3) δ = 7.88 (dd, 2H, J = 6.5, 1.6 Hz), 7.46 (dd, 2H, J = 7.1, 2.2 Hz), 6.18 (dd, 1H, J = 20.2, 14.7 Hz), 6.02 (dd, 1H, J = 14.7, 4.4 Hz), 5.80 (dd, 1H, J = 20.2, 4.4 Hz), 4.11-4.01 (m, 1H), 2.59 (s, 3H), 2.55 (d ABq, 2H, JAB = 16.9 Hz, JAIX = 6.0 Hz, JBX = 6.5 Hz), 1.30 (d, 3H, J = 6.0 Hz), 0.23 (s, 6H)
**Silicon-Tethered Alkyne 231**

A solution of 4-pentyn-2-ol (0.57 mL, 6 mmol, 1.2 equiv), 3-bromopyridine (0.48 mL, 5 mmol, 1 equiv), CuI (95.2 mg, 0.5 mmol, 0.10 equiv), PdCl$_2$(PPh$_3$)$_2$ (176 mg, 0.25 mmol, 0.05 equiv) and Et$_3$N (20 mL) was degassed by freeze-pump-thaw (3 times) and refluxed under Ar$_{(g)}$ overnight. The reaction mixture was quenched with sat. NH$_4$Cl$_{(aq)}$ (20 mL) and extracted with DCM (3 x 20 mL). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated *in vacuo*. Purification by column chromatography on silica gel (2.5 x 15 cm; eluted with 50% EtOAc/hexanes) gave the alcohol (576 mg, 71%) as a brown oil. To a 50 mL RBF with magnetic stir bar under Ar$_{(g)}$ was added alcohol (392 mg, 2.4 mmol, 1 equiv), DCM (15 mL), imidazole (327 mg, 4.8 mmol, 2 equiv) and DMAP (59 mg, 0.48 mmol, 0.2 equiv). The orange solution was cooled to 0°C (ice/H$_2$O bath) then vinyl(dimethylchlorosilane (0.50 mL, 3.6 mmol, 1.5 equiv) was added dropwise via syringe. The resulting yellow suspension stirred at rt overnight. The reaction was quenched with sat. NH$_4$Cl$_{(aq)}$ (15 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 15 mL) then the combined organic layers were dried over MgSO$_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 12 cm; gradient elution with 10%-25% EtOAc/hexanes) gave alkyne 231 as a pale yellow oil (373 mg, 63%).

R$_f$ (25% EtOAc/hexanes) = 0.45

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.60$ (d, 1H, $J = 1.4$ Hz), 8.46 (dd, 1H, $J = 4.9$, 1.7 Hz), 7.64 (dt, 1H, $J = 7.9$, 1.9 Hz), 7.18 (ddd, 1H, $J = 7.9$, 4.9, 0.8 Hz), 6.15 (dd, 1H, $J = 20.4$, 14.8 Hz),
5.99 (dd, 1H, J = 14.8, 4.0 Hz), 5.78 (dd, 1H, J = 20.0, 4.0 Hz), 4.07-3.99 (m, 1H), 2.52 (d ABq, 2H, $J_{AB} = 16.4$ Hz, $J_{AX} = 6.0$ Hz, $J_{BX} = 6.8$ Hz), 1.27 (d, 3H, J = 6.0 Hz), 0.20 (s, 6H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 152.5, 148.2, 138.6, 137.8, 133.4, 123.1, 121.1, 91.3, 78.9, 67.8, 30.4, 23.6, -1.4$

FT-IR (NaCl, thin film) $\nu = 3049, 2970, 2905, 1561, 1476, 1408, 1378, 1253, 1128, 1098, 1004, 837, 736$ cm$^{-1}$

Anal. calcd for C$_{14}$H$_{19}$NOSi: C 68.52, H 7.80, N 5.71; found: C 68.88, H 8.10, N 5.88.
Diene 232

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (28.5 mg, 0.075 mmol, 0.10 equiv) and alkyne 65 (206 mg, 0.75 mmol, 1 equiv) in toluene (3 mL) were combined and stirred at 70°C for 1.5 h. The residue was purified via column chromatography (silica gel 2.5 x 5 cm; gradient elution with 3%-5% ether/hexanes) to give 232 as a clear oil (183.1 mg, 89%).

R_f (5% ether/hexanes) = 0.24

^1H NMR (300 MHz, CDCl_3) δ = 7.19 (d, 2H, J = 8.4 Hz), 6.88 (d, 2H, J = 9.0 Hz), 6.54 (s, 1H), 5.87 (d, 1H, J = 3.0 Hz), 5.21 (d, 1H, J = 2.7 Hz), 4.10-4.00 (m, 1H), 3.82 (s, 3H), 2.86 (dd, 1H, J = 14.7, 1.8 Hz), 2.28 (ddd, 1H, J = 14.4, 10.2, 1.8 Hz), 1.23 (d, 3H, J = 6.0 Hz), 0.30 (s, 3H), 0.23 (s, 3H)

^13C NMR (75 MHz, CDCl_3) δ = 158.4, 151.6, 141.5, 130.6, 130.6, 123.1, 121.3, 113.8, 70.1, 55.4, 40.1, 24.6, -0.1, -0.7

FT-IR (NaCl, thin film) ν = 3030, 2962, 1607, 1510 cm⁻¹

Anal. calcd for C_{16}H_{22}O_{2}Si: C 70.03, H 8.08; found: C 69.94, H 7.87.
Diene 233

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 229 (71.1 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 6 h. The residue was purified via column chromatography (silica gel 1.5 x 4.5 cm; eluted with 20% ether/hexanes) to give 233 as a clear oil (53.9 mg, 76%).

$R_f$ (25% ether/hexanes) = 0.29

$^1H$ NMR (300 MHz, CDCl$_3$) $\delta$ = 7.91 (d, 2H, $J = 8.4$ Hz), 7.32 (d, 2H, $J = 8.4$ Hz), 6.58 (s, 1H), 5.91 (d, 1H, $J = 2.7$ Hz), 5.26 (d, 1H, $J = 2.4$ Hz), 4.11-4.01 (m, 1H), 2.83 (dd, 1H, $J = 4.4, 1.8$ Hz), 2.58 (s, 3H), 2.29 (ddd, 1H, $J = 14.4, 9.9, 1.5$ Hz), 1.23 (d, 3H, $J = 6.0$ Hz), 0.30 (s, 3H), 0.24 (s, 3H)

$^{13}C$ NMR (75 MHz, CDCl$_3$) $\delta$ = 197.7, 151.5, 145.3, 143.0, 135.2, 129.4, 128.5, 122.6, 122.4, 70.0, 40.3, 26.7, 24.5, -0.2, -0.8

FT-IR (NaCl, thin film) $\nu$ = 3046, 2969, 2897, 1683, 1601, 1505, 1406, 1268, 1122 cm$^{-1}$

Anal. calcd for C$_{17}$H$_{22}$O$_2$Si: C 71.28, H 7.74; found: C 70.96, H 7.39.
Diene 234

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 150 (72.7 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; eluted with 3% ether/hexanes) to give 234 as a pale yellow solid (62.0 mg, 85%).

R_f (5% ether/hexanes) = 0.24

M.P. = 82-84°C

^1H NMR (300 MHz, CDCl₃) δ = 8.20 (d, 2H, J = 9.0 Hz), 7.39 (d, 2H, J = 8.7 Hz), 6.59 (s, 1H), 5.93 (d, 1H, J = 2.7 Hz), 5.31 (d, 1H, J = 2.7 Hz), 4.13-4.04 (m, 1H), 2.81 (dd, 1H, J = 14.4, 1.5 Hz), 2.32 (ddd, 1H, J = 15.6, 9.0, 1.8 Hz), 1.25 (d, 3H, J = 6.3 Hz), 0.32 (s, 3H), 0.26 (s, 3H)

^13C NMR (75 MHz, CDCl₃) δ = 151.3, 147.0, 146.2, 144.9, 129.9, 123.8, 123.0, 121.6, 69.8, 40.3, 24.5, -0.2, -0.8

FT-IR (NaCl, thin film) ν = 3078, 2988, 2948, 2850, 1593, 1517, 1342, 1251, 1114 cm⁻¹

Anal. calcd for C_{15}H_{19}NO₃Si: N 4.84, C 62.25, H 6.62; found: N 4.83, C 62.61, H 6.83.
Diene 235

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.1 mg, 0.024 mmol, 0.10 equiv) and alkyne 66 (63.0 mg, 0.24 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; eluted with 3% ether/hexanes) to give 235 as a pale yellow oil (50.6 mg, 80%).

R_f (5% ether/hexanes) = 0.43

^1H NMR (300 MHz, CDCl_3) δ = 7.15 (s, 4H), 6.56 (s, 1H), 5.88 (d, 1H, J = 2.7 Hz), 5.22 (d, 1H, J = 2.7 Hz), 4.11-4.01 (m, 1H), 2.87 (dd, 1H, J = 14.4, 1.8 Hz), 2.35 (s, 3H), 2.27 (ddd, 1H, J = 14.4, 10.2, 1.8 Hz), 1.22 (d, 3H, J = 6.3 Hz), 0.30 (s, 3H), 0.24 (s, 3H)

^13C NMR (75 MHz, CDCl_3) δ = 151.6, 142.3, 136.3, 135.1, 129.3, 129.1, 123.5, 121.5, 70.1, 40.1, 24.6, 21.4, -0.1, -0.7

FT-IR (NaCl, thin film) ν = 3045, 2969, 1706, 1610, 1376, 1251, 1115, 1043 cm^-1

Anal. calcd for C_{16}H_{22}OSi: C 74.36, H 8.58; found: C 74.21, H 8.21.
Diene 236

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 67 (69.2 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; eluted with hexanes) to give 236 as a clear oil (55.7 mg, 80%).

R_f (5% ether/hexanes) = 0.53

^1H NMR (300 MHz, CDCl_3) δ = 6.87 (s, 3H), 6.53 (s, 1H), 5.86 (d, 1H, J = 2.7 Hz), 5.21 (d, 1H, J = 2.7 Hz), 4.10-4.02 (m, 1H), 2.88 (dd, 1H, J = 14.7, 1.8 Hz), 2.32-2.22 (m, 7H), 1.24 (d, 3H, J = 6.0 Hz), 0.31 (s, 3H), 0.23 (s, 3H)

^13C NMR (75 MHz, CDCl_3) δ = 151.7, 142.6, 138.0, 137.8, 128.3, 127.2, 123.7, 121.4, 70.3, 40.1, 24.6, 21.6, -0.2, -0.7

FT-IR (NaCl, thin film) ν = 3042, 2977, 2919, 2862, 1599, 1444, 1376, 1251, 1116, 1051 cm⁻¹

Anal. calcd for C_{17}H_{24}OSi: C 74.94, H 8.88; found: C 75.19, H 8.73.
**Diene 237**

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 64 (66.8 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4.5 cm; eluted with 3% ether/hexanes) to give 237 as a pale yellow oil (54.2 mg, 81%).

$$R_f (5\% \text{ ether/hexanes}) = 0.39$$

$^1H$ NMR (300 MHz, CDCl$_3$) $\delta = 7.23$-$7.18$ (m, 2H), $7.05$-$6.99$ (m, 2H), $6.53$ (s, 1H), $5.88$ (d, 1H, $J = 2.7$ Hz), $5.23$ (d, 1H, $J = 2.7$ Hz), $4.10$-$4.00$ (m, 1H), $2.80$ (dd, 1H, $J = 14.7$, 2.1 Hz), $2.25$ (ddd, 1H, $J = 15.0$, 9.9, 1.5 Hz), $1.23$ (d, 3H, $J = 6.3$ Hz), $0.31$ (s, 3H), $0.24$ (s, 3H)

$^{13}C$ NMR (75 MHz, CDCl$_3$) $\delta = 163.2$, 160.0, 151.4, 143.0, 134.0, 131.0, 130.9, 122.4, 121.8, 115.4, 115.2, 70.0, 40.0, 24.5, -0.2, -0.8

FT-IR (NaCl, thin film) $\nu = 3046$, 2970, 2896, 1601, 1507, 1377, 1251, 1225, 1115, 1043 cm$^{-1}$

Anal. calcd for C$_{15}$H$_{19}$FOSi: C 68.66, H 7.30; found: C 68.68, H 7.02.
Diene 238

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne 230 (69.6 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; eluted with 3% ether/hexanes) to give 238 as a clear oil (66.4 mg, 95%).

**Rf** (5% ether/hexanes) = 0.35

**¹H NMR** (300 MHz, CDCl₃) δ = 7.41-7.17 (m, 4H), 6.58 (s, 1H), 5.94 (d, 1H, J = 2.7 Hz), 5.28 (d, 1H, J = 2.7 Hz), 4.11-4.04 (m, 1H), 2.64 (dd, 1H, J = 14.1, 2.1 Hz), 2.18 (ddd, 1H, J = 14.1, 9.9, 1.8 Hz), 1.21 (d, 3H, J = 6.3 Hz), 0.34 (s, 3H), 0.26 (s, 3H)

**¹³C NMR** (75 MHz, CDCl₃) δ = 151.3, 144.3, 136.4, 134.4, 131.0, 129.6, 128.2, 126.5, 122.1, 120.9, 70.3, 40.2, 24.5, -0.3, -0.8

**FT-IR** (NaCl, thin film) ν = 3048, 2969, 2929, 1468, 1253, 1115, 977 cm⁻¹

**Anal.** calcd for C₁₅H₁₉ClOSi: C 64.61, H 6.87; found: C 64.68, H 6.92.
Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (9.1 mg, 0.024 mmol, 0.12 equiv) and alkyne 231 (49.9 mg, 0.20 mmol, 1 equiv) in toluene (0.8 mL) were combined and stirred at 70°C for 5 h. The residue was purified via column chromatography (silica gel 1.5 x 12 cm; eluted with 25% ether/hexanes) to give 239 as an orange oil (25.8 mg, 52%).

**Diene 239**

\[ \text{Diene 239} \]

\[ \begin{align*}
\text{O} & \quad \text{Si} & \quad \text{N} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{align*} \]

\[ \text{Rf (30% ether/hexanes) = 0.13} \]

**\(^1\text{H NMR}\) (300 MHz, CDCl}_3\) \(\delta = 8.50\) (d, 1H, \(J = 2.1\) Hz), 8.43 (dd, 1H, \(J = 4.8, 1.5\) Hz), 7.55-7.51 (m, 1H), 7.25 (app dd, 1H, \(J = 7.8, 4.8\) Hz), 6.49 (s, 1H), 5.90 (d, 1H, \(J = 2.7\) Hz), 5.26 (d, 1H, \(J = 2.7\) Hz), 4.11-4.00 (m, 1H), 2.77 (dd, 1H, \(J = 14.4, 1.8\) Hz), 2.27 (ddd, 1H, \(J = 14.4, 9.9, 1.8\) Hz), 1.22 (d, 3H, \(J = 6.3\) Hz), 0.30 (s, 3H), 0.23 (s, 3H)

**\(^{13}\text{C NMR}\) (75 MHz, CDCl}_3\) \(\delta = 151.3, 150.4, 147.6, 145.5, 136.3, 133.7, 123.3, 122.4, 119.7, 70.0, 40.1, 24.5, -0.2, -0.8\)

**FT-IR\) (NaCl, thin film) \(\nu = 2968, 2927, 1421, 1376, 1252, 1128 \text{ cm}^{-1}\)

**Anal.** calcd for C\(_{14}\)H\(_{19}\)NOSi: C 68.52, H 7.80, N 5.71; found: C 68.53, H 8.11, N 5.75.
Silicon-Tethered Alkyne 240

\[ \text{C}_\text{dH}_{13} \]

\[ n\text{BuLi (2.4 M in hexanes, 12.5 mL, 30 mmol, 1.5 equiv) was added dropwise} \]
to a stirred solution of cyclopropylacetylene (2.5 mL, 30 mmol, 1.5 equiv) in dry THF (30 mL) at -78°C under Ar\((g)\). After complete addition the solution was stirred at -78°C for 1 h. Next a solution of 1,2-epoxyoctane (3.1 mL, 30 mmol, 1 equiv) in dry HMPA (7 mL, 40 mmol, 2 equiv) was added and the reaction mixture was allowed to warm to rt. After being stirred at rt overnight, the reaction mixture was poured into water (100 mL) and extracted with ether. The combined organic layers were washed with brine, dried over MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give the alcohol as a pale yellow oil.

To a 100 mL RBF equipped with magnetic stir bar under Ar\((g)\) was added alcohol (1.9 g, 9.8 mmol, 1 equiv), DCM (65 mL), imidazole (1.0 g, 14.7 mmol, 1.5 equiv) and DMAP (180 mg, 1.47 mmol, 0.15 equiv). The solution was cooled to 0°C (ice/H\(_2\)O bath) then vinyldimethylchlorosilane (1.6 mL, 11.8 mmol, 1.2 equiv) was added dropwise via syringe. The resulting white suspension stirred at rt overnight. The reaction was quenched with sat. NH\(_4\)Cl\((aq)\) (50 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 50 mL) then the combined organic layers were dried over MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 15 cm; eluted with 1% ether/hexanes) gave alkyne 240 as a clear oil (1.78 g, 66%).

\[ \text{R}_f (5\% \text{ ether/hexanes}) = 0.59 \]

\[^1\text{H NMR} \text{ (400 MHz, CDCl}_3\text{)} \delta = 6.15 \text{ (dd, 1H, } J = 20.4, 14.8 \text{ Hz)}, 5.99 \text{ (dd, 1H, } J = 15.2, 4.0 \text{ Hz)}, 5.76 \text{ (dd, 1H, } J = 20.0, 4.0 \text{ Hz)}, 3.72-3.69 \text{ (m, 1H)}, 2.23 \text{ (d ABq, 2H, } J_{\text{AB}} = 16.4 \text{ Hz, } J_{\text{AX}} = \]


6.0 Hz, $J_{BX} = 6.0$ Hz), 1.60-1.53 (m, 1H), 1.45-1.15 (m, 10H), 0.88 (t, 3H, $J = 6.7$ Hz), 0.71-0.65 (m, 1H), 0.64-0.58 (m, 1H), 0.19 (s, 6H)

$^1$H NMR (100 MHz, CDCl$_3$) $\delta =$ 138.2, 133.1, 84.9, 73.0, 72.1, 36.9, 32.0, 29.5, 28.1, 25.6, 22.8, 14.3, 8.0, -0.2, -1.2

FT-IR (NaCl, thin film) $\nu =$ 2957, 2931, 2858, 1466, 1252, 1097, 1060 cm$^{-1}$

Anal. calcd for C$_{17}$H$_{30}$OSi: C 73.31, H 10.86; found: C 73.39, H 10.57.
Diene 241

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (7.2 mg, 0.019 mmol, 0.10 equiv) and alkyne 240 (53.7 mg, 0.19 mmol, 1 equiv) in toluene (0.8 mL) were combined and stirred at 70°C for 1 h. The residue was purified via column chromatography (silica gel 1.5 x 6 cm; gradient elution with hexanes-3% ether/hexanes) to give 241 as a clear oil (39.7 mg, 74%).

R_f (hexanes) = 0.69

^1H NMR (300 MHz, CDCl_3) δ = 5.63 (d, 1H, J = 3.0 Hz), 5.03 (d, 1H, J = 2.7 Hz), 4.92 (d, 1H, J = 9.6 Hz), 4.11-4.00 (m, 1H), 2.67 (dd, 1H, J = 14.7, 1.8 Hz), 2.24 (ddd, 1H, J = 14.7, 9.0, 1.5 Hz), 1.59-1.28 (m, 8H), 0.90-0.86 (m, 6H), 0.79-0.73 (m, 2H), 0.41-0.36 (m, 2H), 0.22 (s, 3H), 0.18 (s, 3H)

^13C NMR (75 MHz, CDCl_3) δ = 151.4, 138.7, 128.3, 119.4, 73.9, 38.2, 37.4, 32.1, 29.5, 25.9, 22.9, 14.3, 10.5, 7.6, 7.5, 0.1, -0.6

FT-IR (NaCl, thin film) ν = 3002, 2957, 2929, 2857, 1250, 1046 cm^{-1}

Anal. calcd for C_{17}H_{30}OSi: C 73.31, H 10.86; found C 73.53, H 10.66.
Silicon-Tethered Alkyne 242

A solution of 4-pentyn-2-ol (0.94 mL, 10 mmol, 1 equiv), (E)-1-iodooct-1-ene\textsuperscript{214} (2.9 g, 12 mmol, 1.2 equiv), CuI (190 mg, 1.0 mmol, 0.10 equiv), PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (351 mg, 0.5 mmol, 0.05 equiv), Et\textsubscript{3}N (20 mL) and THF (20 mL) was degassed by freeze-pump-thaw (3 times) and refluxed under Ar\textsubscript{(g)} for 1 h. The reaction mixture was quenched with sat. NH\textsubscript{4}Cl\textsubscript{(aq)} (35 mL) and extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine, dried over MgSO\textsubscript{4}, filtered and concentrated \textit{in vacuo}. The residue was purified by flash chromatography on silica gel (4.5 x 15 cm; gradient elution with 10%-25% EtOAc/hexanes) to give the alcohol (1.21 g, 62\%) as an orange oil. To a 100 mL RBF equipped with a magnetic stir bar under Ar\textsubscript{(g)} was added the alcohol (1.09 g, 5.6 mmol, 1 equiv), DCM (37 mL), imidazole (763 mg, 11.2 mmol, 2 equiv) and DMAP (137 mg, 1.12 mmol, 0.2 equiv). The yellow solution was cooled to 0°C (ice/H\textsubscript{2}O bath) then vinyldimethylchlorosilane (0.93 mL, 6.7 mmol, 1.2 equiv) was added via syringe. The resulting yellow suspension stirred at rt overnight. The reaction was quenched with sat. NH\textsubscript{4}Cl\textsubscript{(aq)} (30 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 15 mL) then the combined organic layers were dried over MgSO\textsubscript{4}, filtered and concentrated \textit{in vacuo} to give an orange oil. Purification by column chromatography (silica gel 2.5 x 12 cm; eluted with 1% ether/hexanes) gave alkyne 242 as a yellow oil (750 mg, 48\%).

\textbf{R}_f\ (5\% \text{ether/hexanes}) = 0.52

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \textsuperscript{δ} = 6.16 (dd, 1H, \textit{J} = 20.0, 14.8 Hz), 6.09-5.99 (m, 2H), 5.79 (dd, 1H, \textit{J} = 20.0, 4.0 Hz), 5.44 (doublet of quintets, 1H, \textit{J} = 15.6, 2.0 Hz), 3.97-3.93 (m, 1H), 2.41 (d
ABq, 2H, $J_{AB} = 16.8$ Hz, $J_{AX} = 6.0$ Hz, $J_{BX} = 6.0$ Hz), 2.07 (q, 2H, $J = 7.6$ Hz), 1.40-1.23 (m, 11H), 0.88 (t, 3H, $J = 6.4$ Hz), 0.20 (s, 6H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 144.0, 138.0, 133.3, 109.9, 85.8, 81.0, 68.1, 33.2, 31.9, 30.4, 29.0, 28.97, 23.5, 22.8, 14.3, -1.4

FT-IR (NaCl, thin film) ν = 3019, 2960, 2929, 1457, 1252, 1128, 1097 cm$^{-1}$

Anal. calcd for C$_{17}$H$_{30}$OSi: C 73.31, H 10.86; found: C 73.51, H 11.11.
Diene 243

Following the general procedure as described for compound 132, Cp*Ru(COD)Cl (8.5 mg, 0.023 mmol, 0.15 equiv) and alkyne 242 (41.8 mg, 0.15 mmol, 1 equiv) in toluene (0.6 mL) were combined and stirred at 70°C for 16 h. The residue was purified via column chromatography (silica gel 2.5 x 5.5 cm; gradient elution with 2%-3% ether/hexanes) to give 243 as a yellow oil (25.5 mg, 61%).

\[ R_f (5\% \text{ ether/hexanes}) = 0.41 \]

\(^1\text{H NMR}\) (400 MHz, CDCl\textsubscript{3}) \(\delta = 6.27-6.12 \text{ (m, 2H)}, 5.81-5.73 \text{ (m, 2H)}, 5.13 \text{ (d, 1H, } J = 2.7 \text{ Hz)}, 4.11-4.03 \text{ (m, 1H)}, 2.68 \text{ (dd, 1H, } J = 14.8, 1.9 \text{ Hz)}, 2.19 \text{ (dd, 1H, } J = 14.6, 9.6 \text{ Hz)}, 2.12 \text{ (q, 2H, } J = 7.2 \text{ Hz)}, 1.43-1.24 \text{ (m, 10H)}, 0.89 \text{ (t, 4H, } J = 6.4 \text{ Hz)}, 0.25 \text{ (s, 3H)}, 0.19 \text{ (s, 3H)}

\(^{13}\text{C NMR}\) (100 MHz, CDCl\textsubscript{3}) \(\delta = 151.2, 139.3, 136.0, 126.2, 123.4, 120.5, 70.0, 39.2, 33.4, 32.0, 29.7, 29.2, 24.5, 22.8, 14.3, 0.1, -0.6\)

\textbf{FT-IR} (NaCl, thin film) \(\nu = 2928, 976 \text{ cm}^{-1}\)

\textbf{Anal.} calcd for C\textsubscript{17}H\textsubscript{30}OSi: C 73.31, H 10.86; found: C 73.31, H 10.88.
To a 100 mL RBF equipped with a magnetic stir bar under Ar\((g)\) was added 5-phenylpent-4-yn-2-ol\(^{212}\) (801 mg, 5 mmol, 1 equiv) and THF (20 mL). The solution was cooled to 0°C (ice/H\(_2\)O bath) and sodium hydride (220 mg, 5.5 mmol, 1.1 equiv) was added in one portion. After stirring at 0°C for 15 min, allyl bromide (0.47 mL, 5.5 mmol, 1.1 equiv) was added dropwise. The pale brown suspension stirred at rt for 2 h then was quenched with sat. NH\(_4\)Cl\((aq)\) (20 mL). The aqueous layer was extracted with ether (3 x 50 mL) then the combined organics were dried over MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give an orange oil. Purification via column chromatography (silica 2.5 x 14 cm; gradient elution with 2%-4% ether/hexanes) gave alkyne \textbf{244} as a clear oil (300 mg, 30%).

\(R_f\) (5% ether/hexanes) = 0.34

\textbf{\(^1H\ NMR\) (400 MHz, CDCl\(_3\))} \(\delta = 7.43\text{-}7.40\) (m, 2H), 7.30\text{-}7.27 (m, 3H), 6.00\text{-}5.90 (m, 1H), 5.32 (dq, 1H, \(J = 17.6, 1.6\) Hz), 5.19 (dq, 1H, \(J = 10.4, 1.2\) Hz), 4.08 (dt, 2H, \(J = 5.6, 1.6\) Hz), 3.76\text{-}3.69 (m, 1H), 2.72 (dd, 1H, \(J = 16.4, 4.8\) Hz), 2.52 (dd, 1H, \(J = 16.8, 7.2\) Hz), 1.34 (d, 3H, \(J = 6.0\) Hz)

\textbf{\(^{13}C\ NMR\) (100 MHz, CDCl\(_3\))} \(\delta = 135.3, 131.7, 128.4, 127.9, 124.0, 117.0, 87.1, 82.3, 73.9, 70.0, 27.2, 20.0\)

\textbf{FT-IR} (NaCl, thin film) \(\nu = 2976, 2930, 1599, 1491, 1128\) cm\(^{-1}\)

\textbf{Anal.} calcd for C\(_{14}\)H\(_{16}\)O: C 83.96, H 8.05; found: C 83.95, H 7.93.
Following the general procedure as described for compound 132, Cp*Ru(COD)C; (10.3 mg, 0.027 mmol, 0.10 equiv) and alkyne 244 (53.5 mg, 0.27 mmol, 1 equiv) in toluene (1.1 mL) were combined and stirred at 70°C for 2.5 h. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; 3% ether/hexanes) to give 245 as a clear oil (32.6 mg, 61%).

_**Diene 245**_

\[
\text{Rf (5% ether/hexanes) = 0.20}
\]

_**H NMR** (300 MHz, CDCl₃) \( \delta = 7.39-7.23 \) (m, 5H), \( 6.71 \) (d, 1H, \( J = 2.6 \) Hz), \( 5.22 \) (d, 1H, \( J = 2.7 \) Hz), \( 4.86 \) (s, 1H), \( 4.38 \) (d, 1H, \( J = 12.7 \) Hz), \( 4.19 \) (dt, 1H, \( J = 12.6, 1.7 \) Hz) 3.59-3.50 (m, 1H), \( 2.86 \) (dd, 1H, \( J = 14.5, 2.5 \) Hz), \( 2.32-2.22 \) (m, 1H), \( 1.24 \) (d, 3H, \( J = 6.3 \) Hz)

_**C NMR** (75 MHz, CDCl₃) \( \delta = 145.4, 137.4, 137.2, 129.5, 128.4, 127.0, 124.7, 109.5, 73.2, 72.2, 38.0, 21.9

_**FT-IR** (NaCl, thin film) \( \nu = 2973, 2931, 1271, 1493, 1450, 1386, 1127 \) cm\(^{-1}\)

_**Anal.** calcd for C\(_{14}\)H\(_{16}\)O: C 83.96, H 8.05; found: C 84.15, H 8.48.
Diels-Alder Adduct 256

To a 15 mL glass tube equipped with a magnetic stir bar was added diene 227 (56.4 mg, 0.19 mmol, 1 equiv), N-methylmaleimide (22 mg, 0.20 mmol, 1.05 equiv) and toluene (0.4 mL). The vessel was sealed with a teflon screw cap and the clear solution stirred at rt for 24 h. TLC analysis indicated complete consumption of the starting material. The reaction mixture was placed directly on silica gel for purification (silica gel 2.5 x 12 cm; gradient elution with 25%-60% EtOAc/hexanes) to give 256 as a white solid (73.1 mg, 94%).

\[ R_f (20\% \text{ EtOAc/hexanes}) = 0.08 \]

M.P.: 160-161°C

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\)) \(\delta = 7.23-7.16\) (m, 3H), 7.03-7.00 (m, 2H), 3.60 (d, 1H, \(J = 7.2\) Hz), 3.28 (dd, 1H, \(J = 9.0, 7.5\) Hz), 3.05 (m, 1H), 2.79 (app dd, 1H, \(J = 18.3, 4.2\) Hz), 2.63 (dd, 1H, \(J = 18.3, 10.8\) Hz), 2.36 (s, 3H), 2.22 (app d, 1H, \(J = 16.8\) Hz), 1.98 (dd, 1H, \(J = 16.8, 1.8\) Hz), 1.61-1.49 (m, 3H), 1.41-1.26 (m, 4H), 1.13-1.00 (m, 3H), 0.23 (s, 3H), 0.20 (s, 3H)

\(^13\text{C NMR}\) (75 MHz, CDCl\(_3\)) \(\delta = 180.2, 178.3, 145.6, 136.8, 129.3, 128.5, 128.3, 127.7, 73.8, 47.4, 45.0, 39.5, 37.0, 36.7, 26.0, 24.0, 22.3, 22.2, 22.1, 0.2, -0.6

FT-IR (NaCl, thin film) \(\nu = 2934, 1706, 1434, 1382, 1251, 1023\) cm\(^{-1}\)

Anal. calcd for C\(_{24}\)H\(_{31}\)NO\(_3\)Si: C 70.38, H 7.63, N 3.42; found: C 70.23, H 7.29, N 3.81.
Alcohol 257

To a 25 mL RBF equipped with a magnetic stir bar under Ar(g) was added diene 132 (60.8 mg, 0.25 mmol, 1 equiv) and THF (5 mL). To the clear solution was added TBAF∙3H₂O (158 mg, 0.50 mmol, 2 equiv) in one portion. The pale yellow solution stirred at rt for 1 h. TLC analysis indicated complete consumption of the starting material. The reaction mixture was concentrated in vacuo to give a yellow oil. Purification by column chromatography (silica gel 1.5 x 10 cm; gradient elution with 11%-14% ether/hexanes) gave 257 as a white oil (42.4 mg, 90%).

Rᵣ (10% ether/hexanes) = 0.10

¹H NMR (300 MHz, CDCl₃) δ = 7.45-7.23 (m, 5H), 6.70 (s, 1H), 6.50 (dd, 1H, J = 17.7, 11.1 Hz), 5.36 (d, 1H, J = 17.7 Hz), 5.18 (d, 1H, J = 10.8 Hz), 4.15-4.06 (m, 1H), 2.78 (dd, 1H, J = 13.5, 8.7 Hz), 2.60 (dd, 1H, J = 13.8, 4.8 Hz), 1.73 (br s, 1H), 1.23 (d, 3H, J = 6.3 Hz)

¹³C NMR (75 MHz, CDCl₃) δ = 140.8, 137.1, 136.8, 134.3, 129.0, 128.3, 127.1, 113.7, 67.0, 36.1, 23.2

FT-IR (NaCl, thin film) ν = 3356, 2969, 1606, 1492 cm⁻¹

Anal. calcd for C₁₃H₁₆O: C 82.94, H 8.57; found: C 82.63, H 8.28.
Hydroxy Silane 258

To a 25 mL Schlenk tube equipped with a magnetic stir bar under Ar (g) was added diene 132 (58.1 mg, 0.24 mmol, 1 equiv) and ether (1 mL). The clear solution was cooled to 0°C (ice/water bath) and MeLi (0.34 mL, 0.58 mmol, 2.2 equiv) was added dropwise via syringe. The pale yellow solution stirred at 0°C for 10 min then at rt for 1 h. TLC analysis indicated complete consumption of the starting material. The reaction mixture was quenched with sat. NH₄Cl (aq) (2 mL). The aqueous layer was extracted with ether (2 x 3 mL) and the combined organics were dried over MgSO₄, filtered, and concentrated in vacuo to give 258 as a clear oil (54.3 mg, 87%).

Rf (10% EtOAc/hexanes) = 0.24

¹H NMR (300 MHz, CDCl₃): δ = 7.39-7.31 (m, 4H), 7.28-7.21 (m, 1H), 6.50 (s, 1H), 5.84 (d, 1H, J = 3.0 Hz), 5.52 (d, 1H, J = 2.7 Hz), 4.00-3.89 (m, 1H), 2.72 (dd, 1H, J = 13.8, 8.7 Hz), 2.47 (ddd, 1H, J = 14.1, 4.8, 0.9 Hz), 1.73 (br s, 1H), 1.18 (d, 3H, J = 6.3 Hz), 0.22 (s, 3H)

¹³C NMR (75 MHz, CDCl₃) δ = 155.5, 143.7, 137.9, 129.2, 128.4, 126.7, 126.2, 66.7, 39.7, 23.0, -0.3

FT-IR (NaCl, thin film) ν = 3368, 2964, 1493, 1249, 1120, 1075 cm⁻¹

Anal. calcd for C_{16}H_{24}OSi: C 73.79, H 9.29; found C 73.39, H 9.09.
**Keto Ester 262**

*With Acetic Anhydride:* To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar was added a solution of diene 132 (63 mg, 0.26 mmol, 1 equiv) in DMF (13 mL), potassium hydrogen fluoride (61 mg, 0.78 mmol, 3 equiv), acetic anhydride (0.61 mL, 6.5 mmol, 25 equiv) and 30% hydrogen peroxide (0.7 mL, 6.5 mmol, 25 equiv). The clear solution stirred at rt for 5 h. TLC analysis indicated consumption of the starting material. The reaction mixture was poured into H$_2$O (20 mL) then extracted with ether (3 x 20 mL). The combined organics were washed with H$_2$O and brine (20 mL each), dried over MgSO$_4$, filtered, and concentrated in vacuo to give a clear oil. Purification by column chromatography (silica gel 1.5 x 13 cm; 10% EtOAc/hexanes) gave 262 as a clear oil (23.1 mg, 40%).

\[ \text{R}_f (20\% \text{ EtOAc/hexanes}) = 0.52 \]

$^1$H NMR (300 MHz, CDCl$_3$) \( \delta = 7.36-7.24 \) (m, 3H), 7.21-7.17 (m, 2H), 5.32-5.22 (m, 1H), 3.69 (s, 2H), 2.80 (dd, 1H, \( J = 16.5, 7.2 \) Hz), 2.56 (dd, 1H, \( J = 16.5, 5.7 \) Hz), 1.97 (s, 3H), 1.21 (d, 3H, \( J = 6.3 \) Hz)

$^{13}$C NMR (151 MHz, CDCl$_3$) \( \delta = 205.2, 170.4, 133.8, 129.6, 129.0, 127.4, 67.2, 50.7, 47.8, 21.4, 20.1 \)

FT-IR (NaCl, thin film) \( \nu = 3031, 2983, 2935, 1737, 1498, 1374, 1246, 1135, 1043 \) cm$^{-1}$

Anal. calcd for C$_{13}$H$_{16}$O$_3$: C 70.89, H 7.32; found: C 70.56, H 7.07.

*With Propionic Anhydride:* To an oven-dried 50 mL RBF equipped with a magnetic stir bar was added diene 132 (62.8 mg, 0.26 mmol, 1 equiv), DMF (10 mL), potassium hydrogen fluoride (61
mg, 0.78 mmol, 3 equiv), propionic anhydride (0.83 mL, 6.5 mmol, 25 equiv) and 30% hydrogen peroxide (0.7 mL, 6.5 mmol, 25 equiv). The clear solution stirred at rt for 3.5 h. TLC analysis indicated consumption of the starting material. The reaction mixture was poured into H₂O (20 mL) then extracted with ether (3 x 20 mL). The combined organics were washed with H₂O and brine (20 mL each), dried over MgSO₄, filtered, and concentrated in vacuo to give a clear oil. Purification by column chromatography (silica gel 1.5 x 13 cm; gradient elution with 10%-20% ether/hexanes) gave 262 as a clear oil (32.2 mg, 56%).

Rᶠ (20% EtOAc/hexanes) = 0.50

¹H NMR (400 MHz, CDCl₃) δ = 7.36-7.19 (m, 5H), 5.31-5.23 (m, 1H), 3.70 (s, 2H), 2.80 (dd, 1H, J = 16.4, 7.2 Hz), 2.57 (dd, 1H, J = 16.8, 6.0 Hz), 1.97 (s, 3H), 1.22 (d, 3H, J = 6.4 Hz)
**RuHCl(CO)(PCy₃)₂**

To a flame-dried 3-neck 250 mL RBF equipped with a reflux condenser and magnetic stir bar under Ar (g) was added RuCl₃·3H₂O (2.62 g, 10 mmol, 1 equiv) and 2-methoxyethanol (50 mL, degassed for 30 min). After stirring at rt for 10 min, PCy₃ (8.24 g, 29.4 mmol, 2.94 equiv) was quickly added in 2 equal portions. The reaction vessel was subjected to 2 cycles of vacuum/Ar (g) then was placed under Ar (g). The brown reaction mixture was heated to reflux for 20 min then NEt₃ (6 mL, 43 mmol, 4.3 equiv) was added. The dark brown reaction mixture continued to stir at reflux for 6 h. (Note: Over time, the reaction became an orange suspension.) After 6 h the reaction was cooled to rt and needle-filtered. The resulting orange powder was washed with toluene (2 x 15 mL, degassed 30 min) and ether (15 mL, degassed 30 min), needle-filtered after each wash then dried *in vacuo* to give RuHCl(CO)(PCy₃)₂ (6.9 g, 95%). Spectroscopic data corresponded to what was reported in the literature.²¹⁵

**¹H NMR** (400 MHz, C₆D₆) δ = -24.2 (t, 1H, Jₚ₋H = 17.7 Hz)

**³¹P NMR** (162 MHz, C₆D₆) δ = 46.4
RuHCl(CO)(PrBu₂Me)$_2$

To an oven-dried 3-neck 50 mL RBF equipped with a reflux condenser and magnetic stir bar under Ar$_{(g)}$ was added RuCl$_3$·3H$_2$O (1 g, 3.8 mmol, 1 equiv). The vessel was subjected to 2 cycles of vacuum/Ar$_{(g)}$, placed under Ar$_{(g)}$, then 2-methoxyethanol (25 mL, degassed 30 min) and PrBu$_2$Me (3.7 mL, 19.1 mmol, 5 equiv) were added. The resulting dark brown reaction mixture stirred at reflux for 72 h then was cooled to rt. (Note: Upon cooling, orange crystals began to form.) Once cooled to rt, the suspension was further cooled to -10°C (salt/ice/H$_2$O bath) to further induce precipitation. After 2 h, the suspension was needle-filtered and the resulting orange crystalline powder was washed with ether (5 mL, degassed 30 min), needle-filtered and dried in vacuo to give RuHCl(CO)(PrBu$_2$Me)$_2$ (1.29 g, 70%). Spectroscopic data corresponded to what was reported in the literature.$^{52}$

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ = -24.9 (t, 1H, $J_{P-H}$ = 15.7 Hz)

$^{31}$P NMR (162 MHz, C$_6$D$_6$) $\delta$ = 49.3
**RuHCl(CO)(PrBu₂Cy)₂**

To an oven-dried 25 mL three-neck round bottom flask equipped with a magnetic stir bar and reflux condenser was added RuCl₃·3H₂O (173 mg, 0.66 mmol, 1 equiv). The system was subjected to three cycles of vacuum/Ar(g) then placed under a positive stream of Ar(g). To the ruthenium was added degassed 2-methoxyethanol (10 mL) then PrBu₂Cy (0.85 mL, 3.3 mmol, 5 equiv). The dark brown solution stirred in the dark at 125°C for 72 h. At this time, the orange/brown suspension was cooled to rt then further cooled to -15°C (salt/ice/H₂O bath). After 30 min the suspension was needle-filtered and the resulting crystals were washed with degassed ether (2 x 3 mL) and dried *in vacuo* to give RuHCl(CO)(PrBu₂Cy)₂ as orange crystals (280 mg, 68%).

**¹H NMR** (400 MHz, C₆D₆) δ = 2.46 (d, 2H, J = 10.4 Hz), 2.29-2.26 (m, 2H), 1.69-1.37 (m, 54H), -24.48 (t, 1H, Jₚ-H = 17.4 Hz)

**³¹P NMR** (162 MHz, C₆D₆) δ = 73.1

**FT-IR** (KBr pellet) ν = 2915, 2144 (Ru-H), 1897 (CO) cm⁻¹

**Anal.** calcd for C₂₉H₅₉ClOP₂Ru: C 55.98, H 9.56; found C 56.07, H 9.66.
**RuHCl(CO)(PCy2tBu)₂**

To an oven-dried 25 mL three-neck round bottom flask equipped with a magnetic stir bar and reflux condenser was added RuCl₃·3H₂O (200 mg, 0.76 mmol, 1 equiv). The system was subjected to three cycles of vacuum/Arₕ then placed under a positive stream of Arₕ. To the ruthenium was added degassed 2-methoxyethanol (10 mL) then PCy₂tBu (1.0 mL, 3.8 mmol, 5 equiv). The dark brown solution stirred in the dark at 125°C for 72 h. At this time, the reaction mixture was cooled to rt then further cooled to -15°C (salt/ice/H₂O bath) to induce precipitation. After 1 h, the resulting suspension was needle-filtered and the resulting powder was washed with degassed ether (2 x 3 mL) and dried *in vacuo* to give RuHCl(CO)(PCy₂tBu)₂ as a dark orange powder (320 mg, 63%).

**¹H NMR** (400 MHz, C₆D₆) δ = 2.72-2.58 (m, 4H), 2.24-2.06 (m, 8H), 1.84-1.14 (m, 50H), -22.0 (t, 1H, J_P-H = 17.6 Hz)

**³¹P NMR** (162 MHz, C₆D₆) δ = 58.9

**FT-IR** (KBr pellet) ν = 2849, 2083 (Ru-H), 1900 (CO) cm⁻¹

7.0 SPECTRA
LAK-S-225
yellow oil
LAK-1-132
Crop A

\[
\text{O} \quad \text{O} \\
\text{NH} \\
70 \quad \text{Bn}
\]

\[
\begin{align*}
7.34 & \quad 2.88 \\
7.32 & \quad 2.66 \\
7.27 & \quad 2.73 \\
7.26 & \quad 2.73 \\
7.18 & \quad 2.15 \\
7.16 & \quad 2.15 \\
5.62 & \\
4.51 & \\
4.15 & \\
4.13 & \\
2.85 & \\
3.99 & \\
0.03 & \\
1.00 & \\
2.01 & \\
2.00 & 
\end{align*}
\]
LAK-1-152 crop A
(hashes labeled on the structure refer to the protons at that location)
(#s labeled on the structure refer to the protons at that location)
LAK-1-252
chrome

TBSO

Me

81

ppm
LAK-2-166
LAK-2-07 (2)

![Chemical Structure Image]

![NMR Spectrum Image]
LAK-3-157 carbon
LAK-3-145 proton
LAK-3-145 carbon

![Chemical Structure]
LAK-3-146 proton
LAK-3-146 carbon
LAK-3-148 proton
LAX-3-148 carbon

104

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
LAK-3-165 carbon
LAK-3-151 carbon
LAK-3-154 carbon
carbon

LAK-6-49

126

[Chemical structure image]
134
(from MVK)
LAK-2-97

134
(from MVK)
LAK-2-199

134
(from ethylene)
LK-2-199

(it's labeled on the structure refer to the protons at that location)
LAK-2-232
carbon

![Carbon spectrum](image_url)

135
LAK-2-235

carbon
(It's labeled on the structure refer to the protons at that location.)
LAK-2-157 NOESY

(#'s labeled on the structure refer to the protons at that location)
#5 labeled on the structure. Refer to the protons at that location.
LAK-4-119

carbon

Me₃Si

\[\text{Ph} \]

\[\text{215} \]

\[\text{O} \]

\[\text{Si} \]

\[\text{Ph} \]

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
LAK-3-283

carbon
LAK-5-200
carbon
LAK-5-210
carbon
LAK-5-209-2
carbon
LAK-3-285

carbon
LAK-4-156

carbon
LAK-4-202

carbon

C₆H₁₃

241
LAK-4-89

[Chemical structure image]

244
LAK-4-119

carbon
LAX-5-048
crude, carbon
LAK-6-251-2

(obtained using propionic anhydride)
RuHCl(CO)(PCy₃)₂

¹H NMR
RuHCl\((CO)\)(PCy_3)_2

$^{31}\text{P NMR}$
RuHCl(CO)(PrBu₂Me)₂

¹H NMR
RuHCl(CO)(PrBu$_2$Me)$_2$
$^{31}$P NMR
RuHCl(CO)(PrBu₂Cy)₂

¹H NMR
RuHCl(CO)(PrBu2Cy)2

**1H NMR**

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**Data:****

- **NAME**: LAX-3-73
- **EXPN0**: 1
- **PROCNO**: 1
- **Date**: 20141827
- **Time**: 9:13
- **INSTRUM**: spect
- **PROBHD**: 5 mm C500EO BB
- **POLNOC**: zz30
- **TD**: 65536
- **SOLVENT**: C606
- **NS**: 128
- **DS**: 2
- **SW**: 39682.539 Hz
- **FIDRES**: 0.605587 Hz
- **AQ**: 0.8258836 sec
- **RG**: 134.49
- **DW**: 12.600 usec
- **DE**: 18.00 usec
- **TE**: 298.0 K
- **DL**: 1.00000000 sec
- **TDS**: 1

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**Channel 1:**

- **SFQ1**: 400.130000 MHz
- **NUT1**: 1M
- **1**: 12.00 usec
- **S1**: 62536
- **SF**: 400.1299966 MHz
- **NSW**: 5M
- **SBB**: 0
- **LB**: 0.30 Hz
- **GB**: 0
- **PC**: 1.00

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**Graph:**

The graph shows a spectral peak at approximately -24.5 ppm with a peak width at half maximum (pwhm) of 0.10 Hz.
RuCl(CO)(PrBu₂Cy)₂

³¹P NMR

73.078 ppm
RuHCl(CO)(PCy₂tBu)₂

$^1$H NMR
RuHCl(CO)(PCy₃Bu)₂

¹H NMR
RuHCl(CO)(PCy_{2}Bu)_{2}

^{31}P NMR
8.0 VITAE
Lauren Kaminsky

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Education

Syracuse University, Syracuse, NY
*Thesis*: Ruthenium-Catalyzed Transformations for the Synthesis of Conjugated Dienes
*Advisor*: Dr. Daniel A. Clark

**B.S. in Chemistry, cum laude, June 2010**
**Minor in Mathematics**
York College of Pennsylvania, York, PA
*Advisor*: Dr. Kathleen Halligan

Research Experience

**Research Assistant**, Department of Chemistry
Syracuse University, August 2010 – May 2015
*Advisor*: Dr. Daniel A. Clark

*Research Focus:*
- Scalable, multi-step syntheses for various chiral and non-chiral silicon-tethered enyne substrates
- Development of a ruthenium-hydride catalyzed intermolecular coupling of silicon-tethered alkynes with vinyl boronates to give highly stereo- and regioselective tetrasubstituted 1,3-dienes
- Development of a ruthenium-catalyzed cycloisomerization of silicon-tethered 1,7-enynes to selectively give exocyclic 1,3-dienes
- Synthesis of novel ruthenium and osmium hydrides for the use in organocatalytic methodology development

**Independent Study Research**, Department of Chemistry
York College of Pennsylvania, 2008 – 2010
*Advisor*: Dr. Kathleen Halligan

*Research Focus:*
• Worked in collaboration with the USDA-ARS Plant Mycotoxin Research group in California towards the synthesis of a tricyclic natural product as a means to combat the navel orangeworm

Skills and Techniques

• Multi-step syntheses of organic compounds
  ➢ Experience in small and large scale synthesis
• Handling of a large variety of air-sensitive organic and inorganic reagents
• Schlenk-line techniques
• Preparation of organometallic compounds
• Glovebox use for reagent storage, reagent handling and reactions
• Chromatography
  ➢ Flash column, Thin Layer, Preparative Thin Layer Spectroscopy
• 1D and 2D NMR (Proton, Carbon, Boron, Phosphorus), IR
• Excellent record-keeping with laboratory notebooks and chemical inventory
• Detail-oriented
  ➢ Wrote standard operating procedures for new instruments
• Knowledge of chemistry software programs
  ➢ ChemDraw, Bruker Topspin

Teaching Experience

Teaching Assistant, Syracuse University, 2011 – 2013
• Laboratory and recitation instructor for undergraduate organic chemistry courses (classes of 20-30 students)

Student Tutor, York College of Pennsylvania, 2008 – 2010

Student Laboratory Assistant, York College of Pennsylvania, 2007 – 2010

Awards

Graduate Assistance in Areas of National Need Fellowship, 2010 – 2012

Departmental Recognition, Department of Physical Sciences, York College of Pennsylvania, 2010

Outstanding College Chemistry Major, Southeastern Pennsylvania Section of the American Chemical Society, 2010
Publications


Presentations

32\(^{\text{nd}}\) Annual Graduate Student Symposium, The State University of New York, Buffalo, NY, May 2014

38\(^{\text{th}}\) Northeast Regional Meeting of the American Chemical Society, Rochester, NY, October 2012

239\(^{\text{th}}\) American Chemical Society National Meeting, Chemical Education Division, San Francisco, CA, March 2010 (Poster Presentation)
References

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Kathleen M. Halligan
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