The Rh(I)-Catalyzed Cyclocarbonylation of Allenol Esters to Prepare α-Acetoxy 4-Alkylidene Cyclopent-3-en-2-ones

by

Matthew Michael Davis

B.S., Chemistry, Hope College, 2004

Submitted to the Graduate Faculty of Arts and Sciences in partial fulfillment of the requirements for the degree of

Master of Science

University of Pittsburgh

2009
This thesis was presented

by

Matthew Michael Davis

It was defended on

July 15th, 2009

and approved by

Professor Dennis P. Curran, Department of Chemistry

Professor Tara Y. Meyer, Department of Chemistry

Thesis Advisor: Professor Kay M. Brummond, Department of Chemistry
The Rh(I)-Catalyzed Cyclocarbonylation of Allenol Esters to Prepare α-Acetoxy 4-Alkylidene Cyclopent-3-en-2-ones

Matthew Michael Davis, M.S.
University of Pittsburgh, 2009

The Rh(I)-catalyzed allenic cyclocarbonylation reaction is an effective method for forming 4-alkylidene cyclopentenones. The scope of this methodology was expanded to include the cyclocarbonylation of allenol acetates to provide α-acetoxy-4-alkylidene cyclopentenones. The diastereoselectivity of the [3,3]-sigmatropic rearrangement to form the allenol acetates and cyclocarbonylation reaction were examined. During the course of the Rh(I)-catalyzed cyclocarbonylation reaction two rhodium metallocycle intermediates were observed and structures are postulated based upon \(^1\text{H}\) and \(^{13}\text{C}\) NMR data. Liberation of the acetate to the free alcohol was also accomplished yielding α-hydroxy-4-alkylidene cyclopentenones.
# TABLE OF CONTENTS

LIST OF TABLES ........................................................................................................................................ VII

LIST OF FIGURES ........................................................................................................................................ VIII

LIST OF SCHEMES ....................................................................................................................................... IX

ACKNOWLEDGEMENTS ................................................................................................................................. X

ABBREVIATIONS .......................................................................................................................................... XI

1.0 INTRODUCTION ....................................................................................................................................... 1

1.1 ALPHA-HYDROXY CARBONYLS .................................................................................................................. 1

1.2 CYCLOCARBONYLATION REACTIONS OF ENOL ETHERS AND ENOL ESTERS .................................................. 3

1.3 SYNTHETIC AVAILABILITY OF ALLENOL ACETATES .............................................................................. 5

1.4 SUBSTRATE DESIGN ................................................................................................................................... 7

2.0 RESULTS AND DISCUSSION ..................................................................................................................... 8

2.1 PREPARATION OF PROPARGYL ACETATES ............................................................................................ 8

2.2 FORMATION OF ALLENOL ACETATES FROM PROPARGYL ACETATES ......................................................... 12

2.3 RHODIUM(I)-CATALYZED CYCLOCARBONYLATION REACTION OF ALLENOL ACETATES TO FORM ALPHA-ACETOXY CYCLOPENTADIENONES.............................................................................................................................. 17
LIST OF TABLES

Table 1. Catalyst Screening for Rearrangement ................................................................. 13

Table 2. Rearrangement of 39c-ax and 39c-eq ..................................................................... 14

Table 3. Preparation of Allenol Acetates\textsuperscript{a} .......................................................... 16

Table 4. [Rh(CO)\textsubscript{2}Cl\textsubscript{2}] Catalyzed Cyclocarbonylation Reactions\textsuperscript{a} ......................................................... 18

Table 5. Isomerization of Allenol Acetate 42c ..................................................................... 21

Table 6. \textsuperscript{13}C Chemical Shifts of 42c, 57, 58, and 48c in d\textsubscript{8}-toluene (\textdelta C, mult, J\textsubscript{Rh-C} in Hz) .......... 24
LIST OF FIGURES

Figure 1. Stereochemical Assignment of the Major Diastereomer of 37a-eq ........................................ 9
Figure 2. Conjugated Dienol Acetate 50 .......................................................... 18
Figure 3. $^{13}$C NMR spectrum (in d$_8$-toluene at 23 °C) (a) 42c, (b) 42c and [Rh(CO)$_2$Cl]$_2$ after 20 h at rt under Ar, proposed as 57, (c) 42c and [Rh(CO)$_2$Cl]$_2$ after stirring an additional 17 h at 90 °C under Ar, proposed as 58, (d) Spectrum of isolated 48c. .......................................................... 23
LIST OF SCHEMES

Scheme 1. Formation of α-Hydroxy Carbonyl Compounds ............................................................... 1
Scheme 2. Synthesis of Thapsigargin and Guanacastepene A .......................................................... 2
Scheme 3. Pauson-Khand Reaction of Chiral Enol Ethers ............................................................... 3
Scheme 4. Pauson-Khand Reaction of Enol Ethers and Enol Esters .............................................. 4
Scheme 5. Formation of Bicyclo[5.3.0]undecadienones .............................................................. 5
Scheme 6. Transition Metal Catalyzed Rearrangement of Propargyl Acetates to Allenol Acetates ................................................................. 6
Scheme 7. Metal-Catalyzed Isomerization of Allenol Acetates ................................................... 6
Scheme 8. Dynamic Kinetic Resolution ...................................................................................... 7
Scheme 9. Substrate Design ................................................................................................. 7
Scheme 10. Preparation of Ketones 37a-c .................................................................................. 8
Scheme 11. Preparation of Propargyl Acetates 39a-f ................................................................. 10
Scheme 12. Preparation of Propargyl Acetates 41a-g ............................................................... 11
Scheme 13. [Rh(OCOCF$_3$)$_2$]$_2$ Catalyzed Rearrangement of 43 ........................................ 14
Scheme 14. The [Rh(CO)$_2$Cl]$_2$ Catalyzed Cyclocarbonylation Reaction of Tetrasubstituted Allenol Esters ......................................................................................... 19
Scheme 15. Preparation and Cyclocarbonylation of Allene-ynes 55a and 55c ......................... 20
Scheme 16. Deprotection of 49c .......................................................................................... 25
ACKNOWLEDGEMENTS

I would like to thank my research advisor Professor Kay M. Brummond for the time and support she has given me throughout my graduate career. I also would like to thank Dr. Curran and Dr. Meyer for serving on my committee for both my comprehensive and masters examinations. Thanks to all Brummond group members past and present for their advice and support. You guys have been great and I really appreciate the good times we’ve had together. I would like to thank my parents for supporting me in whatever I do. Finally I would like to thank my wife Kathy for her near infinite support and patience. Graduate school would have been a much sadder place without you.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac</td>
<td>Acetyl</td>
</tr>
<tr>
<td>AcCl</td>
<td>Acetyl Chloride</td>
</tr>
<tr>
<td>Ac&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Acetic Anhydride</td>
</tr>
<tr>
<td>aq</td>
<td>Aqueous</td>
</tr>
<tr>
<td>atm</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>Bz</td>
<td>Benzoyl</td>
</tr>
<tr>
<td>calcd</td>
<td>Calculated</td>
</tr>
<tr>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Wavenumbers</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical Shift</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-&lt;i&gt;N,N&lt;/i&gt;-Dimethylaminopyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>&lt;i&gt;N,N&lt;/i&gt;-Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>dr</td>
<td>Diastereomeric Ratio</td>
</tr>
<tr>
<td>ee</td>
<td>Enantiomeric Excess</td>
</tr>
<tr>
<td>EI</td>
<td>Electron Impact</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray Ionization</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
</tr>
<tr>
<td>EtOAc</td>
<td>Ethyl Acetate</td>
</tr>
</tbody>
</table>
h  hour(s)
IR  infrared
J  coupling constant (in NMR spectroscopy)
LDA  lithium diisopropylamide
liq  Liquid
Me  Methyl
min  Minutes
n-Bu  Normal Butyl
n-Pr  Normal Propyl
NMO  N-Methylmorpholine-N-Oxide
NMR  Nuclear Magnetic Resonance
nOe  Nuclear Overhauser Effect
Ph  Phenyl
Piv  Pivaloyl
PNB  para-Nitro Benzoyl
ppm  Parts Per Million
rt  Room Temperature
T  Temperature
Tf  Trifluoromethanesulfonyl
THF  Tetrahydrofuran
TLC  Thin Layer Chromatography
TMS  Trimethylsilyl
1.0 INTRODUCTION

1.1 ALPHA-HYDROXY CARBONYLS

α-Hydroxy carbonyls are important building blocks in organic synthesis and are present in a number of biologically active compounds. A variety of methods exist to prepare α-hydroxy carbonyls, and the most commonly used protocol is the oxidation of enolates or silyl enol ethers (Scheme 1). In view of the incompatibilities of some functional groups to these enolization/oxidation conditions and in consideration of redox economy, synthetic alternatives to this late-stage oxidation strategy would be useful.

![Scheme 1. Formation of α-Hydroxy Carbonyl Compounds](image)

Representative examples of biologically active molecules that would benefit from efficient synthetic access to α-hydroxy carbonyls are the thapsigargin guaianolides and the guanacastepene diterpenes. Relevant examples of each family are thapsigargin (3) and guanacastepene A (6) (Scheme 2). Thapsigargin is a potent histamine liberator and has proven useful in the study of Ca$^{2+}$ signaling pathways. Guanacastepene A has shown activity against
drug resistant strains of *Staphylococcus aureus* and *Enterococcus faecalis*. In the synthesis of thapsigargin, installation of the C-2 siloxy group of 2 was accomplished via a Rubottom oxidation of the corresponding silyl enol ether of ketone 1. The high diastereoselectivity of this transformation (dr 95:5) results from the approach of dimethyldioxirane from the less sterically hindered face of the silyl enol ether. For the synthesis of guanacastepene A, conversion of ketone 4 to the α-hydroxy ketone 5 is accomplished in an analogous manner; however, the diastereoselectivity results from equilibration of the α-hydroxy carbonyl carbon C-1. An alternative approach to the stereoselective synthesis of α-hydroxy carbonyls is needed whereby reagent control is used.

Scheme 2. Synthesis of Thapsigargin and Guanacastepene A
1.2 CYCLOCARBONYLATION REACTIONS OF ENOL ETHERS AND ENOL ESTERS

Since its discovery in 1973, the Pauson-Khand cyclocarbonylation reaction has proven to be a powerful method for the formation of functionalized cyclopentenone containing compounds. However, missing from the cyclocarbonylation reaction arsenal is efficient access to an α-hydroxy carbonyl via an enol ether or enol ester precursor. Schore demonstrated that α-alkoxy cyclopentenones could be prepared from enol ether precursors using a Pauson-Khand reaction and subsequently a number of groups have rendered the reaction asymmetric. However, relatively harsh conditions are required for the conversion of an α-alkoxy cyclopentenone to an α-hydroxy cyclopentenone. Thus after serving as a control element in the reaction, the alkoxy group is typically removed reductively (Scheme 3).

Scheme 3. Pauson-Khand Reaction of Chiral Enol Ethers

The Co$_2$(CO)$_8$-mediated Pauson–Khand reaction of vinyl ether 12a gave a 31% yield of α-ethoxy cyclopentenone 13a. Reaction of analogous vinyl ester 12b to form an α-benzyloxy cyclopentenone results in concurrent loss of the ester through a proposed single electron transfer process (Scheme 4).
Scheme 4. Pauson-Khand Reaction of Enol Ethers and Enol Esters

It was hypothesized that a Rh(I)-catalyzed cyclocarbonylation of the related allenol esters to afford $\alpha$-acetoxy cyclopentadienones would be possible due to the mildness of the reaction conditions and the unlikelihood of a rhodium catalyst to undergo a single electron transfer.\(^{14}\) Using conditions developed by Narasaka,\(^{15}\) Brummond and coworkers have demonstrated a selective cyclocarbonylation reaction with the distal double bond of the allene.\(^{16}\) Subsequently, the allenic Rh(I)-catalyzed cyclocarbonylation reaction was demonstrated as an efficient method to synthesize a variety of alkylidene cyclopentenones including bicyclo[5.3.0]undecadienones 16, 18, and 20;\(^{17}\) a long sought after ring system previously inaccessible to cyclocarbonylation methodology (Scheme 5).\(^{18}\) In addition, this methodology was applied to the synthesis of the carbocyclic core of guanacastepene A (22).\(^{19}\) Furthermore, the utility of this methodology was demonstrated by Mukai and coworkers in the total synthesis of (+)-achalensolide (25).\(^{20}\)
1.3 SYNTHETIC AVAILABILITY OF ALLENOL ACETATES

Allenol esters are often prepared from propargyl acetates via a formal [3,3]-sigmatropic rearrangement using a variety of transition metal catalysts, such as Ag,\textsuperscript{21} Rh,\textsuperscript{22} Cu,\textsuperscript{23} Pt,\textsuperscript{24} and Au\textsuperscript{25} (Scheme 6).
Scheme 6. Transition Metal Catalyzed Rearrangement of Propargyl Acetates to Allenol Acetates

This is an atom economical alternative to a more common method of forming allenes via an $S_{N}2'$ reaction of a propargyl ester, which results in loss of the ester.\textsuperscript{26} A potential disadvantage to preparing allenol acetates via transition metal catalysis, is the rapid isomerization of allenol acetates under metal catalysis (Scheme 7).\textsuperscript{27}

We envisioned that the rapid isomerization could be exploited in asymmetric synthesis via a dynamic kinetic resolution if $k_2$ or $k_2'$ is faster than either $k_1$ or $k_3$ (Scheme 8). Furthermore, it is predicted that the use of a chiral rhodium catalyst will preferentially give one isomer over
the other (i.e. \( k_1 > k_3 \) or \( k_3 > k_1 \)).\(^{28,29}\) While the use of dynamic kinetic asymmetric transformations (DYKAT) are becoming more commonplace, there are few examples involving allenes.\(^{30-33}\)

![Scheme 8. Dynamic Kinetic Resolution](image)

### 1.4 SUBSTRATE DESIGN

Once the feasibility of the cyclocarbonylation reaction of allenol acetates to produce \( \alpha \)-acetoxy carbonyls was established, several cyclocarbonylation substrates were examined. Guided by a number of natural product substructures the scope of the cyclocarbonylation reaction was explored as follows: 1) The chain length of the tether between the allene and alkyne was varied (\( n = 1-4 \)); 2) Substitution on the allene and the tether were altered (Scheme 9). The stereochemical consequences of the [3,3]-sigmatropic rearrangement of propargyl acetate 32 to allenol acetate 33 and the cyclocarbonylation reaction to give 34 were examined by imbedding the allene into a conformationally anchored cyclohexane ring.

![Scheme 9. Substrate Design](image)
2.0 RESULTS AND DISCUSSION

2.1 PREPARATION OF PROPARGYL ACETATES

Preparation of cyclohexane-based substrates began by alkylating the lithium enolate of dimethyl hydrazone \(35^{34}\) with alkynyl halides or triflates (\(36a-c\)) (Scheme 10). Acidic hydrolysis\(^{35}\) gave ketones \(37a-eq, 37c-eq,\) and \(37c-ax\) \((n = 1, 3)\) in 44%, 50%, and 33% yields. Ketone \(37b-eq\) was obtained in only 5% yield, possibly due to a competing E2 elimination of the triflate to form a conjugated enyne prior to alkylation. The diastereomers of \(37c\) were separated via column chromatography and the major diastereomer was carried forward.

\[
\begin{align*}
\text{N} & \quad \text{1. n-BuLi} \\
\text{N} & \quad \text{2. X} \quad \text{TMS} \\
\text{3. oxalic acid} & \quad \text{TMS}
\end{align*}
\]

\(n = 1 \quad 36a \quad X = \text{Br} \quad 37a-eq 44\%\)

\(n = 2 \quad 36b \quad X = \text{OTf} \quad 37b-eq 5\%\)

\(n = 3 \quad 36c \quad X = I \quad 37c-eq 50\%\)

Scheme 10. Preparation of Ketones 37a-c

The major diastereomer of \(37a-eq\) was assigned as having a chair conformation with the alkyne side chain equatorial based on \(^1\text{H}\) NMR and \(^1\text{H}-^1\text{H}\) COSY experiments (Figure 1). Proton resonance G is assigned as being adjacent to the \(t\)-Bu group based on the two large (12.0 Hz) coupling constants consistent with axial-axial coupling and two small (3.0 Hz) coupling constants consistent with axial-equatorial coupling. COSY correlation was observed between \(H_G\) and

\[\]

8
proton resonances $H_B$, $H_F$, $H_H$, and $H_I$ indicating that they are on carbons adjacent to $H_G$. Resonances $H$ and $I$ proved most informative. Resonance $H$ was assigned based on the three large (12.0 Hz) couplings attributed to two axial-axial and one geminal coupling and a small (3.0 Hz) coupling attributed to an axial-equatorial coupling. Resonance $I$ was assigned based on the three large (2$\times$12.5 Hz and 14.0 Hz) couplings attributed to two axial-axial and one geminal coupling. The three large coupling constants observed for $H_I$ support the side chain having an equatorial orientation. If the side chain was axial, then $H_I$ would have two large coupling constants from an axial-axial and a geminal coupling along with a smaller constant for an axial-equatorial coupling. The same rationale was applied to assign the stereochemistry of ketones 37b-eq and 37c-eq.

Addition of ethynyl or 1-propynylmagnesium bromide to 37a-c-eq gave the propargyl alcohols resulting from axial addition of the Grignard reagent $38a-d-ax$ in 45-68% yields and the propargyl alcohols resulting from equatorial addition $38a-d-eq$ in 17-41% yields (Scheme 11). The major diastereomers were assigned based on the predisposition of small nucleophiles to add...
axially to substituted cyclohexanones.\textsuperscript{36} Separation of the two diastereomers of 38 was readily accomplished via column chromatography. The major diastereomers were acetylated using triethylamine, DMAP, and acetic anhydride yielding a single diastereomer of propargyl acetates 39\textit{a-d-ax} in 71-93\% yield. Two substrates were prepared to examine the electronic and steric effects of the carboxy group. A bulky pivaloyl group was appended to the corresponding propargyl alcohol using trimethylacetic anhydride and catalytic Sc(OTf)\textsubscript{3} to give 39\textit{e-ax} in 82\% yield.\textsuperscript{37} An electron withdrawing \textit{p}-nitrobenzoate was attached to propargyl alcohol 38\textit{c-ax} using 4-nitrobenzoyl chloride and DMAP to give 39\textit{f-ax} in 74\% yield.\textsuperscript{38}

![Diagram of chemical structures](image)

**Scheme 11. Preparation of Propargyl Acetates 39\textit{a-f}**

Propargyl acetates containing a simple alkyl chain were prepared using two different methods (Scheme 12). Propargyl acetates 41\textit{a-d} (\(n = 1, 2\)) were prepared by addition of ethynylmagnesium bromide or 1-propynylmagnesium bromide to aldehyde 40\textit{a} or ketones 40\textit{b-}
followed by in situ acetylation with acetyl chloride furnishing the desired products in 55-82% yields. For propargyl acetate 41e (R² = n-Pr) addition of the lithiate of 1-pentyne to ketone 55c gave the propargyl alcohol, which was then acetylated using triethylamine, DMAP, and acetic anhydride to obtain propargyl acetate 41e in 49% yield over two steps.

Propargyl acetates 41f-g (n = 3, 4) were prepared by reacting a slight excess of the sodium salt of methyl acetoacetate with iodides 36c and 36d. After aqueous workup, the crude material still containing a small amount of methyl acetoacetate, was subjected to Krapcho decarboxylation by heating the ketoester to 130 °C with lithium chloride in wet DMSO to obtain 8-(trimethylsilyl)oct-7-yn-2-one and 9-(trimethylsilyl)non-8-yn-2-one. Subjecting the crude 8-(trimethylsilyl)oct-7-yn-2-one and 9-(trimethylsilyl)non-8-yn-2-one to ethynylmagnesium bromide proved more straightforward than isolating the ketones. After chromatographic purification, the resulting propargyl alcohols were acetylated using triethylamine, DMAP, and acetic anhydride to obtain propargyl acetates 41f and 41g in 38% and 22% yields over 4 steps.

Scheme 12. Preparation of Propargyl Acetates 41a-g
2.2 FORMATION OF ALLENOL ACETATES FROM PROPARGYL ACETATES.

Previously reported conditions to form allenol acetates were screened for efficiency and diastereosepecificity. Treating \textbf{39c-ax} with AuCl$_3$ at 60 °C (Table 1, entry 1) gave complete conversion of allene-yn \textbf{39c-ax} to \textbf{42c} in 30 min as 1:1 ratio of diastereomers.$^{22}$ Performing the same reaction at room temperature gave \textbf{42c} as a 1:1 mixture of diastereomers in 30 min (entry 2). Lowering the temperature to -30 °C resulted in an incomplete reaction after 5 h and afforded a 1:1 diastereomeric mixture of \textbf{42c} (entry 3). Increasing the temperature to 90 °C decreased the reaction time giving full conversion to allenol acetate \textbf{42c} in 12 min and a 1:1 dr (entry 4). Two Ag(I) catalysts (AgBF$_4$ and AgSbF$_6$) were examined (entries 5-8) with no significant changes in stereoselectivity, but significant loss of the TMS group was observed.$^{44,45}$ [Rh(OCOCF$_3$)$_2$]$_2$ gave only a trace amount of product after 14 h (entry 9).$^{22}$ Using the PtCl$_2$ conditions reported by Malacria,$^{24}$ clean conversion to \textbf{42c} was observed, with a 1:1 dr and required prolonged reaction times (entry 10). Among the conditions examined, AuCl$_3$ afforded the allenol acetates in the highest yields and the shortest reaction times. The reaction temperature had a marginal effect on the diastereoselectivity.
Table 1. Catalyst Screening for Rearrangement

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>mol %</th>
<th>T (°C)</th>
<th>time (h)</th>
<th>Conversion%$^a$ (isolated yield %)</th>
<th>dr$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AuCl₃</td>
<td>10</td>
<td>60</td>
<td>0.5</td>
<td>100 (71)</td>
<td>1:1</td>
</tr>
<tr>
<td>2</td>
<td>AuCl₃</td>
<td>10</td>
<td>rt</td>
<td>0.5</td>
<td>100 (74)</td>
<td>1:1</td>
</tr>
<tr>
<td>3</td>
<td>AuCl₃</td>
<td>20</td>
<td>-30</td>
<td>5</td>
<td>55</td>
<td>1:1</td>
</tr>
<tr>
<td>4</td>
<td>AuCl₃</td>
<td>10</td>
<td>90</td>
<td>0.2</td>
<td>100 (62)</td>
<td>1:1</td>
</tr>
<tr>
<td>5</td>
<td>AgBF₄</td>
<td>50</td>
<td>rt</td>
<td>4</td>
<td>84$^c$</td>
<td>1:1</td>
</tr>
<tr>
<td>6</td>
<td>AgSbF₆</td>
<td>10</td>
<td>60</td>
<td>3</td>
<td>83</td>
<td>2:1</td>
</tr>
<tr>
<td>7</td>
<td>AgSbF₆</td>
<td>10</td>
<td>rt</td>
<td>19</td>
<td>90$^c$</td>
<td>1:1</td>
</tr>
<tr>
<td>8</td>
<td>AgSbF₆/PPPh₃</td>
<td>20</td>
<td>rt</td>
<td>17</td>
<td>73</td>
<td>1:1</td>
</tr>
<tr>
<td>9</td>
<td>[Rh(OCOCF₃)$_2$]</td>
<td>2</td>
<td>60</td>
<td>14</td>
<td>2</td>
<td>1:1</td>
</tr>
<tr>
<td>10</td>
<td>PtCl₂</td>
<td>10</td>
<td>40</td>
<td>96</td>
<td>100</td>
<td>1:1</td>
</tr>
</tbody>
</table>

$^a$Conversion determined by $^1$H NMR, $^b$Diastereomeric ratio determined by comparing the allenyl protons in the $^1$H NMR, $^c$Significant loss of TMS observed by $^1$H NMR

Interestingly, while reacting both 39c-ax and 39c-eq independently with AuCl₃ at room temperature showed little difference in reaction time, yield, or dr (entries 1 and 2, Table 2), when [Rh(OCOCF₃)$_2$] was used significant differences in reaction times for the two diastereomers were observed (compare entries 3 and 4). With the alkyne cis to the t-butyl group 39c-ax only trace amounts of product were observed after 72 h (entry 3). Conversely, the other diastereomer 39c-eq (entry 4) showed complete conversion to 42c in 4 h in 94% yield.
Table 2. Rearrangement of 39c-ax and 39c-eq

<table>
<thead>
<tr>
<th>entry</th>
<th>R1</th>
<th>R2</th>
<th>catalyst (mol %)</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>dr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CCH</td>
<td>OAc</td>
<td>AuCl₃ (10)</td>
<td>0.5</td>
<td>74</td>
<td>1:1</td>
</tr>
<tr>
<td>2</td>
<td>OAc</td>
<td>CCH</td>
<td>AuCl₃ (10)</td>
<td>0.5</td>
<td>80</td>
<td>1:1</td>
</tr>
<tr>
<td>3</td>
<td>CCH</td>
<td>OAc</td>
<td>[Rh(OCOCF₃)₂]₂ (2)</td>
<td>72</td>
<td>2^a</td>
<td>1:1</td>
</tr>
<tr>
<td>4</td>
<td>OAc</td>
<td>CCH</td>
<td>[Rh(OCOCF₃)₂]₂ (2)</td>
<td>4</td>
<td>94</td>
<td>1:1</td>
</tr>
</tbody>
</table>

^a Approximate conversion by ^1H NMR

Similar results were seen when 43 (7:1 dr) was reacted with [Rh(OCOCF₃)₂]₂ (Scheme 13). After 5 h at 60 °C, the minor diastereomer possessing a trans relationship between the alkyne and the t-butyl group was completely converted to product 44, and no change was observed for the major diastereomer of 43-ax, based on ^1H NMR. Thus, the stereochemistry of the propargyl acetate significantly impacts the reaction time of the rearrangement when using [Rh(OCOCF₃)₂]₂ with the axially oriented alkyne being slowest. It is postulated that developing 1,3-diaxial interactions of the alkyne coordinated to [Rh(OCOCF₃)₂]₂ slows this reaction.

Scheme 13. [Rh(OCOCF₃)₂]₂ Catalyzed Rearrangement of 43

With AuCl₃-catalyzed rearrangement conditions in hand, propargyl acetates 39a-c-ax were transformed to the trisubstituted allenol acetates 42a-c using AuCl₃ in 74–84% yield as ~1:1 mixtures of diastereomers (Table 3, entries 1-3). Tetrasubstituted allenol acetate 42d was
isolated in 53% yield (entry 4) due to the incomplete consumption of starting material and the instability of 42d. (Decomposition products were observed within 4 h of 42d standing in CDCl₃ at rt.) Treating sterically demanding propargyl ester 39e-ax to AuCl₃ readily formed allene-yne 42e in 1 h (91%, 2:1 dr) (entry 5). Subjecting p-nitrobenzoate ester 39f-ax to AuCl₃-catalyzed conditions gave allene-yne 42f in 87% yield in a 1.4:1 dr (entry 6). Reacting the secondary propargyl acetate 41a to the AuCl₃-catalyzed reaction conditions yielded only trace amounts of the 1,3-disubstituted allene (entry 7). The temperature was increased to 60 °C using AuCl₃ and the [Rh(OCOCF₃)₂]₂ and PtCl₂ conditions gave no improvement. Tertiary propargyl acetates 41b and 41c (entries 8 and 9) rearranged to give the desired allenol acetates 45b and 45c in 46% and 67% yields. Longer reaction times were required compared to the analogous cyclohexane based propargyl acetates (compare entries 1 and 2 to entries 8 and 9). Substituting an alkyl group for the proton on the terminus of the alkyne had little effect on the yield for the rearrangement of the linear system compared to the analogous cyclohexane based system (compare entries 9 and 10 to 3 and 4). Propargyl acetates 41f and 41g (n = 3, 4) reacted in significantly shorter reaction times and gave both 45f and 45g in 79% and 77% yields respectively (entries 12 and 13). It is possible that the remoteness of the appending alkyne minimizes coordination of the gold catalyst allowing for more rapid catalyst turnover, and limits potential side reactions. Reacting propargyl acetate 46a (R = H)¹⁷ to AuCl₃ gave allene-yne 47a in near quantitative yield as a 1.3:1 dr (entry 14). However, treating propargyl acetate 46b (R = Me)¹⁷ to AuCl₃ gave allene-yne 47b in a 43% yield (entry 15). (After 19 h propargyl acetate 46b was still observed in the crude ¹H NMR along with the appearance of a byproduct containing alkene resonances by ¹H NMR.)
Table 3. Preparation of Allenol Acetates

<table>
<thead>
<tr>
<th>entry</th>
<th>propargyl acetate</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>dr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39a-ax, n = 1 R¹ = H, R² = Me</td>
<td>3</td>
<td>84</td>
<td>1:1</td>
</tr>
<tr>
<td>2</td>
<td>39b-ax, n = 2 R¹ = H, R² = Me</td>
<td>0.5</td>
<td>80</td>
<td>1:1:1</td>
</tr>
<tr>
<td>3</td>
<td>39c-ax, n = 3 R¹ = H, R² = Me</td>
<td>0.5</td>
<td>74</td>
<td>1:1</td>
</tr>
<tr>
<td>4</td>
<td>39d-ax, n = 3 R¹ = Me, R² = Me</td>
<td>5</td>
<td>53</td>
<td>1.2:1</td>
</tr>
<tr>
<td>5</td>
<td>39e-ax, n = 3 R¹ = H, R² = t-Bu</td>
<td>0.8</td>
<td>91</td>
<td>2:1</td>
</tr>
<tr>
<td>6</td>
<td>39f-ax, n = 3 R¹ = H, R² = p-NO₂-C₄H₄</td>
<td>16</td>
<td>87</td>
<td>1.4:1</td>
</tr>
<tr>
<td>7</td>
<td>41a, n = 1, R¹ = H, R² = H</td>
<td>20</td>
<td>trace⁴</td>
<td>NA</td>
</tr>
<tr>
<td>8</td>
<td>41b, n = 1, R¹ = Me, R² = H</td>
<td>19</td>
<td>46</td>
<td>NA</td>
</tr>
<tr>
<td>9</td>
<td>41c, n = 2, R¹ = Me, R² = H</td>
<td>4</td>
<td>67⁵</td>
<td>NA</td>
</tr>
<tr>
<td>10</td>
<td>41d, n = 2, R¹ = Me, R² = Me</td>
<td>1.5</td>
<td>64</td>
<td>NA</td>
</tr>
<tr>
<td>11</td>
<td>41e, n = 2, R¹ = Me, R² = n-Pr</td>
<td>1.5</td>
<td>58</td>
<td>NA</td>
</tr>
<tr>
<td>12</td>
<td>41f, n = 3, R¹ = Me, R² = H</td>
<td>0.5</td>
<td>79</td>
<td>NA</td>
</tr>
<tr>
<td>13</td>
<td>41g, n = 4, R¹ = Me, R² = H</td>
<td>0.5</td>
<td>77</td>
<td>NA</td>
</tr>
<tr>
<td>14</td>
<td>46a, R = H</td>
<td>4</td>
<td>100</td>
<td>1.3:1</td>
</tr>
<tr>
<td>15</td>
<td>46b, R = Me</td>
<td>19</td>
<td>43</td>
<td>1.5:1</td>
</tr>
</tbody>
</table>

⁴Conditions: AuCl₃ (10 mol %), toluene, rt, ⁵Reacted as a single diastereomer, ⁶Reacted as a 6:1 dr (major diastereomer is shown), ⁷Reacted as a 4:1 dr (major diastereomer is shown), ⁸Reacted as a 5:1 dr (major diastereomer is shown).
2.3 RHODIUM(I)-CATALYZED CYCLOCARBONYLATION REACTION OF ALLENOL ACETATES TO FORM ALPHA-ACETOXY CYCLOPENTADIENONES.

Next the scope and limitations of the Rh(I)-catalyzed cyclocarbonylation reaction of allenol acetates for the formation of bi- and tricyclic ring systems were explored (Table 4). Previously optimized conditions were used to effect the cyclocarbonylation reaction of allenol acetates.\textsuperscript{17} Reaction of allenol acetate 42a to the standard Rh(I) cyclocarbonylation conditions gave only a 19\% yield of 48a in 8 h (entry 1). Allene-yne 42b (entry 2) and 42c (entry 3), underwent cyclocarbonylation to produce 48b and 48c in 67\% and 76\% yields respectively. Formation of the [6-7-5] ring system took significantly longer (17 h, entry 3) than the analogous [6-6-5] ring system (1 h, entry 1). Subjecting 42e to cyclocarbonylation conditions gave a 2.6:1 dr of α-pivaloxy 4-alkylidene cyclopentadione 48e in 51\% yield (entry 4). Cyclocarbonylation of 42f gave the cyclized product 48f as a 1.8:1 mixture of diastereomers in 35\% yield (entry 5). Thus, it appears that neither steric nor electronic changes significantly impact the diastereomeric ratio of the products. Reaction of linear allene-yne 45b (entry 6) gave 49b in 28\% yield along with significant decomposition, indicating that [5-5] ring systems are not efficiently prepared via this methodology. Cyclocarbonylation of allene-yne 45c and 45f was readily accomplished giving 49c and 49f in 53\% and 62\% yields (entry 7 and 8). The reaction of 45g to produce an [8-5] ring system resulted in only trace amounts of the product with the majority of allenol ester rearranging into the conjugated dienol acetate 50 in an ~1:1 Z to E ratio (entry 10 and Figure 2). Cyclocarbonylation of allenol-acetate 47a gave the α-acetoxy 4-alkylidene cyclopentenone 51a in 19 h and 74\% yield.
Figure 2. Conjugated Dienol Acetate 50

Table 4. [Rh(CO)$_2$Cl]$_2$ Catalyzed Cyclocarbonylation Reactions$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>allene-yne</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>dr$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42a, n = 1, R = Me 1:1 dr</td>
<td>8</td>
<td>19</td>
<td>1.3:1</td>
</tr>
<tr>
<td>2</td>
<td>42b, n = 2, R = Me 1:1 dr</td>
<td>1</td>
<td>67</td>
<td>1.2:1</td>
</tr>
<tr>
<td>3</td>
<td>42c, n = 3, R = Me 1:1 dr</td>
<td>17</td>
<td>76</td>
<td>1.9:1</td>
</tr>
<tr>
<td>4</td>
<td>42e, n = 3, R = t-Bu 2:1 dr</td>
<td>18</td>
<td>51</td>
<td>2.3:1</td>
</tr>
<tr>
<td>5</td>
<td>42f, n = 3, R = p-NO$_2$-C$_6$H$_4$ 1.4:1 dr</td>
<td>18</td>
<td>35</td>
<td>1.8:1</td>
</tr>
<tr>
<td>6</td>
<td>45b, n = 1</td>
<td>22</td>
<td>28</td>
<td>NA</td>
</tr>
<tr>
<td>7</td>
<td>45c, n = 2</td>
<td>2</td>
<td>53</td>
<td>NA</td>
</tr>
<tr>
<td>8</td>
<td>45f, n = 3</td>
<td>46</td>
<td>62</td>
<td>NA</td>
</tr>
<tr>
<td>9</td>
<td>45g, n = 4</td>
<td>120</td>
<td>trace$^c$</td>
<td>NA</td>
</tr>
<tr>
<td>10</td>
<td>47a, 1.3:1 dr</td>
<td>19</td>
<td>74</td>
<td>2.3:1</td>
</tr>
</tbody>
</table>

$^a$Conditions: [Rh(CO)$_2$Cl]$_2$ (10 mol %), CO(g) (1 atm), toluene, 90 °C, $^b$Diastereomeric ratio determined comparing proton resonances by $^1$H NMR, $^c$Observed by $^1$H NMR.
Cyclocarbonylation reactions of tetrasubstituted allene 42d afforded a 26% yield of 52 in 69 h and 47b gave a 45% yield of 53 in 47 h via cyclocarbonylation followed by loss of acetic acid (Scheme 14). Linear allenol acetate 45d gave a 49% yield of triene 54d, along with a trace amount of the desilylated product observed in the crude 1H NMR. Similarly, allenol acetate 45e afforded triene 54e in 42% yield along with desilylated 54e' in 13% yield. Compounds 52, 53, and 54d,e proved relatively unstable with observable decomposition by 1H NMR within 24 h in a freezer. Nonetheless, these examples have provided access to the products of a cyclocarbonylation between an alkyne and a cumulene.

Scheme 14. The [Rh(CO)\(_2\)Cl]\(_2\) Catalyzed Cyclocarbonylation Reaction of Tetrasubstituted Allenol Esters
The cyclocarbonylation of allene-ynes 55a and 55c gave cycloadducts 56a and 56c in 32% and 70% yields (Scheme 15), paralleling the yields obtained for analogous [6-5-5] and [6-7-5] ring systems 48a and 48c (Table 4, entries 1 and 3), suggesting that the acetoxy group has little influence on the yields of the cyclocarbonylation reaction. Conversely, the reaction times for the cyclocarbonylation of 55a and 55c were 30 and 40 min, compared to 8 and 17 h for 48a and 48c suggesting that the acetoxy group has a large effect on the reaction time.

![Scheme 15. Preparation and Cyclocarbonylation of Allene-ynes 55a and 55c](image)

2.4 DIASTEREOSELECTIVE CONSIDERATIONS

To probe the origin of the slight increase in dr (1:1 to 2:1) for the transformation of 42c to 48c, the cyclocarbonylation of diastereomERICALLY enriched allene-yne 42c was performed in d8-toluene and monitored via 1H NMR (Table 5). Starting with 3:1 dr of 42c, rapid isomerization of the allenol acetate was observed giving a 1:1 dr of allenol acetates in 40 min with no evidence of cyclocarbonylation products (entries 1 and 2). Performing the reaction at room temperature slowed the rate of isomerization but still resulted in a 1:1 dr of allenes after 7 h with no evidence of cyclocarbonylation products (entries 3 and 4). Heating allene 42c in the absence of rhodium catalyst for 24 h at 90 °C resulted in no change in dr. Additionally subjecting a 5:1 dr of
cyclocarbonylation product 48c to reaction conditions resulted in no change in dr after three days. Thus, under the Rh(I)-catalyzed cyclocarbonylation conditions rapid isomerization of the allenol acetates is occurring prior to cyclocarbynylation.

Table 5. Isomerization of Allenol Acetate 42c

<table>
<thead>
<tr>
<th>entry</th>
<th>starting dr (major/minor)</th>
<th>[Rh(CO)₂Cl]₂ (mol %)</th>
<th>T (°C)</th>
<th>time³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3:1</td>
<td>10</td>
<td>90</td>
<td>40 min²</td>
</tr>
<tr>
<td>2</td>
<td>1:3</td>
<td>10</td>
<td>90</td>
<td>40 min²</td>
</tr>
<tr>
<td>3</td>
<td>3:1</td>
<td>10</td>
<td>rt</td>
<td>7 h²</td>
</tr>
<tr>
<td>4</td>
<td>1:3</td>
<td>10</td>
<td>rt</td>
<td>7 h²</td>
</tr>
<tr>
<td>5</td>
<td>3:1</td>
<td>0</td>
<td>90</td>
<td>24³</td>
</tr>
<tr>
<td>6</td>
<td>1:3</td>
<td>0</td>
<td>90</td>
<td>24³</td>
</tr>
</tbody>
</table>

³Time until 1:1 dr was observed. ²Run under CO atm, ³No epimerization observed after 24 h under Ar.

During the course of our studies of the isomerization of allenol acetates, we noted by ¹H NMR, the formation of new resonances not characteristic of starting material 42c or product 48c. It was postulated that these new resonances may be a rhodium metallocycle stabilized by coordination of the acetoxy carbonyl. This hypothesis was supported by the disappearance of these resonances and a decrease to 1:1 dr from 2:1 dr observed for 48c performing the reaction with 10 mol% triphenylphosphine, a competing coordinating ligand.

To further probe and characterize the postulated metallocycle intermediate, allenol ester 42c (1:1 dr) was reacted with a full equivalent of [Rh(CO)₂Cl]₂ in d₈-toluene and the reaction progress was monitored by ¹H NMR and the resulting products were characterized by ¹³C NMR
(Figure 3a-d). After 20 h at rt under argon the resonances for the starting material (Figure 3a) were gone and pairs of new resonances appeared in a 1:1 ratio (Figure 3b). The appearance of resonances at 211.0 (d, $J_{\text{Rh-C}} = 27.0$ Hz) and 211.4 (d, $J_{\text{Rh-C}} = 26.3$ Hz) suggest two diastereomeric carbonyl carbons attached to the rhodium$^{46,47}$ and the resonances at 182.8 (d, $J_{\text{Rh-C}} = 86.3$ Hz, 2C) and 183.5 (d, $J_{\text{Rh-C}} = 86.3$ Hz) suggest diastereomeric rhodium bound carbon monoxides.$^{48}$ Disappearance of the resonances for the alkyne carbons of the two diastereomers of 42c at 108.3, 108.3, 85.1, and 84.9 ppm were also observed. Furthermore, the signals at 102.4 (d, $J_{\text{Rh-C}} = 27.2$ Hz) and 102.2 (d, $J_{\text{Rh-C}} = 26.8$ Hz) are consistent with a carbon attached to both a rhodium and an acetoxy group.$^{47}$

Heating this same NMR sample at 90 °C under argon produced new resonances in an apparent 1:1 ratio (Figure 3c) that were not consistent with either starting material 42c (Figure 3a) or cyclocarbonylation product 48c (Figure 3d). Disappearance of the resonances at 211.0 (d, $J_{\text{Rh-C}} = 27.0$ Hz) and 211.4 (d, $J_{\text{Rh-C}} = 26.3$ Hz) and new resonances at 180.1 (d, $J_{\text{Rh-C}} = 73.4$ Hz), $\delta = 184.6$ (d, $J_{\text{Rh-C}} = 81.4$ Hz) and 184.5 (d, $J_{\text{Rh-C}} = 81.2$ Hz) were observed. Additional resonances proposed to result from $sp^2$ hybridized carbons at 158.9 (d, $J_{\text{Rh-C}} = 24.8$ Hz) and 159.3 (d, $J_{\text{Rh-C}} = 27.5$ Hz), resonances at 144.4 (d, $J_{\text{Rh-C}} = 2.4$ Hz), 143.4 (d, $J_{\text{Rh-C}} = 2.6$ Hz), 141.2 (d, $J_{\text{Rh-C}} = 1.8$ Hz), 140.5 (d, $J_{\text{Rh-C}} = 1.4$ Hz) were observed with significantly smaller $^{103}$Rh coupling constants suggesting a greater distance from the rhodium. The $^{13}$C signals at 106.2 (d, $J_{\text{Rh-C}} = 24.9$ Hz) and 106.0 (d, $J_{\text{Rh-C}} = 25.0$ Hz) appear to still be consistent with a carbon attached to both a rhodium and an acetoxy group. Based upon these experiments, compounds 57 and 58 (Table 6) are proposed as intermediates corresponding to the spectra in Figure 3b and 3c, respectively.
These postulated intermediates are further supported by the following experiments: 1) Changing the atmosphere in the NMR tube from argon to CO and allowing to react for an additional 19 h at rt resulted in reappearance of the peaks for the first intermediate in a 1:1 ratio (figure 3b); 2) Heating, the resultant mixture at 90 °C under CO led to the appearance of resonances consistent with cyclocarbonylation product 48c in a 2:1 dr (Figure 3d). After approximately 75% conversion to 48c, the resonances for the postulated rhodium intermediate 57 had changed to a 3:1 ratio by $^1$H NMR indicating that one diastereomer was reacting preferentially over the other. This rare example of a trapped Rh(III) intermediate in the cyclocarbonylation reaction is most likely enabled by the coordination of the appending acetoxy ligand.

![Figure 3](image-url)

**Figure 3.** $^{13}$C NMR spectrum (in d$_8$-toluene at 23 °C) (a) 42c, (b) 42c and [Rh(CO)$_2$Cl]$_2$ after 20 h at rt under Ar, proposed as 57, (c) 42c and [Rh(CO)$_2$Cl]$_2$ after stirring an additional 17 h at 90 °C under Ar, proposed as 58, (d) Spectrum of isolated 48c.
Table 6. $^{13}$C Chemical Shifts of 42c, 57, 58, and 48c in d$_8$-toluene (δC, mult, $J_{\text{Rh-C}}$ in Hz)

<table>
<thead>
<tr>
<th>Position</th>
<th>42c</th>
<th>57</th>
<th>58</th>
<th>48c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>168.3, s</td>
<td>184.9, s</td>
<td>183.9, s</td>
<td>169.0, s</td>
</tr>
<tr>
<td>1$^a$</td>
<td>168.3, s</td>
<td>185.0, s</td>
<td>183.8, s</td>
<td>169.2, s</td>
</tr>
<tr>
<td>2</td>
<td>111.8, s</td>
<td>102.2, d, 26.8</td>
<td>106.0, d, 25.0</td>
<td>74.4, s</td>
</tr>
<tr>
<td>2$^a$</td>
<td>111.8, s</td>
<td>102.4, d, 27.2</td>
<td>106.2, d, 24.9</td>
<td>73.6, s</td>
</tr>
<tr>
<td>3</td>
<td>187.0, s</td>
<td>159.4, s$^b$</td>
<td>141.2, d, 1.4</td>
<td>131.8, s</td>
</tr>
<tr>
<td>3$^a$</td>
<td>186.9, s</td>
<td>158.3, s$^b$</td>
<td>140.5, d, 1.8</td>
<td>131.9, s</td>
</tr>
<tr>
<td>4</td>
<td>122.8, s</td>
<td>142.7, s$^b$</td>
<td>161.4, s</td>
<td>148.2, s</td>
</tr>
<tr>
<td>4$^a$</td>
<td>123.0, s</td>
<td>143.1, s$^b$</td>
<td>160.9, s</td>
<td>147.6, s</td>
</tr>
<tr>
<td>5</td>
<td>84.9, s</td>
<td>140.0, s$^b$</td>
<td>143.4, d, 2.6</td>
<td>179.6, s</td>
</tr>
<tr>
<td>5$^a$</td>
<td>85.1, s</td>
<td>140.3, s$^b$</td>
<td>144.6, d, 2.4</td>
<td>181.2, s</td>
</tr>
<tr>
<td>6</td>
<td>108.3, s</td>
<td>134.8, s$^b$</td>
<td>159.3, d, 27.5</td>
<td>139.7, s</td>
</tr>
<tr>
<td>6$^a$</td>
<td>108.3, s</td>
<td>133.6, s$^b$</td>
<td>158.9, d, 24.8</td>
<td>139.6, s</td>
</tr>
<tr>
<td>7</td>
<td>–</td>
<td>211.0, d, 27.0</td>
<td>–</td>
<td>202.6, s</td>
</tr>
<tr>
<td>7$^a$</td>
<td>–</td>
<td>211.4, d, 26.3</td>
<td>–</td>
<td>203.0, s</td>
</tr>
<tr>
<td>CO</td>
<td>–</td>
<td>182.8, d, 86.3</td>
<td>184.5, d, 81.2</td>
<td>–</td>
</tr>
<tr>
<td>CO$^a$</td>
<td>–</td>
<td>183.5, d, 86.3</td>
<td>184.6, d, 81.4</td>
<td>–</td>
</tr>
<tr>
<td>CO</td>
<td>–</td>
<td>–</td>
<td>180.1, d, 73.7</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$Minor diastereomer, $^b$Carbon assignment is interchangeable.
Removal of the acetate group was achieved. Subjecting acetate 49c to \( \text{K}_2\text{CO}_3 \) in MeOH/H\(_2\)O gave alcohol 59 in 60% yield (Scheme 16). This demonstrates the synthetic utility of the Rh(I)-catalyzed allenic cyclocarbonylation reaction for accessing \( \alpha \)-hydroxy containing cyclopentadienones.

![Scheme 16. Deprotection of 49c](image_url)
3.0 CONCLUSION

We have demonstrated the first Rh(I)-catalyzed cyclocarbonylation reaction for the formation of \(\alpha\)-acetoxy 4-alkylidene cyclopentenones from allenol acetates. Both cyclohexane and linear allene-ynes [6-5] and [7-5] ring systems were prepared in good yields, however [5-5] ring systems proved less successful. The \(\alpha\)-acetoxy cyclopentadienone product was prepared from trisubstituted allenol acetates, while tetrasubstituted allenol acetates gave elimination products. Intermediate rhodium(III) metallocycles were characterized by \(^{13}\text{C}\) and \(^1\text{H}\) NMR; representing a rare example of trapping a cyclocarbonylation intermediate. Liberation of the acetate from the \(\alpha\)-acetoxy-4-alkylidene cyclopentadienone was readily accomplished yielding an \(\alpha\)-hydroxy ketone. Studies are underway to expand the scope of this reaction and increase the stereoselectivity of this reaction.
4.0 EXPERIMENTAL

General Methods

Unless otherwise noted, all reactions were performed under a nitrogen atmosphere using standard syringe, cannula, and septum techniques. All commercially available compounds were used as received unless otherwise noted. Tetrahydrofuran (THF) and dichloromethane (CH$_2$Cl$_2$) were purified using a solvent purification system passing through a column containing Q5 reagent and a column containing activated alumina for THF and passing through a column containing activated alumina for CH$_2$Cl$_2$. Toluene, triethylamine (NEt$_3$), and diisopropylamine were freshly distilled from CaH$_2$ prior to use. Acetic anhydride (Ac$_2$O) was distilled from P$_2$O$_5$ and stored over 4 Å molecular sieves. Flash chromatography was performed using silica gel (32-63 µm particle size, 60 Å pore size). Thin layer chromatography (TLC) was performed using silica gel plates (60 F$_{254}$, 250 µm). All $^1$H and $^{13}$C NMR spectra were obtained on 300 MHz instruments at room temperature unless otherwise specified. Chemical shifts (δ) are reported relative to tetramethylsilane (CDCl$_3$: δ$_{C}$ = 77.0 ppm; residual CHCl$_3$ in CDCl$_3$: δ$_{H}$ = 7.27 ppm). IR spectra were obtained using an FT-IR instrument as a thin film. Diastereomers were not separated for characterization unless stated otherwise. Diastereomeric ratios were assigned using $^1$H NMR integrations.
4-Tert-butyl-2-(3-(trimethylsilyl)prop-2-ynyl)cyclohexanone (37a-eq).

A flame-dried, 15 mL single-necked round-bottomed flask equipped with a stir-bar was charged with 4-tert-butylcyclohexanone N,N-dimethylhydrazone34 (169 mg, 0.861 mmol) and THF (4.3 mL). The solution was cooled in an ice/H₂O bath and n-BuLi (0.64 mL, 1.6 M in hexanes, 1.0 mmol) was added dropwise via syringe forming a canary yellow solution. After 1 h in an ice/H₂O bath, 3-(trimethylsilyl)propargyl bromide (0.15 mL, 1.1 mmol) was added dropwise via syringe. The resulting solution was warmed to rt and stirred overnight. The reaction was diluted with Et₂O and H₂O. The aq layer was separated and extracted with Et₂O (3×). The combined organic layers were concentrated in vacuo in a 10 mL round-bottomed flask. The residue was diluted with Et₂O (3.3 mL) and a stir-bar was added to the flask. A saturated aq oxalic acid solution (1.3 mL) was added with vigorous stirring at rt; after 6 h, the reaction was diluted with H₂O and Et₂O. The aq layer was separated and extracted with Et₂O (3×). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 95:5, v/v) affording the title compound (100 mg, 44%) as a slightly yellow oil as a single diastereomer. 

37a-eq

R<sub>f</sub> = 0.50  (hexanes/EtOAc, 90:10, v/v); <sup>1</sup>H NMR (500 MHz, CDCl₃) δ: 2.63 (dd, <i>J</i> = 17.0, 4.0 Hz, 1H), 2.49-2.43 (m, 2H), 2.39 (ddd, <i>J</i> = 13.5, 4.0, 2.5 Hz, 1H), 2.30 (tdd, <i>J</i> = 14.0, 6.0, 1.0 Hz, 1H), 2.16 (dd, <i>J</i> = 17.5, 9.0 Hz, 1H), 2.10-2.06 (m, 1H), 1.59, (tt, <i>J</i> = 12.0, 3.0 Hz, 1H), 1.41 (qd, <i>J</i> = 13.0, 4.5 Hz, 1H), 1.14 (dt, <i>J</i> = 12.5, 14.0 Hz, 1H), 0.91 (s, 9H), 0.11 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl₃) δ: 210.9, 105.4, 85.9, 48.7, 46.9, 41.2, 34.0, 32.5, 28.5, 27.5, 20.1, 0.0; IR: 2959, 2176, 1716, 1249, 843 cm⁻¹; MS <i>m/z</i> (relative intensity): 264 (8%, M⁺), 249 (52%), 74, (46%), 72 (91%), 55 (100%); HRMS-EI (<i>m/z</i>): [M]⁺ calcd for C₁₆H₂₈OSi, 264.1909; found, 264.1907. 

O
4-Tert-butyl-2-(4-(trimethylsilyl)but-3-ynyl)cyclohexanone (37b-eq).

A flame-dried, single-necked 50 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with 4-tert-butylocyclohexanone N,N-dimethylhydrazone (500 mg, 2.55 mmol) and THF (12.8 mL). The solution was cooled to -78 °C and n-BuLi (1.9 mL, 1.6 M in hexanes, 3.0 mmol) was added dropwise via syringe. The reaction was stirred at -78 °C for 6 h and freshly prepared 4-trimethylsilyl-3-butyn-1-yl triflate (1.05 g, 3.8 mmol) in THF (3.8 mL) was added via cannula at -78 °C. The solution was stirred at -78 °C for 16 h then warmed to -40 °C over 3.5 h and saturated aq NH₄Cl was added. The solution was diluted with Et₂O and H₂O and warmed to rt. The aq layer was separated and extracted with Et₂O (3×). The combined organic layers were concentrated in vacuo in a 100 mL round-bottomed flask. The residue was diluted with Et₂O (10 mL) and a stir-bar was added to the flask. A saturated aq oxalic acid solution (3.8 mL) was added with vigorous stirring at rt; after 1 h the reaction was diluted with H₂O and Et₂O. The aq layer was separated and extracted with Et₂O (3×). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. The residue was taken up in pentanes and filtered. Following concentration in vacuo the crude oil was purified via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v then hexanes/CH₂Cl₂, 7:3 to 1:0, v/v) affording the title compound (36 mg, 5%) as a colorless oil as a single diastereomer. Rf = 0.63 (hexanes/EtOAc, 90:10, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 2.52-2.40 (m, 1H), 2.40-2.33 (m, 2H), 2.29 (t, J = 7.2 Hz, 2H), 2.19-1.97 (m, 3H), 1.60 (tt, J = 12.0, 3.0 Hz, 1H), 1.52-1.29 (m, 2H), 1.14 (q, J = 12.3 Hz, 1H), 0.92 (s, 9H), 0.14 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 213.0, 107.0, 84.8, 48.4, 47.2, 41.7, 35.0, 32.4, 28.8, 28.1, 27.6, 17.6, 0.2; IR: 2958, 2174, 1714, 1365,
1249, 842 cm\(^{-1}\); MS \(m/z\) (relative intensity): 278 (45%, \(M^+\)), 263 (30%), 154 (68%), 139 (83%), 97 (53%), 74 (90%), 72 (98%), 55 (100%); HRMS-EI \((m/z)\): [M]\(^+\) calcd for C\(_{17}\)H\(_{30}\)OSi, 278.2066; found, 278.2063.

4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexanone (37c).

A flame-dried, 100 mL single-necked round-bottomed flask equipped with a stir-bar was charged with 4-tert-butylcyclohexanone \(N,N\)-dimethylhydrazone (1.02 g, 5.20 mmol) and THF (26 mL). The solution was cooled in an ice/H\(_2\)O bath and \(n\)-BuLi (5.3 mL, 1.6 M in hexanes, 8.5 mmol) was added dropwise via syringe forming a canary yellow solution. After stirring for 1 h in an ice/H\(_2\)O bath, 1-iodo-5-(trimethylsilyl)-4-pentyne (1.70 g, 6.38 mmol) was added dropwise via syringe. The resulting solution was warmed to rt and stirred overnight. The reaction was quenched with a saturated aq NH\(_4\)Cl solution and diluted with Et\(_2\)O, H\(_2\)O, and brine. The aq layer was separated and extracted with Et\(_2\)O (3\(\times\)). The combined organic layers were concentrated in vacuo in a 200 mL round-bottomed flask. The residue was diluted with Et\(_2\)O (20 mL) and a stir-bar was added to the flask. A saturated aq oxalic acid solution (8 mL) was added with vigorous stirring at rt; after 1 h the reaction was diluted with H\(_2\)O and Et\(_2\)O. The aq layer was separated and extracted with Et\(_2\)O (3\(\times\)). The combined organic layers were washed with brine, dried over MgSO\(_4\), filtered, and concentrated in vacuo. The residue was taken up in pentanes, filtered, and concentrated in vacuo. The crude material was purified via flash chromatography (pentanes/Et\(_2\)O, 95:5 to 8:2, v/v) affording 597 mg \(37c\)-eq, 219 mg (\(37c\)-eq/\(37c\)-ax 1:2:1), 442 mg \(37c\)-ax with a combined mass of 1.258 g (83%) as a slightly yellow oil as an \(~1.5:1\) dr. \(37c\)-eq: \(R_f = 0.61\) (hexanes/EtOAc,
90:10, v/v); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 2.39 (ddd, $J = 13.5, 5.0, 3.0$ Hz, 1H), 2.33 (ddd, $J = 13.5, 6.0, 1.5$ Hz, 1H), 2.31-2.28 (m, 1H), 2.22 (m, 2H), 2.15-2.07 (m, 2H), 1.88-1.82 (m, 1H), 1.61-1.50 (m, 3H), 1.44 (qd, $J = 13.0, 4.5$ Hz, 1H), 1.29-1.23 (m, 1H), 1.15 (q, $J = 12.5$ Hz, 1H), 0.91 (s, 9H), 0.14 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 213.1, 107.3, 84.4, 49.2, 47.1, 41.7, 35.2, 32.4, 28.7, 27.6, 26.3, 20.1, 0.13; IR: 2957, 2174, 1715, 1249, 842 cm$^{-1}$; MS m/z (relative intensity): 292 (13%, M$^+$), 277 (17%), 235 (14%), 179 (21%), 154 (37%), 138 (41%), 109 (40%), 75 (84%), 73 (88%), 57 (100%); HRMS-El (m/z): [M]$^+$ calcd for C$_{18}$H$_{32}$OSi, 292.2222; found, 292.2215.

37c-ax $R_1 = 0.58$ (hexanes/EtOAc, 90:10, v/v); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 2.37 (ddd, $J = 15.0, 14.0, 6.0$ Hz, 1H), 2.35-2.31 (m, 1H), 2.26-2.22 (m, 1H), 2.18 (t, $J = 7.0$ Hz, 2H), 1.98-1.94 (m, 1H), 1.81-1.75 (m, 2H), 1.63-1.44 (m, 4H), 1.43-1.36 (2H), 0.86 (s, 9H), 0.09 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 215.1, 106.6, 84.7, 48.6, 41.1, 38.2, 32.1, 31.6, 30.3, 27.3, 26.9, 26.0, 19.5, 0.0

4-Tert-butyl-1-ethynyl-2-(3-(trimethylsilyl)prop-2-ynyl)cyclohexanol (38a).

A flame-dried, single-necked 10 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with the major diastereomer of 37a-eq (100 mg, 0.378 mmol) and THF (1.9 mL). The solution was cooled in an ice/H$_2$O bath and ethynylmagnesium bromide (2.3 mL, 0.5 M in THF, 1.2 mmol) was added rapidly via syringe and the solution was allowed to warm to rt. After 90 min, the reaction was complete by TLC and the solution was diluted with Et$_2$O and H$_2$O. The aq layer was separated and extracted with Et$_2$O ($3 \times$). The combined organic layers were washed with brine, dried over MgSO$_4$, filtered, and

31
concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded 32 mg 54a-ax, 19 mg (54a-ax/54a-eq 1.5:1), 45 mg 54a-eq with a combined mass of 95 mg (86%) as off white solids in an ~1:1:1 dr. 38a-ax: Rf = 0.13 (hexanes/EtOAc, 95:5, v/v); 1H NMR (500 MHz, CDCl3) δ: 3.18 (bs, 1H), 2.67 (dd, J = 17.0, 7.0 Hz, 1H), 2.52 (s, 1H), 2.20 (dd, J = 17.0, 7.5 Hz, 1H), 2.08 (dt, J = 12.5, 3.0 Hz, 1H), 1.88 (dq, J = 13.0, 3.0 Hz, 1H), 1.78-1.71 (m, 2H), 1.56 (td, J = 12.5, 3.5 Hz, 1H), 1.33 (qd, J = 12.0, 3.5 Hz, 1H), 1.10 (tt, J = 12.0, 3.0 Hz, 1H), 0.98 (q, J = 13.0 Hz, 1H), 0.87 (s, 9H), 0.15 (s, 9H); 13C NMR (75 MHz, CDCl3) δ 106.6, 86.9, 84.1, 74.7, 73.0, 47.2, 46.9, 40.7, 32.3, 30.8, 27.5, 24.4, 22.4, 0.0; IR: 3295, 2956, 2175, 1250, 841 cm⁻¹; MS m/z (relative intensity): 290 (8%, M⁺), 275 (11%), 233 (23%), 74 (97%), 72 (96%), 55 (100%); HRMS-EI (m/z): [M]⁺ calcd for C18H30OSi, 290.2066; found, 290.2074.

38a-eq: Rf = 0.18 (hexanes/EtOAc, 95:5, v/v); 1H NMR (500 MHz, CDCl3) δ: 2.64 (dd, J = 17.0, 4.0 Hz, 1H), 2.54 (dd, J = 17.0, 8.5 Hz, 1H), 2.46 (s, 1H), 2.34 (s, 1H), 2.10 (dt, J = 14.0, 3.5 Hz, 1H), 1.85 (dq, J = 13.0, 2.0 Hz, 1H), 1.75-1.55 (m, 3H), 1.38 (qd, J = 12.5, 3.0 Hz, 1H), 1.29 (q, J = 12.5 Hz, 1H), 1.12 (tt, J = 12.0, 3.0 Hz, 1H), 0.89 (s, 9H), 0.15 (s, 9H); 13C NMR (75 MHz, CDCl3) δ 106.3, 87.7, 87.2, 71.7, 69.1, 47.4, 45.1, 40.4, 32.6, 27.4, 26.5, 22.2, 21.5, 0.0

### 4-Tert-butyl-1-ethynyl-2-(4-(trimethylsilyl)but-3-ynyl)cyclohexanol (38b).

4-Tert-butyl-1-ethynyl-2-(4-(trimethylsilyl)but-3-ynyl)cyclohexanol (38b).

A flame-dried, single-necked 10 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with a single diastereomer of 37b-eq (34 mg, 0.12 mmol) and THF (0.61 mL). The solution was cooled in an ice/H2O bath and ethynylmagnesium bromide (0.73 mL, 0.5 M in THF, 0.37 mmol) was added rapidly via syringe
and the solution was allowed to warm to rt. After 40 min the reaction was complete by TLC and the solution was diluted with Et₂O and H₂O. The aq layer was separated and extracted with Et₂O (3 ×). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded 21 mg 37b-ax and 7 mg 37b-eq with a combined mass of 28 mg (76%) as a slightly yellow oil as a 2.6:1 dr. Diastereomers were separated by flash chromatography. 38b-ax:

Rₜ = 0.45 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 2.49 (s, 1H), 2.44-2.21 (m, 2H), 2.18 (s, 1H), 2.13-2.02 (m, 2H), 1.82-1.25 (m, 6H), 1.12-0.94 (m, 2H), 0.87 (s, 9H), 0.14 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 107.6, 84.9, 84.8, 74.3, 72.6, 47.2, 47.0, 41.4, 32.3, 30.2, 29.9, 27.6, 24.7, 18.3, 0.2; IR: 3469, 3308, 2954, 2173, 1366, 1249, 843; MS m/z (relative intensity): 304 (36%, M⁺), 289 (50%), 286 (78%), 271 (39%), 261 (39%), 74 (90%), 72 (98%), 55 (100%); HRMS-EI (m/z): [M]⁺ calcd for C₁₅H₃₂OSi, 304.2222; found, 304.2210.

38b-eq:

Rₜ = 0.51 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 2.44 (s, 1H), 2.42-2.07 (m, 4H), 1.78-1.68 (m, 2H), 1.62 (s, 1H), 1.63-1.26 (m, 4H), 1.12-0.92 (m, 2H), 0.87 (s, 9H), 0.16 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 107.4, 88.2, 84.7, 71.5, 69.2, 47.3, 45.4, 40.7, 32.5, 30.2, 27.5, 26.8, 21.6, 18.1, 0.2.

4-Tert-butyl-1-ethynyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexanol (38c).

A flame-dried, single-necked 50 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with the major diastereomer 37c-eq (597 mg, 2.04 mmol) and THF (10 mL). The solution was cooled in an ice/H₂O bath and ethynylmagnesium bromide (12.2 mL, 0.5 M in THF, 6.10 mmol) was added
rapidly via syringe and the solution was allowed to warm to rt. After 1.5 h the reaction was complete by TLC and the solution was quenched with saturated aq NH₄Cl solution. The volume was reduced in vacuo and the remaining solution was diluted with Et₂O and H₂O. The aq layer was separated and extracted with Et₂O (3×). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. Purification of the crude oil (2:1 dr by crude ¹H NMR) via flash chromatography (hexanes/EtOAc, 97.5:2.5 to 8:2 v/v) afforded 146 mg 38c-ax and 439 mg 38c-eq with a combined mass of 585 mg (90%) as a slightly yellowish oil. 38c-ax: Rf = 0.50 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (500 MHz, CDCl₃) δ: 2.46 (s, 1H), 2.26-2.21 (m, 2H), 2.17 (s, 1H), 2.05 (dt, J = 12.0, 3.5 Hz, 1H), 1.92-1.85 (m, 1H), 1.80 (dq, J = 13.0, 3.0 Hz, 1H), 1.74-1.67 (m, 2H), 1.52 (td, J = 13.0, 3.5 Hz, 1H), 1.52-1.43 (m, 1H), 1.37 (tt, J = 10.0, 3.0 Hz, 2H), 1.32-1.28 (m, 1H), 1.04 (tt, J = 12.0, 3.0 Hz, 1H), 0.95 (q, J = 12.0 Hz, 1H), 0.86 (s, 9H), 0.14 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 107.6, 85.0, 84.5, 74.1, 72.6, 47.1, 47.0, 41.2, 32.2, 30.1, 29.8, 27.6, 26.7, 24.6, 20.6, 0.1; IR: 3518, 3309, 2952, 2174, 1366, 1249, 844 cm⁻¹; MS m/z (relative intensity): 318 (16%, M⁺), 285 (12%), 261 (20%), 245 (29%), 149 (27%), 75 (38%), 73 (100%), 57 (70%); HRMS-EI (m/z): [M⁺] calcd for C₂₀H₃₄OSi, 318.2379; found, 318.2365.

38c-eq: Rf = 0.57 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (500 MHz, CDCl₃) δ 2.41 (s, 1H), 2.27-2.23 (m, 2H), 2.10 (dt, J = 14.0, 3.0 Hz, 1H), 2.04-1.96 (m, 1H), 1.73-1.66 (m, 3H), 1.63 (s, 1H), 1.57-1.43 (m, 3H), 1.34-1.26 (m, 2H), 1.04 (tt, J = 9.5, 2.5 Hz, 1H), 0.99 (q, J = 11.5 Hz, 1H), 0.86 (s, 9H), 0.15 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 107.5, 88.4, 84.4, 71.2, 69.4, 47.3, 45.7, 40.5, 32.5, 30.5, 27.5, 27.0, 27.0, 21.6, 20.2, 0.2

34
A flame-dried, single-necked 15 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with the major diastereomer of 37c (351 mg, 1.19 mmol) and THF (4 mL). The solution was cooled in an ice/H₂O bath and 1-propynylmagnesium bromide (4.8 mL, 0.5 M in THF, 2.4 mmol) was added rapidly via syringe and the solution was allowed to warm to rt. After 2.5 h the reaction was complete by TLC and the reaction was diluted with H₂O, Et₂O, and brine (to break up the emulsion). The aq layer was separated and extracted with Et₂O (3 ×). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. Purification of the crude (3:1 dr by crude ¹H NMR) oil via flash chromatography (hexanes/EtOAc, 95:5 to 8:2 v/v) afforded 186 mg 54d-ax and 70 mg 54d-eq separate diastereomers of the title compound with a combined mass of 256 mg (63%) as a faintly yellow oil. 38d-ax: Rᵢ = 0.52 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (500 MHz, CDCl₃) δ: 2.25-2.20 (m, 2H), 2.07 (bs, 1H), 1.98 (dt, J = 12.5, 3.5 Hz, 1H), 1.88-1.81 (m, 1H), 1.84 (s, 3H), 1.75 (dq, J = 13.0, 2.5 Hz, 1H), 1.70-1.64 (m, 2H), 1.50-1.44 (m, 2H), 1.34-1.20 (m, 3H), 1.01 (tt, J = 12.0, 3.5 Hz, 1H), 0.90 (q, J = 12.5 Hz, 1H), 0.85 (s, 9H), 0.14 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 107.7, 84.4, 81.9, 80.2, 72.9, 47.5, 47.2, 41.6, 32.3, 30.3, 30.0, 27.6, 26.8, 24.9, 20.3, 3.5, 0.1; IR: 3406, 2951, 2866, 2246, 2174, 1366, 1249, 1031, 843 cm⁻¹; MS m/z (relative intensity): 332 (6%, M⁺), 317 (9%), 275 (20%), 259 (24%), 167 (46%), 95 (63%), 74 (84%), 72 (100%); HRMS-EI (m/z): [M⁺] calcd for C₂₁H₃₆O₁Si, 332.2535; found, 332.2522.

38d-eq: Rᵢ = 0.61 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (500 MHz, CDCl₃) δ: 2.26-2.23 (m, 2H), 2.04 (dt, J = 14.0, 3.0 Hz, 1H), 1.99-1.92 (m, 1H), 1.83 (s, 3H), 1.74-1.61 (m, 3H), 1.55-
1.45 (m, 3H), 1.41-1.20 (m, 3H), 1.04-0.03 (m, 2H), 0.85 (s, 9H), 0.15 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 107.7, 84.2, 84.0, 79.0, 69.5, 47.4, 46.1, 41.0, 32.5, 30.7, 27.5, 27.3, 27.1, 21.8, 20.3, 3.6, 0.2

4-Tert-butyl-1-ethynyl-2-(3-(trimethylsilyl)prop-2-ynyl)cyclohexyl acetate (39a-ax).

A flame-dried, single-necked 5 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with 38a (45 mg, 0.16 mmol) ~7:1 38a-ax/38a-eq, N,N-dimethyl-4-aminopyridine (20 mg, 0.16 mmol), and NEt$_3$ (0.21 mL, 1.5 mmol). The solution was cooled in an ice/H$_2$O bath and acetic anhydride (0.07 mL, 0.7 mmol) was added via syringe. The solution was warmed to rt. After 19 h the mixture was diluted with Et$_2$O and passed through a plug of silica gel. The filtrate was concentrated in vacuo the crude oil was purified via flash chromatography (hexanes/EtOAc, 95:5, v/v) affording the title compound (48 mg, 93%) as a slightly yellow oil in ~6:1 dr. 39a-ax: R$_f$ = 0.57 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (300 MHz, CDCl$_3$) δ: 2.88-2.84 (m, 1H), 2.97 (dd, J = 16.8, 3.6 Hz, 1H), 2.62 (s, 1H), 2.22 (dd, J = 16.8, 10.8 Hz, 1H), 2.26-2.09 (m, 1H), 2.02 (s, 3H), 1.98-1.85 (m, 1H), 1.77-1.56 (m, 1H), 1.46-1.41 (m, 2H), 1.23-1.03 (m, 2H), 1.87 (s, 9H), 0.16 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 169.2, 106.1, 85.7, 79.7, 79.0, 77.1, 46.8, 46.0, 36.0, 32.3, 29.0, 27.4, 24.3, 21.9, 21.4; IR: 3273, 2958, 2175, 1749, 1367, 1230, 843 cm$^{-1}$; MS m/z (relative intensity): 332 (8%, M$^+$), 317 (8%), 257 (22%), 215 (27%), 117 (89%), 74 (86%), 72 (100%), 55 (98%); HRMS-EI (m/z): [M]$^+$ calcd for C$_{20}$H$_{32}$O$_2$Si, 332.2172; found, 332.2176.
4-Tert-butyl-1-ethynyl-2-(4-(trimethylsilyl)but-3-ynyl)cyclohexyl acetate (39b-ax).

A flame-dried, single-necked 5 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with an 8:1 mixture of 54b-ax/54b-eq (21 mg, 0.069 mmol), N,N-dimethyl-4-aminopyridine (9 mg, 0.07 mmol), and NEt₃ (0.2 mL, 1.4 mmol). The flask was cooled in an ice/H₂O bath and acetic anhydride (0.26 mL, 2.8 mmol) was added via syringe. The solution was warmed to rt and stirred for 17 h. The solution was diluted with Et₂O, passed through a plug of silica gel, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (22 mg, 92%) as a slightly yellow oil as single diastereomer. 39b-ax: Rᵣ = 0.60 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 2.89-2.84 (m, 1H), 2.62 (s, 1H), 2.42-2.16 (m, 2H), 2.10-2.02 (m, 1H), 2.04 (s, 3H), 1.86-1.68 (m, 3H), 1.52-1.37 (m, 3H), 1.18-1.02 (m, 2H), 0.87 (s, 9H), 0.16 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 169.3, 107.4, 84.6, 80.6, 79.7, 76.5, 46.9, 45.5, 36.2, 32.3, 29.8, 29.4, 27.5, 24.2, 22.1, 18.1, 0.2; IR: 3278, 2957, 2174, 1747, 1367, 843 cm⁻¹; MS m/z (relative intensity): 346 (4%, M⁺), 331 (57%), 117 (72%), 72 (100%); HRMS-EI (m/z): [M]⁺ calcd for C₂₁H₃₄O₂Si, 346.2328; found, 346.2329.

4-Tert-butyl-1-ethynyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexyl acetate (39c).

A flame-dried, single-necked 25 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with the major diastereomer of 38c-ax (390 mg, 1.22 mmol), THF (12.2 mL), N,N-dimethyl-4-aminopyridine (80 mg, 0.65 mmol), and NEt₃ (0.94 mL, 6.7 mmol). The solution was cooled in an ice/H₂O bath
and acetic anhydride (0.57 mL, 6.0 mmol) was added via syringe. The solution was allowed to return to rt and stirred for 4 d, whereupon consumption of 33c was observed by TLC brine and saturated aq NH₄Cl were added. The aq layer was separated and extracted with Et₂O (3 ×). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 9:1 v/v) afforded the title compound (335 mg, 76%) as a slightly yellow oil as a single diastereomer. 39c-ax: Rƒ = 0.44 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 2.86-2.81 (m, 1H), 2.59 (s, 1H), 2.23 (t, J = 7.2 Hz, 2H), 2.03 (s, 3H), 1.90-1.78 (m, 2H), 1.72-1.61 (m, 3H), 1.55-1.37 (m, 3H), 1.33-1.21 (m, 1H), 1.15-1.04 (m, 2H), 0.86 (s, 9H), 0.14 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 169.2, 107.5, 84.4, 80.6, 80.0, 76.3, 46.9, 45.7, 36.2, 32.3, 30.0, 29.7, 27.5, 26.8, 24.2, 22.0, 20.1, 0.2; IR: 3309, 2954, 2174, 1747, 1230, 844 cm⁻¹; HRMS-ESI (m/z): [M + Na]⁺ calcd for C₂₂H₃₆O₂NaSi, 383.2382; found, 383.2376.

39c-eq: Rƒ = 0.60 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (500 MHz, CDCl₃) δ: 3.02 (dt, J = 14.5, 3.5 Hz, 1H), 2.53 (s, 1H), 2.31-2.20 (m, 2H), 2.05 (s, 3H), 2.07-2.00 (m, 1H), 1.77-1.63 (m, 2H), 1.62-1.55 (2 H), 1.54-1.44 (m, 2H), 1.40-1.31 (m, 1H), 1.14-1.05 (m, 3H), 0.87 (s, 9H), 0.16 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 169.3, 107.5, 84.5, 84.0, 76.4, 73.4, 46.9, 46.8, 35.4, 32.4, 30.4, 27.4, 27.3, 27.0, 21.7, 21.6, 20.2, 0.2.

4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)-1-(prop-1-ynyl)cyclohexyl acetate (39d-ax).

A flame-dried, single-necked 5 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with the major diastereomer of 38d-ax (186 mg, 0.560 mmol), NEt₃ (0.78 mL, 5.6 mmol), and N,N-dimethyl-4-aminopyridine (69 mg, 0.56 mmol). The solution was
cooled in an ice/H₂O bath and acetic anhydride (0.26 mL, 2.8 mmol) was added via syringe. The solution was warmed to rt and stirred 21 h. The solution was transferred to a separatory funnel and diluted with Et₂O and H₂O. The organic layer was separated and washed with saturated aq NH₄Cl, brine, dried over MgSO₄, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (174 mg, 83%) as a slightly yellow oil as single a diastereomer. R_f = 0.67 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (500 MHz, CDCl₃) δ: 2.73 (dt, J = 12, 3.5 Hz, 1H), 2.23-2.19 (m, 2H), 1.98 (s, 3H), 1.86 (s, 3H), 1.86-1.77 (m, 1H), 1.75-1.71 (m, 1H), 1.67-1.58 (m, 3H), 1.49-1.30 (m, 3H, 1.26-1.18 (m, 1H), 1.07-9.98 (m, 2H), 0.84 (s, 9H), 0.12 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 169.3, 107.6, 84.2, 84.1, 80.8, 76.0, 46.8, 46.0, 36.4, 32.2, 30.1, 29.8, 27.5, 26.8, 24.3, 22.1, 20.2, 3.6, 0.1; IR: 2954, 2250, 2174, 1745, 1366, 1235, 1019, 843; 374 MS m/z (relative intensity): (5%, M⁺), 359 (4%), 331 (24%), 317 (20%), 275 (34%), 257 (39%), 219 (54%), 194 (68%), 117 (100%), 74 (89%), 72 (95%); HRMS-EI (m/z): [M⁺] calcd for C₂₃H₃₈O₂Si, 374.2641; found, 374.2631.

(1S,2S,4S)-4-Tert-butyl-1-ethynyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexyl pivalate (39e-ax).

To a flame-dried, 5 mL round-bottomed flask containing a Teflon-coated stir-bar was added the major diastereomer of 38c-ax (185 mg, 0.581 mmol), CH₃CN (2.3 mL), and trimethylacetic anhydride (0.17 mL, 0.84 mmol). A solution of Sc(OTf)₃ (0.06 mL, 0.1 M in CH₃CN, 0.006 mmol) was added via syringe, immediately the reaction turned a reddish color. After 20 min at rt, consumption of 38c-ax was observed via TLC. The reaction was then quenched with saturated aq NaHCO₃ and diluted with H₂O and Et₂O. The aq layer was separated and extracted with Et₂O (3×). The combined organic layers
were washed with brine, dried over MgSO\textsubscript{4}, filtered and concentrated in vacuo. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (191 mg, 82%) as a solid as a single diastereomer. R\textsubscript{f} = 0.78 (hexanes/EtOAc, 80:20, v/v); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\): 2.87-2.79 (m, 1H), 2.55 (s, 1H), 2.22 (t, J = 7.0 Hz, 2H), 1.90-1.82 (m, 1H), 1.82-1.77 (m, 1H), 1.72-1.60 (m, 3H), 1.53-1.42 (m, 1H), 1.41-1.32 (m, 2H), 1.31-1.22 (m, 1H), 1.17 (s, 9H), 1.12-1.01 (m, 2H), 0.85 (s, 9H), 0.13 (s, 9H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 176.4, 107.4, 84.3, 80.7, 79.2, 76.0, 46.9, 45.9, 39.2, 36.1, 32.2, 30.0, 29.5, 27.5, 27.1, 26.8, 24.2, 20.2, 0.1; IR: 3311, 2957, 2869, 2174, 1739, 1478, 1366, 1249, 1155, 843 cm\textsuperscript{-1}; MS m/z (relative intensity): 402 (13%, M\textsuperscript{+}), 387 (43%), 301 (49%), 243 (44%), 227 (45%), 171 (61%), 159 (84%), 73 (100%); HRMS-EI (m/z): [M]\textsuperscript{+} calcd for C\textsubscript{25}H\textsubscript{42}O\textsubscript{2}Si, 402.2954; found, 402.2950.

\[
\text{(1S,2S,4S)-4-Tert-butyl-1-ethynyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexyl 4-nitrobenzoate (39f-ax).}
\]

To a flame-dried 5 mL round-bottomed flask containing a Teflon-coated stir-bar was added the major diastereomer of 38c-ax (103 mg, 0.323 mmol), \textit{N},\textit{N}-dimethyl-4-aminopyridine (10 mg, 0.08 mmol), and 4-nitrobenzoyl chloride (92 mg, 1.1 mmol). Pyridine (1.6 mL) were added, the flask was equipped with an internal reflux condenser, and placed in a 80 °C oil bath. After 23 h at 80 °C consumption of starting material was observed via TLC. The majority of the solvent was removed in vacuo. The residue was dissolved with CH\textsubscript{2}Cl\textsubscript{2} and saturated aq NaHCO\textsubscript{3}, brined, and H\textsubscript{2}O were added. The mixture was shaken and the organic layer was separated. The organic layer was dried over MgSO\textsubscript{4}, filtered and concentrated in vacuo. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (112 mg, 74%). R\textsubscript{f} = 0.64 (hexanes/EtOAc, 80:20, v/v); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\): 8.31-8.27 (m, 2H), 8.18-8.15 (m, 2H), 2.99 (dt, J = 12.0, 3.5 Hz, 1H), 2.71
(s, 1H), 2.29 (t, J = 7.0 Hz, 2H), 2.01-1.86 (m, 3H), 1.83-1.70 (m, 2H), 1.66-1.37 (m, 4H), 1.23-1.09 (m, 2H), 0.90 (s, 9H), 0.11 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 162.8, 150.4, 136.4, 130.6, 123.5, 107.2, 84.7, 82.0, 79.9, 77.3, 46.8, 46.0, 36.3, 32.3, 30.3, 29.8, 27.5, 26.8, 24.3, 20.4, 0.1; IR: 3300, 2956, 2867, 2173, 1731, 1530, 1348, 1282, 1261, 1098, 842 cm$^{-1}$; MS m/z (relative intensity): 467 (13%, M$^+$), 452 (34%), 300 (30%), 224 (91%), 150 (77%), 73 (100%); HRMS-EI (m/z): [M$^+$] calcd for C$_{27}$H$_{37}$NO$_4$Si, 467.2492; found, 467.2500.

**7-(Trimethylsilyl)hepta-1,6-diyne-3-yl acetate (41a).**

A flame-dried, single-necked 25 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with 5-(trimethylsilyl)pent-4-ynal (250 mg, 1.62 mmol) and THF (5.4 mL). The solution was cooled in an ice/H$_2$O bath and ethynylmagnesium bromide (9.7 mL, 0.5 M in THF, 4.9 mmol) was added rapidly via syringe. After 1 h in an ice/H$_2$O bath, consumption of 5-(trimethylsilyl)pent-4-ynal was observed by TLC and acetyl chloride (0.58 mL, 8.1 mmol) was added via syringe. After stirring 1 h, the reaction was complete by TLC and the solution was diluted with Et$_2$O, H$_2$O, and brine. The aq layer was separated and extracted with Et$_2$O (3 ×). The combined organic layers were washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (197 mg, 55%) as a slightly yellow oil. R$_f$ = 0.59 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (300 MHz, CDCl$_3$) δ: 5.36 (td, J = 6.3, 1.8 Hz, 1H), 2.45 (d, J = 2.1 Hz, 1H), 2.33 (t, J = 7.2 Hz, 2H), 2.02 (s, 3H), 1.98-1.90 (m, 2H), 0.08 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 169.4, 104.8, 85.4, 80.3, 74.0, 62.3, 33.3, 20.7, 15.6, -0.1; IR: 3290, 2961, 2177, 2123, 1747, 1372, 1230, 1047, 845, 761 cm$^{-1}$; MS m/z (relative intensity): 207 (46%, M$^+$), 147 (68%), 117 (89%), 74 (98%), 72 (100%); HRMS-EI (m/z): [M – CH$_3$]$^+$ calcd for C$_{11}$H$_{15}$O$_2$Si, 207.0841; found, 207.0841.
3-Methyl-7-(trimethylsilyl)hepta-1,6-diyne-3-yl acetate (41b).

A flame-dried, single-necked 10 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with 6-(trimethylsilyl)hex-6-yn-2-one (80 mg, 0.48 mmol) and THF (1.6 mL). The solution was cooled in an ice/H$_2$O bath and ethynylmagnesium bromide (2.8 mL, 0.5 M in THF, 1.4 mmol) was added rapidly via syringe. The solution was allowed to slowly warm to rt. After 40 min consumption of 6-(trimethylsilyl)hex-6-yn-2-one was observed by TLC and acetyl chloride (0.17 mL, 2.4 mmol) was added via syringe. After stirring 1 h the reaction was complete by TLC and the solution was diluted with Et$_2$O and the solvent was removed in vacuo. The residue was diluted with Et$_2$O and H$_2$O. The aq layer was separated and extracted with Et$_2$O (3×). The combined organic layers were washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (93 mg, 82%) as a slightly yellow oil. R$_f$ = 0.60 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (300 MHz, CDCl$_3$) δ: 2.54 (s, 1H), 2.41 (t, $J$ = 8.1 Hz, 2H), 2.22-2.12 (m, 1H), 2.06-2.41 (m, 1H), 1.99 (s, 3H), 1.66 (s, 3H), 0.11 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 169.0, 106.0, 84.7, 82.7, 73.9, 73.8, 40.5, 26.2, 21.7, 15.1, -0.01; IR: 3284, 2960, 2177, 1748, 1248, 1087, 845 cm$^{-1}$; MS m/z (relative intensity): 221 (44%, M – CH$_3$), 193 (25%), 161 (29%), 117 (90%), 74 (95%), 72 (100%); HRMS-EI (m/z): [M – CH$_3$]$^+$ calcd for C$_{12}$H$_{17}$O$_2$Si, 221.0998; found, 221.0989.

3-Methyl-8-(trimethylsilyl)octa-1,7-diyne-3-yl acetate (41c).

A flame-dried, single-necked 10 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with 7-(trimethylsilyl)hept-6-yn-2-one (181 mg, 0.993 mmol) and THF (3.3 mL). The solution was cooled in an ice/H$_2$O bath and ethynylmagnesium
bromide (6.0 mL, 0.5 M in THF, 3.0 mmol) was added rapidly via syringe. After 30 min in an ice/H₂O bath, consumption of 7-(trimethylsilyl)hept-6-yn-2-one was observed by TLC and acetyl chloride (0.35 mL, 4.9 mmol) was added via syringe. After stirring an additional 75 min, the reaction was complete by TLC and the solution was diluted with Et₂O, H₂O, and brine. The aq layer was separated and extracted with Et₂O (3×). The combined organic layers were washed with brine (2×), dried over MgSO₄, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (204 mg, 82%) as a slightly yellow oil. Rf = 0.57 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 2.53 (s, 1H), 2.22 (t, J = 7.2 Hz, 2H), 2.04-1.93 (m, 1H), 1.98 (s, 3H), 1.90-1.78 (m, 1H), 1.71-1.57 (m, 2H), 1.64 (s, 3H), 0.09 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 169.1, 106.6, 84.8, 83.4, 74.3, 73.4, 40.5, 26.3, 23.4, 21.8, 19.6, 0.0; IR: 3286, 2959, 2174, 1747, 1369, 1249, 844 cm⁻¹; MS m/z (relative intensity): 235 (50%, M – CH₃), 175 (60%), 117 (99%), 75 (95%), 73 (100%); HRMS-EI (m/z): [M – CH₃]⁺ calcd for C₁₃H₁₉O₂Si, 235.1154; found, 235.1161.

4-Methyl-9-(trimethylsilyl)nona-2,8-diyn-4-yl acetate (41d).

To a flame-dried, 25 mL round-bottomed flask equipped with a Teflon-coated stir-bar was added 7-(trimethylsilyl)hept-6-yn-2-one (318 mg, 1.74 mmol) and THF (5.8 mL). The solution was cooled in an ice/H₂O bath and 1-propynylmagnesium bromide (10.5 mL, 0.5 M in THF, 5.25 mmol) was added via syringe. The reaction was stirred for 1h in an ice/H₂O bath until consumption of starting material was observed via TLC. Acetyl chloride (0.62 mL, 8.7 mmol) was added via syringe and the reaction was warmed to rt. After 2 h at rt, the starting material was consumed by TLC and the reaction was diluted with Et₂O and H₂O. The aq layer was separated and extracted with Et₂O (2×). The
combined organic layers were washed with brine, dried over MgSO\(_4\), filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 90:10, v/v) afforded the title compound (380 mg, 83%). R\(_f\) = 0.58 (hexanes/EtOAc, 80:20, v/v); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 2.23 (t, \(J = 6.9\) Hz, 2H), 2.05-1.91 (m, 1H), 1.98 (s, 3H), 1.86-1.77 (m, 1H), 1.82 (s, 3H), 1.75-1.62 (m, 2H), 1.62 (s, 3H), 0.12 (s, 9H); \(^1^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 169.3, 106.9, 84.7, 81.3, 79.2, 75.4, 41.0, 26.7, 23.7, 22.0, 19.8, 3.6, 0.1; IR: 2959, 2921, 2250, 2175, 1745, 1369, 1247, 1169, 1017, 844.1 cm\(^{-1}\). MS m/z (relative intensity): 264 (46%, M\(^+\)), 250 (35%), 223 (96%), 149 (95%), 148 (97%), 96 (100%); HRMS-EI (m/z): [M]\(^+\) calcd for C\(_{15}\)H\(_{24}\)O\(_2\)Si, 264.1546; found, 264.1542.

6-Methyl-1-(trimethylsilyl)undeca-1,7-diyn-6-ol (60e).

To a flame-dried 50 mL round-bottomed flask equipped with a Teflon-coated stir-bar was added THF (13.4 mL) and 1-pentyne (0.66 mL, 6.7 mmol). The solution was cooled to -78 °C and n-BuLi (0.79 ml, 1.6 M in hexanes, 1.3 mmol) was added via syringe. The reaction was stirred 30 min at -78 °C and a solution of 7-(trimethylsilyl)hept-6-yn-2-one (153 mg, 0.840 mmol) in THF (0.8 mL) was added via syringe. The solution was warmed to rt. After 1 h at rt, consumption of starting material was observed via TLC and the reaction was quenched with saturated aq NH\(_4\)Cl and diluted with Et\(_2\)O and H\(_2\)O. The aq layer was separated and extracted with Et\(_2\)O (3×). The combined organic layers were washed with brine, dried over MgSO\(_4\), filtered and concentrated in vacuo. Purification of the crude material via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (141 mg, 67%). R\(_f\) = 0.56 (hexanes/EtOAc, 80:20, v/v); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 2.27-2.19 (m, 2H), 2.16 (s, 1H), 2.13 (t, \(J = 6.9\) Hz, 2H), 1.76-1.64 (m, 4H), 1.48 (sext, \(J = 7.2\) Hz, 2 H), 1.43 (s, 3H), 0.94 (t, \(J = 7.5\) Hz, 3H), 0.11 (s 9H); \(^1^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 107.1, 84.6,
6-Methyl-1-(trimethylsilyl)undeca-1,7-diyn-6-yl acetate (41e).

To a flame-dried, 5 mL round-bottomed flask equipped with a stir-bar was added 60e (141 mg, 0.563 mmol), CH$_2$Cl$_2$ (1.1 mL), NEt$_3$ (0.31 mL, 2.2 mmol), and N,N-dimethyl-4-aminopyridine (22 mg, 0.18 mmol). The mixture was cooled in an ice/H$_2$O bath and acetic anhydride (0.11 mL, 1.2 mmol) was added via syringe. The reaction was warmed to rt and stirred for 11 h. The solution was then diluted with H$_2$O and Et$_2$O and quenched with the addition of saturated aq NH$_4$Cl. The aq layer was separated and extracted with Et$_2$O (3×). The combined organic layers were washed with brined, dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification of the crude material via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (120 mg, 73%). R$_f$ = 0.64 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 2.27-2.22 (m, 2H), 2.17 (t, $J = 7.0$ Hz, 2H), 2.01-1.95 (m, 1H), 1.99 (s, 3H), 1.86-1.80 (m, 1H), 1.73-1.66 (m, 2H), 1.64 (s, 3H), 1.51 (sext, $J = 7.0$ Hz, 2H), 0.96 (t, $J = 7.5$ Hz, 3H), 0.14 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 169.2, 107.0, 85.7, 85.0, 80.3, 75.5, 41.0, 26.8, 23.8, 22.0, 20.6, 19.8, 13.4, 0.1; IR: 2961, 2873, 2245, 2175, 1746, 1368, 1246, 843 cm$^{-1}$; MS m/z (relative intensity): 292 (3%, M$^+$), 291 (6%), 277 (32%), 250 (24%), 126 (45%), 117 (100%), 111 (70%), 96 (47%), 83 (69%); HRMS-EI (m/z): [M – CH$_3$]$^+$ calcd for C$_{18}$H$_{25}$O$_2$Si, 277.1624; found, 277.1625.
3-Methyl-9-(trimethylsilyl)nona-1,8-diyn-3-ol (60f).

To a flame-dried, 50 mL round-bottomed flask containing a Teflon-coated stir-bar was added NaH (426 mg, 60% dispersion in mineral oil, 10.7 mmol) and THF (7.6 mL). The resulting suspension was cooled in an ice/H$_2$O bath and methyl acetoacetate (1.39 mL, 11.4 mmol) was added via syringe. The reaction was stirred 5 min in an ice/H$_2$O bath and then warmed to rt. After 10 min at rt a solution of 5-iodo-1-(trimethylsilyl)-1-pentyne (2.024 g, 7.60 mmol) in DMF (7.6 mL) was added via syringe. The reaction was stirred 16 h at rt and then diluted with H$_2$O and Et$_2$O. The aq layer was separated and extracted with Et$_2$O (3×). The combined organic layers were washed with brine (3×), dried over MgSO$_4$, filtered, and concentrated in vacuo for 2.282 g. The residue was transferred to a 100 mL round-bottomed flask containing a Teflon-coated stir-bar along with DMSO (38 mL), H$_2$O (0.16 mL, 8.9 mmol), and LiCl (979 mg, 23.1 mmol). The flask was equipped with a coil type reflux condenser that was open to the atmosphere and placed in a preheated 130 °C oil bath. After 23 h no starting material ($R_f = 0.51$ (hexanes/EtOAc, 80:20, v/v)) was observed by TLC. The reaction was cooled to rt and diluted with H$_2$O and Et$_2$O. The aq layer was separated and extracted with Et$_2$O (4×). The combined organic layers were washed with brine (4×), dried over MgSO$_4$, filtered, and concentrated in vacuo yielding 1.315 g of 8-(trimethylsilyl)oct-7-yn-2-one. To a flame-dried 100 mL flask containing a Teflon-coated stir-bar was added 697 mg of the crude material and THF (36 mL). The solution was cooled in an
ice/H$_2$O bath and ethynylmagnesium bromide (21 mL, 0.5 M in THF, 11 mmol) was added via syringe. After 1 h in an ice/H$_2$O bath consumption of the ketone ($R_f = 0.58$ (hexanes/EtOAc, 80:20, v/v)) was observed by TLC and the reaction was quenched with saturated aq NH$_4$Cl. The reaction mixture was diluted with Et$_2$O and H$_2$O. The aq layer was separated and extracted with Et$_2$O (3×). The combined organic layers were washed with brine, dried over MgSO$_4$, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 9:1 v/v) affording the title compound (529 mg, 59%). $R_f = 0.49$ (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 2.42 (s, 1H), 2.25 (bs, 1H), 2.23 (t, J = 6.3 Hz, 2H), 1.69-1.51 (m, 6H), 1.47 (s, 3H), 0.12 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 107.2, 87.6, 84.6, 71.3, 67.9, 42.8, 29.6, 28.5, 23.7, 19.7, 0.1; IR: 3288, 2955, 2174, 1747, 1246, 844 cm$^{-1}$ 3403, 3307, 2950, 2866, 2173, 1372, 1250, 844, 760; MS m/z (relative intensity): 222 (37%, M$^+$), 207 (82%), 189 (45%), 139 (48%), 75 (100%); HRMS-EI (m/z): [M]$^+$ calcd for C$_{13}$H$_{22}$OSi, 222.1440; found, 222.1439.

3-Methyl-9-(trimethylsilyl)nona-1,8-diyn-3-yl acetate (41f).

To a flame-dried 5 mL round-bottomed containing a Teflon-coated stir-bar was added 60f (200 mg, 0.899 mmol), CH$_2$Cl$_2$ (1.8 mL), NEt$_3$ (0.50 mL, 3.6 mmol), and N,N-dimethyl-4-aminopyridine (32 mg, 0.26 mmol). The mixture was cooled in an ice/H$_2$O bath and acetic anhydride (0.17 mL, 1.8 mmol) was added via syringe. The reaction was warmed to rt and stirred for 22 h until no starting material was observed by TLC. The reaction was opened and diluted with H$_2$O and Et$_2$O. The aq layer was separated and extracted with Et$_2$O (3×). The combined organic layers were washed with brined, dried over MgSO$_4$, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 95:5 v/v) affording the title compound (155 mg, 65%). $R_f =$
0.64 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 2.53 (s, 1H), 2.24 (t, $J = 6.9$ Hz, 2H), 2.01 (s, 3H), 1.98-1.87 (m, 1H), 1.86-1.76 (m, 1H), 1.67 (s, 3H), 1.65-1.48 (m, 4H), 0.13 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 169.2, 107.0, 84.7, 83.8, 74.7, 73.2, 40.8, 28.3, 26.3, 23.2, 21.8, 19.7, 0.1; IR: 3288, 2955, 2868, 2174, 1747, 1369, 1246, 844 cm$^{-1}$; MS m/z (relative intensity): 249 (51%, M -CH$_3$), 207 (36%), 189 (90%), 148 (75%), 118 (87%), 83 (91%), 59 (100%); HRMS-EI (m/z): [M – CH$_3$]$^+$ calcd for C$_{14}$H$_{21}$O$_2$Si, 249.1311; found, 249.1310.

3-Methyl-10-(trimethylsilyl)deca-1,9-diyn-3-ol (60g).

To a flame-dried, 25 mL round-bottomed flask containing a Teflon-coated stir-bar was added NaH (231 mg, 60% dispersion in mineral oil, 5.78 mmol) and THF (4.3 mL). The resulting suspension was cooled in an ice/H$_2$O bath and methyl acetoacetate (0.69 mL, 6.4 mmol) was added via syringe. The reaction was warmed to rt. After stirring 40 min a solution of 6-iodo-1-(trimethylsilyl)-1-hexyne (1.20 g, 4.3 mmol) in DMF (4.3 mL) was added via syringe. The reaction was stirred 15 h and then diluted with H$_2$O and Et$_2$O. The aq layer was separated and extracted with Et$_2$O (2×). The combined organic layers were washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo for 1.042 g. The ketoester (737 mg) was transferred to a 25 mL round-bottomed flask containing a Teflon-coated stir-bar along with DMSO (12 mL), H$_2$O (0.06 mL, 3.3 mmol), and LiCl (364 mg, 8.59 mmol). The flask was equipped with a coil type reflux condenser open to the atmosphere and placed in a preheated 130 °C oil bath. After 21
h stirring no starting material ($R_f = 0.53$ (hexanes/EtOAc, 80:20, v/v)) was observed by TLC. The reaction was cooled to rt and diluted with H$_2$O and Et$_2$O. The aq layer was separated and extracted with Et$_2$O (4×). The combined organic layers were washed with brine (4×), dried over MgSO$_4$, filtered, and concentrated in vacuo in a 50 mL round-bottomed flask yielding 521 mg of 9-(trimethylsilyl)non-8-yn-2-one. To the 50 mL flask was added a stir-bar and THF (11.2 mL). The solution was cooled in an ice/H$_2$O bath and ethynylmagnesium bromide (13.4 mL, 0.5 M in THF, 6.7 mmol) was added via syringe. After 1 h in an ice/H$_2$O bath consumption of the crude ketone ($R_f = 0.66$ (hexanes/EtOAc, 80:20, v/v)) was observed by TLC and the reaction was quenched with saturated aq NH$_4$Cl. The reaction mixture was diluted with Et$_2$O and H$_2$O. The aq layer was separated and extracted with Et$_2$O (3×). The combined organic layers were washed with brine (2×), dried over MgSO$_4$, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 9:1 v/v) affording the title compound (204 mg, 28% over three steps). $R_f = 0.53$ (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 2.42 (s, 1H), 2.22 (t, $J = 7.2$ Hz, 2H), 2.17 (s, 1H), 1.69-1.38 (m, 9H), 1.48 (s, 3H), 0.13 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 107.4, 87.7, 84.4, 71.3, 67.9, 43.2, 29.7, 28.7, 28.4, 24.0, 19.7, 0.1; IR: 3394, 3307, 2940, 2862, 1733, 1271, 1120, 1083, 843, 760 cm$^{-1}$; MS m/z (relative intensity): 221 (44%, M –CH$_3$)), 203 (21%), 153 (24%), 145 (35%), 109 (100%), 96 (85%); HRMS-EI (m/z): [M – CH$_3$]$^+$ calcd for C$_{13}$H$_{21}$OSi, 221.1361; found, 221.1355.

3-Methyl-10-(trimethylsilyl)deca-1,9-diyn-3-yl acetate (41g).

To a 15 mL round-bottomed flask containing a Teflon-coated stir-bar was added 60g (204 mg, 0.863 mmol), CH$_2$Cl$_2$ (1.7 mL), NEt$_3$ (0.48 mL, 3.4 mmol), and $N,N$-dimethyl-4-aminopyrididine (31 mg, 0.26 mmol). The mixture was cooled in an ice/H$_2$O bath and acetic anhydride (0.16 mL, 1.7 mmol) was added via syringe. The reaction was warmed to rt.
After 17 h further consumption of 60g was no longer observed by TLC. The reaction was diluted with H₂O and Et₂O. The aq layer was separated and extracted with Et₂O (3×). The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 95:5 v/v) affording the title compound (184 mg, 77%). Rᶠ = 0.69 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 2.52 (s, 1H), 2.20 (t, J = 6.9 Hz, 2H), 1.99 (s, 3H), 1.97-1.87 (m, 1H), 1.82-1.72 (m, 1H), 1.63 (s, 3H), 1.56-1.37 (m 6H), 0.11 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 169.2, 107.3, 84.4, 83.8, 74.7, 73.1, 41.1, 28.5, 28.3, 26.3, 23.5, 21.8, 19.7, 0.1; IR: 3287, 2942, 2864, 2173, 2118, 1747, 1369, 1244, 1042, 844 cm⁻¹; MS m/z (relative intensity): 279 (9%, M+1), 263 (32%), 235 (72%), 203 (86%), 97 (100%), 79 (98%).

**General Procedure for the AuCl₃ Catalyzed Allenol Ester Formation:** A flame-dried, 5 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with AuCl₃ (0.1 equiv) in a glove box. The flask was removed from the glove box, wrapped in aluminum foil, and placed under N₂. A solution of propargyl acetate in toluene (0.2 M, toluene degassed by bubbling with nitrogen for ~5 min) was added rapidly via cannula. The reaction was stirred at rt in a darkened hood. When the reaction was complete as observed by TLC, the mixture was passed through a plug of silica gel using hexanes/EtOAc and concentrated in vacuo. The crude material was purified via flash chromatography.
2-(4-Tert-butyl-2-(3-(trimethylsilyl)prop-2-yny)l)cyclohexylidene)vinyl acetate (42a).

Following the General Procedure for the AuCl₃ Catalyzed Allenol Acetate Formation, AuCl₃ (2 mg, 0.01 mmol) and propargyl acetate 39a-ax (19 mg, 0.057 mmol, ~6:1 dr (major/minor)) were reacted in toluene (0.29 mL) for 3 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (16 mg, 84%) as a colorless oil in an ~1:1 dr. Rₐ = 0.67 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 7.39* (t, J = 2.1 Hz, 0.5H), 7.34** (t, J = 2.4, 0.5H), 2.50-2.43 (m, 2H), 2.34-1.88 (m, 4H), 2.21-2.03 (m, 2H), 2.14 (s, 1.5H), 2.13 (s, 1.5H), 1.31-1.10 (m, 2H), 0.97-0.82 (m, 1H), 0.90* (s, 4.5H), 0.89** (s, 4.5H), 0.15 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 185.6*, 185.5**, 168.7, 121.7*, 121.7**, 111.4**, 111.1*, 105.9**, 105.9*, 86.0, 47.6**, 47.4*, 40.5*, 40.4**, 34.0, 32.3**, 33.1*, 32.6**, 32.6*, 28.2*, 28.0*, 27.5*, 27.5**, 24.7*, 24.6**, 21.0**, 20.9*, 0.13; IR: 2957, 2175, 1976, 1757, 1367, 1213, 1036, 842 cm⁻¹; HRMS-ESI (m/z): [M + Na]⁺ calcd for C₂₀H₃₂O₂NaSi, 355.2069; found, 355.2062.

*diastereomer 1; **diastereomer 2
Spectra Recorded as ~1:1 mixture of diastereomers

2-(4-Tert-butyl-2-(4-(trimethylsilyl)but-3-yny)l)cyclohexylidene)vinyl acetate (42b).

Following the General Procedure for the AuCl₃ Catalyzed Allenol Ester Formation, AuCl₃ (2 mg, 0.01 mmol) and propargyl acetate 39b-ax (20 mg, 0.058 mmol) were reacted in toluene (0.29 mL) for 40 min. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (16 mg, 80%) as a colorless oil in an ~1:1 dr. Rₐ = 0.71 (hexanes/EtOAc, 80:20, v/v);
\(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.38* (t, \(J = 2.5\) Hz, 0.5H), 7.36** (t, \(J = 2.5\) Hz, 0.5H), 2.51-2.46 (m, 1H), 2.31-2.27 (m, 2H), 2.18-2.12 (m, 1H), 2.15** (s, 1.5H), 2.15* (s, 1.5H), 2.11-2.05 (m, 1H), 2.05-1.96 (m, 1H), 1.96-1.90 (m, 1H), 1.84-1.74 (m, 1H), 1.48-1.40 (m, 1H), 1.23-1.11 (m, 2H), 0.95-0.81 (m, 1H), 0.89** (s, 4.5H), 0.88* (s, 4.5H), 0.16* (s, 4.5H), 0.15** (s, 4.5H); 

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 186*, 185**, 168.8, 122.9*, 122.8**, 110.9*, 110.8**, 107.4*, 107.3**, 84.6, 47.8**, 47.7*, 40.3**, 40.2*, 34.7*, 34.5**, 33.6*, 33.6**, 32.5*, 32.5*, 32.3, 28.5**, 28.4*, 27.6*, 27.6**, 21.1**, 21.0*, 17.6**, 17.5*, 0.2; IR: 2953, 2173, 1974, 1756, 1367, 1214, 1035, 842 cm\(^{-1}\); HRMS-ESI (m/z): [M + Na]\(^{+}\) calcd for C\(_{21}\)H\(_{34}\)O\(_2\)NaSi, 369.2226; found, 369.2211.

Spectra Recorded as ~1:1 mixture of diastereomers

*diastereomer 1; **diastereomer 2

**2-(4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexylidene)vinyl acetate (42c).**

Following the General Procedure for the AuCl\(_3\) Catalyzed Allenol Ester Formation, AuCl\(_3\) (4 mg, 0.01 mmol) and propargyl acetate 38c (58 mg, 0.16 mmol) were reacted in toluene (0.81 mL) for 40 min.

Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (33 mg, 74%) as a colorless oil in an ~1:1 dr. Diastereomers were separated via flash chromatography (hexanes/CH\(_2\)Cl\(_2\)/benzene, 16:4:1 v/v/v). Major Diastereomer 42c: \(R_f = 0.17\) (hexanes/CH\(_2\)Cl\(_2\)/benzene, 16:4:1 v/v/v); \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.37* (t, \(J = 2.5\) Hz, 0.75H), 7.35** (t, \(J = 3\) Hz, 0.25H), 2.50-2.45 (m, 1H), 2.23-2.19 (m, 2H), 2.15** (s, 0.75H), 2.14* (s, 2.25H), 2.16-1.89 (m, 5H), 1.67-1.53 (m, 4H), 1.36-1.09 (m, 3H), 0.95-0.74 (m, 1H), 0.88** (s, 2.25H), 0.87* (s, 6.75), 0.15 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 185.9, 168.8,
123.2, 110.8, 107.5, 84.3, 47.7, 40.9, 35.1, 33.7, 33.2, 32.5, 28.4, 27.6, 26.3, 20.9, 20.1, 0.2; IR: 2954, 2174, 1975, 1751, 1367, 1215, 1036, 842 cm\(^{-1}\); HRMS-ESI (m/z): \([M + Na]^+\) calcd for C\(_{22}\)H\(_{36}\)O\(_2\)NaSi, 383.2382; found, 383.2354.

Spectra Recorded as ~3:1 mixture of diastereomers

Minor Diastereomer 42c: \(R_f = 0.17\) (hexanes/CH\(_2\)Cl\(_2\)/benzene, 16:4:1 v/v/v); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.37\* (t, \(J = 2.5\) Hz, 0.25H), 7.35 (t, \(J = 2.5\) Hz, 0.75H), 2.51-2.44 (m, 1H), 2.26-2.18 (m, 2H), 2.15** (s, 2.25H), 2.14* (s, 0.75H), 2.12-1.89 (m, 4H), 1.68-1.52 (m, 4H), 1.35-1.11 (m, 4H), 0.96-0.82 (m, 1H), 0.89** (s, 2.25H), 0.87* (s, 6.75H), 0.15, (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 185.7, 168.8, 123.2, 110.7, 107.6, 84.4, 47.9, 40.9, 34.9, 33.6, 33.0, 32.5, 28.5, 27.6, 26.3, 21.1, 20.1, 0.2

Spectra Recorded as ~1:3 mixture of diastereomers

*diastereomer 1; **diastereomer 2

\[1-(4\text{-}\text{tert-butyl-2-(5\text{-(trimethylsilyl)pent-4-}}\text{ynyl)cyclohexylidene})\text{prop-1-en-2-yi acetate (42d).}\]

Following the General Procedure for the AuCl\(_3\) Catalyzed Allenol Ester Formation, AuCl\(_3\) (3 mg, 0.01 mmol) and propargyl acetate 39d-ax (56 mg, 0.15 mmol, major diastereomer) were reacted in toluene (0.75 mL) for 5 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (30 mg, 54%) as a colorless oil in an ~1:1 dr. \(R_f = 0.67\) (hexanes/EtOAc, 80:20, v/v); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 2.50-2.40 (m, 1H), 2.28-2.15 (m, 2H), 2.11* (s, 1.5H), 2.10** (s, 1.5H), 2.05-1.86 (m, 4H), 1.97** (s, 1.5H), 1.95* (s, 1.5H), 1.69-1.48 (m, 3H), 1.34-1.23 (m, 1H), 1.23-1.00 (m, 2H), 0.93-0.80 (m, 1H), 0.87* (s, 4.5H), 0.86**
(s, 4.5H), 0.15 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 187.7, 169.1*, 169.0**, 120.2**, 120.0*, 118.7**, 118.6*, 107.8**, 107.8*, 48.0*, 47.8**, 41.3*, 40.9**, 35.4*, 35.1**, 33.3**, 33.2*, 33.2**, 32.5, 28.6*, 28.6**, 27.6*, 27.6**, 26.6*, 26.3**, 21.3*, 21.1**, 20.1**, 20.0*, 18.7**, 18.4*, 0.2; IR: 2954, 2174, 1981, 1750, 1366, 1221, 1125, 842 cm$^{-1}$; MS $m/z$ (relative intensity): 374 (7%, M$^+$), 359 (49%), 358 (53%), 331 (29%), 194 (100%), 117 (39%), 75 (34%); HRMS-EI ($m/z$): [M]$^+$ calcd for C$_{23}$H$_{38}$O$_2$Si, 374.2641; found, 374.2639.

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~1:1 mixture of diastereomers

2-((2S,4S)-4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexylidene)vinyl pivalate (42e).

Following the General Procedure for the AuCl$_3$ Catalyzed Allenol Ester Formation, AuCl$_3$ (2 mg, 0.01 mmol) and propargyl acetate 39e-ax (39 mg, 0.097 mmol, 1 diastereomer) were reacted in toluene (0.48 mL) for 50 min. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (35 mg, 91%) as a colorless oil in an ~2:1 dr. $R_f$ = 0.81 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.34* (t, $J = 2.0$ Hz, 0.66H), 7.30** (t, $J = 2.5$ Hz, 0.33H), 2.51-2.45 (m, 1H), 2.26-1.84 (m, 6H), 1.66-1.48 (m, 3H), 1.38-1.09 (m, 3H), 1.26** (s, 3H), 1.25* (s, 6H), 0.96-0.83 (m, 1H), 0.89** (s, 3H), 0.87* (s, 6H), 0.15** (s, 3H), 0.14* (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 186.0*, 186.0**, 176.4**, 176.4*, 122.3, 110.9*, 110.8**, 107.6**, 107.5*, 84.3**, 84.1*, 47.9**, 47.8*, 41.2*, 40.8**, 39.0*, 38.9**, 35.8*, 34.7**, 34.6**, 33.6*, 33.5*, 33.4**, 32.8**, 32.5**, 32.5*, 31.6*, 28.6*, 28.4**, 27.6**, 27.6*, 27.1, 26.4*, 25.9**, 25.3**, 22.6*, 20.7**, 20.1**, 20.1*, 14.1*, 0.2; IR: 3066, 2958, 2867, 2174, 1990, 1741, 1480, 1249, 1133, 843 cm$^{-1}$; MS $m/z$ (relative intensity): 402
(12%, M⁺), 387 (15%), 263 (20%), 180 (62%), 159 (54%), 119 (65%), 117 (66%), 85 (71%), 73 (100%), 57 (97%); HRMS-EI (m/z): [M⁺] calcd for C₂₅H₄₂O₂Si, 402.2954; found, 402.2940.

*diastereomer 1; ** diastereomer 2

Spectra Recorded as ~2:1 mixture of diastereomers

2-((2S,4S)-4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexyldiene)vinyl 4-nitrobenzoate (42f).

Following the General Procedure for the AuCl₃ Catalyzed Allenol Ester Formation, AuCl₃ (2 mg, 0.01 mmol) and propargyl acetate 39f-ax (40 mg, 0.086 mmol, 1 diastereomer) were reacted in toluene (0.43 mL) for 16 h. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (35 mg, 87%) as a colorless oil in an ~1:1 dr. Rf = 0.78 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (500 MHz, CDCl₃) δ: 8.33-8.26 (m, 4H), 7.60* (t, J = 2.0 Hz, 0.5H), 7.57** (t, J = 3.0 Hz, 0.5H), 2.56-2.52 (m, 1H), 2.28-1.93 (m; 6H), 1.73-1.55 (m, 3H), 1.41-1.32 (m, 1H), 1.31-1.14 (m, 2H), 1.02-0.06 (m, 1H), 0.91** (s, 4.5H), 0.87* (s, 4.5H), 0.12** (s, 4.5H), 0.09* (s, 4.5H); ¹³C NMR (75 MHz, CDCl₃) δ: 186.3*, 186.2**, 162.6**, 162.6*, 150.6, 135.1**, 135.0*, 131.0**, 131.0*, 124.3**, 124.2*, 123.6, 111.2*, 111.1**, 107.4**, 107.3*, 84.5**, 84.4*, 47.8**, 47.7*, 41.0, 35.2*, 34.8**, 33.6*, 33.5**, 33.2*, 33.0**, 32.5**, 32.5**, 28.5, 27.6**, 27.6*, 26.3*, 26.2**, 20.6, 0.1; IR: 2953, 2863, 2173, 1982, 1733, 1531, 1279, 1250, 1100, 845 cm⁻¹; MS m/z (relative intensity): 467 (35%, M⁺), 452 (55%), 329 (82%), 300 (92%), 224 (84%), 171 (67%), 104 (86%), 73 (100%), 58 (95%); HRMS-EI (m/z): [M⁺] calcd for C₂₇H₃₇NO₄Si, 467.2492; found, 467.2512.

* diastereomer 1; ** diastereomer 2

Spectra Recorded as ~1:1 mixture of diastereomers
3-Methyl-7-(trimethylsilyl)hepta-1,2-dien-6-ynyl acetate (45b).

Following the General Procedure for the AuCl₃ Catalyzed Allenol Ester Formation, AuCl₃ (4 mg, 0.01 mmol) and propargyl acetate 41b (28 mg, 0.12 mmol) were reacted in toluene (0.60 mL) for 19 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (13 mg, 46%) as a colorless oil. Rf = 0.65 (hexanes/EtOAc, 90:10, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 7.33 (q, J = 2.1 Hz, 1H), 2.41-2.25 (m, 4H), 2.14 (s, 3H), 1.86 (d, J = 2.1 Hz, 3H), 0.15 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 190.2, 169.3, 115.1, 111.1, 106.9, 85.6, 34.7, 21.5, 21.1, 18.9, 0.7; IR: 2959, 2176, 1979, 1752, 1214, 1051, 842 cm⁻¹; HRMS-EI (m/z): [M⁺] calcd for C₁₃H₂₀O₂Si, 236.1232; found, 236.1234.

3-Methyl-8-(trimethylsilyl)octa-1,2-dien-7-ynyl acetate (45c).

Following the General Procedure for the AuCl₃ Catalyzed Allenol Ester Formation, AuCl₃ (7 mg, 0.02 mmol) and propargyl acetate 41c (39 mg, 0.16 mmol) were reacted in toluene (0.78 mL) for 4 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (27 mg, 67%) as a colorless oil. Rf = 0.68 (hexanes/EtOAc, 90:10, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 7.32 (q, J = 2.1 Hz, 1H), 2.27 (t, J = 6.9 Hz, 2H), 2.22-2.08 (m, 2H), 2.14 (s, 3H), 1.85 (d, J = 2.1 Hz, 3H), 1.68 (quint J = 7.5 Hz, 2H) 0.14 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 189.4, 168.8, 115.3, 110.0, 106.8, 84.9, 34.0, 26.1, 20.9, 20.6, 19.3, 0.1; IR: 2956, 2174, 1976, 1750, 1250, 1215, 1056, 843 cm⁻¹.
4-Methyl-9-(trimethylsilyl)nona-2,3-dien-8-yn-2-yl acetate (45d).

Following the General Procedure for the AuCl₃ Catalyzed Allenol Ester Formation, AuCl₃ (3 mg, 0.01 mmol) and propargyl acetate 41d (42 mg, 0.16 mmol) were reacted in toluene (0.80 mL) for 1.5 h. Purification via flash chromatography (hexanes/EtOAc, 95: 5, v/v) afforded the title compound (27 mg, 64%) as a colorless oil. Rₚ = 0.66 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 2.25 (t, J = 6.9 Hz, 2H), 2.13 (td, J = 7.5, 3.0 Hz, 2H), 2.10 (s, 3H), 1.93 (s, 3H), 1.79 (s, 3H), 1.68 (quint, J = 7.2 Hz, 2H), 0.15 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 191.4, 168.9, 119.2, 110.7, 107.1, 84.7, 33.9, 26.1, 21.1, 20.2, 19.2, 18.4, 0.1; IR: 2956, 2901, 2174, 1983, 1753, 1433, 1368, 1249, 1220, 1126, 843 cm⁻¹; MS m/z (relative intensity): 264 (14%, M⁺), 263 (45%), 222 (54%), 221 (50%), 149 (60%), 117 (62%), 98 (100%), 83 (80%), 73 (98%); HRMS: m/z calculated for C₁₅H₂₄O₂Si, 264.1546; found, 264.1539.

6-Methyl-11-(trimethylsilyl)undeca-4,5-dien-10-yn-4-yl acetate (45e).

Following the General Procedure for the AuCl₃ Catalyzed Allenol Ester Formation, AuCl₃ (12 mg, 0.04 mmol) and propargyl acetate 41e (120 mg, 0.41 mmol) were reacted in toluene (2.0 mL) for 80 min. Purification via flash chromatography (hexanes/EtOAc, 99:1, v/v) afforded the title compound (69 mg, 58%) as a colorless oil. Rₚ = 0.67 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 2.25 (t, J = 6.9 Hz, 2H), 2.20-2.12 (m, 4H), 2.10 (s, 3H), 1.80 (s, 3H), 1.69 (quint, J = 6.9, 2H), 1.43 (sext, J = 7.2 Hz, 2H), 0.95 (t, J = 7.2 Hz, 3H), 0.13 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 191.1, 168.9, 122.8, 111.7, 107.1, 84.7, 34.0, 33.8, 26.2, 21.1, 20.3, 19.7, 19.4, 13.6, 0.1; IR: 2959, 2174, 1979, 1753, 1367,
1214, 842.3 cm$^{-1}$; MS $m/z$ (relative intensity): 277 (8%, M – CH$_3$), 250 (38%), 249 (41%), 177 (39%), 117 (68%), 83 (98%), 73 (100%); HRMS-EI ($m/z$): [M – CH$_3$]$^+$ calcd for C$_{16}$H$_{25}$O$_2$Si, 277.1624; found, 277.1621.

**3-Methyl-9-(trimethylsilyl)nona-1,2-dien-8-ylnyl acetate (45f).**

Following the General Procedure for the AuCl$_3$ Catalyzed Allenol Ester Formation, AuCl$_3$ (4 mg, 0.01 mmol) and propargyl acetate 41f (32 mg, 0.12 mmol) were reacted in toluene (0.61 mL) for 30 min. Purification via flash chromatography (hexanes/EtOAc, 9:1, v/v) afforded the title compound (25 mg, 79%) as a colorless oil. R$_f$ = 0.69 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.30 (sext, $J$ = 2.1 Hz, 1H), 2.26-2.20 (m, 2H), 2.16-2.02 (m, 2H), 2.13 (s, 3H), 1.83 (d, $J$ = 2.1 Hz, 3H), 1.61-1.49 (m, 4H), 0.14 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 189.4, 168.8, 115.7, 109.7, 107.2, 84.6, 34.6, 28.0, 26.3, 20.9, 20.4, 19.6, 0.1; IR: 3065, 2943, 2862, 2174, 1976, 1750, 1456, 1369, 1249, 1215, 1066, 1039, 843 cm$^{-1}$; MS $m/z$ (relative intensity): 249 (36%, M-CH$_3$), 222 (26%), 117 (100%), 75 (97%), 109 (88%), 84 (88%), 73 (95%); HRMS-EI (m/z): [M – CH$_3$]$^+$ calcd for C$_{14}$H$_{21}$O$_2$Si, 249.1311; found, 249.1308.

**3-Methyl-10-(trimethylsilyl)deca-1,2-dien-9-ylnyl acetate (45g).**

Following the General Procedure for the AuCl$_3$ Catalyzed Allenol Ester Formation, AuCl$_3$ (5 mg, 0.02 mmol) and propargyl acetate 41g (37 mg, 0.13 mmol) were reacted in toluene (0.66 mL) for 30 min. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (28 mg, 77%) as a colorless oil. R$_f$ = 0.63 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.29 (sext, $J$ = 2.1 Hz, 1H), 2.22 (t, $J$ = 6.9 Hz, 2H), 2.13 (s, 3H), 2.16-2.01 (m, 2H), 1.83 (d, $J$ = 2.1 Hz,
3H), 1.60-1.37 (m, 6H), 0.14 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 189.3, 168.8, 115.9, 109.7, 107.5, 84.4, 34.9, 28.4, 28.3, 26.6, 20.9, 20.5, 19.8, 0.2; IR: 3065, 2935, 2859, 2174, 1976, 1750, 1457, 1368, 1249, 1215, 1068, 1041, 842 cm$^{-1}$; MS m/z (relative intensity): 278 (26%, M$^+$), 263 (13%), 249 (20%), 236 (100%), 218 (64%), 145 (65%); HRMS-EI (m/z): [M]$^+$ calcd for C$_{16}$H$_{26}$O$_2$Si, 278.1702; found, 278.1702.

$$\text{2-(2-(5-(Trimethylsilyl)pent-4-ynyl)-4-oxocyclohexyldene)vinyl acetate-4-monoethylene ketal (47a).}$$

Following the General Procedure for the AuCl$_3$ Catalyzed Allenol Ester Formation, AuCl$_3$ (2 mg, 0.007 mmol) and propargyl acetate 45a (27 mg, 0.074 mmol, 4:1 dr (major/minor)) were reacted in toluene (0.37 mL) for 4 h. Purification via flash chromatography (hexanes/EtOAc, 9:1, v/v) afforded the title compound (27 mg, quant) as a colorless oil in an ~1:1 dr. R$_f$ = 0.44 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.41* (s, 0.5H), 7.38** (t, J = 2.4 Hz, 0.5H), 4.03-3.98 (m, 4H), 2.44-2.35 (m, 3H), 2.24-2.18 (m, 2H), 2.15 (s, 3H), 1.96-1.86 (m, 2H), 1.79-1.27 (m, 6H), 0.13 (9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 186.9, 168.7, 120.7, 111.2*, 111.0**, 108.4**, 108.3*, 107.3, 84, 64.5, 41.8*, 41.5**, 38.0**, 37.9*, 35.3, 32.5*, 32.2**, 30.0, 26.1, 20.9, 19.9, 0.2; IR: 2954, 2173, 1976, 1751, 1368, 1215, 1060, 843 cm$^{-1}$; HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{20}$H$_{30}$O$_4$NaSi, 385.1811; found, 385.1809.

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~1:1 mixture of diastereomers
1-(2-(5-(Trimethylsilyl)pent-4-ynyl)-4-oxocyclohexylidene)prop-1-en-2-yl acetate-4-monoethylene ketal (47b).

Following the General Procedure for the AuCl$_3$ Catalyzed Allenol Ester Formation, AuCl$_3$ (7 mg, 0.02 mmol) and propargyl acetate 46b (106 mg, 0.281 mmol, 5:1 dr) were reacted in toluene (1.4 mL) for 19 h. Purification via flash chromatography (hexanes/EtOAc, 90:10, v/v) afforded the title compound (45 mg, 43%) as a colorless oil in an ~1.5:1 dr. $R_f = 0.43$ (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 4.00-3.93 (m, 4H), 2.42-2.36 (m, 1H), 2.34-2.17 (m, 4H), 2.10 (s, 3H), 1.96* (s, 1.76), 1.95** (s, 1.14H), 1.93-1.81 (m, 2H), 1.70-1.59 (m, 2H), 1.58-1.47 (m, 2H), 1.47-1.28 (m, 2H), 0.14 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 188.7**, 188.6*, 168.9*, 168.8**, 120.5*, 120.3**, 116.1*, 116.0**, 108.5**, 108.4*, 107.6, 84.2, 64.4, 42.0**, 41.7*, 35.5*, 35.4**, 32.4**, 32.3*, 29.7**, 29.5*, 26.4**, 26.1*, 21.2**, 21.1*, 19.9*, 19.9**, 18.7*, 18.3**, 0.2; IR: 2954, 2173, 1982, 1751, 1438, 1369, 1249, 1221, 1123, 843 cm$^{-1}$; MS $m/z$ (relative intensity): 376 (35%, M$^+$), 360 (31%), 333 (76%), 158 (86%), 110 (95%), 99 (78%), 87 (88%), 73 (100%); HRMS-EI ($m/z$): [M]$^+$ calcd for C$_{21}$H$_{32}$O$_4$Si, 376.2070; found, 376.2069.

$^*$ diastereomer 1; $^{**}$ diastereomer 2

Spectra Recorded as ~1.5:1 mixture of diastereomers

60
General Procedure for the [Rh(CO)₂Cl]₂ Catalyzed Cyclocarbonylation Reaction: A flame-dried, test tube (10 × 100 mm) equipped with a Teflon-coated stir-bar was charged with allene-yne and toluene (0.1 M). The tube was evacuated for 3-5 s (via a needle through the septa) and refilled with CO(g) (from a balloon) (3×). To the allene-yne solution was added [Rh(CO)₂Cl]₂ (0.10 equiv) in one portion and the test tube was evacuated and refilled with CO(g) (3×). The test tube was placed in a preheated 90 °C oil bath and stirred under CO(g). After the reaction was complete by TLC, the mixture was cooled to rt, passed through a short plug of silica gel using hexanes/EtOAc and concentrated in vacuo. The crude material was purified by flash chromatography.

6-Tert-butyl-2,3,4,5,6,7,7a,8-octahydro-1-(trimethylsilyl)-2-oxocyclopenta[a]inden-3-yl acetate (48a).

Following the General Procedure for the [Rh(CO)₂Cl]₂ Catalyzed Cyclocarbonylation Reaction, allene-yne 42a (19 mg, 0.057 mmol, ~1:1 dr) and [Rh(CO)₂Cl]₂ (2 mg, 0.005 mmol) were reacted in toluene (0.57 mL) for 8 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (4 mg, 19%) as a slightly yellowish oil in an ~2:1 dr. Rf = 0.47 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 5.66* (s, 0.6H), 5.62** (s, 0.4H), 3.07** (d, J = 19.2 Hz, 0.4H), 3.05* (d, J = 19.5 Hz, 0.6H), 2.98-2.84 (m, 1H), 2.72-2.64 (m, 1H), 2.44-2.31 (m, 1H), 2.26-1.94 (m, 3H), 2.17** (s, 1.2H), 2.15* (s, 1.8H), 1.33-1.25 (m, 1H), 1.19-0.88 (m, 2H), 0.89 (s, 9H), 0.21 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 206.8, 194.2**, 193.7*, 170.5, 154.2**, 153.7*, 136.3*, 135.6**, 135.6*, 127.9**, 127.8*, 69.3*, 69.1**, 50.1**, 49.1*, 47.5**, 47.2*, 36.2**, 36.0*, 35.3*, 35.0**, 32.5*, 28.1**, 22.7**, 27.6*, 27.6*, 27.5**, 20.8**, 20.8*, -1.3; IR: 2953, 1746, 1701, 1559, 1230, 842 cm⁻¹.
*diastereomer 1; **diastereomer 2

Spectra Recorded as ~2:1 mixture of diastereomers

7-Tert-butyl-2,4,5,5a,6,7,8,9-octahydro-3-(trimethylsilyl)-2-oxo-1H-cyclopenta[a]naphthalen-1-yl acetate (48b).

Following the General Procedure for the [Rh(CO)$_2$Cl]$_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne 42b (14 mg, 0.040 mmol) and [Rh(CO)$_2$Cl]$_2$ (2 mg, 0.005 mmol) were reacted in toluene (0.39 mL) for 1 h.

Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (10 mg, 67%) as a slightly yellow oil in an ~1:1 dr. R$_f$ = 0.55 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (500 MHz, CDCl$_3$) δ: 5.75** (s, 0.5H), 5.71* (d, $J$ = 1.0 Hz, 0.5H), 2.92* (dt, $J$ = 16.5, 4.0 Hz, 0.5H), 2.83** (dt, $J$ = 17.0, 5.5 Hz, 0.5H), 2.60** (ddd, $J$ = 17.0, 10.5, 5.0, Hz, 0.5H), 2.54* (ddd, $J$ = 14.5, 6.3, 3.0 Hz, 0.5H), 2.46-2.37 (m, 1H), 2.32-2.19 (m, 1H), 2.17* (s, 1.5H), 2.14** (s, 1.5H), 2.11-1.98 (m, 4H), 1.57-1.49** (m, 0.5H), 1.46-1.37* (m, 0.5H), 1.13-0.95 (m, 2H), 0.89** (s, 4.5H), 0.88* (s, 4.5H), 0.94-0.82 (m, 1H), 0.24** (s, 4.5H), 0.23* (s, 4.5H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 204.6, 178.4*, 178.2**, 170.1**, 170.0*, 145.8**, 145.4*, 134.1**, 133.4*, 129.7*, 129.3**, 70.7**, 70.5*, 47.1**, 47.1*, 37.9*, 37.4**, 36.0*, 35.2**, 32.4, 30.8**, 30.7**, 29.3*, 29.0**, 27.7**, 27.5*, 27.5, 27.0*, 26.1**, 20.9*, 20.8**, -0.6; IR: 2952, 1745, 1699, 1543, 1367, 844 cm$^{-1}$; HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{22}$H$_{34}$O$_3$NaSi: 397.2175; found: 397.2158.

Spectra Recorded as ~1:1 mixture of diastereomers

*diastereomer 1; **diastereomer 2
Following the General Procedure for the [Rh(CO)2Cl]2 Catalyzed Cyclocarbonylation Reaction, allene-yne 42c (16 mg, 0.044 mmol, ~1:1 dr) and [Rh(CO)2Cl]2 (3 mg, 0.006 mmol) were reacted in toluene (0.91 mL) for 17 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (13 mg, 76%) as a slightly yellowish oil in an ~2.3:1 dr. Rf = 0.58 (hexanes/EtOAc, 80:20, v/v); 1H NMR (300 MHz, CDCl3) δ: 5.82* (s, 0.7), 5.77 (s, 0.3H), 3.02** (t, J = 5.4 Hz, 0.3H), 2.96* (t, J = 5.4 Hz, 0.7H), 2.86* (dd, J = 9.9, 4.5 Hz, 0.7H), 2.79** (dd, J = 11.4, 5.0 Hz, 0.3H), 2.58-2.34 (m, 2H), 2.15* (s, 2.1H), 2.14 (m, 0.9H), 2.02-1.57 (m, 7H), 1.52-1.04 (m, 5H), 0.94-0.81 (m, 1H), 0.86 (s, 9H), 0.26 (s, 9H); 13C NMR (75 MHz, CDCl3) δ: 203.8**, 203.6*, 182.5**, 181.3*, 170.0**, 169.9*, 149.7*, 149.0**, 139.3*, 139.1**, 130.6**, 130.4*, 74.4*, 73.5**, 47.4*, 46.9**, 46.2*, 43.7**, 37.9*, 35.4*, 35.2*, 35.1*, 35.0**, 34.6**, 34.4*, 33.1**, 32.5**, 32.4*, 28.4*, 27.8**, 27.5*, 27.4**, 23.0*, 21.7**, 20.9*, 0.3; IR: 2942, 1746, 1695, 1510, 1510, 1367, 1228, 843 cm⁻¹; HRMS-EI (m/z): [M + Na]+ calcd for C23H36O3NaSi, 411.2331; found, 411.2308.

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~2.3:1 mixture of diastereomers
(8S,10aE)-8-Tert-butyl-1,2,4,5,6,6a,7,8,9,10-decahydro-3-(trimethylsilyl)-2-oxobenz[e]azulen-1-yl pivalate (48e).

Following the General Procedure for the \([\text{Rh(CO)}_2\text{Cl}]_2\) Catalyzed Cyclocarbonylation Reaction, allene-yne 42e (35 mg, 0.087 mmol, ~2:1 dr) and \([\text{Rh(CO)}_2\text{Cl}]_2\) (4 mg, 0.01 mmol) were reacted in toluene (0.86 mL) for 18 h. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (19 mg, 51%) as a slightly yellow oil in an ~2.6:1 dr. R\(_f\) = 0.70 (hexanes/EtOAc, 80:20, v/v); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 5.85* (s, 0.65H), 5.75** (s, 0.25), 3.03-2.93 (m, 1H), 2.87-2.78 (m, 1H), 2.56-2.47 (m, 1H), 2.42-2.32 (m, 1H), 2.07-1.60 (m, 7H), 1.55-1.46 (m, 1H), 1.36 (tt, \(J\) = 8.0, 3.5 Hz, 1H), 1.32-1.13 (m, 2H), 1.26* (s, 6.5H) 1.24** (s, 2.4H), 0.86** (s, 2.2H), 0.85 (s, 6.4H), 0.25 (s, 9H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 203.8**, 203.4*, 181.7**, 180.6*, 177.6*, 177.5**, 149.2*, 148.5**, 139.0*, 138.8**, 130.8**, 130.7*, 74.5*, 73.7**, 47.3*, 46.8**, 45.8*, 43.6**, 38.9**, 38.8*, 37.7*, 35.2*, 35.0*, 34.8**, 34.7*, 34.4**, 34.3**, 32.9**, 32.5**, 32.4*, 28.7*, 27.8**, 27.4*, 27.3, 27.2**, 23.2*, 21.7**, -0.2; IR: 2954, 2866, 1734, 1695, 1478, 1248, 843 cm\(^{-1}\); MS \(m/z\) (relative intensity): 430 (33%, \(M^+\)), 415 (15%), 345 (43%), 328 (71%), 313 (60%), 271 (44%), 159 (45%), 121 (89%), 75 (100%); HRMS-EI (\(m/z\)): [M]+ calcd for C\(_{26}\)H\(_{42}\)O\(_3\)Si, 430.2903; found, 430.2902.

* diastereomer 1; ** diastereomer 2

Spectra Recorded as ~2.6:1 mixture of diastereomers
(8S,10aE)-8-Tert-butyl-1,2,4,5,6,6a,7,8,9,10-decahydro-3-
(trimethylsilyl)-2-oxobenzo[e]azulen-1-yl 4-nitrobenzoate (48f).

Following the General Procedure for the [Rh(CO)₂Cl₂] Catalyzed
Cyclocarbonylation Reaction, allene-yne 42f (35 mg, 0.075 mmol, ~1:1 dr)
and [Rh(CO)₂Cl₂] (3 mg, 0.01 mmol) were reacted in toluene (0.74 mL) for
18 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5 to 80:20, v/v) afforded the
title compound (13 mg, 35%) as a slightly yellowish oil in an ~2:1 dr. R_f = 0.65 (hexanes/EtOAc,
80:20, v/v); ¹H NMR (500 MHz, CDCl₃) δ: 8.30-8.10 (m, 4H), 6.06* (s, 0.66H), 6.01 (s, 0.33H),
3.08-3.00 (m, 1H), 2.93-2.86 (m, 1H), 2.59-2.36 (m, 2H), 2.09-1.62 (m, 8H), 1.56-1.46 (m, 1H),
1.38-1.18 (m, 2H), 1.10 (q, J = 12.5, 1H), 1.05-0.82 (m, 3H), 0.84** (s, 0.33H), 0.75* (s,
0.66H), 0.28 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 203.0**, 202.7*, 182.6**, 181.4*, 163.9**,
163.7*, 150.6**, 150.6*, 150.4*, 149.6*, 139.5*, 139.3**, 135.3**, 135.3*, 131.0, 130.2**,
129.9*, 123.4, 75.8*, 75.0**, 47.2*, 47.0**, 46.4*, 43.8**, 38.0*, 35.5*, 35.3*, 35.0*, 35.0**,
34.7**, 34.4**, 33.2**, 32.5**, 32.3*, 28.6*, 27.8**, 27.3, 23.0*, 21.7**, -0.3; IR: 2949, 2865,
1731, 1693, 1345, 1320, 1261, 1120, 1100, 844, 718 cm⁻¹; MS m/z (relative intensity): 495 (14%,
M⁺), 480 (12%), 329 (62%), 271 (48%), 104 (100%), 91 (98%); HRMS-EI (m/z): [M]⁺ calcd for
C₂₀H₃₇NO₅Si, 495.2441; found, 495.2440.

* diastereomer 1; ** diastereomer 2

Spectra Recorded as ~2:1 mixture of diastereomers
**1,2,4,5-Tetrahydro-6-methyl-3-(trimethylsilyl)-2-oxopentalen-1-yl acetate (49b).**

Following the General Procedure for the [Rh(CO)$_2$Cl]$_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne 45b (13 mg, 0.055 mmol) and [Rh(CO)$_2$Cl]$_2$ (3 mg, 0.006 mmol) were reacted in toluene (0.56 mL) for 22 h. Purification via flash chromatography (hexanes/EtOAc, 9:1, v/v) afforded the title compound (4 mg, 28%) as a slightly yellow oil. R$_f$ = 0.35 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (300 MHz, CDCl$_3$) δ: 5.65 (s, 1H), 2.85-2.72 (m, 4H), 2.17 (s, 3H), 1.95 (s, 3H), 0.21 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 194.8, 170.4, 147.2, 140.1, 127.8, 124.8, 69.4, 40.4, 27.8, 20.7, 15.5, -1.3; IR: 2955, 2918, 1745, 1699, 1558, 1229, 839 cm$^{-1}$; HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{14}$H$_{20}$O$_3$NaSi: 287.1079; found: 287.1080.

**1,2,4,5,6-Pentahydro-7-methyl-3-(trimethylsilyl)-2-oxo-2H-inden-1-yl acetate (49c).**

Following the General Procedure for [Rh(CO)$_2$Cl]$_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne 45c (22 mg, 0.088 mmol) and [Rh(CO)$_2$Cl]$_2$ (3 mg, 0.006 mmol) were reacted in toluene (0.87 mL) for 1.5 h. Purification via flash chromatography (hexanes/EtOAc, 9:1, v/v) afforded the title compound (13 mg, 53%) as a slightly yellowish oil. R$_f$ = 0.36 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (300 MHz, CDCl$_3$) δ: 5.73 (s, 1H), 2.79 (dd, $J$ = 17.1, 6.0, 4.8 Hz, 1H), 2.57 (ddd, $J$ = 16.8, 10.2, 4.8 Hz, 1H), 2.32-2.19 (m, 2H), 2.14 (s, 3H), 1.96-1.73 (m, 2H), 1.83 (s, 3H), 0.24 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 204.3, 177.7, 170.0, 139.6, 133.4, 131.7, 70.6, 31.3, 27.3, 21.8, 20.7, 20.4, -0.6; IR: 2955, 1746, 1696, 1542, 1223, 841 cm$^{-1}$; MS m/z (relative intensity): 278 (15%, M$^+$), 236 (35%), 235 (32%), 220 (56%), 218 (72%), 117 (71%), 74 (82%), 72 (100%); HRMS-EI (m/z): [M]$^+$ calcd for C$_{15}$H$_{22}$O$_3$Si, 278.1338; found, 278.1327.
(8E)-1,2,4,5,6,7-Hexahydro-8-methyl-3-(trimethylsilyl)-2-oxoazulen-1-yl acetate (49f).

Following the General Procedure for the [Rh(CO)₂Cl]₂ Catalyzed Cyclocarbonylation Reaction, allene-yne 45f (27 mg, 0.10 mmol) and [Rh(CO)₂Cl]₂ (3 mg, 0.008 mmol) were reacted in toluene (1.0 mL) for 46 h. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (18 mg, 62%) as a slightly yellow oil. R_f = 0.43 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 5.73 (s, 1H), 2.87 (dt, J = 14.7, 5.4 Hz, 1H), 2.81-2.70 (m, 1H), 2.51-2.32 (m, 2H), 2.15 (s, 3H), 1.94-1.72 (m, 4H), 1.85 (s, 3H), 0.25 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 204.4, 181.8, 170.0, 143.5, 136.8, 134.5, 73.5, 34.1, 30.6, 25.9, 24.1, 23.7, 20.7, -0.2; IR: 2937, 2865, 1746, 1697, 1528, 1369, 1246, 1224, 1049, 842.1 cm⁻¹; MS m/z (relative intensity): 292 (14%, M⁺), 266 (24%), 249 (21%), 232 (71%), 217 (28%), 117 (51%), 75 (88%), 73 (100%); HRMS-EI (m/z): [M⁺] calcd for C₁₆H₂₄O₃Si, 292.1495; found, 292.1485.

3-Methyl-10-(trimethylsilyl)deca-1,3-dien-9-ylnyl acetate (50).

Following the General Procedure for the [Rh(CO)₂Cl]₂ Catalyzed Cyclocarbonylation Reaction, allene-yne 45g (26 mg, 0.093 mmol) and [Rh(CO)₂Cl]₂ (4 mg, 0.01 mmol) were reacted in toluene (0.99 mL) for 120 h. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (3 mg, 12%) as a slightly yellow colored oil. R_f = 0.71 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (500 MHz, CDCl₃) δ 7.30* (d, J = 13.0 Hz, 0.5H), 6.90** (d, J = 7.0 Hz, 0.5H), 6.08* (d, J = 12.5 Hz, 0.5H), 5.53* (t, J = 7.5Hz, 0.5H), 5.44** (t, J = 7.0 Hz, 0.5H), 5.28** (d, J = 7.5 Hz, 0.5H), 2.26-2.21 (m, 1H), 2.18-2.10 (m, 2H), 2.17* (s,
0.5H), 2.15** (s, 0.5H), 1.95* (s, 1.5H), 1.74** (s, 1.5H), 1.55-1.45 (m, 4H), 0.14 (s, 9H); \(^{13}\)C
NMR (75 MHz, CDCl\(_3\)) \(\delta\) 168.2*, 167.6**, 134.2**, 133.0**, 132.2*, 131.0*, 130.8**, 130.0*,
120.5*, 116.6**, 107.3*, 107.3**, 84.5, 28.5**, 28.6*, 28.2*, 28.2**, 27.5**, 27.4*, 20.8**,
20.8*, 19.7, 15.6*, 12.5**; IR: 2923, 2852, 2174, 1760, 1459, 1369, 1213, 842 cm\(^{-1}\); MS \(m/z\)
(relative intensity): 278 (8%, \(M^+\)), 263 (37%, \(M+1\)), 249 (30%), 203 (48%), 131 (50%), 119
(79%), 117 (80%), 86 (66%), 84 (88%), 75 (60%), 73 (100%); HRMS-EI \((m/z)\): [\(M^+\)] calcd for
C\(_{16}\)H\(_{28}\)O\(_2\)Si, 278.1702; found: 278.1700.

*E isomer; **Z isomer

Spectra Recorded as ~1:1 mixture of E/Z isomers

Following the General Procedure for the [Rh(CO)\(_2\)Cl\(_2\)] Catalyzed
Cyclocarbonylation Reaction, allene-yne \(47a\) (25 mg, 0.069 mmol, ~1:1 dr)
and [Rh(CO)\(_2\)Cl\(_2\)] (4 mg, 0.01 mmol) were reacted in toluene (0.68 mL) for 18
h. Purification via flash chromatography (hexanes/EtOAc, 8:2, v/v) afforded
the title compound (20 mg, 74%) as a slightly yellowish oil in an ~2:1 dr. \(R_f =
0.13\) (hexanes/EtOAc, 80:20, v/v); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 5.82* (s, 0.7H), 5.76** (s,
0.3H), 4.04-3.93 (m, 4H), 3.04-2.64 (m, 3H), 2.44-2.17 (m, 2H), 2.14 (s, 2.1H)*, 2.13** (s,
0.9H), 2.00-1.40 (m, 8H), 0.26 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 203.5**, 203.3*, 181.7**,
180.3*, 170.0**, 169.0*, 146.7*, 145.8**, 140.0**, 139.8*, 132.5*, 132.0**, 108.4*, 108.4**,
74.3*, 73.5**, 64.5, 64.4*, 64.3**, 43.6, 41.6*, 41.5**, 39.9, 35.3*, 35.2**, 34.4*, 34.4**,
34.3*, 33.8**, 31.5*, 3.3**, 23.0, 21.6**, 20.8*, -0.3; IR: 2947, 2055, 1744, 1695, 1227, 843
cm\(^{-1}\); HRMS-EI \((m/z)\): [\(M + Na^+\)] calcd for C\(_{21}\)H\(_{30}\)O\(_5\)NaSi, 413.1760; found, 413.1752.

*diastereomer 1; **diastereomer 2

68
Spectra Recorded as ~2:1 mixture of diastereomers

8-Tert-butyl-4,5,6,6a,7,8,9,10-octahydro-1-methylene-3-
(trimethylsilyl)benzo[e]azulen-2(1H)-one (52).

Following the General Procedure for the [Rh(CO)$_2$Cl]$_2$ Catalyzed
Cyclocarbonylation Reaction, allene-yne 42d (39 mg, 0.10 mmol, ~1:1 dr) and
[Rh(CO)$_2$Cl]$_2$ (4 mg, 0.01 mmol) were reacted in toluene (1.1 mL) for 69 h.
Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title
compound (9 mg, 26%) as a slightly yellow oil. R$_f$ = 0.69 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR
(500 MHz, CDCl$_3$) δ: 6.06 (s, 1H), 5.57 (s, 1H), 2.95 (ddd, $J$ = 16.0, 6.0, 4.5 Hz, 1H), 2.83-2.77
(m, 2H), 2.68-2.61 (m, 1H), 2.55 (ddd, $J$ = 14.5, 6.5, 5.0 Hz, 1H), 1.92-1.81 (m, 2H), 1.78-1.67
(m, 3H), 1.64-1.56 (m, 1H), 1.51-1.37 (m, 2H), 1.24 (q, $J$ = 12.5 Hz, 1H), 0.89 (s, 9H), 0.27 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 198.6, 180.4, 150.4, 143.2, 136.9, 131.6, 115.0, 45.1, 42.3,
34.4, 34.0, 32.9, 32.3, 30.6, 27.2, 25.2, 23.1, 0.0; IR: 2951, 2865, 1754, 1683, 1625, 1529, 1366,
1247, 842 cm$^{-1}$.

(10aZ)-5,6,6a,7,9,10-Hexahydro-1-methylene-3-
(trimethylsilyl)benzo[e]azulene-2,8(1H,4H)-dione-8-monoethylene ketal (53).

Following the General Procedure for the [Rh(CO)$_2$Cl]$_2$ Catalyzed
Cyclocarbonylation Reaction, allene-yne 47b (36 mg, 0.096 mmol, 1.5:1 dr) and
[Rh(CO)$_2$Cl]$_2$ (4 mg, 0.01 mmol) were reacted in toluene (0.68 mL) for 47 h.
Purification via flash chromatography (hexanes/EtOAc, 85:15, v/v) afforded the title compound
(15 mg, 45%) as a slightly yellow oil. R$_f$ = 0.30 (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (500
MHz, CDCl$_3$) δ: 6.07 (s, 1H), 5.55 (s, 1H), 4.02-3.91 (m, 4H), 2.97 (dt, $J$ = 15.0, 4.5 Hz, 1H)
2.96-2.88 (m, 1H), 2.82-2.69 (m, 3H), 1.95 (dt, \( J = 14.0, 5.5 \) Hz, 1H), 1.92-1.61 (m, 7H), 0.27 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 198.4, 179.5, 147.9, 142.6, 137.5, 133.5, 115.5, 108.8, 64.2, 64.1, 41.1, 37.2, 34.2, 33.6, 31.2, 28.7, 23.3, -0.0; IR: 2949, 2893, 1683, 1624, 1530, 1247, 1120, 842 cm\(^{-1}\); MS m/z (relative intensity): 360 (9\%, M + 16), 344 (16\%, M\(^+\)), 99 (100\%), 86 (54\%), 73 (66\%); HRMS-El (m/z): [M]\(^+\) calcd for C\(_{20}\)H\(_{28}\)O\(_3\)Si, 344.1808; found, 344.1811.

5,6-Dihydro-7-methyl-1-methylene-3-(trimethylsilyl)-1H-inden-2(4H)-one (54d).

Following the General Procedure for the \([\text{Rh}(\text{CO})_2\text{Cl}]_2\) Catalyzed Cyclocarbonylation Reaction, allene-yne 45d (21 mg, 0.079 mmol) and \([\text{Rh}(\text{CO})_2\text{Cl}]_2\) (2 mg, 0.005 mmol) were reacted in toluene (0.80 mL) for 2.5 h. Purification via flash chromatography (hexanes/EtOAc, 95:5 to 80:20, v/v) afforded the title compound (9 mg, 49\%) as a slightly yellow oil. R\(_f\) = 0.65 (hexanes/EtOAc, 80:20, v/v); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \): 6.06 (s, 1H), 5.61 (s, 1H), 2.72 (t, \( J = 6.3 \) Hz, 2H), 2.35 (t, \( J = 5.7 \) Hz, 2H), 2.12 (s, 3H), 1.83 (quint, \( J = 6.3 \) Hz, 2H), 0.23 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \): 198.4, 175.2, 140.0, 139.2, 132.8, 130.4, 114.6, 33.3, 27.3, 21.9, 21.3, -0.4; IR: 2951, 2823, 1685, 1647, 1545, 1246, 842 cm\(^{-1}\); MS m/z (relative intensity): 248 (14\%, M + 16), 232 (38\%, M\(^+\)), 217 (100\%), 191 (12\%), 167 (34\%); HRMS-El (m/z): [M]\(^+\) calcd for C\(_{14}\)H\(_{20}\)OSi, 232.1283; found, 232.1281.

(1Z)-5,6-Dihydro-7-methyl-3-(trimethylsilyl)-1-propylidene-1H-inden-2(4H)-one (54e).

Following the General Procedure for the \([\text{Rh}(\text{CO})_2\text{Cl}]_2\) Catalyzed Cyclocarbonylation Reaction allene-yne 45e (35 mg, 0.12 mmol) and
[Rh(CO)$_2$Cl]$_2$ (4 mg, 0.010 mmol) were reacted in toluene (1.2 mL) for 1.5 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5 to 90:10, v/v) afforded 53e (13 mg, 42%) and 53e' (3 mg, 13%) as yellow oils. 53e: $R_f = 0.73$ (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (500 MHz, CDCl$_3$) δ: 6.40 (t, $J = 7.5$ Hz, 1 H), 2.92 (quint, $J = 7.5$ Hz, 2H), 2.67 (t, $J = 6.5$ Hz, 2H), 2.31 (t, $J = 6.0$ Hz, 2H), 2.09 (s, 3H), 1.79 (quint, $J = 6.0$ Hz, 2H), 1.10 (t, $J = 7.5$ Hz, 3H), 0.25 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 200.6, 172.5, 141.2, 136.4, 134.3, 132.1, 131.7, 33.9, 27.2, 22.0, 21.6, 21.1, 14.2, -0.2; IR: 2954, 2870, 1674, 1640, 1553, 1246, 840 cm$^{-1}$; MS m/z (relative intensity): 276 (24% M + 16), 260 (58%, M$^+$), 244 (100%), 229 (29%), 215 (27%); HRMS-EI (m/z): [M]$^+$ calcd for C$_{16}$H$_{24}$Si, 260.1596; found, 260.1590.

(1Z)-5,6-Dihydro-7-methyl-1-propylidene-1H-inden-2(4H)-one (54e').

$R_f = 0.44$ (hexanes/EtOAc, 80:20, v/v); $^1$H NMR (500 MHz, CDCl$_3$) δ: 6.46 (t, $J = 7.5$ Hz, 1 H), 5.84 (s, 1H), 2.93 (quint, $J = 7.5$ Hz, 2H), 2.61 (t, $J = 6.0$ Hz, 2H), 2.32 (t, $J = 5.5$ Hz, 2H), 2.10 (s, 3H), 1.80 (quint, $J = 6.0$ Hz, 2H), 1.11 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 196.4, 165.6, 142.1, 136.8, 131.8, 130.2, 124.7, 34.0, 26.1, 21.9, 21.4, 21.1, 14.1; IR: 2932, 2872, 1695, 1583, 1456, 1372, 1247, 1179, 844 cm$^{-1}$; MS m/z (relative intensity): 188 (100%, M$^+$), 173 (52%), 91 (41%); HRMS-EI (m/z): [M]$^+$ calcd for C$_{13}$H$_{16}$O, 188.1201; found, 188.1195.

(3-(5-Tert-butyl-2-vinylidenecyclohexyl)prop-1-ynyl)trimethylsilane (55a).

A flame-dried, 25 mL, 2-necked round-bottomed flask containing a Teflon-coated stir-bar was equipped with an internal condenser and AlCl$_3$ (49 mg, 0.37 mmol) was added. The flask was flushed with N$_2$ and THF (9.3 mL) was added. The solution was cooled in an ice/H$_2$O bath and lithium aluminum hydride was added (1.1 mL,
1.0 M in Et₂O, 1.1 mmol) via syringe. After 15 min in an ice/H₂O bath, a solution of 38a (154 mg, 0.530 mmol) ~2:1 dr (38a-eq/38a-ax) in THF (5.3 mL) was added dropwise via cannula, then heated to reflux. After 3.5 h consumption of starting material was observed via TLC and the reaction was cooled in an ice/H₂O bath. The reaction was carefully quenched by the addition of saturated aq Rochelle’s salt and diluted with Et₂O and H₂O. The aq layer was separated and extracted with Et₂O (3×). The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 95:5, v/v) affording the title compound (47 mg, 33%) as a single diastereomer. \( R_f = 0.91 \) (hexanes/EtOAc, 80:20, v/v); \(^1\)H NMR (300 MHz, CDCl₃) δ: 4.74-4.64 (m, 7H), 0.88 (s, 9H); \(^1^3\)C NMR (75 MHz, CDCl₃) δ: 202.0, 106.7, 104.9, 85.7, 76.2, 47.7, 38.4, 33.8, 32.6, 31.8, 27.9, 27.5, 24.8, 0.2; IR: 2957, 2863, 2176, 1960, 1440, 1249, 843 cm⁻¹; MS m/z (relative intensity): 274 (20%, M⁺), 259 (38%), 217 (50%), 86 (79%), 84 (87%), 73 (100%), 59 (66%), 57 (93%); HRMS-EI (m/z): [M]⁺ calcd for C₁₈H₃₀Si, 274.2117; found, 274.2111.

(5-((1S,5S)-5-Tert-butyl-2-vinyldenecyclohexyl)pent-1-ynyl)trimethylsilane (55c).

A flame-dried 15 mL 2 neck round-bottomed flask containing a Teflon-coated stir-bar equipped with an internal condenser and AlCl₃ (18 mg, 0.13 mmol) was added. The flask was flushed with N₂ and THF (3.1 mL) was added. The solution was cooled in an ice/H₂O bath and lithium aluminum hydride was added (0.35 mL, 1.0 M in Et₂O, 0.35 mmol) via syringe. The solution was stirred 15 min in an ice/H₂O bath. A solution of 38c-ax (56 mg, 0.18 mmol) in THF (1.8 mL) was added dropwise via cannula. The
solution was then heated to reflux. After 5 h consumption of starting material was observed via TLC and the reaction was cooled in an ice/H₂O bath. The reaction was quenched with the addition of saturated aq Rochelle’s salt and diluted with Et₂O and H₂O. The aq layer was separated and extracted with Et₂O (3×). The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 97.5:2.5 to 90:10, v/v) affording the title compound (15 mg, 28%) as a single diastereomer. Rₚ = 0.92 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 4.67 (t, J = 3.9 Hz, 2H); 2.38 (dt, J = 12.9, 2.7 Hz, 1H), 2.22 (t, J = 7.2 Hz, 2H), 2.03-1.74 (m, 4H) 1.68-1.53 (m, 2H), 1.35-1.02 (m, 4H), 0.92-0.78 (m, 1H), 0.87 (s, 9H), 0.16 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 202.4, 107.8, 106.0, 84.3, 75.4, 48.0, 38.9, 35.0, 33.4, 32.5, 32.3, 28.3, 27.6, 26.6, 20.1, 0.2; IR: 2953, 2854, 2175, 1958, 1441, 1365, 1249, 841 cm⁻¹; MS m/z (relative intensity): 302 (34%, M⁺), 171 (32%), 73 (100%), 57 (82%); HRMS-EI (m/z): [M]⁺ calcd for C₂₀H₃₄Si, 302.2430; found, 302.2421.

6-Tert-butyl-4,5,6,7,7a,8-hexahydro-1-((trimethylsilyl)cyclopenta[a]inden-2(3H)-one (56a).

Following the General Procedure for the [Rh(CO)₂Cl]₂ Catalyzed Cyclocarbonylation Reaction, allene-yne 55a (14 mg, 0.051 mmol) and [Rh(CO)₂Cl]₂ (2 mg, 0.005 mmol) reacted in toluene (0.5 mL) for 30 min. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5 to 95:5, v/v) afforded the title compound (5 mg, 32%) as a slightly yellowish oil. Rₚ = 0.57 (hexanes/EtOAc, 80:20, v/v); ¹H NMR (300 MHz, CDCl₃) δ: 3.03 (dd, J = 18.9, 6.3 Hz, 1H), 2.86-2.80 (m, 1H), 2.82 (1/2 ABq, J = 18.0 Hz, 1H), 2.68 (1/2 ABq, J = 18.0 Hz, 1H), 2.64 (ddd, J = 13.5, 3.9, 2.4 Hz, 1H), 2.35 (d,
Following the General Procedure for the $[\text{Rh(CO)}_2\text{Cl}]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne 55c (13 mg, 0.043 mmol) and $[\text{Rh(CO)}_2\text{Cl}]_2$ (2 mg, 0.005 mmol) was reacted in toluene (0.43 mL) for 40 min. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (10 mg, 70%) as a slightly yellowish oil. $R_f = 0.63$ (hexanes/EtOAc, 80:20, v/v); $^1\text{H NMR}$ (300 MHz, CDCl$_3$) $\delta$: 3.05 (1/2 ABq, $J = 18.0$ Hz, 1H), 2.96 (1/2 ABq, $J = 18.0$ Hz, 1H), 2.91-2.84 (m, 2H), 2.57 (dt, $J = 13.8$, 3.9 Hz, 1H), 2.44-2.33 (m, 1H), 2.06-1.93 (m, 2H), 1.93-1.58 (m, 5H), 1.57-1.26 (m, 3H), 1.24-1.06 (m, 2H), 0.96-0.87 (m, 1H), 0.87 (s, 9H), 0.25 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl$_3$) $\delta$: 208.8, 181.3, 144.7, 142.8, 130.5, 47.6, 44.8, 43.6, 37.3, 36.0, 35.5, 35.4, 32.4, 28.1, 27.5, -0.1; IR: 2939, 2863, 1680, 1515, 1246, 842 cm$^{-1}$; MS $m/z$ (relative intensity): 330 (64%, M$^+$), 315 (100%), 73 (68%), 57 (53%); HRMS-EI ($m/z$): [M]$^+$ calcld for C$_{21}$H$_{34}$OSi, 330.2379; found, 330.2383.

(5-((1S,5S)-5-Tert-butyl-2-vinylidene cyclohexyl)pent-1-ynyl)trimethylsilane (56c).
To a flame-dried, 5 mL round-bottomed flask equipped with a stir-bar was added 22c (12 mg, 0.043 mmol), MeOH (0.44 mL), K2CO3 (8 mg, 0.06 mmol), and H2O (0.44 mL). After 16 h at rt, consumption of 49c was observed via TLC. The reaction mixture was diluted with Et2O and quenched by the addition of saturated aq NH4Cl. The solution was diluted with H2O and Et2O. The aq layer was separated and extracted with Et2O (3×). The combined organic layers were washed with brine, dried over MgSO4, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 80:20, v/v) afforded the title compound (6 mg, 60%) as an off-white solid. Rf = 0.24 (hexanes/EtOAc, 80:20, v/v); 1H NMR (300 MHz, CDCl3) δ: 4.42 (s, 1H), 2.77 (ddd, J = 17.1, 6.0, 4.8 Hz, 1H), 2.69 (bs, 1H), 2.57 (ddd, J = 16.8, 10.2, 4.8 Hz, 1H), 2.31-2.18 (m, 2H), 2.03 (s, 3H), 1.96-1.72 (m, 2H), 0.24 (s, 9H); 13C NMR (75 MHz, CDCl3) δ: 210.0, 178.3, 140.3, 134.0, 131.9, 70.9, 31.2, 27.4, 21.9, 20.6, -0.6; IR: 3348, 2948, 2905, 1666, 1532, 1429, 837 cm⁻¹. MS m/z (relative intensity): 237 (19%), 236 (100%, M⁺), 235 (54%), 221 (77%), 117 (72%); HRMS-EI (m/z): [M]⁺ calcd for C13H20O2Si, 236.1233; found, 236.1235.
d₈-Toluene was obtained from a freshly opened bottle and deoxygenated by bubbling with N₂ ~5 min prior to use. An oven dried NMR tube, equipped with septa was evacuated and refilled with Ar (3×). A solution of allene-yne 42c (0.56 mL, 0.1 M in d₈-toluene [prepared by dissolving 40 mg 41c in d₈-toluene (1.11 ml)], 0.56 mmol) was added via syringe followed by [Rh(CO)₂Cl]₂ (0.56 mL, 0.1 M in d₈-toluene [prepared by sonicating 34 mg [Rh(CO)₂Cl]₂ in d₈-toluene (0.87 ml)], 0.56 mmol). The tube was shaken and allowed to stand at rt in a darkened hood under Ar. Progress of the reaction was monitored by ¹H NMR, for the disappearance of resonances corresponding to the allene protons of 42c at δ = 7.60 (bs) and 7.58 (bs) ppm and the appearance of new resonances at δ = 7.50 (d, J = 3.0 Hz) and 7.40 (d, J = 3.0 Hz) ppm. After 20 h complete consumption of 42c was observed and the tube was placed in a 90 °C oil bath under Ar. The
reaction was monitored periodically by $^1$H NMR, showing disappearance of ($\delta = 7.50$ (d, $J = 3.0$ Hz) and 7.40 (d, $J = 3.0$ Hz) ppm) and appearance of new resonances at ($\delta = 7.17$ (d, $J = 3.0$ Hz) and 6.98 (d, $J = 3.0$ Hz) ppm) by $^1$H NMR. The transformation was complete after 17 h. The NMR tube was then evacuated and refilled with CO (3×), vigorously shaken, and sonicated for 2 min. The solution was maintained under CO atmosphere at rt periodically shaking, monitoring for disappearance of ($\delta = 7.17$ (d, $J = 3.0$ Hz) and 6.98 (d, $J = 3.0$ Hz) ppm) and reappearance of ($\delta = 7.50$ (d, $J = 3.0$ Hz) and 7.40 (d, $J = 3.0$ Hz) ppm) by $^1$H NMR. After 17 h the transformation was complete. The NMR tube was then placed in a 90 °C oil bath under CO, shaking each time the CO balloon was refilled, monitoring for disappearance of ($\delta = 7.50$ (d, $J = 3.0$ Hz) and 7.40 (d, $J = 3.0$ Hz) ppm) and appearance of 48c resonances ($\delta = 5.86$ (s) and 5.79 (s) ppm) by $^1$H NMR. After 80 h 74% conversion was observed by comparing the integrations of protons for 57 ($\delta = 7.50$ (d, $J = 3.0$ Hz) and 7.40 (d, $J = 3.0$ Hz) ppm in a 3:1 ratio) and 48c ($\delta = 5.86$ ppm (s) and 5.79 ppm (s) in a 1:2 ratio)

**Spectra Recorded as ~1:1 mixture of diastereomers**

\[\text{Spectra Recorded as ~1:1 mixture of diastereomers}\]
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 184.6** (d, $J = 81.4$ Hz), 184.5* (d, $J = 81.2$ Hz), 183.9*, 183.8**, 180.1 (d, $J = 73.7$ Hz), 161.4*, 160.9**, 159.3* (d, $J = 27.5$ Hz), 158.9** (s, $J = 24.8$ Hz), 144.6** (d, $J = 2.4$ Hz), 143.4* (d, $J = 2.6$ Hz), 141.2* (d, $J = 1.4$ Hz), 140.5** (d, $J = 1.8$ Hz), 106.2** (d, $J = 24.9$ Hz), 106.0* (d, $J = 25.0$ Hz), 48.5*, 47.6**, 43.8*, 42.7**, 38.1, 34.1**, 33.1*, 32.6*, 32.5**, 31.3*, 31.1**, 30.6*, 30.0**, 27.8**, 27.6*, 27.5**, 26.9**, 23.7, 18.0, 2.6**, 2.5*.

*diastereomer 1; **diastereomer 2

Spectra Recorded as $\sim$1:1 mixture of diastereomers
$^1$H Spectra Recorded at 500 MHz in $d_8$-toluene at Room Temperature
$^{13}$C Spectra Recorded at 75 MHz in $d_8$-toluene at Room Temperature
Expansions of $^{13}$C NMR Spectra Recorded at 75 MHz in $d_5$-toluene at Room Temperature
APPENDIX A

$^1$H AND $^{13}$C SPECTRA FOR NEW COMPOUNDS
MMD4052P
301B

TMS
Me
OAc

41c
42c
1:3 dr
$\text{OAc}$

$\text{TMS}$

$49c$


