Mild and Phosphine-Free Iron-Catalyzed Cross-Coupling of Non-activated Secondary Alkyl Halides with Alkynyl Grignard Reagents

Chi Wai Cheung, Peng Ren, and Xile Hu*

Laboratory of Inorganic Synthesis and Catalysis
Institute of Chemical Sciences and Engineering
Ecole Polytechnique Fédérale de Lausanne (EPFL)
ISIC-LSCI, BCH 3305, Lausanne 1015 (Switzerland)

E-mail: xile.hu@epfl.ch

Supporting Information

<table>
<thead>
<tr>
<th>Content</th>
<th>Page no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>General Considerations</td>
<td>S2</td>
</tr>
<tr>
<td>Supplementary Experimental Results</td>
<td></td>
</tr>
<tr>
<td>(A) Optimizations of Iron-Catalyzed Cross-Coupling of Non-activated Secondary Alkyl Iodides with Alkynyl Grignard Reagents</td>
<td>S5</td>
</tr>
<tr>
<td>(B) Optimizations of Iron-Catalyzed Cross-Coupling of Non-activated, Sterically-Hindered Secondary Alkyl Iodides with Alkynyl Grignard Reagent</td>
<td></td>
</tr>
<tr>
<td>(C) Optimizations of Iron-Catalyzed Cross-Coupling of Non-activated Secondary Alkyl Bromides with Alkynyl Grignard Reagent</td>
<td></td>
</tr>
<tr>
<td>(D) Optimizations of Iron-Catalyzed Cross-Coupling of Non-activated Primary Alkyl Iodide with Alkynyl Grignard Reagents</td>
<td></td>
</tr>
<tr>
<td>(E) Optimizations of Iron-Catalyzed Cross-Coupling of Non-activated Primary Alkyl Bromide with Alkynyl Grignard Reagent</td>
<td></td>
</tr>
<tr>
<td>(F) Substrate Scope of Iron-Catalyzed Cross-Coupling of Non-activated Secondary Alkyl Halides with Alkynyl Grignard Reagents: Supplementary Results</td>
<td></td>
</tr>
<tr>
<td>Experimental Section</td>
<td>S11</td>
</tr>
<tr>
<td>References</td>
<td>S52</td>
</tr>
<tr>
<td>NMR Spectra</td>
<td>S54</td>
</tr>
</tbody>
</table>
General Considerations

General Analytical Information

Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz instruments at ambient temperature. All $^1$H NMR spectra were measured in part per million (ppm) relative to the signals for tetramethylsilane (TMS) added into the deuterated chloroform (CDCl$_3$) (0 ppm) unless otherwise stated.$^{[1]}$ Data for $^1$H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, m = multiplet, ovrlp = overlap, br = broad), coupling constants, and integration. All $^{13}$C NMR spectra were reported in ppm relative to CDCl$_3$ (77.16 ppm) unless otherwise stated,$^{[1]}$ and were obtained with complete $^1$H decoupling. All GC analyses were performed on a Perkin-Elmer Clarus 400 GC system with a FID detector. All GC-MS analyses were performed on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector. HPLC analyses were performed on an Agilent Technologies 1260 Infinity LC system with CHIRALCEL® OB-H column for the separation of (3-iodobutyl)benzene ($S_16$, $S_17$) (starting material) and with CHIRALPACK® IB column for the separation of 2-((8-methyl-10-phenyldec-6-y1oxy)tetrahydro-2$H$-pyran (3f) (substituted alkyne product), using a solvent mixture of hexane/isopropanol as an eluent. High-resolution mass spectra (HRMS) by electrospray ionization (ESI) method were performed at the EPFL ISIC Mass Spectroscopy Service with a Micro Mass QTOF Ultima spectrometer. HRMS by atmospheric pressure photoionization (APPI) method were performed on a hybrid linear ion trap Fourier transform ion cyclotron resonance mass spectrometer (LTQ FT-ICR MS, Thermo Scientific, Bremen, Germany) equipped with a 10 T superconducting superconducting agent (Oxford Instruments Nanoscience, Abingdon, UK).

General Reagent Information

Unless otherwise noted, all chemicals used in the preparations of starting materials and in the iron-catalyzed cross-coupling reactions of alkyl halides with alkynyl Grignard reagents were commercially available and were used as received without further purifications. Solvents (tetrahydrofuran (THF), 1,4-dioxane, acetonitrile (MeCN), dimethyl sulfoxide (DMSO), $N,N$-dimethylformamide (DMF), and dichloromethane (CH$_2$Cl$_2$)) were purified and dehydrated using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glove box without exposure to air. Anhydrous $N$-methylpyrrolidone (NMP) (99.8% purity) and anhydrous dimethylacetamide (DMA) (99.8% purity) were purchased from Aldrich Chemical Co. or Acros Chemicals in Sure-Seal bottles and stored under nitrogen. Iron(II) bromide (FeBr$_2$) (98% purity) was purchased from Aldrich Chemical Co. or Acros Chemicals. Iron(II) bromide (FeBr$_2$) [99.999% purity (containing 0.4-3.2 ppm of Co, Cu, Mn, and Cr), beads, -10 mesh] and 1-propynylmagnesium bromide (0.50 M solution in THF) were purchased from Aldrich Chemical Co.. All the secondary alkyl halides (starting materials) and the corresponding substituted alkyne products were in form of racemic mixtures unless otherwise noted. For the 1,3- and 1,4-di-substituted cyclohexyl halides and substituted alkyne products, only one form of enantiomers was shown to demonstrate the diastereomeric ratios (d.r.).
The following known starting materials (alkyl halides and terminal alkynes) were commercially available and used without further purifications:

(i) **Alkyl Halides**

- Iodocyclohexane
- Bromocyclohexane
- Bromocyclopentane
- (2-bromopropyl)benzene
- 2-iodobutane
- 1-bromodecane
- 1-iodoheptane
- (bromomethyl)cyclopropane
- 1-chloro-3-iodopropane
- 1-bromo-3-chloropropane
- 1-bromo-6-chlorohexane
- 1-bromo-4-chlorobutane
- (4-bromobutoxy)benzene
- (3-bromoproxy)benzene

(ii) **Alkynes**

- Hex-1-yne
- Oct-1-yne
- Dec-1-yne
- Ethynylcyclohexane
- Ethynylcyclopropane
- 3,3-Dimethylbut-1-yne
- 1-Ethynylcyclohex-1-ene
- Ethynyltrimethylsilane
- Triethyl(ethynyl)silane
- Ethynyltriisopropylsilane
- Ethynylbenzene
- 1-(tert-butyl)-4-ethynylbenzene
- 4-Ethynyl-\(N,N\)-dimethylaniline
- 1-Ethynyl-4-fluorobenzene
- 1-Chloro-4-ethynylbenzene

The following known starting materials (alkyl halides and terminal alkynes) were prepared according to the literature procedures:[2-13]
General Manipulation Considerations

All manipulations for the iron-catalyzed cross-coupling reactions of alkyl halides with alkynyl Grignard reagents were set up in a 30 mL Teflon-screw cap test tubes under an inert nitrogen (N\textsubscript{2}) atmosphere using glove box techniques. The test tubes were then sealed with air-tight electrical tapes and the reaction mixtures were stirred on bench-top. Flash column chromatography was performed using silica gel (Silicycle, ultra pure grade). The solvent system as an eluent for column chromatography is presented as a ratio of solvent volumes. Yields reported in the publication are of isolated materials. All
new starting materials and substituted alkyne products were characterized by $^1$H NMR and $^{13}$C NMR spectroscopies and high-resolution mass spectrometry (HRMS). In case the new compounds could not be detected by HRMS, the compounds ([M]) were then detected by GCMS analysis and their purities were further determined by GC-MS analysis. All known starting materials and substituted alkyne products were characterized by $^1$H NMR and $^{13}$C NMR spectroscopies and the spectra were further compared with the literature values if available.

**Supplementary Experimental Results**

**Table S1. Optimizations of Iron-Catalyzed Cross-Coupling of Non-activated Secondary Alkyl Iodides with Alkynyl Grignard Reagents$^{[a]}$**

![Chemical Reaction]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metal catalyst (x mol%)</th>
<th>Alkynyl Grignard reagent (y equiv)</th>
<th>Solvent (mL)</th>
<th>Additive (z equiv)</th>
<th>Yield of product (%)$^{[b]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCl$_3$ (5)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>Fe$_2$(SO$_4$)$_3$ (5)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>K$_4$[Fe(CN)$_6$].3H$_2$O (5)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>K$_3$[Fe(CN)$_6$] (5)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>FeCp$_2$ (5)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Fe(NO$_3$)$_3$.9H$_2$O (5)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>Fe(ClO$_4$)$_2$.6H$_2$O (5)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>38</td>
</tr>
<tr>
<td>8</td>
<td>FeSO$_4$ (5)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>FeCl$_2$ (5)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>31</td>
</tr>
<tr>
<td>10</td>
<td>FeBr$_2$ (5)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>64</td>
</tr>
<tr>
<td>11</td>
<td>FeI$_2$ (5)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>49</td>
</tr>
<tr>
<td>12</td>
<td>FeF$_2$ (10)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>FeBr$_2$ (10)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>71</td>
</tr>
<tr>
<td>14</td>
<td>FeBr$_2$ (20)</td>
<td>1.2</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>51</td>
</tr>
<tr>
<td>15</td>
<td>FeBr$_2$ (10)</td>
<td>1.0</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>64</td>
</tr>
<tr>
<td>16</td>
<td>FeBr$_2$ (10)</td>
<td>1.5</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>81</td>
</tr>
<tr>
<td>17</td>
<td>FeBr$_2$ (10)</td>
<td>1.7</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>70</td>
</tr>
<tr>
<td>18</td>
<td>FeBr$_2$ (10)</td>
<td>3.0</td>
<td>NMP (1.5)</td>
<td>---</td>
<td>33</td>
</tr>
<tr>
<td>19</td>
<td>FeBr$_2$ (10)</td>
<td>1.5</td>
<td>NMP (2.0)</td>
<td>---</td>
<td>86</td>
</tr>
<tr>
<td>20</td>
<td>FeBr$_2$ (10)</td>
<td>1.5</td>
<td>NMP (3.0)</td>
<td>---</td>
<td>73</td>
</tr>
<tr>
<td>21</td>
<td>FeBr$_2$ (10)</td>
<td>1.5</td>
<td>NMP (2.0)</td>
<td>---</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>FeBr$_2$ (10)</td>
<td>1.2</td>
<td>DMSO (1.5)</td>
<td>---</td>
<td>20</td>
</tr>
<tr>
<td>23</td>
<td>FeBr$_2$ (10)</td>
<td>1.2</td>
<td>DMA (1.5)</td>
<td>---</td>
<td>55</td>
</tr>
</tbody>
</table>
The conditions for the general Fe-catalyzed cross-coupling of non-activated secondary alkyl iodides with alkynyl Grignard reagents were optimized. Various transition metal catalysts were tested in the cross-coupling of iodocyclohexane with 1-propynylmagnesium bromide in NMP solvent at room temperature. Among a range of iron(III) and iron(II) salts being tested (Table S1, entries 1-12), FeBr₂ was found to be the optimal catalyst (Table S1, entry 10). Further optimization showed that the use of 10 mol% FeBr₂, 1.5 equiv of 1-propynylmagnesium bromide, and 2 mL of NMP solvent afforded the substituted alkyne in the highest yield (Table S1, entry 19). Without FeBr₂ added, no product was obtained (Table S1, entry 21). The variation of other solvents and additives, however, did not further enhance the yield or even decreased the yield (Table S1, entries 22-38). Additionally, the use of transition metal salts other than iron salts did not catalyze the reaction (Table S1, entries 39-48). Furthermore, FeBr₃ did not catalyze the reaction as efficiently as FeBr₂ (Table S1, entry 49). Thus, the conditions of entry 19 were employed for the general Fe-catalyzed cross-coupling of non-activated secondary alkyl iodides with alkynyl Grignard reagents.

---

1. Reaction conditions: iodocyclohexane (0.50 mmol), 1-propynylmagnesium bromide (0.5 M in THF, 0.50-1.5 mmol, 1.0-3.0 mL), metal catalyst (5-20 mol%), solvent (1.5-3.0 mL), and additive (0.05 mmol-1.0 mmol), N₂ atm, rt, 16 h. [b] Calibrated GC yield using n-dodecane as internal standard. [c] Bis[2-(N,N-dimethylamino)ethyl] ether. [d] Tetramethylethylenediamine.
The conditions of Fe-catalyzed cross-coupling of sterically hindered, non-activated secondary alkyl iodides with alkynyl Grignard reagents were optimized. By using 3-iodononane as the model substrate, the general reaction protocol developed in Table S1 was initially employed for the alkynylation process. However, only a low yield of substituted product was obtained (Table S2, entry 1). The use of other solvents did not promote the product yield (Table S2, entries 2-3). Further optimizations showed that the addition of O-TMEDA (2 equiv) provided the highest product yield (Table S2, entry 4). Thus, the conditions of entry 4 were employed for the general Fe-catalyzed cross-coupling of non-activated, sterically hindered secondary alkyl iodides with alkynyl Grignard reagents. Additionally, 20 mol% of FeBr₂ was employed in the subsequent scope study to ensure complete conversion of alkyl iodides.

Table S3. Optimizations of Iron-Catalyzed Cross-Coupling of Non-activated Secondary Alkyl Bromides with Alkynyl Grignard Reagents[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>RBr</th>
<th>R’ (x equiv)</th>
<th>FeBr₂ (y mol%)</th>
<th>Additive (z equiv)</th>
<th>Yield of product (%)[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>SiMe₃ (1.5)</td>
<td>10</td>
<td>---</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>SiMe₃ (1.5)</td>
<td>10</td>
<td>O-TMEDA[c] (2)</td>
<td>45</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 3-iodononane (0.50 mmol), 1-propynylmagnesium bromide (0.5 M in THF, 0.75-1.5 mmol, 1.5-3.0 mL), FeBr₂ (10 mol%), solvent (2.0 mL), and additive (0.5-1.0 mmol), N₂ atm, rt, 16 h. [b] Uncorrected GC yield using n-dodecane as internal standard. [c] 6 h. [d] Bis[2-(N,N-dimethylamino)ethyl] ether. [e] Tetramethylethylenediamine.
**Table S4. Optimizations of Iron-Catalyzed Cross-Coupling of Non-activated Primary Alkyl Iodides with Alkynyl Grignard Reagents**

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>FeBr₂ (x mol%)</th>
<th>Solvent</th>
<th>Additive (y equiv)</th>
<th>Yield of product (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>10</td>
<td>NMP</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>Ph</td>
<td>10</td>
<td>NMP</td>
<td>O-TMEDA[c] (2)</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>Ph</td>
<td>10</td>
<td>THF</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>Ph</td>
<td>10</td>
<td>THF</td>
<td>O-TMEDA[d] (2)</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>Ph</td>
<td>0</td>
<td>THF</td>
<td>O-TMEDA[d] (2)</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Me</td>
<td>20</td>
<td>NMP</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>Me</td>
<td>20</td>
<td>THF</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>8</td>
<td>Me</td>
<td>20</td>
<td>THF</td>
<td>O-TMEDA[d] (2)</td>
<td>30</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1-iodohexane (0.50 mmol), alkynylmagnesium bromide (0.5 M in THF, 0.75 mmol, 1.5 mL), FeBr₂ (10 or 20 mol%), solvent (2.0 mL), and additive (1.0 mmol), N₂ atm, rt, 16 h. [b] Uncorrected GC yield using n-dodecane as internal standard. [c] Bis[2-(N,N-dimethylamino)ethyl] ether.
low yield of substituted product was obtained even when O-TMEDA was added (Table S4, entries 1 and 2). When O-TMEDA (2 equiv) in conjunction with THF solvent were employed, the highest yield of substituted alkyne product was obtained (Table S4, entries 4 and 8). Without FeBr₂, no product was obtained (Table S4, entry 5). Thus, the conditions of entry 4 were employed for the Fe-catalyzed cross-coupling of non-activated primary alkyl iodides with alkynyl Grignard reagents.

Table S5. Optimizations of Iron-Catalyzed Cross-Coupling of Non-activated Primary Alkyl Bromides with Alkynyl Grignard Reagents

![Chemical Structure]

<table>
<thead>
<tr>
<th>Entry</th>
<th>RBr</th>
<th>Solvent</th>
<th>Additive (x equiv)</th>
<th>Yield of Product (%)[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RBr</td>
<td>NMP</td>
<td>---</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>RBr</td>
<td>THF</td>
<td>O-TMEDA[^c] (2)</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>PhOBr</td>
<td>NMP</td>
<td>---</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>PhOBr</td>
<td>THF</td>
<td>O-TMEDA[^c] (2)</td>
<td>91</td>
</tr>
</tbody>
</table>

\[^a\] Reaction conditions: 1-bromoalkane (0.50 mmol), alkynylmagnesium bromide (0.5 M in THF, 0.75 mmol, 1.5 mL), FeBr₂ (10 mol%), solvent (2.0 mL), and additive (1.0 mmol), N₂ atm, rt, 16 h. \[^b\] Uncorrected GC yield using \(n\)-dodecane as internal standard. \[^c\] Bis[2-(N,N-dimethylamino)ethyl] ether.

The conditions of Fe-catalyzed cross-coupling of non-activated primary alkyl bromides with alkynyl Grignard reagents were optimized. By using 1-bromoocatane and (3-bromopropoxy)benzene as the model substrates, we found that the use of O-TMEDA (2 equiv) in conjunction with THF solvent could provide the highest yield of substituted alkyne products (Table S5, entries 2 and 4). Thus, the conditions of entries 2 and 4 were employed for the Fe-catalyzed cross-coupling of non-activated primary alkyl bromides with alkynyl Grignard reagents. Additionally, 20 mol% of FeBr₂ was employed in the subsequent scope study to ensure complete conversion of alkyl bromides.
Scheme S1. Substrate Scope of Iron-Catalyzed Cross-Coupling of Non-activated Secondary Alkyl Halides with Alkynyl Grignard Reagents: Supplementary Results\textsuperscript{[a]}

\[
\begin{array}{c}
R-X + \text{Br-Mg} \rightleftharpoons R' \\
(1.5 \text{ equiv}) \quad \text{FeBr}_2 (10 \text{ mol\%}) \quad \text{THF / NMP, rt, 16 h} \\
\end{array}
\]

P1 \hspace{1cm} X = I, 31%

P2 \hspace{1cm} X = I, 29%

P3 \hspace{1cm} X = I, 37% (d.r. = 10.0:1) (d.r. of RX: 10.3:1)

P4 \hspace{1cm} X = I, 32% (d.r. = 49:1) (d.r. of RX: 15.4:1)

P5 \hspace{1cm} X = I, 38%

P6 \hspace{1cm} X = I, 38%

P7 \hspace{1cm} X = I, 45%

P8 \hspace{1cm} X = I, 28%

P9 \hspace{1cm} X = I, 29%

[a] Reaction conditions: alkyl halide (1.0 mmol), alkynylmagnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), FeBr\textsubscript{2} (10 mol\%), and NMP (4.0 mL), N\textsubscript{2} atm, rt, 16 h; yields are of isolated products.
Experimental Section

Preparation of Alkyl Halides from Alkyl Alcohols (General Procedure A): A 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer was charged with triphenylphosphine (1.4 equiv), imidazole (1.4 equiv), and dichloromethane (300 mL). The reaction mixture was stirred at room temperature until the white solids dissolved to form a clear solution. Iodine (1.4 equiv) were then added slowly in a few portions into the reaction mixture, and the resulting mixture was stirred until all iodine granules dissolved. Alkyl alcohol (1.0 equiv) was then slowly added into the reaction mixture, and the resulting mixture was stirred overnight. The brown mixture was diluted with hexanes and then filtered to remove the solid residues. The filtrate was then concentrated in vacuo with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using hexanes (or a mixture of hexanes and EtOAc) as an eluent to afford the alkyl iodide product.

Preparation of Alkyl Iodides from Benzaldehydes (General Procedure B): A 250 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer was charged with benzaldehyde (1.0 equiv), 3-buten-1-ol (2.0 equiv), iodine (1.0 equiv), and dichloromethane (CH$_2$Cl$_2$, 100 mL). The resulting mixture was stirred under reflux until benzaldehyde was consumed as determined by GCMS analysis. After cooling to room temperature, the reaction mixture was washed with additional CH$_2$Cl$_2$ (50 mL) and saturated Na$_2$S$_2$O$_3$ solution (50 mL). The aqueous solution was further washed with CH$_2$Cl$_2$ (2 x 20 mL). The combined organic fractions were concentrated in vacuo with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using a mixture of hexanes and EtOAc as an eluent to afford the alkyl iodide product.

Preparation of Alkyl Iodides from Alkyl Mesylates (General Procedure C): A 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer was charged with alkyl alcohol (1.0 equiv), mesyl chloride (1.2-1.5 equiv), triethylamine (1.5 equiv), and dichloromethane (CH$_2$Cl$_2$, 200 mL). The reaction mixture was stirred at room temperature for 2 h, followed by washing with excess CH$_2$Cl$_2$ (50 mL) and HCl solution (~1 M (aq), 100 mL). The aqueous solution was further washed with CH$_2$Cl$_2$ (2 x 50 mL). The combined organic layers were then dried with anhydrous Na$_2$SO$_4$, filtered, and concentrated with the aid of a rotary evaporator. The residue was dried in vacuo to afford a crude product of alkyl mesylate in approximately quantitative yield. Subsequently, a 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer was charged with alkyl mesylate (~1.0 equiv), sodium iodide (2.5-3.0 equiv), and solvent (acetone or DMF, 100 mL). The reaction mixture was then stirred at elevated temperature (acetone: 60 °C; DMF: 100 °C) overnight. After cooling to room temperature. After cooling to room temperature, the reaction mixture was washed with CH$_2$Cl$_2$ (50 mL) and water (400 mL). The aqueous solution was further washed with CH$_2$Cl$_2$ (2 x 50 mL). The combined organic fractions were concentrated in vacuo with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using a mixture of hexanes and EtOAc as an eluent to afford the alkyl iodide product.
Preparation of Alkyl Iodide from Nitrogen-Containing Heterocycle (General Procedure D): A 500 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stirrer was charged with N-containing heterocycle (1.0 equiv) and sodium hydride (1.3-1.5 equiv, 60% NaH suspension in oil used). The flask was degassed and refilled with N₂ (this process was repeated for 3 times). Anhydrous DMF (80 mL) was then slowly added into the flask under N₂, and the reaction mixture was stirred at room temperature for 2 h. 1-Bromo-3-chloropropane (1.3-1.5 equiv) was the added into the flask under N₂ via syringe, and the reaction mixture was stirred at room temperature overnight. The reaction mixture was then washed with CH₂Cl₂ (50 mL) and water (400 mL). The aqueous solution was further washed with CH₂Cl₂ (2 x 50 mL). The combined organic layer was dried with anhydrous Na₂SO₄, filtered, and concentrated with the aid of a rotary evaporator. The residue was dried in vacuo to afford a crude product of 1-chloro-3-(heteroaryl)propane in approximately quantitative yield. Subsequently, a 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer was charged with 1-chloro-3-(heteroaryl)propane (~1.0 equiv), sodium iodide (2.5-3.0 equiv), and acetone (100 mL). The reaction mixture was then stirred at elevated temperature at 60 °C overnight. After cooling to room temperature, the reaction mixture was washed with CH₂Cl₂ (50 mL) and water (400 mL). The aqueous solution was further washed with CH₂Cl₂ (2 x 50 mL). The combined organic fractions were concentrated in vacuo with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using a mixture of hexanes and EtOAc as an eluent to afford the alkyl iodide product.

Preparations of Alkynes (General Procedure E): A 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer was charged with chloro-substituted terminal alkyne (1.0-1.3 equiv), K₂CO₃ (2 equiv), 4-substituted phenol (1.0-1.3 equiv), sodium iodide (0.2-0.5 equiv), and DMF (60 mL). The reaction mixture was stirred at 70 °C overnight. After cooling to room temperature, the reaction mixture was washed with CH₂Cl₂ (50 mL) and water (400 mL). The aqueous solution was further washed with CH₂Cl₂ (2 x 50 mL). The combined organic fractions were concentrated in vacuo with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using a mixture of hexanes and EtOAc as an eluent to afford the funcionalized terminal alkyne product.

1-Iodo-3-methylcyclohexane (S1).[5] Following the general procedure A, the title compound was prepared using cis/trans-3-methylcyclohexan-1-ol (6.85 g, 60 mmol), triphenylphosphine (22.0 g, 84 mmol), imidazole (5.72 g, 84 mmol), and iodine (21.3 g, 84 mmol). After work up, the crude product was purified by flash chromatography with silica gel using hexanes as an eluent to afford 1-iodo-3-methylcyclohexane (S1) as colorless oil (6.50 g, 29 mmol, 48%). The diastereomeric ratio (d.r.: trans:cis = 6.4:1) of S1 was determined by ¹H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers.[14] ¹H NMR (400 MHz, CDCl₃): δ 4.85 (s, 0.9 H), 4.15 (t, J = 12.2 Hz, 0.1 H), 2.40-1.96 (m, 3 H), 1.83-1.68 (ovrlp, 2 H), 1.63-1.48 (ovrlp, 2 H), 1.27 (t, J = 11.0 Hz, 1 H), 1.03 (t, J = 11.2 Hz, 1 H), 0.93-0.88 (ovrlp, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 49.3, 44.8, 40.3,
Iodobicyclo[2.2.1]heptane \([S4]\). Following the general procedure A, the title compound was prepared using bicyclo[2.2.1]heptan-2-ol (5.0 g, 44.6 mmol), triphenylphosphine (14.4 g, 62.4 mmol), imidazole (4.25 g, 62.4 mmol), and iodine (15.8 g, 62.4 mmol). After work up, the crude product was purified by flash chromatography with silica gel using hexanes as an eluent to afford 2-Iodobicyclo[2.2.1]heptane \([S4]\) as colorless oil (7.48 g, 33.7 mmol, 76%). The diastereomeric ratio (d.r.: \(\text{exo:endo} = 4.3:1\)) of \(S4\) was determined by \(^1\)H NMR spectroscopy of the isolated product. The major \(\text{exo}\)-isomer was determined by comparing the chemical shift of \(ipso\)-C-H proton of the product with that...
of the reported compound.\textsuperscript{[15]} \textbf{\textit{H} NMR} (400 MHz, CDCl$_3$): $\delta$ 4.26-4.24 (m, 0.2 H), 3.98-3.97 (m, 0.8 H), 2.60 (s, 0.8 H), 2.40 (s, 0.2 H), 2.24-2.22 (m, 2 H), 2.12-2.06 (m, 1 H), 1.93-1.82 (m, 1 H), 1.62-1.42 (m, 2 H), 1.40-1.31 (m, 1 H), 1.26-1.22 (m, 1 H), 1.10 (t, $J = 9.4$ Hz, 1 H). \textbf{\textit{C} NMR} (exo-isomer (major), 100 MHz, CDCl$_3$): $\delta$ 48.1, 45.3, 38.1, 36.4, 30.4, 28.8, 28.5.

\textbf{1,4-Diiodocyclohexane (S5)}.\textsuperscript{[16]} Following the general procedure A, the title compound was prepared using cyclohexane-1,4-diol (2.32 g, 20 mmol, 1.0 equiv), triphenylphosphine (31.5 g, 120 mmol, 6.0 equiv), imidazole (8.17 g, 120 mmol, 6.0 equiv), and iodine (30.5 g, 120 mmol, 6 equiv). The crude product was purified by flash chromatography with silica gel using hexanes as an eluent to afford 1,4-diiodocyclohexane containing a small amount of impurity. The product was heated \textit{in vacuo} to remove the low-boiling impurity. The resulting product was further purified by flash chromatography with silica gel using hexanes as an eluent to afford a pure 1,4-diiodocyclohexane (S5) as a white solid (2.59 g, 7.7 mmol, 39\%). The diastereomeric ratio (d.r. = 2.8:1) of S5 was determined by GCMS analysis. The major diastereoisomer could not be determined due to the broadening and overlapping of the characteristic ipso-C-H protons by \textbf{\textit{H} NMR} spectroscopy. \textbf{\textit{H} NMR} (400 MHz, CDCl$_3$): $\delta$ 4.51-4.41 (ovrlp, 2 H), 2.28-2.19 (m, 4 H), 2.06-1.96 (m, 4 H). \textbf{\textit{C} NMR} (major diastereoisomer, 100 MHz, CDCl$_3$): $\delta$ 39.0 (br), 37.4, 29.5 (br).

\textbf{(2-Iodopropyl)benzene (S6)}.\textsuperscript{[17]} Following the general procedure A, the title compound was prepared using 1-phenylpropan-2-ol (10.5 g, 76.8 mmol), triphenylphosphine (28.2 g, 107.5 mmol), imidazole (7.32 g, 107.5 mmol), and iodine (27.3 g, 107.5 mmol). The crude product was purified by flash chromatography with silica gel using hexanes as an eluent to afford (2-iodopropyl)benzene (S6) as colorless oil (16.6 g, 67.5 mmol, 88\%). \textbf{\textit{H} NMR} (400 MHz, CDCl$_3$): 7.32-7.24 (ovrlp, 3 H), 7.17 (d, $J = 6.5$ Hz, 2 H), 4.33 (sex, $J = 6.8$ Hz, 1 H), 3.31-3.26 (m, 1 H), 3.08-3.03 (m, 1 H), 1.89 (d, $J = 6.5$ Hz, 3 H).

\textbf{2-Iodononane (S7)}. Following the general procedure A, the title compound was prepared using 1-phenylpropan-2-ol (10.1 g, 70 mmol), triphenylphosphine (25.7 g, 98 mmol), imidazole (6.67 g, 98 mmol), and iodine (24.9 g, 98 mmol). The crude product was purified by flash chromatography with silica gel using hexanes as an eluent to afford (2-iodopropyl)benzene (S7) as colorless oil (15.7 g, 61.7 mmol, 88\%). \textbf{\textit{H} NMR} (400 MHz, CDCl$_3$): $\delta$ 4.19 (sex, $J = 6.5$ Hz, 1 H), 1.93 (d, $J = 6.6$ Hz, 3 H), 1.86-1.79 (m, 1 H), 1.65-1.56 (m, 1 H), 1.51-1.24 (ovrlp, 10 H), 0.89 (t, $J = 6.5$ Hz, 3 H). \textbf{\textit{C} NMR} (100 MHz, CDCl$_3$): $\delta$ 43.1, 31.9, 31.1, 29.9, 29.3, 29.1, 28.9, 22.8, 14.3. \textbf{HRMS}: [M] could not be detected by HRMS (ESI and APPI). \textbf{GCMS}: [M] = 254 detected which corresponds to C$_9$H$_{10}$I; the purity was further confirmed by GCMS.
4-Iodo-2-phenyltetrahydro-2H-pyran (S8). Following the general procedure B, the title compound was prepared using benaldehyde (4.24 g, 40 mmol), 3-buten-1-ol (5.77 g, 80 mmol), and iodine (10.2 g, 40 mmol). The crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (15:1) as an eluent to afford 4-iodo-2-phenyltetrahydro-2H-pyran (S8) as brown oil (6.33 g, 22.0 mmol, 55%). The diastereomeric ratio (d.r.: cis:trans = 15.7:1) of S8 was determined by 1H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers. 1H NMR (400 MHz, CDCl3): δ 7.35-7.24 (ovrlp, 5 H), 4.92 (s, 0.06 H), 4.84 (d, J = 10.2 Hz, 0.06 H), 4.44-4.36 (m, 0.94 H), 4.31 (d, J = 10.9 Hz, 0.94 H), 4.05-3.98 (ovrlp, 1 H), 3.61-3.55 (m, 1 H), 2.55 (d, J = 12.4 Hz, 1 H), 2.40-1.84 (ovrlp, 3 H). 13C NMR (major diastereoisomer, 100 MHz, CDCl3): δ 141.2, 128.6, 127.9, 125.8, 81.4, 69.6, 47.7, 39.6, 22.1.

4-Iodo-2-(4-methoxyphenyl)tetrahydro-2H-pyran (S9). Following the general procedure B, the title compound was prepared using 4-methoxybenaldehyde (5.45 g, 40 mmol), 3-buten-1-ol (5.77 g, 80 mmol), and iodine (10.2 g, 40 mmol). After work up, the crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (10:1) as an eluent to afford 4-iodo-2-(4-methoxyphenyl)tetrahydro-2H-pyran (S9) as viscous brown oil (2.35 g, 7.4 mmol, 19%). The diastereomeric ratio (d.r.: cis:trans = 3.0:1) of S9 was determined by 1H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers. 1H NMR (400 MHz, CDCl3): δ 7.26-7.21 (ovrlp, 2 H), 6.84 (d, J = 8.1 Hz, 2 H), 4.87 (s, 0.2 H), 4.76 (d, J = 10.3 Hz, 0.2 H), 4.34 (t, J = 11.5 Hz, 0.8 H), 4.21 (d, J = 10.8 Hz, 0.8 H), 4.03-3.92 (ovrlp, 1.2 H), 3.74 (s, 3 H), 3.51 (t, J = 11.2 Hz, 0.8 H), 2.50-1.78 (m, 4 H). 13C NMR (major diastereoisomer, 100 MHz, CDCl3): δ 159.0, 133.3, 127.0, 113.7, 80.7, 69.3, 55.2, 47.4, 39.4, 22.4.

2-(4-Fluorophenyl)-4-iodotetrahydro-2H-pyran (S10). Following the general procedure B, the title compound was prepared using 4-fluorobenaldehyde (4.96 g, 40 mmol), 3-buten-1-ol (5.77 g, 80 mmol),
and iodine (10.2 g, 40 mmol). After work up, the crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (15:1) as an eluent to afford 2-(4-fluorophenyl)-4-iodotetrahydro-2H-pyran (S10) as brown oil (8.21 g, 26.8 mmol, 67%). The diastereomeric ratio (d.r.: cis:trans = 10.1:1) of S10 was determined by $^1$H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers.$^{[14]}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29 (dd, $^3$J$_{HH}$ = 7.8 Hz, $^4$J$_{HF}$ = 5.8 Hz, 2 H), 7.02 ($^3$J$_{HH}$ = 8.5 Hz, $^3$J$_{HF}$ = 8.5 Hz, 2 H), 4.91 (s, 0.1 H), 4.81 (d, $J$ = 10.3 Hz, 0.1 H), 4.42-4.34 (m, 0.9 H), 4.29 (d, $J$ = 10.8 Hz, 0.9 H), 4.06-3.97 (ovrlp, 1 H), 3.60-3.54 (m, 1 H), 2.52 (d, $J$ = 12.8 Hz, 1 H), 2.39-1.80 (ovrlp, 3 H). $^{13}$C NMR (major diastereoisomer, 100 MHz, CDCl$_3$): $\delta$ 162.2 (d, $^1$J$_{CF}$ = 244.4 Hz), 137.0 (d, $^2$J$_{CF}$ = 3.1 Hz), 127.5 (d, $^2$J$_{CF}$ = 8.0 Hz), 115.4 (d, $^2$J$_{CF}$ = 21.2 Hz), 80.5, 69.5, 47.6, 39.4, 21.7. HRMS (APPI): Calcd for C$_{11}$H$_{11}$FIO [M-H]: 304.9834; Found: 304.9833.

4-Iodo-2-(4-(trifluoromethyl)phenyl)tetrahydro-2H-pyran (S11). Following the general procedure B, the title compound was prepared using 4-(trifluoromethyl)benaldehyde (1.2 g, 8.8 mmol), 3-buten-1-ol (1.27 g, 17.6 mmol), and iodine (2.23 g, 8.8 mmol). After work up, the crude product was purified by flash chromatography with silica gel using hexanes as an eluent to afford 4-iodo-2-(4-(trifluoromethyl)phenyl)tetrahydro-2H-pyran (S11) as brown oil (981 mg, 2.76 mmol, 31%). The diastereomeric ratio (d.r.: cis:trans = 3.3:1) of S11 was determined by $^1$H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers.$^{[14]}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.59 (d, $J$ = 7.7 Hz, 2 H), 7.46-7.25 (ovrlp, 2 H), 4.91-4.88 (ovrlp, 0.4 H), 4.43-4.36 (ovrlp, 1.6 H), 4.08-4.00 (ovrlp, 1.2 H), 3.65-3.55 (m, 0.8 H), 2.56 (d, $J$ = 12.2 Hz, 0.8 H), 2.36-2.32 (ovrlp, 1.2 H), 2.22-2.13 (ovrlp, 1 H), 1.97 (s, 0.8 H), 1.80 (t, $J$ = 12.8 Hz, 0.2 H). $^{13}$C NMR (major diastereoisomer, 100 MHz, CDCl$_3$): $\delta$ 145.1, 129.9 (q, $^2$J$_{CF}$ = 32.1 Hz), 126.0, 125.5 (q, $^3$J$_{CF}$ = 3.4 Hz), 124.2 (q, $^1$J$_{CF}$ = 270.3 Hz), 80.4, 69.5, 47.5, 39.4, 21.1. HRMS (APPI): Calcd for C$_{12}$H$_{12}$F$_3$IO [M]: 355.9853; Found: 355.9879.

Benzy1 3-iodoazetidine-1-carboxylate (S12).$^{[5]}$ Following the general procedure C, the title compound was prepared using benzy1 3-iodoazetidine-1-carboxylate (5.05 g, 24.5 mmol), mesyl chloride (4.21 g, 2.8 mL, 36.8 mmol), and triethylamine (3.72 g, 5.1 mL, 36.8 mmol), followed by the iodination of the crude benzy1 3-((methylsulfonyl)oxy)azetidine-1-carboxylate product with sodium iodide (11.0 g, 73.5 mmol) in DMF (Note: No reaction occurred when acetone solvent was used). After work up, the crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (10:1) as an eluent to afford benzy1 3-iodoazetidine-1-carboxylate (S12) as brown oil (5.08 g, 9.6 mmol, 39%). $^1$H NMR (400 MHz, CDCl$_3$): 7.36-7.29 (ovrlp, 5 H), 5.08 (s, 2 H), 4.68 (t, $J$ = 8.4 Hz, 2 H), 4.43 (qu, $J$ = 5.2 Hz, 1 H), 4.34-4.31 (m, 2 H).
**Ethyl 3-iodobutanoate (S13).** Following the general procedure C, the title compound was prepared using ethyl 3-hydroxybutanoate (3.97 g, 30 mmol), mesyl chloride (4.12 g, 2.8 mL, 36 mmol), and triethylamine (4.6 g, 6.2 mL, 45 mmol), followed by the iodination of the crude ethyl 3-((methylsulfonyl)oxy)butanoate product with sodium iodide (11.2 g, 75 mmol) in acetone. After work up, the crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (10:1) as an eluent to afford ethyl 3-iodobutanoate (S13) as colorless oil (4.62 g, 19.1 mmol, 64%).

\[^1H\text{NMR}\quad (400\text{ MHz, CDCl}_3): \delta 4.39\text{ (s, }J = 7.0\text{ Hz, }1\text{ H}), 4.11\text{ (q, }J = 7.0\text{ Hz, }2\text{ H), }2.96\text{--}2.90\text{ (m, }1\text{ H), }2.87\text{--}2.81\text{ (m, }1\text{ H), }1.87\text{ (d, }J = 6.7\text{ Hz, }3\text{ H), }1.21\text{ (t, }J = 7.0\text{ Hz, }3\text{ H).}\]

\[^{13}C\text{NMR}\quad (100\text{ MHz, CDCl}_3): \delta 170.5, 61.0, 48.0, 28.8, 18.6, 14.3.\]

**9-(3-Iodopropyl)-9H-carbazole (S14).** Following the general procedure D, the title compound was prepared using carbazole (10.0 g, 60 mmol), sodium hydride (2.17 g, 90 mmol, 3.62 g of 60% NaH suspension in oil used), and 1-bromo-3-chloropropane (14.2 g, 8.9 mL, 90 mmol), followed by iodination of the crude 1-(3-chloropropyl)-1H-carbazole product with NaI (23.5 g, 150 mmol). After work up, the crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (15:1) as an eluent to afford 1-(3-iodopropyl)-1H-indole (S14) as a pale-yellow solid (18.1 g, 54 mmol, 90%).

\[^1H\text{NMR}\quad (400\text{ MHz, CDCl}_3): \delta 8.10\text{ (d, }J = 7.7\text{ Hz, }2\text{ H), }7.50\text{--}7.45\text{ (ovrlp, }4\text{ H), }7.27\text{--}7.21\text{ (m, }2\text{ H), }4.43\text{ (d, }J = 6.6\text{ Hz, }2\text{ H), }3.16\text{ (d, }J = 6.4\text{ Hz, }2\text{ H), }2.41\text{ (qu, }J = 6.5\text{ Hz, }2\text{ H).}\]

\[^{13}C\text{NMR}\quad (100\text{ MHz, CDCl}_3): \delta 140.3, 125.9, 123.0, 120.5, 119.2, 108.7, 43.1, 32.8, 3.2.\]

**HRMS (ESI): Calcd for C\textsubscript{15}H\textsubscript{15}IN [M+H]: 336.0249; Found: 366.0257.**

**1-(3-Iodopropyl)-1H-indole (S15).** Following the general procedure D, the title compound was prepared using indole (4.11 g, 35.0 mmol), sodium hydride (1.10 g, 45.5 mmol, 1.83 g of 60% NaH suspension in oil used), and 1-bromo-3-chloropropane (7.16 g, 4.5 mL, 45.5 mmol), followed by iodination of the crude 1-(3-chloropropyl)-1H-indole product with NaI (13.1 g, 87.5 mmol). After work up, the crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (15:1) as an eluent to afford 1-(3-iodopropyl)-1H-indole (S15) as pale-yellow oil (3.94 g, 13.8 mmol, 39%).

\[^1H\text{NMR}\quad (400\text{ MHz, CDCl}_3): \delta 7.61\text{ (d, }J = 7.6\text{ Hz, }1\text{ H), }7.31\text{ (d, }J = 8.0\text{ Hz, }1\text{ H), }7.18\text{ (t, }J = 7.5\text{ Hz, }1\text{ H), }7.11\text{--}7.05\text{ (ovrlp, }2\text{ H), }6.46\text{ (s, }1\text{ H), }4.14\text{ (t, }J = 6.0\text{ Hz, }2\text{ H), }2.95\text{ (t, }J = 6.2\text{ Hz, }2\text{ H), }2.18\text{ (qu, }J = 6.2\text{ Hz, }2\text{ H).}\]

\[^{13}C\text{NMR}\quad (100\text{ MHz, CDCl}_3): \delta 135.8, 128.7, 128.0, 121.7, 121.1, 119.6, 109.4, 101.5, 46.1, 33.4, 3.4.\]

**HRMS (ESI): Calcd for C\textsubscript{11}H\textsubscript{13}IN [M+H]: 286.0093; Found: 286.0080.**
Synthesis of Enantioenriched Alkyl Halides:

\[
\text{(R)}: (S) = 79:21
\]

(\text{R})-(3-Iodobutyl)benzene (S16). Following the general procedure A and the similar literature procedure,\[6\] the title compound was prepared using (\text{S})-4-phenylbutan-2-ol (185 mg, 1.23 mmol, 1.0 equiv), triphenylphosphine (969 mg, 3.69 mmol, 3.0 equiv), imidazole (251 mg, 3.69 mmol, 3.0 equiv), and iodine (937 mg, 3.69 mmol, 3.0 mmol). The crude product was purified by flash chromatography with silica gel using hexanes as an eluent to afford enantioenriched (\text{R})-(3-iodobutyl)benzene (S16) (288 mg, 1.11 mmol, 90%). The enantiomeric ratio of (S16) ((\text{R}):(\text{S}) = 79:21) was determined by HPLC analysis as shown below. The identification and purity of (S16) were further determined by GCMS and HPLC analysis by comparing with authentic and racemic (\text{R})/(\text{S})-(3-iodobutyl)benzene synthesized from (\text{R})/(\text{S})-phenylbutan-2-ol.\[5\] The \(^1\)H NMR of (S16) was in agreement with that of (\text{R})/(\text{S})-(3-iodobutyl)benzene.\[5\] The HPLC separation of S16 was shown below.

HPLC separation of enantio-enriched (R)-(3-iodobutyl)benzene

\[
\begin{align*}
\text{(S)}-(3-\text{iodobutyl})\text{benzene} & \quad \text{enantiomeric ratio:} \\
\text{(R)}-(3-\text{iodobutyl})\text{benzene} & \quad (\text{R}) : (\text{S}) = 79 : 21
\end{align*}
\]

\[
\begin{align*}
\text{(S)}-4\text{-phenylbutan-2-ol} & \quad \text{PPh}_3 \text{ (3 equiv), I}_2 \text{ (3 equiv)} \\
& \quad \text{imidazole (3 equiv)} \\
& \quad \text{DCM, rt, overnight} \\
\text{(R)}-(3-\text{iodobutyl})\text{benzene (S16)} & \quad (\text{R}) : (\text{S}) = 79 : 21 \\
& \quad \text{90%}
\end{align*}
\]
(R)-(3-Iodobutyl)benzene (S17). The title compound was prepared according to the literature procedure. In a nitrogen-filled glovebox, an oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stirrer bar was charged with (S)-4-phenylbutan-2-ol (150 mg, 1.0 mmol, 1.0 equiv), trimethylsilyl iodide (242 mg, 172 µL, 1.1 mmol, 1.1 equiv), and anhydrous CH₂Cl₂ (10 mL). The reaction mixture was stirred at room temperature for 13 h. The reaction mixture was then washed with CH₂Cl₂ (20 mL) and saturated Na₂S₂O₃ solution (20 mL). The aqueous solution was further washed with CH₂Cl₂ (2 x 10 mL). The combined organic fractions were concentrated with the aid of a rotary evaporator. The crude product was purified by flash chromatography with silica gel using hexanes as an eluent to afford enantiomERICALLY enriched (R)-(3-iodobutyl)benzene (S17) (82 mg, 0.31 mmol, 31%). The enantiomeric ratio of (S17) ((R):(S) = 98:2) was determined by HPLC analysis. The identification and purity of (S17) were further determined by GCMS and HPLC analysis by comparing with authentic and racemic (R)/(S)-(3-iodobutyl)benzene synthesized from (R)/(S)-phenylbutan-2-ol.\(^5\) The HPLC separation of S17 was shown below.

HPLC separation of enantio-enriched (R)-(3-iodobutyl)benzene

\[\text{(R)} : \text{(S)} = 98 : 2\]
1-Bromo-4-(hex-5-yn-1-yloxy)benzene (S18). Following the general procedure E, the title compound was prepared using 6-chloro-1-hexyne (1.77 g, 15.2 mmol, 1.0 equiv), K₂CO₃ (4.20 g, 30.4 mmol, 2.0 equiv), 4-bromophenol (3.42 g, 19.8 mmol, 1.3 equiv), and sodium iodide (1.14 g, 7.6 mmol, 0.5 equiv). After work up, the crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (20:1) as an eluent to afford 1-bromo-4-(hex-5-yn-1-yloxy)benzene (S18) as pale-yellow oil (2.41 g, 9.52 mmol, 63%).

**1H NMR** (400 MHz, CDCl₃): δ 7.34 (d, J = 8.6 Hz, 2 H), 6.74 (d, J = 8.6 Hz, 2 H), 3.91 (t, J = 6.1 Hz, 2 H), 2.27-2.23 (m, 1 H), 1.98 (s, 1 H), 1.88 (d, J = 6.7 Hz, 2 H), 1.69 (d, J = 7.2 Hz, 2 H).

**13C NMR** (100 MHz, CDCl₃): δ 158.1, 132.2, 116.3, 112.7, 84.1, 68.9, 67.5, 28.2, 25.0, 18.2.

**HRMS** (ESI): Calcd for C₁₂H₁₃BrOAg [M+Ag]: 358.9201; Found: 358.9230.

1-Chloro-4-(hex-5-yn-1-yloxy)benzene (S19). Following the general procedure E, the title compound was prepared using 6-chloro-1-hexyne (2.33 g, 20 mmol, 1.0 equiv), K₂CO₃ (5.52 g, 40 mmol, 2.0 equiv), 4-chlorophenol (3.34 g, 26 mmol, 1.3 equiv), and sodium iodide (1.50 g, 10 mmol, 0.5 equiv). After work up, the crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (20:1) as an eluent to afford 1-chloro-4-(hex-5-yn-1-yloxy)benzene (S19) as pale-yellow oil (3.37 g, 16.2 mmol, 62%).

**1H NMR** (400 MHz, CDCl₃): δ 7.21 (d, J = 8.4 Hz, 2 H), 6.80 (d, J = 8.4 Hz, 2 H), 3.91 (t, J = 6.1 Hz, 2 H), 2.27-2.23 (m, J = 2 H), 1.98 (s, 1 H), 1.88 (d, J = 6.7 Hz, 2 H), 1.69 (d, J = 7.2 Hz, 2 H).

**13C NMR** (100 MHz, CDCl₃): δ 157.7, 129.4, 125.5, 115.8, 84.1, 68.9, 67.5, 28.2, 25.0, 18.2. **HRMS**: [M] could not be detected by HRMS (ESI). **GCMS**: [M] = 208 detected which corresponds to C₁₂H₁₃ClO; the purity was further confirmed by GCMS.

Methyl(4-(pent-4-yn-1-yloxy)phenyl)sulfane (S20). Following the general procedure E, the title compound was prepared using 5-chloro-1-pentyne (4.00 g, 39 mmol, 1.3 equiv), K₂CO₃ (8.29 g, 60 mmol, 2.0 equiv), 4-(methylthio)phenol (4.21 g, 30 mmol, 1.0 equiv), and sodium iodide (900 mg, 6.0 mmol, 0.2 equiv). After work up, the crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (20:1) as an eluent to afford methyl(4-(pent-4-yn-1-yloxy)phenyl)sulfane (S20) as pale-yellow oil (4.88 g, 23.7 mmol, 79%).

**1H NMR** (400 MHz, CDCl₃): δ 7.25 (d, J = 8.3 Hz, 2 H), 6.84 (d, J = 8.3 Hz, 2 H), 4.02 (t, J = 5.9 Hz, 2 H), 2.43-2.36 (ovrlp, 5 H), 2.01-1.92 (ovrlp, 3 H). **13C**
NMR (100 MHz, CDCl₃): δ 157.5, 130.2, 128.9, 115.3, 83.5, 69.0, 66.3, 28.2, 18.1, 15.2. HRMS (ESI): Calcd for C₁₂H₁₄OSAg [M+Ag]: 312.9816; Found: 312.9803.

1-(2-Iodopropyl)-4-methoxybenzene (S21). Step (1): A 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer was charged with 1-(4-methoxyphenyl)propan-2-one (9.85 g, 60 mmol, 1.0 equiv) and methanol (300 mL). The reaction mixture was cooled in an ice-water bath, and NaBH₄ (6.81 g, 180 mmol, 3.0 equiv) was slowly added into the reaction mixture in a few portions. The resulting reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was dried in vacuo with the aid of a rotary evaporator, and the residue was then washed with water (400 mL) and CH₂Cl₂ (100 mL). The aqueous fraction was further washed with CH₂Cl₂ (2 x 100 mL). The combined organic fractions were dried with anhydrous Na₂SO₄, filtered, and dried with the aid of a rotary evaporator. The residue was dried in vacuo to afford a crude 1-(4-methoxyphenyl)propan-2-ol as a viscous, colorless oil. Step (2): Following the general procedure A, the title compound was prepared using 1-phenylpropan-2-ol (prepared from the preceding procedure, ~60 mmol), triphenylphosphine (22.0 g, 84 mmol), imidazole (5.72 g, 84 mmol), and iodine (21.3 g, 84 mmol). The crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (10:1) as an eluent to afford 1-(2-iodopropyl)-4-methoxybenzene (S21) as colorless oil (11.1 g, 40.2 mmol, 67%).

1H NMR (400 MHz, CDCl₃): δ 7.10 (d, J = 8.2 Hz, 2 H), 6.84 (d, J = 8.2 Hz, 2 H), 4.29 (sex, J = 7.0 Hz, 1 H), 3.79 (s, 3 H), 3.25-3.20 (m, 1 H), 3.02-2.96 (m, 1 H), 1.88 (d, J = 6.8 Hz, 2 H).

13C NMR (100 MHz, CDCl₃): δ 158.5, 132.0, 130.1, 113.9, 55.3, 48.7, 29.6, 28.0. HRMS (APPI): Calcd for C₁₀H₁₃IO [M]: 276.0017; Found: 276.0011.

4-(2-Iodopropyl)-1,2-dimethoxybenzene (S22). Step (1): A 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer was charged with 1-(3,4-dimethoxyphenyl)propan-2-one (11.7 g, 60 mmol, 1.0 equiv) and methanol (300 mL). The reaction mixture was cooled in an ice-water bath, and NaBH₄ (6.81 g, 180 mmol, 3.0 equiv) was slowly added into the reaction mixture in a few portions. The resulting reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was dried in vacuo with the aid of a rotary evaporator, and the residue was then washed with water (400 mL) and CH₂Cl₂ (100 mL). The aqueous fraction was further washed with CH₂Cl₂ (2 x 100 mL). The combined organic fractions were dried with anhydrous Na₂SO₄, filtered, and dried with the aid of a rotary evaporator. The residue was dried in vacuo to afford a crude 1-(3,4-dimethoxyphenyl)propan-2-ol as a white solid. Step (2): Following the general procedure A, the title compound was prepared using 1-(3,4-dimethoxyphenyl)propan-2-ol (prepared from the preceding procedure, ~60 mmol), triphenylphosphine (22.0 g, 84 mmol), imidazole (5.72 g, 84 mmol), and iodine (21.3 g, 84 mmol). The crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (10:1) as an eluent to afford 4-(2-iodopropyl)-1,2-dimethoxybenzene (S22) as viscous, colorless oil (16.4 g, 53.6 mmol, 89%).

1H NMR (400 MHz, CDCl₃): δ 6.81 (d, J = 7.9 Hz, 1 H), 6.73-6.71 (ovrlp, 2 H), 4.32 (sex, J = 6.9 Hz, 1 H), 3.88 (s, 3 H), 3.86 (s, 3 H), 3.26-3.21 (m, 1 H), 3.02-2.97 (m, 1 H), 1.89 (d, J = 6.7 Hz,
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.23 (t, $J = 7.5$ Hz, 2 H), 6.72 (t, $J = 7.2$ Hz, 1 H), 6.66 (d, $J = 7.9$ Hz, 2 H), 4.35 (sex, $J = 7.2$ Hz, 1 H), 3.90-3.85 (m, 1 H), 3.52-3.46 (m, 1 H), 3.00 (s, 3 H), 1.85 (d, $J = 6.7$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.2, 129.4, 116.9, 111.8, 63.2, 39.8, 25.9, 25.8. HRMS (ESI): Calcd for C$_{16}$H$_{24}$N $[M+H]$; 230.1909; Found: 230.1913.

**N-(2-iodopropyl)-N-methylaniline (S23). Step (1):** A 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer and capped with a rubber septum was charged with N-methylaniline (6.43 g, 60.0 mmol, 1.0 equiv), propylene oxide (10.5 g, 12.6 mL 180 mmol, 3.0 equiv), and ethanol (200 mL). The reaction mixture was then heated at 90 °C overnight. The reaction mixture was dried in vacuo with the aid of a rotary evaporator, and the residue was then washed with water (400 mL) and CH$_2$Cl$_2$ (100 mL). The aqueous fraction was further washed with CH$_2$Cl$_2$ (2 x 100 mL). The combined organic fractions were dried with anhydrous Na$_2$SO$_4$, filtered, and dried in vacuo with the aid of a rotary evaporator. The residue was dried in vacuo to afford a crude 1-(methyl(phenyl)amino)propan-2-ol as a yellow oil. **Step (2):** Following the general procedure A, the title compound was prepared using 1-(methyl(phenyl)amino)propan-2-ol (prepared from the preceding procedure, ~60 mmol), triphenylphosphine (22.0 g, 84 mmol), imidazole (5.72 g, 84 mmol), and iodine (21.3 g, 84 mmol). The crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (8:1) as an eluent to afford N-(2-iodopropyl)-N-methylaniline (S23) as brown oil (12.5 g, 45.5 mmol, 76%).

**Ethyl (2-Bromopropyl)(2-methoxyphenyl)carbamate (S24). Step (1):** A 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer and capped with a rubber septum was charged with 2-methoxyaniline (18.5 g, 16.9 mL, 150 mmol, 1.0 equiv), triethylamine (18.2 g, 25.0 mL 180 mmol, 1.2 equiv), and CH$_2$Cl$_2$ (200 mL). Bromopropanoyl bromide (32.4 g, 15.7 mL, 150 mmol, 1.0 equiv) was then added dropwise into the reaction mixture, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with aqueous HCl solution (1 M, 300 mL), and the aqueous fraction was further washed with CH$_2$Cl$_2$ (2 x 50 mL). The combined organic fractions were then washed with water (200 mL), dried with anhydrous Na$_2$SO$_4$, filtered, and dried in vacuo with the aid of a rotary evaporator. The residue was dried in vacuo to afford a crude 2-bromo-N-(2-methoxyphenyl)propanamide. **Step (2):** A 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer and capped with a rubber septum was charged with 2-bromo-N-(2-methoxyphenyl)propanamide (prepared from the preceding procedure) and dry THF (200 mL), and borane-THF solution (1 M in THF, 180 mmol, 180 mL) was then added into the reaction mixture. The resulting solution was stirred at room temperature for 15 min and then heated at 50 °C in an oil bath overnight. After the reaction, water (50 mL) was added and the
reaction mixture was stirred for 15 min to deactivate any unreacted BH₃. The crude reaction mixture was dried in vacuo with the aid of a rotary evaporator, and the residue was then washed with CH₂Cl₂ (200 mL) and water (200 mL). The aqueous fraction was further washed with CH₂Cl₂ (2 x 50 mL). The combined organic fractions were then dried with anhydrous Na₂SO₄, filtered, and dried in vacuo with the aid of a rotary evaporator. The residue was dried in vacuo to afford a crude N-(2-bromopropyl)-2-methoxyaniline. Step (3): A 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirrer was charged with N-(2-bromopropyl)-2-methoxyaniline (prepared from the preceding procedure), (~4.88 g, ~20 mmol, ~1.0 equiv), 2.6-lutidine (2.57 g, 2.8 mL, 24 mmol, 1.2 equiv), and diethyl ether (100 mL). Ethyl chloroformate (2.17 g, 1.9 mL, 2.0 mmol, 1.0 equiv) was then added slowly into the reaction mixture, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with aqueous HCl solution (1 M, 50 mL) and EtOAc (100 mL), and the aqueous fraction was further washed with EtOAc (2 x 50 mL). The combined organic fractions were then washed with water (200 mL), dried with anhydrous Na₂SO₄, filtered, and dried in vacuo with the aid of a rotary evaporator. The crude product was purified by flash chromatography with silica gel using hexanes/EtOAc (20:1) and then hexanes/EtOAc (10:1) as eluents to afford ethyl (2-bromopropyl)(2-methoxyphenyl)carbamate (S24) as a viscous, colorless oil (3.05 g, 9.6 mmol, 48%, as a mixture of rotamers in a ratio of 2.8:1). ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.23 (ovrlp, 2 H), 6.96-6.92 (ovrlp, 2 H), 4.35-4.05 (ovrlp, 4 H), 3.82 (s, 3 H), 3.74-3.49 (m, 1 H), 1.72 (d, J = 6.3 Hz, 3 H), 1.33 (t, J = 6.4 Hz, 0.8 H), 1.11 (t, J = 6.8 Hz, 2.2 H). GCMS: [M] = 315 and 317 which corresponds to C₁₃H₁₈BrNO₃.

Preparations of Alkynyl Grignard Reagents. Alkynyl Grignard reagents were prepared according to the literature procedure.[13] In a nitrogen-filled glove box, an oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stirrer bar was charged with terminal alkynes (1.0 equiv) and THF (1.0 mL of THF was added when 1.0 equiv of terminal alkyne was added), followed by the slow addition of ethylmagnesium bromide via syringe (1.0 M in THF, 1.0 mL of EtMgBr solution was added when 1.0 equiv of terminal alkyne was added) (Caution: exothermic reaction; ethane gas was evolved). The reaction mixture was stirred at room temperature for 15 min to form a clear solution. The reaction mixture was then stirred at 50 °C in an oil bath for 1 h to form an alkynyl Grignard reagent (alkynyl magnesium bromide) solution (0.5 M in THF). The scale of alkynyl Grignard reagent ranged from 3.0 mmol to 7.5 mmol.

Optimizations of Iron-Catalyzed Cross-Coupling of Non-activated Secondary Alkyl Halides with Alkynyl Grignard Reagents (Table 1, Tables S1-S3). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stirrer bar was charged with FeBr₂ (98% purity, 10.8 mg, 0.05 mmol, 0.10 equiv), secondary alkyl halide (0.5 mmol, 1.0 equiv), and NMP solvent (2.0 mL), followed by the addition of alkynyl Grignard reagent solution (0.5 M in THF, 1.5 mL, 1.5 equiv). The reaction mixture was stirred at room temperature for 16 h to form a deep brown or black solution. After the reaction, n-dodecane (109 µL, 0.50 mmol, 1.0 equiv) was added into the crude product mixture, and the crude product was washed with EtOAc (5 mL) and water (20 mL). A small portion of the organic fraction was filtered through a plug of silica gel and then subjected to GC analysis to determine the GC yields of alkylated alkyne product using n-dodecane as an internal standard.
**Optimizations of Iron-Catalyzed Cross-Coupling of Non-activated Primary Alkyl Halides with Alkynyl Grignard Reagents (Tables S4-S5).** An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stirrer bar was charged with FeBr₂ (98% purity, 10.8 mg, 0.05 mmol, 0.10 equiv), primary alkyl halide (0.5 mmol, 1.0 equiv), bis[2-(N,N-dimethylamino)ethyl] ether (321 mg, 377 µL, 1.0 mmol, 2.0 equiv), and THF solvent (2.0 mL), followed by the addition of alkynyl Grignard reagent solution (0.5 M in THF, 1.5 mL, 1.5 equiv). The reaction mixture was stirred at room temperature for 16 h to form a deep brown or black solution. After the reaction, n-dodecane (109 µL, 0.50 mmol, 1.0 equiv) was added into the crude product mixture, and the crude product was washed with EtOAc (5 mL) and water (20 mL). A small portion of the organic fraction was filtered through a plug of silica gel and then subjected to GC analysis to determine the GC yield of substituted alkyne product using n-dodecane as an internal standard.

**Substrate Scope for Iron-Catalyzed Cross-Coupling of Non-activated Secondary Alkyl Halides with Alkynyl Grignard Reagents (General Procedure F):** An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stirrer bar was charged with FeBr₂ (98% purity, 22 mg, 0.10 mmol, 0.10 equiv), secondary alkyl halide (1.0 mmol, 1.0 equiv), and NMP solvent (4.0 mL), followed by the addition of alkynyl Grignard reagent solution (0.5 M in THF, 3.0 mL, 1.5 equiv). The reaction mixture was stirred at room temperature for 16 h to form a deep brown or black solution. After the reaction, the crude product was washed with EtOAc (10 mL) and water (30 mL). The aqueous fraction was further washed with EtOAc (2 x 10 mL). The combined organic fractions were concentrated in vacuo with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography with silica gel using a solvent mixture (EtOAc, hexanes) as an eluent to afford the substituted alkyne product.

**Substrate Scope for Iron-Catalyzed Cross-Coupling of Non-activated Primary Alkyl Halides with Alkynyl Grignard Reagents (General Procedure G).** An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stirrer bar was charged with FeBr₂ (98% purity, 43 mg, 0.20 mmol, 0.20 equiv), primary alkyl halide (1.0 mmol, 1.0 equiv), bis[2-(N,N-dimethylamino)ethyl] ether (O-TMEDA) (321 mg, 377 µL, 2.0 mmol, 2.0 equiv), and THF solvent (4.0 mL), followed by the addition of alkynyl Grignard reagent solution (0.5 M in THF, 3.0 mL, 1.5 equiv). The reaction mixture was stirred at room temperature for 16 h to form a deep brown or black solution. After the reaction, the crude product was washed with EtOAc (10 mL) and water (30 mL). The aqueous fraction was further washed with EtOAc (2 x 10 mL). The combined organic fractions were concentrated in vacuo with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography with silica gel using a solvent mixture (EtOAc, hexanes) as an eluent to afford the isolated substituted alkyne product.
1-(Cyclohexylethynyl)-4-methoxybenzene (2a). Following the general procedure F, the title compound was prepared using iodocyclohexane (210 mg, 130 \( \mu \)L 1.0 mmol) and ((4-methoxyphenyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (60:1) and then hexanes/EtOAc (40:1) as eluents to afford 1-(cyclohexylethynyl)-4-methoxybenzene (2a) as colorless oil (128 mg, 0.60 mmol, 60%).

**\( ^{1}H \) NMR (400 MHz, CDCl\(^{3}\))**: \( \delta \) 7.32 (d, \( J = 8.3 \) Hz, 2 H), 6.78 (d, \( J = 8.4 \) Hz, 2 H), 3.78 (s, 3 H), 2.58-2.52 (m, 1 H), 1.87-1.85 (m, 2 H), 1.78-1.71 (m, 2 H), 1.56-1.48 (ovrlp, 3 H), 1.38-1.30 (ovrlp, 3 H).

**\( ^{13}C \) NMR (100 MHz, CDCl\(^{3}\))**: \( \delta \) 159.1, 132.9, 116.4, 113.8, 92.9, 80.3, 55.3, 33.0, 29.8, 26.1, 25.1.

(4-(Cyclohexylethynyl)phenyl)(methyl)sulfane (2b). Following the general procedure F, the title compound was prepared using iodocyclohexane (210 mg, 130 \( \mu \)L 1.0 mmol) and ((4-methylthio)phenyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as an eluent to afford (4-(cyclohexylethynyl)phenyl)(methyl)sulfane (2b) as viscous yellow oil (151 mg, 0.65 mmol, 65%).

**\( ^{1}H \) NMR (400 MHz, CDCl\(^{3}\))**: \( \delta \) 7.29 (d, \( J = 8.1 \) Hz, 2 H), 7.13 (d, \( J = 8.1 \) Hz, 2 H), 2.59-2.53 (m, 1 H), 2.44 (s, 3 H), 1.89-1.83 (m, 2 H), 1.77-1.70 (m, 2 H), 1.56-1.47 (ovrlp, 3 H), 1.38-1.28 (ovrlp, 3 H).

**\( ^{13}C \) NMR (100 MHz, CDCl\(^{3}\))**: \( \delta \) 138.1, 131.9, 126.1, 120.7, 94.6, 80.3, 32.8, 29.8, 26.0, 25.0, 15.7.

**HRMS (ESI)**: Calcd for C\(_{15}\)H\(_{18}\)SAg [M+Ag]: 337.0180; Found: 337.0178.

(Cyclohexylethynyl)trimethylsilane (2c).

(i) From Iodocyclohexane. Following the general procedure F, the title compound was prepared using iodocyclohexane (210 mg, 130 \( \mu \)L 1.0 mmol) and ((trimethylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford (cyclohexylethynyl)trimethylsilane (2c) as deep brown oil (93 mg, 0.51 mmol, 51%).

**\( ^{1}H \) NMR (400 MHz, CDCl\(^{3}\))**: \( \delta \) 2.41-2.35 (m, 1 H), 1.82-1.76 (m, 2 H), 1.73-1.66 (m, 2 H), 1.53-1.40 (ovrlp, 3 H), 1.32-1.24 (ovrlp, 3 H), 0.14 (s, 9 H).

**\( ^{13}C \) NMR (100 MHz, CDCl\(^{3}\))**: \( \delta \) 112.0, 83.8, 32.8, 30.2, 26.0, 25.0, 0.4.

(ii) From Bromocyclohexane. Following the general procedure F, the title compound was prepared using bromocyclohexane (163 mg, 124 \( \mu \)L 1.0 mmol), ((trimethylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), FeBr\(_{2}\) (43 mg, 0.20 mmol), and O-TMEDA (321 mg, 381 \( \mu \)L). The crude product was purified by flash chromatography using hexanes as an eluent to afford (cyclohexylethynyl)trimethylsilane (2c) as brown oil (86 mg, 0.48 mmol, 48%). Spectral and analytical data were identical to those reported for the same compound above.
2-((7-Cyclohexylhept-6-yn-1-yl)oxy)tetrahydro-2H-pyran (2d). Following the general procedure F, the title compound was prepared using iodocyclohexane (210 mg, 130 µL 1.0 mmol) and (7-((tetrahydro-2H-pyran-2-yl)oxy)hept-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (10:1) as an eluent to afford 2-((7-cyclohexylhept-6-yn-1-yl)oxy)tetrahydro-2H-pyran (2d) as colorless oil (186 mg, 0.67 mmol, 67%). ¹H NMR (400 MHz, CDCl₃): δ 4.58 (s, 1 H), 3.89-3.85 (m, 1 H), 3.77-3.71 (m, 1 H), 3.53-3.47 (m, 1 H), 3.42-3.36 (m, 1 H), 2.31 (s, 1 H), 2.17 (t, J = 6.2 Hz, 2 H), 1.87-1.65 (ovrlp, 6 H), 1.62-1.43 (ovrlp, 11 H), 1.40-1.25 (ovrlp, 5 H). ¹³C NMR (100 MHz, CDCl₃): δ 98.8, 84.8, 79.9, 67.5, 62.3, 33.2, 30.8, 29.4, 29.2, 29.1, 26.0, 25.6, 25.5, 25.0, 19.7, 18.8. HRMS (ESI): Calcd for C₁₈H₃₁O₂ [M+H]: 279.2324; Found: 279.2326.

9-(6-Cyclohexylhex-5-yn-1-yl)-9H-carbazole (2e). Following the general procedure F, the title compound was prepared using iodocyclohexane (210 mg, 130 µL 1.0 mmol) and (6-(9H-carbazol-9-yl)hex-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (50:1) as an eluent to afford 9-(6-cyclohexylhex-5-yn-1-yl)-9H-carbazole (2e) as viscous colorless oil (119 mg, 0.36 mmol, 36%). ¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, J = 7.6 Hz, 2 H), 7.47-7.40 (ovrlp, 4 H), 7.22 (t, J = 6.9 Hz, 2 H), 4.32 (d, J = 7.0 Hz, 2 H), 2.33-2.15 (ovrlp, 3 H), 2.00 (qu, J = 7.3 Hz, 2 H), 1.77-1.65 (ovrlp, 4 H), 1.60-1.46 (ovrlp, 3 H), 1.39-1.20 (ovrlp, 5 H). ¹³C NMR (100 MHz, CDCl₃): δ 140.5, 125.7, 123.0, 120.4, 118.8, 108.8, 85.6, 79.2, 42.7, 33.2, 29.3, 28.0, 26.7, 26.1, 25.1, 18.6. HRMS (ESI): Calcd for C₂₄H₂₈N [M+H]: 330.2222; Found: 330.2220.

((3-Methylcyclohexyl)ethynyl)benzene (2f). Following the general procedure F, the title compound was prepared using 1-iodo-3-methylcyclohexane (S1) (224 mg, 1.0 mmol) and (phenylethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford ((3-methylcyclohexyl)ethynyl)benzene (2f) as pale-yellow oil (125 mg, 0.63 mmol, 63%). The diastereomeric ratio (d.r.: cis : trans = 9.0:1) of 2f was determined by ¹H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers.¹⁴ ¹H NMR (400 MHz, CDCl₃): δ 7.41-7.37 (m, 2 H), 7.28-7.24 (ovrlp, 3 H), 2.99 (s, 0.1 H), 2.44 (t, J = 11.4 Hz, 0.9 H), 2.01 (d, J = 10.4 Hz, 2 H), 1.81-1.64 (m, 2 H), 1.40-1.23 (ovrlp, 4 H), 1.13-1.04 (m, 1 H), 0.91 (d, J = 6.4 Hz, 3 H). ¹³C NMR (major diastereoisomer, 100 MHz, CDCl₃): δ 131.7, 128.3, 127.5, 124.2, 94.7, 80.0,
41.8, 34.6, 32.9, 32.5, 30.5, 26.0, 22.7. **HRMS (APPI):** Calcd for C\textsubscript{13}H\textsubscript{18} [M]: 198.1404; Found: 198.1403.

4-(6-(4-Methylcyclohexyl)hex-5-yn-1-yl)morpholine (2g). Following the general procedure F, the title compound was prepared using 1-iodo-4-methylcyclohexane (S2) (224 mg, 1.0 mmol) and (6-morpholinohex-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (2:1) as an eluent to afford 4-(6-(4-methylcyclohexyl)hex-5-yn-1-yl)morpholine (2g) as colorless oil (147 mg, 0.54 mmol, 54%). The diastereomeric ratio (d.r.: trans:cis > 50:1) of 2g was determined by GCMS analysis. The major diastereoisomer could not be determined due to the broadening and overlapping of the characteristic ipso-C-H proton signals by \textsuperscript{1}H NMR spectroscopy. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 3.71 (br s, 4 H), 2.66 (s, 0.3 H), 2.43 (br s, 4 H), 2.37-2.32 (m, 2 H), 2.19 (qu, \(J = 6.5\) Hz, 2 H), 2.09 (t, \(J = 11.5\) Hz, 0.7 H), 1.89 (d, \(J = 11.8\) Hz, 1 H), 1.62-1.46 (ovrlp, 8 H), 1.34-1.25 (ovrlp, 3 H), 0.92-0.85 (ovrlp, 4 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 85.2, 84.0, 80.7, 79.2, 67.0, 58.6, 53.8, 34.6, 33.6, 32.1, 32.0, 31.0, 30.8, 29.8, 29.5, 27.2, 27.1, 26.9, 25.7, 22.6, 22.3, 18.7 (Observed complexity due to the mixture of diastereoisomers). **HRMS (ESI):** Calcd for C\textsubscript{17}H\textsubscript{30}NO [M+H]: 264.2327; Found: 264.2315.

\(\text{Bu}\)\textsuperscript{3}\textsuperscript{Bu} \(\equiv \) \textsuperscript{3}N

1-(tert-Butyl)-4-((4-(tert-butyl)cyclohexyl)ethynyl)benzene (2h). Following the general procedure F, the title compound was prepared using 1-(tert-butyl)-4-iodocyclohexane (S3) (266 mg, 1.0 mmol) (S3) and ((4-(tert-butyl)phenyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford 1-(tert-butyl)-4-((4-(tert-butyl)cyclohexyl)ethynyl)benzene (2h) as off-white solid (147 mg, 0.50 mmol, 50%). The diastereomeric ratio (d.r.: trans:cis > 50:1) of 2h was determined by \textsuperscript{1}H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers.\textsuperscript{[14]} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.35-7.25 (ovrlp, 4 H), 2.32 (t, \(J = 11.8\) Hz, 1 H), 2.10 (d, \(J = 11.8\) Hz, 2 H), 1.82-1.77 (m, 2 H), 1.45-1.35 (m, 2 H), 1.29 (s, 9 H), 1.03-0.98 (ovrlp, 3 H), 0.85 (s, 9 H). \textsuperscript{13}C NMR (major diastereoisomer, 100 MHz, CDCl\textsubscript{3}): δ 150.6, 131.4, 125.2, 121.2, 94.1, 80.1, 47.5, 34.8, 33.9, 32.6, 31.3, 30.6, 27.6, 27.1. **HRMS (APPI):** Calcd for C\textsubscript{22}H\textsubscript{32} [M]: 296.2506; Found: 296.2499.

\(\text{Dec-1-yn-1-yl} \equiv \text{Dec-1-yl} \equiv \text{Dec-1-yl}

2-(Dec-1-yn-1-yl)bicyclo[2.2.1]heptane (2i). Following the general procedure F, the title compound was prepared using 2-iodobicyclo[2.2.1]heptane (S4) (222 mg, 1.0 mmol) and dec-1-yn-1-ylmagnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (100:1) as eluents to afford 2-(dec-1-yn-1-yl)bicyclo[2.2.1]heptane (2i) as brown oil (163.3 mg, 0.70 mmol, 70%). The diastereomeric ratio of 2i
was not determined due to the overlapping of signals in both $^1$H NMR spectroscopy and GCMS analysis. $^1$H NMR (400 MHz, CDCl$_3$): δ 2.60-2.11 (ovrlp, 5 H), 1.91-1.58 (m, 2 H), 1.51-1.42 (ovrlp, 4 H), 1.35-1.11 (ovrlp, 14 H), 0.88 (t, $J = 6.0$ Hz, 3 H). $^{13}$C NMR (major diastereoisomer, 100 MHz, CDCl$_3$): δ 86.0, 79.9, 43.9, 39.8, 36.6, 36.3, 33.2, 32.0, 29.4, 29.3, 29.0, 24.1, 22.8, 18.9, 14.2. HRMS (ESI): Calcd for C$_{17}$H$_{28}$Ag [M+Ag]: 339.1242; Found: 339.1255.

**((Bicyclo[2.2.1]heptan-2-yl)ethynyl)triethylsilane (2j).** Following the general procedure F, the title compound was prepared using 2-iodobicyclo[2.2.1]heptane (S4) (222 mg, 1.0 mmol) and ((triethylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford ((bicyclo[2.2.1]heptan-2-yl)ethynyl)triethylsilane (2j) as brown oil (183 mg, 0.78 mmol, 78%). The diastereomeric ratio (d.r. = 2.8:1) of 2j was estimated by $^1$H NMR spectroscopy and the ratio was found to be comparable to that estimated from the $^{13}$C NMR spectroscopy. (Note: The major diastereoisomer could not be determined due to the overlapping of characteristic ipso C-H proton signals with other proton signals.) $^1$H NMR (400 MHz, CDCl$_3$): δ 2.65-2.62 (m, 0.3 H), 2.33-2.26 (ovrlp, 2.4 H), 2.21 (s, 0.3 H), 1.95-1.54 (ovrlp, 3 H), 1.48 (s, 1 H), 1.30-1.13 (ovrlp, 4 H), 1.01-0.95 (ovrlp, 9 H), 0.62-0.52 (ovrlp, 6 H). $^{13}$C NMR (major diastereoisomer, 100 MHz, CDCl$_3$): δ 114.6, 80.5, 44.2, 39.8, 36.7, 36.4, 34.2, 28.9, 24.2, 7.7, 4.8. HRMS (ESI): Calcd for C$_{15}$H$_{26}$SiAg [M+Ag]: 341.0855; Found: 341.0855.

**Ethyl 3-((4-(tert-butyl)phenyl)ethynl)cyclohexane-1-carboxylate (2k).** Following the general procedure F, the title compound was prepared using ethyl 3-iodocyclohexane-1-carboxylate (282 mg, 1.0 mmol) and ((4-(tert-butyl)phenyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford ethyl 3-((4-(tert-butyl)phenyl)ethynyl)cyclohexane-1-carboxylate (2k) as viscous, deep-brown oil (284 mg, 0.91 mmol, 91%). The diastereomeric ratio (d.r.: cis:trans = 6.5:1) of 2k was determined by $^1$H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers.$^{[14]}$ $^1$H NMR (400 MHz, CDCl$_3$): δ 7.36-7.25 (m, 4 H), 4.13 (q, $J = 7.0$ Hz, 2 H), 3.05-2.24 (m, 3 H), 2.09-1.53 (ovrlp, 5 H), 1.45-1.38 (m, 2 H), 1.29 (s, 9 H), 1.25 (t, $J = 7.2$ Hz, 3 H). $^{13}$C NMR (major diastereoisomer, 100 MHz, CDCl$_3$): δ 175.3, 150.9, 131.4, 125.3, 120.8, 92.6, 80.7, 60.4, 43.0, 35.2, 34.8, 32.6, 31.3, 29.8, 28.3, 25.1, 14.4. HRMS (ESI): Calcd for C$_{21}$H$_{29}$O$_2$ [M+H]: 313.2168; Found: 313.2163.

**Ethyl 3-(6-(4-chlorophenoxy)hex-1-yn-1-yl)cyclohexane-1-carboxylate (2l).** Following the general
Procedure F, the title compound was prepared using ethyl 3-iodocyclohexene-1-carboxylate (282 mg, 1.0 mmol) and (6-(4-chlorophenoxy)hex-1-yn-1-yl)magnesium bromide (synthesized from S19, 0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford ethyl 3-(6-(4-chlorophenoxy)hex-1-yn-1-yl)cyclohexene-1-carboxylate (2l) as pale-yellow oil (158 mg, 0.44 mmol, 44%). The diastereomeric ratio (d.r. = 1.9:1) of 2l was determined by GCMS analysis. (Note: The major diastereoisomer could not be determined by $^1$H NMR spectroscopy due to the overlapping of characteristic ipso C-H proton signals with other proton signals.) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.71 (d, $J$ = 9.8 Hz, 2 H), 7.15 (d, $J$ = 8.4 Hz, 2 H), 5.11 (q, $J$ = 6.7 Hz, 2 H), 3.84 (d, $J$ = 5.8 Hz, 2 H), 2.85-2.16 (ovrlp, 4 H), 1.90-1.80 (ovrlp, 5 H), 1.72-1.50 (ovrlp, 4 H), 1.47-1.39 (m, 1 H), 1.35-1.22 (ovrlp, 5 H). $^{13}$C NMR (major diastereoisomer, 100 MHz, CDCl$_3$): $\delta$ 175.3, 157.7, 129.3, 125.4, 115.9, 84.4, 79.7, 67.8, 60.3, 43.0, 35.6, 32.9, 29.3, 28.35, 28.31, 25.6, 25.1, 18.5, 14.3. HRMS (ESI): Calcd for C$_{21}$H$_{27}$ClO$_3$Ag [M+Ag]: 469.0700; Found: 469.0710.

1,4-Di(hex-1-yn-1-yl)cyclohexane (2m). Following the general procedure F, the title compound was prepared using 1,4-diiodocyclohexane (S5) (336 mg, 1.0 mmol) and hex-1-yn-1-ylmagnesium bromide (0.5 M in THF, 3.0 mmol, 6.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (100:1) and then hexanes/ EtOAc (50:1) as eluents to afford 1,4-di(hex-1-yn-1-yl)cyclohexane (2m) as deep-brown oil (195 mg, 0.80 mmol, 80%). The diastereomeric ratio (d.r. = 2.2:1) of 2m was determined by GCMS analysis. (Note: The major diastereoisomer could not be determined by $^1$H NMR spectroscopy due to the broadening and overlapping of characteristic ipso C-H proton signals.) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.41 (s, 0.7 H), 2.26 (s, 1.3 H), 2.18-2.12 (m, 4 H), 1.95-1.88 (m, 2 H), 1.77-1.71 (m, 2 H), 1.63-1.53 (m, 2 H), 1.48-1.26 (ovrlp, 10 H), 0.93-0.88 (ovrlp, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 84.1, 83.8, 80.9, 80.3, 32.0, 31.5, 31.4, 30.1, 28.8, 28.2, 22.1, 22.0, 18.6, 18.5, 14.2, 13.7 (Observed complexity due to the mixture of diastereoisomers). HRMS (ESI): Calcd for C$_{18}$H$_{28}$Ag [M+Ag]: 351.1242; Found: 351.1228.

Terbutyl 4-(cyclohex-1-en-1-yl)ethynyl)piperidine-1-carboxylate (2n). Following the general procedure F, the title compound was prepared using tert-butyl 4-iodopiperidine-1-carboxylate (311 mg, 1.0 mmol) and (cyclohex-1-en-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/ EtOAc (30:1) as eluents to afford tert-butyl 4-(cyclohex-1-en-1-yl)ethynyl)piperidine-1-carboxylate (2n) as viscous brown oil (179 mg, 0.62 mmol, 62%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.03 (s, 1 H), 3.71-3.65 (m, 2 H), 3.23-3.18 (m, 2 H), 2.71-2.65 (m, 1 H), 2.13-2.04 (ovrlp, 4 H), 1.80-1.73 (m, 2 H), 1.64-1.54 (ovrlp, 6 H), 1.45 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.9, 133.8, 120.8, 89.0, 83.8, 79.5, 42.4, 31.7, 29.7, 28.6, 27.6, 25.7, 22.5, 21.7. HRMS (ESI): Calcd for C$_{18}$H$_{27}$NO$_2$Ag [M+Ag]: 396.1093; Found: 396.1077.
**tert-Butyl 4-((trimethylsilyl)ethyl)piperidine-1-carboxylate (2o).**

(i) With FeBr$_2$ (98% purity): Following the general procedure F, the title compound was prepared using tert-butyl 4-iodopiperidine-1-carboxylate (311 mg, 1.0 mmol) and ((trimethylsilyl)ethyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (20:1) as eluents to afford tert-butyl 4-((trimethylsilyl)ethyl)piperidine-1-carboxylate (2o) as pale-brown oil (242 mg, 0.86 mmol, 86%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.67-3.64 (m, 2 H), 3.24-3.18 (m, 2 H), 2.63-2.57 (m, 1 H), 1.77-1.74 (m, 2 H), 1.61-1.53 (m, 2 H), 1.45 (s, 9 H), 0.15 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.6, 108.8, 85.6, 79.2, 41.9, 31.2, 28.4, 27.7, 0.1. HRMS (ESI): Calcd for C$_{15}$H$_{26}$NO$_2$Si [M+H]: 282.1889; Found: 282.1893.

(ii) With FeBr$_2$ (99.999% purity): Following the general procedure F, the title compound was prepared using tert-butyl 4-iodopiperidine-1-carboxylate (311 mg, 1.0 mmol), ((trimethylsilyl)ethyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), and FeBr$_2$ (99.999% purity, 22 mg, 0.10 mmol). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (20:1) as eluents to afford tert-butyl 4-((trimethylsilyl)ethyl)piperidine-1-carboxylate (2o) as pale-brown oil (242 mg, 0.86 mmol, 88%). Spectral and analytical data were identical to those reported for the same compound above.

**N,N-diethyl-4-((tetrahydro-2H-pyran-4-yl)ethynyl)benzamide (2p).** Following the general procedure F, the title compound was prepared using 4-iodotetrahydro-2H-pyran (212 mg, 1.0 mmol) and 4-(diethylcarbamoyl)phenyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (2:1) as an eluent to afford N,N-diethyl-4-((tetrahydro-2H-pyran-4-yl)ethynyl)benzamide (2p) as viscous, pale-yellow oil (110 mg, 0.39 mmol, 39%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43 (d, $J$ = 7.6 Hz, 2 H), 7.30 (d, $J$ = 7.7 Hz, 2 H), 3.98-3.92 (m, 2 H), 3.57-3.53 (ovrlp, 4 H), 3.23 (br s, 2 H), 2.88-2.82 (m, 1 H), 1.95-1.88 (m, 2 H), 1.80-1.72 (m, 2 H), 1.25 (br s, 3 H), 1.11 (br s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 170.7, 136.5, 131.6, 126.4, 124.6, 93.6, 81.0, 66.4, 43.3, 39.4, 32.3, 26.9, 14.2, 13.0. HRMS (ESI): Calcd for C$_{18}$H$_{24}$NO$_2$ [M+H]: 286.1807; Found: 286.1810.

**4-(6-(4-bromophenoxy)hex-1-yn-1-yl)tetrahydro-2H-pyran (2q).** Following the general procedure F, the title compound was prepared using 4-iodotetrahydro-2H-pyran (212 mg, 1.0 mmol) and 6-(4-bromophenoxy)hex-1-yn-1-yl)magnesium bromide (synthesized from S20, 0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford 4-(6-(4-bromophenoxy)hex-1-yn-1-yl)tetrahydro-2H-pyran (2q) as viscous, pale-yellow oil (168 mg, 0.50 mmol, 50%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35 (d, $J$ = 8.6 Hz, 2 H), 6.76 (d, $J$ = 8.6 Hz, 2 H), 5.53 (ovrlp, 4 H), 3.23 (br s, 3 H), 2.88-2.82 (m, 1 H).
was purified by flash chromatography using hexanes/EtOAc (40:1) as an eluent to afford ((triisopropylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was prepared using trimethyl((tetrahydro-2H-pyran)iodotetrahydro-2H-pyran (2r). Following the general procedure F, the title compound was prepared using 4-iodotetrahydro-2H-pyran (212 mg, 1.0 mmol) and (cyclohex-1-en-1-ylethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (20:1) as eluents to afford 4-iodotetrahydro-2H-pyran (2r) as brown oil (146 mg, 0.77 mmol, 77%). 1H NMR (400 MHz, CDCl3): δ 6.13 (s, 1 H), 4.01-3.98 (m, 2 H), 3.61-3.57 (m, 2 H), 2.85-2.79 (m, 1 H), 2.22-2.15 (ovrlp, 4 H), 1.95-1.90 (m, 2 H), 1.79-1.67 (ovrlp, 6 H). 13C NMR (100 MHz, CDCl3): δ 133.7, 120.8, 89.3, 83.3, 66.4, 32.5, 29.6, 26.7, 25.8, 22.4, 21.6. HRMS: [M] could not be detected by HRMS (ESI) and HRMS (APPI). GCMS: [M] = 190 detected which corresponds to C13H18O; the purity was further confirmed by GCMS.

Trimethyl((tetrahydro-2H-pyran-4-yl)ethynyl)silane (2s).
(i) With FeBr2 (98% purity): Following the general procedure F, the title compound was prepared using 4-iodotetrahydro-2H-pyran (212 mg, 1.0 mmol) and (trimethylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (20:1) as eluents to afford trimethyl((tetrahydro-2H-pyran-4-yl)ethynyl)silane (2s) as brown oil (150 mg, 0.82 mmol, 82%). 1H NMR (400 MHz, CDCl3): δ 3.91-3.86 (m, 2 H), 3.51-3.46 (m, 2 H), 2.67-2.61 (m, 1 H), 1.85-1.78 (m, 2 H), 1.69-1.61 (m, 2 H), 0.15 (s, 9 H). 13C NMR (100 MHz, CDCl3): δ 109.4, 85.3, 66.3, 32.2, 27.2, 0.3. HRMS: [M] could not be detected by HRMS (ESI) and HRMS (APPI). GCMS: [M] = 182 detected which corresponds to C10H18OSi; the purity was further confirmed by GCMS.

(ii) With FeBr2 (99.999% purity): Following the general procedure F, the title compound was prepared using 4-iodotetrahydro-2H-pyran (212 mg, 1.0 mmol), ((trimethylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), and FeBr2 (99.999% purity, 22 mg, 0.10 mmol). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (20:1) as eluents to afford trimethyl((tetrahydro-2H-pyran-4-yl)ethynyl)silane (2s) as brown oil (147 mg, 0.81 mmol, 81%). Spectral and analytical data were identical to those reported for the same compound above.

Triisopropyl((tetrahydro-2H-pyran-4-yl)ethynyl)silane (2t). Following the general procedure F, the title compound was prepared using 4-iodotetrahydro-2H-pyran (212 mg, 1.0 mmol) and ((triisopropylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (40:1) as an eluent to afford...
triisopropyl((tetrahydro-2H-pyran-4-yl)ethynyl)silane (2t) as pale-yellow oil (255 mg, 0.96 mmol, 96%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.92-3.88 (m, 2 H), 3.56-3.52 (m, 2 H), 2.75-2.69 (m, 1 H), 1.87-1.82 (m, 2 H), 1.70-1.63 (m, 2 H), 1.10-1.01 (ovrlp, 21 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 111.2, 81.4, 65.9, 32.4, 26.9, 18.7, 11.3. HRMS (ESI): Calcd for C$_{16}$H$_{30}$OSiAg [M+Ag]: 373.1117; Found: 273.1109.

Triisopropyl((2-phenyltetrahydro-2H-pyran-4-yl)ethynyl)silane (2u). Following the general procedure F, the title compound was prepared using 4-iodo-2-phenyltetrahydro-2H-pyran (S8) (288 mg, 1.0 mmol) and ((triisopropylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford triisopropyl((2-phenyltetrahydro-2H-pyran-4-yl)ethynyl)silane (2u) as pale-brown oil (271 mg, 0.79 mmol, 79%). The diastereomeric ratio (d.r.: cis:trans = 24.0:1) of 2u was determined by $^1$H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers.$^{[14]}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33-7.20 (ovrlp, 5 H), 4.85-4.25 (m, 1 H), 4.15-3.99 (m, 1 H), 3.55 (t, $J$ = 10.8 Hz, 1 H), 3.07 (s, 0.04 H), 2.69 (t, $J$ = 11.6 Hz, 0.96 H), 2.12 (d, $J$ = 12.7 Hz, 1 H), 1.89 (d, $J$ = 11.8 Hz, 1 H), 1.83-1.75 (m, 1 H), 1.70-1.59 (m, 1 H), 1.12-1.04 (ovrlp, 21 H). $^{13}$C NMR (major diastereoisomer, 100 MHz, CDCl$_3$): $\delta$ 142.5, 128.5, 127.6, 125.9, 111.4, 80.4, 79.3, 67.9, 40.6, 32.7, 29.0, 18.7, 11.3. HRMS (ESI): Calcd for C$_{22}$H$_{34}$OSiAg [M+Ag]: 449.1430; Found: 449.1439.

Triethyl((2-(4-methoxyphenyl)tetrahydro-2H-pyran-4-yl)ethynyl)silane (2v). Following the general procedure F, the title compound was prepared using 4-iodo-2-(4-methoxyphenyl)tetrahydro-2H-pyran (S9) (318 mg, 1.0 mmol) and ((triethylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford triethyl((2-(4-methoxyphenyl)tetrahydro-2H-pyran-4-yl)ethynyl)silane (2v) as brown oil (285 mg, 0.86 mmol, 86%). The diastereomeric ratio (d.r.: cis:trans = 9.4:1) of 2v was determined by $^1$H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers.$^{[14]}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18 (d, $J$ = 8.2 Hz, 2 H), 6.78 (d, $J$ = 8.3 Hz, 2 H), 4.69-4.12 (m, 1 H), 4.05-3.87 (m, 1 H), 3.69 (s, 3 H), 3.84 (t, $J$ = 11.5 Hz, 1 H), 2.98 (s, 0.1 H), 2.59 (t, $J$ = 11.8 Hz, 0.9 H), 2.00 (t, $J$ = 12.7 Hz, 1 H), 1.80 (t, $J$ = 12.7 Hz, 1 H), 1.73-1.66 (m, 1 H), 1.63-1.54 (m, 1 H), 0.98-0.87 (ovrlp, 9 H), 0.58-0.45 (ovrlp, 6 H). $^{13}$C NMR (major diastereoisomer, 100 MHz, CDCl$_3$): $\delta$ 159.1, 134.7, 127.2, 113.8, 110.9, 81.6, 78.9, 67.9, 55.3, 40.3, 32.6, 28.9, 7.55, 4.61. HRMS (ESI): Calcd for C$_{20}$H$_{31}$O$_2$Si [M+H]: 331.2093; Found: 331.2084.
Triethyl((2-(4-fluorophenyl)tetrahydro-2H-pyran-4-yl)ethynyl)silane (2w).

(i) With FeBr₂ (98% purity): Following the general procedure F, the title compound was prepared using 2-(4-fluorophenyl)-4-iodotetrahydro-2H-pyran (S10) (306 mg, 1.0 mmol) and ((triethylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford triethyl((2-(4-fluorophenyl)tetrahydro-2H-pyran-4-yl)ethynyl)silane (2w) as brown oil (295 mg, 0.93 mmol, 93%). The diastereomeric ratio (d.r.: cis:trans = 9.1:1) of 2w was estimated by 1H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers. [14] 1H NMR (400 MHz, CDCl₃): δ 7.30 (dd, 3JHH = 7.6 Hz, 4JHF = 5.8 Hz, 2 H), 7.01 (dd, 3JHH = 8.3 Hz, 3JHF = 8.3 Hz, 2 H), 4.80-4.23 (m, 1 H), 4.14-3.98 (m, 1 H), 3.55 (t, 1J = 11.7 Hz, 1 H), 3.07 (s, 0.1 H), 2.69 (t, 1J = 11.8 Hz, 0.9 H), 2.09 (d, 1J = 13.0 Hz, 1 H), 1.89 (d, 1J = 12.0 Hz, 1 H), 1.81-1.74 (m 1 H), 1.72-1.58 (m, 1 H), 1.06-0.95 (m, 9 H), 0.66-0.53 (m, 6 H). 13C NMR (major diastereoisomer, 100 MHz, CDCl₃): δ 162.3 (d, 1JCF = 243.9 Hz), 138.2 (d, 4JCF = 3.0 Hz), 127.6 (d, 3JCF = 8.0 Hz), 115.3 (d, 2JCF = 21.2 Hz), 110.6, 81.8, 78.6, 67.9, 40.4, 32.5, 28.9, 7.6, 4.6. HRMS (ESI): Calcd for C₁₉H₂₇F₆OSiAg [M+Ag]: 425.0866; Found: 425.0861.

(ii) With FeBr₂ (99.999% purity): Following the general procedure F, the title compound was prepared using 2-(4-fluorophenyl)-4-iodotetrahydro-2H-pyran (S10) (306 mg, 1.0 mmol), ((triisopropylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), and FeBr₂ (99.999% purity, 22 mg, 0.10 mmol). The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford triisopropyl((2-(4-fluorophenyl)tetrahydro-2H-pyran-4-yl)ethynyl)silane (2w) as brown oil (305 mg, 0.96 mmol, 96%). The diastereomeric ratio (d.r.: cis:trans = 9:1) of 2w was estimated by 1H NMR spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers. [14] Spectral and analytical data were identical to those reported for the same compound above.

Triisopropyl((2-(4-(trifluoromethyl)phenyl)tetrahydro-2H-pyran-4-yl)ethynyl)silane (2x).

Following the general procedure F, the title compound was prepared using 4-iodo-2-(4-(trifluoromethyl)phenyl)tetrahydro-2H-pyran (S11) (356 mg, 1.0 mmol) and ((triisopropylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford triisopropyl((2-(4-(trifluoromethyl)phenyl)tetrahydro-2H-pyran-4-yl)ethynyl)silane (2x) as pale-brown oil (358 mg, 0.87 mmol, 87%). The diastereomeric ratio (d.r.: cis:trans = 24.0:1) of 2x was determined by 1H NMR.
spectroscopy by comparing the integrations of ipso C-H protons of both cis- and trans-isomers.\textsuperscript{[14]} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.59 (d, $J = 7.6$ Hz, 2 H), 7.45 (d, $J = 7.4$ Hz, 2 H), 4.90 (d, $J = 11.0$ Hz, 0.06 H), 4.34 (d, $J = 11.1$ Hz, 0.94 H), 4.16 (d, $J = 8.7$ Hz, 1 H), 4.05 (t, $J = 11.6$ Hz, 0.06 H), 3.57 (t, $J = 11.8$ Hz, 0.94 H), 3.10 (s, 0.06 H), 2.72 (t, $J = 11.6$ Hz, 0.94 H), 2.14 (d, $J = 12.8$ Hz, 1 H), 1.93 (d, $J = 12.4$ Hz, 1 H), 1.84-1.72 (m, 1 H), 1.65-1.55 (m, 1 H), 1.12-1.01 (ovrlp, 21 H). \textsuperscript{13}C NMR (major diastereoisomer, 100 MHz, CDCl\textsubscript{3}): $\delta$ 146.5, 129.8 (q, $^1J_{CF} = 32.2$ Hz), 126.1, 125.4 (q, $^3J_{CF} = 3.6$ Hz), 124.3 (q, $^1J_{CF} = 270.3$ Hz), 110.9, 80.7, 78.5, 67.9, 40.6, 32.8, 28.9, 18.7, 11.3. HRMS (ESI): Calcd for C\textsubscript{23}H\textsubscript{34}F\textsubscript{3}OSi [M+H]: 411.2331; Found: 411.2350.

2-(((7-((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)hept-6-yn-1-yl)oxy)tetrahydro-2H-pyran (2y). Following the general procedure F, the title compound was prepared using 3\textbeta;iodo-5-cholestene (497 mg, 1.0 mmol) and (7-((tetrahydro-2H-pyran-2-yl)oxy)hept-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (10:1) as eluents to afford 2-(((7-((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)hept-6-yn-1-yl)oxy)tetrahydro-2H-pyran (2y) as an off-white, low-melting solid (284 mg, 0.50 mmol, 50%). The diastereomeric ratio (d.r.: major : minor = 7.0:1) of 2y was determined by \textsuperscript{1}H NMR spectroscopy by comparing the integrations of olefinic protons of both major and minor isomers. The major isomer was determined by comparing the chemical shift of olefinic C-H proton and ipso C-H proton of the major isomer with that of structurally similar and well-defined compound.\textsuperscript{[5]} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 5.30 (s, 0.9 H), 4.96 (s, 0.1 H), 4.58 (s, 1 H), 3.89-3.84 (m, 1 H), 3.77-3.71 (m, 1 H), 3.51-3.49 (m, 1 H), 3.42-3.36 (m, 1 H), 2.77 (s, 0.1 H), 2.46-2.11 (ovrlp, 4.9 H), 2.02-1.26 (ovrlp, 34 H), 1.16-1.07 (ovrlp, 4 H), 0.99 (s, 3 H), 0.91 (d, $J = 5.6$ Hz, 3 H), 0.86 (d, $J = 5.6$ Hz, 6 H), 0.67 (s, 3 H). \textsuperscript{13}C NMR (major diastereoisomer, 100 MHz, CDCl\textsubscript{3}): $\delta$ 141.8, 120.6, 98.8, 84.6, 80.0, 67.5, 67.4, 62.3, 56.9, 56.2, 50.3, 42.4, 39.9, 39.7, 39.6, 39.1, 36.8, 36.3, 35.9, 31.92, 31.87, 31.3, 30.8, 29.8, 29.4, 29.1, 28.3, 28.1, 25.61, 25.59, 24.4, 23.9, 22.9, 22.7, 20.9, 19.7, 19.4, 18.8, 11.9. HRMS (ESI): Calcd for C\textsubscript{39}H\textsubscript{64}O\textsubscript{2}Na [M+Na]: 587.4804; Found: 587.4796.

Benzyl 3-((triisopropylsilyl)ethynyl)azetidine-1-carboxylate (3a). Following the general procedure F, the title compound was prepared using benzyl 3-iodoazetidine-1-carboxylate (S12) (317 mg, 1.0 mmol) and ((triisopropylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude
product was purified by flash chromatography using hexanes and then hexanes/EtOAc (20:1) as eluents to afford benzyl 3-(triisopropylsilyl)ethynyl)azetidine-1-carboxylate (3a) as pale-brown oil (372 mg, 0.85 mmol, 85%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39-7.31 (ovrlp, 5 H), 5.10 (s, 2 H), 4.23 (t, $J = 8.2$ Hz, 2 H), 4.00 (t, $J = 7.2$ Hz, 2 H), 3.41 (qu, $J = 6.6$ Hz, 1 H), 1.11-1.00 (ovrlp, 21 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 156.1, 136.5, 128.5, 128.1, 128.0, 107.6, 84.5, 66.8, 56.0, 20.6, 18.6, 11.2. HRMS (ESI): Calcd for C$_{22}$H$_{34}$NO$_2$Si [M+H]: 372.2359; Found: 372.2361.

(Cyclopentylethynyl)cyclohexane (3b). Following the general procedure F, the title compound was prepared using bromocyclopentane (149 mg, 1.0 mmol), (cyclohexylethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), FeBr$_2$ (43 mg, 0.20 mmol), and O-TMEDA (321 mg, 381 µL). The crude product was purified by flash chromatography using hexanes as an eluent to afford (cyclopentylethynyl)cyclohexane (3b) as pale-yellow oil (123 mg, 0.70 mmol, 70%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.61-2.54 (m, 1 H), 2.32 (s, 1 H), 1.91-1.83 (m, 2 H), 1.79-1.68 (ovrlp, 6 H), 1.58-1.49 (ovrlp, 4 H), 1.42-1.35 (m, 2 H), 1.29-1.26 (ovrlp, 4 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 84.6, 84.2, 34.4, 33.4, 30.5, 29.3, 26.2, 25.1, 25.0. HRMS: [M] could not be detected by HRMS (ESI and APPI). GCMS: [M] = 176 detected which corresponds to C$_{13}$H$_{20}$; the purity was further confirmed by GCMS.

2-(Dec-1-yn-1-yl)-2,3-dihydro-$^1$H-indene (3c). Following the general procedure F, the title compound was prepared using 2-iodo-2,3-dihydro-$^1$H-indene (244 mg, 1.0 mmol) and dec-1-yn-1-ylmagnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (100:1) as eluents to afford 2-(dec-1-yn-1-yl)-2,3-dihydro-$^1$H-indene (3c) as pale-brown oil (161 mg, 0.63 mmol, 63%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.17-7.09 (ovrlp, 4 H), 3.20-3.12 (ovrlp, 3 H), 2.99-2.93 (m, 2 H), 2.15 (t, $J = 6.5$ Hz, 2 H), 1.47 (qu, $J = 6.5$ Hz, 2 H), 1.37-1.20 (ovrlp, 10 H), 0.88 (t, $J = 6.7$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 142.4, 126.5, 124.4, 83.3, 80.6, 40.8, 32.0, 30.6, 29.4, 29.3, 29.2, 29.0, 22.8, 18.9, 14.3. HRMS (ESI): Calcd for C$_{19}$H$_{26}$Ag [M+Ag]: 361.1086; Found: 361.1095.

Dec-1-yn-1-ylcycloheptane (3d).$^{[25]}$ Following the general procedure F, the title compound was prepared using iodo(cycloheptane (224 mg, 1.0 mmol) and dec-1-yn-1-ylmagnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford dec-1-yn-1-ylcycloheptane (3d) as pale-brown oil (152 mg, 0.65 mmol, 65%). $^1$H NMR
(400 MHz, CDCl₃): δ 2.55 (s, 1 H), 2.15 (t, J = 6.4 Hz, 2 H), 1.83-1.76 (m, 2 H), 1.71-1.60 (ovrlp, 4 H), 1.60-1.44 (ovrlp, 8 H), 1.36-1.23 (ovrlp, 10 H), 0.88 (t, J = 6.5 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 85.4, 80.5, 35.3, 32.0, 31.4, 29.42, 29.39, 29.3, 29.0, 28.0, 25.7, 22.8, 18.9, 14.2.

(3,3-Dimethylbut-1-yn-1-yl)cyclooctane (3e). Following the general procedure F, the title compound was prepared using iodocyclooctane (238 mg, 1.0 mmol) and (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford (3,3-dimethylbut-1-yn-1-yl)cyclooctane (3e) as yellow oil (152 mg, 0.65 mmol, 65%). ¹H NMR (400 MHz, CDCl₃): δ 2.52 (s, 1 H), 1.83-1.69 (ovrlp, 4 H), 1.65-1.43 (ovrlp, 10 H), 1.19 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ 89.1, 83.8, 32.4, 31.7, 30.8, 30.2, 27.6, 25.6, 24.6. HRMS (APPI): Calcd for C₁₄H₂₄ [M]: 192.1829; Found: 192.1873.

2-((8-Methyl-10-phenyldec-6-yn-1-yl)oxy)tetrahydro-2H-pyran (3f). Following the general procedure F, the title compound was prepared using (3-iodobutyl)benzene (260 mg, 1.0 mmol) and (7-((tetrahydro-2H-pyran-2-yl)oxy)hept-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (15:1) as eluents to afford 2-((8-methyl-10-phenyldec-6-yn-1-yl)oxy)tetrahydro-2H-pyran (3f) as pale-yellow oil (202 mg, 0.62 mmol, 62%). ¹H NMR (400 MHz, CDCl₃): δ 7.27 (t, J = 7.2 Hz, 2 H), 7.20-7.15 (ovrlp, 3 H), 4.57 (s, 1 H), 3.86 (t, J = 7.5 Hz, 1 H), 3.75 (q, J = 6.8 Hz, 1 H), 3.51-3.46 (m, 1 H), 3.39 (q, J = 6.2 Hz, 1 H), 2.84-2.77 (m, 1 H), 2.72-2.65 (m, 1 H), 2.39 (sex, J = 6.2 Hz, 1 H), 2.21 (t, J = 6.0 Hz, 2 H), 1.85-1.61 (ovrlp, 6 H), 1.58-1.48 (ovrlp, 8 H), 1.15 (d, J = 6.7 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 142.4, 128.6, 128.3, 125.8, 98.9, 84.6, 80.8, 67.6, 62.4, 39.2, 33.8, 30.8, 29.4, 29.1, 25.62, 25.59, 21.6, 19.7, 18.8. HRMS (ESI): Calcd for C₂₂H₃₃O₂ [M]+: 329.2480; Found: 329.2470.

(3,6,6-Trimethylhept-4-yn-1-yl)benzene (3g). Following the general procedure F, the title compound was prepared using (3-iodobutyl)benzene (260 mg, 1.0 mmol) and (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford (3,6,6-trimethylhept-4-yn-1-yl)benzene (3g) as colorless oil (115 mg, 0.54 mmol, 54%). ¹H NMR (400 MHz, CDCl₃): δ 7.27 (t, J = 7.3 Hz, 1 H), 7.21-7.15 (ovrlp, 3 H), 2.83-2.76 (m, 1 H), 2.73-2.65 (m, 1 H), 2.37 (sex, J = 6.9 Hz, 1 H), 1.70-1.64 (m, 2 H), 1.22 (s, 9 H), 1.13 (d, J = 6.8 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 142.6, 128.7, 128.4, 125.8, 89.9, 82.7, 39.4, 33.9, 31.7, 27.5, 25.5, 21.7. HRMS (ESI): Calcd for C₁₆H₂₂Ag [M+Ag]: 321.0772; Found: 321.0779.
Triisopropyl(3-methyl-5-phenylpent-1-yn-1-yl)silane (3h). Following the general procedure F, the title compound was prepared using (3-iodobutyl)benzene (260 mg, 1.0 mmol) and ((triisopropylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford triisopropyl(3-methyl-5-phenylpent-1-yn-1-yl)silane (3h) as pale-yellow oil (278 mg, 0.88 mmol, 88%).

\[
\begin{align*}
\text{Si} & \quad \text{Pr}_3 \\
& \\
\end{align*}
\]

\text{H NMR} (400 MHz, CDCl}_3): \delta 7.27 (t, \text{J} = 7.2 \text{ Hz}, 2 \text{ H}), 7.21-7.16 (ovrlp, 3 \text{ H}), 2.89-2.83 (m, 1 \text{ H}), 2.77-2.70 (m, 1 \text{ H}), 2.46 (sex, \text{J} = 6.9 \text{ Hz}, 2 \text{ H}), 1.72 (q, \text{J} = 7.4 \text{ Hz}, 2 \text{ H}), 1.19 (d, \text{J} = 6.7 \text{ Hz}, 3 \text{ H}), 1.11-1.06 (ovrlp, 21 \text{ H}).

\text{13C NMR} (100 MHz, CDCl}_3): \delta 142.4, 128.7, 128.5, 125.9, 113.5, 80.5, 39.2, 33.9, 26.7, 21.5, 18.8, 11.4. \text{HRMS} (ESI): Calcd for C21H34SiAg [M+Ag]: 421.1481; Found: 421.1487.

2,2,5-Trimethyldodec-3-yne (3i). Following the general procedure F, the title compound was prepared using 2-iodononane (S7) (254 mg, 1.0 mmol) and (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford 2,2,5-trimethyldodec-3-yne (3i) as yellow oil (153 mg, 0.73 mmol, 73%).

\[
\begin{align*}
\text{H NMR} (400 MHz, CDCl}_3): \delta 2.35 (sex, \text{J} = 6.8 \text{ Hz}, 3 \text{ H}), 1.19 (s, \text{J} = 6.8 \text{ Hz}, 3 \text{ H}), 0.89 (t, \text{J} = 6.6 \text{ Hz}, 3 \text{ H}).
\end{align*}
\]

\text{13C NMR} (100 MHz, CDCl}_3): \delta 89.1, 83.3, 37.6, 32.0, 31.7, 30.8, 29.6, 29.5, 27.5, 25.9, 22.9, 21.8, 14.3. \text{HRMS} (ESI): Calcd for C15H28 [M+Ag]: 208.2143; Found: 208.2141.

Ethyl 3,6,6-trimethylhept-4-ynoate (3j). Following the general procedure F, the title compound was prepared using ethyl 3-iodobutanoate (S13) (242 mg, 1.0 mmol) and (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford ethyl 3,6,6-trimethylhept-4-ynoate (3j) as brown oil (106 mg, 0.54 mmol, 54%).

\[
\begin{align*}
\text{H NMR} (400 MHz, CDCl}_3): \delta 4.15 (q, \text{J} = 7.1 \text{ Hz}, 2 \text{ H}), 2.90 (sex, \text{J} = 7.0 \text{ Hz}, 1 \text{ H}), 2.49-2.44 (m, 1 \text{ H}), 2.37-2.32 (m, 1 \text{ H}), 1.27 (t, \text{J} = 7.1 \text{ Hz}, 3 \text{ H}), 1.18-1.17 (ovrlp, 12 \text{ H}).
\end{align*}
\]

\text{13C NMR} (100 MHz, CDCl}_3): \delta 171.9, 89.6, 81.3, 60.4, 42.5, 31.4, 27.3, 23.0, 21.3, 14.4. \text{HRMS} (ESI): Calcd for C12H21O2 [M+H]: 197.1542; Found: 197.1535.
N-methyl-N-(2,5,5-trimethylhex-3-yn-1-yl)aniline (3k). Following the general procedure F, the title compound was prepared using N-(2-iodopropyl)-N-methylaniline (S23) (275 mg, 1.0 mmol) and (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes as eluents to afford N-methyl-N-(2,5,5-trimethylhex-3-yn-1-yl)aniline (3k) as brown oil (180 mg, 0.78 mmol, 78%). 1H NMR (400 MHz, CDCl3): δ 7.21 (t, J = 7.7 Hz, 2 H), 6.68-6.64 (ovrpl, 3 H), 3.40-3.35 (m, 1 H), 3.31-3.26 (m, 1 H), 3.01 (s, 3 H), 2.80 (sex, J = 7.0 Hz, 1 H), 1.16 (s, 9 H), 1.12 (d, J = 7.0 Hz, 3 H). 13C NMR (100 MHz, CDCl3): δ 149.1, 129.2, 115.9, 111.8, 90.1, 81.4, 59.3, 39.6, 31.4, 27.4, 25.1, 19.3. GCMS: [M] = 275 detected which corresponds to C16H23N; the purity was further confirmed by GCMS.

Ethyl (2-Methoxyphenyl)(2-methyl-(triisopropylsilyl)but-3-yn-1-yl)carbamate (3l). Following the general procedure F, the title compound was prepared using ethyl (2-bromopropyl)(2-methoxyphenyl)carbamate (S24) (158 mg, 0.50 mmol), ((triisopropylsilyl)ethyl)magnesium bromide (0.5 M in THF, 0.75 mmol, 1.5 mL), FeBr2 (22 mg, 0.10 mmol), O-TMEDA (160 mg, 191 µL), and NMP (2.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (10:1) as eluents to afford ethyl (2-methoxyphenyl)(2-methyl-(triisopropylsilyl)but-3-yn-1-yl)carbamate (3l) as pale yellow oil (181 mg, 0.43 mmol, 87%). 1H NMR (400 MHz, CDCl3): δ 7.31-7.22 (ovrpl, 2 H), 6.95-6.90 (ovrpl, 2 H), 4.24-3.94 (ovrpl, 3 H), 3.81 (s, 3 H), 3.45-3.23 (m, 1 H), 2.83-2.55 (m, 1 H), 1.22 (t, J = 8.6 Hz, 3 H), 1.12-1.04 (ovrpl, 24 H). 13C NMR (100 MHz, CDCl3): δ 156.6, 155.6, 130.7, 130.2, 130.0, 128.8, 128.6, 120.8, 120.6, 120.4, 112.1, 111.6, 111.4, 81.2, 61.7, 61.5, 55.7, 55.5, 55.0, 54.4, 54.2, 29.8, 26.9, 26.7, 26.6, 18.7, 14.7, 11.3 (observed complexity due to the mixture of 2 rotamers). GCMS: [M] = 417 detected which corresponds to C24H39NO3Si; the purity was further confirmed by GCMS.

2,6,9,9-Tetramethyldec-2-en-7-yne (3m). Following the general procedure F, the title compound was prepared using 6-iodo-2-methylhept-2-ene (238 mg, 1.0 mmol) and (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford 2,6,9,9-tetramethyldec-2-en-7-yne (3m) as pale-yellow oil (138 mg, 0.72 mmol, 72%). 1H NMR (400 MHz, CDCl3): δ 5.12 (s, 1 H), 2.37 (sex, J = 6.9 Hz, 1 H), 2.16-2.05 (m, 2 H), 1.69 (s, 3 H), 1.63 (s, 3 H), 1.38 (q, J = 6.4 Hz, 2 H), 1.19 (s, 9 H), 1.10 (d, J = 6.8 Hz, 3 H). 13C NMR (100 MHz, CDCl3): δ 131.8, 124.5, 89.3, 83.1, 37.8, 31.7, 30.8, 26.1, 25.9, 25.5, 21.7, 17.8. HRMS (APPI): Calcd for C14H24 [M]: 192.1874; Found: 192.1873.
From (2-iodopropyl)benzene: Following the general procedure F, the title compound was prepared using (2-iodopropyl)benzene (S6) (246 mg, 1.0 mmol) and ((4-(tert-buty1)phenyl)ethynyl)magnesium bromide (0.5 M in THF, 0.75 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford the crude product. The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (10:1) as eluents to afford 1-(tert-butyl)-4-(3-methyl-4-phenylbut-1-yn-1-yl)benzene (3n) as viscous, deep-brown oil (264 mg, 0.95 mmol, 95%). \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 7.30-7.16 (ovrlp, 9 H), 2.87 (d, \(J = 8.2\) Hz, 2 H), 2.79-2.70 (m, 1 H), 1.27 (s, 9 H), 1.23 (d, \(J = 5.8\) Hz, 3 H). \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) 150.7, 139.8, 131.3, 129.5, 128.2, 126.4, 125.2, 121.1, 93.4, 81.7, 43.4, 34.7, 31.3, 28.7, 20.8. \text{HRMS} (ESI): Calcd for C\(_{21}\)H\(_{24}\)Ag \([M+Ag]^+\): 383.0929; Found: 383.0921.

From (2-bromopropyl)benzene: Following the general procedure F, the title compound was prepared using (2-bromopropyl)benzene (199 mg, 1.0 mmol), ((4-(tert-buty1)phenyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), FeBr\(_2\) (43 mg, 0.20 mmol), and O-TMEDA (321 mg, 381 \(\mu\)L). The crude product was purified by flash chromatography using hexanes/EtOAc (50:1) as eluents to afford 1-(tert-butyl)-4-(3-methyl-4-phenylbut-1-yn-1-yl)benzene (3l) as deep-brown oil (229 mg, 0.83 mmol, 83%). Spectral and analytical data were identical to those reported for the same compound above.

\(\text{N,N-dimethyl-4-(3-methyl-4-phenylbut-1-yn-1-yl)aniline (3o).}\) Following the general procedure F, the title compound was prepared using (2-iodopropyl)benzene (S6) (123 mg, 0.50 mmol), FeBr\(_2\) (11 mg, 0.050 mmol), ((4-(dimethylamino)phenyl)ethynyl)magnesium bromide (0.5 M in THF, 0.75 mmol, 1.5 mL), and NMP (2.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (10:1) as an eluent to afford \(\text{N,N-dimethyl-4-(3-methyl-4-phenylbut-1-yn-1-yl)aniline (3o)}\) as viscous, pale-yellow oil (86 mg, 0.33 mmol, 65%). \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 7.32-7.19 (ovrlp, 7 H), 6.59 (d, \(J = 8.4\) Hz, 2 H), 2.93-2.84 (ovrlp, 8 H), 2.78-2.71 (m, 1 H), 1.23 (d, \(J = 6.0\) Hz, 3 H). \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) 149.8, 140.0, 132.6, 129.5, 128.2, 126.3, 112.0, 111.1, 91.6, 82.1, 43.5, 40.4, 28.8, 20.9. \text{HRMS} (ESI): Calcd for C\(_{19}\)H\(_{22}\)N \([M+H]^+\): 264.1752; Found: 264.1742.

\(4-(4-(4-methoxyphenyl)-3-methylbut-1-yn-1-yl)-\text{N,N-dimethylaniline (3p).}\) Following the general procedure F, the title compound was prepared using 1-(2-iodopropyl)-4-methoxybenzene (S21) (138 mg, 0.50 mmol), FeBr\(_2\) (11 mg, 0.050 mmol), ((4-(dimethylamino)phenyl)ethynyl)magnesium bromide (0.5 M in THF, 0.75 mmol, 1.5 mL), and NMP (2.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (10:1) as an eluent to afford 4-(4-(4-methoxyphenyl)-3-methylbut-1-yn-1-yl)-\text{N,N-dimethylaniline (3p)} as viscous, pale-yellow oil (72 mg, 0.25 mmol, 50%).
**1H NMR** (400 MHz, CDCl₃): 7.24 (d, J = 8.2 Hz, 2 H), 7.19 (d, J = 8.0 Hz, 2 H), 6.84 (d, J = 8.1 Hz, 2 H), 6.60 (d, J = 8.3 Hz, 2 H), 3.78 (s, 3 H), 2.93 (s, 6 H), 2.86-2.80 (ovrlp, 2 H), 2.72-2.66 (m, 1 H), 1.22 (d, J = 5.8 Hz, 3 H). **13C NMR** (100 MHz, CDCl₃): δ 158.1, 149.8, 132.6, 132.1, 130.4, 113.6, 112.0, 111.2, 91.7, 82.1, 55.3, 42.6, 40.4, 29.0, 20.8. **HRMS** (ESI): Calcd for C₂₀H₂₄NO [M+H]: 294.1858; Found: 294.1853.

Triethyl(4-(4-methoxyphenyl)-3-methylbut-1-yn-1-yl)silane (3q). Following the general procedure F, the title compound was prepared using 1-(2-iodopropyl)-4-methoxybenzene (S21) (276 mg, 1.0 mmol) and ((triethylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 0.75 mmol, 1.5 mL), and NMP (2.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (10:1) as an eluent to afford triethyl(4-(4-methoxyphenyl)-3-methylbut-1-yn-1-yl)silane (3q) as deep-brown oil (271 mg, 0.94 mmol, 94%). **1H NMR** (400 MHz, CDCl₃): 7.13 (d, J = 7.6 Hz, 2 H), 6.81 (d, J = 7.6 Hz, 2 H), 3.77 (s, 3 H), 2.76-2.60 (ovrlp, 3 H), 1.15 (d, J = 5.2 Hz, 3 H), 0.96 (t, J = 7.4 Hz, 9 H), 0.55 (q, J = 7.6 Hz, 6 H). **13C NMR** (100 MHz, CDCl₃): δ 158.2, 131.8, 130.4, 113.5, 112.7, 82.1, 55.3, 42.3, 29.3, 20.7, 7.58, 4.65. **HRMS** (ESI): Calcd for C₁₈H₂₆OSiAg [M+H]: 395.0960; Found: 395.0968.

4-(4-(3,4-dimethoxyphenyl)-3-methylbut-1-yn-1-yl)-N,N-dimethylaniline (3r). Following the general procedure F, the title compound was prepared using 4-(2-iodopropyl)-1,2-dimethoxybenzene (S22) (153 mg, 0.50 mmol), FeBr₂ (11 mg, 0.050 mmol), ((4-(dimethylamino)phenylethynyl)magnesium bromide (0.5 M in THF, 0.75 mmol, 1.5 mL), and NMP (2.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (10:1) as an eluent to afford 4-(4-(3,4-dimethoxyphenyl)-3-methylbut-1-yn-1-yl)-N,N-dimethylaniline (3r) as viscous yellow oil (82 mg, 0.25 mmol, 51%). **1H NMR** (400 MHz, CDCl₃): 7.23 (d, J = 8.4 Hz, 2 H), 6.86 (s, 1 H), 6.79 (ovrlp s, 2 H), 6.59 (d, J = 8.5 Hz, 2 H), 3.85 (s, 3 H), 3.83 (s, 3 H), 2.93 (s, 6 H), 2.88-2.80 (ovrlp, 2 H), 2.76-2.67 (m, 1 H), 1.24 (d, J = 6.2 Hz, 3 H). **13C NMR** (100 MHz, CDCl₃): δ 149.7, 148.5, 147.5, 132.6, 132.5, 121.3, 112.7, 111.9, 111.0, 110.9, 91.7, 82.3, 55.9, 55.8, 43.0, 40.4, 29.0, 20.9. **HRMS** (ESI): Calcd for C₂₁H₂₆NO₂ [M+H]: 324.1964; Found: 324.1968.

(2-Ethyl-5,5-dimethylhex-3-yn-1-yl)benzene (3s). Following the general procedure F, the title compound was prepared using (2-iodobutyl)benzene (260 mg, 1.0 mmol) and (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford (2-ethyl-5,5-dimethylhex-3-yn-1-yl)benzene (3s) as pale-yellow oil (169 mg, 0.79 mmol, 79%). **1H NMR** (400 MHz, CDCl₃): δ 7.28-7.16 (ovrlp, 5 H), 2.75-2.65 (m, 2 H), 2.46 (qu, J = 5.5 Hz, 1 H), 1.54-1.43 (m, 1 H), 1.09-1.00 (m, 2 H), 1.00-0.90 (m, 2 H), 0.70-0.60 (m, 2 H), 0.40-0.30 (m, 1 H), 0.30-0.20 (m, 1 H), 0.10-0.00 (m, 1 H).
1.40-1.31 (m, 1 H), 1.16 (s, 9 H), 0.99 (t, \( J = 7.2 \) Hz, 3 H). 13C NMR (100 MHz, CDCl₃): \( \delta \) 140.3, 129.6, 128.0, 126.1, 91.3, 81.4, 41.7, 35.5, 31.5, 27.9, 27.5, 11.8. HRMS (APPI): Calcd for C₁₆H₂₂ [M]: 214.1723; Found: 214.1716.

5-Ethyl-2,2-dimethylundec-3-yne (3t). Following the general procedure F, the title compound was prepared using 3-iodononane (254 mg, 1.0 mmol), (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), FeBr₂ (43 mg, 0.20 mmol), and O-TMEDA (321 mg, 381 \( \mu L \)). The crude product was purified by flash chromatography using hexanes as an eluent to afford 5-ethyl-2,2-dimethylundec-3-yne (3t) as yellow oil (141 mg, 0.68 mmol, 68%). 1H NMR (400 MHz, CDCl₃): \( \delta \) 2.18 (qu, \( J = 6.6 \) Hz, 1 H), 1.48-1.41 (m, 2 H), 1.39-1.25 (ovrlp, 10 H), 1.19 (s, 9 H), 0.96 (t, \( J = 7.3 \) Hz, 3 H), 0.89 (t, \( J = 6.8 \) Hz, 3 H). 13C NMR (100 MHz, CDCl₃): \( \delta \) 90.3, 81.9, 35.3, 33.4, 32.0, 31.7, 30.5, 29.4, 28.6, 27.5, 22.8, 14.3, 11.9. HRMS (ESI): Calcd for C₁₅H₂₈Ag [M+Ag]: 315.1242; Found: 315.1248.

5-Ethyl-8,8-dimethylnon-1-en-6-yne (3u). Following the general procedure F, the title compound was prepared using 5-iodohept-1-ene (224 mg, 1.0 mmol), (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), FeBr₂ (43 mg, 0.20 mmol), and O-TMEDA (321 mg, 381 \( \mu L \)). The crude product was purified by flash chromatography using hexanes as an eluent to afford 5-ethyl-8,8-dimethylnon-1-en-6-yne (3u) as volatile, pale-yellow oil (84 mg, 0.47 mmol, 47%). 1H NMR (400 MHz, CDCl₃): \( \delta \) 5.88-5.78 (m, 1 H), 5.03 (d, \( J = 17.0 \) Hz, 1 H), 4.95 (d, \( J = 10.0 \) Hz, 1 H), 2.24-2.08 (ovrlp, 3 H), 1.50-1.42 (m, 2 H), 1.29-1.23 (m, 2 H), 1.20 (s, 9 H), 0.97 (t, \( J = 7.3 \) Hz, 3 H). 13C NMR (100 MHz, CDCl₃): \( \delta \) 139.0, 114.6, 90.8, 81.3, 34.5, 32.9, 31.9, 31.7, 30.8, 28.5, 11.9. HRMS (APPI): Calcd for C₁₃H₂₂ [M]: 178.1715; Found: 178.1716.

5-Butyl-2,2-dimethylnon-3-yne (3v). Following the general procedure F, the title compound was prepared using 5-iodononane (254 mg, 1.0 mmol), (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), FeBr₂ (43 mg, 0.20 mmol), and O-TMEDA (321 mg, 381 \( \mu L \)). The crude product was purified by flash chromatography using hexanes as an eluent to afford 5-butyl-2,2-dimethylnon-3-yne (3v) as volatile, pale-brown oil (152 mg, 0.73 mmol, 73%). 1H NMR (400 MHz, CDCl₃): \( \delta \) 2.23 (s, 1 H), 1.47-1.26 (ovrlp, 12 H), 1.19 (s, 9 H), 0.90 (t, \( J = 6.4 \) Hz, 6 H). 13C NMR (100 MHz, CDCl₃): \( \delta \) 90.1, 82.2, 35.4, 31.70, 31.65, 29.8, 27.5, 22.8, 14.3. HRMS (ESI): Calcd for C₁₅H₂₈Ag [M+Ag]: 315.1242; Found: 315.1260.
2-(Cyclohexylethynyl)-5-methylthiophene (P1). Following the general procedure F, the title compound was prepared using iodocyclohexane (210 mg, 130 μL, 1.0 mmol) and ((5-methylthiophen-2-yl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford ethyl 2-(cyclohexylethynyl)-5-methylthiophene (P1) as pale-brown oil (64 mg, 0.31 mmol, 31%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.90 (d, $J = 3.0$ Hz, 1 H), 6.57 (d, $J = 3.0$ Hz, 1 H), 2.60-2.54 (m, 1 H), 2.43 (s, 3 H), 1.87-1.85 (m, 2 H), 1.77-1.70 (m, 2 H), 1.57-1.47 (ovrlp, 3 H), 1.37-1.29 (ovrlp, 3 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.5, 131.1, 125.0, 121.9, 97.6, 74.0, 32.7, 30.1, 26.0, 25.1, 15.5.

HRMS (APPI): Calcd for C$_{13}$H$_{16}$S [M]: 204.0967; Found: 204.0967.

4-((5-Methylthiophen-2-yl)ethynyl)tetrahydro-2H-pyran (P2). Following the general procedure F, the title compound was prepared using 4-iodotetrahydro-2H-pyran (212 mg, 1.0 mmol) and ((5-methylthiophen-2-yl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford 4-((5-methylthiophen-2-yl)ethynyl)tetrahydro-2H-pyran (P2) as brown oil (59 mg, 0.29 mmol, 29%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.93 (d, $J = 3.0$ Hz, 1 H), 6.59 (d, $J = 2.8$ Hz, 1 H), 3.96-3.91 (m, 2 H), 3.53 (t, $J = 8.8$ Hz, 2 H), 2.87-2.81 (m, 1 H), 2.33 (s, 3 H), 1.92-1.85 (m, 2 H), 1.78-1.69 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.0, 131.5, 125.1, 121.3, 95.3, 75.0, 66.5, 32.2, 27.2, 15.4. HRMS (ESI): Calcd for C$_{12}$H$_{15}$OS [M+Ag]: 207.0844; Found: 207.0861.

1-Chloro-4-((4-methylcyclohexyl)ethynyl)benzene (P3). Following the general procedure F, the title compound was prepared using 1-iodo-4-methylcyclohexane (S2) (224 mg, 1.0 mmol) and ((4-chlorophenyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford 1-chloro-4-((4-methylcyclohexyl)ethynyl)benzene (P3) as an off-white solid (85 mg, 0.37 mmol, 37%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34-7.29 (ovrlp, 2 H), 7.26-7.22 (ovrlp, 2 H), 2.90 (s, 0.1 H), 2.35 (t, $J = 11.8$ Hz, 0.9 H), 2.02 (d, $J = 11.8$ Hz, 2 H), 1.85-1.71 (m, 2 H), 1.59-1.36 (ovrlp, 4 H), 0.99-0.88 (ovrlp, 4 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 133.4, 132.9, 128.6, 122.7, 95.8, 79.1, 34.6, 33.1, 32.0, 30.1, 22.7. HRMS: [M] could not be detected by HRMS (ESI). GCMS: [M] = 232 detected which corresponds to C$_{15}$H$_{17}$Cl; The purity was further confirmed by GCMS.

1-((4-(tert-Butyl)cyclohexyl)ethynyl)-4-fluorobenzene (P4). Following the general procedure F, the title compound was prepared using 1-iodo-4-(tert-butyl)cyclohexane (S3) (266 mg, 1.0 mmol) and ((4-fluorophenyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was
purified by flash chromatography using hexanes as an eluent to afford 1-((4-(tert-butyl)cyclohexyl)ethyl)ethyl)-4-fluorobenzene (P4) as a low-melting, off-white solid (82 mg, 0.32 mmol, 32%). ¹H NMR (400 MHz, CDCl₃): δ 7.36 (dd, 3J_HH = 7.6 Hz, 4J_HF = 5.7 Hz, 2 H), 6.96 (dd, 3J_HH = 8.5 Hz, 2J_HF = 8.5 Hz, 2 H), 2.32 (t, J = 12.0 Hz, 1 H), 2.09 (d, J = 12.7 Hz, 2 H), 1.83-1.78 (m, 2 H), 1.45-1.35 (m, 2 H), 1.03-0.98 (ovrlp, 3 H), 0.85 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ 162.1 (d, 1J_CF = 246.7 Hz), 133.5 (d, 3J_CF = 8.0 Hz), 120.2 (d, 4J_CF = 2.9 Hz), 115.4 (d, 2J_CF = 21.8 Hz), 94.4, 79.1, 47.5, 33.8, 32.6, 30.5, 27.6, 27.0. HRMS (APPI): Calcd for C₁₈H₂₃F [M]: 258.1780; Found: 258.1778.

[Chemical structure image]

4-(5-(4-(Methylthio)phenoxy)pent-1-yn-1-yl)tetrahydro-2H-pyran (P5). Following the general procedure F, the title compound was prepared using 4-iodotetrahydro-2H-pyran (212 mg, 1.0 mmol) and (5-(4-(methylthio)phenoxy)pent-1-yn-1-yl)magnesium bromide (synthesized from (S20), 0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford 4-(5-(4-(methylthio)phenoxy)pent-1-yn-1-yl)tetrahydro-2H-pyran (P5) as an off-white solid (110 mg, 0.38 mmol, 38%). ¹H NMR (400 MHz, CDCl₃): δ 7.18 (d, J = 8.4 Hz, 2 H), 6.77 (d, J = 8.4 Hz, 2 H), 3.96 (t, J = 6.1 Hz, 2 H), 3.82-3.77 (m, 2 H), 3.39 (t, J = 9.0 Hz, 2 H), 2.50 (s, 1 H), 2.36 (s, 3 H), 2.30 (t, J = 6.3 Hz, 2 H), 1.88 (qu, J = 6.4 Hz, 2 H), 1.74-1.67 (m, 2 H), 1.57-1.49 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 157.7, 130.3, 128.9, 115.4, 83.5, 80.1, 66.7, 66.5, 32.8, 28.8, 26.4, 18.2, 15.6. HRMS (ESI): Calcd for C₁₇H₂₂O₂S [M+H]: 291.1419; Found: 291.1422.

[Methyl(4-(3-methylpent-1-yn-1-yl)phenyl)sulfane (P6). Following the general procedure F, the title compound was prepared using 2-iodobutane (184 mg, 1.0 mmol) and (4-(methylthio)phenyl)ethyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford methyl(4-(3-methylpent-1-yn-1-yl)phenyl)sulfane (P6) as yellow oil (77 mg, 0.38 mmol, 38%). ¹H NMR (400 MHz, CDCl₃): δ 7.30 (d, J = 7.8 Hz, 2 H), 7.14 (d, J = 7.8 Hz, 2 H), 2.57 (sex, J = 6.6 H, 1 H), 2.46 (s, 3 H), 1.53 (sex, J = 6.4 H, 2 H), 1.23 (d, J = 6.8 Hz, 3 H), 1.04 (t, J = 7.1 H, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 138.1, 132.0, 126.2, 120.8, 94.8, 80.6, 30.1, 28.3, 20.8, 15.8, 11.9. HRMS (APPI): Calcd for C₁₃H₁₇S [M+H]: 205.1001 Found: 205.1001.

1-(tert-Butyl)-4-(3,7-dimethyloct-6-en-1-yn-1-yl)benzene (P7). Following the general procedure F, the title compound was prepared using 6-iodo-2-methylhept-2-ene (184 mg, 1.0 mmol) and (4-(tert-butyl)phenyl)ethyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford 1-(tert-butyl)-4-(3,7-dimethyloct-6-en-1-yn-1-yl)benzene (P7) as pale-yellow oil (121 mg, 0.45 mmol, 45%). ¹H NMR (400 MHz, CDCl₃): δ 7.33-7.27 (m, 4 H), 5.14 (s, 1 H), 2.63 (sex, J = 6.4 Hz, 1 H), 2.21-2.15 (m, 2 H), 1.70 (s, 3 H), 1.65 (s, 3 H), 1.58-1.48 (m, 2 H), 1.29 (s, 9 H), 1.24 (d, J = 6.7 Hz, 3 H). ¹³C NMR (100 MHz,
CDCl₃): δ 150.7, 132.1, 131.4, 125.3, 124.2, 121.3, 94.1, 81.0, 37.4, 34.8, 31.4, 26.2, 26.1, 25.9, 21.3, 17.9. **HRMS (APPI):** Calcd for C₂₀H₂₈ [M]: 268.2186; Found: 268.2186.

Trimethyl(3-methyl-5-phenylpent-1-yn-1-yl)silane (P8).[27] Following the general procedure F, the title compound was prepared using (3-iodobutyl)benzene (260 mg, 1.0 mmol) and ((trimethylsilyl)ethyl)ynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford trimethyl(3-methyl-5-phenylpent-1-yn-1-yl)silane (P8) as viscous, deep-brown oil (65 mg, 0.28 mmol, 28%).

**1H NMR** (400 MHz, CDCl₃): δ 7.28 (t, J = 7.2 Hz, 2 H), 7.22-7.16 (ovrlp, 3 H), 2.84-2.77 (m, 1 H), 2.74-2.67 (m, 1 H), 2.44 (sex, J = 7.0 Hz, 1 H), 1.79-1.65 (m, 2 H), 1.18 (d, J = 6.8 Hz, 3 H), 0.17 (s, 9 H).

**13C NMR** (100 MHz, CDCl₃): δ 142.2, 128.6, 128.5, 125.9, 111.7, 84.9, 38.8, 33.8, 26.5, 21.1, 0.44.

2-((9-(3,4-dimethoxyphenyl)-8-methylnon-6-yn-1-yl)oxy)tetrahydro-2H-pyran (P9). Following the general procedure F, the title compound was prepared using 4-(2-iodopropyl)-1,2-dimethoxybenzene (S22) (306 mg, 1.0 mmol) and ((4-(dimethylamino)phenyl)ethyl)ynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (10:1) and then hexanes/EtOAc (6:1) as eluents to afford 2-((9-(3,4-dimethoxyphenyl)-8-methylnon-6-yn-1-yl)oxy)tetrahydro-2H-pyran (P9) as viscous, pale-yellow oil (109 mg, 0.29 mmol, 29%).

**1H NMR** (400 MHz, CDCl₃): δ 6.79-6.73 (ovrlp, 3 H), 4.57 (s, 1 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 3.76-3.70 (m, 1 H), 3.52-3.47 (m, 1 H), 3.40-3.35 (m, 1 H), 2.72 (sex, J = 6.2 Hz, 1 H), 2.68-2.56 (ovrlp, 2 H), 2.15 (t, J = 6.0 Hz, 2 H), 1.86-1.79 (m, 1 H), 1.73-1.68 (m, 1 H), 1.63-1.40 (ovrlp, 11 H), 1.13 (d, J = 5.7 Hz, 3 H).

**13C NMR** (100 MHz, CDCl₃): δ 148.4, 147.3, 132.5, 121.2, 112.4, 110.8, 98.8, 84.4, 80.9, 67.4, 62.2, 55.8, 55.7, 43.1, 30.7, 29.3, 28.9, 28.1, 25.5, 25.4, 20.9, 19.6, 18.7. **GCMS:** [M] = 374 detected which corresponds to C₂₃H₄₅O₄.

1-(tert-Butyl)-4-(5-chloropent-1-yn-1-yl)benzene (4a). (i) From 1-chloro-3-iodopropane. Following the general procedure G, the title compound was prepared using 1-chloro-3-iodopropane (204 mg, 1.0 mmol), ((4-(tert-butyl)phenyl)ethyl)ynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), and FeBr₂ (22 mg, 0.10 mmol). The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford 1-(tert-butyl)-4-(5-chloropent-1-yn-1-yl)benzene (4a) as deep-brown oil (205 mg, 0.88 mmol, 88%).

**1H NMR** (400 MHz, CDCl₃): δ
7.34-7.29 (ovrlp, 4 H), 3.69 (t, \( J = 6.2 \text{ Hz} \), 2 H), 2.58 (t, \( J = 6.6 \text{ Hz} \), 2 H), 2.03 (qu, \( J = 6.5 \text{ Hz} \), 2 H), 1.29 (s, 9 H). \(^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta 151.1, 131.4, 125.3, 120.7, 87.4, 81.7, 43.9, 34.8, 31.7, 31.3, 17.0 \). \( \text{HRMS (APPI): Calcd for C}_{15}\text{H}_{19}\text{Cl} [M]: 234.1174; Found: 234.1170.}  

(ii) From 1-bromo-3-chloropropane. Following the general procedure G, the title compound was prepared using 1-bromo-3-chloropropane (204 mg, 1.0 mmol) and ((4-(tert-butyl)phenyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford 1-(tert-butyl)-4-(5-chloropent-1-yn-1-yl)benzene (4a) as deep-brown oil (212 mg, 0.90 mmol, 90%). Spectral and analytical data were identical to those reported for the same compound above.

\( \text{SiEt}_3\text{Cl} \)

(6-Chlorohex-1-yn-1-yl)triethylsilane (4b). Following the general procedure G, the title compound was prepared using 1-bromo-4-chlorobutane (172 mg, 1.0 mmol) and ((triethylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and hexanes/EtOAc (50:1) as eluents to afford (6-chlorohex-1-yn-1-yl)triethylsilane (4b) as brown oil (183 mg, 0.79 mmol, 79%). \( \text{HRMS (ESI): Calcd for C}_{12}\text{H}_{23}\text{ClSiAg} [M+Ag]: 337.0312; Found: 337.0312.}  

(8-Chlorooct-1-yn-1-yl)cyclohexane (4c). Following the general procedure G, the title compound was prepared using 1-bromo-6-chlorohexane (200 mg, 1.0 mmol) and (cyclohexylethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and hexanes/EtOAc (50:1) as eluents to afford (8-chlorooct-1-yn-1-yl)cyclohexane (4c) as brown oil (143 mg, 0.63 mmol, 63%). \( \text{HRMS (ESI): Calcd for C}_{14}\text{H}_{23}\text{ClAg} [M+Ag]: 333.0545; Found: 333.0545.}  

9-(non-4-yn-1-yl)-9H-carbazole (4d). Following the general procedure G, the title compound was prepared using 9-(3-iodopropyl)-9H-carbazole (S14) (335 mg, 1.0 mmol), hex-1-yn-1-ylmagnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), and FeBr\(_2\) (22 mg, 0.10 mmol). The crude product was
purified by flash chromatography using hexanes and then hexanes/EtOAc (100:1) as eluents to afford 9-(non-4-yn-1-yl)-9H-carbazole (4d) as brown oil (169 mg, 0.59 mmol, 59%). \[^1\text{H} \text{NMR}\] (400 MHz, CDCl\(_3\)): \(\delta\) 8.06 (d, \(J = 7.3\) Hz, 2 H), 7.44-7.37 (ovrlp, 4 H), 7.22-7.16 (m, 2 H), 4.35 (t, \(J = 6.3\) Hz, 2 H), 2.23-2.13 (ovrlp, 4 H), 1.97 (qu, \(J = 6.3\) Hz, 2 H), 1.56-1.41 (ovrlp, 4 H), 0.94 (t, \(J = 6.6\) Hz, 3 H). \[^{13}\text{C} \text{NMR}\] (100 MHz, CDCl\(_3\)): \(\delta\) 140.6, 125.7, 123.0, 120.4, 118.9, 108.8, 81.6, 79.1, 41.7, 31.3, 28.4, 22.1, 18.6, 16.7, 13.8. \[^{15}\text{N}\]MS (ESI): Calcd for C\(_{21}\)H\(_{24}\)N [M+H]: 290.1909; Found: 290.1901.

**9-(5-Cyclopropypent-4-yn-1-yl)-9H-carbazole (4e).** Following the general procedure G, the title compound was prepared using 9-(3-iodopropyl)-9H-carbazole (S14) (335 mg, 1.0 mmol) and (cyclopropylethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (100:1) as eluents to afford 9-(5-cyclopropypent-4-yn-1-yl)-9H-carbazole (4e) as brown oil (116 mg, 0.42 mmol, 42%). \[^1\text{H} \text{NMR}\] (400 MHz, CDCl\(_3\)): \(\delta\) 8.06 (d, \(J = 7.5\) Hz, 2 H), 7.45-7.39 (ovrlp, 4 H), 7.23-7.17 (m, 2 H), 4.36 (t, \(J = 6.6\) Hz, 2 H), 2.12 (t, \(J = 5.8\) Hz, 2 H), 1.98 (qu, \(J = 6.5\) Hz, 2 H), 1.29-1.22 (m, 1 H), 0.76-0.70 (m, 2 H), 0.68-0.64 (m, 2 H). \[^{13}\text{C} \text{NMR}\] (100 MHz, CDCl\(_3\)): \(\delta\) 140.6, 125.7, 123.0, 120.4, 119.0, 108.8, 84.6, 74.5, 41.7, 28.3, 16.6, 8.1, -0.3. \[^{15}\text{N}\]MS (ESI): Calcd for C\(_{20}\)H\(_{20}\)N [M+H]: 274.1596; Found: 274.1598.

**9-(5-(Cyclohex-1-en-1-yl)pent-4-yn-1-yl)-9H-carbazole (4f).** Following the general procedure G, the title compound was prepared using 9-(3-iodopropyl)-9H-carbazole (S14) (335 mg, 1.0 mmol), (cyclohex-1-en-1-ylethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), and FeBr\(_2\) (22 mg, 0.10 mmol). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (200:1) as eluents to afford 9-(5-(cyclohex-1-en-1-yl)pent-4-yn-1-yl)-9H-carbazole (4f) as viscous brown oil (188 mg, 0.60 mmol, 60%). \[^1\text{H} \text{NMR}\] (400 MHz, CDCl\(_3\)): \(\delta\) 8.07 (d, \(J = 7.6\) Hz, 2 H), 7.47-7.41 (ovrlp, 4 H), 7.21 (t, \(J = 6.5\) Hz, 2 H), 6.10 (s, 1 H), 4.41 (t, \(J = 6.6\) Hz, 2 H), 2.30 (t, \(J = 6.3\) Hz, 2 H), 2.19-2.15 (m, 2 H), 2.11-2.02 (ovrlp, 4 H), 1.68-1.56 (ovrlp, 4 H). \[^{13}\text{C} \text{NMR}\] (100 MHz, CDCl\(_3\)): \(\delta\) 140.6, 133.9, 125.7, 123.0, 121.0, 120.4, 119.0, 108.8, 86.1, 83.7, 41.7, 29.7, 28.2, 25.7, 22.5, 21.7, 17.2. \[^{15}\text{N}\]MS (ESI): Calcd for C\(_{23}\)H\(_{24}\)N [M+H]: 314.1909; Found: 314.1921.
9-(5-(Trimethylsilyl)pent-4-yn-1-yl)-9H-carbazole (4g). Following the general procedure G, the title compound was prepared using 9-(3-iodopropyl)-9H-carbazole (S14) (335 mg, 1.0 mmol), ((trimethylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), and FeBr₂ (22 mg, 0.10 mmol). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (200:1) as eluents to afford 9-(5-(trimethylsilyl)pent-4-yn-1-yl)-9H-carbazole (4g) as viscous brown oil (158 mg, 0.52 mmol, 52%). ¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, J = 7.5 Hz, 2 H), 7.47-7.42 (ovrlp, 4 H), 7.22 (t, J = 6.6 Hz, 2 H), 4.42 (t, J = 6.4 Hz, 2 H), 2.23 (t, J = 6.1 Hz, 2 H), 2.05 (qu, J = 6.3 Hz, 2 H), 0.23 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ 140.6, 125.7, 123.0, 120.5, 119.0, 108.8, 106.4, 86.1, 41.6, 27.8, 17.7, 0.3. HRMS (ESI): Calcd for C₂₀H₂₄NSi [M+H]: 306.1678; Found: 306.1684.

1-(6,6-Dimethylhept-4-yn-1-yl)-1H-indole (4h). Following the general procedure G, the title compound was prepared using 1-(3-iodopropyl)-1H-indole (S15) (285 mg, 1.0 mmol), (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL), and FeBr₂ (22 mg, 0.10 mmol). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford 1-(6,6-dimethylhept-4-yn-1-yl)-1H-indole (4h) as brown oil (168 mg, 0.70 mmol, 70%). ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, J = 7.5 Hz, 1 H), 7.39 (d, J = 8.0 Hz, 1 H), 7.11-7.08 (ovrlp, 2 H), 6.48 (s, 1 H), 4.24 (t, J = 6.4 Hz, 2 H), 2.10 (t, J = 6.2 Hz, 2 H), 1.95 (qu, J = 6.4 Hz, 2 H), 1.25 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ 136.0, 128.7, 128.2, 121.4, 121.0, 119.4, 109.5, 101.1, 90.6, 77.1, 44.8, 31.5, 29.4, 27.6, 16.2. HRMS (ESI): Calcd for C₁₇H₂₃N [M+H]: 240.1752; Found: 240.1750.

2,2-Dimethyltetradec-3-yne (4i). Following the general procedure G, the title compound was prepared using 1-bromodecane (221 mg, 1.0 mmol) and (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford 2,2-dimethyltetradec-3-yne (4i) as pale-brown oil (150 mg, 0.68 mmol, 68%). ¹H NMR (400 MHz, CDCl₃): δ 2.12 (t, J = 6.9 Hz, 2 H), 1.46 (qu, J = 6.8 Hz, 2 H), 1.35-1.23 (ovrlp, 14 H), 1.19 (s, 9 H), 0.88 (t, J = 6.6 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 89.1, 78.7, 32.1, 31.6, 30.8, 29.8, 29.7, 29.5, 29.4, 29.3, 29.0, 22.9, 18.8, 14.3. HRMS (APPI): Calcd for C₁₆H₃₀ [M]: 222.2343; Found: 222.2342.
Triisopropyl(6-phenoxyhex-1-yn-1-yl)silane (4j). Following the general procedure G, the title compound was prepared using (4-bromobutoxy)benzene (229 mg, 1.0 mmol) and ((triisopropylsilyl)ethynyl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford triisopropyl(6-phenoxyhex-1-yn-1-yl)silane (4j) as pale yellow oil (309 mg, 0.93 mmol, 93%). 

\[ \text{SiPr}_3 \text{Si} \text{C} \text{C} \text{SiPr}_3 \]

8.8-Dimethylnon-6-yn-1-yl acetate (4k). Following the general procedure G, the title compound was prepared using 5-iodopentyl acetate (256 mg, 1.0 mmol) and (3,3-dimethylbut-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (50:1) as eluents to afford 8,8-dimethylnon-6-yn-1-yl acetate (4k) as pale-yellow oil (140 mg, 0.67 mmol, 67%). 

\[ \text{O} \text{C} \text{O} \text{Bu} \]

Large-Scale Synthesis for Iron-Catalyzed Cross-Coupling of Non-activated Secondary Alkyl Halides with Alkynyl Grignard Reagents (General Procedure H). An oven-dried 250 mL round-bottom flask capped with a rubber septum and equipped with a Teflon-coated magnetic stirrer bar was charged with FeBr\(_2\) (98% purity, 0.10 equiv), secondary alkyl halide (1.0 equiv), and NMP solvent, followed by the slow addition of alkynyl Grignard reagent solution (in THF, 1.5 equiv). The reaction mixture was stirred at room temperature for 16 h to form a black solution. After the reaction, the crude product was washed with EtOAc (20 mL) and water (60 mL). The aqueous fraction was further washed with EtOAc (2 x 20 mL). The combined organic fractions were concentrated \textit{in vacuo} with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography with silica gel using a solvent mixture (EtOAc, hexanes) as an eluent to afford the isolated alkylated alkyne product.

\textbf{(i) 5 mmol Scale Synthesis.} Following the general procedure H, the title compound was prepared using 4-iodotetrahydro-2\(H\)-pyran (1.06 g, 5.0 mmol), ((trimethylsilyl)ethynyl)magnesium bromide (0.75 M in
THF, 7.5 mmol, 10 mL) (prepared by ethynyltrimethylsilane (737 mg, 7.5 mmol), ethylmagnesium bromide (1 M in THF, 7.5 mL), and THF (2.5 mL)), FeBr₂ (108 mg, 0.50 mmol), and NMP (20 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (20:1) as eluents to afford trimethyl((tetrahydro-2H-pyran-4-yl)ethynyl)silane (2s) as brown oil (699 mg, 3.83 mmol, 77%). Spectral and analytical data were identical to those reported for the same compound above based on 1.0 mmol scale.

(ii) 20 mmol Scale Synthesis. Following the general procedure H, the title compound was prepared using 4-iodotetrahydro-2H-pyran (4.24 g, 20.0 mmol), ((trimethylsilyl)ethynyl)magnesium bromide (1 M in THF, 30.0 mmol, 30 mL) (prepared by ethynyltrimethylsilane (2.95 g, 30.0 mmol) and ethylmagnesium bromide (1 M in THF, 30 mL)), FeBr₂ (413 mg, 2.0 mmol), and NMP (40 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (20:1) as eluents to afford trimethyl((tetrahydro-2H-pyran-4-yl)ethynyl)silane (2s) as brown oil (2.68 g, 14.9 mmol, 75%). Spectral and analytical data were identical to those reported for the same compound above based on 1.0 mmol scale.

(iii) 10 mmol Scale Synthesis. Following the general procedure H, the title compound was prepared using tert-butyl 4-iodopiperidine-1-carboxylate (3.11 g, 10.0 mmol) and ((trimethylsilyl)ethynyl)magnesium bromide (0.75 M in THF, 15.0 mmol, 20 mL) (prepared by ethynyltrimethylsilane (1.47 g, 15.0 mmol), ethylmagnesium bromide (1 M in THF, 15 mL), and THF (5.0 mL)), FeBr₂ (216 mg, 1.0 mmol), and NMP (40 mL). The crude product was purified by flash chromatography using hexanes and then hexanes/EtOAc (20:1) as eluents to afford tert-butyl 4-((trimethylsilyl)ethynyl)piperidine-1-carboxylate (2o) as pale-brown oil (2.62 g, 9.31 mmol, 93%). Spectral and analytical data were identical to those reported for the same compound above based on 1.0 mmol scale.

Mechanistic Studies on Iron-Catalyzed Cross-Coupling of Non-activated Alkyl Halides with Alkynyl Grignard Reagents

(A) Reaction with Enantioenriched (3-Iodobutyl)benzene (General Procedure I). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stirrer bar was charged with FeBr₂ (98% purity, 0.10 equiv), enantioenriched (3-iodobutyl)benzene (1.0 equiv), and NMP solvent, followed by the addition of 7-((tetrahydro-2H-pyran-2-yl)oxy)hept-1-yn-1-yl)magnesium bromide (0.5 M in THF, 1.5 equiv). The reaction mixture was stirred at room temperature for 16 h to form a deep brown solution. After the reaction, the crude product was washed with EtOAc (10 mL) and water (30 mL). The aqueous fraction was further washed with EtOAc (2 x 10 mL). The combined organic fractions were concentrated in vacuo with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography with silica gel using hexanes and then hexanes/EtOAc (10:1) as eluents to afford the isolated substituted alkyne product, 2-((8-methyl-10-phenyldec-6-yn-1-yl)oxy)tetrahydro-2H-pyran (3f).

(i) Reaction of (R)-(3-iodobutyl)benzene ((R):(S) = 79:21) (S16). Following the general procedure I, the title compound was prepared using (R)-(3-iodobutyl)benzene ((R):(S) = 79:21) (S16) (130 mg, 0.50
mmol), (7-((tetrahydro-2H-pyran-2-yl)oxy)hept-1-yn-1-yl)magnesium bromide (0.5 M in THF, 0.75 mmol, 1.5 mL), FeBr₂ (11 mg, 0.05 mmol), and NMP (2.0 mL). A racemic mixture of 2-((8-methyl-10-phenyldec-6-yn-1-yl)oxy)tetrahydro-2H-pyran (3f) ((R):(S) = 50:50) was obtained as pale-yellow oil (140 mg, 0.43 mmol, 85%). The HPLC separation of the racemic product 3f was shown below and was shown to be similar to that from the reaction of (R)/(S)-(3-iodobutyl)benzene (Scheme 2, 3f).

(ii) Reaction of (R)-(3-iodobutyl)benzene ((R):(S) = 98:2) (S17). Following the general procedure I, the title compound was prepared using (R)-(3-iodobutyl)benzene ((R):(S) = 98:2) (S17) (80 mg, 0.30 mmol), (7-((tetrahydro-2H-pyran-2-yl)oxy)hept-1-yn-1-yl)magnesium bromide (0.5 M in THF, 0.45 mmol, 0.90 mL), FeBr₂ (6.5 mg, 0.03 mmol), and NMP (1.2 mL). A racemic mixture of 2-((8-methyl-10-phenyldec-6-yn-1-yl)oxy)tetrahydro-2H-pyran (3f) ((R):(S) = 50:50) was obtained as pale-yellow oil (48 mg, 0.15 mmol, 49%). The HPLC separation of the racemic product 3f was shown below and was shown to be similar to that from the reaction of (R)/(S)-(3-iodobutyl)benzene (Scheme 2, 3f).
HPLC separation of product 2-((8-methyl-10-phenyldec-6-yn-1-yl)oxy)tetrahydro-2H-pyranyl from enantio-enriched (R)-(3-iodobutyl)benzene ((R) : (S) = 98 : 2)

![HPLC separation graph](image)

3f (racemic product): (R) : (S) = 50 : 50

(B) Reaction with Radical Clock Substrate. Following the general procedure G, the title compound was prepared using cyclopropylmethyl bromide (135 mg, 1.0 mmol) and oct-1-yn-1-ylmagnesium bromide (0.5 M in THF, 1.5 mmol, 3.0 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford dodec-1-en-5-yne (4l) as pale-brown oil (41 mg, 0.25 mmol, 25%).

Dodec-1-en-5-yne (4l).[^1] \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 5.91-5.81 (m, 1 H), 5.07 (d, \(J = 17.4\) Hz, 1 H), 5.01 (d, \(J = 10.2\) Hz, 1 H), 2.26-2.21 (ovrlp, 4 H), 2.14 (t, \(J = 6.0\) Hz, 2 H), 1.47 (qu, \(J = 6.8\) Hz, 2 H), 1.41-1.24 (ovrlp, 6 H), 0.89 (t, \(J = 6.7\) Hz, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 137.4, 115.5, 80.9, 79.5, 33.6, 31.5, 29.2, 28.7, 22.7, 18.9, 18.8, 14.2.

[^1]: Reference or citation
References:


NMR Spectra

List of Spectra of Compounds

<table>
<thead>
<tr>
<th>¹H and ¹³C NMR Spectra</th>
<th>Page no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting Materials – Alkyl Halides and Terminal Alkynes (S1-S23)</td>
<td>S55</td>
</tr>
<tr>
<td>Substituted Alkyne Products from Six-Membered Cyclic Alkyl Halides (2a-2y)</td>
<td>S77</td>
</tr>
<tr>
<td>Substituted Alkyne Products from Cyclic and Acyclic Alkyl Halides (3a-3u)</td>
<td>S102</td>
</tr>
<tr>
<td>Substituted Alkyne Products from Secondary Alkyl Halides</td>
<td></td>
</tr>
<tr>
<td>(Supplementary Results) (P1-P9)</td>
<td>S124</td>
</tr>
<tr>
<td>Substituted Alkyne Products from Primary Alkyl Halides (4a-4l)</td>
<td>S133</td>
</tr>
</tbody>
</table>
$^1$H and $^{13}$C NMR of 1-Iodo-3-methylcyclohexane (S1)

d.r. of diastereoisomers:
1,3-trans (major) : 1,3-cis (minor) = 0.77 : 0.12 = 6.4 : 1
$^1$H and $^{13}$C NMR of 1-Iodo-4-methylcyclohexane (S2)

d.r. of diastereoisomers:
1,4-cis (major) : 1,4-trans (minor) = 0.72 : 0.07 = 10.3 : 1
$^1$H and $^{13}$C NMR of 1-(tert-Butyl)-4-iodocylohexane (S3)

d.r. of diastereoisomers:
1,4-cis (major) : 1,4-trans (minor)
= 0.77 : 0.05 = 15.4 : 1
$^1$H and $^{13}$C NMR of 2-Iodobicyclo[2.2.1]heptane (S4)

d.r. of diastereoisomers:
exo-isomer (major) : endo-isomer (endo)
$= 0.81 : 0.19 = 4.3 : 1$
$^1$H and $^{13}$C NMR of 1,4-Diiodocyclohexane (S5)

d.r. of diastereoisomers = 2.8 : 1 (by GC)
$^1$H and $^{13}$C NMR of (2-Iodopropyl)benzene (S6)
$^1$H and $^{13}$C NMR of 2-Iodononane (S7)
$^1$H and $^{13}$C NMR of 4-Iodo-2-phenyltetrahydro-2$H$-pyran (S8)

![NMR spectrum of S8](image1)

d.r. of diastereoisomers:
1,3-cis (major) : 1,3-trans (minor) = 0.94 : 0.06 = 15.7 : 1

![NMR spectrum of S8](image2)
$^1$H and $^{13}$C NMR of 4-Iodo-2-(4-methoxyphenyl)tetrahydro-2$H$-pyran (S9)

d.r. of diastereoisomers:
1,3-cis (major) : 1,3-trans (minor) = 0.75 : 0.25 = 3.0 : 1
$^1$H and $^{13}$C NMR of 2-(4-Fluorophenyl)-4-iodotetrahydro-$2H$-pyran (S10)

d.r. of diastereoisomers:
1,3-cis (major) : 1,3-trans (minor)
= 0.91 : 0.09 = 10.1 : 1
$^1$H and $^{13}$C NMR of 4-Iodo-2-(4-(trifluoromethyl)phenyl)tetrahydro-2H-pyran (S11)

d.r. of diastereoisomers:
1,3-cis (major) : 1,3-trans (minor) = 1.57 : 0.47 = 3.3 : 1

H(C4) overlaps with H(C2)
$^1$H and $^{13}$C NMR of Benzyl 3-iodoazetidine-1-carboxylate (S12)
$^1$H and $^{13}$C NMR of Ethyl 3-iodobutanoate (S13)
$^1$H and $^{13}$C NMR of 9-(3-Iodopropyl)-9H-carbazole (S14)
$^1$H and $^{13}$C NMR of 1-(3-Iodopropyl)-1H-indole (S15)

\[ \text{S15} \]

[Diagram of 1-(3-Iodopropyl)-1H-indole]

[Chemical shift spectra for $^1$H and $^{13}$C NMR]
$^1$H and $^{13}$C NMR of 1-Bromo-4-(hex-5-yn-1-yloxy)benzene (S18)
$^1$H and $^{13}$C NMR of 1-Chloro-4-(hex-5-yn-1-yl)oxy)benzene (S19)
$^1$H and $^{13}$C NMR of Methyl(4-(pent-4-yn-1-yl oxy)phenyl)sulfane (S20)
$^1$H and $^{13}$C NMR of 1-(2-Iodopropyl)-4-methoxybenzene (S21)
$^1$H and $^{13}$C NMR of 4-(2-Iodopropyl)-1,2-dimethoxybenzene (S22)
$^1$H and $^{13}$C NMR of N-(2-iodopropyl)-N-methylaniline (S23)


$^1$H and $^{13}$C NMR of Ethyl (2-Bromopropyl)(2-methoxyphenyl)carbamate (S24)

[Chemical structure and NMR spectra image]

S76
$^1$H and $^{13}$C NMR of 1-(Cyclohexylethynyl)-4-methoxybenzene (2a)
$^1$H and $^{13}$C NMR of (4-(Cyclohexylethynyl)phenyl)(methyl)sulfane (2b)
$^1$H and $^{13}$C NMR of (Cyclohexylethynyl)trimethylsilane (2c)
$^1$H and $^{13}$C NMR of 2-((7-Cyclohexylhept-6-yn-1-yl)oxy)tetrahydro-2H-pyran (2d)
$^1$H and $^{13}$C NMR of 9-(6-Cyclohexylhex-5-yn-1-yl)-9H-carbazole (2e)
$^1$H and $^{13}$C NMR of ((3-Methylcyclohexyl)ethynyl)benzene (2f)

d.r. of diastereoisomers:
1,3-cis (major) : 1,3-trans (minor) = 0.90 : 0.10 = 9.0 : 1
$^1$H and $^{13}$C NMR of 4-(6-(4-Methycyclohexyl)hex-5-yn-1-yl)morpholine (2g)

d.r. of diastereoisomers difficult to be determined by $^1$H NMR;
d.r. = 1.9 : 1 (by GCMS)
$^1$H and $^{13}$C NMR of 1-(tert-Butyl)-4-((4-(tert-butyl)cyclohexyl)ethynyl)benzene (2h)

d.r. of diastereoisomers:
1,4-trans (major) : 1,4-cis (minor)
= 0.92 : 0.01 = 92 : 1 (> 50 : 1)
$^1$H and $^{13}$C NMR of 2-(Dec-1-yn-1-yl)bicyclo[2.2.1]heptane (2i)

d.r. of diastereoisomers: difficult to be determined by $^1$H NMR due to overlapping of H signals
$^1$H and $^{13}$C NMR of ((Bicyclo[2.2.1]heptan-2-yl)ethynyl)triethylsilane (2j)

\[ \text{d.r. of diastereoisomers:} \sim [(2.43-1.0)/2] : 0.26 \sim 0.72 : 0.26 \sim 2.8 : 1 \]
$\text{H and } ^{13}\text{C NMR of Ethyl 3-((4-(tert-butyl)phenyl)ethynyl)cyclohexane-1-carboxylate (2k)}$

\[
\text{EtO}_2\text{C} \quad \begin{array}{c}
\text{EtO}_2\text{C} \\
\text{tBu}
\end{array}
\]

d.r. of diastereoisomers:
1,3-cis (major) : 1,3-trans (minor)
= 0.78 : 0.12 = 6.5 : 1.
$^1$H and $^{13}$C NMR of Ethyl 3-(6-(4-chlorophenoxy)hex-1-yn-1-yl)cyclohexane-1-carboxylate (2l)

d.r. of diastereoisomers difficult to be determined by $^1$H NMR.
d.r. of diastereoisomers = 1.9 : 1 (determined by GCMS)
$^1$H and $^{13}$C NMR of 1,4-Di(hex-1-yn-1-yl)cyclohexane (2m)

\[
\text{d.r. of stereoisomers = 2.2 : 1 (by GCMS)}
\]
\(^1\)H and \(^{13}\)C NMR of tert-Butyl 4-(cyclohex-1-en-1-ylythynyl)piperidine-1-carboxylate (2n)

BocN

BocN
$^1$H and $^{13}$C NMR of tert-Butyl 4-((trimethylsilyl)ethynyl)piperidine-1-carboxylate (2o)
§H and \textsuperscript{13}C NMR of \(N,N\)-diethyl-4-\((\text{tetrahydro-2H-pyran-4-yl})\text{ethynyl}\)benzamide (2p)
$^{1}$H and $^{13}$C NMR of 4-(6-(4-bromophenoxy)hex-1-yn-1-yl)tetrahydro-2$H$-pyran (2q)
$^1$H and $^{13}$C NMR of 4-(Cyclohex-1-en-1-ylethynyl)tetrahydro-2H-pyran (2r)
$^1$H and $^{13}$C NMR of Trimethyl((tetrahydro-2H-pyran-4-yl)ethynyl)silane (2s)
$^1$H and $^{13}$C NMR of triisopropyl((tetrahydro-2H-pyran-4-yl)ethynyl)silane (2t)
$^1$H and $^{13}$C NMR of Triisopropyl((2-phenyltetrahydro-2H-pyran-4-yl)ethynyl)silane (2u)

D.r. of stereoisomers:
1,3-cis (major) : 1,3-trans (minor) = 96 : 4 = 24.0 : 1

1,3-cis isomer

1,3-trans isomer
$^1$H and $^{13}$C NMR of Triethyl(2-(4-methoxyphenyl)tetrahydro-2H-pyran-4-yl)ethynyl)silane (2v)

d.r. of sereoisomers:
1,3-trans (major) : 1,3-cis (minor) = 0.85 : 0.9 = 9.4 : 1.
$^1$H and $^{13}$C NMR of Triethyl((2-(4-fluorophenyl)tetrahydro-2$H$-pyran-4-yl)ethynyl)silane (2w)

d.r. of stereoisomers:
1,3-cis (major) : 1,3-trans (cis) = 0.82 : 0.09 = 9.1 : 1.
$^1$H and $^{13}$C NMR of Triisopropyl((2-(4-(trifluoromethyl)phenyl)tetrahydro-2H-pyran-4-yl)ethynyl)silane (2x)

d.r. of diastereoisomers:
1,3-cis (major) : 1,3-trans (minor) = 0.94 : 0.06 = 15.7 : 1.
$^1$H and $^{13}$C NMR of 2-((7-((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)hept-6-yn-1-yl)oxy)tetrahydro-2$^H$-pyran (2y)
$^1$H and $^{13}$C NMR of Benzyl 3-((triisopropylsilyl)ethynyl)azetidine-1-carboxylate (3a)
$^1$H and $^{13}$C NMR of (Cyclopentylethynyl)cyclohexane (3b)
$^1$H and $^{13}$C NMR of 2-(Dec-1-yn-1-yl)-2,3-dihydro-1H-indene (3c)
$^1$H and $^{13}$C NMR of Dec-1-yn-1-ylcycloheptane (3d)
$^1$H and $^{13}$C NMR of (3,3-Dimethylbut-1-yn-1-yl)cyclooctane (3e)
$^1$H and $^{13}$C NMR of 2-((8-Methyl-10-phenyldec-6-yn-1-yl)oxy)tetrahydro-2$H$-pyran (3f)
$^{1}$H and $^{13}$C NMR of (3,6,6-Trimethylhept-4-yn-1-yl)benzene (3g)
$^1$H and $^{13}$C NMR of Triisopropyl(3-methyl-5-phenylpent-1-yn-1-yl)silane (3h)
$^1$H and $^{13}$C NMR of 2,2,5-Trimethyldodec-3-yne (3i)
$^1$H and $^{13}$C NMR of Ethyl 3,6,6-trimethylhept-4-ynoate (3j)
$\text{H and }^{13}\text{C NMR of } N\text{-methyl-}N\text{-}(2,5,5\text{-trimethylhex-3-yn-1-yl})\text{aniline (3k)}$
$^1$H and $^{13}$C NMR of Ethyl (2-Methoxyphenyl)(2-methyl-4-(triisopropylsilyl)but-3-yn-1-yl)carbamate (3l)
$^1$H and $^{13}$C NMR of 2,6,9,9-Tetramethyldec-2-en-7-yne (3m)
$^1$H and $^{13}$C NMR of 1-(tert-Butyl)-4-(3-methyl-4-phenylbut-1-yn-1-yl)benzene (3n)
$^1$H and $^{13}$C NMR of N,N-dimethyl-4-(3-methyl-4-phenylbut-1-yn-1-yl)aniline (3o)
$^{1}H$ and $^{13}C$ NMR of 4-(4-(4-methoxyphenyl)-3-methylbut-1-yn-1-yl)-$N,N$-dimethylaniline (3p)
$^1$H and $^{13}$C NMR of Triethyl(4-(4-methoxyphenyl)-3-methylbut-1-yn-1-yl)silane (3q)
$^1$H and $^{13}$C NMR of 4-(4-(3,4-dimethoxyphenyl)-3-methylbut-1-yn-1-yl)-$N,N$-dimethylaniline (3r)
$^1$H and $^{13}$C NMR of (2-Ethyl-5,5-dimethylhex-3-yn-1-yl)benzene (3s)
$^1$H and $^{13}$C NMR of 5-Ethyl-2,2-dimethylundec-3-yne (3t)
$^1$H and $^{13}$C NMR of 5-Ethyl-8,8-dimethylnon-1-en-6-yne (3u)
${}^1$H and ${}^{13}$C NMR of 5-Butyl-2,2-dimethylnon-3-yne (3v)
$^1$H and $^{13}$C NMR of 2-(Cyclohexylethynyl)-5-methylthiophene (P1)
$^1$H and $^{13}$C NMR of 4-((5-Methylthiophen-2-yl)ethynyl)tetrahydro-2H-pyran (P2)
$^1$H and $^{13}$C NMR of 1-Chloro-4-((4-methylcyclohexyl)ethynyl)benzene (P3)

d.r. of stereoisomers:
1,4-trans (major) : 1,4-cis (minor) = 0.80 : 0.08 = 10.0 : 1.
$^1$H and $^{13}$C NMR of 1-((4-(tert-Butyl)cyclohexyl)ethynyl)-4-fluorobenzene (P4)

d.r. of diastereoisomers:
1,4-trans (major) : 1,4-cis (minor) = 0.98 : 0.02 = 49.0 : 1.
$^1$H and $^{13}$C NMR of 4-(5-(4-(Methylthio)phenoxy)pent-1-yn-1-yl)tetrahydro-2H-pyran (P5)
$^1$H and $^{13}$C NMR of Methyl(4-(3-methylpent-1-yn-1-yl)phenyl)sulfane (P6)
$^1$H and $^{13}$C NMR of 1-(tert-Butyl)-4-(3,7-dimethyloct-6-en-1-yn-1-yl)benzene (P7)
$^1$H and $^{13}$C NMR of Trimethyl(3-methyl-5-phenylpent-1-yn-1-yl)silane (P8)
$^1$H and $^{13}$C NMR of 2-((9-(3,4-dimethoxyphenyl)-8-methylnon-6-yn-1-yl)oxy)tetrahydro-2H-pyran (P9)
$^1$H and $^{13}$C NMR of 1-(tert-Butyl)-4-(5-chloropent-1-yn-1-yl)benzene (4a)
$^1$H and $^{13}$C NMR of (6-Chlorohex-1-yn-1-yl)triethylsilane (4b)
$^1$H and $^{13}$C NMR of (8-chlorooct-1-yn-1-yl)cyclohexane (4c)
$^1$H and $^{13}$C NMR of 9-(non-4-yn-1-yl)-9H-carbazole (4d)
$^1$H and $^{13}$C NMR of 9-(5-Cyclopropylpent-4-yn-1-yl)-9H-carbazole (4e)
$^1$H and $^{13}$C NMR of 9-(5-(Cyclohex-1-en-1-yl)pent-4-yn-1-yl)-9H-carbazole (4f)
$^1$H and $^{13}$C NMR of 9-(5-(Trimethylsilyl)pent-4-yn-1-yl)-9H-carbazole (4g)
$^1$H and $^{13}$C NMR of 1-(6,6-Dimethylhept-4-yn-1-yl)-1H-indole (4h)
$^1$H and $^{13}$C NMR of 2,2-Dimethyltetradec-3-yne (4i)
$^1$H and $^{13}$C NMR of Triisopropyl(6-phenoxyhex-1-yn-1-yl)silane (4j)
$^1$H and $^{13}$C NMR of 8,8-Dimethylnon-6-yn-1-yl acetate (4k)
$^1$H and $^{13}$C NMR of Dodec-1-en-5-yne (4l)