

Highly regio- and chemoselective [2 +2 +2] cycloaddition of  
1,6-heptadiynes with allenes catalyzed by cobalt complexes

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**Supporting Information**

**General procedure for the [2 + 2 +2] cycloaddition of 1,6-heptadiynes with allenes:** CoI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (42 mg, 0.05 mmol) and Zn (180 mg, 2.75 mmol) were placed in a screw-capped vessel. The vial was sealed with septum and flushed several times with nitrogen. Diyne (1.00 mmol), allene (1.3 mmol), and 1,2-dichloroethane (2.00 mL) were injected into the reaction mixture via a syringe. The septum was removed, and the vial was sealed with a screw cap quickly under nitrogen. The reaction mixture was stirred at 80 °C for 8 h. The crude reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, filtered through a thin Celite pad, and concentrated *in vacuo*. The residue was chromatographed on a silica gel column (hexane/EtOAc = 9/1) to give pure product.

Products **4a-l** and **6a-d** were obtained according to this procedure. Spectral data for compounds **4a-l** and **6a-d** are listed below.

**Dimethyl 5-(cyclohexylmethyl)-2,3-dihydro-1H-2,2-indenedicarboxylate 4a:** colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.05 (d, *J* = 8.0 Hz, 1H) 6.94 (s, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 3.72 (s, 6H), 3.54 (s, 4H), 2.40 (d, *J* = 7.0 Hz, 2H), 1.65 – 0.88 (m, 11H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 172.23, 140.23, 139.68, 136.95, 127.95, 124.89, 123.64, 60.37, 52.92, 43.93, 40.52, 40.25, 39.83, 33.14, 26.54, 26.28; HRMS calcd for C<sub>20</sub>H<sub>26</sub>O<sub>4</sub> 330.1831, found 330.1832.

**Dimethyl 5-(cyclopentylmethyl)-2,3-dihydro-1H-2,2-indenedicarboxylate 4b:** colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.06 (d, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 3.74 (s, 6H), 3.55 (s, 4H), 2.54 (d, *J* = 7.5 Hz, 2H), 2.03 (m, 1H), 1.70 – 1.18 (m, 8H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 172.20, 141.24, 139.75, 136.92, 127.55, 124.49, 123.73, 60.37, 52.88, 42.02, 41.87, 40.50, 40.23, 32.42, 24.85; HRMS calcd for C<sub>19</sub>H<sub>24</sub>O<sub>4</sub> 316.1675, found 316.1676.

**Dimethyl 5-pentyl-2,3-dihydro-1H-2,2-indenedicarboxylate 4c:** colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.07 (d, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 6.96 (d, *J* = 7.5 Hz,

1H), 3.73 (s, 6H), 3.55 (s, 4H), 2.53 (t,  $J = 8.0$  Hz, 2H), 1.60 – 1.55 (m, 2H), 1.32 – 1.27 (m, 4H), 0.88 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.18, 141.84, 139.85, 136.95, 127.16, 124.14, 123.84, 60.40, 52.90, 40.49, 40.23, 35.75, 31.52, 31.37, 22.51, 14.00; HRMS calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_4$  304.1675, found 304.1667.

**Dimethyl 5-(2,2-dimethylpropyl)-2,3-dihydro-1H-2,2-indenedicarboxylate 4d:** colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.05 (d,  $J = 7.5$  Hz, 1H), 6.92 (s, 1H), 6.90 (d,  $J = 8.0$  Hz, 1H), 3.72 (s, 6H), 3.56 (s, 4H), 2.42 (s, 2H), 0.88 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.26, 139.23, 138.56, 137.12, 129.26, 126.15, 123.23, 60.39, 52.92, 50.00, 40.55, 40.30, 31.65, 29.36; HRMS calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_4$  304.1675, found 304.1679.

**Dimethyl 5-benzyl-2,3-dihydro-1H-2,2-indenedicarboxylate 4e:** colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.97 – 7.29 (m, 8H), 3.91 (s, 2H), 3.75 (s, 6H), 3.53 (s, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.15, 141.19, 140.16, 140.00, 137.58, 128.90, 128.44, 127.73, 126.03, 124.68, 124.10, 60.37, 52.95, 42.97, 40.47, 40.23; HRMS calcd for  $\text{C}_{20}\text{H}_{20}\text{O}_4$  324.1362, found 324.1358.

**5-(Cyclohexylmethyl)-1,3-dihydroisobenzofuran 4f:** colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.11 (d,  $J = 7.5$  Hz, 1H), 7.01 (d,  $J = 9.0$  Hz, 1H), 6.99 (s, 1H), 5.07 (s, 4H), 2.47 (d,  $J = 7.0$  Hz, 2H), 1.64 – 0.88 (m, 11H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.62, 139.08, 136.34, 128.25, 121.53, 120.42, 73.49, 73.44, 43.92, 39.92, 33.10, 26.51, 26.28; HRMS calcd for  $\text{C}_{15}\text{H}_{20}\text{O}$  216.1514, found 216.1512.

**5-(Cyclohexylmethyl)-2,3-dihydro-1H-2-isoindolyl(4-methylphenyl)sulfone 4g:** colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.74 (d,  $J = 8.5$  Hz, 2H), 7.28 (d,  $J = 8.0$  Hz, 2H), 7.03 (d,  $J = 7.5$  Hz, 1H), 6.97 (d,  $J = 8.0$  Hz, 1H), 6.91 (s, 1H), 4.56 (s, 4H), 2.40 (d,  $J = 7.5$  Hz, 2H), 2.39 (s, 3H), 1.64 – 0.84 (m, 11H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.56, 141.21, 135.99, 133.74, 133.31, 129.76, 128.70, 127.60, 123.15,

122.10, 53.63, 53.50, 43.83, 39.81, 29.68, 26.44, 26.21, 21.47; HRMS calcd for  $C_{22}H_{27}NO_2S$  369.1762, found 369.1759.

**5-(2,2-Dimethylpropyl)-2,3-dihydro-1H-2-isoindolyl(4-methylphenyl)sulfone 4h:**

colorless oil;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.74 (d,  $J = 8.0$  Hz, 2H), 7.28 (d,  $J = 8.0$  Hz, 2H), 7.03 (d,  $J = 8.0$  Hz, 1H), 6.96 (d,  $J = 8.0$  Hz, 1H), 6.89 (s, 1H), 4.57 (s, 4H), 2.42 (s, 2H), 2.38 (s, 3H), 0.89 (s, 9H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  143.56, 139.50, 135.60, 133.77, 133.51, 129.96, 129.76, 127.61, 124.36, 121.70, 53.65, 53.51, 49.90, 31.65, 29.25, 21.48; HRMS calcd for  $C_{20}H_{25}NO_2S$  343.1606, found 343.1602.

**5-(Cyclohexylmethyl)-2,3-dihydro-1H-2,2-indenedicarbonitrile 4i:** colorless oil;

$^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.15 (d,  $J = 7.5$  Hz, 1H), 7.05 (d,  $J = 7.5$  Hz, 1H), 7.03 (s, 1H), 3.68 (s, 4H), 2.45 (d,  $J = 7.0$  Hz, 2H), 1.67 – 0.85 (m, 11H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  142.26, 136.12, 133.40, 129.59, 125.37, 124.28, 116.46, 44.67, 44.47, 43.83, 39.80, 33.06, 29.69, 26.45, 26.22; HRMS calcd for  $C_{18}H_{20}N_2$  264.1626, found 264.1624.

**5,5-Dimethyl-4'-(cyclohexylmethyl)spiro[hexane-1,3-dione-2,1'-indane] 4j:**

colorless oil;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.01 (d,  $J = 8.0$  Hz, 1H), 6.91 (s, 1H), 6.89 (d,  $J = 8.0$  Hz, 1H), 3.41 (s, 2H), 3.40 (s, 2H), 2.70 (d,  $J = 14.0$  Hz, 2H), 2.65 (d,  $J = 14.0$  Hz, 2H), 2.39 (d,  $J = 7.5$  Hz, 2H), 1.64 – 1.10 (m, 9H), 1.02 (s, 3H), 1.00 (s, 3H), 0.91 – 0.84 (m, 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  206.87, 140.53, 139.67, 136.59, 128.26, 125.15, 123.88, 71.71, 51.69, 44.17, 40.08, 38.96, 38.36, 33.38, 30.81, 28.77, 28.48, 26.80, 26.54; HRMS calcd for  $C_{23}H_{30}O_2$  338.2246, found 338.2244.

**5,5-Dimethyl-4'-butylspiro[hexane-1,3-dione-2,1'-indane] 4k:** colorless oil;

$^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.02 (d,  $J = 7.5$  Hz, 1H), 6.96 (s, 1H), 6.94 (d,  $J = 8.0$  Hz, 1H), 3.43 (s, 2H), 3.41 (s, 2H), 2.70 (d,  $J = 14.0$  Hz, 2H), 2.65 (d,  $J = 14.0$  Hz, 2H), 2.51 (t,  $J = 8.0$  Hz, 2H), 1.58 – 1.23 (m, 7H), 1.02 (s, 3H), 1.00 (s, 3H), 0.88 (t,  $J =$

6.8 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.61, 141.91, 139.60, 136.33, 127.24, 124.14, 123.83, 71.47, 51.43, 38.73, 38.09, 35.76, 31.52, 31.36, 30.57, 28.53, 28.22, 22.52, 14.01; HRMS calcd for  $\text{C}_{21}\text{H}_{28}\text{O}_2$  312.2089, found 312.2090.

**5-(Cyclohexylmethyl)-2,3-dihydro-1H-indene 4l:** colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.10 (d,  $J = 8.0$  Hz, 1H), 6.99 (s, 1H), 6.88 (d,  $J = 8.0$  Hz, 1H), 2.86 – 2.83 (m, 4H), 2.41 (d,  $J = 8.0$  Hz, 2H), 2.03 (m, 2H), 1.67 – 0.90 (m, 11H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.07, 141.31, 139.17, 126.96, 125.17, 123.79, 43.98, 39.95, 33.20, 32.79, 32.46, 26.58, 26.33, 25.48; HRMS calcd for  $\text{C}_{16}\text{H}_{22}$  214.1721, found 214.1728.

**Dimethyl 6-(cyclohexylmethyl)-4-(1,1,1-trimethylsilyl)-2,3-dihydro-1H-2,2-indenedicarboxylate 6a:** colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.02 (s, 1H), 6.95 (s, 1H), 3.72 (s, 6H), 3.57 (s, 2H), 3.53 (s, 2H), 2.40 (d,  $J = 7.0$  Hz, 2H), 1.67 – 0.89 (m, 11H), 0.27 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.22, 142.21, 139.35, 138.90, 134.74, 133.56, 125.77, 60.56, 52.91, 44.05, 41.18, 40.02, 39.78, 33.17, 26.56, 26.29, -0.82; HRMS calcd for  $\text{C}_{23}\text{H}_{34}\text{O}_4\text{Si}$  402.2226, found 402.2235.

**Dimethyl 6-pentyl-4-(1,1,1-trimethylsilyl)-2,3-dihydro-1H-2,2-indenedicarboxylate 6b:** colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.08 (s, 1H), 7.00 (s, 1H), 3.72 (s, 6H), 3.57 (s, 2H), 3.53 (s, 2H), 2.52 (t,  $J = 8.0$  Hz, 2H), 1.57 – 1.55 (m, 2H), 1.33 – 1.30 (m, 4H), 0.88 (t,  $J = 6.8$  Hz, 3H), 0.27 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.19, 142.28, 141.03, 139.13, 135.05, 132.75, 125.00, 60.62, 52.92, 41.17, 40.02, 35.89, 31.69, 31.47, 22.53, 14.03, -0.84; HRMS calcd for  $\text{C}_{21}\text{H}_{32}\text{O}_4\text{Si}$  376.2070, found 376.2070.

**6-(Cyclohexylmethyl)-1,3-dihydro-4-isobenzofuranyl(trimethyl)silane 6c:** colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.11 (s, 1H), 6.99 (s, 1H), 5.10 (s, 2H), 5.05 (s, 2H), 2.47 (d,  $J = 7.0$  Hz, 2H), 1.68 – 0.88 (m, 11H), 0.25 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.48, 139.73, 138.03, 133.85, 132.24, 122.23, 73.92, 73.11,

43.99, 39.90, 33.15, 26.54, 26.29, -0.92; HRMS calcd for C<sub>18</sub>H<sub>28</sub>OSi 288.1909, found 288.1906.

**6-(Cyclohexylmethyl)-4-phenyl-1,3-dihydroisobenzofuran 6d:** colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.43 – 7.31 (m, 5H), 7.08 (s, 1H), 6.98 (s, 1H), 5.12 (s, 2H), 5.16 (s, 2H), 2.52 (d, *J* = 7.5 Hz, 2H), 1.68 – 0.81 (m, 11H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 141.48, 140.33, 139.96, 135.49, 134.39, 128.61, 128.27, 127.82, 127.32, 120.52, 73.62, 73.36, 43.93, 39.94, 33.15, 26.51, 26.28; HRMS calcd for C<sub>21</sub>H<sub>24</sub>O 292.1827, found 292.1821.