**Cobalt-Catalyzed Carbocyclization of *o*-Iodobenzaldehydes and
o-Iodophenylketones with Alkynes**

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Supporting Information

Experimental Section

General Procedure: A round-bottom side-arm flask (25 mL) containing *o*-iodobenzaldehydes or *o*-iodophenylketones **1** (1.00 mmol), CoI₂(dppe) (0.050 mmol, 5.0 mol%) and zinc powder (2.75 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled CH₃CN (3.0 mL) and an alkyne (1.50 mmol) were added to the system and the reaction mixture was stirred at 80 °C for 3 h. The reaction mixture was cooled to room temperature, diluted with dichloromethane and then stirred in the air for 15 min. The mixture was filtered through a short Celite and silica gel pad and washed with dichloromethane several times. The filtrate was concentrated and the residue was purified on a silica gel column using hexane-ethyl acetate as eluent to afford the cyclization products **3**. Compounds **3a-s** were synthesized according this procedure and the spectral data of these compounds are as follows.

2,3-Diphenyl-1H-inden-1-ol (3a): ¹H NMR (400 MHz, CDCl₃): δ = 1.99 (d, *J* = 8.8 Hz, 1H), 5.68 (d, *J* = 8.8 Hz, 1H), 7.28~7.45 (m, 13H), 7.65 (dd, *J* = 6.8 Hz, *J* = 0.8 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 77.30, 120.62, 123.67, 126.31, 127.28, 127.76, 128.25, 128.65, 128.77, 129.03, 129.20, 133.99, 134.68, 139.64, 143.72, 143.81, 144.21; HRMS calcd for C₂₁H₁₆O 284.1201, found 284.1211.

6,7-Diphenyl-5H-indeno[5,6-d][1,3]dioxol-5-ol (3b): ¹H NMR (400 MHz, CDCl₃): δ = 1.84 (d, *J* = 8.8 Hz, 1H), 5.56 (d, *J* = 8.8 Hz, 1H), 5.96 (d, *J* = 8.4 Hz, 2H), 6.64 (s, 1H), 7.19~7.42 (m, 11H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 76.72, 101.24,

102.11, 105.53, 127.03, 127.86, 128.28, 128.88, 128.92, 128.96, 133.98, 134.73, 138.06, 138.27, 139.26, 142.80, 146.65, 148.07; HRMS calcd for C₂₂H₁₆O₃ 328.1099, found 328.1082

5-*tert*-Butyl-2,3-diphenyl-1H-inden-1-ol (3c): ¹H NMR (400 MHz, CDCl₃): δ = 1.35 (s, 9H), 1.99 (d, *J* = 7.2 Hz, 1H), 5.67 (d, *J* = 7.2 Hz, 1H), 7.22~7.47 (m, 12H), 7.61 (d, *J* = 7.6 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 31.45, 34.87, 76.93, 117.67, 123.26, 127.15, 127.70, 128.02, 128.21, 128.79, 129.08, 129.18, 134.15, 134.80, 139.87, 141.46, 143.71, 144.09, 152.10; HRMS calcd for C₂₅H₂₄O 340.1827, found 340.1836

2,3-Dipropyl-1H-inden-1-ol (3d): ¹H NMR (400 MHz, CDCl₃): δ = 0.98~1.02 (m, 6H), 1.53~1.91 (m, 4H), 1.91 (br, 1H), 2.37~2.45 (m, 4H), 4.94 (s, 1H), 7.10~7.17 (m, 2H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 14.27, 21.74, 22.76, 27.19, 27.65, 76.83, 118.57, 123.02, 124.82, 128.13, 137.66, 144.13, 144.96, 145.14; HRMS calcd for C₁₅H₂₀O 216.1514, found 216.1518.

3-Butyl-2-phenyl-1H-inden-1-ol (3e): ¹H NMR (400 MHz, CDCl₃): δ = 0.95 (t, *J* = 7.2 Hz, 3H), 1.41~1.73 (m, 4H), 1.85 (br, 1H), 2.65 (t, *J* = 8.0 Hz, 2H), 5.49 (s, 1H),

7.24~7.56 (m, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 13.81, 23.00, 25.71, 30.75, 77.47, 119.63, 123.37, 125.90, 127.12, 127.96, 128.50, 128.76, 135.03, 140.07, 1443.19, 143.71, 144.51; HRMS calcd for $\text{C}_{19}\text{H}_{20}\text{O}$ 264.1514, found 264.1502.

2-Butyl-3-phenyl-1H-inden-1-ol (3e'): ^1H NMR (400 MHz, CDCl_3): δ = 0.86 (t, J = 8.0 Hz, 3H), 1.25-1.65 (m, 4H), 1.75 (d, J = 9.2 Hz, 1H), 2.46 (t, J = 8.4 Hz, 2H), 5.13 (d, J = 9.2 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 7.17~7.47 (m, 7H), 7.53 (d, J = 7.2 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 13.84, 22.81, 25.75, 31.86, 77.32, 119.70, 123.38, 125.34, 127.44, 128.38, 128.45, 128.74, 134.50, 138.56, 143.95, 144.61, 147.26; HRMS calcd for $\text{C}_{19}\text{H}_{20}\text{O}$ 264.1514, found 264.1525.

2-Methyl-3-trimethylsilyl-1H-inden-1-ol (3f): ^1H NMR (400 MHz, CDCl_3): δ = 0.36 (s, 9H), 1.87 (d, J = 9.6 Hz, 1H), 2.14 (s, 3H), 4.75 (d, J = 9.6 Hz, 1H), 7.11 (td, J = 7.2 Hz, J = 1.2 Hz, 1H), 7.21~7.30 (m, 2H), 7.45 (d, J = 7.2 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 0.33, 14.19, 80.87, 121.49, 123.17, 124.42, 128.30, 135.57, 144.79, 146.87, 157.69; HRMS calcd for $\text{C}_{13}\text{H}_{18}\text{OSi}$ 218.1127, found 218.1131

2-Phenyl-3-trimethylsilyl-1H-inden-1-ol (3g): ^1H NMR (400 MHz, CDCl_3): δ = 0.13 (s, 9H), 1.92 (br, 1H), 5.35 (s, 1H), 7.23 (td, J = 3.6 Hz, J = 0.8 Hz, 1H), 7.31~7.46 (m, 7H), 7.56 (d, J = 7.2 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 0.21, 80.71, 122.63, 123.60, 125.37, 127.87, 127.98, 128.47, 129.29, 137.22, 139.12,

144.68, 146.45, 161.10; HRMS calcd for C₁₈H₂₀OSi 280.1283, found 280.1278.

5-tert-Butyl-2-phenyl-3-trimethylsilyl-1H-inden-1-ol (3h): ¹H NMR (400 MHz, CDCl₃): δ = 0.20 (s, 9H), 1.44 (s, 9H), 1.95 (d, *J* = 7.6 Hz, 1H), 5.36 (d, *J* = 7.6 Hz, 1H), 7.33~7.57 (m, 8H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 0.28, 31.51, 34.78, 80.43, 119.90, 122.19, 123.11, 127.75, 127.90, 129.25, 137.38, 139.16, 141.75, 146.47, 151.66, 161.31; HRMS calcd for C₂₂H₂₈OSi 336.1909, found 336.1900.

1-Methyl-2,3-diphenyl-1H-indenol (3i): ¹H NMR (400 MHz, CDCl₃): δ = 1.58 (s, 3H), 1.98 (s, 1H), 7.21~7.33 (m, 13H), 7.51 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 23.9, 83.2, 120.7, 121.8, 126.5, 127.2, 127.5, 127.9, 128.4, 128.4, 129.2, 129.4, 134.6, 134.6, 138.6, 142.1, 146.9, 149.4; HRMS calcd for C₂₂H₁₈O 298.1358, found 298.1357.

2,3-Dipropyl-1H-inden-1-ol (3j): ¹H NMR (400 MHz, CDCl₃): δ = (q, *J*=7.2 Hz, 6H), 1.50 (s, 3H), 1.52~1.71 (m, 4H), 1.80 (s, 1H), 2.24~2.40 (m, AB type, 2H), 2.44 (t, *J*=7.2 Hz, 2H), 7.13~7.17 (m, 2H), 7.25 (t, *J*=7.2 Hz, 1H), 7.37 (d, *J*=6.4 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 14.29, 14.74, 21.68, 22.19, 23.49, 27.10, 27.37, 82.42, 118.68, 121.17, 125.06, 127.99, 136.32, 142.85, 147.87, 149.45; HRMS calcd

for C₁₆H₂₂O 230.1671, found 230.1665.

3-Butyl-1-methyl-2-phenyl-1H-indenol (3k): ¹H NMR (400 MHz, CDCl₃): δ = 0.85 (t, *J* = 7.6 Hz, 3H), 1.32 (q, *J* = 6.4 Hz, 2H), 1.43 (s, 3H), 1.51 (m, 2H), 1.92 (s, 1H), 2.47 (t, *J* = 8 Hz, 2H), 7.22~7.46 (m, 9H); ¹³C{¹H} NMR (400 MHz, CDCl₃): δ = 13.8, 22.8, 23.6, 25.5, 30.7, 82.8, 119.7, 121.5, 126.1, 127.2, 128.1, 128.3, 129.0, 135.3, 138.6, 142.4, 146.9, 149.3; HRMS calcd for C₂₀H₂₂O 278.1671, found 278.1665.

2-Butyl-1-methyl-3-phenyl-1H-indenol (3k'): ¹H NMR (400 MHz, CDCl₃): δ = 0.79 (t, *J* = 6.0 Hz, 3H), 1.23 (q, *J* = 7.2 Hz, 2H), 1.46~1.59 (m, 2H), 1.60 (s, 3H), 2.28 (m, 1H), 2.39 (m, 1H), 6.99 (dd, *J* = 6.8 Hz, *J* = 6.8 Hz, 1H), 7.16 (m, 2H), 7.33 (m, 2H), 7.43 (t, *J* = 5.6 Hz, 4H).

1,2-Dimethyl-3-(1,1,1-trimethylsilyl)-1H-indenol (3l): ¹H NMR (400 MHz, CDCl₃): δ = 0.32 (s, 9H), 1.42 (s, 3H), 1.49 (s, 1H), 2.02 (s, 3H), 7.10 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.19 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 0.4, 11.9, 23.2, 83.3, 121.6, 121.7, 124.5, 128.1, 133.0, 145.6, 149.2, 161.2; HRMS calcd for C₁₄H₂₀OSi 232.1283, found 232.1281.

1-Methyl-2-phenyl-3-trimethylsilanyl-1H-inden-1-ol(3m): δ = 0.03 (s, 9H), 1.42 (s, 3H), 1.83 (s, 1H), 7.20~7.58 (m, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 0.01, 23.78, 84.00, 122.15, 122.63, 125.67, 127.61, 127.86, 128.41, 129.43, 137.09, 137.72, 145.19, 148.90, 163.51; HRMS calcd for $\text{C}_{19}\text{H}_{22}\text{OSi}$ 194.1440, found 294.1435.

2,3-Diethyl-1-methyl-1H-indenol (3n): ^1H NMR (400 MHz, CDCl_3): δ = 1.16 (t, J = 8.0 Hz, 3H), 1.16 (t, J = 7.6 Hz, 3H), 1.47 (s, 3H), 2.28~2.47 (m, 4H), 7.11~7.14 (m, 2H), 7.24 (td, J = 7.2 Hz, J = 1.2 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 13.2, 14.7, 17.5, 18.3, 23.3, 82.5, 118.6, 121.2, 125.1, 128.1, 137.6, 142.6, 148.6, 149.4; HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}$ 202.1358, found 202.1359.

Ethyl 1-hydroxy-1-methyl-3-(1,1,1-trimethylsilyl)-1H-2-indenecarboxylate (3o): ^1H NMR (400 MHz, CDCl_3): δ = 0.38 (s, 9H), 1.38 (t, J = 7.2 Hz, 3H), 1.63 (s, 3H), 3.32 (brs, 1H), 4.26~4.40 (m, 2H), 7.24~7.32 (m, 2H), 7.47 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 0.86, 14.4, 25.6, 61.0, 83.1, 122.5, 125.3, 128.3, 128.7, 143.7, 150.0, 151.4, 152.8, 166.4; HRMS calcd for $\text{C}_{16}\text{H}_{22}\text{SiO}_3$ 290.1338, found 290.1334.

3-Hexyl-1-hydroxy-1-methyl-1H-indene-2-carboxylic acid methyl ester (3p): ^1H NMR (400 MHz, CDCl_3): δ = 0,87 (t, J = 7.2 Hz, 3H), 1.22~1.42 (m, 6H), 1.57-1.62 (m, 2H), 1.65 (s, 3H), 2.89 (q, J = 7.2 Hz, 2H), 3.43 (s, 1H), 3.86 (s, 3H), 7.32~7.40 (m, 3H), 7.50 (dd, J = 6 Hz, J = 1.2 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 14.29, 22.77, 26.00, 26.95, 29.12, 29.79, 31.81, 51.49, 81.72, 122.12, 122.44, 128.76, 129.48, 134.81, 140.75, 150.34, 155.96, 166.11; HRMS calcd for $\text{C}_{18}\text{H}_{24}\text{O}_3$ 288.1725, found 288.1716.

5-Methoxy-1-methyl-2,3-diphenyl-1H-1-indenol (3q): ^1H NMR (400 MHz, CDCl_3): δ = 1.55 (s, 3H), 1.96 (s, 1H), 3.77 (s, 3H), 6.76 (m, 2H), 7.20~7.39 (m, 8H), 7.40 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3): δ = 24.1, 55.5, 82.7, 107.5, 110.9, 122.4, 127.3, 127.5, 127.9, 128.5, 129.2, 129.3, 134.5, 134.7, 138.3, 141.6, 143.8, 148.2, 160.4; HRMS calcd for $\text{C}_{23}\text{H}_{20}\text{O}_2$ 328.1463, found 328.1466.

1-Butyl-5-methoxy-2,3-diphenyl-1H-1-indenol (3r): ^1H NMR (400 MHz, CDCl_3): δ = 0.63 (t, J = 7.6 Hz, 3H), 0.77~1.79 (m, 4H), 1.80 (td, J = 8 Hz, J = 4.4 Hz, 1H), 1.95 (s, 1H), 1.98 (td, J = 8 Hz, J = 4.4 Hz, 1H), 3.77 (s, 3H), 6.72 (m, 2H), 7.16-7.38

(m, 11H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 13.7, 22.6, 25.5, 36.6, 55.4, 85.7, 107.3, 110.8, 122.6, 127.2, 127.5, 127.8, 128.5, 129.2, 129.2, 134.6, 134.8, 139.6, 140.1, 144.7; HRMS calcd for $\text{C}_{26}\text{H}_{26}\text{O}_2$ 370.1933, found 370.1923.

5-Methoxy-1,2,3-triphenyl-1H-indenol (3s): ^1H NMR (400 MHz, CDCl_3): δ = 2.37 (s, 1H), 3.74 (s, 3H), 6.65 (dd, J = 8 Hz, J = 2.4 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 7.02 (m, 6H), 7.19~7.39 (m, 8H), 7.48 (d, J = 7.6 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 55.4, 86.3, 107.6, 111.4, 123.7, 124.9, 126.9, 127.2, 127.7, 128.7, 128.7, 129.1, 129.4, 133.8, 134.6, 140.1, 142.0, 143.0, 144.3, 148.7, 160.2; HRMS calcd for $\text{C}_{28}\text{H}_{22}\text{O}_2$ 390.1620, found 390.1622.

NOE Experiments: In the case of **3e**, the selective irradiation of H_e at δ 5.13 led to enhancement of the signals of H_b at δ 7.43 by 2.94%, hydroxyl proton at δ 1.85 by 5.39% and H_c at δ 7.35 by 8.48%. Similarly, the selective irradiation of H_d (methylene protons) at δ 2.46 caused an enhancement of the signals of H_a at δ 7.22 by 3.92% and H_c at δ 7.35 by 3.62%. The NOE results strongly support the proposed structure of product **3e**. The NOE experimental data for compound **3e**, **3f** and **3l** are shown below.

3e

3f

3l

Cc1c(C[Si](C)(C)C)c2ccccc12O **3f**

1.984
1.583
1.538