**Synthesis of Indenes by the Palladium-Catalyzed Carboannulation of
Internal Alkynes**

Daohua Zhang, Eul Kgun Yum, Zhijian Liu and Richard C. Larock*

*Department of Chemistry
Iowa State University, Ames, IA 50011*

SUPPLEMENTARY MATERIAL

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Experimental Section

Diethyl (2-iodophenyl)malonate (Compound 1).

Diethyl (2-iodophenyl)malonate was prepared in two steps from commercially available (2-iodophenyl)acetic acid. To a solution of (2-iodophenyl)acetic acid (1.00 g, 3.82 mmol) in 3 mL of ethanol was added 0.3 mL of concentrated sulfuric acid. The solution was then allowed to reflux for 3 h. The solution was poured into 8 mL of H₂O and extracted with 3 × 5 mL of ether. The ether extract was washed with 5 mL of H₂O, 5 mL of 5 % NaHCO₃, and 5 mL of brine, dried (Na₂SO₄) and filtered. The solvent was evaporated under reduced pressure, and the mixture was chromatographed using 4: 1 hexanes/EtOAc to afford ethyl (2-iodophenyl)acetate (1.45 g, 95 %) as a white solid: mp 125-126 °C; ¹H NMR (CDCl₃) δ 1.26 (t, *J* = 7.2 Hz, 3 H), 3.77 (s, 2 H), 4.17 (q, *J* = 7.2 Hz, 2 H), 6.94 (m, 1 H), 7.28 (m, 2 H), 7.82 (d, *J* = 8.0 Hz, 1 H).

To a solution of ethyl (2-iodophenyl)acetate (0.54 g, 1.9 mmol) in 10 mL of diethyl carbonate was added NaH (0.19 g, 8.0 mmol). The resulting mixture was then allowed to stir at room temperature for 12 h. The mixture was poured into 20 mL of satd NH₄Cl (aq) and extracted with 3 × 10 mL of CH₂Cl₂. The ether extract was dried (Na₂SO₄) and filtered. The solvent was evaporated under reduced pressure, and the mixture was chromatographed using 5:1 hexanes/EtOAc to afford diethyl (2-iodophenyl)malonate (0.59 g, 88%) as a yellow oil: ¹H NMR (CDCl₃) δ 1.27 (t, *J* = 7.2 Hz, 6 H), 4.24 (m, 4 H), 5.12 (s, 1 H), 7.00 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.36 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.47 (dd, *J* = 1.5, 7.5 Hz, 1 H), 7.86 (dd, *J* = 1.5, 7.5 Hz, 1 H); ¹³C NMR (CDCl₃) δ 14.3, 62.2, 62.4, 101.9, 128.8, 129.9, 130.0, 136.7, 139.8, 168.0; IR (CHCl₃, cm⁻¹) 2955, 2924, 1753, 1736, 1468; HRMS calcd for C₁₃H₁₅IO₄ 362.0015, found 362.0013.

Diethyl (2-iodo-4,5-dimethoxyphenyl)malonate (Compound 8).

Diethyl (2-iodo-4,5-dimethoxyphenyl)malonate (**8**) was prepared in two steps from commercially available 2-iodo-4,5-dimethoxyphenylacetic acid in the same manner as the preparation of diethyl (2-iodophenyl)malonate (**1**). Diethyl (2-iodo-4,5-dimethoxyphenyl)malonate was obtained in an 84% yield as a yellow oil: ¹H NMR (CDCl₃) δ 1.29 (t, *J* = 7.2 Hz, 6 H), 3.86 (s, 6 H), 4.24 (m, 4 H), 5.05 (s, 1 H), 7.06 (s, 1 H), 7.24 (s, 1 H);

^{13}C NMR (CDCl_3) δ 14.1, 56.0, 56.2, 89.8, 112.2, 121.4, 128.6, 149.4, 168.0; IR (CHCl_3 , cm^{-1}) 3055, 2937, 1749, 1733, 1029; HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{IO}_6$ 422.0226, found 422.0234.

Diethyl (2-bromophenyl)malonate (Compound 10).

Diethyl (2-bromophenyl)malonate (**10**) was prepared in two steps from commercially available 2-bromophenylacetic acid in the same manner as the preparation of diethyl (2-iodophenyl)malonate (**1**). Diethyl (2-bromophenyl)malonate was obtained as a yellow oil: ^1H NMR (CDCl_3) δ 1.25 (t, $J = 7.2$ Hz, 6 H), 4.24 (m, 4 H), 5.20 (s, 1 H), 7.16 (dt, $J = 1.5, 8.0$ Hz, 1 H), 7.31 (dt, $J = 1.5, 7.8$ Hz, 1 H), 7.46 (dd, $J = 1.4, 8.0$ Hz, 1 H), 7.62 (dd, $J = 1.5, 8.0$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 14.1, 57.3, 62.1, 125.2, 127.7, 129.7, 130.3, 132.9, 133.0, 167.7; IR (CHCl_3 , cm^{-1}) 3055, 2983, 1750, 1734, 1308; HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{BrO}_4$ 314.0154, found 314.0157.

Ethyl cyano(2-iodophenyl)acetate (Compound 11).

To a solution of (2-iodophenyl)acetonitrile (0.50 g, 2.1 mmol) in 10 mL of diethyl carbonate was added NaH (0.19 g, 8.0 mmol). The resulting mixture was then allowed to stir at room temperature for 12 h. The mixture was poured into 20 mL of satd NH_4Cl (aq) and extracted with 3×10 mL of CH_2Cl_2 . The ether extract was dried (Na_2SO_4) and filtered. The solvent was evaporated under reduced pressure, and the mixture was chromatographed using 3:1 hexanes/EtOAc to afford ethyl cyano(2-iodophenyl)acetate (0.54 g, 82%) as a yellow oil: ^1H NMR (CDCl_3) δ 1.31 (t, $J = 7.2$ Hz, 3 H), 4.30 (m, 2 H), 5.19 (s, 1 H), 7.10 (dt, $J = 1.5, 7.8$ Hz, 1 H), 7.44 (dt, $J = 1.2, 7.5$ Hz, 1 H), 7.60 (dd, $J = 1.5, 7.8$ Hz, 1 H), 7.90 (dd, $J = 1.2, 7.8$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 14.2, 48.3, 63.8, 100.0, 115.6, 129.5, 129.6, 131.1, 134.1, 140.4, 164.3; IR (CHCl_3 , cm^{-1}) 3070, 2957, 1743, 1466, 1217; HRMS calcd for $\text{C}_{11}\text{H}_{10}\text{INO}_2$ 314.9756, found 314.9760.

Ethyl (2-iodophenyl)(phenylsulfonyl)acetate (Compound 14).

Ethyl (2-iodophenyl)(phenylsulfonyl)acetate was prepared in two steps from commercially available 2-iodobenzyl bromide. 2-Iodobenzyl phenyl sulfone was prepared according to a modified literature procedure.¹ To a solution of 2-iodobenzyl bromide (0.59 g, 2.0 mmol) in DMF (4 mL) was added NaSO_2Ph (0.50 g, 3.0 mmol). The reaction mixture was stirred at 80 $^\circ\text{C}$

for 10 min, then poured into water and stirred vigorously for 30 min. The precipitate was filtered, washed with water and dried *in vacuo*. Recrystallization from 2:1 CH₂Cl₂/hexane afforded 2-iodobenzyl phenyl sulfone (0.45 g, 63%) as bright colorless needles: mp 131-132 °C; ¹H NMR (CDCl₃) δ 4.59 (s, 2 H), 7.00 (dt, *J* = 1.5, 7.8 Hz, 1 H), 7.44-7.53 (m, 3 H), 7.60-7.66 (m, 3 H), 7.73 (dd, *J* = 0.9, 7.8 Hz, 1 H). To a solution of 2-iodobenzyl phenyl sulfone (0.72 g, 2.0 mmol) in 10 mL of diethyl carbonate was added NaH (0.19 g, 8.0 mmol). The resulting mixture was then allowed to stir at room temperature for 12 h. The mixture was poured into 20 mL of satd NH₄Cl (aq) and extracted with 3 × 10 mL of CH₂Cl₂. The ether extract was dried (Na₂SO₄) and filtered. The solvent was evaporated under reduced pressure, and the mixture was chromatographed using 2:1 hexanes/EtOAc to afford ethyl (2-iodophenyl)(phenylsulfonyl)acetate (0.67 g, 78%) as a white solid: mp 118-119 °C; ¹H NMR (CDCl₃) δ 1.15 (t, *J* = 7.2 Hz, 3 H), 4.15 (m, 2 H), 5.73 (s, 1 H), 7.00 (dt, *J* = 1.6, 7.8 Hz, 1 H), 7.33 (t, *J* = 7.5 Hz, 1 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.58 (t, *J* = 7.2 Hz, 1 H), 7.65 (d, *J* = 7.6 Hz, 2 H), 7.71 (t, *J* = 8.0 Hz, 1 H), 7.97 (dd, *J* = 1.5, 7.8 Hz, 1 H); ¹³C NMR (CDCl₃) δ 14.0, 62.9, 103.8, 128.6, 129.1, 129.5, 131.1, 131.2, 134.5, 137.5, 140.0, 164.1; IR (CHCl₃, cm⁻¹) 3068, 2984, 1741, 1328, 1157; HRMS calcd for C₁₆H₁₅ISO₄ 329.9736, found 329.9742.

General procedure for the palladium-catalyzed carboannulation of alkynes.

Palladium acetate (0.0125 mmol), LiCl (Mallinckrodt, 0.25 mmol) or *n*-Bu₄NCl (Lancaster, 0.25 mmol), the appropriate base (0.50 mmol), the aryl halide (0.25 mmol), the alkyne (0.50-1.25 mmol), and DMF (5 ml) were added to a 2 dram vial equipped with a stirring bar and teflon-lined screwcap. After being heated for the appropriate time at 80 °C, the reaction mixture was diluted with diethyl ether and washed with satd NH₄Cl (aq) and water. The organic layer was dried over anhydrous MgSO₄, filtered, concentrated, and the product was purified by flash column chromatography using hexane/EtOAc as the eluent. The following compounds were prepared using this general procedure.

Diethyl 2-*tert*-butyl-3-methyl-1*H*-indene-1,1-dicarboxylate (Compound 2).

This compound was obtained as a pale yellow oil in 86% isolated yield from the reaction of diethyl 2-iodophenylmalonate (**1**) and 4,4-dimethyl-2-pentyne using *n*-Bu₄NCl and KOAc, and stirring for 48 h at 80 °C: ¹H NMR (CDCl₃) δ 1.16 (t, *J* = 7.2 Hz, 6 H), 1.36 (s, 9 H), 2.29 (s, 3 H), 4.13 (m, 4 H), 7.13 (dt, *J* = 1.2, 7.5 Hz, 1 H), 7.19 (d, *J* = 7.8 Hz, 1 H), 7.31 (dt, *J* = 1.6, 7.5 Hz, 1 H), 7.47 (dt, *J* = 0.6, 7.5 Hz, 1 H); ¹³C NMR (CDCl₃) δ 13.5, 14.1, 30.3, 34.4, 61.6, 70.9, 118.5, 122.3, 125.6, 128.5, 137.6, 140.7, 147.6, 149.1, 169.1; IR (CHCl₃, cm⁻¹) 2928, 2908, 1757, 1736, 1223, 1055; HRMS calcd for C₂₀H₂₆O₄ 330.1831, found 330.1835.

Diethyl 2,3-di-*n*-propyl-1*H*-indene-1,1-dicarboxylate (Compound 3).

This compound was obtained as a pale yellow oil in 72% isolated yield from the reaction of diethyl 2-iodophenylmalonate (**1**) and 4-octyne using KOAc and LiCl, and stirring for 48 h at 80 °C: ¹H NMR (CDCl₃) δ 0.98 (m, 6 H), 1.22 (t, *J* = 6.9 Hz, 6 H), 1.47 (m, 2 H), 1.63 (m, 2 H), 2.52 (t, *J* = 8.1 Hz, 4 H), 4.18 (m, 4 H), 7.14-7.28 (m, 3 H), 7.55 (d, *J* = 7.5 Hz, 1 H); ¹³C NMR (CDCl₃) δ 14.2, 14.3, 15.0, 21.9, 23.3, 28.0, 29.7, 61.9, 71.6, 119.3, 124.8, 125.5, 128.5, 140.6, 140.7, 142.9, 145.9, 169.1; IR (CHCl₃, cm⁻¹) 3067, 2959, 1732, 1466, 1367, 1229; HRMS calcd for C₂₁H₂₈O₄ 344.1988, found 344.1990.

Diethyl 2,3-diphenyl-1*H*-indene-1,1-dicarboxylate (Compound 4).

This compound was obtained as pale yellow crystals in 70% isolated yield from the reaction of diethyl 2-iodophenylmalonate (**1**) and diphenylacetylene using KOAc and *n*-Bu₄NCl, and stirring for 48 h at 80 °C: mp 85-87 °C; ¹H NMR (CDCl₃) δ 1.07 (t, *J* = 7.2 Hz, 6 H), 4.14 (m, 4 H), 7.15-7.36 (m, 13 H), 7.69 (d, *J* = 7.2 Hz, 1 H); ¹³C NMR (CDCl₃) δ 13.8, 61.9, 72.8, 121.3, 124.6, 126.7, 127.3, 127.6, 128.5, 128.7, 129.6, 130.3, 134.3, 135.1, 140.6, 141.0, 144.8, 145.1, 168.3; IR (CHCl₃, cm⁻¹) 3057, 3019, 2982, 1727, 1466, 1216; HRMS calcd for C₂₇H₂₄O₄ 412.1675, found 412.1680.

Diethyl 3-methyl-2-trimethylsilyl-1*H*-indene-1,1-dicarboxylate (Compound 5).

This compound was obtained as a pale yellow oil in 81% isolated yield from the reaction of diethyl 2-iodophenylmalonate (**1**) and 1-trimethylsilyl-1-propyne using LiCl and K₂CO₃, and stirring for 48 h at 80 °C: ¹H NMR (CDCl₃) δ 0.43 (s, 9 H), 1.36 (t, *J* = 7.2 Hz, 6 H), 2.41 (s, 3

H), 4.30 (m, 4 H), 7.35-7.49 (m, 3 H), 7.78 (d, $J = 7.2$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 0.55, 14.2, 14.2, 62.0, 73.58, 119.2, 124.4, 126.5, 128.6, 140.8, 143.5, 146.4, 152.5, 169.2; IR (CHCl_3 , cm^{-1}) 2957, 1732, 1466, 1246; HRMS calcd for $\text{C}_{19}\text{H}_{26}\text{O}_4\text{Si}$ 346.1600, found 346.1604.

Diethyl 3-methyl-2-phenyl-1*H*-indene-1,1-dicarboxylate (Compound 6).

This compound was obtained as pale yellow crystals in 63% isolated yield from the reaction of diethyl 2-iodophenylmalonate (**1**) and 1-phenyl-1-propyne using KOAc and LiCl, and stirring for 48 h at 80 °C: mp 72-74 °C; ^1H NMR (CDCl_3) δ 1.07 (t, $J = 7.2$ Hz, 6 H), 2.12 (s, 3 H), 4.11 (m, 4 H), 7.25-7.63 (m, 9 H); ^{13}C NMR (CDCl_3) δ 12.2, 14.1, 61.9, 72.9, 120.0, 124.5, 126.6, 127.6, 127.9, 128.9, 130.1, 135.7, 139.7, 140.8, 141.0, 146.1, 168.6; IR (CHCl_3 , cm^{-1}) 2984, 1729, 1472, 1246; HRMS calcd for $\text{C}_{22}\text{H}_{22}\text{O}_4$ 350.1518, found 350.1523.

Diethyl 3-hydroxymethyl-2-phenyl-1*H*-indene-1,1-dicarboxylate (Compound 7).

This compound was obtained as a pale yellow oil in 51% isolated yield from the reaction of diethyl 2-iodophenylmalonate (**1**) and 3-phenyl-2-propyn-1-ol using KOAc and LiCl, and stirring for 48 h at 80 °C: ^1H NMR (CDCl_3) δ 1.07 (t, $J = 7.2$ Hz, 6 H), 2.39 (s, 1 H), 4.09 (m, 4 H), 4.54 (d, $J = 3.0$ Hz, 1 H), 7.34 (m, 7 H), 7.56 (d, $J = 7.2$ Hz, 1 H), 6.63 (d, $J = 7.5$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 14.0, 57.6, 62.2, 73.2, 121.3, 124.8, 126.8, 128.1, 128.2, 129.1, 130.0, 134.6, 141.0, 142.6, 143.4, 144.0, 168.2; IR (CHCl_3 , cm^{-1}) 3458, 3062, 2989, 2936, 2904, 1732, 1246; HRMS calcd for $\text{C}_{22}\text{H}_{22}\text{O}_6$ 366.1512, found 366.1521.

Ethyl 2-*tert*-butyl-5,6-dimethoxy-3-methyl-1*H*-indene-1,1-dicarboxylate (Compound 9).

This compound was obtained as a pale yellow oil in 74% isolated yield from the reaction of diethyl (2-iodo-4,5-dimethoxyphenyl)malonate (**8**) and 4,4-dimethyl-2-pentyne using KOAc and $n\text{-Bu}_4\text{NCl}$, and stirring for 48 h at 80 °C: ^1H NMR (CDCl_3) δ 1.17 (t, $J = 7.2$ Hz, 6 H), 1.34 (s, 9 H), 2.28 (s, 3 H), 3.86 (s, 3 H), 3.92 (s, 3 H), 4.12 (m, 4 H), 6.74 (s, 1 H), 7.06 (s, 1 H); ^{13}C NMR (CDCl_3) δ 13.7, 14.1, 30.3, 34.4, 56.3, 56.6, 61.6, 70.4, 102.3, 106.5, 132.6, 137.2, 140.5, 147.8, 149.8, 169.3; IR (CHCl_3 , cm^{-1}) 3054, 2983, 1754, 1734, 1497, 1265; HRMS calcd for $\text{C}_{22}\text{H}_{30}\text{O}_6$ 390.2042, found 390.2048.

Ethyl 2-*tert*-butyl-1-cyano-3-methyl-1*H*-indene-1-carboxylate (Compound 12).

This compound was obtained as a pale yellow oil in 65% isolated yield from the reaction of ethyl cyano(2-iodophenyl)acetate (**11**) and 4,4-dimethyl-2-pentyne using K_2CO_3 and LiCl, and stirring for 48 h at 80 °C: 1H NMR ($CDCl_3$) δ 1.25 (t, $J = 7.2$ Hz, 3 H), 1.44 (s, 9 H), 2.29 (s, 3 H), 4.23 (m, 2 H), 7.26 (m, 2 H), 7.38 (m, 1 H), 7.53 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.4, 14.1, 30.3, 34.4, 58.1, 63.4, 117.2, 119.6, 122.0, 126.9, 130.0, 138.4, 140.0, 145.4, 146.8, 167.1; IR ($CHCl_3$, cm^{-1}) 3014, 2964, 1747, 1222; HRMS calcd for $C_{18}H_{21}NO_2$ 283.1572, found 283.1576.

Ethyl 1-cyano-3-methyl-2-triisopropylsilyl-1H-indene-1-carboxylate (Compound 13).

This compound was obtained as a pale yellow oil in 52% isolated yield from the reaction of ethyl cyano(2-iodophenyl)acetate (**11**) and 1-triisopropylsilyl-1-propyne using K_2CO_3 and LiCl, and stirring for 48 h at 80 °C: 1H NMR ($CDCl_3$) δ 1.18 (m, 21 H), 1.52 (m, 3 H), 2.35 (s, 3 H), 4.17 (t, $J = 7.2$ Hz, 4 H), 7.33 (m, 2 H), 7.44 (m, 1 H), 7.60 (d, $J = 7.6$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.0, 13.7, 15.5, 19.1, 19.4, 60.7, 63.2, 117.8, 120.1, 122.0, 127.5, 129.6, 135.9, 142.9, 145.7, 156.6, 166.6; IR ($CHCl_3$, cm^{-1}) 3019, 2927, 1735, 1217; HRMS calcd for $C_{23}H_{33}NO_2Si$ 383.2281, found 383.2286.

Ethyl 1-phenylsulfonyl-2,3-di-*n*-propyl-1H-indene-1-carboxylate (Compound 15).

This compound was obtained as a pale yellow oil in 45% isolated yield from the reaction of ethyl (2-iodophenyl)(phenylsulfonyl)acetate (**14**) and 4-octyne using K_2CO_3 and LiCl, and stirring for 48 h at 80 °C: 1H NMR ($CDCl_3$) δ 1.84 (t, $J = 7.2$ Hz, 3 H), 1.07 (m, 5 H), 1.31 (t, $J = 7.2$ Hz, 3 H), 1.53 (m, 2 H), 2.18 (t, $J = 8.0$ Hz, 2 H), 2.42 (m, 1 H), 2.97 (m, 1 H), 4.29 (q, $J = 7.2$ Hz, 4 H), 6.89 (dd, $J = 1.5, 6.8$ Hz, 1 H), 7.14 (t, $J = 7.6$ Hz, 2 H), 7.26 (m, 4 H), 7.38 (m, 1 H), 7.82 (dd, $J = 1.8, 7.2$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 14.9, 15.3, 21.5, 23.3, 28.2, 29.0, 62.9, 85.2, 119.3, 125.9, 126.9, 127.7, 129.6, 130.0, 133.5, 136.8, 136.9, 146.1, 147.2, 165.3; IR ($CHCl_3$, cm^{-1}) 3016, 2963, 1716, 1419, 1224; HRMS calcd for $C_{24}H_{28}SO_4$ 412.1708, found 412.1713.

Reference

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