Supporting Information

Tetraorganoindates as Nucleophilic Coupling Partners in Pd-Catalyzed Cross-Coupling Reactions

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Typical experimental procedure: To a solution of InCl₃ (30.5 mg, 0.138 mmol) in THF (1 mL) at -78 °C was added *n*-BuLi (0.55 mmol, 1.55M in hexane) under a nitrogen atmosphere. The mixture was stirred for 30 min, the cooling bath was removed, and the reaction mixture was warmed to room temperature over 30 min. The solution of *n*-Bu₄InLi (0.138 mmol, ~0.138 M in dry THF) was subsequently added to a mixture of Pd(PPh₃)₄ (23.1mg, 4 mol%) and 4-iodotoluene (109.0 mg, 0.5 mmol) in THF (1 mL) under a nitrogen atmosphere. The reaction mixture was warmed to 60 °C over 40 min and heated at reflux for 1 h. After cooling to room temperature, the reaction mixture was quenched with NaHCO₃ (sat. aq.). The aqueous layer was extracted with ether (3 x 20 mL), and the combined organic phases were sequentially washed with water and brine, dried with MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:hexane=1:50 for elution) to give 4-*n*-butyltoluene (**2**) (67.2 mg, 91 %).

¹H NMR (400 MHz, CDCl₃) δ 7.07 (s, 4H), 2.56 (t, 7.73, 2H), 2.31 (s, 3H) 1.54-1.60 (m, 2H), 1.32-1.37 (m, 2H), 0.92(t, *J* = 7.34 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 139.84, 134.93, 128.90, 128.29, 35.21, 33.81, 22.37, 20.99, 13.97; IR (film) 3155, 2959, 2929, 2858, 1639, 1466, 1380, 1167, 1096, 912, 742, 650 cm⁻¹; HRMS (EI) calcd for C₁₁H₁₆ M⁺ 148.1252, found 148.1254.

4-Methyl styrene(1) ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 8.09$ Hz, 2H), 7.12 (d, $J = 7.95$ Hz, 2H), 6.69 (dd, $J = 17.49, 11.14$ Hz, 1H), 5.70 (d, $J = 17.49$ Hz, 1H), 5.18 (d, $J = 11.14$ Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.65, 137.13, 135.24, 129.63, 126.54, 113.18, 21.62; IR (film) 1638, 1472 cm^{-1} ; HRMS (EI) calcd for $\text{C}_9\text{H}_{10} \text{M}^+$ 118.0783, found 118.0782.

4-Isobutyltoluene(3) ^1H NMR (400 MHz, CDCl_3) δ 7.07 (d, $J = 8.01$ Hz, 2H), 7.02 (d, $J = 8.00$ Hz, 2H), 2.43 (d, $J = 7.16$ Hz, 2H), 2.32 (s, 3H), 1.81-1.85 (m, 2H), 0.99 (d, $J = 6.59$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.60, 134.98, 128.99, 128.75, 45.02, 30.27, 22.37, 21.01; IR (film) 3154, 2984, 2901, 1640, 1470 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{16} \text{M}^+$ 148.1252, found 148.1250.

4-sec-Butyltoluene(4) ^1H NMR (400 MHz, CDCl_3) δ 7.06-7.11 (m, 4H), 2.53-2.58 (m, 1H), 2.32 (s, 3H), 1.54-1.61 (m, 2H), 1.21 (d, $J = 6.95$ Hz, 3H), 0.82 (t, $J = 7.37$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.67, 135.14, 128.92, 126.91, 41.25, 31.20, 22.37, 21.95, 12.28; IR (film) 3155, 2962, 2928, 1639, 1467 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{16} \text{M}^+$ 148.1252, found 148.1253.

4-Methyl-biphenyl(5) ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 7.84$ Hz, 2H), 7.49 (d, $J = 8.11$ Hz, 2H), 7.42 (t, $J = 7.62$ Hz, 2H), 7.32 (t, $J = 7.32$ Hz, 1H), 7.24 (d, $J = 7.46$ Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.57, 138.76, 137.42, 129.88, 129.11, 127.57, 127.39, 127.37, 21.50; IR (film) 3156, 2986, 1639, 1470 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{12} \text{M}^+$ 168.0939, found 168.0934.

4'-Methyl-1,2-diphenylacetylene(6) ^1H NMR (400 MHz, CDCl_3) δ 7.51-7.53 (m, 2H), 7.42 (d, $J = 8.07$ Hz, 2H), 7.31-7.35 (m, 3H), 7.14 (d, $J = 7.87$ Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.78, 131.95, 131.90, 129.52, 128.71, 128.47, 123.89, 120.59, 89.96, 89.12, 21.91; IR (film) 2250, 1640, 1468 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{12} \text{M}^+$ 192.0939, found 192.0940.

1-Methyl naphthalene(7) ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 4.50$ Hz, 1H), 7.82-7.84 (m, 1H), 7.69 (d, $J = 4.05$ Hz, 1H), 7.44-7.52 (m, 2H), 7.36 (t, $J = 7.53$ Hz, 1H), 7.30 (d, $J = 6.92$ Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.24, 133.52, 128.50, 126.53, 126.35, 125.69, 125.55, 125.51, 124.09, 19.36; IR (film) 3155, 1598, 1467 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{10} \text{M}^+$ 142.0783, found 142.0783.

1-Vinyl naphthalene(8) ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 7.72$ Hz, 1H), 7.82-7.84 (m, 1H), 7.76 (d, $J = 8.16$ Hz, 1H), 7.71 (d, $J = 10.10$ Hz, 1H), 7.43-7.50 (m, 4H), 5.80 (d, $J = 17.31$ Hz, 1H), 5.46 (d, $J = 10.80$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.04, 134.82, 134.03, 131.55, 128.96, 128.55, 126.50, 126.20, 126.08, 124.21, 124.07, 117.55; IR (film) 3155, 3050, 1687, 1467 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{10}\text{M}^+$ 154.0783, found 154.0779.

1-Phenylethynyl naphthalene(9) ^1H NMR (400 MHz, CDCl_3) δ 8.44 (d, $J = 8.35$ Hz, 1H), 7.84 (t, $J = 9.00$ Hz, 2H), 7.76 (d, $J = 6.99$ Hz, 1H), 7.64-7.66 (m, 2H), 7.52 (t, $J = 6.90$ Hz, 1H), 7.51 (t, $J = 7.75$ Hz, 1H), 7.34-7.42 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.26, 133.20, 131.66, 130.35, 128.75, 128.42, 128.37, 128.30, 126.76, 126.41, 126.21, 125.27, 123.40, 120.89, 94.30, 87.51; IR (film) 2250, 1640, 1468 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{12}\text{M}^+$ 228.0939, found 228.0941.

4-*n*-Butyl acetophenone(10) ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.08$ Hz, 2H), 7.26 (d, $J = 8.06$ Hz, 2H), 2.66 (t, $J = 7.72$ Hz, 2H), 2.58 (s, 3H), 1.58-1.65 (m, 2H), 1.31-1.40 (m, 2H), 0.93 (t, $J = 7.34$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.88, 148.81, 134.92, 128.61, 128.47, 35.69, 33.26, 26.55, 22.32, 13.90; IR (film) 3154, 2960, 1793, 1677, 1466 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{16}\text{O M}^+$ 176.1201, found 176.1201.

3-Nitro styrene(11) ^1H NMR (400 MHz, CDCl_3) δ 8.24-8.25 (m, 1H), 8.09-8.11 (m, 1H), 7.70 (d, $J = 7.71$ Hz, 1H), 7.49 (t, $J = 7.97$ Hz, 1H), 6.76 (dd, $J = 17.56, 10.87$ Hz, 1H), 5.89 (d, $J = 17.56$ Hz, 1H), 5.44 (d, $J = 10.87$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.99, 139.65, 135.13, 132.49, 129.86, 122.81, 121.26, 117.48; IR (film) 3155, 1637, 1532, 1470, 1350 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_7\text{NO}_2\text{M}^+$ 149.0477, found 149.0483.

4-*n*-Butyl anisole(12) ^1H NMR (400 MHz, CDCl_3) δ 7.08 (d, $J = 8.56$, 2H), 6.82 (d, $J = 6.74$ Hz, 2H), 3.78 (s, 3H), 2.54 (t, $J = 7.70$ Hz, 2H), 1.52-1.60 (m, 2H), 1.30-1.38 (m, 2H), 0.92 (t, $J = 7.34$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.60, 135.02, 129.25, 113.64, 55.24, 34.73, 33.92, 22.31, 13.97; IR (film) 3155, 2959, 1639, 1466, 1244 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{16}\text{O M}^+$ 164.1201, found 164.1201.

4-Isobutyl phenol(13) ^1H NMR (400 MHz, CDCl_3) δ 7.00 (d, $J = 8.42$ Hz, 2H), 6.74 (d, $J = 8.49$ Hz, 2H), 4.63 (s, 1H), 2.39 (d, $J = 7.14$ Hz, 2H), 1.77-1.82 (m, 1H), 0.88 (d,

$J = 6.57$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 130.14, 114.87, 44.52, 30.35, 22.28; IR (film) 3423, 3154, 2984, 1638, 1601, 1468 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{14}\text{O}$ M^+ 150.1045, found 150.1050.

4-*n*-Butyl chlorobenzene(14) ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, $J = 8.37$ Hz, 2H), 7.09 (d, $J = 8.32$ Hz, 2H), 2.57 (t, $J = 7.71$ Hz, 2H), 1.52-1.60 (m, 2H), 1.29-1.38 (m, 2H), 0.92 (t, $J = 7.33$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.29, 131.23, 129.74, 128.29, 34.99, 33.54, 22.25, 13.91; IR (film) 1638, 1491 cm^{-1} ; HRMS(EI) calcd for $\text{C}_{10}\text{H}_{13}\text{Cl}$ M^+ 168.0706, found 168.0704.

2-Phenylethynyl thiophene(15) ^1H NMR (400 MHz, CDCl_3) δ 7.50-7.53 (m, 2H), 7.33-7.36 (m, 3H), 7.28-7.30 (m, 2H), 7.0-7.03 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.51, 131.89, 131.41, 128.42, 128.37, 127.25, 127.10, 93.01, 82.59; IR (film) 2250, 1641, 1470 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_8\text{S}$ M^+ 184.0347, found 184.0341.

2,6-Divinyl pyridine(16) ^1H NMR (400 MHz, CDCl_3) δ 7.60 (t, $J = 7.75$ Hz, 1H), 7.21 (d, $J = 7.81$ Hz, 2H), 6.83 (dd, $J = 17.53, 10.72$ Hz, 2H), 6.25 (d, $J = 17.53$ Hz, 1H), 5.48 (d, $J = 10.72$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.34, 137.05, 136.86, 119.95, 118.29; IR (film) 1639, 1469, 1096 cm^{-1} ; HRMS (EI) calcd for $\text{C}_9\text{H}_9\text{N}$ M^+ 131.0735 found 131.0736.

α -Vinyl styrene(17) ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.35 (m, 5H), 6.62 (dd, $J = 17.34, 11.03$ Hz, 1H), 5.17 (s, 1H), 5.22 (d, $J = 11.03$ Hz, 1H), 5.20 (s, 1H), 5.18 (d, $J = 17.34$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.63, 138.53, 131.37, 129.47, 128.65, 127.69, 118.07, 117.28; IR (film) 1639, 1490, 1468 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{10}$ M^+ 130.0783, found 130.0780.

2-Vinyl naphthalene(18) ^1H NMR (400 MHz, CDCl_3) δ 7.78-7.82 (m, 3H), 7.75 (s, 1H), 7.62-7.65 (m, 2H), 7.44-7.46 (m, 2H), 6.89 (dd, $J = 17.57, 10.90$ Hz, 1H), 5.87 (d, $J = 17.57$ Hz, 1H), 5.33 (d, $J = 10.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.74, 133.81, 132.36, 131.95, 126.95, 126.85, 126.47, 125.17, 125.04, 124.72, 121.97, 112.98; IR (film) 3155, 1639, 1469 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{10}$ M^+ 154.0783, found 154.0784.

4-*tert*-Butyl-1-vinylcyclohexene(19) ^1H NMR (400 MHz, CDCl_3) δ 6.36 (dd, $J = 17.50, 10.70$ Hz, 1H), 5.76-5.70 (m, 1H), 5.04 (d, $J = 17.50$ Hz, 1H), 4.88 (d, $J = 10.70$

Hz, 1H), 1.89-2.31 (m, 6H), 0.84-1.32 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.10, 136.33, 130.40, 110.14, 44.67, 32.59, 27.78, 27.58, 25.55, 24.09; IR (film) 3155, 2962, 1644, 1469 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{20}$ M^+ 164.1565, found 164.1526.

Phenyl vinyl ketone(20) ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 7.22$ Hz, 2H), 7.57-7.60 (m, 1H), 7.47 (t, $J = 3.64$ Hz, 2H), 7.17 (dd, $J = 17.17, 10.59$ Hz, 1H), 6.45 (d, $J = 17.1$ Hz, 1H), 5.94 (d, $J = 8.95$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.105, 137.28, 133.00, 132.39, 130.23, 128.71, 128.63; IR (film) 3154, 1793, 1671, 1470 cm^{-1} ; HRMS (EI) calcd for $\text{C}_9\text{H}_8\text{O}$ M^+ 132.0575, found 132.0573.

1,3-Diphenyl propynone(21) ^1H NMR (400 MHz, CDCl_3) δ 8.22-8.24 (m, 2H), 7.68-7.70 (m, 2H), 7.61-7.66 (m, 1H), 7.47-7.54 (m, 3H), 7.40-7.44 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.46, 137.31, 134.55, 133.50, 131.23, 130.00, 129.12, 129.06, 120.55, 91.55, 87.31; IR (film) 2200, 1793, 1638, 1450 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{10}\text{O}$ M^+ 206.0732, found 206.0733.

Allyl benzene(22) ^1H NMR (400 MHz, CDCl_3) δ 7.18-7.31 (m, 5H), 5.98 (ddt, $J = 16.80, 10.11, 6.75$ Hz, 1H), 5.06-5.11 (m, 2H), 3.39 (d, $J = 6.68$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.46, 137.87, 128.99, 128.82, 126.47, 116.19, 40.65; IR (film) 3033, 1639, 1455 cm^{-1} ; HRMS (EI) calcd for C_9H_{10} M^+ 118.0783, found 118.0782.

1,4-Divinylbenzene(23) ^1H NMR (400 MHz, CDCl_3) δ 7.36 (s, 4H), 6.66-6.73 (m, 2H), 5.74 (d, $J = 17.62$ Hz, 2H), 5.23 (d, $J = 10.95$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.52, 136.89, 126.81, 114.18; IR (film) 3155, 1629, 1468 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{10}$ M^+ 130.0783, found 130.0780.

1,4-Di-*n*-butyl benzene(24) ^1H NMR (400 MHz, CDCl_3) δ 7.08 (s, 4H), 2.57 (t, $J = 1.76$ Hz, 4H), 1.54-1.62 (m, 4H), 1.30-1.40 (m, 4H), 0.92 (t, $J = 7.34$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.04, 128.24, 35.25, 33.76, 22.42, 13.99; IR (film) 2959, 2930, 1638, 1466 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{22}$ M^+ 190.1721, found 190.1721.

1,4-Diphenylbenzene(25) ^1H NMR (400 MHz, CDCl_3) δ 7.68 (s, 4H), 7.64-7.66 (m, 4H), 7.44-7.48 (m, 4H), 7.34-7.38 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.68, 139.10, 127.79, 126.48, 126.32, 126.03; IR (film) 3154, 1639, 1470 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{14}$ M^+ 230.1096, found 230.1093.

1,4-Diphenyl ethynylbenzene(26) ^1H NMR (400 MHz, CDCl_3) δ 7.53-7.55 (m, 2H), 7.51 (s, 2H), 7.35-7.37 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 131.63, 131.54, 128.47, 128.40, 123.09, 123.04, 91.23, 89.10; IR (film) 3154, 2250, 1639, 1472 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{14}$ M^+ 278.1096, found 278.1098.

4-Vinylbiphenyl(27) ^1H NMR (400 MHz, CDCl_3) δ 7.56-7.61 (m, 4H), 7.48-7.50 (m, 2H), 7.42-7.46 (m, 2H), 7.32-7.36 (m, 1H), 6.76 (dd, $J = 17.58, 11.24$ Hz, 1H), 5.79 (d, $J = 17.58$ Hz, 1H), 5.28 (d, $J = 11.24$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.74, 140.59, 136.59, 136.40, 128.78, 127.32, 127.23, 126.96, 126.64, 113.90; IR (film) 3154, 1640, 1470 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{12}$ M^+ 180.0939, found 180.0939.

4'-Phenyl-1,2-diphenylacetylene(28) ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.59 (m, 1H), 7.50-7.55 (m, 5H), 7.40-7.47 (m, 6H), 7.31-7.38 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.08, 139.95, 133.00, 131.99, 131.83, 131.59, 128.87, 128.71, 127.61, 127.19, 126.91, 121.52, 90.51, 88.31; IR (film) 2249, 1639, 1476 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{14}$ M^+ 254.1096, found 254.1084.