

SUPPORTING INFORMATION

Cp*Co(III) and Cu(OAc)₂ Bimetallic Catalyst for Buchwald type C-N Cross Coupling of Arylchlorides and Amines under Base, Inert gas & Solvent-free Conditions

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Experimental Details: The ¹H, ¹³C {¹H} NMR spectra were recorded using JEOL ECS-400 spectrometer (operating at 400 MHz for ¹H and 100 MHz for ¹³C).

Chemicals and reagents: Reactants, reagents, chemicals and solvents available commercially within the country were used.

Procedure for synthesis of Cobalt catalyst

Cobalt catalyst was synthesised through the earlier known methodology.^{R1, R2}

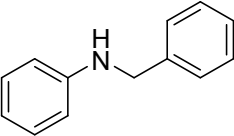
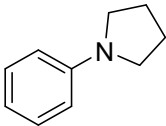
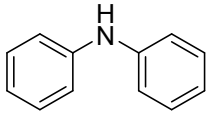
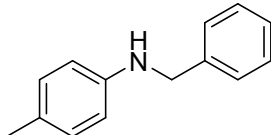
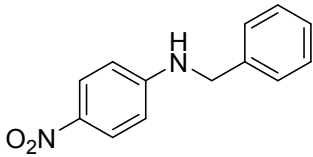
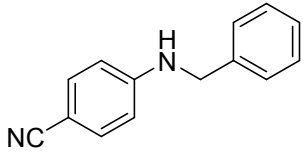
Procedure for Catalytic Reaction

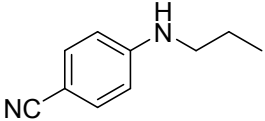
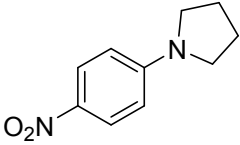
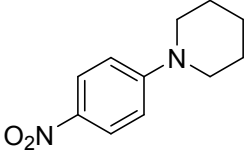
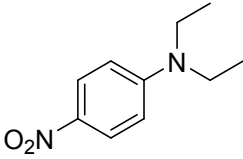
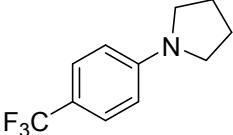
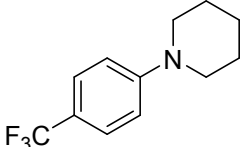
In a 10mL reaction tube, 1 mmol of each primary/secondary amine and aryl halide was considered. Thereafter, 1 mol% of Cp*Co(CO)I₂ and 10 mol% of Cu(OAc)₂ were added into the reaction tube, and the reaction tube was heated at 100 °C for 4h with a continuous stirring. After completion of the reaction, the reaction mixture was cool down to room temperature, and crude product was extracted in aqueous organic layer by using a mixture of ethyl acetate and water. The organic layer was separated and dried over anhydrous Na₂SO₄, and then concentrated on a rotatory evaporator. At last, the final coupling product was isolated in organic layer by passing the residue through celite pad. Most of the coupling products were separated through extraction of aqueous organic layer, however, some of the ortho- substituted products were separated through column chromatography for spectroscopic analysis.

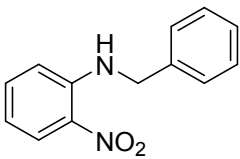
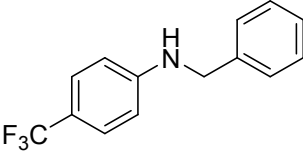
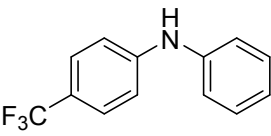
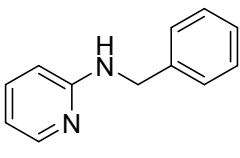
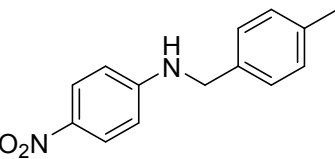
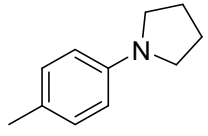
R1 – S. A. Frith, J. Spencer, *Inorganic Syntheses* **1990**, 28, 273

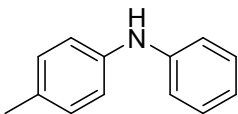
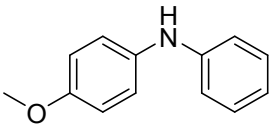
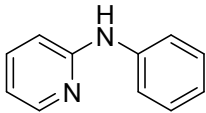
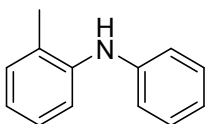
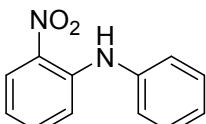
R2 – W. Li, L. Weng, G. Jin, *Inorg. Chem. Commun.* **2004**, 7, 1174

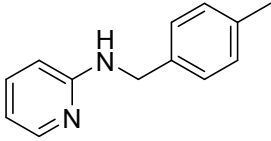
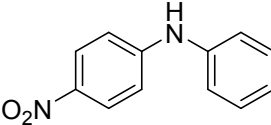
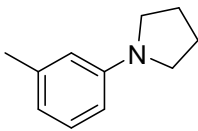
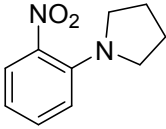
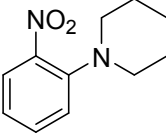
Characterisation Data

	^1H NMR (400 MHz, CDCl_3) δ 1H NMR (400 MHz,) δ 7.36 – 7.26 (m, 5H), 7.18 – 7.14 (m, 2H), 6.70 (tt, J = 7.5, 1.0 Hz, 1H), 6.62 – 6.60 (m, 2H), 4.30 (s, 2H), 3.99 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.10, 139.38, 129.24, 128.60, 127.48, 127.20, 117.51, 112.79, 48.25.
	^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.19 (m, 2H), 6.66 – 6.63 (m, 1H), 6.57 – 6.54 (m, 2H), 3.28 – 3.25 (m, 4H), 2.01 – 1.95 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.92, 129.10, 115.29, 111.58, 47.52, 25.44.
	^1H NMR (400 MHz, CDCl_3) δ 7.26 (t, J = 7.9 Hz, 4H), 7.09 – 7.04 (m, 4H), 6.92 (t, J = 7.3 Hz, 2H), 5.69 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.29, 129.33, 120.97, 117.77.
	^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.21 (m, 5H), 6.98 (d, J = 8.1 Hz, 2H), 6.55 (d, J = 8.1 Hz, 2H), 4.30 (s, 2H), 3.83 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 129.74, 128.60, 127.51, 127.16, 113.03, 48.68, 20.39.
	^1H NMR (400 MHz, CDCl_3) δ 8.09 – 8.05 (m, 2H), 7.36 – 7.33 (m, 5H), 6.58 – 6.56 (m, 2H), 4.93 (s, 1H), 4.43 (d, J = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.02, 136.31, 127.93, 126.83, 126.31, 125.38, 110.29, 98.87, 46.59.
	^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.71 (m, 2H), 7.41 – 7.29 (m, 7H), 6.41 (s, 1H), 4.63 (d, J = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.27, 37.90, 137.82, 132.70, 128.86, 128.40, 127.97, 127.76, 44.25.

	¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.69 (m, 2H), 7.39 – 7.36 (m, 2H), 6.39 (s, 1H), 3.42 – 3.37 (m, 2H), 1.63 (h, J = 7.4 Hz, 2H), 0.98 (d, J = 7.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.57, 137.48, 133.17, 128.74, 128.33, 41.85, 22.86, 11.44.
	¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.10 (m, 2H), 6.49 – 6.45 (m, 2H), 3.42 – 3.39 (m, 4H), 2.11 – 2.05 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 151.82, 136.52, 126.36, 110.41, 47.90, 25.43.
	¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.08 (m, 2H), 6.81 – 6.77 (m, 2H), 3.45 (d, J = 5.1 Hz, 4H), 1.69 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 154.88, 137.41, 126.16, 112.30, 48.37, 25.28, 24.24.
	¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.09 (m, 2H), 6.59 – 6.57 (m, 2H), 3.46 (q, J = 7.1 Hz, 4H), 1.23 (t, J = 7.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 152.20, 136.25, 126.52, 106.80, 44.95, 12.40.
	¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 8.9 Hz, 2H), 6.52 (d, J = 8.7 Hz, 2H), 3.30 – 2.35 (m, 4H), 2.04 – 1.97 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 149.77, 126.38 (q, J = 3.6 Hz), 125.42 (q, 270.0 Hz), 116.59 (q, J = 32.6 Hz), 110.83, 47.51, 25.47.
	¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.27 – 3.25 (m, 4H), 1.71 – 1.58 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 153.79, 126.33 (q, J = 3.6 Hz), 124.88 (q, 270.6 Hz), 119.53 (q, J = 32.2), 114.59, 49.31, 25.42, 24.28.

	¹H NMR (400 MHz, CDCl₃) δ 8.44 (s, 1H), 8.20 (dd, J = 8.6, 1.6 Hz, 1H), 7.33 – 7.26 (m, 6H), 6.67 (ddd, J = 8.3, 7.0, 1.2 Hz, 1H), 4.56 (d, J = 5.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 144.22, 136.31, 135.22, 127.91, 126.67, 126.01, 125.85, 114.70, 113.17, 46.06.
	¹H NMR (400 MHz,) δ 7.39 – 7.27 (m, 7H), 6.60 (d, J = 8.6 Hz, 2H), 4.35 (s, 3H). ¹³C NMR (101 MHz,) δ 150.45, 138.44, 128.79, 127.52, 127.35, 126.62 (q, J = 3.6 Hz), 124.97 (q, 270.2 Hz), 118.96 (q, J = 32.6), 111.95, 47.75.
	¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 8.4 Hz, 2H), 7.42 – 7.28 (m, 2H), 7.21 – 7.07 (m, 2H), 7.07 – 6.87 (m, 3H), 5.91 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 146.73, 141.11, 129.55, 126.69 (q, J = 3.5 Hz), 124.60 (q, 270.8 Hz), 122.92, 121.61 (q, J = 32.7 Hz), 120.00, 115.31.
	¹H NMR (400 MHz, CDCl₃) δ 8.09 – 8.07 (m, 1H), 7.40 – 7.24 (m, 6H), 6.57 (ddd, J = 7.1, 5.1, 0.7 Hz, 1H), 6.36 (d, J = 8.4 Hz, 1H), 5.04 (s, 1H), 4.49 (d, J = 5.8 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 158.62, 148.13, 139.15, 137.49, 128.62, 127.38, 127.21, 113.11, 106.77, 46.29.
	¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 9.2 Hz, 2H), 7.25 – 7.13 (m, 4H), 6.56 (d, J = 9.2 Hz, 2H), 4.81 (s, 1H), 4.38 (d, J = 5.3 Hz, 2H), 2.36 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 129.63, 127.38, 126.41, 111.29, 47.45, 21.12.
	¹H NMR (400 MHz, CDCl₃) δ 7.02 (d, J = 7.2 Hz, 2H), 6.50 – 6.48 (m, 2H), 3.23 (q, J = 4.4 Hz, 4H), 2.24 (s, 3H), 1.97 (dt, J = 6.1, 3.5 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 145.06, 128.59, 123.42, 110.77, 46.81, 24.36, 19.25.

	^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.21 (m, 2H), 7.08 (d, J = 8.3 Hz, 2H), 7.03 – 6.96 (m, 4H), 6.87 (t, J = 7.3 Hz, 1H), 5.58 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.88, 139.22, 129.86, 128.80, 128.25, 119.23, 117.84, 115.79, 19.64.
	^1H NMR (400MHz, CDCl_3): 7.23 – 7.19 (t, 2H), 7.08 (d, J = 8.7 Hz, 1H), 6.90 – 6.81 (m, 5H), 3.80 (s, 3H). ^{13}C NMR (100MHz, CDCl_3): 155.35, 145.24, 135.78, 129.39, 122.28, 119.64, 116.50, 115.70, 114.74, 55.67.
	^1H NMR (400 MHz, CDCl_3) δ 8.21 – 8.20 (d, 1H), 7.51 – 7.47 (m, 1H), 7.33 (d, J = 3.8 Hz, 4H), 7.05 (tt, J = 5.5, 3.3 Hz, 1H), 6.88 (d, J = 8.3 Hz, 1H), 6.74 – 6.73 (m, 1H), 6.61 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.95, 148.42, 140.42, 137.70, 129.30, 122.83, 120.34, 115.07, 108.21.
	^1H NMR (400 MHz, CDCl_3) δ 7.22 (dt, J = 16.5, 7.8 Hz, 4H), 7.13 (t, J = 7.5 Hz, 1H), 6.96 – 6.87 (m, 4H), 5.37 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.79, 140.04, 129.78, 128.19, 128.17, 128.14, 128.12, 128.11, 127.10, 125.59, 120.80, 119.30, 117.57, 116.32, 116.31, 116.30, 116.29, 116.28, 116.27, 116.26, 116.25, 116.24, 16.75.
	^1H NMR (400 MHz, CDCl_3) δ 9.50 (s, 1H), 8.21 (dd, J = 8.6, 1.4 Hz, 1H), 7.47 – 7.34 (m, 3H), 7.28 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 6.77 (td, J = 7.7, 7.0, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.11, 138.71, 135.71, 129.75, 126.69, 125.68, 124.41, 117.51, 116.05.

	¹H NMR (400 MHz, CDCl₃) δ 8.10 – 8.09 (m, 1H), 7.41 – 7.37 (m, 1H), 7.26 – 7.21 (m, 2H), 7.14 (d, J = 7.9 Hz, 2H), 6.58 (dd, J = 7.0, 5.1 Hz, 1H), 6.36 (d, J = 8.3 Hz, 1H), 4.88 (s, 1H), 4.45 (d, J = 5.7 Hz, 2H), 2.33 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.66, 148.20, 137.45, 136.88, 136.05, 129.30, 127.39, 113.07, 106.74, 46.11, 21.09.
	¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 9.1 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.22 – 7.19 (m, 3H), 6.94 (d, J = 9.1 Hz, 2H), 6.28 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 150.13, 139.81, 139.47, 129.76, 126.25, 124.69, 121.93, 113.69.
	¹H NMR (400 MHz, CDCl₃) δ 7.15 – 7.06 (m, 1H), 6.48 (d, J = 7.4 Hz, 1H), 6.39 (s, 2H), 3.26 (t, J = 6.4 Hz, 4H), 2.31 (s, 3H), 1.97 (dq, J = 9.4, 6.1, 4.8 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 148.05, 138.78, 128.99, 116.34, 112.36, 108.88, 47.58, 25.43, 21.85.
	¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, J = 8.2, 1.6 Hz, 1H), 7.36 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 6.90 (d, J = 8.6 Hz, 1H), 6.70 (t, J = 7.6 Hz, 1H), 3.25 – 3.17 (m, 4H), 1.98 (dt, J = 9.6, 4.6 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 142.76, 137.04, 132.98, 126.73, 115.89, 115.44, 50.36, 25.73.
	¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, J = 8.1, 1.5 Hz, 1H), 7.43 (td, J = 8.1, 7.4, 1.6 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 6.99 – 6.90 (m, 1H), 3.03 – 2.96 (m, 4H), 1.69 (q, J = 5.6 Hz, 4H), 1.58 (q, J = 5.8 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 147.00, 142.57, 133.39, 125.96, 120.85, 120.56, 52.90, 25.94, 24.00.

