A New Efficient Catalytic System for the Chemoselective Cobalt-Catalyzed Cross-Coupling of Aryl Grignard Reagents with Primary and Secondary Alkyl Bromides

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1- General

All reactions were carried out under a nitrogen atmosphere. All starting materials were purchased from commercial sources and used without any further purification. Anhydrous THF was purchased from commercial source. Yields refer to isolated yields of compounds estimated to be $\geq 97\%$ pure as determined by ^1H -NMR (400 MHz), ^{13}C -NMR (100 MHz) and GC analysis (capillary column 30m x 0.25mm x 0.25 μm). All compounds give satisfactory centesimal analysis. The analytical data for the known compounds were found to match with the literature data.

Ionization for High Resolution Mass Spectra (HRMS) was obtained by electronic impact (EI, 70 eV). Mass spectra are reported as m/z .

The Grignard solutions were titrated according to the procedure described by Watson¹.

2- Typical Procedure : synthesis of *s*-butylbenzene (3d).

A dry and nitrogen flushed 250 mL four-necked flask, equipped with a mechanical stirrer, a thermometer, a nitrogen inlet and a septum, was charged with THF (25 mL), 2-bromobutane (6.85 g, 50 mmol), CoCl_2 (325 mg, 5 mol%) and TMEDA (0.29 g, 5 mol%). The reaction mixture was cooled to 0°C then a solution of phenylmagnesium bromide in THF (61 mL, 0.9 M, 55 mmol) was added in 50 min. After completion of the addition, the reaction mixture was stirred for 30 min then quenched with aqueous HCl 1M (100 mL). The aqueous layer was extracted with ether (3 x 50 mL), then the combined organic layers were dried with MgSO_4 and concentrated *in vacuo*. The crude product is then distilled under reduced pressure (55°C , 10 Torr) to yield 6.31g (94%) of *s*-butylbenzene as a colorless oil.

3- Analytical Data

^1H (400MHz, CDCl_3) $\delta(\text{ppm})$: 0.69 (t, $J = 7.33$ Hz, 3H), 1-1.3 (m, 13H), 1.49 (m, 6H), 2.19 (t, $J = 7.33$ Hz, 2H), 2.30 (m, 1H), 4.03 (q, $J = 7.33$ Hz, 2H), 7.11 (d, $J = 7.33$ Hz, 2H), 7.16 (t, $J = 7.33$ Hz, 1H), 7.27 (t, $J = 7.33$ Hz, 2H).

^{13}C (100MHz, CDCl_3) $\delta(\text{ppm})$: 12.18, 14.23, 24.93, 27.55, 29.08, 29.30, 29.41, 29.64, 29.75, 29.69, 29.80, 34.47, 36.61, 47.84, 60.11, 125.68, 127.70 (2C), 128.09 (2C), 146.03, 174.01.

Micro-analysis : calcd (%) : C = 78.90 , H = 10.59, O = 10.51

found (%) : C = 79.17, H = 10.48, O = 10.35

^1H (400MHz, CDCl_3) $\delta(\text{ppm})$: 0,96 (t, 7.33 Hz, 3H), 1,33 (m, 2H), 1,65 (m, 2H), 2,57 (t, J = 7.33 Hz, 2H), 7,18 (d, J = 7.79 Hz, 2H), 7,21 (t, J = 7.79 Hz, 1H), 8,09 (t, J = 7.79 Hz, 2H).

^{13}C (100MHz, CDCl_3) $\delta(\text{ppm})$: 24.6, 27.4, 34.1, 38.2, 128.7, 130.4 (2C), 132.8 (2C), 138.0.

Micro-analysis : calcd (%) : C = 89.49, H = 10.51

found (%) : C = 89.61, H = 10.39

^1H (400MHz, CDCl_3) $\delta(\text{ppm})$: 0.88 (t, J = 6.87 Hz, 3H), 1.27 (m, 10H), 1.60 (m, 2H), 2.61 (t, J = 7.79 Hz, 2H), 7.16 (m, 3H), 7.26 (m, 2H).

^{13}C (100MHz, CDCl_3) $\delta(\text{ppm})$: 14.12, 22.68, 29.28, 29.36, 29.50, 31.58, 31.89, 35.99, 125.50, 128.18 (2C), 128.37 (2C), 142.93.

Micro-analysis : calcd (%) : C = 88.35, H = 11.65

found (%) : C = 88.65, H = 11.35

^1H (400MHz, CDCl_3) $\delta(\text{ppm})$: 0.87 (t, J = 6.87 Hz, 3H), 1.28 (m, 10H), 1.58 (quint. , J = 7.79 Hz, 2H), 2.53 (t, J = 7.79 Hz, 2H), 3.79 (s, 3H), 6.82 (d, J = 8.70 Hz, 2H), 7.09 (d, J = 8.70 Hz, 2H).

^{13}C (100MHz, CDCl_3) $\delta(\text{ppm})$: 14.12, 22.67, 29.28 (2C), 29.49, 31.80, 31.88, 35.02, 55.17, 113.54 (2C), 129.20 (2C), 135.01, 157.47.

Micro-analysis : calcd (%) : C = 81.76 , H = 10.98, O = 7.26

found (%) : C = 81.64, H = 11.12, O = 7.24

¹H (400MHz, CDCl₃) δ(ppm) : 0.83 (t, J = 7.33 Hz, 3H), 1.24 (d, J = 6.87 Hz, 3H), 1.59 (quint. , J = 7.33 Hz, 2H), 2.58 (s, J = 7.33 Hz, 1H), 7.17 (m, 3H), 7.28 (d, J = 7.33 Hz, 2H).

¹³C (100MHz, CDCl₃) δ(ppm) : 12.27, 21.85, 31.16, 41.65, 125.73 (2C), 127.03 (2C), 128.20, 147.63.

Micro-analysis : calcd (%) : C = 89.49, H = 10.51

found (%) : C = 89.32, H = 10.68

¹H (400MHz, CDCl₃) δ(ppm) : 1.25 (m, 1H), 1.42 (m, 4H), 1.75 (m, 1H), 1.84 (m, 4H), 2.49 (m, 1H), 7.20 (m, 3H), 7.27 (m, 2H).

¹³C (100MHz, CDCl₃) δ(ppm) : 26.14 (2C), 26.89, 34.43 (2C), 44.56, 125.79 (2C), 126.79 (2C), 128.24, 148.05.

Micro-analysis : calcd (%) : C = 89.94, H = 10.06

found (%) : C = 89.86, H = 10.14

¹H (400MHz, CDCl₃) δ(ppm) : 1.23 (m, 1H), 1.37 (quint. , J = 8.70 Hz, 4H), 1.75 (m, 1H), 1.83 (m, 4H), 2.44 (m, 1H), 3.78 (s, 3H), 6.83 (d, J = 9.62 Hz, 2H), 7.13 (d, J = 9.62 Hz, 2H).

¹³C (100MHz, CDCl₃) δ(ppm) : 26.13, 26.91(2C), 34.69 (2C), 43.64, 55.20, 113.57 (2C), 127.60 (2C), 140.34, 157.56.

Micro-analysis : calcd (%) : C = 82.06, H = 9.53, O = 8.41

found (%) : C = 81.99, H = 9.66, O = 8.35

^1H (400MHz, CDCl_3) $\delta(\text{ppm})$: 1.25 (m, 1H), 1.38 (m, 4H), 1.75 (m, 1H), 1.83 (m, 4H), 2.95 (m, 1H), 3.80 (s, 3H), 6.83 (d, $J = 7.79$ Hz, 1H), 6.91 (t, $J = 7.33$ Hz, 1H), 7.16 (d, $J = 7.33$ Hz, 1H), 7.18 (t, $J = 7.79$ Hz, 1H).

^{13}C (100MHz, CDCl_3) $\delta(\text{ppm})$: 26.41 (2C), 27.07, 33.17, 36.64 (2C), 55.29, 110.21, 120.47, 126.41, 126.46, 136.15, 156.60.

Micro-analysis : calcd (%) : C = 82.06, H = 9.53 , O = 8.41

found (%) : C = 81.98, H = 9.69, O = 8.33

^1H (400MHz, CDCl_3) $\delta(\text{ppm})$: 0.82 (t, $J = 7.33$ Hz, 3H), 0.83 (t, $J = 6.87$ Hz, 3H), 1.0-1.3 (m, 10H), 1.52 (m, 2H), 1.60 (m, 2H), 2.44 (m, 1H), 7.14 (d, $J = 7.33$ Hz, 2H), 7.17 (t, $J = 7.33$ Hz, 1H), 7.27 (t, $J = 7.33$ Hz, 2H).

^{13}C (100MHz, CDCl_3) $\delta(\text{ppm})$: 14.03, 14.08, 22.56, 22.79, 27.29, 29.85, 31.98, 36.69, 36.94, 46.03, 125.64, 127.65 (2C), 128.10 (2C), 146.44.

Micro-analysis : calcd (%) : C = 88.00, H = 12.00

found (%) : C = 88.28, H = 11.72

^1H (400MHz, CDCl_3) $\delta(\text{ppm})$: 0.75 (t, $J = 7.33$ Hz, 3H), 0.76 (t, $J = 6.87$ Hz, 3H), 1.0-1.25 (m, 10H), 1.49 (m, 4H), 3.00 (m, 1H), 3.72 (s, 3H), 6.77 (d, $J = 7.79$ Hz, 1H), 6.83 (t, $J = 7.33$ Hz, 1H), 7.04 (d, $J = 7.79$ Hz, 1H), 7.06 (t, $J = 7.79$ Hz, 1H).

^{13}C (100MHz, CDCl_3) $\delta(\text{ppm})$: 14.17 (2C), 22.70, 22.98, 27.29, 29.85, 32.18, 35.64, 35.89, 37.37, 55.56, 110.63, 120.59, 126.33, 127.52, 134.86, 157.77.

Micro-analysis : calcd (%) : C = 82.20, H = 11.36, O = 6.44

found (%) : C = 82.31, H = 11.22, O = 6.47

¹H (400MHz, CDCl₃) δ(ppm) : 1.48 (quint. , J = 7.33 Hz, 2H), 1.62 (quint. , J = 7.33 Hz, 2H), 1.80 (quint. , J = 7.33 Hz, 2H), 2.57 (t, J = 7.33 Hz, 2H), 3.53 (t, J = 7.33 Hz, 2H), 3.79 (s, 3H), 6.83 (d, J = 7.79 Hz, 2H), 7.10 (d, J = 7.79 Hz, 2H).

¹³C (100MHz, CDCl₃) δ(ppm) : 26.44, 30.98, 32.47, 34.77, 45.04, 55.20, 113.63, 129.20(2C), 134.36 (2C), 157.61.

Micro-analysis : calcd (%) : C = 67.76, H = 8.06, O = 7.52, Cl = 16.67

found (%) : C = 67.75, H = 8.18, O = 7.41, Cl = 16.66

¹H (400MHz, CDCl₃) δ(ppm) : 1.98 (s, 3H), 2.90 (t, J = 7.33 Hz, 2H), 3.79 (s, 3H), 4.26 (t, J = 7.33 Hz, 2H), 7.20 (d, J = 7.79 Hz, 2H), 7.27 (d, J = 7.79 Hz, 2H).

¹³C (100MHz, CDCl₃) δ(ppm) : 20.60, 34.78, 55.17, 64.65, 126.29, 128.23 (2C), 128.63 (2C), 137.54, 170.68.

Micro-analysis : calcd (%) : C = 68.02, H = 7.27, O = 24.71

found (%) : C = 68.09, H = 7.04, O = 24.87

¹H (400MHz, CDCl₃) δ(ppm) : 1.24 (t, J = 7.33 Hz, 3H), 1.36 (q, J = 7.79 Hz, 2H), 1.62 (m, 4H), 2.30 (t, J = 7.33 Hz, 2H), 2.54 (t, J = 7.79 Hz, 2H), 3.79 (s, 3H), 4.10 (q, J = 7.33 Hz, 2H), 6.82 (d, J = 8.20 Hz, 2H), 7.09 (d, J = 8.70 Hz, 2H).

¹³C (100MHz, CDCl₃) δ(ppm) : 14.18, 24.75, 28.59, 31.30, 34.20, 34.70, 55.13, 60.12, 113.54 (2C), 129.15 (2C), 134.50, 157.51, 173.76.

Micro-analysis : calcd (%) : C = 71.97, H = 8.86, O = 19.17

found (%) : C = 71.73, H = 9.07, O = 19.20

¹H (400MHz, CDCl₃) δ(ppm) : 1.17 (t, J = 7.33 Hz, 3H), 1.30 (quint., J = 7.79 Hz, 2H), 1.52 (quint., J = 7.79 Hz, 2H), 1.59 (quint., J = 7.79 Hz, 2H), 2.22 (t, J = 7.79 Hz, 2H), 2.52 (t, J = 7.79 Hz, 2H), 3.74 (s, 3H), 4.05 (q, J = 7.33 Hz, 2H), 6.76 (d, J = 7.79 Hz, 1H), 6.80 (t, J = 7.33 Hz, 1H), 7.04 (d, J = 7.33 Hz, 1H), 7.09 (t, J = 7.79 Hz, 1H).

¹³C (100MHz, CDCl₃) δ(ppm) : 14.23, 24.84, 29.00, 29.40, 29.94, 34.32, 55.19, 60.13, 110.17, 120.28, 126.84, 129.72, 130.93, 157.39, 173.90.

Micro-analysis : calcd (%) : C = 71.97, H = 8.86, O = 19.17

found (%) : C = 72.15, H = 8.93, O = 18.92

¹H (400MHz, CDCl₃) δ(ppm) : 1.12 (t, J = 7.33 Hz, 3H), 1.15 (t, J = 7.33 Hz, 3H), 1.38 (m, 2H), 1.65 (m, 4H), 2.27 (t, J = 7.33 Hz, 2H), 2.61 (t, J = 7.79 Hz, 2H), 3.27 (q, J = 7.33 Hz, 2H), 3.35 (q, J = 7.33 Hz, 2H), 7.17 (m, 3H), 7.26 (m, 2H).

¹³C (100MHz, CDCl₃) δ(ppm) : 13.03, 14.30, 25.53, 29.06, 31.30, 32.94, 35.72, 39.91, 41.81, 125.51, 128.14 (2C), 128.32 (2C), 142.57, 172.04.

Micro-analysis : calcd (%) : C = 77.68, H = 10.19, O = 6.47, N = 5.66

found (%) : C = 77.54, H = 10.57, O = , N = 5.54

¹H (400MHz, CDCl₃) δ(ppm) : 1.07 (d, J = 6.87 Hz, 6H), 1.31 (quint., J = 7.33 Hz, 2H), 1.58 (quint., J = 7.79 Hz, 4H), 2.41 (t, J = 6.87 Hz, 2H), 2.54 (m, 3H), 3.77 (s, 3H), 6.81 (d, J = 8.70 Hz, 2H), 7.07 (d, J = 8.70 Hz, 2H).

^{13}C (100MHz, CDCl_3) $\delta(\text{ppm})$: 18.20 (2C), 23.53, 28.77, 31.51, 34.74, 40.17, 40.73, 55.15, 113.54 (2C), 129.16 (2C), 134.59, 157.51, 215.00.

Micro-analysis : calcd (%) : C = 77.38, H = 9.74, O = 12.88

found (%) : C = 77.59, H = 9.49, O = 12.92

^1H (400MHz, CDCl_3) $\delta(\text{ppm})$: 0.99 (d, $J = 6.87$ Hz, 6H), 1.26 (quint., $J = 6.87$ Hz, 2H), 1.53 (m, 4H), 2.37 (t, $J = 6.87$ Hz, 2H), 2.53 (t, $J = 6.87$ Hz, 2H), 3.70 (m, 1H), 3.72 (s, 3H), 6.75 (d, $J = 7.79$ Hz, 1H), 6.79 (t, $J = 7.33$ Hz, 1H), 7.03 (d, $J = 7.33$ Hz, 1H), 7.07 (t, $J = 7.79$ Hz, 1H).

^{13}C (100MHz, CDCl_3) $\delta(\text{ppm})$: 18.25 (2C), 23.67, 29.17, 29.59, 29.99, 40.26, 40.79, 55.19, 110.17, 120.27, 126.83, 129.73, 130.98, 157.42, 215.09.

Micro-analysis : calcd (%) : C = 77.38, H = 9.74, O = 12.88

found (%) : C = 77.71, H = 9.52, O = 12.77

4- References

1. Watson, S. C.; Eastham, J. F. *J. Organometal. Chem.* 1967, 9, 165.