

SUPPLEMENTARY INFORMATION

Ni(II)/Al(0) Mediated Benzylic Csp³-Csp³ Coupling in Aqueous Media

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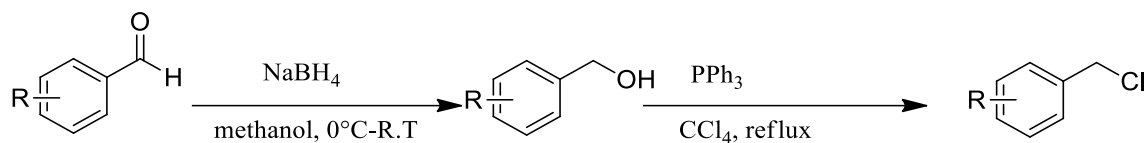
General Methods

Solvents were distilled before use. All other reagents (Sigma Aldrich or Spectrochem) were used as received. Ultrapure distilled water (Millipore-Q) was used to prepare aqueous solution. All reactions requiring inert atmosphere were carried out under argon atmosphere. Reactions were monitored by Thin Layer Chromatography (TLC) on 0.25 mm silica gel plates (60 F254 grade) with UV light as detecting agent. Silica gel (100–200 mesh) was used for column chromatography. ¹H (400 MHz), ¹³C (101 MHz) NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: δ 7.261 ppm). Data are reported as follows: chemical shifts, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), coupling constant (Hz). ¹³C chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: δ 77.0 ppm).

Preparation of Starting Materials

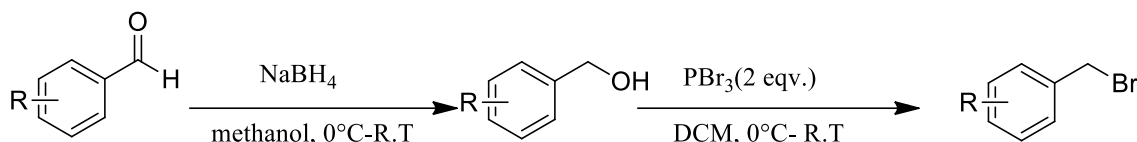
All organic reactions presented hereafter were conducted in small scale. Reaction parameters such as catalyst concentration and solvent were varied to obtain better results. In most cases, the reaction progress was monitored by TLC.

Scheme 1.1.1: Preparation of Benzyl Chloride Derivatives



Benzyl alcohol derivatives were prepared from the corresponding aldehydes and NaBH₄ in methanol medium. Benzyl chloride derivatives were prepared using Appel reaction involving triphenyl phosphine and CCl₄. The final product was purified by column chromatography.

Scheme 1.1.2: Preparation of Benzyl Bromide Derivatives



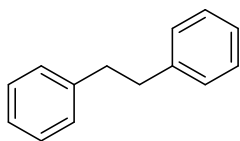
Benzyl bromide derivatives were prepared using Phosphorous tribromide (PBr₃) in DCM medium. The final product was purified by column chromatography.

1.2 General Procedure for the Homo-Coupling of Benzyl halides

To a suspension of aluminium powder (1.2 eq) in water (5 mL), Ni(NO₃)₂·6H₂O (10 mol%) was added and the reaction mixture was degassed using argon. The suspension was stirred at room temperature for 5 min. Benzyl halide (3 mmol) was added slowly to the reaction mixture, and the mixture was stirred at room temperature for 48 h under argon. The mixture slowly turned into a clear solution and the bibenzyl crystals were seen to be floating on top of the solution. The mixture was quenched with hydrochloric acid (4M, 5 mL) and extracted with dichloromethane. The combined organic extract was washed with water and dried over Na₂SO₄. The solvent was removed and the residue was purified by chromatography or recrystallization. All products gave satisfactory spectroscopic data and were compared with authentic sample wherever available.

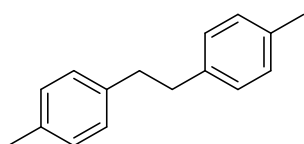
Spectral Data for Coupling Products

1, 2-Diphenylethane (2a):¹



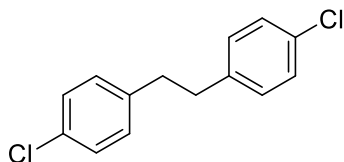
White solid; ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.22 (m, *J* = 11.4, 4.6, 2.7 Hz, 4H), 7.22 – 7.14 (m, 6H), 2.90 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 141.81, 128.47, 128.35, 125.93, 37.97.

1, 2-Di-*p*-tolylethane (2b):¹



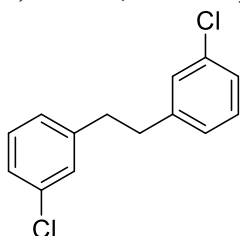
White Solid; ¹H NMR (400 MHz, CDCl₃) δ 7.09 (s, 8H), 2.86 (s, 4H), 2.32 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 138.89, 135.32, 129.02, 128.31, 37.66, 21.04.

1, 2-Bis-(4-chlorophenyl) ethane (2c):²



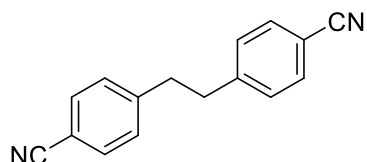
White solid; ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, *J* = 8.4 Hz, 4H), 7.04 (d, *J* = 8.4 Hz, 4H), 2.85 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 139.63, 131.78, 129.86, 128.47, 37.05.

1, 2-Bis-(3-chlorophenyl) ethane (2d):³



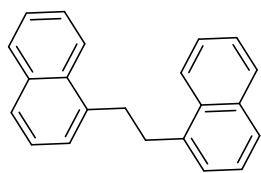
White solid; ¹H NMR (400 MHz, CDCl₃) δ 7.21–7.14 (m, 6H), 7.06–7.01 (m, 2H), 2.87 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 142.10, 134.12, 129.62, 128.51, 126.61, 126.35, 37.21.

1, 2-Di-(4-cyanophenyl) ethane (2e):⁴



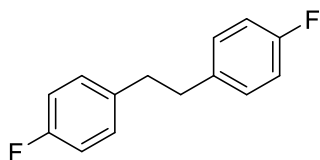
White solid; ^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, $J = 8.4$ Hz 4H), 7.21 (d, $J = 8.4$ Hz 4H), 2.97 (s, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 146.02, 132.22, 129.21, 118.74, 110.20, 37.17.

1, 2-Di-(naphthalen-1-yl) ethane (2f):⁵



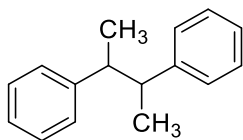
White solid; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (dd, $J = 8.1, 1.0$ Hz, 2H), 7.91–7.88 (m, 2H), 7.76 (d, $J = 8.1$ Hz, 2H), 7.57–7.48 (m, 3H), 7.44–7.34 (m, $J = 8.3, 7.5, 4.2$ Hz, 3H), 3.58 – 3.49 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.00, 132.9, 131.50, 128.64, 126.63, 125.90, 125.74, 125.61, 125.50, 122.05, 35.10

1, 2-Bis-(4-fluorophenyl) ethane (2g):⁵



White solid; ^1H NMR (400 MHz, CDCl_3) δ 7.10–7.04 (m, 4H), 6.98–6.91 (m, 4H), 2.86 (s, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.56, 160.14, 136.94, 129.87, 129.79, 115.17, 114.96, 37.15.

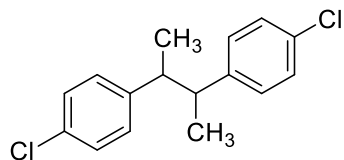
Butane-2, 3-diyl dibenzene (2h):^{1, 6}



White solid; ^1H NMR (400 MHz, CDCl_3) δ 7.34–7.27 (m, 2H), 7.24–7.12 (m, 5H), 7.11–7.05 (m, 1H), 7.00 (dt, $J = 3.2, 2.0$ Hz, 2H), 2.97–2.89 (m, 1H), 2.84–2.75 (m,

1H), 1.29–1.25 (m, 3H), 1.04–1.00 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 146.56, 145.90, 128.37, 127.91, 127.86, 127.69, 126.13, 125.78, 47.34, 46.55, 21.13, 18.03.

4, 4'-(butane-2, 3-diyl)-bis-(chlorobenzene) (2i)



White solid; ¹H NMR (400 MHz, CDCl₃) δ 7.27–7.23 (m, 2H), 7.13–7.06 (m, 4H), 6.88–6.84 (m, 2H), 2.87–2.79 (m, 1H), 2.78–2.69 (m, 1H), 1.24 (dd, *J* = 6.7, 4.9 Hz, 3H), 0.99 (dd, *J* = 4.6, 1.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.43, 143.90, 131.80, 131.49, 129.14, 128.97, 128.49, 128.05, 46.58, 46.04, 20.63, 18.75.

Figure S1a. *In situ* monitoring of reaction: spectrum showing the formation of bibenzyl and benzyl bromide (for details see text)

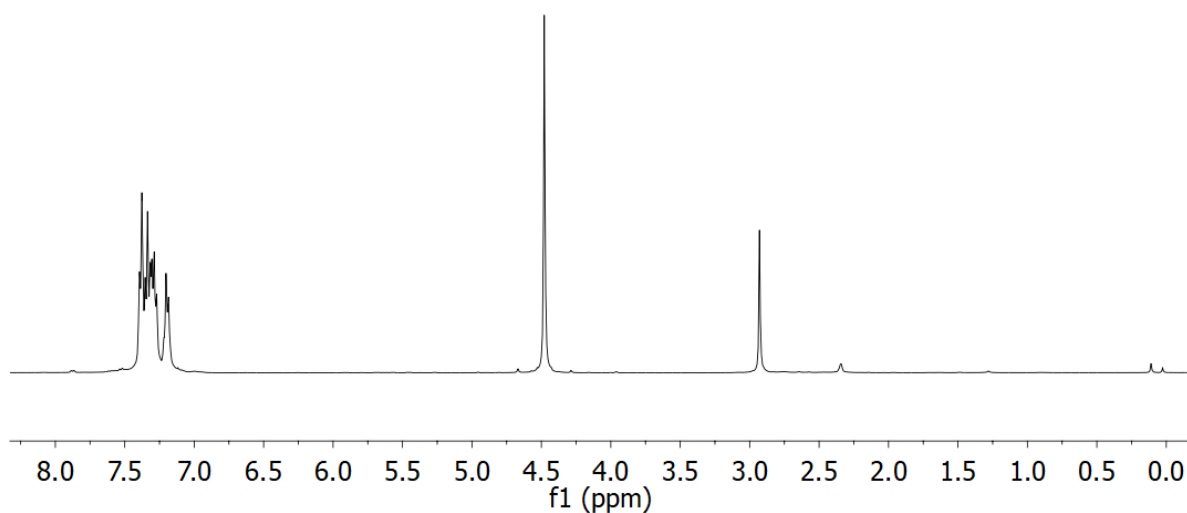
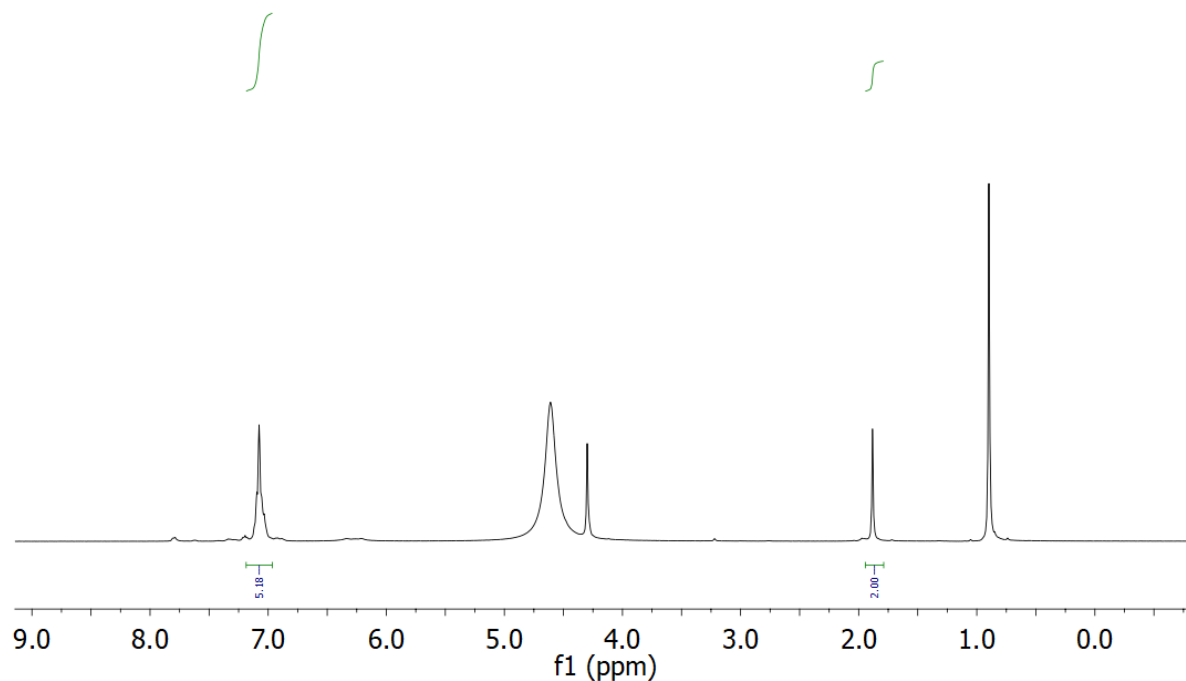


Figure S1b. *In situ* monitoring of reaction: spectrum showing the formation of benzylaluminium species (for details see text)



References

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