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Supporting Information

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TRANSITION-METAL FREE SUZUKI – TYPE COUPLING REACTIONS

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Experimental details

^{1}H and ^{13}C NMR data for the compounds prepared

Experimental details

General experimental: All reactions were carried out in air and all chemicals were used as purchased. Microwave reactions were conducted using a focused microwave unit. The machine consists of a continuous focused microwave power delivery system with operator selectable power output from 0-300 W. Reactions were performed in glass vessels (capacity 10 mL) sealed with a septum. The pressure is controlled by a load cell connected to the vessel *via* a 14-gauge needle which penetrates just below the septum surface. The temperature of the contents of the vessel was monitored using a calibrated infrared temperature control mounted under the reaction vessel. All experiments were performed using a stirring option whereby the contents of the vessel are stirred by means of a rotating magnetic plate located below the floor of the microwave cavity and a Teflon-coated magnetic stir bar in the vessel. For more detailed description of the apparatus see: http://www.cemsynthesis.com. Conventional heating experiments were performed in an oil bath using identical reaction vessels to those used for the microwave experiments. The oil was pre-heated before placing the reaction vessel in. ^{1}H and ^{13}C NMR spectra were recorded at 293 K on a Bruker Advance 360 MHz spectrometer. Product yields refer to isolated yields of compounds estimated to be ≥95% pure as determined by ^{1}H and ^{13}C NMR analysis. Products were characterized by comparison of ^{1}H and ^{13}C NMR data with that in the literature.¶

General procedure for the microwave-assisted reactions: In a 10 mL glass tube was placed aryl halide (1.0 mmol), arylboronic acid (1.3 mmol), Na_2CO_3 (400 mg, 3.8 mmol), tetrabutylammonium bromide (322 mg, 1.0 mmol), 2 mL water and a magnetic stir bar. The vessel was sealed with a septum and placed into the microwave cavity. Microwave irradiation of 100 W was used, the temperature being ramped from r.t. to 150 ºC. Once 150 ºC was reached, the reaction mixture was held at this temperature for 5 min. After allowing the mixture to cool to room temperature, the reaction vessel was opened and the contents poured into a separating funnel. Water and diethyl ether (30 mL of each) were added and the organic material extracted and removed. After further extraction of the aqueous layer with ether, combining the organic washings and drying them over $MgSO_4$, the ether was removed *in-vacuuo* leaving the crude product. The product was purified and isolated by chromatography after, in the cases where the starting aryl halide was a liquid, firstly removing un-reacted aryl halide by heating the crude residue whilst under a vacuum on a Schlenk line.

General procedure for the conventionally heated reactions on a 1 mmol scale: The method was as for the microwave-assisted procedure except that after sealing the tube with a septum it was placed into an oil bath pre-heated to 150 ºC rather than into the microwave cavity. The reaction mixture was held in the oil for the specified time before removing, allowing the vessel and contents to cool and then the product extracted and purified in an identical manner to that in the microwave protocol.

Spectroscopic data

Biphenyl: ^{1}H NMR ($CDCl_3$) δ 7.77-7.74 (m, 4H), 7.61-7.56 (m, 4H), 7.52- 7.47 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 141.76, 129.32, 127.80, 127.71.

4-Nitrobiphenyl: ^{1}H NMR ($CDCl_3$) δ 8.12-8.09 (m, 2H), 7.57-7.53 (m, 2H), 7.48- 7.44 (m, 2H), 7.37-7.27 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 147.96, 147.42, 139.07, 129.59, 129.38, 128.16, 127.79, 124.49.

4-Acetylbiphenyl: ^{1}H NMR ($CDCl_3$) δ 7.86&7.84 (d, J= 8.4 Hz, 2H), 7.51-7.44 (m, 4H), 7.38- 7.21 (m, 3H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 198.16, 146.17, 140.26, 136.25, 129.36, 129.32, 128.64, 127.67, 127.62, 27.06.

4-Methylbiphenyl: ^{1}H NMR ($CDCl_3$) δ 7.73 (dd, J_1= 7.3 Hz, J_2= 1.5 Hz, 2H), 7.65&7.62 (d, J= 8.0 Hz, 2H), 7.58-7.53 (m, 2H), 7. 45 (dd, J_1= 7.3 Hz, J_2= 1.5 Hz, 1H), 7.37&7.33 (d, J= 8.0 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 141.66, 138.86, 137.50, 130.00, 129.23, 127.51, 127.48, 21.62.

2-Methylbiphenyl: ^{1}H NMR ($CDCl_3$) δ 7.56- 7.51 (m, 2H), 7.50-7.48 (m, 3H), 7.44-7.40 (m, 4H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 140.89, 140.86, 134.26, 129.24, 128.73, 128.12, 127.00, 126.18, 125.69, 124.70, 19.41.

4-Methoxylbiphenyl: ^{1}H NMR ($CDCl_3$) δ 7.69-7.64 (m, 4H), 7.55-7.51 (m, 2H), 7.42 (t, J= 7.3 Hz, 1H), 7.10&7.08 (d, J=8.7 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 160.32, 141.64, 134.89, 129.93, 129.32, 127.90, 127.85, 115.38, 56.45.

3-Methoxylbiphenyl: ^{1}H NMR ($CDCl_3$) δ 7.74&7.72 (d, J=7.6 Hz, 2H), 7.58-7.54 (m, 2H), 7.50-7.46 (m, 2H), 7.33&7.31 (d, J=7.8 Hz, 1H), 7.28 (s, 1H), 7.04&7.02 (dd, J_1= 8.2 Hz, J_2= 2.5 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 160.46, 143.23, 141.60, 130.29, 129.27, 127.94, 127.71, 120.19, 13.41, 113.17, 55.74.

2-Methoxylbiphenyl: ^{1}H NMR ($CDCl_3$) δ 7.44-7.42 (m, 2H), 7.32-7.28 (m, 2H), 7.23-7.18 (m, 3H), 6.94-6.85 (m, 2H), 3.68 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 156.92, 139.02, 131.37, 131.19, 130.04, 129.11, 128.47, 127.40, 121.31, 111.68, 55.99.

4-Aminobiphenyl: ^{1}H NMR ($CDCl_3$) δ 7.69-7.66 (m, 2H), 7.55-7.50 (m, 4H), 7.42-7.38 (m, 1H), 6.84&6.82 (d, J= 8.5 Hz, 2H), 3.77 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 146.42, 141.66, 131.93, 129.23, 128.50, 126.91, 126.79, 115.91.

Biphenyl-4-carbaldehyde: ^{1}H NMR ($CDCl_3$) δ 9.89 (br s, 1H), 7.80&7.78 (d, J= 8.2 Hz, 2H), 7.60&7.57 (d, J= 8.2 Hz, 2H), 7.49-7.47 (m, 2H), 7.36-7.25 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 192.35, 147.53, 140.07, 135.60, 130.69, 129.46, 128.92, 128.07, 127.78.

Biphenyl-4-carboxylic acid methyl ester: ^{1}H NMR ($CDCl_3$) δ 7.98&7.96 (d, J= 8.4 Hz, 2H), 7.52-7.46 (m, 4H), 7.33-7.24 (m, 3H), 3.79 (s, 3H).

4-Carboxybiphenyl: ^{1}H NMR (d_6- DMSO) δ 13 (br s), 8.08&8.06 (d, J= 8.2 Hz, 2H), 7.76&7.74 (d, J= 8.2 Hz, 2H), 7.68&7.66 (d, J= 7.4 Hz, 2H), 7.45-7.34 (m, 3H); ^{13}C NMR (d_6- DMSO) δ 169.21, 146.28, 140.99, 131.97, 131.62, 130.97, 130.17, 128.88, 128.71.

2,6-Dimethylbiphenyl: ^{1}H NMR ($CDCl_3$) δ 7.57-7.53 (m, 2H), 7.48-7.46 (m, 1H), 7.30-7.23 (m, 5H), 1.94 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 140.79, 140.02, 134.95, 127.94, 127.34, 126.21, 125.96, 125.53, 19.78.

2-Phenylpyridine: ^{1}H NMR ($CDCl_3$) δ 8.63-8.61 (m, 1H), 7.93-7.90 (m, 2H), 7.69-7.64 (m, m, 2H), 7.42-7.32 (m, 3H), 7.18-7.13 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 157.88, 150.07, 139.79, 137.16, 129.35, 129.15, 127.32, 122.51, 121.00.

4-Acetyl- 4'-methylbiphenyl: ^{1}H NMR ($CDCl_3$) δ 7.85&7.82 (d, J= 8.4 Hz, 2H), 7.49&7.47 (d, J= 8.4 Hz, 2H), 7.36&7.34 (d, J= 8.1 Hz, 2H), 7.11&7.09 (d, J= 8.1 Hz, 2H), 2.44 (s, 3H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 198.12, 146.04, 138.64, 137.27, 135.97, 130.14, 129.35, 127.50, 127.31, 27.03, 21.61

¶ Literature NMR data for comparison

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