EXPERIMENTAL

General Methods: All experiments were carried out under an atmosphere of dry argon. Toluene and benzene were distilled under an atmosphere of dry argon from molten sodium. Chlorobenzene was distilled under an atmosphere of dry argon from calcium chloride. All chemicals were purchased from Aldrich Chemical company and were used without purification. ^{1}H and ^{13}C were recorded on a Varian UNITY 300 MHz or a VARIAN 500 MHz spectrometers.

General Procedure for the Preparation of Biaryl Compounds 5a-k. Method A (Scheme 2, Table 1). A solution of TTMSS (0.992 g, 4 mmol), AIBN (0.656 g, 4 mmol), the corresponding bromide **2a-f** (2 mmol) in 10 mL of the adequate solvent **4a-c**, was added dropwise by a syringe pump during 8 h, to 20 mL of the same **4a-c** solvent, stirred at 80 ºC (bath temperature). After being stirred at the same temperature until 24 h, full consumption of **2** was observed (TLC analysis). The pale yellow solution was concentrated *in vacuo*, providing a crude product that was purified using flash chromatography to yield the corresponding biaryl compound **5**.

2-Phenylpyridine 5a[1] The general procedure using **2a** (0.316 g) as bromide and benzene (**4a)** as solvent gave, after flash chromatography (silicagel, hexanes:ethyl acetate (90:10)), a colorless liquid (127 mg, 41%). This product was identical in all respects to an authentic sample obtained from Aldrich. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.69 (td, 1 H, *J*= 4.7 and 1.4 Hz), 8.01 (dd, 2 H, *J*= 8.4 and 1.6 Hz), 7.69 (m, 2 H), 7.45 (m, 3 H), 7.19 (dd, 1 H, *J*= 8.8 and 4.7 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 157.1, 149.4, 139.2, 136.5, 128.8, 128.5, 126.7, 121.8, 120.3.

3-Phenylpyridine 5b[1,2] The general procedure using **2b** as bromide (0.316 g) and benzene (**4a)** as solvent gave, after flash chromatography (silicagel, hexanes:ethyl acetate (80:20)), a colorless liquid (230 mg, 74%). This product was identical in all respects to an authentic sample obtained from Aldrich**.** ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.83 (dd, 1 H, *J*= 2.6 and 0.9 Hz), 8.57 (dd, 1 H, *J*= 4.9 and 1.6 Hz), 7.85 (ddd, 1 H, *J*= 7.7, 2.6 and 1.6 Hz), 7.56 (dd, 2 H, *J*= 8.2 and 1.4 Hz), 7.45 (m, 3H), 7.34 (ddd, 1 H, *J*= 7.7, 4.9 and 0.9 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 148.3, 148.2, 137.7, 136.4, 134.2, 128.9, 127.9, 127.0, 123.3.

4-Phenylpyridine 5c[3] The general procedure using **2c** as bromide (0.316 g of the base free, freshly obtained from the comercial avaible 4-bromopyridine hydrochloride) and benzene (**4a)** as solvent gave, after flash chromatography (silicagel, hexanes:ethyl acetate (80:20)), a white solid (m.p= 70-72 ºC) (171 mg, 55%). This product was identical in all respects to an authentic sample obtained from Aldrich**.** ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.55 (dd, 2 H, *J*= 4.4 and 1.6 Hz), 7.53 (m, 2 H), 7.37 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 149.9, 147.8, 137.6, 128.8, 128.7, 126.6, 121.2.

2-(2´-Chlorophenyl)pyridine 5d[4,5] **and 2-(4´-chlorophenyl)pyridine 5e**[4] The general procedure using **2a** as bromide (0.316 g) and chlorobenzene (**4b)** as solvent, gave a mixture of products. After separation by flash chromatography (silicagel, hexanes:ethyl acetate (90:10), pure compounds **5d** and **5e** were obtained (296 mg (78%) of **5d** (Rf= 0.35) and 23 mg (6 %) of **5e** (Rf= 0.45)). **5d** ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.73 (ddd, 1 H, *J*= 5.0, 1.7 and 1.1 Hz), 7.75 (dt, 1 H, *J*= 8.7 and 1.7 Hz), 7.63 (td, 1 H, *J*= 7.7 and 1.1 Hz), 7.57 (m, 1 H), 7.46 (m, 1 H), 7.33 (m, 2 H), 7.27 (ddd, 1 H, *J*= 7.7, 5.0 and 1.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 156.9, 149.5, 139.2, 135.8, 132.1, 131.5, 130.0, 129.4, 127.0, 124.8, 122.3. **5e** ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.67 (d, 1 H, *J*= 4.5 Hz), 7.93 (d, 2 H, *J*= 8.6 Hz), 7.75 (dt, 1 H, *J*= 7.2 and 1.6 Hz), 7.69 (bd, 1 H, *J*= 7.2 Hz), 7.44 (d, 2 H, *J*= 8.6 Hz), 7.24 (ddd, 1 H, *J*= 7.2, 4.5 and 1.6 Hz).

2-(2´-Methylphenyl)pyridine 5f,[4-6] **2-(3´-methylphenyl)pyridine 5g**[4,5] **and 2-(4´-methylphenyl)pyridine 5h.**[4-6] The general procedure using **2a** as bromide (0.316 g) and toluene (**4c)** as solvent gave a mixture of products. After

separation by flash chromatography (silicagel, dichloromethane:ethyl acetate (100:2.5)), pure compounds **5f**, **5g** and **5h** were obtained (101 mg (30 %) of **5f** (Rf= 0.35), 54 mg (16 %) of **5g** (Rf= 0.41) and 51 mg (15 %) of **5h** (Rf= 0.40)). **5f** ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.68 (ddd, 1 H, *J*= 4.8, 1.8 and 1.0 Hz), 7.72 (dt, 1 H, *J*= 7.7 and 1.8 Hz), 7.37 (td, 1 H, *J*= 7.7 and 1.0 Hz), 7.36 (m, 1 H), 7.27 (m, 3 H), 7.22 (ddd, 1 H, *J*= 7.7, 4.8 and 1.0 Hz), 2.34 (s, 3H). **5g** ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.68 (ddd, 1 H, *J*= 4.8, 1.5 and 1.0 Hz), 7.82 (bs, 1 H), 7.73 (dt, 1 H, *J*= 8.0 and 1.5 Hz), 7.70 (m, 2 H), 7.34 (t, 1 H, *J*= 7.6 Hz), 7.21 (m, 1 H), 7.20 (ddd, 1 H, *J*= 8.0, 4.8 and 1.9 Hz), 2.42 (s, 3H). **5h** ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.67 (d 1 H, *J*= 4.4 Hz), 7.86 (d, 2 H, *J*= 8.1 Hz), 7.70 (m, 2 H), 7.26 (d, 2 H, *J*= 8.1 Hz), 7.20 (m, 1 H), 2.44 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 157.2, 149.3, 138.6, 136.4, 136.3, 129.2, 126.5, 121.5, 120.0, 21.0.

4-Methylbiphenyl 5i[7-9] The general procedure using **2d** as bromide (0.342 g) and benzene (**4a)** as solvent gave, after flash chromatography (silicagel, hexanes:ethyl acetate (95:5)), a white solid (m.p= 46-47 ºC)(171 mg, 51%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, 2 H, *J*= 8.3 and 1.2 Hz), 7.50 (d, 2 H, *J*= 8.1 Hz), 7.42 (t, 2 H, *J*= 8.3 Hz), 7.31 (td, 1 H, *J*= 8.3 and 1.2 Hz), 7.25 (d, 2 H, *J*= 8.1 Hz), 2.39 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 142.4, 139.6, 138.1, 130.4, 129.7, 127.9, 127.8, 127.7, 21.1.

4-Methoxylbiphenyl 5j[8,10,11] The general procedure using **2e** as bromide (0.374 g) and benzene (**4a)** as solvent gave, after flash chromatography (silicagel, hexanes:ethyl acetate (95:5)), a white solid (m.p= 86-87 ºC)(184 mg, 50%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.56 (m, 4 H), 7.43 (t, 2 H, *J*= 7.5 Hz), 7.32 (tt, 1 H, *J*= 7.5 and 1.2 Hz), 6.99 (d, 2 H, *J*= 8.8 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.1, 55.3.

Biphenyl 4-carboxylic acid methyl ester 5k [12-15] The general procedure using **2f** as bromide (0.430 g) and benzene (**4a)** as solvent gave, after flash chromatography (silicagel, hexanes:ethyl acetate (95:5)), a white solid (m.p= 76-77 ºC)(220 mg, 52%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.04 (d, 2 H, *J*= 8.4 Hz), 7.59 (d, 2 H, *J*= 8.4 Hz), 7.56 (dd, 2 H, *J*= 7.4 and 1.3 Hz), 7.44 (dd, 2 H, *J*= 7.4 and 7.2 Hz), 7.33 (tt, 1 H, *J*= 7.2 and 1.3 Hz), 3.89 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 166.9, 145.5, 139.9, 130.0, 128.8, 128.6, 128.1, 127.2, 126.9, 52.0.

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