Supporting Information

For

Synthesis of Ortho Substituted Arylboronic Esters by In Situ Trapping of Unstable Lithio Intermediates.

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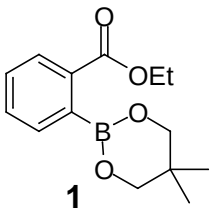
General Methods. All reactions involving air-sensitive reagents were performed under N_2 using syringe-septum cap techniques. All glassware was flame-dried prior to use. Flash column chromatography (FC) was performed using silica gel (Merck, 40-63 mesh). TLC was performed using Merck silica gel 60 F_{254} aluminum sheets. Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ on a 300 MHz Varian spectrometer with tetramethylsilane/$CDCl_3$ as internal standards. For clarity the coupling patterns are reported as they appear. For AA'XX' coupling patterns $J_{app} = J_{AX} + J_{AX'}$ is reported. The multiplicity of ^{13}C-NMR signals were assigned from APT-spectra.

Materials. All solvents and reagents were obtained from Fluka or Aldrich and used without further purification except THF which was distilled from Na/benzophenone under nitrogen. $Pd(PPh_3)_4$ was prepared as previously described.[1]

General Procedure for preparation of ortho substituted arylboronic esters:

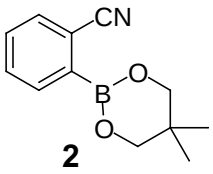
To a solution of 2,2,6,6-tetramethylpiperidine (38.8 mmol, 6.54 mL) in THF (40 mL), 1.6 M *n*-Butyllithium (37.5 mmol, 23.4 mL) was added at –10°C. The mixture was stirred for 10 min and cooled to –78°C before $B(O\text{-}iPr)_3$ (50 mmol, 11.5 mL) was added. Stirring was continued for 5 min before the substrate (25 mmol) was added neat via syringe. The mixture was stirred at –78°C for 2 hours and subsequently warmed to rt over 3-4 hours and quenched with saturated NH_4Cl (100 mL). Extraction with EtOAc (3 x 100 mL), drying of the combined organic phases (Na_2SO_4) and evaporation of the

solvent. The crude product was dissolved in toluene (100 mL) and 2,2-dimethyl-1,3-propandiol (30 mmol, 3.13 g) was added. The mixture was stirred overnight at rt. The toluene phase was washed with water (3 x 50 mL) and the combined aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The CH_2Cl_2-phase was washed once with water (50 mL) and combined with the toluene extract from above. Drying (Na_2SO_4) and removal of the solvent gave the crude products.



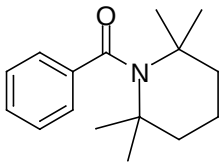
1

Ethyl benzoate yielded ethyl 2-(5,5-dimethyl-[1,3,2]dioxaborinan-2-yl)-benzoate (**1**) as a yellow oil, which was analytically pure. Yield: 92 %. ^{1}H NMR (300 MHz, $CDCl_3$): 7.93 (td, 1H, *J* = 7.8, 0.9 Hz), 7.48-7.52 (m, 2H), 7.35-7.42 (m, 1H), 4.38 (q, 2H, *J* = 7.1 Hz), 3.79 (s, 4H), 1.39 (t, 3H, *J* = 7.1 Hz), 1.11 (s, 6H). ^{13}C NMR(75 MHz, $CDCl_3$): 168.6 (s), 133.1 (s), 131.9 (d), 131.2 (d), 128.6 (d), 128.3 (d), 72.4 (t), 61.6 (t), 31.6 (s), 21.9 (q), 14.2 (q). Anal. calcd. for $C_{14}H_{19}BO_4$ (crude product): C 64.15, H 7.31. Found C 63.78, H 7.27.

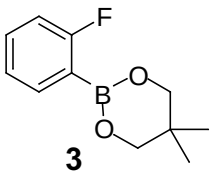


2

Benzonitrile yielded a 3.5:1 mixture of 2-(5,5-dimethyl-[1,3,2]dioxaborinan-2-yl)-benzonitrile (**2**) and *N*-benzoyl-2,2,6,6-tetramethylpiperidine (see below). Recrystalization from heptane gave off-white crystals, mp 112˚C. Yield: 61 %. ^{1}H NMR(300 MHz, $CDCl_3$): 7.87-7.92 (m, 1H), 7.68 (ddd, 1H, *J* = 7.3, 1.6, 0.6), 7.56 (td, 1H, *J* = 7.5, 1.5 Hz), 7.49 (td, 1H, *J* = 7.5, 1.5 Hz), 3.84 (s, 4H), 1.05 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 135.1 (d), 133.6 (d), 131.5 (d), 130.5 (d), 119.6 (s), 116.6 (s), 72.4 (t), 31.6 (s), 21.6 (q). Anal. calcd. for $C_{12}H_{14}NBO_2$: C 67.02, H 6.56, N 6.51. Found: C 67.15 H 6.42, N 6.51.

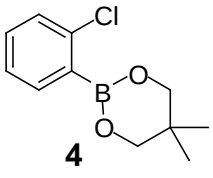


N-benzoyl-2,2,6,6-tetramethylpiperidine: ^{1}H NMR (300 MHz, $CDCl_3$): 7.75-7.85 (m, 2H), 7.30-7.30 (m, 3H), 1.71-1.79 (m, 2H), 1.57-1.62 (m, 4H), 1.21 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.5 (s), 143.7 (s), 129.7 (d), 128.0 (d), 127.8 (d), 55.0 (s), 40.5 (t), 29.4 (q), 17.4 (t).



3

Fluorobenzene yielded 2-(2-fluorophenyl)-5,5-dimethyl-[1,3,2]dioxaborinane (**3**) as slightly orange crystals, which were analytically pure, mp 37-40°C. Yield: 98 %. Recrystalization from heptane gave white crystals, mp 40°C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.69-7.76 (m, 1H), 7.39 (dddd, 1H, *J* = 8.3, 7.3, 5.5, 1.9 Hz), 7.11 (tt, 1H, *J* = 7.3, 0.7 Hz), 7.00 (m, 1H), 3.80 (s, 4H), 1.04 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 167.3 (s($d_{C\text{-}F}$), $J_{C\text{-}F}$ = 249 Hz), 136.3 (d($d_{C\text{-}F}$), $J_{C\text{-}F}$ = 8 Hz), 132.5 (d($d_{C\text{-}F}$), $J_{C\text{-}F}$ = 9 Hz), 123.5 (d($d_{C\text{-}F}$), $J_{C\text{-}F}$ = 3 Hz), 115.3 (d($d_{C\text{-}F}$), $J_{C\text{-}F}$ = 25 Hz), 72.3 (t), 31.6 (s), 21.6 (q). Anal. calcd. for $C_{11}H_{14}BFO_2$ (crude product): C 63.51, H 6.78. Found: C 63.46, H 6.80.



4

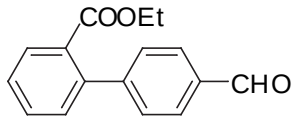
Chlorobenzene yielded 2-(2-chlorophenyl)-5,5-dimethyl-[1,3,2]dioxaborinane (**4**) as slightly orange crystals, which were analytically pure, mp 35°C. Yield: 96%. Recrystalization from heptane gave white crystals mp 36°C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.63 (dd, 1H, *J* = 7.4, 1.6 Hz), 7.30-7.36 (m, 1H), 7.28 (td, 1H, *J* = 7.0, 1.8 Hz), 7.20 (td, 1H, *J* = 7.1, 1.6 Hz), 3.79 (s, 4H), 1.04 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 138.6 (s), 135.5 (d), 131.1 (d), 129.4 (d), 125.8 (d), 72.4 (t), 31.6 (s), 21.7 (q). Anal.

cacld. for $C_{11}H_{14}BClO_2$ (crude product): C 58.85, H 6.29. Found C 59.13, H 6.09

General Procedures for preparation of biaryls:

General Procedure A:

In a nitrogen atmosphere the boronic ester **1** (1 mmol) and the appropriate aryl halide (1.2 mmol) were dissolved in dioxane (10 mL) and $K_3PO_4 \cdot 3H_2O$ (2 mmol, 532 mg) and $Pd(PPh_3)_4$ (3 mol%, 35 mg) were added. The reaction mixture was stirred at 100 ^oC for 4 h, and then cooled to room temperature. Addition of sat. aqueous NH_4Cl (25 mL) followed by extraction with EtOAc (3x20 mL), drying ($MgSO_4$) and evaporation *in vacuo* provided the crude product which was purified by column chromatography (heptane/EtOAc, 10:1).

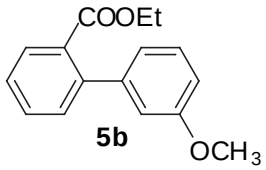


5a

4'-Formyl-biphenyl-2-carboxylic acid ethyl ester (5a): Boronic ester **1** and 4-bromobenzaldehyde (table 2, entry 1) produced 204 mg (80%) (**5a**) as a colorless oil. A correct microanalysis could not be obtained, ^{1}H-NMR spectrum included.

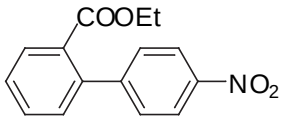
R_f (heptane:EtOAc, 3:1) 0.40. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.95-7.90 (m, 3H), 7.57 (dt, 1H, *J* = 1.4, 7.5 Hz), 7.51-7.45 (m, 3H), 7.36 (d, 1H, *J* = 7.5 Hz), 4.10 (q, 2H, 7.1 Hz), 1.03 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1 (d), 168.0

(s), 148.1 (s), 141.4 (s), 135.1 (s), 131.5 (d), 130.7 (s), 130.4 (d), 130.2 (d), 129.4 (d), 129.2 (d), 128.1 (d), 60.9 (t), 13.5 (q).



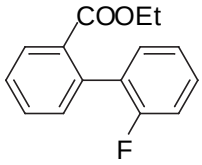
5b

3'-Methoxy-biphenyl-2-carboxylic acid ethyl ester (**5b**)**:** Boronic ester **1** and 3-iodoanisole (table 2, entry 2) produced 192 mg (75%) of **5b** as a colorless oil.[2] R_f (heptane:EtOAc, 3:1) 0.51. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, 1H, *J* = 7.6, 1.5 Hz), 7.52 (tt, 1H, *J* = 7.5, 1.5 Hz), 7.45-7.36 (m, 2H), 7.29 (t, 1H, *J* = 8.1 Hz), 6.94-6.85 (m, 3H), 4.10 (q, 2H, *J* = 7.1 Hz), 3.82 (s, 3H), 1.03 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0 (s), 159.4 (s), 142.9 (s), 142.2 (s), 131.5 (s), 131.1 (d), 130.5 (d), 129.6 (d), 129.0 (d), 127.3 (d), 121.0 (d), 113.9 (d), 112.8 (d), 60.9 (t), 55.1 (q), 13.5 (q).



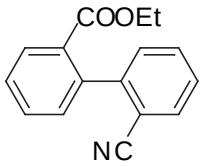
5c

4'-Nitro-biphenyl-2-carboxylic acid ethyl ester (5c): Boronic ester **1** and 4-iodonitrobenzene (table 2, entry 3) produced 228 mg (84%) of (**5c**) as colorless crystals; mp 74-75°C (heptane)(reported[3] mp 65-66 °C). R_f (heptane:EtOAc, 3:1) 0.49. ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5 (s), 148.7 (s), 147.0 (s), 140.7 (s), 131.7 (d), 130.5 (d), 130.5 (s), 130.4 (d), 129.4 (d), 128.5 (d), 123.2 (d), 61.1 (t), 13.6 (q).



5d

2'-Fluoro-biphenyl-2-carboxylic acid ethyl ester (5d): Boronic ester **1** and 2-bromofluorobenzene (table 2, entry 4) produced 176 mg (72%) of (**5d**) as a colorless oil.[4] R_f (heptane:EtOAc, 3:1) 0.57.

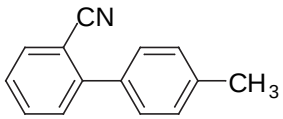


5e

2'-Cyano-biphenyl-2-carboxylic acid ethyl ester (5e): Boronic ester **1** and 2-bromobenzonitrile (table 2, entry 5) produced 178 mg (70%) of (**5e**) as a colorless oil. R_f (heptane:EtOAc, 3:1) 0.36. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.10 (dd, 1H, *J* = 7.7, 1.4 Hz), 7.72 (dd, 1H, *J* = 7.7, 1.4 Hz), 7.65-7.58 (m, 2H), 7.52 (dt, 1H, *J* = 1.4, 7.7 Hz), 7.45 (dt, 1H, *J* = 1.3, 7.6 Hz), 7.37-7.31 (m, 2H), 4.13 (q, 2H, *J* = 7.1 Hz), 1.07 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7 (s), 146.1 (s), 139.4 (s), 132.3 (d), 132.2 (d), 132.0 (d), 131.0 (d), 130.9 (d), 130.1(s), 129,5 (d), 128.8 (d), 127.5 (d), 118,1 (s), 112.4 (s), 60.9 (t), 13.6 (q). Anal. Calcd. for $C_{16}H_{13}NO_2$ C: 76.48 H: 5.21 N: 5.57, found: C: 76.41 H: 5.17 N: 5.67.

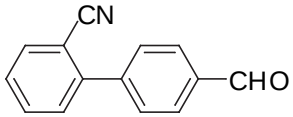
General Procedure B:

In a nitrogen atmosphere the boronic ester **2-4** (1 mmol) and the appropriate aryl halide (1.2 mmol) were dissolved in toluene (10 mL) and EtOH (1 mL), 2M K_2CO_3 (1 mL), and $Pd(PPh_3)_4$ (3 mol%, 35 mg) was added. The reaction mixture was stirred at 100 °C for 5 h, and then cooled to room temperature. Addition of sat. aqueous NH_4Cl (25 mL) followed by extraction with EtOAc (3x20 mL), drying ($MgSO_4$) and evaporation *in vacuo* provided the crude product which was purified by column chromatography (heptane/EtOAc, 10:1)



5f

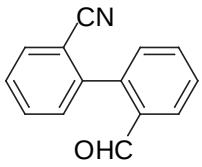
4'-Methyl-biphenyl-2-carbonitrile (5f): Boronic ester **2** and 4-iodotoluene (table 2, entry 6) produced 139 mg (72%) of (**5f**) as colorless crystals, mp 51-52°C (heptane/EtOAc)(reported[5] mp 48-49.5 °C). R_f (heptane:EtOAc, 3:1) 0.53. ^{1}H- and ^{13}C-NMR was identical with that previously reported.[6]



5g

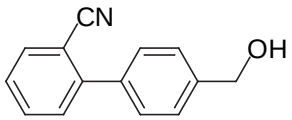
4'-Formyl-biphenyl-2-carbonitrile (5g): Boronic ester **2** and 4-bromobenzaldehyde (table 2, entry 7) produced 152 mg (73%) of **(5g)** as colorless crystals, mp 159-160 °C (heptane/EtOAc). R_f (heptane:EtOAc, 3:1) 0.24. A correct microanalysis could not be

obtained, ^{1}H-NMR spectrum included. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.02 (d, 2H, J_{app} = 8.5 Hz), 7.82 (ddd, 1H, *J* = 7.5, 1.3, 0.6 Hz), 7.74 (d, 2H, J_{app} = 8.1 Hz), 7.70 (dd, 1H, *J* = 7.6, 1.4 Hz), 7.55 (ddd, 1H, *J* = 7.9, 1.3, 0.5 Hz), 7.54 (dt, 1H, *J* = 1.3, 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9 (d), 144.0 (s), 144.0 (s), 136.2 (s), 133.9 (d), 133.1 (d), 130.1 (d), 130.0 (d), 129.6 (d), 128.6 (d), 118.3 (s), 111.2 (s).



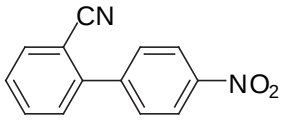
5h

2'-Formyl-biphenyl-2-carbonitrile (5h): Boronic ester **2** and 2-bromobenzaldehyde (table 2, entry 8) produced 190 mg (91%) of **(5h)** as colorless crystals, mp 117-118°C (heptane). R_f (heptane:EtOAc, 3:1) 0.29. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.06(dd, 1H, *J* = 7.6, 1.4 Hz), 7.85 (dd, 1H, *J* = 7.7, 1.4 Hz), 7.72 (dd, 1H, *J* = 7.5, 1.4 Hz), 7.67 (dd, *J* = 7.8, 1.4 Hz), 7.55 (dt, 1H, *J* = 1.3, 7.6 Hz), 7.45 (dd, 1H, *J* = 7.7, 1.2 Hz), 7.43 (dd, 1H, *J* = 7.7, 0.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9 (d), 142.2 (s), 140.9 (s), 133.9 (d), 133.9 (s), 133.1 (d), 132.5 (d), 131.2 (d), 131.1 (d), 129.5 (d), 129.4 (d), 128.6 (d), 117.7 (s), 113.0 (s). Anal. calcd. for $C_{14}H_9NO$ C: 81.14, H: 4.38, N: 6.76, found C: 81.34, H: 4.20, N: 6.55.



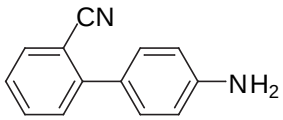
5i

4'-Hydroxymethyl-biphenyl-2-carbonitrile (5i): Boronic ester **2** and 4-bromobenzylalcohol (table 2, entry 9) produced 159 mg (76%) of (**5i**) as colorless crystals, mp 119-120°C (heptane/EtOAc). R_f (heptane:EtOAc, 3:1) 0.09. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.77 (ddd, 1H, *J* = 7.7, 1.3, 0.4 Hz), 7.65 (dt, 1H, *J* = 1.4, 7.8 Hz), 7.56 (d, 2H, J_{app} = 8.4 Hz), 7.53-7.48 (m, 3H), 7.45 (dt, 1H, *J* = 1.3, 7.6 Hz), 4.78 (br s, 2H), 1.73 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2 (s), 141.5 (s), 137.4 (s), 133.8 (d), 132.9 (d), 130.0 (d), 128.9 (d), 127.6 (d), 127.2 (d), 118.8 (s), 111.2 (s), 64.8 (t). Anal. calcd. for $C_{14}H_{11}NO$ C: 80.36, H: 5.30, N: 6.69, found C: 80.15, H: 5.11, N:6.68.



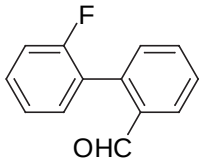
5j

4'-Nitro-biphenyl-2-carbonitrile (5j): Boronic ester **2** and 4-iodo-nitrobenzene (table 2, entry 10) produced 190 mg (84%) of (**5j**) as light brown crystals, mp 127-128 °C (heptane/EtOAc) (reported[7] mp 179-180 °C). R_f (heptane:EtOAc, 3:1) 0.33. ^{1}H-NMR differs from that previously reported.[6] ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.37 (d, 2H, J_{app} = 8.8 Hz), 7.86-7.82 (m, 1H), 7.77-7.70 (m, 3H), 7.60-7.53 (m, 2H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9 (s), 144.5 (s), 142.9 (s), 134.0 (d), 133.3 (d), 130.0 (d), 129.9 (d), 129.0 (d), 124.0 (d), 118.0 (s), 111.2 (s).



5k

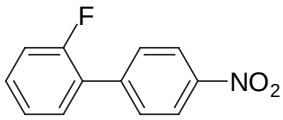
4'-Amino-biphenyl-2-carbonitrile (5k): Boronic ester **2** and 4-iodoaniline (table 2, entry 11) produced 103 mg (53%) of (**5k**) as colorless crystals, mp 115-116 °C (heptane) (reported[8] mp 119 °C). R_f (heptane:EtOAc, 3:1) 0.16. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.70 (ddd, 1H, *J* = 7.9 , 1.4, 0.5 Hz), 7.57 (dt, 1H, *J* = 1.4, 7.4 Hz), 7.46 (ddd, 1H, *J* = 7.9, 1.3, 0.5 Hz), 7.38 (d, 2H, J_{app} = 8.7 Hz), 7.32 (dt, 1H, *J* = 7.4, 1.3 Hz), 6.76 (d, 2H, J_{app} = 8.7 Hz), 3.87 (br s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2 (s), 145.7 (s), 133.8 (d), 132.8 (d), 129.9 (d), 129.7 (d), 128.0 (s), 126.6 (d), 119.3 (s), 115.0 (d),110.6 (s).



5l

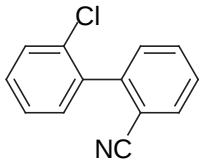
2'-Fluoro-biphenyl-2-carbaldehyde (5l): Boronic ester **3** and 2-bromobenzaldehyde (table 2, entry 12) produced (85%) of (**5l**) as a colorless oil. R_f (heptane:EtOAc, 3:1) 0.56. A correct microanalysis could not be obtained, ^{1}H-NMR spectrum included. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.92 (dd, 1H, *J* = 3.0, 0.7 Hz), 8.05 (dd, 1H, *J* = 7.7, 1.5 Hz), 7.68 (dt, 1H, *J* = 1.5, 7.5 Hz), 7.55 (br t, 1H, *J* = 7.6 Hz), 7.49-7.40 (m, 2H), 7.35 (dt, 1H, *J* = 1.9 7.5 Hz), 7.27 (dt, 1H, *J* = 1.1, 7.2 Hz), 7.19 (dt, 1H, *J* = 1.1, 8.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6 (d,(d_{C-F}), J_{C-F} = 2 Hz), 159.6 (s,(d_{C-F}), J_{C-F} = 247 Hz), 138.9 (s), 133.9 (s), 133.8 (d), 132.0 (d,(d_{C-F}), J_{C-F} = 2 Hz), 131.4 (d,(d_{C-F}), J_{C-F} = 0.8 Hz), 130.5 (d,(d_{C-F}), J_{C-F} = 8 Hz), 128.5 (d), 127.7 (d), 125.5 (s,(d_{C-F}), J_{C-F} = 15 Hz), 124.5 (d,(d_{C-F}), J_{C-F} = 3 Hz), 115.7 (d,(d_{C-F}), J_{C-F} = 22 Hz).



5m

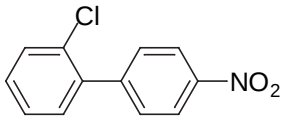
2-Fluoro-4'-nitro-biphenyl (5m): Boronic ester **3** and 4-iodonitrobenzene (table 2, entry 13) produced (86%) of (**5m**) as colorless crystals. mp 73-75 °C (ethanol) (reported[9] mp 74.5 °C). R_f (heptane:EtOAc, 3:1) 0.60. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.30 (d, 2H, J_{app} = 8.9 Hz), 7.72 (dd, 2H, J_{app} = 8.9, 1.5 Hz), 7.50-7.38 (m, 2H), 7.28 (dt, 1H, J = 1.1, 7.5 Hz), 7.21 (ddd, 1H, J = 10.8, 8.3, 0.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7 (s,(d_{C-F}), J_{C-F} = 250.0 Hz), 147.3 (s), 142.4 (s,(d_{C-F}), J_{C-F} = 1.2 Hz), 130.7 (d,(d_{C-F}), J_{C-F} = 8.5 Hz), 130.6 (d,(d_{C-F}), J_{C-F} = 2.8 Hz), 129.3 (d,(d_{C-F}), J_{C-F} = 3.3 Hz), 126.8 (s,(d_{C-F}), J_{C-F} = 13.0 Hz), 124.8 (d,(d_{C-F}), J_{C-F} = 3.7 Hz) 123.7 (d), 116.5 (d,(d_{C-F}), J_{C-F} = 22 Hz).



5n

2'-Chloro-biphenyl-2-carbonitrile (5n): Boronic ester **4** and 2-bromobenzonitrile (table 2, entry 14) produced 198 mg (94%) of (**5n**) as colorless crystals, mp 67-68 °C (EtOAc/heptane). R_f (heptane:EtOAc, 3:1) 0.49. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.77

(ddd, 1H, *J* = 7.7, 1.3, 0.5 Hz). 7.66 (dt, 1H, *J* = 1.3, 7.7 Hz), 7.55-7.34 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1 (s), 137.0 (s), 133.0 (s), 132.9 (d), 132.4 (d), 131.1 (d), 130.8 (d), 130.2 (d), 130.0 (d), 128,3 (d), 127.0 (d), 117.9 (s), 113.0 (s). Anal. Calcd. for $C_{13}H_8ClN$: C 73.08, H 3.77, N 6.65. Found C 72.96, H 3.79, N 6.56.



5o

2-Chloro-4'-nitro-biphenyl (5o): Boronic ester **4** and 4-iodonitrobenzene (table 2, entry 15) produced (80%) of (**5o**) as colorless crystals. mp 71-73 °C (ethanol) (reported[10] mp 79-80 °C). R_f (heptane:EtOAc, 3:1) 0.62. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.30 (d, 2H, J_{app} = 8.9 Hz), 7.62 (d, 2H, J_{app} = 8.9 Hz), 7.54-7.49 (m, 1H), 7.39-7.33 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.3 (s), 145.9 (s), 138.3 (s), 132,3 (s), 131.0 (d), 130.5 (d), 130.3 (d), 129.8 (d), 127.2 (d), 123.4 (d).

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