Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

A Novel Transmetallation of Arylzinc Species into Arylboronates from Aryl Halides in a Barbier Procedure

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General Information

GC analysis were carried out using a gas chromatograph Varian 3300 provided with a 25-m CPSIL5CB capillary column. Mass spectra were recorded with a GCQ Thermoelectron spectrometer coupled to a gas chromatograph Varian (35-m CPSIL5CB/MS capillary column). Column chromatographies were performed on silica gel 60, 70-230 mesh with CH_2Cl_2/ethyl acetate as eluent. ^{1}H and ^{13}C spectra were recorded in $CDCl_3$, on a Bruker ARX (200 MHz) and ^{11}B NMR ^{13}C spectra were recorded in $CDCl_3$, on a Bruker AC- 200 SY (300 MHz). All solvents and reagents were purchased and used without further purification. No inert atmosphere was required.

Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constants (*J*) are measured in hertz (Hz). The following abbreviations are used to describe multiplicities s=singlet, d=doublet, t=triplet, q=quartet, b=broad, m=multiplet.

Typical procedure for preparation of arylboronates from aryl Halides bearing an electro-withdrawing group (Procedure A) : A solution of 220 mg (0.1 equiv) of $CoBr_2$, 1g (1.5 equiv) of zinc dust and 250µl (0.3equiv) of allyl chloride in acetonitrile (6 mL) was stirred at room temperature, and activated by 100ml of trifluoroacetic acid. The medium was stirred for 5 minutes and the temperature increased. To this resulting grey solution were successively added aryl halide (10 mmol) and B-bromocatechol-borane (10 mmol). The mixture was stirred until total consumption of the aryl halide is achieved (ca.1h). The amount of the corresponding arylboronate was measured by GC using an internal reference (dodecane, 200 µL). Then, 2 ml of tetrahydrofuran was added to this thick solution and 10 mmol of pinacol. The mixture was stirred until total conversion of aryl-catecholborane into aryl-pinacolborane. An inert atmosphere was not required. The mixture was then hydrolysed with NH_4Cl followed by diethyl ether extraction. The combined organic layers were washed with saturated NaCl solution, dried over MgSO4 and the solvent was evaporated to give the crude arylboronic ester. Purification by flash chromatography (CH_2Cl_2: Ethyl acetate 95:5) afforded the pure arylboronate

Typical procedure for preparation of arylboronates from aryl Halides bearing an electro-donating group (Procedure B) : A solution of 220 mg (0.1 equiv) of $CoBr_2$, 1g (1.5 equiv) of zinc dust and 250µl (0.3equiv) of allyl chloride in acetonitrile (6 mL) was stirred at room temperature, and activated by 100ml of trifluoroacetic acid. The medium was stirred for 5

minutes and the temperature increased. To this resulting grey solution were successively added aryl halide (10 mmol) and B-Chlorocatechol-borane (10 mmol). The mixture was stirred until total consumption of the aryl halide is achieved (ca.1h). The amount of the corresponding arylboronate was measured by GC using an internal reference (dodecane, 200 μL). Then, 2 ml of tetrahydrofuran was added to this thick solution and 10 mmol of pinacol. The mixture was stirred until total conversion of aryl-catecholborane into aryl-pinacolborane. An inert atmosphere was not required. The mixture was then hydrolysed with NH_4Cl followed by diethyl ether extraction. The combined organic layers were washed with saturated NaCl solution, dried over MgSO4 and the solvent was evaporated to give the crude arylboronic ester. Purification by flash chromatography (CH_2Cl_2: Ethyl acetate 95:5) afforded the pure arylboronate

Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (entry 1)

CAS registry number 269409-99-6 [1]

The procedure employed for this compound was A.

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.91 (d, 1H), 7.49-7.37 (m, 3H), 4.35 (q, 2H), 1.39 (s, 12H), 1.35 (t, 3H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS)167.97, 130.42, 130.13, 129.87, 129.79, 128.81, 128.47, 83.87, 61.17, 24.81, 14.28 ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) *δ* 33.21; EI-MS *m/z* 277(M+1), 261, 218, 189, 147 131, 103, 78

Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (entry 2)

CAS registry number 269410-00-6 [1]

The procedure employed for this compound was A**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 8.27 (s, 1H), 7.95 (d, J= 7.7 Hz, 1H), 7.78 (d, J=7.7 Hz, 1H), 7.23 (d, J=7.7 Hz, 1H), 4.19 (q, 2H), 1.2 (t, 3H), 1.10 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) δ 166.29, 145.48, 138.96, 135.6, 132.16, 129.62, 127.55, 83.75, 60.59, 24.68, 14.23; EI-MS *m/z* 276 (M,), 261, 233, 205, 187, 177, 167, 149, 131, 118, 103, 85

Ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (entry 3 and 4)

CAS registry number 195062-62-5 [2, 1]

The procedure employed for this compound was A**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 8.0 (d, J=8.3 Hz, 2H), 7.82 (d, J=8.3 Hz, 2H), 4.15 (q, 2H), 1.4 (t, 3H), 1.3 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) δ 166.44, 134.66, 132.47, 128.31, 83.95, 60.83, 24.65, 14.24; ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) δ 32.26; EI-MS *m/z* 276 (M, 100), 261, 233, 205, 187, 177, 167, 149, 131, 118, 103, 85

4,4,5,5-tetramethyl-2-(4-trifluoromethyl-phenyl)-1,3,2-dioxaborolane (entry 5)

CAS registry number 214360-65-3 [3, 1]

The procedure employed for this compound was A**.**

^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 7.85(d, 2H), 7.50 (d, 2H), 1.30 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, TMS); 135.0, 132.89 (q, J (CF) = 32.0 Hz), 124.30 (q, J (CF) = 3.3 Hz), 124.15, (q, J (CF) = 272.4 Hz), 84,25, 24.78 ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) δ 30.82; EI-MS *m/z* 273 (M+1), 257, 229, 186, 166, 117, 86, 58

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (entry 6)

CAS registry number 171364-80-0 [4, 5]

The procedure employed for this compound was A**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.98 (d, J= 8.1 Hz, 2H), 7.74 (d, J= 8.1 Hz, 1H), 3.9 (s, 3H), 1.36 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) δ 166,83, 133.95, 132.2, 128.47, 84.0, 51.93, 24.73 ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) δ 30.57; EI-MS *m/z* 262 (M), 247, 231, 203, 187, 177, 167, 149, 131, 118, 103, 85

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzonitrile (entry 7)

CAS registry number 138642-62-3 [6]

The procedure employed for this compound was A**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.80 (d, 1H), 7.60 (m, 1H), 7.45-7.2 (m, 2H), 1.30 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) 135.78, 133.4, 131.46, 134.0, 131.06, 118.9, 117.2, 84.43, 24.70, 14.23; ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) *δ* 30.74; EI-MS *m/z* 229 (M), 214, 199, 188, 170, 116, 103, 85, 77, 69, 57

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzonitrile (entry 8)

CAS registry number 171364-82-2 [2, 5]

The procedure employed for this compound was A**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.85 (d, 2H), 7.60 (d, 2H), 1.30 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) δ 135.10, 131.12, 118.87, 114.19, 84.49, 24.86 ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) *δ* 32.16; EI-MS *m/z* 230 (M+1), 214, 186, 172, 143, 104, 85, 57

(4-chloro-phenyl)-4,4,5,5-teramethyl-1,3,2-dioxaborolane (entry 9)

CAS registry number 195062-61-4 [2]

The procedure employed for this compound was A**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.65 (d, J= 8.2Hz, 2H), 7.2 (d, J= 8.2Hz, 2H), 1.25 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) 137.28, 136.02, 135.74, 127.88, 127.64, 83.74, 24.72 ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) *δ* 33.58; EI-MS *m/z* 238 (M), 223, 207, 195, 181, 152, 139, 117, 85, 57

1-4- (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenylethanone (entry 10)

CAS registry number 171364-81-1 [4, 2, 5]

The procedure employed for this compound was A**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.80 (m, 4H), 2.5 (s, 3H), 1.24 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) 198.30, 145.66, 138.89, 134.85, 127.19, 84.12, 24.91, 24.70 ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) δ 32.19; EI-MS *m/z* 246 (M), 231, 203, 189, 160, 145, 131, 85, 57

2-(4-Methoxyphenyl)-4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (entry 11)

CAS registry number 171364-79-7 [4, 2, 3, 1, 5]

The procedure employed for this compound was B**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.95 (d, 2H), 6.95 (d, 2h), 3.9 (s, 3H), 1.45 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) 162.05, 136.55, 113.24, 83.42, 54.89, 24.63 ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) δ 30.8; EI-MS *m/z* 234 (M), 219, 191, 175, 161, 148, 134, 121, 109, 77, 65

2-(2-Methoxyphenyl)-4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (entry 12)

CAS registry number 190788-60-4 [4, 7]

The procedure employed for this compound was B**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.95 (d, 1H), 7.6 (t, 1H) 7.15-6.95 (m, 2H), 4.0 (s, 3H), 1.50 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) 164.01, 136.69, 132.42, 120.06, 110.26,83.24, 55.54, 24.76 ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) δ 31.3; EI-MS *m/z* 234 (M), 219, 203, 189, 175, 161, 148, 133, 118, 105, 91, 77, 65

4,4,5,5-tetramethyl -2-(4-methylsulfanyl-phenyl)-(1,3,2)dioxaborolane (entry 13)

CAS registry number 190788-58-0 [8]

The procedure employed for this compound was B**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.76 (d, 2H), 7.24 (d, 2H), 2.46 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) 142.76, 135.18, 124.93, 83.67, 24.92, 14.94; ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) δ 32.37

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolyl)-N,N-dimethylaniline (entry 14)

CAS registry number 171364-78-6 [2, 1]

The procedure employed for this compound was B**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.60 (d, 2H), 7.6 (t, 1H) 6.6 (d, 2H), 2.87 (s, 6H), 1.23 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) 152.36, 136.14, 135.88, 111.09, 82.97, 40.02, 24.83 EI-MS *m/z* 247 (M), 232, 188, 174, 148, 122, 77

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) thiophene

CAS registry number 193978-23-3 [2]

The procedure employed for this compound was A**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.4 (m, 2H), 7.0 (t, 1H), 1.18 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) 136.74, 131.93, 128, 83.80, 24.41 ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) δ 30.78; EI-MS *m/z* 210 (M), 195, 179, 167, 150, 137, 124, 111, 85, 57

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) thiophene

CAS registry number 214360-70-0 [9]

The procedure employed for this compound was A**.**

^{1}H NMR (200 MHz, $CDCl_3$, 293 K, TMS) δ 7.78 (d, 1H), 7.29-7.16 (m, 2H), 1.18 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K, TMS) 136.50, 131.73, 125.32, .83.46, 24.59 ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$) δ 30.63; EI-MS *m/z* 210 (M), 195, 167, 152, 137, 124, 111, 97, 85, 57

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