Supporting Information for
Copper-Mediated Synthesis of Mono-Fluoro Aryl Acetates via Decarboxylative Cross-Coupling

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Contents

I. General Considerations S-1
II. Competition Studies S-2
III. General Procedure for the Copper Catalyzed Synthesis of Mono-Fluoro Aryl Acetates via Decarboxylative Cross-Coupling S-3
IV. Characterization Data S-4
V. References S-10
VI. 1H and 13C DEPT Spectra S-11

I. General Considerations

Unless noted, all reactions were setup under inert atmosphere employing standard schlenk technique or by the use of an N2-filled glovebox. All glassware was oven-dried prior to use. Flash chromatography was performed as described by Still and co-workers1 (SiliaFlash P60, 40-63μm, 60A silica gel, Silicycle) or by automated flash chromatography (Isolera, HP-SIL or Ultra SNAP silica cartridges, Biotage). Analytical thin-layer chromatography was performed using glass plates pre-coated with silica (SiliaPlate G TLC - Glass-Backed, 250μm, Silicycle). TLC plates were visualized by UV light and/or staining with aqueous basic potassium permanganate. Unless otherwise noted, all reagents were obtained from commercial vendors and used as supplied. Mono ethyl fluoro malonate was synthesized according to literature procedure from diethyl fluoromalonate.2 Other fluoro malonate half esters were prepared according to literature procedure.3 Aryl boroxines were prepared by dehydration of the corresponding boronic acid according to established methods.4 Aryl boronic esters were synthesized according to literature procedures.5 Select 13C NMR spectra display an artefact signal at 189 or 206 ppm.
II. Competition Studies

\[
\begin{align*}
\text{EtO} & \text{CO}_2\text{H} \\
F & H \\
50 \text{ mol\%} \\
\text{EtO} & \text{CO}_2\text{H} \\
H & H \\
50 \text{ mol\%} \\
\rightarrow & \\
\text{EtO} & \text{CO}_2\text{H} \\
F & H \\
200 \text{ mol\% } \text{Ar--Bneop} \\
40 \text{ mol\% } \text{Cu(OTf)}_2 \\
\rightarrow & \\
\text{EtO} & \text{CO}_2\text{H} \\
F & H \\
2a & <2\% \\
600 \text{ mol\% } \text{NEt}_3 \\
\text{DMA, rt in air} \\
\rightarrow & \\
\text{EtO} & \text{CO}_2\text{H} \\
F & H \\
\text{S1} & >45\%
\end{align*}
\]

![Graph of yield over time](image)

**Standard Conditions for Mono Fluoro Malonate Half Esters**

\[
\begin{align*}
\text{EtO} & \text{CO}_2\text{H} \\
F & H \\
50 \text{ mol\%} \\
\text{EtO} & \text{CO}_2\text{H} \\
H & H \\
50 \text{ mol\%} \\
\rightarrow & \\
\text{EtO} & \text{CO}_2\text{H} \\
F & H \\
250 \text{ mol\% } \text{Ar--boroxine} \\
50 \text{ mol\% } \text{Cu(OTf)}_2 \\
\rightarrow & \\
\text{EtO} & \text{CO}_2\text{H} \\
F & H \\
300 \text{ mol\% } \text{NEt}_3 \\
\text{DMA, rt in air} \\
\rightarrow & \\
\text{EtO} & \text{CO}_2\text{H} \\
F & H \\
\text{S1} \\
\end{align*}
\]

![Graph of yield over time](image)
III. General Procedure for the Copper Catalyzed Synthesis of Mono-Fluoro Aryl Acetates via Decarboxylative Cross-Coupling

**Procedure A (0.50 mmol scale)** In an atmosphere controlled glovebox Cu(OTf)$_2$ (90.4 mg, 0.250 mmol, 0.50 equiv.) and aryl boronic ester (1.25 mmol, 2.5 equiv.) or aryl boroxine (0.42 mmol, 2.5 equiv. Ar-B) were added sequentially to a 1 dram screw-top vial charged with a stir bar. The fluoro malonic half ester (0.50 mmol, 1.0 equiv.) was added as a solution in anhydrous DMA (1.0 mL). Additional DMA (2 x 0.6 mL) was used to quantitatively transfer the solution to the reaction mixture. The solution was stirred until the majority of the solid had dissolved, followed by the addition of NEt$_3$ (0.2 mL, 1.5 mmol, 3.0 equiv.). The vial was sealed with a PTFE-lined cap, removed from the glovebox, and the PTFE septum pierced with an 18 gauge needle. The reaction mixture was gently stirred at room temperature. Upon reaction completion (24 to 72 h), the reaction mixture was diluted with EtOAc (60 mL), and washed sequentially with NH$_4$Cl (60 mL), 0.5 M NaOH (2 x 60 mL), and brine (60 mL). The organic layer was dried with Na$_2$SO$_4$, concentrated in vacuo, and purified by silica gel chromatography. Note, the needle gauge and vial size can influence the reaction rates and overall efficiency. Reactions conducted without the use of a glovebox gave similar results. Cu(OTf)$_2$ and aryl boroxines are hydroscopic and should be stored under inert gas.

**Procedure B (0.2 mmol scale):** In an atmosphere controlled glovebox Cu(OTf)$_2$ (36.2 mg, 0.10 mmol, 0.50 equiv.) and aryl boronic ester (0.5 mmol, 2.5 equiv.) or aryl boroxine (0.17 mmol, 2.5 equiv. Ar-B) were added sequentially to a 0.5 dram screw-top vial charged with a stir bar. The fluoro malonic half ester (0.20 mmol, 1.0 equiv.) was added as a solution in anhydrous DMA (0.5 mL). Additional DMA (2 x 0.2 mL) was used to quantitatively transfer the solution to the reaction mixture. The solution was stirred until the majority of the solid had dissolved, followed by the addition of NEt$_3$...
(0.09 mL, 0.6 mmol, 3.0 equiv.). The vial was sealed with a PTFE-lined cap, removed from the glovebox, and the PTFE septum pierced with an 20 gauge needle. The reaction mixture was gently stirred at room temperature and worked up after completion according the procedure described above.

**Procedure C (2.0 mmol scale, no glovebox):** To a 4 dram with a stirbar was added Cu(OTf)₂ (362 mg, 1.0 mmol, 0.50 equiv.) and 3-bromophenylboroxine (914 mg, 1.67 mmol, 2.5 equiv. Ar-B). DMA (8.9 mL) was used to quantitatively transfer (with rinsing) the fluoro malonic half ester (300 mg, 2.0 mmol, 1.0 equiv.) into the vial. The solution was stirred until the majority of the solid had dissolved, followed by the addition of NEt₃ (0.84 mL, 6.0 mmol, 3.0 equiv.). The vial was sealed with a PTFE-lined cap, and the PTFE septum was pierced with two 18 gauge needles. The reaction mixture was gently stirred at room temperature (72% yield based on calibrated 1H NMR).

**IV. Characterization Data**

![Chemical structure of 2a](image)

**2a** Prepared according to Procedure A from the corresponding aryl boroxine (229 mg, 0.42 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (75 mg, 0.50 mmol, 1.0 equiv.), 49 h. Isolated in 73% yield after purification by column chromatography (10:1 Hex/EtOAc) as a light yellow oil.

- **¹H NMR** (CDCl₃, 700 MHz) δ 7.63 – 7.61 (m, 1H), 7.54 – 7.51 (m, 1H), 7.41 – 7.38 (m, 1H), 7.29 – 7.26 (m, 1H), 5.72 (d, J = 47.4 Hz, 1H), 4.30 – 4.20 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H);
- **¹³C NMR** (CDCl₃, 176 MHz) δ 167.9 (d, J = 27.1 Hz), 136.3 (d, J = 21.3 Hz), 132.6, 130.3, 129.5 (d, J = 6.7 Hz), 125.0 (d, J = 6.2 Hz), 122.8, 88.4 (d, J = 187.6 Hz), 62.1, 14.0;
- **¹⁹F NMR** (CDCl₃, 377 MHz) δ –182.3 (d, J = 47.4 Hz);

![Chemical structure of 2b](image)

**2b** Prepared according to Procedure A from the corresponding aryl boroxine (235 mg, 0.42 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (75 mg, 0.50 mmol, 1.0 equiv.), 49 h. Isolated in 70% yield after purification by column chromatography (gradient, 100% to 90% Hex/EtOAc) as a light yellow oil.

- **¹H NMR** (CDCl₃, 700 MHz) δ 7.45 – 7.40 (m, 2H), 7.35 – 7.33 (m, 1H), 7.26 – 7.23 (m, 1H), 5.78 (d, J = 47.6 Hz, 1H), 4.30 – 4.21 (m, 2H), 1.26 (t, J = 7.17 Hz);
- **¹³C NMR** (CDCl₃, 126 MHz) δ 167.8 (d, J = 26.9 Hz), 149.4 (d, J = 1.8 Hz), 136.4 (d, J = 21.3 Hz), 130.3, 124.6 (d, J = 6.7 Hz), 121.9, 120.4 (q, J = 258.9 Hz), 119.0 (d, J = 7.02 Hz), 88.4 (d, J = 187.7 Hz), 62.1, 14.0;
- **¹⁹F NMR** (CDCl₃, 377 MHz) δ –58.0 (s, 3F), –183.2 (d, J = 47.5 Hz, 1F);
- **HRMS (EI):** calcd for C₁₁H₁₀F₃O₃ [M⁺]: 266.0566. Found 266.0569.
2c Prepared according to Procedure A from the corresponding aryl boroxine (167 mg, 0.42 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (75 mg, 0.50 mmol, 1.0 equiv.), 48 h. Isolated in 55% yield after purification by column chromatography (20:1 Hex/EtOAc) as a light yellow oil.

1H NMR (CDCl₃, 700 MHz) δ 7.32 – 7.29 (m, 1H), 7.05 – 7.02 (m, 1H), 7.00 – 6.99 (m, 1H), 6.94 – 6.91 (m, 1H), 5.73 (d, J = 48.0 Hz, 1H), 4.30 – 4.28 (m, 2H), 3.81 (s, 3H), 1.26 (t, J = 7.18 Hz, 3H);

13C NMR (CDCl₃, 176 MHz) δ 168.4 (d, J = 27.5 Hz), 159.8, 135.6 (d, J = 20.1 Hz), 129.9, 118.9 (d, J = 6.6 Hz), 115.4 (d, J = 2.1 Hz), 111.8 (d, J = 6.7 Hz), 89.2 (d, J = 185.7 Hz), 61.8, 55.3, 14.0;

19F NMR (CDCl₃, 377 MHz) δ –180.4 (d, J = 47.5 Hz);


2d Prepared according to Procedure A from the corresponding aryl boroxine (186 mg, 0.42 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (75 mg, 0.50 mmol, 1.0 equiv.), 47 h. 66% yield based on calibrated 1H NMR, isolated in 56% yield (17:1 product:diarylation at the α position) yield after purification by column chromatography (2:1 Tol/Hex to 100% Tol) as a light yellow oil.

1H NMR (CDCl₃, 700 MHz) δ 8.36 – 8.35 (m, 1H), 8.27 – 8.25 (m, 1H), 7.83 – 7.81 (m, 1H), 7.63 – 7.60 (m, 1H), 5.76 (d, J = 47.2 Hz, 1H), 4.32 – 4.22 (m, 2H), 1.31 (t, J = 7.14 Hz, 3H);

13C NMR (CDCl₃, 176 MHz) δ 167.3 (d, J = 26.6 Hz), 148.4, 136.4 (d, J = 21.6), 132.0 (d, J = 6.5 Hz), 129.9, 124.3 (d, J = 1.1 Hz), 121.5 (d, J = 7.5 Hz), 88.0 (d, J = 189.0 Hz), 62.4, 14.0;

19F NMR (CDCl₃, 377 MHz) δ –184.4 (d, J = 47.1 Hz);


2e Prepared according to Procedure A from the corresponding aryl neopentyl boronic ester (283 mg, 1.25 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (75 mg, 0.5 mmol, 1.0 equiv.), 48 h. Isolated in 59% yield after purification by column chromatography (20:1 Hex/EtOAc) as a light yellow oil.

1H NMR (CDCl₃, 498 MHz) δ 7.06 – 7.02 (m, 2H), 6.89 – 6.83 (m, 1H), 5.76 (d, J = 47.5 Hz, 1H), 4.35 – 4.24 (m, 2H), 1.31 (t, J = 7.14 Hz, 3H);

13C NMR (CDCl₃, 176 MHz) δ 167.4 (d, J = 26.6 Hz), 163.8 (d, J = 12.4 Hz), 162.3 (d, J = 12.8 Hz), 109.4 (ddd, J = 21.8, 7.5, 7.3 Hz), 104.9 (td, J = 25.2, 1.0 Hz), 88.0 (dt, J = 188.8, 2.2), 62.3, 14.0;

19F NMR (CDCl₃, 377 MHz) δ –184.3 (m, 2F), −184.4 (d, J = 47.5 Hz, 1F);

2f Prepared according to Procedure A from the corresponding aryl boroxine (173 mg, 0.42 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (75 mg, 0.50 mmol, 1.0 equiv.), 43 h. Isolated in 58% yield after purification by column chromatography (20:1 Hex:EtOAc) as a light yellow oil.

$^1$H NMR (CDCl$_3$, 700 MHz) δ 7.51 – 7.48 (m, 1H), 7.43 – 7.41 (m, 1H), 7.39 – 7.29 (m, 2H), 6.19 (d, $J = 46.5$ Hz, 1H), 4.31 – 4.22 (m, 2H), 1.26 (t, $J = 7.2$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 176 MHz) δ 168.0 (d, $J = 27.5$ Hz), 133.6 (d, $J = 4.4$ Hz), 132.4 (d, $J = 20.8$ Hz), 130.9 (d, $J = 2.4$ Hz), 129.9, 128.6 (d, $J = 6.3$ Hz), 127.3, 86.2 (d, $J = 184.6$ Hz), 62.0, 14.0;

$^{19}$F NMR (CDCl$_3$, 377 MHz) δ –180.9 (d, $J = 46.7$ Hz);

HRMS (EI): calcd for C$_{10}$H$_{10}$ClFO$_2$ [M$^+$]: 216.0353. Found 216.0355.

2g Prepared according to Procedure A from the corresponding aryl boroxine (287 mg, 0.42 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (75 mg, 0.50 mmol, 1.0 equiv.), 49 h. Isolated in 59% yield after purification by column chromatography (Hex/EtOAc gradient, 98:2 to 80:20) as a clear, light-yellow oil.

$^1$H NMR (CDCl$_3$, 700 MHz) δ 7.75 – 7.72 (m, 2H), 7.21 – 7.18 (m, 2H), 5.70 (d, $J = 47.5$ Hz, 1H), 4.28 – 4.18 (m, 2H), 1.25 (t, $J = 7.1$ Hz);

$^{13}$C NMR (CDCl$_3$, 126 MHz) δ 168.0 (d, $J = 27.3$ Hz), 137.9, 134.0 (d, $J = 20.9$ Hz), 128.3 (d, $J = 6.3$ Hz), 95.7 (d, $J = 2.8$ Hz), 88.8 (d, $J = 186.7$ Hz), 62.0, 14.0;

$^{19}$F NMR (CDCl$_3$, 377 MHz) δ –181.9 (d, $J = 47.6$ Hz);


2h Prepared according to Procedure A from the corresponding aryl boroxine (229 mg, 0.42 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (75 mg, 0.50 mmol, 1.0 equiv.), 53 h. Isolated in 65% yield after purification by column chromatography (Hex/EtOAc gradient, 98:2 to 80:20) as a light yellow oil.

$^1$H NMR (CDCl$_3$, 700 MHz) δ 7.54 – 7.52 (m, 2H), 7.35 – 7.32 (m, 2H), 5.72 (d, $J = 47.6$ Hz, 1H), 4.28 – 4.18 (m, 2H), 1.25 (t, $J = 7.1$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 126 MHz) δ 168.0 (d, $J = 27.5$ Hz), 133.3 (d, $J = 20.9$ Hz), 132.0, 128.2 (d, $J = 6.3$ Hz), 123.8 (d, $J = 2.6$ Hz), 88.7 (d, $J = 186.6$ Hz), 62.0, 14.0;

$^{19}$F NMR (CDCl$_3$, 377 MHz) δ –181.5 (d, $J = 47.6$ Hz);

HRMS (EI): calcd for C$_{10}$H$_{10}$BrFO$_2$ [M$^+$]: 259.9848. Found 259.9850.
2i Prepared according to Procedure A from the corresponding aryl boroxine (173 mg, 0.42 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (75 mg, 0.50 mmol, 1.0 equiv.), 48 h. Isolated in 69% yield after purification by column chromatography (20:1 Hex/EtOAc) as a light yellow oil.

\[ ^1H \text{ NMR (CDCl}_3, 700 \text{ MHz}) \delta 7.42 – 7.38 \text{ (m, 4H), } 5.73 \text{ (d, } J = 47.6 \text{ Hz, 1H), } 4.29 – 4.19 \text{ (m, 2H), 1.25 (t, } J = 7.15 \text{ Hz, 3H);} \]

\[ ^{13}C \text{ NMR (CDCl}_3, 176 \text{ MHz}) \delta 168.1 \text{ (d, } J = 27.5 \text{ Hz), 135.6 \text{ (d, } J = 2.4 \text{ Hz), 132.8 \text{ (d, } J = 21.1 \text{ Hz), 129.1, 127.9 (d, } J = 6.3 \text{ Hz), 88.6 (d, } J = 186.6 \text{ Hz), 62.0, 14.0;} \]

\[ ^{19}F \text{ NMR (CDCl}_3, 377 \text{ MHz}) \delta -181.0 \text{ (d, } J = 47.5 \text{ Hz);} \]


2j Prepared according to Procedure B from the corresponding aryl neopentyl boronic ester (123 mg, 0.50 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (30 mg, 0.20 mmol, 1.0 equiv.), 48 h. Isolated in 49% yield after purification by column chromatography (Hex/EtOAc gradient, 90:10 to 50:50) as a yellow oil.

\[ ^1H \text{ NMR (CDCl}_3, 700 \text{ MHz}) \delta 7.66 – 7.63 \text{ (m, 2H), 7.01 – 7.00 \text{ (m, 1H), 5.70 (d, } J = 47.2 \text{ Hz, 1H), 4.30 – 4.19 \text{ (m, 2H), 3.95 (s, 3H), 1.26 (t, } J = 7.1 \text{ Hz, 3H);} \]

\[ ^{13}C \text{ NMR (CDCl}_3, 126 \text{ MHz}) \delta 167.8 \text{ (d, } J = 27.7 \text{ Hz), 162.0 \text{ (d, } J = 1.5 \text{ Hz), 132.7 \text{ (d, } J = 5.8 \text{ Hz), 132.2 (d, } J = 6.3 \text{ Hz), 127.1 (d, } J = 22.0 \text{ Hz), 115.6, 111.7, 102.4, 87.9 (d, } J = 187.3 \text{ Hz), 62.2, 56.3, 14.1;} \]

\[ ^{19}F \text{ NMR (CDCl}_3, 377 \text{ MHz}) \delta -179.9 \text{ (d, } J = 47.3 \text{ Hz);} \]


2k Prepared according to Procedure A from the corresponding aryl neopentyl boronic ester (396 mg, 1.25 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (75 mg, 0.50 mmol, 1.0 equiv.), 49 h. Isolated in 76% yield after purification by column chromatography (Hex/EtOAc gradient, 100:0 to 90:10) as a light yellow oil.

\[ ^1H \text{ NMR (CDCl}_3, 700 \text{ MHz}) \delta 7.38 – 7.36 \text{ (m, 1H), 7.06 – 7.03 \text{ (m, 1H), 5.98 (d, } J = 46.9 \text{ Hz, 1H), 4.32 – 4.22 \text{ (m, 2H), 3.97 (d, } J = 1.5 \text{ Hz, 3H), 1.27 (t, } J = 7.1 \text{ Hz, 3H);} \]

\[ ^{13}C \text{ NMR (CDCl}_3, 126 \text{ MHz}) \delta 167.4 \text{ (dd, } J = 27.4, 1.3 \text{ Hz), 153.8 (dd, } J = 255.0, 4.3 \text{ Hz), 145.6 (d, } J = 12.6 \text{ Hz), 128.5 Hz (dd, } J = 4.0, 0.9 \text{ Hz), 123.3 (dd, } J = 5.5, 3.1 \text{ Hz), 123.0 (dd, } J = 21.2, 12.9 \text{ Hz), 119.5 (t, } J = 3.0 \text{ Hz), 83.1 (dd, } J = 186.1, 4.3 \text{ Hz), 62.2, 61.6 (d, } J = 5.0 \text{ Hz), 14.0;} \]

\[ ^{19}F \text{ NMR (CDCl}_3, 377 \text{ MHz}) \delta -131.4 \text{ (dd, } J = 6.5, 1.6 \text{ Hz, 1F), -181.5 (d, } J = 47.0 \text{ Hz, 1F);} \]

2l Prepared according to Procedure B from the corresponding aryl boroxine (81 mg, 0.13 mmol, 2.0 equiv. Ar–B) and fluoro malonic half ester (30 mg, 0.20 mmol, 1.0 equiv.), 48 h. Isolated in 67% yield after purification by column chromatography (Hex/EtOAc gradient, 98:2 to 82:18 to 18%) as a colorless oil.

$^1$H NMR (CDCl$_3$, 700 MHz) δ 7.31 – 7.29 (m, 1H), 7.18 – 7.17 (m, 1H), 7.15 – 7.14 (m, 1H), 5.78 (d, $J$ = 47.4 Hz, 1H), 4.25 (m, 2H), 3.85 (s, 3H), 1.26 (t, $J$ = 7.18 Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 126 MHz) δ 167.7 (d, $J$ = 26.9 Hz), 161.1 Hz, 136.7 (d, $J$ = 21.2 Hz), 132.4 (q, $J$ = 32.9 Hz), 123.4 (q, $J$ = 271.9 Hz), 115.4 – 115.2 (m), 115.1 – 115.0 (m), 112.1 – 112.0 (m), 88.5 (d, $J$ = 187.7 Hz), 62.2, 55.7, 14.0;

$^{19}$F NMR (CDCl$_3$, 377 MHz) δ –63.0 (s, 3F), –183.4 (d, $J$ = 47.7 Hz, 1F);


2m Prepared according to Procedure A from the corresponding aryl neopentyl boronic ester (261 mg, 1.25 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (75 mg, 0.50 mmol, 1.0 equiv.), 50 h. Isolated in 51% yield after purification by column chromatography (Hex/EtOAc gradient, 94:6 to 50:50) light yellow oil.

$^1$H NMR (CDCl$_3$, 700 MHz) δ 8.29 – 8.26 (m, 1H), 7.93 – 7.89 (m, 1H), 7.28 – 7.26 (m, 1H), 5.99 (d, $J$ = 46.7 Hz, 1H), 4.32 – 4.22 (m, 2H), 1.27 (t, $J$ = 7.2 Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 126 MHz) δ 167.1 (d, $J$ = 27.5 Hz), 160.6 (dd, $J$ = 241.5, 4.6 Hz), 149.1 (dd, $J$ = 15.0, 2.4 Hz), 139.4 (dd, $J$ = 5.8, 3.8 Hz), 121.8 (d, $J$ = 4.5 Hz), 117.2 (dd, $J$ = 22.3, 29.4 Hz), 83.3 (dd, $J$ = 186.2, 2.4 Hz), 62.4, 14.0;

$^{19}$F NMR (CDCl$_3$, 377 MHz) δ –70.9 (d, $J$ = 7.4 Hz, 1F), –184.4 (d, $J$ = 46.8 Hz, 1F);


2n Prepared according to Procedure B, with the modification of using 1,2-dichloroethane as the solvent, from the corresponding aryl neopentyl boronic ester (95.4 mg, 0.430 mmol, 2.15 equiv. Ar–B) and fluoro malonic half ester (30.0 mg, 0.20 mmol, 1.0 equiv.), 48 h. The solvent was removed in vacuo and the product was isolated in 43% after purification by column chromatography (Hex/EtOAc gradient, 20:80 to 0:100) yellow oil.

$^1$H NMR (CDCl$_3$, 700 MHz) δ 8.60 – 8.59 (m, 2H), 5.75 (d, $J$ = 47.1 Hz, 1H), 4.32 – 4.23 (m, 2H), 4.03 (s, 3H), 1.27 (t, $J$ = 7.05 Hz, 3H);
$^{13}$C NMR (CDCl$_3$, 126 MHz) δ 167.4 (d, $J = 27.5$ Hz), 166.3 (d, $J = 1.5$ Hz), 158.2 (d, $J = 5.3$ Hz), 121.8 (d, $J = 22.1$ Hz), 85.5 (d, $J = 187.0$ Hz), 62.5, 55.3, 14.0;

$^{19}$F NMR (CDCl$_3$, 377 MHz) δ $-181.5$ (d, $J = 47.5$ Hz);


4a Prepared according to Procedure B from the corresponding aryl boroxine (92 mg, 0.167 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (32.8 mg, 0.20 mmol, 1.0 equiv.), 48 h. Isolated in 69% yield after purification by column chromatography (Hex/EtOAc gradient, 99:1 to 88:12) as a pale yellow oil.

$^1$H NMR (CDCl$_3$, 400 MHz) δ 7.65 – 7.64 (m, 1H), 7.56 – 7.52 (m, 1H), 7.43 – 7.40 (m, 1H), 7.32 – 7.27 (m, 1H), 5.71 (d, $J = 47.8$ Hz, 1H), 5.13 (hept, $J = 6.3$ Hz, 1H), 1.30 (d, $J = 6.3$ Hz, 3H), 1.22 (d, $J = 6.3$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 126 MHz) δ 167.4 (d, $J = 27.0$ Hz), 136.5 (d, $J = 20.5$ Hz), 132.5 (d, $J = 1.9$ Hz), 130.3, 129.5 (d, $J = 6.9$ Hz), 125.0 (d, $J = 6.4$ Hz), 122.7, 88.5 (d, $J = 187.8$ Hz), 70.1, 21.7, 21.5;

$^{19}$F NMR (CDCl$_3$, 377 MHz) δ $-182.2$ (d, $J = 47.7$ Hz);


4b Prepared according to Procedure A from the corresponding aryl boroxine (229 mg, 0.417 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (107 mg, 0.50 mmol, 1.0 equiv.), 44 h. Isolated in 59% yield after purification by column chromatography (Hex/EtOAc gradient, 98:2 to 82:18) as a yellow oil.

$^1$H NMR (CDCl$_3$, 700 MHz) δ 7.61 – 7.60 (m, 1H), 7.53 – 7.51 (m, 1H), 7.38 – 7.36 (m, 1H), 7.36 – 7.31 (m, 3H), 7.28 – 7.24 (m, 3H), 5.77 (d, $J = 47.4$ Hz, 1H), 5.21 (dd, $J = 39.7, 12.3$ Hz, 2H);

$^{13}$C NMR (CDCl$_3$, 126 MHz) δ 167.6 (d, $J = 27.0$ Hz), 136.1 (d, $J = 20.7$ Hz), 134.7, 132.7 (d, $J = 1.8$ Hz), 130.3, 129.6 (d, $J = 6.9$ Hz), 128.7, 128.7, 128.3, 125.1 (d, $J = 6.3$ Hz), 122.8, 88.4 (d, $J = 188.3$ Hz), 67.6;

$^{19}$F NMR (CDCl$_3$, 377 MHz) δ $-182.1$ (d, $J = 47.8$ Hz);


4c Prepared according to Procedure B from the corresponding aryl boroxine (92 mg, 0.167 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (41 mg, 0.20 mmol, 1.0 equiv.), 20 h. Isolated in 56% yield after purification by column chromatography (Hex/EtOAc gradient, 98:2 to 80:20) as a yellow oil.

$^1$H NMR (CDCl$_3$, 500 MHz) δ 7.66 – 7.64 (m, 1H), 7.59 – 7.54 (m, 1H), 7.43 – 7.40 (m, 1H), 7.34 – 7.30 (m, 1H), 5.87 (d, $J = 49.6$ Hz, 1H), 4.65 – 4.50 (m, 2H);
**13C NMR** (CDCl₃, 126 MHz) δ 166.5 (d, J = 28.7 Hz), 135.1 (d, J = 21.4 Hz), 133.2 (d, J = 2.0 Hz), 130.5, 129.5 (d, J = 5.9 Hz), 125.0 (d, J = 6.0 Hz), 123.0, 122.4 (q, J = 278.8 Hz), 88.0 (d, J = 188.7 Hz), 61.1 (d, J = 36.8 Hz);

**19F NMR** (CDCl₃, 498 MHz) δ –73.7 (t, J = 8.2 Hz, 3F), –182.7 (d, J = 47.1 Hz, 1F)

**HRMS (EI):** calcd for C₁₀H₇BrF₄O₂[⁺][M]: 313.9566. Found 313.9568.

**4d** Prepared according to Procedure B from the corresponding aryl boroxine (92 mg, 0.167 mmol, 2.5 equiv. Ar–B) and fluoro malonic half ester (32 mg, 0.20 mmol, 1.0 equiv.), 45 h. Isolated in 74% yield after purification by column chromatography (Hex/EtOAc gradient, 99:1 to 90:10) as a yellow oil.

**1H NMR** (CDCl₃, 700 MHz) δ 7.64 – 7.62 (m, 1H), 7.54 – 7.51 (m, 1H), 7.41 – 7.38 (m, 1H), 7.29 – 7.26 (m, 1H), 5.89 – 5.83 (m, 1H), 5.76 (d, J = 47.1 Hz, 1H), 5.28 – 5.23 (m, 2H), 4.71 – 4.64 (m, 2H);

**13C NMR** (CDCl₃, 126 MHz) δ 167.7 (d, J = 27.7 Hz), 136.2 (d, J = 21.2 Hz), 132.7 (d, J = 1.7 Hz), 130.9, 130.3, 129.6 (d, J = 6.8 Hz), 125.1 (d, J = 6.3 Hz), 122.8, 119.4, 88.4 (d, J = 188.2 Hz), 66.4;

**19F NMR** (CDCl₃, 498 MHz) δ –182.2 (d, J = 48.6 Hz)

**HRMS (EI):** calcd for C₁₁H₁₀BrFO₂[⁺][M]: 271.9848. Found 271.9848.

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less successful aryl boroxine examples (<30% yield)

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**V. References**

Anis, AF-03-153-A
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.6 °C -> actual temp = 27.8 °C, coldid probe

Department of Chemistry, University of Alberta

Recorded on: v700, Feb 18 2017
Pulse Sequence: PRESAT

Acq. Time(s): 5
Relaxation Delay(s): 0.1

Sweep Width(Hz): 8389.26
Hz per mm(Hz/mm): 25.73

Digital Res.(Hz/pt): 0.13
Completed Scans: 32

2a
Anis, AF-03-153-A
175.974 MHz C13 DEPT1q in CDCl3 (ref. to CDC3 @ 77.06 ppm)
temp 27.5 °C -> actual temp = 27.0 °C, coldid probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-04-025
699.762 MHz H1 1D in cdc13 (ref. to CDC13 @ 7.26 ppm)
temp 27.6 C -> actual temp = 27.6 C, solid probe

Department of Chemistry, University of Alberta

Recorded on: v700, Mar 18 2017
Pulse Sequence: PRESAT
Sweep Width (Hz): 8369.26
Digital Res. (Hz/pt): 0.13
Acquisition Time(s): 5
Hz per min (Hz/min): 23.32
Relaxation Delay(s): 0.1
Completed Scans: 16

This is a chemical spectroscopy report, likely an NMR spectrum, showing the chemical shifts and peaks for compound 2b.
Anis, AF-04-925
125.868 MHz C13 DEPTq in cdcl3 (ref. to CDC3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
DEPTq:135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Department of Chemistry, University of Alberta

Anis, AF-03-159-A
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
Anis, AF-03-159-A
175.974 MHz C13 DEPTq in cdc3 (ref. to CDC3 @ 77.06 ppm)
temp 27.5 °C -> actual temp = 27.0 °C, coldid probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-03-153-B
699.762 MHz H1 1D in cdcl3 (ref. to CDC13 @ 7.26 ppm)
temp 27.5°C -> actual temp = 27.9°C, coldid probe
Anis, AF-03-153-B
175.9 T4 MHz C13 DEPTq in cdc3 (ref. to CDC13 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-03-187-C
699.762 MHz H1 1D in cdc13 (ref. to CDC13 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.5 C, coldid probe

![Chemical Structure](image)

Department of Chemistry, University of Alberta

Recorded on: v700, Mar 13 2017
Pulse Sequence: PRESAT
Digital Res.(Hz/pt): 0.13
Hz per mm/(Hz/mm): 26.25
Completed Scans: 16

Acquisition Time(s): 5
Relaxation Delay(s): 0.1
Anis, AF-03-187-C
175.974 MHz C13 DEPTq in ccdCl3 (ref. to CDC13 @ 77.06 ppm)
temp 27.5 C -> actual temp 27.0 C, coldid probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-03-155-A
699.762 MHz H1 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
Anis, AF-03-155-A
175.974 MHz C13 DEPTq in cdcl3 (ref. to CDC13 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-04-047-A

699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C => actual temp = 27.0 C, coldid probe
Agilent Technologies

Anis, AF-04-047-A
125.686 MHz C13 DEPTq in cdc13 (ref. to CDC13 @ 77.06 ppm)
temp 27.7 C => actual temp = 27.0 C, colldual probe
DEPTq 135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2

Department of Chemistry, University of Alberta
Recorded on: u500, Mar 25 2017
Pulse Sequence: DEPT_chempack

S24
Anis, AF-04-041-A
699.762 MHz H1 1D in cdc3 (ref. to CDC3 @ 7.26 ppm)
temp 27.5 C → actual temp = 27.9 C, coldid probe
Anis, AF-04-041-A
125.688 MHz C13 DEPTq in dcd3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colidual probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-03-187-A
699.762 MHz H1 1D in cdc3 (ref. to CDC3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
Anis, AF-03-187-A
175.973 MHz C13 DEPTq in cdcl3 (ref. to CDC13 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.8 C, coldid probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-04-079
699.762 MHz H1 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 °C → actual temp = 27.0 °C, coldid probe
Anis, AF-04-079
125.688 MHz C13 DEPTq in cdc3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C => actual temp = 27.0 C, cold dual probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-04-039
699.762 MHz H1 1D in ccdCl3 (ref. to CDC13 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe

Department of Chemistry, University of Alberta
Recorded on: v700, Mar 20 2017  
Sweep Width(·Hz): 8389.26  
Sweep Width(·Hz): 8389.26
Sweep Width(·Hz): 8389.26  
Sweep Width(·Hz): 8389.26
Acquisition Time(s): 5  
Acquisition Time(s): 5
Acquisition Time(s): 5  
Acquisition Time(s): 5
Digital Res. (·Hz/d): 0.13  
Digital Res. (·Hz/d): 0.13
Digital Res. (·Hz/d): 0.13  
Digital Res. (·Hz/d): 0.13
Hz per mm(·Hz/mm): 26.26  
Hz per mm(·Hz/mm): 26.26
Hz per mm(·Hz/mm): 26.26  
Hz per mm(·Hz/mm): 26.26
Completed Scans: 16  
Completed Scans: 16
Completed Scans: 16  
Completed Scans: 16
129.68 MHz C13 DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, coelcical probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-04-081 699.762 MHz H1 1D in cdcl3 (ref. to CDC13 @ 7.26 ppm) temp 27.5 C -> actual temp = 27.0 C, coldid probe
Anis, AF-04-081
125.668 MHz C13 DEPTq in cdc3 (ref. to CDC11 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, cold dual probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

C13n edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-04-031
699.762 MHz H1 1D in cdc3 (ref. to CDC3 @ 7.26 ppm)
temp 27.5°C -> actual temp = 27.0°C, cold probe
Anis, AF-04-031
125.66 MHz C13 DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C → actual temp = 27.0 C, cold dual probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-04-101-C
698.762 MHz H1 1D in cdc5 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
Anis, AF-04-101-C
125.600 MHz C13 DEPTq in cdcl3 (ref. to CDC13 @ 77.06 ppm)
temp 27.7 C → actual temp = 27.8 C, cold1 dual probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
AF-04-105
399.764 MHz H1 1D in cdCl3 (ref. to CDCl3 @ 7.26 ppm)
temp 26.5 C → actual temp = 27.3 C, autosol probe

Department of Chemistry, University of Alberta

Recorded on: 400, Apr 27 2017
Pulse Sequence: s2pul

Sweep Width(Hz): 4801.92
Digital Res.(Hz/pdt): 0.07
Acquisition Time(s): 4.998
Hz per mm(Hz/mm): 14.99
Relaxation Delay(s): 0.1
Completed Scans: 16
Anis, AF-04-105
125.888 MHz C13 DEPTq in dcds (ref. to CDC13 @ 77.06 ppm)
 temp 27.7 °C -> actual temp = 27.0 °C, colddual probe
 DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-04-089
699.762 MHz H1 1D in cdc13 (ref. to CDC13 @ 7.26 ppm)
temp 27.5°C -> actual temp = 27.0°C, coldid probe
Anis, AF-04-069
125.668 MHz C13 DEPTq in cdc3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C → actual temp = 27.9 C, coldfual probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
PM-11-133-A
400.118 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 29.9 C -> actual temp = 27.0 C, autosdb probe
Anis, PM-11-133-A
125.688 MHz C13 DEPTq in cdCl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.9 C, colddual probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2
Anis, AF-04-151
699.763 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C => actual temp = 27.8 C, coldid probe

[Diagram of molecule labeled 4d]

S45
Anis, AF-04-151
125.888 MHz C13 DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C → actual temp = 27.0 C, cold dual probe
DEPTq-135, C & CH2 same, CH & CH3 opposite side of solvent signal

CHn edited spectrum, CH & CH3 opposite side of CH2, quaternaries same side as CH2