Supporting Information
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A Convenient Synthesis of Tri- and Tetramethylbenzaldehydes from Readily Available Phenols

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General Procedure for formylation of phenols: Alumini um trichloride (4.82 g, 36 mmol) was added to a solution of phenol (4 mL, 33 mmol) in anhydrous CH$_2$Cl$_2$ (50 mL) under argon and the solution was stirred for 10 minutes. Dichloromethyl methyl ether (3.3 mL, 36 mmol) was added dropwise via a syringe pump at 7.7 mL/hr. The reaction was left to stir for a further 10 minutes before cold water (200 mL) was added slowly. After stirring for a further 10 minutes, the organic layer was separated and washed with brine (100 mL) and water (150 mL), dried with MgSO$_4$, filtered and concentrated to give the crude aldehyde.

General Procedure for synthesis of aryl trifluoromethanesulfonates: Triethylamine (4.04 g, 40 mmol) was added to a solution of phenol (2 g, 13 mmol) in anhydrous CH$_2$Cl$_2$ (13 mL) at -78°C under argon and the solution stirred for 30 minutes. Trifluoromethylsulfonate anhydride (2.5 mL, 15 mmol, 1.1 eq) was added dropwise via a syringe pump at 7.7 mL/hr. The reaction was left to stir for a further 2 hrs. The reaction mixture was diluted with CH$_2$Cl$_2$ (15 mL) and washed with saturated NaHCO$_3$ (20 mL), brine (20 mL) and water (20 mL), dried (MgSO$_4$), filtered and concentrated to give the corresponding aryl trifluoromethanesulfonate.

General Procedure for Suzuki cross-coupling with methylboronic acid: Potassium carbonate (397 mg, 3 mmol) and PdCl$_2$(dpdpf).CH$_2$Cl$_2$ (116 mg, 10 mol%) were added to a solution of aryl trifluoromethanesulfonate (400 mg, 1 mmol) in THF (25 mL) which was left to stir for 5 minutes. Water (HPLC grade, 1.25 mL) was added, followed by methyl boronic acid (255 mg, 4 mmol). The reaction was heated at reflux overnight. Ethyl acetate (7 mL) was added and the organic layer separated and washed with water (2 × 10 mL), dried with MgSO$_4$, filtered and concentrated to give the crude methylbenzene.
2-Hydroxy-3,5-dimethylbenzaldehyde (3)

Purification by column chromatography with 100% petrol; brown viscous oil (3.2 g, 65%); \( R_f = 0.97 \) (1 : 1 EtOAc : petrol); \( \nu_{\text{max}} \) 3201 (O-H), 2921 (C-H), 1646 (C=O), 1467 (aromatic), 1260 (C-O) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) 11.09 (s, 1H, -OH), 9.81 (s, 1H, CHO), 7.20 (br s, 1H, 4-H), 7.15 (s, 1H, 6-H), 2.29 (s, 3H, 5-Me), 2.23 (s, 3H, 3-Me); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) 196.8 (CHO), 158.0 (C\(_q\)), 139.1 (CH), 131.0 (CH), 128.6 (C\(_q\)), 126.6 (C\(_q\)), 119.9 (C\(_q\)), 20.3 (CH\(_3\)), 15.1 (CH\(_3\)); HRMS (El) calcd. for C\(_9\)H\(_{10}\)O\(_2\) [M]+ 150.0680, found 150.0681.

2-Hydroxy-3,6-dimethylbenzaldehyde (5)

Purification by dry load flash column gradient method 0-40% EtOAc: petrol isolated minor isomer as a pale green oil (720 mg, 15%); \( R_f = 0.87 \) (1 : 1 EtOAc : petrol); \( \nu_{\text{max}} \) 2926 (C-H), 1633 (C=O), 1458 (aromatic), 1424 (aromatic), 1232 (C-O) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) 12.1 (s, 1H, OH), 10.3 (s, 1H, CHO), 7.24 (d, 1H, \( J = 7.4 \) Hz, 4-H), 6.62 (d, 1H, \( J = 7.4 \) Hz, 5-H), 2.57 (s, 3H, 6-Me), 2.21 (s, 3H, 3-Me); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) 195.8 (CHO), 161.7 (C\(_q\)), 139.5 (C\(_q\)), 138.4 (CH), 125.1 (C\(_q\)), 121.3 (CH), 118.1 (C\(_q\)), 18.1 (CH\(_3\)), 15.1 (CH\(_3\)); HRMS (El) calcd. for C\(_9\)H\(_{10}\)O\(_2\) [M]+ 150.0680, found 150.0669.
4-Hydroxy-3,5-dimethylbenzaldehyde (7)\(^3\)

![Chemical Structure](attachment:image.png)

Compound used directly without purification; purple-pink powder (3.5 g, 71%). M.p. 92-95°C [lit. 112-114°C]; R\(_f\) = 0.73 (1:1 EtOAc : petrol); IR\(_{max}\) 3248 (O-H), 2915 (C-H), 1664 (C=O), 1591 (aromatic), 1488 (aromatic), 1200 (C-O) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) 9.81 (s, 1H, CHO), 7.54 (s, 2H, 2-H), 5.38 (s, 1H, OH), 2.31 (s, 6H, 3-Me); \(^13\)C NMR (150 MHz, CDCl\(_3\)) 191.6 (CHO), 158.1 (C\(_q\)), 131.1 (2 \times CH), 129.5 (C\(_q\)), 123.8 (2 \times C\(_q\)), 15.9 (2 \times CH\(_3\)); HRMS (EI) calcd. for C\(_9\)H\(_{10}\)O\(_2\) [M]+150.0680, found 150.0673.

4-Hydroxy-2,3-dimethylbenzaldehyde (9)\(^4\) and 2-Hydroxy-3,4-dimethylbenzaldehyde (10)\(^5\)

The crude product contained a 1:0.4 ratio of aldehydes 9 and 10. The two compounds could be separated by column chromatography (0-30% EtOAc: petrol); combined yield of 44%.

9: White crystals (1.36g, 28%); m.p 155-157 °C [lit. 160-171 °C]; R\(_f\) = 0.51 (1:1 EtOAc: petrol); IR\(_{max}\) 3251 (O-H), 2953 (C-H), 1651 (C=O), 1580 (aromatic), 1251 (C-O) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) 10.2 (s, 1H, CHO), 7.54 (d, 1H, J = 8.5 Hz, 6-H), 6.76 (d, 1H, J = 8.5 Hz, 5-H), 5.62 (s, 1H, OH), 2.61 (s, 3H, 2-Me), 2.22 (s, 3H, 3-Me); \(^13\)C NMR (150 MHz, CDCl\(_3\)) 192.0 (CHO), 158.5 (C\(_q\)), 142.3 (C\(_q\)), 131.1 (CH), 128.3 (C\(_q\)), 124.1 (C\(_q\)), 113.1 (CH), 14.9 (CH\(_3\)), 11.4 (CH\(_3\)); HRMS (CI) calcd. for C\(_9\)H\(_{11}\)O\(_2\) [M+H]\(^+\) 151.0680, found 151.0753.
10: Yellow powder (750 mg, 16%); m.p. 43-45 °C; R_f = 0.91 (1: 1 EtOAc : petrol); IRυ max 3200 (O-H), 2839 (C-H), 1645 (C=O), 1620 (aromatic), 1499 (aromatic), 1230 (C-O) cm⁻¹; ¹H NMR (600 MHz, CDCl₃) 11.37 (s, 1H, OH), 9.81 (s, 1H, CHO), 7.29 (d, 1H, J = 7.9 Hz, 6-H), 6.83 (d, 1H, J = 7.9 Hz, 5-H), 2.33 (s, 3H, 4-Me), 2.17 (s, 3H, 3-Me); ¹³C NMR (150 MHz, CDCl₃) 196.1 (CHO), 159.9 (C_q), 147.3 (C_q), 130.9 (CH), 125.0 (C_q), 121.6 (CH), 118.6 (C_q), 21.1 (CH₃), 10.8 (CH₃); HRMS (Cl) calcd. for C₉H₁₁O₂ [M+H]⁺ 151.0680, found 151.0752.

4-Hydroxy-2,3,5-trimethylbenzaldehyde (13)⁶

Prepared according to the general procedure but only 1.1 eq of dichloromethyl methyl ether and AlCl₃ were used with respect to the phenol.

Yellow viscous oil (2.9 g, 60%); m.p. 123-125 °C; R_f = 0.91 (1: 1 EtOAc : petrol); IRυ max 3356 (O-H), 2926 (C-H), 1657 (C=O), 1570 (aromatic), 1290 (C-O) cm⁻¹; ¹H NMR (600 MHz, CDCl₃) 10.1 (s, 1H, CHO), 7.49 (s, 2H, 6-H), 5.31 (d, 1H, J = 6.1 Hz, OH), 2.57 (s, 3H, 2-Me), 2.28 (s, 3H, 5-Me), 2.21 (s, 3H, 3-Me); ¹³C NMR (150 MHz, CDCl₃) 192.1 (CHO), 157.1 (C_q), 139.7 (C_q), 132.6 (CH), 127.8 (C_q), 123.2 (C_q), 120.5 (C_q), 15.7 (CH₃), 14.7 (CH₃), 11.7 (CH₃); HRMS (Cl) calcd. for C₁₀H₁₃O₂ [M + H]⁺ 165.0837, found 165.0906.
2-Formyl-4,6-dimethylphenyl trifluoromethanesulfonate (4)

\[
\begin{array}{c}
\text{O} \\
\text{S-CF}_3 \\
\text{O} \\
\text{3} \\
\text{4} \\
\text{5} \\
\text{6}
\end{array}
\]

Purified by column chromatography (0-40% EtOAc in petrol); Yellow viscous oil (2.4 g, 64%). \( R_f = 0.91 \) (1: 1 EtOAc : petrol); IR
\( \nu_{\text{max}} \) 2883 (C-H), 1701 (C=O), 1598 (aromatic), 1407 (O=S=O), 1207 (C-O), 1136 (C-F) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) 10.19 (s, 1H, CHO), 7.62 (d, 1H, \( J = 2.0 \) Hz, 3-H), 7.38 (d, 1H, \( J = 2.0 \) Hz 5-H), 2.42 (s, 3H, 6-Me), 2.40 (s, 3H, 4-Me); \(^1\)3C NMR (150 MHz, CDCl\(_3\)) 187.4 (CHO), 145.9 (C\(_\text{q}\)), 139.1 (C\(_\text{q}\)), 138.8 (CH), 132.5 (C\(_\text{q}\)), 129.2 (C\(_\text{q}\)), 128.5 (CH), 118.4 (q, \( J = 321 \) Hz, C\(_\text{q}\)), 20.9 (CH\(_3\)), 16.5 (CH\(_3\)) ; HRMS (EI) calcd. for \( \text{C}_{10}\text{H}_{9}\text{F}_3\text{O}_4\text{S} \ [\text{M}]^+ \) 282.0174, found 282.0174.

2-Formyl-3,6-dimethylphenyl trifluoromethanesulfonate (6)

\[
\begin{array}{c}
\text{O} \\
\text{S-CF}_3 \\
\text{O} \\
\text{3} \\
\text{4} \\
\text{5} \\
\text{6}
\end{array}
\]

Prepared according to the general procedure but 2.2 eq. of trifluoromethanesulfonic anhydride were used and 3.2 eq triethylamine.

Purified column chromatography (0-20% EtOAc in petrol); red-brown oil (925 mg, 34%). \( R_f = 0.72 \) (1: 1 EtOAc : petrol); IR
\( \nu_{\text{max}} \) 2981 (C-H ald), 1612 (C=O ald), 1455 (aromatic), 1350 (O=S=O), 1207 (C-O), 1132 (C-F) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) 10.4 (s, 1H, H-CHO), 7.41 (d, 1H, \( J = 8.0 \) Hz, 4-H), 7.21 (d, 1H, \( J = 8.0 \) Hz, 5-H), 2.60 (s, 3H, 6-Me), 2.42 (s, 3H, 3-Me); \(^1\)3C NMR (150 MHz, CDCl\(_3\)) 189.9 (CHO), 148.9 (C\(_\text{q}\)), 140.8 (C\(_\text{q}\)), 136.7 (CH), 132.0 (CH), 130.2 (C\(_\text{q}\)), 128.0 (C\(_\text{q}\)), 121.4 (q, \( J = 299.3 \) Hz, C\(_\text{q}\)), 20.8 (CH\(_3\)), 16.5 (CH\(_3\)); HRMS (Cl) calcd. for \( \text{C}_{10}\text{H}_{9}\text{F}_3\text{O}_4\text{S} \ [\text{M}]^+ \) 282.0174, found 282.0110.
4-Formyl-2, 6-dimethylphenyl trifluoromethanesulfonate (8)

Prepared according to the general procedure but 1.9 eq. of trifluoromethanesulfonic anhydride and 3.2 eq. of triethylamine were used.

Purified by column chromatography (0-20% EtOAc in petrol); yellow oil (88 mg, 53%); R_f = 0.89 (1:1 EtOAc: petrol); IR\text{\nu}_{\text{max}} 2922-2864 (ald C-H), 1701 (ald C=O), 1604 (aromatic), 1290 (O=S=O), 1212 (C-O), 1132 (C-F) cm^{-1}; ^1\text{H} NMR (600 MHz, CDCl_3) 9.96 (s, 1H, CHO), 7.66 (br s, 2H, H-3, 5), 7.30 (d, 1H, J = 7.8 Hz, 5-H), 7.34 (d, 1H, J = 7.8 Hz 6-H), 2.47 (s, 6H, 6-Me and 2-Me); ^13\text{C} NMR (150 MHz, CDCl_3) 191.1 (CHO), 150.8 (C\text{q}), 135.4 (C\text{q}), 133.1 (2 \times C\text{q}), 131.2 (2 \times CH), 118.7 (q, J = 321 Hz, C\text{q}), 17.5 (2 \times CH_3); HRMS (CI) calcd. for C_{10}H_{10}F_3O_4S [M+H]^+ 283.0174, found 283.0237.

4-Formyl-2,3-dimethylphenyl trifluoromethanesulfonate (11) and 6-formyl-2,3-dimethylphenyl trifluoromethanesulfonate (12)

Prepared according to the general procedure from a mixture of aldehydes 9 and 10, using 1.2 eq. of trifluoromethanesulfonic anhydride and 3 eq of triethylamine.

Purification by dry load gradient method 0-20% EtOAc: Petrol. Isolated as a mixture of the two isomers 11 and 12 as a yellow oil (1.8 g, 95%).

11: R_f = 0.92 (1 : 1 EtOAc : petrol); IR\text{\nu}_{\text{max}} 2881 (C-H ald), 1695 (C=O ald), 1423 (aromatic), 1390 (O=S=O), 1213 (C-O), 1137 (C-F) cm^{-1}; ^1\text{H} NMR (600 MHz, CDCl_3) 10.2 (s, 1H, CHO), 7.75 (d, 1H, J = 7.8 Hz, 5-H), 7.34 (d, 1H, J = 7.8 Hz 6-H), 2.41 (s, 3H, 2-Me), 2.34 (s, 3H, 3-
4-Formyl-2, 3, 6-trimethylphenyl trifluoromethanesulfonate (14)

Prepared according to the general procedure but 1.7 eq. of trifluoromethanesulfonic anhydride and 3.2 eq. of triethylamine were used.

Purified by column chromatography (0-10% EtOAc in petrol); yellow oil (250 mg, 46%). Rf = 0.93 (1:1 EtOAc: petrol); IRνmax 2956 (ald C-H), 1699 (ald C=O), 1407 (aromatic), 1209 (O=S=O), 1136 (C-O), 1040 (C-F) cm⁻¹; ¹H NMR (600 MHz, CDCl₃) 10.30 (s, 1H, H-CHO), 7.61 (s, 1H, 5-H), 2.60 (s, 3H, 2-Me), 2.43 (s, 3H, 6-Me), 2.34 (s, 3H, 3-Me); ¹³C NMR (150 MHz, CDCl₃) 191.9 (CHO), 150.2 (Cq), 139.9 (Cq), 133.6 (Cq), 132.6 (CH), 132.3 (Cq), 129.6 (Cq), 118.6 (q, J = 319.4 Hz, Cq), 17.2 (CH₃), 14.7 (CH₃), 14.0 (CH₃); HRMS (EI) calcd. for C₁₁H₁₁F₃O₄S [M⁺] 296.0330, found 296.0324.
2,3,5-Trimethylbenzaldehyde (1a)

Prepared according to the general procedure.

Purified by column chromatography (30% EtOAc in petrol); brown oil (208 mg, 99%); \( R_f = 0.82 \) (1:1 EtOAc:petrol); IR \( \nu_{\max} \) 2923 (C-H ald), 1692 (C=O ald), 1478 (aromatic) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) 10.28 (s, 1H, CHO), 7.46 (s, 1H, 6-H), 7.20 (s, 1H, 4-H), 2.52 (s, 3H, 2-Me), 2.33 (s, 3H, 5-Me), 2.30 (s, 3H, 3-Me); \(^1^3\)C NMR (150 MHz, CDCl\(_3\)) 193.5 (CHO), 138.3 (C\(_q\)), 136.4 (CH), 136.3 (C\(_q\)), 135.4 (C\(_q\)), 134.3 (C\(_q\)), 130.1 (CH), 21.2 (CH\(_3\)), 20.2 (CH\(_3\)), 14.3 (CH\(_3\)); HRMS (EI) calcd. for C\(_{10}\)H\(_{12}\)O \([M]^+\) 148.0888, found 148.0876.

2,3,6-Trimethylbenzaldehyde (1b)

Prepared according to the general procedure.

Purification by column chromatography (0-10% EtOAc in petrol); orange-yellow oil (209 mg, 99%); \( R_f = 0.91 \) (1:1 EtOAc : petrol); IR \( \nu_{\max} \) 2930 (C-H ald), 1687 (C=O ald), 1461 (aromatic) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) 10.64 (s, 1H, CHO), 7.22 (d, 1H, \( J = 7.7 \) Hz, 4-H), 6.98 (d, 1H, \( J = 7.7 \) Hz, 5-H), 2.52 (s, 3H, 6-Me), 2.48 (s, 3H, 2-Me), 2.29 (s, 3H, 3-Me); \(^1^3\)C NMR (150 MHz, CDCl\(_3\)) 194.9 (CHO), 139.1 (C\(_q\)), 138.2 (C\(_q\)), 135.7 (C\(_q\)), 134.5 (CH), 133.3 (C\(_q\)), 129.1
(CH), 20.5 (CH₃), 20.2 (CH₃), 15.6 (CH₃); HRMS (EI) calcd. for C₁₀H₁₂O [M]⁺ 148.0888, found 148.0873.

3,4,5-Trimethylbenzaldehyde (1c)¹¹
Prepared according to the general procedure using 8 (500 mg), methylboronic acid (5 eq.), K₂CO₃ (3 eq.) and PdCl₂(dppf).dcm (15 mol%).

\[
\begin{array}{c}
\text{O} \\
\text{6} \\
\text{5} \\
\text{4} \\
\text{3} \\
\text{2} \\
\text{6} \\
\end{array}
\]

Purified by column chromatography (0-10% EtOAc in petrol); yellow oil (159 mg, 61%); Rₚ = 0.93 (1 : 1 EtOAc : petrol); IRυ max 2929 (C-H ald), 1694 (C=O ald), 1406 (aromatic) cm⁻¹; ¹H NMR (600 MHz, CDCl₃) 9.90 (s, 1H, H-1), 7.51 (s, 2H, 2-H and 6-H), 2.36 (s, 6H, 3-Me and 5-Me), 2.25 (s, 3H, 4-Me); ¹³C NMR (150 MHz, CDCl₃) 192.7 (CHO), 143.2 (C_q), 137.5 (2 × C_q), 133.9 (C_q), 129.0 (2 × CH), 20.7 (2 × CH₃), 16.2 (CH₃); HRMS (EI) calcd. for C₁₀H₁₂O [M]⁺ 148.0888, found 148.0878.

2,3,4-Trimethylbenzaldehyde (1d)¹²
Prepared according to the general procedure using a mixture of 11 and 12 (500 mg), methylboronic acid (3 eq.), K₂CO₃ (2 eq.) and PdCl₂(dppf).dcm (10 mol%).

\[
\begin{array}{c}
\text{O} \\
\text{6} \\
\text{5} \\
\text{4} \\
\text{3} \\
\text{2} \\
\end{array}
\]
Purified by column chromatography (0-40% EtOAc in petrol); yellow oil (255 mg, 97%); R_f = 0.89 (1: 1 EtOAc : petrol); IRν_{max} 2935 (C-H ald), 1693 (C=O ald), 1680 (aromatic), 1593 (aromatic) cm^{-1}; ^1H NMR (600 MHz, CDCl₃) 10.26 (s, 1H, CHO), 7.56 (d, 1H, J = 7.7 Hz, 6-H), 7.16 (d, 1H, J = 7.7 Hz, 5-H), 2.60 (s, 3H, 3-Me), 2.36 (s, 3H, 4-Me), 2.24 (s, 3H, 2-Me); ^13C NMR (150 MHz, CDCl₃) 193.2 (CHO), 143.5 (C_q), 139.2 (C_q), 137.0 (C_q), 132.8 (C_q), 129.7 (CH), 127.8 (CH), 21.7 (CH₃), 15.4 (CH₃), 14.9 (CH₃); HRMS (CI) calcd. for C_{10}H_{13}O [M +H]^+ 149.0888, found 149.0959.

2,3,4,5-Tetramethylbenzaldehyde (1e)

Prepared according to the general procedure using 14 (800 mg), methylboronic acid (5 eq.), K₂CO₃ (3 eq.) and PdCl₂(dppf).dcn (15 mol%).

Purified by column chromatography (0-10% EtOAc in petrol); yellow oil (438 mg, 80%); R_f = 0.93 (1 : 1 EtOAc : petrol); IRν_{max} 2931 (C-H ald), 1688 (C=O), 1600 (aromatic) cm^{-1}; ^1H NMR (600 MHz, CDCl₃) 10.25 (s, 1H, H-CHO), 7.46 (s, 1H, 6-H), 2.58 (s, 3H, 4-Me), 2.33 (s, 3H, 5-Me), 2.27 (s, 3H, 2-Me), 2.25(s, 3H, 3-Me); ^13C NMR (150 MHz, CDCl₃) 193.5 (CHO), 142.2 (C_q), 136.8 (CH), 136.7 (C_q), 134.3 (C_q), 132.3 (C_q), 130.8 (CH), 21.8 (CH₃), 17.0 (CH₃), 15.9 (CH₃), 14.8 (CH₃); HRMS (EI) calcd. for C_{11}H_{14}O [M]^+ 162.1045, found 162.1035.
Methyl-2,4-dimethyl-3,6-bis(trifluoromethyl)sulfonyl)oxy)benzoate (14)

Prepared according to the general procedure using methyl 2,5-dihydroxy-4,6-dimethylbenzoate 2f (1.35 g), trifluoromethanesulfonic anhydride (2.2 eq) and triethylamine (3 eq).

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{S} \\
\text{CF}_3 & \quad \text{CF}_3 \\
\text{O} & \quad \text{S} \\
\text{CF}_3 & \quad \text{CF}_3
\end{align*}
\]

Purified by column chromatography (20% EtOAc in petrol); yellow viscous oil (3.0 g, 98%); \( R_f = 0.68 \) (1 : 1 EtOAc : petrol); \( \nu_{\max} \) IR 1740 (C=O), 1420 (aromatic), 1399 (O=S=O), 1206 (C-O), 1130 (C-F) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) 7.22 (s, 1H, 5-H), 3.94 (s, 3H, Me), 2.45 (s, 3H, 4-Me), 2.37 (s, 3H, 2-Me); \(^1^3\)C NMR (150 MHz, CDCl\(_3\)) 164.6 (C\(_q\)), 148.9 (C\(_q\)), 145.2 (C\(_q\)), 138.6 (C\(_q\)), 127.9 (C\(_q\)), 124.3 (C\(_q\)), 123.6 (CH), 118.6 (q, \( J = 320.6 \) Hz, C\(_q\)), 118.4 (q, \( J = 320.6 \) Hz, C\(_q\)), 53.1 (CH\(_3\)), 20.5 (CH\(_3\)), 11.1 (CH\(_3\)); HRMS (CI) calcd. for C\(_{12}\)H\(_{11}\)F\(_6\)O\(_8\)S\(_2\) [M + H]\(^+\) 460.9721, found 460.9785.

Methyl-2, 3, 4, 6-tetramethylbenzoate (15)

Prepared according to the general procedure using 14 (1 g), methylboronic acid (10 eq.), K\(_2\)CO\(_3\) (3 eq.) and PdCl\(_2\)(dpff).dcm (15 mol%).

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{S} \\
\text{CF}_3 & \quad \text{CF}_3 \\
\text{O} & \quad \text{S} \\
\text{CF}_3 & \quad \text{CF}_3
\end{align*}
\]

Purified by column chromatography (0-10% EtOAc in petrol); orange yellow oil (447 mg, 87%); \( R_f = 0.68 \) (1:4 EtOAc : petrol); \( \nu_{\max} \) IR 2949 (C-H), 1730 (C=O), 1435 (aromatic), 1268 (C-O) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) 6.86 (s, 1H, 5-H), 3.90 (s, 3H, Me), 2.25 (s, 3H, 6-Me), 2.22
(s, 3H, 4-Me), 2.20 (s, 3H, 3-Me), 2.15 (s, 3H, 2-Me); $^{13}$C NMR (150 MHz, CDCl$_3$) 171.5 (C$_q$), 137.7 (C$_q$), 132.9 (C$_q$), 132.8 (C$_q$), 132.5 (C$_q$), 131.3 (C$_q$), 129.3 (CH), 52.0 (CH$_3$), 20.9 (CH$_3$), 19.3 (CH$_3$), 17.6 (CH$_3$), 15.3 (CH$_3$); HRMS (EI) calcd. for C$_{12}$H$_{16}$O$_2$ [M]$^+$ 192.1150, found 192.1153.

2, 3, 4, 6-Tetramethylphenyl)methanol$^{15}$

Diisobutylaluminium hydride (10 M solution in diethyl ether, 0.039 mL, 0.39 mmol) was added to a solution of 15 (50 mg, 0.26 mmol, 1 eq) in toluene (3 mL) at -78 °C under argon. The reaction was stirred for 4 hrs at -78°C then CH$_2$Cl$_2$ (5 mL) was added and the reaction mixture was washed with brine (5 mL) and water (2 × 10 mL), dried with MgSO$_4$, filtered and evaporated. Purification by column chromatography (20% EtOAc in petrol) gave the alcohol as a colourless oil (27 mg, 63%).

R$_f$ = 0.81 (1 : 1 EtOAc : petrol); IR$_{\text{v max}}$ 3383 (O-H), 2921 (C-H), 1443 (aromatic), 1265 (C-O) cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) 6.88 (s, 1H, H-5), 4.74 (s, 2H, H-7), 2.37 (s, 3H, 6-Me), 2.35 (s, 3H, 2-Me), 2.26 (s, 3H, 4-Me), 2.18 (s, 3H, 3-Me); $^{13}$C NMR (150 MHz, CDCl$_3$) 136.5 (C$_q$), 136.2 (C$_q$), 134.4 (C$_q$), 134.1 (C$_q$), 133.5 (C$_q$), 129.8 (CH), 59.9 (CH$_2$), 20.9 (CH$_3$), 19.5 (CH$_3$), 15.91 (CH$_3$), 15.88 (CH$_3$); HRMS (EI) calcd. for C$_{11}$H$_{16}$O [M]$^+$ 164.1201, found 164.1195.

2, 3, 4, 6-Tetramethylbenzaldehyde (1f)$^{16}$

Oxalyl chloride (0.3 mL, 0.6 mmol, 2 M solution in CH$_2$Cl$_2$, 1.1 eq) and anhydrous DMSO (78 μl, 1 mmol, 2 eq) were added to CH$_2$Cl$_2$ (3 mL) under argon at -78°C. After stirring for 15 minutes, 16 (90 mg, 0.55 mmol, 1 eq) and NEt$_3$ (0.23 mL, 2 mmol, 3 eq) were added and the
reaction was left to stir for 3 hrs, then diluted with CH₂Cl₂ (5 mL) and washed with aqueous saturated sodium carbonate (15 mL), followed by brine (15 mL) and water (15 mL), dried with MgSO₄, filtered and evaporated. The crude material was purified by column chromatography (20% EtOAc in petrol) to give the aldehyde as a yellow oil (17 mg, 18%); Rf = 0.89 (1 : 1 EtOAc: petrol); IRυ max 2924 (C-H), 1690 (C=O), 1596 (aromatic) cm⁻¹; ¹H NMR (600 MHz, CDCl₃) 10.60 (s, 1H, H-CHO), 6.90 (s, 1H, 5-H), 2.52 (s, 3H, 4-Me), 2.51 (s, 3H, 6-Me), 2.30 (s, 3H, 3-Me), 2.19 (s, 3H, 2-Me); ¹³C NMR (150 MHz, CDCl₃) 194.5 (CHO), 142.2 (C q), 139.2 (C q), 137.9 (C q), 134.3 (C q), 131.5 (C q), 131.2 (CH), 21.5 (CH₃), 20.5 (CH₃), 15.9 (CH₃), 15.3 (CH₃); HRMS (El) calcd. for C₁₁H₁₄O [M]+ 162.1045, found 162.1031.
References
