Supporting Information

Oxidation of Hydroxyl-Substituted Organotrifluoroborates

Gary A. Molander and Daniel E. Petrillo*

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania,

Philadelphia, Pennsylvania 19104-6323

Contents:

Experimental Data	S1
References	S19
NMR spectra	S20

General. Standard bench top techniques were employed for handling air-sensitive reagents.¹

THF was distilled from Na/benzophenone ketyl. Acetone was distilled from K₂CO₃. CH₂Cl₂ was dried by passing through a column of activated alumina. All other solvents were HPLC

grade and used as received. Borane-pyridine complex was purified by passing through a plug of silica gel, eluting with 2:1 Et₂O/hexanes.² Powdered molecular sieves were activated by heating at 180 °C at 0.001 Torr for 18 h. Melting points (°C) were determined using a Thomas–Hoover melting point apparatus and are uncorrected. ¹H, ¹³C, ¹¹B, and ¹⁹F NMR spectra were recorded at 500 MHz, 126 MHz, 128 MHz, and 471 MHz, respectively. Analytical thin-layer chromatography (TLC) was performed on silica gel plates (0.25 mm) precoated with a fluorescent indicator. Visualization was effected with ultraviolet light or KMnO₄ (in aq K₂CO₃/NaOH). Standard flash chromatography procedures³ were followed using 40–63 μm silica gel (200 X 400 mesh).

slurried in H₂O (15 mL) at 0 °C in an ice/water bath. KHF₂ (1.56 g, 20.0 mmol) was added all at once as a solid. The mixture was stirred for 2 h at 0 °C at which point H₂O (6 mL) was used to rinse the neck and sides of the flask. After stirring for an additional 2 h, CH₂Cl₂ (15 mL) was added followed by *n*-Bu₄NOH (1.61M, 6.25 mL, 10.1 mmol) via syringe. After stirring for 0.5 h, the biphasic mixture was transferred to a separatory funnel, rinsing with CH₂Cl₂ (10 mL). The layers were shaken and separated and the aqueous layer was further extracted with CH₂Cl₂ (10 mL, 15 mL). The combined organic layers were dried (Na₂SO₄) and concentrated to give an oil which solidified to yellow crystals (3.70 g, 89% yield): mp 98-99 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 4.56 (s, 2H), 2.93-2.89 (m, 8H), 1.42-1.36 (m, 8H), 1.28 (sextet, *J* = 7.3, 8H), 0.91 (t, *J* = 7.3, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 128.2, 132.1, 125.8, 65.7, 58.3, 23.8, 19.6, 13.7; ¹¹B (128 MHz, CDCl₃) δ 2.8 (br s); ¹⁹F NMR (471 MHz, CDCl₃) δ -142.0 (m); IR (film) 3511, 2962, 2876 cm⁻¹; HRMS calcd. for C₇H₇BF₃O

[M-(NBu₄)]⁺ 175.0542, found 175.0545. Anal calcd. for C₂₃H₄₃BF₃NO: C, 66.18; H, 10.38.

Found: C, 65.91; H, 10.56.

Tetra-*n*-butylammonium 3-Hydroxymethylphenyltrifluoroborate (1b). This compound was synthesized from 3-hydroxymethylboronic acid according to the procedure used for **1a** to give a yellow oil which solidified upon standing (785

mg, 94% yield): mp 55-57 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.60 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 4.62 (s, 2H), 3.11-3.08 (m, 8H), 1.56-1.50 (m, 8H), 1.37 (sextet, *J* = 7.3 Hz, 8H), 0.97 (t, *J* = 7.3 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 138.9, 131.3, 130.9, 127.0, 124.7, 66.0, 58.3, 23.7, 19.6, 13.7; ¹¹B NMR (128 MHz, CDCl₃) δ 2.87 (br s); ¹⁹F NMR (471 MHz, CDCl₃) δ -142.1 (m); IR (film) 3515, 2963, 2876 cm⁻¹; HRMS calcd. for C₇H₇BF₃O [M-(NBu₄)]⁺ 175.0542, found 175.0551.

Potassium 4-Hydroxyethylphenyltrifluoroborate (3a). 4-

Acetylphenylboronic acid (1.00 g, 6.10 mmol) was dissolved in anhyd EtOH (5.0 mL) and cooled 0 °C with an ice/water bath. NaBH₄ (579 mg, 15.2 mmol) was added all at once as a solid. After stirring for 16 h, additional EtOH (5.0 mL) was added and the mixture was stirred for 4 h. The soln was cooled to 0 °C and treated with 1N HCl (30 mL, 30 mmol). The mixture was then extracted with EtOAc (3 X 15 mL), dried (Na₂SO₄), and concentrated. The crude boronic acid was then dissolved in MeOH (10 mL) and cooled to 0 °C. Satd aq KHF₂ (6.8 mL, 31 mmol) was added dropwise via syringe. The mixture was stirred at 0 °C for 2 h, concentrated, and placed under high-vacuum (0.001 Torr) for 3 h. The dried solids were triturated with hot acetone (3 X 20 mL) and filtered to remove inorganic

salts. The resulting filtrate was concentrated and Et₂O was added to precipitate a white solid (1.15 g, 83%): mp >210 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.26 (d, *J* = 7.7 Hz, 2H) 7.05 (d, *J* = 7.6 Hz, 2H), 4.85 (d, *J* = 4.1 Hz, 1H), 4.63-4.59 (m, 1H), 1.28 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (126 MHz, DMSO- *d*₆) δ 143.6, 130.9, 123.3, 68.5, 26.0; ¹¹B NMR (128 MHz, DMSO- *d*₆) δ 2.30 (br s); ¹⁹F NMR (471 MHz, DMSO- *d*₆) δ -139.2 (m); IR (KBr) 3368, 2973, 2875, 1610 cm⁻¹; HRMS calcd. for C₈H₉BF₃O [M-K]⁻ 189.0698, found 189.0704.

Tetra-*n*-butylammonium 4-(1-

Hydroxyethyl)phenyltrifluoroborate (1c). Potassium 4-(1-

hydroxyethyl)phenyltrifluoroborate (228 mg, 1.00 mmol) was

slurried in CH₂Cl₂ (2.2 mL). *n*-Bu₄NOH (1.61M, 0.620 mL, 1.00 mmol) was added dropwise via syringe. The mixture was stirred for 5 min then transferred to a separatory funnel rinsing with CH₂Cl₂ (3 mL). H₂O (1 mL) was added and the layers were shaken and separated. The aqueous layer was further extracted with CH₂Cl₂ (3 mL). The combined organic layers were dried (Na₂SO₄) and the mixture was concentrated to give a light yellow solid (415 mg, 96% yield): mp 119-122 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 4.80 (q, *J* = 6.4, 1H), 2.99-2.95 (m, 8H), 1.88 (br s, 1H), 1.46-1.39 (m, 11H), 1.29 (sextet, *J* = 7.3 Hz, 8H), 0.92 (t, *J* = 7.3 Hz, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 142.9, 132.0, 123.9, 70.7, 58.4, 25.2, 23.8, 19.6, 13.7; ¹¹B NMR (128 MHz, CDCl₃) δ 2.17 (br s); ¹⁹F NMR (471 MHz, CDCl₃) δ -141.8 (m); IR (film) 3510, 2964, 2876, 1607, 1484 cm⁻¹; HRMS calcd. for C₈H₉BF₃O [M-(NBu₄)]⁻ 189.0699, found 189.0695.

Potassium 3-(1-Hydroxyethyl)phenyltrifluoroborate (3b). This compound was synthesized from 3-acetylphenyltrifluoroborate according to the procedure

described for **3a** to give a white crystalline solid (1.17 g, 90% yield): mp 189-192

°C; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 7.28 (s, 1H), 7.16-7.14 (m, 1H), 7.02-6.99 (m, 2H), 4.81 (d, J = 4.8 Hz, 1H), 4.62-4.57 (m, 1H), 1.27 (d, J = 6.4 Hz, 3H); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 144.5, 129.7, 128.6, 125.8, 122.0, 68.9, 26.1; ^{11}B NMR (128 MHz, $\text{DMSO-}d_6$) 2.87 (br s); ^{19}F NMR (471 MHz, $\text{DMSO-}d_6$) -139.3 (m); IR (KBr) 3600, 3539, 2982, 2875, 1420 cm^{-1} ; HRMS calcd. for $\text{C}_8\text{H}_9\text{BF}_3\text{O} [\text{M-K}]^-$ 189.0698, found 189.0707.

Potassium 4-(1-Hydroxypropyl)phenyltrifluoroborate (3c). Potassium 4-bromophenyltrifluoroborate (526 mg, 2.00 mmol) was dissolved in THF (20 mL) and cooled to -78°C . $n\text{-BuLi}$ in hexanes (2.44M, 0.830 mL, 2.02

mmol) was added dropwise via syringe. The mixture was stirred at low temperature for 1 h at which point propionaldehyde (114 mg, 2.04 mmol) was added. The mixture was stirred for 45 min at low temperature, then allowed to warm to room temperature for 1 h. The mixture was cooled to 0°C and treated with satd aq KHF_2 (4.5M, 2.2 mL, 9.9 mmol). The resulting slurry was stirred for 30 min, concentrated, then placed under high vacuum (0.001 Torr). The dried solids were triturated with hot acetone (3 X 10 mL) and filtered to remove inorganic salts. The resulting filtrate was concentrated and Et_2O was added to precipitate a white solid (430 mg, 89% yield) that was 93% pure as judged by ^1H NMR spectroscopy: mp $>205^\circ\text{C}$; ^1H NMR (500 MHz, acetone- d_6) δ 7.41 (d, J = 7.4 Hz, 2H), 7.06 (d, J = 7.7 Hz, 2H), 4.43-4.40 (m, 1H), 3.64-3.63 (m, 1H), 1.70-1.63 (m, 2H), 0.86-0.83 (m, 3H); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 142.3, 130.9, 124.0, 74.2, 39.0, 32.1, 10.3; ^{11}B NMR (128 MHz, $\text{DMSO-}d_6$) δ 1.83 (br s); ^{19}F NMR (471 MHz,

DMSO-*d*₆) δ -139.5 (m); IR (KBr) 3422, 2969, 2931, 2969, 2369, 2169, 1610, 1457. HRMS calcd. for C₉H₁₁BF₃O [M-K]⁻ 203.0855 found, 203.0860.

Tetra-*n*-butylammonium 3-(1-Hydroxyethyl)phenyltrifluoroborate (1d). This

compound was synthesized from potassium 3-(1-hydroxyethyl)phenyltrifluoroborate according to the procedure described for **1c** to give a yellow solid (449 mg, 100% yield): mp 73-75 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.61 (s, 1H), 7.54 (d, *J* = 7.0 Hz, 1H), 7.22-7.15 (m, 2H), 4.84 (q, *J* = 6.4 Hz, 1H), 3.14-3.11 (m, 8H), 1.70 (s, 1H), 1.58-1.52 (m, 8H), 1.48 (d, *J* = 6.5 Hz, 2H), 1.38 (sextet, *J* = 7.4 Hz, 8H), 0.97 (t, *J* = 7.3 Hz, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 143.6, 131.2, 129.1, 127.0, 122.8, 71.2, 58.4, 25.1, 23.8, 19.6, 13.7; ¹¹B NMR (128 MHz, CDCl₃) δ 2.91 (br s); ¹⁹F (471 MHz, CDCl₃) δ -142.0 (br s); IR (film) 3512, 2964, 2876, 1485 cm⁻¹; HRMS calcd. for C₈H₉BF₃O [M-(NBu₄)]⁻ 189.0699, found 189.0697.

Tetra-*n*-butylammonium 6-Hydroxhexyltrifluoroborate (1e).

2,5-Dimethylhexa-2,4-diene⁴ (1.45 g, 13.2 mmol) was dissolved in THF (7.8 mL) and cooled to 0 °C. BH₃•THF in THF (1.0M, 6.0 mL, 6.00 mmol) was added dropwise via syringe. The mixture was stirred at 0 °C for 3 h. A portion of this solution (15.0 mL, 5.70 mmol) was added dropwise to 2-(hex-5-enyloxy)-tetrahydro-2*H*-pyran (920 mg, 5.0 mmol) in THF (34 mmol) at 0 °C. The solution was stirred for 2 h at 0 °C then 1 h at room temperature. The mixture was then cooled to 0 °C and treated with H₂O (1.0 mL) and stirred for 15 min. Aq formaldehyde (37%, 0.5 mL) was then added and the mixture was stirred for 14 h. The mixture was partitioned between EtOAc (50 mL), H₂O (25 mL), and brine (25 mL) and the

layers were shaken and separated. The aqueous layer was extracted with EtOAc (2 X 25 mL) then concentrated. The resulting oil was dissolved in MeOH (12.0 mL) and treated with *p*-toluenesulfonic acid (85 mg, 0.50 mmol). The mixture was stirred overnight then partitioned between EtOAc (15 mL), satd aq NaHCO₃ (10 mL) and H₂O (15 mL). The layers were shaken and separated, and the aqueous layer was extracted with EtOAc (2 X 15 mL). The combined organic layers were washed with brine (10 mL), dried (Na₂SO₄) and concentrated. Flash chromatography provided a glassy solid (310 mg, 42%), a portion of which (0.128 mg, 0.878 mmol) was dissolved in H₂O (2.8 mL) and cooled to 0 °C. The slurry was treated with KHF₂ (137 mg, 1.75 mmol). The mixture was stirred for 2 h at which point CH₂Cl₂ (3 mL) was added. *n*-Bu₄NOH (1.61M, 0.55 mL, 0.886 mmol) was added dropwise via syringe. The mixture was stirred for 30 min, then transferred to a separatory funnel with CH₂Cl₂ (3.0 mL). The layers were shaken and separated and the aqueous layer was extracted with CH₂Cl₂ (3.0 mL). The combined organic layers were dried (Na₂SO₄) and concentrated to give a yellow, waxy solid (0.245 g, 68%): mp 61-64 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.60-3.54 (m, 2H), 3.21-3.17 (m, 8H), 1.59-1.50 (m, 10H), 1.40 (sextet, *J* = 7.3, 8H), 1.29 (m, 6H), 0.96 (t, *J* = 7.3 Hz, 12H) 0.20 (br s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 63.1, 58.7, 33.4, 33.1, 26.0, 25.6, 24.0, 19.7, 13.7; ¹¹B NMR (128 MHz, CDCl₃) δ 4.28 (br s); ¹⁹F NMR (471 MHz, CDCl₃) δ 140.3 (m); IR (film) 3503, 2963, 2931, 2876, 1465; HRMS calcd. for C₆H₁₃BF₃O [M-(NBu₄)]⁻ 169.1012, found 169.1007.

Potassium 11-Hydroxydodecyltrifluoroborate (3d). Borane-pyridine complex² (0.890 mL, 8.81 mmol) was dissolved in CH₂Cl₂ (5.0 mL) and cooled to 0 °C. Iodine (1.11 g, 4.37 mmol) was added portionwise and the mixture was stirred for 15 min. Dodec-11-en-2-ol⁵ (0.767 g, 4.17 mmol) was added dropwise via syringe and the

mixture was stirred for 18 h at room temperature. It was cooled to 0 °C in an ice/water bath and quenched with MeOH (1.0 mL). The mixture was concentrated then partitioned between Et₂O (30 mL) and 1N HCl (15 mL). The layers were shaken and separated, and the aqueous layer was further extracted with Et₂O (2 X 15 mL). The combined organic layers were then dried (MgSO₄) and concentrated. The crude boronic acid was dissolved in MeOH (5.0 mL) and cooled to 0 °C. KHF₂ (4.5M, 2.8 mL, 12.6 mmol) was added dropwise via syringe. The mixture was stirred for 2 h then concentrated and placed on high vacuum (0.001 Torr). The dried solids were triturated with hot 20% methanol/acetone and filtered to remove inorganic salts. The resulting filtrate was concentrated and Et₂O was added to precipitate a white solid (353 mg, 29% yield): mp >210 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 4.26-4.25 (m, 1H), 3.55 (m, 1H), 1.22-1.01 (m, 21H), -0.08 (m, 2H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 65.7, 33.2, 29.5, 29.3, 29.2, 29.2 (2), 25.7, 25.4, 23.6, 23.6; ¹¹B NMR (128 MHz, DMSO-*d*₆) δ 4.34 (br s); ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -137.2 (m); IR (KBr) 3370, 2918, 2850, 2669, 2338, 1468 cm⁻¹; HRMS calcd. for C₁₂H₂₂BF₃O [M-K]⁻ 253.1950, found 253.1939.

Tetra-*n*-butylammonium 11-Hydroxydodecyltrifluoroborate (1f).

This compound was synthesized from potassium 11-hydroxydodecyltrifluoroborate according to the procedure described for **1c** to give a yellow oil (121 mg, 98% yield): ¹H NMR (500 MHz, CDCl₃) δ 3.75 (m, 1H), 3.22-3.20 (m, 8H), 1.60-1.59 (m, 8H), 1.44-1.23 (m, 26H), 1.15 (m, 3H), 0.98 (t, *J* = 7.3 Hz, 12H), 0.20 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 68.1, 58.6, 39.4, 33.9, 30.1, 29.9, 29.8, 29.7, 26.1, 25.8, 24.0, 23.5, 19.7, 13.6; ¹¹B NMR (128 MHz, CDCl₃) δ 4.90 (br s); ¹⁹F NMR (471 MHz, CDCl₃) δ -137.2 (m); IR (film) 3497, 2963, 2924, 2853, 2876, 1488, 1465 cm⁻¹; HRMS calcd. for C₁₂H₂₂BF₃O [M-

(NBu₄)]⁺ 253.1950, found 253.1938.

Tetra-*n*-butylammonium (*E*)-6-Hydroxyhex-1-

enyltrifluoroborate (1g). In a resealable tube, distilled

catecholborane⁶ (1.50 mL, 14.0 mmol) was added dropwise via syringe to 5-hexyn-1-ol (650 mg, 6.63 mmol) at 0 °C. The mixture was stirred for 40 min until the bubbling ceased, at which point it was sealed and placed in a 75 °C oil bath. The mixture was stirred for 23 h then cooled to 0 °C and diluted with EtOAc (5 mL). The mixture was carefully quenched with H₂O (5 mL) and stirred for 1 h at which point it was transferred to a separatory funnel, rinsing with EtOAc (5 mL). The layers were shaken and separated, and the aqueous layer was extracted with EtOAc (4 X 10 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. Flash chromatography (30% EtOAc/hexanes to 5% MeOH/CH₂Cl₂) provided the crude boronic acid as a glass (490 mg, 51% yield). This was dissolved in H₂O (5 mL) and cooled to 0 °C. KHF₂ (532 mg, 6.81 mmol) was added and the mixture was stirred at 0 °C for 1 h. CH₂Cl₂ (5 mL) was added followed by tetra-*n*-butylammonium hydroxide (1.61M, 2.10 mL, 3.38 mmol). After stirring for 20 min, the mixture was transferred to a separatory funnel and the layers were shaken and separated. The aqueous layer was extracted with CH₂Cl₂ (5 mL) and the combined organic layers were dried (Na₂SO₄). The organic layer was concentrated and placed on high-vacuum to give a yellow solid (1.16 g, 83% yield, 43% yield from 5-hexyn-1-ol): mp 89-91 °C; ¹H NMR (500 MHz, CDCl₃) δ 5.82-5.79 (m, 1H), 5.50-5.46 (m, 1H), 3.56 (t, *J* = 6.7 Hz, 2H), 3.20-3.16 (m, 8H), 2.01-2.00 (m, 2H), 1.61-1.53 (m, 10H), 1.43-1.35 (m, 10H), 0.96 (t, *J* = 7.3 Hz, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 135.9, 62.9, 58.6, 35.6, 32.6, 25.7, 24.0, 19.7, 13.7; IR (film)

3510, 2962, 2876, 1638, 1473 cm^{-1} ; ^{11}B NMR (128 MHz, CDCl_3) δ 1.37 (br s); ^{19}F NMR (CDCl_3 , 471 MHz) δ -140.4 (br s); HRMS calcd. for $\text{C}_6\text{H}_{11}\text{BF}_3\text{O}$ $[\text{M}-(\text{NBu}_4)]^-$ 167.0855, found 167.0866.

Dodec-11-yn-2-ol. Undec-10-ynal⁷ (0.810 g, 4.88 mmol) was

dissolved in THF (12 mL) and cooled to -78°C . MeMgBr

(3.0M, 3.60 mL, 10.8 mmol) was added dropwise via syringe. The mixture was stirred for 2 h at low temperature then allowed to warm for 1 h. The resulting slurry was then cooled to 0°C and aq HCl (1.0M, 11 mL, 11.0 mmol) was added dropwise via syringe. The mixture was stirred for 10 min then extracted with EtOAc (3 X 15 mL). The combined organic layers were washed with brine (5 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (15% EtOAc/hexanes) provided a colorless oil (0.631 mg, 71%): R_f 0.20 (15% EtOAc/hexanes); ^1H NMR (500 MHz, CDCl_3) δ 3.78-3.77 (m, 1H), 2.18-2.14 (m, 2H), 1.93-.1.92 (m, 1H), 1.54-1.48 (m, 2H), 1.41-1.29 (m, 12H), 1.19-1.16 (m, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 84.8, 68.2, 68.1, 39.4, 29.6, 29.5, 29.0, 28.7, 28.5, 25.8, 23.5, 18.4; IR (film) 3356, 3312, 2930, 2119, 1464, 1432; HRMS calcd. for $\text{C}_{12}\text{H}_{21}$ $[\text{M}-\text{OH}]^+$ 165.1644, found 165.1639.

Potassium (E)-11-Hydroxydodec-1-enyltrifluoroborate

(3e). In a resealable tube, dodec-11-yn-1-ol (493 mg, 2.71 mmol) was treated with distilled catecholborane⁶ (0.610 mL, 5.69 mmol) at 0°C . The mixture was stirred until the bubbling ceased, at which point it was sealed and placed in a 75°C oil bath. The mixture was stirred for 18.5 h then cooled to 0°C and diluted with EtOAc (5 mL). The mixture was carefully quenched with H_2O (5 mL) and stirred for 1 h at which point it was transferred to a separatory funnel, rinsing with EtOAc (5 mL). The layers were shaken and

separated, and the aqueous layer was extracted with EtOAc (4 X 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. Flash chromatography (30% EtOAc/hexanes to 5% MeOH/CH₂Cl₂) provided the crude boronic acid as a glass (332 mg, 54% yield) which was dissolved in MeOH (6 mL) and cooled to 0 °C. KHF₂ (4.5M, 0.970 mL, 4.4 mmol) was added dropwise via syringe and the mixture was stirred for 1.25 h at which point it was concentrated and placed under high vacuum (0.001 Torr) for 8 h. The dried solids were triturated with hot acetone (6 X 10 mL) and filtered to remove inorganic salts. The resulting filtrate was concentrated and Et₂O was added to precipitate a white solid (290 mg, 68% yield): mp >210 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 5.48-5.42 (m, 1H), 5.21-5.17 (m, 1H), 4.26 (d, *J* = 4.6 Hz, 1H), 3.56-3.53 (m, 1H), 1.86-1.85 (m, 1H), 1.31-1.23 (m, 14H), 1.01 (d, *J* = 6.1 Hz, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 133.5, 65.7, 35.4, 29.3 (2), 29.2, 29.1, 29.0, 28.8, 25.4, 23.6; ¹¹B NMR (128 MHz, DMSO-*d*₆) δ 2.17 (br s); ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -137.6 (s); IR (KBr) 3392, 2922, 2852, 1646, 1466 cm⁻¹; HRMS calcd. for C₁₂H₂₂BF₃O [M-K]⁻ 251.1794, found 251.1798.

Tetra-*n*-butylammonium 11-Hydroxydodec-1-enyltrifluoroborate

(1h). This compound was synthesized from potassium 11-

hydroxydodec-1-enyltrifluoroborate according to the procedure described for **1c** to give a yellow oil (120 mg, 100% yield). ¹H NMR (500 MHz, CDCl₃) δ 5.86-5.80 (m, 1H), 5.49-5.45 (m, 1H), 3.76 (m, 1H), 3.21-3.18 (m, 8H), 1.98-1.97 (m, 2H), 1.60-1.56 (m, 8H), 1.44-1.25 (m, 23H), 1.16 (d, *J* = 6.2 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 136.5, 68.2, 58.6, 39.5, 36.1, 29.8, 29.8, 29.7 (2), 25.9, 24.0, 23.6, 19.8, 13.8; ¹¹B NMR (128 MHz, CDCl₃) δ 1.94

(br s); ^{19}F NMR (471 MHz, CDCl_3) δ -140.2 (s); IR (film) 3509, 2963, 2927, 2976, 2854, 1639, 1465 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{23}\text{BF}_3\text{O}$ $[\text{M}-(\text{NBu}_4)]^-$ 251.1794, found 251.1801.

General Procedure A: TPAP/NMO Oxidation

Tetra-*n*-butylammonium 4-Formylphenyltrifluoroborate (2a).
Tetra-*n*-butylammonium 4-hydroxymethylphenyltrifluoroborate (104 mg, 0.25 mmol), NMO (34.0 mg, 0.290 mmol), powdered 4Å

molecular sieves (125 mg) and CH_2Cl_2 (1.0 mL) were combined in a two-neck 10 mL flask.

TPAP (0.8 mg, 0.002 mmol) was added and the mixture was stirred for 18 h. Upon completion of the reaction, CH_2Cl_2 (5 mL) and H_2O (3 mL) were added and the mixture was transferred to a separatory funnel. The layers were shaken and separated and the aqueous layer was extracted with CH_2Cl_2 (5 mL). The combined organics were washed with 1N HCl (2 X 3 mL), dried (Na_2SO_4) and concentrated to give a yellow oil (95 mg, 91%): ^1H NMR (500 MHz, CDCl_3) δ 9.90 (s, 1H), 7.72 (d, J = 7.9 Hz, 2H), 7.67 (d, J = 7.7 Hz, 2H), 3.02-2.98 (m, 8H), 1.47-1.41 (m, 8H), 1.32-1.24 (m, 8H), 0.90 (t, J = 7.3, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 193.4, 134.6, 132.3, 128.5, 58.5, 23.8, 19.6, 13.6; ^{11}B (128 MHz, CDCl_3) δ 2.59 (br s); ^{19}F NMR (471 MHz, CDCl_3) δ -142.8 d (br s); IR (film) 2964, 2877, 1693, 1660 cm^{-1} ; HRMS calcd. for $\text{C}_7\text{H}_7\text{BF}_3\text{O}$ $[\text{M}-(\text{NBu}_4)]^-$ 173.0386, found 173.0384.

Swern Oxidation:

Tetra-*n*-butylammonium 4-Formylphenyltrifluoroborate (2a).
Oxalyl chloride (50 μL , 0.58 mmol) was dissolved in CH_2Cl_2 (1.0 mL)

and cooled to $-78\text{ }^{\circ}\text{C}$. DMSO (85 μL , 1.20 mmol) was added via syringe and the mixture was stirred for 5 min. A solution of tetra-*n*-butylammonium 4-hydroxymethylphenyltrifluoroborate (0.208 g, 0.500 mmol) in CH_2Cl_2 (1.0 mL) was added dropwise via syringe and the mixture was stirred for 25 min. Et_3N (350 μL , 2.49 mmol) was added and the mixture was stirred at low temperature for an additional 5 min, at which point the cooling bath was removed. After stirring for 2 h, CH_2Cl_2 (5 mL) and H_2O (3 mL) were added and the mixture was transferred to a separatory funnel. The layers were shaken and separated and the organic layer was washed with 0.1M HCl (3 mL) and satd aq NaHCO_3 (3 mL), dried (Na_2SO_4) and concentrated to give a yellow oil which partially solidified (0.187 g, 90% yield). The NMR spectra were identical to those obtained for **2a** using General Procedure A.

Dess-Martin Periodinane Oxidation:

Tetra-*n*-butylammonium 4-Formylphenyltrifluoroborate (2a).

Tetra-*n*-butylammonium 4-hydroxymethylphenyltrifluoroborate (104 mg, 0.250 mmol) was dissolved in CH_2Cl_2 (1.0 mL) and treated with the Dess-Martin reagent (126 mg, 0.300 mmol). The mixture was stirred for 18 h, then treated with CH_2Cl_2 (5 mL), 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (1.5 mL), and satd aq NaHCO_3 (1.5 mL). After stirring for 10 min, the mixture was transferred to a separatory funnel, and the layers were shaken and separated. The aqueous layer was extracted with CH_2Cl_2 (5 mL) and the combined organics were washed with 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (3 mL), satd aq NaHCO_3 (3 mL) and pH 7 buffer (3 mL). The organic layer was dried (Na_2SO_4), and concentrated to give a yellow oil which partially solidified (0.088 g, 86% yield). The NMR spectra were identical to those obtained for **2a** using General Procedure A.

Tetra-*n*-butylammonium 3-Formylphenyltrifluoroborate (2b). This

compound was synthesized from tetra-*n*-butylammonium 3-hydroxymethylphenyltrifluoroborate using General Procedure A to give a dark oil (101 mg, 97% yield): ^1H NMR (500 MHz, CDCl_3) δ 9.98 (s, 1H), 8.11 (s, 1H), 7.92-7.90 (m, 1H), 7.67 (d, $J = 7.6$ Hz, 1H), 7.35 (t, $J = 7.3$ Hz, 1H), 3.11 (m, 8H), 1.53 (m, 8H), 1.35-1.34 (m, 8H), 0.95 (t, $J = 7.2$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 194.2, 138.6, 134.5, 127.4, 126.6, 58.3, 23.6, 19.5, 13.5; ^{11}B (128 MHz, CDCl_3) δ 2.51 (br s); ^{19}F NMR (471 MHz, CDCl_3) δ -142.5 (br s); IR (film) 3002, 2963, 1585, cm^{-1} ; HRMS calcd. for $\text{C}_7\text{H}_5\text{BF}_3\text{O} [\text{M}-(\text{NBu}_4)]^-$ 173.0386, found 173.0378.

Tetra-*n*-butylammonium 4-Acetylphenyltrifluoroborate (2c). This

compound was synthesized from tetra-*n*-butylammonium 4-(1-hydroxyethyl)phenyltrifluoroborate according to General Procedure A to give a clear oil which became a waxy solid upon standing (101 mg, 94% yield): mp 51-55 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 7.8$ Hz, 2H), 7.66 (d, $J = 7.9$ Hz, 2H), 3.03-3.00 (m, 8H), 2.52 (s, 3H), 1.48-1.42 (m, 8H), 1.33-1.26 (m, 8H), 0.91 (t, $J = 7.3$ Hz, 12H); ^{13}C NMR (CDCl_3 , 126 MHz) δ 199.2, 135.0, 132.0, 126.9, 58.5, 26.6, 23.8, 19.6, 13.6; ^{11}B NMR (128 MHz, CDCl_3) δ 1.56 (br s); ^{19}F NMR (471 MHz, CDCl_3) δ -142.7 (m); IR (KBr) 2963, 2876, 1674 cm^{-1} ; HRMS calcd. for $\text{C}_8\text{H}_7\text{BF}_3\text{O} [\text{M}-(\text{NBu}_4)]^-$ 187.0542, found 187.0543.

Tetra-*n*-butylammonium 3-(1-Hydroxyethyl)phenyltrifluoroborate (2d). This

compound was synthesized from tetra-*n*-butylammonium 3-(1-

hydroxyethyl)phenyltrifluoroborate according to General Procedure A to give a clear oil which solidified upon standing (99 mg, 92% yield): mp 63-65 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.17 (s, 1H), 7.79 (d, $J = 7.2$ Hz, 1H), 7.71 (d, $J = 7.8$ Hz, 1H), 7.28-7.25 (m, 1H), 3.05-3.01 (m, 8H), 2.54 (s, 3H), 1.50-1.44 (m, 8H), 1.30 (sextet, $J = 7.4$ Hz, 8H), 0.91 (t, $J = 7.3$ Hz, 12 H); ^{13}C NMR (126 MHz, CDCl_3) δ 200.1, 137.2, 135.8, 132.2, 127.1, 125.7, 58.5, 26.9, 23.8, 19.7, 13.7; ^{11}B (128 MHz, CDCl_3) δ 1.88 (br s); ^{19}F (471 MHz, CDCl_3) δ -142.4 (br s); IR (film) 2963, 2877, 1675, 1588, 1474 cm^{-1} ; HRMS calcd. for $\text{C}_8\text{H}_7\text{BF}_3\text{O}[\text{M}-(\text{NBu}_4)]^-$ 187.0542, found 187.0559.

Tetra-*n*-butylammonium 6-Formylpentyltrifluoroborate (2e).

This compound was synthesized from tetra-*n*-butylammonium 6-hydroxyhexyltrifluoroborate according to General Procedure A (washing with pH 7 buffer instead of 1.0N HCl) to give a dark oil (46 mg, 84% yield) that was >95% pure as judged by ^1H NMR: ^1H NMR (500 MHz, CDCl_3) δ 9.71 (t, $J = 2.1$ Hz, 1H), 3.21 (m, 8H), 2.36 (td, $J = 7.4$, 2.1 Hz, 2H), 1.61 (m, 8H), 1.42-1.32 (m, 14H), 0.98 (t, $J = 7.1$ Hz, 12H), 0.22 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 204.1, 58.7, 44.1, 33.1, 25.6, 23.9, 22.5, 19.7, 13.6; ^{11}B NMR (128 MHz, CDCl_3) δ 3.61 (br s); ^{19}F NMR (471 MHz, CDCl_3) δ -140.5 (m); IR (film) 2963, 2931, 2877, 1721, 1485, 1464; HRMS calcd. for $\text{C}_6\text{H}_{11}\text{BF}_3\text{O}[\text{M}-(\text{NBu}_4)]^-$ 167.0855, found 167.0849.

Tetra-*n*-butylammonium 11-Oxododecyltrifluoroborate (2f).

This compound was synthesized from tetra-*n*-butylammonium 11-hydroxydodecyltrifluoroborate according to General Procedure A to give a dark oil (86 mg, 93% yield). ^1H NMR (500 MHz, CDCl_3) δ 3.22-3.19 (m, 8H), 2.38 (t, $J = 7.4$ Hz, 2H), 2.10 (s, 3H),

1.63-1.57 (m, 8H), 1.53-1.52 (m, 2H), 1.41 (sextet, $J = 7.3$ Hz, 8H), 1.22 (m, 14H), 0.97 (t, $J = 7.3$ Hz, 12H), 0.20 (m, 2H); ^{13}C NMR (500 MHz, CDCl_3) δ 209.6, 58.7, 43.9, 34.0, 30.1, 29.9, 29.9, 29.7, 29.5, 29.3, 26.1, 24.0, 19.8, 13.7; ^{11}B NMR (128 MHz, CDCl_3) δ 4.91 (br s); ^{19}F NMR (471 MHz, CDCl_3) δ -140.3 (s); IR (film) 2923, 2962, 2876, 1713, 1669, 1465; HRMS calcd for $\text{C}_{12}\text{H}_{23}\text{BF}_3\text{O} [\text{M}-(\text{NBu}_4)]^-$ 251.1793, found 251.1785.

Tetra-*n*-butylammonium (*E*)-6-Formylpent-1-

enyltrifluoroborate (2g). This compound was synthesized from

tetra-*n*-butylammonium (*E*)-6-hydroxyhex-1-enyltrifluoroborate according to General Procedure A (washing with pH 7 buffer instead of 1.0N HCl) to give a dark oil (80 mg, 78% yield) that was 93% pure as judged by ^1H NMR: ^1H NMR (500 MHz, CDCl_3) δ 9.71 (t, $J = 1.9$ Hz, 1H), 5.80-5.76 (m, 1H), 5.54-5.50 (m, 1H), 3.20-3.17 (m, 8H), 2.41 (td, $J = 7.4$ Hz, 1.9 Hz, 2H), 2.03-2.02 (m, 2H), 1.69-1.55 (m, 10H), 1.40 (sextet, $J = 7.3$ Hz, 8H), 0.97 (t, $J = 7.3$ Hz, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ 203.7, 134.5, 58.6, 43.5, 35.0, 23.9, 21.9, 19.7, 13.6; ^{11}B NMR (128 MHz, CDCl_3) δ 2.09 (br s); ^{19}F NMR (471 MHz, CDCl_3) δ -140.6 (m); IR (film) 2963, 2876, 1721, 1638, 1474 cm^{-1} ; HRMS calcd. for $\text{C}_6\text{H}_9\text{BF}_3\text{O} [\text{M}-(\text{NBu}_4)]^-$ 165.0698, found 165.0708.

Tetra-*n*-butylammonium 11-Oxododec-1-enyltrifluoroborate (2h).

This compound was synthesized from tetra-*n*-butylammonium 11-hydroxydodec-1-enyltrifluoroborate according to the General Procedure A to give a gray, oily solid (83 mg, 96% yield) that was 93% pure as judged by ^1H NMR: ^1H NMR (500 MHz, CDCl_3) δ 5.84-5.79 (m, 1H), 5.49-5.45 (m, 1H), 3.21-3.17 (m, 8H), 2.38 (t, $J = 7.4$ Hz, 2H), 2.10 (s, 3H), 1.97 (m, 2H), 1.62-1.52 (m, 10H), 1.44-1.23 (m, 18H), 0.97 (t, $J = 7.3$ Hz, 12H); ^{13}C NMR (126

MHz, CDCl₃) δ 209.6, 136.4, 58.6, 43.9, 36.0, 30.0, 29.7, 29.6 (2), 29.5, 29.3, 24.0, 19.8, 13.7; ¹¹B NMR (128 MHz, CDCl₃) δ 2.26 (br s); ¹⁹F NMR (471 MHz, CDCl₃) δ -140.3 (m); IR (film) 2962, 2928, 2876, 1713, 1638, 1466; HRMS calcd for C₁₂H₂₁BF₃O [M-(NBu₄)]⁻ 249.1637, found 249.1627.

General Procedure B: IBX oxidations of Potassium Organotrifluoroborates

Potassium 4-Acetylphenyltrifluoroborate (4a). Potassium 4-(1-hydroxyethyl)phenyltrifluoroborate (114 mg, 0.500 mmol) was dissolved in acetone (5.0 mL). IBX (420 mg, 1.50 mmol) was added all at once and the mixture was heated to reflux. After stirring for 2 h, the mixture was allowed to cool to rt for 0.5 h. Using 20 mL of acetone, the solids were removed via filtration over a coarse sintered glass Buchner funnel. The resulting filtrate was concentrated and Et₂O was added to precipitate the product as a white solid (104 mg, 92% yield): mp >205 °C; ¹H NMR (500 MHz, acetone-*d*₆) δ 7.34 (d, *J* = 7.73 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 2.49 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 198.7, 134.8, 131.9, 126.8, 27.0; ¹¹B NMR (128 MHz, DMSO-*d*₆) δ 1.71 (br s); ¹⁹F NMR (471 MHz, acetone-*d*₆) δ -140.2 (m); IR (KBr) 3081, 3044, 2375, 1677 cm⁻¹; HRMS calcd. for C₈H₇BF₃O [M-K]⁻ 187.0542, found 187.0535.

Potassium 3-Acetylphenyltrifluoroborate (4b). This compound was synthesized from 3-(1-hydroxyethyl)phenyltrifluoroborate according to the general procedure B to give an off-white solid (100 mg, 88% yield): mp 172-174 °C; ¹H NMR (500 MHz, acetone-*d*₆) δ 8.12-8.11 (m, 1H), 7.70-7.66 (m, 2H), 7.22-7.19 (t, *J* = 7.4 Hz, 1H), 2.51 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 198.9, 136.4, 135.2, 131.2, 126.5, 125.0, 26.6; ¹¹B NMR

(128 MHz, DMSO- d_6) δ 2.42 (br s); ^{19}F NMR (471 MHz, acetone- d_6) δ -143.7 (m); IR (KBr) 2375, 1684, 1598, 1578 cm^{-1} ; HRMS calcd. for $\text{C}_8\text{H}_7\text{BF}_3\text{O}$ $[\text{M-K}]^-$ 187.0542, found 187.0545.

Potassium 4-(1-Propionyl)phenyltrifluoroborate (4c). This compound

was synthesized from potassium 4-(1-

hydroxypropyl)phenyltrifluoroborate according to General Procedure B to

give a white solid (89 mg, 74% yield): mp >205 °C; ^1H NMR (500 MHz, acetone- d_6) δ 7.74 (d, J = 7.9 Hz, 2H), 7.58 (d, J = 7.8 Hz, 2H), 2.95 (q, J = 7.3 Hz, 2H), 1.11 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 201.2, 134.4, 131.9, 126.4, 31.4, 8.9; ^{11}B NMR (128 MHz, DMSO- d_6) δ 2.05; ^{19}F NMR (471 MHz, DMSO- d_6) δ -140.2 (br s); IR (KBr) 3031, 2994, 2925, 2369, 2343, 1683 cm^{-1} ; HRMS calcd for $\text{C}_9\text{H}_9\text{BF}_3\text{O}$ $[\text{M-K}]^-$ 201.0699, found 201.0694.

4'-Acetylbiphenyl-4-carbonitrile (5). Tetra-*n*-butylammonium

4- acetylphenyltrifluoroborate (216 mg, 0.50 mmol), prepared

using General Procedure A, was combined with 4-bromobenzonitrile (91.0 mg, 0.500 mmol),

$\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.0500 mmol) and K_2CO_3 (207 mg, 1.50

mmol). The flask was evacuated and filled with N_2 . MeOH (2.0 mL) was added and the

mixture was heated at 70 °C for 16 h. Upon cooling to room temperature, EtOAc (5 mL) and

H_2O (3 mL) were added and the layers were shaken and separated. The aqueous layer was

extracted with EtOAc (3 X 5 mL). The combined organic layers were washed with 1N HCl (2

mL) and brine (2 mL) then dried (Na_2SO_4). The product was purified via flash chromatography

(20% EtOAc/hexanes) to give white crystals (88 mg, 80% yield over two steps); mp 115-116 °C

(lit.⁸ 117-120); R_f 0.18 (20% EtOAc/hexanes). The ^1H and ^{13}C NMR spectral data obtained matched those in the literature.⁹

References:

- (1) Brown, H. C. *Organic Syntheses via Boranes*; Wiley: New York, 1975.
- (2) Clay, J.M.; Vedejs, E. *J. Am. Chem. Soc.* **2005**, *127*, 5766.
- (3) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
- (4) Kalinin, A.V.; Scherer, S.; Snieckus, V. *Angew. Chem. Int. Ed.* **2003**, *42*, 3399.
- (5) Qin, X.; Tzvetkov, T.; Liu, X.; Lee, D.C.; Yu, L.; Jacobs, D.C. *J. Am. Chem. Soc.* **2004**, *126*, 13232.
- (6) Roush, W.R.; Sciotti, R.J. *J. Am. Chem. Soc.* **1998**, *120*, 7411.
- (7) Hopf, H.; Krüger A. *Chem. Eur. J.* **2001**, *7*, 4378.
- (8) Tsuno, Y.; Chong, W.-Y.; Tairaka, Y.; Sawada, M.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 596.
- (9) Ueda, M.; Daitoh, A.; Oh-tani, S.; Miyaura, N. *Tetrahedron* **1998**, *54*, 13079.

^1H -NMR (500 MHz, CDCl_3) Spectrum of **1a**

^{13}C -NMR (126 MHz, CDCl_3) Spectrum of **1a**

¹¹B-NMR (128 MHz, CDCl₃) Spectrum of **1a**

¹⁹F-NMR (471 MHz, CDCl₃) Spectrum of **1a**

¹H-NMR (500 MHz, CDCl₃) Spectrum of **1b**

¹³C-NMR (126 MHz, CDCl₃) Spectrum of **1b**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **1b**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **1b**

¹H-NMR (500 MHz, CDCl₃) Spectrum of **1c**

¹³C-NMR (126 MHz, CDCl₃) Spectrum of **1c**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **1c**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **1c**

^1H -NMR (500 MHz, CDCl_3) Spectrum of **1d**

^{13}C -NMR (126 MHz, CDCl_3) Spectrum of **1d**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **1d**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **1d**

^1H -NMR (500 MHz, CDCl_3) Spectrum of **1e**

¹³C-NMR (126 MHz, CDCl₃) Spectrum of **1e**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **1e**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **1e**

¹H-NMR (500 MHz, CDCl₃) Spectrum of **1f**

¹³C-NMR (126 MHz) Spectrum of **1f**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **1f**

^{19}F -NMR (471 MHz) Spectrum of **1f**

¹H-NMR (500 MHz, CDCl₃) Spectrum of **1g**

^{13}C -NMR (126 MHz, CDCl_3) Spectrum of **1g**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **1g**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **1g**

^1H -NMR (500 MHz, CDCl_3) Spectrum of **1h**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **1h**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **1h**

^1H -NMR (500 MHz, CDCl_3) Spectrum of **2a**
(using General Procedure A)

^{13}C -NMR (126 MHz, CDCl_3) Spectrum of **2a**
(using General Procedure A)

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **2a**
(using General Procedure A)

¹⁹F-NMR (471 MHz, CDCl₃) Spectrum of **2a**
(using General Procedure A)

¹H-NMR (500 MHz, CDCl₃) Spectrum of **2a** (using Swern Oxidation)

^1H -NMR (500 MHz, CDCl_3) Spectrum of **2a** (using Dess-Martin Oxidation)

¹³C-NMR (126 MHz, CDCl₃) Spectrum of **2b**

^{11}B -NMR (126 MHz, CDCl_3) Spectrum of **2b**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **2b**

^1H NMR (500 MHz, CDCl_3) of **2c**

^{13}C -NMR (126 MHz, CDCl_3) Spectrum of **2c**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **2c**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **2c**

^1H -NMR (500 MHz, CDCl_3) Spectrum of **2d**

^{13}C -NMR (126 MHz, CDCl_3) Spectrum of **2d**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **2d**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **2d**

¹H-NMR (500 MHz, CDCl₃) Spectrum of **2e**

^{13}C -NMR (126 MHz, CDCl_3) Spectrum of **2e**

^{11}B -NMR (128 MHz, CDCl_3) of **2e**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **2e**

¹H-NMR (500 MHz, CDCl₃) Spectrum of **2f**

¹³C-NMR (126 MHz, CDCl₃) Spectrum of **2f**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **2f**

^{19}F -NMR (471 MHz, CDCl_3) of **2f**

¹H NMR (500 MHz, CDCl₃) Spectrum of **2g**

^{13}C -NMR (126 MHz, CDCl_3) Spectrum of **2g**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **2g**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **2g**

¹H-NMR (500 MHz, CDCl₃) Spectrum of **2h**

^{13}C -NMR (126 MHz, CDCl_3) Spectrum of **2h**

^{11}B -NMR (128 MHz, CDCl_3) Spectrum of **2h**

^{19}F -NMR (471 MHz, CDCl_3) Spectrum of **2h**

¹H-NMR (500 MHz, DMSO-*d*₆) Spectrum of **3a**

¹³C-NMR (126 MHz, DMSO-*d*₆) Spectrum of **3a**

^{11}B -NMR (128 MHz, $\text{DMSO-}d_6$) Spectrum of **3a**

^{19}F -NMR (471 MHz, $\text{DMSO}-d_6$) Spectrum of **3a**

^1H -NMR (500 MHz, $\text{DMSO}-d_6$) Spectrum of **3b**

^{13}C -NMR (126 MHz, $\text{DMSO}-d_6$) Spectrum of **3b**

^{11}B -NMR (128 MHz, $\text{DMSO-}d_6$) Spectrum of **3b**

^{19}F -NMR (471 MHz, $\text{DMSO}-d_6$) Spectrum of **3b**

^1H -NMR (500 MHz, acetone- d_6) Spectrum of **3c**

^{13}C -NMR (126 MHz, $\text{DMSO}-d_6$) Spectrum of **3c**

^{11}B -NMR (128 MHz, $\text{DMSO}-d_6$) Spectrum of **3c**

^{19}F -NMR (471 MHz, $\text{DMSO-}d_6$) Spectrum of **3c**

¹H-NMR (500 MHz, DMSO-*d*₆) Spectrum of **3d**

^{13}C -NMR (126 MHz, $\text{DMSO-}d_6$) Spectrum of **3d**

^{11}B -NMR (471 MHz, DMSO- d_6) for **3d**

¹⁹F-NMR (471 MHz, DMSO-*d*₆) Spectrum of **3d**

S102

^{13}C -NMR (126 MHz, $\text{DMSO-}d_6$) Spectrum of **3e**

^{11}B -NMR (128 MHz, $\text{DMSO-}d_6$) Spectrum of **3e**

¹H-NMR (500 MHz, acetone-*d*₆) Spectrum of **4a**

^{13}C -NMR (126 MHz, $\text{DMSO}-d_6$) Spectrum of **4a**

^{11}B -NMR (128 MHz, $\text{DMSO}-d_6$) Spectrum of **4a**

^{19}F -NMR (471 MHz, acetone- d_6) Spectrum of **4a**

^1H -NMR (500 MHz, $\text{acetone-}d_6$) Spectrum of **4b**

^{13}C -NMR (126 MHz, $\text{DMSO-}d_6$) Spectrum of **4b**

^{11}B -NMR (128 MHz, $\text{DMSO}-d_6$) Spectrum of **4b**

^{19}F -NMR (471 MHz, acetone- d_6) Spectrum of **4b**

^1H -NMR (500 MHz, acetone- d_6) Spectrum of **4c**

^{13}C -NMR (126 MHz, $\text{DMSO}-d_6$) Spectrum of **4c**

^{11}B -NMR (128 MHz, $\text{DMSO}-d_6$) Spectrum of **4c**

^{19}F -NMR (471 MHz, $\text{DMSO}-d_6$) Spectrum of **4c**