Supporting Information for:

Synthesis of Bifunctional Potassium Acyltrifluoroborates

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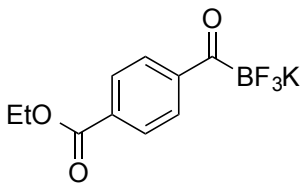
1. General methods:

Reactions involving air- and/or moisture-sensitive reagents were conducted in dry glassware sealed with a rubber septum under an atmosphere of dry N_2. Tetrahydrofuran (THF) was distilled from Na/benzophenone ketyl; all other solvents (acetone, MeCN, DMF, CH_2Cl_2) were used as supplied (ACS or HPLC grade). Starting materials were used as supplied by commercial vendors or prepared by methods described in literature. Thin layer chromatography (TLC) was performed on Merck TLC plates (0.245 mm) pre-coated with silica gel 60 F254 and visualized by UV quenching and/or staining with $KMnO_4$ solution and warming with a heat gun. Flash column chromatography was performed under a forced-flow of air using Silicycle SiliFlash F60 (40-63 µm particle size). ^{1}H NMR was performed on a Varian AV400 (400 MHz) or Bruker Avance III 600 (600 MHz) and spectra are referenced to residual protonated solvent ($CDCl_3$: 7.26 ppm; aceton–d_6: 2.05 ppm; DMSO–d_6: 2.50 ppm, CD_3OD: 3.31 ppm). ^{13}C NMR was performed on a Varian AV 400 (100 MHz) or Bruker Avance III 600 (150 MHz) and spectra are referenced to residual protonated solvent ($CDCl_3$: 77.16 ppm; acetone–d_6: 29.84 ppm; DMSO–d_6: 39.52 ppm, CD_3OD: 49.00 ppm). ^{19}F NMR was performed on a Bruker Avance III (282 MHz) and Bruker DRX500 (470 MHz) and referenced to an external standard of trifluoroacetic acid (−76.53 ppm); trifluoroborate multiplets are reported as the average of the observed signals. ^{11}B NMR was acquired on a Bruker DRX500 (160 MHz) and referenced to an external sample of $BF_3{\cdot}OEt_2$ (0 ppm); trifluoroborate multiplets are reported as an average of the observed signals. All chemical shifts are reported in ppm (δ). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Melting points are uncorrected; as the acyltrifluoroborates precipitate as amorphous powders melting points were not acquired. IR spectra were obtained on a Varian 800 FT-IR (ATR) spectrometer; the wavenumbers of the bands are reported in cm^{-1}. High-resolution mass spectra were obtained by the mass spectrometry service of the ETH Zürich Laboratorium für Organische Chemie on a Bruker Daltonics maXis ESI-QTOF.

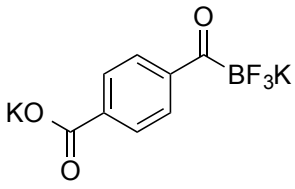
2.Synthesis of bifunctional reagents

Synthesis of potassium 4-(ethyl carboxylate)benzoyltrifluoroborate (3)



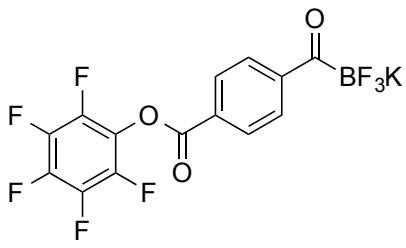
In a flame-dried round-bottom flask under an atmosphere of dry N_2, (ethylthiotrifluoroborate)-methane dimethyliminium (1.25 g, 6.74 mmol, 1.0 equiv) and ethyl 4-iodobenzoate (1.86 g, 6.74 mmol, 1.0 equiv) were dissolved in dry THF (25 mL) and cooled to −78 ºC. *n*-Butyllithium (1.6 M in hexane, 4.6 mL, 7.42 mmol, 1.1 equiv) was added dropwise over 30 min by syringe pump. After addition of *n*-butyllithium, the reaction was stirred for an additional hour at −78 ºC before quenching with acetone (0.5 mL) and a sat. aq KF solution (3 mL). The flask was removed from the cooling bath and stirred for 1 h. CH_2Cl_2 (25 mL) was added to the reaction mixture and filtered. The filter cake was washed with CH_2Cl_2 (25 mL) before the product was extracted from the filter cake with acetone. The filtrate was concentrated *in vacuo* and the product **3** was obtained as a white solid (1.63 g, 5.73 mmol, 85%). Full characterization is reported and not duplicated here.[1]

Synthesis of potassium 4-(carboxy)benzoyltrifluoroborate (4)



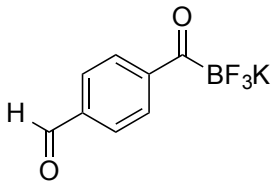
In a flame-dried round-bottom flask under an atmosphere of dry N_2, KAT **3** (1.63 g, 5.75 mmol, 1.0 equiv) and potassium trimethylsiloxide (0.88 g, 6.90 mmol, 1.2 equiv) were suspended in MeCN (20 mL) and stirred at rt overnight. The solvent was removed *in vacuo* and the resulting solid was suspended in CH_2Cl_2 (30 mL). The suspension was filtered and washed with CH_2Cl_2 (100 mL) before the product was extracted from the filter cake with DMF. The solvent was removed *in vacuo* to give product **4** as a white solid (1.42 g, 4.83 mmol, 84%). **m.p.** >250 °C (decomp); **^{1}H NMR** (600 MHz, DMSO–d_6): δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H); **^{13}C NMR** (151 MHz, DMSO–d_6): δ 233.1 (br), 169.2, 143.0, 141.1, 128.2, 126.6; **^{19}F NMR** (470 MHz, DMSO–d_6): δ −141.4; **^{11}B NMR** (160 MHz, DMSO–d_6): δ −0.94; **IR** (thin film): v 1585, 1545, 1387, 1078 cm^{-1}; **ESI-HRMS** calcd for $C_8H_5BF_3O_3$ $[M – K_2 + H]^-$ 217.0291, found 217.0286.

Synthesis of potassium 4-(perfluorophenylcarboxy)benzoyltrifluoroborate (5)



In a flame-dried round-bottom flask under an atmosphere of dry N_2, KAT **4** (1.42 g, 4.82 mmol, 1.0 equiv), perfluorophenyl trifluoroacetate (0.88 g, 5.78 mmol, 1.2 equiv) and N^{i}Pr$_2$Et (0.84 mL, 4.82 mmol, 1.0 equiv) were dissolved in dry DMF (25 mL) and stirred at rt overnight. CH_2Cl_2 (150 mL) was added and the resulting suspension filtered, washed with CH_2Cl_2 (3 x 50 mL) and dried *in vacuo* to afford product **5** as an off-white solid (2.03 g, 4.77 mmol, quant). **m.p.** 210 °C (decomp); **^{1}H NMR** (600 MHz, acetone–d_6): δ 8.25 (d, J = 2.3 Hz, 4H) **^{13}C NMR** (151 MHz, acetone–d_6): δ 235.0 (br), 163.2, 146.6, 143.1 ({^{19}F}), 141.4 ({^{19}F}), 139.7 ({^{19}F}), 138.1 ({^{19}F}), 131.2, 129.5, 129.1; **^{19}F NMR** (470 MHz, acetone–d_6): δ −145.3, −155.0, −160.3, −164.8; **^{11}B NMR** (160 MHz, acetone–d_6): δ −0.90; **IR** (thin film): ν 1757, 1683, 1519, 1207 cm^{-1}; **ESI-HRMS** calcd for $C_{14}H_4BF_8O_3$ [M – K]$^-$ 383.0134, found 383.0126.

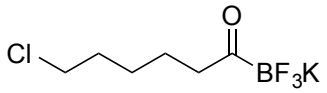
Synthesis of potassium 4-(formyl)benzoyltrifluoroborate (8)



In a flame-dried round-bottom flask under an atmosphere of dry N_2, 4-(diethoxymethyl)benzaldehyde (8.6 mL, 43.2 mmol, 1.0 equiv), benzotriazole (5.15 g, 43.2 mmol, 1.0 equiv), MeOH (3.5 mL, 86.4 mmol, 2.0 equiv) and trimethylorthoformate (14.2 mL, 129.7 mmol, 3.0 equiv) were dissolved in dry THF (200 mL). To this solution was added conc. H_2SO_4 (13 drops). The reaction was stirred for 30 min and subsequently quenched with solid $NaHCO_3$ (12 g) and the reaction mixture was filtered. The filter cake was washed with CH_2Cl_2 (50 mL) and the resulting filtrate was concentrated *in vacuo* to afford crude 1-(methoxy(4-(diethoxymethyl)phenyl)methyl)-1*H*-benzotriazole **7**. Compound **7** was dissolved in dry THF (100 mL) without further purification and cooled to −90 ºC using an acetone/N_2 ice bath. *n*-Butyllithium (1.6 M in hexane, 24.4 mL, 39.0 mmol, 1.0 equiv) was added slowly and the reaction mixture was stirred for 5 min. $B(OMe)_3$ (8.7 mL, 77.9 mmol, 2.0 equiv) was added and the reaction was allowed to stir for 2 h before it was quenched with a sat. aq KHF_2 solution. The reaction flask was removed from the cooling bath and allowed to stir at rt overnight. The solvent was removed *in vacuo* and the residue suspended in CH_2Cl_2 (100 mL), filtered and washed with CH_2Cl_2 (50 mL). The product was

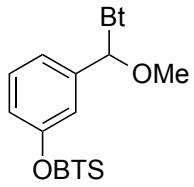
extracted from the filter cake with acetone and dried *in vacuo* to afford KAT **8** as a light yellow solid (1.60 g, 8.0 mmol, 17%). **m.p.** >250 °C (decomp); **^{1}H NMR** (600 MHz, DMSO–d_6): δ 10.06 (s, 1H), 8.06 (d, J = 8.1 Hz, 2H), 7.94 (m, 2H); **^{13}C NMR** (151 MHz, DMSO–d_6): δ 233.2 (br), 193.3, 137.3, 129.3, 128.1, 128.1; **^{19}F NMR** (470 MHz, DMSO–d_6): δ −142.1; **^{11}B NMR** (160 MHz, DMSO–d_6): δ −1.13; **IR** (thin film): v 2915, 1692, 1634, 1299 cm^{-1}; **ESI-HRMS** calcd for $C_8H_5BF_3O_2$ $[M - K]^-$ 201.0340, found 201.0345.

Synthesis of potassium 6-chlorohexanoyltrifluoroborate (11)



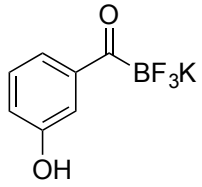
In a flame-dried, 100 mL two-neck flask equipped with a low temperature thermometer under an atmosphere of dry N_2, 1-(6-chloro-1-phenoxyhexyl)-1*H*-benzotriazole **10** (1.09 g, 3.32 mmol, 1.0 equiv) was dissolved in dry THF (50 mL) at rt, and then cooled to –110 °C (reaction mixture measured by internal thermometer) in an EtOH/N_2 ice bath. *n*-Butyllithium (1.54 M in hexane, titrated, 2.2 mL, 3.32 mmol, 1.0 equiv) was added dropwise over 2 min, resulting in a red-brown solution. The reaction was stirred for 25 min, followed by dropwise addition of $B(OMe)_3$ (0.74 mL, 6.64 mmol, 2.0 equiv) resulting in a brownish mixture. If solidification of the reaction mixture was observed, the reaction was warmed to –90 ºC for 30 min, resulting in a clear yellow solution, before cooling to –110 ºC and stirring for an additional 1 h. The reaction was quenched with a sat. aq KHF_2 solution (15 mL) and allowed to warm to rt overnight. The solvent was removed *in vacuo* to give an off-white solid, which was washed with Et_2O (50 mL) and CH_2Cl_2 (50 mL). The product was extracted with acetone to afford the crude product as a white solid. The crude was dissolved in 2 mL acetone and precipitated slowly with Et_2O (20 mL). After filtration, the filter cake was washed with CH_2Cl_2 (20 mL). Potassium 6-chlorohexanoyltrifluoroborate was dried *in vacuo* and obtained as a white solid (0.49 g, 2.07 mmol, 62%). Full characterization is reported and not duplicated here.[2]

Synthesis of 1-(methoxy(3-((*tert*-butyldimethylsilyl)oxy)phenyl)methyl))-1*H*-benzo triazole (12a)



In a flame-dried round-bottom flask under an atmosphere of dry N_2, 3-(*tert*-butyldimethylsiloxy)benzaldehyde (3.90 g, 16.5 mmol, 1.0 equiv), benzotriazole (3.93 g, 33.0 mmol, 2.0 equiv) and trimethylorthoformate (3.6 mL, 33.0 mmol, 2.0 equiv) were dissolved in dry THF (50 mL). To this solution was added conc. H_2SO_4 (4 drops). The reaction was stirred overnight and subsequently concentrated *in vacuo*. Purification by flash column chromatography eluting with 9:1 hexane/EtOAc yielded product **12a** as a colorless oil (4.80 g, 13.0 mmol, 79%). **^{1}H NMR** (600 MHz, acetone–d_6): δ 8.05 (dt, *J* = 7.9 Hz, 1.2 Hz, 1H), 7.46–7.36 (m, 3H), 7.29 (dt, *J* = 7.7 Hz, 0.9 Hz, 1H), 7.16 (s, 1H), 7.08–7.01 (m, 1H), 6.91–6.85 (m, 2H), 3.46 (s, 3H), 0.92 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); **^{13}C NMR** (151 MHz, acetone–d_6): δ 156.7, 147.8, 139.3, 132.1, 130.6, 128.3, 125.0, 121.5, 120.6, 119.9, 118.4, 112.4, 91.4, 57.1, 26.0, 18.7, –4.4; **IR** (thin film): v 3003, 2953, 2858, 1738, 1448, 1364, 1217 cm^{-1}; **ESI-HRMS** calcd for $C_{20}H_{27}N_3NaO_2Si$ $[M + Na]^+$ 392.1765, found 392.1767.

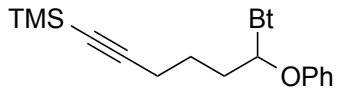
Synthesis of potassium 3-(hydroxy)benzoyltrifluoroborate (12)



In a flame-dried, 100 mL two-neck flask equipped with a low temperature thermometer under an atmosphere of dry N_2, precursor **12a** (4.50 g, 12.1 mmol, 1.0 equiv) was dissolved in dry THF (30 mL) and cooled to −110 ºC (reaction mixture measured by internal thermometer) using an EtOH/N_2 ice bath. *n*-Butyllithium (1.54 M in hexane, titrated, 7.9 mL, 12.1 mmol, 1.0 equiv) was added dropwise over 2 min and the reaction mixture was stirred for 30 min. $B(OMe)_3$ (2.7 mL, 24.2 mmol, 2.0 equiv) was added and the reaction was allowed to stir for 2 h before it was quenched with a sat. aq KHF_2 solution. The reaction flask was removed from the cooling bath and allowed to stir at rt overnight. The solvent was removed *in vacuo* and the residue suspended in CH_2Cl_2, filtered and washed with CH_2Cl_2. The product was extracted from the filter cake with acetone and dried *in vacuo* to afford KAT **12** as a white solid (1.11 g, 4.9 mmol, 40%). **m.p.** >195 °C (decomp); **^{1}H NMR** (600 MHz, acetone–d_6): δ 8.43 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.58 (ddd, *J* = 2.6 Hz, 0.9 Hz, 0.4 Hz, 1H), 7.21 (ddd, *J* = 8.0, 7.6, 0.4 Hz, 1H), 6.93 (ddd, *J* = 8.0 Hz, 2.6 Hz, 1.1 Hz, 1H); **^{13}C NMR** (151 MHz, acetone–d_6): δ 235.5 (br), 158.0, 143.6, 129.5, 120.8, 119.1, 115,8; **^{19}F NMR** (470 MHz,

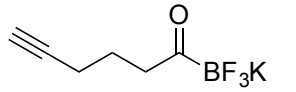
acetone–d_6): δ −144.4; **^{11}B NMR** (160 MHz, acetone–d_6): δ −0.82; **IR** (thin film): ν 3382, 1637, 1589, 1453, 1283 cm^{-1}; **ESI-HRMS** calcd for $C_7H_5BF_3O_2$ [M − K]$^-$ 189.0341, found 189.03439.

Synthesis of 1-1(-phenoxy-6-(trimethylsilyl)hex-5-yn-1-yl (13a)



1-(Phenoxymethyl)-1*H*-benzotriazole (1.42 g, 6.30 mmol, 1.0 equiv) was dissolved in THF (100 mL) at rt and cooled to –78 °C. *n*-Butyllithium (1.54 M in hexane, titrated, 4.5 mL, 6.93 mmol, 1.1 equiv) was added down the side of the flask over 2 min, resulting in a brownish yellow solution. This was stirred at –78 °C for 1 h before (5-iodopent-1-yn-1-yl)trimethylsilane (1.68 g, 6.30 mmol, 1.0 equiv) was added directly into the reaction. The reaction was stirred overnight as the bath gradually warmed to rt, and then quenched with H_2O (60 mL). The layers were separated, the aqueous phase extracted with EtOAc (2 x 50 mL), and the combined organic layers washed with brine (25 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by flash column chromatography eluting with 9:1 hexane/EtOAc gave precursor **13a** (1.80 g, 4.95 mmol, 79%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 8.4 Hz, 1.0 Hz, 1H), 7.81 (dt, *J* = 8.4 Hz, 1.0 Hz, 1H), 7.46 (ddd, *J* = 8.4 Hz, 7.0 Hz, 1.0 Hz, 1H), 7.35 (ddd, *J* = 8.4 Hz, 7.0 Hz, 1.0 Hz, 1H), 7.20–7.16 (m, 2H), 6.98–6.92 (m, 3H), 6.88 (t, *J* = 6.9 Hz, 1H), 2.69–2.59 (m, 1H), 2.47–2.40 (m, 1H), 2.36–2.29 (m, 2H), 1.82–1.72 (m, 1H), 1.54–1.45 (m, 1H), 0.13 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 156.2, 146.9, 131.3, 129.9, 127.9, 124.5, 123.1, 120.4, 116.3, 111.3, 105.8, 88.0, 86.0, 33.9, 23.8, 19.4, 0.2; **IR** (thin film): ν 3063, 3043, 2959, 2899, 2173, 1590, 1494, 1451, 1341 cm^{-1}; **ESI-HRMS** calcd for $C_{21}H_{26}N_3OSi$ [M + H]$^+$ 364.1840, found 364.1842.

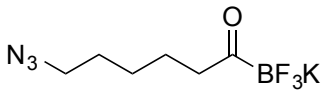
Synthesis of potassium hex-5-ynoyltrifluoroborate (13)



In a flame-dried, 100 mL two-neck flask equipped with a low temperature thermometer under an atmosphere of dry N_2, precursor **13a** (1.80 g, 4.95 mmol, 1.0 equiv) was dissolved in dry THF (50 mL) at rt, and then cooled to –110 °C (reaction mixture measured by internal thermometer) in an EtOH/N_2 ice bath. *n*-Butyllithium (1.35 M in hexane, titrated, 3.7 mL, 4.95 mmol, 1.0 equiv) was added dropwise over 2 min, resulting in a red-brown solution. The mixture

was stirred for 25 min followed by drop-wise addition of $B(OMe)_3$ (1.1 mL, 9.90 mmol, 2.0 equiv), resulting in a brownish mixture. If solidification of the reaction mixture was observed, the reaction was warmed to –90 ºC for 30 min, resulting in a clear yellow solution, before cooling to –110 ºC and stirring for an additional 1 h. The reaction was quenched with a sat. aq KHF_2 solution (15 mL) and allowed to warm to rt overnight. The solvent was removed *in vacuo* to give an off-white solid. The solid was extracted with acetone, the extract concentrated *in vacuo*, suspended in 3 mL sat. aq KHF_2 solution and stirred at 65 ºC overnight. The solvent was removed *in vacuo* and the resulting solid suspended in Et_2O (30 mL). After filtration, the filter cake was washed with CH_2Cl_2 (50 mL). The product was extracted from the filter cake with acetone to yield product **13** as a white solid (0.55 g, 2.72 mmol, 55%). **m.p.** 121 °C (decomp); **^{1}H NMR** (600 MHz, acetone–d_6): δ 2.50 (t, J = 7.2 Hz, 2H), 2.25 (t, J = 2.7 Hz, 1H), 2.13–2.07 (m, 2H), 1.63 (p, J = 7.3 Hz, 2H); **^{13}C NMR** (151 MHz, acetone–d_6): δ 248.5 (br), 85.3, 69.5, 43.9, 22.6, 18.7; **^{19}F NMR** (470 MHz, acetone–d_6): δ −151.0; **^{11}B NMR** (160 MHz, acetone–d_6): δ −1.70; **IR** (thin film): ν 3295, 2951, 2874, 1657 cm^{-1}; **ESI-HRMS** calcd for $C_6H_7BF_3O$ [M – K]$^-$ 163.0549, found 163.0544.

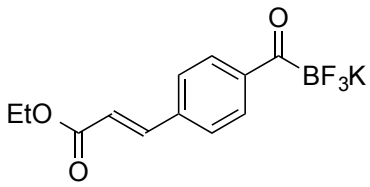
Synthesis of potassium 6-azidohexanoyltrifluoroborate (14)



In a flame-dried round-bottom flask under an atmosphere of dry N_2, **11** (0.44 g, 1.82 mmol, 1.0 equiv), potassium iodide (0.30 g, 1.82 mmol, 1.0 equiv) and sodium azide (0.35 g, 5.46 mmol, 3.0 equiv) were suspended in DMF (10 mL) and stirred at 80 ºC for 6 h. The reaction mixture was filtered and the solvent was concentrate *in vacuo*. The resulting solid was dissolved in acetone and precipitated with Et_2O. After filtration the filter cake was washed with Et_2O (50 mL). The product was extracted from the filter cake with acetone to afford product **14** as a white solid (0.29 g, 1.82 mmol, 64%). **m.p.** >125 °C (decomp); **^{1}H NMR** (600 MHz, acetone–d_6): δ 3.30 (t, J = 6.9 Hz, 2H), 2.42 (t, J = 7.3 Hz, 2H), 1.59–1.52 (m, 2H), 1.48 (p, J = 7.4 Hz, 2H) 1.35–1.27 (m, 2H); **^{13}C NMR** (151 MHz, acetone–d_6): δ 250.9 (br), 51.9, 44.5 (br), 30.3, 27.4, 22.6; **^{19}F NMR** (470 MHz, acetone–d_6): δ −153.5; **^{11}B NMR** (160 MHz, acetone–d_6): δ −1.7; **IR** (thin film): ν 2934, 2862, 2095, 1660 cm^{-1}; **ESI-HRMS** calcd for $C_6H_{10}BF_3N_3O$ [M – K]$^-$ 208.0876, found 208.0876.

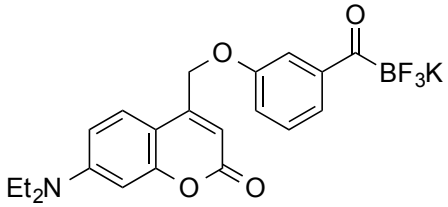
3. Chemoselective transformation

Synthesis of potassium 4-(3-(ethoxy)-3-oxoprop-1-en-1-yl)benzoyltrifluoroborate (16)



In a flame-dried round-bottom flask under an atmosphere of dry N_2, compound **8** (50 mg, 0.21 mmol, 1.0 equiv) and (carbethoxymethylene)triphenylphosphorane **15** (109 mg, 0.31 mmol, 1.5 equiv) were suspended in dry THF (5 mL) and heated to reflux for 16 h. The reaction mixture was allowed to cool to rt, the solvent was removed *in vacuo* and the resulting solid suspended in Et_2O (10 mL). The suspension was filtered and washed with Et_2O (3 x 50 mL). The product was extracted from the filter cake with acetone and dried *in vacuo* to give the product **16** as a white solid (50 mg, 0.16 mmol, 77%). **m.p.** 200 °C (decomp); **^{1}H NMR** (600 MHz, acetone–d_6): δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.72–7.66 (m, 3H), 6.59 (d, *J* = 16.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, acetone–d_6): δ 235.1 (br), 166.9, 144.8, 137.5, 129.7, 129.6, 128.6, 120.0, 60.8, 14.6; **^{19}F NMR** (470 MHz, acetone–d_6): δ −145.0; **^{11}B NMR** (160 MHz, acetone–d_6): δ −0.86; **IR** (thin film): v 2984, 1704, 1636, 1599 cm^{-1}; **ESI-HRMS** calcd for $C_{12}H_{11}BF_3O_3$ $[M - K]^-$ 271.0761, found 271.0757.

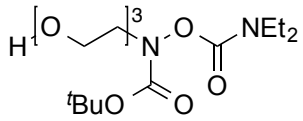
Synthesis of potassium 3-((7-(diethylamino)-2*H*-chromen-2-one)methoxy)benzoyltri fluoroborate (18)



A suspension of potassium 3-(hydroxyl)benzoyltrifluoroborate **12** (50 mg, 0.22 mmol, 1.0 equiv), 4-(bromomethyl)-7-(diethylamino)-2*H*-chromen-2-one **17** (75 mg, 0.24 mmol, 1.1 equiv)[3] and K_2CO_3 (36 mg, 0.26 mmol, 1.2 equiv) in acetone (5 mL) was stirred at 50 ºC for 24 h. The solvent was removed *in vacuo* and the resulting solid suspended in CH_2Cl_2 (20 mL). The suspension was filtered and the filter cake was washed with CH_2Cl_2 (3 x 20 mL) before the product was extracted from the filter cake with DMF to afford product **18** as a yellow solid (77 mg, 0.13 mmol, 77%). **m.p.** >210 °C (decomp); **^{1}H NMR** (600 MHz, acetone–d_6): δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.70 (dd, *J* = 2.7 Hz, 1.2 Hz, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.35 (ddd, *J* = 8.1 Hz, 7.6 Hz, 0.4 Hz, 1H), 7.18 (ddd, *J* = 8.1 Hz, 2.7 Hz, 1.0 Hz, 1H), 6.75 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 6.53 (d, *J* = 2.6 Hz, 1H), 6.21 (t, *J* = 1.3 Hz, 1H), 5.33 (d, *J* =

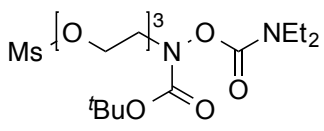
1.3 Hz, 2H), 3.52 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (151 MHz, acetone–d_6): δ 235.0 (br), 161.6, 158.9, 157.4, 152.0, 151.7, 144.1, 129.8, 126.3, 123.5, 118.4, 114.1, 109.5, 107.1, 106.9, 98.1, 66.5, 45.2, 12.8; **^{19}F NMR** (470 MHz, acetone–d_6): δ −144.6; **^{11}B NMR** (160 MHz, acetone–d_6): δ −0.88; **IR** (thin film): v 2970, 2360, 1737, 1725, 1602, 1354, 1230 cm^{-1}; **ESI-HRMS** calcd for $C_{21}H_{20}BF_3NO_4$ $[M - K]^-$ 418.1447, found 418.1441.

Synthesis of *tert*-butyl ((diethylcarbamoyl)oxy)(2-(2-(2-hydroxyethoxy)ethoxy)ethyl) carbamate (19a)



To a solution of 2-(2-(2-chloroethoxy)ethoxy)ethanol (500 mg, 2.98 mmol, 0.43 mL, 1.0 equiv) and *tert*-butyl ((diethylcarbamoyl)oxy)carbamate (825 mg, 3.55 mmol, 1.3 equiv) in DMF (10 mL) were added K_2CO_3 (822 mg, 5.96 mmol, 2.0 equiv) and potassium iodide (495 mg, 2.98 mmol, 1.0 equiv). The reaction mixture was heated to 70 °C and stirred for 16 h, cooled to rt and quenched with H_2O (50 mL). The aqueous phase was extracted with CH_2Cl_2 (4 x 50 mL) and the combined organic layers were dried over Na_2SO_4. Removal of the solvent *in vacuo* gave hydroxylamine alcohol **19a** as a pale yellow oil, which was used in the next step without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$): d 3.81 (br s, 1H), 3.77–3.57 (m, 12H), 3.31 (m, 4H), 1.45 (s, 9H), 1.17 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$): d 154.99, 154.16, 81.87, 72.49, 70.44, 70.42, 67.95, 61.78, 49.98, 42.97 (-N(*C*H_2CH$_3$)$_2$, rotomers), 41.60 (-N(*C*H_2CH$_3$)$_2$, rotomers), 28.18, 14.14 (-N(CH$_2$*C*H$_3$)$_2$, rotomers), 13.37 (-N(CH$_2$*C*H$_3$)$_2$, rotomers); **IR** (thin film): v 3479, 2976, 2935, 2875, 1742, 1423, 1367, 1269, 1132, 922, 746 cm^{-1}; **ESI-HRMS**: calcd for $C_{16}H_{33}N_2O_7^+$ $[M+H]^+$: 347.2282, found 347.2283.

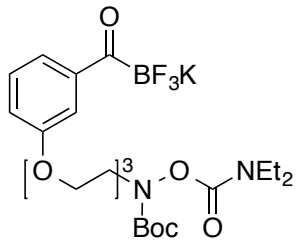
Synthesis of 6-(*tert*-butoxycarbonyl)-3-ethyl-4-oxo-5,9,12-trioxa-3,6-diazatetradecan-14-yl methanesulfonate (19)



To a solution of hydroxylamine **19a** (200 mg, 0.55 mmol, 1.0 equiv) and NEt_3 (114 µL, 0.82 mmol, 1.5 equiv) in CH_2Cl_2 (4 mL) at 0 °C was added methanesulfonyl chloride (51 µL, 0.66 mmol, 1.2 equiv). The reaction mixture was allowed to stir at rt for 2 h before removing the solvent *in vacuo*. The crude material was purified by flash column

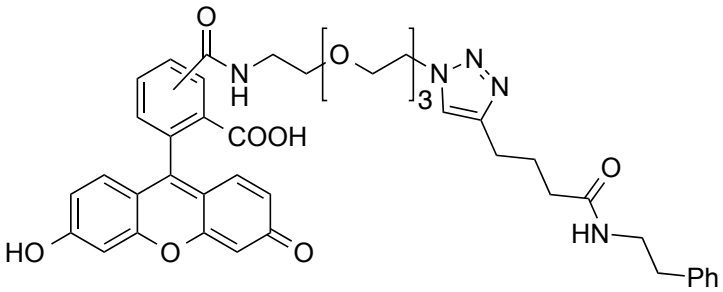
chromatography, eluting with cyclohexane/EtOAc (gradient 1:2→1:3) to give hydroxylamine **19** as a colorless oil (205 mg, 0.47 mmol, 85%).**^{1}H NMR** (400 MHz, $CDCl_3$): d 4.39–4.35 (m, 2H), 3.81 (br s, 2H), 3.78–3.74 (m, 2H), 3.69–3.62 (m, 6H), 3.32 (q, *J* = 6.7 Hz, 4H), 3.07 (s, 3H), 1.46 (s, 9H), 1.18 (t, *J* = 7.1 Hz, 6H);**^{13}C NMR** (101 MHz, $CDCl_3$): d 154.98, 154.16, 81.88, 70.65, 70.32, 69.25, 69.07, 67.95, 49.99, 43.00, 41.63, 37.72, 28.19, 14.16, 13.40; **IR** (thin film): v 2976, 2936, 1741, 1475, 1423, 1352, 1269, 1175, 1132, 1018, 920, 799, 745 cm^{-1}; **ESI-HRMS**: calcd for $C_{17}H_{38}N_3O_9S^+$ $[M+NH_4]^+$ 460.2323, found 460.2321.

Synthesis of potassium 3-((6-(*tert*-butoxycarbonyl)-3-ethyl-4-oxo-5,9,12-trioxa-3,6-diazatetradecan-14-yl)oxy)benzoyltrifluoroborate (20)



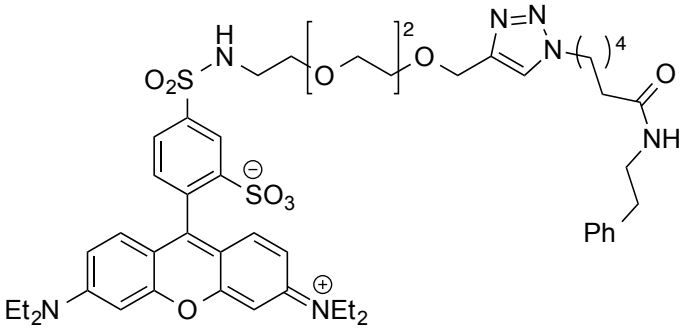
Potassium 3-(hydroxyl)benzoyltrifluoroborate **12** (50 mg, 0.22 mmol, 1.0 equiv), Cs_2CO_3 (143 mg, 0.44 mmol, 2.0 equiv) and 6-(*tert*-butoxycarbonyl)-3-ethyl-4-oxo-5,9,12-trioxa-3,6-diazatetradecan-14-yl methanesulfonate **19** (146 mg, 0.33 mmol, 1.5 equiv) were suspended in acetone (1 mL) and stirred at 65 ºC for 2 days. The mixture was filtered and washed with acetone (2 x 10 mL). The filtrate was concentrated *in vacuo* and the resulting solid dissolved in 3 drops of acetone. Et_2O was slowly added along the flask wall to precipitate the product as a white solid. The precipitate was filtered, washed with Et_2O and dried to afford product **20** as a light yellow oil (95 mg, 0.16 mmol, 75%). **^{1}H NMR** (600 MHz, acetone–d_6): δ 7.71 (d, *J* = 7.4 Hz, 1H), 7.63 (dd, *J* = 2.6 Hz, 1.2 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.00 (ddd, *J* = 8.1 Hz, 2.7 Hz, 1.0 Hz, 1H), 4.16–4.13 (m, 2H), 3.83–3.82 (m, 2H), 3.77–3.72 (m, 1H), 3.71–3.61 (m, 7H), 3.32 (q, *J* = 7.0 Hz, 4H), 1.44 (s, 9H), 1.16 (br.s, 6H); **^{13}C NMR** (151 MHz, acetone–d_6): δ 234.7 (br), 159.6, 155.7, 154.7, 144.1, 129.5, 122.2, 118.1, 114.3, 81.7, 71.4, 71.1, 70.4, 68.5, 68.2, 50.7, 43.6, 42.3, 28.4, 14.5, 13.7; **^{19}F NMR** (470 MHz, acetone–d_6): δ −141.6; **^{11}B NMR** (160 MHz, acetone–d_6): δ −0.80; **IR** (thin film): v 2978, 2935, 2877, 1737, 1633, 1577, 1479, 1428, 1368 cm^{-1}; **ESI-HRMS** calcd for $C_{23}H_{35}BF_3N_2O_8$ $[M - K]^-$ 535.2439, found 535.2444.

Synthesis of 2-(6-Hydroxy-3-oxo-3*H*-xanthen-9-yl)-4(5)-((2-(2-(2-(2-(4-(4-oxo-4-(phenethylamino)butyl)-1*H*-1,2,3-triazol-1-yl)ethoxy)ethoxy)ethoxy)ethyl)carbamoyl) benzoic acid (23)



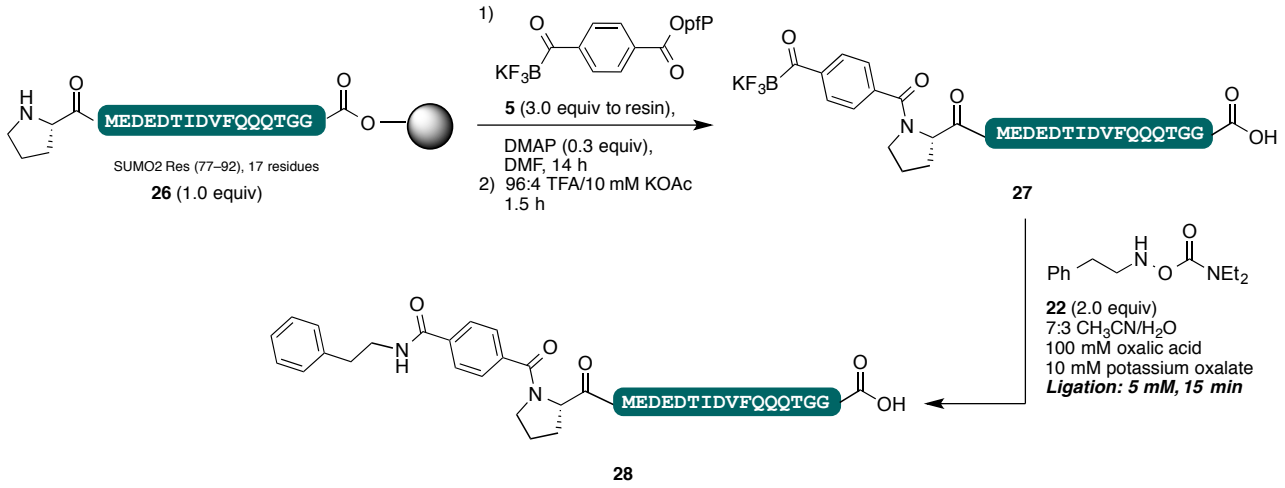
Potassium hex-5-ynoyltrifluoroborate **13** (21 mg, 104 µmol, 2.0 equiv), 4(5)-((2-(2-(2-(2-Azidoethoxy)ethoxy) etho-xy)ethyl)carbamoyl)-2-(6-hydro-xy-oxo-3*H*-xanthen-9-yl)benzoic acid **21**[4] (30 mg, 52 µmol, 1.0 equiv), CuI (10 mg, 52 µmol, 1.0 equiv) and NEt_3 (22 µL, 156 µmol, 3.0 equiv) in 1:1 CH_3CN/H_2O (1mL) was stirred for 12 h at rt. *N,N*-Diethyl-2-(phenethylamino)acetamide **22** (31 mg, 130 µmol, 2.5 equiv) was added the mixture was allowed to stir for 12 h. The reaction mixture was purified directly by preparative HPLC to afford product **23** as a yellow solid (24 mg, 31 µmol, 59%). **m.p.** >90 °C (decomp); **^{1}H NMR** (600 MHz, CD_3OD): δ 8.50 (s, 0.5H), 8.22 (dd, *J* = 8.0 Hz, 1.7 Hz, 0.5H), 8.17–8.12 (m, 1H), 7.80 (dd, *J* = 5.5 Hz, 2.9 Hz, 0.5H), 7.75 (s, 0.5H), 7.68 (s, 0.5H), 7.33 (d, *J* = 8.0 Hz, 0.5H), 7.26–7.22 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.15 (ddt, *J* = 8.7 Hz, 5.4 Hz, 1.3 Hz, 1H), 6.81 (d, *J* = 9.1 Hz, 2H), 6.75 (d, *J* = 8.3 Hz, 2H), 6.66 (d, *J* = 6.3 Hz, 2H), 4.51 (t, *J* = 6.0 Hz, 1H), 4.46 (t, *J* = 6.0 Hz, 1H), 3.86 (t, *J* = 6.0 Hz, 1H), 3.79 (t, *J* = 6.0 Hz, 1H), 3.70 (t, *J* = 5.5 Hz, 1H), 3.67–3.59 (m, 5H), 3.58 (t, *J* = 5.5 Hz, 1H), 3.55–3.52 (m, 1H), 3.52–3.49 (m, 2H), 3.49 (s, 2H), 3.38 (q, *J* = 7.0 Hz, 2H), 2.76 (dt, *J* = 7.3 Hz, 3.0 Hz, 2H), 2.63 (q, *J* = 8.2 Hz, 2H), 2.18 (dt, *J* = 9.6 Hz, 7.5 Hz, 2H), 1.93–1.84 (m, 2H); **^{13}C NMR** (151 MHz, CD_3OD): δ 175.4, 169.9, 168.3, 168.2, 163.4, 160.3, 160.0, 160.0, 159.8, 155.3, 155.1, 148.2, 141.9, 140.5, 137.9, 135.1, 131.0, 130.9, 130.6, 129.8, 129.5, 127.3, 126.8, 126.1, 125.0, 124.5, 115.1, 112.1, 103.6, 71.6, 71.5, 71.5, 71.4, 71.4, 71.2, 70.5, 70.3, 70.3, 51.5, 51.4, 41.9, 41.2, 41.1, 36.5, 36.3, 26.7, 25.7; **IR** (thin film): v 3141, 3089, 2930, 2874, 1756, 1699, 1643, 1614, 1550, 1454, 1249, 1182, 1114 cm^{-1}; **ESI-HRMS** calcd for $C_{43}H_{46}N_5O_{10}$ $[M + H]^+$ 792.3239, found 792.3223.

Synthesis of 2-(6-(Diethylamino)-3-(diethyliminio)-3*H*-xanthen-9-yl)-5-(*N*-(2-(2-(2-((1-(6-oxo-6-(phenethylamino)hexyl)-1*H*-1,2,3-triazol-4-yl)methoxy)ethoxy)ethoxy)ethyl) sulfamoyl)benzenesulfonate (25)



Potassium 6-azidohexanoyltrifluoroborate **14** (20 mg, 41 μmol, 2.0 equiv), 2-(6-(diethylamino)-3-(diethyliminio)-3*H*-xanthen-9-yl)-5-(*N*-(2-(2-(2-(prop-2-yn-1-yl oxy)ethoxy)ethoxy)ethyl)sulfamoyl) benzenesulfonate **24**[5] (30 mg, 82 μmol, 1.0 equiv), CuI (8 mg, 41 μmol, 1.0 equiv) and NEt_3 (5 μL, 41 μmol, 1.0 equiv) in 1:1 CH_3CN/H_2O (1mL) was stirred for 16 h. *N,N*-diethyl-2-(phenethylamino)acetamide **22** (19 mg, 82 μmol, 2.0 equiv) was added and the reaction was allowed to stir for 12 h at rt. Purification by HPLC gave the product as a purple solid (23 mg, 23 μmol, 56%). **m.p.** >210 °C (decomp); **^{1}H NMR** (600 MHz, CD_3OD): δ 8.67 (dd, *J* = 1.9 Hz, 0.4 Hz, 1H), 8.11 (dd, *J* = 7.9 Hz, 1.9 Hz, 1H), 8.02 (s, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.27-7.23 (m, 2H), 7.19-7.15 (m, 3H), 7.11 (s, 1H), 7.09 (s, 1H), 6.98 (dd, *J* = 9.5 Hz, 2.5 Hz, 2H), 6.92 (d, *J* = 2.5 Hz, 2H), 4.62 (s, 2H), 4.36 (t, *J* = 7.1 Hz, 2H), 3.69-3.63 (m, 12H), 3.62-3.59 (m, 2H), 3.57 (dd, *J* = 4.2 Hz, 2.1 Hz, 1 H), 3.56–3.53 (m, 3H), 3.34 (t, *J* = 7.3 Hz, 2H), 3.22 (t, *J* = 5.3 Hz, 2H), 2.75–2.70 (m, 2H), 2.10 (t, *J* = 7.4 Hz, 2H), 1.86 (p, *J* = 7.5 Hz, 2H), 1.57 (p, *J* = 7.5 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 12H), 1.26–1.22 (m, 2H); **^{13}C NMR** (151 MHz, CD_3OD): δ 175.8, 159.4, 157.9, 157.1, 147.3, 145.8, 144.2, 140.5, 135.3, 133.7, 132.5, 129.8, 129.5, 129.3, 127.7, 127.3, 125.4, 115.3, 115.1, 97.0, 71.6, 71.5, 71.3, 70.8, 70.7, 64.9, 51.3, 46.8, 44.2, 41.9, 36.7, 36.5, 30.8, 26.9, 26.3, 12.8; **IR** (thin film): v 2978, 2932, 2871, 1591, 1416, 1338, 1180 cm^{-1}; **ESI-HRMS** calcd for $C_{50}H_{65}N_7O_{10}S_2$ $[M + H]^+$ 988.4307, found 988.4295.

4. Preparation and KAT ligation of potassium acyltrifluoroborate containing SUMO2 C-terminal peptide sequence



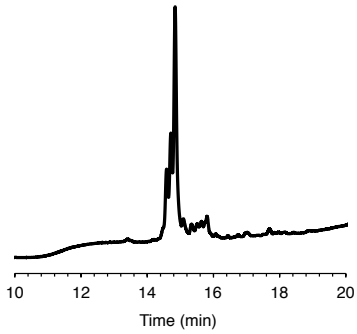
Peptide synthesis: The peptide was synthesized by standard automated Fmoc-SPPS using pre-loaded Fmoc-Gly-HMP-AM resin with a substitution capacity of 0.49 mmol/g.

Coupling of KAT-pfP ester: The *N*-terminal proline containing peptide on-resin **26** (55.0 mg, 27.5 µmol) was treated with a solution of bifunctional KAT-pfP ester **5** (34.8 mg, 82.5 µmol, 3.0 equiv to resin) and DMAP (1.0 mg, 8.2 µmol, 0.3 equiv to resin) in DMF (1.5 mL). The reaction was allowed to proceed for 14 h. The resin was thoroughly washed with DMF (3 x 2 mL) and CH_2Cl_2 (3 x 2 mL) and dried under a stream of nitrogen.

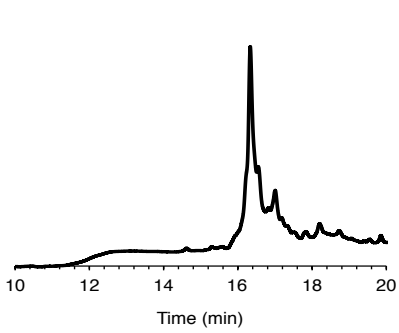
Cleavage of peptide from resin: The peptide containing the KAT group on-resin **27** (55.0 mg) was treated with 96:4 TFA/10 mM KOAc, pH = 4 for 1.5 h. The resin was filtered-off and the filtrate was concentrated in vacuo. The residue was triturated with Et_2O (3 x 5 mL), centrifuged and dried to obtain an off-white solid (22.8 mg, 39% crude yield).

Purification of KAT-peptide: The crude peptide was purified by preparative HPLC using pH 4 buffer systems. Eluent A: 10 mM KOAc buffer, pH = 4; Eluent B: (9:1) CH_3CN/10 mM KOAc buffer, pH = 4 using a gradient of 10 to 95% CH_3CN in 25 min. Column: Phenomenex Jupiter (21.5 x 250 mm), 5 micron, 300 Å; Flow rate: 10 mL/min; UV detection: 220 nm, 254 nm, 280 nm. The product fractions were pooled, frozen and lyophilized to give the desired KAT-peptide along with KOAc. Analytical HPLC and MALDI-FTMS (negative mode) were used to confirm the purity and identity of the isolated product **27**. m/z calculated for **27** $C_{87}H_{123}BF_3N_{20}O_{35}S$ 2107.8239; measured 2106.8127 [M–H].

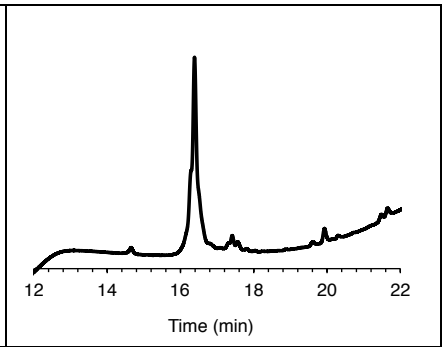
Note: Under MALDI-TOF measurement conditions using HCCA as the matrix, presumably the proto-deborylated and difluoroborate products are observed as the molecular ion peak, which is pronounced for sequences rich in acidic residues.



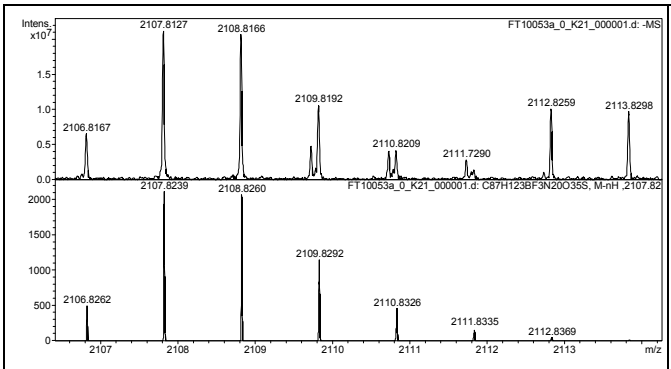
Analytical HPLC of crude peptide ***26***



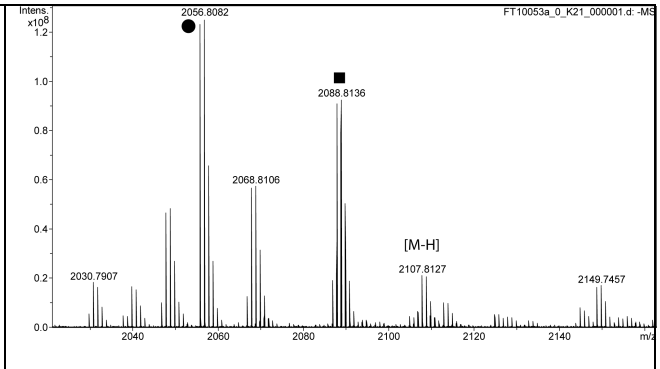
Analytical HPLC of crude KAT-peptide ***27***



Preparative HPLC purified KAT-peptide ***27***



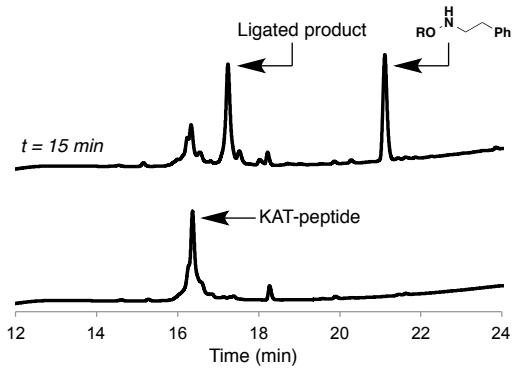
MALDI-HRMS of purified KAT-peptide ***27*** *(–ve ionisation). Top: measured mass, Bottom: calculated isotopic pattern of the product.*



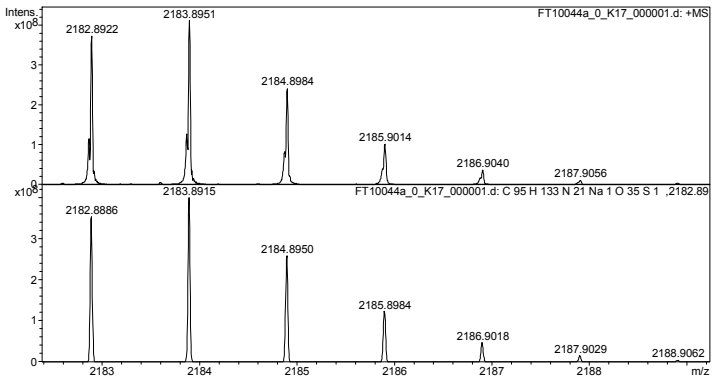
MALDI-HRMS: Depending on the peptide sequence, under MALDI ionisation, presumably the acyldifluoroborate (n) *and proto-deborylated* (●) *products can be observed.*

KAT ligation with purified KAT-peptide: KAT-peptide **27** (4.0 mg, 1.9 µmol, 1.0 equiv) and phenethylcarbamoyl hydroxylamine **22** (0.9 mg, 3.7 µmol, 2.0 equiv) were dissolved in 7:3 CH_3CN/H_2O with 0.1 M oxalic acid and 0.01 M potassium oxalate (373.0 µL, 5 mM) and allowed to react at 25 ºC. The progress of the ligation was monitored by analytical HPLC using a Shiseido capcell pak UG80 C18 column (4.6 x 250 mm) using a gradient of 10 to 95% CH_3CN with 0.1% TFA in 22 min. An aliquot of the ligation mixture (3 µL) was taken at 15 min and 90 min, diluted to 15 µL with ligation solvent and injected on HPLC. No change in the peak ratios was observed after 15 min. The reaction mixture was diluted to 0.9 mL and purified by preparative HPLC using a Phenomenex Jupiter column (21.5 x 250 mm), 5 micron, 300 Å with a gradient of 10 to 95% CH_3CN with 0.1% TFA in 25 min; Flow rate: 10 mL/min; UV detection: 220 nm, 254 nm, 280 nm. The fractions containing the product were pooled, frozen and lyophilized to give the desired KAT-ligated

SUMO 2 C-terminal peptide **28** (1.3 mg, 32% yield for KAT ligation and purification steps). Analytical HPLC and MALDI-FTMS (positive mode) were used to confirm the purity and identity of the ligated product **28**. m/z calculated for **28** $C_{95}H_{133}N_{21}NaO_{35}S$ 2182.8886; measured 2182.8922 [M+Na].



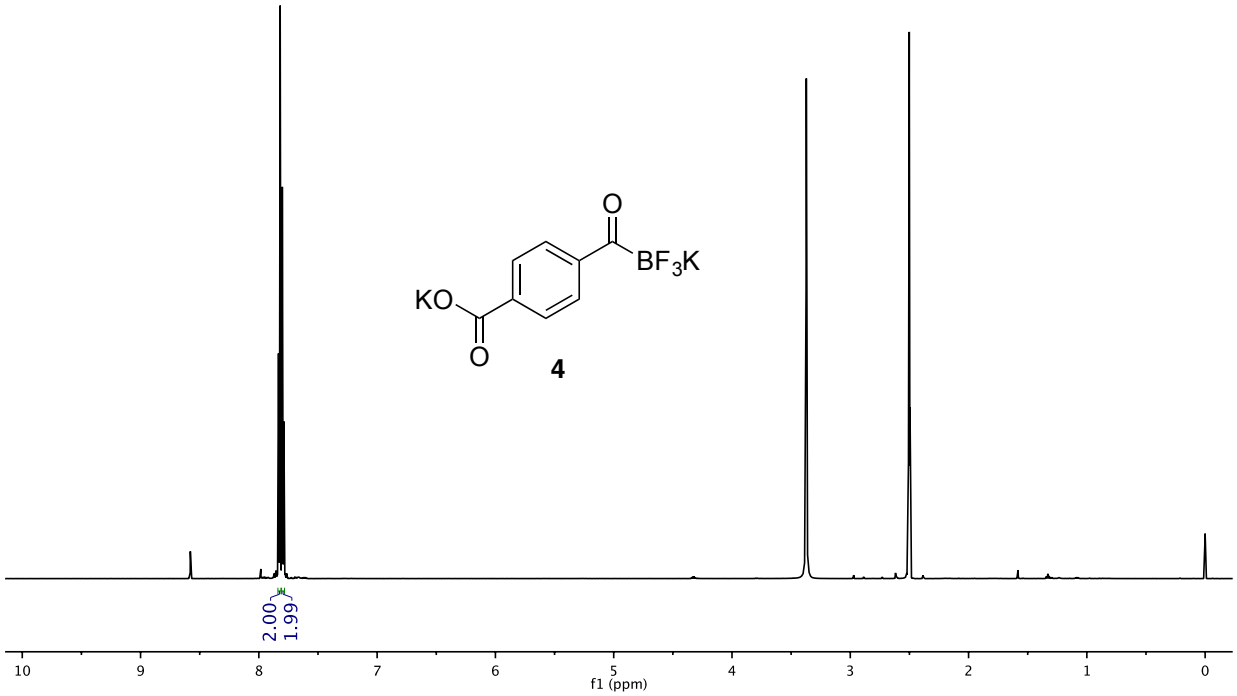
*KAT ligation: HPLC monitoring of the ligation of KAT-peptide **27** with phenethylcarbamoyl hydroxylamine **22***



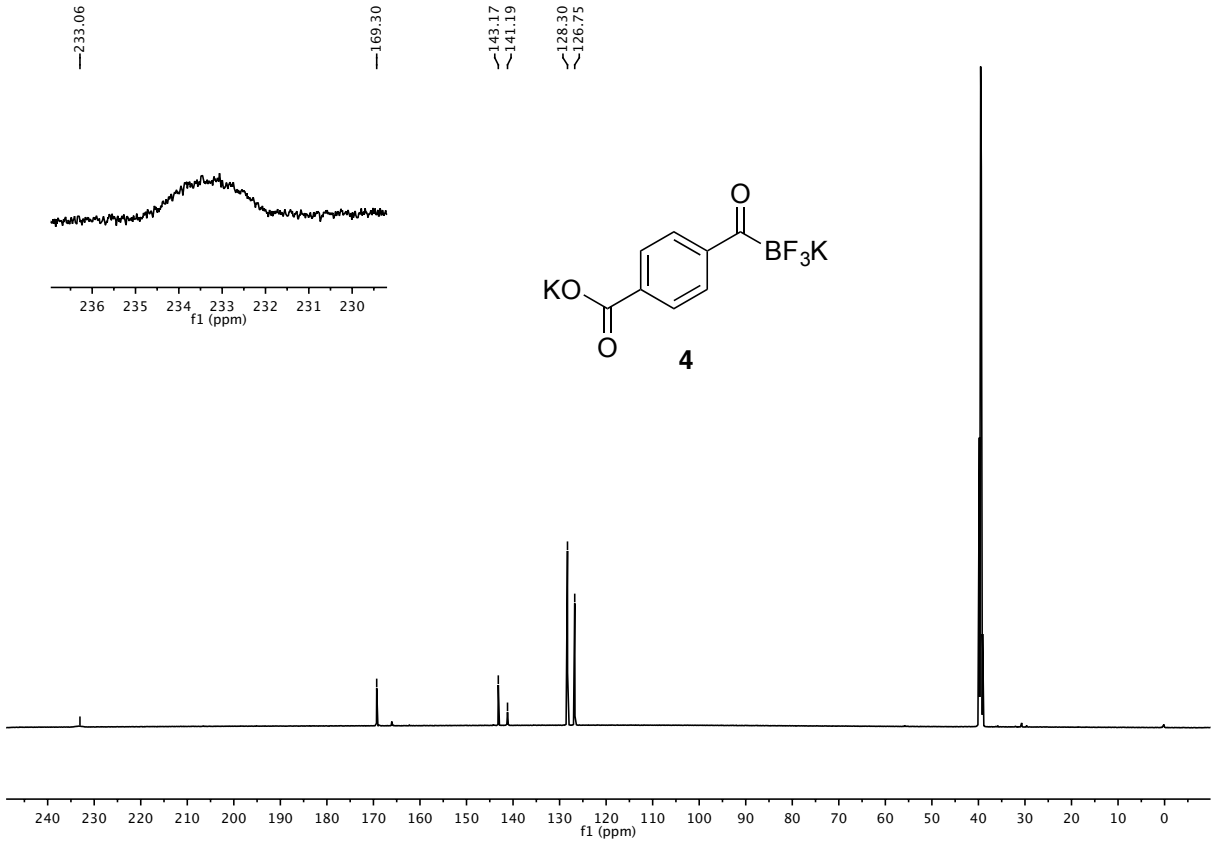
*MALDI-HRMS of ligated, purified peptide **28**. Top: measured mass, Bottom: calculated isotopic pattern of the product*

5. Spectral Data

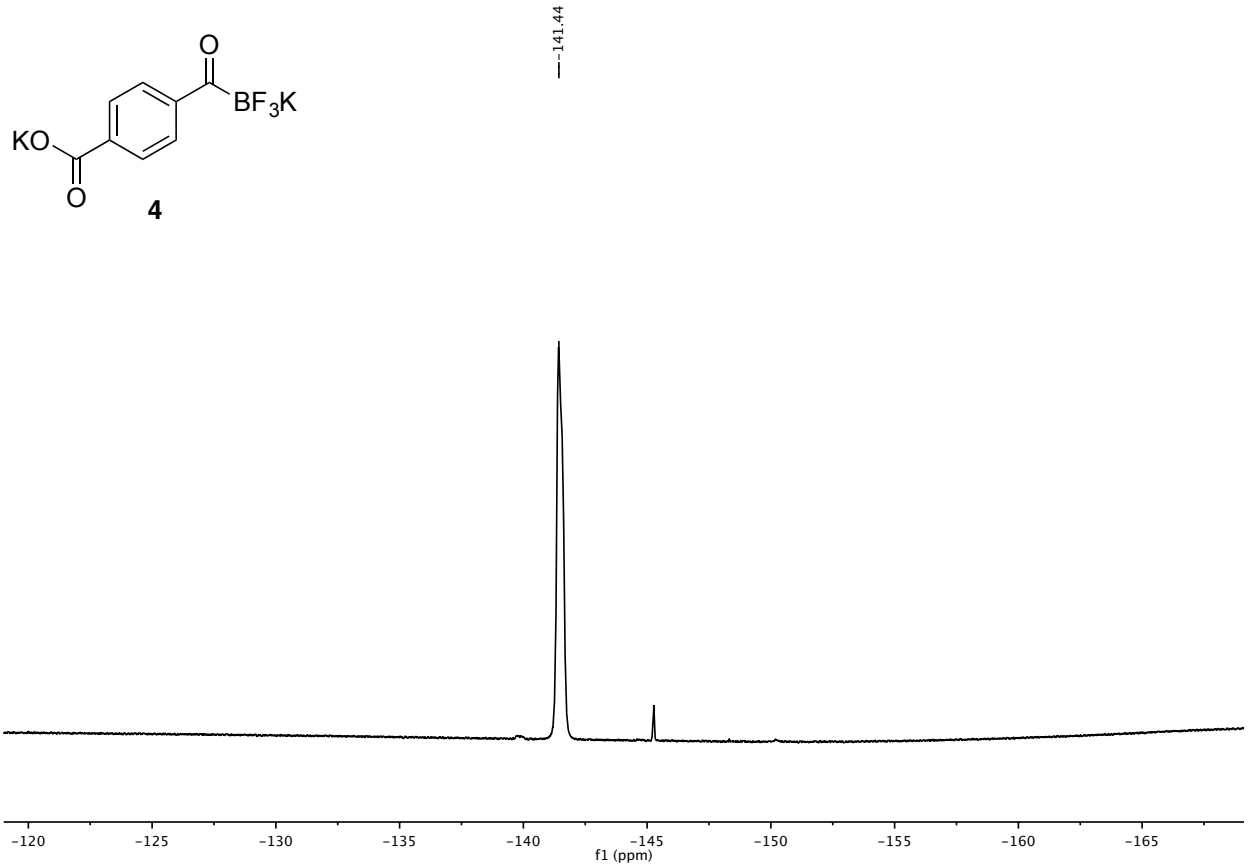
4: ^{1}H NMR (600 MHz, DMSO–d_6)



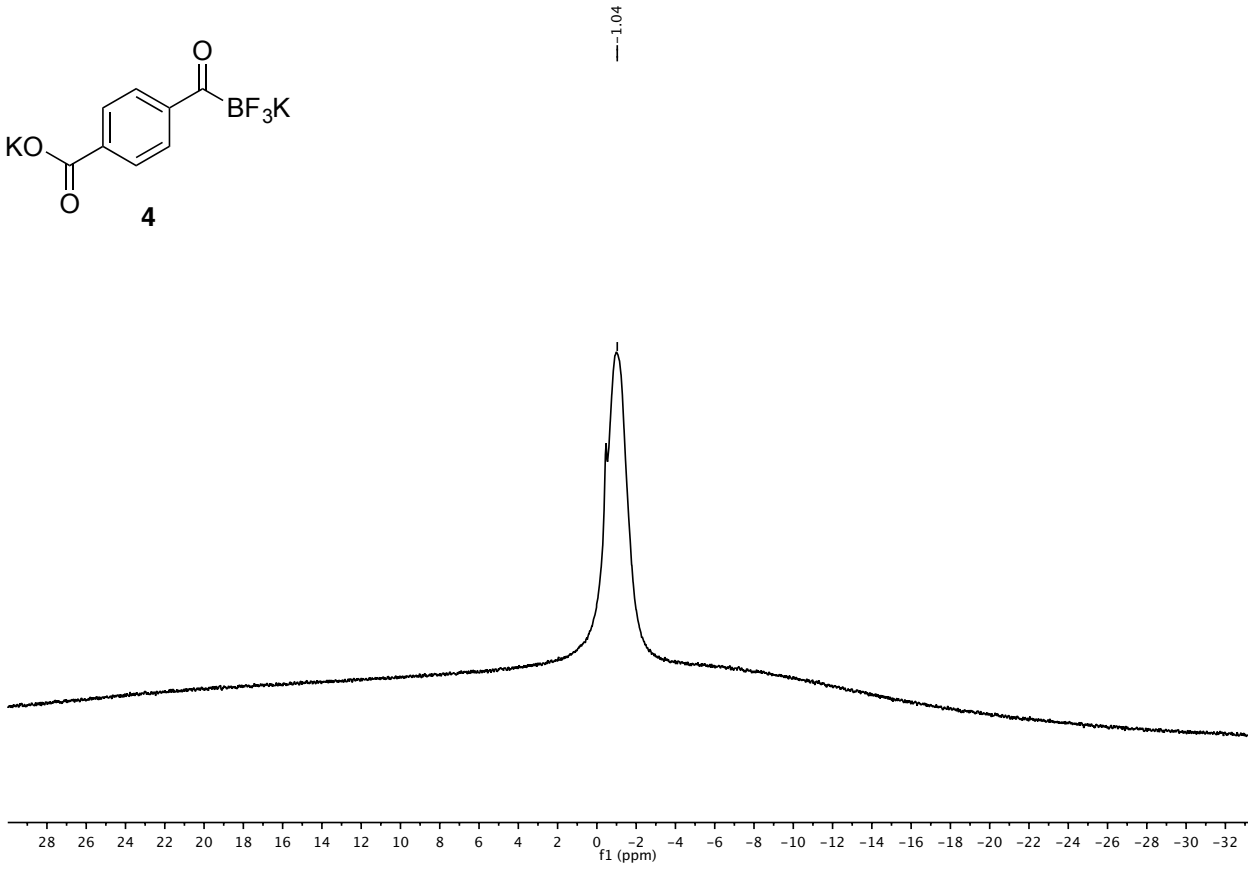
4: ^{13}C NMR (151 MHz, DMSO–d_6)



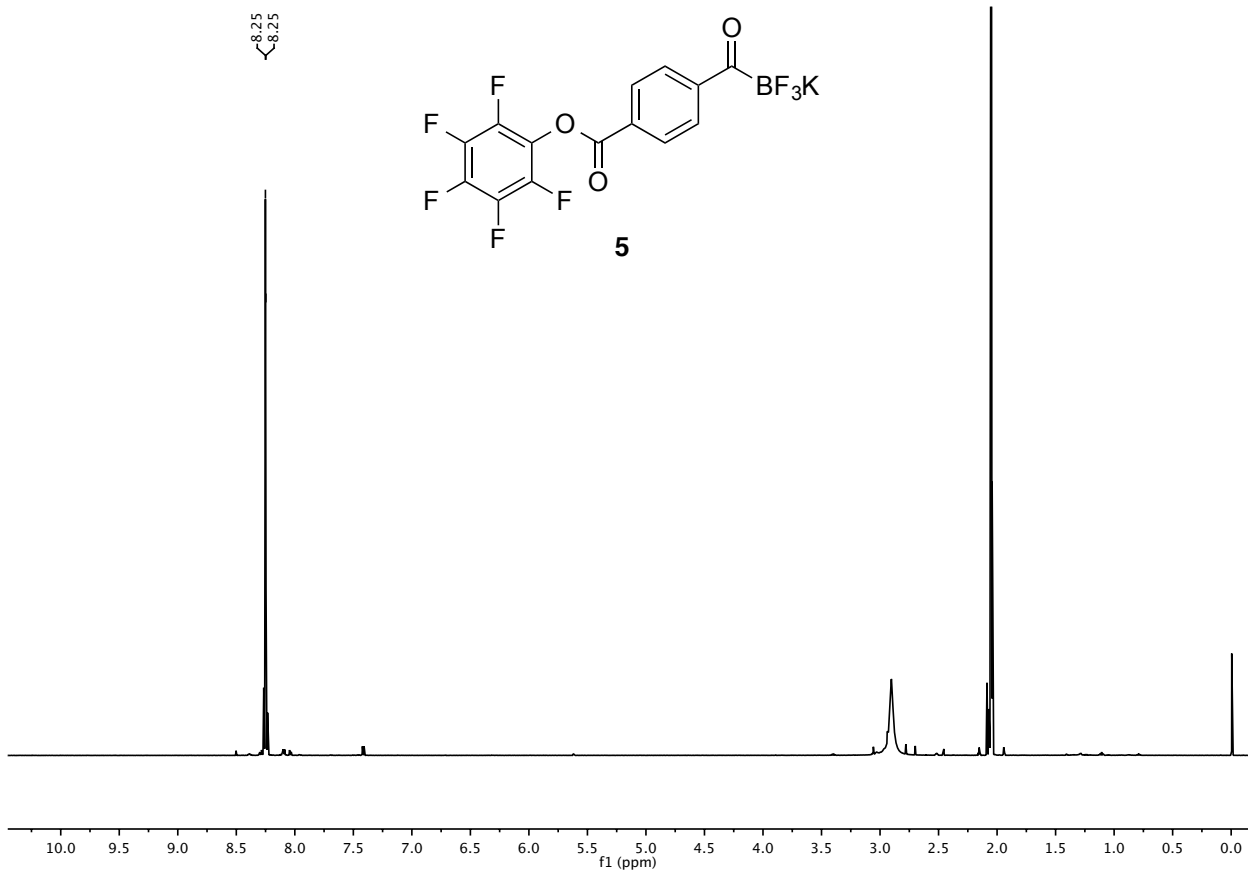
4: ^{19}F NMR (470 MHz, DMSO–d_6)



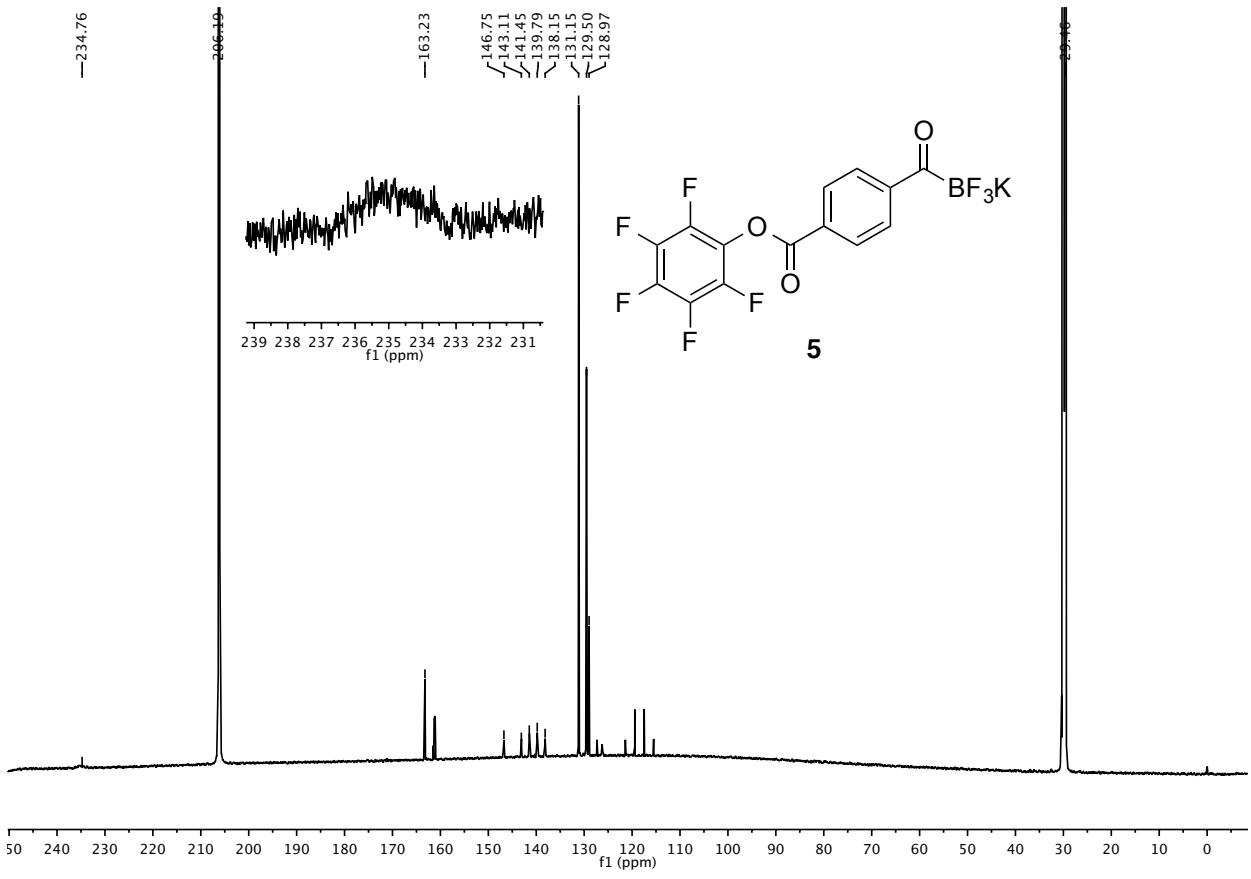
4: ^{11}B NMR (160 MHz, DMSO–d_6)



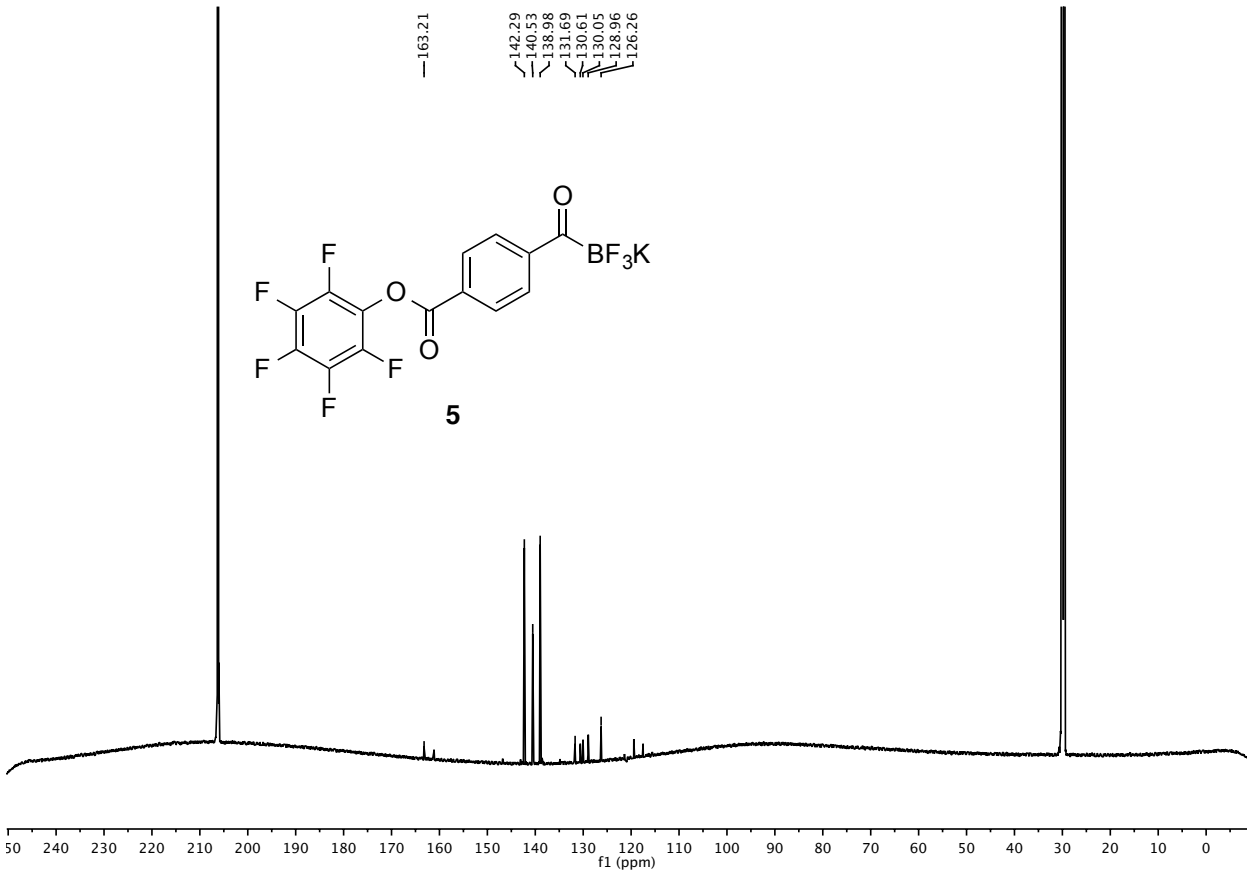
5: ^{1}H NMR (600 MHz, acetone–d_6)



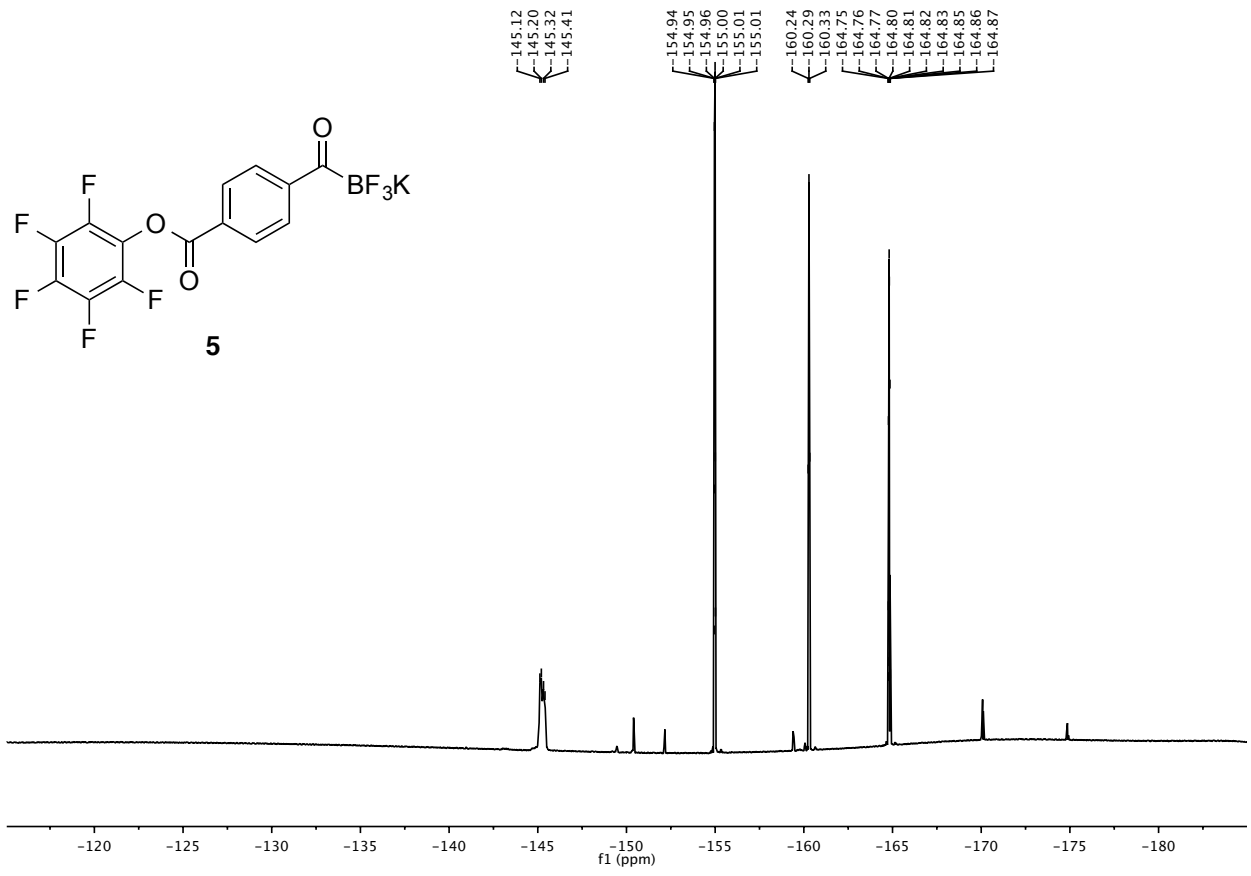
5: ^{13}C NMR (151 MHz, acetone–d_6)



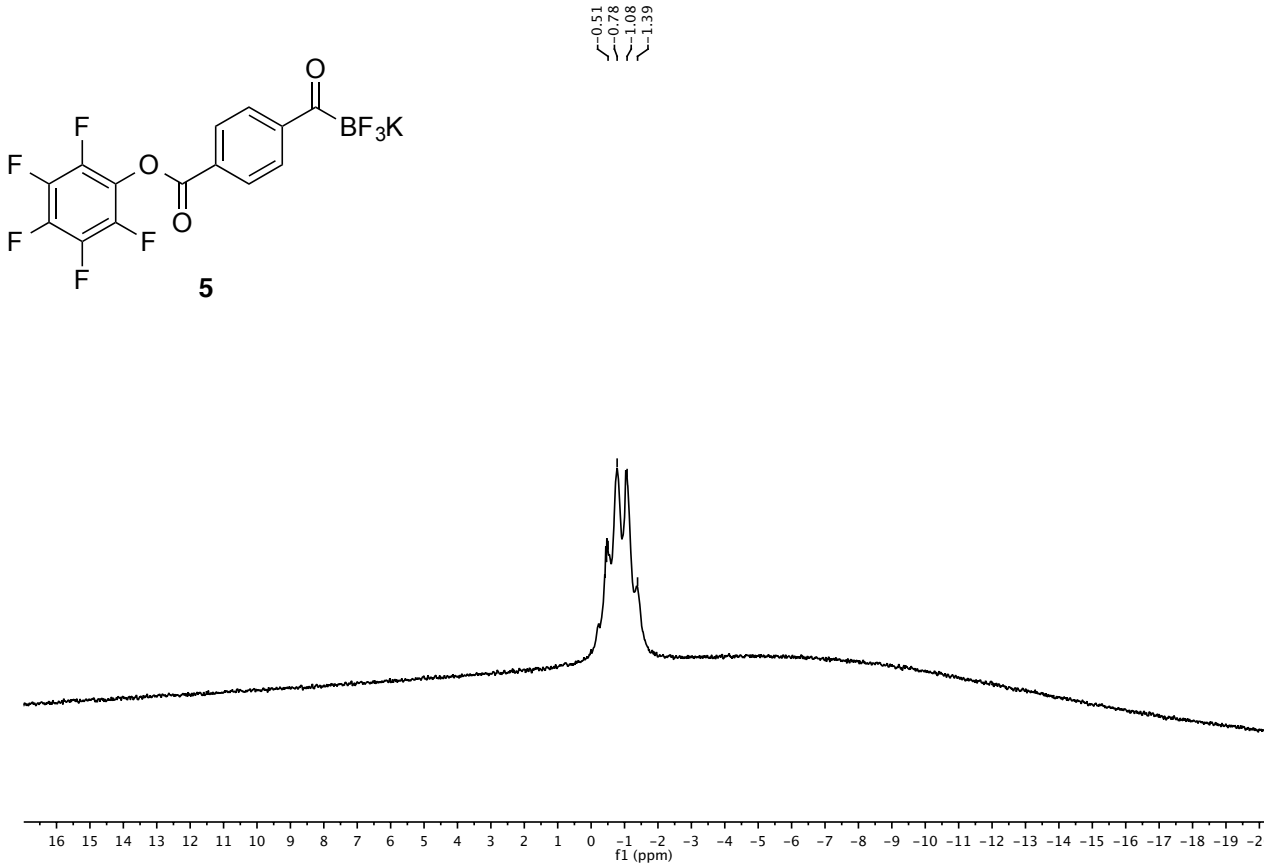
5: ^{13}C NMR decoupled (151 MHz, acetone–d_6)



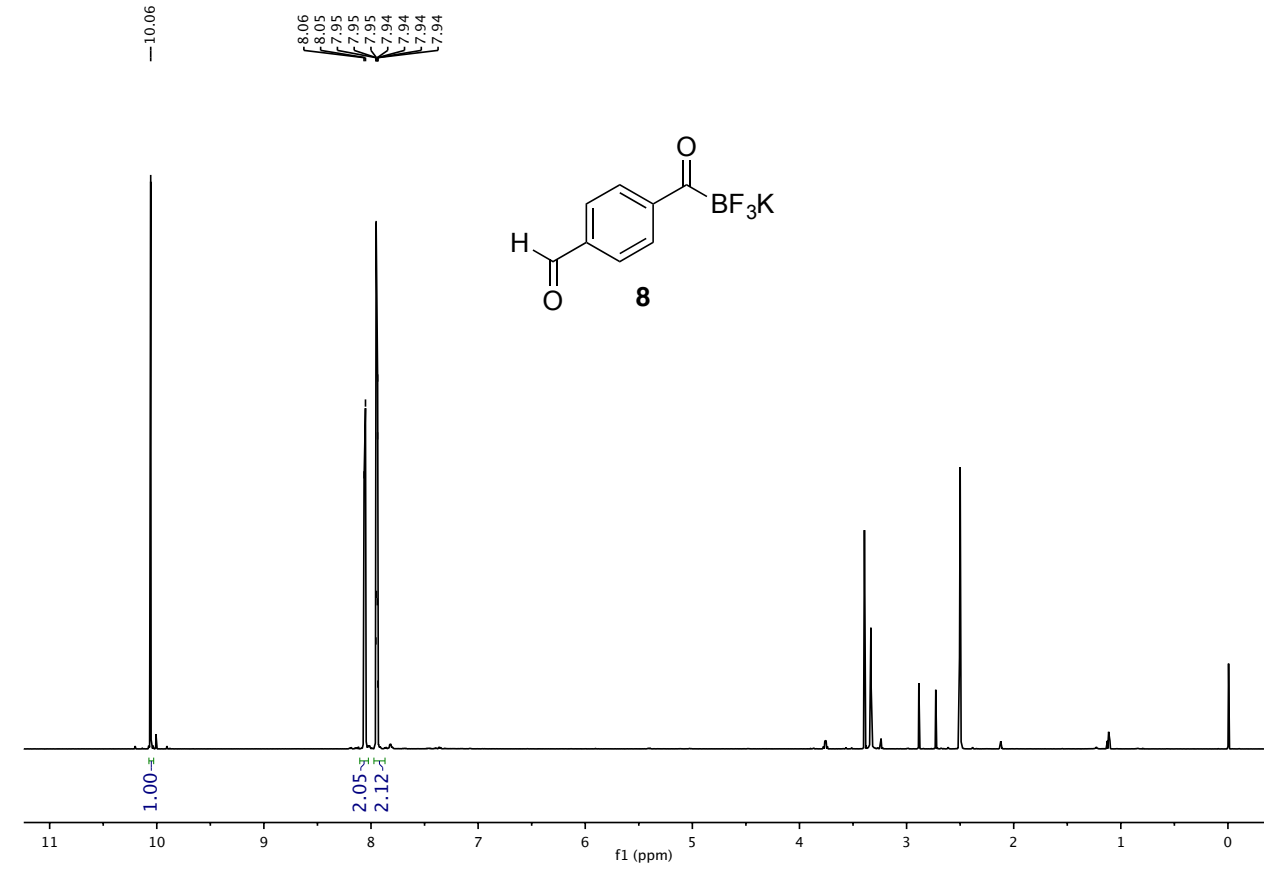
5: ^{19}F NMR (470 MHz, acetone–d_6)



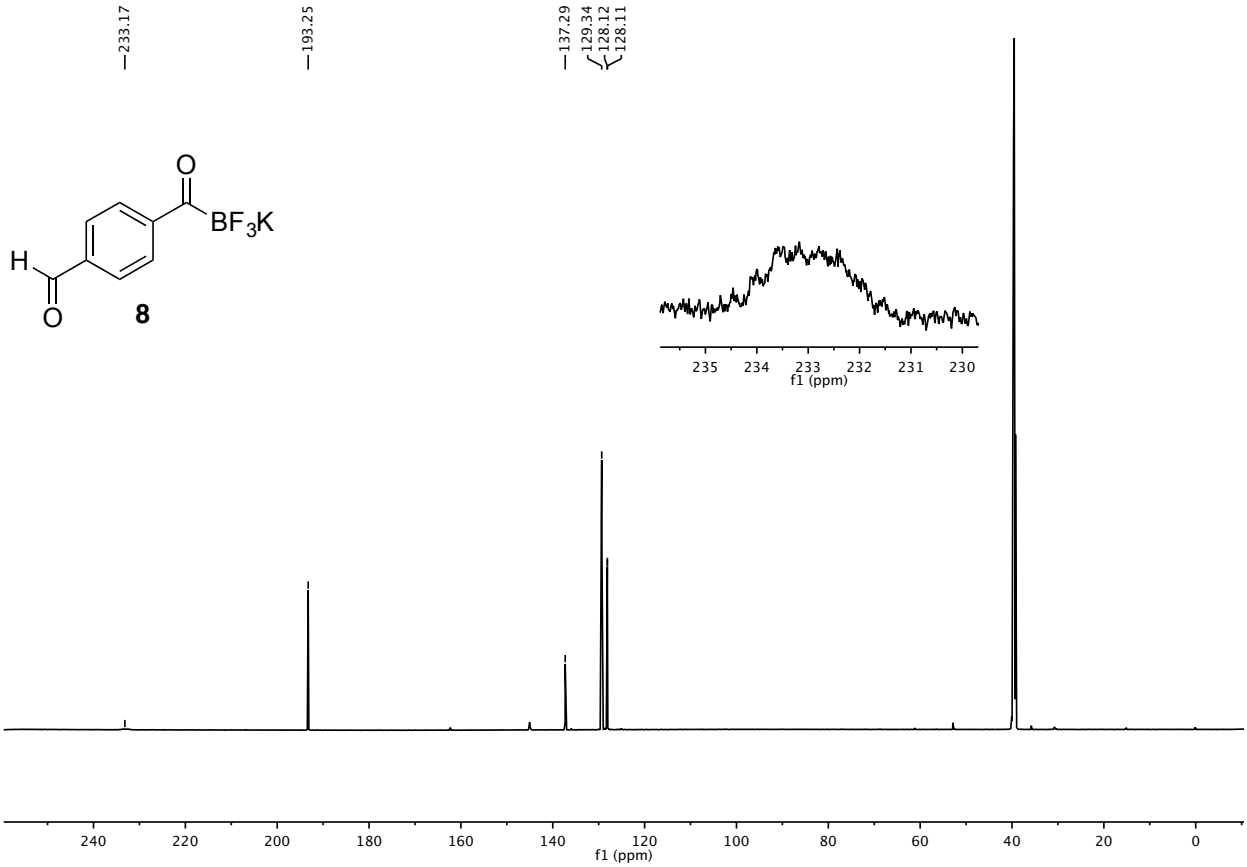
5: ^{11}B NMR (160 MHz, acetone–d_6)



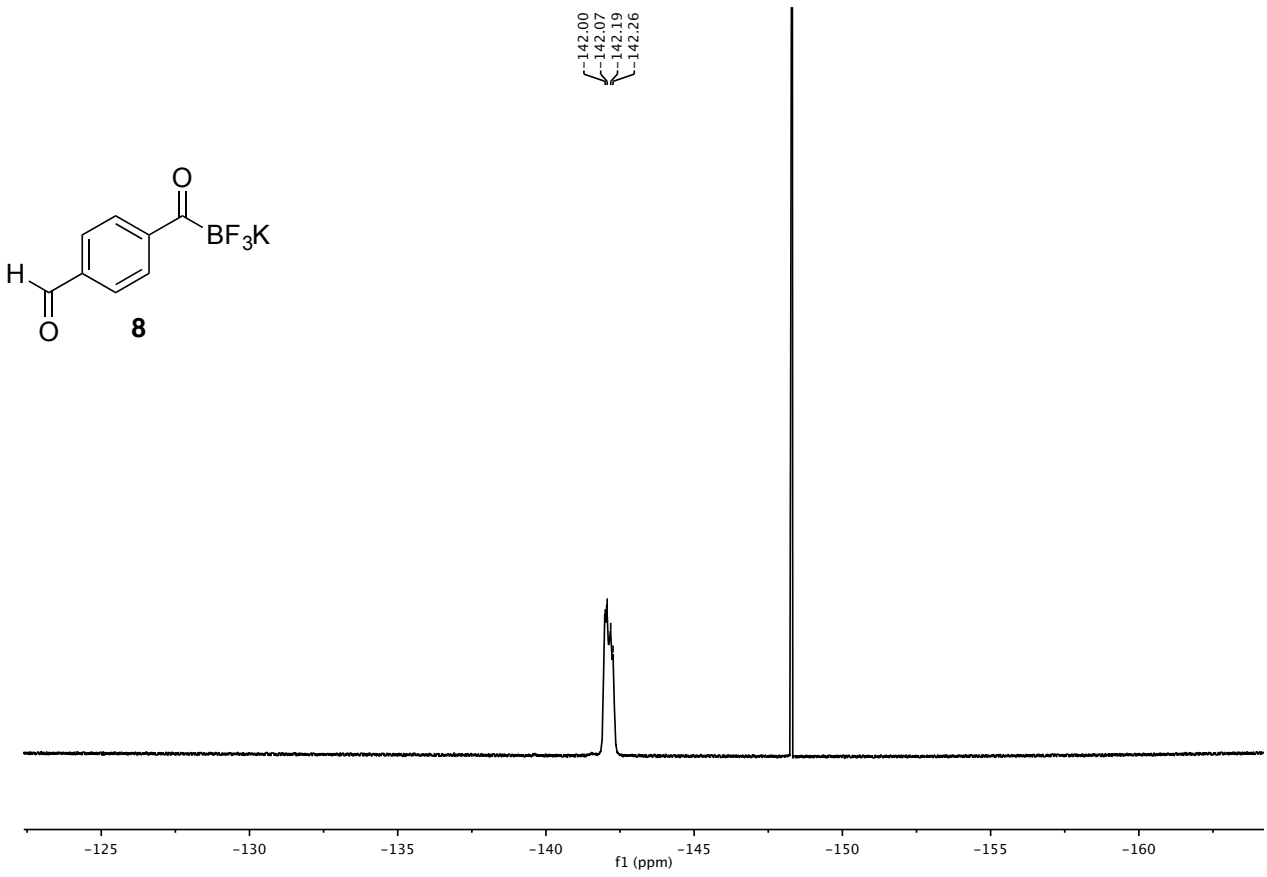
8: ^{1}H NMR (600 MHz, DMSO–d_6)



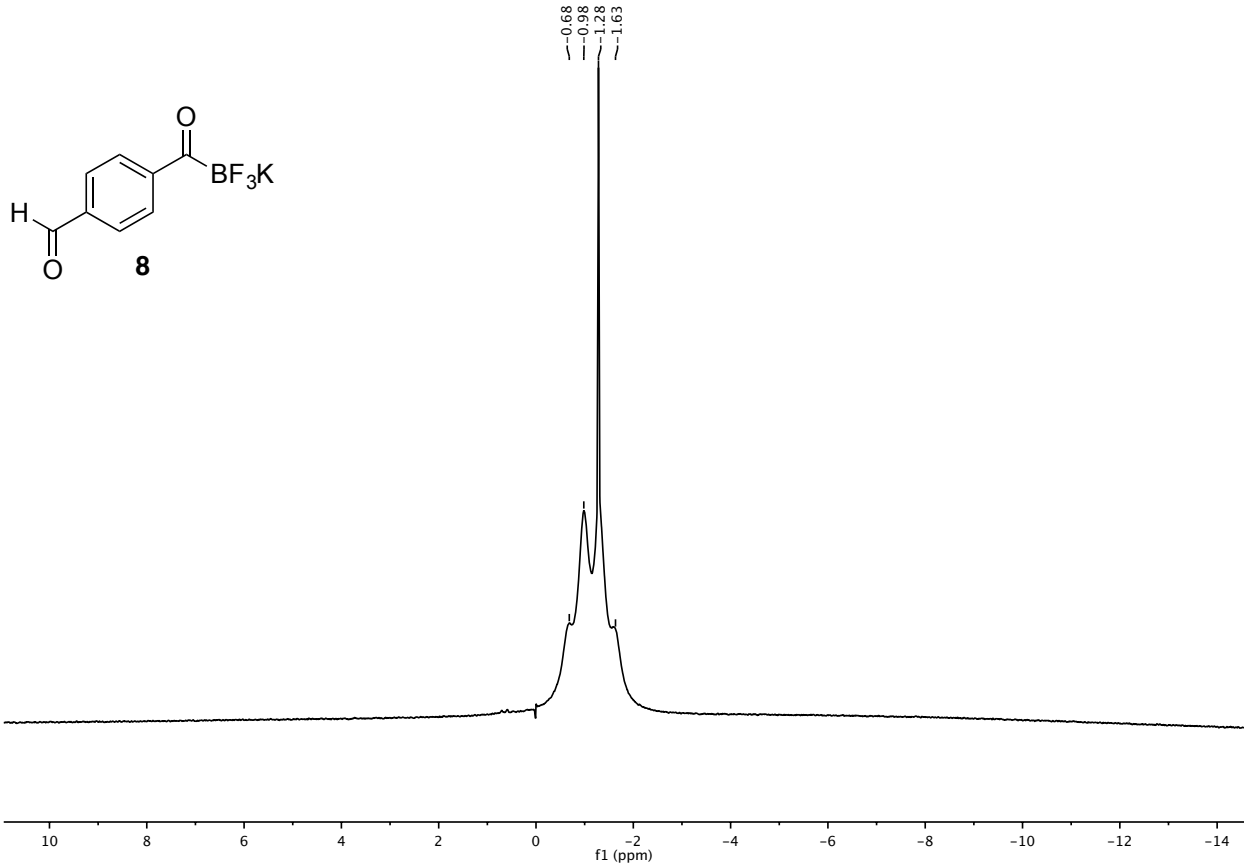
8: ^{13}C NMR (151 MHz, DMSO–d_6)



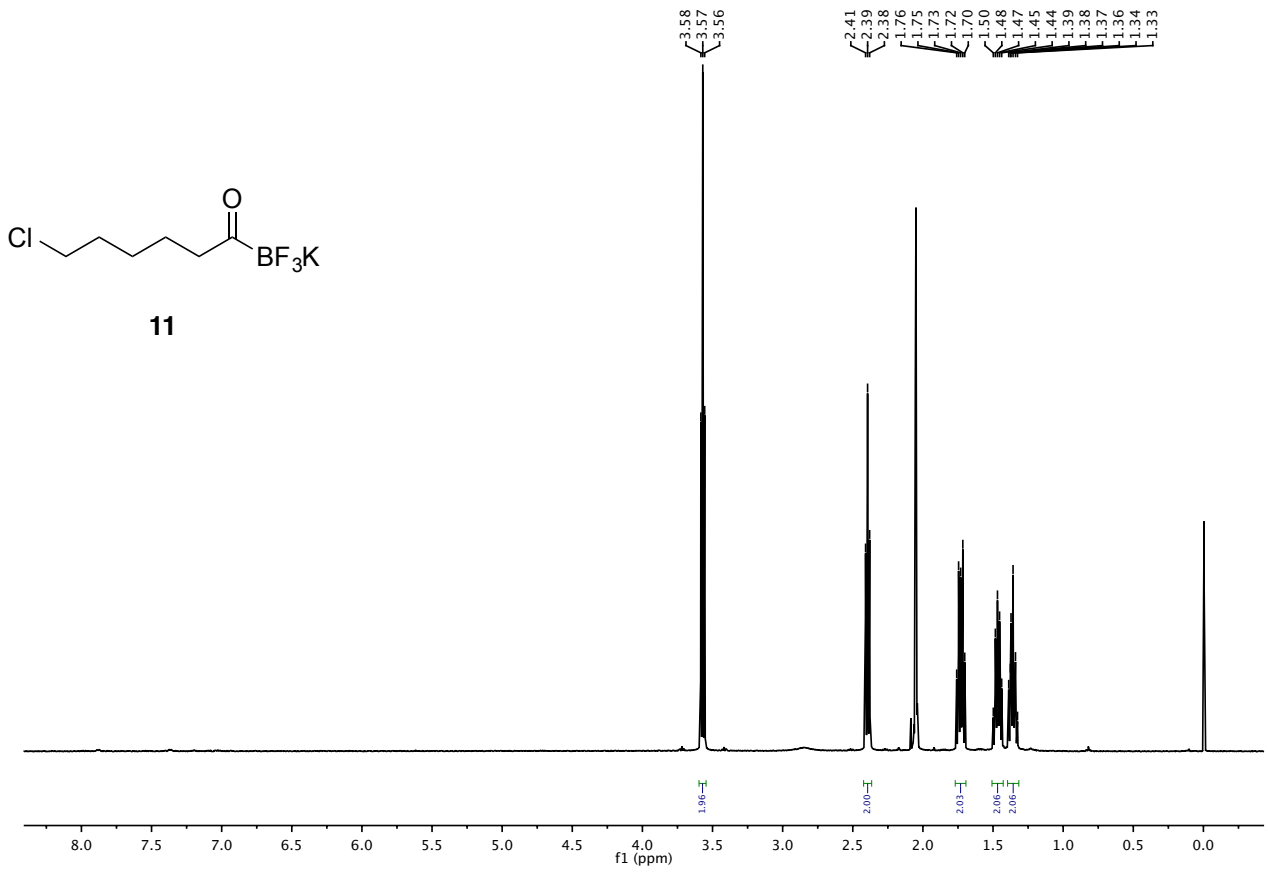
8: ^{19}F NMR (151 MHz, DMSO–d_6)



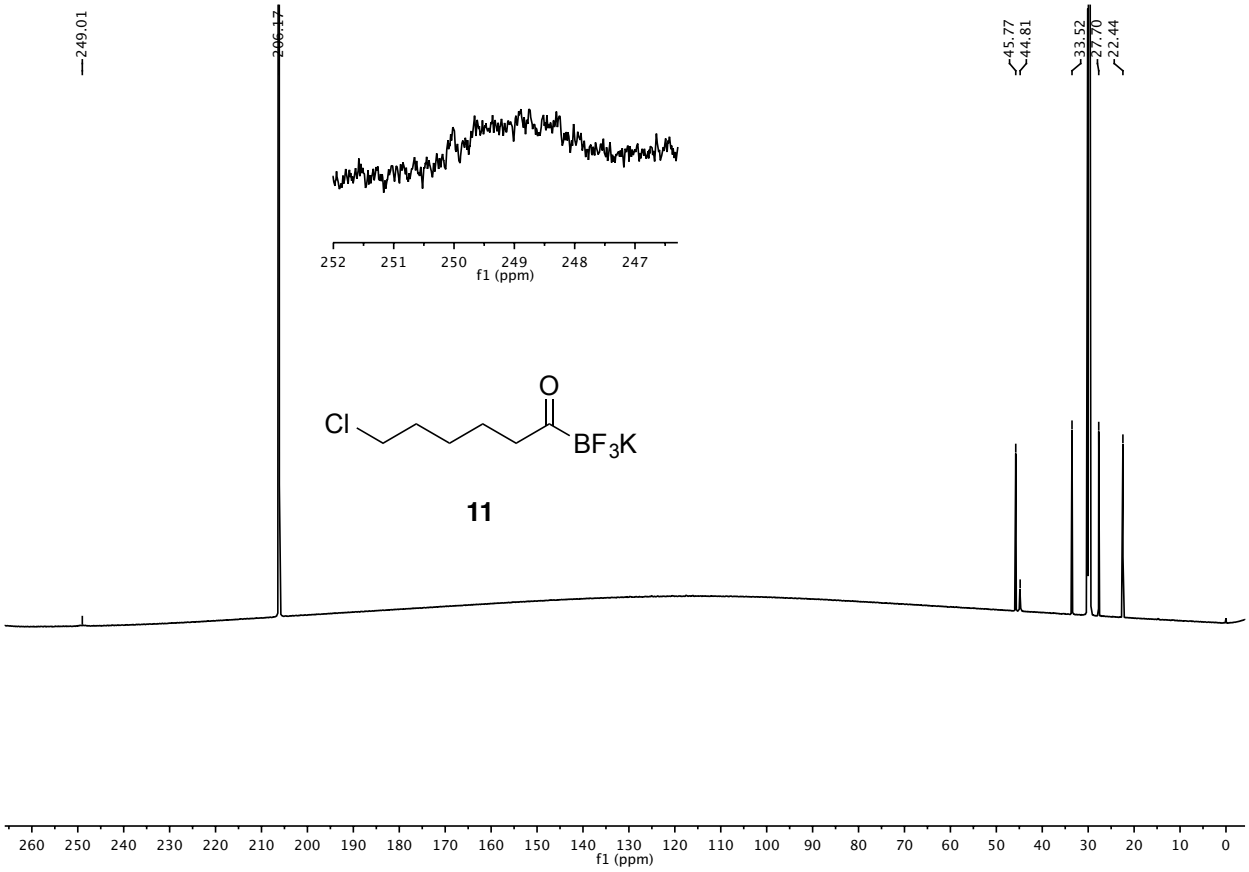
8: ^{11}B NMR (160 MHz, DMSO–d_6)



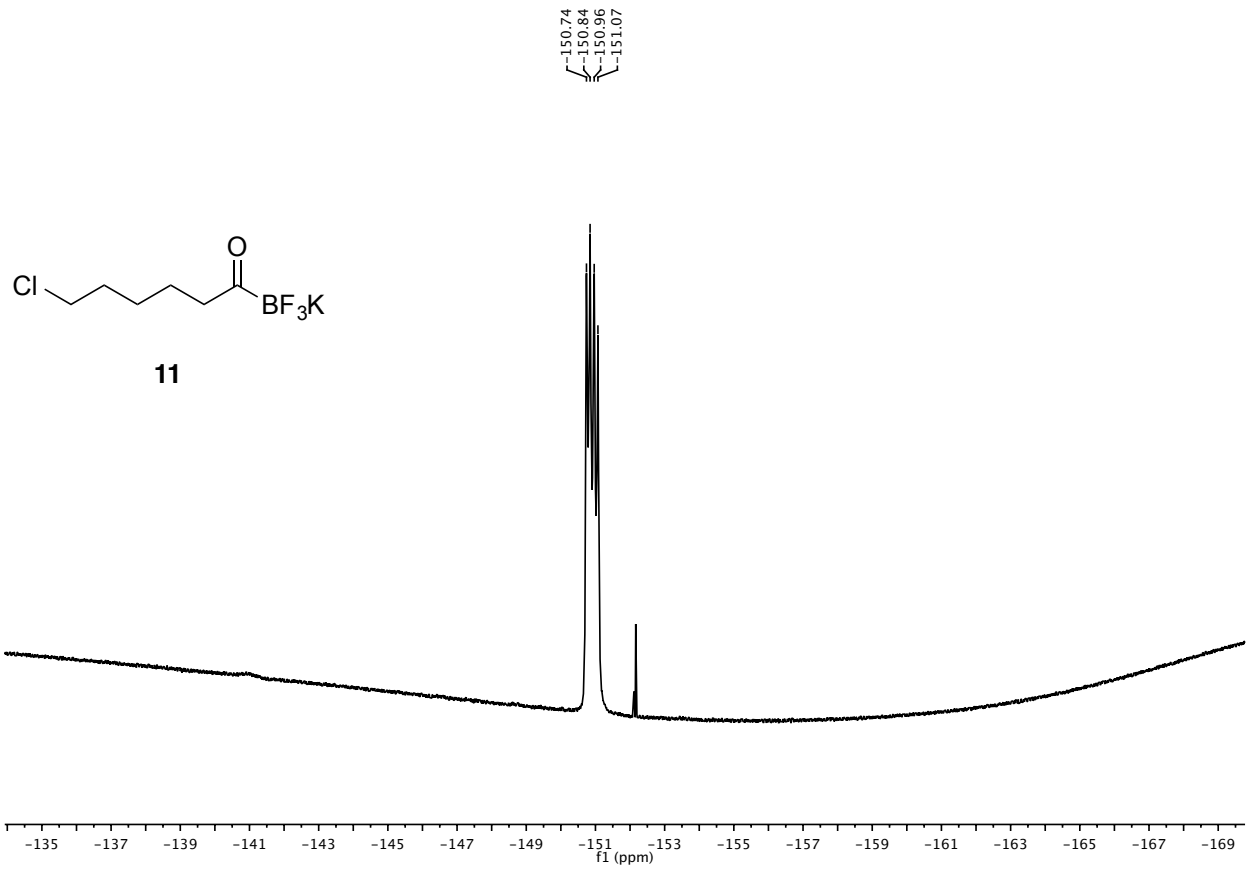
11: ^{1}H NMR (600 MHz, acetone–d_6)



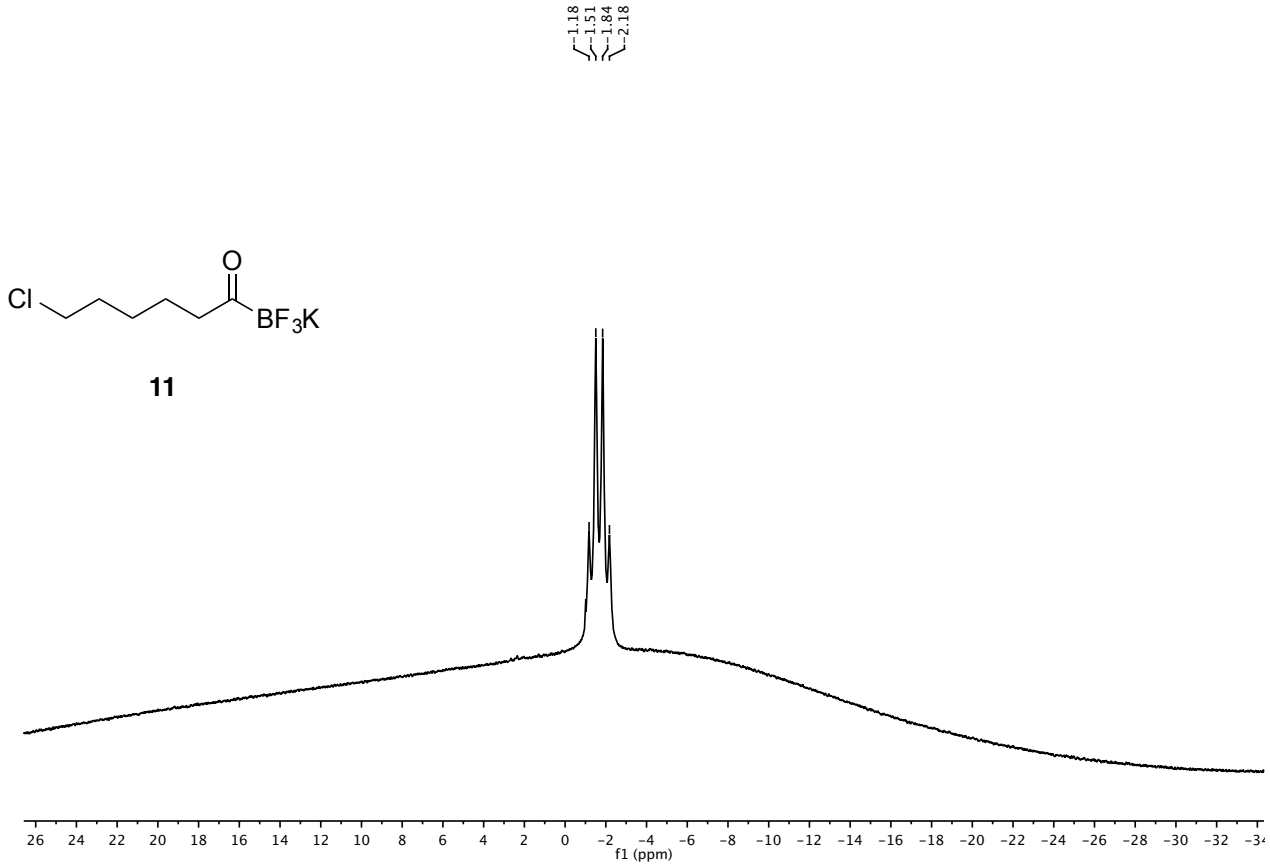
11: ^{12}C NMR (151 MHz, acetone–d_6)



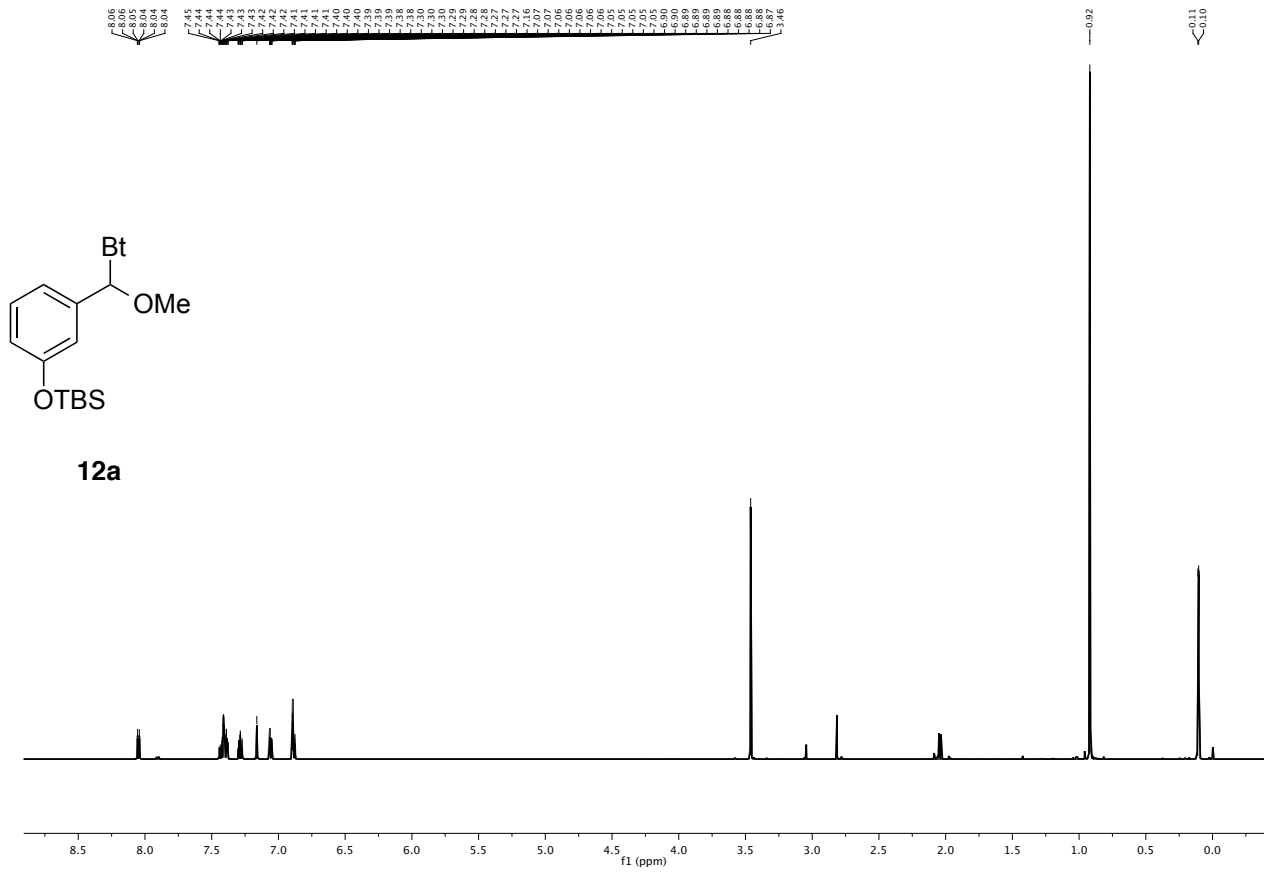
11: ^{19}F NMR (470 MHz, acetone–d_6)



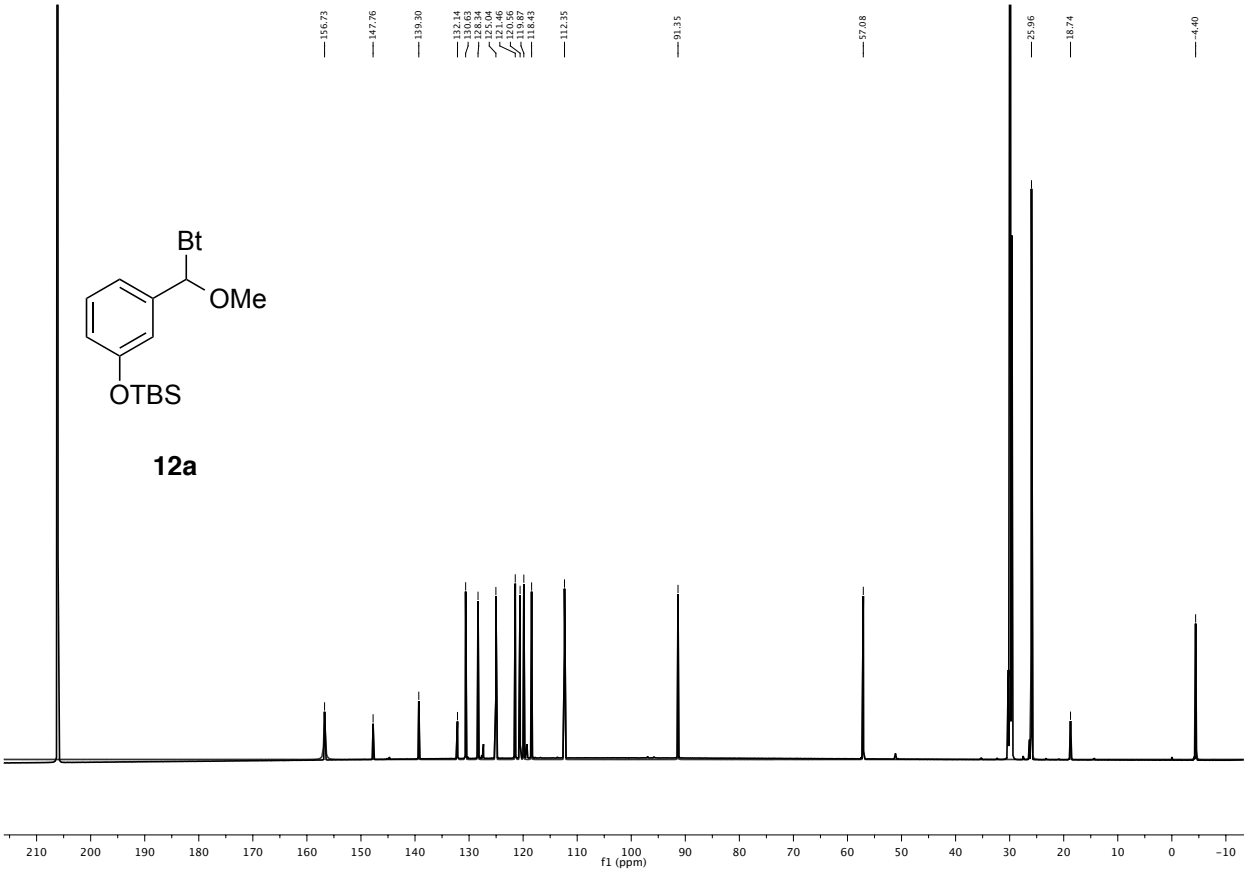
11: ^{11}B NMR (160 MHz, acetone–d_6)



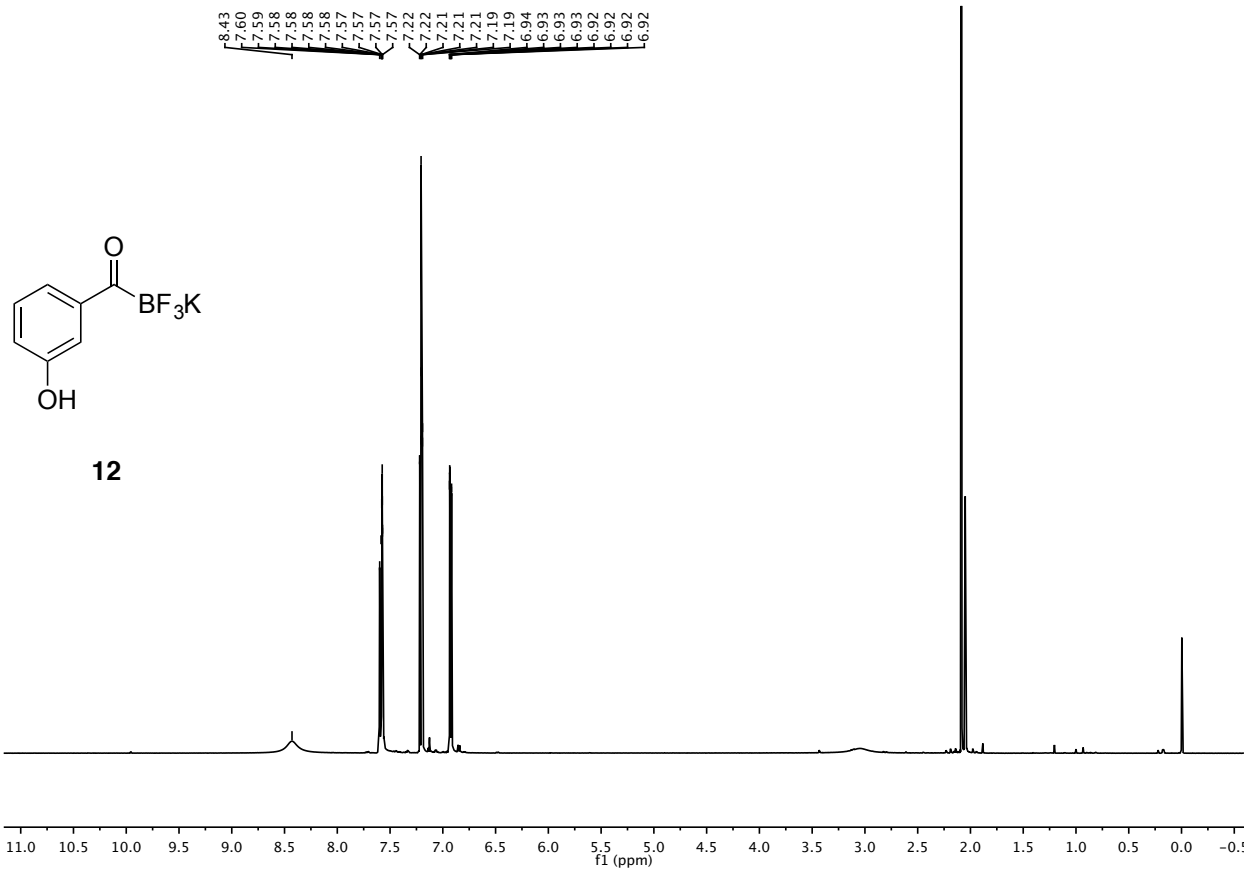
12a: ^{1}H NMR (600 MHz, acetone–d_6)



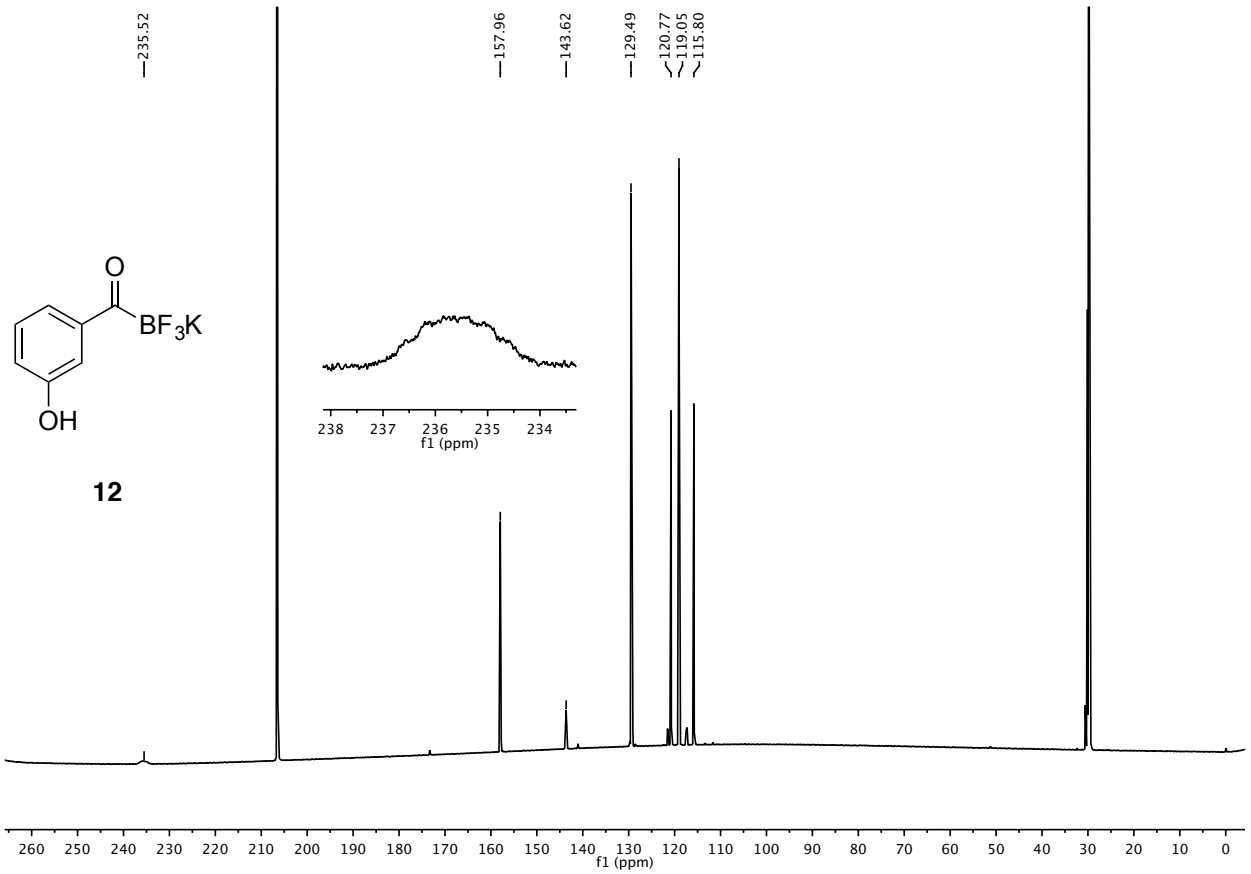
12a: ^{13}C NMR (151 MHz, acetone–d_6)



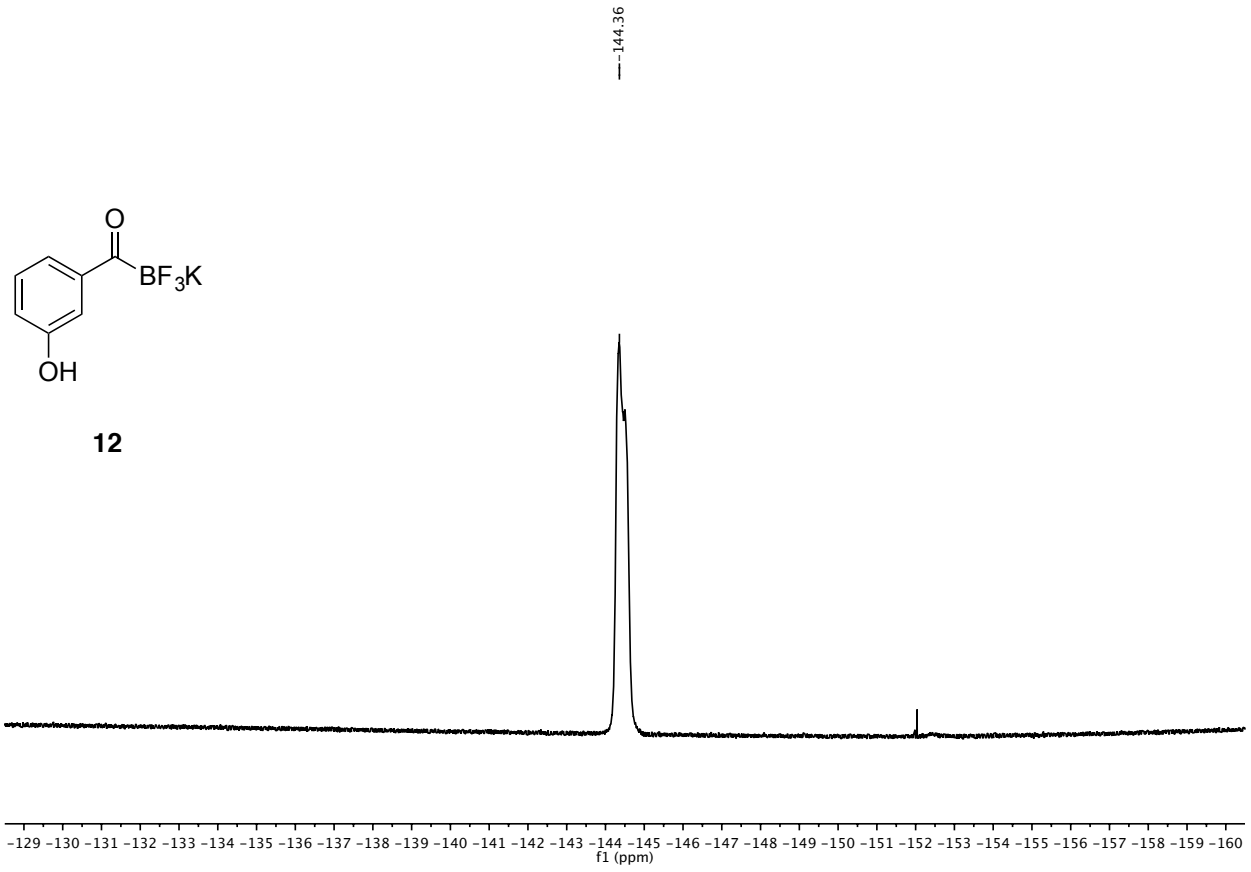
12: ^{1}H NMR (600 MHz, acetone–d_6)



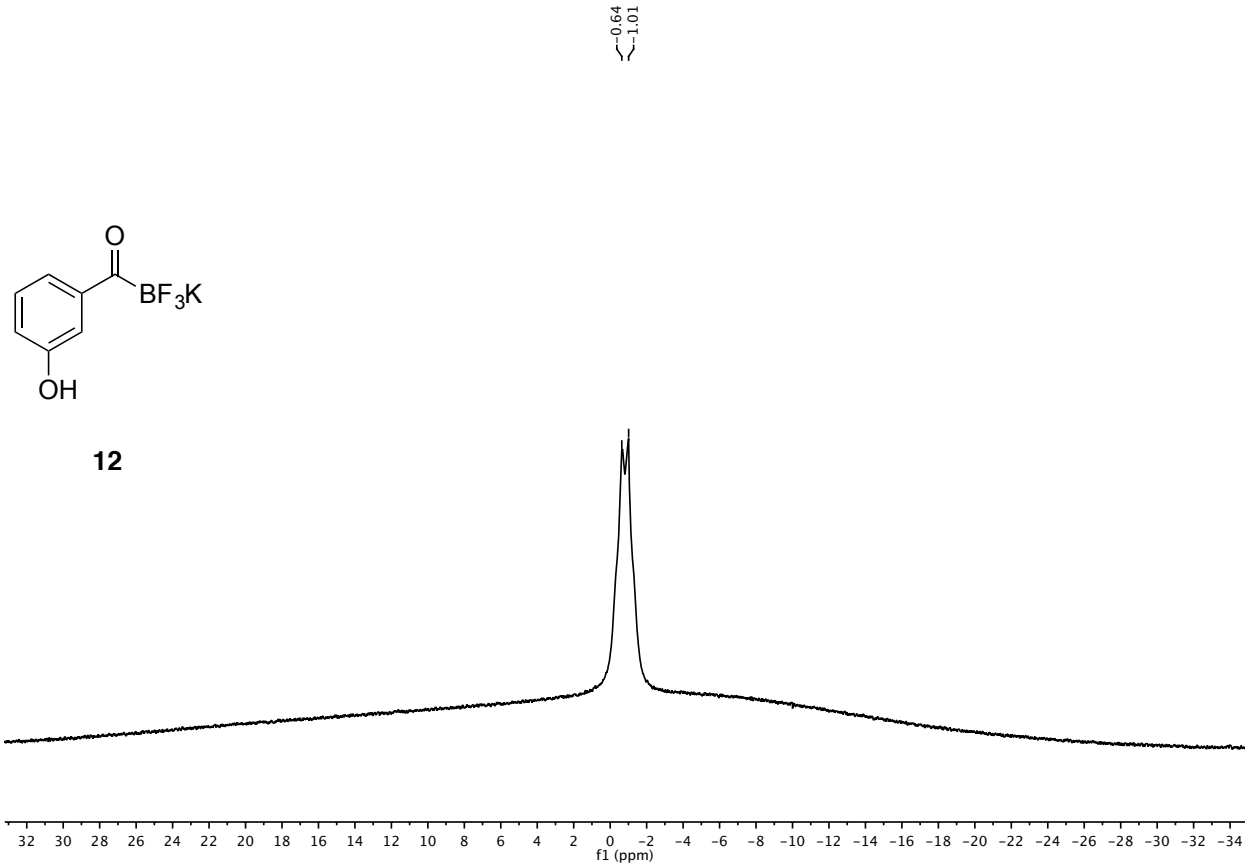
12: ^{13}C NMR (151 MHz, acetone–d_6)



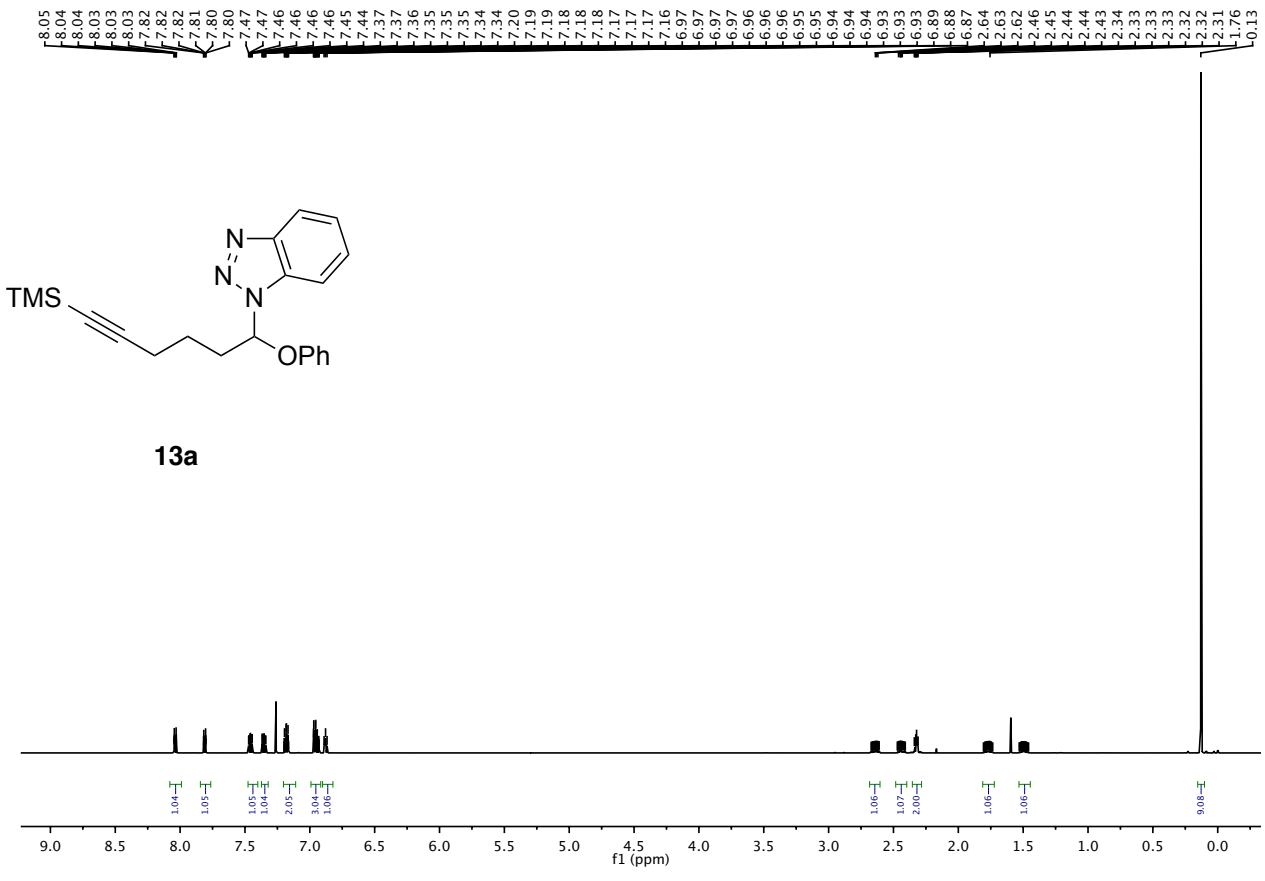
12: ^{19}F NMR (470 MHz, acetone–d_6)



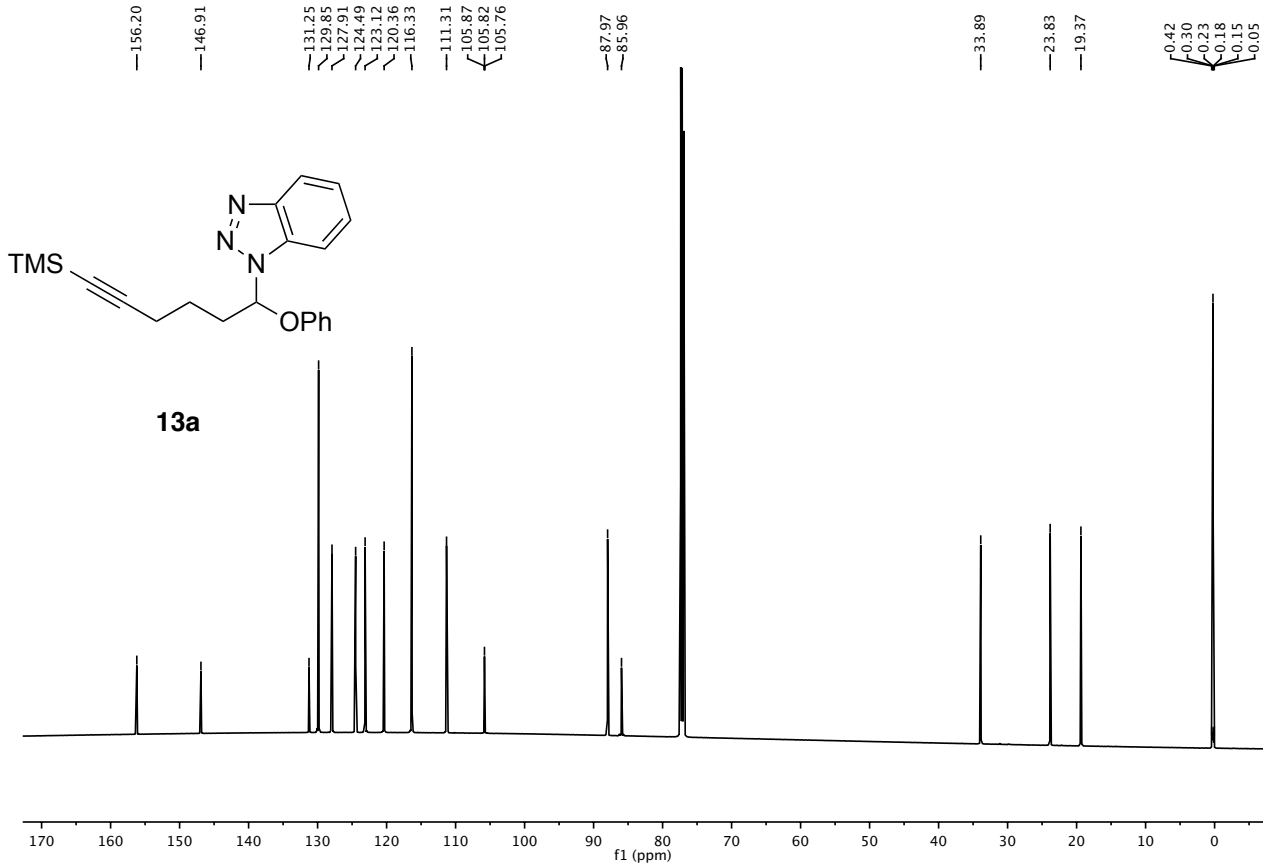
12: ^{11}B NMR (160 MHz, acetone–d_6)



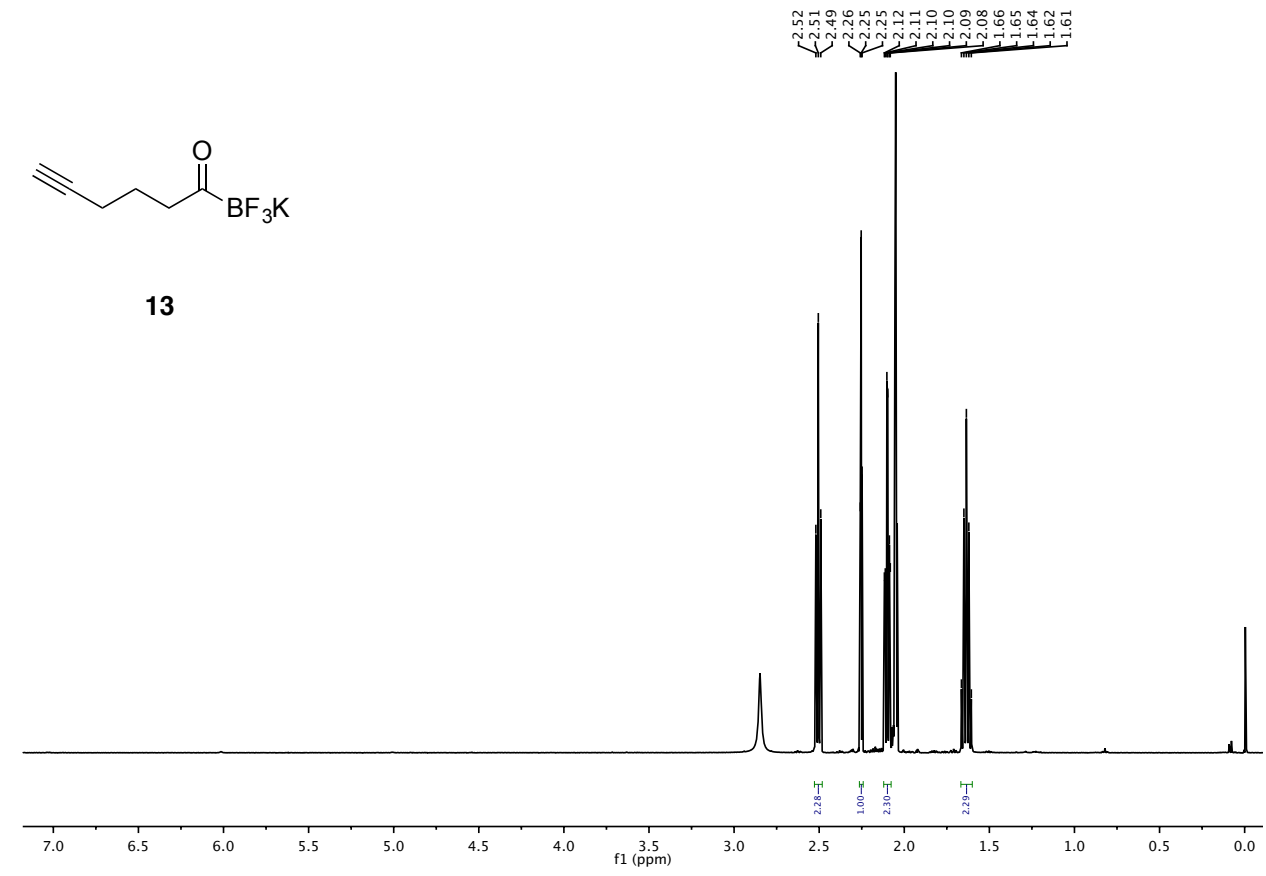
13a: ^{1}H NMR (600 MHz, $CDCl_3$)



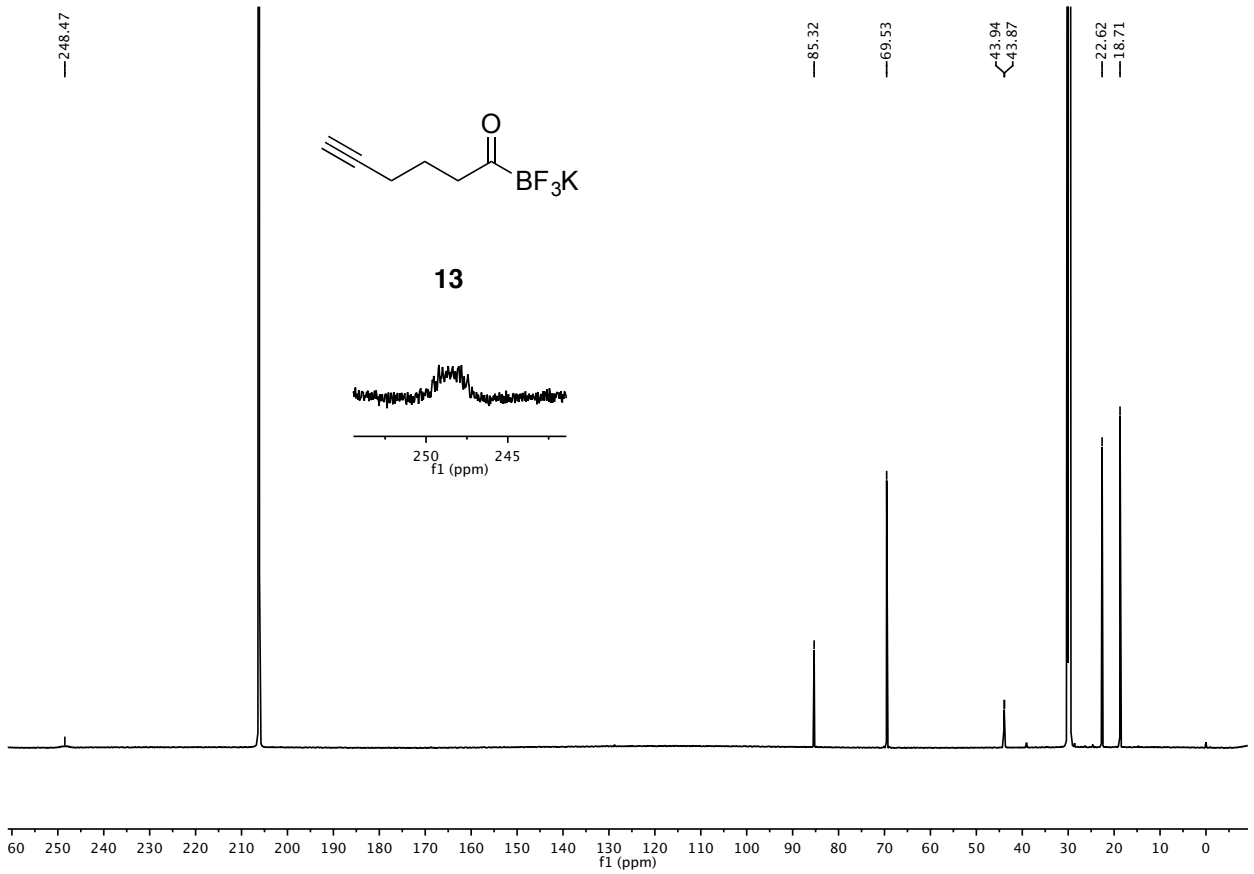
13a: ^{13}C NMR (151 MHz, $CDCl_3$)



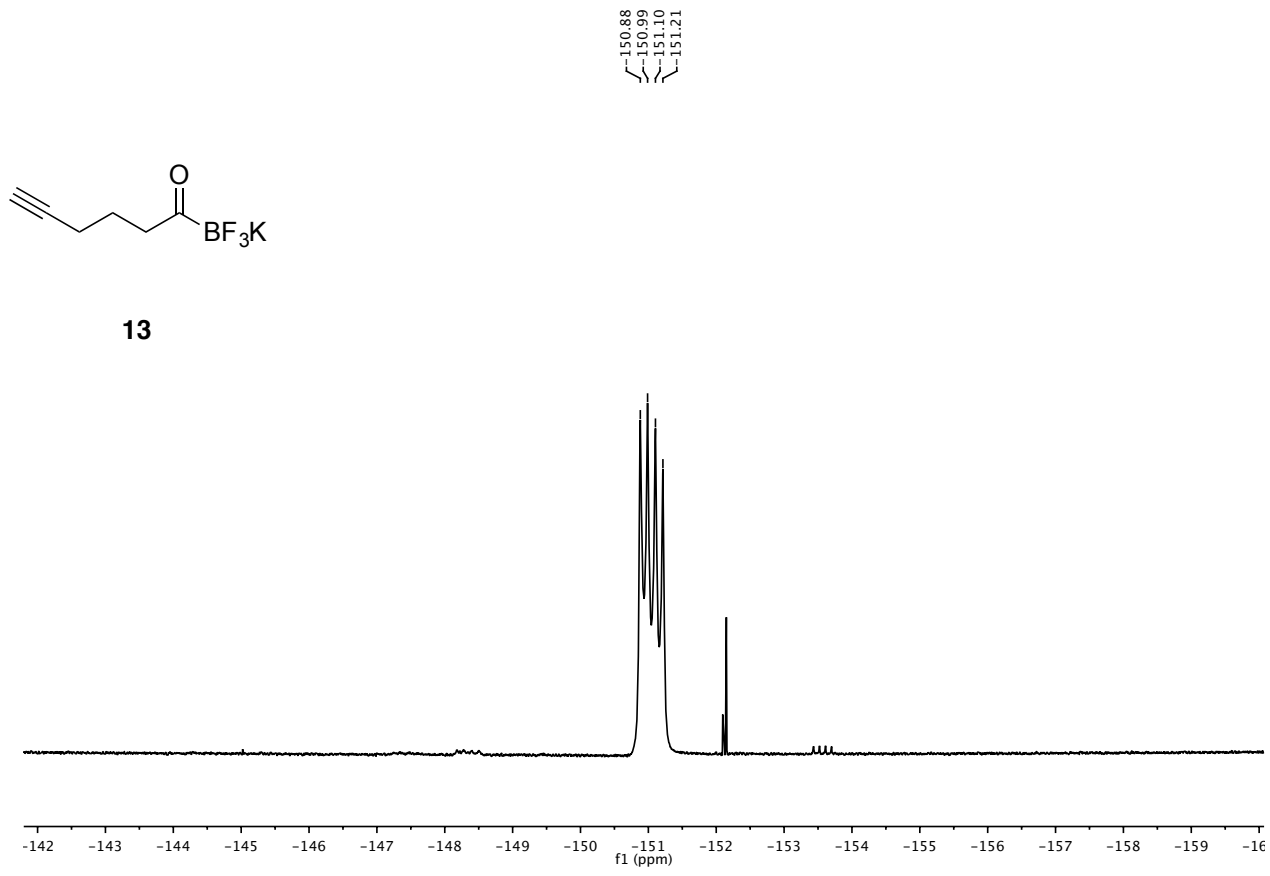
13: ^{1}H NMR (600 MHz, acetone-d_6)



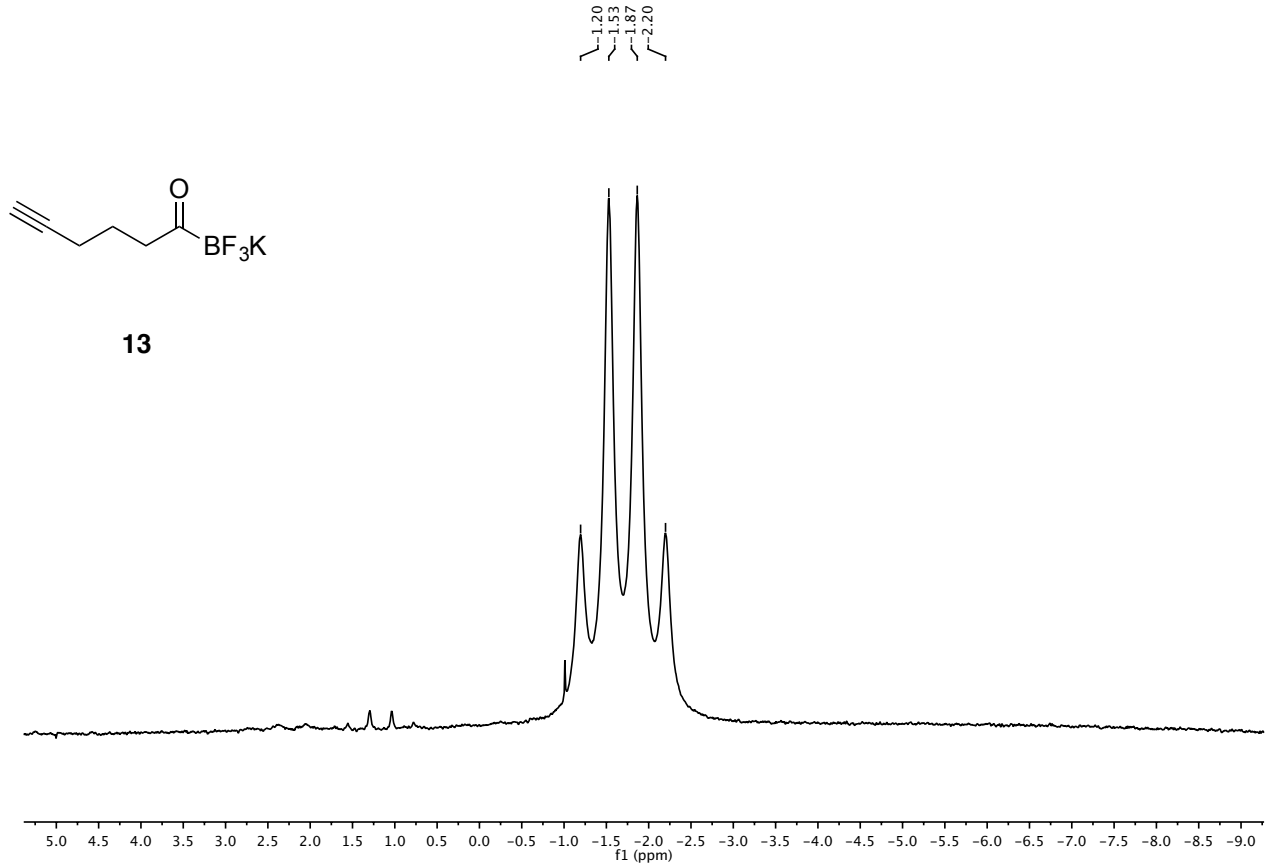
13: ^{12}C NMR (151 MHz, acetone–d_6)



13: ^{19}F NMR (470 MHz, acetone–d_6)

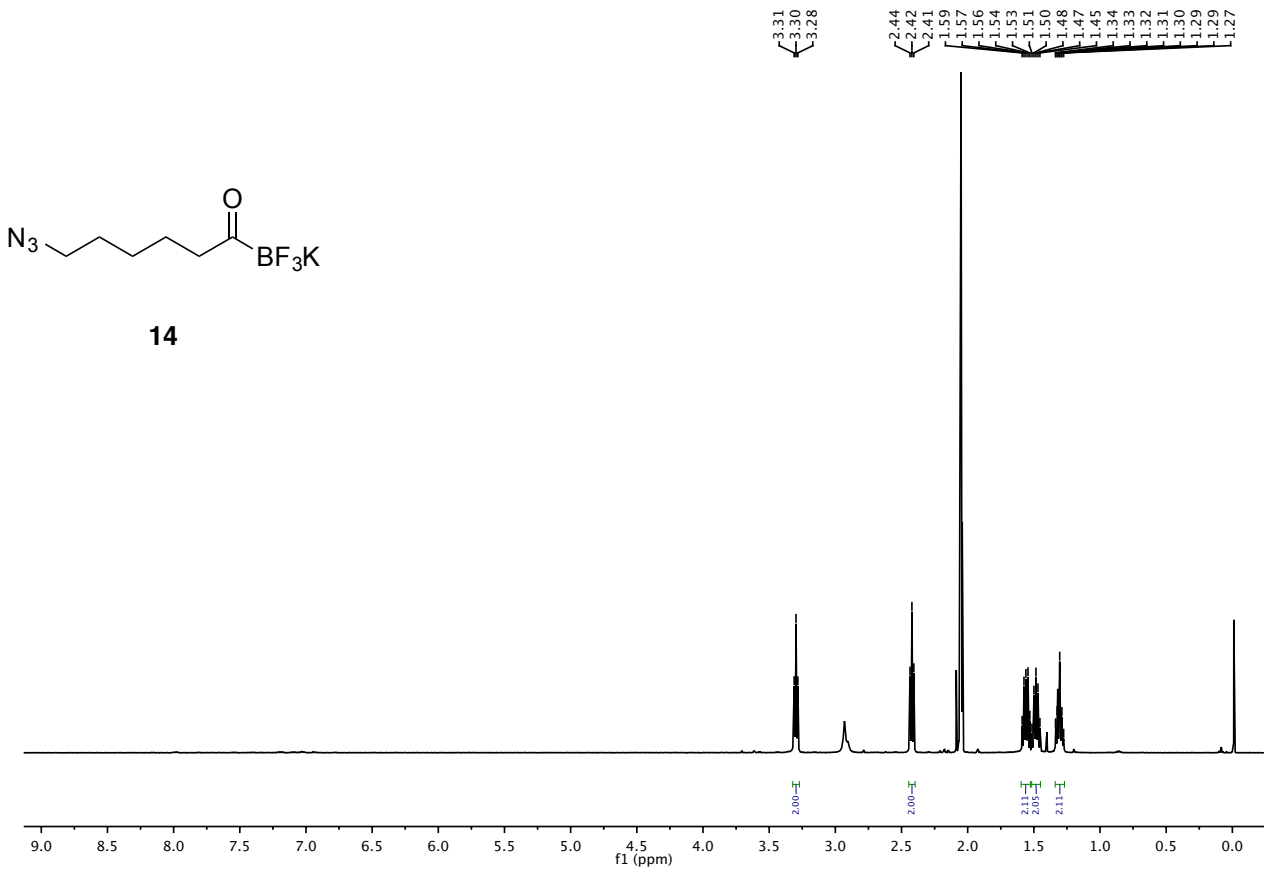


13: ^{11}B NMR (160 MHz, acetone–d_6)



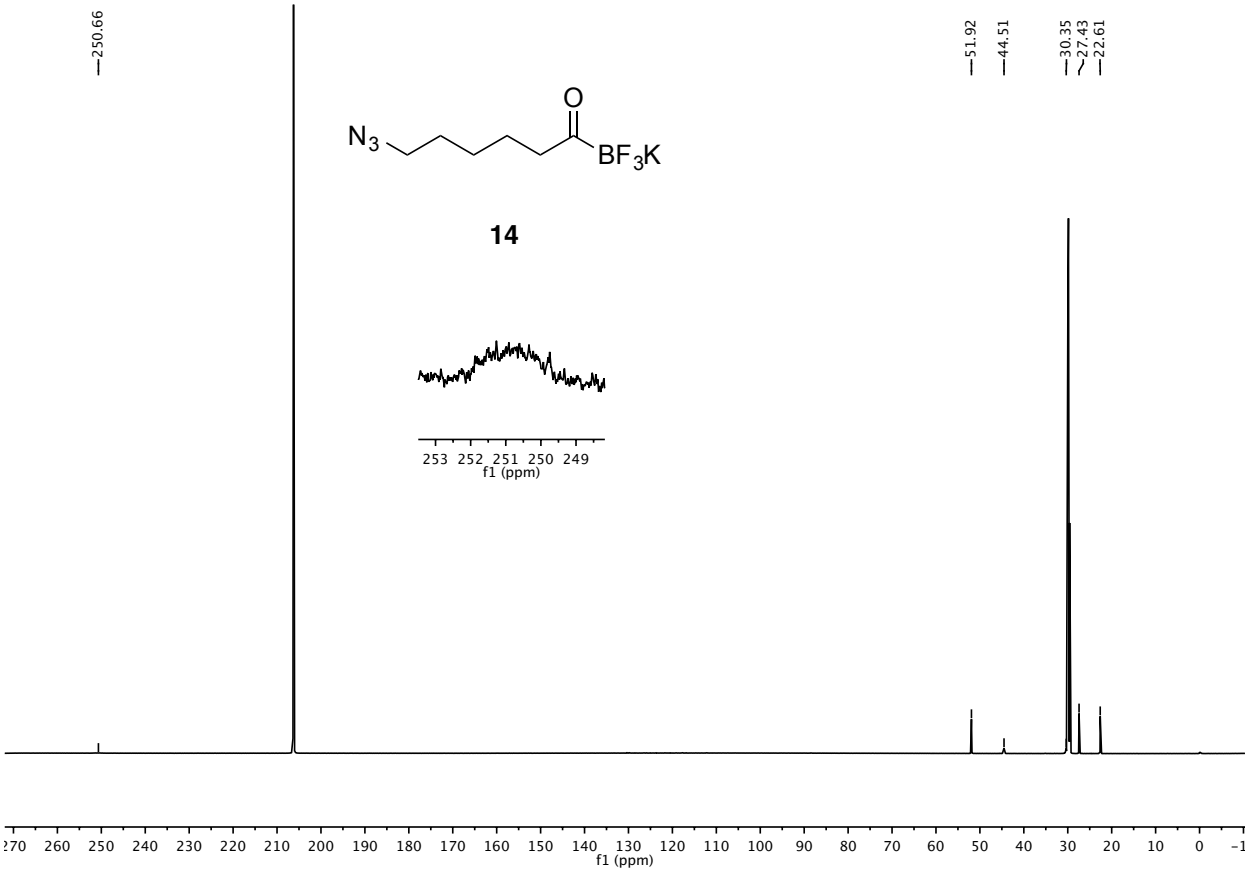
13

14: ^{1}H NMR (600 MHz, acetone–d_6)

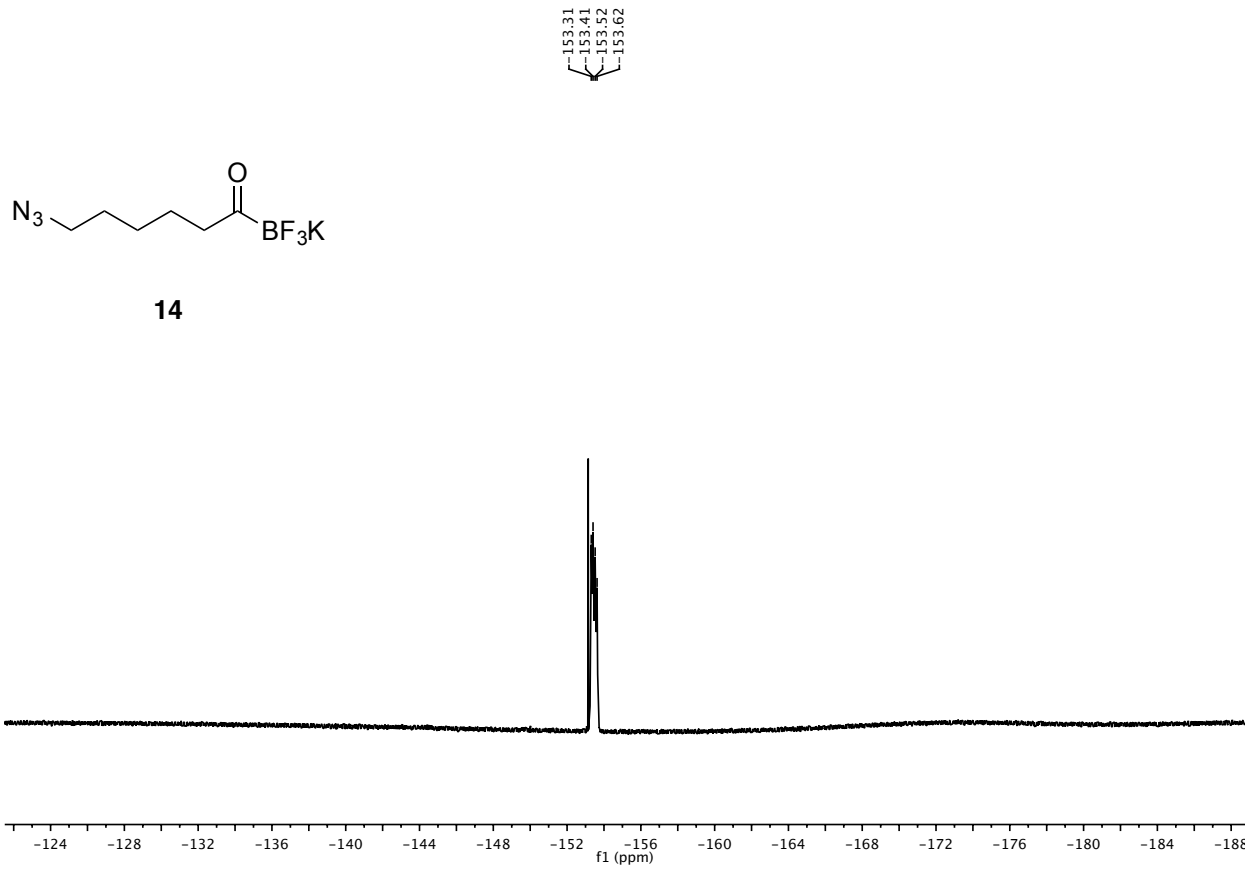


14

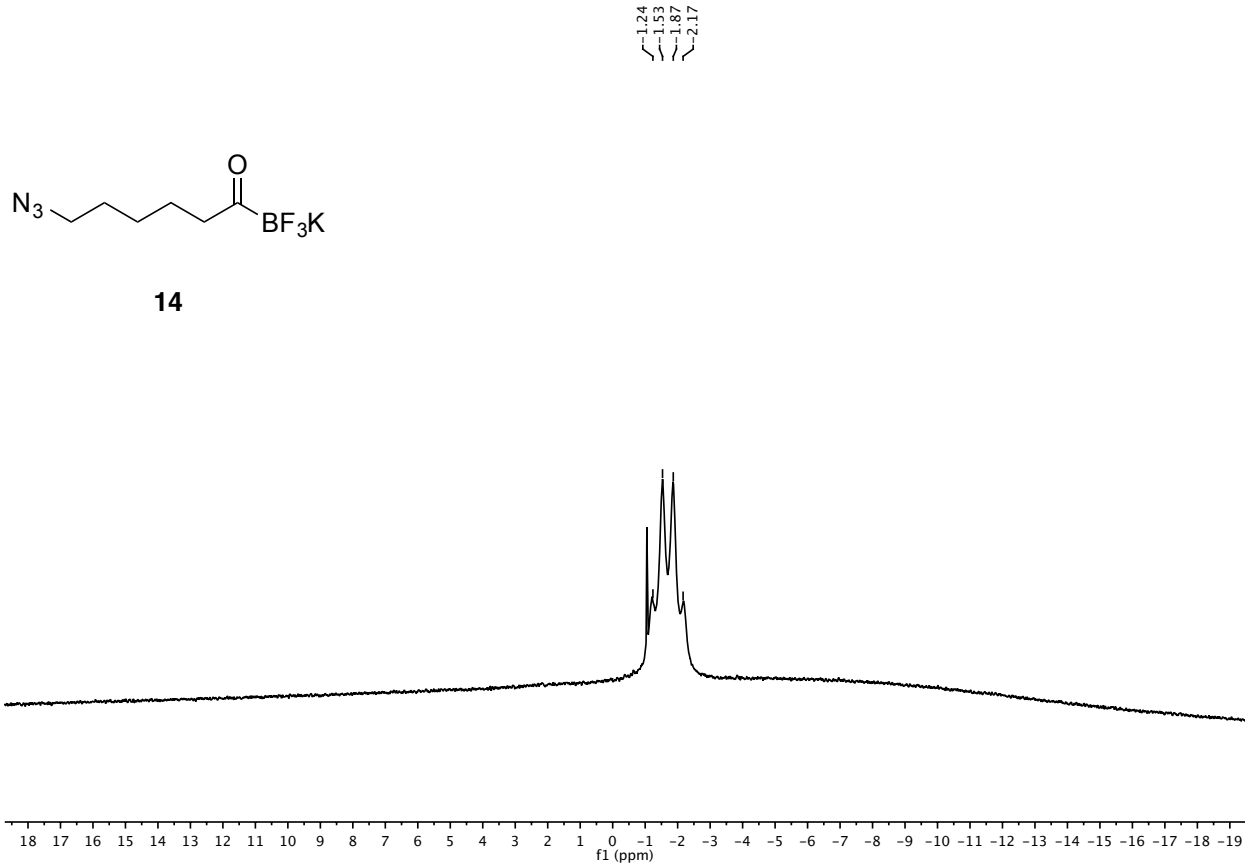
14: ^{13}C NMR (151 MHz, acetone–d_6)



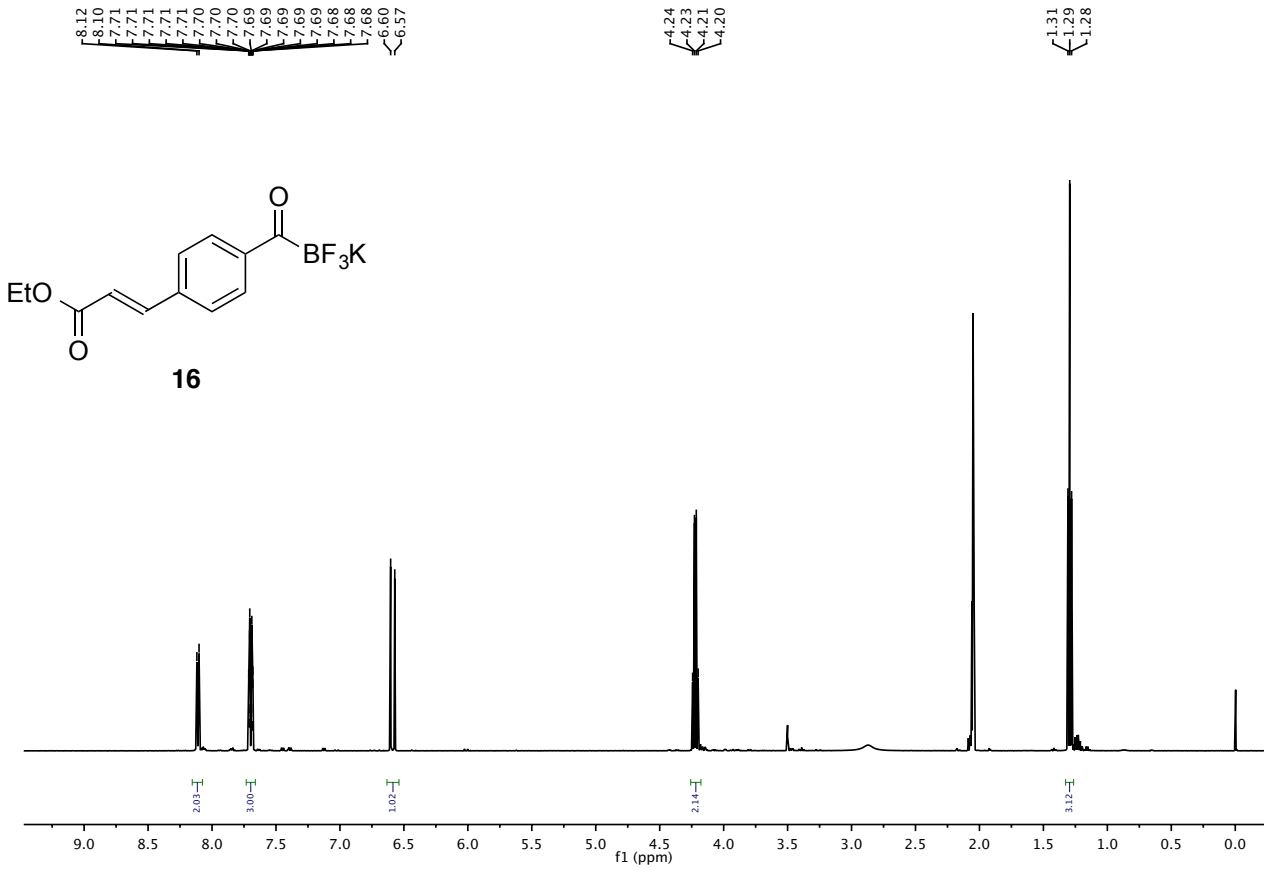
14: ^{19}F NMR (470 MHz, acetone–d_6)



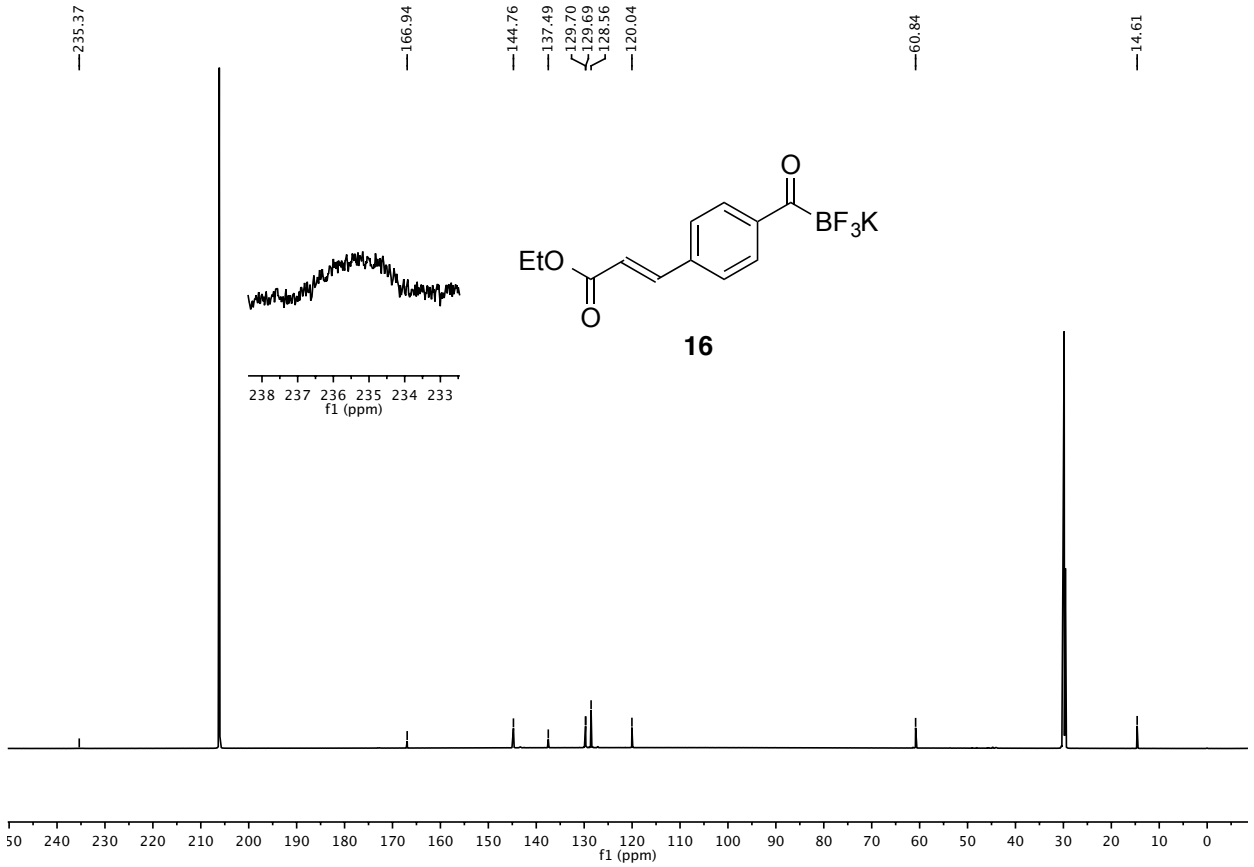
14: ^{11}B NMR (160 MHz, acetone–d_6)



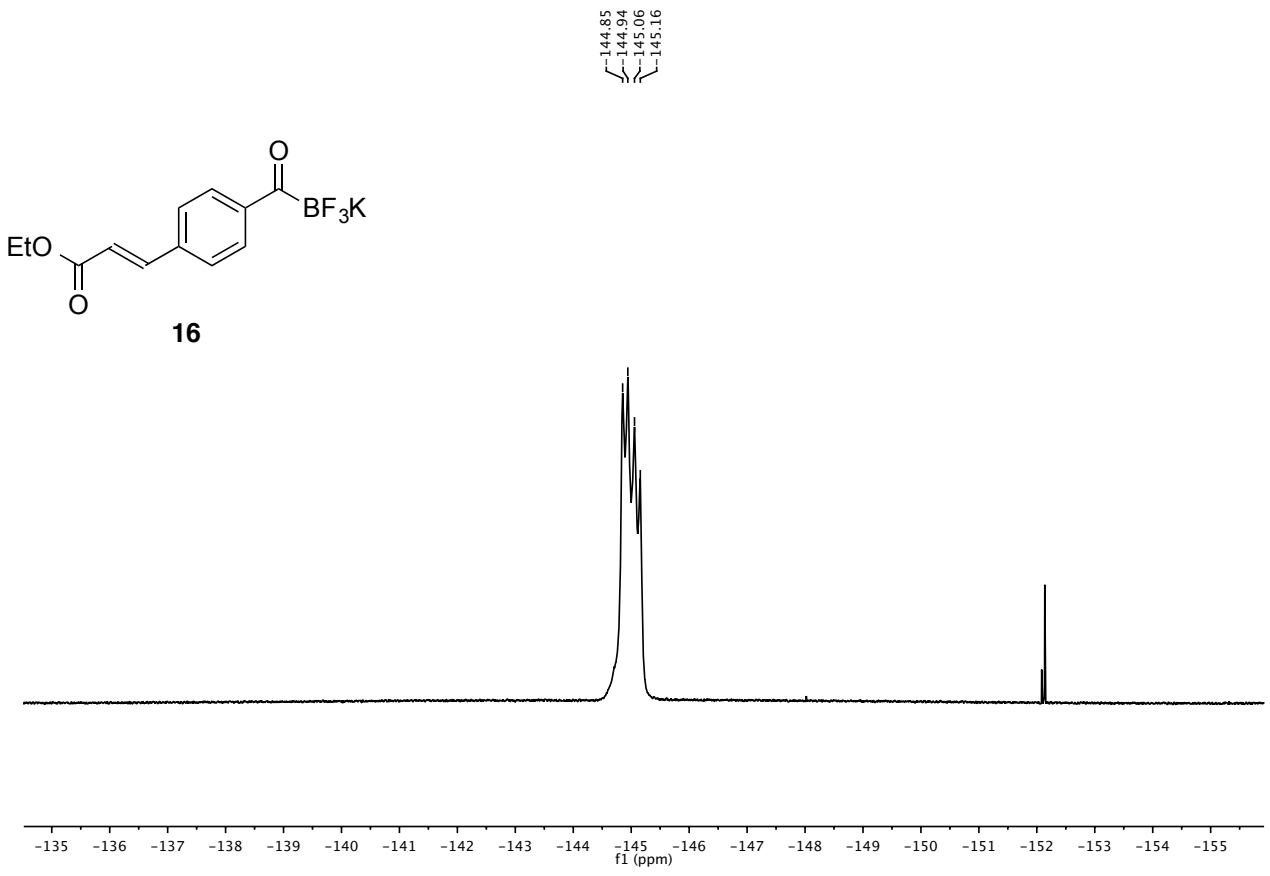
16: ^{1}H NMR (600 MHz, acetone–d_6)



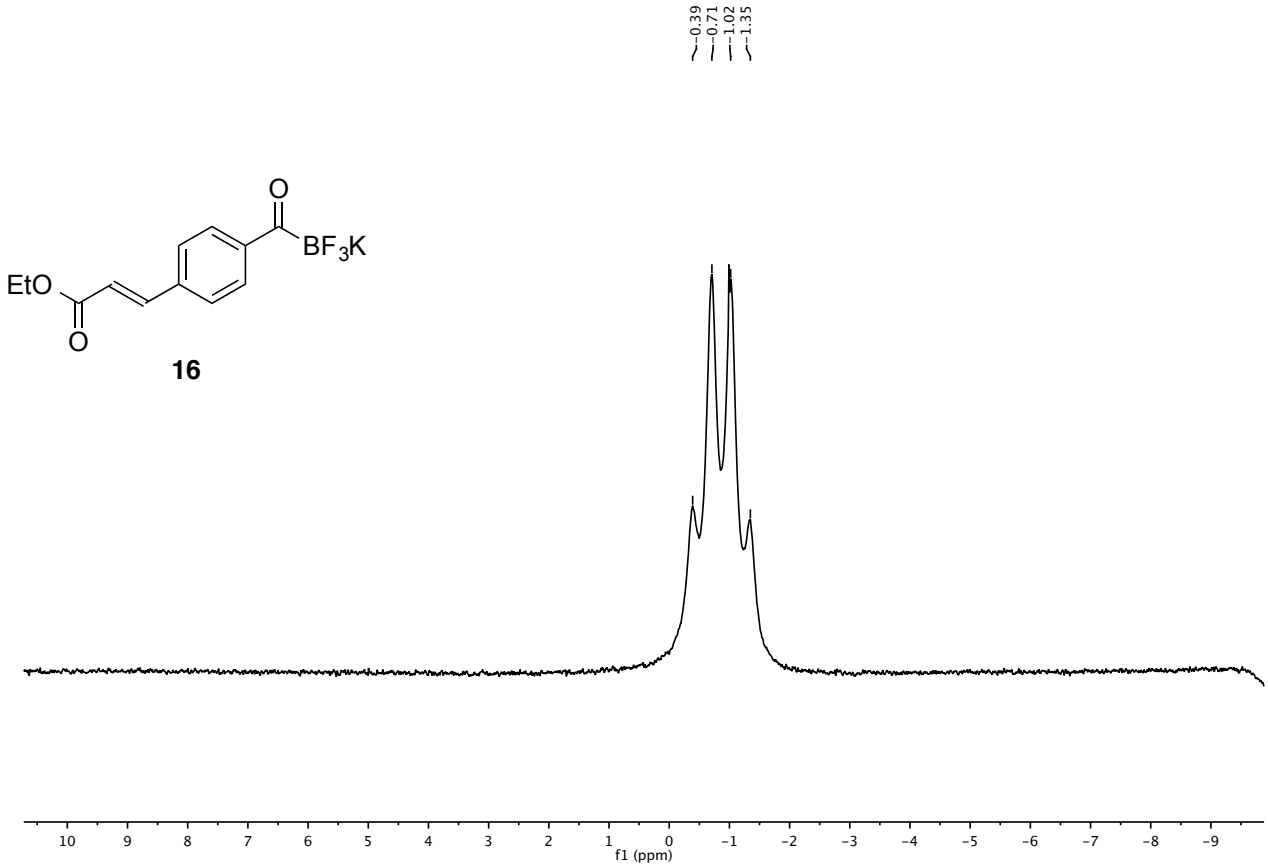
16: ^{13}C NMR (151 MHz, acetone–d_6)



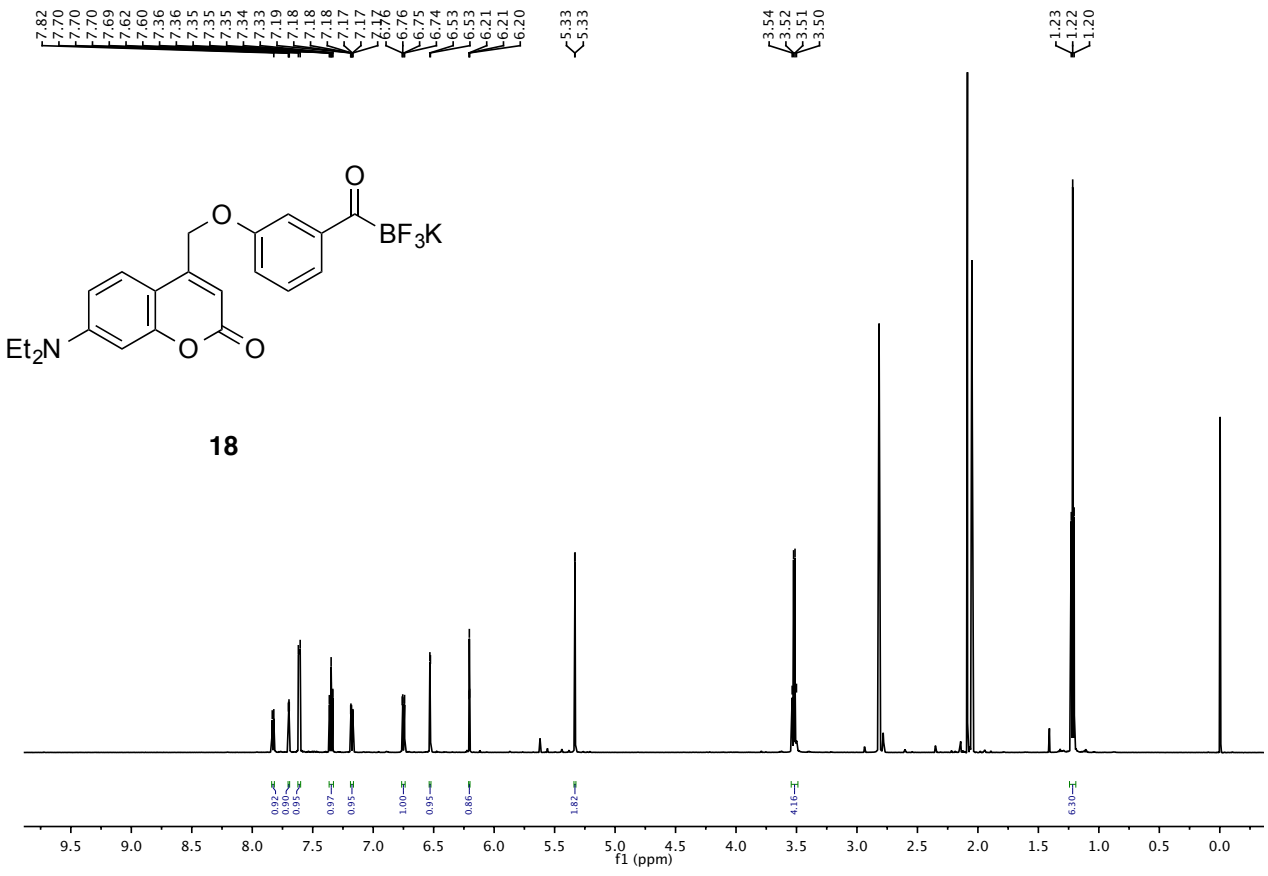
16: ^{19}F NMR (470 MHz, acetone–d_6)



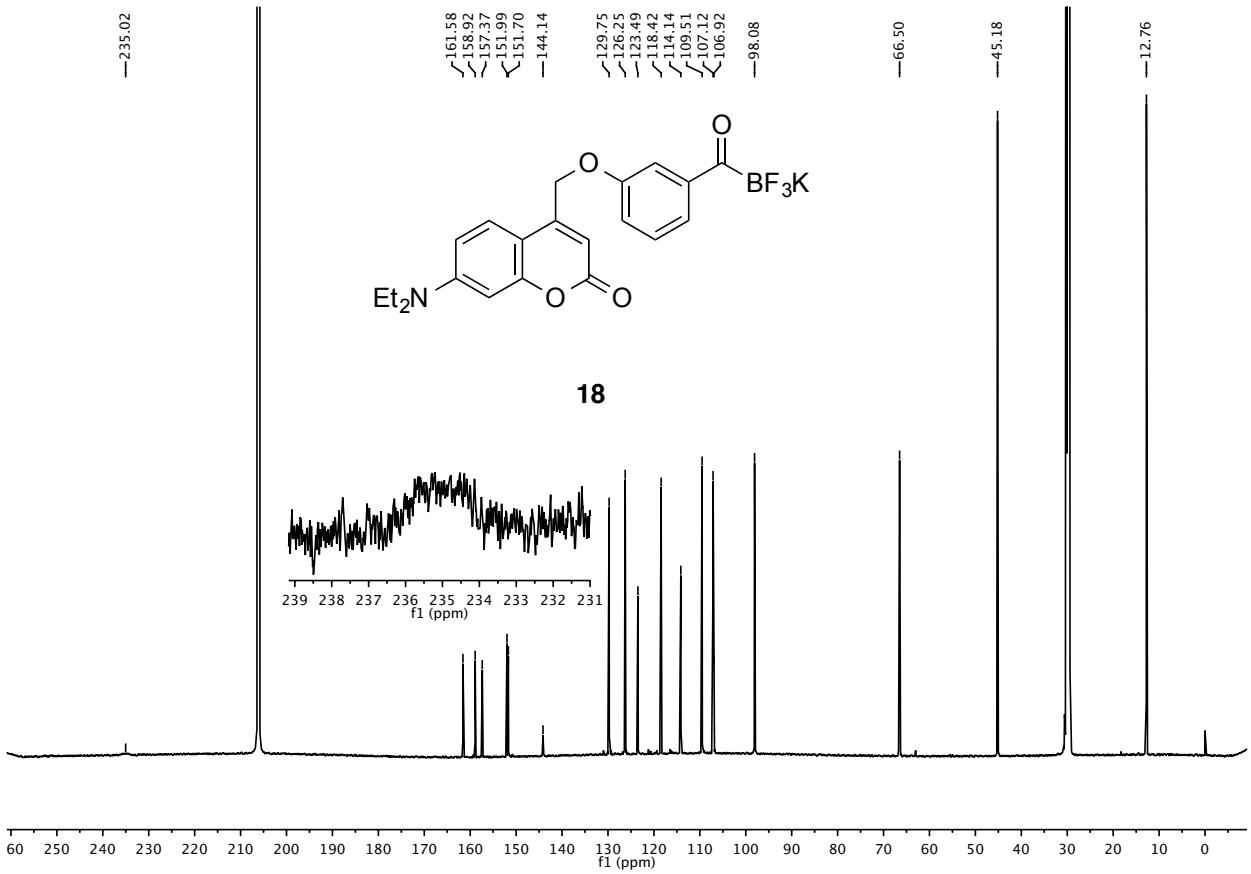
16: ^{11}B NMR (160 MHz, acetone–d_6)



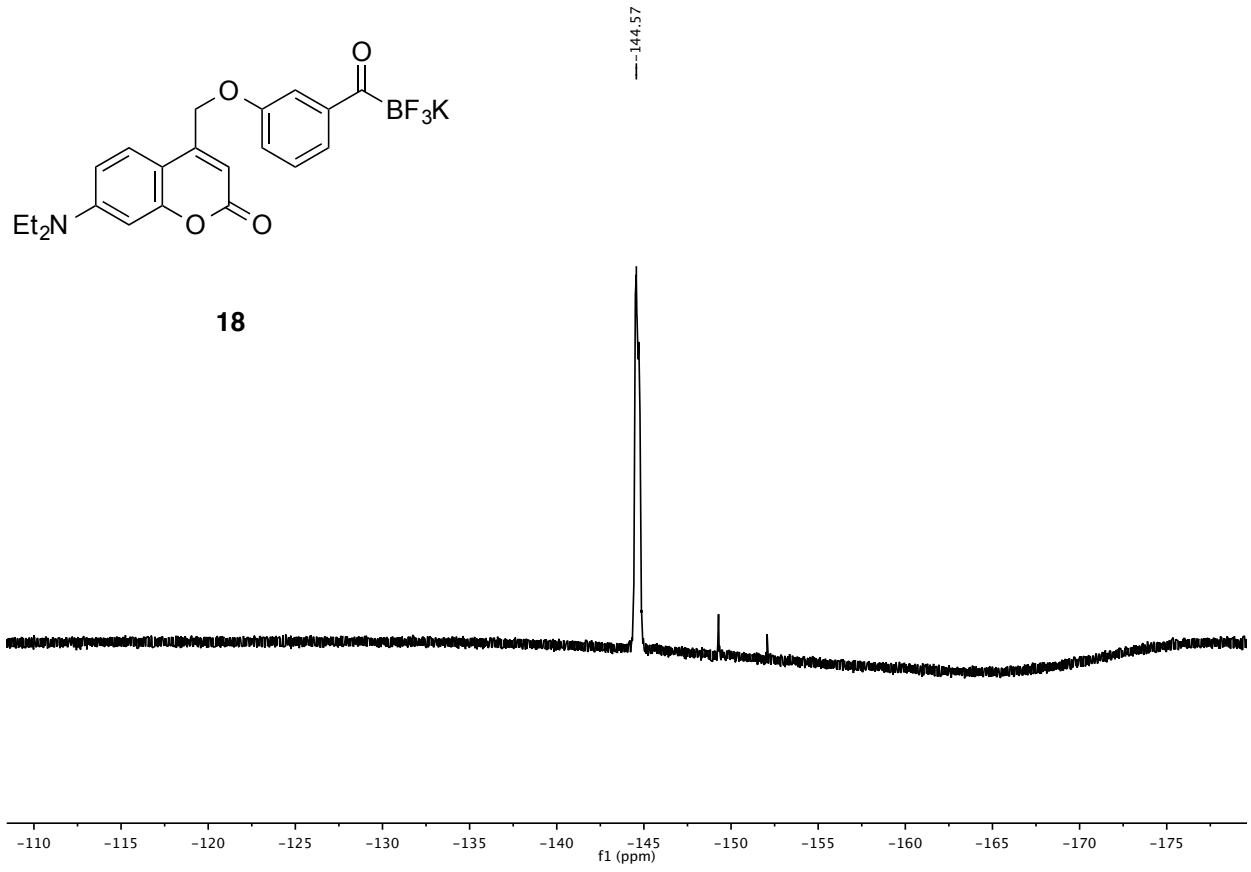
18: ^{1}H NMR (600 MHz, acetone–d_6)



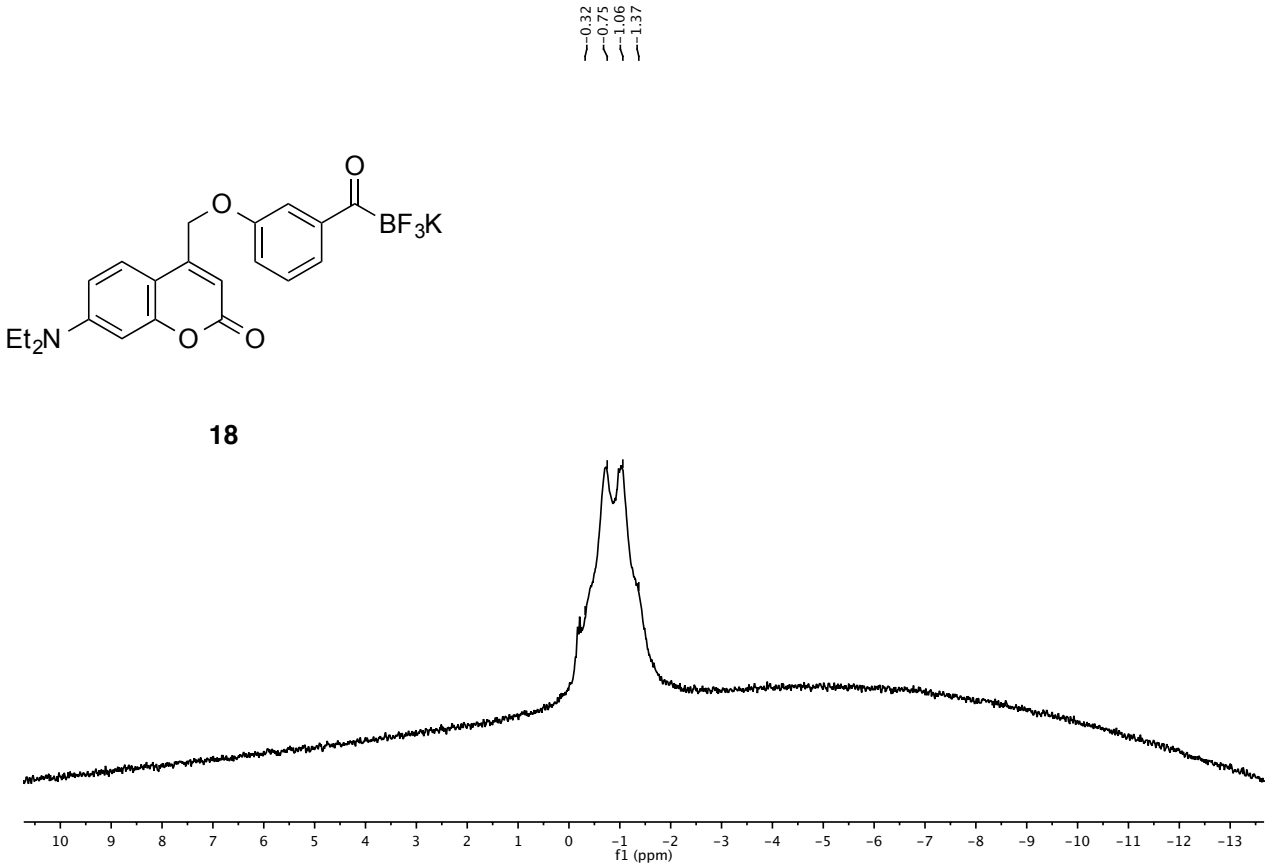
18: ^{13}C NMR (151 MHz, acetone–d_6)



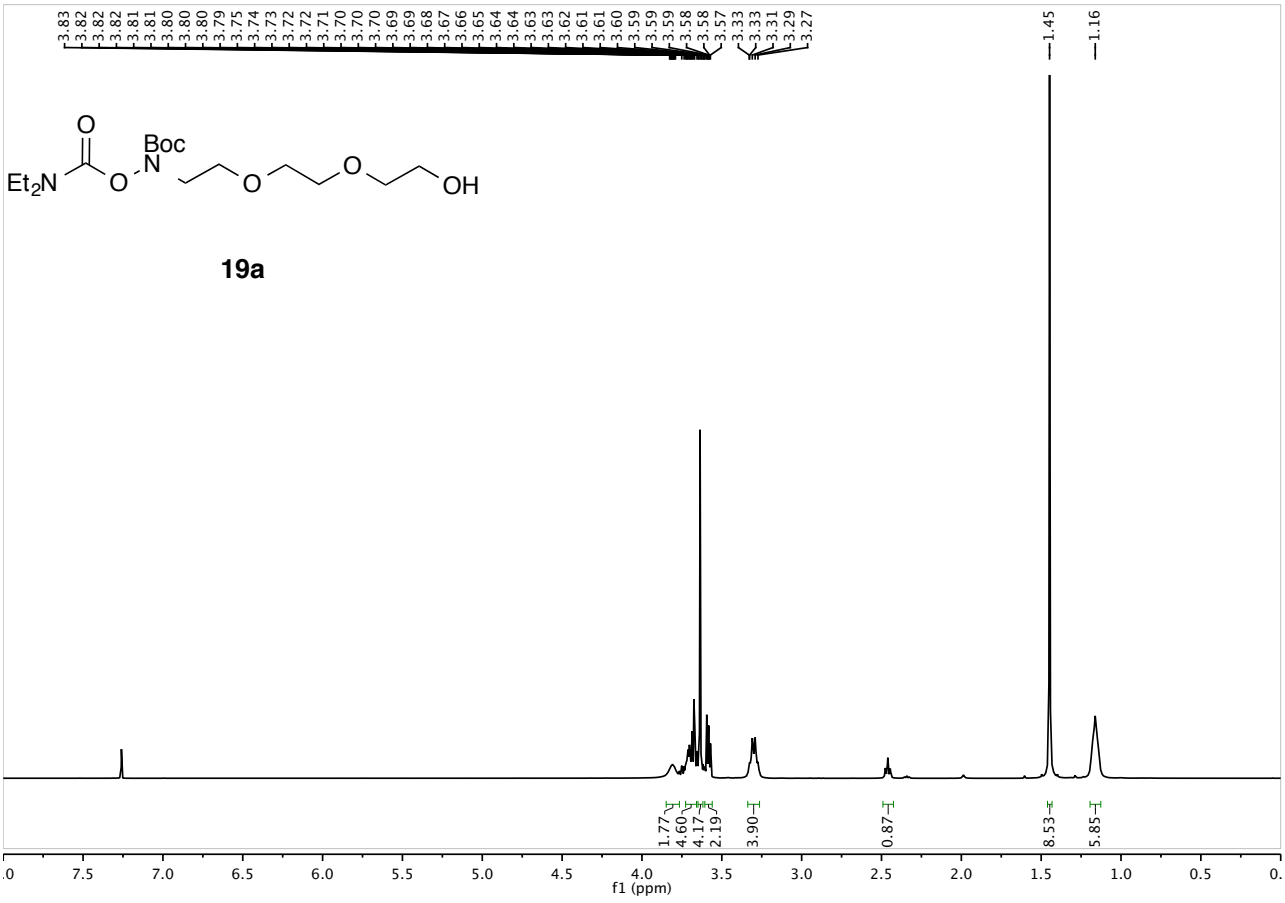
18: ^{19}F NMR (470 MHz, acetone–d_6)



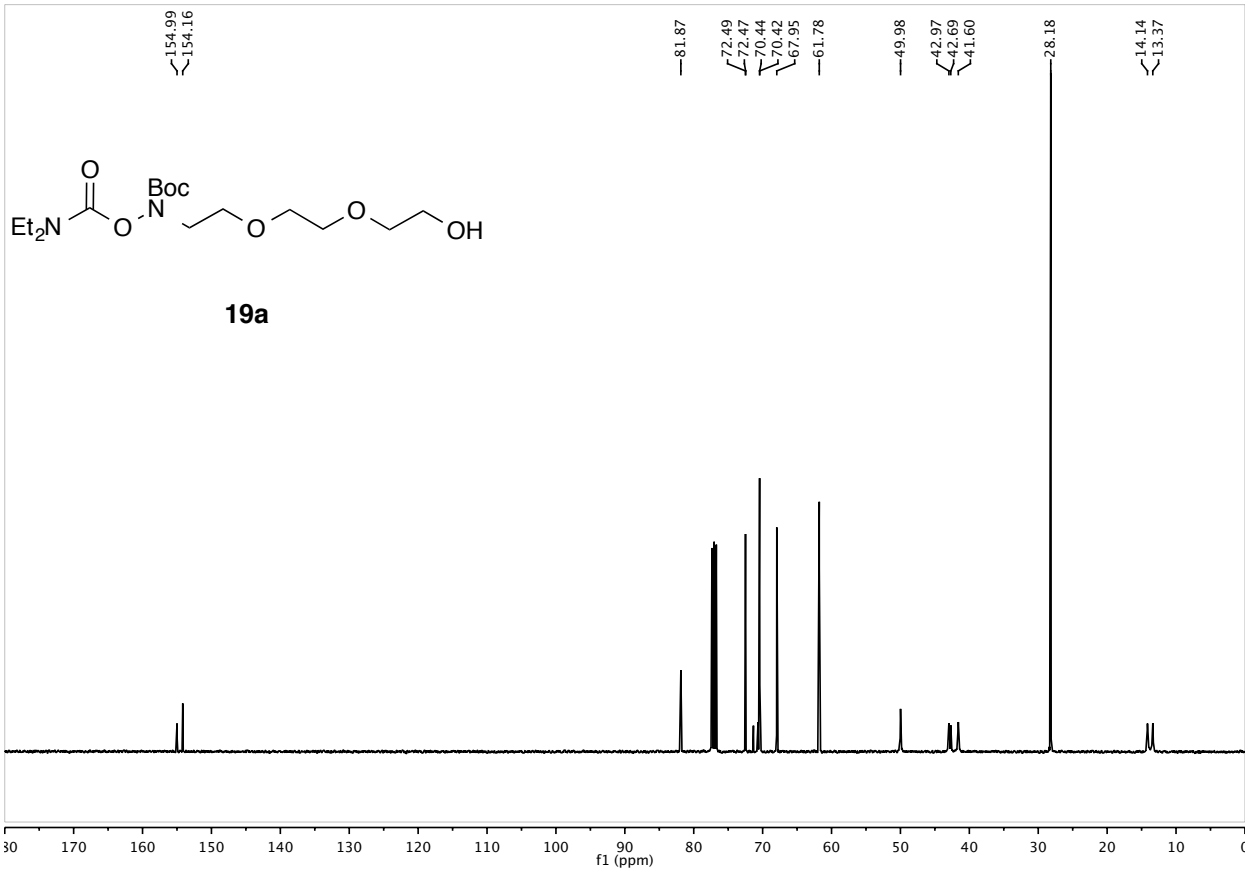
18: ^{11}F NMR (160 MHz, acetone–d_6)



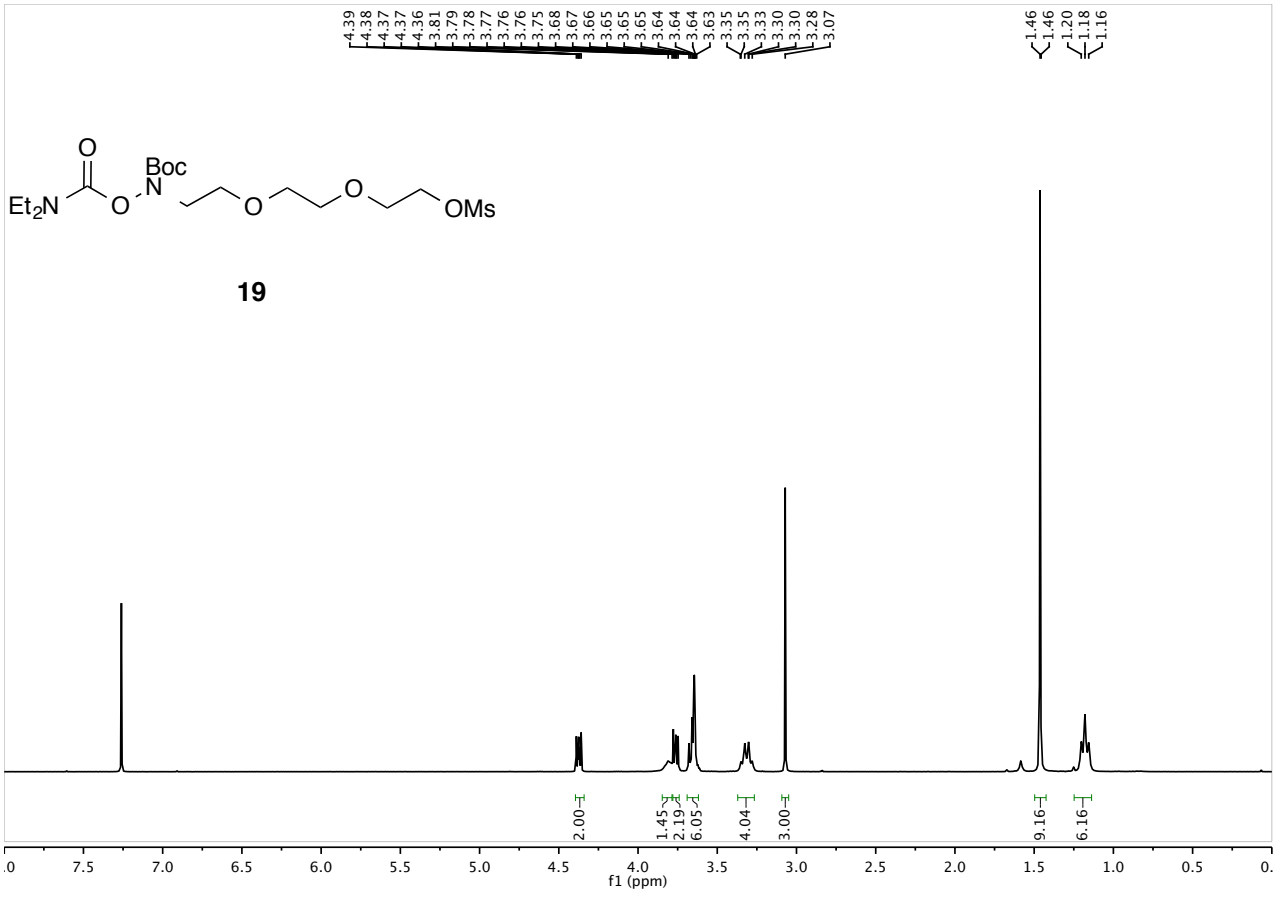
19a: ^{1}H NMR (400 MHz, $CDCL_3$)



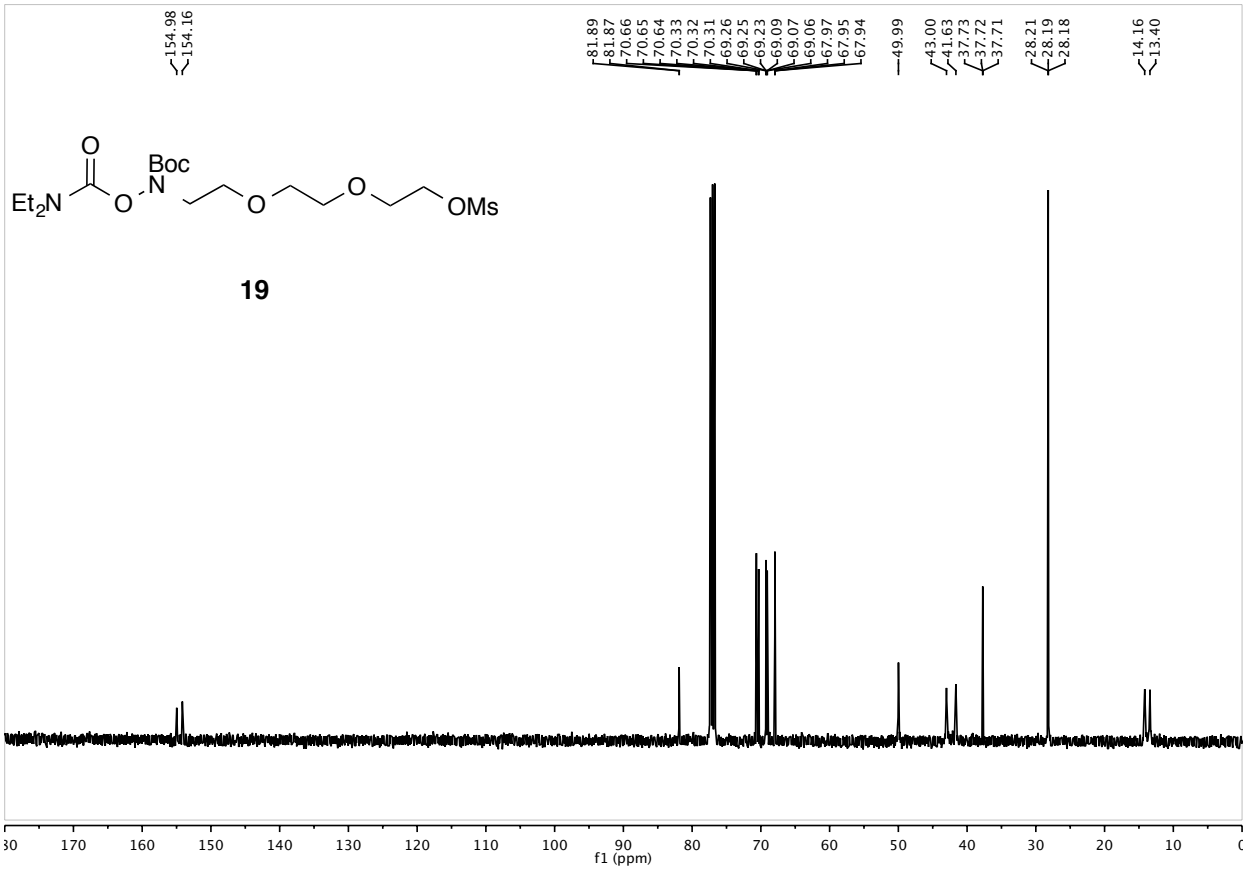
19a: ^{13}C NMR (101 MHz, $CDCl_3$)



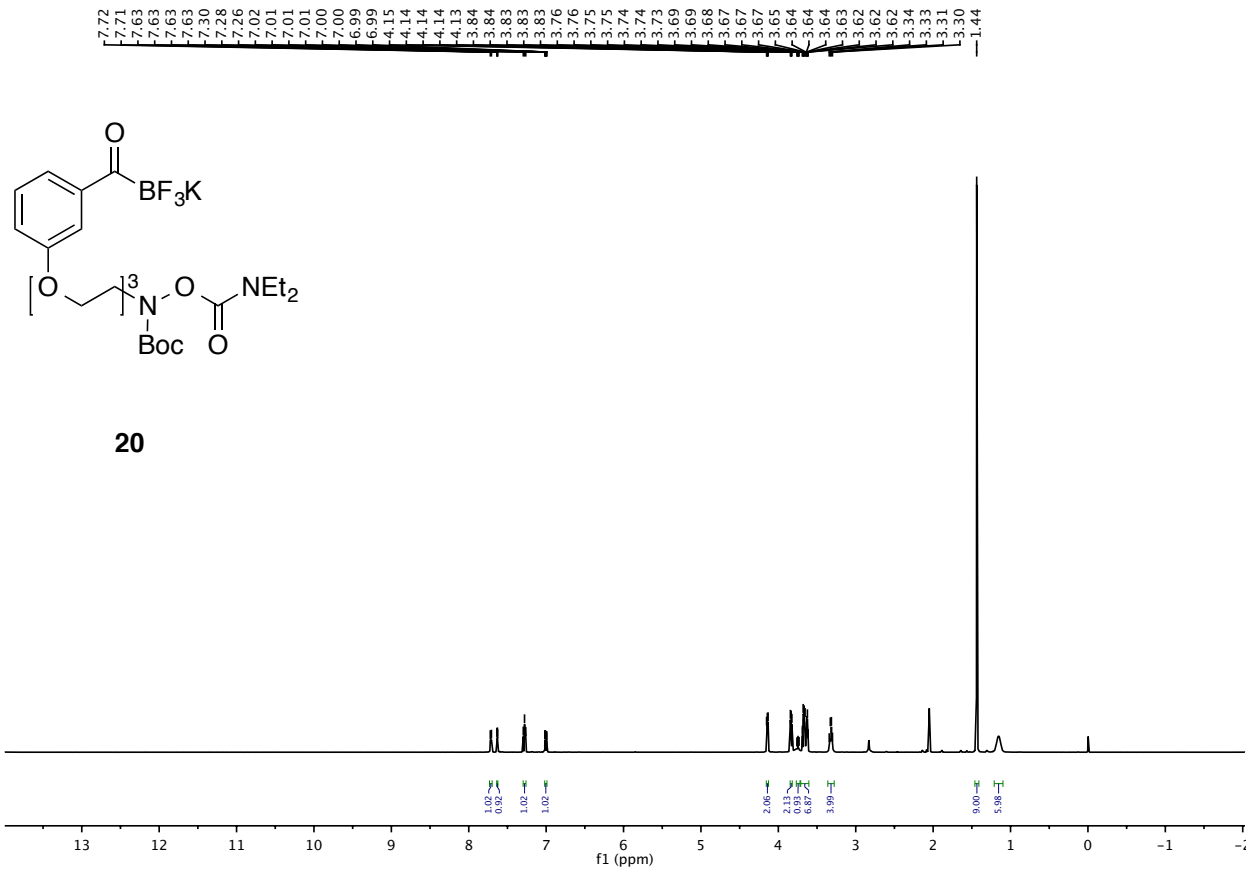
19: ^{1}H NMR (400 MHz, $CDCl_3$)



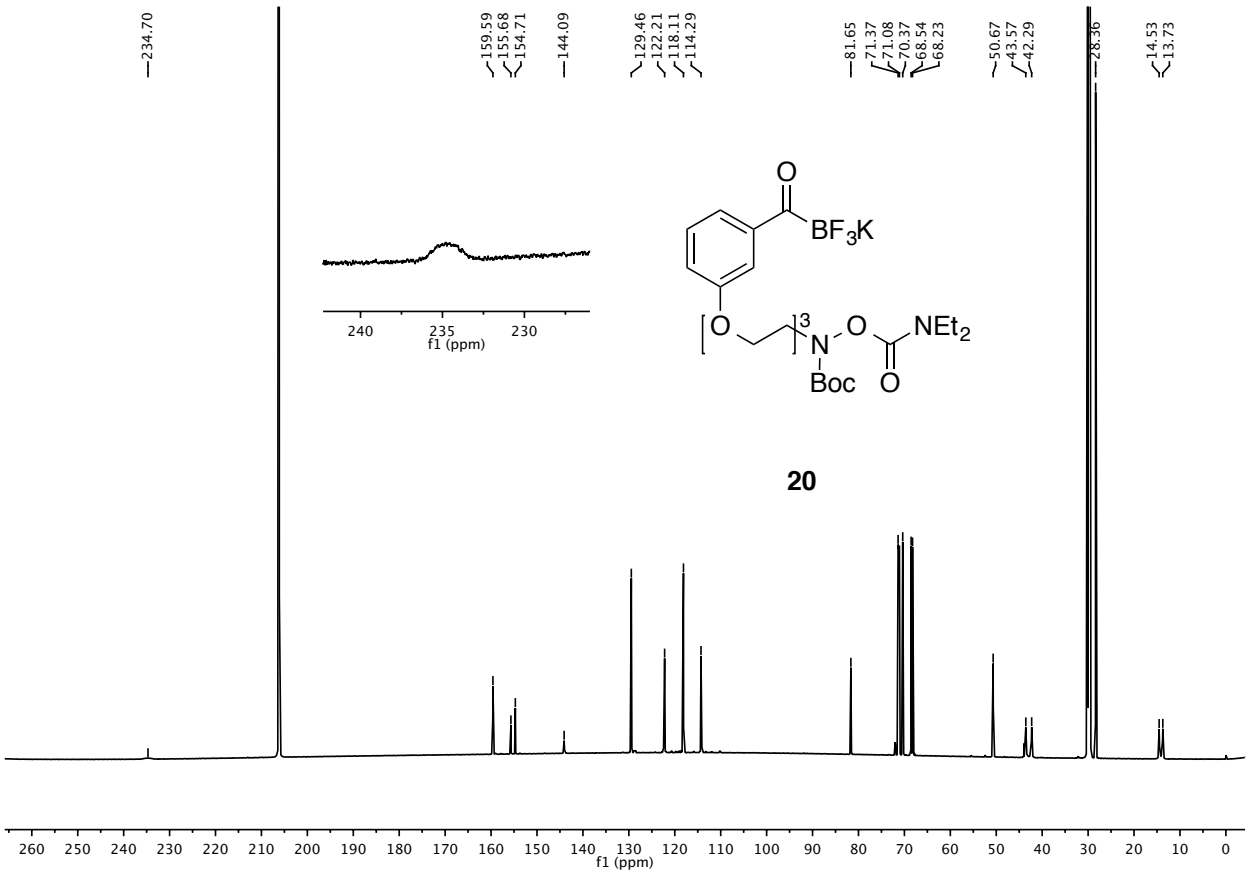
19: ^{13}C NMR (101 MHz, $CDCl_3$)



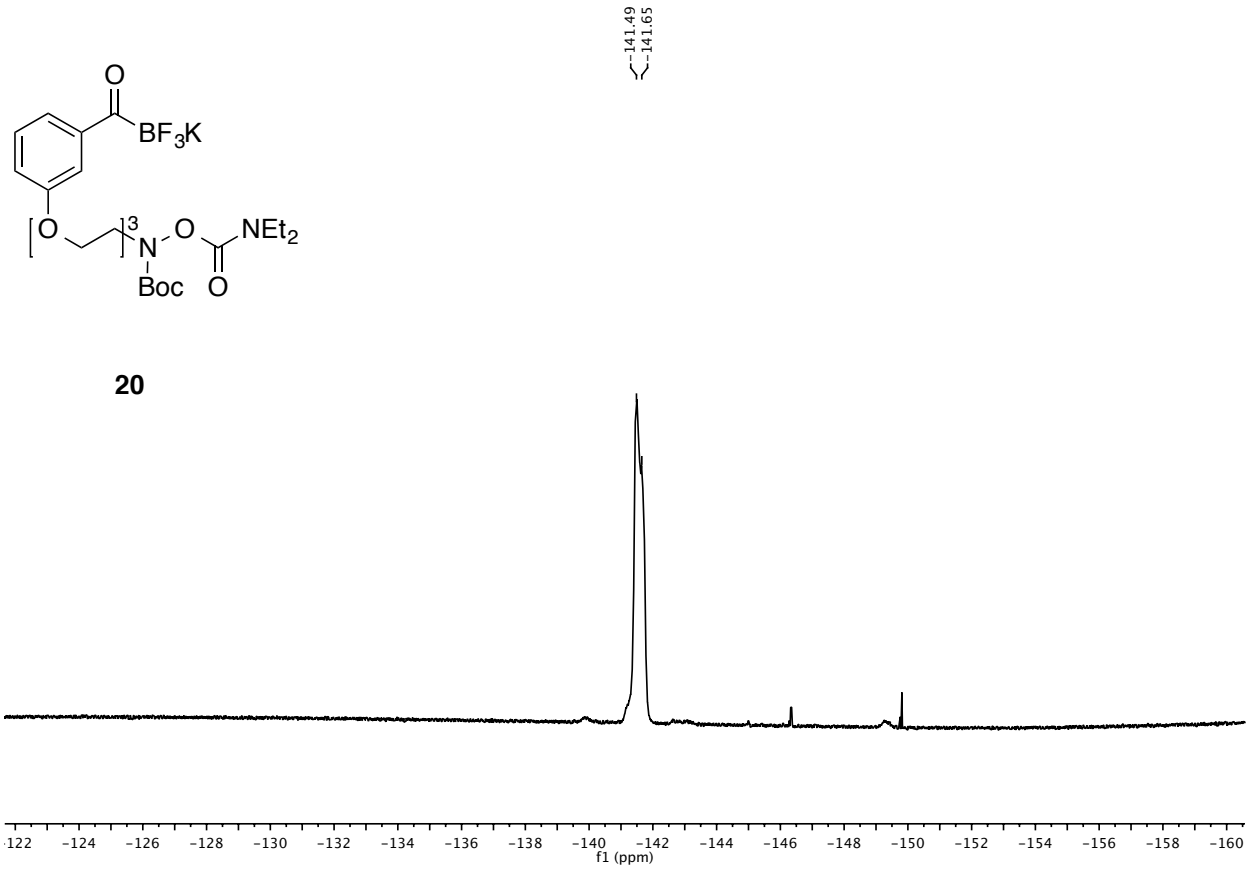
20: ^{1}H NMR (600 MHz, acetone–d_6)



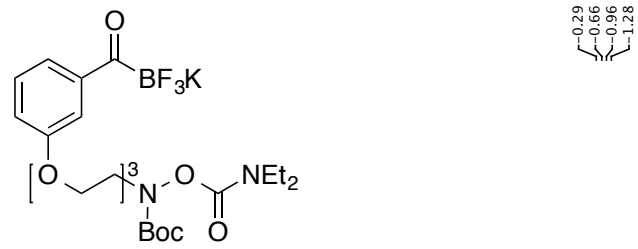
20: ^{13}C NMR (151 MHz, acetone–d_6)



20: ^{19}F NMR (470 MHz, acetone–d_6)

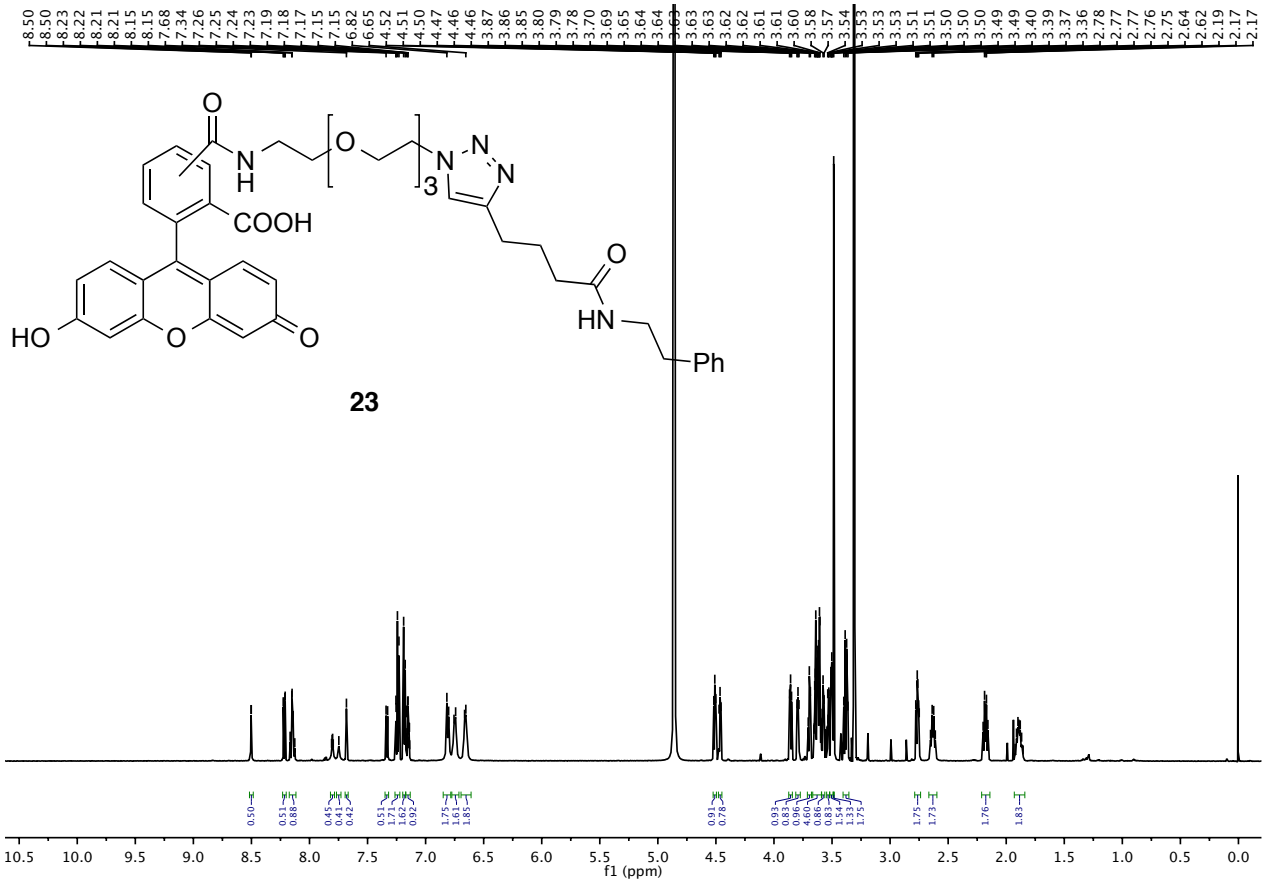


20: ^{11}B NMR (160 MHz, acetone-d_6)



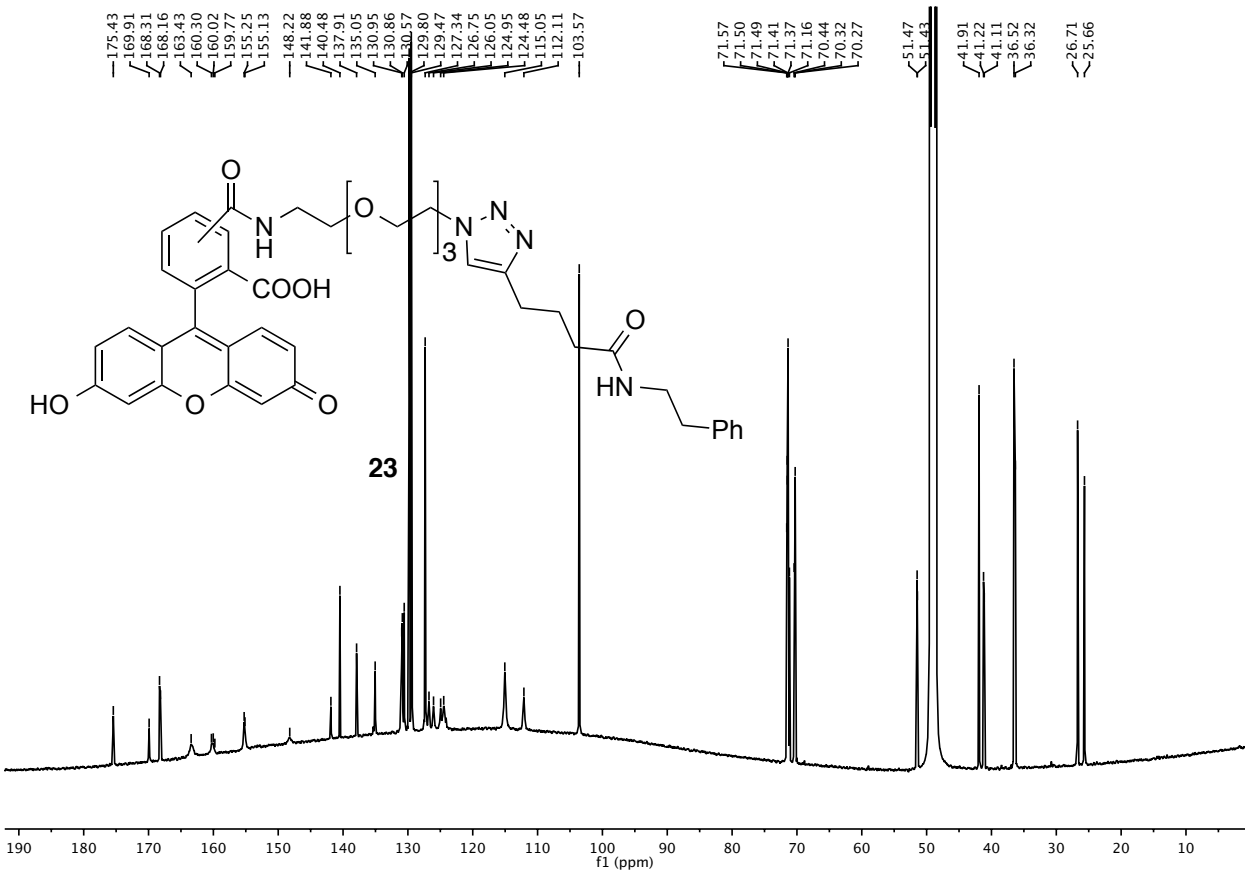
20

23: ^{1}H NMR (600 MHz, CD_3OD)

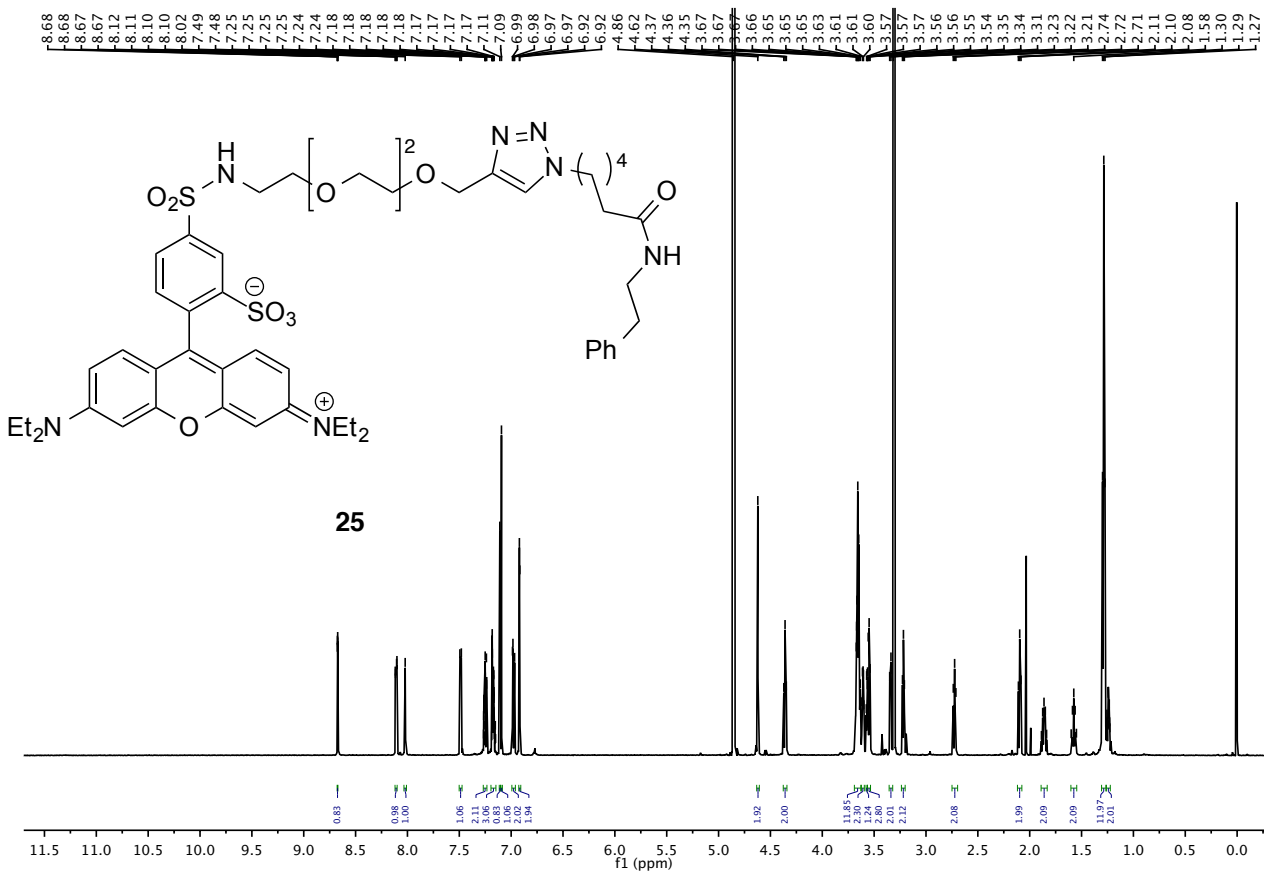


23

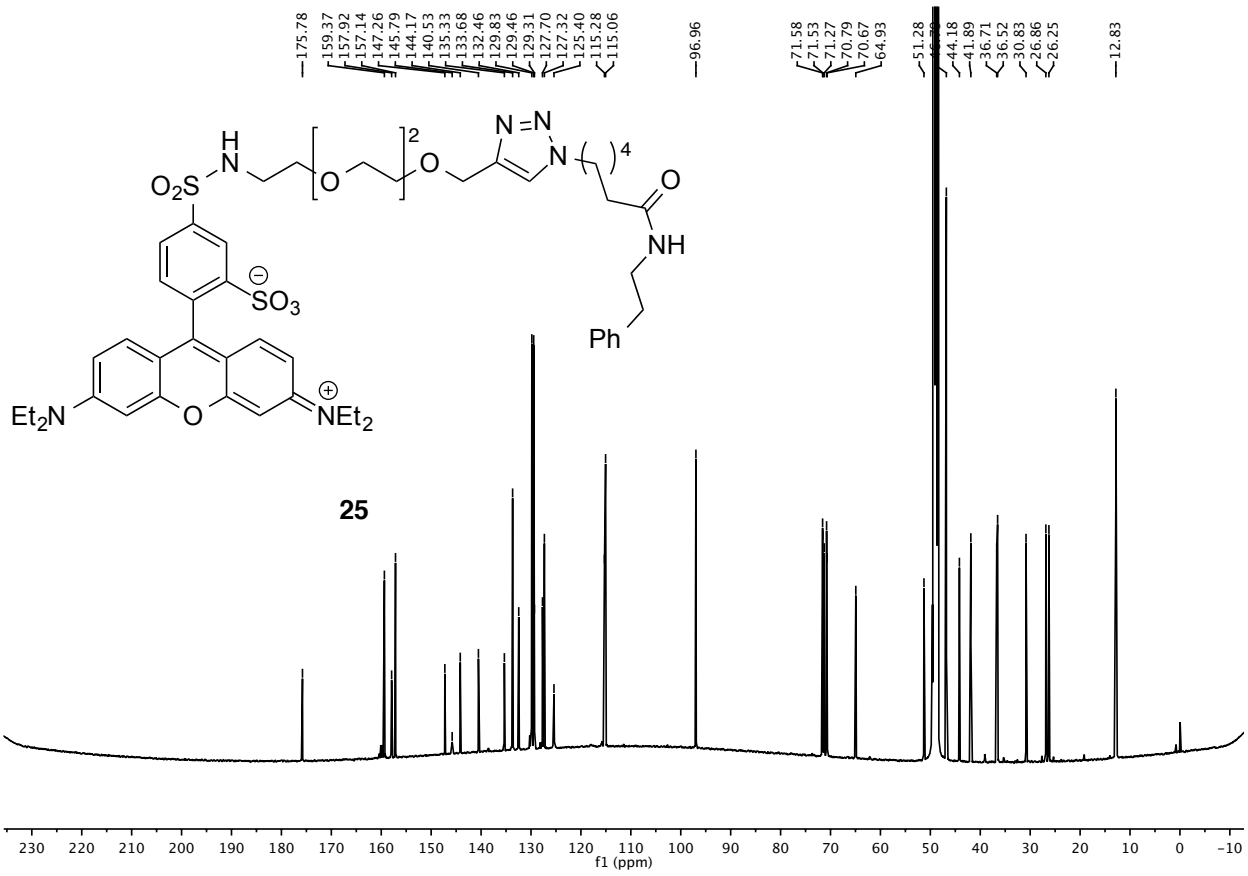
23: ^{13}C NMR (151 MHz, CD_3OD)



25: ^{1}H NMR (600 MHz, CH_3OD)



25: ^{13}C NMR (470 MHz, CD_3OD)



6. References

(1) Erős, G.; Kushida, Y.; Bode, J.W. *Angew. Chem. Int. Ed.* **2014**, *53*, 7604–7607.
(2) Dumas, A.M.; Bode, J.W. *Org. Lett.* **2012**, *14*, 2138–2141.
(3) Seven, I.; Weinrich, T.; Gränz, M.; Grünewald, C.; Brüß, S.; Krstic, I.; Prisner, T.F.; Heckel, A.; Göbel, M.W. *Eur. J. Org. Chem.* **2014**, *19*, 4037–4043.
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(5) Goswami, L.N.; Khan, A.A.; Jalisatg, S.S.; Hawthorne, M.F. *Chem. Commun.* **2014**, *50*, 5793–5795.