Supporting Information for:

Synthesis of Acyltrifluoroborates

Aaron M. Dumas and Jeffrey W. Bode*

Laboratorium für Organische Chemie, Department of Chemistry and Applied Biosciences ETH Zürich, Wolfgang Pauli Strasse 10, 8093 Zürich, Switzerland

Email: bode@org.chem.ethz.ch

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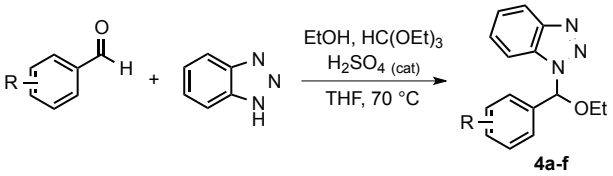
General Methods:

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) and 1,4-dioxane were distilled from Na/benzophenone ketyl; all other solvents (acetone, MeOH, CH_3CN) were used as supplied (ACS or HPLC grade). Starting materials were used as supplied by commercial vendors or prepared per the method described in the corresponding reference. Thin layer chromatography (TLC) was performed on Merck TLC plates (0.25 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 Mercury300 (300 MHz) or Varian AV400 (400 MHz) and spectra are referenced to residual protonated solvent ($CDCl_3$: 7.26 ppm; acetone-d_6: 2.05 ppm; DMSO-d_6: 2.50 ppm; CD_3CN: 1.94 ppm). ^{13}C NMR performed on a Varian AV400 (100 MHz) and spectra are referenced to the solvent ($CDCl_3$: 77.0 ppm; acetone-d_6: 28.92 ppm; DMSO-d_6: 39.98 ppm; CD_3CN: 0.30 ppm); the number of attached protons was determined by either combined DEPT135/DEPT90 or HSQC experiments, and is listed in brackets after the chemical shift value. *Note*: The ^{13}C signal of the boron-bound carbon in acyltrifluoroborates was not detected, most likely due to its slow relaxation and signal splitting from ^{11}B and ^{19}F coupling. ^{19}F NMR was performed on a Varian Mercury300 (282 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•OEt_2 (0 ppm); trifluoroborate multiplets are reported as an average of the observed signals. All chemicals shifts are reported in ppm (δ). LCMS analysis was performed on a Dionex UltiMate 3000 RSLC connected to a Surveyor MSQ Plus mass spectrometer; a reversed–phase RESTEK Pinnacle II C18 (4.6 x 50 mm) column was used, running a gradient of 5 to 100% CH_3CN in H_2O over 4.5 min, 100% CH_3CN for 2.5 min. 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.

CCDC 865601 & 865602 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

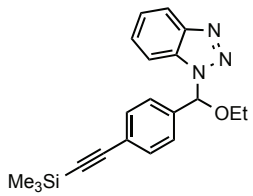
Preparation of Bt-ethoxy *N,O*-acetals 4a-f:



4a-f

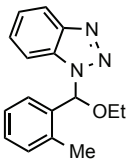
These reactions were performed by a slight modification of the method of Katritzky.[1] The corresponding aldehyde (20.0 mmol, 1.0 equiv), benzotriazole (2.98 g, 25.0 mmol, 1.25 equiv), EtOH (2.33 mL, 40 mmol, 2.0 equiv), and triethylorthoformate (10.0 mL, 60.0 mmol, 3.0 equiv) were dissolved in THF (40 mL) at RT. To this solution was added H_2SO_4 (10 drops), resulting in a white precipitate. The reaction was stirred at RT until the precipitate dissolved (~ 15 min), capped tightly with a plastic cap, and placed at 70 °C for 14 h. The reaction was cooled to RT, diluted with EtOAc (50 mL), washed with saturated $NaHCO_3$ (2 x 25 mL), the combined aqueous layers back extracted with EtOAc (2 x 25 mL), the combined organic layers washed with brine (25 mL), dried over Na_2SO_4, filtered, and concentrated. The acetals were purified by flash column chromatography eluting with 1:19 EtOAc/hexane or recrystallized from EtOH. *Note:* The crude mixture contains both 1- (major) and 2- (minor) benzotriazolyl *N,O*-acetals; for convenience, only the 1benzotriazolyl acetal was isolated and used in the next step.

4a[1], **4b**[1], **4c**[2], **4e**[1] are known compounds; spectroscopic data matched those reported and are not duplicated here.



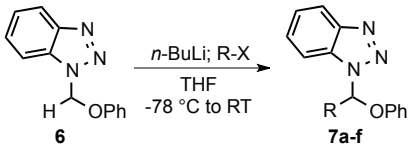
1-(Ethoxy(4-((trimethylsilyl)ethynyl)phenyl)methyl)-1*H*-benzotriazole (4d): Prepared from 4-((trimethylsilyl)ethynyl)benzaldehyde[3] (2.62 g), purified by flash column chromatography, and isolated as a pale yellow oil (3.75 g, 60% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) 8.07–8.04 (m, 1H), 7.45 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.34–7.28 (m, 2H), 7.22–7.18 (m, 2H), 3.76 (dq, J = 9.4 Hz, 7.0 Hz, 1H), 3.46 (dq, J = 9.4 Hz, 7.0 Hz, 1H), 1.25 (t, J = 7.0 Hz, 3H), 0.24 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) 147.0 (C), 136.5 (C), 132.1 (2CH), 131.0 (C), 127.5 (CH), 125.9 (2CH), 124.3 (CH), 123.9 (C), 119.9 (CH), 104.2 (C), 95.3 (C), 89.1 (CH), 65.0 (CH_2), 14.7 (CH_3), –0.14 ($3CH_3$); **HRMS** (ESI) calc'd for $C_{20}H_{23}N_3NaOSi$ $[M + Na]^+$: 372.1503, found: 372.1502.

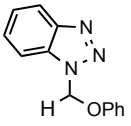
1. Katritzky, A. R.; Lang, H.; Wang, Z.; Zhang, Z.; Song, H. *J. Org. Chem.* **1995**, *60*, 7619–7624.
2. Katritzky, A. R.; Lang, H.; Wang, Z.; Lie, Z. *J. Org. Chem.* **1996**, *61*, 7551–7557.
3. Thorand, S.; Krause, N. *J. Org. Chem.* **1998**, *63*, 8551 – 8553.



1-(Ethoxy(o-tolyl)methyl)-1H-benzotriazole (4f): Prepared from 2-methylbenzaldehyde (2.40 g), purified by recrystallization, and isolated as a white solid (3.1 g, 58% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) 8.07–8.04 (m, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.34–7.28 (m, 2H), 7.22–7.18 (m, 2H), 3.76 (dq, *J* = 9.4 Hz, 7.0 Hz, 1H), 3.46 (dq, *J* = 9.4 Hz, 7.0 Hz, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 0.24 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) 147.0 (C), 136.5 (C), 132.1 (2CH), 131.0 (C), 127.5 (CH), 125.9 (2CH), 124.3 (CH), 123.9 (C), 119.9 (CH), 104.2 (C), 95.3 (C), 89.1 (CH), 65.0 (CH_2), 14.7 (CH_3), –0.14 ($3CH_3$); **HRMS** (ESI) calc'd for $C_{16}H_{17}NaN_3O$ $[M + Na]^+$: 290.1264, found: 290.1268.

Preparation of Bt-phenoxy *N,O*-acetals 7a-f:

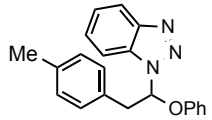




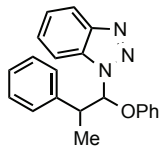
1-(Phenoxymethyl)-1*H*-benzotriazole (6): Prepared by literature methods from benzotriazole; a large-scale synthesis is described here for convenience.[4,6] Formalin (35% CH_2O in water, 27 mL) was cooled to 0 °C and to it was added benzotriazole (20.0 g, 168 mmol, 1.0 equiv). The mixture was stirred at 0 °C for 15 min and warmed to RT for 30 min, over which time it solidified into a solid white mass. This was broken up with a metal spatula, suspended in H_2O (100 mL), filtered, and the solid washed with cold EtOH (2 x 25 mL) and pumped dry to give 1-hydroxymethylbenzotriazole as a white solid (21 g). This was placed in a flask cooled in an ice/water bath, and $SOCl_2$ (60 mL) was added dropwise over 20 min with vigorous stirring. After the end of addition, the flask was placed at 75 °C and the reaction heated to reflux for 1 h (reflux condenser attached to a KOH trap to neutralize vapours). After cooling to RT, the reaction was concentrated on a rotary evaporator, MeOH (50 mL) was added slowly (*caution: exothermic, and acidic gasses are released*), the suspension stirred for 5 min and then concentrated. This MeOH treatment was repeated twice more, and the solid filtered, washed with MeOH (2 x 10 mL) and pumped dry to give 1-chloromethylbenzotriazole as a white powder (19.8 g). This was dissolved in DMF (390 mL), sodium phenoxide (13.7 g, 1.0 equiv relative to amount of product from previous step) was added, and the milky suspension stirred at 70 °C for 16 h. After cooling to RT, the reaction was poured into ice-water (1.5 L), stirred vigorously for 20 min, and then filtered. The white solid was washed with water (3 x 250 mL) and dried under high vacuum to give **6** as a fluffy white powder (26.5 g, 70% yield over 3 steps).

4. Le Borgne, M; Na, Y.M.; Pagniez, F.; Le Baut, G.; Le Pape, P.; Abdala, H. US20040067998, **2004**.

General procedure for lithiation/alkylation of 6: Based on the reported method[5], **6** (2.25 g, 10.0 mmol, 1.0 equiv) was dissolved in THF (100 mL) at RT and cooled to –78 °C. *n*-BuLi (1.6 M in hexane, 6.9 mL, 11.0 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 (occasionally, a greenish precipitate formed, however this seemingly had no effect on the success of the reaction), and the electrophile (11 mmol, 1.1 equiv) added directly into the reaction; liquids were added neat, while solids were added as a solution in THF (5 mL). The reaction was stirred for 16 h 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. The residue was purified by recrystallization or flash column chromatography, as indicated.



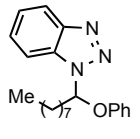
1-(1-Phenoxy-2-(*p*-tolyl)ethyl)-1*H*-benzotriazole (7a): Prepared using α-bromo-*p*-xylene (2.0 g), purified by recrystallization from EtOH, and isolated as an off-white powder (2.8 g, 85% yield). **M.p.** 119–120 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) 8.03 (dt, *J* = 8.3 Hz, 0.9 Hz, 1H), 7.80 (dt, *J* = 8.3 Hz, 0.9 Hz, 1H), 7.46 (ddd, *J* = 8.2 Hz, 7.0 Hz, 1.0 Hz, 1H), 7.35 (ddd, *J* = 8.1 Hz, 7.0 Hz, 1.0 Hz, 1H), 7.18–7.12 (m, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.97–6.88 (m, 4H), 3.77 (dd, *J* = 14.0 Hz, 7.1 Hz, 1H), 3.53 (dd, *J* = 14.0 Hz, 6.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) 156.1 (C), 146.6 (C), 137.0 (C), 131.4 (C), 131.3 (C), 129.6 (2CH), 129.3 (2CH), 129.2 (CH), 127.7 (CH), 124.2 (CH), 123.0 (CH), 120.2 (CH), 116.3 (2CH), 111.1 (CH), 89.0 (CH), 40.9 (CH_2), 21.0 (CH_3); **HRMS** (ESI) calc'd for $C_{21}H_{20}N_3O$ [M + H]$^+$: 330.1601, found: 330.1597.



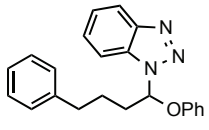
1-(1-Phenoxy-2-phenylpropyl)-1*H*-benzotriazole (7b): Prepared using (1-bromoethyl)benzene (1.5 mL), purified by flash column chromatography eluting with 3:17 EtOAc/hexane (Rf ~ 0.25) and isolated as a pale yellow oil (2.54 g, 77% yield, 1:1 mixture of diastereomers by ^{1}H NMR). **^{1}H NMR** (300 MHz, $CDCl_3$) 8.05 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.92 (dt, *J* = 8.3 Hz, 0.9 Hz, 1H), 7.69 (dt, *J* = 3.0 Hz, 0.9 Hz, 1H), 7.66 (dt, *J* = 2.9 Hz, 1.0 Hz, 1H), 7.47–7.24 (m, 9H), 7.23–7.04 (m, 7H), 7.02–6.85 (m, 6H), 6.82 (d, *J* = 4.6 Hz, 1H), 6.79 (d, *J* = 4.5 Hz, 1H), 6.77–6.70 (m, 2H), 3.97–3.82 (m, 2H), 1.71 (d, *J* = 7.0 Hz, 3H), 1.15 (d, *J* =7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) 156.39 (C), 156.38 (C), 146.6 (C), 146.2 (C), 140.8 (C), 139.5 (C), 131.6 (C), 131.4 (C), 129.7 (2CH), 129.5 (2CH), 128.6 (2CH), 128.4 (2CH), 128.0 (2CH), 127.6 (CH), 127.5 (2CH), 127.44 (CH), 127.36 (CH), 127.33 (CH), 124.3 (CH), 123.9 (CH), 123.02 (CH),

5. Katritzky, A. R.; Wang, Z.; Lang, H. *Organometallics* **1996**, *15*, 486–490.

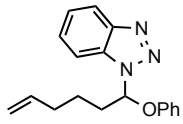
122.97 (CH), 120.0 (CH), 119.9 (CH), 92.7 (CH), 92.2 (CH), 45.0 (CH), 44.8 (CH), 17.6 (CH_3), 16.9 (CH_3); **HRMS** (ESI) calc'd for $C_{21}H_{20}N_3O$ $[M + H]^+$: 330.1601, found: 330.1604.



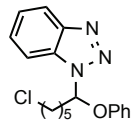
1-(1-Phenoxynonyl)-1*H*-benzotriazole (7c): Prepared using 1-bromooctane (1.9 mL), purified by flash column chromatrography eluting with 1:9 EtOAc/hexane (Rf ~0.3), and isolated as a colourless liquid (2.46 g, 73% yield). Spectroscopic data matched those reported.[6]



1-(1-Phenoxy-4-phenylbutyl)-1*H*-benzotriazole (7d): Prepared using 1-bromo–3–phenylpropane, purified by flash column chromatrography eluting with 3:17 EtOAc/hexane, and isolated as a pale yellow oil (2.61 g, 76% yield). Spectroscopic data matched those reported.[7]



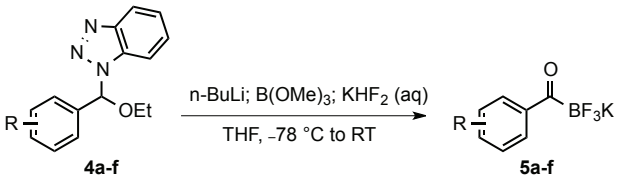
1-(1-Phenoxyhex-5-en-1-yl)-1*H*-benzotriazole (7e): Prepared using 5-bromo-1-pentene (1.3 mL), purified by flash column chromatrography eluting with 3:17 EtOAc/hexane, and isolated as a pale yellow oil (2.44 g, 83% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) 8.03 (dt, *J* = 8.3 Hz, 0.9 Hz, 1H), 7.80 (dt, *J* = 8.4 Hz, 0.9 Hz, 1H), 7.46 (ddd, *J* = 8.2 Hz, 7.0 Hz, 1.1 Hz, 1H), 7.35 (ddd, *J* = 8.0 Hz, 7.0 Hz, 1.1 Hz, 1H), 7.21–7.15 (m, 2H), 6.97–6.81 (m, 3H), 6.84 (t, *J* = 6.9 Hz, 1H), 5.75 (ddt, 16.9 Hz, 10.1 Hz, 6.6 Hz, 1H), 5.05–4.96 (m, 2H), 2.54–2.48 (m, 1H), 2.36–2.30 (m, 1H), 2.18–2.11 (m, 2H), 1.72–1.60 (m, 1H), 1.46–1.34 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) 156.1 (C), 146.7 (C), 137.5 (CH), 131.1 (C), 129.7 (2CH), 127.7 (CH), 124.3 (CH), 122.9 (CH), 120.1 (CH), 116.2 (2CH), 115.5 (CH_2), 111.2 (CH), 88.2 (CH), 34.2 (CH_2), 32.8 (CH_2), 23.9 (CH_2); **HRMS** (ESI) calc'd for $C_{18}H_{20}N_3O$ $[M + H]^+$: 294.1601, found: 294.1601.



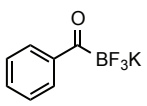
1-(6-Chloro-1-phenoxyhexyl)-1H-benzotriazole (7f): Prepared using 1-bromo-5-chloropentane (1.5 mL), purified by flash column chromatography eluting with 3:17 EtOAc/hexane, and isolated as a pale yellow oil (2.45 g, 74% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) 8.04 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.21–7.15 (m, 2H), 6.97–6.92 (m, 3H), 6.84 (t, *J* = 6.8 Hz, 1H), 3.51 (t, *J* = 6.5 Hz, 2H), 2.55–2.47 (m, 1H), 2.37–2.27 (m, 2H), 1.77 (pentet, *J* = 6.9 Hz, 2H), 1.63–1.50 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) 156.1 (C), 146.7 (C), 131.1 (C), 129.7 (2CH), 127.7 (CH), 124.3 (CH), 122.9 (CH), 120.2 (2CH), 116.2 (CH), 111.1 (CH), 88.1 (CH), 44.6 (CH_2), 34.7 (CH_2), 32.2 (CH_2), 26.1 (CH_2), 24.1 (CH_2); **HRMS** (ESI) calc'd for $C_{18}H_{20}ClN_3O$ $[M + H]^+$: 330.1386, found: 330.1369.

6. Katritzky, A. R.; Serdyuk, L.; Xie, L. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1059–1064.
7. Katritzky, A. R.; Wang, Z.; Lang, H.; Feng, D. *J. Org. Chem.* **1997**, *62*, 4125–4130.

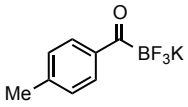
Preparation of Benzoyltrifluoroborates 5a-f:



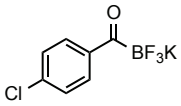
General procedure for synthesis of benzoyltrifluoroborates 5a–f: In a 200 mL flask, **4** (5.5 mmol, 1.1 equiv) was dissolved in THF (70 mL) at RT. The flask was placed in a dry–ice/acetone bath and stirred for at least 15 minutes. *n*-BuLi (1.6 M in hexane, 3.2 mL, 5.0 mmol, 1.0 equiv) was added slowly down the side of the flask over a period of 2–3 min. During this time, an intense green colour developed (blood-red in the case of 1-naphthyl **4e**). The solution was stirred for 5 min following the end of *n*-BuLi addition, and neat $B(OMe)_3$ (1.12 mL, 10.0 mmol, 2.0 equiv) was added dropwise over 2 min directly into the solution. The deep green colour gradually became yellow or brown-yellow after 5-10 minutes of stirring. The flask was kept in the dry-ice/acetone bath for 1 h, and then removed from the bath to stir at RT for 5 minutes. At this time, the septum was removed from the flask, and, with vigorous stirring, four portions of KHF_2 solution (sat. aq.) were added (5 mL per minute, 20 mL total). As the reaction warmed, a biphasic mixture consisting of a milky white aqueous layer and a yellow organic layer formed. This was stirred overnight (~12 hours from the time of KHF_2 addition) over which time the organic layer became wine red. The reaction was concentrated using a rotary evaporator followed by drying on high vacuum (the flask can be placed in a 50 °C oil bath to facilitate drying). A dry white powder with slightly greasy red clumps resulted. This was stirred in acetone (15 mL) for 5 min, and then filtered. The solids were treated in this fashion 3 additional times (60 mL of acetone total), and the combined acetone filtrates were concentrated to ~5 mL volume. This was diluted with Et_2O (25 mL) and stirred until a precipitate formed. Filtration, washing with additional Et_2O (2 x 5 mL), and drying under high vacuum gave the product as a white or yellow solid.



Potassium benzoyltrifluoroborate (5a): Prepared from **4a** (1.39 g) according to the general procedure and isolated as a white solid (502 mg, 47% yield). **^{1}H NMR** (300 MHz, acetone–d_6) 8.07 (d, *J* = 7.8 Hz, 2H), 7.41–7.34 (m, 3H); **^{13}C NMR** (100 MHz, DMSO–d_6) 141.7 (br, C), 131.2 (CH), 128.23 (2CH), 128.21 (2CH); **^{19}F NMR** (282 MHz, acetone–d_6) –142.8; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.08; **IR** (neat) 3344, 1639, 1597, 1579; **HRMS** (ESI^-) calc'd for $C_7H_5BF_3O$ $[M–K]^-$: 173.0391, found: 173.0389.



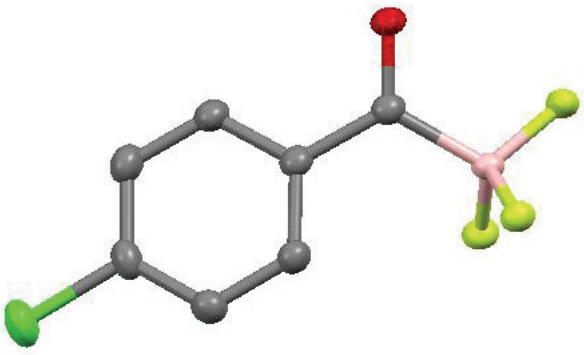
Potassium 4-methylbenzoyltrifluoroborate (5b): Prepared from **4b** (1.47 g) according to the general procedure and isolated as a white solid (398 mg, 35% yield). **^{1}H NMR** (300 MHz, acetone–d_6) 7.97 (d, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, DMSO–d_6)140.79 (C), 128.7 (2CH), 128.4 (app d, *J* = 1.8 Hz, 2CH), 21.5 (CH_3); **^{19}F NMR** (282 MHz, acetone–d_6) –143.0; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.09; **IR** (neat) 1638, 1602, 1572; **HRMS** (ESI$^-$) calc'd for $C_8H_7BF_3O$ [M–K]$^-$: 187.0548, found: 187.0544.

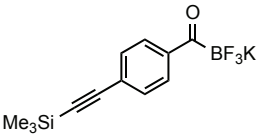


Potassium 4-chlorobenzoyltrifluoroborate (5c): Prepared from **4c** (1.58 g) according to the general procedure and isolated as a white solid (510 mg, 41% yield). **^{1}H NMR** (300 MHz, acetone–d_6) 8.05 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO–d_6)140.2 (br, C), 136.0 (C), 130.1 (app d, *J* = 1.9 Hz, 2CH) 128.4 (2CH); **^{19}F NMR** (282 MHz, acetone–d_6) –143.0; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.14; **IR** (neat) 3083, 1636, 1584; **HRMS** (ESI$^-$) calc'd for $C_7H_4BClF_3O$ [M–K]$^-$: 207.0003, found: 207.0000.

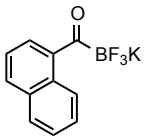
Crystals of **5c** were grown by dissolving ~5 mg in acetone (0.2 mL) in a small glass vial, and diffusing hexane into it by placing the vial in a glass chamber partially filled with hexane. Clear colourless needles were obtained, from which a single crystal was cut.

X-Ray crystal structure of 5c:

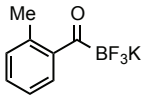




Potassium 4-((trimethylsilyl)ethynyl)benzoyltrifluoroborate (5d): Prepared from **4d** (1.92 g) according to the general procedure and isolated as a pale yellow solid (353 mg, 23% yield). **^{1}H NMR** (300 MHz, DMSO–d_6) 7.86 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 0.24 (s, 9H); **^{13}C NMR** (100 MHz, DMSO–d_6) 141.2 (br, C), 131.7 (2CH), 128.3 (app. d, *J* = 1.8 Hz, C), 124.68 (C), 105.63 (C), 96.19 (C), 0.32 ($3CH_3$); **^{19}F NMR** (282 MHz, DMSO–d_6) –140.3; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.14; **IR** (neat) 2961, 2161, 1635, 1596; **HRMS** (ESI$^-$) calc'd for $C_{12}H_{13}BF_3OSi$ [M–K]$^-$: 269.0789, found: 269.0784.

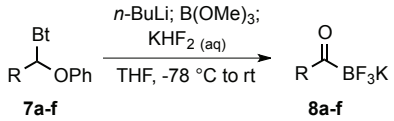


Potassium 1-naphthoyltrifluoroborate (5e): Prepared from **4e** (1.67 g) according to the general procedure and isolated as a pale yellow solid (560 mg, 43% yield). **^{1}H NMR** (400 MHz, DMSO–d_6) 8.51–8.47 (m, 1H), 8.00 (d, *J* = 7.0 Hz, 1H), 7.96 – 7.83 (m, 2H), 7.51 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.49 – 7.44 (m, 2H); **^{13}C NMR** (100 MHz, DMSO–d_6) 133.8 (C), 129.9 (CH), 129.8 (C), 128.4 (CH), 128.3 (app d, *J* = 2.6 Hz, CH), 126.7 (CH), 126.6 (CH), 125.9 (CH), 125.3 (CH); **^{19}F NMR** (282 MHz, DMSO–d_6) –141.2; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.33; **IR** (neat) 3054, 1630, 1615; **HRMS** (ESI^-) calc'd for $C_{11}H_7BF_3O$ $[M–K]^-$: 223.0550, found: 223.0544.



Potassium 2-methylbenzoyltrifluoroborate (5f): Prepared from **4f** (1.47 g) according to the general procedure and isolated as a white solid (373 mg, 33% yield). **^{1}H NMR** (300 MHz, acetone–d_6) 7.99 (d, *J* = 8.2 Hz, 1H), 7.18–7.14 (m, 2H), 7.08–7.05 (m, 1H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, DMSO–d_6) 135.0 (C), 131.0 (CH), 129.5 (CH), 128.9 (app d, *J* = 5.1 Hz, CH), 125.2 (CH), 20.6 (CH_3); **^{19}F NMR** (282 MHz, acetone–d_6) –143.8; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.51; **IR** (neat) 3055, 2927, 1633, 1567; **HRMS** (ESI^-) calc'd for $C_8H_7BF_3O$ $[M–K]^-$: 187.0549, found: 187.0547.

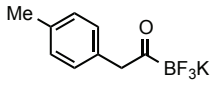
Preparation of Acyltrifluroborates 8a-f:



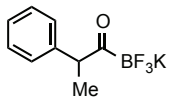
7a-f **8a-f**

General procedure for synthesis of acyltrifluoroborates 8a–f: In a flamed-dried, 200 mL round-bottom flask under an atmosphere of dry N_2, **7** (5.5 mmol, 1.1 equiv) was dissolved in THF (70 mL) at RT, and then cooled to –78 °C in a dry ice/acetone bath. *n*-BuLi (1.6 M in hexane, 3.2 mL, 5.0 mmol, 1.0 equiv) was added dropwise over 2 min, resulting in red–brown solution. Two minutes after the end of *n*-BuLi addition, $B(OMe)_3$ (1.1 mL, 10.0 mmol, 2.0 equiv) was added dropwise over 1 min, over which time the solution became clear and pale yellow. This was stirred at –78 °C for 1 h, removed from the bath, and stirred at RT for 5 min. After this time, the flask was opened to atmosphere and with vigorous stirring, four portions of saturated aqueous KHF_2 solution (5 mL each) were added once per minute, giving a pale yellow THF layer with a lower milky white aqueous phase. This was stirred for 14 h at RT, the THF removed by rotory evaporation, and the water evaporated by placing the flask under high vacuum while immersed in a 50 °C oil bath. Once a dry off–white solid was obtained, this was stirred in Et_2O (20 mL) and filtered (the Et_2O contained **7**, phenol, and benzotriazole). The remaining white solids were stirred in acetone (20 mL) for 5 min at RT, filtered, and the acetone extraction repeated twice more (60 mL of acetone total). The

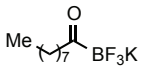
combined acetone liquids were concentrated to ~5 mL, diluted with Et_2O (25 mL) and stirred until a white solid precipitated. This was filtered and dried under high vacuum to give **8**.



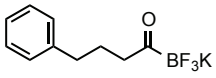
Potassium (2-(*p*-tolyl)acetyl)trifluoroborate (8a): Prepared from **7a** (1.81 g) and isolated as a white powder (489 mg, 40% yield). **^{1}H NMR** (300 MHz, acetone–d_6) 6.99 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 3.64 (s, 2H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, DMSO–d_6) 134.3 (C), 134.2 (C), 130.1 (2CH), 128.7 (2CH), 50.8 (br, CH_2), 21.1 (CH_3); **^{19}F NMR** (282 MHz, acetone–d_6) –148.8; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.60; **IR** (neat) 3025, 1671, 1516; **HRMS** (ESI^-) calc'd for $C_9H_9BF_3O$ $[M–K]^-$: 201.0706, found: 201.0703.



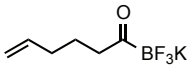
Potassium 2-phenylpropanoyltrifluoroborate (8b): Prepared from **7b** (1.81 g) and isolated by the following modification to the general procedure: the acetone washes were concentrated completely, yielding a yellow oil. This was dissolved in Et_2O (10 mL) and diluted with hexane (20 mL); this solution precipitated a sticky white solid after being kept 14 h at RT. The liquids were decanted away from the solid, the solid stirred vigorously in Et_2O (20 mL) until it was free–flowing, filtered, and pumped dry to give **8b** as a white powder (410 mg, 34% yield). **^{1}H NMR** (300 MHz, acetone–d_6) 7.19–7.06 (m, 5H), 4.20 (q, J = 7.1 Hz, 1H), 1.21 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO–d_6) 142.8 (C), 128.6 (2CH), 128.1 (2CH), 125.7 (CH), 51.7 (br, CH_2), 17.3 (CH_3); **^{19}F NMR** (282 MHz, acetone–d_6) –147.5; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.75; **IR** (neat) 2977, 1653; **HRMS** (ESI^-) calc'd for $C_9H_9BF_3O$ $[M–K]^-$: 201.0706, found: 201.0704.



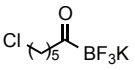
Potassium nonanoyltrifluoroborate (8c): Prepared from **7c** (1.83 g) by the general procedure, with hexane (10 mL) being added in addition after Et_2O to precipitate the salt from the acetone extract, giving the product as a white solid (393 mg, 32% yield). **^{1}H NMR** (400 MHz, acetone–d_6) 2.38 (t, J = 7.4 Hz, 2H), 1.43 (pentet, J = 7.1 Hz, 2H), 1.26 (br m, 10H), 0.87 (t, J = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO–d_6) 44.6 (br, CH_2), 31.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.1 (CH_2), 22.63 (CH_2), 22.55 (CH_2), 14.4 (CH_3); **^{19}F NMR** (282 MHz, acetone–d_6) –149.1; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.69; **IR** (neat) 2924, 2854, 1661; **HRMS** (ESI^-) calc'd for $C_9H_{17}BF_3O$ $[M–K]^-$: 209.1332, found: 201.1330.



Potassium 3-phenylpropanoyltrifluoroborate (8d): Prepared from **7d** (1.89 g) by the general procedure and isolated as a white solid (880 mg, 69% yield). **^{1}H NMR** (300 MHz, acetone–d_6) 7.26–7.12 (m, 5H), 2.52 (t, J = 7.8 Hz, 2H), 2.43 (t, J = 7.3 Hz, 2H), 1.74 (pentet, J = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO–d_6) 143.0 (C), 128.7 (2CH), 128.6 (2CH), 125.95 (CH), 44.0 (br, CH_2), 35.6 (CH_2), 24.7 (CH_2); **^{19}F NMR** (282 MHz, acetone–d_6) –149.0; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.88; **IR** (neat) 2939, 1651; **HRMS** (ESI^-) calc'd for $C_{10}H_{11}BF_3O$ $[M–K]^-$: 215.0862, found: 201.0857.

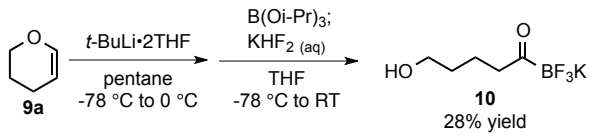


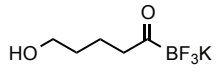
Potassium hex-5-enoyltrifluoroborate (8e): Prepared from **7e** (1.61 g) by the general procedure and isolated as a white solid (291 mg, 28% yield). **^{1}H NMR** (300 MHz, acetone–d_6) 5.79 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.00–4.86 (m, 2H), 2.40 (t, *J* = 7.4 Hz, 2H), 2.03–1.91 (m, 2H), 1.52 (pentet, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO–d_6) 139.5 (CH), 114.9 (CH_2), 44.0 (br, CH_2), 33.7 (CH_2), 21.9 (CH_2); **^{19}F NMR** (282 MHz, acetone–d_6) –149.9; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.90; **IR** (neat) 3079, 2934, 1661; **HRMS** (ESI^-) calc'd for $C_6H_9BF_3O$ $[M–K]^-$: 165.0705, found: 165.0707.



Potassium 6-chlorohexanoyltrifluoroborate (8f): Prepared from **7f** (1.81 g) by the general procedure and isolated as a white solid (405 mg, 34% yield). **^{1}H NMR** (400 MHz, DMSO–d_6) 3.59 (t, *J* = 6.7 Hz, 2H), 2.25 (t, *J* = 7.1 Hz, 2H), 1.75 – 1.59 (m, 2H), 1.42–1.31 (m, 2H), 1.30–1.21 (m, 2H); **^{13}C NMR** (100 MHz, DMSO–d_6) 45.9 (CH_2), 44.4 (br, CH_2) 32.6 (CH_2), 26.9 (CH_2), 21.9 (CH_2); **^{19}F NMR** (282 MHz, acetone–d_6) –149.2; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.62; **IR** (neat) 2940, 2869, 1651; **HRMS** (ESI^-) calc'd for $C_6H_{10}BClF_3O$ $[M–K]^-$: 201.0472, found: 201.0469.

Preparation of Acyltrifluroborates 10 and 11:

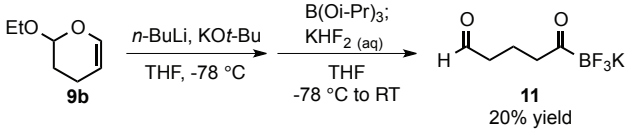


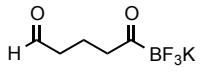


Potassium 5-hydroxypentanoyltrifluoroborate (10): *Caution: t-BuLi is pyrophoric– use appropriate precautions.* Lithiation of DHP was carried out by the procedure of Boeckmann.[8] In a 100 mL flask, 3,4-dihydro-2*H*-pyran (**9a**, 1.1 mL, 12.0 mmol, 1.0 equiv) was dissolved in THF (2.5 mL) at RT and placed in a dry–ice/acetone bath. After stirring for 10 minutes, *t*-BuLi (1.7 mL in pentane, 7.0 mL, 12.0 mmol, 1.0 equiv) was added down the side of the flask over 15 min, resulting in a thick yellow suspension. This was kept at –78 °C for an additional 15 min, placed in an ice-water bath for 30 min (formation of a bright yellow solution), and re–cooled to –78 °C. The reaction was diluted with THF (12 mL, addition down the side of the flask over 2 min) and B(O*i*-Pr)$_3$ (3.0 mL, 13.2 mL, 1.1 equiv) was added dropwise directly into the solution over 10 min (thick white precipitate formed). The reaction was kept at –78 °C for 30 min, removed from the bath, stirred at RT for 30 min, and saturated KHF_2 solution (15 mL) was added in 5 mL portions over 2 min (some smoking upon addition of first aliquot). The reaction was stirred at

8. Boeckman Jr, R. K.; Bruza, K. J. *Tetrahedron* **1981**, *37*, 3997–4006.

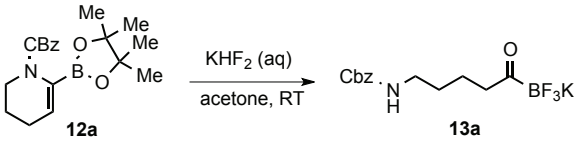
RT for 1 h, placed in a refrigerator overnight (~12 h) and concentrated on a rotary evaporator and under high vacuum with heating until a dry white solid formed. The solids were extracted by stirring in hot CH_3CN (2 x 20 mL), and the product obtained by concentrating the mother liquors to ~10 mL, diluting with Et_2O (30 mL), filtering, and drying the resulting white powder (707 mg, 28% yield). **^{1}H NMR** (400 MHz, DMSO–d_6) 4.25 (t, J = 5.3 Hz, 1H), 3.32 (q, J = 6.3 Hz, 2H), 2.23 (t, J = 6.9 Hz, 2H), 1.34–1.29 (m, 4H); **^{13}C NMR** (100 MHz, DMSO–d_6) 61.3 (CH_2), 44.4 (br, CH_2), 33.2 (CH_2), 19.1 (CH_2); **^{19}F NMR** (282 MHz, acetone–d_6) –149.3; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.68; **IR** (neat) 3543, 1656; **HRMS** (ESI^-) calc'd for $C_5H_9BF_3O_2$ $[M–K]^-$: 169.0654, found: 169.0655.

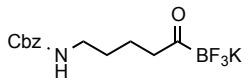




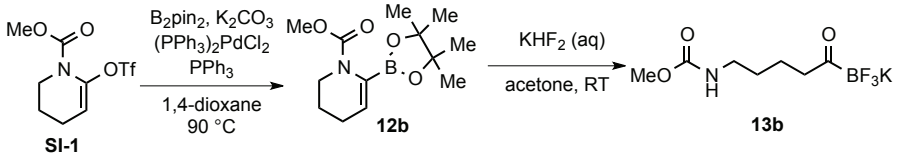
Potassium 5-oxopentanoyltrifluoroborate (11): In a 100 mL flask, *t*-BuOK (1.12 g, 10.0 mmol, 1.0 equiv) was dissolved in THF (24 mL) at RT and cooled to –78 °C in a dry–ice/acetone bath. 2-Ethoxy-3,4-dihydro-2*H*–pyran (**9b**, 1.33 mL, 10.0 mmol, 1.0 equiv) was added dropwise directly into the solution over 2 min, forming a yellow solution. *n*-BuLi (1.7 M in hexane, 5.9 mL, 10.0 mmol, 1.0 equiv) was added down the side of the flask over 10 min, resulting in a gradual darkening of the solution to a bright orange colour. The solution was stirred for 1 h, and then B(O*i*-Pr)$_3$ (3.5 mL, 15.0 mmol, 1.5 equiv) was added dropwise directly into the solution over 5 min. The reaction was kept at –78 °C for 1 h, removed from the bath and stirred at RT for 30 min, over which time the solution became yellow with some white precipitate. The reaction was quenched by the addition of saturated KHF_2 (20 mL) added in four 5 mL portions over 3 min and stirred vigorously for 12 h. The contents of the flask were diluted with Et_2O (20 mL) poured into a separatory funnel, the layers separated, and the organic layer extracted with H_2O (3 x 10 mL). The combined aqueous layers were washed with Et_2O (20 mL), and concentrated under high vacuum with heating until a dry white solid was obtained. This was extracted with acetone (3 x 20 mL), concentrated to ~5 mL and diluted with Et_2O (20 mL). The resulting white powder was filtered and pumped dry. A second crop of equal purity was obtained by extracting the original white solid with additional acetone (2 x 20 mL) and treating the mother liquors as was the first crop. These two crops were combined to give the product as a white powder (408 mg, 20% yield). **^{1}H NMR** (300 MHz, DMSO–d_6) 9.60 (t, J = 1.7 Hz, 1H), 2.33–2.25 (m, 4H), 1.62–1.52 (m, 2H); **^{13}C NMR** (100 MHz, DMSO–d_6) 204.1 (CH), 43.5 (CH_2, overlaps with broad signal, also CH_2), 15.4 (CH_2); **^{19}F NMR** (282 MHz, DMSO–d_6) –146.3; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.91; **IR** (neat) 2883, 1716, 1662; **HRMS** (ESI^-) calc'd for $C_5H_7BF_3O_2$ $[M–K]^-$: 167.0498, found: 169.0497.

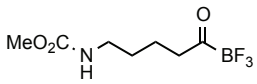
Preparation of Acyltrifluoroborates 13a-b:





Synthesis of 5-(benzyloxylcarbonylamino)pentanoyltrifluoroborate (13a): Known boronate **12a**[9] (480 mg, 1.4 mmol, 1.0 equiv) was dissolved in acetone (7 mL) at RT. With vigorous stirring, saturated aqueous KHF_2 solution (3 mL) was added in 1 mL portions over 2 min. The reaction was stirred at RT for 3 h and then concentrated on high vacuum with heating to give a fine white powder. This was stirred in acetone and filtered (5 x 10 mL), and the combined acetone liquors concentrated. The resulting white solid was dissolved in acetone (5 mL) and diluted with Et_2O (20 mL). The product was isolated by filtering and drying under high vacuum to give a white powder (257 mg, 54% yield). **^{1}H NMR** (300 MHz, acetone–d_6) 7.36–7.31 (m, 5H), 5.63, (br s, 1H), 5.04 (s, 2H), 3.06 (q, J = 6.4 Hz, 2H), 2.39 (t, J = 6.9 Hz, 2H), 1.46–1.38 (m, 4H); **^{13}C NMR** (100 MHz, DMSO–d_6) 156.5 (C), 137.8 (C), 128. (overlapping $2CH_2$ and CH), 128.1 ($2CH_2$), 65.5 (CH_2), 44.2 (br, CH_2), 40.9 (CH_2), 30.0 (CH_2), 19.9 (CH_2); **^{19}F NMR** (282 MHz, acetone–d_6) –148.5; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.88; **IR** (neat) 3309, 1685, 1659, 1535; **HRMS** (ESI^-) calc'd for $C_{13}H_{16}BF_3NO_3$ $[M–K]^-$: 302.1181, found: 302.1182.



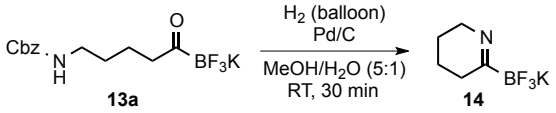


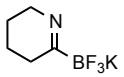
Synthesis of 5-(carbomethoxyamino)pentanoyltrifluoroborate (13b): Vinyl boronate **12b** was prepared based on the reported procedure for coupling N–vinyl triflates with B_2pin_2.[9] Known triflate **SI-1**[10] (1.24 g, 4.28 mmol, 1.0 equiv) was dissolved in 1,4–dioxane (28 mL), and the solution degassed by applying light vacuum and refilling with dry N_2 (three cycles). To this solution were added, in order, B_2pin_2 (1.63 g, 6.42 mmol, 1.5 equiv), $(PPh_3)_2PdCl_2$ (92 mg, 0.13 mmol, 3.0 mol %), PPh_3 (68 mg, 0.26 mmol, 6.0 mol %), and K_2CO_3 (888 mg, 6.42 mmol, 1.5 equiv). The flask was stirred at 90 °C for 12 h, cooled to RT, and diluted with Et_2O (120 mL). The solution was washed with H_2O (2 x 80 mL), dried over Na_2SO_4, filtered, and concentrated to give crude boronate **12b**, which was used without purification.

9. Occhiato, E. G.; Lo Galbo, F.; Guarna, A. *J. Org. Chem.* **2005**, *70*, 7324–7330.
10. Bartali, L.; Guarna, A.; Larini, P.; Occhiato, E. G. *Eur. J. Org. Chem.* **2007**, *2007*, 2152–2163.

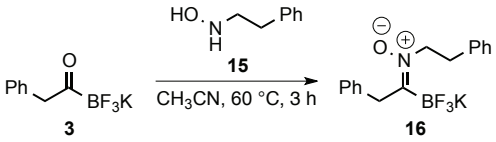
Boronate **12b** was dissolved in acetone (25 mL) at RT and, with vigorous stirring, saturated aqueous KHF_2 solution (15 mL) was added in three 5 mL portions over 2 min. This was stirred at RT for 2 h, then concentrated on a rotary evaporator and under high vacuum (immersed in a 50 °C oil bath). The resulting dry grey solid was stirred in acetone (10 mL), filtered, and treated again with acetone (10 mL). The combined acetone washes were concentrated to ~ 5 mL, and this solution was added to rapidly stirring Et_2O (30 mL). The precipitate was filtered, redissolved in acetone (4 mL), and diluted with Et_2O (20 mL). The resulting solid was filtered and pumped dry to give the product as a beige solid (428 mg, 39% yield over two steps). **^{1}H NMR** (300 MHz, acetone–d_6) 6.15 (br s, 1H), 3.54 (s, 3H), 3.06 (q, *J* = 6.5 Hz, 2H), 2.39 (t, *J* = 6.8 Hz, 2H), 1.46–1.38 (m, 4H); **^{13}C NMR** (100 MHz, DMSO–d_6) 157.1 (C), 51.5 (CH_3), 44.2 (br, CH_2), 40.8 (CH_2), 30.0 (CH_2), 19.9 (CH_2); **^{19}F NMR** (282 MHz, acetone–d_6) –149.4; **^{11}B NMR** (160 MHz, DMSO–d_6) –1.89; **IR** (neat) 3313, 1690, 1660, 1539; **HRMS** (ESI$^-$) calc'd for $C_7H_{12}BF_3NO_3$ [M–K]$^-$: 226.0869, found: 226.0866.

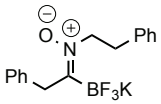
Synthesis of Acyltrifluoroborate Derivatives 14 and 16:





Potassium (3,4,5,6-tetrahydropyridin-2-yl)trifluoroborate (14): N–CBz acyltrifluoroborate **13a** (34.1 mg, 0.1 mmol, 1.0 equiv) was dissolved in 3:1 MeOH/H_2O (3 mL) at RT. The solution was degassed by evacuating the flask under light vacuum and refilling with N_2 (three cycles), and Pd/C (10% wt/wt, 5 mg) was added. The atmosphere was exchanged for H_2 by placing the flask under light vacuum and refilling with a hydrogen from a balloon (three cycles). The reaction was stirred under an H_2 atmosphere (balloon) for 45 min, degassed by placing under light vacuum and refilling with N_2 (three cycles), then filtered through a pad of Celite. The pad was washed with 3:1 MeOH/H_2O (3 x 1 mL), and the combined washes concentrated on a rotovap to remove MeOH, and the water removed on a lyophilizer. The resulting dry white solid was pure **14** (24.4 mg, 99% yield). **^{1}H NMR** (400 MHz, CD_3CN) 3.46 (t, *J* = 5.8 Hz, 2H), 2.74 (t *J* = 6.1 Hz, 2H), 1.84–1.78 (m, 2H), 1.71–1.65 (m, 2H); **^{13}C NMR** (100 MHz, CD_3CN–d_6) 43.7 (CH_2), 28.2 (CH_2), 19.5 (CH_2), 15.9 (CH_2); **^{19}F NMR** (282 MHz, acetone–d_6) –150.8; **^{11}B NMR** (160 MHz, DMSO–d_6) –0.53; **IR** (neat) 2941, 1658, 1444; **HRMS** (ESI$^-$) calc'd for $C_5H_8BF_3N$ [M–K]$^-$: 150.0708, found: 150.0707.

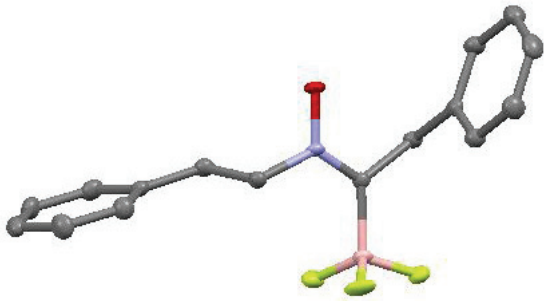




Preparation of nitrone 16: Phenacetyltrifluoroborate **3**[11] (1.16 g, 5.0 mmol, 1.0 equiv) was dissolved in CH_3CN (25 mL) at RT. Hydroxylamine **15** (0.82 g, 6.0 mmol, 1.2 equiv) was added, and the reaction placed in a 60 °C oil bath. After 1.5 h, LCMS analysis of the reaction mixture showed incomplete conversion of the acylborane, and another portion of **15** was added (150 mg). After an additional 1.5 h at 60 °C, the reaction was complete as demonstrated by LCMS analysis. It was cooled to RT, concentrated to ~ 5 mL, and diluted with Et_2O. This was sonicated until a free–flowing powder formed, filtered, and the solid washed with Et_2O (2 x 10 mL). This was ground with a mortar and pestle to break up large pieces and pumped dry on high vacuum to give the nitrone as a white powder (1.6 g, 92% yield). **^{1}H NMR** (300 MHz, acetone–d_6) 7.39 (d, *J* = 7.4 Hz, 2H), 7.27–7.21 (m, 4H), 7.17–7.09 (m, 3H), 7.05–7.00 (m, 1H), 4.16–4.11 (m, 2H), 3.76 (s, 2H), 3.19–3.13 (m, 2H); **^{13}C NMR** (100 MHz, DMSO–d_6) 140.5 (C), 139.8 (C), 129.4 (2CH), 129.1 (2CH), 128.8 (2CH), 128.0 (2CH), 126.5 (CH), 125.3 (CH), 62.7 (CH_2), 35.5 (CH_2), 35.2 (CH_2); **^{19}F NMR** (282 MHz, acetone–d_6) –138.9; **^{11}B NMR** (160 MHz, DMSO–d_6) 0.77; **IR** (neat) 2960, 1603, 1571, 1497, 1453; **HRMS** (ESI^-) calc'd for [$C_{16}H_{16}BF_3NO^-$]: 306.1285, found: 306.1282.

X–ray quality crystals of **16** were grown by dissolving a small amount in a minimum volume of acetone and diffusing Et_2O into it by placing the vial in a chamber partly filled with Et_2O. Clear, colourless rods were obtained from which a crystal was cut.

X-Ray crystal structure of nitrone 16:

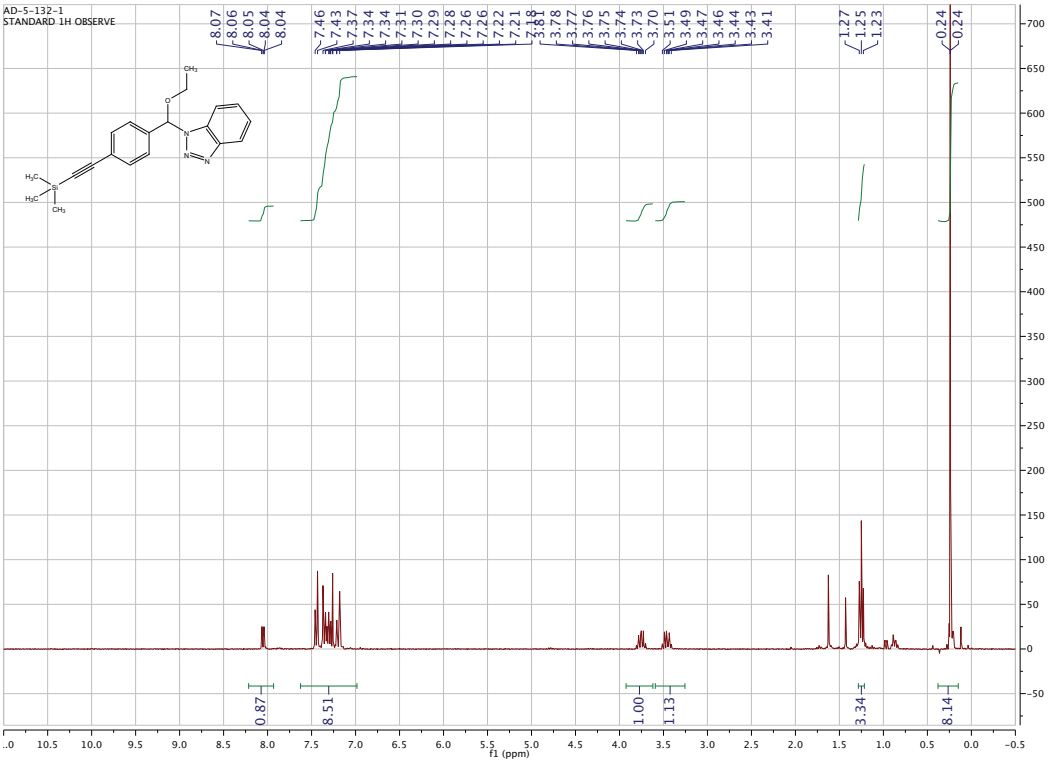


11. Molander, G. A.; Raushel, J.; Ellis, N. M. *J. Org. Chem.* **2010**, *75*, 4304–4306.

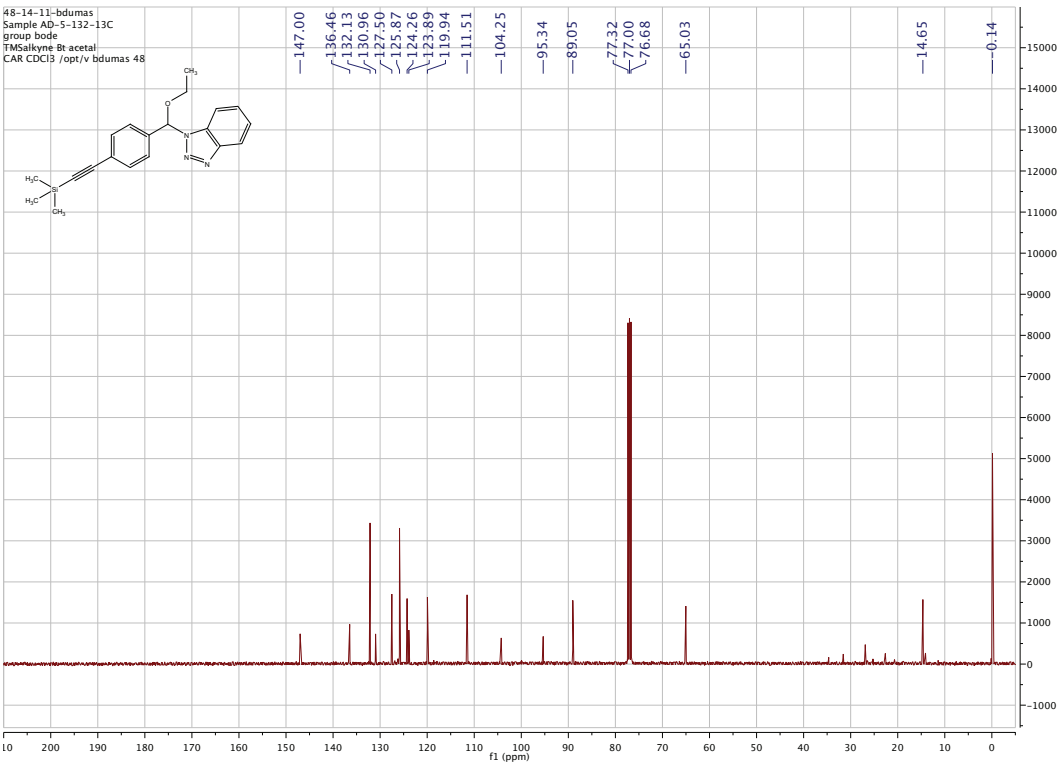
Spectroscopic Data:

1-(Ethoxy(4-((trimethylsilyl)ethynyl)phenyl)methyl)-1*H*-benzotriazole (4d):

^{1}H NMR (300 MHz, $CDCl_3$)

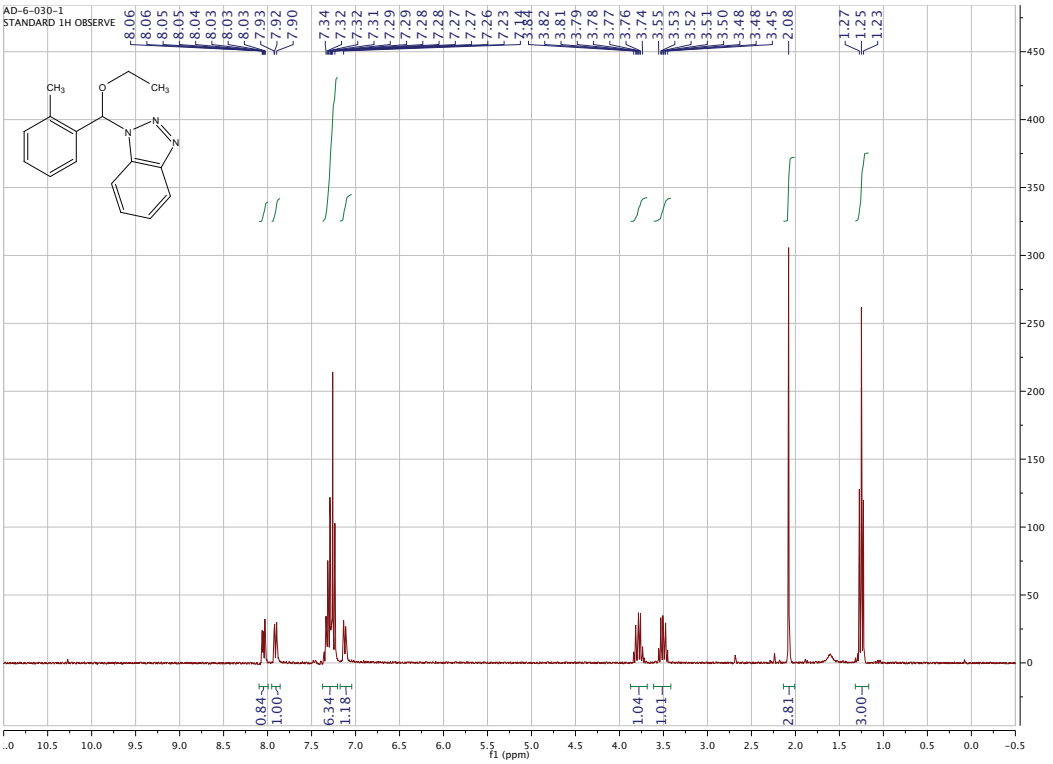


^{13}C NMR (100 MHz, $CDCl_3$)

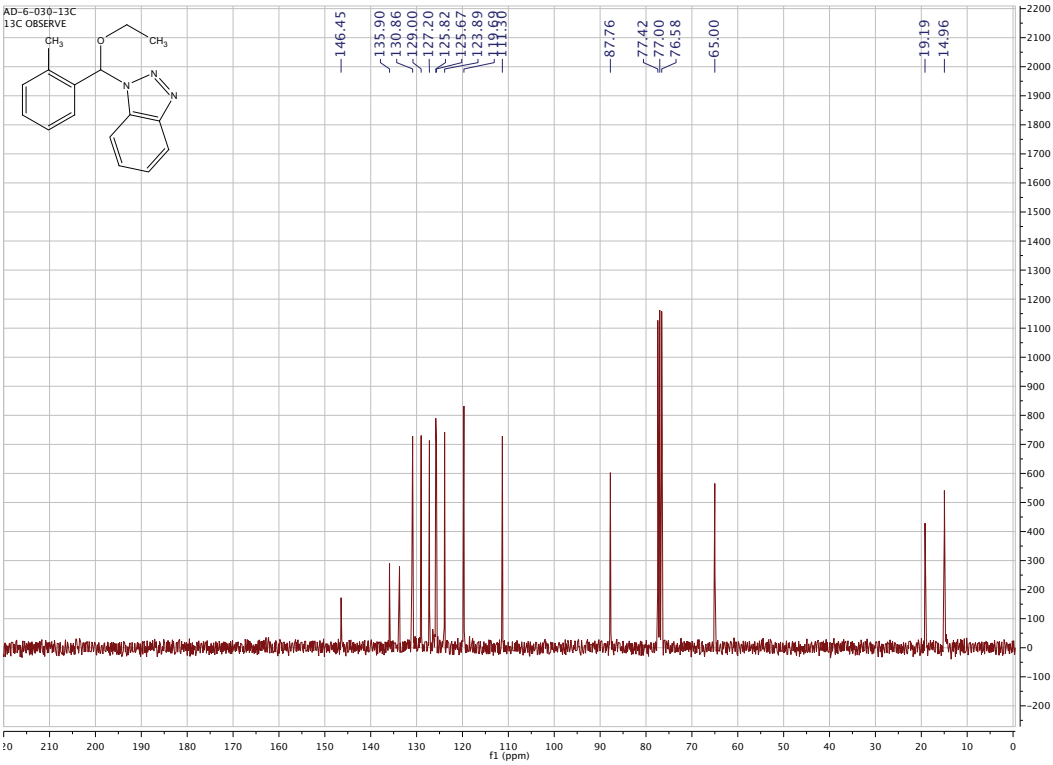


1-(Ethoxy(o-tolyl)methyl)-1H-benzotriazole (4f):

^{1}H NMR (300 MHz, $CDCl_3$)

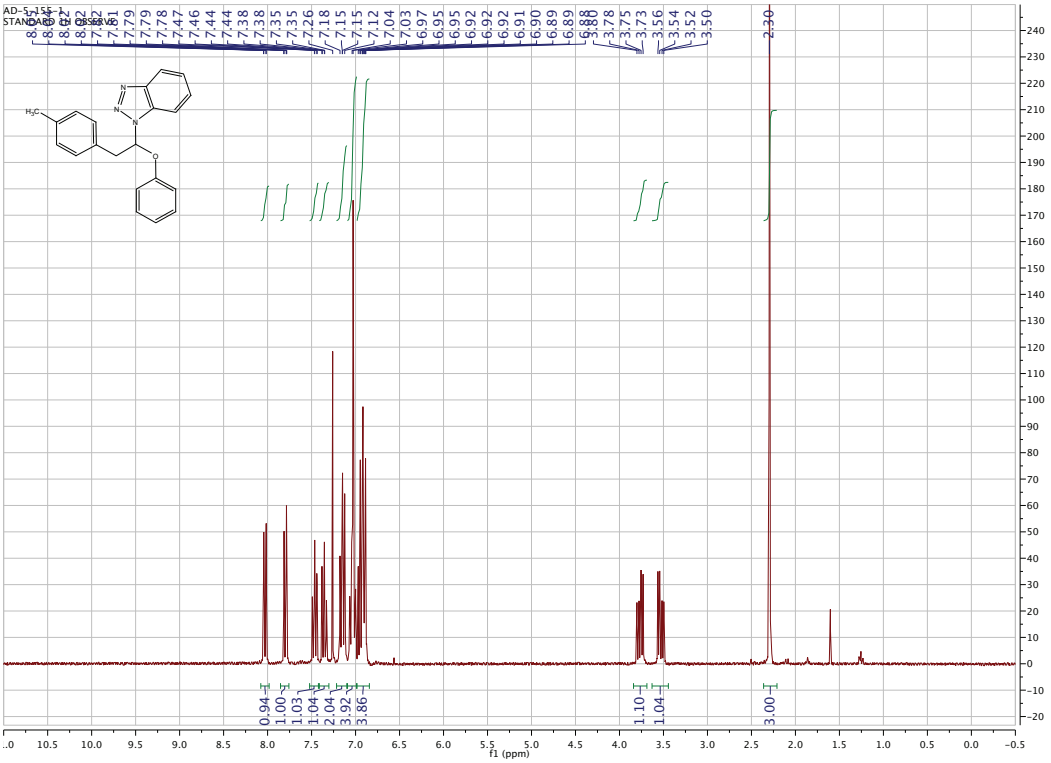


^{13}C NMR (100 MHz, $CDCl_3$)

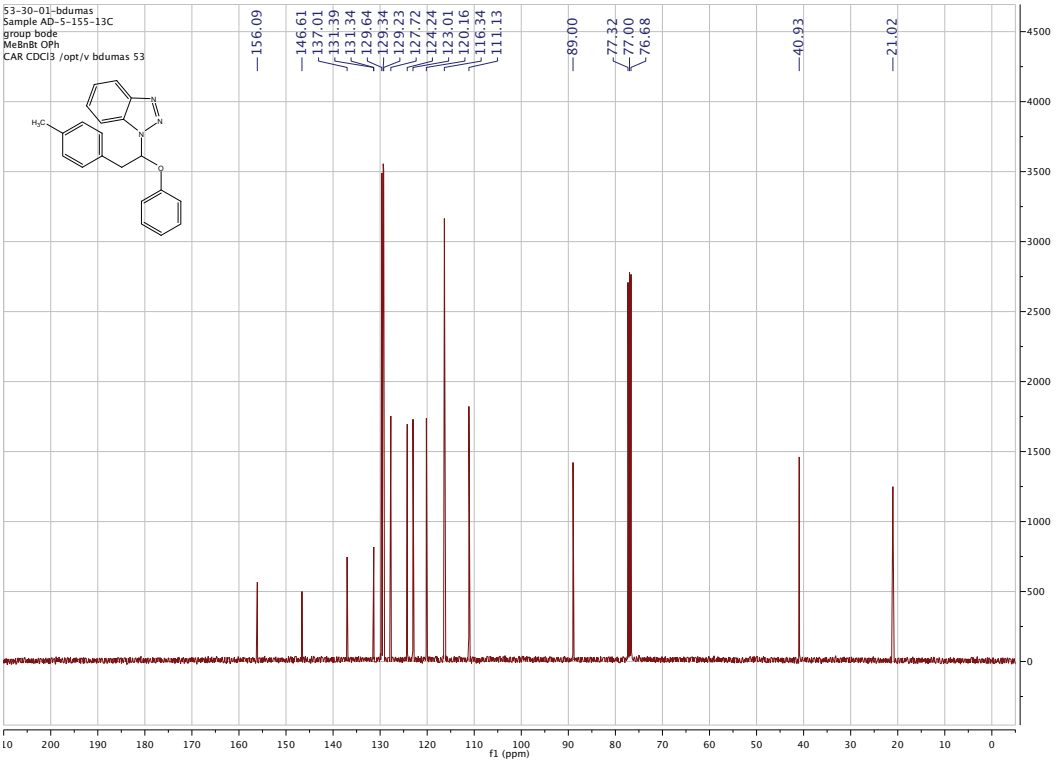


1-(1-Phenoxy-2-(*p*-tolyl)ethyl)-1*H*-benzotriazole (7a):

^{1}H NMR (300 MHz, $CDCl_3$)

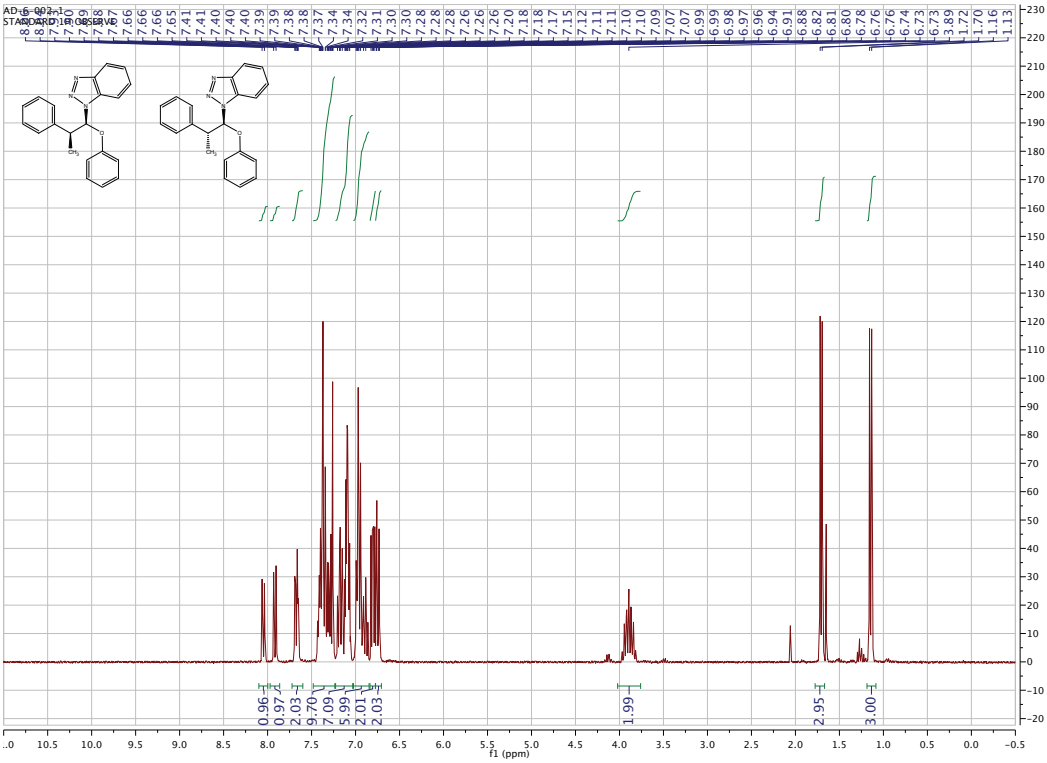


^{13}C NMR (100 MHz, $CDCl_3$)

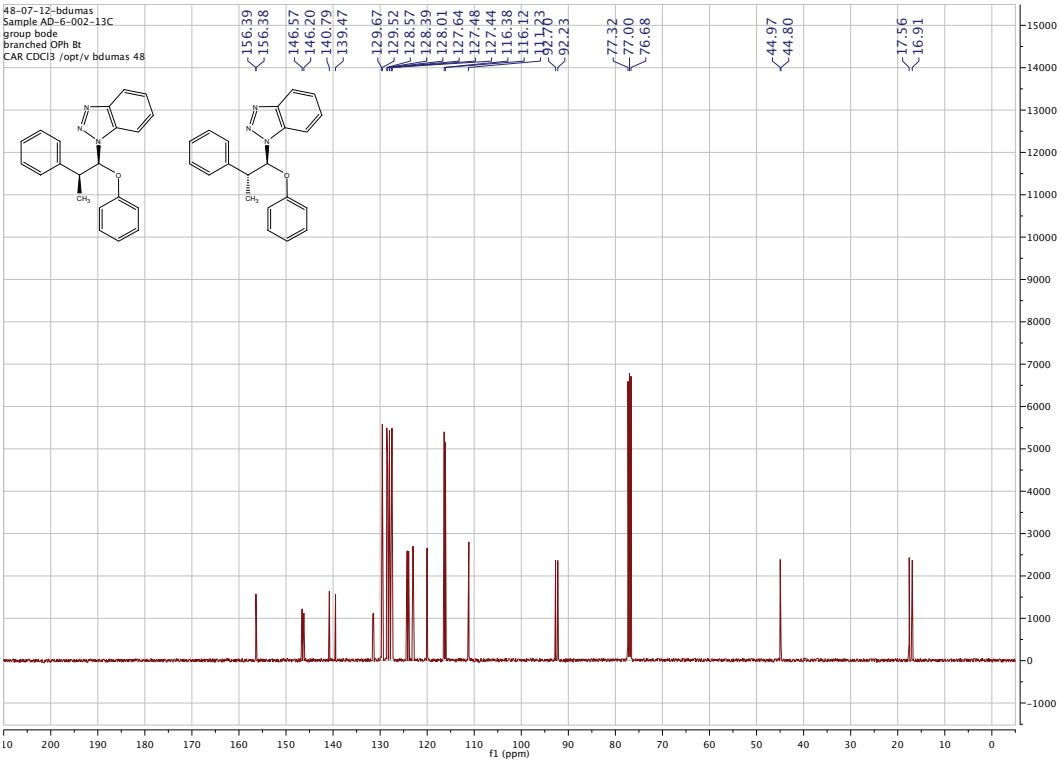


1-(1-Phenoxy-2-phenylpropyl)-1*H*-benzotriazole (7b):

^{1}H NMR (300 MHz, $CDCl_3$)

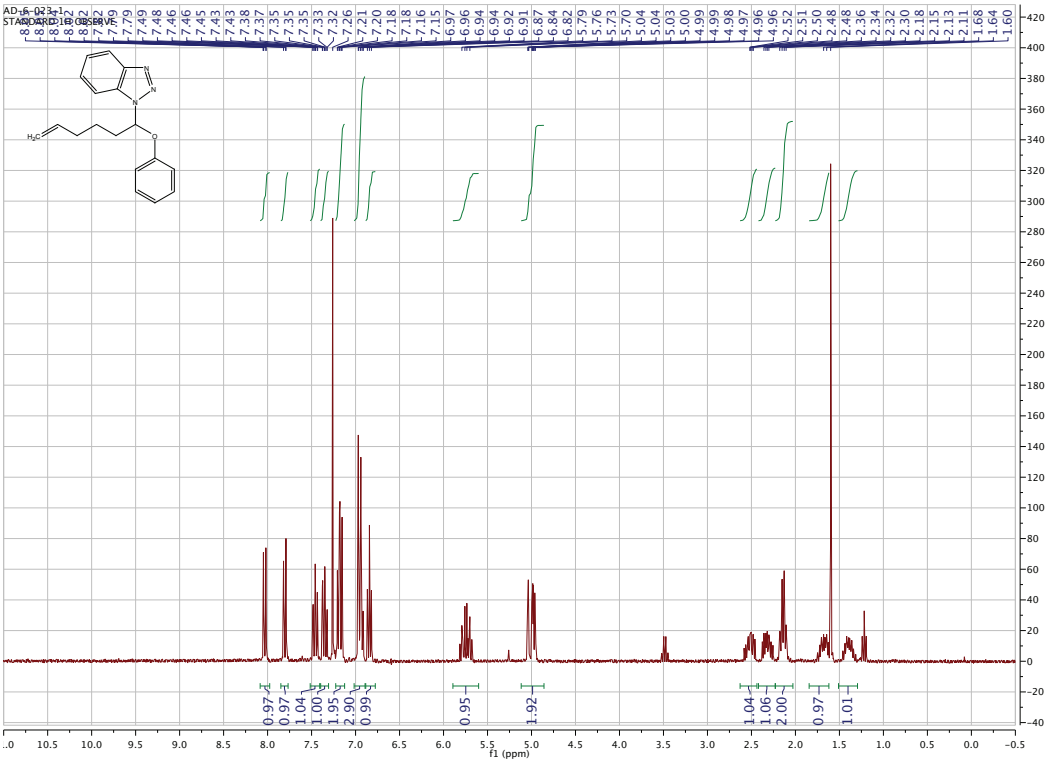


^{13}C NMR (100 MHz, $CDCl_3$)

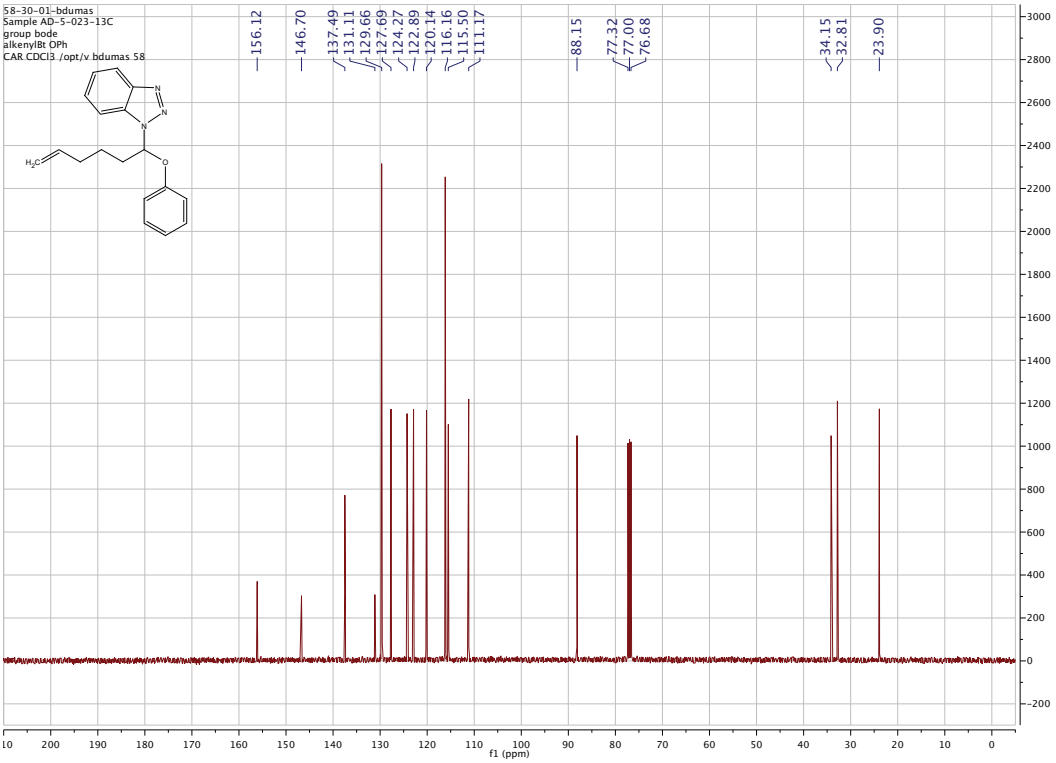


1-(1-Phenoxyhex-5-en-1-yl)-1*H*-benzotriazole (7e):

^{1}H NMR (300 MHz, $CDCl_3$)

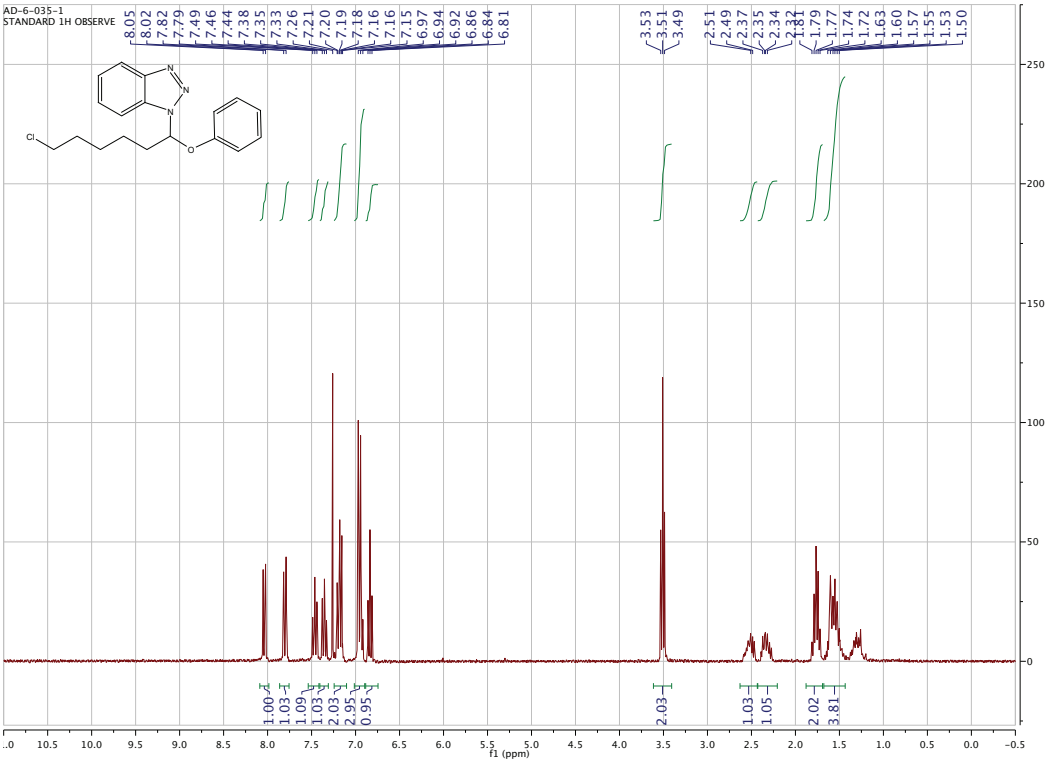


^{13}C NMR (100 MHz, $CDCl_3$)

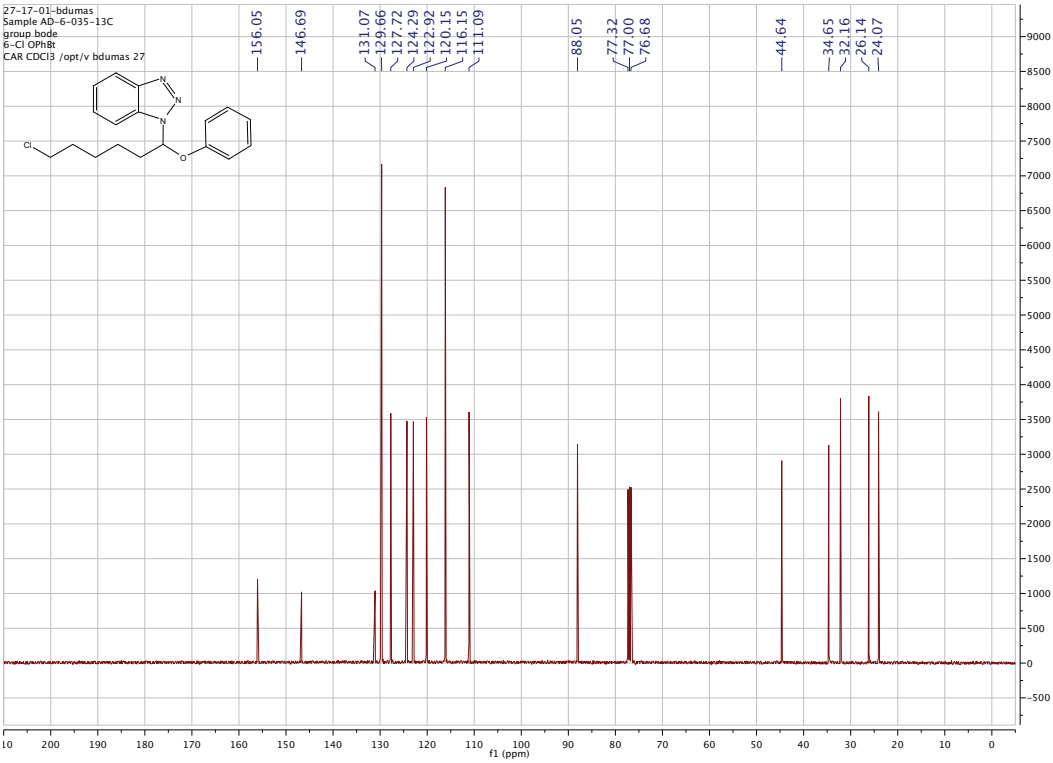


1-(6-Chloro-1-phenoxyhexyl)-1*H*-benzotriazole (7f):

^{1}H NMR (300 MHz, $CDCl_3$)

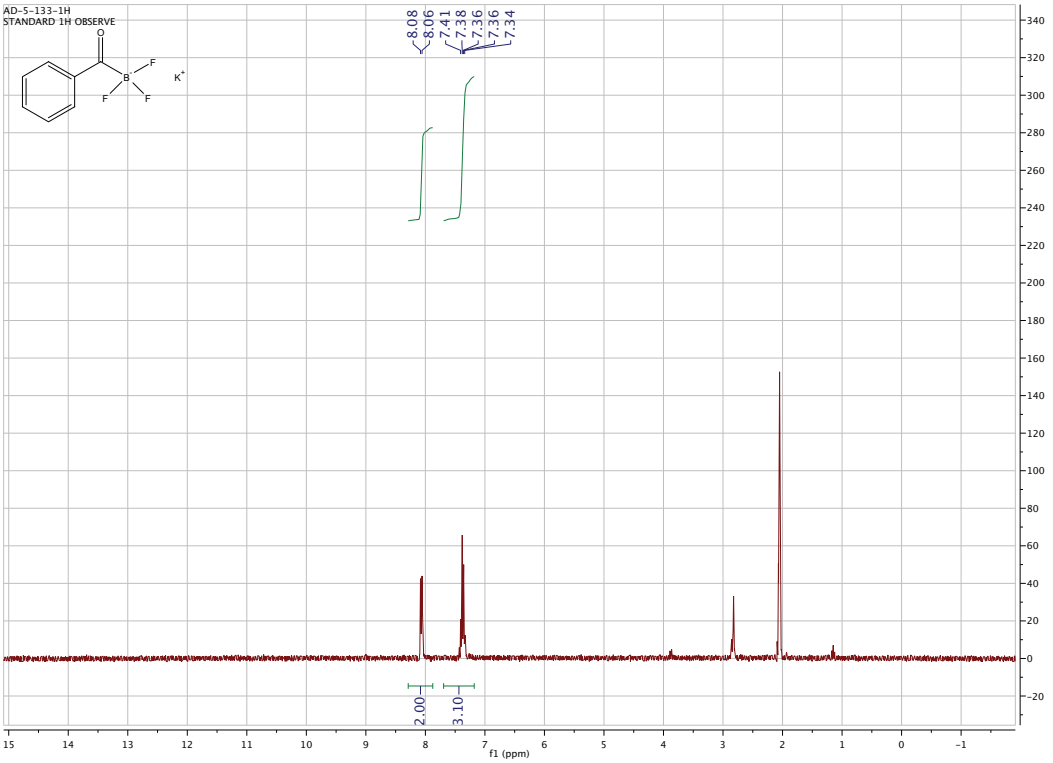


^{13}C NMR (100 MHz, $CDCl_3$)

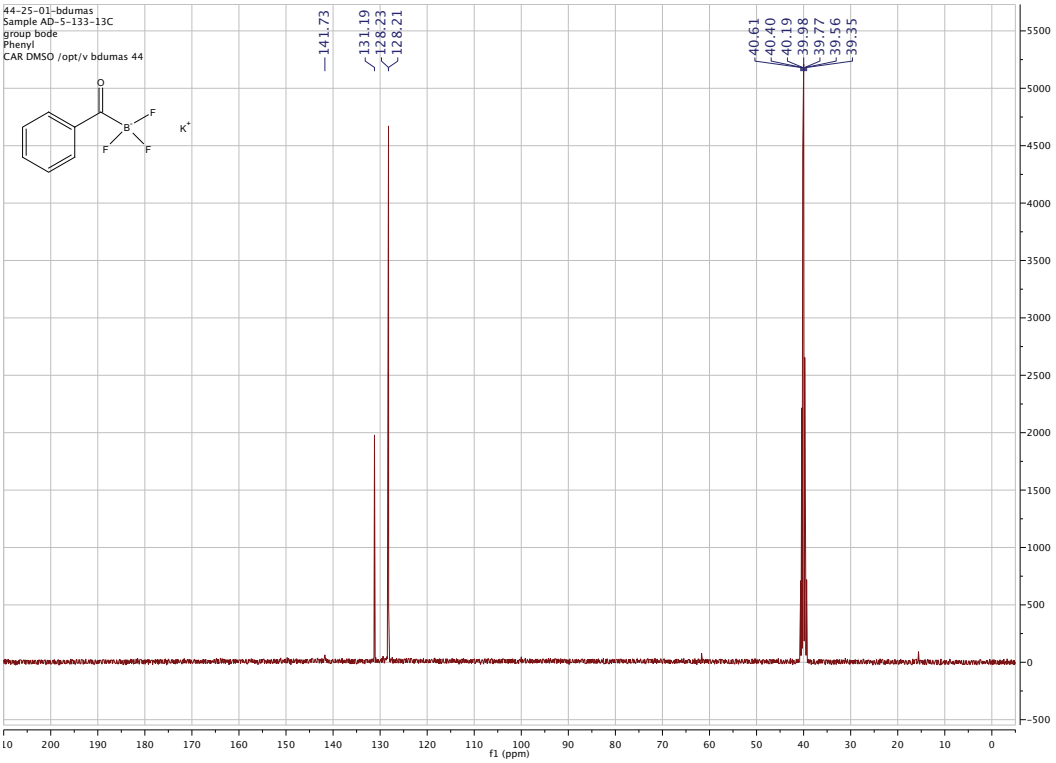


Potassium benzoyltrifluoroborate (5a):

^{1}H NMR (300 MHz, acetone-d_6)

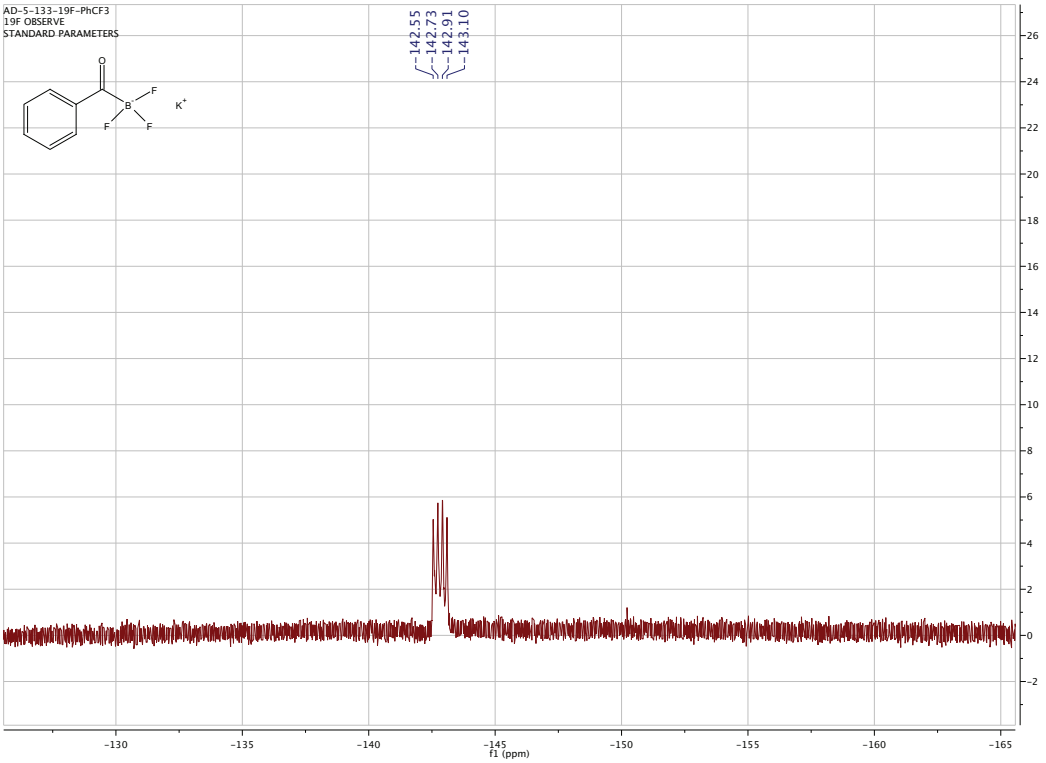


^{13}C NMR (100 MHz, DMSO-d_6)

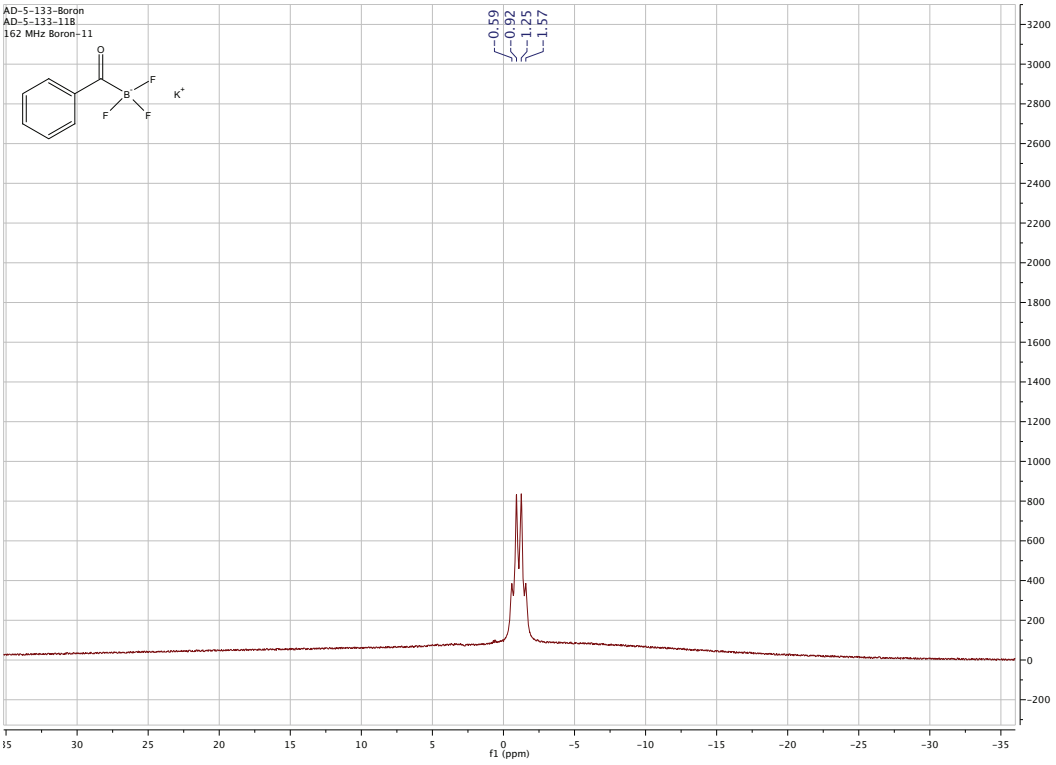


Potassium benzoyltrifluoroborate (5a):

^{19}F NMR (282 MHz, acetone-d_6)

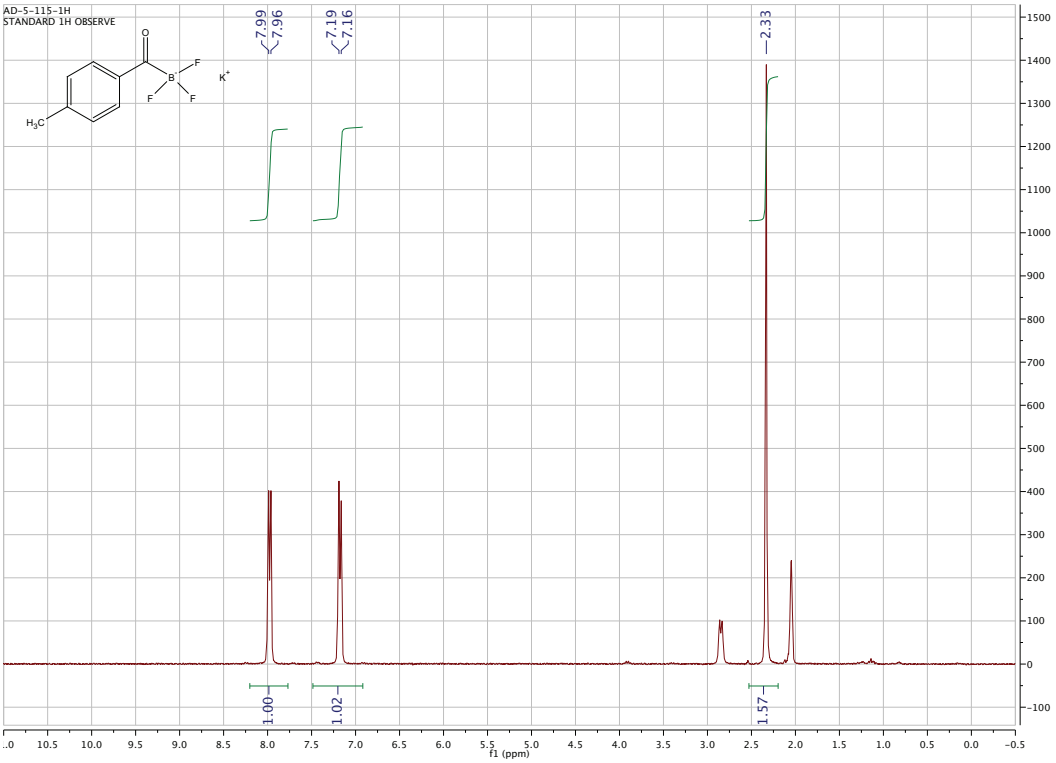


^{11}B NMR (160 MHz, DMSO-d_6)

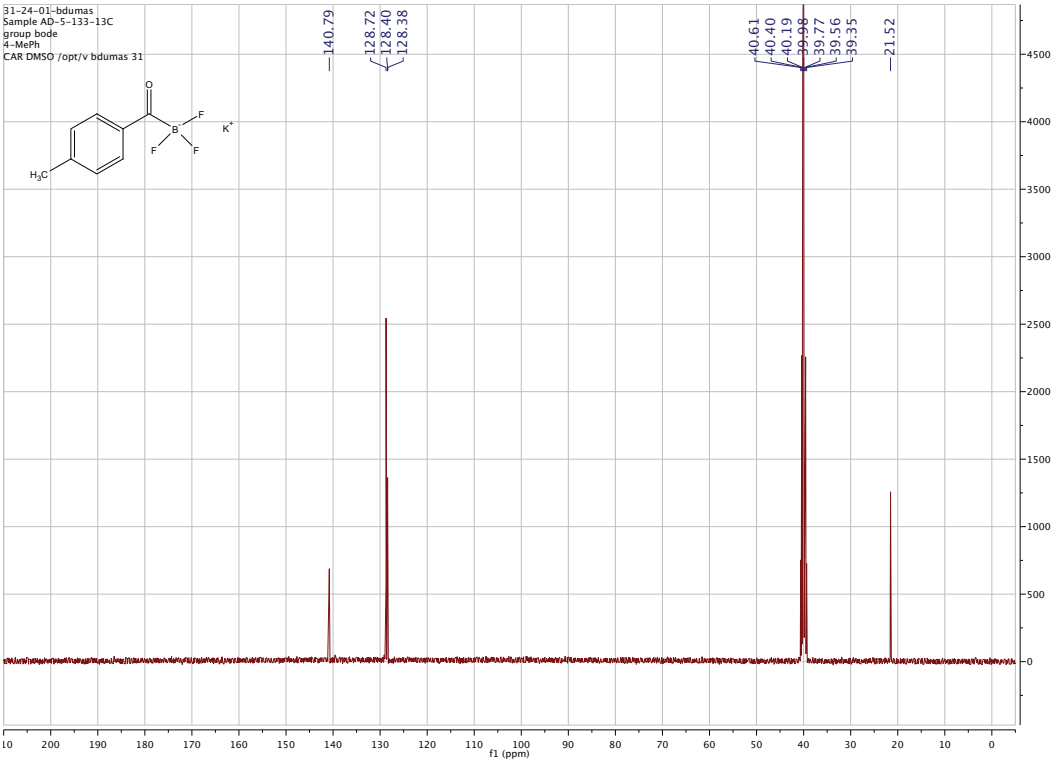


Potassium 4-methylbenzoyltrifluoroborate (5b):

^{1}H NMR (300 MHz, acetone-d_6)

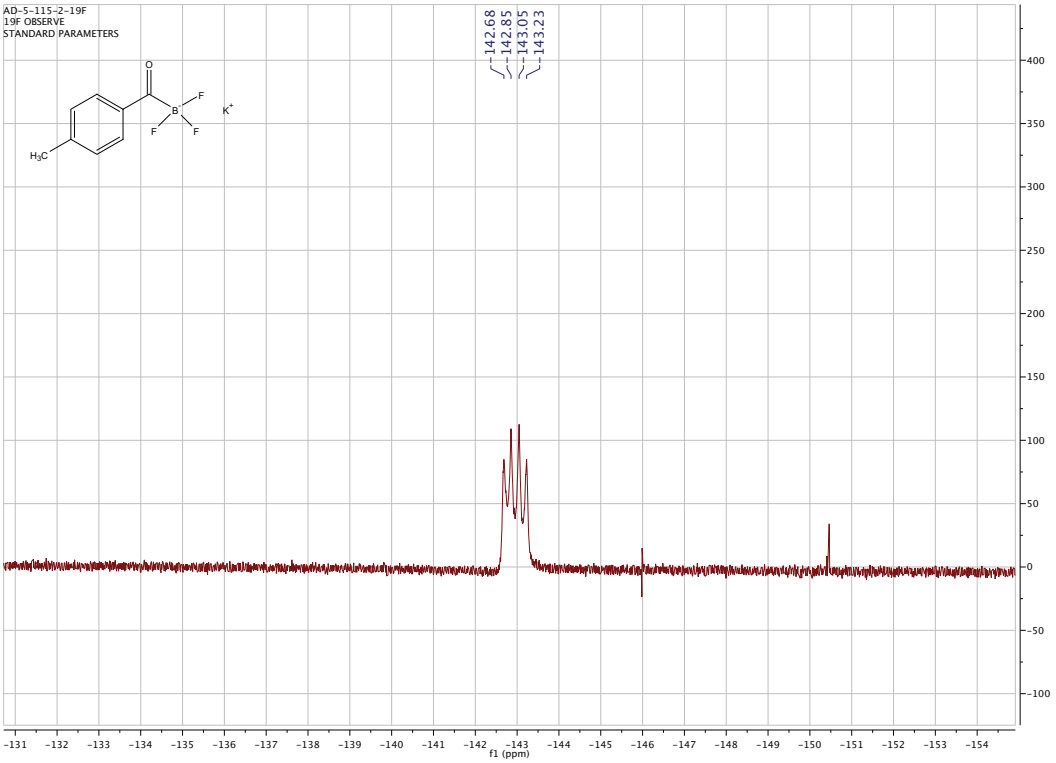


^{13}C NMR (100 MHz, DMSO-d_6)

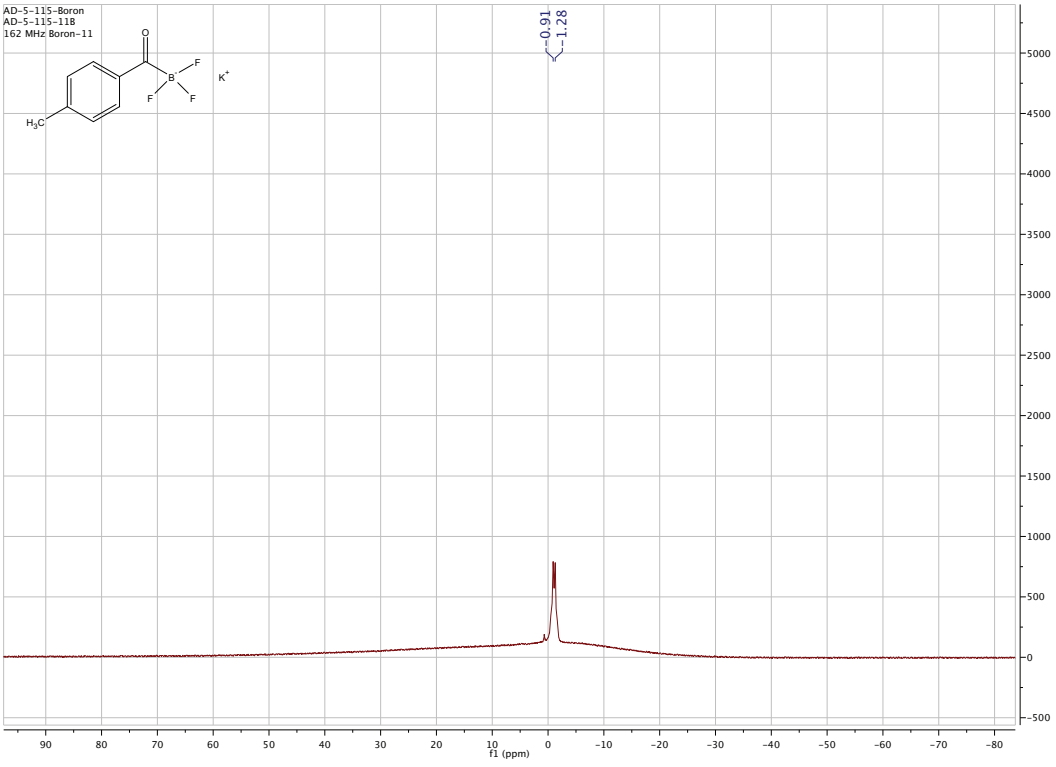


Potassium 4-methylbenzoyltrifluoroborate (5b):

^{19}F NMR (282 MHz, acetone-d_6)

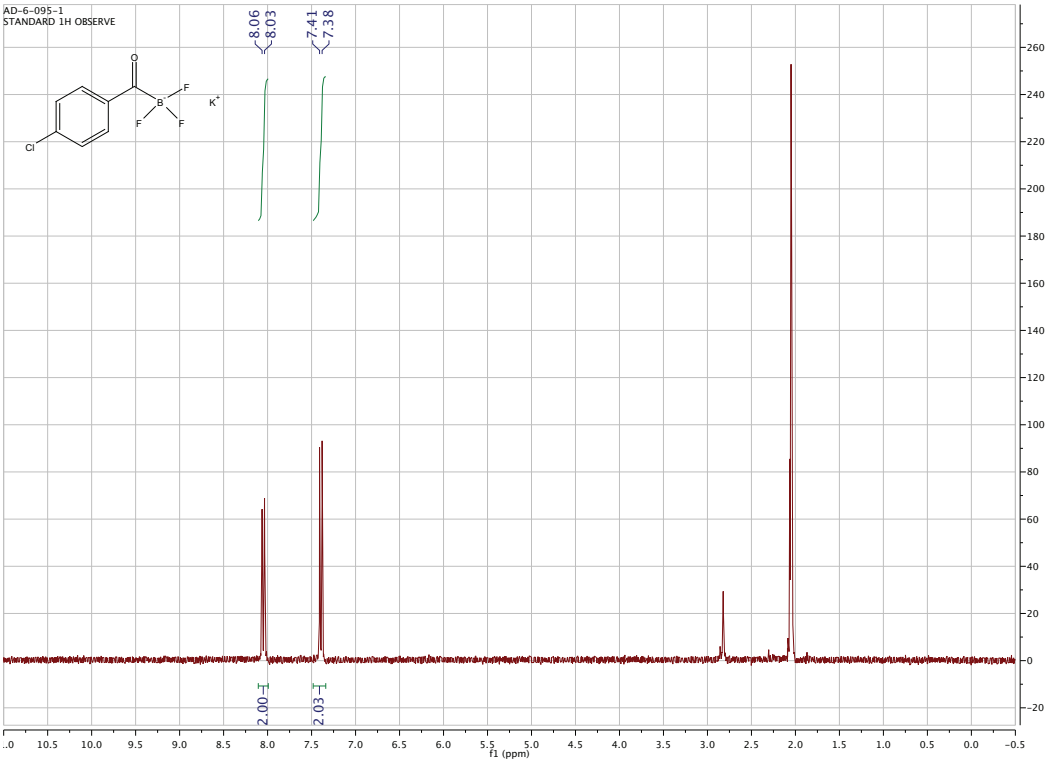


^{11}B NMR (160 MHz, DMSO-d_6)

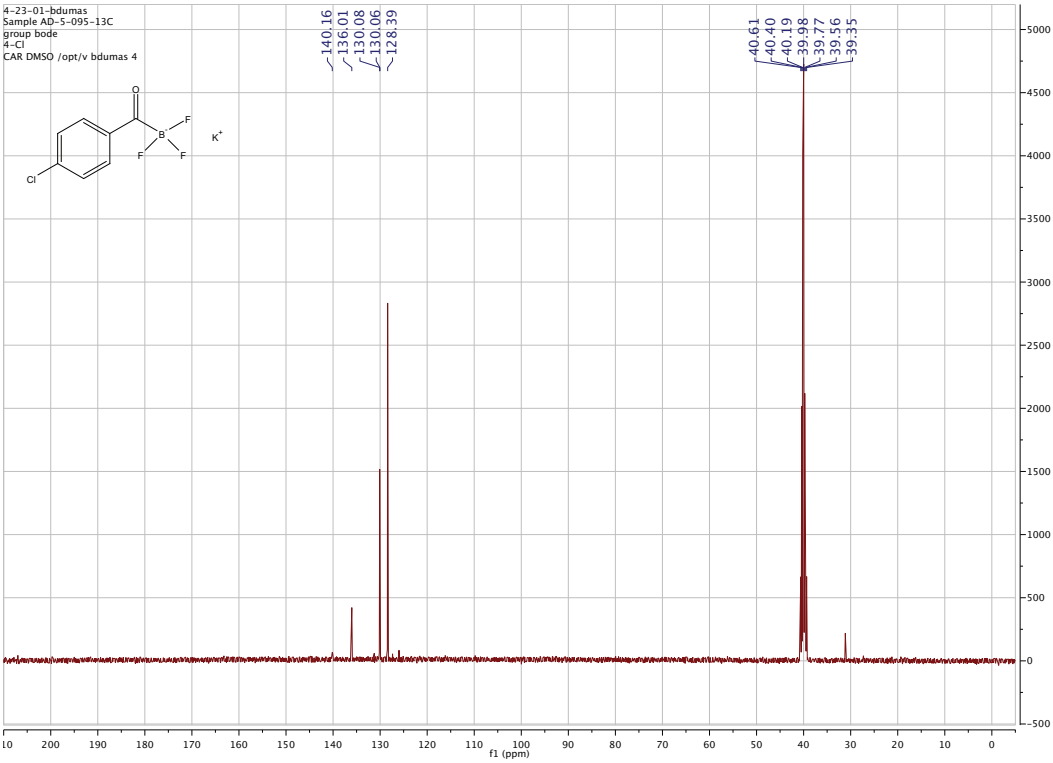


Potassium 4-chlorobenzoyltrifluoroborate (5c):

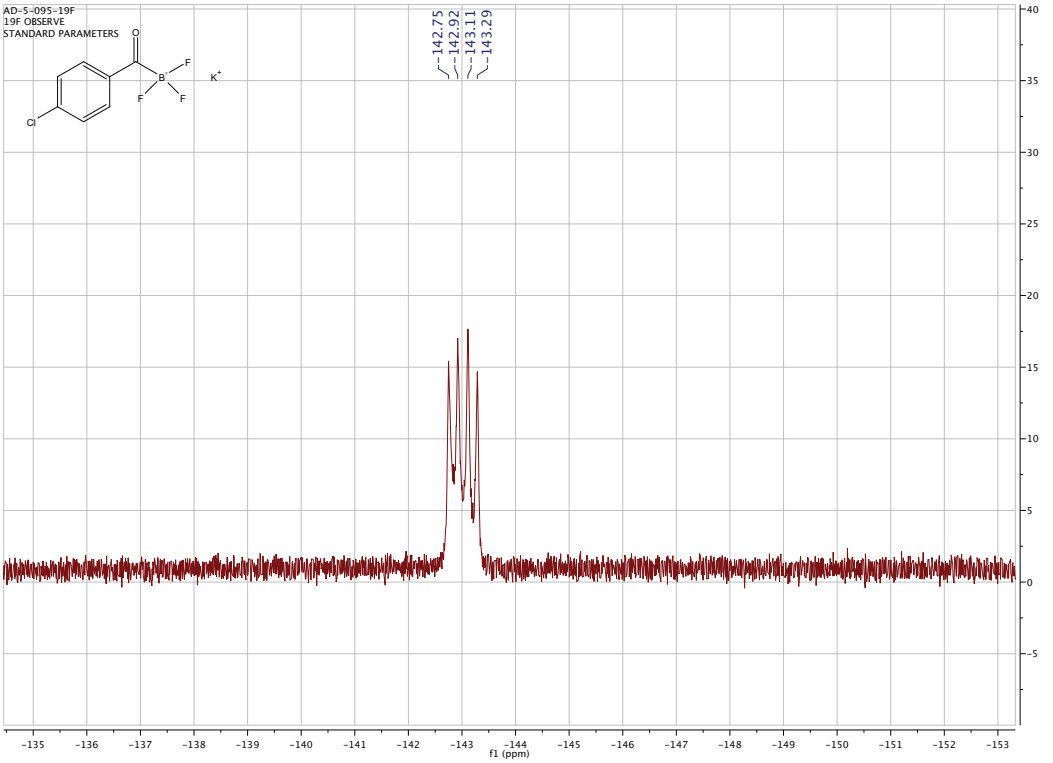
^{1}H NMR (300 MHz, acetone-d_6)



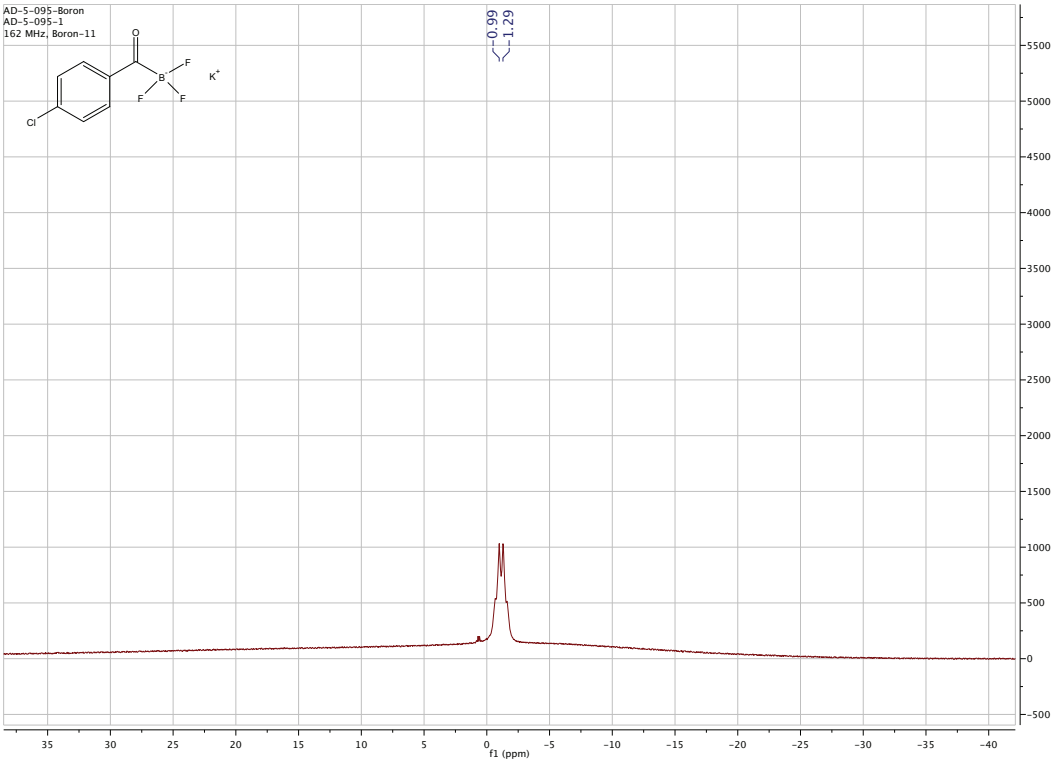
^{13}C NMR (100 MHz, DMSO-d_6)



^{19}F NMR (282 MHz, acetone-d_6)

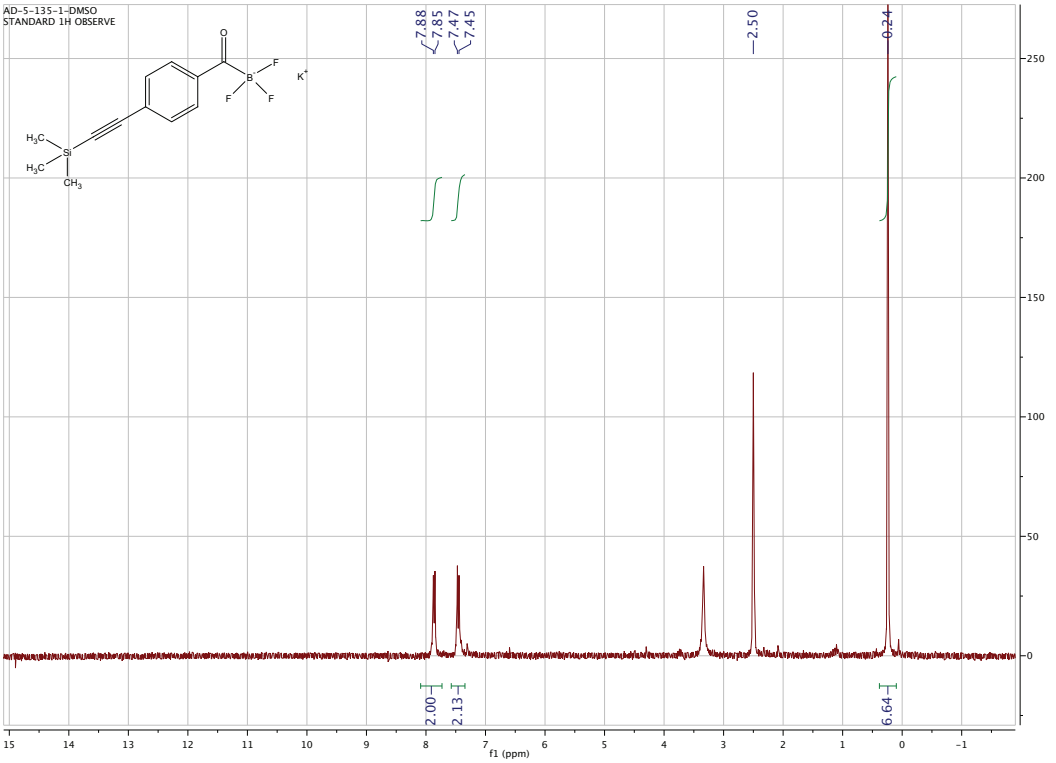


^{11}B NMR (160 MHz, DMSO-d_6)

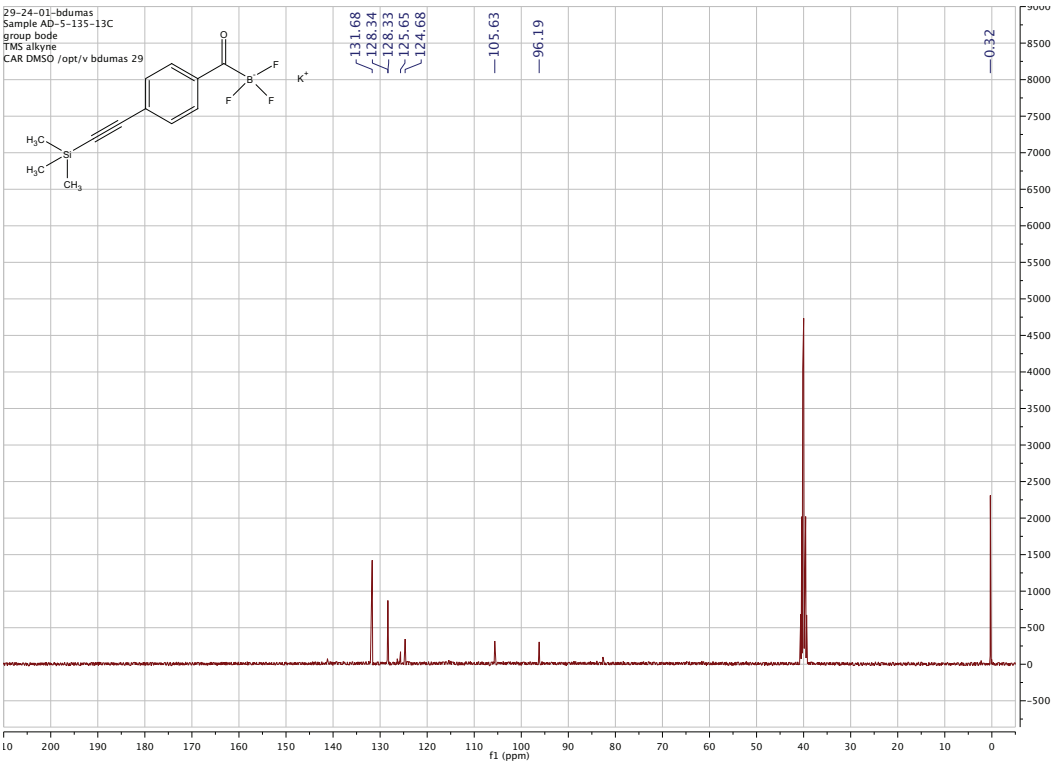


Potassium 4-((trimethylsilyl)ethynyl)benzoyltrifluoroborate (5d):

^{1}H NMR (300 MHz, DMSO-d_6)

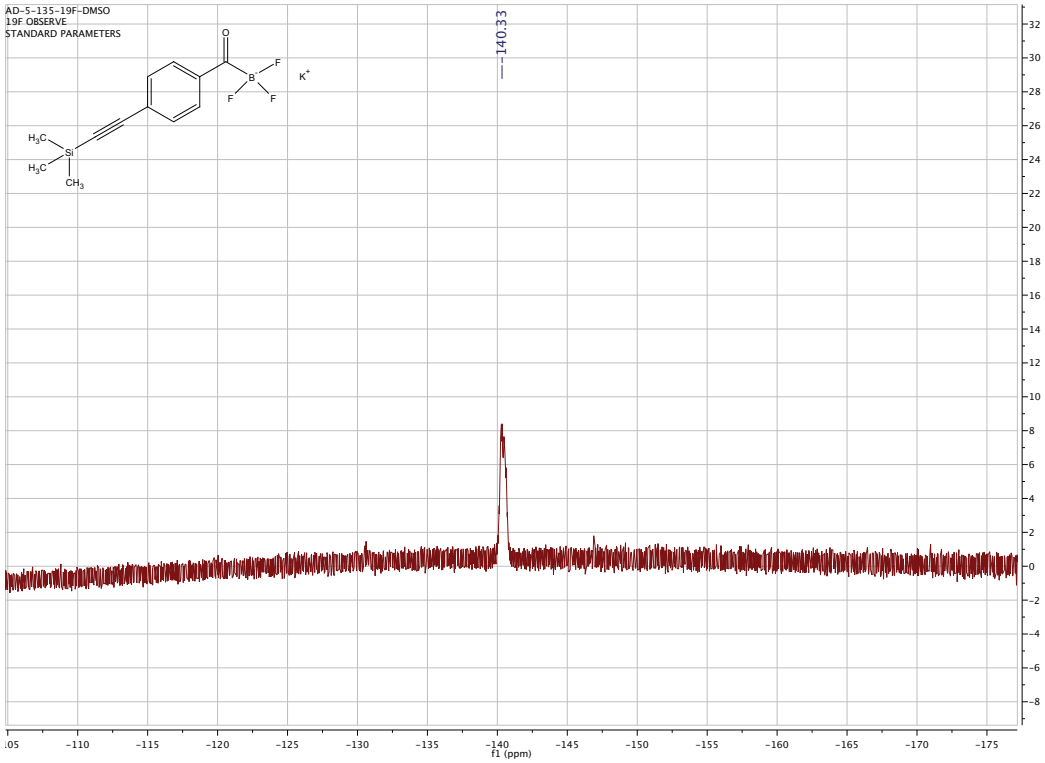


^{13}C NMR (100 MHz, DMSO-d_6)

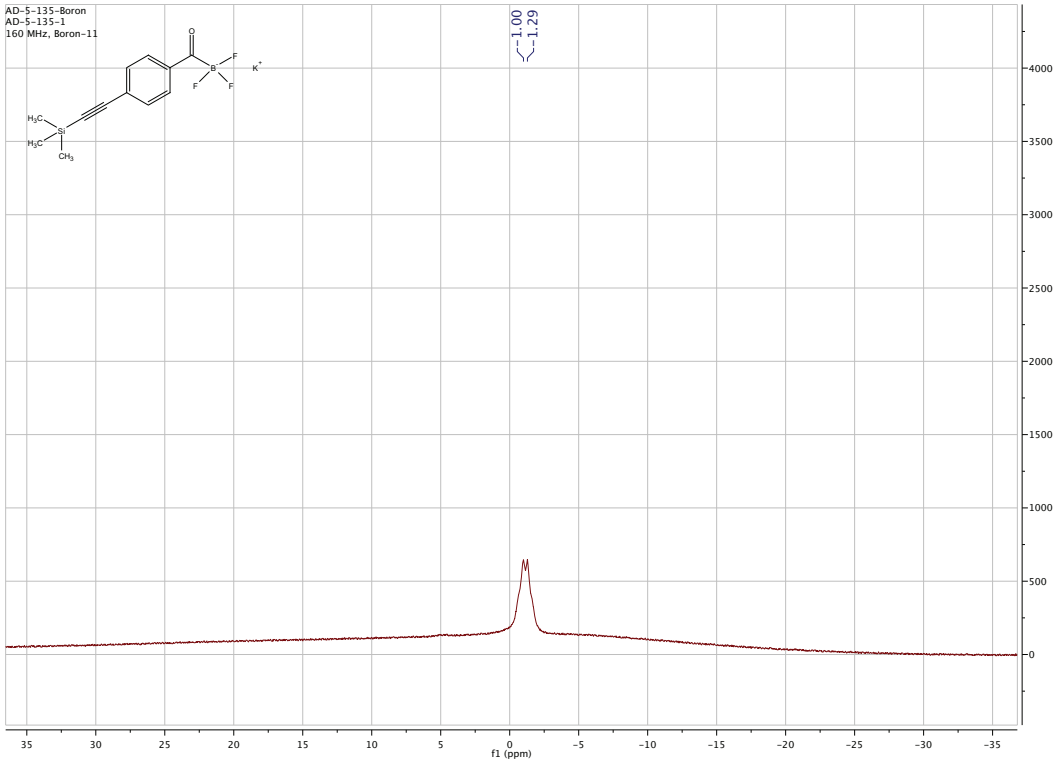


Potassium 4-((trimethylsilyl)ethynyl)benzoyltrifluoroborate (5d):

^{19}F NMR (282 MHz, DMSO-d_6)

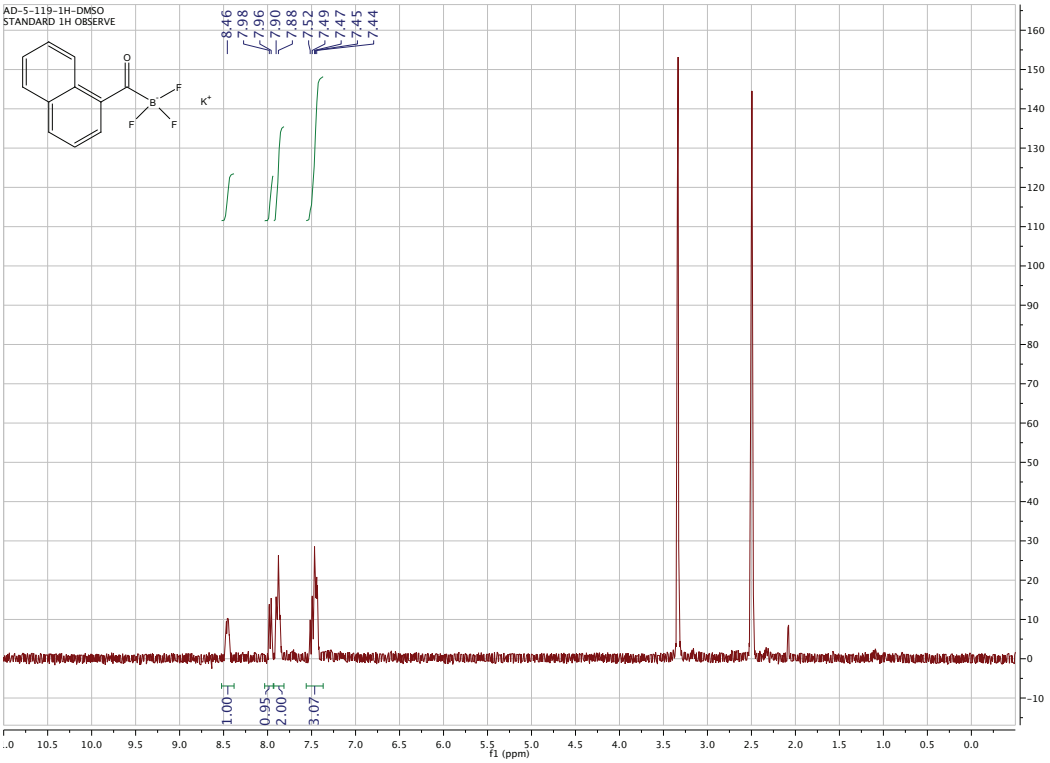


^{11}B NMR (160 MHz, DMSO-d_6)

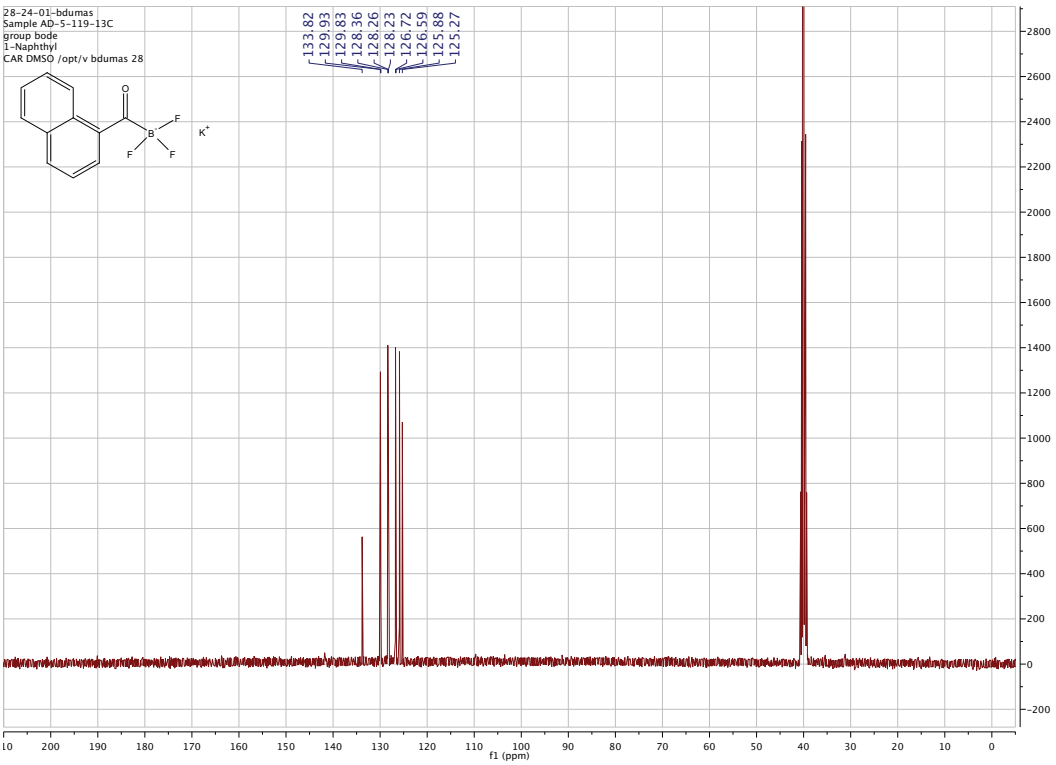


Potassium 1-naphthoyltrifluoroborate (5e):

^{1}H NMR (300 MHz, DMSO-d_6)

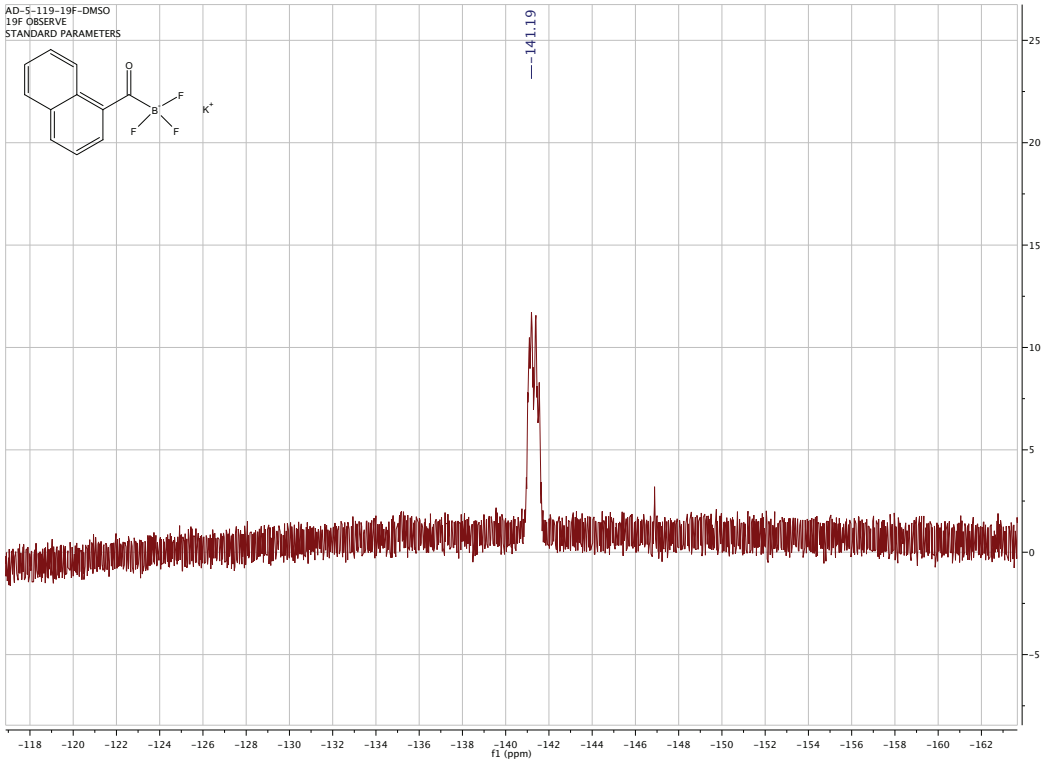


^{13}C NMR (100 MHz, DMSO-d_6)

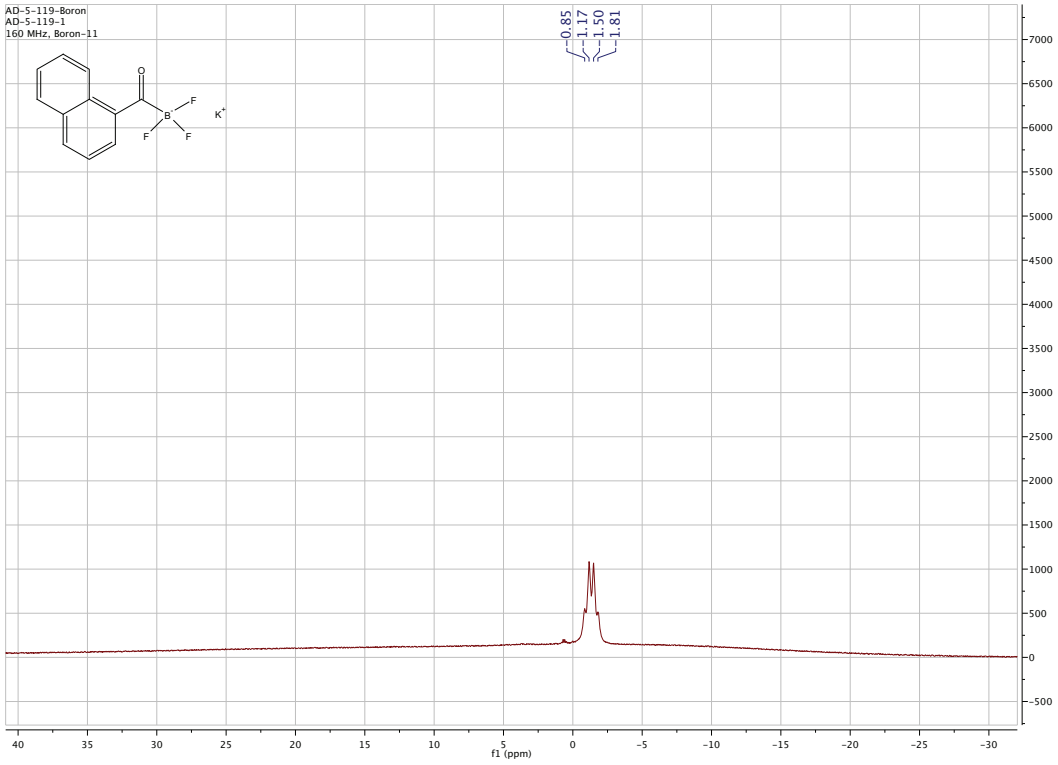


Potassium 1-naphthoyltrifluoroborate (5e):

^{19}F NMR (282 MHz, DMSO-d_6)

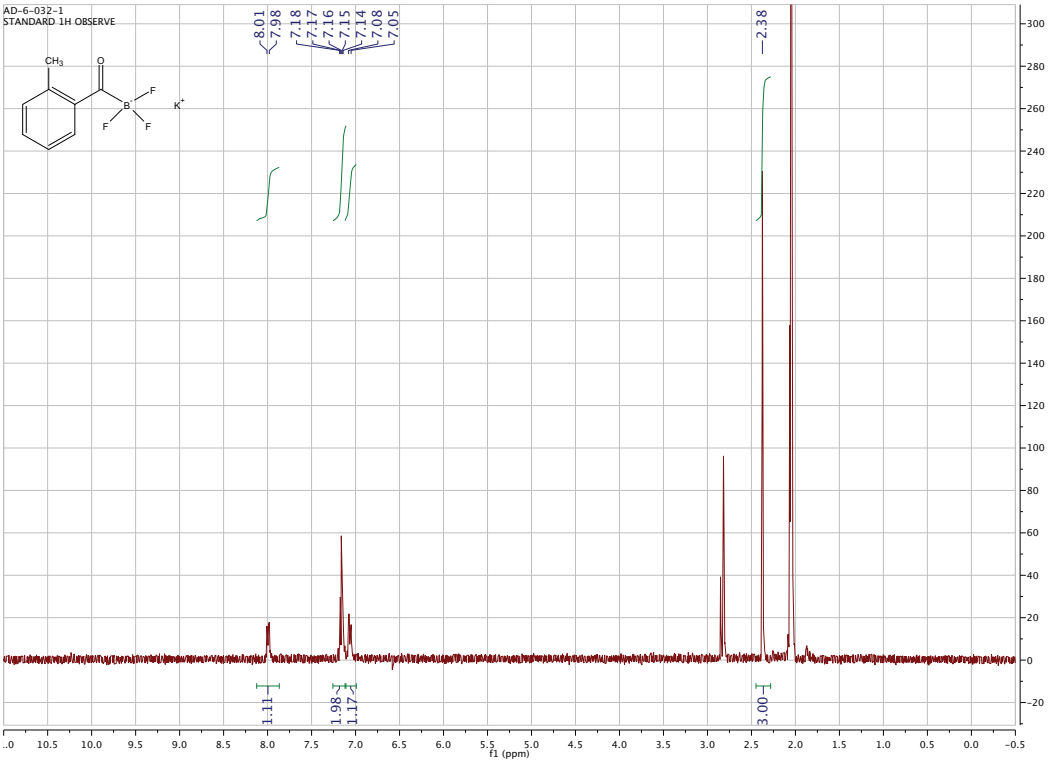


^{11}B NMR (160 MHz, DMSO-d_6)

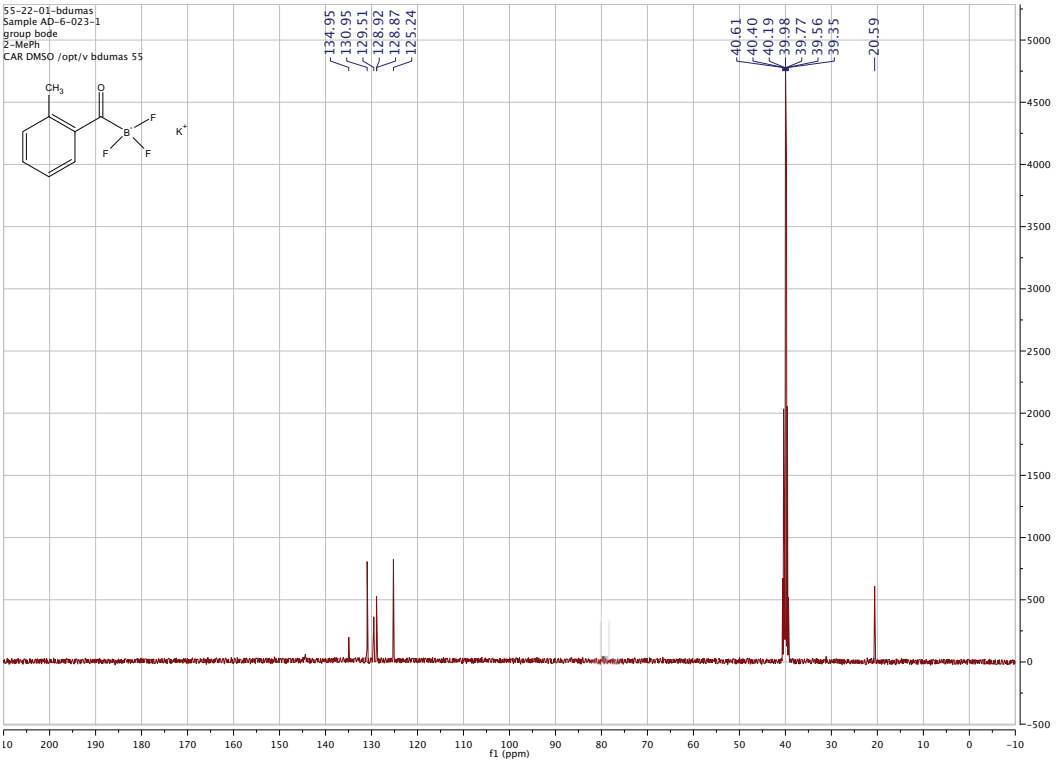


Potassium 2-methylbenzoyltrifluorobrate (5f):

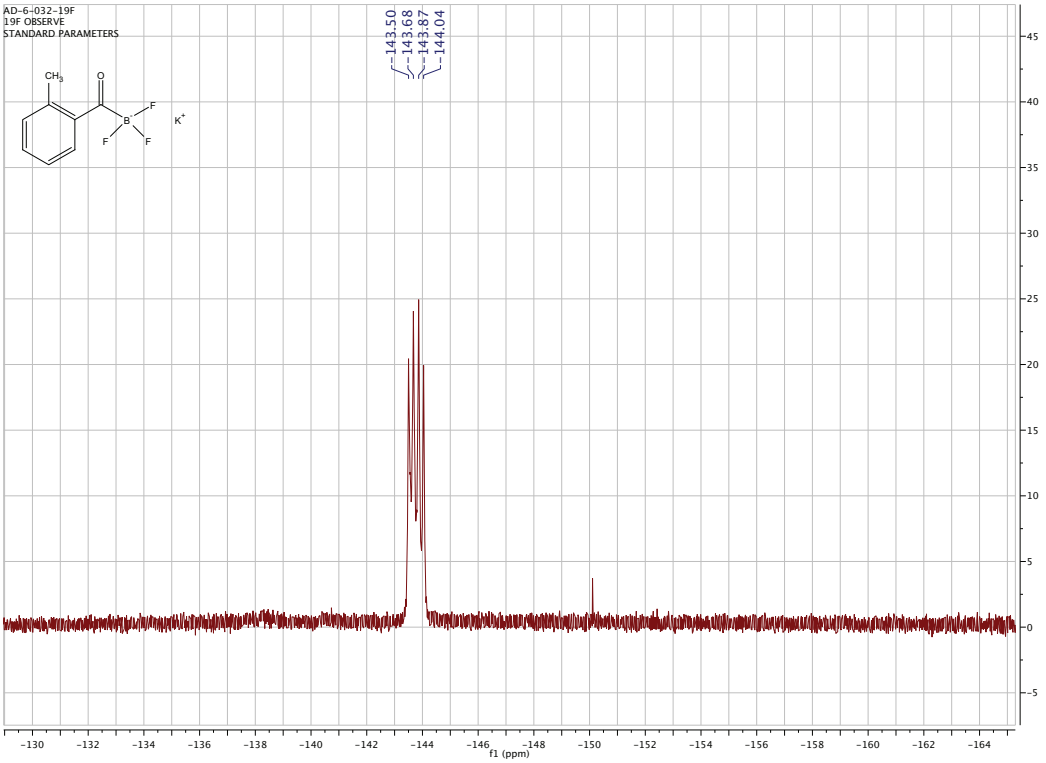
^{1}H NMR (300 MHz, acetone-d_6)



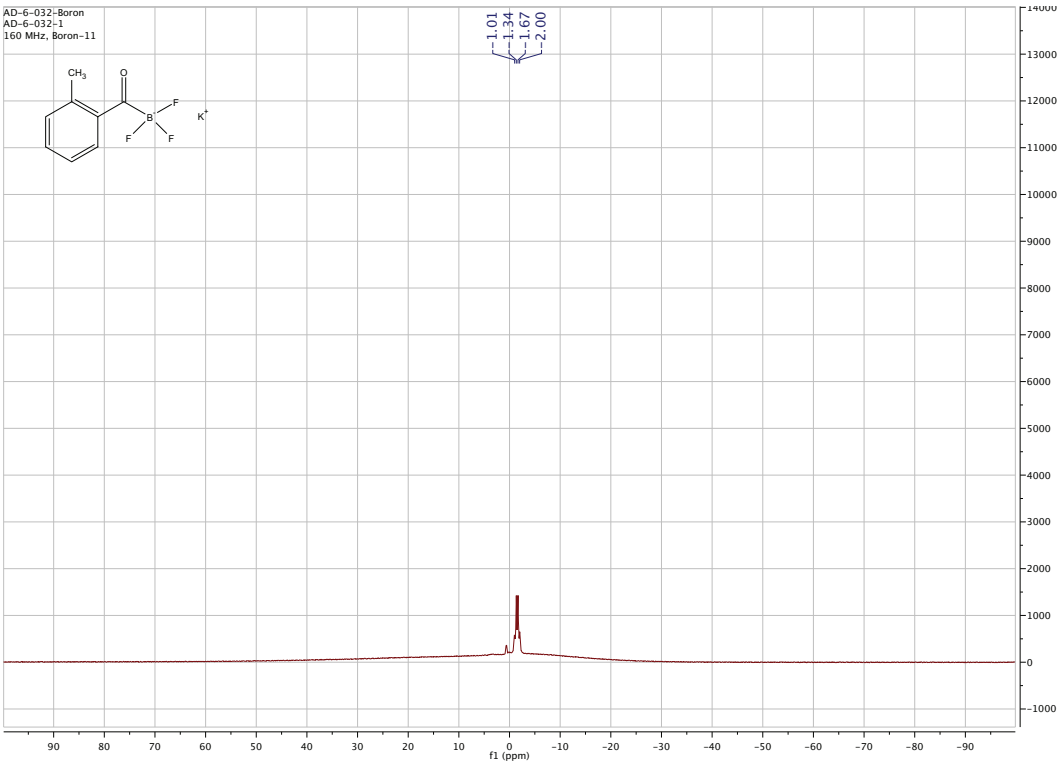
^{13}C NMR (100 MHz, DMSO-d_6)



^{19}F NMR (282 MHz, acetone-d_6)

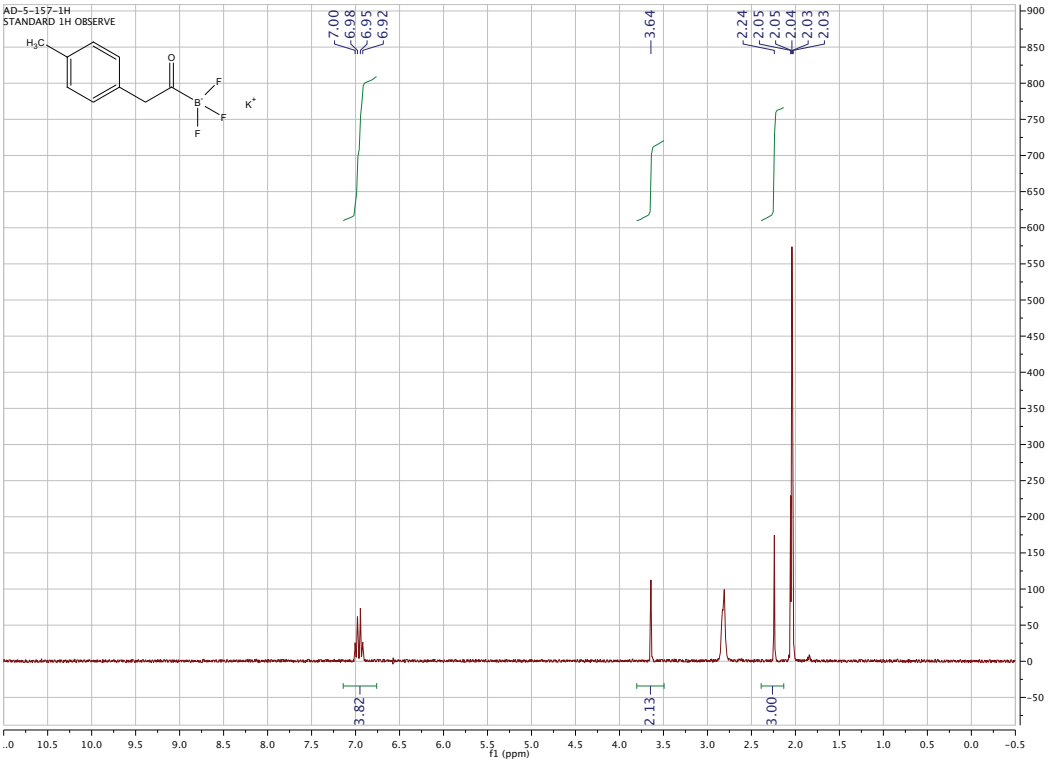


^{11}B NMR (160 MHz, DMSO-d_6)

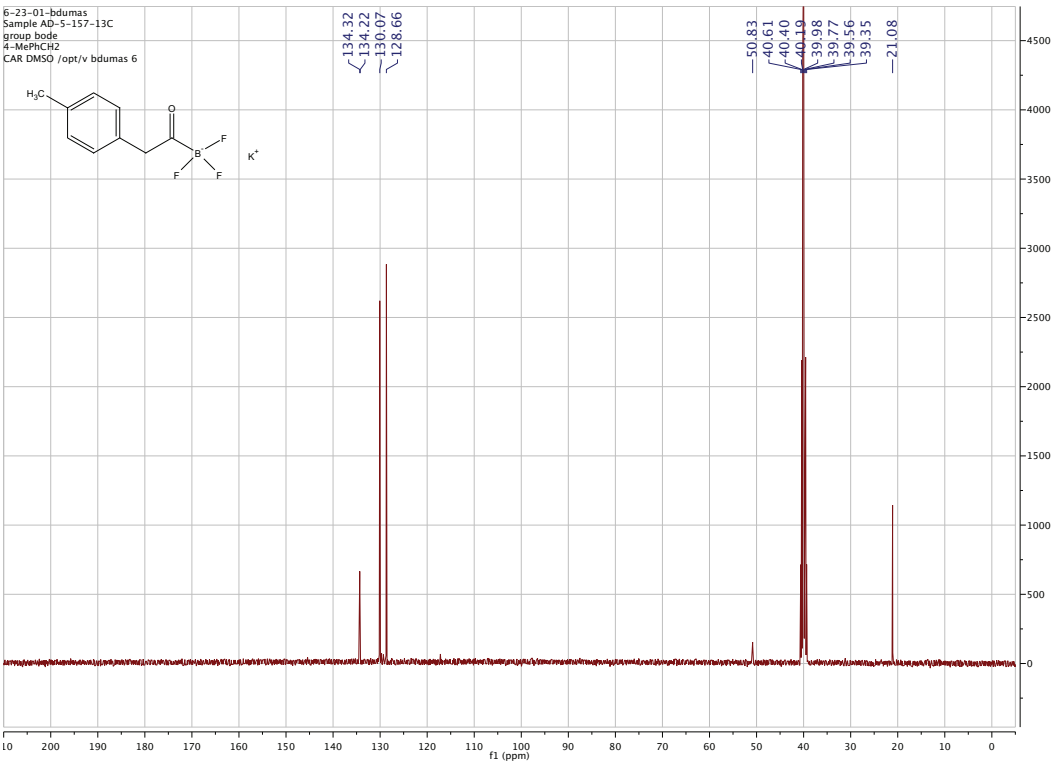


Potassium (2-(*p*-tolyl)acetyl)trifluoroborate (8a):

^{1}H NMR (300 MHz, acetone-d_6)

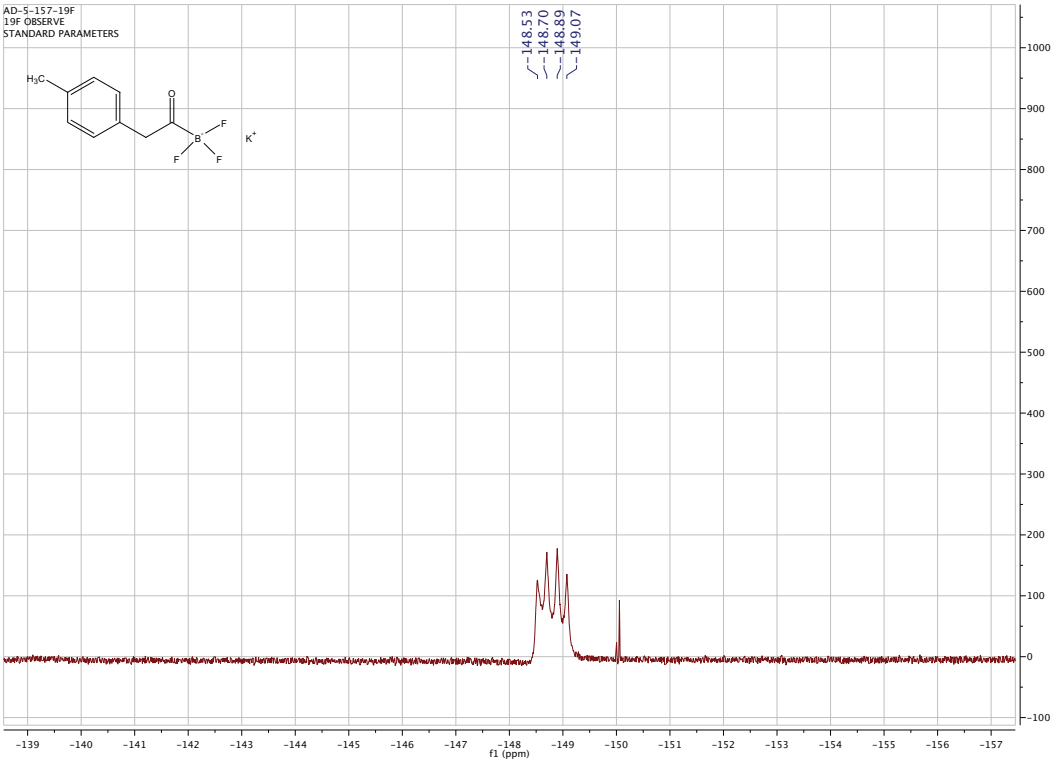


^{13}C NMR (100 MHz, DMSO-d_6)

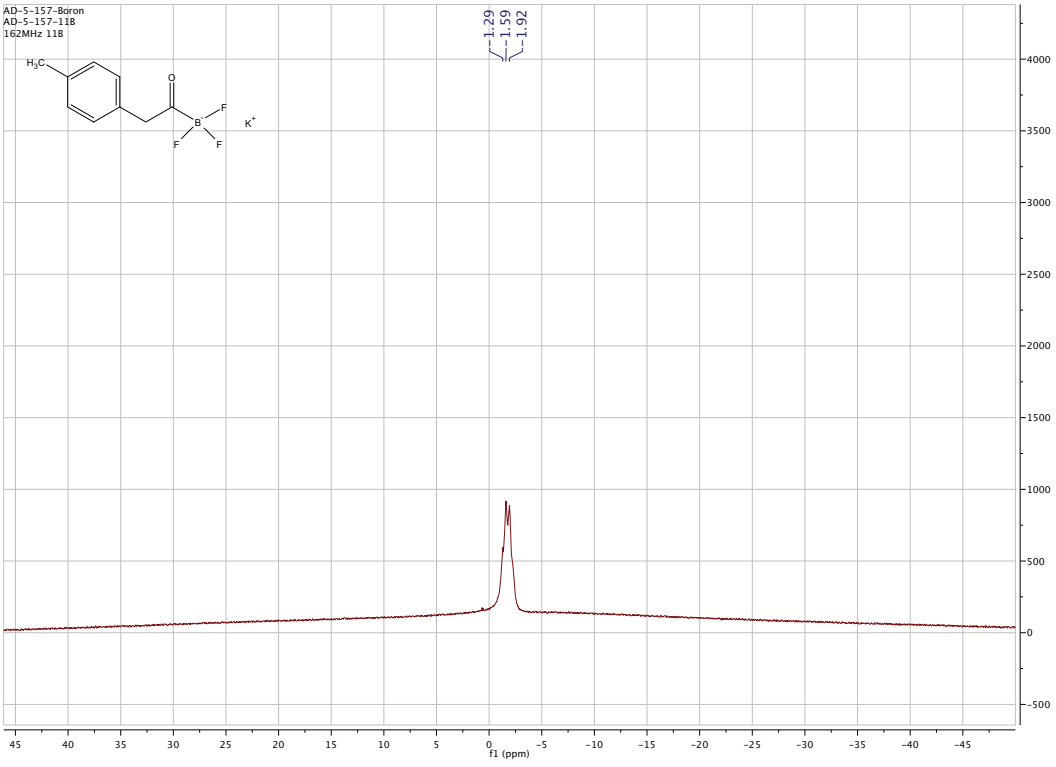


Potassium (2-(*p*-tolyl)acetyl)trifluoroborate (8a):

^{19}F NMR (282 MHz, acetone-d_6)

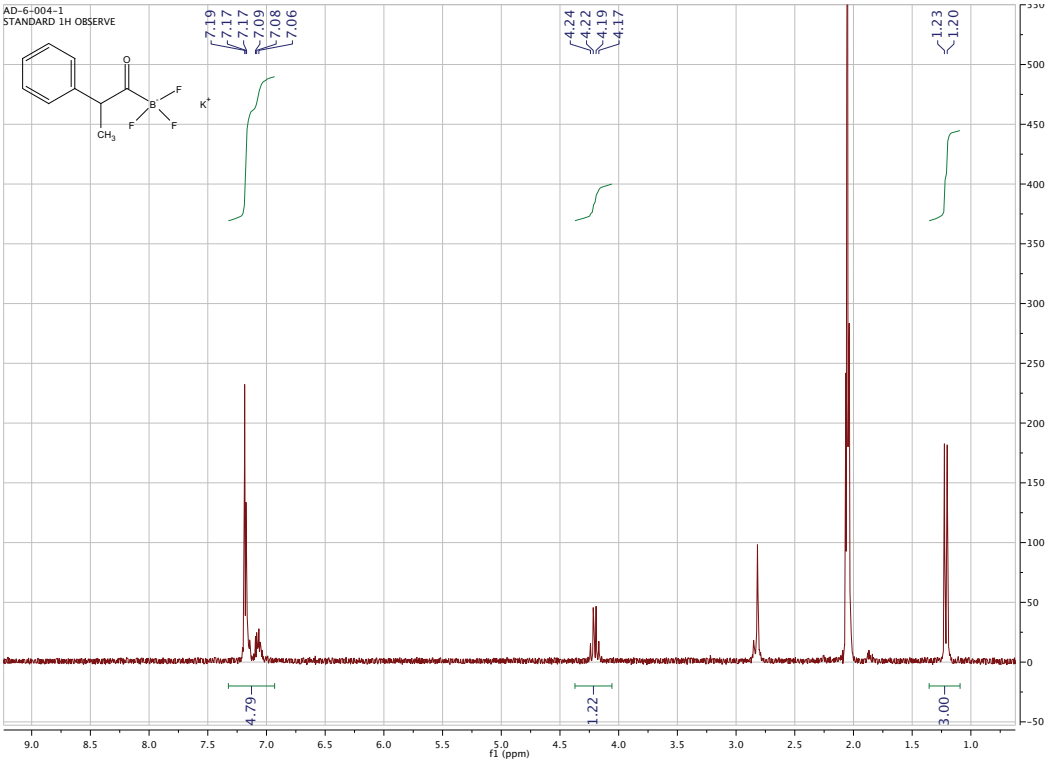


^{11}B NMR (160 MHz, DMSO-d_6)

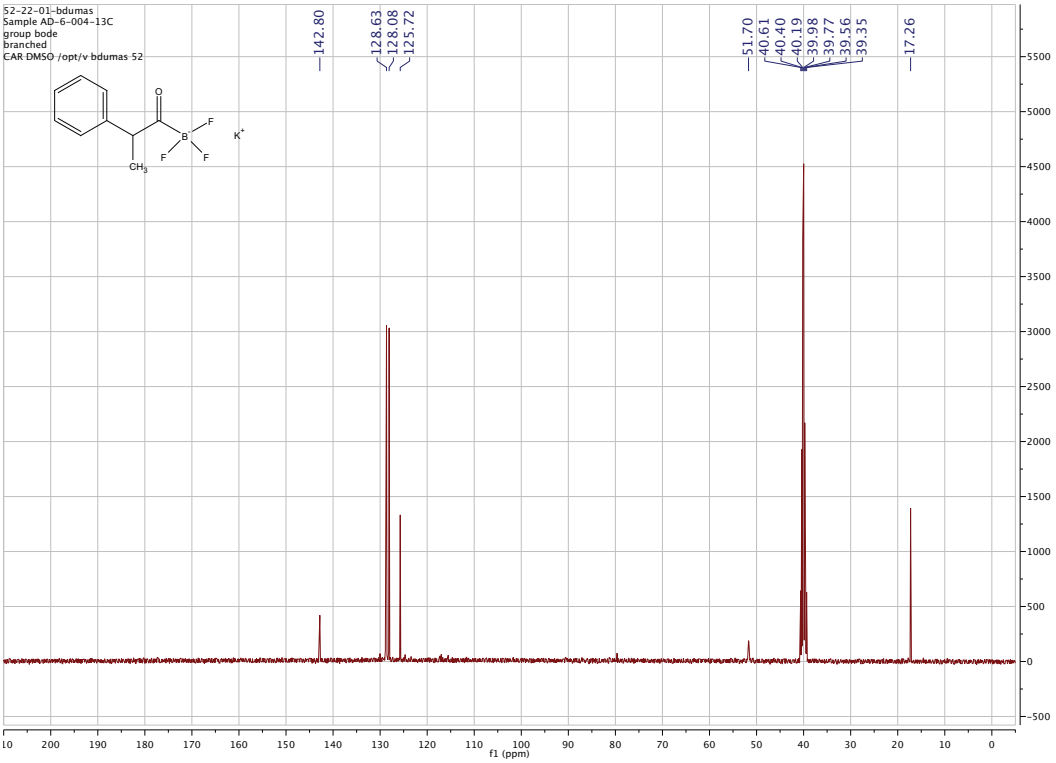


Potassium 2-phenylpropanoyltrifluoroborate (8b):

^{1}H NMR (300 MHz, acetone-d_6)

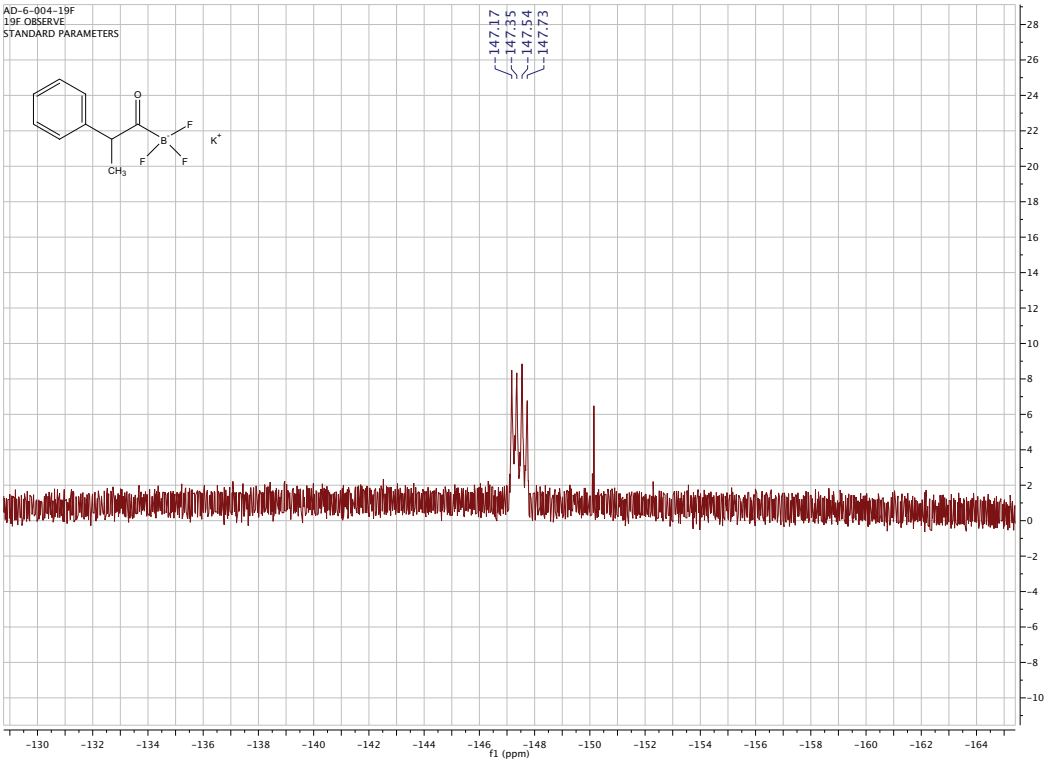


^{13}C NMR (100 MHz, DMSO-d_6)

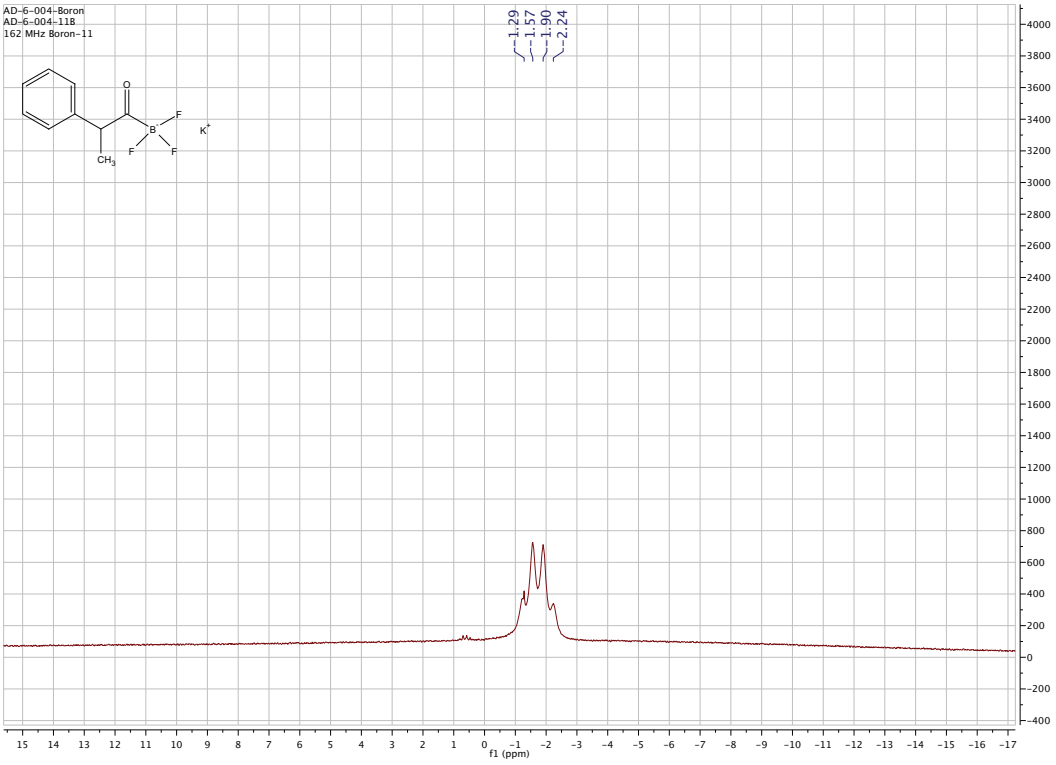


Potassium 2-phenylpropanoyltrifluoroborate (8b):

^{19}F NMR (282 MHz, acetone-d_6)

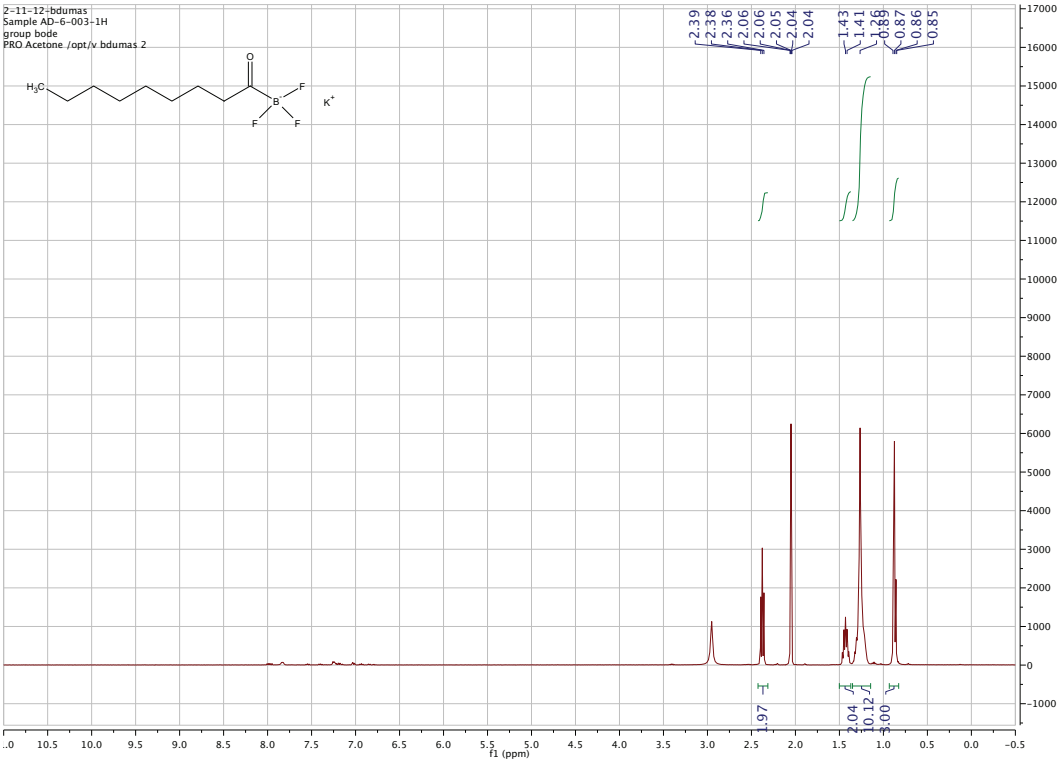


^{11}B NMR (160 MHz, DMSO-d_6)

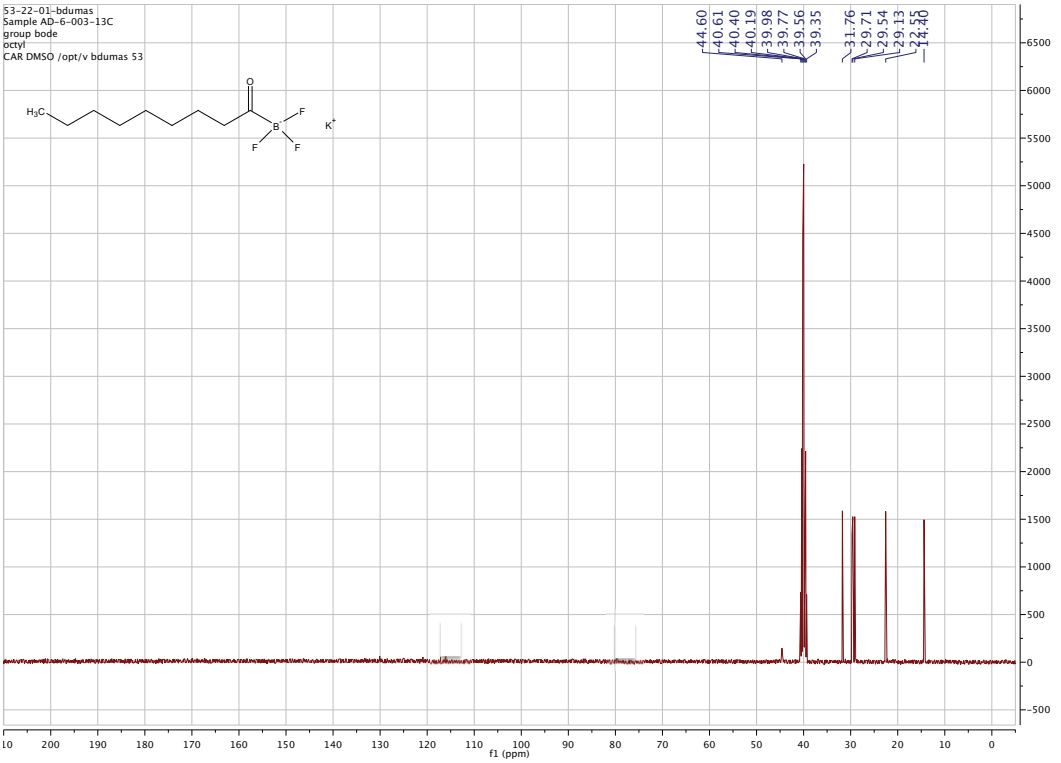


Potassium nonanoyltrifluoroborate (8c):

^{1}H NMR (400 MHz, acetone-d_6)

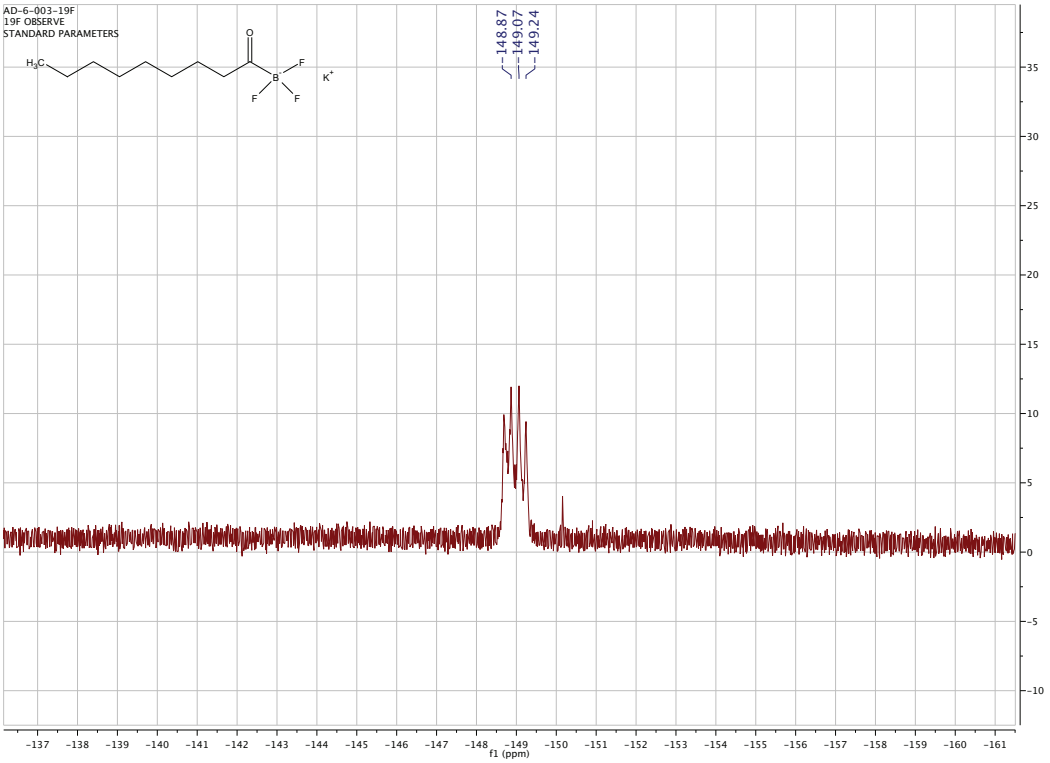


^{13}C NMR (100 MHz, DMSO-d_6)

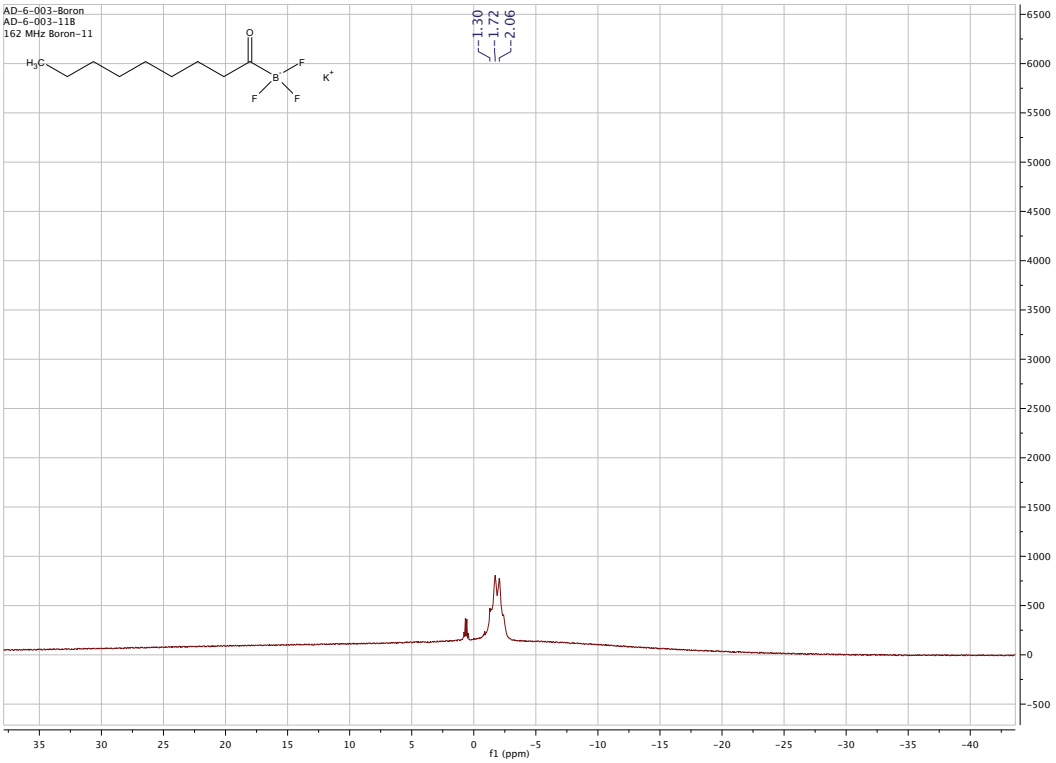


Potassium nonanoyltrifluoroborate (8c):

^{19}F NMR (282 MHz, acetone-d_6)

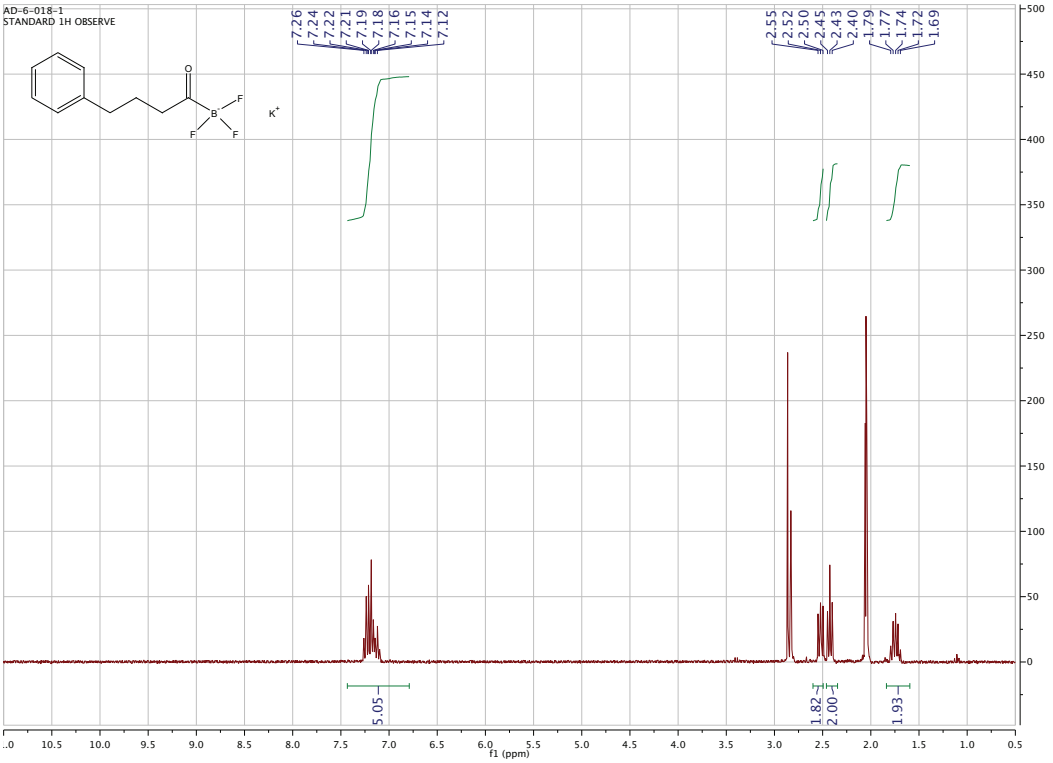


^{11}B NMR (160 MHz, DMSO-d_6)

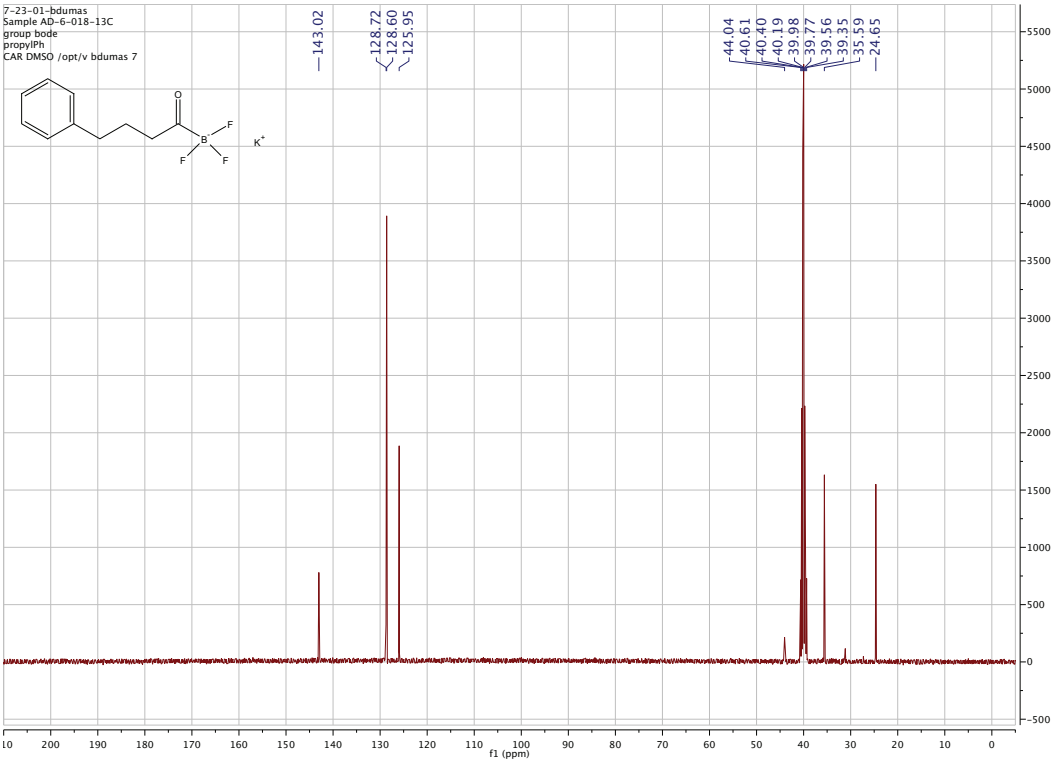


Potassium 3-phenylpropanoyltrifluoroborate (8d):

^{1}H NMR (300 MHz, acetone-d_6)

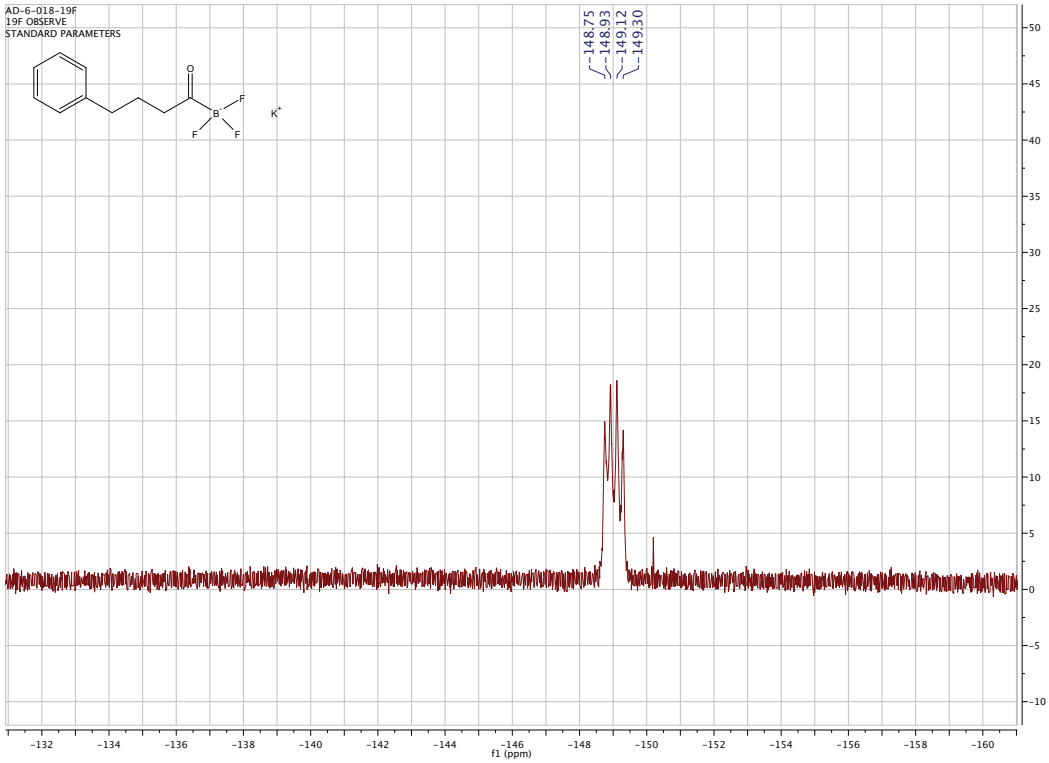


^{13}C NMR (100 MHz, DMSO-d_6)

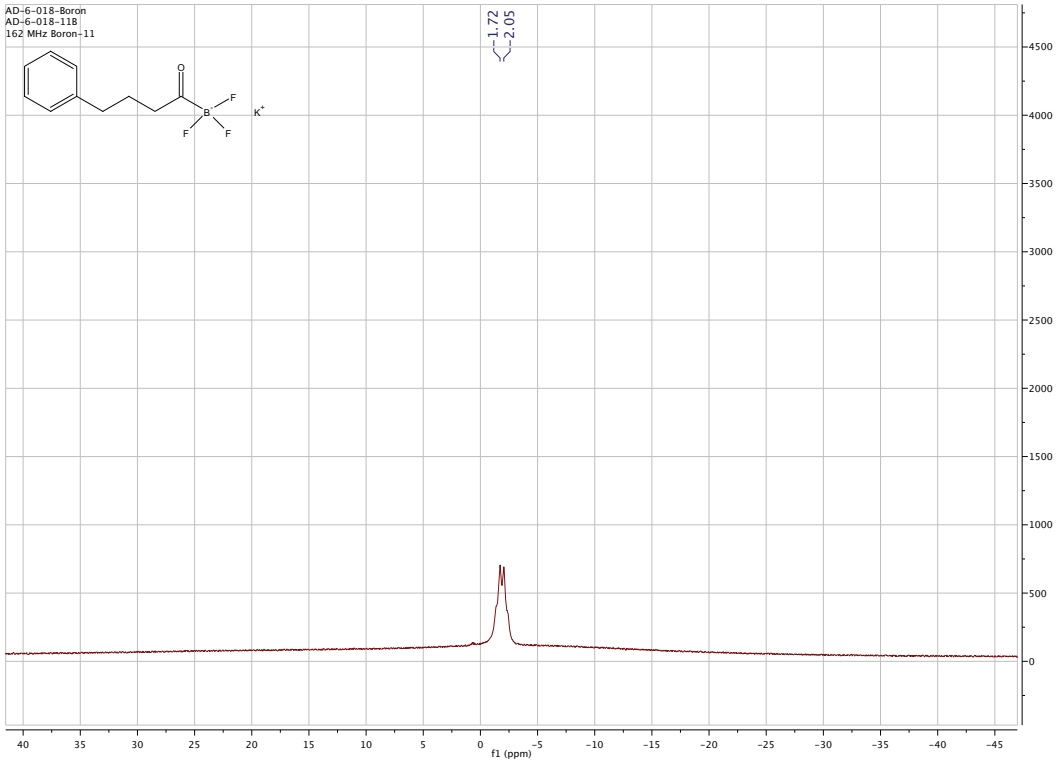


Potassium 3-phenylpropanoyltrifluoroborate (8d):

^{19}F NMR (282 MHz, acetone-d_6)

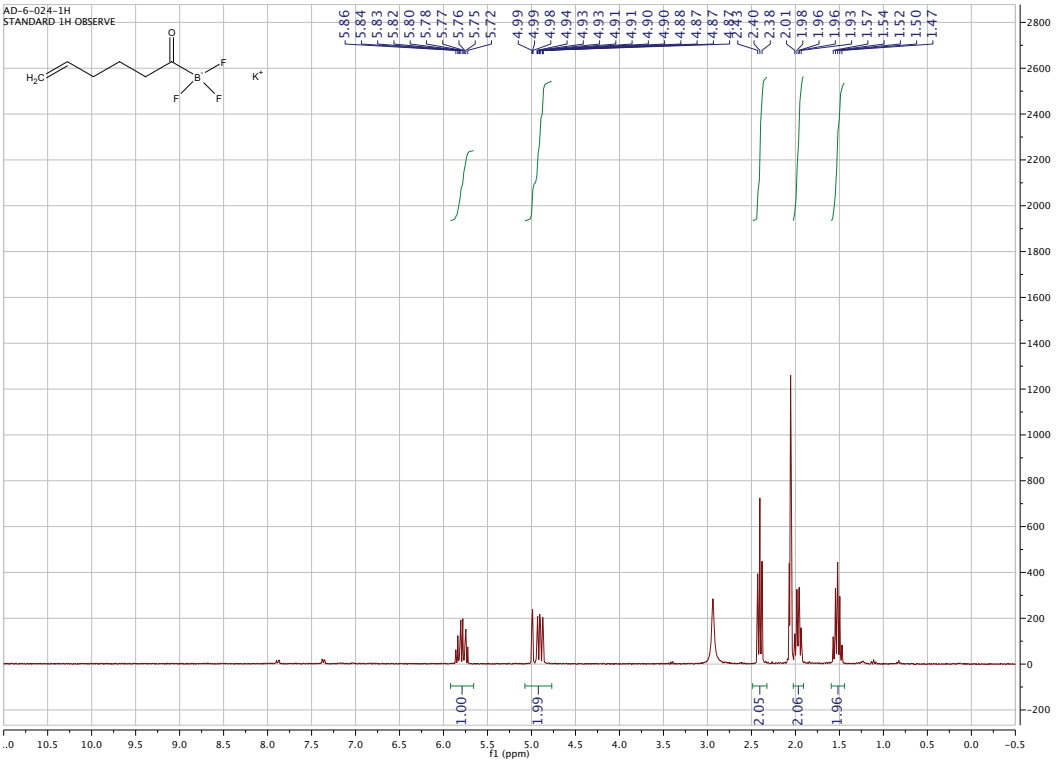


^{11}B NMR (160 MHz, DMSO-d_6)

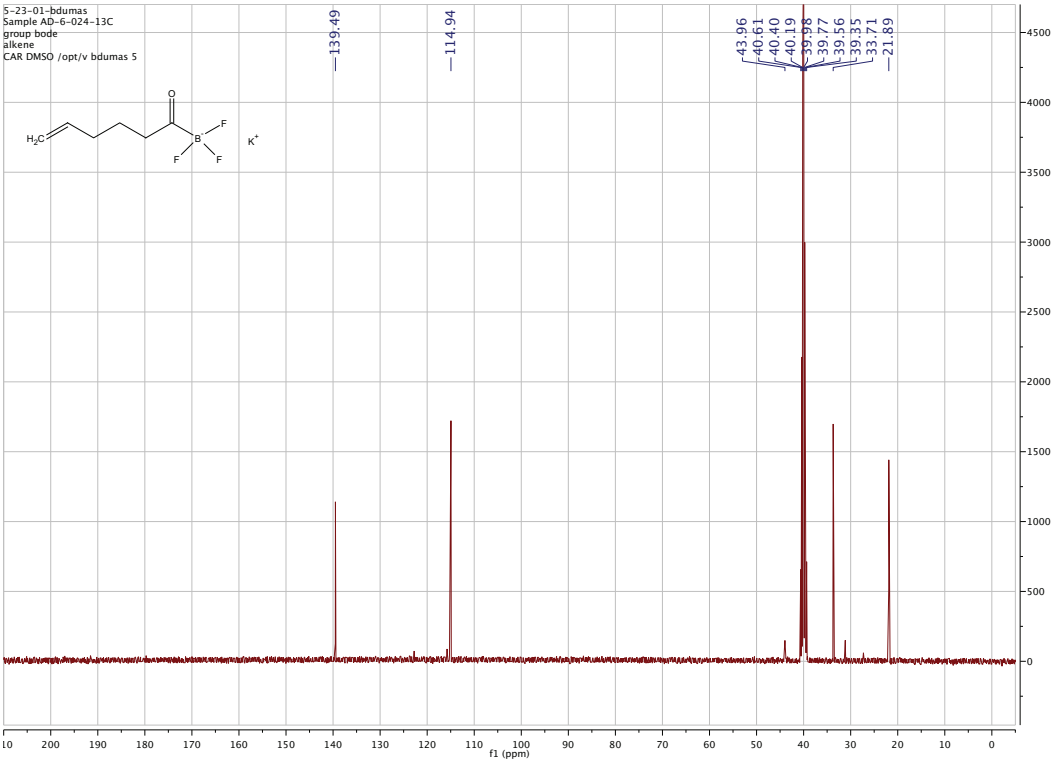


Potassium hex-5-enoyltrifluoroborate (8e):

^{1}H NMR (300 MHz, acetone-d_6)

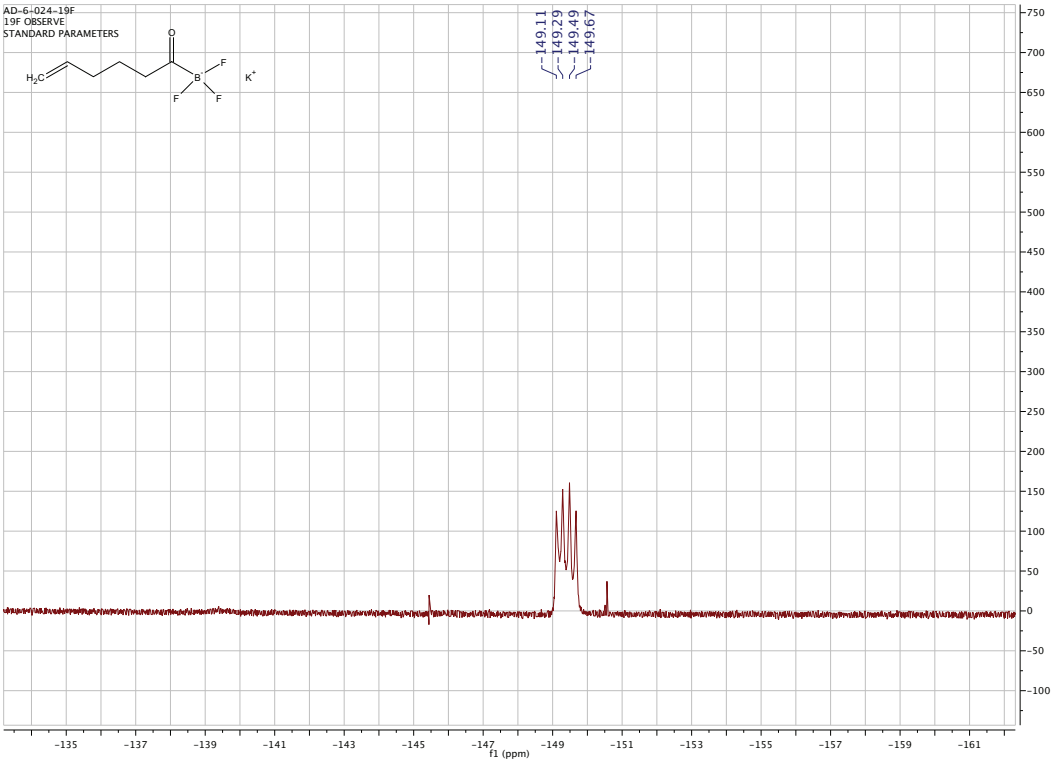


^{13}C NMR (100 MHz, DMSO-d_6)

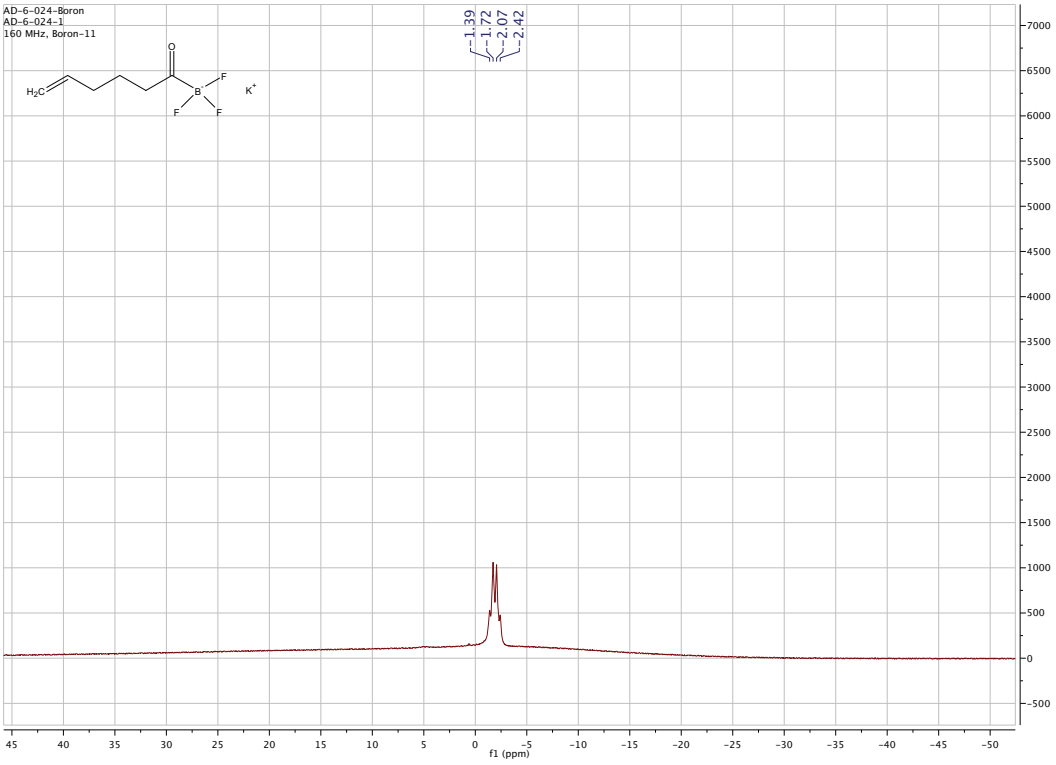


Potassium hex-5-enoyltrifluoroborate (8e):

^{19}F NMR (282 MHz, acetone-d_6)

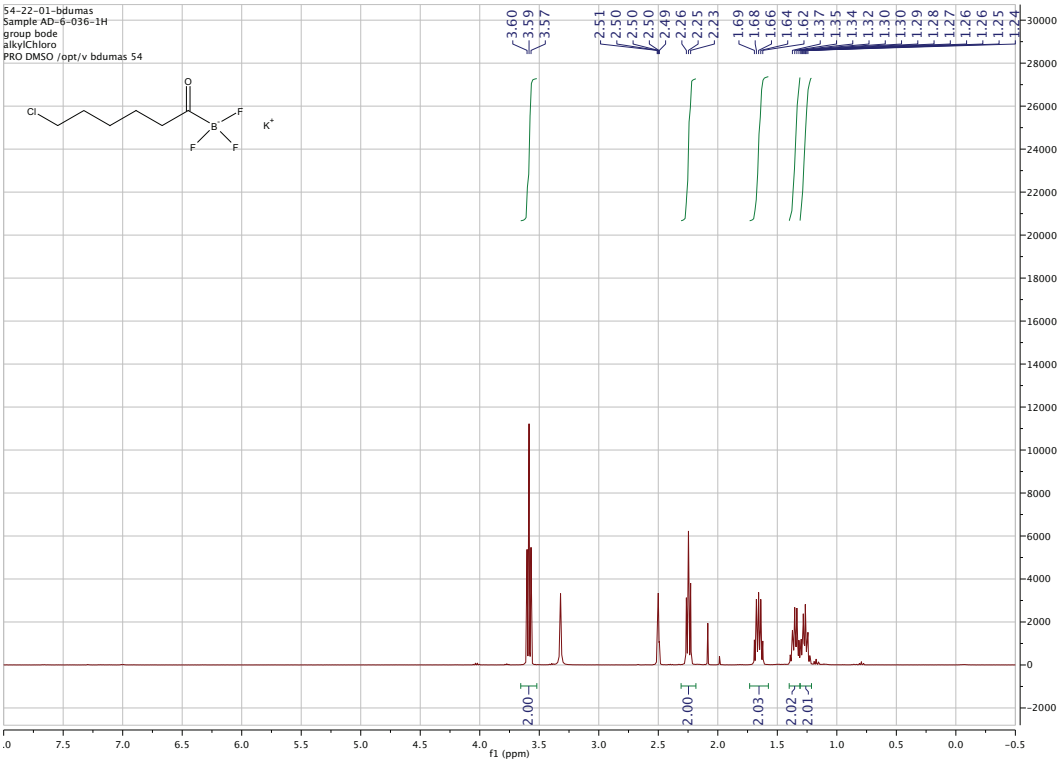


^{11}B NMR (160 MHz, DMSO-d_6)

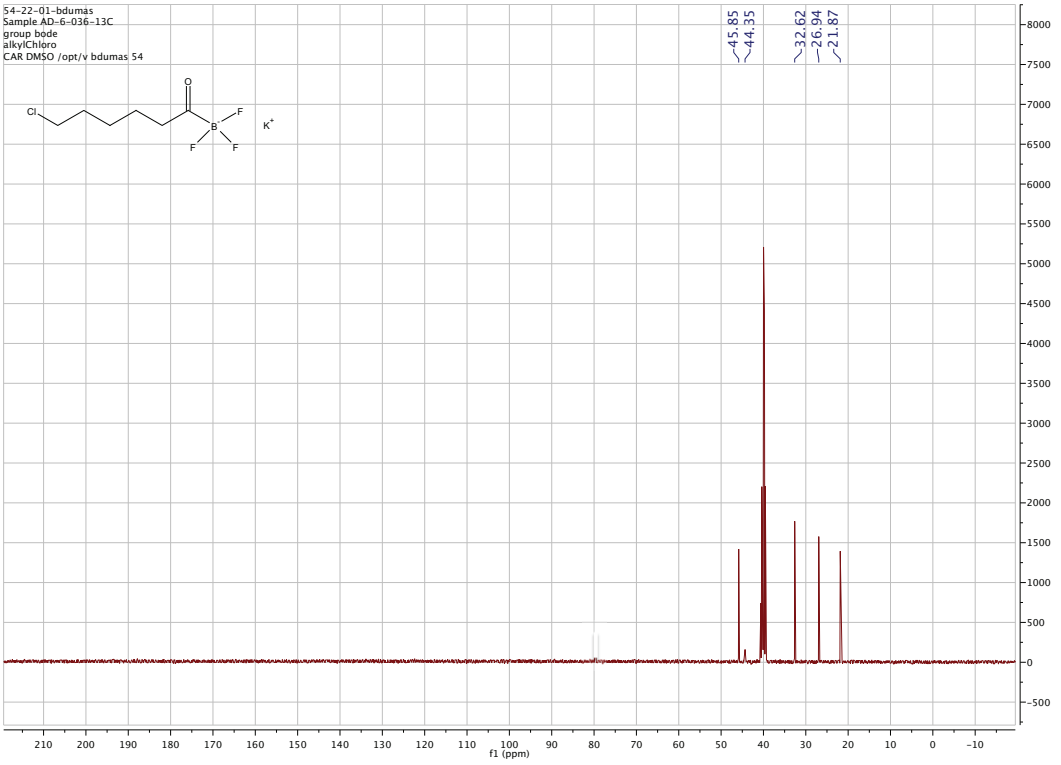


Potassium 6-chlorohexanoyltrifluoroborate (8f):

^{1}H NMR (400 MHz, DMSO-d_6)

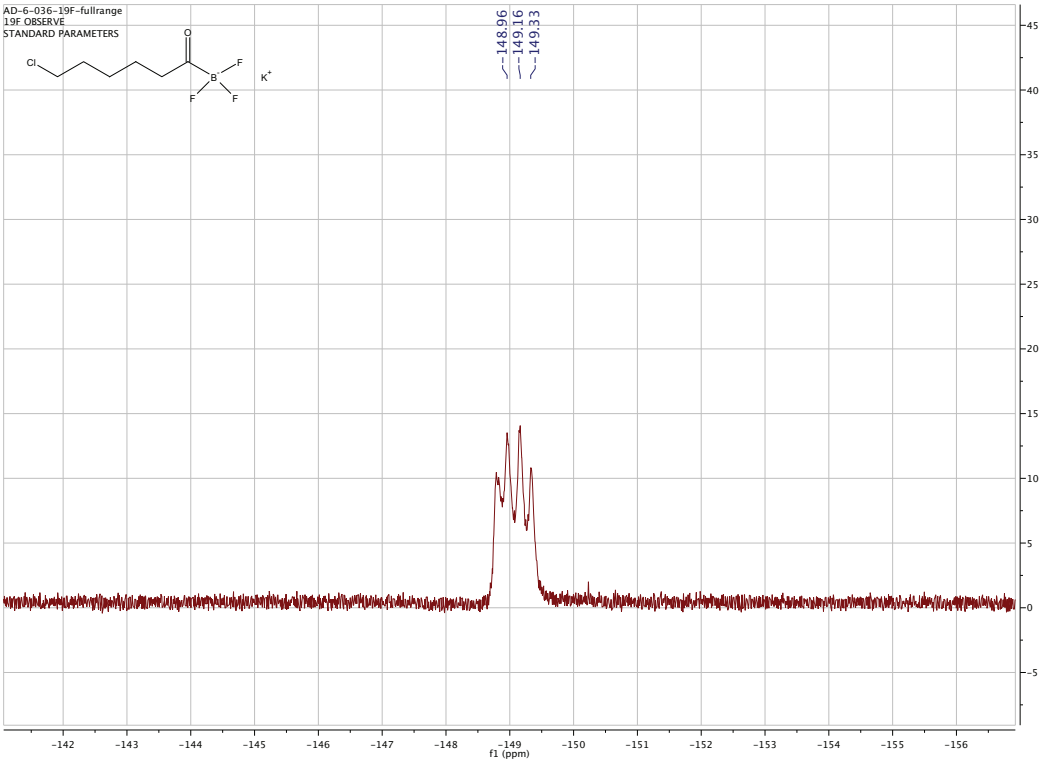


^{13}C NMR (100 MHz, DMSO-d_6)

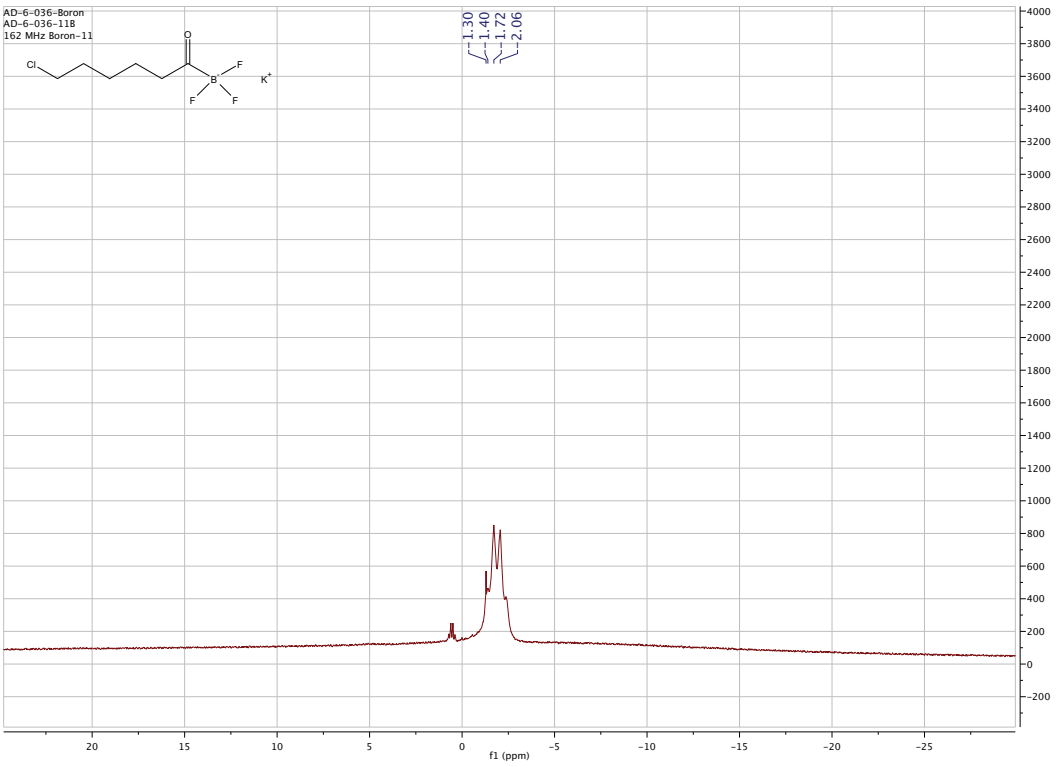


Potassium 6-chlorohexanoyltrifluoroborate (8f):

^{19}F NMR (282 MHz, acetone-d_6)

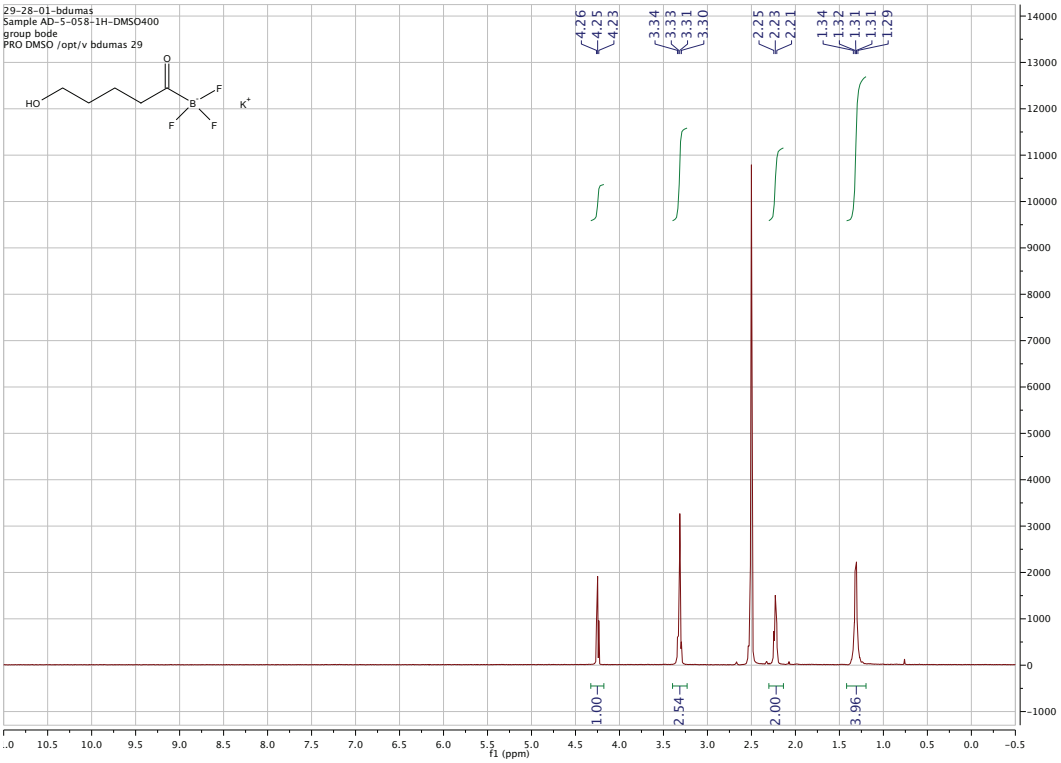


^{11}B NMR (160 MHz, DMSO-d_6)

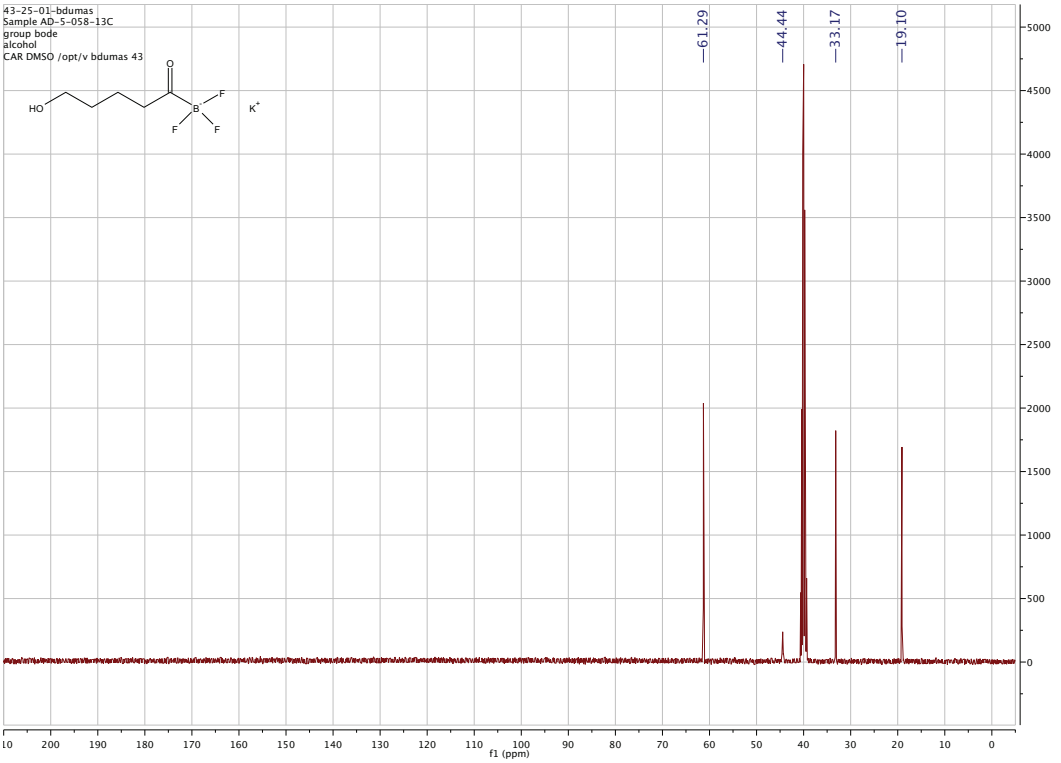


Potassium 5-hydroxypentanoyltrifluoroborate (10):

^{1}H NMR (400 MHz, DMSO-d_6)

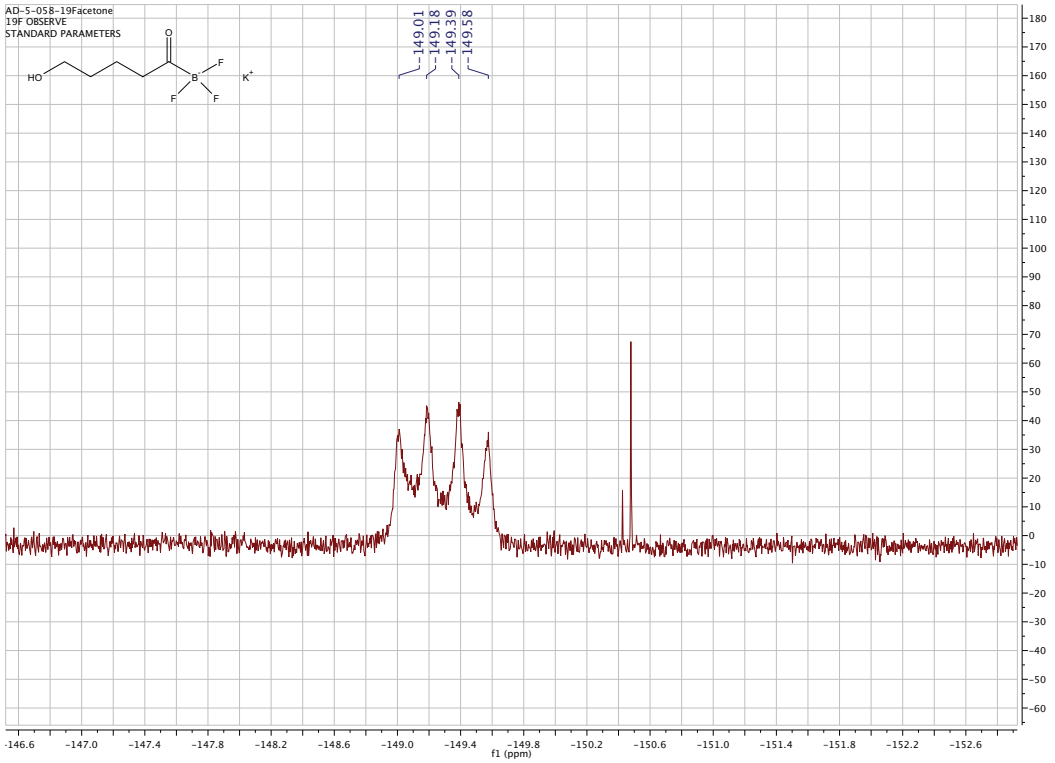


^{13}C NMR (100 MHz, DMSO-d_6)

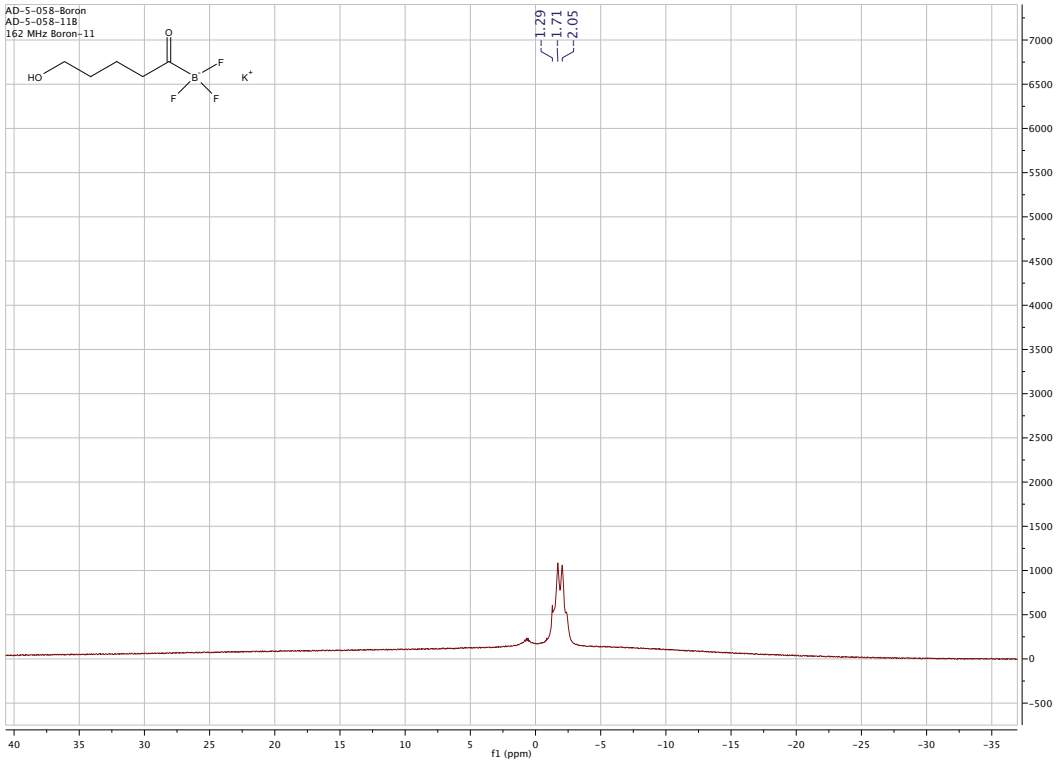


Potassium 5-hydroxypentanoyltrifluoroborate (10):

^{19}F NMR (282 MHz, acetone-d_6)

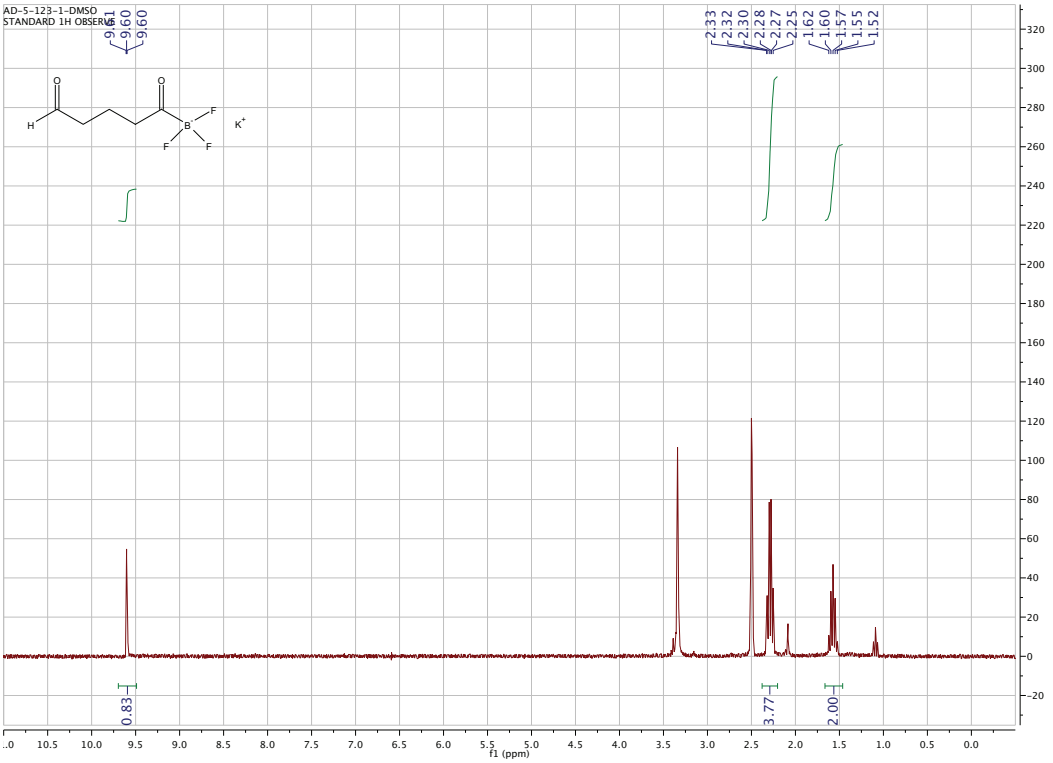


^{11}B NMR (160 MHz, DMSO-d_6)

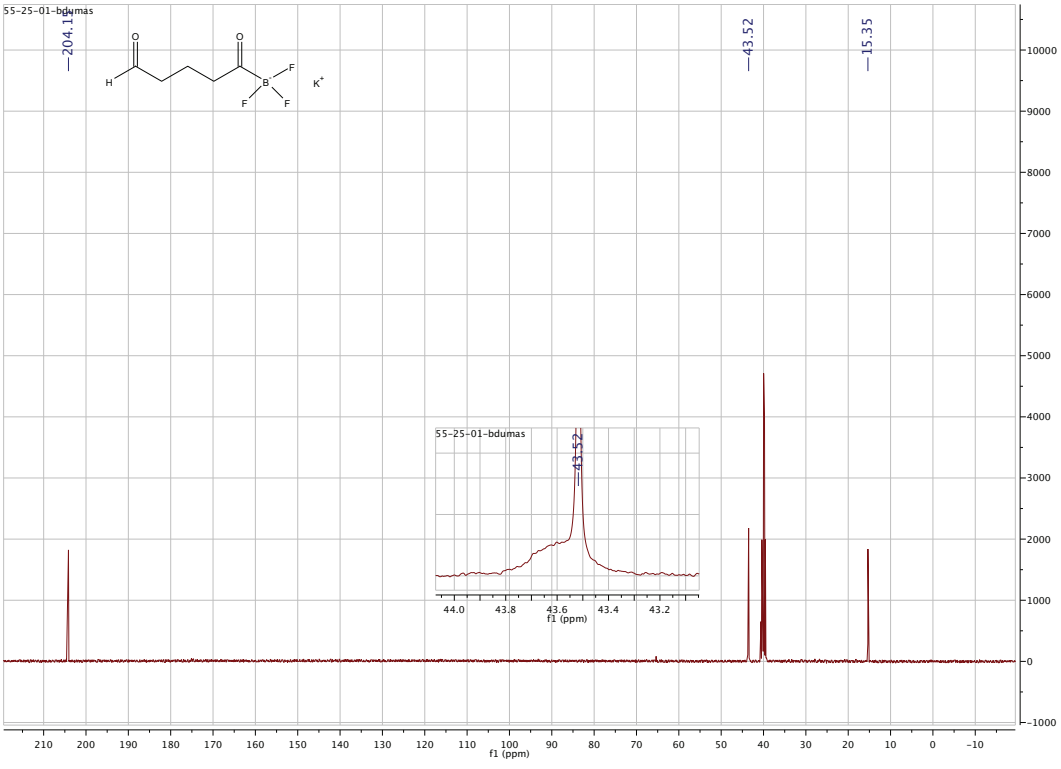


Potassium 5-oxopentanoyltrifluoroborate (11):

^{1}H NMR (300 MHz, DMSO-d_6)

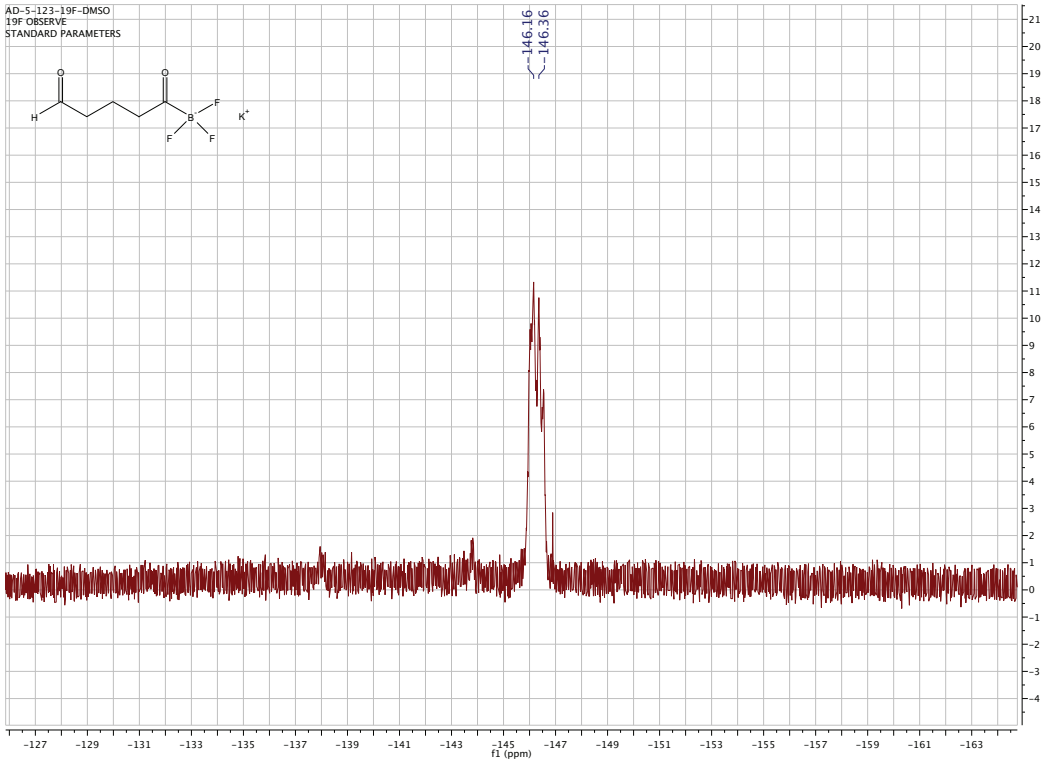


^{13}C NMR (100 MHz, DMSO-d_6)

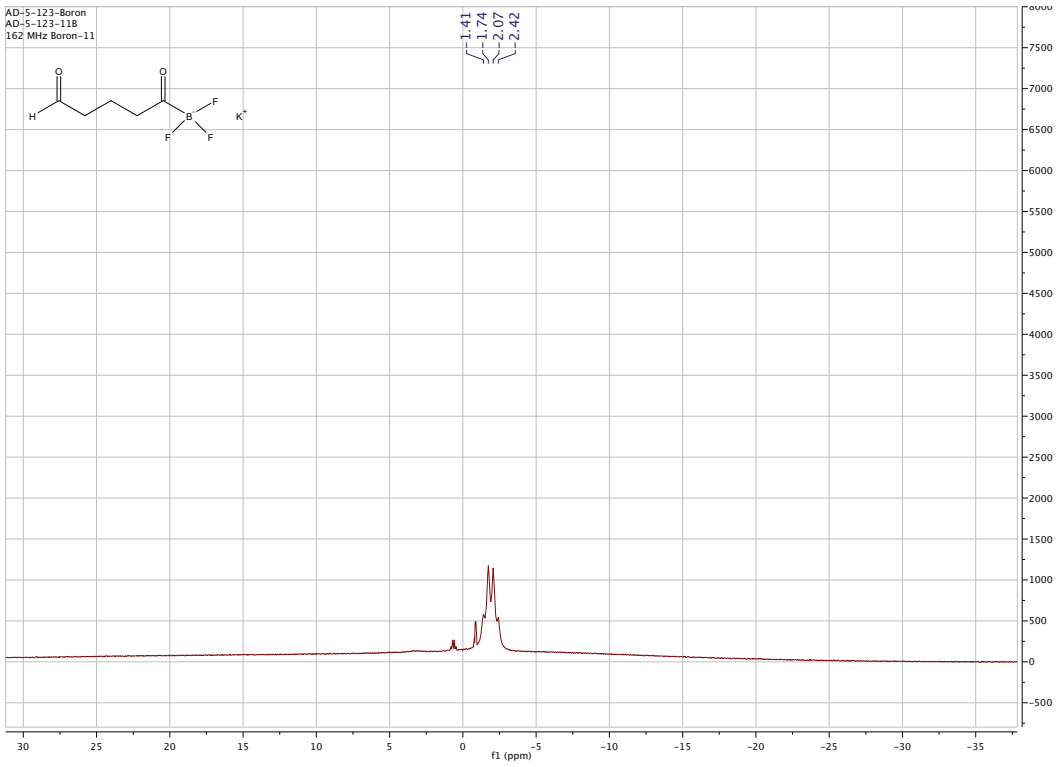


Potassium 5-oxopentanoyltrifluoroborate (11):

^{19}F NMR (282 MHz, acetone-d_6)

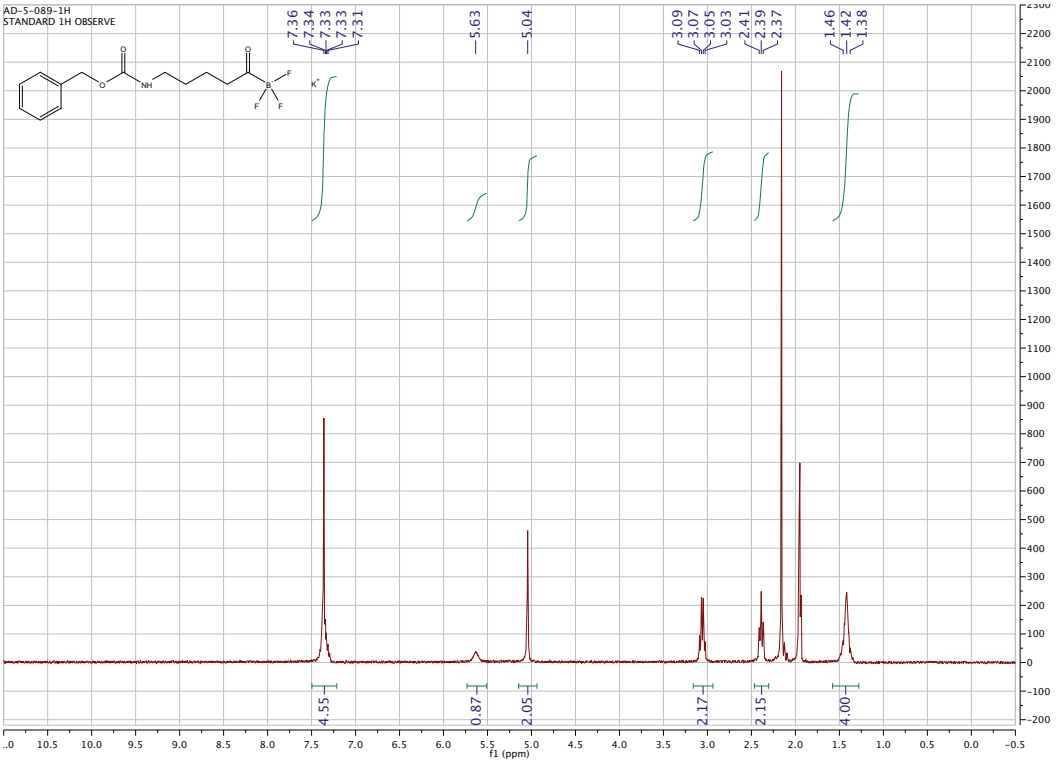


^{11}B NMR (160 MHz, DMSO-d_6)

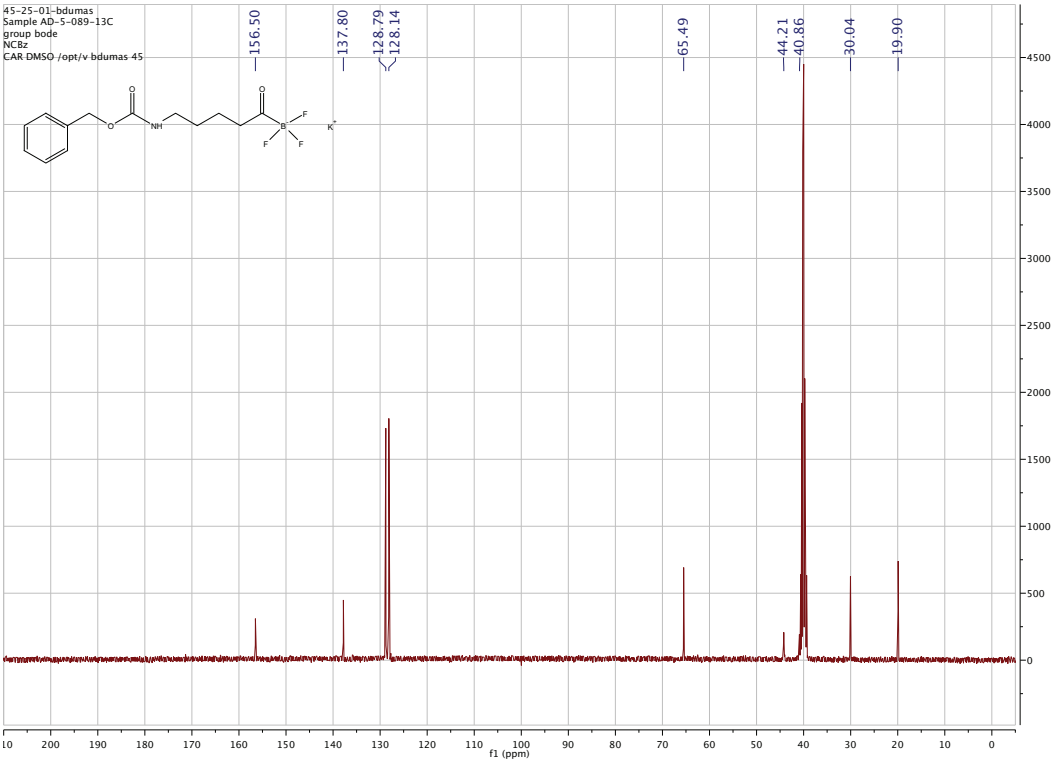


5-(Benzyloxylcarbonylamino)pentanoyltrifluoroborate (13a):

^{1}H NMR (300 MHz, acetone-d_6)

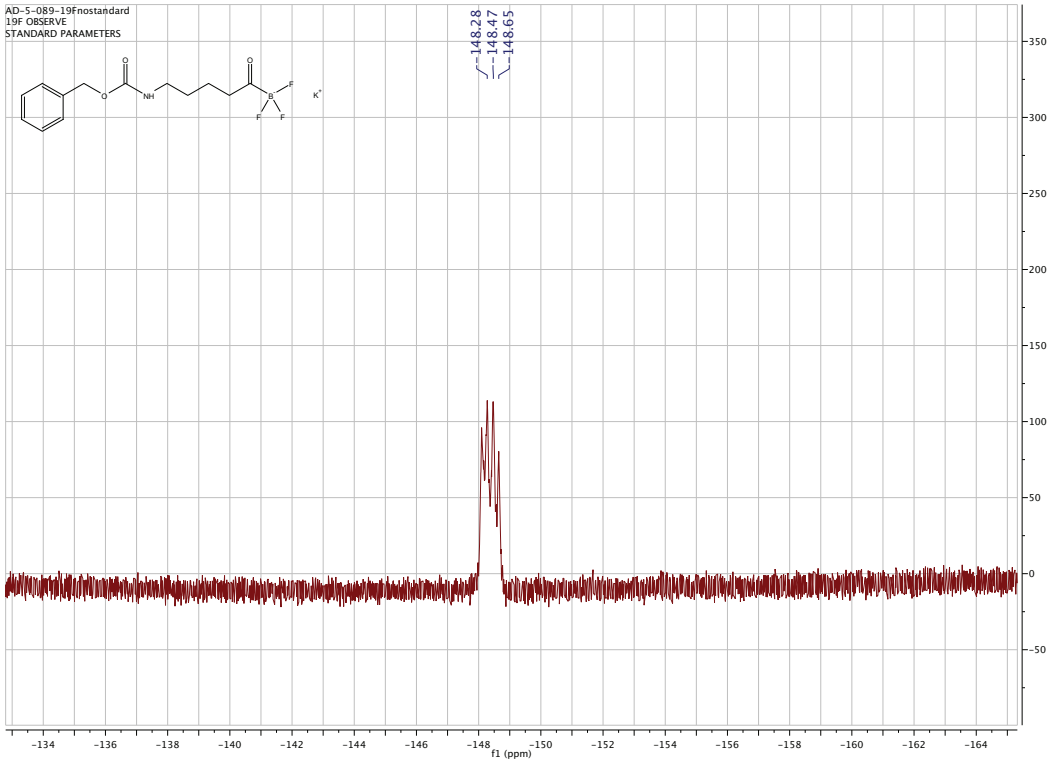


^{13}C NMR (100 MHz, DMSO-d_6)

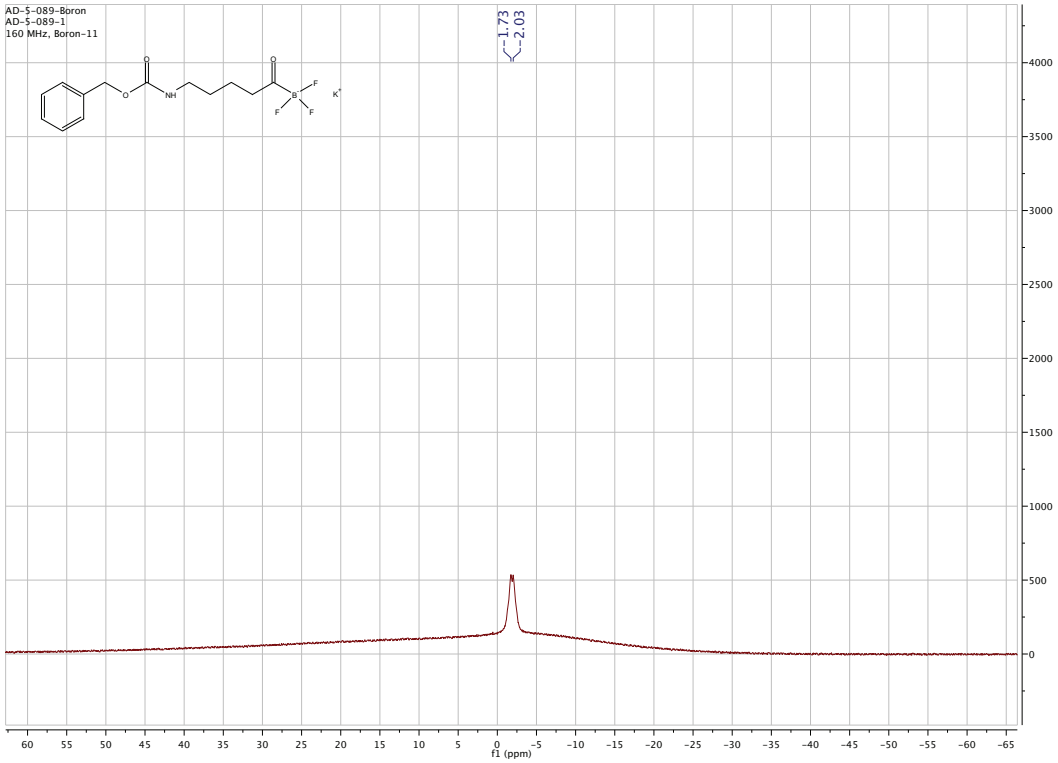


5-(Benzyloxylcarbonylamino)pentanoyltrifluoroborate (13a):

^{19}F NMR (282 MHz, acetone-d_6)

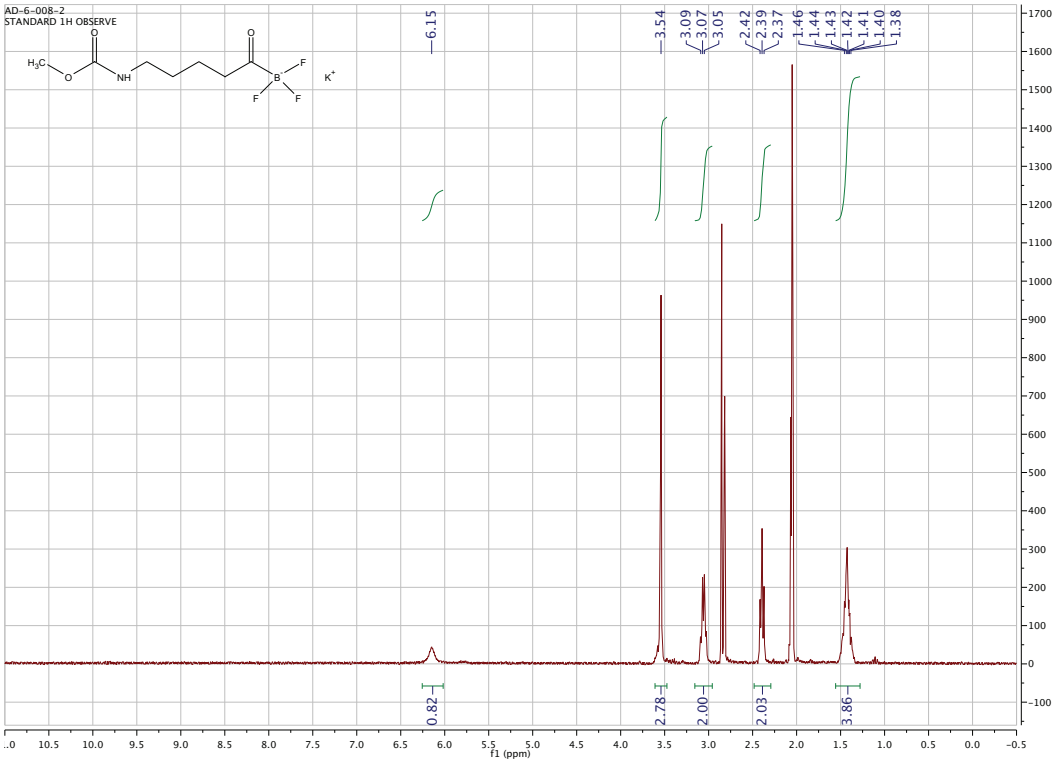


^{11}B NMR (160 MHz, DMSO-d_6)

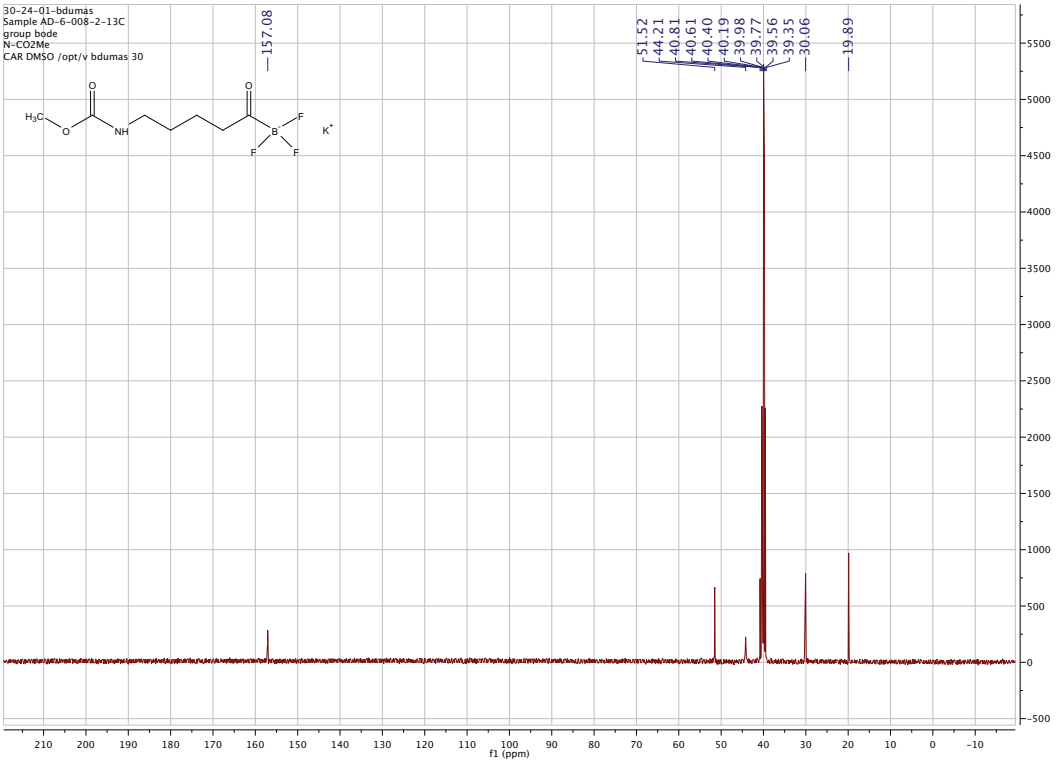


5-(Carbomethoxyamino)pentanoyltrifluoroborate (13b):

^{1}H NMR (300 MHz, acetone-d_6)

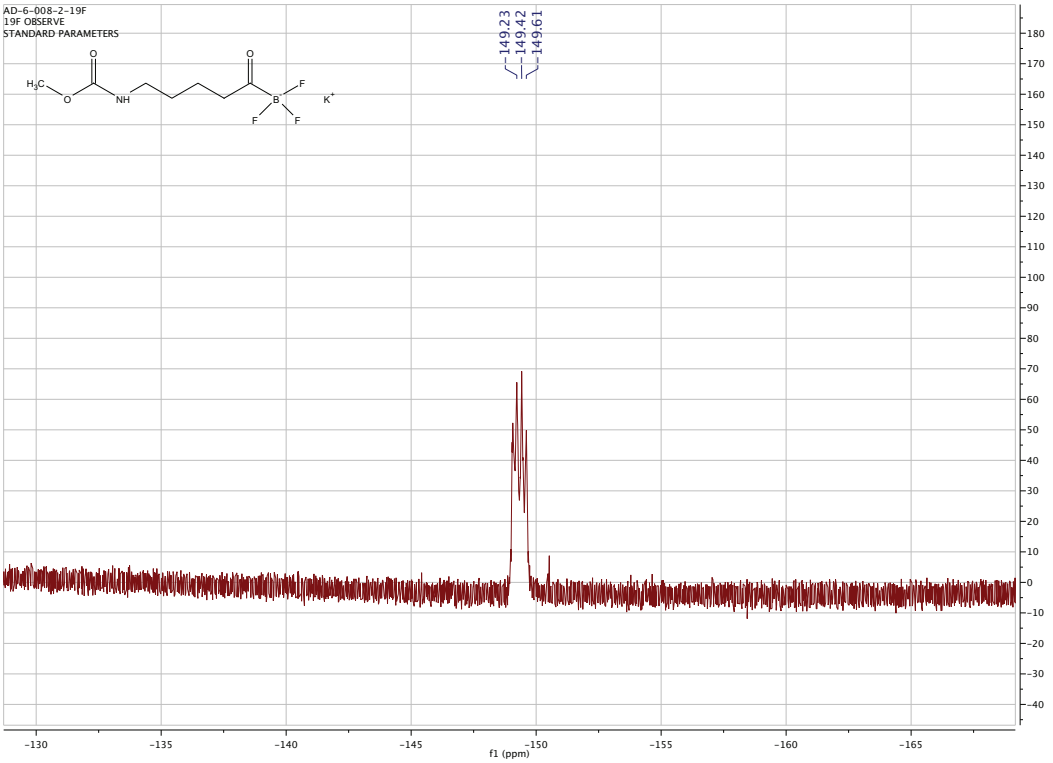


^{13}C NMR (100 MHz, DMSO-d_6)

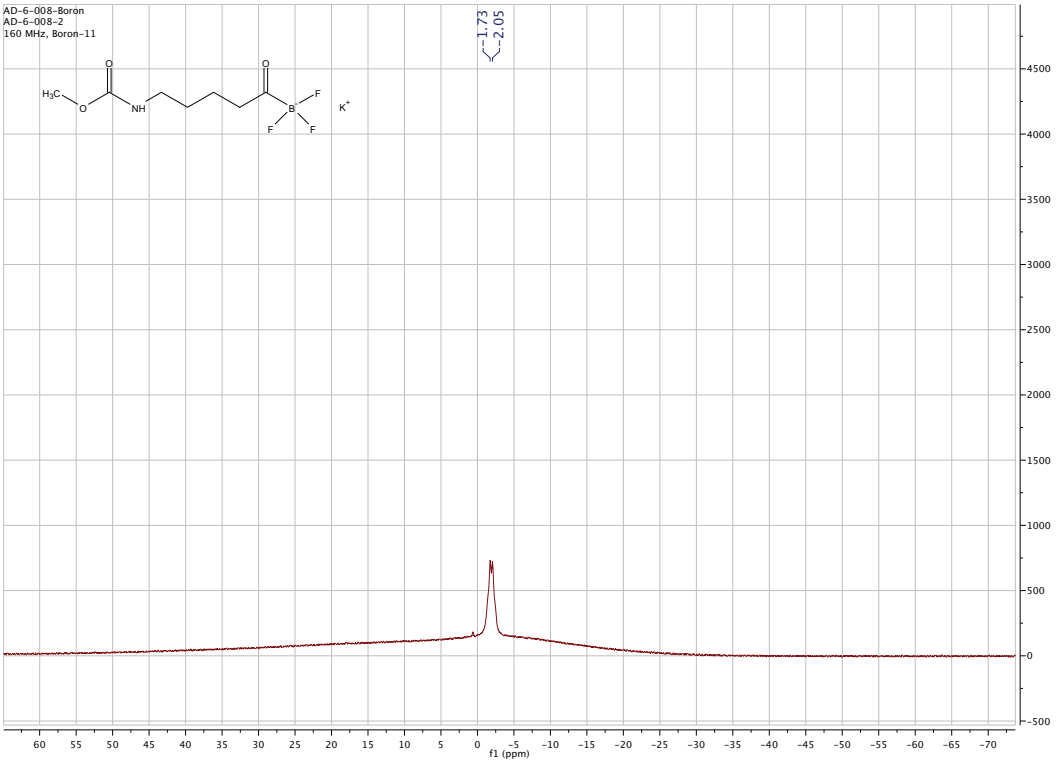


5-(Carbomethoxyamino)pentanoyltrifluoroborate (13b):

^{19}F NMR (282 MHz, acetone-d_6)

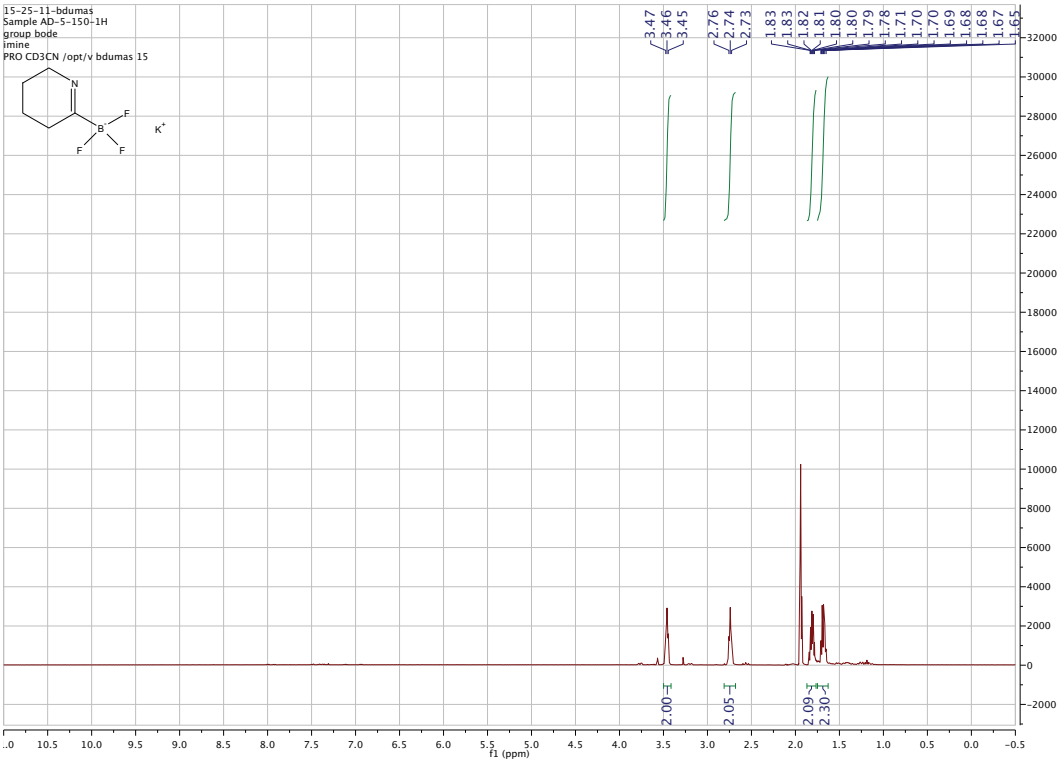


^{11}B NMR (160 MHz, DMSO-d_6)

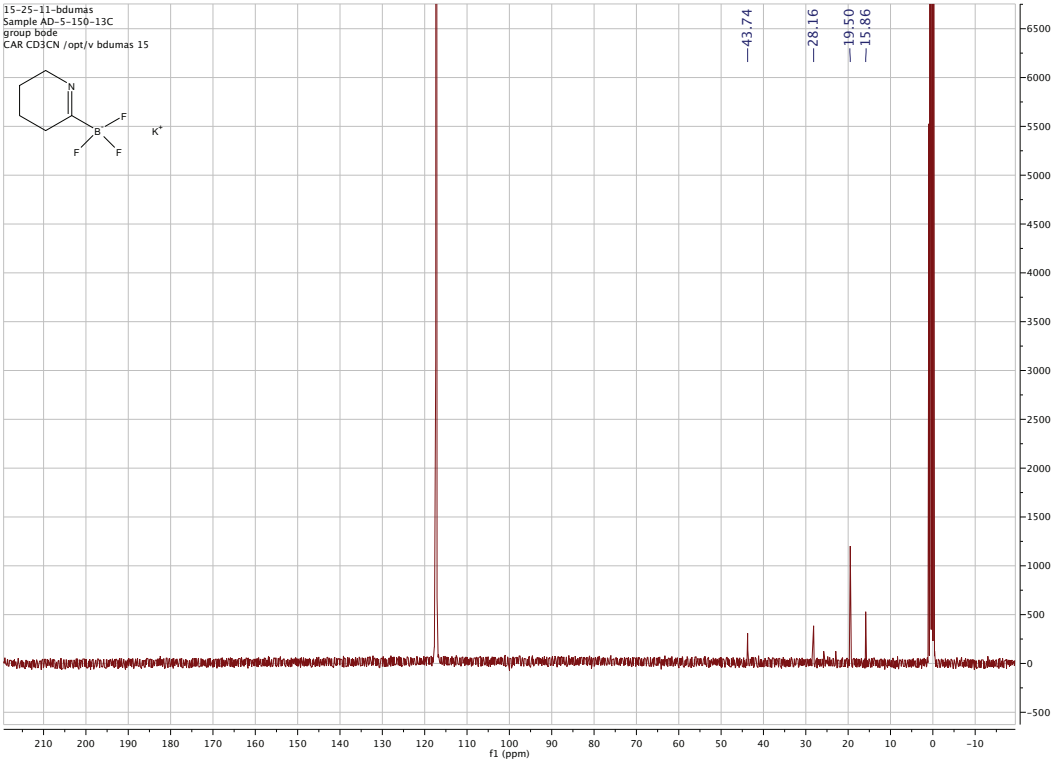


Potassium (3,4,5,6-tetrahydropyridin-2-yl)trifluoroborate (14):

^{1}H NMR (400 MHz, CD_3CN)

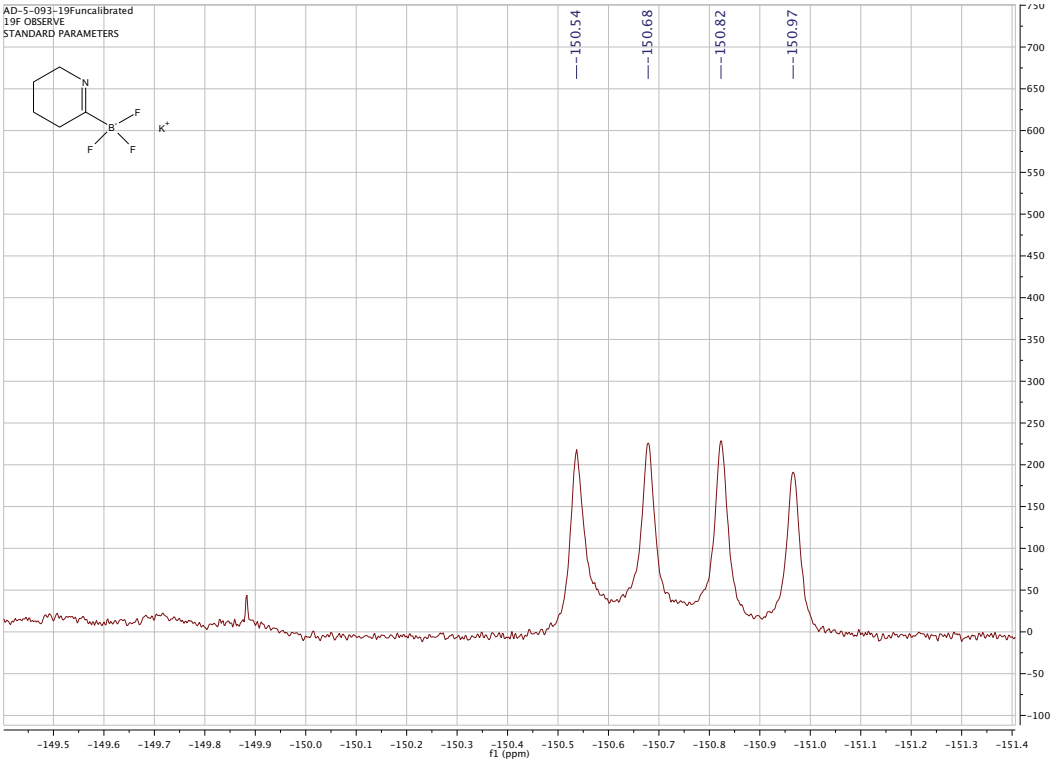


^{13}C NMR (100 MHz, CD_3CN)

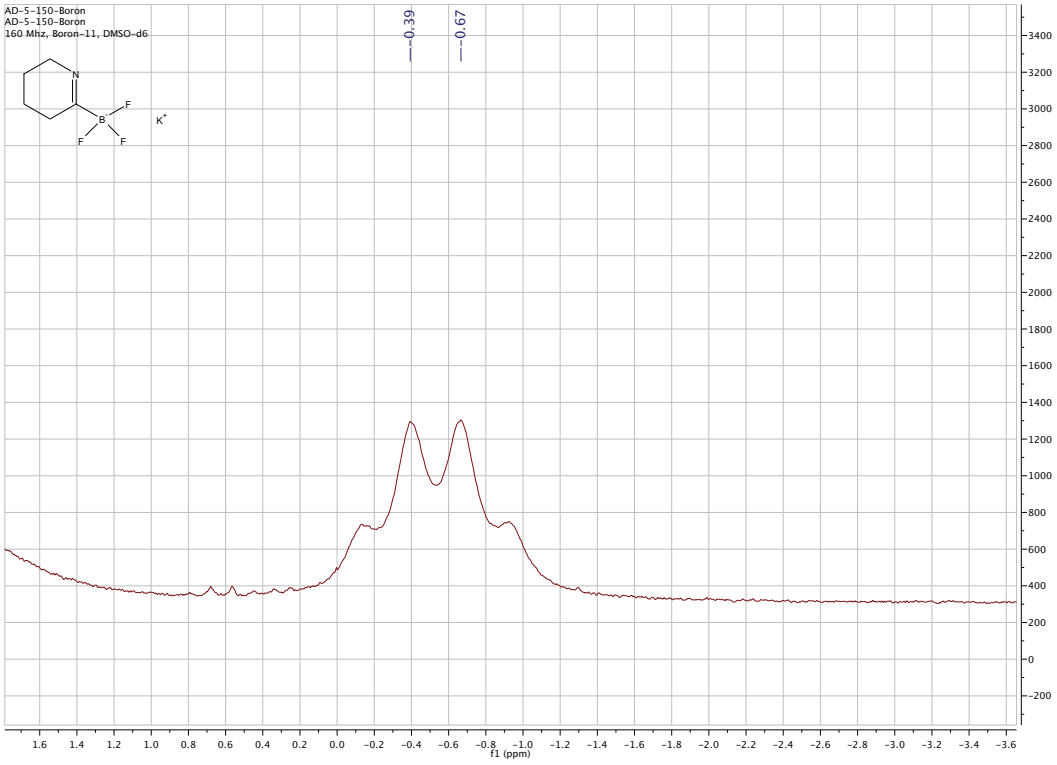


Potassium (3,4,5,6-tetrahydropyridin-2-yl)trifluoroborate (14):

^{19}F NMR (282 MHz, acetone-d_6)

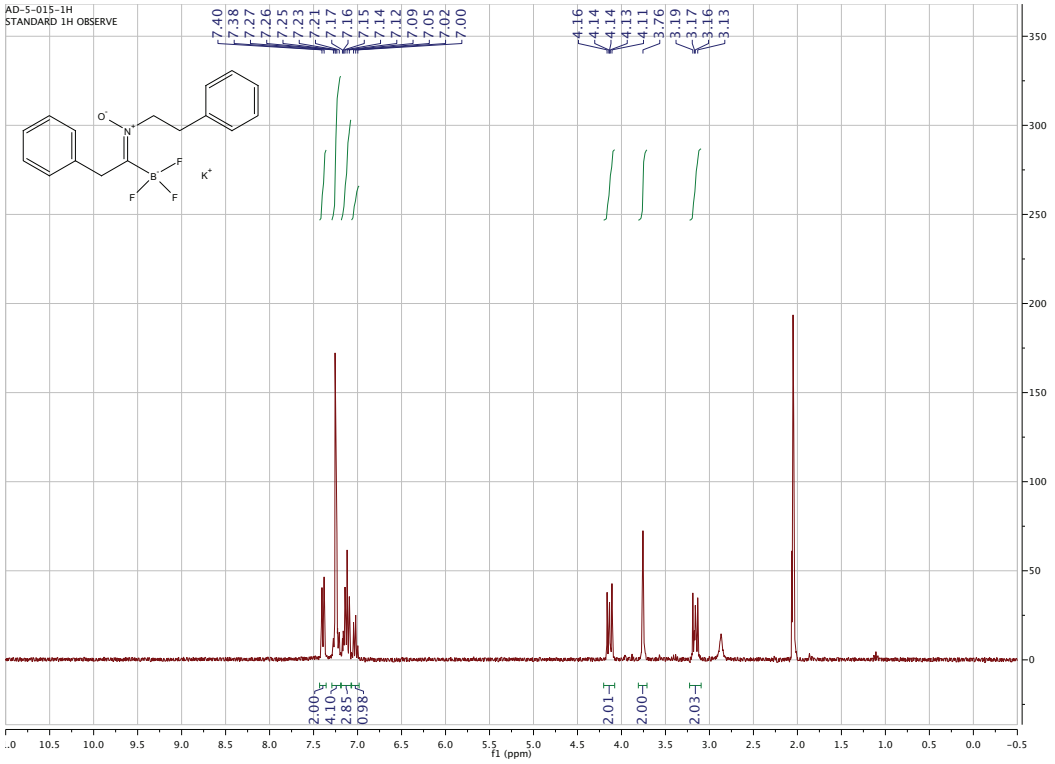


^{11}B NMR (160 MHz, DMSO-d_6)

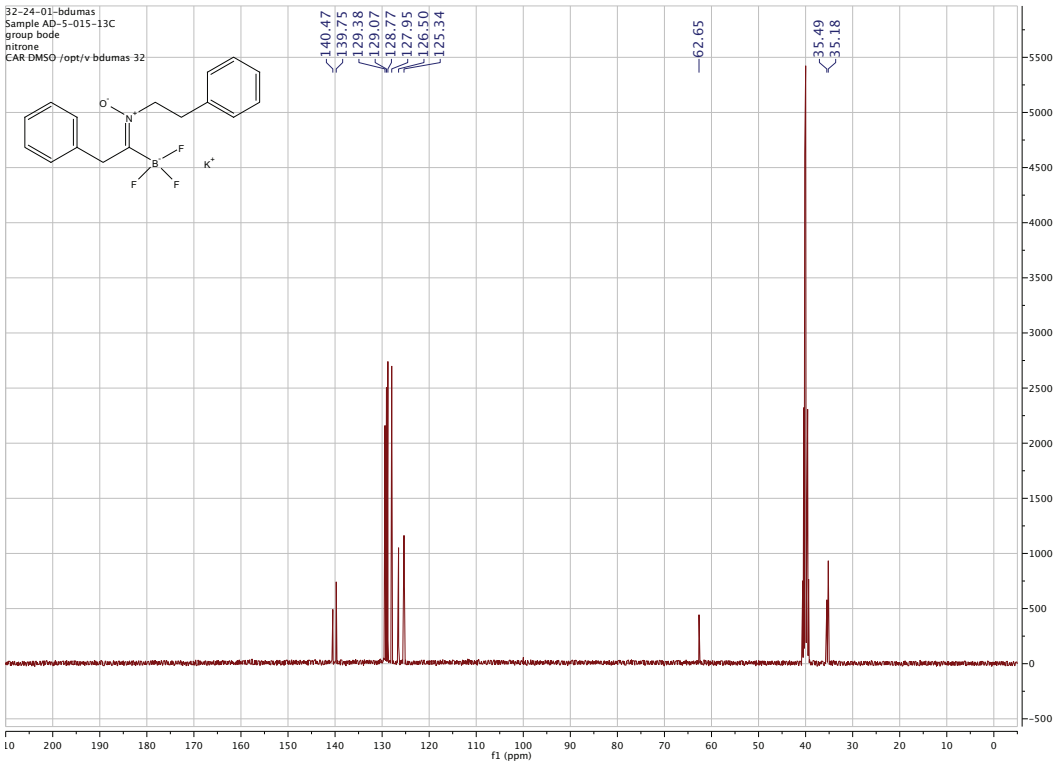


Nitrone 16:

^{1}H NMR (300 MHz, acetone-d_6)

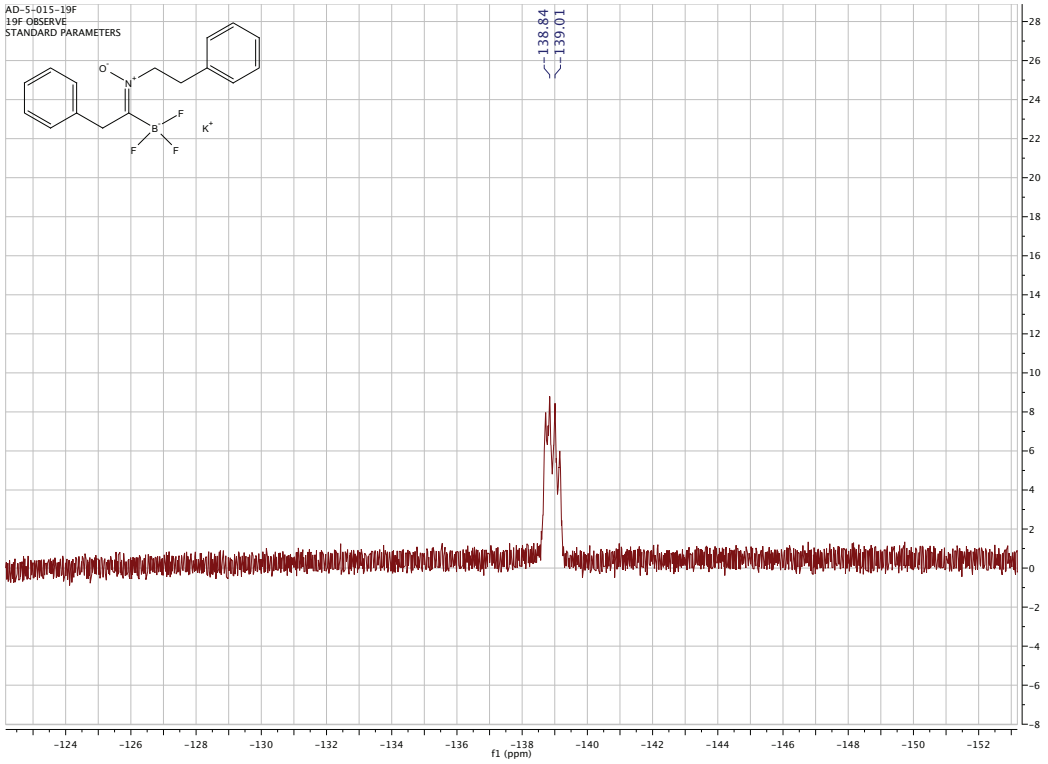


^{13}C NMR (100 MHz, DMSO-d_6)



Nitrone 16:

^{19}F NMR (282 MHz, acetone-d_6)



^{11}B NMR (160 MHz, DMSO-d_6)