Supporting Information

Synthesis of allyl sulfones from potassium allyltrifluoroborates

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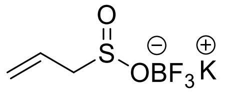
1. General Information

Solvents for the reactions were dried over standard drying agents and freshly distilled prior to use. Commercially available reagents were used as received. All reactions were followed by TLC on E. Merck Kieselgel 60 F254, with detection by UV light. Column chromatography was performed on silica gel (60 Å, 40-63 µm, ROCC). Melting points were recorded with a Fisher Digital Melting Point Analyzer Model 355 apparatus and are uncorrected. IR spectra were recorded as thin films on KBr plates or in KBr with FT-IR Perkin Elmer Spectrum BX (4000 - 450 cm-1). ^1H and ^{13}C-NMR spectra were recorded on a Bruker 300 MHz, in $CDCl_3$, $DMSO_{d6}$ or D_2O at 25 °C. ^{11}B and ^{19}F-NMR spectra were recorded on a Varian 400 MHz in D_2O. Chemical shifts (δ) values are reported in ppm. The residual solvent peaks are used as internal reference ($CDCl_3$ 7.26 ppm, $DMSO_{d6}$ 2.50 ppm, D_2O 4.79 for ^1H-NMR, $CDCl_3$ 77.16 ppm, $DMSO_{d6}$ 39.52 ppm for ^{13}C-NMR), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); *J* in hertz. High-resolution mass-spectra (ESI) were performed on Agilent 1290 Infinity series UPLC connected to Agilent 6230 TOF mass spectrometer (calibration at m/z 121.050873 and m/z 922.009798).

2. Synthetic procedures and product characterization

Potassium 3-((allylsulfinyl)oxy)trifluoroborate 2



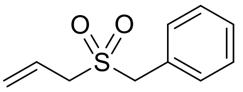
Anh. SO_2 (10 ± 1 mL) was transferred through a vacuum line to a flamed-dried two-neck round bottom flask containing potassium allyltrifluoroborate **1** (50 mg, 0.338 mmol) at -78 °C. After stirring at -78 °C for 30 minutes the excess of SO_2 was evaporated at -20 °C and the residue was dried under reduced pressure. Potassium 3-((allylsulfinyl)oxy)trifluoroborate) **2** (70 mg, 98%) was obtained as a white paste. ^1H-NMR ($DMSO_{d6}$, 300 MHz): δ 5.74 (ddt, 1H, ^3J =17.0, 9.4, 7.5 Hz, CH-allyl), 5.19 - 5.29 (m, 2H, H_2C-allyl), 3.07 - 3.23 (m, 2H, CH_2 SO_2). ^{13}C-NMR ($DMSO_{d6}$,75.5 MHz,): δ 128.3, 121.2, 63.1. ^1H-KMR (D_2O, 400 MHz,): δ 5.87 (ddt, 1H, ^3J= 17.0, 10.4, 7.7 Hz, CH-allyl), 5.43 (dt, 1H, ^3J = 10.4 Hz, ^4J = 0.7 Hz, H_a-C(allyl)), 5.38 (dq, 1H, ^3J= 17.0 Hz, ^4J = 1.2 Hz, H_b-C(allyl)), 3.39 (ddd, 2H, ^4J = 1.2, 0.7 Hz, ^3J= 7.7 Hz, CH_2SO_2). ^{13}C-NMR (D_2O, 100 MHz,): δ 125.9, 122.8, 63.0. ^{11}B-NMR (D_2O, 128 MHz): δ 0.18 (q, ^1J = 15.1 Hz). ^{19}F-NMR (D_2O, 377 MHz): δ 141.38 (q, ^1J= 15.1 Hz).

General Procedure for Preparation of Sulfones

Anh. SO_2 (10 ± 1 mL) was transferred through a vacuum line at -78 °C to a flamed-dried two-neck round bottom flask containing potassium allyltrifluoroborate **1** (50 mg, 0.338 mmol). After stirring at -78 ^oC for 30 minutes the excess of SO_2 was evaporated at -20 ^oC and the residue (product **2**) was dried under reduced pressure and used in the next step.

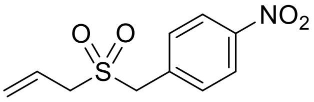
A solution of halide derivative **5** (1.2 equiv.; for **5g**,**f** - 1.5 equiv.) and TBAI (0.1 equiv.) in DMF (1–1.5 mL for 60 – 70 mg of product **2**) was added dropwise to a solution of potassium 3-((allylsulfinyl)oxy)trifluoroborate **2** (1 equiv.) in aqueous solution (0.5 – 1 mL) containing NaOH (0.4 equiv.) or K_2CO_3 (0.4 equiv.) (for the details see Table 3 in manuscript). The resulting emulsion/suspension was stirred for 24 h (for **5f** – 36 h) at room temperature (approximately 20 ^oC) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed several times with brine, dried (Na_2SO_4), evaporated and purified by column chromatography (eluent DCM).

((Allylsulfonyl)methyl)benzene 6a



Compound **6a** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (33.2 mg, 0.224 mmol, 1 equiv.), benzyl bromide (46 mg / 32 μL, 0.269 mmol, 1.2 equiv.), NaOH (3.6 mg, 0.09 mmol, 0.4 equiv.), TBAI (0.008 g, 0.022 mmol, 0.1 equiv.), DMF (1.5 mL), H_2O (0.5 mL). Purified by column chromatography 100% DCM. Yield (34 mg, 77%). Colorless oil. R_f = 0.10 (17 % Hex/EtOAc). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.39-7.43 (m, 5H, H-C(Ar)), 5.93 (ddt, 1H, ^3J = 17.4, 10.2, 7.3 Hz, CH-allyl), 5.53 (dd, 1H, ^3J = 10.1 Hz, ^2J = 0.9 Hz, H_a-C(allyl)), 5.42 (dd, 1H, ^3J = 17.3 Hz, ^2J = 0.9, H_b-C(allyl)), 4.22 (s, 2H, CH_2Ar), 3.59 (d, 2H, ^3J = 7.3 Hz, CH_2SO_2).[1]

1-((Allylsulfonyl)methyl)-4-nitrobenzene 6b



Compound **6b** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (44 mg, 0.297 mmol, 1 equiv.), 1-(bromomethyl)-4-nitrobenzene (77 mg, 0.359 mmol, 1.2 equiv.), NaOH (5 mg, 0.125 mmol, 0.4 equiv.), TBAI (11 mg, 0.030 mmol, 0.1 equiv.), DMF (1.5 mL), H_2O (0.5 mL). Purified by column chromatography 100% DCM. Yield (50 mg, 70%). Amorphous white powder. R_f = 0.26 (DCM). M.p. = 119…120 °C. IR (KBr): 1520, 1510, 1350, 1321, 1295, 1155, 1125, 1105, 1090. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.27 (d, 2H, ^3J = 8.5 Hz, H-C(Ar)), 7.60 (d, 2H, ^3J = 8.5 Hz, H-C(Ar)), 5.96 (ddt, 1H, ^3J =17.3, 10.1, 7.3 Hz, CH-allyl), 5.57 (dd, 1H, ^3J = 10.1 Hz, ^2J = 0.9, H_a-C(allyl)), 5.46 (dd, 1H, ^3J = 17.3 Hz, ^2J = 0.9 Hz, H_b-C(allyl)), 4.31 (s, 2H, CH_2Ar), 3.69 (d, 2H, ^3J = 7.3 Hz,

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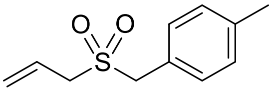
[1] Markovic, D.; Volla, C. M. R.; Vogel, P.; Varela-Alvarez, A.; Sordo, J. A. *Chem. Eur. J.* **2010**, *16*, 5969.

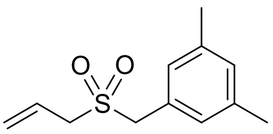
CH_2SO_2). ^{13}C-NMR **(**$CDCl_3$, 75.5 MHz**)**: δ 148.2, 134.6, 132.1, 125.5, 124.8, 124.1, 57.3, 57.0. HRMS m/z calcd. for $C_{10}H_{11}NO_4SNa$ $[M+Na]^+$ 264.0301; found 264.0296.

1-((Allylsulfonyl)methyl)-4-methylbenzene 6c



Compound **6c** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (40 mg, 0.270 mmol, 1 equiv.), 1-(bromomethyl)-4-methylbenzene (60 mg, 0.324 mmol, 1.2 equiv.), NaOH (4.4 mg, 0.110 mmol, 0.4 equiv.), TBAI (10 mg, 0.027 mmol, 0.1 equiv.), DMF (1.5 mL), H_2O (0.5 mL). Purified by column chromatography 100% DCM. Yield (44 mg, 77%). Amorphous white powder. $R_f = 0.48$ (DCM). M.p. = 50…51 °C. IR (KBr): 1515, 1415, 1300, 1285, 1120. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.29 (d, 2H, $^3J = 8.1$ Hz, H-C(Ar)), 7.21 (d, 2H, $^3J = 8.1$ Hz, H-C(Ar)), 5.92 (ddt, 1H, $^3J = 17.1$, 10.1, 7.3 Hz, CH-allyl), 5.52 (dd, 1H, $^3J = 10.1$ Hz, $^2J = 0.7$ Hz, H_a-C(allyl)), 5.41 (dd, 1H, $^3J = 17.1$ Hz, $^2J = 0.7$ Hz, H_b-C(allyl)), 4.18 (s, 2H, CH_2Ar), 3.57 (d, 2H, $^3J = 7.3$ Hz, CH_2SO_2), 2.37 (s, 3H, CH_3). ^{13}C-NMR **(**$CDCl_3$, 75.5 MHz**)**: δ 139.2, 130.7, 129.9, 125.1, 124.9, 124.7, 57.8, 55.9, 21.4. HRMS m/z calcd. for $C_{11}H_{14}O_2SNa$ $[M+Na]^+$ 233.0607; found 233.0598.

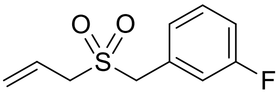
1-((Allylsulfonyl)methyl)-3,5-dimethylbenzene 6d



Compound **6d** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (37 mg, 0.250 mmol, 1 equiv.), 1-(bromomethyl)-3,5-dimethylbenzene (75 mg, 0.374 mmol, 1.5 equiv.), K_2CO_3 (14 mg, 0.101 mmol, 0.4 equiv.), TBAI (9 mg, 0.025 mmol, 0.1 equiv.), DMF (1.5 mL), H_2O (0.5 mL). Purified by column chromatography 100% DCM. Yield (39 mg, 70%). Amorphous white powder. $R_f = 0.42$ (DCM). M.p. = 106 °C. IR (KBr): 2920, 1605, 1310, 1295, 1135, 1120. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.98 - 7.05 (m, 3H, H-C(Ar)), 5.93 (ddt, 1H, $^3J = 17.1$, 10.2, 7.3 Hz, CH-allyl), 5.53 (dd, 1H, $^3J = 10.2$ Hz, $^2J = 1.0$, H_a-C(allyl)), 5.41 (dd, 1H, $^3J = 17.1$ Hz, $^2J = 1.0$ Hz, H_b-C(allyl)), 3.59 (d, 2H, $^3J = 7.3$ Hz, CH_2SO_2), 4.14 (s, 2H, CH_2Ar), 2.33 (s, 6H, $2CH_3$). ^{13}C-NMR **(**$CDCl_3$, 75.5 MHz**)**: δ 138.8, 130.9, 128.7, 127.6, 125.1, 124.9, 58.2, 56.0, 21.4. HRMS m/z calcd. for $C_{12}H_{17}O_2S$ $[M+H]^+$ 225.0944; found 225.0930.

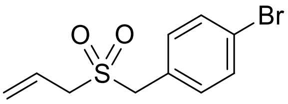
1-((Allylsulfonyl)methyl)-3-fluorobenzene 6e

Compound **6e** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (37 mg, 0.250 mmol, 1 equiv.), 1-(bromomethyl)-3-fluorobenzene (71 mg / 46 μL, 0.375 mmol, 1.5 equiv.), NaOH (4 mg, 0.100 mmol, 0.4 equiv.), TBAI (9 mg, 0.025 mmol,



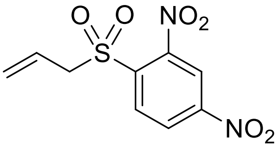
0.1 equiv.), DMF (1 mL), H_2O (1 mL). Purified by column chromatography 100% DCM. Yield (42 mg, 78%). Amorphous white powder. R_f = 0.43 (DCM). M.p. = 73...74 °C. IR (KBr): 2990, 1590, 1320, 1285, 1150, 1130. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.38 (td, 1H, ^3J = 7.7 Hz, $^4J_{HF}$ = 5.8 Hz, H-C(Ar)), 7.07-7.22 (3H, m, H-C(Ar)), 5.94 (ddt, 1H, ^3J = 17.1, 10.2, 7.3 Hz, CH-allyl), 5.55 (dd, 1H, ^3J = 10.2 Hz, ^2J = 1.1 Hz, H_a-C(allyl)), 5.43 (dd, 1H, ^3J = 17.1 Hz, ^2J = 1.1 Hz, H_b-C(allyl)), 4.21 (s, 2H, CH_2Ar), 3.62 (d, 2H, ^3J = 7.3 Hz, CH_2SO_2). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 162.9 ($^1J_{CF}$ = 248.8), 130.7 ($^3J_{CF}$ = 8.6), 129.9 ($^3J_{CF}$ = 8.0), 126.7 ($^4J_{CF}$ = 3.1), 125.2, 124.9, 118.0 ($^2J_{CF}$ = 22.6), 116.3 ($^2J_{CF}$ = 21.0), 57.4, 56.4. HRMS m/z calcd. for $C_{10}H_{12}FO_2S$ $[M+H]^+$ 251.0537; found 251.0519.

1-((Allylsulfonyl)methyl)-4-bromobenzene 6f



Compound **6f** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (44 mg, 0.297 mmol, 1 equiv.), 1-bromo-4-(bromomethyl)benzene (112 mg, 0.447 mmol, 1.5 equiv.), K_2CO_3 (16.5 mg, 0.119 mmol, 0.4 equiv.), TBAI (11 mg, 0.030 mmol, 0.1 equiv.), DMF (1.5 mL), H_2O (0.5 mL). Purified by column chromatography 100% DCM. Yield (57 mg, 70%). Amorphous white powder. R_f = 0.39 (DCM). M.p. = 69...70 °C. IR (KBr): 2940, 1485, 1310, 1295, 1275, 1125. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.55 (d, 2H, ^3J = 8.3 Hz, H-C(Ar)), 7.28 (d, 2H, ^3J = 8.3 Hz, H-C(Ar)), 5.94 (ddt, 1H, ^3J =17.1, 10.2 Hz, CH-allyl), 5.54 (d, 1H, ^3J = 10.2 Hz, H_a-C(allyl)), 5.42 (d, 1H, ^3J = 17.1 Hz, H_b-C(allyl)), 4.16 (s, 2H, CH_2Ar), 3.60 (d, 2H, ^3J = 7.3 Hz, CH_2SO_2). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 132.5, 132.4, 126.7, 125.2, 125.0, 123.7, 57.2, 56.4.

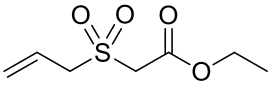
1-(Allylsulfonyl)-2,4-dinitrobenzene 6g



Compound **6g** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (45 mg, 0.304 mmol, 1 equiv.), 1-fluoro-2,4-dinitrobenzene (68 mg / 46 μL, 0.365 mmol, 1.2 equiv.), NaOH (5 mg, 0.125 mmol, 0.4 equiv.), TBAI (11 mg, 0.030 mmol, 0.1 equiv.), DMF (1 mL), H_2O (1 mL). Purified by column chromatography 100% DCM. Yield (75 mg, 91%). Amorphous yellow powder. R_f = 0.52 (DCM). M.p. = 111...112 °C. IR (KBr): 3095, 1555, 1535, 1365, 1350, 1325, 1300, 1150. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.65 (d, 1H, ^4J = 2.2 Hz, H-C(Ar)), 8.56 (dd, 1H, ^3J = 8.6 Hz, ^4J = 2.2 Hz, H-C(Ar)), 8.30 (d, 1H, ^3J = 8.6 Hz, H-C(Ar)), 5.85 (ddt, 1H, ^3J = 17.1, 10.1, 7.5 Hz, CH-allyl), 5.44 (d, 1H, ^3J = 10.1 Hz, H_a-C(allyl)), 5.38 (dd, 1H, ^3J = 17.1 Hz, ^2J = 0.9 Hz,

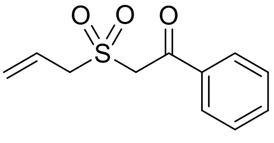
H_b-C(allyl)), 4.35 (d, 2H, ^3J = 7.5 Hz, CH_2SO_2). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 150.8, 149.7, 137.2, 135.0, 126.9, 126.7, 123.5, 120.4, 61.2. HRMS m/z calcd. for $C_9H_9N_2O_6S$ [M+H]$^+$ 273.0176; found 273.0116.

Ethyl 2-(allylsulfonyl)acetate 6h



Compound **6h** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (30 mg, 0.203 mmol, 1 equiv.), ethyl 2-bromoacetate (34 mg / 23 μL, 0.203 mmol, 1 equiv.), K_2CO_3 (11 mg, 0.081 mmol, 0.4 equiv.), TBAI (7.5 mg, 0.020 mmol, 0.1 equiv.), DMF (1 mL), H_2O (1 mL). Purified by column chromatography 100% DCM. Yield (24 mg, 62%). Colorless oil. R$_f$ = 0.36 (DCM). IR (KBr): 2925, 2855, 1740, 1730, 1325, 1140, 1110, 1025. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.95 (ddt, 1H, ^3J = 17.3, 10.0, 7.4 Hz, CH-allyl), 5.52-5.62 (m, 2H, CH_2-allyl), 4.28 (q, 2H, ^3J = 7.1 Hz, CH_2), 4.00 (d, 2H, ^3J = 7.4 Hz, CH_2SO_2), 3.95 (s, 2H, CH_2CO_2), 1.33 (t, 3H, ^3J = 7.1 Hz, CH_3). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 163.3, 126.0, 124.9, 62.8, 57.9, 55.1, 14.1. HRMS m/z calcd. for $C_7H_{13}O_4S$ [M+H]$^+$ 193.0529; found 193.0519.

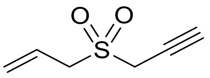
2-(Allylsulfonyl)-1-phenylethanone 6i



Compound **6i** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (30 mg, 0.203 mmol, 1 equiv.), 2-bromo-1-phenylethanone (48 mg, 0.243 mmol, 1.2 equiv.), K_2CO_3 (11 mg, 0.081 mmol, 0.4 equiv.), TBAI (7.5 mg, 0.020 mmol, 0.1 equiv.), DMF (1 mL), H_2O (1 mL). Purified by column chromatography 100% DCM. Yield (29 mg, 64%). Colorless oil. R$_f$ = 0.48 (DCM). IR (KBr): 2920, 1680, 1595, 1320, 1280, 1140, 1125. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.99 (d, 2H, ^3J = 7.7 Hz, H-C(Ar)), 7.66 (1H, t, ^3J = 7.7 Hz, H-C(Ar)), 7.53 (t, 2H, ^3J = 7.7 Hz, H-C(Ar)), 5.98 (ddt, 1H, ^3J = 17.4, 10.0, 7.4 Hz, CH-allyl), 5.52-5.65 (m, 2H, CH_2-allyl), 4.57 (s, 2H, CH_2-CO), 4.02 (d, 2H, ^3J = 7.4 Hz, CH_2SO_2). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 189.5, 135.9, 134.8, 129.3, 129.2, 126.1, 124.9, 58.2, 57.3. HRMS m/z calcd. for $C_{11}H_{13}O_3S$ [M+H]$^+$ 225.0580; found 225.0572.

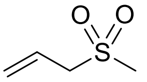
3-(Prop-2-yn-1-ylsulfonyl)prop-1-ene 6j

Compound **6j** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (50 mg, 0.338 mmol, 1 equiv.), propargyl bromide (80% in toluene, 75 mg / 55 μL, 0.507 mmol, 1.5 equiv.), K_2CO_3 (19 mg, 0.138 mmol, 0.4 equiv.), TBAI (12.5 mg, 0.034 mmol, 0.1 equiv.), DMF (1.5 mL), H_2O (1 mL). Purified by column chromatography 100% DCM. Yield (34 mg,



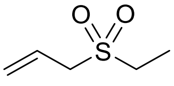
69%). Colorless oil. $R_f = 0.41$ (DCM). IR (KBr): 3270, 2960, 2920, 2130, 1320, 1125. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.95 (ddt, 1H, $^3J = 17.3, 9.9, 7.5$ Hz, CH-allyl), 5.49-5.61 (m, 2H, H_2C-allyl), 3.92 (d, 2H, $^3J = 7.5$ Hz, CH_2SO_2), 3.83 (d, 2H, $^4J = 2.7$ Hz, CH_2-propargyl), 2.53 (t, 1H, $^4J = 2.7$ Hz, CH-propargyl). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 125.8, 124.6, 76.7, 71.7, 55.7, 43.1. HRMS m/z calcd. for $C_6H_9O_2S$ $[M+H]^+$ 145.0318; found 145.0305.

3-(Methylsulfonyl)prop-1-ene 6k



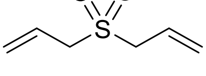
Potassium 3-((allylsulfinyl)oxy)trifluoroborate **2** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (33 mg, 0.223 mmol, 1 equiv.). Then it was dissolved in water (1 mL) containing NaOH (13.4 mg, 335 mmol, 1.5 equiv.). and dimethylsulfate (28 mg / 21 μl, 0.224 mmol, 1 equiv.) was added. The resulting reaction mixture was stirred for 24 h at room temperature and extracted with EtOAc (3×5 mL). The combined organic layers were dried over Na_2SO_4, filtred, evaporated and purified by column chromatography (eluent DCM) yielding 14 mg (53%) of compound **6k** as colorless oil. $R_f = 0.06$ (DCM). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.97 (ddt, 1H, $^3J = 17.3, 10.2, 7.4$ Hz, CH-allyl), 5.42-5.55 (m, 2H, H_2C-allyl), 3.73 (d, 2H, $^3J = 7.4$ Hz, CH_2SO_2), 2.87 (s, 1H, CH_3).[2]

3-(Ethylsulfonyl)prop-1-ene 6o



Compound **6o** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (78 mg, 0.527 mmol, 1 equiv.), iodoethane (99 mg / 51 μL, 0.632 mmol, 1.2 equiv.), NaOH (8 mg, 0.211 mmol, 0.4 equiv.), TBAI (19 mg, 0.053 mmol, 0.1 equiv.), DMF (1 mL), H_2O (1 mL). Purified by column chromatography 100% DCM. Yield (19 mg, 27%). Colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.85 (ddt, 1H, $^3J = 17.1, 10.1, 7.7$ Hz, CH-allyl), 5.46-5.33 (m, 2H, H_2C-allyl), 3.64 (d, 2H, $^3J = 7.7$ Hz, CH_2SO_2), 3.03 (q, 2H, $^3J = 7.3$ Hz, CH_2), 1.31 (t, 3H, $^3J = 7.3$ Hz, CH_3).[3]

3-(Allylsulfonyl)prop-1-ene 6p



Compound **6p** was prepared according to the general procedure from potassium allyltrifluoroborate **1** (64 mg, 0.432mmol, 1 equiv.), 3-bromoprop-1-ene (75 mg / 54 μL, 0.519 mmol, 1.2 equiv.), NaOH (7 mg, 0.173 mmol, 0.4 equiv.), TBAI (16 mg, 0.043 mmol, 0.1 equiv.), DMF (1 mL), H_2O (1 mL). Purified by column chromatography 100% DCM.

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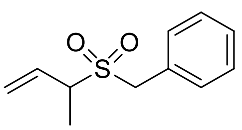
[2] Tsui, G. C.; Lautens, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 8938

[3] Sun, X.; Wang, L.; Zhang, Y. *Synth. Commun.* **1998**, *28*, 1785.

Yield (23 mg, 37%). Colorless oil. ^{1}H-NMR (CDCl$_3$, 300 MHz): δ 5.89 (ddt, 1H, ^3J = 17.5, 10.1, 7.4 Hz, CH-allyl), 5.51-5.35 (m, 2H, CH$_2$-allyl), 3.67 (d, 2H, ^3J = 7.2 Hz, CH$_2$SO$_2$).[4]

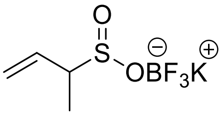
((But-3-en-2-ylsulfonyl)methyl)benzene 9



Into a flask equipped with a dry ice condenser compound **7a** (93 mg, 0.574 mmol) was placed under inert atmosphere. SO$_2$ (20 ml) was slowly condenced into the flask at – 78 °C for 15 min. The resulting reaction mixture was warmed to the boiling point of SO$_2$ (- 10 °C) and additionaly stirred for 30 min. Once the reaction was complete (^{1}H NMR control) excess of SO$_2$ was removed from reaction mixture by evaporation under reduced pressure. The crude **8a** was dissolved in DMF (1.5 mL), solution of NaOH (9 mg, 0.230 mmol, 0.4 equiv.) in 3 mL H$_2$O was slowly added at 0 °C and mixed for 30 min. Benzyl bromide (118 mg / 82 µL, 0.689 mmol, 1.2 equiv.) and TBAI (21 mg, 0.057 mmol, 0.1 equiv.) were added as a solution in DMF (1.5 mL). The resulting reaction mixture was stirred at this temperature for 18 h. Then the reaction mixture was partitioned between EtOAc and brine and the aqueous phase was extracted with EtOAc (10 ml, 3 times). The combined organic phase was washed with brine (5 mL, 10 times), dried (Na$_2$SO$_4$) and the solvent removed under reduced pressure. Column chromatography yielded 38 mg, 31 % of product **9**. Colorless oil. R$_f$ = 0.48 (17 % Hex/EtOAc). ^{1}H-NMR (CDCl$_3$, 300 MHz): δ 7.48 – 7.32 (m, 5H, H-C(Ar)), 5.98 (ddd, 1H, ^3J = 17.2, 10.3, 8.6 Hz, H-C(3)), 5.44 (d, 2H, ^3J = 17.2, 10.3 Hz, H-C(4)), 4.26 (d, 1H, ^2J = 14.1 Hz, H$_a$-C-C(Ar)), 4.19 (d, 1H, ^2J = 14.1 Hz, H$_b$-C-C(Ar)), 3.58 (dq, ^3J = 8.6, 6.7 Hz, H-C-SO$_2$), 1.47 (d, 3H, ^3J = 6.7 Hz, CH$_3$).^{13}C-NMR (CDCl$_3$, 75.5 MHz): δ 132.5, 131.1, 129.0, 127.7, 122.1, 60.5, 56.2, 12.5.

NMR studies of compound **8a** and **8b**: The crude products were dissolved in DMSO$_{d6}$ under inert atmosphere. The NMR spectra were collected at 25 °C.

Potassium ((but-3-en-2-ylsulfinyl)oxy)trifluoroborate 8a



Compound **8a** was prepared from potassium (*Z*)-but-2-en-1-yltrifluoroborate **7a** by a procedure similar to that for preparation of compound **2** (conditions: -10 °C, 30 min): ^{1}H-NMR (DMSO$_{d6}$, 300 MHz): δ 5.77 (dddq, 1H, ^3J = 17.4, 10.0, 6.7 Hz, ^4J = 2.0 Hz, H-C(3)), 5.27 – 5.10 (m, 2H, H$_2$C(4)), 2.93 (q, 1H, ^3J = 6.7 Hz, H-C-SO$_2$), 1.13 (dd, 3H, ^3J = 6.7 Hz, ^4J = 1.5 Hz, CH$_3$). ^{13}C-NMR (DMSO$_{d6}$, 75.5 MHz): δ 134.7, 118.2, 73.5, 25.0.

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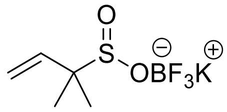
[4] Afrasiabi, R.; Farsani, M. R.; Yadollahi, B. *Tatrahedron Lett.* **2014**, *55*, 3923.

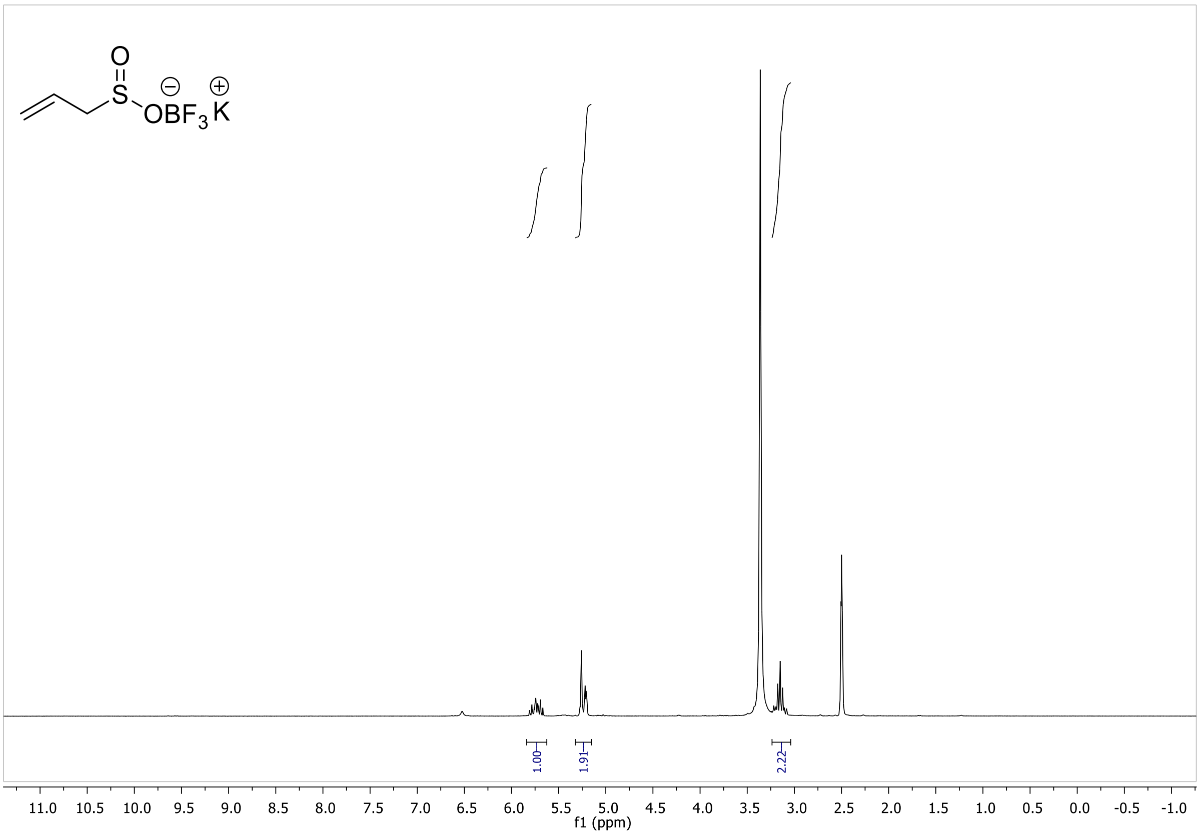
Potassium trifluoro(((2-methylbut-3-en-2-yl)sulfinyl)oxy)borate 8b



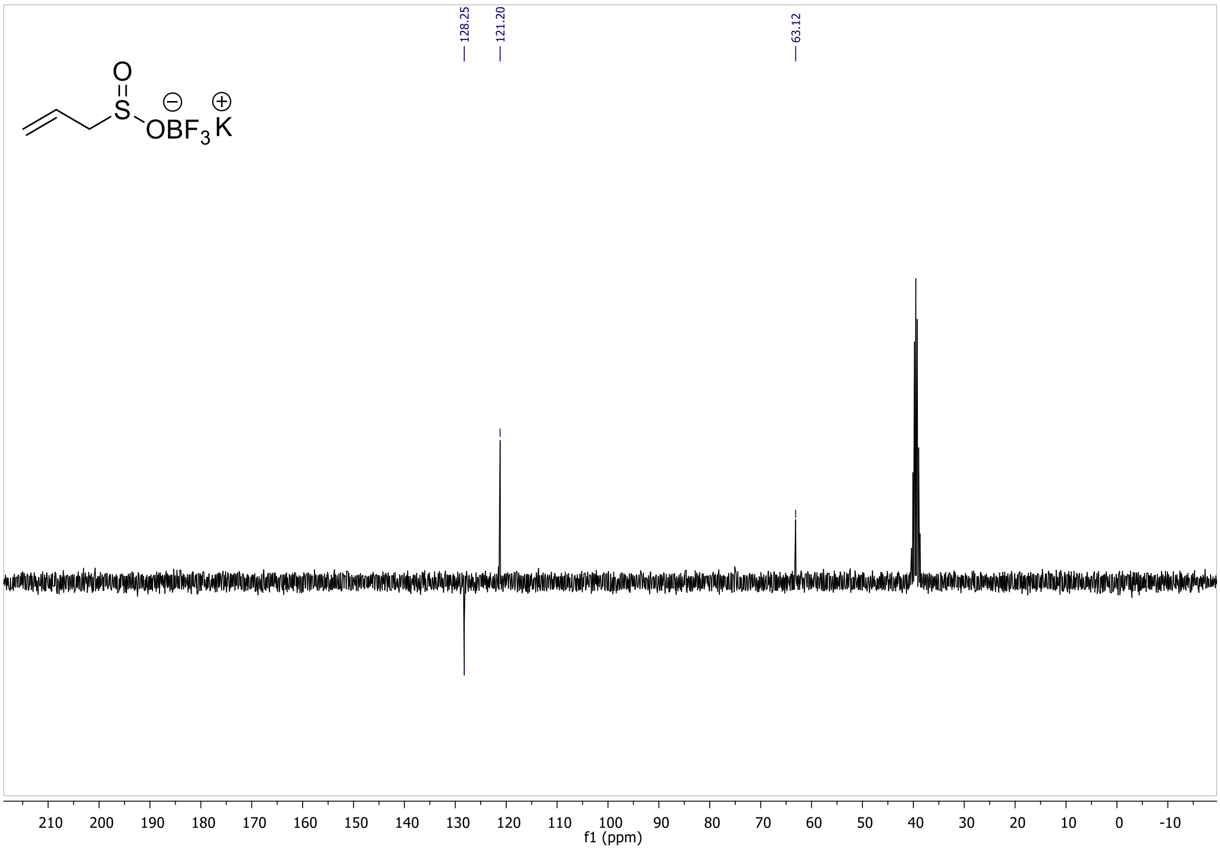
Compound **8b** was prepared from potassium trifluoro(3-methylbut-2-en-1-yl)borate **7b** by a procedure similar to that for preparation of compound **2** (conditions: -10 °C, 2 h): ^{1}H-NMR (DMSO$_{d6}$, 300 MHz): δ 5.80 (dd, 1H, ^3J = 17.4, 10.7 Hz, H-C(3)), 5.17 (dd, 1H, ^3J = 10.7 Hz, ^4J = 1.1 Hz, H$_a$-C(4)), 5.09 (dd, 1H, ^3J = 17.4 Hz, ^4J = 1.1 Hz, H$_b$-C(4)), 1.06 (s, 6H, 2CH$_3$). ^{13}C-NMR (DMSO$_{d6}$, 75.5 MHz): δ 139.8, 115.7, 73.9, 18.6, 18.3.

3. NMR Spectra

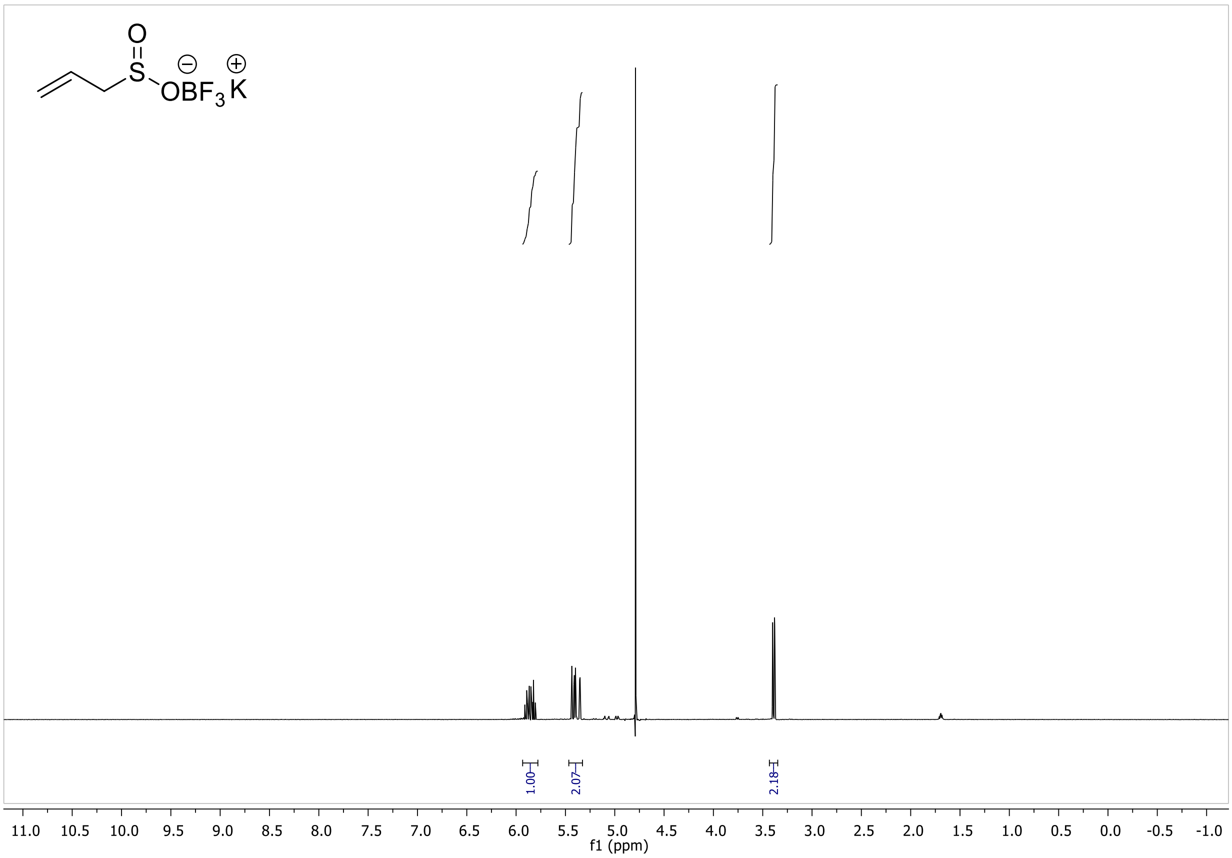
^{1}H-NMR (DMSO$_{d6}$, 300 MHz) spectrum of compound 2::



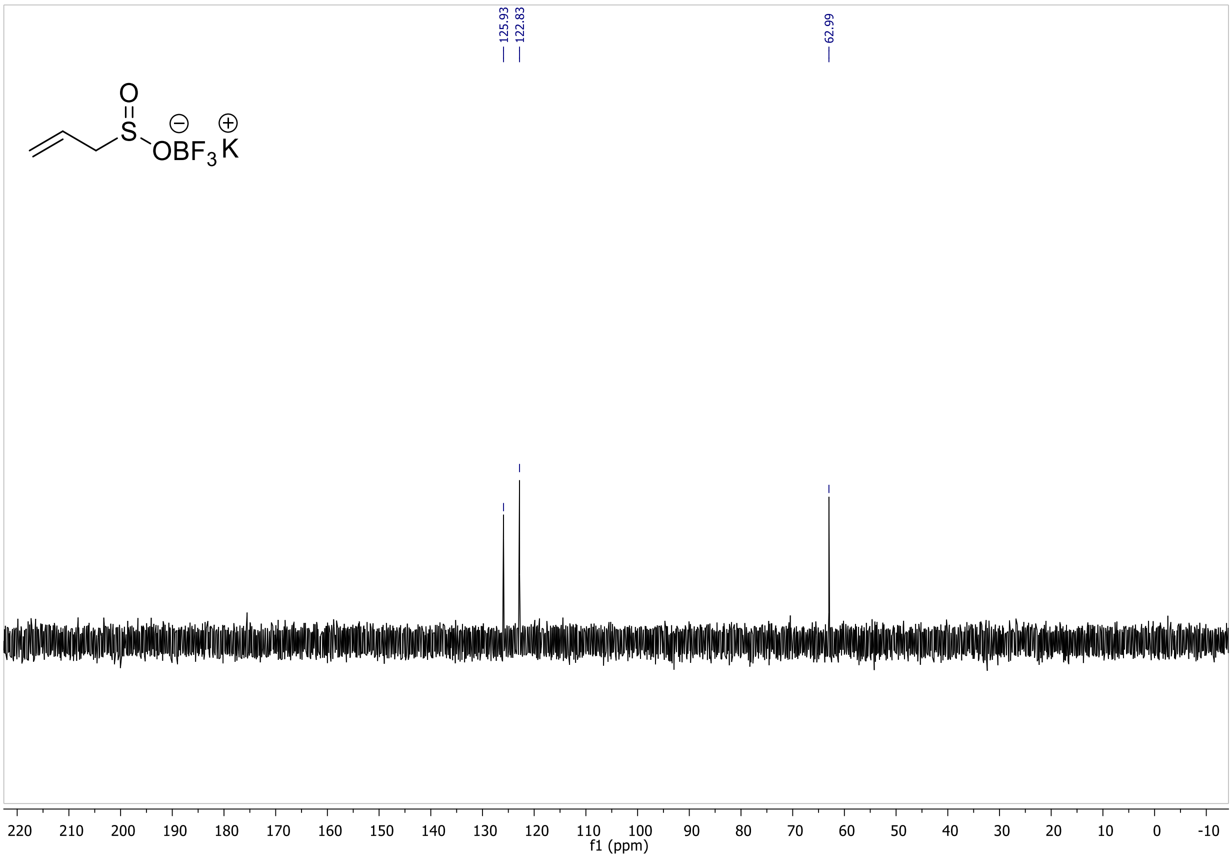
^{13}C-NMR (DMSO$_{d6}$, 75.5 MHz) spectrum of compound 2:



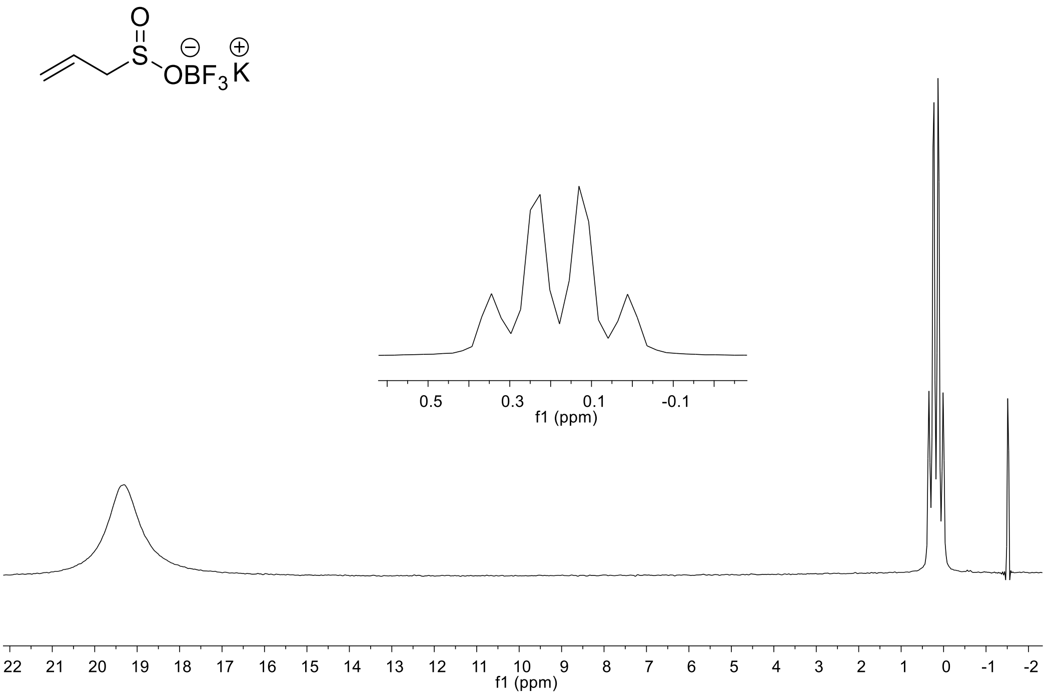
^{1}H-NMR (D_2O, 300 MHz) spectrum of compound 2:



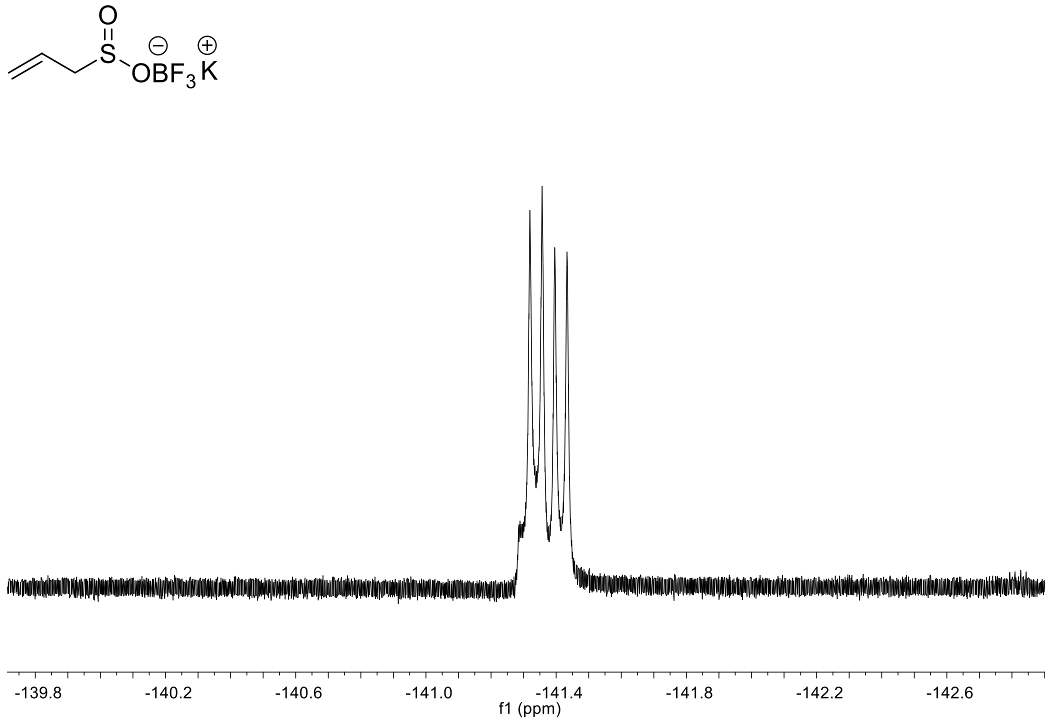
^{13}C-NMR (D_2O, 75.5 MHz) spectrum of compound 2:



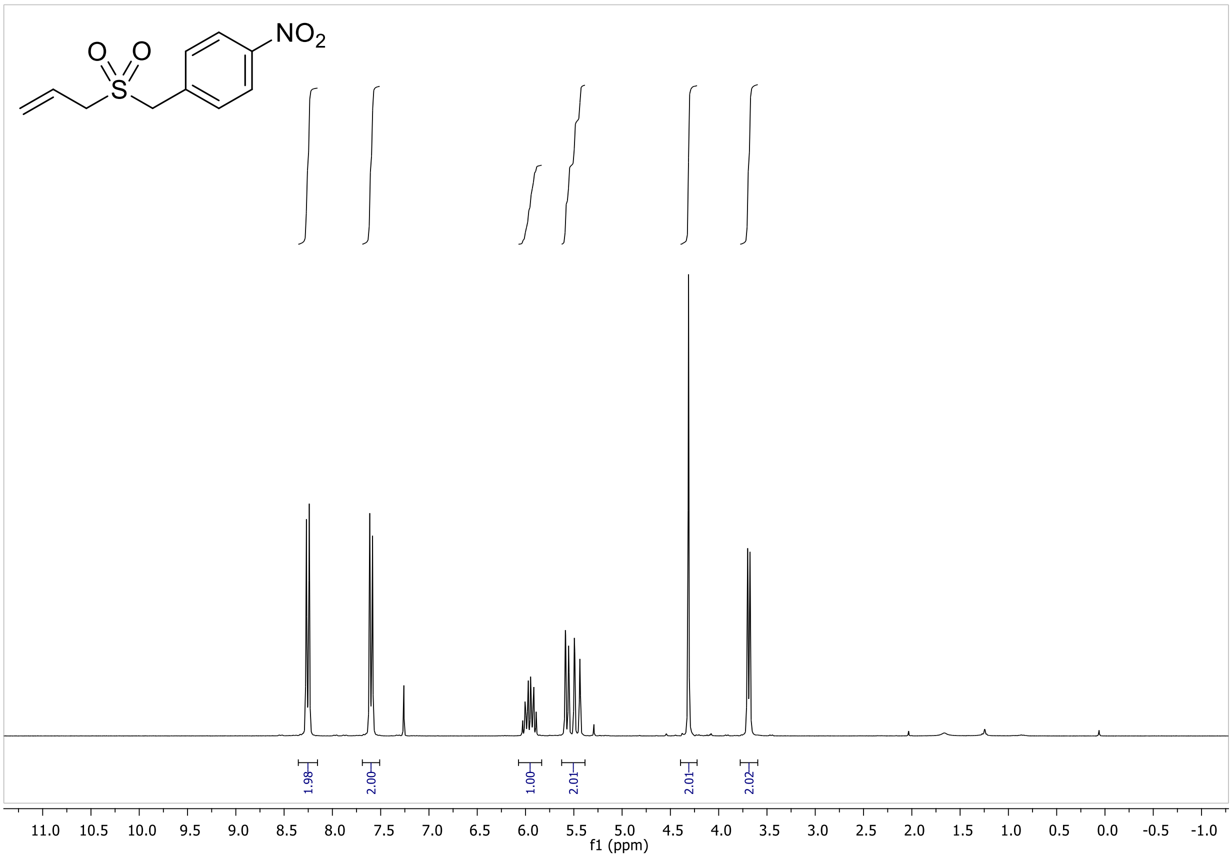
^{11}B-NMR (D_2O, 128 MHz) spectrum of compound 2:



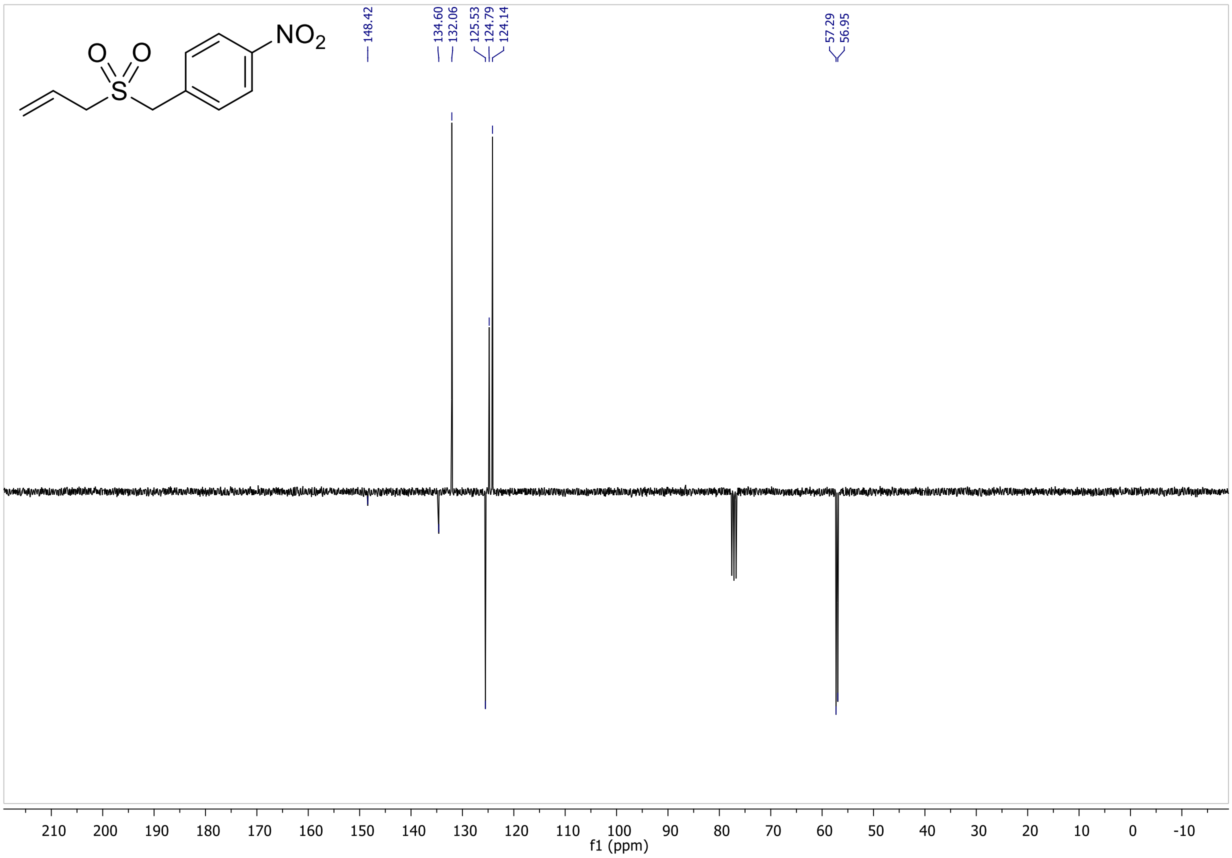
^{19}F-NMR (D_2O, 377 MHz) spectrum of compound 2:



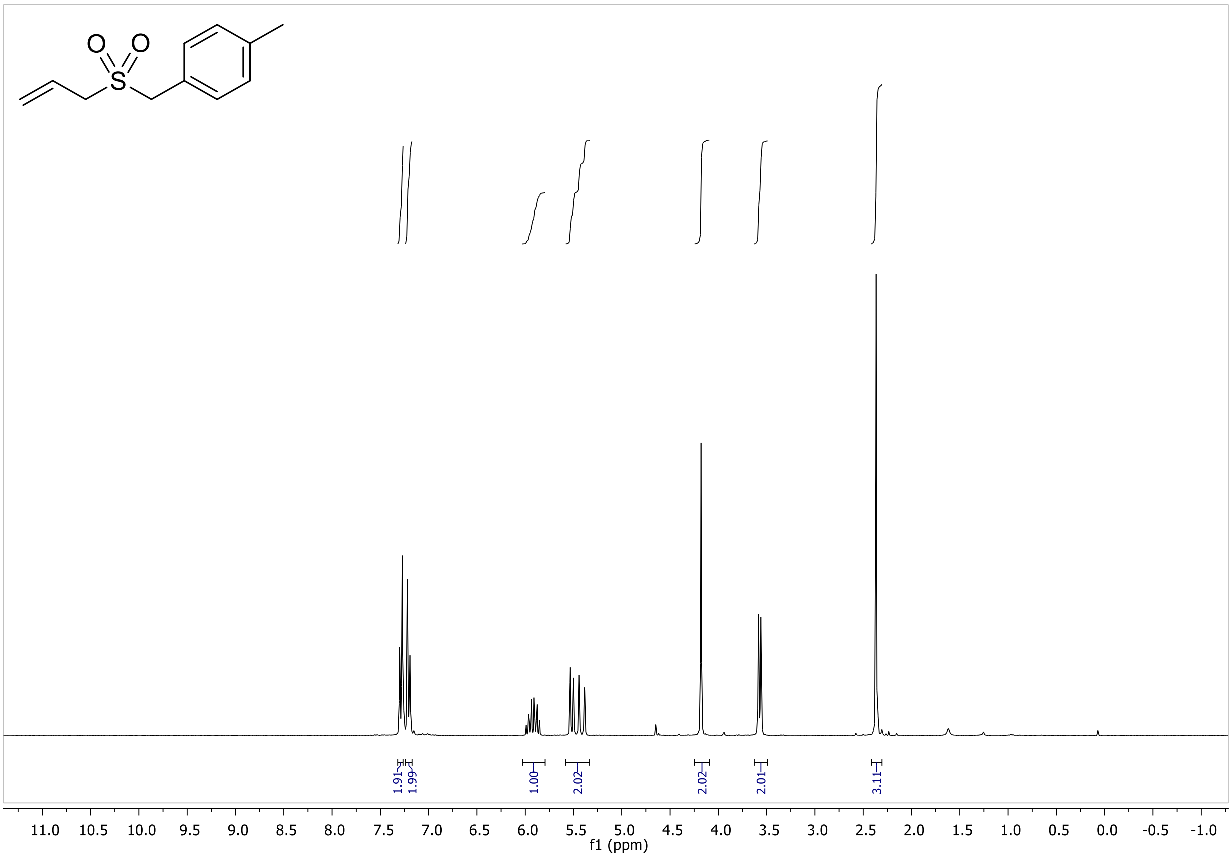
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of compound 6b:



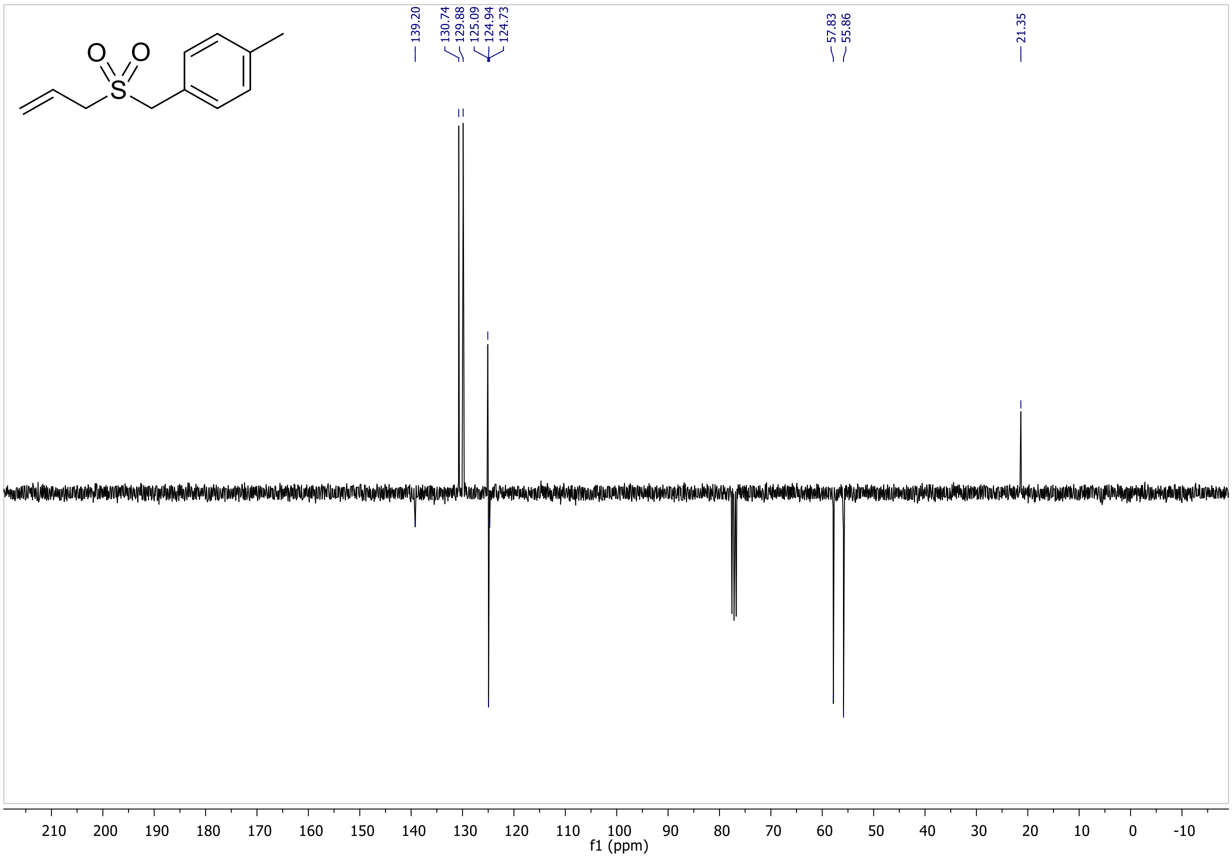
^{13}C-NMR ($CDCl_3$, 75.5 MHz) spectrum of compound 6b:



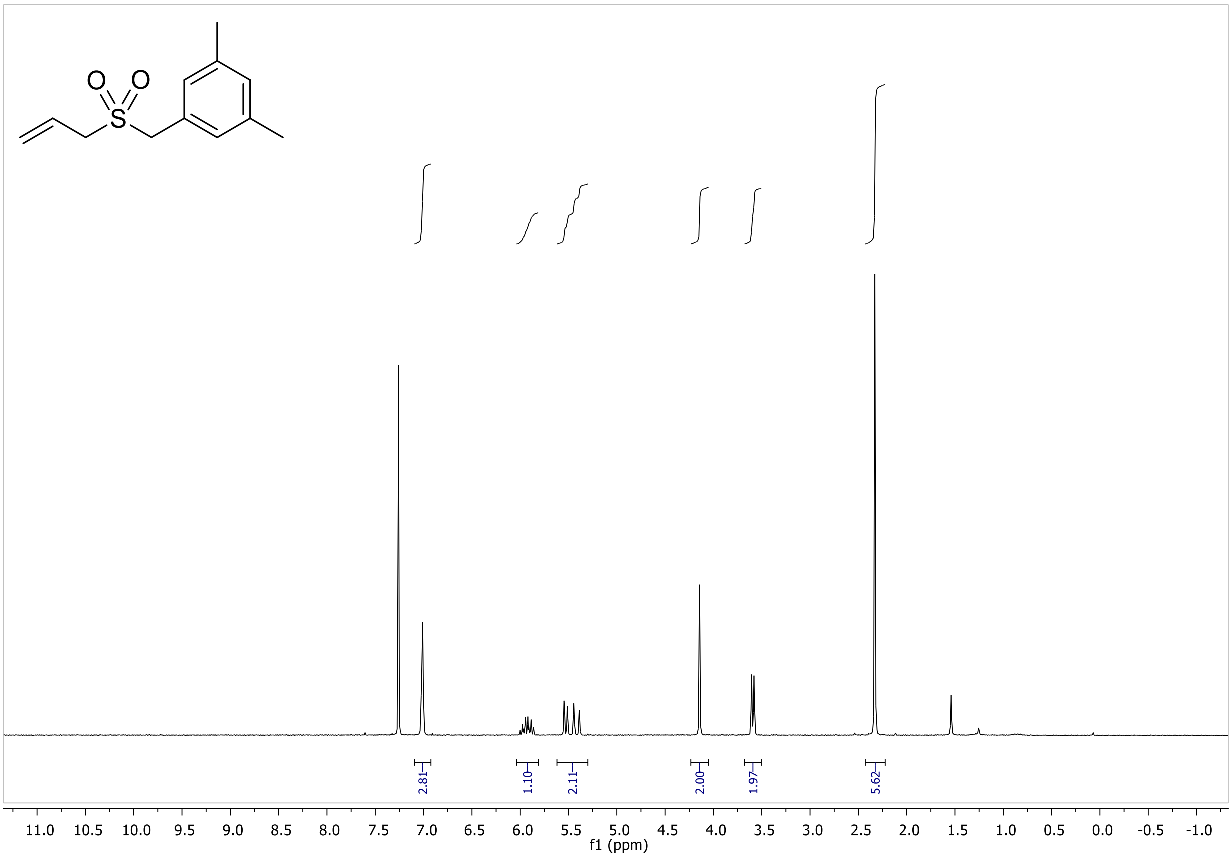
^{1}H-NMR (CDCl$_3$, 300 MHz) spectrum of compound 6c:



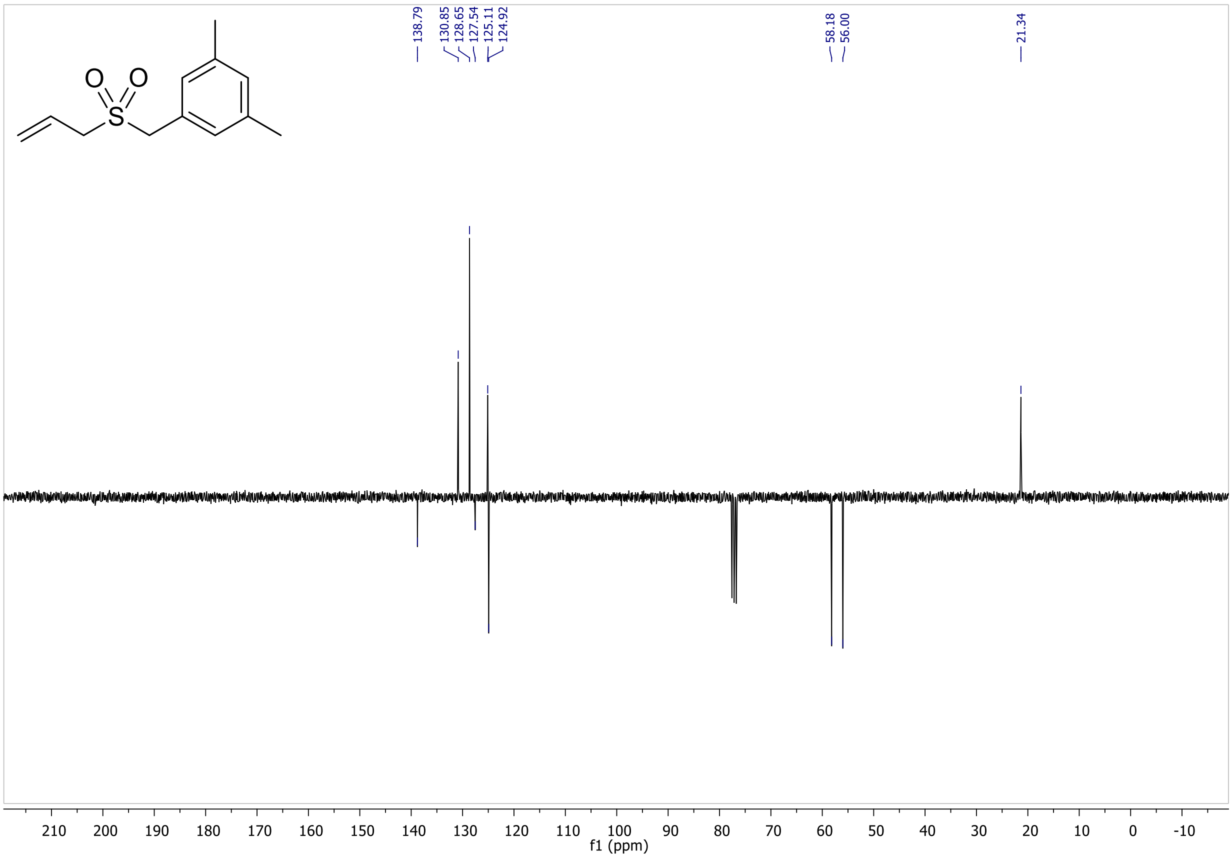
^{13}C-NMR (CDCl$_3$, 75.5 MHz) spectrum of compound 6c:



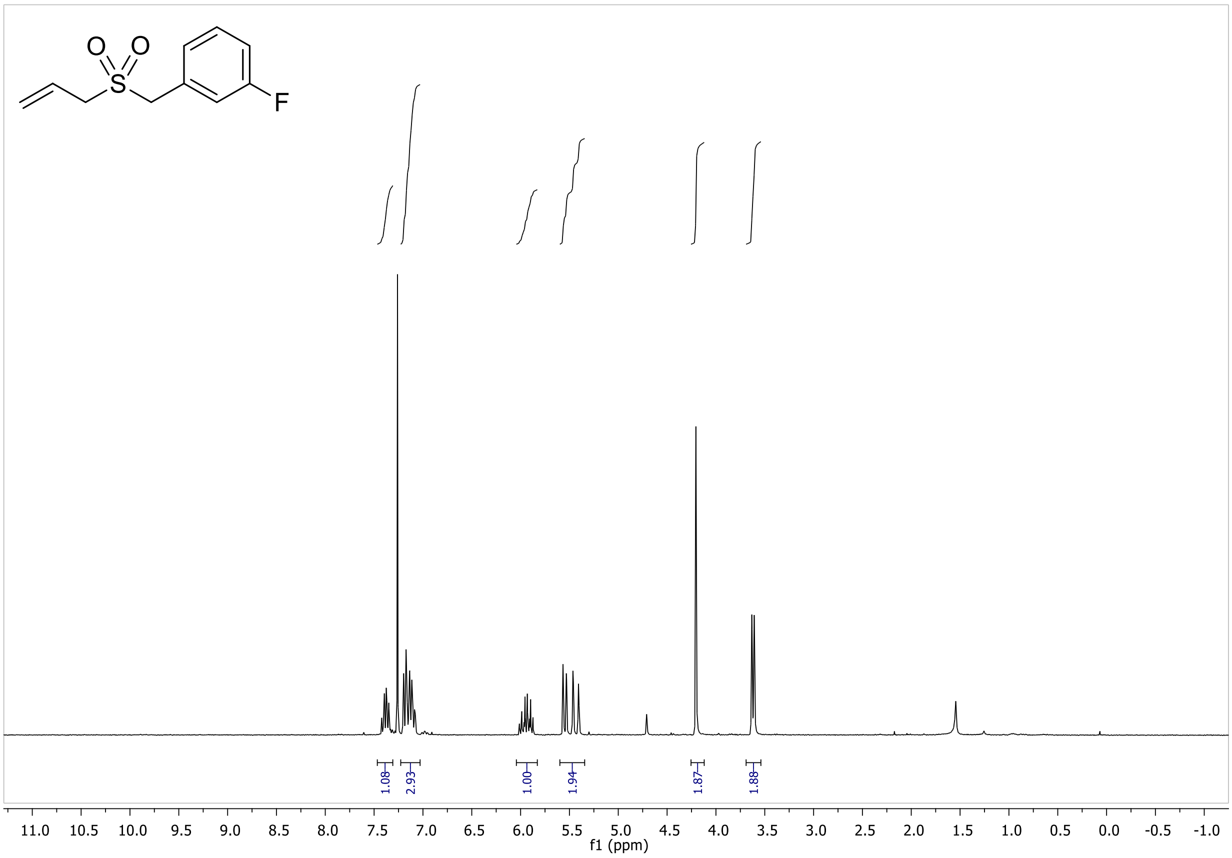
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of compound 6d:



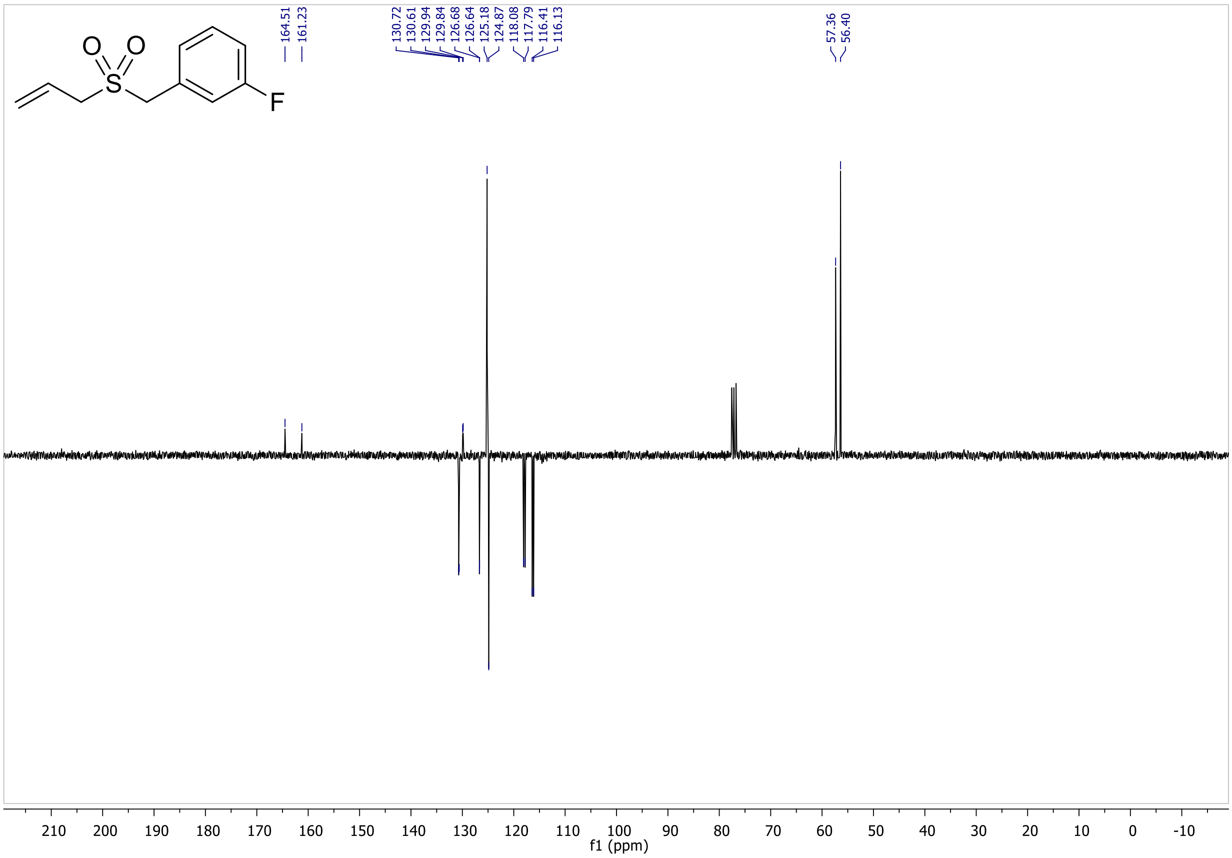
^{13}C-NMR ($CDCl_3$, 75.5 MHz) spectrum of compound 6d:



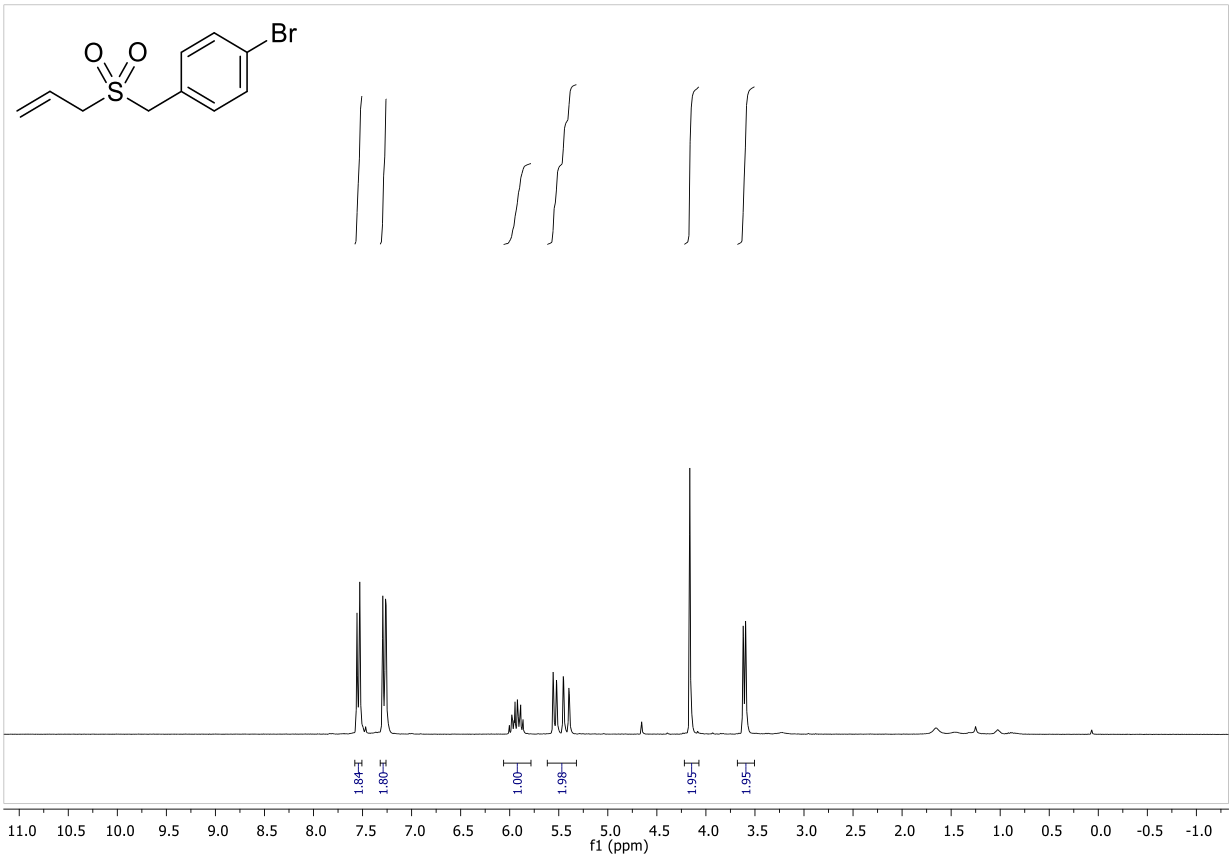
^{1}H-NMR (CDCl$_3$, 300 MHz) spectrum of compound 6e:



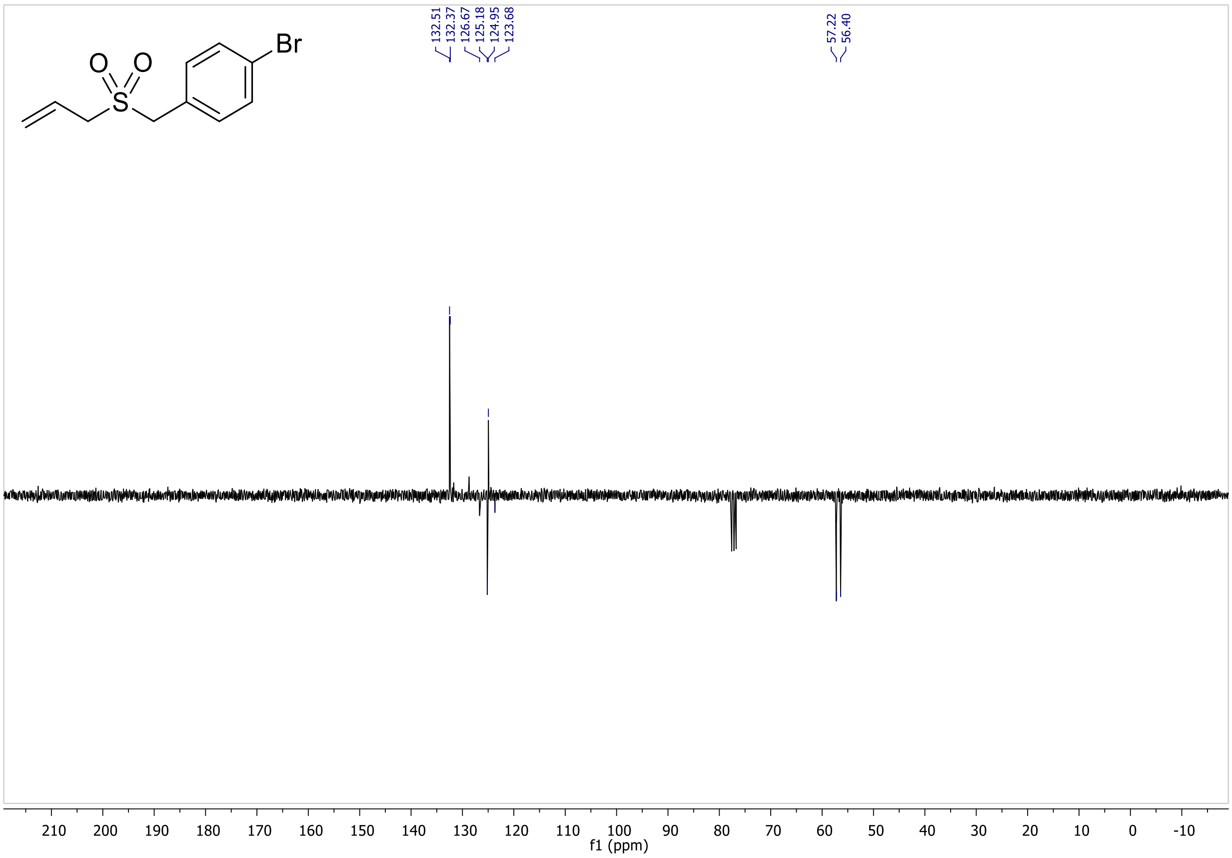
^{13}C-NMR (CDCl$_3$, 75.5 MHz) spectrum of compound 6e:



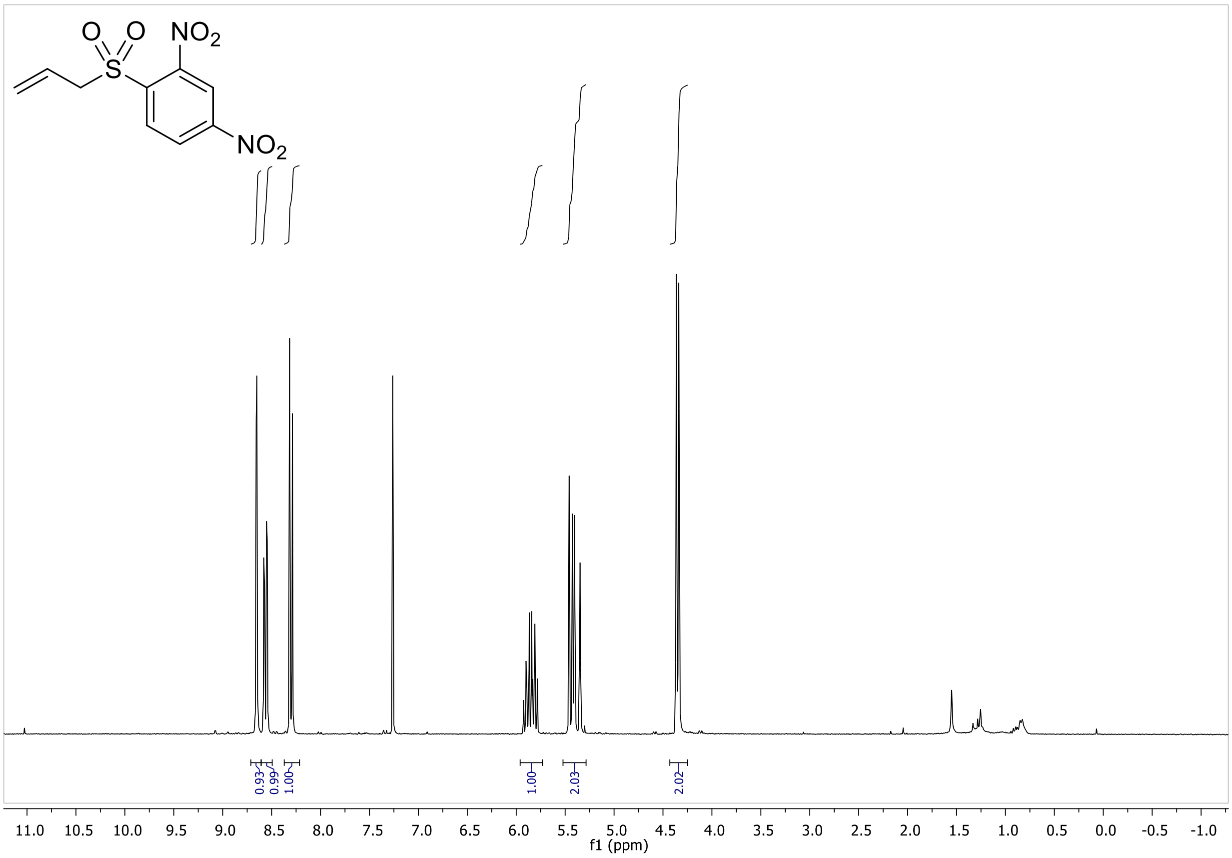
^{1}H-NMR (CDCl$_3$, 300 MHz) spectrum of compound 6f:



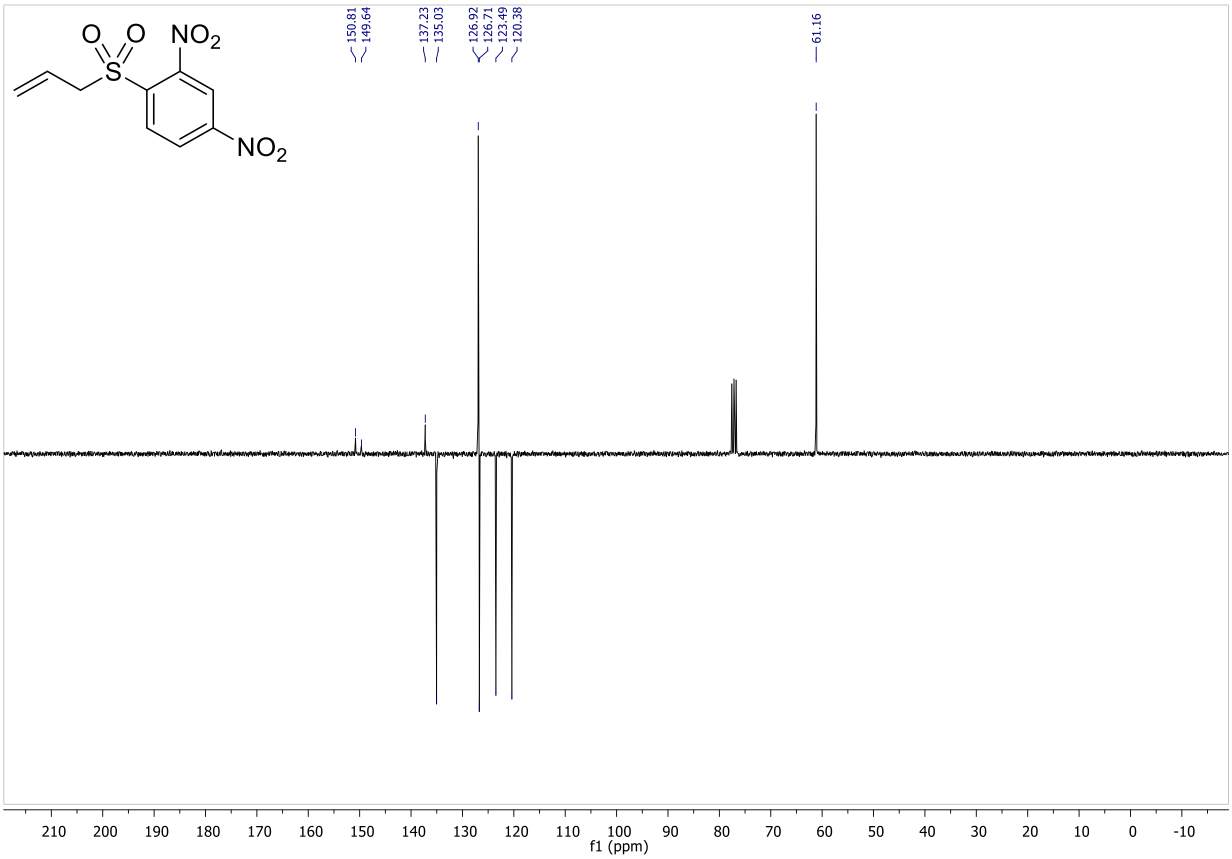
^{13}C-NMR (CDCl$_3$, 75.5 MHz) spectrum of compound 6f:



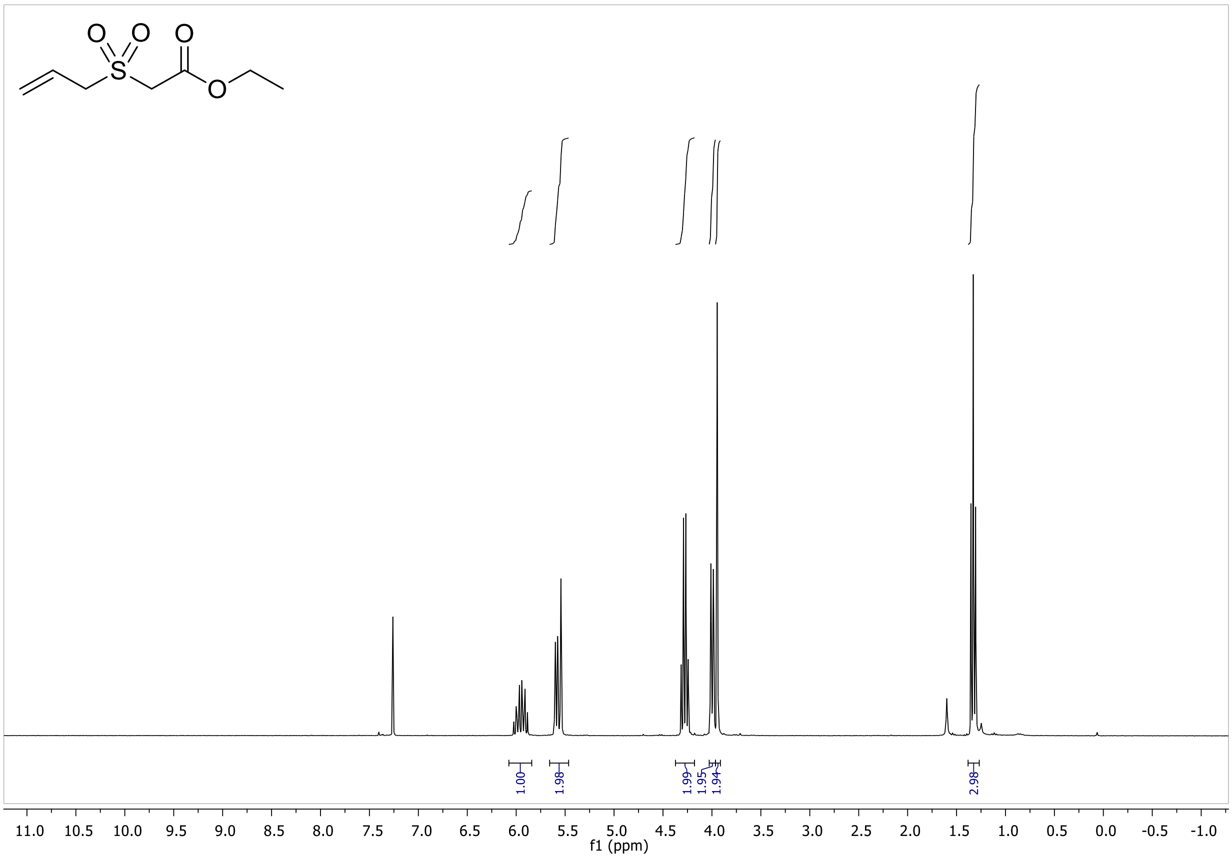
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of compound 6g:



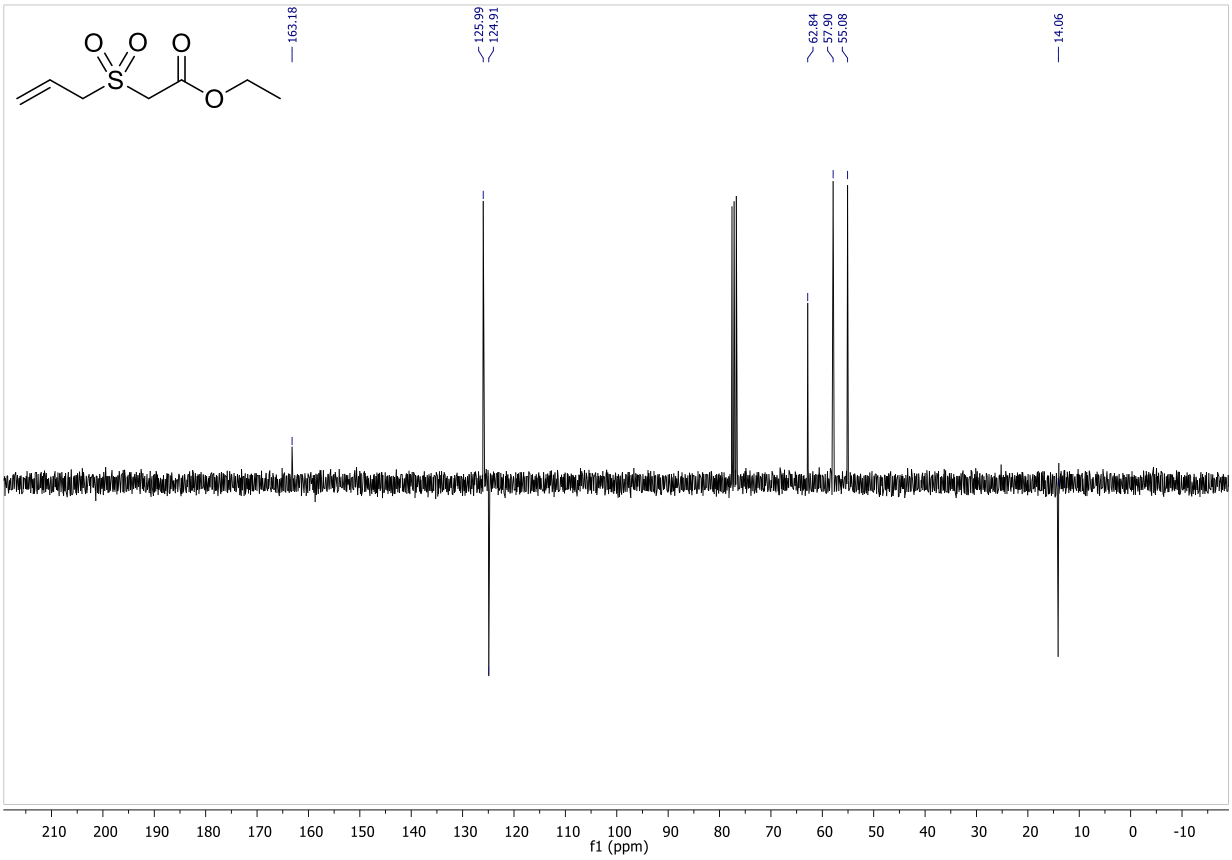
^{13}C-NMR ($CDCl_3$, 75.5 MHz) spectrum of compound 6g:



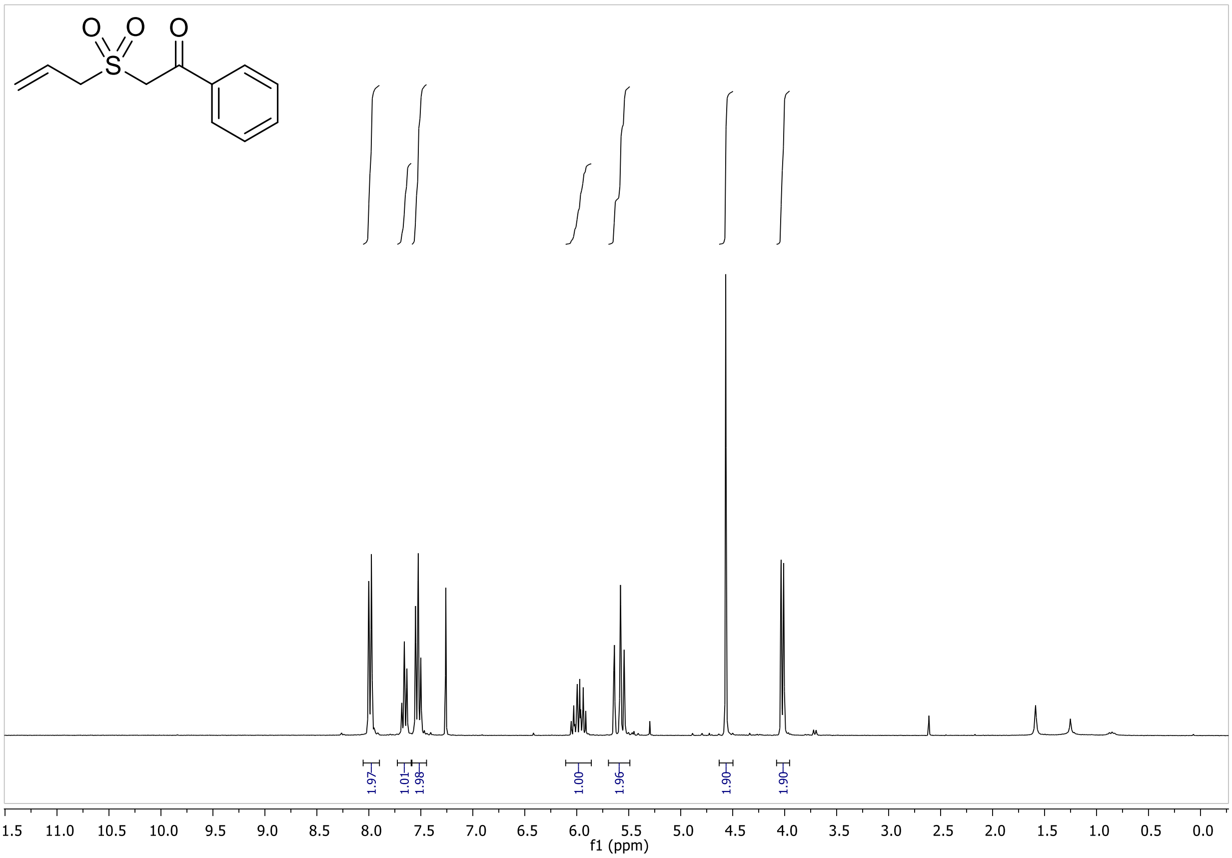
^{1}H-NMR (CDCl$_3$, 300 MHz) spectrum of compound 6h:



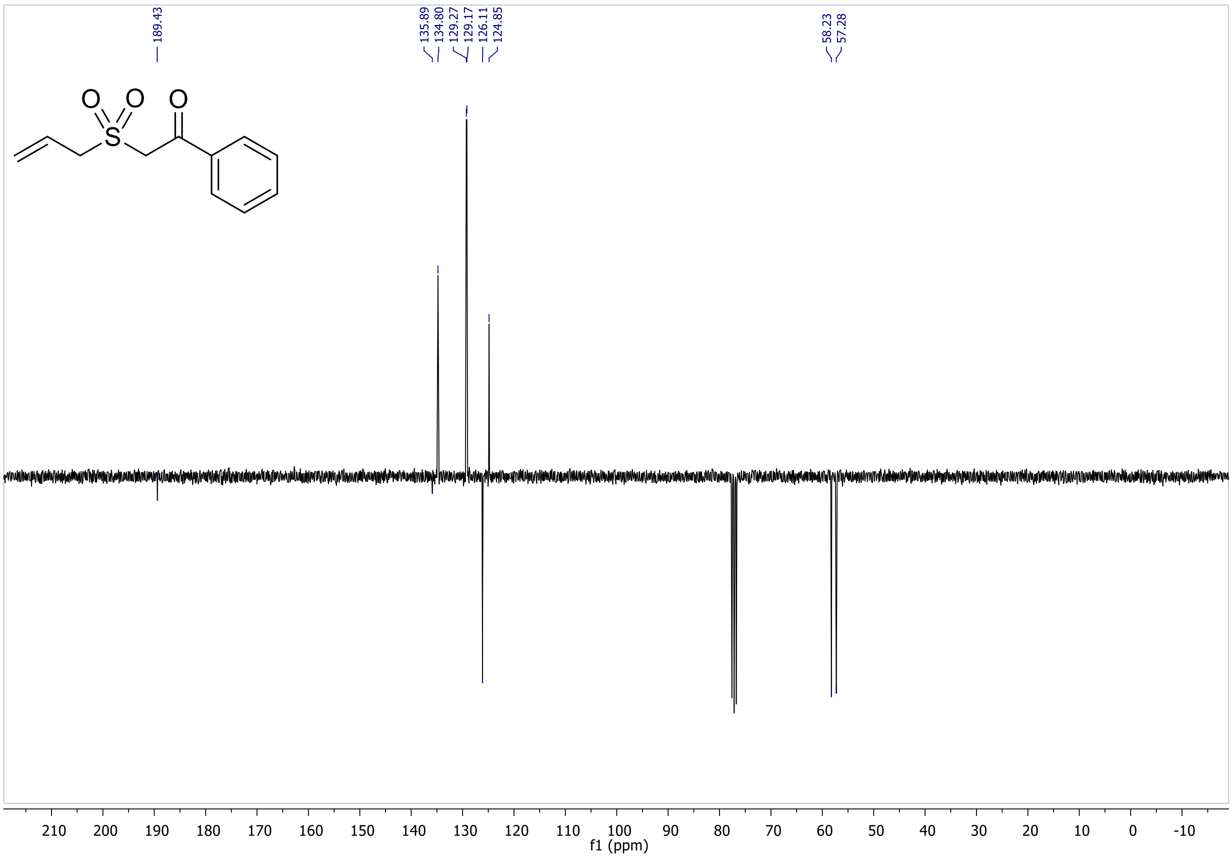
^{13}C-NMR (CDCl$_3$, 75.5 MHz) spectrum of compound 6h:



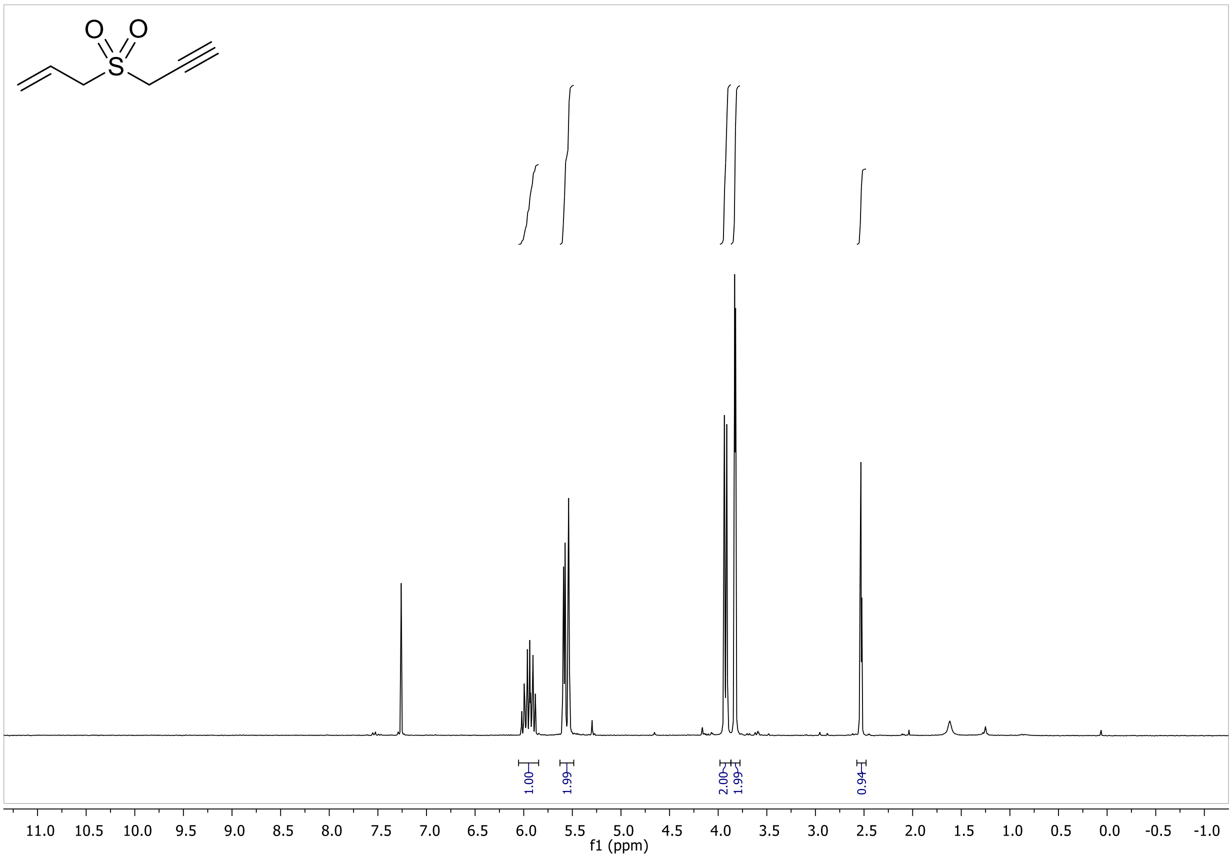
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of compound 6i:



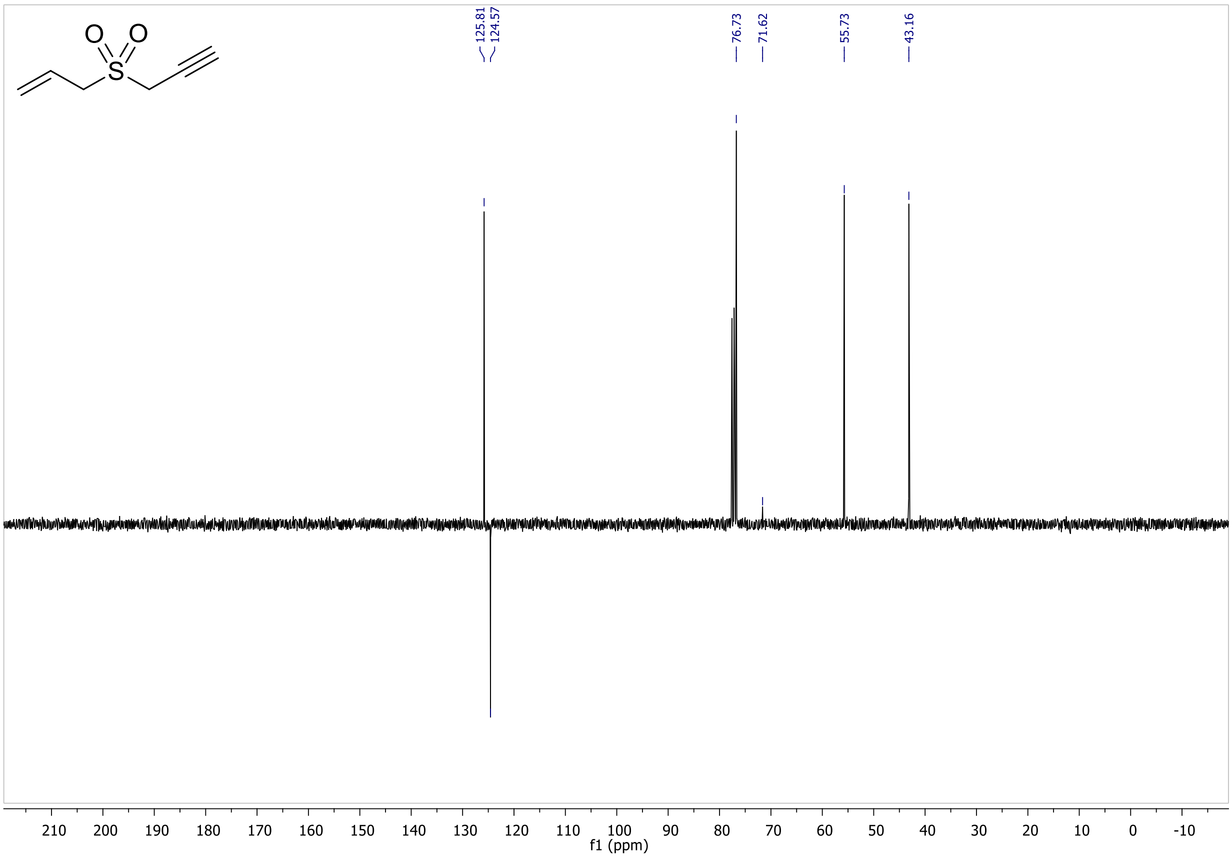
^{13}C-NMR ($CDCl_3$, 75.5 MHz) spectrum of compound 6i:



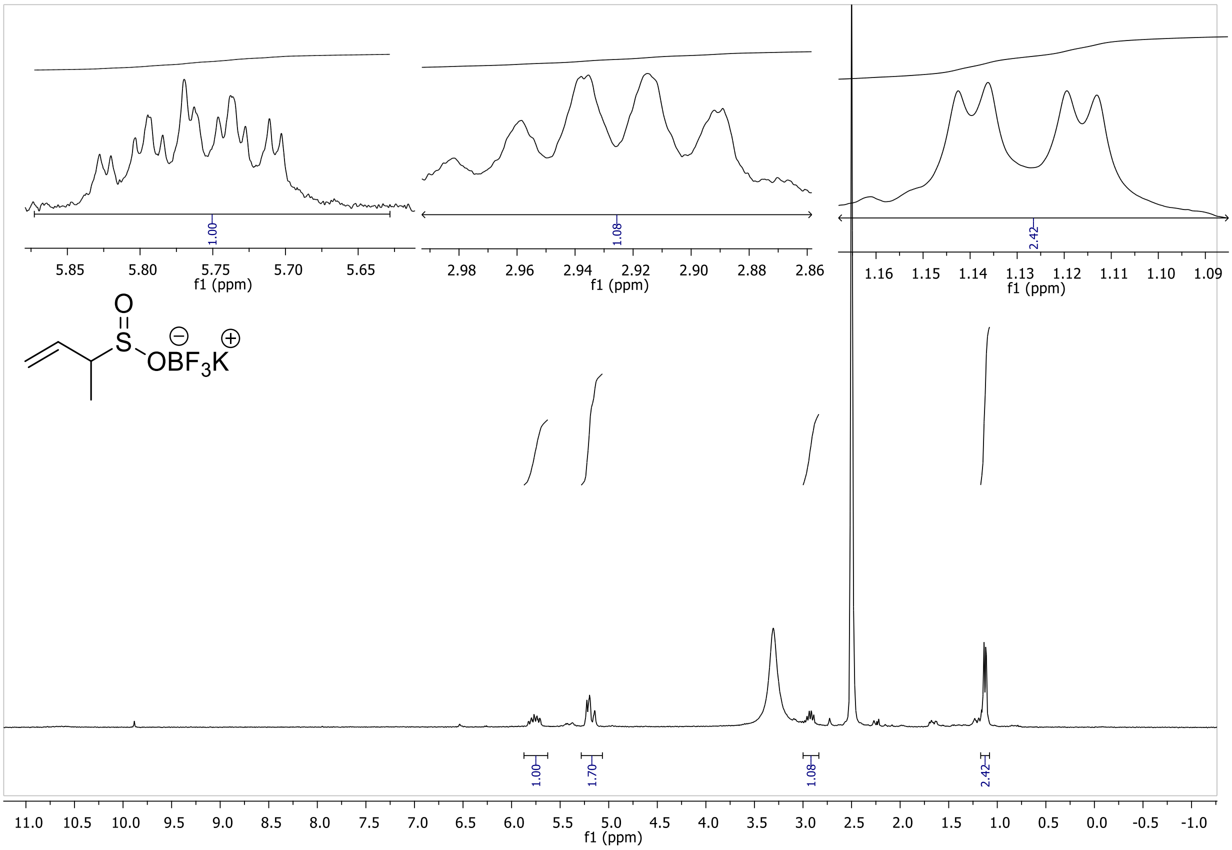
^{1}H-NMR (CDCl$_3$, 300 MHz) spectrum of compound 6j:



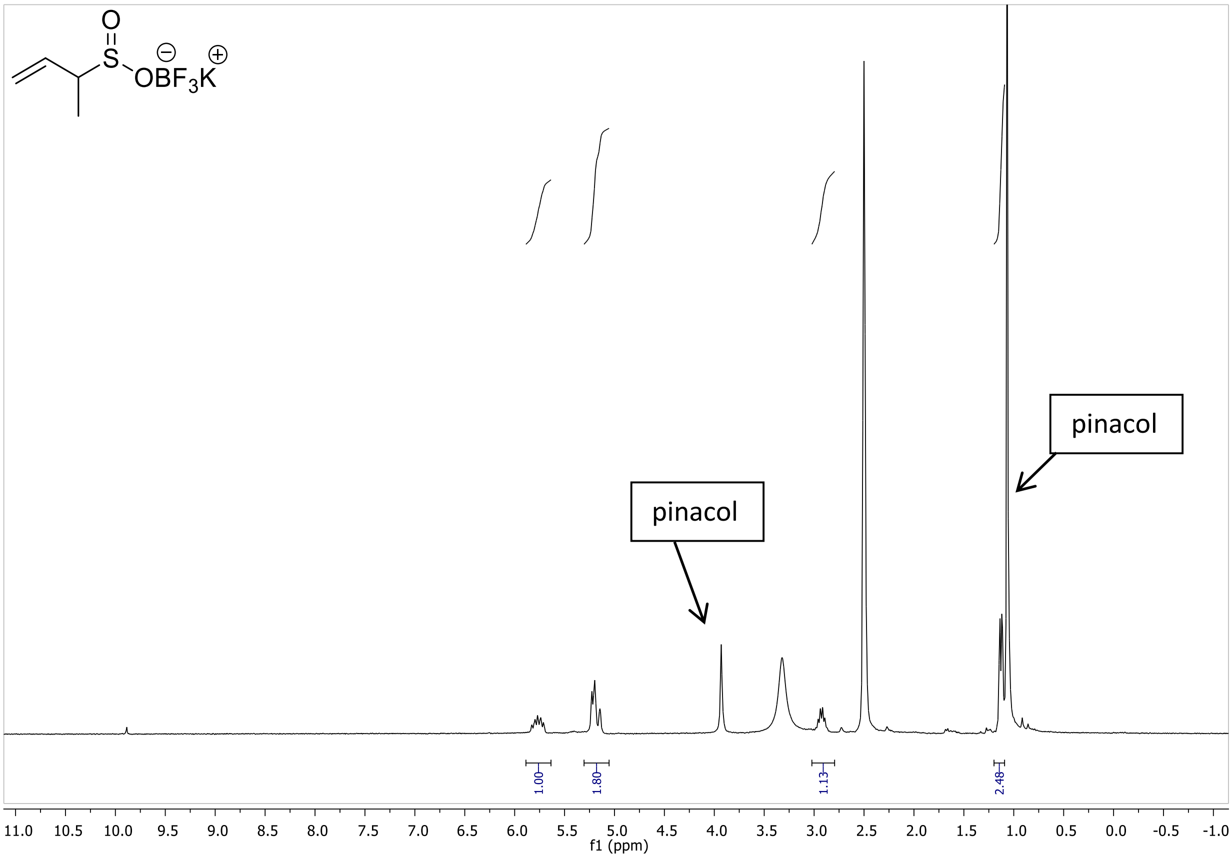
^{13}C-NMR (CDCl$_3$, 75.5 MHz) spectrum of compound 6j:



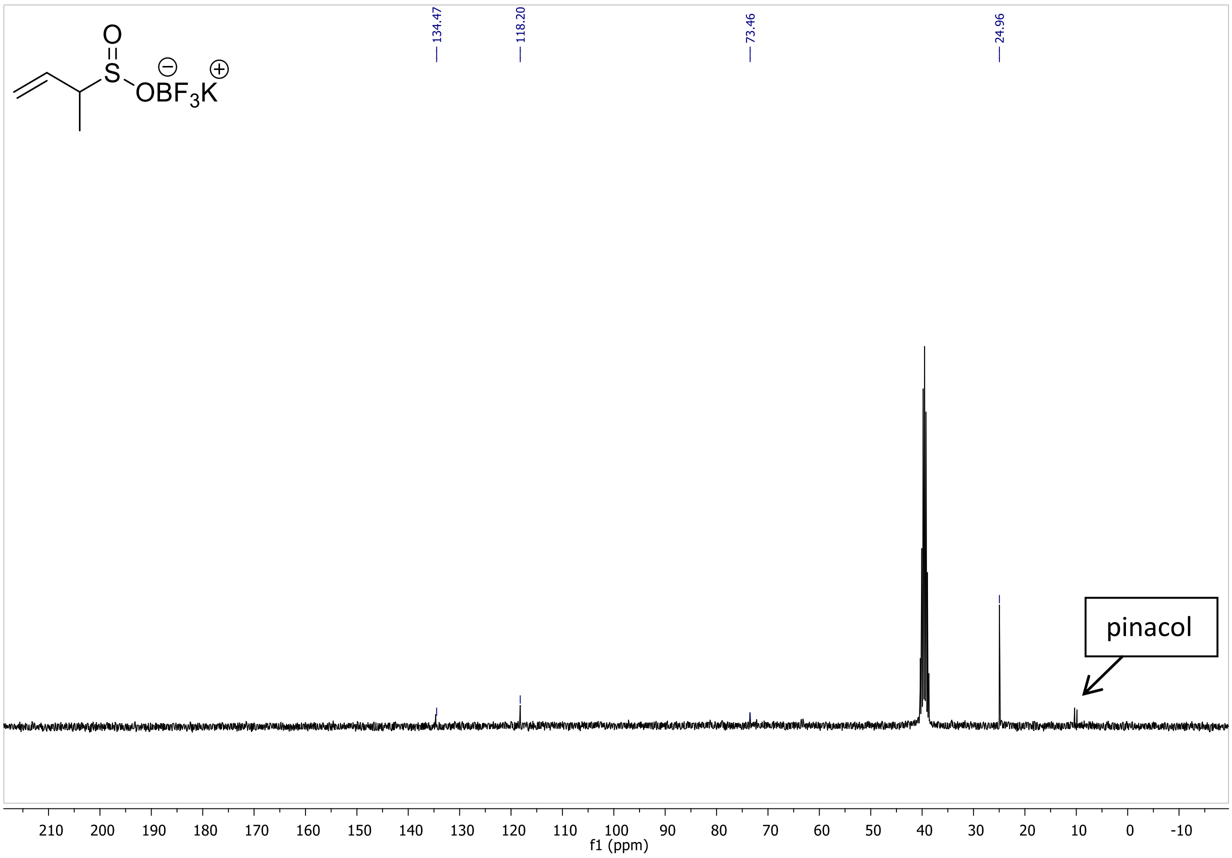
^{1}H-NMR (DMSO$_{d6}$, 300 MHz) spectrum of compound 8a:



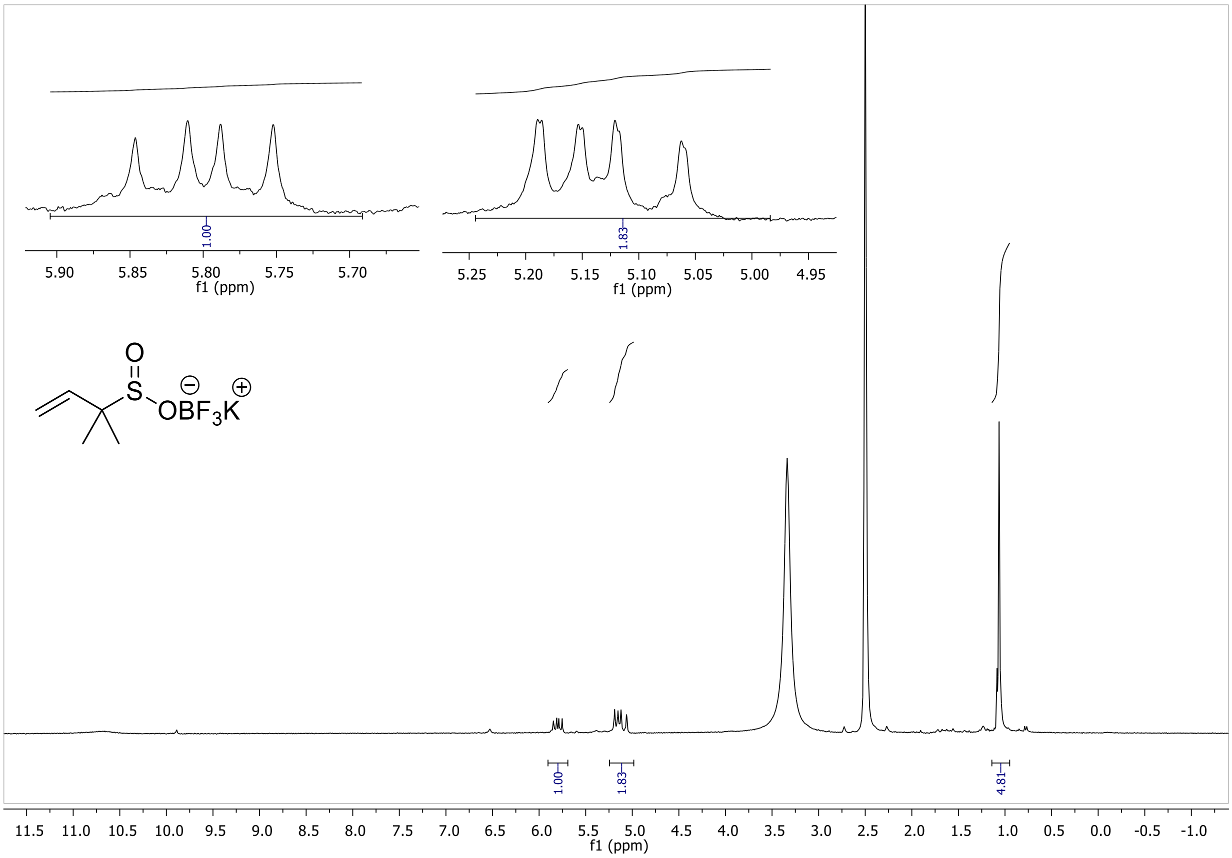
^{1}H-NMR (DMSO$_{d6}$, 300 MHz) spectrum of compound 8a, containing pinacol from the synthesis of starting material 7a:



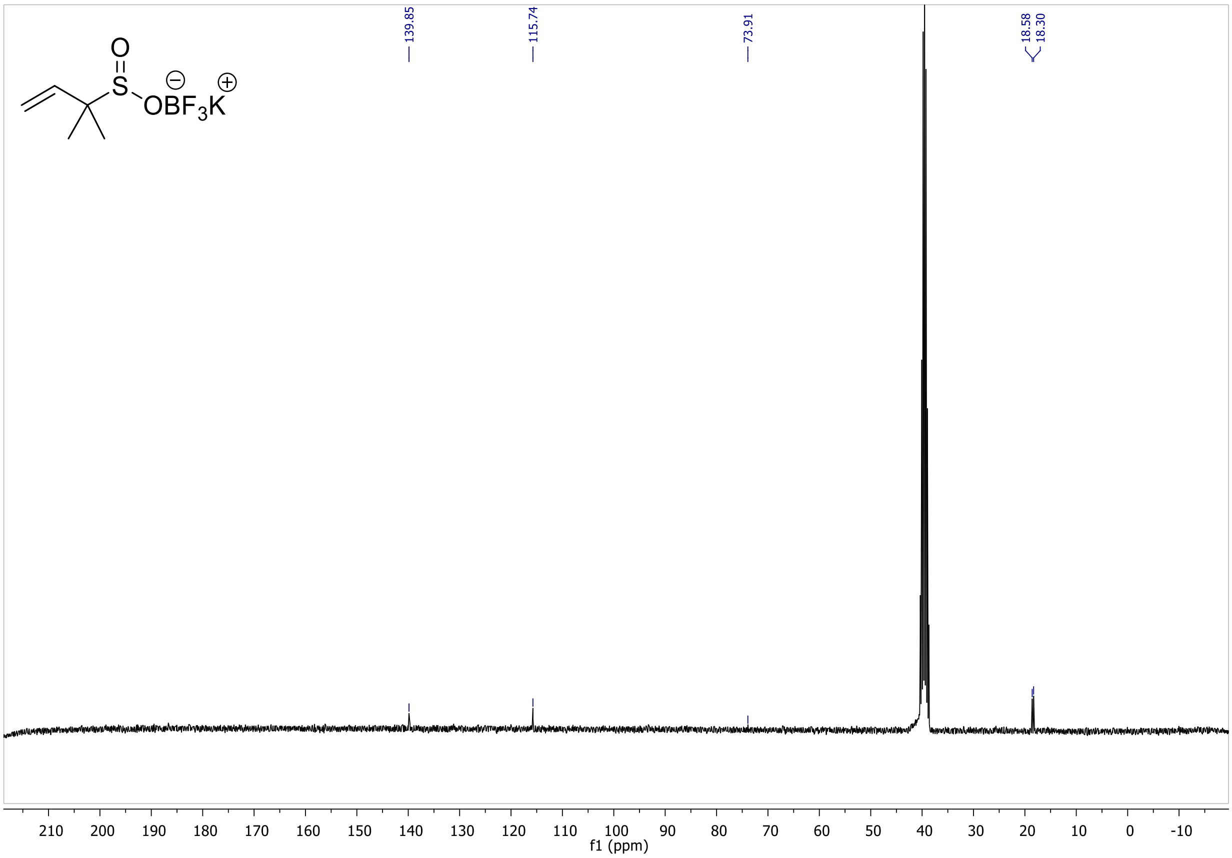
^{3}C-NMR (DMSO$_{d6}$, 75.5 MHz) spectrum of compound 8a, containing pinacol from the synthesis of starting material 7a:



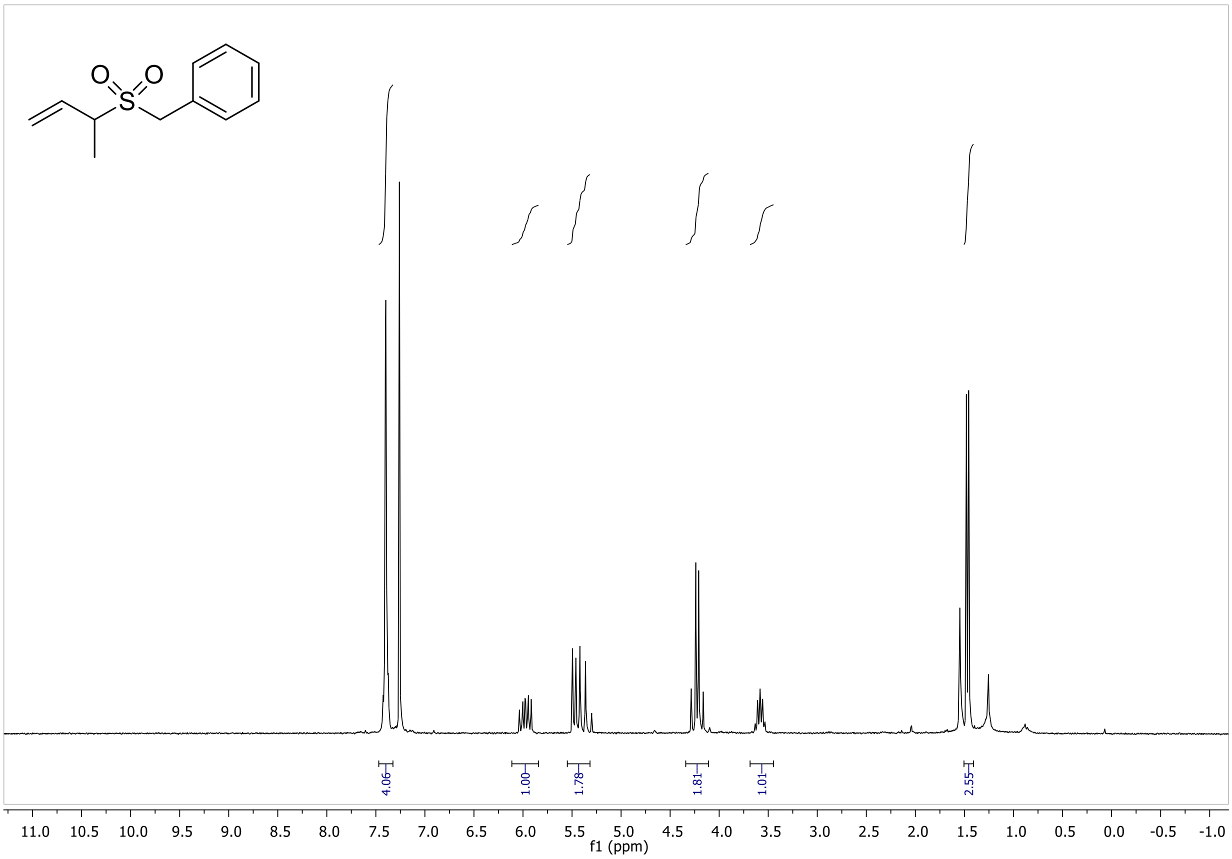
^{1}H-NMR (DMSO$_{d6}$, 300 MHz) spectrum of compound 8b:



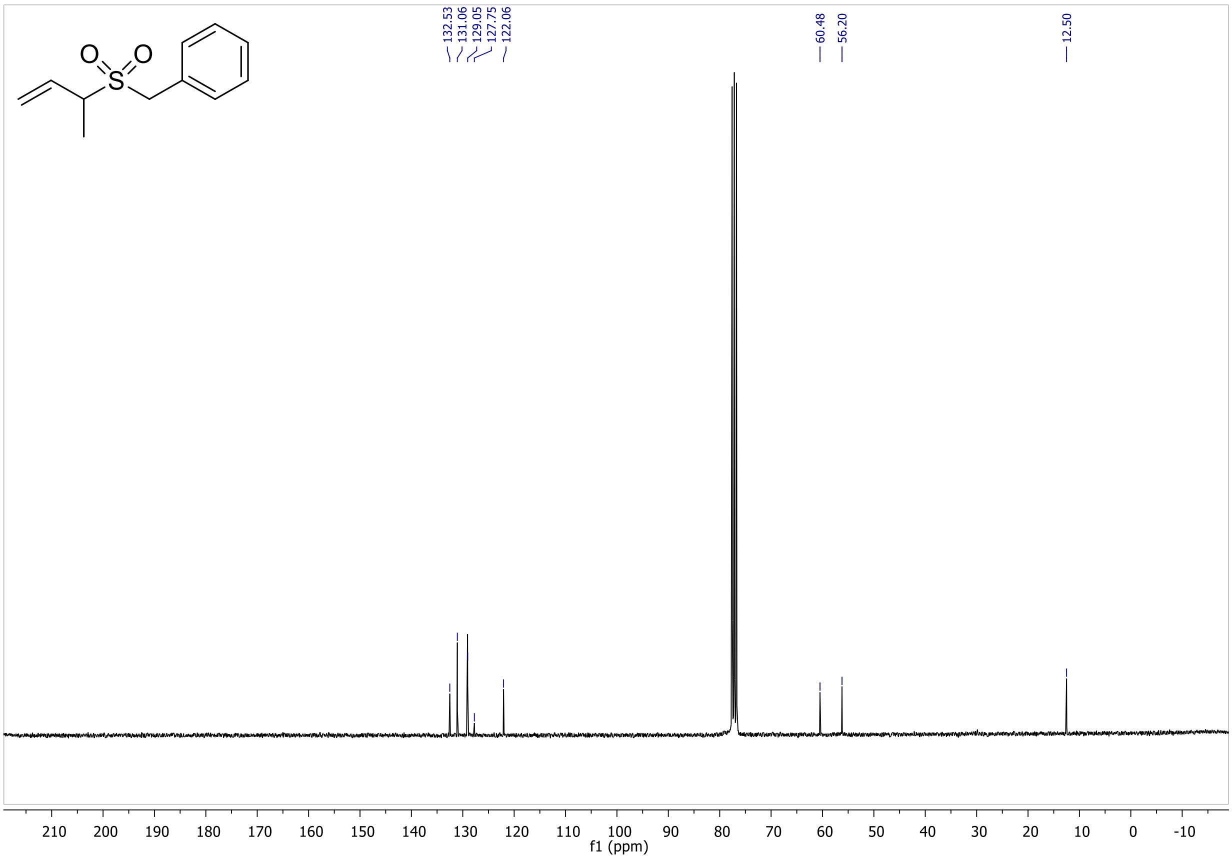
^{13}C-NMR (DMSO$_{d6}$, 75.5 MHz) spectrum of compound 8b:



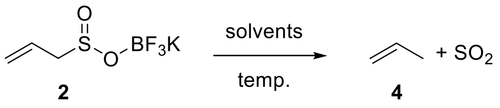
^{1}H-NMR (CDCl$_3$, 300 MHz) spectrum of compound 9:

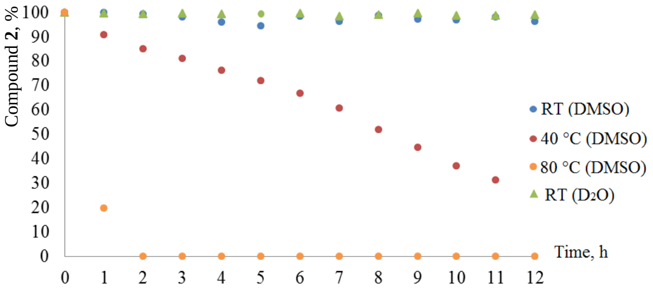


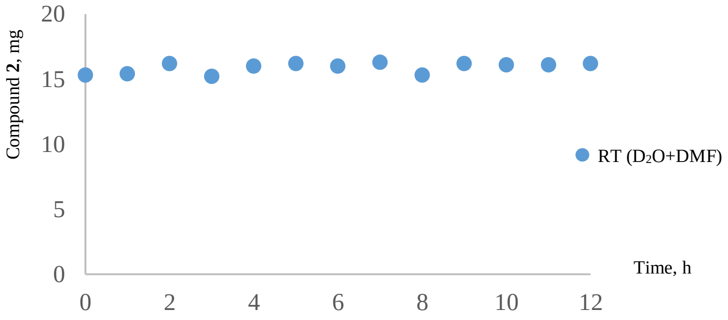
^{13}C-NMR (CDCl$_3$, 75.5 MHz) spectrum of compound 9:

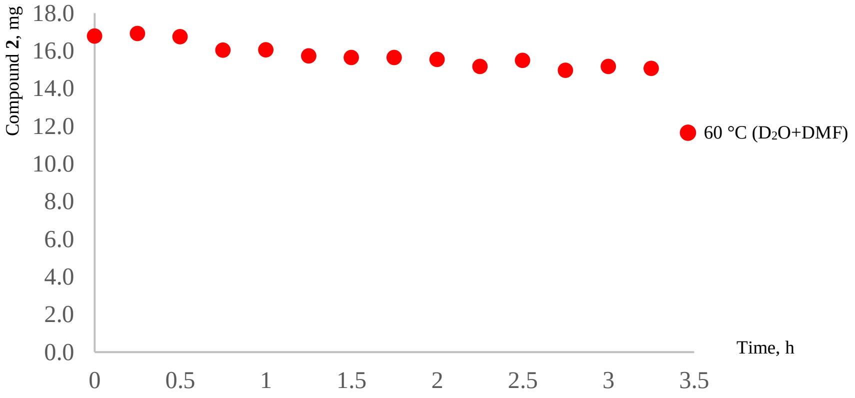


4. Stability studies of compound 2









5. Comparison of ^{11}B-NMR and ^{19}F-NMR chemical shifts of compounds 1 and 2 with literature data for other trifluoroborates.

Characteristic chemical shifts of starting material **1**, product **2** along with the literature examples for compounds of type $YBF_3^-M^+$ are listed in Table 1. The ^{11}B NMR spectra revealed a shift from 4.81 ppm (**1**) to 0.18 ppm (**2**), which along with the ^{1}H and ^{13}C NMR data confirmed the insertion of sulfur dioxide.[1]

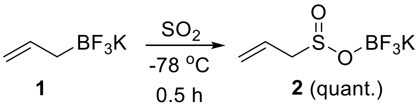


Table 1. Comparison of NMR spectral data for compounds **1** and **2** with substances of type $YBF_3^-M^+$.

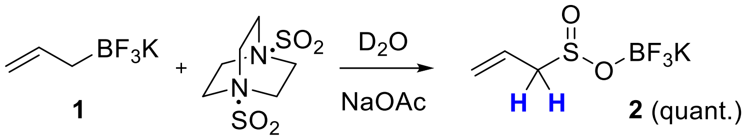
Compound (solvent)	^{19}F NMR (ppm)	$J_{B\text{-}F}$ (Hz)	^{11}B NMR (ppm)	Remarks
1 (D_2O)	-135.0	63.4	4.81	This work
2 (D_2O)	-141.4	15.1	0.18	This work
$[Me_4N]BF_3OAc$ (SO_2, -70 °C)	-135.6	7.3	-[a]	Ref.[2]
$[Me_4N]BF_2(OAc)_2$ (SO_2, -70 °C)	-135.2	15.9	-[a]	Ref.[2]
$[Me_4N]BF_3OTf$ (SO_2, -70 °C)	-137.5	-[a]	-[a]	Ref.[3]
$(CF_3)_2NBF_3K$ (CD_3CN)	-144.9	14.2	-0.66	Ref.[4]

[a] Not reported.

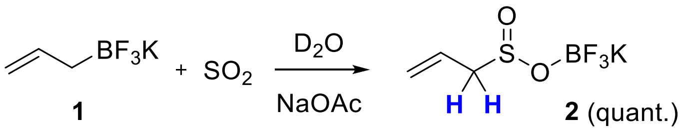
1. From the obtained spectral data one cannot exclude the possibility of a fast equilibrium in solution with the general equation: n $C_3H_5SO_2BF_3K \leftrightarrow (C_3H_5SO_2)_nBF_{(4-n)}K$ + (n-1) KBF_4, although the signals corresponding to KBF_4 were not observed in ^{11}B and ^{19}F NMR spectra.
2. Brownstein, S.; Bornais, J.; Latremouille, G. *Can. J. Chem.* **1978**, *56*, 1419-1422.
3. Brownstein, S.; Latremouille, G. *Can. J. Chem.* **1978**, *56*, 2764-2767.
4. Pawelke, G. *J. Fluorine Chem.* **1988**, *41*, 289-291.

6. Determination of NMR yield for transformation 1+SO_2→2

1. Experiment



2. Experiment



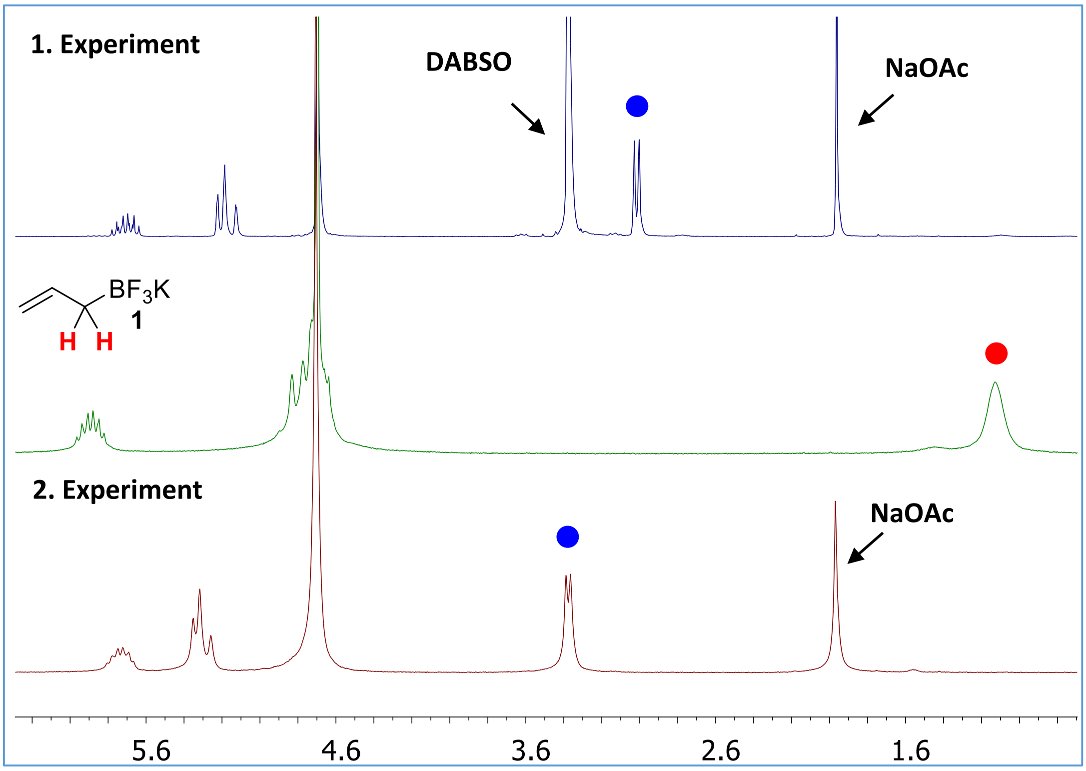


Figure 1. Selected regions of ^{1}H-NMR spectra (300 MHz, D_2O) showing the transformation of allyltrifluoroborate **1** (green spectrum) into potassium 3-((allylsulfinyl)oxy)trifluoroborate **2** using DABSO (1. experiment, blue spectrum) and SO2 (2. experiment, red spectrum).