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# Batch and Flow Electrochemical Synthesis of Allyl Sulfones via Sulfonation of Allyl Trifluoroborates: A Robust, Regioselective, and Scalable Approach

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# 1. General methods and commercial starting materials

Starting materials and solvents for the reactions were acquired from commercial sources (Acros Organics, Aldrich Chemical Co., Alfa Aesar, TCI Chemicals, Fluorochem and/or BLDpharm) unless otherwise specified. For thin layer chromatography (TLC), silica gel plates with fluorescence indicator 254 nm were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of potassium permanganate in water followed by heating. Flash column chromatography was performed using Geduran® Silica Gel 60 (0.040-0.063 nm). Cyclohexane and diethyl ether for flash column chromatography were acquired from commercial sources and were used without previous purification. NMR spectra were acquired on a *Bruker Avance 300 MHz spectrometer*, running at 300 and 75 MHz for $^{1}H$ and $^{13}C$, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for $^{1}H$-NMR; 77.2 ppm for $^{13}C$-NMR). $^{13}C$-NMR was acquired on a broad band decoupled mode. The following abbreviations are used to describe peak patterns when appropriate: s (singlet), bs (broad singlet), d (doublet), bd (broad doublet), t (triplet), q (quartet), p (pentet), h (heptet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublets of doublets), dt (double of triplets), ddt (doublet of doublets of triplets), tt (triplet of triplets). Electrospray ionization has been used for measuring the exact mass (indicated for each case): HRMS (ESI) (Electrospray ionization mass spectroscopy) was acquired with an *Agilent Technologies 6120 Quadrupole LC/MS*. In this technique, *MassWorks software ver. 4.0.0.0 (Cerno Bioscience*) was used for the formula identification. *MassWorks* is a MS calibration software which calibrates for isotope profile as well as for mass accuracy, allowing highly accurate comparisons between calibrated and theoretical spectra.[1]

All the electrodes and equipment (ElectraSyn 2.0) used for the batch electrochemical experiments were acquired from IKA.

## 1.1. Electrochemical-Flow Setup

*-Vapourtec Setup*


**Figure S1.** Vapourtec set-up.

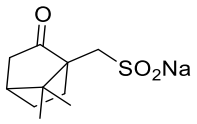
The electrochemical-flow experiments were carried out using a commercially available Vapourtec Ion Electrochemical Reactor and Controller on an E-series Vapourtec equipment. The system (**Figure S1**), consist of a pump, an electrochemical reactor, and a 20 psi Back Pressure Regulator (BPR: 20 psi) at its ending which was connected to the reaction vial for its recirculation.

Materials (**Figure S2**): the electrodes used were Graphite (Flexible Graphite Plain obtained from Vapourtec Ltd.) and Graphite (Flexible Graphite with 3 holes obtained from Vapourtec Ltd.). The electrodes (5 x 5 $cm^2$) are separated by a 0.5 mm membrane with a channel volume of 0.6 mL and an exposed electrode surface area of 12 $cm^2$ (each electrode). A 2 mm electrode spacer was used between the side of the carrier with 2 fluid hole and the plain electrode.

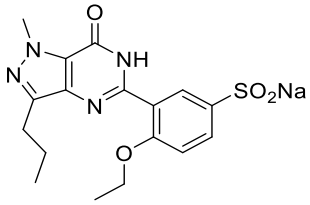

**Figure S2.** Electrochemical-flow reactor and materials.

# 2. General procedure A: Synthesis of starting materials

## 2.1. General procedure A1: Synthesis sodium sulfinates 1n-o



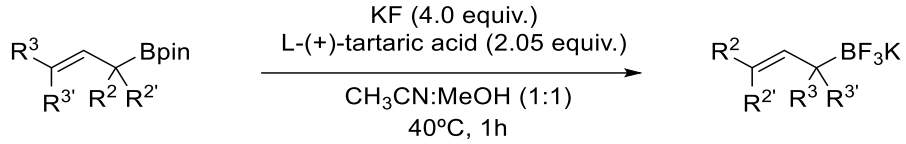

**1n**




**1o**

Starting materials **1a-m** were acquired from commercial sources. Sodium sulfinates **1n** and **1o** were prepared following a procedure described in the literature and spectra data are consistent with those reported.[2]

## 2.2. General procedure A2: Synthesis of potassium allyltrifluoroborate salts



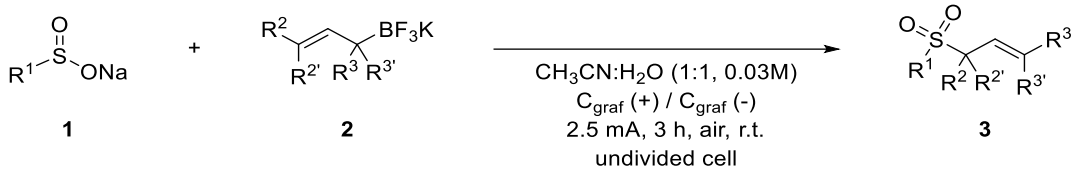

**2**

Starting material **2a** was acquired from commercial sources. Potassium allyltrifluoroborate salts **2b-g** were prepared following a modified procedure described in the literature:[3] To a solution of the corresponding allylboronic acid pinacol ester (1.0 equiv.) in methanol (2 mL/mmol) and acetonitrile (2 mL/mmol) was added a solution of KF (4.0 equiv.) in water (0.1 mL/mmol) and the mixture was stirred until complete dissolution. Then, L-(+)-tartaric acid (2.05 equiv.) in tetrahydrofuran (1.5 mL/mmol of allylboronic acid pinacol ester) was added dropwise and the resulting mixture was stirred for 1 hour at 40ºC. The reaction was cooled to room temperature and acetonitrile (5 mL/mmol of allylboronic acid pinacol ester) was added and stirred for 5 min. Then, solids were filtered, and the solution was concentrated to dryness. Pentane was added to the oily mixture, and it was stirred and sonicated until the precipitation of the corresponding potassium allyltrifluoroborate salt **2**. The salt was filtered and washed with pentane to give pure product **2**.

Spectra data of starting materials **2b-g** are consistent with those reported in the literature.[3]

# 3. General procedure B

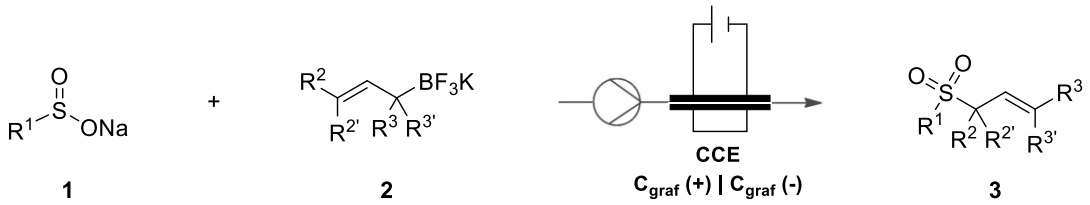
## 3.1. General procedure B1: Electrochemical synthesis of allylsulfones




1 2 3

Sodium sulfinate **1** (0.1 mmol) and potassium allyltrifluoroborate **2** (0.25 mmol) were added to a 5 mL ElectraSyn vial. Acetonitrile (1.5 mL) and distilled water (1.5 mL) were added to the vial and it was stirred until solids were dissolved. Then, carbon graphite electrodes were fitted in the cap of the vial and it was closed. The reaction was set at constant current (2.5 mA) for 3 hours. After that time, the solution was transfer to a round bottom flask, electrodes and vial were rinsed with dichloromethane and then concentrated to dryness. Diethyl ether was added to the flask in order to dissolve the product and then the mixture was filtered and concentrated under reduce pressure. The residue was purified by manual flash column chromatography using the eluents indicated in each case to give final product **3**.

## 3.2. General procedure B2: Electro-flow synthesis of allylsulfones

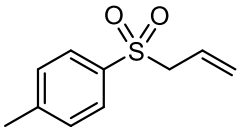



1 2 3

Sodium sulfinate **1** (0.1 mmol) and potassium allyltrifluoroborate **2** (0.25 mmol) were added to a vial equipped with a septum. A 1:1 mixture of acetonitrile: water (4 mL) was added to the vial, and the solution was homogenised by sonication in an ultrasound bath. The above prepared solution is pumped through the system at 150 µL $min^{-1}$ (4 minutes in the electrochemical cell, 17.3 minutes in all the system). Two carbon graphite foils were used as electrodes, a constant current of 2.5 mA (consisting with a potential close to 2.5 V) was applied to the reaction and after 3 hours recirculating (~42 minutes in the electrochemical cell), the flow system was washed with a 1:1 mixture of acetonitrile: water (2 mL) and everything was collected in a 25 mL round-bottom flask. Solvents were removed under reduced pressure, then, the residue was dissolved in water (5 mL) and extracted with ethyl acetate (3 x 5 mL). Organic phase was collected and concentrated to dryness. The residue was purified by manual flash column chromatography using the eluents indicated in each case to give final product **3**.

## 3.3. Experimental Data and Caracterization of Products 3

**1-(Allylsulfonyl)-4-methylbenzene (3a)**



Following the general procedure B1, sodium 4-methylbenzenesulfinate **1a** (17.8 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3a** (80% yield) as a colourless oil. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 80:20.

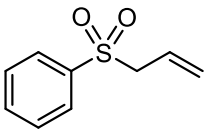
The reaction was scaled up to 1.0 mmol. Procedure B1 was followed using a 10 mL ElectraSyn vial as 4 mL of acetonitrile and 4 mL of distilled water were used as solvents. The reaction was carried out at 5 mA for 16 hours. After workup and purification as described above, **3a** (62% yield) was obtained as a colourless oil that solidifies upon time.

The reaction was carried out under electro-flow conditions. Procedure B2 was followed. After workup and purification as described above, **3a** (92% yield) was obtained as a colourless oil.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.79 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.33 (d, *J* = 10.1 Hz, 1H), 5.15 (d, *J* = 17.1, 1H), 3.79 (d, *J* = 7.4 Hz, 2H), 2.45 (s, 3H) ppm.

Spectra data are consistent with those reported in the literature.[4]

**(Allylsulfonyl)benzene (3b)**

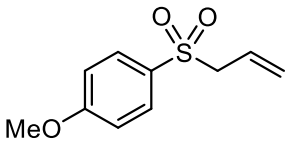


Following the general procedure B1, sodium benzenesulfinate **1b** (16.4 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3b** (83% yield) as a colourless oil. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 80:20.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.92 – 7.83 (m, 2H), 7.75 – 7.62 (m, 1H), 7.59 – 7.48 (m, 2H), 5.79 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.33 (d, *J* = 10.1 Hz, 1H), 5.14 (d, *J* = 17.4 Hz, 1H), 3.81 (d, *J* = 7.4 Hz, 2H) ppm.

Spectra data are consistent with those reported in the literature.[5]

**1-(Allylsulfonyl)-4-methoxybenzene (3c)**

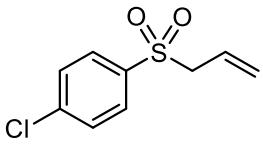


Following a sighly modified procedure B1, sodium 4-methoxybenzenesulfinate **1c** (19.4 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3c** (47% yield) as a colourless oil when $TBAPF_6$ (0.5 equiv.) was used as electrotyte under the standart conditions. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 80:20.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.79 (d, *J* = 9.0 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 5.91 – 5.64 (m, 1H), 5.32 (d, *J* = 10.1 Hz, 1H), 5.14 (d, *J* = 17.0 Hz, 1H), 3.88 (s, 3H), 3.78 (d, *J* = 7.4 Hz, 2H) ppm.

Spectra data are consistent with those reported in the literature.[4]

**1-(Allylsulfonyl)-4-chlorobenzene (3d)**

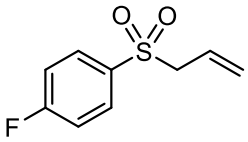


Following the general procedure B1, sodium 4-chlorobenzenesulfinate **1d** (19.9 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3d** (59% yield) as a colourless oil. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 85:15.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.88 – 7.73 (m, 2H), 7.59 – 7.48 (m, 2H), 5.91 – 5.65 (m, 1H), 5.35 (d, *J* = 10.2 Hz, 1H), 5.15 (dt, *J* = 17.1 Hz, 1H), 3.80 (d, *J* = 7.4 Hz, 2H) ppm.

Spectra data are consistent with those reported in the literature.[4]

**1-(Allylsulfonyl)-4-fluorobenzene (3e)**



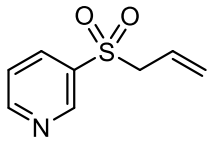
Following the general procedure B1, sodium 4-fluorobenzenesulfinate **1e** (18.2 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3e** (63% yield) as a colourless oil. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 80:20.

The reaction was carried out under electro-flow conditions. Procedure B2 was followed. After workup and purification as described above, **3e** (56% yield) was obtained as a colourless oil.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 9.0, 5.1 Hz, 2H), 7.30 (dd, *J* = 9.0, 0.8 Hz, 2H), 5.85 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.40 (d, *J* = 10.1 Hz, 1H), 5.20 (dd, *J* = 17.4 Hz, 1H), 3.87 (d, *J* = 7.4 Hz, 2H) ppm.

Spectra data are consistent with those reported in the literature.[4]

**3-(Allylsulfonyl)pyridine (3f)**



Following the general procedure B1, sodium pyridine-3-sulfinate **1f** (16.5 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3f** (70% yield) as a colourless oil. Eluent: cyclohexane: diethyl ether, slow gradient from 80:20 to 40:60.

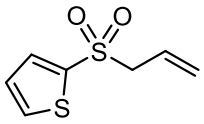
The reaction was carried out under electro-flow conditions. Procedure B2 was followed. After workup and purification as described above, **3f** (59% yield) was obtained as a colourless oil.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 9.08 (bs, 1H), 8.88 (bd, *J* = 4.9 Hz, 1H), 8.15 (dt, *J* = 8.0, 2.2 Hz, 1H), 7.51 (dd, *J* = 8.0, 4.9 Hz, 1H), 5.82 (ddt, *J* = 17.0, 10.1, 7.4 Hz, 1H), 5.38 (d, *J* = 10.1 Hz, 1H), 5.16 (dd, *J* = 17.0 Hz, 1H), 3.86 (d, *J* = 7.4 Hz, 2H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ 154.5, 149.7, 136.6, 134.8, 125.7, 124.4, 123.8, 61.4 ppm.

**HRMS (ESI$^+$)**: calculated for $C_8H_{10}NO_3S$ [M-H]$^+$: 184.0427; found: 184.0487.

**2-(Allylsulfonyl)thiophene (3g)**



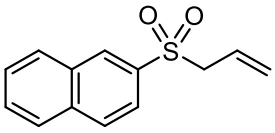
Following the general procedure B1, sodium thiophene-2-sulfinate **1g** (17.0 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3g** (43% yield) as a colourless oil. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 80:20.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.66 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.15 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.85 (ddt, *J* = 17.0, 10.2, 7.4 Hz, 1H), 5.48 – 5.36 (m, 1H), 5.22 (d, *J* = 17.0 Hz, 1H), 3.90 (d, *J* = 7.4 Hz, 2H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ 139.4, 134.8, 134.3, 127.9, 125.2, 124.8, 62.3 ppm.

**HRMS (ESI$^+$)**: calculated for $C_7H_{12}NO_2S_2$ [M-$NH_4$]$^+$: 206.0304; found: 206.0272.

**2-(Allylsulfonyl)naphthalene (3h)**

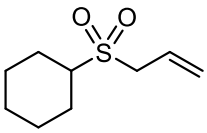


Following a sighly modified procedure B1, sodium naphthalene-2-sulfinate **1h** (21.4 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3h** (31% yield) as a colourless oil when $TBAPF_6$ (0.5 equiv.) was used as electrotyte under the standart conditions. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 90:10.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.74 – 7.60 (m, 2H), 5.83 (ddt, *J* = 17.3, 10.2, 7.4 Hz, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 5.15 (dd, *J* = 17.3 Hz, 1H), 3.89 (d, *J* = 7.4 Hz, 2H) ppm.

Spectra data are consistent with those reported in the literature.[6]

**(Allylsulfonyl)cyclohexane (3i)**

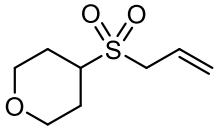


Following a sighly modified procedure B1, sodium cyclohexanesulfinate **1i** (17.0 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3i** (39% yield) as a colourless oil when $TBAPF_6$ (0.5 equiv.) was used as electrotyte under the standart conditions. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 80:20.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 6.06 – 5.77 (m, 1H), 5.60 – 5.36 (m, 2H), 3.69 (d, *J* = 7.3 Hz, 2H), 2.93 (tt, *J* = 12.1, 3.5 Hz, 1H), 2.31 – 2.09 (m, 2H), 2.00 – 1.85 (m, 2H), 1.82 – 1.67 (m, 1H), 1.66 – 1.48 (m, 2H), 1.38 – 1.12 (m, 3H) ppm.

Spectra data are consistent with those reported in the literature.[7]

**4-(Allylsulfonyl)tetrahydro-2*H*-pyran (3j)**



Following the general procedure B1, sodium tetrahydro-2*H*-pyran-4-sulfinate **1j** (17.2 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3j** (63% yield) as a colourless oil. Eluent: cyclohexane: diethyl ether, slow gradient from 80:20 to 40:60.

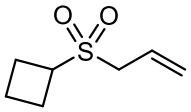
The reaction was carried out under electro-flow conditions. Procedure B2 was followed. After workup and purification as described above, **3j** (43% yield) was obtained as a colourless oil.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 5.94 (ddt, *J* = 17.4, 10.2, 7.3 Hz, 1H), 5.66 – 5.38 (m, 2H), 4.11 (dt, *J* = 11.6, 3.5 Hz, 2H), 3.71 (d, *J* = 7.3 Hz, 2H), 3.49 – 3.32 (m, 2H), 3.27 – 3.09 (m, 1H), 2.07 – 1.89 (m, 4H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ 124.9, 124.7, 66.5 (2C), 56.8, 54.9, 25.1 (2C) ppm.

**HRMS (ESI$^+$)**: calculated for $C_8H_{18}NO_3S$ $[M\text{-}NH_4]^+$: 208.1002; found: 208.0972.

**(Allylsulfonyl)cyclobutene (3k)**

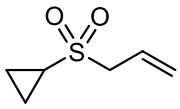


Following the general procedure B1, sodium cyclobutanesulfinate **1k** (14.2 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3k** (43% yield) as a colourless oil. Eluent: cyclohexane: diethyl ether, slow gradient from 80:20 to 60:40.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 5.89 (ddt, *J* = 17.4, 10.2, 7.4 Hz, 1H), 5.49 – 5.31 (m, 2H), 3.85 (p, *J* = 8.3 Hz, 1H), 3.61 (d, *J* = 7.4 Hz, 2H), 2.79 – 2.48 (m, 2H), 2.39 – 2.16 (m, 2H), 2.13 – 1.85 (m, 2H) ppm.

Spectra data are consistent with those reported in the literature.[7]

**(Allylsulfonyl)cyclopropane (3l)**



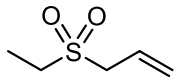
Following the general procedure B1, sodium cyclopropanesulfinate **1l** (12.8 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3l** (88% yield) as a colourless oil. Eluent: cyclohexane: diethyl ether, slow gradient from 80:20 to 60:40.

The reaction was carried out under electro-flow conditions. Procedure B2 was followed. After workup and purification as described above, **3l** (35% yield) was obtained as a colourless oil.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 6.08 – 5.85 (m, 1H), 5.57 – 5.38 (m, 2H), 3.76 (d, *J* = 7.4 Hz, 2H), 2.61 – 2.29 (m, 1H), 1.31 – 1.16 (m, 2H), 1.09 – 0.94 (m, 2H) ppm.

Spectra data are consistent with those reported in the literature.[8]

**3-(Ethylsulfonyl)prop-1-ene (3m)**

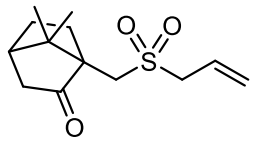


Following the general procedure B1, sodium ethanesulfinate **1m** (11.6 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3m** (47% yield) as a colourless oil. Eluent: cyclohexane: diethyl ether, slow gradient from 80:20 to 60:40.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 5.95 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.55 – 5.36 (m, 2H), 3.71 (d, *J* = 7.4 Hz, 2H), 2.99 (q, *J* = 7.5 Hz, 2H), 1.39 (t, *J* = 7.5 Hz, 3H) ppm.

Spectra data are consistent with those reported in the literature.[9]

**1-((Allylsulfonyl)methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-one (3n)**



Following the general procedure B1, sodium (7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfinate **1n** (23.8 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3n** (38% yield) as a white solid. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 80:20.

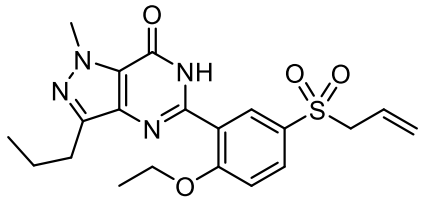
The reaction was carried out under electro-flow conditions. Procedure B2 was followed. After workup and purification as described above, **3n** (30% yield) was obtained as a white solid.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 6.08 – 5.92 (m, 1H), 5.56 – 5.44 (m, 2H), 4.11 (dd, *J* = 14.0, 7.8 Hz, 1H), 3.79 (dd, *J* = 14.0, 6.9 Hz, 1H), 3.47 (d, *J* = 14.9 Hz, 1H), 2.74 (d, *J* = 14.9 Hz, 1H), 2.56 – 2.27 (m, 2H), 2.22 – 1.99 (m, 2H), 1.98 – 1.75 (m, 2H), 1.53 – 1.36 (m, 1H), 1.06 (s, 3H), 0.88 (s, 3H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ 215.6, 125.5, 125.0, 60.6, 59.2, 49.4, 48.9, 42.9, 42.8, 27.3, 25.6, 20.0, 19.9 ppm.

**HRMS (ESI$^+$)**: calculated for $C_{13}H_{24}NO_3S$ $[M\text{-}NH_4]^+$: 274.1471; found: 274.1517.

**5-(5-(Allylsulfonyl)-2-ethoxyphenyl)-1-methyl-3-propyl-1,6-dihydro-7H-pyrazolo[4,3-d]pyrimidin-7-one (3o)**



Following the general procedure B1, sodium 4-ethoxy-3-(1-methyl-7-oxo-3-propyl-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidin-5-yl)benzenesulfinate **1o** (39.8 mg, 0.1 mmol) and potassium allyltrifluoroborate **2a** (37.0 mg, 0.25 mmol) gave product **3o** (30% yield) as a white solid. Eluent: cyclohexane: diethyl ether 40:60.

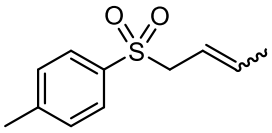
The reaction was carried out under electro-flow conditions. Procedure B2 was followed. After workup and purification as described above, **3o** (28% yield) was obtained as a white solid.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 10.81 (s, 1H), 8.91 (d, *J* = 2.5 Hz, 1H), 7.92 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 5.98 – 5.73 (m, 1H), 5.37 (d, *J* = 10.1 Hz, 1H), 5.27 (d, *J* = 16.6 Hz, 1H), 4.38 (q, *J* = 7.0 Hz, 2H), 4.27 (s, 3H), 3.87 (d, *J* = 7.3 Hz, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 1.86 (h, *J* = 7.4 Hz, 2H), 1.64 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.4 Hz, 3H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ 160.2, 153.8, 147.2, 146.5, 138.5, 132.7, 132.3, 131.8, 125.1, 124.9, 124.7, 121.4, 113.1, 66.4, 61.2, 38.4, 27.8, 22.5, 14.7, 14.2 ppm.

**HRMS (ESI$^+$)**: calculated for $C_{20}H_{25}N_4O_4S$ $[M-H]^+$: 417.1591; found: 417.1573.

**1-(But-2-en-1-ylsulfonyl)-4-methylbenzene (3p)**

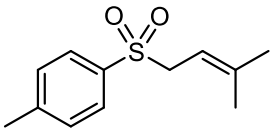


Following a sighly modified procedure B1, sodium 4-methylbenzenesulfinate **1a** (17.8 mg, 0.1 mmol) and potassium but-3-en-2-yltrifluoroborate **2b** (40.5 mg, 0.25 mmol) gave product **3p** (81% yield, 75:25 d.r.) as a colourless oil when the reaction was carried out in 3 mL of a 5:1 mixture of acetonitrile: water, Ni foam was used as counterelectrode and constant current (5 mA) was set during 2 hours. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 80:20.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.81 – 7.68 (m, 4H), 7.33 (d, *J* = 7.9 Hz, 4H), 5.92 – 5.73 (m, 1H, minor), 5.67 – 5.48 (m, 1H, major), 5.48 – 5.36 (m, 2H), 3.83 (d, *J* = 8.0 Hz, 2H, minor), 3.70 (d, *J* = 7.2 Hz, 2H, major), 2.44 (s, 6H), 1.67 (d, *J* = 6.2 Hz, 6H) ppm.

Spectra data are consistent with those reported in the literature.[10]

**1-Methyl-4-((3-methylbut-2-en-1-yl)sulfonyl)benzene (3q)**



Following a sighly modified procedure B1, sodium 4-methylbenzenesulfinate **1a** (17.8 mg, 0.1 mmol) and potassium trifluoro(2-methylbut-3-en-2-yl)borate **2c** (44.0 mg, 0.25 mmol) gave product **3q** (72% yield) as a colourless oil when the reaction was carried out in 3 mL of a 5:1 mixture of acetonitrile: water, Ni foam was used as counterelectrode and constant current (5 mA) was set during 2 hours. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 80:20.

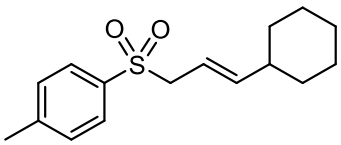
The reaction was scaled up to 1.0 mmol. Modified procedure B1 was followed using a 10 mL ElectraSyn vial as 6.7 mL of acetonitrile and 1.3 mL of distilled water were used as solvents. Ni foam was used as counterelectrode and the reaction was carried out at 5 mA during 16 hours. After workup and purification as described above, **3q** (71% yield) was obtained as a colourless oil that solidifies upon time.

The reaction was carried out under electro-flow conditions. Procedure B2 was followed. After workup and purification as described above, **3q** (65% yield) was obtained as a colourless oil.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.32 (dd, *J* = 8.0 Hz, 2H), 5.18 (t, *J* = 8.0 Hz, 1H), 3.76 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 1.72 (s, 3H), 1.33 (s, 3H) ppm.

Spectra data are consistent with those reported in the literature.[12]

**(*E*)-1-((3-Cyclohexylallyl)sulfonyl)-4-methylbenzene (3r)**

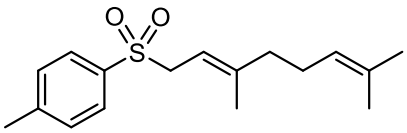


Following a sighly modified procedure B1, sodium 4-methylbenzenesulfinate **1a** (17.8 mg, 0.1 mmol) and potassium (1-cyclohexylallyl)trifluoroborate **2d** (57.5 mg, 0.25 mmol) gave product **3r** (68% yield) as a colourless oil when the reaction was carried out in 3 mL of a 5:1 mixture of acetonitrile: water, Ni foam was used as counterelectrode and constant current (5 mA) was set during 2 hours. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 85:15.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.47 – 5.26 (m, 2H), 3.70 (d, *J* = 6.2 Hz, 2H), 2.44 (s, 3H), 2.03 – 1.82 (m, 1H), 1.76 – 1.46 (m, 4H), 1.34 – 1.03 (m, 4H), 1.02 – 0.73 (m, 2H) ppm.

Spectra data are consistent with those reported in the literature.[11]

**(*E*)-1-((3,7-Dimethylocta-2,6-dien-1-yl)sulfonyl)-4-methylbenzene (3s)**

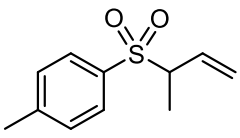


Following a sighly modified procedure B1, sodium 4-methylbenzenesulfinate **1a** (17.8 mg, 0.1 mmol) and potassium (3,7-dimethylocta-1,6-dien-3-yl)trifluoroborate **2e** (61.0 mg, 0.25 mmol) gave product **3s** (41% yield) as a colourless oil when the reaction was carried out in 3 mL of a 5:1 mixture of acetonitrile: water, Ni foam was used as counterelectrode and constant current (5 mA) was set during 2 hours. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 85:15.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.17 (t, *J* = 8.0 Hz, 1H), 5.03 (bs, 1H), 3.78 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.08 – 1.97 (m, 4H), 1.68 (s, 3H), 1.59 (s, 3H), 1.33 (s, 3H) ppm.

Spectra data are consistent with those reported in the literature.[13]

**1-(But-3-en-2-ylsulfonyl)-4-methylbenzene (3t)**



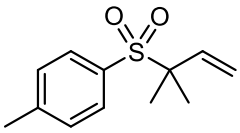
Following a sighly modified procedure B1, sodium 4-methylbenzenesulfinate **1a** (17.8 mg, 0.1 mmol) and potassium (*E*)-but-2-en-1-yltrifluoroborate **2f** (40.5 mg, 0.25 mmol) gave product **3t** (77% yield) as a colourless oil when the reaction was carried out in 3 mL of a 5:1 mixture of acetonitrile: water, Ni foam was used as counterelectrode and constant current (5 mA) was set during 2 hours. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 80:20.

<u>The reaction was carried out under electro-flow conditions.</u> Procedure B2 was followed. After workup and purification as described above, **3t** (55% yield) was obtained as a colourless oil.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.82 (ddd, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.26 (d, *J* = 10.3 Hz, 1H), 5.09 (d, *J* = 17.3 Hz, 1H), 3.69 (p, *J* = 7.1 Hz, 1H), 2.44 (s, 3H), 1.42 (d, *J* = 7.1 Hz, 3H) ppm.

Spectra data are consistent with those reported in the literature.[14]

**1-Methyl-4-((2-methylbut-3-en-2-yl)sulfonyl)benzene (3u)**



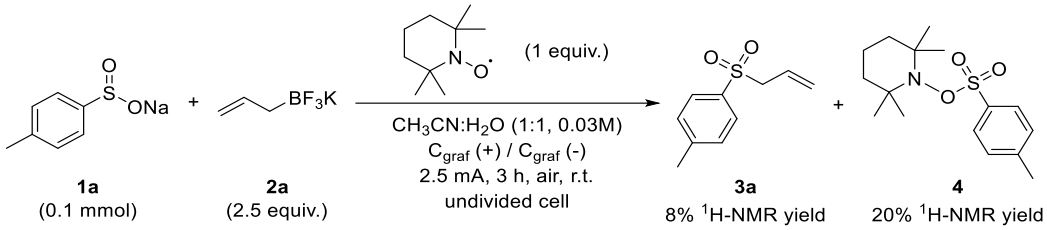
Following a sighly modified procedure B1, sodium 4-methylbenzenesulfinate **1a** (17.8 mg, 0.1 mmol) and potassium trifluoro(3-methylbut-2-en-1-yl)borate **2g** (44.0 mg, 0.25 mmol) gave product **3u** (30% yield) as a colourless oil when the reaction was carried out in 3 mL of a 5:1 mixture of acetonitrile: water, Ni foam was used as counterelectrode and constant current (5 mA) was set during 2 hours. Eluent: cyclohexane: diethyl ether, slow gradient from 95:5 to 80:20.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.02 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.26 (d, *J* = 10.7 Hz, 1H), 5.07 (d, *J* = 17.4 Hz, 1H), 2.43 (s, 3H), 4.13 (s, 6H) ppm.

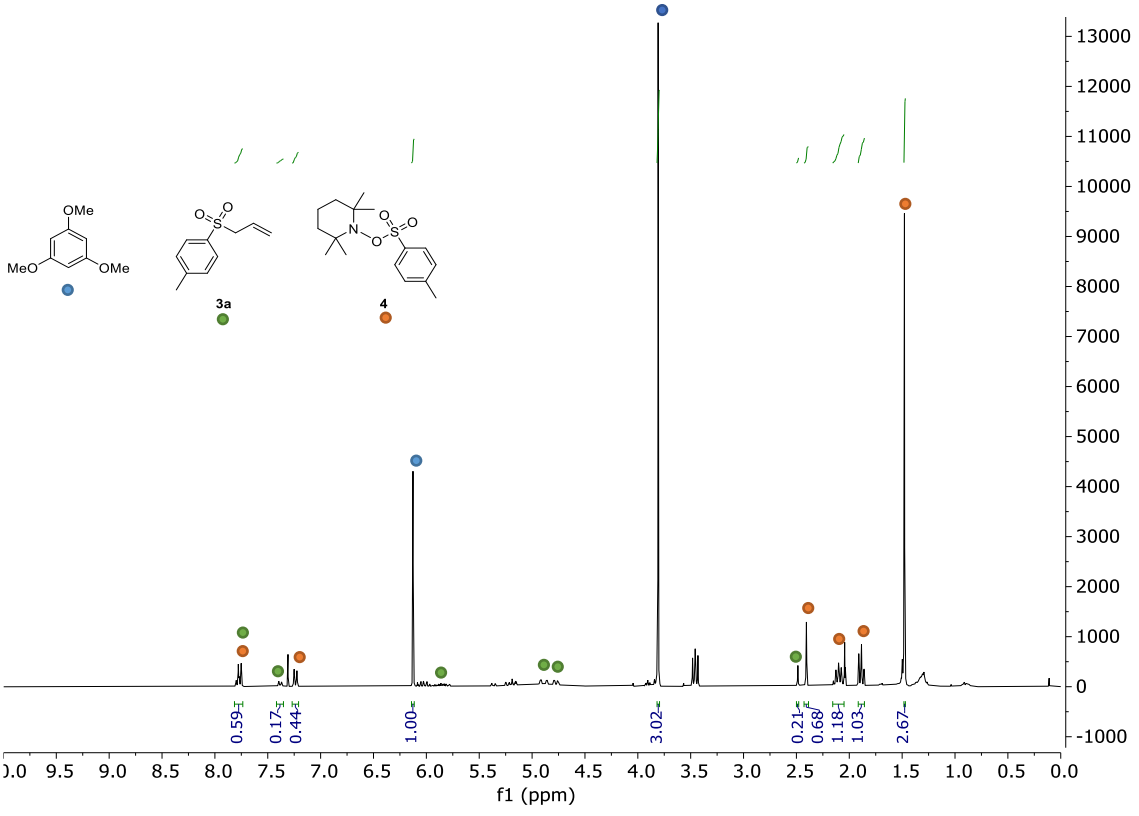
Spectra data are consistent with those reported in the literature.[14]

# 4. Mechanistic studies

## 4.1. Radical scavenger

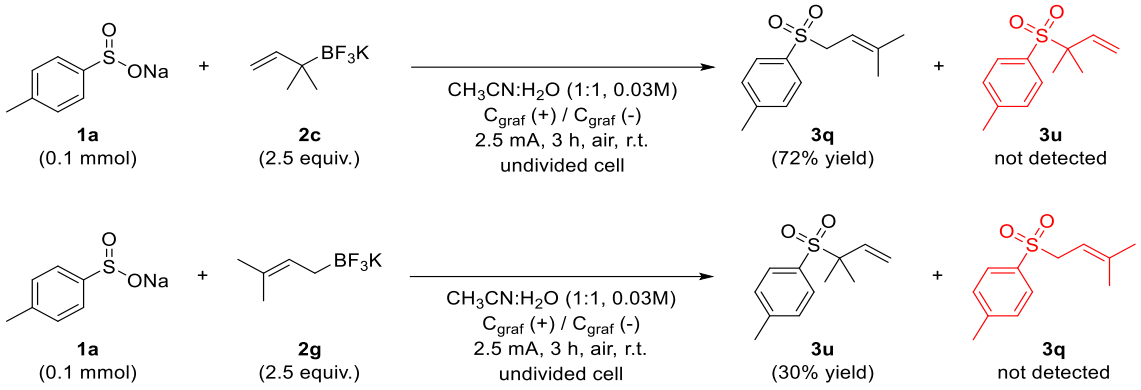


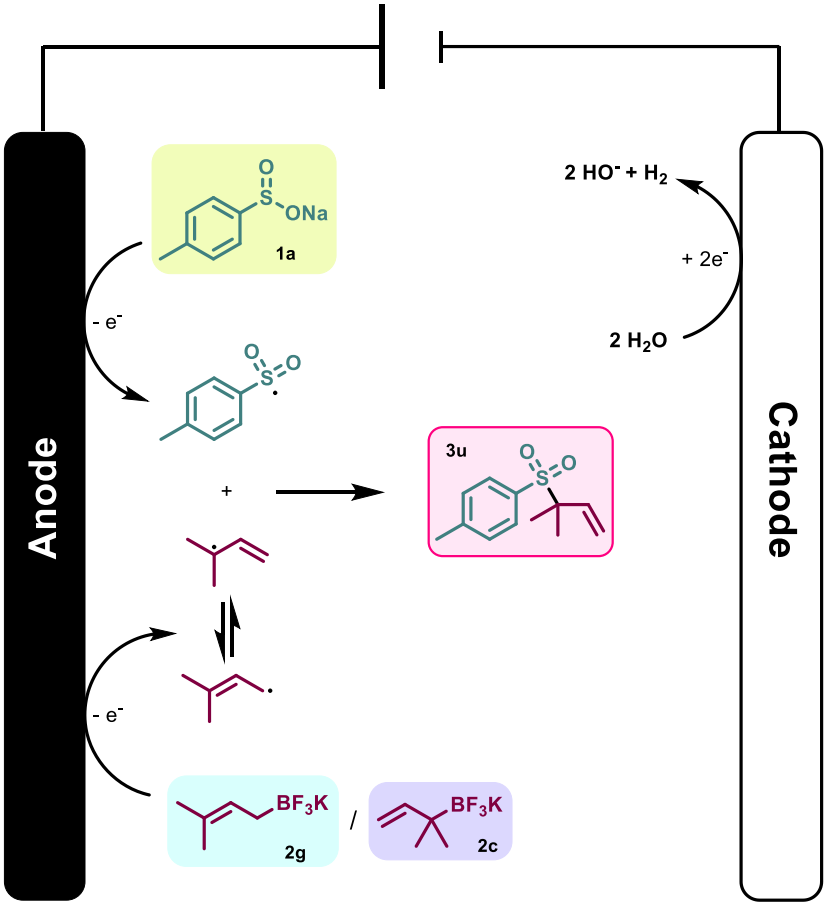

Sodium sulfinate **1a** (0.1 mmol) and potassium allyltrifluoroborate **2a** (0.25 mmol) were added to a 5 mL ElectraSyn vial as well as, the radical scavenger, TEMPO (1 equiv.). Acetonitrile (1.5 mL) and distilled water (1.5 mL) were added to the vial and it was stirred until solids were dissolved. Then, carbon graphite electrodes were fitted in the cap of the vial and it was closed. The reaction was set at constant current (2.5 mA) for 3 hours. After that time, the solution was transfer to a round bottom flask, electrodes and vial were rinsed with dichloromethane and then concentrated to dryness. Diethyl ether was added to the flask in order to dissolve the product and then the mixture was filtered and concentrated under reduce pressure. The residue was analysed by $^{1}$H-NMR using 1,3,5-trimethoxybenzene (5.6 mg, 0.03 mmol) as internal standard and $CDCl_3$ (0.6 mL) as solvent, finding traces of **3a** (8% $^{1}$H-NMR yield) and **4** as major product (20% $^{1}$H-NMR yield), which spectra data are consistent with those reported in the literature.[15]



## 4.2. Discarted mechanism

If a radical-radical recombination mechanism (**Scheme S1**) is taking place due to the oxidation of both substrates (sodium sulfinates (**1**) and potassium allyltrifluoroborate salts (**2**)) at the anode, the reactivity through the most stabilized position of the allylic radical intermediate should be observed experimentally. However, only formation of product **3q** was observed when substrate **2c** was subjected to the standard reaction condition. The same observation was achieved in the case of substrate **2g**, product **3u** was obtained in 30% yield as sole product.




**Scheme S1.** Radical-radical recombination mechanism.

## 4.3. Cyclic Voltammetry

CVs were performed under nitrogen atmosphere at room temperature, using 0.25 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte solution in acetonitrile ($CH_3CN$) or dimethylformamide (DMF). Measurements were carried out by using a commercially available IKA Electrasyn 2.0 Package. A standard IKA three-electrode vial was used as well as the commercially available IKA CV Package. Potentials were referred to Ag/AgCl, KCl 3.0 M reference electrode in water, and measured potentials were calibrated using an internal Fc/Fc+ standard. The working electrode used to perform the experiments was a glassy carbon electrode. The counterelectrode consisted of a Pt electrode. CVs are consistent with those reported in the literature.[16]

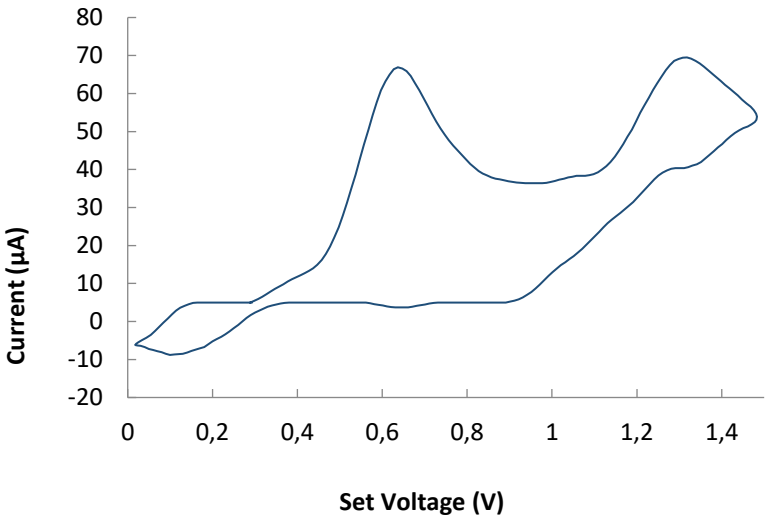



**Figure S3.** CV of sodium sulfinate (**1a**) (blue). It was measured in DMF (0.25 M $TBAPF_6$) at 100 mV/s using glassy carbon electrode as WE, Ag/AgCl as RE and Pt as CE.

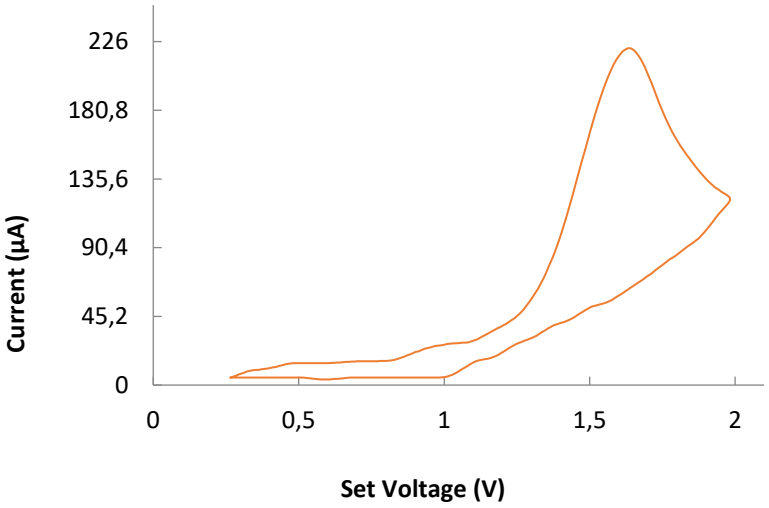



**Figure S4.** CV of potassium allyl-trifluoroborate (**2a**) (orange). It was measured in $CH_3CN$ (0.25 M $TBAPF_6$) at 100 mV/s using glassy carbon electrode as WE, Ag/AgCl as RE and Pt as CE.

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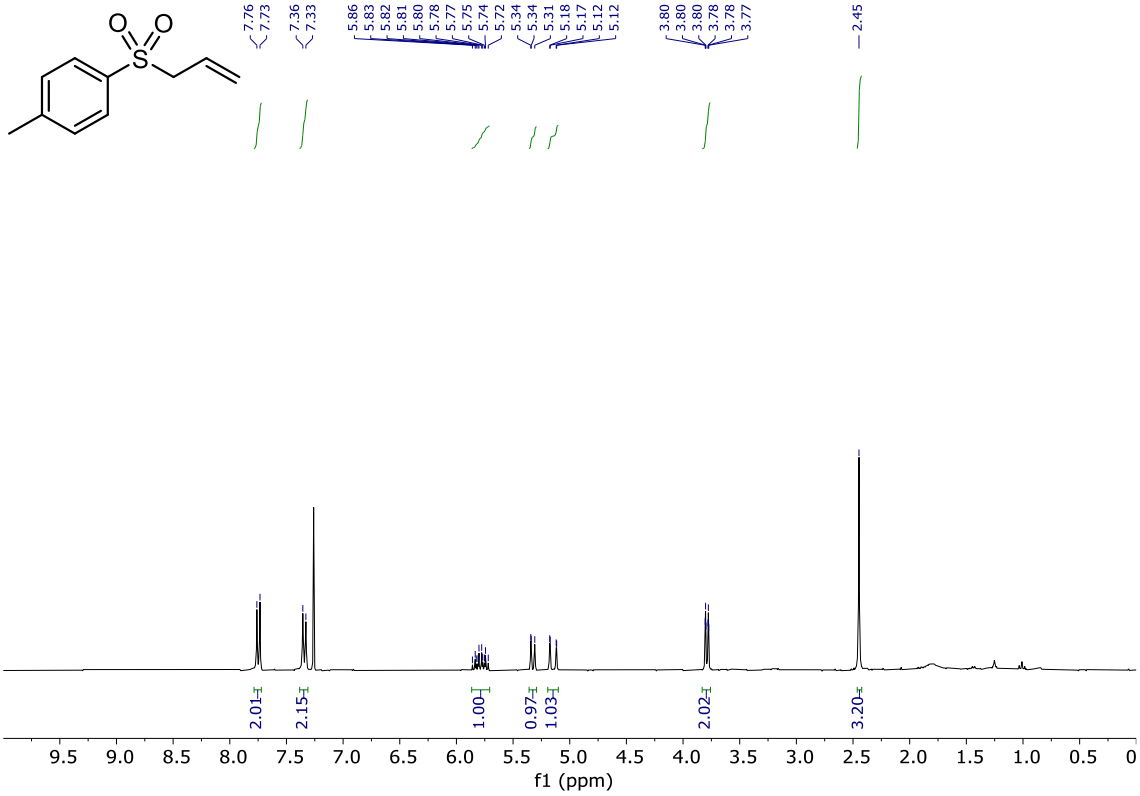
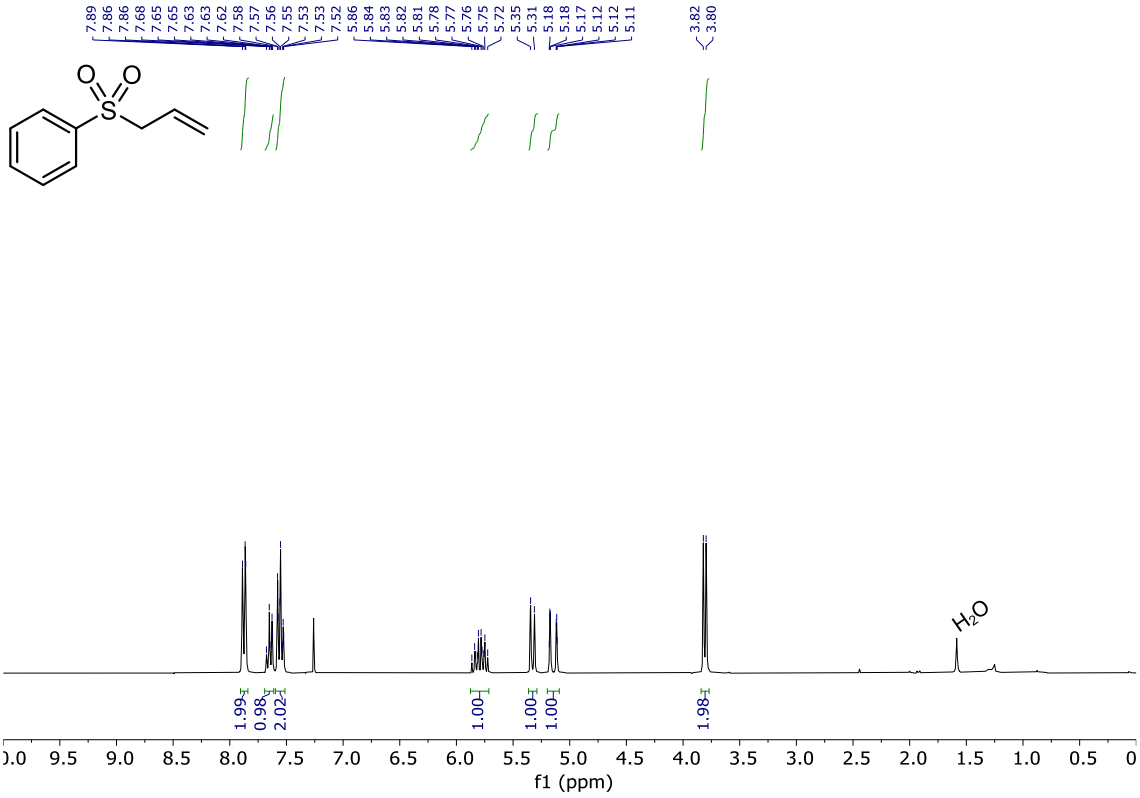
# 6. Nuclear Magnetic Resonance Spectra

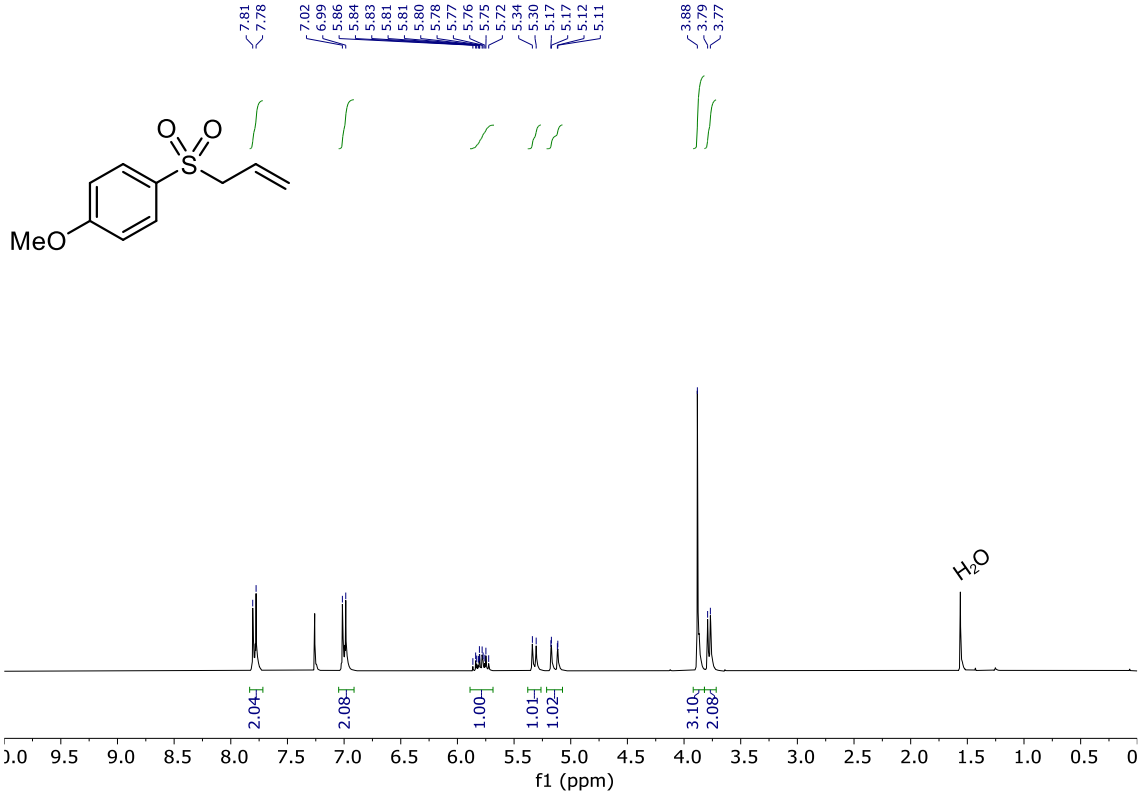
### 1-(Allylsulfonyl)-4-methylbenzene (3a)



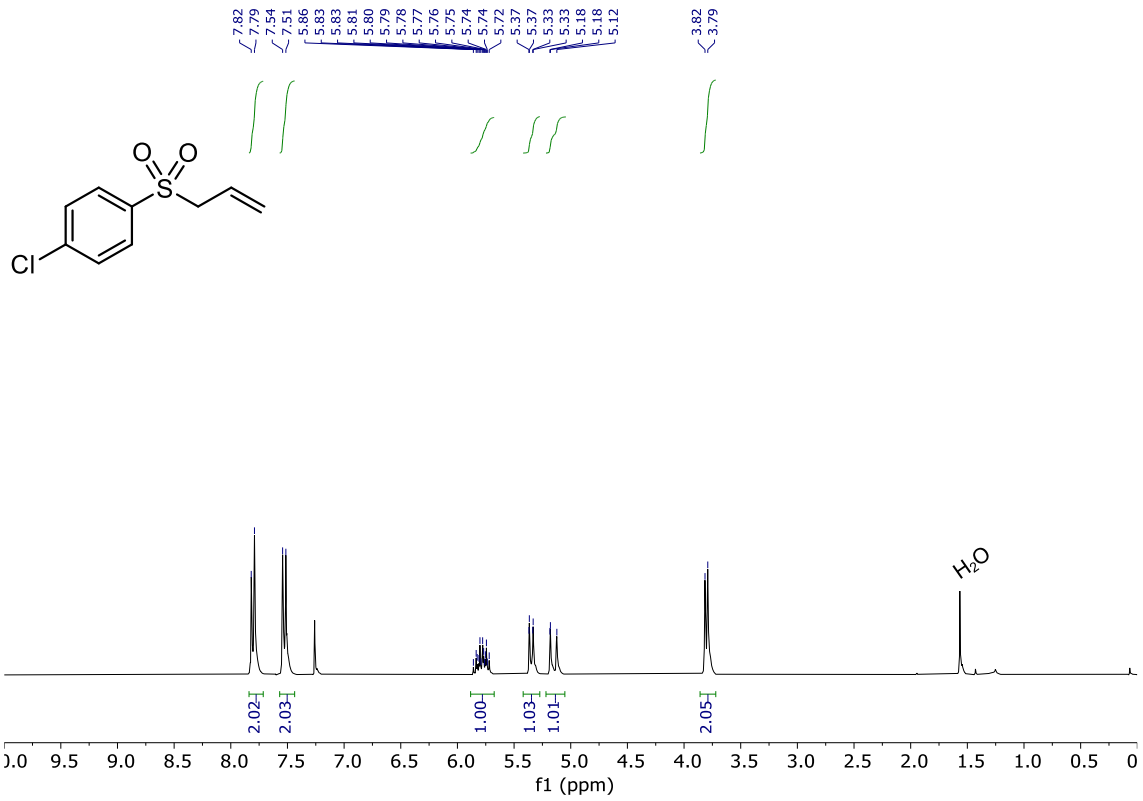

### (Allylsulfonyl)benzene (3b)



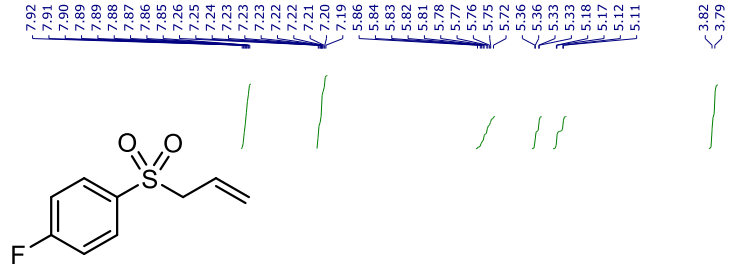
**1-(Allylsulfonyl)-4-methoxybenzene (3c)**

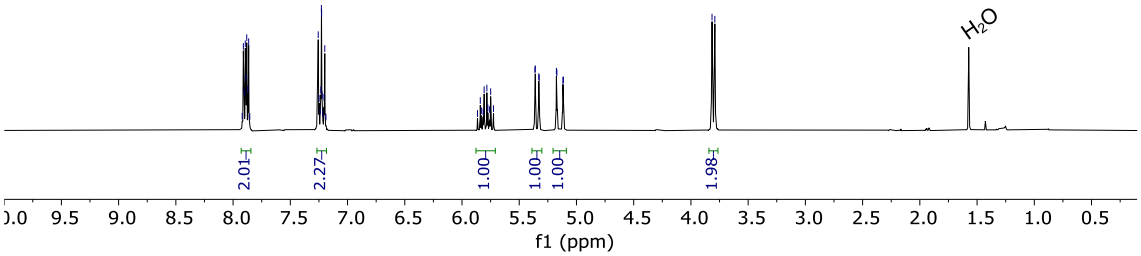



**1-(Allylsulfonyl)-4-chlorobenzene (3d)**

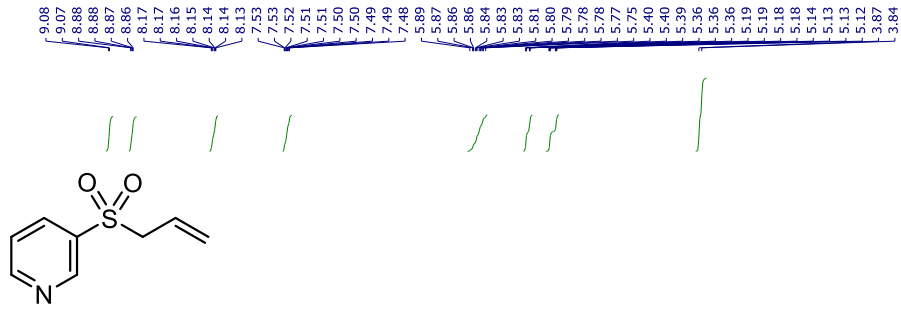


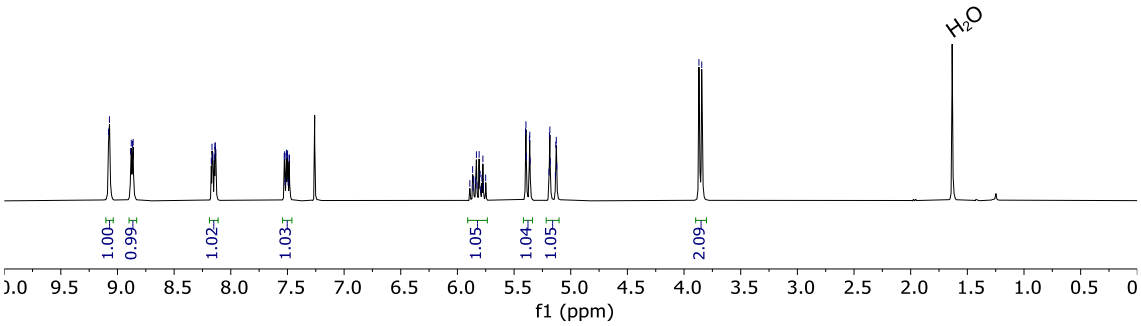
**1-(Allylsulfonyl)-4-fluorobenzene (3e)**



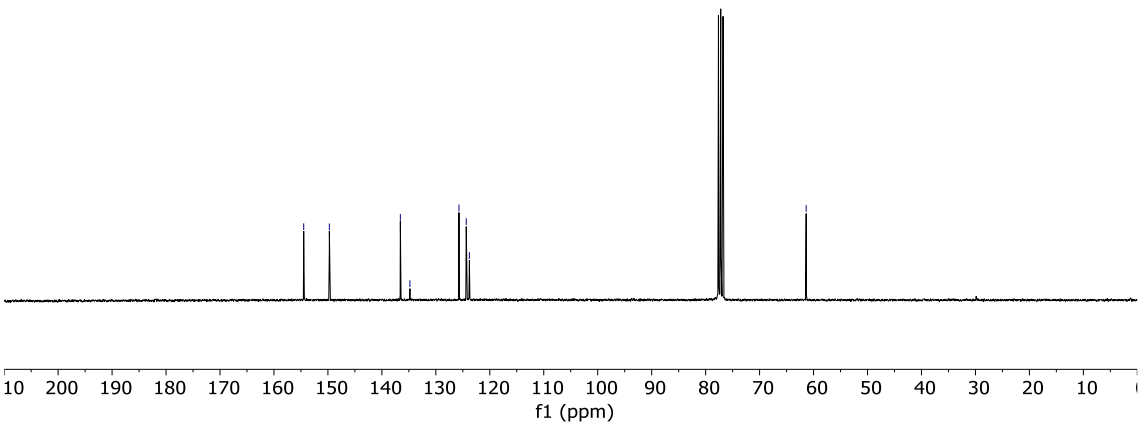



**3-(Allylsulfonyl)pyridine (3f)**

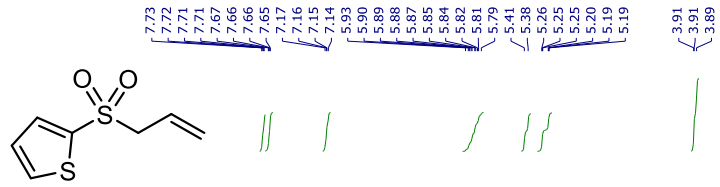


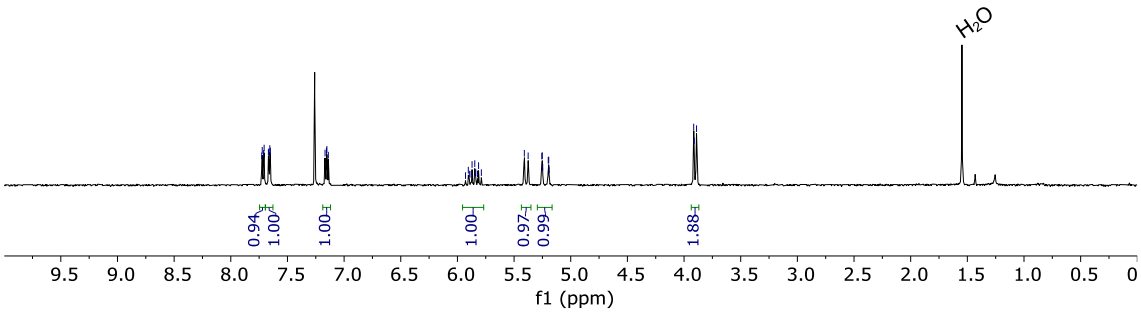



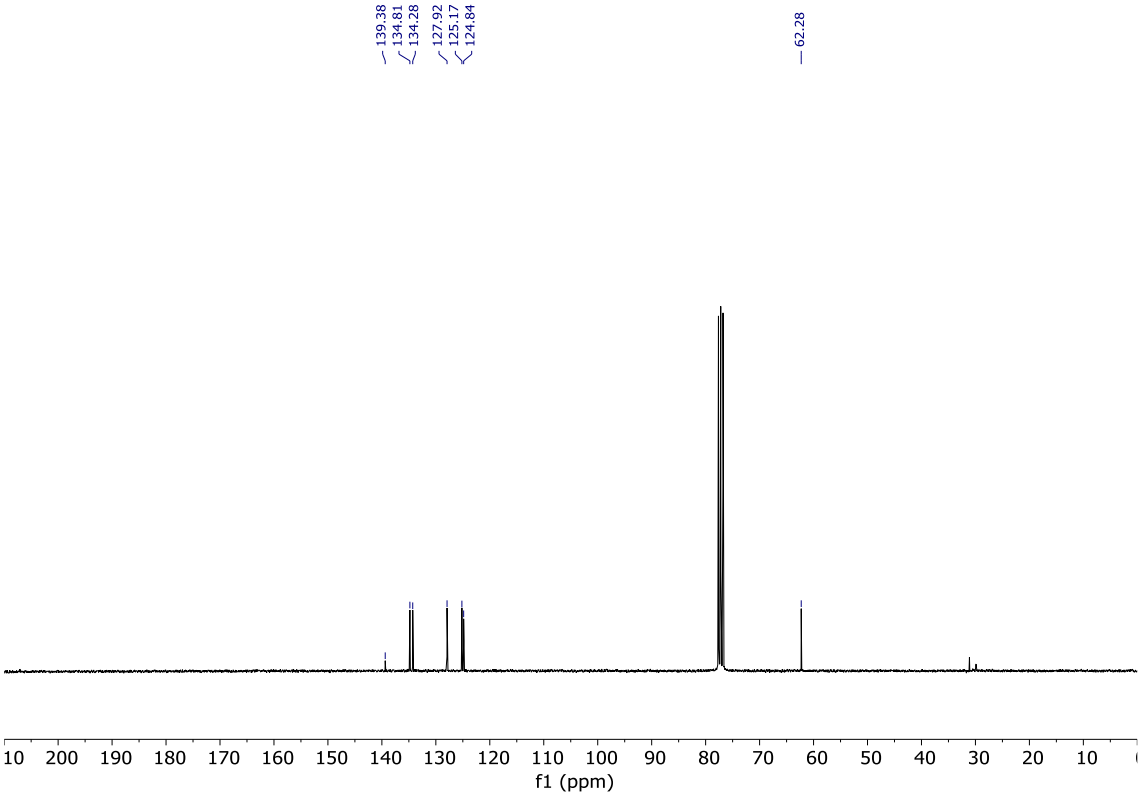




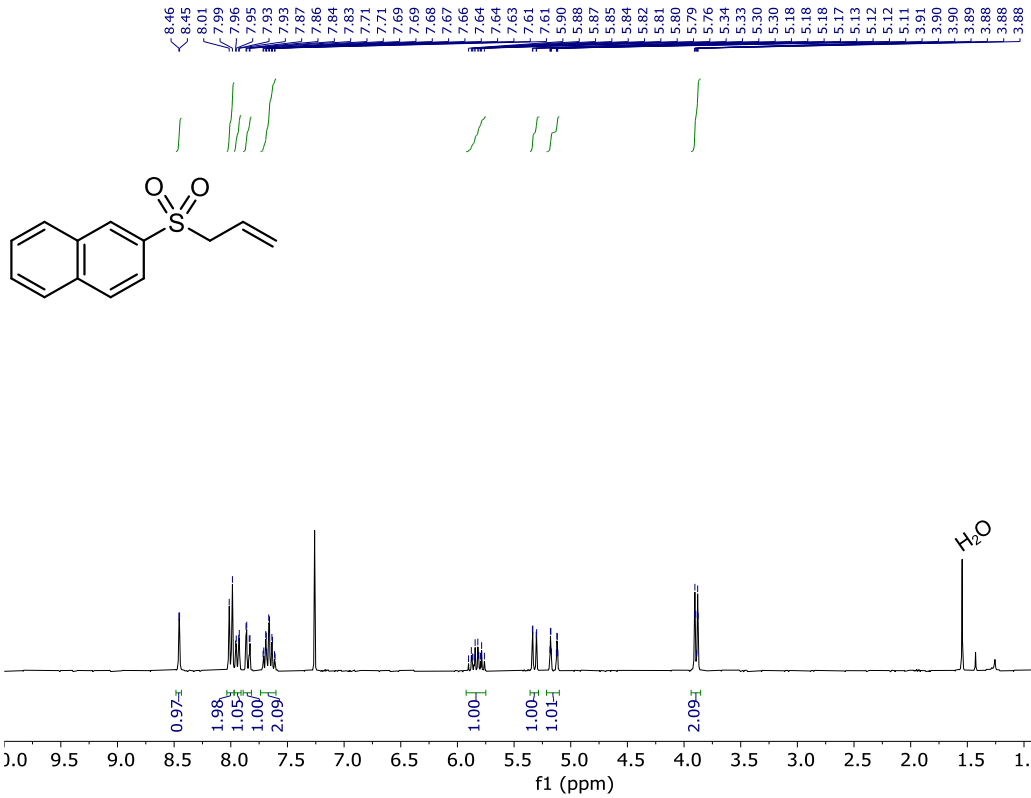
**2-(Allylsulfonyl)thiophene (3g)**



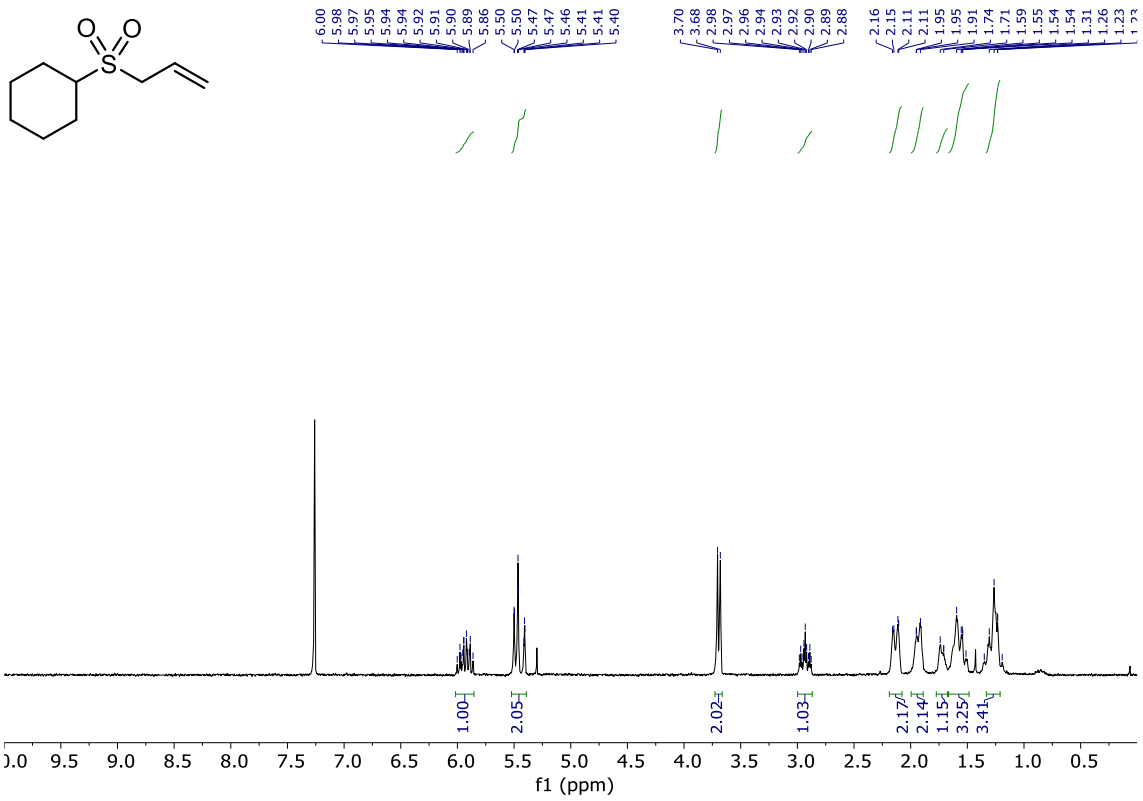



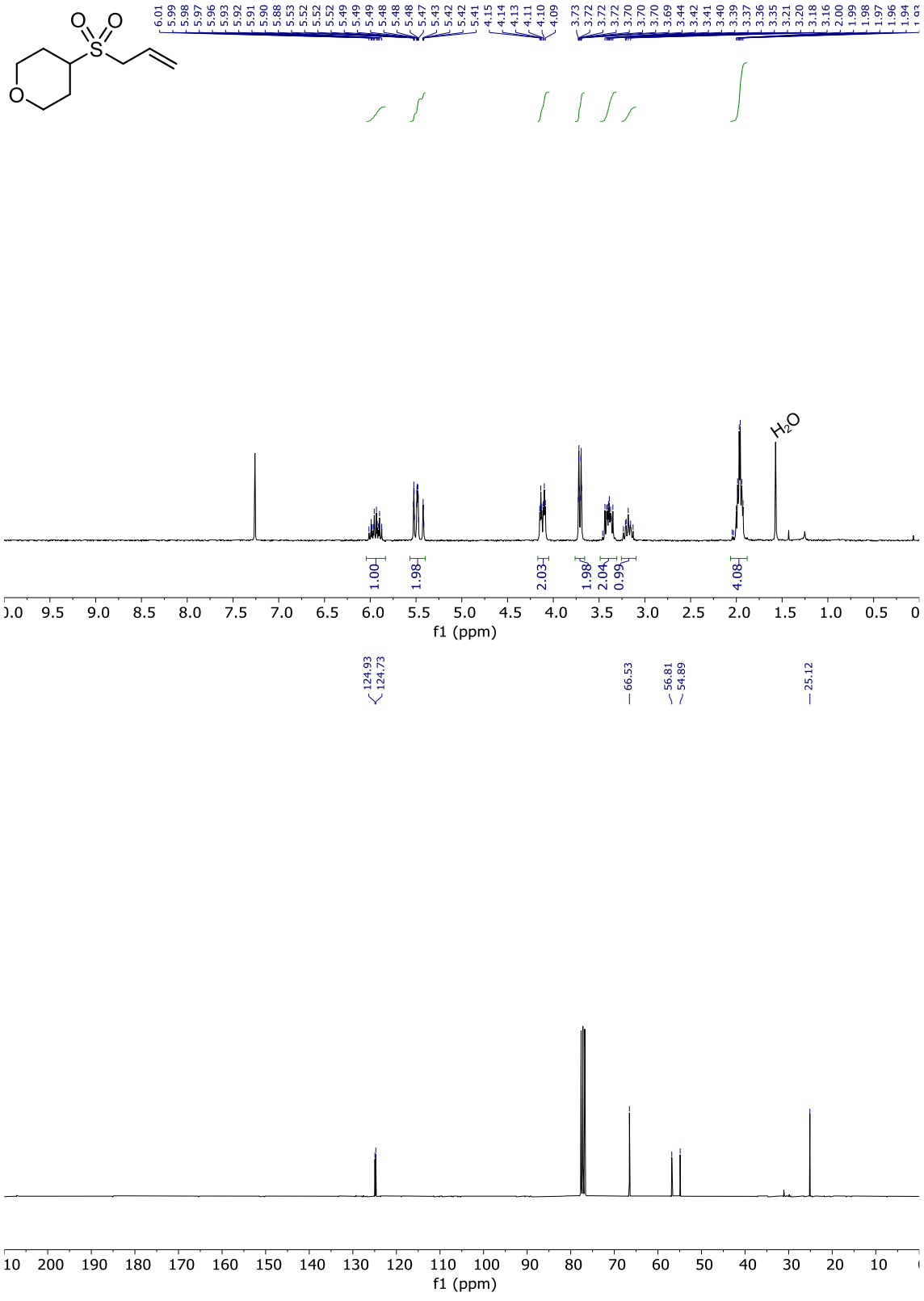
**2-(Allylsulfonyl)naphthalene (3h)**



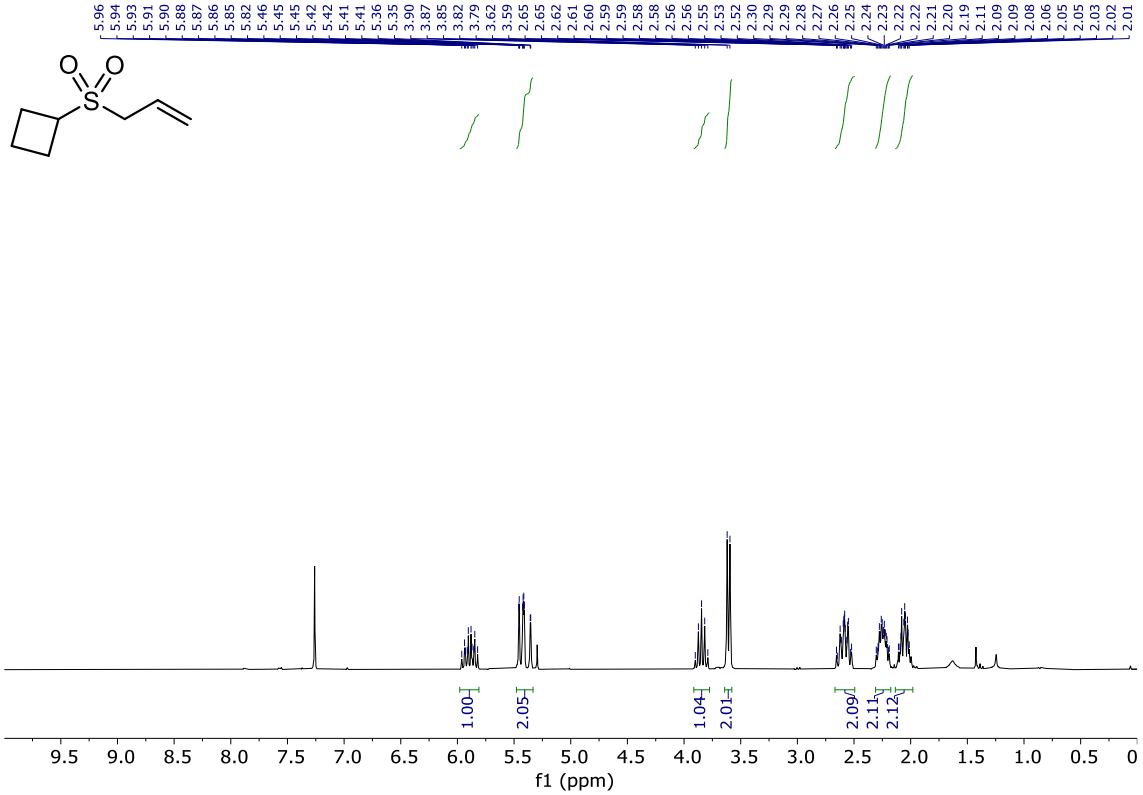

**(Allylsulfonyl)cyclohexane (3i)**



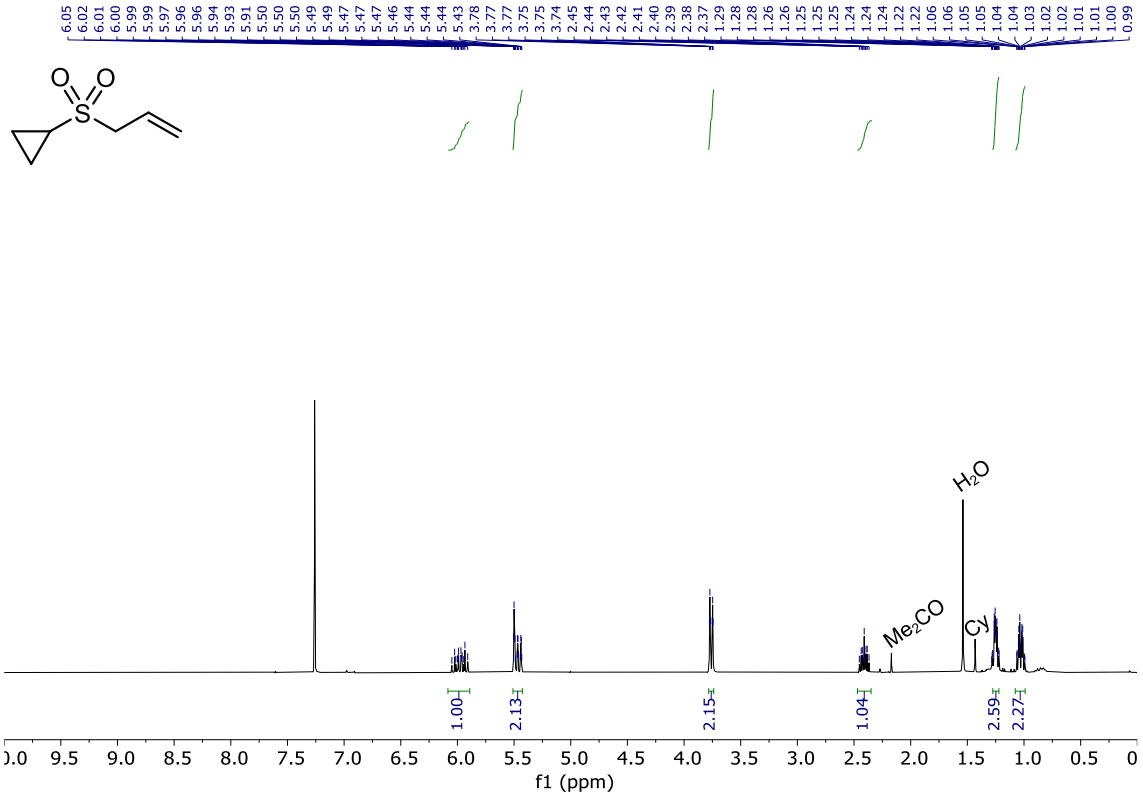
**4-(Allylsulfonyl)tetrahydro-2*H*-pyran (3j)**



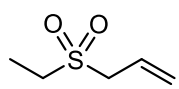
**(Allylsulfonyl)cyclobutene (3k)**



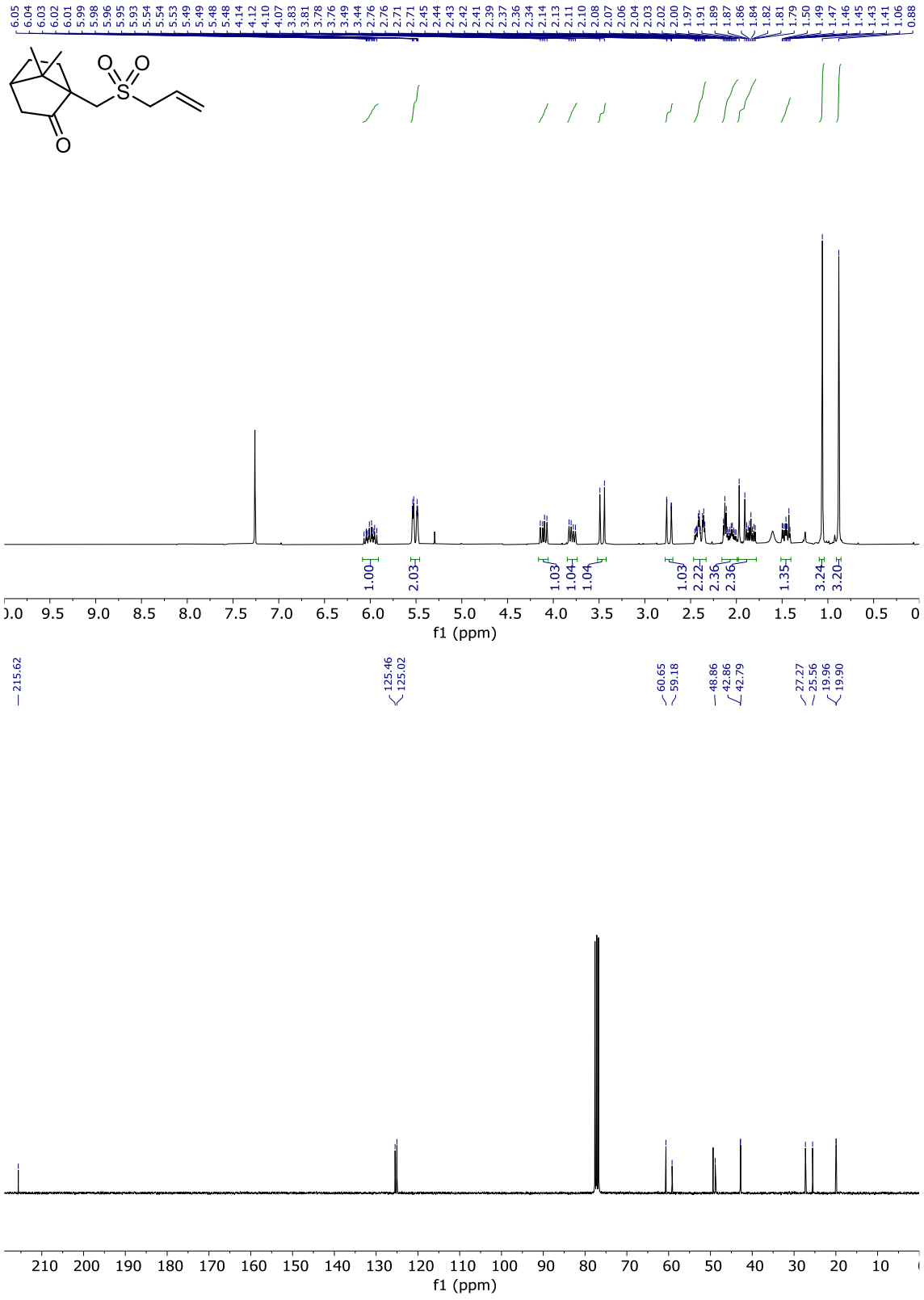

**(Allylsulfonyl)cyclopropane (3l)**



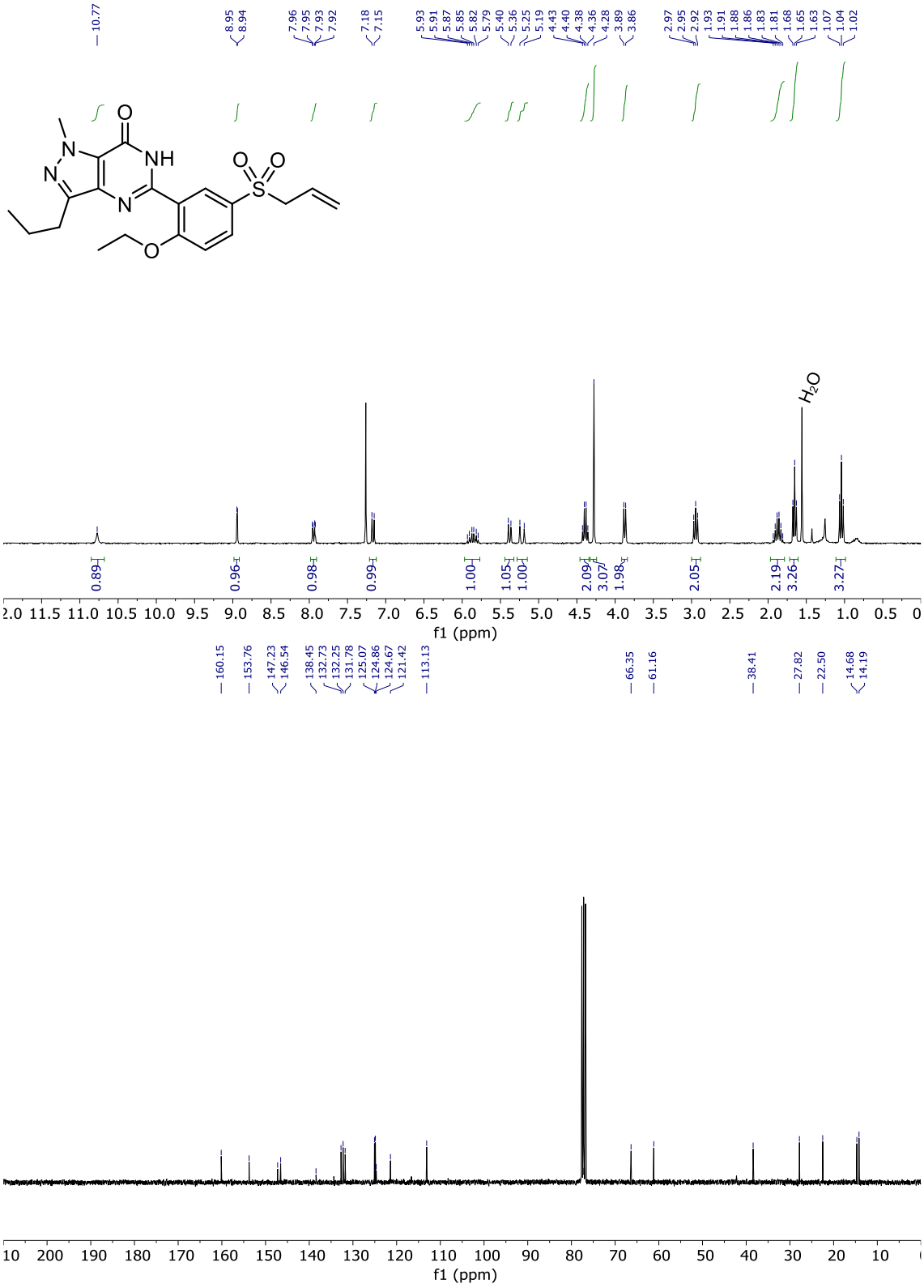
**3-(Ethylsulfonyl)prop-1-ene (3m)**



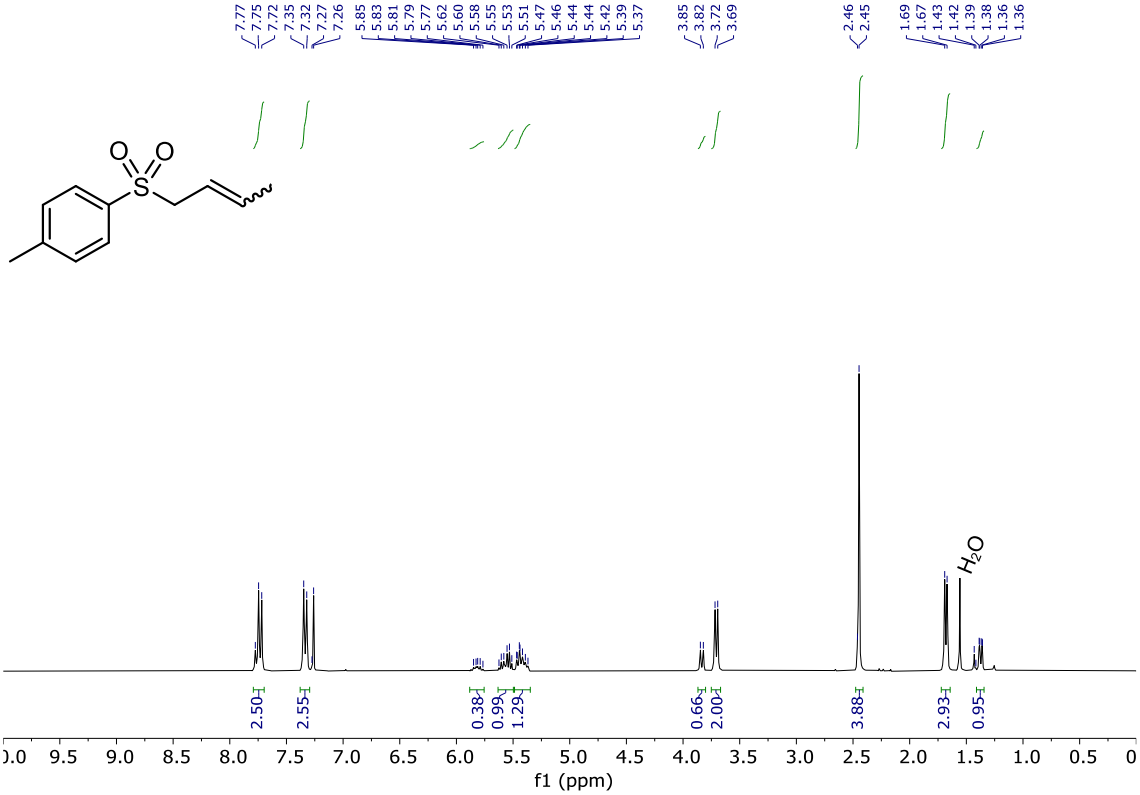
**1-((Allylsulfonyl)methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-one (3n)**



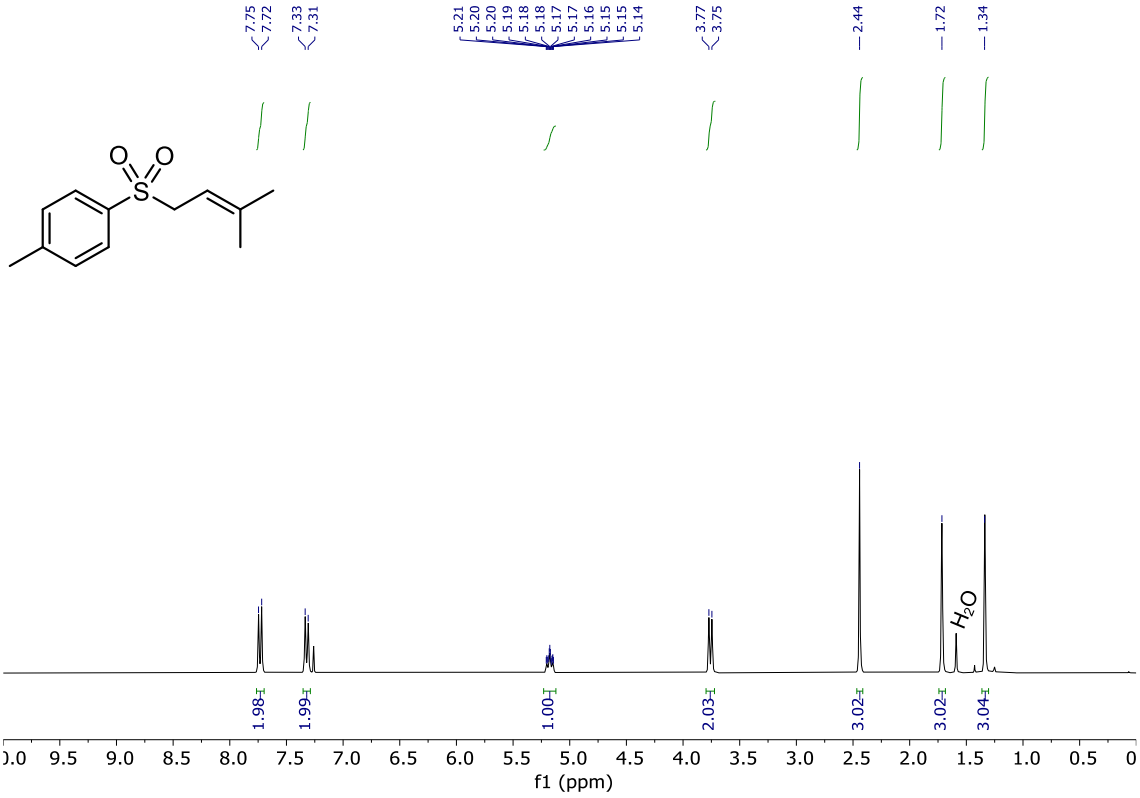
**5-(5-(Allylsulfonyl)-2-ethoxyphenyl)-1-methyl-3-propyl-1,6-dihydro-7H-pyrazolo[4,3-d]pyrimidin-7-one (3o)**



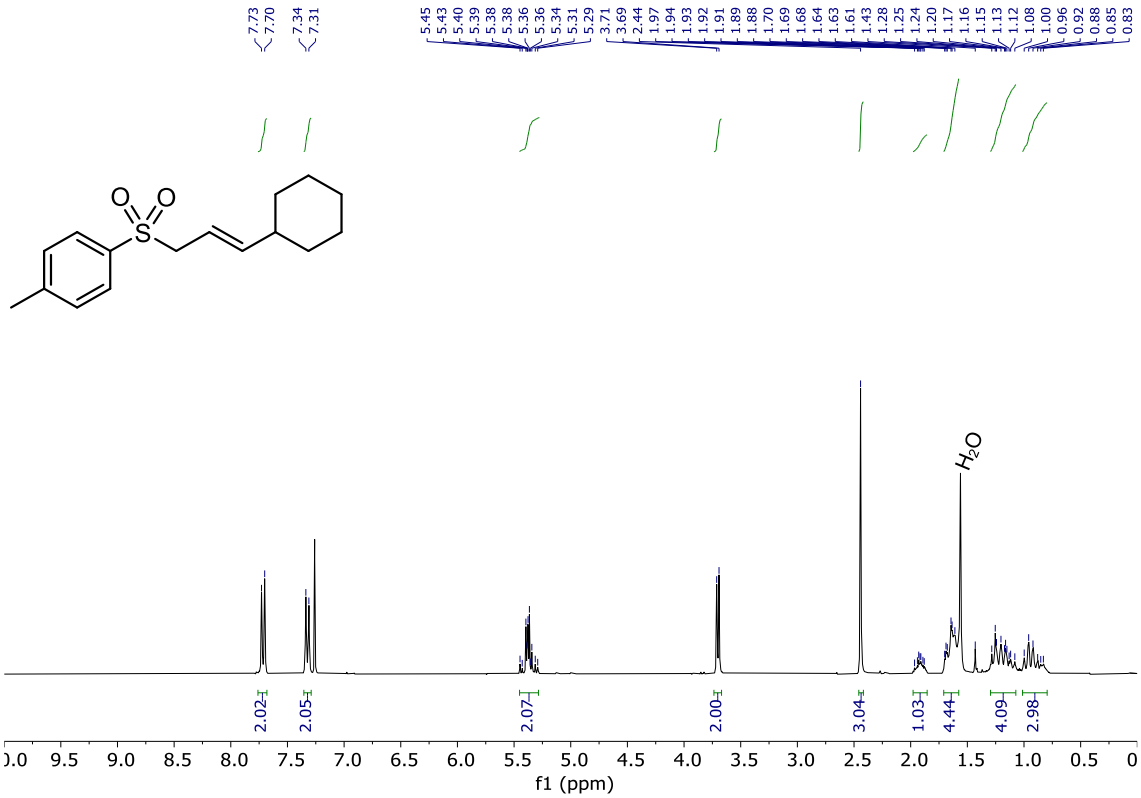
**1-(But-2-en-1-ylsulfonyl)-4-methylbenzene (3p)**



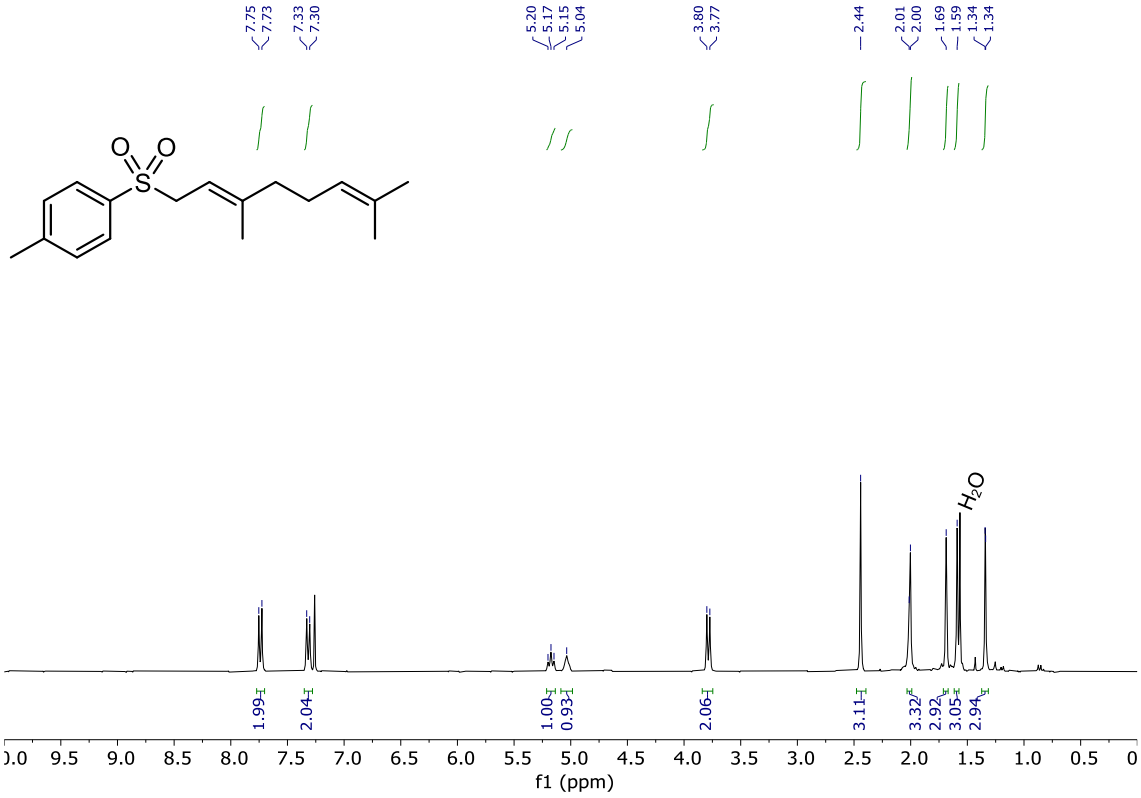

**1-Methyl-4-((3-methylbut-2-en-1-yl)sulfonyl)benzene (3q)**



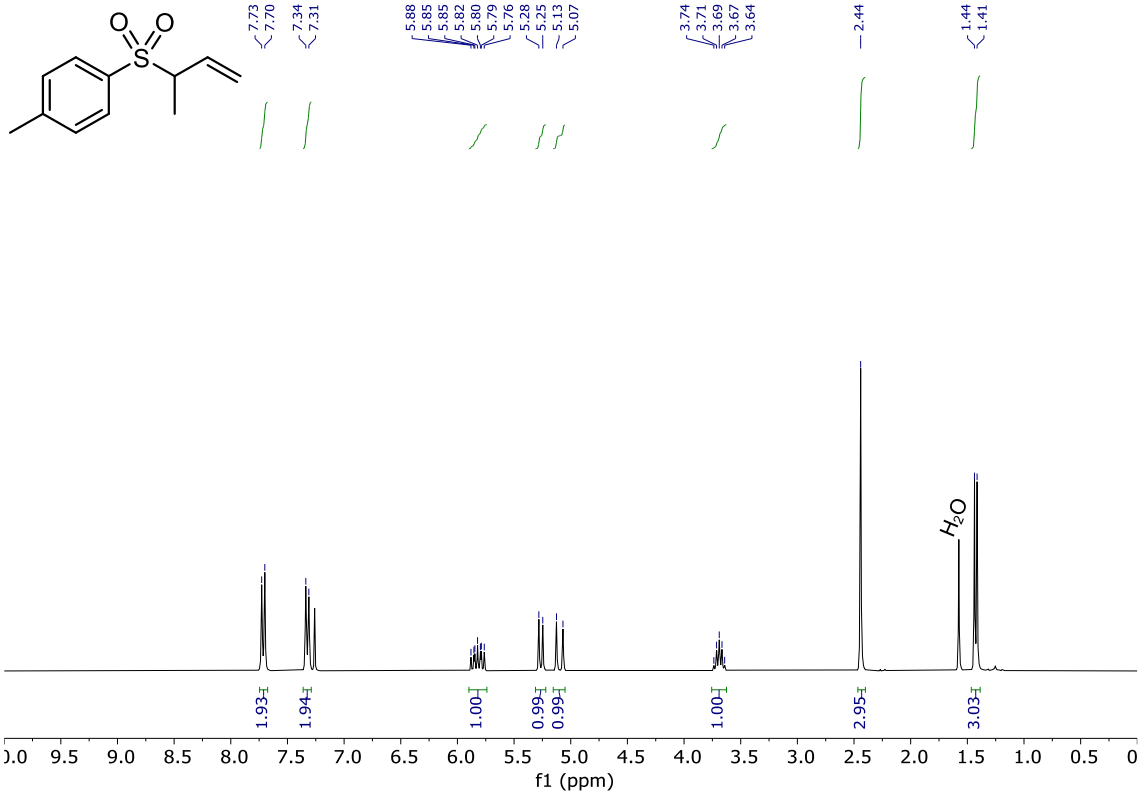
**(*E*)-1-((3-Cyclohexylallyl)sulfonyl)-4-methylbenzene (3r)**




**(*E*)-1-((3,7-Dimethylocta-2,6-dien-1-yl)sulfonyl)-4-methylbenzene (3s)**



**1-(But-3-en-2-ylsulfonyl)-4-methylbenzene (3t)**




**1-Methyl-4-((2-methylbut-3-en-2-yl)sulfonyl)benzene (3u)**