# Synthesis of *S*-Allylic Sulfinamides by the Catalytic Nucleophilic Allylation of *N*-Sulfinylamines

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# Supplementary Information

## 1. General Information

**Reagents and Solvents.** All commercially available reagents were used as received unless otherwise stated.

**Chromatography**. Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien 60F254 0.2 mm precoated plates. Compounds were visualized by exposure to UV light or by dipping the plates into solutions of potassium permanganate followed by gentle heating. Column chromatography was carried out using a Biotage Isolera 4 fitted with Agela Claricep silica gel disposable flash columns.

**Melting Points.** Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. The solvent of recrystallization is reported in parentheses.

**IR Spectra.** Infrared (IR) spectra were recorded on a Bruker platinum alpha FTIR spectrometer on the neat compound using the attenuated total refraction technique.

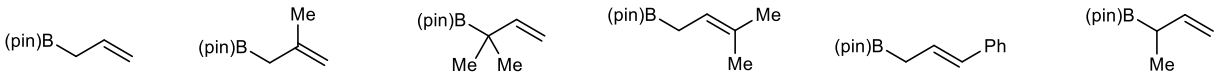
**NMR Spectra.** NMR spectra were acquired on Bruker Ascend 400 or Ascend 500 spectrometers. $^{1}H$ and $^{13}C$ NMR spectra were referenced to external tetramethylsilane via the residual protonated solvent ($^{1}H$) or the solvent itself ($^{13}C$). $^{19}F$ NMR spectra were referenced through the solvent lock ($^{2}H$) signal according to the IUPAC-recommended secondary referencing method following Bruker protocols. All chemical shifts are reported in parts per million (ppm). For $CDCl_3$, the shifts are referenced to 7.26 ppm for $^{1}H$ NMR spectroscopy and 77.16 ppm for $^{13}C$ NMR spectroscopy. $^{13}C$ NMR Assignments were made using the DEPT sequence with secondary pulses at 90° and 135° or using 2D NMR spectroscopy techniques including HSQC and HMBC. Coupling constants (*J*) are quoted to the nearest 0.1 Hz.

**Mass Spectra.** High-resolution mass spectra were recorded using electrospray ionization (ESI) and electron ionization (EI) techniques.

**X-ray Crystallography.** Single crystal X-ray diffraction data for compound **3af** were collected on an Oxford Diffraction GV1000 instrument, (AtlasS2 CCD area detector, mirror-monochromated Cu-Kα radiation source; λ = 1.54184 Å, ω scans). Single crystals were selected, mounted using Fomblin® (YR-1800 perfluoropolyether oil) on a polymer-tipped MiTeGen MicroMount™, and cooled rapidly to 120 K in a stream of cold $N_2$ using an Oxford Cryosystems open flow cryostat.[1] Cell parameters were refined from the observed positions of all strong reflections and absorption corrections were applied using a Gaussian numerical method with beam profile correction (CrysAlisPro).[2] Structures were solved within Olex2[3] by dual space iterative methods (SHELXT)[4] and all non-hydrogen atoms refined by full-matrix least-squares on all unique F2 values with anisotropic displacement parameters

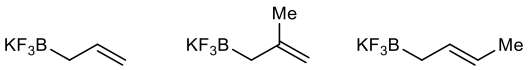
(SHELXL).[5] Hydrogen atoms were refined both freely and with constrained riding geometries and thermal parameters linked to Uiso of their parent atoms. The structure was checked with checkCIF (http://checkcif.iucr.org). CCDC 2475361 contains the data for compound **3af**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## 2. Synthesis of Allylboron Compounds




**2a** **2b** **2c** **2d** **2e** ***rac*-2f**

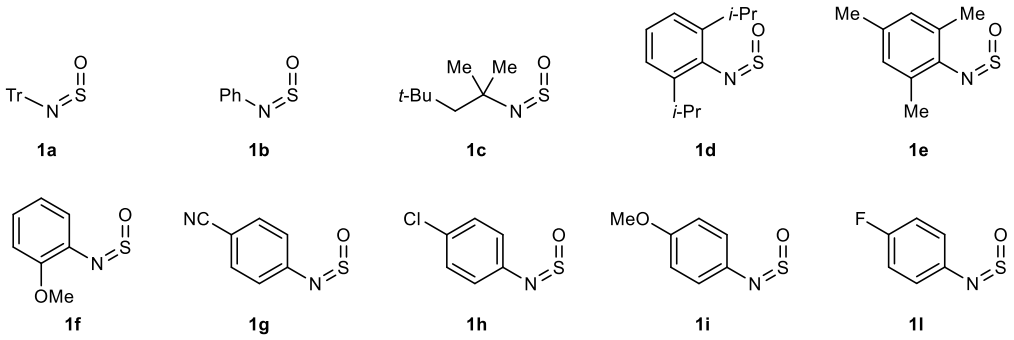
Allylboronate **2a** is commercially available. Allylboronates **2b**–**2d**,[6] **2e**,[7] and *rac*-**2f**[6] were prepared following previously reported procedures.




**8a** **8b** **8c**

Potassium allyltrifluoroborate (**8a**) is commercially available. Potassium allyltrifluoroborates **8a**[8] and **8c**[9] were prepared following previously reported procedures.

## 3. Synthesis of *N*-Sulfinylamines

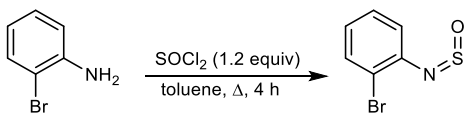



**1a** **1b** **1c** **1d** **1e**

**1f** **1g** **1h** **1i** **1l**

*N*-Sulfinylamine **1b** is commercially available. *N*-Sulfinylamines **1a**,[10] **1c**,[11] **1d**,[12] **1e**,[13] **1f**,[14] **1g**,[15] **1h**,[15] **1i**,[13] and **1l**[15] were prepared according to previously reported procedures.

### (2-Bromophenyl)imino)-λ⁴-sulfanone (1j)

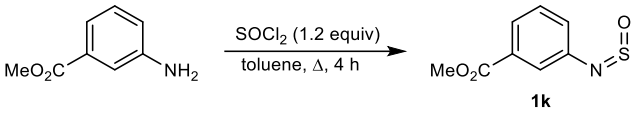



**1j**

To a solution of 2-bromoaniline (660 µL, 5.81 mmol) in toluene (10 mL) at 0 °C was added $SOCl_2$ (509 µL, 6.97 mmol). The mixture was heated to reflux for 4 h, cooled to room temperature, and concentrated *in vacuo*

to leave *N-sulfinylamine* **1j** (705 mg, 56%) as a dark green oil. IR 3062, 1579, 1460, 1437, 1300, 1168, 1019, 754, 656, 465 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.34 (1H, dd, *J* = 8.1, 1.6 Hz, Ar**H**), 7.69 (1H, dd, *J* = 8.1, 1.4 Hz, Ar**H**), 7.36 (1H, td, *J* = 7.7, 1.5 Hz, Ar**H**), 7.23 (1H, td, *J* = 7.7, 1.6 Hz, Ar**H**); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 141.0 (C), 133.7 (CH), 131.2 (CH), 128.6 (CH), 128.3 (CH), 120.4 (C); HRMS (EI) Exact mass calculated for $[C_6H_4NOSBr]^+$: 216.9192, found 216.9162.

### Methyl 3-[(oxo-λ⁴-sulfaneylidene)amino]benzoate (1k)

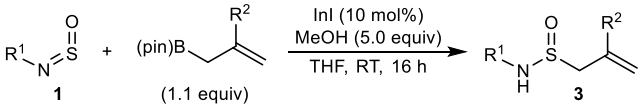



**1k**

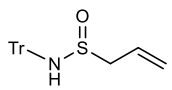
To a solution of methyl-3-aminobenzoate (1.20 g, 8.00 mmol) in toluene (10 mL) at 0 °C was added $SOCl_2$ (707 µL, 9.60 mmol). The mixture was heated to reflux for 4 h, cooled to room temperature, and concentrated *in vacuo* to leave *N-sulfinylamine* **1k** (1.53 g, 97%) as a brown solid. m.p. 105–108 °C ($Et_2O$); IR 2953, 1721, 1438, 1297, 1258, 1160, 1107, 914, 816, 680 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.39 (1H, t, *J* = 1.8 Hz, Ar**H**), 8.05 (2H, ddq, *J* = 7.9, 2.0, 1.2 Hz, Ar**H**), 7.50 (1H, t, *J* = 7.9 Hz, Ar**H**), 3.93 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 166.0 (C), 142.5 (C), 131.4 (CH), 131.2 (CH), 129.6 (C), 128.0 (CH), 120.0 (CH), 52.6 ($CH_3$).

## 4. Indium-Catalyzed Nucleophilic Allylation of *N*-Sulfinylamines

### General Procedure A

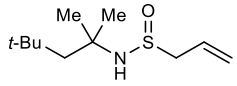



A solution of the *N*-sulfinylamine **1** (0.25 mmol) and InI (6.0 mg, 0.025 mmol in anhydrous THF (1 mL) was heated at 50 °C until the mixture became homogenous. The mixture was cooled to room temperature and the allylboronate **2** (0.275 mmol) was added, followed by MeOH (51.0 µL, 1.25 mmol). The reaction was stirred at room temperature for 16 h, concentrated *in vacuo,* and the residue was purified by column chromatography on silica gel (pentane to 40% EtOAc/pentane) to give the desired *S*-allylic sulfinamide **3**.

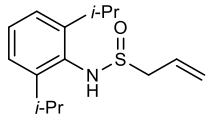



***N*-Tritylprop-2-ene-1-sulfinamide (3aa).** General Procedure A was followed using *N*-sulfinylamine **1a** (76 mg, 0.25 mmol) and allylboronate **2a** (51.6 µL, 0.275 mmol) to give *sulfinamide* **3aa** (63 mg, 73%) as a white solid. $R_f$ = 0.43 (40% EtOAc/pentane); m.p. 143–145 °C ($Et_2O$); IR 3146, 2923, 2853, 1597, 1490, 1200, 1160, 964, 934, 697 $cm^{-1}$; $^1H$ NMR (500

MHz, $CDCl_3$) δ 7.36–7.26 (15H, m, Ar**H**), 6.01 (1H, dddd, *J* = 17.1, 10.2, 9.1, 6.0 Hz, C**H**=$CH_2$), 5.50 (1H, dd, *J* = 10.1, 1.6 Hz, =C**H**$_a$H$_b$), 5.28 (1H, dd, *J* = 17.2, 1.4 Hz, =CH$_a$**H**$_b$), 5.02 (1H, s, N**H**), 3.52 (1H, app ddt, *J* = 12.6, 5.9, 1.1 Hz, SC**H**$_a$H$_b$), 2.99 (1H, dd, *J* = 12.7, 9.0 Hz, SCH$_a$**H**$_b$); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 145.0 (3 × C), 129.2 (6 × CH), 128.2 (6 × CH), 127.5 (3 × CH), 125.8 (CH), 124.3 ($CH_2$), 72.7 (C), 59.8 ($CH_2$); HRMS (ESI) Exact mass calculated for $[C_{22}H_{21}NOSNa]^+$ $[M+Na]^+$: 370.1236, found 370.1234.

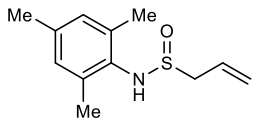



***N*-(2,4,4-Trimethylpentan-2-yl)prop-2-ene-1-sulfinamide (3ca).** General Procedure A was followed using *N*-sulfinylamine **1c** (46 mg, 0.25 mmol) and allylboronate **2a** (51.6 μL, 0.275 mmol) but with the following modification: After stirring for 16 h, saturated aqueous $NaHCO_3$ solution (10 mL) was added, and the mixture was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography on alumina (pentane to 40% EtOAc/pentane) gave *sulfinamide* **3ca** (25 mg, 46%) as a brown oil, $R_f$ = 0.45 (40% EtOAc/pentane); IR; 3197, 2952, 2924, 1673, 1509, 1367, 1045, 968, 923, 529 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.94 (1H, dddd, *J* = 17.2, 10.2, 8.8, 6.2 Hz, C**H**=$CH_2$), 5.50–5.45 (1H, m, =C**H**$_a$H$_b$), 5.33 (1H, dq, *J* = 17.1, 1.2 Hz, =CH$_a$**H**$_b$), 3.71 (1H, s, N**H**), 3.53 (1H, ddt, *J* = 12.7, 6.2, 1.2 Hz, SC**H**$_a$H$_b$), 3.25 (1H, dd, *J* = 12.7, 8.8 Hz, SCH$_a$**H**$_b$), 1.38 (3H, s, C**H**$_3$CNH), 1.37 (3H, s, C**H**$_3$CNH), 1.59 (1H, d, *J* = 14.9 Hz, *t*-BuC**H**$_a$H$_b$), 1.52 (1H, d, *J* = 14.9 Hz, *t*-BuC**H**$_a$H$_b$), 1.00 (9H, s, C(C**H**$_3$)$_3$); $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 126.0 (CH), 123.6 ($CH_2$), 60.0 ($CH_2$), 57.9 (C), 56.2 ($CH_2$), 32.4 ($CH_3$), 31.9 (3 × $CH_3$), 29.7 ($CH_3$), 25.0 (C); HRMS (ESI) Exact mass calculated for $[C_{11}H_{24}NOS]^+$ $[M+H]^+$: 218.1573, found 218.1572.

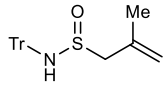



***N*-(2,6-Diisopropylphenyl)prop-2-ene-1-sulfinamide (3da).** General Procedure A was followed using *N*-sulfinylamine **1d** (56 mg, 0.25 mmol) and allylboronate **2a** (51.6 μL, 0.275 mmol) to give *sulfinamide* **3da** (45 mg, 68%) as a white solid. $R_f$ = 0.45 (40% EtOAc/pentane); m.p. 114–117 °C ($Et_2O$); IR 3172, 2963, 2866, 1443, 1332, 990, 930, 749, 641, 421 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.22–7.19 (1H, m, Ar**H**), 7.15–7.14 (2H, m, Ar**H**), 6.16 (1H, dddd, *J* = 17.2, 10.2, 8.9, 6.1 Hz, C**H**=$CH_2$), 5.63–5.61 (2H, m, =C**H**$_a$H$_b$ and N**H**), 5.52 (1H, dd, *J* = 17.1, 1.3 Hz, =CH$_a$**H**$_b$), 3.81 (1H, dd, *J* = 12.5, 12.4 Hz, SC**H**$_a$H$_b$), 3.58 (1H, dd, *J* = 12.8, 9.0 Hz, SCH$_a$**H**$_b$), 3.33 (2H, hept, *J* = 6.9 Hz, 2 × C**H**(CH$_3$)$_2$), 1.23 (6H, d, *J* = 6.8 Hz, CH(C**H**$_3$)$_2$), 1.20 (6H, d, *J* = 6.9 Hz, CH(C**H**$_3$)$_2$); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 145.1 (2 × C), 134.0 (C), 127.1 (CH), 125.4 (CH), 124.4 ($CH_2$), 123.9 (2 × CH), 59.8 ($CH_2$), 28.2 (CH), 24.1 (CH), 23.8

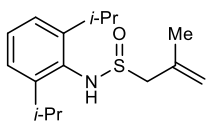
(4 × $CH_3$); HRMS (ESI) Exact mass calculated for $[C_{15}H_{24}NOS]^+$ $[M+H]^+$: 266.1573, found 266.1570.



***N*-Mesitylprop-2-ene-1-sulfinamide (3ea).** General Procedure A was followed using *N*-sulfinylamine **1e** (45 mg, 0.25 mmol) and allylboronate **2a** (51.6 μL, 0.275 mmol) but with the following modification: After stirring for 16 h, saturated aqueous $NaHCO_3$ solution (10 mL) was added, and the mixture was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography on alumina (pentane to 40% EtOAc/pentane) gave *sulfinamide* **3ea** (35 mg, 63%) as a yellow solid. $R_f$ = 0.40 (40% EtOAc/pentane); m.p. 139–142 °C ($Et_2O$); IR 3173, 2917, 1638, 1480, 1148, 1039, 848, 638. 560, 446 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.86 (2H, s, Ar**H**), 6.12 (1H, dddd, *J* = 17.3, 10.3, 8.9, 6.1 Hz, C**H**=$CH_2$), 5.60–5.57 (1H, m, =C**H**$_a$H$_b$), 5.52–5.47 (1H, m, =CH$_a$**H**$_b$), 5.46 (1H, br s, N**H**), 3.76 (1H, ddt, *J* = 12.8, 6.1, 1.2 Hz, SC**H**$_a$H$_b$), 3.55 (1H, dd, *J* = 12.8, 8.9 Hz, SCH$_a$**H**$_b$), 2.28 (6H, s, 2 × ArC**H**$_3$), 2.24 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (100.6 MHz $CDCl_3$) δ 135.8 (C), 134.4 (C), 133.7 (C), 129.6 (2 × CH), 125.4 (CH), 124.4 ($CH_2$), 59.7 ($CH_2$), 20.9 ($CH_3$), 19.1 (2 × $CH_3$); HRMS (ESI) Exact mass calculated for $[C_{12}H_{17}NOSNa]^+$ $[M+Na]^+$: 246.0923, found 246.0923.

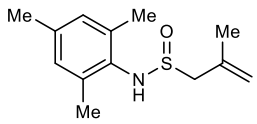


**2-Methyl-*N*-tritylprop-2-ene-1-sulfinamide (3ab).** General Procedure A was followed using *N*-sulfinylamine **1a** (76 mg, 0.25 mmol) and allylboronate **2b** (50.0 mg, 0.275 mmol) to give *sulfinamide* **3ab** (51 mg, 56%) as a white solid. $R_f$ = 0.33 (40% EtOAc/pentane); m.p. 134–138 °C ($Et_2O$); IR 3170, 1492, 1429, 1034, 1009, 914, 755, 698, 566, 434 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.36–7.27 (15H, m, Ar**H**), 5.11 (1H, t, *J* = 1.6 Hz, =C**H**$_a$H$_b$), 5.03 (1H, s, N**H**), 4.87 (1H, s, =CH$_a$**H**$_b$), 3.39 (1H, dd, *J* = 12.4, 0.9 Hz, SC**H**$_a$H$_b$), 3.17 (1H, dd, *J* = 12.4, 0.8 Hz, SCH$_a$**H**$_b$), 1.86 (3H, s, C**H**$_3$); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 145.1 (3 × C), 136.3 (C), 129.2 (6 × CH), 128.2 (6 × CH), 127.5 (3 × CH), 118.4 ($CH_2$), 72.8 (C), 65.0 ($CH_2$), 23.9 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{23}H_{23}NOSNa]^+$ $[M+Na]^+$: 384.1393 found 384.1386.

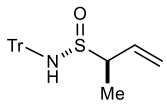


***N*-(2,6-Diisopropylphenyl)-2-methylprop-2-ene-1-sulfinamide (3db).** General Procedure A was followed using *N*-sulfinylamine **1d** (56 mg, 0.25 mmol) and allylboronate **2b** (50.1 mg, 0.275 mmol) to give *sulfinamide* **3db** (44 mg, 63%) as a white solid. $R_f$ = 0.36 (40% EtOAc/pentane); m.p. 122–125 °C ($Et_2O$); IR 3178, 2963, 2496, 1460, 1444, 1380, 1057, 896, 749, 428 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.22–7.19 (1H, m, Ar**H**), 7.15–

7.13 (2H, m, Ar**H**), 5.62 (1H, s, N**H**), 5.25 (1H, t, *J* = 1.5 Hz, =C**H**$_a$H$_b$), 5.10 (1H, dt, *J* = 1.8, 1.0 Hz, =CH$_a$**H**$_b$), 3.73 (1H, dd, *J* = 12.5, 0.9 Hz, SC**H**$_a$H$_b$), 3.60 (1H, dd, *J* = 12.5, 0.8 Hz, SCH$_a$**H**$_b$), 3.35 (2H, hept, *J* = 6.8 Hz, 2 × C**H**(CH$_3$)$_2$), 1.57 (s, 3H, CH$_2$CC**H**$_3$), 1.22 (6H, d, *J* = 6.7 Hz, CH(C**H**$_3$)$_2$), 1.21 (6H, d, *J* = 6.8 Hz, CH(C**H**$_3$)$_2$); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 145.2 (C), 135.7 (C), 134.1 (C), 127.2 (2 × C), 123.9 (2 × CH), 118.8 (CH$_2$), 64.9 (CH$_2$), 28.2 (2 × CH), 24.2 (2 × CH$_3$), 24.0 (CH$_3$), 23.8 (2 × CH$_3$); HRMS (ESI) Exact mass calculated for [C$_{16}$H$_{26}$NOS]$^+$ [M+H]$^+$: 280.1730, found 280.1733.

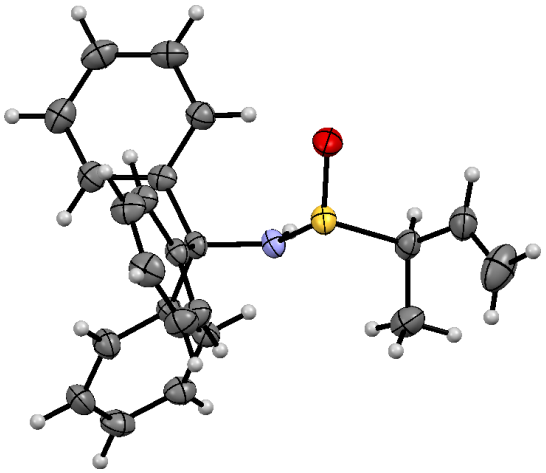


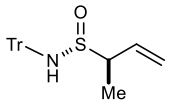

***N*-Mesityl-2-methylprop-2-ene-1-sulfinamide (3eb).** General Procedure A was followed using *N*-sulfinylamine **3e** (45 mg, 0.25 mmol) and allylboronate **2b** (50.1 mg, 0.275 mmol) to give *sulfinamide* **3eb** (35 mg, 59%) as a white solid. R$_f$ = 0.41 (40% EtOAc/pentane); m.p. 123–127 °C (Et$_2$O); IR 3168, 2916, 1476, 1148, 1045, 896, 727, 638, 564, 501 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 6.89 (2H s, Ar**H**), 5.52 (1H, s, N**H**), 5.26 (1H, t, *J* = 1.6 Hz, =C**H**$_a$H$_b$), 5.13–4.92 (1H, m, =CH$_a$**H**$_b$), 3.71 (1H, dd, *J* = 12.6, 0.8 Hz, SC**H**$_a$H$_b$), 3.58 (1H, dd, *J* = 12.6, 0.8 Hz, SCH$_a$**H**$_b$), 2.31 (6H, s, 2 × ArC**H**$_3$), 2.27 (3H, s, ArC**H**$_3$), 2.05 (3H, d, *J* = 1.2 Hz, CH$_2$CC**H**$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 135.8 (C), 135.6 (C), 134.5 (2 × C), 129.6 (C and 2 × CH), 118.9 (CH$_2$), 64.5 (CH$_2$), 24.1 (CH$_3$), 20.8 (CH$_3$), 18.1 (2 × CH$_3$); HRMS (ESI) Exact mass calculated for [C$_{13}$H$_{20}$NOS] [M+H]$^+$: 238.1260, found 238.1260.




**(±)-(*R*,2*R*)-*N*-Tritylbut-3-ene-2-sulfinamide (3af).** General Procedure A was followed using *N*-sulfinylamine **1a** (76 mg, 0.25 mmol) and allylboronate *rac*-**2f** (54.6 mg, 0.275 mmol) but with the following modification: After stirring for 16 h, saturated aqueous NaHCO$_3$ solution (10 mL) was added, and the mixture was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layers were dried (MgSO$_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography on alumina (pentane to 40% EtOAc/pentane) gave *sulfinamide* **3af** (40 mg, 44%) as a white solid. R$_f$ = 0.40 (40% EtOAc/pentane); m.p. 142–145 °C (Et$_2$O); IR 3169, 2977, 1596, 1491, 1370, 1155, 1060, 1030, 955, 696 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36–7.27 (15H, m, Ar**H**), 5.86 (1H, dt, *J* = 17.2, 9.9 Hz, C**H**=CH$_2$), 5.45 (1H, dd, *J* = 10.2, 1.7 Hz, =C**H**$_a$H$_b$), 5.18 (1H, ddd, *J* = 17.2, 1.7, 0.7 Hz, =CH$_a$**H**$_b$), 4.96 (1H, s, N**H**), 2.73 (1H, dq, *J* = 9.6, 7.0 Hz, CH$_3$C**H**), 1.31 (3H, d, *J* = 6.9 Hz, C**H**$_3$); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 145.3 (3 × C), 132.3 (CH), 129.2 (6 × CH), 128.2 (6 × CH), 127.5 (3 × CH), 122.1 (CH$_2$), 72.5 (C), 62.7 (CH), 15.8 (CH$_3$); HRMS (ESI) mass calculated for [C$_{23}$H$_{23}$NOSNa]$^+$ [M+Na]$^+$: 384.1393, found 384.1382.

Slow diffusion of MeOH into a solution of **3af** in CDCl$_3$ gave crystals suitable for X-ray crystallography:

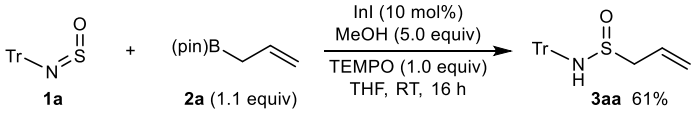





**3af**
CCDC 2475361

ORTEP with ellipsoid probabilities at 50%

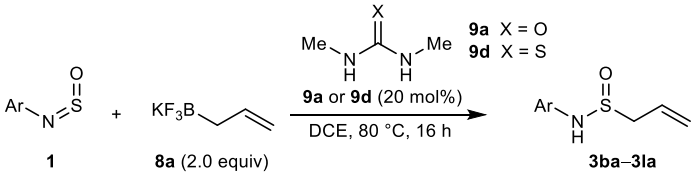
## 5. Reaction of 1a and 2a in the Presence of the Radical Scavenger TEMPO



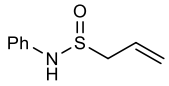

A solution of the *N*-sulfinylamine (46 mg, 0.15 mmol) and InI (3.6 mg, 0.015 mmol) in anhydrous THF (0.5 mL) was heated at 50 °C until the mixture became homogenous. The mixture was cooled to room temperature and the allylboronate **2a** (31.0 µL, 0.165 mmol) was added, followed by MeOH (30.3 µL, 0.750 mmol), and TEMPO (23 mg, 0.15 mmol). The reaction was stirred at room temperature for 16 h, concentrated *in vacuo,* and the residue was purified by column chromatography on silica gel (pentane to 40% EtOAc/pentane) to give the desired *S*-allylic sulfinamide **3aa** as a white solid (32 mg, 61%). For the spectroscopic characterization data of **3aa**, see section 4 above.

## 6. (Thio)urea-Catalyzed Nucleophilic Allylation of *N*-Sulfinylamines

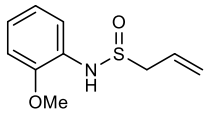
### General Procedure B



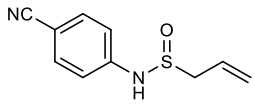

A solution of the *N*-sulfinylamine **1** (0.25 mmol), potassium allyltrifluoroborate (**4a**, 74 mg, 0.50 mmol), and **9a** or **9d** (0.05 mmol) in DCE (1 mL) was heated at reflux for 16 h. The reaction was cooled to room temperature, filtered through a plug of silica using EtOAc as eluent, and concentrated *in vacuo*. Purification of the residue by column chromatography (cyclohexane to 60% EtOAc/cyclohexane) gave the desired *S*-allylic sulfinamide **3**.



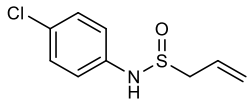
***N*-Phenylprop-2-ene-1-sulfinamide (3ba).** General Procedure B was followed using *N*-sulfinylamine **1b** (28.1 μL, 0.25 mmol) and *N,N′*-dimethylurea (**9a**, 4.4 mg, 0.05 mmol) to give sulfinamide **3ba** (30 mg, 66%) as a yellow oil. $R_f$ = 0.27 (40% EtOAc/pentane); IR 3162, 2959, 1637, 1600, 1496, 1177, 1053, 930, 884, 692 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.32–7.14 (2H, m, Ar**H**), 7.14–6.89 (3H, m, Ar**H**), 6.46 (1H, s, N**H**), 6.02–5.91 (1H, m, C**H**=$CH_2$), 5.53 (1H, dt, *J* = 10.3, 1.6 Hz, =C**H**$_a$H$_b$), 5.44 (1H, dt, *J* = 17.1, 1.3 Hz, =CH$_a$**H**$_b$), 3.92–3.60 (1H, m, SC**H**$_a$H$_b$), 3.57 (1H, dd, *J* = 12.9, 8.5 Hz, SCH$_a$**H**$_b$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 140.8 (C), 129.7 (2 × CH), 125.3 (CH), 124.6 ($CH_2$), 123.7 (CH), 119.1 (2 × CH), 59.2 ($CH_2$); HRMS (ESI) Exact mass calculated for $[C_9H_{11}NOSNa]^+$ $[M+Na]^+$: 204.0454, found 204.0449. The spectroscopic data are consistent with those reported previously.[16]



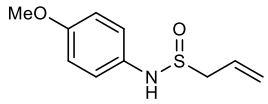
***N*-(2-Methoxyphenyl)prop-2-ene-1-sulfinamide (3fa).** General Procedure B was followed using *N*-sulfinylamine **1f** (42 mg, 0.25 mmol) and *N,N′*-dimethylurea (**9a**, 4.4 mg, 0.05 mmol) to give *sulfinamide* **3fa** (37 mg, 70%) as a brown oil. $R_f$ = 0.33 (40% EtOAc/pentane); IR 3204, 2923, 1597, 1501, 1464, 1290, 1250, 1060, 1026, 745 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.23 (1H, dd, *J* = 7.7, 1.7 Hz, Ar**H**), 6.98 (1H, td, *J* = 7.7, 1.7 Hz, Ar**H**), 6.91 (1H, td, *J* = 7.7, 1.5 Hz, Ar**H**), 6.86 (1H, dd, *J* = 8.0, 1.5 Hz, Ar**H**), 6.51 (1H, s, N**H**), 6.00 (1H, dddd, *J* = 16.8, 10.2, 8.6, 6.4 Hz, C**H**=$CH_2$), 5.55 (1H, dd, *J* = 10.2, 1.4 Hz, =C**H**$_a$H$_b$), 5.46 (1H, dq, *J* = 17.2, 1.4 Hz, =CH$_a$**H**$_b$), 3.85 (3H, s, OC**H**$_3$), 3.77 (1H, dd, *J* = 12.9, 6.4 Hz, SC**H**$_a$H$_b$), 3.55 (1H, dd, *J* = 12.9, 8.6 Hz, SCH$_a$**H**$_b$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 149.0 (C), 130.5 (C), 125.3 (CH), 124.4 ($CH_2$), 123.3 (CH), 121.3 (CH), 117.5 (CH), 111.0 (CH), 59.3 ($CH_2$), 55.9 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{10}H_{13}NOSNa]^+$ $[M+Na]^+$: 234.0559, found 234.0559.



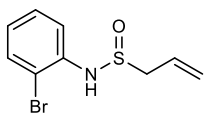
***N*-(4-Cyanophenyl)prop-2-ene-1-sulfinamide (3ga).** General Procedure B was followed using *N*-sulfinylamine **1g** (41 mg, 0.25 mmol) and *N,N′*-dimethylurea (**9a**, 4.4 mg, 0.05 mmol) to give *sulfinamide* **3ga** (33 mg, 64%) as a yellow oil. $R_f$ = 0.31 (40% EtOAc/pentane); IR 3367, 3230, 2924, 2212, 1627, 1604, 1515, 1316, 1173, 830, 545 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.55 (2H, d, *J* = 8.7 Hz, Ar**H**), 7.17–6.89 (2H, m, Ar**H**), 6.82 (1H, s, N**H**), 5.96 (1H, dddd, *J* = 16.8, 10.2, 8.5, 6.4 Hz, C**H**=$CH_2$), 5.59 (1H, dd, *J* = 10.2, 1.2 Hz, =C**H**$_a$H$_b$), 5.48 (1H, dq, *J* = 17.2, 1.3 Hz, =C**H**$_a$H$_b$), 3.83 (1H, ddt, *J* = 13.0, 6.4, 1.0 Hz, SC**H**$_a$H$_b$), 3.60 (1H, dd, *J* = 13.0, 8.5 Hz, SCH$_a$**H**$_b$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 145.5 (C), 133.9 (CH), 125.4 ($CH_2$), 124.6 (CH), 118.9 (C), 117.6 (2 × CH), 106.1 (C), 59.3 ($CH_2$); HRMS (ESI) Exact mass calculated for $[C_{10}H_{11}NOS]^+$ $[M+H]^+$: 207.0587, found 207.0581.



***N*-(4-Chlorophenyl)prop-2-ene-1-sulfinamide (3ha).** General Procedure B was followed using *N*-sulfinylamine **1h** (43 mg, 0.25 mmol) and *N,N′*-dimethyurea (**9a**, 4.4 mg, 0.05 mmol) to give *sulfinamide* **3ha** (26 mg, 48%) as a yellow oil. $R_f$ = 0.22 (40% EtOAc/pentane); IR 3126, 3044, 1636, 1594, 1490, 1271, 1052, 1037, 931, 512 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.23–7.19 (2H, m, Ar**H**), 6.97–6.93 (2H, m, Ar**H**), 6.22 (1H, s, N**H**), 5.95 (1H, dddd, *J* = 16.8, 10.2, 8.4, 6.4 Hz, C**H**=$CH_2$), 5.53 (1H, dd, *J* = 10.2, 1.4 Hz, =C**H**$_a$H$_b$), 5.44 (1H, dd, *J* = 17.2, 1.3 Hz, =CH$_a$**H**$_b$), 3.71 (1H, ddt, *J* = 13.0, 6.3, 1.1 Hz, SC**H**$_a$H$_b$), 3.57 (1H, dd, *J* = 13.0, 8.5 Hz, SCH$_a$**H**$_b$); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ 139.6 (C), 129.6 (2 × CH), 128.8 (C), 125.2 (CH), 124.7 ($CH_2$), 120.2 (2 × CH), 59.2 ($CH_2$); HRMS (ESI) Exact mass calculated for $[C_9H_{10}ClNOSNa]^+$ $[M+Na]^+$: 238.0064, found 238.0064.

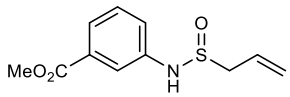


***N*-(4-Methoxyphenyl)prop-2-ene-1-sulfinamide (3ia).** General Procedure B was followed using *N*-sulfinylamine **1i** (42 mg, 0.25 mmol) and *N,N′*-dimethyurea (**9a**, 4.4 mg, 0.05 mmol) but with a slight modification in that DCE (2 mL) was used (instead of 1 mL) to give *sulfinamide* **3ia** (20.4 mg, 38%) as a brown oil. $R_f$ = 0.36 (40% EtOAc/pentane); IR 3146, 2923, 1514, 1461, 1231, 1185, 1034, 923, 726, 524 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.04–7.00 (2H, m, Ar**H**), 6.84–6.80 (2H, m, Ar**H**), 6.03–5.92 (2H, N**H** and C**H**=$CH_2$), 5.52 (1H, ddt, *J* = 10.2, 1.4, 0.7 Hz, =C**H**$_a$H$_b$), 5.43 (1H, dq, *J* = 17.1, 1.3 Hz, =CH$_a$**H**$_b$), 3.77 (3H, s, OC**H**$_3$), 3.76–3.71 (1H, m, SC**H**$_a$H$_b$), 3.52 (1H, ddt, *J* = 13.0, 8.5, 0.9 Hz, SCH$_a$**H**$_b$); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ 157.1 (C), 133.1 (C), 125.4 (CH), 124.4 ($CH_2$), 123.2 (2 × CH), 114.9 (2 × CH), 59.0 ($CH_2$), 55.7 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{10}H_{14}NOS]^+$ $[M+H]^+$: 212.0740, found 212.0745.

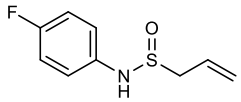


***N*-(2-Bromophenyl)prop-2-ene-1-sulfinamide (3ja).** General Procedure B was followed using *N*-sulfinylamine **1j** (55 mg, 0.25 mmol) and *N,N′*-dimethylthiourea (**9b**, 5.2 mg, 0.05 mmol) but with a slight modification in that DCE (1.25 mL) was used (instead of 1 mL) to give sulfinamide **3ja** (38 mg, 58%) as an orange oil. $R_f$ = 0.51 (40% EtOAc/pentane); IR 3194, 2923, 1619, 1587, 1478, 1292, 1060, 1024, 931, 745 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.51 (1H, dd, *J* = 8.0, 1.5 Hz, Ar**H**), 7.35 (1H, dd, *J* = 8.1, 1.6 Hz, Ar**H**), 7.29–7.26 (1H, m, Ar**H**), 6.90 (1H, ddd, *J* = 8.0, 7.3, 1.6 Hz, Ar**H**), 6.66 (1H, s, N**H**), 6.09 (1H, dddd, *J* = 17.2, 10.2, 9.0, 6.0 Hz, C**H**=$CH_2$) 5.69–5.61 (1H, m, =C**H**$_a$H$_b$), 5.55 (1H, dq, *J* = 17.2, 1.3 Hz, =CH$_a$**H**$_b$) 3.94–3.69 (1H, m, SC**H**$_a$H$_b$), 3.55 (1H, dd, *J* = 13.0, 9.0 Hz, SCH$_a$**H**$_b$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 139.0 (C), 133.1 (CH), 128.8 (CH), 125.5 ($CH_2$), 124.6 (CH), 124.1 (CH), 118.0 (CH), 113.6 (C),

59.0 ($CH_2$); HRMS (ESI) Exact mass calculated for $[C_9H_{10}BrNOSNa]^+$ $[M+Na]^+$: 281.9559, found 281.9559.

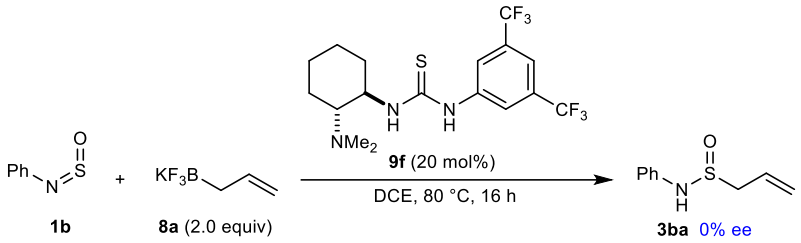


**Methyl 3-[(allylsulfinyl)amino]benzoate (3ka).** General Procedure B was followed using *N*-sulfinylamine **1k** (49 mg, 0.25 mmol), allyl trifluoroborate and *N,N′*-dimethylthiourea (**9b**, 4.4 mg, 0.05 mmol) in DCE (1 mL) to give sulfinamide **3ka** (36 mg, 60%) as a colorless oil. $R_f$ = 0.37 (40% EtOAc/pentane); IR 3155, 1721, 1589, 1471, 1294, 1220, 1054, 1000, 754, 690 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.80–7.57 (2H, m, Ar**H**), 7.33 (1H, tt, *J* = 7.8, 1.5 Hz, Ar**H**), 7.24–7.17 (1H, m, Ar**H**), 6.45 (1H, s, N**H**), 6.10–5.86 (1H, m, C**H**=$CH_2$), 5.62–5.53 (1H, m, =C**H**$_a$H$_b$), 5.47 (1H, dq, *J* = 17.1, 1.2 Hz, =CH$_a$**H**$_b$), 3.90 (3**H**, s, $CH_3$), 3.87–3.72 (1H, m, SC**H**$_a$H$_b$), 3.59 (1H, ddt, *J* = 12.9, 8.6, 0.8 Hz, SCH$_a$**H**$_b$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 166.6 (C), 141.4 (C), 131.6 (CH), 129.7 (C), 125.1 (CH), 124.8 ($CH_2$), 124.6 (CH), 122.9 (CH), 119.6 (CH), 59.3 ($CH_2$), 52.4 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{11}H_{13}NOSNa]^+$ $[M+Na]^+$: 262.0508, found 262.0502.



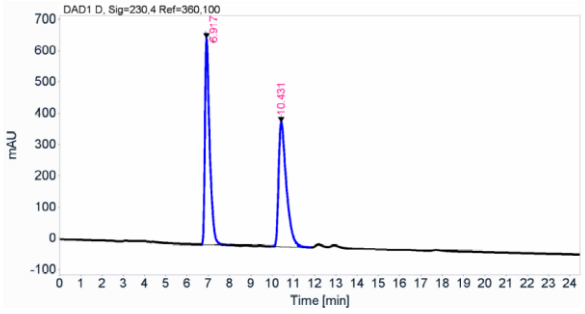
***N*-(4-Fluorophenyl)prop-2-ene-1-sulfinamide (3la).** General Procedure B was followed using *N*-sulfinylamine **1l** (39 mg, 0.25 mmol), allyl trifluoroborate (74 mg, 0.50 mmol), and *N,N′*-dimethylthiourea (**9b**, 4.4 mg, 0.05 mmol) in DCE (1 mL) to give sulfinamide **3la** (22 mg, 44%) as an orange oil. $R_f$ = 0.23 (40% EtOAc/pentane); IR 3167, 1637, 1585, 1506, 1211, 1053, 896, 830, 505 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.04–6.95 (4H, m, Ar**H**), 6.16 (1H, br s, N**H**), 5.98 (1H, dddd, *J* = 16.9, 10.2, 8.5, 6.4 Hz, C**H**=$CH_2$), 5.57–5.52 (1H, m, =C**H**$_a$H$_b$), 5.45 (1H, dd, *J* = 17.1, 1.3 Hz, =CH$_a$**H**$_b$), 3.76 (1H, dddd, *J* = 13.0, 6.4, 1.4, 0.7 Hz, SC**H**$_a$H$_b$), 3.54 (1H, ddt, *J* = 12.9, 8.5, 0.8 Hz, SCH$_a$**H**$_b$); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 159.7 (C, d, *J* = 243.0 Hz), 136.6 (C, d, *J* = 2.8 Hz), 125.2 (CH), 124.7 ($CH_2$), 121.8 (2 × CH, d, *J* = 8.0 Hz), 116.4 (2 × CH, d, *J* = 22.7 Hz), 59.2 ($CH_2$); $^{19}F$ NMR (376 MHz, $CDCl_3$) δ –119.2; HRMS (ESI) Exact mass calculated for $[C_9H_{10}FNOSNa]^+$ $[M+Na]^+$: 222.0359, found 222.0351.

## 7. Chiral Thiourea-Catalyzed Nucleophilic Allylation of *N*-Sulfinylamine 1b




The reaction of *N*-sulfinylamine **1b** with potassium allyltrifluoroborate (**8a**) in the presence of chiral thiourea **9f** (20 mol%) gave **3ba** in good conversion (>90%) but with 0% ee. Enantiomeric excess was determined by HPLC using a Chiralcel OD-H column (90:10 isohexane:*i*-PrOH, 1.0 mL/min, 230 nm, 25 °C); $t_r$ (one enantiomer) = 7.0 min, $t_r$ (opposite enantiomer) = 10.5 min, 0% ee.

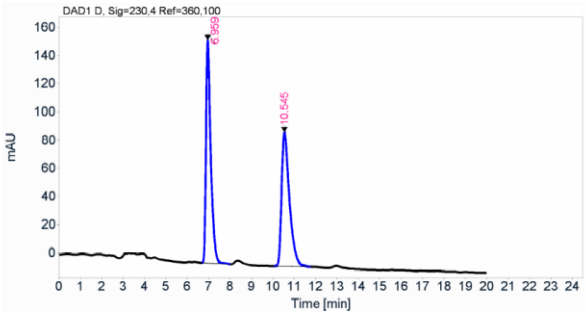
Using *N*,*N*-dimethylurea (**9a**)




Signal: DAD1 D, Sig=230,4 Ref=360,100

| RT [min] | Type | Width [min] | Area | Height | Area% |
|---|---|---|---|---|---|
| 6.917 | BB | 0.2258 | 10125.975 | 657.1190 | 50.23 |
| 10.431 | BV | 0.3770 | 10034.843 | 396.8622 | 49.77 |

Using chiral thiourea **9f**

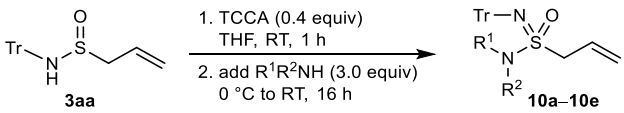



Signal: DAD1 D, Sig=230,4 Ref=360,100

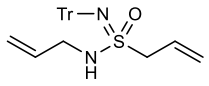
| RT [min] | Type | Width [min] | Area | Height | Area% |
|---|---|---|---|---|---|
| 6.959 | BB | 0.2282 | 2439.614 | 157.9732 | 50.12 |
| 10.545 | BB | 0.3799 | 2428.053 | 95.0804 | 49.88 |

## 8. Further Manipulations

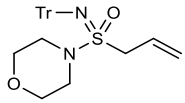
### General Procedure C: Preparation of Sulfonimidamides from *S*-Allylic Sulfinamide 3aa



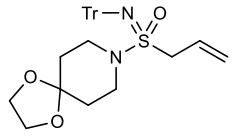

To a solution of *S*-allylic sulfinamide **3aa** (50 mg, 0.14 mmol) in THF (0.5 mL) at room temperature was added trichloroisocyanuric acid (TCCA) (13 mg, 0.056 mmol) and the resulting mixture was stirred at room temperature for 1 h. The mixture was cooled to 0 °C and the appropriate amine (0.42 mmol) was added. The mixture was warmed to room temperature and stirred for 16 h. The reaction was diluted with $H_2O$ (1 mL) and extracted with EtOAc (2 × 5 mL). The combined organic layers were dried ($Na_2SO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (pentane to 60% EtOAc/pentane) gave the desired sulfonimidamide **10**.



***N*-Allyl-*N'*-tritylprop-2-ene-1-sulfonimidamide (10a).** General Procedure C was followed using allylamine (32.4 uL, 0.43 mmol) to give *sulfonimidamide* **10a** (46 mg, 79%) as a white solid. $R_f$ = 0.50 (30% EtOAc/pentane); m.p. 109–112 °C ($Et_2O$); IR 2923, 1641, 1164, 1082, 922, 772, 701, 636, 580 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.58–7.45 (6H, m, Ar**H**), 7.30–7.22 (6H, m, Ar**H**), 7.23–7.16 (3H, m, Ar**H**), 6.13 (1H, ddt, *J* = 17.3, 10.2, 7.3 Hz, C**H**=$CH_2$), 5.55–5.24 (3H, m, C**H**=$CH_2$ and =C$\mathbf{H}_2$), 5.30 (1H, s, N**H**), 5.01–4.84 (2H, m, =C$\mathbf{H}_2$), 3.88 (1H, dd, *J* = 13.6, 7.0 Hz, SC$\mathbf{H}_a$$H_b$), 3.79 (1H, dd, *J* = 13.6, 7.5 Hz, SC$H_a$$\mathbf{H}_b$), 3.24–3.11 (2H, m, NC$\mathbf{H}_2$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 148.2 (3 × C), 134.3 (CH), 129.0 (6 × CH), 127.9 (CH), 127.6 (6 × CH), 126.5 (3 × CH), 122.9 ($CH_2$), 116.8 ($CH_2$), 71.6 (C), 62.2 ($CH_2$), 46.7 ($CH_2$); HRMS (ESI) Exact mass calculated for $[C_{25}H_{26}N_2NaOS]^+$ $[M+Na]^+$: 425.1658, found 425.1651.

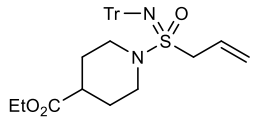


**4-(*N*-Tritylallylsulfonimidoyl)morpholine (10b).** General Procedure C was followed using morpholine (37.8 uL, 0.43 mmol) to give *sulfonimidamide* **10b** (40 mg, 64%) as a white solid. $R_f$ = 0.46 (30% EtOAc/pentane); m.p. 150–152 °C ($Et_2O$); IR 2920, 1490, 1158, 1142, 1066, 929, 751, 700, 635, 510 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (6H, m, Ar**H**), 7.28–7.24 (6H, m, Ar**H**), 7.22–7.18 (3H, m, Ar**H**), 6.17 (1H, ddt, *J* = 17.4, 10.3, 7.3 Hz, $CH_2$C**H**=), 5.51–5.45 (2H, m, =C$\mathbf{H}_2$), 3.93 (1H, ddt, *J* = 13.5, 7.1, 1.1 Hz, SC$\mathbf{H}_a$$H_b$), 3.73 (1H, dd, *J* = 13.3, 7.4, 1.1 Hz, SC$H_a$$\mathbf{H}_b$), 3.20 (2H, ddd, *J* = 11.2, 6.3, 3.0 Hz, OC$\mathbf{H}_2$), 3.07 (2H, ddd, *J* = 11.1, 6.1, 3.0 Hz, OC$\mathbf{H}_2$), 2.98 (2H, dd, *J* = 12.1, 6.2, 3.0 Hz, NC$\mathbf{H}_2$), 2.91 (2H, ddd, *J* = 11.9, 6.3, 3.1 Hz, NC$\mathbf{H}_2$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 148.1 (3 × C), 129.2 (6 × C), 127.4 (6 × C), 126.4 (3 × CH), 123.2 ($CH_2$), 71.6 (C), 66.3 (2 × $CH_2$), 57.4 ($CH_2$), 46.5 ($CH_2$); HRMS (ESI) Exact mass calculated for $[C_{26}H_{28}N_2NaO_2S]^+$ $[M–H]^+$: 455.1764, found 455.1767.

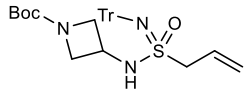


**8-(*N*-Tritylallylsulfonimidoyl)-1,4-dioxa-8-azaspiro[4.5]decane (10c).** General Procedure C was followed using 8-aza-1,4-dioxaspiro[4.5]decane (55.3 uL, 0.43 mmol) to give *sulfonimidamide* **10c** (51 mg, 74%) as a yellow oil. $R_f$ = 0.55 (30% EtOAc/pentane); m.p. 126–129 °C ($Et_2O$); IR 2962, 2874, 1312, 12745, 1179, 1143, 1043, 751, 703 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.51–7.50 (6H, m, Ar**H**), 7.28–7.24 (6H, m, Ar**H**), 7.22–7.19 (3H, m, Ar**H**), 6.17 (1H, ddt, *J* = 17.3, 10.2, 7.3 Hz, $CH_2$C**H**=), 5.49–5.44 (2H, m, =C$\mathbf{H}_2$), 3.92 (1H, ddt, *J* = 13.5, 7.2, 1.1 Hz, SC$\mathbf{H}_a$$H_b$), 3.87 (4H, s, 2 × OC$\mathbf{H}_2$), 3.69 (1H, ddt, *J* = 13.5, 7.5, 1.1 Hz, SC$H_a$$\mathbf{H}_b$), 3.13–3.03 (4H, m, 2 × NC), 1.27 (2H, dddd, *J* = 11.5, 7.4, 4.2, 1.5 Hz, NC$\mathbf{H}_2$), 1.18–1.04 (2H, m, NC$\mathbf{H}_2$); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 148.2 (3 × C), 129.3 (6 × CH), 127.4 (7 × CH), 126.3 (3 × CH), 123.0 ($CH_2$), 106.7 (C), 71.6 (C), 64.4 (2 × $CH_2$), 57.8 ($CH_2$), 44.4 (2 × $CH_2$),

34.3 (2 × $CH_2$); HRMS (ESI) Exact mass calculated for $[C_{29}H_{32}N_2NaO_3S]^+$ $[M+Na]^+$: 511.2026, found 511.2029.

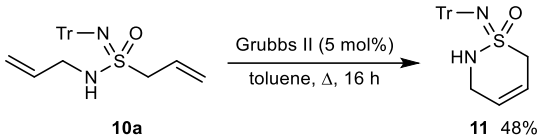


**Ethyl 1-(*N*-tritylallylsulfonimidoyl)piperidine-4-carboxylate (10d).** General Procedure C was followed using ethyl piperidine-4-carboxylated (66.5 uL) to give *sulfonimidamide* **10d** (30 mg, 42%) as a yellow oil. $R_f$ = 0.45 (30% EtOAc/pentane); IR 2979, 1727, 1491, 1446, 1281, 1206, 1179, 1143, 1035, 772, 702 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.60–7.42 (6H, m, Ar**H**), 7.33–7.24 (6H, m, Ar**H**), 7.21–7.17 (3H, m, Ar**H**), 6.14 (1H, ddt, *J* = 17.3, 10.2, 7.3 Hz, $CH_2C\mathbf{H}$=), 5.47–5.41 (2H, m, =C$\mathbf{H}_2$), 4.11 (2H, q, *J* = 7.1 Hz, OC$\mathbf{H}_2$), 3.91 (1H, ddt, *J* = 13.5, 6.9, 1.1 Hz, SC$\mathbf{H}_a$H$_b$), 3.71 (1H, ddt, *J* = 13.5, 7.6, 1.1 Hz, SCH$_a$$\mathbf{H}_b$), 3.47 (2H, dt, *J* = 12.1, 4.0 Hz, NC$\mathbf{H}_2$), 2.46 (1H, ddd, *J* = 12.3, 11.0, 2.9 Hz, C**H**C=O), 2.32 (1H, ddd, *J* = 12.5, 11.0, 2.8 Hz, NC$\mathbf{H}_a$H$_b$), 2.06 (1H, tt, *J* = 10.9, 3.8 Hz, NCH$_a$$\mathbf{H}_b$), 1.60–1.43 (2H, m, $NCH_2C\mathbf{H}_2$), 1.32–1.26 (1H, m, $NCH_2C\mathbf{H}_a$ 1.25 (3H, t, *J* = 7.1 Hz, $CH_2C\mathbf{H}_3$), 1.08–0.92 (1H, m, $NCH_2CH_a$); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 174.5 (C), 148.1 (3 × C), 129.3 (6 × CH), 127.5 (CH), 127.4 (6 × CH), 126.3 (3 × CH), 122.9 ($CH_2$), 71.6 (C), 60.5 ($CH_2$), 58.6 ($CH_2$), 45.6 ($CH_2$), 45.1 ($CH_2$), 40.5 (CH), 27.8 ($CH_2$), 27.5 ($CH_2$), 14.3 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{30}H_{34}N_2NaO_3S]^+$ $[M+Na]^+$: 525.2182, found 525.2180.



***tert*-Butyl [1-(*N*-tritylallylsulfonimidoyl)azetidin-3-yl]carbamate (10e).** General Procedure C was followed using 3-(Boc-amino)azetidine (74 mg, 0.43 mmol) to give *sulfonimidamide* **10e** (56 mg, 75%) as a white crystalline solid. $R_f$ = 0.42 (30% EtOAc/pentane); m.p. 160–162 °C ($Et_2O$); IR 2978, 1716, 1446, 1294, 1157, 1031, 909, 752, 729, 660 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.54–7.51 (6H, m, Ar**H**), 7.30–7.26 (6H, m, Ar**H**), 7.24–7.20 (3H, m, Ar**H**), 5.98 (1H, ddt, *J* = 17.3, 10.2, 7.3 Hz, $CH_2C\mathbf{H}$=), 5.42–5.05 (2H, m, =C$\mathbf{H}_2$), 4.49–4.47 (1H, br m, C**H**N or N**H**), 4.08 (1H, br s, C**H**N or N**H**), 3.83 (1H, t, *J* = 7.7 Hz, C$\mathbf{H}_2$N), 3.77–3.74 (1H, m, C$\mathbf{H}_2$N), 3.62 (1H, ddt, *J* = 13.6, 7.3, 1.1 Hz, SC$\mathbf{H}_a$H$_b$), 3.51 (1H, dd, *J* = 14.2, 7.1 Hz, SCH$_a$$\mathbf{H}_b$), 3.29 (2H, ddd, *J* = 12.0, 7.9, 5.8 Hz, C$\mathbf{H}_2$N), 1.44 (9H, s, C(C$\mathbf{H}_3$)$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 154.8 (C), 148.4 (3 × C), 129.3 (6 × CH), 127.8 (CH), 127.6 (6 × CH), 126.5 (3 × CH), 122.5 ($CH_2$), 80.1 (C), 71.6 (C), 59.4 ($CH_2$), 58.72 ($CH_2$), 58.65 ($CH_2$), 38.7 (CH), 28.5 (3 × $CH_3$); HRMS (ESI) Exact mass calculated for $[C_{30}H_{35}N_3NaO_3S]^+$ $[M+H]^+$: 540.2291, found 516.2280.

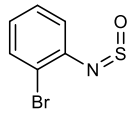
**1-(Tritylimino)-1,2,3,6-tetrahydro-1λ$^6$,2-thiazine 1-oxide (11)**



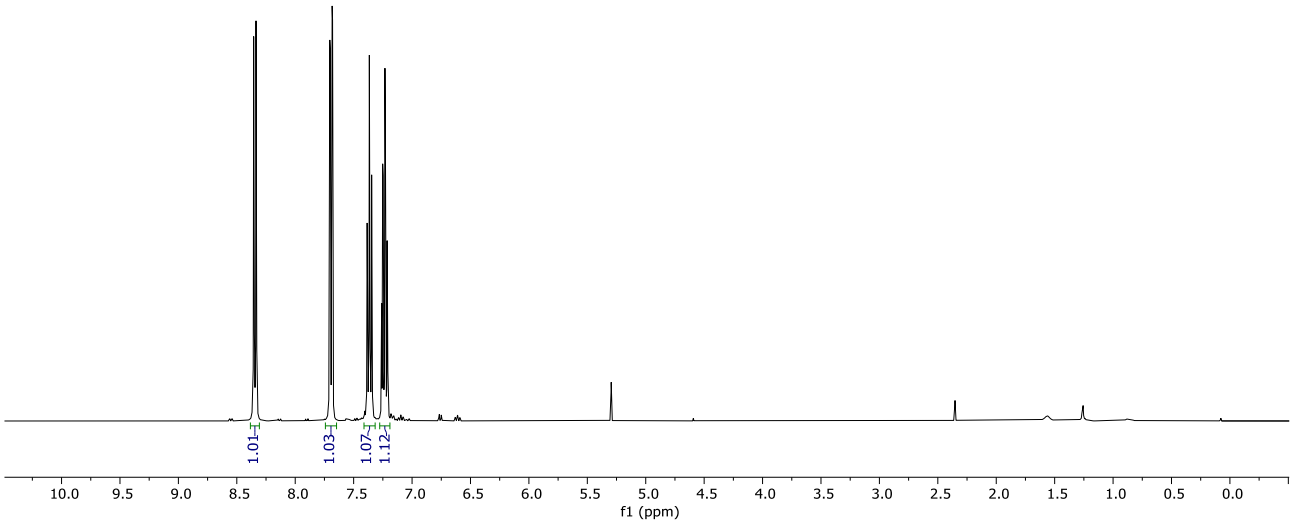

**10a** **11** 48%

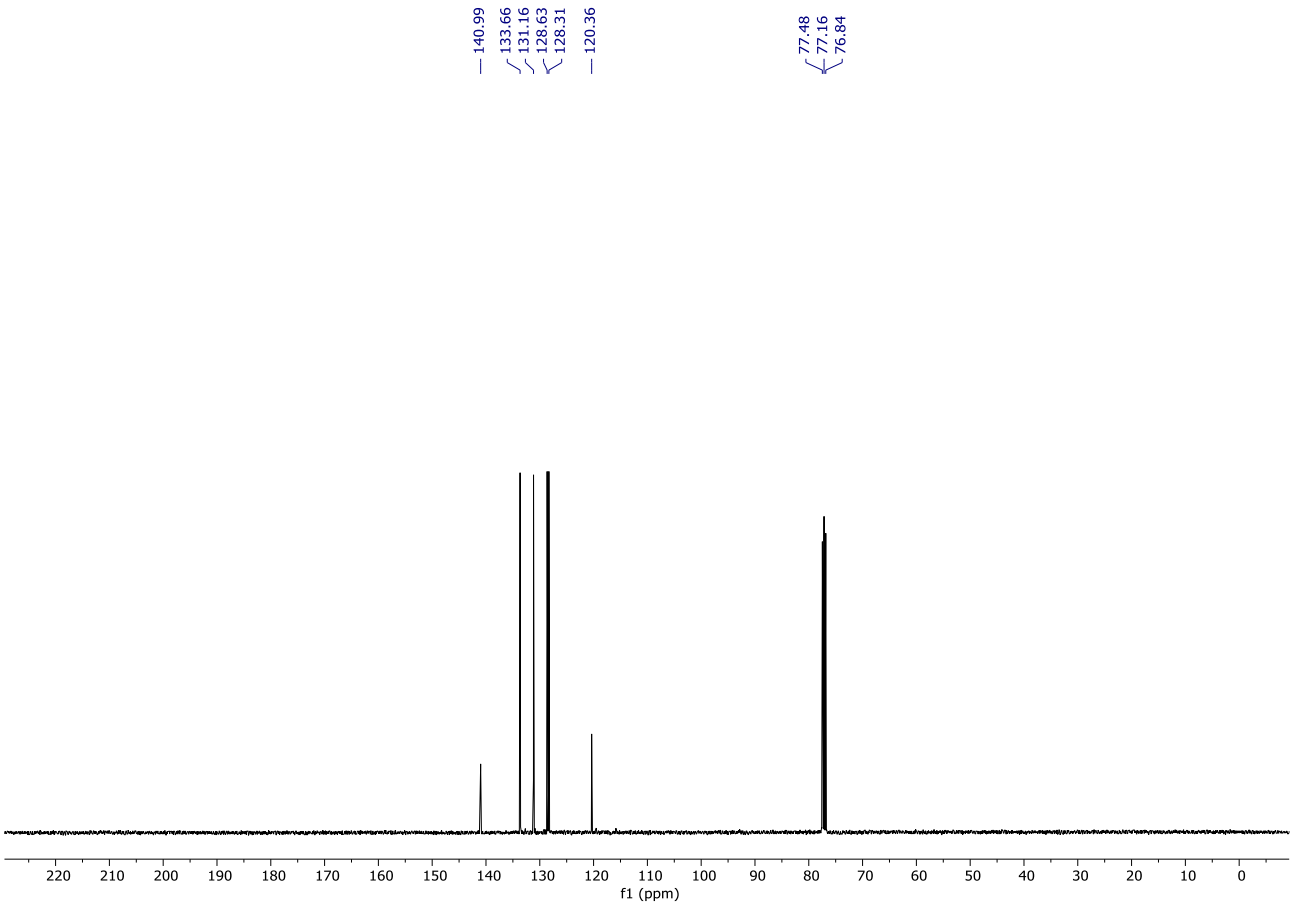
To a solution of sulfonimidamide **10a** (50.0 mg, 0.12 mmol) in degassed toluene (12.4 mL) was added Grubbs second generation catalyst (5.3 mg, 0.06 mmol) in one portion and the reaction was heated at reflux for 16 h. The reaction was cooled to room temperature, filtered through a pad of celite using EtOAc as eluent, and concentrated *in vacuo*. Purification of the residue by column chromatography (pentane to 40% EtOAc/pentane) gave the *cyclic sulfonimidamide* as a yellow oil (22 mg, 48%). $R_f$ = 0.18 (30% EtOAc/pentane); IR 1594, 1489, 1446, 1376, 1295, 1186, 748, 703, 641, 518 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.57–7.55 (6H, m, Ar**H**), 7.28–7.25 (6H, m, Ar**H**), 7.22–7.18 (3H, m, Ar**H**), 5.75–5.70 (1H, m, =C**H**), 5.69–5.63 (1H, m, =C**H**), 3.66–3.59 (1H, m, SC**H**$_a$H$_b$), 3.53–3.50 2H, m, NC**H**$_2$), 3.49–3.43 (1H, m, SCH$_a$**H**$_b$), 3.30 (1H, br s, N**H**); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.9 (3 × C), 129.1 (6 × CH), 127.6 (6 × CH), 126.6 (3 × CH), 125.3 (CH), 120.5 (CH), 71.8 (C), 53.3 ($CH_2$), 46.1 ($CH_2$); HRMS (ESI) Exact mass calculated for $[C_{23}H_{22}N_2OSNa]^+$ $[M+Na]^+$: 397.1345, found 397.1345.

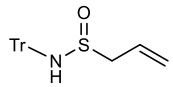
## 9. NMR Spectra



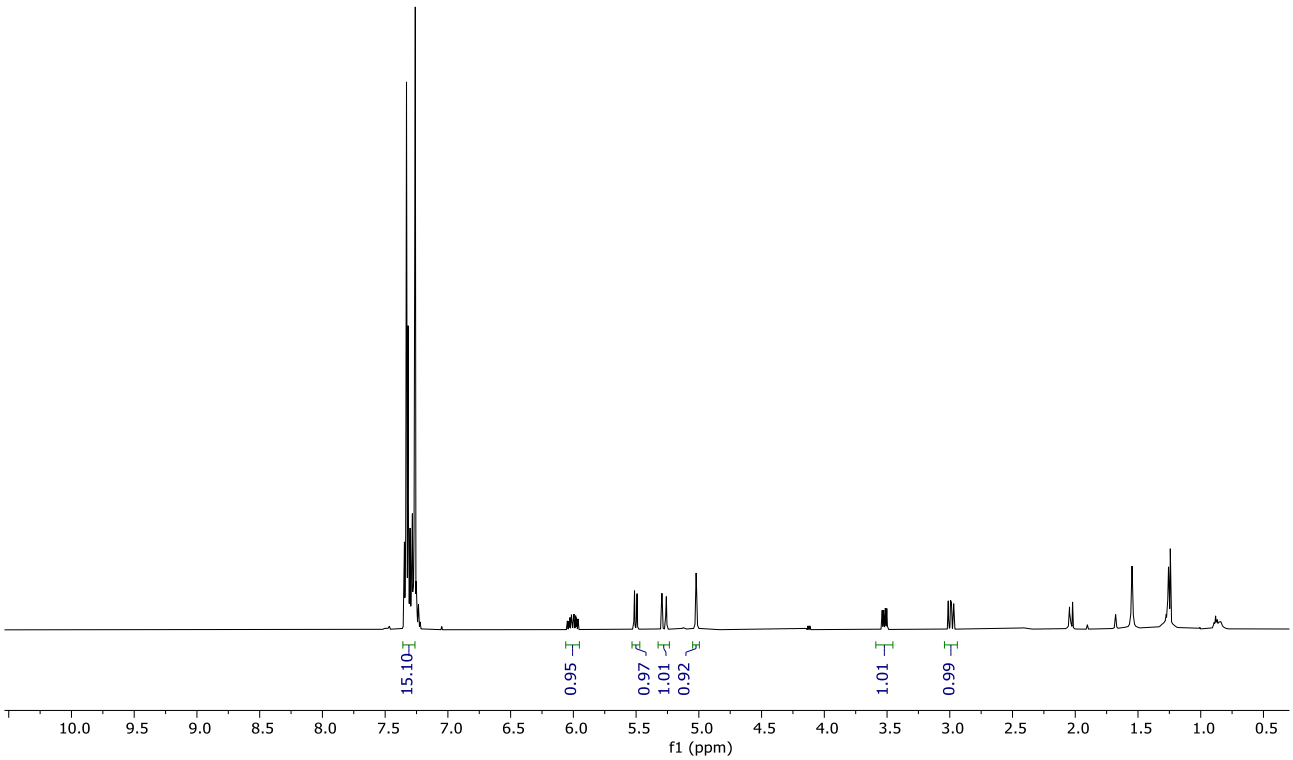

**1j**

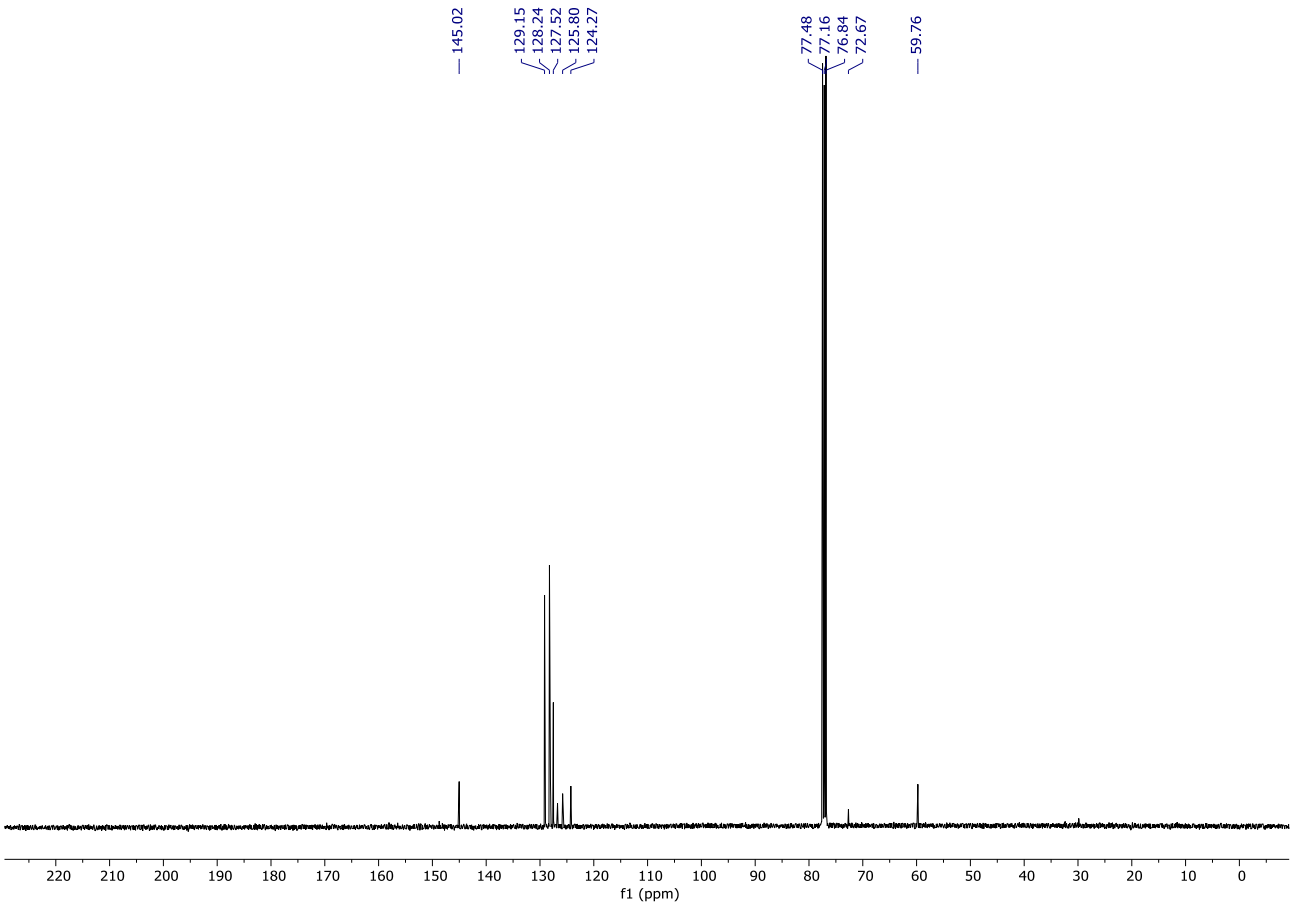


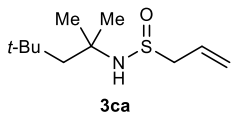




O
Tr
N
H
S

**3aa**

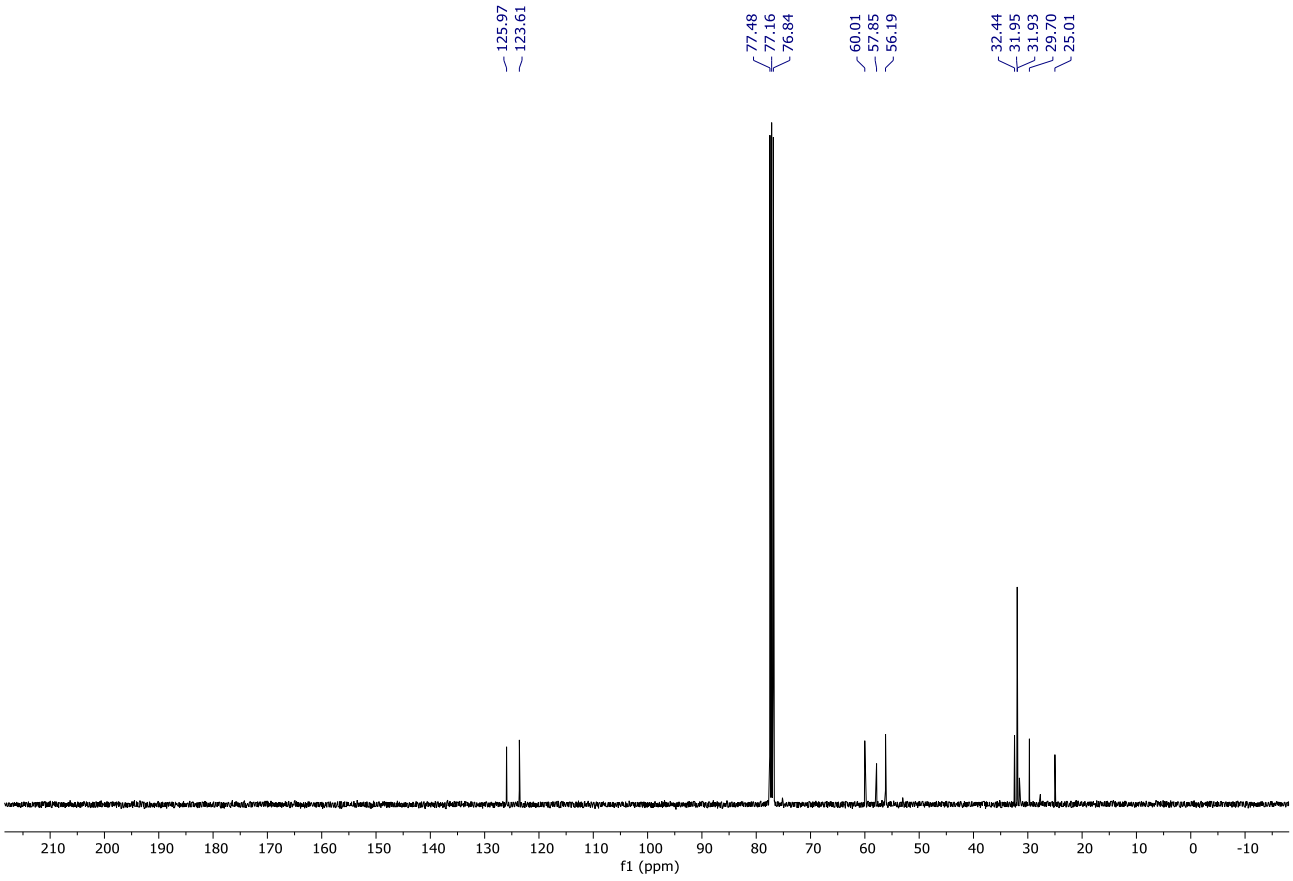

15.10
0.95
0.97
1.01
0.92
1.01
0.99
f1 (ppm)

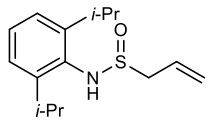

145.02
129.15
128.24
127.52
125.80
124.27
77.48
77.16
76.84
72.67
59.76
f1 (ppm)


Me
Me
O
t-Bu
S
N
H

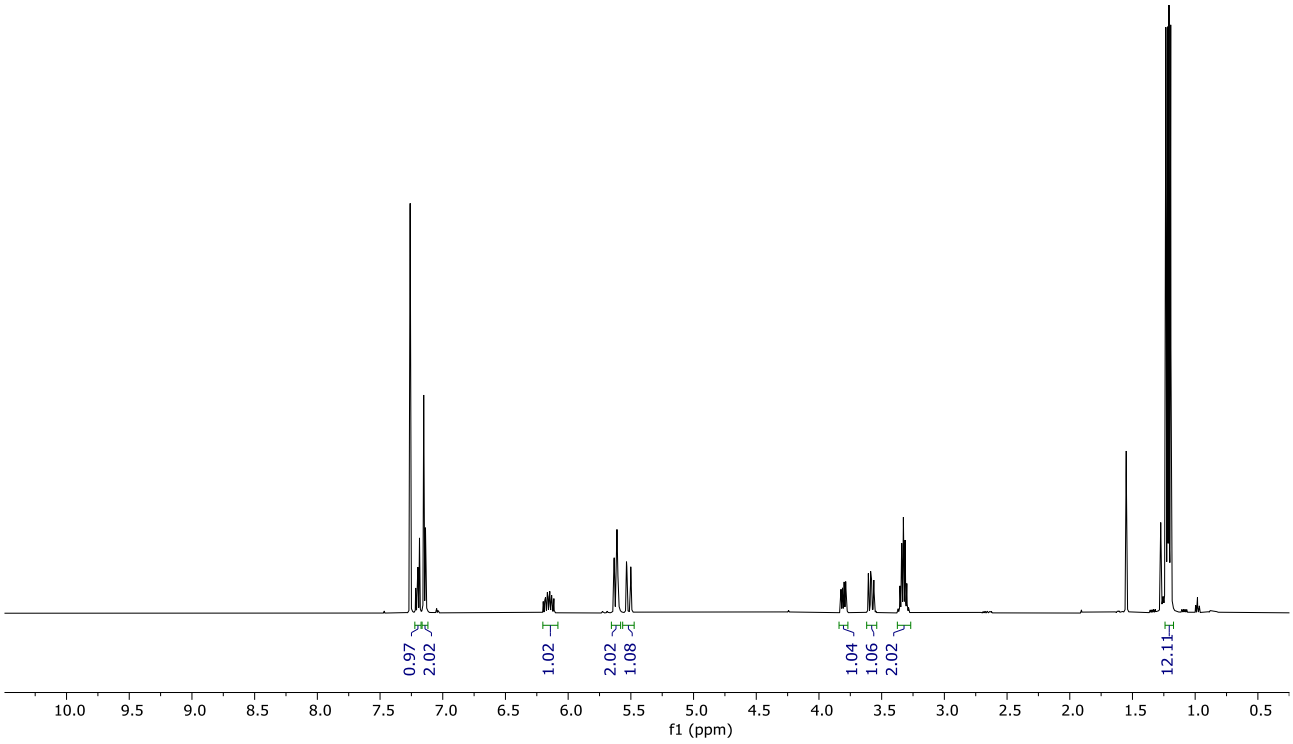
**3ca**

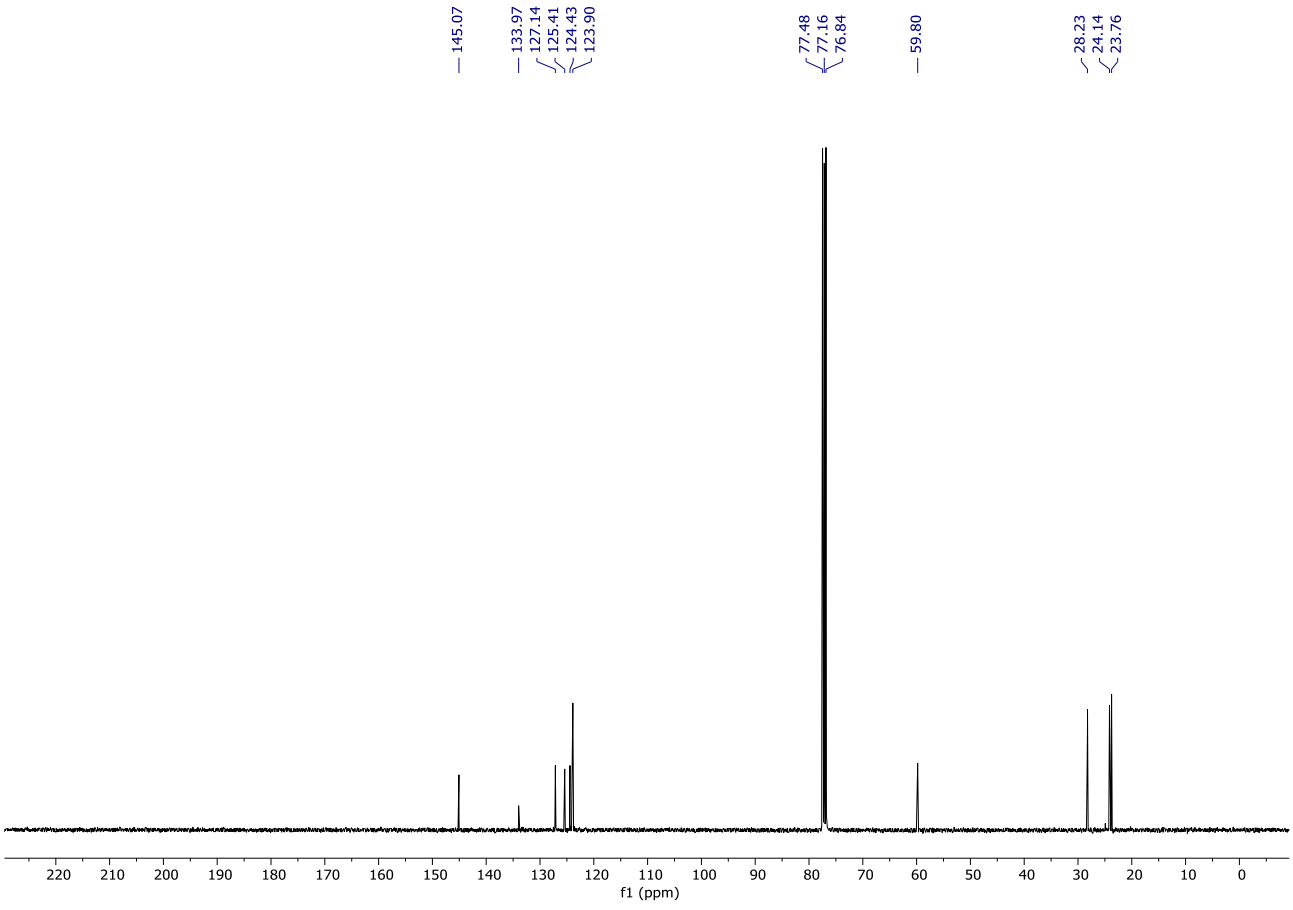

1.00
0.99
1.12
0.91
0.97
0.97
1.20
1.69
5.68
8.81
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

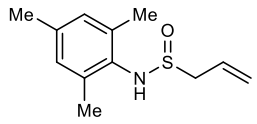

125.97
123.61
77.48
77.16
76.84
60.01
57.85
56.19
32.44
31.95
31.93
29.70
25.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


i-Pr
O
S
N
H
i-Pr

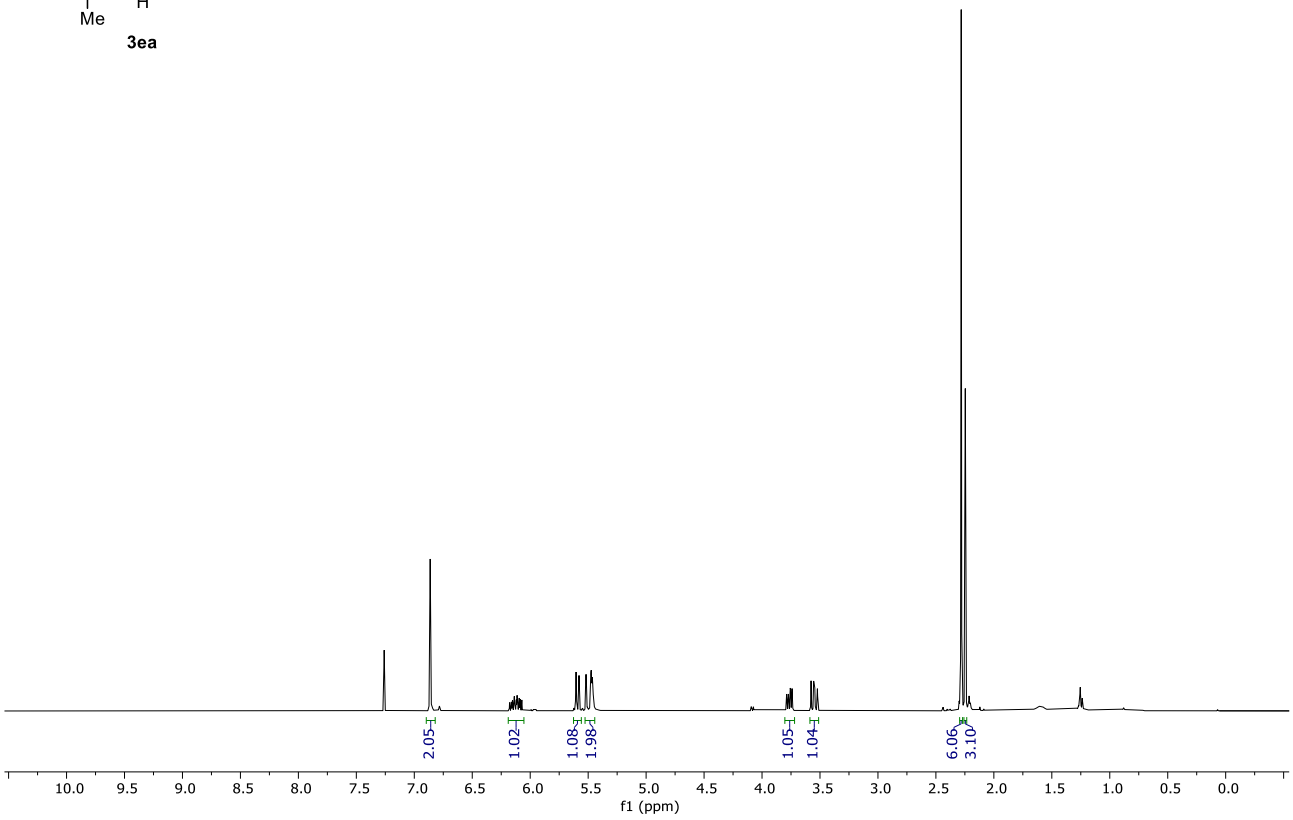
**3da**

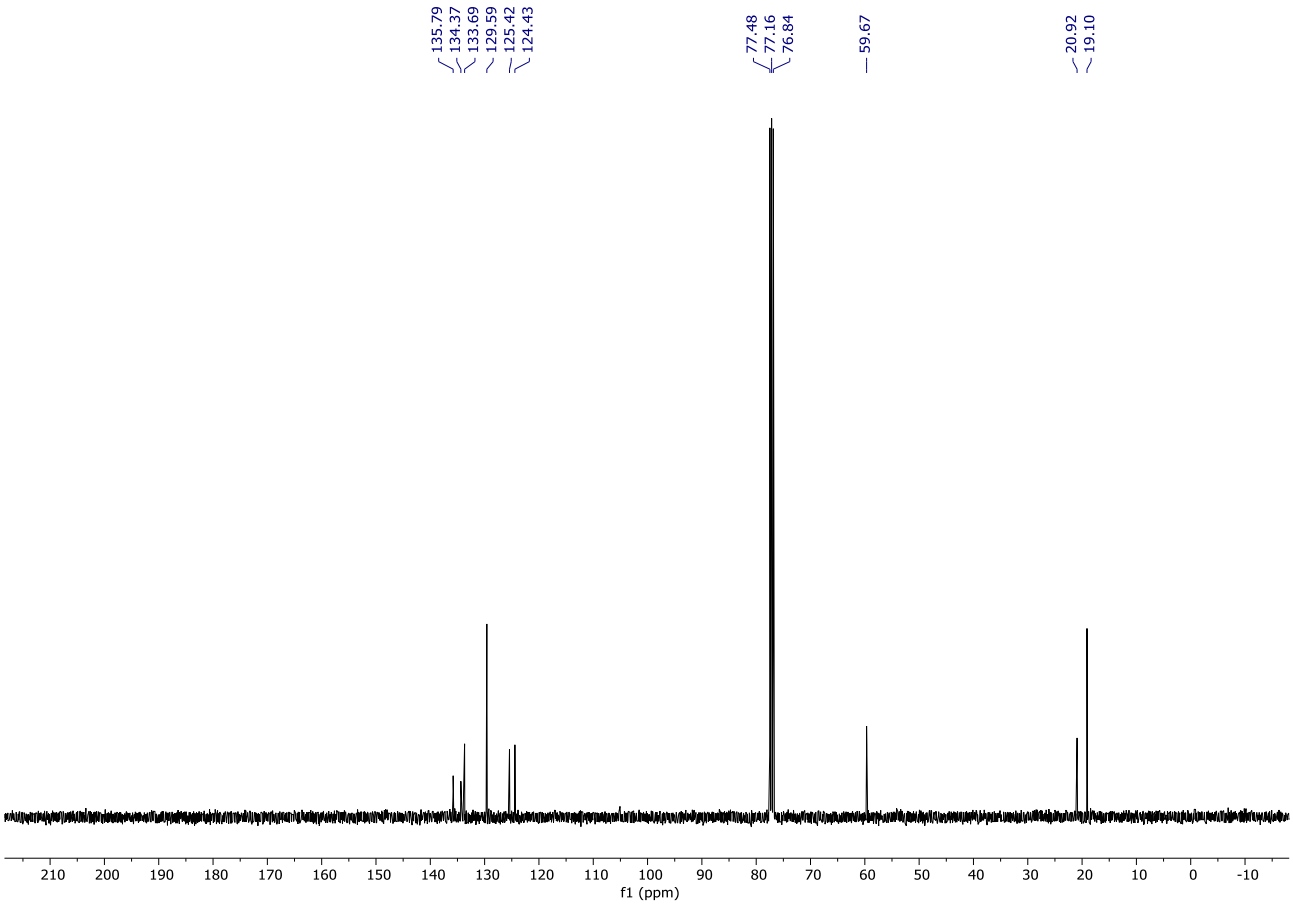

0.97
2.02
1.02
2.02
1.08
1.04
1.06
2.02
12.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

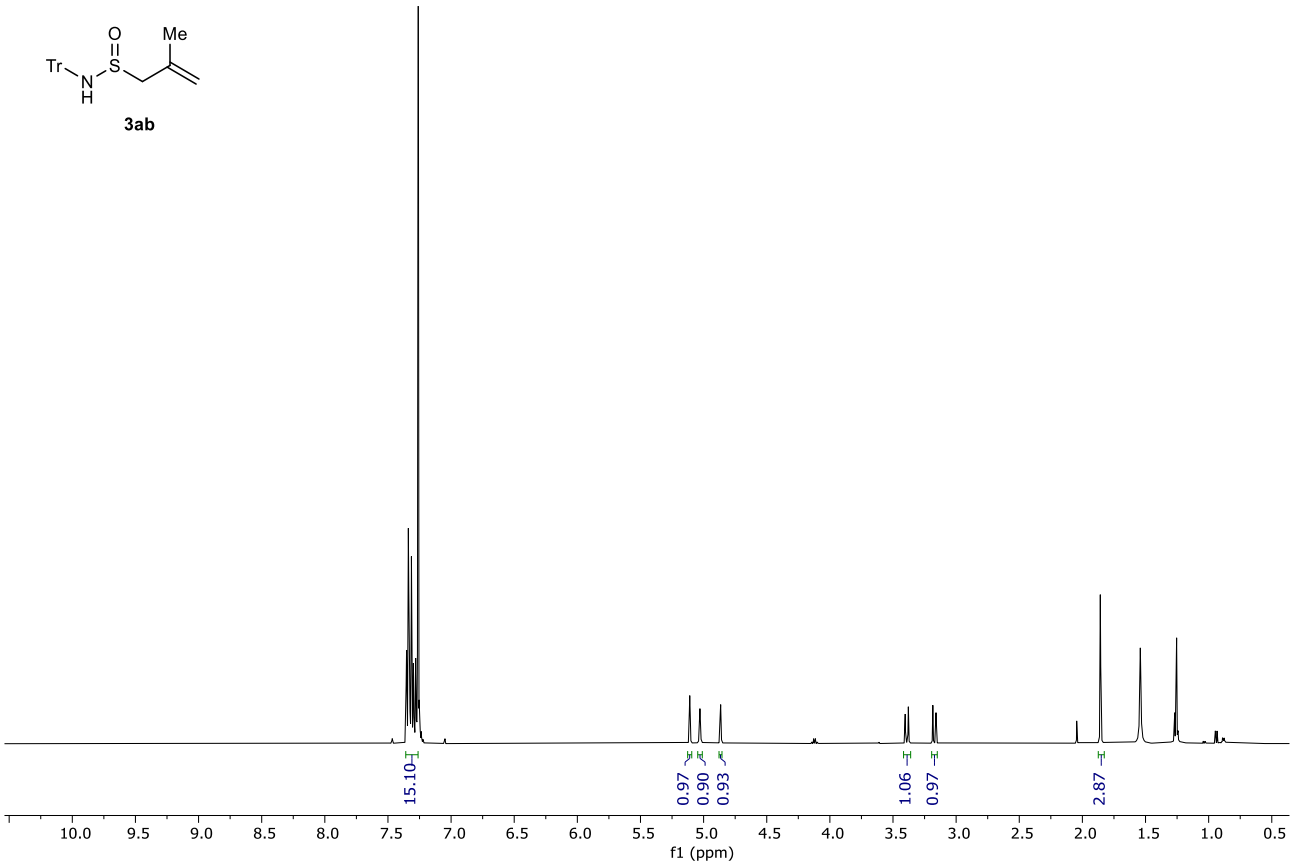

145.07
133.97
127.14
125.41
124.43
123.90
77.48
77.16
76.84
59.80
28.23
24.14
23.76
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

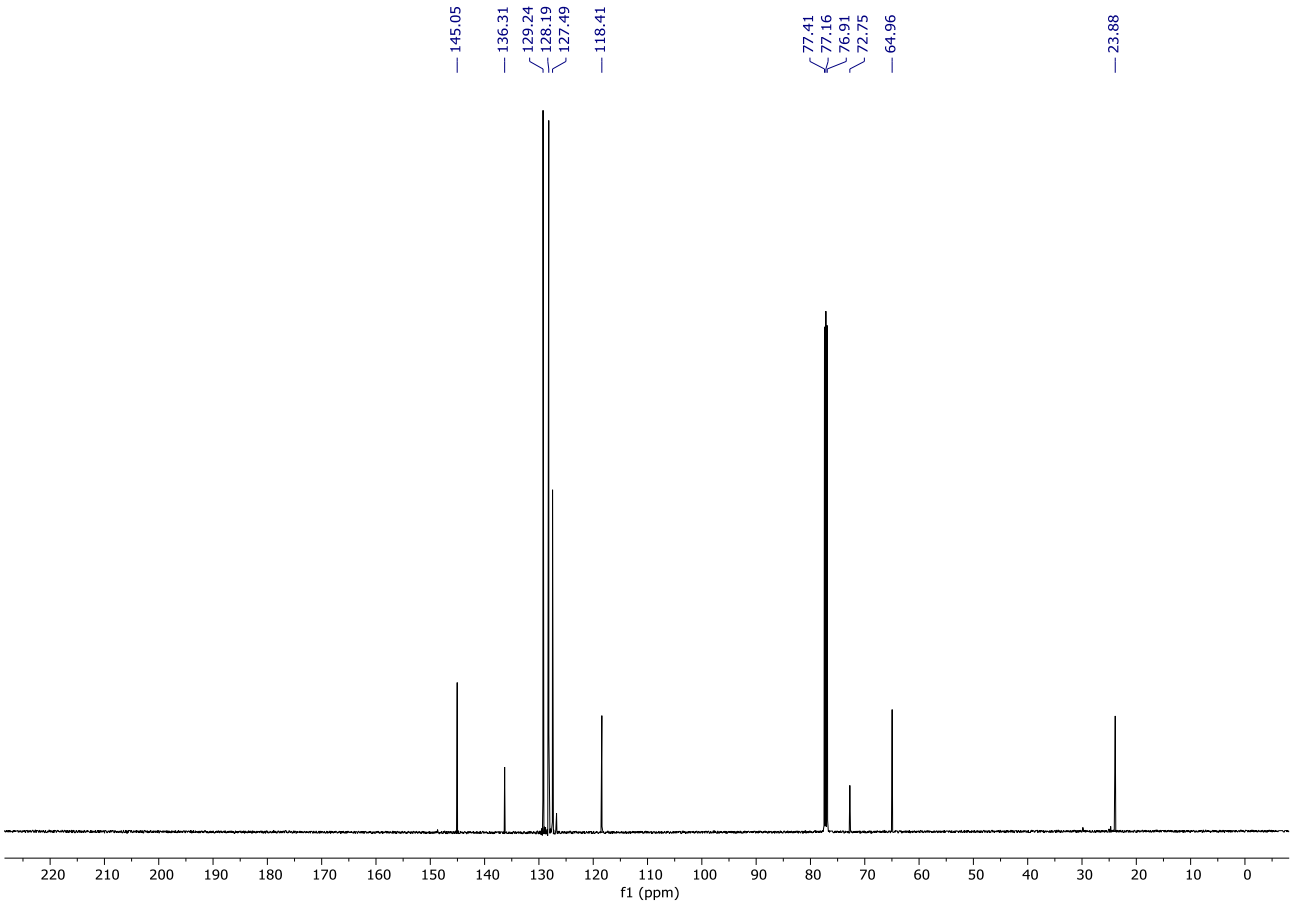

Me
Me
O
S
N
H
Me

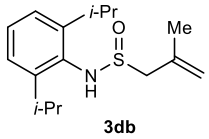
**3ea**


2.05
1.02
1.08
1.98
1.05
1.04
6.06
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


135.79
134.37
133.69
129.59
125.42
124.43
77.48
77.16
76.84
59.67
20.92
19.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

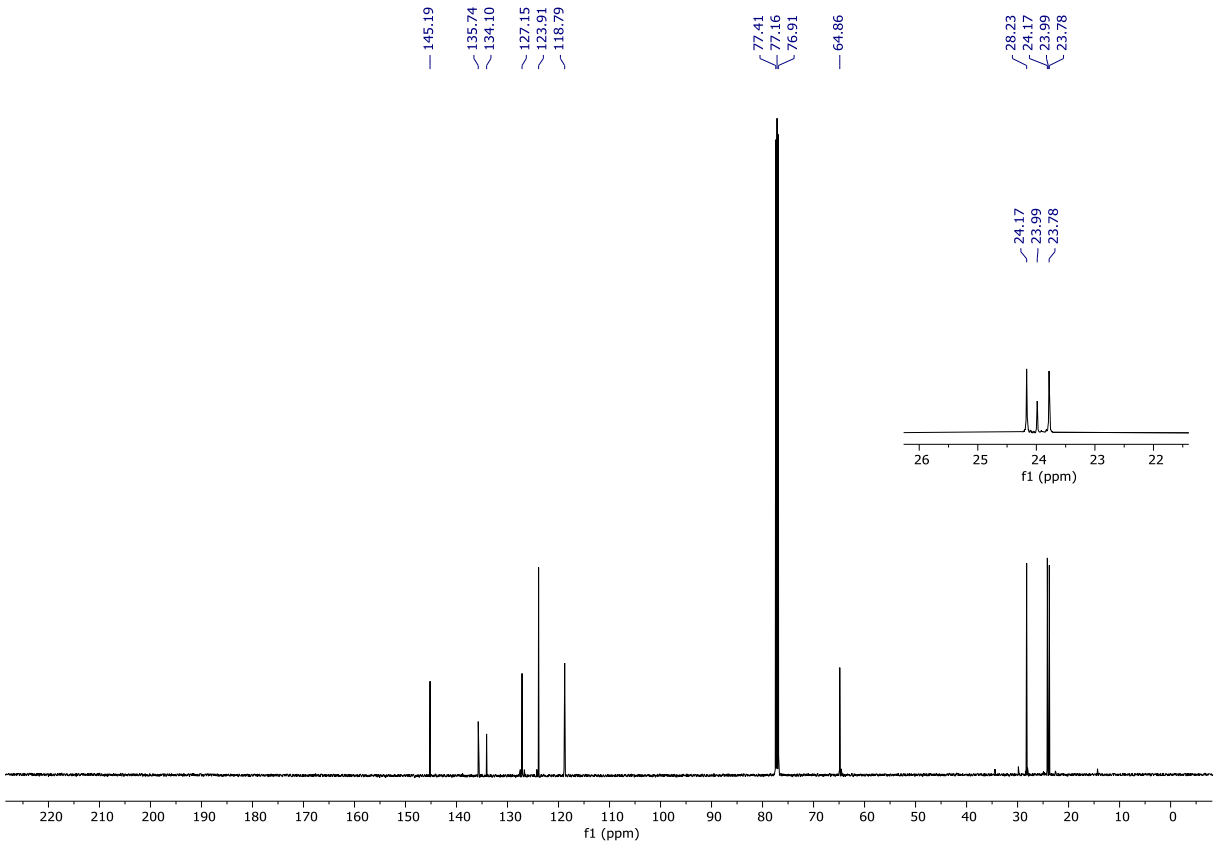

Tr
N
H
O
S
Me
3ab
15.10
0.97
0.90
0.93
1.06
0.97
2.87
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

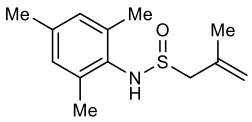

145.05
136.31
129.24
128.19
127.49
118.41
77.41
77.16
76.91
72.75
64.96
23.88
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


i-Pr
O
Me
S
N
H
i-Pr

**3db**

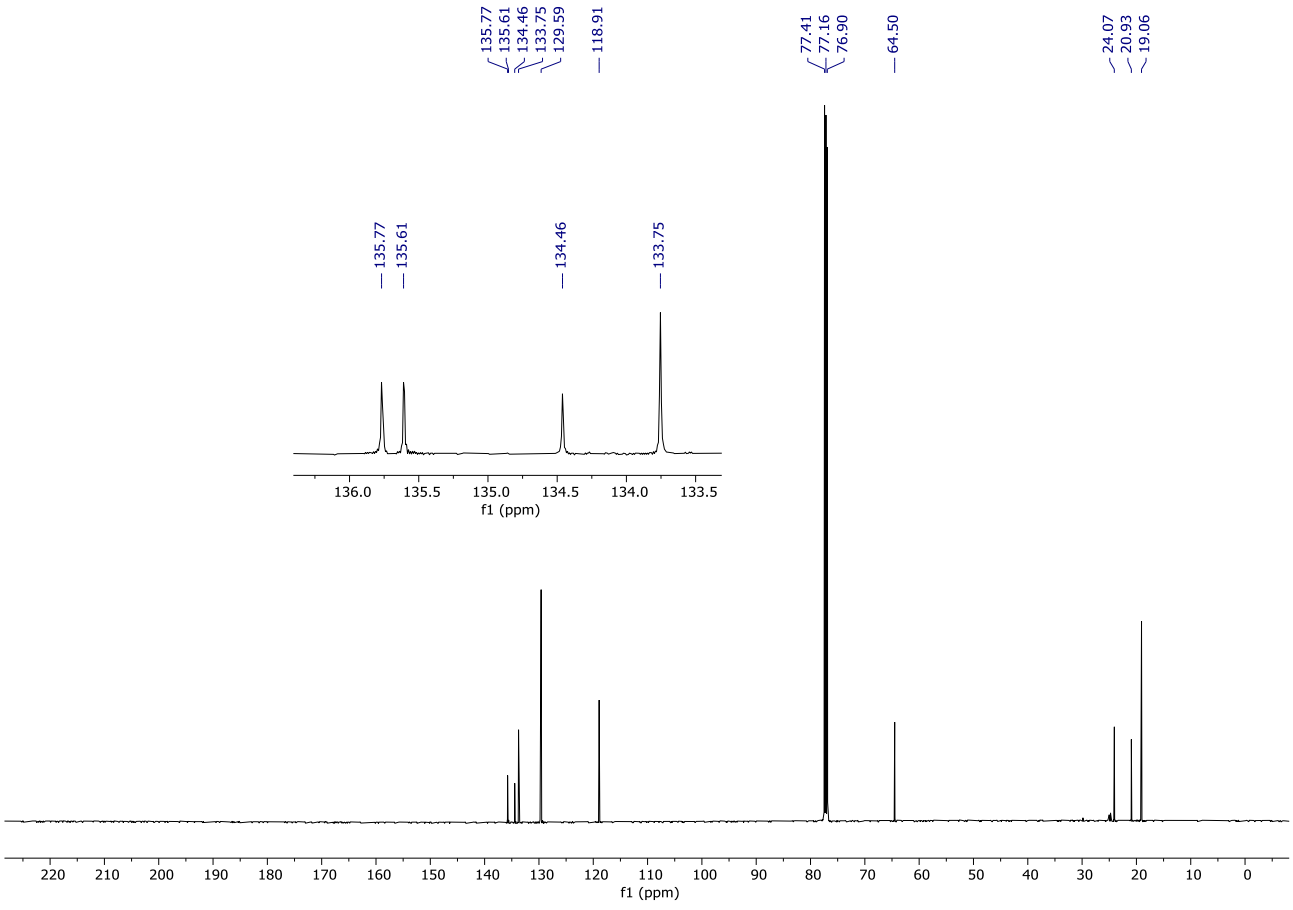

0.95
2.05
1.03
1.07
1.12
1.12
1.09
2.08
3.81
11.77
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

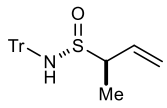

145.19
135.74
134.10
127.15
123.91
118.79
77.41
77.16
76.91
64.86
28.23
24.17
23.99
23.78
24.17
23.99
23.78
26 25 24 23 22
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
Me
O
Me
S
N
H
Me

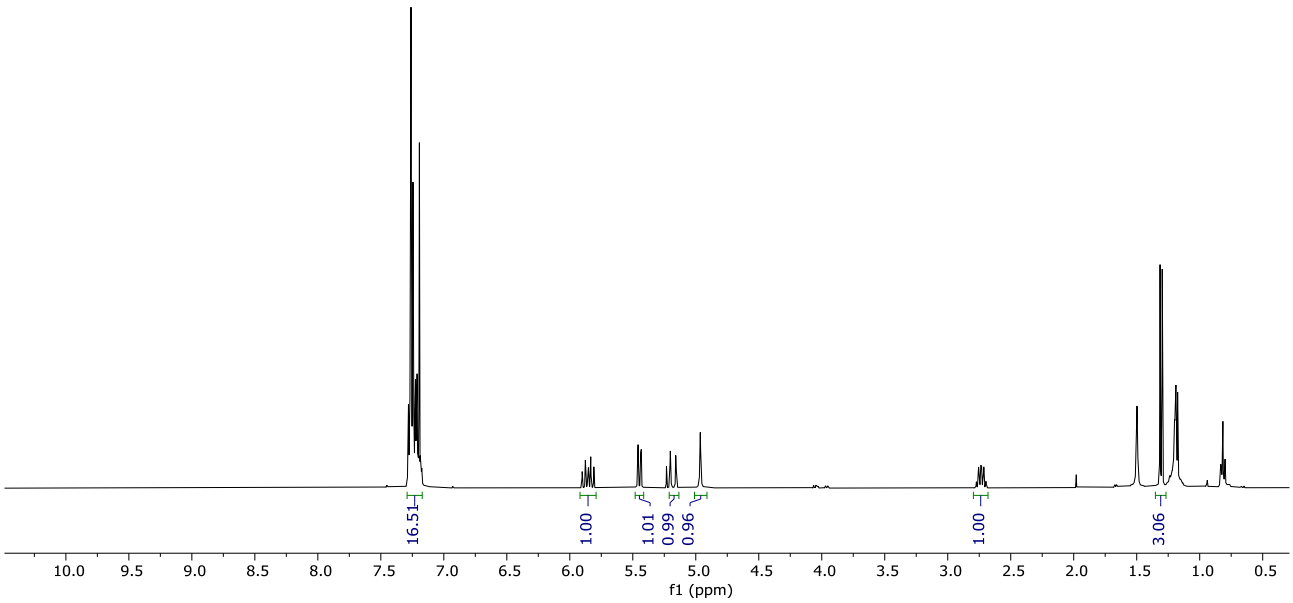
**3eb**

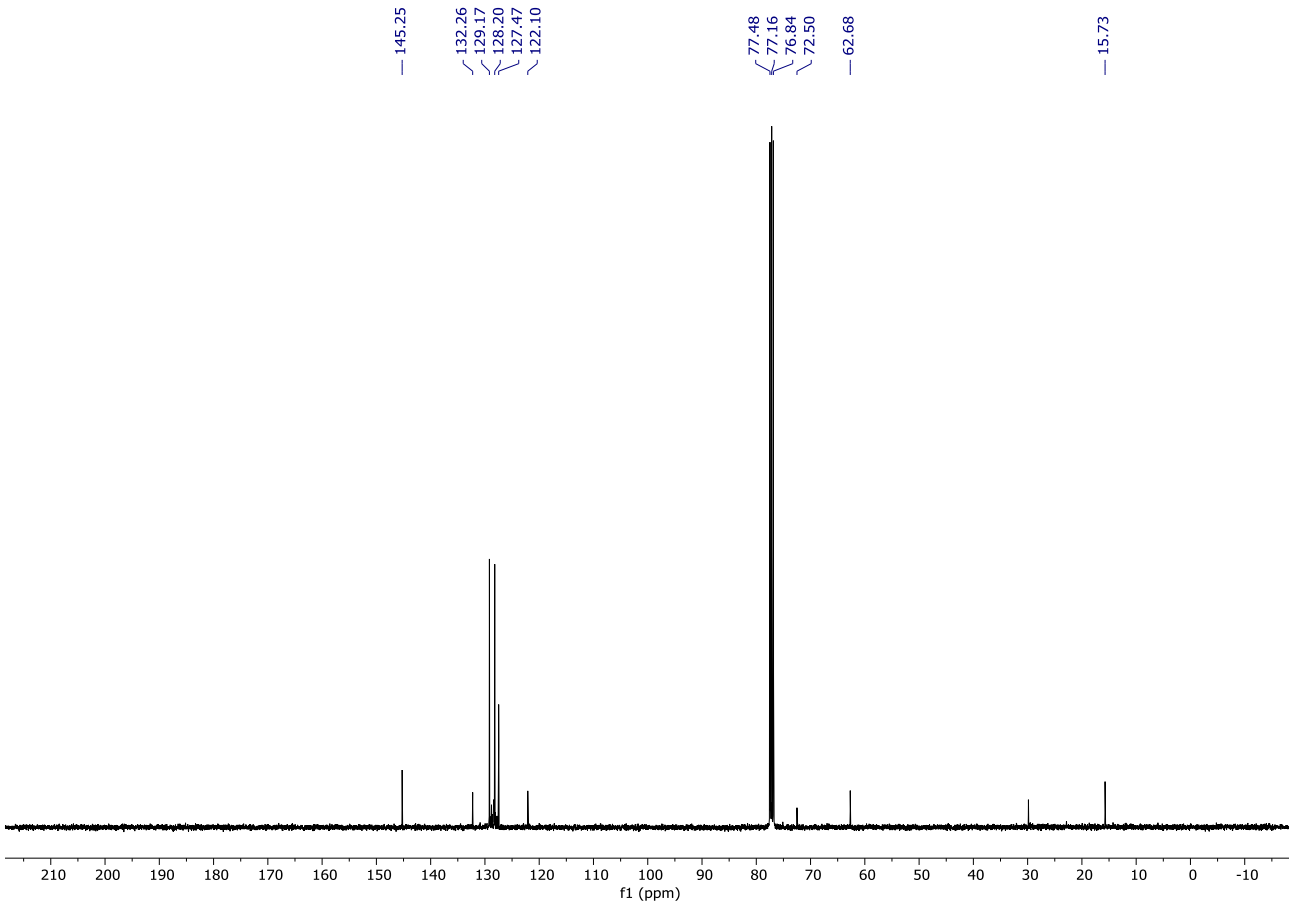

2.00
0.96
1.02
1.05
1.04
1.05
6.19
3.10
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

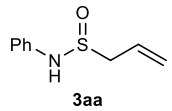

135.77
135.61
134.46
133.75
129.59
118.91
77.41
77.16
76.90
64.50
24.07
20.93
19.06
135.77
135.61
134.46
133.75
136.0 135.5 135.0 134.5 134.0 133.5
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Tr
N
H
S
O
Me

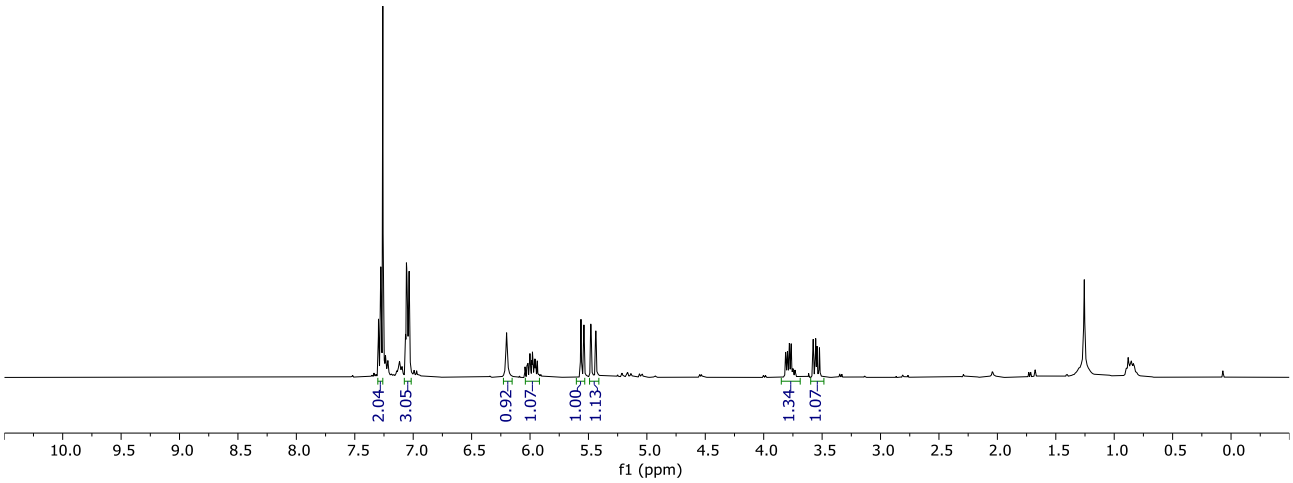
**3af**

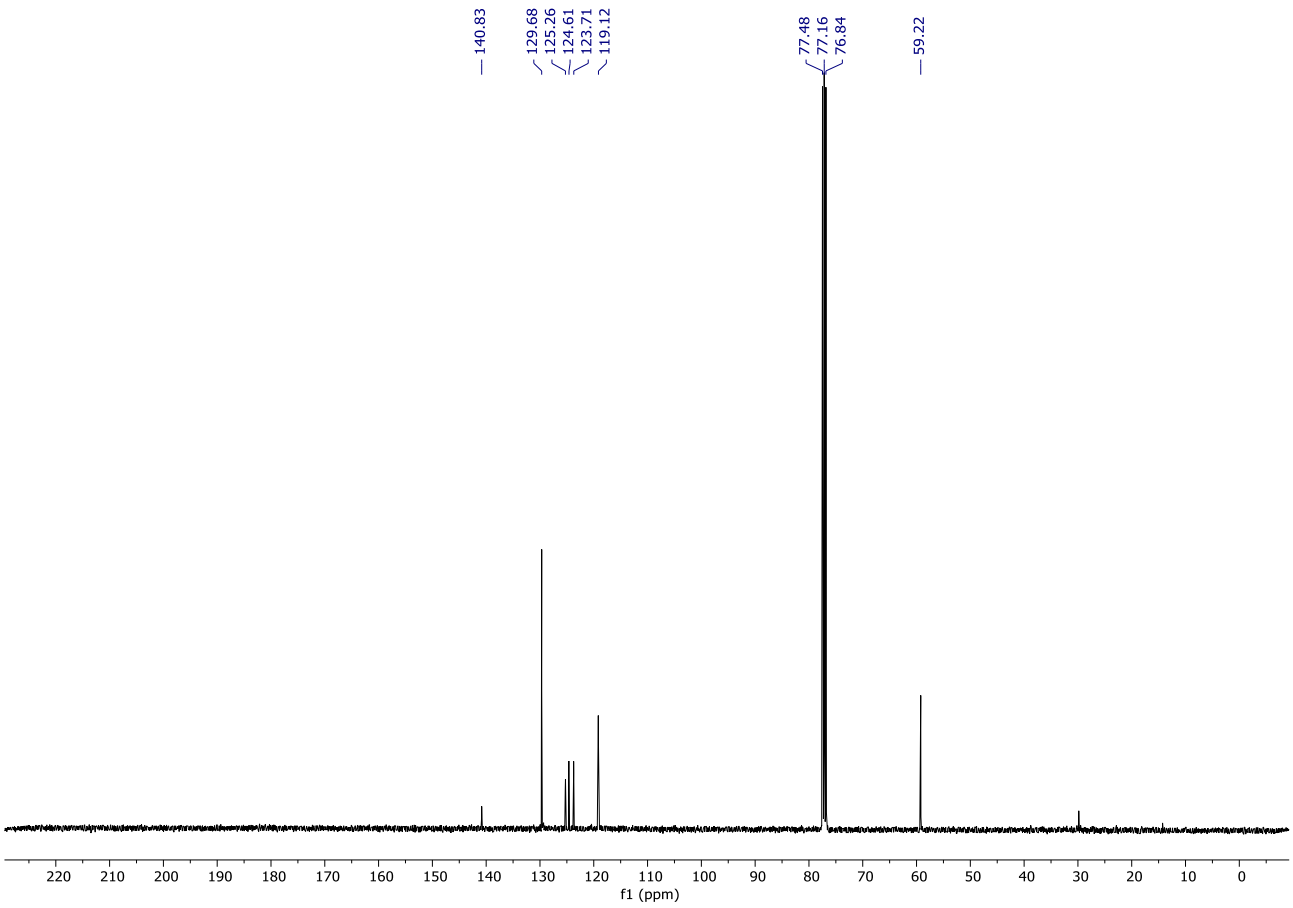

16.51
1.00
1.01
0.99
0.96
1.00
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

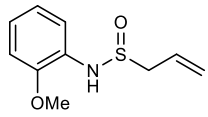

145.25
132.26
129.17
128.20
127.47
122.10
77.48
77.16
76.84
72.50
62.68
15.73
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
N
H
S
O

**3aa**

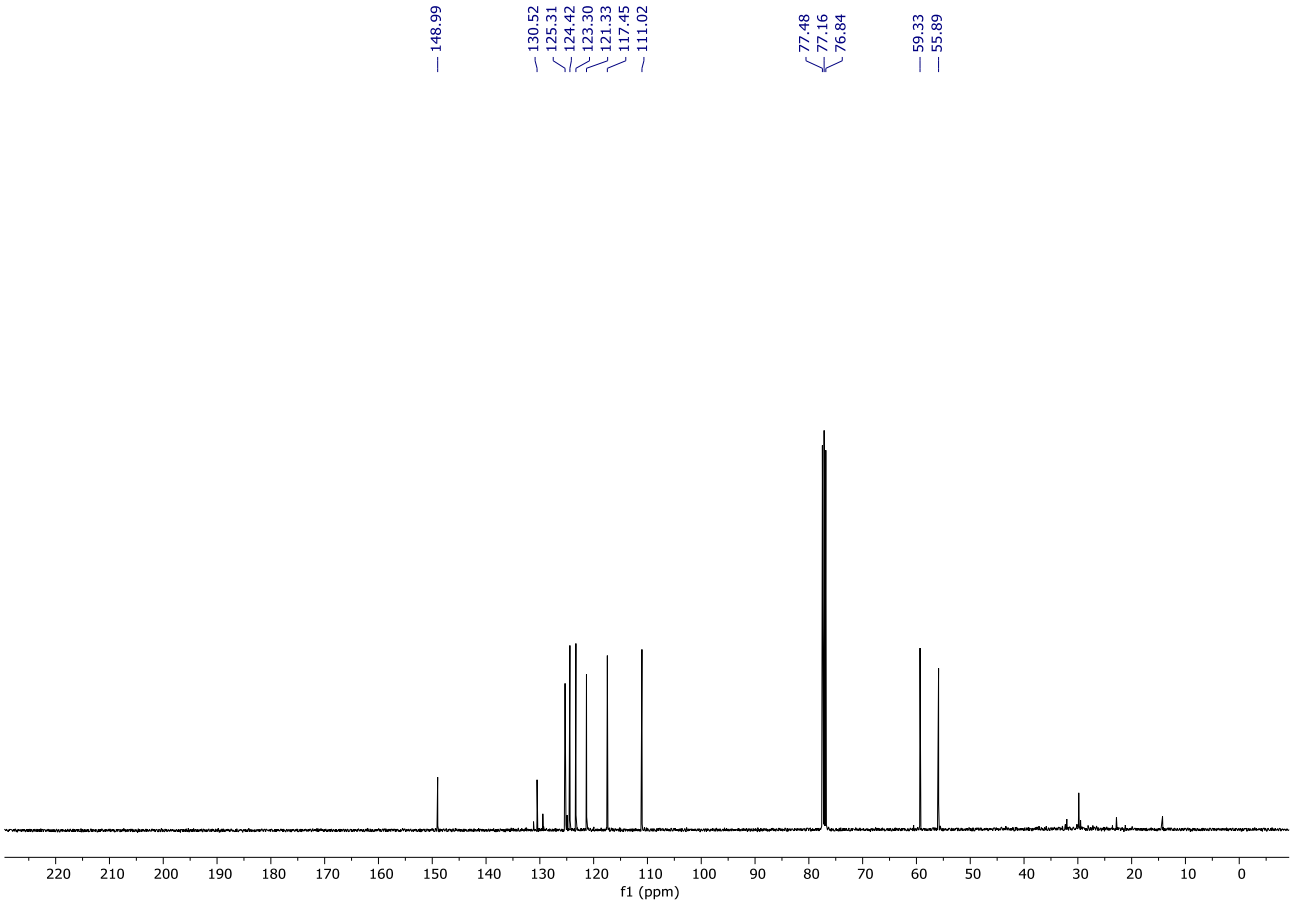

2.04
3.05
0.92
1.07
1.00
1.13
1.34
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

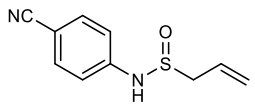

140.83
129.68
125.26
124.61
123.71
119.12
77.48
77.16
76.84
59.22
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
S
N
H
OMe

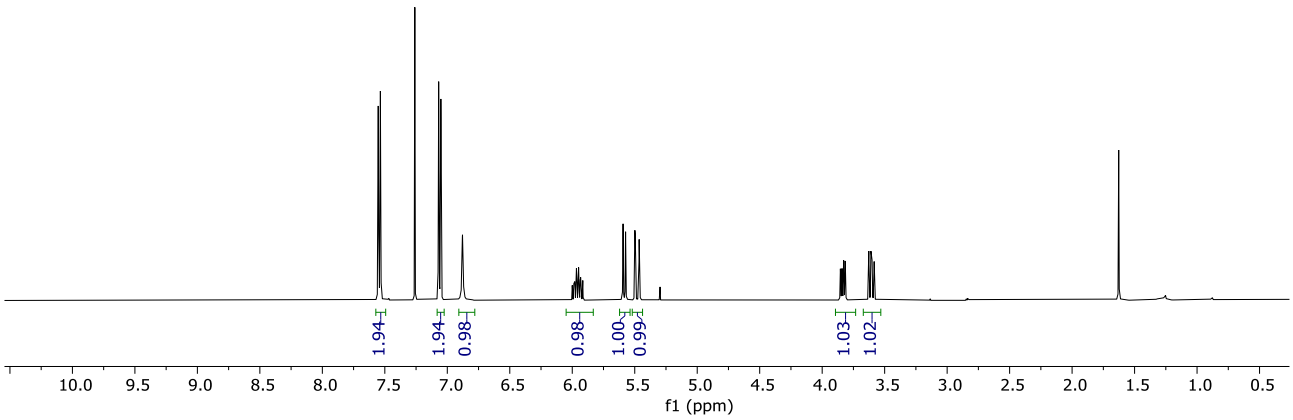
**3fa**

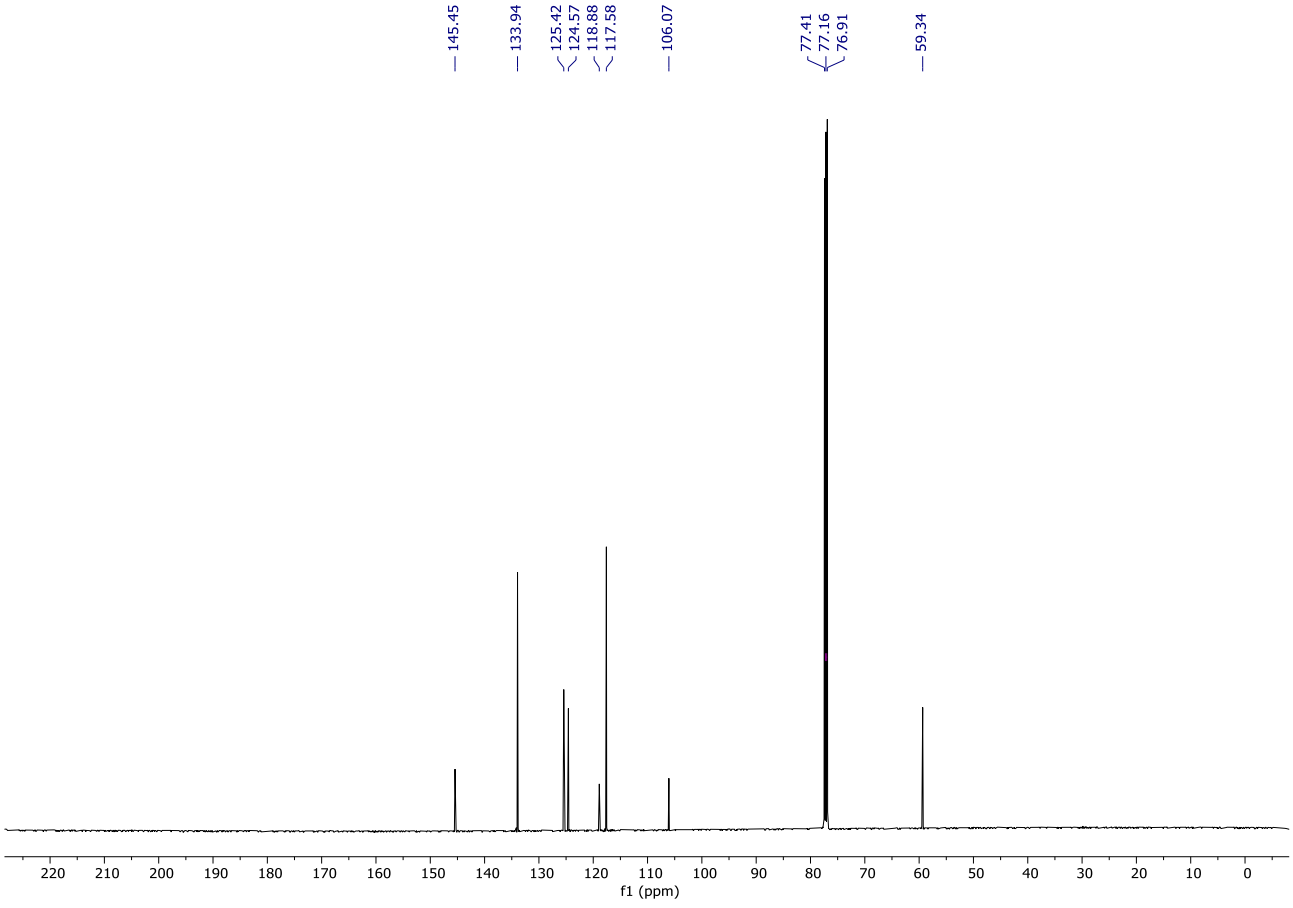

0.92
3.02
0.94
0.98
0.97
0.98
3.00
1.04
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

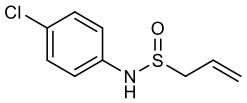

148.99
130.52
125.31
124.42
123.30
121.33
117.45
111.02
77.48
77.16
76.84
59.33
55.89
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NC
O
S
N
H

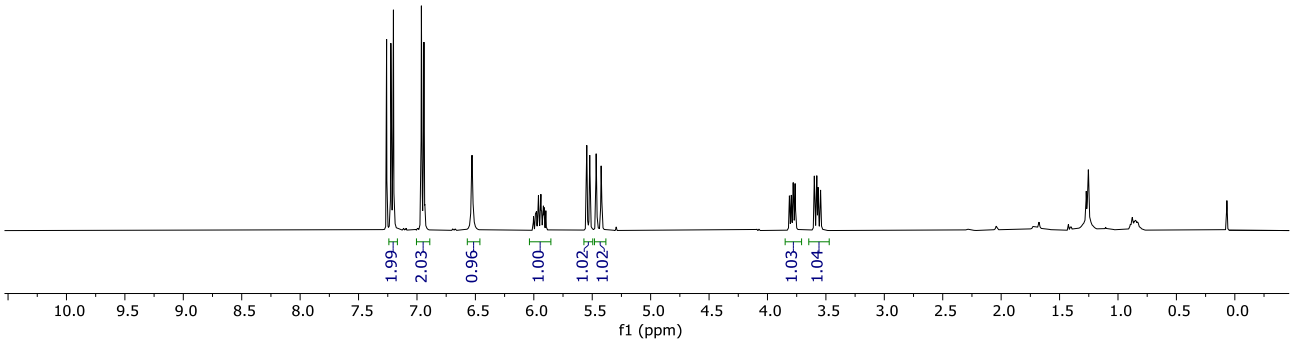
**3ga**

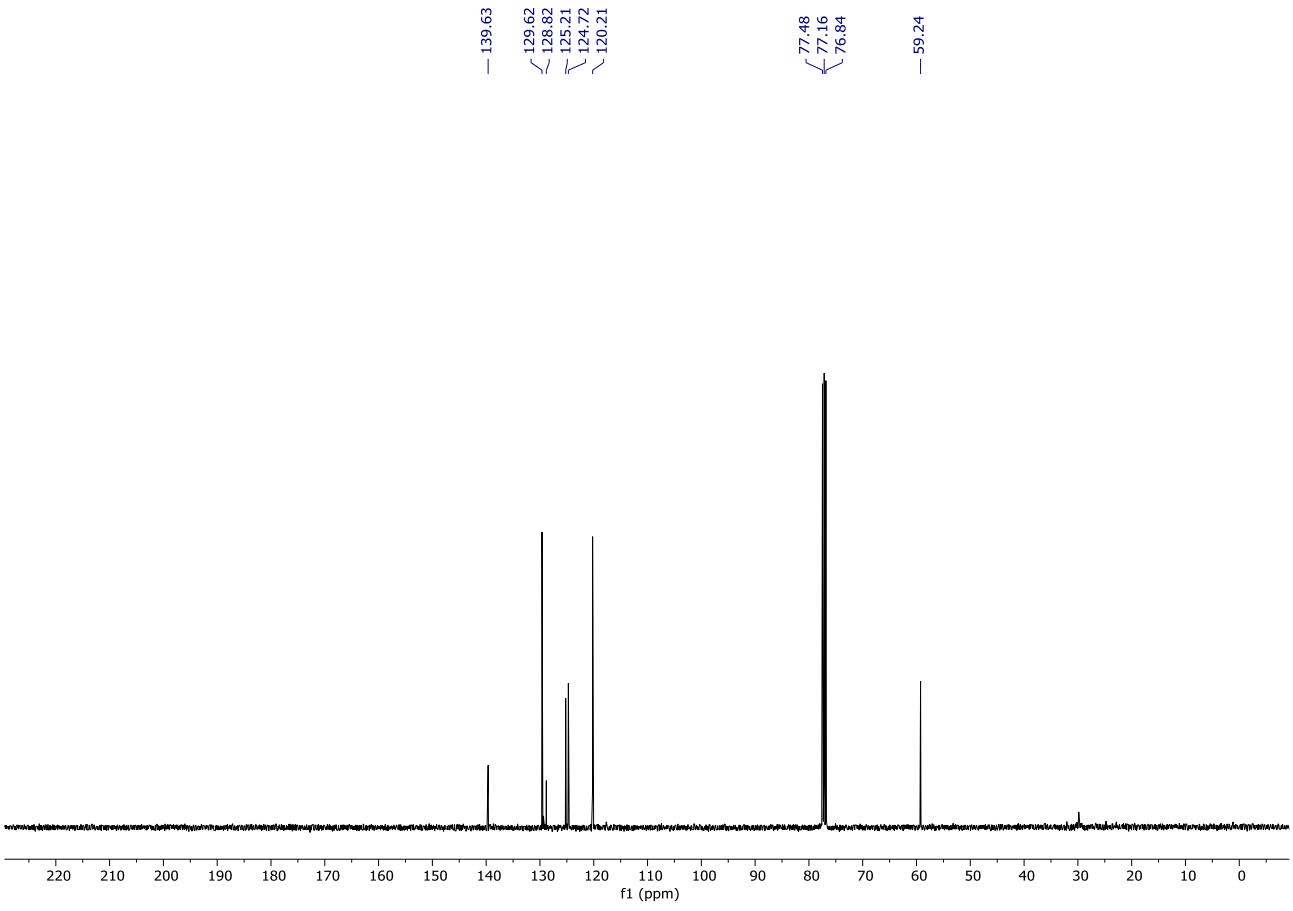

1.94
1.94
0.98
0.98
1.00
0.99
1.03
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

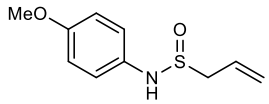

145.45
133.94
125.42
124.57
118.88
117.58
106.07
77.41
77.16
76.91
59.34
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
O
S
N
H

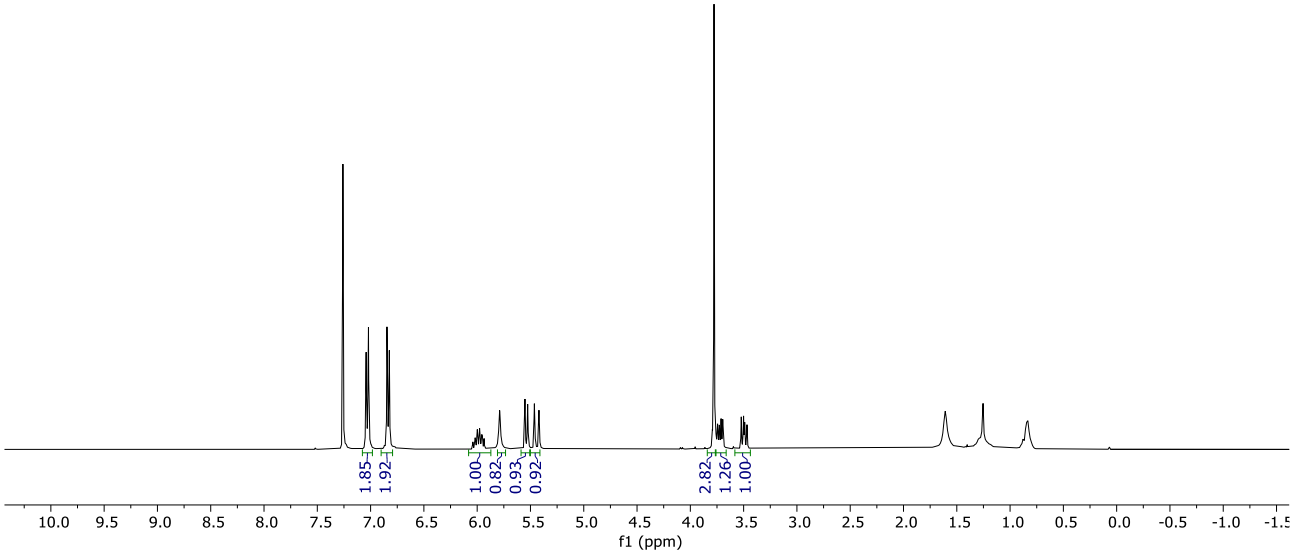
**3ha**

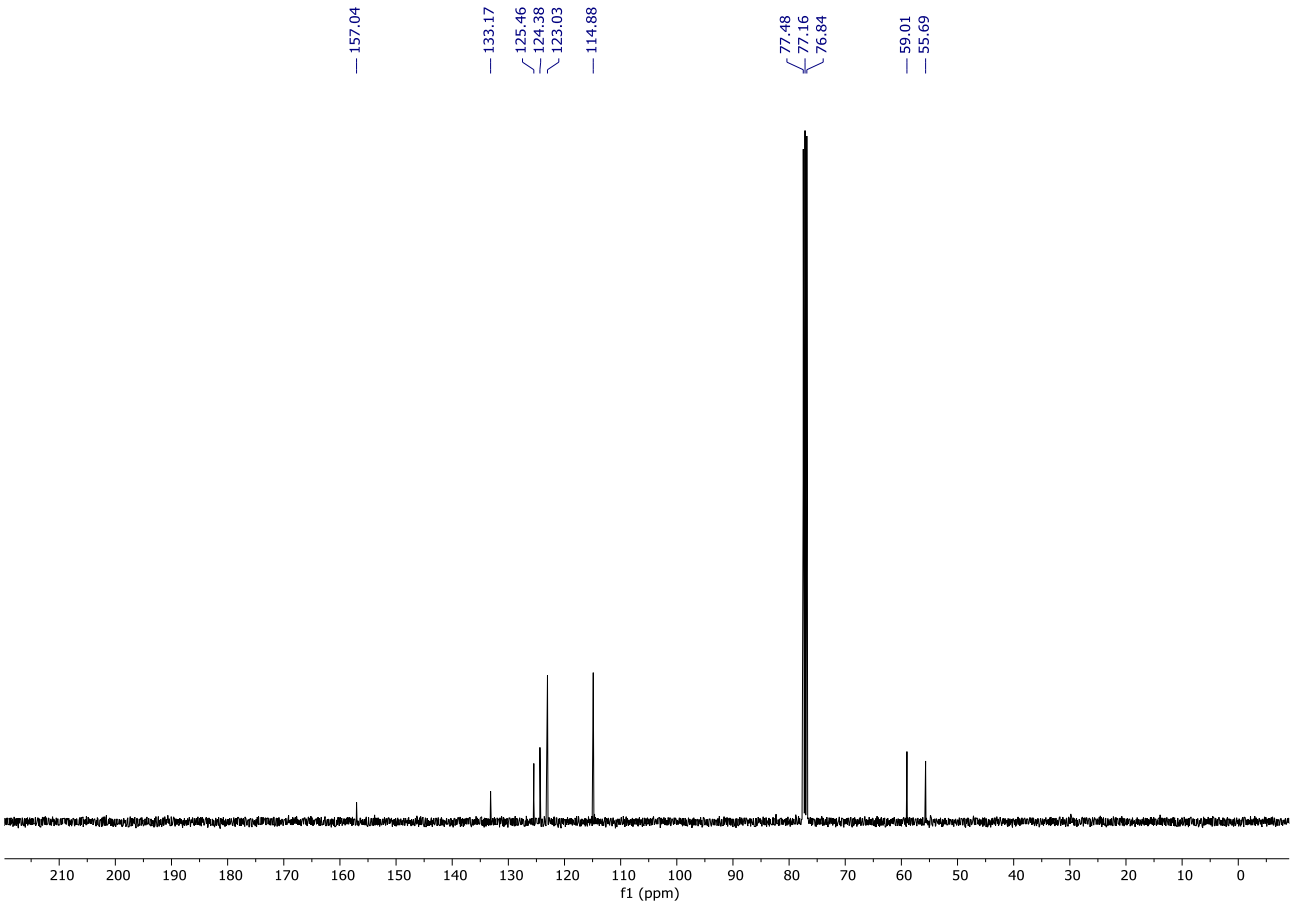

1.99
2.03
0.96
1.00
1.02
1.02
1.03
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

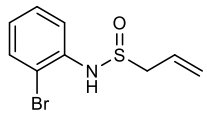

139.63
129.62
128.82
125.21
124.72
120.21
77.48
77.16
76.84
59.24
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeO
O
S
N
H

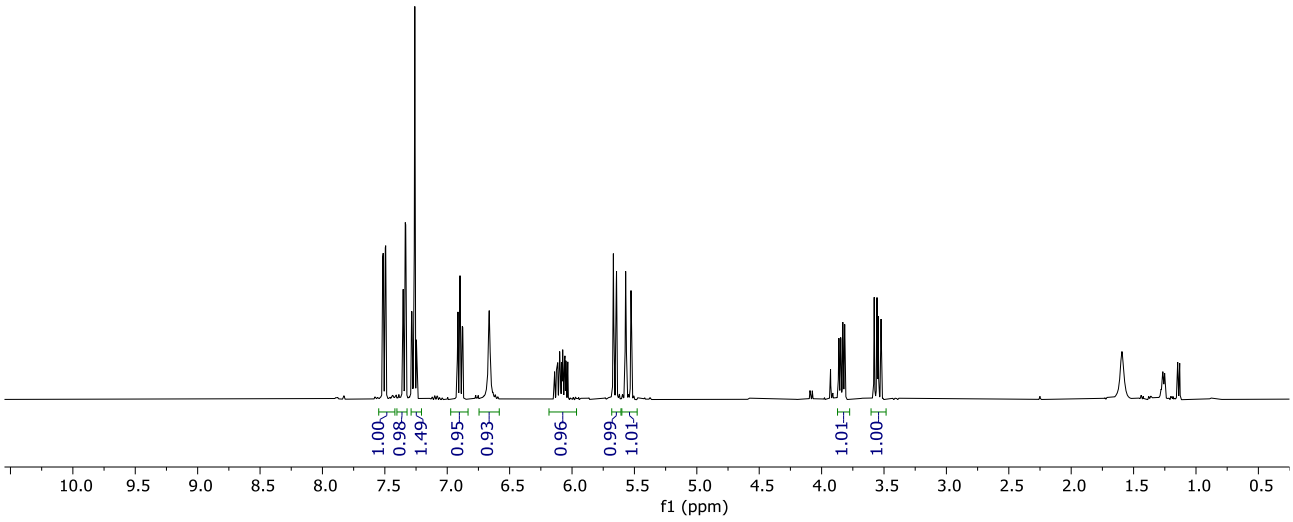
**3ia**

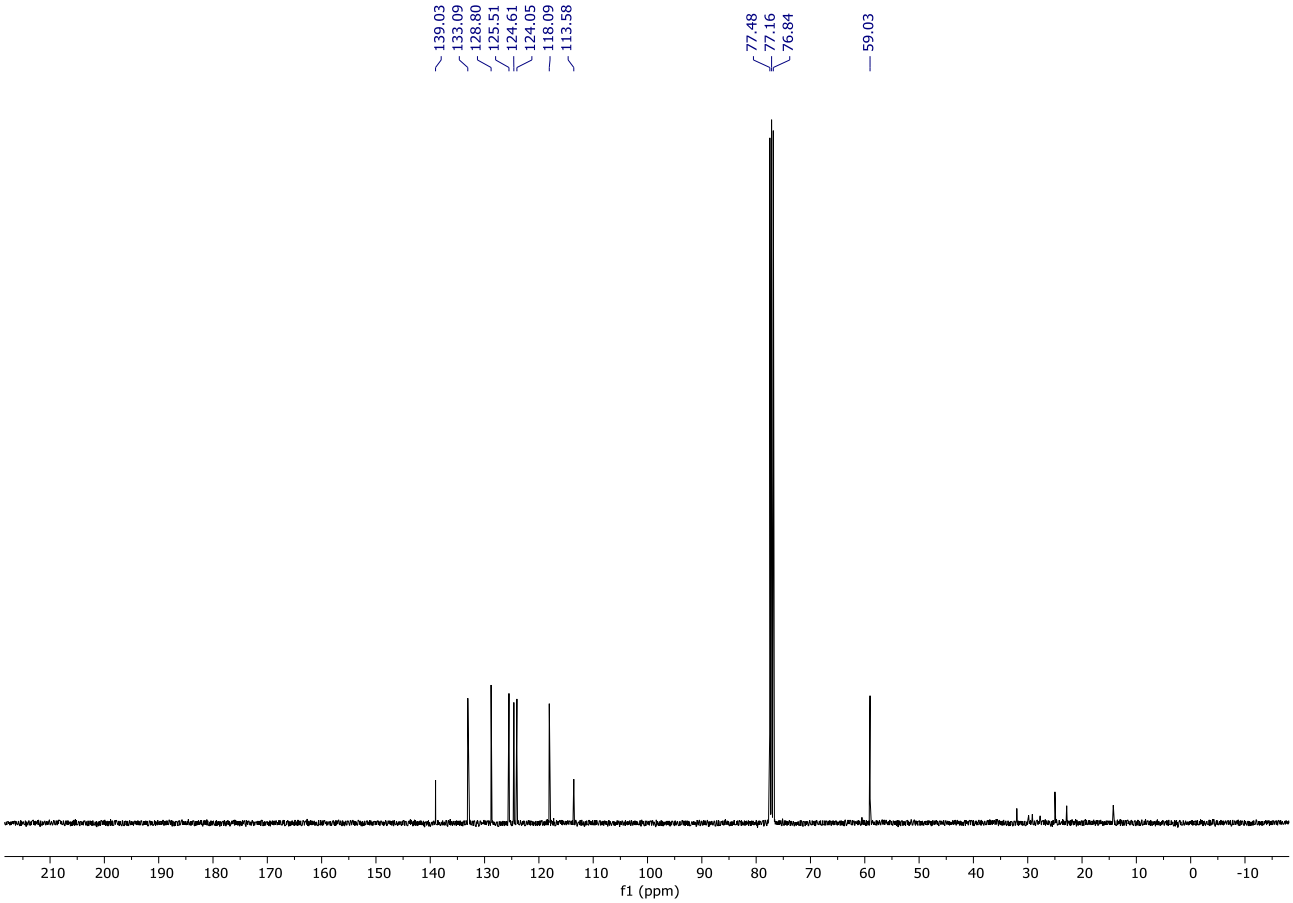

1.85
1.92
1.00
0.82
0.93
0.92
2.82
1.26
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

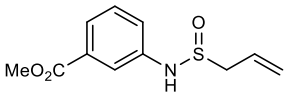

157.04
133.17
125.46
124.38
123.03
114.88
77.48
77.16
76.84
59.01
55.69
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
S
N
H
Br

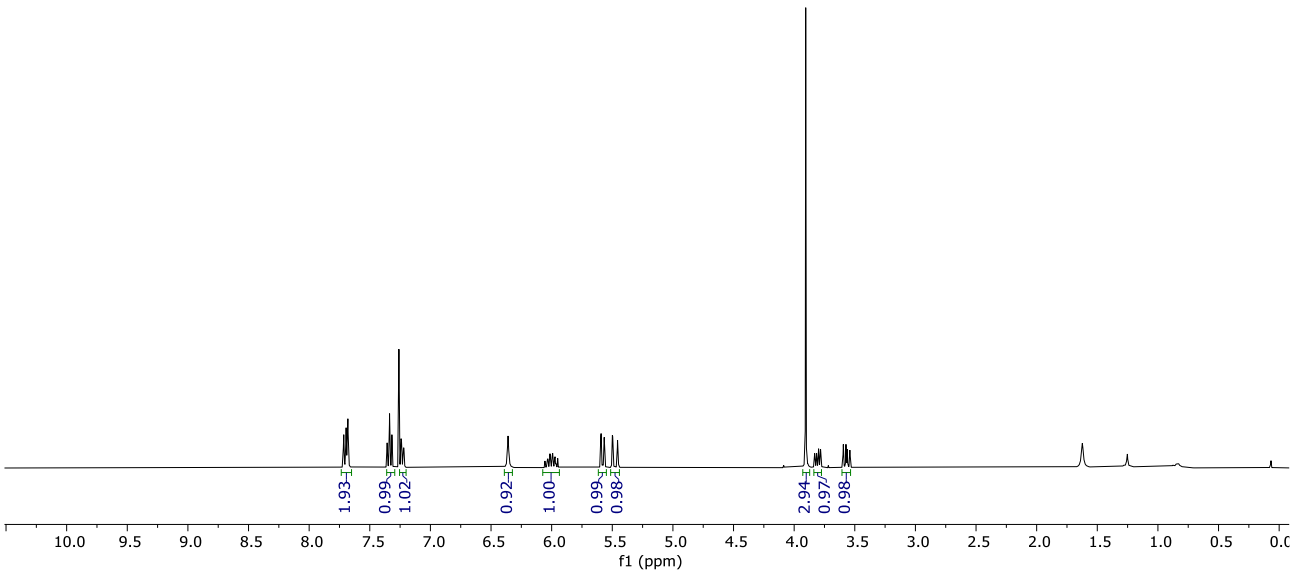
**3ja**

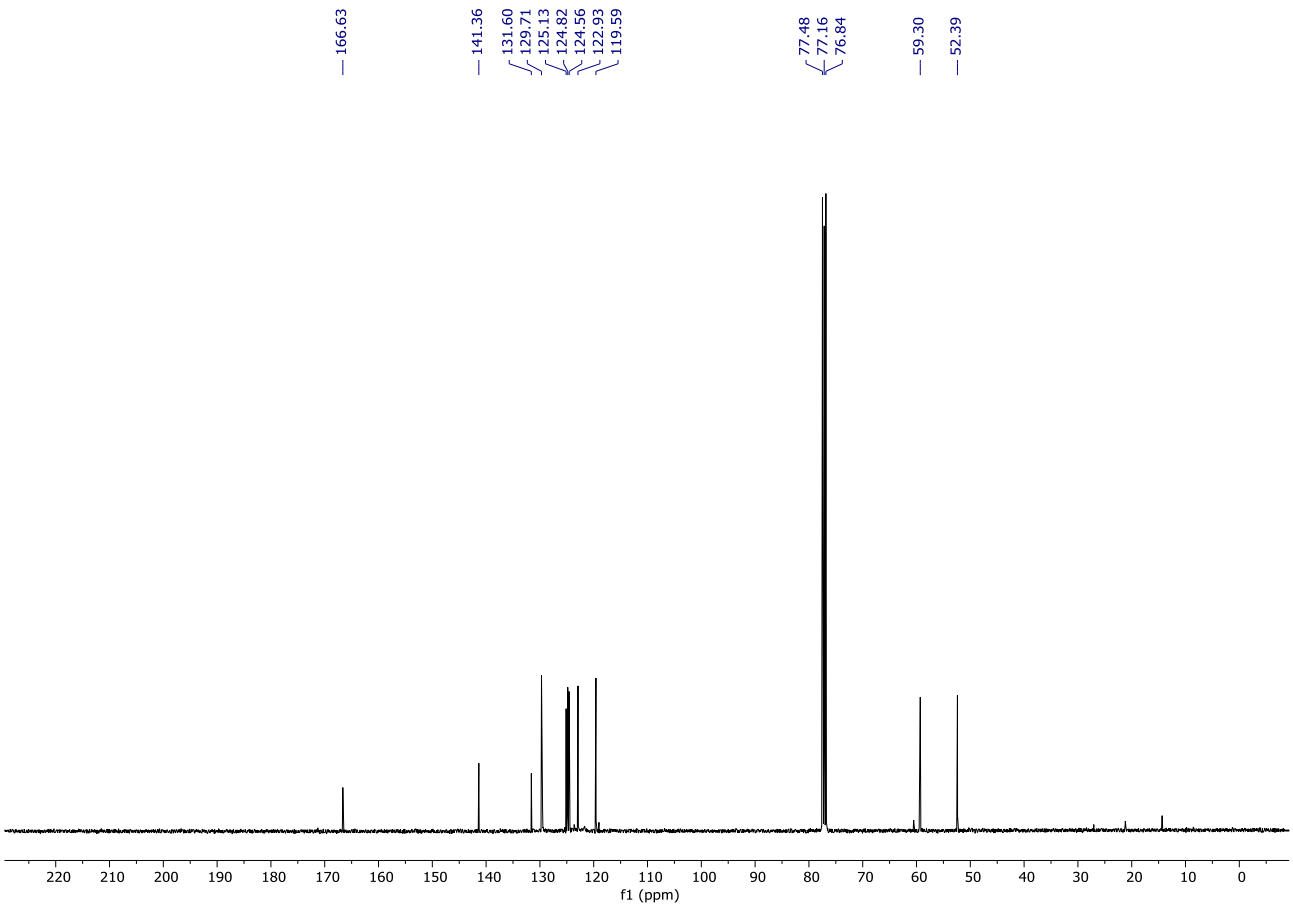

1.00
0.98
1.49
0.95
0.93
0.96
0.99
1.01
1.01
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

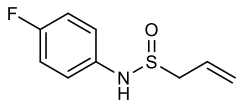

139.03
133.09
128.80
125.51
124.61
124.05
118.09
113.58
77.48
77.16
76.84
59.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



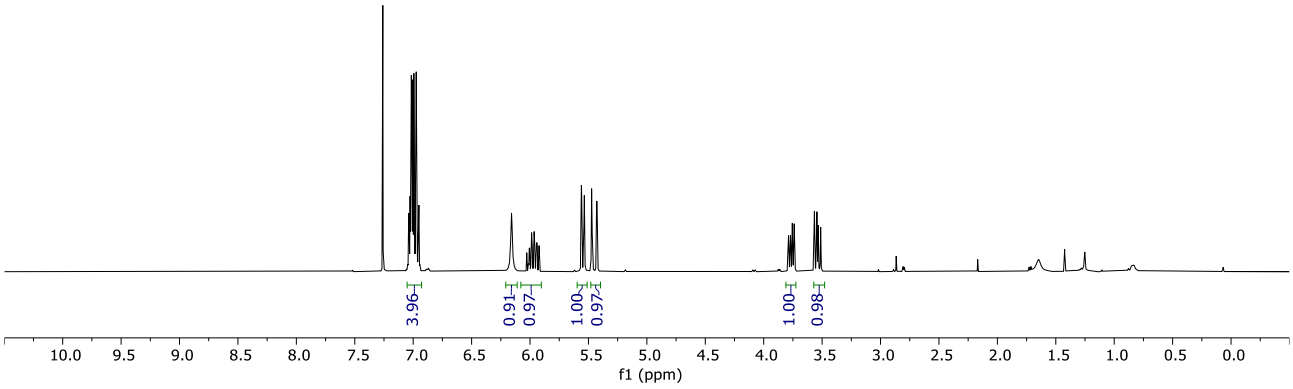
**3ka**

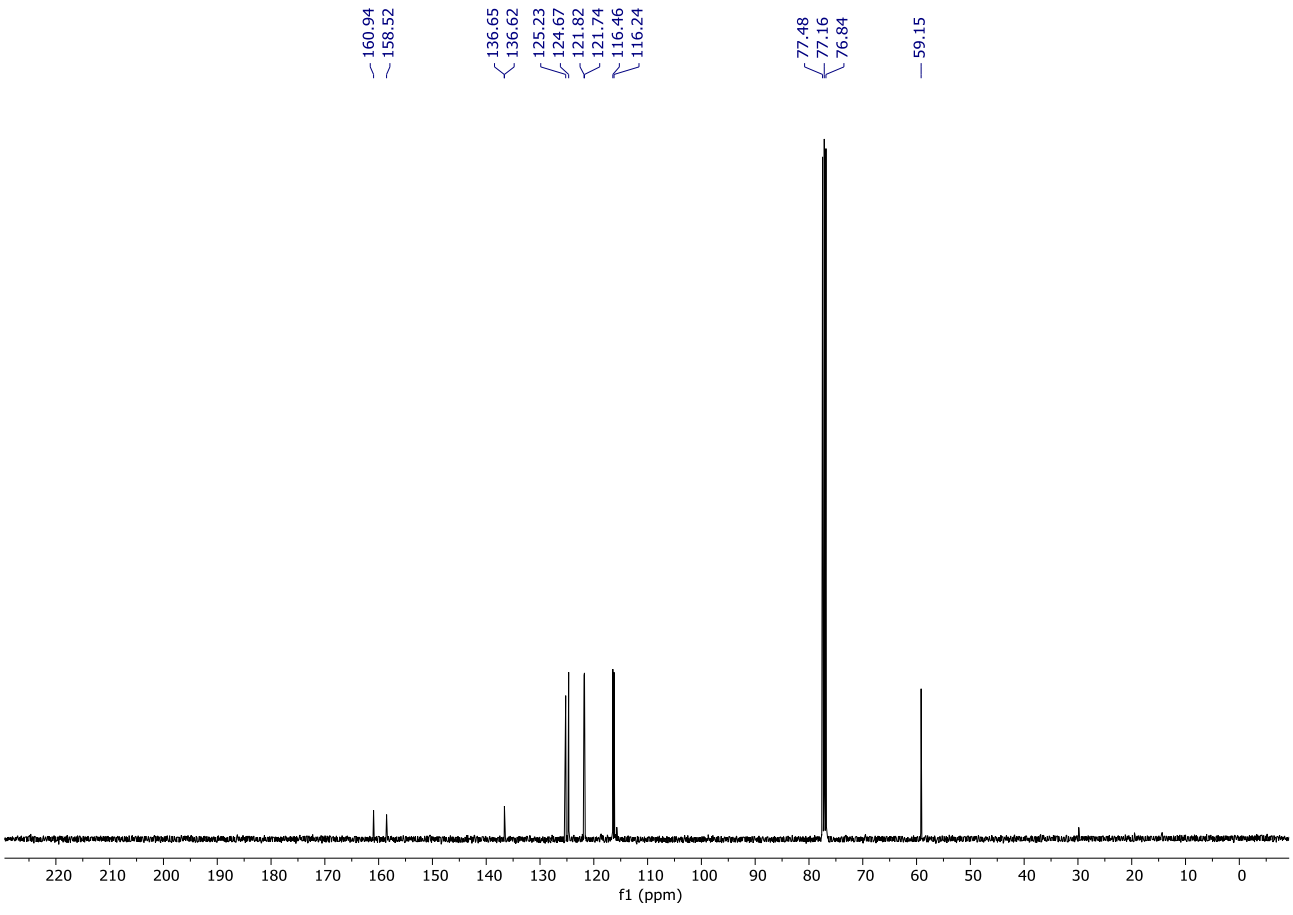

1.93
0.99
1.02
0.92
1.00
0.99
0.98
2.94
0.97
0.98
f1 (ppm)

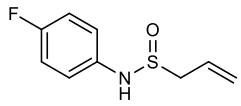

166.63
141.36
131.60
129.71
125.13
124.82
124.56
122.93
119.59
77.48
77.16
76.84
59.30
52.39
f1 (ppm)



**3la**

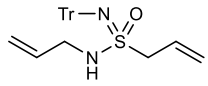

3.96
0.91
0.97
1.00
0.97
1.00
0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.94
158.52
136.65
136.62
125.23
124.67
121.82
121.74
116.46
116.24
77.48
77.16
76.84
59.15
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

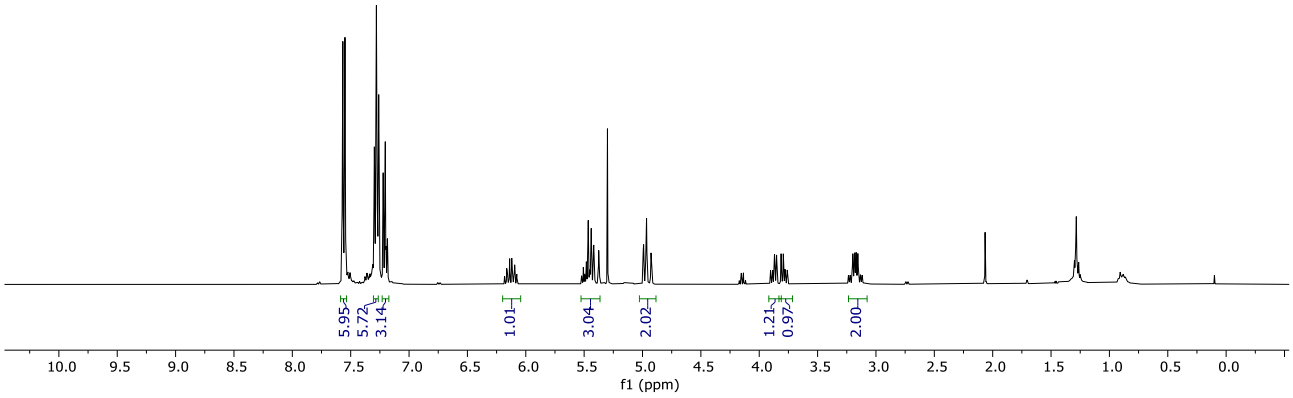

F
O
S
N
H

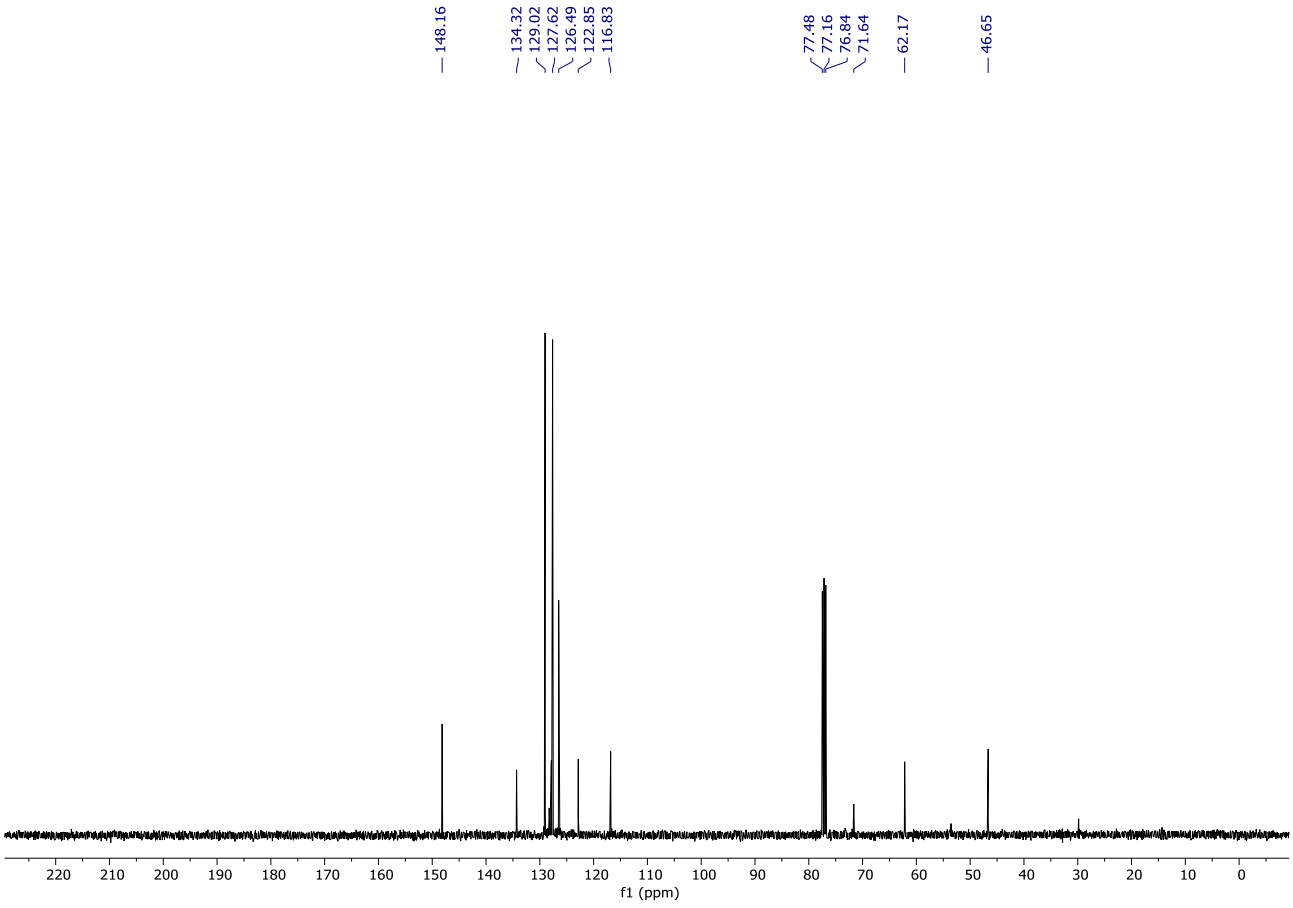
**3la**

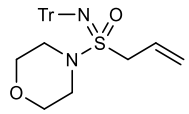

-119.19
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


Tr—N
O
S
N
H

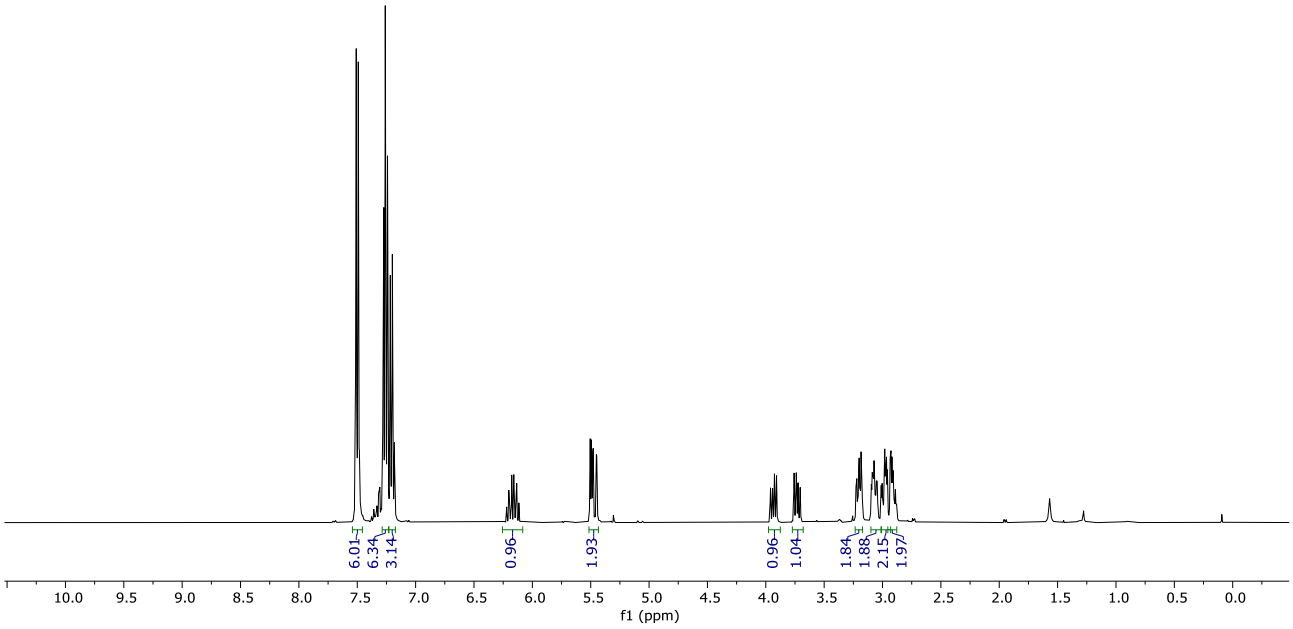
**10a**

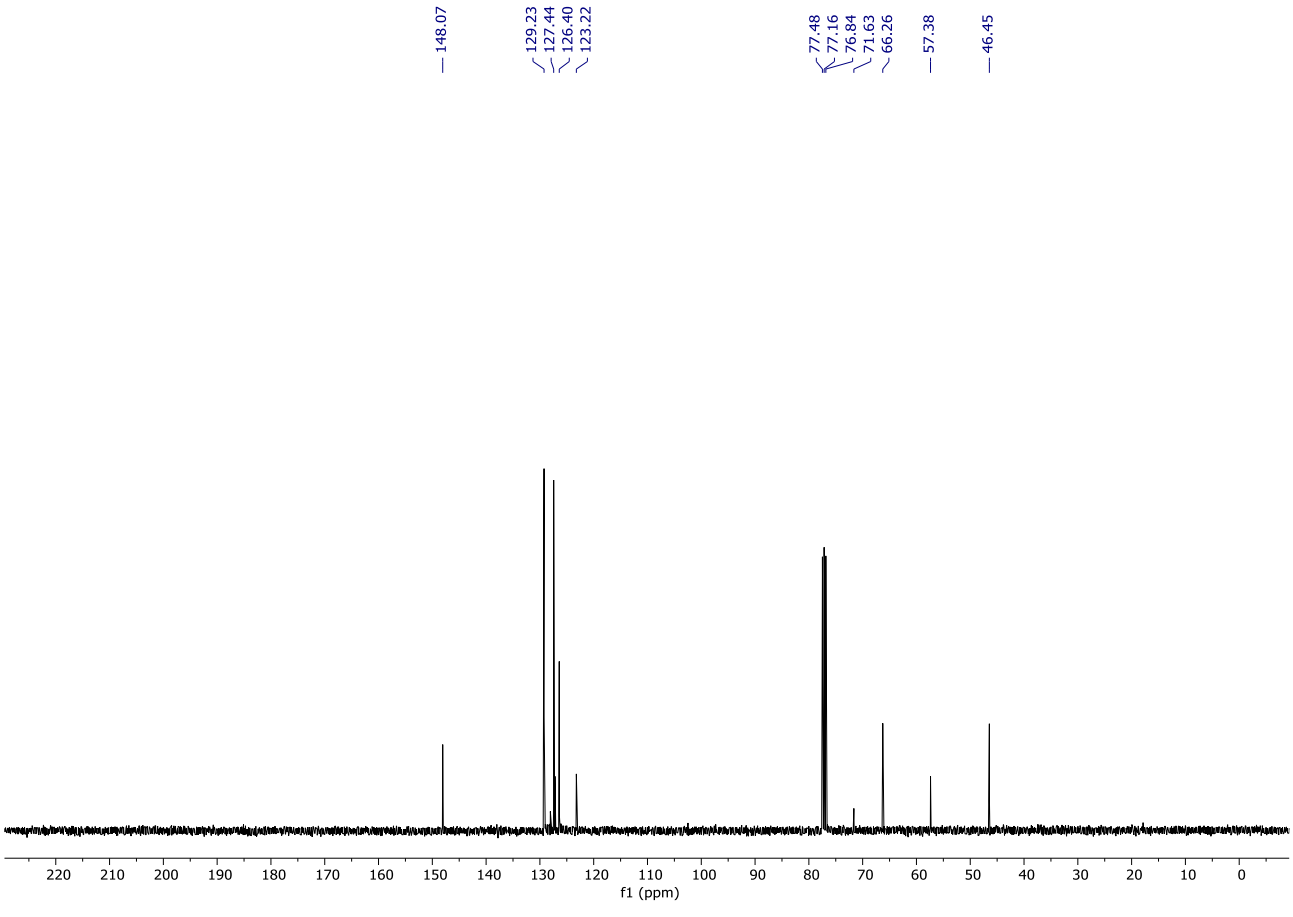

5.95
5.72
3.14
1.01
3.04
2.02
1.21
0.97
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

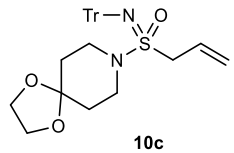

148.16
134.32
129.02
127.62
126.49
122.85
116.83
77.48
77.16
76.84
71.64
62.17
46.65
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Tr—N
O
S
N
O

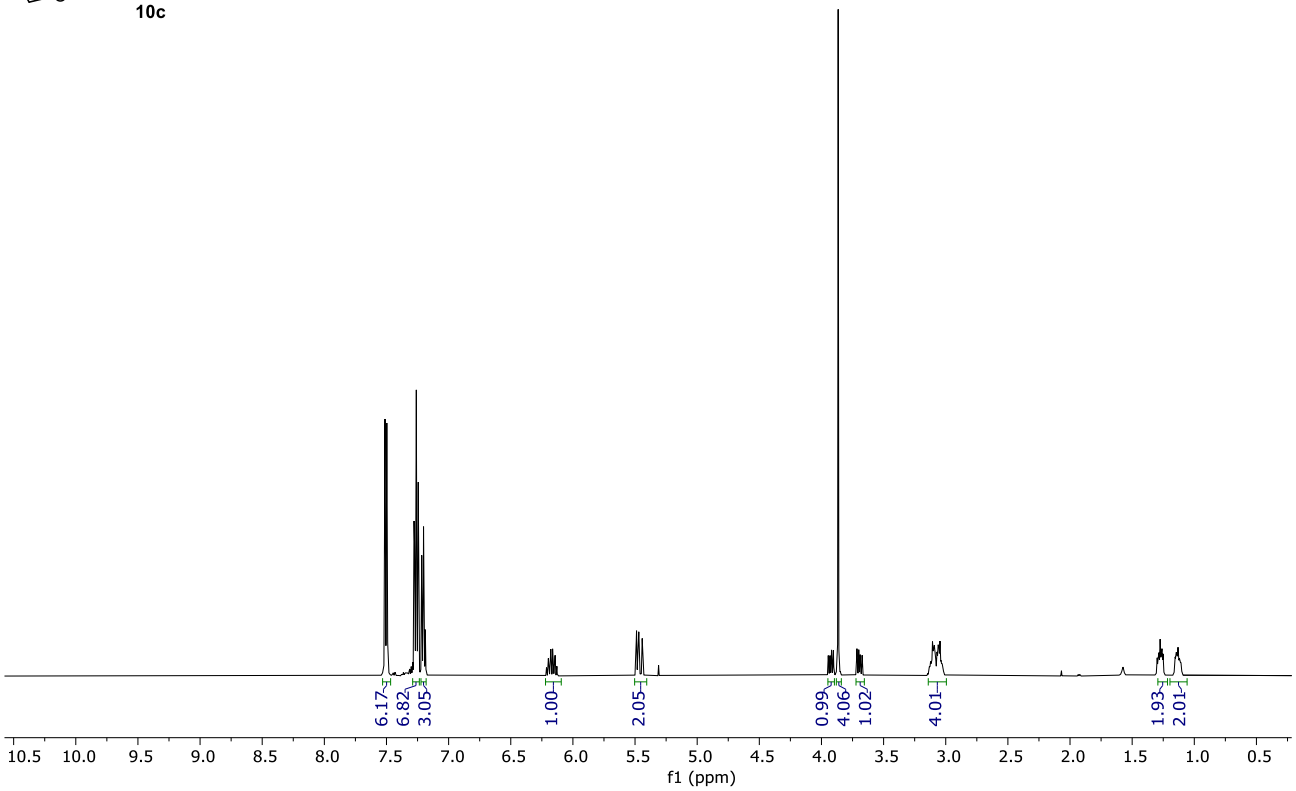
**10b**

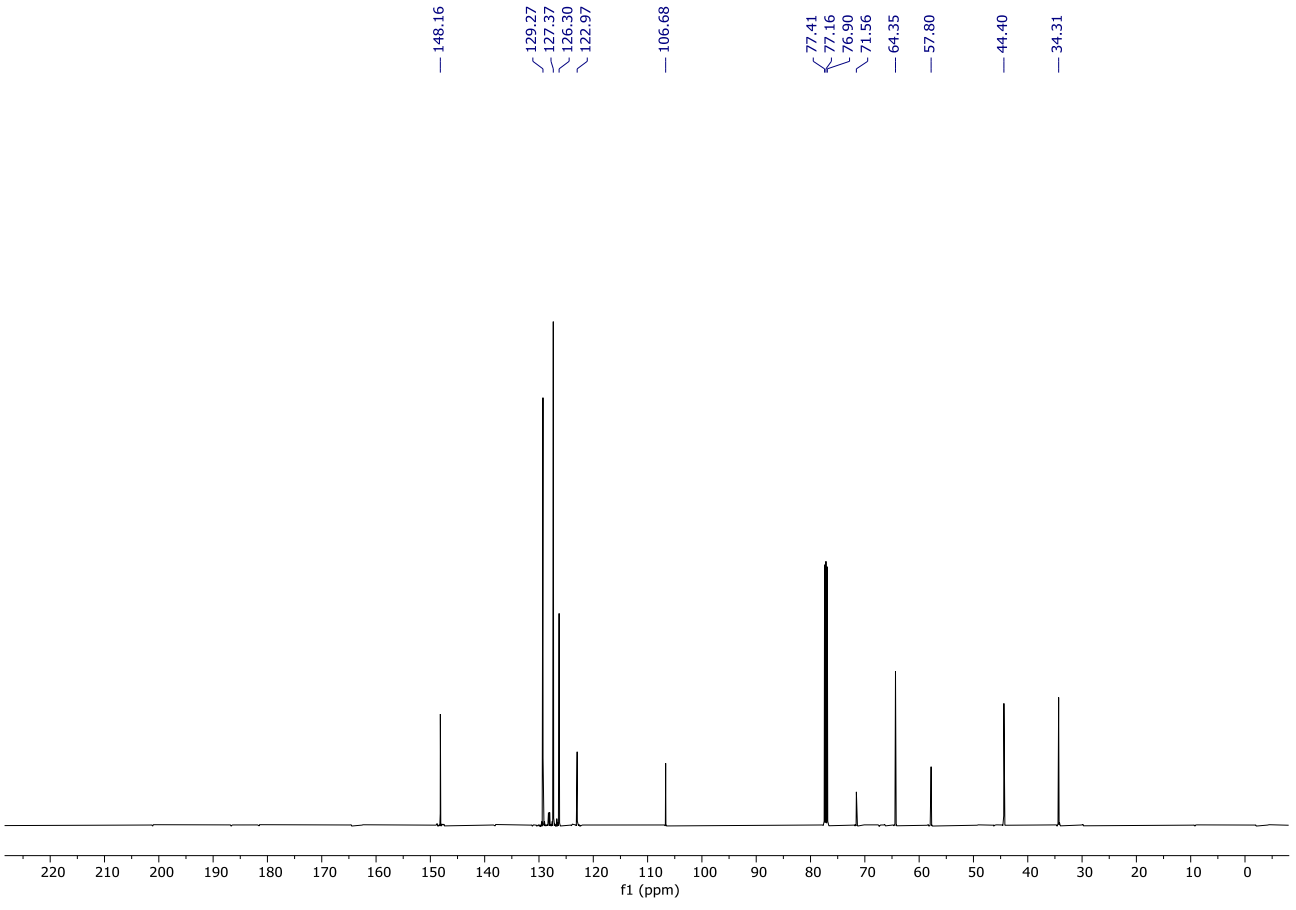

6.01
6.34
3.14
0.96
1.93
0.96
1.04
1.84
1.88
2.15
1.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

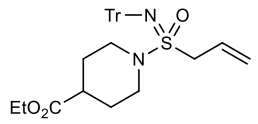

148.07
129.23
127.44
126.40
123.22
77.48
77.16
76.84
71.63
66.26
57.38
46.45
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Tr—N
O
S
N
O
O

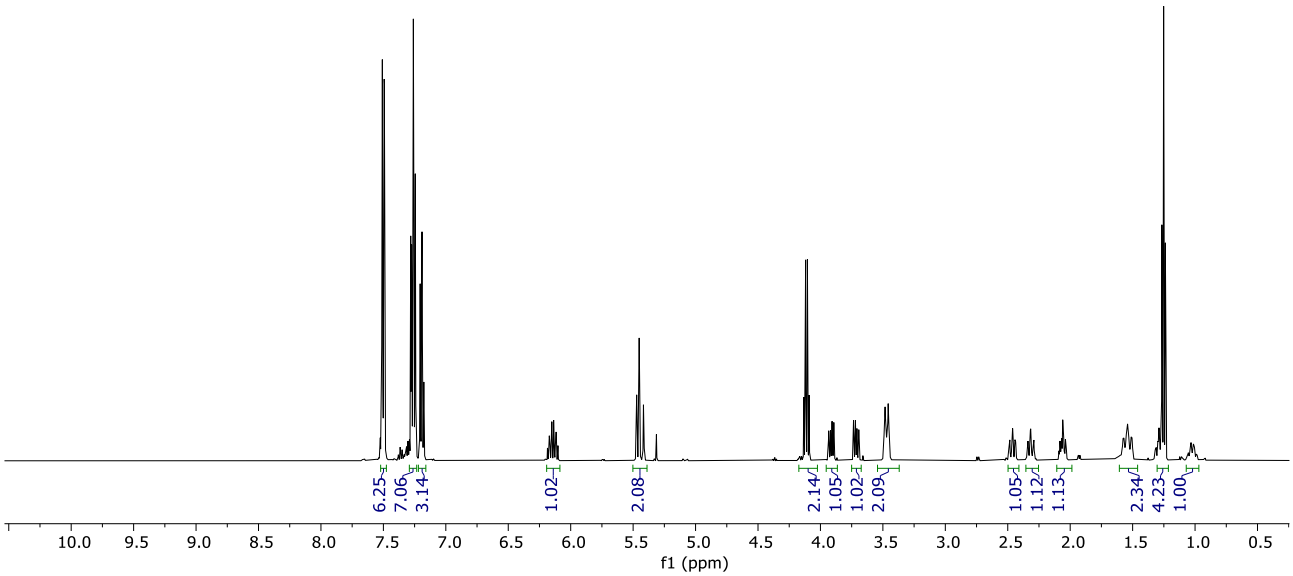
**10c**

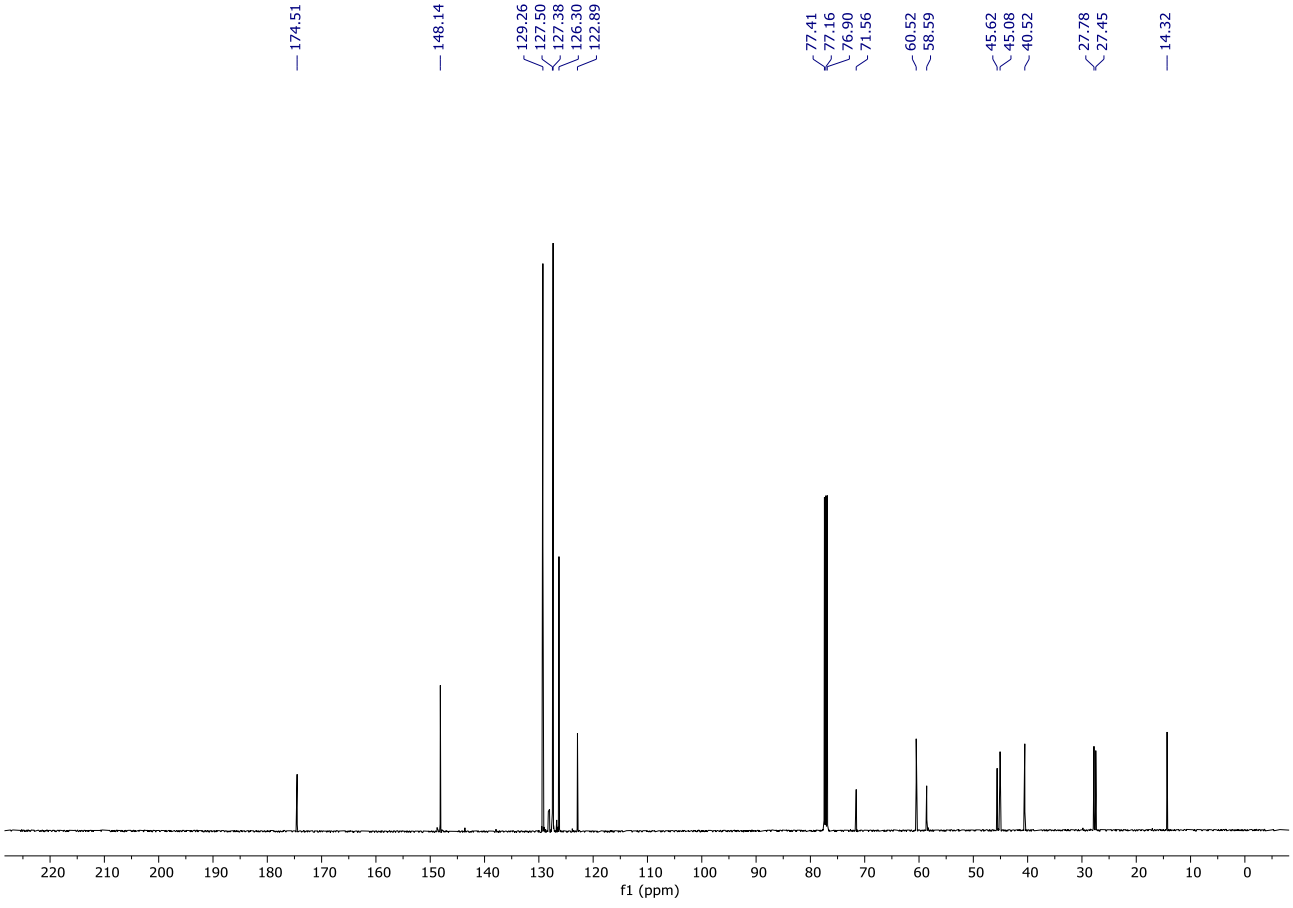

6.17
6.82
3.05
1.00
2.05
0.99
4.06
1.02
4.01
1.93
2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

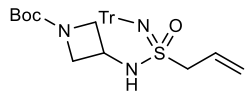

148.16
129.27
127.37
126.30
122.97
106.68
77.41
77.16
76.90
71.56
64.35
57.80
44.40
34.31
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Tr—N
O
S
N
EtO2C

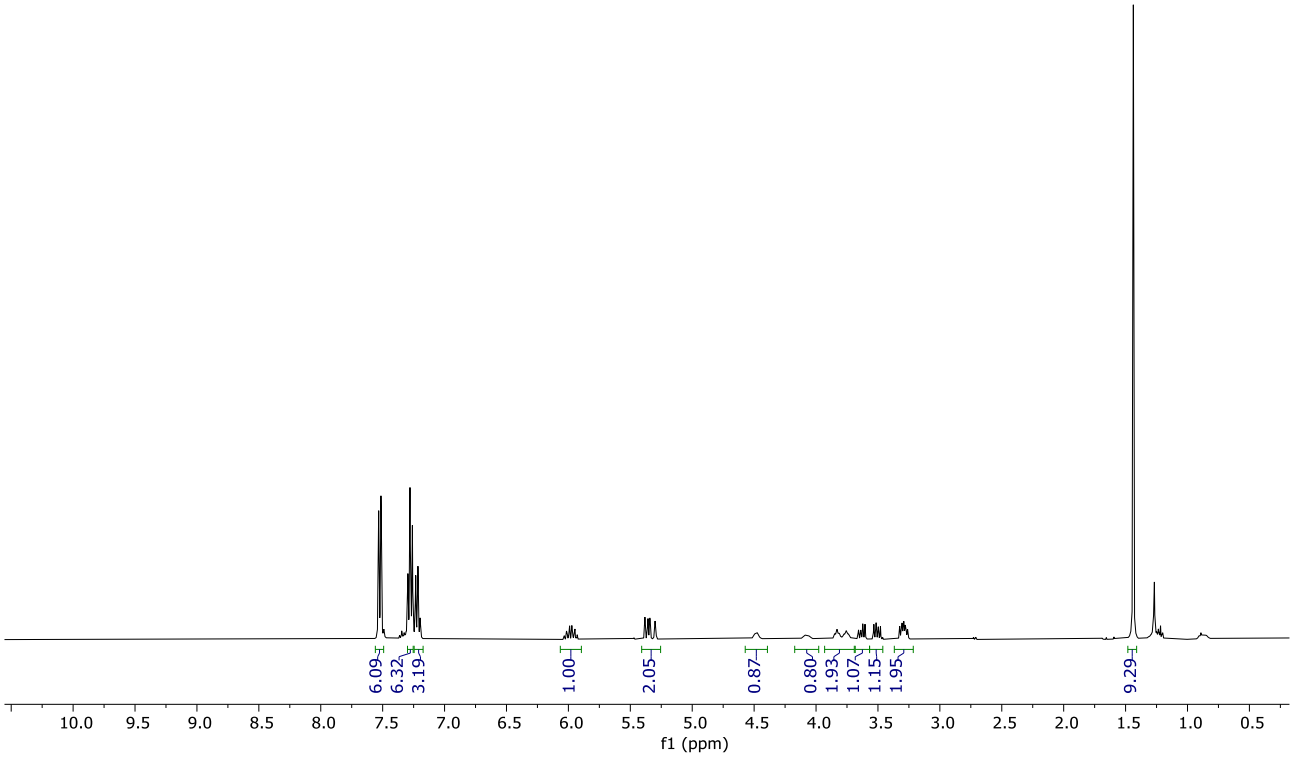
**10d**

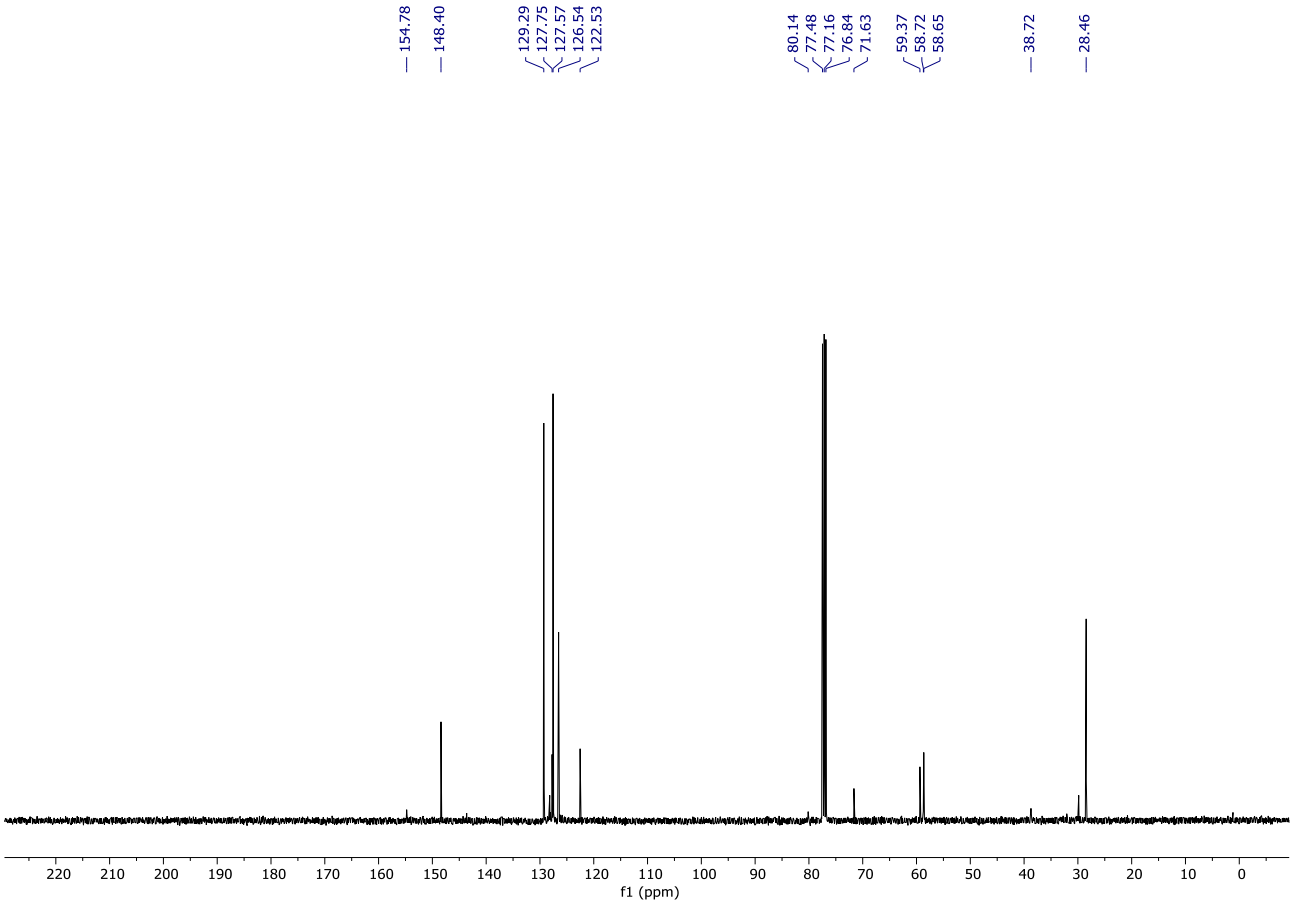

6.25
7.06
3.14
1.02
2.08
2.14
1.05
1.02
2.09
1.05
1.12
1.13
2.34
4.23
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

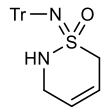

174.51
148.14
129.26
127.50
127.38
126.30
122.89
77.41
77.16
76.90
71.56
60.52
58.59
45.62
45.08
40.52
27.78
27.45
14.32
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Boc
N
Tr
N
O
S
N
H

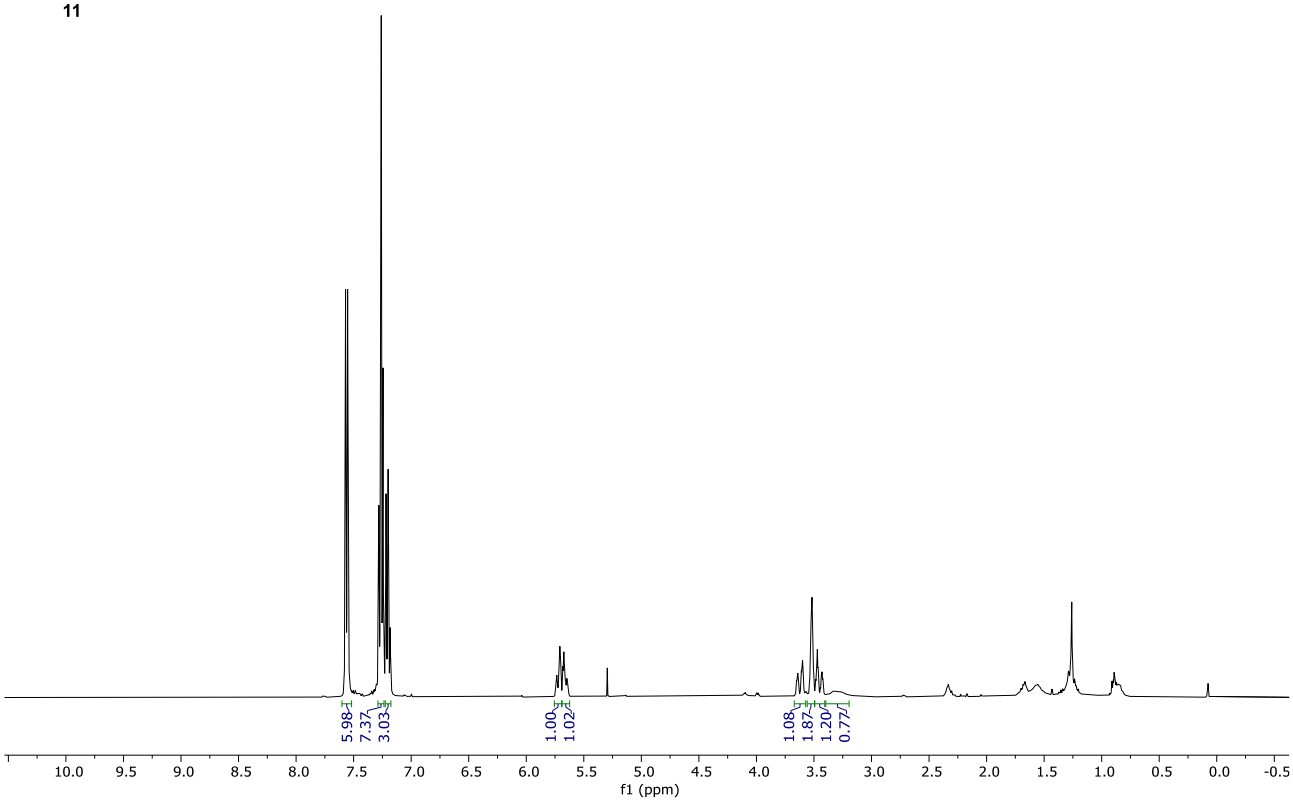
**10e**

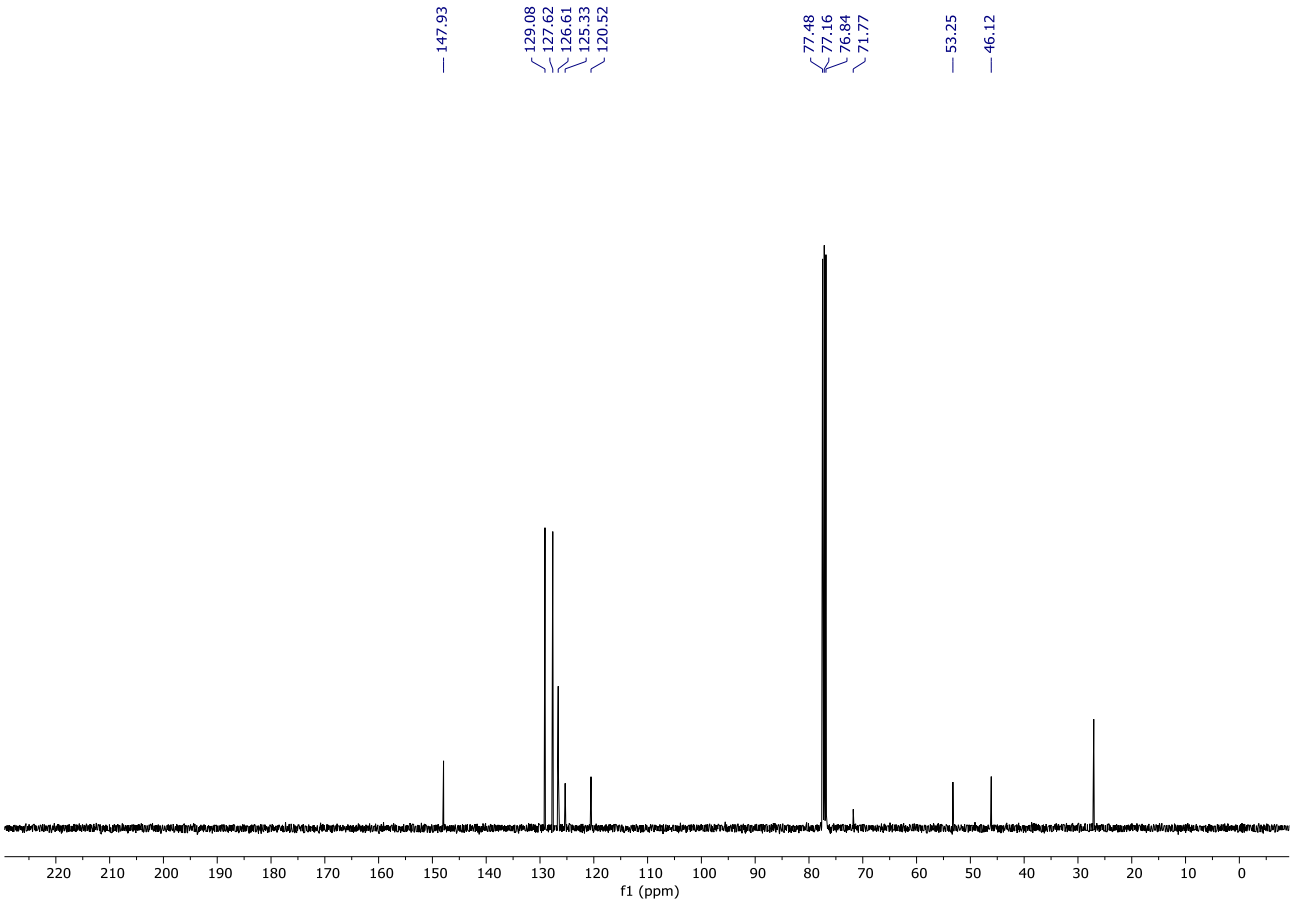

6.09
6.32
3.19
1.00
2.05
0.87
0.80
1.93
1.07
1.15
1.95
9.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


154.78
148.40
129.29
127.75
127.57
126.54
122.53
80.14
77.48
77.16
76.84
71.63
59.37
58.72
58.65
38.72
28.46
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Tr—N
O
S
HN

**11**


5.98
7.37
3.03
1.00
1.02
1.08
1.87
1.20
0.77
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


147.93
129.08
127.62
126.61
125.33
120.52
77.48
77.16
76.84
71.77
53.25
46.12
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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