

## Supporting Information

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## 1. General

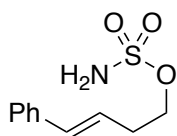
New compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, and HRMS.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer ( $^1\text{H}$  NMR, 400 MHz;  $^{13}\text{C}$  NMR, 100 MHz).  $^1\text{H}$  NMR chemical shifts were determined relative to  $\text{Me}_4\text{Si}$  (0.0 ppm) in  $\text{CDCl}_3$ .  $^{13}\text{C}$  NMR chemical shifts were determined relative to  $\text{CDCl}_3$  (77.0 ppm). Infrared spectra were recorded on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. High-resolution mass spectra were obtained on JEOL JMS-700 (magnetic sector type mass spectrometer) and JEOL JMS-T100LP mass spectrometers. Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. All reactions were carried out under nitrogen. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd.) or Chromatorex NH (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F<sub>254</sub> and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating.

## 2. Materials

Phenyl sulfamate was prepared according to the reported procedure.<sup>1</sup> Dehydrated acetonitrile was used from a solvent purification system. All other solvents and reagents were purchased and used as obtained.

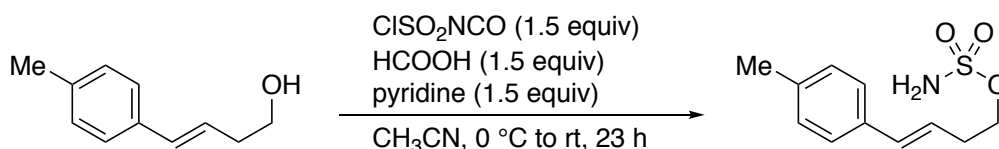
### 3. Preparation of unsaturated sulfamate esters

#### (*E*)-4-phenylbut-3-en-1-yl sulfamate (1a)



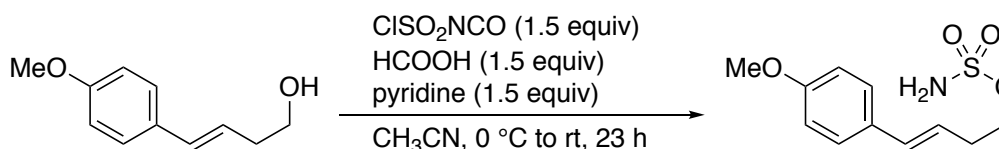
This compound was prepared according to the reported procedure.<sup>2</sup>

#### (*E*)-4-(*p*-tolyl)but-3-en-1-yl sulfamate (1b)



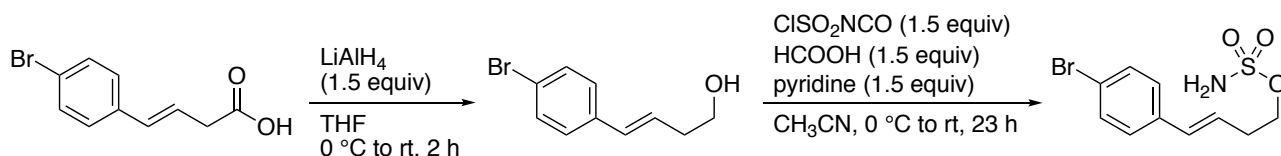
According to the reported procedure,<sup>2</sup> the reaction using ClSO<sub>2</sub>NCO (340  $\mu$ L, 3.9 mmol), formic acid (150  $\mu$ L, 3.9 mmol), (*E*)-4-(*p*-tolyl)but-3-en-1-ol (427 mg, 2.6 mmol), CH<sub>3</sub>CN (3 mL), and pyridine (360  $\mu$ L, 3.9 mmol) in DMA (3 mL) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (467 mg, 74% yield). mp: 78–79 °C; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.11 (dt, *J* = 16.0, 6.8 Hz, 1H), 4.74 (brs, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 2.65 (tdd, *J* = 6.8, 6.8, 1.2 Hz, 2H), 2.33 (s, 3H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.4, 134.0, 133.2, 129.3, 126.0, 122.8, 70.6, 32.4, 21.2; IR: (ATR) 3375, 1545, 1512, 1350, 1194, 1161, 962, 932, 797, 781 cm<sup>-1</sup>; HRMS: (CI) calcd for (C<sub>11</sub>H<sub>16</sub>NO<sub>3</sub>S) 242.0851 ([M+H]<sup>+</sup>) found *m/z* 242.0848

#### (*E*)-4-(4-methoxyphenyl)but-3-en-1-yl sulfamate (1c)



According to the reported procedure,<sup>2</sup> the reaction using ClSO<sub>2</sub>NCO (305  $\mu$ L, 3.5 mmol), formic acid (130  $\mu$ L, 3.5 mmol), (*E*)-4-(4-methoxyphenyl)but-3-en-1-ol (390 mg, 2.2 mmol), CH<sub>3</sub>CN (3 mL), and pyridine (325  $\mu$ L, 3.5 mmol) in DMA (3 mL) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (477 mg, 84% yield). mp: 88–89 °C; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30–7.21 (m, 2H), 6.87–6.81 (m, 2H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.02 (dt, *J* = 15.6, 6.4 Hz, 1H), 4.79 (brs, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.81 (s, 3H), 2.64 (dt, *J* = 6.4, 6.4 Hz, 2H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.1, 132.8, 129.6, 127.3, 121.6, 114.0, 70.7, 55.3, 32.4; IR: (ATR) 3362, 3273, 1510, 1354, 1169, 937, 897, 841, 768, 748 cm<sup>-1</sup>; HRMS: (CI) calcd for (C<sub>11</sub>H<sub>16</sub>NO<sub>4</sub>S) 258.0800 ([M+H]<sup>+</sup>) found *m/z* 258.0798

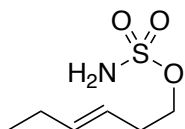
### (*E*)-4-(4-bromophenyl)but-3-en-1-yl sulfamate (1d)



According to the reported procedure,<sup>3</sup> (*E*)-4-(4-bromophenyl)but-3-en-1-ol was prepared using  $\text{LiAlH}_4$  (285 mg, 7.5 mmol), THF (40 mL), and (*E*)-4-(4-bromophenyl)but-3-enoic acid (1.18 g, 5.0 mmol). The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc = 70:30) to give the mixture of product and by-product, which was used next step without further purification.

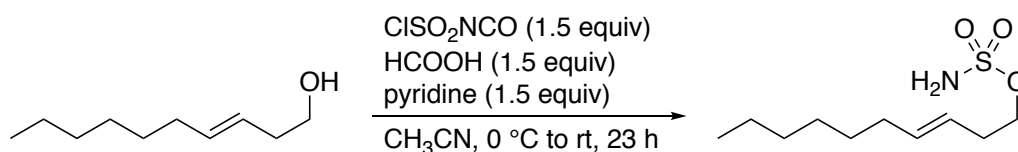
According to the reported procedure,<sup>2</sup> the reaction using  $\text{ClSO}_2\text{NCO}$  (390  $\mu\text{L}$ , 4.5 mmol), formic acid (170  $\mu\text{L}$ , 4.5 mmol), the mixture (709 mg),  $\text{CH}_3\text{CN}$  (4 mL), and pyridine (420  $\mu\text{L}$ , 4.5 mmol) in DMA (4 mL) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) then recrystallization gave the product as a colorless solid (367 mg, 25% yield). mp: 97–98 °C;  $^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46–7.39 (m, 2H), 7.24–7.18 (m, 2H), 6.46 (d,  $J$  = 16.0 Hz, 1H), 6.17 (dt,  $J$  = 16.0, 6.8 Hz, 1H), 4.71 (brs, 2H), 4.32 (t,  $J$  = 6.8 Hz, 2H), 2.66 (tdd,  $J$  = 6.8, 6.8, 1.6 Hz, 2H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.7, 132.2, 131.7, 127.7, 124.8, 121.3, 70.3, 32.4; IR: (ATR) 3354, 3264, 1341, 1165, 964, 930, 796, 700  $\text{cm}^{-1}$ ; HRMS: (EI) calcd for ( $\text{C}_{10}\text{H}_{12}\text{BrNO}_3\text{S}$ ) 304.9721 ( $\text{M}^+$ ) found  $m/z$  304.9725

### (*E*)-hex-3-en-1-yl sulfamate (1e)



This compound was prepared according to the reported procedure.<sup>4</sup>

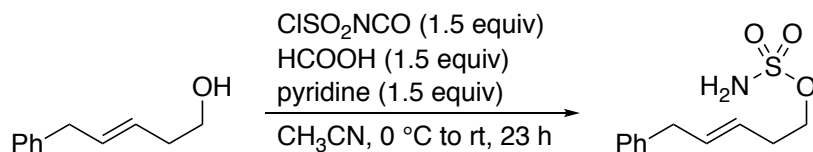
### (*E*)-dec-3-en-1-yl sulfamate (1f)



According to the reported procedure,<sup>2</sup> the reaction using  $\text{ClSO}_2\text{NCO}$  (520  $\mu\text{L}$ , 6.0 mmol), formic acid (230  $\mu\text{L}$ , 6.0 mmol), (*E*)-dec-3-en-1-ol (641 mg, 4.0 mmol),  $\text{CH}_3\text{CN}$  (6 mL), and pyridine (560  $\mu\text{L}$ , 6.0 mmol) in DMA (6 mL) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (586 mg, 62% yield). mp 38–39 °C;  $^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.63–5.51 (m, 1H), 5.42–5.30 (m, 1H), 4.90 (brs, 2H), 4.20 (t,  $J$  = 6.8 Hz, 2H), 2.44 (dtd,  $J$  = 6.8, 6.8, 1.2 Hz, 2H), 2.00 (dt,  $J$  = 6.8, 6.8 Hz, 2H), 1.39–1.20 (m, 8H), 0.88 (t,  $J$  = 6.8 Hz, 3H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.8, 123.4, 71.0, 32.6, 32.0, 31.7, 29.2, 28.8, 22.6, 14.1; IR: (ATR) 3372, 3291, 2918, 2851, 1342, 1173, 914, 781  $\text{cm}^{-1}$ ;

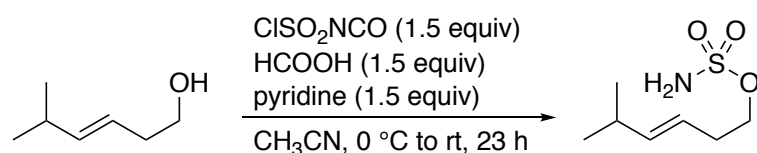
HRMS: (CI) calcd for (C<sub>10</sub>H<sub>22</sub>NO<sub>3</sub>S) 236.1320 ([M+H]<sup>+</sup>) found *m/z* 236.1317

**(E)-5-phenylpent-3-en-1-yl sulfamate (1g)**



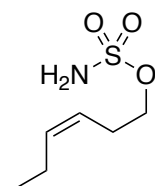
According to the reported procedure,<sup>2</sup> the reaction using ClSO<sub>2</sub>NCO (650 μL, 7.5 mmol), formic acid (285 μL, 7.5 mmol), (E)-5-phenylpent-3-en-1-ol (810 mg, 5.0 mmol), CH<sub>3</sub>CN (6 mL), and pyridine (695 μL, 7.5 mmol) in DMA (6 mL) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless liquid (808 mg, 68% yield). <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ 7.34–7.14 (m, 5H), 5.75 (dtt, *J* = 15.2, 6.8, 1.6 Hz, 1H), 5.47 (dtt, *J* = 15.2, 6.8, 1.6 Hz, 1H), 4.76 (brs, 2H), 4.21 (t, *J* = 6.8 Hz, 2H), 3.35 (d, *J* = 6.8 Hz, 2H), 2.48 (tdd, *J* = 6.8, 6.8, 1.6 Hz, 2H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ 140.2, 133.1, 128.4, 126.1, 125.2, 70.6, 38.9, 31.8 (one sp<sup>2</sup> signal was not observed because of overlapping); IR: (ATR) 3377, 3287, 1356, 1174, 966, 916, 783, 745 cm<sup>-1</sup>; HRMS: (CI) calcd for (C<sub>11</sub>H<sub>16</sub>NO<sub>3</sub>S) 242.0851 ([M+H]<sup>+</sup>) found *m/z* 242.0848

**(E)-5-methylhex-3-en-1-yl sulfamate (1h)**



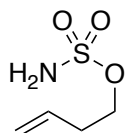
According to the reported procedure,<sup>2</sup> the reaction using ClSO<sub>2</sub>NCO (575 μL, 6.6 mmol), formic acid (250 μL, 6.6 mmol), (E)-5-methylhex-3-en-1-ol (504 mg, 4.4 mmol), CH<sub>3</sub>CN (6 mL), and pyridine (610 μL, 6.6 mmol) in DMA (6 mL) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 50:50) gave the product as a colorless liquid (658 mg, 77% yield). <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ 5.55 (dtt, *J* = 15.2, 6.4, 1.2 Hz, 1H), 5.33 (dtd, 15.2, 6.8, 1.6 Hz, 1H), 4.75 (brs, 2H), 4.20 (t, *J* = 6.8 Hz, 2H), 2.44 (tdd, *J* = 6.8, 6.8, 1.2 Hz, 2H), 2.26 (dq, *J* = 6.4, 6.4, 6.4 Hz, 1H), 0.97 (d, *J* = 6.4 Hz, 6H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ 141.8, 120.5, 71.1, 32.0, 31.0, 22.3; IR: (ATR) 3362, 3267, 2959, 2868, 1339, 1169, 970, 926, 837, 810 cm<sup>-1</sup>; HRMS: (CI) calcd for (C<sub>7</sub>H<sub>16</sub>NO<sub>3</sub>S) 194.0851 ([M+H]<sup>+</sup>) found *m/z* 194.0847

**(Z)-hex-3-en-1-yl sulfamate (1i)**



This compound was prepared according to the reported procedure.<sup>4</sup>

### but-3-en-1-yl sulfamate (1j)



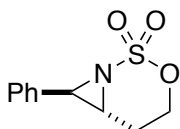
This compound was prepared according to the reported procedure.<sup>2</sup>

### 4. Intramolecular aziridination of unsaturated sulfamate esters

**Typical procedure:** A heat-gun-dried reaction flask containing a magnetic stir bar was charged with NaI (0.44 mmol), sulfamate ester **1** (0.2 mmol), and CH<sub>3</sub>CN (5 mL). To the mixture, *t*-BuOCl (0.44 mmol) was added, and the mixture was stirred at room temperature for 1 h in the dark. The reaction was quenched by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aq. (1 M, 5 mL), and extracted with Et<sub>2</sub>O (3 x 10 mL). Collected organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel gave the product.

### Product data

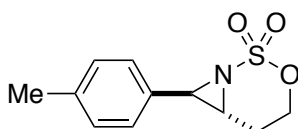
#### *trans*-7-phenyl-3-oxa-2-thia-1-azabicyclo[4.1.0]heptane 2,2-dioxide (2a)



According to the typical procedure, the reaction using NaI (66.1 mg, 0.44 mmol), (*E*)-4-phenylbut-3-en-1-yl sulfamate (45.6 mg, 0.20 mmol), CH<sub>3</sub>CN (5 mL), and *t*-BuOCl (50 μL, 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (35.9 mg, 80% yield). <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ 7.40–7.32 (m, 3H), 7.32–7.20 (m, 2H), 4.77 (ddd, *J* = 12.4, 6.4, 6.4 Hz, 1H), 4.53 (ddd, *J* = 12.4, 6.4, 6.4 Hz, 1H), 3.88 (d, *J* = 4.4 Hz, 1H), 3.26 (ddd, *J* = 6.4, 4.4, 2.4 Hz, 1H), 2.50 (dddd, *J* = 14.4, 6.4, 6.4, 6.4 Hz, 1H), 2.40 (dddd, *J* = 14.4, 6.4, 6.4, 2.4 Hz, 1H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ 134.1, 128.7, 126.2, 68.8, 50.5, 47.7, 18.7 (one sp<sup>2</sup> signal was not observed because of overlapping)

The analytical data for this compound were in excellent agreement with the reported data.<sup>2</sup>

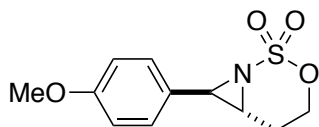
#### *trans*-7-(*p*-tolyl)-3-oxa-2-thia-1-azabicyclo[4.1.0]heptane 2,2-dioxide (2b)



According to the typical procedure, the reaction using NaI (66.3 mg, 0.44 mmol), (*E*)-4-(*p*-tolyl)but-3-en-1-yl sulfamate (46.7 mg, 0.19 mmol), CH<sub>3</sub>CN (5 mL), and *t*-BuOCl (50 μL, 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (36.8 mg, 79% yield). The

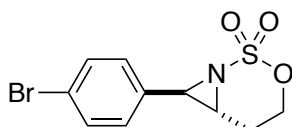
configuration of the product was determined by comparing their  $^1\text{H}$  NMR signals with product **2a**. mp: 105–106 °C;  $^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22–7.13 (m, 4H), 4.77 (ddd,  $J = 12.4, 6.4, 6.4$  Hz, 1H), 4.53 (ddd,  $J = 12.4, 6.4, 6.4$  Hz, 1H), 3.85 (d,  $J = 4.4$  Hz, 1H), 3.25 (ddd,  $J = 6.4, 4.4, 2.4$  Hz, 1H), 2.49 (dddd,  $J = 15.2, 6.4, 6.4, 6.4$  Hz, 1H), 2.44–2.26 (m, 1H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.7, 131.1, 129.4, 126.2, 68.8, 50.3, 47.7, 21.2, 18.8; IR: (ATR) 2924, 1726, 1360, 1260, 1117, 878, 783  $\text{cm}^{-1}$ ; HRMS: (CI) calcd for ( $\text{C}_{11}\text{H}_{14}\text{NO}_3\text{S}$ ) 240.0694 ( $[\text{M}+\text{H}]^+$ ) found  $m/z$  240.0699

***trans*-7-(4-methoxyphenyl)-3-oxa-2-thia-1-azabicyclo[4.1.0]heptane 2,2-dioxide (2c)**



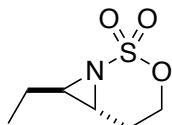
According to the typical procedure at 0 °C, the reaction using NaI (66.4 mg, 0.44 mmol), (*E*)-4-(4-methoxyphenyl)but-3-en-1-yl sulfamate (51.2 mg, 0.20 mmol),  $\text{CH}_3\text{CN}$  (5 mL), and *t*-BuOCl (50  $\mu\text{L}$ , 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (45.6 mg, 90% yield). The configuration of the product was determined by comparing their  $^1\text{H}$  NMR signals with product **2a**. mp: 115–117 °C;  $^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25–7.18 (m, 2H), 6.91–6.83 (m, 2H), 4.76 (ddd,  $J = 12.4, 6.4, 6.4$  Hz, 1H), 4.52 (ddd,  $J = 12.4, 6.4, 6.4$  Hz, 1H), 3.84 (d,  $J = 4.4$  Hz, 1H), 3.80 (s, 3H), 3.25 (ddd,  $J = 6.4, 4.4, 2.0$  Hz, 1H), 2.49 (dddd,  $J = 14.4, 6.4, 6.4, 6.4$  Hz, 1H), 2.38 (dddd,  $J = 14.4, 6.4, 6.4, 2.0$  Hz, 1H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.0, 127.5, 126.0, 114.1, 68.8, 55.3, 50.3, 47.6, 18.7; IR: (ATR) 3263, 2895, 1510, 1339, 1238, 1169, 1084, 1003, 932, 887, 775  $\text{cm}^{-1}$ ; HRMS: (CI) calcd for ( $\text{C}_{11}\text{H}_{14}\text{NO}_4\text{S}$ ) 256.0644 ( $[\text{M}+\text{H}]^+$ ) found  $m/z$  256.0641

***trans*-7-(4-bromophenyl)-3-oxa-2-thia-1-azabicyclo[4.1.0]heptane 2,2-dioxide (2d)**



According to the typical procedure, the reaction using NaI (67.9 mg, 0.45 mmol), (*E*)-4-(4-bromophenyl)but-3-en-1-yl sulfamate (61.2 mg, 0.20 mmol),  $\text{CH}_3\text{CN}$  (5 mL), and *t*-BuOCl (50  $\mu\text{L}$ , 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 60:40) gave the product as a colorless solid (48.2 mg, 79% yield). The configuration of the product was determined by comparing their  $^1\text{H}$  NMR signals with product **2a**. mp: 135–136 °C;  $^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53–7.40 (m, 2H), 7.21–7.13 (m, 2H), 4.83–4.74 (m, 1H), 4.53 (ddd,  $J = 12.0, 6.4, 6.4$  Hz, 1H), 3.83 (d,  $J = 4.4$  Hz, 1H), 3.22 (ddd,  $J = 6.4, 4.4, 2.4$  Hz, 1H), 2.50 (dddd,  $J = 15.2, 6.4, 6.4, 6.4$  Hz, 1H), 2.41 (dddd,  $J = 15.2, 6.4, 6.4, 2.4$  Hz, 1H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.2, 131.9, 127.9, 122.8, 68.8, 50.4, 47.1, 18.7; IR: (ATR) 1491, 1362, 1176, 1047, 951, 910, 872, 827, 771  $\text{cm}^{-1}$ ; HRMS: (CI) calcd for ( $\text{C}_{10}\text{H}_{11}\text{BrNO}_3\text{S}$ ) 303.9643 ( $[\text{M}+\text{H}]^+$ ) found  $m/z$  303.9642

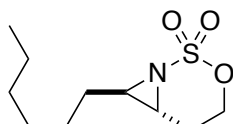
***trans*-7-ethyl-3-oxa-2-thia-1-azabicyclo[4.1.0]heptane 2,2-dioxide (2e)**



According to the typical procedure, the reaction using NaI (66.9 mg, 0.45 mmol), (*E*)-hex-3-en-1-yl sulfamate (35.8 mg, 0.20 mmol), CH<sub>3</sub>CN (5 mL), and *t*-BuOCl (50 μL, 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless liquid (21.6 mg, 61% yield). <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ 4.66 (ddd, *J* = 12.8, 6.8, 6.0 Hz, 1H), 4.39 (ddd, *J* = 12.8, 7.2, 6.0 Hz, 1H), 3.04 (ddd, *J* = 6.0, 4.4, 2.4 Hz, 1H), 2.85 (ddd, *J* = 7.2, 4.4, 4.4 Hz, 1H), 2.42 (dddd, *J* = 15.2, 6.0, 6.0, 6.0 Hz, 1H), 2.30 (dddd, *J* = 15.2, 7.2, 6.8, 2.4 Hz, 1H), 1.77–1.65 (m, 1H), 1.58–1.46 (m, 1H), 1.06 (dd, *J* = 7.2, 7.2 Hz, 3H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ 68.5, 48.3, 47.7, 24.5, 18.9, 10.2

The analytical data for this compound were in excellent agreement with the reported data.<sup>4</sup>

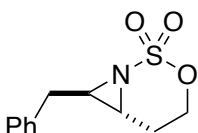
***trans*-7-hexyl-3-oxa-2-thia-1-azabicyclo[4.1.0]heptane 2,2-dioxide (2f)**



According to the typical procedure, the reaction using NaI (66.0 mg, 0.44 mmol), (*E*)-dec-3-en-1-yl sulfamate (47.9 mg, 0.20 mmol), CH<sub>3</sub>CN (5 mL), and *t*-BuOCl (50 μL, 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless liquid (40.0 mg, 84% yield). The configuration of the product was determined by comparing their <sup>1</sup>H NMR signals with product **2e**.

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ 4.66 (ddd, *J* = 12.4, 6.0, 6.0 Hz, 1H), 4.39 (ddd, *J* = 12.4, 6.0, 6.0 Hz, 1H), 3.01 (ddd, *J* = 6.4, 4.4, 2.4 Hz, 1H), 2.86 (ddd, *J* = 5.2, 5.2, 4.4 Hz, 1H), 2.48–2.36 (m, 1H), 2.28–2.16 (m, 1H), 1.69–1.56 (m, 1H), 1.56–1.41 (m, 3H), 1.41–1.18 (m, 6H), 0.89 (t, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ 68.4, 47.9, 47.2, 31.6, 31.3, 28.7, 26.1, 22.5, 19.0, 14.0; IR: (ATR) 2955, 2928, 2859, 1364, 1179, 928, 893, 779, 754 cm<sup>-1</sup>; HRMS: (CI) calcd for (C<sub>10</sub>H<sub>20</sub>NO<sub>3</sub>S) 234.1164 ([M+H]<sup>+</sup>) found *m/z* 234.1167

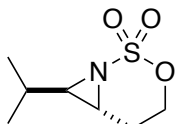
***trans*-7-benzyl-3-oxa-2-thia-1-azabicyclo[4.1.0]heptane 2,2-dioxide (2g)**



According to the typical procedure, the reaction using NaI (67.0 mg, 0.45 mmol), (*E*)-5-phenylpent-3-en-1-yl sulfamate (48.4 mg, 0.20 mmol), CH<sub>3</sub>CN (5 mL), and *t*-BuOCl (50 μL, 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 60:40) gave the product as a colorless liquid (38.9 mg, 81% yield). The configuration of the product was determined by comparing their <sup>1</sup>H NMR signals with product **2e**.

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ 7.38–7.18 (m, 5H), 4.64 (ddd, *J* = 12.0, 6.4, 6.4 Hz, 1H), 4.36 (ddd, *J* = 12.0, 6.4, 6.0 Hz, 1H), 3.16–3.01 (m, 3H), 2.79 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.41 (dddd, *J* = 15.2, 6.4, 6.4, 6.4 Hz, 1H), 2.20 (dddd, *J* = 15.2, 6.4, 6.0, 2.0 Hz, 1H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ 135.9, 128.8, 128.7, 127.1, 68.5, 47.2, 46.8, 37.3, 18.7; IR: (ATR) 2922, 2853, 1362, 1176, 779, 748, 700 cm<sup>-1</sup>; HRMS: (CI) calcd for (C<sub>11</sub>H<sub>14</sub>NO<sub>3</sub>S) 240.0694 ([M+H]<sup>+</sup>) found *m/z* 240.0691

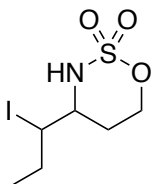
#### ***trans*-7-isopropyl-3-oxa-2-thia-1-azabicyclo[4.1.0]heptane 2,2-dioxide (2h)**



According to the typical procedure, the reaction using NaI (66.8 mg, 0.45 mmol), (*E*)-5-methylhex-3-en-1-yl sulfamate (38.4 mg, 0.20 mmol), CH<sub>3</sub>CN (5 mL), and *t*-BuOCl (50 μL, 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 60:40) gave the product as a colorless liquid (33.5 mg, 88% yield). The configuration of the product was determined by comparing their <sup>1</sup>H NMR signals with product **2e**.

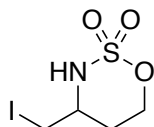
<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ 4.67 (ddd, *J* = 12.0, 6.4, 6.4 Hz, 1H), 4.39 (ddd, *J* = 12.0, 6.4, 6.4 Hz, 1H), 3.07 (ddd, *J* = 6.4, 4.4, 2.0 Hz, 1H), 2.65 (dd, *J* = 6.8, 4.4 Hz, 1H), 2.41 (dddd, *J* = 14.4, 6.4, 6.4, 6.4 Hz, 1H), 2.22 (dddd, *J* = 14.4, 6.4, 6.4, 2.0 Hz, 1H), 1.55 (dq, *J* = 6.8, 6.8, 6.8 Hz, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ 68.5, 52.8, 47.0, 30.3, 19.1, 19.0, 18.8; IR: (ATR) 2965, 2932, 2874, 1362, 1177, 1043, 991, 893, 872, 773 cm<sup>-1</sup>; HRMS: (CI) calcd for (C<sub>7</sub>H<sub>14</sub>NO<sub>3</sub>S) 192.0694 ([M+H]<sup>+</sup>) found *m/z* 192.0695

#### **4-(1-iodopropyl)-1,2,3-oxathiazinane 2,2-dioxide (3)**



According to the typical procedure, the reaction using NaI (66.9 mg, 0.45 mmol), (*Z*)-hex-3-en-1-yl sulfamate (35.6 mg, 0.20 mmol), CH<sub>3</sub>CN (5 mL), and *t*-BuOCl (50 μL, 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (32.7 mg, 54% yield). mp: 72–75 °C; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ 4.81 (ddd, *J* = 12.8, 12.0, 2.4 Hz, 1H), 4.57 (ddd, *J* = 12.0, 5.6, 1.6 Hz, 1H), 4.23 (d, *J* = 11.2 Hz, 1H), 4.10 (ddd, *J* = 8.0, 5.6, 2.4 Hz, 1H), 3.15 (dddd, *J* = 12.0, 11.2, 2.4, 2.4 Hz, 1H), 2.26–2.06 (m, 2H), 2.02–1.88 (m, 1H), 1.63 (dddd, *J* = 14.0, 2.4, 2.4, 1.6 Hz, 1H), 1.07 (dd, *J* = 7.2, 7.2 Hz, 3H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ 70.7, 58.4, 43.4, 31.3, 31.2, 14.5; IR: (ATR) 3223, 2965, 1350, 1192, 1169, 986, 862, 787 cm<sup>-1</sup>; HRMS: (CI) calcd for (C<sub>6</sub>H<sub>13</sub>NO<sub>3</sub>SI) 305.9661 ([M+H]<sup>+</sup>), found *m/z* 305.9665

#### 4-(iodomethyl)-1,2,3-oxathiazinane 2,2-dioxide (4)



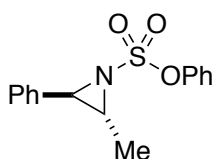
According to the typical procedure, the reaction using NaI (65.4 mg, 0.44 mmol), but-3-en-1-yl sulfamate (32.4 mg, 0.21 mmol), CH<sub>3</sub>CN (5 mL), and *t*-BuOCl (50  $\mu$ L, 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) then gel permeation chromatography gave the product as a colorless liquid (21.4 mg, 36% yield). <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.79 (ddd, *J* = 12.4, 12.0, 2.4 Hz, 1H), 4.59 (ddd, *J* = 12.0, 4.8, 1.6 Hz, 1H), 4.22 (d, *J* = 10.0 Hz, 1H), 3.59–3.48 (m, 1H), 3.44 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.36 (dd, *J* = 10.8, 4.0 Hz, 1H), 2.00 (dddd, *J* = 14.8, 12.4, 12.0, 4.8 Hz, 1H), 1.78 (dddd, *J* = 14.8, 2.4, 2.4, 1.6 Hz, 1H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>)  $\delta$  70.9, 54.3, 29.9, 9.6; IR: (ATR) 3252, 2963, 1418, 1356, 1179, 995, 862, 775 cm<sup>-1</sup>; HRMS: (CI) calcd for (C<sub>4</sub>H<sub>9</sub>NO<sub>3</sub>SI) 277.9348 ([M+H]<sup>+</sup>), found *m/z* 277.9344

#### 5. Intermolecular aziridination of alkenes with a sulfamate ester

**Typical procedure:** A heat-gun-dried reaction flask containing a magnetic stir bar was charged with NaI (0.44 mmol), alkene (0.4 mmol), phenyl sulfamate (0.2 mmol), and CH<sub>3</sub>CN (1 mL). To the mixture, *t*-BuOCl (0.44 mmol) was added, and the mixture was stirred at room temperature for 1 h in the dark. The reaction was quenched by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aq. (1 M, 5 mL), and extracted with Et<sub>2</sub>O (3 x 10 mL). Collected organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel gave the product.

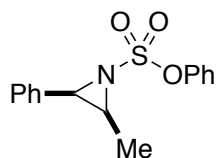
#### Product data

##### phenyl (*E*)-2-methyl-3-phenylaziridine-1-sulfonate (*trans*-8)



According to the typical procedure, the reaction using NaI (66.8 mg, 0.45 mmol), CH<sub>3</sub>CN (1 mL), *trans*- $\beta$ -methylstyrene (47.5 mg, 0.40 mmol), phenyl sulfamate (35.1 mg, 0.20 mmol) and *t*-BuOCl (50  $\mu$ L, 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 90:10) then gel permeation chromatography gave the product as a colorless liquid (42.3 mg, 73% yield). <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40–7.31 (m, 3H), 7.31–7.22 (m, 3H), 7.22–7.12 (m, 4H), 3.71 (d, *J* = 4.4 Hz, 1H), 2.96 (qd, *J* = 5.6, 4.4 Hz, 1H), 1.75 (d, *J* = 5.6 Hz, 3H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.4, 134.5, 129.4, 128.6, 127.1, 126.5, 122.1, 50.9, 48.5, 13.5 (one sp<sup>2</sup> signal was not observed because of overlapping); IR: (ATR) 3064, 1487, 1368, 1190, 1169, 1146, 872, 783 cm<sup>-1</sup>; HRMS: (EI) calcd for (C<sub>15</sub>H<sub>15</sub>NO<sub>3</sub>S) 289.0773 (M<sup>+</sup>), found *m/z* 289.0770

### phenyl (*Z*)-2-methyl-3-phenylaziridine-1-sulfonate (*cis*-8)

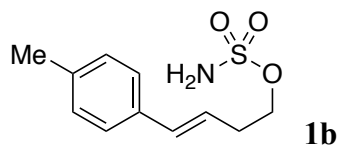


According to the typical procedure, the reaction using NaI (65.7 mg, 0.44 mmol), CH<sub>3</sub>CN (1 mL), *cis*- $\beta$ -methylstyrene (47.4 mg, 0.40 mmol), phenyl sulfamate (34.2 mg, 0.20 mmol) and *t*-BuOCl (50  $\mu$ L, 0.44 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 90:10) then gel permeation chromatography gave the product as a colorless solid (40.8 mg, 71% yield). mp: 60–62 °C; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44–7.24 (m, 10H), 4.03 (d, *J* = 7.2 Hz, 1H), 3.25 (dq, *J* = 7.2, 6.0 Hz, 1H), 1.10 (d, *J* = 6.0 Hz, 3H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.4, 131.8, 129.7, 128.4, 128.2, 127.6, 127.2, 121.8, 47.6, 44.1, 11.5; IR: (ATR) 3071, 1364, 1188, 1142, 878, 793, 764 cm<sup>-1</sup>; HRMS: (EI) calcd for (C<sub>15</sub>H<sub>15</sub>NO<sub>3</sub>S) 289.0773 (M<sup>+</sup>), found *m/z* 289.0776

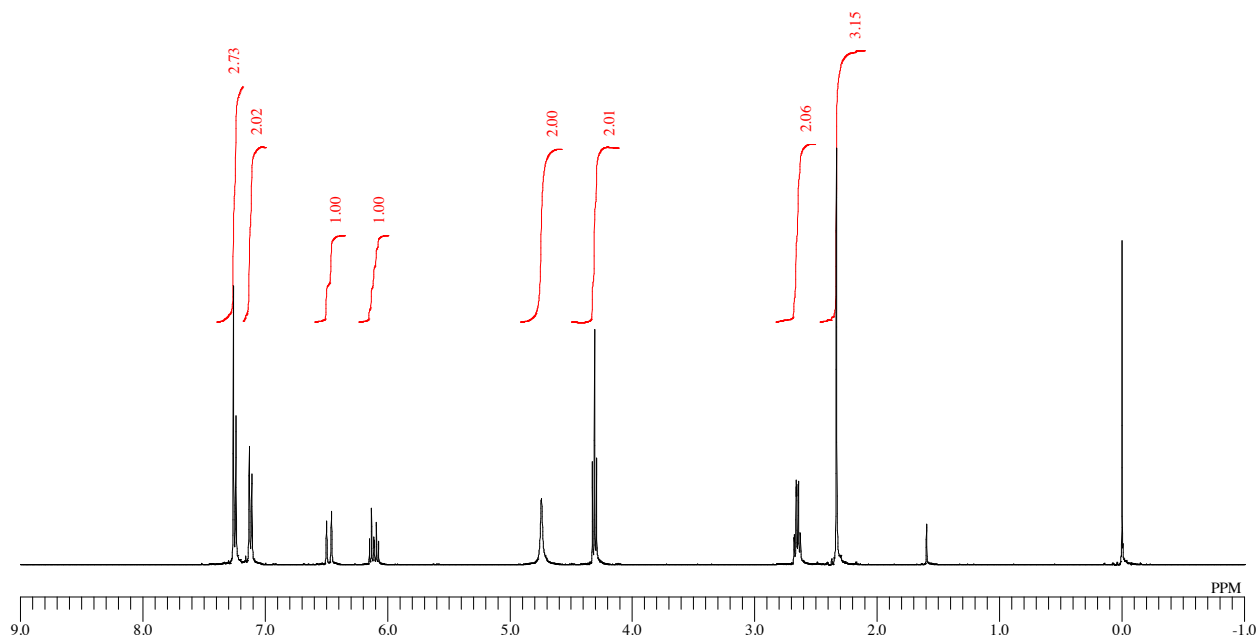
## 6. References

- (1) Petrova, E.; Rasina, D.; Jirgensons, A. *Eur. J. Org. Chem.* **2017**, 1773.
- (2) Guthikonda, K.; When, P. M.; Caliendo, B. J.; Du Bois, J. *Tetrahedron* **2006**, 62, 11331.
- (3) Spivey, A. C.; Laraia, L.; Bayly, A. R.; Rzepa, H. S.; White, A. J. P. *Org. Lett.* **2010**, 12, 900.
- (4) Duran, F.; Leman, L.; Ghini, A.; Burton, G.; Dauban, P.; Dodd, R. H. *Org. Lett.* **2002**, 4, 2481.

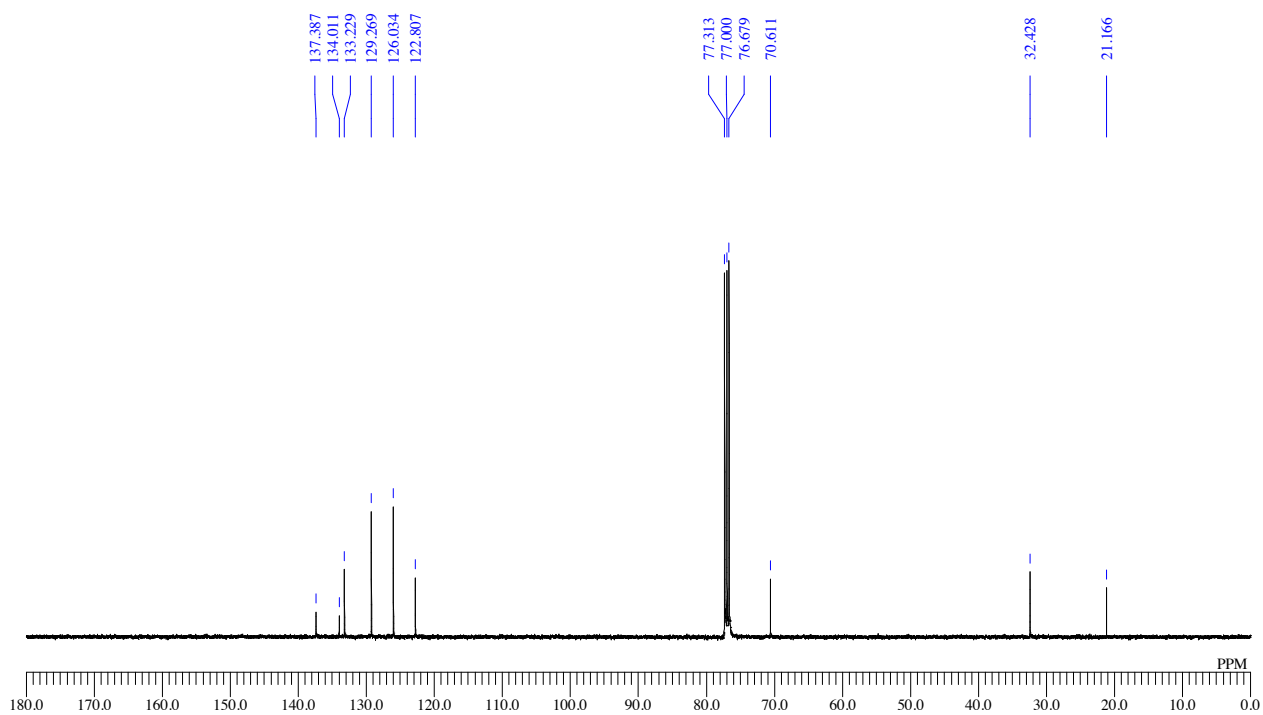
## 7. NMR spectra

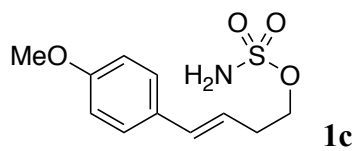


$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )

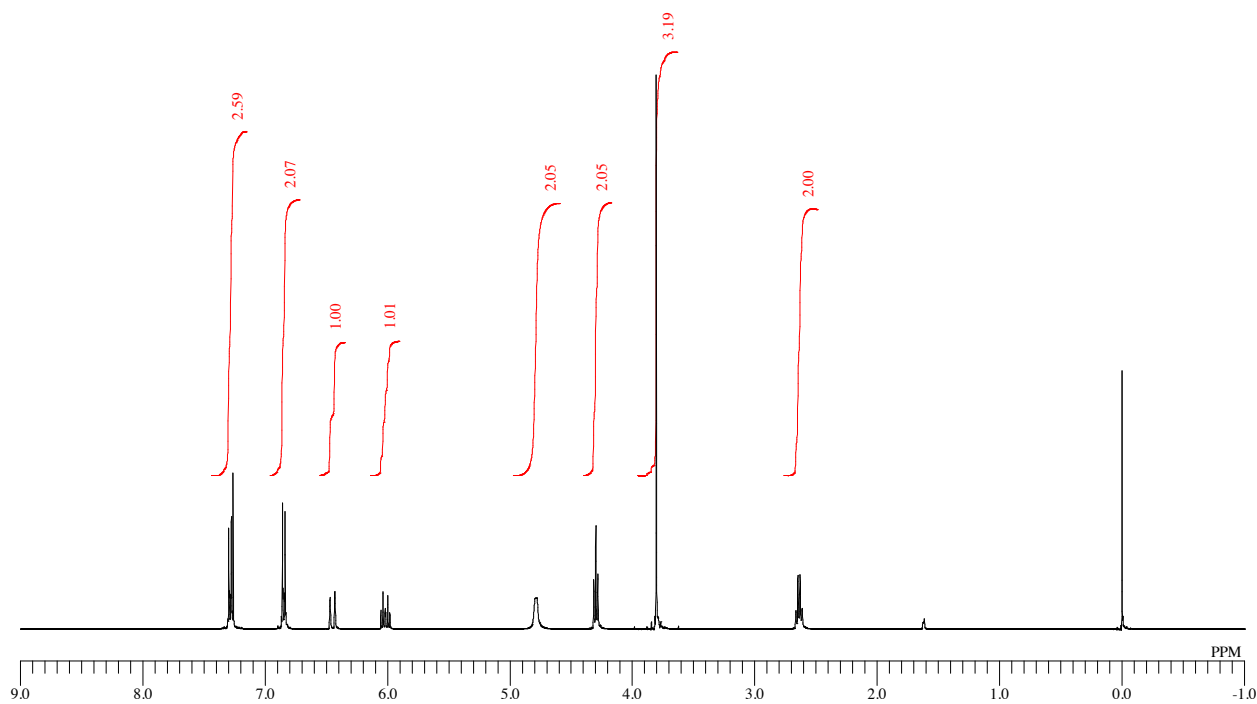


$^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )

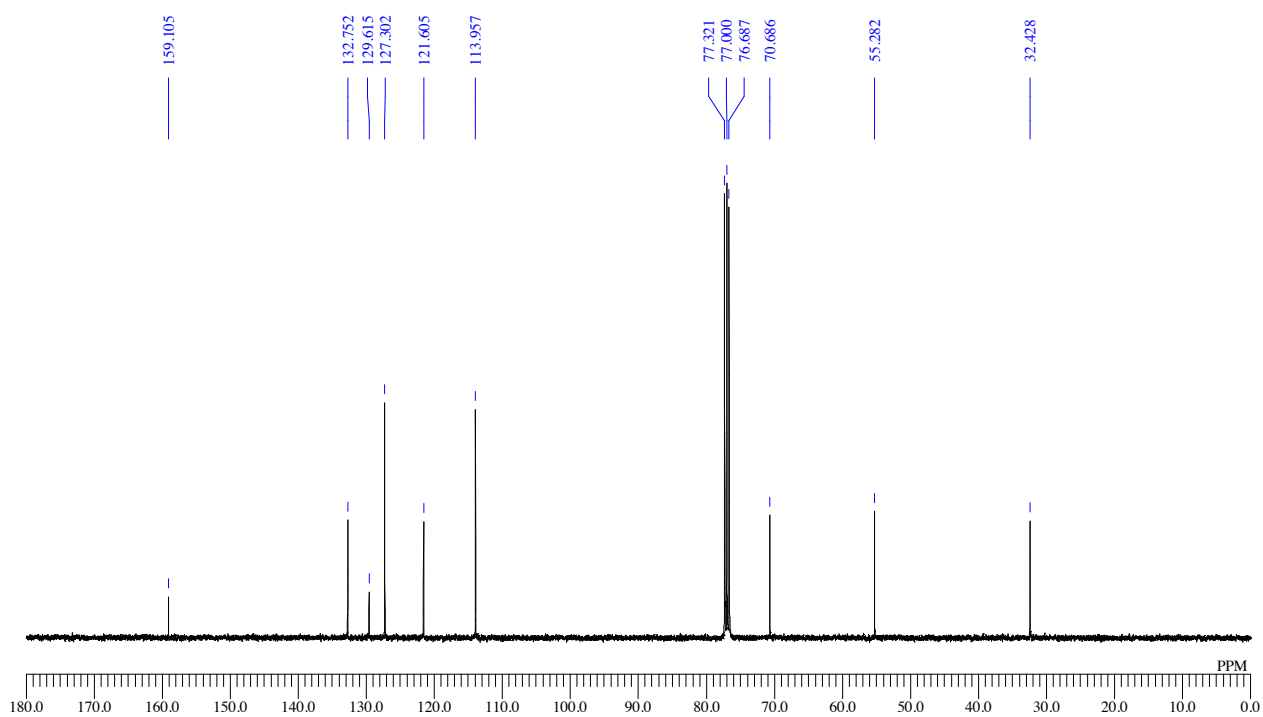


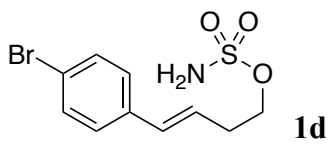


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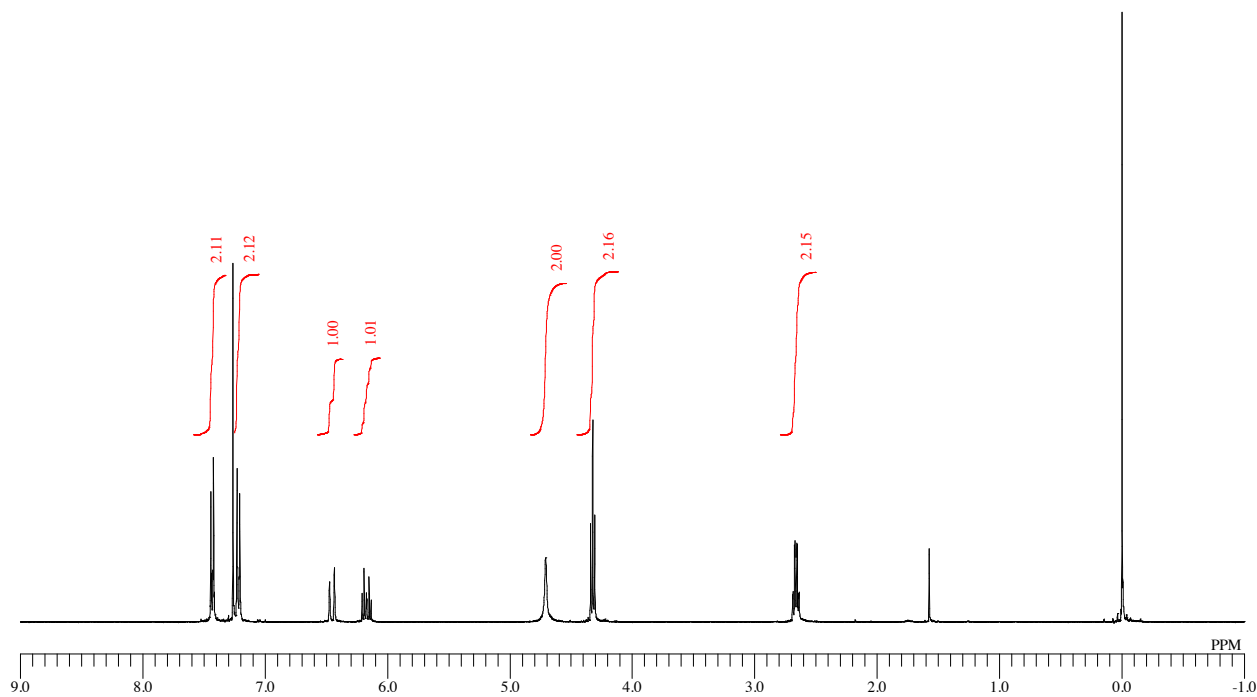


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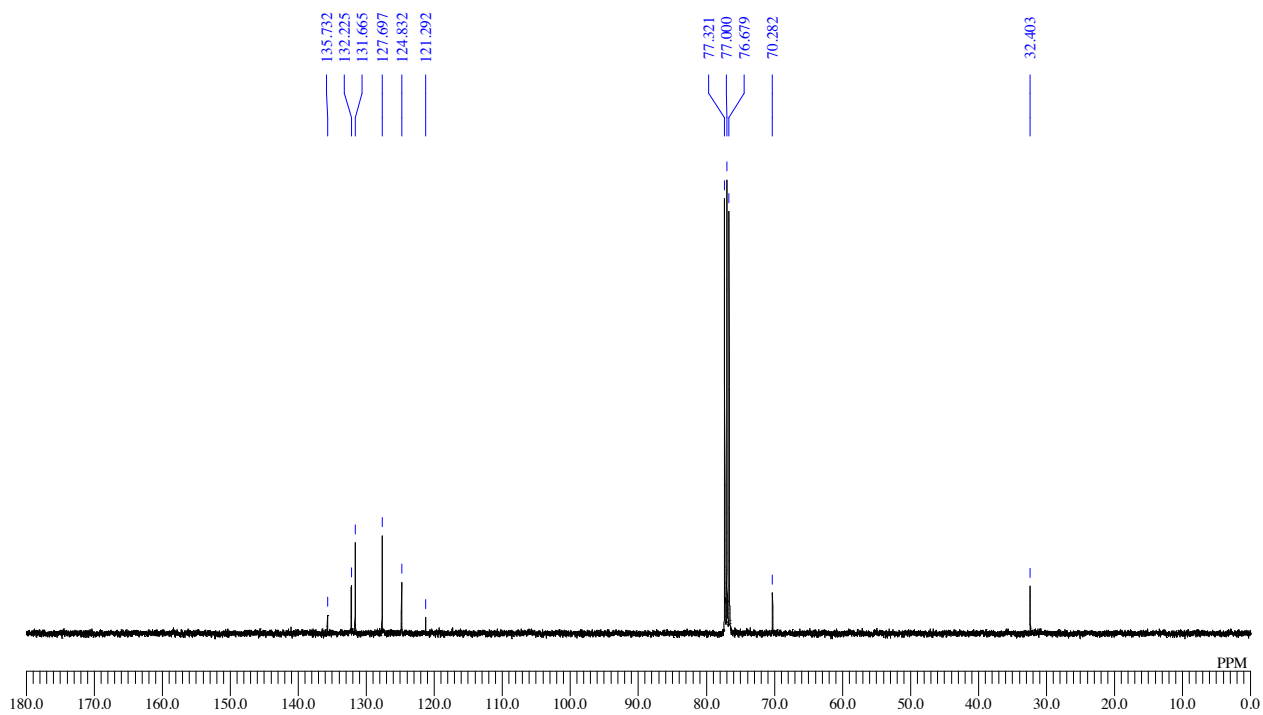


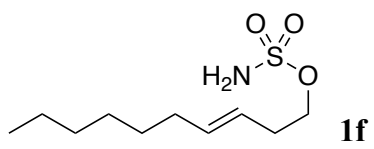


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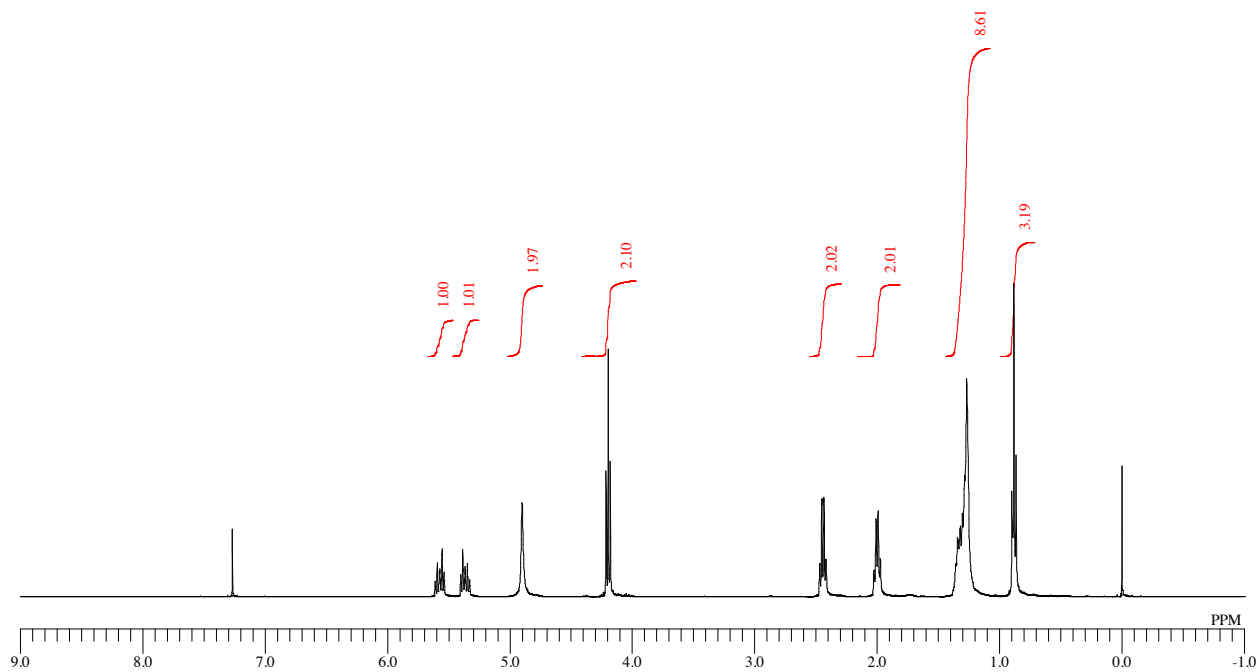


$^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )

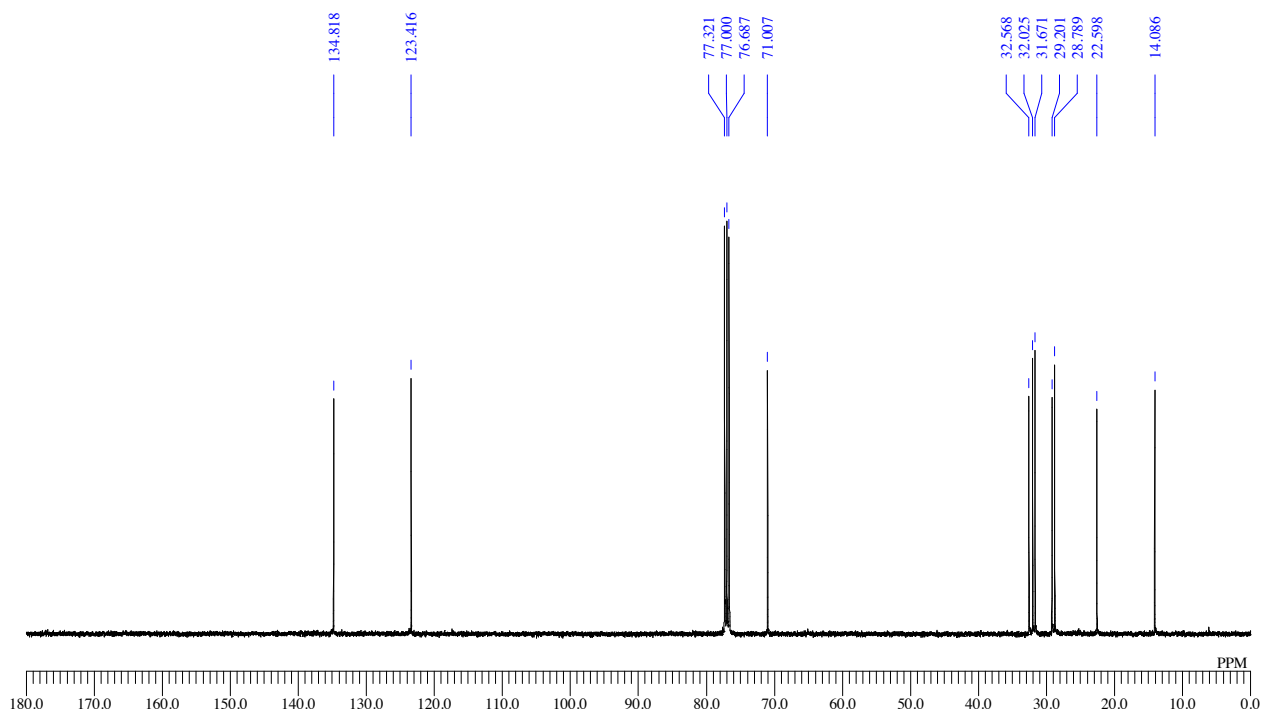


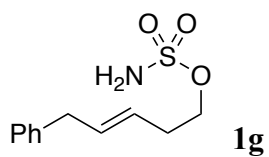


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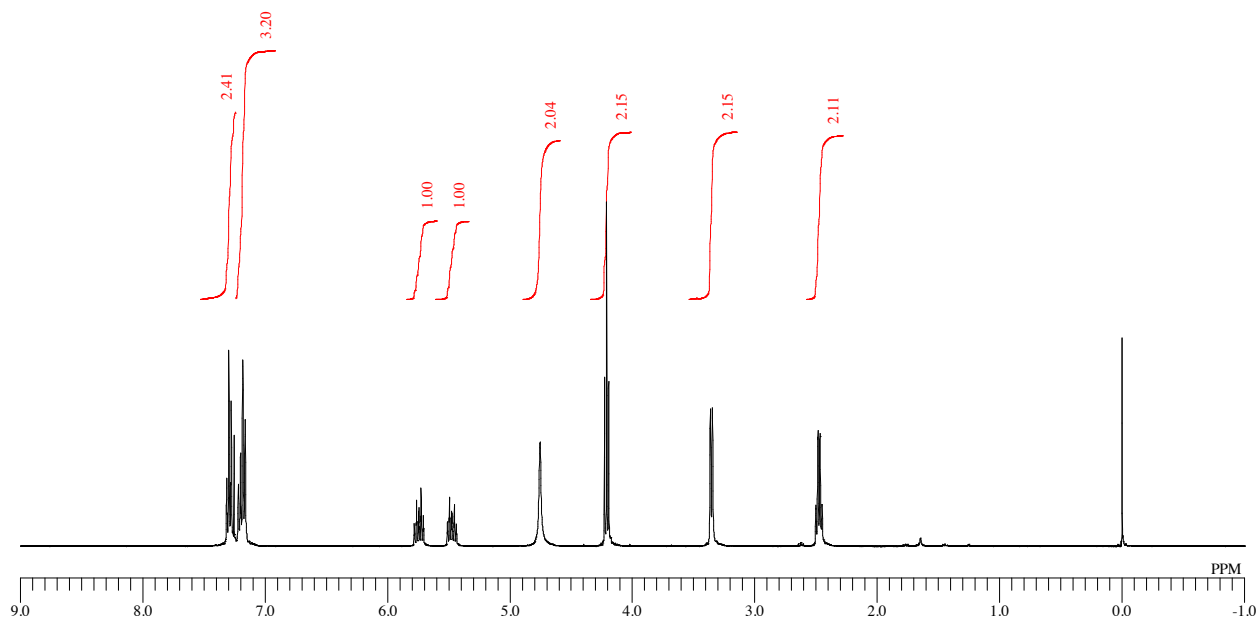


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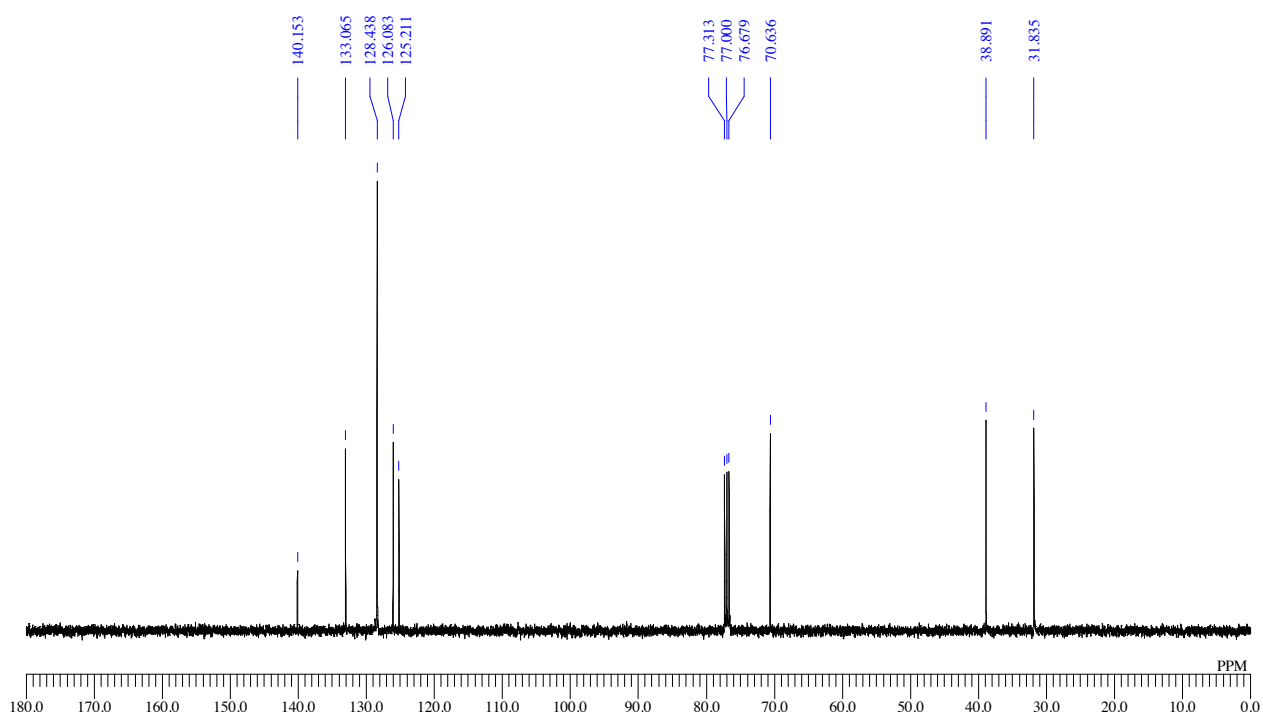


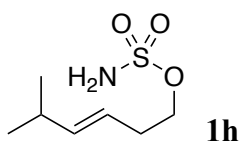


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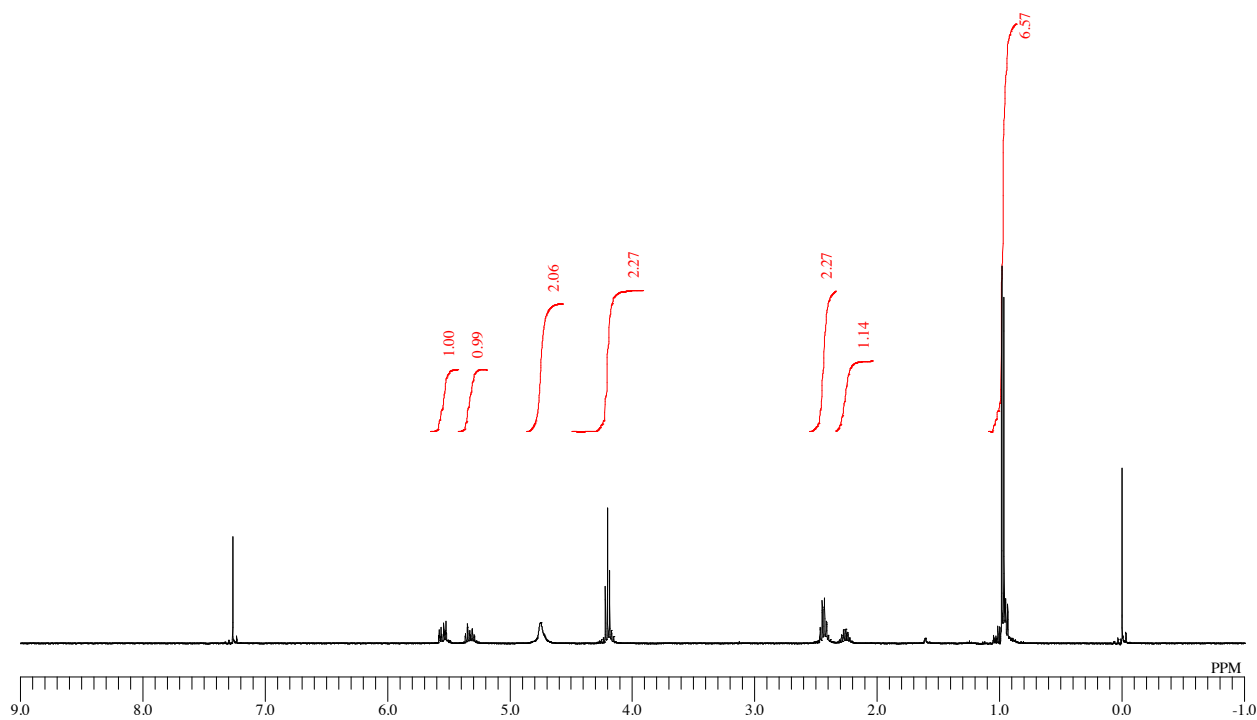


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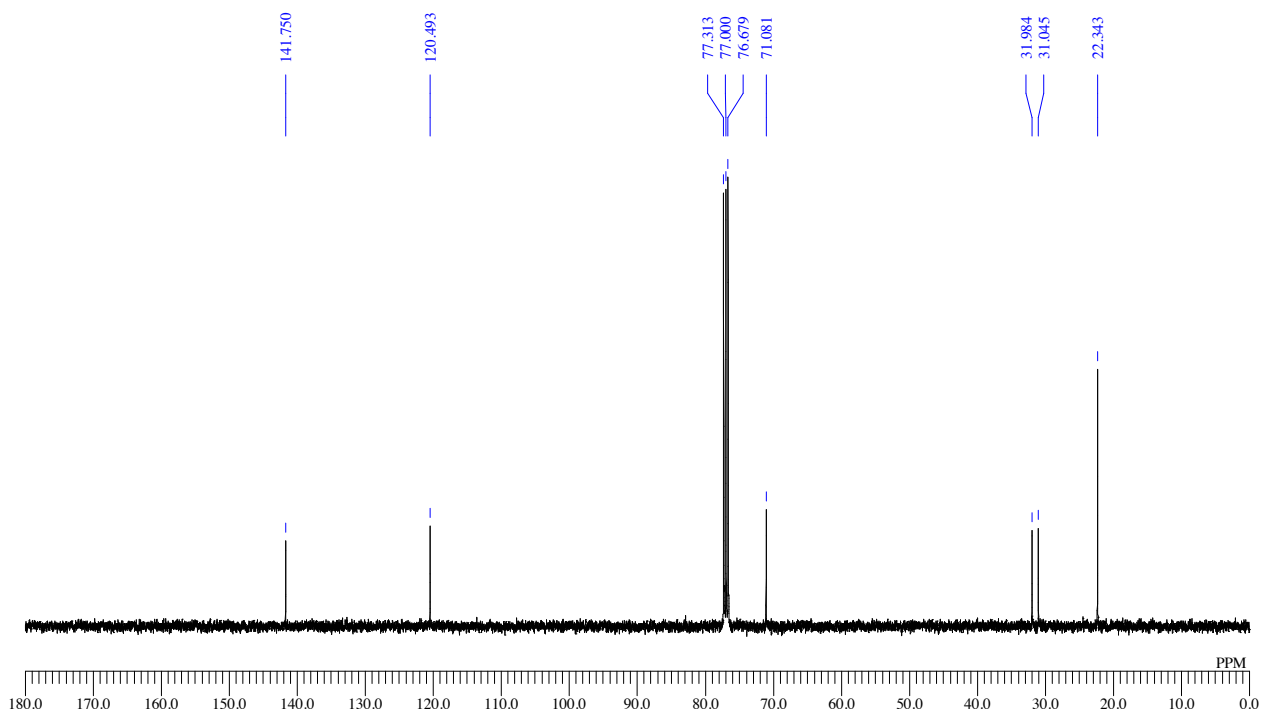


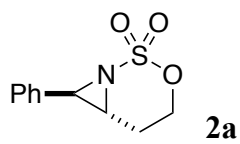


$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )

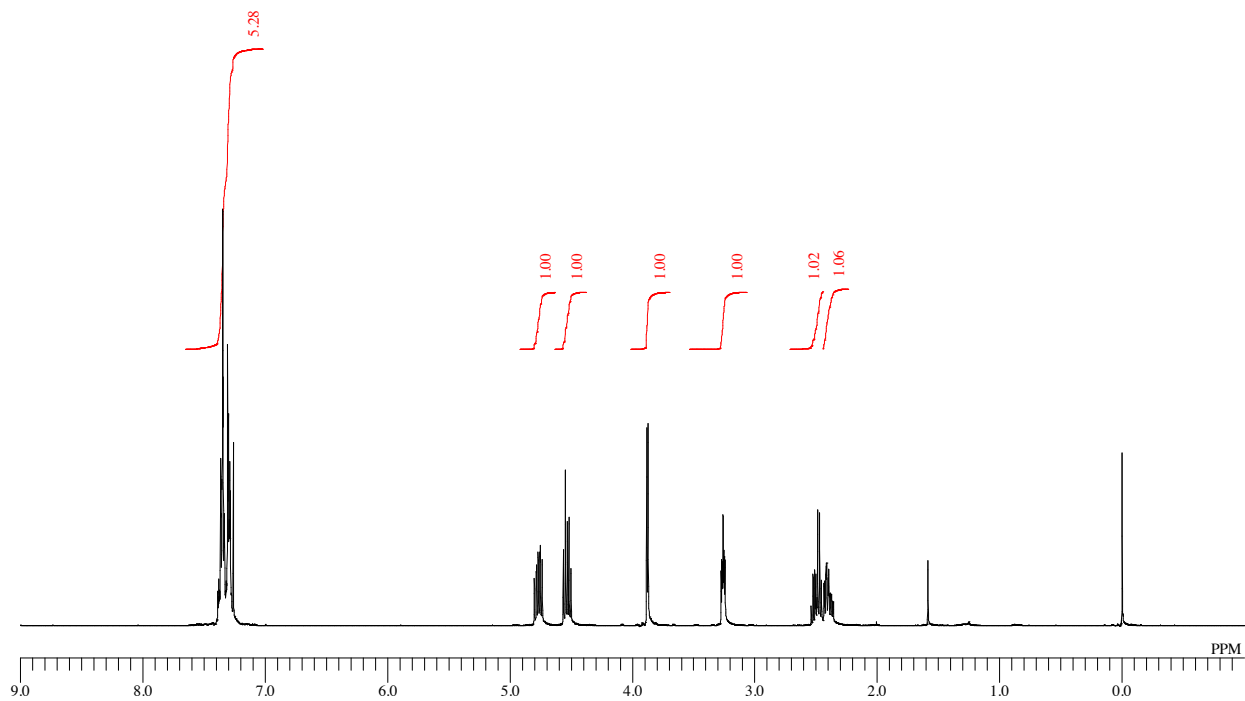


$^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )

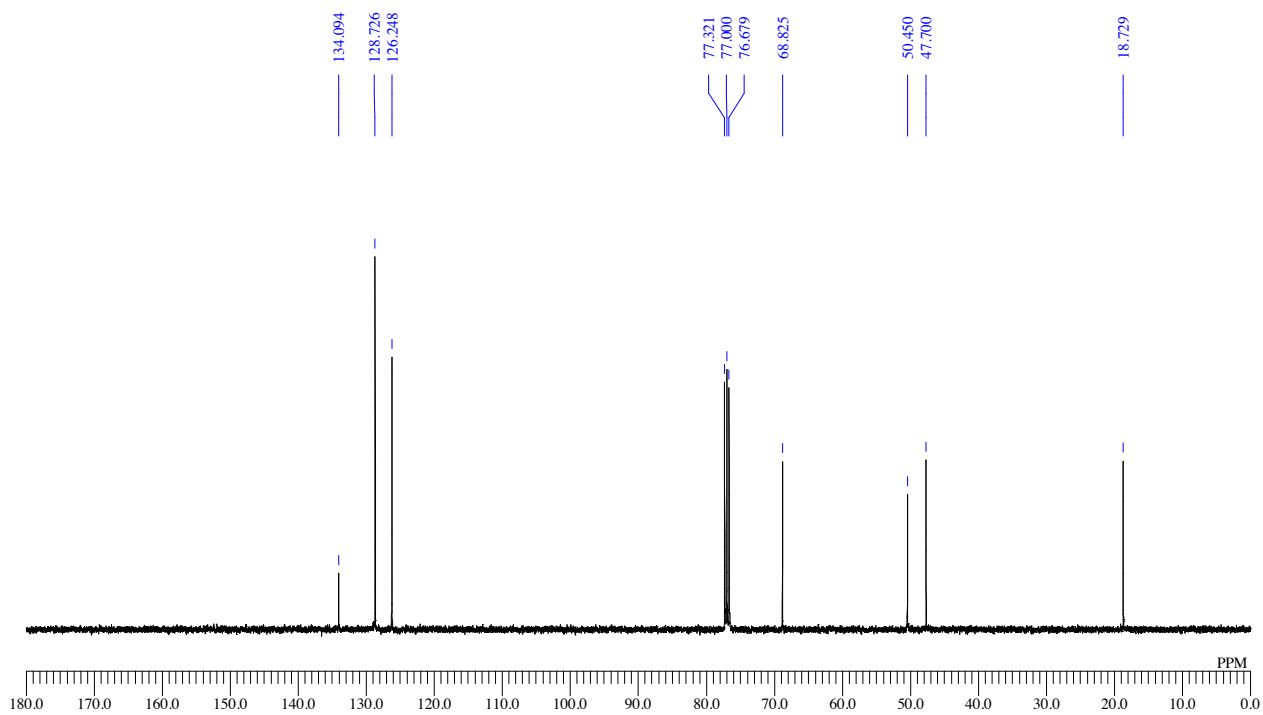


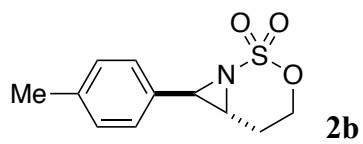


$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )

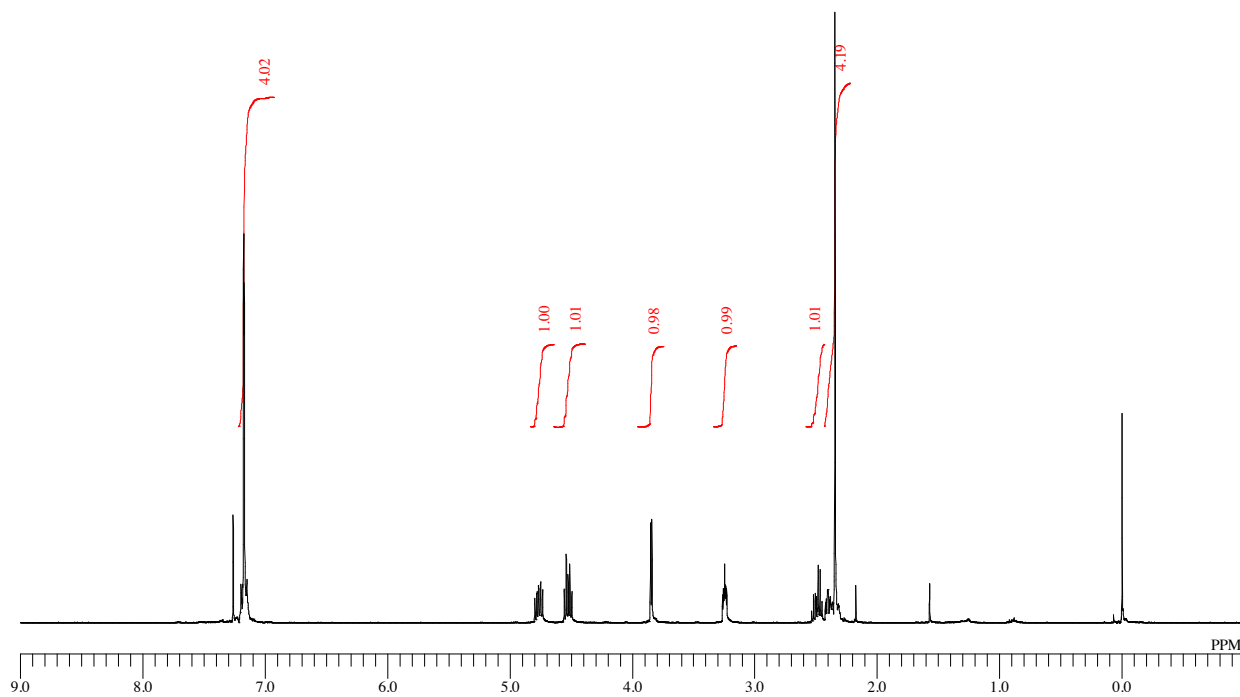


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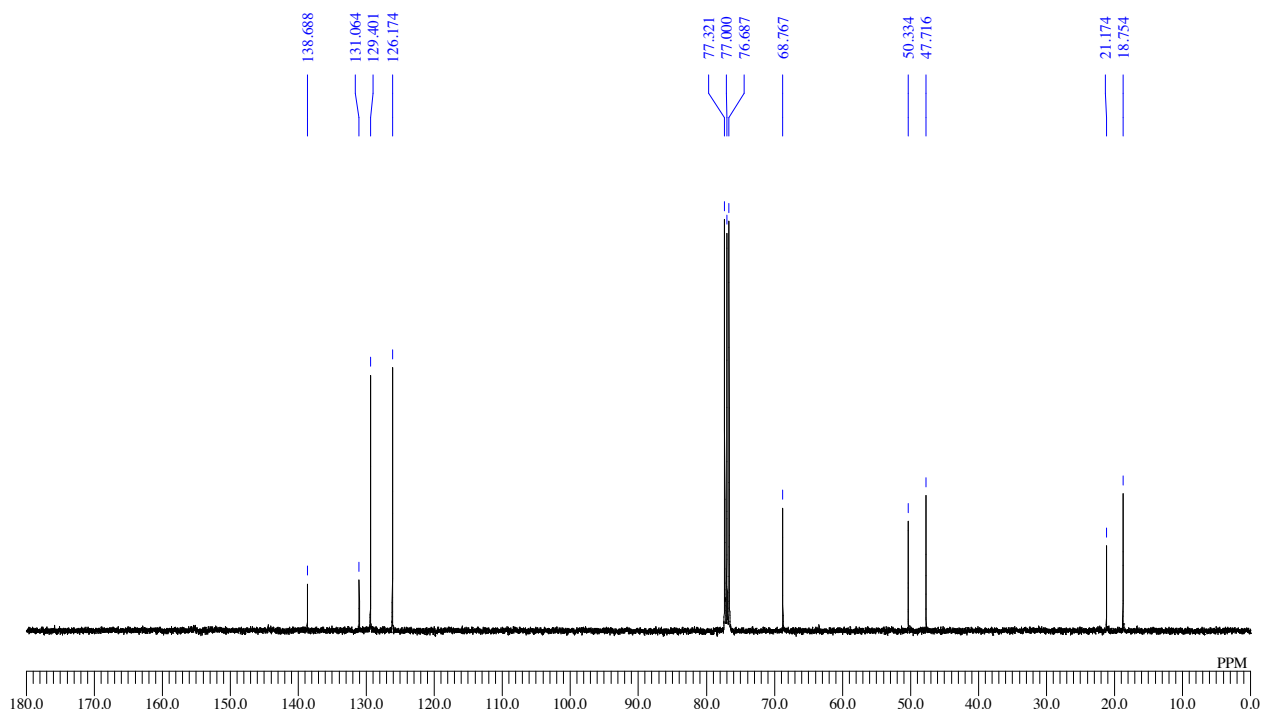


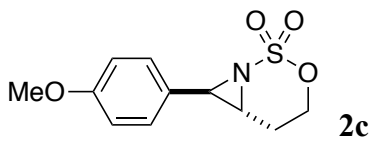


$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )

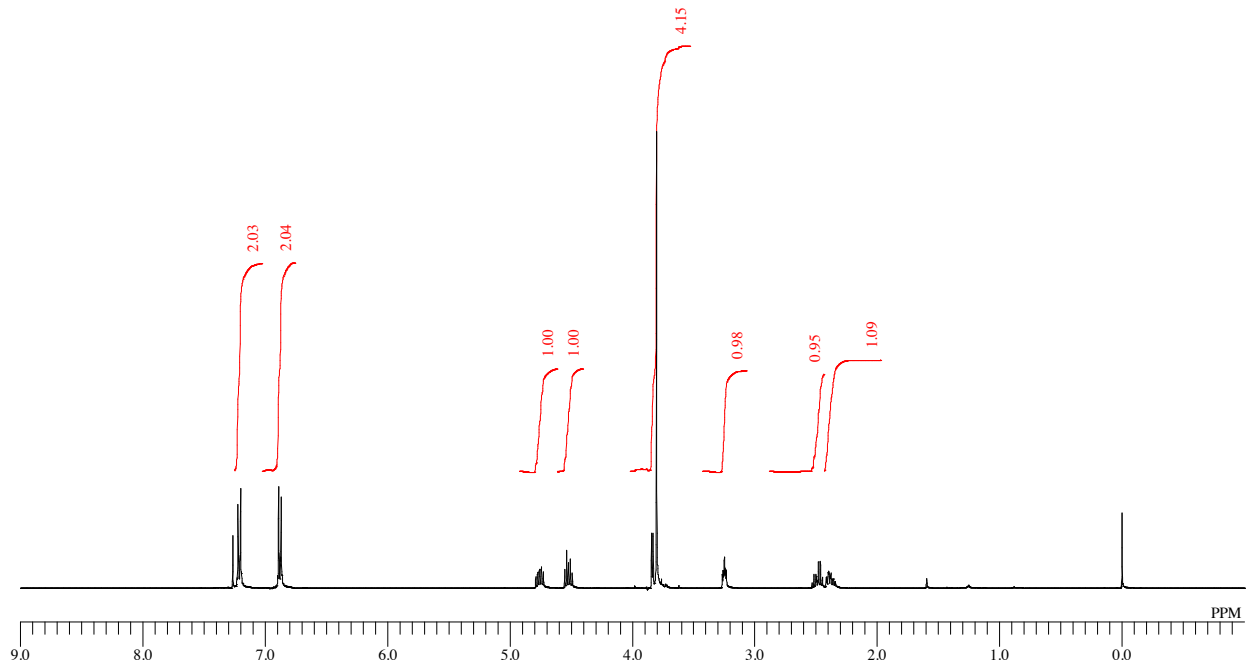


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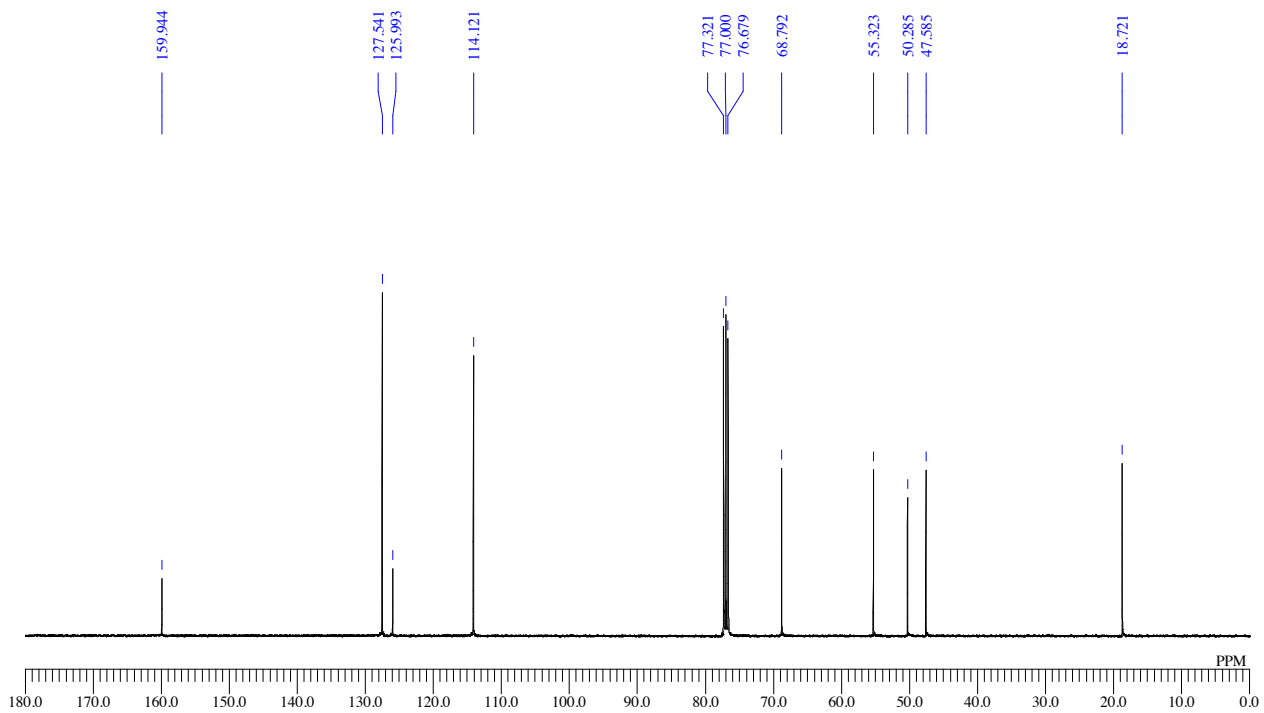


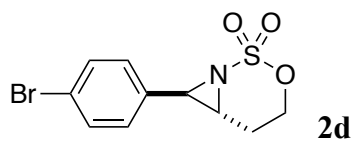


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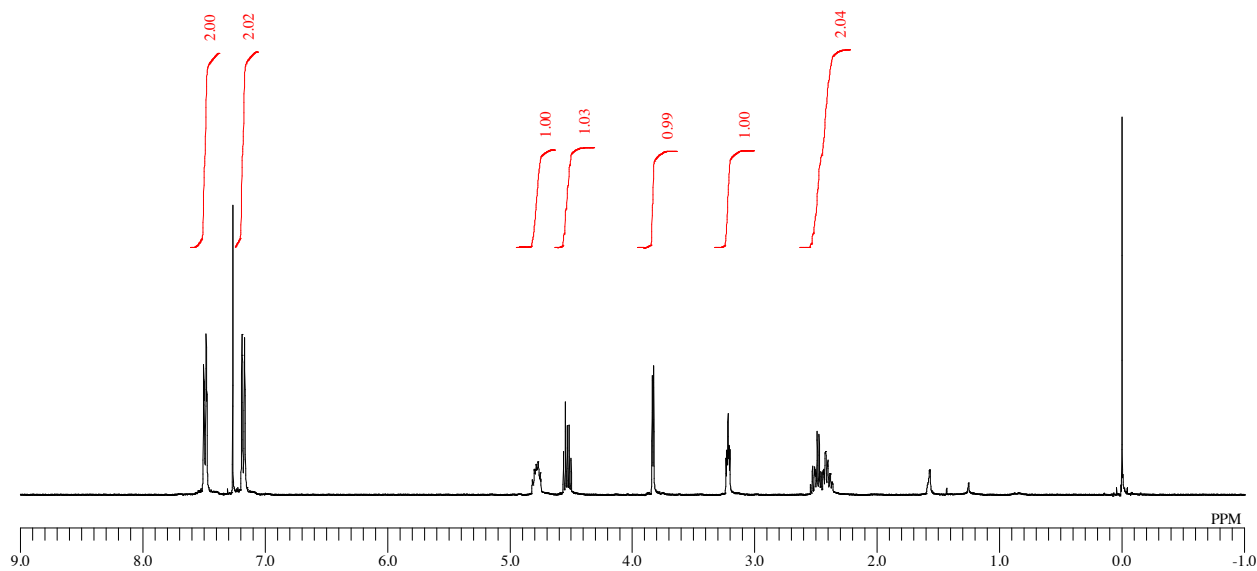


$^{13}\text{C NMR}$ : (100 MHz,  $\text{CDCl}_3$ )

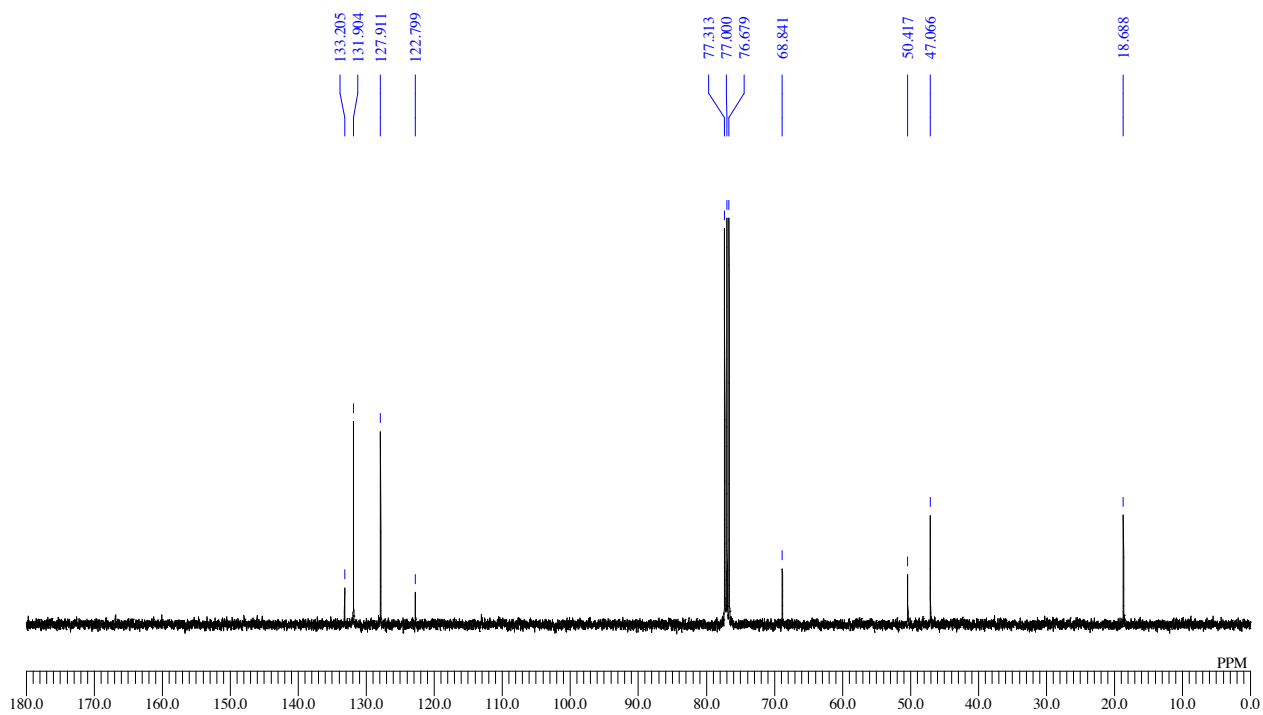


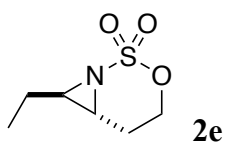


$^1\text{H NMR}$ : (400 MHz,  $\text{CDCl}_3$ )

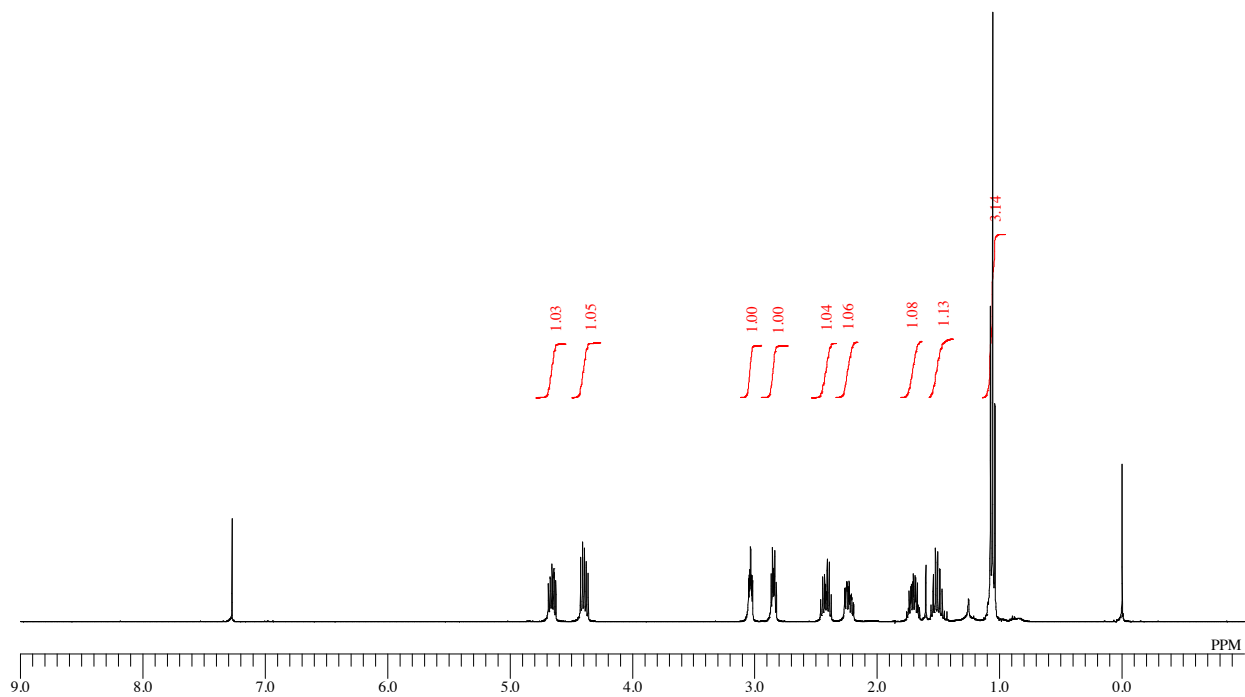


$^{13}\text{C NMR}$ : (100 MHz,  $\text{CDCl}_3$ )

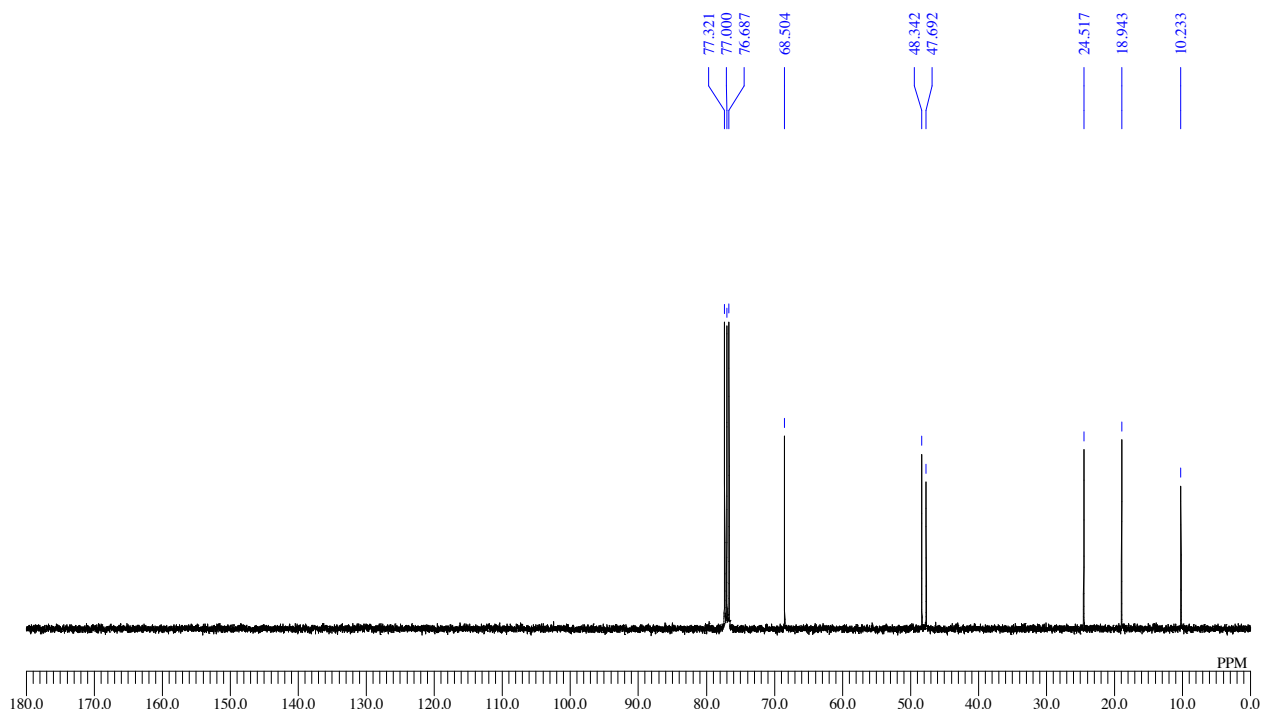


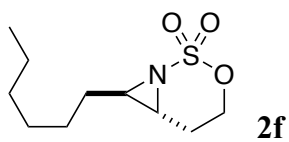


$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )

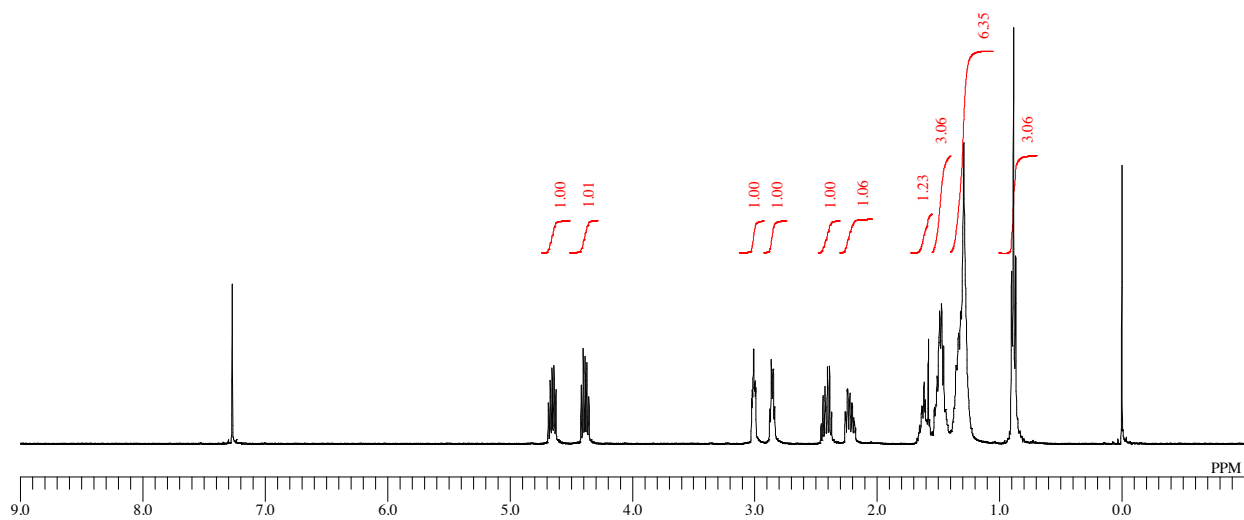


$^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )

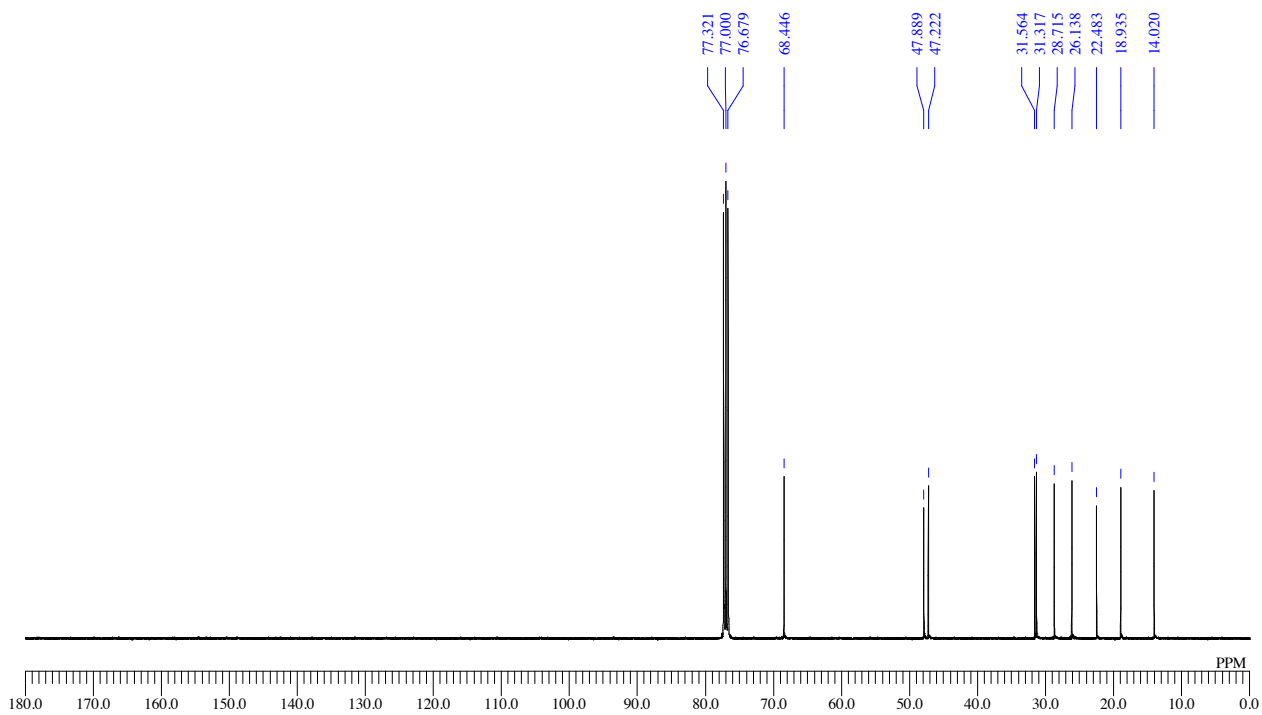


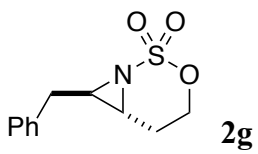


$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )

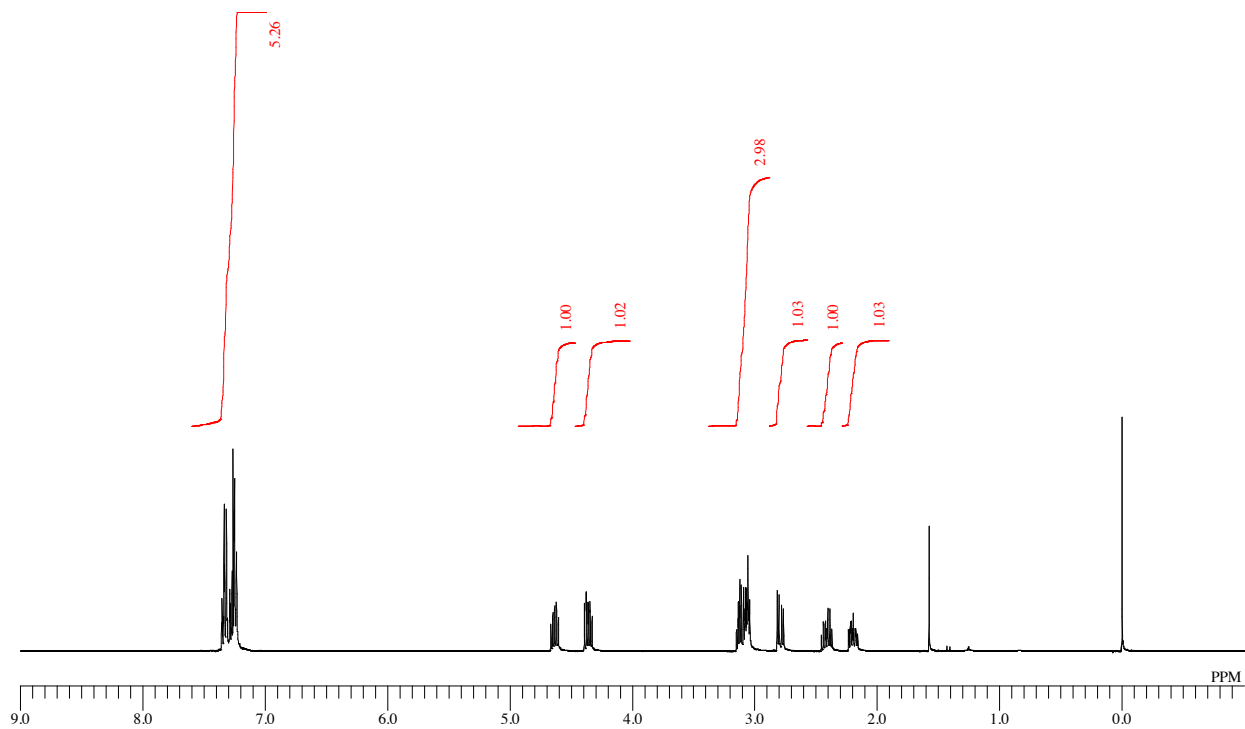


$^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )

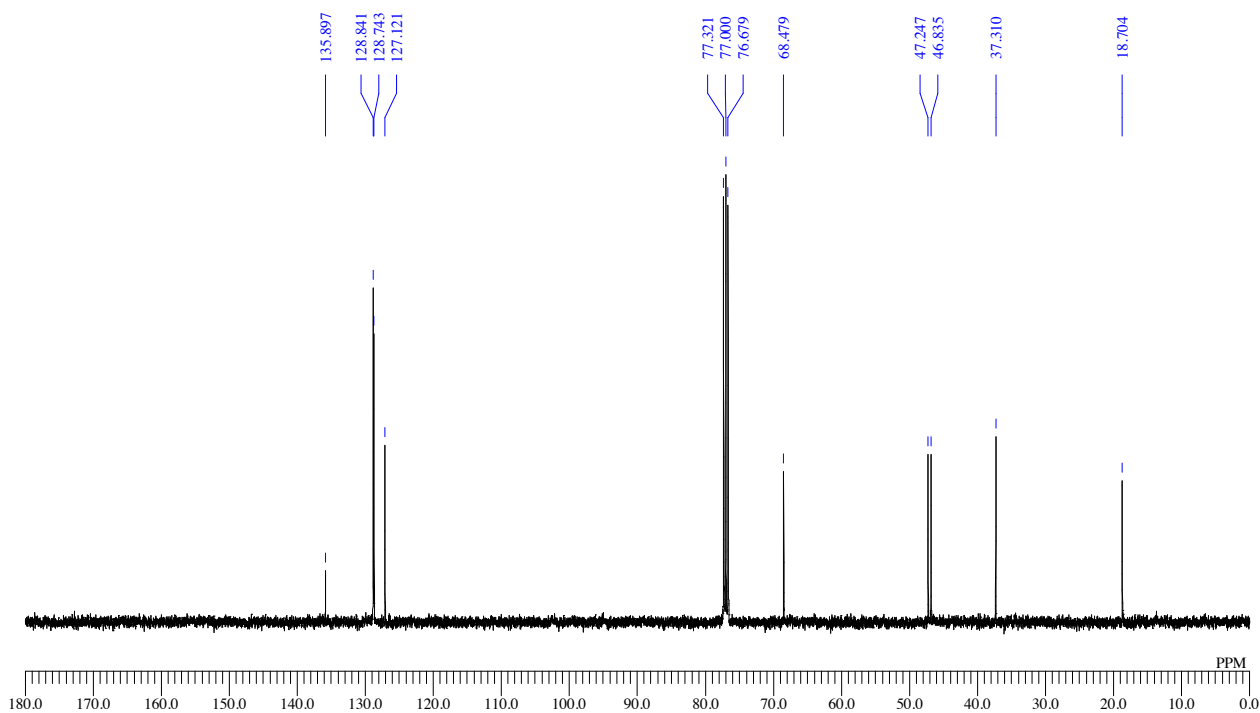


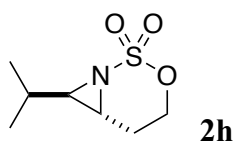


$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )

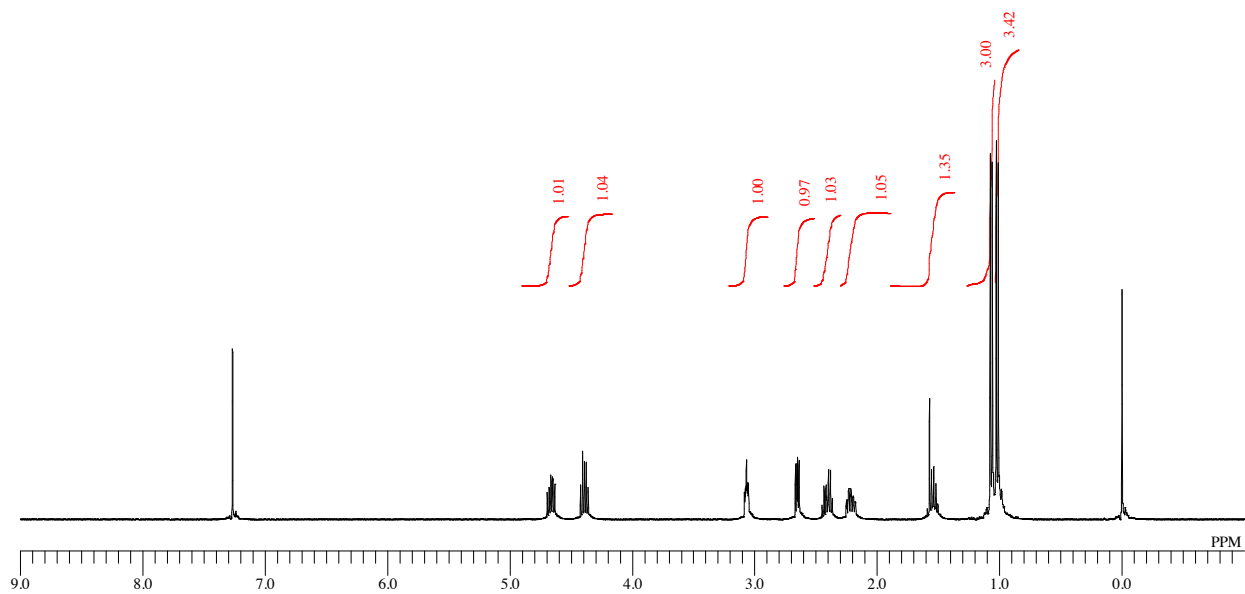


$^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )

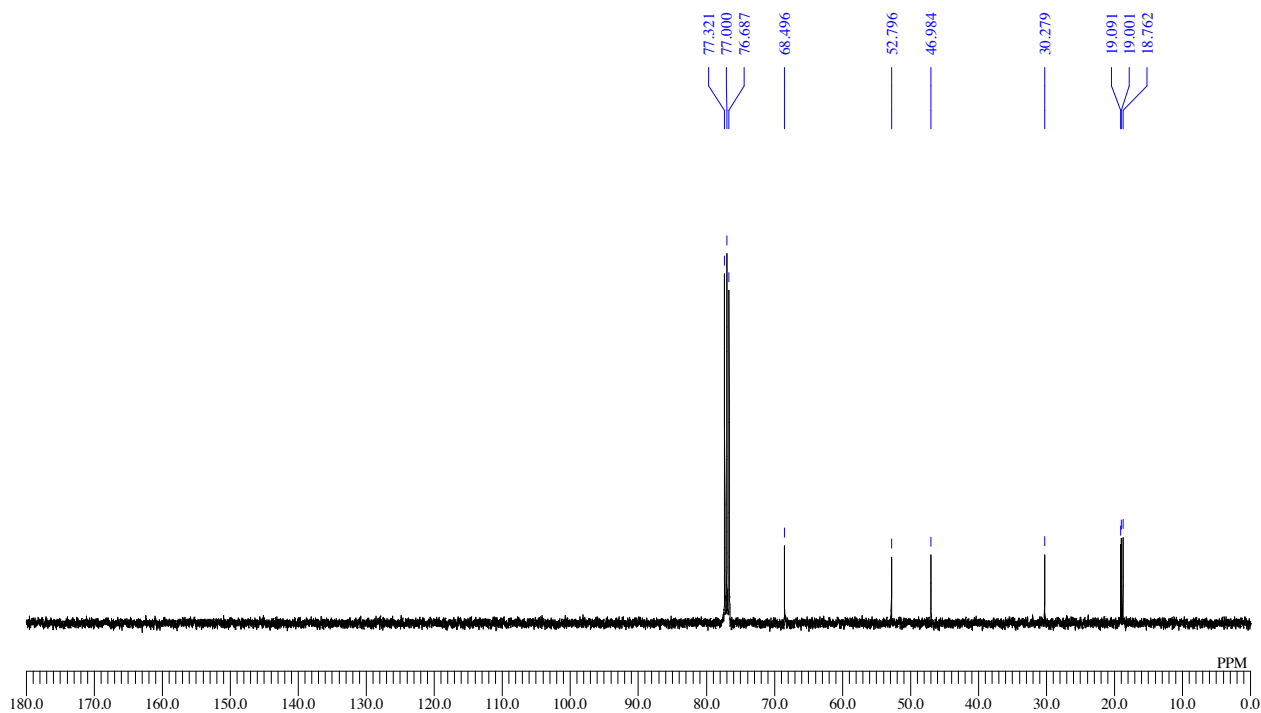


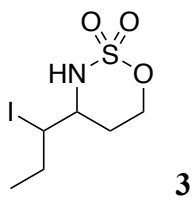


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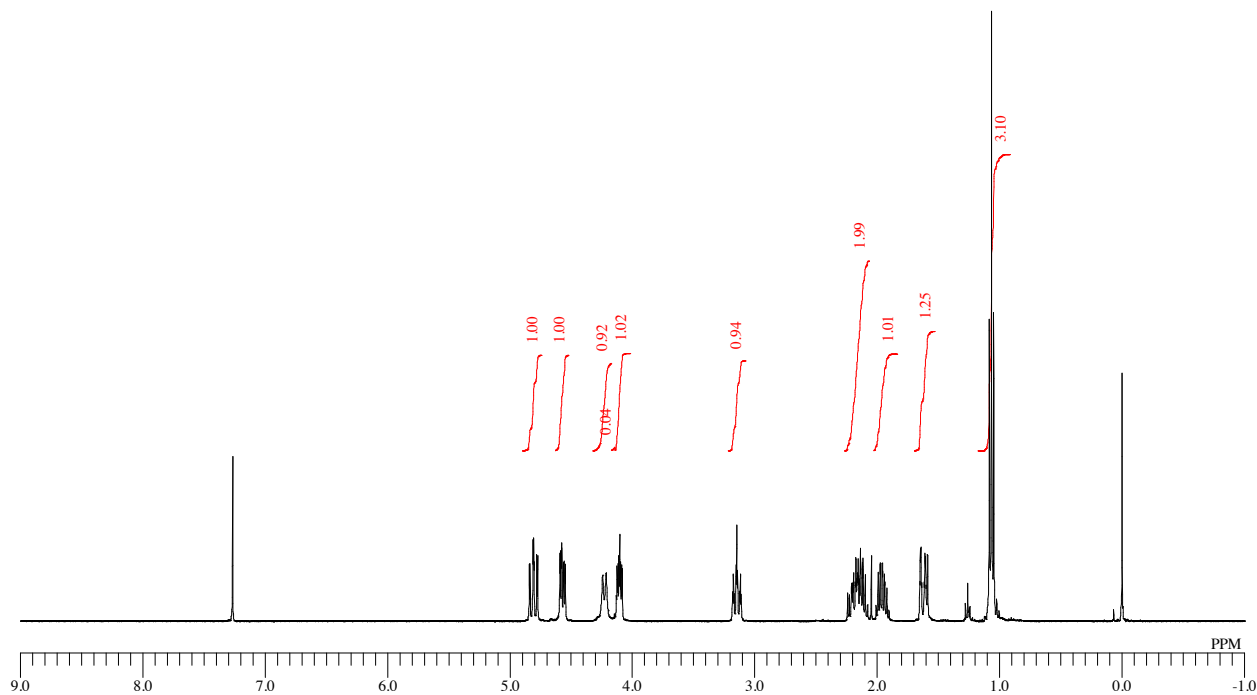


$^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )

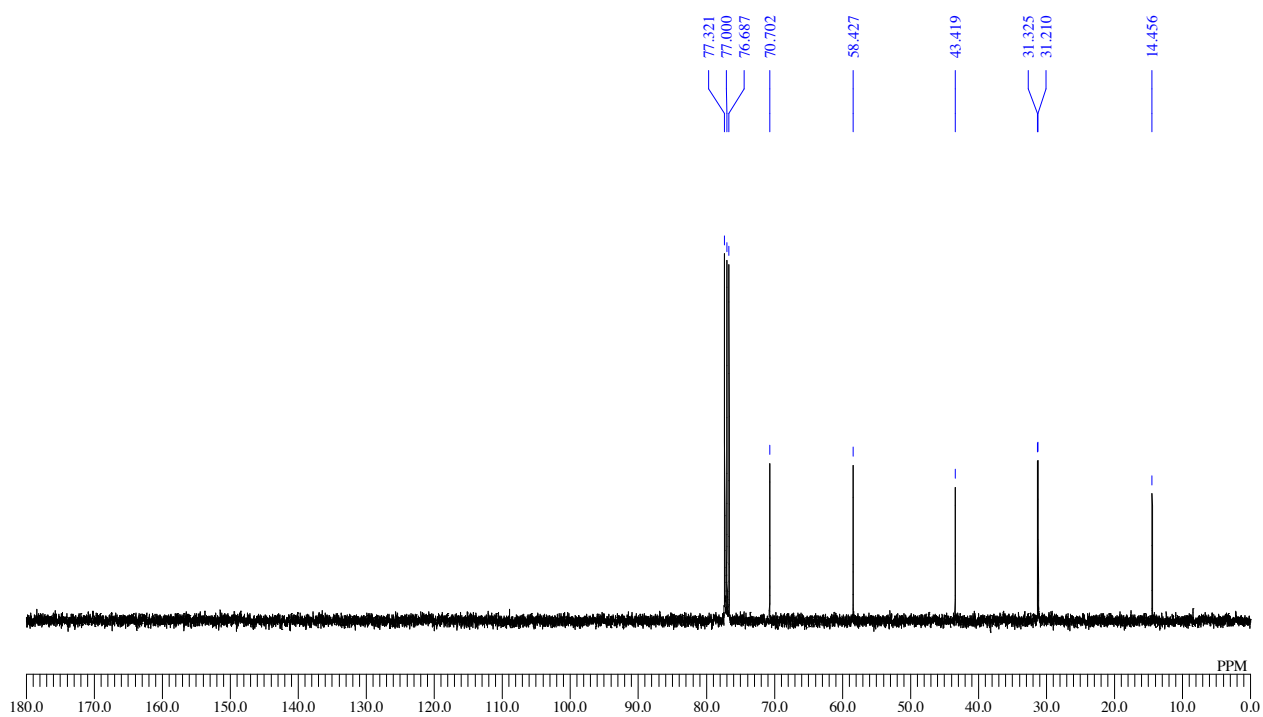


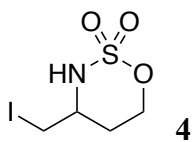


<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

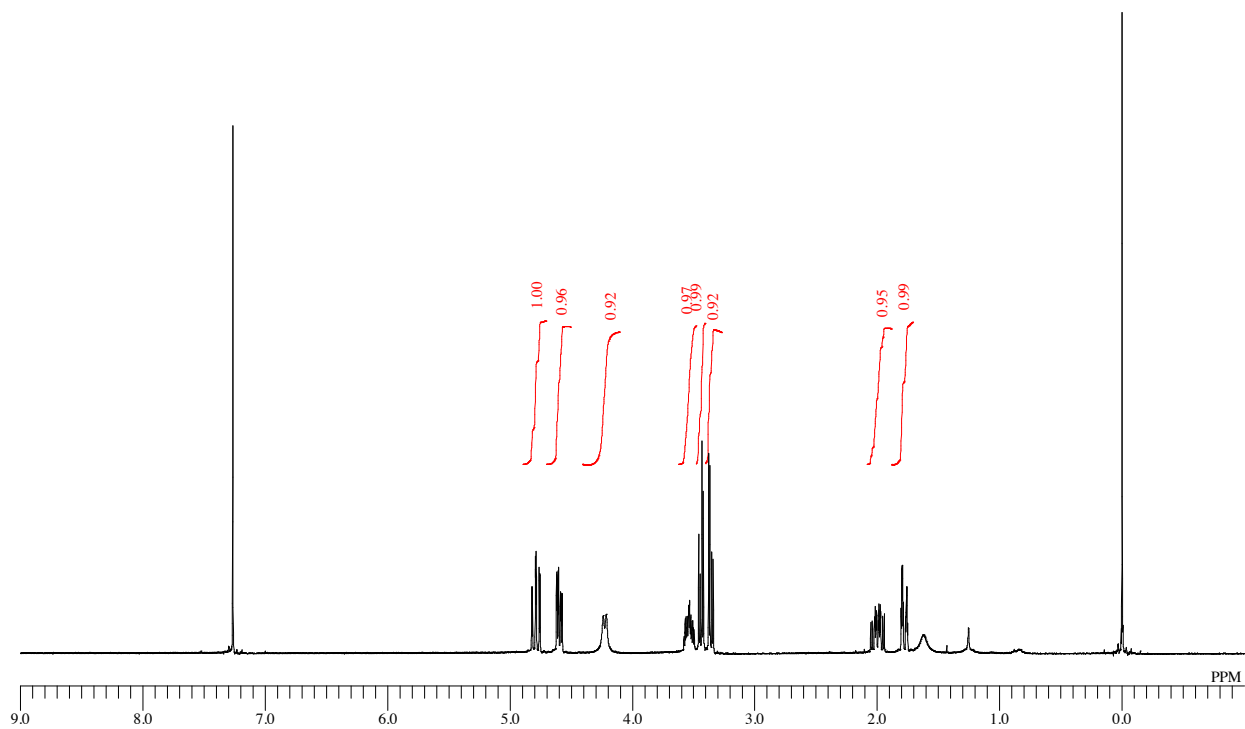


<sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>)

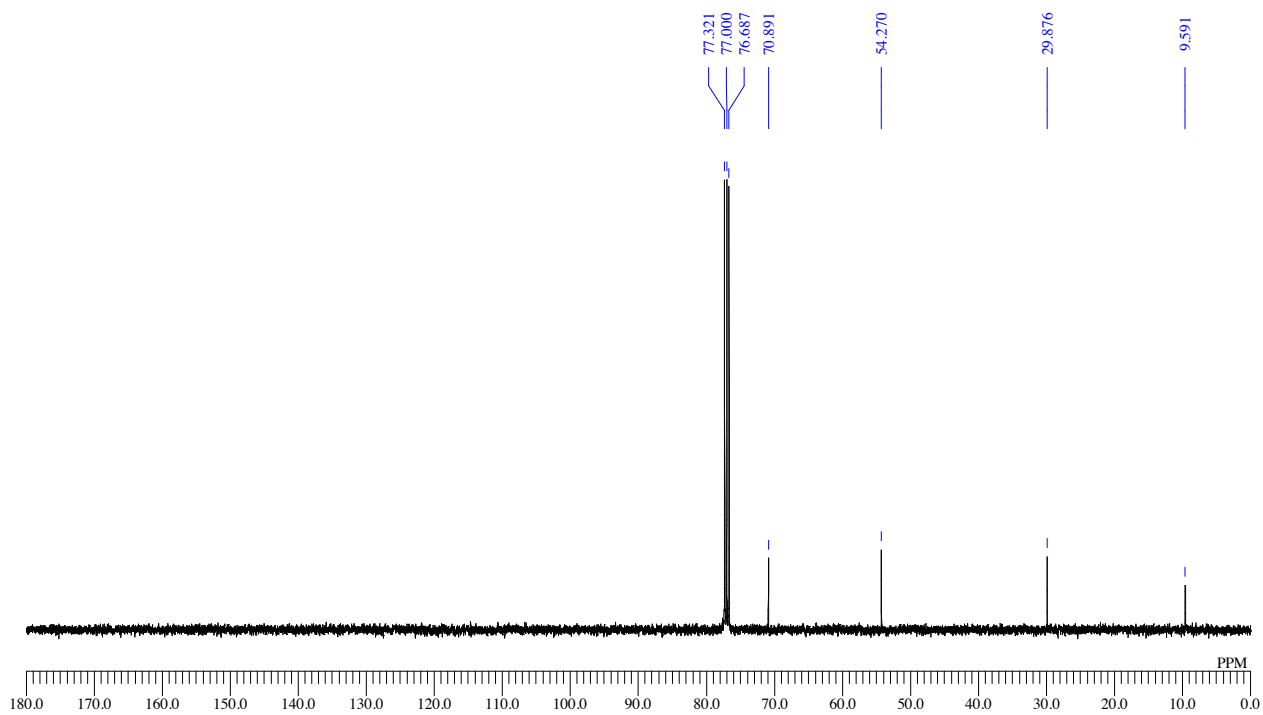


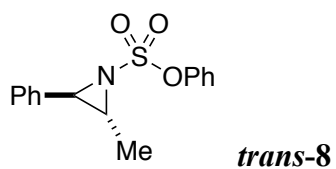


$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )

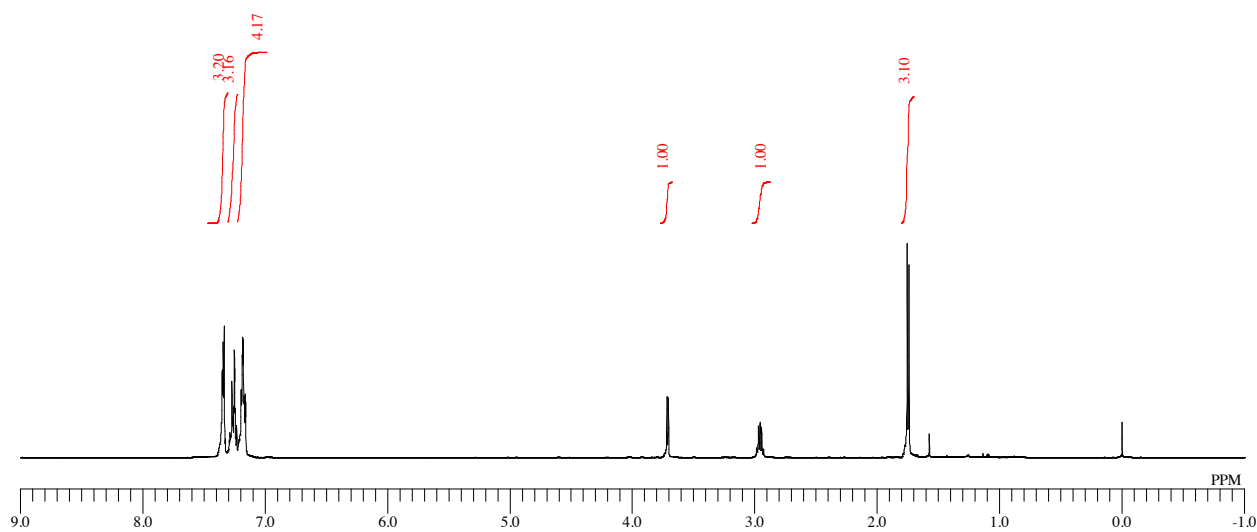


$^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )

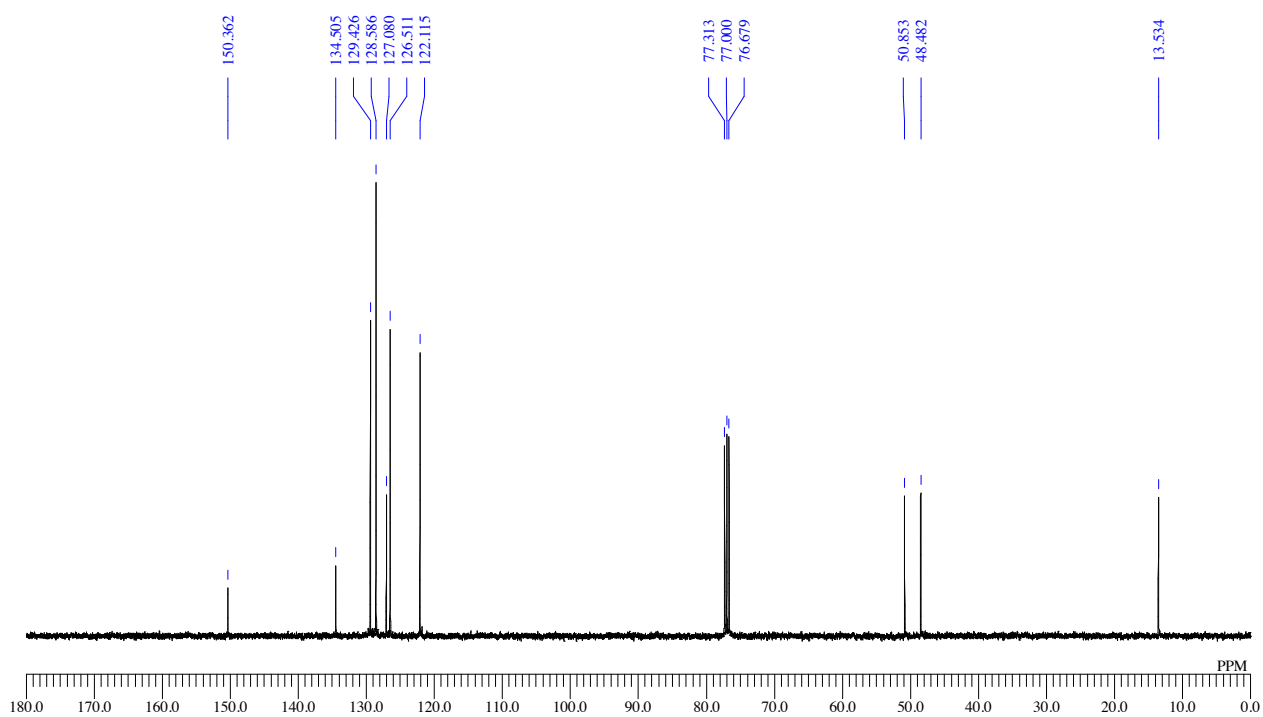


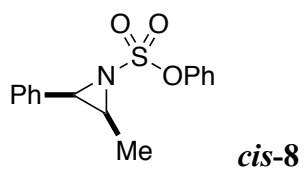


$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )

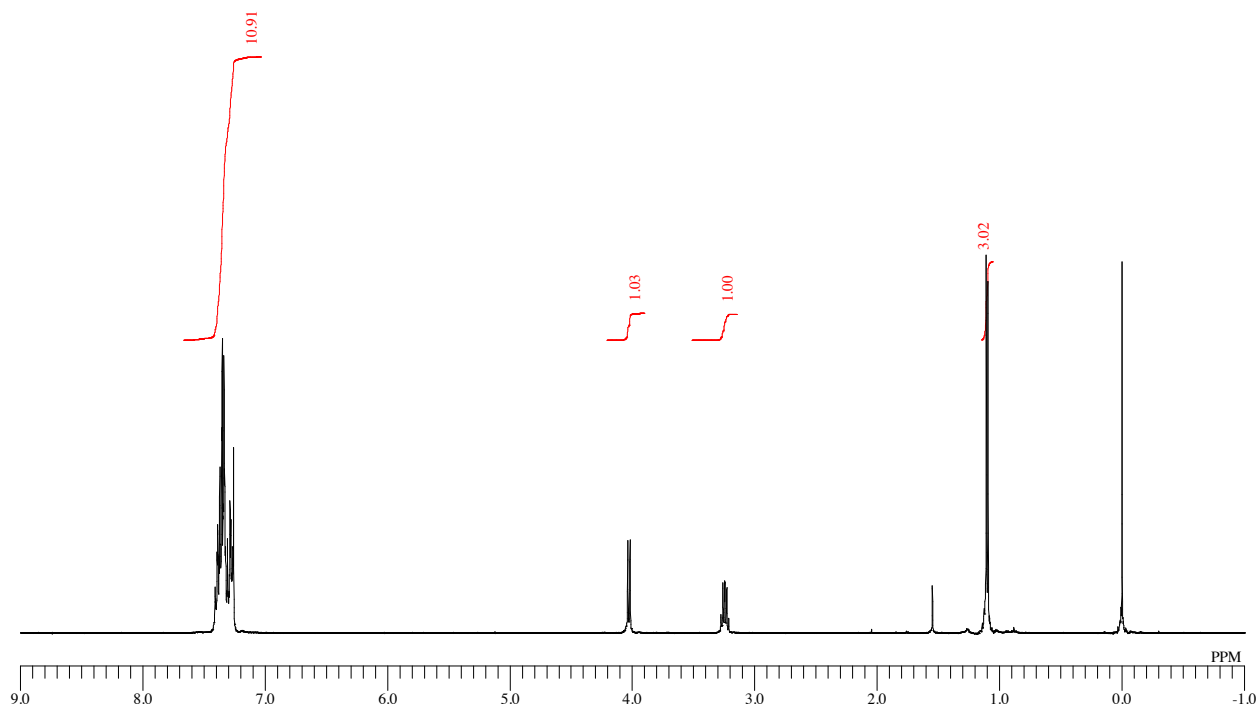


$^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )





$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )

