

**Silver-catalyzed stereoselective Meyer-Schuster-type rearrangement:  
Synthesis of densely substituted  $\alpha$ -iodo,  $\alpha,\beta$ -unsaturated thioesters**

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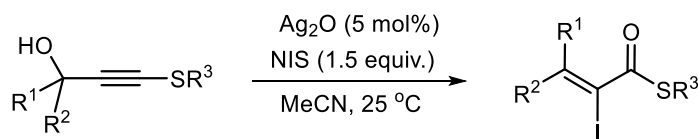
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## 1. General Information

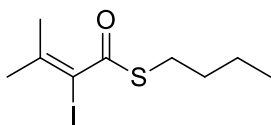
Unless otherwise stated, all glassware was dried before use and all reactions were performed under an atmosphere of argon. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminum plates coated with silica gel F254 with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm, iodine and by staining using vanillin solution. Flash column chromatography was performed using silica (230-400 mesh, Merck and co.). Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers ( $= 1/\lambda$ ) are reported in  $\text{cm}^{-1}$ . Mass spectra were obtained using an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). All  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded using a 400 MHz spectrometer at 298K (frequency for  $^1\text{H}$ ). Chemical shifts were given in parts per million (ppm,  $\delta$ ), referenced to TMS, defined at  $\delta = 0.0$  ppm ( $^1\text{H}$  NMR) and to the solvent peak of  $\text{CDCl}_3$ , defined at  $\delta = 77.00$  ( $^{13}\text{C}$  NMR). Coupling constants are quoted in Hz ( $J$ ).  $^1\text{H}$  NMR splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (qt), sextet (sext), heptet (hept), septet (se) and nonet (n). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m).

## 2. General procedure for the synthesis of $\alpha$ -iodo, $\alpha\beta$ -unsaturated thioesters



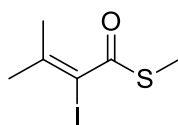
*N*-iodo-succinimide (1.5 equiv., 0.375 mmol, 0.0844g),  $\text{Ag}_2\text{O}$  (5 mol %, 0.0029g) and dry MeCN (1mL) were added to a flame-dried Schlenk flask containing thioalkyne (0.25 mmol), under argon atmosphere. The reaction was stirred until the complete consumption of the substrate. The reaction was monitored by TLC and after the complete consumption of thioalkyne the solvent was removed and the crude product was purified on flash column chromatography using a gradient of hexane and ethyl acetate as eluent (98:2 hexane /ethyl acetate).

### **S-butyl 2-iodo-3-methylbut-2-enethioate (1)**



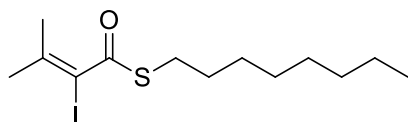
Yellow oil. **Yield:** 95% (0.071 g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 2.95 (t, *J* = 7.4 Hz, 2H), 2.07 (s, 3H), 2.06 (s, 3H), 1.61 (qt, *J* = 7.3, 2H), 1.42 (sext, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.3, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 193.1, 147.1, 91.4, 31.3, 30.8, 30.4, 22.3, 22.0, 13.6. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 2961, 2929, 2865, 1660, 1436, 1240, 1124, 1030, 857, 787. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>9</sub>H<sub>15</sub>IOS 298.9967, found 298.9955.

### **S-methyl 2-iodo-3-methylbut-2-enethioate (2)**



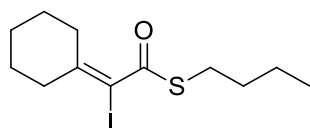
Yellow oil. **Yield:** 38% (0.0246g). This product is volatile and despite full conversion, isolated yield is lowered due to loss of mass during the removal of the solvent. Yields determined by <sup>1</sup>H NMR using mesitylene as internal standard: 90%. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 2.39 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 193.3, 147.9, 91.2, 31.1, 22.5, 13.6. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>6</sub>H<sub>9</sub>IOS 256.9497, found 256.9492.

### **S-octyl 2-iodo-3-methylbut-2-enethioate (3)**



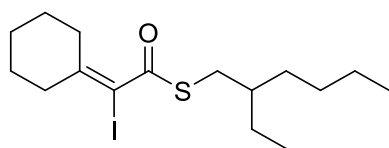
Yellow oil. **Yield:** 92% (0.0844g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 2.94 (t, *J* = 7.1 Hz, 2H), 2.07 (s, 6H), 1.62 (qt, *J* = 7.3 Hz, 2H), 1.44-1.35 (m, 2H), 1.35-1.24 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 193.0, 147.1, 91.5, 31.7, 30.8, 30.7, 29.2, 29.1, 29.0, 28.8, 22.6, 22.3, 14.1. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 2961, 2923, 2859, 1667, 1584, 1444, 1252, 1119, 1116, 972, 787, 736. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>23</sub>IOS 355.0593, found 355.0591.

### **S-butyl 2-cyclohexylidene-2-iodoethanethioate (4)**



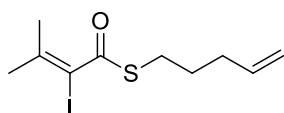
Yellow oil. **Yield:** 90% (0.0502g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 2.96 (t, *J* = 7.4 Hz, 2H), 2.48-2.40 (m, 4H), 1.68 - 1.52 (m, 8H), 1.42 (sext, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 193.2, 152.1, 87.7, 40.0, 33.1, 31.3, 29.9, 28.0, 27.4, 25.8, 22.0, 13.6. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>19</sub>IOS 339.0280, found 339.0279.

**S-(2-ethylheptyl) 2-cyclohexylidene-2-iodoethanethioate (5)**



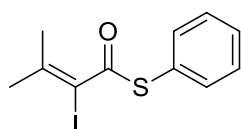
Yellow oil. **Yield:** 88% (0.093g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 3.00 (d, *J* = 6.1 Hz, 2H), 2.51 – 2.38 (m, 4H), 1.68 – 1.61 (m, 2H), 1.60 – 1.52 (m, 5H), 1.44 – 1.23 (m, 9H), 0.92 – 0.88 (m, 6H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 193.2, 151.8, 87.6, 39.8, 39.2, 33.9, 33.0, 32.4, 28.8, 27.9, 27.4, 25.8 (2C), 22.9, 14.0, 10.9. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 2960, 2923, 2852, 1660, 1609, 1450, 1119, 1112, 1054, 978, 768, 723. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>29</sub>IOS 395.0906, found 395.0913.

**S-pent-4-en-1-yl 2-iodo-3-methylbut-2-enethioate (6)**



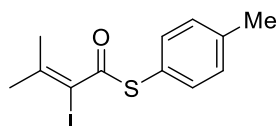
Yellow oil. **Yield:** 65% (0.051g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 5.78 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.03 (dd, *J* = 16.9, 1.7 Hz, 1H), 4.99 (dd, *J* = 10.1, 1.7 Hz, 1H), 2.93 (t, *J* = 6.9 Hz, 2H), 2.15 (q, *J* = 6.9 Hz, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.71 (qt, *J* = 7.4 Hz, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 192.8, 147.3, 137.3, 115.5, 91.4, 32.7, 30.9, 30.0, 28.4, 22.3. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 2955, 2916, 2846, 1660, 1603, 1463, 1138, 1080, 800, 723. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>10</sub>H<sub>16</sub>IOS 310.9967, found 310.9972.

**S-phenyl 2-iodo-3-methylbut-2-enethioate (7)**



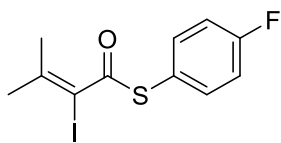
Yellow oil. **Yield:** 52% (0.048 g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.41 (m, 5H), 2.14 (s, 3H), 2.10 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 190.9, 148.9, 134.6, 129.6, 129.3, 128.6, 90.6, 31.1, 22.8. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 3063, 2923, 2846, 1673, 1577, 1444, 1125, 1016, 856, 787, 742, 678. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>11</sub>H<sub>11</sub>IOS 318.9654, found 318.9651.

**S-(*p*-tolyl) 2-iodo-3-methylbut-2-enethioate (9)**



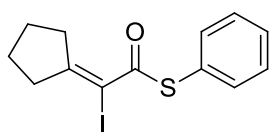
Yellow oil. **Yield:** 65% (0.054 g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.33 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 191.3, 148.7, 139.9, 134.5, 130.1, 124.9, 90.6, 31.0, 22.7, 21.3. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 3063, 2923, 2846, 1673, 1577, 1444, 1125, 1016, 856, 787, 742, 678. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>13</sub>IOS 332.9810, found 332.9812.

### ***S*-(4-fluorophenyl) 2-iodo-3-methylbut-2-enethioate (10)**



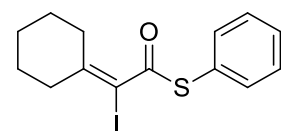
Yellow oil. **Yield:** 45% (0.038 g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.46 – 7.40 (m, 2H), 7.17 – 7.10 (m, 2H), 2.14 (s, 3H), 2.11 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 190.8 (d, *J* = 1.3 Hz), 163.5 (d, *J* = 250.4 Hz), 149.5, 136.7 (d, *J* = 8.6 Hz), 123.9 (d, *J* = 3.5 Hz), 116.6 (d, *J* = 22.1 Hz), 90.4, 31.3, 22.9. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -110.74. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 3063, 2923, 2846, 1673, 1577, 1444, 1125, 1016, 856, 787, 742, 678. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>11</sub>H<sub>10</sub>FIO<sub>2</sub> 336.9559, found 336.9562.

### ***S*-phenyl 2-cyclopentylidene-2-iodoethanethioate (11)**



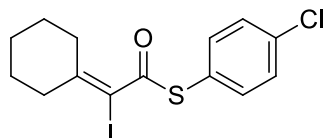
Yellow oil. **Yield:** 90% (0.102 g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.41 (m, 5H), 2.82 - 2.76 (m, 2H), 2.54 - 2.48 (m, 2H), 1.89 (qt, *J* = 6.9 Hz, 2H), 1.72 (qt, *J* = 7.0 Hz, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 188.2, 170.2, 134.6, 130.6, 129.4, 129.1, 88.3, 45.1, 37.3, 28.5, 24.8. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>13</sub>IO<sub>2</sub> 344.9810, found 344.9803.

### ***S*-phenyl 2-cyclohexylidene-2-iodoethanethioate (12)**



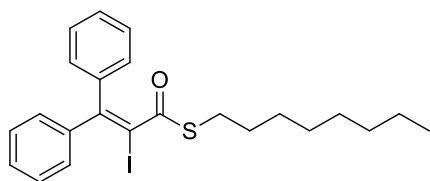
Yellow oil. **Yield:** 84% (0.075 g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.51 - 7.40 (m, 5H), 2.56-2.53 (m, 2H), 2.46-2.43 (m, 2H), 1.66 - 1.63 (m, 2H), 1.60-1.57 (m, 4H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 190.9, 153.3, 134.4, 129.6, 129.2, 127.9, 86.7, 39.9, 33.3, 28.0, 27.4, 25.7. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 3063, 2929, 2852, 1667, 1615, 1437, 1227, 1112, 1049, 978, 742, 692. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>15</sub>IO<sub>2</sub> 358.9967, found 358.9964.

### ***S*-(4-chlorophenyl) 2-cyclohexylidene-2-iodoethanethioate (13)**



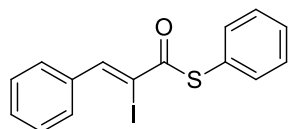
Yellow oil. **Yield:** 94% (0.068 g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.43 - 7.37 (m, 4H), 2.55-2.52 (m, 2H), 2.47- 2.43 (m, 2H), 1.68 - 1.63 (m, 2H), 1.60-1.57 (m, 4H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 190.7, 154.3, 136.0, 129.8, 129.6, 126.8, 86.8, 40.4, 33.8, 28.3, 27.8, 26.0. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 3056, 2929, 2916, 2857, 1756, 1660, 1571, 1469, 1387, 1214, 1049, 819, 767. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>14</sub>ClIO<sub>2</sub> 392.9577, found 392.9564.

### **S-octyl 2-iodo-3,3-diphenylprop-2-enethioate (14)**



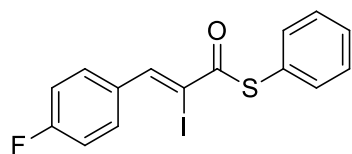
Yellow oil. **Yield:** 90% (0.108g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.34 (m, 3H), 7.29 – 7.22 (m, 5H), 7.20 – 7.17 (m, 2H), 2.78 (t, *J* = 7.2 Hz, 2H), 1.39 (qt, *J* = 7.0 Hz, 2H), 1.32 – 1.14 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 193.9, 153.6, 143.5, 139.4, 129.5, 129.0, 128.6, 128.5, 128.2, 128.0, 94.7, 31.7, 30.2, 29.0 (2C), 28.8, 28.5, 22.6, 14.1. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 3063, 2954, 2916, 2846, 1736, 1654, 1577, 1437, 1233, 1169, 1080, 927, 749, 697. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>23</sub>H<sub>27</sub>IOS 479.0906, found 479.0914.

### **(Z)-S-phenyl 2-iodo-3-phenylprop-2-enethioate (15)**



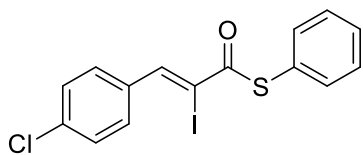
Yellow solid, melting point: 71 °C. **Yield:** 93% (0.086 g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.29 (s, 1H), 7.81 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.49 (dd, *J* = 6.8, 3.1 Hz, 2H), 7.47 – 7.43 (m, 6H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 187.5, 146.0, 144.7, 134.9, 134.8, 134.3, 130.4, 129.7, 129.2, 128.3, 99.0. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 3056, 2955, 2913, 2841, 1648, 1584, 1437, 1271, 1175, 1067, 1016, 831, 742, 685. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>11</sub>IOS 366.9654, found 366.9663.

### **(Z)-S-phenyl 3-(4-fluorophenyl)-2-iodoprop-2-enethioate (16)**



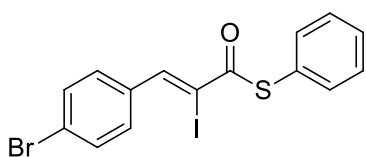
Yellow solid, melting point: 79 °C. **Yield:** 60 % (0.065g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.26 (s, 1H), 7.89 – 7.81 (m, 2H), 7.53 – 7.42 (m, 5H), 7.20 – 7.11 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 187.6, 163.7 (d, *J* = 250.0 Hz), 144.8, 134.9, 132.1 (d, *J* = 8.6 Hz), 131.0 (d, *J* = 3.4 Hz), 129.8, 129.3, 128.2, 115.6 (d, *J* = 20.0 Hz), 98.8 (d, *J* = 1.7 Hz). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): -111.81. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 3056, 2980, 2929, 2852, 1667, 1596, 1500, 1233, 1157, 1068, 870, 831, 780, 736. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>10</sub>FIOS 384.9559, found 384.9563.

**(Z) - S-phenyl 3-(4-chlorophenyl)-2-iodoprop-2-enethioate (17)**



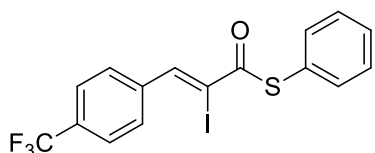
Yellow solid, melting point: 73 °C. **Yield:** 56% (0.057 g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.24 (s, 1H), 7.80 – 7.73 (m, 2H), 7.50 – 7.40 (m, 7H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 187.6, 144.6, 136.4, 134.8, 133.4, 131.0, 129.9, 129.4, 128.7, 128.1, 99.8. **IR** (ν<sub>max</sub>, cm<sup>-1</sup>): 3056, 2980, 2910, 2852, 1667, 1577, 1476, 1271, 1068, 1004, 883, 812, 742, 678. **HRMS** (ESI-TOF) m/z: [M+H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>10</sub>ClIOS 400.9264, found 400.9266.

**(Z)-S-phenyl 3-(4-bromophenyl)-2-iodoprop-2-enethioate (18)**



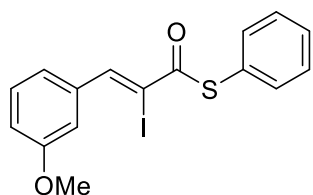
Yellow solid, melting point: 74 °C. **Yield:** 80 % (0.089g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.21 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.51 – 7.42 (m, 5H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 187.6, 144.7, 134.8, 133.8, 131.7, 131.2, 129.9, 129.3, 128.1, 124.8, 99.9. **IR** (ν<sub>max</sub>, cm<sup>-1</sup>): 3050, 2923, 2840, 1667, 1571, 1469, 1398, 1265, 1061, 1010, 876, 845, 812, 742, 678. **HRMS** (ESI-TOF) m/z: [M+Na]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>10</sub>BrIOS 444.8759, found 444.8742.

**(Z)-S-phenyl 2-iodo-3-(4-(trifluoromethyl)phenyl)prop-2-enethioate (19)**



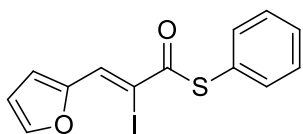
White solid, melting point: 75 °C. **Yield:** 60 % (0.065g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.28 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.44 (m, 5H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 187.7, 144.2, 138.8 (q, *J* = 1.2 Hz), 134.8, 131.7 (q, *J* = 32.7 Hz), 130.0, 129.7, 129.4, 127.9, 125.4 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 275.0 Hz), 101.9. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): -62.87. **IR** (ν<sub>max</sub>, cm<sup>-1</sup>): 3075, 2916, 2845, 1667, 1596, 1475, 1322, 1175, 1119, 1068, 883, 831, 742. **HRMS** (ESI-TOF) m/z: [M+H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>10</sub>F<sub>3</sub>IOS 434.9527, found 434.9519.

**(Z) - S-phenyl (Z)-2-iodo-3-(3-methoxyphenyl)prop-2-enethioate (20)**



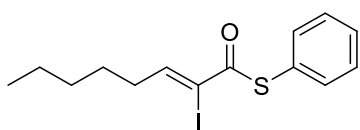
Brown solid, melting point: 71 °C. **Yield:** 39 % (0.037g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.26 (s, 1H), 7.51 – 7.40 (m, 7H), 7.37 - 7.32 (m, 2H), 3.86 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, cdcl<sub>3</sub>) δ 187.7, 159.3, 145.9, 136.2, 134.9, 129.8, 129.5, 129.3, 122.6, 116.5, 114.3, 99.2, 55.4. **HRMS** (ESI-TOF) m/z: [M+H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>13</sub>O<sub>2</sub>S 396.9759, found 396.9766.

**(Z)-S-phenyl 3-(furan-2-yl)-2-iodoprop-2-enethioate(21)**



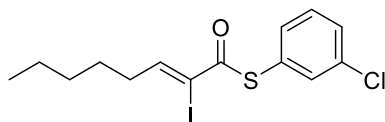
Yellow solid, **melting point:** 70 °C. **Yield:** 35% (0.036g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.41 (s, 1H), 7.68 (d, *J* = 1.6 Hz, 1H), 7.64 (d, *J* = 3.6 Hz, 1H), 7.50 – 7.41 (m, 5H), 6.62 (dd, *J* = 3.6, 1.6 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 186.9, 150.5, 145.8, 134.9, 133.7, 129.7, 129.3, 128.5, 117.6, 112.4, 92.9. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. For C<sub>13</sub>H<sub>9</sub>IO<sub>2</sub>S 356.9446, found 356.9446.

**(Z)-S-phenyl 2-iodooct-2-enethioate (22)**



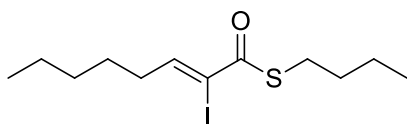
Yellow oil. **Yield:** 80 % (0.0763g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.47 – 7.40 (m, 5H), 7.29 (t, *J* = 7.0 Hz, 1H), 2.41 (q, *J* = 7.2 Hz, 2H), 1.57 (qt, *J* = 7.3 Hz, 2H), 1.39 – 1.35 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 186.1, 151.9, 134.9, 129.7, 129.2, 128.1, 103.7, 37.2, 31.4, 27.2, 22.4, 13.9. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>17</sub>IOS 361.0123, found 361.0142.

**(Z)-S-(3-chlorophenyl) 2-iodooct-2-enethioate (23)**



Yellow oil. **Yield:** 55% (0.053g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.50 – 7.46 (m, 1H), 7.45 – 7.27 (m, 4H), 2.44 (q, *J* = 7.2 Hz, 2H), 1.62 – 1.55 (m, 2H), 1.44 – 1.35 (m, 4H), 0.95 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 185.3, 152.4, 134.7, 134.6, 133.0, 130.2, 129.9, 129.8, 103.1, 37.2, 31.4, 27.2, 22.4, 13.9. **HRMS** (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>16</sub>ClIOS 394.9733, found 394.9719.

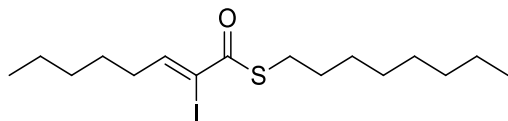
**(Z)-S-butyl 2-iodooct-2-enethioate (24)**



Yellow oil. **Yield:** 66% (0.051g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.16 (t, *J* = 7.0 Hz, 1H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.36 (q, *J* = 7.0 Hz, 2H), 1.65 – 1.49 (m, 4H), 1.47 – 1.30 (m, 6H), 0.96 – 0.91 (m, 6H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 188.2, 150.6, 104.9, 37.1, 31.4, 31.3, 30.6, 27.2, 22.4, 22.0, 13.9, 13.6. **IR** (*v*<sub>max</sub>, cm<sup>-1</sup>): 2955, 2929, 2852, 1660, 1610, 1456, 1265, 1080, 806, 723, 647. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>21</sub>IOS 341.0436, found 341.0431.

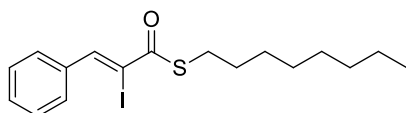


**(Z)-S-octyl 2-iodooct-2-enethioate (25)**

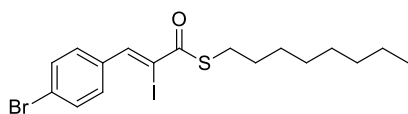


Yellow oil. **Yield:** 66% (0.065g). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.09 (t, *J* = 7.0 Hz, 1H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.29 (q, *J* = 7.0 Hz, 2H), 1.54 (qt, *J* = 7.4 Hz, 2H), 1.46 (qt, *J* = 7.4 Hz, 2H), 1.30 – 1.26 (m, 4H), 1.24 – 1.16 (m, 10H), 0.85 – 0.80 (m, 6H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 188.2, 150.6, 104.9, 37.1, 31.8, 31.4, 31.0, 29.2, 29.1 (2C), 28.9, 27.2, 22.6, 22.4, 14.1, 13.9. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>29</sub>IOS 397.1062, found 397.1043.

**(Z)-S-octyl 2-iodo-3-phenylprop-2-enethioate (26)**



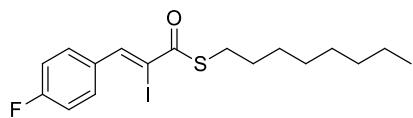
Yellow oil. **Yield:** 88% (0.089 g) isomers mixture, *E:Z* (36:62). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.19 (s, 1H), 7.79 – 7.74 (m, 2H), 7.45 – 7.40 (m, 3H), 7.36 (s, 0,6H), 7.32 – 7.24 (m, 3H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 1.2H), 1.65 (qt, *J* = 7.4 Hz, 2H), 1.55 (qt, *J* = 7.3 Hz, 1.2H), 1.45 – 1.37 (m, 2H), 1.43 – 1.20 (m, 14H), 0.90 – 0.86 (m, 4.8H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 193.5, 189.6, 145.1, 144.1, 135.8, 135.2, 130.1, 129.6, 128.9, 128.4, 128.3, 128.2, 100.5, 91.5, 31.8, 31.7, 31.5, 31.4, 30.1, 29.9, 29.2, 29.11, 29.06, 28.9, 28.8, 28.6, 22.6 (2C), 14.1 (2C). **IR** (ν<sub>max</sub>, cm<sup>-1</sup>): 3063, 2954, 2916, 2846, 1648, 1589, 1444, 1258, 1067, 1016, 774, 692. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>23</sub>IOS 403.0593, found 403.0599.



**(Z)-S-octyl 3-(4-bromophenyl)-2-iodoprop-2-enethioate (27)**

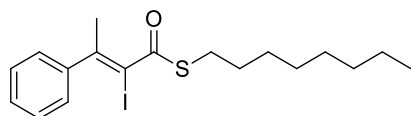
Yellow oil. **Yield:** 81% (0.085 g) isomers mixture, *E:Z* (46:54). Major isomer: **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.03 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 1.57 (qt, *J* = 7.3 Hz, 2H), 1.36-1.29 (m, 2H), 1.27-1.16 (m, 8H), 0.81 (t, *J* = 6.7 Hz, 4H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 189.6, 143.7, 134.1, 131.6, 131.1, 124.5, 101.4, 31.8, 31.6, 29.7, 29.1, 29.0, 28.9, 22.6, 14.1. **IR** (ν<sub>max</sub>, cm<sup>-1</sup>): 2954, 2916, 2840, 1654, 1577, 1482, 1398, 1265, 1074, 1004, 889, 806, 768. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>22</sub>BrIOS 480.9698, found 480.9660.

**(Z)-S-octyl 3-(4-fluorophenyl)-2-iodoprop-2-enethioate (28)**



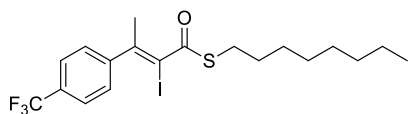
Yellow oil. **Yield:** 74% (0.079 g) isomers mixture, *E:Z* (36:62). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.15 (s, 1H), 7.85 – 7.75 (m, 2H), 7.31 (s, 0.6H), 7.28 – 7.22 (m, 1.2H), 7.17 – 7.09 (m, 2H), 7.03 – 6.96 (m, 1.2H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 1.2H), 1.65 (qt, *J* = 7.4 Hz, 2H), 1.56 (qt, *J* = 7.3 Hz, 1.2H), 1.41 (qt, *J* = 7.0 Hz, 2H), 1.36 – 1.22 (m, 14H), 0.91 – 0.85 (m, 4.8H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 193.3, 189.5, 163.5 (d, *J* = 250.0 Hz), 163.4 (d, *J* = 250.0 Hz), 143.8, 142.9, 132.0 (d, *J* = 3.0 Hz), 131.9 (d, *J* = 8.5 Hz), 131.1 (d, *J* = 3.4 Hz), 130.3 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 20.0 Hz), 115.4 (d, *J* = 20.0 Hz), 100.33, 100.31, 91.4, 91.3, 31.8, 31.7, 31.5, 30.0, 29.14, 29.11, 29.07, 29.0, 28.9, 28.8, 22.6, 22.5, 14.07, 14.05. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** -108.87. **IR** ( $\nu_{\max}$ , cm<sup>-1</sup>): 2954, 2923, 2846, 1730, 1660, 1596, 1507, 1456, 1227, 1157, 1080, 882, 826, 780, 742. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>22</sub>FIO<sub>2</sub>S 421.0498, found 421.0484.

**(Z)-S-octyl 2-iodo-3-phenylbut-2-enethioate (29)**



Yellow oil. **Yield:** 94% (0.098 g) isomers mixture, *E:Z* (50:50). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.26 (m, 4H), 7.24 – 7.17 (m, 4H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.70 (t, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 2.31 (s, 3H), 1.66 (qt, *J* = 7.4 Hz, 2H), 1.40 (qt, *J* = 7.3 Hz, 2H), 1.37 – 1.10 (m, 20H), 0.91 – 0.84 (m, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 193.45, 193.41, 150.1, 149.3, 145.1, 139.8, 128.4, 128.3, 128.1, 127.9, 127.7, 126.9, 94.9, 92.1, 31.7 (2C), 30.6, 30.4, 30.1, 29.2, 29.1, 29.0 (2C), 28.9, 28.83, 28.81, 28.4, 23.4, 22.6 (2C), 14.1 (2C). **IR** ( $\nu_{\max}$ , cm<sup>-1</sup>): 3056, 2923, 2852, 1673, 1590, 1476, 1437, 1106, 1023, 965, 761, 742, 692. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>26</sub>IO<sub>2</sub>S 417.0749, found 417.0752.

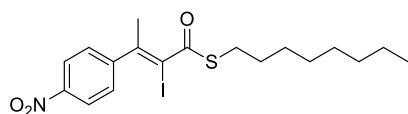
**(Z)-S-octyl 2-iodo-3-(4-(trifluoromethyl)phenyl)but-2-enethioate (30)**



Yellow oil. **Yield:** 80% (0.057g) isomers mixture, *E:Z* (45:55). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.30 (m, 4H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 2.31 (s, 3H), 1.67 (qt, *J* = 7.4 Hz, 2H), 1.41 (qt, *J* = 7.4 Hz, 2H), 1.37 – 1.10 (m, 20H), 0.91 – 0.84 (m, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 193.2, 193.1, 148.6, 148.5, 147.7, 143.4, 130.2 (q, *J* = 30.0

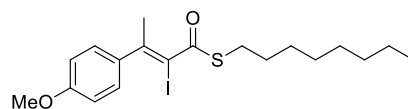
Hz), 130.1 (q,  $J = 30.0$  Hz), 128.1, 127.5, 125.6 (q,  $J = 4.0$  Hz), 125.2 (q,  $J = 4.0$  Hz), 123.9 (q,  $J = 270$  Hz), 121.2 (q,  $J = 270$  Hz), 96.4, 92.9, 31.8, 31.7, 30.6, 30.3, 30.1, 29.2, 29.1, 29.05, 29.01, 28.9, 28.84, 28.82, 28.4, 23.2, 22.6, 22.5, 14.08, 14.05.  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ ): -62.69. **IR** ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2954, 2923, 2859, 1660, 1609, 1405, 1322, 1163, 1125, 1061, 1022, 838, 774, 736, 608. **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{24}\text{F}_3\text{IOS}$  485.0623, found: 485.0613.

**(Z)-S-octyl 2-iodo-3-(4-nitrophenyl)but-2-enethioate (31)**



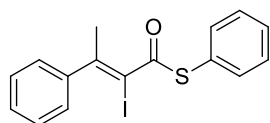
Yellow solid, melting point: 78 °C. **Yield:** 72% (0.053 g).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (d,  $J = 8.3$  Hz, 2H), 7.39 (d,  $J = 8.3$  Hz, 2H), 2.73 (t,  $J = 7.2$  Hz, 2H), 2.42 (s, 3H), 2.00 – 1.82 (m, 2H), 1.48 – 1.09 (m, 10H), 0.87 (t,  $J = 7.0$  Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.9, 147.4, 147.0, 146.5, 128.6, 123.5, 97.6, 31.7, 30.3, 29.0, 28.9, 28.8, 28.5, 23.1, 22.6, 14.1. **IR** ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3094, 2916, 2846, 1654, 1584, 1507, 1469, 1335, 1106, 1009, 857, 755, 704, 614. **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{18}\text{H}_{24}\text{INO}_3\text{S}$  462.0600, found 462.0593.

**(Z)-S-octyl 2-iodo-3-(4-methoxyphenyl)but-2-enethioate (32)**



Yellow solid, melting point: 77 °C. **Yield:** 88% (0.094g).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 – 7.14 (m, 2H), 6.95 – 6.90 (m, 2H), 3.84 (s, 3H), 2.33 (t,  $J = 7.4$  Hz, 2H), 1.81 (s, 3H), 1.42 (qt,  $J = 7.1$  Hz, 2H), 1.30 – 1.10 (m, 10H), 0.87 (t,  $J = 7.0$  Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.7, 160.4, 157.2, 130.1, 129.0, 114.2, 98.5, 55.3, 34.7, 31.7, 29.4, 28.9 (2C), 28.7, 28.5, 22.5, 14.0. **IR** ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2954, 2923, 2846, 1680, 1603, 1500, 1290, 1253, 1176, 1030, 825, 704. **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{27}\text{IO}_2\text{S}$  447.0855, found 447.0871.

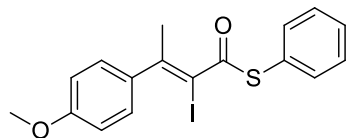
**(Z)-S-phenyl 2-iodo-3-phenylbut-2-enethioate (33)**



Yellow solid, melting point: 76 °C. **Yield:** 65% (0.063 g) isomers mixture, *E:Z* (33:67).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.51 (m, 2H), 7.49 – 7.44 (m, 3H), 7.42 – 7.25 (m, 7H), 7.20 – 7.15 (m, 2H), 7.12 – 7.09 (m, 1H), 2.45 (s, 1.5H), 2.37 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.6, 191.5, 151.3, 151.2, 145.0, 139.7, 134.7,

134.4, 129.8, 129.5, 129.3, 129.1, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 127.3, 126.8, 93.6, 91.0, 30.2, 23.7. **HRMS** (ESI-TOF)  $m/z$ :  $[M+H]^+$  calcd. for  $C_{16}H_{13}IOS$  380.9810, found 380.9804.

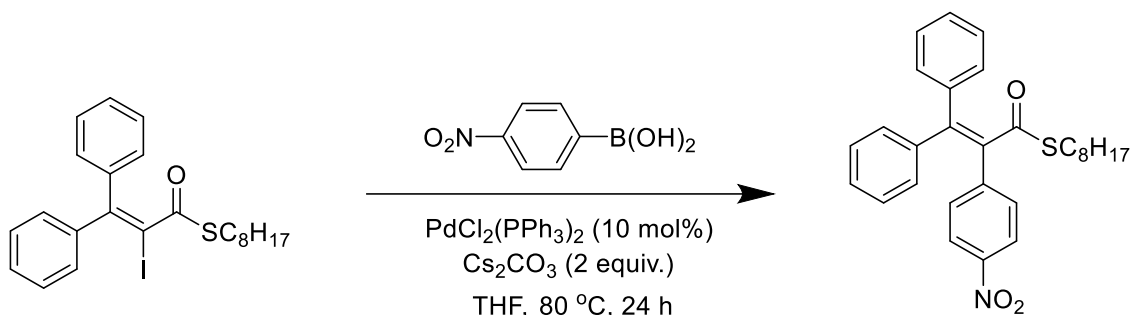
**(Z)-S-phenyl 2-iodo-3-(4-methoxyphenyl)but-2-enethioate (34)**



Yellow solid, melting point: 79 °C. **Yield:** 41% (0.0416g).  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.17 – 7.10 (m, 7H), 6.73 – 6.68 (m, 2H), 3.73 (s, 3H), 2.66 (s, 3H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  197.8, 159.5, 147.7, 133.3, 132.5, 132.3, 130.7, 128.6, 127.9, 113.2, 95.3, 55.1, 29.3. **IR** ( $\nu_{max}$ ,  $cm^{-1}$ ): 3056, 2929, 2833, 1692, 1596, 1495, 1297, 1253, 1169, 1023, 825, 742, 678. **HRMS** (ESI-TOF)  $m/z$ :  $[M+H]^+$  calcd. for  $C_{17}H_{15}IO_2S$  410.9916, found 410.9925.

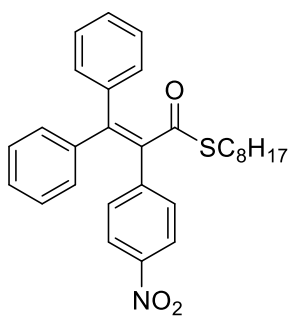
### 3. General procedure for coupling reaction

#### 3.1. Suzuki coupling reaction



**Procedure:** 4-nitrophenylboronic acid (0.071g, 0.42 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.0182g, 0.026 mmol),  $\text{Cs}_2\text{CO}_3$  (0.0847 g, 0.26 mmol) and dry THF (2 mL) were added to a sealed reaction tube containing compound **12b** (0.0622 g, 0.13 mmol). The sealed tube was submerged in an oil bath at 80 °C and stirred for 24h. After this period, the reaction was quenched with 5 mL  $\text{H}_2\text{O}$  and the organic phase was extracted with 3x10 mL EtOAc. The solvent was removed and the crude product was purified on flash column chromatography using a gradient of hexane and ethyl acetate as eluent (96:4 hexane/ethyl acetate).

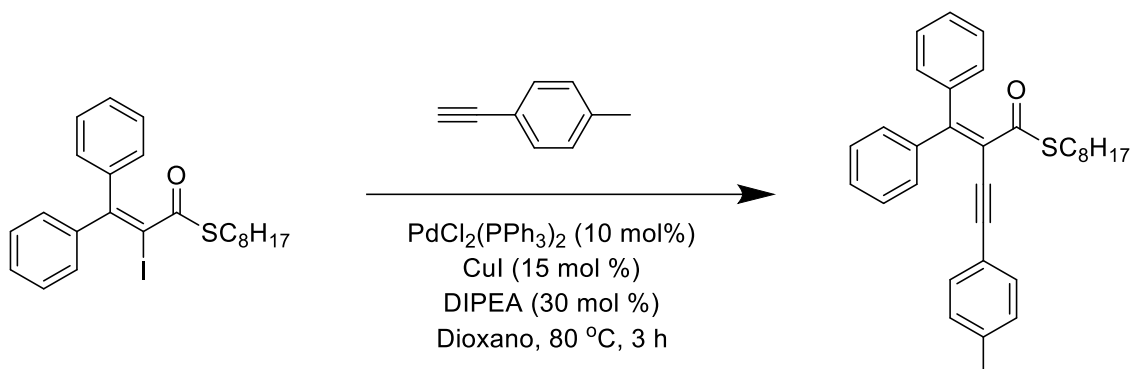
#### *S*-octyl 2-(4-nitrophenyl)-3,3-diphenylprop-2-enethioate (**39**)



Yellow solid, melting point: 90 °C. **Yield:** 74 % (0.039 g).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 8.01 (m, 2H), 7.36 – 7.27 (m, 7H), 7.24 – 7.12 (m, 3H), 7.01 – 6.95 (m, 2H), 2.82 (t,  $J = 7.2$  Hz, 2H), 1.46 – 1.37 (m, 2H), 1.30 - 1.25 (m, 10H), 0.89 (t,  $J = 7.0$  Hz, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 147.9, 146.7, 144.9, 140.1, 139.8, 138.0, 131.1, 130.9, 130.0, 128.9, 128.5, 128.2(2C), 123.5, 31.8, 29.8, 29.1, 29.0(2C), 28.6, 22.6, 14.1.

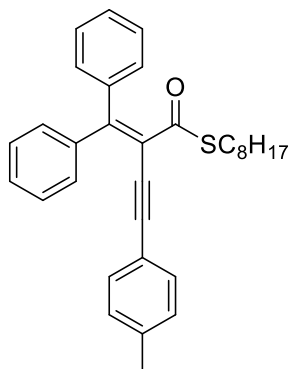
**HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. For  $\text{C}_{29}\text{H}_{32}\text{NO}_3\text{S}$  474.2103, found 474.2098.

### 3.2. Sonogoshira coupling reaction



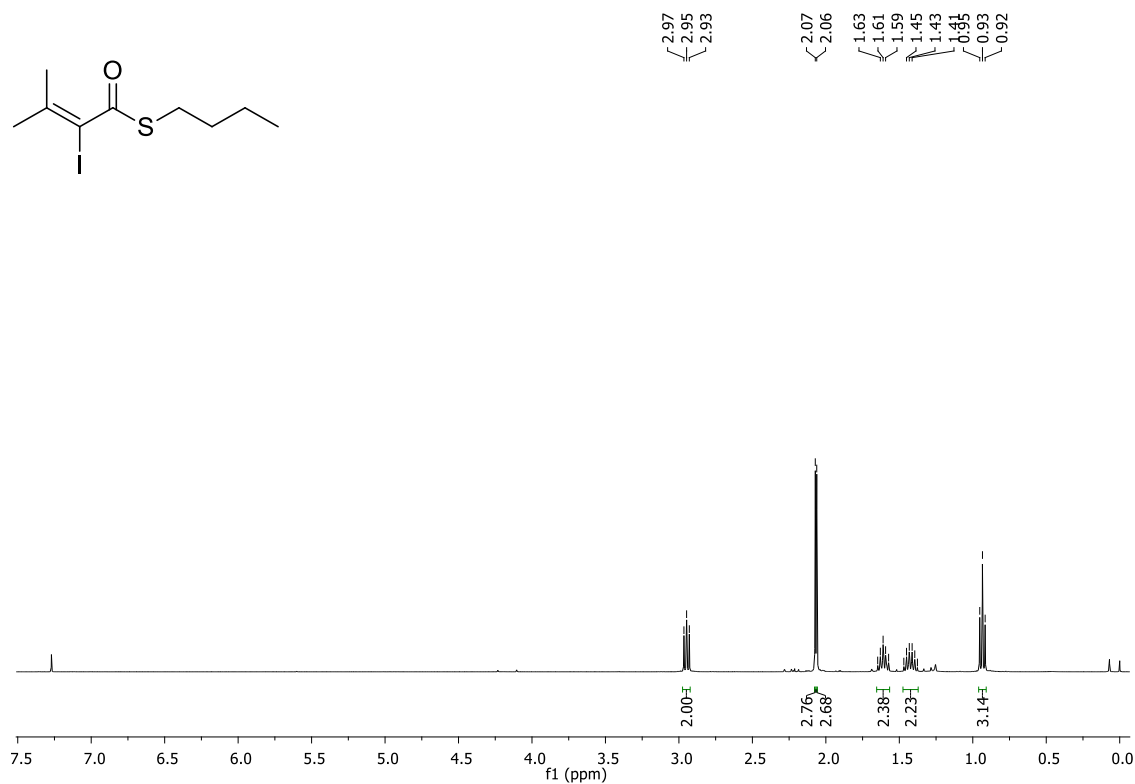
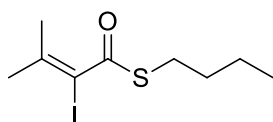
**Procedure:** *p*-tolylacetylene (0.0465g, 0.4 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.0084g, 0.012 mmol), CuI (0.0033g, 0.017 mmol), DIPEA (0.052g, 0.4 mmol) and 1mL dioxane were added to a sealed reaction tube containing compound **12b** (0.050g, 0.1 mmol). Under inert environment and reflux system at 80°C the reaction mixture was stirred vigorously for 3h. After this period, the reaction was quenching with 5 mL H<sub>2</sub>O and the organic phase was extracted with 3x10 mL EtOAc. The solvent was removed and the crude product was purified on flash column chromatography using a gradient of hexane and ethyl acetate as eluent (98:2 hexane /ethyl acetate).

#### S-octyl 2-(diphenylmethylene)-4-(*p*-tolyl)but-3-ynethioate (**40**)

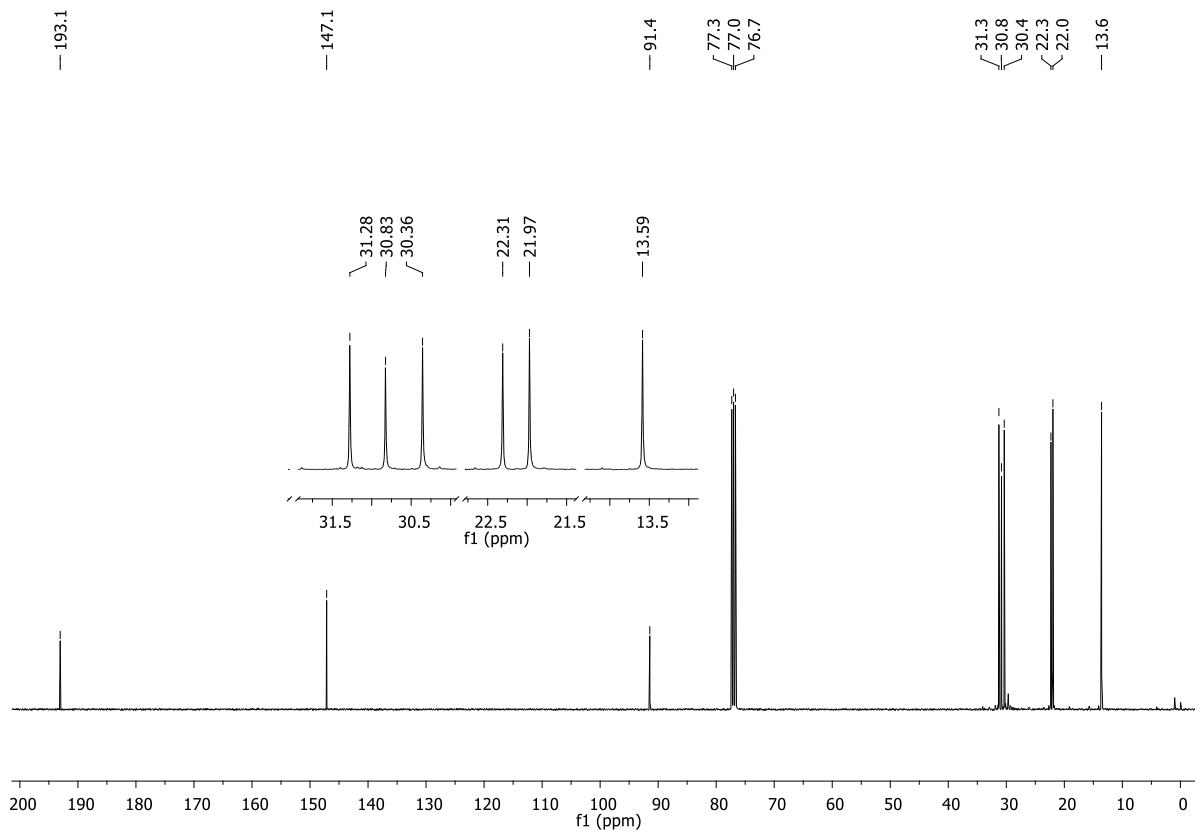


Yellow solid, melting point: 95 °C. **Yield:** in 83% (0.0367 g). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.55 – 7.47 (m, 2H), 7.38 – 7.18 (m, 10H), 7.09 (d, *J* = 7.8 Hz, 2H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.34 (s, 3H), 1.52 - 1.47 (m, 2H), 1.29-1.23 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 192.2, 153.6, 140.4, 140.3, 138.8, 131.2, 130.5, 129.8, 129.0 (2C), 128.5, 128.3, 127.9, 127.7, 121.0, 119.8, 96.2, 86.9, 31.8, 29.7, 29.1 (2C), 28.8, 22.6, 21.5, 14.1. **HRMS (ESI-TOF)** *m/z*:

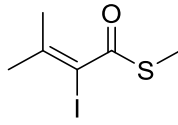
[*M*+Na]<sup>+</sup> calcd. for C<sub>32</sub>H<sub>34</sub>OS 467.2409, found 467.2383.



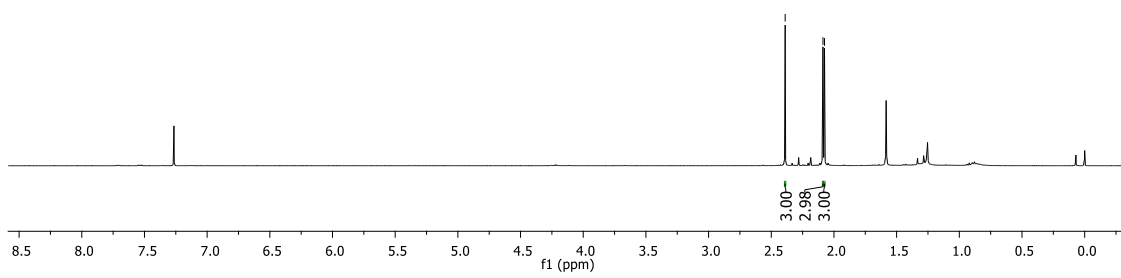
<sup>1</sup>H NMR spectrum for compound **1** in CDCl<sub>3</sub>, 400 MHz



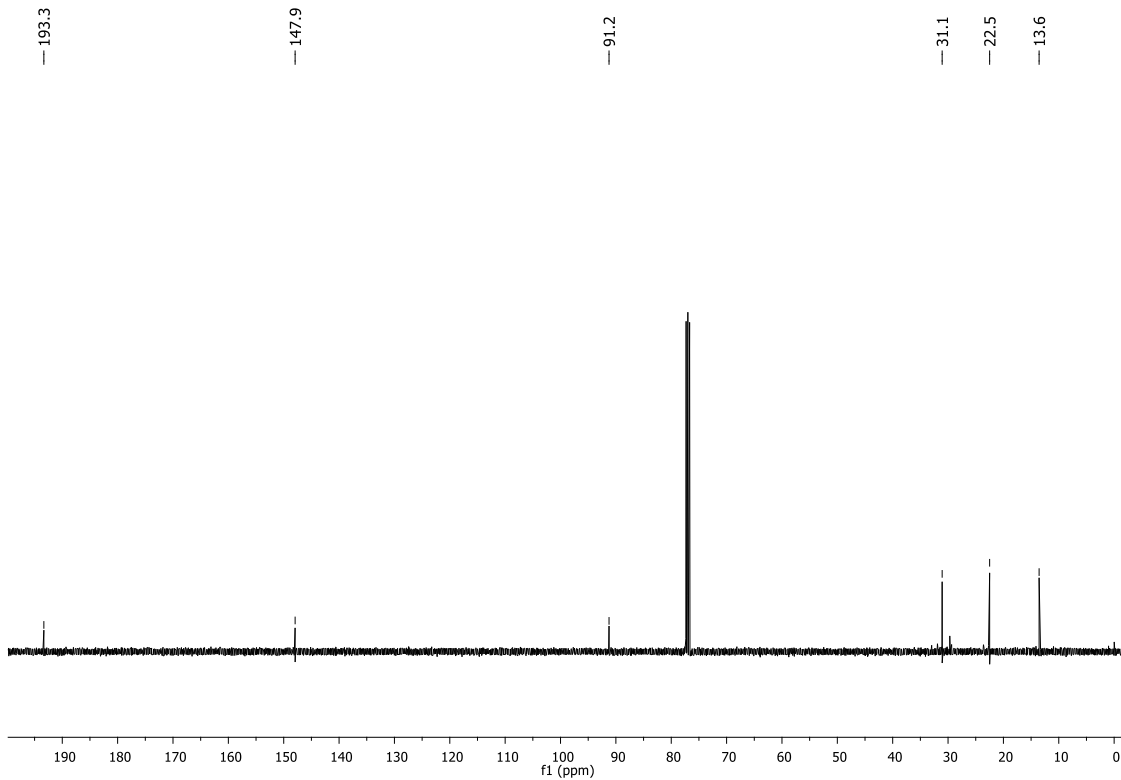
<sup>13</sup>C NMR spectrum for compound **1** in CDCl<sub>3</sub>, 100 MHz



2.39  
2.09  
2.08

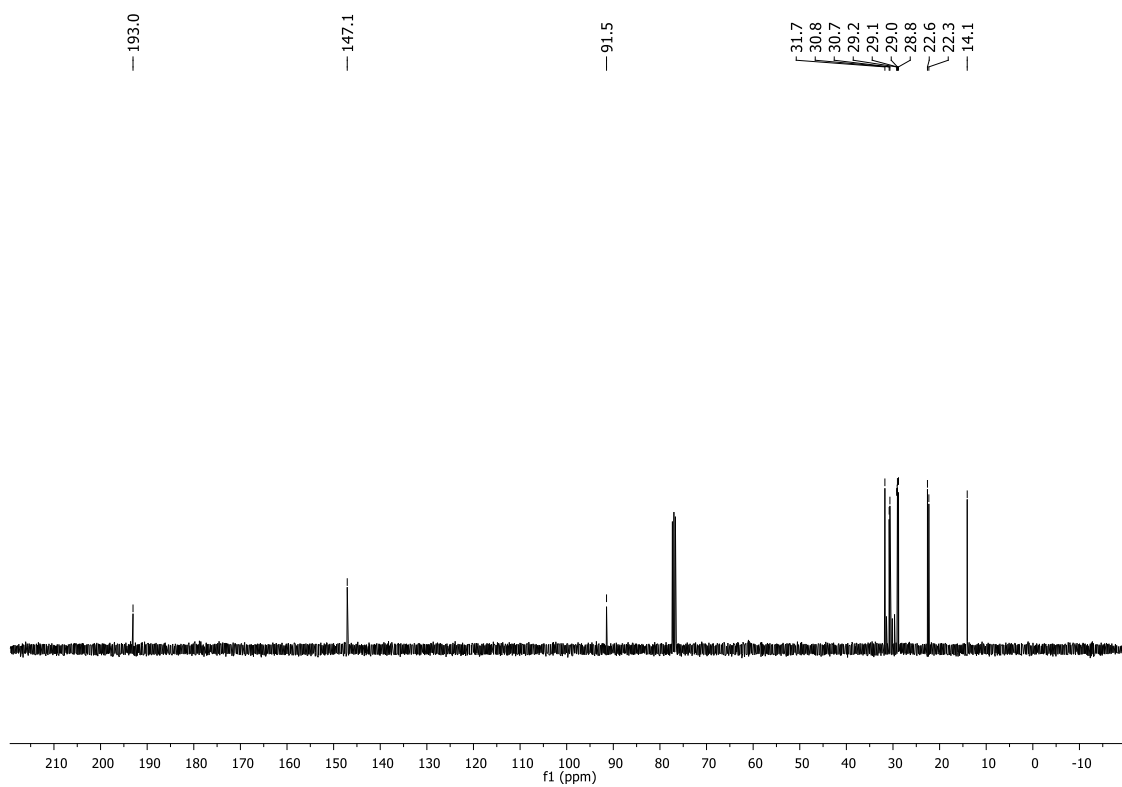
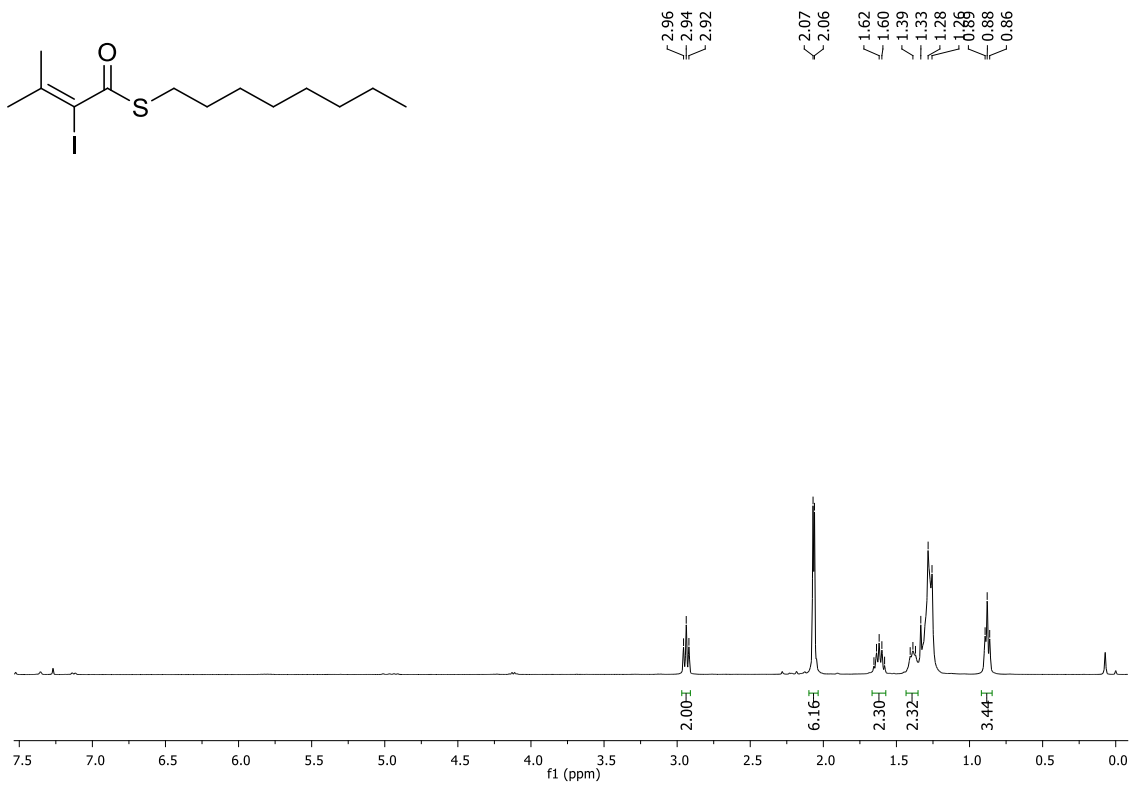


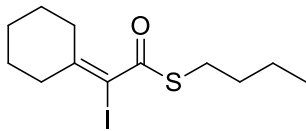
<sup>1</sup>H NMR spectrum for compound **2** in CDCl<sub>3</sub>, 400 MHz



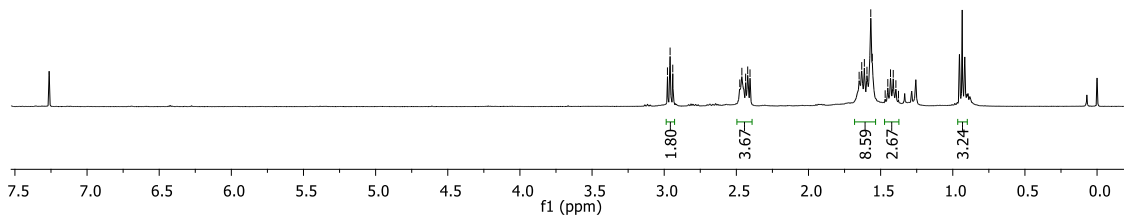
<sup>13</sup>C NMR spectrum for compound **2** in CDCl<sub>3</sub>, 100 MHz



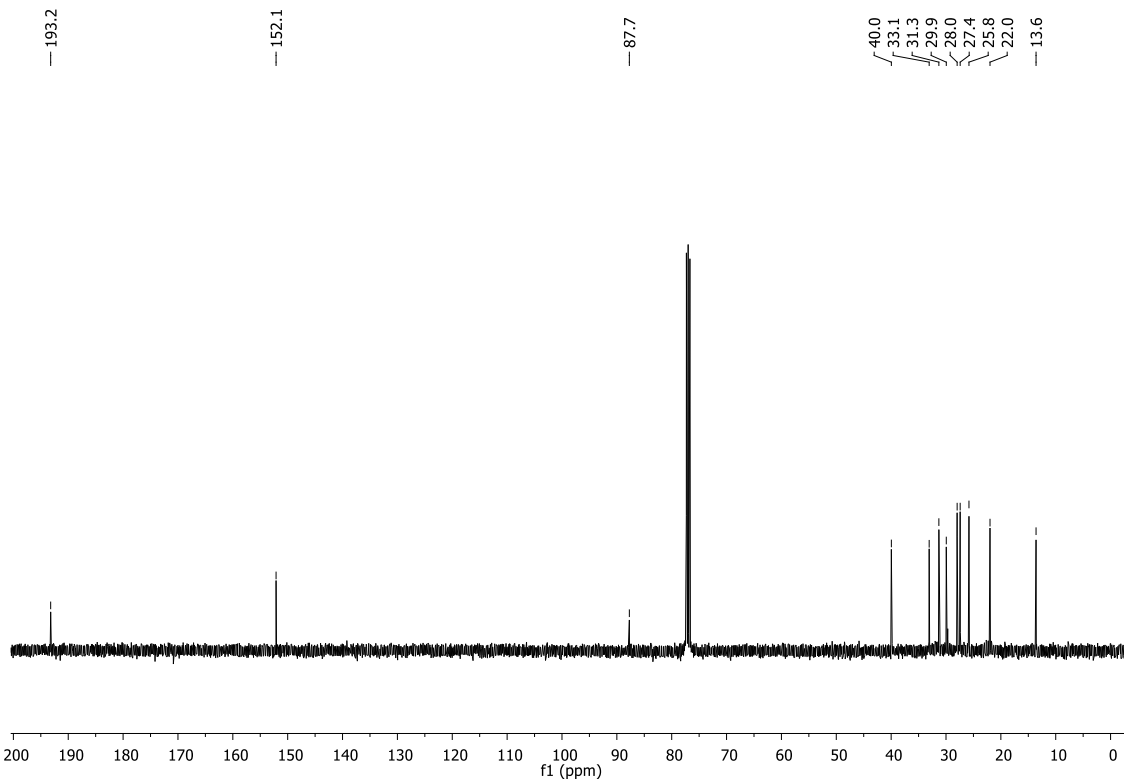




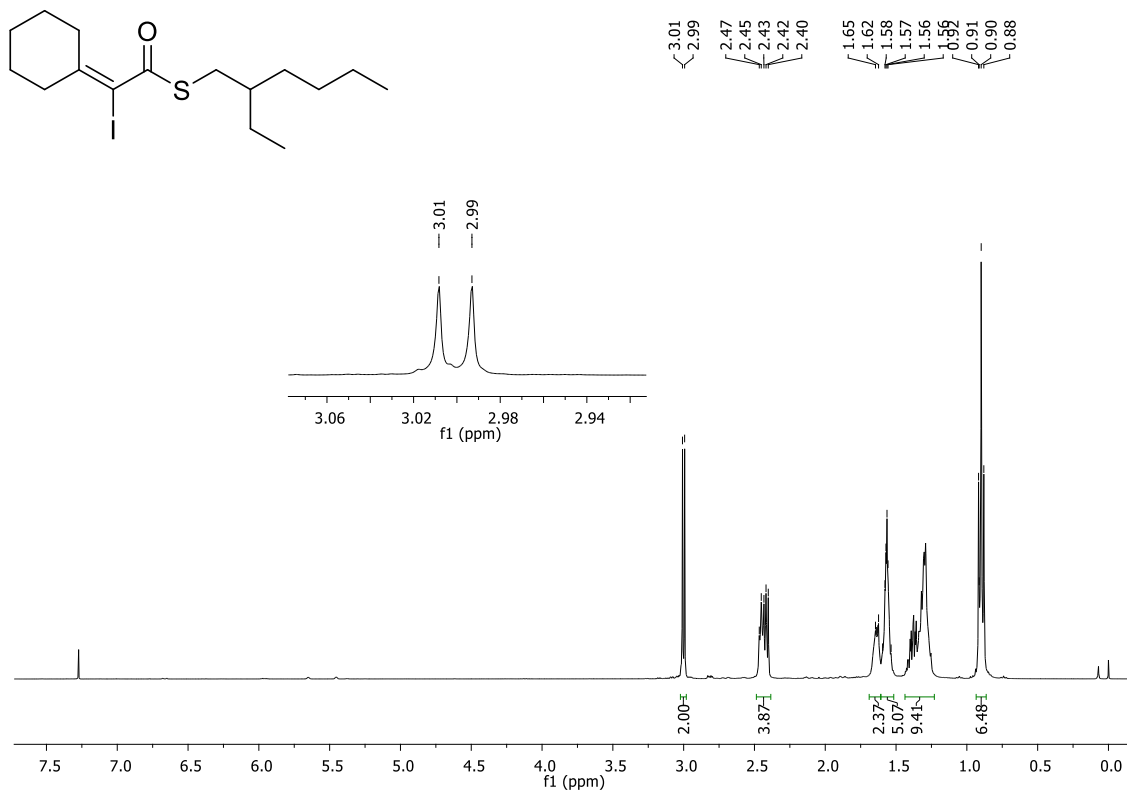
2.98  
2.96  
2.94  
2.48  
2.46  
2.44  
2.42  
2.41  
1.65  
1.63  
1.61  
1.59  
1.57  
1.56  
1.47  
1.45  
1.43  
1.41  
1.39  
1.38



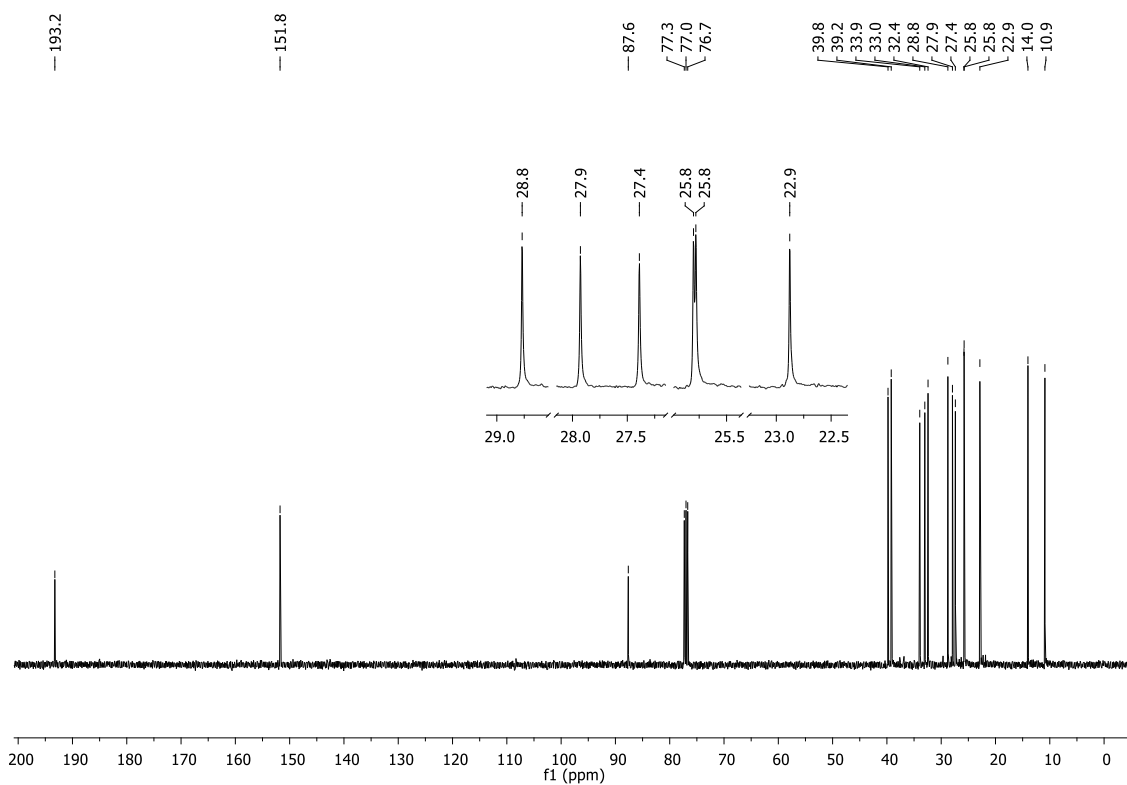
$^1\text{H}$  NMR spectrum for compound **4** in  $\text{CDCl}_3$ , 400 MHz



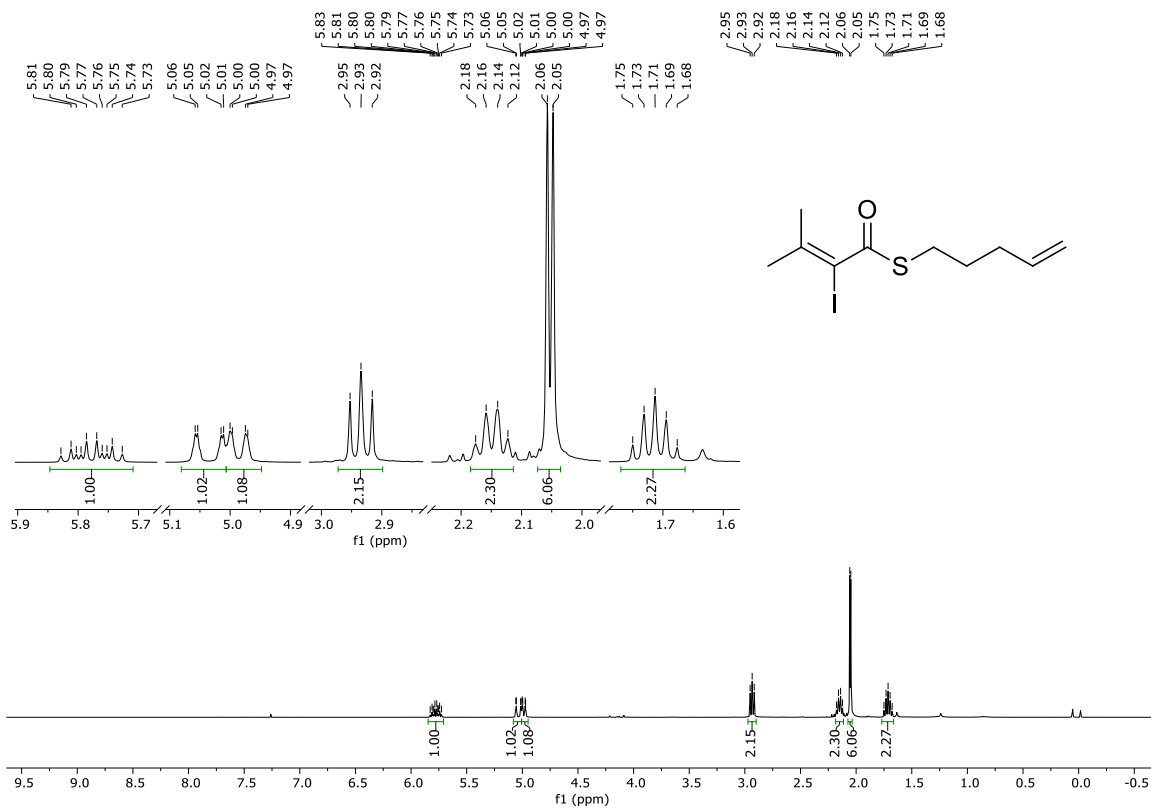
$^{13}\text{C}$  NMR spectrum for compound **4** in  $\text{CDCl}_3$ , 100 MHz



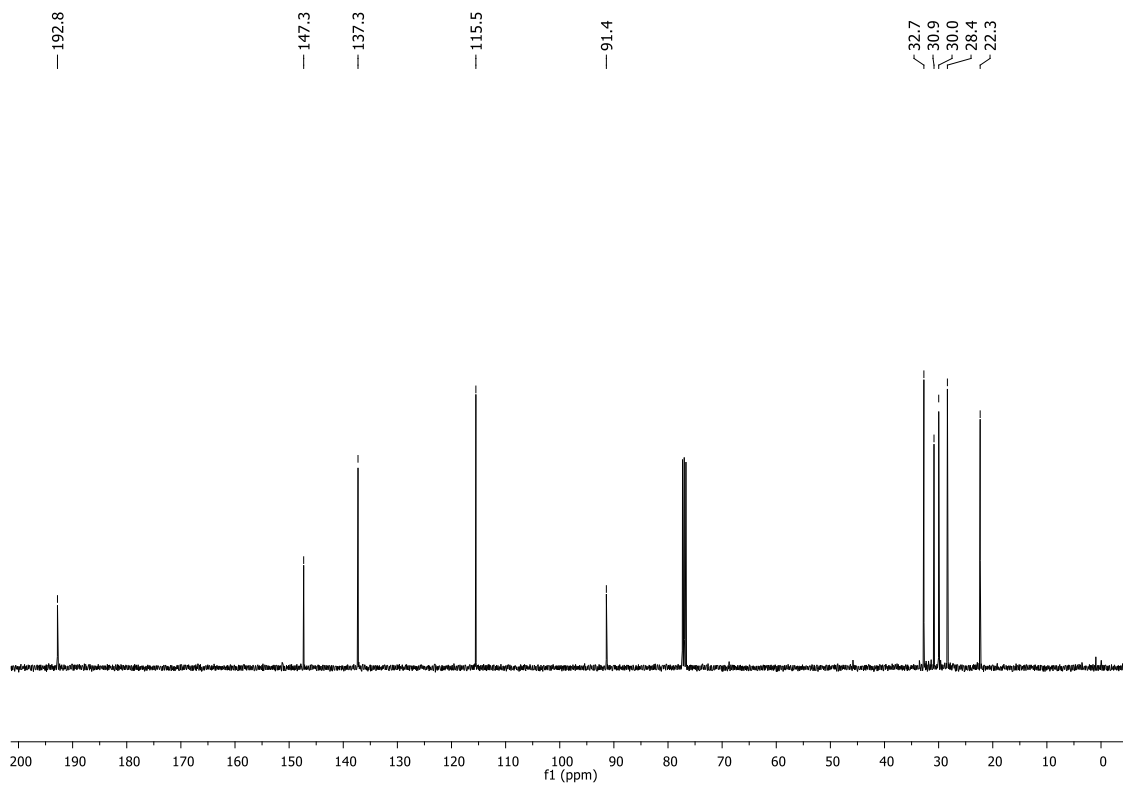
<sup>1</sup>H NMR spectrum for compound 5 in CDCl<sub>3</sub>, 400 MHz



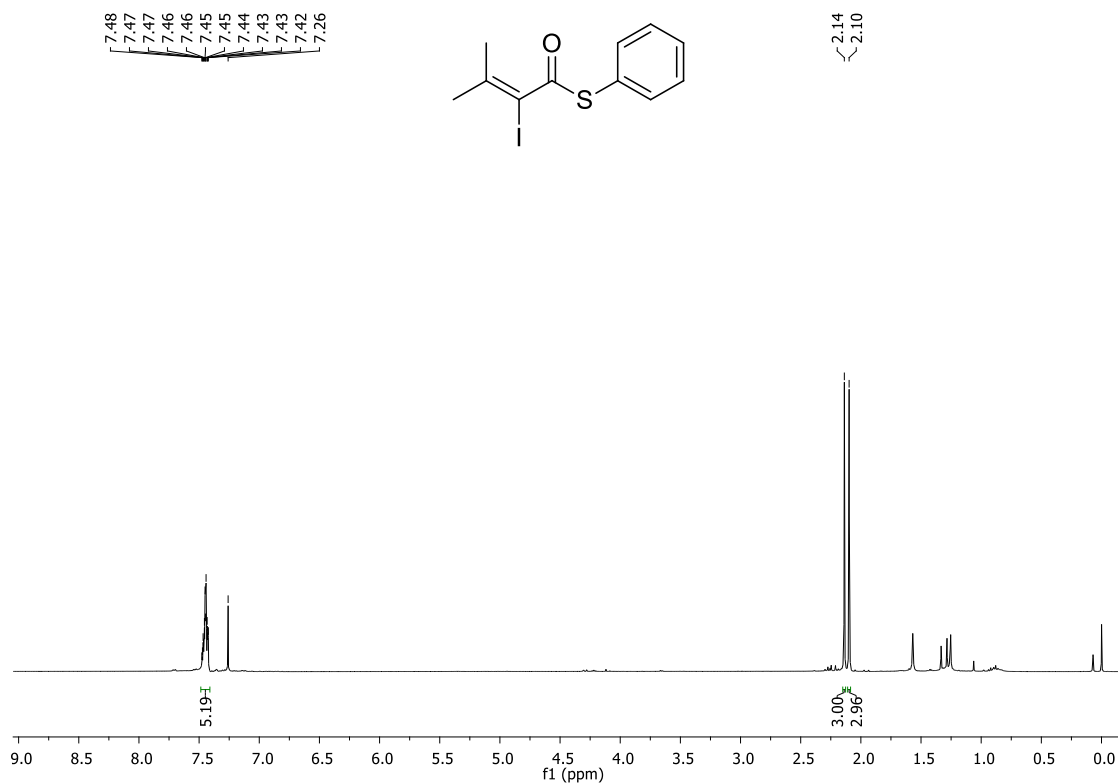
<sup>13</sup>C NMR spectrum for compound 5 in CDCl<sub>3</sub>, 100 MHz



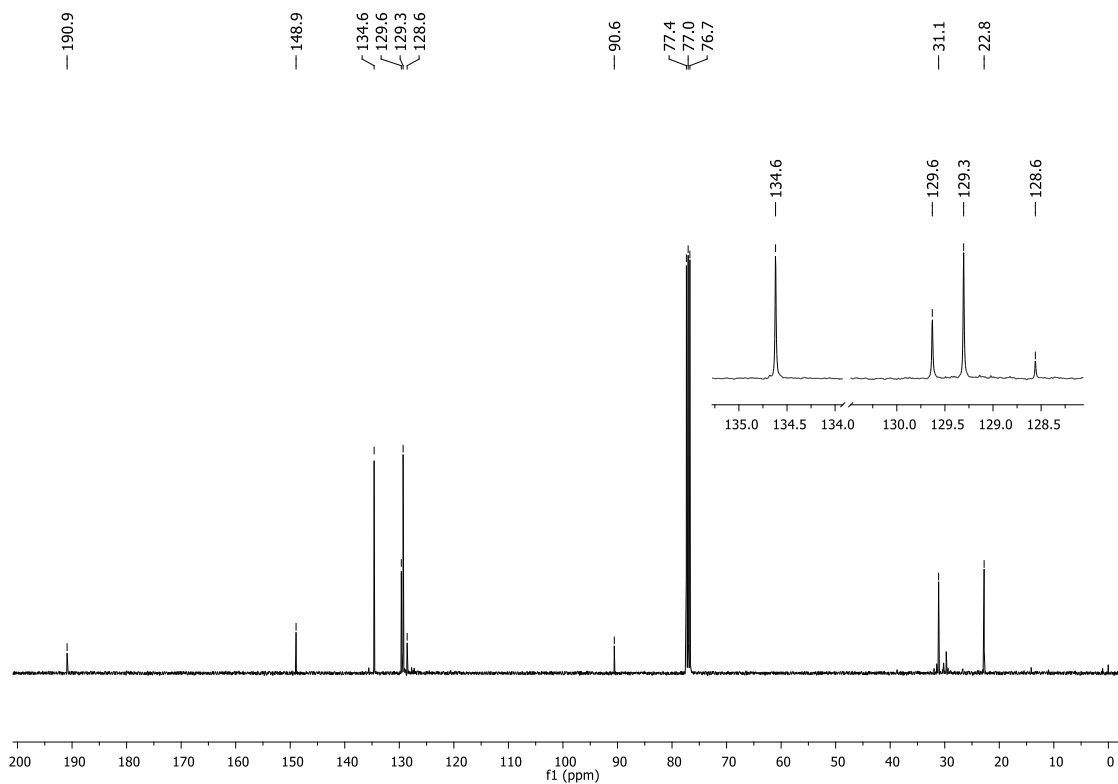
<sup>1</sup>H NMR spectrum for compound 6 in CDCl<sub>3</sub>, 400 MHz



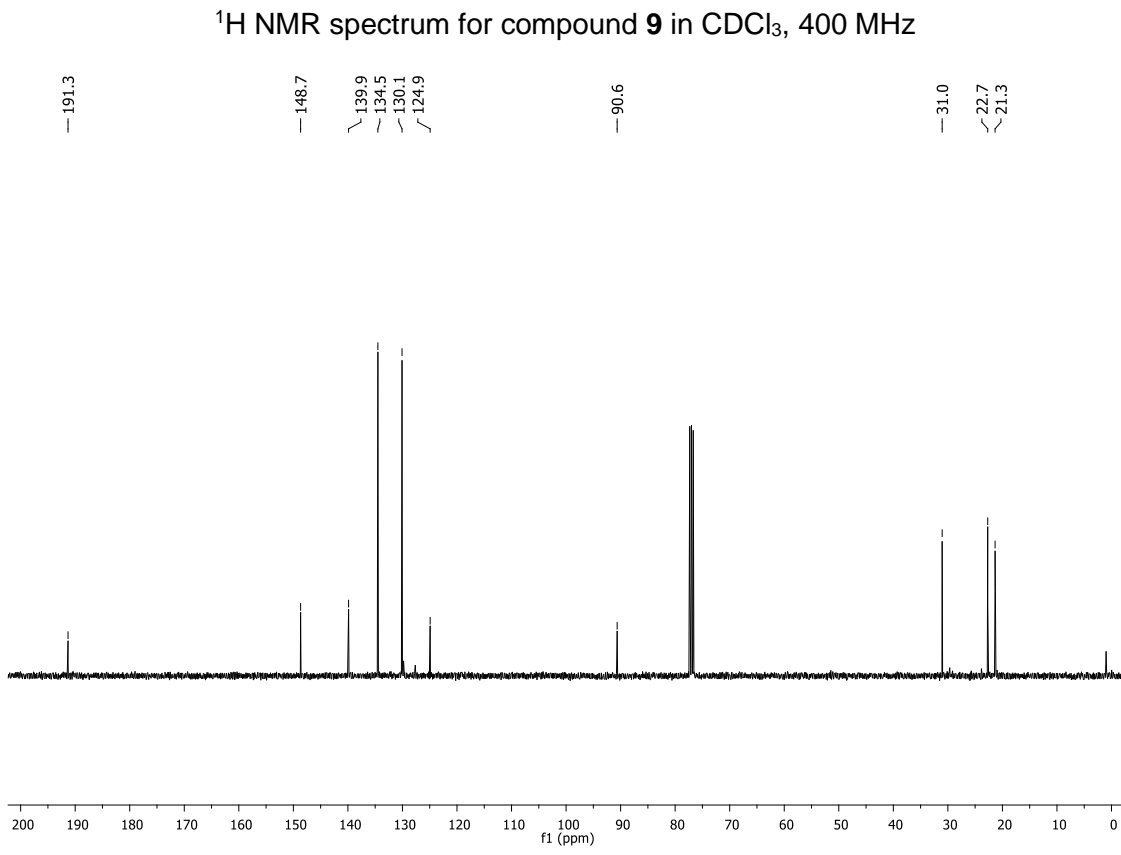
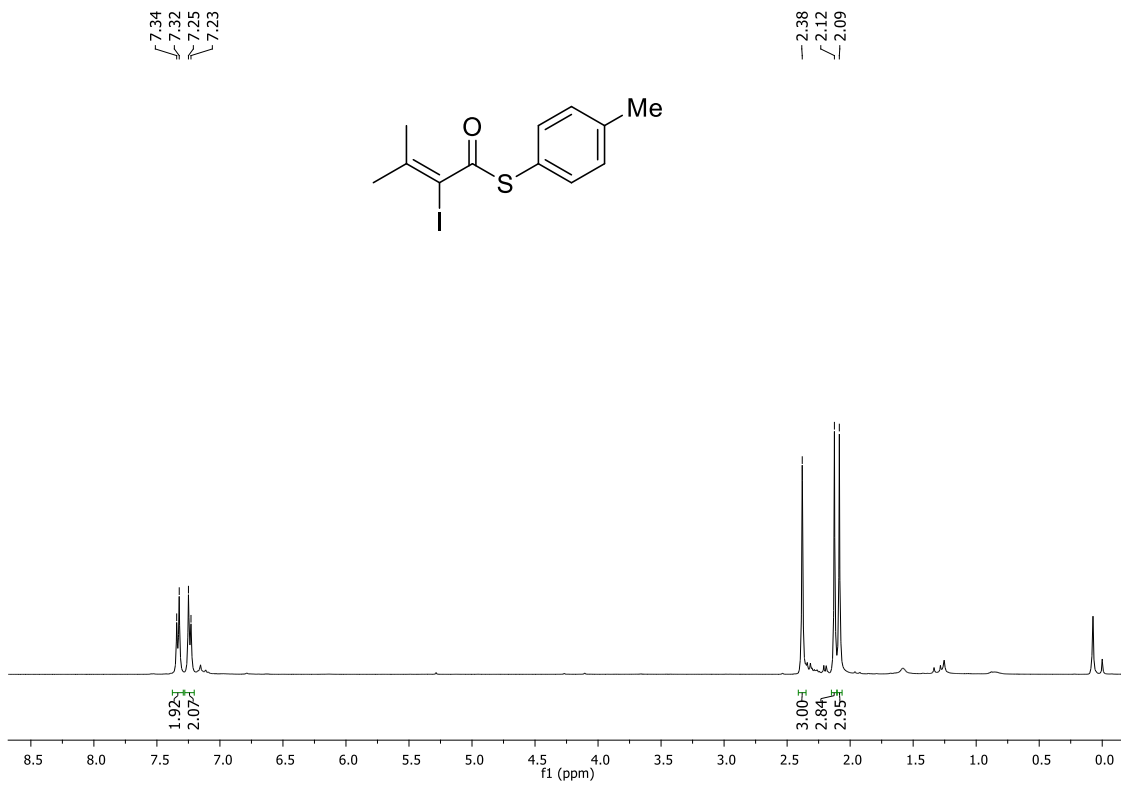
<sup>13</sup>C NMR spectrum for compound 6 in CDCl<sub>3</sub>, 100 MHz

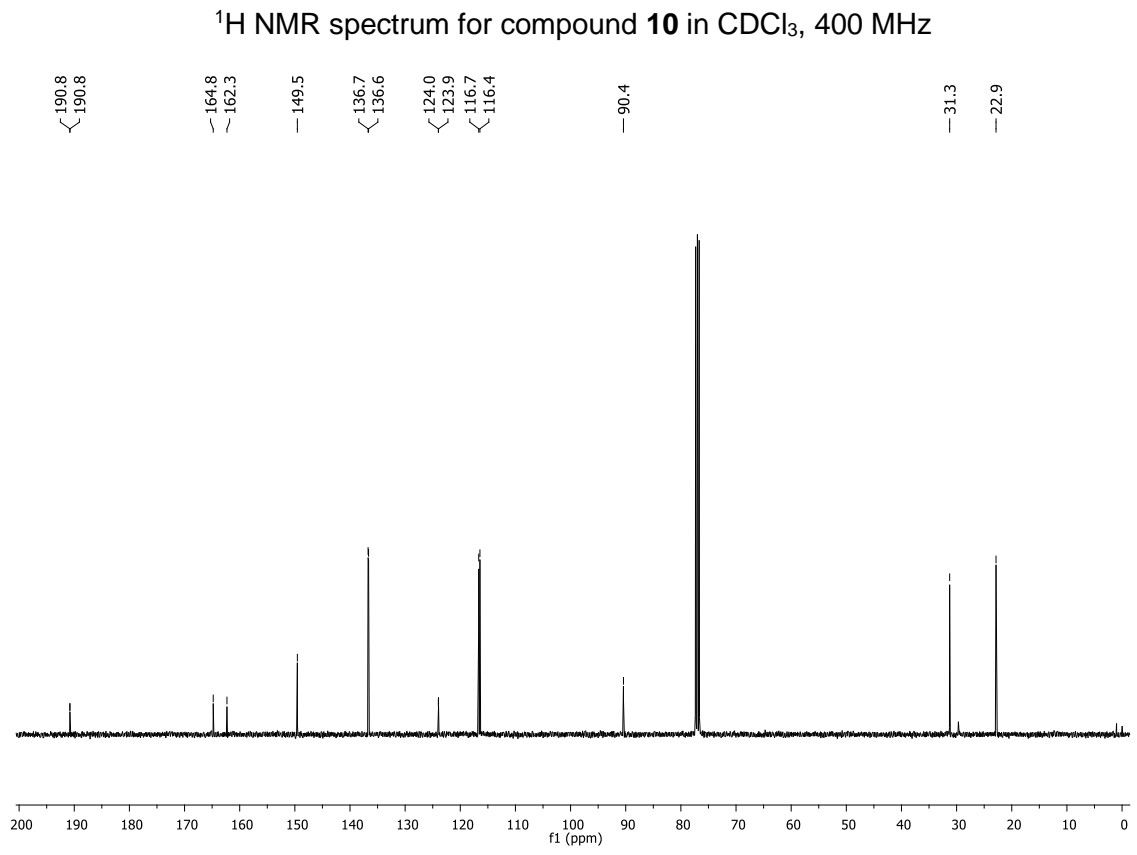
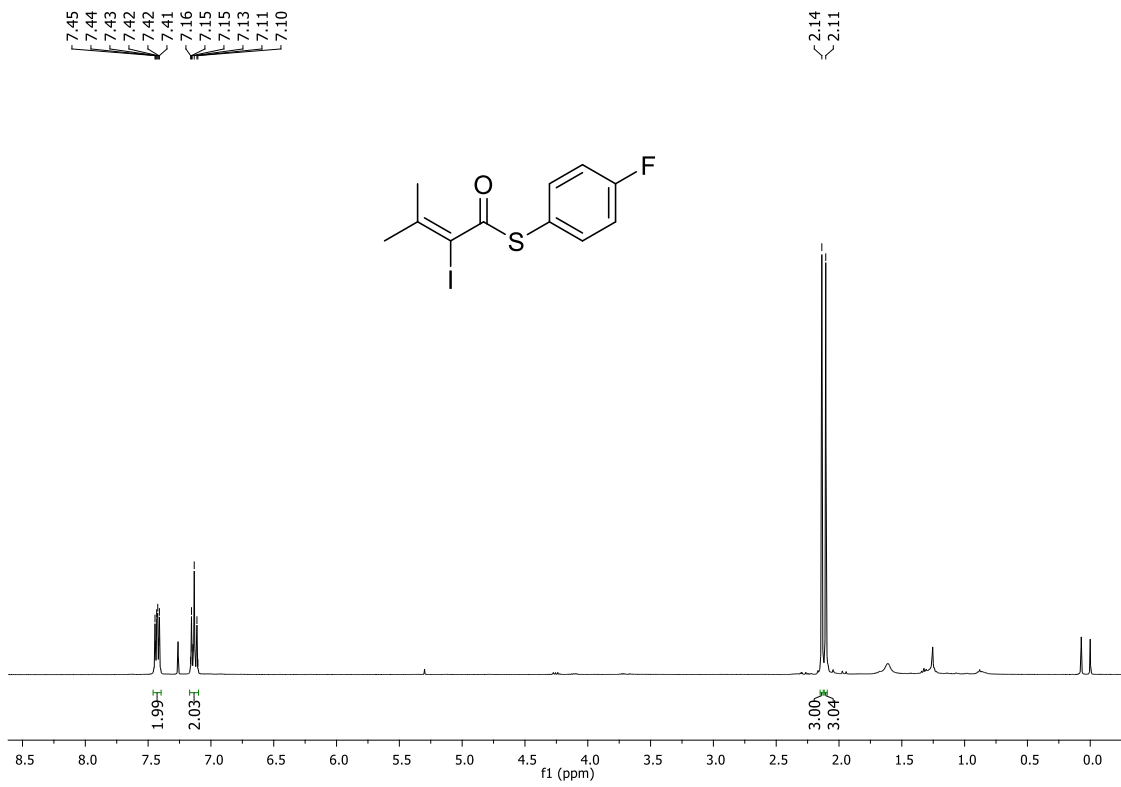


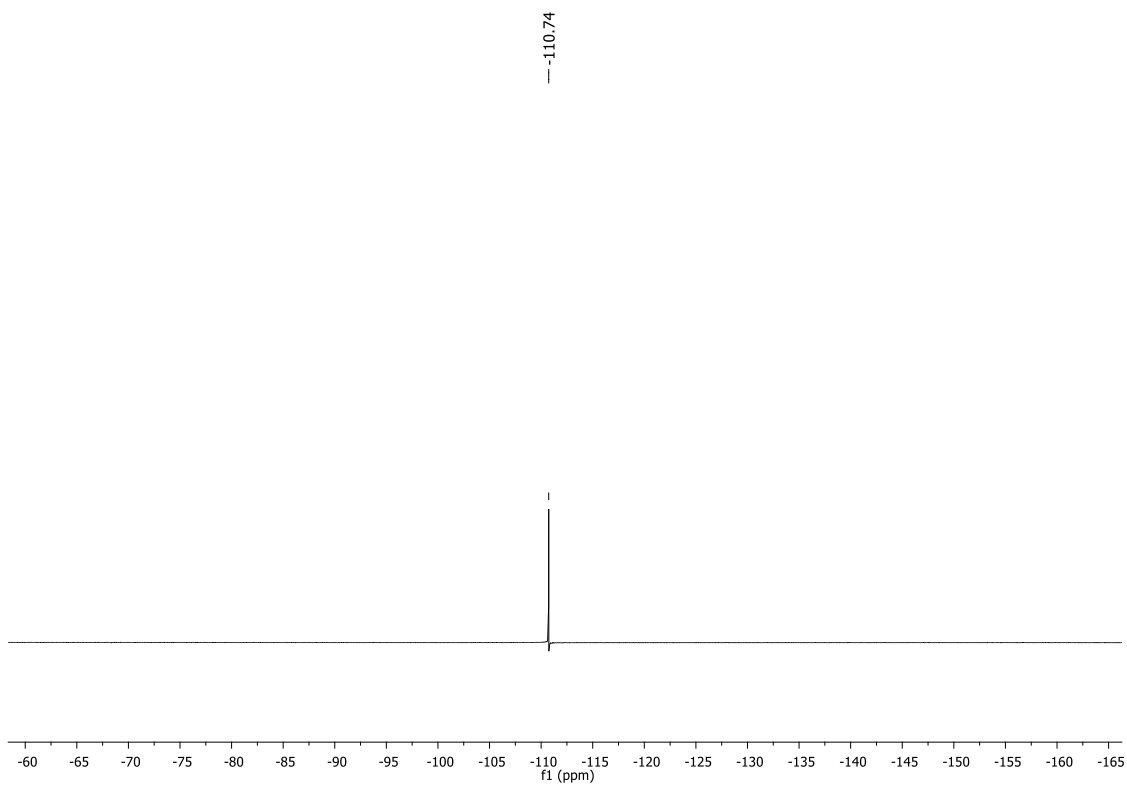
<sup>1</sup>H NMR spectrum for compound 7 in CDCl<sub>3</sub>, 400 MHz



<sup>13</sup>C NMR spectrum for compound 7 in CDCl<sub>3</sub>, 100 MHz

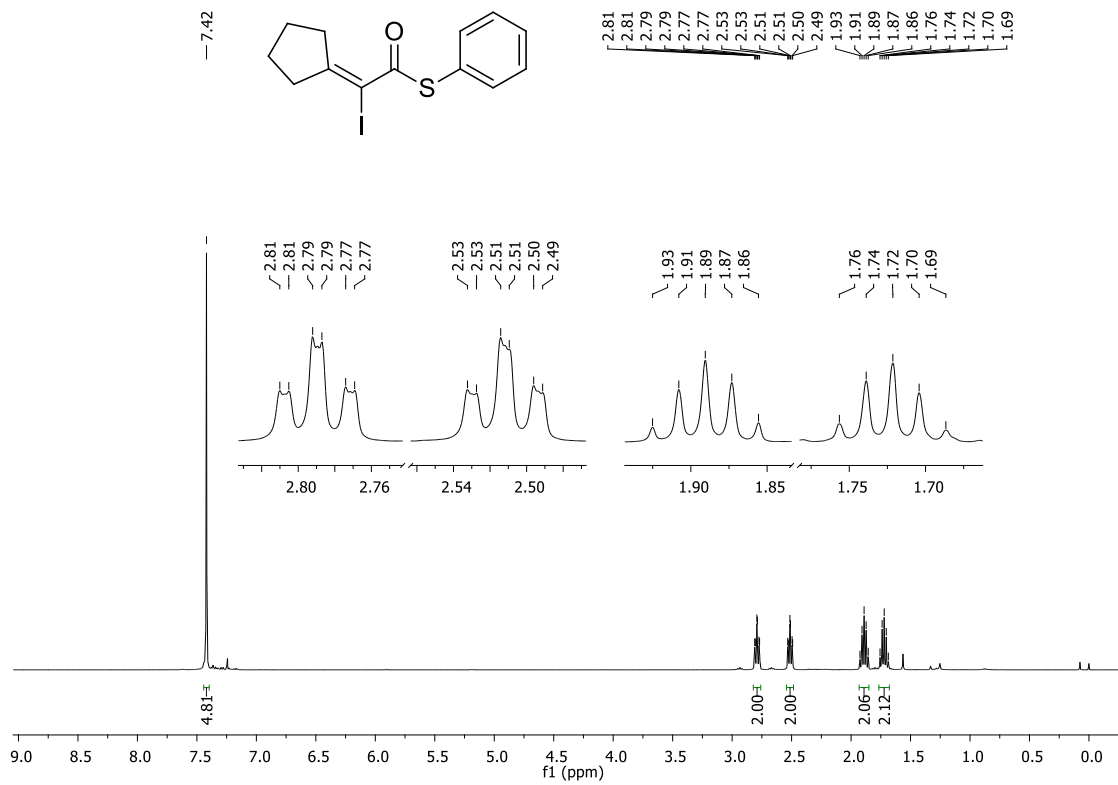




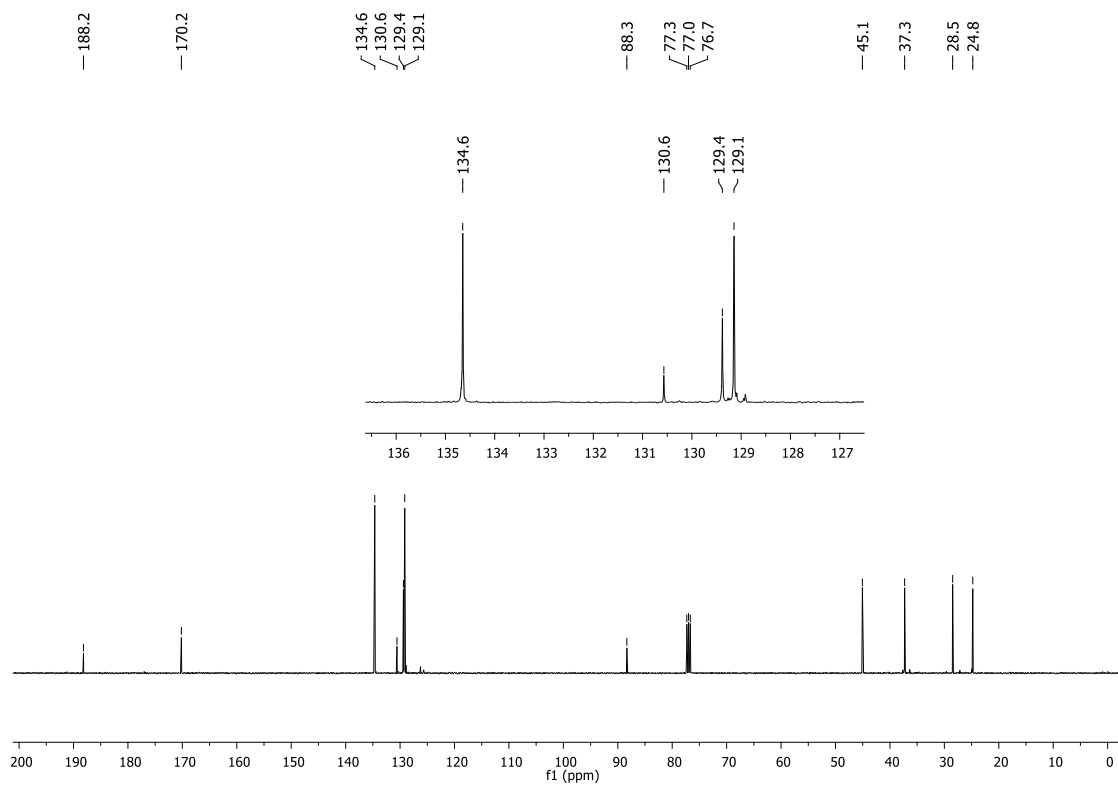


$^{19}\text{F}$  NMR spectrum for compound **10** ( $\text{CDCl}_3$ , 376 MHz)

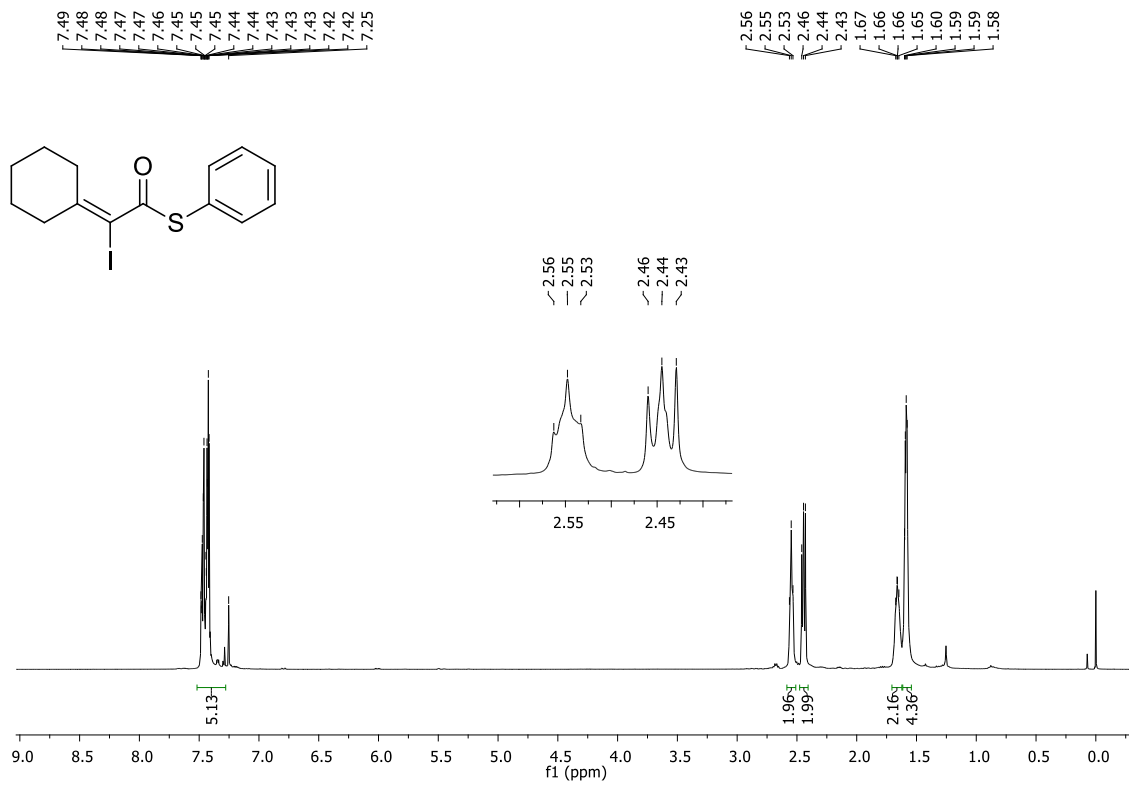




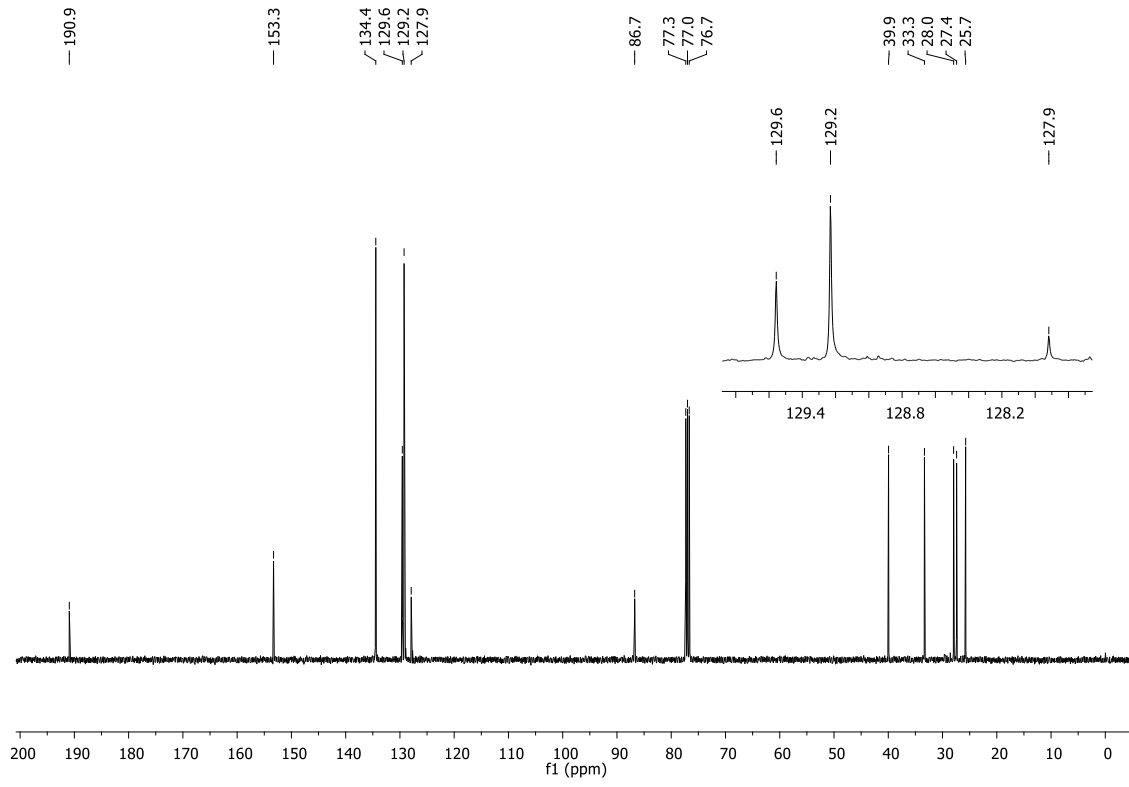
<sup>1</sup>H NMR spectrum for compound 11 in CDCl<sub>3</sub>, 400 MHz



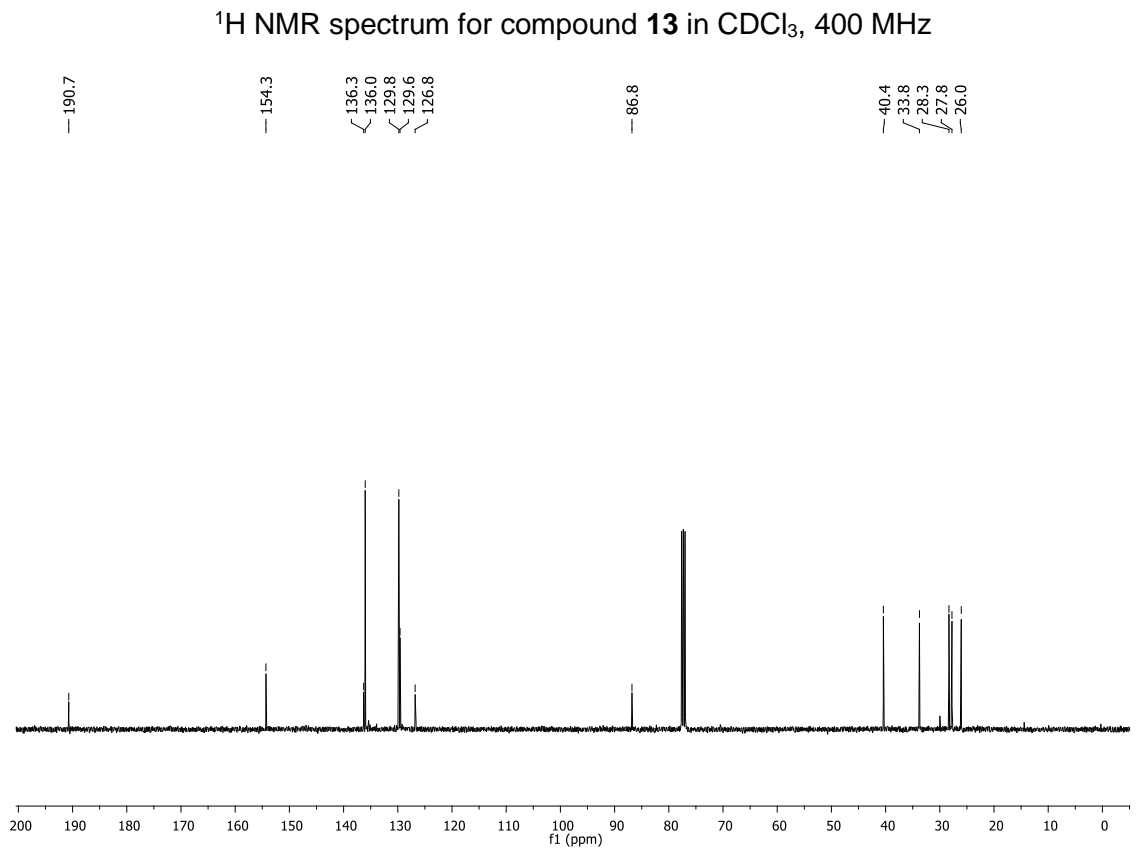
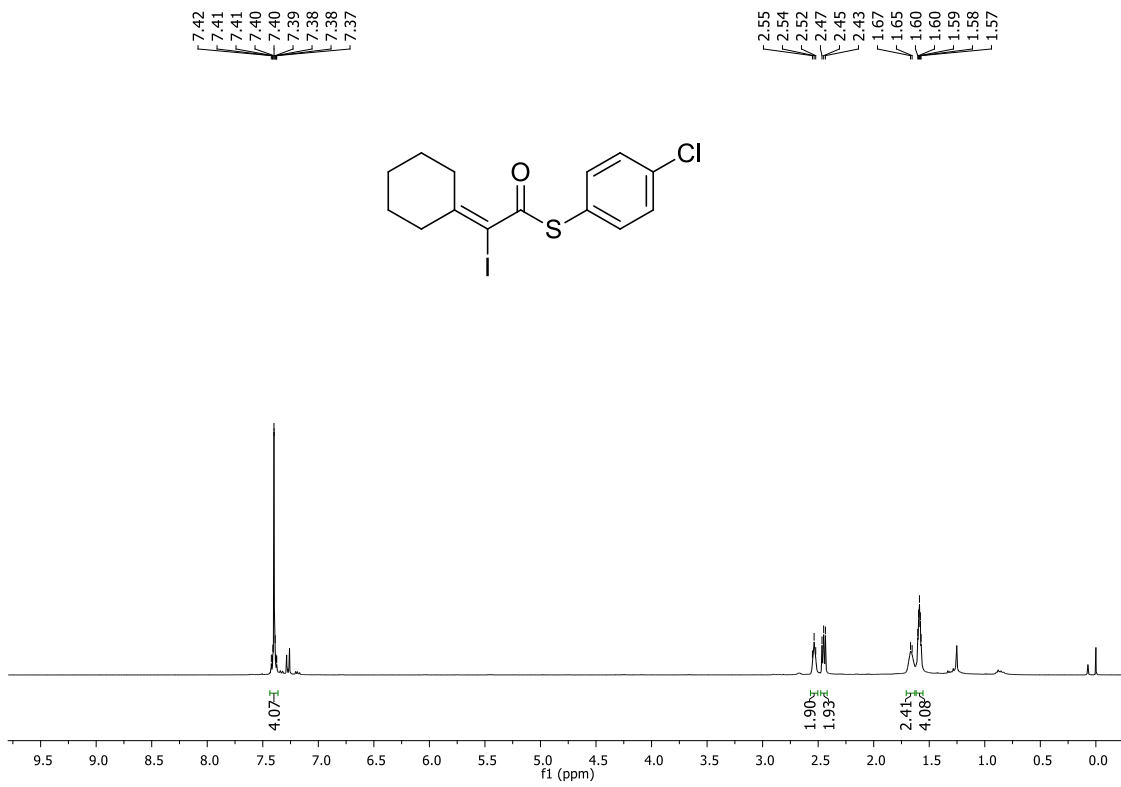
<sup>13</sup>C NMR spectrum for compound 11 in CDCl<sub>3</sub>, 100 MHz

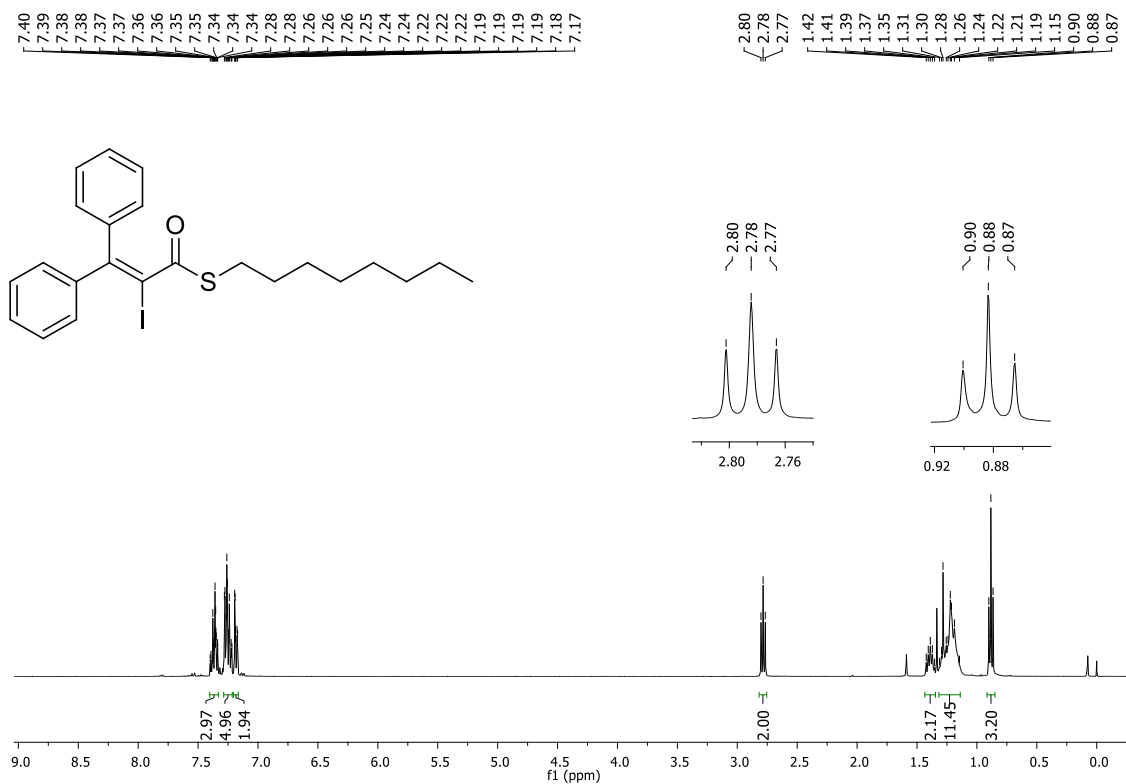


<sup>1</sup>H NMR spectrum for compound 12 in CDCl<sub>3</sub>, 400 MHz

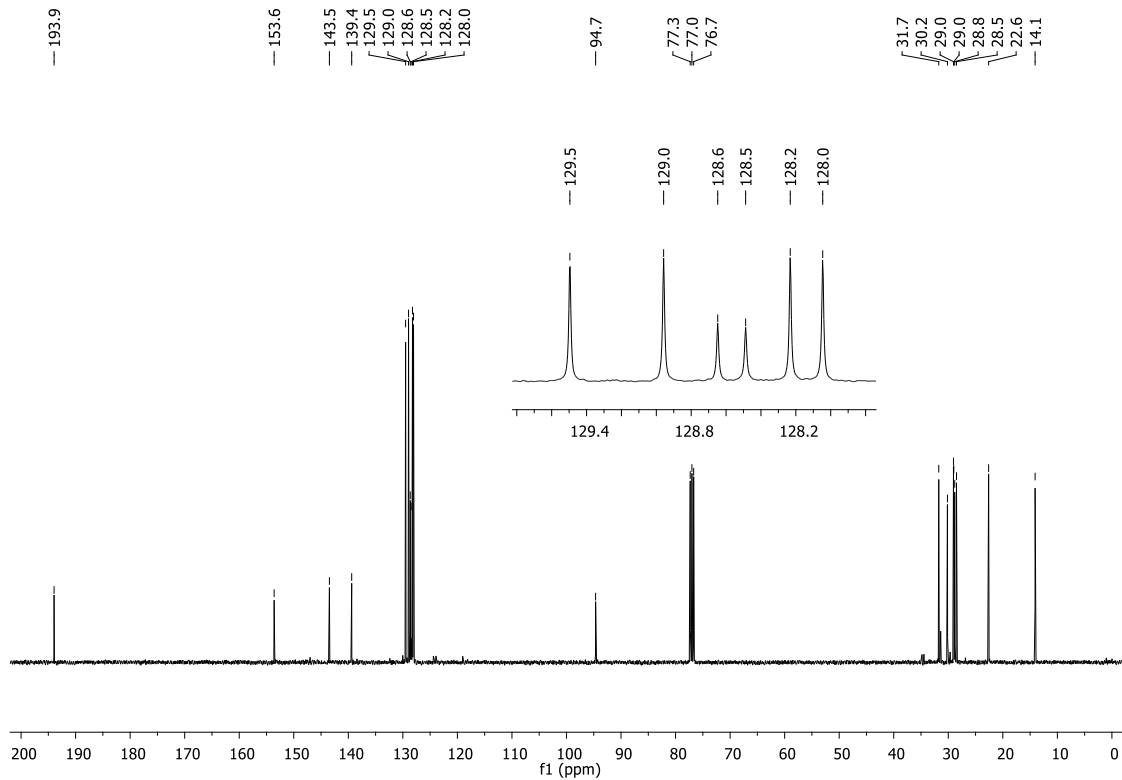


<sup>13</sup>C NMR spectrum for compound 12 in CDCl<sub>3</sub>, 100 MHz

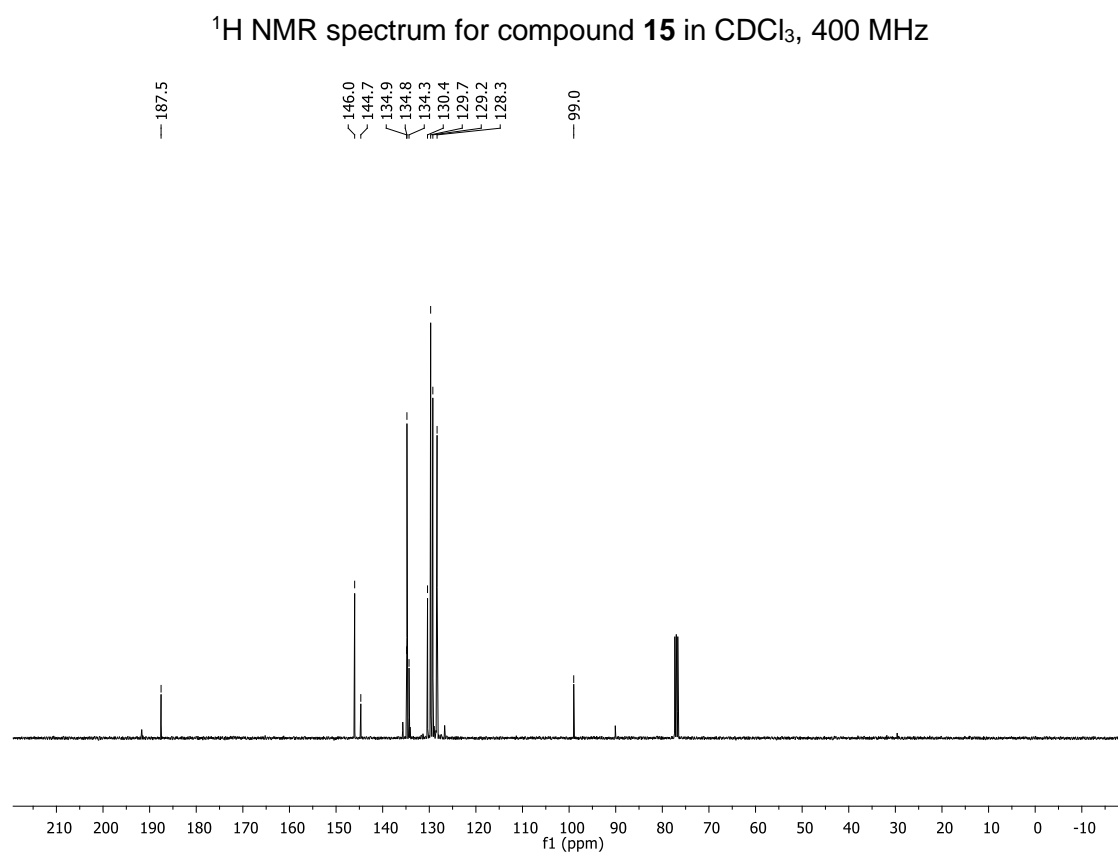
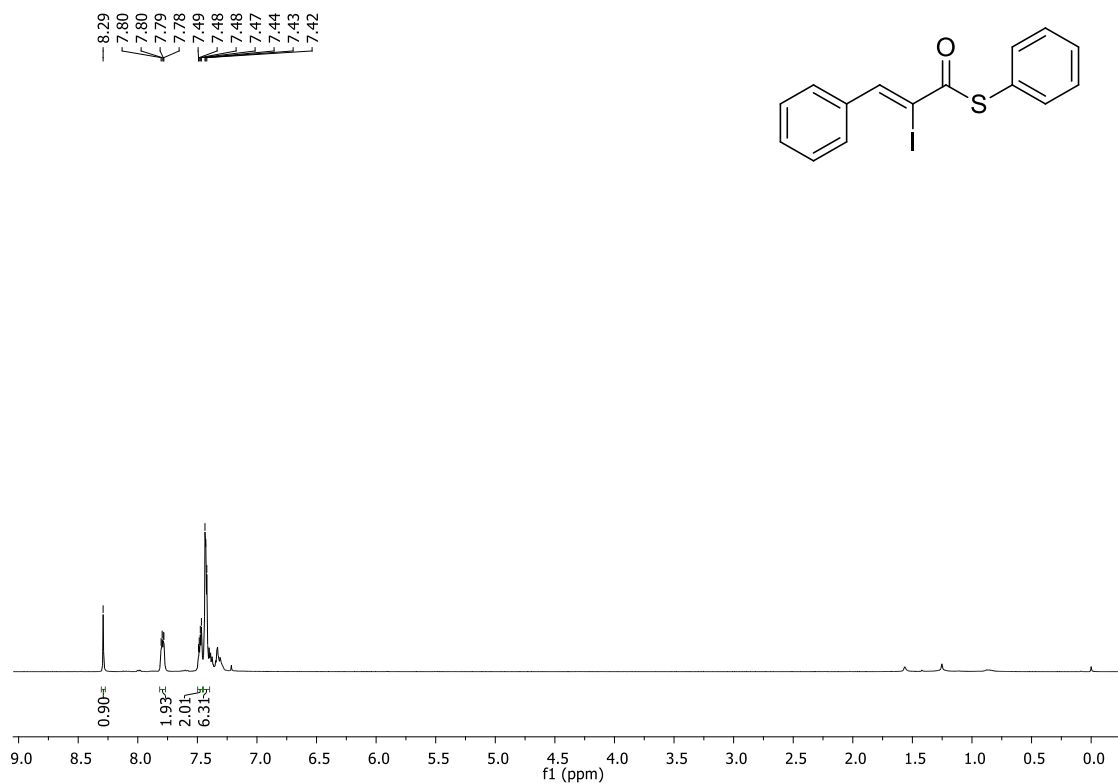


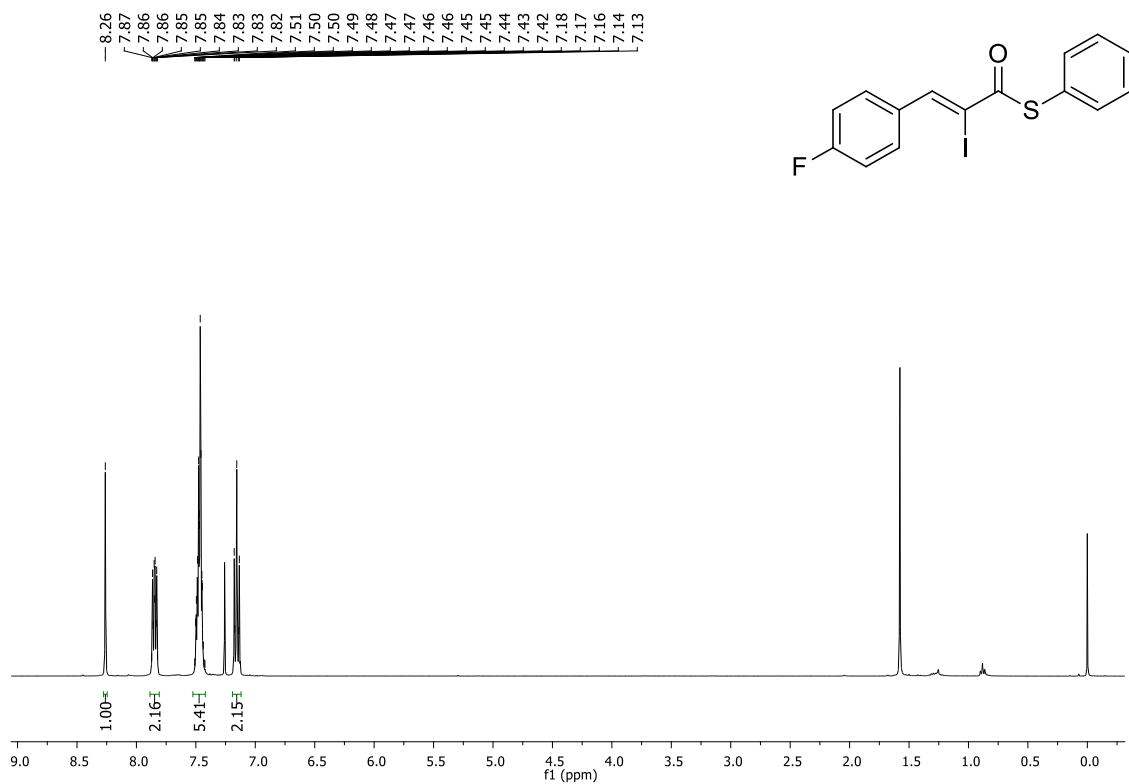


<sup>1</sup>H NMR spectrum for compound 14 in CDCl<sub>3</sub>, 400 MHz

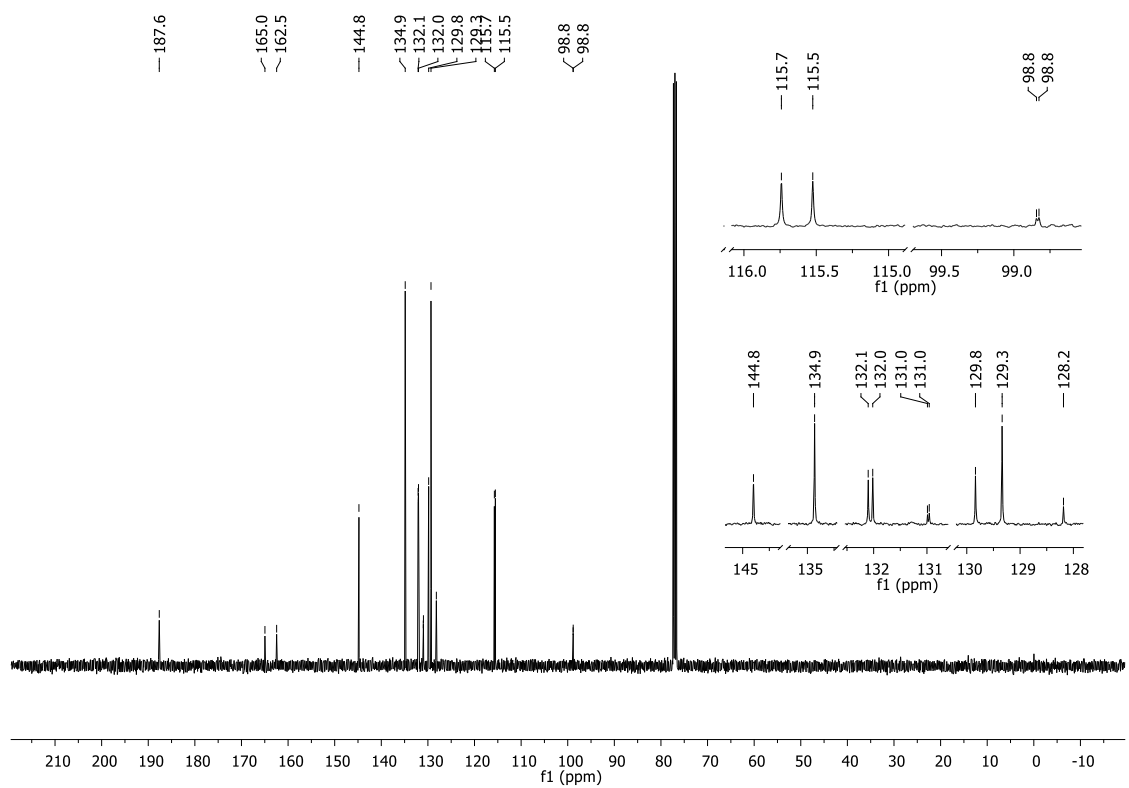


<sup>13</sup>C NMR spectrum for compound 14 in CDCl<sub>3</sub>, 100 MHz

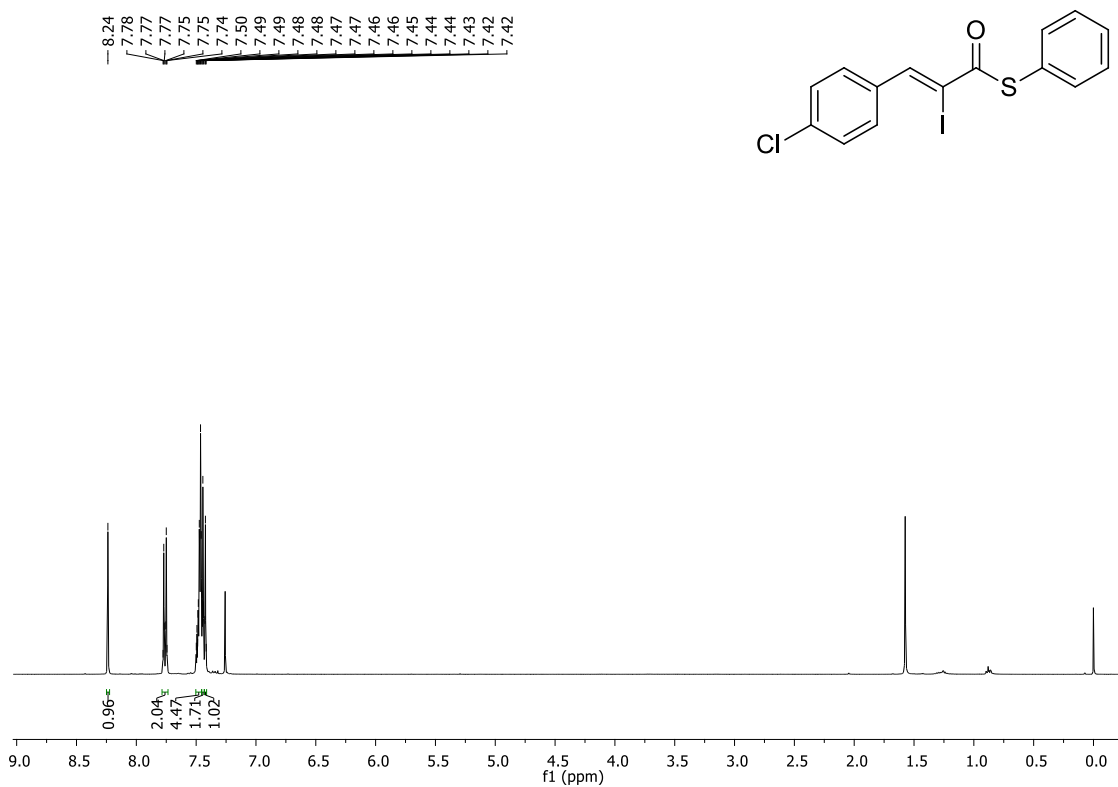




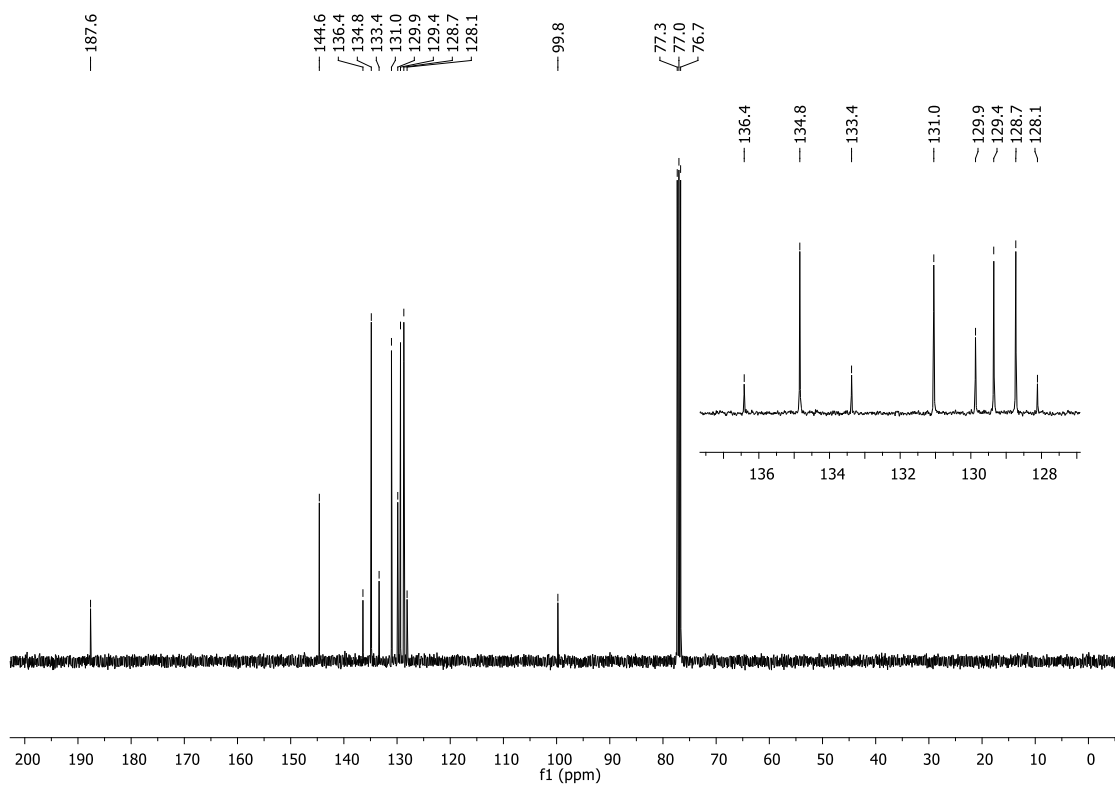
<sup>1</sup>H NMR spectrum for compound **16** in CDCl<sub>3</sub>, 400 MHz



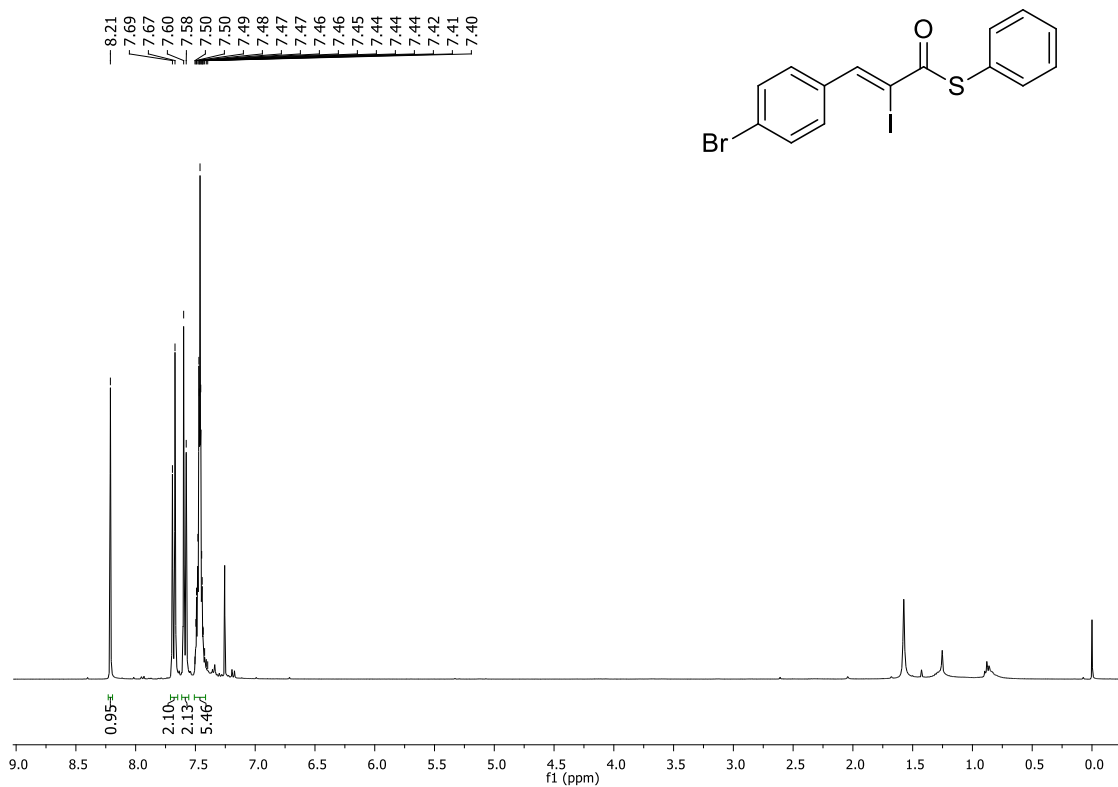
<sup>13</sup>C NMR spectrum for compound **16** in CDCl<sub>3</sub>, 100 MHz



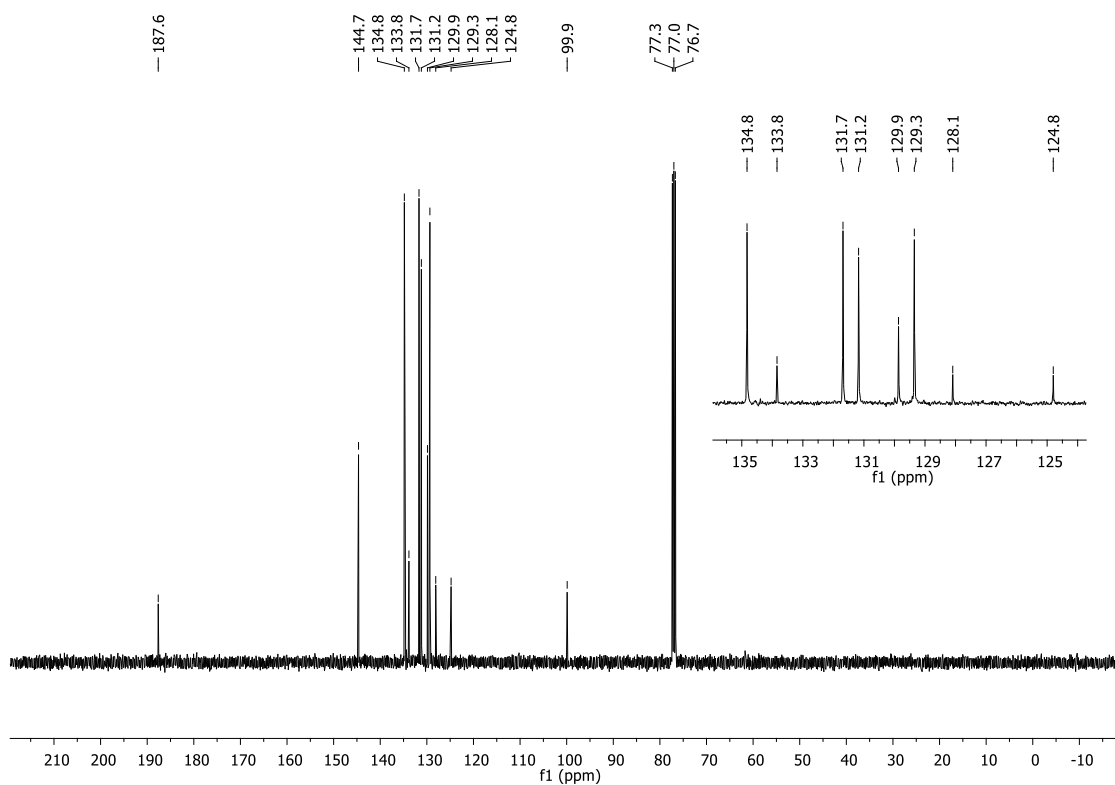
<sup>1</sup>H NMR spectrum for compound 17 in CDCl<sub>3</sub>, 400 MHz



<sup>13</sup>C NMR spectrum for compound 17 in CDCl<sub>3</sub>, 100 MHz

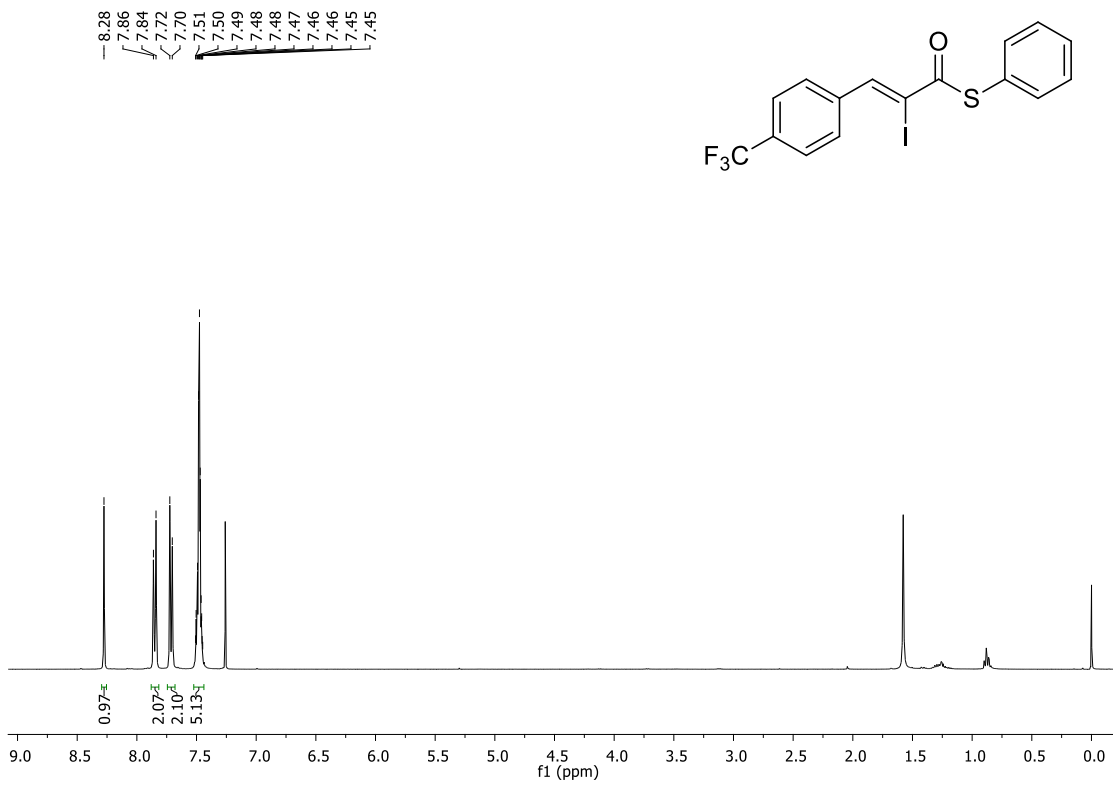


<sup>1</sup>H NMR spectrum for compound **18** in CDCl<sub>3</sub>, 400 MHz

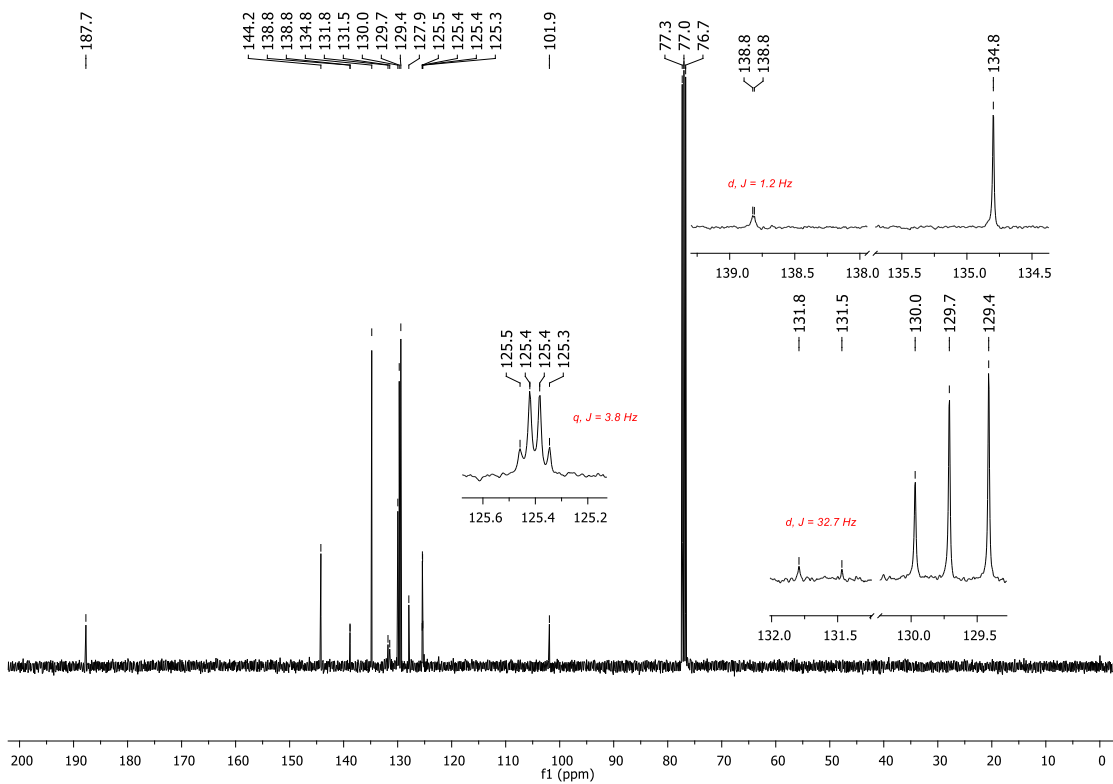


<sup>13</sup>C NMR spectrum for compound **18** in CDCl<sub>3</sub>, 100 MHz

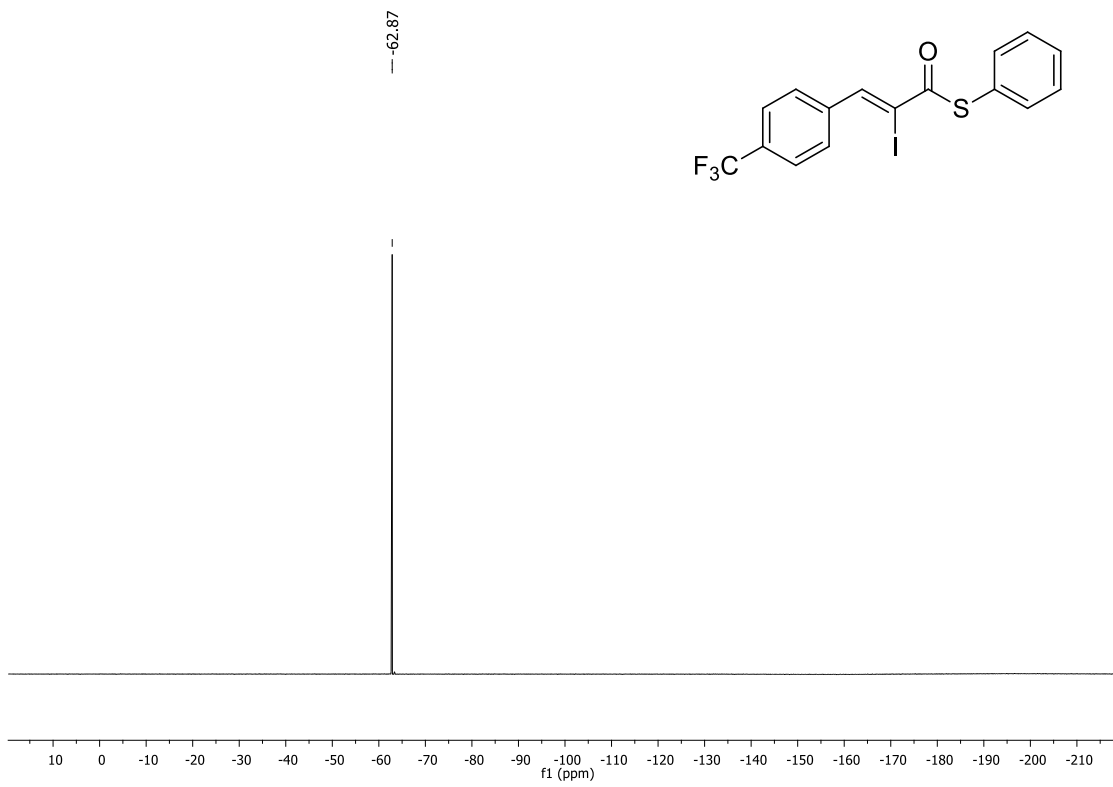




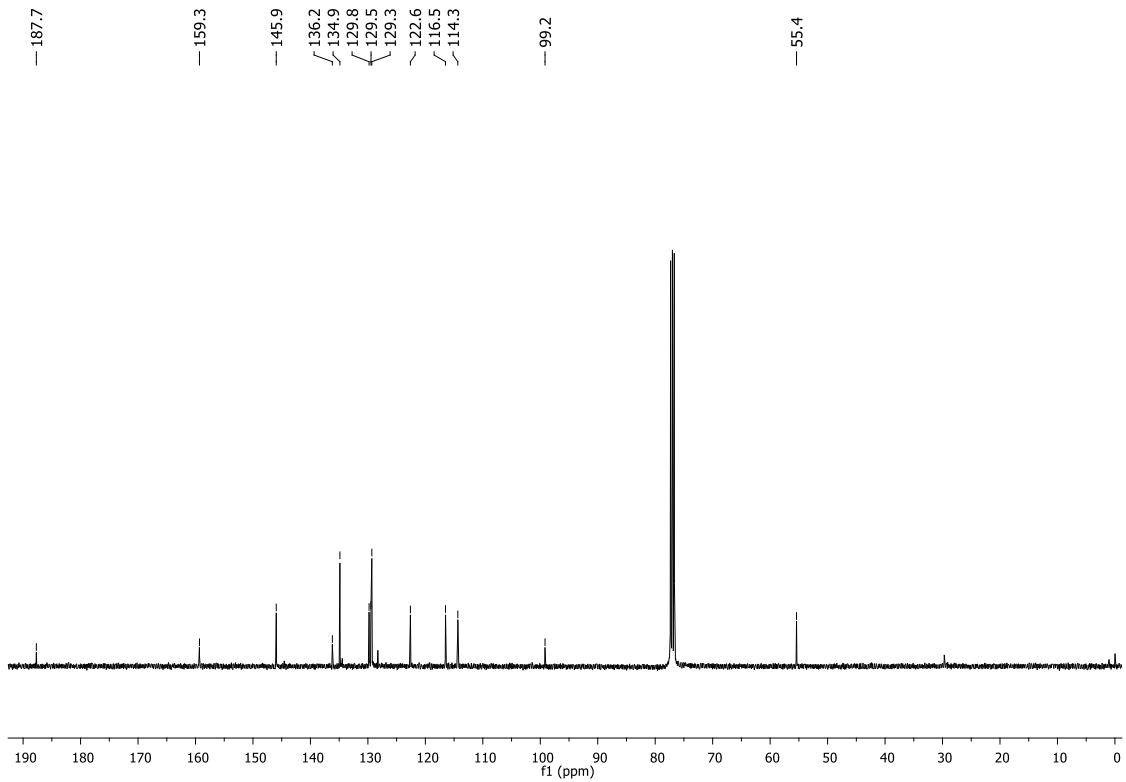
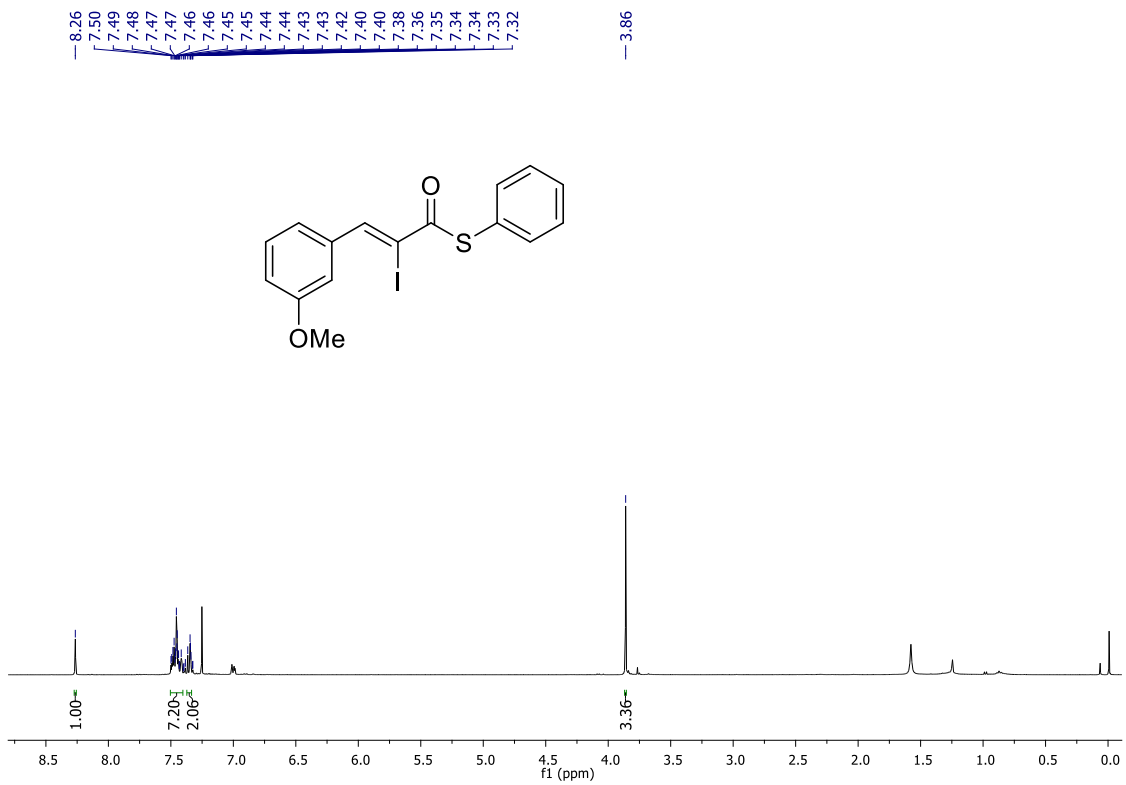
<sup>1</sup>H NMR spectrum for compound **19** in CDCl<sub>3</sub>, 400 MHz

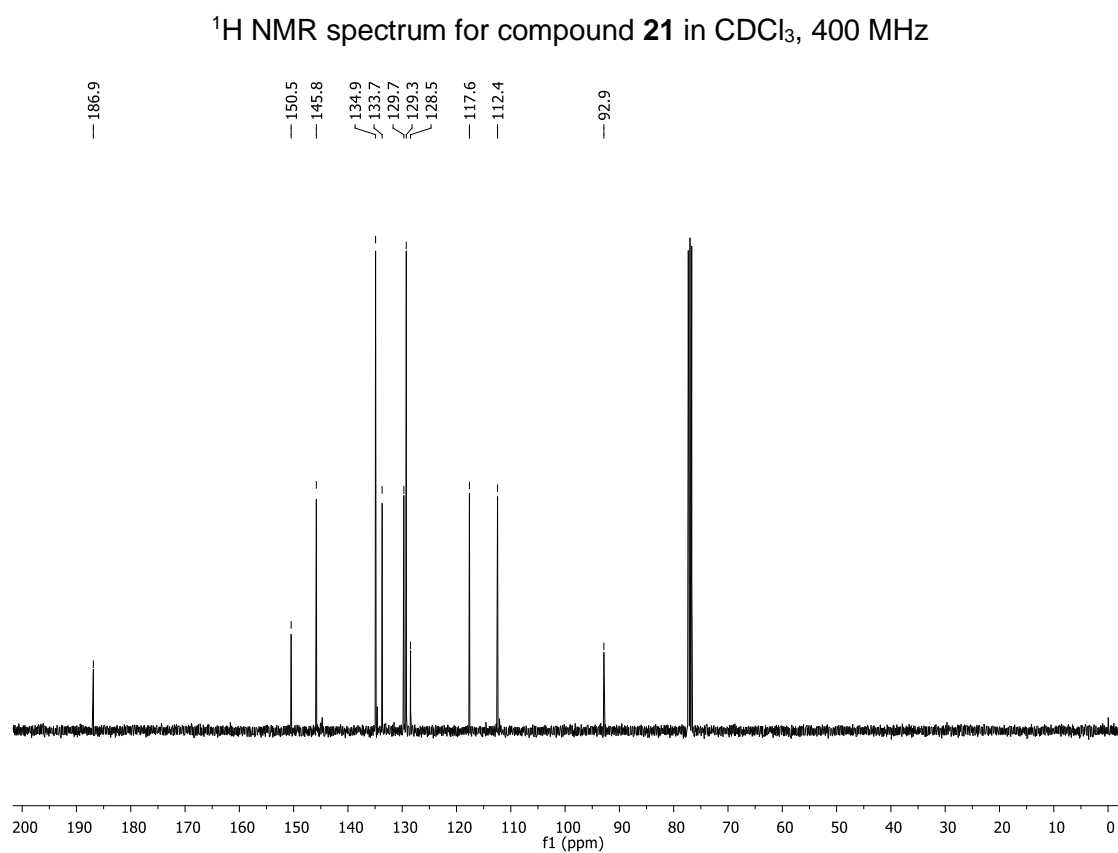
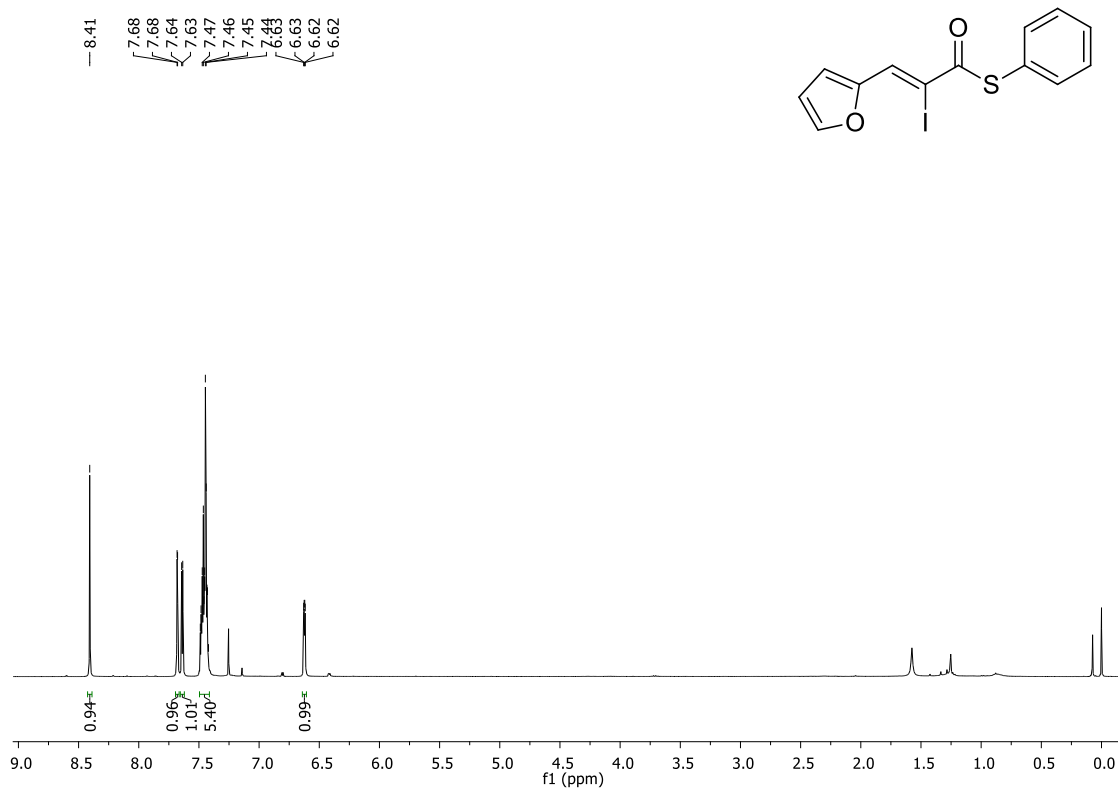


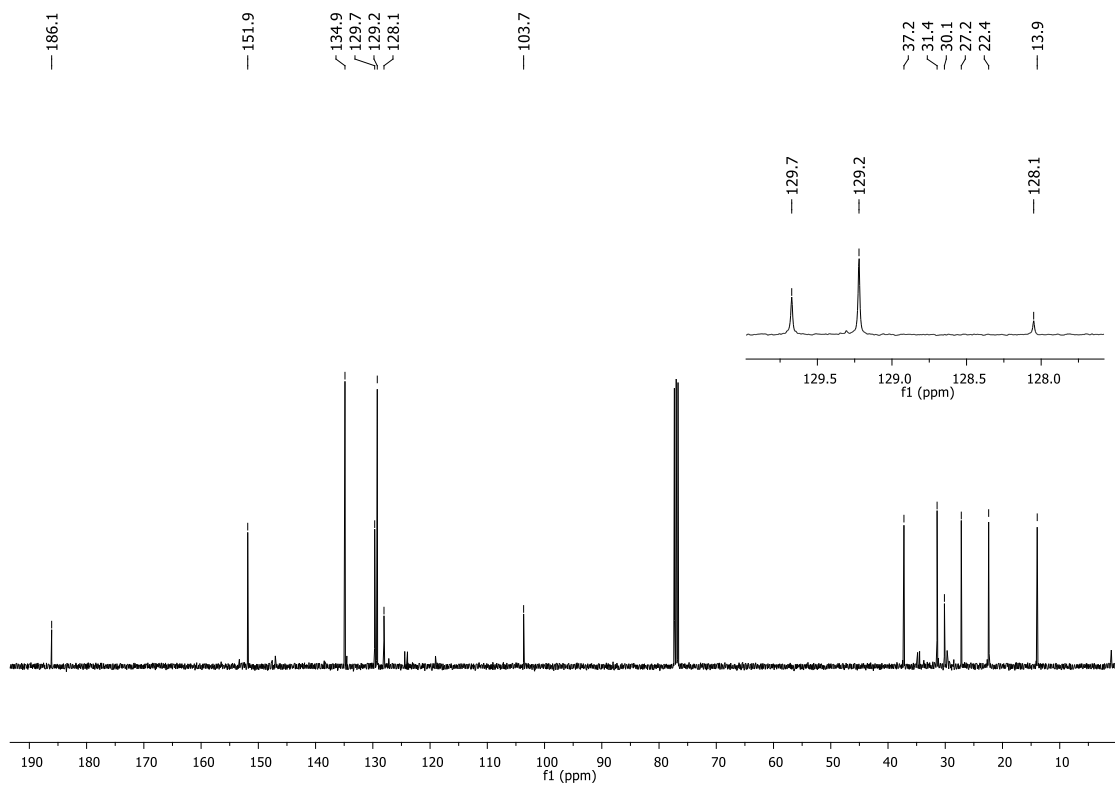
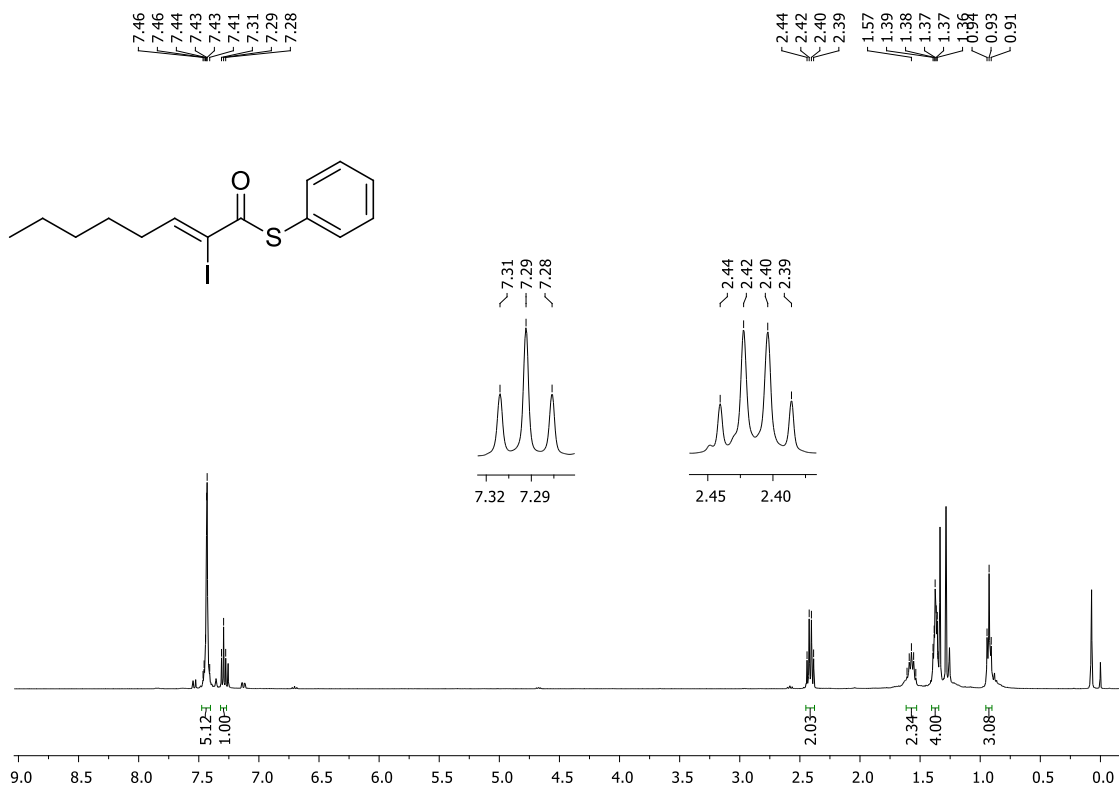
<sup>13</sup>C NMR spectrum for compound **19** in CDCl<sub>3</sub>, 100 MHz

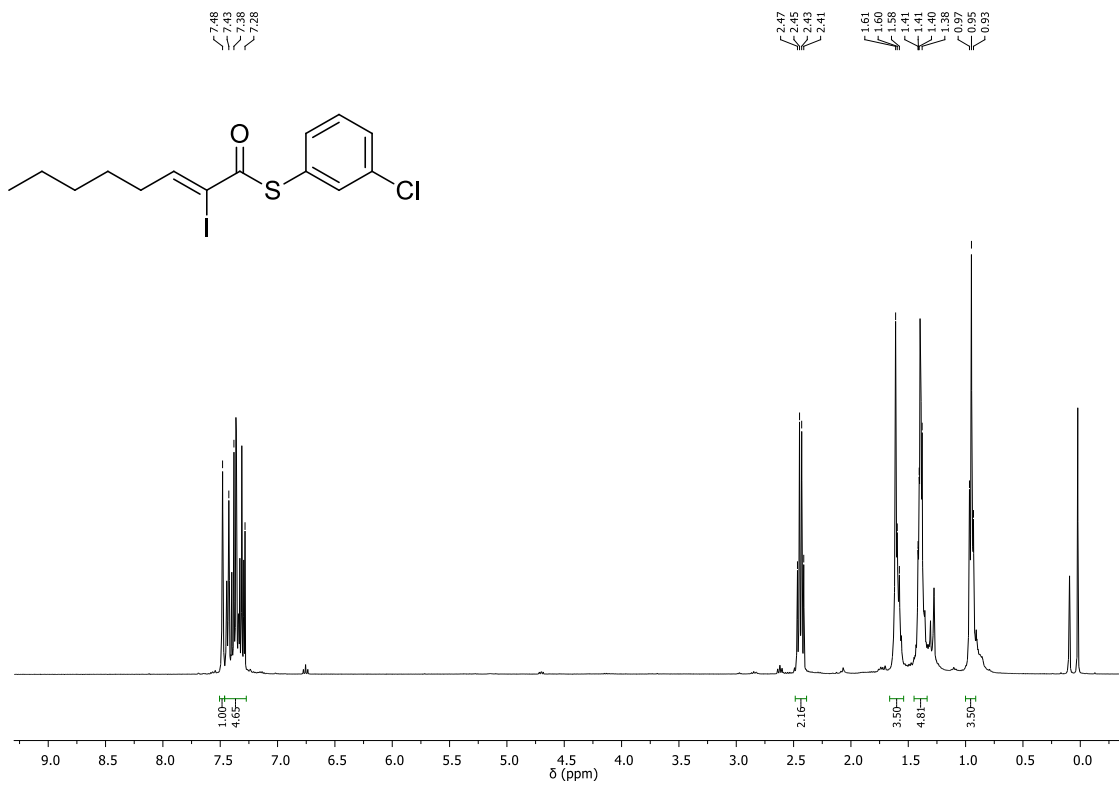


$^{19}\text{F}$  NMR spectrum for compound **19** ( $\text{CDCl}_3$ , 376 MHz)

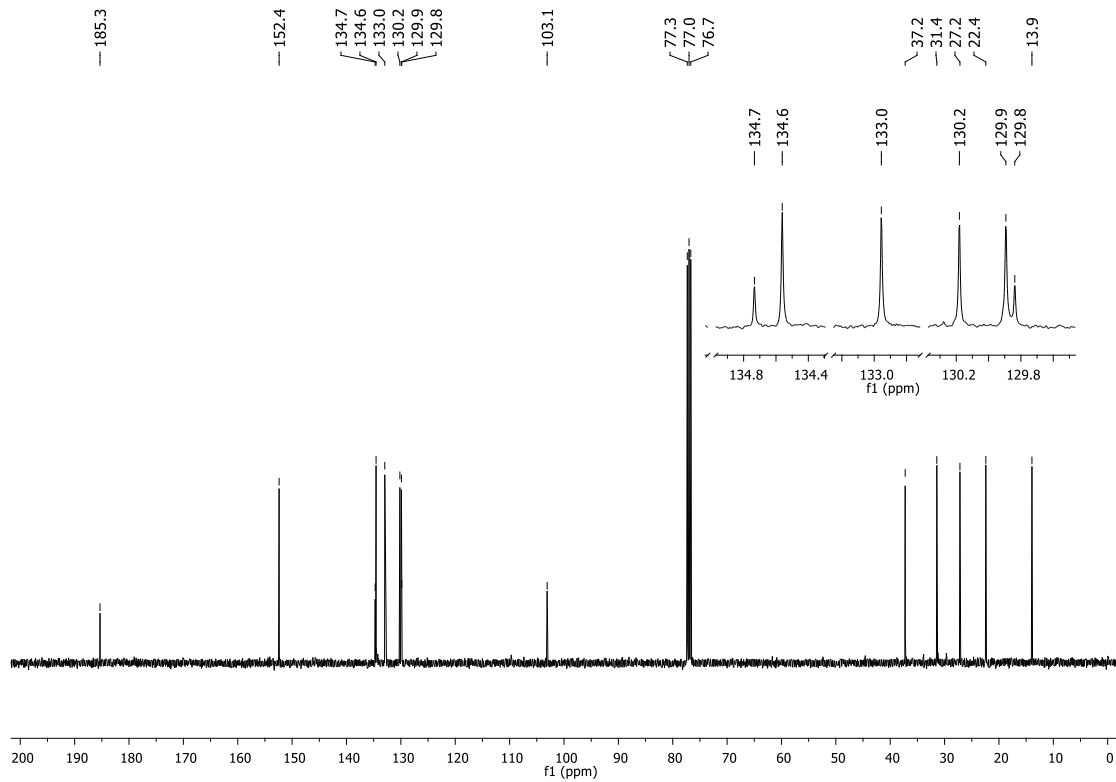




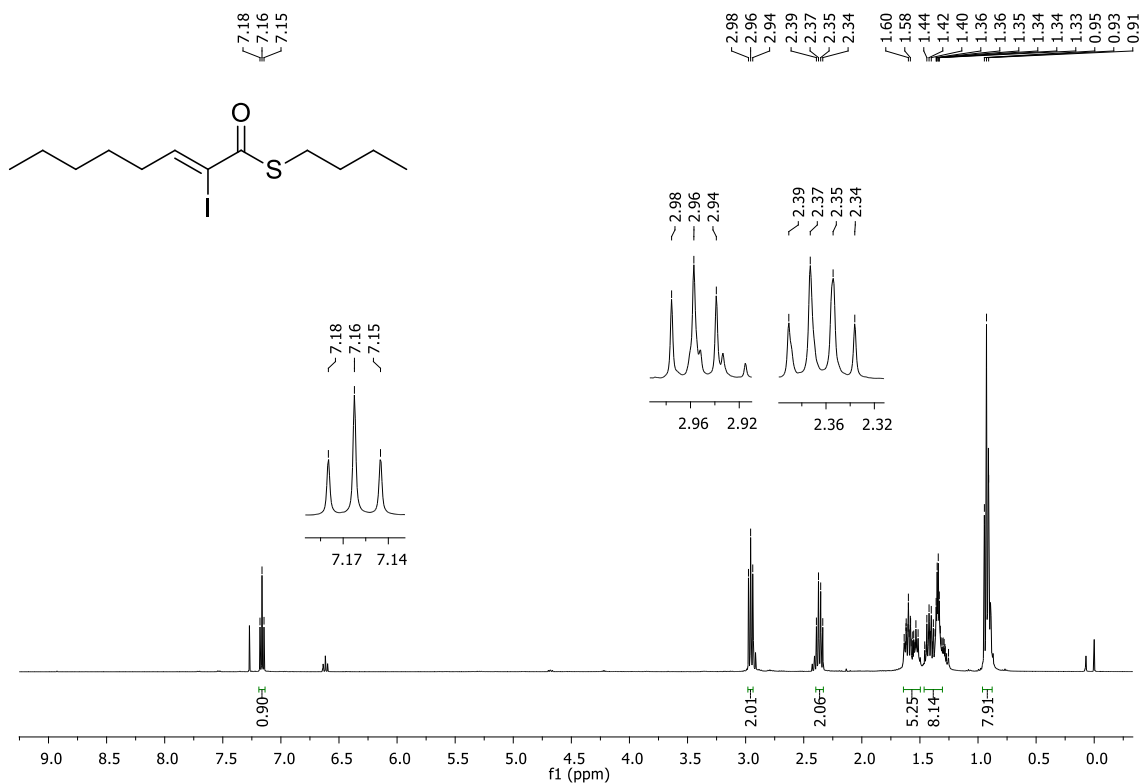




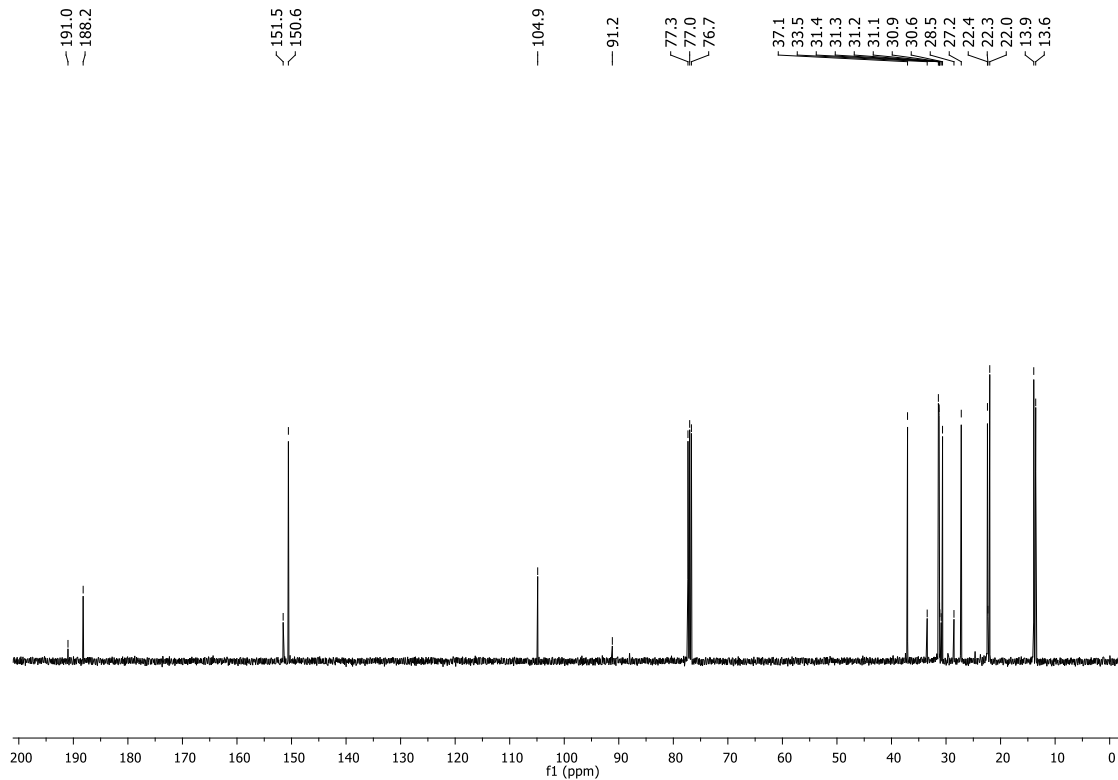
<sup>1</sup>H NMR spectrum for compound **23** in CDCl<sub>3</sub>, 400 MHz



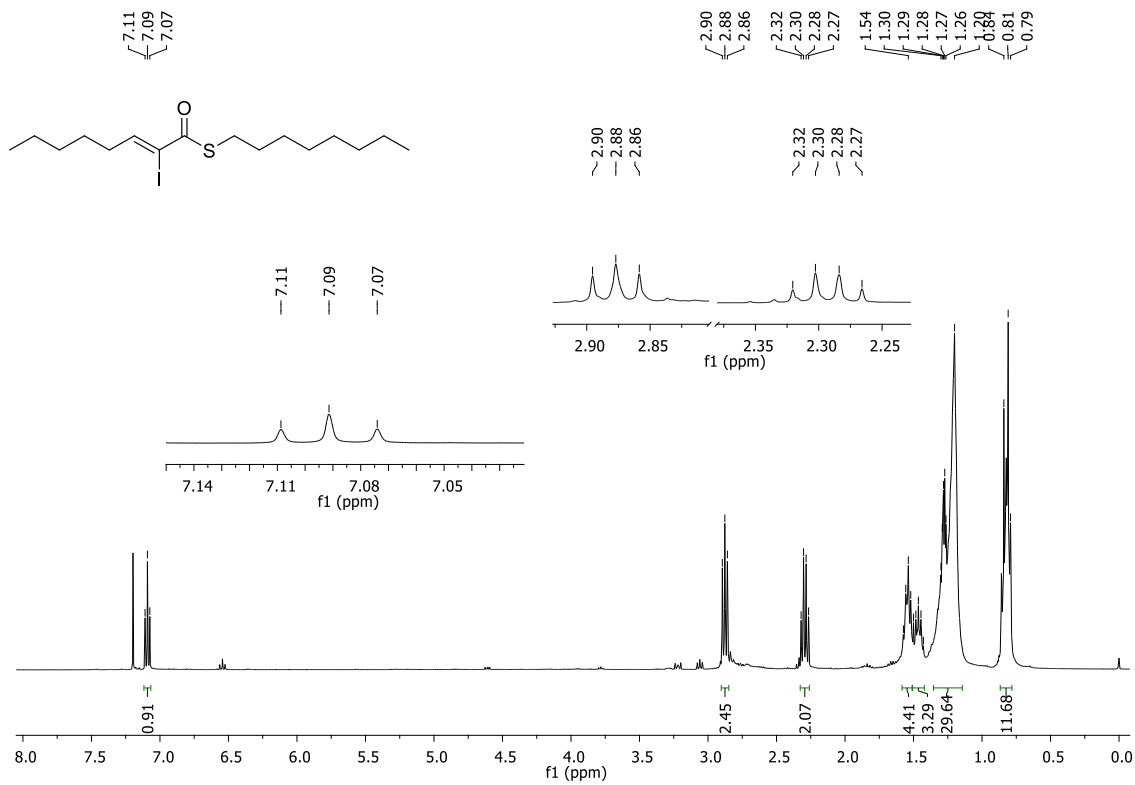
<sup>13</sup>C NMR spectrum for compound **23** in CDCl<sub>3</sub>, 100 MHz



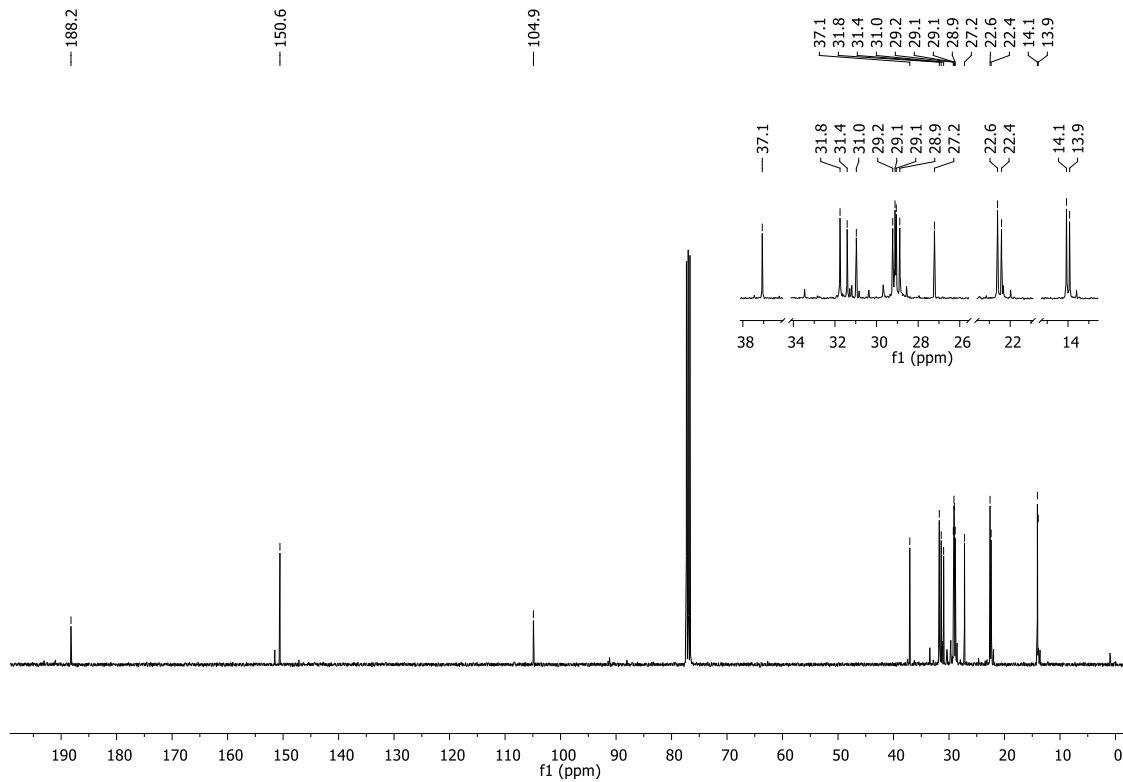
<sup>1</sup>H NMR spectrum for compound **24** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 400 MHz



<sup>13</sup>C NMR spectrum for compound **24** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 100 MHz

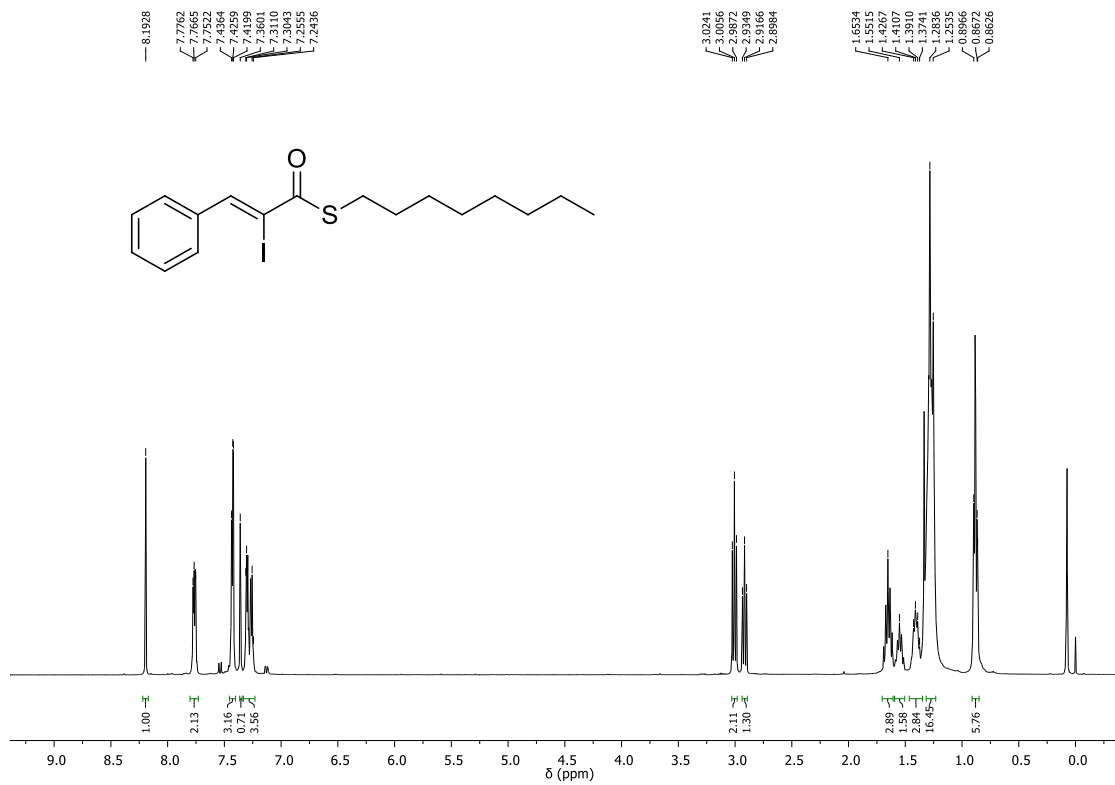


<sup>1</sup>H NMR spectrum for compound **25** in CDCl<sub>3</sub>, 400 MHz

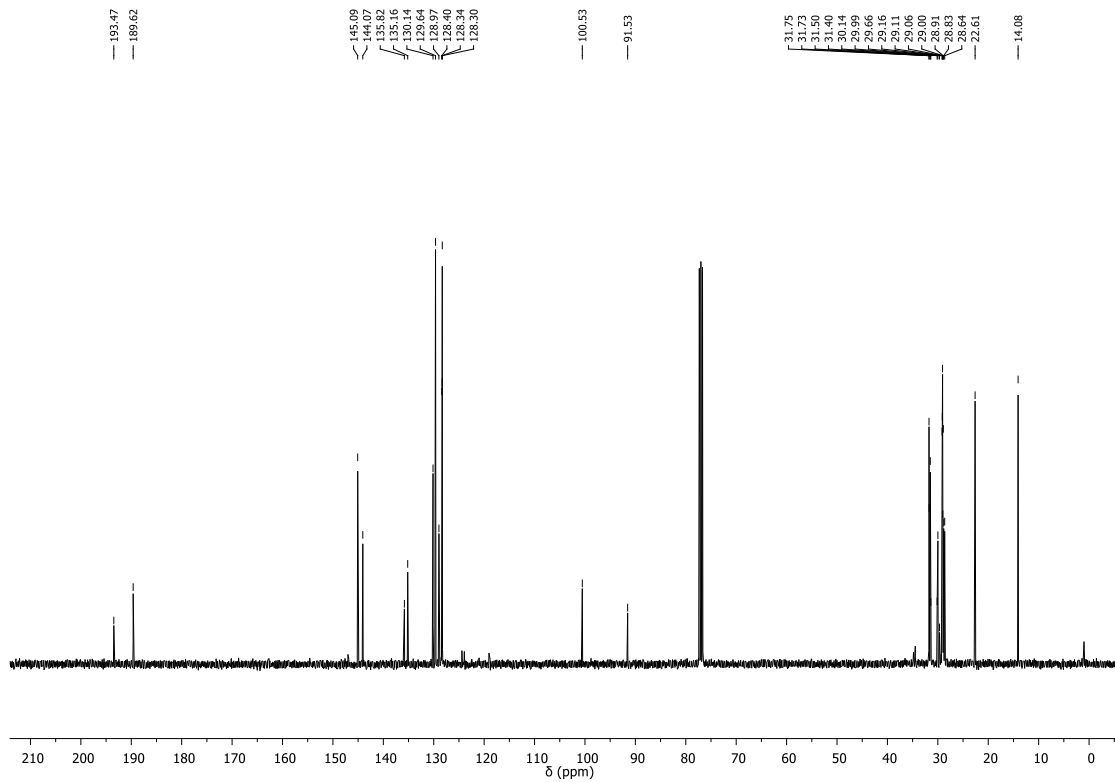


<sup>13</sup>C NMR spectrum for compound **25** in CDCl<sub>3</sub>, 100 MHz

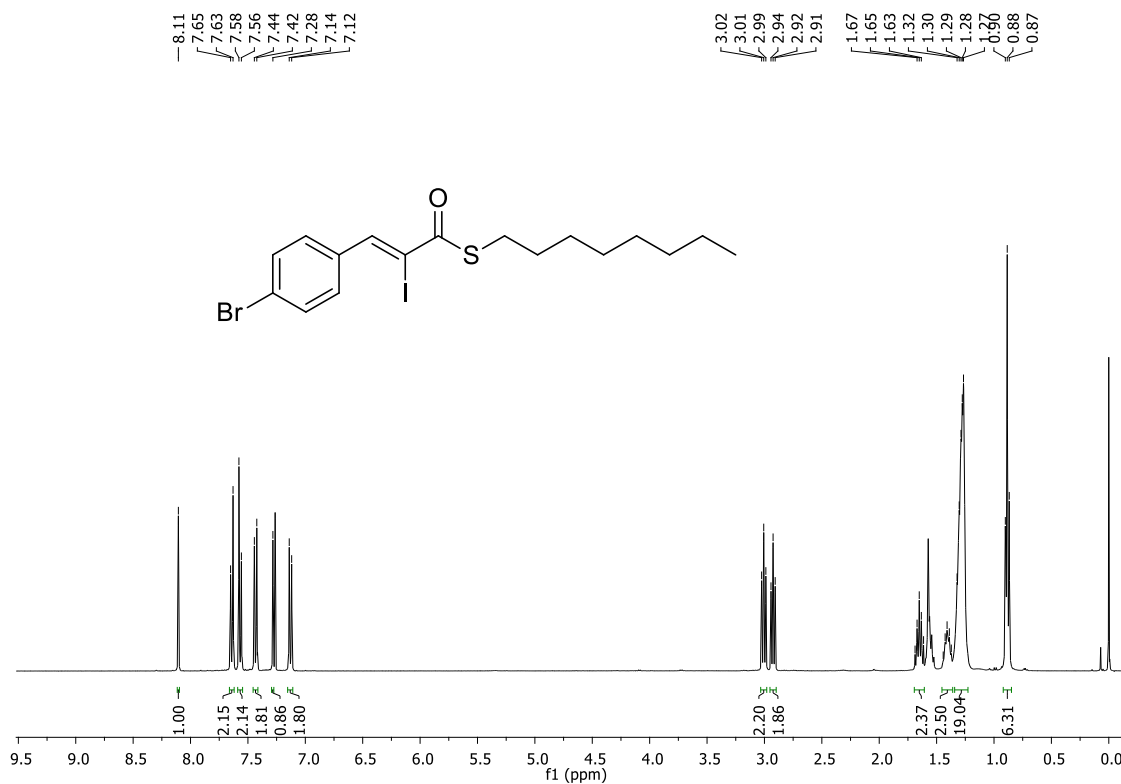




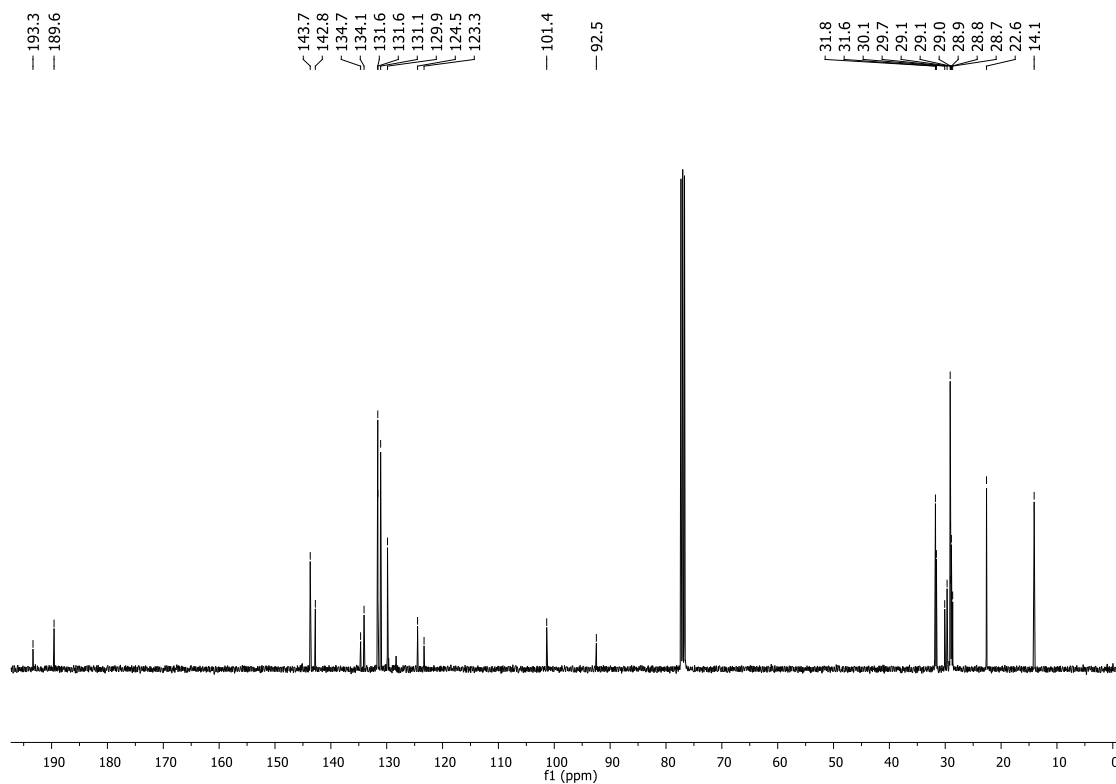
<sup>1</sup>H NMR spectrum for compound **26** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 400 MHz



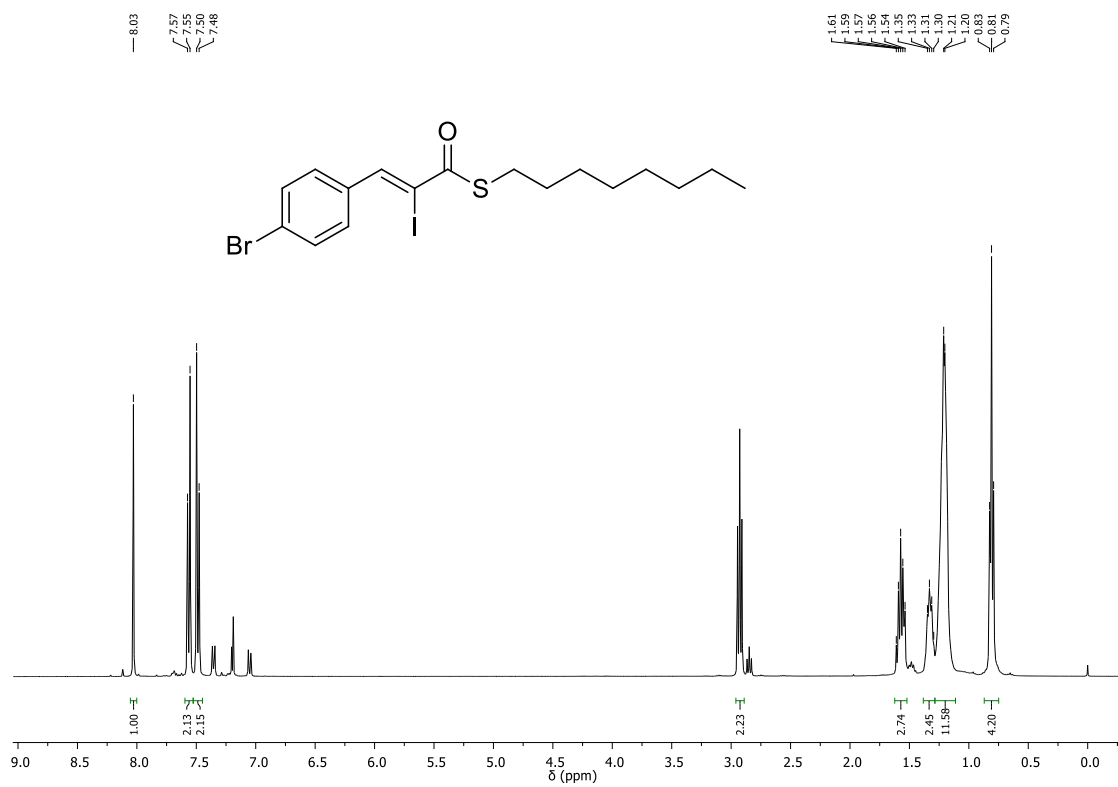
<sup>13</sup>C NMR spectrum for compound **26** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 100 MHz



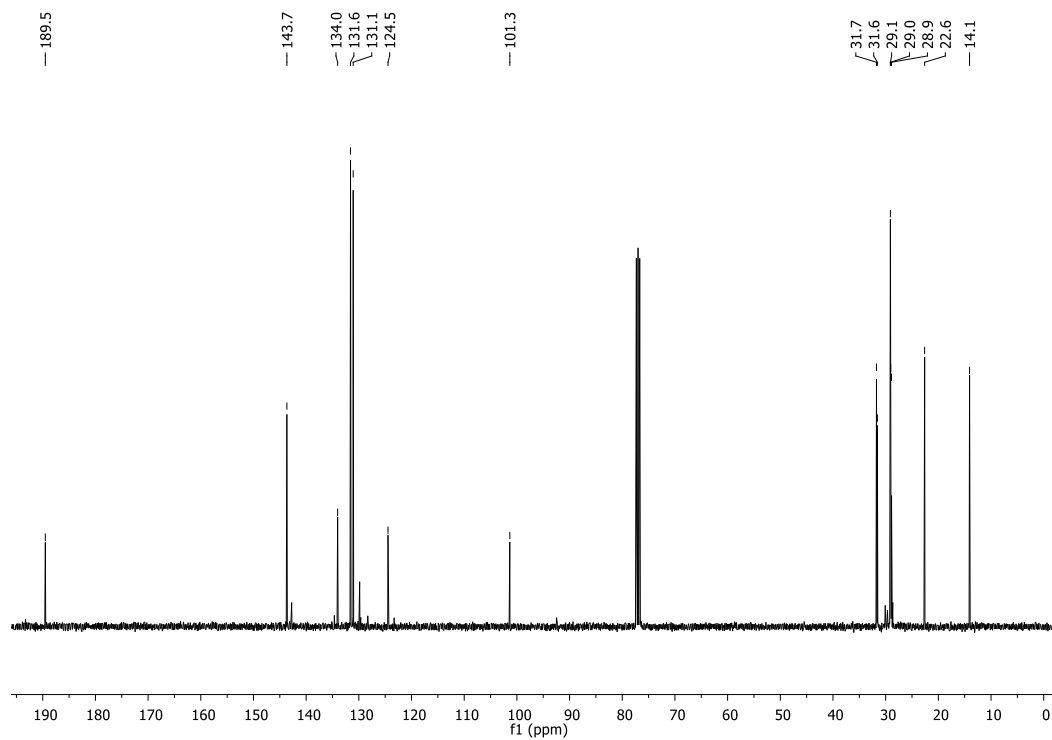
<sup>1</sup>H NMR spectrum for compound **27** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 400 MHz



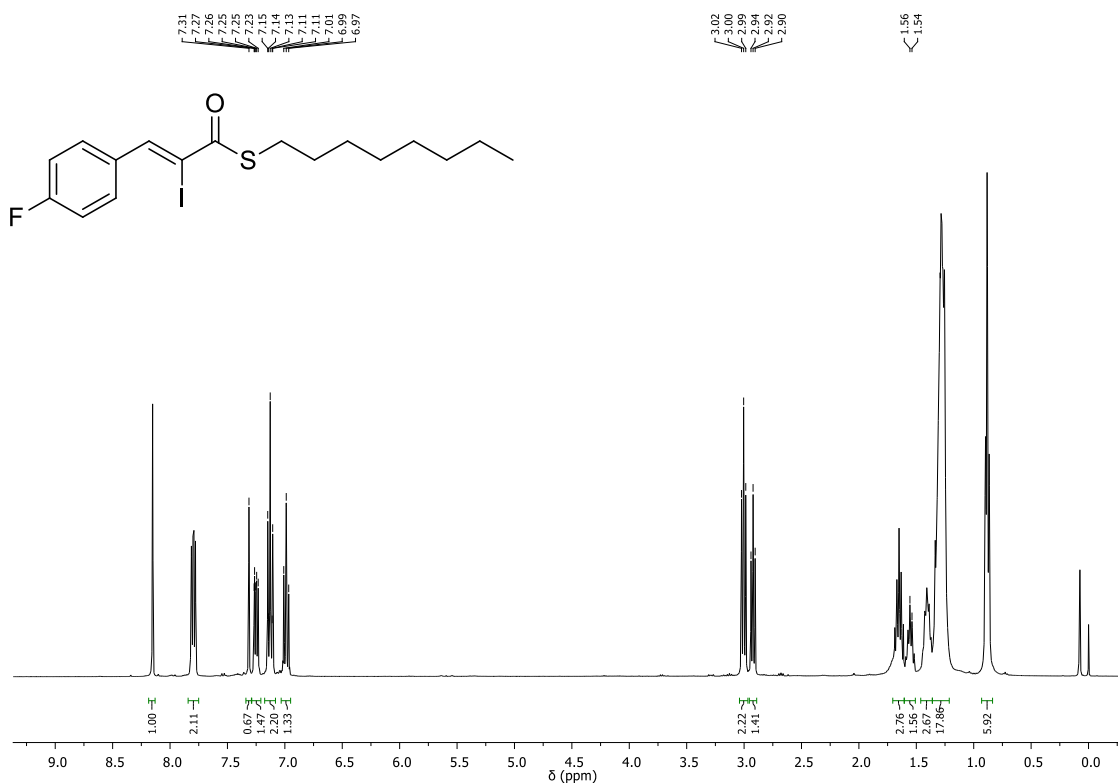
<sup>13</sup>C NMR NMR spectrum for compound **27** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 400 MHz



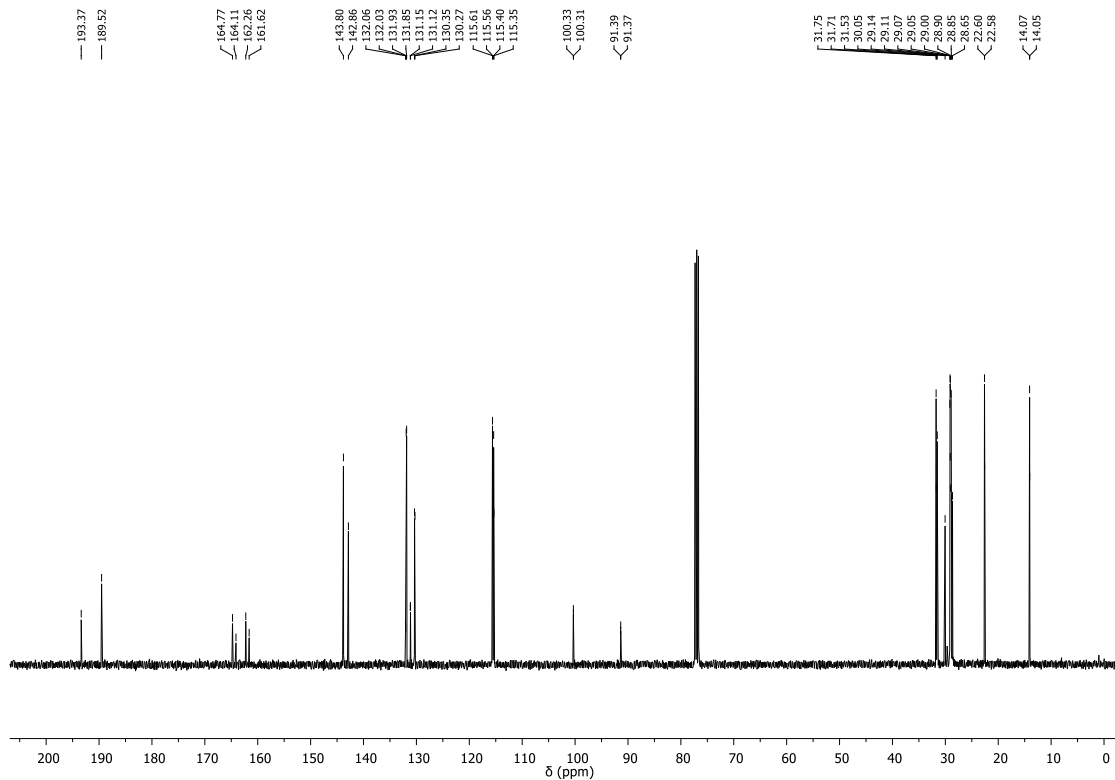
<sup>1</sup>H NMR spectrum for compound **27** (Z isomer major) in CDCl<sub>3</sub>, 400 MHz



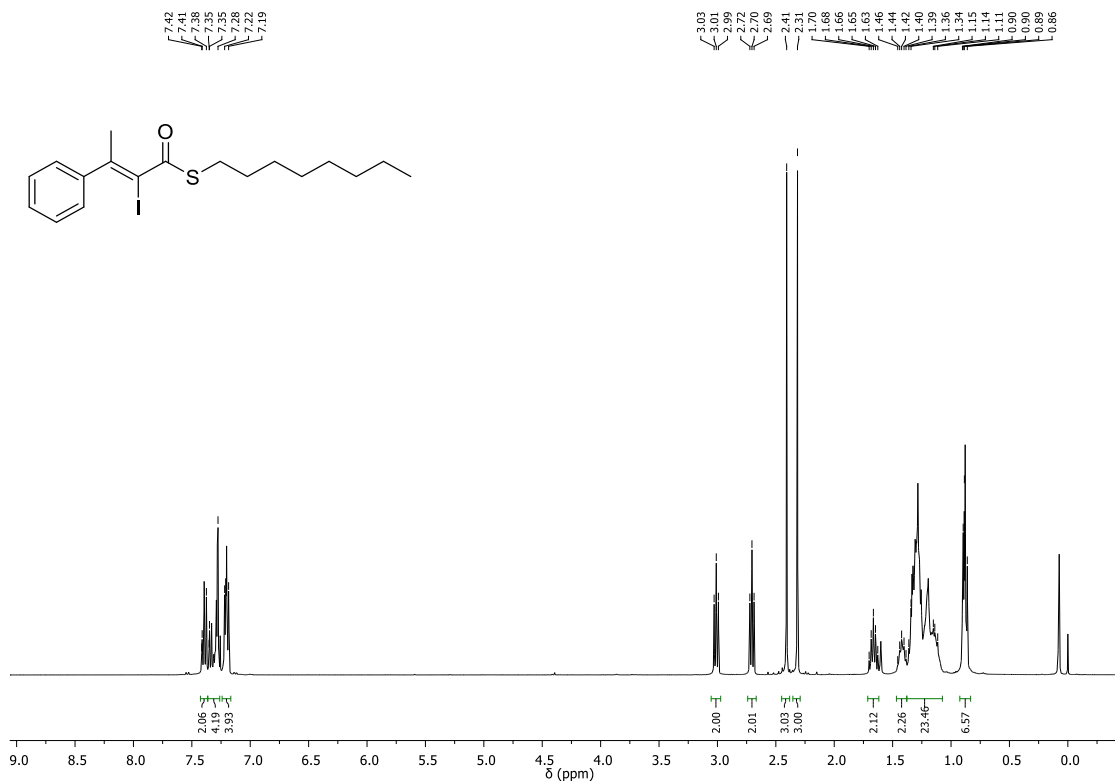
<sup>13</sup>C NMR spectrum for compound **27** (Z isomer major) in CDCl<sub>3</sub>, 100 MHz



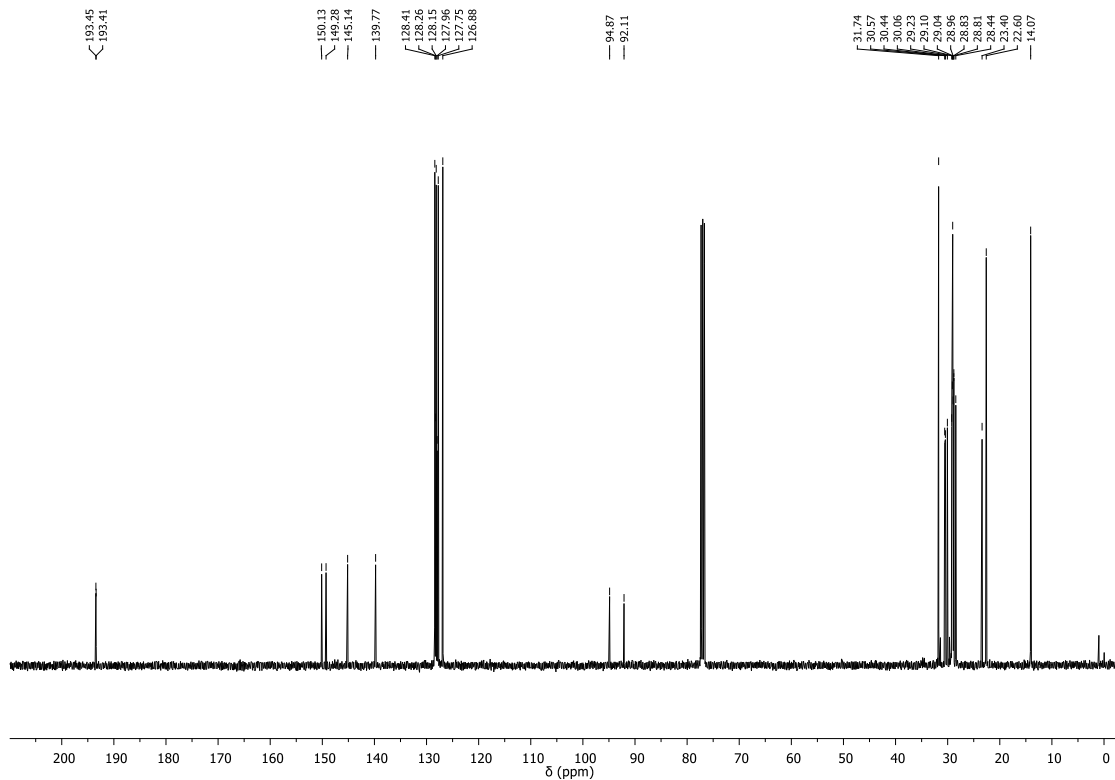
<sup>1</sup>H NMR spectrum for compound **28** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 400 MHz



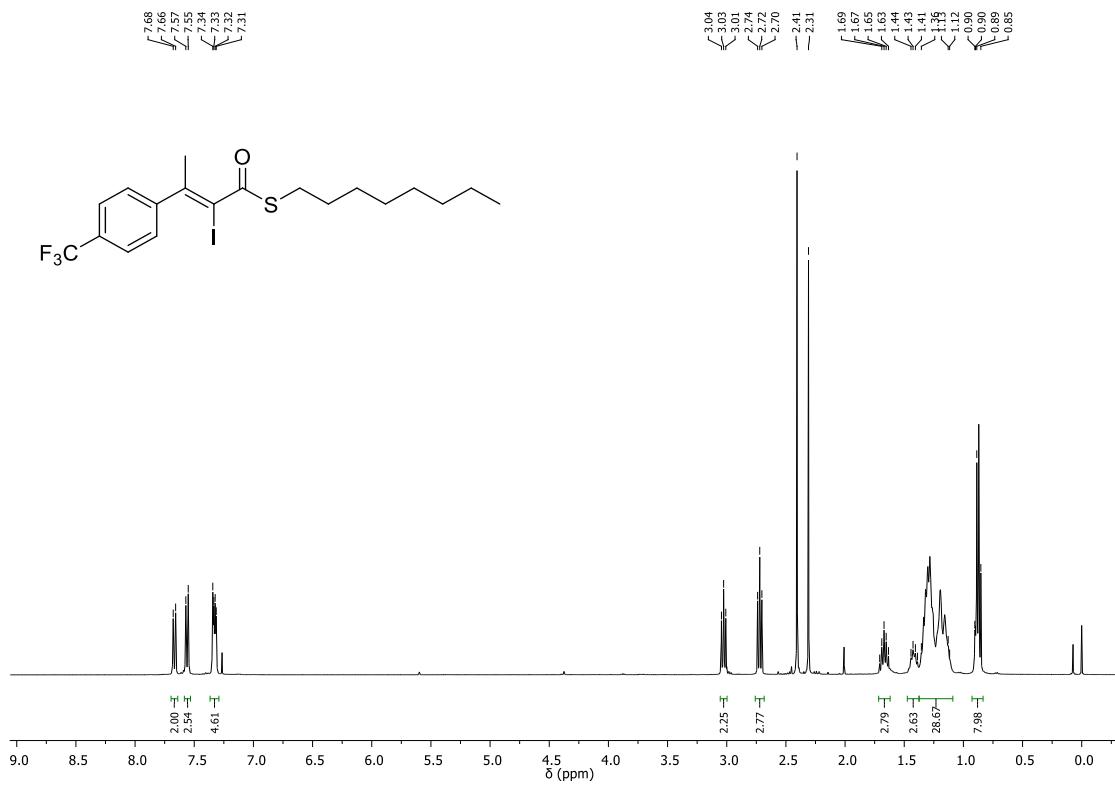
<sup>13</sup>C NMR spectrum for compound **28** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 100 MHz



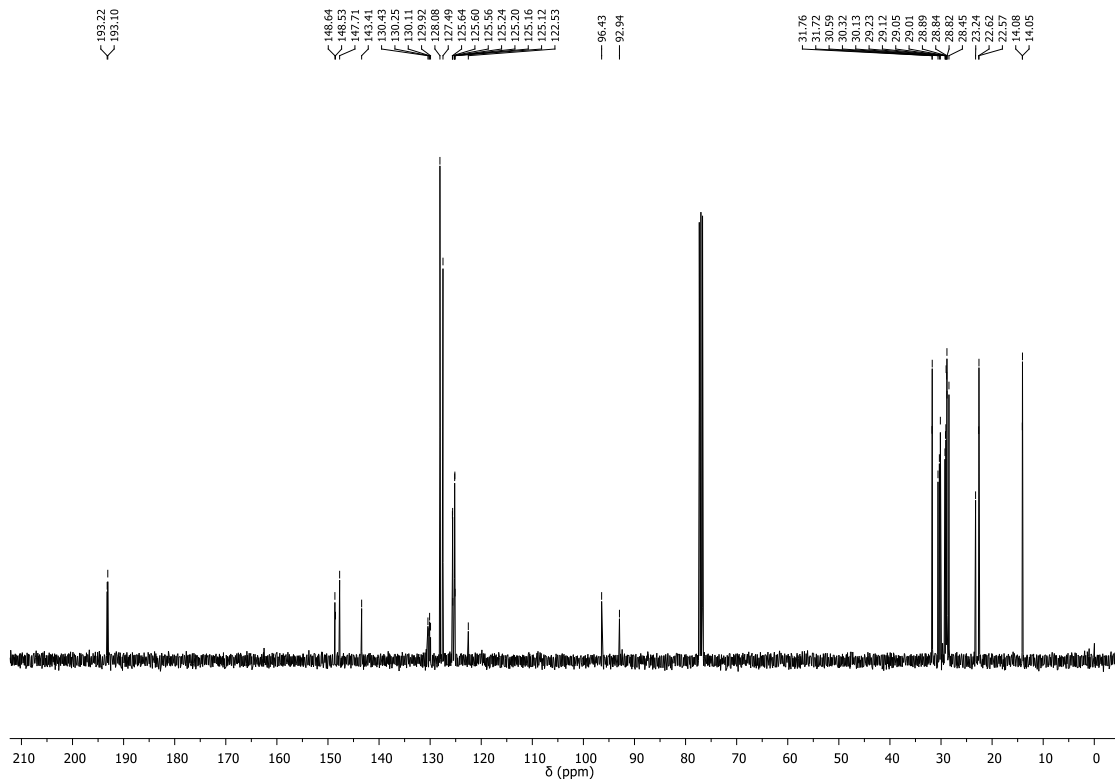
<sup>1</sup>H NMR spectrum for compound **29** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 400 MHz



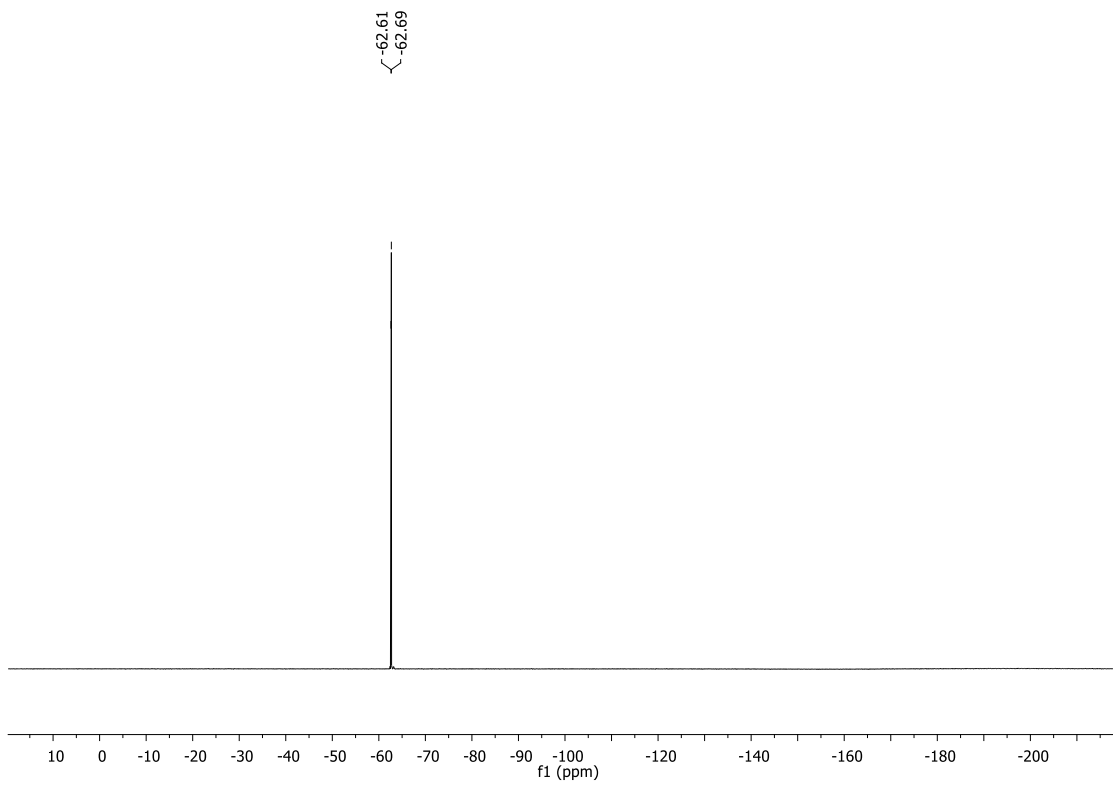
<sup>13</sup>C NMR spectrum for compound **29** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 100 MHz



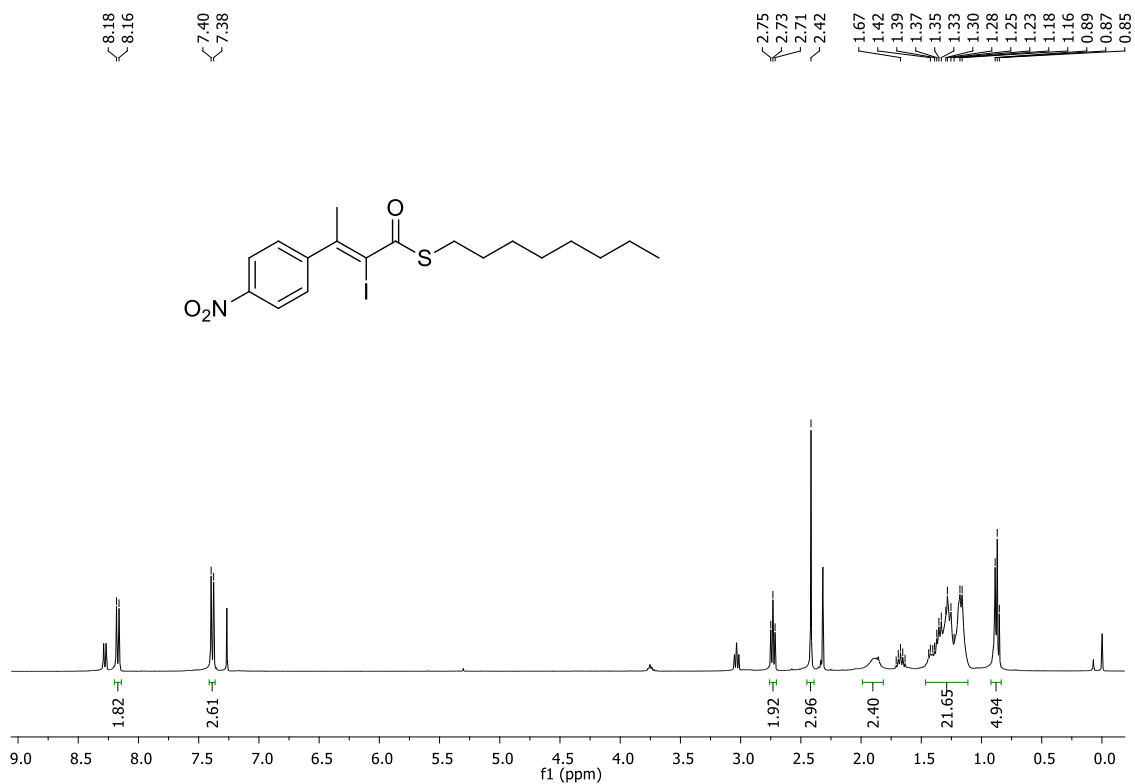
<sup>1</sup>H NMR spectrum for compound **30** (*Z/E* isomer's mixture) in CDCl<sub>3</sub>, 400 MHz



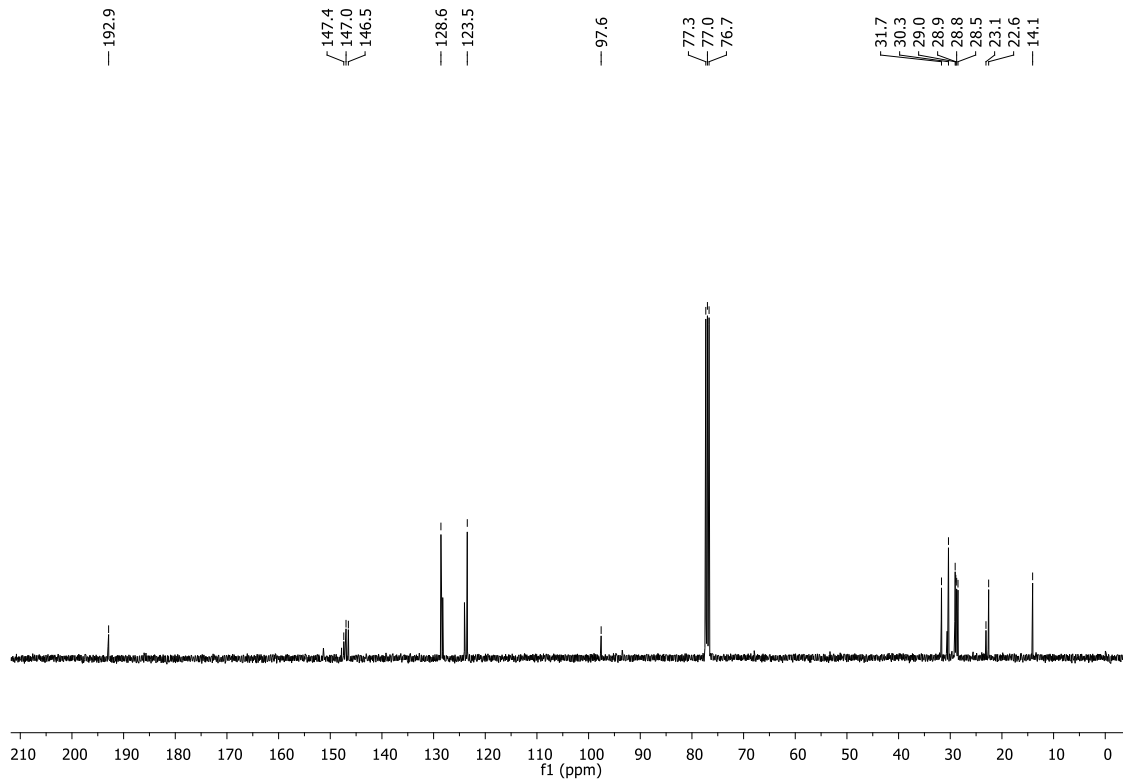
<sup>13</sup>C NMR spectrum for compound **30** (*Z/E* isomer's mixture) in CDCl<sub>3</sub>, 100 MHz



$^{19}\text{F}$  NMR spectrum for compound **30** ( $\text{CDCl}_3$ , 376 MHz)

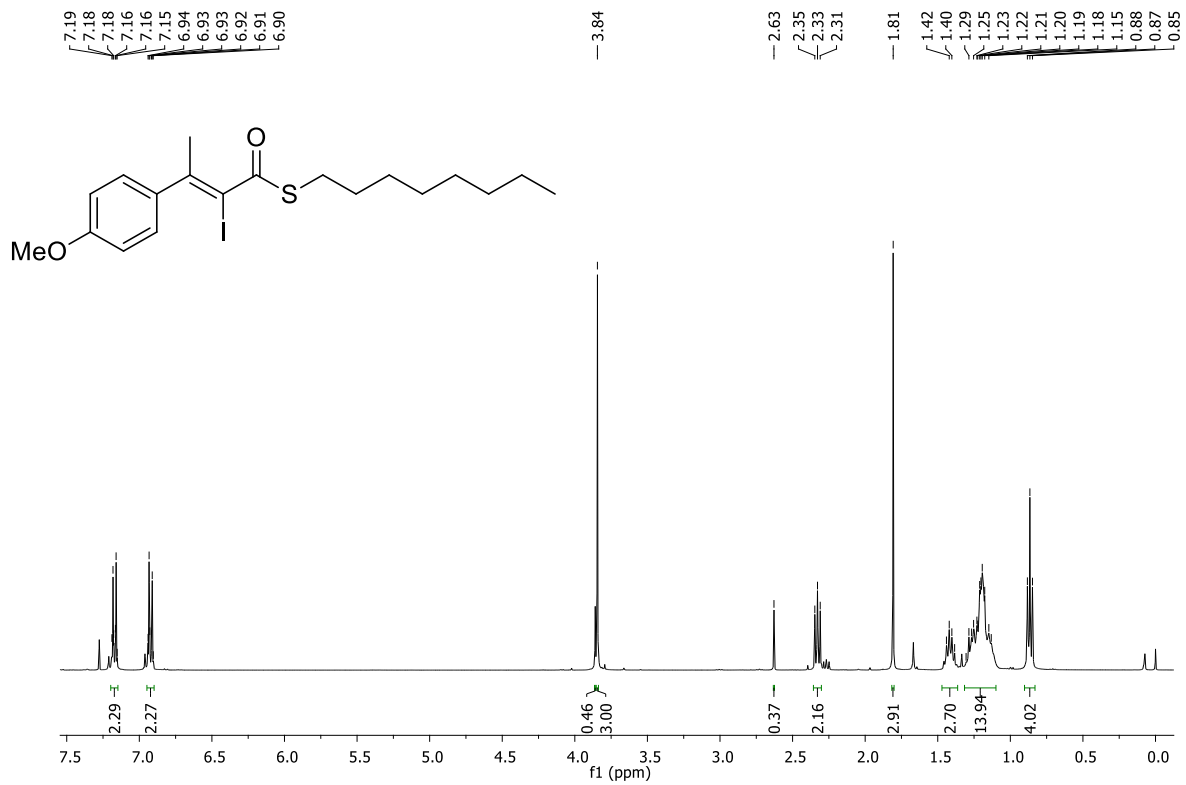


<sup>1</sup>H NMR spectrum for compound **31** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 400 MHz

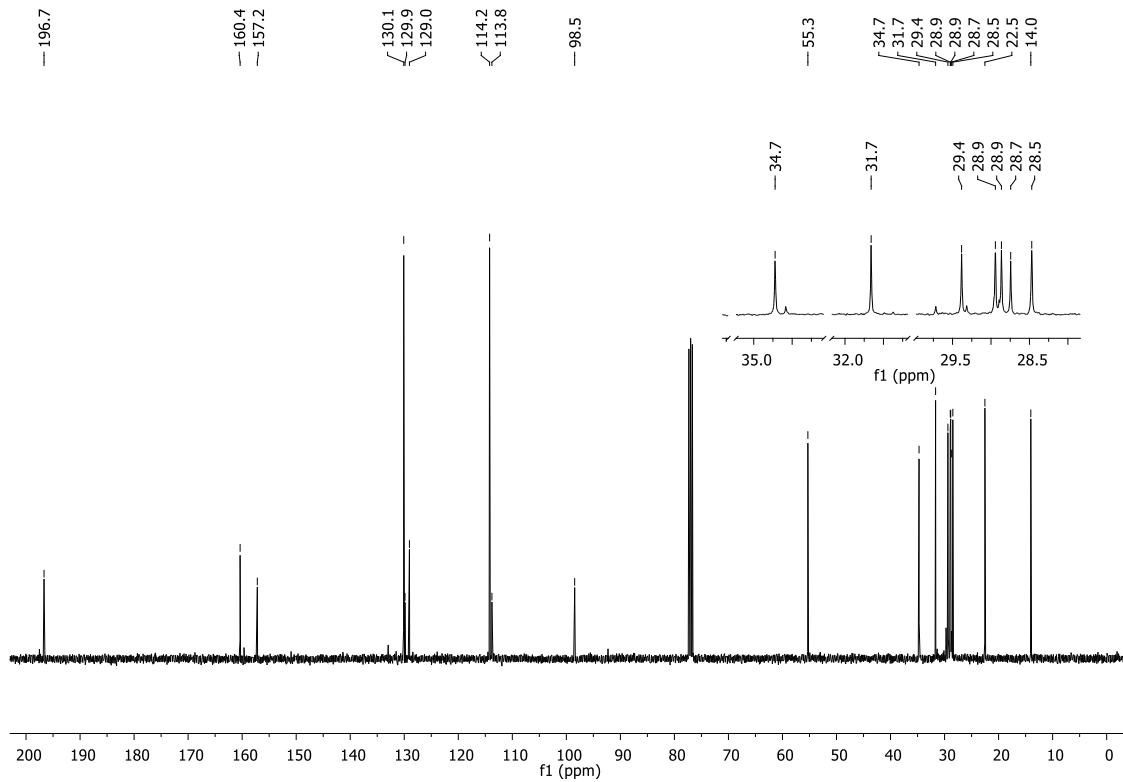


<sup>13</sup>C NMR spectrum for compound **31** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 100 MHz

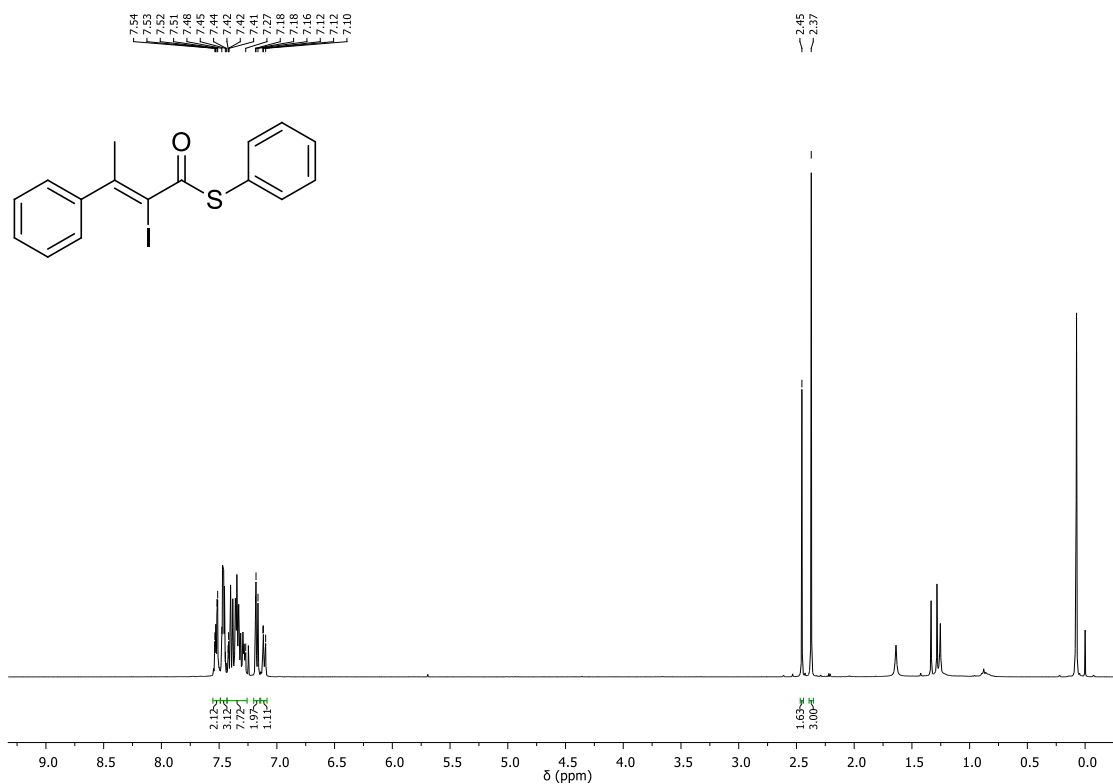




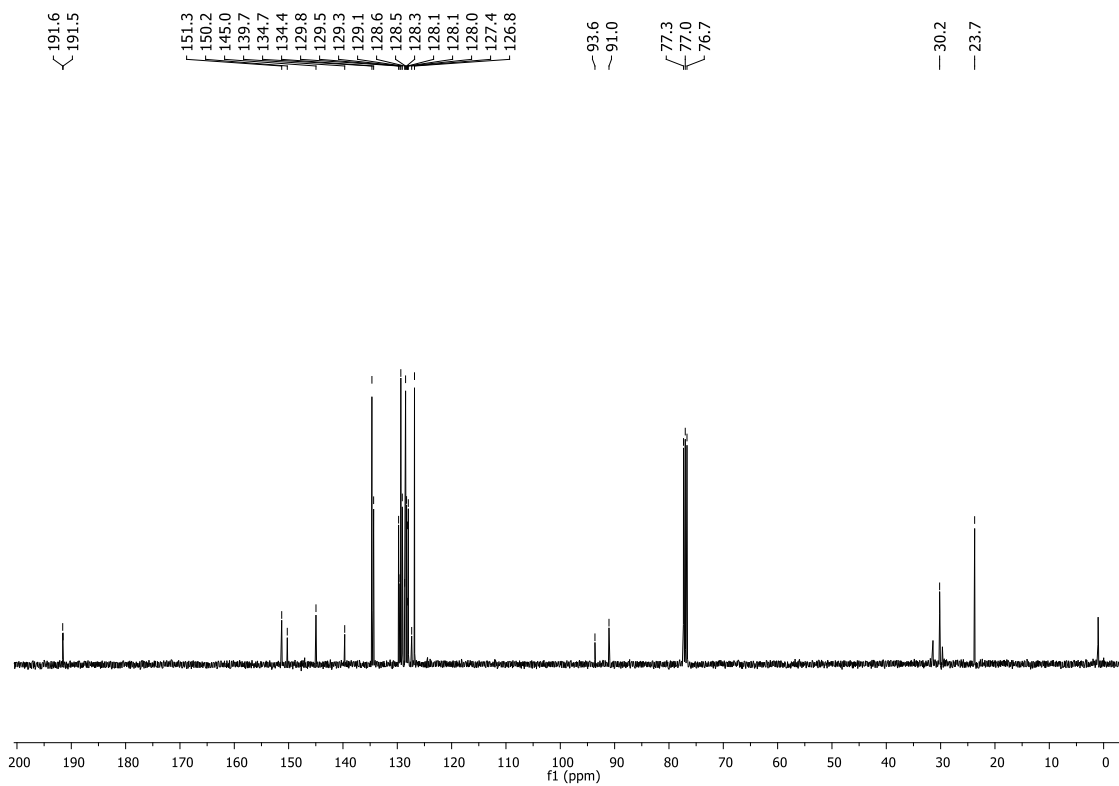
<sup>1</sup>H NMR spectrum for compound **32** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 400 MHz



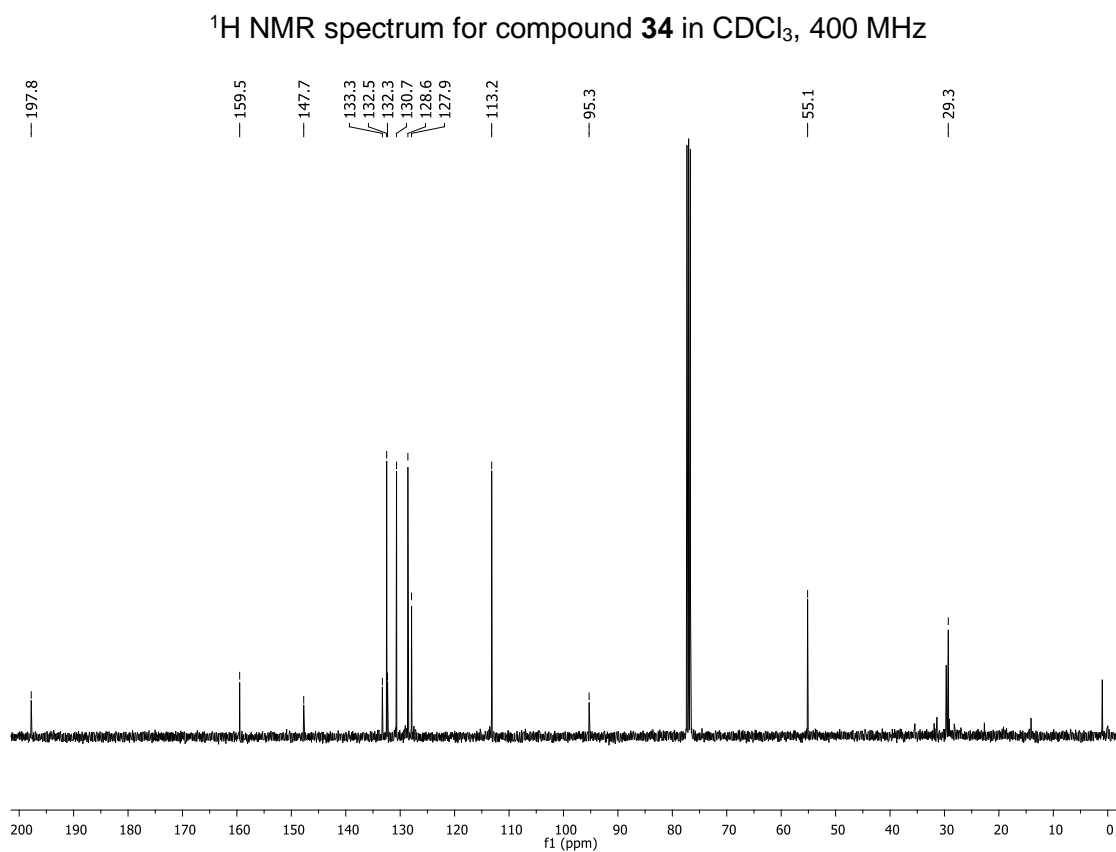
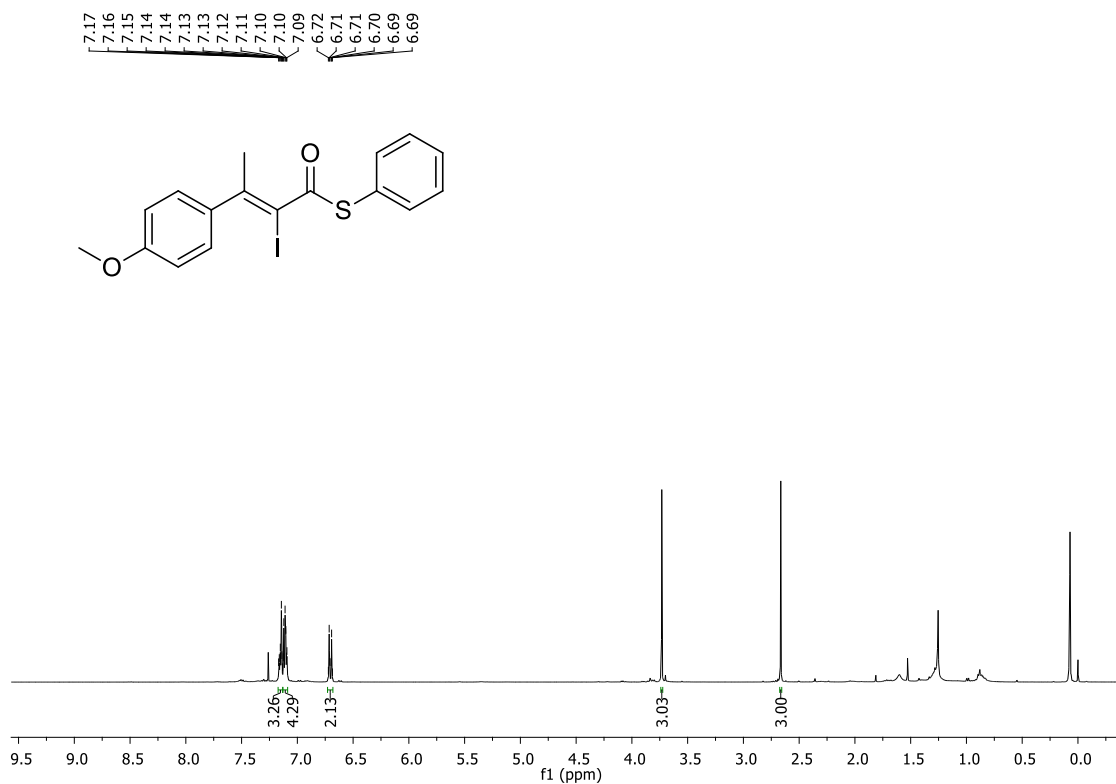
<sup>13</sup>C NMR spectrum for compound **32** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 100 MHz

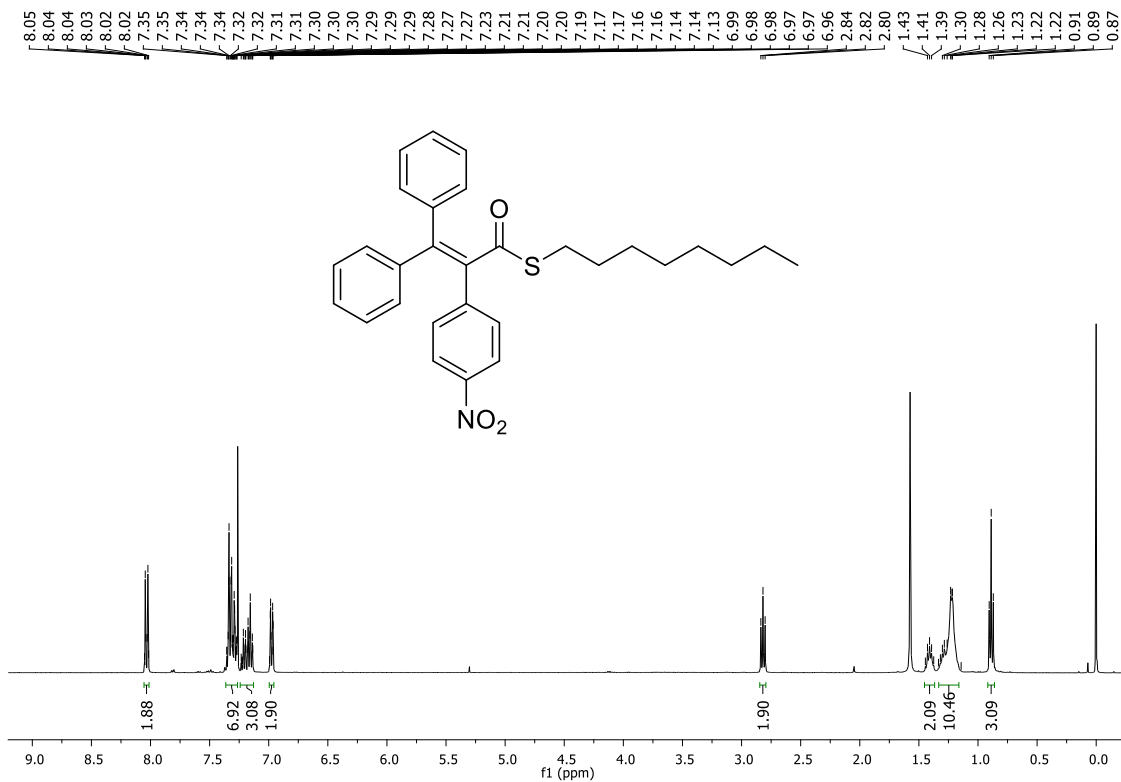


<sup>1</sup>H NMR spectrum for compound **33** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 400 MHz

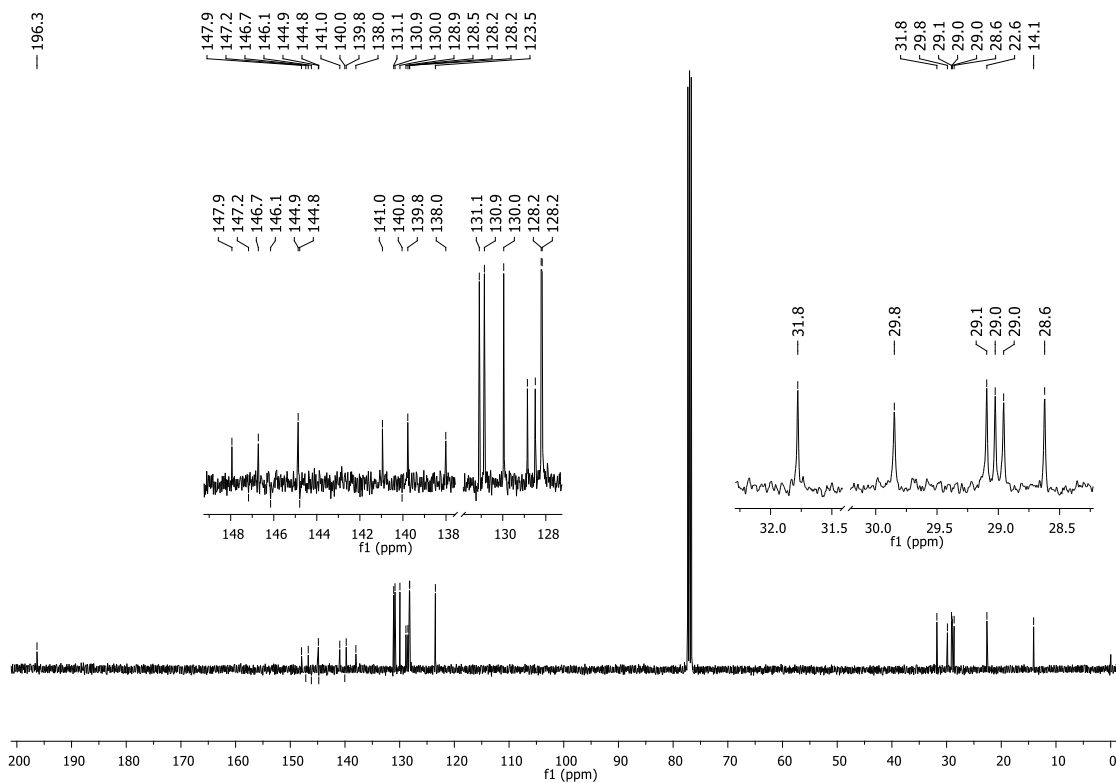


<sup>13</sup>C NMR spectrum for compound **33** (Z/E isomer's mixture) in CDCl<sub>3</sub>, 100 MHz





<sup>1</sup>H NMR spectrum for compound **39** in CDCl<sub>3</sub>, 400 MHz



<sup>13</sup>C NMR spectrum for compound **39** in CDCl<sub>3</sub>, 100 MHz

