

## Supporting information

### Enabling iron catalyzed Doyle-Kirmse rearrangement reactions with in-situ generated diazo compounds

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## **GENERAL INFORMATIONS:**

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich and Alfa Aesar. Amino acetonitrile hydrochloride used in this manuscript was purchased from Alfa Aesar, though it can be readily synthesized on 50 mmol scale in a single step starting from formaldehyde, ammonium hydroxide and sodium cyanide, followed by precipitation of the hydrochloride salt with 69% yield.<sup>[1]</sup>

Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume.

<sup>1</sup>H-NMR, <sup>19</sup>F-NMR and <sup>13</sup>C-NMR were recorded on a Varian AV600 or AV400 spectrometer in CDCl<sub>3</sub>. Data are reported in the following order: chemical shift ( $\delta$ ) in ppm; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), p (pentelet) m (multiplet); coupling constants (J) are in Hertz (Hz).

EI MS data were recorded on a Shimadzu GCMS system (QP 2010 SE and GC2010plus, CP-Sil-8-MS column, 30m, 0.25 $\mu$ m ID, method: 60°C 5min, 20K/min to 300°C and keep for 20min). HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization.

IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm<sup>-1</sup>).

Syringe pump: Chemyx Inc. Model Fusion 710.

## **IMPORTANT SAFETY NOTE:**

*Safety hazards of diazo acetonitrile and trifluoro diazoethane, described within this manuscript, have not been investigated. However, it should be noted these particular diazo compound were reported to be highly explosive.*

*Handling of diazo compounds should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred handling of diazoalkanes during the preparation of this manuscript, yet the reader should be aware of carcinogenicity and explosiveness of the herein described diazo compounds. General safety precautions when working with diazomethane and its derivatives should be followed. Any reactions described in this manuscript should not be performed without strict risk assessment and proper safety precautions.*

## **STANDARD PROCEDURE FOR THE REARRANGEMENT REACTION**

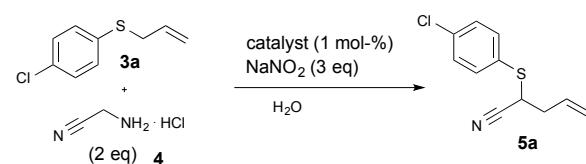
FeTPPCl (1 mol-%), amine hydrochloride (2eq) and allyl or propargyl sulfide (0.2 mmol, 1eq) were dissolved in 0.5 mL of thoroughly degassed water and 0.05 mL degassed dichloromethane under argon atmosphere. NaNO<sub>2</sub> (3 eq) was dissolved in 1 mL degassed water and added via syringe pump over 10 h at room temperature. The resulting mixture was stirred additional 5 h at room temperature. The aqueous phase was extracted with dichloromethane (three times) and the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was re-

moved under reduced pressure and the residue was purified with column chromatography on silica gel (pentane  $\rightarrow$  pentane: diethyl ether 20:1) to afford the desired rearrangement product.

#### STANDARD PROCEDURE FOR LARGE SCALE REARRANGEMENT REACTION

FeTPPCl (1 mol-% or 0.1 mol-%), amine hydrochloride (2eq) and allyl or progargyl sulfide (2 or 8 mmol, 1eq) were dissolved in 5 mL of thoroughly degassed water (20 mL for 8 mmol scale) and 0.5 mL degassed dichloromethane (2 mL for 8 mmol scale) under argon atmosphere. NaNO<sub>2</sub> (3 eq) was dissolved in 10 mL degassed water (40 mL for 8 mmol scale) and added via syringe pump over 10 h at room temperature. The resulting mixture was stirred additional 5 h at room temperature. The aqueous phase was extracted with dichloromethane (three times) and the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified with column chromatography on silica gel (pentane  $\rightarrow$  pentane: diethyl ether 20:1) to afford the desired rearrangement product.

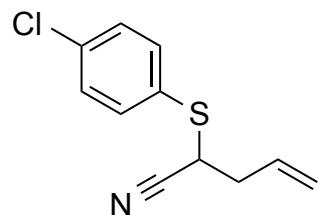
#### OPTIMIZATION OF REACTION CONDITIONS



entry <sup>[a]</sup>	catalyst	mol-%	concentration	yield
1	Mn(acac) <sub>2</sub>	1	0.05 M	no reaction
2	Mn(acac) <sub>3</sub>	1	0.05 M	no reaction
3	Mn(salen)	1	0.05 M	no reaction
4	Co(acac) <sub>2</sub>	1	0.05 M	traces
5	Co(acac) <sub>3</sub>	1	0.05 M	no reaction
6	Fe(acac) <sub>3</sub>	1	0.05 M	traces
7	Cu(acac) <sub>2</sub>	1	0.05 M	no reaction
8	FeBr <sub>2</sub>	1	0.05 M	no reaction
9	Co(salen)	1	0.05 M	41
10	Rh <sub>2</sub> OAc <sub>4</sub>	1	0.05 M	47
11	FeTPPCl	1	0.05 M	92

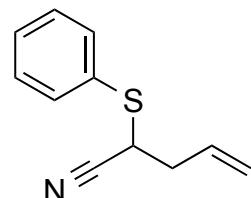
[a] reaction conditions: 0.2 mmol **3a**, 1 mol-% catalyst, 2 eq **4** were suspended in H<sub>2</sub>O. NaNO<sub>2</sub> (3 eq) dissolved in 1 mL water was added 10 h at rt; the resulting mixture was stirred for 5 h at rt; isolated yields.

**2-((4-chlorophenyl)thio)pent-4-enenitrile**



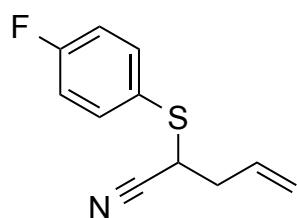
Compound **5a** was prepared according to general procedure, using corresponding allyl sulfide (37 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 95% yield (42 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.65 – 7.50 (m, 2H), 7.43 – 7.30 (m, 2H), 5.84 (ddt, *J* = 16.3, 10.7, 7.0 Hz, 1H), 5.32 – 5.08 (m, 2H), 3.71 (dd, *J* = 7.9, 6.7 Hz, 1H), 2.69 – 2.33 (m, 2H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 136.3, 136.2, 131.6, 129.7, 128.7, 120.2, 118.5, 36.9, 36.5 ppm; HRMS (ESI): m/z calc. for [C<sub>11</sub>H<sub>10</sub>NCINaS]: 246.01147, found 246.01146; IR (KBr): 3833, 2920, 2343, 2090, 1860, 1443, 1077, 963, 805 cm<sup>-1</sup>.

**2-(phenylthio)pent-4-enenitrile**



Compound **5b** was prepared according to general procedure, using corresponding allyl sulfide (30 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 87% yield (33 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.63 – 7.59 (m, 2H), 7.42 – 7.37 (m, 3H), 5.86 (ddt, *J* = 16.9, 9.9, 6.9 Hz, 1H), 5.32 – 5.14 (m, 2H), 3.73 (dd, *J* = 8.1, 6.5 Hz, 1H), 2.74 – 2.44 (m, 2H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 134.7, 131.8, 130.4, 129.6, 129.5, 120.0, 118.8, 36.9, 36.6 ppm; HRMS (ESI): m/z calc. for [C<sub>11</sub>H<sub>11</sub>NNaS]: 212.05044, found 212.05051; IR (KBr): 3467, 3068, 2992, 2922, 2668, 2324, 2098, 1892, 1747, 1435, 989, 925, 745, 693 cm<sup>-1</sup>.

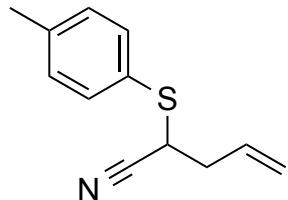
**2-((4-fluorophenyl)thio)pent-4-enenitrile**



Compound **5c** was prepared according to general procedure, using corresponding allyl sulfide (34 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 88% yield (36 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.68 – 7.52 (m, 2H), 7.13 – 7.02 (m, 2H), 5.84 (ddt, *J* = 16.4, 10.7, 6.9 Hz, 1H), 5.31 – 5.17 (m, 2H), 3.67 (m, 1H), 2.67

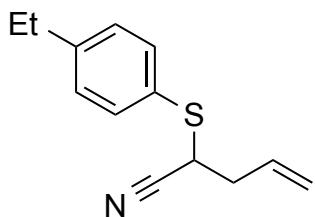
– 2.40 (m, 2H) ppm; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>): δ -110.18 ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 164.7, 163.1, 137.6 (d, *J* = 8.5 Hz), 131.7, 125.3 (d, *J* = 3.0 Hz), 120.1, 118.6, 116.7 (d, *J* = 22.0 Hz), 37.3, 36.5 ppm; HRMS (ESI): m/z calc. for [C<sub>11</sub>H<sub>10</sub>NFNaS]: 230.04104, found 230.04103; IR (KBr): 3413, 3080, 2922, 2667, 2321, 1894, 1644, 1586, 1485, 1227, 991, 928, 829 cm<sup>-1</sup>.

#### 2-((4-methylphenyl)thio)pent-4-enenitrile



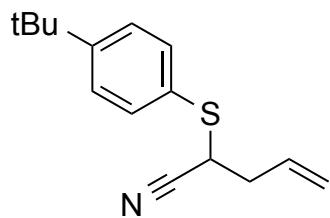
Compound **5d** was prepared according to general procedure, using corresponding allyl sulfide (33 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane → pentane : diethyl ether 20:1) as a colorless liquid in 90% yield (37 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.53 – 7.47 (m, 2H), 7.22 – 7.17 (m, 2H), 5.85 (ddt, *J* = 16.9, 9.9, 6.9 Hz, 1H), 5.33 – 5.02 (m, 2H), 3.67 (dd, *J* = 8.1, 6.5 Hz, 1H), 2.71 – 2.45 (m, 2H), 2.37 (s, 3H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 140.1, 135.2, 131.9, 130.3, 126.6, 119.9, 118.8, 37.2, 36.6, 21.3 ppm; HRMS (ESI): m/z calc. for [C<sub>12</sub>H<sub>13</sub>NNaS]: 226.06609, found 226.06627; IR (KBr): 3456, 3073, 2923, 2323, 2242, 2100, 1905, 1743, 1488, 1435, 1211, 1104, 990, 925, 809 cm<sup>-1</sup>.

#### 2-((4-ethylphenyl)thio)pent-4-enenitrile



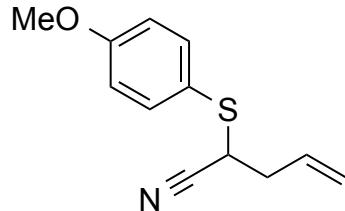
Compound **5e** was prepared according to general procedure, using corresponding allyl sulfide (36 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane → pentane : diethyl ether 20:1) as a colorless liquid in 94% yield (41 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.59 – 7.46 (m, 2H), 7.24 – 7.16 (m, 2H), 5.86 (ddt, *J* = 17.0, 9.9, 6.9 Hz, 1H), 5.29 – 5.17 (m, 2H), 3.68 (dd, *J* = 8.2, 6.5 Hz, 1H), 2.67 (m, 2H), 2.61 – 2.48 (m, 2H), 1.24 (t, *J* = 7.6 Hz, 3H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 146.3, 135.2, 131.9, 129.1, 126.9, 119.9, 118.9, 37.1, 36.6, 28.6, 15.3 ppm; HRMS (ESI): m/z calc. for [C<sub>13</sub>H<sub>15</sub>NNaS]: 240.08174, found 240.08173; IR (KBr): 3454, 3076, 2967, 2238, 1909, 1642, 1488, 1433, 1183, 1109, 988, 925, 828, 767 cm<sup>-1</sup>.

#### 2-((4-tert-butylphenyl)thio)pent-4-enenitrile



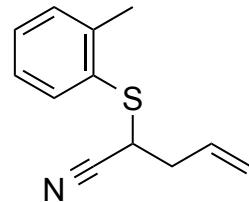
Compound **5f** was prepared according to general procedure, using corresponding allyl sulfide (41 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 92% yield (45 mg). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.61 – 7.46 (m, 2H), 7.43 – 7.35 (m, 2H), 5.85 (ddt, J = 16.9, 9.9, 6.9 Hz, 1H), 5.33 – 5.14 (m, 1H), 3.67 (dd, J = 8.0, 6.6 Hz, 1H), 2.71 – 2.41 (m, 1H), 1.31 (s, 9H) ppm; <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 153.1, 134.7, 131.9, 126.8, 126.5, 119.8, 118.9, 37.0, 36.6, 34.8, 31.2 ppm; GC-MS: m/z (%): 245.0 [M] 55%, 230.0 [M-CH<sub>3</sub>] 100%, 203.9 [M-C<sub>3</sub>H<sub>5</sub>] 15%, 91.0 [M-C<sub>8</sub>H<sub>12</sub>NS] 51%; IR (KBr): 3081, 2962, 2871, 2322, 2237, 1993, 1643, 1594, 1488, 1395, 1365, 1267, 1200, 1117, 1088, 1013, 991, 925, 830 cm<sup>-1</sup>.

#### 2-((4-methoxyphenyl)thio)pent-4-enenitrile



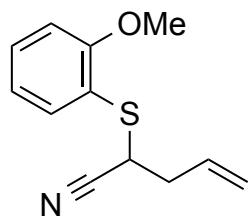
Compound **5f** was prepared according to general procedure, using corresponding allyl sulfide (36 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 90% yield (39 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.62 – 7.50 (m, 2H), 6.94 – 6.87 (m, 2H), 5.83 (ddt, J = 16.9, 9.9, 6.9 Hz, 1H), 5.26 – 5.17 (m, 2H), 3.81 (s, 3H), 3.60 (dd, J = 8.1, 6.7 Hz, 1H), 2.52 (m, 2H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 161.2, 137.4, 131.9, 120.4, 119.7, 118.8, 114.9, 55.4, 27.5, 36.5 ppm; HRMS (ESI): m/z calc. for [C<sub>12</sub>H<sub>13</sub>ONNaS]: 242.06101, found 242.06108; IR (KBr): 3078, 2938, 2096, 1888, 1742, 1588, 1489, 1288, 1246, 1174, 1101, 1026, 925, 827 cm<sup>-1</sup>.

#### 2-((2-methylphenyl)thio)pent-4-enenitrile



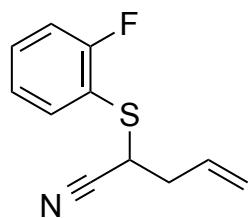
Compound **5h** was prepared according to general procedure, using corresponding allyl sulfide (33 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a colorless liquid in 98% yield (40 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.60 (dd, J = 7.5, 1.1 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 5.89 (ddt, J = 17.1, 10.2, 7.0 Hz, 1H), 5.31 – 5.13 (m, 2H), 3.71 (dd, J = 8.0, 6.3 Hz, 1H), 2.72 – 2.58 (m, 2H), 2.51 (s, 3H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 141.8, 135.1, 131.8, 130.9, 130.3, 129.6, 127.0, 120.0, 118.8, 36.6 (d, J = 28.1 Hz), 20.9 ppm; HRMS (ESI): m/z calc. for [C<sub>12</sub>H<sub>13</sub>NNaS]: 226.06609, found 226.06615; IR (KBr): 3066, 2924, 2325, 2239, 2105, 1908, 1740, 1458, 1216, 1046, 988, 926, 752 cm<sup>-1</sup>.

**2-((2-methoxyphenyl)thio)pent-4-enenitrile**



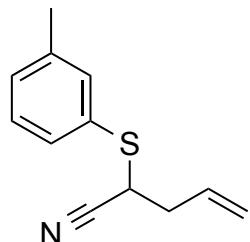
Compound **5i** was prepared according to general procedure, using corresponding allyl sulfide (36 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 96% yield (42 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.19 – 7.12 (m, 2H), 6.97 – 6.92 (m, 1H), 5.86 (ddt, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.30 – 5.22 (m, 2H), 3.83 (s, 3H), 3.75 (dd, *J* = 8.0, 6.5 Hz, 1H), 2.59 (m, 2H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 159.9, 131.8, 131.5, 130.2, 126.5, 120.0, 119.3, 118.83, 115.6, 55.4, 36.8, 36.6 ppm; HRMS (ESI): m/z calc. for [C<sub>12</sub>H<sub>13</sub>ONNaS]: 242.06101, found 242.06122; IR (KBr): 3073, 2939, 2838, 2098, 1580, 1473, 1433, 1274, 1245, 1021, 925, 752, 684 cm<sup>-1</sup>.

**2-((2-fluorophenyl)thio)pent-4-enenitrile**



Compound **5j** was prepared according to general procedure, using corresponding allyl sulfide (34 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 88% yield (36 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.67 – 7.60 (m, 1H), 7.47 – 7.37 (m, 1H), 7.22 – 7.10 (m, 2H), 5.88 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.40 – 5.10 (m, 2H), 3.89 (dd, *J* = 8.2, 6.1 Hz, 1H), 2.77 – 2.48 (m, 2H) ppm; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>): δ = -106.37 ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 163.7, 162.1, 137.0, 132.2 (d, *J* = 8.3 Hz), 131.5, 125.1 (d, *J* = 3.7 Hz), 120.2, 118.3, 117.6 (d, *J* = 17.9 Hz), 116.3 (d, *J* = 22.9 Hz), 36.6, 35.9 (d, *J* = 2.8 Hz) ppm; HRMS (ESI): m/z calc. for [C<sub>11</sub>H<sub>10</sub>NFNaS]: 230.04102, found 230.04102; IR (KBr): 3078, 2923, 2092, 1919, 1740, 1576, 1471, 1442, 1261, 1223, 990, 928, 822, 757 cm<sup>-1</sup>.

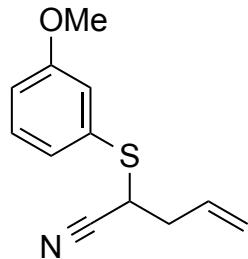
**2-((3-methylphenyl)thio)pent-4-enenitrile**



Compound **5k** was prepared according to general procedure, using corresponding allyl sulfide (33 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was

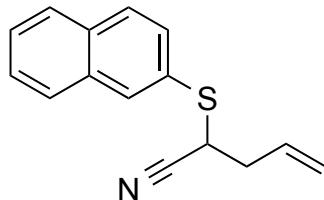
obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 86% yield (35 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.44 – 7.37 (m, 2H), 7.31 – 7.26 (m, 1H), 7.23 – 7.17 (m, 1H), 5.86 (ddt, *J* = 17.0, 9.9, 6.9 Hz, 1H), 5.33 – 5.13 (m, 2H), 3.72 (dd, *J* = 8.1, 6.5 Hz, 1H), 2.68 – 2.51 (m, 2H), 2.37 (s, 3H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 139.4, 135.1, 131.9, 131.5, 130.4, 130.2, 129.3, 119.9, 118.8, 36.9, 36.6, 21.3 ppm; HRMS (ESI): m/z calc. for [C<sub>12</sub>H<sub>13</sub>NNaS]: 226.06609, found 226.06618; IR (KBr): 3461, 2923, 2676, 2337, 2096, 1881, 1742, 1436, 1372, 1215, 1091, 991, 925, 778, 687 cm<sup>-1</sup>.

#### 2-((3-methoxyphenyl)thio)pent-4-enenitrile



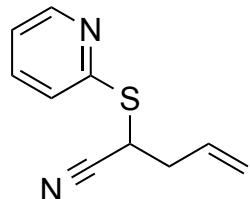
Compound **5l** was prepared according to general procedure, using corresponding allyl sulfide (36 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPP<sup>+</sup>Cl<sup>-</sup> (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 91% yield (40 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.35 – 7.20 (m, 1H), 7.20 – 7.11 (m, 2H), 6.92 (ddd, *J* = 8.3, 2.5, 1.0 Hz, 1H), 5.85 (ddt, *J* = 16.9, 9.8, 6.9 Hz, 1H), 5.38 – 5.08 (m, 2H), 3.81 (s, 3H), 3.73 (dd, *J* = 7.9, 6.7 Hz, 1H), 2.58 (m, 2H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 159.9, 131.8, 131.5, 130.2, 126.4, 119.9, 119.3, 118.8, 115.6, 55.4, 36.8, 36.6 ppm; HRMS (ESI): m/z calc. for [C<sub>12</sub>H<sub>13</sub>ONNaS]: 242.06101, found 242.06122; IR (KBr): 3073, 2939, 2098, 1580, 1473, 1433, 1274, 1245, 1069, 1021, 925, 752 cm<sup>-1</sup>.

#### 2-(naphthalen-2-ylthio)pent-4-enenitrile



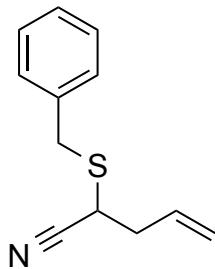
Compound **5m** was prepared according to general procedure, using corresponding allyl sulfide (40 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPP<sup>+</sup>Cl<sup>-</sup> (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 87% yield (42 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.13 (d, *J* = 1.8 Hz, 1H), 7.88 – 7.83 (m, 3H), 7.64 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.56 – 7.51 (m, 2H), 5.89 (ddt, *J* = 16.9, 9.9, 6.9 Hz, 1H), 5.31 – 5.24 (m, 2H), 3.82 (dd, *J* = 8.2, 6.3 Hz, 1H), 2.66 – 2.56 (m, 2H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 134.6, 133.5, 133.4, 131.8, 130.7, 129.2, 127.9, 127.8, 127.6, 127.3, 126.9, 120.1, 118.8, 36.9, 36.7 ppm; HRMS (ESI): m/z calc for [C<sub>15</sub>H<sub>13</sub>NNaS]: 262.06610, found 262.06609; IR (KBr): 3850, 2924, 2342, 2094, 1854, 1619, 1441, 1343, 1247, 1135, 927, 818 cm<sup>-1</sup>.

**2-(pyridin-2-ylthio)pent-4-enenitrile**



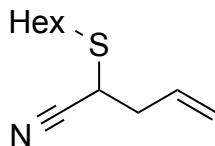
Compound **5n** was prepared according to general procedure, using corresponding allyl sulfide (30 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 10:1) as a yellow liquid in 87% yield (33 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.48 (ddd, J = 4.9, 1.9, 0.9 Hz, 1H), 7.56 (td, J = 7.7, 1.9 Hz, 1H), 7.20 (dt, J = 8.0, 1.1 Hz, 1H), 7.08 (ddd, J = 7.4, 4.9, 1.1 Hz, 1H), 5.92 (ddt, J = 17.0, 10.1, 6.9 Hz, 1H), 5.35 – 5.23 (m, 2H), 4.92 (dd, J = 7.8, 6.1 Hz, 1H), 2.80 – 2.64 (m, 2H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 154.6, 149.7, 136.6, 131.9, 122.4, 120.7, 120.1, 119.4, 36.3, 31.1 ppm; HRMS (ESI): m/z calc for [C<sub>10</sub>H<sub>11</sub>N<sub>2</sub>S]: 191.06375, found 191.06375; IR (KBr): 3834, 3518, 3413, 3051, 2985, 2907, 2659, 2328, 2238, 1994, 2108, 1808, 1694, 1577, 1498, 1452, 1415, 1281, 1175, 1123, 1084, 1043, 988, 927, 761, 722, 675 cm<sup>-1</sup>.

**2-((benzyl)thio)pent-4-enenitrile**



Compound **5o** was prepared according to general procedure, using corresponding allyl sulfide (33 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 96% yield (39 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.40 – 7.32 (m, 4H), 7.31 – 7.25 (m, 2H), 5.77 (ddt, J = 17.5, 9.7, 7.0 Hz, 1H), 5.22 – 5.17 (m, 2H), 4.08 – 3.88 (m, 2H), 3.33 (dd, J = 7.8, 6.3 Hz, 1H), 2.62 – 2.41 (m, 2H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 36.2, 131.8, 128.9, 128.83, 127.7, 119.8, 118.4, 36.1 (d, J = 25.3 Hz), 31.8 ppm; HRMS (ESI): m/z calc. for [C<sub>12</sub>H<sub>13</sub>NNaS]: 226.06609 found 226.06612; IR (KBr): 3450, 3069, 3024, 2920, 2662, 2324, 2102, 1895, 1741, 1441, 1365, 1220, 991, 924, 766, 703 cm<sup>-1</sup>.

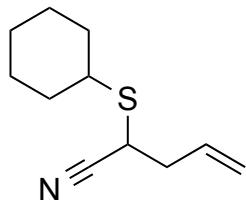
**2-(hexylthio)pent-4-enenitrile**



Compound **5p** was prepared according to general procedure, using corresponding allyl sulfide (32 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a

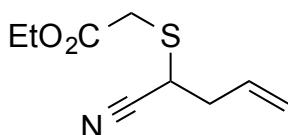
colorless liquid in 93% yield (37 mg).  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.85$  (ddt,  $J = 17.1, 10.2, 7.0$  Hz, 1H), 5.30 – 5.19 (m, 2H), 3.55 (dd,  $J = 8.0, 6.4$  Hz, 1H), 2.84 – 2.69 (m, 2H), 2.69 – 2.50 (m, 2H), 1.74 – 1.58 (m, 2H), 1.44 – 1.35 (m, 2H), 1.31 (dtt,  $J = 10.7, 6.9, 3.8$  Hz, 4H), 0.89 (t,  $J = 6.9$  Hz, 3H) ppm;  $^{13}\text{C-NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta = 132.0, 119.7, 118.8, 36.7, 32.6, 31.9, 31.3, 28.9, 28.4, 22.5, 13.9$  ppm; HRMS (ESI): m/z calc for  $[\text{C}_{11}\text{H}_{19}\text{NNaS}]$ : 220.11307, found 220.11304; IR (KBr): 2928, 2237, 2077, 1862, 1642, 1443, 1281, 1101, 928, 729  $\text{cm}^{-1}$ .

#### 2-(cyclohexylthio)pent-4-enenitrile



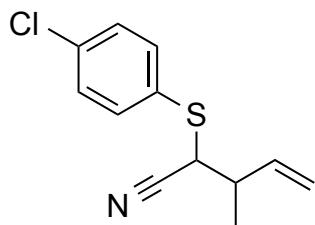
Compound **5q** was prepared according to general procedure, using corresponding allyl sulfide (31 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 93% yield (36 mg).  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.84$  (ddt,  $J = 17.1, 10.1, 7.0$  Hz, 1H), 5.37 – 5.16 (m, 2H), 3.60 (t,  $J = 7.1$  Hz, 1H), 2.97 (m, 1H), 2.55 (m, 2H), 2.10 – 1.90 (m, 2H), 1.82 – 1.71 (m, 2H), 1.45 – 1.20 (m, 5H) ppm;  $^{13}\text{C-NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta = 132.0, 119.7, 119.3, 44.5, 36.8, 33.5, 32.9, 30.9, 25.9, 25.6, 25.5$  ppm; HRMS (ESI): m/z calc for  $[\text{C}_{11}\text{H}_{18}\text{NS}^+]$ : 196.11545, found 196.11491; IR (KBr): 2923, 2338, 2096, 1742, 1443, 1368, 1215, 995, 859  $\text{cm}^{-1}$ .

#### ethyl 2-((1-cyanobut-3-en-1-yl)thio)acetate



Compound **5r** was prepared according to general procedure, using corresponding allyl sulfide (32 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a colorless liquid in 99% yield (40 mg).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.83$  (ddt,  $J = 17.1, 10.1, 7.0$  Hz, 1H), 5.30 – 5.22 (m, 2H), 4.20 (q,  $J = 7.2$  Hz, 2H), 3.93 (t,  $J = 7.1$  Hz, 1H), 3.56 (d,  $J = 15.7$  Hz, 1H), 3.38 (d,  $J = 15.7$  Hz, 1H), 2.59 (tt,  $J = 7.0, 1.2$  Hz, 2H), 1.28 (t,  $J = 7.1$  Hz, 3H) ppm;  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 169.2, 131.4, 120.1, 118.1, 61.9, 36.1, 33.2, 32.9, 14.1$  ppm; HRMS (ESI): m/z calc for  $[\text{C}_9\text{H}_{13}\text{NO}_2\text{SNa}^+]$ : 222.05592, found 222.05577; IR (KBr): 2971, 2337, 2095, 1876, 1729, 1400, 1278, 1157, 1019, 928  $\text{cm}^{-1}$ .

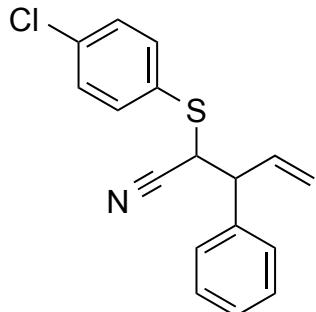
#### 2-((4-chlorophenyl)thio)-3-methylpent-4-enenitrile



diastereomeric ratio: 1:1

Compound **5s** was prepared according to general procedure, using corresponding allyl sulfide (40 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 85% yield (40 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.57 – 7.50 (m, 2H), 7.41 – 7.32 (m, 2H), 5.91 – 5.74 (m, 1H), 5.28 – 5.16 (m, 2H), 3.89 – 3.36 (m, 1H), 2.66 (m, 1H), 1.30 (m, 3H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 137.9, 137.1, 136.0, 135.9, 135.9, 135.6, 135.5, 129.7, 129.7, 118.1, 117.9, 117.9, 117.5, 44.1, 43.9, 40.3, 40.0, 18.2, 17.2 ppm; GC-MS: m/z (%): 236.9 [M] 20%, 155.9 [M-C<sub>5</sub>H<sub>7</sub>N] 40%; IR (KBr): 2920, 2335, 2105, 1743, 1368, 1215, 1024, 699 cm<sup>-1</sup>.

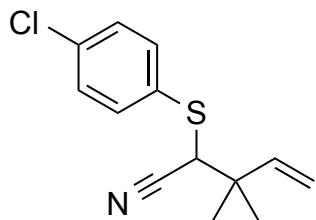
**2-((4-chlorophenyl)thio)-3-phenylpent-4-enenitrile**



diastereomeric ratio: 2:1

Compound **5t** was prepared according to general procedure, using corresponding allyl sulfide (52 mg, 0.2 mmol, 1 eq.), aminoacetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 96% yield (58 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.61 – 7.15 (m, 9H), 6.16 (dd, *J* = 16.9, 11.4, 10.2, 8.1 Hz, 1H), 5.43 – 5.16 (m, 2H), 3.98 (t, *J* = 7.5 Hz, 1H), 3.69 (t, *J* = 8.0 Hz, 1H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 138.6, 138.4, 136.1, 135.9, 135.9, 135.8, 135.2, 129.7, 129.7, 129.4, 129.2, 129.0, 128.9, 128.2, 128.1, 127.9, 127.8, 119.7, 119.1, 117.9, 117.9, 51.7, 51.4, 43.5, 43.4 ppm; HRMS (ESI): m/z calc for [C<sub>17</sub>H<sub>15</sub>ClNS<sup>+</sup>]: 300.06082, found 300.06052; IR (KBr): 2915, 2343, 2100, 1869, 1473, 1091, 1004, 928, 819, 714 cm<sup>-1</sup>.

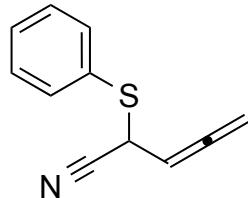
**2-((4-chlorophenyl)thio)-3,3-dimethylpent-4-enenitrile**



Compound **5u** was prepared according to general procedure, using corresponding allyl sulfide (43 mg, 0.2 mmol, 1 eq.), amino acetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 98% yield (49mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.58 – 7.48 (m, 2H), 7.40 – 7.30 (m, 2H), 5.92 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.24 – 5.11 (m, 2H), 3.55 (s, 1H), 1.33

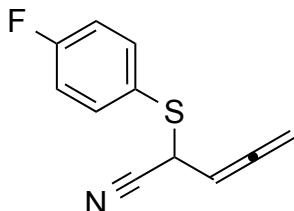
(d,  $J = 1.2$  Hz, 6H) ppm;  $^{13}\text{C}$ -NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.0, 135.7, 130.7, 118.2, 115.2, 50.4, 40.5, 24.9, 24.7$  ppm; GC-MS: m/z (%): 250.9 [M] 5%, 142.9 [ $\text{M-C}_7\text{H}_{10}\text{N}$ ] 33%, 69.0 [ $\text{M-C}_8\text{H}_5\text{ClNS}$ ] 100%; IR (KBr): 2673, 2337, 2096, 1743, 1378, 1214  $\text{cm}^{-1}$ .

**2-(phenylthio)-4 $\lambda^5$ -penta-3,4-dienenitrile**



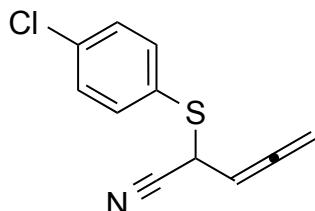
Compound **7a** was prepared according to general procedure, using corresponding propargyl sulfide (30 mg, 0.2 mmol, 1 eq.), amino acetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane  $\rightarrow$  pentane : diethyl ether 20:1) as a yellow liquid in 97% yield (36 mg).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.70 - 7.54$  (m, 2H), 7.46 – 7.33 (m, 3H), 5.22 (q,  $J = 6.6$  Hz, 1H), 4.97 (ddd,  $J = 12.0, 6.6, 2.8$  Hz, 1H), 4.86 – 4.65 (m, 1H), 4.32 (dt,  $J = 6.6, 2.6$  Hz, 1H) ppm;  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 208.8, 135.7, 135.0, 129.9, 129.2, 116.9, 85.8, 80.0, 36.7$  ppm; HRMS (ESI): m/z calc for  $[\text{C}_{11}\text{H}_{10}\text{NS}^+]$ : 188.05285, found 188.05269; IR (KBr): 2927, 2671, 2335, 2095, 1937, 1738, 1576, 1448, 1089, 857, 721  $\text{cm}^{-1}$ .

**2-((4-fluorophenyl)thio)-4 $\lambda^5$ -penta-3,4-dienenitrile**



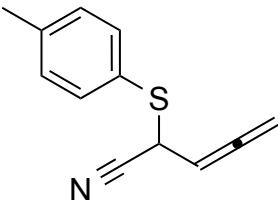
Compound **7b** was prepared according to general procedure, using corresponding propargyl sulfide (33 mg, 0.2 mmol, 1 eq.), amino acetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane  $\rightarrow$  pentane : diethyl ether 20:1) as a yellow liquid in 83% yield (34 mg).  $^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.63 - 7.57$  (m, 2H), 7.10 (m, 2H), 5.21 (q,  $J = 6.6$  Hz, 1H), 5.00 (ddd,  $J = 12.1, 6.6, 2.8$  Hz, 1H), 4.80 (ddd,  $J = 12.1, 6.5, 2.5$  Hz, 1H), 4.29 (dt,  $J = 6.5, 2.6$  Hz, 1H) ppm;  $^{13}\text{C}$ -NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta = 208.8, 165.0, 163.3, 138.5$  (d,  $J = 8.4$  Hz), 124.7 (d,  $J = 3.3$  Hz), 116.5 (d,  $J = 21.7$  Hz), 85.7, 80.1, 37.0 ppm;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta = -109.78$  ppm; HRMS (ESI): m/z calc for  $[\text{C}_{11}\text{H}_8\text{FNNaS}^+]$ : 228.02537, found 228.02495; IR (KBr): 2927, 2683, 2341, 2095, 1742, 1587, 1478, 1221, 840, 719  $\text{cm}^{-1}$ .

**2-((4-chlorophenyl)thio)-4 $\lambda^5$ -penta-3,4-dienenitrile**



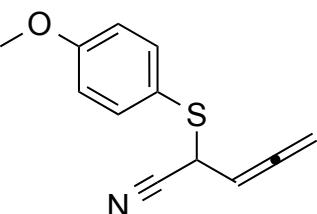
Compound **7c** was prepared according to general procedure, using corresponding propargyl sulfide (37 mg, 0.2 mmol, 1 eq.), amino acetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 89% yield (40 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.56 – 7.50 (m, 2H), 7.39 – 7.33 (m, 2H), 5.20 (qd, J = 6.6, 0.6 Hz, 1H), 5.00 (dddd, J = 12.1, 6.6, 2.8, 0.6 Hz, 1H), 4.83 (dddd, J = 12.1, 6.5, 2.5, 0.6 Hz, 1H), 4.31 (dtd, J = 6.5, 2.6, 0.6 Hz, 1H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 208.8, 137.1, 136.7, 129.5, 127.9, 116.6, 85.7, 80.3, 36.7 ppm; HRMS (ESI): m/z calc for [C<sub>11</sub>H<sub>9</sub>CINS<sup>+</sup>]: 222.01387, found 222.01357; IR (KBr): 2916, 2675, 2339, 2096, 1776, 1471, 1091, 1011, 840, 725 cm<sup>-1</sup>.

**2-((4-methylphenyl)thio)-4λ<sup>5</sup>-penta-3,4-dienenitrile**



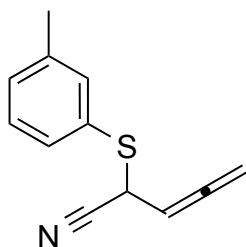
Compound **7d** was prepared according to general procedure, using corresponding propargyl sulfide (37 mg, 0.2 mmol, 1 eq.), amino acetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 98% yield (39 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.55 – 7.45 (m, 2H), 7.20 (m, 2H), 5.22 (q, J = 6.6 Hz, 1H), 4.99 (ddd, J = 11.9, 6.6, 2.8 Hz, 1H), 4.82 (ddd, J = 11.9, 6.5, 2.5 Hz, 1H), 4.29 (dt, J = 6.6, 2.6 Hz, 1H), 2.38 (s, 3H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): 208.7, 140.5, 135.9, 130.0, 126.1, 116.9, 85.9, 79.9, 36.9, 21.3 ppm; HRMS (ESI): m/z calc for [C<sub>12</sub>H<sub>11</sub>NNaS]: 224.05044, found 224.05049; IR (KBr): 3065, 3024, 2920, 2664, 2329, 2103, 1951, 1787, 1701, 1595, 1491, 1428, 1400, 1303, 1265, 1016, 857, 810 cm<sup>-1</sup>.

**2-((4-methoxyphenyl)thio)-4λ<sup>5</sup>-penta-3,4-dienenitrile**



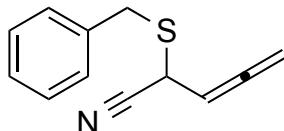
Compound **7e** was prepared according to general procedure, using corresponding propargyl sulfide (36 mg, 0.2 mmol, 1 eq.), amino acetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 85% yield (38 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.55 (m, 2H), 6.98 – 6.75 (m, 2H), 5.21 (q, J = 6.6 Hz, 1H), 4.97 (ddd, J = 11.9, 6.5, 2.7 Hz, 1H), 4.80 (ddd, J = 11.9, 6.5, 2.4 Hz, 1H), 4.23 (dt, J = 6.6, 2.6 Hz, 1H), 3.83 (s, 3H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 208.7, 161.4, 138.2, 119.9, 116.9, 114.7, 85.9, 79.8, 55.4, 37.3 ppm; HRMS (ESI): m/z calc for [C<sub>12</sub>H<sub>11</sub>NNaOS]: 240.04536, found 240.04539; IR (KBr): 2931, 2678, 2342, 2092, 1928, 1746, 1587, 1474, 1252, 1025, 835 cm<sup>-1</sup>.

**2-((3-methylphenyl)thio)-4 $\lambda^5$ -penta-3,4-dienenitrile**



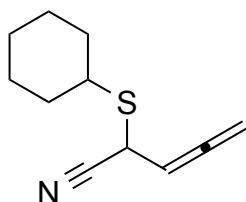
Compound **7f** was prepared according to general procedure, using corresponding propargyl sulfide (33 mg, 0.2 mmol, 1 eq.), amino acetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 95% yield (38 mg).  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.46 – 7.39 (m, 2H), 7.31 – 7.17 (m, 2H), 5.24 (q,  $J$  = 6.5 Hz, 1H), 5.00 (ddd,  $J$  = 11.9, 6.6, 2.8 Hz, 1H), 4.85 (ddd,  $J$  = 11.9, 6.5, 2.5 Hz, 1H), 4.33 (dt,  $J$  = 6.7, 2.6 Hz, 1H), 2.37 (s, 3H) ppm;  $^{13}\text{C-NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 208.8, 139.2, 136.0, 132.4, 130.7, 129.6, 129.1, 116.9, 85.9, 80.0, 36.7, 21.2 ppm; HRMS (ESI): m/z calc for  $[\text{C}_{12}\text{H}_{11}\text{NNaS}]$ : 224.05044, found 224.05052; IR (KBr): 3057, 2920, 2329, 2114, 1951, 1791, 1696, 1591, 1473, 1428, 1363, 1265, 1170, 856, 782, 689  $\text{cm}^{-1}$ .

**2-(benzylthio)-4 $\lambda^5$ -penta-3,4-dienenitrile**



Compound **7g** was prepared according to general procedure, using corresponding propargyl sulfide (33 mg, 0.2 mmol, 1 eq.), amino acetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a yellow liquid in 88% yield (35 mg).  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.39 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 5.17 (q,  $J$  = 6.5 Hz, 1H), 5.10 (m, 2H), 4.04 – 3.90 (m, 3H) ppm;  $^{13}\text{C-NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 208.7, 135.8, 129.1, 128.8, 127.8, 116.7, 85.8, 80.5, 35.9, 31.7 ppm; HRMS (ESI): m/z calc for  $[\text{C}_{12}\text{H}_{11}\text{NNaS}]$ : 224.05044, found 224.05043; IR (KBr): 3063, 3028, 2916, 2665, 2329, 2110, 1952, 1779, 1696, 1493, 1352, 1427, 1320, 1247, 1167, 1070, 858, 700  $\text{cm}^{-1}$ .

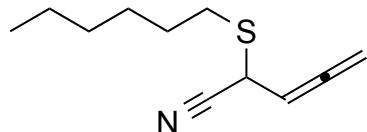
**2-(cyclohexylthio)-4 $\lambda^5$ -penta-3,4-dienenitrile**



Compound **7h** was prepared according to general procedure, using corresponding propargyl sulfide (31 mg, 0.2 mmol, 1 eq.), amino acetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a colorless liquid in 93% yield (38 mg).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.22 (q,  $J$  = 6.5 Hz, 1H), 5.09 (dt,  $J$  = 6.0, 2.7 Hz, 2H), 4.21 (dt,  $J$  = 6.3, 2.9 Hz, 1H), 2.98 (ddd,  $J$  = 10.3, 6.6, 3.6

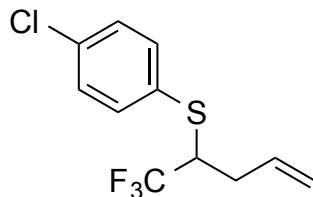
Hz, 1H), 2.20 – 1.91 (m, 2H), 1.86 – 1.70 (m, 2H), 1.68 – 1.57 (m, 1H), 1.47 – 1.16 (m, 5H) ppm;  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 208.4, 117.5, 86.5, 80.3, 44.5, 33.4, 33.1, 30.8, 25.9, 25.7, 25.5 ppm; HRMS (ESI): m/z calc for  $[\text{C}_{11}\text{H}_{16}\text{NS}^+]$ : 194.09980, found 194.09962; IR (KBr): 2924, 2339, 2094, 1941, 1741, 1442, 1354, 1220, 999, 856, 727  $\text{cm}^{-1}$ .

**2-(hexylthio)-4 $\lambda^5$ -penta-3,4-dienenitrile**



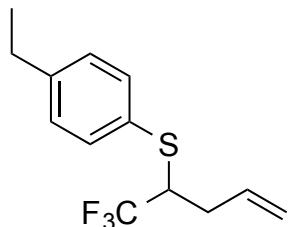
Compound **7i** was prepared according to general procedure, using corresponding propargyl sulfide (35 mg, 0.2 mmol, 1 eq.), amino acetonitrile hydrochloride (36 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane  $\rightarrow$  pentane : diethyl ether 20:1) as a colorless liquid in 90% yield (37 mg).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.31 – 5.01 (m, 3H), 4.16 (dt,  $J$  = 6.1, 2.9 Hz, 1H), 2.86 – 2.59 (m, 2H), 1.75 – 1.57 (m, 2H), 1.45 – 1.13 (m, 6H), 0.95 – 0.78 (m, 3H) ppm;  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 208.5, 116.9, 86.5, 80.3, 32.2, 31.3, 31.2, 28.7, 28.5, 22.5, 13.9 ppm; HRMS (ESI): m/z calc for  $[\text{C}_{11}\text{H}_{18}\text{NS}^+]$ : 196.11545, found 196.11536; IR (KBr): 2926, 2339, 2096, 1741, 1447, 1218, 855  $\text{cm}^{-1}$ .

**(4-chlorophenyl)(1,1,1-trifluoropent-4-en-2-yl)sulfane**



Compound **9a** was prepared according to general procedure, using corresponding allyl sulfide (37 mg, 0.2 mmol, 1 eq.), 2,2,2-trifluoro ethylamine hydrochloride (53 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane) as a yellow liquid in 83% yield (44 mg).  $^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.47 – 7.41 (m, 2H), 7.33 – 7.27 (m, 2H), 5.92 (ddt,  $J$  = 16.9, 9.9, 6.9 Hz, 1H), 5.22 (ddt,  $J$  = 13.8, 3.9, 1.5 Hz, 2H), 3.33 (dq,  $J$  = 10.0, 8.2, 4.1 Hz, 1H), 2.66 (dddt,  $J$  = 15.0, 6.8, 4.1, 1.3 Hz, 1H), 2.37 (dddt,  $J$  = 14.9, 9.7, 7.0, 1.2 Hz, 1H) ppm;  $^{13}\text{C}$ -NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 135.2, 134.9, 132.9, 131.2, 129.3, 126.3 (q,  $J$  = 279.8 Hz), 118.9, 52.6 (q,  $J$  = 28.3 Hz), 32.8 ppm;  $^{19}\text{F}$ -NMR (564 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -70.08 (d,  $J$  = 8.1 Hz) ppm; HRMS (ESI): m/z calc for  $[\text{C}_{11}\text{H}_{10}\text{ClF}_3\text{S}^+]$ : 266.01361, found 266.01384; IR (KBr): 3083, 2923, 2855, 2111, 1643, 1573, 1475, 1440, 1347, 1290, 1251, 1161, 1096, 1012, 922, 821  $\text{cm}^{-1}$ .

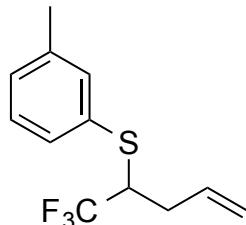
**(4-ethylphenyl)(1,1,1-trifluoropent-4-en-2-yl)sulfane**



Compound **9b** was prepared according to general procedure, using corresponding allyl sulfide (36 mg, 0.2 mmol, 1 eq.), 2,2,2-trifluoro ethylamine hydrochloride (53 mg, 0.4 mmol, 2

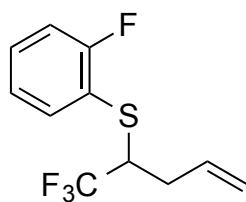
eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCl (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane) as a yellow liquid in 96% yield (50 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.51 – 7.36 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 5.96 (ddt, *J* = 17.1, 10.4, 6.9 Hz, 1H), 5.27 – 5.15 (m, 2H), 3.31 (dq, *J* = 9.5, 8.4, 4.3 Hz, 1H), 2.72 – 2.50 (m, 2H), 2.46 – 2.30 (m, 1H), 1.23 (t, *J* = 7.6 Hz, 3H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 145.1, 134.2, 133.25, 132.5, 129.4, 128.8, 128.7, 126.5 (q, *J* = 279.4 Hz), 118.6, 52.7 (q, *J* = 28.1 Hz), 32.9 (d, *J* = 2.7 Hz), 28.5, 15.3 ppm; <sup>19</sup>F-NMR (564 MHz, CDCl<sub>3</sub>): δ = -70.03 (d, *J* = 8.2 Hz) ppm; HRMS (ESI): m/z calc for [C<sub>13</sub>H<sub>15</sub>F<sub>3</sub>S]: 260.08466, found 260.08448; IR (KBr): 3080, 2969, 2933, 2107, 1644, 1492, 1441, 1348, 1250, 1161, 1101, 920, 828 cm<sup>-1</sup>.

**(3-methylphenyl)(1,1,1-trifluoropent-4-en-2-yl)sulfane**



Compound **9c** was prepared according to general procedure, using corresponding allyl sulfide (33 mg, 0.2 mmol, 1 eq.), 2,2,2-trifluoro ethylamine hydrochloride (53 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCl (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane) as a yellow liquid in 83% yield (41 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.34 – 7.27 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.14 – 7.09 (m, 1H), 5.95 (ddt, *J* = 17.1, 10.4, 6.9 Hz, 1H), 5.27 – 5.10 (m, 2H), 3.39 (dddt, *J* = 12.6, 9.7, 6.8, 4.3 Hz, 1H), 2.72 – 2.62 (m, 1H), 2.40 (dddt, *J* = 14.8, 9.4, 6.8, 1.2 Hz, 1H), 2.34 (s, 3H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 138.9, 134.0, 133.2, 132.7, 130.4, 129.2, 128.9, 126.5 (q, *J* = 279.5 Hz), 118.6, 52.4 (q, *J* = 28.0 Hz), 33.0, 21.2 ppm; <sup>19</sup>F-NMR (564 MHz, CDCl<sub>3</sub>): δ = -70.09 (d, *J* = 8.3 Hz) ppm; HRMS (ESI): m/z calc for [C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>S]: 246.06901, found 246.06834; IR (KBr): 3082, 2924, 1644, 1475, 1440, 1348, 1250, 1161, 1101, 921, 778, 688 cm<sup>-1</sup>.

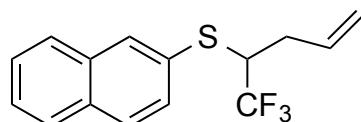
**(2-fluorophenyl)(1,1,1-trifluoropent-4-en-2-yl)sulfane**



Compound **9d** was prepared according to general procedure, using corresponding allyl sulfide (34 mg, 0.2 mmol, 1 eq.), 2,2,2-trifluoro ethylamine hydrochloride (53 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCl (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane) as a yellow liquid in 92% yield (47 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.60 – 7.42 (m, 1H), 7.38 – 7.27 (m, 1H), 7.17 – 6.97 (m, 2H), 6.14 – 5.75 (m, 1H), 5.28 – 5.06 (m, 2H), 3.50 (dtq, *J* = 12.6, 8.9, 4.5 Hz, 1H), 2.73 – 2.58 (m, 1H), 2.41 (dt, *J* = 15.7, 8.3 Hz, 1H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 136.2, 132.8, 131.0 (d, *J* = 8.2 Hz), 124.6 (d, *J* = 3.8 Hz), 118.7, 116.1 (d, *J* = 22.8 Hz), 50.8 (m), 32.9 ppm; <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>): δ = -70.30 (d, *J* = 8.2 Hz), -106.84 (d, *J* = 7.4

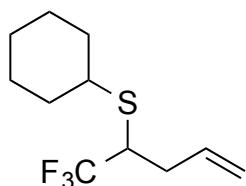
Hz) ppm; GC-MS: m/z (%): 249.9 [M] 37%, 208.8 [M-C<sub>3</sub>H<sub>5</sub>] 41%, 127.0 [M-C<sub>5</sub>H<sub>6</sub>F<sub>3</sub>] 80%. IR (KBr): 3958, 3451, 3059, 2926, 2658, 2326, 2243, 2105, 1947, 1734, 1590, 1460, 1376, 1321, 1271, 1155, 1046, 940, 857 cm<sup>-1</sup>.

**naphthalen-2-yl(1,1,1-trifluoropent-4-en-2-yl)sulfane**



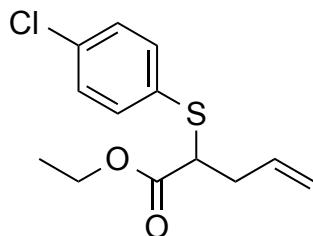
Compound **9e** was prepared according to general procedure, using corresponding allyl sulfide (40 mg, 0.2 mmol, 1 eq.), 2,2,2-trifluoro ethylamine hydrochloride (53 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane) as a yellow liquid in 93% yield (53 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.00 (d, J = 1.8 Hz, 1H), 7.87 – 7.73 (m, 3H), 7.61 – 7.42 (m, 3H), 5.98 (ddt, J = 17.1, 10.3, 6.9 Hz, 1H), 5.46 – 5.09 (m, 2H), 3.76 – 3.31 (m, 1H), 2.92 – 2.55 (m, 1H), 2.50 – 2.36 (m, 1H) ppm; <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 133.5, 133.1, 132.9, 132.8, 130.2, 128.8, 127.7, 127.6, 126.8, 126.7, 118.8, 52.4 (q, J = 28.2 Hz), 33.0 ppm; <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ = -69.97 (d, J = 8.2 Hz) ppm; GC-MS: m/z (%): 282.9 [M] 6%, 125.1 [M-C<sub>5</sub>H<sub>6</sub>F<sub>3</sub>S] 15%, 115.0 [M-C<sub>6</sub>H<sub>7</sub>F<sub>3</sub>S] 100%; IR (KBr): 3450, 3002, 2321, 2107, 1749, 1366, 1216, 1026 cm<sup>-1</sup>.

**cyclohexyl(1,1,1-trifluoropent-4-en-2-yl)sulfane**



Compound **9f** was prepared according to general procedure, using corresponding allyl sulfide (31 mg, 0.2 mmol, 1 eq.), 2,2,2-trifluoro ethylamine hydrochloride (53 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCL (1 mol-%, 1.4 mg). The product was obtained after column chromatography (silica, pentane) as a yellow liquid in 82% yield (39 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.60 – 7.42 (m, 1H), 7.38 – 7.27 (m, 1H), 7.17 – 6.97 (m, 2H), 6.14 – 5.75 (m, 1H), 5.28 – 5.06 (m, 2H), 3.50 (dtq, J = 12.6, 8.9, 4.5 Hz, 1H), 2.73 – 2.58 (m, 1H), 2.41 (dt, J = 15.7, 8.3 Hz, 1H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 133.5, 126.9 (q, J = 278.8 Hz), 118.2, 46.0 (q, J = 28.3 Hz), 44.6, 25.9, 25.8, 25.6 ppm; <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ = -70.78 (d, J = 8.3 Hz) ppm; HRMS (ESI): m/z calc for [C<sub>11</sub>H<sub>17</sub>F<sub>3</sub>S]: 238.10031, found 238.10018; IR (KBr): 3082, 2931, 2855, 2661, 2111, 1643, 1445, 1346, 1289, 1252, 1154, 1099, 994, 919, 685 cm<sup>-1</sup>.

**ethyl 2-((4-chlorophenyl)thio)pent-4-enoate**

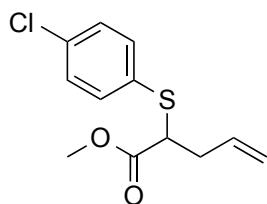


Compound **9g** was prepared according to general procedure, using corresponding allyl sulfide (31 mg, 0.2 mmol, 1 eq.), ethyl glycine hydrochloride (56 mg, 0.4 mmol, 2 eq.), sodium ni-

trite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCl (2 mol-%, 2.8 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a colorless liquid in 79% yield (43 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.46 – 7.37 (m, 2H), 7.33 – 7.24 (m, 2H), 5.79 (ddt, J = 17.0, 10.2, 6.9 Hz, 1H), 5.28 – 5.04 (m, 2H), 4.14–4.08 (m, 2H), 3.65 (dd, J = 8.7, 6.4 Hz, 1H), 2.71 – 2.57 (m, 1H), 2.54 – 2.44 (m, 1H), 1.18 (t, J = 7.1 Hz, 3H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 171.3, 134.4, 134.3, 133.6, 131.5, 129.0, 118.2, 61.2, 50.2, 35.6, 14.0 ppm; HRMS (ESI): m/z calc for [C<sub>13</sub>H<sub>15</sub>ClNaO<sub>2</sub>S<sup>+</sup>]: 293.03735, found 293.03708; IR (KBr): 3078, 2981, 2323, 2101, 1907, 1730, 1473, 1379, 1261, 1158, 1094, 1012, 921, 819 cm<sup>-1</sup>.

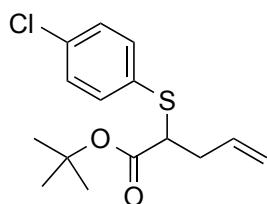
The NMR data is in accordance with the literature.<sup>[2]</sup>

**methyl 2-((4-chlorophenyl)thio)pent-4-enoate**



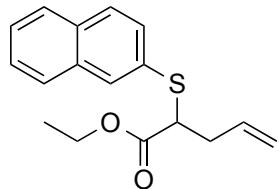
Compound **9h** was prepared according to general procedure, using corresponding allyl sulfide (31 mg, 0.2 mmol, 1 eq.), methyl glycine hydrochloride (56 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCl (2 mol-%, 2.8 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a colorless liquid in 55% yield (28 mg). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.41 – 7.36 (m, 2H), 7.31 – 7.27 (m, 2H), 5.78 (ddt, J = 17.2, 10.4, 6.9 Hz, 1H), 5.33 – 4.98 (m, 2H), 3.67 (s, 3H), 2.77 – 2.56 (m, 1H), 2.54 – 2.45 (m, 1H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 171.8, 134.5, 134.4, 133.5, 131.3, 129.1, 118.2, 52.2, 50.2, 35.6 ppm; HRMS (ESI): m/z calc for [C<sub>12</sub>H<sub>13</sub>ClNaO<sub>2</sub>S<sup>+</sup>]: 279.02170, found: 279.02115; IR (KBr): 3078, 2949, 2664, 2324, 2095, 1907, 1734, 1639, 1471, 1340, 1267, 1157, 1093, 1003, 920, 821 cm<sup>-1</sup>.

**tert-butyl 2-((4-chlorophenyl)thio)pent-4-enoate**



Compound **9i** was prepared according to general procedure, using corresponding allyl sulfide (31 mg, 0.2 mmol, 1 eq.), *tert*-butyl glycine hydrochloride (67 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCl (2 mol-%, 2.8 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a colorless liquid in 47% yield (28 mg). <sup>1</sup>H NMR (600 MHz, Chloroform-d) δ 7.47 – 7.36 (m, 2H), 7.34 – 7.23 (m, 2H), 5.80 (ddt, J = 17.1, 10.2, 6.7 Hz, 1H), 5.23 – 5.06 (m, 2H), 3.58 (dd, J = 8.9, 6.2 Hz, 1H), 2.61 – 2.52 (m, 1H), 2.48 – 2.42 (m, 1H), 1.37 (s, 9H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 170.4, 134.1, 133.9, 133.8, 132.0, 128.9, 117.9, 81.7, 50.8, 35.7, 27.8 ppm; HRMS (ESI): m/z calc for [C<sub>15</sub>H<sub>19</sub>ClNaO<sub>2</sub>S<sup>+</sup>]: 321.06865, found: 321.06790; IR (KBr): 3078, 2977, 2930, 2660, 2320, 2095, 1906, 1726, 1640, 1474, 1368, 1249, 1145, 1096, 1009, 919, 822 cm<sup>-1</sup>.

**ethyl 2-(naphthalen-2-ylthio)pent-4-enoate**



Compound **9j** was prepared according to general procedure, using corresponding allyl sulfide (40 mg, 0.2 mmol, 1 eq.), ethyl glycine hydrochloride (56 mg, 0.4 mmol, 2 eq.), sodium nitrite (41 mg, 0.6 mmol, 3 eq.) and FeTPPCl (2 mol-%, 2.8 mg). The product was obtained after column chromatography (silica, pentane -> pentane : diethyl ether 20:1) as a colorless liquid in 56% yield (32 mg). <sup>1</sup>H NMR (600 MHz, Chloroform-d) δ = 7.96 (d, J = 1.7 Hz, 1H), 7.88 – 7.74 (m, 3H), 7.56 – 7.45 (m, 3H), 5.84 (ddt, J = 17.2, 10.2, 6.8 Hz, 1H), 5.24 – 5.00 (m, 2H), 4.21 – 4.02 (m, 2H), 3.82 (dd, J = 8.7, 6.2 Hz, 1H), 2.92 – 2.61 (m, 1H), 2.60 – 2.53 (m, 1H), 1.14 (t, J = 7.1 Hz, 3H) ppm; <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>): δ = 171.6, 133.8, 133.5, 132.6, 131.9, 130.5, 129.9, 128.4, 127.6, 127.5, 126.5, 126.4, 118.0, 61.2, 50.2, 35.8, 14.0 ppm; HRMS (ESI): m/z calc for [C<sub>17</sub>H<sub>18</sub>NaO<sub>2</sub>S<sup>+</sup>]: 309.09197, found: 309.09122; IR (KBr): 3056, 2980, 2319, 2106, 1912, 1729, 1584, 1497, 1442, 1261, 1135, 1028, 922, 854, 813, 745 cm<sup>-1</sup>.

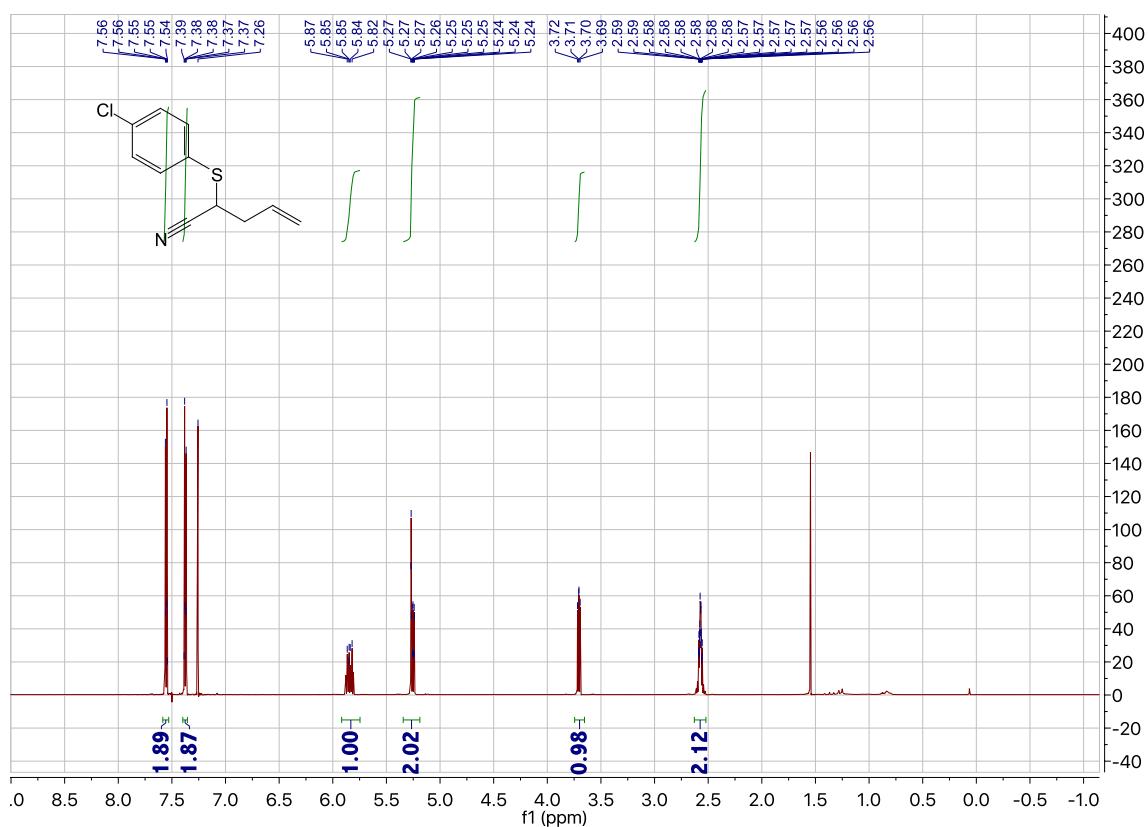
The NMR data is in accordance with the literature.<sup>[3]</sup>

## REFERENCES

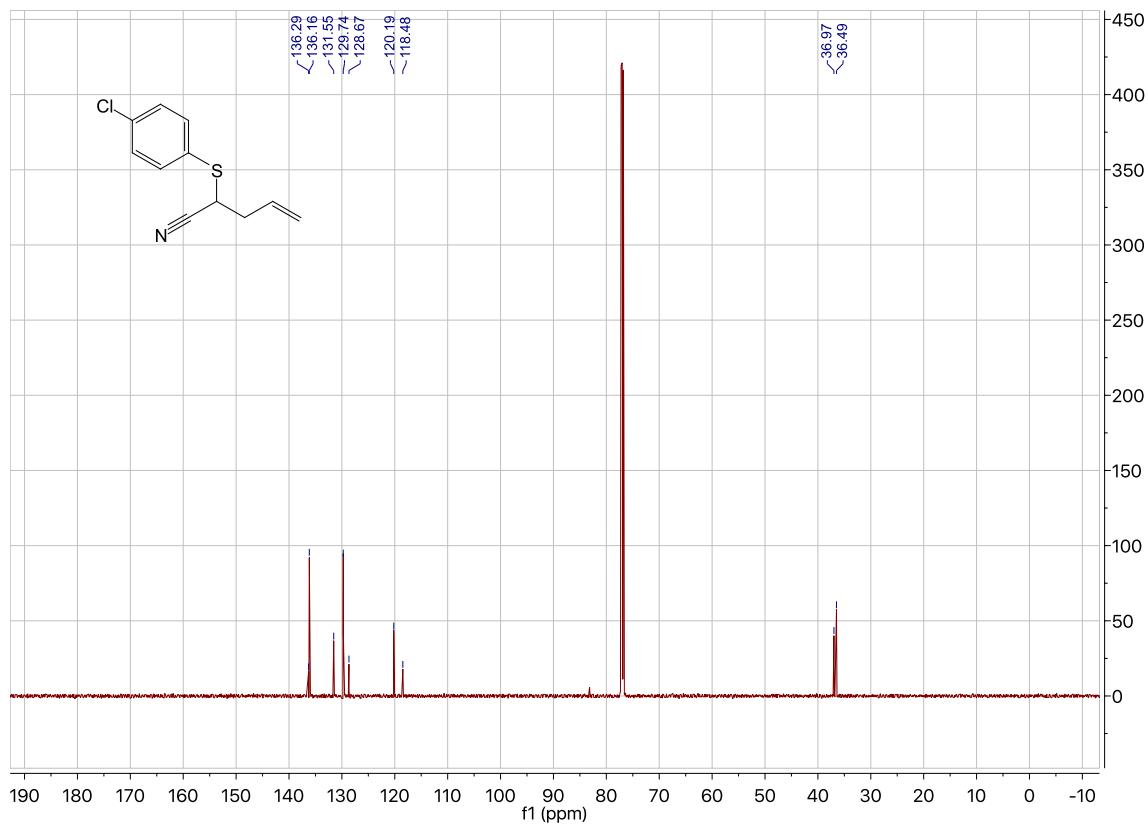
- <sup>[1]</sup> B. Binkowski, L. P. Encell, M. Hall, M. B. Robers, M. R. Slater, K. V. Wood, M. G. Wood, (Promega Corporation), 2012, WO2012061530
- <sup>[2]</sup> V. Tyagi, G. Sreenilayam, P. Bajaj, A. Tinoco, R. Fasan, *Angew. Chem. Int. Ed.*, **2016**, *55*, 13562-13566.
- <sup>[3]</sup> X. Xu, C. Li, Z. Tao, Y. Pan, *Green Chem.*, **2017**, *19*, 1245-1249.

**compound: 5a**

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

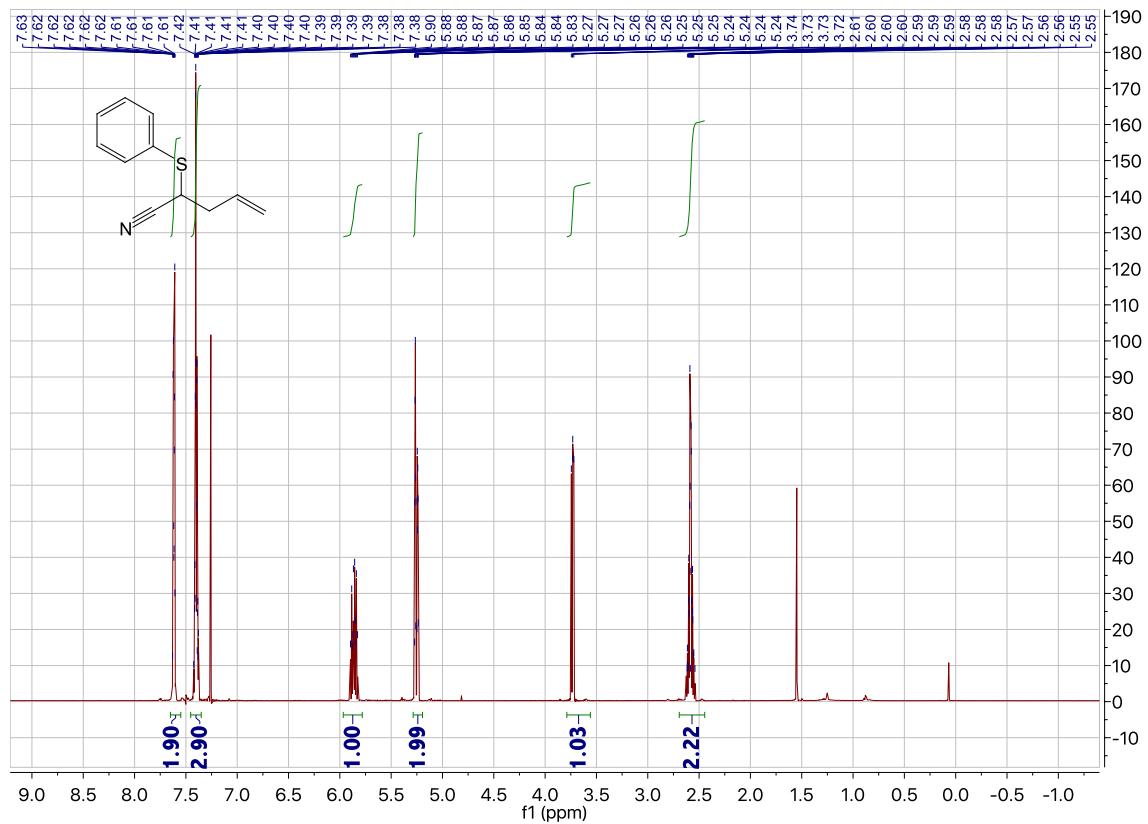


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

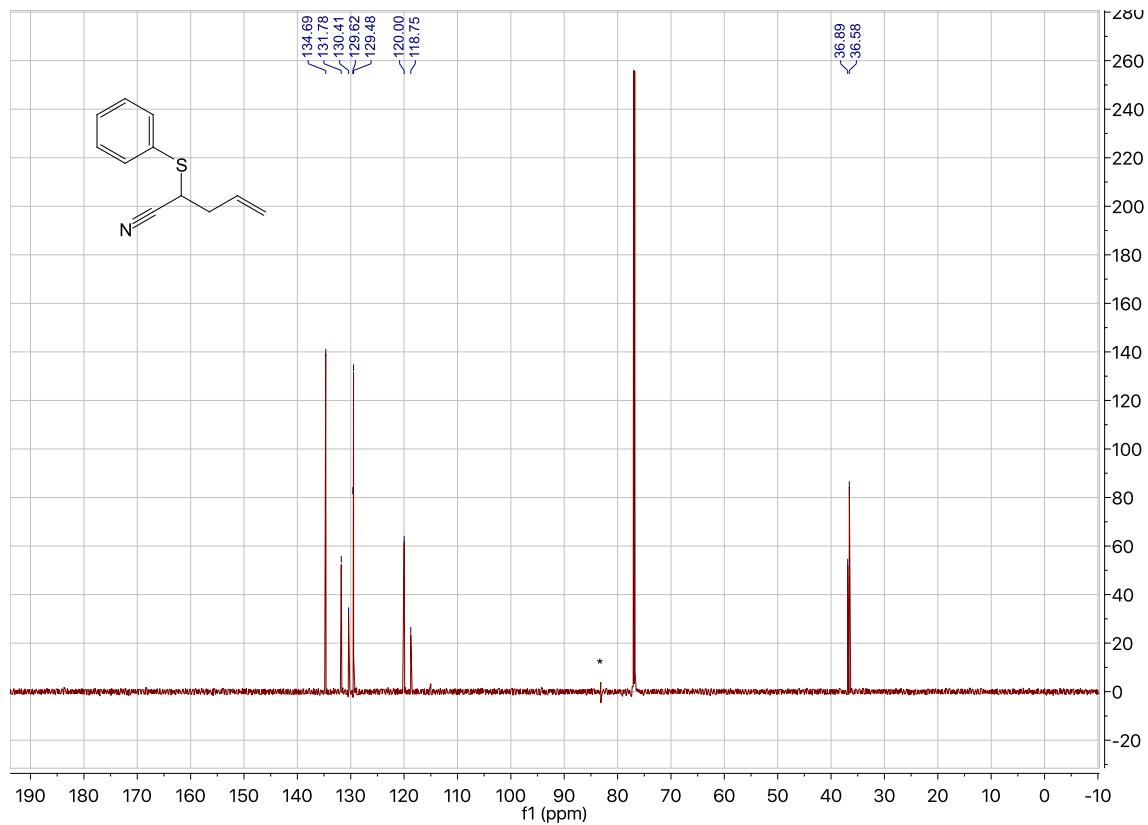


## **compound: 5b**

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

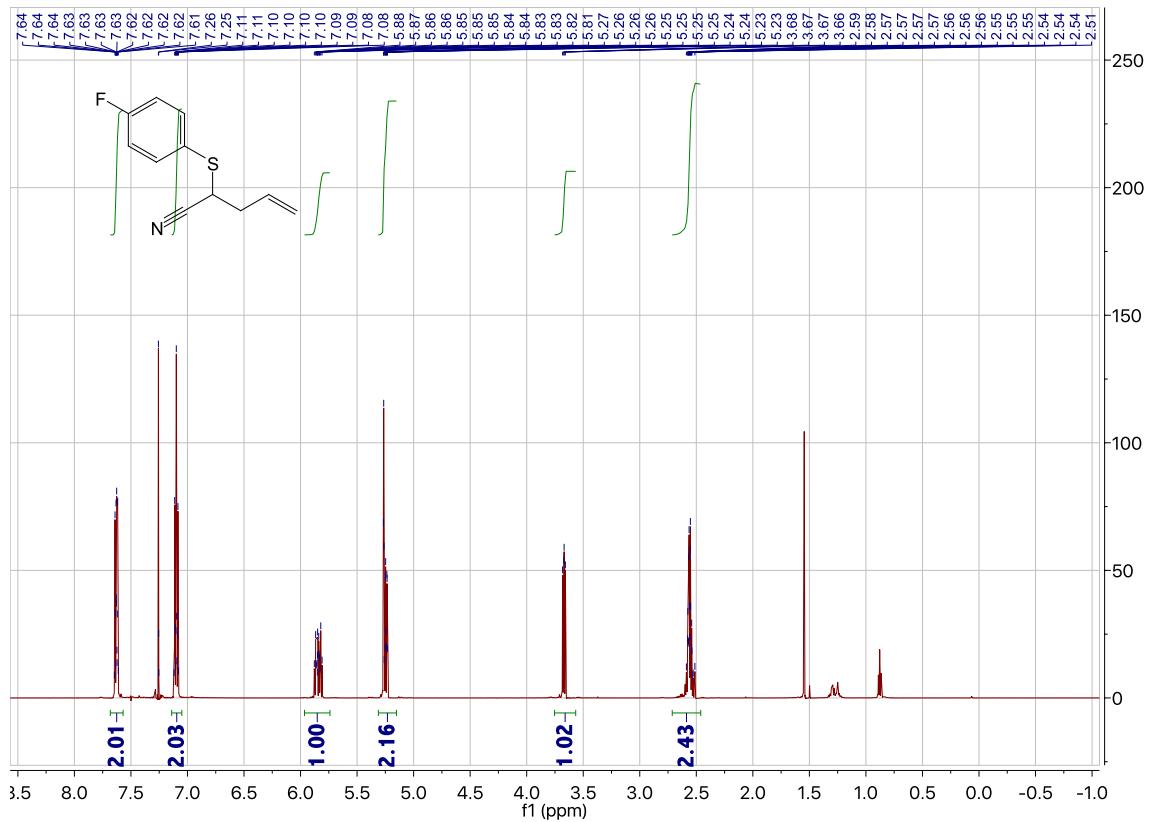


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

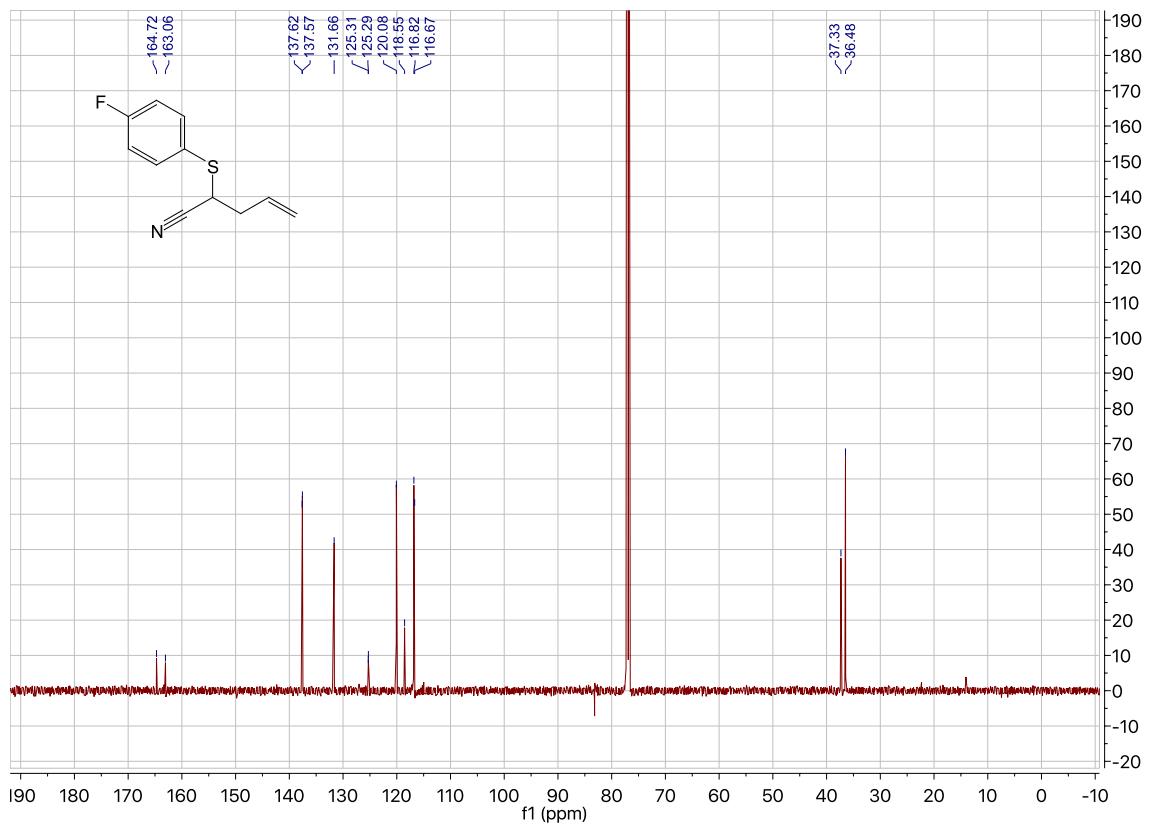


### compound: 5c

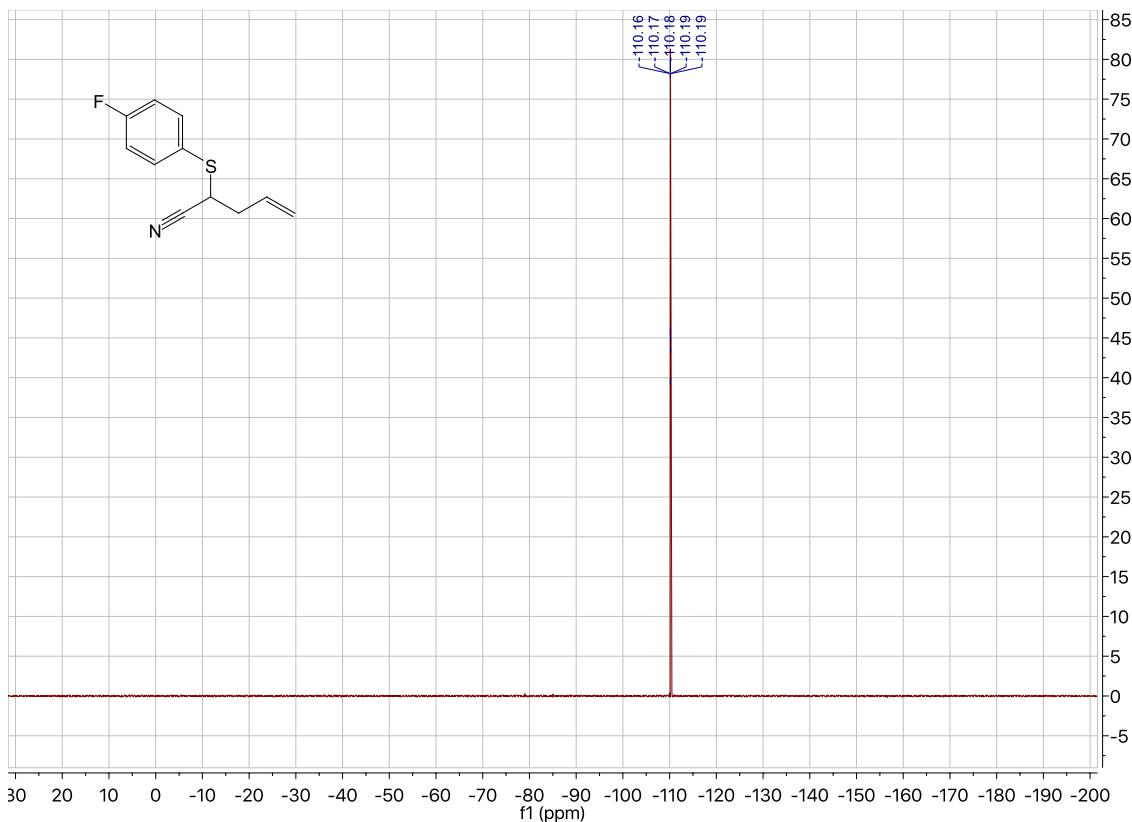
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

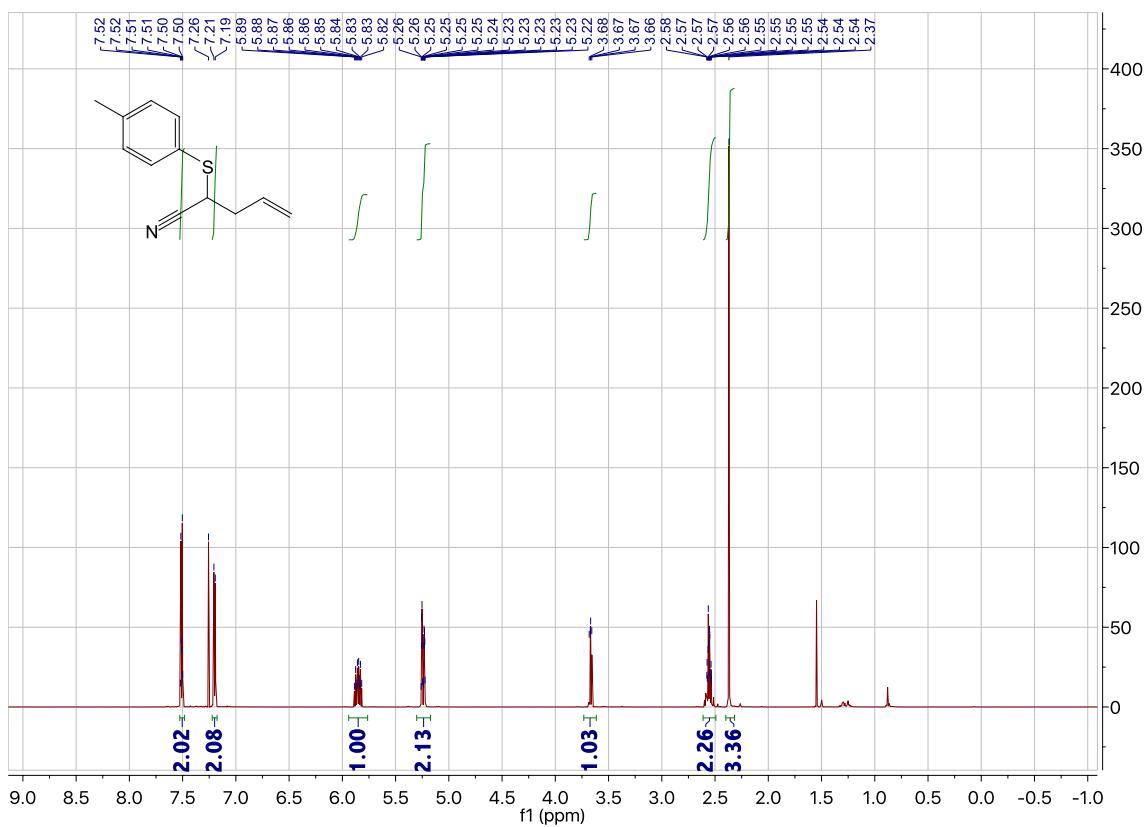


<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)

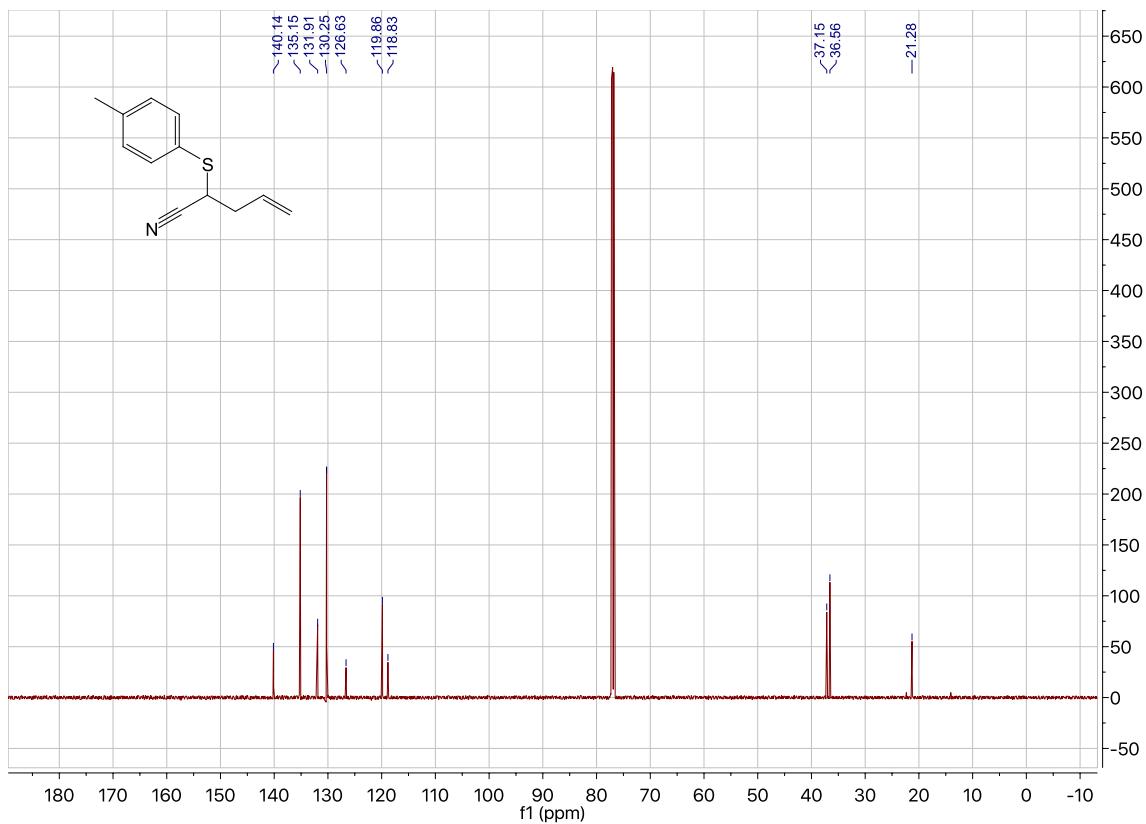


**compound: 5d**

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

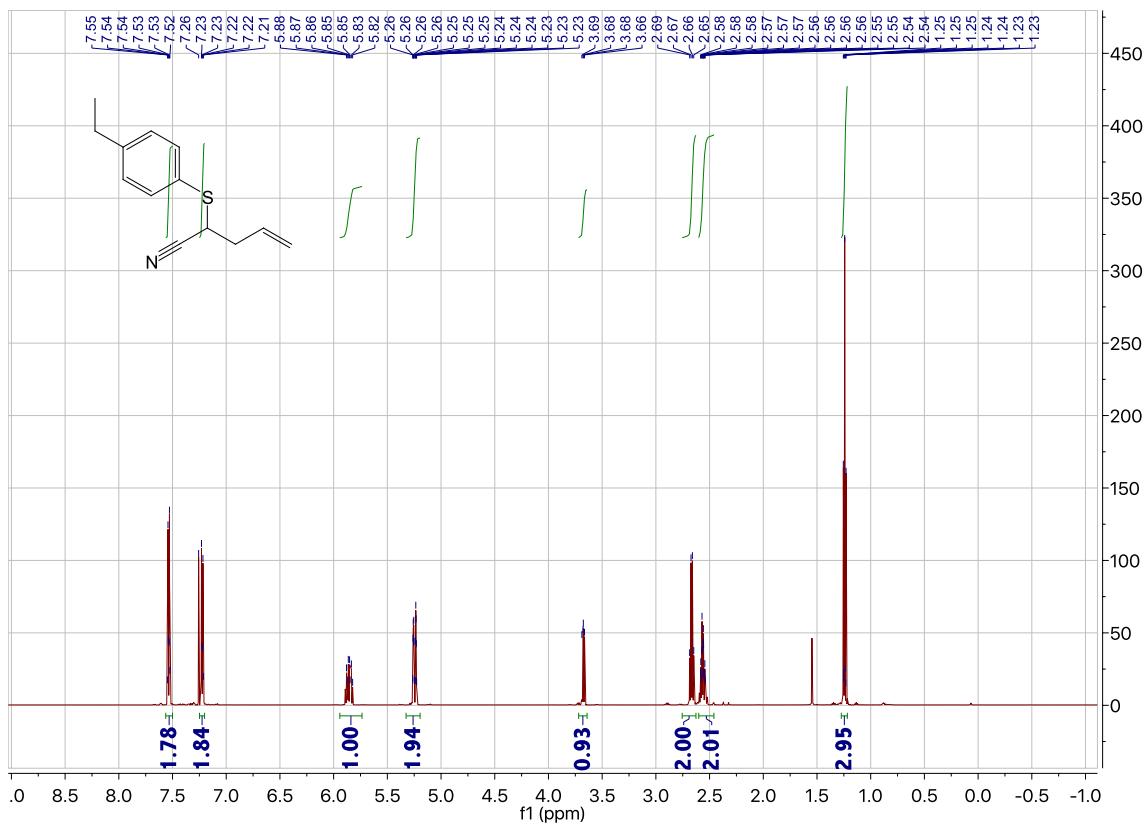


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

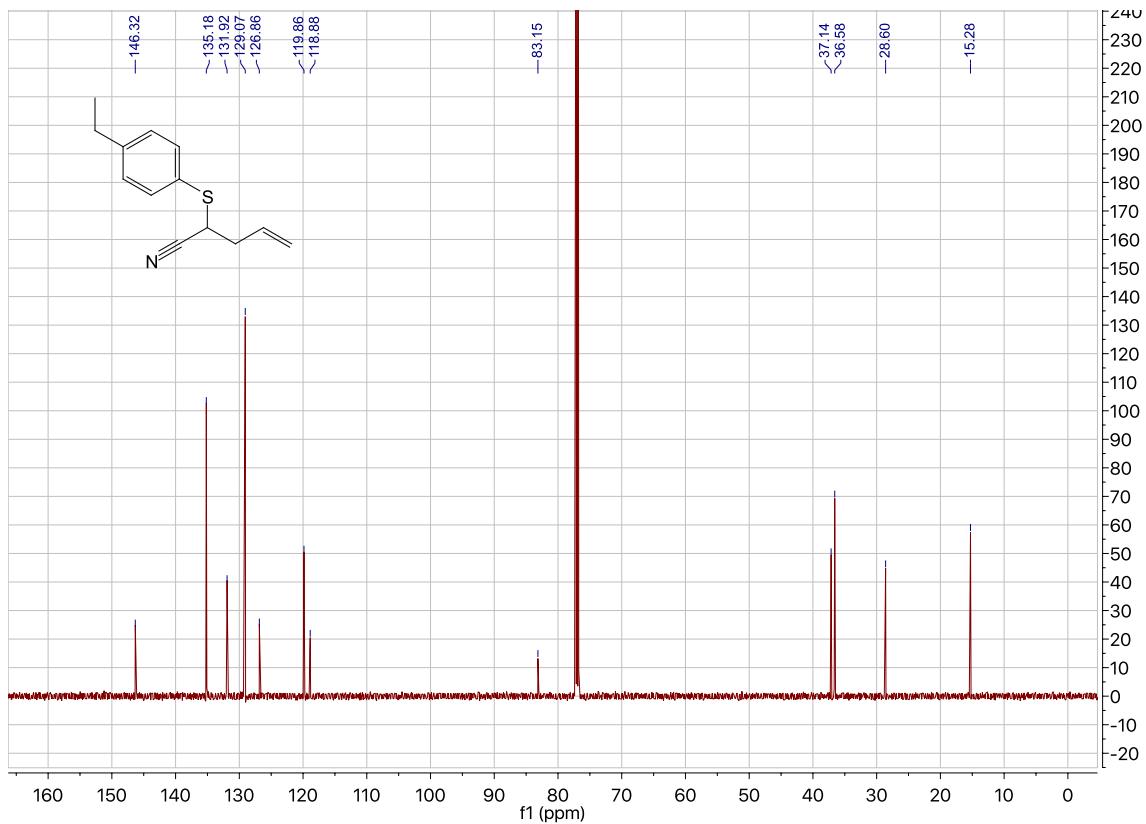


**compound: 5e**

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

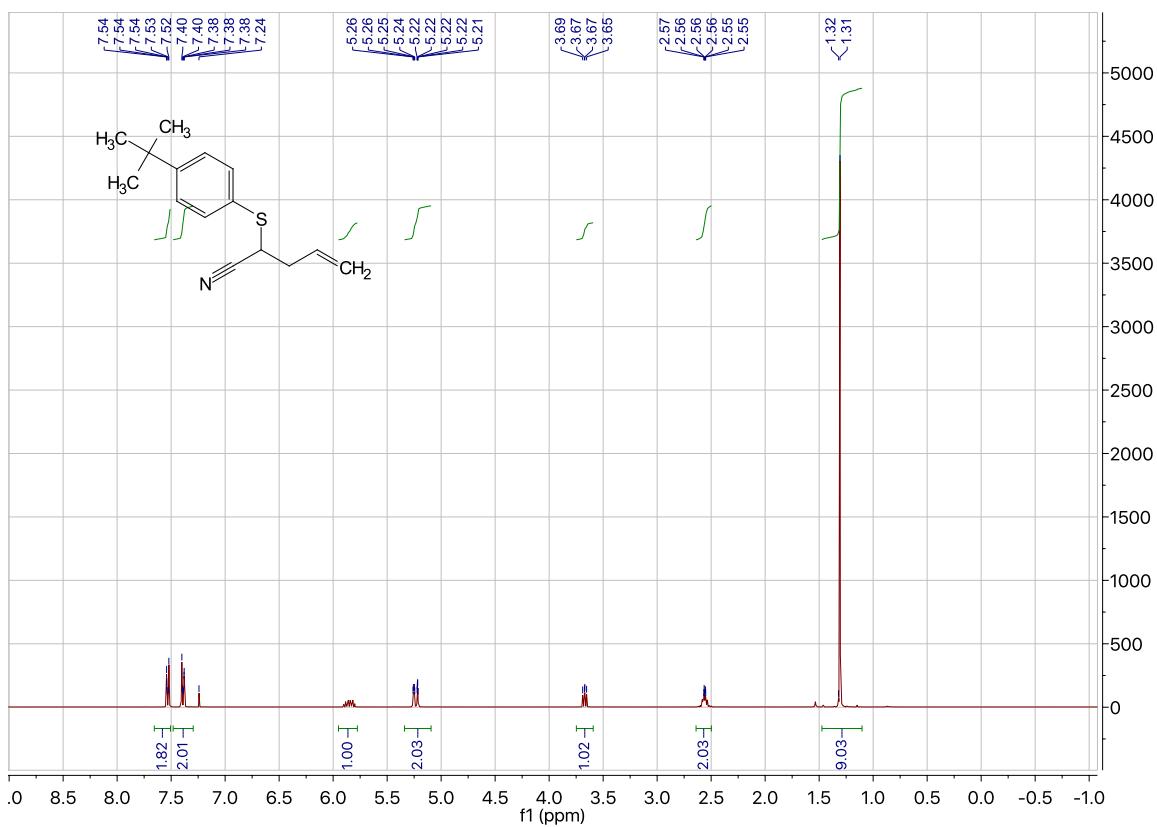


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

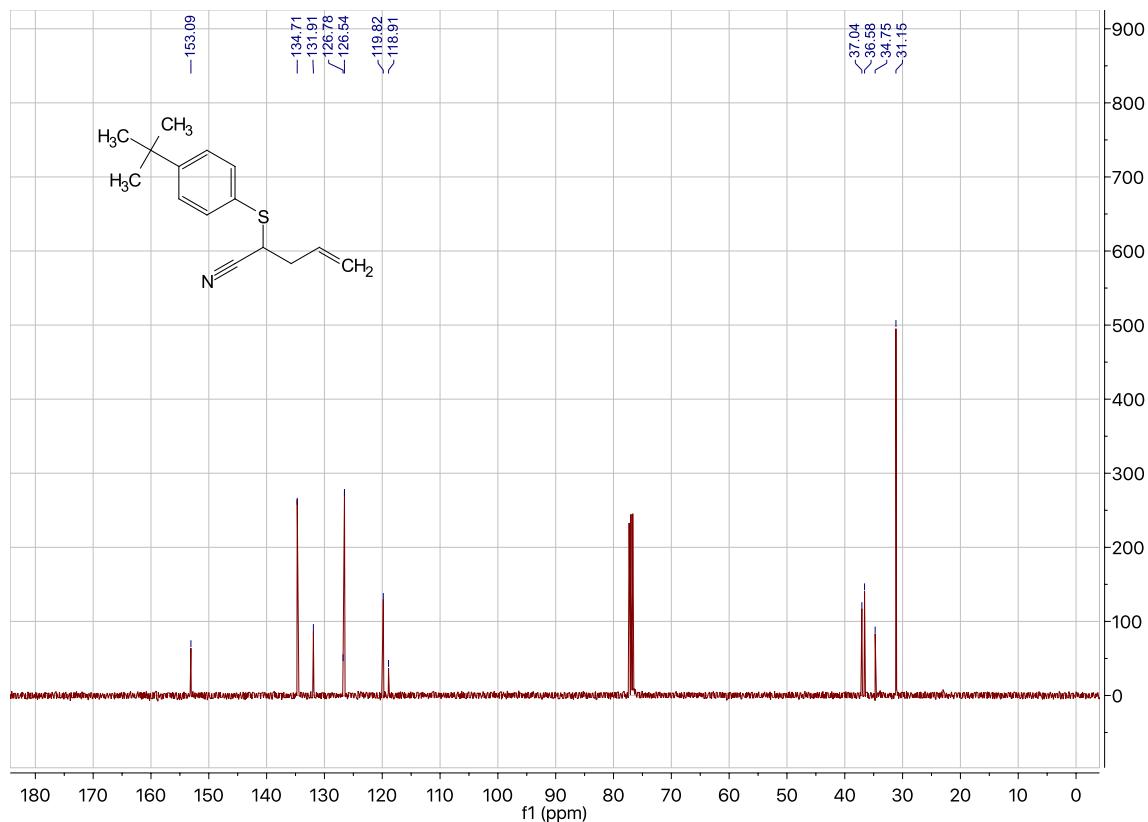


compound: 5f

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

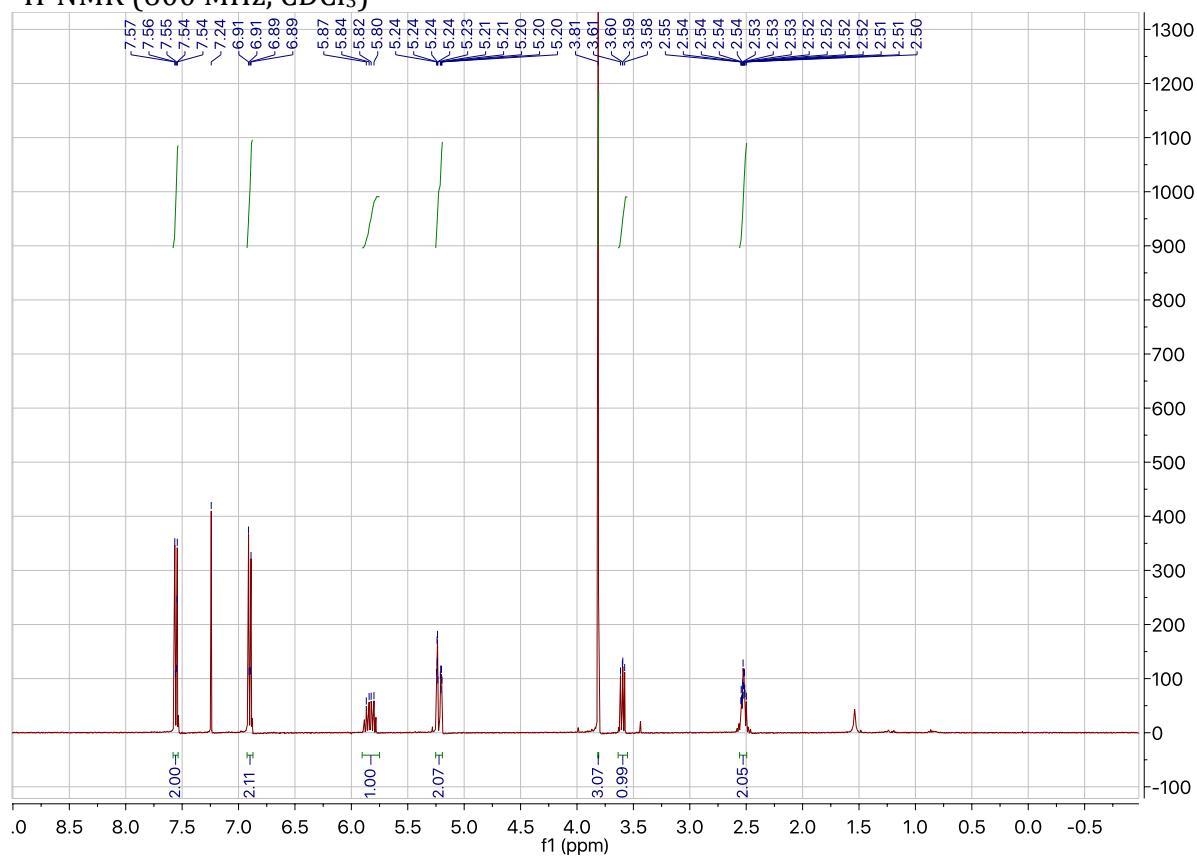


<sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>)

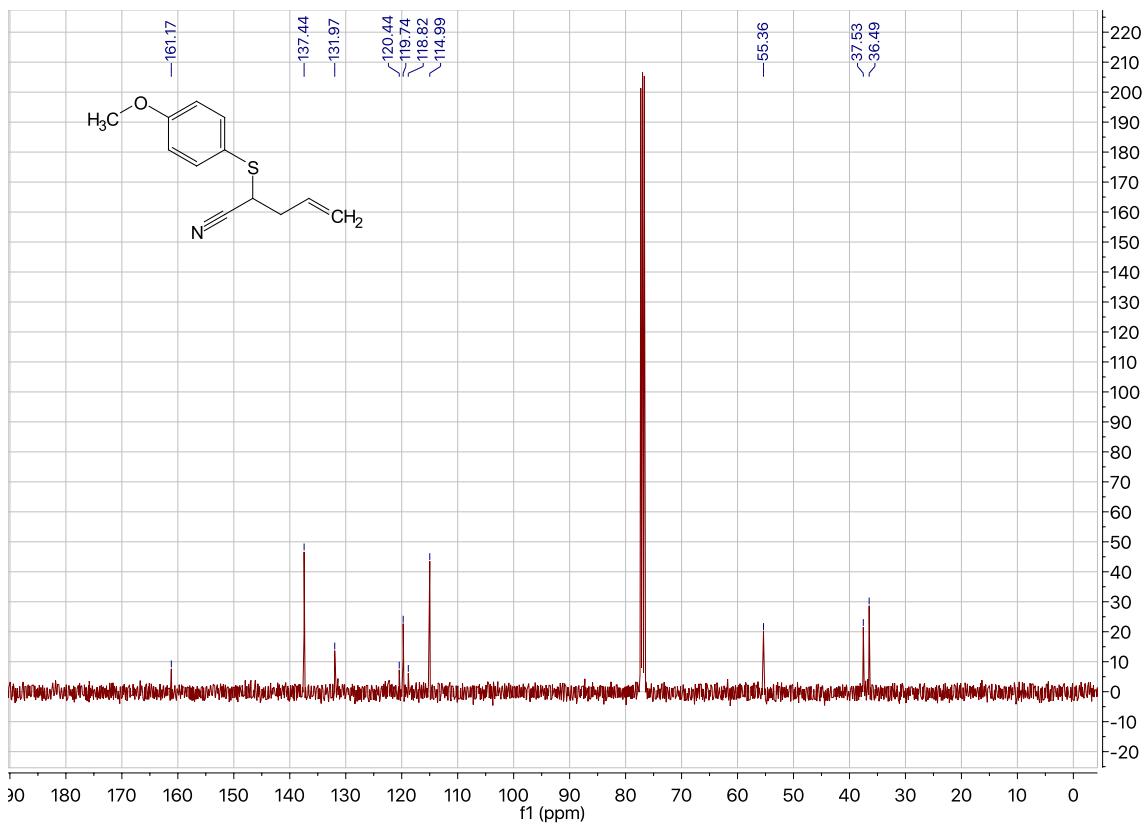


compound: 5g

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

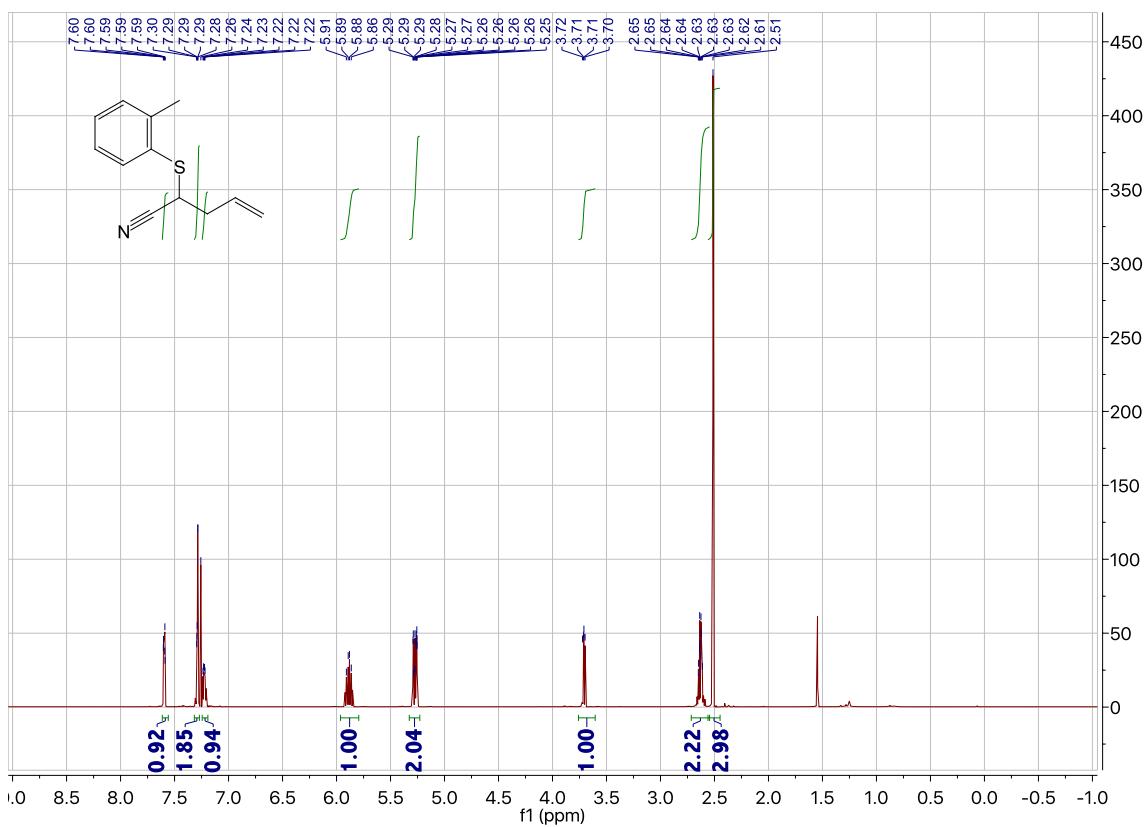


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

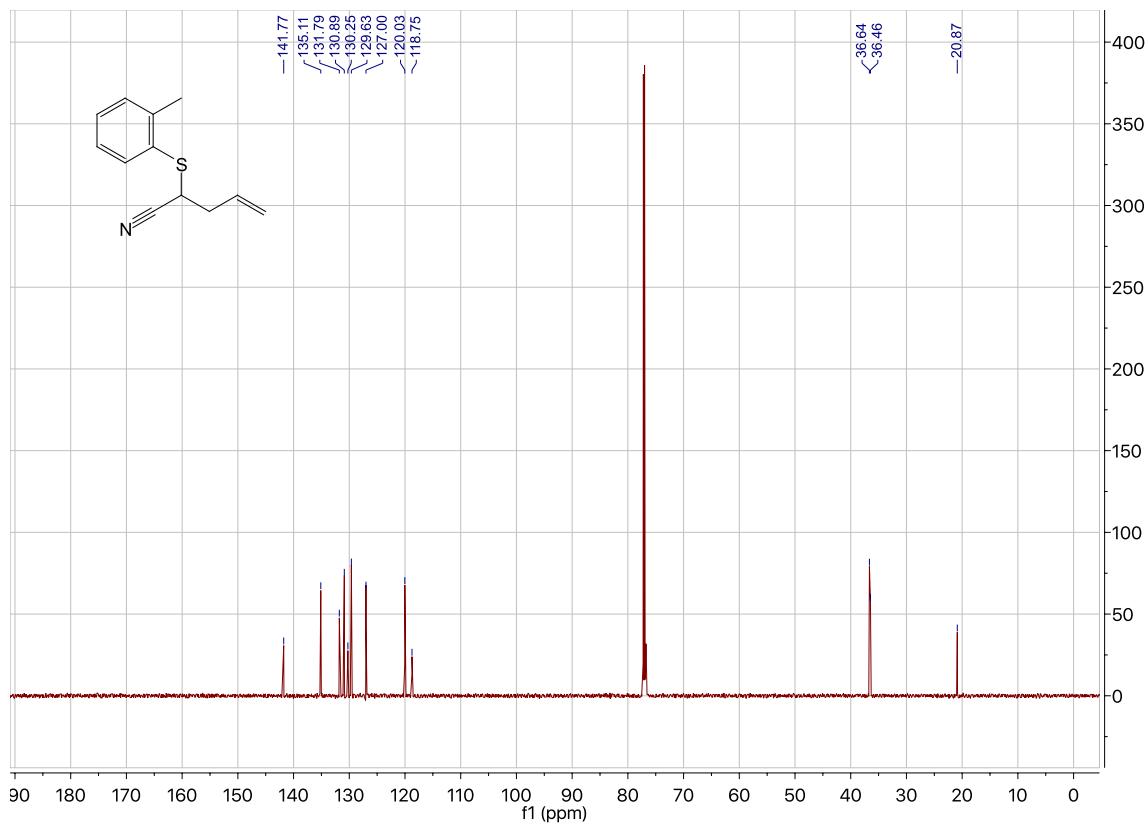


### compound: 5h

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

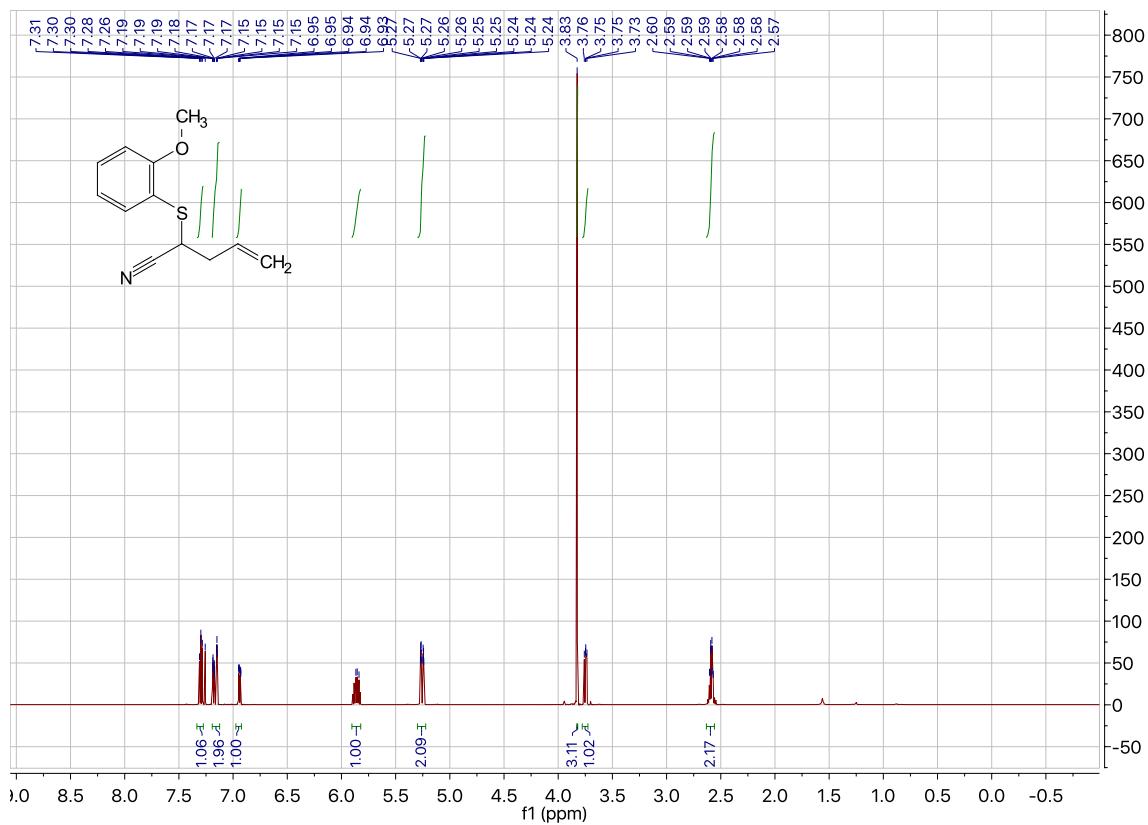


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

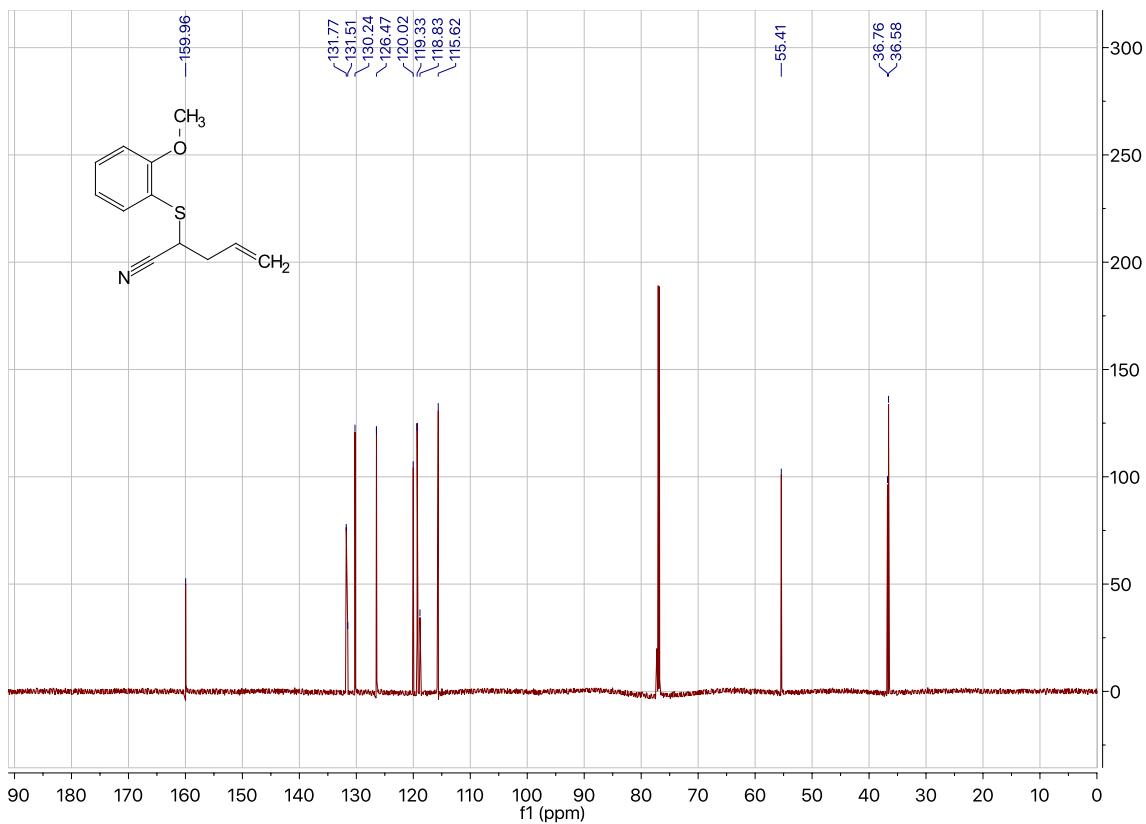


compound: 5i

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

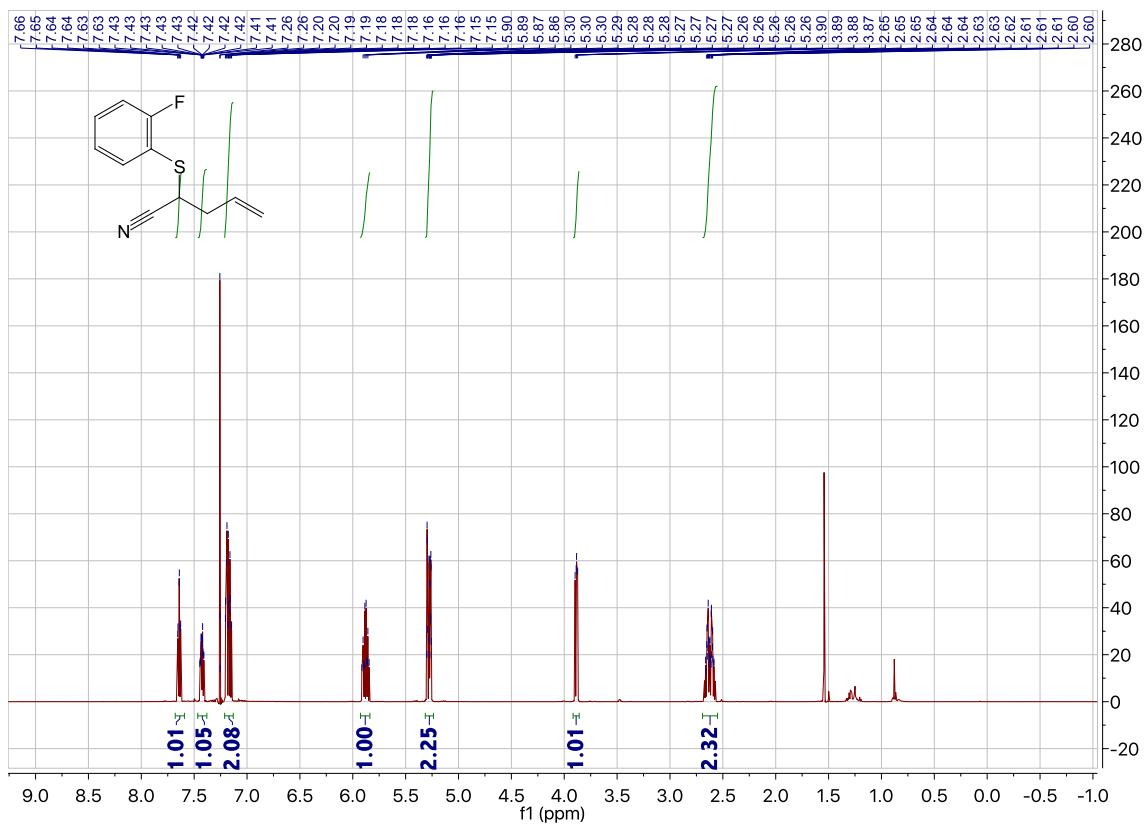


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

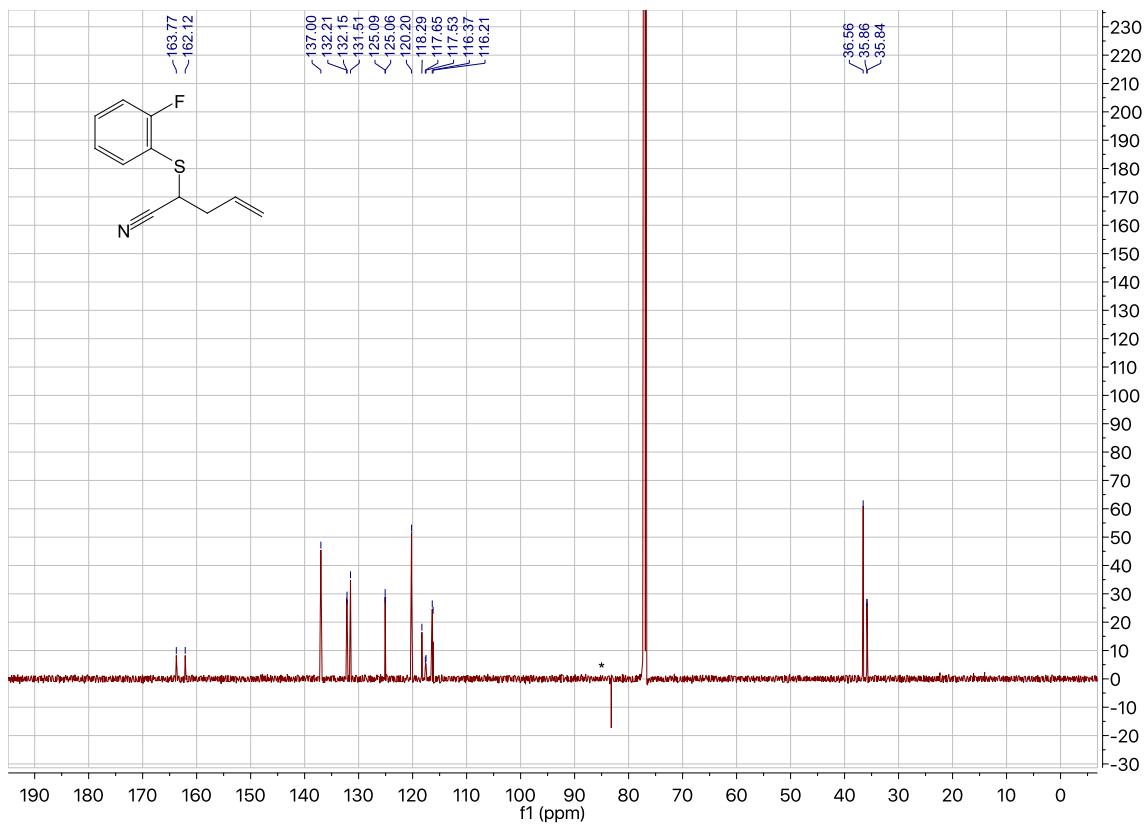


### compound: 5j

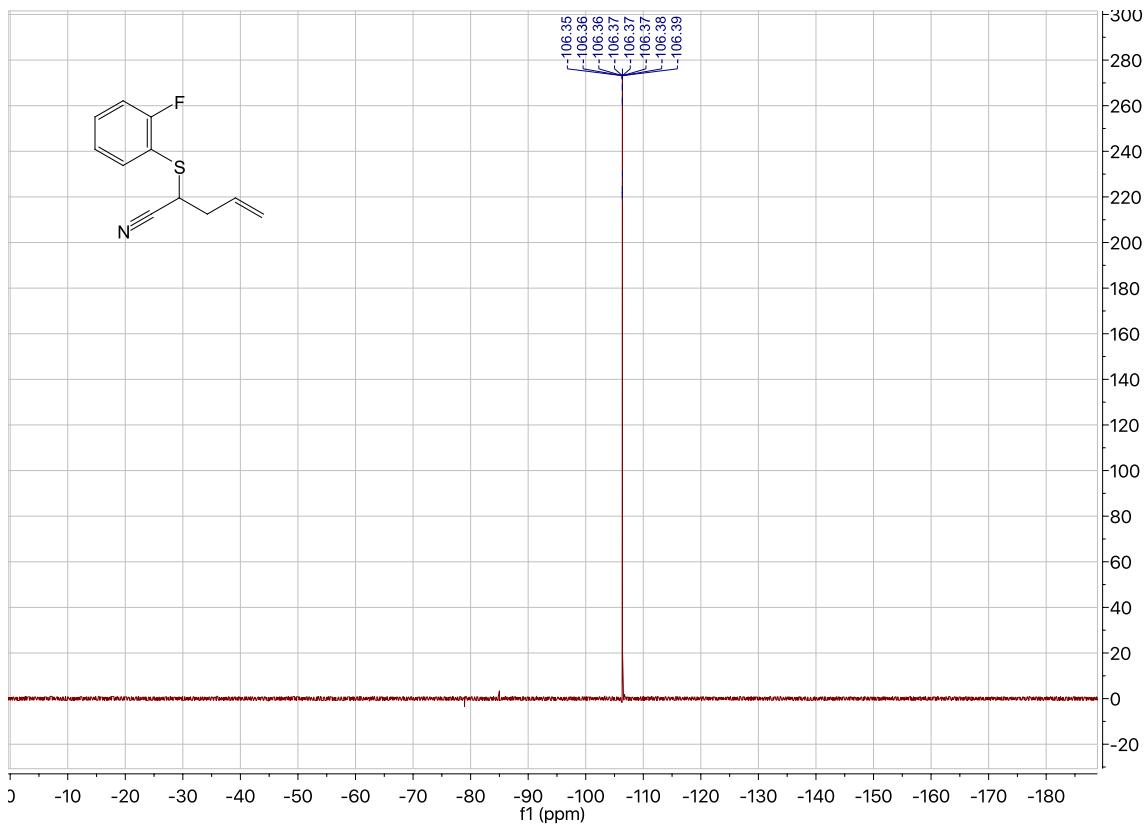
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

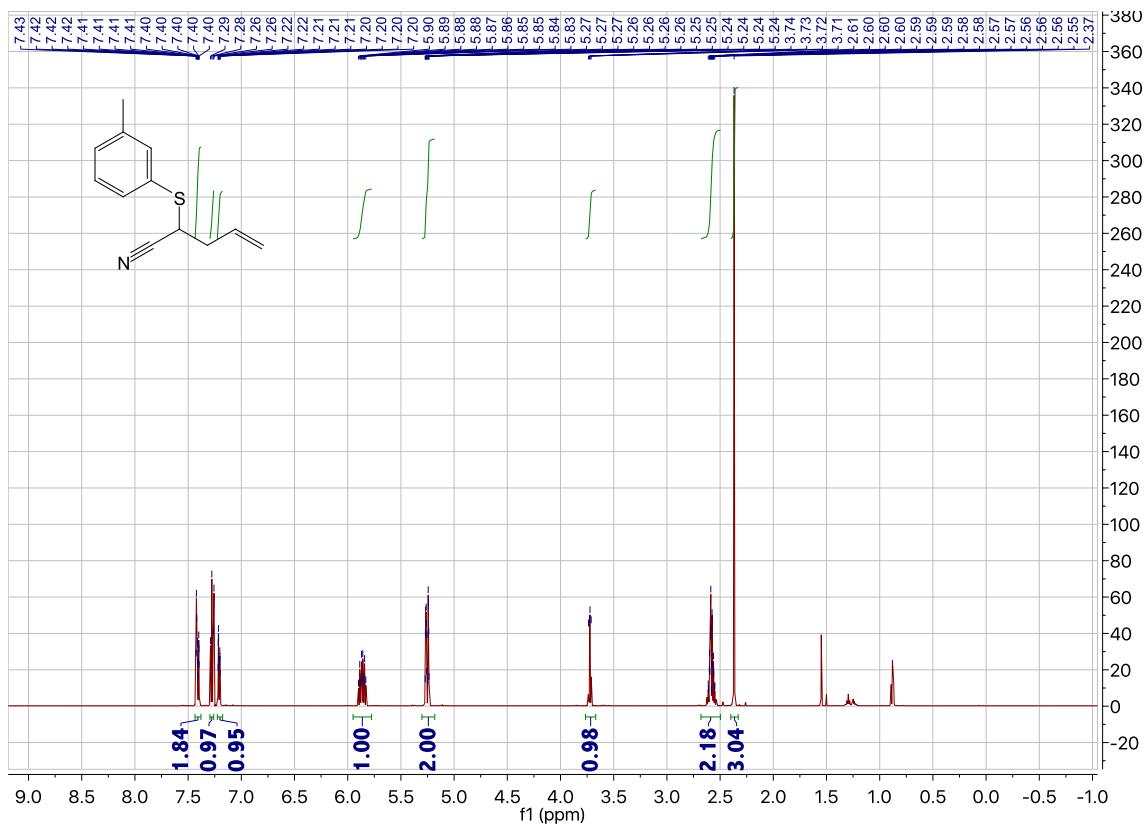


<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)

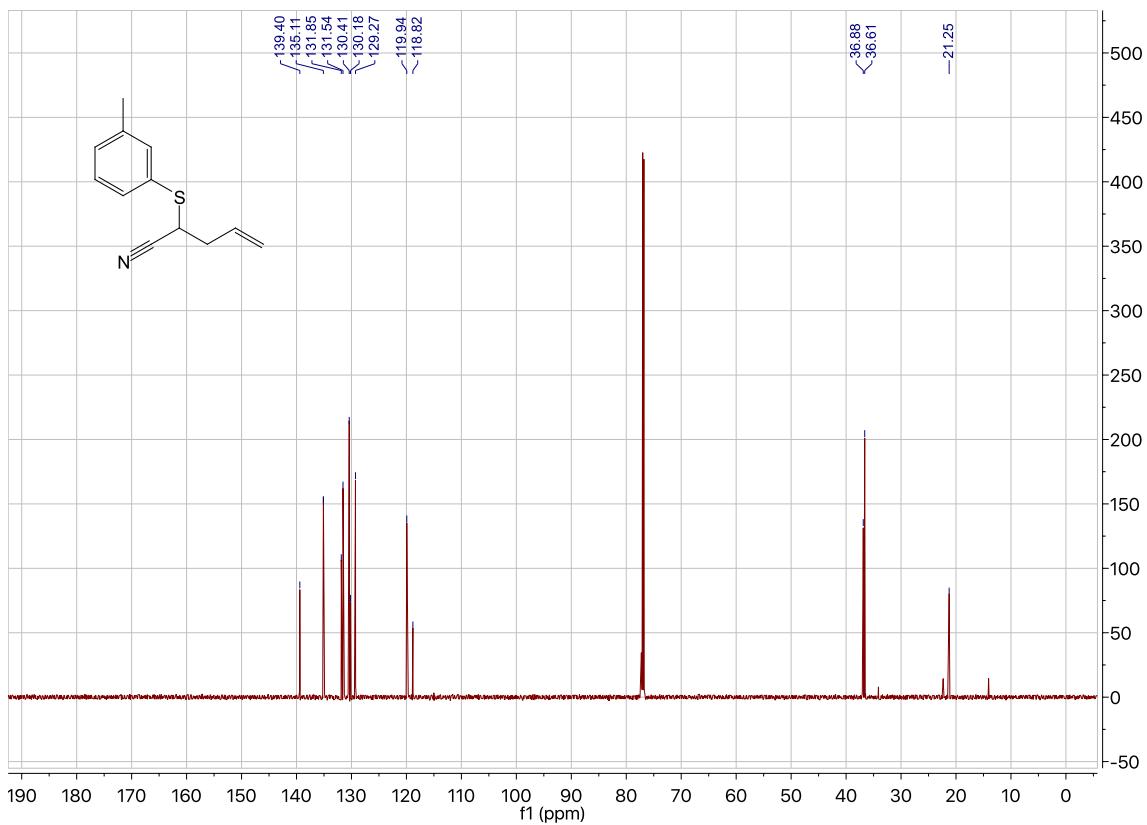


### compound: 5k

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

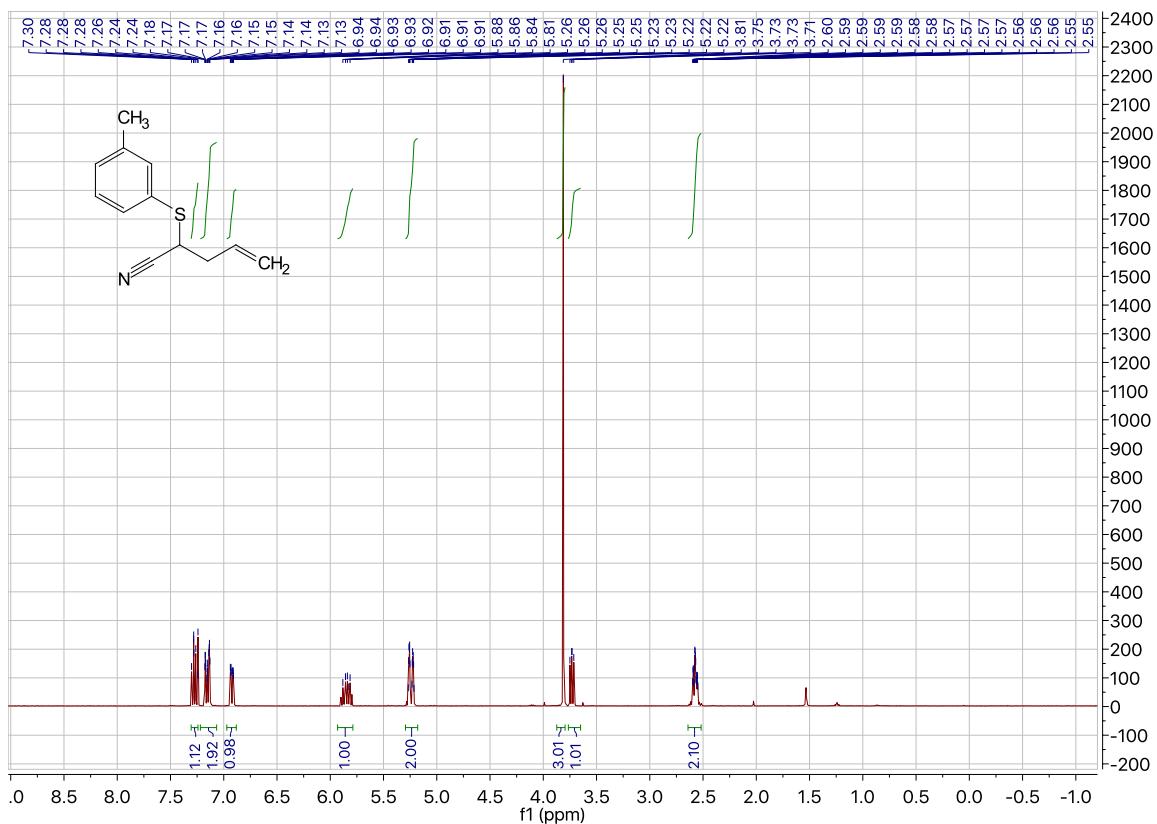


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

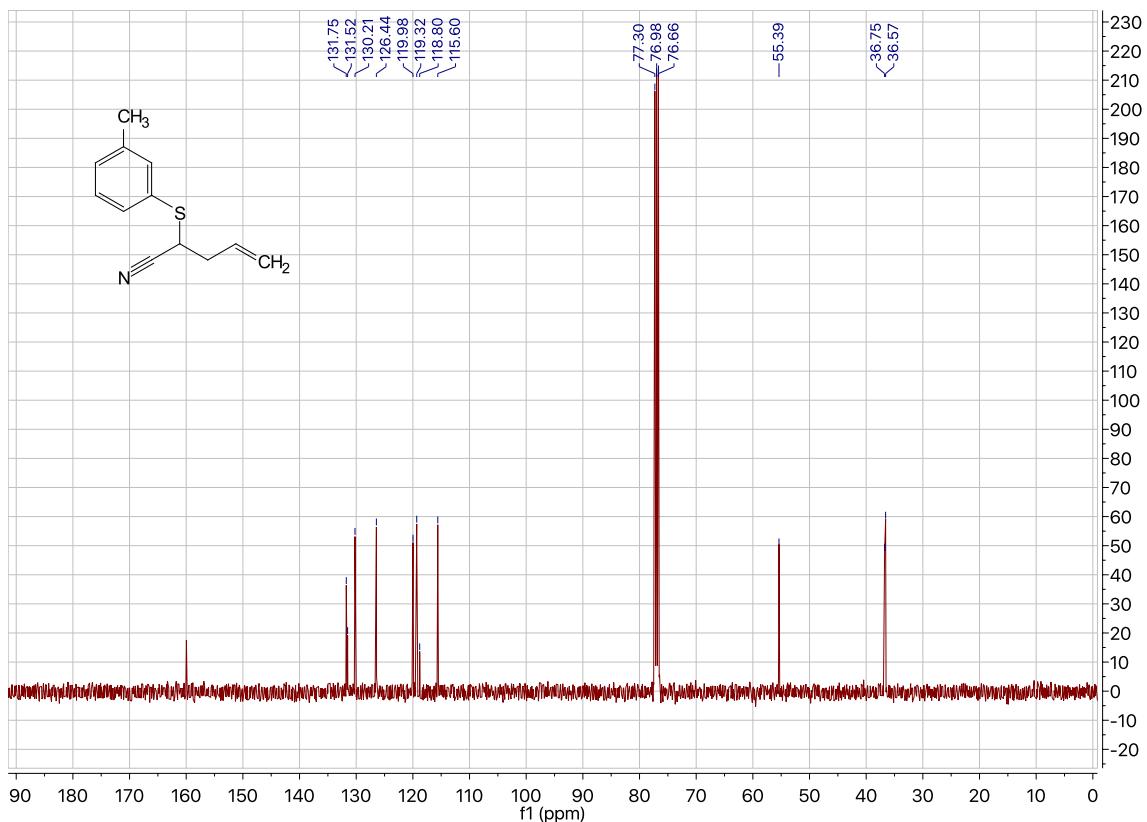


compound: 5l

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

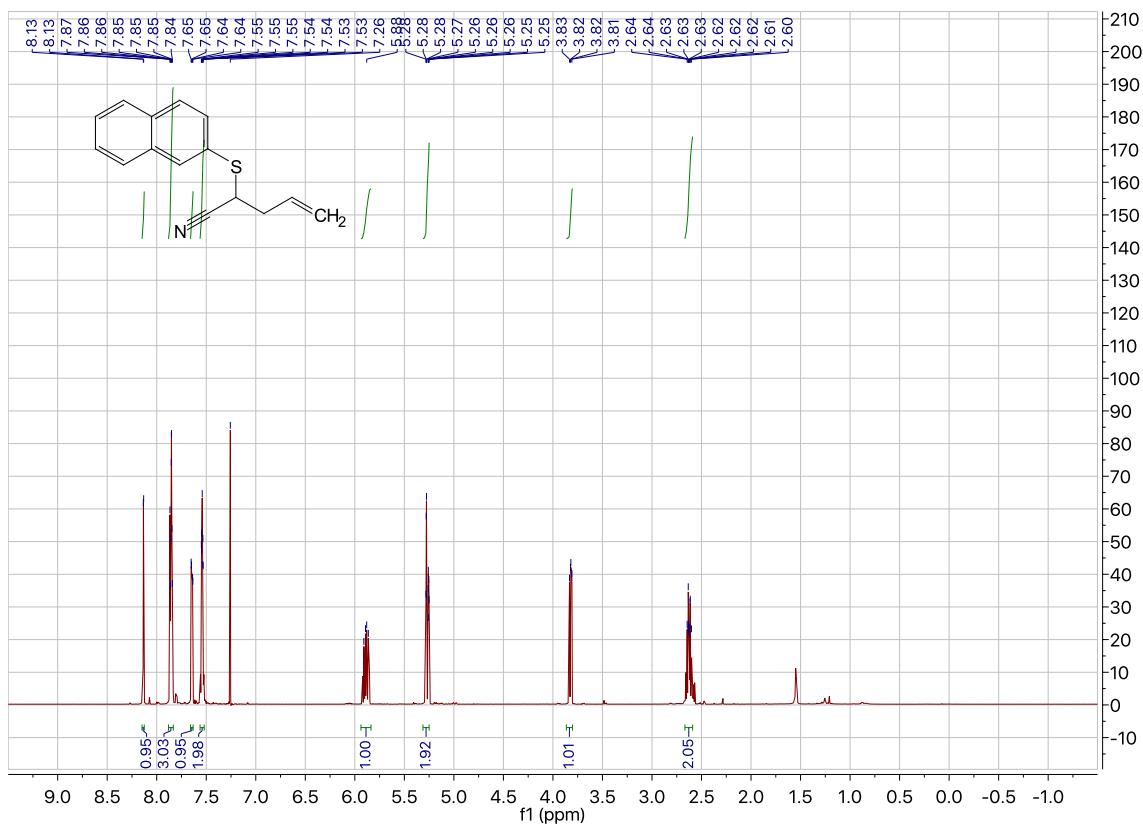


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

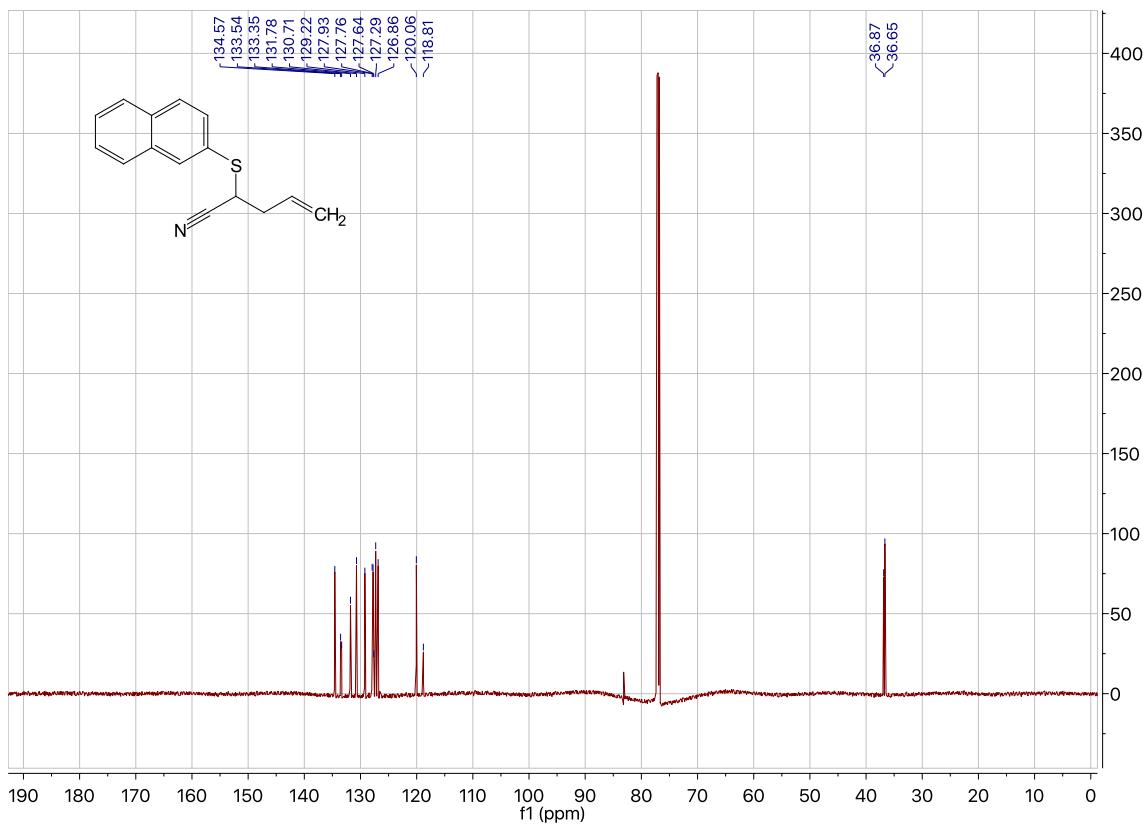


compound: **5m**

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

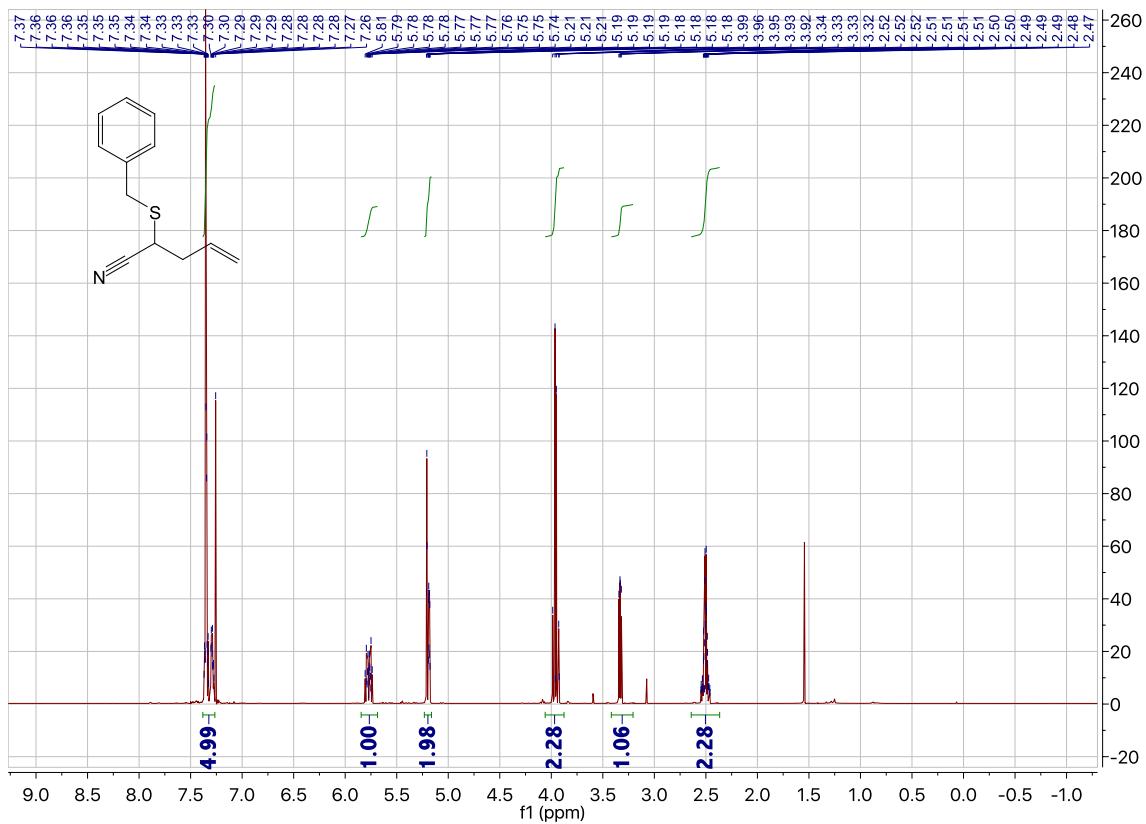


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

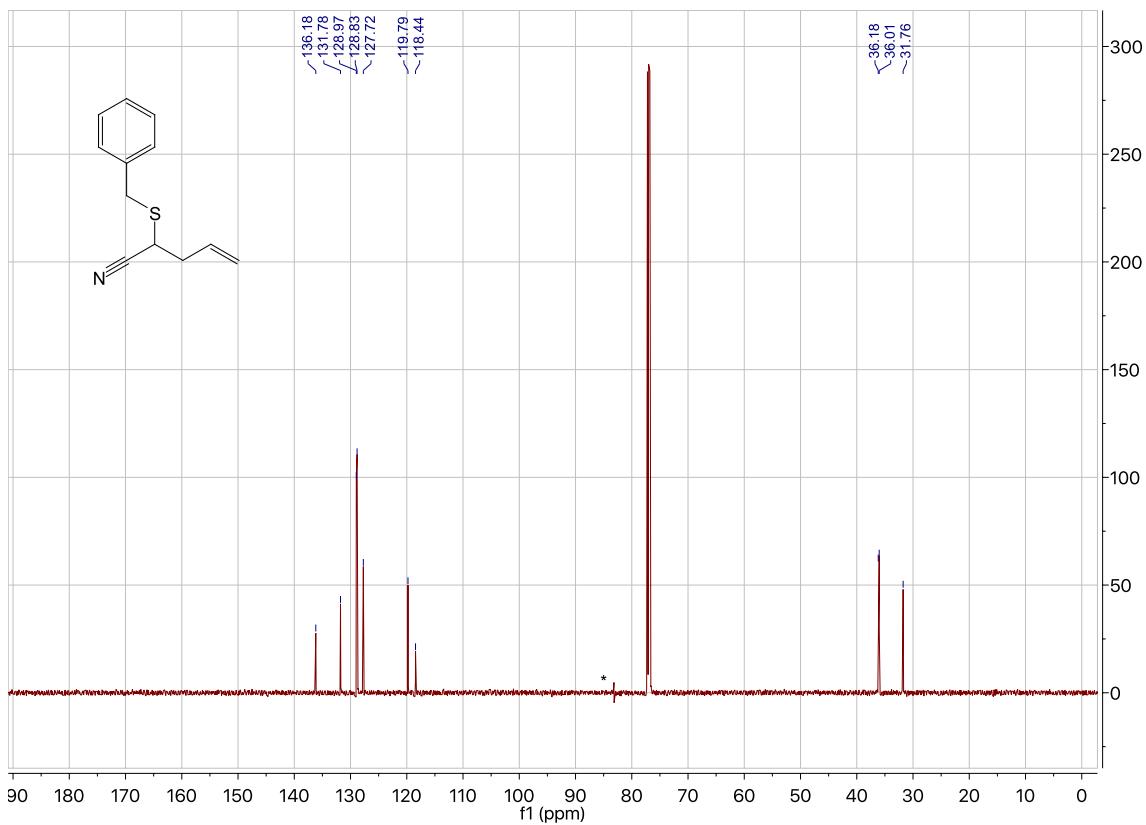


compound: **5n**

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

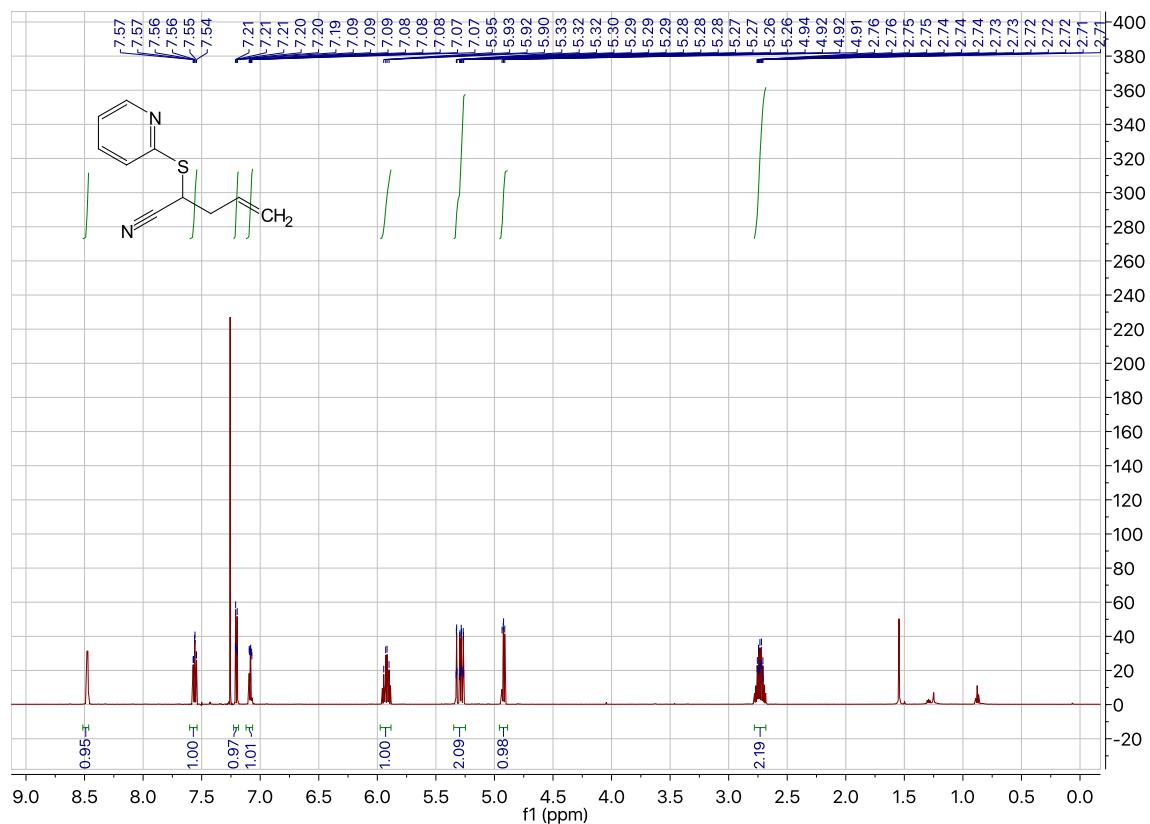


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

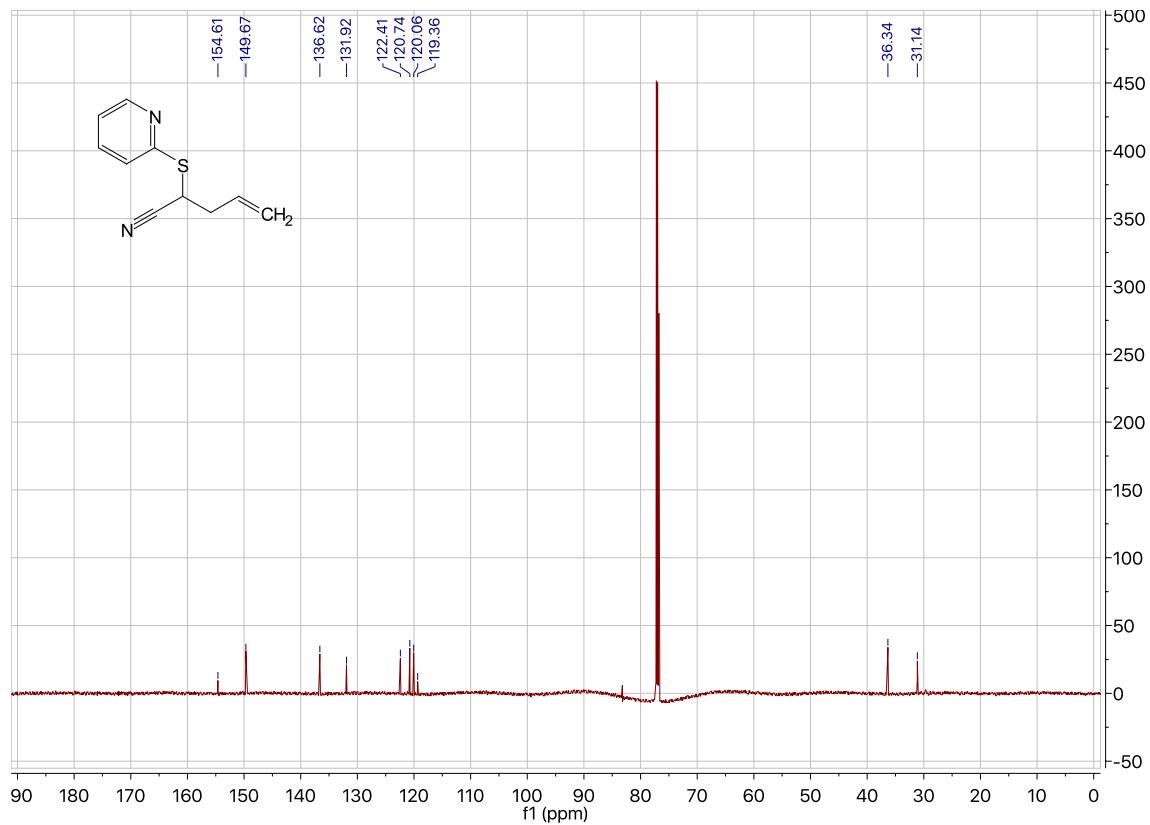


## compound: 5o

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

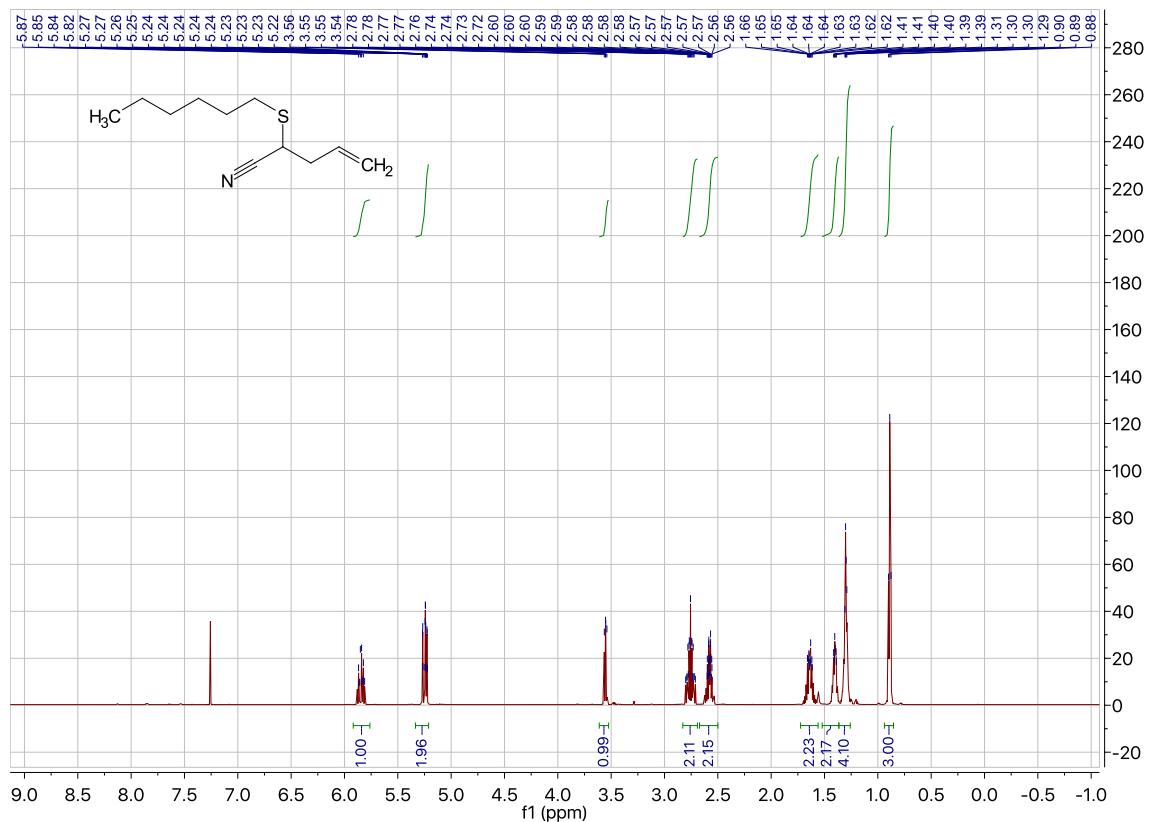


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

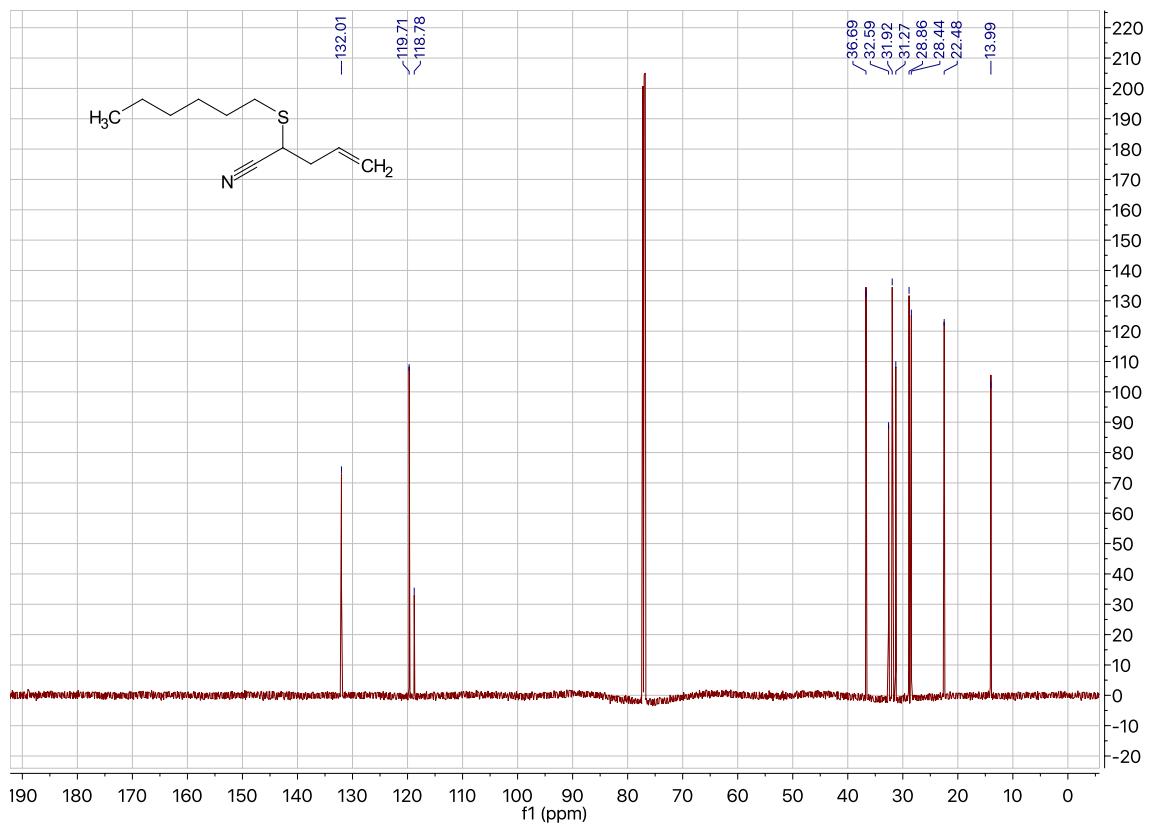


compound: 5p

$^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ )

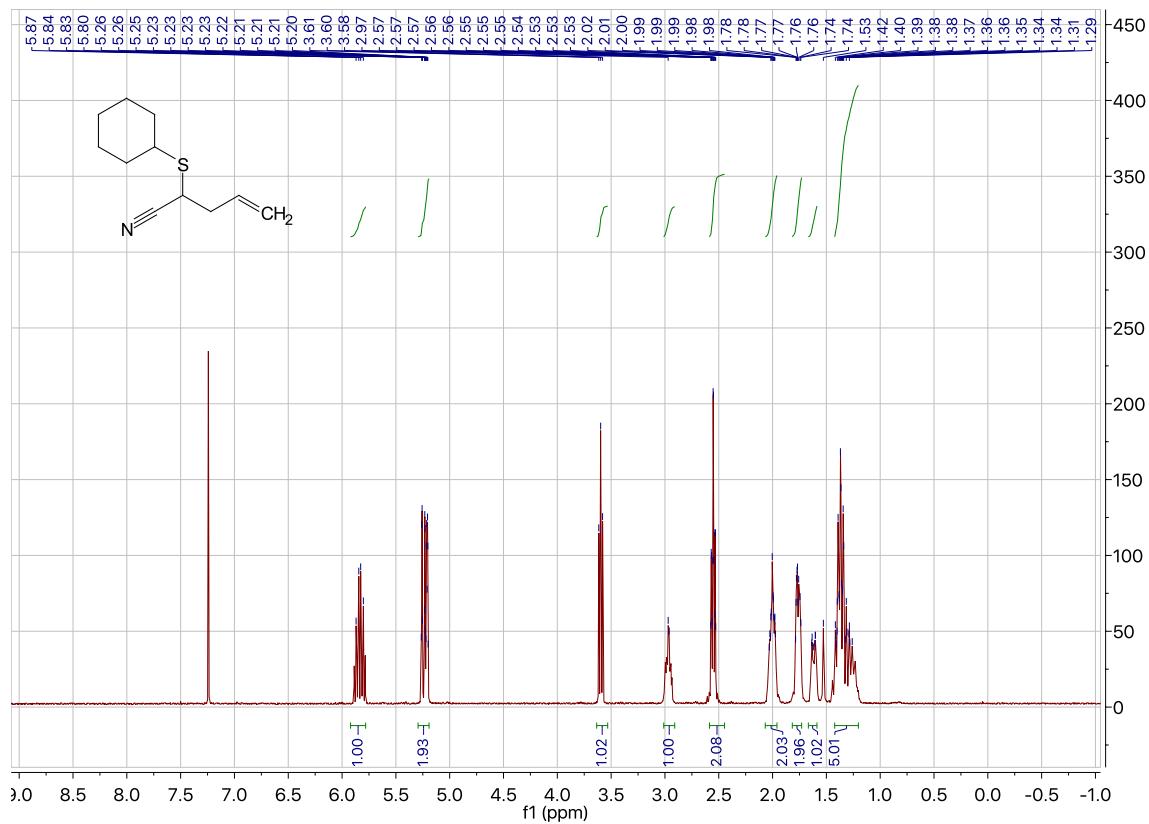


$^{13}\text{C}$ -NMR (151 MHz,  $\text{CDCl}_3$ )

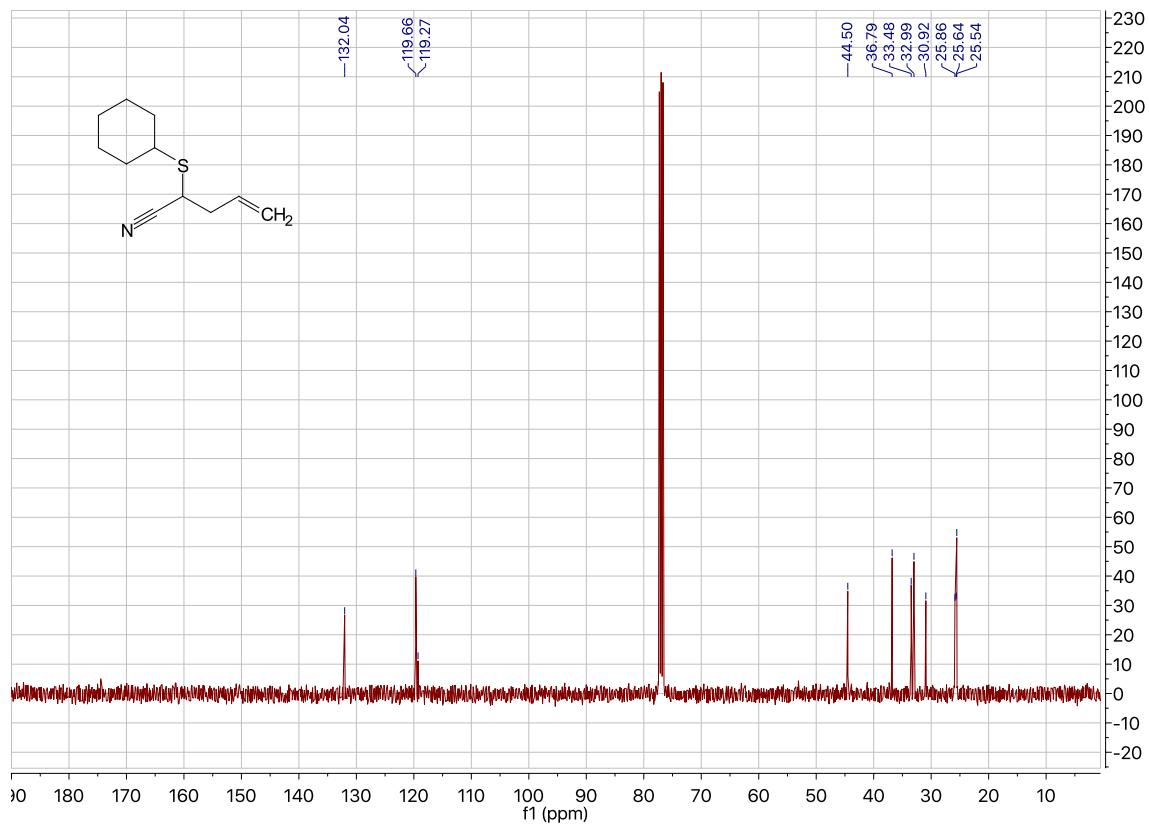


compound: 5q

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

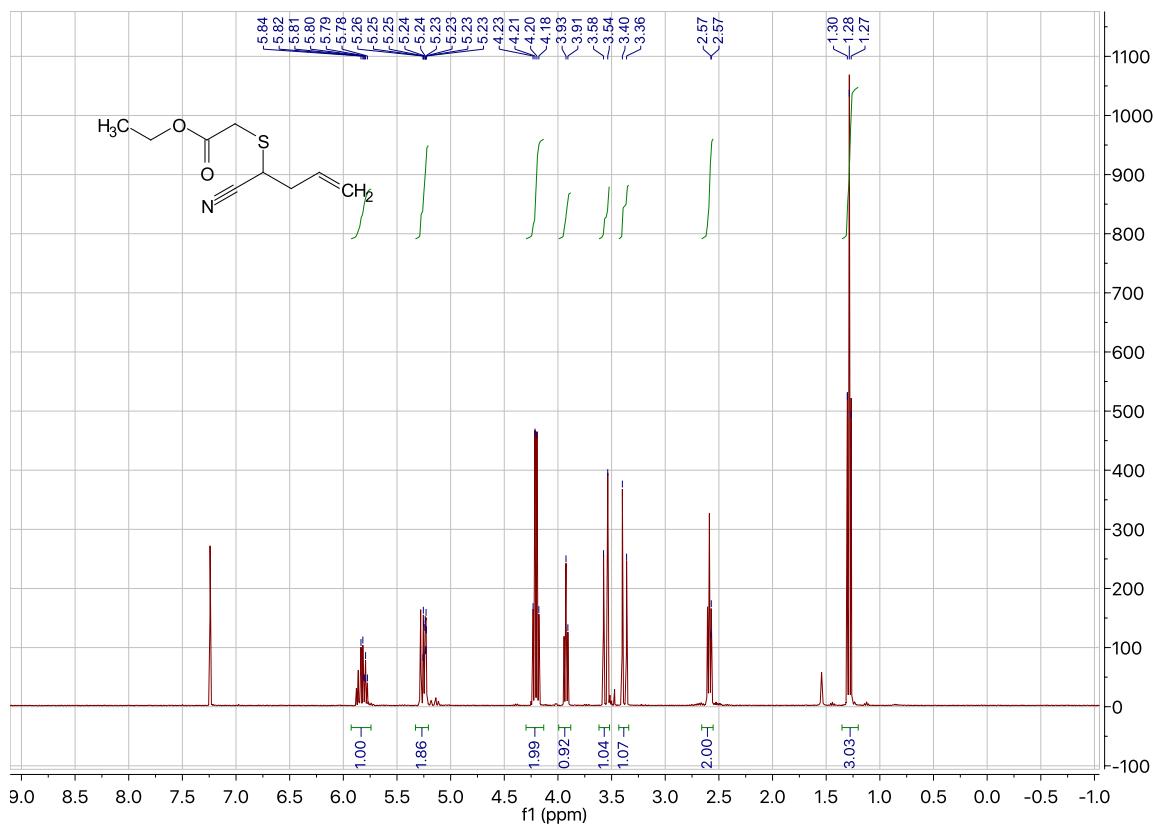


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

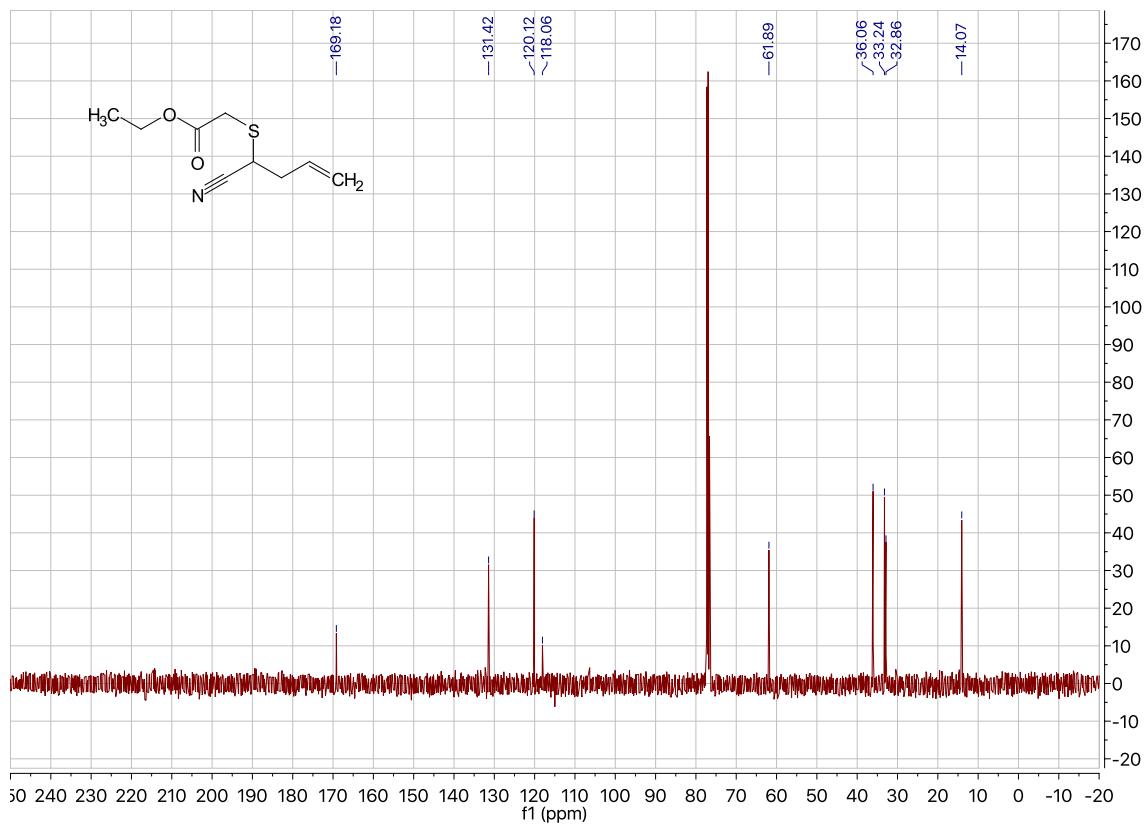


compound: 5r

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

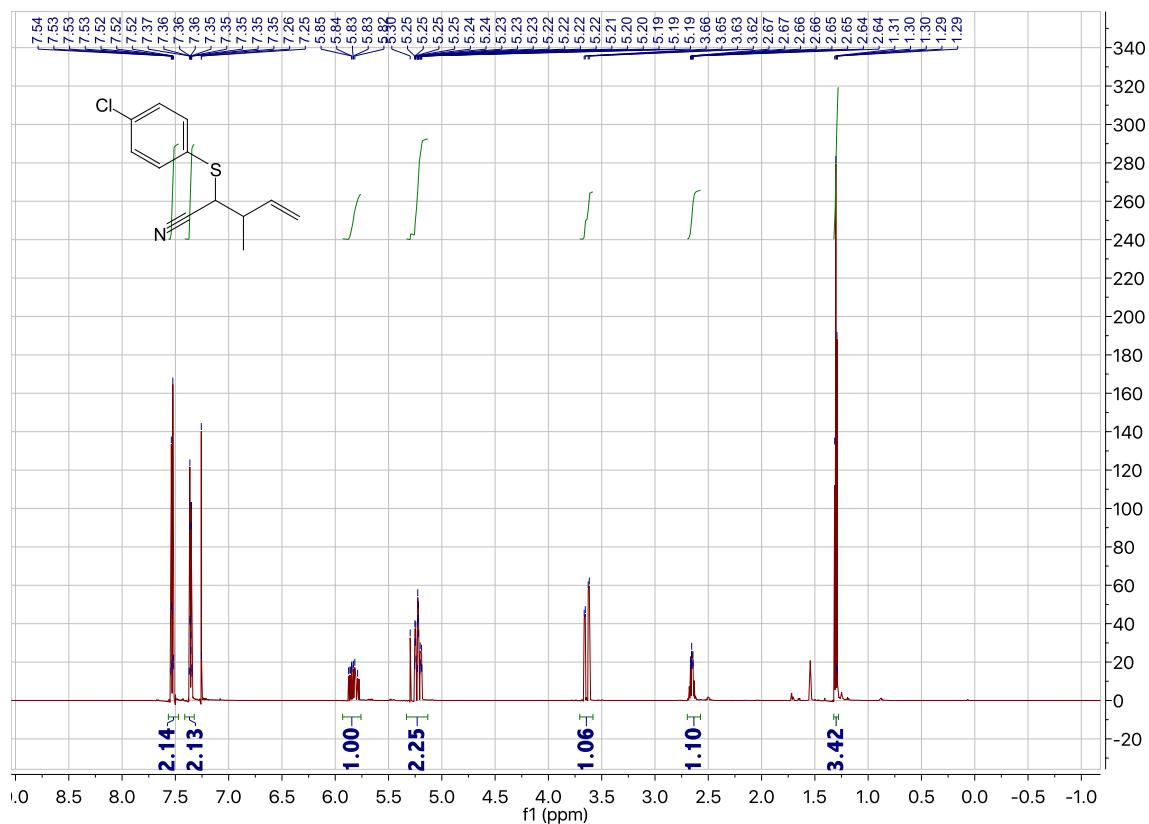


<sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>)

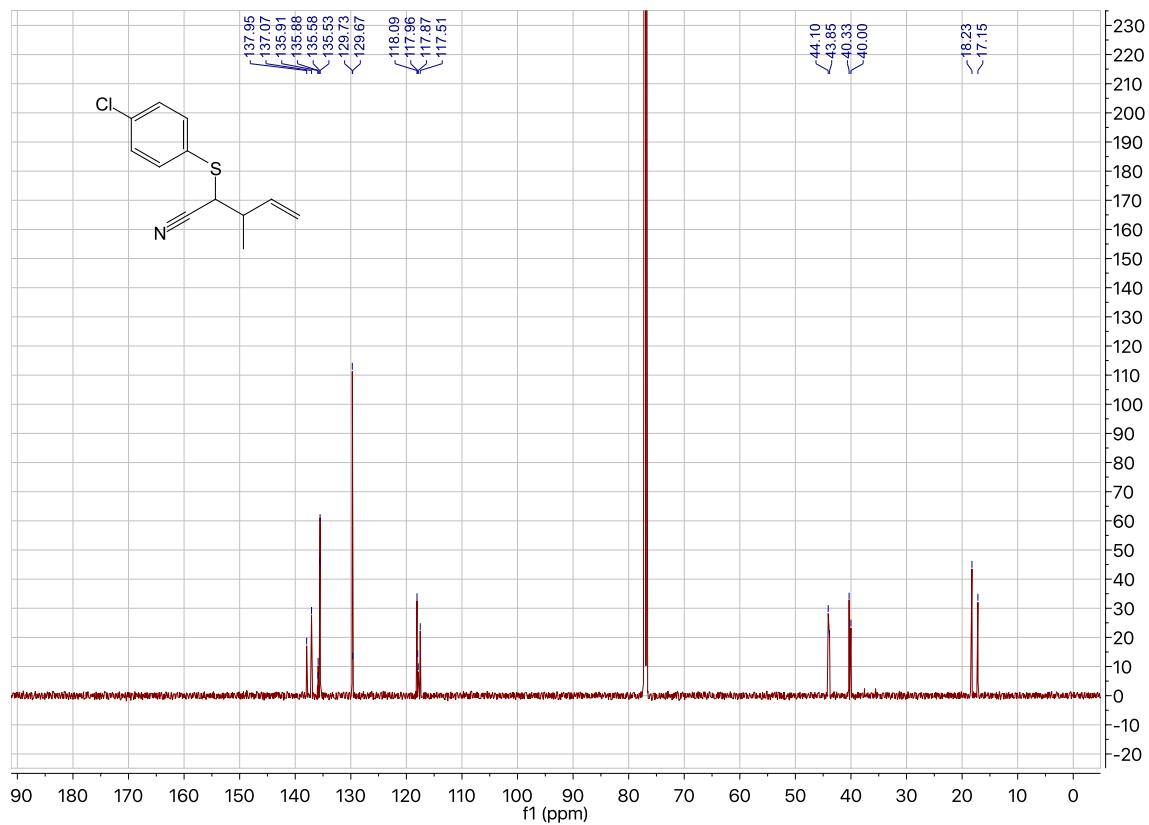


compound: 5s

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

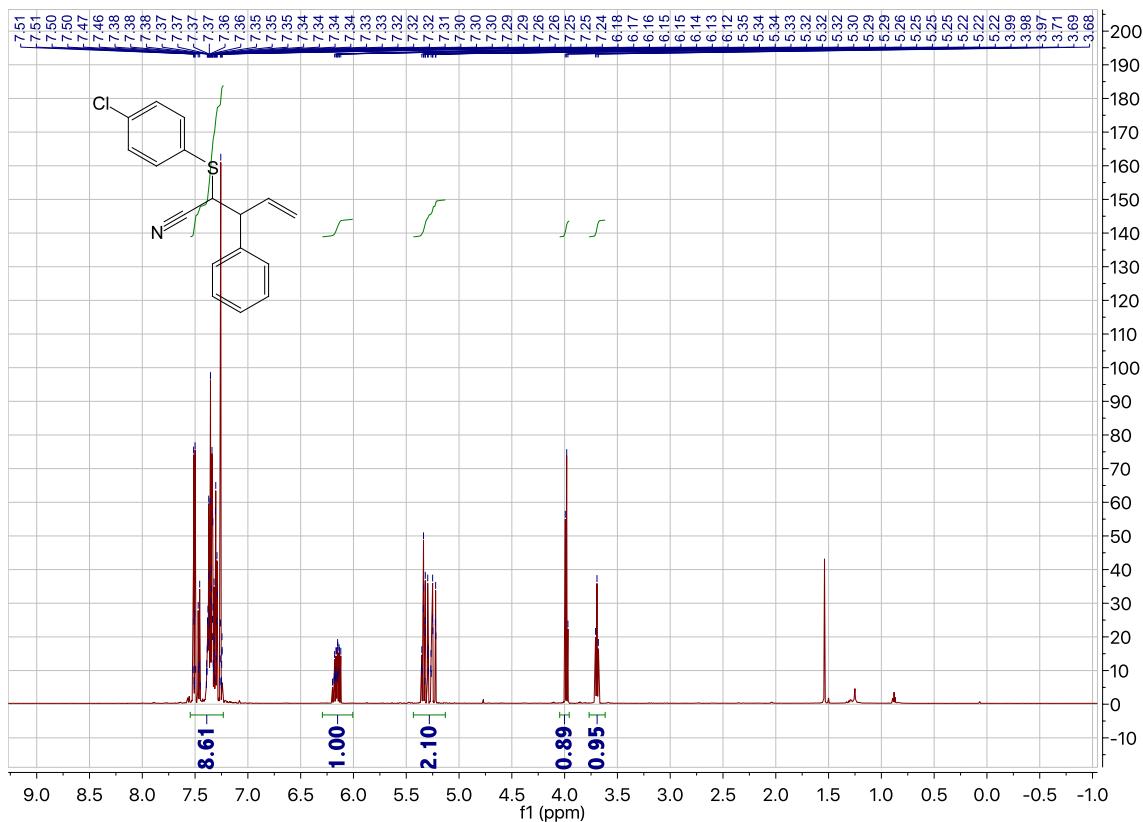


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

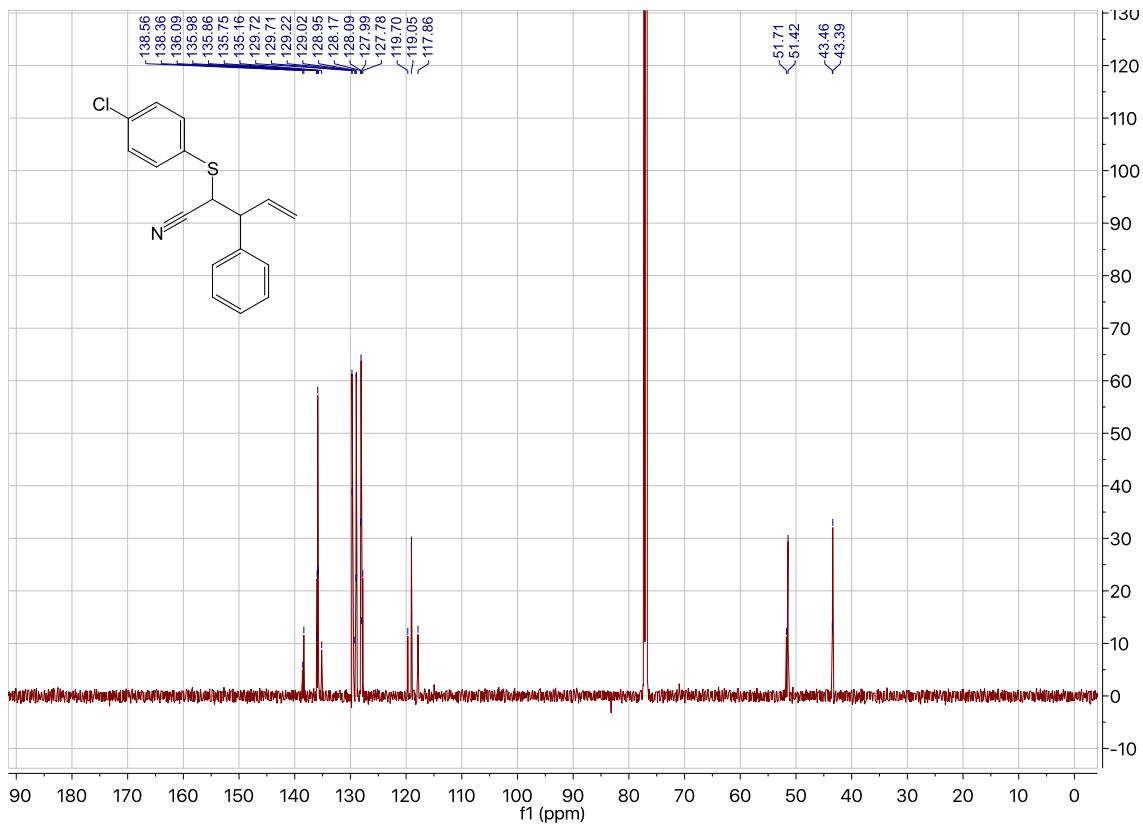


compound: **5t**

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

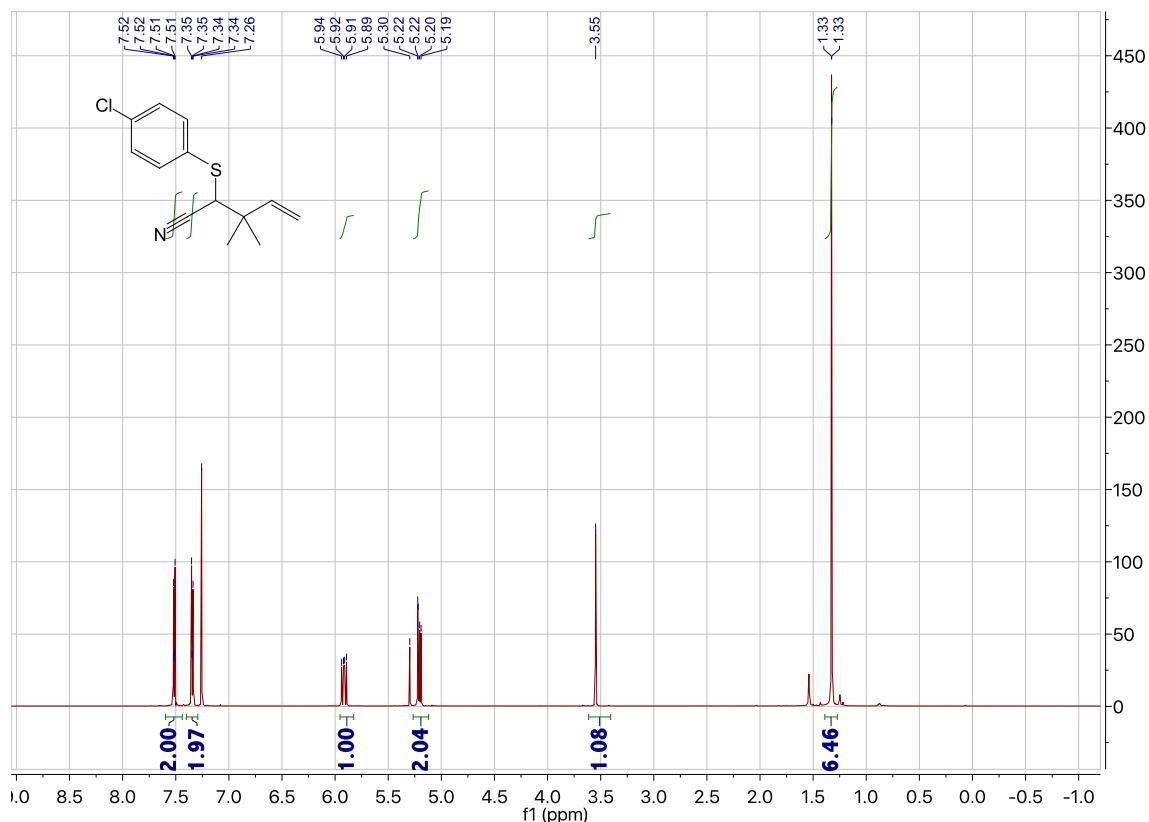


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

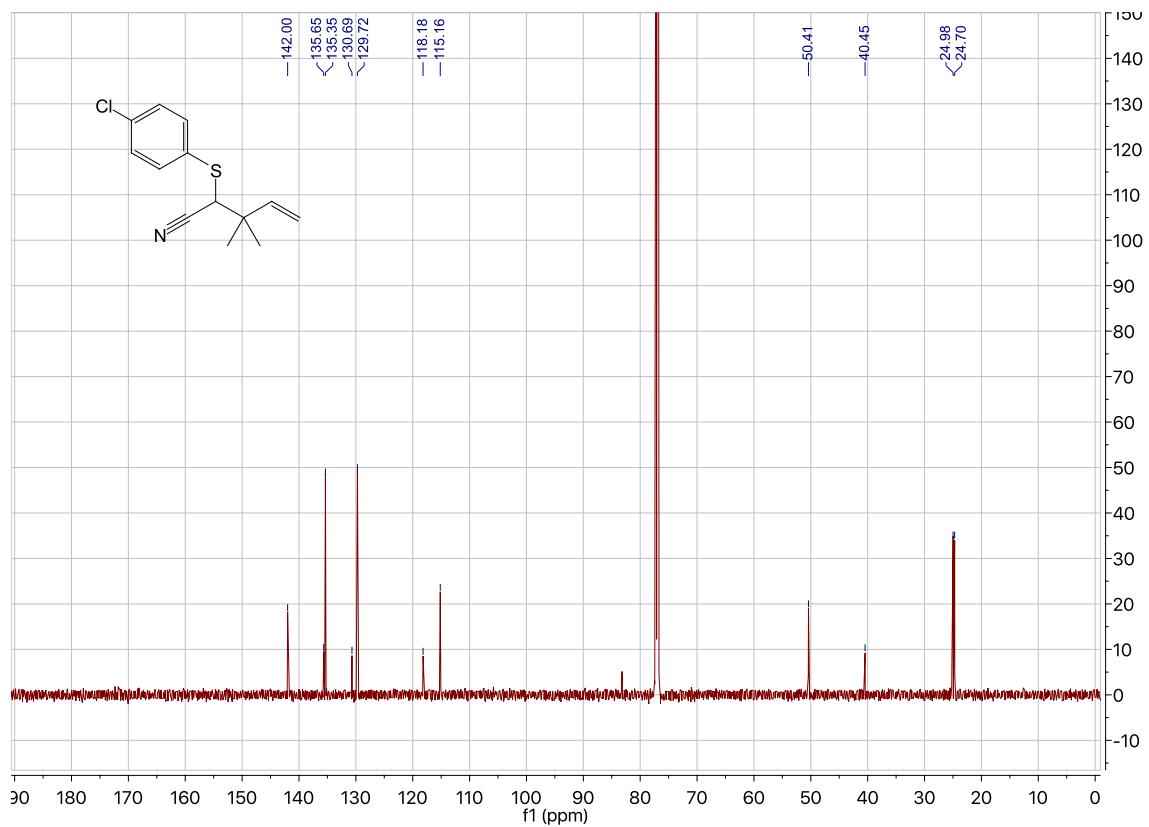


compound: **5u**

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

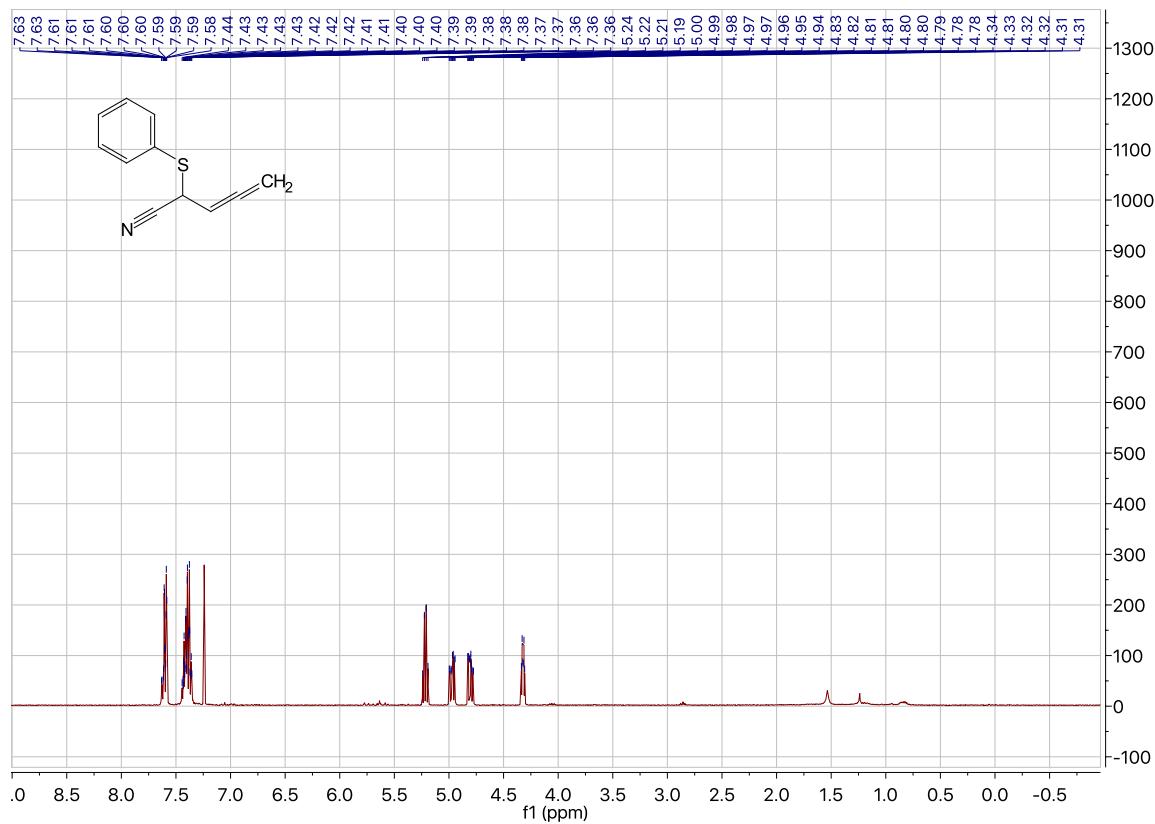


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

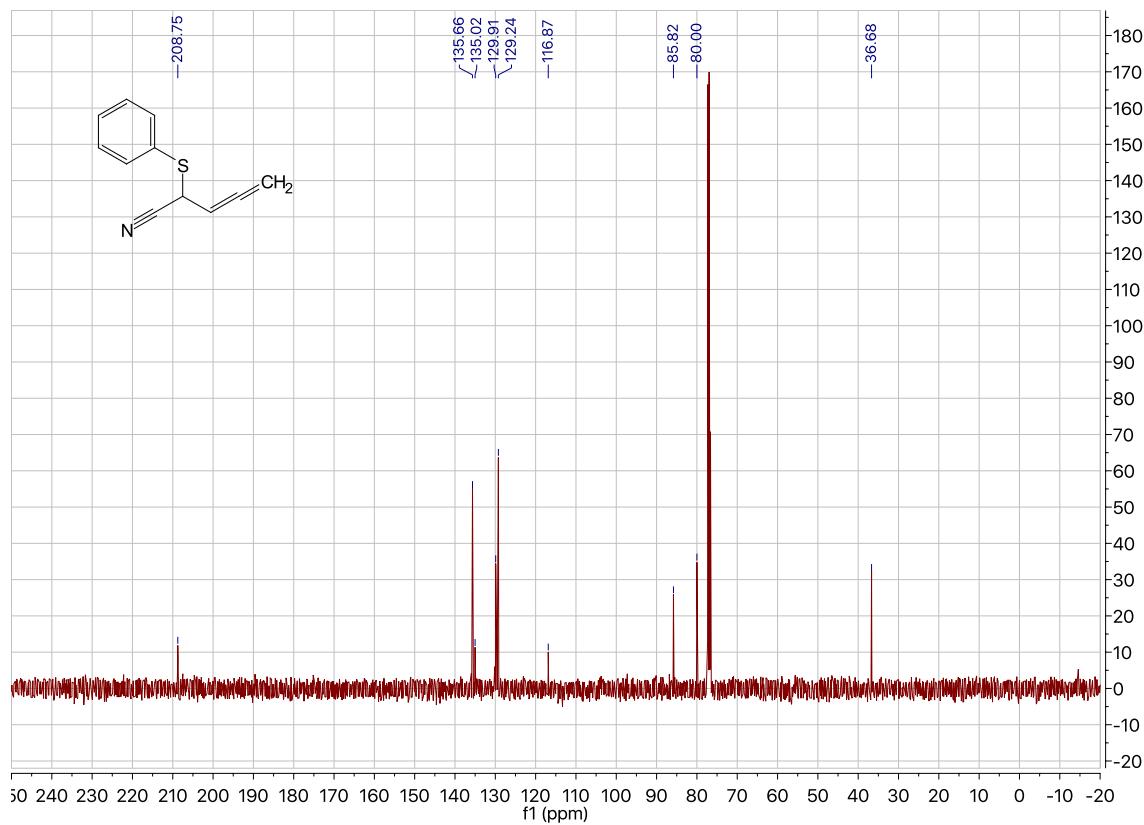


compound: 7a

$^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ )

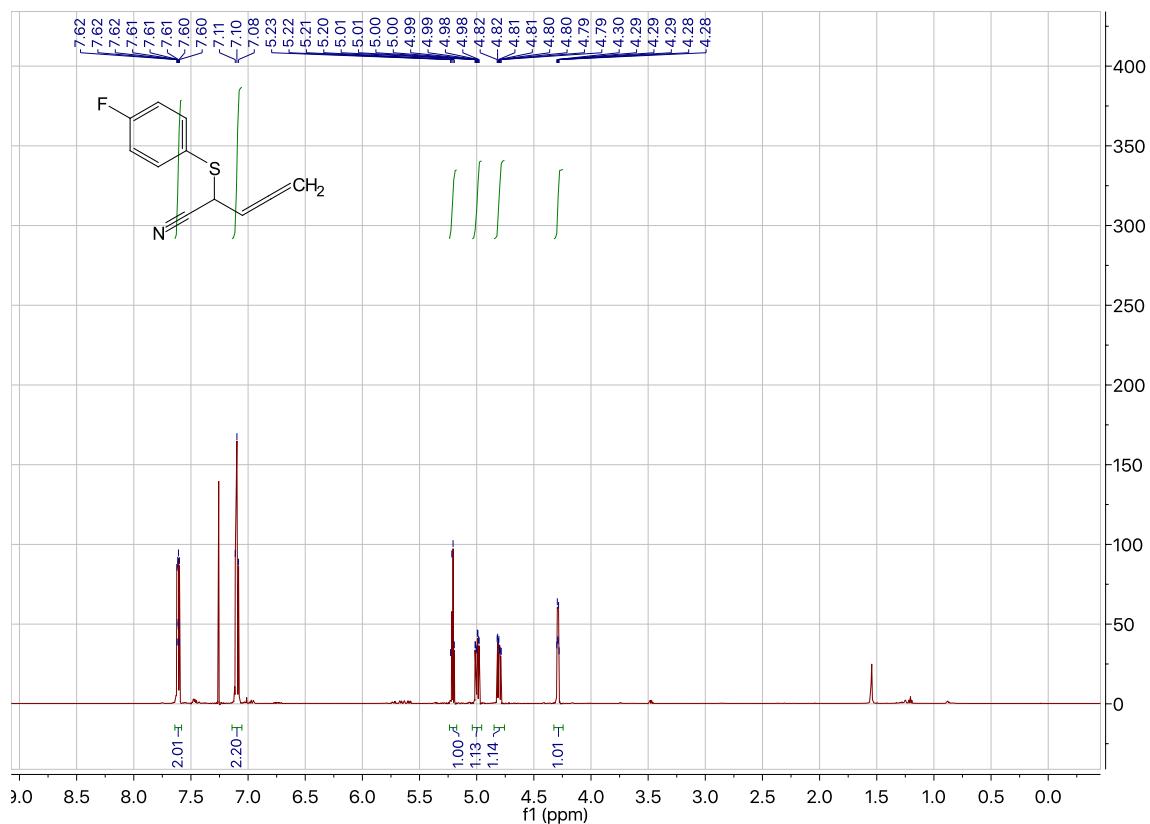


$^{13}\text{C}$ -NMR (151 MHz,  $\text{CDCl}_3$ )

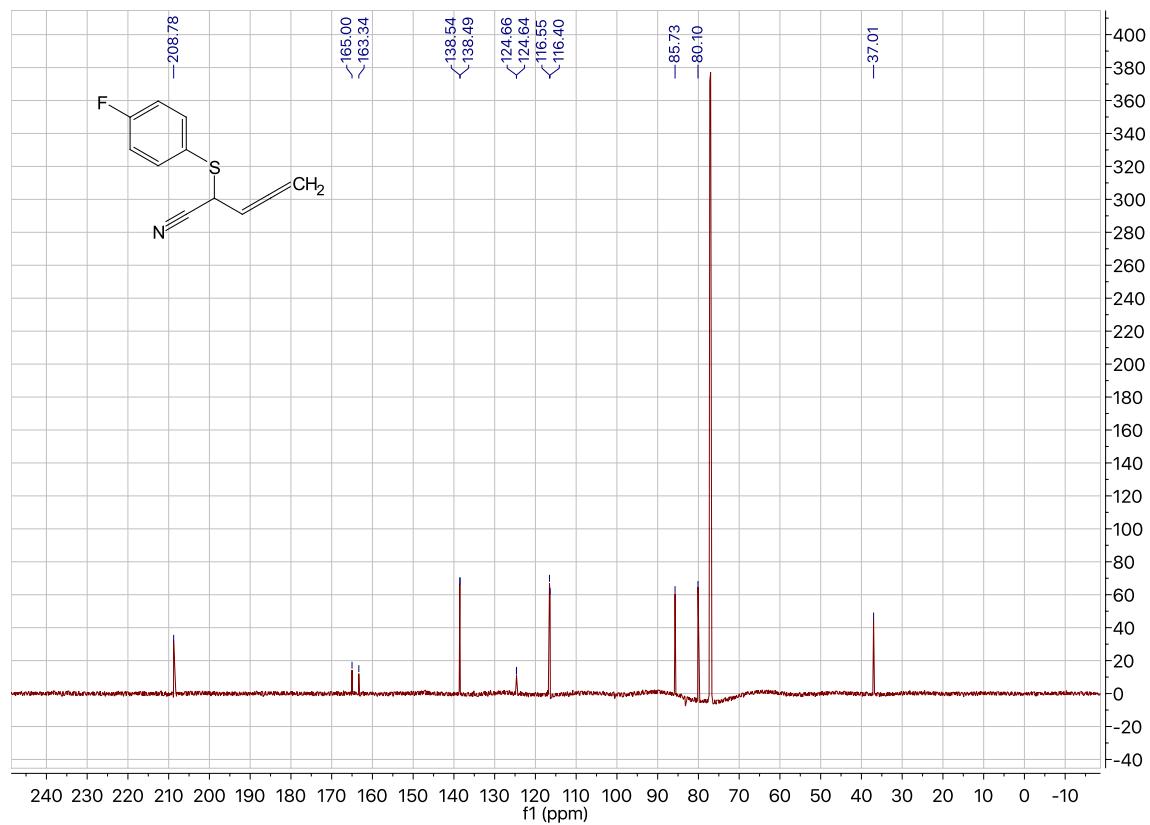


### compound: 7b

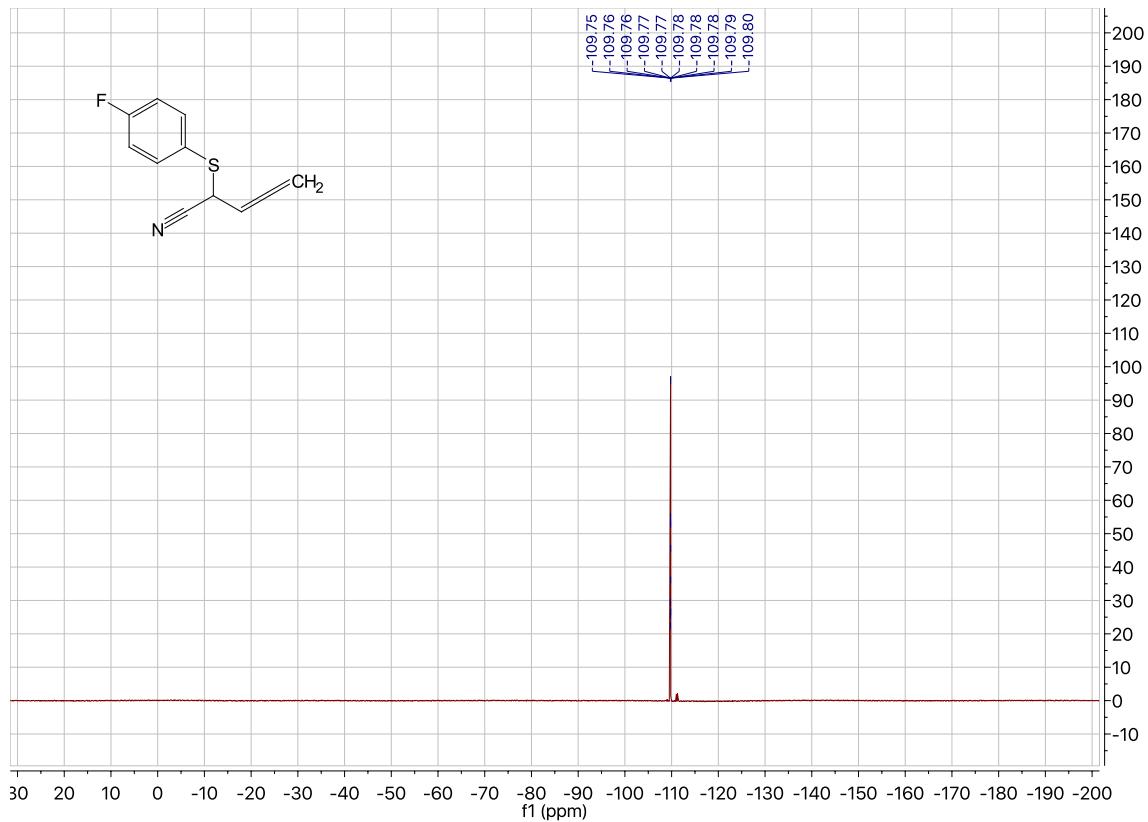
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

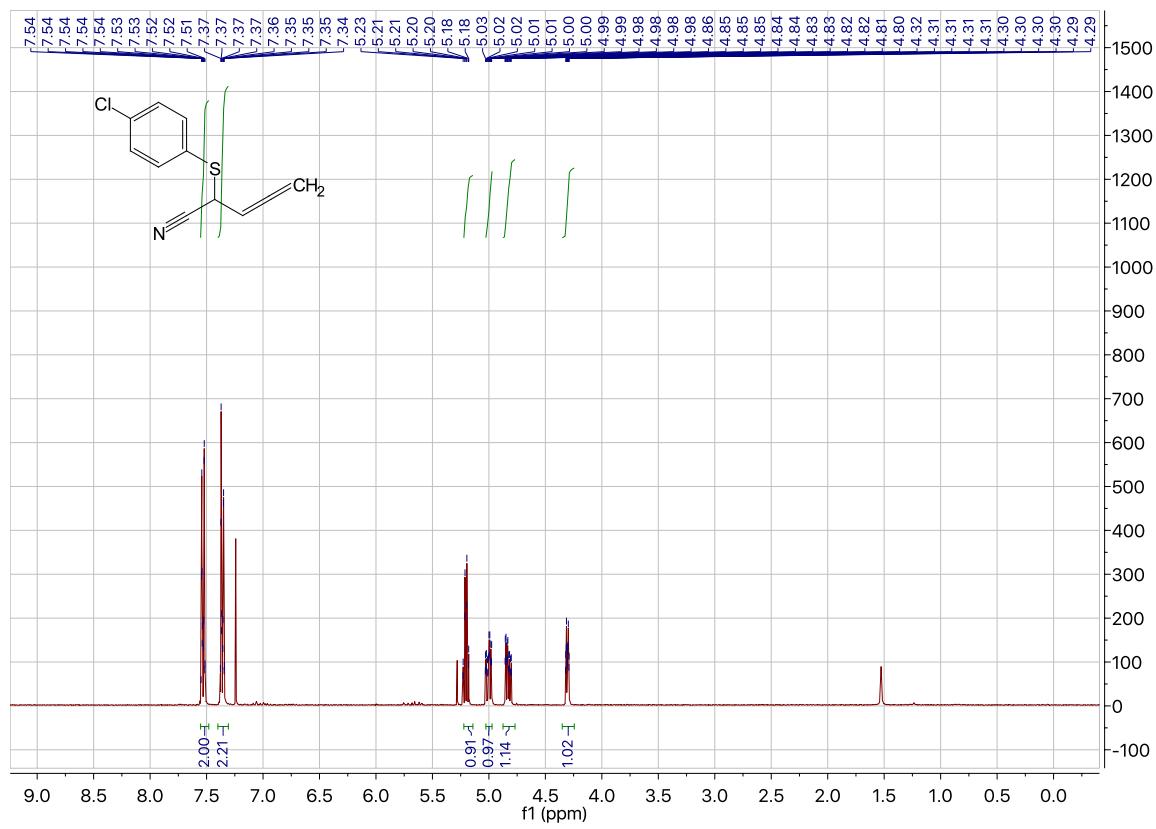


<sup>19</sup>F-NMR (564 MHz, CDCl<sub>3</sub>)

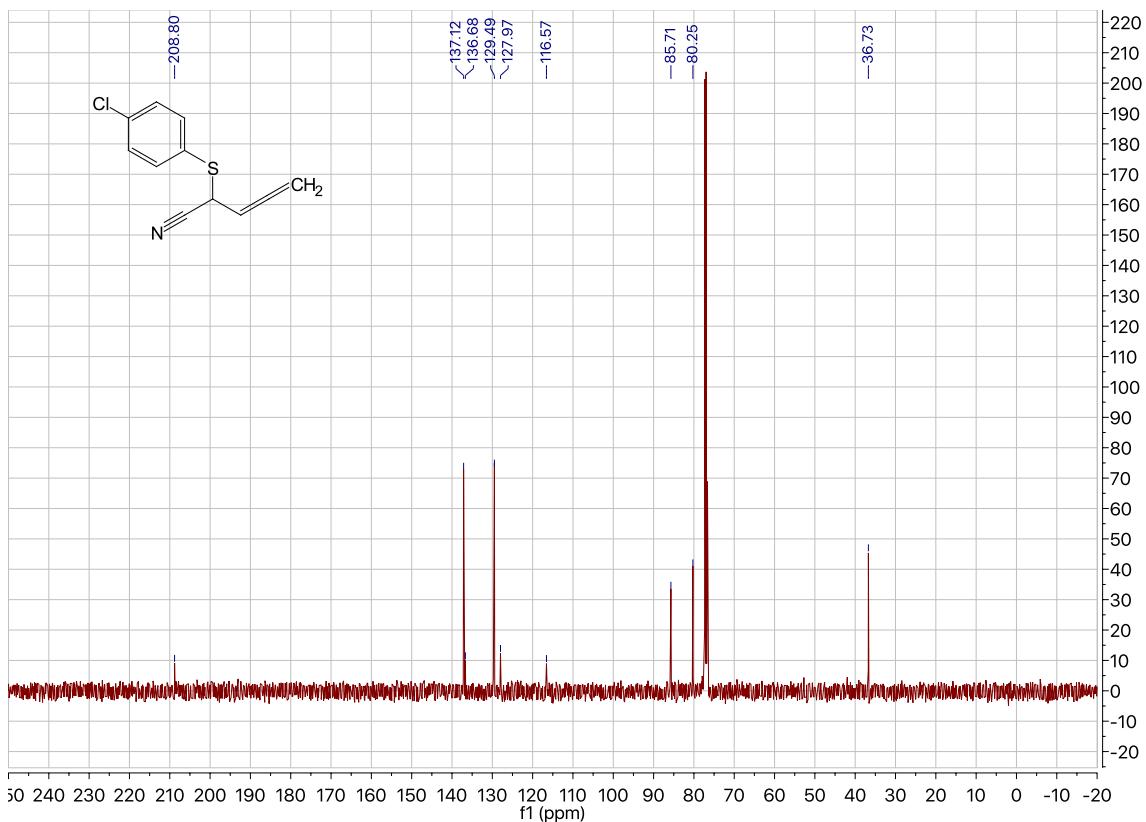


### compound: 7c

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

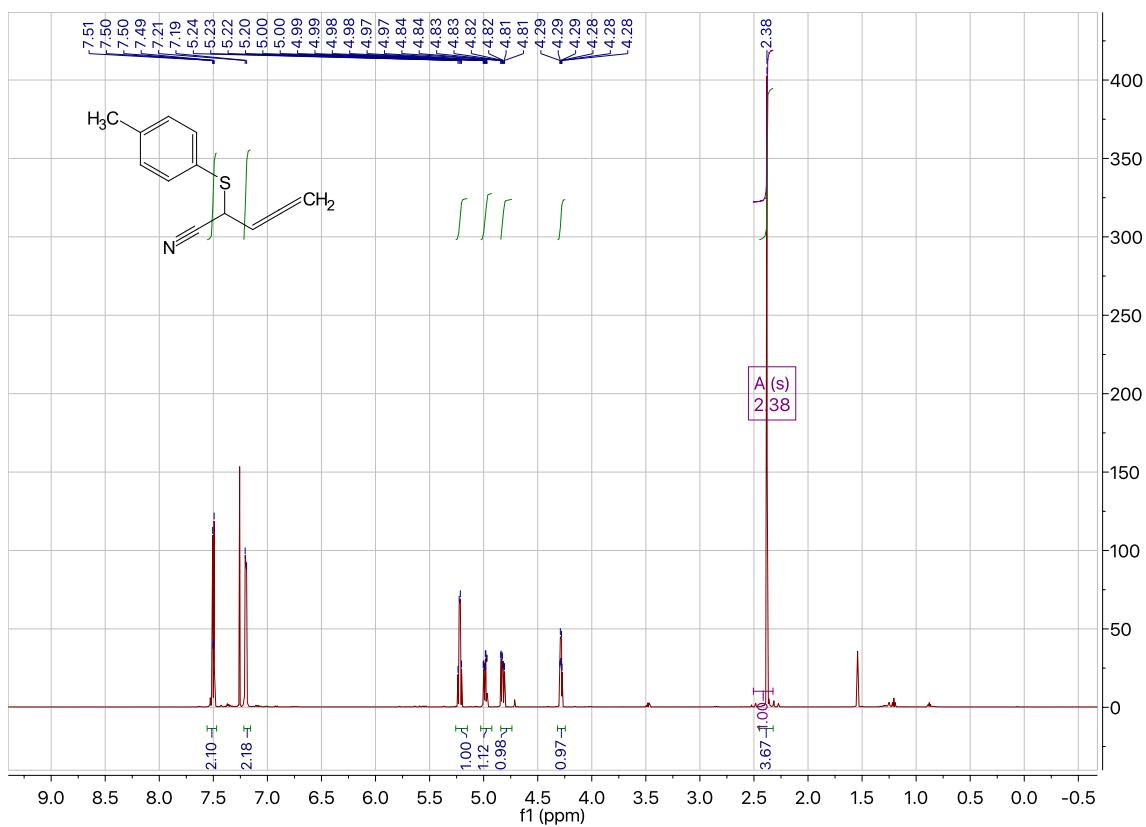


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

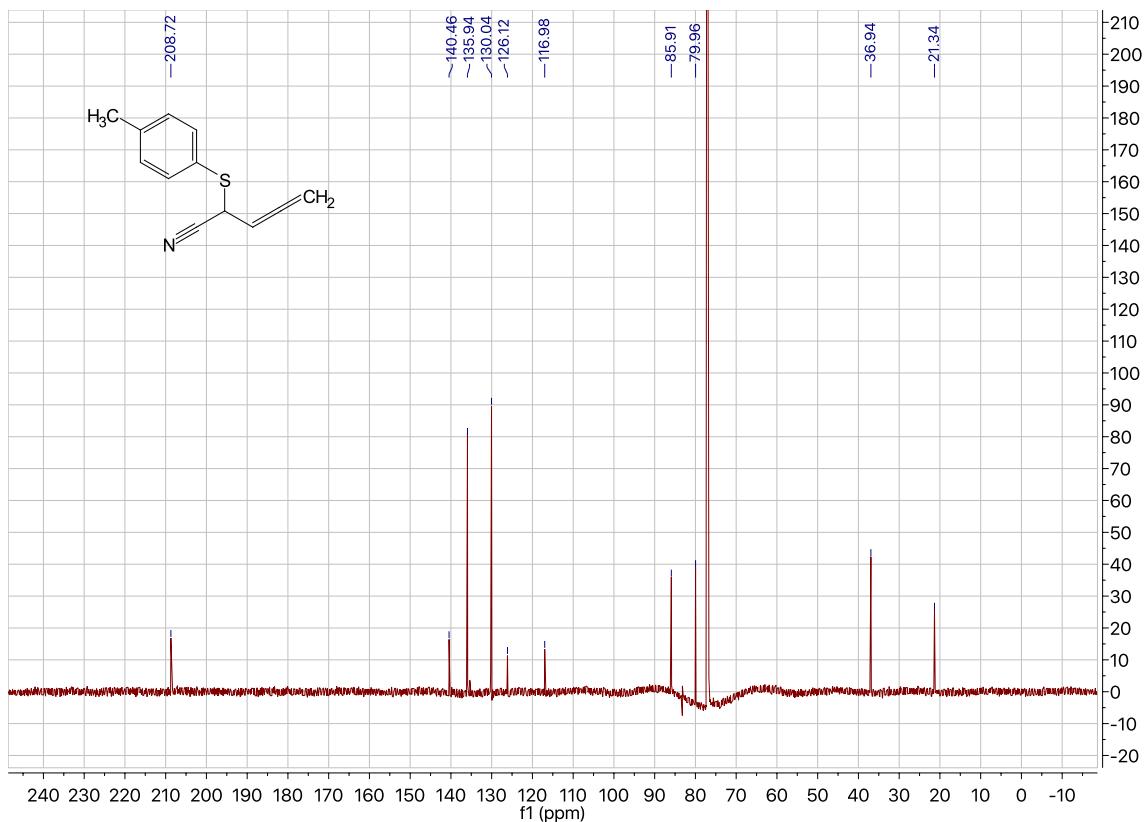


compound: 7d

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

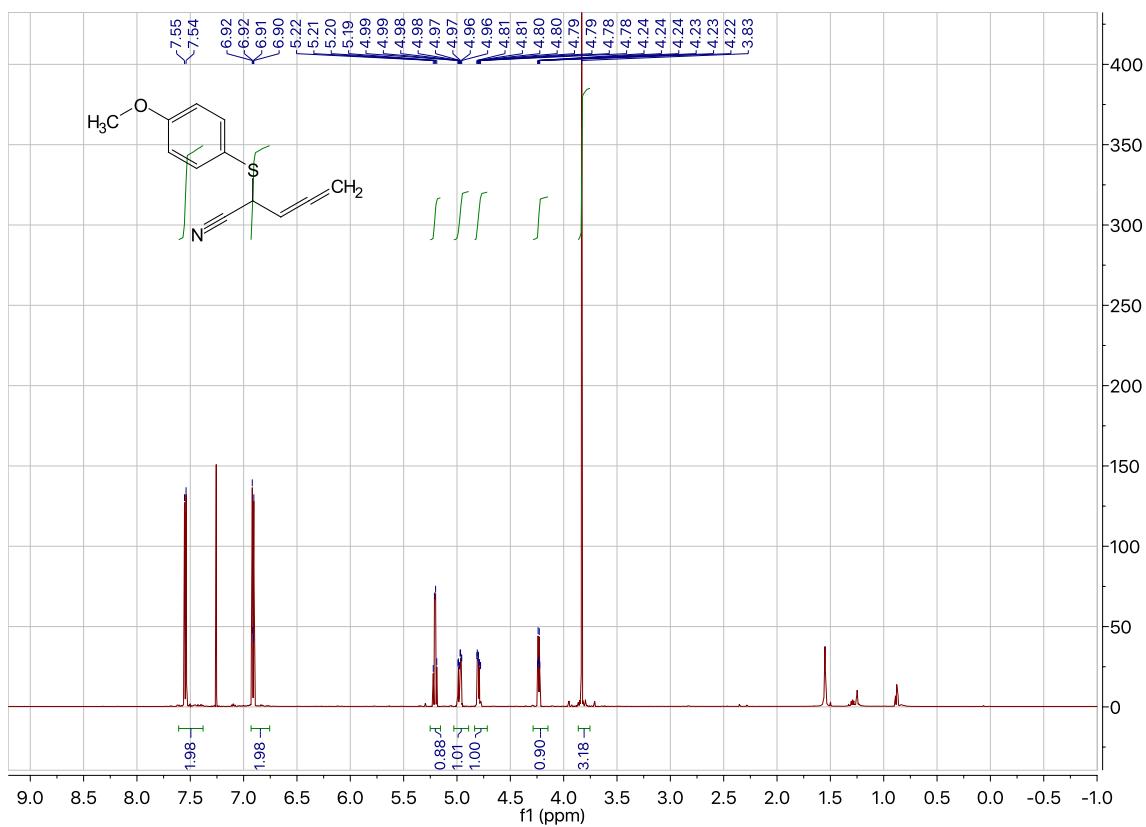


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

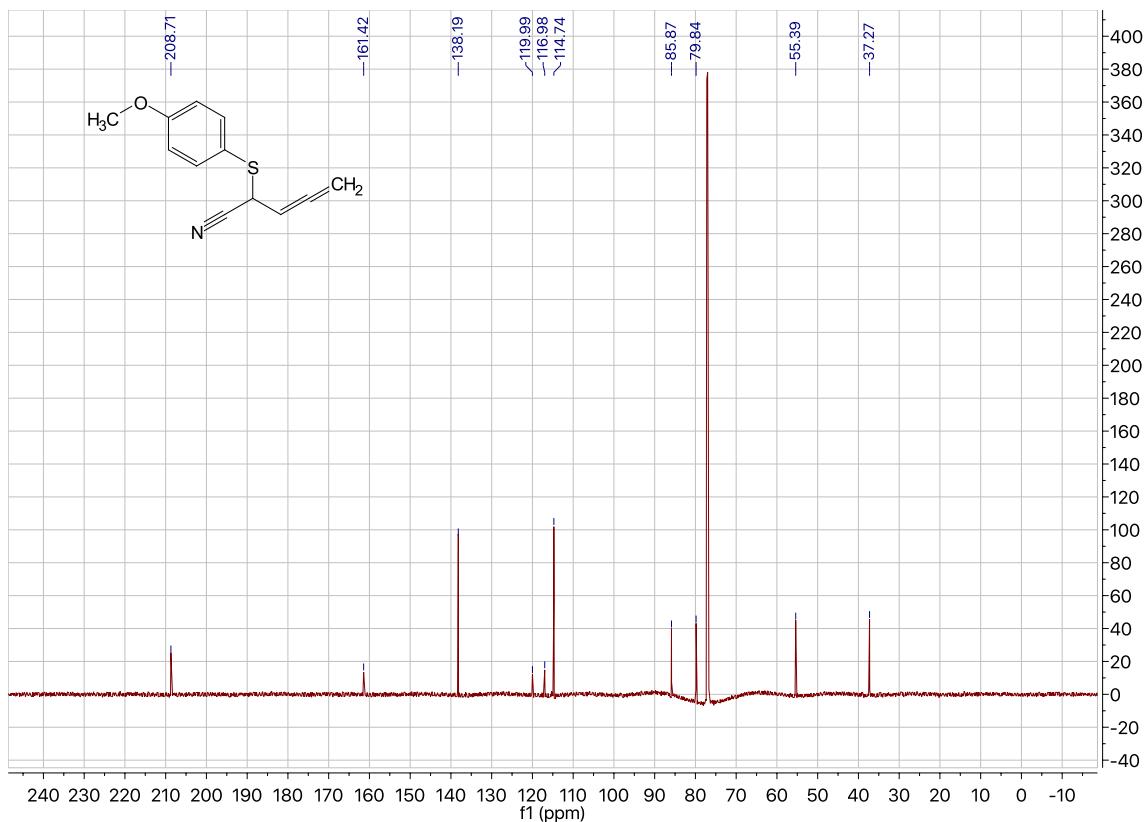


### compound: 7e

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

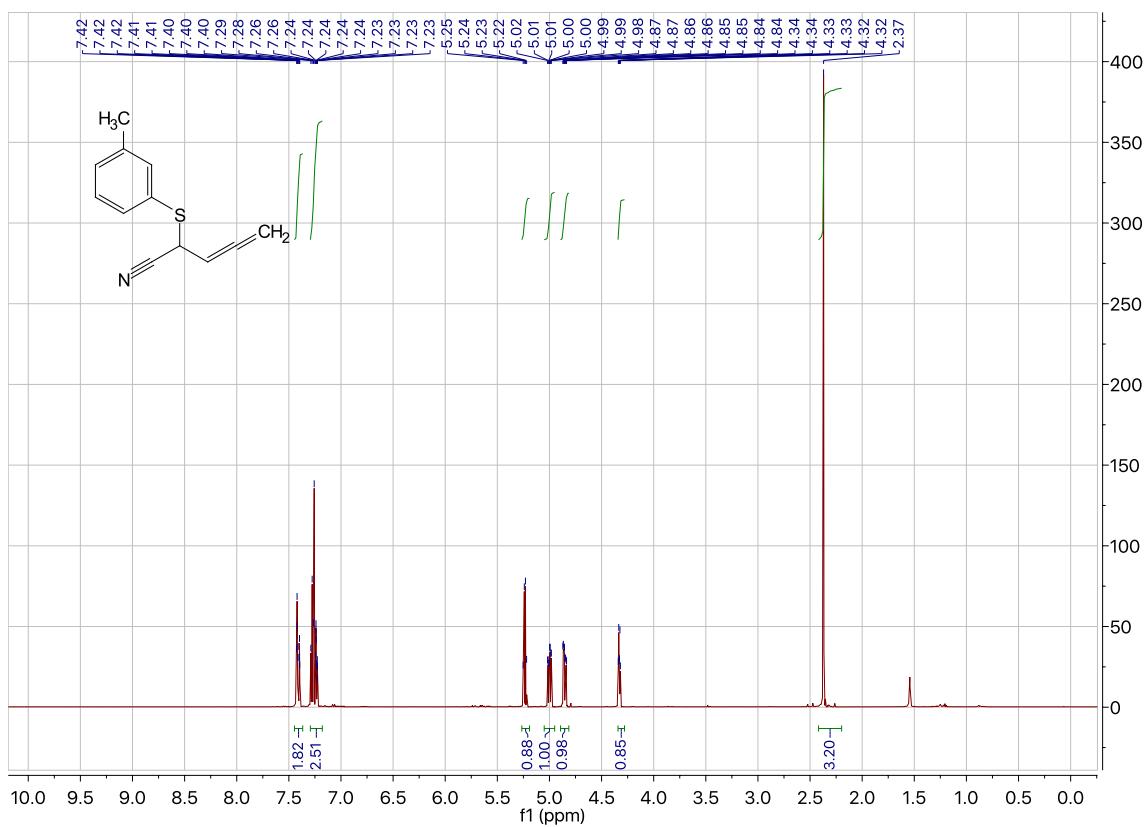


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

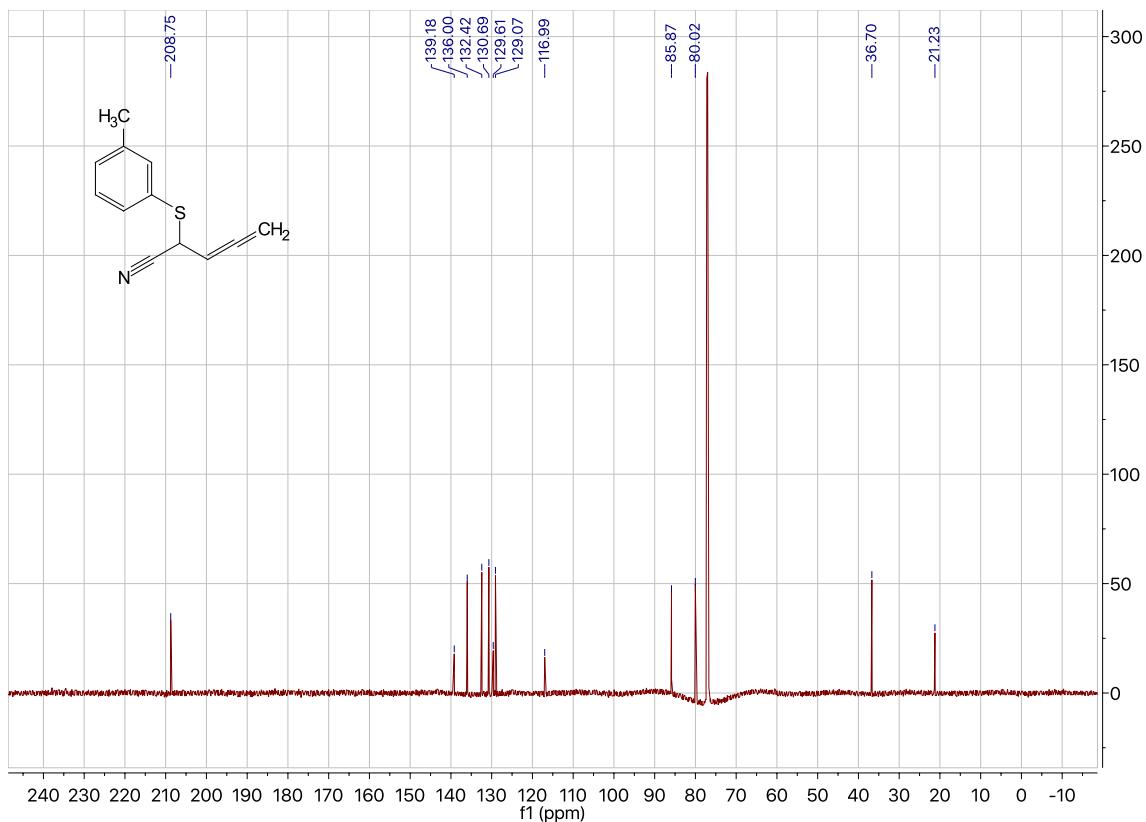


compound: 7f

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

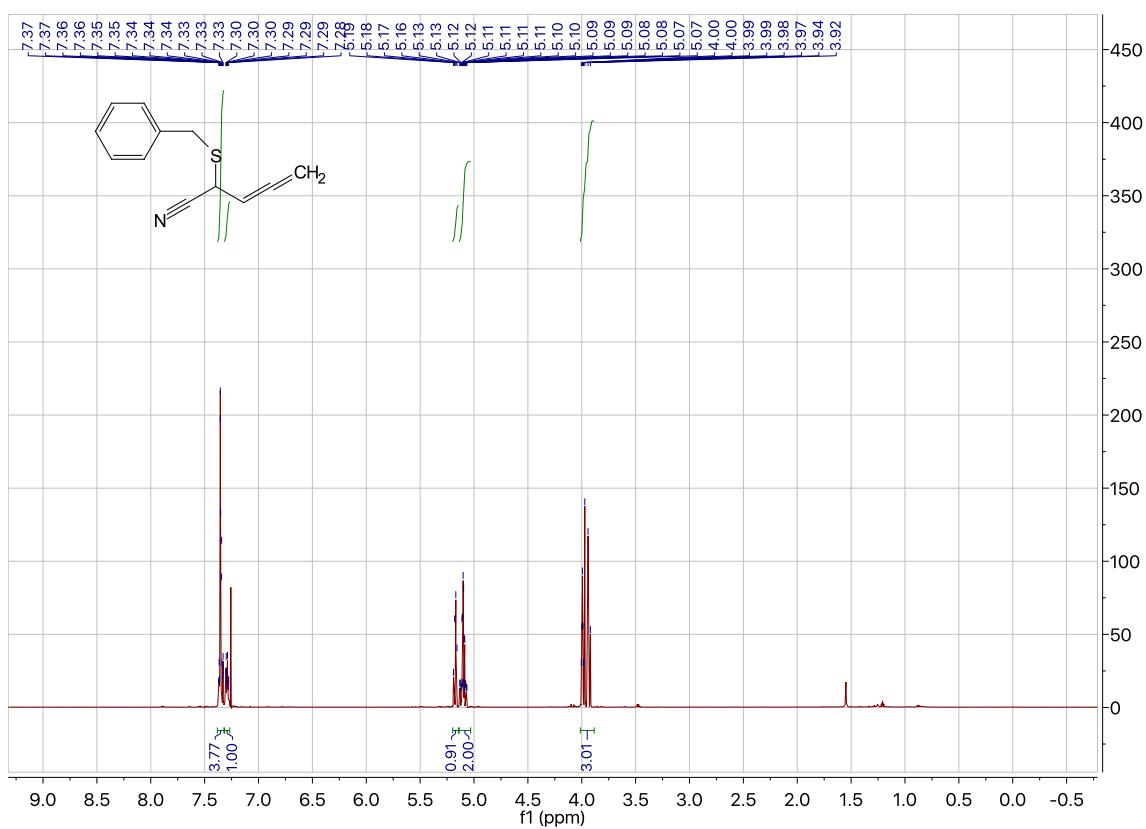


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

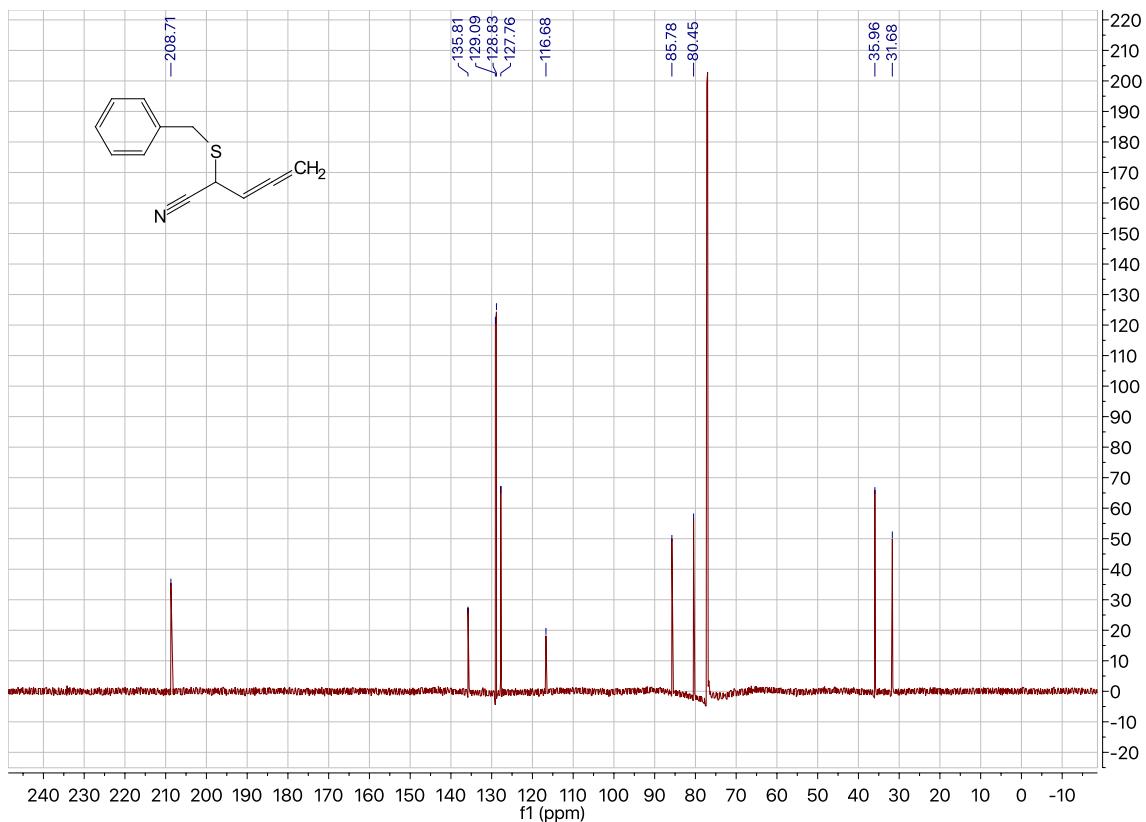


compound: 7g

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

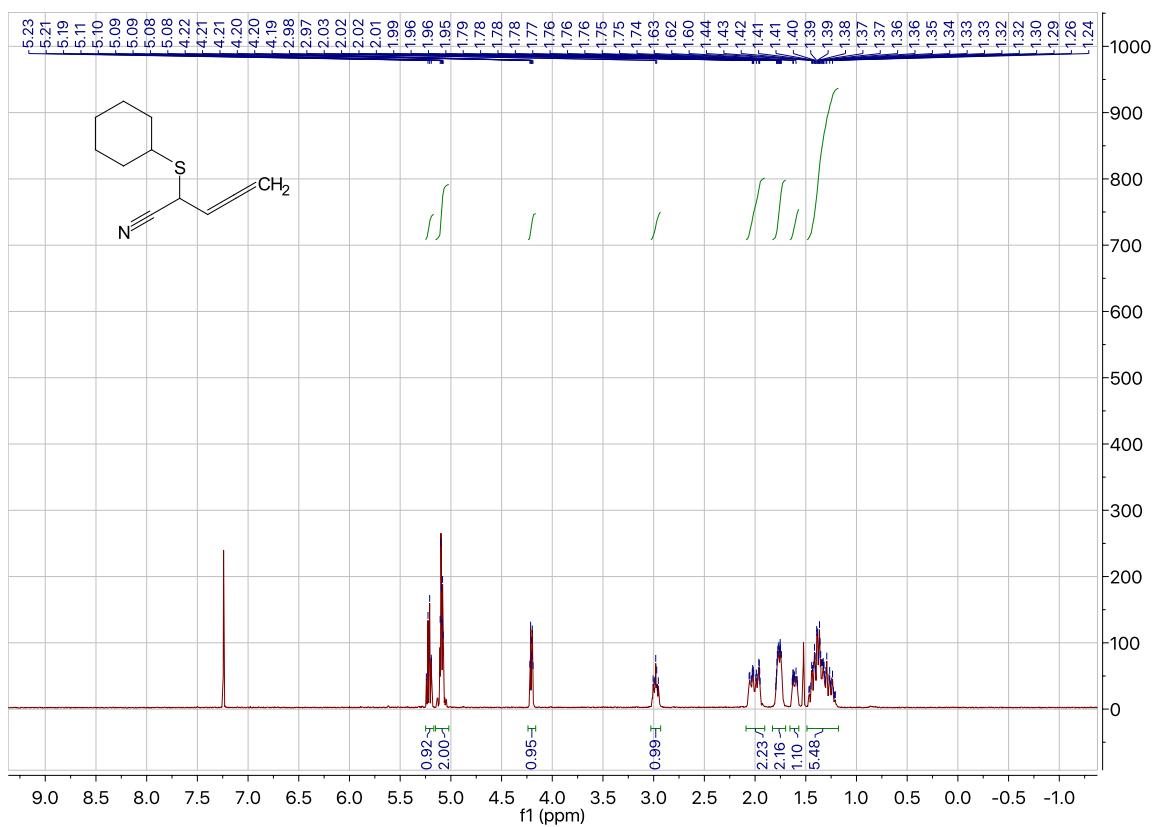


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

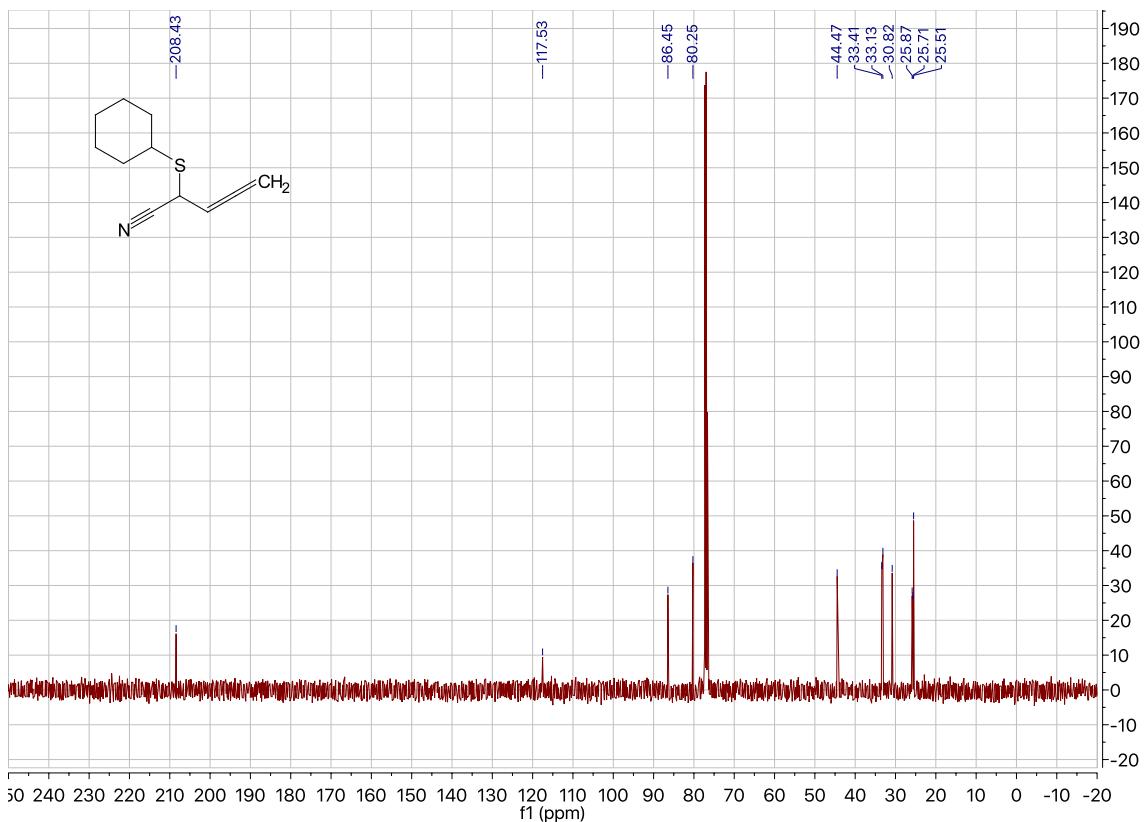


compound: 7h

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

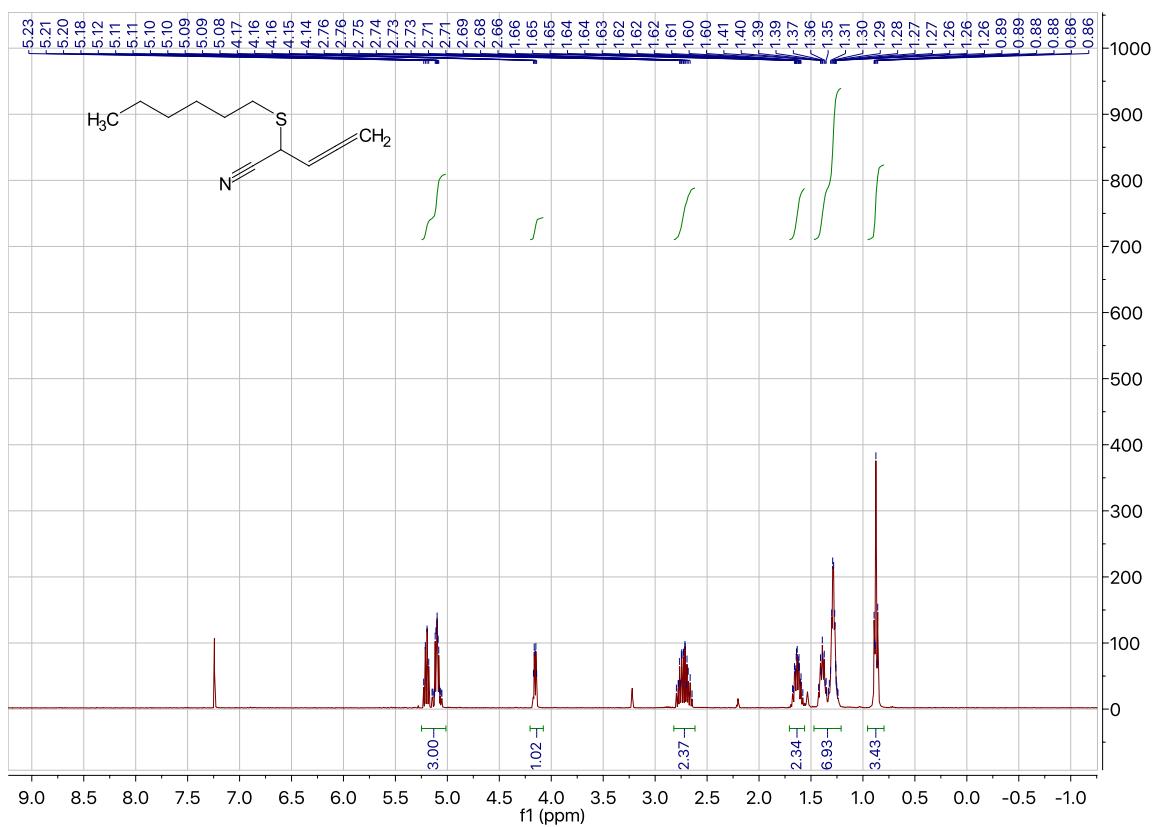


<sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>)

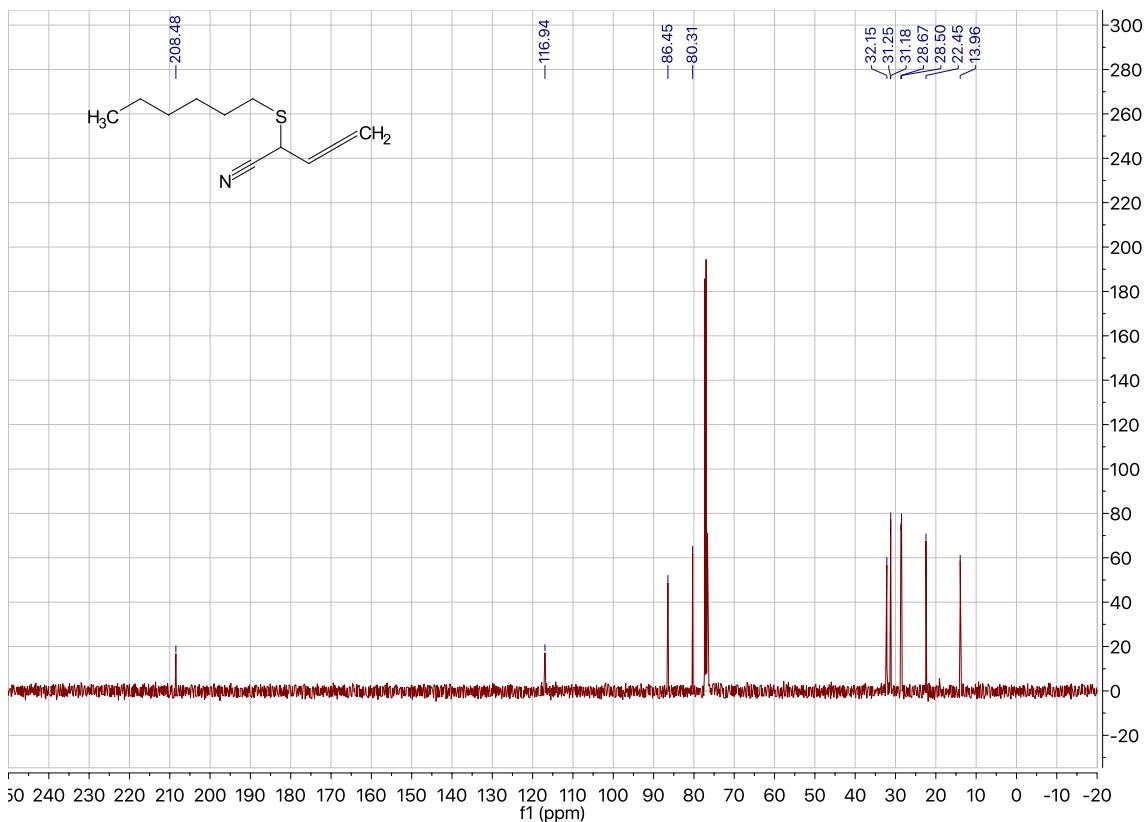


### compound: 7i

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

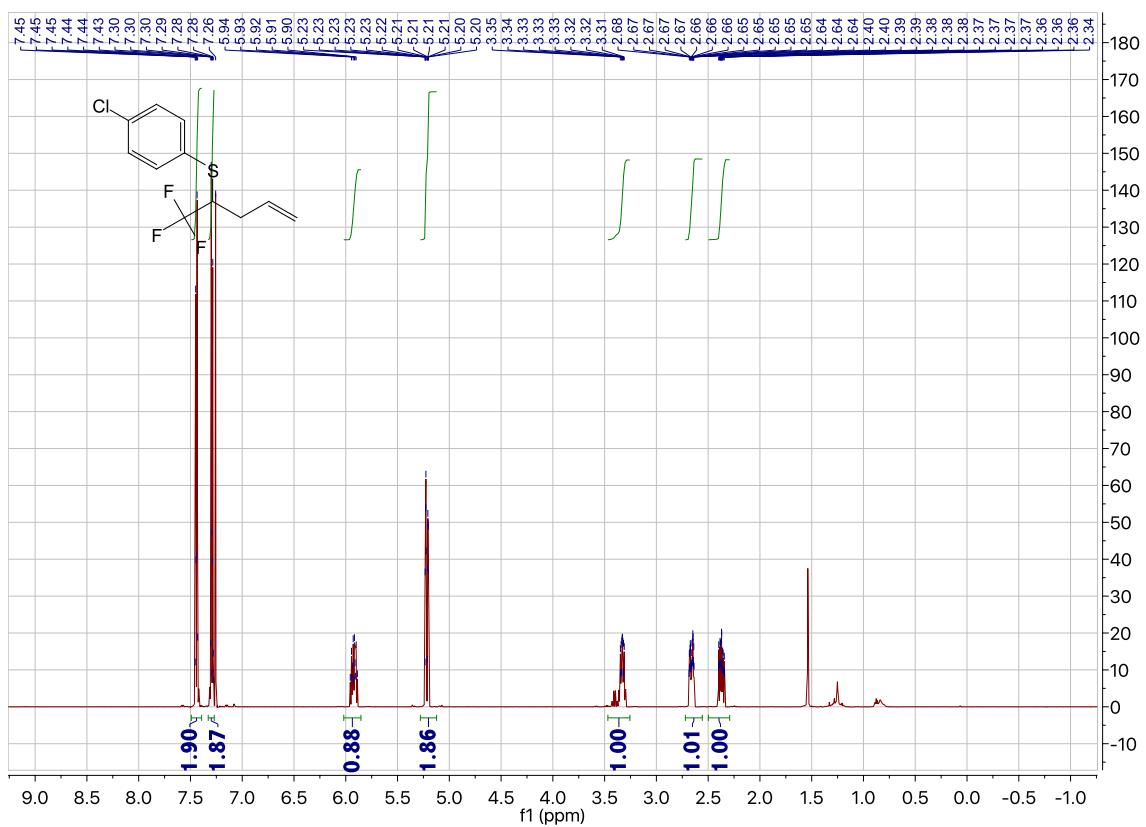


<sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>)

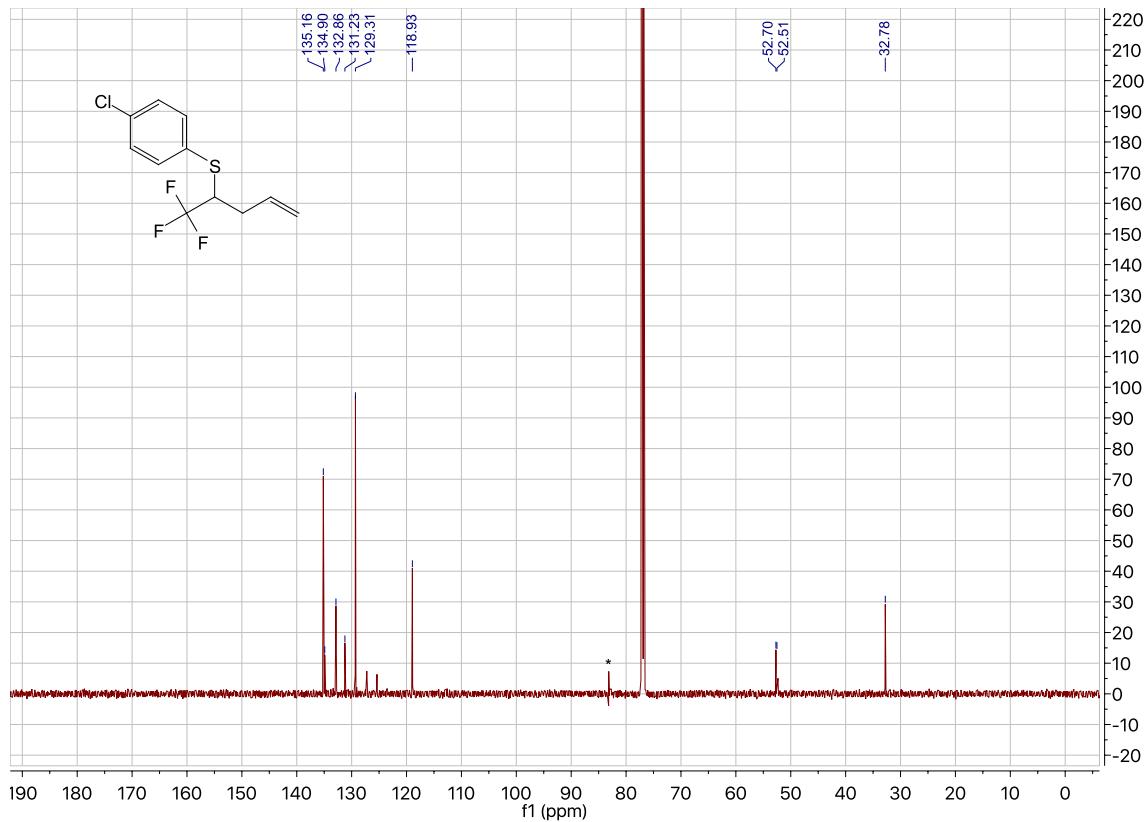


compound: 9a

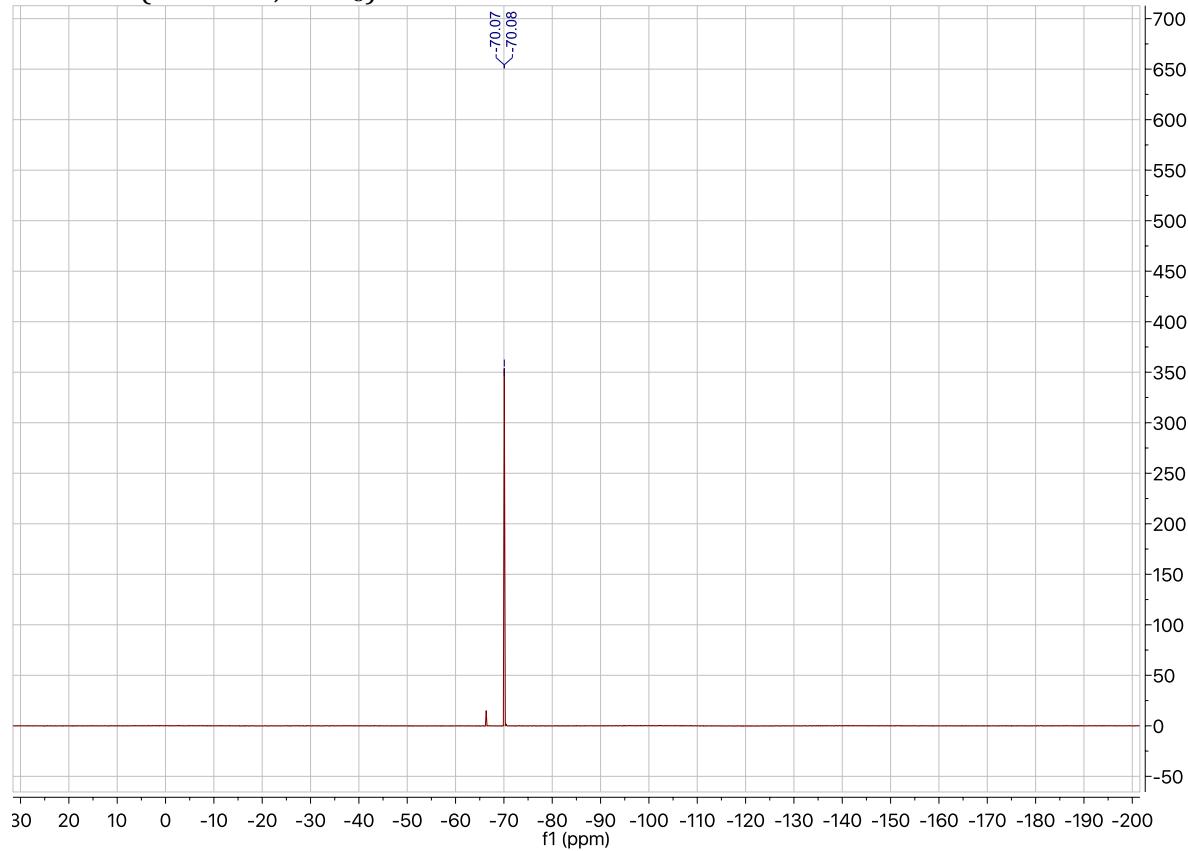
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$ -NMR (151 MHz,  $\text{CDCl}_3$ )

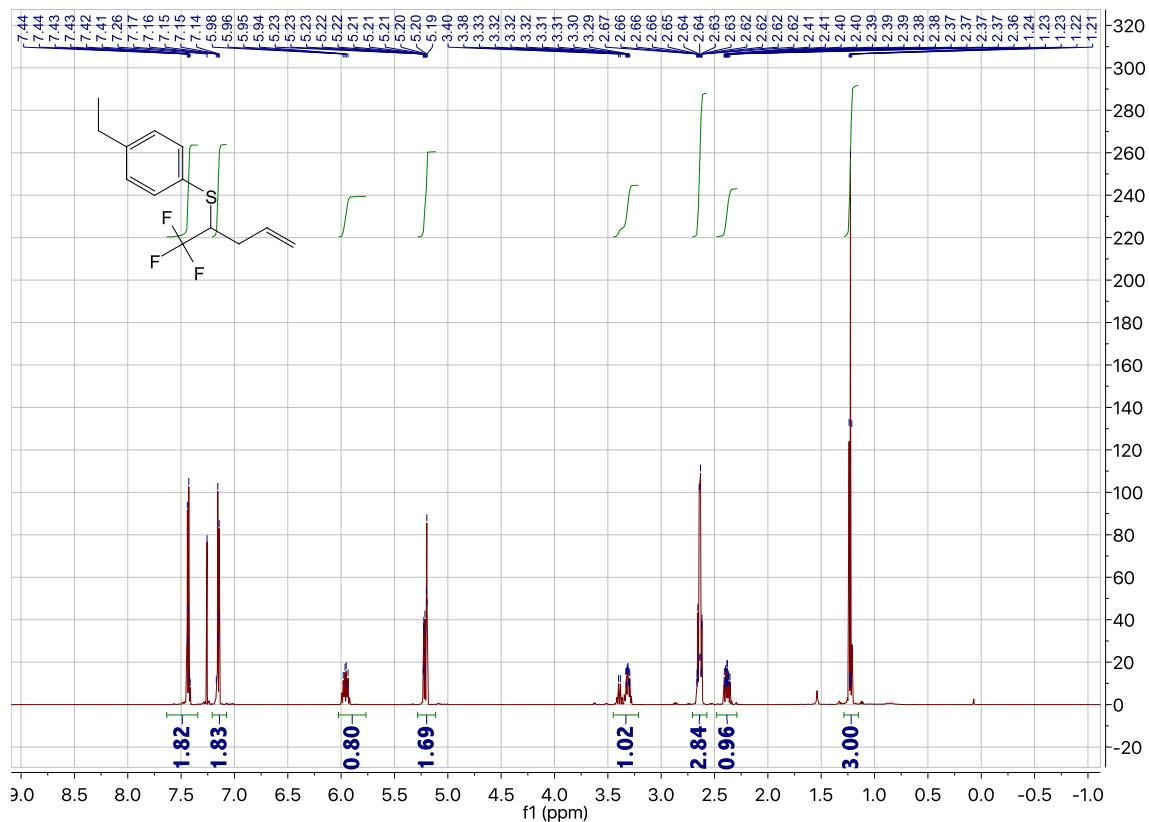


$^{19}\text{F}$ -NMR (564 MHz,  $\text{CDCl}_3$ )

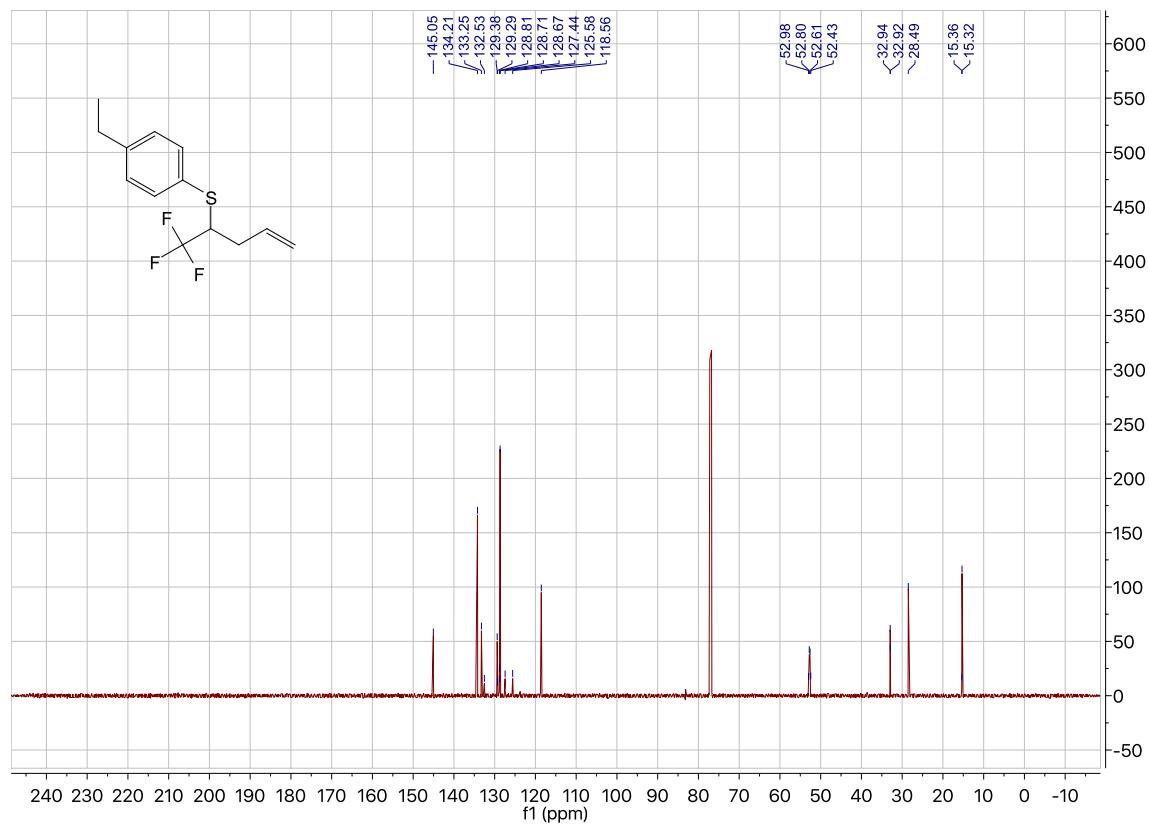


compound: **9b**

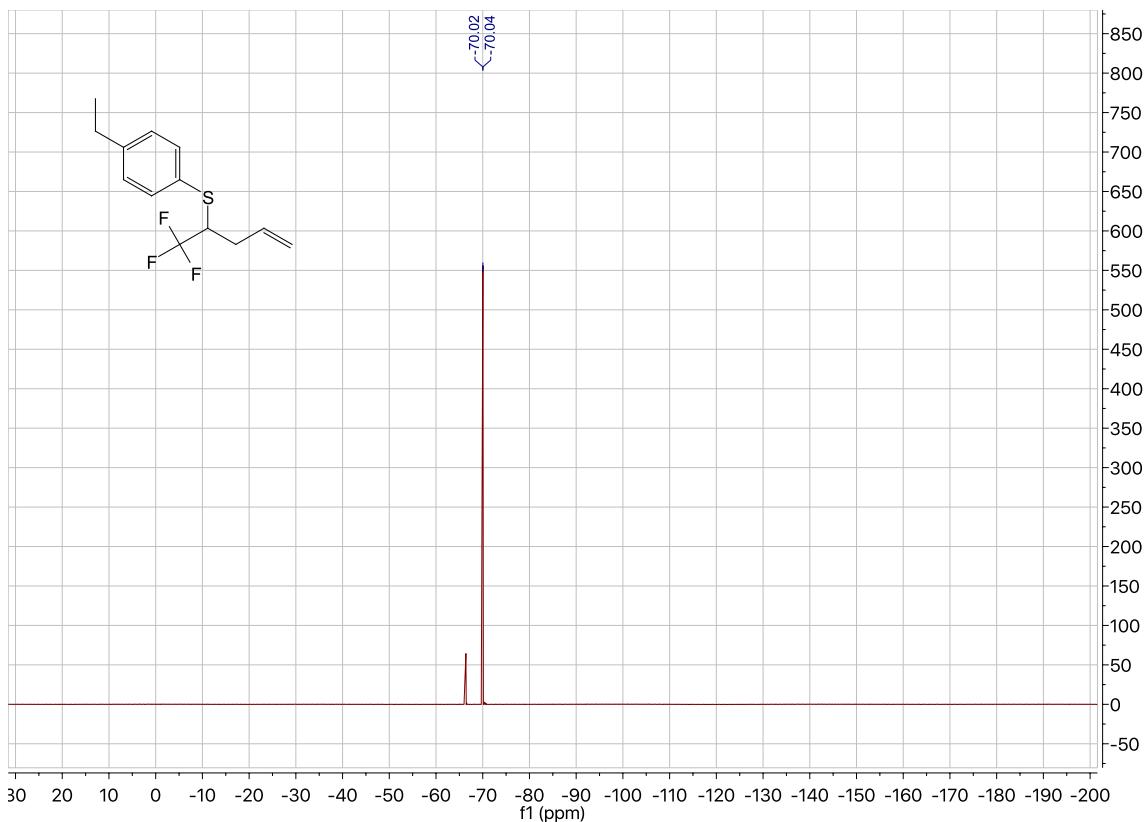
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

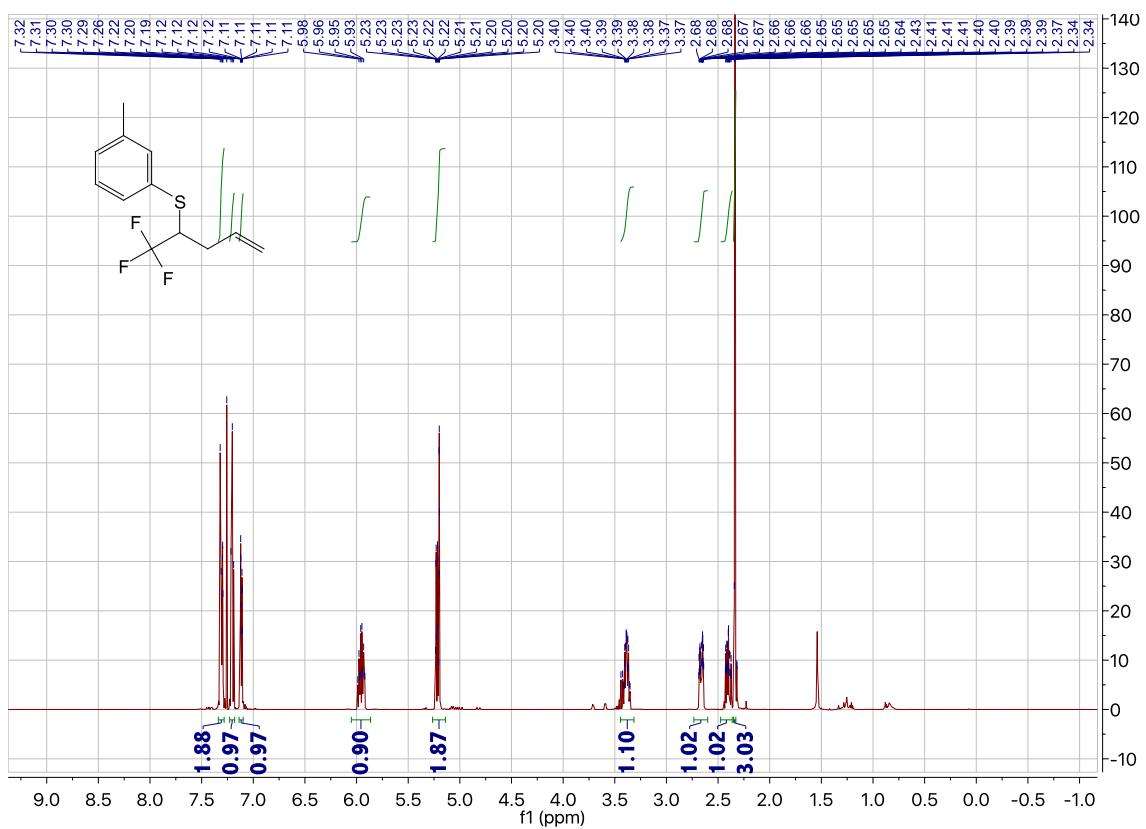


<sup>19</sup>F-NMR (564 MHz, CDCl<sub>3</sub>)

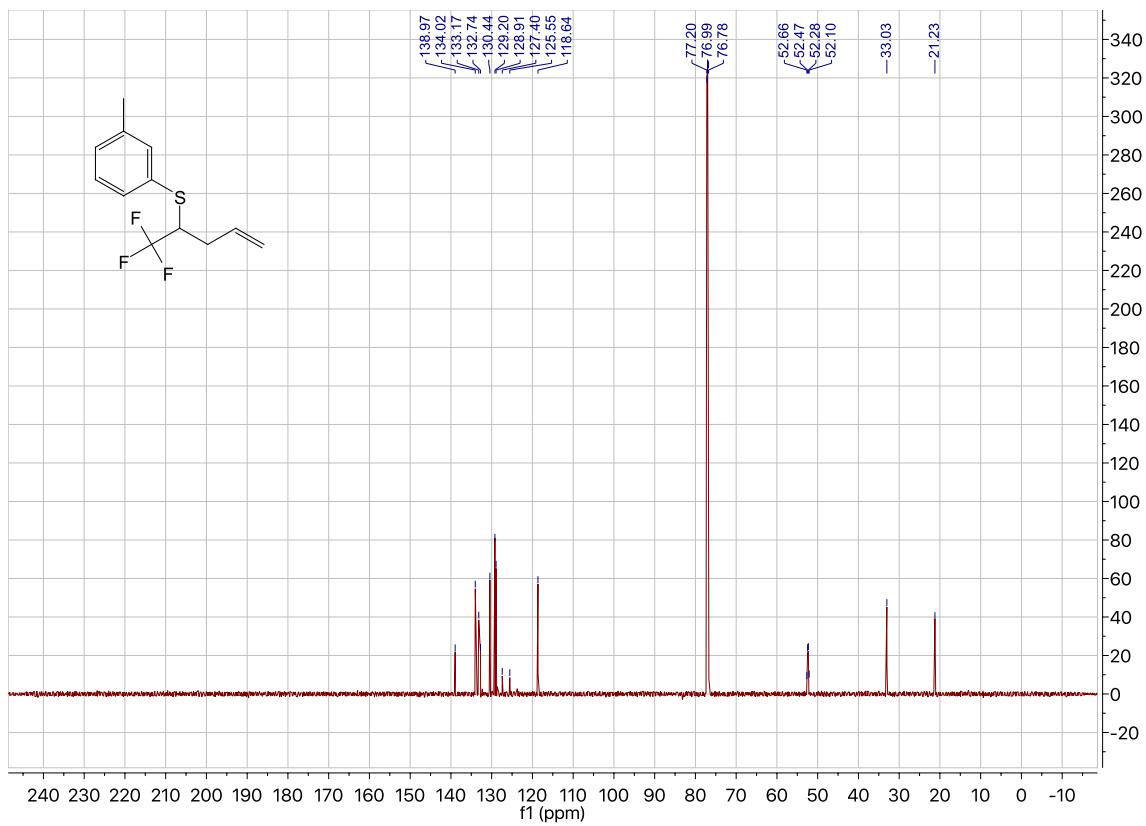


### compound: 9c

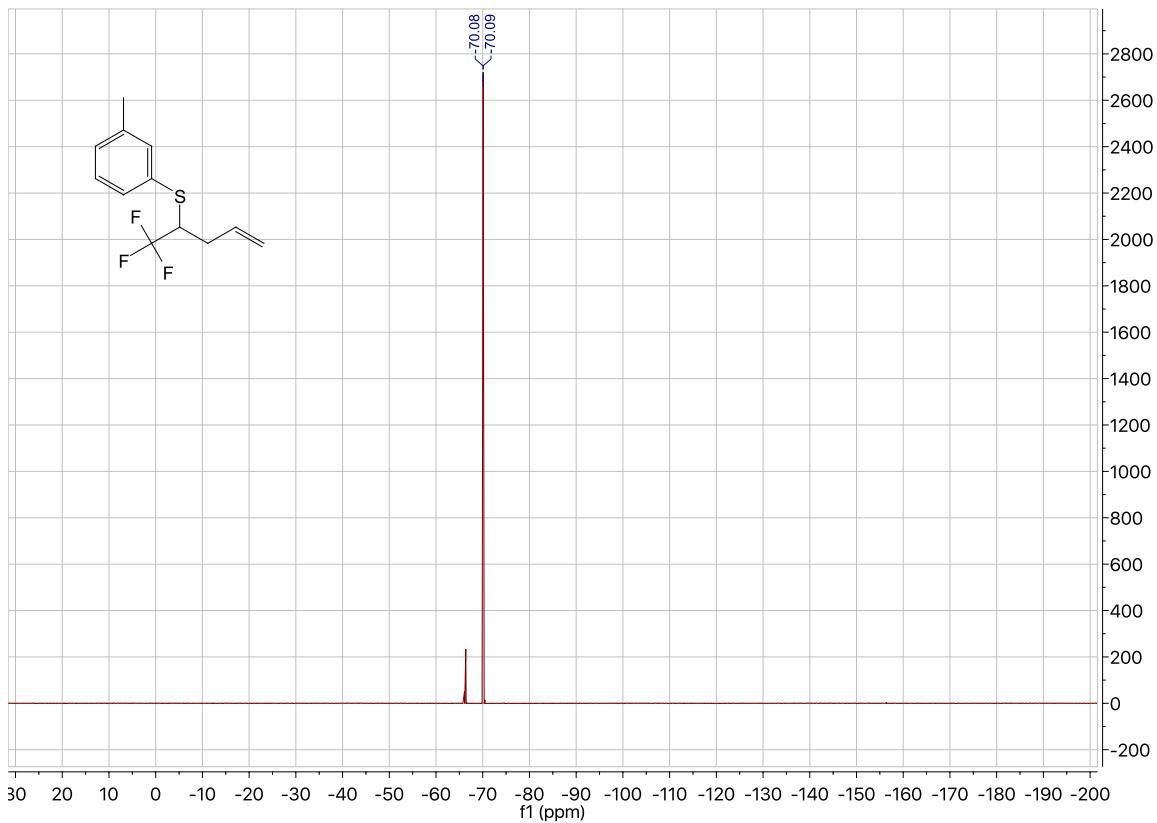
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$ -NMR (151 MHz,  $\text{CDCl}_3$ )

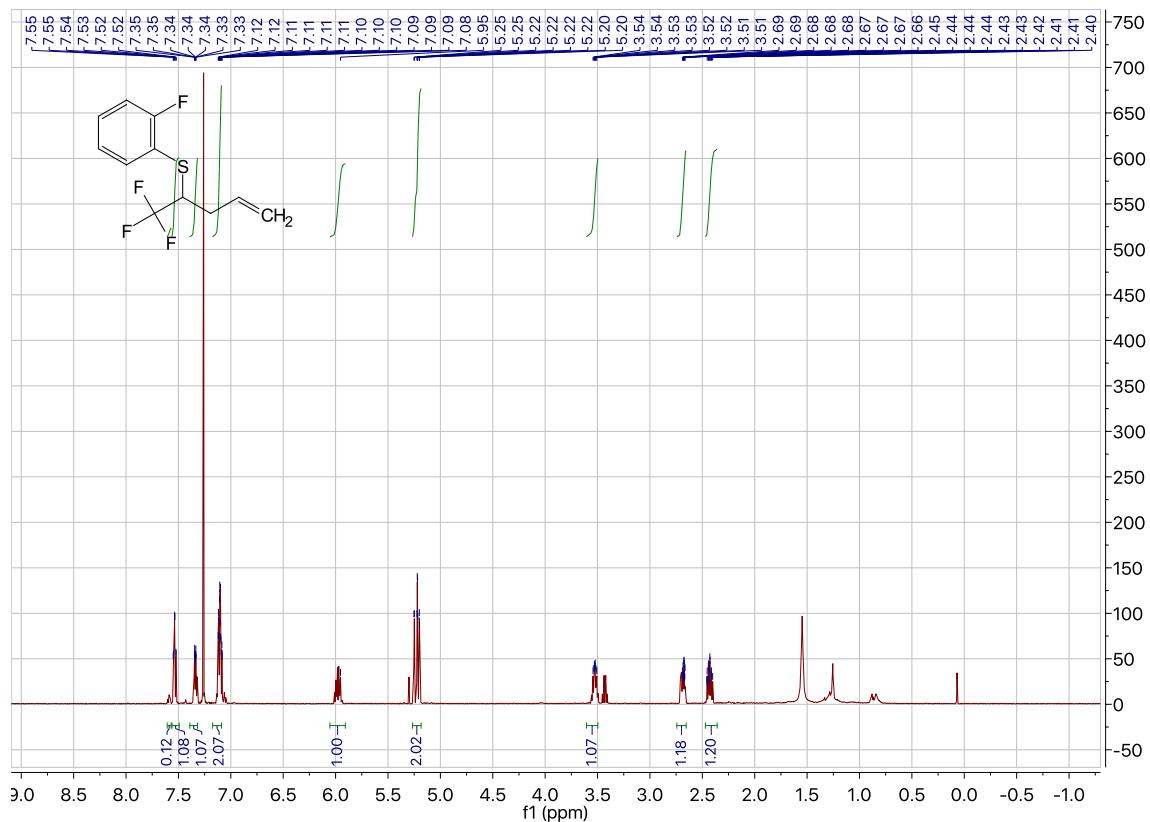


$^{19}\text{F}$ -NMR (564 MHz,  $\text{CDCl}_3$ )

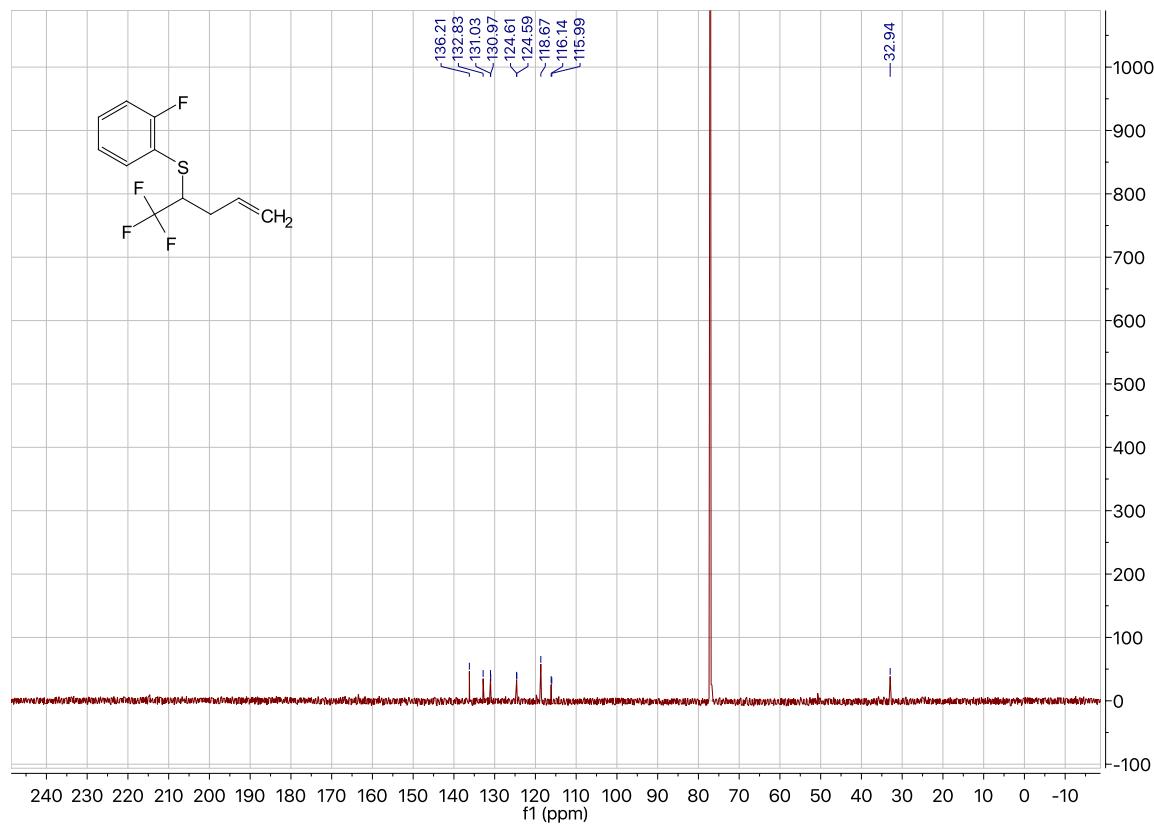


### compound: **9d**

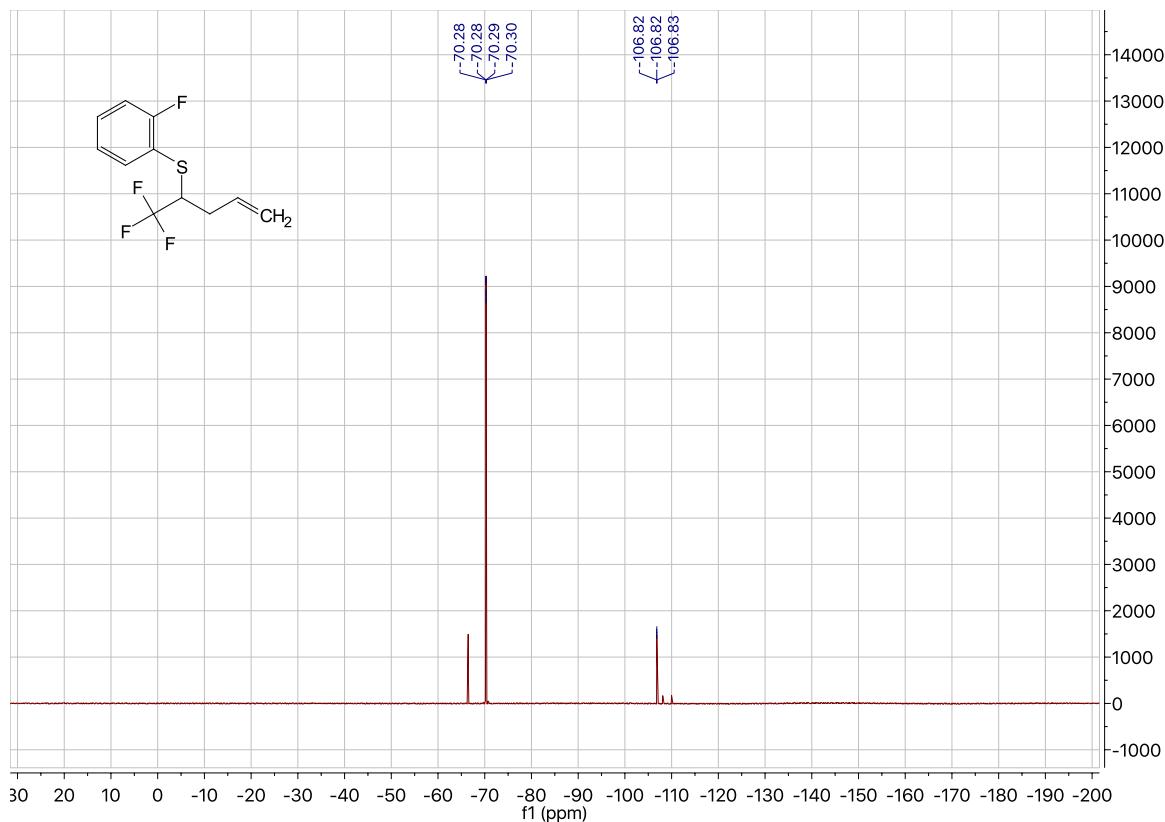
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

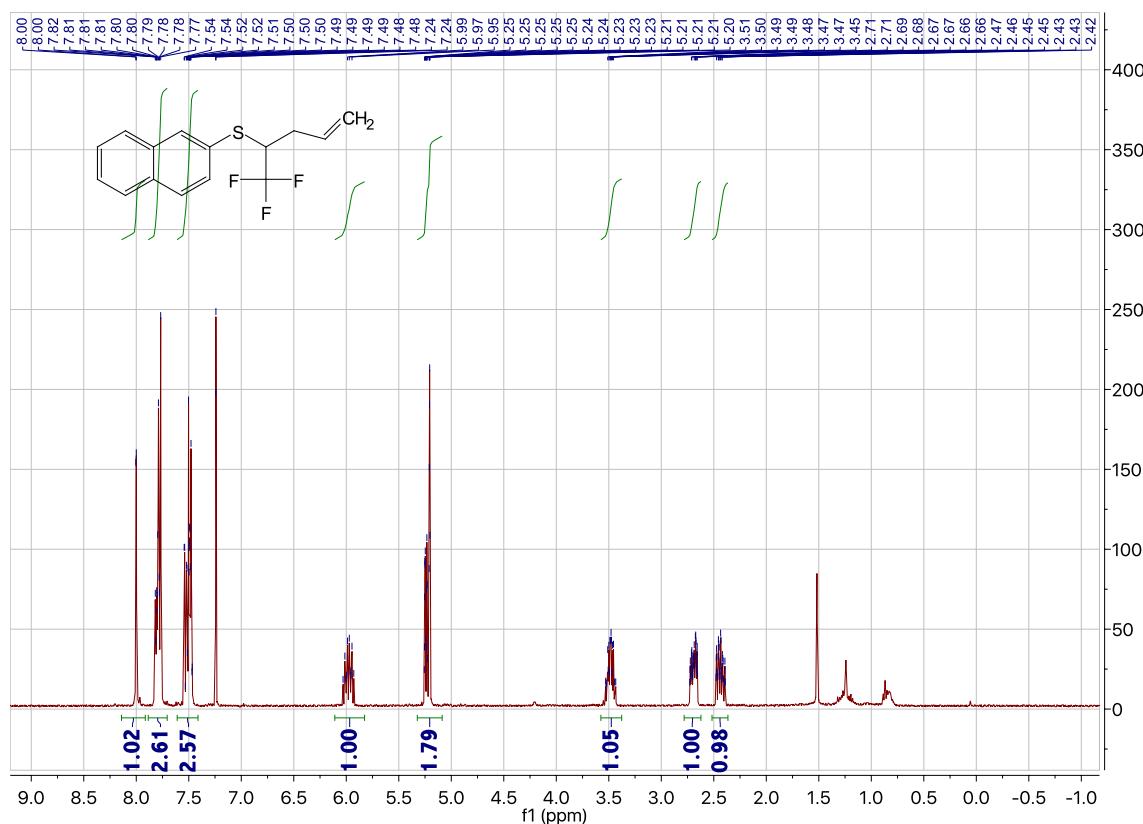


<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>)

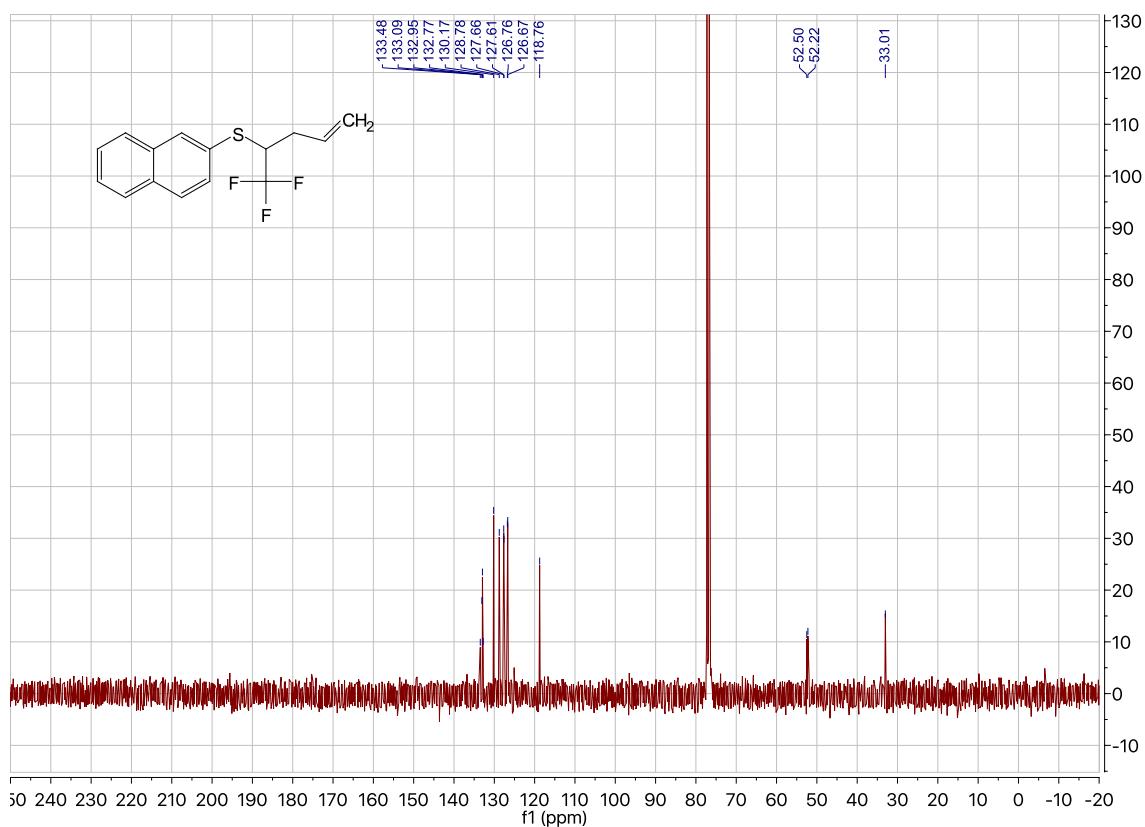


compound: 9e

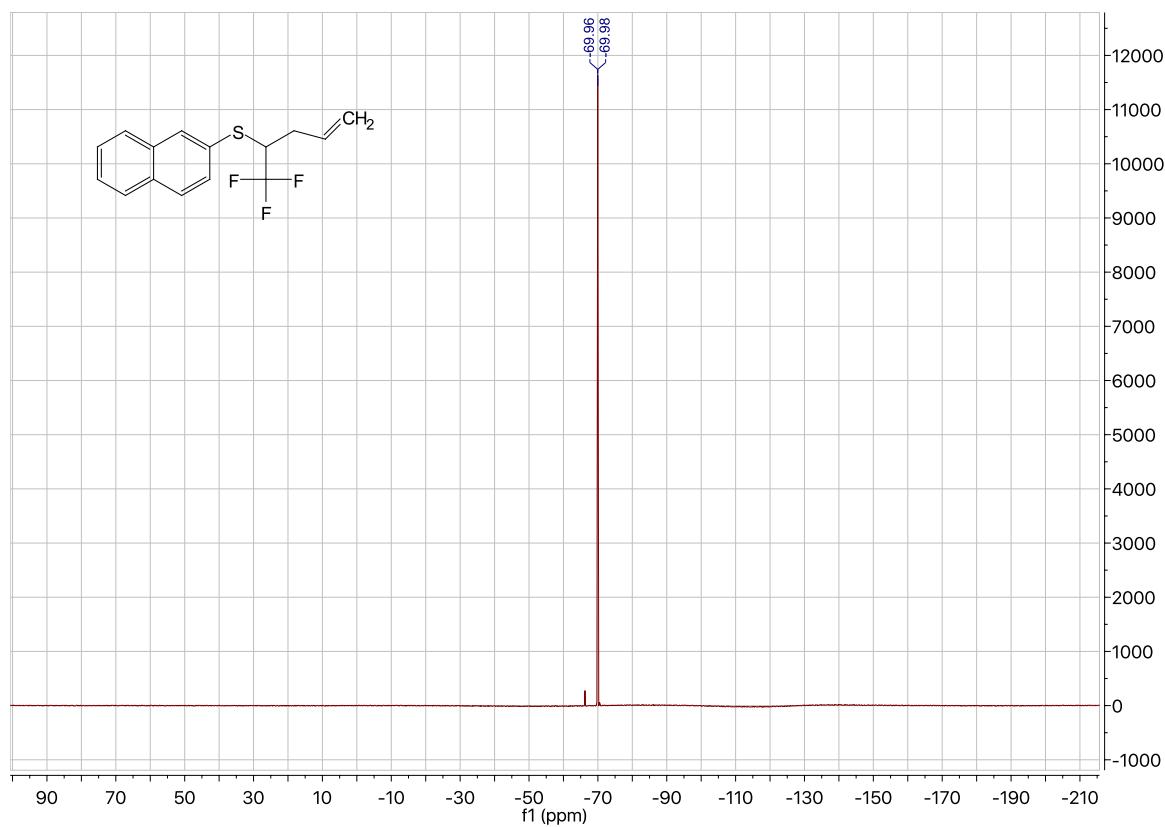
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>)

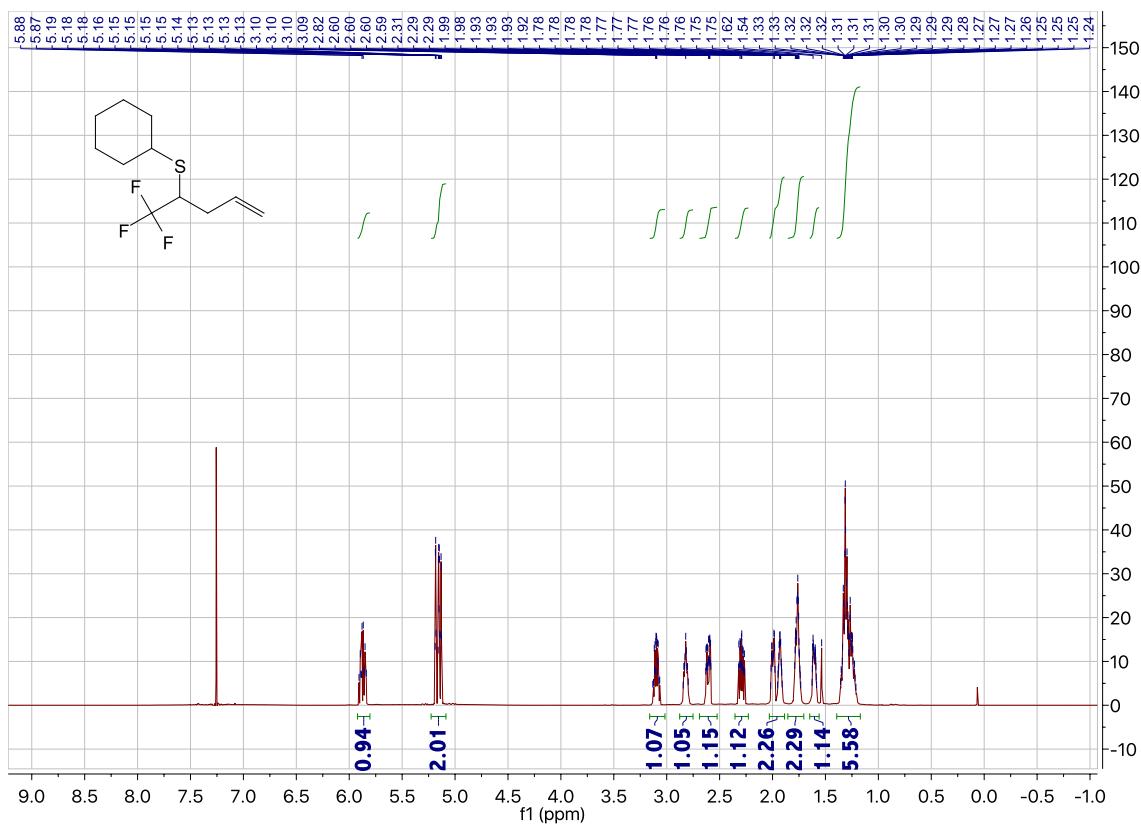


<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>)

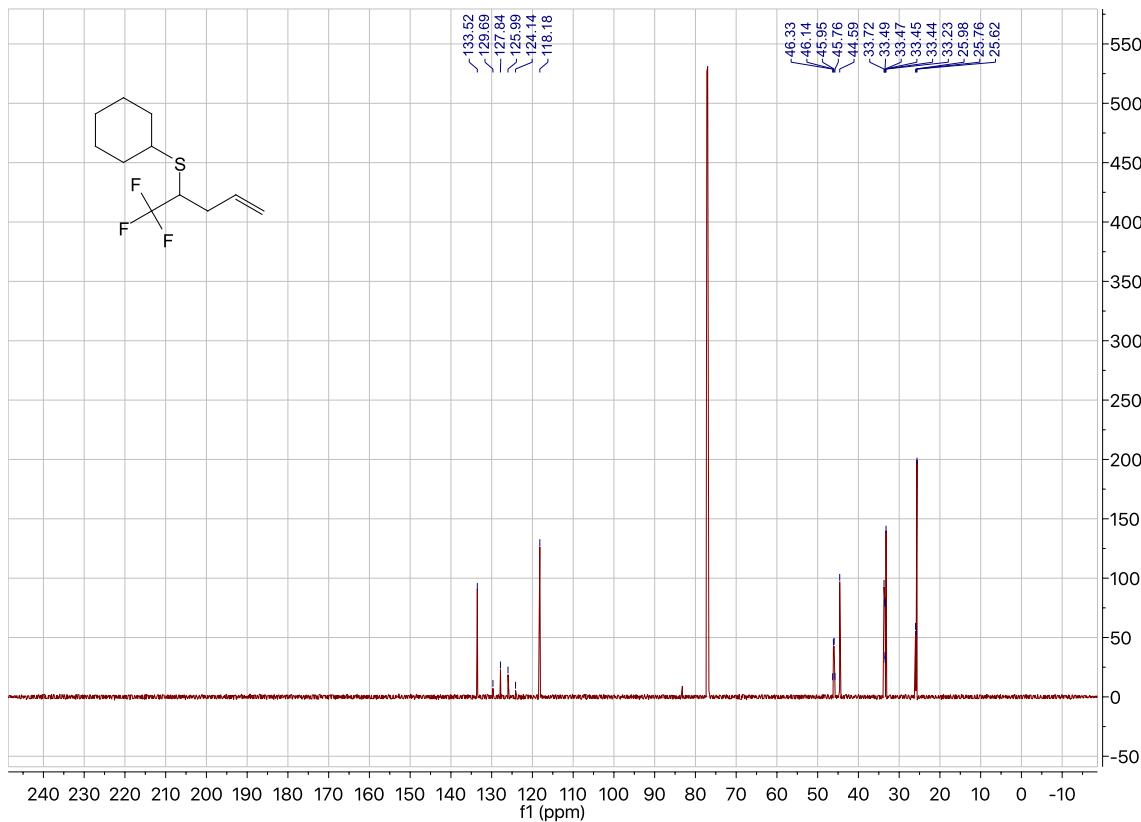


**compound: 9f**

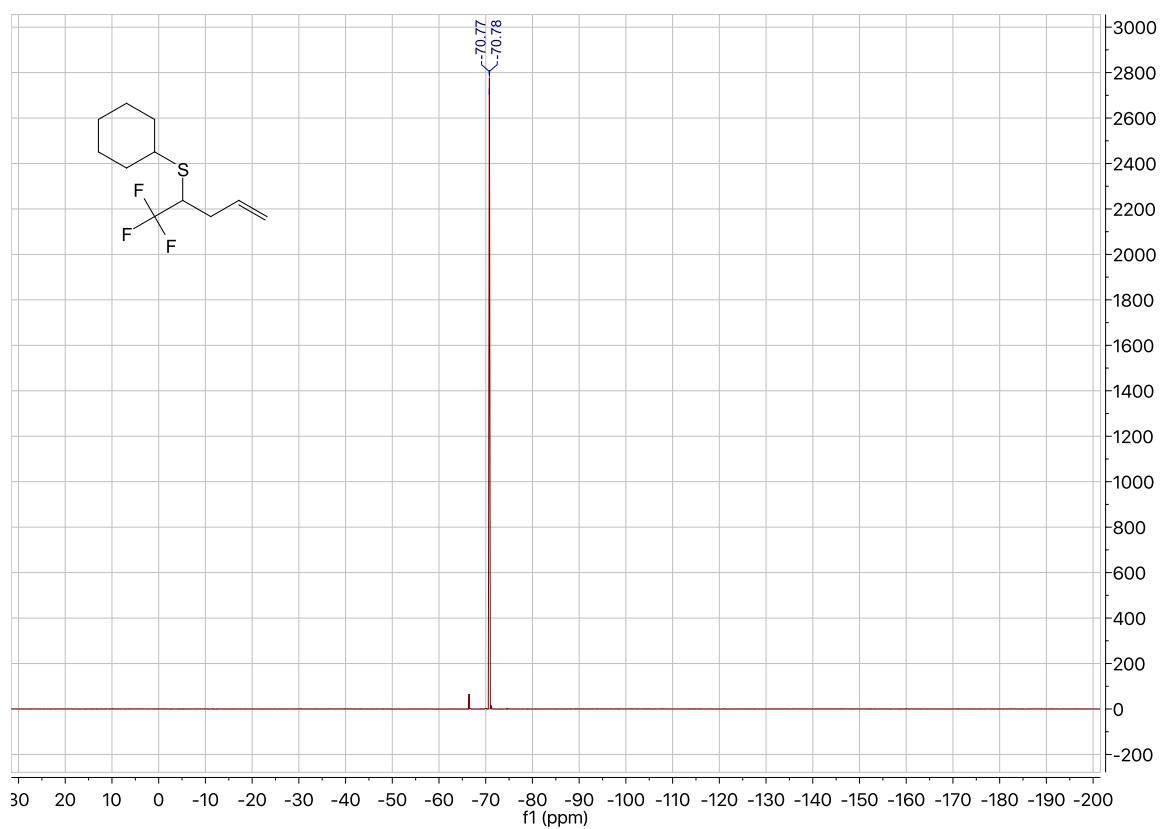
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

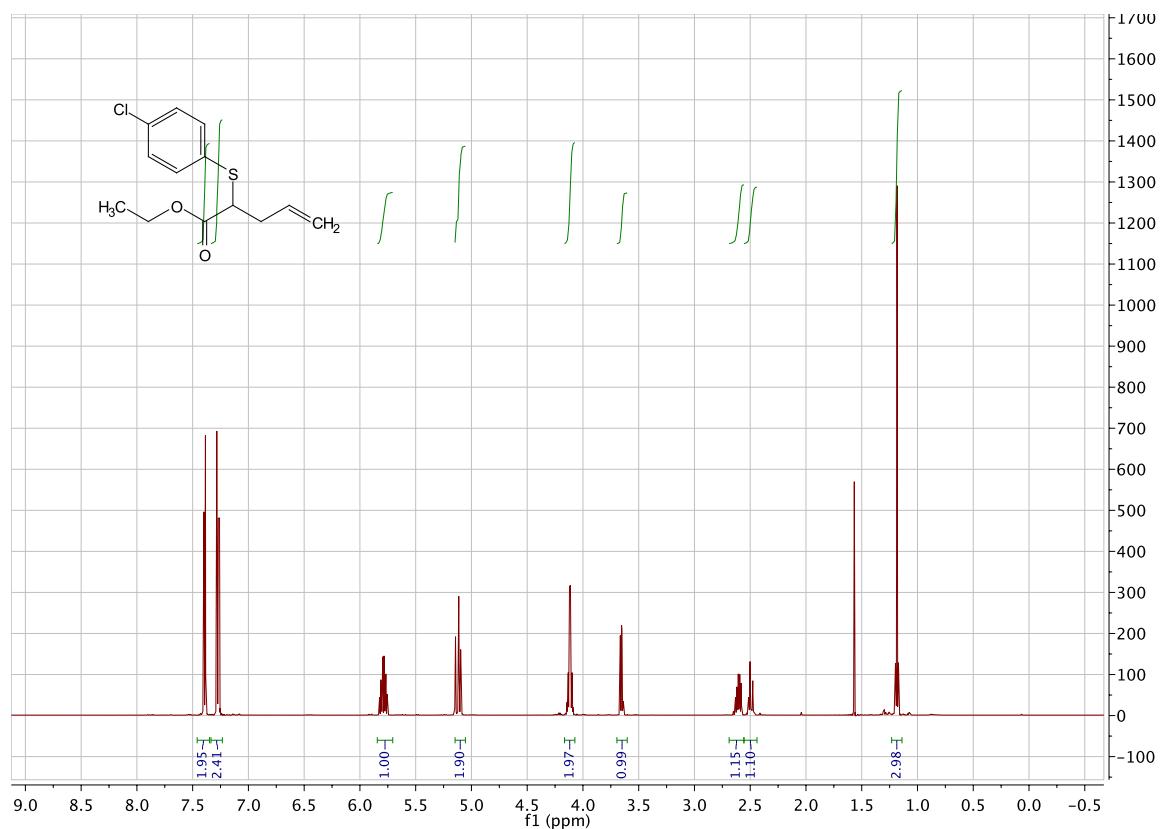


<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>)

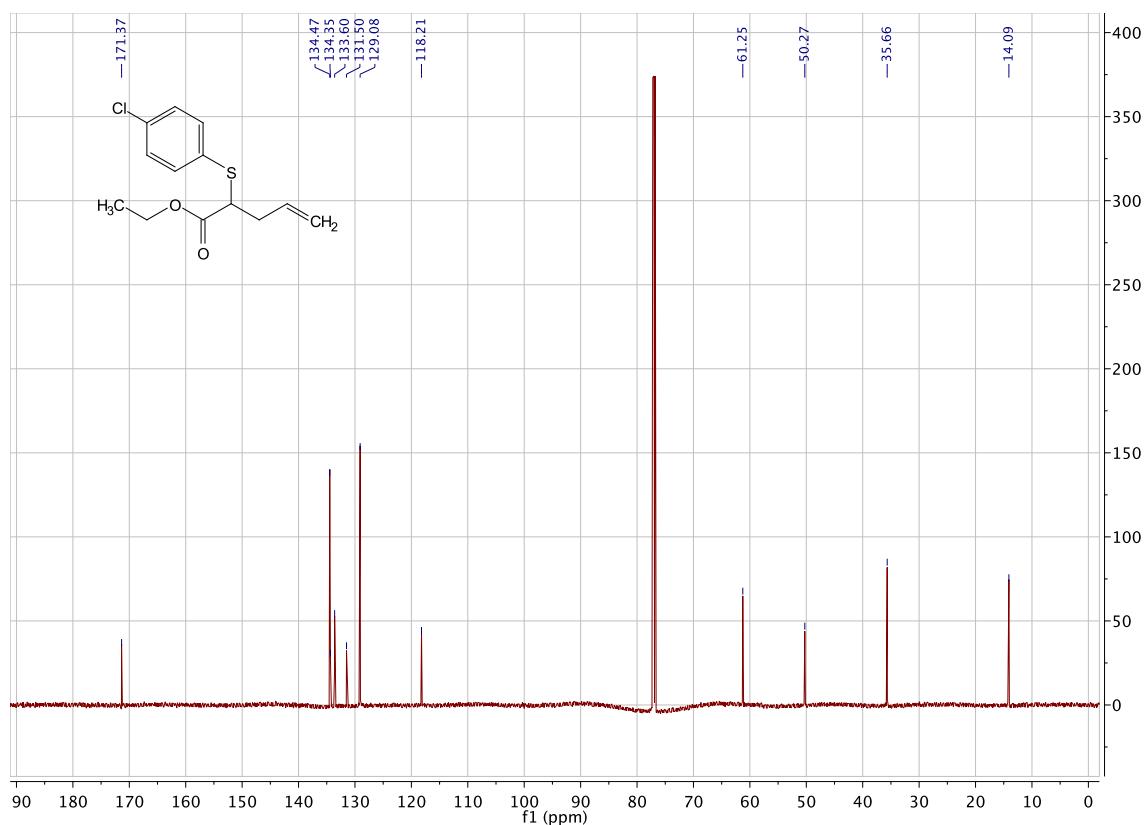


compound: 9g

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

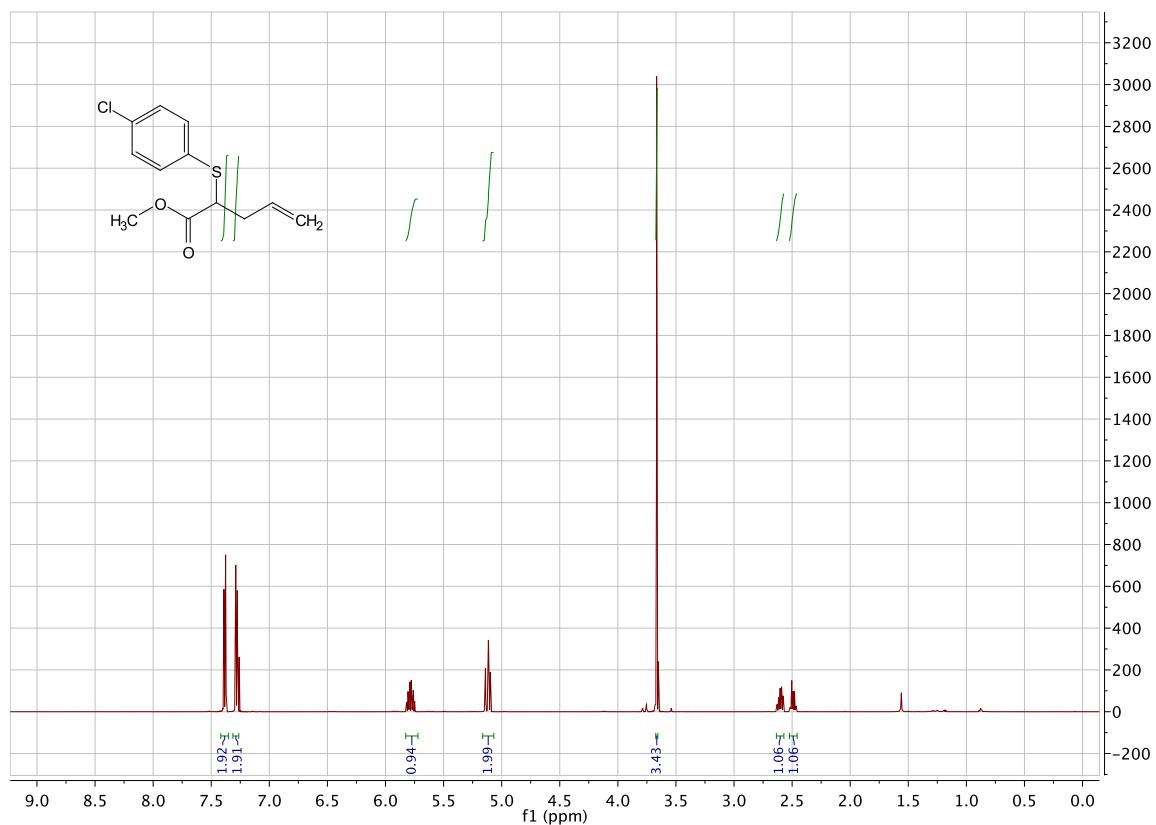


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

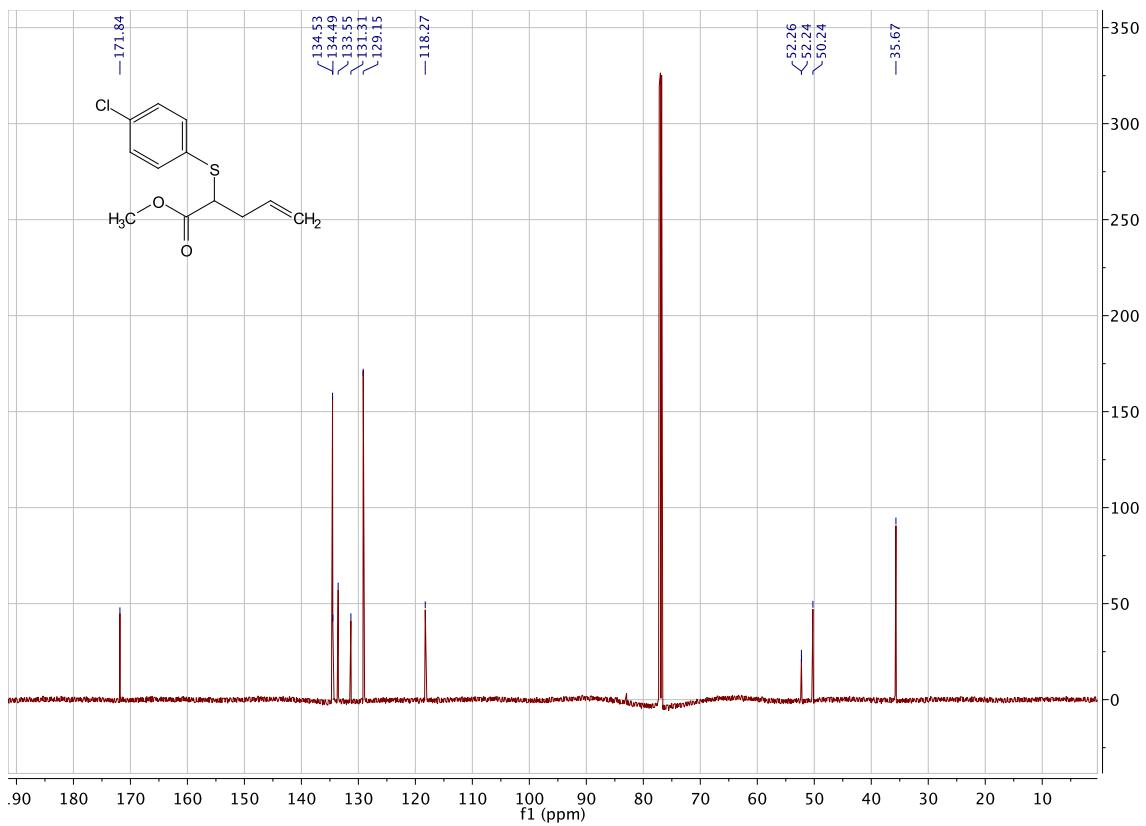


compound: 9h

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

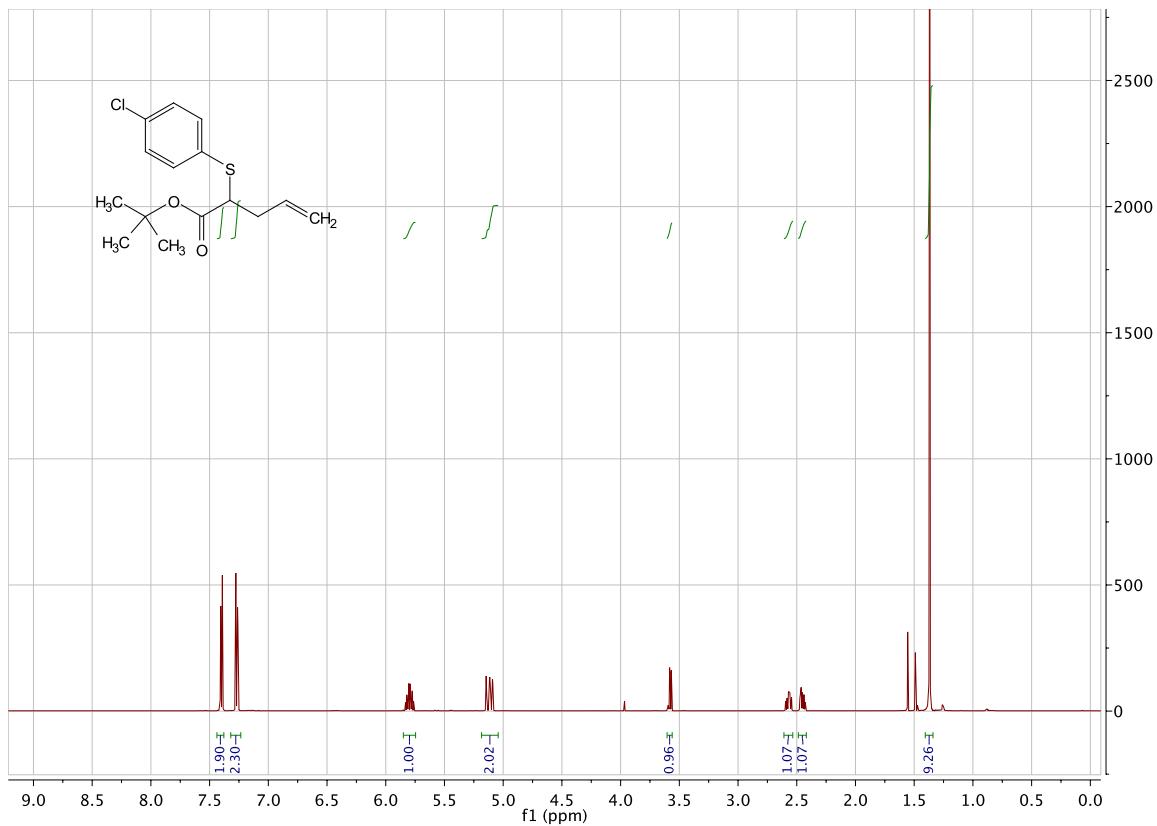


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

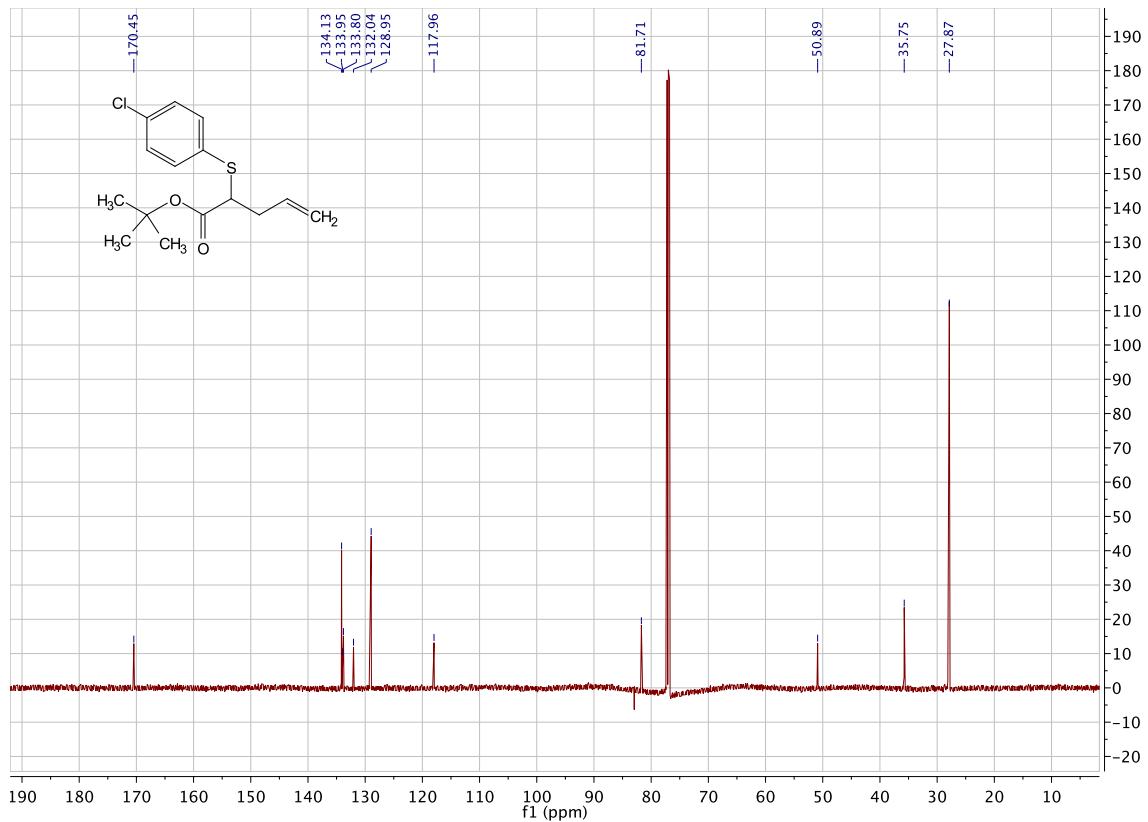


compound: 9i

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)

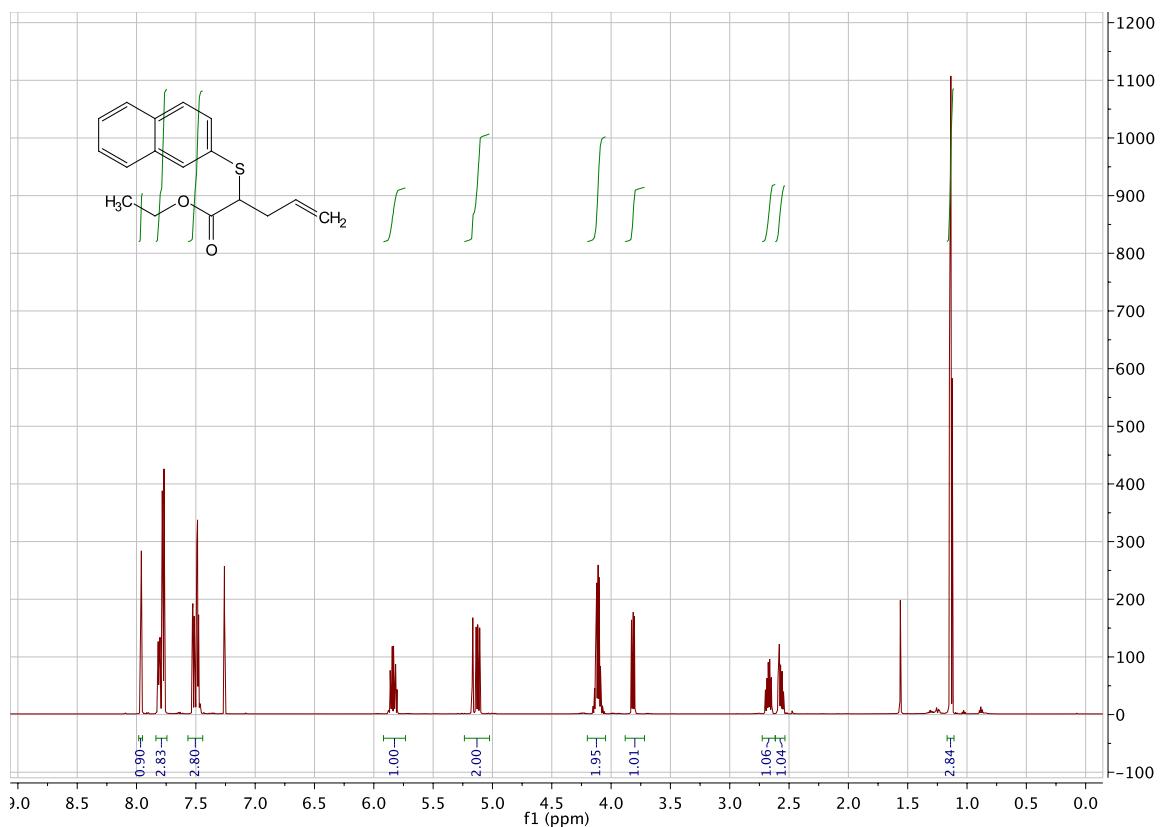


<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)



compound: 9j

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)

