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Supporting information

The α-alkylation of Carbonyl Sulfoxonium Ylides: Studies and Applications in the Synthesis of New Sulfur Heterocycles

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1 General Information

Commercially available reagents were used without further purification unless otherwise specified. All solvents were dried and distilled prior to use according to the standard procedures. Reactions were stirred magnetically and conducted in flame- or oven-dried glassware equipped with tightly fitted rubber septa and under an ultra-purified argon (>99.999%) atmosphere, unless otherwise specified. Temperatures above room temperature were maintained by use of a mineral oil bath heated on a hotplate.

Microwave experiments were performed in a microwave synthesis reactor (AntonPaar Monowave 300), powers from 0 to 850 W, and pressures from 0 to 30 bar, using sealed glass vials (2 mL) equipped with a snap cap and a silicon septum.

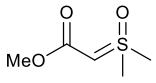
Reactions were monitored by thin-layer chromatography (TLC) employing Merck silica gel 60 F_{254} precoated plates (0.25 mm). Column flash chromatography was performed using silica gel 601 (particle size 0.063−0.210 mm) or using Biotage IsoleraTM Prime (Snap Ultra 10 g). All of the yields refer to isolated products after column chromatography.

^{1}H NMR spectra were recorded on 400 (Agilent Technologies, 400/54 Premium Shielded) or 500 MHz (Agilent Technologies, 500/54 Premium Shielded) spectrometers and the chemical shifts (δ) are reported in parts per million relative to tetramethylsilane as an internal standard or residual solvents from $CDCl_3$ (7.26 ppm) or dimethyl sulfoxide (DMSO)-d_6 (2.50 ppm). ^{13}C NMR spectra were recorded on 100 MHz or 125 MHz spectrometers, and chemical shifts (δ) are given from $CDCl_3$ (77.0 ppm) or DMSO-d_6 (39.5). Infrared spectra were obtained using Fourier-transform infrared spectroscopy (FT-IR) at 4.0 cm^{-1} resolution (Bruker, model ALPHA) and are reported in wavenumbers. Melting points were determined using a digital melting point apparatuss (Fisatom, model 430D). High-resolution mass spectra (HRMS) were recorded using a UPLC H-class liquid chromatograph connected to a Waters Xevo G2-XS QToF mass spectrometer via an electrospray ionization (ESI) interface.

2 General procedure A: Synthesis of carbonyl sulfoxonium ylides

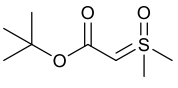
The synthesis of carbonyl sulfoxonium ylides was performed through a modified procedure[1-5]. In a 125 mL flame-dried round bottom flask attached to a reflux condenser, under argon atmosphere, 3.0 g of potassium *tert*-butoxide (27.2 mmol, 4.0 equiv) and 27.0 mL of anhydrous THF were added. Then, 4.48 g of trimethylsulfoxonium iodide (20.4 mmol, 3.0 equiv) was added in one portion. The suspension was heated at reflux for 2 h. After this time, the mixture was cooled at 0 °C, followed by the slow addition of the appropriate benzoyl chloride, chloroformate or carbonate (6.8 mmol, 1.0 equiv). The reaction mixture temperature was slowly increased to room temperature, and this mixture was stirred for an additional 3 h (or overnight for carbonates). Then, the solvent was removed on a rotary evaporator. After that, 70 mL of water was added, and the product was extracted with a 3:1 CH_2Cl_2/i-PrOH mixture (8 × 20 mL). The organic phase was washed with brine (3 × 10 mL) and dried over Na_2SO_4, and the solvent was removed on a rotary evaporator. The crude material was purified by solubilization in the minimal amount of hot EtOAc (10−15 mL), followed by the slow addition of 15 mL of hexanes. The solid was filtered and washed with two portions of a 2:1 mixture of hexanes/EtOAc (2 × 10 mL), furnishing the respective sulfoxonium ylide. For compounds where was not possible to obtain a precipitate after evaporation of all volatiles, the crude mixture was purified by flash chromatography (Eluent MeOH/EtOAc 0-5%).

Methyl 2-(dimethyl(oxo)- λ⁶-sulfaneylidene)acetate (1a)



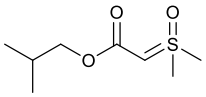
Prepared according to the general procedure A from dimethyl carbonate (0.613 g, 6.8 mmol), potassium *tert*-butoxide (3.05 g, 27.2 mmol, 4.0 equiv), and trimethylsulfoxonium iodide (4.49 g, 20.4 mmol, 3.0 equiv). Yield: 35% (0.357 g, 2.38 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) 3.96 (s, 1H), 3.63 (s, 3H), 3.39 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) 167.5, 55.2, 50.2, 42.4. In good agreement with previously reported data[3].

***t*-Butyl-2-(dimethyl(oxo)- λ⁶-sulfanylidene)acetate (1b)**



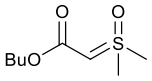
Prepared according to the general procedure A from di-*tert*-butyl dicarbonate (1.48 g, 6.8 mmol), potassium *tert*-butoxide (3.05 g, 27.2 mmol, 4.0 equiv), and trimethylsulfoxonium iodide (4.49 g, 20.4 mmol, 3.0 equiv). Yield: 67% (0.88 g, 4.6 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 1H), 3.36 (s, 6H), 1.47 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 78.6, 56.6, 42.4, 28.9. In good agreement with previously reported data[3].

Isobutyl 2-(Dimethyl(oxo)- λ^6-sulfanylidene)-3-oxo-3- (phenylamino)propanoate (1c)



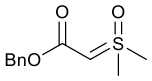
Prepared according to the general procedure A from isobutyl chloroformate (0.93 g, 6.8 mmol), potassium *tert*-butoxide (3.05 g, 27.2 mmol, 4.0 equiv), and trimethylsulfoxonium iodide (4.49 g, 20.4 mmol, 3.0 equiv). Yield: 73% (0.96 g, 5.0 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 1H), 3.82 (d, *J* = 6.7 Hz, 2H), 3.39 (s, 6H), 1.91 (hept, *J* = 6.6 Hz, 1H), 0.93 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 69.2, 55.1, 42.5, 28.2, 19.4. In good agreement with previously reported data[5].

Butyl 2-(dimethyl(oxo)-λ^6-sulfanylidene)acetate (1d)



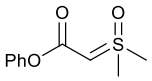
Prepared according to the general procedure A from butyl chloroformate (0.92 g, 6.8 mmol), potassium *tert*-butoxide (3.05 g, 27.2 mmol, 4.0 equiv), and trimethylsulfoxonium iodide (4.49 g, 20.4 mmol, 3.0 equiv). Yield: 37% (0.48 g, 2.5 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.03 (s, 2H), 3.95 (s, 1H), 3.39 (s, 6H), 1.60 (s, 2H), 1.38 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 62.7, 55.1, 42.4, 31.3, 19.3, 13.9. In good agreement with previously reported data[2].

Benzyl 2-(dimethyl(oxo)- λ^6-sulfanylidene) acetate (1e)



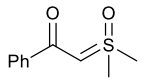
Prepared according to the general procedure A from benzyl chloroformate (1.16 g, 6.8 mmol), potassium *tert*-butoxide (3.05 g, 27.2 mmol, 4.0 equiv), and trimethylsulfoxonium iodide (4.49 g, 20.4 mmol, 3.0 equiv). Yield: 55% (0.85 g, 3.8 mmol). Yellow solid. Rf= 0.45 (2% MeOH/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.32 (m, 4H), 7.30-7,27 (m, 1H), 5.10 (s, 2H), 4.03 (s, 1H), 3.35 (s, 6H). ^{13}C NMR (126 MHz, CDCl3) d 166.9, 137.4, 128.5, 128.0, 127.7, 64.5, 55.5, 42.3. In good agreement with previously reported data[13].

Phenyl 2-(dimethyl(oxo)- λ^6-sulfanylidene) acetate (1f)



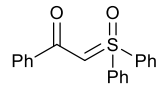
Prepared according to the general procedure A from phenyl chloroformate (1.06 g, 6.8 mmol), potassium *tert*-butoxide (3.05 g, 27.2 mmol, 4.0 equiv), and trimethylsulfoxonium iodide (4.49 g, 20.4 mmol, 3.0 equiv). Yield: 60% (0.86 g, 4.1 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.21 – 7.13 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 4.16 (s, 1H), 3.40 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) d 165.7, 151.5, 129.2, 125.0, 122.3, 55.8, 42.4. In good agreement with previously reported data[3].

2-(Dimethyl(oxo)- λ^6-sulfanylidene)-1-phenylethan-1-one (1g)



Prepared according to the general procedure A from benzyl chloride (0.96 g, 6.8 mmol), potassium *tert*-butoxide (3.05 g, 27.2 mmol, 4.0 equiv), and trimethylsulfoxonium iodide (4.49 g, 20.4 mmol, 3.0 equiv). Yield: 75% (1.0 g, 5.1 mmol). RMN ^{1}H (500 MHz, $CDCl_3$) δ 7.80-7.79 (m, 2H), 7.43-7.37 (m, 3H), 4,99 (s, 1H), 3,50 (s, 6H). RMN ^{13}C (126 MHz, $CDCl_3$) δ 182.3, 138.8, 130.7, 126.5, 68.4, 42,4. In good agreement with previously reported data[2].

2-(oxodiphenyl-λ^6-sulfaneylidene)-1-phenylethan-1-one (1h)



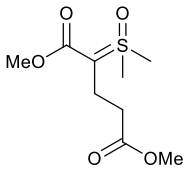
Diphenylmethylsulfoxonium tetrafluoroborate was prepared from the alkylation of diphenylsulfide with trimethyloxonium tetrafluoroborate followed by oxidation with *m*-CPBA[6-7]. Then, the carbonyl sulfoxonium ylide was prepared according to a modification of the general procedure A. Diphenylmethylsulfoxonium tetrafluoroborate (0.608 g, 2 mmol, 3.0 equiv) was added in a single portion in a 10 mL round-bottom flask coupled to a reflux condenser, under argon atmosphere, containing potassium *tert*-butoxide (0.298 g, 2.66 mmol, 4.0 equiv) and 3.0 mL of anhydrous THF. The suspension was heated to reflux for 2 h, cooled to 0 °C for the slow addition of benzoyl chloride in anhydrous THF (0.0942 g, 0.67 mmol, 1 equiv in 1 mL of THF), and stirred at room temperature overnight. Then, the reaction mixture was filtered on celite (washed with DCM) and the solvent was removed on a rotary evaporator. The product was purified using Biotage IsoleraTM Prime (Snap Ultra 10 g, Eluent EtOAc/Hex). White solid (0.162 g, 75%), m.p. = 141-143 °C, Rf = 0.29 (EtOAc:Hex 1:1). RMN ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11-8.03 (m, 4H), 7.92-7.85 (m, 2H), 7.62-7.52 (m, 6H), 7.47-7.35 (m, 3H), 5.45 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.4, 139.0, 138.3, 133.4, 131.1, 129.9, 128.2, 127.7, 127.2, 67.7. IR ν_{max} (cm^{-1}): 3062, 1594, 1554, 1475, 1363, 1178, 1080, 893, 754, 710. HRMS (ESI-TOF): calculated for $C_{20}H_{17}O_2S$ [M+H$^+$]: 321.0949, found: 321.0953.

3 General Procedure B: Synthesis of α-alkyl carbonyl sulfoxonium ylides

To a 2 mL glass microwave vial equipped with a magnetic stir bar was added sulfoxonium ylide (0.256 mmol, 1 equiv), capped with a rubber septum and filled with ultra-purified argon (99.999%). Then, dry THF (0.5 mL), DBU (19.1 µL, 0.128 mmol, 0.5 equiv), and Michael acceptor (0.768 mmol, 3 equiv) were added. The rubber septum was removed and the microwave vial was quickly capped with a Teflon microwave cap. The reaction was heated to 150 °C for 105 min. Then, the solvent was removed under reduced pressure to furnish a crude product that was

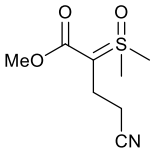
purified by flash column chromatography, using silica gel 60 (200-400 mesh) as a stationary phase (Eluent MeOH/EtOAc 0-5%) or using Isolera Biotage (Snap Ultra 10 g, Eluent EtOAc/ Hex).

Dimethyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)pentanedioate (2a)



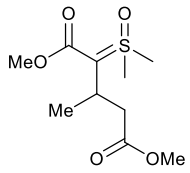
Prepared according to the general procedure B from sulfoxonium ylide **1a** (0.0384 g, 0.256 mmol) and methyl acrylate (0.0661 g, 69.6 µL, 0.768 mmol). White solid (37.3 mg, 61% yield), m.p. = 40-41 °C, Rf = 0.44 (5% MeOH:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 3.62 (s, 3H), 3.38 (s, 6H), 2.60 (t, *J* = 6.8 Hz, 2 H), 2.45 (t, *J* = 6.8 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1, 167.1, 51,3, 50,0, 43,4, 35,9, 19,3. IR ν_{max} (cm^{-1}): 3013, 2942, 1727, 1614, 1435, 1332, 1261, 1138, 1090, 1016, 984, 826, 752, 608. HRMS (ESI-TOF): calculated for $C_9H_{17}O_5S$ [M+H]$^+$: 237.0797, found: 237.0800.

Methyl 4-cyano-2-(dimethyl(oxo)-λ^6-sulfaneylidene)butanoate (2b)



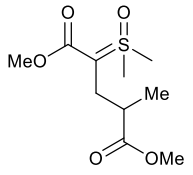
Prepared according to the general procedure B from sulfoxonium ylide **1a** (0.0384 g, 0.256 mmol) and acrylonitrile (0.0408 g, 50.3 µL, 0.768 mmol). White solid (34.9 mg, 67% yield), m.p. = 51-53 °C, Rf = 0.52 (5% MeOH:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.62 (s, 3H), 3.41 (s, 6H), 2.61 (t, *J* = 6.3 Hz, 2 H), 2.48 (t, *J* = 6.3 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1, 167.1, 51.3, 50.0, 43.4, 35.9, 19.3. IR ν_{max} (cm^{-1}): 3012, 2923, 2856, 2318, 2241, 1616, 1432, 1337, 1306, 1147, 1091, 1015, 977, 933, 799, 750, 684. HRMS (ESI-TOF): calculated for $C_8H_{14}NO_3S$ [M+H]$^+$: 204.0694, found: 204.0702.

Dimethyl 2-(dimethyl(oxo)- λ^6-sulfaneylidene)-3-methylpentanedioate (2c)



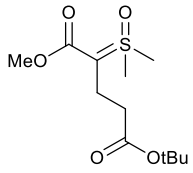
Prepared according to the general procedure B from sulfoxonium ylide **1a** (0.0384 g, 0.256 mmol) and methyl crotonate (0.0769 g, 81.3 µL, 0.768 mmol). White solid (7.7 mg, 12% yield), m.p. = 78-79 °C, Rf = 0.43 (5% MeOH:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 3H), 3.61 (s, 3H), 3.37 (s, 3H), 3.32 (s, 3H), 3.12 (m, 1H), 2.84 (m, 1H), 2.41(dd, *J* = 15.4, 5.4 Hz, 1H), 1.22 (d, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 167.1, 51.4, 49.9, 44.5, 43.2, 40.6, 29.8, 26.4, 22,4. IR ν_{max} (cm^{-1}): 2938, 1724, 1614, 1438, 1328, 1252, 1165, 1111, 1020, 937, 755. HRMS (ESI-TOF): calculated for $C_{10}H_{19}O_5S$ [M+H]$^+$: 251.0953, found: 251.0957.

Dimethyl 2-(dimethyl(oxo)- λ^6-sulfaneylidene)-4-methylpentanedioate (2d)



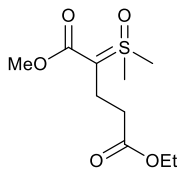
Prepared according to the general procedure B from sulfoxonium ylide **1a** (0.0384 g, 0.256 mmol) and methyl metacrylate (0.0769 g, 81.8 µL, 0.768 mmol). White solid (28.4 mg, 44% yield), m.p. = 39-40 °C, Rf = 0.41 (5% MeOH:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 3H), 3.60 (s, 3H), 3.37 (s, 3H), 3.35 (s, 3H), 2.60 (m, 2H), 2.45 (m, 1H), 1.12 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.1, 174.1, 51.4, 50.0, 43.4, 41.1, 35.9, 28.0, 19.3, 16.3. IR ν_{max} (cm^{-1}): 3013, 2950, 1725, 1612, 1437, 1337, 1258, 1149, 1116, 1018, 982, 938, 826, 756, 687. HRMS (ESI-TOF): calculated for $C_{10}H_{19}O_5S$ [M+H]$^+$: 251.0953, found: 251.0955.

5-(*tert*-butyl) 1-methyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)pentanedioate (2e)



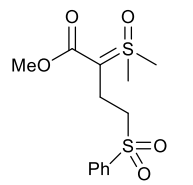
Prepared according to the general procedure B from sulfoxonium ylide **1a** (0.0384 g, 0.256 mmol) and *tert*-butyl acrylate (0.0984 g, 112.5 µL, 0.768 mmol). Yellow solid (34.9 mg, 49% yield), m.p. = 46-48 °C, Rf = 0.42 (5% MeOH:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.61 (s, 3H), 3.37 (s, 6H), 2.54 (d, J = 7.0 Hz, 2H), 2.35 (d, J = 7.0 Hz, 2H), 1.42 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 167.0, 80.0, 50.0, 43.5, 42.6, 37.1, 28.1, 19.5. IR ν_{max} (cm^{-1}): 2975, 2932, 1719, 1616, 1437, 1335, 1141, 1090, 1018, 982, 939, 847, 755. HRMS (ESI-TOF): calculated for $C_{12}H_{23}O_5S$ [M+H]$^+$: 279.1266, found: 279.1269.

5-ethyl 1-methyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)pentanedioate (2f)



Prepared according to the general procedure B from sulfoxonium ylide **1a** (0.0384 g, 0.256 mmol) and ethyl acrylate (0.0769 g, 81.8 µL, 0.768 mmol). White solid (38.4 mg, 60% yield), m.p. = 95-97 °C, Rf = 0.38 (5% MeOH:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.11 (q, *J* = 7.1 Hz, 2H), 3.37 (s, 6H), 2.56 (t, *J* = 6,4 Hz, 2H), 2.45 (t, *J* = 6,4 Hz, 2H), 1.47 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 166.8, 78.2, 60.1, 43.7, 35.9, 29.0, 27.8, 20.1, 14.3. IR ν_{max} (cm^{-1}): 2974, 2926, 1725, 1612, 1446, 1349, 1253, 1133, 1085, 1018, 978, 935, 852, 742. HRMS (ESI-TOF): calculated for $C_{10}H_{19}O_5S$ [M+H]$^+$: 251.0953, found: 251.0958.

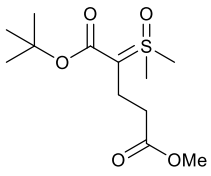
Methyl-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-(phenylsulfonyl)butanoate (2g)



Prepared according to the general procedure B from sulfoxonium ylide **1a** (0.0384 g, 0.256 mmol) and phenyl vinyl sulfone (0.129 g, 0.768 mmol). Pale brown solid (24.7 mg, 30% yield), m.p. = 124-126 °C, Rf = 0.19 (EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98-7.91 (m, 2H), 7.68-7.62 (m, 1H), 7.61-7.53 (m, 2H), 3.58

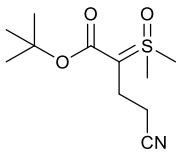
(s, 3H), 3.37 (s, 6H), 3.25 (t, J = 7.2 Hz, 2H), 2.67 (t, J = 7.2 Hz, 2H).[13]C NMR (126 MHz, $CDCl_3$) δ 171.0, 139.4, 133.5, 129.1, 128.1, 56.8, 50.1, 43.5. IR ν_{max} (cm^{-1}): 3015, 2927, 1731, 1621, 1441, 1340, 1285, 1236, 1204, 1145, 1084, 1021, 746. HRMS (ESI-TOF): calculated for $C_{13}H_{19}O_5S_2$ $[M+H]^+$: 319.0674, found: 319.0678.

1-(*tert*-butyl) 5-methyl 2-(dimethyl(oxo)- λ⁶-sulfaneylidene)pentanedioate (2h)



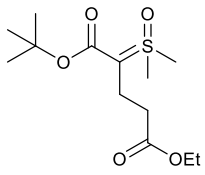
Prepared according to the general procedure B from sulfoxonium ylide **1b** (0.0492 g, 0.256 mmol) and methyl acrylate (0.0661 g, 69.6 µL, 0.768 mmol). Brownish solid (42.8 mg, 61% yield), m.p. = 64-65 °C, Rf = 0.40 (5% MeOH:EtOAc). [1]H NMR (500 MHz, $CDCl_3$) δ 3.64 (s, 3H), 3.35 (s, 6H), 2.55 (d, J = 6.5 Hz, 2H), 2.45 (d, J = 6.5 Hz, 2H), 1.45 (s, 9H). [13]C NMR (126 MHz, $CDCl_3$) δ 174.2, 166.7, 78.2, 51.3, 43.7, 42.6, 35.7, 28.9, 20.2. IR ν_{max} (cm^{-1}): 2968, 2930, 1729, 1614, 1440, 1348, 1254, 1131, 1085, 1015, 978, 935, 849, 744, 618. HRMS (ESI-TOF): calculated for $C_{12}H_{23}O_5S$ $[M+H]^+$: 279.1266, found: 279.1266.

***tert*-butil-4-ciano-2-(dimetil(oxo)-λ⁶-sulfanoylideno)butanoato (2i)**



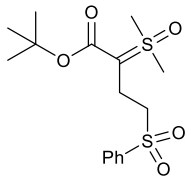
Prepared according to the general procedure B from sulfoxonium ylide **1b** (0.0492 g, 0.256 mmol) and acrylonitrile (0.0408 g, 50.3 µL, 0.768 mmol). Yellow solid (40.2 mg, 64% yield), m.p. = 107-108 °C, Rf = 0.68 (5% MeOH:EtOAc). [1]H NMR 3.41 (s, 6H), 2.58 (m, 2H), 2.49 (m, 2H), 1.47 (s, 9H). [13]C NMR (101 MHz, $CDCl_3$) δ 166.8, 120.6, 78.5, 56.2, 44.0, 28.9, 20.0, 19.5. IR ν_{max} (cm^{-1}): 3009, 2974, 2924, 2444, 1603, 1389, 1314, 1246, 1184, 1140, 1089, 1019, 981, 946, 901, 850, 807, 761, 734, 689, 605. HRMS (ESI-TOF): calculated for $C_{11}H_{19}NO_3SNa$ $[M+Na]^+$: 268.1086, found: 268.0983.

1-(*tert*-butyl) 5-ethyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)pentanedioate (2j)



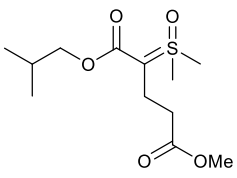
Prepared according to the general procedure B from sulfoxonium ylide **1b** (0.0492 g, 0.256 mmol) and ethyl acrylate (0.0769 g, 81.8 µL, 0.768 mmol). White solid (45.4 mg, 61% yield), m.p. = 70-72 °C, Rf = 0.35 (5% MeOH:EtOAc). [1]H NMR δ 4.11 (d, *J* = 7.1 Hz, 2H), 3.37 (s, 6H), 2.56 (t, *J* = 6.4 Hz, 2H), 2.45 (t, *J* = 6.4 Hz, 2H), 1.47 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H). [13]C NMR (126 MHz, $CDCl_3$) δ 173.9, 166.8, 78.2, 60.1, 43.7, 35.9, 29.0, 27.8, 20.1, 14.3. IR ν_{max} (cm^{-1}): 2974, 2926, 1612, 1446, 1349, 1253, 1133, 1085, 1018, 978, 935, 852, 742. HRMS (ESI-TOF): calculated for $C_{13}H_{25}O_5S$ $[M+H]^+$: 293.1417, found: 293.1425.

***tert*-butyl-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-(phenylsulfonyl)butanoate (2k)**



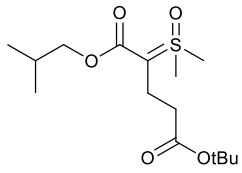
Prepared according to the general procedure B from sulfoxonium ylide **1b** (0.0492 g, 0.256 mmol) and phenyl vinyl sulfone (0.129 g, 0.768 mmol). Pale brown solid (23.5 mg, 25% yield), m.p. = 100-102 °C, Rf = 0.43 (EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 17.9 Hz, 2H), 3.35 (s, 6H), 3.25 (s, 2H), 2.62 (s, 2H), 1.39 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.27, 139.50, 133.59, 129.29, 128.28, 78.73, 56.96, 43.93, 29.03, 18.24. IR ν_{max} (cm^{-1}): 2972, 2927, 1616, 1448, 1342, 1250, 1142, 1016, 739, 690. HRMS (ESI-TOF): calculated for $C_{16}H_{25}O_5S_2$ $[M+H]^+$: 361.1143, found: 361.1137.

1-isobutyl 5-methyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)pentanedioate (2l)



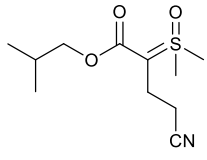
Prepared according to the general procedure B from sulfoxonium ylide **1c** (0.0492 g, 0.256 mmol) and methyl acrylate (0.0661 g, 69.6 µL, 0.768 mmol). White solid (35.5 mg, 58% yield), m.p. = 57-58 °C, Rf = 0.40 (EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78 (d, *J* = 6.3 Hz, 2H), 3.64 (s, 3H), 3.37 (s, 6H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.47 (t, *J* = 6.5 Hz, 2H), 1.96-1.88 (m, 1H), 0.92 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1, 68.9, 51.3, 43.5, 35.8, 28.2, 19.3. IR ν_{max} (cm^{-1}): 3015, 2958, 1729, 1611, 1437, 1312, 1141, 1087, 1017, 757. HRMS (ESI-TOF): calculated for $C_{12}H_{23}O_5S$ $[M+H]^+$ 279.1266, found 279.1272.

5-(*tert*-butyl) 1-isobutyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)pentanedioate (2m)



Prepared according to the general procedure B from sulfoxonium ylide **1c** (0.0492 g, 0.256 mmol) and *tert*-butyl acrylate (0.0984 g, 112.5 µL, 0.768 mmol). Pale yellow solid (47.8 mg, 60% yield), m.p. = 62-63 °C, Rf = 0.51 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (d, *J* = 6.5 Hz, 2H), 3.36 (s, 6H), 2.54 (t, *J* = 7.0 Hz, 2H), 2.36 (t, *J* = 6.4 Hz, 2H), 1.94-1.87 (m, 1H), 1.40 (s, 9H), 0.92 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 167.0, 80.0, 68.9, 43.6, 37.2, 28.3, 28.3, 19.4. IR ν_{max} (cm^{-1}): 2966, 2931, 1721, 1613, 1394, 1313, 1142, 1086, 1017, 939, 844, 758. HRMS (ESI-TOF): calculated for $C_{15}H_{29}O_5S$ $[M+H]^+$ 321.1736, found 321.1739.

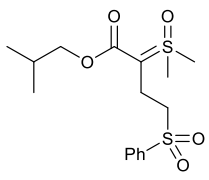
Isobutyl 4-cyano-2-(dimethyl(oxo)- λ^6-sulfaneylidene)butanoate (2n)



Prepared according to the general procedure B from sulfoxonium ylide **1c** (0.0492 g, 0.256 mmol) and acrylonitrile (0.0408 g, 50.3 µL, 0.768 mmol). Yellow oil (38.0 mg, 62% yield), Rf = 0.51 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$)

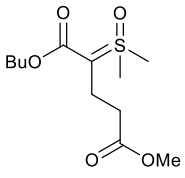
δ 3.82 (d, *J* = 6.5 Hz, 2H), 3.43 (s, 6H), 2.64 (t, *J* = 6.4 Hz, 2H), 2.51 (t, *J* = 6.4 Hz, 1H), 2.04-1.79 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 120.6, 69.1, 55.7, 44.0, 28.3, 19.8, 19.8, 19.4. IR ν_{max} (cm^{-1}): HRMS (ESI-TOF): calculated for $C_{11}H_{20}NO_3S$ $[M+H]^+$ 246.1164, found 246.1170.

Isobutyl-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-(phenylsulfonyl)butanoate (2o)



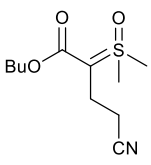
Prepared according to the general procedure B from sulfoxonium ylide **1c** (0.0492 g, 0.256 mmol) and phenyl vinyl sulfone (0.129 g, 0.768 mmol). Pale brown solid (46 mg, 51% yield), Rf = 0.52 (EtOAc), m.p.=118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 7.63-7.60 (m, 1H), 7.56-7.52 (m, 2H), 3.73 (d, *J*=6.2 Hz, 2H), 3.34 (s, 6H), 3.23 (t, *J* = 7.0 Hz, 2H), 2.66 (t, *J* = 7.2 Hz, 2H), 0.86 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 139.4, 133.6, 129.3, 128.2, 69.1, 57.0, 43.7, 28.2, 19.4. IR ν_{max} (cm^{-1}): 3016, 2960, 1615, 1469, 1283, 1143, 1082, 1019, 743, 690. HRMS (ESI-TOF): calculated for $C_{16}H_{25}O_5S_2$ [M+H]: 361.1143, found: 361.1143.

1-butyl 5-methyl 2-(dimethyl(oxo)- λ^6-sulfaneylidene)pentanedioate (2p)



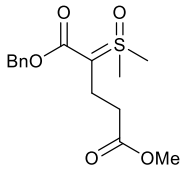
Prepared according to the general procedure B from sulfoxonium ylide **1d** (0.0492 g, 0.256 mmol) and methyl acrylate (0.0661 g, 69.6 µL, 0.768 mmol). Yellow solid (36.2 mg, 52% yield), m.p. = 69-71 °C, Rf = 0.52 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (t, =6.7 Hz, 2H), 3.62 (s, 3H), 3.35 (s, 6H), 2.58 (t, *J* = 6.8 Hz, 2H), 2.43 (t, *J* = 6.8 Hz, 2H), 1.63-1.54 (m, 2H), 1.41-1.33 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 166.8, 62.5, 51.4, 43.6, 35.8, 31.4, 28.2, 19.5, 13.9. IR ν_{max} (cm^{-1}): 2955, 2874, 1729, 1612, 1437, 1309, 1144, 1090, 1019, 980, 758. HRMS (ESI-TOF): calculated for $C_{12}H_{22}O_5SNa$ $[M+Na]^+$ 301.1086, found 301.1089.

Butyl 4-cyano-2-(dimethyl(oxo)-λ^6-sulfaneylidene)butanoate (2q)



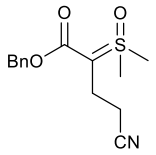
Prepared according to the general procedure B from sulfoxonium ylide **1d** (0.0492 g, 0.256 mmol) and acrylonitrile (0.0408 g, 50.3 µL, 0.768 mmol). White solid (36.8 mg, 60 % yield), m.p. = 79-80 °C, Rf = 0.53 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (t, *J* = 6.5 Hz, 2H), 3.40 (s, 6H), 2.62 (t, *J* = 6.4 Hz, 2H), 2.48 (t, *J* = 6.4 Hz, 1H), 1.63-1.56 (m, 2H), 1.42-1.33 (m, 3H), 0.93 (t, J= 7.4Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 120.7, 62.7, 55.8, 44.0, 31.4, 19.8, 19.7, 19.5, 13.9. IR ν_{max} (cm^{-1}): 2959, 2932, 1616, 1393, 1334, 1309, 1154, 1093, 1019, 939, 760. HRMS (ESI-TOF): calculated for $C_{11}H_{20}NO_3S$ $[M+H]^+$ 246.1164, found 246.1170.

1-benzyl 5-methyl 2-(dimethyl(oxo)- λ^6-sulfaneylidene)pentanedioate (2r)



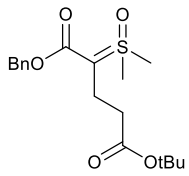
Prepared according to the general procedure B from sulfoxonium ylide **1e** (0.0579 g, 0.256 mmol) and methyl acrylate (0.0661 g, 69.6 µL, 0.768 mmol). Yellowish solid (39,2 mg, 49% yield), m.p. = 37-38 °C, Rf = 0.61 (5% MeOH:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7,36-7,27 (m, 5H), 5,11 (s, 2H), 3,61 (s, 3H), 3,38 (s, 6H), 2,66 (t, *J* = 6,9 Hz, 2H), 2,48 (t, *J* = 6,1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 174.1, 137.8, 128.4, 127.5, 64.3, 51.3, 43.4, 35.9, 19.4. IR ν_{max} (cm^{-1}): 3020, 2941, 1728, 1617, 1440, 1378, 1307, 1261, 1142, 1038, 1016, 938, 831, 746, 699. HRMS (ESI-TOF): calculated for $C_{15}H_{21}O_5S$ [M+H]: 313.1110, found: 313.1109.

Benzyl 4-cyano-2-(dimethyl(oxo)- λ^6-sulfaneylidene)butanoate 2s



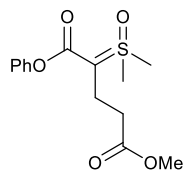
Prepared according to the general procedure B from sulfoxonium ylide **1e** (0.0579 g, 0.256 mmol) and acrylonitrile (0.0408 g, 50.3 µL, 0.768 mmol). Pale yellow solid (42.6 mg, 61% yield), m.p. = 65-66 °C, Rf = 0.50 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 4H), 7.32-7.30 (m, 1H), 5.10 (s, 2H), 3.44 (s, 6H), 2.66 (t, *J*=6.4 Hz, 2H), 2.48 (t, *J*=6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 137.6, 128.6, 127.9, 127.7, 120.7, 64.6, 56.2, 43.9, 19.8, 19.7. IR ν_{max} (cm^{-1}): 3024, 2928, 2244, 1619, 1383, 1334, 1305, 1148, 1089, 1017, 979, 750, 699. HRMS (ESI-TOF): calculated for $C_{14}H_{18}NO_3S$ $[M+H]^+$ 280.1007, found 280.1008.

1-benzyl 5-(*tert*-butyl) 2-(dimethyl(oxo)- λ^6-sulfaneylidene)pentanedioate (2t)



Prepared according to the general procedure B from sulfoxonium ylide **1e** (0.0579 g, 0.256 mmol) and *tert*-butyl acrylate (0.0984 g, 112.5 µL, 0.768 mmol). Yellow solid (37.2 mg, 42% yield), m.p. = 67-68 °C, Rf = 0.50 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38-7.33 (m, 4H), 7.30-7.25 (m, 1H), 5.12 (s, 2H), 3.38 (s, 6H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.40 (t, *J* = 6.4 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 166.5, 138.0, 128.5, 127.6, 80.1, 64.3, 43.6, 37.1, 28.3. IR ν_{max} (cm^{-1}): 2977, 2930, 1721, 1618, 1367, 1306, 1148, 1087, 980, 939, 845, 754.HRMS (ESI-TOF): calculated for $C_{18}H_{27}O_5S$ $[M+H]^+$ 355.1579, found 355.1585.

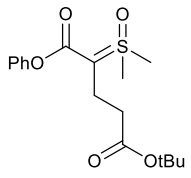
5-metil-1-fenil-2-(dimetil(oxo)-λ^6-sulfanoilideno)pentanodioato (2u)



Prepared according to the general procedure B from sulfoxonium ylide **1f** (0.0543 g, 0.256 mmol) and methyl acrylate (0.0661 g, 69.6 µL, 0.768 mmol). Yellow oil (42,8 mg, 56% yield), Rf = 0.70 (5% MeOH:EtOAc). ^{1}H NMR 7.36-7.33 (m, 2H), 7.17-7.14 (m, 1H), 7.10-7.09 (m, 2H), 3.66 (s, 3H), 3.42 (s, 6H), 2.78 (t,

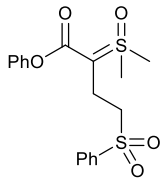
J = 6.9 Hz, 2H), 2.59 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 165.0, 151.5, 129.1, 124.7, 122.2, 51.4, 43.2, 35.9, 19.4. IR ν_{max} (cm^{-1}): 3017, 2927, 1729, 1636, 1491, 1437, 1343, 1260, 1194, 1126, 1052, 1015, 981, 940, 825, 782, 745, 693, 617. HRMS (ESI-TOF): calculated for $C_{14}H_{19}O_5S$ [M+H]: 299.0953, found: 299.0958.

5-(*tert*-butyl) 1-phenyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)pentanedioate (2v)



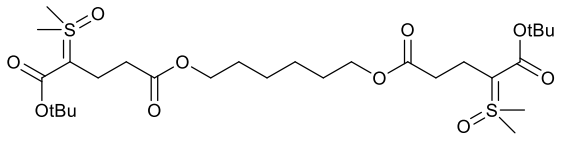
Prepared according to the general procedure B from sulfoxonium ylide **1f** (0.0543 g, 0.256 mmol) and *tert*-butyl acrylate (0.0984 g, 112.5 µL, 0.768 mmol). White solid (42.5 mg, 50% yield), m.p. = 128-129 °C, Rf = 0.48 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37-7.32 (m, 2H), 7.18-7.14 (m, 1H), 7.11-7.09 (m, 2H), 3.42 (s, 6H), 2.72 (t, *J* = 6.4 Hz, 2H), 2.51 (t, *J* = 6.4 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 165.2, 151.7, 129.3, 124.8, 122.4, 80.3, 59.4, 43.3, 37.3, 28.4, 28.2, 19.2. IR ν_{max} (cm^{-1}): 2978, 2930, 1724, 1639, 1344, 1199, 1152, 981, 749. HRMS (ESI-TOF): calculated for $C_{17}H_{25}O_5S$ $[M+H]^+$ 341.1423, found 341.1423.

Phenyl-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-(phenylsulfonyl)butanoate (2w)



Prepared according to the general procedure B from sulfoxonium ylide **1f** (0.0543 g, 0.256 mmol) and phenyl vinyl sulfone (0.129 g, 0.768 mmol). Pale brown wax (50.4 mg, 53% yield), Rf = 0.50 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.63-7.60 (m, 1H), 7.56-7.54 (m, 2H), 7.36-7.32 (m, 2H), 7.18-7.14 (m, 1H), 7.04 (d, *J*= 7.8 Hz, 2H), 3.41 (s, 6H), 3.38 (t, *J* = 7.0 Hz, 2H), 2.83 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 164.6, 151.3, 139.4, 133.7, 129.3, 129.3, 128.2, 125.0, 122.2, 115.4, 60.5, 56.9, 43.3, 17.3. IR ν_{max} (cm^{-1}): 3018, 2926, 1641, 1340, 1287, 1195, 1143, 1113, 1087, 1013, 741, 691. HRMS HRMS (ESI-TOF): calculated for $C_{18}H_{21}O_5S_2$ [M+H]: 381.0830, found: 381.0825.

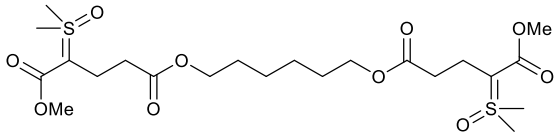
1,1'-di-*tert*-butyl-O'^{5},O^5-(hexane-1,6-dil)bis(2-(dimetil(oxo)-λ^6-sulfanoylideno)pentanodioato) (2x)



Prepared according to a modification of the general procedure B from sulfoxonium ylide **1b** (0.196 g, 1.02 mmol) and 1,6-hexanediol diacrylate (0.115 g, 113.7 µL, 0.508 mmol). Purification by column flash chromatography, using silica gel 60 (200-400 mesh) as a stationary phase (Eluent MeOH/EtOAc 0-20%). Yellow Solid (46.5 mg, 15 % yield), m.p. = 88-89 °C, Rf = 0.10 (MeOH:EtOAc 5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4,02 (t, *J* = 6,7 Hz, 4H), 3,36 (s, 12 H), 2,54 (t, *J* = 6,3 Hz, 4H), 2,44 (t, *J* = 6,5 Hz, 4H), 1,61 (m, 4H),

1,45 (s, 18H), 1,35 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 167.9, 78.3, 64.2, 43.8, 41.1, 36.0, 29.1, 28.6, 25.7, 20.3. IR ν_{max} (cm^{-1}): 2930, 2863, 1725, 1612, 1388, 1345, 1311, 1252, 1169, 1134, 1086, 1016, 979, 936, 788, 759. HRMS (ESI-TOF): calculated for $C_{28}H_{51}O_{10}S_2$ $[M+H]^+$ 611.2924, found 611.2925.

O'^{5},O^5-(hexane-1,6-diyl)-1,1'-dimethyl-bis(2-(dimethyl(oxo)-λ^6-sulfaneylidene)pentanedioate) (2y)

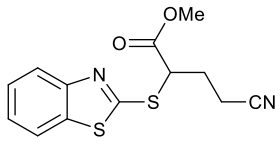


Prepared according to a modification of the general procedure B from sulfoxonium ylide **1a** (0.192 g, 1.28 mmol) and 1,6-hexanediol diacrylate (0.145 g, 143.4 µL, 0.640 mmol). Purification by column flash chromatography, using silica gel 60 (200-400 mesh) as a stationary phase (Eluent MeOH/EtOAc 0-20 %). Pale brown wax (84.3 mg, 25% yield), Rf = 0.10 (MeOH:EtOAc 5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (s, t, *J* = 6,7 Hz 4H), 3.62 (s, 6H), 3.37 (s, 12H), 2.59 (t, *J*= 6,4 Hz, 4H), 2.43 (t, *J* = 6,4 Hz, 4H), 1.62 (s, 6H), 1.36 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 167.0, 64.2, 50.1, 43.5, 40.8, 36.0, 28.5, 25.6, 19.5. IR ν_{max} (cm^{-1}): 2932, 2860, 1725, 1619, 1439, 1341, 1311, 1258, 1178, 1146, 1092, 982, 939, 758. HRMS (ESI-TOF): calculated for $C_{22}H_{39}O_{10}S_2$ $[M+H]^+$ 527.1985, found 527.1992.

4 General Procedure C: Synthesis of mercaptobenzothiazole derivatives

To a 4 mL reaction vial with a Teflon-coated septum screw-top was added sulfoxonium ylide (0.1 mmol, 1.0 equiv), 2-mercaptobenzothiazole (16.7 mg, 0.1 mmol, 1.0 equiv) and 500 µL of ACN. The reaction mixture was stirred at 60 °C for 24 h. The solvent was removed under reduced pressure to furnish crude product that was purified using Biotage IsoleraTM Prime (Snap Ultra 10 g, Eluent EtOAc/ Hex).

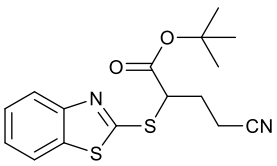
Methyl 2-(benzo[d]thiazol-2-ylthio)-4-cyanobutanoate (3a)



Prepared according to the general procedure C from methyl 4-cyano-2-(dimethyl(oxo)-λ^6-sulfaneylidene)butanoate **2b** (0.0203 g, 0.1 mmol). Pale yellow solid (20.2 mg, 69% yield), m.p. = 69-70 °C, Rf = 0.35 (EtOAc:Hex 1:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.46-7.42 (m, 1H), 7.36-7.32 (m, 1H), 4.81 (t, *J* = 6.8 Hz, 1H), 3.81 (s, 3H), 2.67-2.63 (m, 2H), 2.58-2.49 (m, 1H), 2.47-2.38 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 162.7, 152.9, 135.8, 126.5, 125.1, 122.2, 121.3, 118.6, 53.4, 48.4, 28.2, 15.1. IR ν_{max} (cm^{-1}): 2953, 1734, 1458, 1427, 1237,

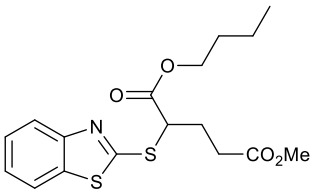
1126, 993, 758, 727. HRMS (ESI-TOF): calculated for $C_{13}H_{13}N_2O_2S_2$ $[M+H]^+$ 293.0418, found 293.0413.

tert-butyl 2-(benzo[d]thiazol-2-ylthio)-4-cyanobutanoate (3b)



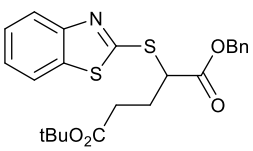
Prepared according to the general procedure C from *tert*-butyl 4-cyano-2-(dimethyl(oxo)-λ^6-sulfaneylidene)butanoate **2i** (0.0245 g, 0.1 mmol). Pale yellow solid (17.4 mg, 52% yield), m.p. = 75-76 °C, Rf = 0.37 (EtOAc:Hex 1:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J*=7.9 Hz, 1H), 7.46-7.42 (m, 1H), 7.36-7.29 (m, 1H), 4.64 (t, *J* = 6.8 Hz, 1H), 2.69-2.61 (m, 2H), 2.54-2.38 (m, 1H), 2.45-2.38 (m, 1H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 163.2, 153.0, 127.3, 126.4, 125.0, 122.1, 121.3, 112.1, 83.5, 49.9, 28.0, 15.1. IR ν_{max} (cm^{-1}): 3604, 2977, 2931, 1725, 1490, 1459, 1318, 1146, 995, 755. HRMS (ESI-TOF): calculated for $C_{16}H_{19}N_2O_2S_2$ $[M+H]^+$ 335.0888, found 335.0898.

1-butyl 5-methyl 2-(benzo[d]thiazol-2-ylthio)pentanedioate (3c)



Prepared according to the general procedure C from 1-butyl 5-methyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)pentanedioate **2p** (0.0278 g, 0.1 mmol). Purification by preparative thin layer chromatography, pale yellow solid (18.4 mg, 50% yield), m.p. = 78-79 °C, Rf = 0.39 (EtOAc:Hex 1:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.42 (ddd, *J* = 8.2, 7.3, 1.3 Hz, 1H), 7.31 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 4.83-4.69 (m, 1H), 4.26 – 4.09 (m, 2H), 3.68 (s, 3H), 2.62 – 2.55 (m, 2H), 2.45 (dq, *J* = 14.4, 7.3 Hz, 1H), 2.38-2.27 (m, 1H), 1.65-1.61 (m, 1H), 1.60-1.56 (m,1H), 1.38 -1.29 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 170.8, 164.0, 153.1, 135.8, 126.3, 124.8, 122.0, 121.2, 65.9, 51.9, 49.5, 31.3, 30.6, 27.3, 19.2, 13.7. IR ν_{max} (cm^{-1}): 2958, 2872, 1736, 1461, 1429, 1170, 994, 758.HRMS (ESI-TOF): calculated for $C_{17}H_{22}NO_4S_2$ $[M+H]^+$ 368.0990, found 368.1006.

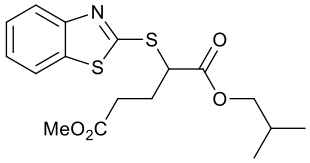
1-benzyl 5-(_tert_-butyl) 2-(benzo[d]thiazol-2-ylthio)pentanedioate (3d)



Prepared according to the general procedure C from 1-benzyl-5-(*tert*-butyl)-2-(dimethyl(oxo)-λ^6-sufaneyldene)pentanedioate **2t** (0.0354 g, 0.1 mmol). Pale yellow oil (31.4 mg, 71% yield), Rf = 0.35 (EtOAc:Hex 1:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ .81 (d, J = 8.2 Hz, 1H), 7.74 (d, *J*=7.9 Hz, 1H), 7.41 (ddd, *J* = 8.2, 7.3, 1.3 Hz, 1H), 7.33-7.27 (m, 6H), 5.24-5.15 (m, 2H), 4.78 (t, *J* = 6.8 Hz, 1H), 2.48-2.44 (m, 2H), 2.42-2.35 (m, 1H), 2.33-2.24 (m, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 170.8, 163.9, 153.1, 135.8, 135.5, 128.6, 128.4, 128.3, 126.2, 124.7, 122.1, 121.2,

81.0, 67.6, 49.5, 32.7, 28.2, 27.2. IR ν_{max} (cm^{-1}): 2976, 2930, 1729, 1458, 1428, 1368, 1237, 1148, 994, 756, 728. HRMS (ESI-TOF): calculated for $C_{23}H_{26}NO_4S_2$ $[M+H]^+$ 444.1303, found 444.1317.

1-isobutyl 5-methyl 2-(benzo[d]thiazol-2-ylthio)pentanedioate (3e)

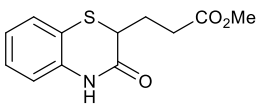


Prepared according to the general procedure C from 1-isobutyl 5-methyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)pentanedioate **2l** (0.0278 g, 0.1 mmol). Yellow oil (19.4 mg, 53% yield), Rf = 0.33 (EtOAc:Hex 1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 4.77 (t, *J*=7.1 Hz, 1H), 3.95 (qd, *J* = 10.6, 6.6 Hz, 2H), 3.68 (s, 3H), 2.59 (td, *J* = 7.4, 6.6, 3.6 Hz, 2H), 2.46 (dq, *J* = 14.4, 7.3 Hz, 1H), 2.39 – 2.28 (m, 1H), 1.93 (dq, *J* = 13.4, 6.7 Hz, 1H), 0.91 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 170.8, 164.0, 153.1, 135.8, 126.3, 124.8, 122.0, 121.2, 72.1, 51.9, 49.5, 31.3, 27.8, 27.3, 19.1. IR ν_{max} (cm^{-1}): 2959, 1734, 1461, 1428, 1309, 1157, 993, 758, 727. HRMS (ESI-TOF): calculated for $C_{17}H_{22}NO_4S_2$ $[M+H]^+$ 368.0990, found 368.1001.

5 General Procedure D: Synthesis of [1,4]-benzothiazin-3-ones derivatives

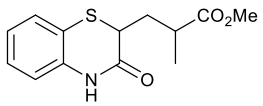
To a 4 mL reaction vial with a Teflon-coated septum screw-top was added alkylated sulfur ylide (0.256 mmol, 1 equiv) and 512 µL of MeCN. To this solution was added 2-aminothiophenol (28.0 µL, 0.304 mmol, 1.2 equiv) and the reaction mixture was stirred at 60 °C for 48 h. The solvent was removed under reduced pressure to furnish a crude product that was purified using Isolera Biotage (Snap Ultra 10 g, Eluent EtOAc/Hex).

Methyl-3-(3-oxo-3,4-dihydro-2H-benzo[b][1,4]thiazin-2-yl)propanoate (4a)



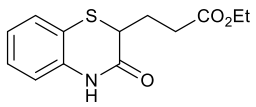
Prepared according to the general procedure D from dimethyl-2-(dimethyl(oxo)-λ^6-sulfaneylidene)pentanedioate **2a** (0.0605 g, 0.256 mmol). Yellowish solid (27.0 mg, 42% yield), m.p. = 118-120 °C, Rf = 0.29 (30% EtOAc:Hex).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 3.67 (s, 3H), 3.51 (dd, *J* = 8.6, 6.4 Hz, 1H), 2.63-2.49 (m, 2H), 2.29-2.22 (m, 1H), 1.98-1.90 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 167.8, 136.0, 128.5, 127.5, 124.2, 118.3, 117.1, 51.9, 41.9, 31.1, 25.1. IR ν_{max} (cm^{-1}): 3208, 3054, 2953, 1734, 1671, 1585, 1479, 1369, 1216, 753. In good agreement with previously reported data.[8]

methyl 2-methyl-3-(3-oxo-3,4-dihydro-2H-benzo[b][1,4]thiazin-2-yl)propanoate (4b)



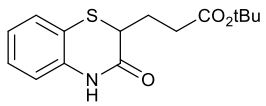
Prepared according to the general procedure D from dimethyl 2-(dimethyl(oxo)- λ^6-sulfaneylidene)-4-methylpentanedioate **2d** (0.0641 g, 0.256 mmol). Yellowish oil (24.4 mg, 36% yield), Rf = 0.28 (30% EtOAc:Hex). ^{1}H NMR (400 MHz, $CDCl_3$) Mixture of diastereoisomers δ 8.68 (s, 1H), 8.67 (s, 1H), 7.31 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.30 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.02 (m, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 3.67 (s, 3H), 3.53 (dd, *J* = 15,5, 6.2 Hz, 1H), 3.49 (dd, *J* = 15,5, 6.2 Hz, 1H), 2.85-2.71 (m, 2H), 2.39-2.32 (m, 1H), 2.06-1.93 (m, 1H), 1.69-1.63 (m, 1H), 1.22 (d, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) Mixture of diastereoisomers δ 176.04, 175.74, 167.58, 167.47, 135.89, 135.82, 128.38, 128.33, 127.28, 127.26, 124.00, 123.93, 118.33, 118.30, 116.90, 51.84, 40.64, 40.38, 36.96, 36.61, 33.23, 33.04, 29.95, 29.67, 17.64, 16.97. IR ν_{max} (cm^{-1}): HRMS (ESI-TOF): calculated for $C_{13}H_{16}NO_3S$ $[M+H]^+$ 266.0851, found 266.0854.

Ethyl-3-(3-oxo-3,4-dihydro-2H-benzo[b][1,4]thiazin-2-yl)propanoate (4c)



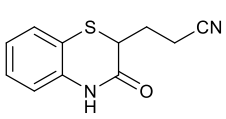
Prepared according to the general procedure D from 5-ethyl 1-methyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)pentanedioate **2f** (0.0641 g, 0.256 mmol). Yellowish solid (53.0 mg, 78% yield), m.p. = 88-89 °C, Rf = 0.35 (30% EtOAc:Hex).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.02 (m, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 3.67 (s, 3H), 3.53 (dd, *J* = 15,5, 6.2 Hz, 1H), 3.49 (dd, *J* = 15,5, 6.2 Hz, 1H), 2.85-2.71 (m, 2H), 2.9-2.22 (m, 1H), 1.98-1.90 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 168.0, 136.0, 128.4, 127.4, 124.1, 118.2, 117.2, 60.9, 41.9, 31.4, 25.2, 14.3. IR ν_{max} (cm^{-1}): 3206, 3053, 2978, 2907, 1729, 1666, 1585, 1478, 1372, 1157, 1030, 751, 656. HRMS (ESI-TOF): calculated for $C_{13}H_{16}NO_3S$ $[M+H]^+$ 266.0851, found 266.0857.

***tert*-butyl-3-(3-oxo-3,4-dihydro-2H-benzo[b][1,4]thiazin-2-yl)propanoate (4d)**



Prepared according to the general procedure D from 5-(*tert*-butil)-1-metil-2-(dimetil(oxo)-λ^6-sulfanoylideno)pentanodioato **2e** (0.0713 g, 0.256 mmol). Yellowish solid (46.6 mg, 62% yield), m.p. = 112-113 °C, Rf = 0.30 (30% EtOAc:Hex). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.30 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.17 (td, *J* = 7.7, 1.4 Hz, 1H), 7.01 (td, *J* = 7.6, 1.3 Hz, 1H), 6.91 (dd, *J* = 8.0, 1.3 Hz, 1H), 3.49 (dd, *J* = 8.6, 6.3 Hz, 1H), 2.54-2.37 (m, 2H), 2.24 – 2.15 (m, 1H), 1.93-1.84 (m, 1H), 1.43 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 168.1, 136.0, 128.4, 127.4, 124.1, 118.3, 117.2, 80.8, 42.0, 32.5, 28.2, 25.3. IR ν_{max} (cm^{-1}): 3204, 2976, 1724, 1667, 1585, 1478, 1365, 1248, 1144, 846, 750, 656. HRMS (ESI-TOF): calculated for $C_{15}H_{19}NO_3SNa$ $[M+H]^+$ 316.0983, found 316.0992.

3-(3-oxo-3,4-dihydro-2H-benzo[b][1,4]thiazin-2-yl)propanenitrile (4e)

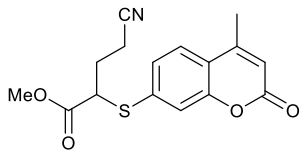


Prepared according to the general procedure D from methyl 4-cyano-2-(dimethyl(oxo)-λ^6-sulfaneylidene)butanoate **2b** (0.0520 g, 0.256 mmol). Yellowish solid (30.7 mg, 55% yield), m.p. = 114-116 °C, Rf = 0.28 (30% EtOAc:Hex). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.33 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.06 (td, *J* = 7.6, 1.3 Hz, 1H), 6.97 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.57 (dd, *J* = 8.5, 6.3 Hz, 1H), 2.71 – 2.56 (m, 2H), 2.32 (dtd, *J* = 14.0, 7.6, 6.3 Hz, 1H), 1.99 (dtd, *J* = 14.0, 7.6, 6.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 135.8, 128.4, 127.9, 124.5, 118.6, 117.6, 117.5, 41.0, 25.6, 15.0. IR ν_{max} (cm^{-1}): 3215, 3053, 2969, 1667, 1584, 1478, 1373, 1306, 753. HRMS (ESI-TOF): calculated for $C_{11}H_{11}N_2OS$ $[M+H]^+$ 219.0592, found 219.0596.

6 General Procedure E: Synthesis of 7-mercapto-cumarin derivative

To a 4 mL reaction vial with a Teflon-coated septum screw-top was added methyl 4-cyano-2-(dimethyl(oxo)-λ^6-sulfaneylidene)butanoate (20.3 mg, 0.1 mmol, 1.0 equiv), 7-mercapto-4-methylcoumarin (19.2 mg, 0.1 mmol, 1.0 equiv) and 500 µL of ACN. The reaction was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to furnish a crude product that was purified using Biotage IsoleraTM Prime (Snap Ultra 10 g, Eluent EtOAc/ Hex).

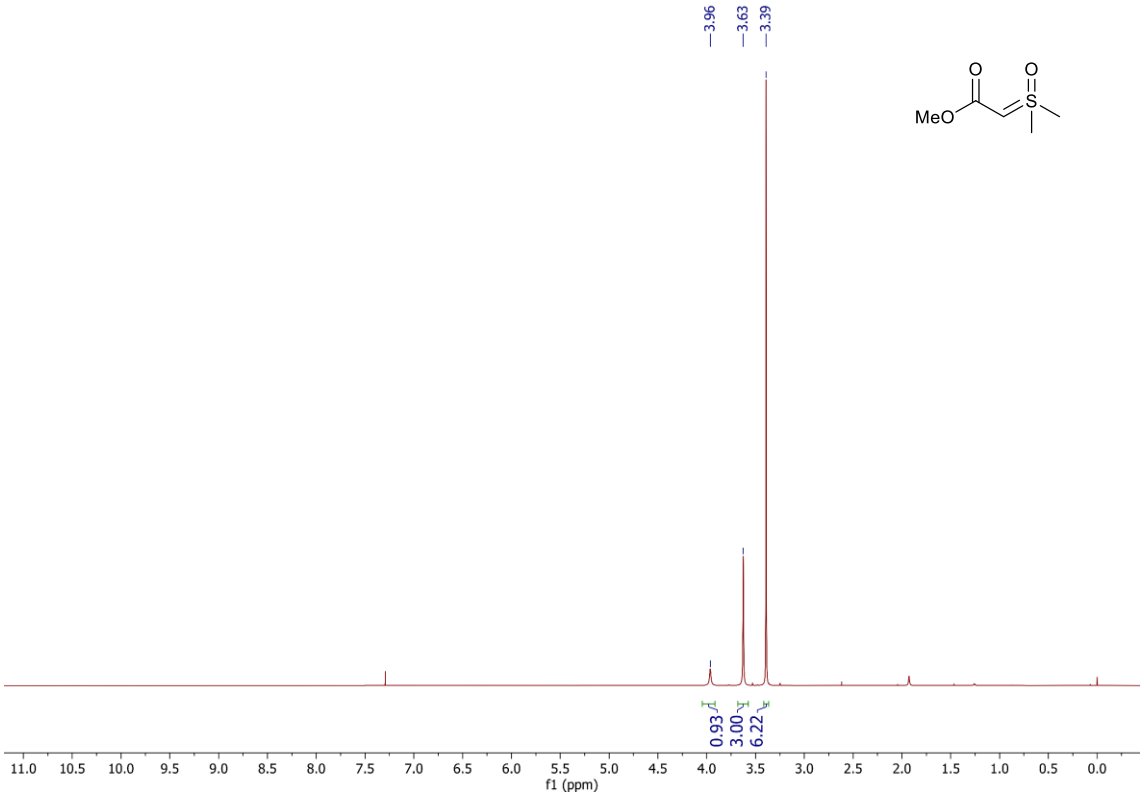
Methyl 4-cyano-2-((4-methyl-2-oxo-2H-chromen-7-yl)thio)butanoate (5a)



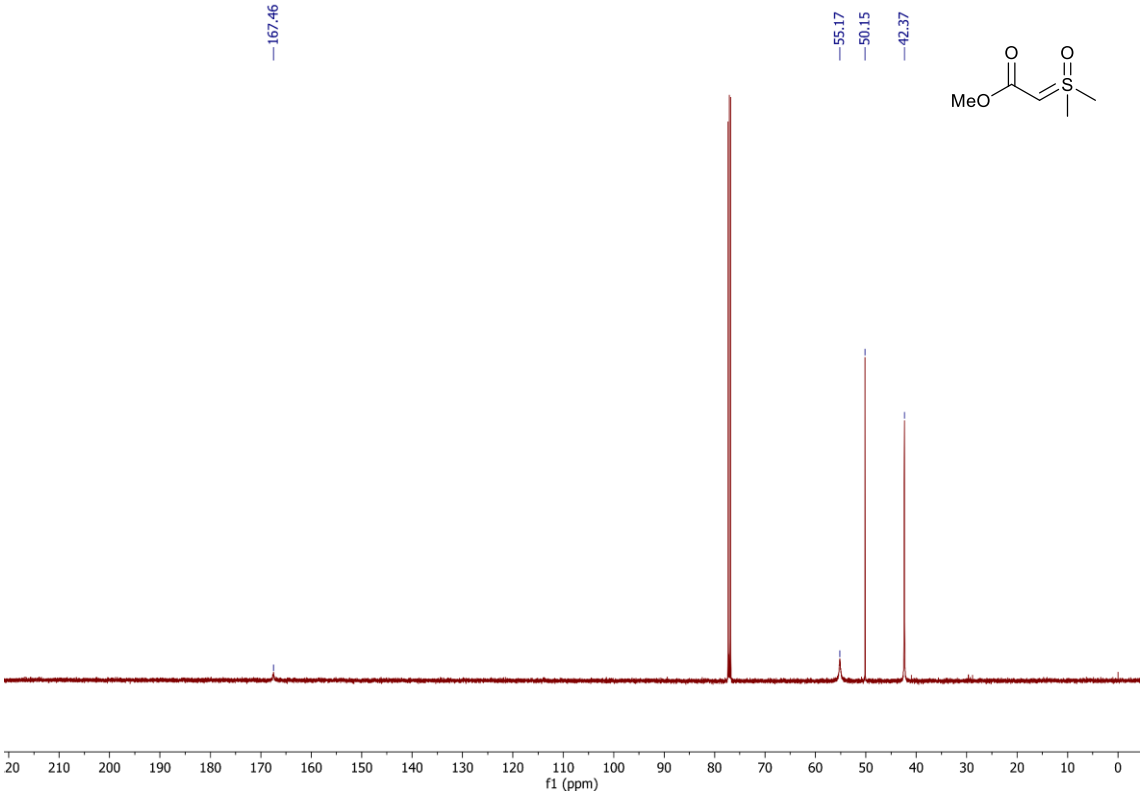
The product was isolated as a yellow oil (24.7 mg, 78% yield), Rf = 0.45 (EtOAc:Hex 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J*=8.3 Hz, 1H), 7.38 (d, *J*=1.8 Hz, 1H), 7.34 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.29 (q, *J* = 1.3 Hz, 1H), 3.89 (t, *J* = 7.4 Hz, 1H), 3.77 (s, 3H), 2.60 (qt, *J* = 17.1, 7.1 Hz, 2H), 2.43 (d, *J* = 1.3 Hz, 3H), 2.30 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.14 (dq, *J* = 14.3, 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 162.7, 152.9, 135.8, 126.5, 125.1, 122.2, 121.3, 118.6, 53.4, 48.4, 28.2, 15.1. HRMS (ESI-TOF): calculated for $C_{16}H_{15}NO_4SNa$ $[M+Na]^+$ 340.0619, found 340.0628.

7 ^{1}H and ^{13}C NMR Spectra

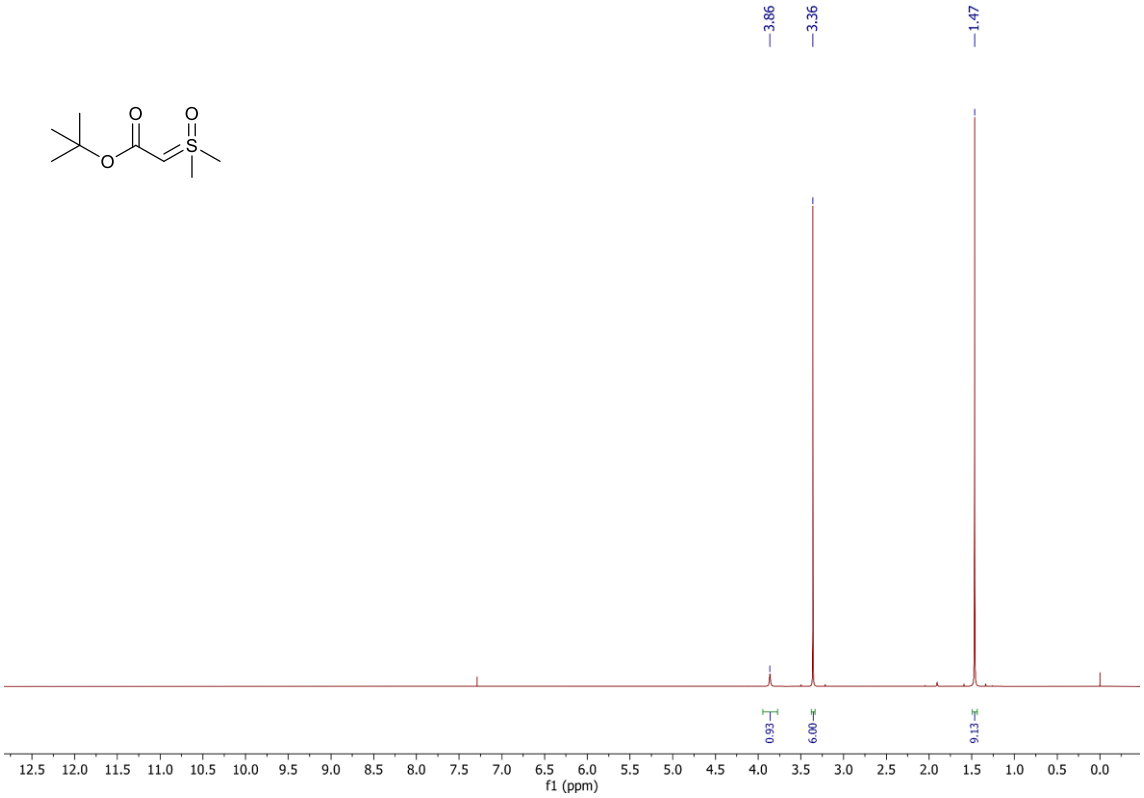
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **1a**



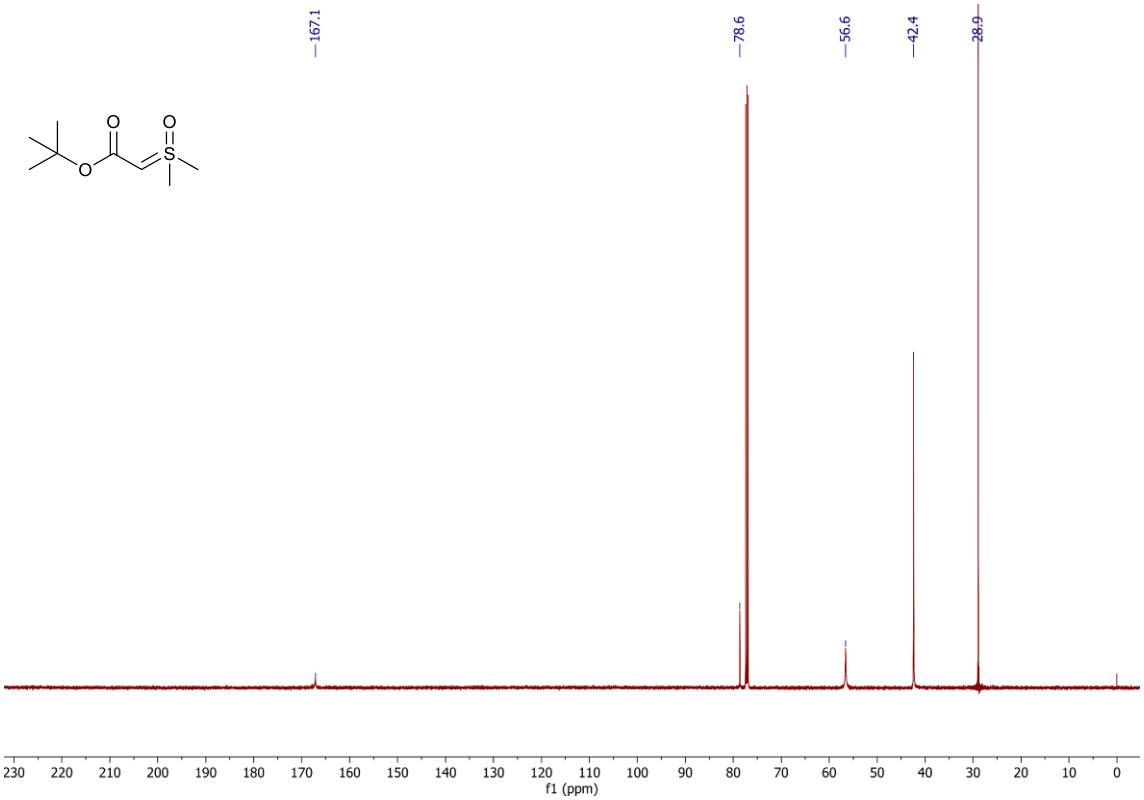
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **1a**



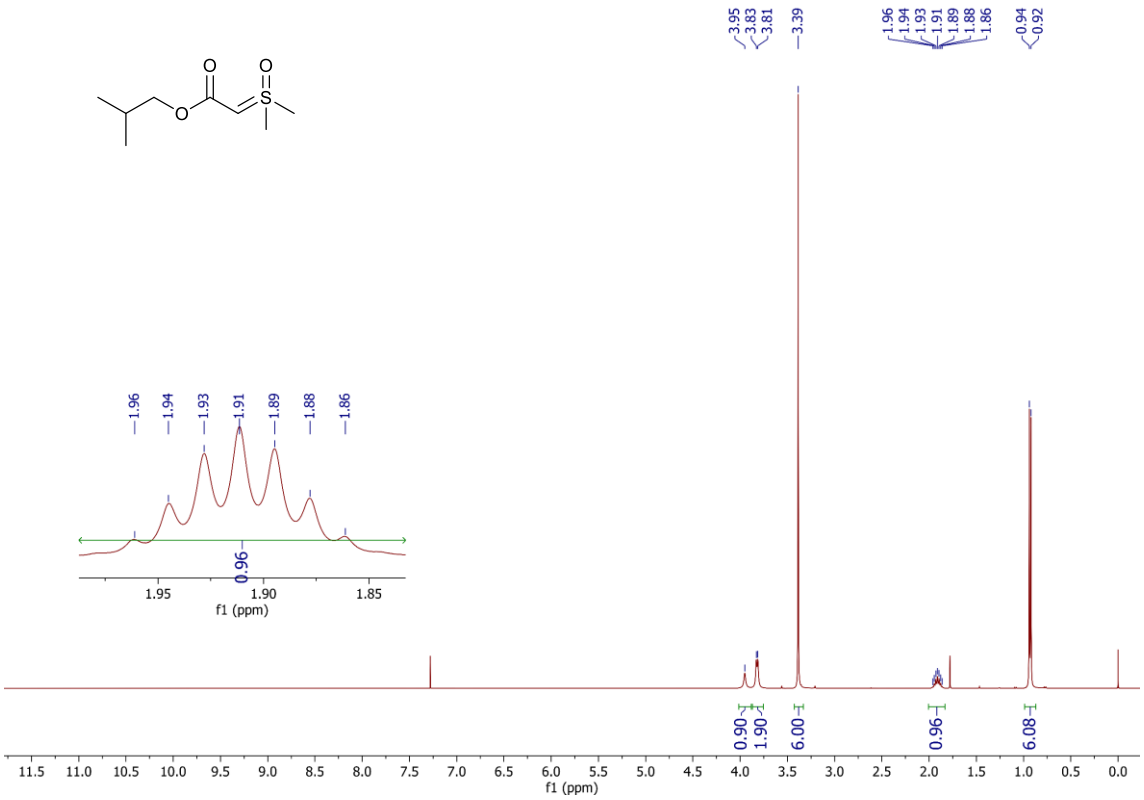
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **1b**



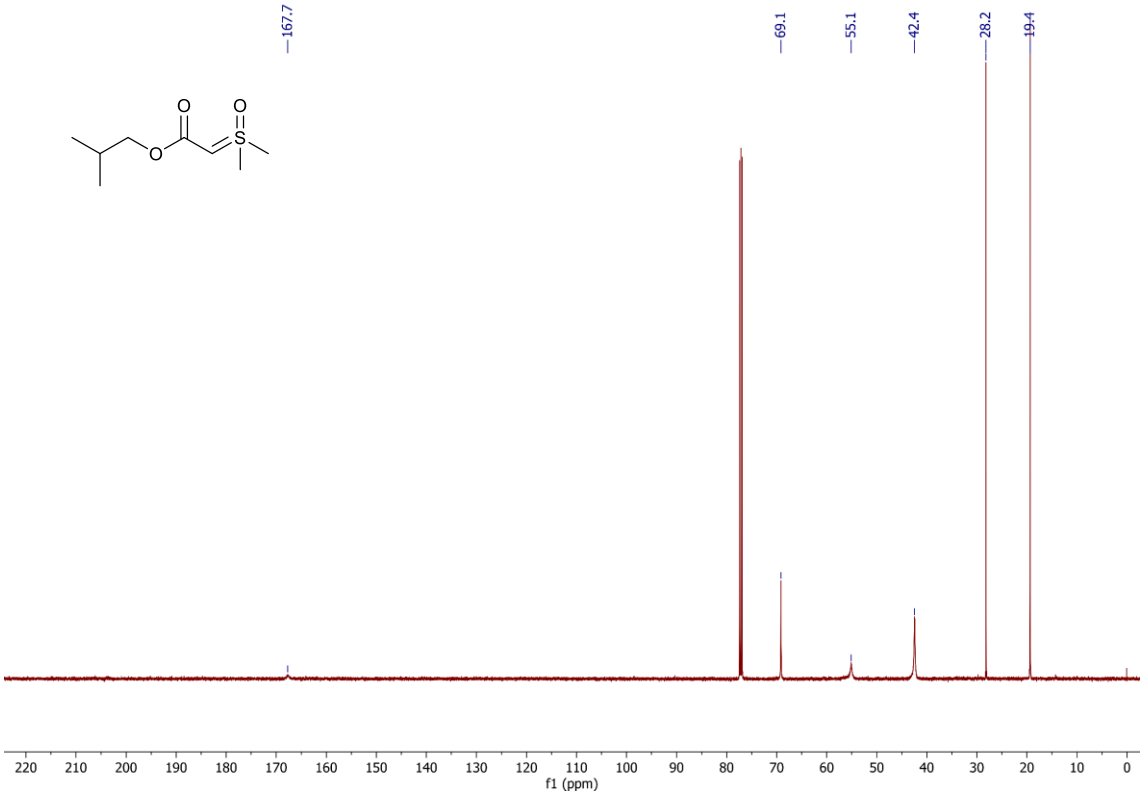
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **1b**



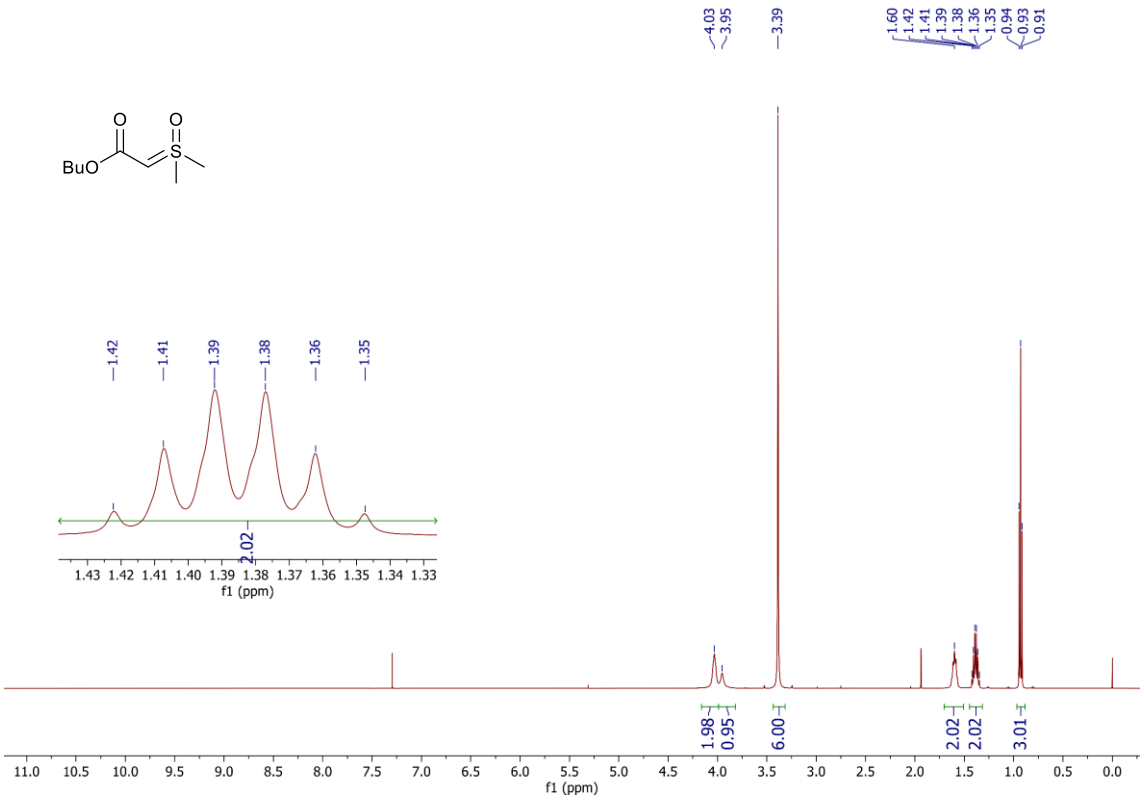
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **1c**



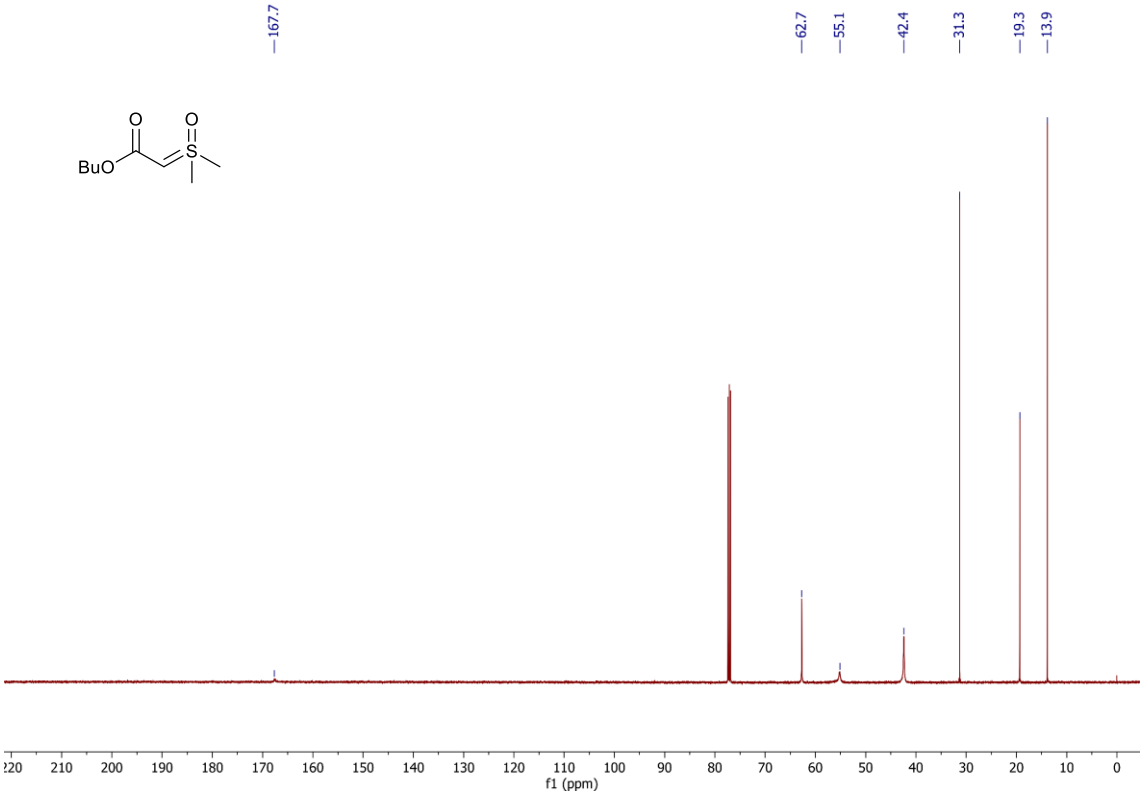
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **1c**



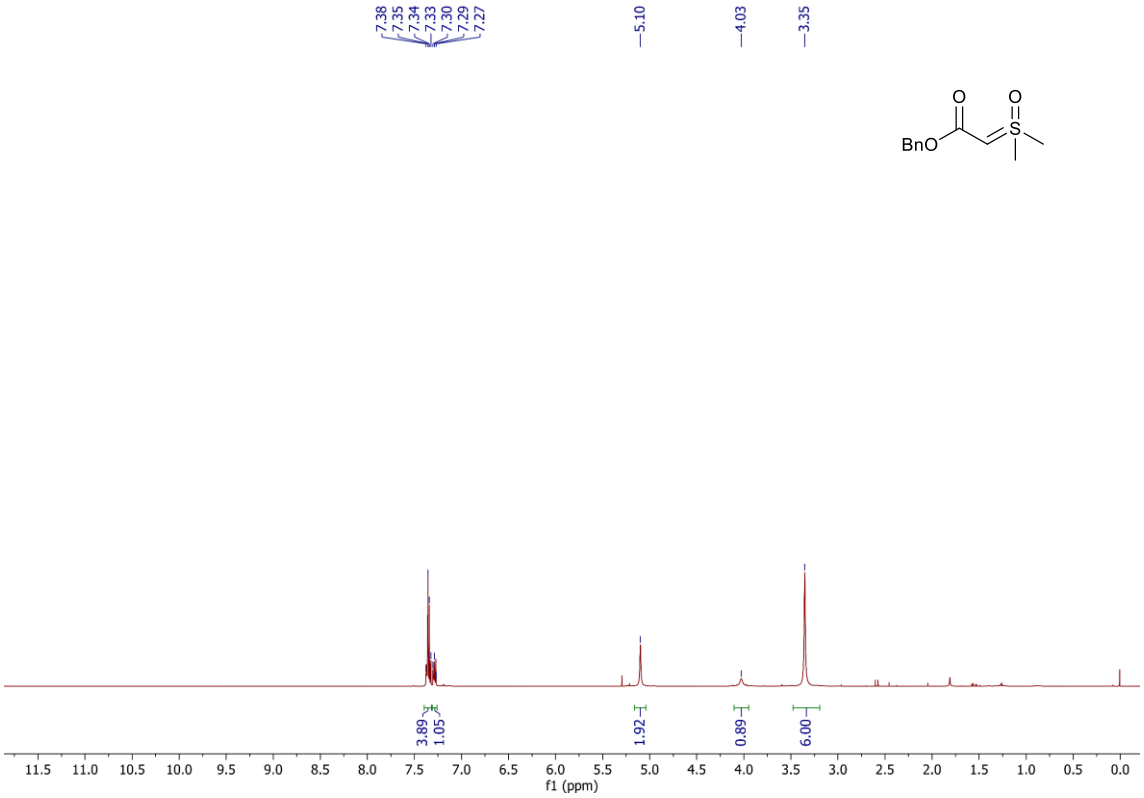
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **1d**



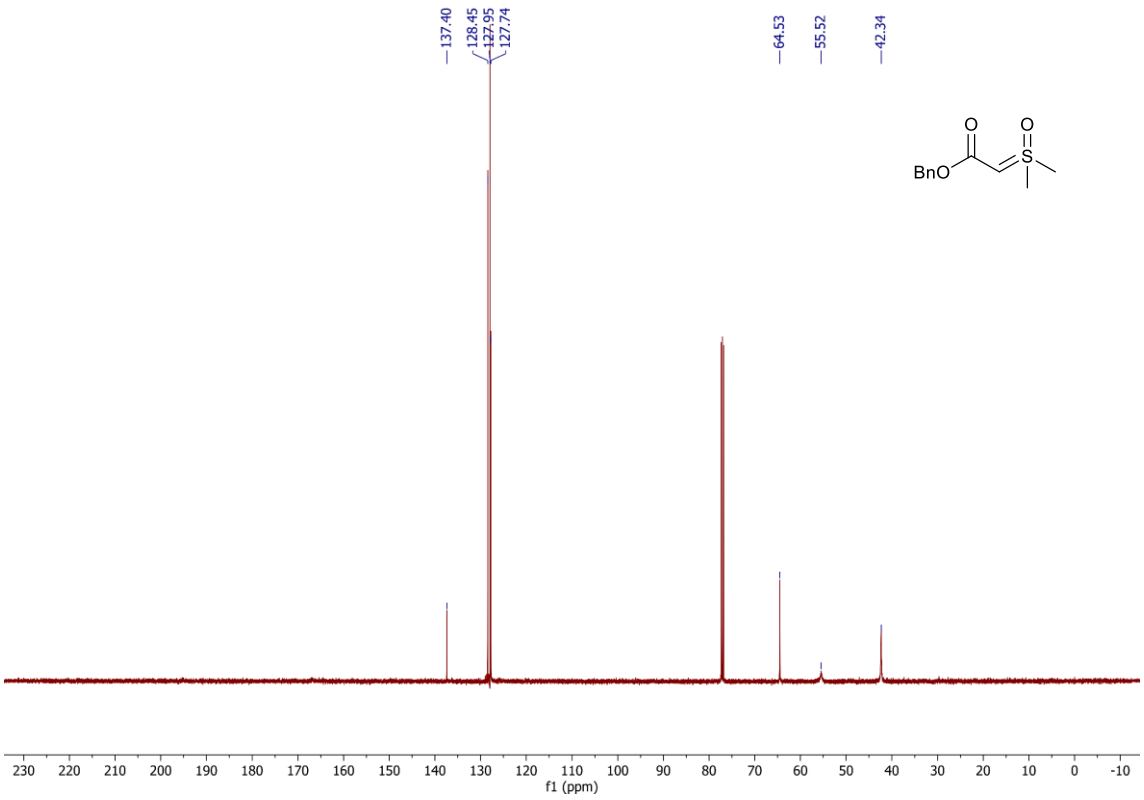
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **1d**



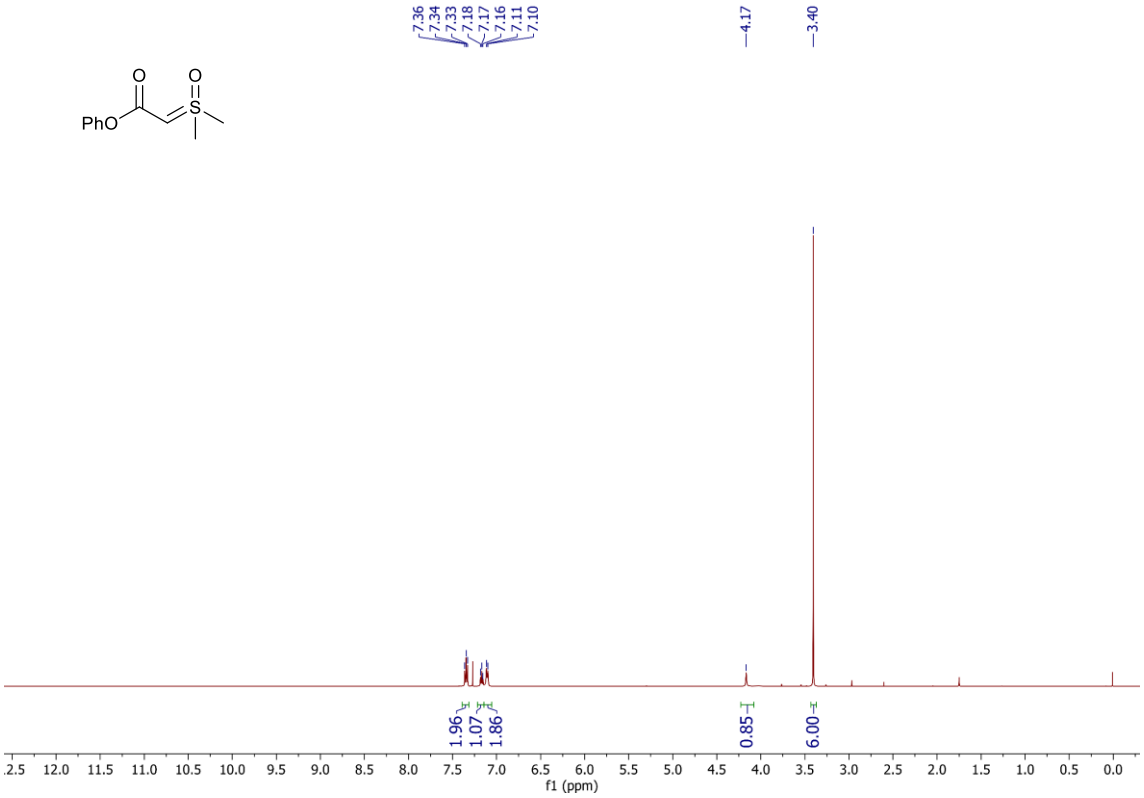
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **1e**



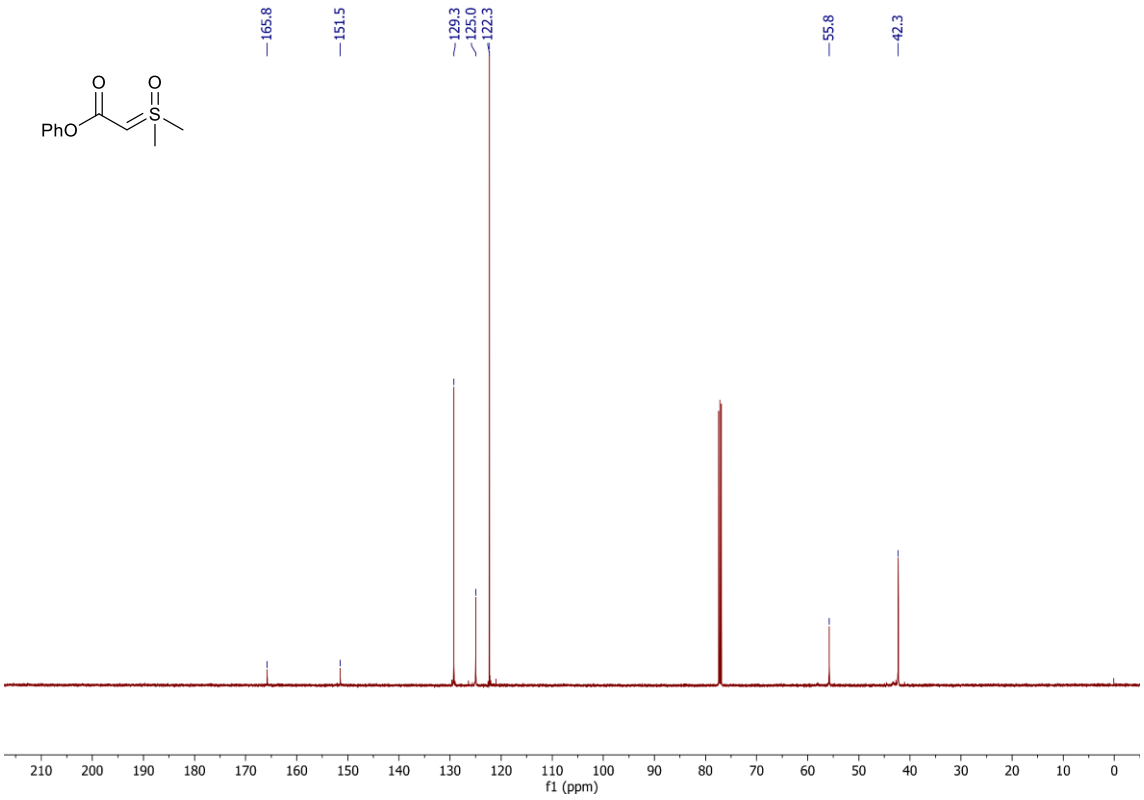
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **1e**



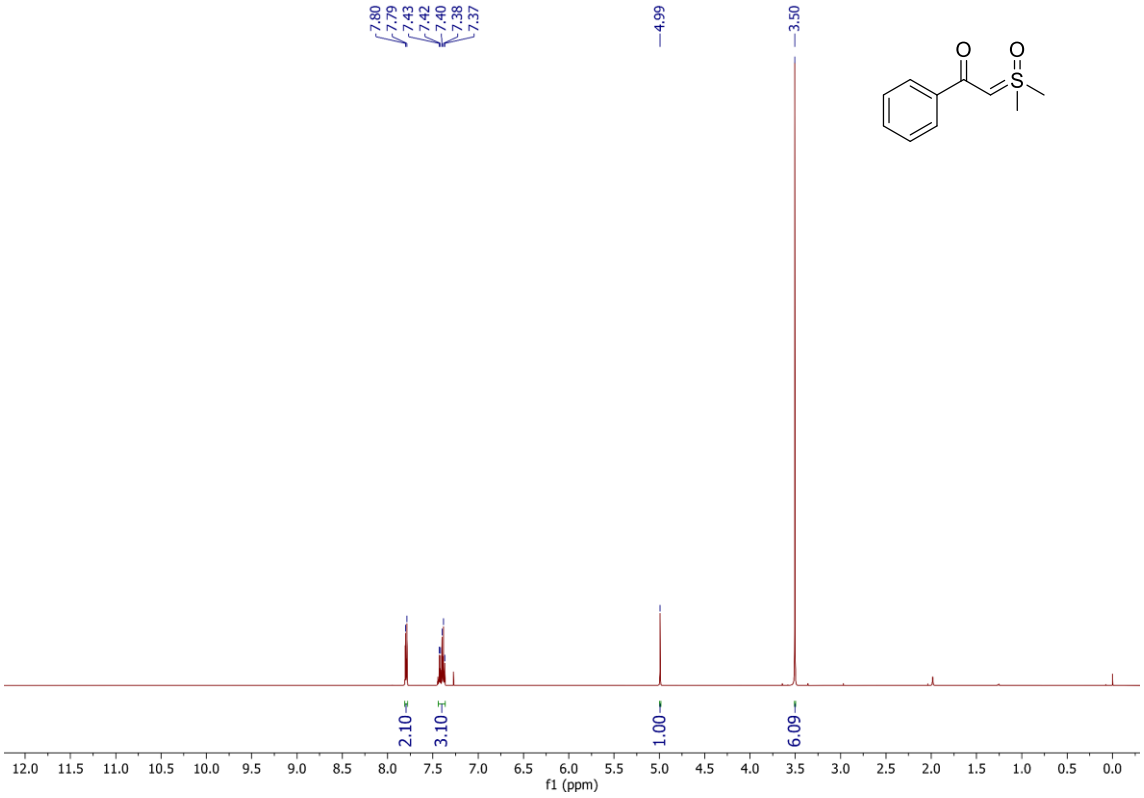
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **1f**



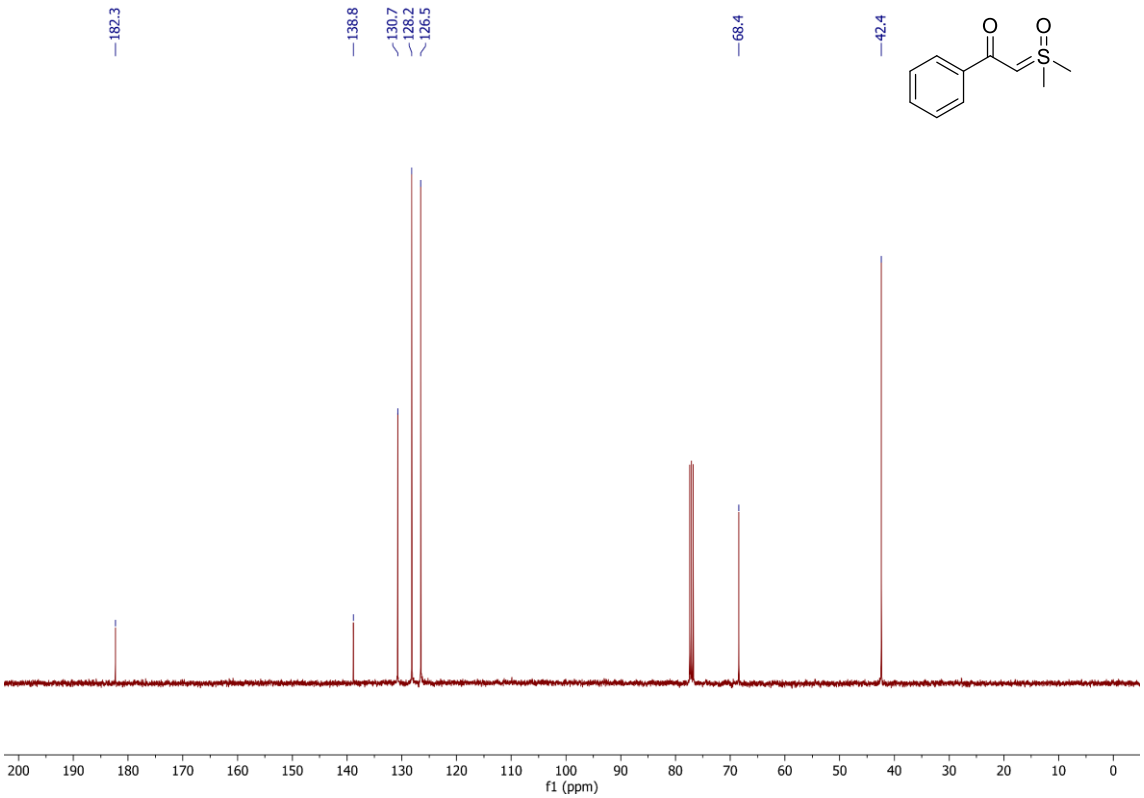
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **1f**



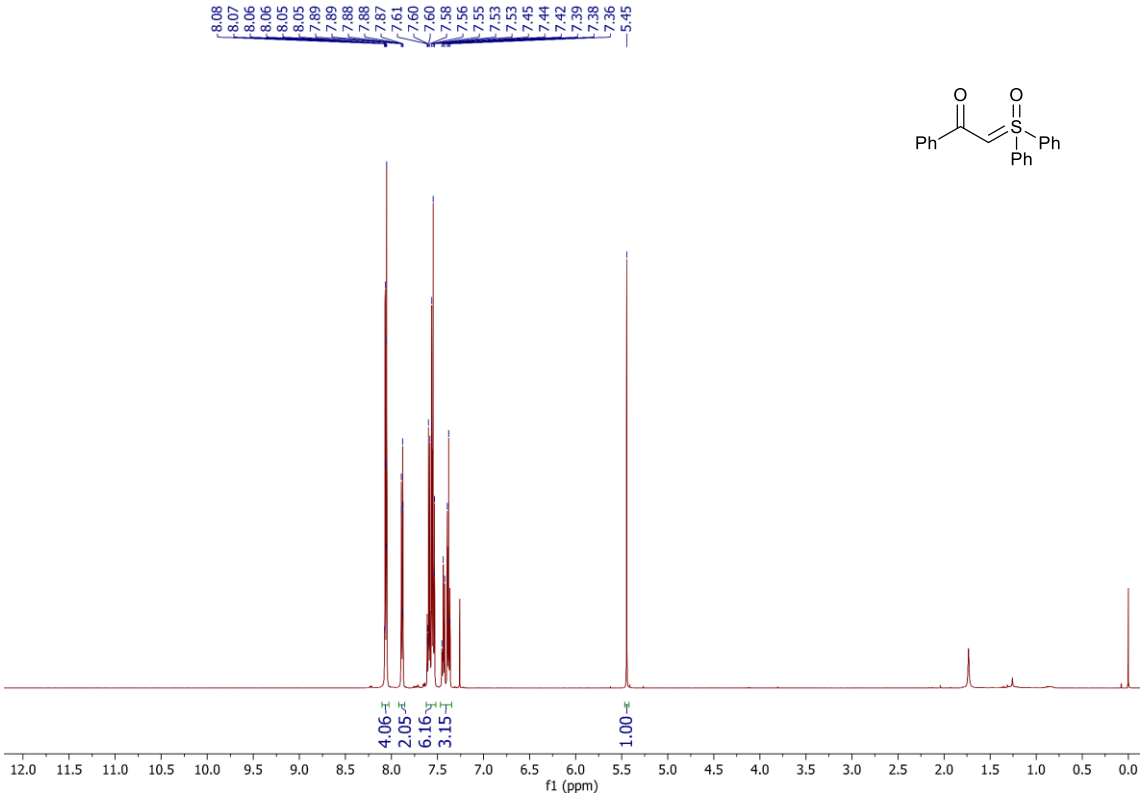
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **1g**



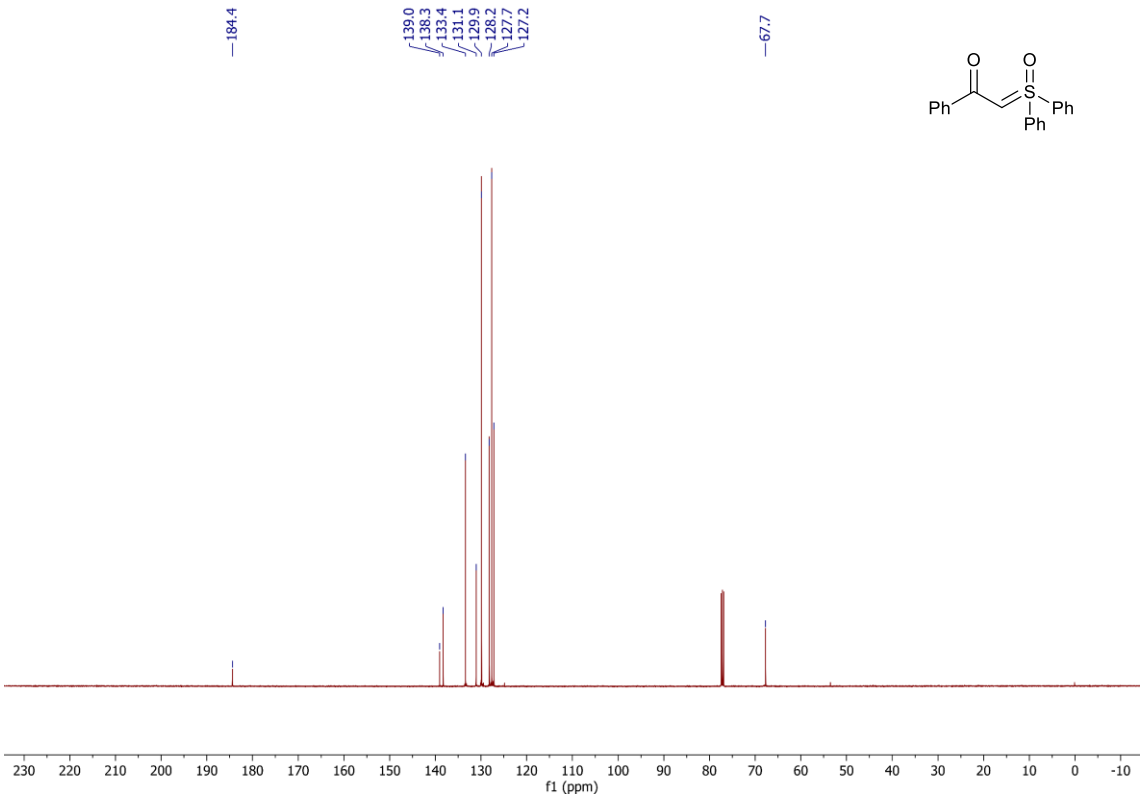
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **1g**



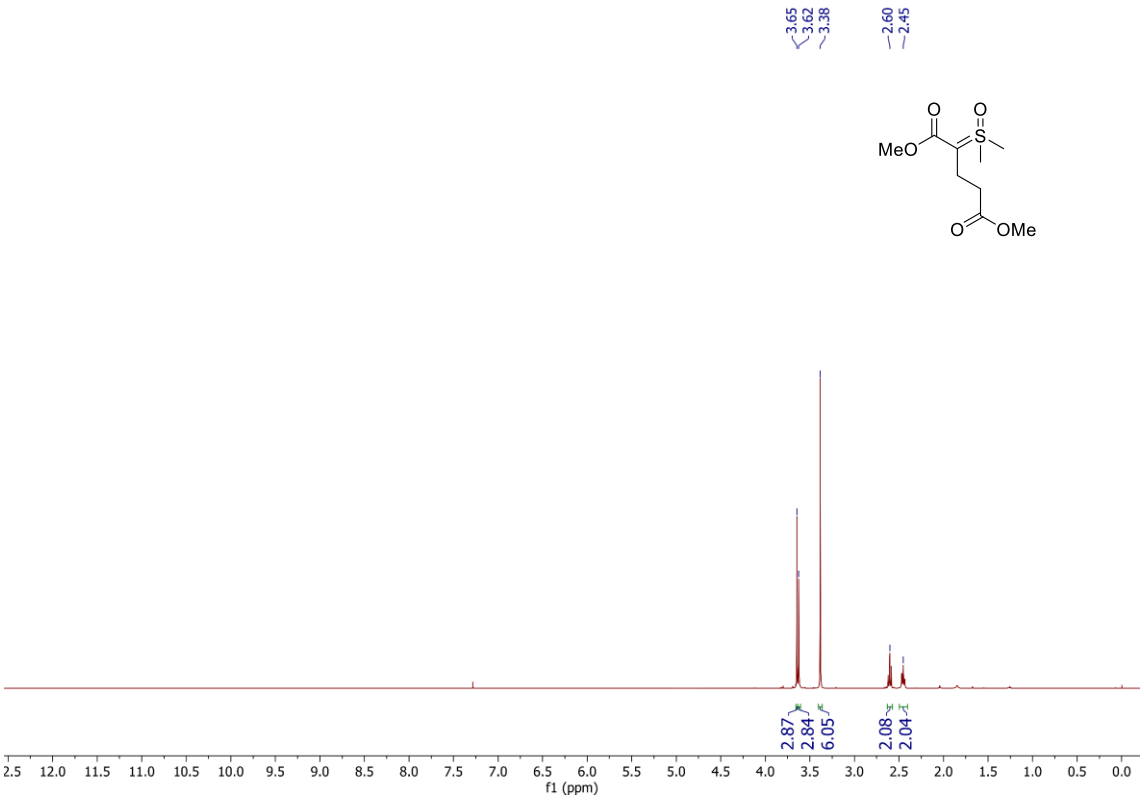
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **1h**



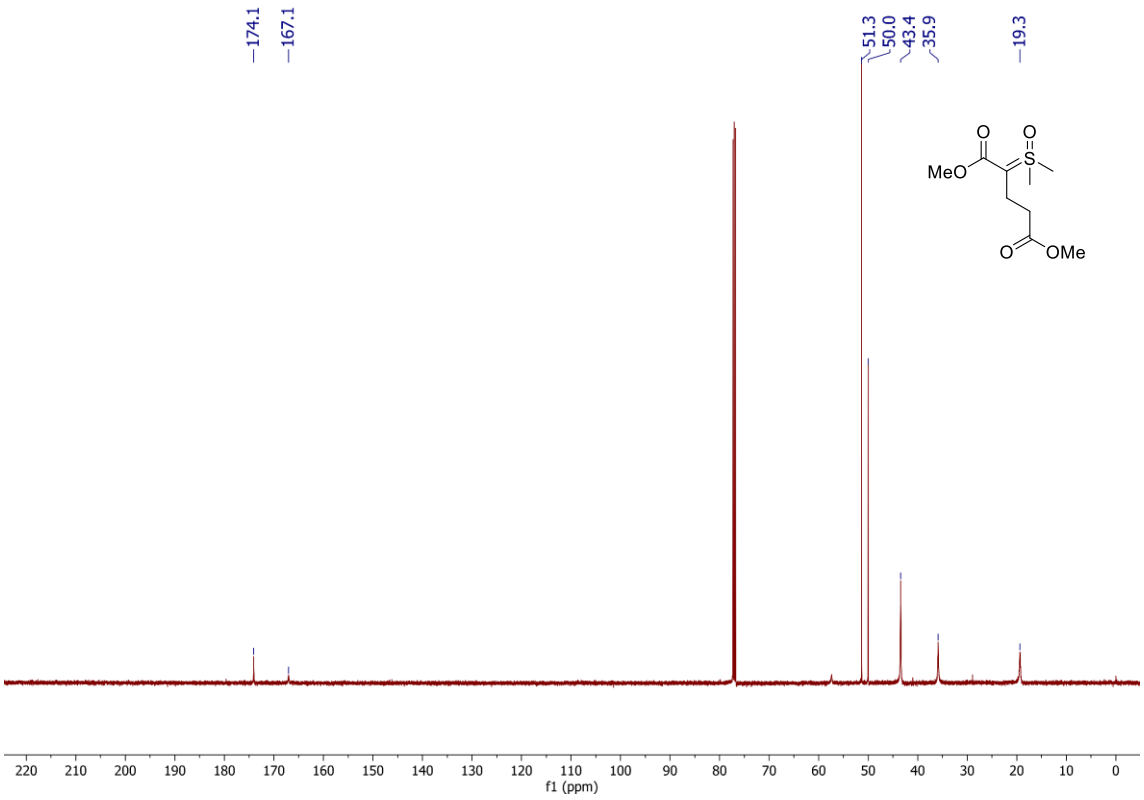
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **1h**



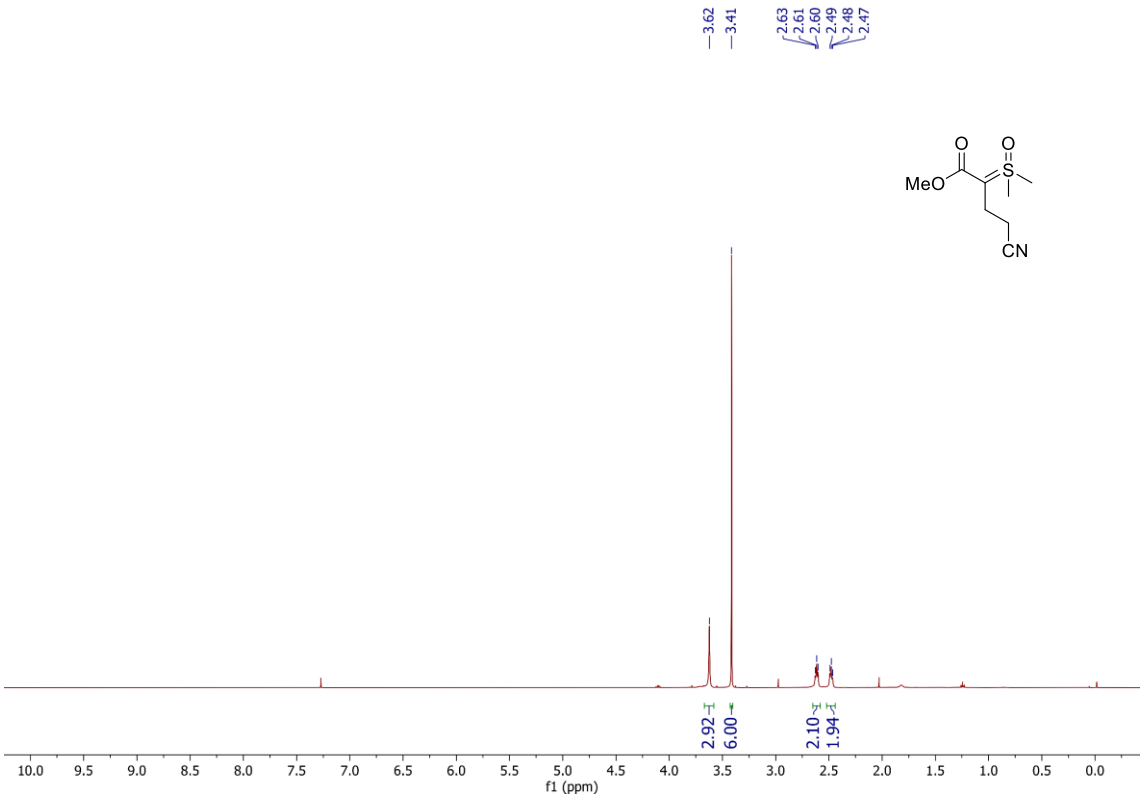
^{1}H NMR spectra (600 MHz, $CDCl_3$) of compound **2a**



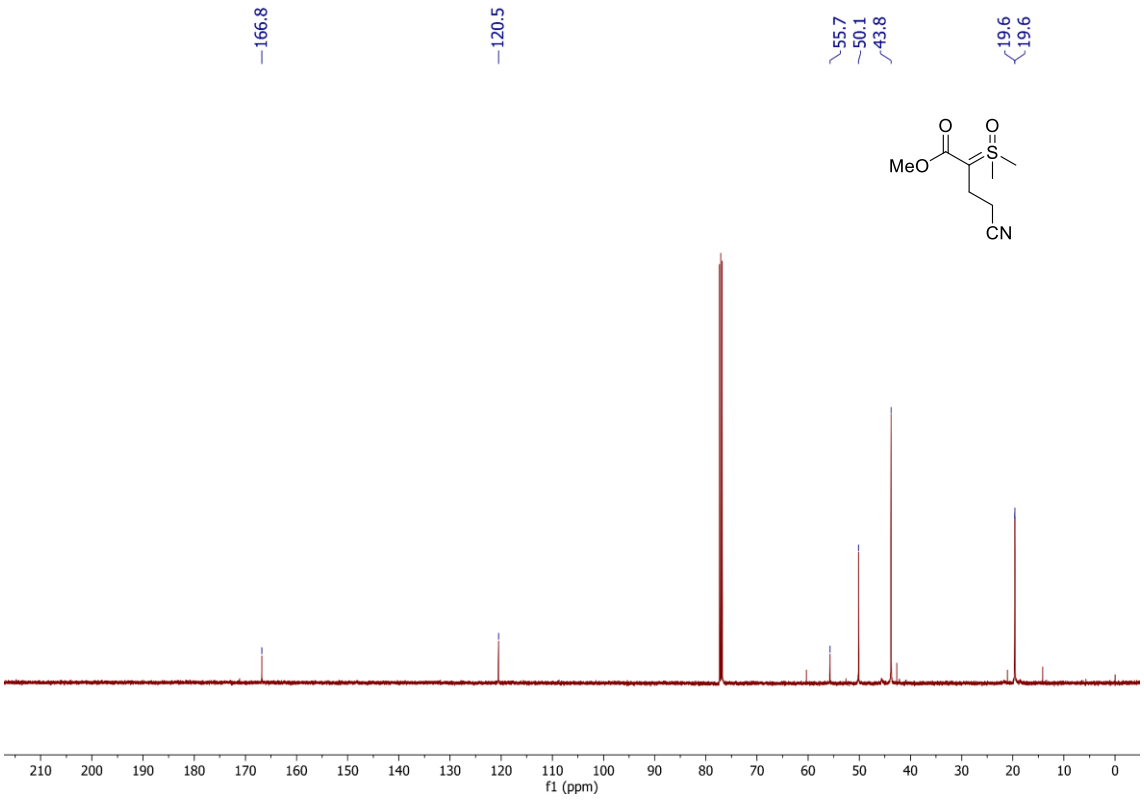
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2a**



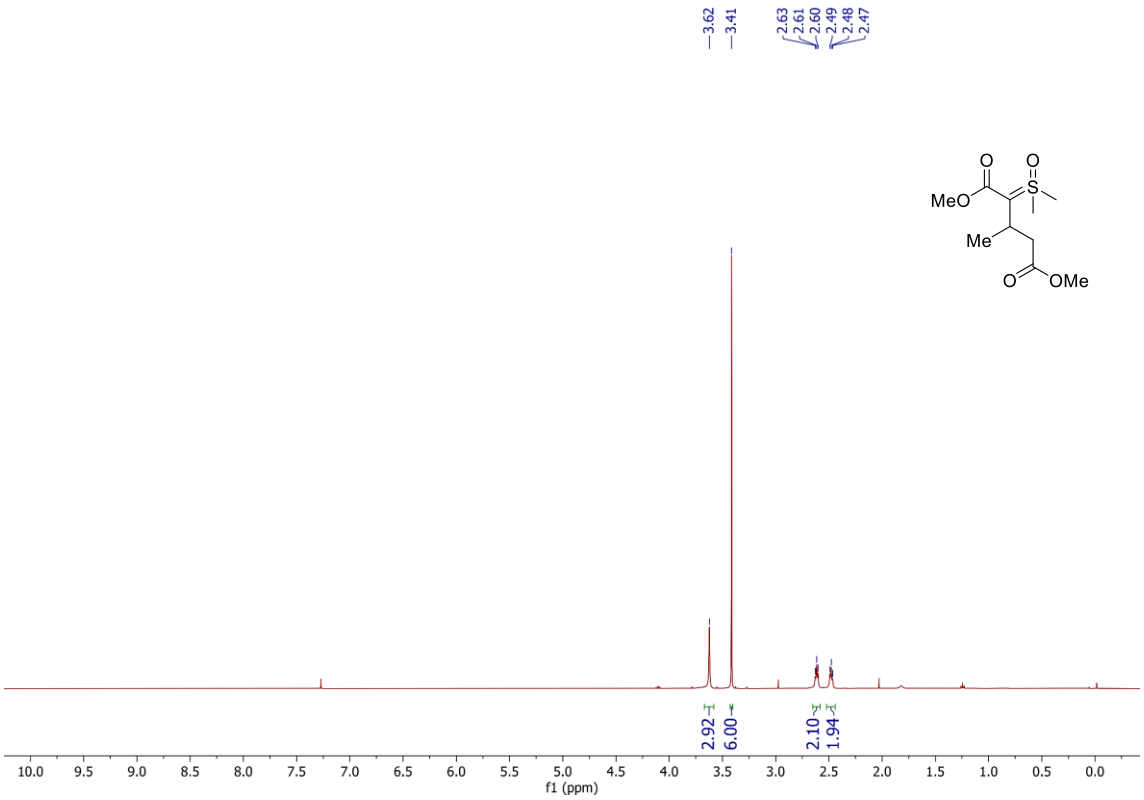
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **2b**



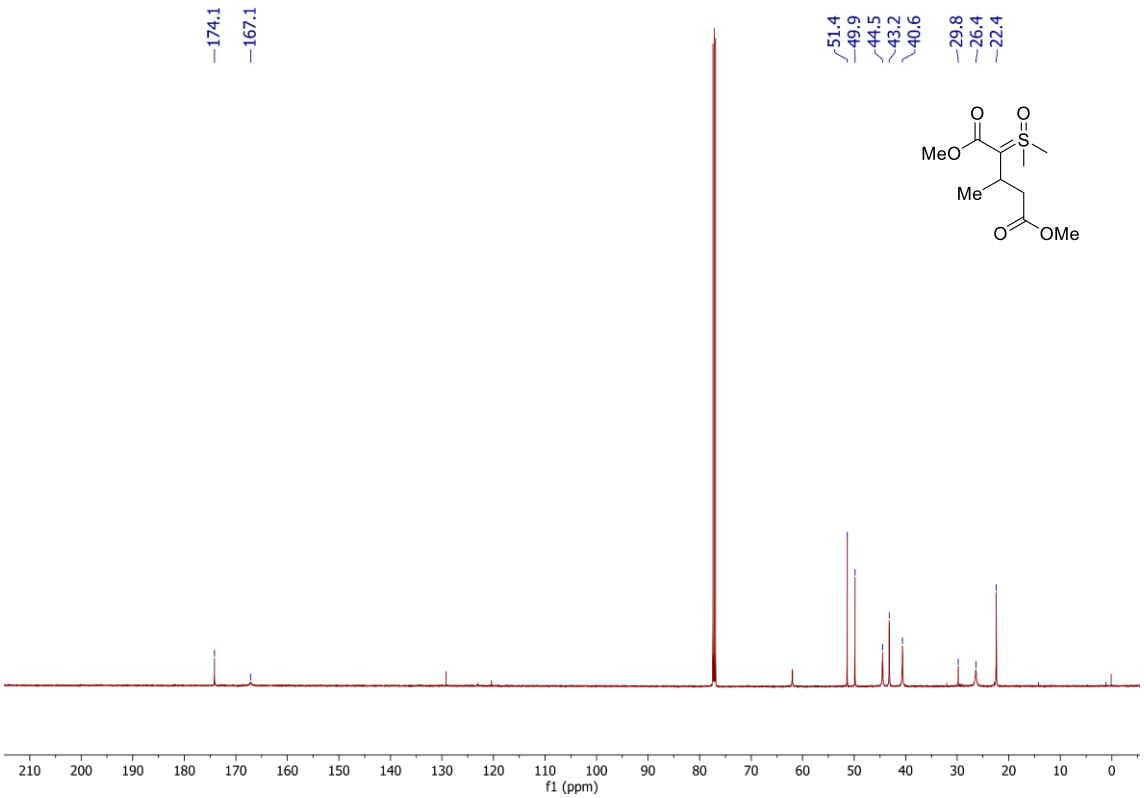
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2b**



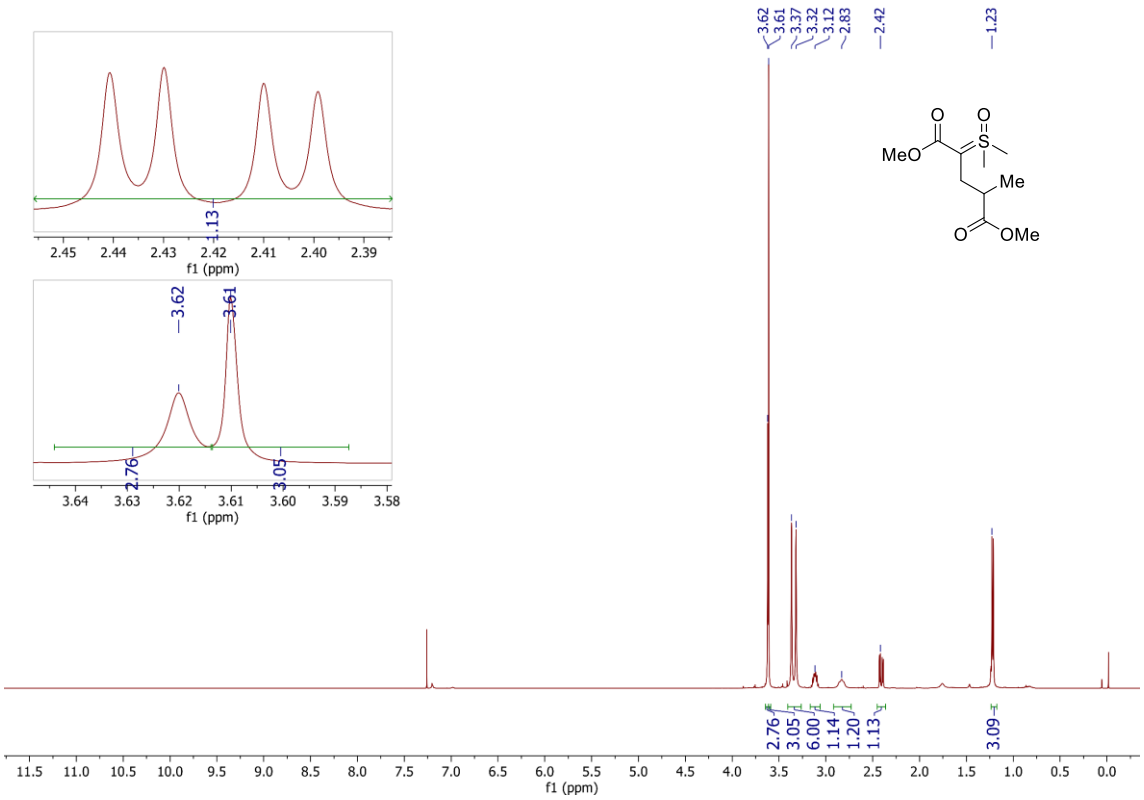
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2c**



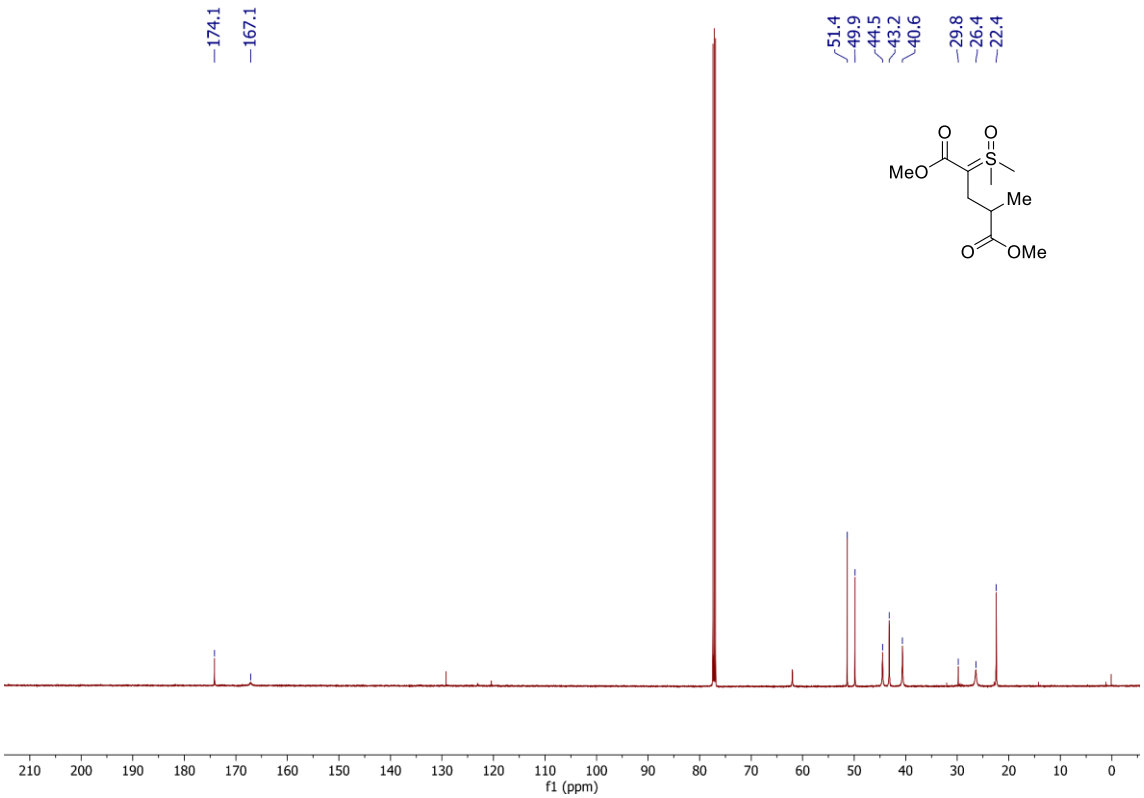
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2c**



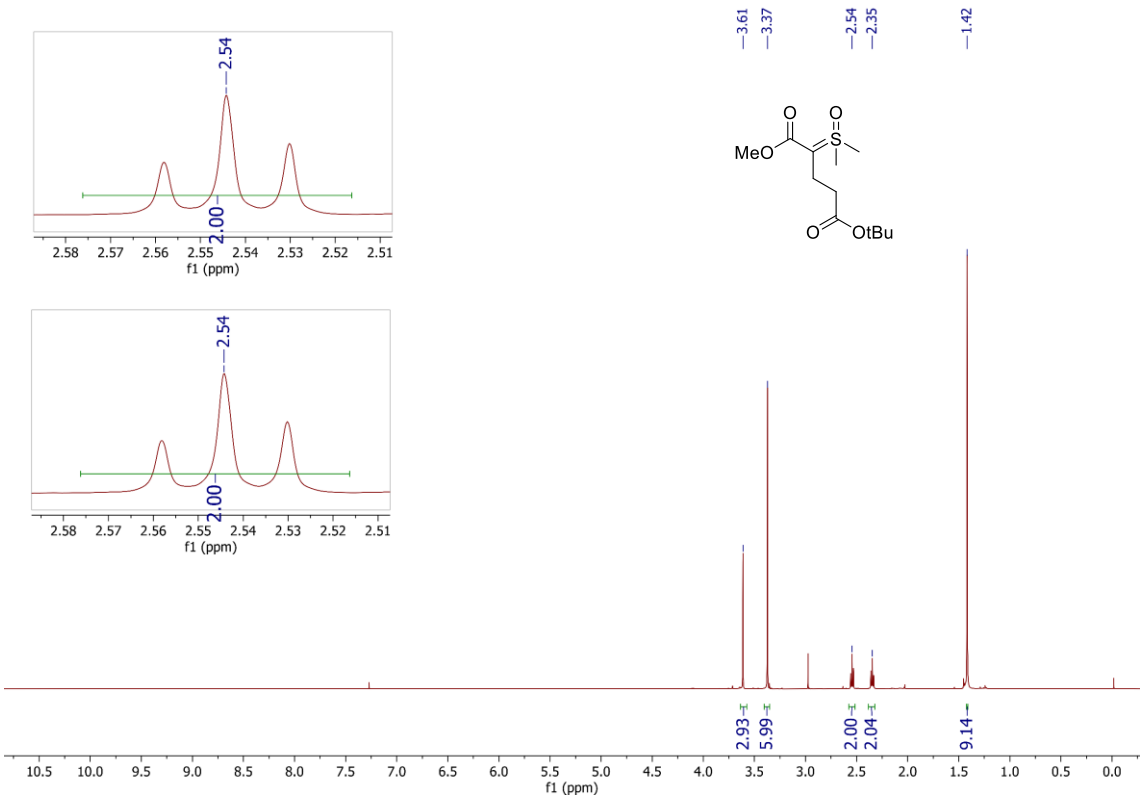
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2d**



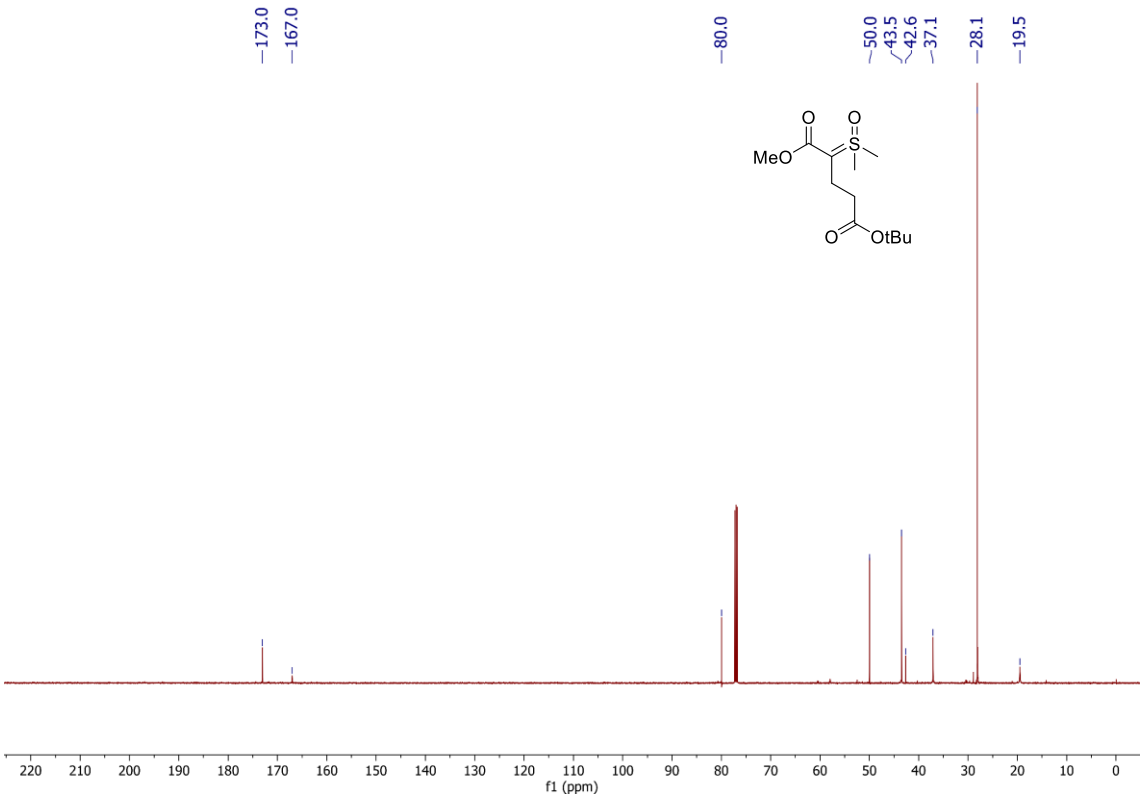
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2d**



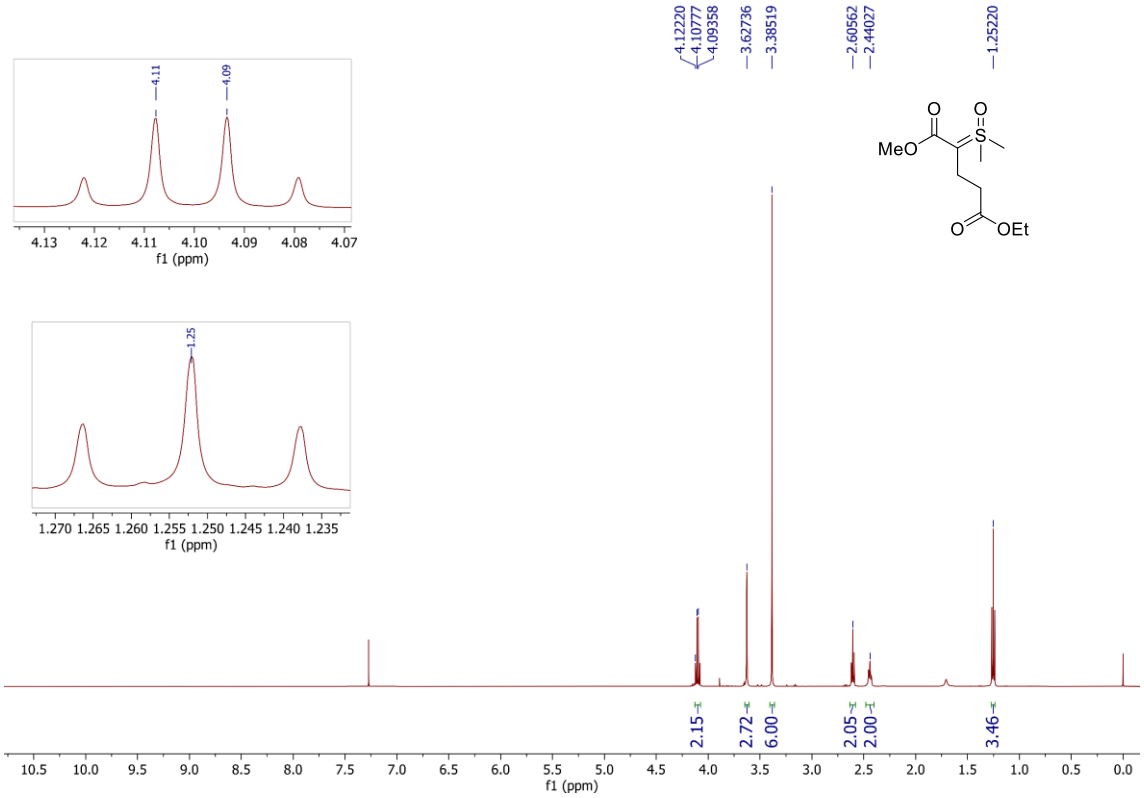
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2e**



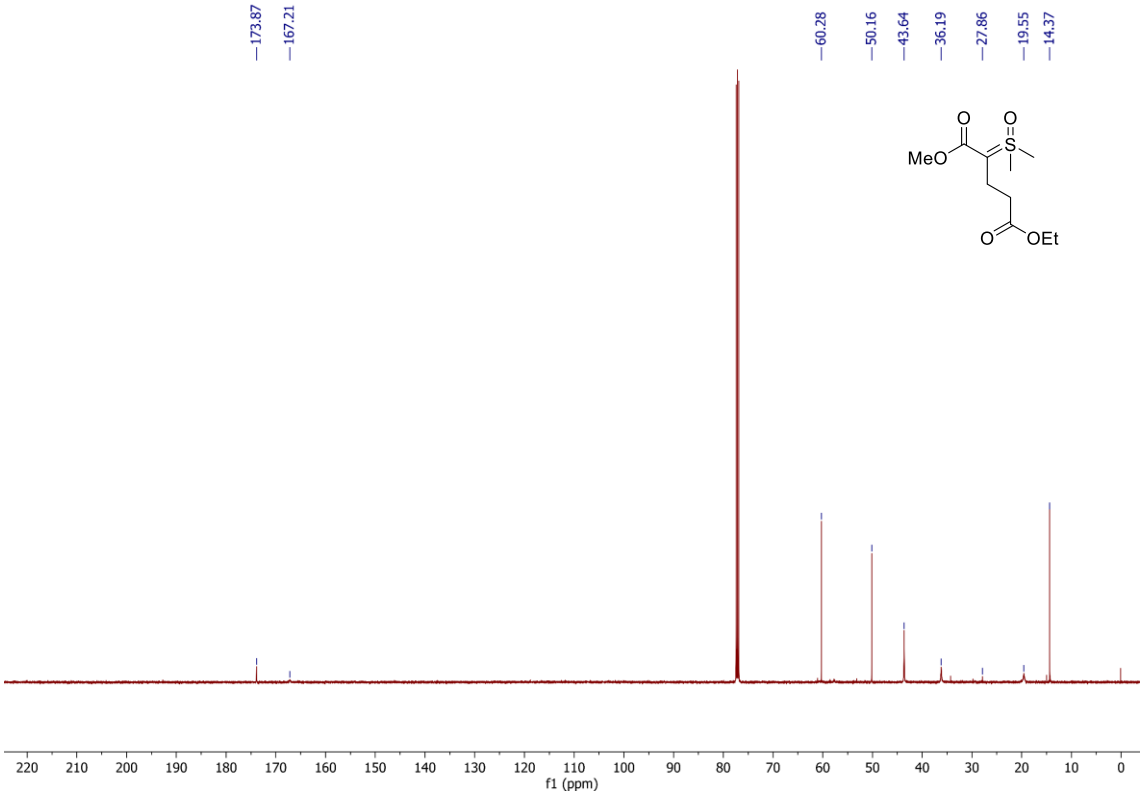
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2e**



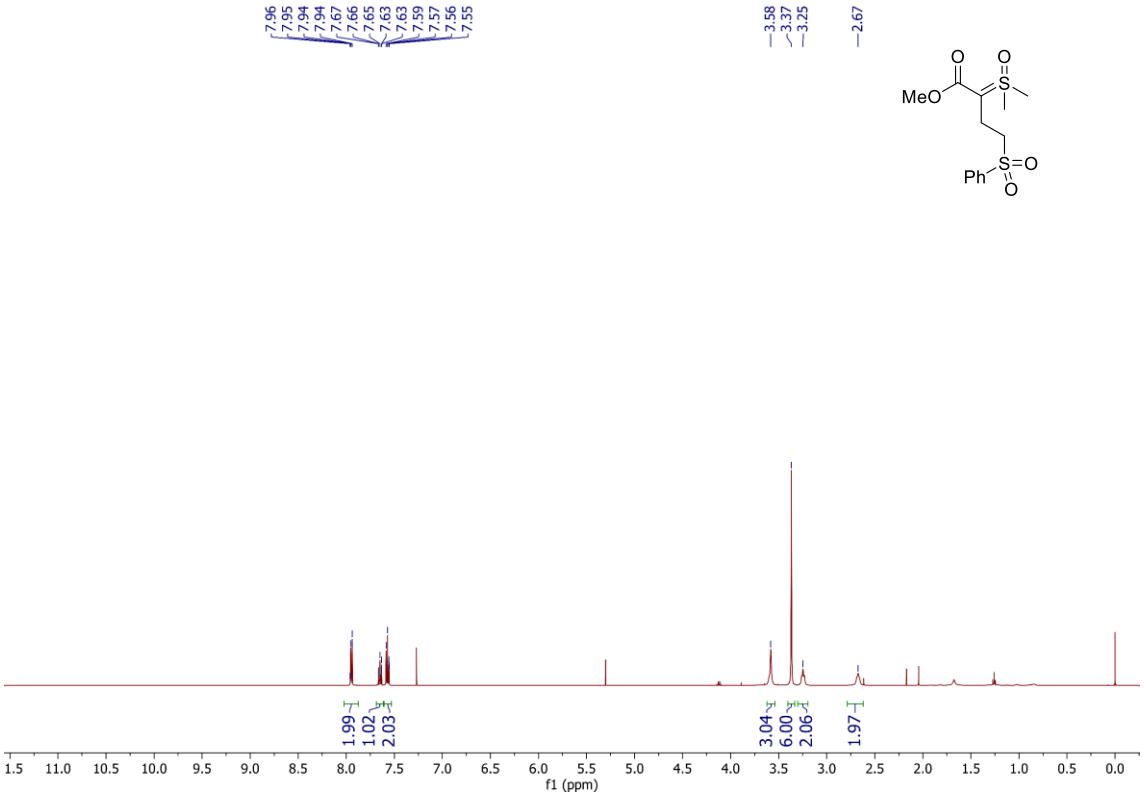
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **2f**



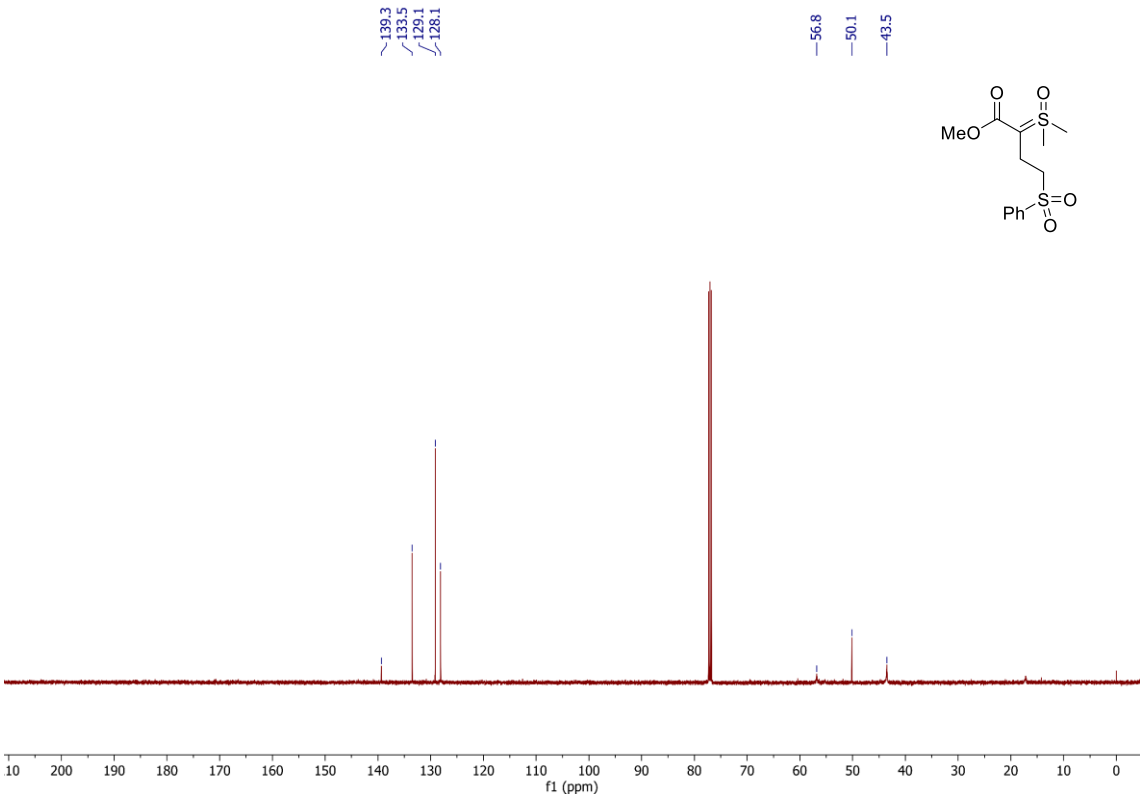
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2f**



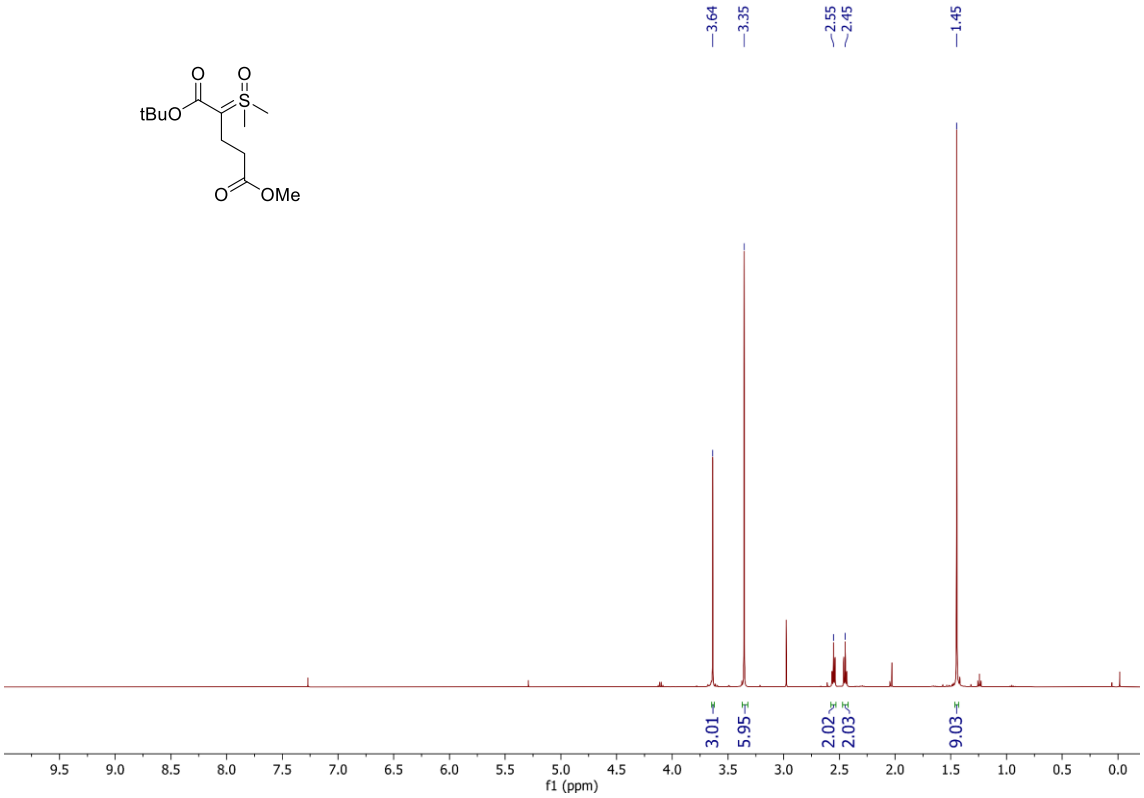
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2g**



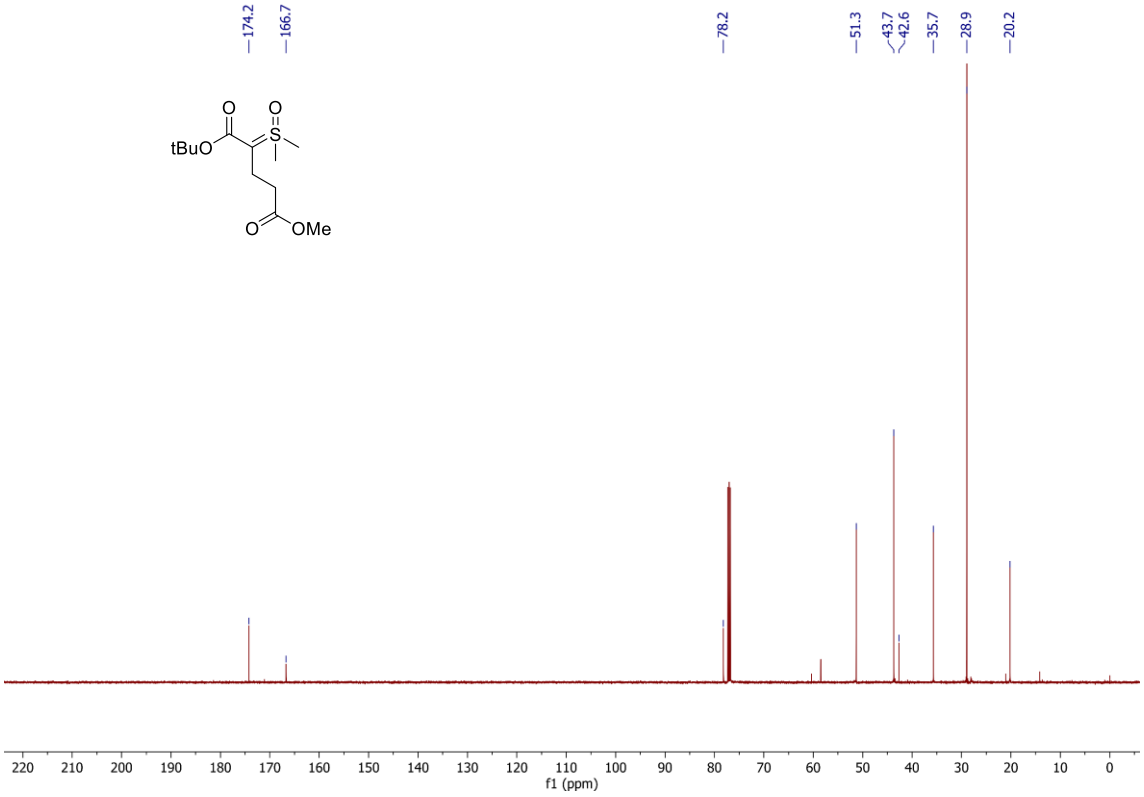
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2g**



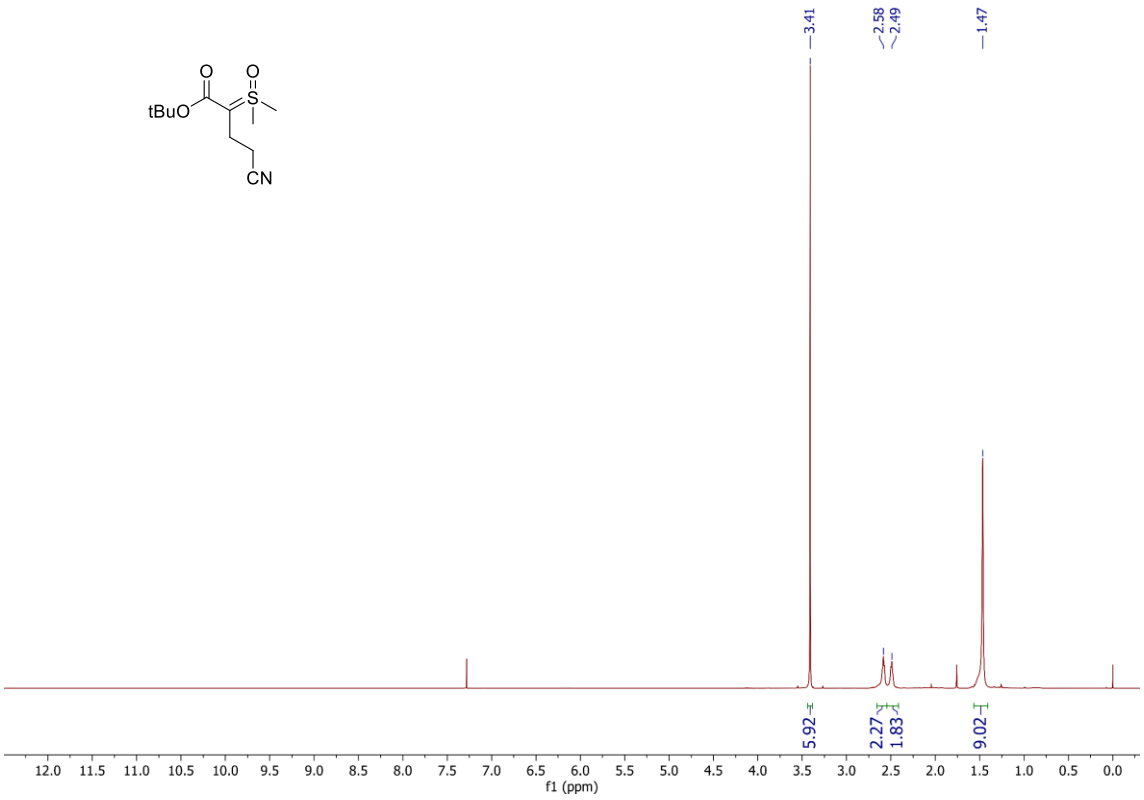
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **2h**



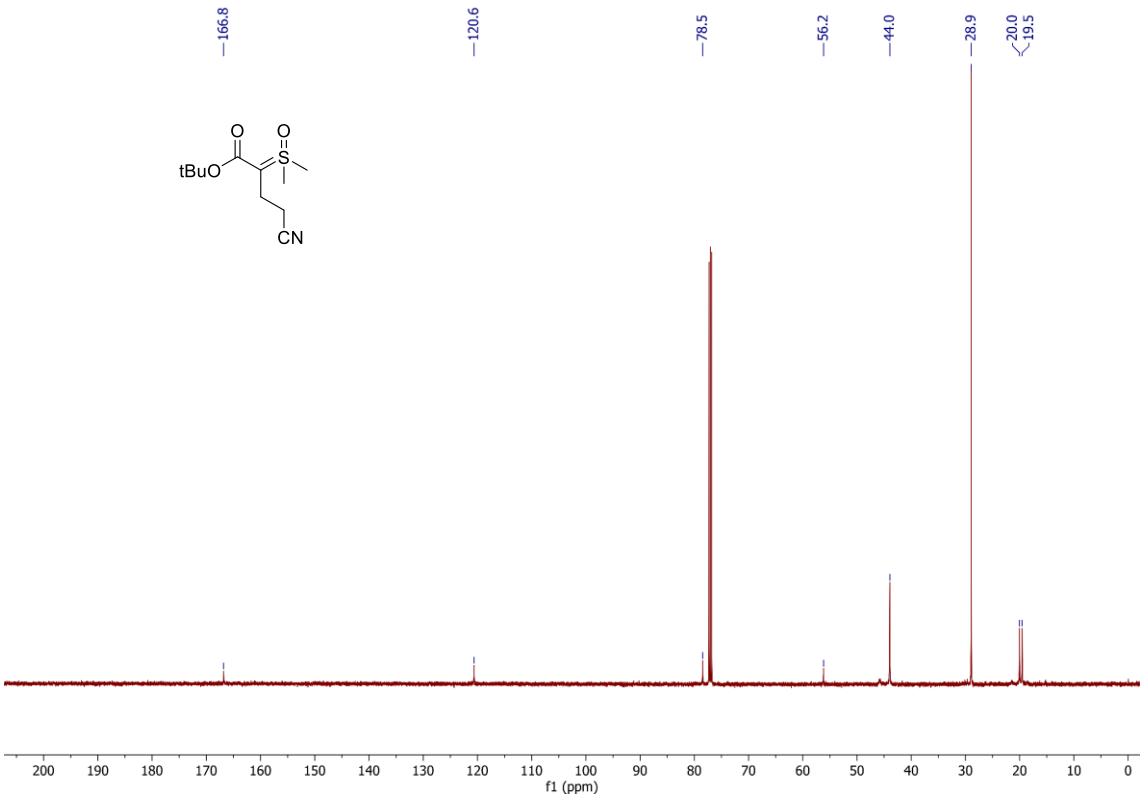
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2h**



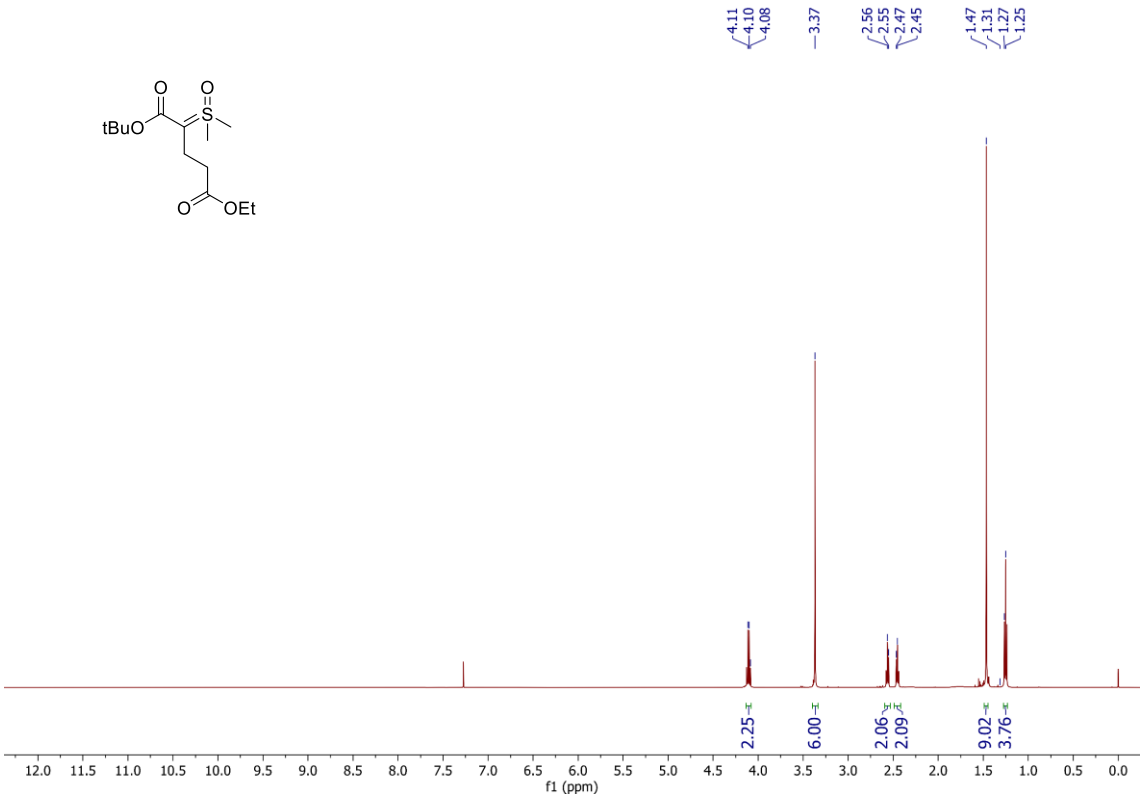
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **2i**



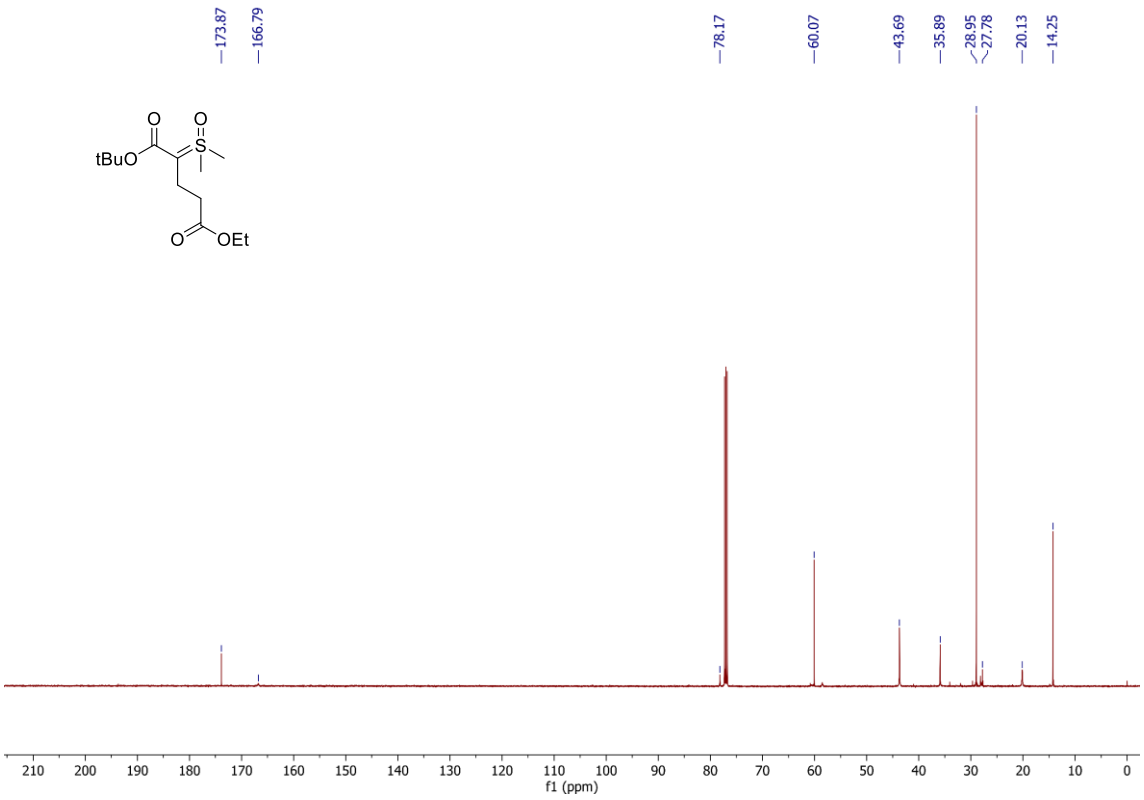
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2i**



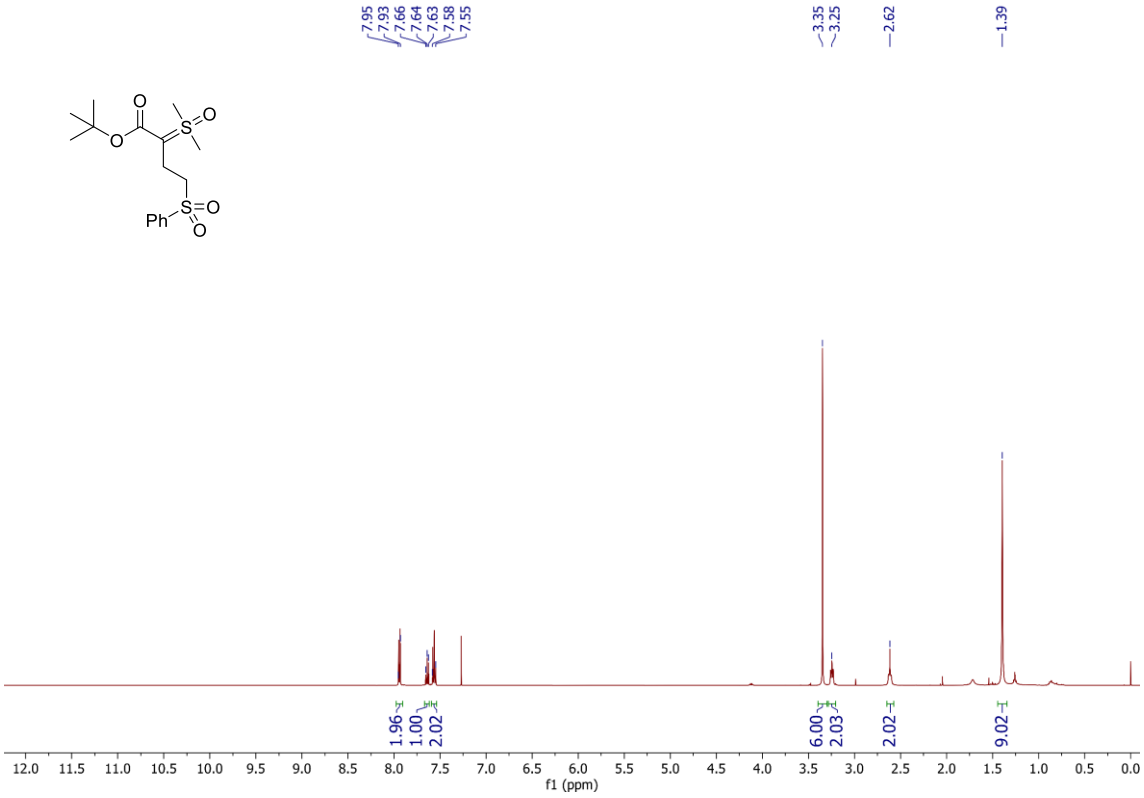
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2j**



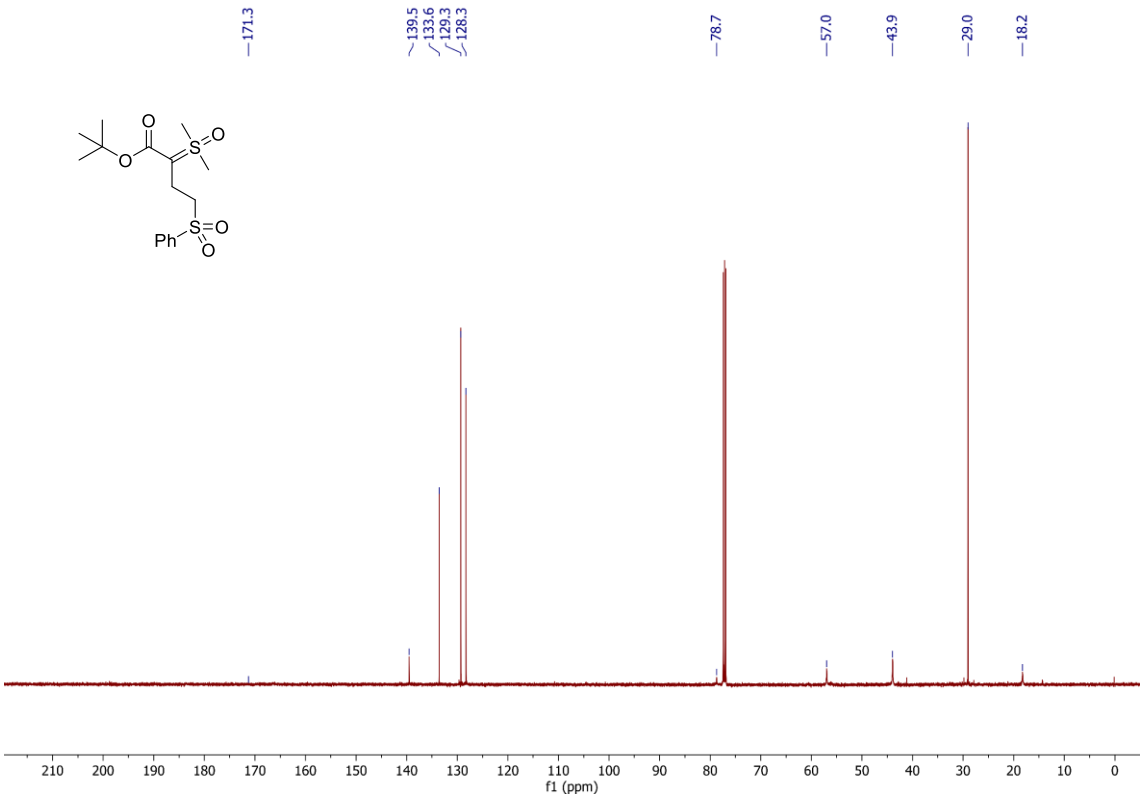
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2j**



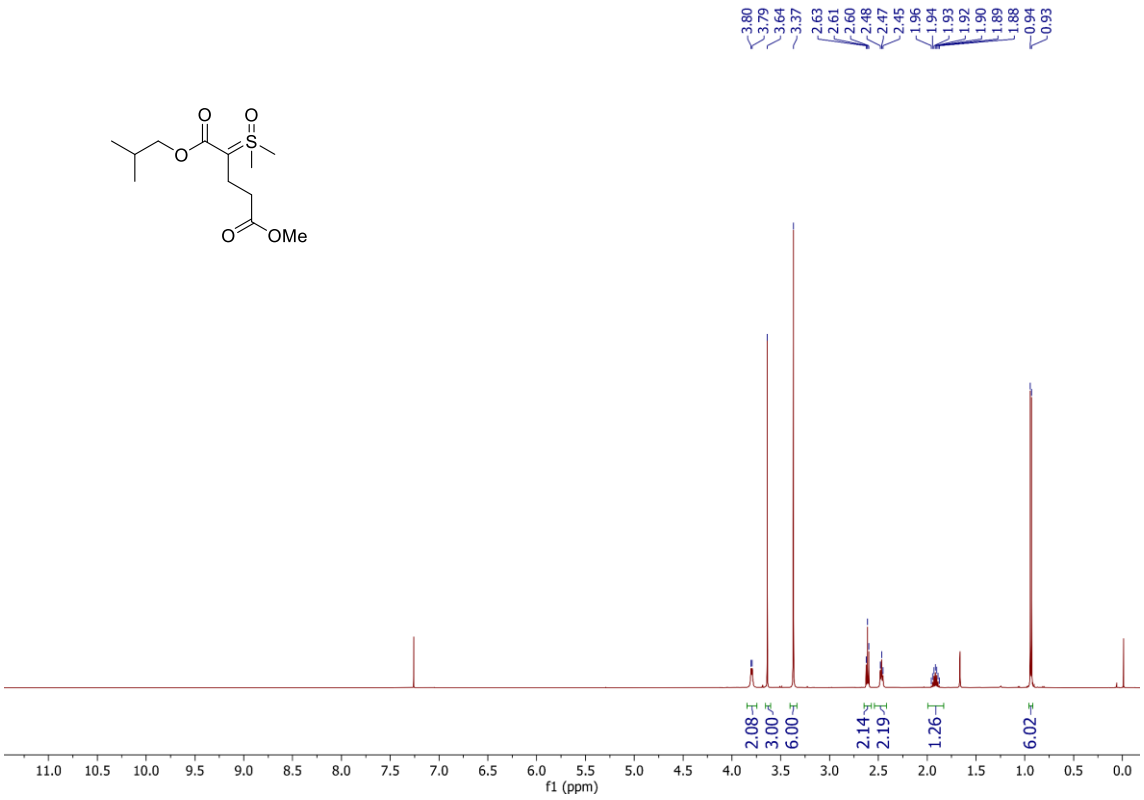
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **2k**



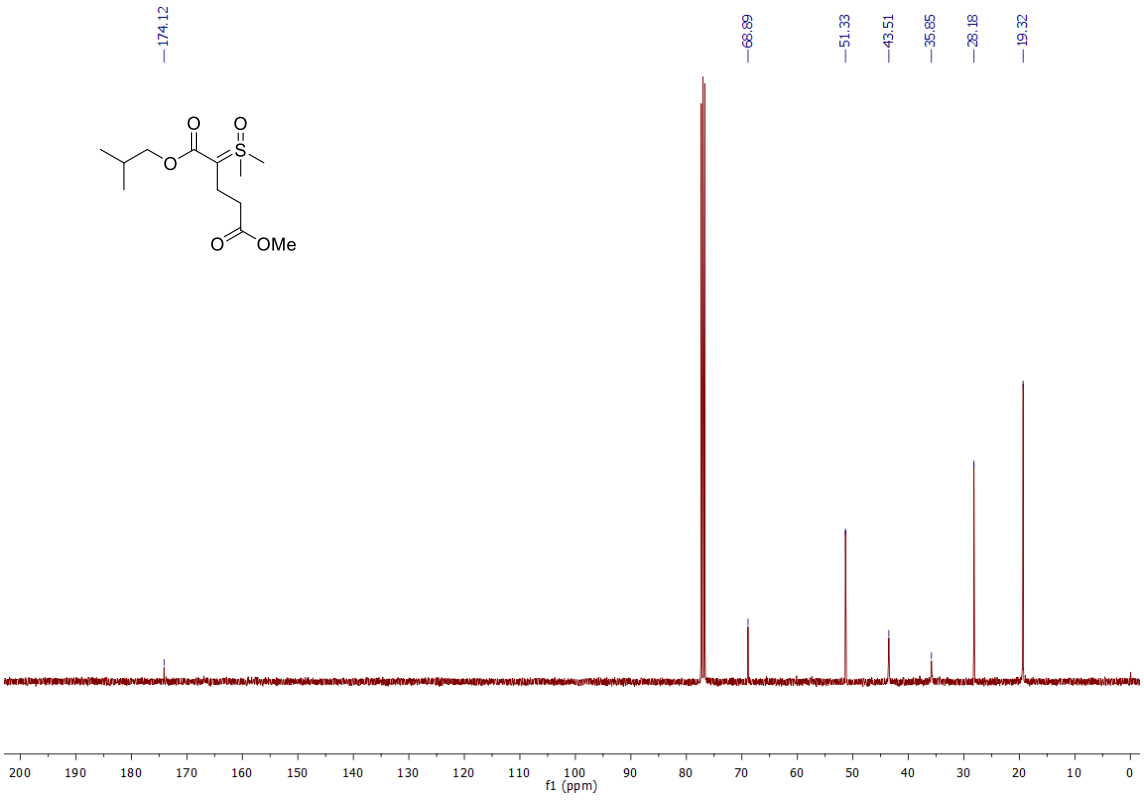
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2k**



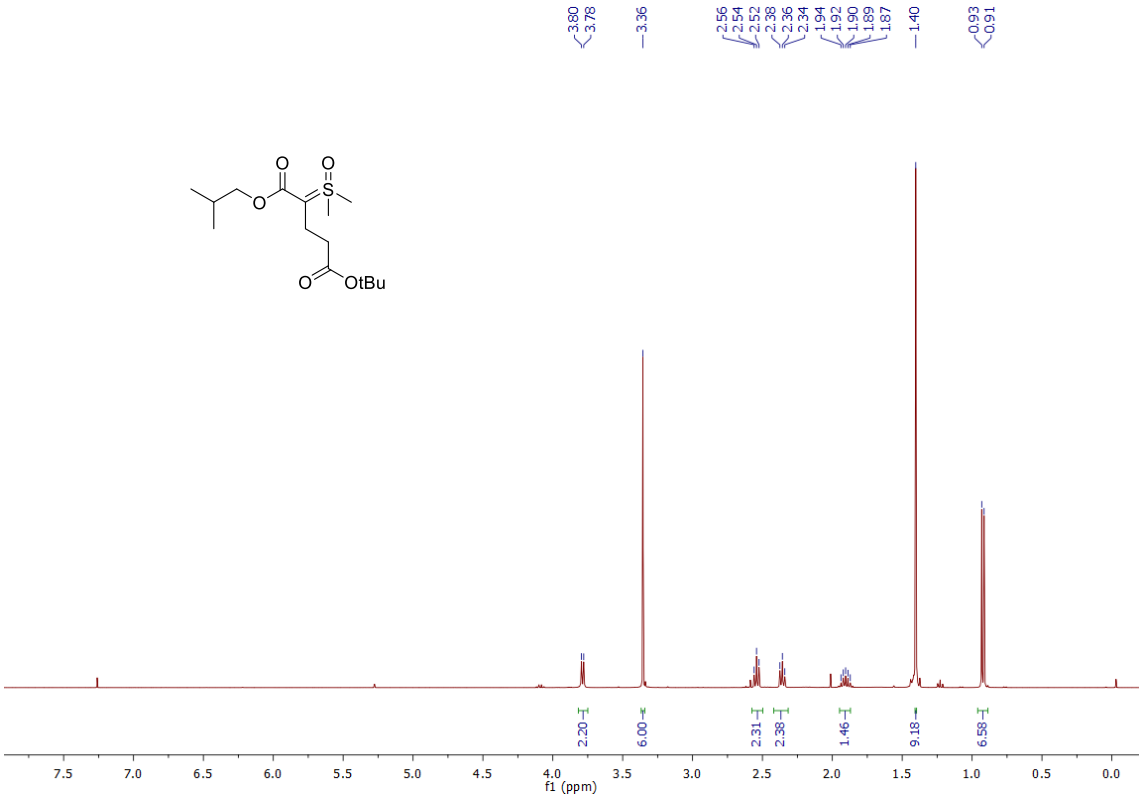
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **2l**



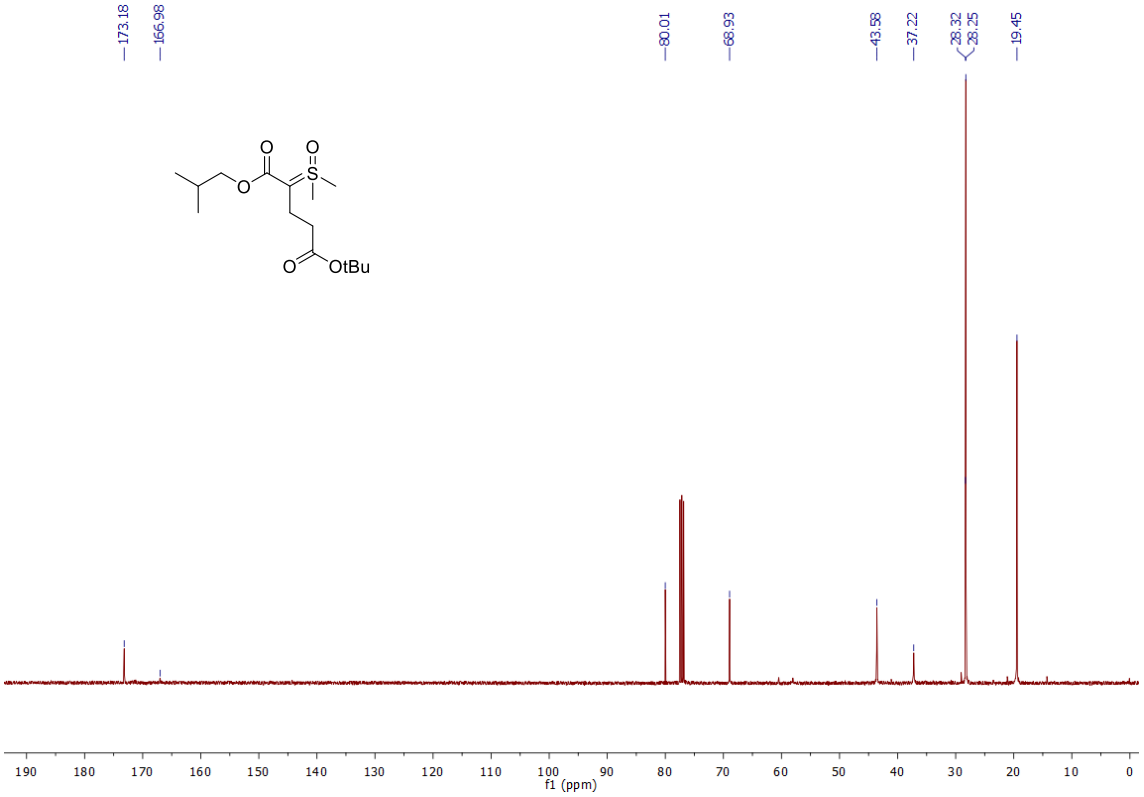
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2l**



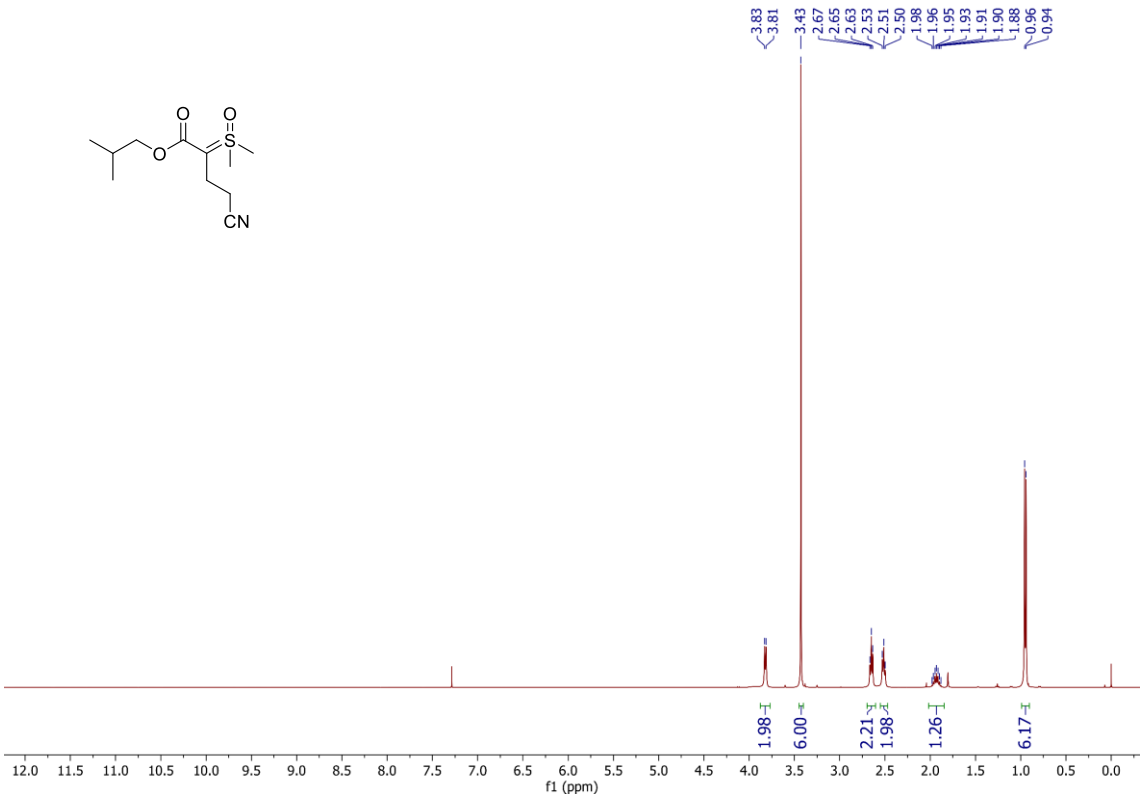
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **2m**



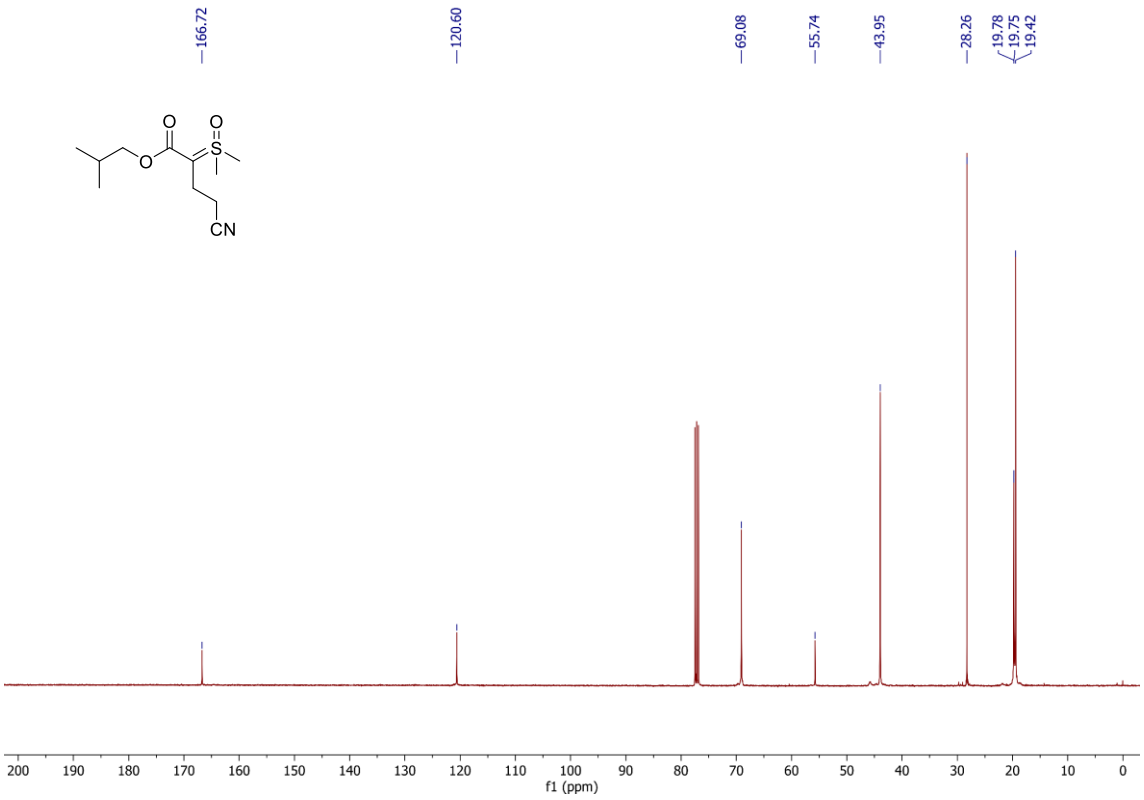
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2m**



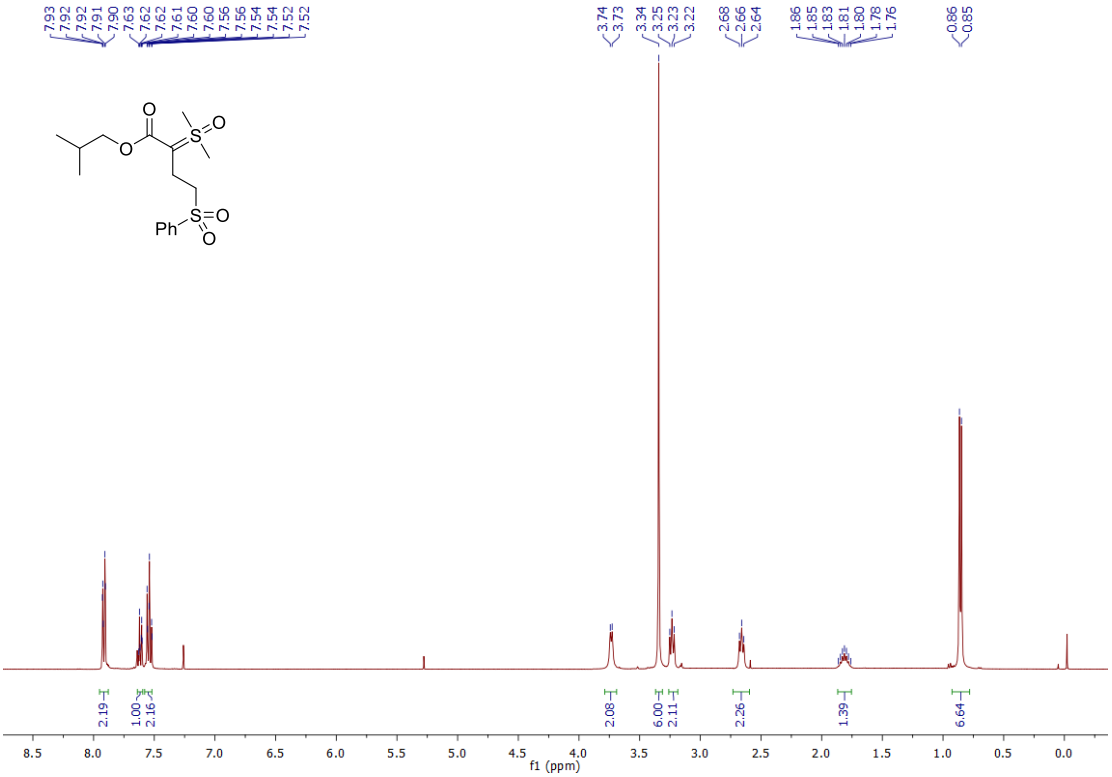
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2n**



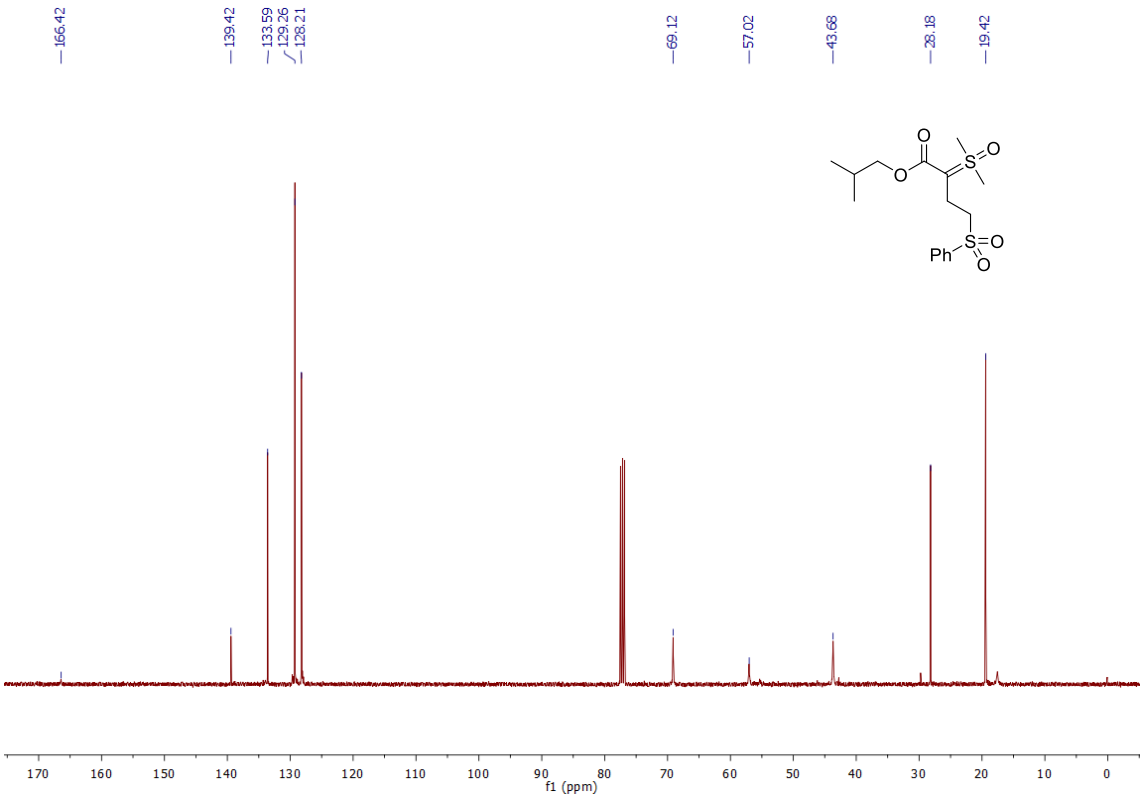
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2n**



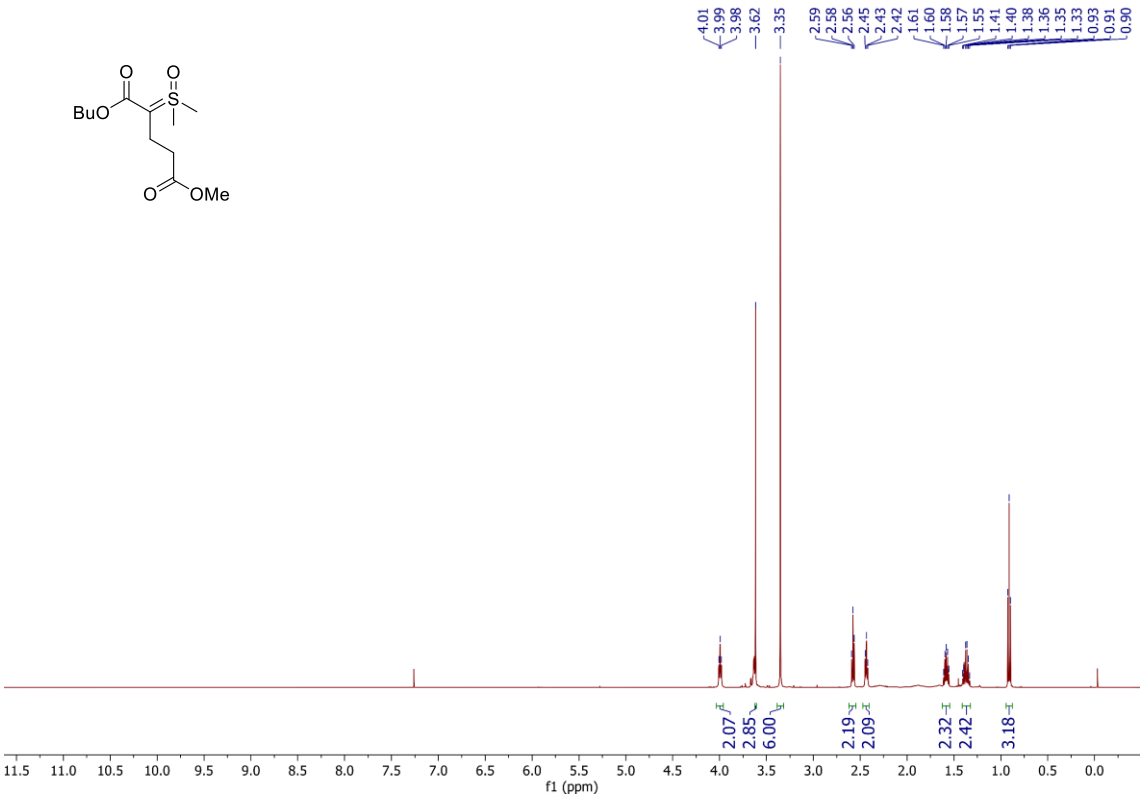
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2o**



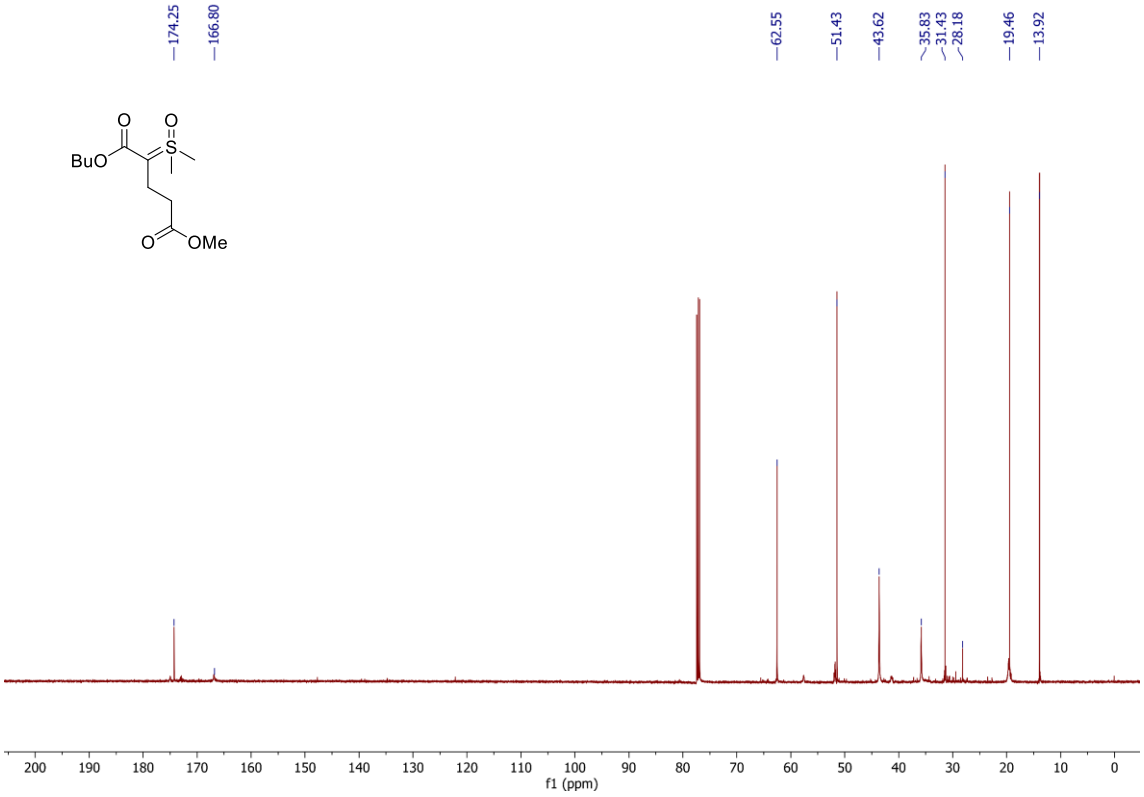
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2o**



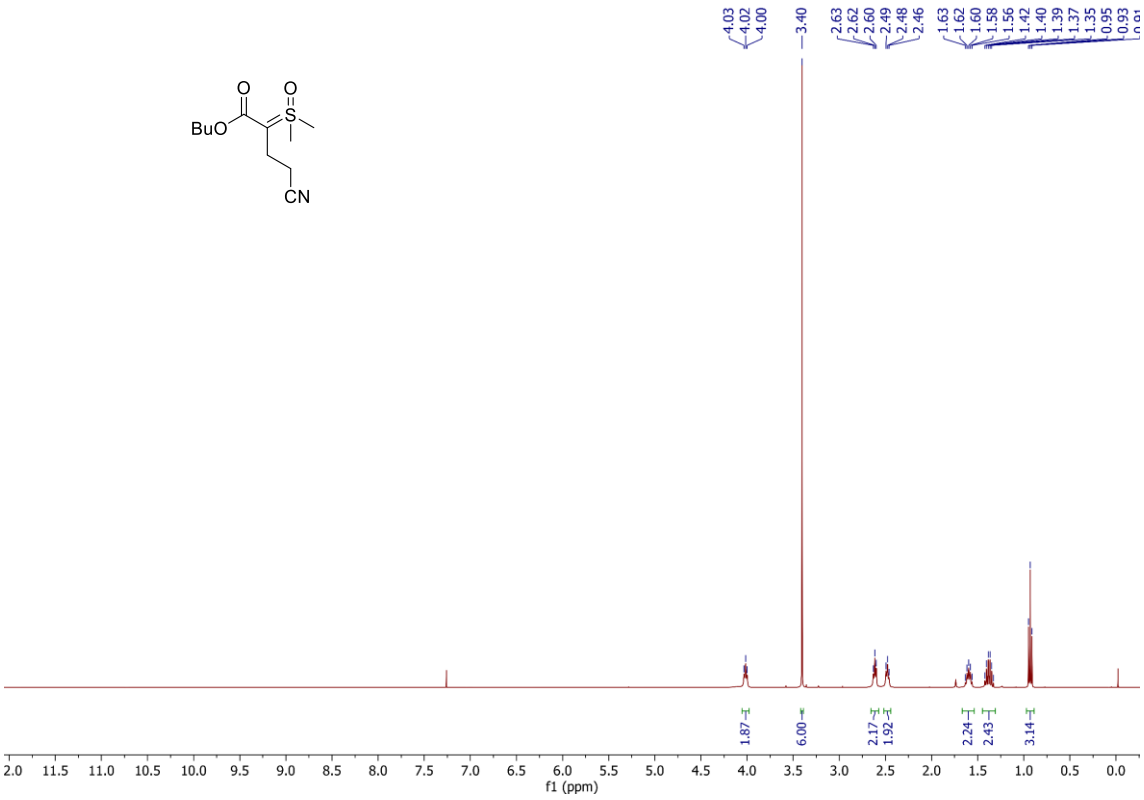
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2p**



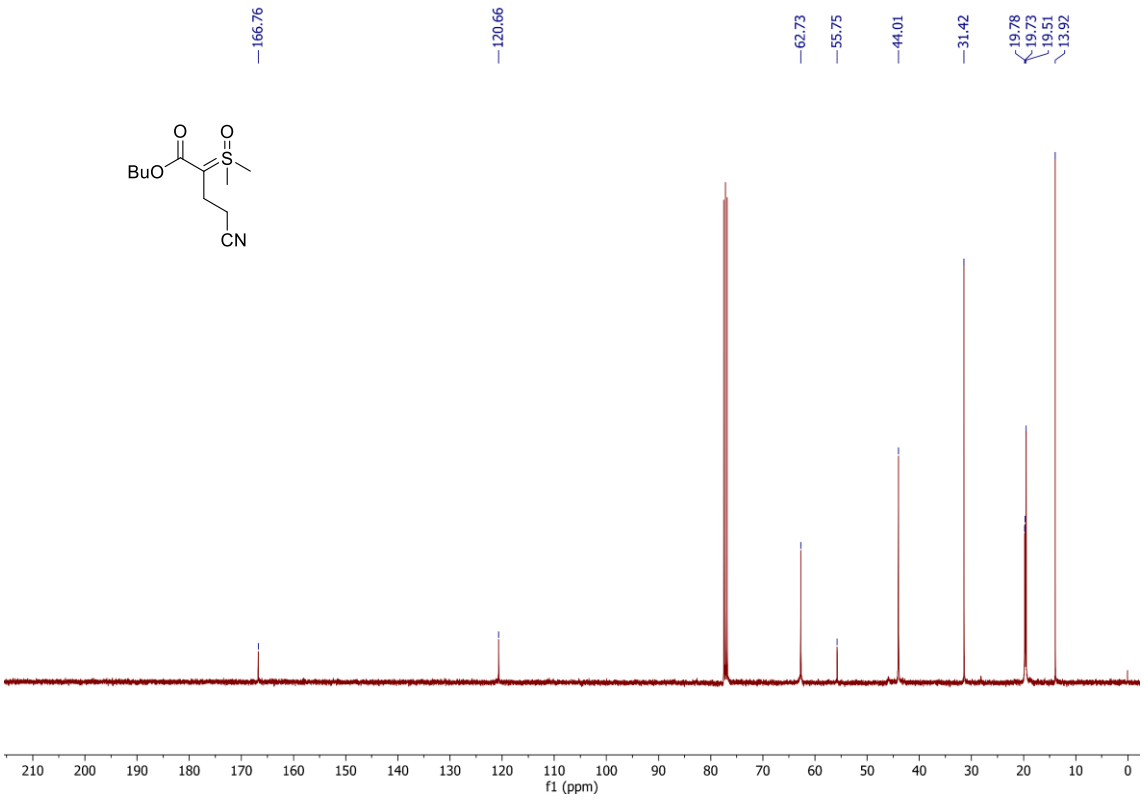
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2p**



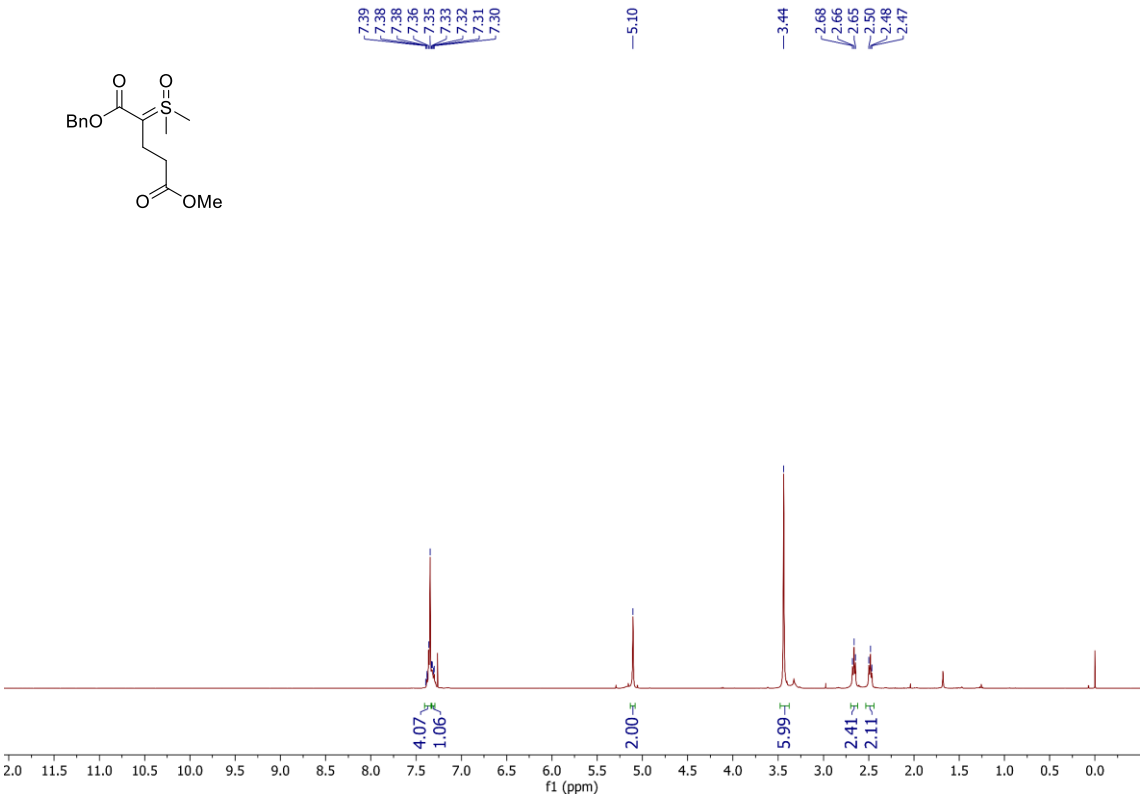
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2q**



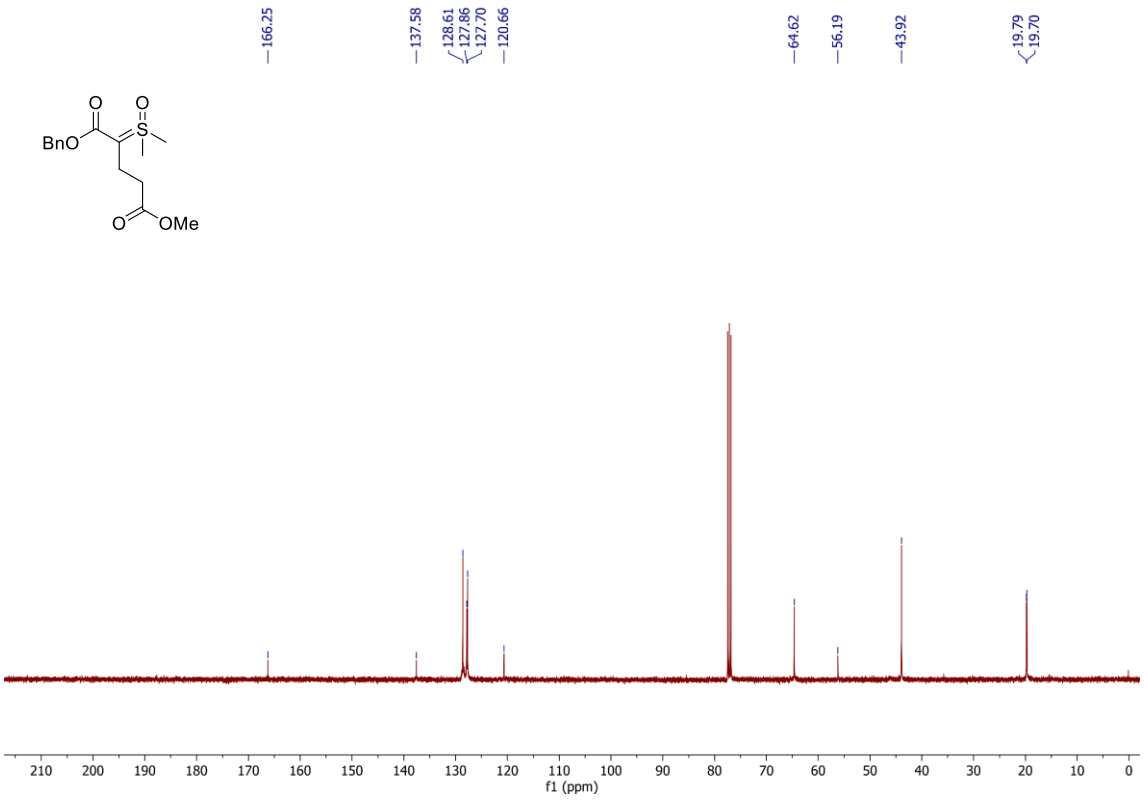
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **2q**



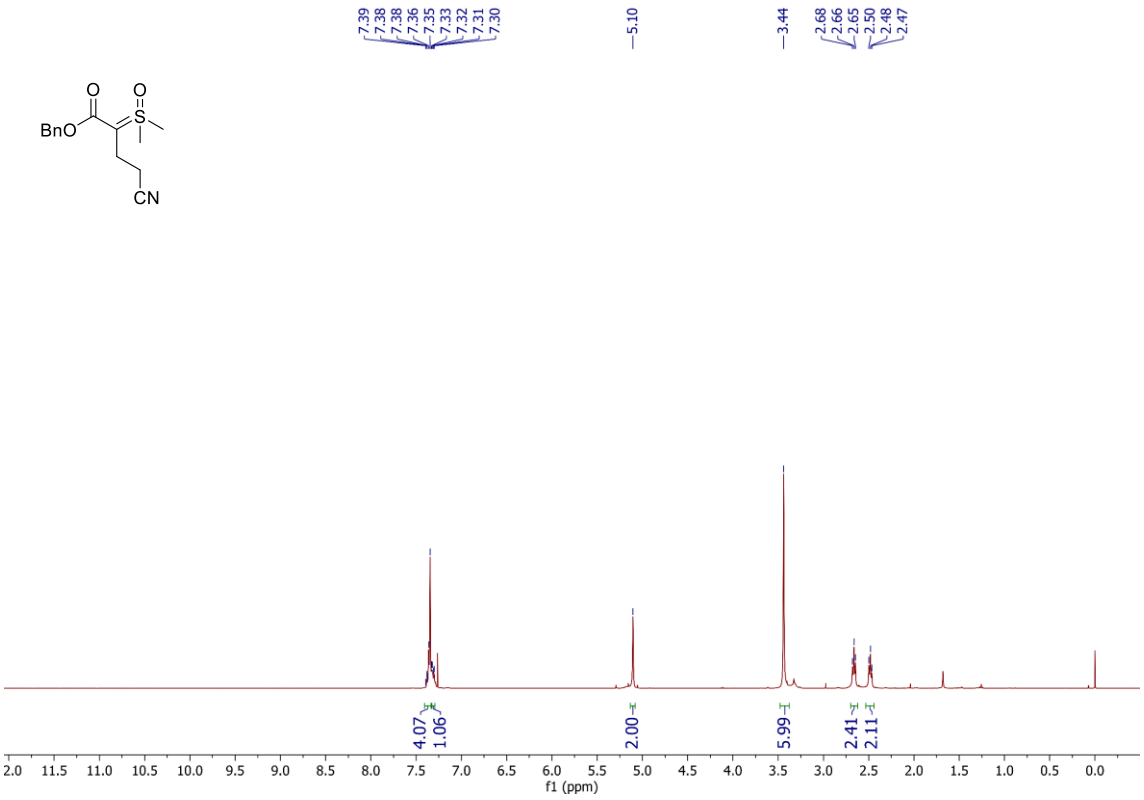
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2r**



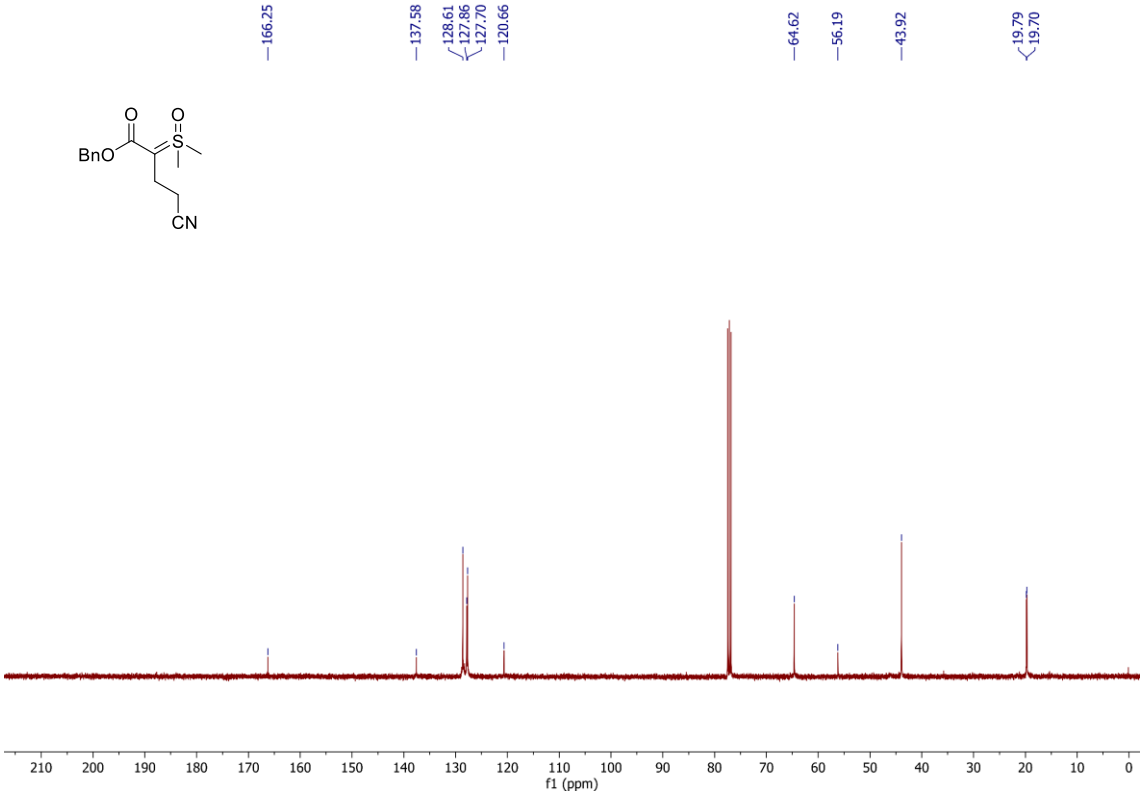
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2r**



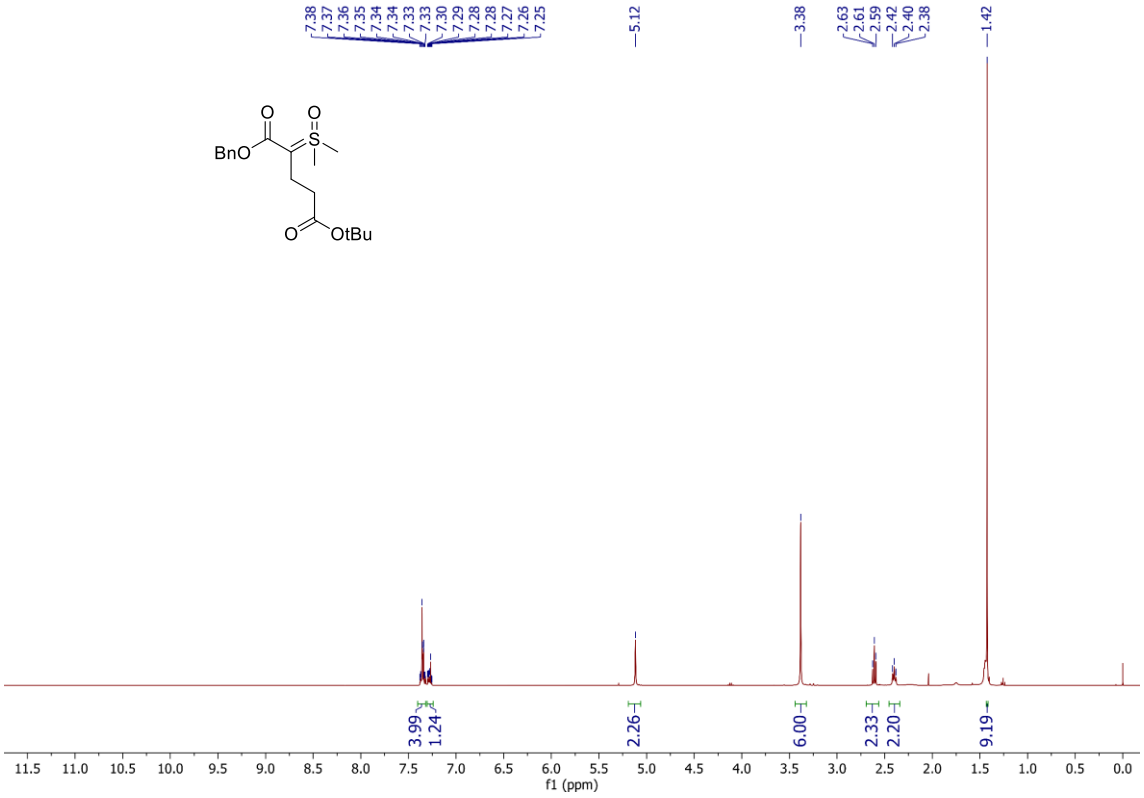
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2s**



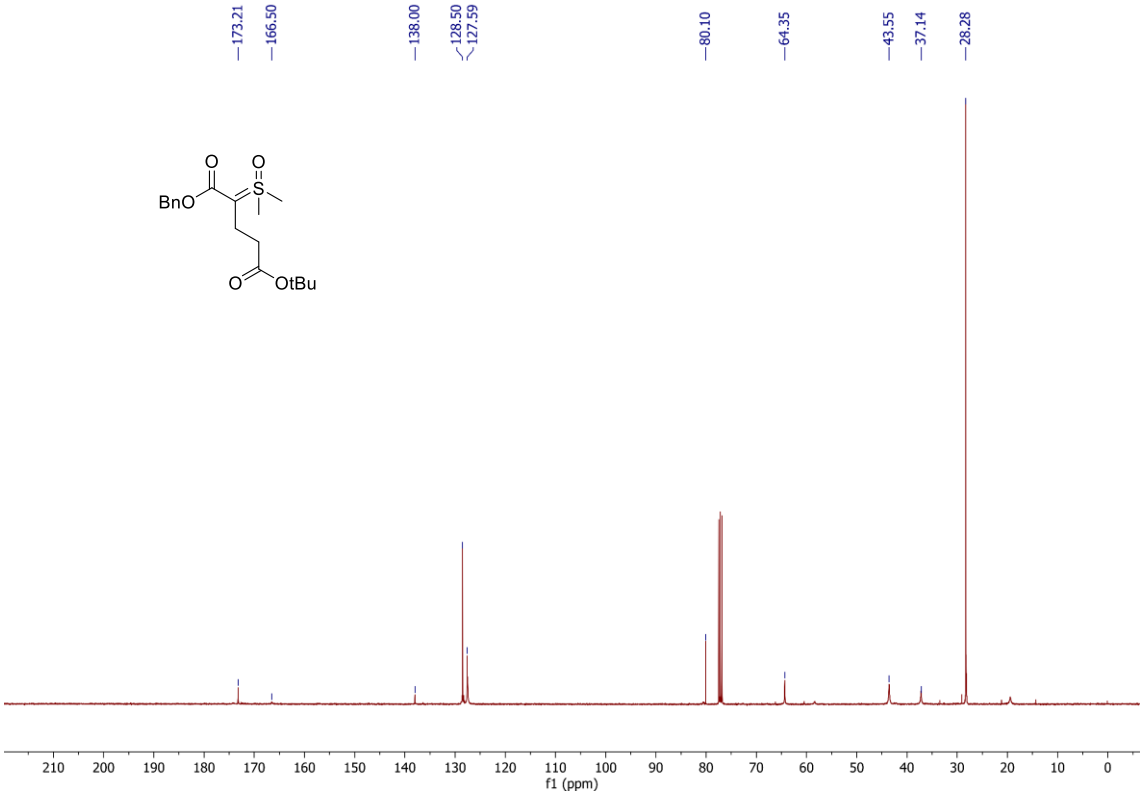
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2s**



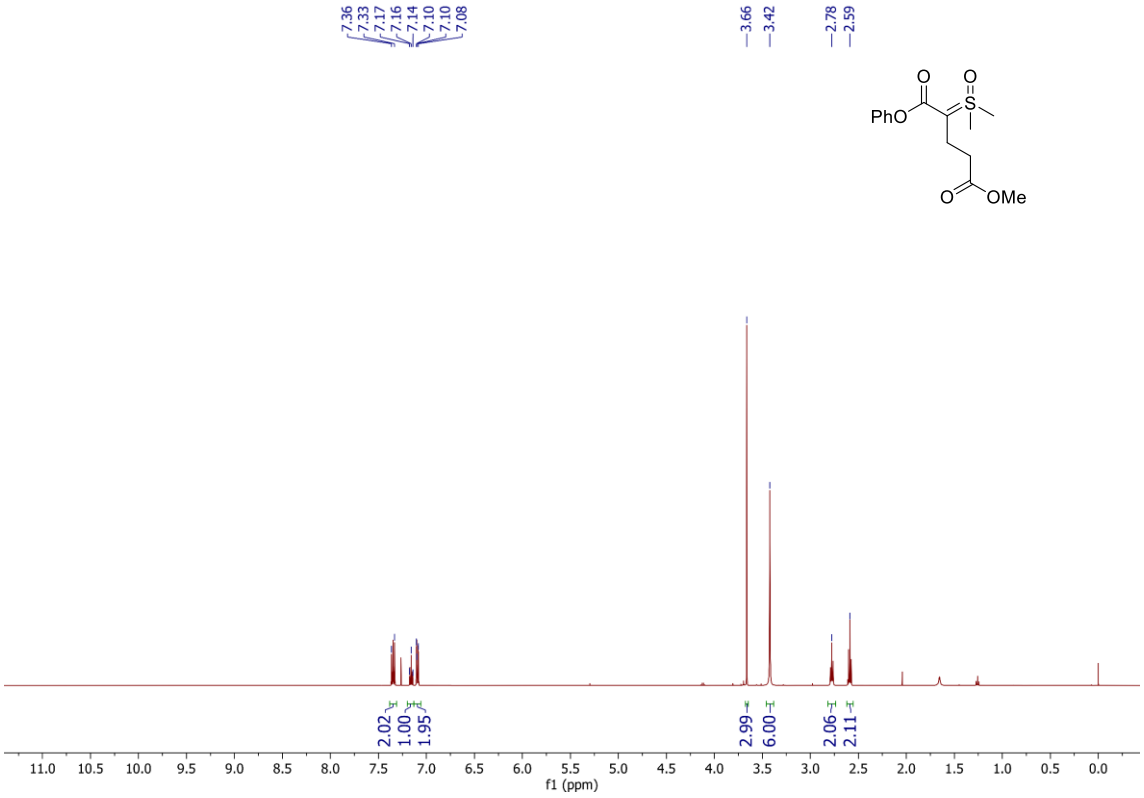
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2t**



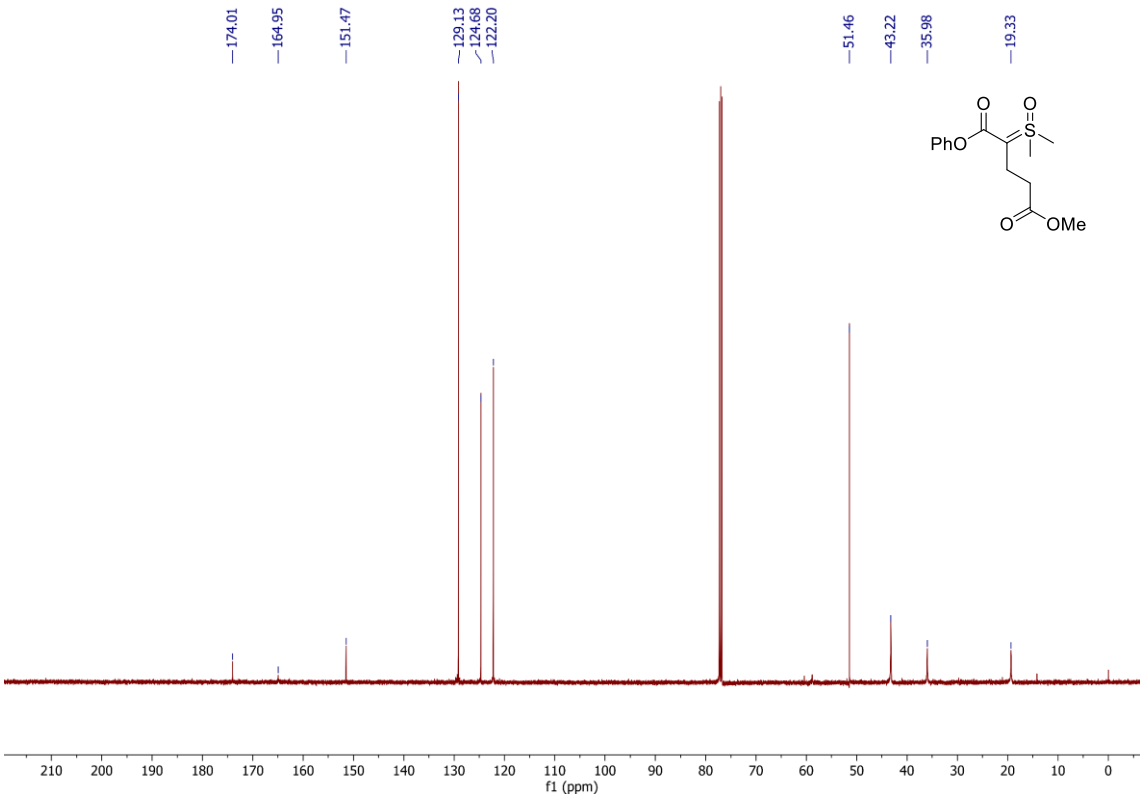
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **2t**



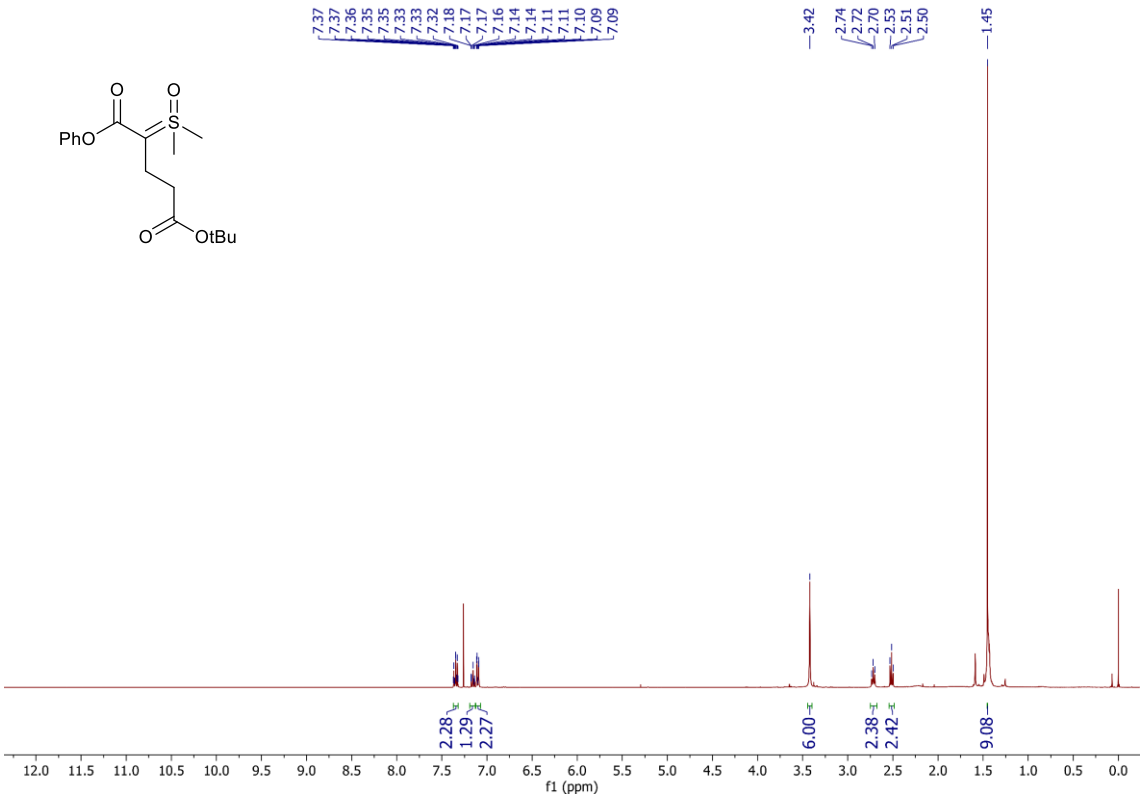
^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **2u**



^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2u**



^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2v**



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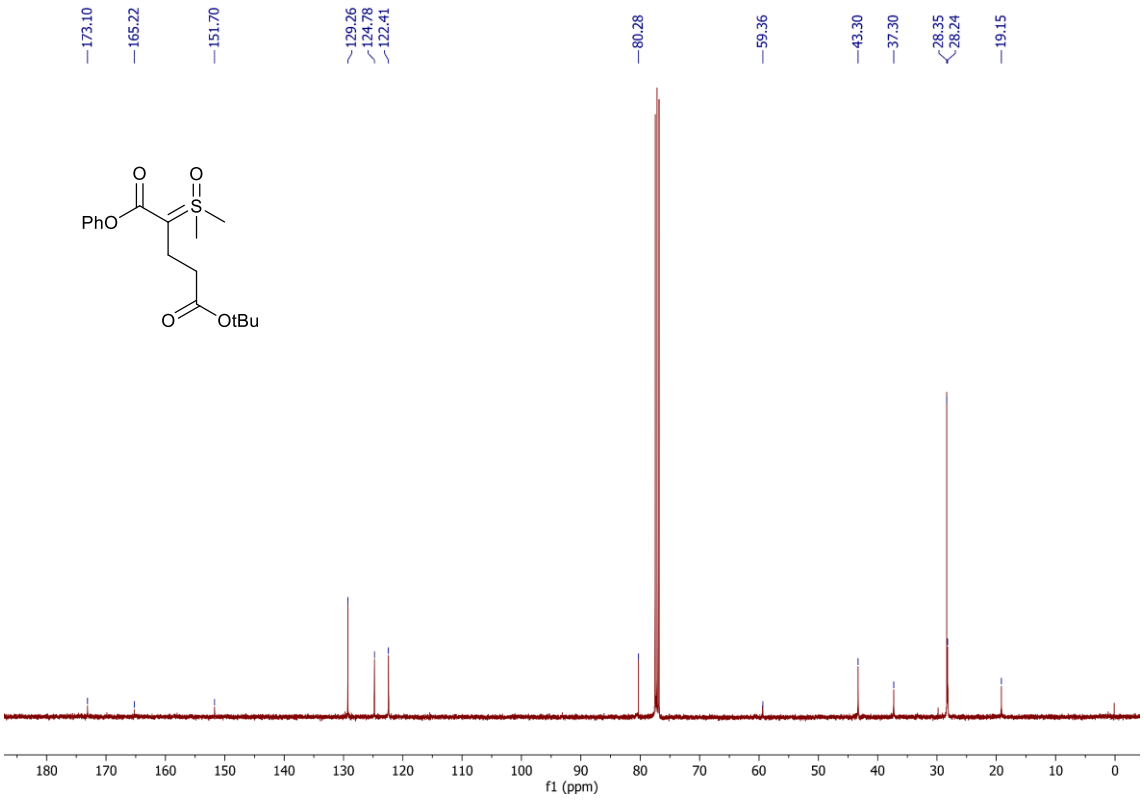

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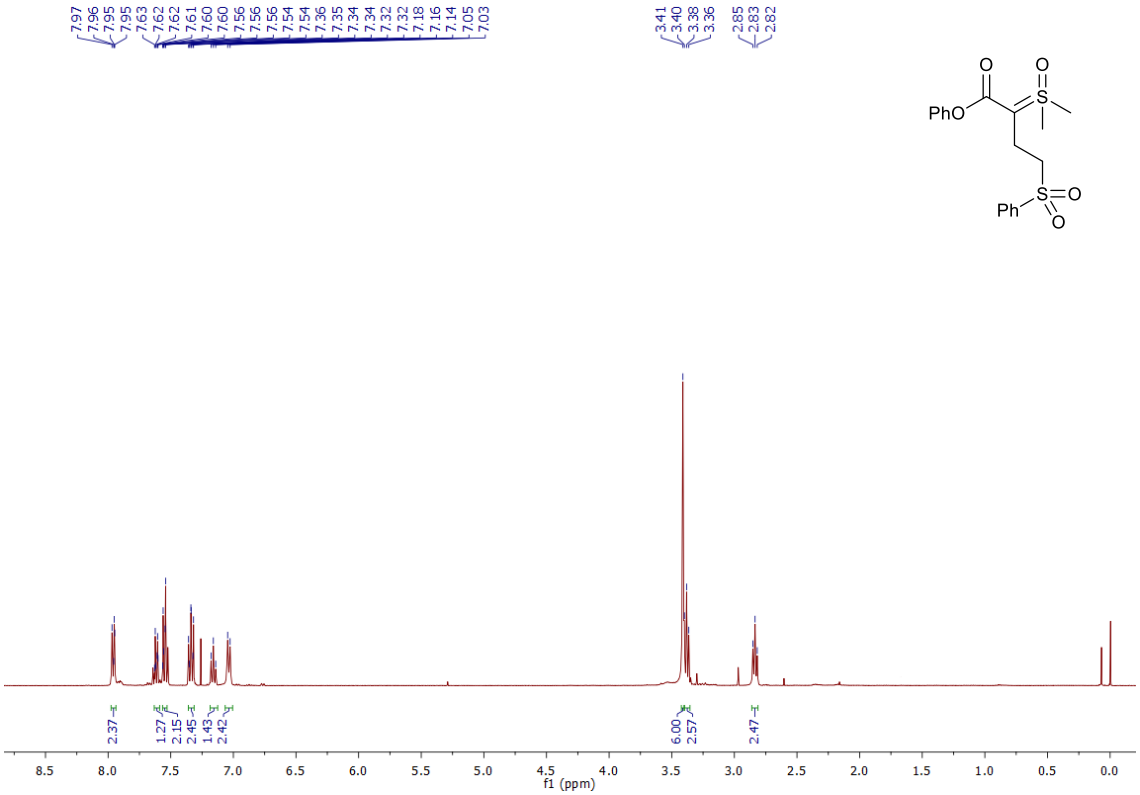

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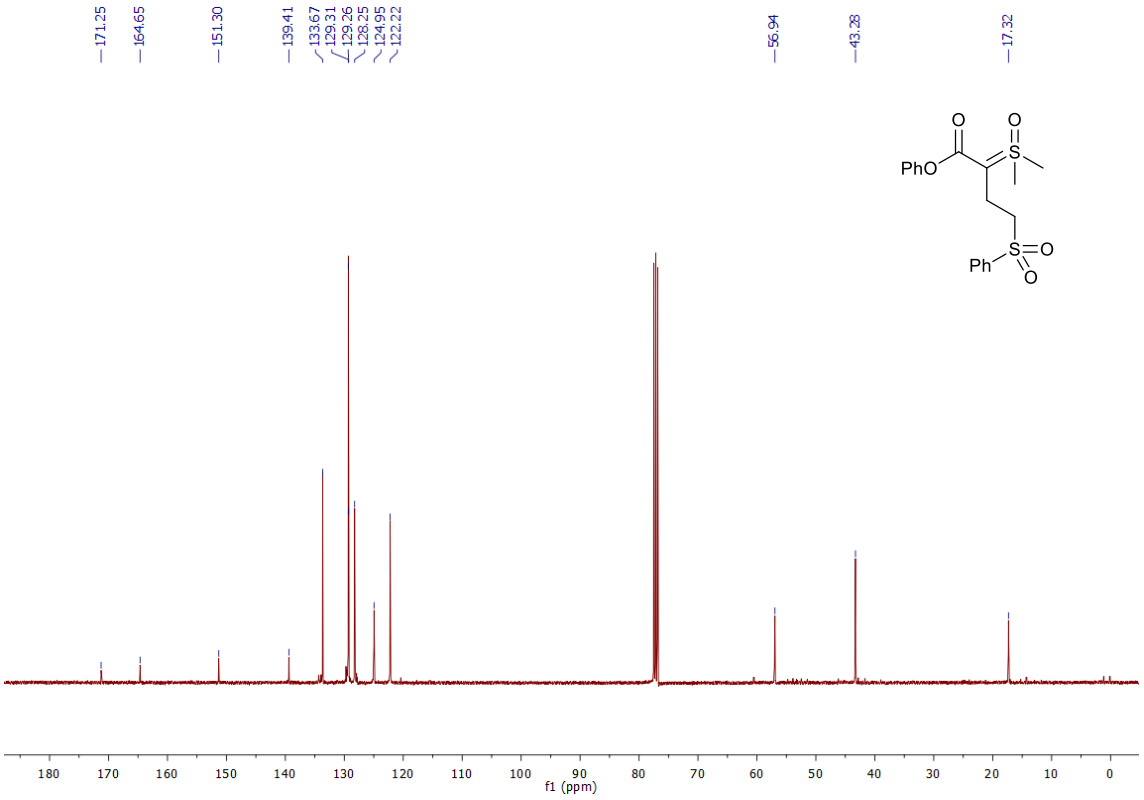
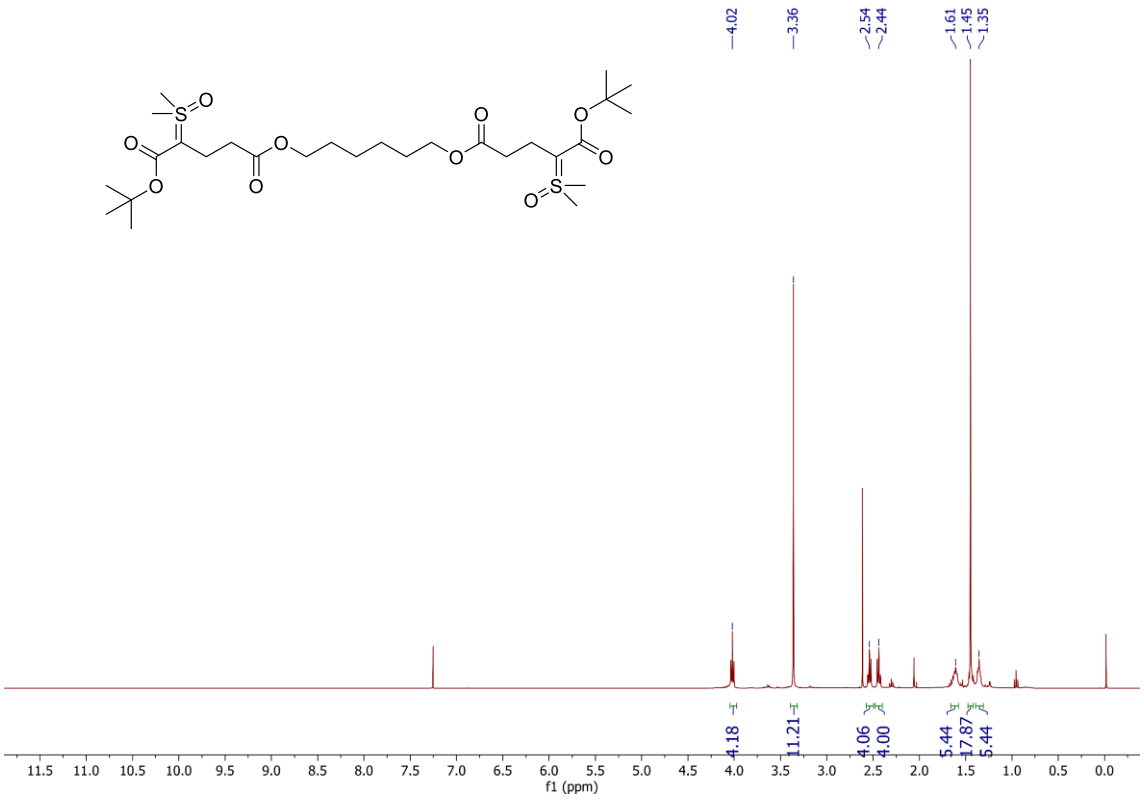
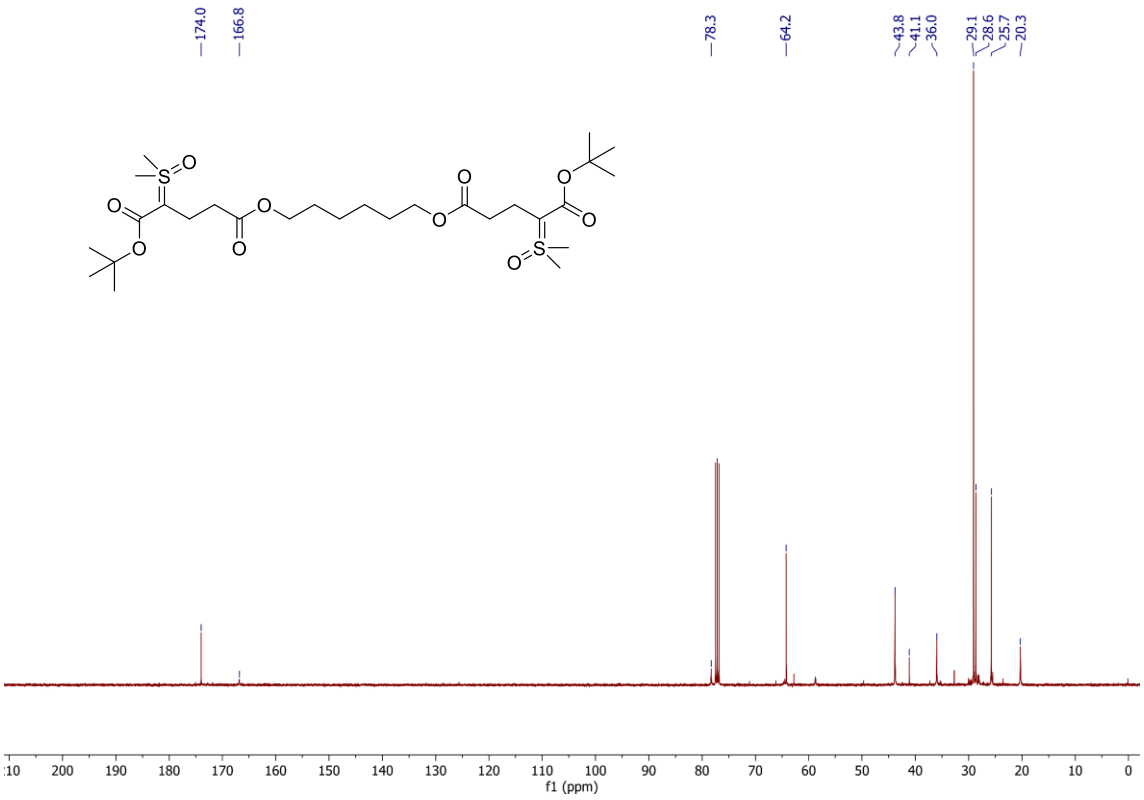


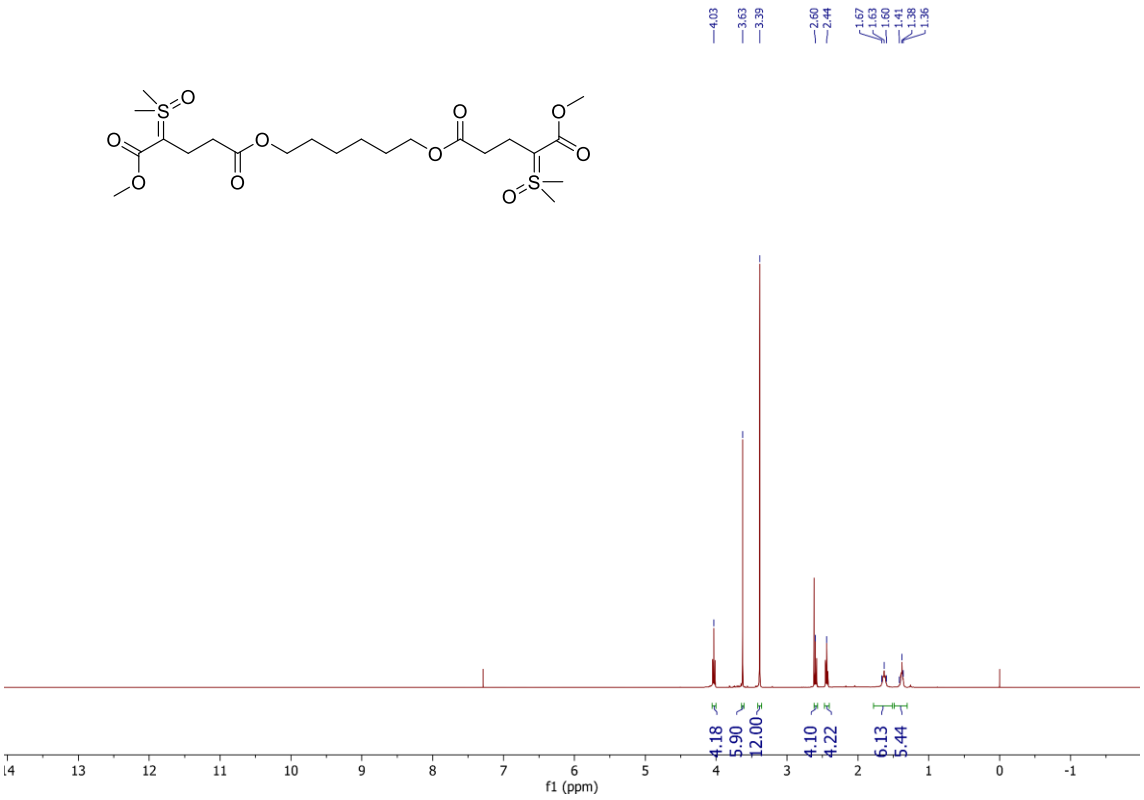
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2x**



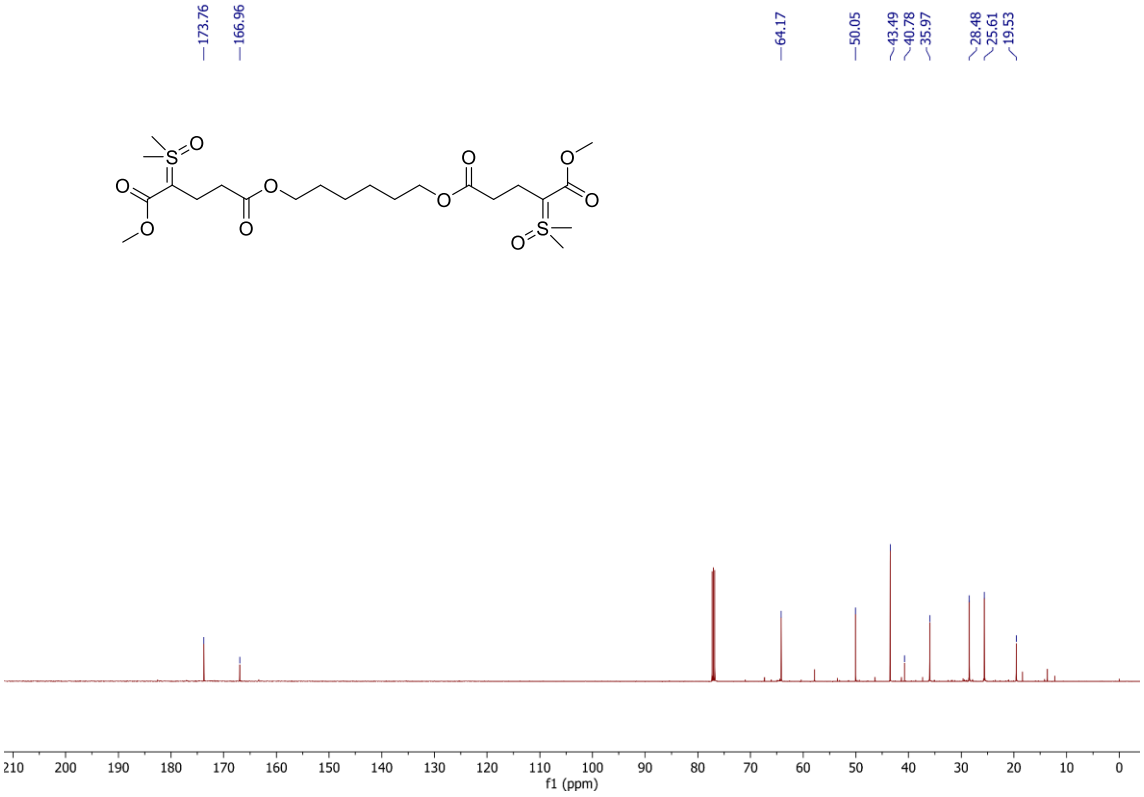
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2x**



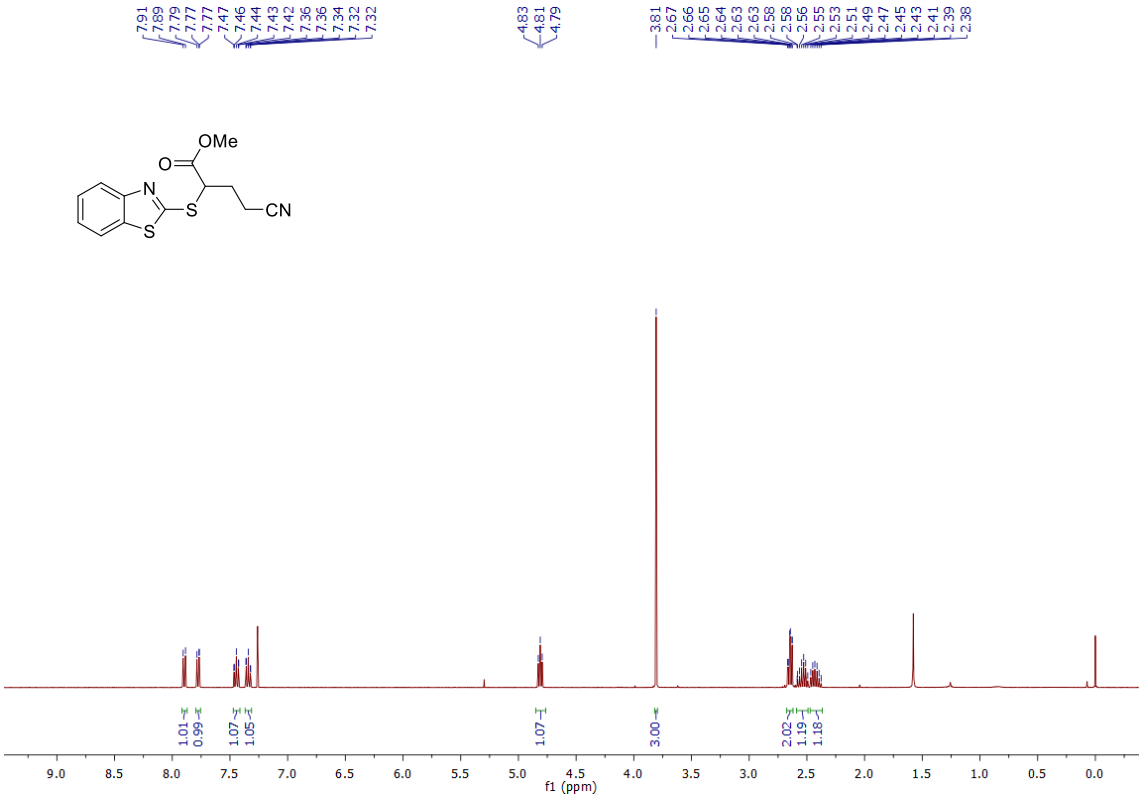
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2y**



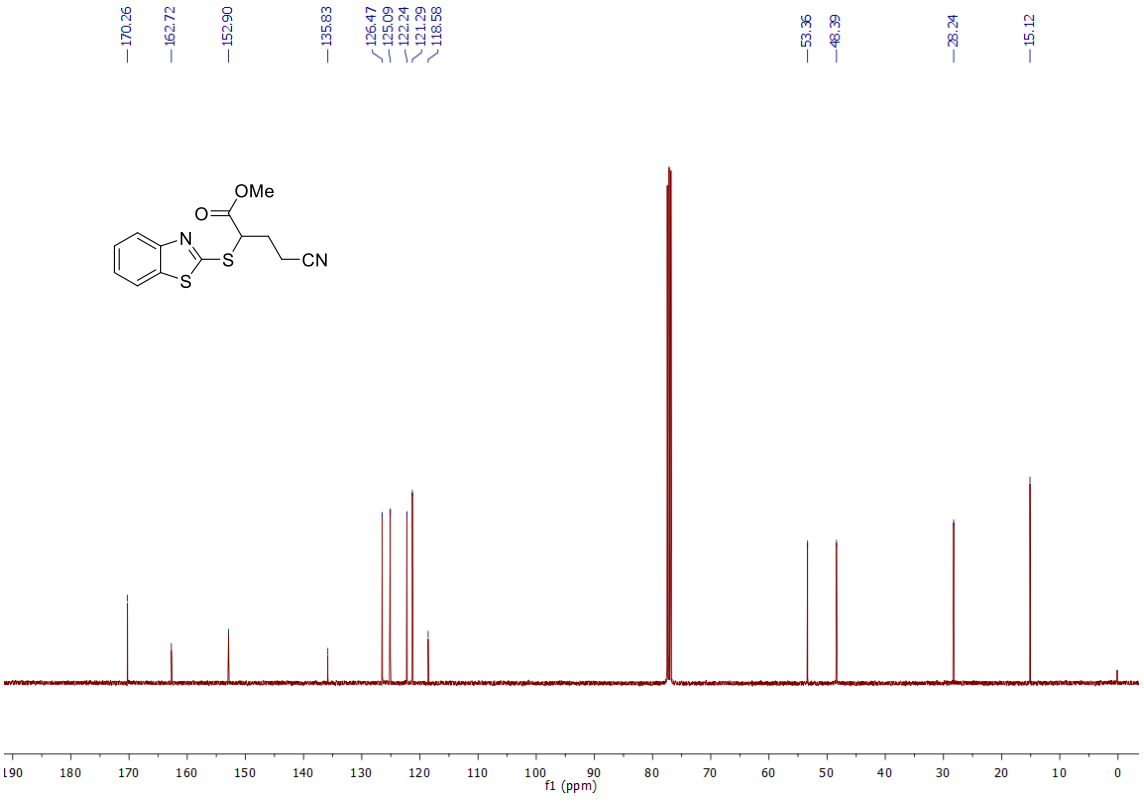
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **2y**



^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3a**



^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **3a**



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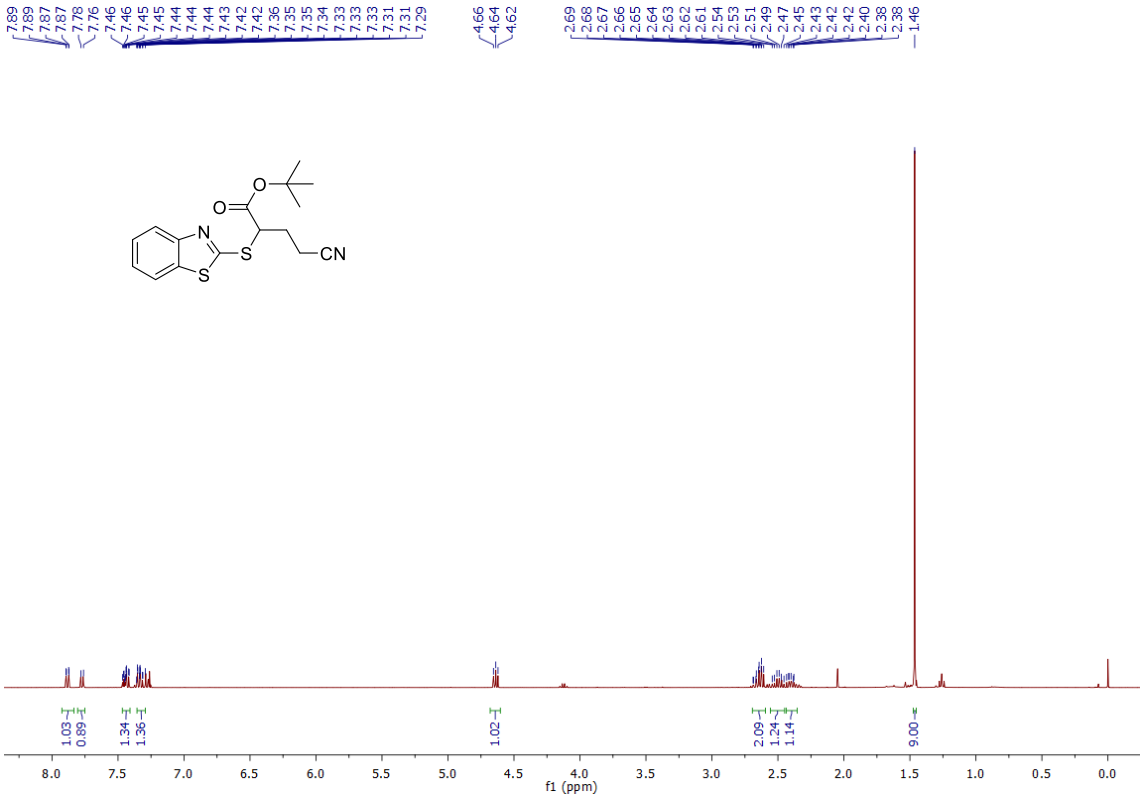
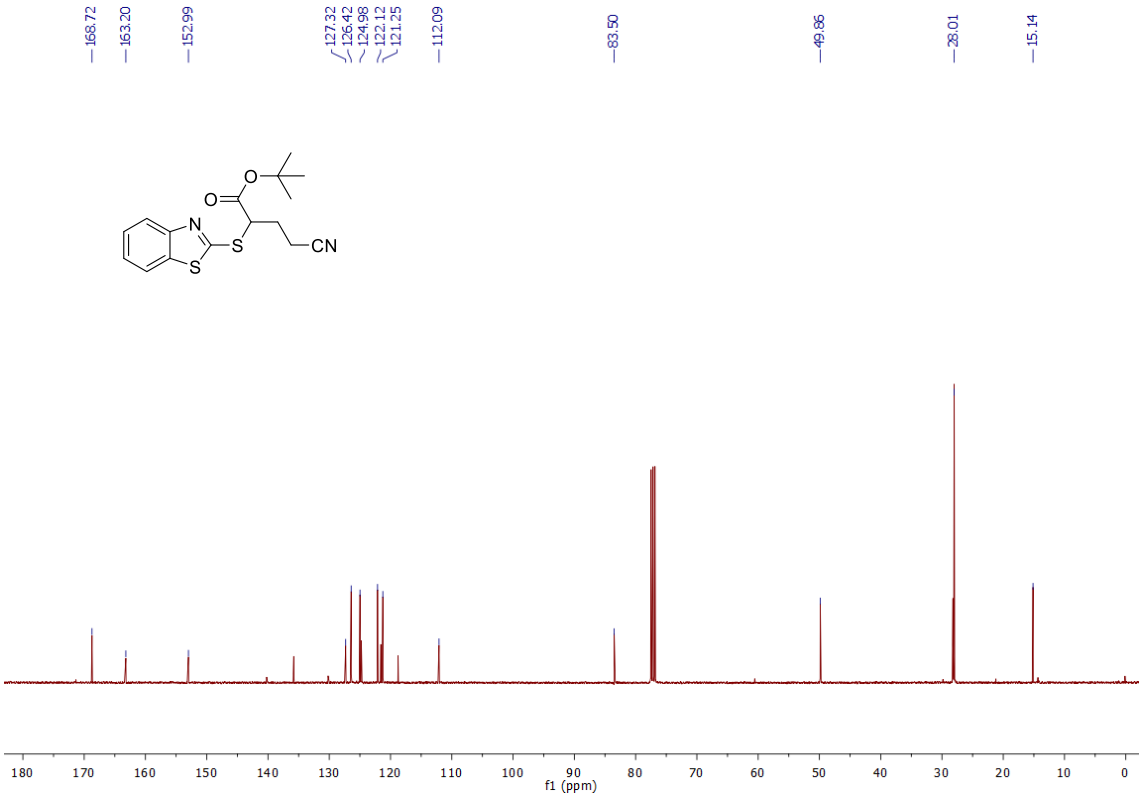
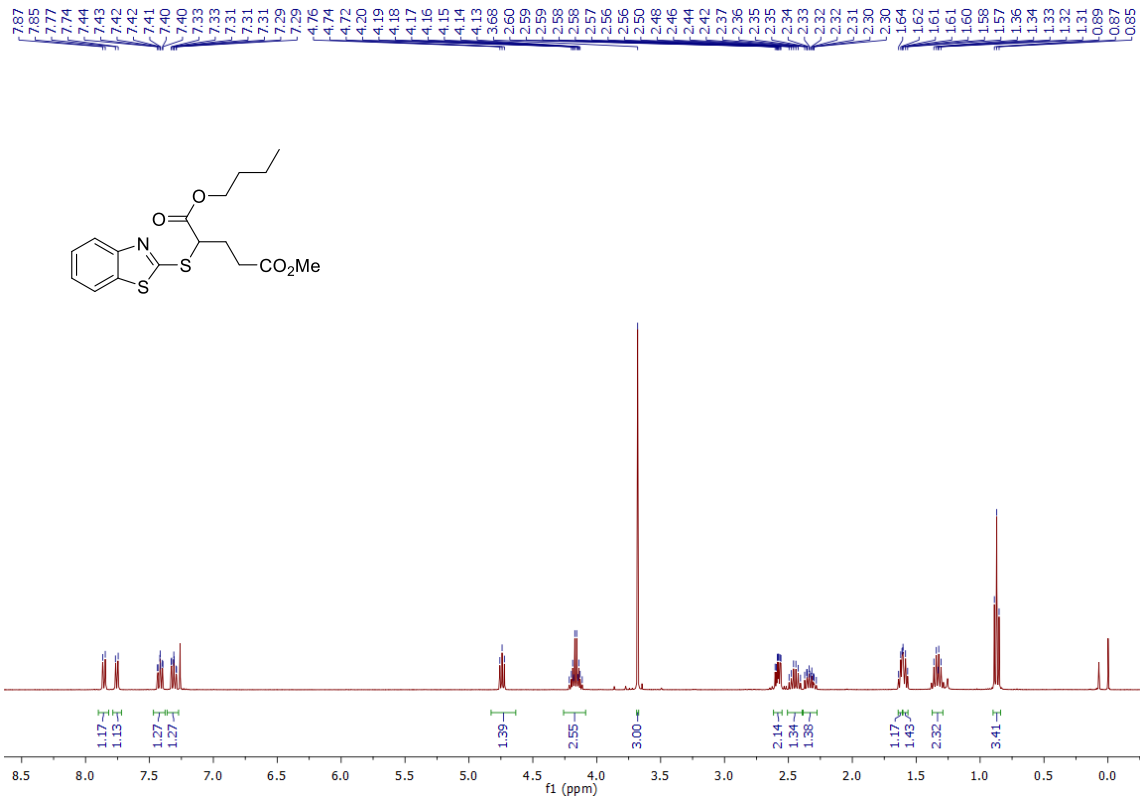


^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **3b**



^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3c**



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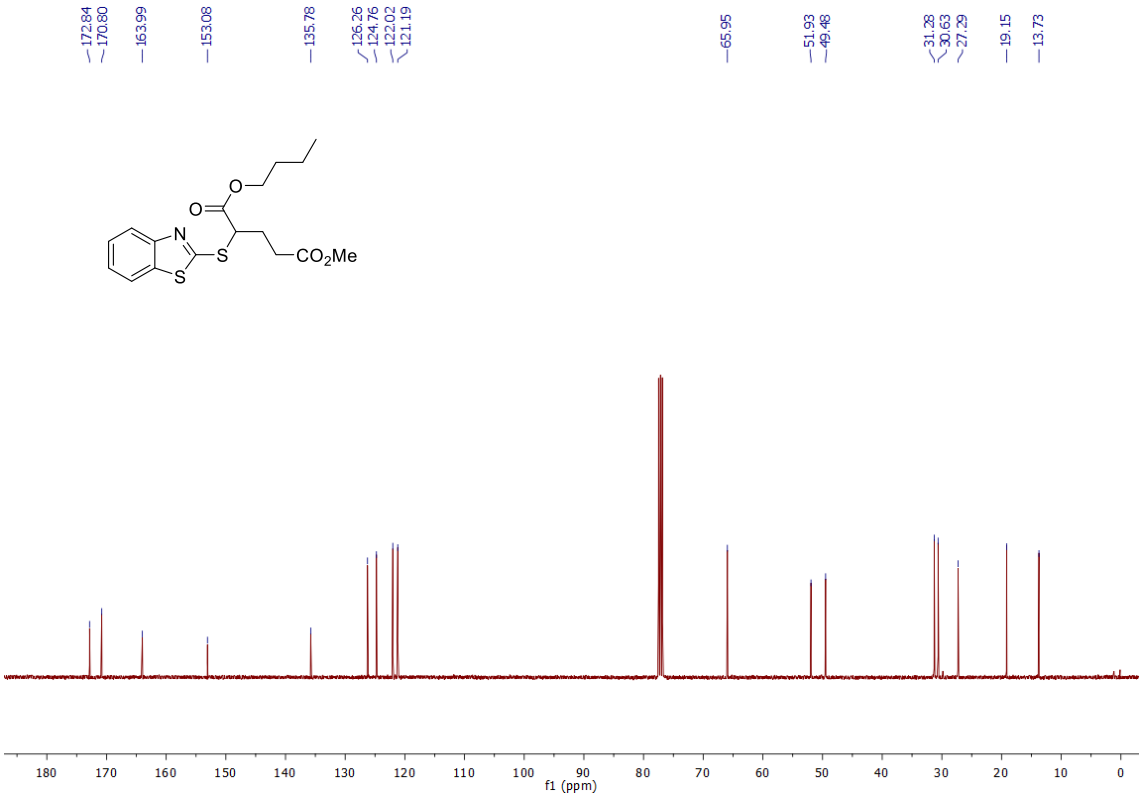
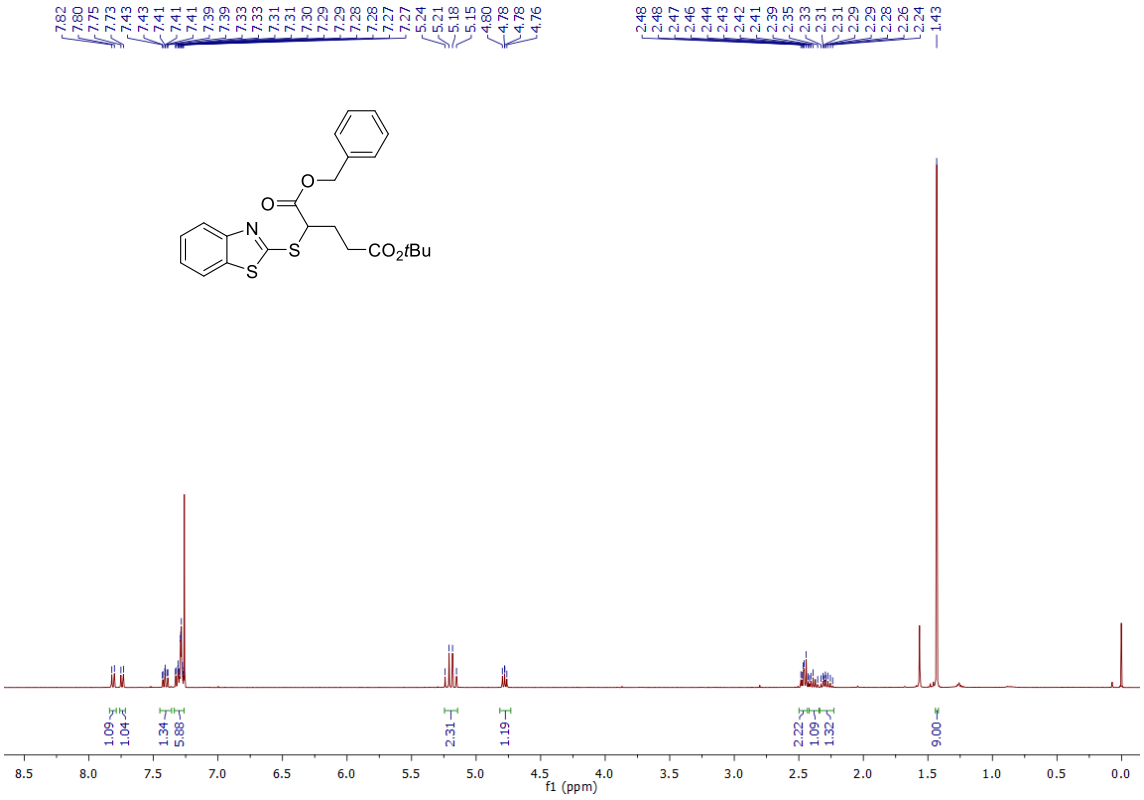
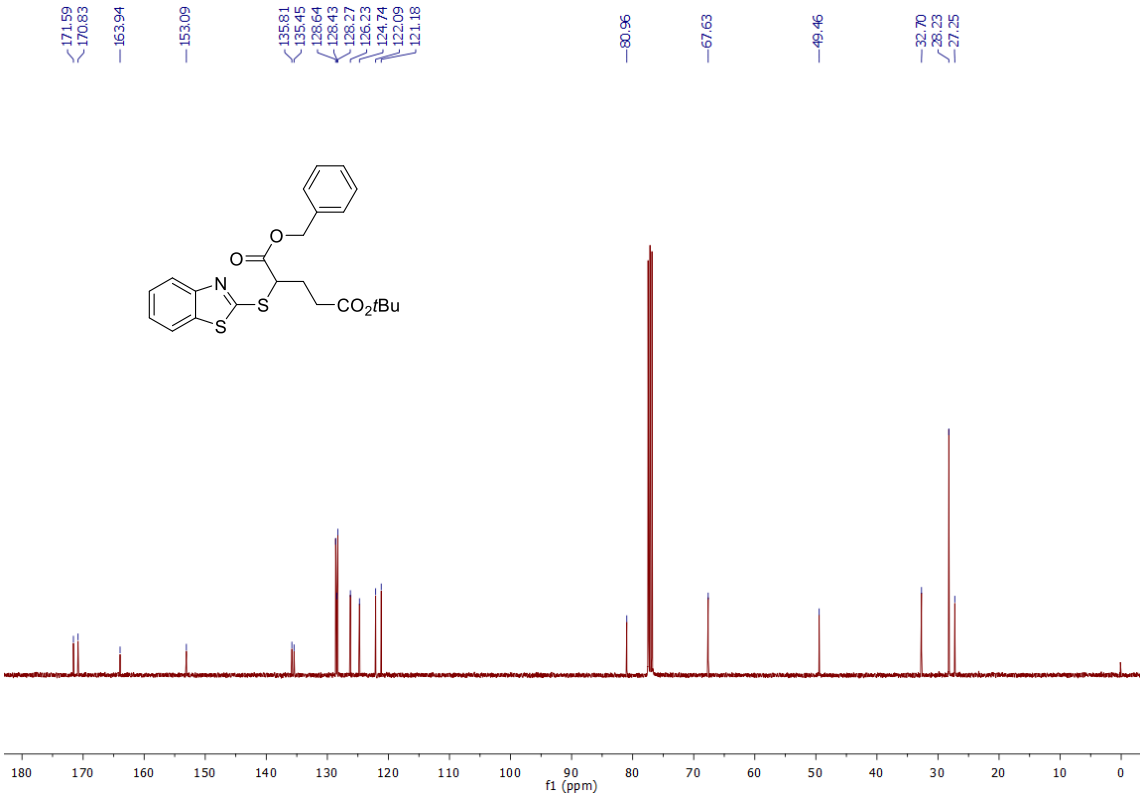


^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3d**



^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **3d**



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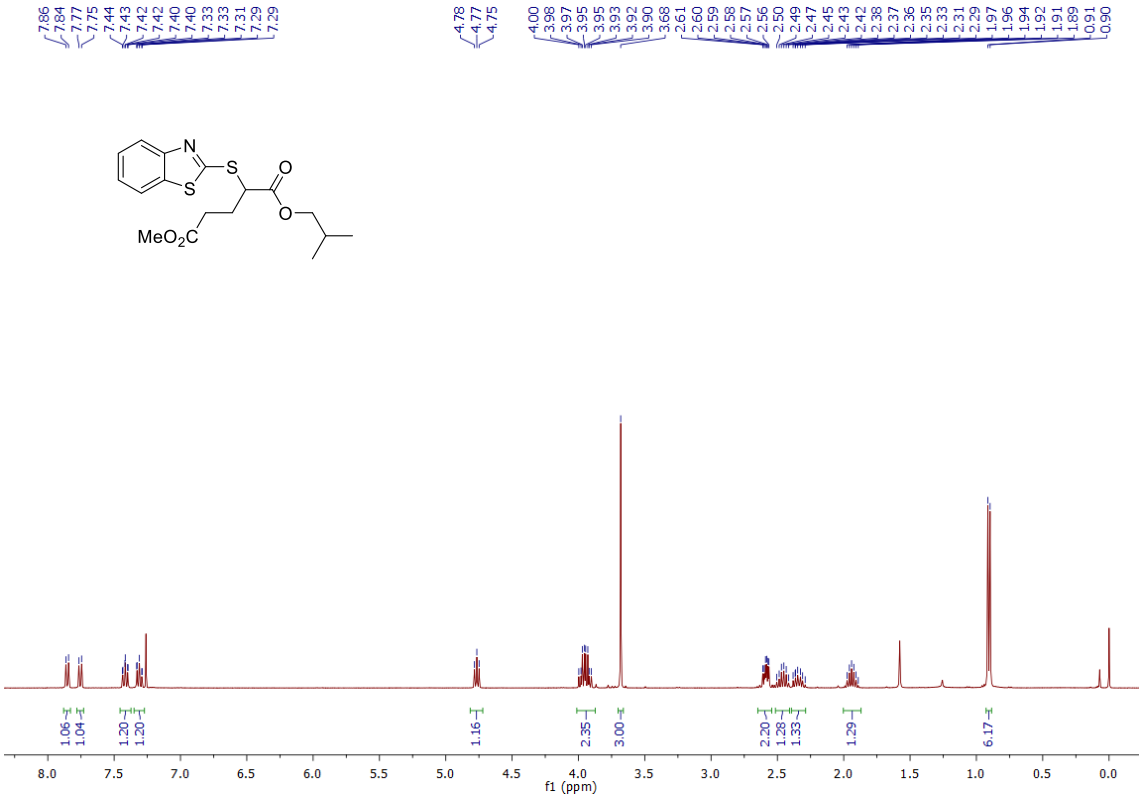

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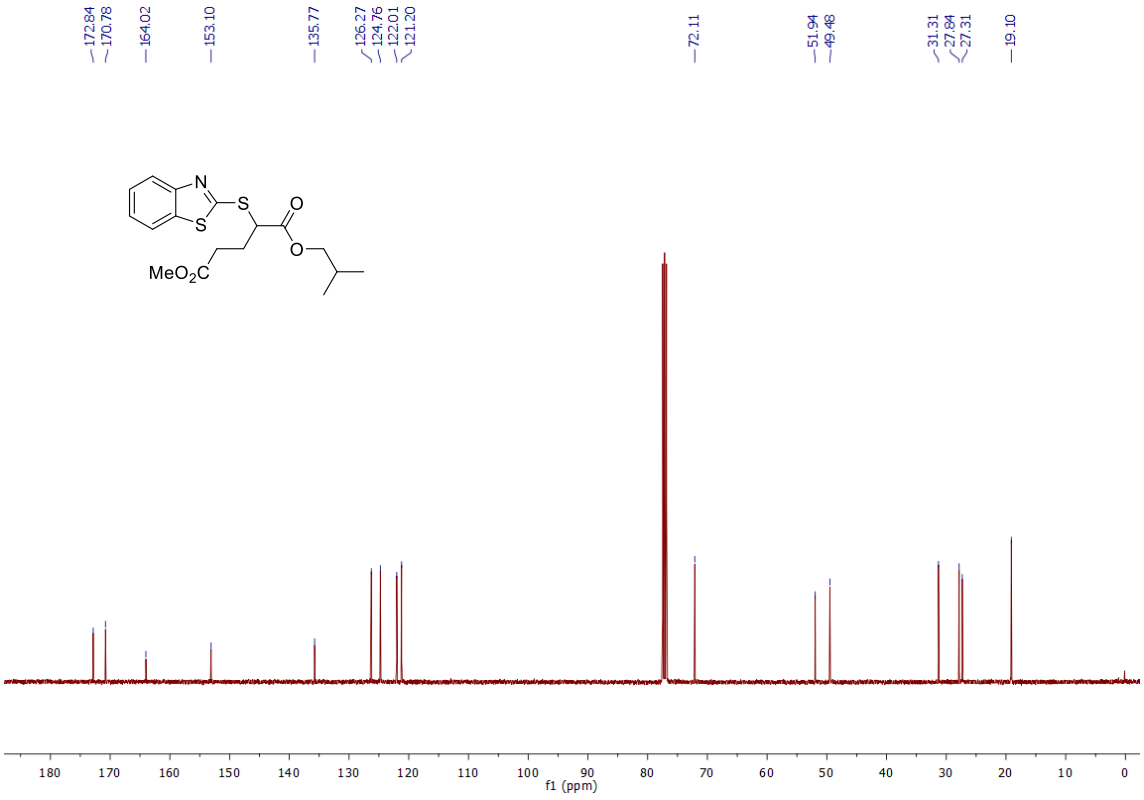
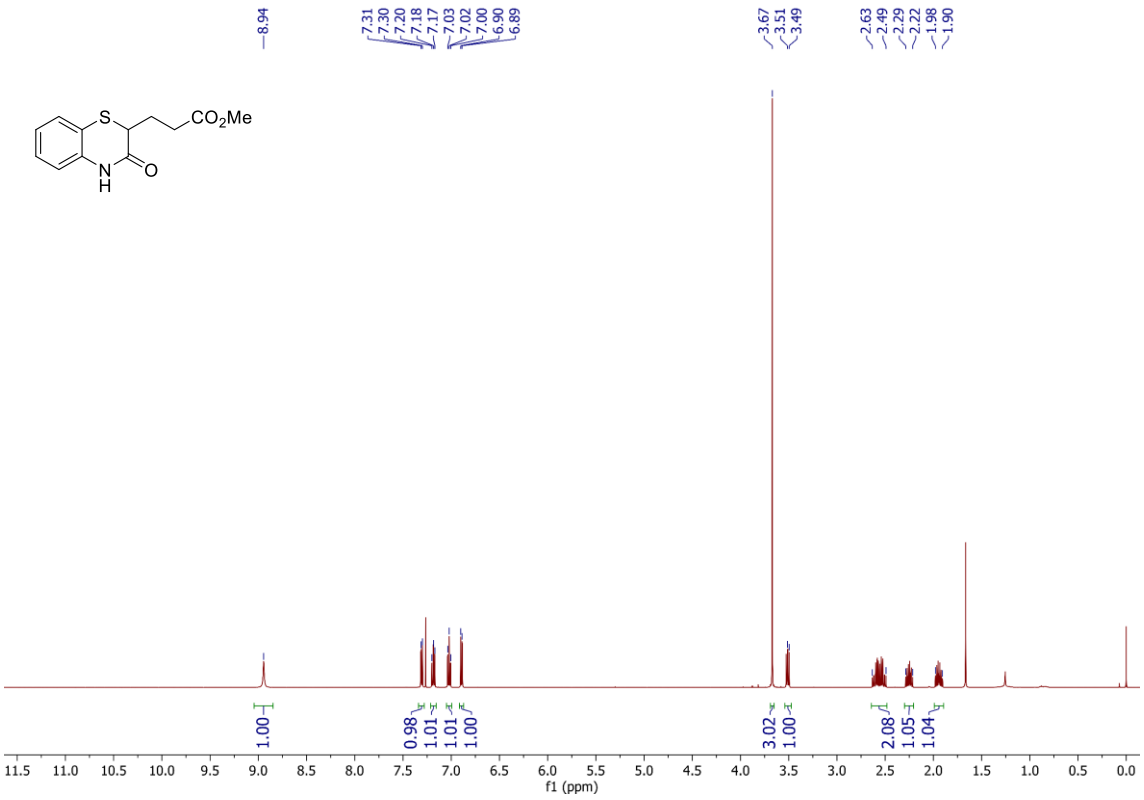
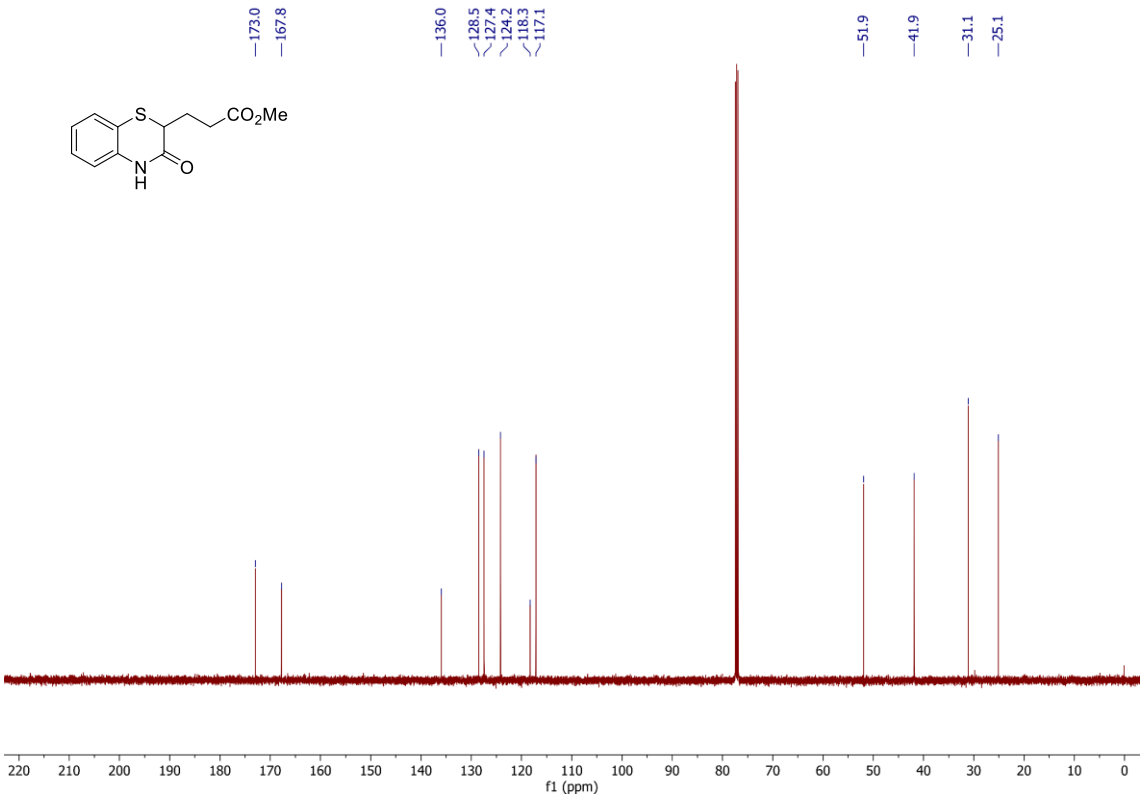


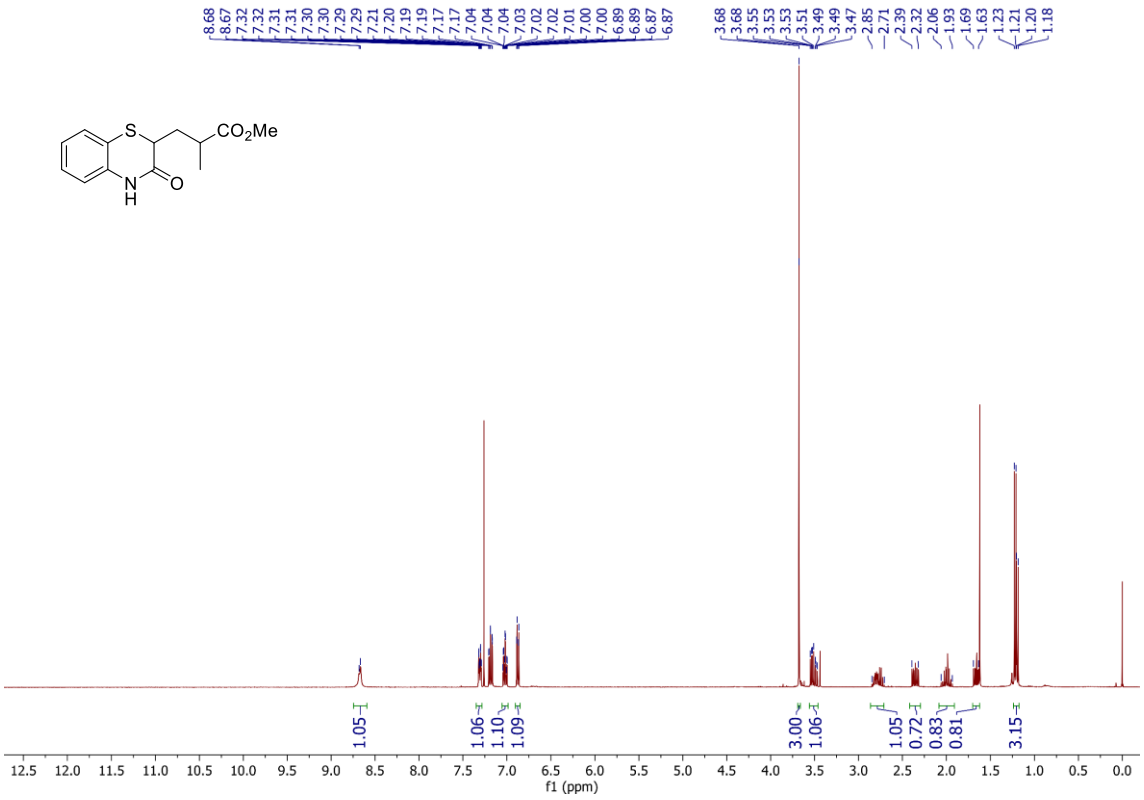
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4a**



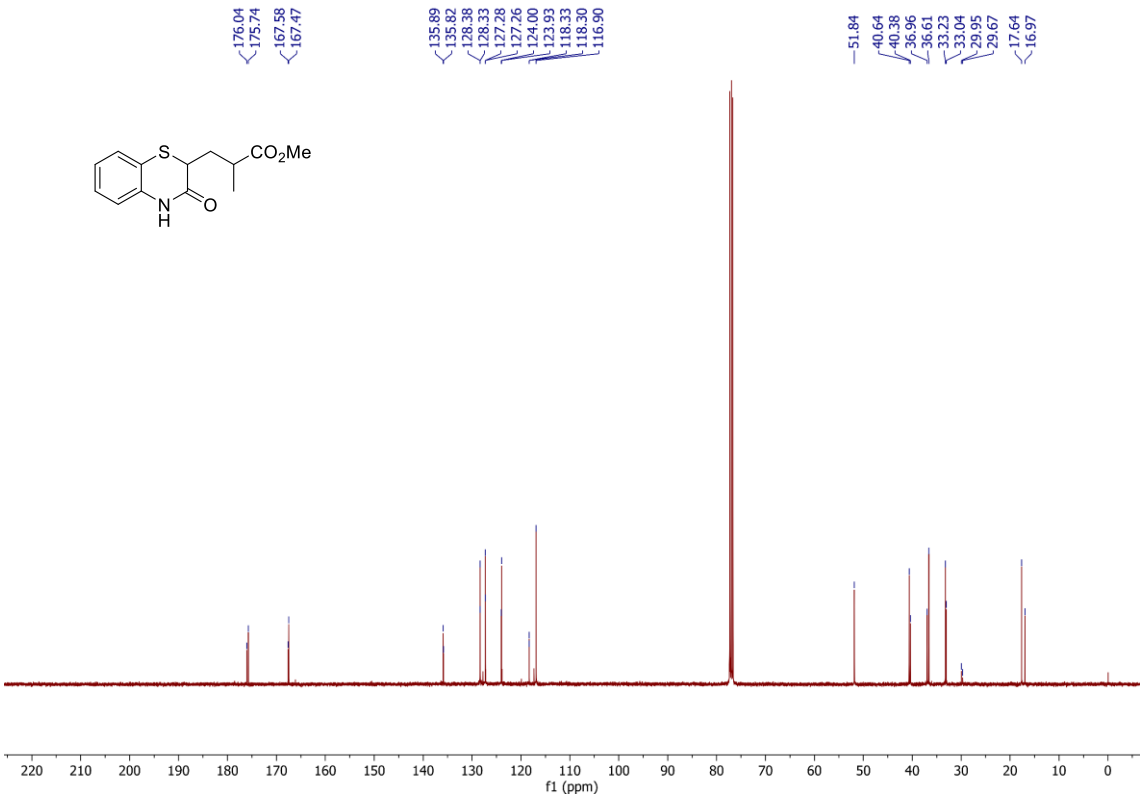
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **4a**



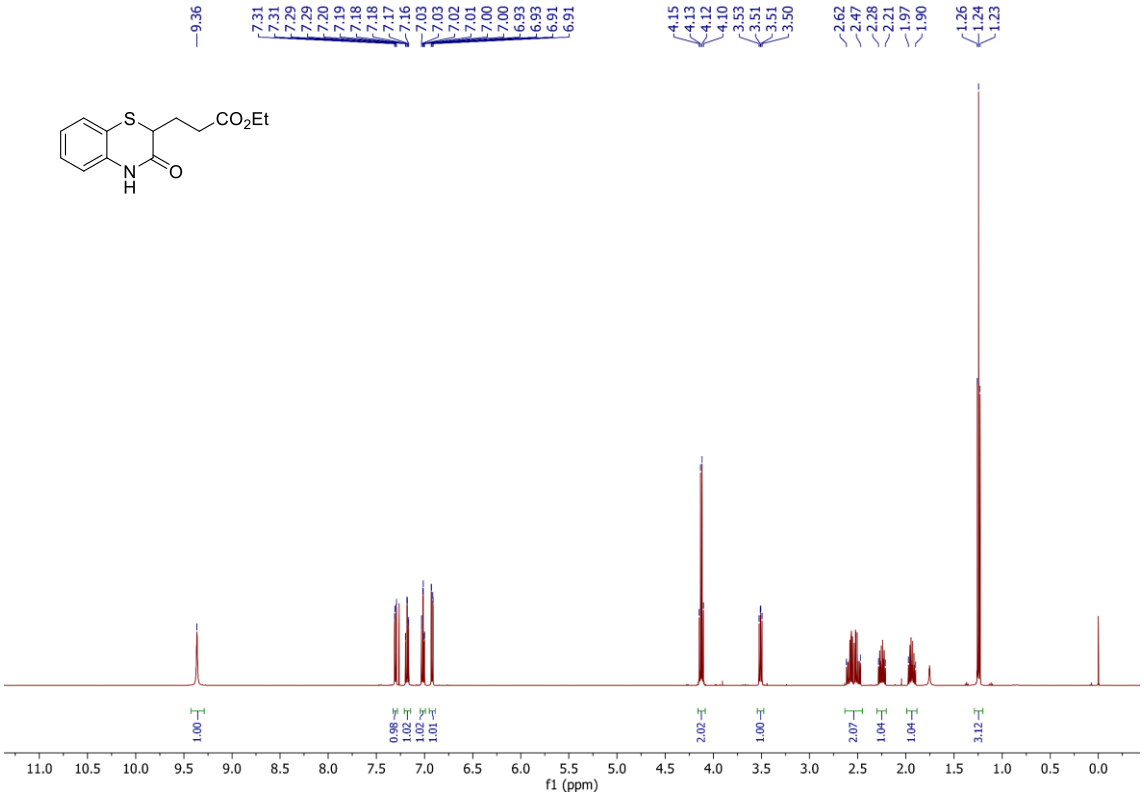
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4b**



^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **4b**



^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4c**



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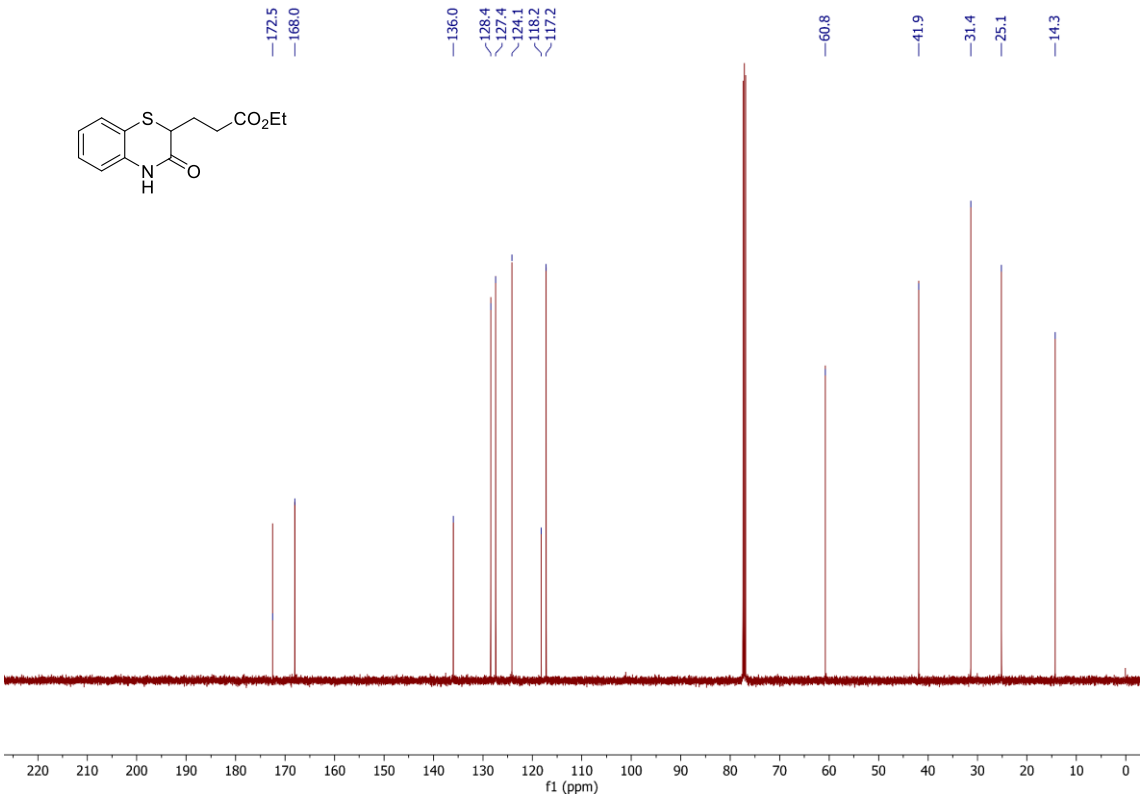
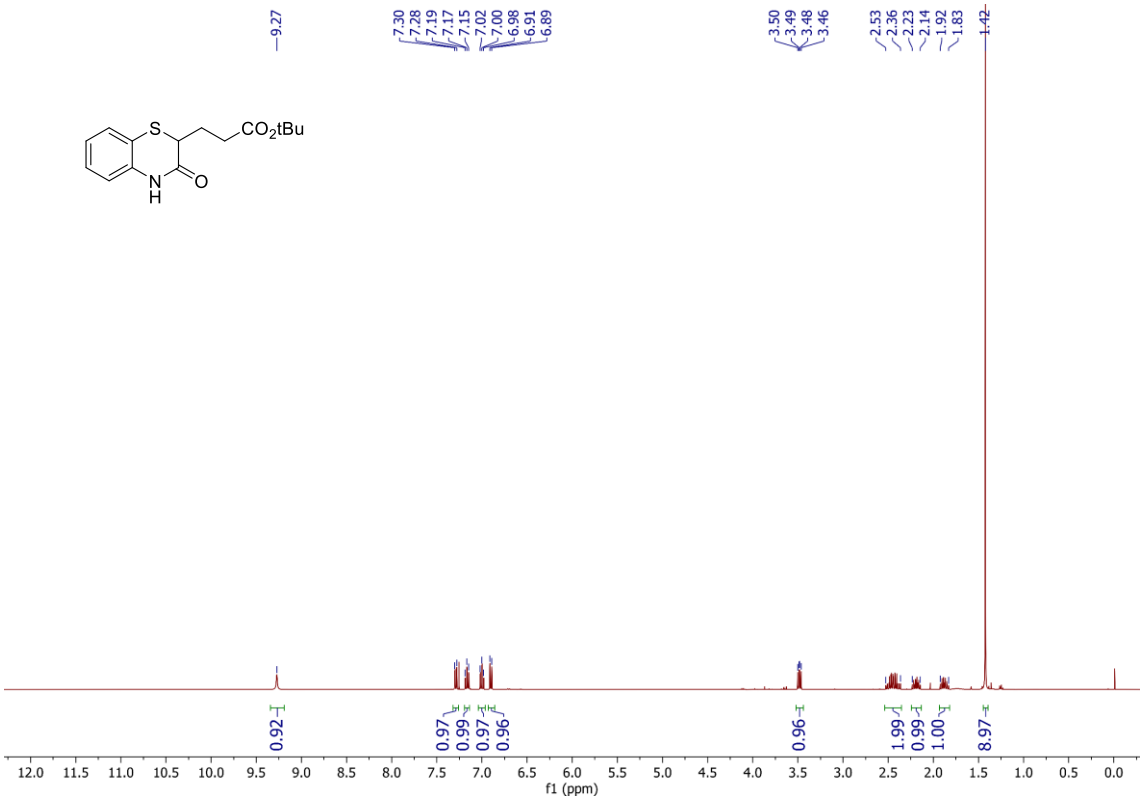
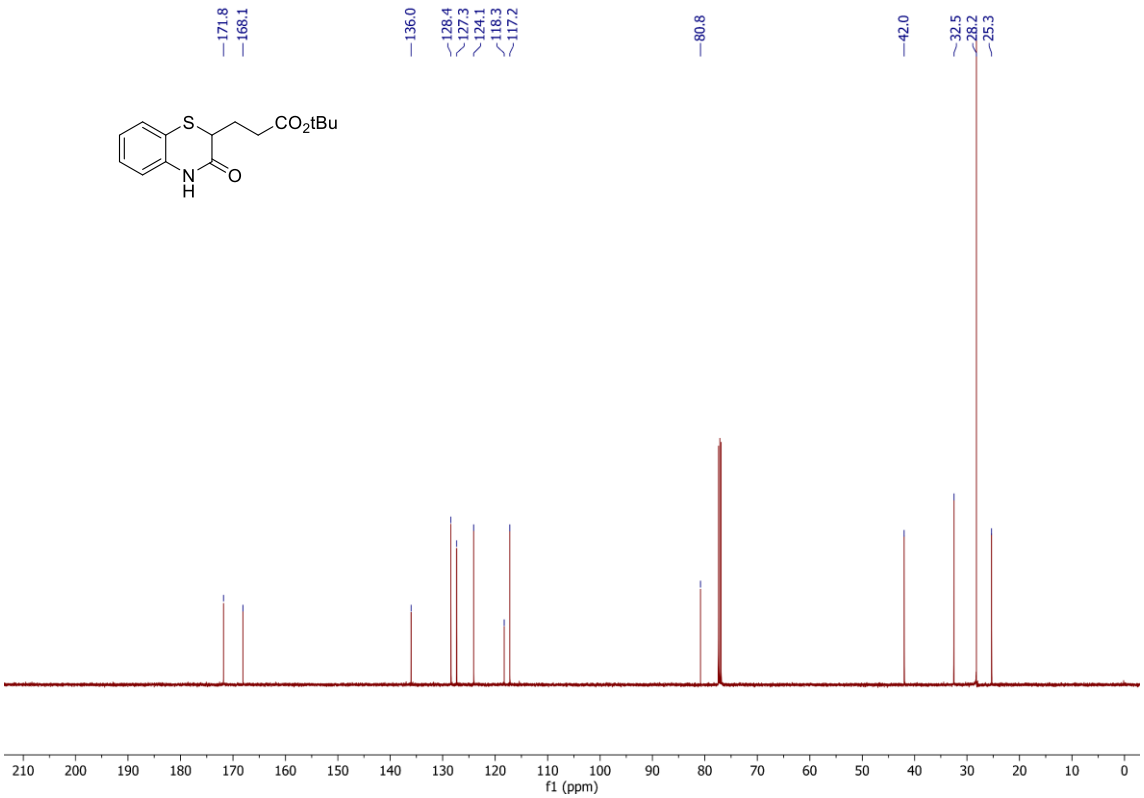


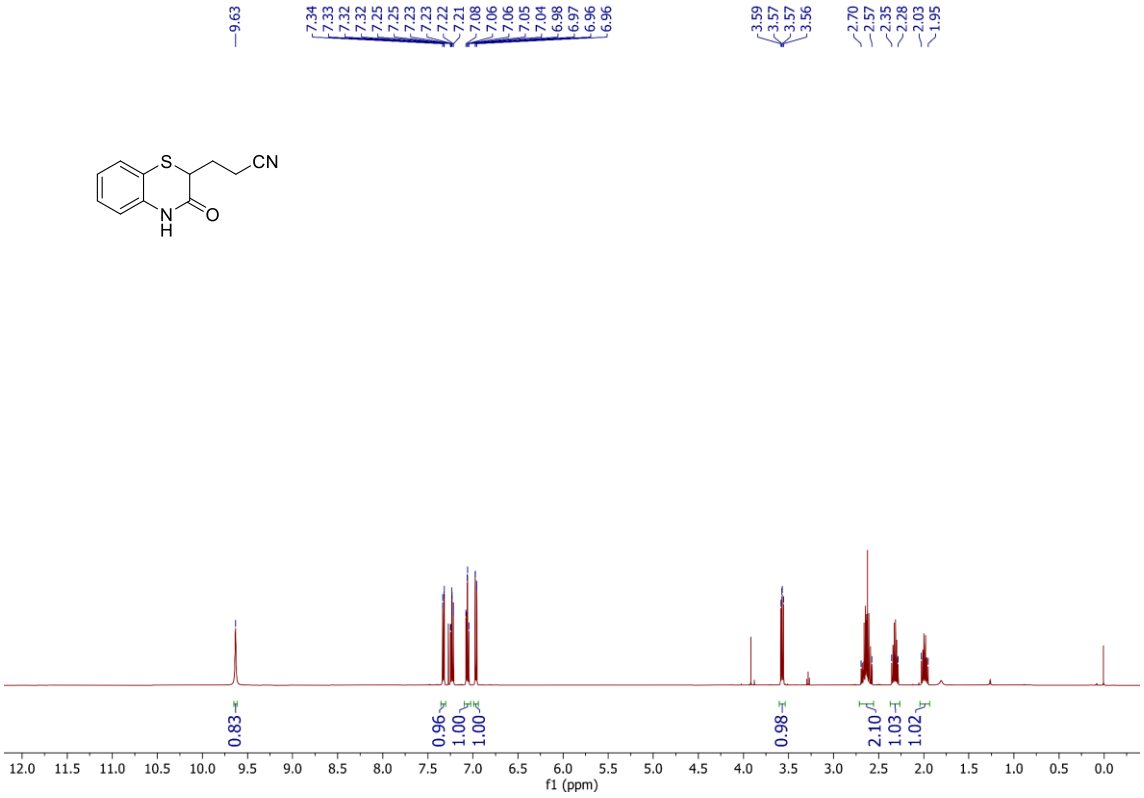
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4d**



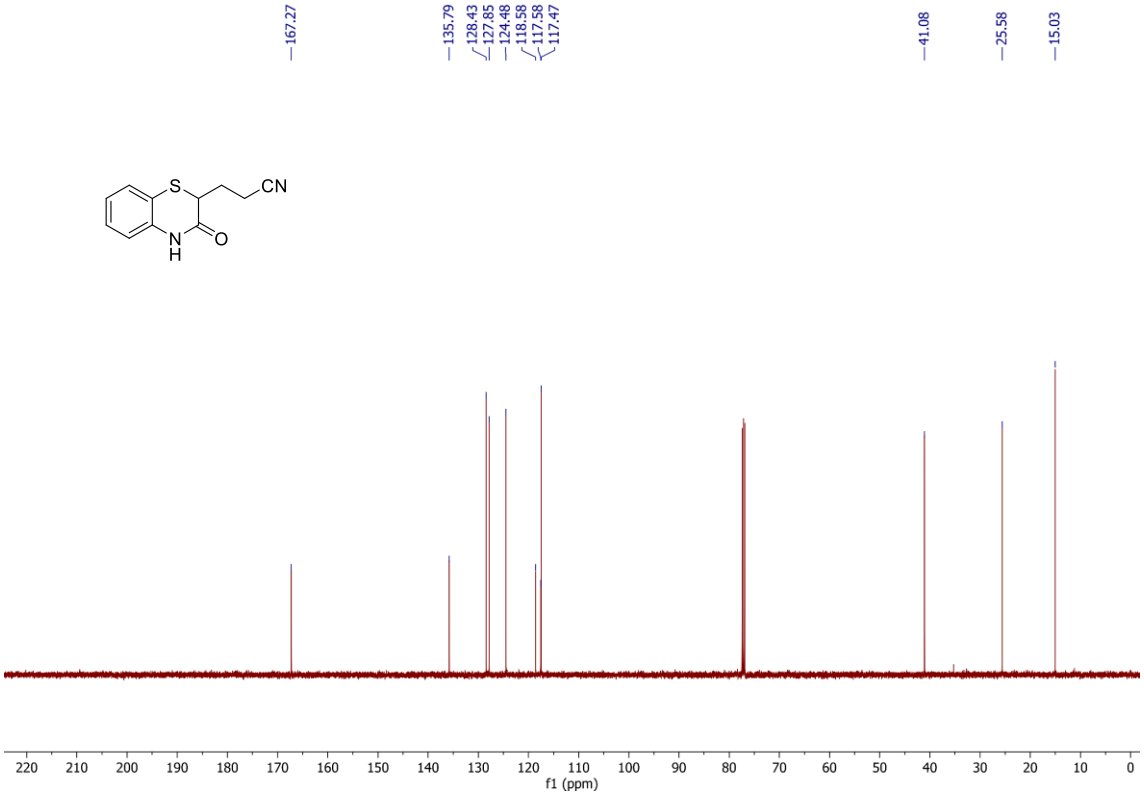
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **4d**



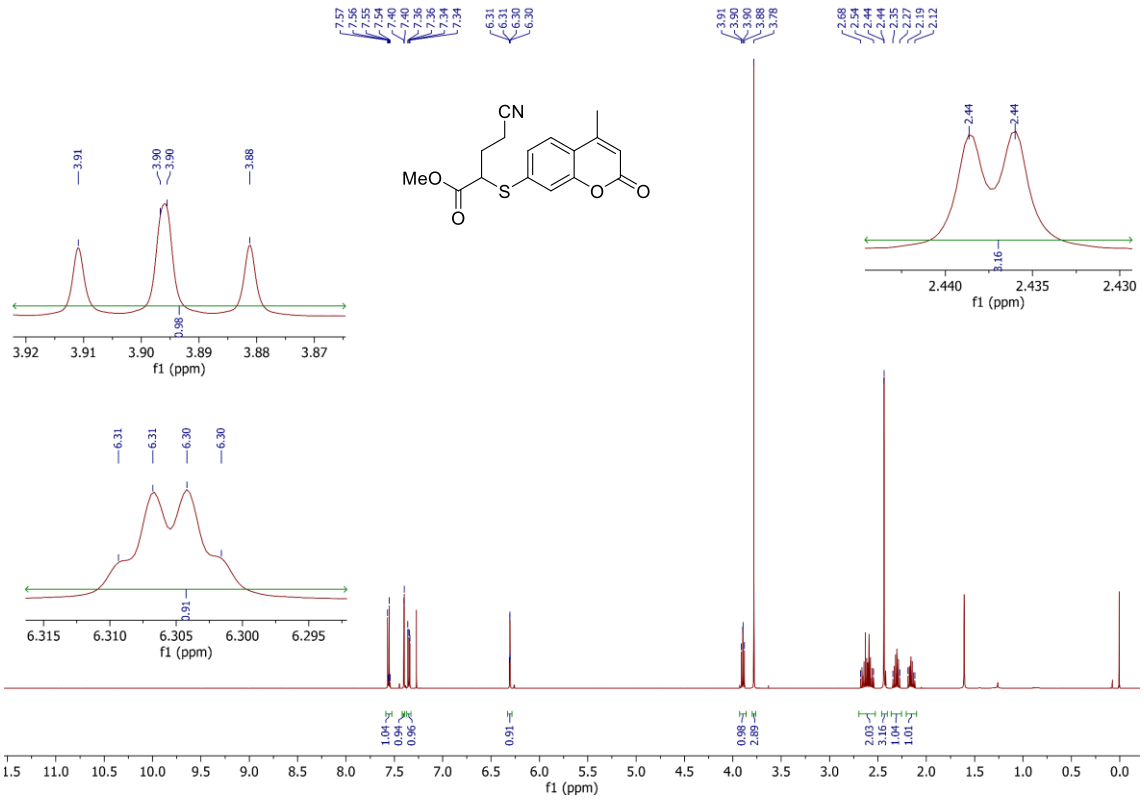
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4e**



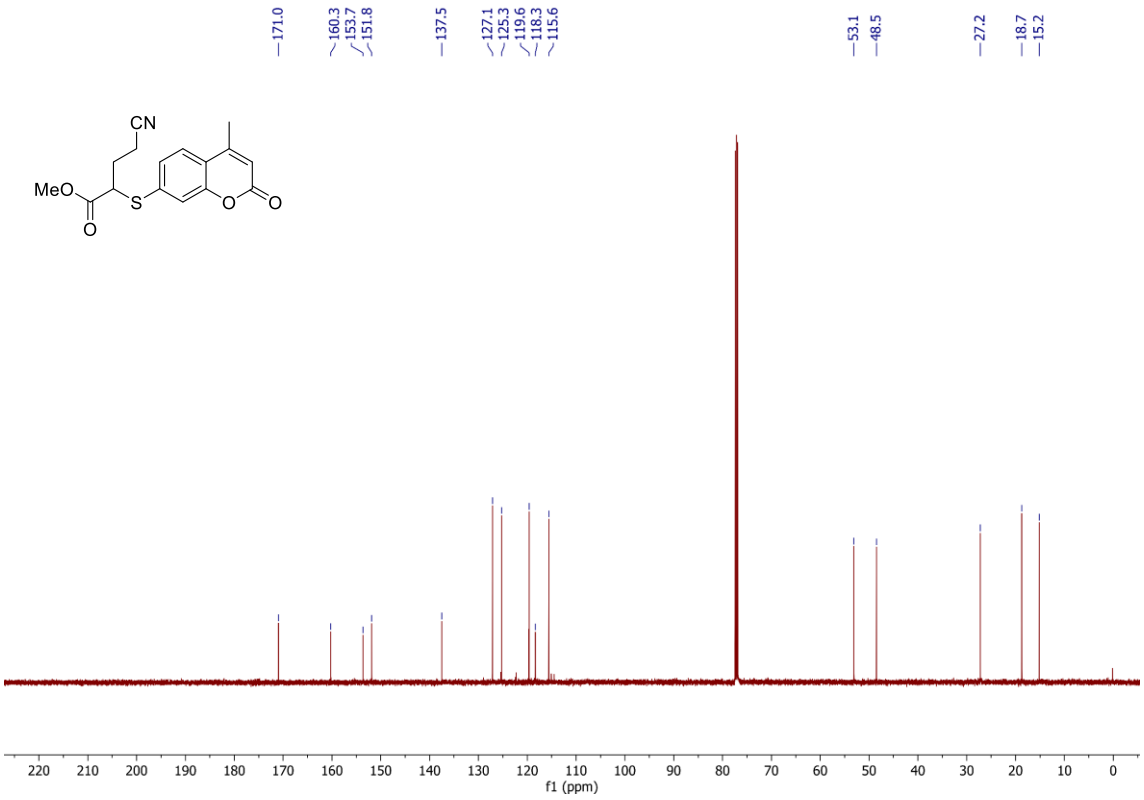
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **4e**



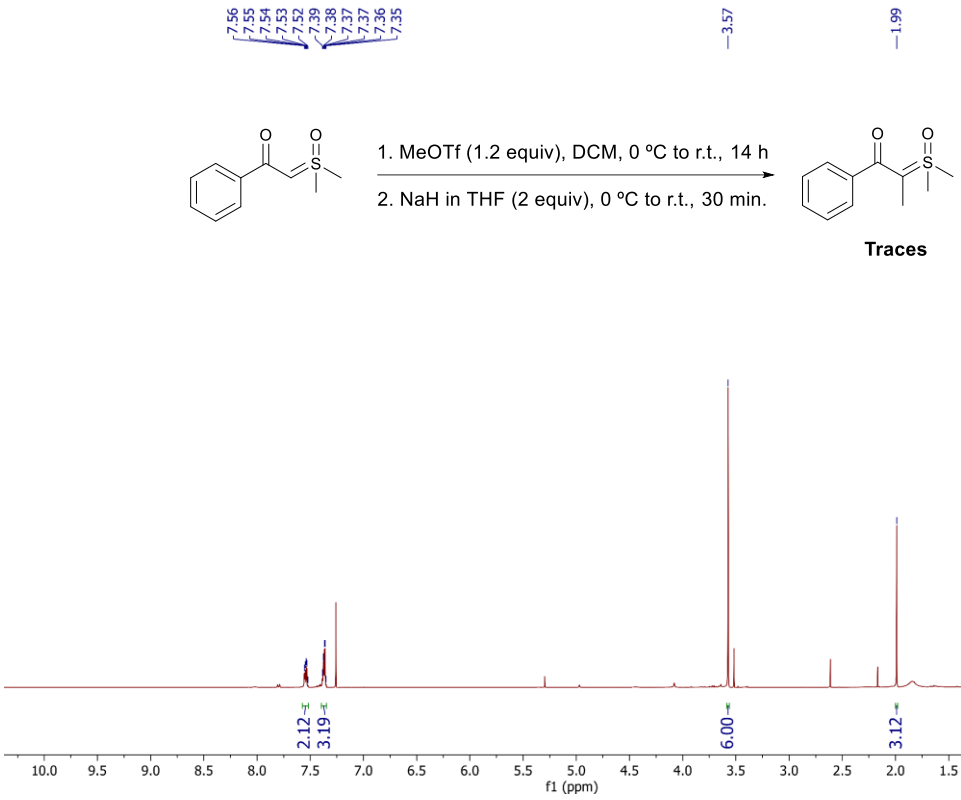
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5a**



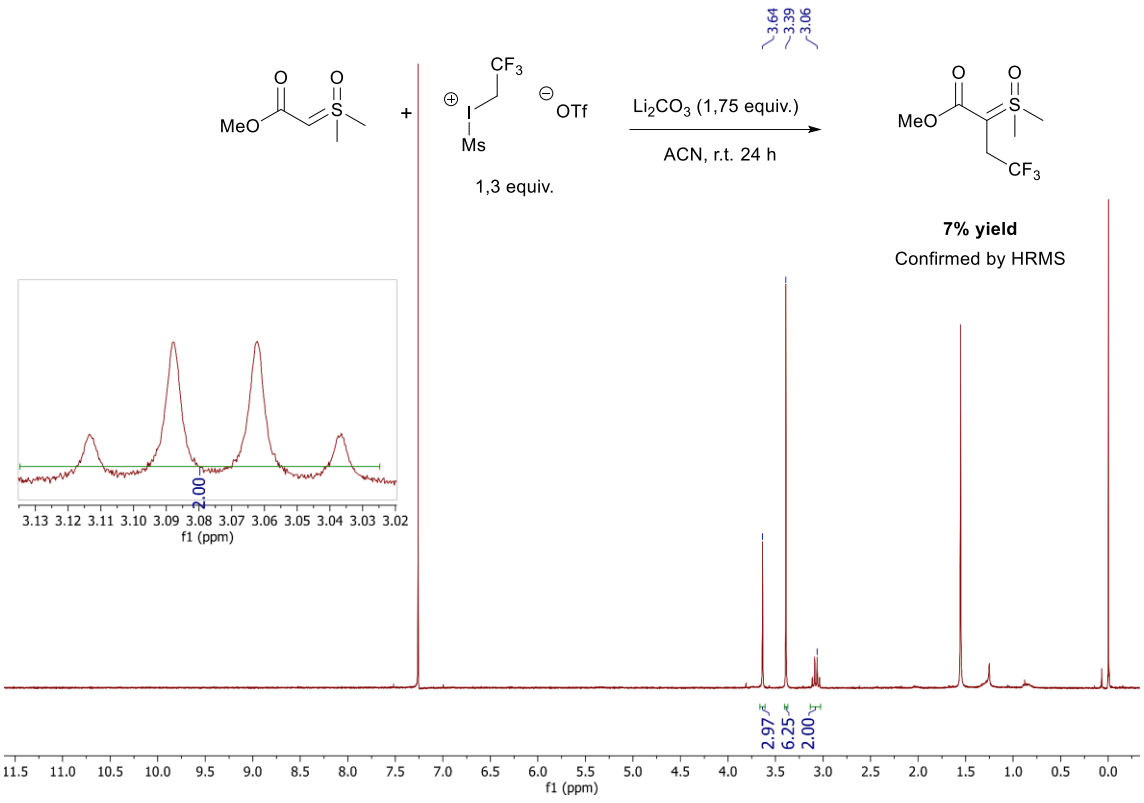
^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **5a**



^{1}H NMR spectra (400 MHz, $CDCl_3$) of the product mentioned in the Table 1-Entry 16



^{1}H NMR spectra (400 MHz, $CDCl_3$) of the product mentioned in the Table 1-Entry 26



8 References

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