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Alkynyl sulfoxides as α-sulfinyl carbene equivalents: Gold-catalysed oxidative cyclopropanation

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General Experimental

Commercially available chemicals/reagents were purchased from major suppliers (Sigma-Aldrich, Fisher, Acros, Alfa Aesar, Strem, Fluorochem or VWR) and used without further purification unless otherwise stated. All catalysis reactions were carried out under argon in heat gun-dried glassware unless otherwise stated. Solvents were purified using a Pure Solv-MD solvent purification system except for $CHCl_3$ and 1,4-dioxane which were dried over activated 3 Å molecular sieves and were transferred under argon. For reactions above room temperature pre-heated Asynt DrySyn heating blocks on stirrer hotplates were employed and the temperature was controlled using an external probe. The following cooling baths were used: 0 °C (ice/water), -10 °C (NaCl/ice) and -78 °C (dry ice/acetone). Reactions were monitored by thin layer chromatography using Merck silica gel 60 F254 (aluminium support) TLC plates which were developed using standard visualizing agents: UV fluorescence (254 nm), potassium permanganate/Δ or vanillin/Δ. Flash column chromatography: Flash column chromatography was performed using Fluorochem silica gel 60 (0.043-0.063 mm) as the stationary phase. Infrared spectra were recorded neat on a Perkin-Elmer Spectrum 100 FTIR spectrometer. Wavelengths (ν) of selected absorbencies are reported in cm^{-1}. Mass spectra were obtained using Waters GCT Premier (EI), Waters LCT (ES) or Waters Synapt (ES) spectrometers. High resolution spectra used a lock-mass to adjust the calibrated mass scale. MS data are reported as m/z (relative intensity). ^{1}H NMR and ^{13}C NMR experiments were recorded using Bruker AVIII400 (^{1}H = 400 MHz, ^{13}C = 101 MHz) or AVIII300 (^{1}H = 300 MHz, ^{13}C = 75 MHz) spectrometers at 300 K. ^{13}C NMR spectra were recorded using either the UDEFT or the PENDANT pulse sequences from the Bruker standard pulse program library. 2D HSQC and HMBC NMR spectra were recorded using the Bruker standard pulse program library. Spectra were processed using MestReNova 10.0. Chemical shifts (δ) are given in ppm relative to TMS and are calibrated using residual solvent peaks ($CDCl_3$: $\delta_C \equiv 77.16$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; DMSO-d_6: $\delta_C \equiv 39.52$ ppm; residual DMSO in DMSO-d_6: $\delta_H \equiv 2.50$ ppm).[1] Spectral data for ^{1}H NMR spectroscopy is reported as follows: Chemical shift (multiplicity, coupling constant, number of protons); and for ^{13}C NMR spectroscopy: Chemical shift. The following abbreviations were used for multiplicity in ^{1}H NMR: s (singlet), d (doublet), t (triplet), q (quadruplet), quin (quintuplet), br. (broad), m (multiplet), app. (apparent). Coupling constants (*J*) are quoted in Hz to one decimal place. Melting points were measured in open capillaries using Stuart Scientific melting point apparatus and are uncorrected.

*m*CPBA was purified by washing with a pH 7 phosphate buffer unless otherwise stated: A buffer solution was prepared from 0.1 M NaOH (154 mL) and 0.2 M KH_2PO_4 (94 mL) and made up to 376 mL with distilled water. *m*CPBA (77% w/w, 10 g) was dissolved in diethyl ether (100 mL) and washed four times with the buffer solution. The organic extract was dried over $MgSO_4$ and carefully evaporated (**CAUTION -** potential explosive) under reduced pressure to yield pure *m*CPBA (7.3 g).[2]

Experimental Procedures and Spectroscopic Data

Preparation of Starting Materials

Sodium benzenesulfonothioate
Prepared in 83% yield according to a literature procedure.[3] Data is in agreement with literature values.[3]

1,1-Dibromo-8-methylnona-1,7-diene
Prepared in 74% yield according to a literature procedure.[4] Data matches that reported in the literature.[5]

(2,2-Dibromovinyl)cyclohexane
Prepared in 47% yield according to a literature procedure.[4] Data matches that reported in the literature.[6]

1-Ethynyl-4-methylbenzene
Prepared in 43% yield according to a literature procedure.[7] Data matches that reported in the literature.[8]

1-Ethynyl-4-methoxybenzene
Prepared in 90% yield according to a literature procedure.[7] Data matches that reported in the literature.[7]

1-Ethynyl-2-isopropylbenzene
Prepared in 91% yield according to a literature procedure.[9] Data is in agreement with literature values.[8]

2-(2,2-Dibromovinyl)naphthalene
Prepared in 84% yield according to a literature procedure.[4] Data matches that reported in the literature.[10]

2-(2,2-Dibromovinyl)furan
Prepared in 64% yield according to a literature procedure.[11] Data is in agreement with literature values.[11]

3-Bromo-2-ethynylthiophene
Prepared in 24% yield over three steps from 3-bromothiophene according to a literature procedure.[12] Data is in agreement with literature values.[12b]

3-(Prop-2-yn-1-yloxy)prop-1-ene
Prepared in 36% yield according to the literature procedure.[13] Data matches that reported in the literature.[13]

(*E*)-(3-(Prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene
Prepared in 49% yield according to a literature procedure.[14] Data matches that reported in the literature.[14]

***N*-(4-Ethynylphenyl)acetamide**

Prepared in 3 steps in a 44% yield according to a literature procedure.[15] Data matches that reported in the literature.[15b]

1-(2,2-Dibromovinyl)-4-(trifluoromethyl)benzene

Prepared in 74% yield according to a literature procedure.[4] Data matches that reported in the literature.[4]

1-(2,2-Dibromovinyl)-4-fluorobenzene

Prepared in 79% yield according to a literature procedure.[4] Data matches that reported in the literature.[4]

3,5-Dichloropyridine 1-oxide

Prepared in 84% yield according to a literature procedure.[2] Data is in agreement with literature values.[16]

Chloro[2-dicyclohexyl(2',6'-dimethoxybiphenyl)phosphine] gold(I)

Prepared in 80% yield according to a literature procedure.[17] Data is in agreement with literature values.[17]

2-Dicyclohexyl(2',6'-dimethoxybiphenyl)phosphine gold(I) bis(trifluoromethanesulfonyl)imide

Prepared in 85% yield according to a literature procedure.[18] Data is in agreement with literature values.[18]

***S*-Methyl benzenesulfonothioate**

Prepared in 85% yield according to a literature procedure.[19] Data is in agreement with literature values.[19]

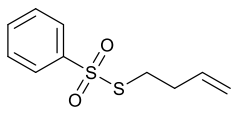
(*E*)-(4-Bromo-but-1-enyl)benzene ((E)-(4-Chloro-but-1-enyl)benzene (3:1 mixture)

Prepared in 39% yield according to a literature procedure.[20] Data is in agreement with literature values.[20]

Methyl benzenesulfinate

Prepared in 83% yield according to a literature procedure.[21] Data is in agreement with literature values.[21]

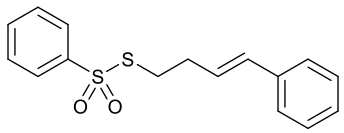
***S*-(But-3-en-1-yl) benzenesulfonothioate (S1)**



S1 was prepared following a literature procedure.[24] Sodium benzenesulfonothioate (7.60 g, 38.7 mmol, 1.0 eq) was added to a RBF and the flask was evacuated and refilled with argon (× 3). Anhydrous DMF (60 mL) was added and the mixture was stirred at rt. 4-bromo-1-butene (4.0 mL, 40 mmol, 1.03 eq.) was added over 5 minutes by syringe and the mixture was stirred for 4 days. The mixture was poured into ice/water (200 mL) and was extracted Et_2O (6 × 50 mL). The combined organics were washed with $NaHCO_3$ (sat) solution (50 mL), brine (3 × 50 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by column chromatography (9:1 hexane:EtOAc) to afford **1** (8.90 g, 86%) as a pale orange oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 – 7.87 (m, 2H), 7.75 – 7.49 (m, 3H), 5.67 (ddt, *J* = 17.0, 10.4, 6.7 Hz,

1H), 5.08 – 4.96 (m, 2H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.41 – 2.28 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.0 (C), 134.8 (CH), 133.8 (CH), 129.4 (2CH), 127.1 (2CH), 117.7 (CH_2), 35.3 (CH_2), 32.9 (CH_2); IR (neat): *v* = 3068, 2981, 1641, 1582, 1447, 1322, 1308, 1293, 1139, 1076, 714; HR-MS (ES-TOF): *m/z*: calcd for $C_{10}H_{12}O_2S_2Na$: 251.0179, found 251.0176 $[M + Na]^+$.

(*E*)-*S*-(4-Phenylbut-3-en-1-yl) benzenesulfonothioate



(*E*)-*S*-(4-Phenylbut-3-en-1-yl) benzenesulfonothioate was prepared following a literature procedure.[24] Sodium benzenesulfonothioate (981 mg, 5.0 mmol, 1.2 eq.) was added to a RBF and the flask was evacuated and refilled with argon (× 3). Anhydrous DMF (7 mL) was added and the mixture was stirred at rt for 10 minutes. (*E*)-(4-Bromo-but-1-enyl)benzene (1.00 g, 4.0 mmol from a 3:1 mixture with its chloro-analogue, 1.0 eq.) was added over 5 minutes by syringe and the mixture was stirred at rt for 2.5 days. The mixture was poured into ice/ water (20 mL) and was extracted with Et_2O (6 × 15 mL). The combined organics were washed with $NaHCO_3$ (sat) solution (15 mL), brine (3 × 15 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by column chromatography (95:5 hexane:EtOAc to 9:1 hexane:EtOAc) to afford the sulfonothioate (930 mg, 76%) as a viscous orange oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 – 7.91 (m, 2H), 7.71 – 7.51 (m, 3H), 7.33 – 7.28 (m, 4H), 7.25 – 7.19 (m, 1H), 6.34 (dt, *J* = 15.8, 1.3 Hz, 1H), 6.04 (dt, *J* = 15.8, 7.2 Hz, 1H), 3.15 (t, *J* = 7.2 Hz, 2H), 2.53 (app qd, *J* = 7.2, 1.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.0 (C), 136.9 (C), 133.8 (CH), 132.9 (CH), 129.5 (2CH), 128.7 (2CH), 127.7 (2CH), 127.1 (2CH), 126.3 (2CH), 35.8 (CH_2), 32.3 (CH_2); IR (neat): *v* = 3060, 3026, 2933, 1597, 1581, 1446, 1307, 1320, 1138, 1076, 966, 744, 714, 684, 594; HR-MS (ES-TOF): *m/z*: calcd for $C_{16}H_{16}O_2NaS_2$: 327.0489, found 327.0484 $[M + Na]^+$.

Preparation of Alkynyl Sulfoxides

Alkynyl Thioethers

General Procedure 1: Preparation of alkynyl thioethers (GP1)

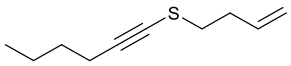
Dibromoolefin (1.1 eq.) and anhydrous THF (0.2 M) were added to a flame dried two-neck RBF under argon. The flask was cooled to -78 °C. *n*-BuLi (2.5 M in hexane) (2.3 eq.) was added dropwise and on complete addition the mixture was stirred at 78 °C for an hour before *S*-(but-3-en-1-yl) benzenesulfonothioate (**S1**) (1.0 eq.) was added dropwise. The reaction was allowed to warm to rt overnight. The reaction was quenched with NH_4Cl (sat) (0.2 M with respect to the alkyne) and the mixture was extracted Et_2O (3 × reaction volume), the organics were washed with brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure and the residue was purified by column chromatography.

General Procedure 2: Preparation of alkynyl thioethers (GP2)

Alkyne (1.1 eq.) and anhydrous THF (0.2 M) were added to a flame dried two-neck RBF under argon. The flask was cooled to -78 °C. LiHMDS (1 M in ethylbenzene) (1.1 eq.) was added dropwise and on complete addition the mixture was stirred at -78 °C for an hour before *S*-(but-3-en-1-yl) benzenesulfonothioate (**S1**) (1.0 eq.) was added dropwise. The reaction was allowed to warm to rt overnight. The reaction was quenched with NH_4Cl (sat) (0.2 M with respect to alkyne added) and the mixture was extracted Et_2O (3 × reaction volume), the organics were

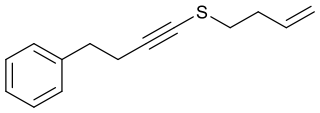
washed with brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure and the residue was purified by column chromatography.

But-3-en-1-yl(hex-1-yn-1-yl)sulfane (S2a)



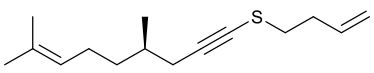
S2a was prepared according to a literature procedure.[25] 1-Hexyne (822 mg, 10.0 mmol) and THF (50 mL) were added to a 50 mL three-neck RBF. The mixture was cooled to -78 °C and *n*-BuLi (6.7 mL, 11.0 mmol, 1.1 eq.) was added dropwise. After complete addition the mixture was stirred for 1 h at -78 °C before addition of sulfur (321 mg, 10.0 mmol, 1.0 eq.) the resulting red solution was stirred for a further 1 h at -78 °C before warming to 0 °C slowly. 4-bromo-1-butene (1.35 g, 1.0 mL, 10.0 mmol, 1.0 eq.) was added and the mixture was stirred for 2 h at 0 °C and left to warm to rt for 13 h. The mixture was quenched with NH_4Cl (50 mL of a saturated solution), extracted with Et_2O (3 × 30 mL), washed with brine (50 mL), dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography (hexane) to afford **S2a** (1.03g, 61%) as a pale yellow oil; ^{1}H NMR (300 MHz $CDCl_3$): δ = 5.84 (ddt, *J* = 17.3, 10.4, 6.6 Hz, 1H), 5.12 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.07 (dd, *J* = 10.4, 1.3 Hz, 1H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.48 (td, *J* = 7.4, 6.6 Hz, 2H) 2.30 (t, *J* = 6.8, 2H), 1.55 – 1.34 (m, 4H), 0.91 (t, *J* = 7.1, 3H); ^{13}C NMR (101 MHz $CDCl_3$): δ = 136.0 (CH), 116.6 (CH_2), 94.8 (C), 67.8 (C), 34.6 (CH_2), 33.4 (CH_2), 30.9 (CH_2), 22.0 (CH_2), 19.9 (CH_2), 13.6 (CH_3); IR (neat): *v* = 3079, 2960, 2929, 2167, 1641, 1571, 1442, 1417, 752, 689. HR-MS (ES-TOF): *m/z* calcd. for $C_{10}H_{16}S$ 168.0973, found 168.0979 $[M + H]^+$.

But-3-en-1-yl(4-phenylbut-1-yn-1-yl)sulfane (S2b)



S2b was prepared according to a literature procedure.[25] 4-Phenyl-1-butyne (391 mg, 3.0 mmol, 1.0eq.) and THF (15 mL) were added to a 50 mL three-neck RBF. The mixture was cooled to -78 °C and *n*-BuLi (2.0 mL, 3.3 mmol, 1.1 eq.) was added dropwise. After complete addition the mixture was stirred for 1 h at -78 °C before addition of sulfur (96.3 mg, 3.0 mmol, 1.0 eq.) the resulting red solution was stirred for a further 1 h at -78 °C before warming to 0 °C slowly. 4-bromo-1-butene (405 mg, 0.30 mL, 3.0 mmol, 1.0 eq.) was added and the mixture was stirred for 2 h at 0 °C and left to warm to rt for 2 h. The mixture was quenched with NH_4Cl (20 mL of a saturated solution), extracted with Et_2O (3 × 10 mL), washed with brine (20 mL), dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography (hexane) to afford **S2b** (214 mg, 33%) as a pale yellow oil; ^{1}H NMR (300 MHz $CDCl_3$): δ = 7.36 – 7.21 (m, 5H), 5.84 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 1H), 5.17-5.05 (m, 2H), 2.87 (t, *J* = 7.5 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.64 (t, *J* = 7.4 Hz, 2H), 2.44 (td, *J* = 7.5, 6.6 Hz, 2H); ^{13}C NMR (101 MHz $CDCl_3$): δ = 140.6 (C), 135.9 (CH), 128.5 (2CH), 128.4 (2CH), 126.3 (CH), 116.6 (CH_2), 93.8 (C), 69.0 (C), 35.2 (CH_2), 34.5 (CH_2), 33.4 (CH_2), 22.3 (CH_2); IR (neat): *v* = 3063, 3027, 2923, 1640, 1537, 1453, 1337, 1276, 1030, 993, 915, 747, 697; HR-MS (ES-TOF): *m/z* calcd. for $C_{14}H_{16}S$ 217.1048, found 217.1051 $[M + H]^+$.

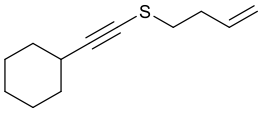
(R)-But-3-en-1-yl(4,8-dimethylnon-7-en-1-yn-1-yl)sulfane (S2c)



S2c was prepared according to **GP2** using 1,1-dibromo-8-methylnona-1,7-diene (828 mg, 2.67 mmol), *n*-BuLi (2.4 M in hexanes) (2.2 mL, 5.5 mmol), **S1** (547 mg, 2.40 mmol) and THF (20 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (hexane) provided **S2c** (346 mg, 62%) as a colourless oil; $[\alpha]_D^{21}$ 11.60 (*c* 0.010 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$):

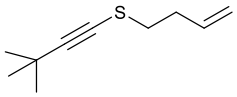
δ = 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.17 – 5.03 (m, 3H), 2.76 – 2.68 (m, 2H), 2.53 – 2.43 (m, 2H), 2.24 (qd, *J* = 16.8, 6.2 Hz, 2H), 1.98 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.75 – 1.58 (m, 7H), 1.52 – 1.37 (m, 1H), 1.32 – 1.16 (m, 1H), 0.98 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.1 (CH), 131.6 (C), 124.6 (CH), 116.7 (CH_2), 93.7 (C), 68.8 (C), 36.2 (CH_2), 34.8 (CH_2), 33.6 (CH_2), 32.5 (CH), 27.5 (CH_2), 25.9 (CH_3), 25.7 (CH_2), 19.6 (CH_3), 17.8 (CH_3); IR (neat): ν = 2964, 2914, 1641, 1445, 1377, 1277, 1222, 993, 916, 825; HR-MS (EI-TOF): *m/z*: calcd for $C_{15}H_{24}S$: 236.1599, found 236.1604 $[M + H]^+$.

But-3-en-1-yl(cyclohexylethynyl)sulfane (S2d)



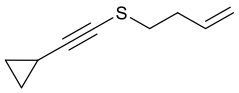
S2d was prepared according to **GP1** using (2,2-dibromovinyl)cyclohexane (630 mg, 2.35 mmol), *n*-BuLi (2.5 M in hexanes) (2.0 mL, 4.9 mmol), **S1** (448 mg, 2.14 mmol) and THF (10 mL). The reaction time was 17 hours. Aqueous work-up and purification by column chromatography (hexane) provided **S2d** (260 mg, 63%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.85 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.12 (dd, *J* = 17.0. 1.6 Hz, 1H), 5.07 (dd, *J* = 10.2, 1.6 Hz, 1H), 2.71 (t, *J* = 7.2 Hz, 2H), 2.55 – 2.41 (m, 3H), 1.73 (ddt, *J* = 14.7, 12.0, 6.0 Hz, 4H), 1.55 – 1.37 (m, 3H), 1.37 – 1.20 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.1 (CH), 116.7 (CH_2), 99.0 (C), 67.9 (C), 34.8 (CH_2), 33.5 ($2CH_2$), 32.8 (CH_2), 30.5 (CH), 26.0 ($2CH_2$), 25.0 (CH_2); IR (neat): *v* = 2928, 2853, 1641, 1496, 1447, 993, 910, 730; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{18}S$: 194.1129, found 194.1134 $[M + H]^+$.

But-3-en-1-yl(3,3-dimethylbut-1-yn-1-yl)sulfane (S2e)



S2e was prepared according to **GP3** using 3,3-dimethyl-1-butyne (400 µL, 3.30 mmol), LiHMDS (1 M, 3.30 mL, 3.30 mmol), **S1** (678 mg, 3.00 mmol) and THF (10 mL). The reaction time was 20 hours. Aqueous workup and purification by column chromatography (hexane) provided **S2e** (336 mg, 67%) as a colourless oil; ^{1}H NMR (300 MHz $CDCl_3$): δ = 5.85 (ddt, *J* = 17.2, 10.2, 6.6, 1H), 5.12 (dd, *J* = 17.2, 1.7, 1H), 5.07 (dd, *J* = 10.2, 1.7, 1H), 2.71 (t, *J* = 7.2, 2H), 2.48 (td, *J* = 7.2, 6.6, 2H), 1.23 (s, 9H); ^{13}C NMR (101 MHz $CDCl_3$): δ = 136.2 (CH), 116.7 (CH_2), 103.0 (C), 66.7 (C), 34.8 (CH_2), 33.5 (CH_2), 31.2 ($3CH_3$), 29.0 (C); IR (neat): *v* = 2963, 2865, 1706, 1640, 1467, 1393, 1362, 1218, 991, 914, 744. HR-MS (ES-TOF): *m/z* calcd. for $C_{10}H_{16}S$ 168.0973, found 168.0976 $[M + H]^+$.

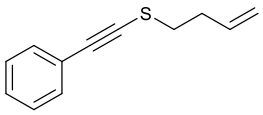
But-3-en-1-yl(cyclopropylethynyl)sulfane (S2f)



S2f was prepared according to a literature procedure.[25] Cyclopropylacetylene (198.3 mg, 3.00 mmol, 1.0 eq.) and THF (15 mL) were added to a 50 mL three-neck RBF. The mixture was cooled to -78 °C and n-BuLi (2.0 mL, 3.3 mmol, 1.1 eq.) was added dropwise. After complete addition the mixture was stirred for 1 h at -78 °C before addition of sulfur (66.3 mg, 3.0 mmol, 1.0 eq.) the resulting red solution was stirred for a further 1 h at -78 °C before warming to 0 °C slowly. 4-bromo-1-butene (405 mg, 0.3 mL, 3.0 mmol, 1.0 eq.) was added and the mixture was stirred for 2 h at 0 °C and left to warm to rt for 15 h. The mixture was quenched with NH_4Cl (20 mL of a saturated solution), extracted with Et_2O (3 × 10 mL), washed with brine (20 mL), dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography (hexane) to afford **S2f** (139 mg, 30%) as a pale yellow oil; ^{1}H NMR (300 MHz $CDCl_3$): δ = 5.86 (ddt, *J* = 17.2, 10.3, 6.6 Hz, 1H), 5.12 (dd, *J* = 17.2, 1.7 Hz, 1H,), 5.06 (dd, *J* = 10.3, 1.7 Hz, 1H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.48 (td, *J* = 7.4, 6.6 Hz, 2H) 1.34 (tt, *J* = 7.5, 6.0 Hz, 1H), 0.84-0.78 (m,

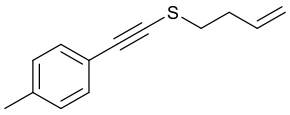
2H), 0.77-0.72 (m, 2H); ^{13}C NMR (101 MHz $CDCl_3$): δ = 135.9 (CH,), 116.6 (CH_2), 98.6 (C), 63.8 (C), 34.7 (CH_2), 33.4 (CH_2), 9.0 ($2CH_2$), 0.8 (CH); IR (neat): *v* = 3080, 3011, 2979, 1640, 1429, 989, 916, 839, 810, 725; HR-MS (ES-TOF): *m/z* calcd. for $C_9H_{13}S$ 153.0738, found 153.0735 [M + H]$^+$.

But-3-en-1-yl(phenylethynyl)sulfane (S2g)



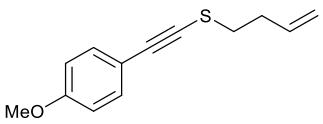
S2g was prepared according to **GP3** using phenylacetylene (563 mg, 5.5 mmol), LiHMDS (1 M, 5.5 mL, 5.5 mmol), **1** (1.14 g, 5.0 mmol) and THF (25 mL). The reaction time was 19 hours. Aqueous workup and purification by column chromatography (hexane) provided **S2g** (804 mg, 94%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 – 7.37 (m, 2H), 7.34 – 7.27 (m, 3H), 5.88 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.16 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.10 (dd, *J* = 10.2, 1.6 Hz, 1H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.57 (dt, *J* = 7.4, 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ =135.8 (CH), 131.7 (2CH), 128.5 (2CH), 128.3 (C), 117.1 (CH_2), 93.5 (C), 35.1 (CH_2), 33.7 (CH_2); IR (neat): ν = 3079, 2979, 2927, 2166, 1640, 1595, 1487, 1442, 915, 752, 688; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{12}S$: 188.0660, found 188.0663 [M + H]$^+$.

But-3-en-1-yl(p-tolylethynyl)sulfane (S2h)



S2h was prepared according to a literature procedure.[25] 1-Ethynyl-4-methylbenzene (190 mg, 1.64 mmol, 1.0 eq.) and THF (8 mL) were added to a 50 mL three-neck RBF. The mixture was cooled to -78 °C and *n*-BuLi (2.5 M in hexanes) (0.72 mL, 1.8 mmol, 1.0 eq.) was added dropwise. On complete addition the mixture was stirred for 1 hour at -78 °C before addition of sulfur (52.6 mg, 1.64 mmol, 1.0 eq.). The resulting red solution was stirred for a further hour at -78 °C before warming to 0 °C over 1 hour. 4 Bromo-1-butene (167 µL, 1.64 mmol, 1.0 eq.) was added and the mixture was stirred for 2 hours at 0 °C and left to warm to rt for 16 hours. The mixture was quenched with NH_4Cl (10 mL of a saturated solution), extracted with Et_2O (3 × 10 mL), washed with brine (10 mL), dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography (hexane) to afford **S2h** (222 mg, 67%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.88 (ddt, *J* = 17.0, 10.2, 6.4 Hz, 1H), 5.15 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.20 – 5.07 (dd, 10.2, 1.6 Hz, 2H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.56 (dt, *J* = 7.5, 6.4 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.4 (C), 135.8 (CH), 131.7 (2CH), 129.2 (2CH), 120.5 (C), 116.9 (CH_2), 93.5 (C), 78.2 (C), 35.1 (CH_2), 33.6 (CH_2), 21.6 (CH_3); IR (neat): ν = 3079, 3028, 2979, 2921, 2166, 1641, 1506, 1434, 1417, 916, 813; HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{15}S$: 203.0894, found 203.0893 [M + H]$^+$.

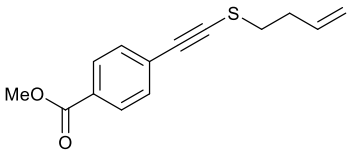
But-3-en-1-yl((4-methoxyphenyl)ethynyl)sulfane (S2i)



S2i was prepared according to a literature procedure.[25] 1-Ethynyl-4-methoxybenzene (170 mg, 1.29 mmol, 1.0 eq.) and THF (7 mL) were added to a 50 mL three-neck RBF. The mixture was cooled to -78 °C and *n*-BuLi (2.5 M in hexanes) (0.57 mL, 1.42 mmol, 1.0 eq.) was added dropwise. After complete addition the mixture was stirred for 1 h at -78 °C before addition of sulfur (41.3 mg, 1.29 mmol, 1.0 eq.) the resulting red solution was stirred for a further 1 h at -78 °C before warming to 0 °C slowly. 4 Bromo-1-butene (131 µL, 1.29 mmol, 1.0 eq.) was added and the mixture was stirred for 2 h at 0 °C and left to warm to rt for

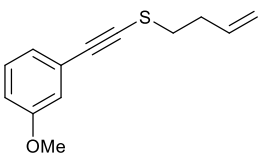
16 h. The mixture was quenched with NH_4Cl (10 mL of a saturated solution), extracted with Et_2O (3 × 10 mL), washed with brine (10 mL), dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography (hexane) to afford **2i** (222 mg, 67%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 – 7.35 (m, 2H), 6.85 – 6.81 (m, 2H), 5.87 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.15 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.10 (dd, *J* = 10.2, 1.6 Hz, 1H), 3.81 (s, 3H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.55 (dt, *J* = 7.4, 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.8 (C), 135.9 (CH), 133.5 (2CH), 116.9 (CH_2), 115.7 (C), 114.1 (2CH), 93.2 (C), 55.4 (CH_3), 35.1 (CH_2), 33.6 (CH_2); IR (neat): ν = 2933, 2837, 1604, 1505, 1289, 1245, 1171, 1030, 917, 829, 810, 777; HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{15}OS$: 219.0844, found 219.0836 $[M + H]^+$.

Methyl-4-((but-3-en-1-ylthio)ethynyl)benzoate (S2l)



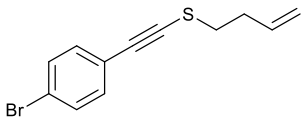
S2l was prepared according to **GP2** using methyl 4-ethynylbenzoate (333 mg, 2.08 mmol), LiHMDS 1 M (2.08 mL, 2.08 mmol), **S1** (432 mg, 1.89 mmol) and THF (10 mL). The reaction time was 16 hours. Aqueous work-up and purification by column chromatography (hexane) provided **S2l** (428 mg, 92%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 5.87 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.16 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.11 (d, *J* = 10.2, 1,6 Hz, 1H), 3.91 (s, 3H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.63 – 2.51 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7 (C), 135.5 (CH), 131.0 (2CH), 129.6 (2CH), 129.1 (C), 128.3 (C), 117.2 (CH_2), 93.1 (C), 83.5 (C), 52.3 (CH_3), 35.1 (CH_2), 33.6 (CH_2); IR (neat): ν = 2951, 2162, 1717, 1603, 1434, 1270, 1174, 1270, 1174, 1105, 1017, 855, 766; HR-MS (ES-TOF): *m/z*: calcd for $C_{14}H_{15}O_2S$: 247.0793, found 247.0789 $[M + H]^+$.

But-3-en-1-yl((3-methoxyphenyl)ethynyl)sulfane (S2n)



S2n was prepared according to **GP2** using 3-methoxyphenylacetylene (265 mg, 2.00 mmol), LiHMDS (1 M, 2.00 mL, 2.00 mmol), **S1** (415 mg, 1.82 mmol) and THF (10 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (hexane) provided **S2n** (346 mg, 91%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (t, *J* = 8.1 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.94 (dd, *J* = 2.6, 1.4 Hz, 1H), 6.85 (ddd, *J* = 8.1, 2.6, 1.0 Hz, 1H), 5.88 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 1H), 5.16 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.10 (dd, *J* = 10.2, 1.6 Hz, 1H), 3.80 (s, 3H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.57 (dt *J* = 7.5, 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.4 (C), 135.8 (CH), 129.5 (CH), 124.3 (C), 124.1 (CH), 117.0 (CH_2), 116.3 (CH), 114.8 (CH), 93.4 (C), 79.2 (C), 55.4 (CH_3), 35.0 (CH_2), 33.6 (CH_2); IR (neat): *v* = 3076, 2962, 2935, 2835, 2162, 1640, 1593, 1573, 1283, 1157, 1041, 775, 684; HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{15}OS$: 219.0844, found 219.0838 $[M + H]^+$.

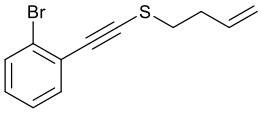
((4-Bromophenyl)ethynyl)(but-3-en-1-yl)sulfane (S2o)



S2o was prepared according to **GP2** using 4-bromophenylacetylene (240 mg, 1.32 mmol), LiHMDS 1 M (1.32 mL, 1.32 mmol), **S1** (275 mg, 1.21 mmol) and THF (7 mL). The reaction time was 16 hours. Aqueous work-up and purification by column chromatography (hexane) provided **2o** (190 mg, 59%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.6 Hz, 2H) 7.08 (d, *J* = 8.6 Hz, 2H), 5.68 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 4.97 (dd, *J* = 17.0, 1.6 Hz, 1H), 4.92 (dd, *J* = 10.2, 1.6 Hz, 1H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.39 (dt, *J* = 7.4, 6.6 Hz, 2H);

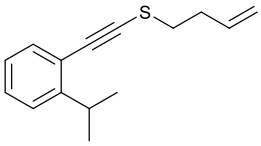
^{13}C NMR (101 MHz, $CDCl_3$): δ = 135.6 (CH), 132.9 (2CH), 131.7 (2CH), 122.5 (C), 122.3 (C), 117.1 (CH_2), 92.4 (C), 80.8 (C), 35.0 (CH_2), 33.6 (CH_2); IR (neat): *v* = 3078, 2978, 2925, 2164, 1640, 1583, 1483, 1393, 1069, 1009, 819; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{12}S^{79}Br$: 266.9843, found 266.9837 $[M + H]^+$.

((2-Bromophenyl)ethynyl)(but-3-en-1-yl)sulfane (S2p)



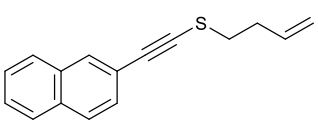
S2p was prepared according to **GP2** using 2-bromophenylacetylene (195 mg, 1.08 mmol), LiHMDS 1 M (1.08 mL, 1.08 mmol), **S1** (223 mg, 0.98 mmol) and THF (5 mL). The reaction time was 16 hours. Aqueous work-up and purification by column chromatography (hexane) provided **S2p** (183 mg, 70%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.24 (app dt, *J* = 7.7, 1.4 Hz, 1H), 7.17 – 7.08 (m, 1H), 5.88 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.18 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.2, 1.6 Hz, 1H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.63 (dt, *J* = 7.4, 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 135.7 (CH), 132.8 (CH), 132.5 (CH), 129.0 (CH), 126.9 (CH), 125.7 (C), 125.0 (C), 117.1 (CH_2), 92.2 (C), 84.9 (C), 35.2 (CH_2), 33.7 (CH_2); IR (neat): *v* = 3075, 2978, 2926, 2170, 1640, 1585, 1465, 1432, 1025, 918, 750; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{12}S^{79}Br$: 266.9843, found 266.9841 $[M + H]^+$.

But-3-en-1-yl((2-isopropylphenyl)ethynyl)sulfane (S2q)



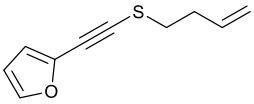
S2q was prepared according to **GP2** using 1-ethynyl-2-isopropylbenzene (300 mg, 2.08 mmol), LiHMDS (1 M, 2.08 mL, 2.08 mmol), **S1** (431 mg, 1.89 mmol) and THF (10 mL). The reaction time was 20 hours. Aqueous workup and purification by column chromatography (hexane) provided **S2q** (350 mg, 80%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (dd, *J* = 4.6, 3.6 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.12 (ddd, *J* = 7.7, 5.2, 3.6 Hz, 1H), 5.89 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.16 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.2, 1.6 Hz, 1H), 3.51 – 3.35 (m, 1H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.58 (dt, *J* = 7.4, 6.6 Hz, 2H), 1.28 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.5 (C), 135.8 (CH), 132.3 (CH), 128.5 (CH), 125.6 (CH), 125.0 (CH), 122.4 (C), 117.0 (CH_2), 92.3 (C), 82.4 (C), 35.2 (CH_2), 33.8 (CH_2), 31.7 (CH), 23.3 ($2CH_3$); IR (neat): *v* = 3048, 2961, 2927, 2868, 2163, 1641, 916, 754. The mass ion could not be identified in order to obtain HRMS. HRMS for the corresponding sulfoxide was obtained.

But-3-en-1-yl(naphthalen-2-ylethynyl)sulfane (S2r)



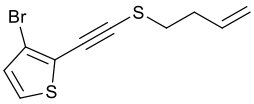
S2r was prepared according to **GP1** using 2-(2,2-dibromovinyl)naphthalene (550 mg, 1.76 mmol), *n*-BuLi (1.5 mL, 3.7 mmol) and **S1** (365 mg, 1.60 mmol). The reaction time was 18 hours. Aqueous work-up and purification by column chromatography (hexane) provided **S2r** (248 mg, 65%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (s, 1H), 7.86 – 7.73 (m, 3H), 7.51-7.45 (m, 3H), 5.91 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.19 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.10 (dd, *J* = 10.2, 1.6 Hz, 1H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.61 (dt, *J* = 7.5, 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 135.7 (CH), 133.1 (C), 132.8 (C), 131.3 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 126.7 (2CH), 120.9 (C), 117.0 (CH_2), 93.9 (C), 79.7 (C), 35.1 (CH_2), 33.7 (CH_2); IR (neat): ν = 3057, 2979, 2928, 2156, 1640, 1626, 1596, 1501, 1272, 918, 857, 816, 746; HR-MS (ES-TOF): *m/z*: calcd for $C_{16}H_{15}S$: 239.0894, found 239.0899 $[M + H]^+$.

2-((But-3-en-1-ylthio)ethynyl)furan (S2s)



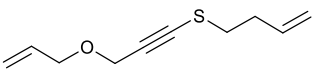
S2s was prepared according to **GP1** using 2-(2,2-dibromovinyl)furan (670 mg, 2.66 mmol), *n*-BuLi (2.4 M in hexanes) (2.3 mL, 5.6 mmol) and **S1** (552 mg, 2.42 mmol). The reaction time was 18 hours. Aqueous workup and purification by column chromatography (pentane) provided **S2s** (191 mg, 44%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (dd, *J* = 1.9, 0.7 Hz, 1H), 6.64 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.39 (dd, *J* = 3.4, 1.9 Hz, 1H), 5.85 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.15 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.09 (dd, *J* = 10.2, 1.6 Hz, 1H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.53 (dt, *J* = 7.5, 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.1 (CH), 137.4 (C), 135.6 (CH), 117.1 (CH_2), 117.1 (CH), 111.2 (CH), 85.3 (C), 83.4 (C), 35.3 (CH_2), 33.5 (CH_2); IR (neat): ν = 3079, 2979, 2925, 2154, 1640, 1565, 1461, 1015, 917, 745; HR-MS (EI-TOF): *m/z*: calcd for $C_{10}H_{10}OS$: 178.0452, found 178.0454 $[M + H]^+$.

3-Bromo-2-((but-3-en-1-ylthio)ethynyl)thiophene (S2t)



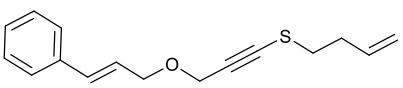
S2t was prepared according to **GP2** using 3-bromo-2-ethynylthiophene (335 mg, 1.78 mmol), LiHMDS (1 M, 1.78 mL, 1.78 mmol), **S1** (369 mg, 1.62 mmol) and THF (9 mL). The reaction time was 16 hours. Aqueous work-up and purification by column chromatography (hexane) provided **S2s** (238 mg, 55%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 5.4 Hz, 1H), 6.95 (d, *J* = 5.4 Hz, 1H), 5.87 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.18 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.2, 1.6 Hz, 1H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.60 (dt, *J* = 7.4, 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 135.6 (CH), 130.1 (CH), 127.4 (CH), 121.3 (C), 117.2 (CH_2), 117.1 (C), 88.4 (C), 84.5 (C), 35.4 (CH_2), 33.5 (CH_2); IR (neat): *v* = 3105, 3081, 2978, 2925, 2153, 1640, 1499, 1416, 917, 862, 708; HR-MS (ES-TOF): *m/z*: calcd for $C_{10}H_9S_2{}^{79}Br$: 271.9329, found 271.9335 $[M + H]^+$.

(3-(Allyloxy)prop-1-yn-1-yl)(but-3-en-1-yl)sulfane (S2u)



A flame dried (50 mL) 3-neck RBF was charged with 3-(prop-2-yn-1-yloxy)prop-1-ene (60% in Et_2O (760 µl, 4.00 mmol) and THF (20 mL). The mixture was cooled to -78 °C and *n*-BuLi (2.4 M in hexane) (1.8 mL, 1.2 equiv, 4.4 mmol) was added dropwise. On complete addition the mixture was stirred for an hour at 78 °C before the dropwise addition of **1** (827 mg, 3.63 mmol). The reaction mixture was allowed to warm to rt over 16 hours. The mixture was quenched NH_4Cl (20 mL), the organic layer was removed and the aqueous layer extracted with Et_2O (3 × 10 mL). The combined organic portions were washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by column chromatography (hexane) providing **S2u** (376 mg, 57%) as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.99 – 5.74 (m, 2H), 5.38 – 5.03 (m, 4H), 4.26 (s, 2H), 4.06 (dt, *J* = 5.8, 1.3 Hz, 2H), 2.81 – 2.72 (m, 2H), 2.55 – 2.43 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 135.7 (CH), 134.2 (CH), 118.0 (CH_2), 117.0 (CH_2), 90.7 (C), 90.7 (C), 70.5 (CH_2), 58.4 (CH_2), 34.7 (CH_2), 33.5 (CH_2); IR (neat): ν = 3080, 2980, 2847, 2179, 1641, 1420, 1279, 1124, 1074, 991, 917; HR-MS (AP-TOF): m/z: calcd for $C_{10}H_{15}OS$: 183.0844, found 183.0852 $[M + H]^+$.

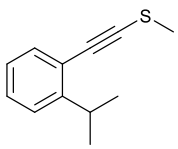
But-3-en-1-yl(3-(cinnamyloxy)prop-1-yn-1-yl)sulfane (S2v)



A flame dried (50 mL) 3-neck RBF was charged with (E)-(3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene (692 mg, 1.1 equiv, 4.00 mmol) and THF (20 mL). The mixture was

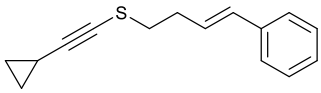
cooled to -78 °C and *n*-BuLi (2.35 M in hexane) (1.9 mL, 1.2 equiv, 4.4 mmol) was added dropwise. On complete addition the mixture was stirred for an hour at -78 °C before the dropwise addition of **S1** (820 mg, 1.0 equiv, 3.6 mmol). The reaction mixture was allowed to warm to rt over 16 hours. The mixture was quenched NH_4Cl (20 mL), the organic layer was removed and the aqueous layer extracted with Et_2O (3 × 10 mL). The combined organics were washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by column chromatography (hexane) providing **S2v** (683 mg, 66%) as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (m, 5H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.32 (dt, *J* = 15.9, 6.2 Hz, 1H), 5.87 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.23 – 5.07 (m, 2H), 4.34 (s, 2H), 4.27 (d, *J* = 6.2 Hz, 2H), 2.80 (t, *J* = 7.4 Hz, 2H), 2.55 – 2.45 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.7 (C), 135.7 (CH), 133.4 (CH), 128.7 (2CH), 127.9 (CH), 126.7 (2CH), 125.3 (CH), 117.0 (CH_2), 90.7 (C), 70.1 (C), 58.3 (CH_2), 34.7 (CH_2), 33.5 (CH_2); IR (neat): ν = 3027, 2845, 2179, 1640, 1495, 1448, 1350, 1073, 966, 916, 744, 692; HR-MS (ES-TOF): *m/z*: calcd for $C_{16}H_{19}OS$: 259.1157, found 259.1159 $[M + H]^+$.

((2-Isopropylphenyl)ethynyl)(methyl)sulfane (S3)



S3 was prepared according to **GP2** using 1-ethynyl-2-isopropylbenzene (144 mg, 1.00 mmol), LiHMDS (1 M, 1.00 mL, 1.00 mmol), *S*-methyl benzenesulfonothioate (167 mg, 0.91 mmol) and THF (5 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (hexane) provided **S3** (82 mg, 50%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 – 7.25 (m, 1H), 7.15 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.14 (d, *J* = 1.0 Hz, 1H), 7.00 (ddd, *J* = 7.7, 5.3, 3.4 Hz, 1H), 3.30 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.38 (s, 3H), 1.15 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.4 (C), 132.2 (CH), 128.4 (CH), 125.5 (CH), 124.9 (CH), 122.2 (C), 90.7 (C), 84.1 (C), 31.6 (CH), 23.1 ($2CH_3$), 19.6 (CH_3); IR (neat): *v* = 3062, 2961, 2927, 2868, 2164, 1596, 1481, 1444, 1312, 1082, 976, 754; HR-MS (EI-TOF): *m/z*: calcd for $C_{12}H_{14}S$: 245.1000, found 245.1004 $[M + H]^+$.

(E)-(Cyclopropylethynyl)(4-phenylbut-3-en-1-yl)sulfone (S5)



S5 was prepared according to **GP2** using cyclopropylacetylene (168 µl, 2.00 mmol), LiHMDS (1 M, 2.00 mL, 2.00 mmol), **S2** (554 mg, 1.82 mmol) and THF (10 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (hexane) provided **S5** (308 mg, 74%) as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 – 7.27 (m, 4H), 7.25 – 7.18 (m, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.78 (dd, *J* = 10.7, 4.1 Hz, 2H), 2.69 – 2.58 (m, 2H), 1.37 (tt, *J* = 8.3, 5.0 Hz, 1H), 0.85 – 0.70 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.4 (C), 131.9 (CH), 128.7 (2CH), 127.7 (CH), 127.4 (CH), 126.2 (2CH), 98.8 (C), 64.0 (C), 35.2 (CH_2), 32.9 (CH_2), 9.1 ($2CH_2$), 0.9 (CH); IR (neat): *v* = 3025, 2924, 2167, 1598, 1493, 1448, 1350, 1268, 1192, 1053, 1028, 987, 963, 839, 810, 740, 691; HR-MS (EI-TOF): *m/z*: calcd for $C_{15}H_{16}S$: 228.0977, found 228.0973 $[M + H]^+$.

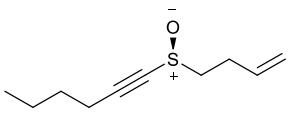
Alkynyl Sulfoxides

General Procedure 3: Preparation of alkynyl sulfoxides (GP 3)

A round-bottomed flask (RBF) equipped with a stirrer bar under argon was charged with alkynyl thioether (1.0 eq.) and CH_2Cl_2 (0.1 M). The mixture was cooled to 0 °C and *m*CPBA (1.0

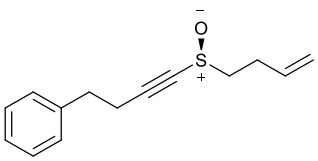
eq.) was added in 5 portions over 10 mins. The reaction was allowed to warm to rt. On reaction completion the mixture was washed with $NaHCO_3$ (3 × 10 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by column chromatography (using 3-5 inches of silica) to provide the alkynyl sulfoxide.

(±)-1-(But-3-en-1-ylsulfinyl)hex-1-yne (9a)



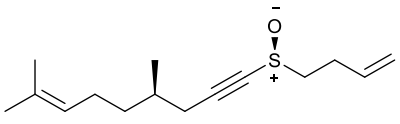
9a was prepared according to **GP3** using **S2a** (371 mg, 2.21 mmol), *m*CPBA (381.4 mg, 2.21 mmol) and CH_2Cl_2 (22 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided **9a** as a pale yellow oil (308 mg, 76%); ^{1}H NMR (300 MHz $CDCl_3$): δ = 5.66 (ddt, *J* = 17.2, 10.3, 6.6, 1H), 5.17 (dd, *J* = 17.2, 1.4, 1H), 5.12 (dd, *J* = 10.3, 1.4, 1H), 3.09 (t, *J* = 7.7, 2H), 2.63 (m, 2H), 2.44 (t, *J* = 7.0, 2H), 1.60 – 1.37 (m, 4H), 0.93 (t, *J* = 7.3, 3H); ^{13}C NMR (101 MHz $CDCl_3$): δ = 134.7 (CH), 117.4 (CH_2), 106.1 (C), 56.4 (C), 55.5 (CH_2), 29.8 (CH_2), 26.6 (CH_2), 22.1 (CH_2), 19.5 (CH_2), 13.6 (CH_3); IR (neat): ν = 2959, 2933, 2873, 2181, 1641, 1466, 1056, 916; HR-MS (ES-TOF): *m/z*: calcd for $C_{10}H_{16}OSNa$ 207.0820, found 207.0825. $[M + Na]^+$.

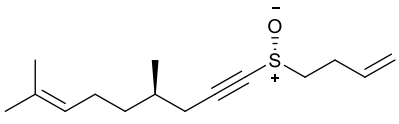
(±)-(4-(But-3-en-1-ylsulfinyl)but-3-yn-1-yl)benzene (9b)



9b was prepared according to **GP3** using **S2b** (85.9 mg, 0.40 mmol), *m*CPBA (69.0 mg, 0.40 mmol) and CH_2Cl_2 (4 mL). The reaction time was 3.5 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided **9b** as a pale yellow oil (67.4 mg, 73%). ^{1}H NMR (300 MHz $CDCl_3$): δ = 7.38 – 7.22 (m, 5H), 5.85 (ddt, *J* = 17.1, 10.2, 6.6, 1H), 5.17 (dd, *J* = 17.1, 1.4, 1H), 5.15 (dd, *J* = 10.2, 1.4, 1H), 3.07 (app t, *J* = 7.7, 2H), 2.94 (t, *J* = 7.2, 2H), 2.78 (t, *J* = 7.2, 2H), 2.70 – 2.44 (m, 2H); ^{13}C NMR (101 MHz $CDCl_3$): δ = 140.8 (C), 136.1 (CH), 128.7 ($2CH_2$), 128.6 ($2CH_2$), 126.5 (CH), 116.8 (CH_2), 94.0 (C), 69.2 (C), 35.4 (CH_2), 34.7 (CH_2), 33.6 (CH_2), 22.5 (CH_2). IR: ν_{max} (cm^{-1}) 3028, 2925, 2182, 1780, 1641, 1454, 1338, 1055, 994, 920, 748, 700, 626; HRMS (ES-TOF): *m/z* calcd. for $C_{14}H_{17}OS$ 233.1000, found 233.1004 $[M + H]^+$.

(4R)-1-((S)-but-3-en-1-ylsulfinyl)-4,8-dimethylnon-7-en-1-yne and (4R)-1-((R)-but-3-en-1-ylsulfinyl)-4,8-dimethylnon-7-en-1-yne (9c)

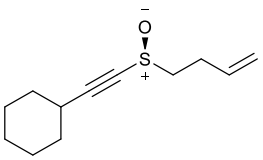




9c was prepared according to **GP3** using **S2c** (156 mg, 0.66 mmol), *m*CPBA (113 mg, 0.66 mmol) and CH_2Cl_2 (7 mL). The reaction time was 19 hours. Aqueous workup and purification by column chromatography (9:1 hexane:EtOAc) afforded **9c** (118 mg, 71%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.86 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.23 – 4.99 (m, 3H), 3.09 (t, *J* = 7.7 Hz, 2H), 2.75 – 2.51 (m, 2H), 2.38 (qd, *J* = 17.2, 6.3 Hz, 2H), 2.07 – 1.90 (m, 2H), 1.76 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.43 (ddt, *J* = 13.3, 8.5, 6.5 Hz, 1H), 1.35 – 1.19 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.7 (CH), 132.0 (C), 124.1 (CH), 117.4 (CH_2), 104.9 (C), 78.0 (C), 55.5 (CH_2), 36.2 (CH_2), 31.8 (CH), 27.0 (CH_2), 26.6 (CH_2), 25.8 (CH_3), 25.5 (CH_2), 19.6 (CH_3), 17.8 (CH_3); IR (neat): ν = 2964, 2916, 2180, 1641,

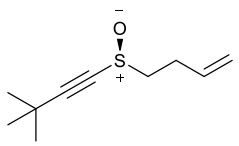
1444, 1379, 1060, 993, 915, 617; HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{25}OS$: 253.1626, found 253.1631 $[M+H]^+$.

(±)-((But-3-en-1-ylsulfinyl)ethynyl)cyclohexane (9d)



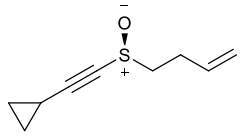
9d was prepared according to **GP3** using **S2d** (225 mg, 1.16 mmol), *m*CPBA (200 mg, 1.16 mmol) and CH_2Cl_2 (12 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (hexane to 4:1 hexane:EtOAc) provided **9d** (140 mg, 57%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.86 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.17 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.12 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.09 (t, *J* = 7.7 Hz, 2H), 2.74 – 2.50 (m, 3H), 1.91 – 1.77 (m, 2H), 1.76 – 1.66 (m, 2H), 1.60 – 1.45 (m, 3H), 1.43 – 1.23 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.7 (CH), 117.4 (CH_2), 109.4 (C), 76.8 (C), 55.5 (CH_2), 31.6 (CH_2), 29.9 (CH), 26.7 ($2CH_2$), 25.7 ($2CH_2$), 24.7 (CH_2); IR (neat): *v* = 2930, 2855, 2177, 1641, 1448, 1057, 915, 650; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{18}ONaS$: 233.0973, found 233.0976 $[M + Na]^+$.

(±)-4-((3,3-Dimethylbut-1-yn-1-yl)sulfinyl)but-1-ene (9e)



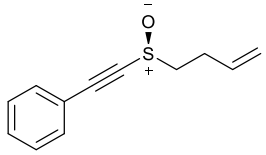
9e was prepared according to **GP3** using **S2e** (336 mg, 2.00 mmol), *m*CPBA (345 mg, 2.00 mmol) and CH_2Cl_2 (20 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (hexane to 4:1 hexane:EtOAc) provided **9e** (190 mg 52%) as a colourless oil; ^{1}H NMR (300 MHz $CDCl_3$): δ = 5.81 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 1H), 5.14 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.08 (dd, *J* = 10.2, 1.4 Hz, 1H), 3.08 (td, *J* = 7.7, 2.1 Hz, 2H), 2.67 – 2.51 (m, 2H), 1.25 (s, 9H); ^{13}C NMR (101 MHz $CDCl_3$): δ = 134.7 (CH), 117.5 (CH_2), 112.9 (C), 73.2 (C), 55.5 (CH_2), 30.2 ($3CH_3$), 29.9 (C), 26.7 (CH_2); IR (neat): ν = 2973, 2928, 2870, 2162, 1720, 1642, 1575, 1456, 1365, 1252, 1141, 1060, 918, 838, 768, 752, 701; HRMS (ES-TOF) *m/z* calcd. for $C_{10}H_{17}OS$ $[M+H]^+$ 185.1000 found 185.1001.

(±)-((But-3-en-1-ylsulfinyl)ethynyl)cyclopropane (9f)



9f was prepared according to **GP3** using sulfide **S2f** (91.4 mg, 0.60 mmol), *m*CPBA (104 mg, 0.60 mmol) and CH_2Cl_2 (6 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided **9f** as a pale yellow oil (68.7 mg, 68%); ^{1}H NMR (300 MHz $CDCl_3$): δ = 5.82 (ddt, *J* = 17.2, 10.3, 6.6, 1H), 5.14 (dd, *J* = 17.2, 1.5, 1H), 5.10 (dd, *J* = 10.3, 1.5, 1H), 3.04 (app t, *J* = 7.7, 2H), 2.74 – 2.51 (m, 2H), 1.43 (tt, *J* = 8.2, 5.1, 1H), 1.03 – 0.91 (m, 4H); ^{13}C NMR (101 MHz $CDCl_3$): δ = 134.7 (CH), 117.4 (CH_2), 109.6 (C,), 72.1 (C), 55.5 (CH_2), 26.7 (CH_2), 9.6 ($2CH_2$), 0.33 (C); IR (neat): ν = 3080, 3012, 2920, 2178, 1641, 1441, 1348, 1277, 1052, 995, 916, 828, 781; HR-MS (ES-TOF): *m/z*: calcd for $C_9H_{13}S$ 169.0687, found 169.0692. $[M + H]^+$.

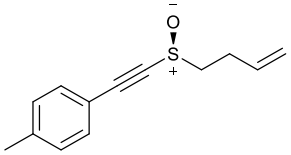
(±)-((But-3-en-1-ylsulfinyl)ethynyl)benzene (9g)



9g was prepared according to **GP3** using sulfide **S2g** (266 mg, 1.41 mmol), *m*CPBA (243 mg, 1.41 mmol) and CH_2Cl_2 (14 mL). The reaction time was 2 hours. Aqueous work-up and column chromatography (9:1 hexane:EtOAc) provided **9g** (220 mg, 77%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 – 7.50 (m, 2H), 7.50

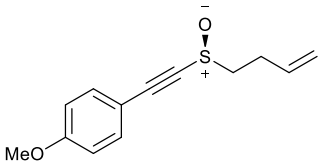
– 7.34 (m, 3H), 5.90 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.21 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.15 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.23 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 2H), 2.82 – 2.60 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.6 (CH), 132.4 (2CH), 130.8 (CH), 128.8 (2CH), 119.9 (C), 117.7 (CH_2), 102.7 (C), 85.1 (C), 55.4 (CH_2), 26.7 (CH_2); IR (neat): ν = 3068, 2920, 2164, 1719, 1574, 1282, 1244, 1057, 1023, 917, 832, 753, 688; HRMS (ES) *m/z* calcd. for $C_{12}H_{12}OSNa$ 227.0507, found 227.0504 [M + Na]$^+$.

(±)-1-((But-3-en-1-ylsulfinyl)ethynyl)-4-methylbenzene (9h)



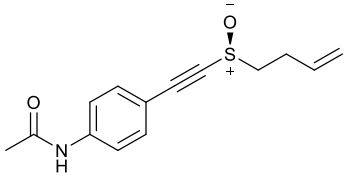
9h was prepared according to **GP3** using **S2h** (180 mg, 0.89 mmol), *m*CPBA (154 mg, 0.89 mmol) and CH_2Cl_2 (9 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (9:1 hexane:EtOAc) provided **9h** (143 mg, 74%) as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.89 (ddt, *J* = 17.0, 10.1, 6.6 Hz, 1H), 5.21 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.14 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.29 – 3.14 (m, 2H), 2.84 – 2.57 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.4 (C), 134.6 (CH), 132.4 (2CH), 129.5 (2CH), 117.6 (CH_2), 116.8 (C), 103.2 (C), 84.5 (C), 55.4 (CH_2), 26.7 (CH_2), 21.9 (CH_3); IR (neat): ν = 2923, 2243, 2162, 1605, 1508, 1055, 908, 817, 730; HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{14}OSNa$: 241.0663, found 241.0670 [M + Na]$^+$.

(±)-1-((But-3-en-1-ylsulfinyl)ethynyl)-4-methoxybenzene (9i)



9i was prepared according to **GP3** using **S2i** (151 mg, 0.69 mmol), *m*CPBA (120 mg, 0.69 mmol) and CH_2Cl_2 (7 mL). The reaction time was 2 hours. Aqueous work-up followed by column chromatography (4:1 hexane:EtOAc) provided **9i** (124 mg, 75%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.90 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.21 (dd, *J* = 16.9, 1.5 Hz, 1H), 5.15 (dd, *J* = 10.1, 1.5 Hz, 1H), 3.84 (s, 3H), 3.21 (t, *J* = 7.2 Hz, 2H), 2.79 – 2.61 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.6 (C), 139.3 (C), 134.7 (CH), 134.3 (2CH), 117.6 (CH_2), 114.5 (2CH), 103.4 (C), 84.1 (C), 55.6 (CH_3), 55.4 (CH_2), 26.8 (CH_2); IR (neat): ν = 3077, 2918, 2840, 2156, 1641, 1602, 1507, 1295, 1251, 1172, 1024, 832, 762; HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{15}O_2S$: 235.0793, found 235.0799 [M + H]$^+$.

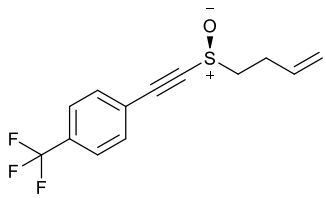
(±)-*N*-(4-((but-3-en-1-ylsulfinyl)ethynyl)phenyl)acetamide (9j)



A flame dried 2-neck RBF under argon was charged with *N*-(4-ethynylphenyl)acetamide (320 mg, 1.01 mmol, 1.1 eq.) and anhydrous THF (10 mL). The flask was cooled to -78 °C. LiHMDS (1 M in ethylbenzene) (4.02 mL, 4.02 mmol, 2.2 eq.) was added dropwise and on complete addition the mixture was stirred at -78 °C for an hour before **S1** (417 mg, 1.83 mmol, 1.0 eq.) was added dropwise. The reaction was allowed to warm to rt for 16 hours. The reaction was quenched with NH_4Cl (10 mL of a saturated solution) and the mixture was extracted with Et_2O (3 × 10 mL), the organics were washed with brine (10 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and most impurities were removed by column chromatography (7:3 hexane:EtOAc) to provide (370 mg) of a 1.8:1 ratio of sulfide **S2j** to *N*-(4-ethynylphenyl)acetamide. (**S2j** was used as a 1.8:1 mixture of alkynyl sulfide to alkyne) **9j** was prepared according to **GP3** using **S2j** (225 mg,

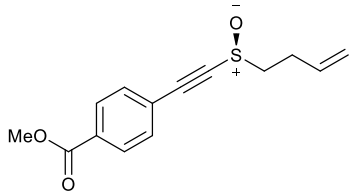
0.92 mmol), *m*CPBA (158 mg, 0.92 mmol) and CH_2Cl_2 (9 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (1:1 hexane:EtOAc to EtOAc) provided **9j** (176 mg, 74%) as a yellow solid; mp: 73-74 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (s, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 7.0 Hz, 2H), 5.89 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.27 – 5.10 (m, 2H), 3.32 – 3.15 (m, 2H), 2.81 – 2.56 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.0 (C), 140.7 (C), 134.4 (CH), 133.5 (2CH), 119.6 (2CH), 117.8 (CH_2), 114.4 (C), 103.7 (C), 84.3 (C), 55.3 (CH_2), 26.8 (CH_2), 24.8 (CH_3); IR (neat): ν = 3307, 3257, 3096, 2980, 2163, 1688, 1592, 1525, 1509, 1313, 1022, 839; HR-MS (ES-TOF): *m/z*: calcd for $C_{14}H_{16}NO_2S$: 262.0902, found 262.0900 $[M + H]^+$.

(±)-1-((But-3-en-1-ylsulfinyl)ethynyl)-4-(trifluoromethyl)benzene (9k)



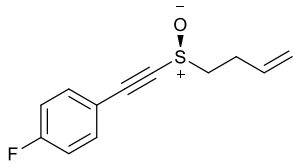
9k was prepared in 2 steps according to **GP1** and **GP3** starting from 1-(2,2-dibromovinyl)-4-(trifluoromethyl)benzene (825 mg, 2.50 mmol), *n*-BuLi (2.2 mL, 5.2 mmol), **S1** (517 mg, 2.27 mmol) and THF (12 mL). The reaction time was 16 hours. Aqueous work-up and removal of most impurities by column chromatography (hexane) provided the crude sulfide **S2k** (537 mg). Sulfide **2k** (195 mg) was dissolved in CH_2Cl_2 (7 mL), the mixture was cooled to 0 °C and *m*CPBA (118 mg, 0.68 mmol) was added in 5 portions over 10 minutes. The reaction time was 2 hours. The mixture was washed with $NaHCO_3$ (10 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by column chromatography (9:1 hexane:EtOAc) to yield **9k** (130 mg, 59% over 2 steps); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (s, 4H), 5.89 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.26 – 5.13 (m, 2H), 3.31 – 3.18 (m, 2H), 2.84 – 2.60 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.3 (CH), 134.7 (q, *J* = 32.6 Hz, C) 132.6 (2CH), 125.8 (d, *J* = 3.2 Hz, 2CH), 123.6 (q, *J* = 271.4 Hz, C), 123.6 (C), 117.9 (CH_2), 100.6 (C), 87.4 (C), 55.3 (CH_2), 26.7 (CH_2); IR (neat): *v* = 2981, 2170, 1643, 1615, 1321, 1241, 1128, 1065, 842, 655; HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{11}OF_3NaS$: 295.0380, found 295.0371 $[M + Na]^+$.

(±)-Methyl 4-((but-3-en-1-ylsulfinyl)ethynyl)benzoate (9l)



9l was prepared according to **GP3** using **S2l** (246 mg, 1.00 mmol), *m*CPBA (173 mg, 1.00 mmol) and CH_2Cl_2 (10 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (17:3 hexane:EtOAc) provided **9l** (206 mg, 77%) as a pale orange oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 5.89 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.22 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.16 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.93 (s, 3H), 3.30 – 3.19 (m, 2H), 2.83 – 2.59 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C), 134.4 (CH), 132.3 (2CH), 131.8 (C), 129.8 (2CH), 124.2 (C), 117.8 (CH_2), 101.3 (C), 87.6 (C), 55.3 (CH_2), 52.6 (CH_3), 26.7 (CH_2); IR (neat): ν = 2952, 2166, 1436, 1275, 1107, 1060, 769; HR-MS (ES-TOF): *m/z*: calcd for $C_{14}H_{14}O_3NaS$: 285.0561, found 285.0567 $[M + Na]^+$.

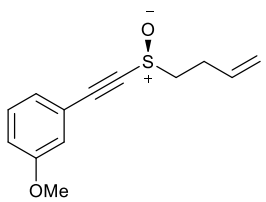
(±)-1-((But-3-en-1-ylsulfinyl)ethynyl)-4-fluorobenzene (9m)



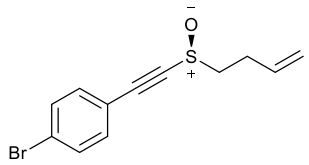
9m was prepared in 2 steps from 1-(2,2-dibromovinyl)-4-fluorobenzene. Sulfide **S2m** was prepared according to **GP1** using 1-(2,2-dibromovinyl)-4-fluorobenzene (840 mg, 3.0 mmol), *n*-BuLi (2.7 mL, 6.2 mmol), THF (15 mL) and **S1** (616 mg, 2.7 mmol). The reaction time was 16 hours. Purification by column chromatography (hexane) afforded **S2m** (90% pure) 65%. **9m** was prepared according to **GP3** using **S2m** (97 mg, 0.47 mmol), *m*CPBA (81 mg, 0.47 mmol) and CH_2Cl_2 (5 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (9:1 hexane:EtOAc) provided **9m** (76 mg, 73%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 – 7.46 (m, 2H), 7.17 – 7.00 (m, 2H), 5.89 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.21 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.15 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.31 – 3.13 (m, 2H), 2.82 – 2.59 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.0 (d, *J* = 253.6 Hz, C), 134.6 (d, *J* = 8.8 Hz, 2CH), 134.4 (CH), 117.7 (CH_2), 116.3 (d, *J* = 22.4 Hz, 2CH), 116.0 (d, *J* = 2.8 Hz, C) 101.6 (C), 85.0 (C), 55.3 (CH_2), 26.7 (CH_2); IR (neat): ν = 3077, 2981, 2919, 2165, 1641, 1598, 1505, 1233, 1216, 1157, 1054, 918, 837, 775; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{12}OSF$: 223.0593, found 223.0601 $[M + H]^+$.

(±)-1-((But-3-en-1-ylsulfinyl)ethynyl)-3-methoxybenzene (9n)

9n was prepared according to **GP3** using **S2n** (218 mg, 1.00 mmol), *m*CPBA (173 mg, 1.00 mmol) and CH_2Cl_2 (10 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (8:2 hexane:EtOAc) afforded **9n** (170 mg 72%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 – 7.25 (m, 1H), 7.16 – 7.09 (m, 1H), 7.08 – 6.96 (m, 2H), 5.89 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.26 – 5.11 (m, 2H), 3.81 (s, 3H), 3.23 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 2H), 2.85 – 2.58 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.5 (C), 134.5 (CH), 129.9 (CH), 124.8 (CH), 120.7 (C), 117.7 (CH_2), 117.3 (CH), 117.0 (CH), 102.6 (C), 84.8 (C), 55.5 (CH_3), 55.3 (CH_2), 26.7 (CH_2); IR (neat): *v* = 3076, 2939, 2837, 2159, 1641, 1594, 1574, 1487, 1287, 1156, 1042, 683; HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{15}O_2S$: 235.0793, found 235.0796 $[M + H]^+$.

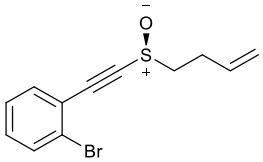


(±)-1-Bromo-4-((but-3-en-1-ylsulfinyl)ethynyl)benzene (9o)



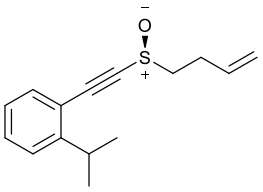
9o was prepared according to **GP3** using **S2o** (180 mg, 0.67 mmol), *m*CPBA (117 mg, 0.67 mmol) and CH_2Cl_2 (7 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (9:1 hexane:EtOAc) provided **9o** (153 mg, 80%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 5.89 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.21 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.15 (dd, *J* = 10.2, 1.4 Hz, 1H), 3.34 – 3.12 (m, 2H), 2.85 – 2.55 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.4 (CH), 133.7 (2CH), 132.2 (2CH), 125.6 (C), 118.7 (C), 117.8 (CH_2), 101.5 (C), 86.2 (C), 55.3 (CH_2), 26.7 (CH_2); IR (neat): *v* = 3080, 2978, 2914, 2163, 1640, 1583, 1483, 1394, 1056, 762; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{11}ONaS^{79}Br$: 304.9612, found 304.9620 $[M + Na]^+$

(±)-1-Bromo-2-((but-3-en-1-ylsulfinyl)ethynyl)benzene (9p)



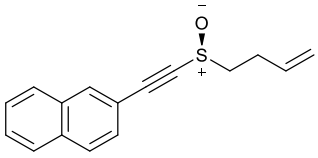
9p was prepared according to **GP3** using **S2p** (175 mg, 0.65 mmol), *m*CPBA (114 mg, 0.65 mmol) and CH_2Cl_2 (7 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (9:1 hexane:EtOAc) provided **9p** (157 mg, 85%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 – 7.54 (m, 2H), 7.40 – 7.26 (m, 2H), 5.90 (ddt, *J* = 17.0, 10.1, 6.6 Hz, 1H), 5.22 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.15 (dd, *J* = 10.1, 1.5 Hz, 1H), 3.35 – 3.20 (m, 2H), 2.87 – 2.63 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.5 (CH), 134.4 (CH), 132.9 (CH), 131.8 (CH), 127.5 (CH), 126.1 (C), 122.3 (C), 117.7 (CH_2), 100.0 (C), 89.2 (C), 55.4 (CH_2), 26.7 (CH_2); IR (neat): *v* = 3077, 2979, 2917, 2167, 1675, 1640, 1584, 1057, 1045, 754; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{12}OS^{79}Br$: 282.9808, found 282.9792 $[M + H]^+$.

(±)-1-((But-3-en-1-ylsulfinyl)ethynyl)-2-isopropylbenzene (9q)



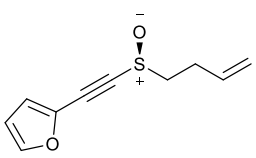
9q was prepared according to **GP3** using **S2q** (230 mg, 1.00 mmol), *m*CPBA (173 mg, 1.00 mmol) and CH_2Cl_2 (10 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (17:3 hexane:EtOAc) provided **9q** (218 mg, 89%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.41 (td, *J* = 7.7, 1.4 Hz, 1H), 7.32 (d, *J* = 6.7 Hz, 1H), 7.19 (td, *J* = 7.7, 1.4 Hz, 1H), 5.90 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.21 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.15 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.39 (dt, *J* = 13.8, 6.9 Hz, 1H), 3.24 (t, *J* = 7.7 Hz, 2H), 2.87 – 2.58 (m, 2H), 1.27 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.0 (C), 134.6 (CH), 133.4 (CH), 131.2 (CH), 126.0 (CH), 125.5 (CH), 118.6 (C), 117.6 (CH_2), 101.7 (C), 88.4 (C), 55.4 (CH_2), 32.0 (CH), 26.8 (CH_2), 23.3 (CH_3), 23.3 (CH_3); IR (neat): *v* = 3067, 2963, 2870, 2157, 1641, 1482, 1444, 1056, 758; HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{19}OS$: 247.1157, found 247.1155 $[M + H]^+$.

(±)-2-((But-3-en-1-ylsulfinyl)ethynyl)naphthalene (9r)



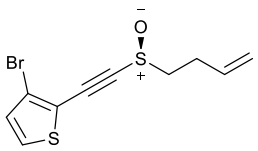
9r was prepared according to **GP3** using sulfide **S2r** (90 mg, 0.38 mmol), *m*CPBA (65 mg, 0.38 mmol) and CH_2Cl_2 (4 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (9:1 hexane:EtOAc) provided **9r** as a colourless oil (73 mg, 79%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 0.9 Hz, 1H), 7.85 (dd, *J* = 7.2, 3.7 Hz, 3H), 7.56 (app tdd, *J* = 8.7, 6.9, 1.8 Hz, 3H), 5.92 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.24 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.17 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.35 – 3.20 (m, 2H), 2.89 – 2.62 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.6 (CH), 133.9 (C), 133.5 (CH), 132.7 (C), 128.6 (CH), 128.3 (CH), 128.1 (CH), 128.1 (CH), 127.8 (CH), 127.2 (CH), 117.7 (CH_2), 117.0 (C), 103.2 (C), 85.3 (C), 55.4 (CH_2), 26.8 (CH_2); IR (neat): ν = 3057, 2924, 2154, 1720, 1641, 1277, 1056, 916, 818, 749; HR-MS (ES-TOF): *m/z*: calcd for $C_{16}H_{15}OS$: 255.0844, found 255.0841 $[M + H]^+$.

(±)-2-((But-3-en-1-ylsulfinyl)ethynyl)furan (9s)



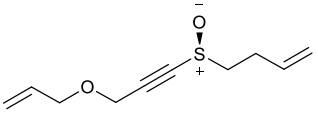
9s was prepared according to **GP3** from **S2s** (54.3 mg, 0.30 mmol), *m*CPBA (52.0 mg, 0.30 mmol) and CH_2Cl_2 (3 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided **9s** (41.4 mg, 70%) as a colourless oil. The product was seen to degrade when neat and so was used directly in the catalysis reaction on its preparation.

(±)-3-Bromo-2-((but-3-en-1-ylsulfinyl)ethynyl)thiophene (9t)



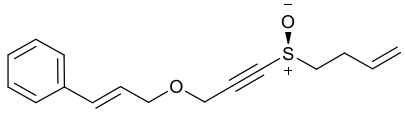
9t was prepared according to **GP3** from **S2t** (82.0 mg, 0.30 mmol), *m*CPBA (52.0 mg, 0.30 mmol) and CH_2Cl_2 (3 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided **9t** (60.7 mg, 70%) as a colourless oil. The product was seen to degrade when neat and so was used directly in the catalysis reaction on its preparation.

(±)-4-((3-(Allyloxy)prop-1-yn-1-yl)sulfinyl)but-1-ene (9u)



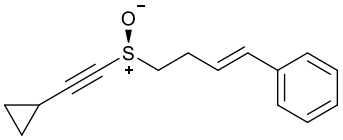
9u was prepared according to **GP3** using **S2u** (249 mg, 1.36 mmol), *m*CPBA (233 mg, 1.36 mmol) and CH_2Cl_2 (13 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided **9u** (217 mg, 80%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.95 – 5.76 (m, 2H), 5.36 – 5.08 (m, 4H), 4.34 (s, 2H), 4.06 (dt, *J* = 5.8, 1.3 Hz, 2H), 3.14 (dd, *J* = 11.6, 4.1 Hz, 2H), 2.76 – 2.51 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.3 (CH), 133.3 (CH), 118.7 (CH_2), 117.7 (CH_2), 99.7 (C), 82.9 (C), 71.3 (CH_2), 57.3 (CH_2), 55.1 (CH_2), 26.5 (CH_2); IR (neat): ν = 3081, 2850, 2181, 1641, 1435, 1351, 1058, 990, 919; HR-MS (ES-TOF): *m/z*: calcd for $C_{10}H_{15}O_2S$: 199.0793, found 199.0799 $[M + H]^+$.

(±)-(*E*)-(3-((3-(But-3-en-1-ylsulfinyl)prop-2-yn-1-yl)oxy)prop-1-en-1-yl)benzene (9v)



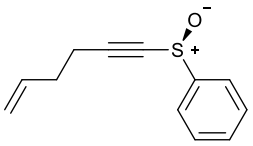
9v was prepared according to **GP3** using **S2v** (500 mg, 1.93 mmol), *m*CPBA (333 mg, 1.93 mmol) and CH_2Cl_2 (19 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided **9v** (353 mg, 66%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 – 7.21 (m, 5H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.25 (dt, *J* = 15.9, 6.3 Hz, 1H), 5.85 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.25 – 5.09 (m, 2H), 4.41 (s, 2H), 4.25 (dd, *J* = 6.3, 1.3 Hz, 2H), 3.28 – 3.06 (m, 2H), 2.79 – 2.52 (m, 2H); This compound proved unstable and prevented collection of useful ^{13}C NMR data. IR (neat): ν = 2850, 2180, 1641, 1599, 1495, 1448, 1352, 1057, 990, 968, 918, 744, 692; HR-MS (ES-TOF): *m/z*: calcd for $C_{16}H_{19}O_2S$: 275.1106, found 275.1113 $[M + H]^+$.

(*E*)-(4-((Cyclopropylethynyl)sulfinyl)but-1-en-1-yl)benzene (14)



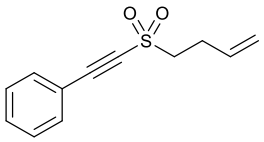
14 was prepared according to **GP3** using **S5** (280 mg, 1.23 mmol), *m*CPBA (212 mg, 1.23 mmol) and CH_2Cl_2 (12 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided **14** (208 mg, 69%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 – 7.18 (m, 5H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.89 – 2.66 (m, 2H), 1.51 – 1.41 (m, 1H), 1.03 – 0.85 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.0 (C), 132.7 (CH), 128.7 (2CH), 127.6 (CH), 126.2 (2CH), 126.1 (CH), 109.8 (C), 72.0 (C), 55.8 (CH_2), 26.0 (CH_2), 9.7 (CH), 0.3 ($2CH_2$); IR (neat): *v* = 3025, 2179, 1598, 1493, 1444, 1059, 967, 829, 745, 694; HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{17}OS$: 245.1000, found 245.1004 $[M + H]^+$.

(±)-(Hex-5-en-1-yn-1-ylsulfinyl)benzene (17)



17 was prepared according to an adapted literature procedure.[26] Mg turnings (1.73 g, 72.0 mmol, 2.3 eq.) and a pellet of iodine were added to a two-neck RBF fitted with a condenser and the mixture was purged with argon. Et_2O (30 mL) was added followed by slow addition of allyl bromide (6.14 mL, 72.0 mmol, 2.3 eq.). The solution was stirred for 2 hours at rt. The reaction mixture was cooled to -10 °C, propargyl chloride (3.45 mL, 30 mmol, 1.0 eq.) was added slowly and the solution was stirred for 5 hours allowing to warm to rt. After cooling to 0 °C, methyl benzenesulfinate (9.37 g, 60 mmol, 2.0 eq.) was added dropwise and the solution was stirred at rt for 16 hours. The reaction was quenched by the addition of sat. NH_4Cl solution (30 mL) at 0 °C and the aqueous layer was extracted with Et_2O (5 × 20 mL), washed with brine (20 mL) and the organic layers were dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by column chromatography (9:1 hexane:EtOAc) affording **17** as a yellow oil (1.23 g, 26%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 – 7.75 (m, 2H), 7.59 – 7.50 (m, 3H), 5.79 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H,), 5.06 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.06 (dd, *J* = 10.2, 1.4 Hz, 1H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.31 (dt, *J* = 7.2, 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.4 (C), 135.7 (CH), 131.7 (CH), 129.6 (2CH), 125.1 (2CH), 116.8 (CH_2), 106.2 (C), 78.2 (C), 31.7 (CH_2), 19.7 (CH_2); IR (neat): ν = 3078, 2981, 2913, 2180, 1643, 1581, 1476, 1444, 1188, 1086, 1052, 985, 917, 885, 788, 749, 687; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{12}ONaS$: 227.0507, found 227.0502 [M + Na]$^+$.

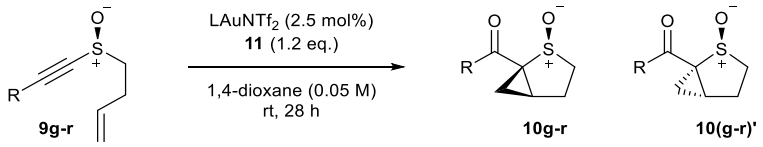
((But-3-en-1-ylsulfonyl)ethynyl)benzene



A RBF under argon was charged with **2b** (130 mg, 0.69 mmol), and CH_2Cl_2 (10 mL). The mixture was cooled to 0 °C and *m*CPBA (238 mg, 1.38 mmol, 2.0 eq.) was added in 5 portions over 10 mins. The mixture was stirred for 3 hours allowing to warm to rt. The mixture was cooled to 0 °C and *m*CPBA (59 mg, 0.35 mmol, 0.5 eq.) was added in one portion. The reaction was stirred for a further hour. The mixture was washed with $NaHCO_3$ (3 × 10 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by column chromatography (9:1 hexane:EtOAc) providing **4b** (129 mg, 85%) as a viscous colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 – 7.60 (m, 2H), 7.59 – 7.51 (m, 1H), 7.50 – 7.40 (m, 2H), 5.89 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.30 – 5.14 (m, 2H), 3.44 – 3.34 (m, 2H), 2.83 – 2.70 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 133.4 (CH), 133.0 (2CH), 131.9 (CH), 129.0 (2CH), 117.8 (CH_2), 117.7 (C), 92.8 (C), 83.3 (C), 57.5 (CH_2), 27.3 (CH_2); IR (neat): ν = 3082, 2922, 2181, 1643, 1490, 1444, 1319, 1232, 1136, 847, 756, 687; HR-MS (AP-TOF): *m/z*: calcd for $C_{12}H_{13}O_2S$: 221.0636, found 221.0630 [M + H]$^+$.

Catalysis Reactions

Table of catalysis results at room temperature



Entry	R	**9**	% Yield of **10**
1	Ph	**g**	73
2	4-MeC_6H_4	**h**	75
3	4-MeOC_6H_4	**i**	74[b]
4	4-AcNHC_6H_4	**j**	79[c]
5	4-$F_3C$$C_6H_4$	**k**	30
6	4-$MeO_2C$$C_6H_4$	**l**	54
7	4-FC_6H_4	**m**	54
8	3-MeOC_6H_4	**n**	54
9	4-BrC_6H_4	**o**	54
10	2-BrC_6H_4	**p**	50
11	2-*i*PrC_6H_4	**q**	50
12	2-Napthyl	**r**	65[a]

Reactions were run on a 0.3 mmol scale. [a] 0.2 mmol scale. [b] 19 h. [c] 20 h.

Structural assignment of major and minor diastereomers 10a-t.

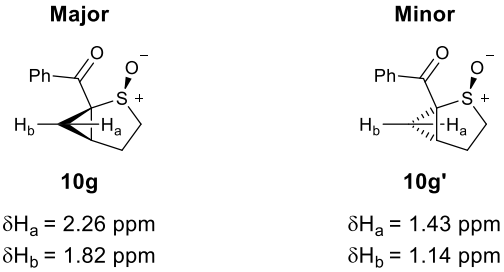


Fig S1. ^{1}H NMR chemical shifts in catalysis product **10g** and **10g'**

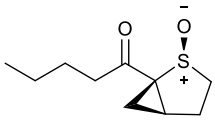
The structure of the major diastereomer **10g** was determined by X-ray crystallography. The structures of major diastereomers **10a-f** and **10h-t** were assigned by analogous key characteristic chemical shifts in the ^{1}H NMR spectra, which remain consistent across the series **10a-t**. In every case, for the major diastereomer a distinctive proton α to the sulfoxide resonates between 3.52 and 3.58 ppm, 0.4 ppm downfield of the same proton in the ^{1}H NMR spectrum of the minor diastereomer. The methylene cyclopropyl hydrogens in the major diastereomer are are shifted downfield compared to the analogous protons in the minor diastereomer, presumably due to the anisotropic effect exerted by the promimal sulfinyl group (Fig S1).[22] Data is reported for the major diastereomer the structures of which are shown in the inserts.

Cyclopropanation products

General procedure 4 (GP4) Gold catalysed reactions of alkynyl sulfoxides

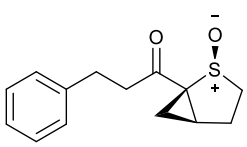
A Radleys tube under argon was charged with 3,5-dichloropyridine-*N*-oxide (1.2 eq.) and alkynyl sulfoxide (1.0 eq.) in 1,4-dioxane (¼ of the total solvent volume). $SPhosAuNTf_2$ (2.5 to 5 mol%) was added followed by 1,4-dioxane (¾ of the total solvent volume, the final concentration is 0.05 M) and the tube was heated at the specified temperature and with stirring until completion or no further reaction was observed by TLC analysis. The mixture was filtered through a pad of silica, washing with EtOAc, concentrated and purified by column chromatography.

(±)-1-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)pentan-1-one (10a)



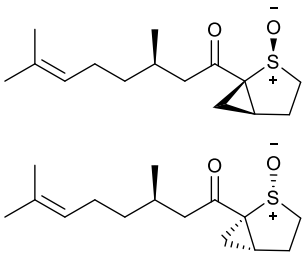
10a was prepared according to **GP4** using **9a** (36.8 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), $SPhosAuNTf_2$ (8.8 mg, 5 mol%) and 1,4 dioxane (4 mL). The reaction time was 17 hours. Purification by column chromatography (EtOAc to 95:5 EtOAc:MeOH) afforded **10a** (29.4 mg, 72%) a pale yellow oil as a 6:1 mixture of diastereomers; ^{1}H NMR (300 MHz $CDCl_3$): δ 3.57 – 3.47 (m, 1H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.54 – 2.45 (m, 1H), 2.44 – 2.36 (m, 1H,), 2.33 – 2.25 (m, 2H), 2.04 (app t, *J* = 5.7 Hz, 1H), 1.83 (dd, *J* = 8.4, 5.7 Hz, 1H), 1.59 (tt, *J* = 7.5, 7.4 Hz, 2H), 1.31 (app q, *J* = 7.5 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz $CDCl_3$): δ 203.7 (C,), 58.6 (C), 50.7 (CH_2), 40.7 (CH_2), 35.2 (CH), 25.5 (CH_2), 25.3 (CH_2), 22.1 (CH_2), 17.7 (CH_2), 13.8 (CH_3). IR (neat): *v* = 2957, 2933, 2871, 1687, 1450, 1375, 1260, 1055, 1031, 992, 875. HR-MS (ES-TOF): *m/z* calcd. for $C_{10}H_{17}O_2S$ 201.0949, found 201.0950 $[M + Na]^+$.

(±)-1-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)-3-phenylpropan-1-one (10b)



10b was prepared according to **GP4** using **9b** (23.2 mg, 0.10 mmol), 3,5-dichloropyridine-*N*-oxide (19.7 mg, 0.12 mmol), $SPhosAuNTf_2$ (4.4 mg, 5 mol%) and 1,4-dioxane (2 mL). The reaction time was 3.5 hours. Purification by column chromatography (EtOAc to 95:5 EtOAc:MeOH) afforded **10b** (15.7 mg, 63%) as a pale yellow oil as a 6:1 mixture of diastereomers; ^{1}H NMR (300 MHz $CDCl_3$): δ = 3.50 (ddd, *J* = 13.2, 6.9, 2.9 Hz, 1H), 3.20 – 3.17 (m, 2H), 2.97 (t, *J* = 7.4 Hz, 2H), 2.55 – 2.45 (m, 1H), 2.45 – 2.35 (m, 1H), 2.31 – 2.24 (m, 2H), 2.07 (app t, *J* = 5.9 Hz, 1H), 1.86 (dd, *J* = 8.4, 5.9 Hz, 1H); ^{13}C NMR (101 MHz $CDCl_3$): δ = 202.9 (C), 140.4 (C), 128.6 (2CH), 128.5 (2CH), 126.3 (CH), 58.9 (C), 50.9 (CH_2), 42.9 (CH_2), 35.6 (CH), 29.7 (CH_2), 25.4 (CH_2), 18.1 (CH_2); IR (neat): *v* = 3410, 3028, 2931, 1689, 1584, 1536, 1400, 1372, 1251, 1107, 1058, 967, 842, 730, 699, 615; HR-MS (ES-TOF): *m/z* calcd. for $C_{14}H_{17}O_2S$ 249.0949, found 249.0952 $[M + Na]^+$.

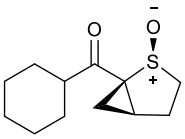
(3S)-3,7-Dimethyl-1-(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)oct-6-en-1-one (10c)



10c was prepared according to **GP4** using **9c** (50.4 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), $SPhosAuNTf_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 21 hours. Purification by column chromatography (1:1 hexane:EtOAc to EtOAc) afforded **10c** (37.8 mg, 70%) as a colourless oil (d.r. ratio 10:10:1:1, assignment of the two major diastereomers is observed in the ^{13}C NMR); ^{1}H NMR (300 MHz,

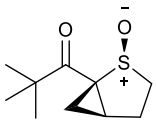
$CDCl_3$): δ = 5.08 (dtd, *J* = 7.0, 2.7, 1.3 Hz, 1H), 3.58 – 3.45 (m, 1H), 2.93 – 2.62 (m, 2H), 2.59 – 2.38 (m, 2H), 2.37 – 2.25 (m, 2H), 2.19-2.05 (m, 1H), 2.10 – 2.04 (m, 1H), 1.97 (td, *J* = 14.0, 7.1 Hz, 2H), 1.85 (dd, *J* = 7.9, 5.8 Hz, 1H), 1.67 (s, 3H), 1.59 (s, 4H), 1.43 – 1.15 (m, 3H), 0.93 (dd, *J* = 6.6, 2.0 Hz, 3H); Major diastereomer 1;^{13}C NMR (101 MHz, $CDCl_3$): 203.5 (C), 131.7 (C), 124.3 (CH), 59.3 (C), 51.3 (CH_2), 50.1 (CH_2), 48.6 (CH_2), 37.0 (CH_2), 35.5 (CH), 28.8 (CH), 25.8 (CH_3), 25.6 (CH_2), 19.9 (CH_3), 18.1 (CH_2), 17.8 (CH_3); Major diastereomer 2 δ = 203.5 (C), 131.7 (C), 124.3 (CH), 59.2 (C), 51.1 (CH_2), 50.1 (CH_2), 48.6 (CH_2), 36.9 (CH_2), 35.4 (CH), 28.8 (CH), 25.8 (CH_3), 25.6 (CH_2), 19.8 (CH_3), 18.0 (CH_2), 17.8 (CH_3); IR (neat): *v* = 3458, 2961, 2924, 1688, 1446, 1375, 1287, 1241, 1100, 1057, 1031, 989; HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{24}O_2NaS$: 291.1395, found 291.1393 $[M + Na]^+$.

(±)-Cyclohexyl(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10d)



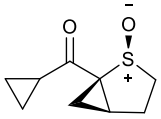
10d was prepared according to **GP4** using **9d** (42.7 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), $SPhosAuNTf_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 24 hours. Purification by column chromatography (1:1 hexane:EtOAc to EtOAc) afforded **10d** (20.6 mg, 45%) as a white solid as a 7:1 mixture of diastereomers; mp: 86-87 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.60 – 3.48 (ddd, *J* = 10.2, 6.2, 4.8, 1H), 3.17 – 3.01 (m, 1H), 2.59 – 2.47 (m, 1H), 2.45 – 2.36 (m, 1H), 2.34 – 2.27 (m, 2H), 2.08 – 2.02 (m, 1H), 2.02 – 1.95 (m, 1H), 1.85 (dd, *J* = 8.5, 5.6 Hz, 1H), 1.80 (dd, *J* = 9.1, 3.2 Hz, 2H), 1.75 – 1.63 (m, 2H), 1.56 – 1.11 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 207.1 (C), 58.3 (C), 51.8 (CH_2), 48.7 (CH), 36.2 (CH), 28.8 (CH_2), 28.5 (CH_2), 25.8 (CH_2), 25.7 (CH_2), 25.5 ($2CH_2$), 18.0 (CH_2); IR (neat): *v* = 2980, 2925, 2853, 1667, 1442, 1382, 1332, 1267, 1259, 1057, 1041, 980, 874; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{18}O_2NaS$: 249.0925, found 249.0920 $[M + Na]^+$.

(±)-2,2-Dimethyl-1-((1S,2R)-2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)propan-1-one (10e)



10e was prepared according to **GP4** using **9e** (36.9 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), $SPhosAuNTf_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 25 hours. ^{1}H NMR analysis using 1,2,4,5 tetramethyl benzene as internal standard showed a d.r. of 12:1. Purification by column chromatography (EtOAc) afforded **10e** (28.0 mg, 70%) as a colourless oil as a 12:1 mixture of diastereomers; ^{1}H NMR (300 MHz $CDCl_3$): δ = 3.51 (ddd, *J* = 13.2, 6.8, 4.9 Hz, 1H), 2.65 (ddd, *J* = 13.2, 6.8, 4.9 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.38 – 2.29 (m, 2H), 2.03 (app t, *J* = 5.7 Hz, 1H), 1.78 (dd, *J* = 8.6, 5.7 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (101 MHz $CDCl_3$): δ = 207.0 (C), 58.3 (C), 53.7 (CH_2), 45.4 (C), 36.6 (CH), 26.7 ($3CH_3$), 25.9 (CH_2), 18.5 (CH_2); IR (neat): *v* = 3470, 2971, 2871, 1678, 1478, 1367, 1225, 1169, 1091, 1057, 994. HR-MS (ES-TOF): *m/z* calcd. for $C_{10}H_{16}O_2S$ 200.0871, found 200.0879 $[M + H]^+$.

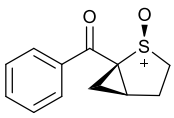
(±)-Cyclopropyl(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10f)



10f was prepared according to **GP4** using **9f** (17.0 mg, 0.10 mmol), 3,5-dichloropyridine-*N*-oxide (19.7 mg, 0.12 mmol), $SPhosAuNTf_2$ (4.4 mg, 5 mol%) and 1,4 dioxane (2 mL). The reaction time was 17 hours. Purification by column chromatography (EtOAc to 95:5 EtOAc:MeOH) afforded **10f** (15.8 mg, 86%) a pale yellow oil as a 10:1 mixture of diastereomers; ^{1}H NMR (300 MHz $CDCl_3$): δ =3.55 (app dt, *J* = 13.5, 4.8 Hz, 1H), 2.56 – 2.50 (m, 1H), 2.50 – 2.46 (m, 1H), 2.43 – 2.38 (m, 1H,), 2.38 – 2.29 (m, 2H), 2.12 (app t, *J* = 6.1 Hz, 1H), 1.88 (dd, J = 8.6, 6.1 Hz, 1H), 1.22 – 1.13 (m, 2H), 1.09 – 0.99

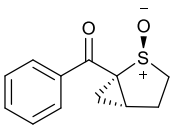
(m, 2H); ^{13}C NMR (101 MHz $CDCl_3$): δ = 203.8 (C), 59.3 (C), 50.6 (CH_2), 34.5 (CH), 25.5 (CH_2), 18.7 (CH), 17.8 (CH_2), 12.8 ($2CH_2$); IR (neat): *v* = 3412, 2934, 1167, 1445, 1394, 1250, 1057, 1022, 988, 872, 885, 677; HR-MS (ES-TOF): *m/z* calcd. for $C_9H_{12}O_2SNa$ 207.0456, found 207.0461 $[M + Na]^+$.

(±)-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)(phenyl)methanone (10g)



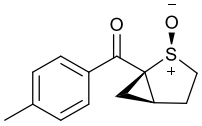
10g was prepared according to **GP4** using **9g** (61.2 mg, 0.30 mmol), 3,5-dichloropyridine-*N*-oxide (59.1 mg, 0.36 mmol), $SPhosAuNTf_2$ (13.2 mg, 5 mol%) and 1,4-dioxane (6 mL). The reaction time was 45 min. ^{1}H NMR analysis showed a d.r. ratio of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded **10g** (52.8 mg, 80%) as an off-white solid as a single diastereomer. When run on the same scale with $SPhosAuNTf_2$ (6.6 mg, 2.5 mol%), **10g** was obtained as a single diastereomer (48.2 mg, 73%) as an off white solid after 28 hours; mp: 77-78 °C (Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 – 7.92 (m, 2H), 7.65 – 7.56 (m, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 3.53 (ddd, *J* = 12.9, 7.7, 4.3 Hz, 1H), 2.79 – 2.64 (m, 2H), 2.56 – 2.34 (m, 2H), 2.26 (t, *J* = 5.9 Hz, 1H), 1.82 (dd, *J* = 8.7, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.5 (C), 136.9 (C), 133.5 (CH), 129.5 (2CH), 128.8 (2CH), 59.7 (C), 54.4 (CH_2), 34.0 (CH), 26.5 (CH_2), 19.5 (CH_2); IR (neat): ν = 3078, 3006, 2989, 2934, 2860, 1661, 1600, 1449, 1442, 1060, 754, 692, 662; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{12}O_2NaS$: 243.0456, found 243.0458 $[M + Na]^+$.

(±)-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)(phenyl)methanone (10g')



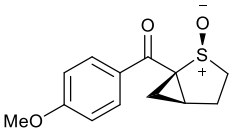
The minor diastereomer **10g'** was isolated from a separate reaction run; mp: 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 – 8.02 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 3.12 (dd, *J* = 14.4, 7.1 Hz, 1H), 3.02 – 2.85 (m, 2H), 2.67 (ddd, *J* = 14.4, 12.4, 7.1 Hz, 1H), 2.40 (dd, *J* = 13.2, 7.0 Hz, 1H), 1.43 (dd, *J* = 8.2, 6.6 Hz, 1H), 1.14 (app t, *J* = 6.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.0 (C), 137.3 (C), 133.6 (CH), 129.0 (2CH), 128.8 (2CH), 58.7 (C), 50.4 (CH_2), 27.5 (CH), 25.5 (CH_2), 18.4 (CH_2); IR (neat): ν = 3082, 3009, 2990, 2934, 2865, 1667, 1597, 1286, 1022, 989, 775; HR-MS (EI-TOF): *m/z*: calcd for $C_{12}H_{12}O_2S$: 220.0558 found 220.0556 $[M + H]^+$.

(±)-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)(p-tolyl)methanone (10h)



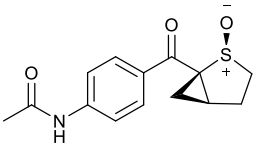
10h was prepared according to **GP4** using **9h** (65.4 mg, 0.30 mmol), 3,5-dichloropyridine-*N*-oxide (59.1 mg, 0.36 mmol), $SPhosAuNTf_2$ (6.6 mg, 2.5 mol%) and 1,4-dioxane (6 mL). The reaction time was 28 hours. ^{1}H NMR analysis using 1,2,4,5-tetramethylbenzene as internal standard showed a d.r. of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded **10h** (53.0 mg, 75%) as a colourless oil as a single diastereomer after 28 hours; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 3.49 (ddd, *J* = 13.1, 7.7, 4.3 Hz, 1H), 2.73 – 2.62 (m, 2H), 2.52 – 2.29 (m, 2H), 2.39 (s, 3H), 2.24 – 2.17 (t, *J* = 5.9 Hz, 1H), 1.75 (dd, *J* = 8.7, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.8 (C), 144.4 (C), 134.2 (C), 129.6 (2CH), 129.4 (2CH), 59.4 (C), 54.5 (CH_2), 33.3 (CH), 26.4 (CH_2), 21.8 (CH_3), 19.1 (CH_2); IR (neat): ν = 3463, 2926, 1760, 1660, 1605, 1571, 1281, 1180, 1055, 1029, 734; HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{14}O_2NaS$: 257.0612, found 257.0605 $[M + Na]^+$.

(±)-(4-Methoxyphenyl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10i)



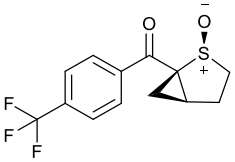
10i was prepared according to **GP4** using **9i** (70.2 mg, 0.30 mmol), 3,5-dichloropyridine-*N*-oxide (59.1 mg, 0.36 mmol), SPhosAuNTf$_2$ (13.2 mg, 5 mol%) and 1,4-dioxane (6 mL). The reaction time was 1 hour. ^{1}H NMR analysis showed a d.r. ratio of 8:1. Purification by column chromatography (1:1 hexane:EtOAc to EtOAc) afforded **10i** (58.5 mg, 78%) as a colourless oil as a single diastereomer. When run on the same scale with SPhosAuNTf$_2$ (6.6 mg, 2.5 mol%), **10i** was obtained as a single diastereomer (53.0 mg, 72%) after 19 hours. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 – 7.99 (m, 2H), 7.04 – 6.95 (m, 2H), 3.53 (ddd, *J* = 13.1, 7.8, 4.3 Hz, 1H), 2.77 – 2.64 (m, 2H), 2.55 – 2.31 (m, 2H), 2.22 (t, *J* = 5.9 Hz, 1H), 1.71 (dd, *J* = 8.7, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.2 (C), 164.1 (C), 132.3 (2CH), 129.6 (C), 114.1 (2CH), 59.1 (C), 55.7 (CH_3) 54.7 (CH_2), 32.4 (CH) 26.4 (CH_2), 18.8 (CH_2); IR (neat): ν = 3452, 2934, 1731, 1655, 1597, 1573, 1510, 1285, 1258, 1170, 1024, 841; HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{14}O_3NaS$: 273.0561, found 273.0570 $[M + Na]^+$.

(±)-N-(4-(2-Oxido-2-thiabicyclo[3.1.0]hexane-1-carbonyl)phenyl)acetamide (10j)



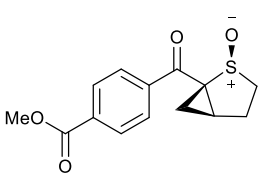
10j was prepared according to **GP4** using **9j** (78.3 mg, 0.30 mmol), 3,5-dichloropyridine-*N*-oxide (59.1 mg, 0.36 mmol), SPhosAuNTf$_2$ (6.6 mg, 2.5 mol%) and 1,4-dioxane (6 mL). The reaction time was 20 hours. ^{1}H NMR analysis showed a d.r. of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded **10j** (66.0 mg, 79%) as a white solid as a single diastereomer. When run on 0.2 mmol scale with SPhosAuNTf$_2$ (8.8 mg, 5 mol%), **10j** (44.0 mg, 79%) was obtained as a single diastereomer after 4 hours. mp: 170-172 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48 (s, 1H), 7.99 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 3.58 (ddd, *J* = 12.9, 7.8, 4.0 Hz, 1H), 2.81 – 2.64 (m, 2H), 2.59 – 2.34 (m, 2H), 2.22 (t, *J* = 6.0 Hz, 1H), 2.18 (s, 3H), 1.77 (dd, *J* = 8.6, 6.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.3 (C), 169.1 (C), 143.6 (C), 131.8 (C), 131.1 (2CH), 119.0 (2CH), 59.1 (C), 54.4 (CH_2), 33.0 (CH_3), 26.4 (CH_2), 24.8 (CH), 18.9 (CH_2); IR (neat): ν = 3086, 3039, 2958, 1678, 1662, 1597, 1579, 1286, 1117, 885; HR-MS (ES-TOF): *m/z*: calcd for $C_{14}H_{15}NO_3NaS$: 300.0670, found 300.0658 $[M + Na]^+$.

(±)-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)(4-(trifluoromethyl)phenyl)methanone (10k)



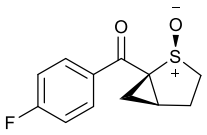
10k was prepared according to **GP4** using **9k** (54.4 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf$_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 17 hours. ^{1}H NMR analysis showed a d.r. of 8:1; Purification by column chromatography (1:1 hexane:EtOAc to EtOAc) afforded **10k** (35.6 mg, 63%) as a colourless oil, as a single diastereomer. When run on 0.3 mmol scale with SPhosAuNTf$_2$ (6.6 mg, 2.5 mol%), **10j** (26.0 mg, 30%) was obtained as a single diastereomer after 28 hours. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 3.57 (ddd, *J* = 13.2, 7.3, 4.2 Hz, 1H), 2.82 – 2.64 (m, 2H), 2.55 – 2.36 (m, 2H), 2.31 (t, *J* = 5.9 Hz, 1H), 1.85 (dd, *J* = 8.7, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.2 (C), 139.8 (C), 134.7 (q, *J* = 32.7 Hz, C), 129.8 (2CH), 125.8 (d, *J* = 3.2 Hz, 2CH), 123.4 (q, *J* = 272.4 Hz, C), 59.4 (C), 53.8 (CH_2), 34.4 (CH), 26.2 (CH_2), 19.8 (CH_2); IR (neat): *v* = 2937, 1673, 1409, 1323, 1279, 1167, 1112, 1063, 855; HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{11}O_2NaSF_3$: 311.0330, found 311.0327 $[M + Na]^+$.

(±)-Methyl 4-(2-oxido-2-thiabicyclo[3.1.0]hexane-1-carbonyl)benzoate (10l)



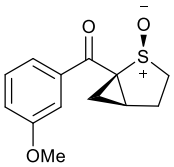
10l was prepared according to **GP4** using **9l** (52.5 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf$_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 20 hours. ^{1}H NMR analysis showed a d.r. of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded **10l** (35.6 mg, 64%) as an off white solid. When run on 0.3 mmol scale with SPhosAuNTf$_2$ (6.6 mg, 2.5 mol%), **10l** (38.5 mg, 54%) was obtained as a single diastereomer after 28 hours. mp: 63-64 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 – 8.12 (m, 2H), 8.04 – 7.98 (m, 2H), 3.94 (s, 3H), 3.55 (ddd, *J* = 13.2, 7.5, 4.2 Hz, 1H), 2.80 – 2.62 (m, 2H), 2.54 – 2.38 (m, 2H), 2.33 – 2.26 (t, *J* = 5.9 Hz, 1H), 1.86 (dd, *J* = 8.7, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.6 (C) 166.2 (C), 140.3 (C), 134.1 (C), 129.9 (2CH), 129.3 (2CH), 59.7 (C), 54.0 (CH_2), 52.6 (CH_3), 34.7 (CH), 26.3 (CH_2), 19.7 (CH_2); IR (neat): ν = 3493, 3094, 3022, 2960, 2936, 1716, 1665, 1436, 1273, 1031, 763; HR-MS (ES-TOF): *m/z*: calcd for $C_{14}H_{14}O_4NaS$: 301.0510, found 301.0500 $[M + Na]^+$.

(±)-(4-Fluorophenyl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10m)



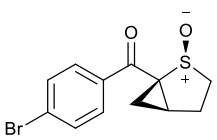
10m was prepared according to **GP4** using **9m** (66.6 mg, 0.30 mmol), 3,5-dichloropyridine-*N*-oxide (59.1 mg, 0.36 mmol), SPhosAuNTf$_2$ (13.2 mg, 5 mol%) and 1,4-dioxane (6 mL). The reaction time was 17 hours. ^{1}H NMR analysis showed a d.r. ratio of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded **10m** (53.6 mg, 68%) as a colourless viscous oil, as a single diastereomer. When run on 0.3 mmol scale with SPhosAuNTf$_2$ (6.6 mg, 2.5 mol%), **10m** (38.5 mg, 54%) was obtained as a single diastereomer after 28 hours. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 – 7.99 (m, 2H), 7.23 – 7.10 (m, 2H), 3.56 (ddd, *J* = 13.2, 7.6, 4.1 Hz, 1H), 2.78 – 2.64 (m, 2H), 2.54 – 2.33 (m, 2H), 2.25 (t, *J* = 5.9 Hz, 1H), 1.76 (dd, *J* = 8.7, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.8 (C), 166.1 (d, *J* = 255.8 Hz, C), 133.1 (C), 132.5 (d, *J* = 9.4 Hz, 2CH), 116.0 (d, *J* = 22.1 Hz, 2CH), 59.1 (C), 54.2 (CH_2), 33.2 (CH), 26.3 (CH_2), 19.2 (CH_2); IR (neat): ν = 3070, 2937, 1663, 1596, 1506, 1280, 1230, 1027, 844, 609; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{12}O_2FS$: 239.0542, found 239.0547 $[M + H]^+$.

(±)-3-Methoxyphenyl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10n)



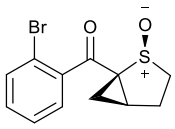
10n was prepared according to **GP4** using **9n** (46.9 mg, 0.20 mmol), 3,5 dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf$_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 18 hours. ^{1}H NMR analysis showed a d.r. ratio of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded **10n** (35.0 mg, 70%) as colourless oil as a single diastereomer. When run on 0.3 mmol scale with SPhosAuNTf$_2$ (6.6 mg, 2.5 mol%), **10n** (40.0 mg, 54%) was obtained as a single diastereomer after 28 hours. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 – 7.54 (m, 1H), 7.49 (dd, *J* = 2.4, 1.7 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.13 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.85 (s, 3H), 3.53 (ddd, *J* = 13.2, 7.6, 4.1 Hz, 1H), 2.76 – 2.61 (m, 2H), 2.52 – 2.32 (m, 2H), 2.25 (t, *J* = 5.9 Hz, 1H), 1.80 (dd, *J* = 8.7, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.4 (C), 159.8 (C), 138.1 (C), 129.8 (CH), 122.0 (CH), 120.4 (CH), 113.4 (CH), 59.5 (C), 55.6 (CH_3), 54.2 (CH_2), 34.0 (CH), 26.3 (CH_2), 19.4 (CH_2); IR (neat): *v* = 2939, 1722, 1663, 1596, 1580, 1279, 1030, 787; HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{14}O_3SNa$: 273.0561, found 273.0563 $[M + Na]^+$.

(±)-4-Bromophenyl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10o)



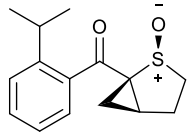
10o was prepared according to **GP4** using **9o** (56.6 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf$_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 3 hours. ^{1}H NMR analysis showed a d.r. of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded **10o** (42.0 mg, 74%) as a white solid as a single diastereomer. When run on 0.3 mmol scale with SPhosAuNTf$_2$ (6.6 mg, 2.5 mol%), **10o** (49.3 mg, 54%) was obtained as a single diastereomer after 28 hours. mp: 78-80 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 – 7.82 (m, 2H), 7.67 – 7.59 (m, 2H), 3.54 (ddd, *J* = 13.2, 7.5, 4.1 Hz, 1H), 2.78 – 2.61 (m, 2H), 2.53 – 2.32 (m, 2H), 2.25 (t, *J* = 6.0 Hz, 1H), 1.76 (dd, *J* = 8.7, 6.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.5 (C), 135.5 (C), 132.1 (2CH), 131.1 (2CH), 128.8 (C), 59.2 (C), 54.0 (CH_2), 33.6 (CH), 26.2 (CH_2), 19.3 (CH_2); IR (neat): ν = 3082, 3068, 2991, 1647, 1410, 1275, 1013, 874, 756; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{11}O_2SNa^{79}Br$: 320.9561, found 320.9550 $[M + Na]^+$.

(±)-(2-Bromophenyl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10p)



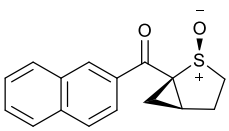
10p was prepared according to **GP4** using **9p** (85.0 mg, 0.30 mmol), 3,5-dichloropyridine-*N*-oxide (59.1 mg, 0.36 mmol), SPhosAuNTf$_2$ (6.6 mg, 2.5 mol%) and 1,4-dioxane (5 mL). The reaction time was 28 hours. ^{1}H NMR analysis using 1,2,4,5 tetramethyl benzene as internal standard showed a d.r. of 8:1; Purification by column chromatography (3:7 hexane:EtOAc) afforded **10p** (44.3 mg, 50%) as a white solid as a single diastereomer after 28 hours. mp: 120-122 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 – 7.59 (m, 1H), 7.49 – 7.41 (m, 1H), 7.41 – 7.32 (m, 2H), 3.60 – 3.48 (m, 1H), 2.73 – 2.63 (m, 1H), 2.59 – 2.39 (m, 3H), 2.31 – 2.16 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.2 (C), 140.2 (C), 133.0 (CH), 131.9 (CH), 128.4 (CH), 128.0 (CH), 118.4 (C), 60.4 (C), 52.4 (CH_2), 40.2 (CH), 26.6 (CH_2), 19.1 (CH_2); IR (neat): ν = 3049, 3006, 2924, 1662, 1589, 1426, 1326, 1054, 1026, 754; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{11}O_2SNa^{79}Br$: 320.9561, found 320.9551 $[M + Na]^+$.

(±)-2-Isopropylphenyl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10q)



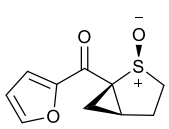
10q was prepared according to **GP4** using **9q** (49.3 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf$_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 28 hours. Purification by column chromatography (3:7 hexane:EtOAc) afforded **10q** (27.5 mg, 52%) as a colourless oil, as a 7:1 mixture of diastereomers. When run on 0.3 mmol scale with SPhosAuNTf$_2$ (6.6 mg, 2.5 mol%), **10q** (39.4 mg, 50%) was obtained as a 7:1 mixture of diastereomers after 28 hours. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 – 7.32 (m, 2H), 7.29 – 7.24 (m, 1H), 7.21 (dd, *J* = 6.0, 2.2 Hz, 1H), 3.45 – 3.35 (m, 1H), 3.03 – 2.87 (m, 1H), 2.64 – 2.45 (m, 2H), 2.36 – 2.28 (m, 2H), 2.25 – 2.15 (m, 1H), 1.96 (dd, *J* = 8.7, 5.7 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 201.7 (C), 146.4 (C), 137.2 (C), 130.9 (CH), 126.6 (CH), 126.3 (CH), 125.7 (CH), 61.1 (C), 52.4 (CH_2), 37.2 (CH), 30.5 (CH), 26.1 (CH_2), 24.2 (CH_3), 24.0 (CH_3), 19.1 (CH_2); IR (neat): *v* = 3039, 3084, 2959, 1677, 1663, 1597, 1579, 1286, 1263, 1056, 762; HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{18}O_2NaS$: 285.0925, found 285.0932 $[M + Na]^+$.

(±)-Naphthalen-2-yl(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10r)



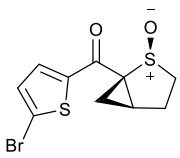
10r was prepared according to **GP4** using **9r** (50.9 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf$_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 28 hours. ^{1}H NMR analysis showed a d.r. ratio of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded **10r** (37.7 mg, 70%) as a white solid as a single diastereomer. When run on the same scale with SPhosAuNTf$_2$ (4.4 mg, 2.5 mol%), **10r** (35.1 mg, 65%) was obtained as a single diastereomer after 28 hours. mp: 108-109 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.65 (s, 1H), 8.09 – 7.83 (m, 4H), 7.67 – 7.52 (m, 2H), 3.56 (ddd, *J* = 13.0, 7.7, 4.2 Hz, 1H), 2.85 – 2.61 (m, 2H), 2.62 – 2.38 (m, 2H), 2.33 (t, *J* = 5.9 Hz, 1H), 1.86 (dd, *J* = 8.6, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.3 (C), 135.8 (C), 134.1 (C), 132.4 (C), 132.1 (CH), 130.1 (CH), 128.9 (CH), 128.7 (CH), 127.9 (CH), 127.1 (CH), 124.7 (CH), 59.6 (C), 54.4 (CH_2), 33.6 (CH), 26.4 (CH_2), 19.5 (CH_2); IR (neat): ν = 3065, 3021, 2930, 1651, 1628, 1365, 1292, 1181, 1125, 1051, 1001, 813; HR-MS (ES TOF): *m/z*: calcd for $C_{16}H_{15}O_2S$: 271.0793, found 271.0798 $[M + H]^+$.

(±)-Furan-2-yl(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10s)



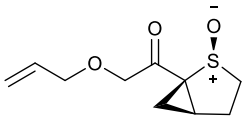
10s was prepared according to **GP4** using **9s** (41.4 mg, 0.21 mmol), 3,5-dichloropyridine-*N*-oxide (41.0 mg, 0.25 mmol), SPhosAuNTf$_2$ (9.0 mg, 5 mol%) and 1,4-dioxane (4.2 mL). The reaction time was 28 hours. Purification by column chromatography (1:4 hexane:EtOAc) afforded **10s** (33.3 mg, 74%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 – 7.58 (m, 2H), 6.58 (dd, *J* = 3.7, 1.7 Hz, 1H), 3.57 (dt, *J* = 13.1, 5.0 Hz, 1H), 2.88 – 2.77 (m, 1H), 2.68 – 2.53 (m, 1H), 2.44 – 2.33 (m, 2H), 2.18 (t, *J* = 6.1 Hz, 1H), 1.91 (dd, *J* = 8.6, 6.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 182.5 (C), 151.5 (C), 147.4 (CH), 120.9 (CH), 112.8 (CH), 58.1 (C), 52.0 (CH_2), 33.8 (CH), 25.5 (CH_2), 18.3 (CH_2); IR (neat): ν = 3425, 3127, 2935, 1635, 1563, 1461, 1390, 1297, 1138, 1055, 1017, 991, 884, 768; HR-MS (AP-TOF): *m/z*: calcd for $C_{10}H_{11}O_3S$: 211.0429, found 211.0425 $[M + H]^+$.

(±)-(5-Bromothiophen-2-yl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10t)



10t was prepared according to **GP4** using **9t** (60.7 mg, 0.21 mmol), 3,5-dichloropyridine-*N*-oxide (41.0 mg, 0.25 mmol), SPhosAuNTf$_2$ (9.0 mg, 5 mol%) and 1,4-dioxane (4.2 mL). The reaction time was 28 hours. Purification by column chromatography (1:4 hexane:EtOAc) afforded **10t** (44.4 mg, 73%) as a white solid, as a single diastereomer; mp: 116-118 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 5.1 Hz, 1H), 7.13 (d, *J* = 5.1 Hz, 1H), 3.68 – 3.52 (m, 1H), 2.72 – 2.39 (m, 4H), 2.13 (t, *J* = 6.2 Hz, 1H), 2.07 (dd, *J* = 8.3, 6.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.2 (C), 135.1 (C), 132.9 (CH), 132.1 (CH), 115.2 (C), 60.8 (C), 54.5 (CH_2), 36.6 (CH), 27.8 (CH_2), 16.8 (CH_2); IR (neat): ν = 3082, 3068, 2989, 1650, 1411, 1277, 1011, 755; HR-MS (ES-TOF): *m/z*: calcd for $C_{10}H_9O_2NaS_2{}^{79}Br$: 326.9125, found 326.9131 $[M + Na]^+$.

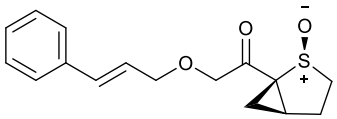
(±)-2-(Allyloxy)-1-(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)ethan-1-one (10u)



10u was prepared according to **GP4** using **9u** (39.7 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf$_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 21 hours. Purification by column chromatography (EtOAc to 1:9 MeOH:EtOAc) afforded **10u** (27.0

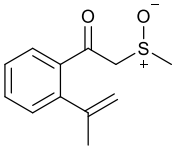
mg, 63%) as a colourless oil as a 10:1 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.92 (ddt, *J* = 17.0, 10.4, 5.8 Hz, 1H), 5.37 – 5.17 (m, 2H), 4.64 (d, *J* = 17.0 Hz, 1H), 4.52 (d, *J* = 17.0 Hz, 1H), 4.11 – 4.05 (m, 2H), 3.52 (dt, *J* = 13.1, 5.2 Hz, 1H), 2.63 – 2.48 (m, 2H), 2.32 (ddd, *J* = 5.9, 4.4, 2.0 Hz, 2H), 2.14 – 2.06 (m, 1H), 1.94 (dd, *J* = 8.6, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.4 (C), 133.5 (CH), 118.8 (CH_2), 74.4 (CH_2), 72.7 (CH_2), 58.1 (C), 52.3 (CH_2), 36.9 (CH), 25.9 (CH_2), 18.6 (CH_2); IR (neat): *v* = 3451, 2935, 1703, 1423, 1250, 1140, 1092, 992, 926, 730; HR-MS (AP-TOF): *m/z*: calcd for $C_{10}H_{15}O_3S$: 215.0742, found 215.0746 $[M + H]^+$.

(±)-2-(Cinnamyloxy)-1-(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)ethan-1-one (10v)



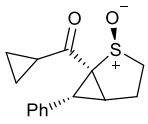
10v was prepared according to **GP4** using **9v** (54.8 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), $SPhosAuNTf_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 21 hours. Purification by column chromatography (EtOAc to 1:19 MeOH:EtOAc) afforded **10v** (38.0 mg, 65%) as a white semi-solid, as a 10:1 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 – 7.22 (m, 5H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.30 (dt, *J* = 16.0, 6.3 Hz, 1H), 4.71 (d, *J* = 17.0 Hz, 1H), 4.60 (d, *J* = 17.0 Hz, 1H), 4.36 – 4.19 (m, 2H), 3.59 – 3.48 (m, 1H), 2.65 – 2.50 (m, 2H), 2.38 – 2.26 (m, 2H), 2.16 – 2.07 (m, 1H), 1.95 (dd, *J* = 8.6, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.5 (C), 136.3 (C), 134.1 (CH), 128.7 (2CH), 128.1 (CH), 126.7 (2CH), 124.7 (CH), 74.4 (CH_2), 72.4 (CH_2), 58.1 (C), 52.2 (CH_2), 37.0 (CH), 25.9 (CH_2) 18.8 (CH_2); IR (neat): *v* = 2934, 1704, 1495, 1449, 1248, 1137, 1093, 1058, 1031, 968, 872, 735, 693; HR-MS (AP-TOF): *m/z*: calcd for $C_{16}H_{19}O_3S$: 291.1055, found 291.1059 $[M + H]^+$.

1-Isopropyl-2-((methylsulfinyl)ethynyl)benzene (12)



1-Isopropyl-2-((methylsulfinyl)ethynyl)benzene (**12**) was prepared according to **GP3** from **S3** (74.1 mg, 0.39 mmol), *m*CPBA (67.3 mg, 0.39 mmol) and CH_2Cl_2 (4 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided **12** (60.3 mg, 75%) as a colourless oil which was used directly in the catalysis according to **GP4**: **12** (41.2 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.24 mmol), $SPhosAuNTf_2$ (4.4 mg, 2.5 mol%) and 1,4-dioxane (4 mL). The reaction time was 24 hours. Purification by column chromatography (7:3 hexane:EtOAc) afforded **13** (9.0 mg, 22%) as an off white solid; mp: 104-106 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (ddd, *J* = 15.2, 7.6, 1.3 Hz, 2H), 7.42 – 7.30 (m, 2H), 5.29 – 5.26 (m, 1H), 4.90 (d, *J* = 0.5 Hz, 1H), 4.33 (d, *J* = 14.3 Hz, 1H), 4.14 (d, *J* = 14.4 Hz, 1H), 2.76 (s, 3H), 2.18 (dd, *J* = 1.3, 0.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$); δ = 197.2 (C), 144.8 (C), 143.2 (C), 137.9 (C), 132.2 (CH), 128.8 (CH), 128.7 (CH), 127.9 (CH), 118.2 (CH_2), 65.4 (CH_2), 40.0 (CH_3), 24.0 (CH_2); IR (neat): ν = 2916, 1679, 1594, 1288, 1039, 770; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{14}O_2S$: 222.0715, found 222.0713 $[M + H]^+$.

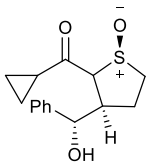
(±)-Cyclopropyl(2-oxido-6-phenyl-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (15)



Prepared according to **GP4** using sulfoxide **14** (97.7 mg, 0.40 mmol), 3,5-dichloropyridine-*N*-oxide (78.6 mg, 0.48 mmol), $SPhosAuNTf_2$ (17.6 mg, 5 mol%) and dioxane (8 mL). The reaction time was 3 hours. Purification by column chromatography (1:1 hexane:EtOAc) to (2:1 hexane:EtOAc) afforded **15** (41.6 mg, 40%) as a white solid, stereochemistry is undefined; mp: 107-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.22 (m, 5H), 3.77 (d, *J* = 6.8 Hz, 1H), 3.58 (dt, *J* = 13.1, 5.8 Hz, 1H), 3.17 (dt, *J* = 6.8, 3.3 Hz, 1H), 2.83 – 2.70 (m, 1H), 2.61 – 2.50 (m, 2H), 2.39 – 2.28 (m, 1H), 1.07

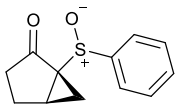
– 0.94 (m, 1H), 0.92 – 0.83 (m, 1H), 0.82 – 0.71 (m, 1H), 0.67 – 0.58 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 201.1 (C), 133.3 (C), 129.2 (2CH), 128.4 (CH), 127.7 (2CH), 68.3 (C), 53.6 (CH_2), 35.4 (CH), 33.9 (CH), 27.1 (CH_2), 21.3 (CH), 12.6 (CH_2), 12.2 (CH_2); IR (neat): *v* = 2983, 2941, 2871, 1659, 1601, 1497, 1447, 1396, 1249, 1218, 1058, 1032, 968, 896, 747, 702; HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{16}O_2NaS$: 283.0769, found 283.0775 $[M + Na]^+$.

(±)-Cyclopropyl(3-(hydroxy(phenyl)methyl)-1-oxidotetrahydrothiophen-2-yl)methanone (16)



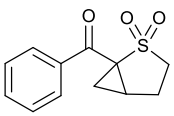
The relative stereochemistry of **16** at the benzylic position was assigned assuming a stereospecific hydrative cyclisation of the alkene which appears consistent with the data.[23]. Prepared from the same reaction eluting with (EtOAc) yielding **16** (24.5 mg, 22%); mp: 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (dt, *J* = 15.1, 7.4 Hz, 4H), 7.27 (t, *J* = 6.3 Hz, 1H), 4.86 (t, *J* = 5.1 Hz, 1H), 4.24 (dd, *J* = 4.7, 1.5 Hz, 1H), 3.74 (d, *J* = 4.7 Hz, 1H), 3.22 – 3.05 (m, 2H), 2.78 – 2.60 (m, 2H), 2.44 – 2.29 (m, 1H), 1.69 (ddd, *J* = 12.4, 7.8, 4.6 Hz, 1H), 1.00 – 0.80 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 205.4 (C), 143.7 (C), 128.8 (2CH), 127.9 (CH), 126.0 (2CH), 80.0 (CH), 74.8 (CH), 53.1 (CH_2), 52.2 (CH), 29.6 (CH_2), 21.3 (CH), 12.4 (CH_2), 12.3 (CH_2); IR (neat): *v* = 3314, 3063, 3011, 2935, 1677, 1604, 1380, 1063, 1028, 1041, 998, 760, 703; HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{18}O_3SNa$: 301.0874, found 301.0878 $[M + Na]^+$.

(±)-1-(Phenylsulfinyl)bicyclo[3.1.0]hexan-2-one (18 and 18')



18/**18'** were prepared according to **GP4** using **17** (40.8 mg, 0.20 mmol), 3,5-dichloropyridine-*N*-oxide (39.4 mg, 0.12 mmol), $SPhosAuNTf_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 20 hours. ^{1}H NMR analysis using 1,2,4,5-tetramethylbenzene as internal standard showed the formation of **18**/**18'** (62%) as a 1.6:1 mixture of diastereomers. Structure elucidation of **18**/**18'** was achieved by separation of mixed fractions using column chromatography (2:1 hexane:EtOAc) to afford: diastereomer 1 as an oily solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 – 7.74 (m, 2H), 7.50 (dd, *J* = 5.0, 1.9 Hz, 3H), 2.80 – 2.70 (m, 2H), 2.38 – 2.23 (m, 6H), 2.13 – 2.01 (m, 2H), 1.75 (dd, *J* = 8.6, 5.3 Hz, 2H), 1.24 (t, *J* = 5.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 208.4 (C), 143.5 (C), 131.3 (CH), 129.1 (2CH), 124.7 (2CH), 54.3 (C), 34.3 (CH_2), 30.3 (CH), 21.5 (CH_2), 15.4 (CH_2); IR (neat): ν = 3059, 2946, 2879, 1718, 1582, 1477, 1443, 1276, 1083, 1041, 1022, 749, 689; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{13}O_2S$: 221.0636, found 221.0638 $[M+ H]^+$; and then diastereomer 2 as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 – 7.58 (m, 2H), 7.52 – 7.46 (m, 3H), 2.44 (dt, *J* = 8.7, 5.0 Hz, 1H), 2.29 – 1.91 (m, 4H), 1.90 – 1.74 (m, 1H), 1.48 (t, *J* = 5.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 208.5 (C), 143.2 (C), 131.5 (CH), 129.2 (2CH), 124.6 (2CH), 55.4 (C), 33.6 (CH_2), 26.5 (CH), 21.1 (CH_2), 18.8 (CH_2); IR (neat): ν = 3060, 2944, 2880, 1721, 1582, 1476, 1443, 1274, 1084, 1030, 956, 748, 690; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{13}O_2S$: 221.0636, found 221.0631 $[M + H]^+$.

(±)-(2,2-Dioxido-2-thiabicyclo[3.1.0]hexan-1-yl)(phenyl)methanone (6b)



6b was prepared according to **GP4** using **4b** (66.0 mg, 0.30 mmol), 3,5-dichloropyridine-*N*-oxide (59.1 mg, 0.36 mmol), $SPhosAuNTf_2$ (6.6 mg, 2.5 mol%) and 1,4-dioxane (6 mL). The reaction time was 28 hours. Purification by column chromatography (7:3 hexane:EtOAc), followed by recrystallisation from hot EtOH afforded **6b** (56.0 mg, 79%) as a white solid; mp: 118-119 °C (EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 – 8.09 (m, 2H), 7.68 – 7.58 (m, 1H), 7.56 – 7.46 (m, 2H), 3.34 – 3.03 (m,

2H), 2.79 (dt, *J* = 8.6, 5.7 Hz, 1H), 2.63 – 2.46 (m, 1H), 2.32 (dd, *J* = 13.7, 7.7 Hz, 1H), 1.85 (t, *J* = 6.6 Hz, 1H), 1.77 – 1.68 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.7 (C), 136.5 (C), 134.3 (CH), 129.7 (2CH), 128.8 (2CH), 50.6 (C), 48.6 (CH_2), 25.4 (CH), 19.7 (CH_2), 18.4 (CH_2); IR (neat): *v* = 3039, 3086, 2958, 1678, 1662, 1597, 1452, 1302, 1286, 1117, 885; HR-MS (ES-TOF): *m/z*: calcd for $C_{12}H_{12}O_3NaS$: 259.0405, found 259.0416 $[M + Na]^+$.

Crystal Structure Determination of 10g:

Crystal Data for $C_{12}H_{12}O_2S$ (M =220.28 g/mol): triclinic, space group P-1 (no. 2), a = 6.2782(3) Å, b = 7.1917(3) Å, c = 12.4920(6) Å, α = 86.275(4)°, β = 75.966(4)°, γ = 66.086(4)°, V = 499.87(4) Å^3, Z = 2, T = 100.01(11) K, μ(CuKα) = 2.667 mm^{-1}, Dcalc = 1.463 g/cm^3, 7653 reflections measured (7.3° ≤ 2Θ ≤ 144.236°), 1939 unique (R_{int} = 0.0218, R_{sigma} = 0.0170) which were used in all calculations. The final R1 was 0.0390 (I > 2σ(I)) and wR_2 was 0.0963 (all data).

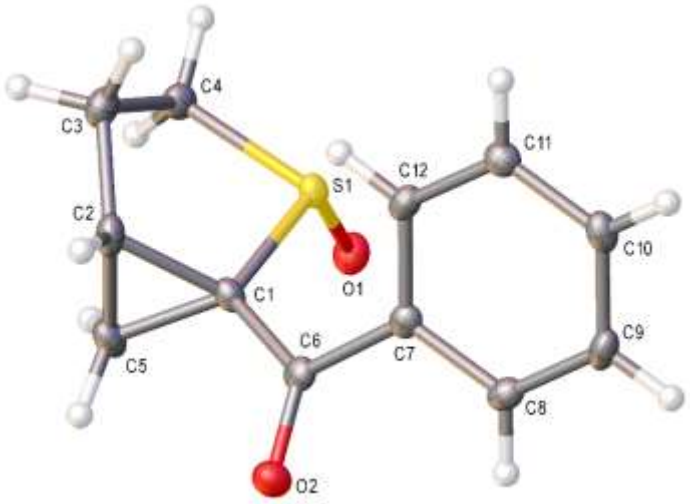


Fig. S1: Crystal structure of **10g** with ellipsoids drawn at the 50% probability level.

The dataset was measured on an Agilent SuperNova diffractometer using an Atlas detector. The data collection was driven and processed and an absorption correction was applied using CrysAlisPro.[24] The structure was solved using ShelXS[25] and refined by a full-matrix least-squares procedure on F^2 in ShelXL.[25] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. Figures and reports were produced using OLEX2.[26]

The CIF for the crystal structure of 10g has been deposited with the CCDC and have been given the deposition number CCDC 1528851. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

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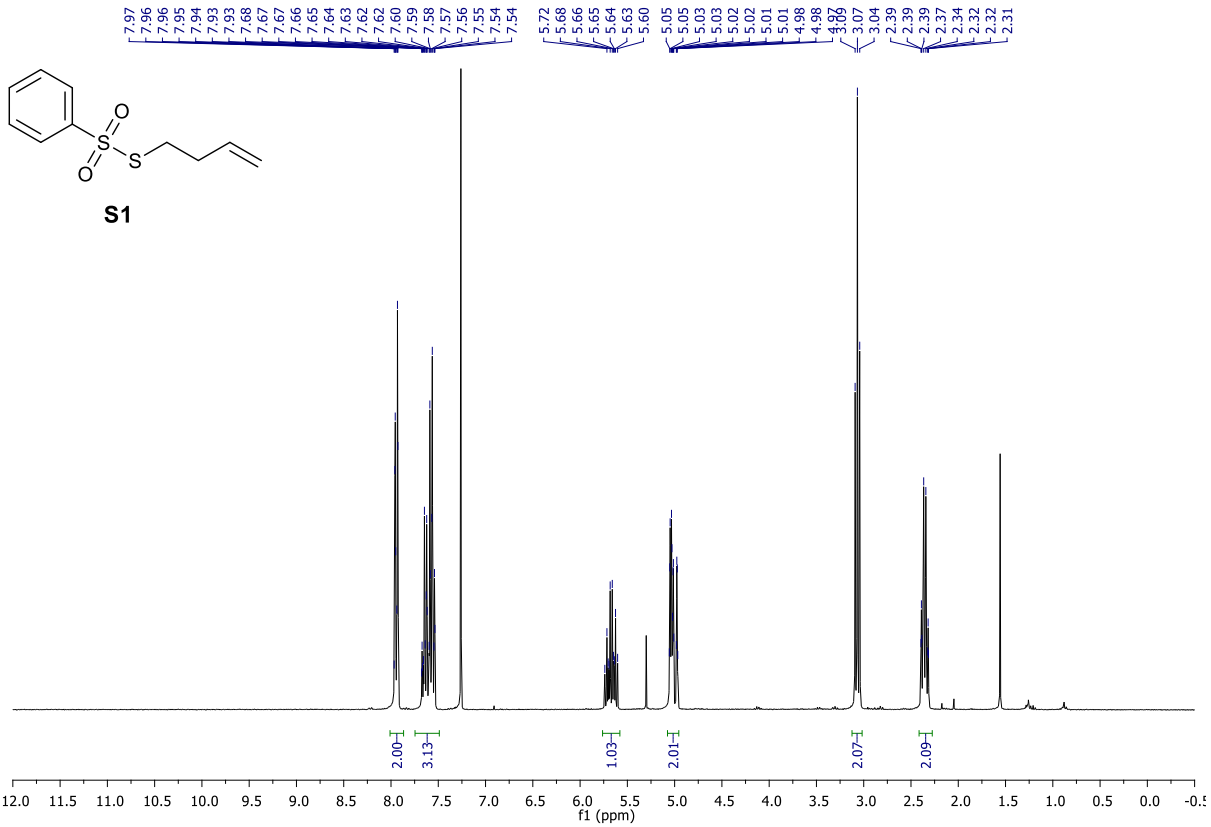
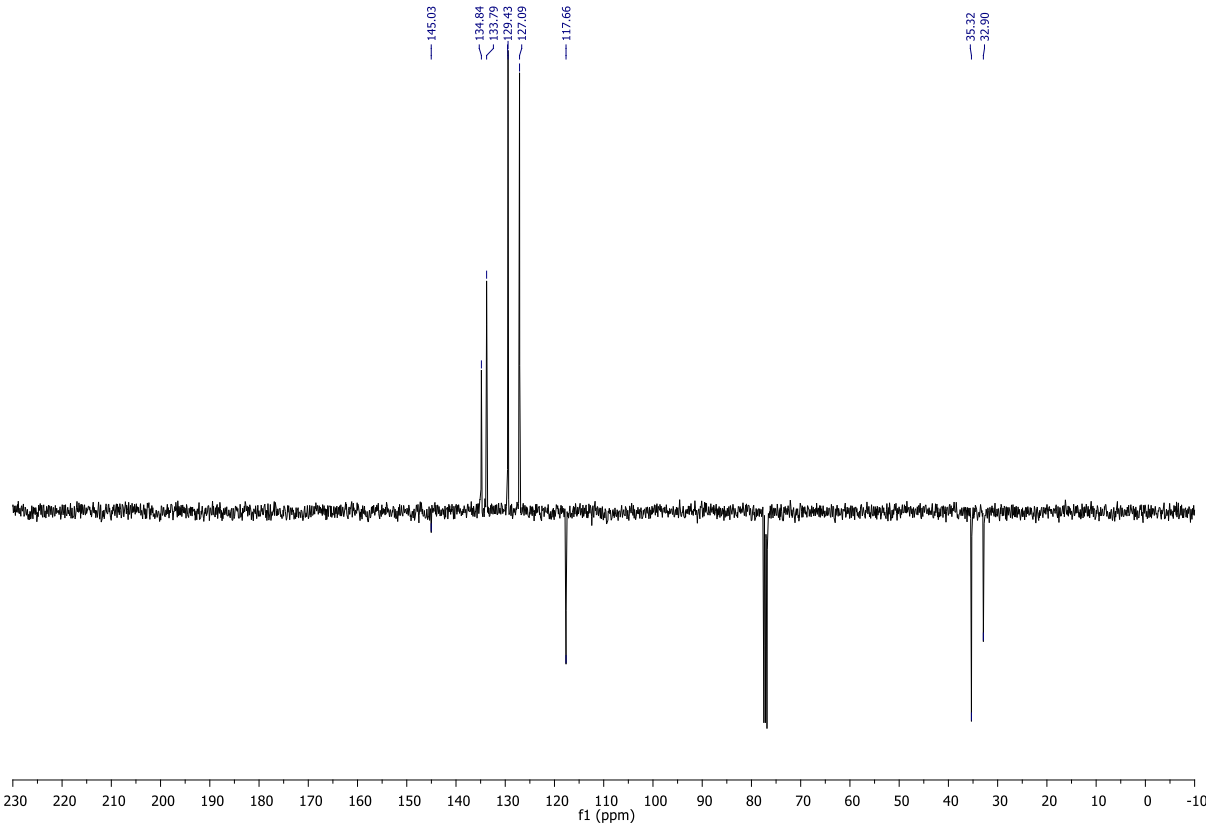
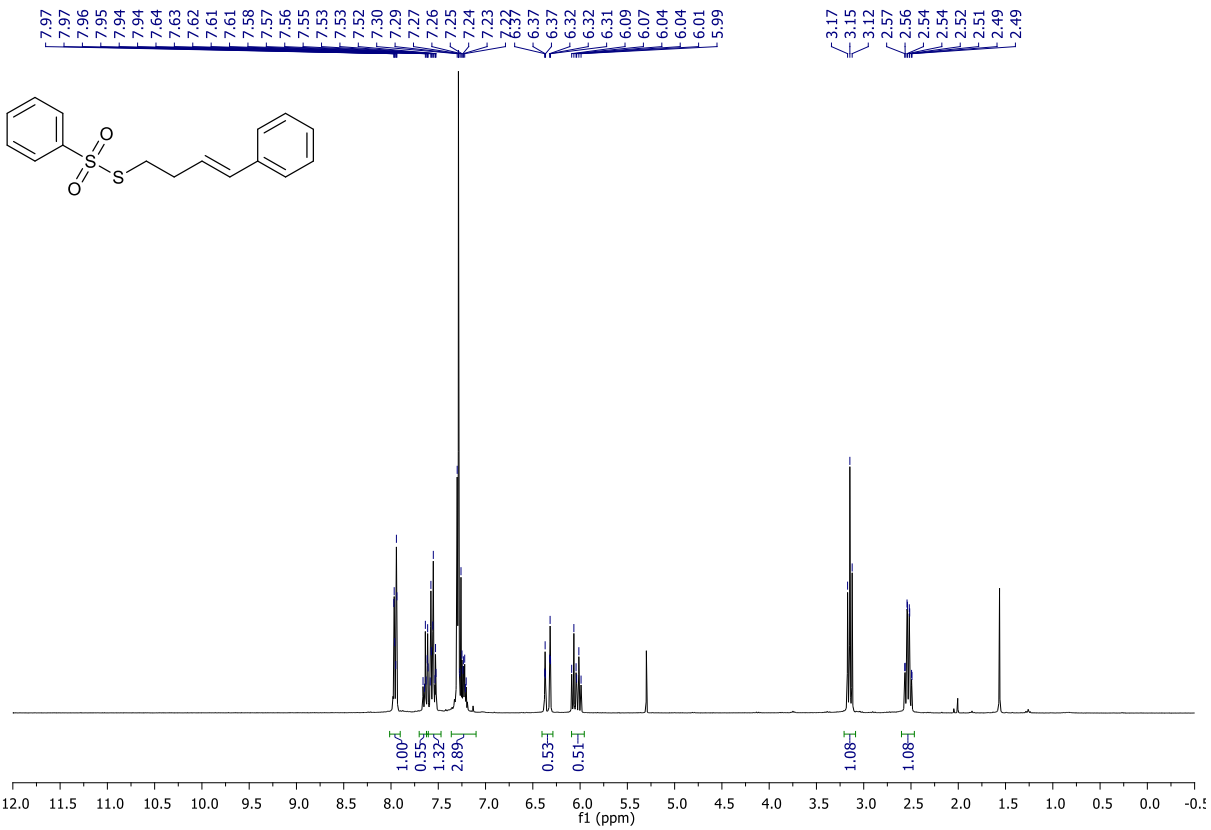
^{1}H NMR and ^{13}C NMR Spectra of New Compounds



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7.24
7.23
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6.31
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6.07
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6.04
6.01
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3.12
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2.54
2.52
2.51
2.49
2.49
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1.08
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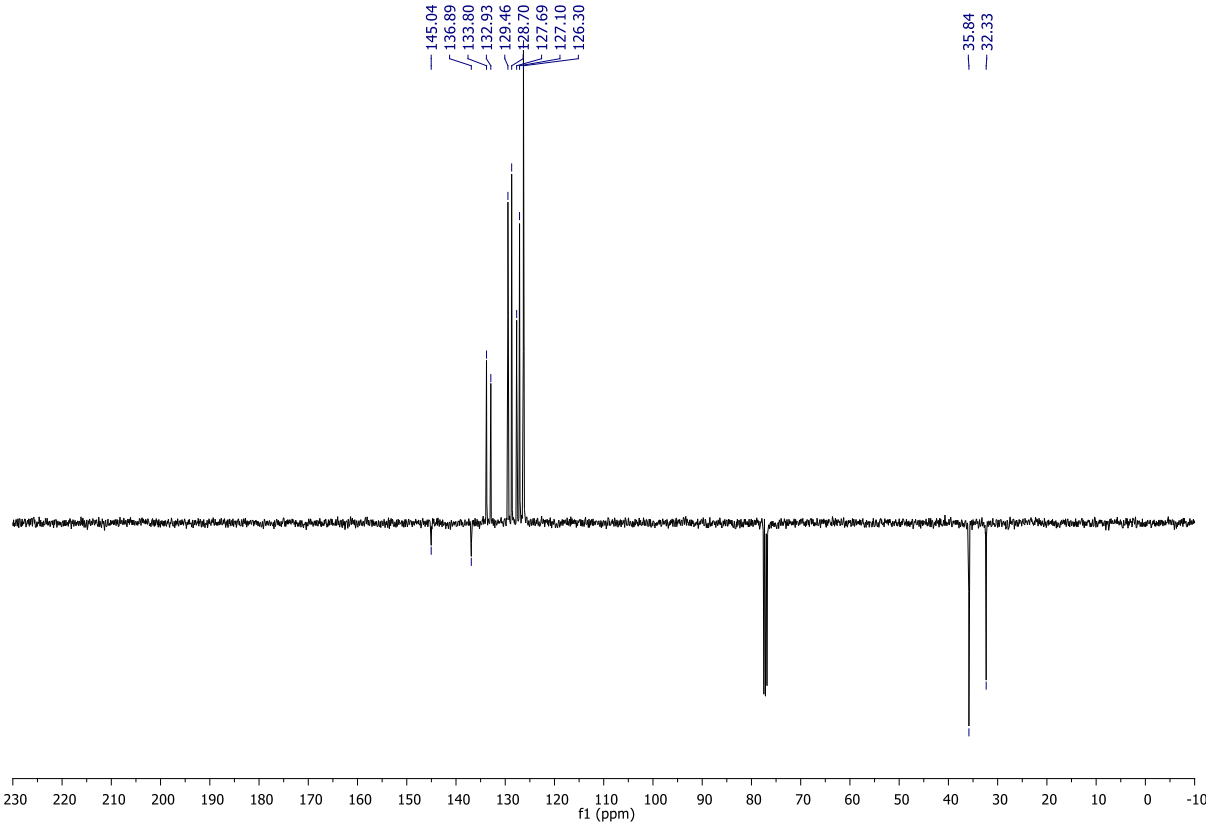
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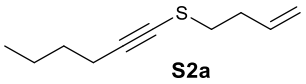
f1 (ppm)

Alkynyl Thioethers



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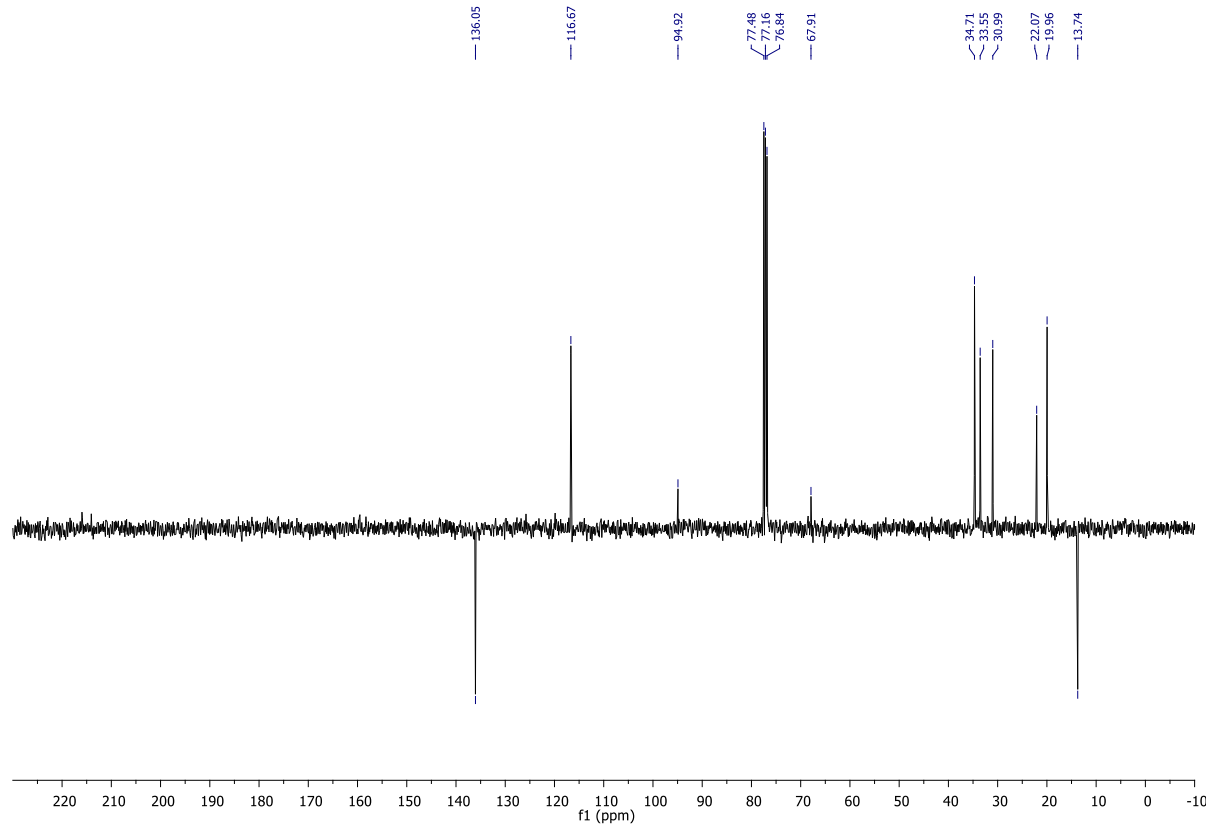

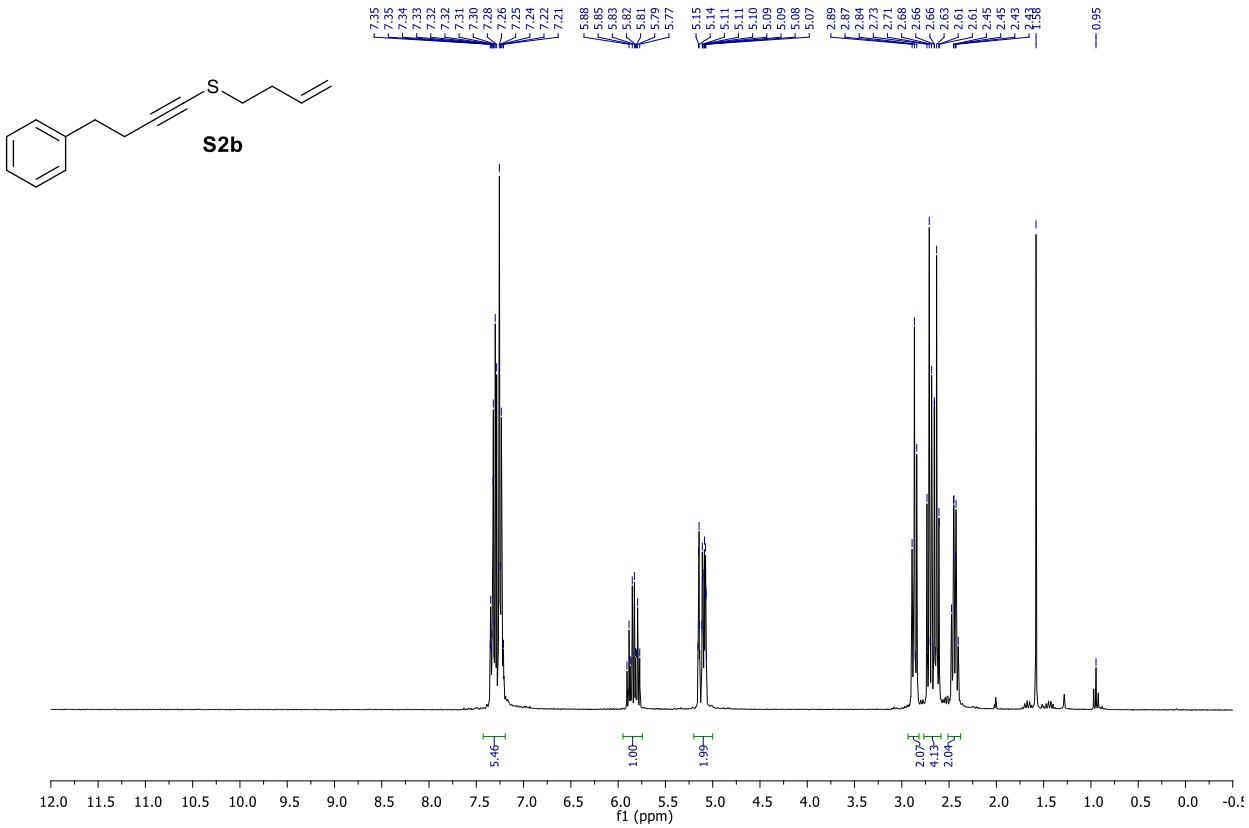
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5.15 5.14 5.11 5.11 5.10 5.09 5.09 5.08 5.07
2.89 2.87 2.84 2.73 2.71 2.68 2.66 2.66 2.63 2.61 2.61 2.45 2.45 2.43 1.58
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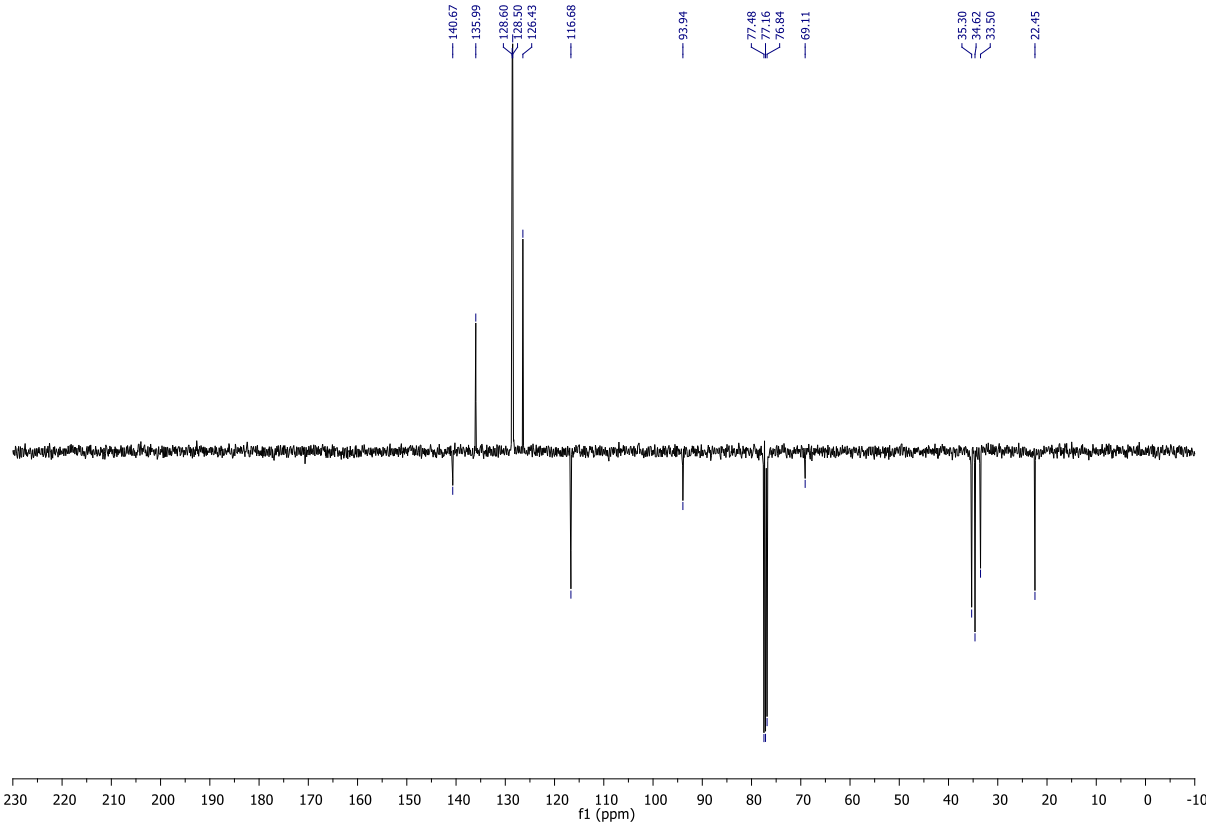
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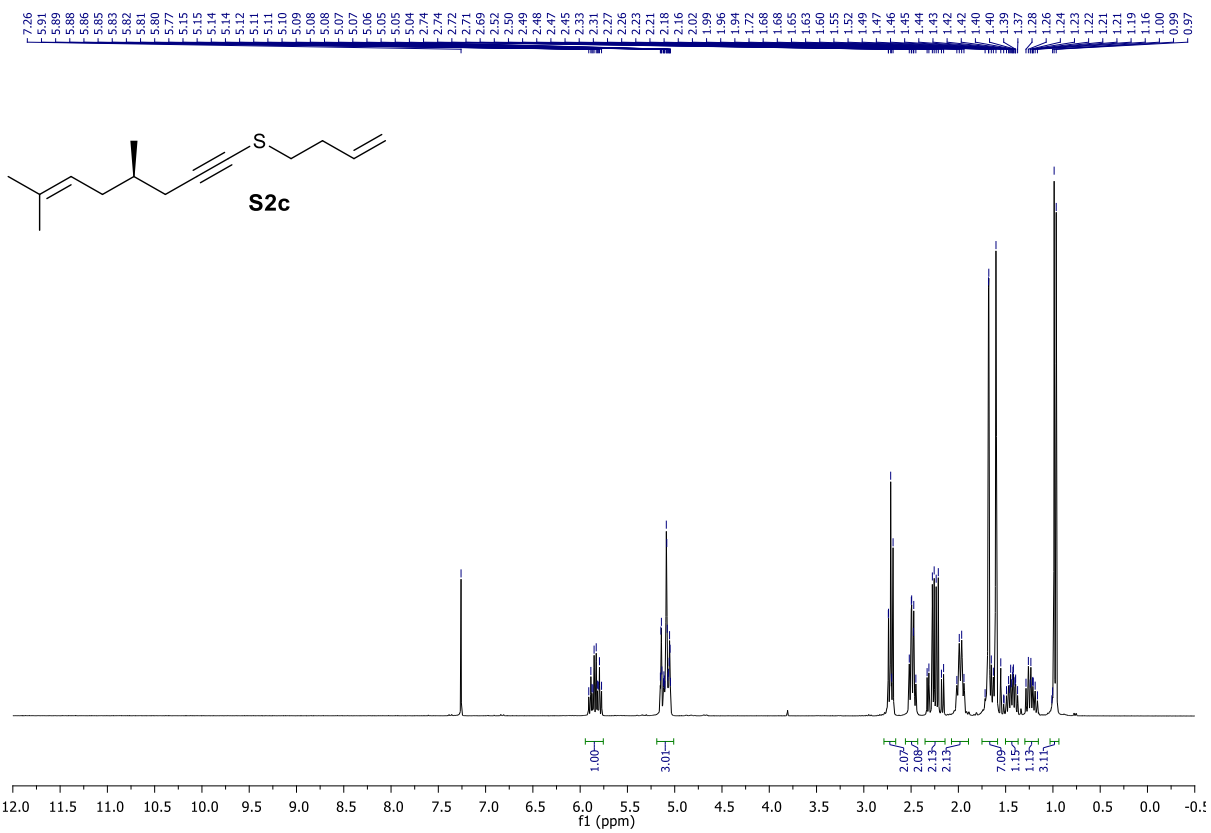
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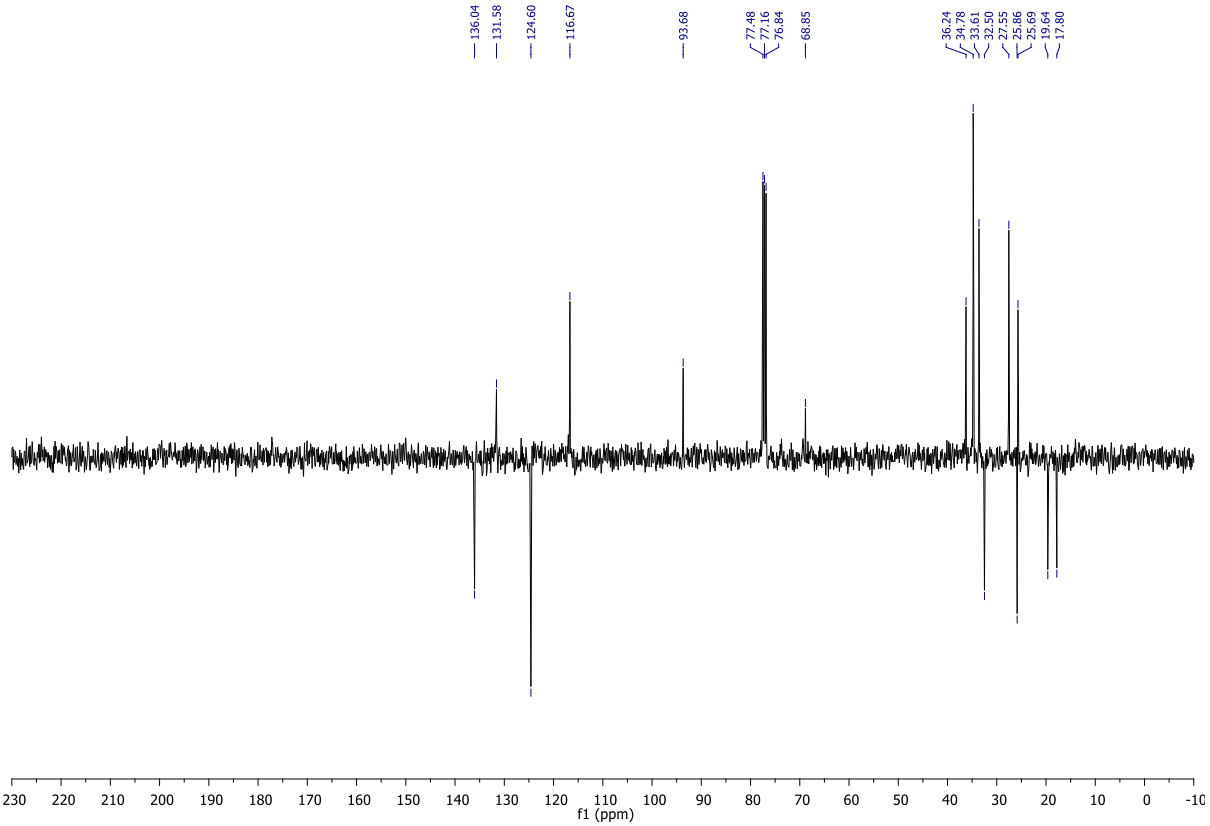
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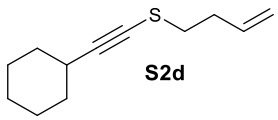
S

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5.15
5.15
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5.09
5.09
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5.05
5.05
5.05
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2.69
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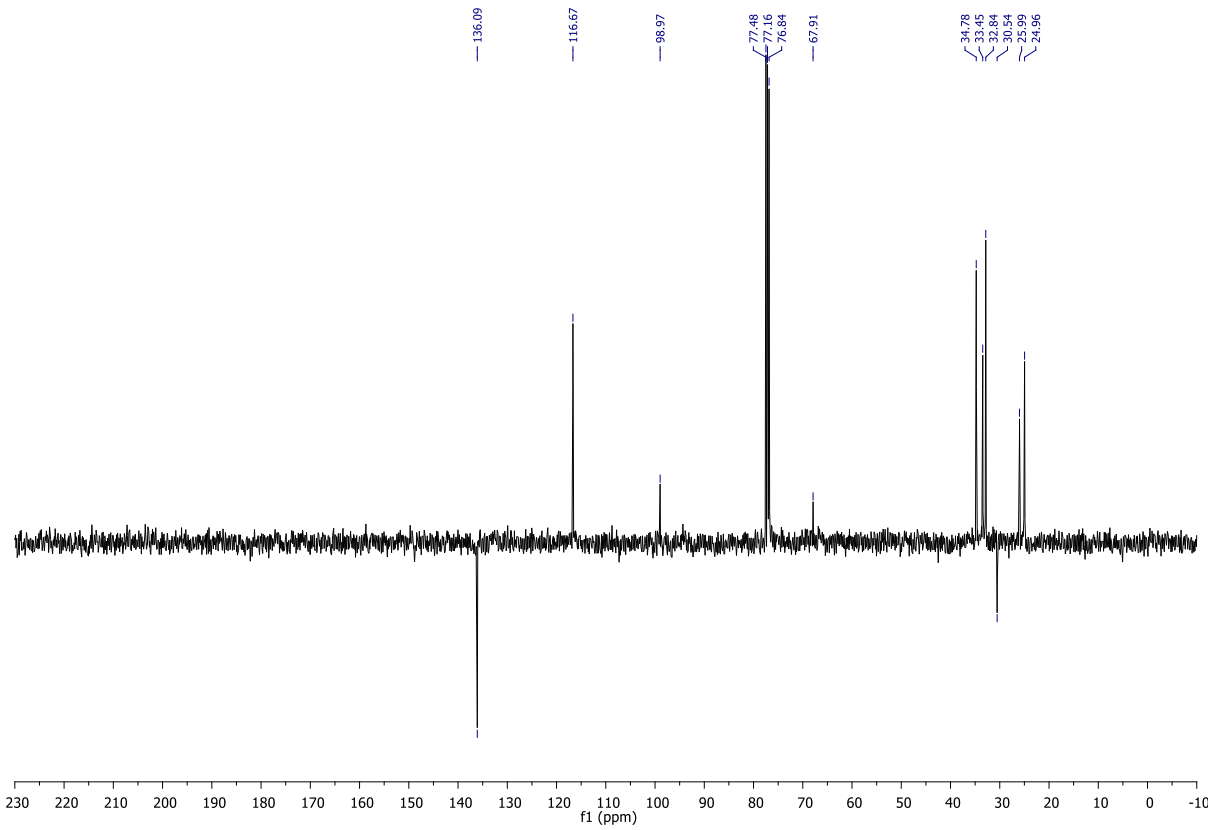
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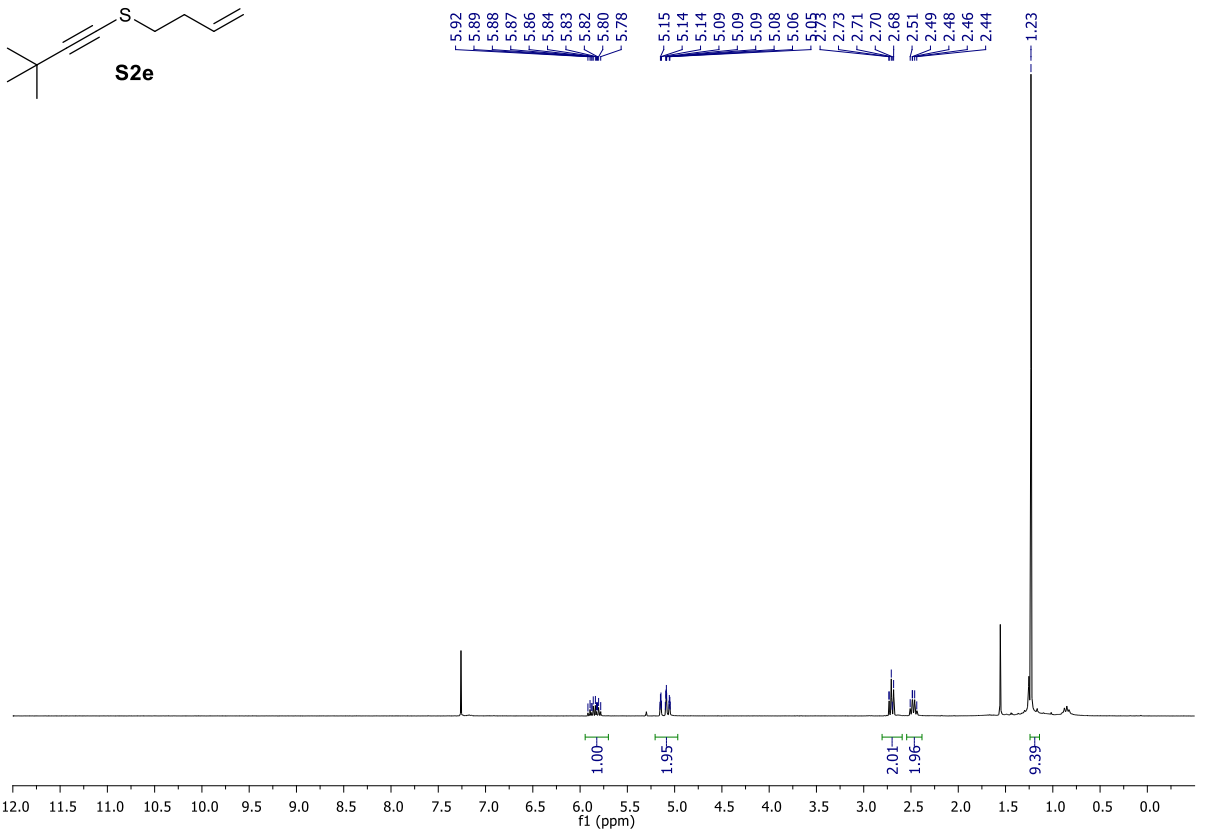
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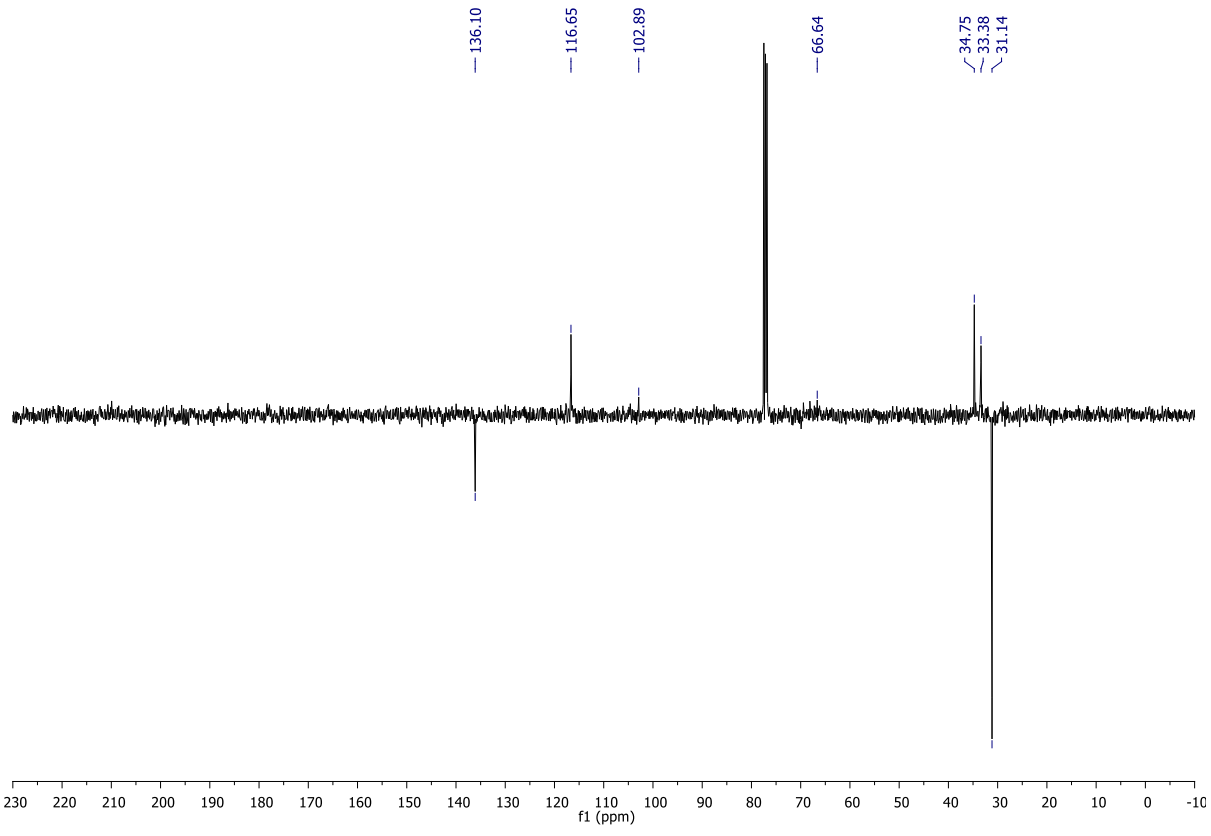
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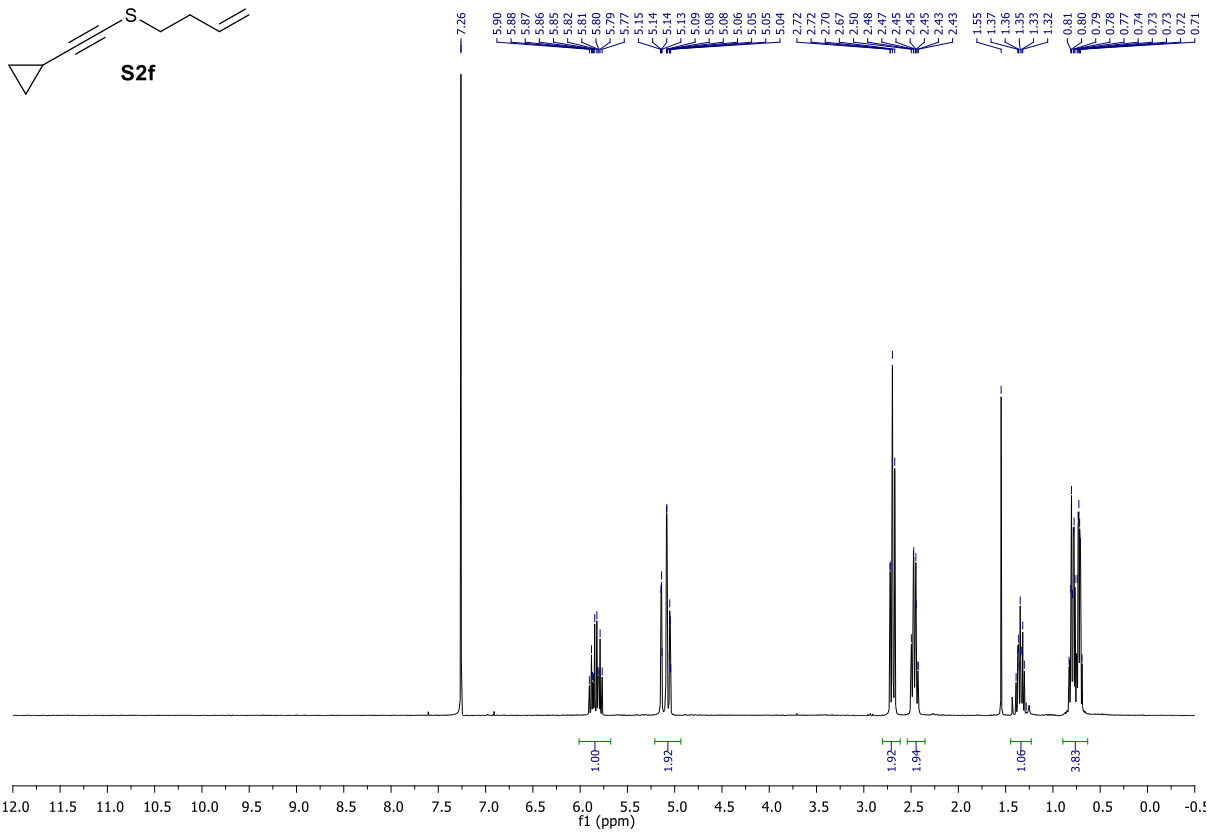
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5.77
5.15
5.14
5.14
5.13
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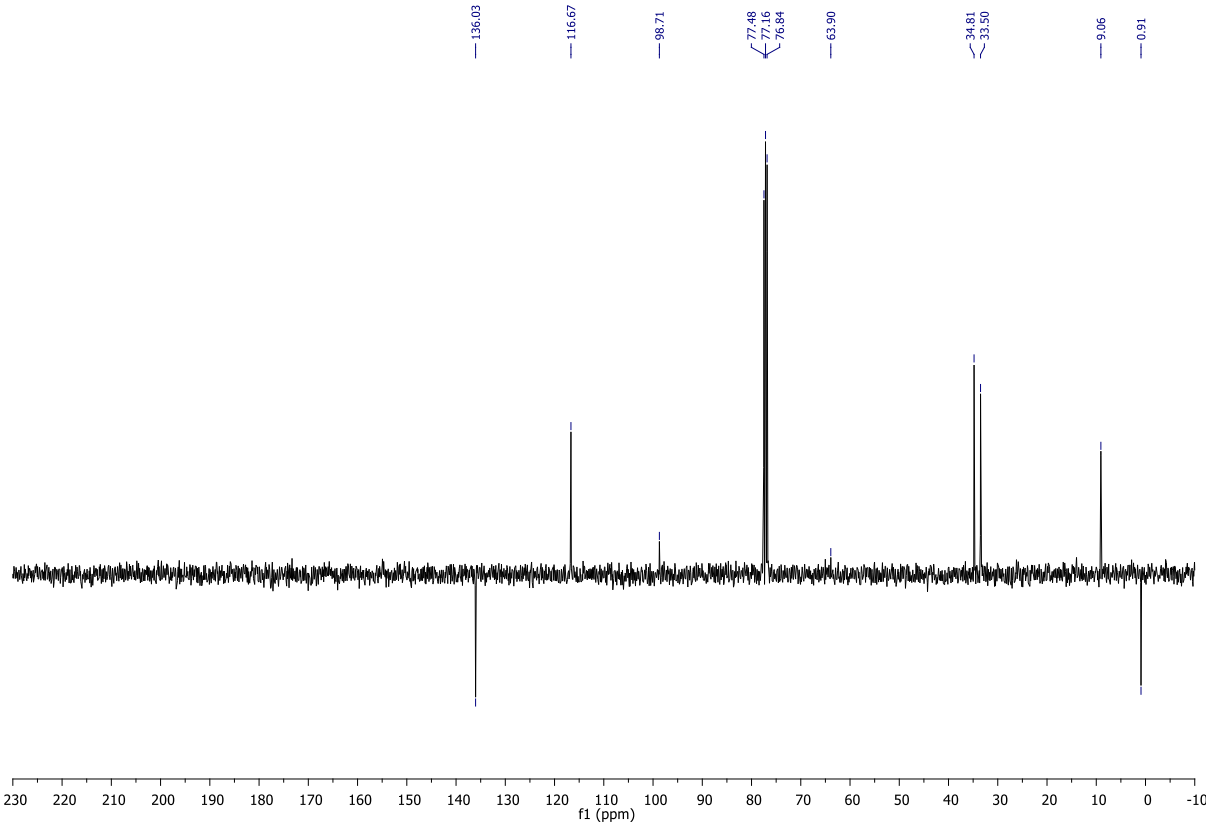
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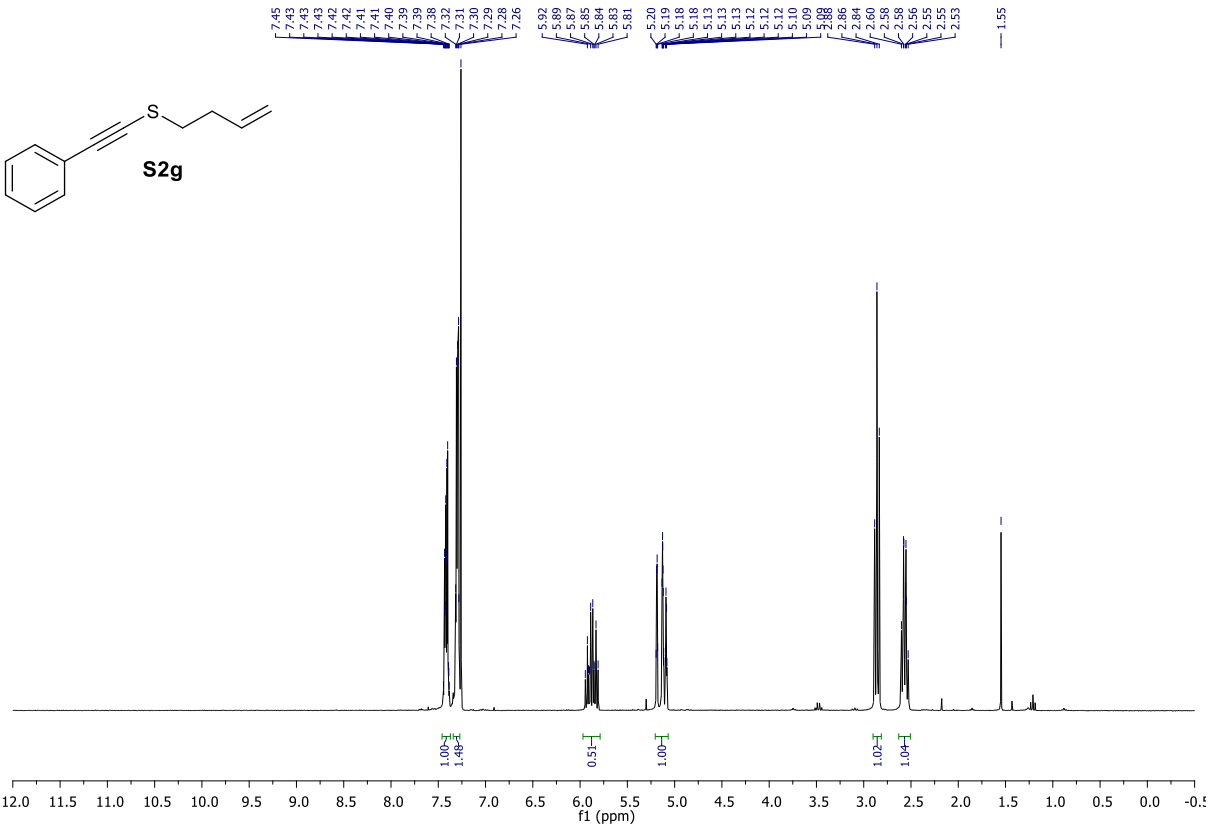
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5.92 5.89 5.87 5.85 5.84 5.83 5.81
5.20 5.19 5.18 5.18 5.13 5.13 5.12 5.12 5.12 5.10 5.09 5.09
2.88 2.86 2.84 2.60 2.58 2.58 2.56 2.55 2.55 2.53
1.55
1.00 1.48 0.51 1.00 1.02 1.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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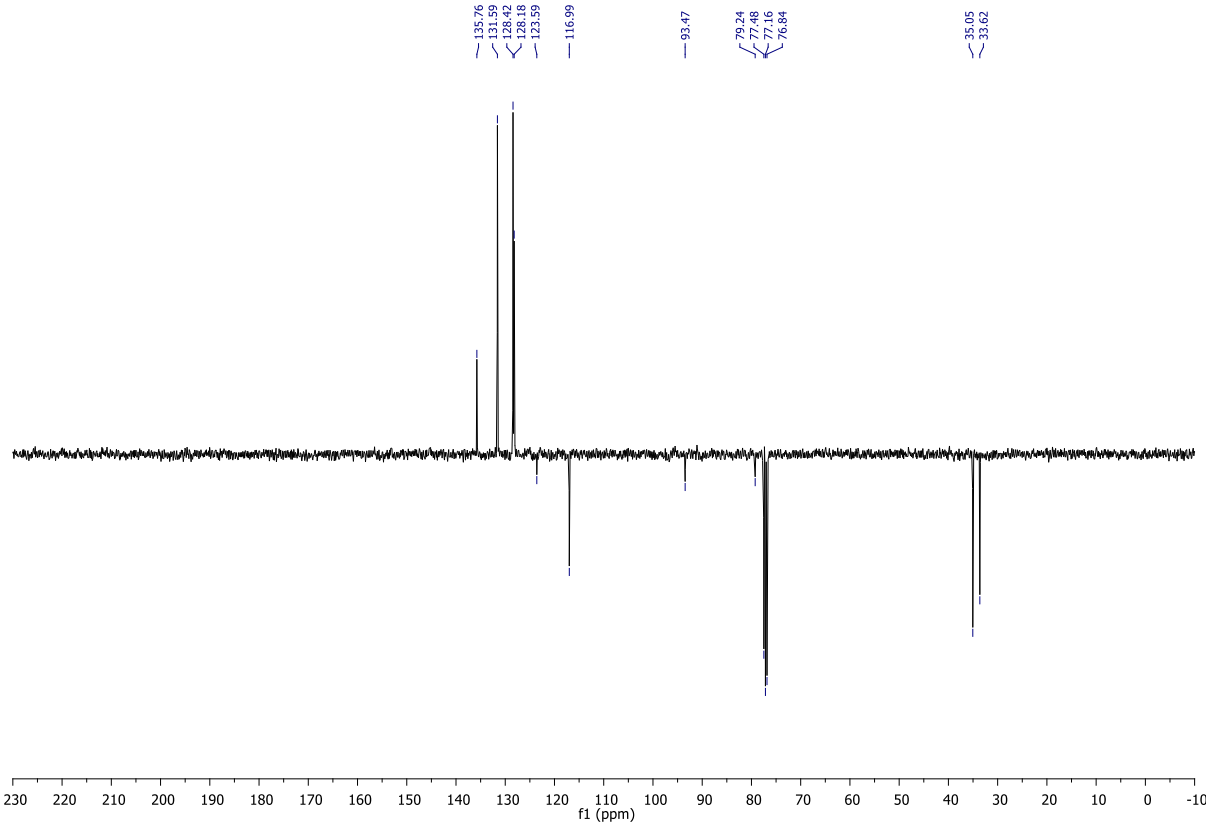
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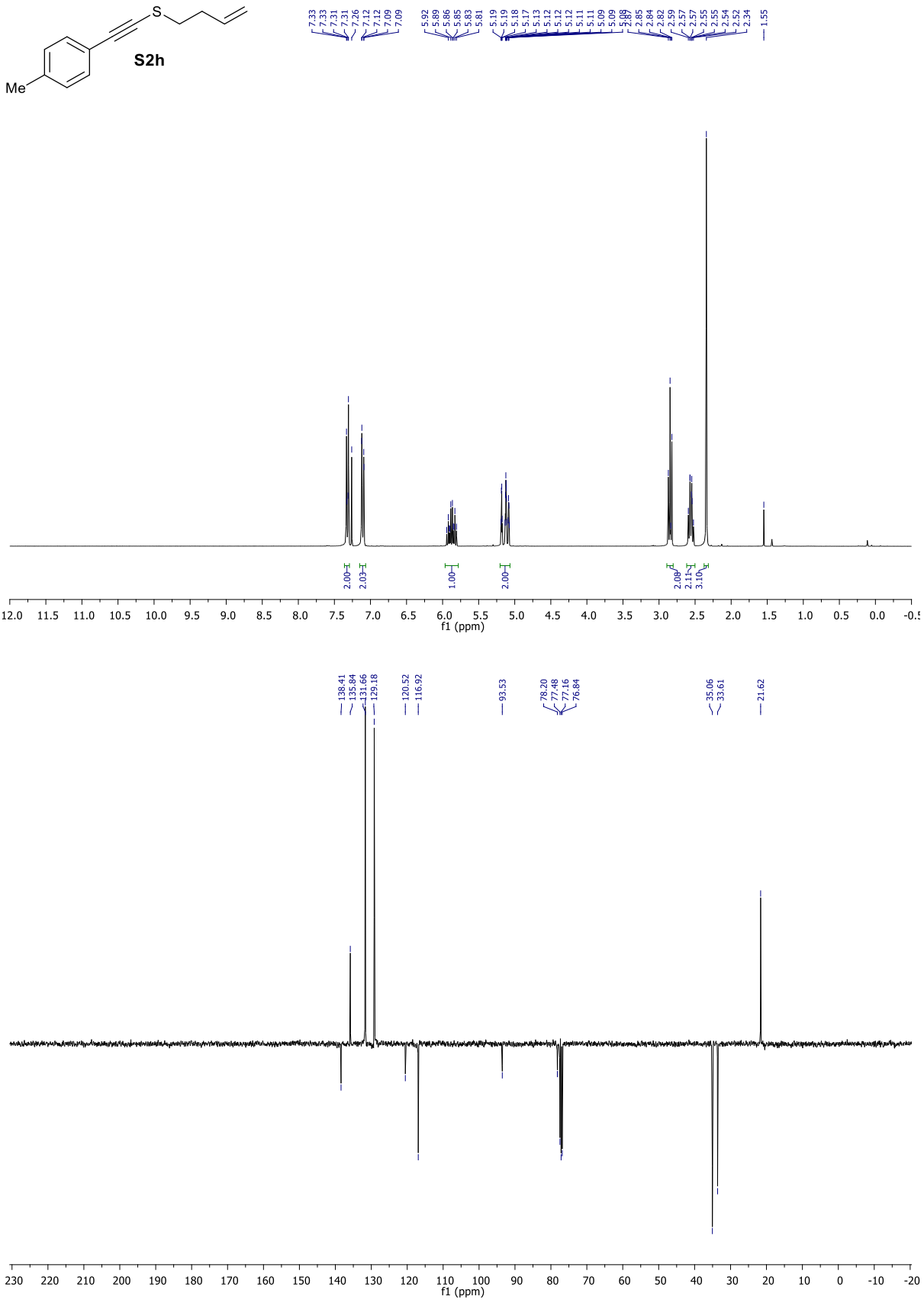
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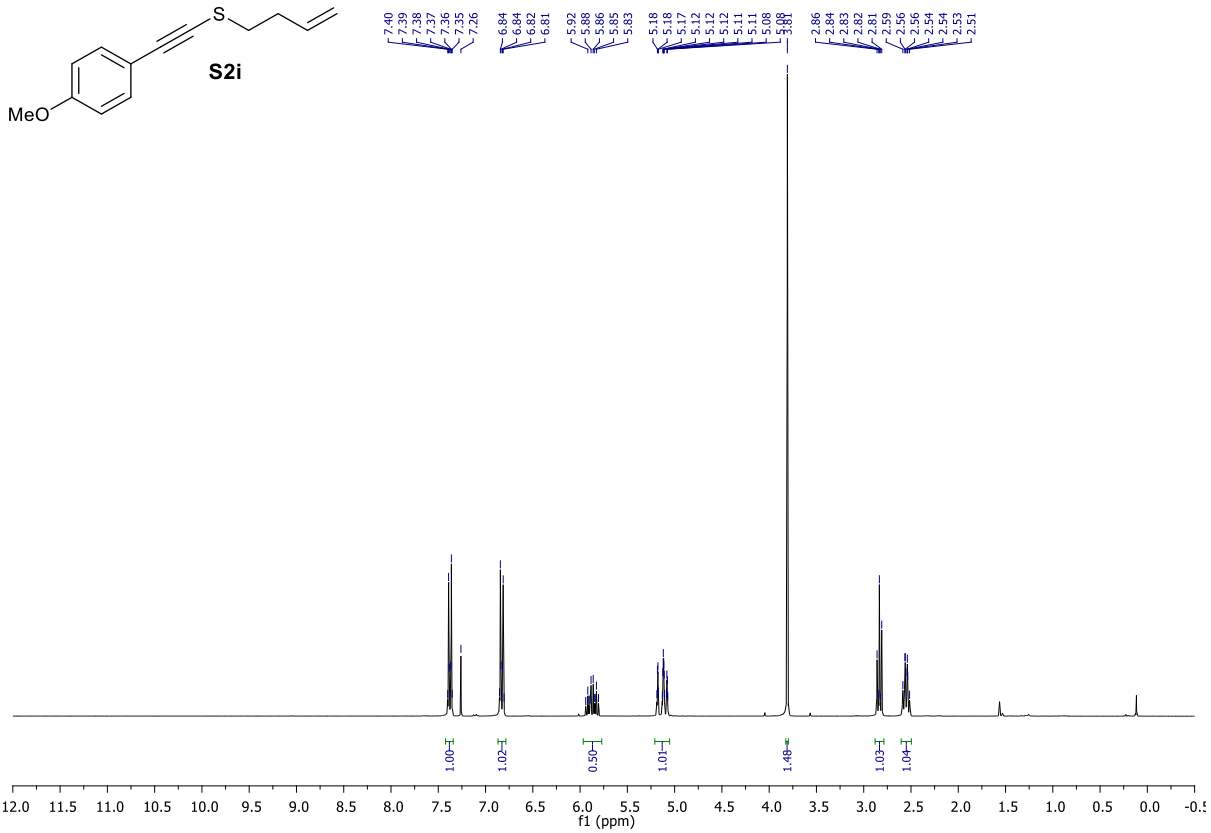
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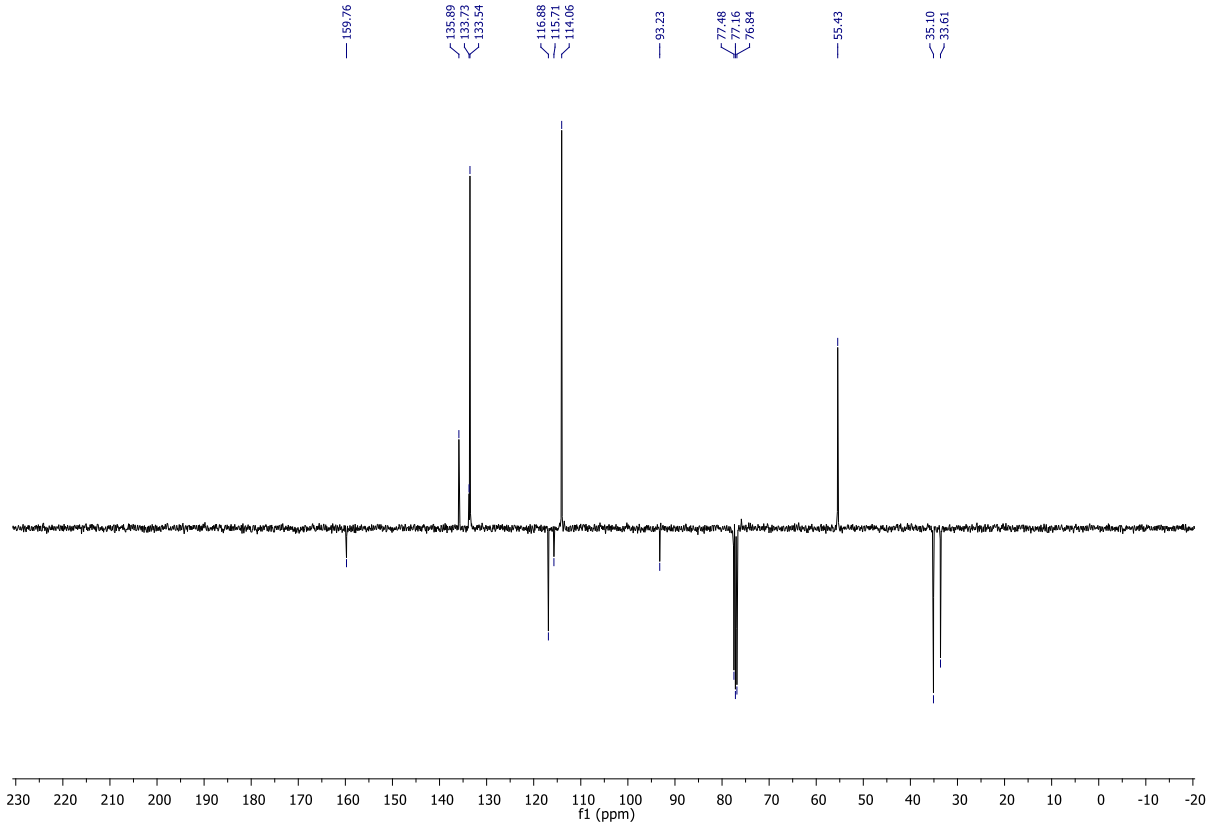
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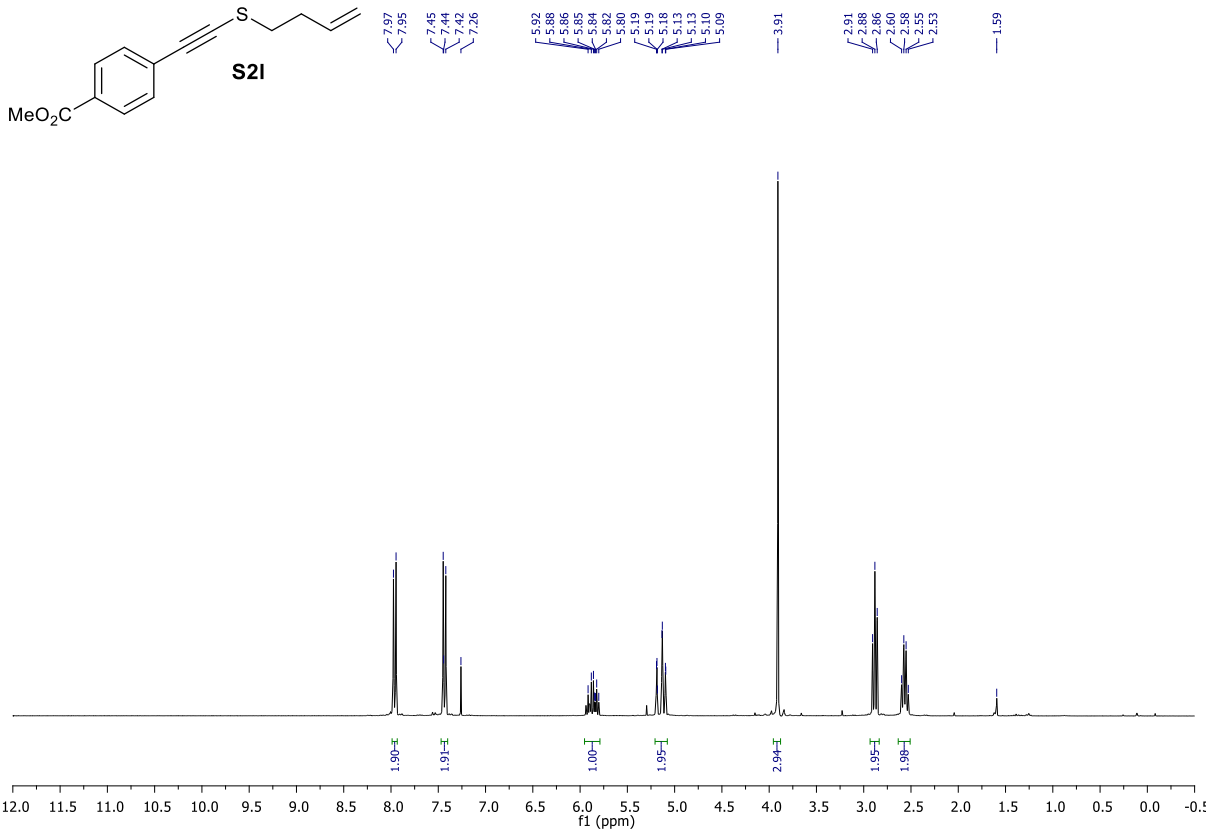
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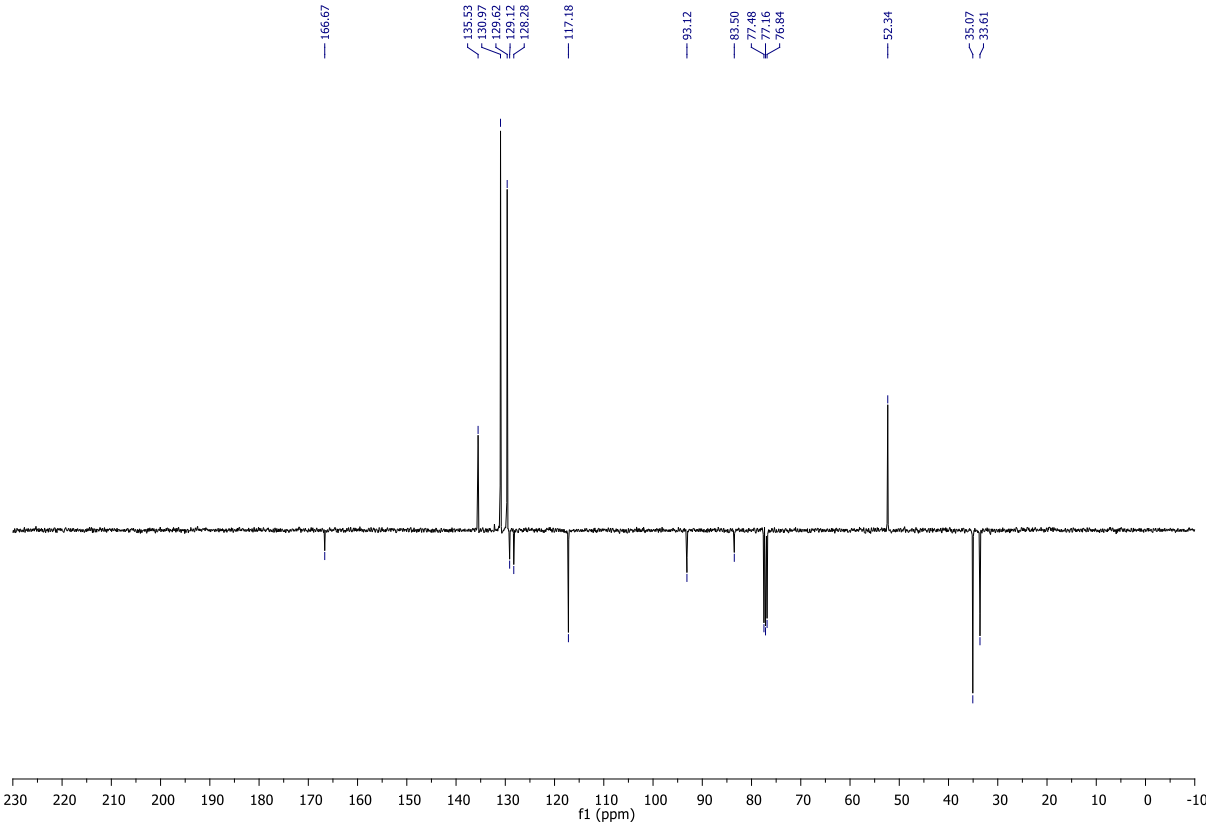
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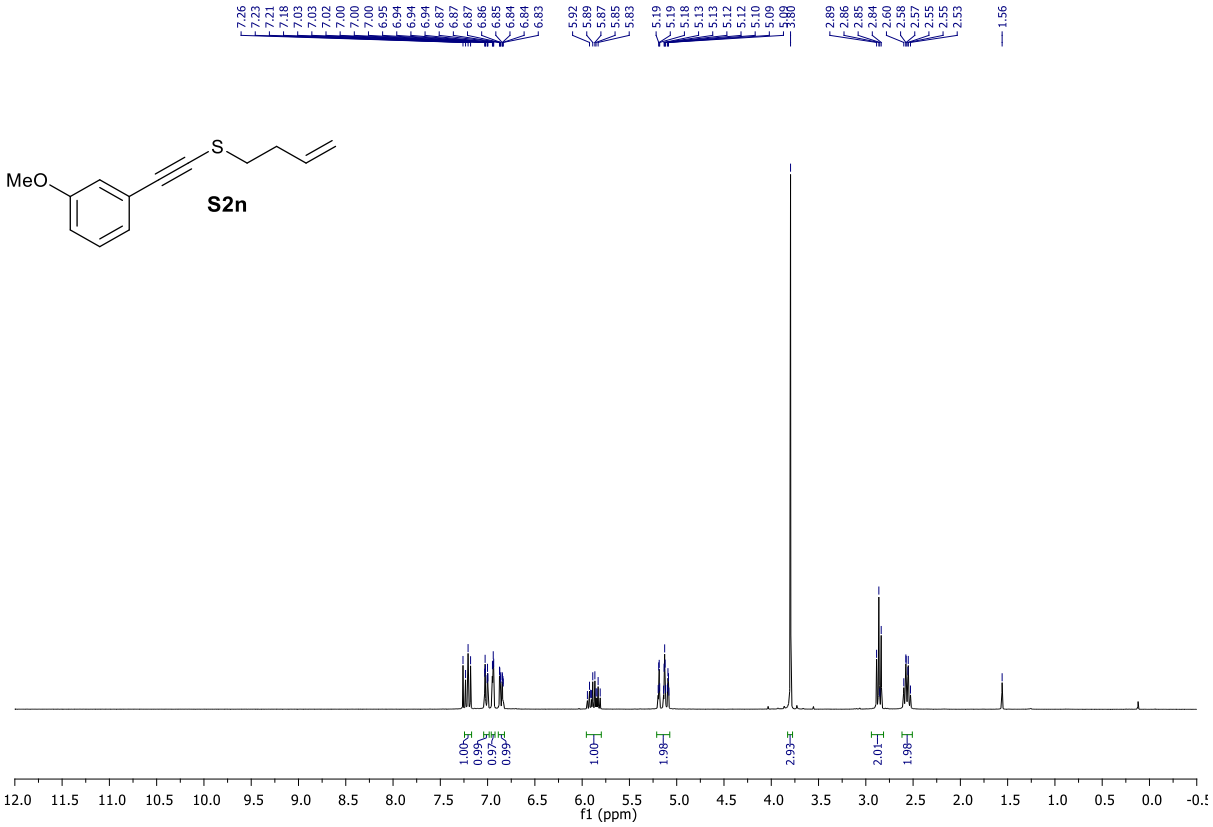
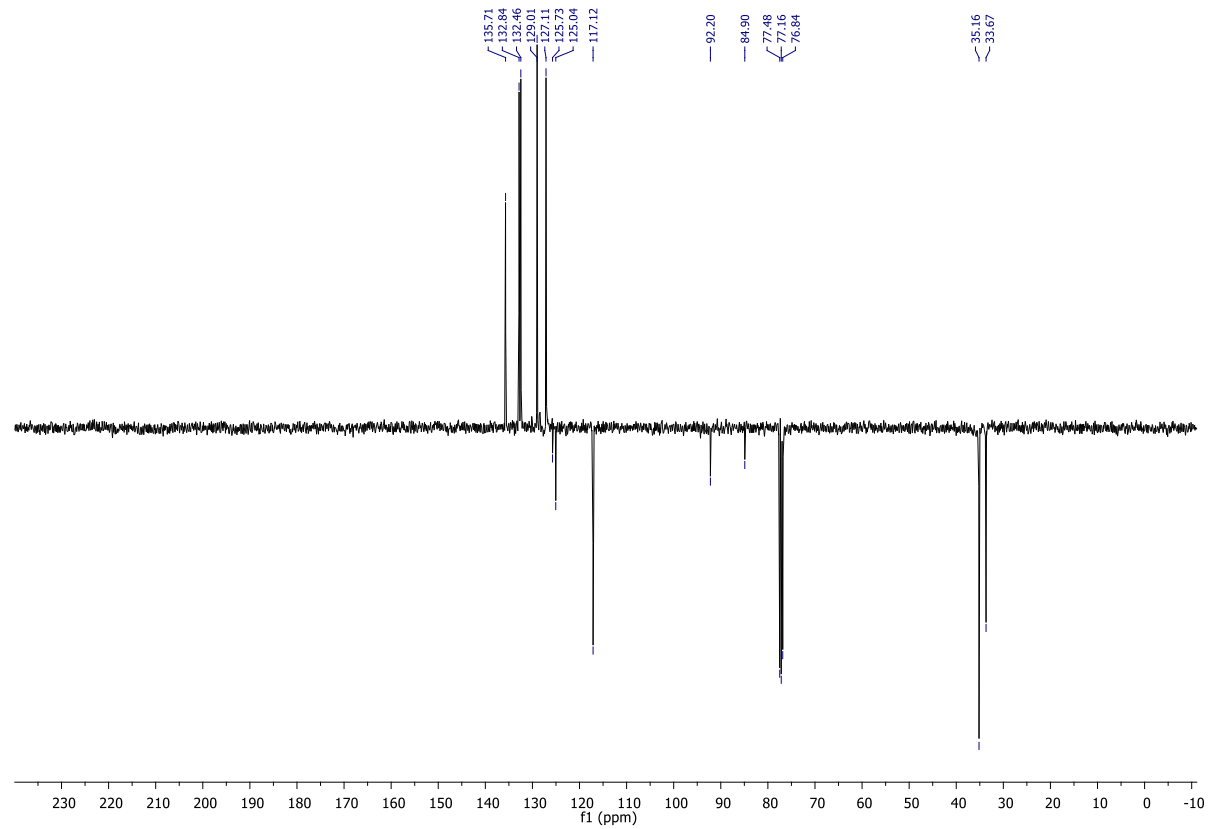
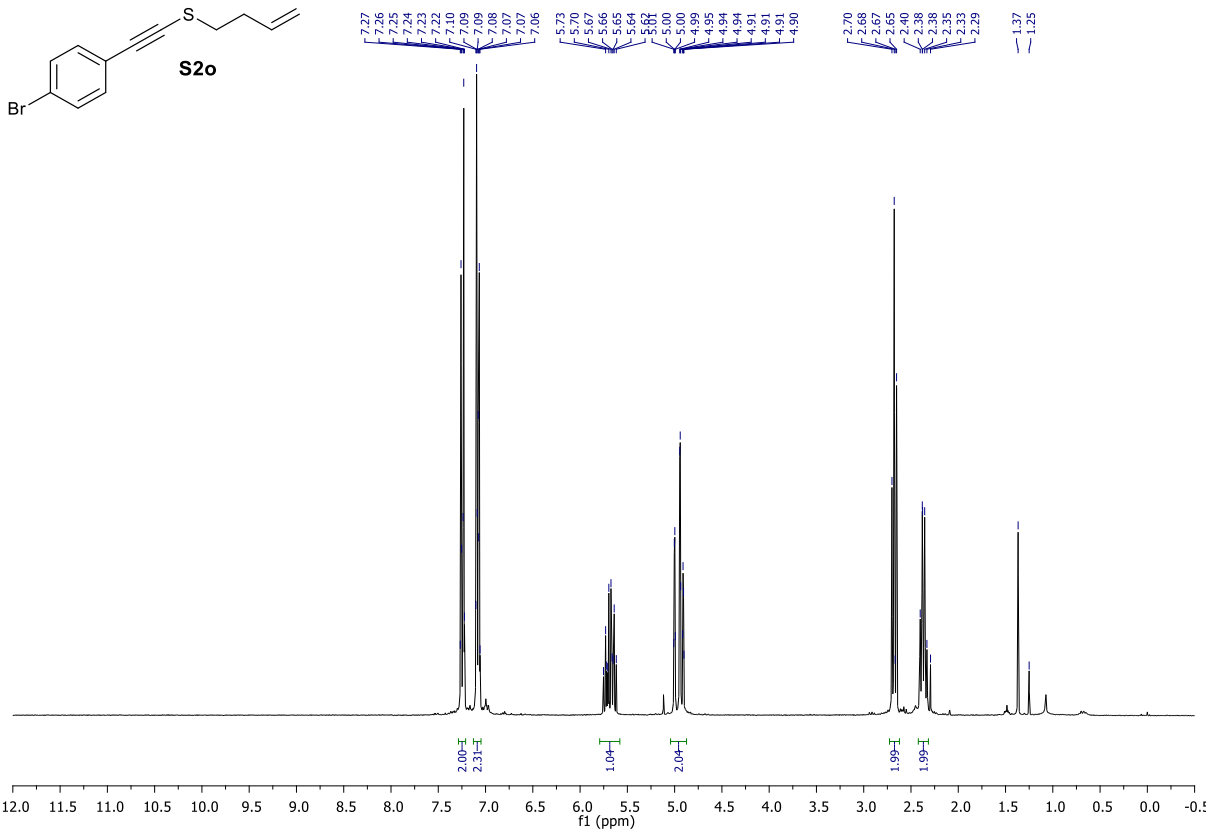
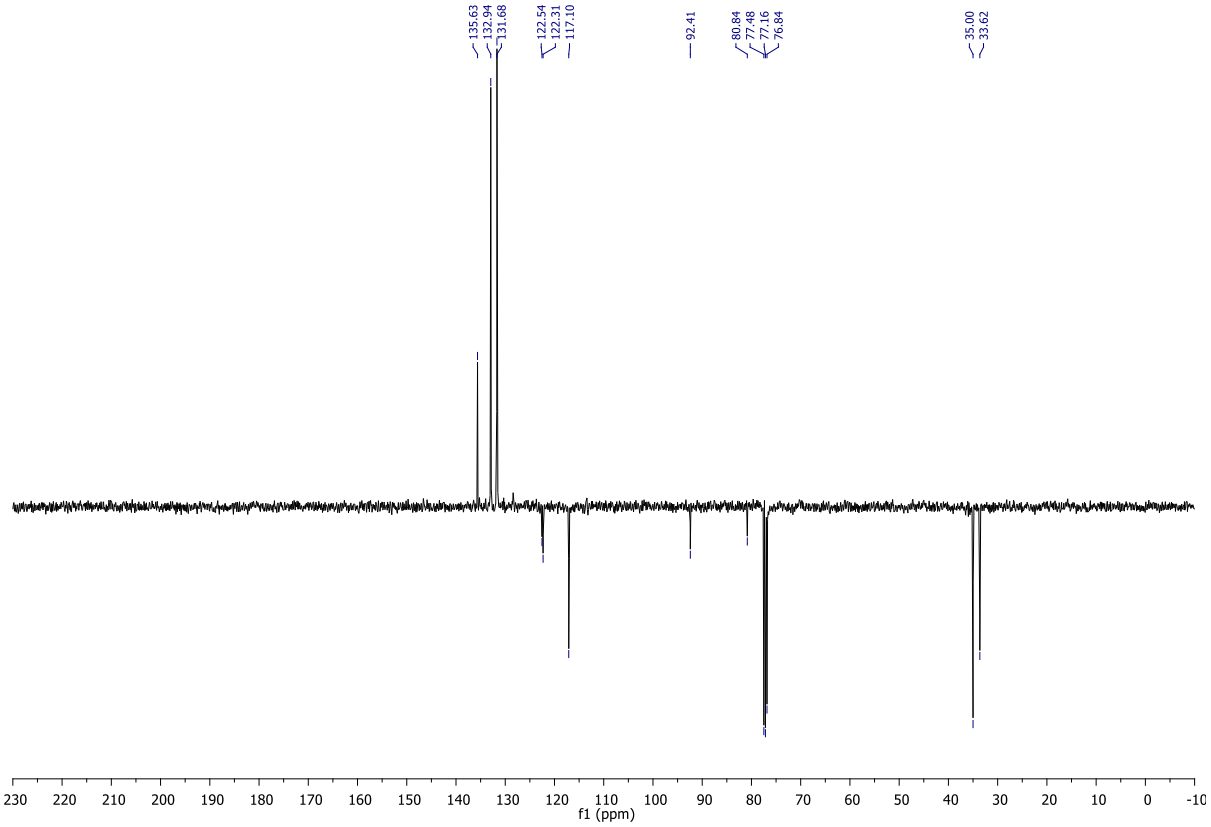
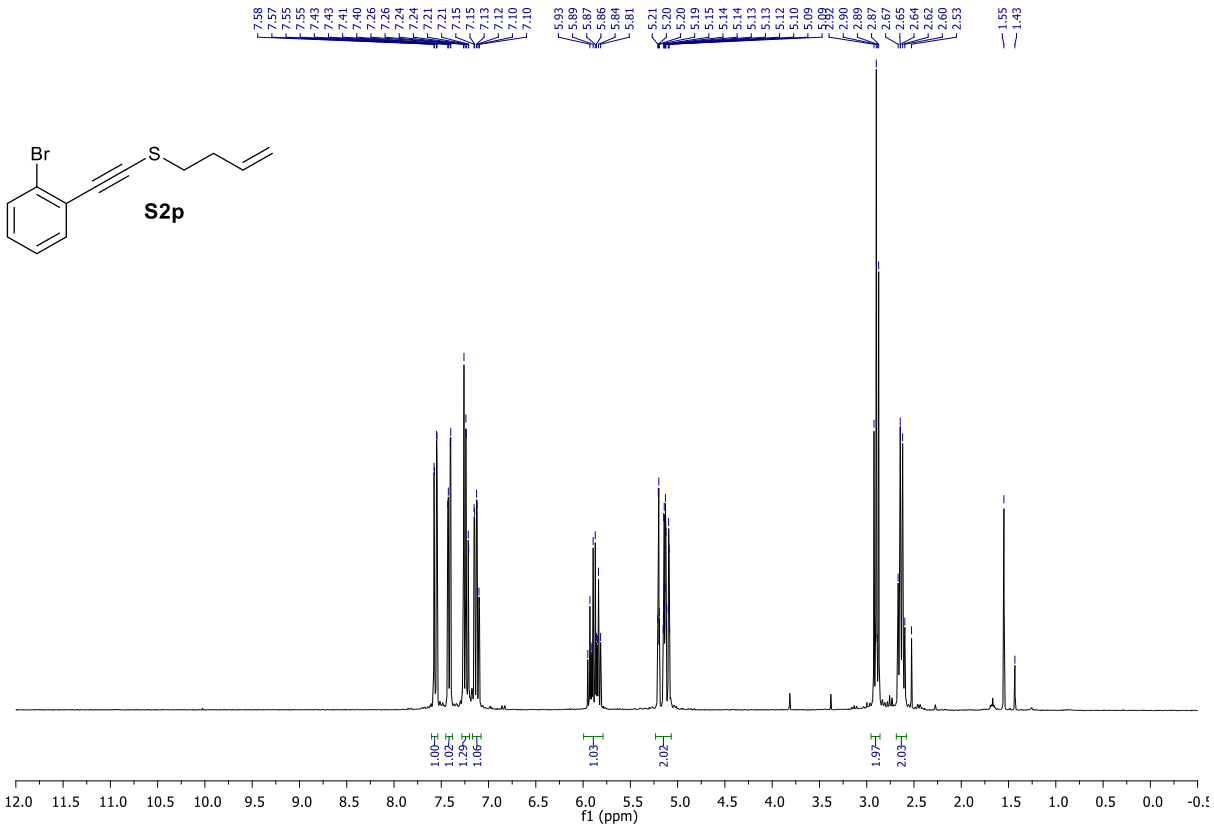
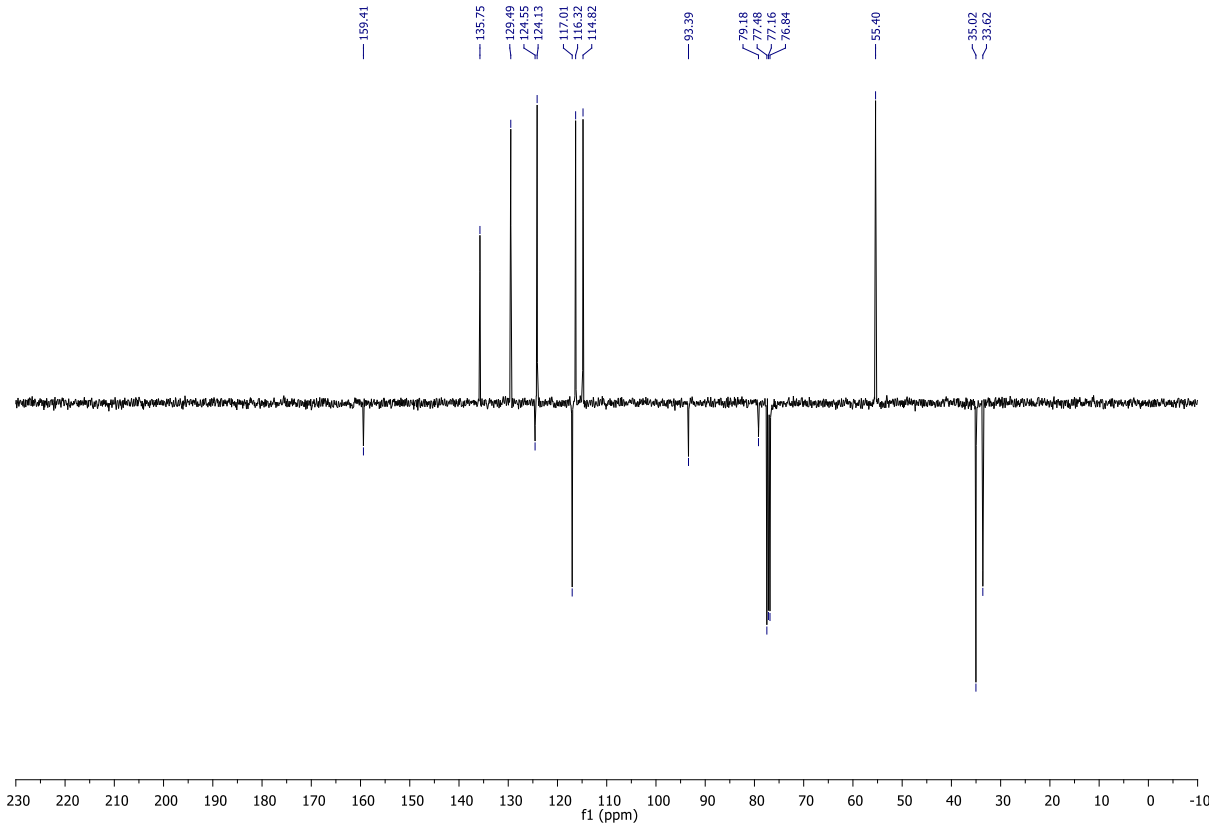

MeO
S
S2n
f1 (ppm)

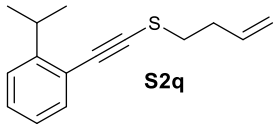

f1 (ppm)


S
Br
S2o
7.27
7.26
7.25
7.24
7.23
7.22
7.10
7.09
7.09
7.08
7.07
7.07
7.06
5.73
5.70
5.67
5.66
5.65
5.64
5.00
5.00
4.99
4.95
4.94
4.94
4.91
4.91
4.91
4.90
2.70
2.68
2.67
2.65
2.40
2.38
2.38
2.35
2.33
2.29
1.37
1.25
2.00
2.31
1.04
2.04
1.99
1.99
f1 (ppm)


135.63
132.94
131.68
122.54
122.31
117.10
92.41
80.84
77.48
77.16
76.84
35.00
33.62
f1 (ppm)


Br
S
S2p
f1 (ppm)


f1 (ppm)


S

S2q

7.41
7.38
7.38
7.28
7.27
7.27
7.26
7.26
7.24
7.15
7.14
7.13
7.12
7.12
7.11
7.11
7.09
5.93
5.90
5.88
5.86
5.84
5.82
5.20
5.19
5.19
5.18
5.14
5.13
5.13
5.10
5.10
5.09
3.47
3.45
3.43
3.40
3.38
2.89
2.87
2.86
2.84
2.62
2.60
2.59
2.57
2.55
1.55
1.28
1.25
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1.08
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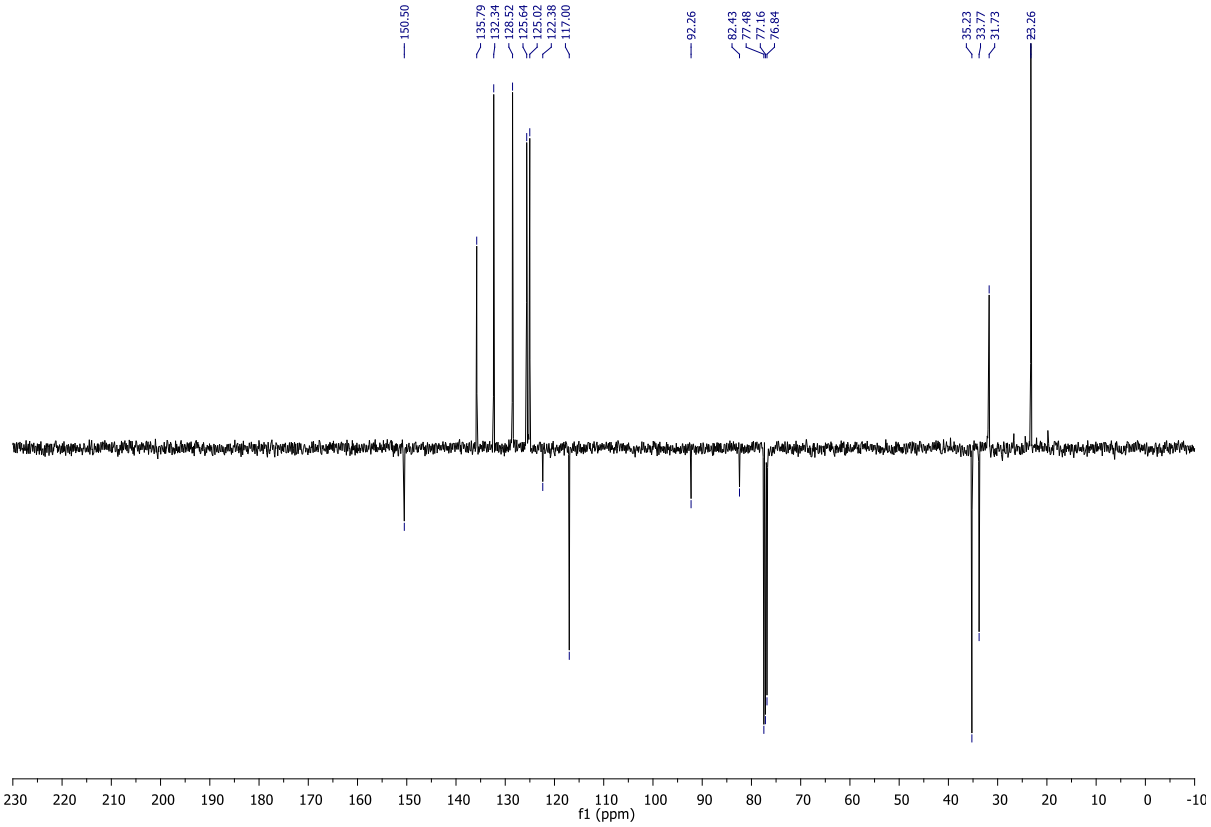
2.07
1.08
2.05
2.14
3.02
3.07
f1 (ppm)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135.79
132.34
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125.64
125.02
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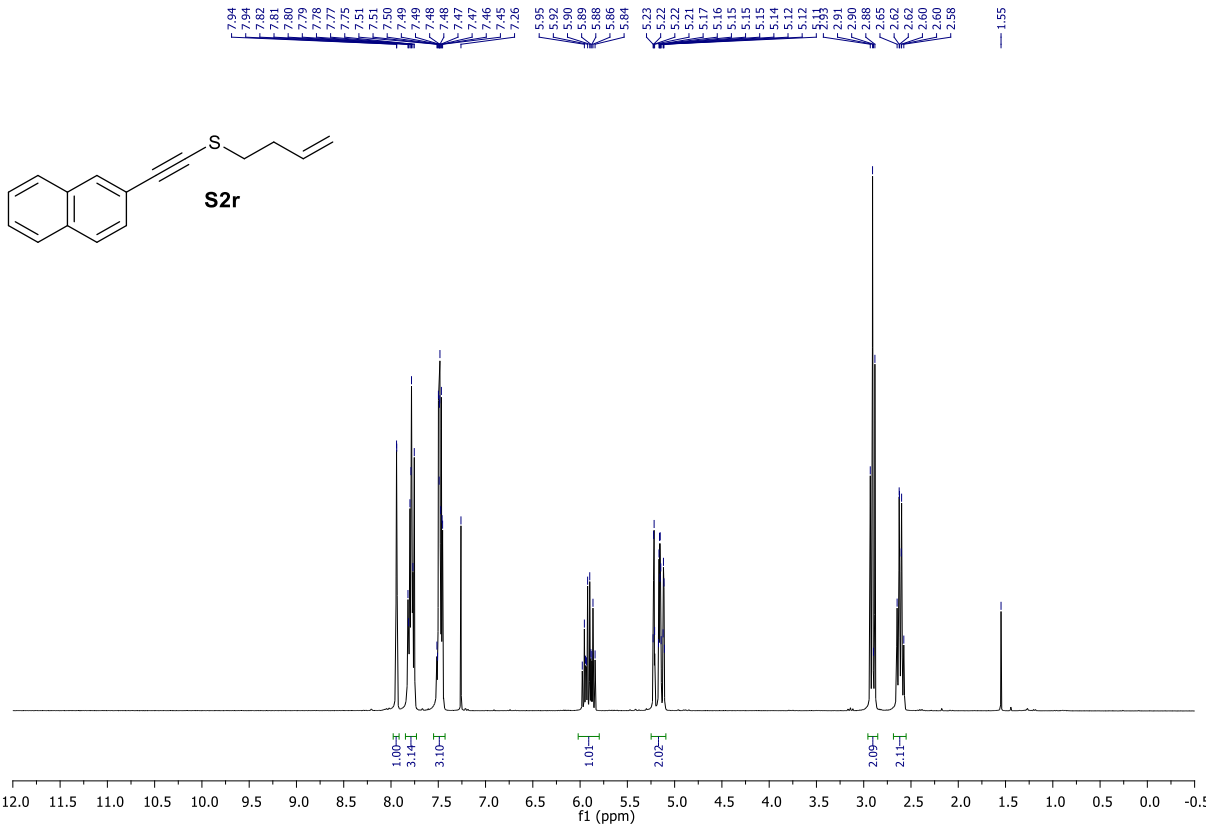
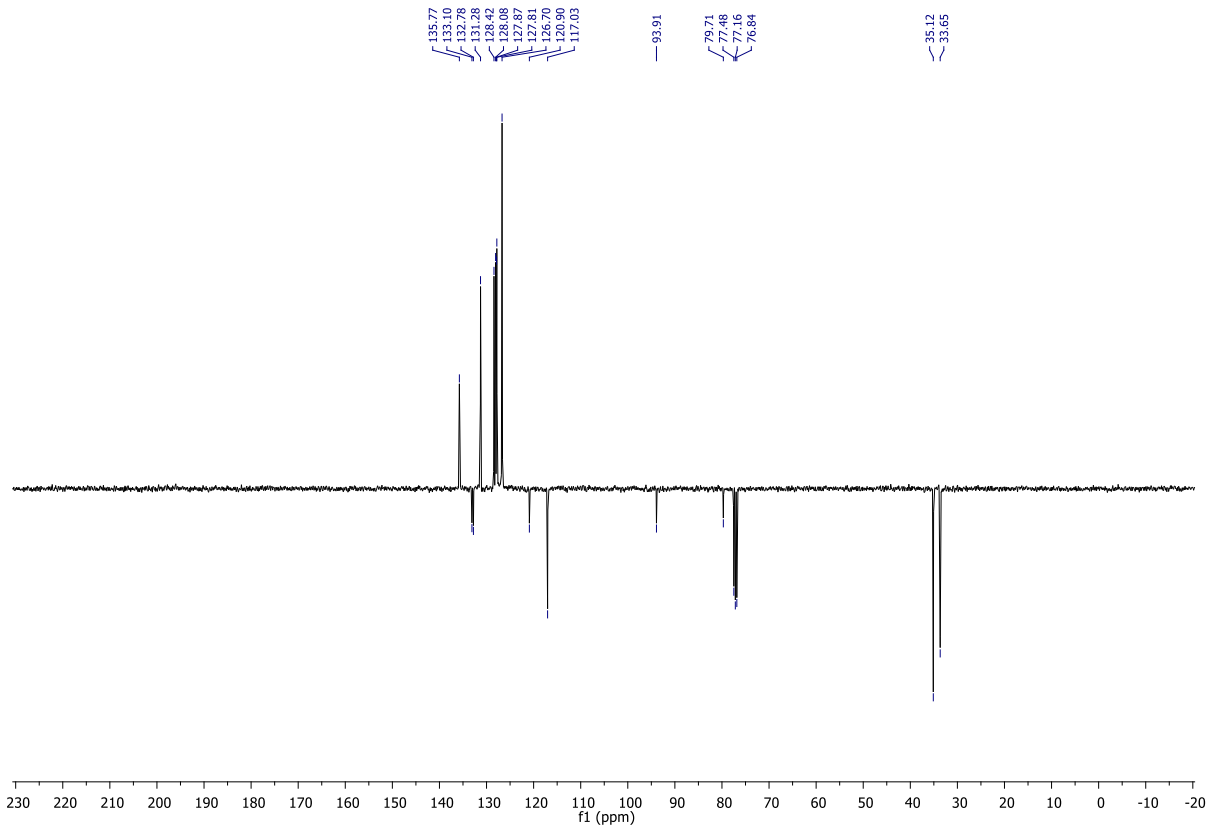
82.43
77.48
77.16
76.84
35.23
33.77
31.73
23.26
f1 (ppm)


7.94
7.94
7.82
7.81
7.80
7.79
7.78
7.77
7.75
7.51
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.26
5.95
5.92
5.90
5.89
5.88
5.86
5.84
5.23
5.22
5.22
5.21
5.17
5.16
5.15
5.15
5.14
5.12
5.12
2.91
2.90
2.88
2.65
2.62
2.62
2.60
2.60
2.58
1.55
S
S2r
1.00
3.14
3.10
1.01
2.02
2.09
2.11
f1 (ppm)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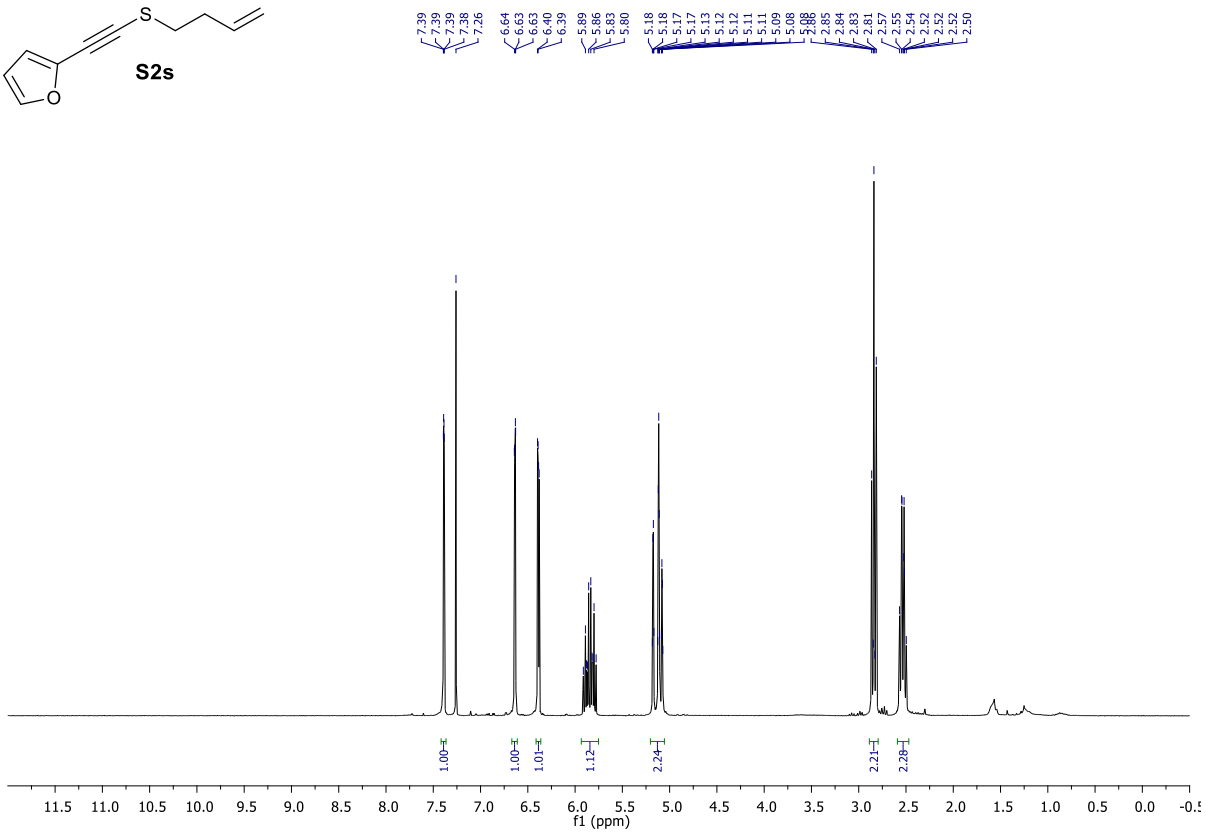
131.28
128.42
128.08
127.87
127.81
126.70
120.90
117.03
93.91
79.71
77.48
77.16
76.84
35.12
33.65
f1 (ppm)


S
O
S2s
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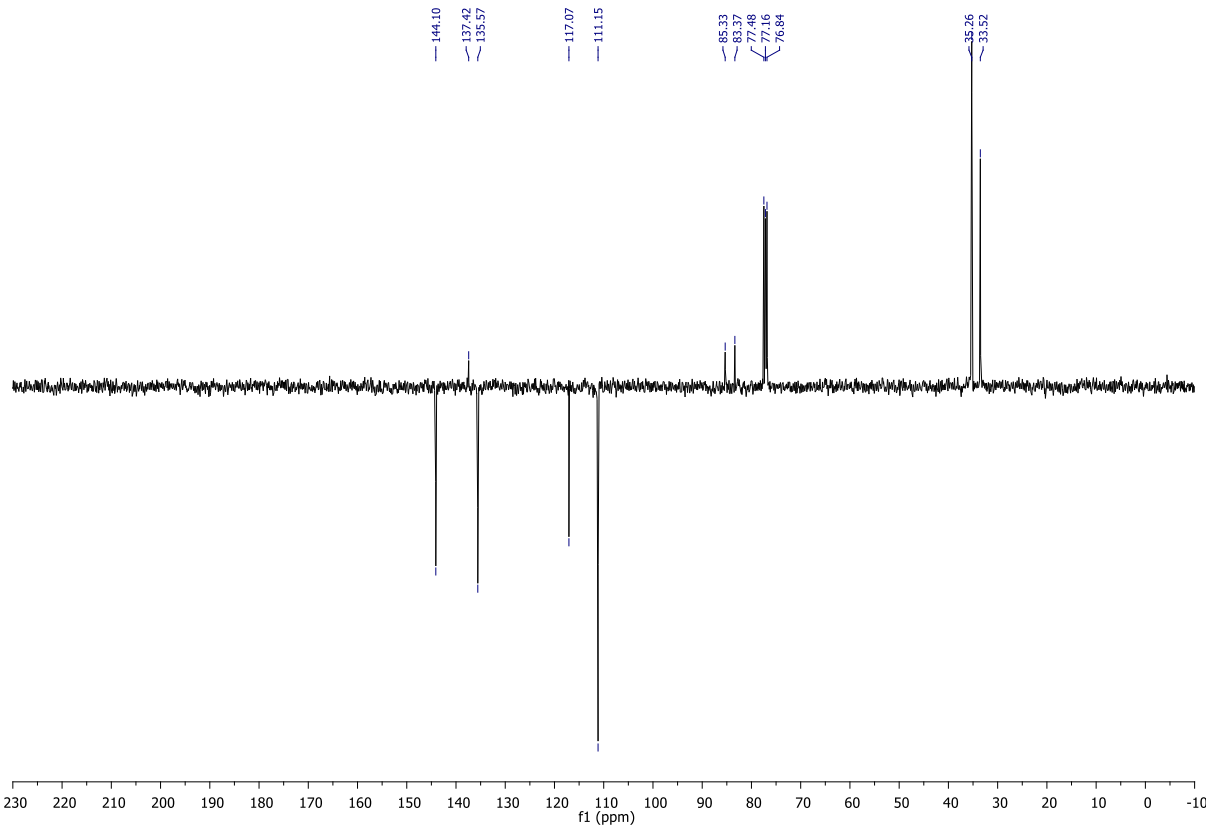
7.39
7.39
7.38
7.26
6.64
6.63
6.63
6.40
6.39
5.89
5.86
5.83
5.80
5.18
5.18
5.17
5.17
5.13
5.12
5.12
5.11
5.11
5.09
5.08
5.08
2.88
2.85
2.84
2.83
2.81
2.57
2.55
2.54
2.52
2.52
2.52
2.50
1.00
1.00
1.01
1.12
2.24
2.21
2.28
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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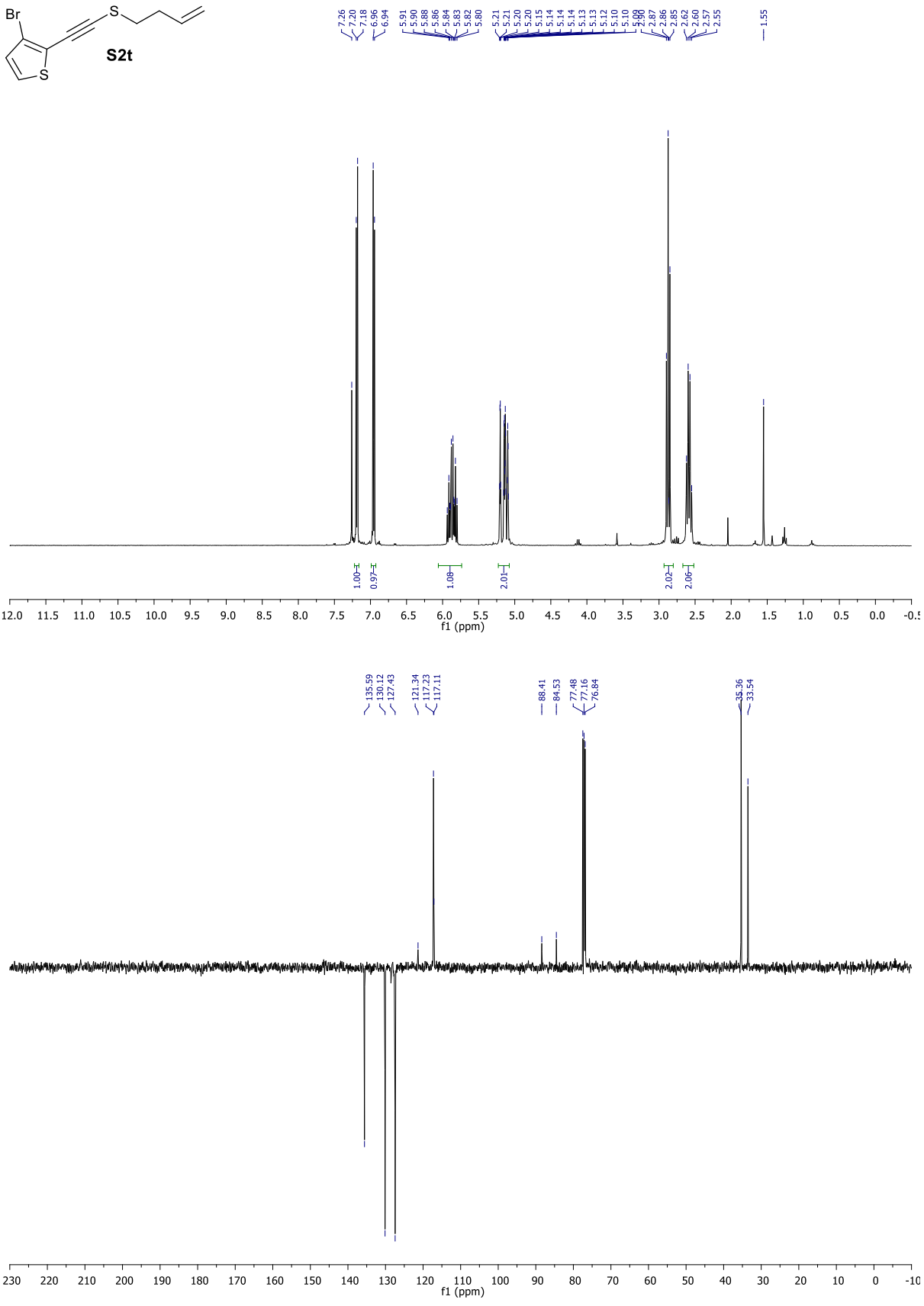
137.42
135.57
117.07
111.15
85.33
83.37
77.48
77.16
76.84
35.26
33.52
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
S
S
S2t
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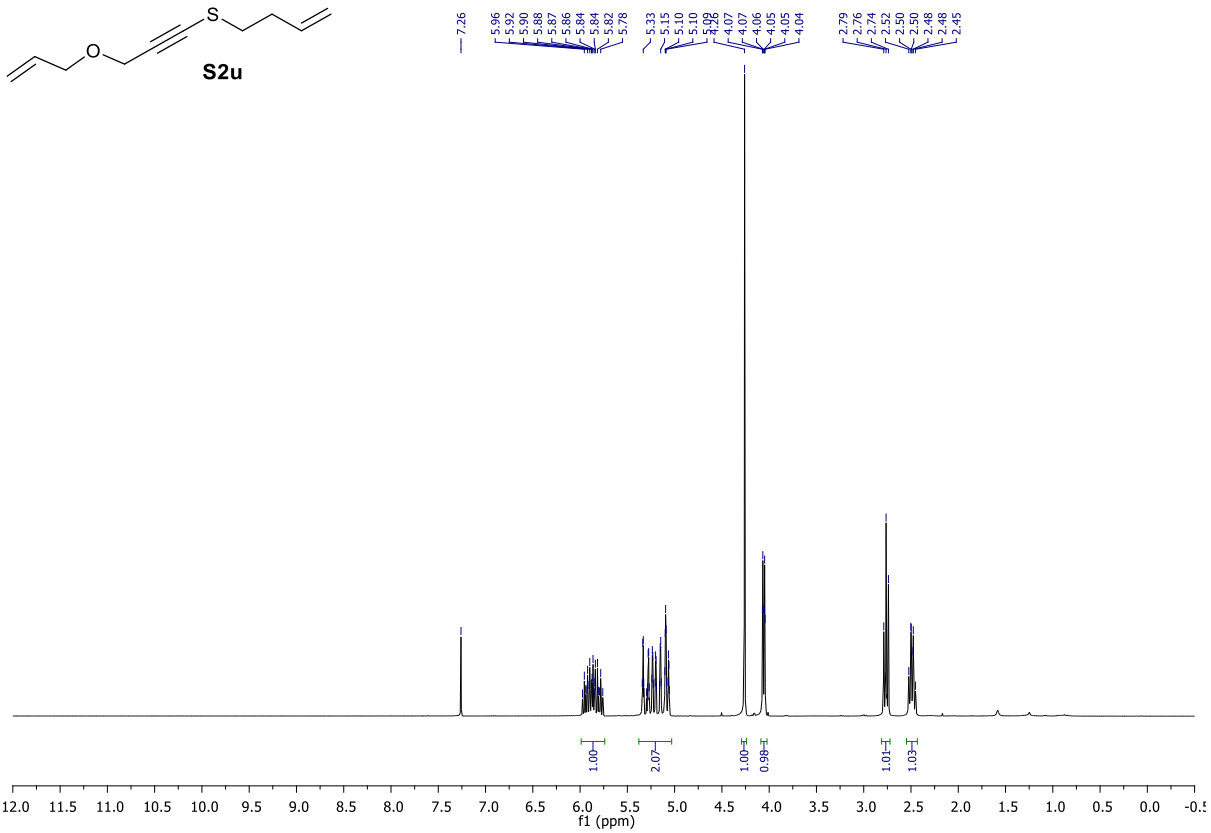
7.20
7.18
6.96
6.94
5.91
5.90
5.88
5.86
5.84
5.83
5.82
5.80
5.21
5.21
5.20
5.20
5.15
5.14
5.14
5.13
5.13
5.12
5.10
5.10
5.08
5.08
2.90
2.87
2.86
2.85
2.62
2.60
2.57
2.55
1.55
1.00
0.97
1.08
2.01
2.02
2.06
f1 (ppm)
135.59
130.12
127.43
121.34
117.23
117.11
88.41
84.53
77.48
77.16
76.84
35.36
33.54
f1 (ppm)


S2u
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5.90
5.88
5.87
5.86
5.84
5.84
5.82
5.78
5.33
5.15
5.10
5.10
5.08
4.28
4.07
4.07
4.06
4.05
4.05
4.04
2.79
2.76
2.74
2.52
2.50
2.50
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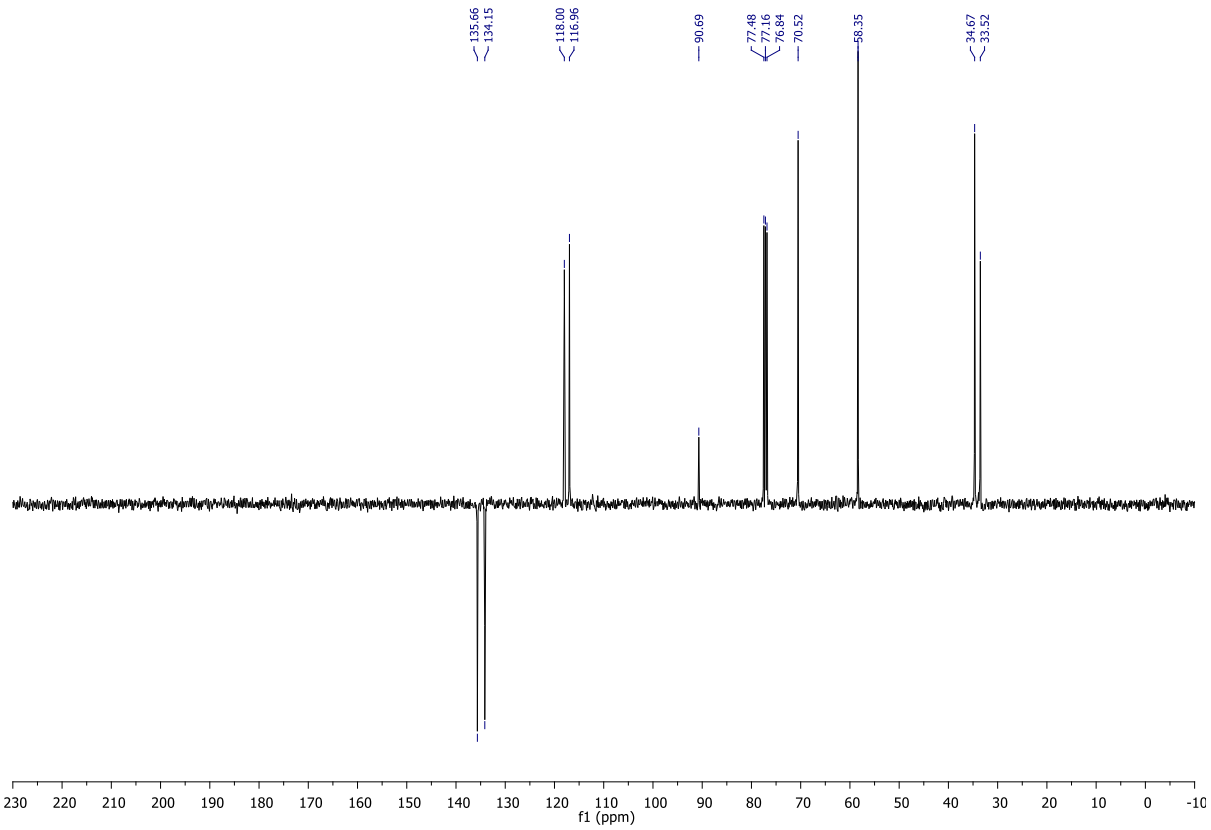
2.48
2.45
1.00
2.07
1.00
0.98
1.01
1.03
f1 (ppm)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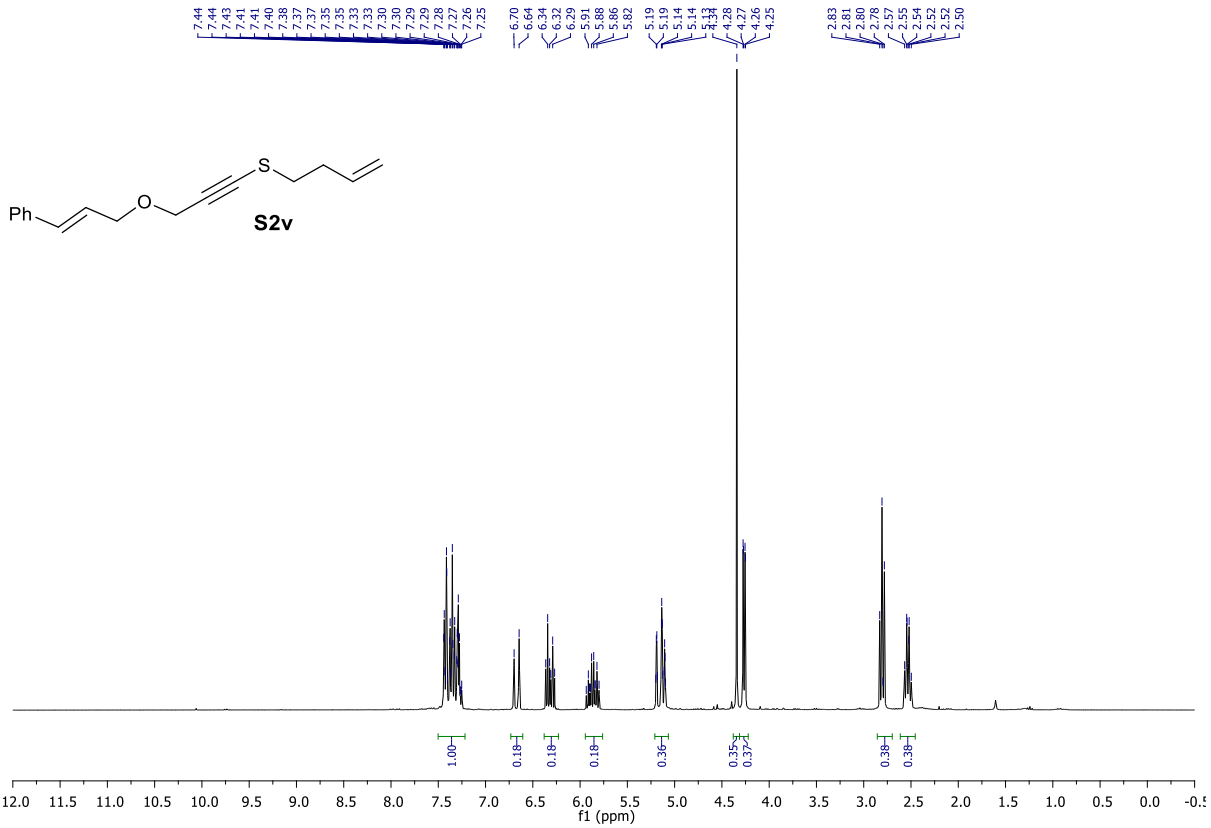
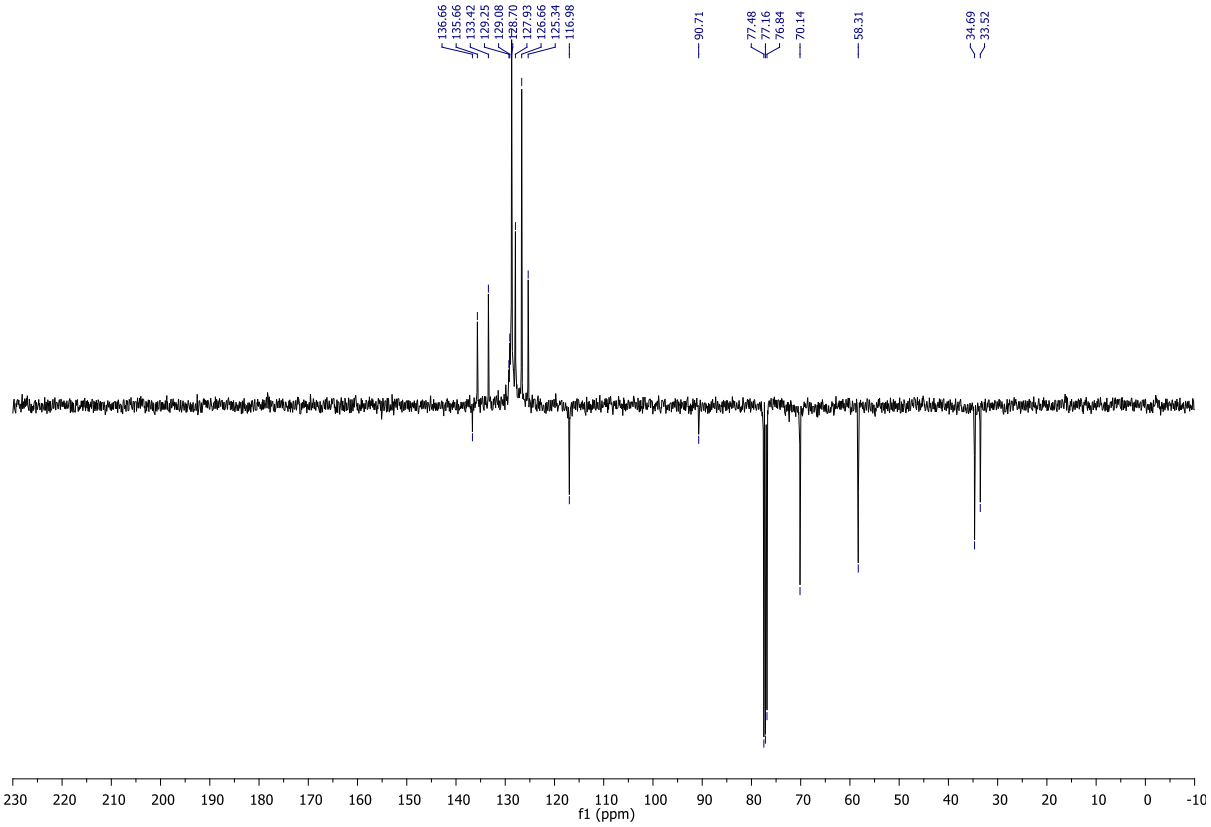
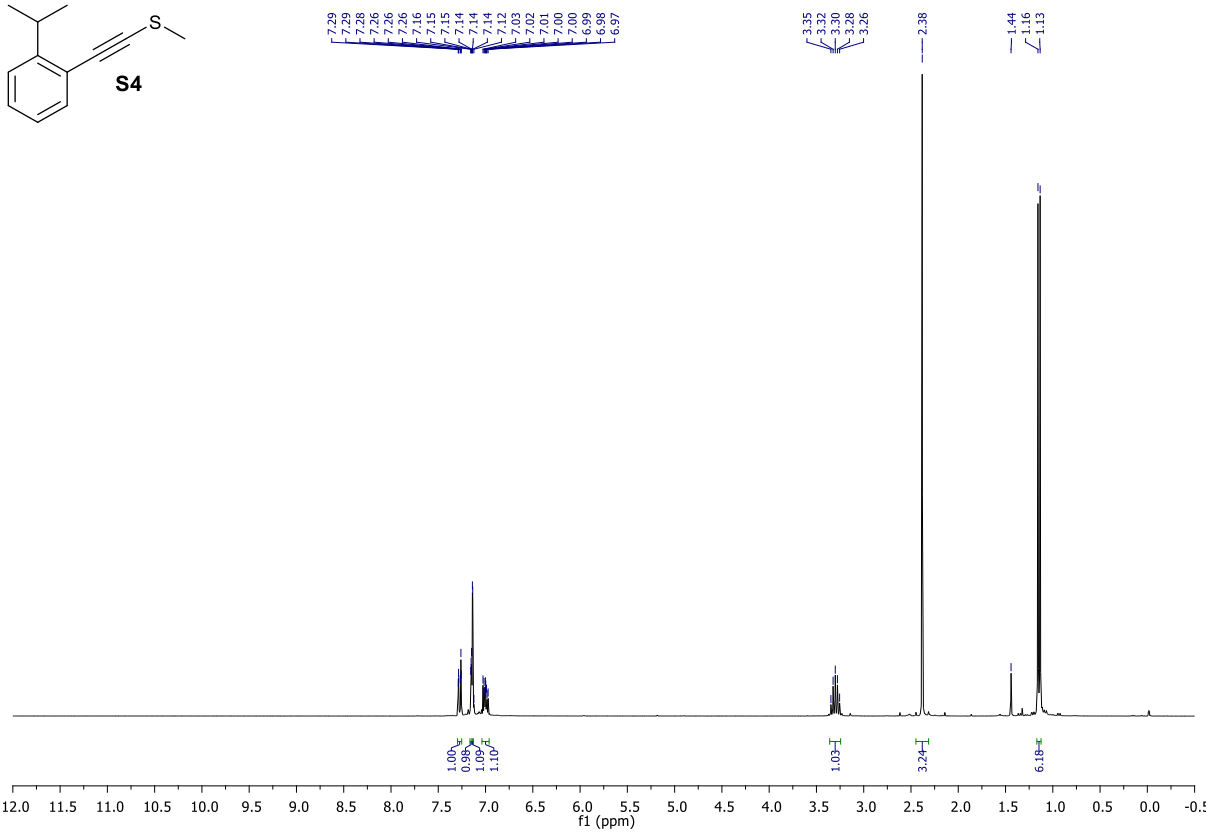
76.84
70.52
58.35
34.67
33.52
f1 (ppm)


Ph
O
S
S2v
f1 (ppm)


f1 (ppm)


S4
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7.28
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7.26
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7.16
7.15
7.15
7.14
7.14
7.14
7.12
7.03
7.02
7.01
7.00
7.00
6.99
6.98
6.97
3.35
3.32
3.30
3.28
3.26
2.38
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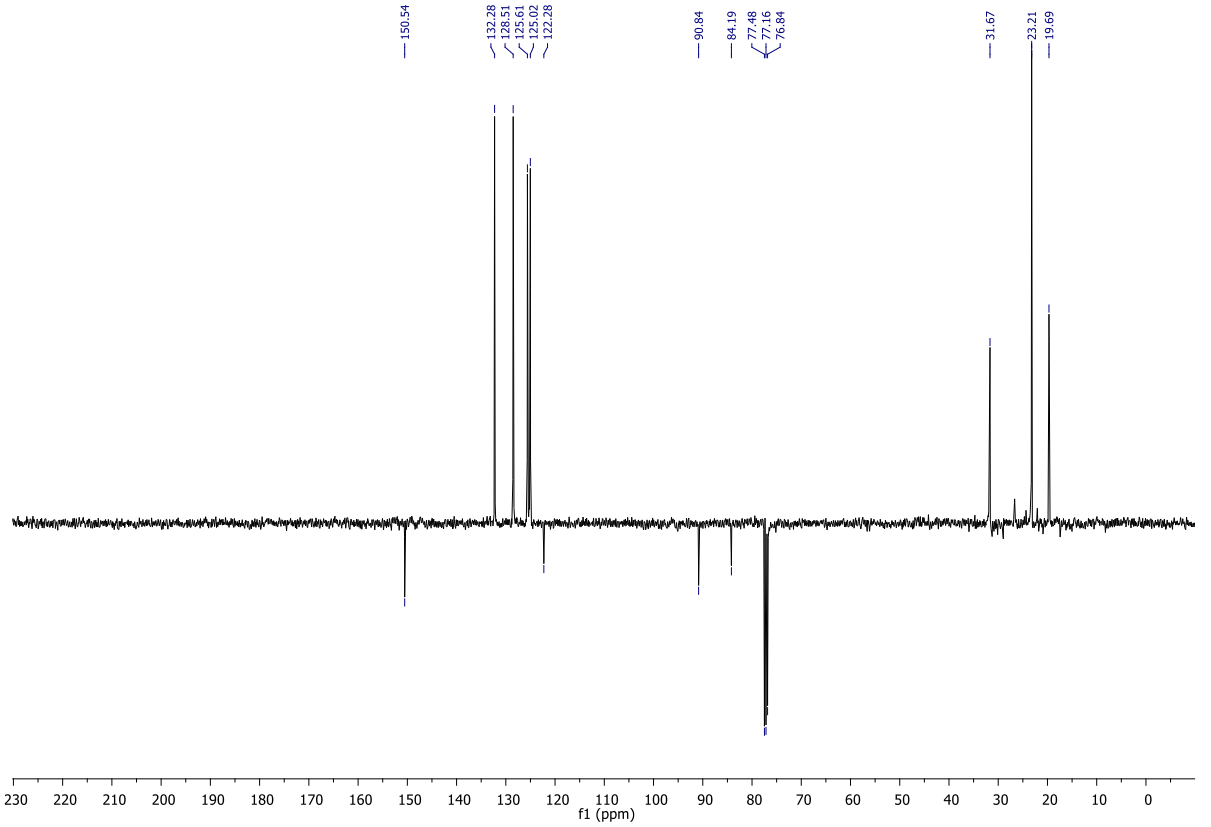
1.13
1.00
0.98
1.09
1.10
1.03
3.24
6.18
f1 (ppm)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84.19
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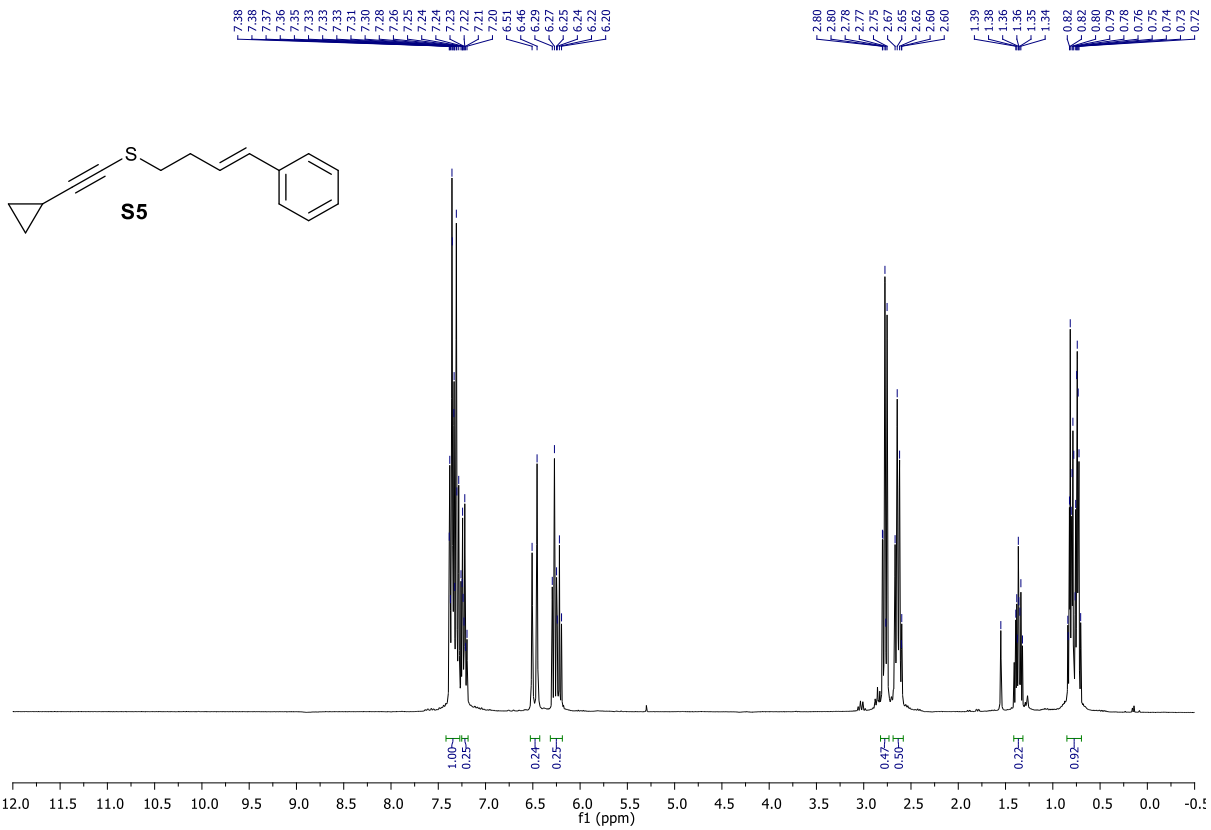
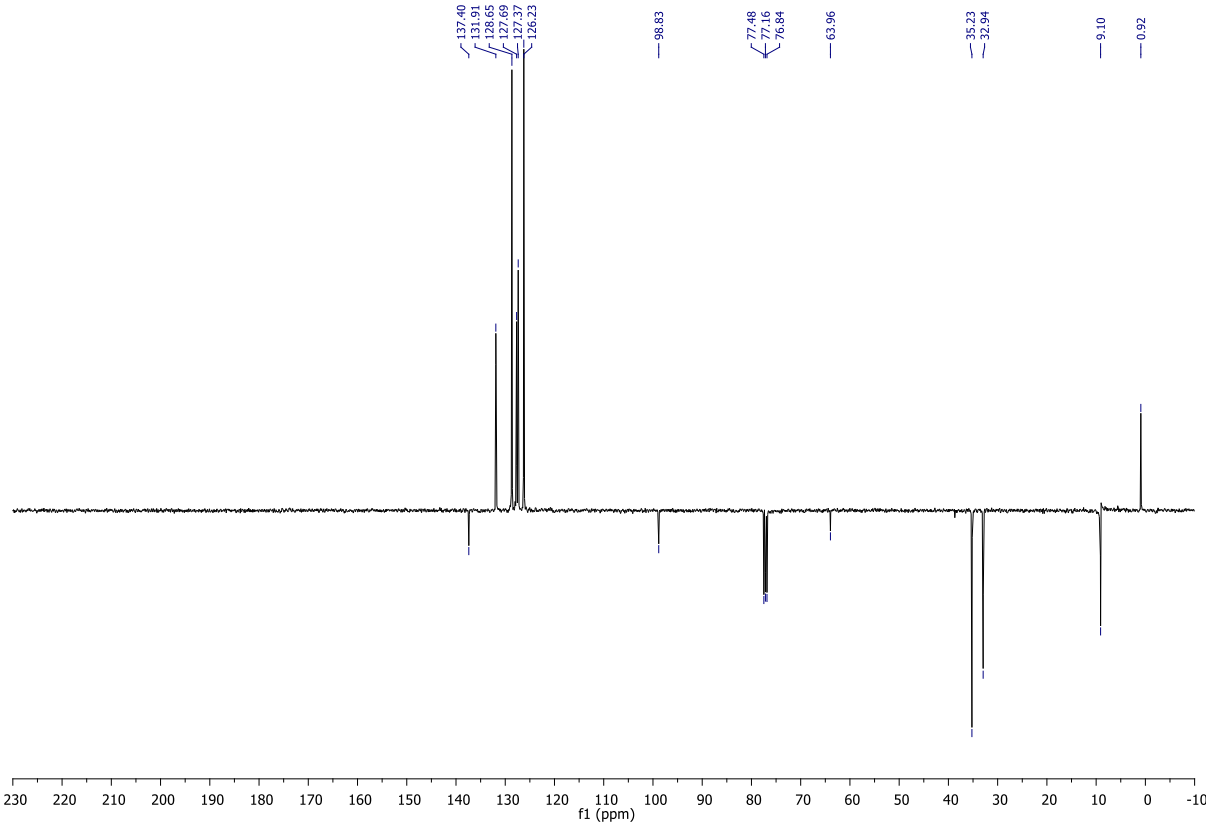
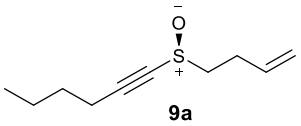
77.16
76.84
31.67
23.21
19.69
f1 (ppm)

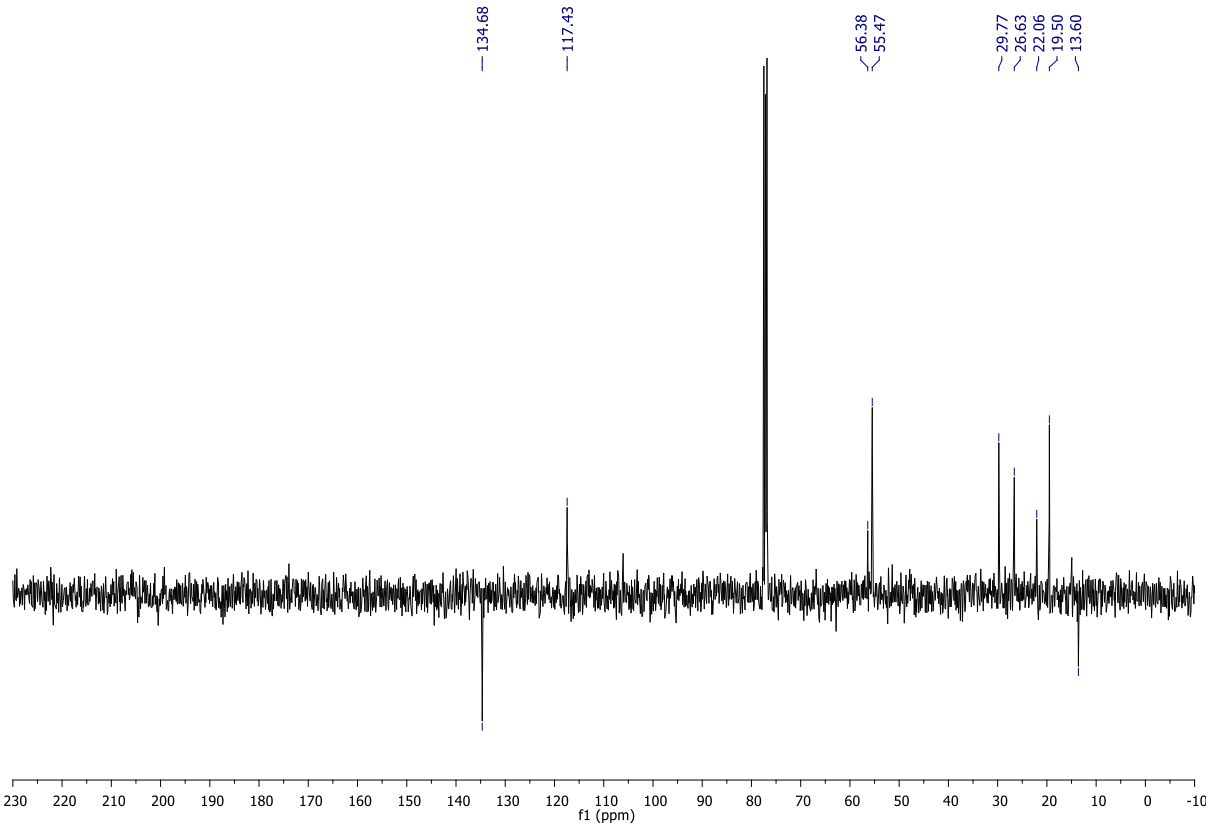

S
S5
f1 (ppm)

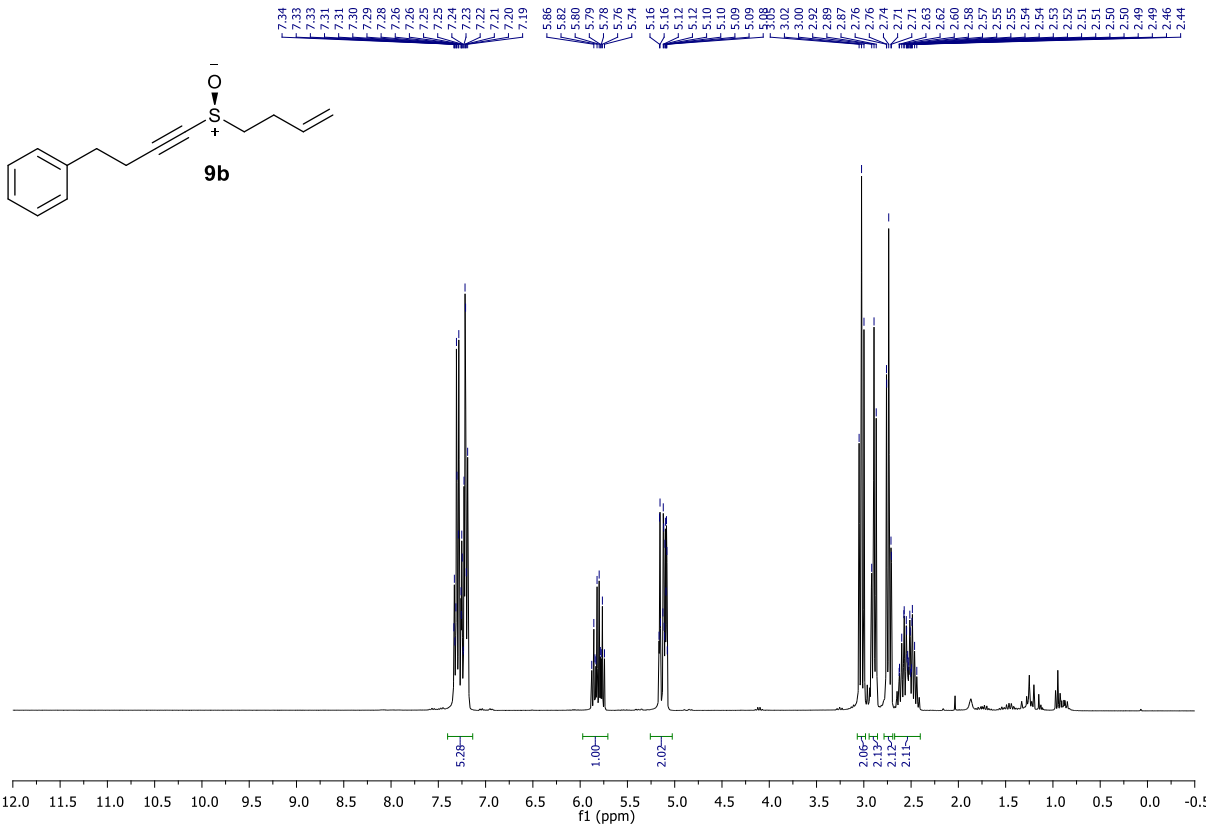

f1 (ppm)

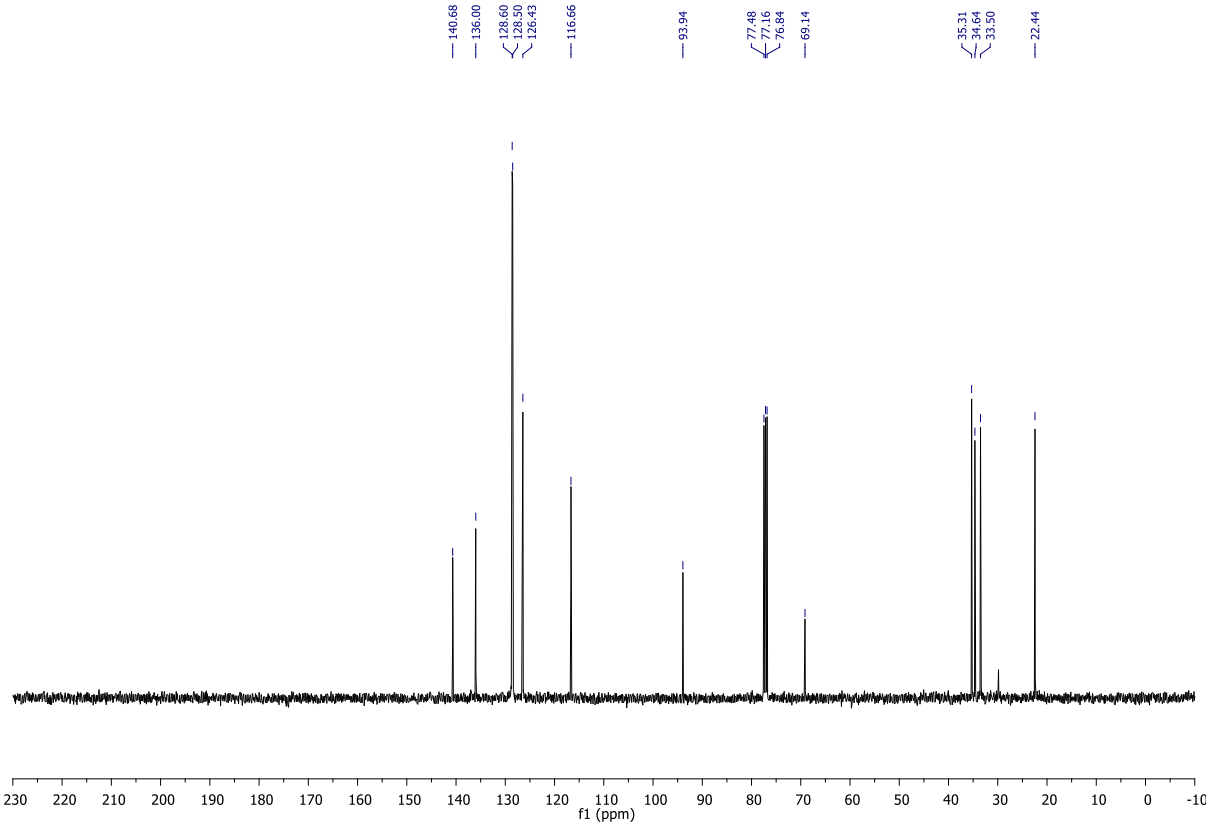
Alkynyl Sulfoxides

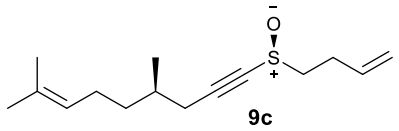


9a




9b
f1 (ppm)


f1 (ppm)



9c

7.26
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5.88
5.87
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5.82
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5.20
5.19
5.14
5.14
5.13
5.10
5.10
5.07
5.07
5.06
5.05
5.04
3.11
3.09
3.06
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2.64
2.62
2.61
2.59
2.45
2.42
2.40
2.36
2.34
2.28
1.99
1.97
1.78
1.75
1.68
1.60
1.42
1.30
1.28
1.02
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1.00
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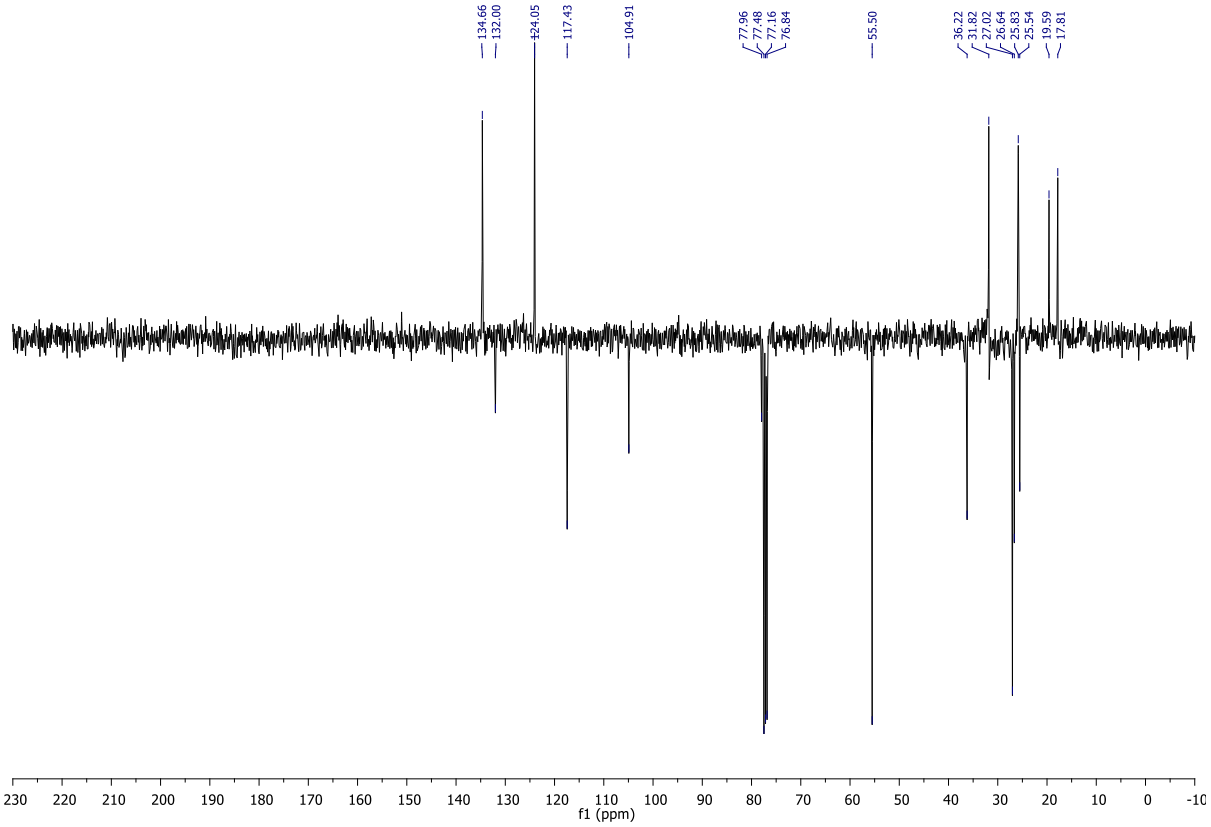
3.04
1.16
1.21
3.04
f1 (ppm)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76.84
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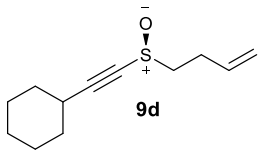
36.22
31.82
27.02
26.64
25.83
25.54
19.59
17.81
f1 (ppm)


O
S
+
9d

7.26
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5.87
5.85
5.84
5.83
5.81
5.79
5.20
5.14
5.13
5.09
3.12
3.09
3.07
2.62
2.61
2.59
2.59
1.86
1.84
1.82
1.81
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1.71
1.70
1.68
1.54
1.52
1.49
1.37
1.34
1.33
1.31
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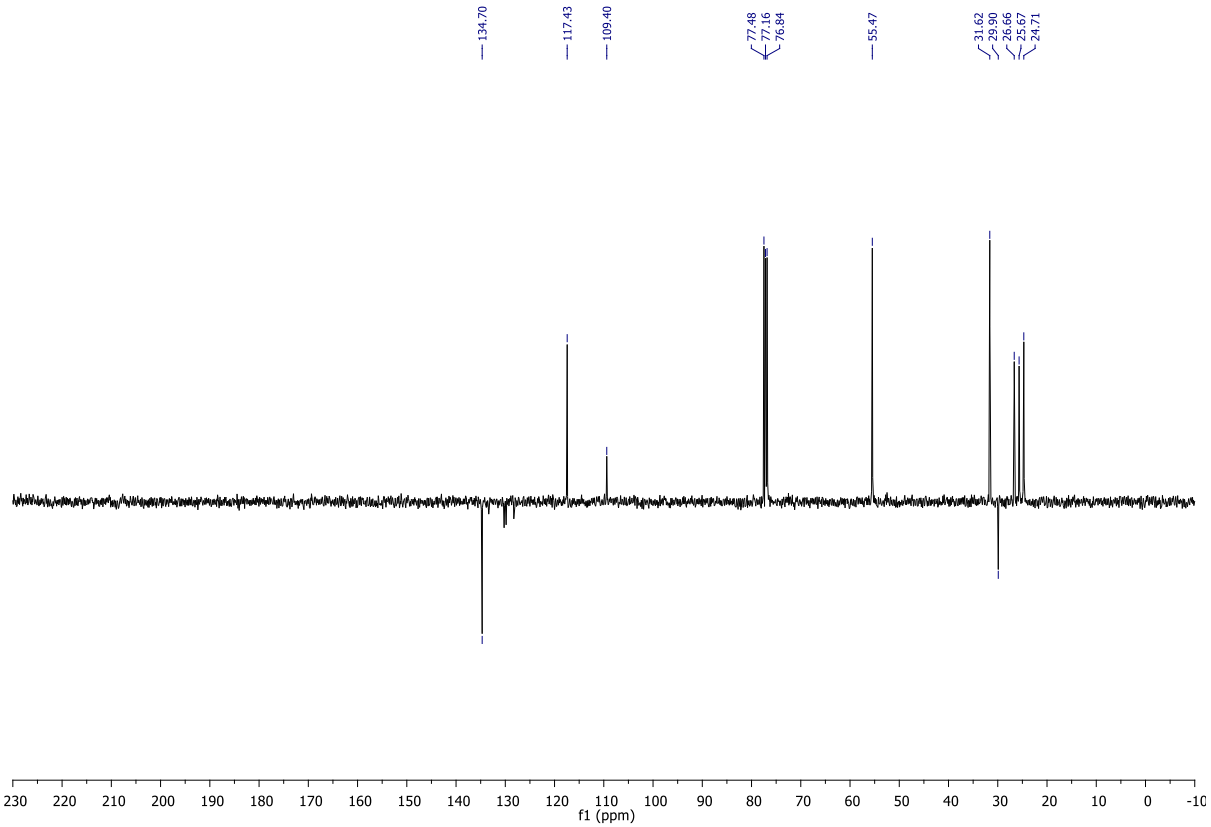
1.04
0.59
1.89
3.09
1.99
2.11
3.07
3.40
f1 (ppm)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29.90
26.66
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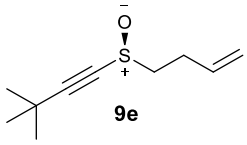
24.71
f1 (ppm)



9e

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5.91
5.90
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5.85
5.84
5.83
5.82
5.80
5.21
5.20
5.20
5.19
5.15
5.14
5.14
5.13
5.13
5.11
5.10
5.10
5.10
3.11
3.08
3.05
2.69
2.69
2.64
2.63
2.62
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2.58
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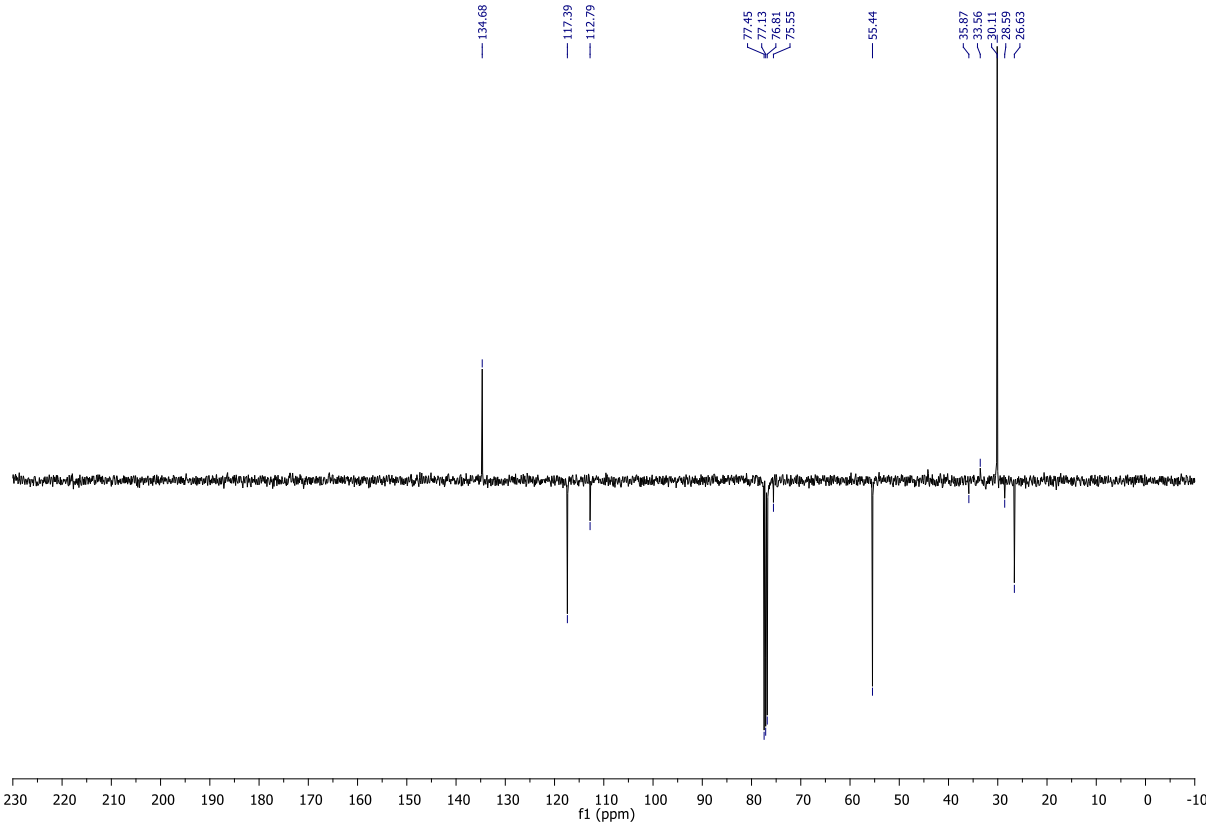
2.54
2.53
1.29
0.98
2.02
1.89
2.05
9.00
f1 (ppm)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55.44
35.87
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30.11
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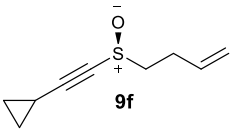
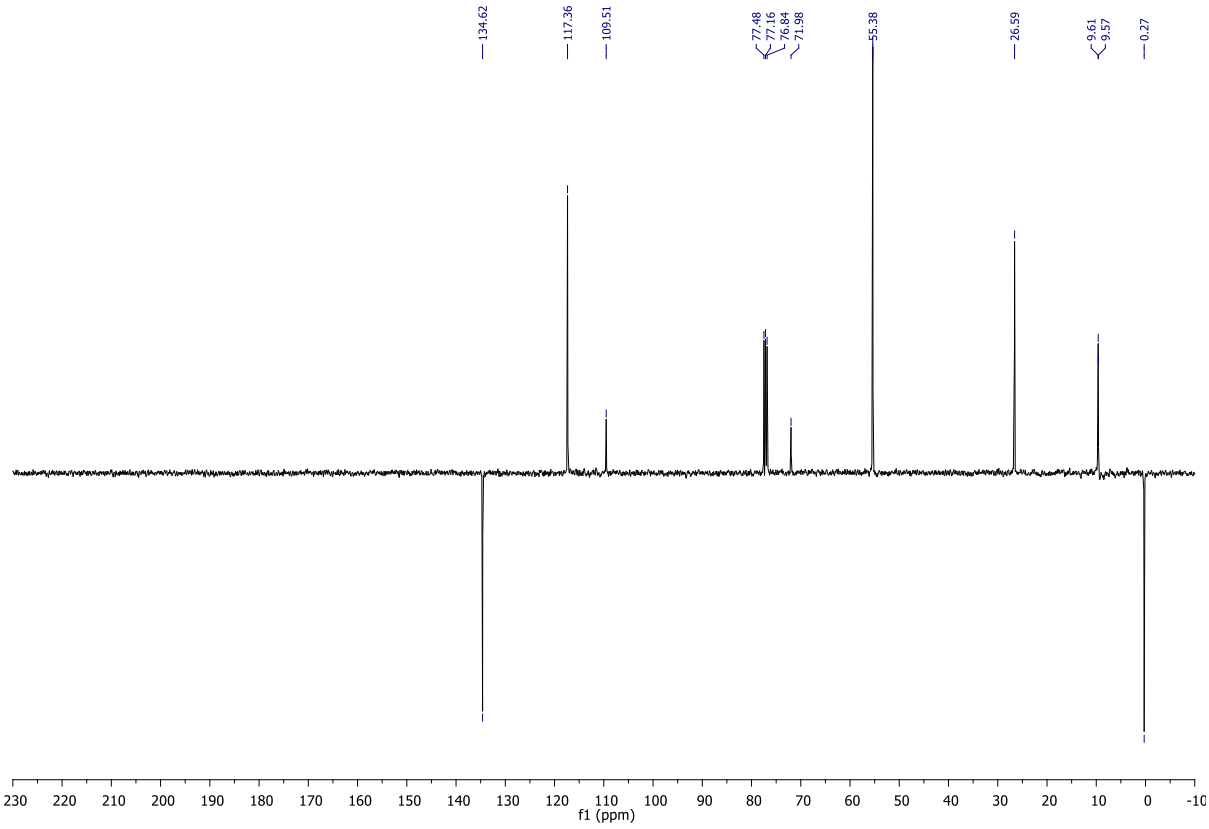
26.63
f1 (ppm)



9f

7.23
5.85
5.83
5.82
5.81
5.80
5.77
5.76
5.75
5.74
5.72
5.13
5.12
5.08
5.07
5.06
5.04
5.03
5.02
3.03
3.00
2.98
2.57
2.54
2.53
2.50
1.42
1.40
1.37
0.93
0.92
0.91
0.90
0.89
0.87
0.86
0.85
0.84
0.83
1.00
1.99
2.01
2.03
1.12
4.32
f1 (ppm)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117.36
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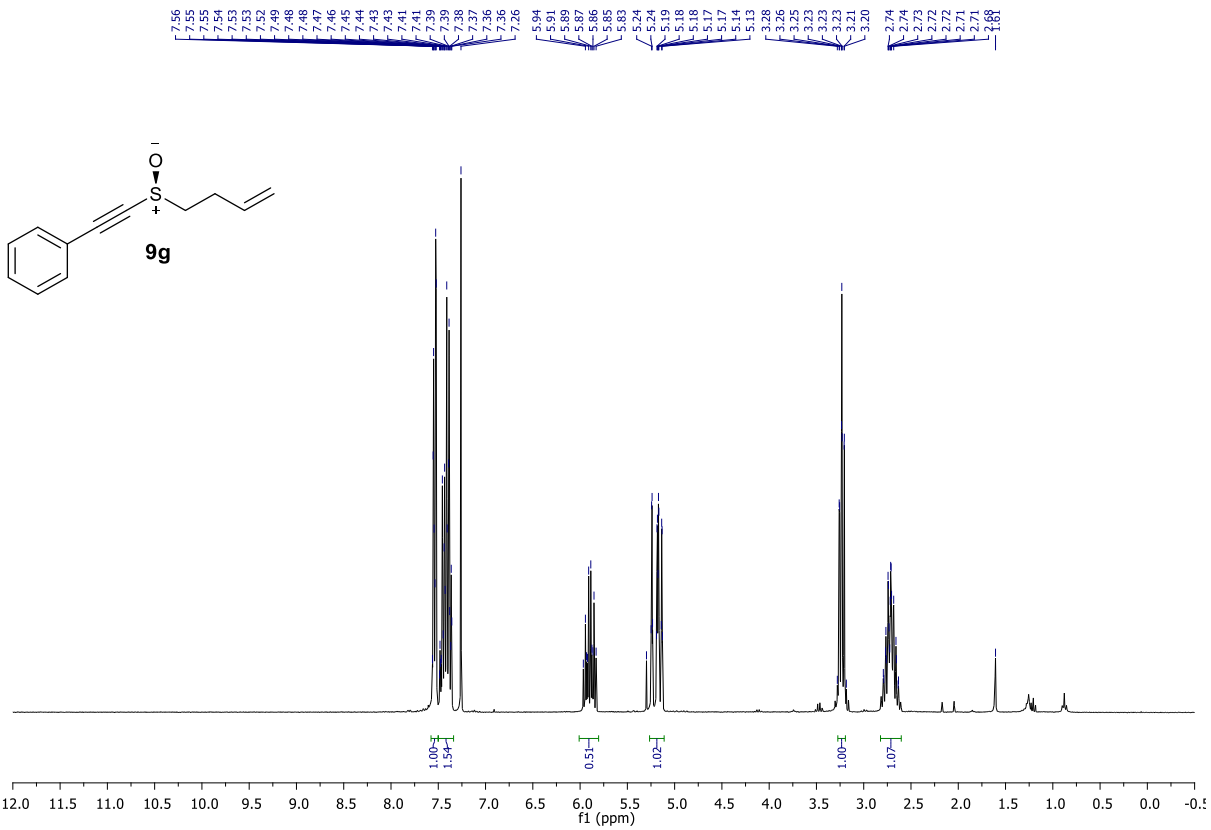
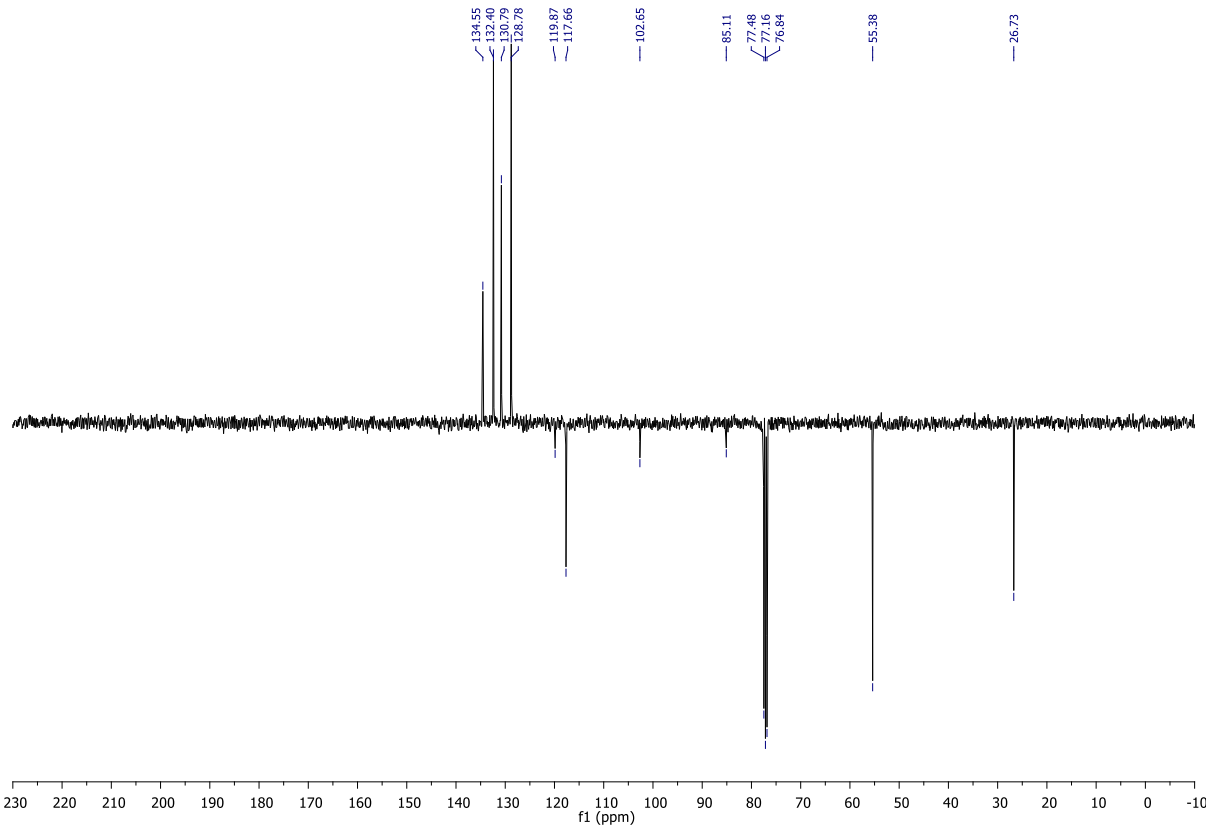
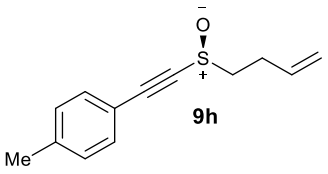
77.48
77.16
76.84
71.98
55.38
26.59
9.61
9.57
0.27
f1 (ppm)


9g
f1 (ppm)


f1 (ppm)


O
S
+
Me

9h

7.44
7.42
7.41
7.26
7.20
7.17
5.94
5.93
5.91
5.88
5.87
5.86
5.85
5.83
5.24
5.23
5.23
5.18
5.17
5.17
5.16
5.16
5.13
5.13
3.24
3.24
3.22
3.21
3.19
3.19
2.73
2.73
2.72
2.71
2.70
2.70
2.68
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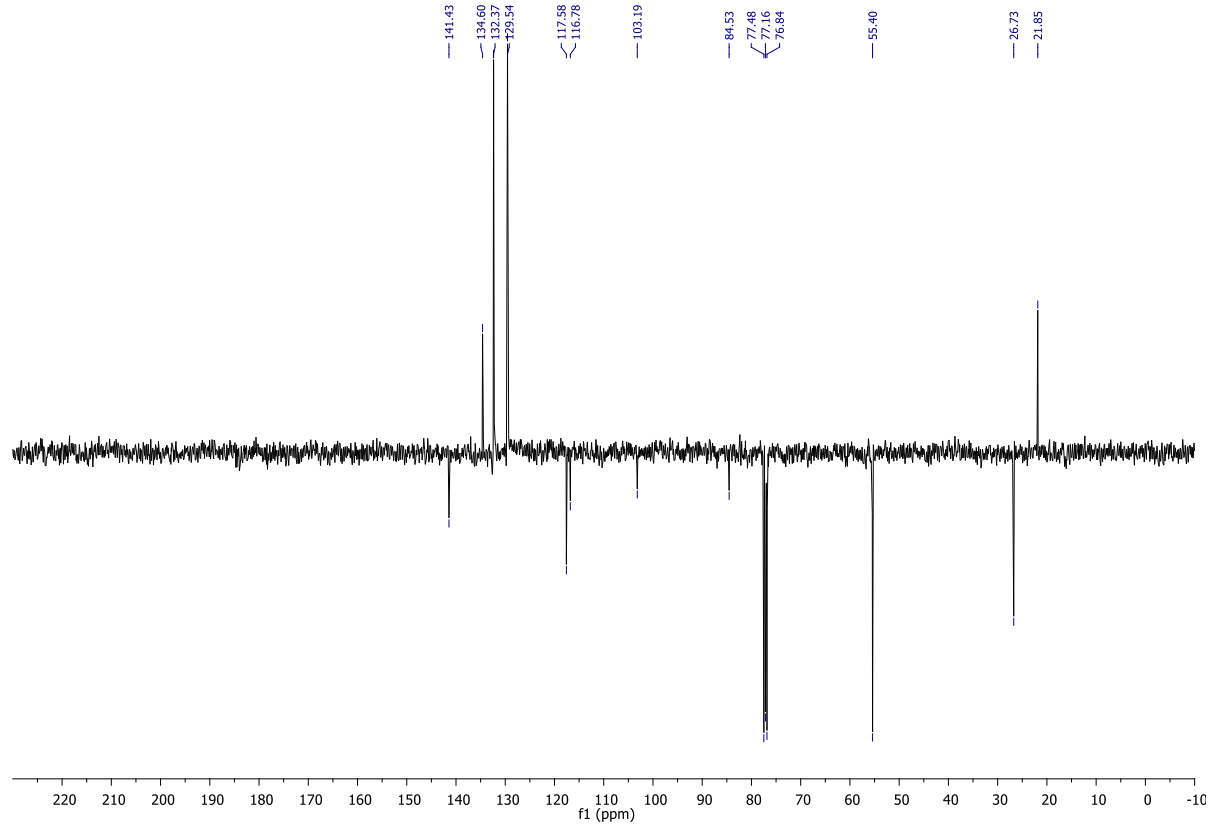
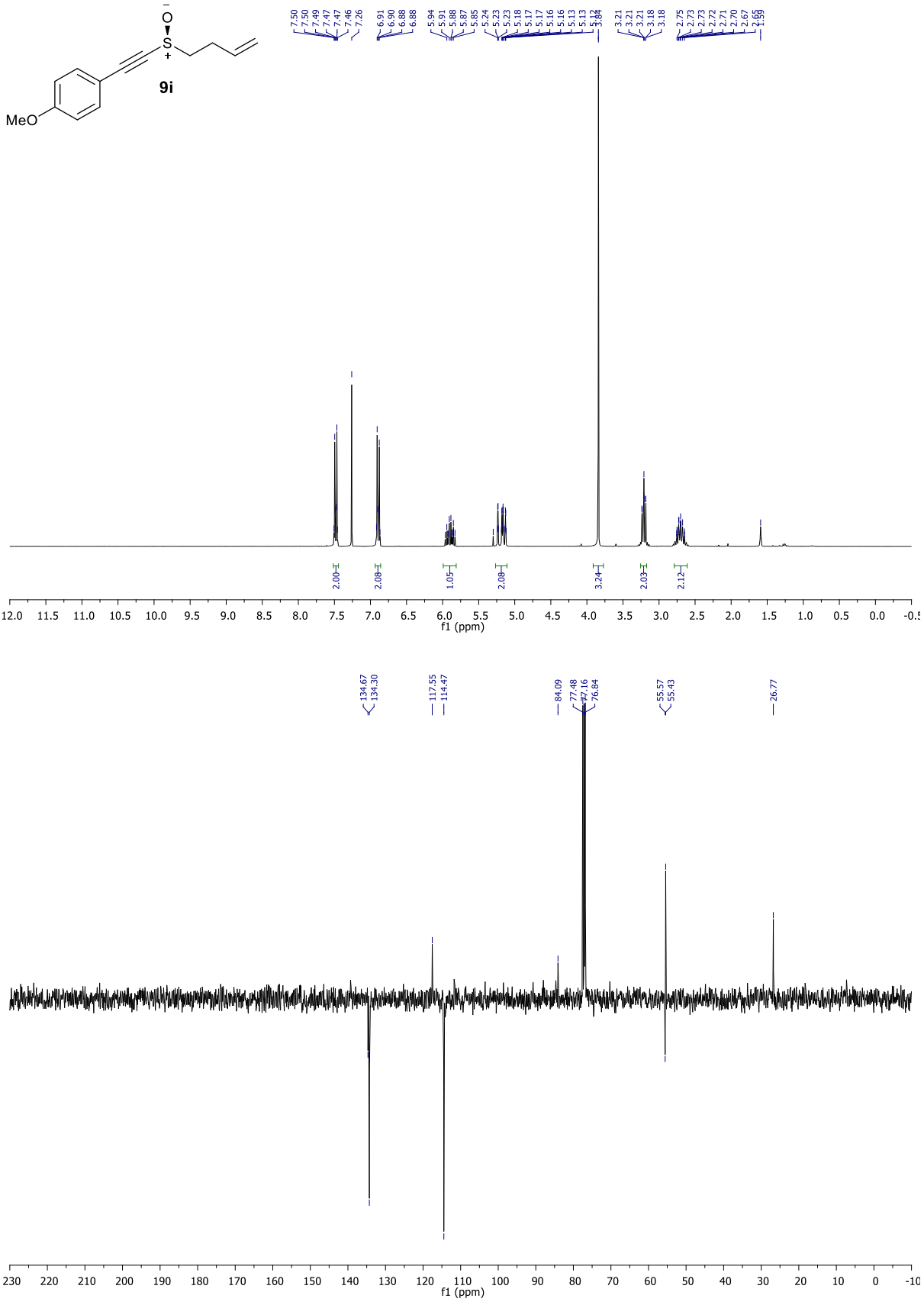
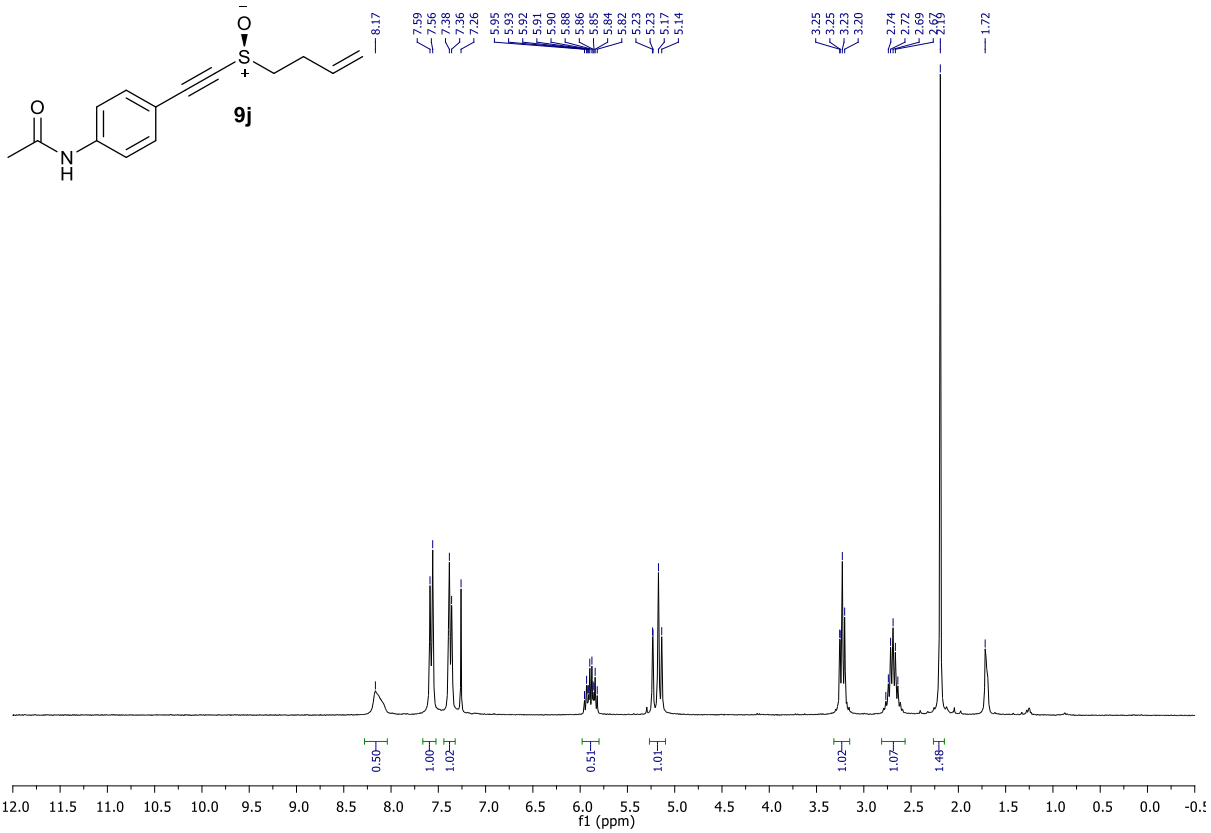
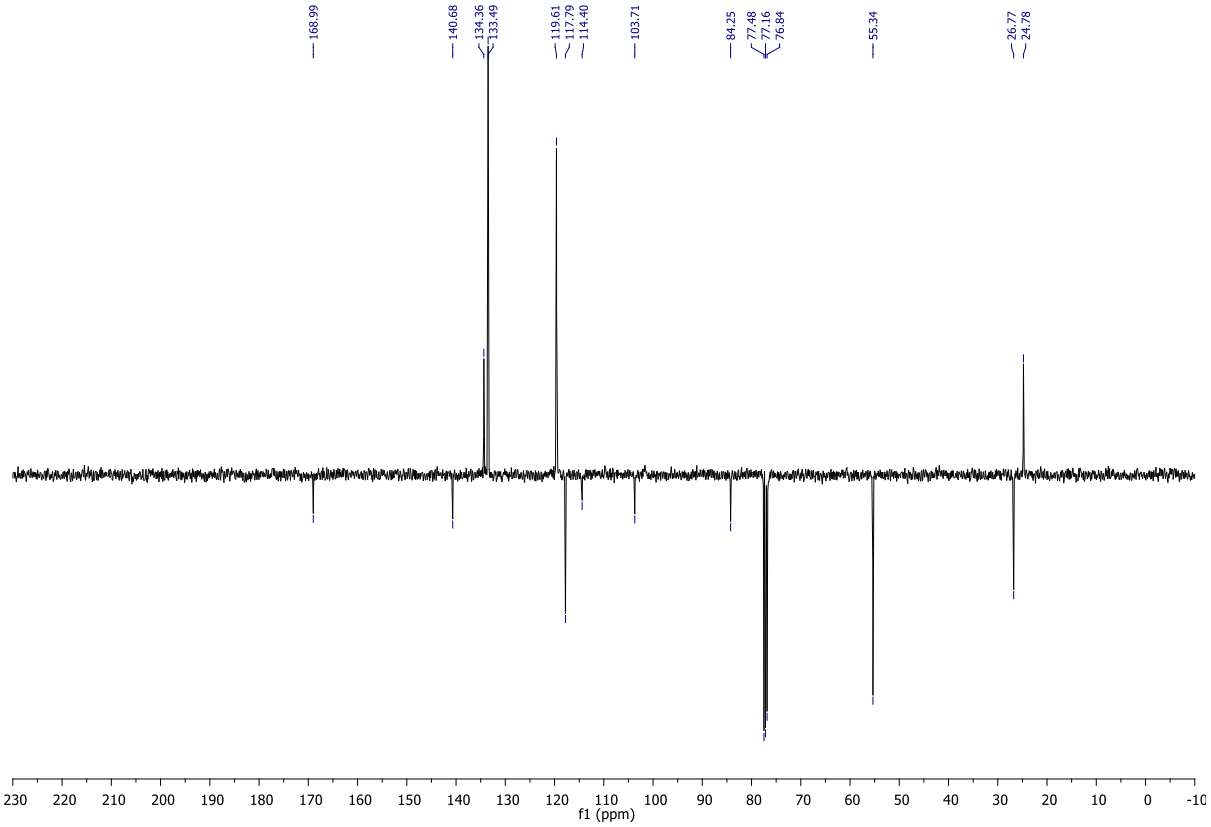
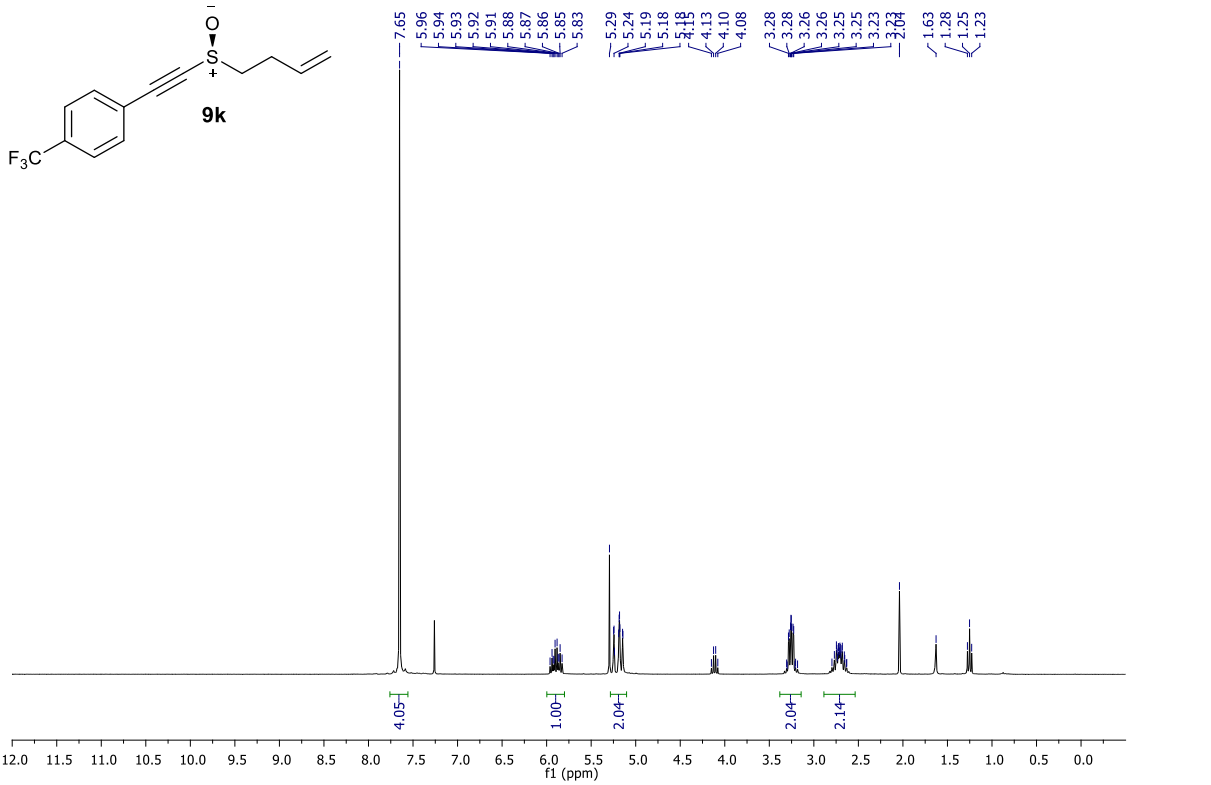
1.80
1.89
0.92
1.87
1.94
2.04
3.00
f1 (ppm)

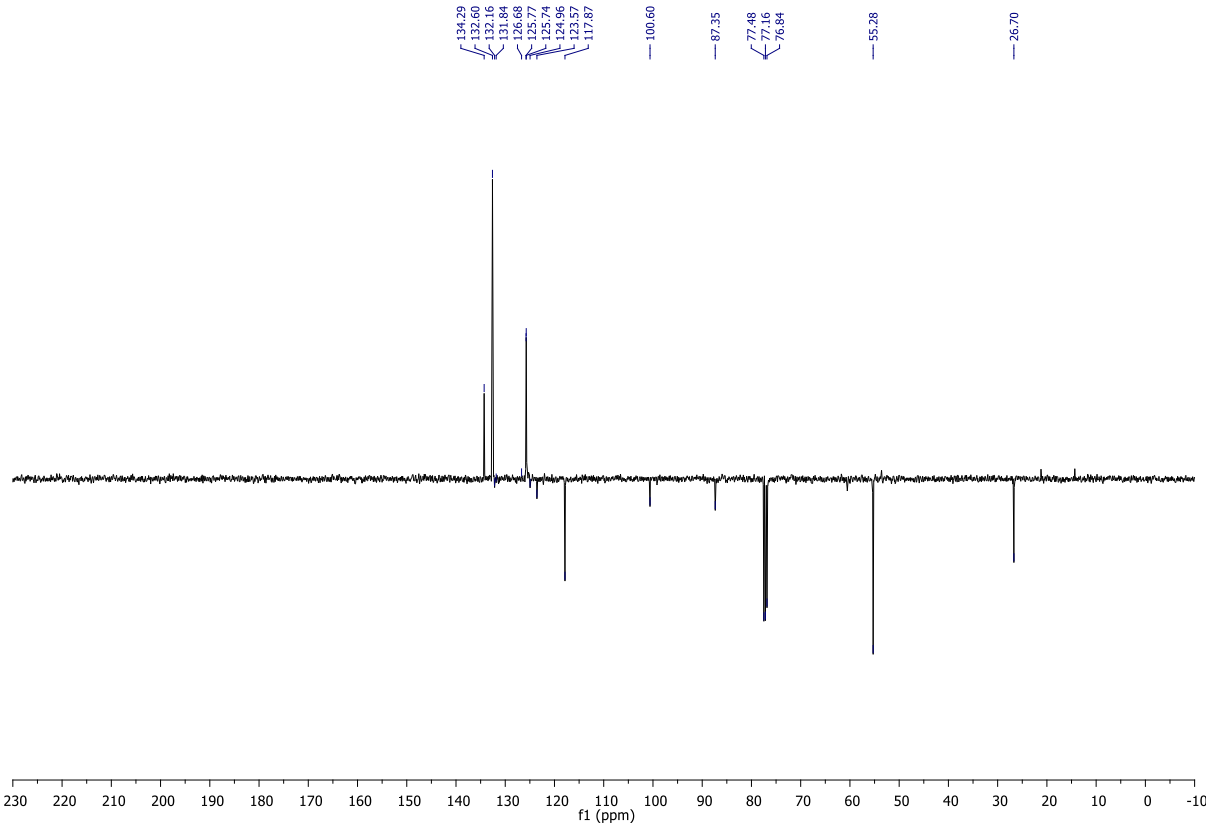

141.43
134.60
132.37
129.54
117.58
116.78
103.19
84.53
77.48
77.16
76.84
55.40
26.73
21.85
f1 (ppm)


9i
MeO
f1 (ppm)
f1 (ppm)


9j
8.17
7.59
7.56
7.38
7.36
7.26
5.95
5.93
5.92
5.91
5.90
5.88
5.86
5.85
5.84
5.82
5.23
5.23
5.17
5.14
3.25
3.25
3.23
3.20
2.74
2.72
2.69
2.67
2.19
1.72
0.50
1.00
1.02
0.51
1.01
1.02
1.07
1.48
f1 (ppm)


168.99
140.68
134.36
133.49
119.61
117.79
114.40
103.71
84.25
77.48
77.16
76.84
55.34
26.77
24.78
f1 (ppm)


9k
F3C
7.65
5.96
5.94
5.93
5.92
5.91
5.88
5.87
5.86
5.85
5.83
5.29
5.24
5.19
5.18
4.13
4.10
4.08
3.28
3.26
3.25
3.23
2.04
1.63
1.28
1.25
1.23
4.05
1.00
2.04
2.04
2.14
f1 (ppm)


134.29
132.60
132.16
131.84
126.68
125.77
125.74
124.96
123.57
117.87
100.60
87.35
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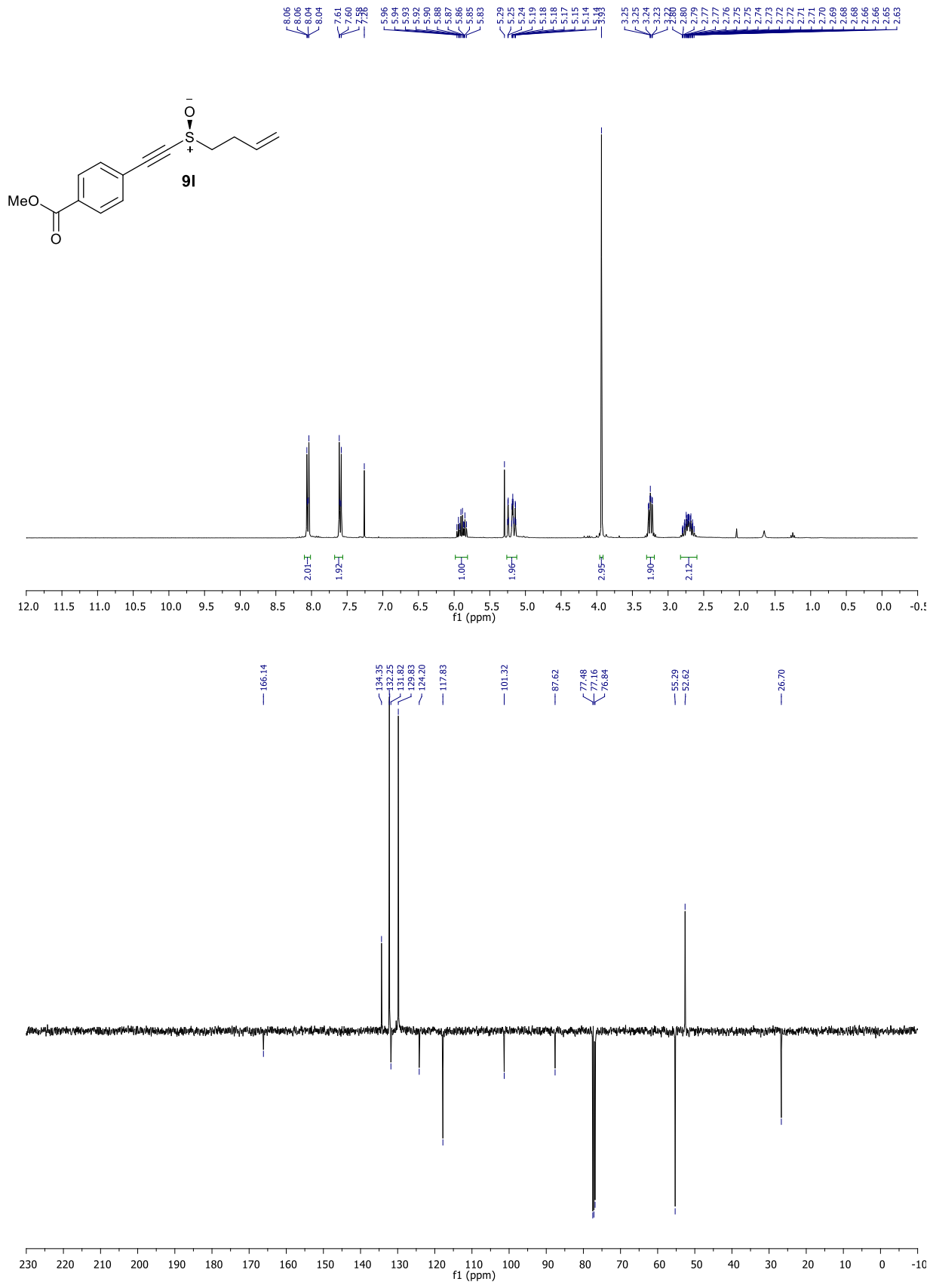
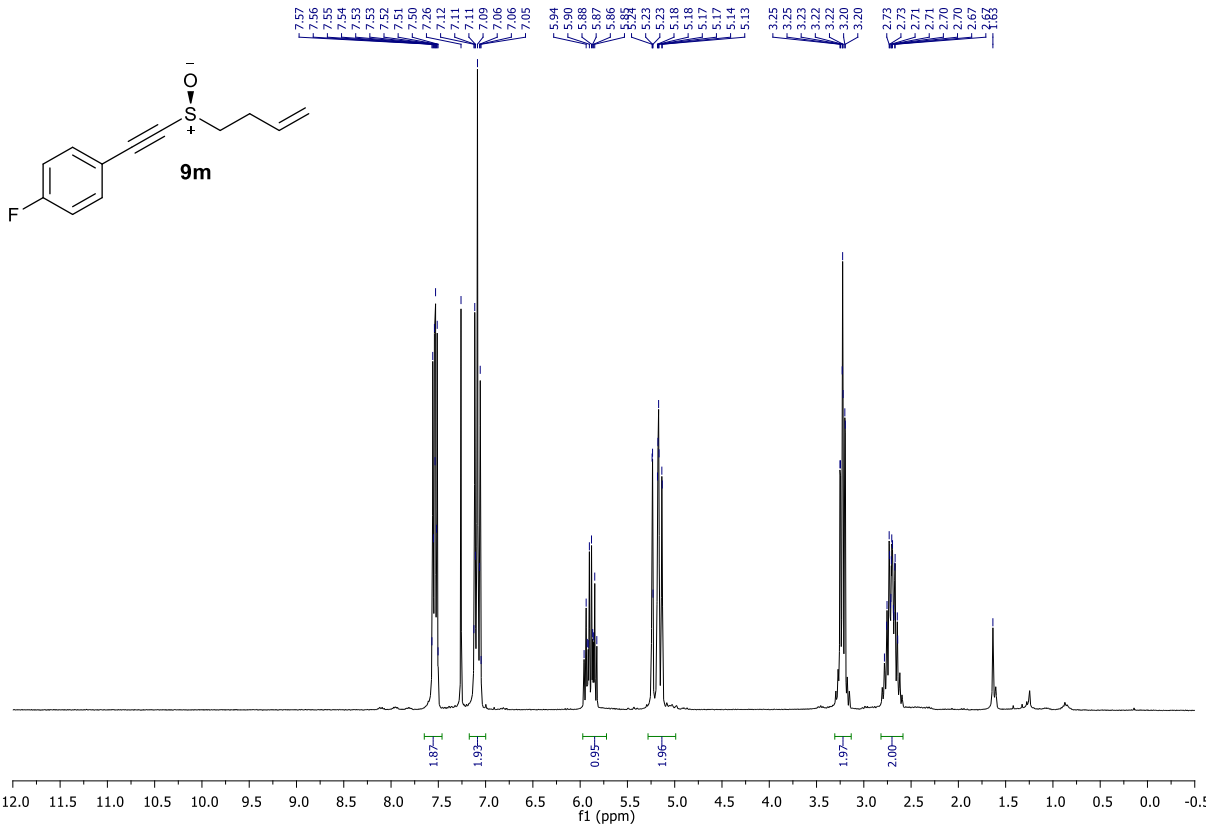
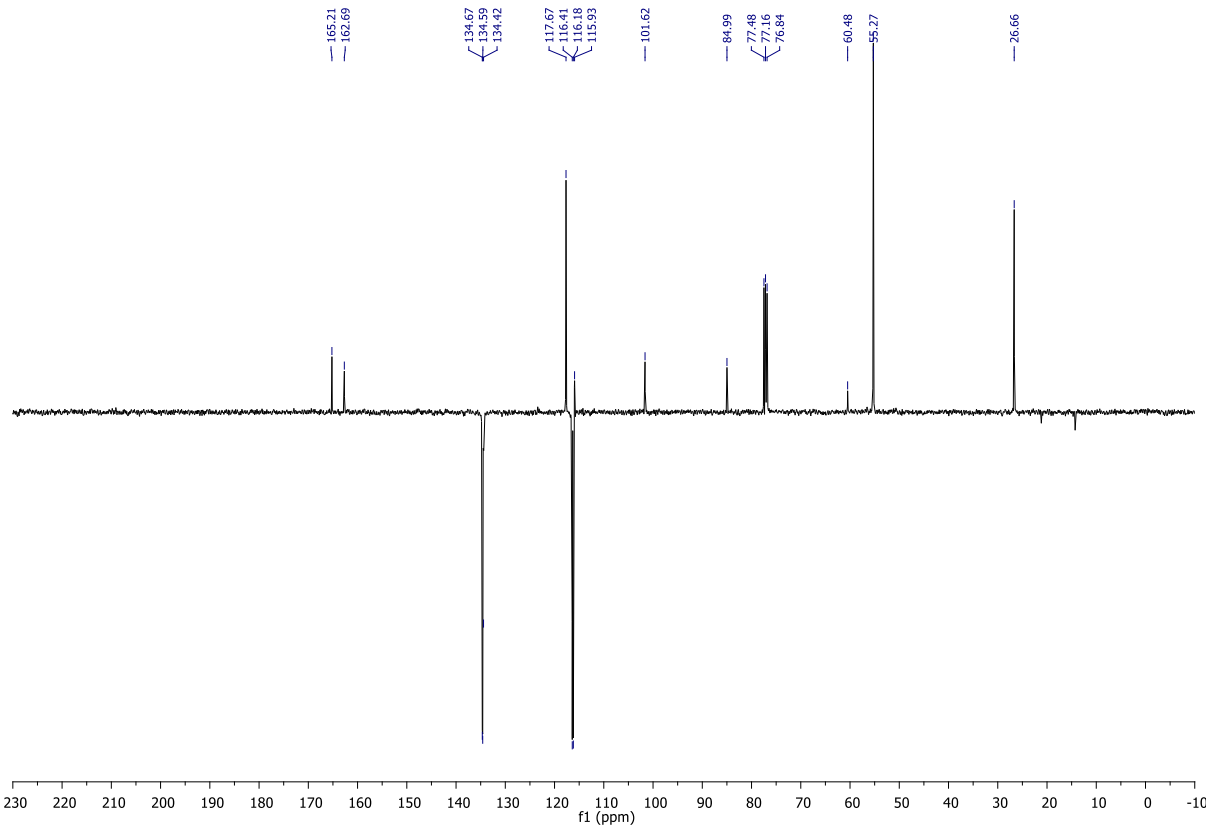
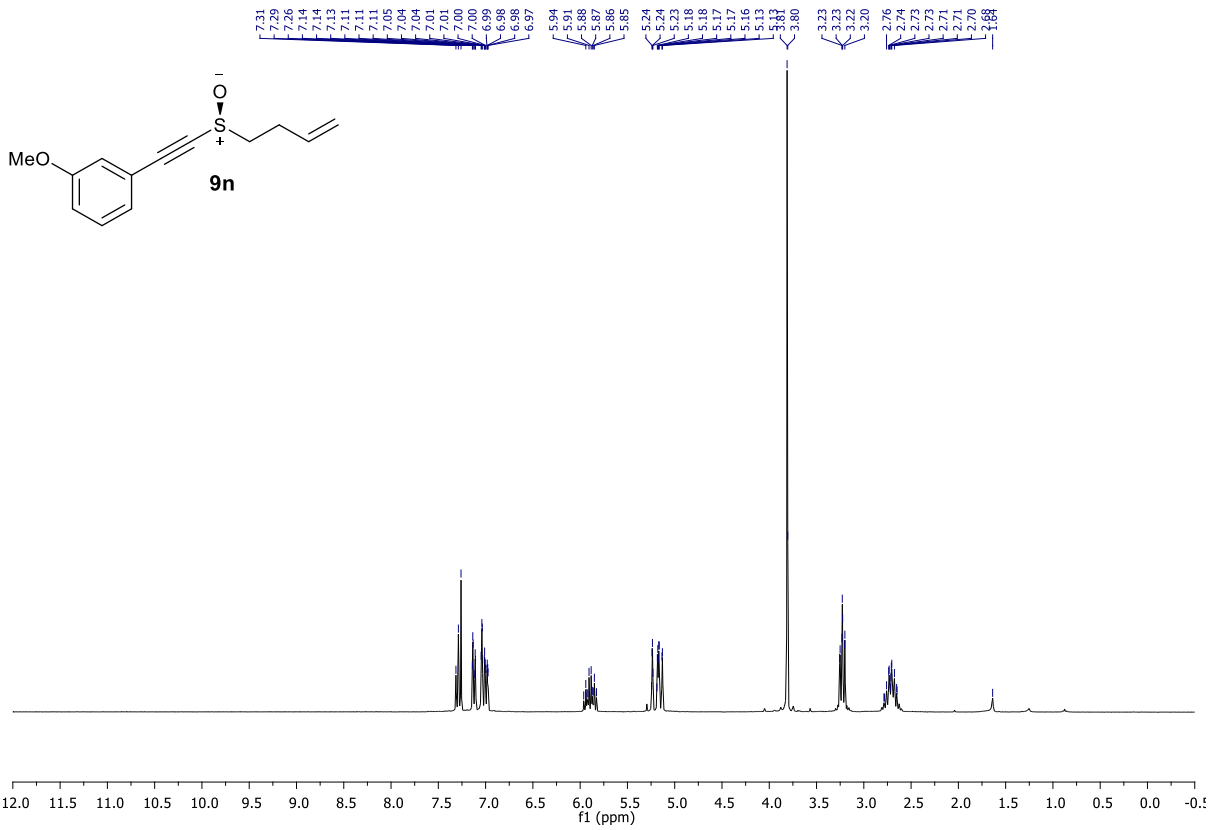
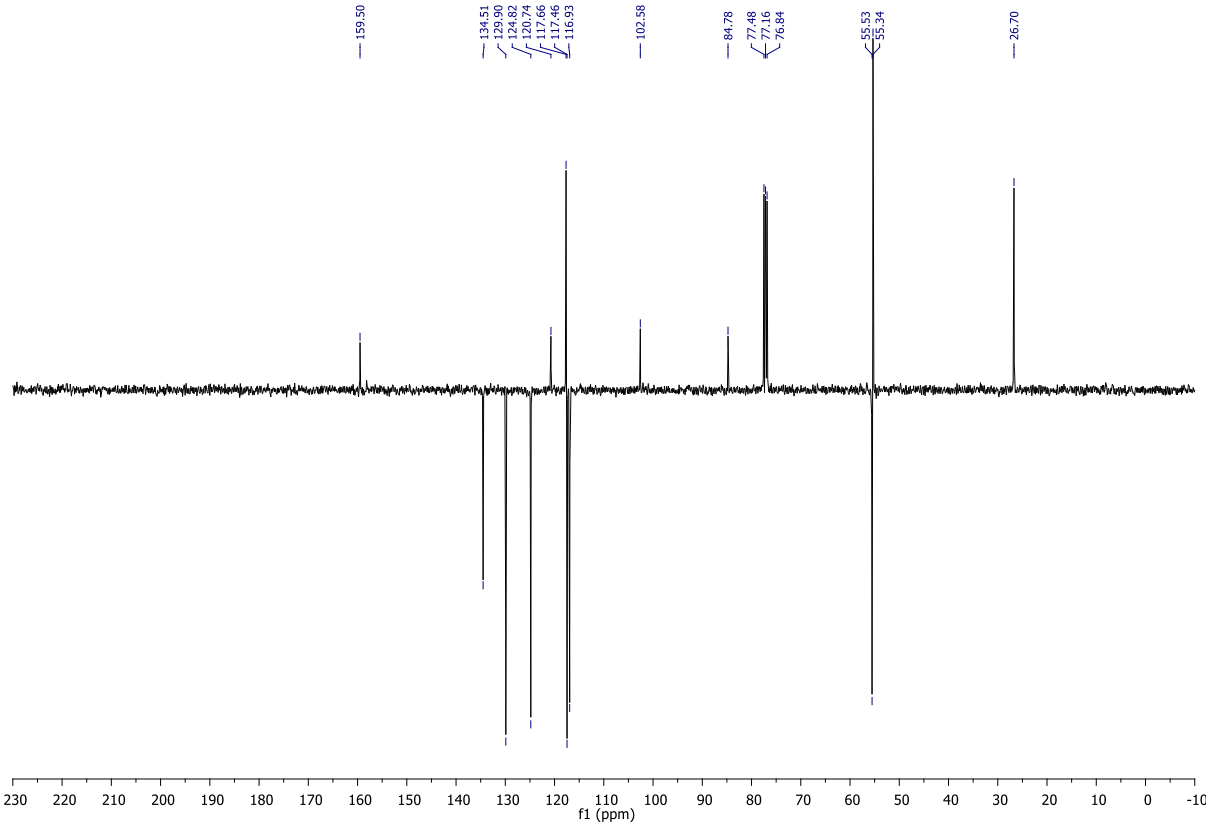
77.16
76.84
55.28
26.70
f1 (ppm)

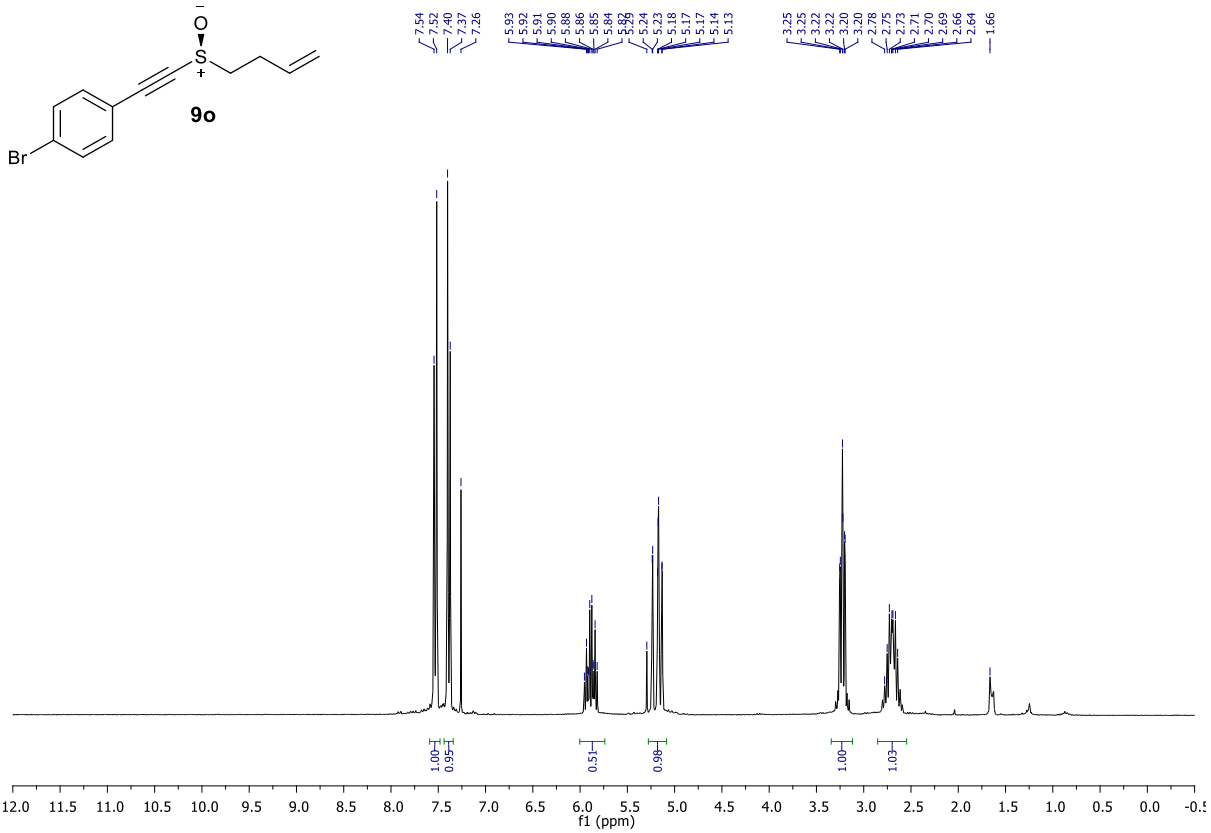

9l
MeO
O
S
+
f1 (ppm)

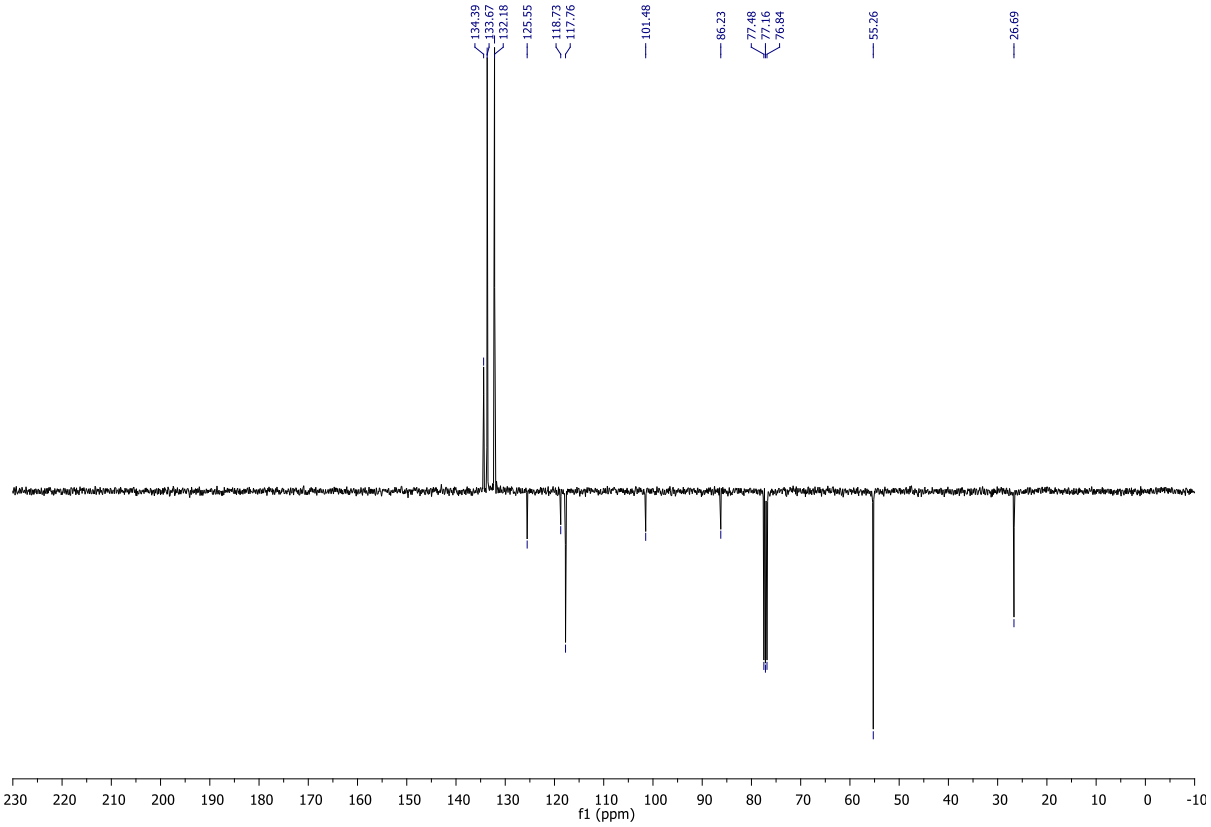

9m
F
O
S
7.57 7.56 7.55 7.54 7.53 7.53 7.52 7.51 7.50 7.26 7.12 7.11 7.11 7.09 7.06 7.06 7.05
5.94 5.90 5.88 5.87 5.86 5.85 5.24 5.23 5.23 5.18 5.18 5.17 5.17 5.14 5.13
3.25 3.25 3.23 3.22 3.22 3.20 3.20
2.73 2.73 2.71 2.71 2.70 2.70 2.67 1.67 1.63
1.87 1.93 0.95 1.96 1.97 2.00
f1 (ppm)

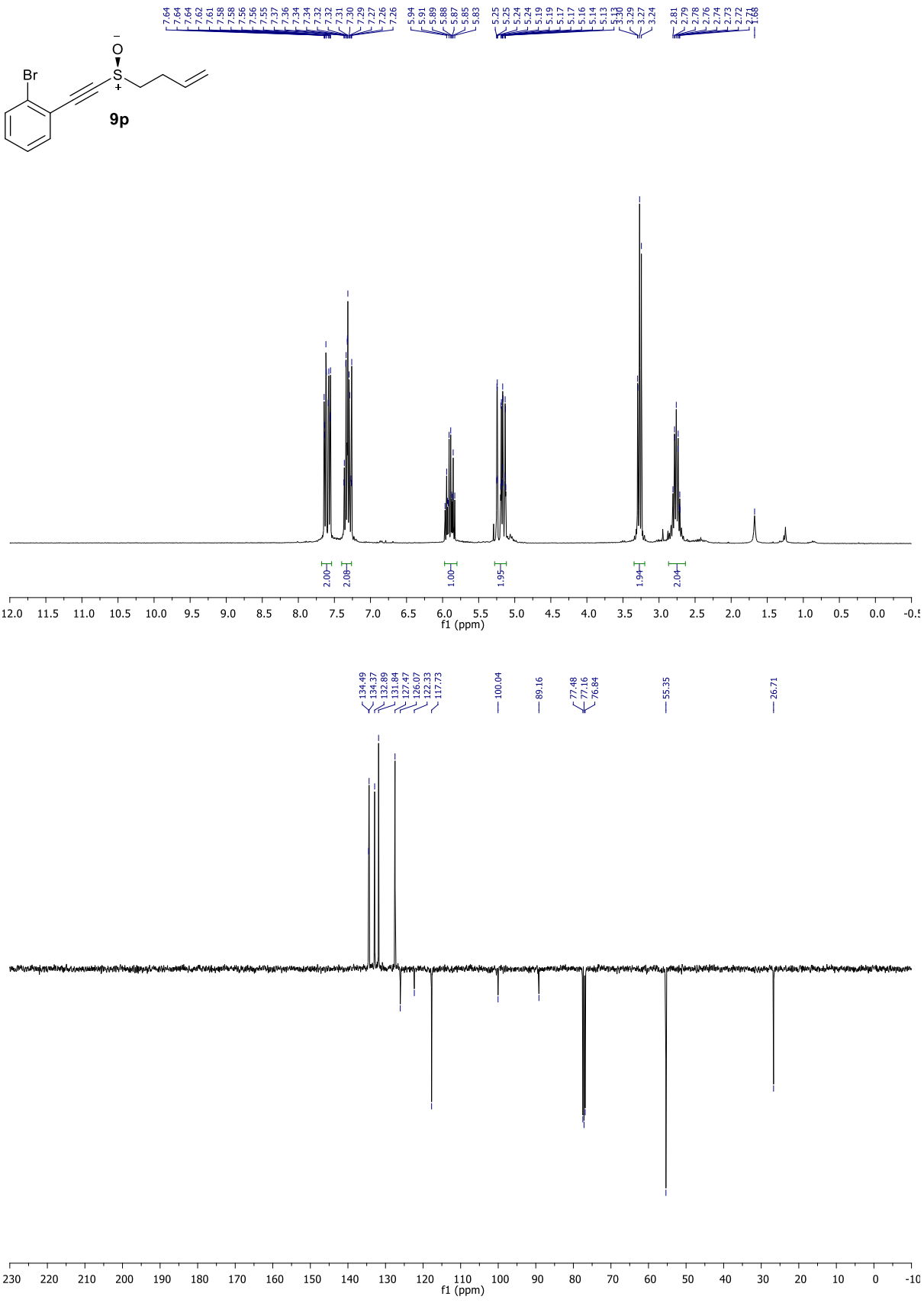

165.21 162.69
134.67 134.59 134.42
117.67 116.41 116.18 115.93
101.62
84.99
77.48 77.16 76.84
60.48
55.27
26.66
f1 (ppm)

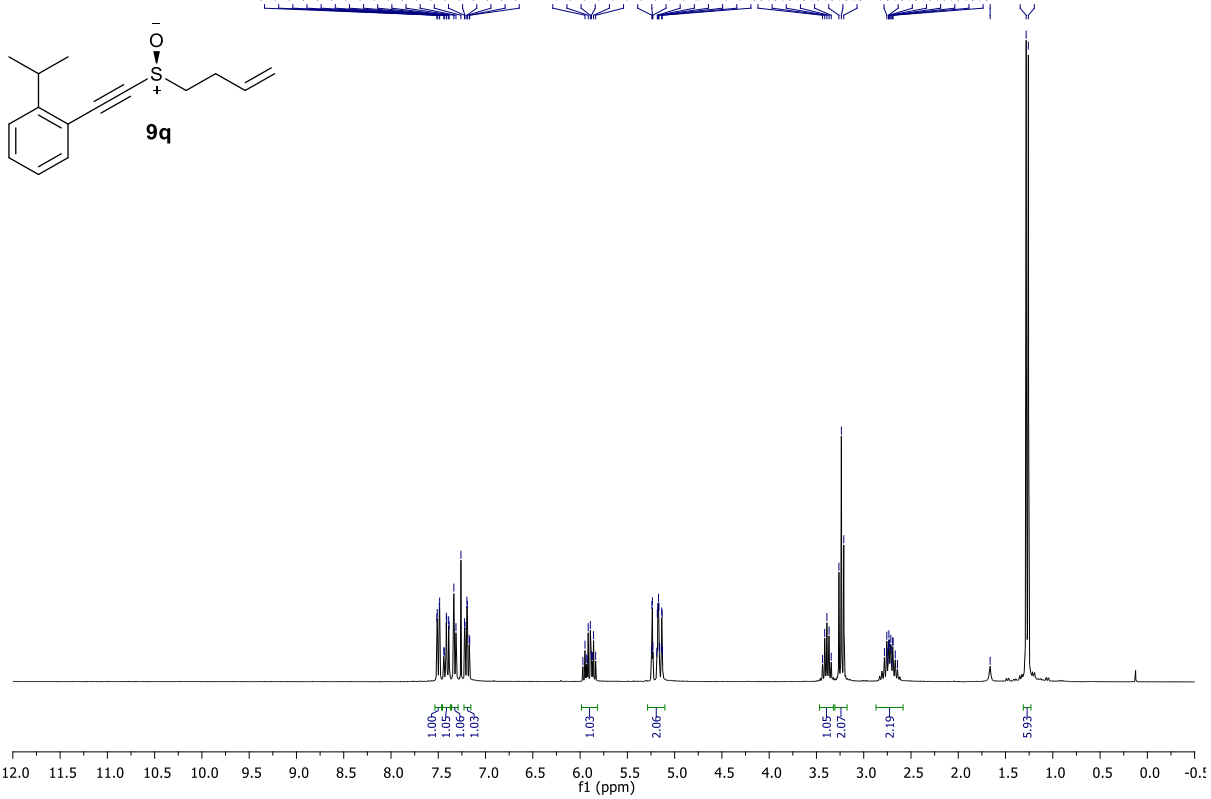

MeO
O
S
+
−
9n
f1 (ppm)

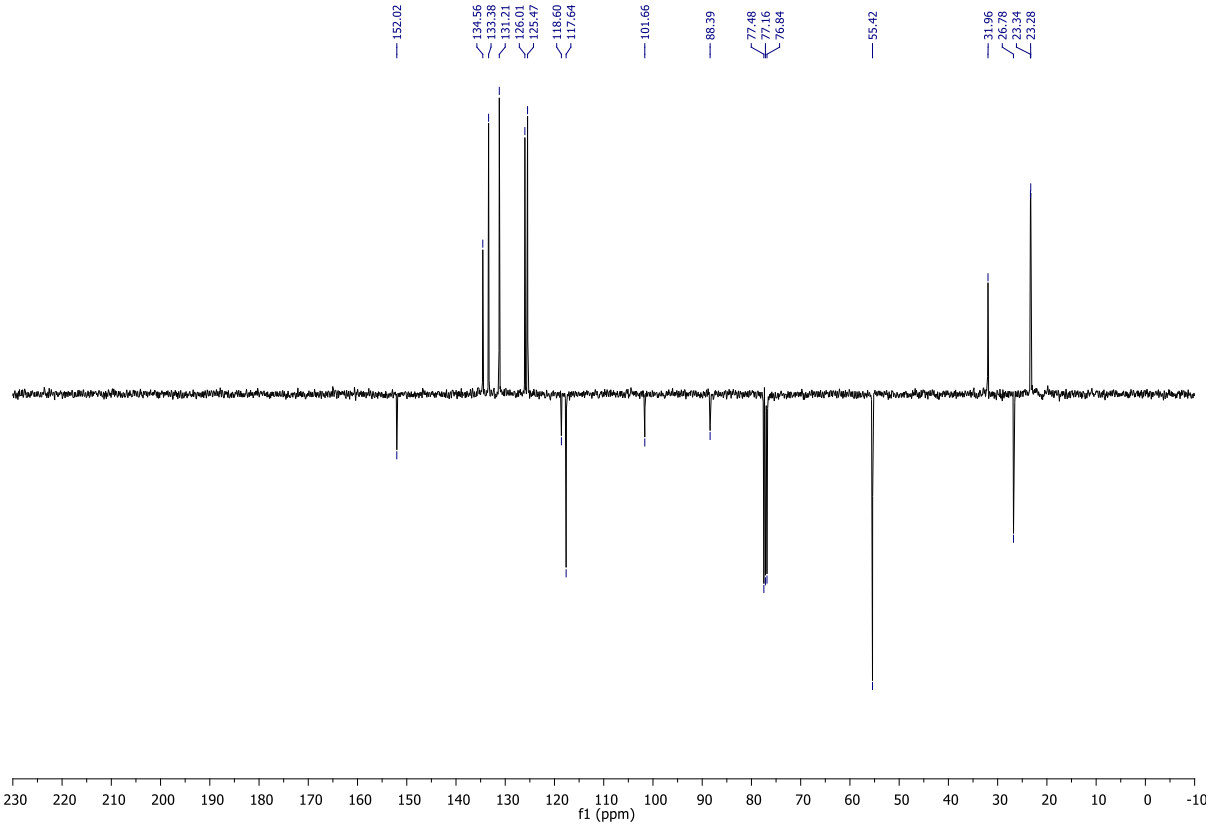

159.50
134.51
129.90
124.82
120.74
117.66
117.46
116.93
102.58
84.78
77.48
77.16
76.84
55.53
55.34
26.70
f1 (ppm)

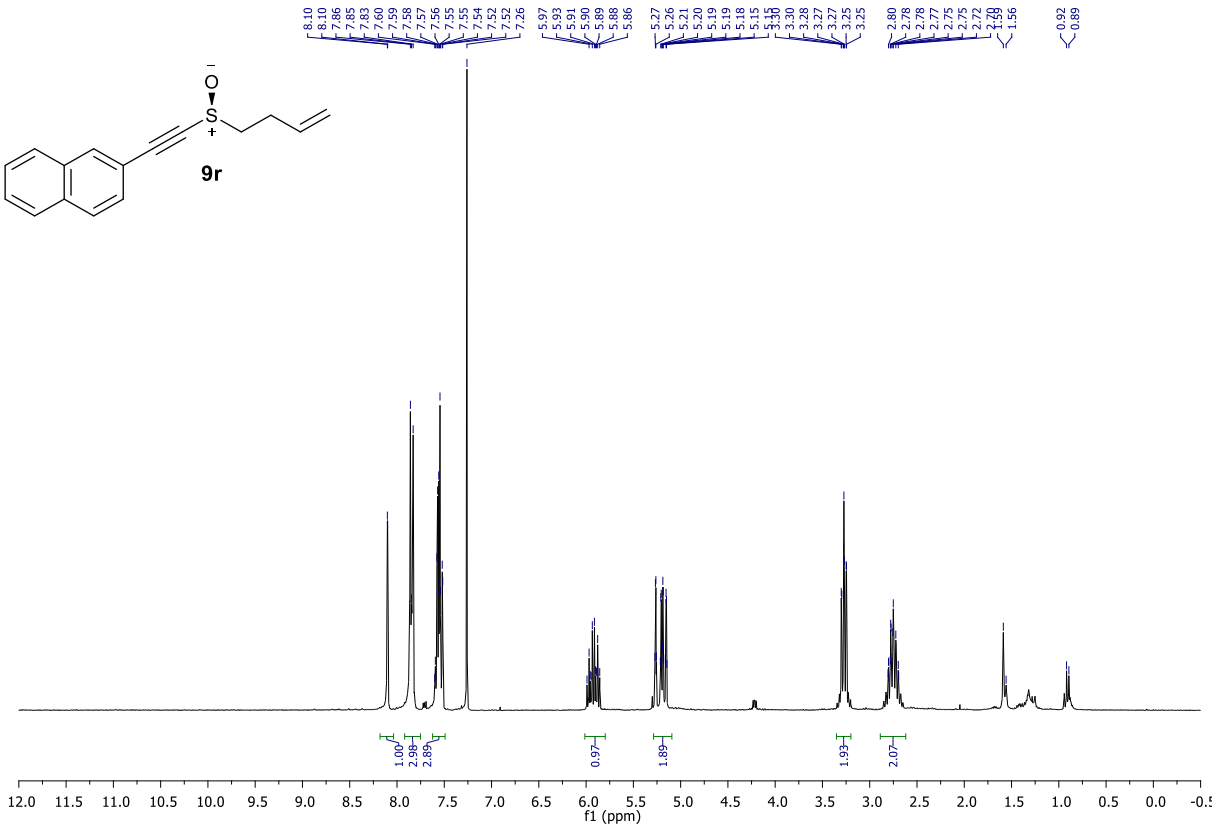

9o
Br
O
S
+
7.54
7.52
7.40
7.37
7.26
5.93
5.92
5.91
5.90
5.88
5.86
5.85
5.84
5.24
5.23
5.18
5.17
5.17
5.14
5.13
3.25
3.25
3.22
3.22
3.20
3.20
2.78
2.75
2.73
2.71
2.70
2.69
2.66
2.64
1.66
1.00
0.95
0.51
0.98
1.00
1.03
f1 (ppm)

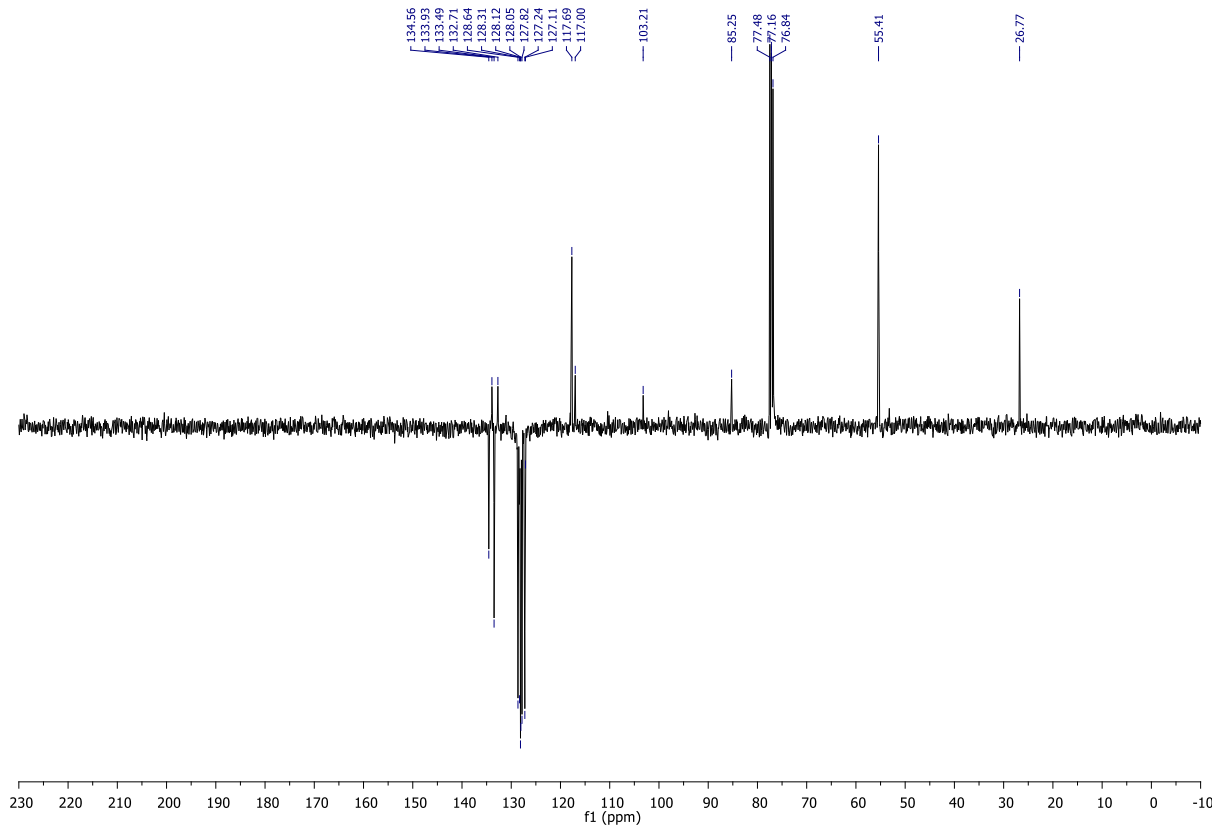

134.39
133.67
132.18
125.55
118.73
117.76
101.48
86.23
77.48
77.16
76.84
55.26
26.69
f1 (ppm)

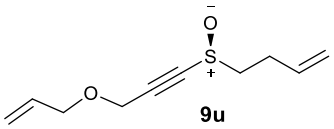

Br
O
S
+
9p
f1 (ppm)
f1 (ppm)


9q
7.51 7.51 7.49 7.49 7.44 7.44 7.42 7.41 7.39 7.39 7.34 7.31 7.26 7.22 7.22 7.20 7.19 7.17 7.17
5.95 5.91 5.89 5.88 5.86 5.84 5.24 5.24 5.23 5.18 5.18 5.17 5.17 5.14 3.41 3.39 3.37 3.34 3.26 3.24 3.21
2.76 2.74 2.73 2.73 2.71 2.71 2.69 1.28 1.26
1.05 1.05 1.06 1.03 1.03 2.06 1.05 2.07 2.19 5.93
f1 (ppm)


152.02 134.56 133.38 131.21 126.01 125.47 118.60 117.64 101.66 88.39 77.48 77.16 76.84 55.42 31.96 26.78 23.34 23.28
f1 (ppm)


9r
f1 (ppm)


f1 (ppm)


O
S
+
O

9u

7.26
5.92
5.88
5.88
5.86
5.86
5.85
5.83
5.82
5.81
5.79
5.34
5.33
5.19
5.14
4.34
4.08
4.07
4.07
4.06
4.05
4.05
3.16
3.16
3.14
3.11
2.67
2.66
2.64
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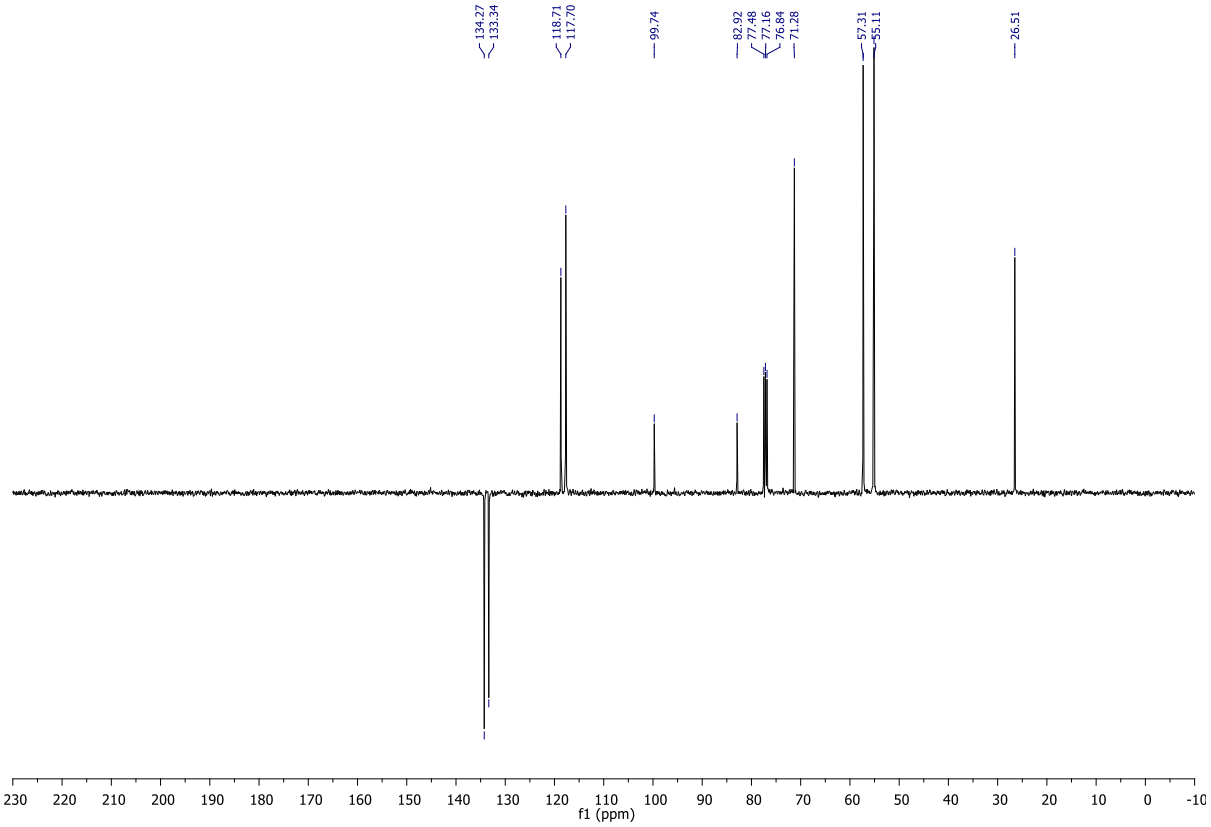
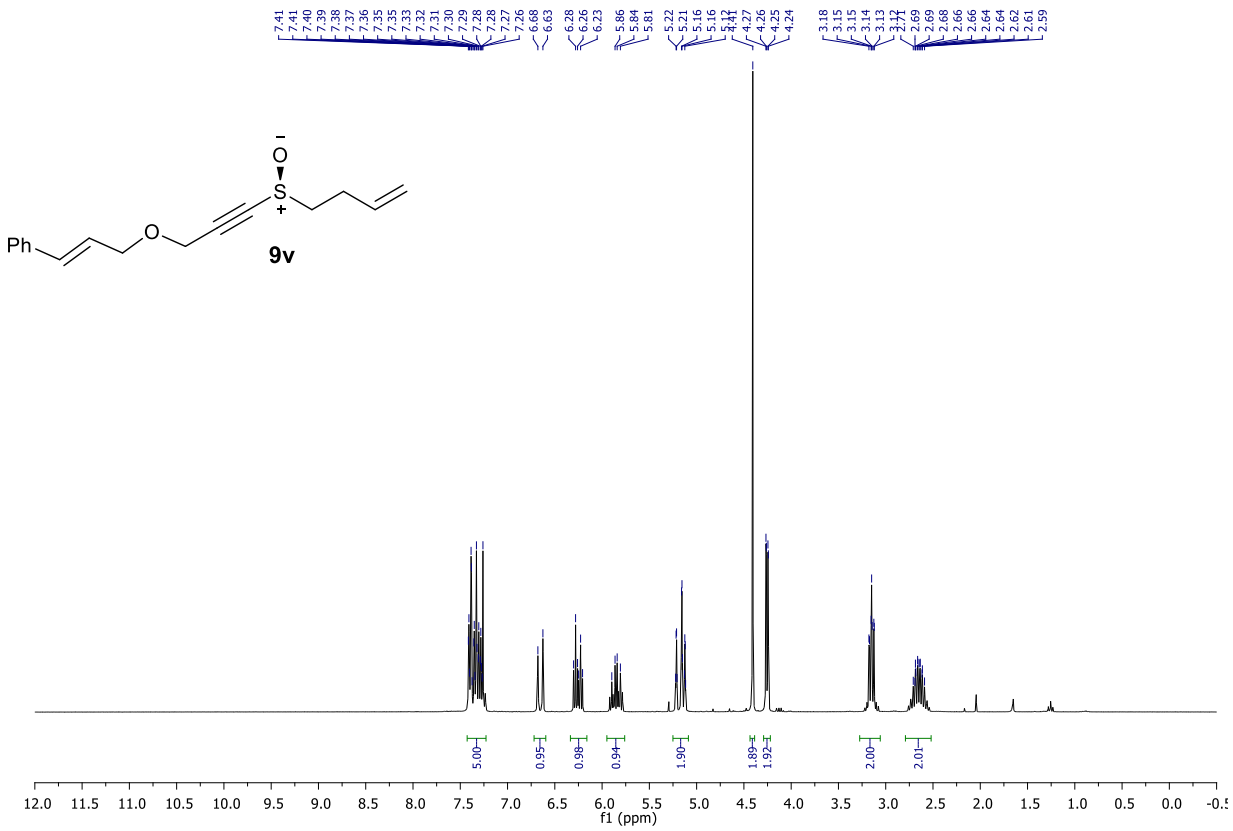
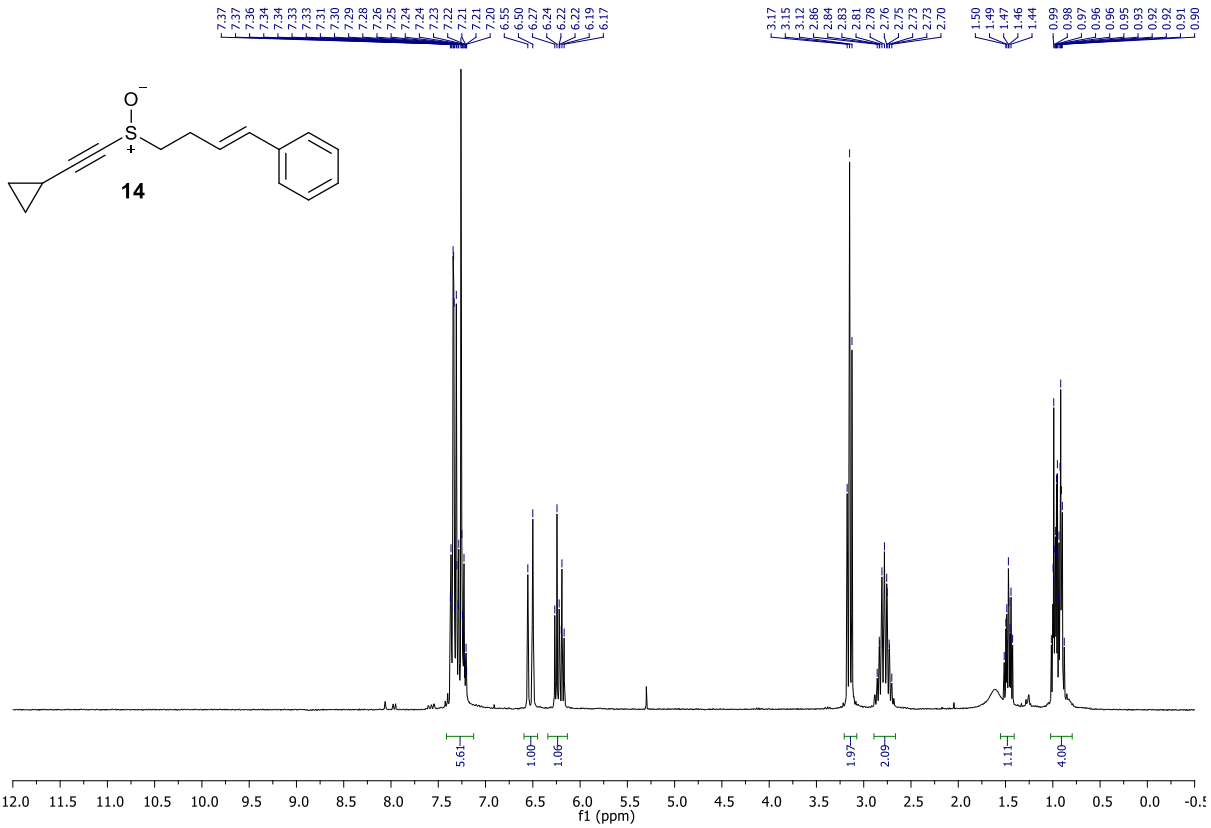
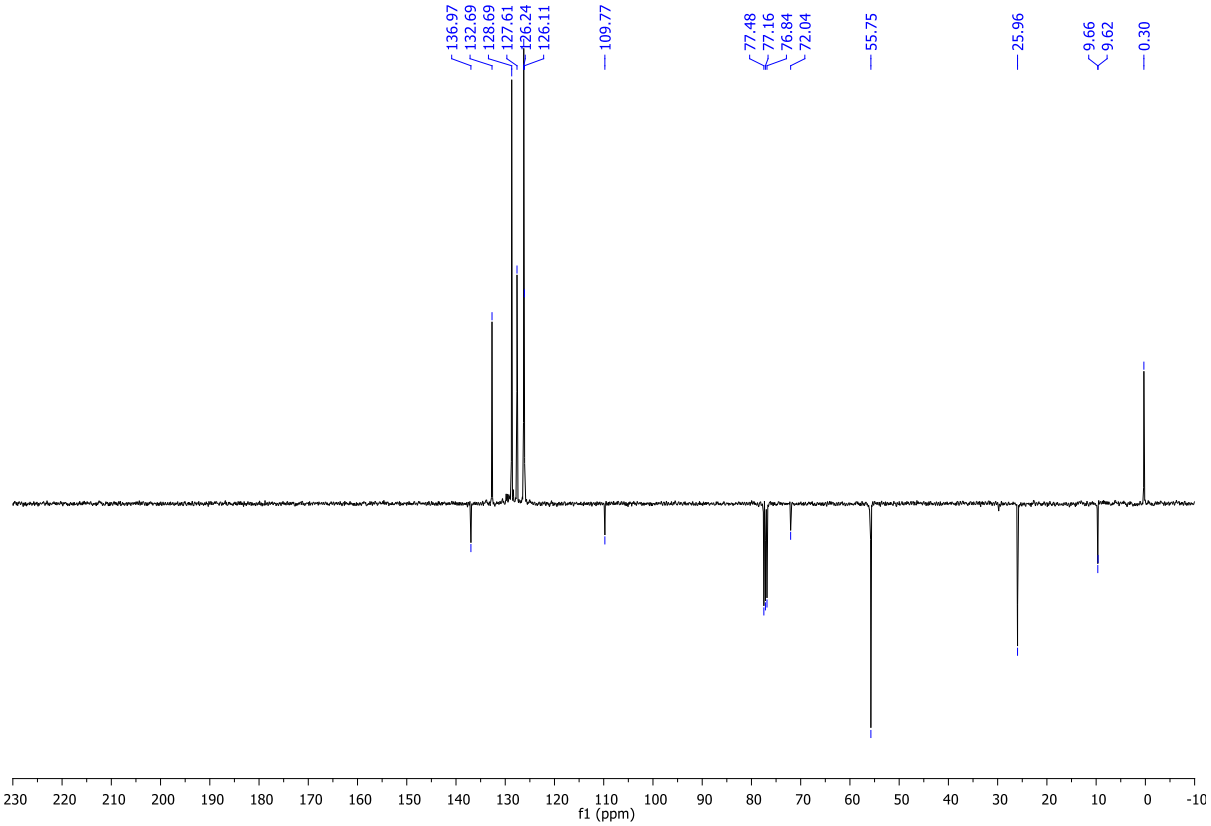
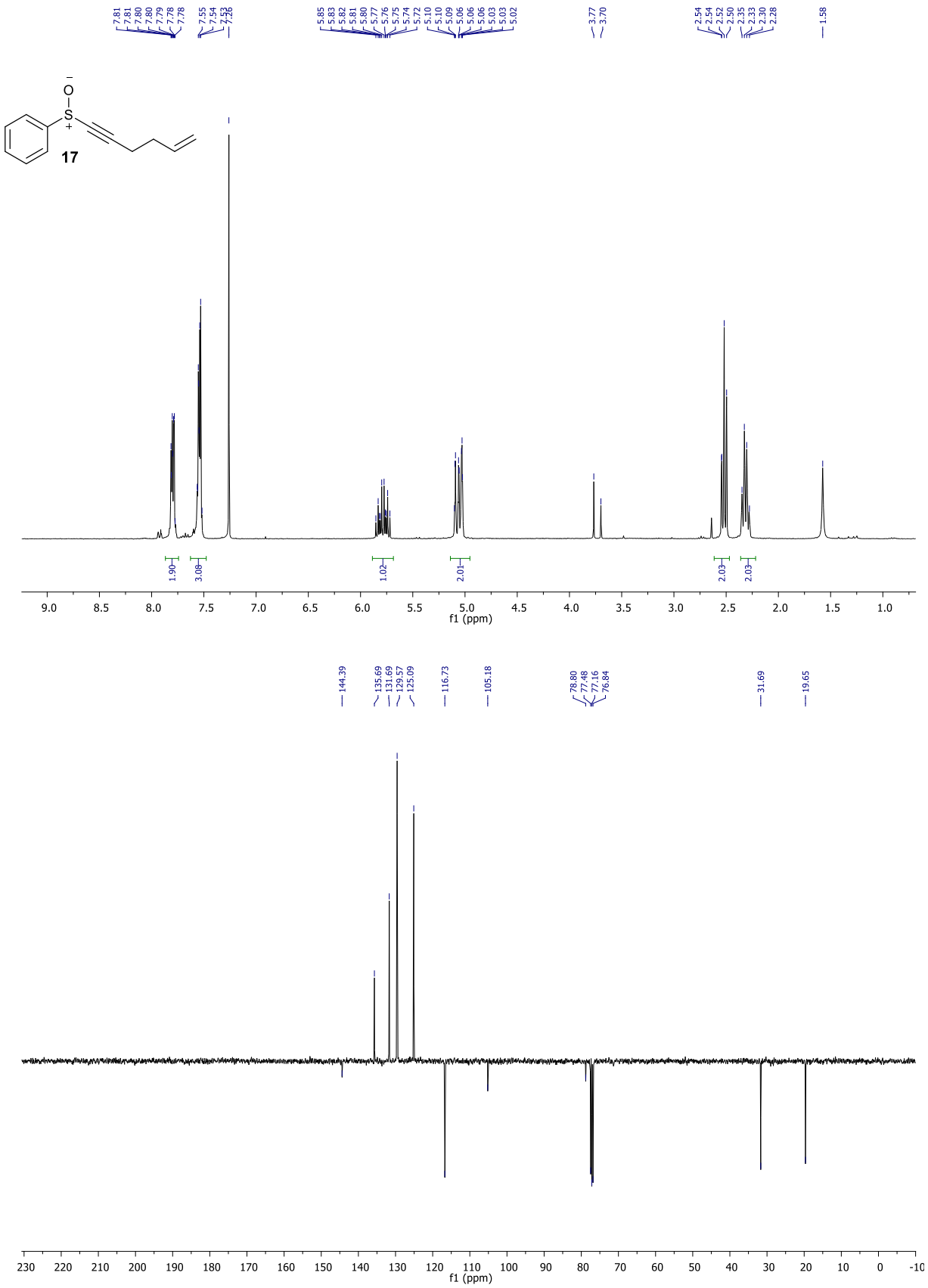
1.04
1.03
1.10
1.11
f1 (ppm)


134.27
133.34
118.71
117.70
99.74
82.92
77.48
77.16
76.84
71.28
57.31
55.11
26.51
f1 (ppm)


Ph
O
O
S
+
9v
f1 (ppm)


14
f1 (ppm)


f1 (ppm)


7.81
7.81
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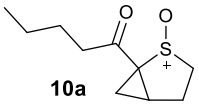
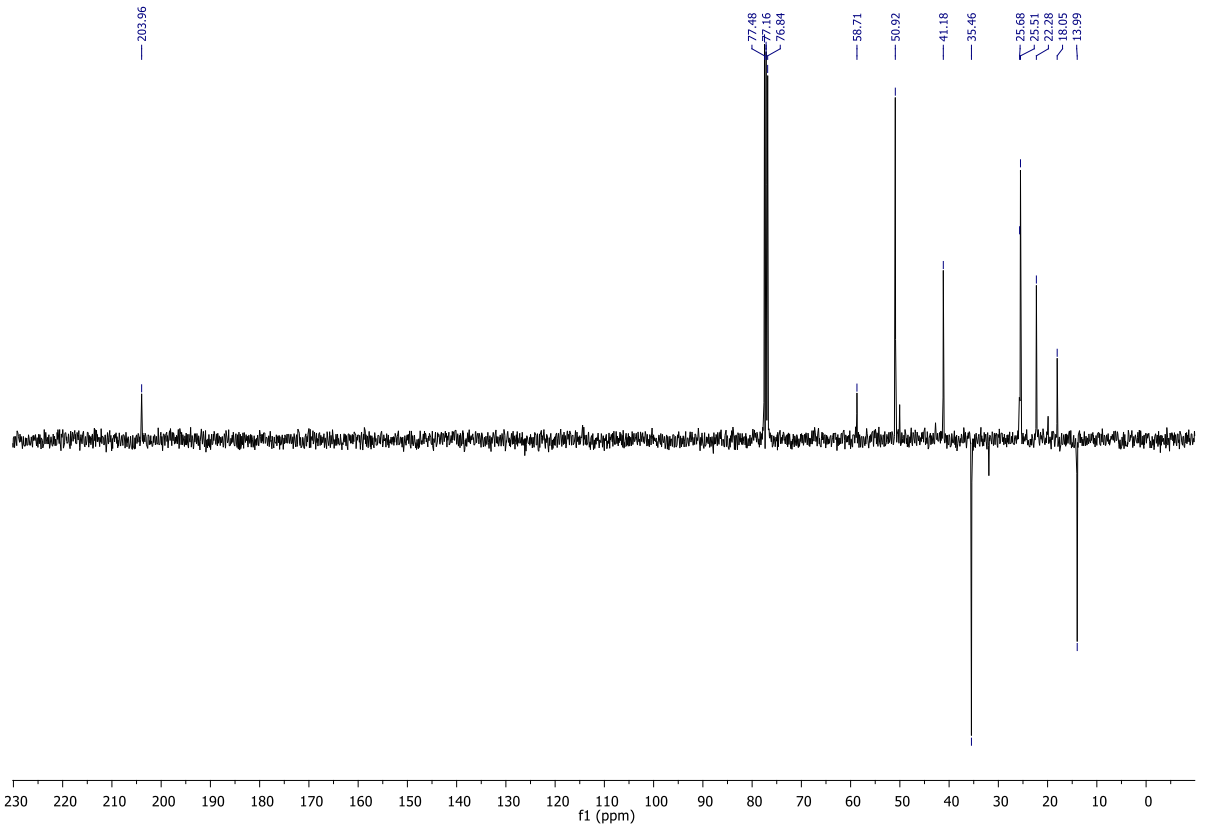
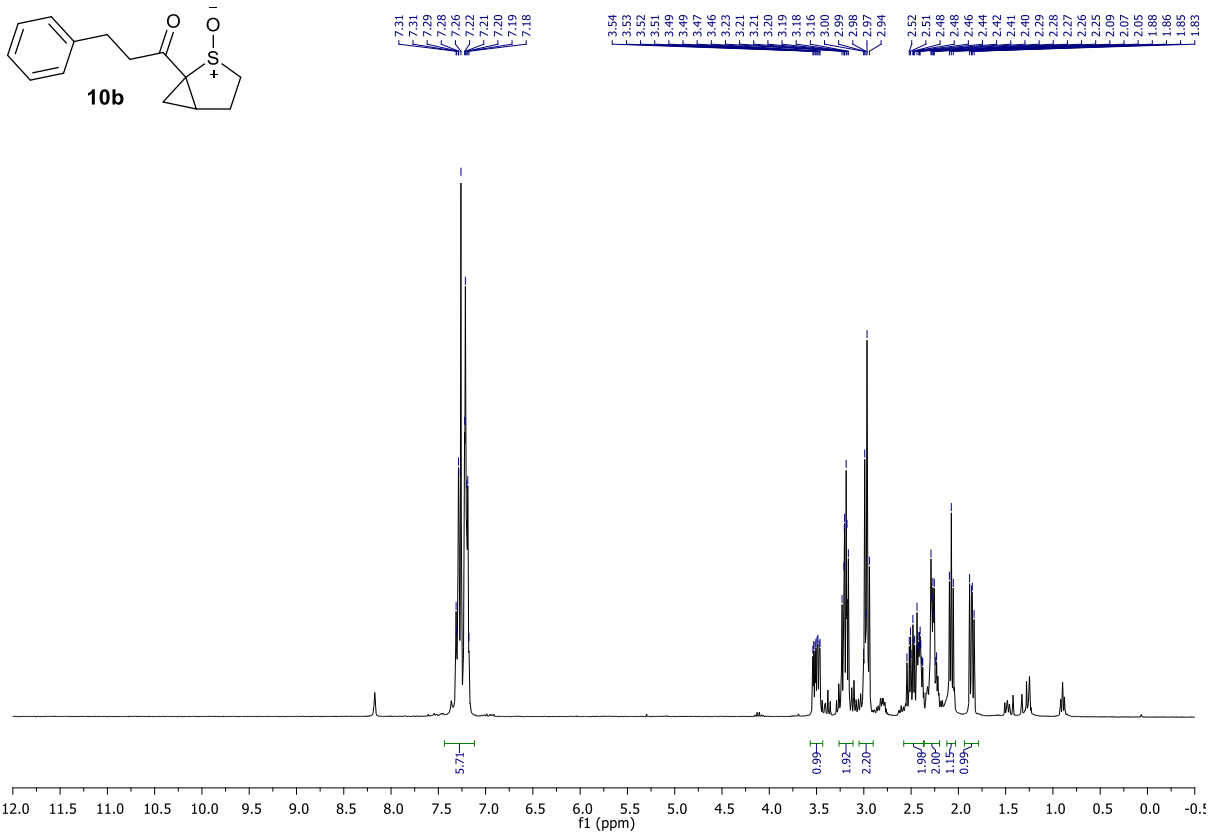
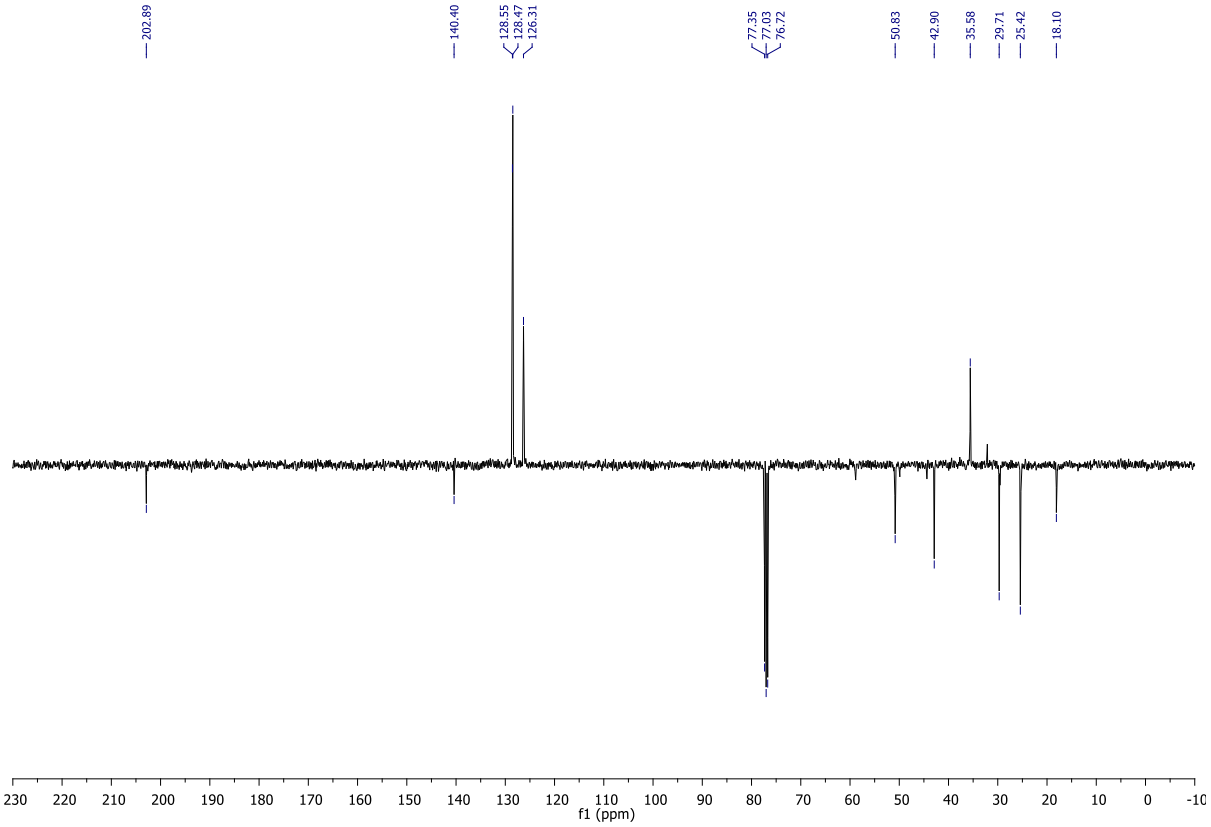
7.80
7.79
7.78
7.78
7.55
7.54
7.53
7.28
5.85
5.83
5.82
5.81
5.80
5.77
5.76
5.75
5.74
5.72
5.10
5.09
5.06
5.06
5.06
5.03
5.03
5.02
3.77
3.70
2.54
2.54
2.52
2.50
2.35
2.33
2.30
2.28
1.58
O
S
17
1.90
3.08
1.02
2.01
2.03
2.03
f1 (ppm)
144.39
135.69
131.69
129.57
125.09
116.73
105.18
78.80
77.48
77.16
76.84
31.69
19.65
f1 (ppm)

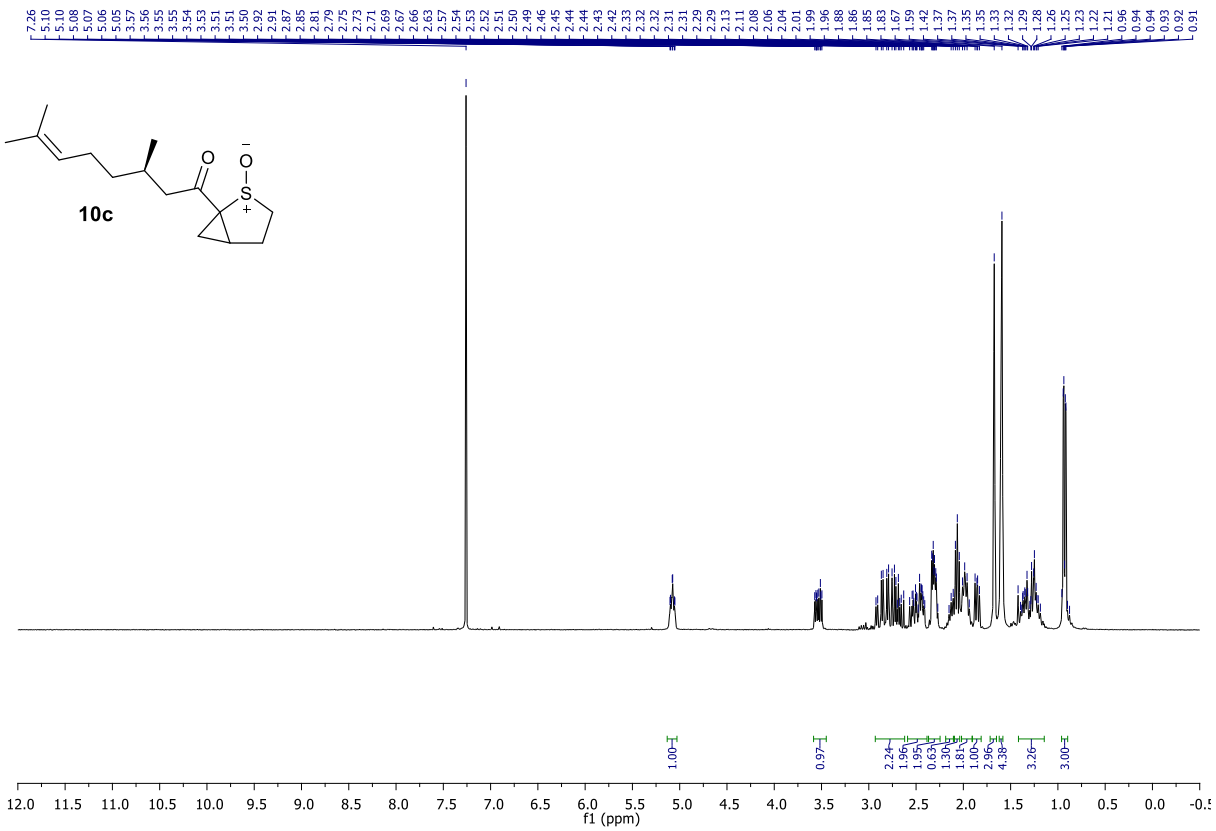
Products of Catalysis

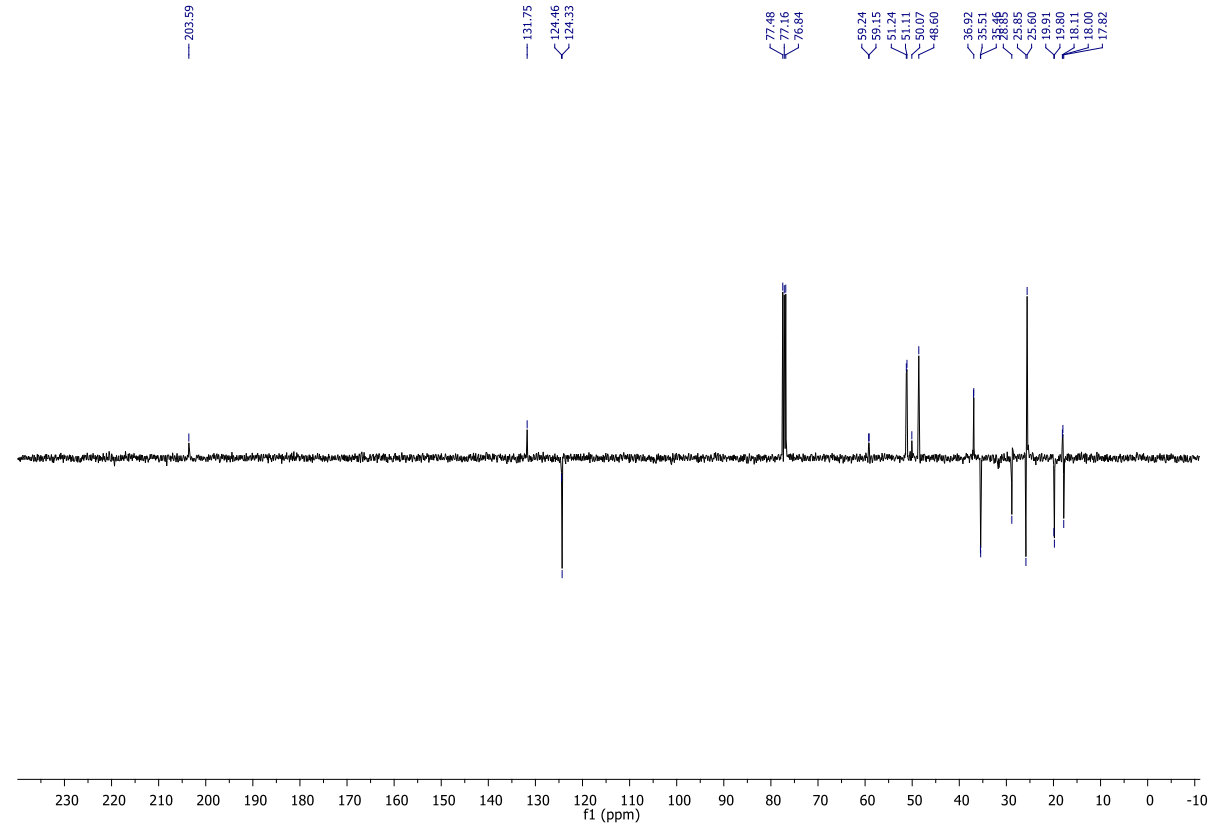


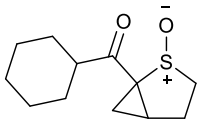



10b
7.31
7.31
7.29
7.28
7.26
7.22
7.21
7.20
7.19
7.18
3.54
3.53
3.52
3.51
3.49
3.49
3.47
3.46
3.23
3.21
3.21
3.20
3.19
3.18
3.16
3.00
2.99
2.98
2.97
2.94
2.52
2.51
2.48
2.48
2.46
2.44
2.42
2.41
2.40
2.29
2.28
2.27
2.26
2.25
2.09
2.07
2.05
1.88
1.86
1.85
1.83
5.71
0.99
1.92
2.20
1.98
2.00
1.15
0.99
f1 (ppm)


202.89
140.40
128.55
128.47
126.31
77.35
77.03
76.72
50.83
42.90
35.58
29.71
25.42
18.10
f1 (ppm)

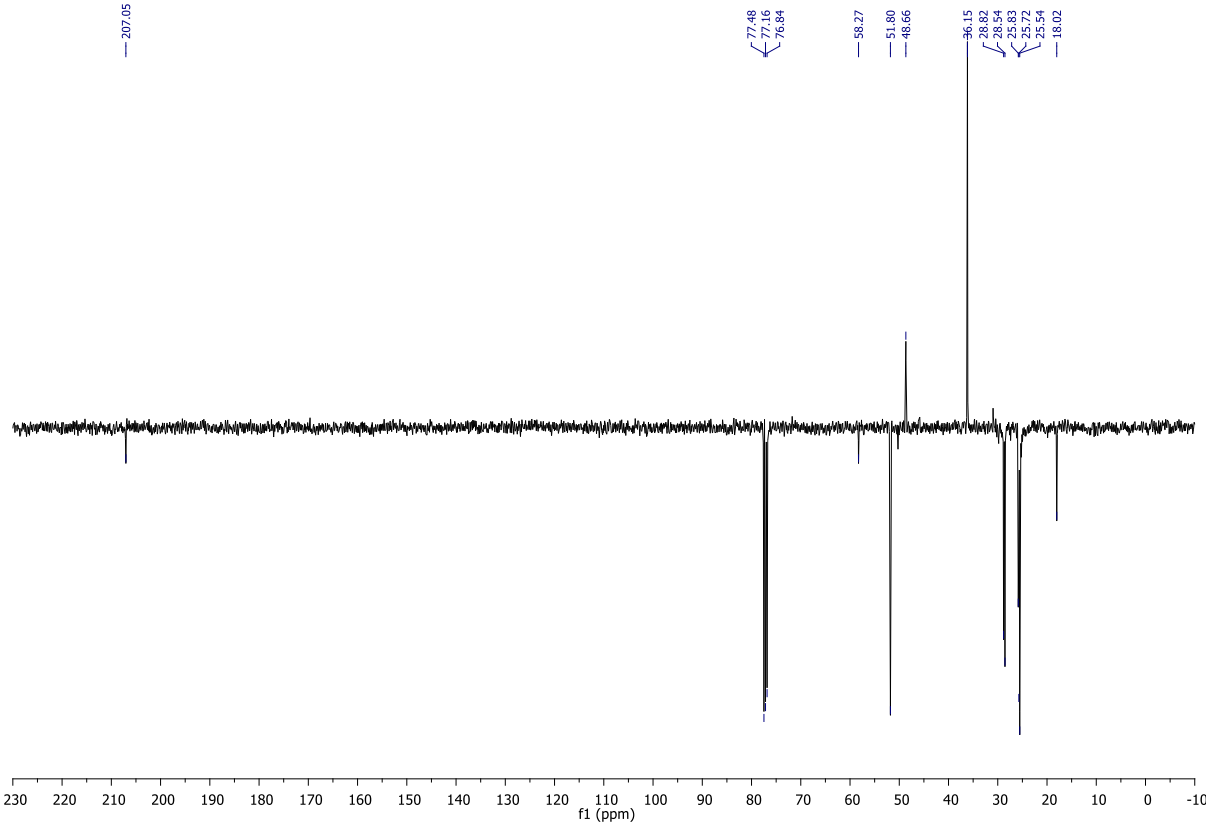

10c
f1 (ppm)

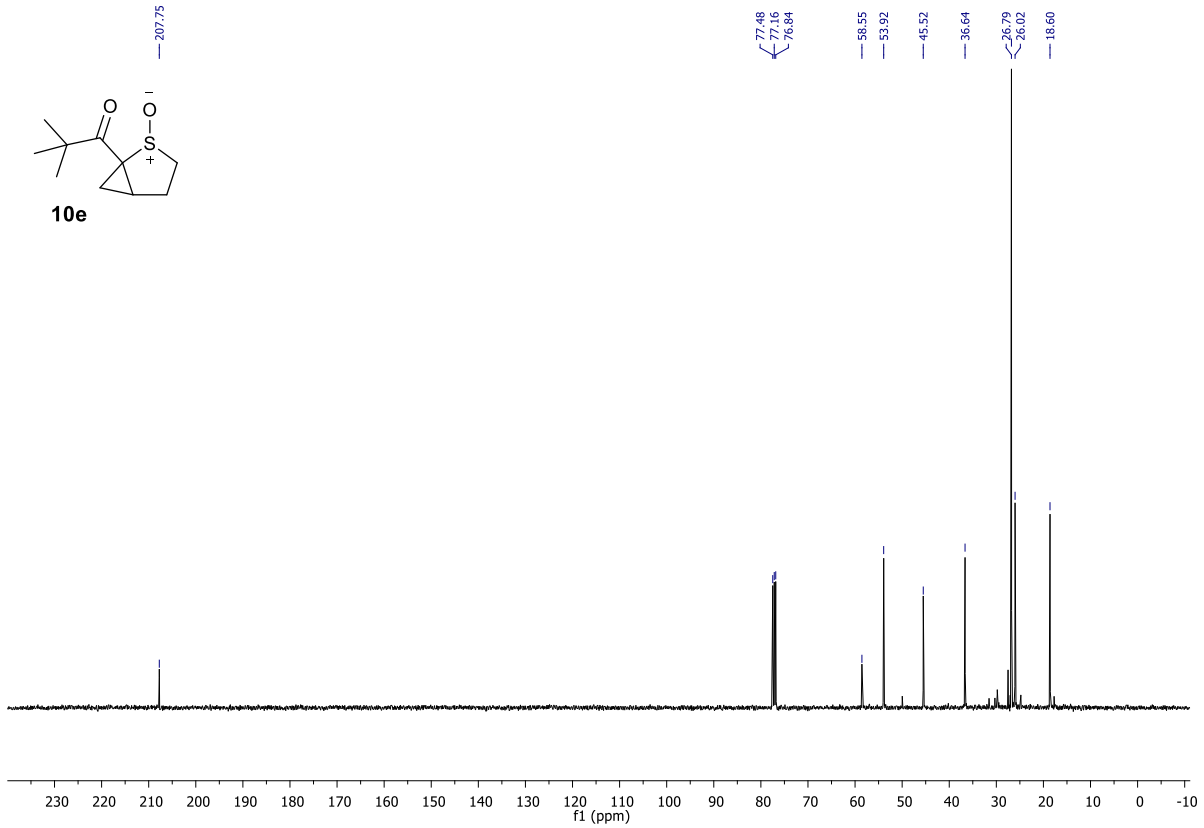

f1 (ppm)



10d

7.26
3.57
3.56
3.55
3.54
3.53
3.52
3.50
3.10
3.09
3.08
2.34
2.33
2.32
2.31
2.06
2.04
2.02
1.87
1.85
1.84
1.82
1.81
1.80
1.78
1.77
1.72
1.40
1.36
1.35
1.33
1.32
1.00
1.10
1.11
1.06
2.08
1.10
1.04
2.04
2.30
1.99
6.91
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


207.05
77.48
77.16
76.84
58.27
51.80
48.66
36.15
28.82
28.54
25.83
25.72
25.54
18.02
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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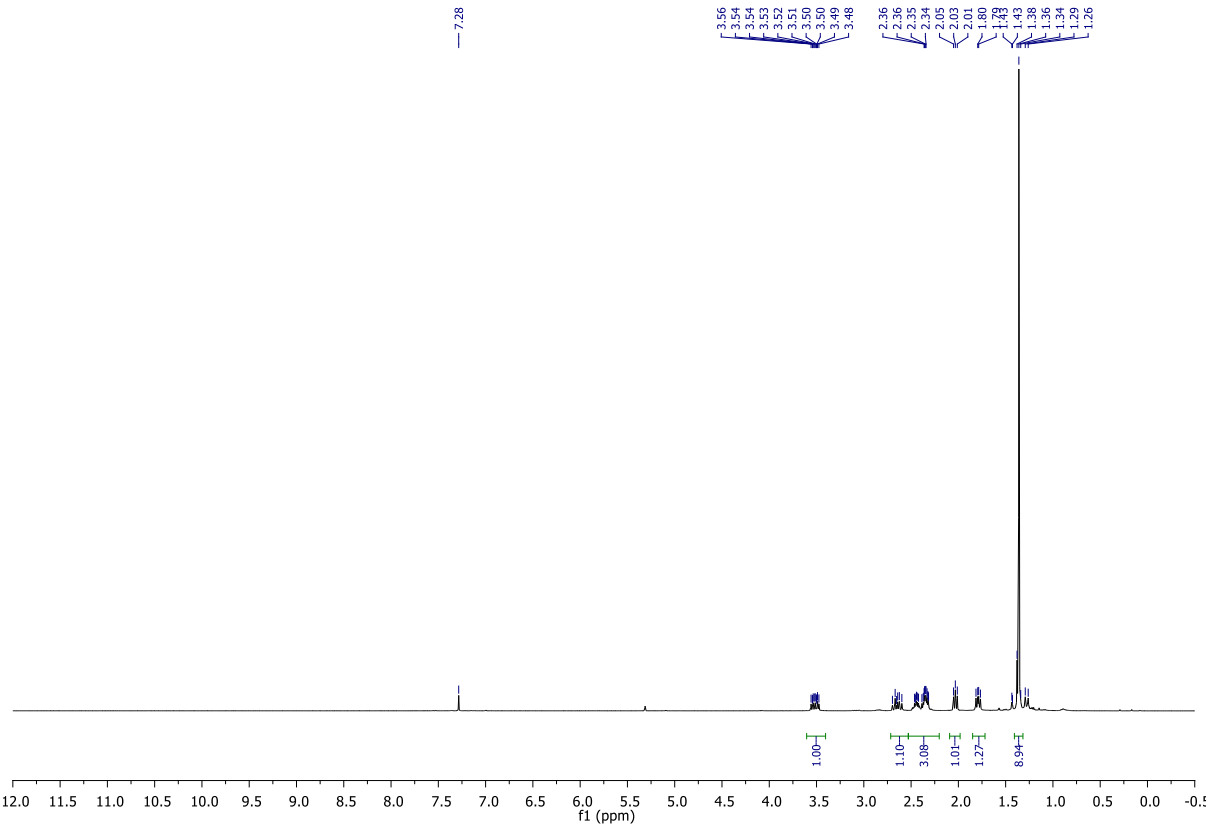
76.84
58.55
53.92
45.52
36.64
26.79
26.02
18.60
O
O
S
+
10e
f1 (ppm)


7.28
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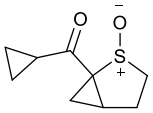
3.54
3.54
3.53
3.52
3.51
3.50
3.50
3.49
3.48
2.36
2.36
2.35
2.34
2.05
2.03
2.01
1.80
1.43
1.43
1.38
1.36
1.34
1.29
1.26
1.00
1.10
3.08
1.01
1.27
8.94
f1 (ppm)



10f

7.26
3.59
3.58
3.56
3.55
3.53
3.53
3.52
2.51
2.50
2.47
2.43
2.35
2.35
2.34
2.12
1.90
1.88
1.20
1.19
1.18
1.17
1.17
1.15
1.07
1.06
1.05
1.04
1.03
1.03
1.03
1.00
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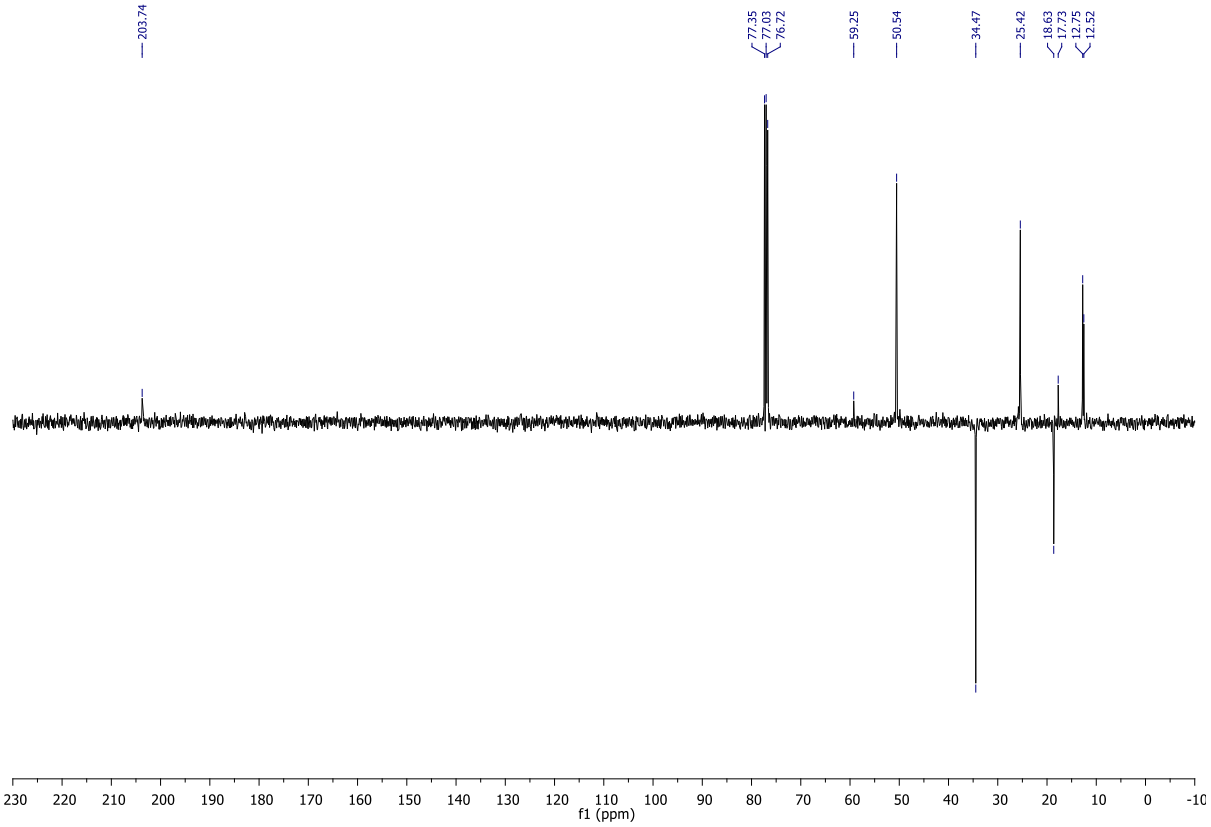
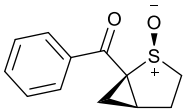
1.05
1.08
2.27
2.30
f1 (ppm)


203.74
77.35
77.03
76.72
59.25
50.54
34.47
25.42
18.63
17.73
12.75
12.52
f1 (ppm)



10g

8.00
7.99
7.99
7.98
7.97
7.96
7.63
7.63
7.62
7.61
7.60
7.60
7.58
7.58
7.58
7.58
7.53
7.53
7.51
7.51
7.49
7.48
7.48
7.26
3.56
3.55
3.54
3.52
3.52
3.51
3.49
3.48
2.73
2.73
2.70
2.44
2.28
2.26
1.83
1.82
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1.85
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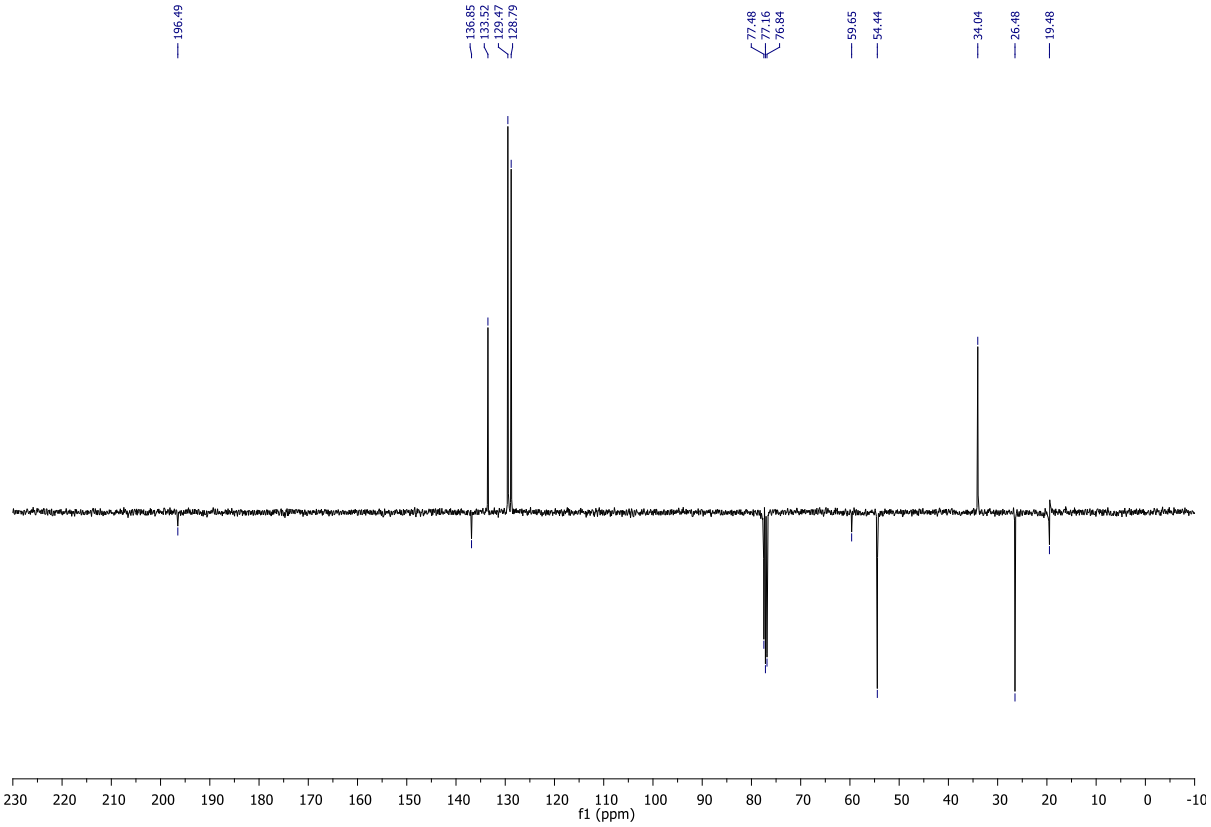
1.84
1.00
1.93
2.01
0.97
0.94
f1 (ppm)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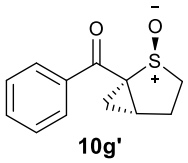
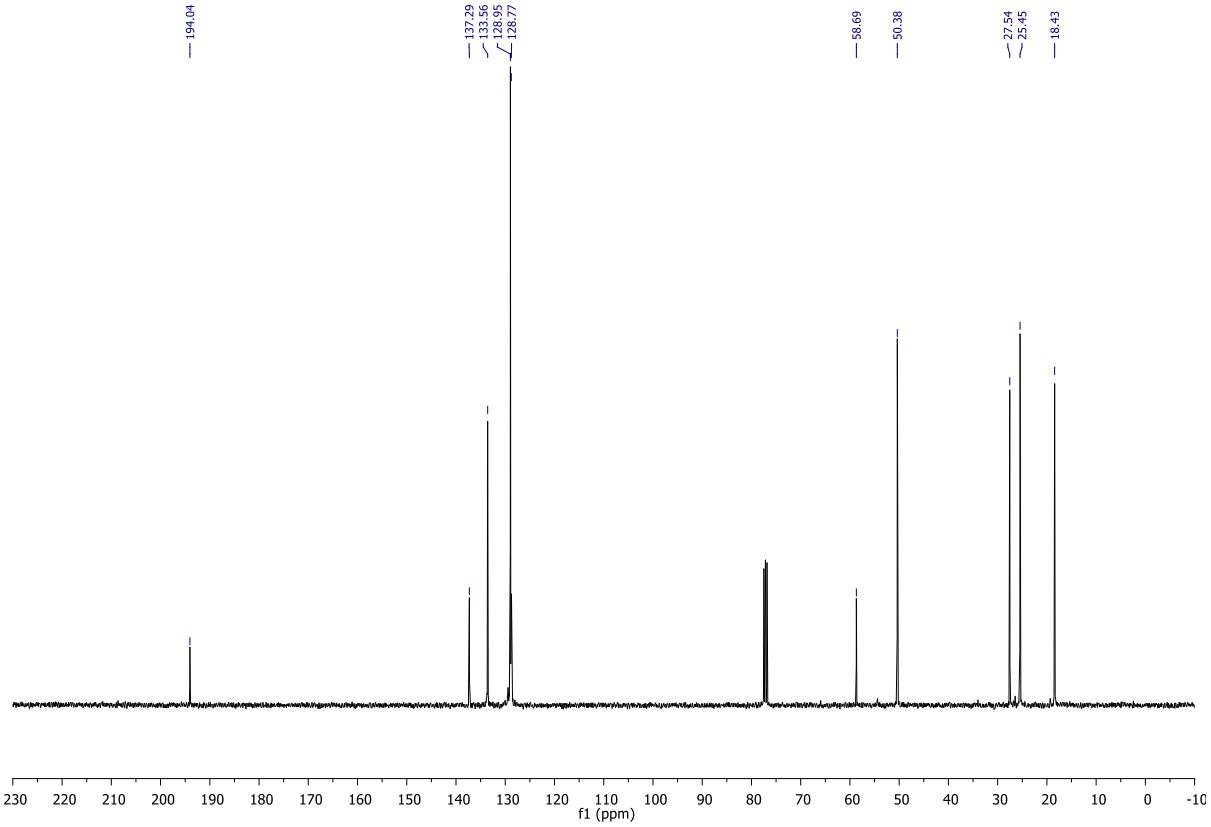
136.85
133.52
129.47
128.79
77.48
77.16
76.84
59.65
54.44
34.04
26.48
19.48
f1 (ppm)



10g'

8.07
8.05
8.05
7.61
7.60
7.58
7.51
7.49
7.48
3.14
3.12
3.11
3.09
3.01
2.99
2.99
2.98
2.98
2.97
2.96
2.95
2.94
2.93
2.92
2.91
2.90
2.89
2.87
2.87
2.86
2.71
2.70
2.68
2.68
2.67
2.66
2.65
2.63
2.42
2.40
2.39
2.37
1.45
1.44
1.43
1.42
1.16
1.14
1.13
2.00
1.07
2.08
1.07
2.14
1.13
1.16
1.07
1.03
f1 (ppm)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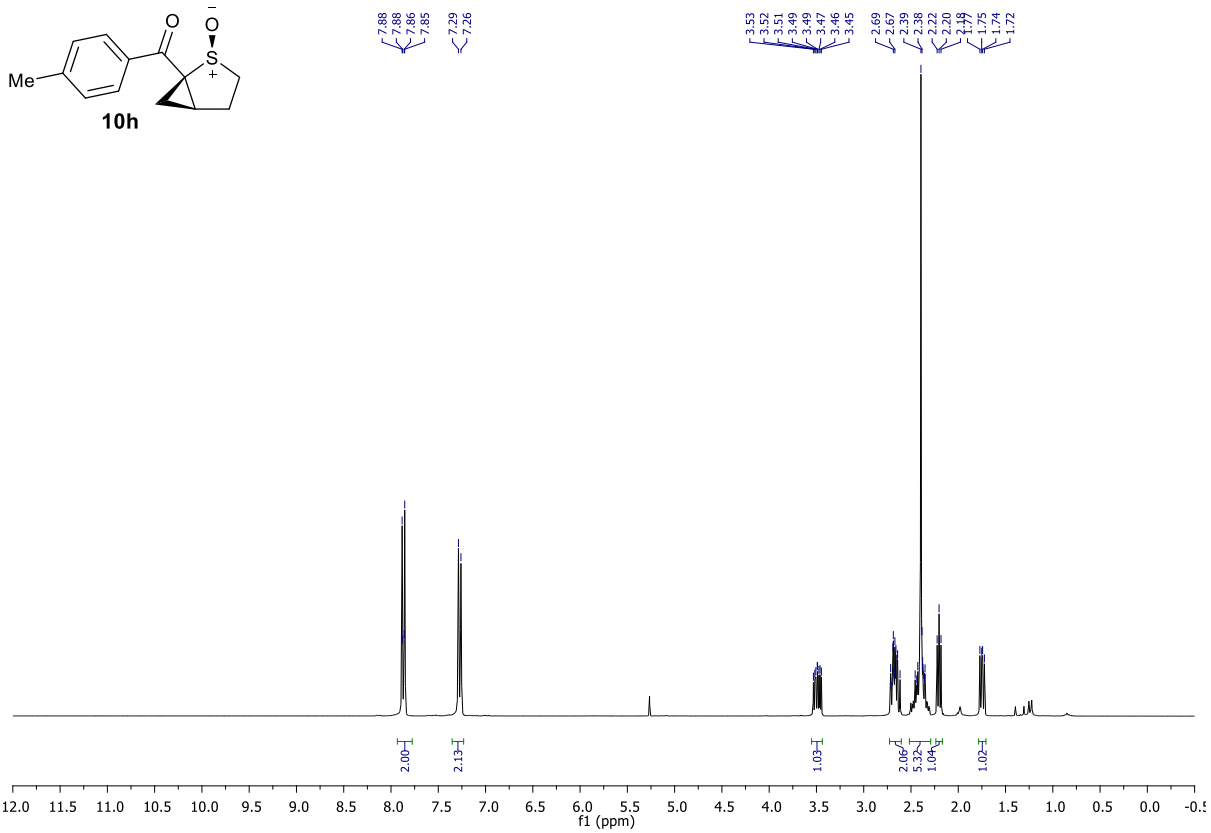
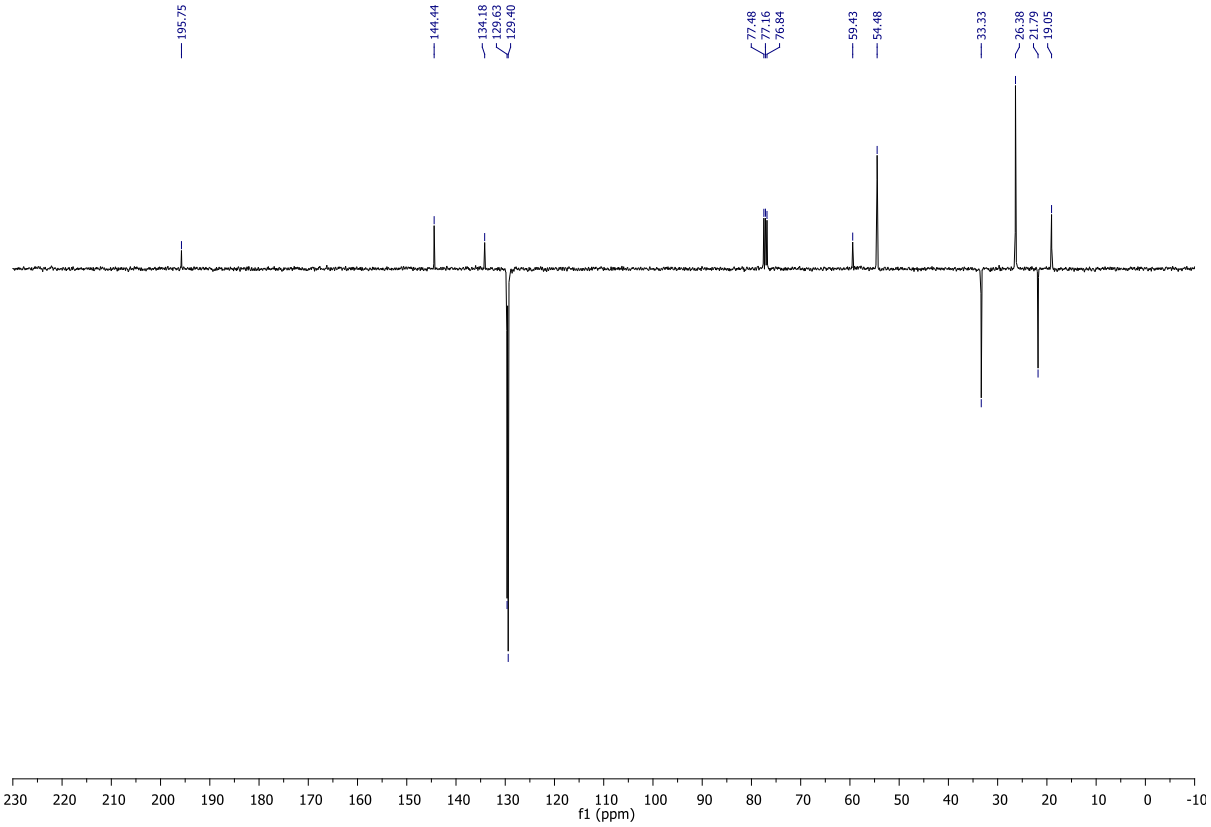
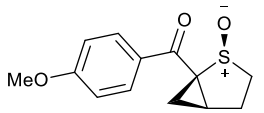
137.29
133.56
128.95
128.77
58.69
50.38
27.54
25.45
18.43
f1 (ppm)

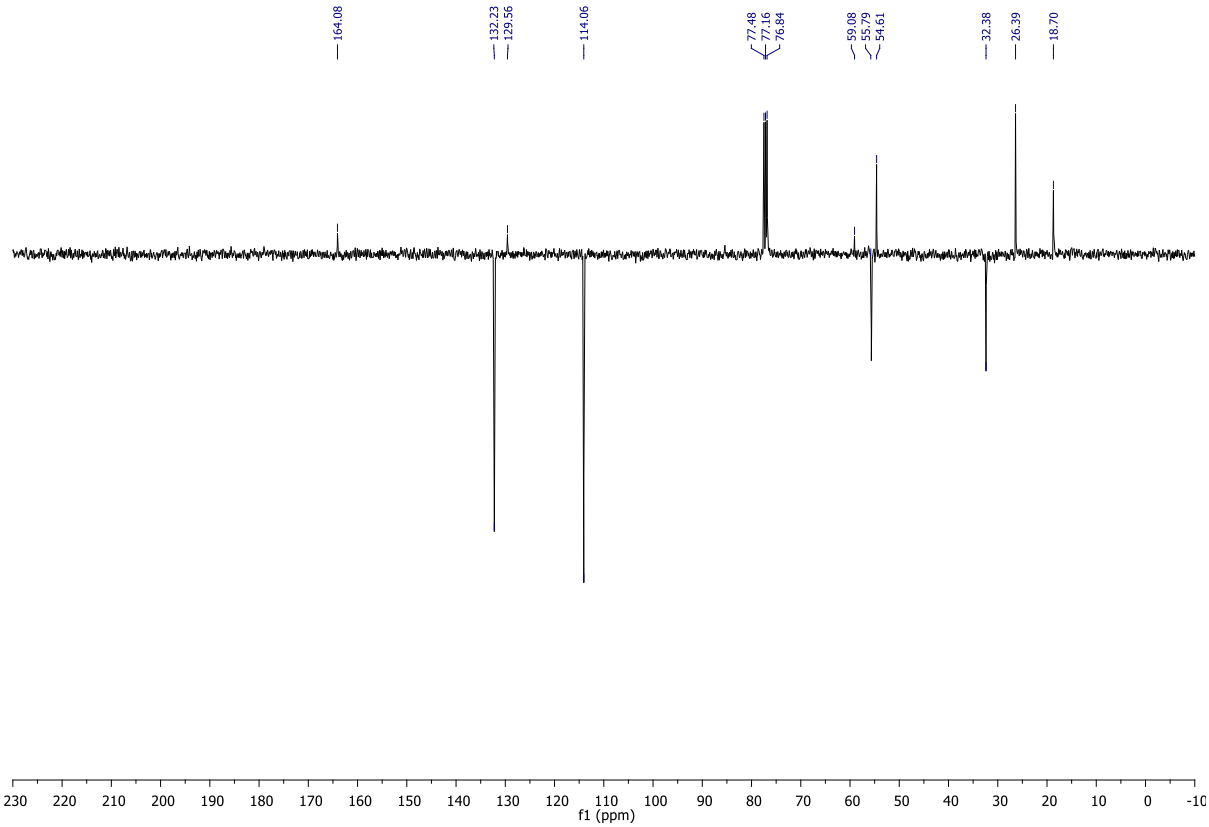

Me
O
O
S
+
10h
7.88
7.88
7.86
7.85
7.29
7.26
3.53
3.52
3.51
3.49
3.49
3.47
3.46
3.45
2.69
2.67
2.39
2.38
2.22
2.20
2.18
1.77
1.75
1.74
1.72
2.00
2.13
1.03
2.06
5.32
1.04
1.02
f1 (ppm)

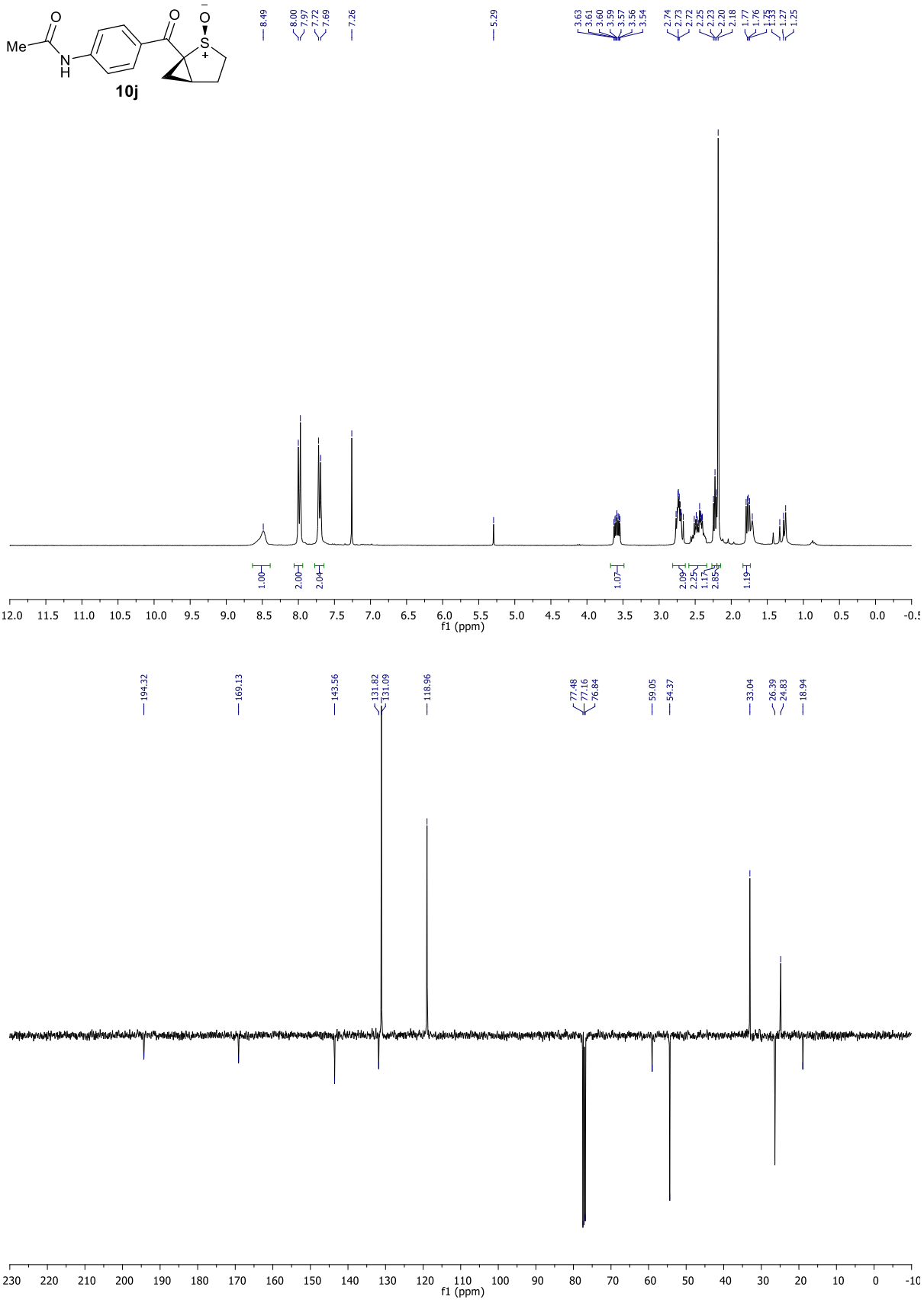

195.75
144.44
134.18
129.63
129.40
77.48
77.16
76.84
59.43
54.48
33.33
26.38
21.79
19.05
f1 (ppm)

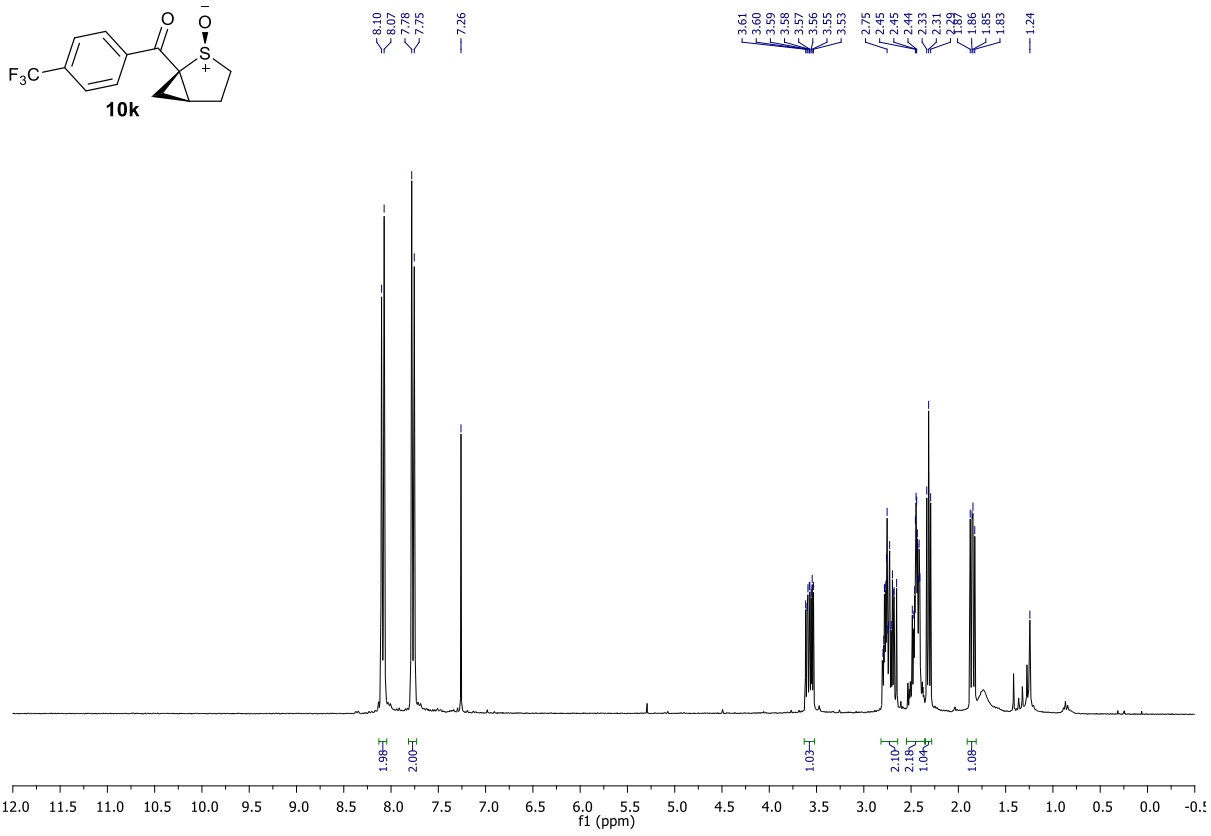

MeO
O
O
S
+

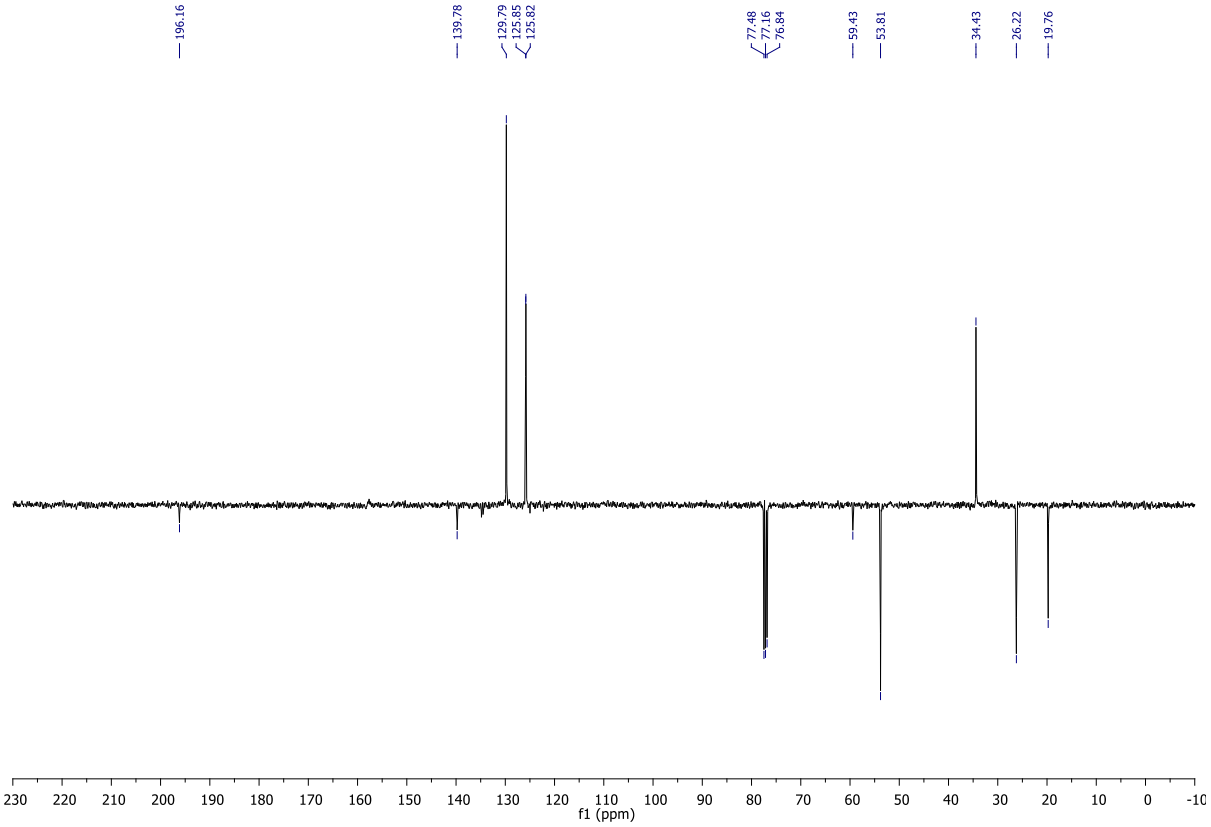
10i

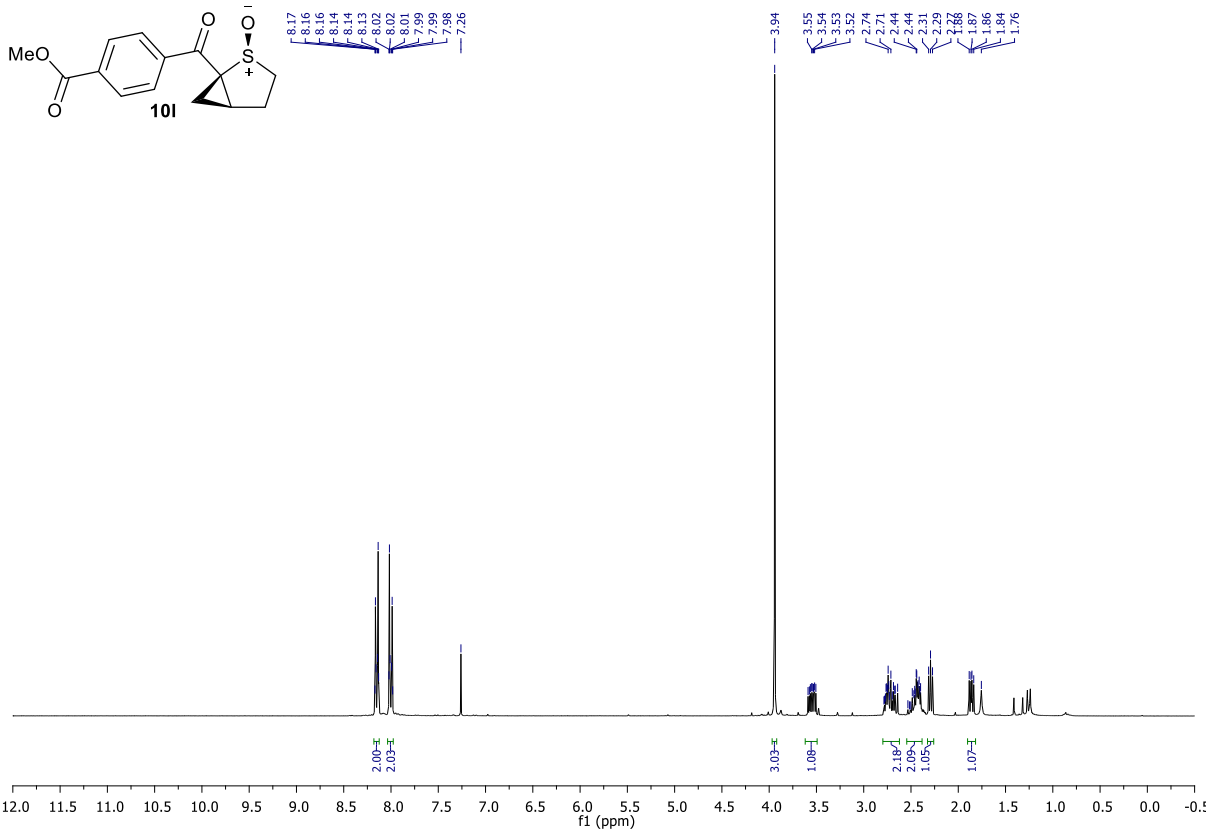
8.05
8.02
7.00
6.97
3.88
3.57
3.56
3.55
3.53
3.51
3.50
3.49
2.71
2.69
2.68
2.68
2.21
1.73
1.71
1.70
1.68
1.66
1.63
1.93
1.97
2.94
1.00
1.95
2.02
1.02
1.24
f1 (ppm)

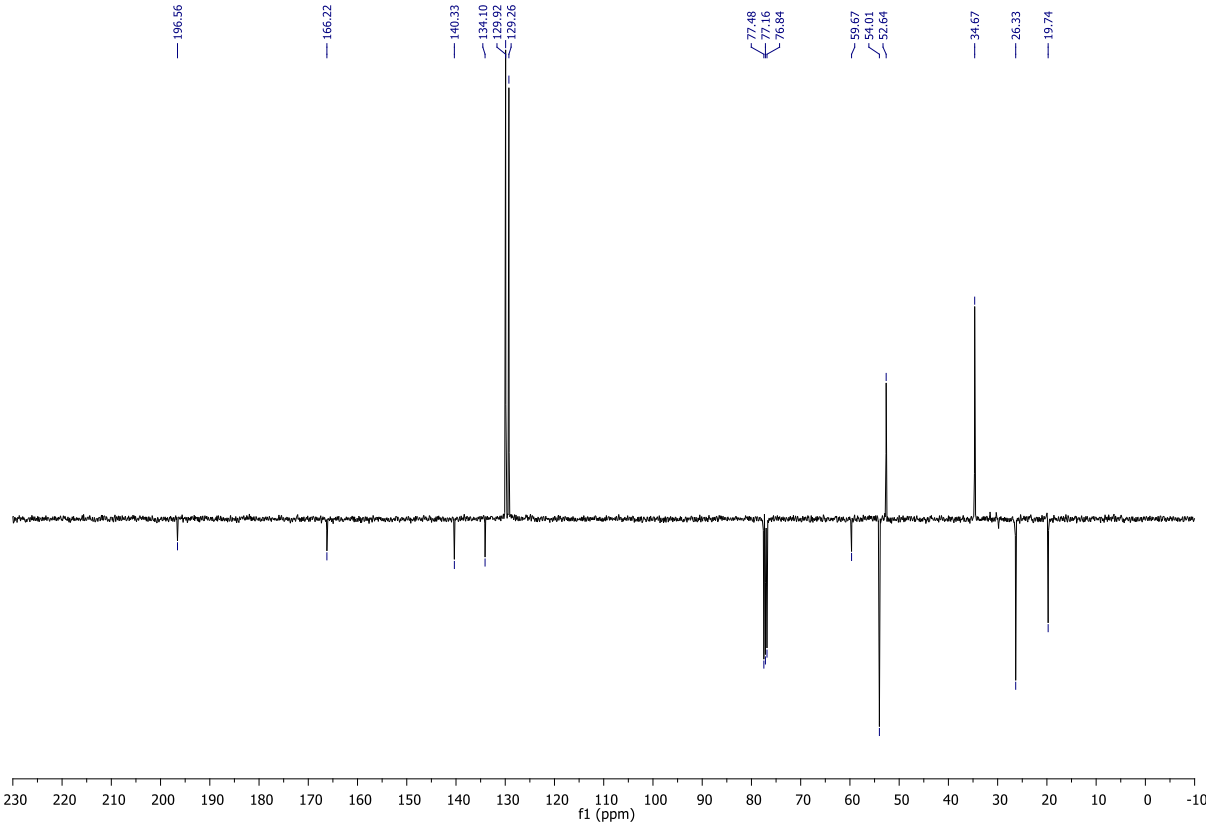

164.08
132.23
129.56
114.06
77.48
77.16
76.84
59.08
55.79
54.61
32.38
26.39
18.70
f1 (ppm)


10j
8.49
8.00
7.97
7.72
7.69
7.26
5.29
3.63
3.61
3.60
3.59
3.57
3.56
3.54
2.74
2.73
2.72
2.25
2.23
2.20
2.18
1.77
1.76
1.33
1.27
1.25
1.00
2.00
2.04
1.07
2.09
2.25
1.17
2.85
1.19
f1 (ppm)
194.32
169.13
143.56
131.82
131.09
118.96
77.48
77.16
76.84
59.05
54.37
33.04
26.39
24.83
18.94
f1 (ppm)


10k
8.10
8.07
7.78
7.75
7.26
3.61
3.60
3.59
3.58
3.57
3.56
3.55
3.53
2.75
2.45
2.45
2.44
2.33
2.31
2.30
1.87
1.86
1.85
1.83
1.24
1.98
2.00
1.03
2.10
2.18
1.04
1.08
f1 (ppm)


196.16
139.78
129.79
125.85
125.82
77.48
77.16
76.84
59.43
53.81
34.43
26.22
19.76
f1 (ppm)


MeO
O
O
O
S
+
10l
8.17
8.16
8.16
8.14
8.14
8.13
8.02
8.02
8.01
7.99
7.99
7.98
7.26
3.94
3.55
3.54
3.53
3.52
2.74
2.71
2.44
2.44
2.31
2.29
1.88
1.87
1.86
1.84
1.76
2.00
2.03
3.03
1.08
2.18
2.09
1.05
1.07
f1 (ppm)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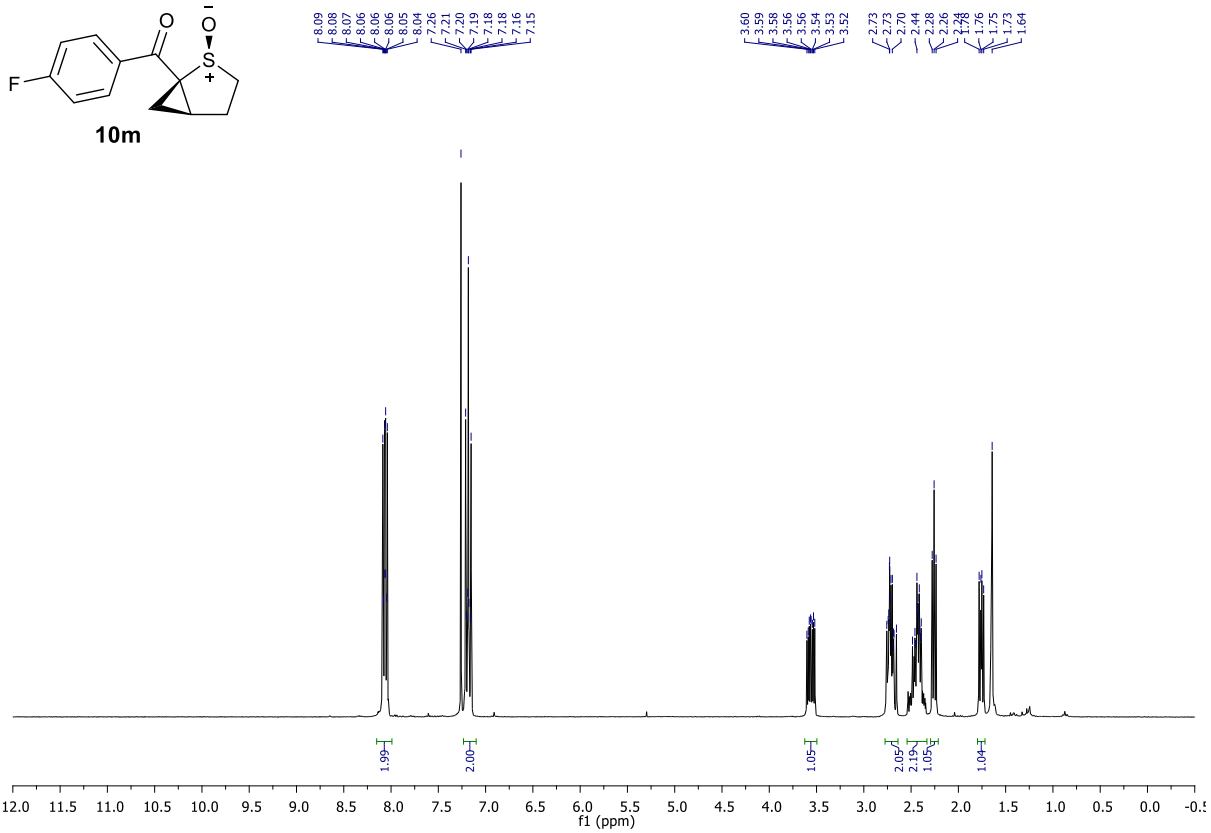
166.22
140.33
134.10
129.92
129.26
77.48
77.16
76.84
59.67
54.01
52.64
34.67
26.33
19.74
f1 (ppm)


10m
F
O
O
S
+
8.09
8.08
8.07
8.06
8.06
8.06
8.06
8.05
8.04
7.26
7.21
7.20
7.19
7.18
7.18
7.16
7.15
3.60
3.59
3.58
3.56
3.56
3.54
3.53
3.52
2.73
2.73
2.70
2.44
2.28
2.26
1.76
1.76
1.75
1.73
1.64
1.99
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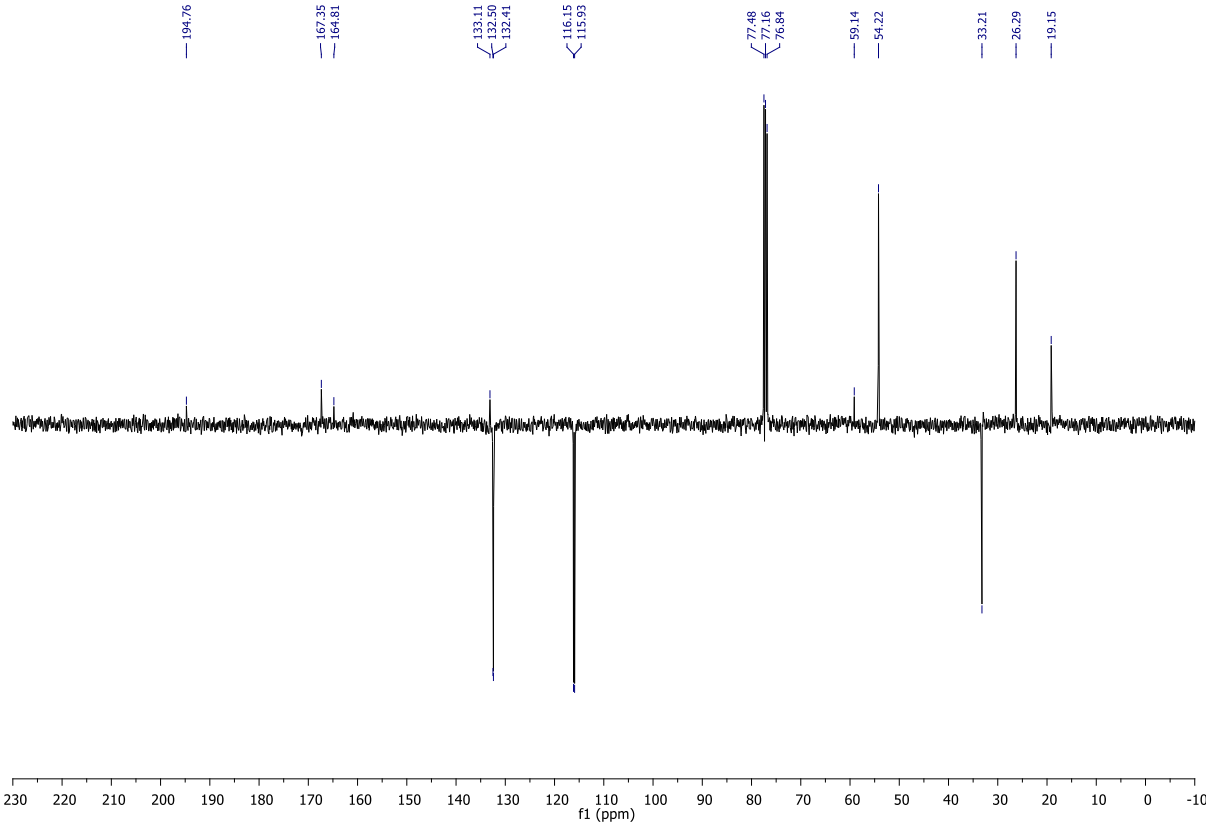
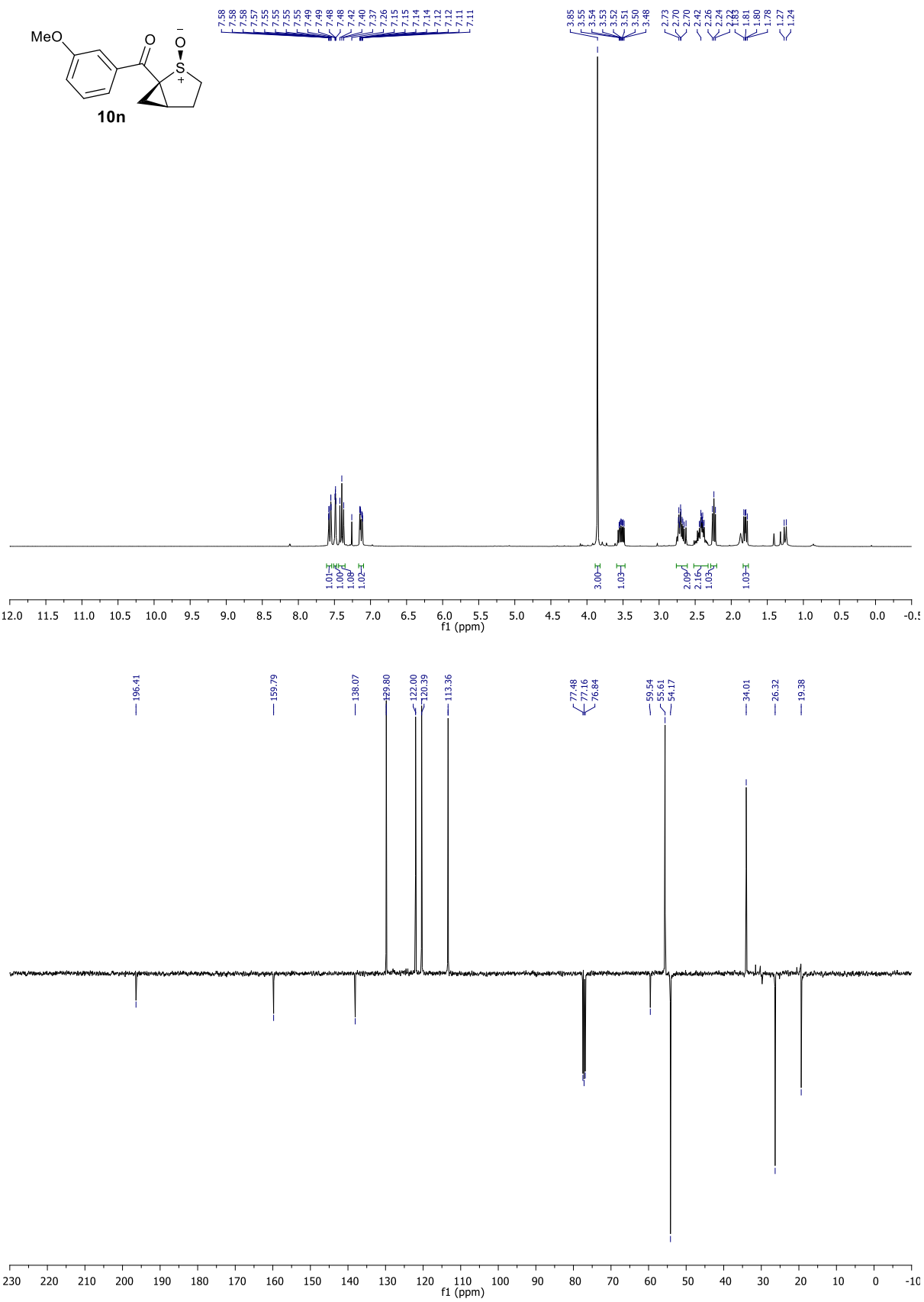
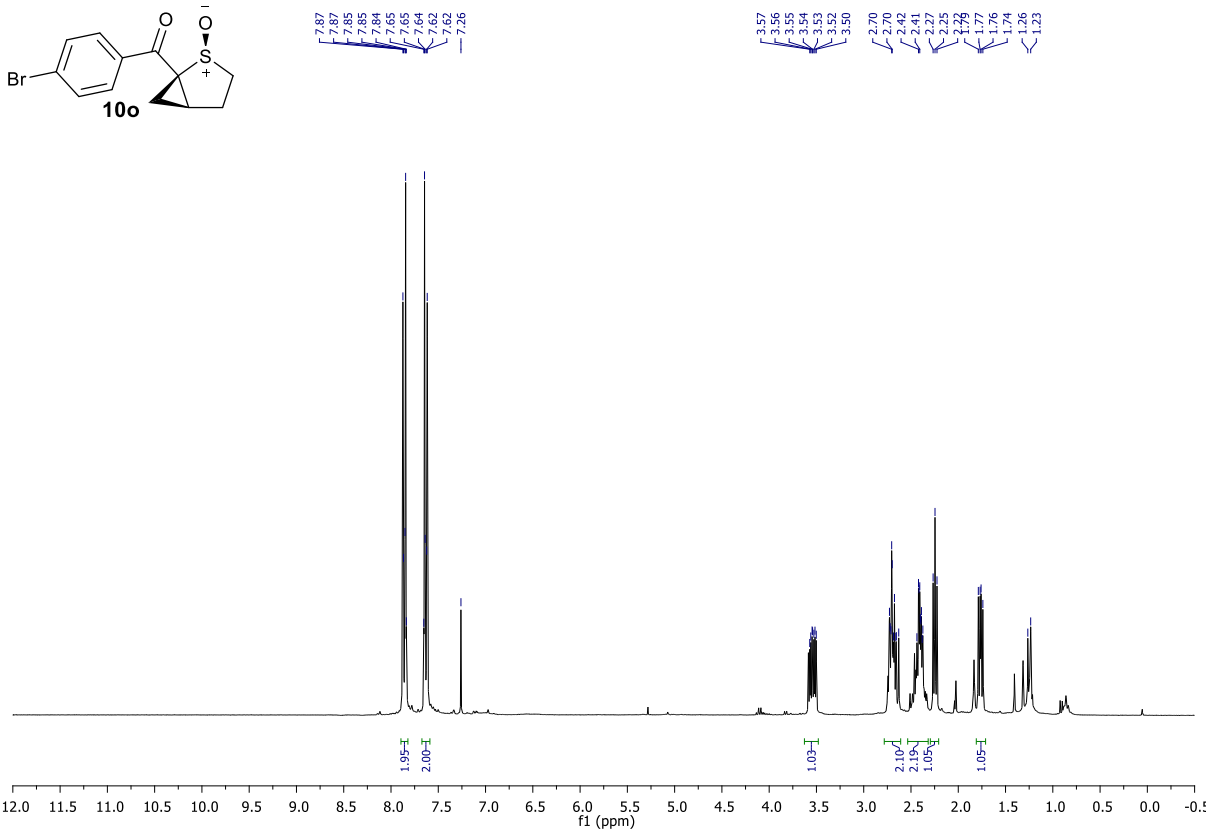
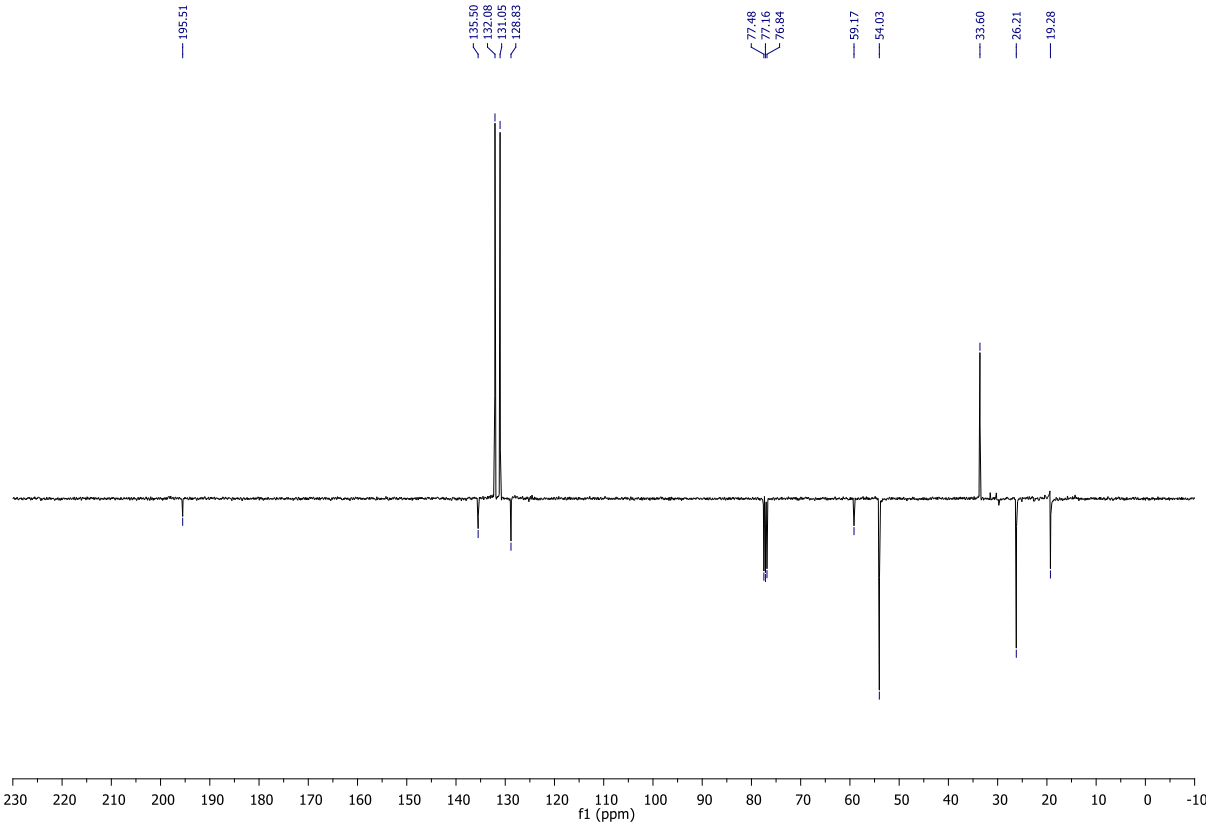
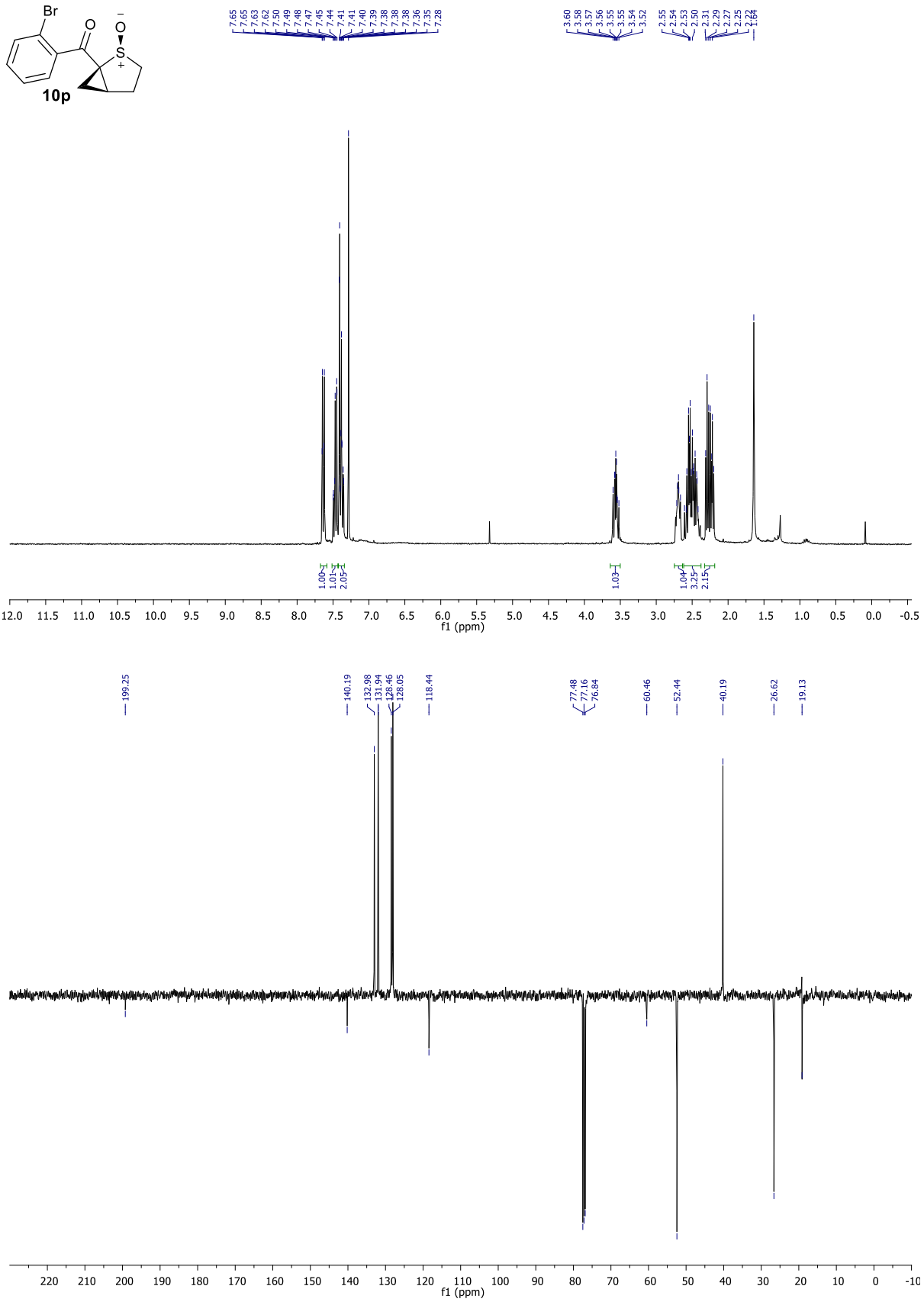
2.05
2.19
1.05
1.04
f1 (ppm)

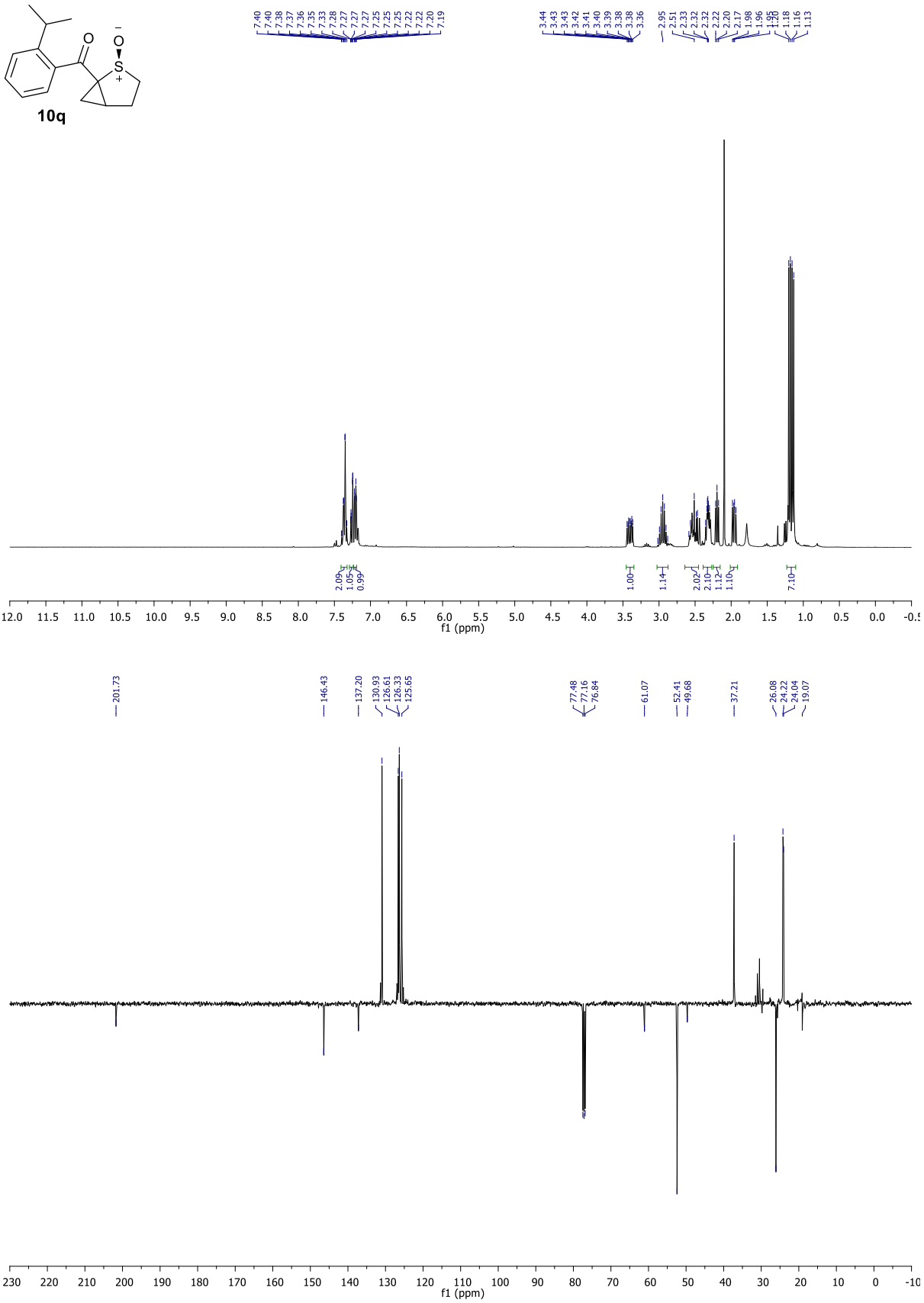

194.76
167.35
164.81
133.11
132.50
132.41
116.15
115.93
77.48
77.16
76.84
59.14
54.22
33.21
26.29
19.15
f1 (ppm)

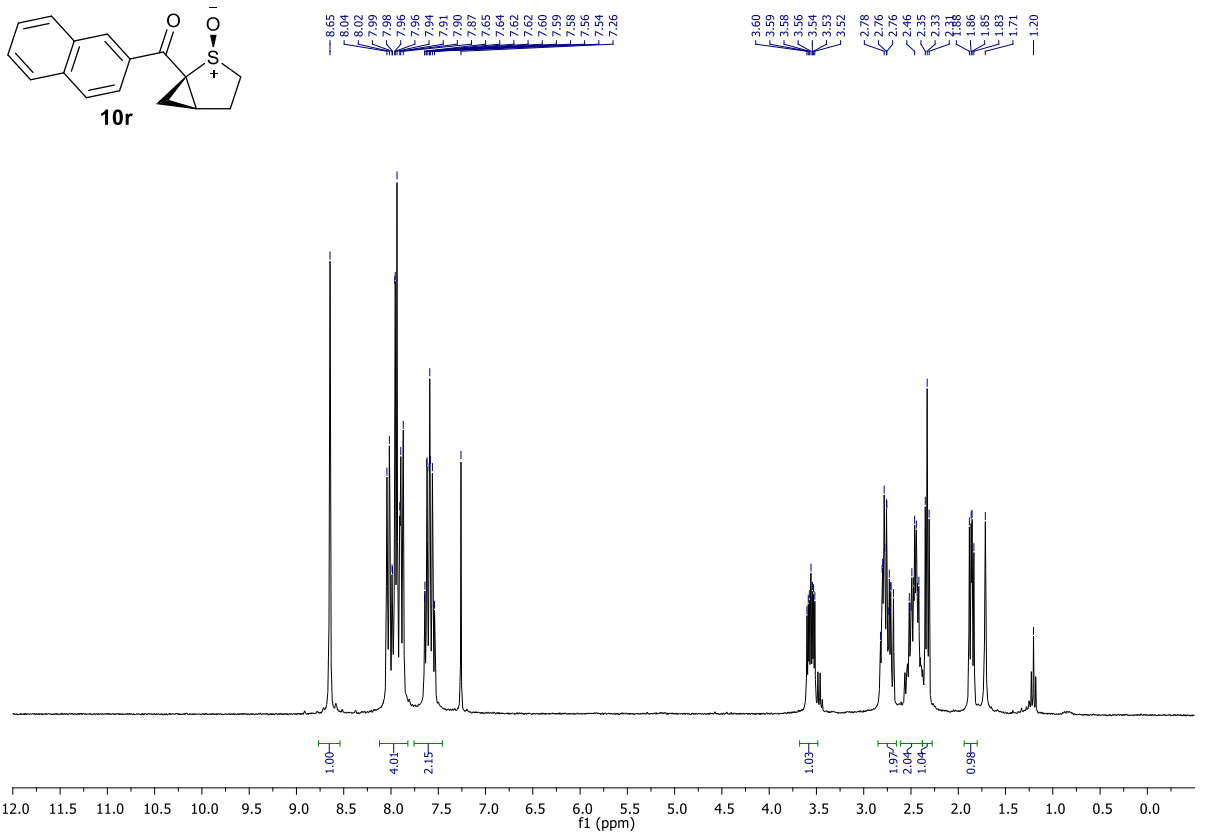

MeO
O
O
S
+
10n
f1 (ppm)
f1 (ppm)

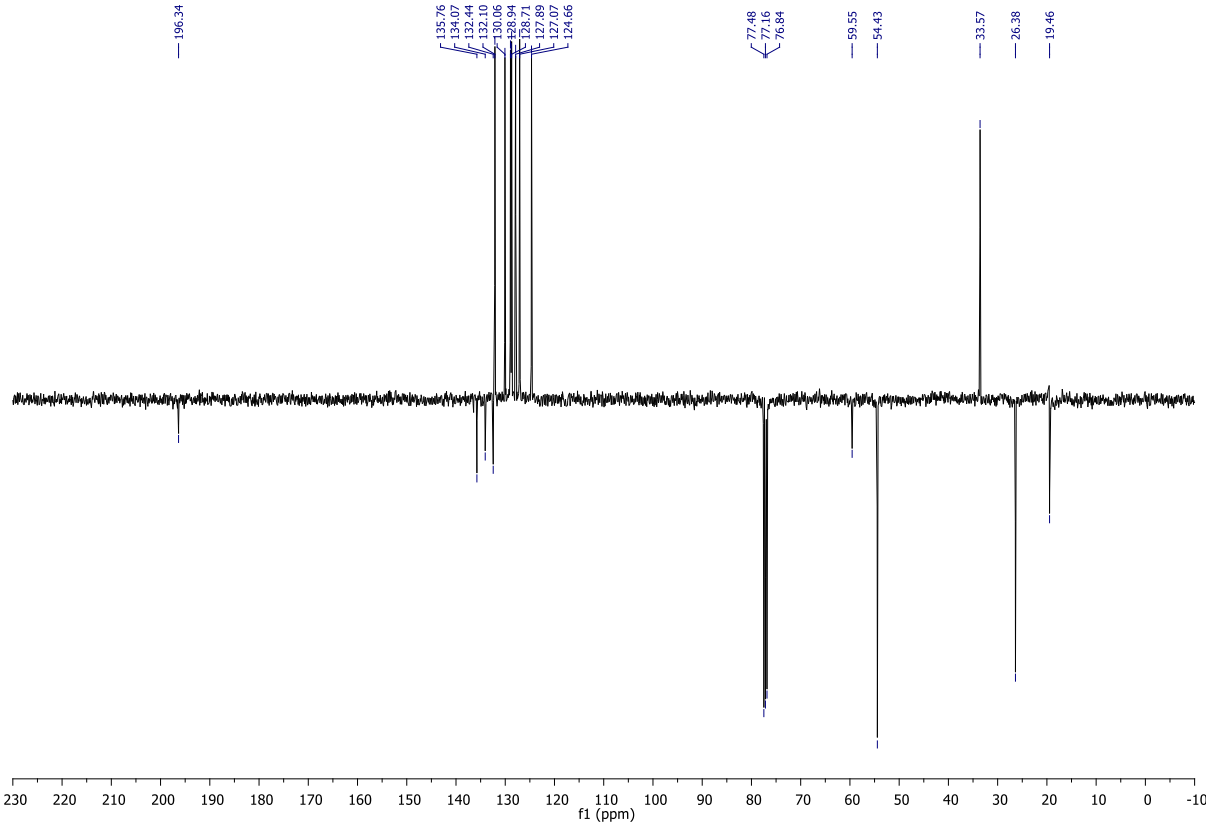

10o
Br
O
O
S
+
7.87
7.87
7.85
7.85
7.84
7.84
7.65
7.64
7.62
7.62
7.26
3.57
3.56
3.55
3.54
3.53
3.52
3.50
2.70
2.70
2.42
2.41
2.27
2.25
1.77
1.76
1.74
1.26
1.23
1.95
2.00
1.03
2.10
2.19
1.05
1.05
f1 (ppm)

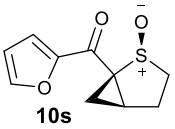

195.51
135.50
132.08
131.05
128.83
77.48
77.16
76.84
59.17
54.03
33.60
26.21
19.28
f1 (ppm)


Br
O
O
S
+
10p
7.65
7.65
7.63
7.62
7.50
7.49
7.48
7.47
7.45
7.44
7.41
7.41
7.40
7.39
7.38
7.38
7.36
7.35
7.28
3.60
3.58
3.57
3.56
3.55
3.55
3.54
3.52
2.55
2.54
2.53
2.50
2.31
2.29
2.27
2.25
1.64
1.00
1.01
2.05
1.03
1.04
3.25
2.15
f1 (ppm)
199.25
140.19
132.98
131.94
128.46
128.05
118.44
77.48
77.16
76.84
60.46
52.44
40.19
26.62
19.13
f1 (ppm)


10q
f1 (ppm)
f1 (ppm)

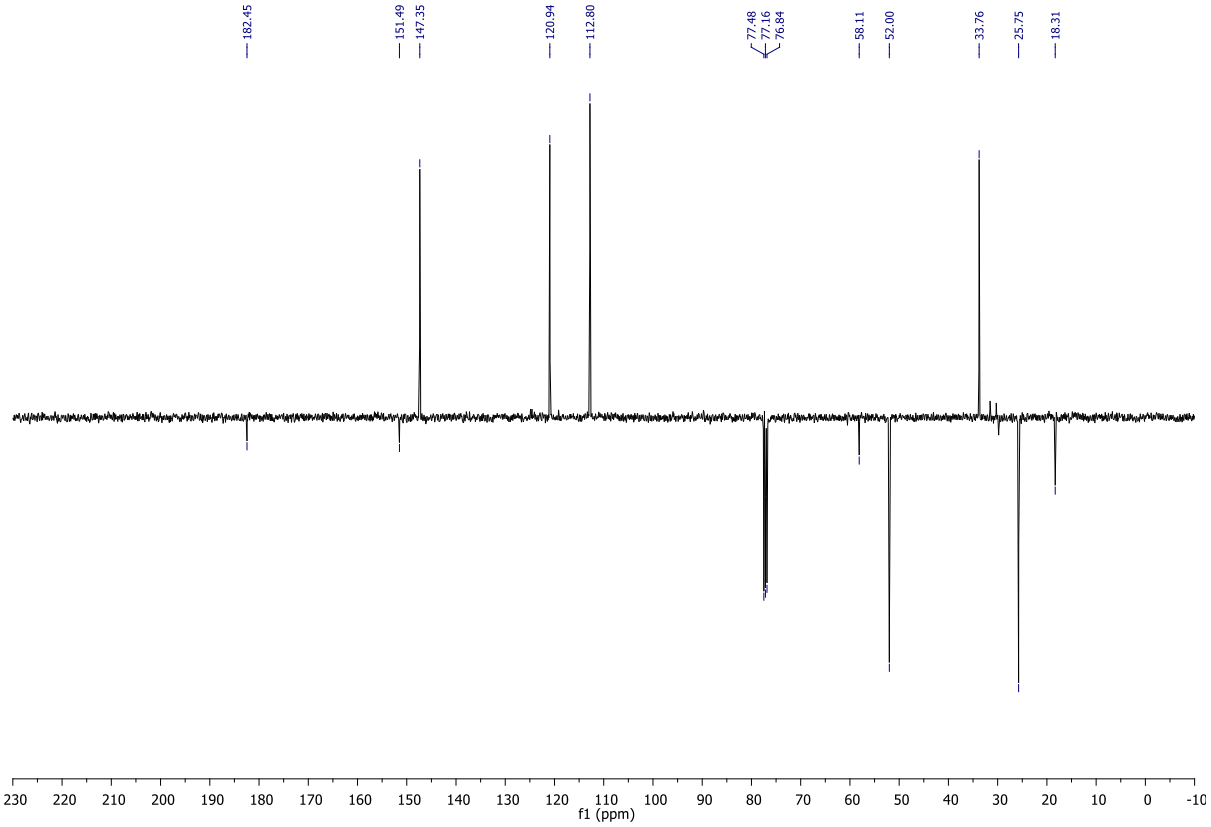

10r
8.65
8.04
8.02
7.99
7.98
7.96
7.96
7.94
7.91
7.90
7.87
7.65
7.64
7.62
7.62
7.60
7.59
7.58
7.56
7.54
7.26
3.60
3.59
3.58
3.56
3.54
3.53
3.52
2.78
2.76
2.76
2.46
2.35
2.33
2.31
1.88
1.86
1.85
1.83
1.71
1.20
1.00
4.01
2.15
1.03
1.97
2.04
1.04
0.98
f1 (ppm)


196.34
135.76
134.07
132.44
132.10
130.06
128.94
128.71
127.89
127.07
124.66
77.48
77.16
76.84
59.55
54.43
33.57
26.38
19.46
f1 (ppm)



10s

7.65
7.65
7.64
7.62
7.61
7.60
7.60
7.26
6.59
6.59
6.58
6.57
3.61
3.60
3.58
3.57
3.55
3.53
2.39
2.39
2.38
2.36
2.20
2.18
2.16
1.94
1.92
1.91
1.28
1.24
1.23
1.99
1.00
1.09
1.08
1.15
2.20
1.11
1.26
f1 (ppm)


182.45
151.49
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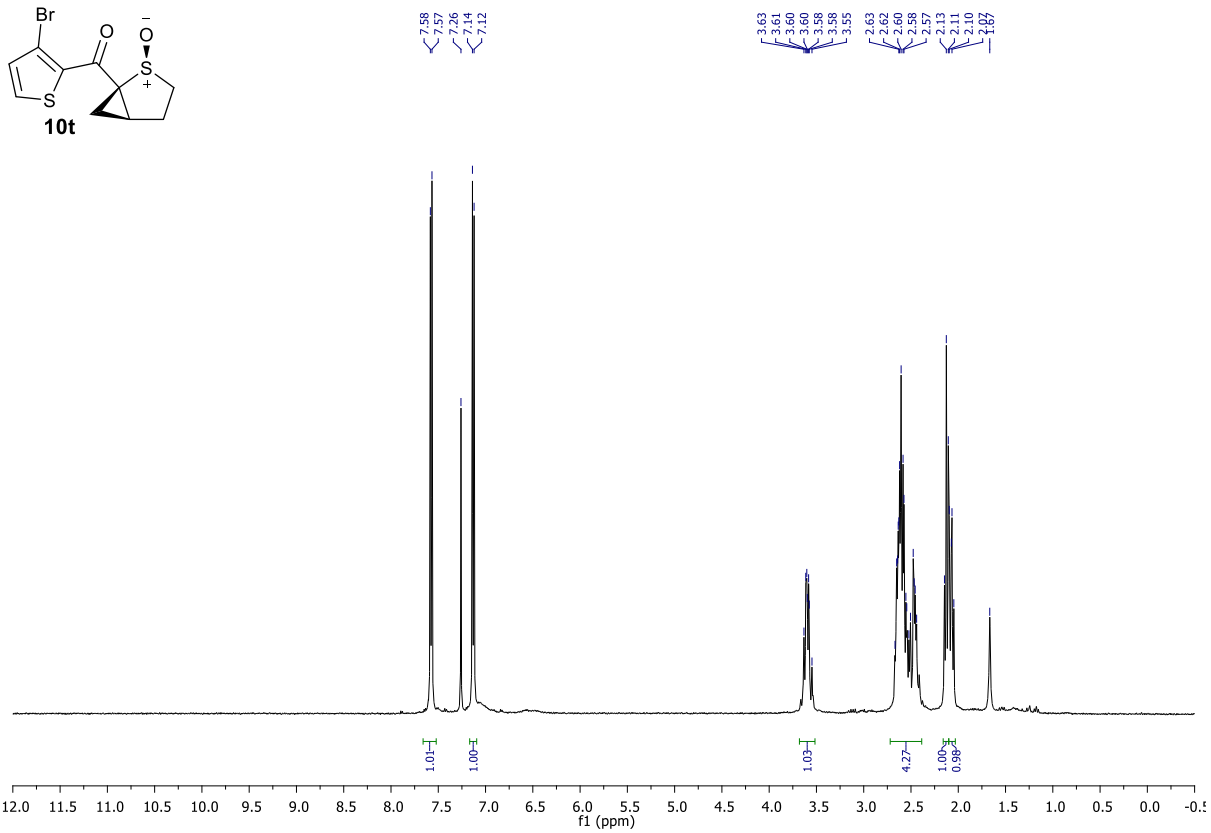
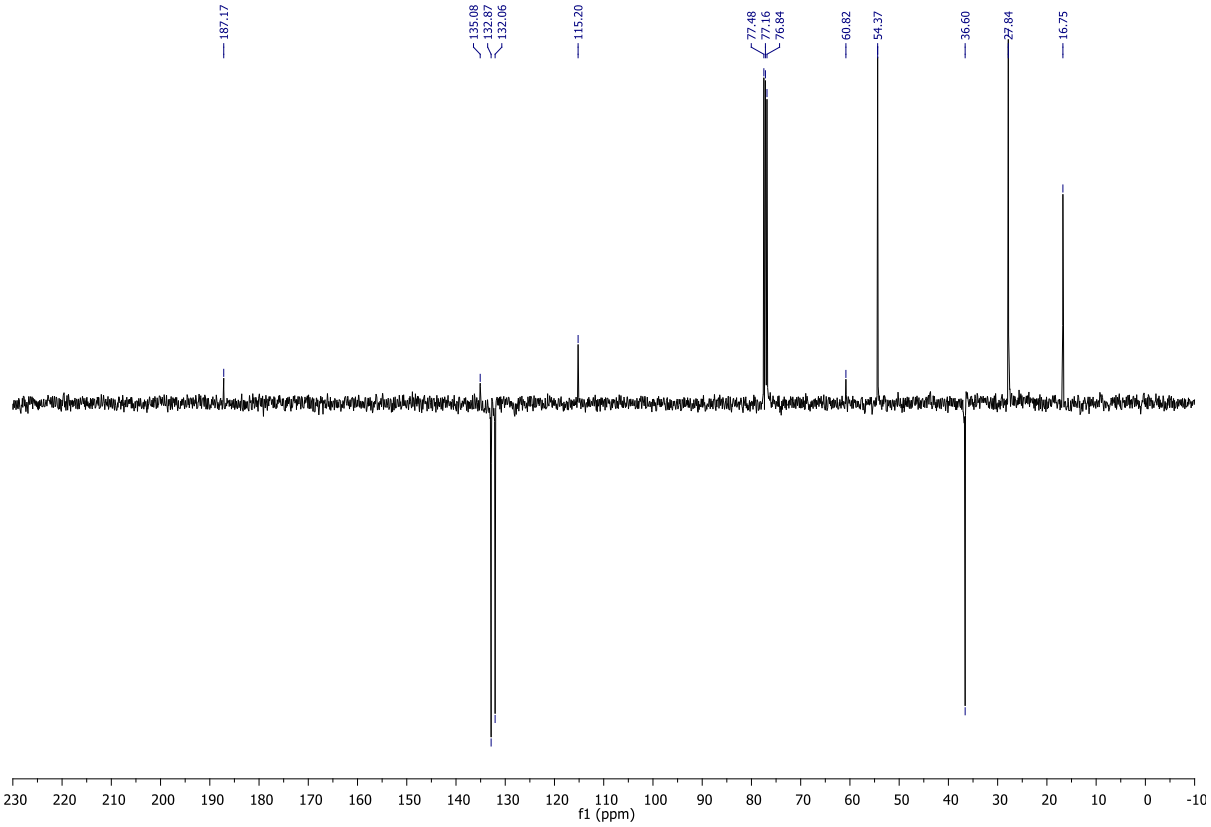
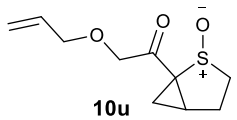
112.80
77.48
77.16
76.84
58.11
52.00
33.76
25.75
18.31
f1 (ppm)

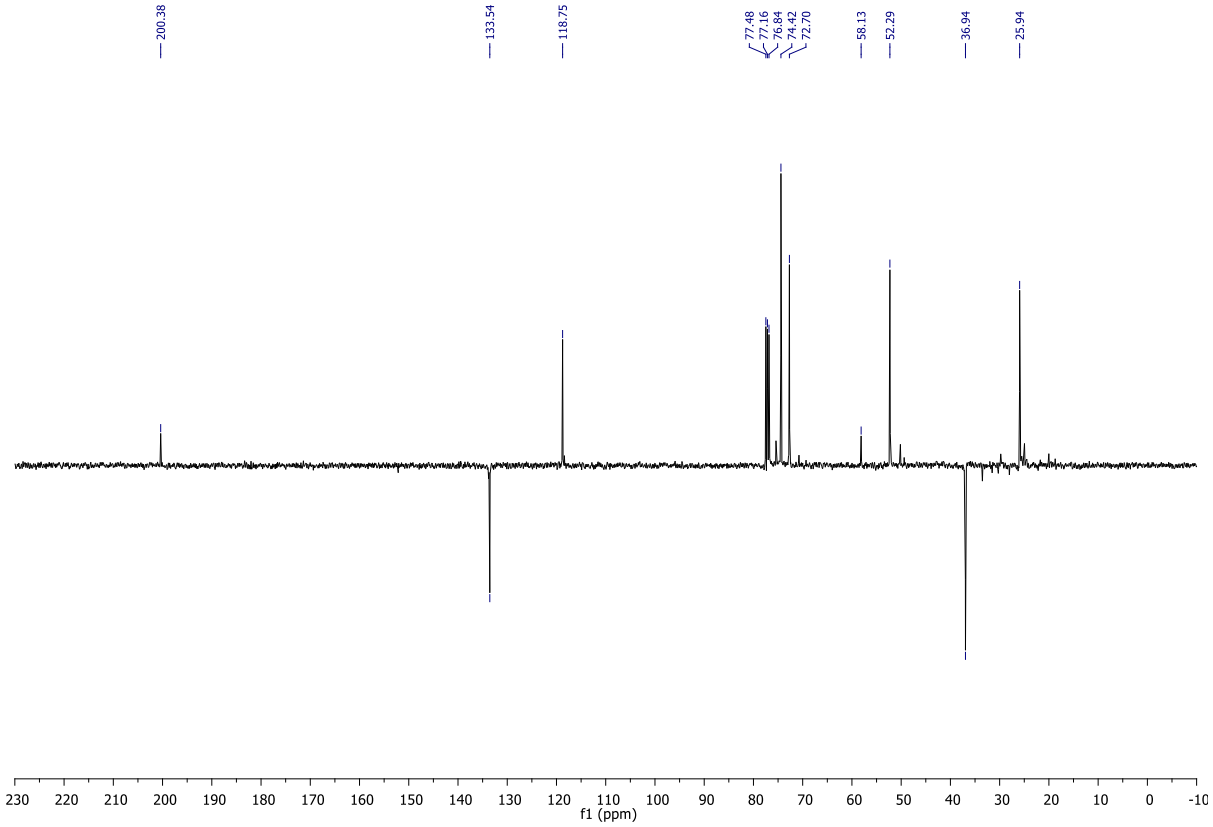

Br
O
O
S
S
10t
7.58
7.57
7.26
7.14
7.12
3.63
3.61
3.60
3.60
3.58
3.58
3.55
2.63
2.62
2.60
2.58
2.57
2.13
2.11
2.10
1.07
1.07
1.01
1.00
1.03
4.27
1.00
0.98
f1 (ppm)

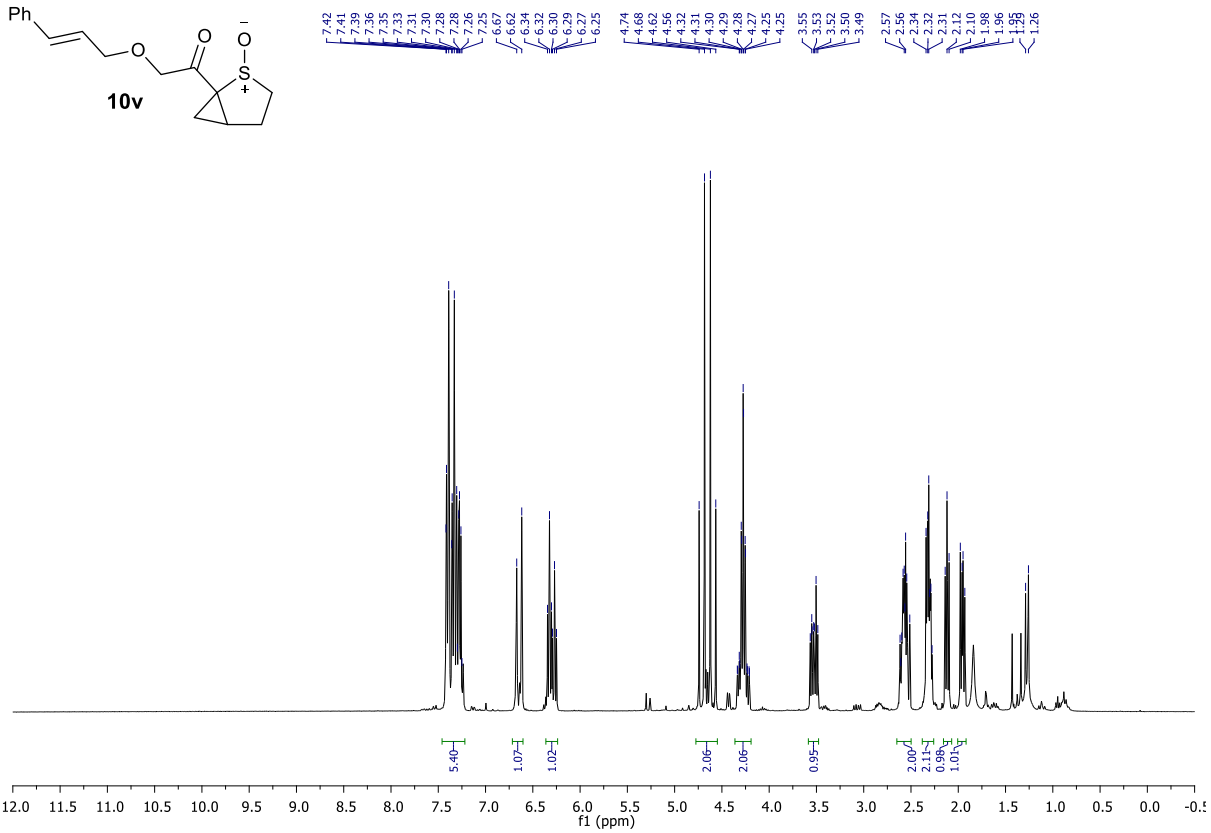

187.17
135.08
132.87
132.06
115.20
77.48
77.16
76.84
60.82
54.37
36.60
27.84
16.75
f1 (ppm)

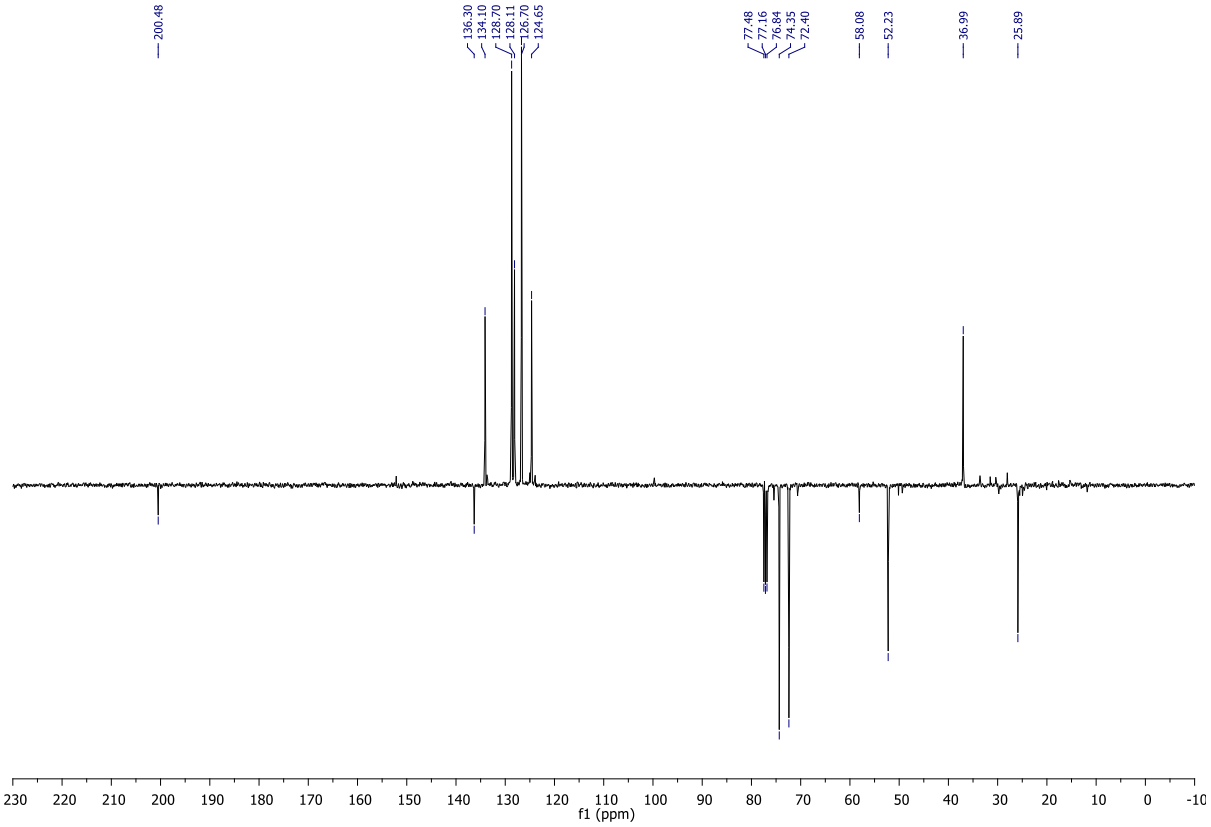

O
O
O
S
+
−

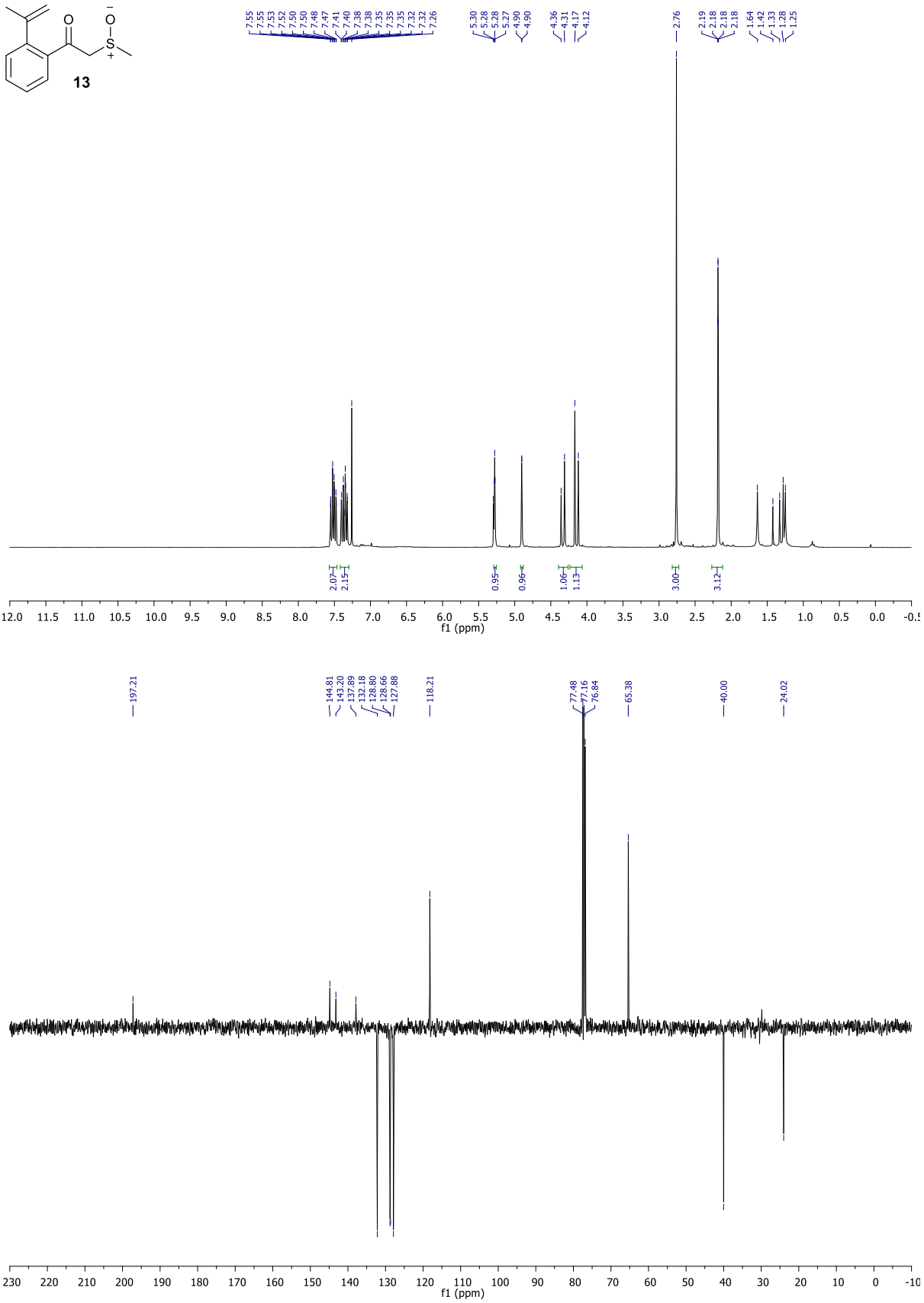
10u

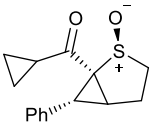
7.26
5.97
5.95
5.93
5.93
5.91
5.89
5.87
5.87
5.87
5.85
5.84
5.33
5.33
5.26
5.25
4.66
4.61
4.55
4.49
4.09
4.09
4.07
3.54
3.52
3.51
3.50
3.48
2.57
2.55
2.53
2.34
2.33
2.32
2.10
1.96
1.93
1.40
1.31
1.26
1.23
1.00
2.10
2.08
0.09
2.06
0.98
1.99
2.08
0.98
1.07
f1 (ppm)


200.38
133.54
118.75
77.48
77.16
76.84
74.42
72.70
58.13
52.29
36.94
25.94
f1 (ppm)


Ph
O
O
O
S
+
10v
7.42
7.41
7.39
7.36
7.35
7.33
7.31
7.30
7.28
7.28
7.26
7.25
6.67
6.62
6.34
6.32
6.30
6.29
6.27
6.25
4.74
4.68
4.62
4.56
4.32
4.31
4.30
4.29
4.28
4.27
4.25
4.25
3.55
3.53
3.52
3.50
3.49
2.57
2.56
2.34
2.32
2.31
2.12
2.10
1.98
1.96
1.26
5.40
1.07
1.02
2.06
2.06
0.95
2.00
2.11
0.98
1.01
f1 (ppm)

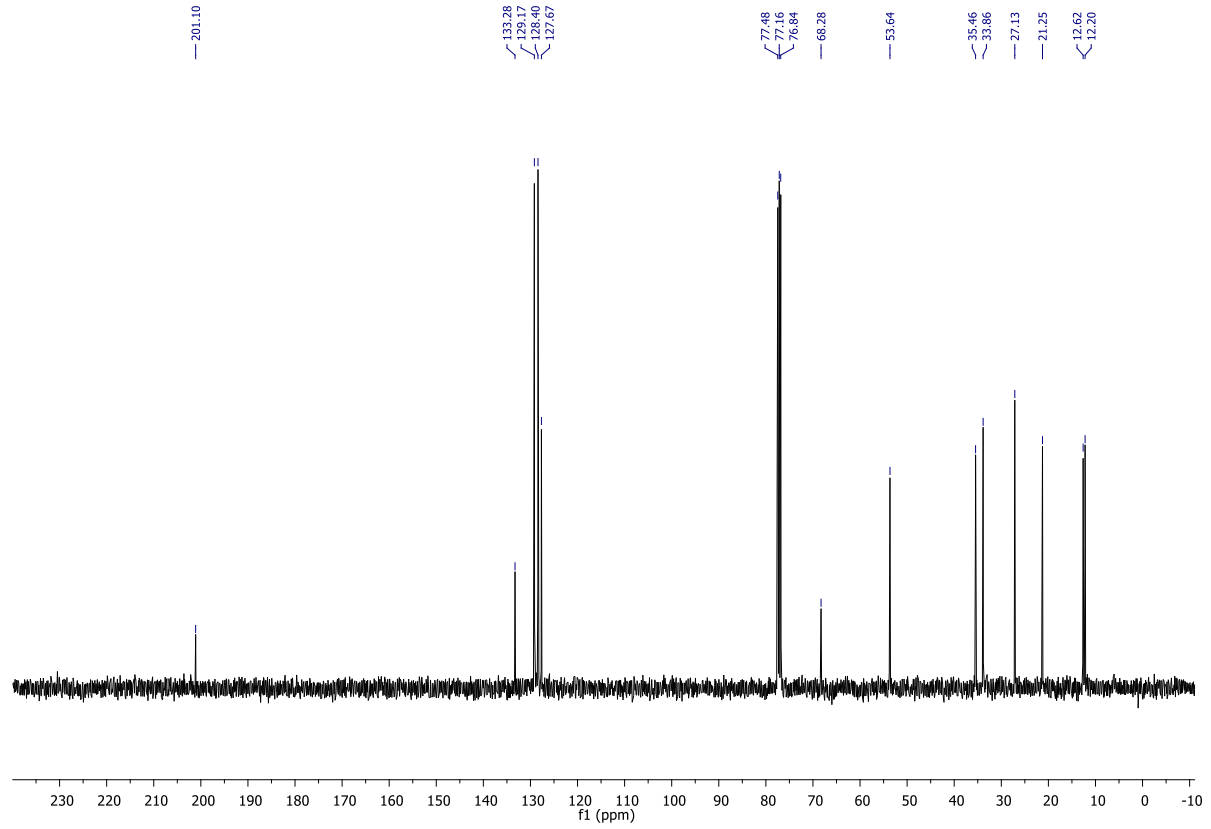

200.48
136.30
134.10
128.70
128.11
126.70
124.65
77.48
77.16
76.84
74.35
72.40
58.08
52.23
36.99
25.89
f1 (ppm)

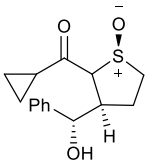

13
7.55
7.55
7.53
7.52
7.50
7.50
7.48
7.47
7.41
7.40
7.38
7.38
7.35
7.35
7.35
7.32
7.32
7.26
5.30
5.28
5.28
5.27
4.90
4.90
4.36
4.31
4.17
4.12
2.76
2.19
2.18
2.18
2.18
1.64
1.42
1.33
1.28
1.25
2.07
2.15
0.95
0.96
1.06
1.13
3.00
3.12
f1 (ppm)
197.21
144.81
143.20
137.89
132.18
128.80
128.66
127.88
118.21
77.48
77.16
76.84
65.38
40.00
24.02
f1 (ppm)


O
O
S
+
Ph

15

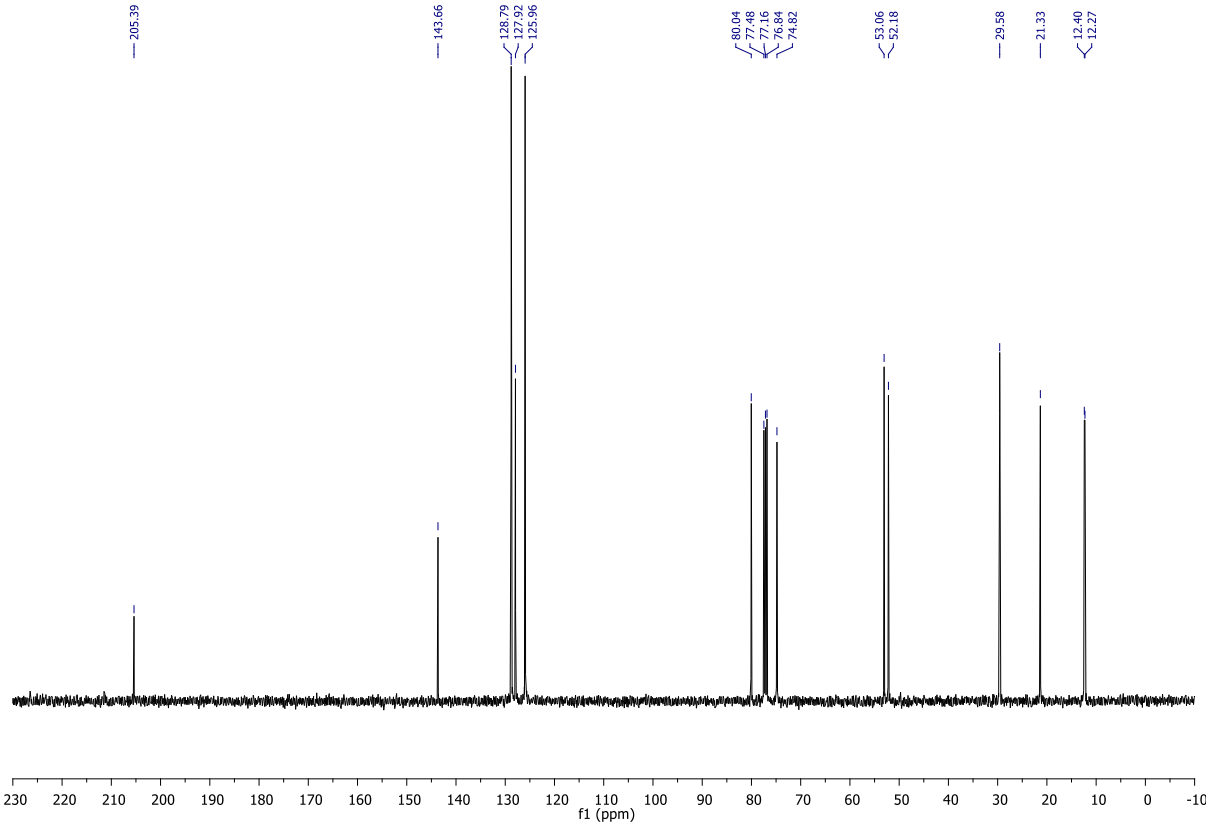
7.32
7.32
7.30
7.28
7.27
7.25
7.23
3.78
3.77
3.62
3.60
3.59
3.58
3.57
3.55
3.18
3.17
2.74
2.56
2.55
2.55
2.54
2.53
2.53
1.85
1.01
1.00
0.99
0.89
0.88
0.86
0.86
0.78
0.77
0.76
0.63
0.63
0.62
5.14
0.94
1.07
1.00
1.05
1.99
0.98
1.01
1.14
1.04
1.06
f1 (ppm)


201.10
133.28
129.17
128.40
127.67
77.48
77.16
76.84
68.28
53.64
35.46
33.86
27.13
21.25
12.62
12.20
f1 (ppm)

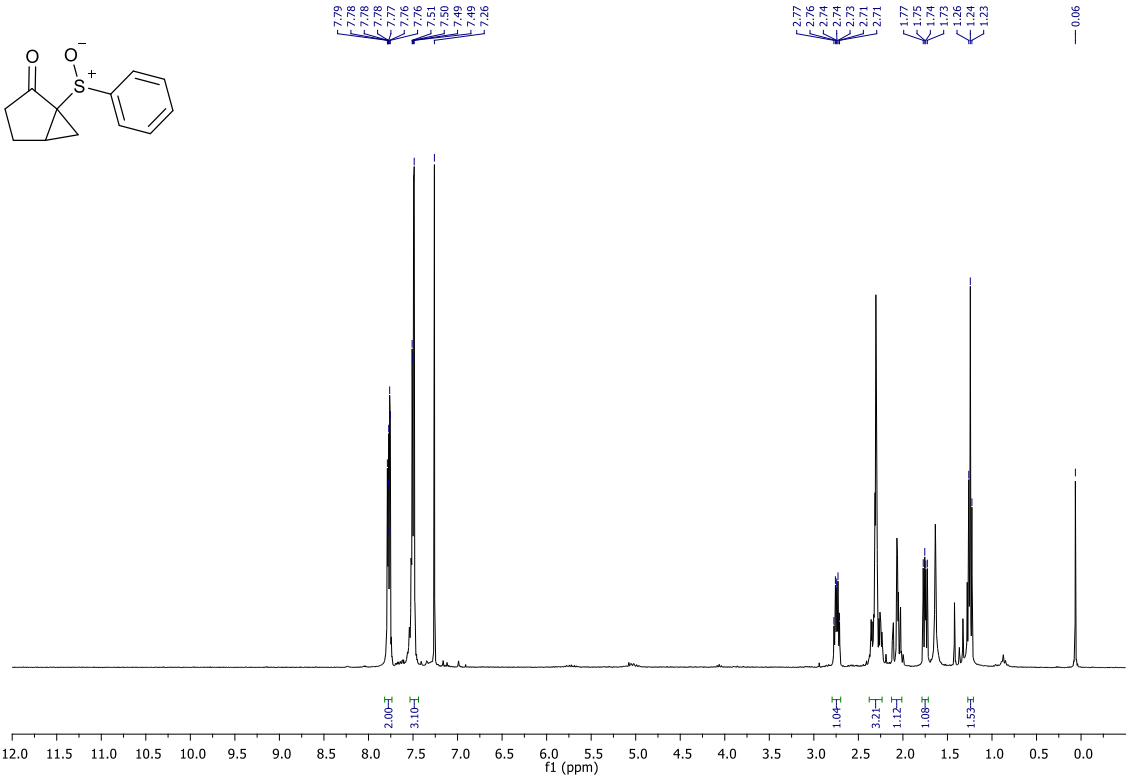

O
O
S
+
Ph
H
OH

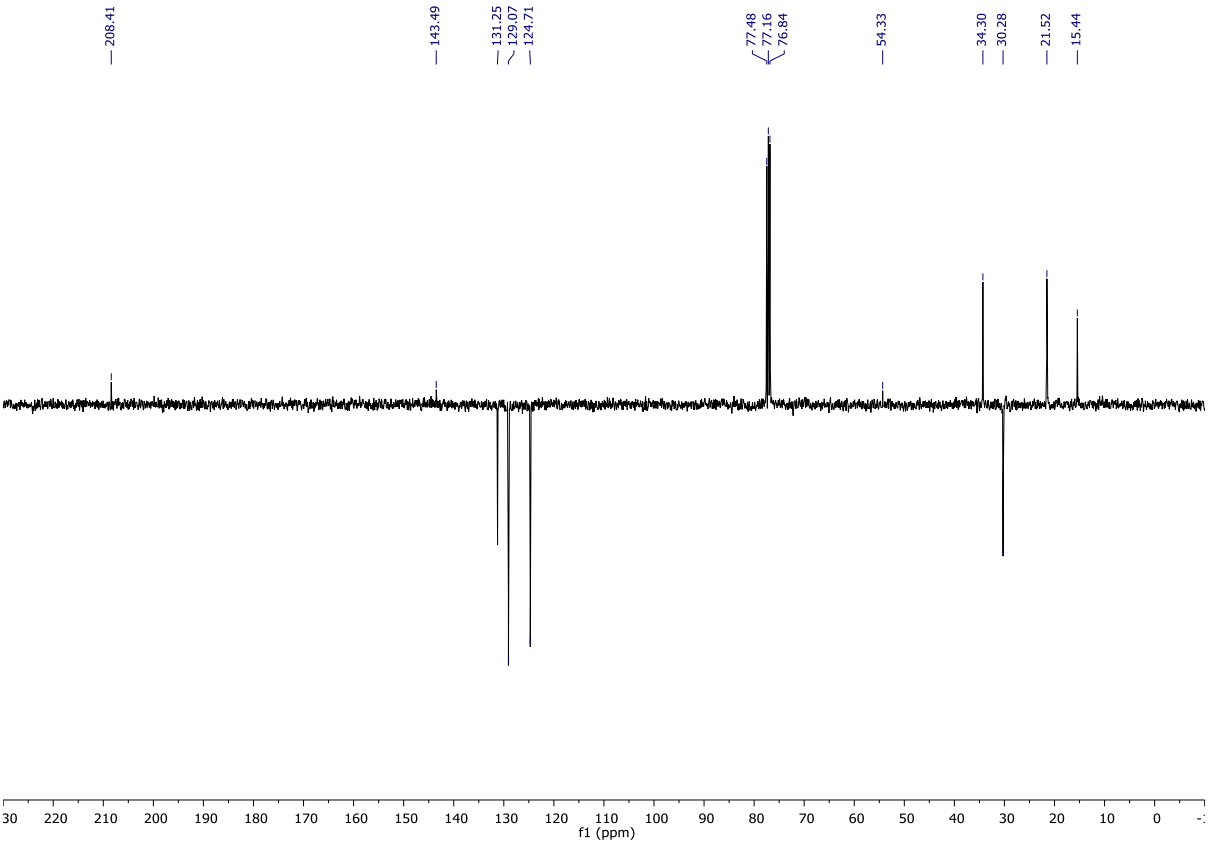
16

7.40
7.39
7.37
7.35
7.33
7.28
7.27
7.26
7.25
7.25
4.87
4.86
4.84
4.25
4.25
4.24
4.24
3.75
3.74
3.17
3.12
3.11
3.10
2.72
2.71
2.70
2.69
2.68
2.35
1.74
1.70
1.69
1.68
0.97
0.97
0.96
0.96
0.94
0.93
0.92
0.90
0.87
0.85
0.85
0.84
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

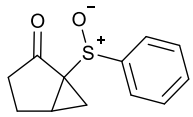

205.39
143.66
128.79
127.92
125.96
80.04
77.48
77.16
76.84
74.82
53.06
52.18
29.58
21.33
12.40
12.27
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

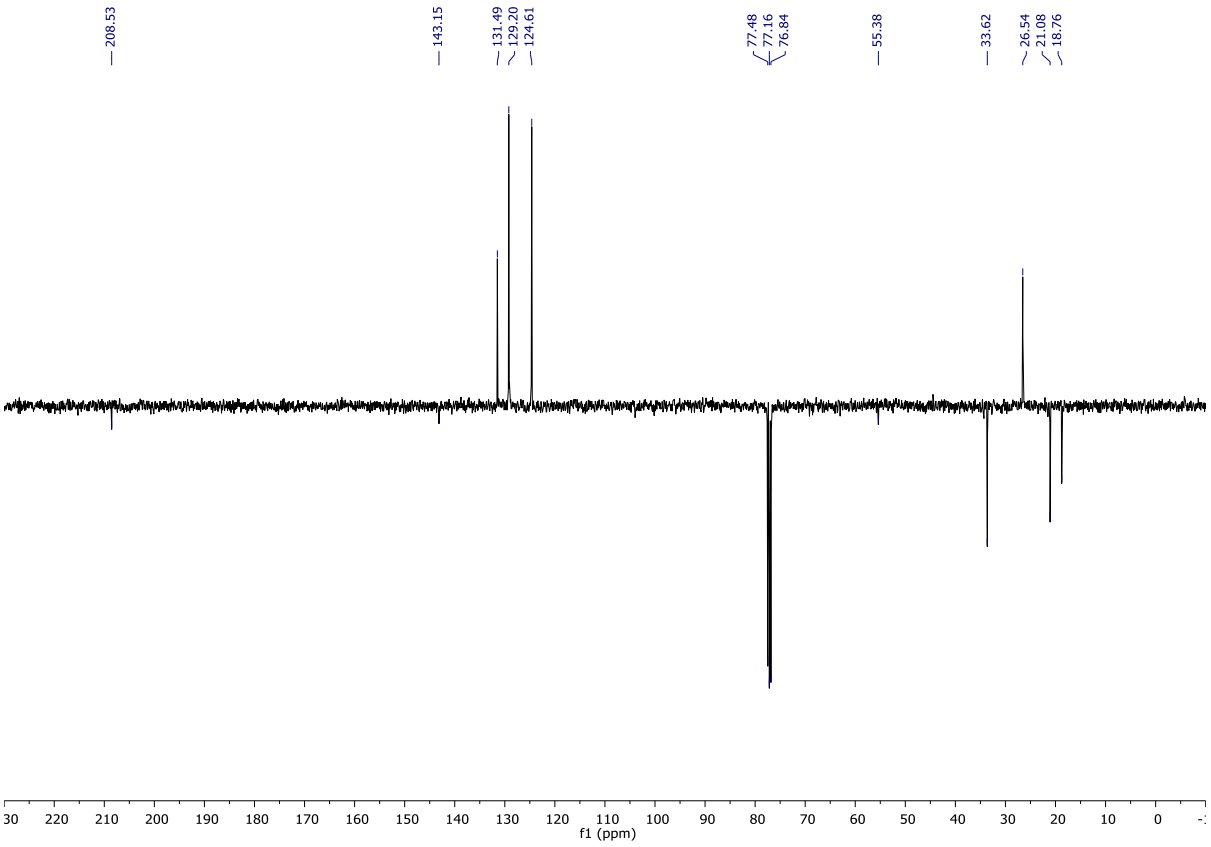
18/18' Diastereomer 1

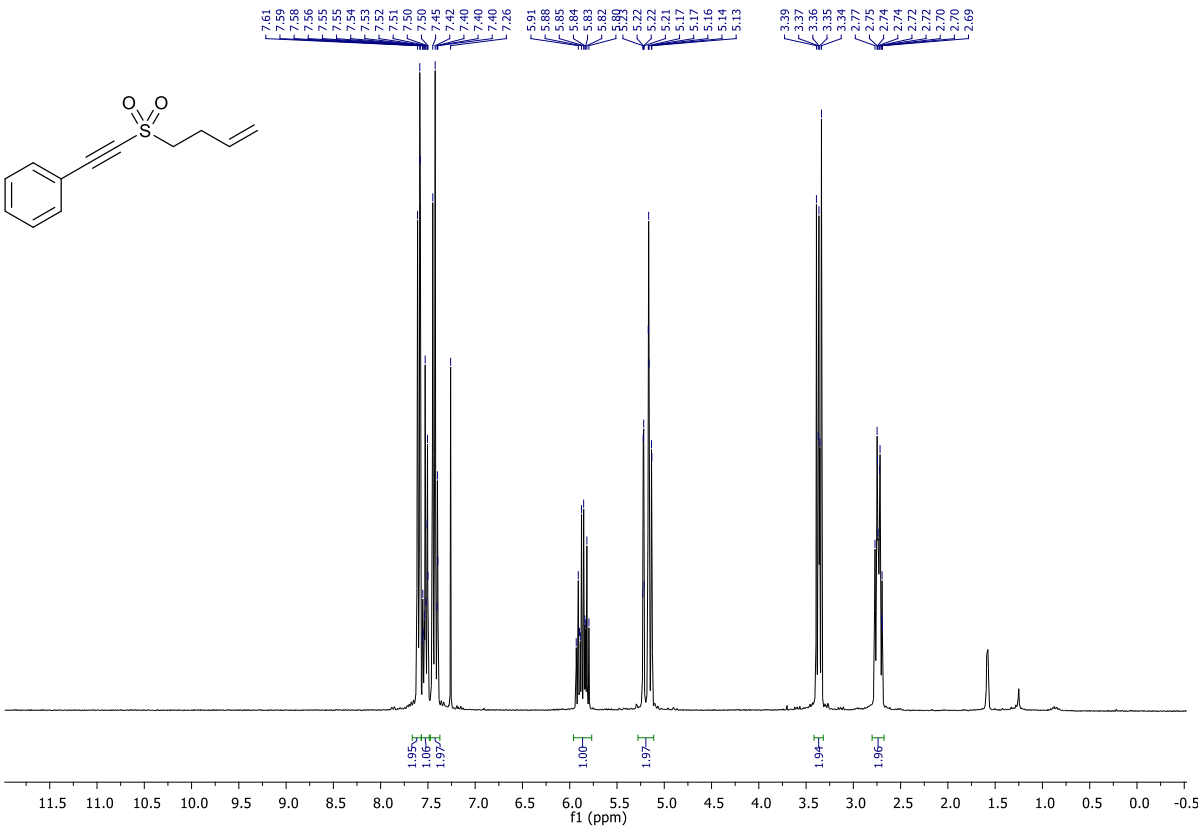


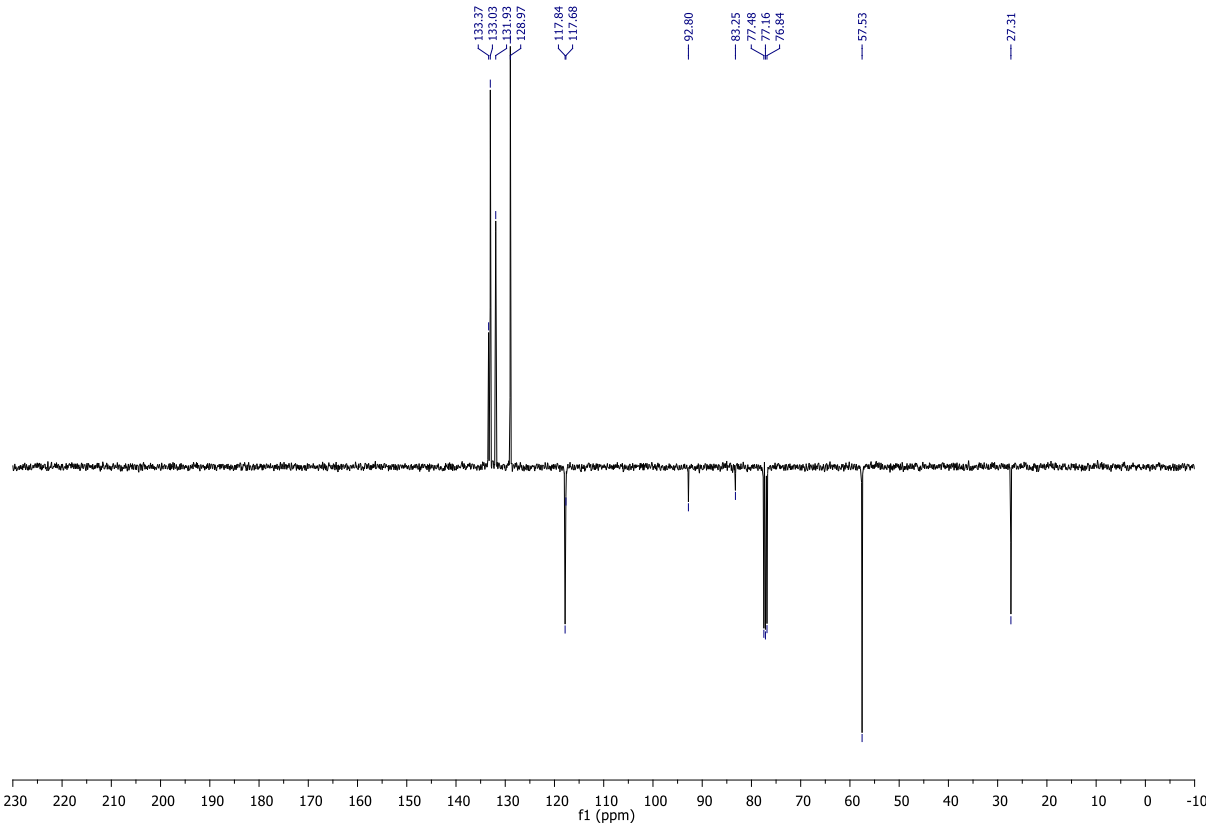


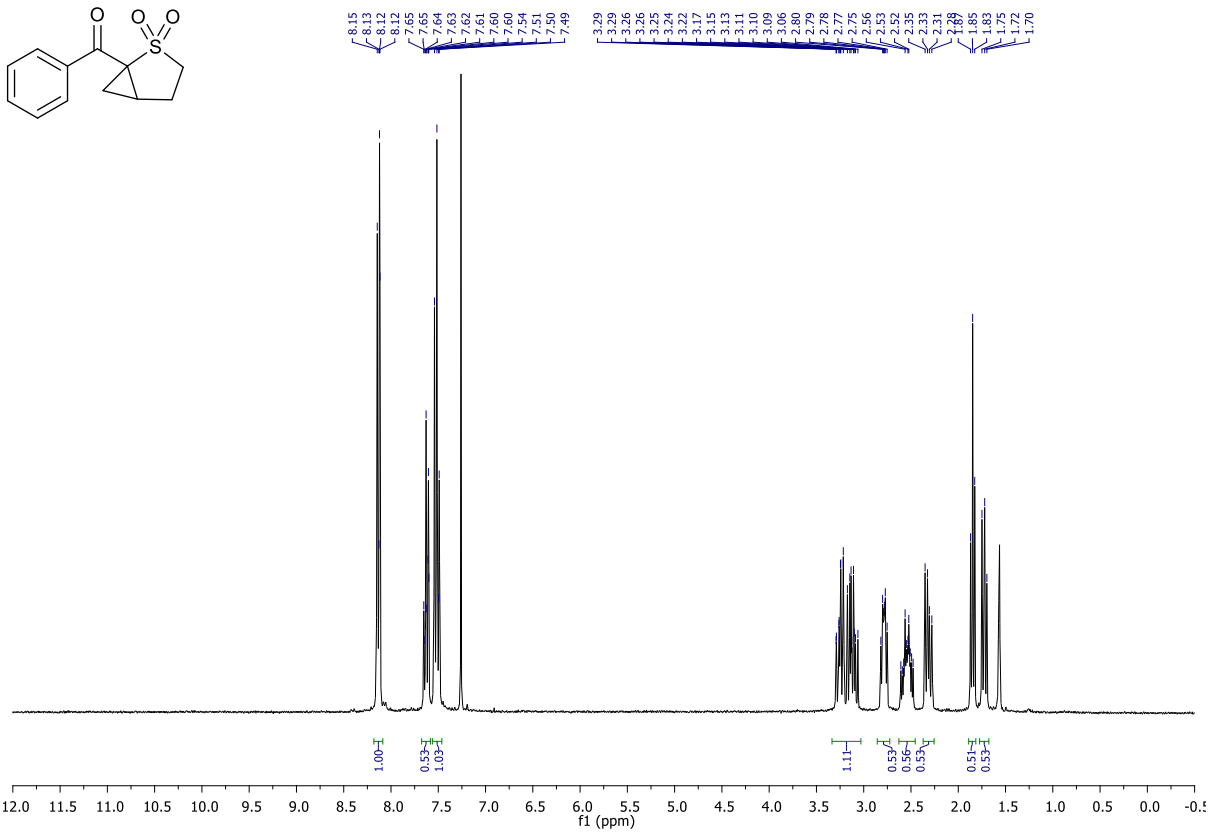
18/18' Diastereomer 2

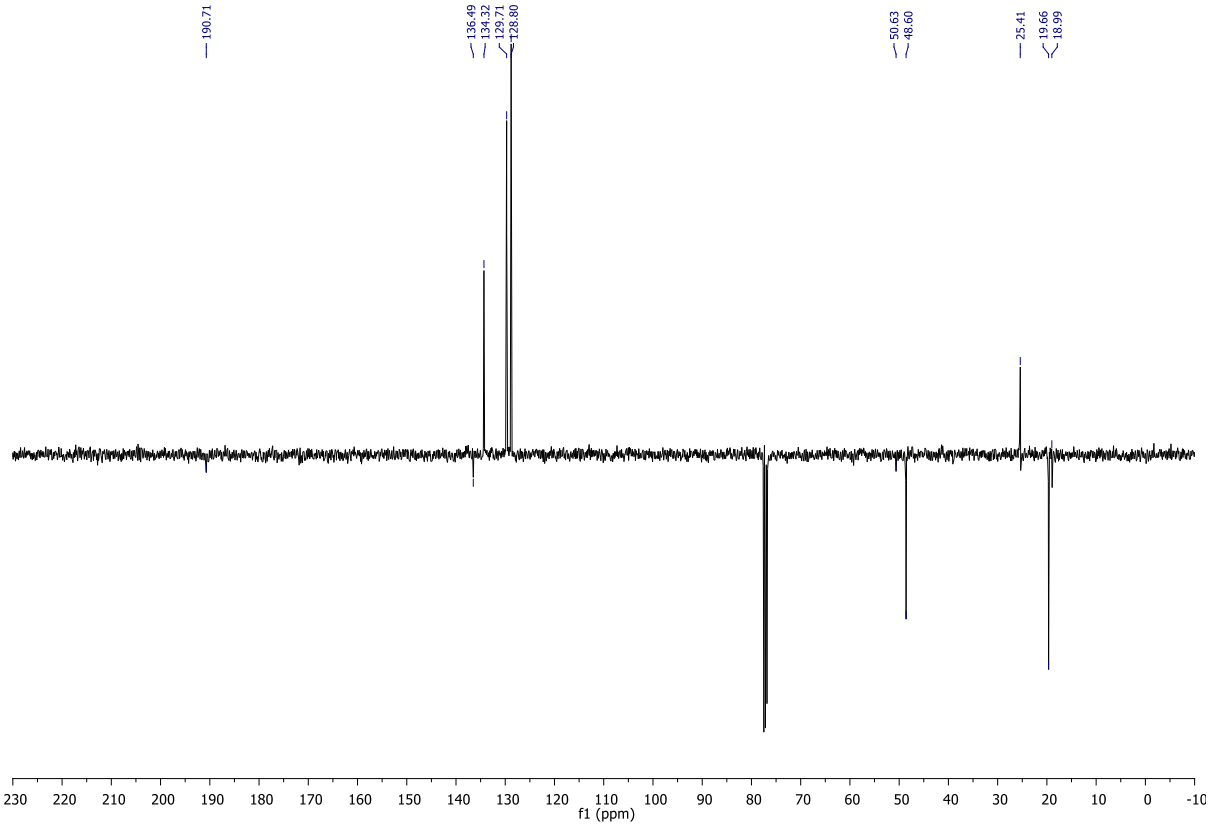





7.61
7.59
7.58
7.56
7.55
7.55
7.54
7.53
7.52
7.51
7.50
7.50
7.45
7.42
7.40
7.40
7.40
7.26
5.91
5.88
5.85
5.84
5.83
5.82
5.80
5.23
5.22
5.22
5.21
5.17
5.17
5.16
5.14
5.13
3.39
3.37
3.36
3.35
3.34
2.77
2.75
2.74
2.74
2.72
2.72
2.70
2.70
2.69
O
O
S
1.95
1.06
1.97
1.00
1.97
1.94
1.96
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


133.37
133.03
131.93
128.97
117.84
117.68
92.80
83.25
77.48
77.16
76.84
57.53
27.31
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.15
8.13
8.12
8.12
7.65
7.65
7.64
7.63
7.62
7.61
7.60
7.60
7.54
7.51
7.50
7.49
3.29
3.29
3.26
3.26
3.25
3.24
3.22
3.17
3.15
3.13
3.11
3.10
3.09
3.06
2.80
2.79
2.78
2.77
2.75
2.56
2.53
2.52
2.35
2.33
2.31
1.89
1.85
1.83
1.75
1.72
1.70
1.00
0.53
1.03
1.11
0.53
0.56
0.53
0.51
0.53
f1 (ppm)


190.71
136.49
134.32
129.71
128.80
50.63
48.60
25.41
19.66
18.99
f1 (ppm)