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Rhodium-Catalyzed Addition of Sulfonylhydrazines to Allenes: Regioselective Synthesis of Branched Allylic Sulfones

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S1 (General)

FCC (Flash Column Chromatography) was accomplished using MACHEREY-NAGEL silica gel 60® (230-400 mesh).

TLC (Thin Layer Chromatography) was performed on aluminum plates pre-coated with silica gel (MERCK, 60F254), which were visualized by UV fluorescence (λ_{max} = 254 nm) and/or by staining with 1% w/v $KMnO_4$ in 0.5 M aqueous K_2CO_3.

NMR (Nuclear Magnetic Resonance) spectra were acquired on a BRUKER Avance 400 spectrometer (400 MHz or 300 MHz and 100.6 MHz for ^1H and ^{13}C respectively) and/or on a VARIAN Mercury (250 MHz and 63 MHz for ^1H and ^{13}C respectively). All ^1H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 7.26 ppm ($CHCl_3$). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.16 ppm) and were obtained with 1H-decoupling. Data for ^1H NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sx, sextet; m, multiplet; app, apparent; br, broad signal), coupling constant (Hz), integration. Data for ^{13}C NMR spectra are described in terms of chemical shift (δ in ppm).

HRMS (High resolution mass spectra) were obtained on a FINNIGAN MAT 8200 instrument (CI/NH_3: 110 eV; EI: 70 eV). **MS-CI** (Chemical ionization mass spectrometry) was performed on a TSQ 700 or MAT 95XL mass spectrometer from Thermo Fisher Scientific Inc. at an ionization energy of 110 eV and a source temperature of 200 °C. Ammonia or isobutene were used as reactant gases.

S2 (Materials)

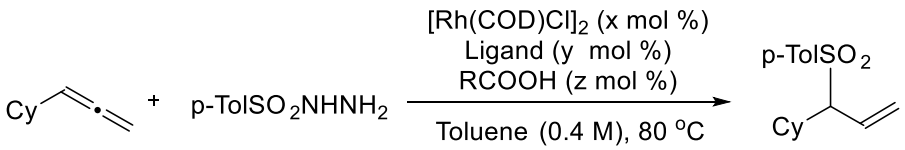
Solvents: Toluene was freshly distilled over Sodium/Benzophenone and degassed with argon prior to use. Solvents employed for work-up and column chromatography were purchased in technical grade quality and distilled by rotary evaporator before use.

Substrates: Terminal allenes, Sulfonyl hydrazides and p-Toluenesulfinic acid, if commercially available, were purchased from Sigma-Aldrich, ABCR, Alfa Aesar and used without further purification. tert-butyldimethyl(pent-4-yn-1-yloxy)silane was synthesized according to literature procedures [1]. Sulfonyl hydrazides, which are not commercially available, were synthesized in one step according to a literature procedure starting from corresponding Sulfonyl cholorides.

Ligands and catalysts: The ligands were purchased from Sigma-Aldrich, ABCR, Alfa Aesar and used without further purification. $[Rh(COD)Cl]_2$ was prepared from $RhCl_3(H_2O)_x$ and 1,5-cyclooctadiene following the procedure described by Bosnich and co-workers [2].

S3 (Optimization)

Optimization of Rhodium/Benzoic Acid Catalyzed Hydrosulfination

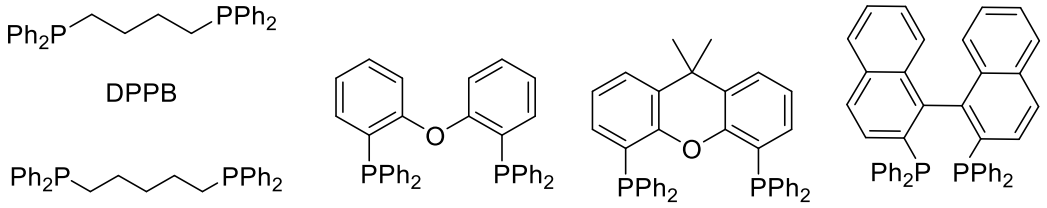


S1 **S2**

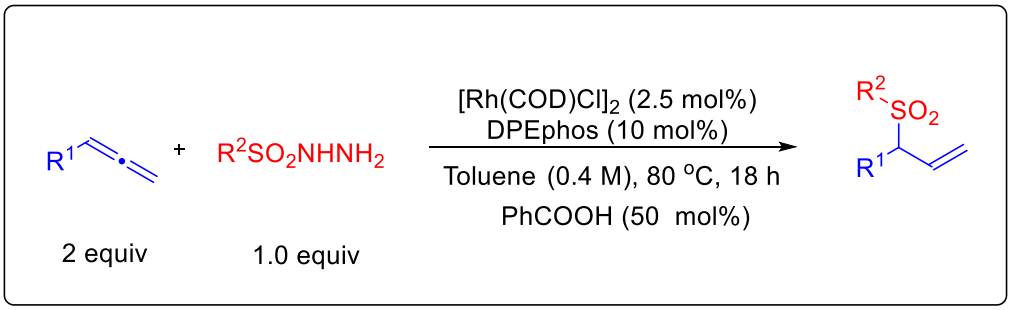
entry	ligand	S1/S2 (equiv.)	x/y (mol %)	z	R	yield (%)[a]
1	DPEphos	1.5/1	2.5/10	20	Ph	55
2	DPEphos	1.5/1	2.5/10	50	Ph	60
3	DPEphos	1.5/1	2.5/10	100	Ph	58
4	**DPEphos**	**2/1**	**2.5/10**	**50**	**Ph**	**80**
5	DPPB	2/1	2.5/10	50	Ph	12
6	DPPPent	2/1	2.5/10	50	Ph	14
7	BINAP	2/1	2.5/10	50	Ph	65
8	Xantphos	2/1	2.5/10	50	Ph	40
9	DPEphos	2/1	2.5/10	25	Ph	59
10	DPEphos	2/1	2.5/10	75	Ph	76
11	DPEphos	2/1	2.5/10	100	Ph	33
12	DPEphos	2/1	2.5/10	50	p-CF_3-Ph	69
13	DPEphos	2/1	2.5/10	50	p-CH_3-Ph	26
14	DPEphos	2/1	0/0	0	---	n.r.
15	DPEphos	2/1	0/0	50	Ph	n.r.
16	DPEphos	2/1	0/10	50	Ph	n.r.
17	DPEphos	2/1	2.5/no	50	Ph	n.r.

[a] ^{1}H NMR yield of the branched product in the crude reaction mixture was determined by using 1,3,5-trimethoxybenzene as internal standard. DPPB = 1,4-Bis(diphenylphosphino)butane, DPPPent = 1,5-bis(diphenylphosphino)pentane.

Ligand:



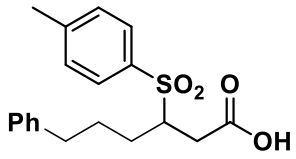
S4 (General Procedure for Rhodium Catalyzed Hydrosulfination)



The reaction was performed in a 5.0 ml Schlenk tube under N_2. $[Rh(COD)Cl]_2$ (4.9 mg, 0.01 mmol, 2.5 mol%), DPEphos (21.5 mg, 0.04 mmol, 10 mol%), benzoic acid (24.4 mg, 0.20 mmol, 50 mol%), sulfonyl hydrazide (0.4 mmol, 1.0 equiv) were dissolved in Toluene (1.0 mL), then allene (0.8 mmol, 2 equiv.) was added and the tube was sealed. The reaction mixture was stirred at 80 °C for 18 hours. After cooling to room temperature, the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography on silica gel and dried *in vacuo*.

S5 (Derivatization of Branched Allylic Sulfones)

Synthesis of 6-phenyl-3-tosylhexanoic acid (4ac)

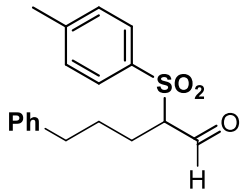


The reaction was performed according to the modified literature procedure [3]. A mixture of **4ab** (99.7 mg, 0.3 mmol), $PhI(OAc)_2$ (193.0 mg, 0.6 mmol), and TEMPO (14.0 mg, 0.09 mmol) was stirred in aq. CH_3CN (1.5 ml) at room temperature overnight. The mixture was extracted with ethyl acetate, then the organic phase was extracted with aq. $NaHCO_3$. The aqueous solution was acidified to pH 1 using 1 N HCl, then extracted with

ethyl acetate. The combined organic phases were dried over $MgSO_4$ and concentrated. The crude product was purified by FCC on silica gel to afford the product as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 - 7.80 (m, 2 H), 7.15 - 7.39 (m, 8 H), 7.01 - 7.12 (m, 2 H), 3.45 - 3.62 (m, 1 H), 2.95 (dd, *J*=17.2, 5.7 Hz, 1 H), 2.64 - 2.74 (m, 1 H), 2.43 - 2.63 (m, 6 H), 2.37 (t, *J*=7.5 Hz, 1 H), 1.86 - 2.02 (m, 2 H), 1.48 - 1.82 (m, 4 H), 1.19 - 1.39 (m, 3 H), **^{13}C NMR** ($CDCl_3$,101MHz) δ = 175.3, 145.2, 141.2, 134.2, 130.0, 129.1, 128.6, 128.5, 126.2, 60.8, 35.1, 33.2, 28.3, 26.3, 21.8 ppm; **HRMS**: calculated for $C_{19}H_{26}NO_4S$ $[M+NH_4]^+$ 364.1583, found 364.1579.

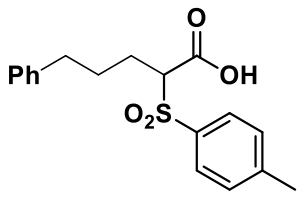
Synthesis of 5-phenyl-2-tosylpentanal (4ad)



The reaction was performed according to the modified literature procedure [4]. **3ab** (157.2 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (5.0 ml, 0.1 M) and cooled to – 78 °C. Ozone was directly bubbled in the solution. When the solution remained light blue about 5 min, indicating excess ozone, the ozone flow was stopped and N_2 was bubbled for 15 min to remove excess of ozone. To the reaction mixture was added PPh_3 (196.7 mg, 0.75 mmol) at – 78 °C, and the resulting solution was stirred at r.t. for 2 hours. The crude reaction mixture was concentrated and purified by FCC on silica gel to afford the product as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.57 - 9.78 (m, 1 H), 7.59 - 7.72 (m, 2 H), 7.31 - 7.41 (m, 2 H), 7.00 - 7.30 (m, 6 H), 3.67 - 3.92 (m, 1 H), 2.61 (t, J=7.6 Hz, 3 H), 2.38 - 2.52 (m, 4 H), 1.92 - 2.11 (m, 3 H), 1.58 - 1.76 (m, 3 H), 1.17 - 1.34 (m, 1 H), **^{13}C NMR** ($CDCl_3$,101MHz) δ = 193.5, 145.9, 140.9, 134.5, 130.2, 128.8, 128.6, 128.4, 126.2, 74.9, 35.5, 28.4, 23.4, 21.8 ppm **HRMS**: calculated for $C_{18}H_{19}O_3S$ $[M-H]^-$ 315.1060, found 315.1133.

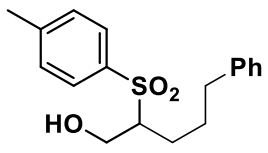
Synthesis of 5-phenyl-2-tosylpentanoic acid (4ad)



The reaction was performed according to the modified literature procedure [5]. **3ab** (157.2 mg, 0.5 mmol) was dissolved in a CH_2Cl_2 (5.0 ml, 0.1 M) and cooled to – 78 °C. Ozone was directly bubbled in the solution. When the solution remained light blue about 5 min, indicating excess ozone, the ozone flow was stopped and N_2 was bubbled for 15 min to remove excess of ozone. The resulting solution was treated with a mixture of 2 mL formic acid and 2 mL 30% H_2O_2. The mixture was extracted with ethyl acetate, then the organic phase was extracted with eq. $NaHCO_3$ and the aqueous reacidified to pH using 5% aq. Citric acid. Finally, re-extraction with ethyl acetate, dried over $MgSO_4$, filtered and concentrated. The crude mixture was purified by FCC on silica gel to afford the product as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, J=7.2 Hz, 2 H), 7.07 - 7.32 (m, 5 H), 6.99 (d, J=6.8 Hz, 2 H), 5.49 - 6.39 (m, 1 H), 4.03 (br. s., 1 H), 2.42 - 2.57 (m, 2 H), 2.35 (s, 3 H), 1.98 (br. s., 1 H), 1.81 (br. s., 1 H), 1.70 (br. s., 1 H), 1.55 ppm (br. s., 1 H), **^{13}C NMR** ($CDCl_3$,101MHz) δ = 145.4, 141.4, 129.9, 129.4, 128.5, 128.4, 125.9, 35.2, 28.5, 26.9, 21.7 ppm; **HRMS**: calculated for $C_{18}H_{24}NO_4S$ $[M+NH_4]^+$ 350.1426, found 350.1421.

Synthesis of 5-phenyl-2-tosylpentan-1-ol (4af)



The reaction was performed according to the modified literature procedure [4]. **3ab** (157.2 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (5.0 ml, 0.1 M) and cooled to – 78 °C. Ozone was directly bubbled in the solution. When

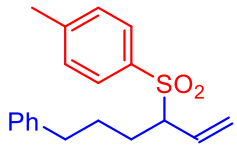
the solution remained light blue about 5 min, indicating excess ozone, the ozone flow was stopped and N_2 was bubbled for 15 min to remove excess of ozone. The solvent was removed via rotary evaporation, the resulted ozonide was dissolved in methanol (5.0 ml), then $NaBH_4$ (189.2 mg, 5 mmol) was added at 0 ^oC. The resulting slurry was stirred at r.t. for 10 hours, then HCl (aq. 1.0 N) was slowly added to the mixture at 0 ^oC to quenched excess $NaBH_4$. Water and Et_2O were added and the aqueous phase was separated, and extracted with Et_2O. The combined organic phases were washed with brined, $MgSO_4$, then filtered and concentrated under vacuum. The crude product was purified by FCC on silica gel to afford the product as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 - 7.81 (m, 2 H), 7.31 - 7.40 (m, 2 H), 7.14 - 7.29 (m, 3 H), 6.97 - 7.11 (m, 2 H), 3.80 - 3.98 (m, 2 H), 3.06 (dtd, J=5.4, 3.6, 1.9 Hz, 1 H), 2.57 (t, J=6.4 Hz, 2 H), 2.47 (s, 3 H), 1.73 - 1.87 (m, 2 H), 1.50 - 1.70 ppm (m, 2 H), **^{13}C NMR** ($CDCl_3$,101MHz) δ = 145.2, 141.3, 134.4, 130.1, 128.9, 128.5, 128.4, 126.1, 66.2, 59.6, 35.6, 28.4, 24.6, 21.8 ppm; **HRMS**: calculated for $C_{18}H_{22}NaO_3S$ $[M+Na]^+$ 341.1187, found 341.1183.

S6 (Characterization of Branched Allylic Sulfones)

1) Hydrosulfination of p-Toluenesulfonyl Hydrazide with Terminal Allenes (3a-3t)

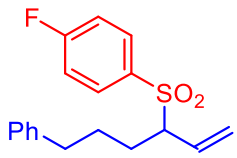
1.1) 1-methyl-4-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3a**)



The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and p-toluenesulfonyl hydrazide (74.5 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.40) to afford the product as a colorless oil (100.0 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.47 - 1.63 (m, 1 H) 1.65 - 1.79 (m, 2 H) 2.08 - 2.21 (m, 1 H) 2.44 (s, 3 H) 2.52 - 2.69 (m, 2 H) 3.47 (td, J=9.95, 3.47 Hz, 1 H) 5.02 (dt, J=17.05, 0.95 Hz, 1 H) 5.27 (dd, J=10.10, 1.14 Hz, 1 H) 5.60 (ddd, J=17.05, 10.23, 9.35 Hz, 1 H) 7.06 - 7.37 (m, 7 H) 7.63 - 7.76 (m, 2 H). **^{13}C NMR** ($CDCl_3$,101MHz) δ =144.6, 141.6, 134.6, 130.5, 129.5, 129.3, 128.5, 128.4, 126.1, 123.6, 70.0, 35.5, 28.6, 26.8, 21.7 ppm; **HRMS**: calculated for $C_{19}H_{22}O_2S$ $[M+H]^+$ 315.1341, found 315.1414.

1.2) 1-fluoro-4-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3b**)

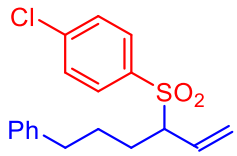


The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and 4-fluorobenzenesulfonohydrazide (76.0 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.42) to afford the product as a white solid (96.0 mg, 75%).

m.p.: 51-51.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.72 - 7.90 (m, 2 H), 7.04 - 7.36 (m, 8 H), 5.60 (ddd, *J*=17.1, 10.2, 9.3 Hz, 1 H), 5.20 - 5.37 (m, 1 H), 5.01 (dt, *J*=17.1, 0.9 Hz, 1 H), 3.47 (td, *J*=9.9, 3.5 Hz, 1 H), 2.62 (td,

J=9.2, 6.3 Hz, 2 H), 2.07 - 2.23 (m, 1 H), 1.66 - 1.85 (m, 2 H), 1.49 - 1.66 (m, 2 H). **^{13}C NMR** ($CDCl_3$,101MHz) δ =167.2, 164.6, 141.5, 133.6, 132.2, 130.4, 128.5, 128.4, 126.1, 123.9, 116.1, 70.2, 35.5, 28.5, 26.6 ppm; **HRMS**: calculated for $C_{18}H_{19}O_2FNaS$ $[M+Na]^+$ 341.0987, found 341.0982.

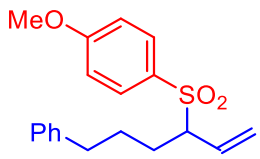
1.3) 1-chloro-4-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3c**)



The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and 4-chlorobenzenesulfonohydrazide (80.0 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.44) to afford the product as a colorless oil (105.0 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 - 7.93 (m, 2 H), 7.38 - 7.62 (m, 2 H), 6.90 - 7.30 (m, 6 H), 5.46 - 5.76 (m, 1 H), 5.30 (dd, *J*=10.2, 0.7 Hz, 1 H), 4.80 - 5.09 (m, 1 H), 3.47 (td, *J*=9.9, 3.3 Hz, 1 H), 2.48 - 2.81 (m, 2 H), 2.00 - 2.35 (m, 1 H), 1.47 - 1.87 (m, 4 H). **^{13}C NMR** ($CDCl_3$,101MHz) δ = 141.4, 140.5, 136.0, 130.8, 130.3, 129.2, 128.5, 128.4, 126.2, 124.1, 70.1, 35.5, 28.4, 26.5 ppm; **HRMS**: calculated for $C_{18}H_{19}ClNaO_2S$ $[M+Na]^+$ 357.0692, found 357.0691.

1.4) 1-methoxy-4-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3d**)

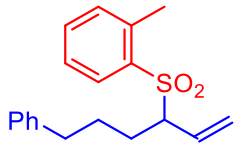


The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and 4-methoxybenzenesulfonohydrazide (80.8 mg, 0.4 mmol). The crude product was purified by flash column

chromatography on silica gel (EA / CH = 1:4, R_f = 0.31) to afford the product as a colorless oil (130.0 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.67 - 7.80 (m, 2 H), 7.21 - 7.31 (m, 2 H), 7.08 - 7.21 (m, 3 H), 6.90 - 7.03 (m, 2 H), 5.60 (ddd, *J*=17.1, 10.2, 9.2 Hz, 1 H), 5.28 (dd, *J*=10.2, 1.4 Hz, 1 H), 5.03 (dt, *J*=17.0, 1.0 Hz, 1 H), 3.88 (s, 3 H), 3.45 (t, *J*=9.9 Hz, 1 H), 2.61 (ddd, *J*=12.1, 8.7, 6.2 Hz, 2 H), 2.06 - 2.24 (m, 1 H), 1.65 - 1.82 (m, 2 H), 1.47 - 1.65 (m, 2 H). **^{13}C NMR** ($CDCl_3$,101MHz) δ = 163.8, 141.6, 131.5, 130.7, 129.2, 128.5, 128.4, 126.1, 123.5, 114.1, 70.2, 55.7, 35.6, 28.6, 26.9 ppm; **HRMS**: calculated for $C_{19}H_{22}NaO_3S$ $[M+Na]^+$ 353.1187, found 353.1182.

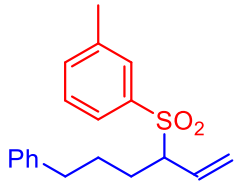
1.5) 1-methyl-2-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3e**)



The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and 2-methylbenzenesulfonohydrazide (74.5 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.42) to afford the product as a white solid (110.0 mg, 88%).

m.p.: 42-43 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.88 (dd, *J*=7.9, 1.5 Hz, 1 H), 7.42 - 7.54 (m, 1 H), 7.05 - 7.38 (m, 8 H), 5.53 - 5.72 (m, 1 H), 5.22 (dd, *J*=10.2, 1.0 Hz, 1 H), 4.96 (dt, *J*=17.1, 0.9 Hz, 1 H), 3.44 - 3.63 (m, 1 H), 2.53 - 2.72 (m, 5 H), 2.12 (dd, *J*=6.5, 3.3 Hz, 1 H), 1.66 - 1.91 (m, 2 H), 1.47 - 1.66 (m, 2 H); **^{13}C NMR** ($CDCl_3$,101MHz) δ = 141.6, 138.5, 136.0, 133.6, 132.6, 131.6, 130.5, 128.5, 128.4, 126.3, 126.1, 123.5, 69.3, 35.6, 28.5, 26.3, 20.9 ppm; **HRMS**: calculated for $C_{19}H_{22}NaO_2S$ $[M+Na]^+$ 337.1238, found 337.1239.

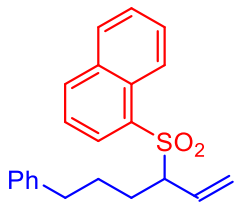
1.6) 1-methyl-3-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3f**)



The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and 3-methylbenzenesulfonohydrazide (74.5 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.46) to afford the product as a white solid (110.0 mg, 88%).

m.p.: 58.5 - 59 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53 - 7.68 (m, 2 H), 7.35 - 7.48 (m, 2 H), 7.06 - 7.32 (m, 6 H), 5.61 (ddd, *J*=17.1, 10.2, 9.3 Hz, 1 H), 5.28 (dt, *J*=10.2, 0.7 Hz, 1 H), 5.02 (dt, *J*=17.1, 0.9 Hz, 1 H), 3.38 - 3.59 (m, 1 H), 2.61 (ddd, *J*=11.4, 8.7, 6.3 Hz, 2 H), 2.39 - 2.47 (m, 3 H), 2.07 - 2.19 (m, 1 H), 1.66 - 1.81 (m, 2 H), 1.49 - 1.63 (m, 2 H); **^{13}C NMR** ($CDCl_3$,101MHz) δ = 141.6, 139.1, 137.5, 134.5, 130.5, 129.5, 128.7, 128.4, 126.5, 126.1, 123.7, 69.9, 35.6, 28.5, 26.7, 21.5 ppm; **HRMS**: calculated for $C_{19}H_{22}NaO_2S$ $[M+Na]^+$ 337.1238, found 337.1234.

1.7) 1-((6-phenylhex-1-en-3-yl)sulfonyl)naphthalene (**3g**)

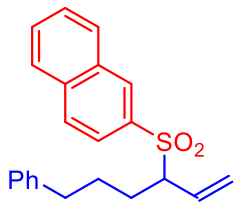


The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and naphthalene-1-sulfonohydrazide (88.8 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.34) to afford the product as a light yellow oil (85.0 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 - 8.75 (m, 1 H), 8.00 - 8.18 (m, 2 H), 7.83 - 7.95 (m, 1 H), 7.41 - 7.69 (m, 3 H), 6.92 - 7.24 (m, 6 H), 5.56 (ddd, J=17.1, 10.2, 9.4 Hz, 1 H), 5.03 (dd, J=10.1, 1.1 Hz, 1 H), 4.69 (dt,

J=17.1, 0.9 Hz, 1 H), 3.72 (td, J=10.2, 3.5 Hz, 1 H), 2.34 - 2.67 (m, 2 H), 1.99 - 2.20 (m, 1 H), 1.38 - 1.89 (m, 5 H). **^{13}C NMR** ($CDCl_3$,101MHz) δ = 141.6, 139.1, 137.5, 134.5, 130.5, 129.5, 128.7, 128.4, 126.5, 126.1, 123.7, 69.9, 35.6, 28.5, 26.7, 21.5 ppm; **HRMS**: calculated for $C_{22}H_{22}NaO_2S$ $[M+Na]^+$ 373.1305, found 373.1302.

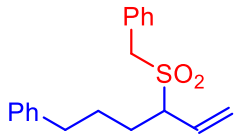
1.8) 2-((6-phenylhex-1-en-3-yl)sulfonyl)naphthalene (**3h**)



The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and naphthalene-2-sulfonohydrazide (88.8 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.42) to afford the product as a white solid (127.0 mg, 91%).

m.p.: 91 - 92 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.32 - 8.50 (m, 1 H), 7.89 - 8.08 (m, 3 H), 7.75 - 7.87 (m, 1 H), 7.56 - 7.78 (m, 2 H), 7.04 - 7.38 (m, 5 H), 5.68 (ddd, J=17.1, 10.3, 9.4 Hz, 1 H), 5.29 (dd, J=10.1, 1.1 Hz, 1 H), 5.03 (dt, J=17.1, 0.9 Hz, 1 H), 3.48 - 3.71 (m, 1 H), 2.52 - 2.77 (m, 2 H), 2.12 - 2.30 (m, 1 H), 1.50 - 1.89 (m, 4 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.5, 135.4, 134.6, 132.1, 131.1, 130.4, 129.6, 129.3, 129.0, 128.5, 128.4, 128.4, 128.0, 127.6, 126.1, 124.0, 123.8, 70.0, 35.5, 28.5, 26.7 ppm. **HRMS:** calculated for $C_{22}H_{22}NaO_2S$ $[M+Na]^+$ 373.1305, found 373.1306.

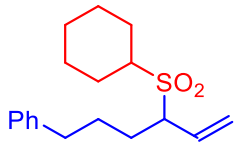
1.9) (4-(benzylsulfonyl)hex-5-en-1-yl)benzene (**3i**)



The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and phenylmethanesulfonohydrazide (74.4 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.46) to afford the product as a white solid (114.0 mg, 91%).

m.p.: 55 – 55.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.22 - 7.44 (m, 8 H), 7.05 - 7.22 (m, 3 H), 5.72 - 5.93 (m, 1 H), 5.53 (dd, *J*=10.2, 1.1 Hz, 1 H), 5.25 - 5.41 (m, 1 H), 4.08 - 4.32 (m, 2 H), 3.37 (td, *J*=10.1, 3.5 Hz, 1 H), 2.60 (ddd, *J*=8.5, 6.6, 4.7 Hz, 2 H), 2.00 - 2.23 (m, 1 H), 1.66 - 1.85 (m, 2 H), 1.42 - 1.60 (m, 1 H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.5, 131.5, 131.0, 129.0, 128.5, 128.5, 127.8, 126.1, 123.7, 65.7, 56.7, 35.5, 28.4, 25.4 ppm. **HRMS:** calculated for $C_{19}H_{22}NaO_2S$ $[M+Na]^+$ 373.1238, found 373.1232.

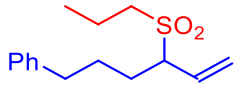
1.10) (4-(cyclohexylsulfonyl)hex-5-en-1-yl)benzene (**3j**)



The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and cyclohexanesulfonohydrazide (71.2 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.37) to afford the product as a colorless oil (99.0 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.11 - 7.33 (m, 4 H), 5.77 (dt, *J*=17.2, 10.0 Hz, 1 H), 5.24 - 5.50 (m, 2 H), 3.55 (td, *J*=10.2, 3.5 Hz, 1 H), 2.93 - 3.12 (m, 1 H), 2.57 - 2.74 (m, 2 H), 2.08 - 2.23 (m, 2 H), 1.84 - 2.05 (m, 3 H), 1.66 - 1.81 (m, 2 H), 1.47 - 1.64 (m, 3 H), 1.12 - 1.32 (m, 3 H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.7, 132.0, 128.5, 128.5, 126.1, 122.7, 63.9, 57.9, 35.6, 28.4, 26.1, 25.3, 25.2, 25.2, 25.0, 23.3 ppm. **HRMS:** calculated for $C_{18}H_{26}NaO_2S$ $[M+Na]^+$ 329.1551, found 329.1552.

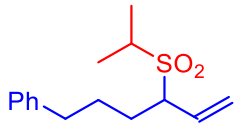
1.11) (4-(propylsulfonyl)hex-5-en-1-yl)benzene (**3k**)



The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and propane-1-sulfonohydrazide (55.2 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.34) to afford the product as a colorless oil (103.0 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02 - 7.28 (m, 5 H), 5.61 - 5.79 (m, 1 H), 5.39 (dd, J=10.3, 1.1 Hz, 1 H), 5.21 - 5.34 (m, 1 H), 3.36 (td, J=10.0, 3.5 Hz, 1 H), 2.75 - 2.92 (m, 2 H), 2.49 - 2.66 (m, 2 H), 2.03 - 2.18 (m, 1 H), 1.63 - 1.86 (m, 4 H), 1.43 - 1.62 (m, 1 H), 0.98 (t, J=7.4 Hz, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 142.1, 132.0, 128.3, 128.1, 126.2, 122.1, 63.8, 50.1, 36.2, 28.0, 26.3, 16.3, 14.1 ppm. **HRMS:** calculated for $C_{15}H_{22}NaO_2S$ $[M+Na]^+$ 289.1238, found 289.1233.

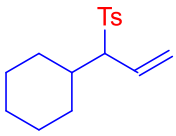
1.12) (4-(isopropylsulfonyl)hex-5-en-1-yl)benzene (**3l**)



The reaction was performed with hexa-4,5-dien-1-ylbenzene (126.4 mg, 0.8 mmol) and propane-2-sulfonohydrazide (55.2 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.33) to afford the product as a light yellow oil (80.0 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02 - 7.27 (m, 6 H), 5.58 - 5.82 (m, 1 H), 5.36 (dd, J=10.3, 1.1 Hz, 1 H), 5.18 - 5.30 (m, 1 H), 3.50 (td, J=10.2, 3.5 Hz, 1 H), 3.21 (quin, J=6.9 Hz, 1 H), 2.58 (dt, J=8.6, 6.3 Hz, 2 H), 2.01 - 2.16 (m, 1 H), 1.63 - 1.81 (m, 2 H), 1.43 - 1.61 (m, 1 H), 1.20 - 1.34 (m, 7 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.0, 129.8, 128.2, 127.9, 126.1, 122.0, 64.1, 49.7, 36.1, 28.1, 26.3, 16.0, 14.4 ppm. **HRMS:** calculated for $C_{15}H_{22}NaO_2S$ $[M+Na]^+$ 289.1238, found 289.1236.

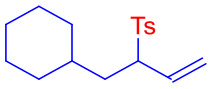
1.13) 1-((1-cyclohexylallyl)sulfonyl)-4-methylbenzene (**3m**)



The reaction was performed with propa-1,2-dien-1-ylcyclohexane (97.6 mg, 0.8 mmol) and p-toluenesulfonyl hydrazide (74.5 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.45) to afford the product as a white solid (90.0 mg, 81%).

m.p.: 112 –114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.73 - 7.66 (m, 2 H), 7.32 - 7.27 (m, 2 H), 5.84 (ddd, J = 17.0, 10.2 Hz, 1 H), 5.21 (dd, J = 10.2, 1.5 Hz, 1 H), 4.82 (ddd, J = 17.1, 1.5, 0.6 Hz, 1 H), 3.27 (dd, J = 10.4, 3.5 Hz, 1 H), 2.42 (s, 3 H), 2.39 - 2.29 (m, 1 H), 2.17 - 2.08 (m, 1 H), 1.79 - 1.70 (m, 2 H), 1.69 - 1.55 (m, 2 H), 1.41 - 1.03 (m, 5 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.3, 136.0, 129.4, 129.0, 128.9, 123.7, 75.6, 36.7, 32.1, 28.8, 26.5, 26.2, 26.1, 21.7 ppm. **HRMS:** calculated for $C_{16}H_{22}NaO_2S$ $[M+Na]^+$ 301.12382, found 301.12390.

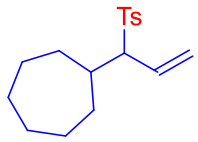
1.14) 1-((1-cyclohexylbut-3-en-2-yl)sulfonyl)-4-methylbenzene (**3n**)



The reaction was performed with buta-2,3-dien-1-ylcyclohexane (108.8 mg, 0.8 mmol) and p-toluenesulfonyl hydrazide (74.5 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.45) to afford the product as a yellow oil (70.0 mg, 60%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.51 - 7.71 (m, 2 H), 7.10 - 7.34 (m, 2 H), 5.52 (ddd, *J*=17.1, 10.1, 9.3 Hz, 1 H), 5.20 (dd, *J*=10.2, 1.2 Hz, 1 H), 4.96 (dt, *J*=17.1, 0.9 Hz, 1 H), 3.38 - 3.61 (m, 1 H), 2.26 - 2.51 (m, 3 H), 1.80 (ddd, *J*=13.5, 10.1, 3.4 Hz, 1 H), 1.41 - 1.67 (m, 7 H), 1.01 - 1.32 (m, 4 H), 0.85 - 0.98 (m, 1 H), 0.61 - 0.81 (m, 1 H).

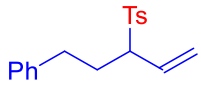
1.15) (1-tosylallyl)cycloheptane (**3o**)



The reaction was performed with propa-1,2-dien-1-ylcycloheptane (108.8 mg, 0.8 mmol) and p-toluenesulfonyl hydrazide (74.5 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.46) to afford the product as a colorless oil (71.0 mg, 81%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.58 - 7.81 (m, 2 H), 7.16 - 7.42 (m, 3 H), 5.90 (dt, *J*=17.0, 10.2 Hz, 1 H), 5.27 (dd, *J*=10.1, 1.5 Hz, 1 H), 4.89 (ddd, *J*=17.0, 1.4, 0.6 Hz, 1 H), 3.34 (dd, *J*=10.3, 2.9 Hz, 1 H), 2.54 (ddd, *J*=13.3, 6.9, 3.3 Hz, 1 H), 2.45 (s, 3 H), 2.11 - 2.31 (m, 1 H), 1.21 - 1.83 (m, 12 H).

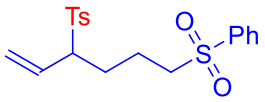
1.16) 1-methyl-4-((5-phenylpent-1-en-3-yl)sulfonyl)benzene (**3p**)



The reaction was performed with penta-3,4-dien-1-ylbenzene (115.2 mg, 0.8 mmol) and p-toluenesulfonyl hydrazide (74.5 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.36) to afford the product as a yellow soild (90.0 mg, 75%).

m.p.: 59 –60 °C; **^{1}H NMR** (250 MHz, $CDCl_3$) δ = 7.63 - 7.56 (m, 2 H), 7.26 - 7.08 (m, 5 H), 7.07 - 7.00 (m, 2 H), 5.66 - 5.50 (m, 1 H), 5.28 (dd, J = 1.3, 10.3 Hz, 1 H), 5.00 (td, J = 1.0, 17.0 Hz, 1 H), 3.46 - 3.34 (m, 1 H), 2.76 - 2.60 (m, 1 H), 2.53 - 2.28 (m, 5 H), 1.98 - 1.79 (m, 1 H); **^{13}C NMR** (63 MHz, $CDCl_3$) δ = 144.6, 140.1, 134.4, 130.3, 129.5, 129.3, 128.6, 128.5, 126.3, 124.1, 69.0, 32.4, 28.5, 21.7; **HRMS:** calculated for $C_{18}H_{20}NaO_2S$ $[M+Na]^+$ 323.1082, found 323.1081.

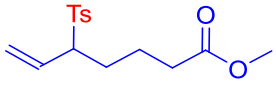
1.17) 1-methyl-4-((6-(phenylsulfonyl)hex-1-en-3-yl)sulfonyl)benzene (**3q**)



The reaction was performed with (hexa-4,5-dien-1-ylsulfonyl)benzene (177.6 mg, 0.8 mmol) and p-toluenesulfonyl hydrazide (74.5 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, Rf = 0.30) to afford the product as a white solid (136.0 mg, 90%).

m.p.: 113 –114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.82 - 7.96 (m, 2 H), 7.51 - 7.74 (m, 5 H), 7.20 - 7.40 (m, 3 H), 5.56 (ddd, *J*=17.1, 10.2, 9.3 Hz, 1 H), 5.28 (dd, *J*=10.2, 0.9 Hz, 1 H), 5.03 (dt, *J*=17.1, 0.8 Hz, 1 H), 3.32 - 3.48 (m, 1 H), 2.93 - 3.18 (m, 2 H), 2.44 (s, 3 H), 2.05 - 2.27 (m, 1 H), 1.89 (d, *J*=9.5 Hz, 1 H), 1.62 - 1.78 (m, 2 H), 1.57 (s, 1 H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ = 145.0, 139.1, 134.2, 134.0, 129.8, 129.7, 129.5, 129.3, 128.1, 124.3, 69.5, 55.7, 26.0, 21.8, 20.2 ppm. **HRMS:** calculated for $C_{19}H_{22}NaO_4S_2$ $[M+Na]^+$ 401.0857, found 401.0855.

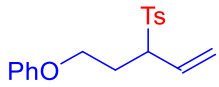
1.18) methyl 5-tosylhept-6-enoate (**3r**)



The reaction was performed with methyl hepta-5,6-dienoate (112.0 mg, 0.8 mmol) and p-toluenesulfonyl hydrazide (74.5 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.16) to afford the product as a colorless oil (82.0 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 - 7.80 (m, 2 H), 7.19 - 7.40 (m, 2 H), 5.42 - 5.71 (m, 1 H), 5.29 (dd, *J*=10.2, 0.8 Hz, 1 H), 5.05 (dt, *J*=17.1, 0.9 Hz, 1 H), 3.58 - 3.69 (m, 3 H), 3.46 (td, *J*=9.9, 3.3 Hz, 1 H), 2.43 (s, 3 H), 2.21 - 2.37 (m, 2 H), 1.95 - 2.18 (m, 1 H), 1.63 - 1.83 (m, 2 H), 1.39 - 1.61 (m, 1 H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ = 173.3, 144.7, 134.5, 130.2, 129.5, 129.3, 123.8, 69.8, 51.7, 33.5, 26.5, 22.1, 21.7 ppm. **HRMS:** calculated for $C_{15}H_{20}NaO_4S$ $[M+Na]^+$ 319.0980, found 319.0978.

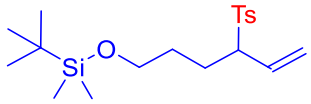
1.19) 1-methyl-4-((5-phenoxypent-1-en-3-yl)sulfonyl)benzene (**3s**)



The reaction was performed with (penta-3,4-dien-1-yloxy)benzene (128.0 mg, 0.8 mmol) and p-toluenesulfonyl hydrazide (74.5 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.36) to afford the product as a colorless oil (110.0 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 - 7.82 (m, 2 H), 7.13 - 7.42 (m, 5 H), 6.70 - 7.04 (m, 3 H), 5.69 (ddd, *J*=17.2, 10.2, 9.3 Hz, 1 H), 5.23 - 5.39 (m, 1 H), 5.09 (dt, *J*=17.1, 0.9 Hz, 1 H), 4.09 (ddd, *J*=9.6, 5.5, 4.4 Hz, 1 H), 3.77 - 4.01 (m, 2 H), 2.63 (dddd, *J*=14.1, 9.4, 5.7, 3.7 Hz, 1 H), 2.44 (s, 3 H), 2.05 (ddt, *J*=14.1, 10.7, 4.5 Hz, 1 H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.6, 144.8, 134.5, 129.7, 129.6, 129.6, 129.3, 124.2, 121.2, 114.7, 66.8, 64.1, 27.4, 21.8 ppm. **HRMS:** calculated for $C_{18}H_{24}NO_3S$ $[M+NH_4]^+$ 334.1477, found 334.1471.

1.20) tert-butyldimethyl((4-tosylhex-5-en-1-yl)oxy)silane (**3t**)

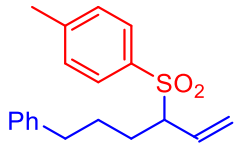


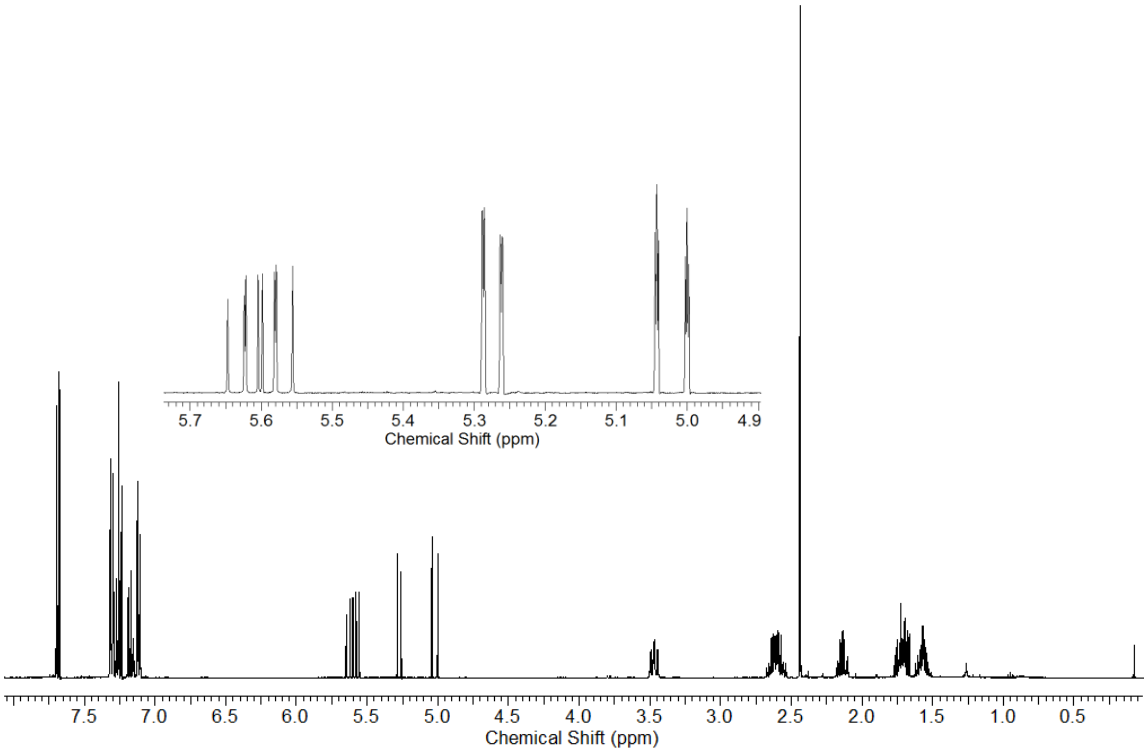
The reaction was performed with tert-butyl(hexa-4,5-dien-1-yloxy)dimethylsilane (169.6 mg, 0.8 mmol) and p-toluenesulfonyl hydrazide (74.5 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:4, R_f = 0.40) to afford the product as a colorless oil (90.0 mg, 61%).

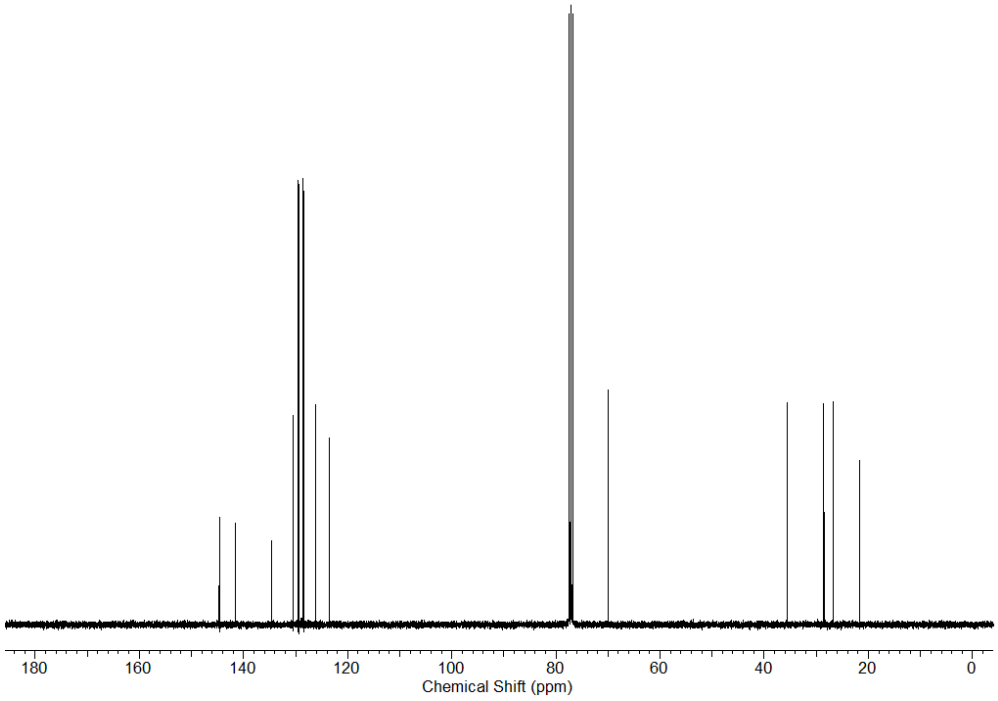
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, J=8.3 Hz, 2 H), 7.31 (dd, J=8.6, 0.8 Hz, 2 H), 5.52 - 5.71 (m, 1 H), 5.25 - 5.41 (m, 1 H), 5.11 (s, 1 H), 3.58 (t, J=6.1 Hz, 2 H), 2.43 (s, 3 H), 2.03 - 2.21 (m, 1 H), 1.36 - 1.75 (m, 4 H), 0.85 ppm (s, 9 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.6, 134.7, 130.5, 129.5, 129.4, 128.6, 123.6, 69.8, 62.4, 29.7, 26.0, 24.1, 21.7, 18.4 ppm. **HRMS:** calculated for $C_{19}H_{36}NO_3SSi$ $[M+NH_4]^+$ 386.2185, found 386.2180.

S7 (^{1}H NMR and ^{13}C NMR spectra)

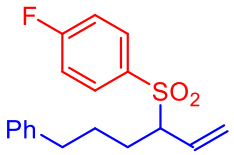
1.1) 1-methyl-4-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3a**)

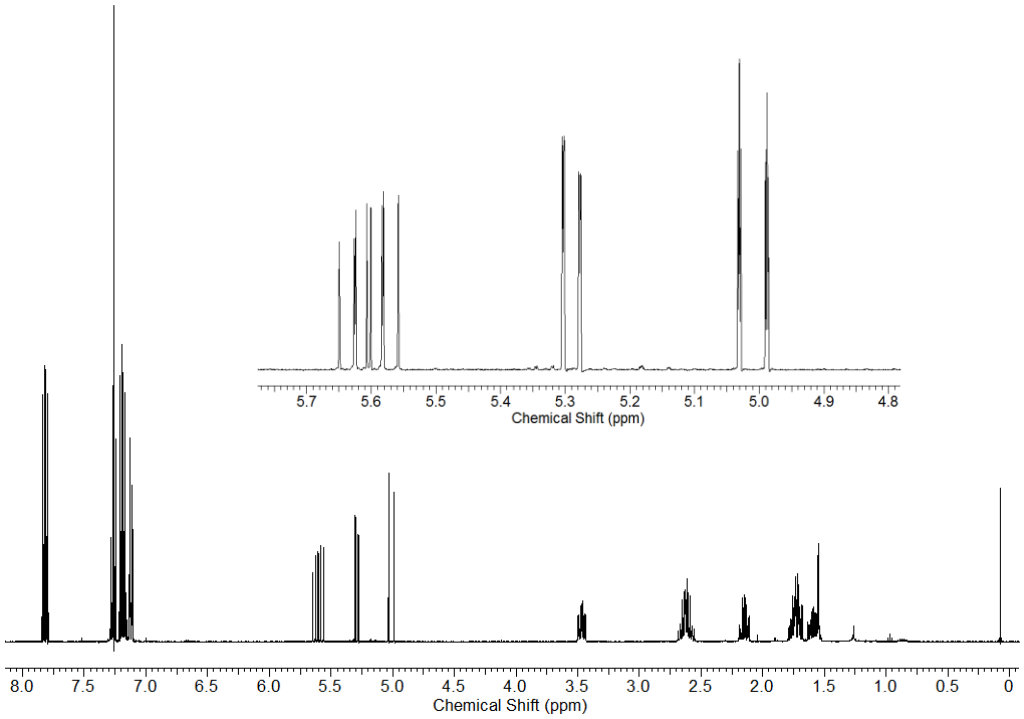


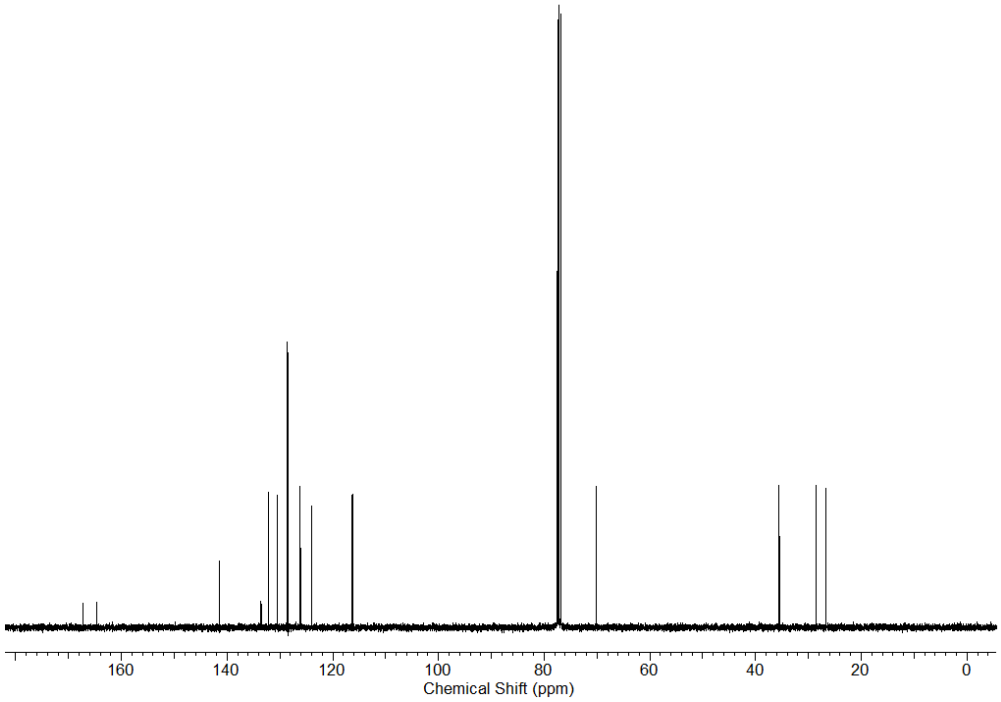




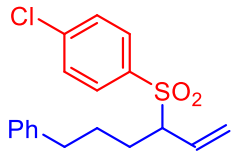
1.2) 1-fluoro-4-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3b**)

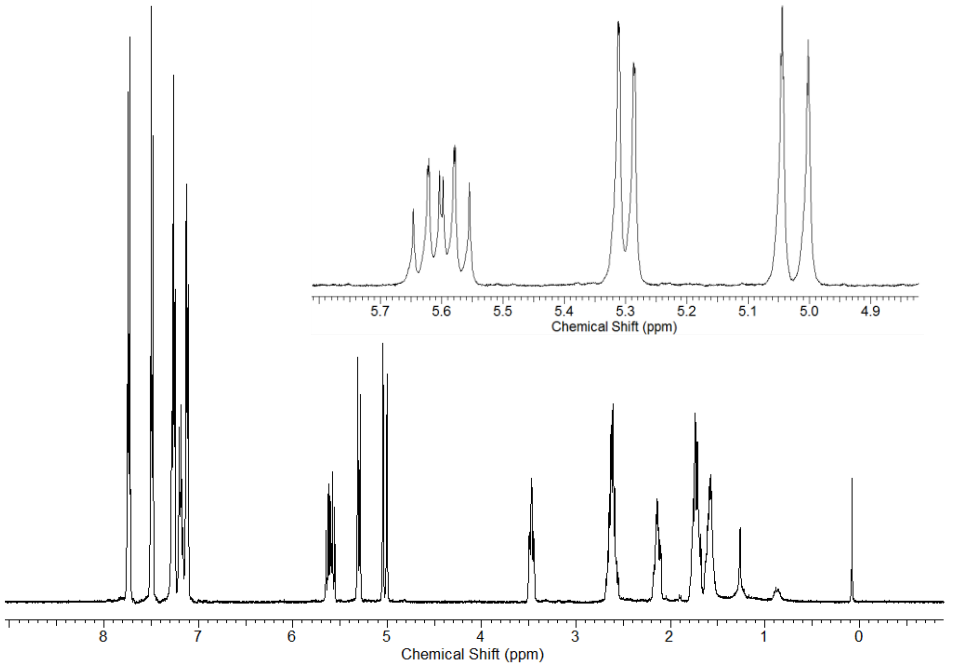


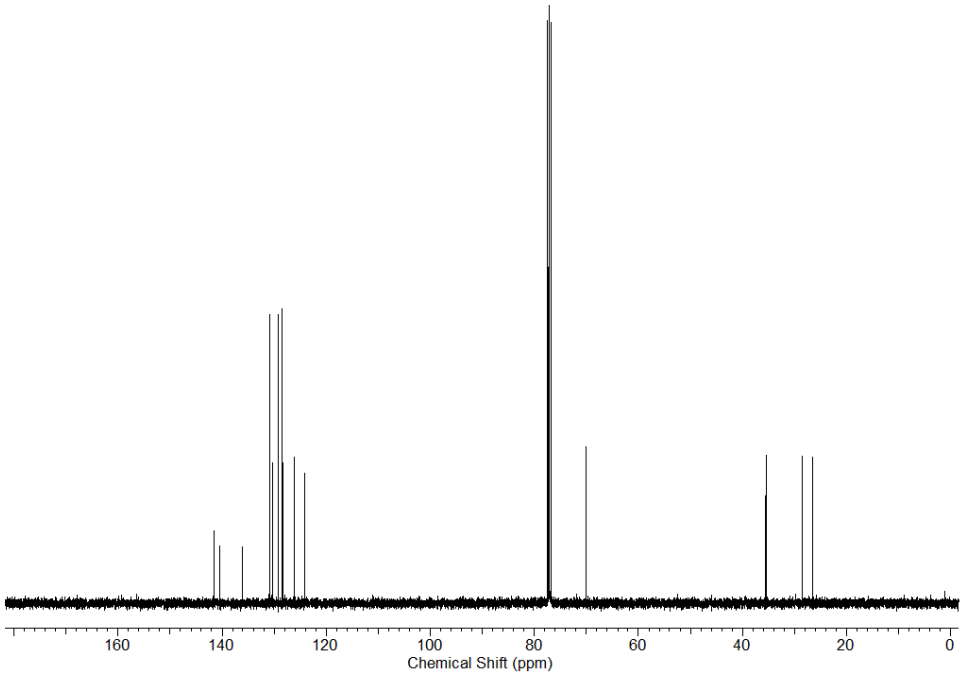




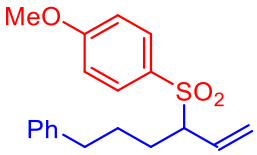
1.3) 1-chloro-4-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3c**)

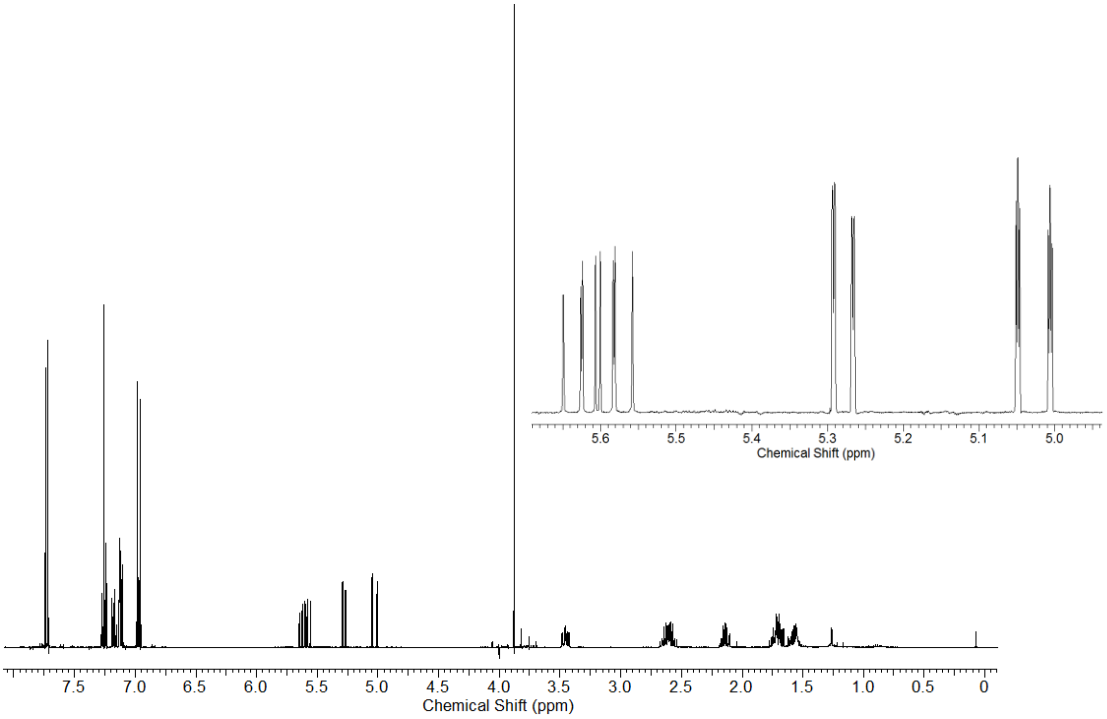


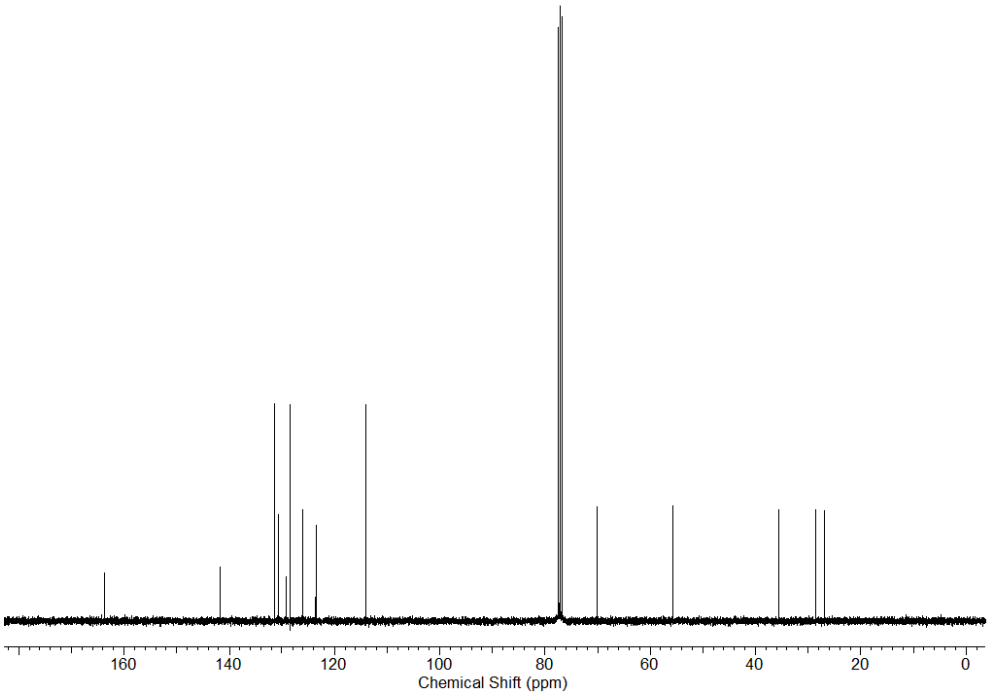




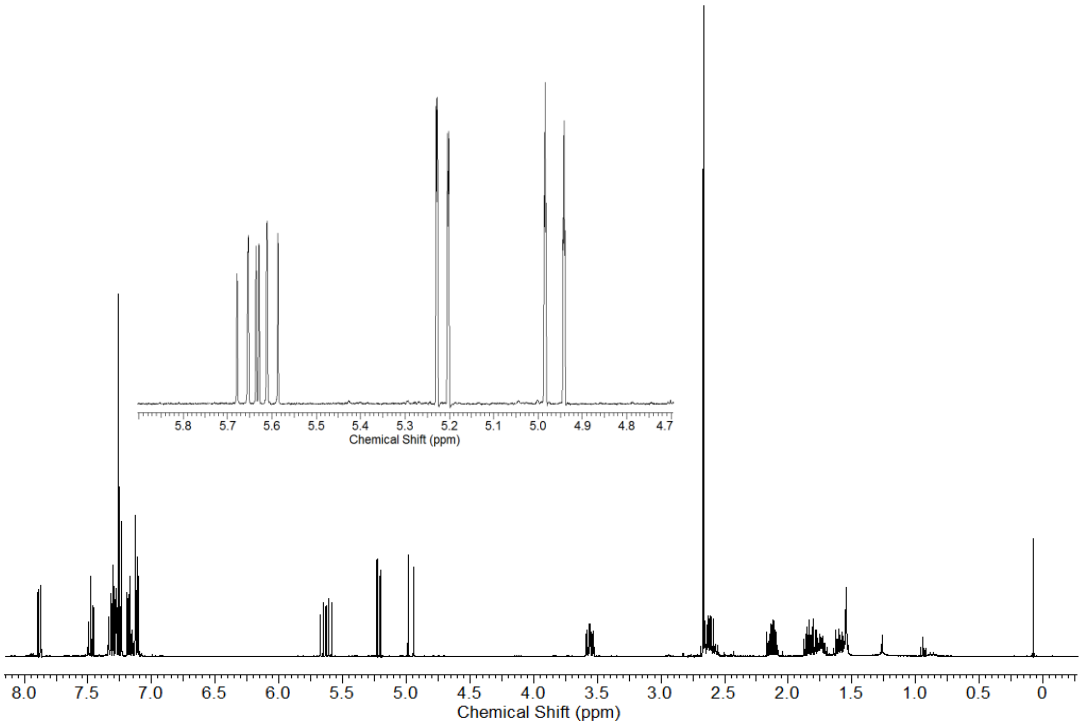
1.4) 1-methoxy-4-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3d**)

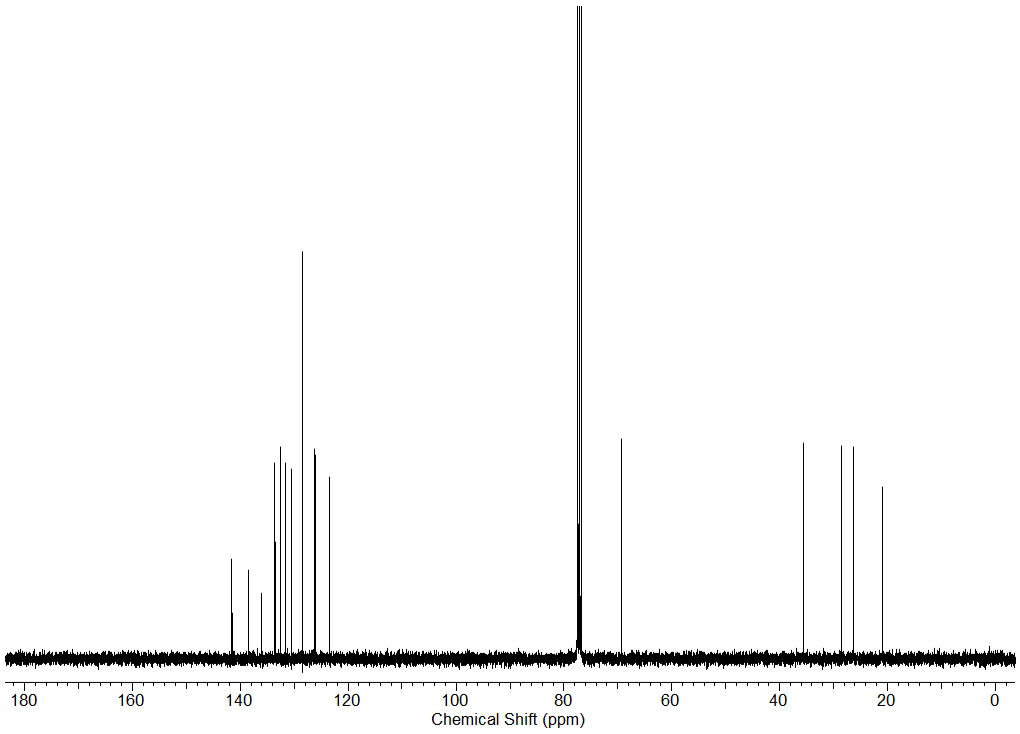




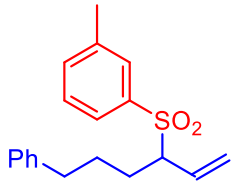


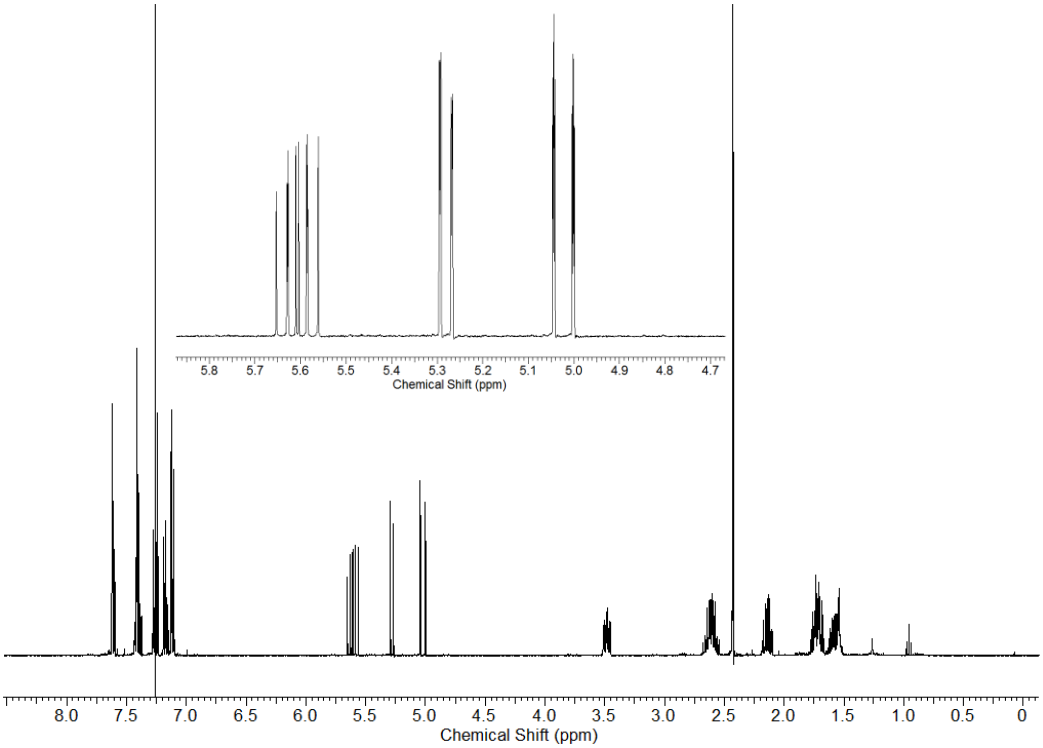
1.5) 1-methyl-2-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3e**)

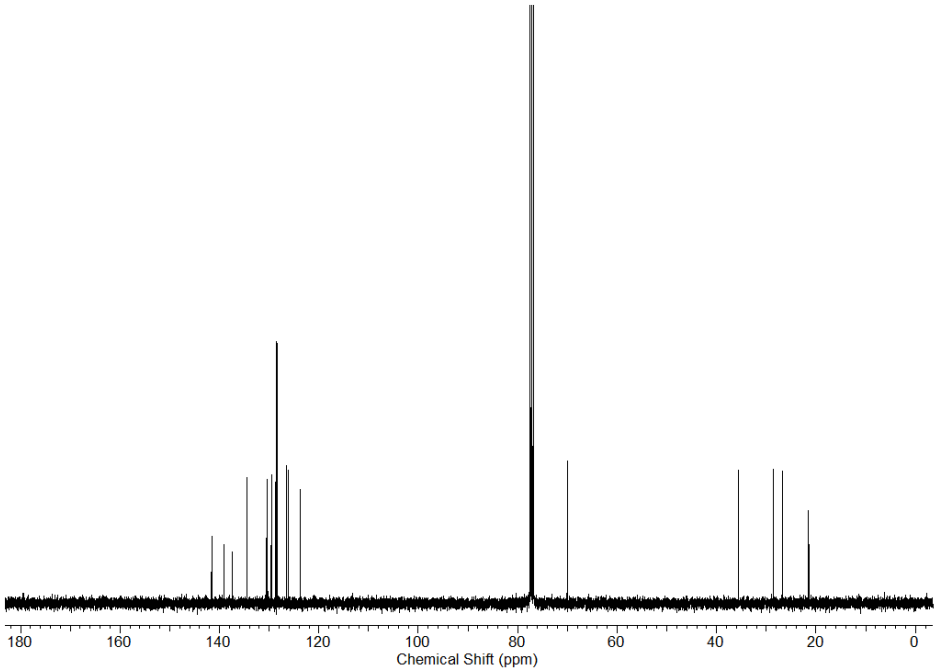




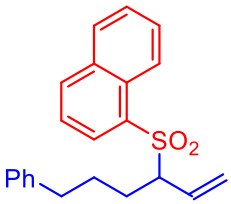
1.6) 1-methyl-3-((6-phenylhex-1-en-3-yl)sulfonyl)benzene (**3f**)

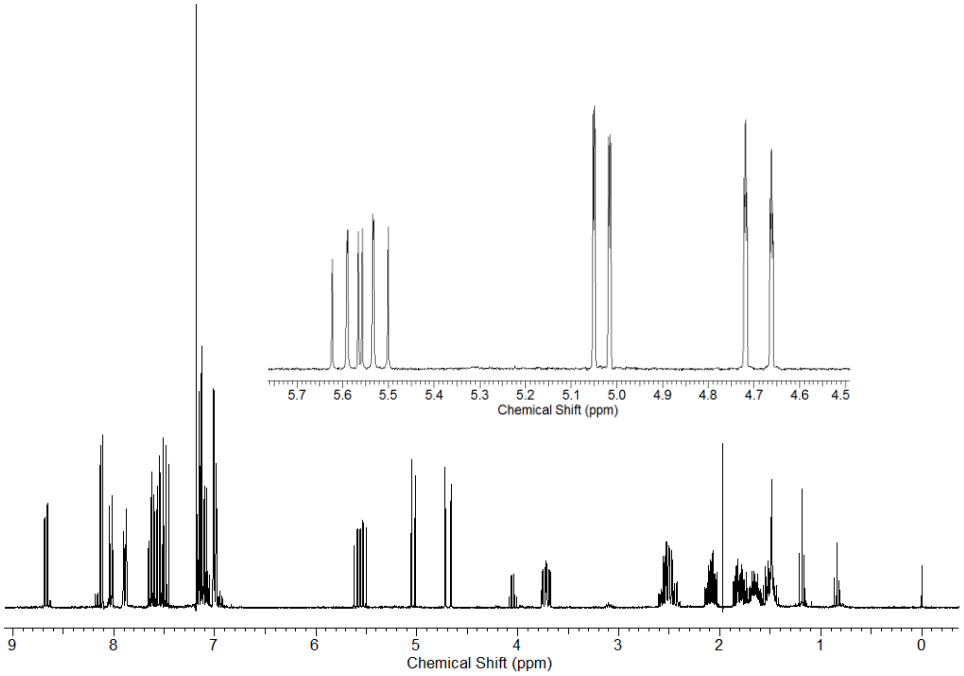


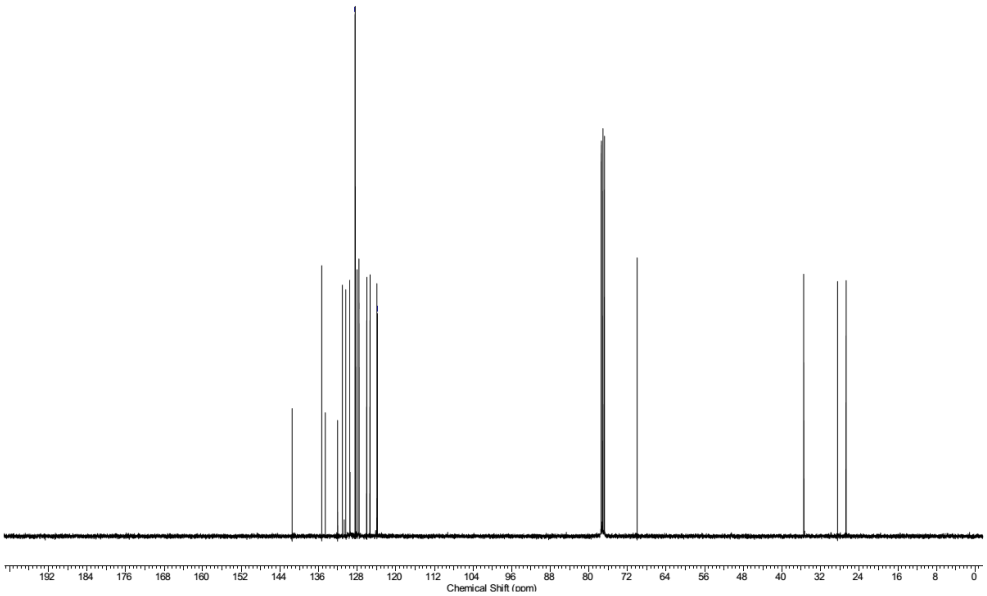




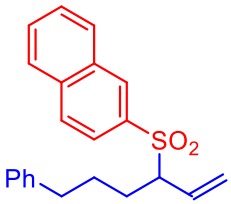
1.7) 1-((6-phenylhex-1-en-3-yl)sulfonyl)naphthalene (**3g**)

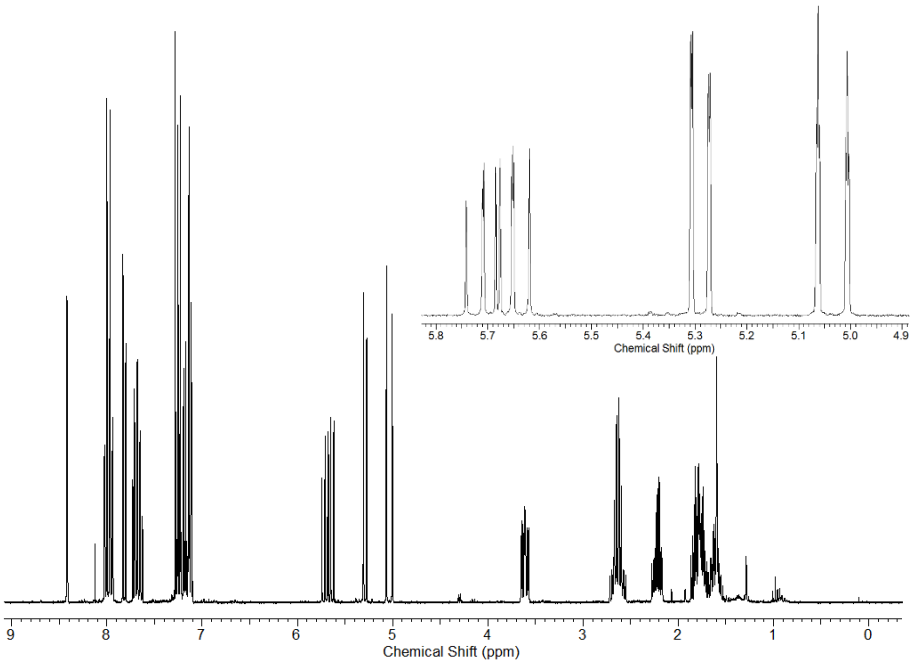


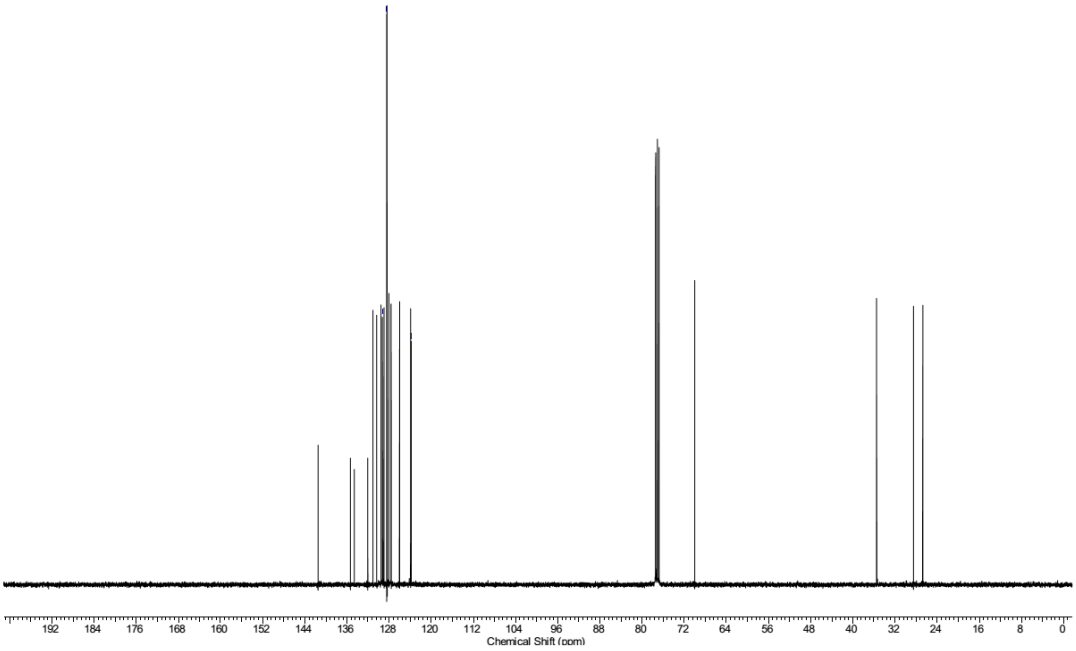




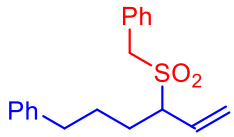
1.8) 2-((6-phenylhex-1-en-3-yl)sulfonyl)naphthalene (**3h**)

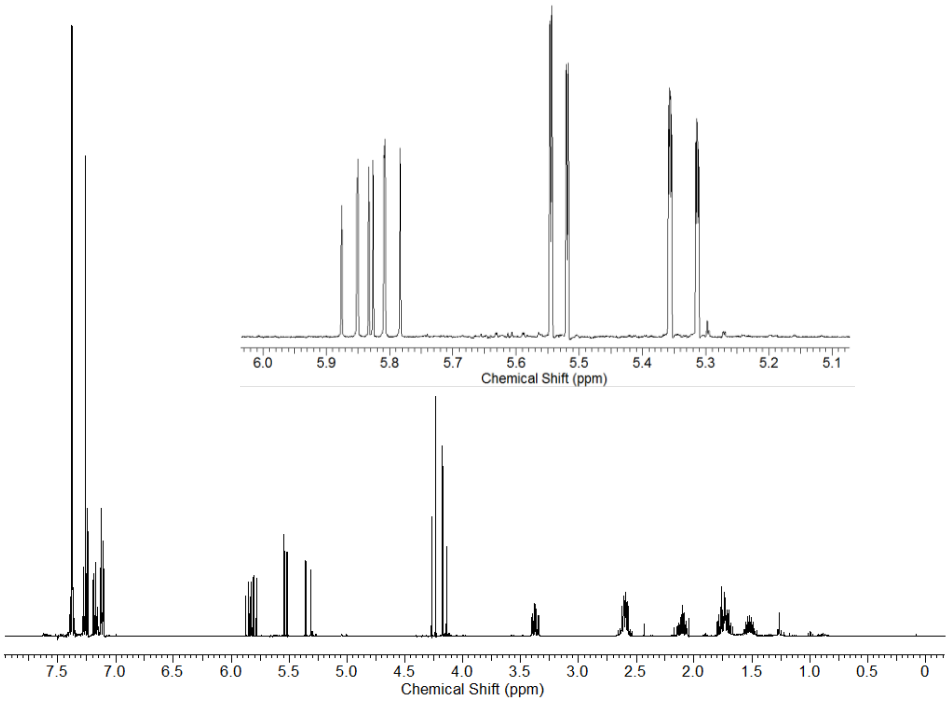


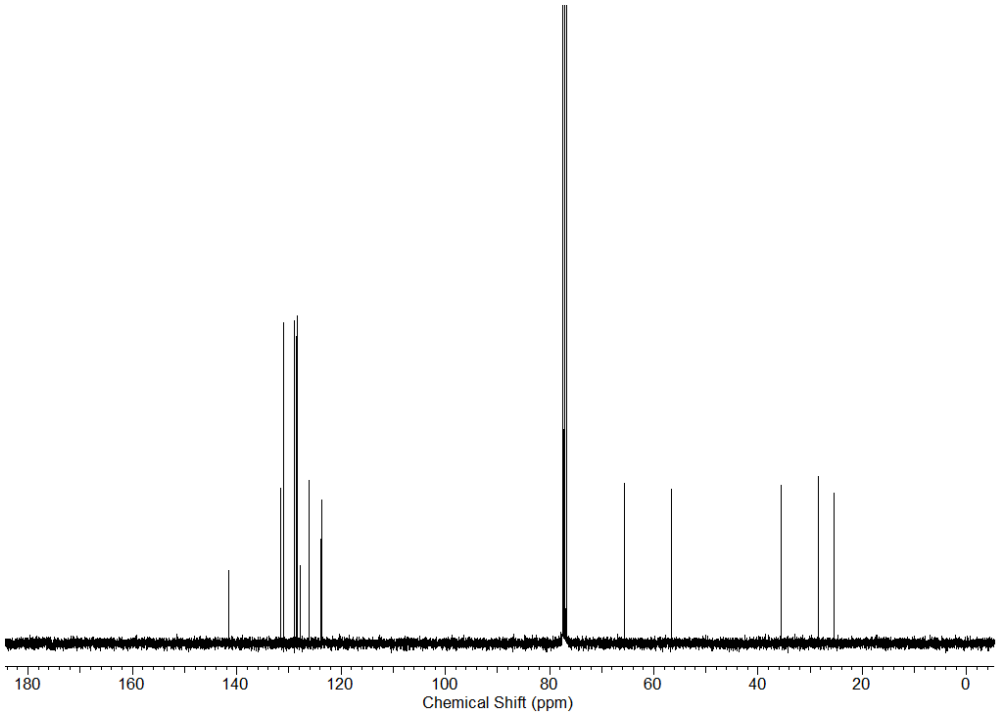




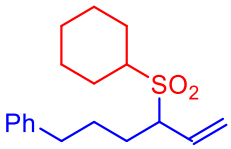
1.9) (4-(benzylsulfonyl)hex-5-en-1-yl)benzene (**3i**)

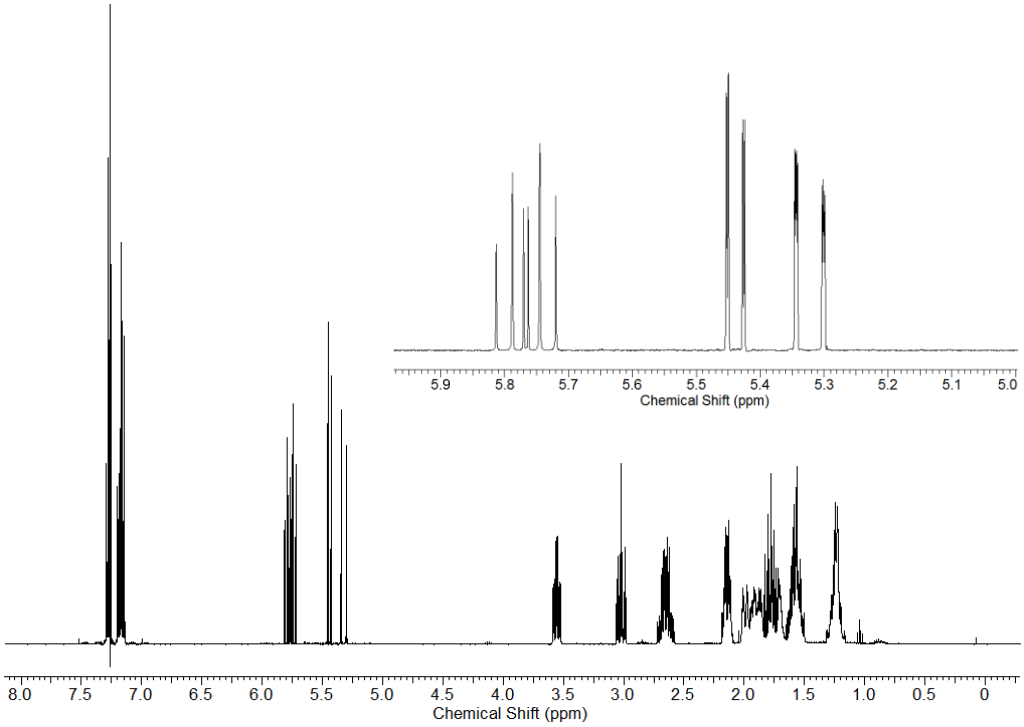


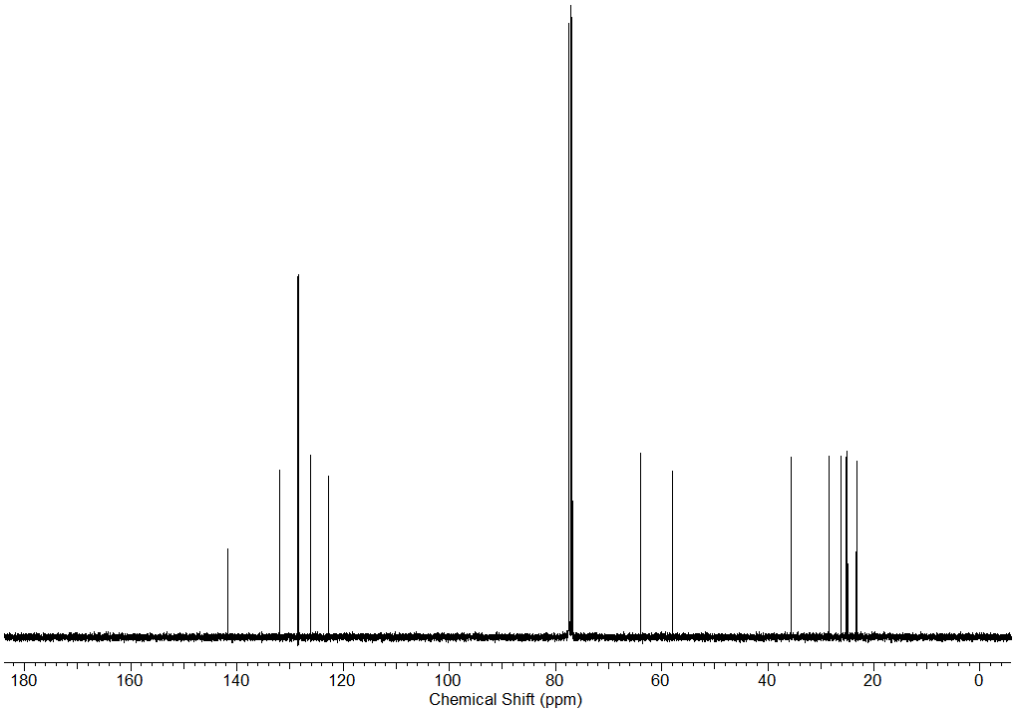




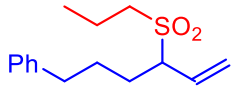
1.10) (4-(cyclohexylsulfonyl)hex-5-en-1-yl)benzene (**3j**)

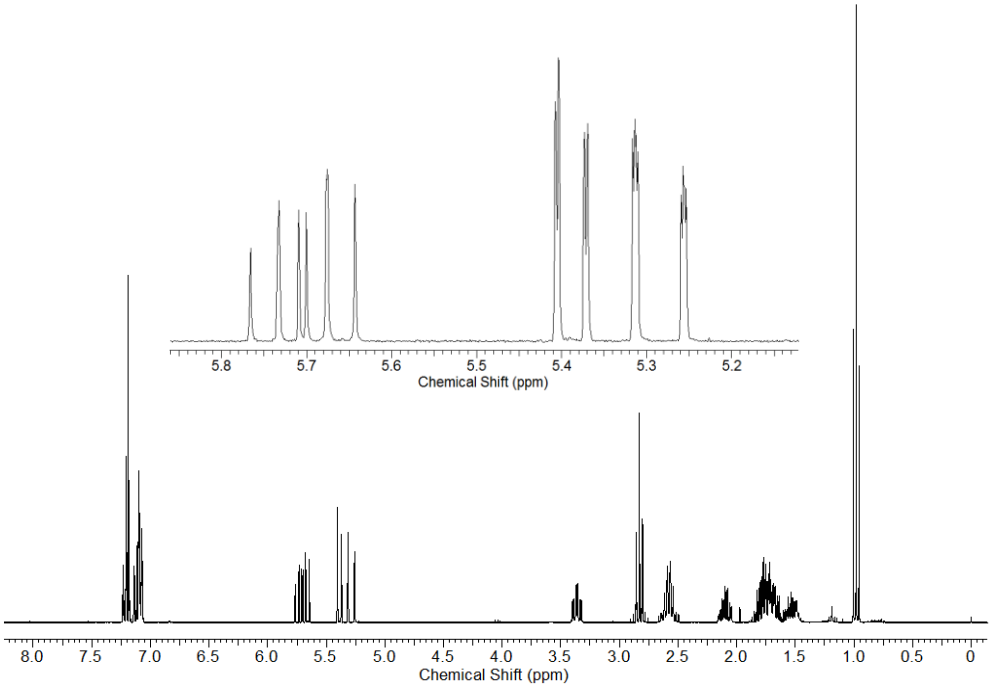


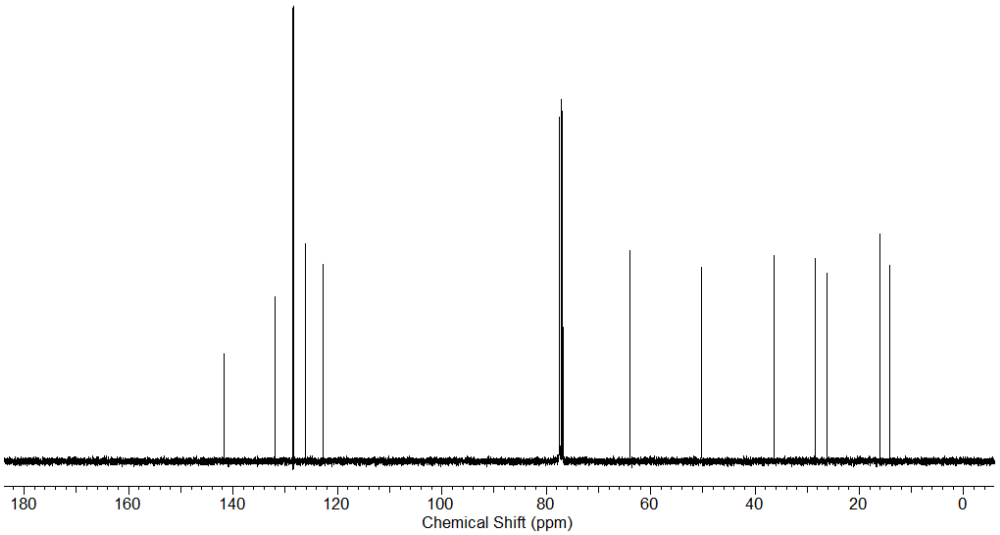




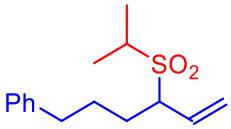
1.11) (4-(propylsulfonyl)hex-5-en-1-yl)benzene (**3k**)

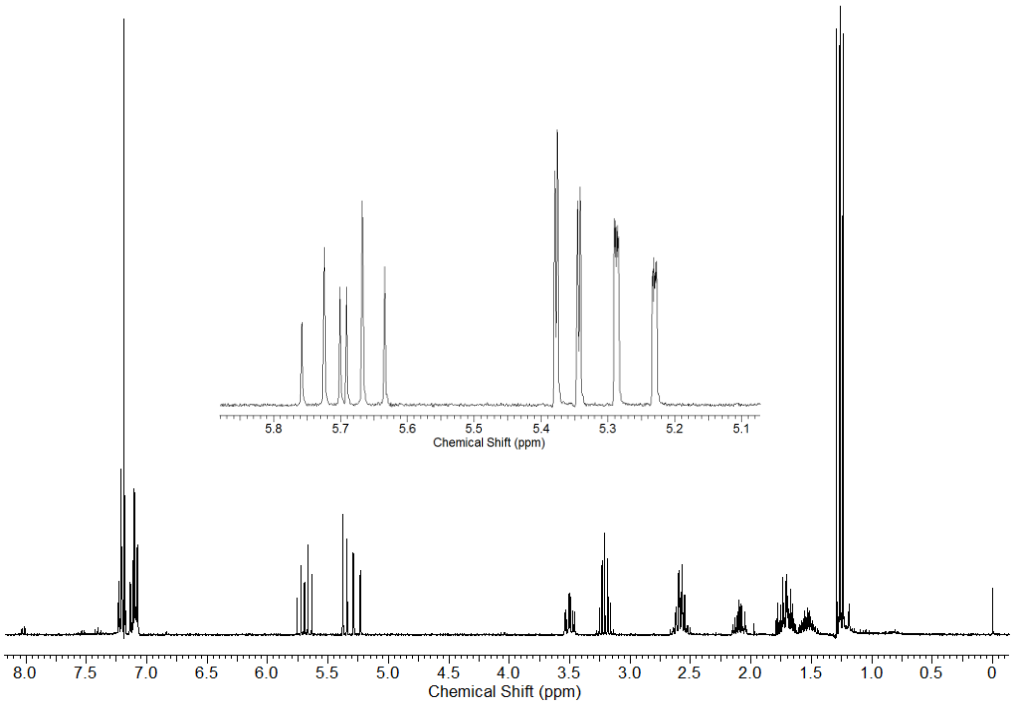


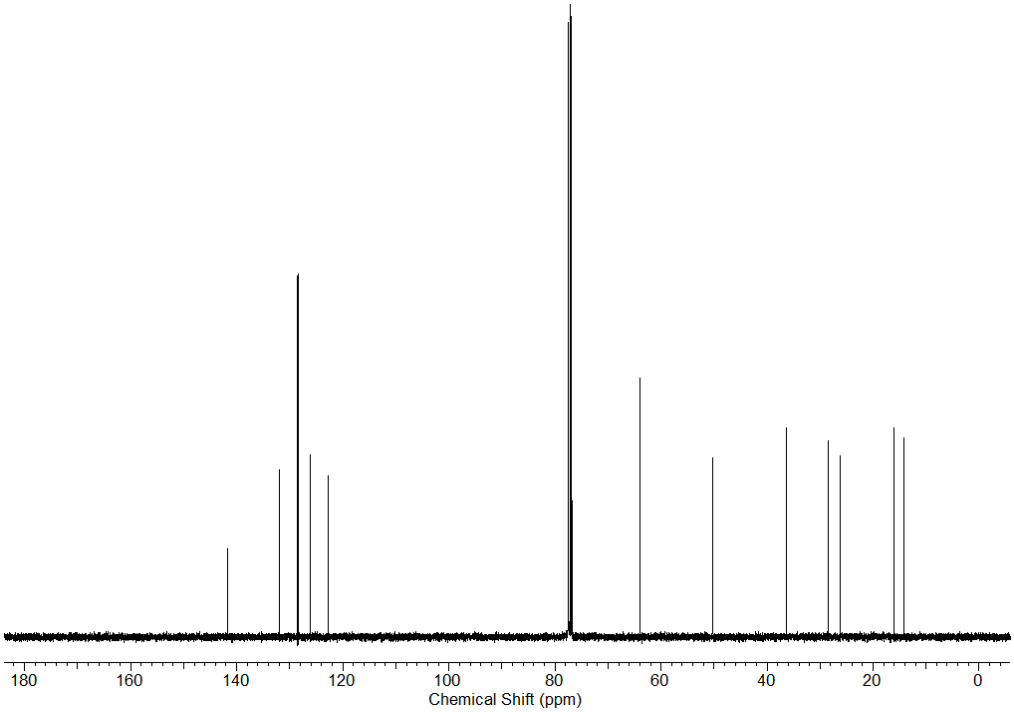




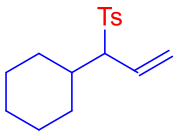
1.12) (4-(isopropylsulfonyl)hex-5-en-1-yl)benzene (**3l**)

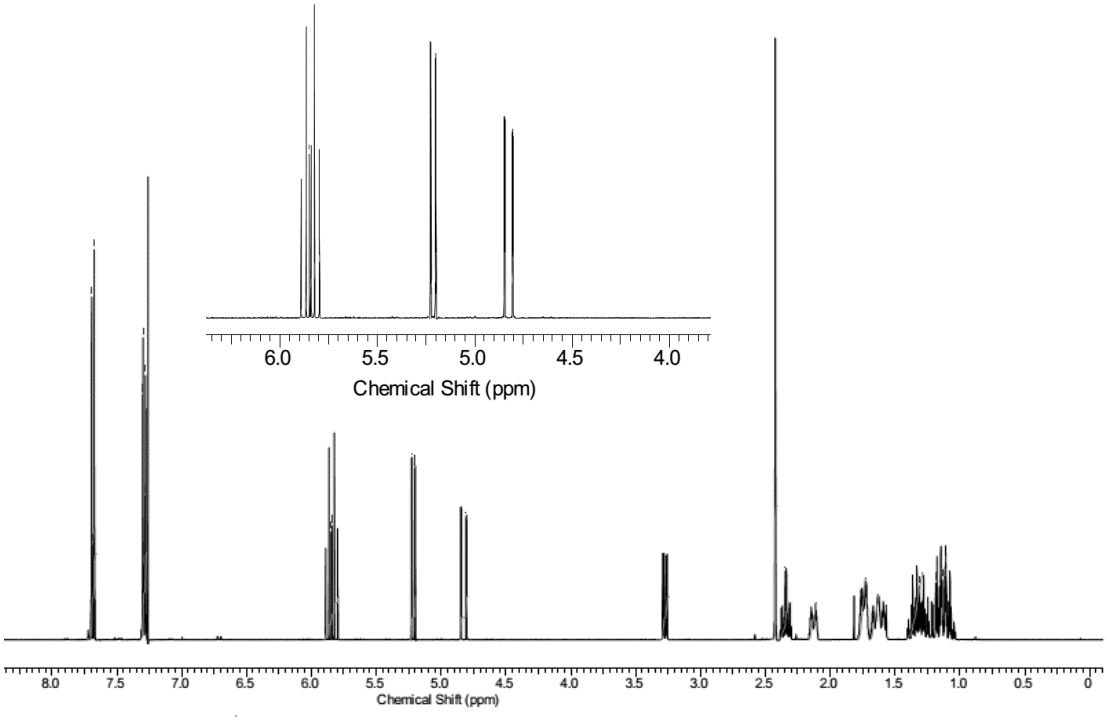


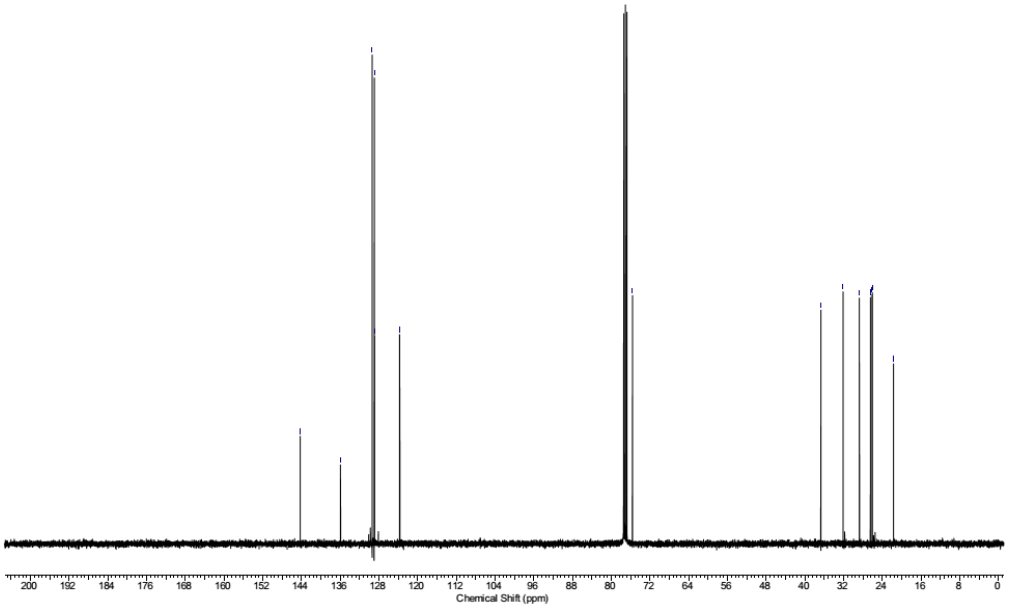




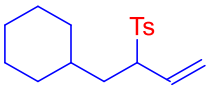
1.13) 1-((1-cyclohexylallyl)sulfonyl)-4-methylbenzene (**3m**)

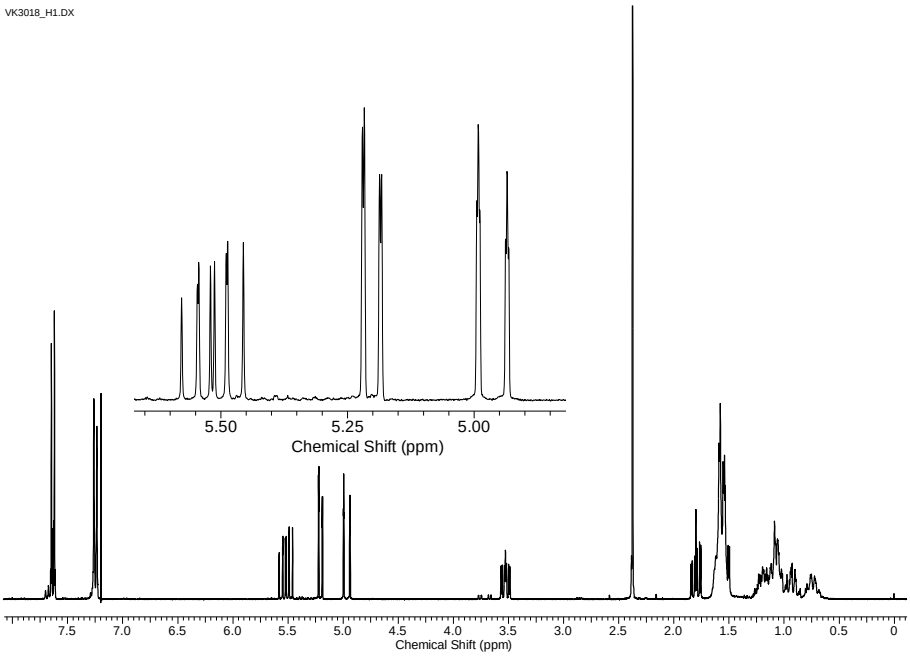




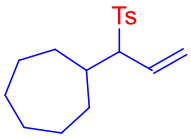


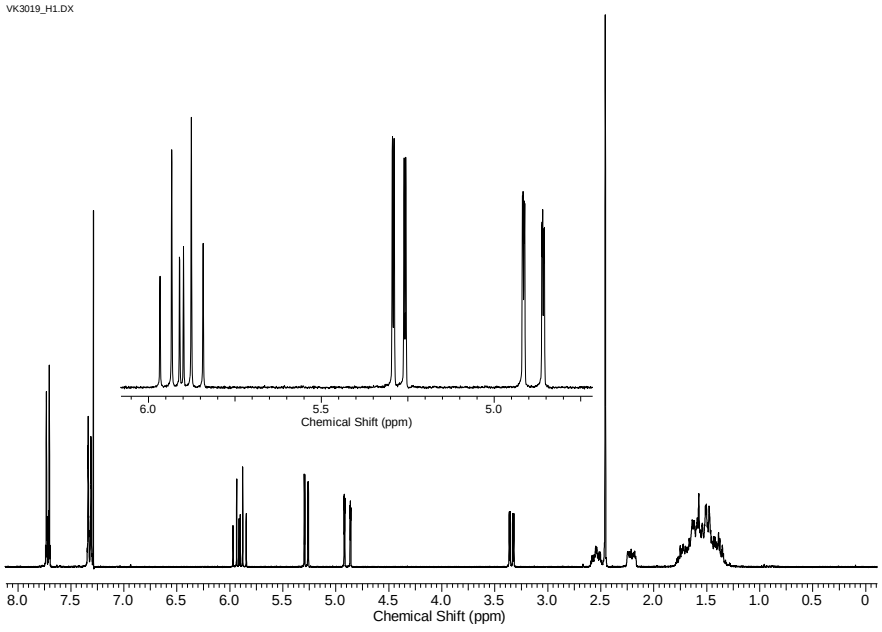
1.14) 1-((1-cyclohexylbut-3-en-2-yl)sulfonyl)-4-methylbenzene (**3n**)



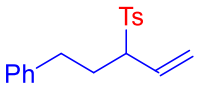


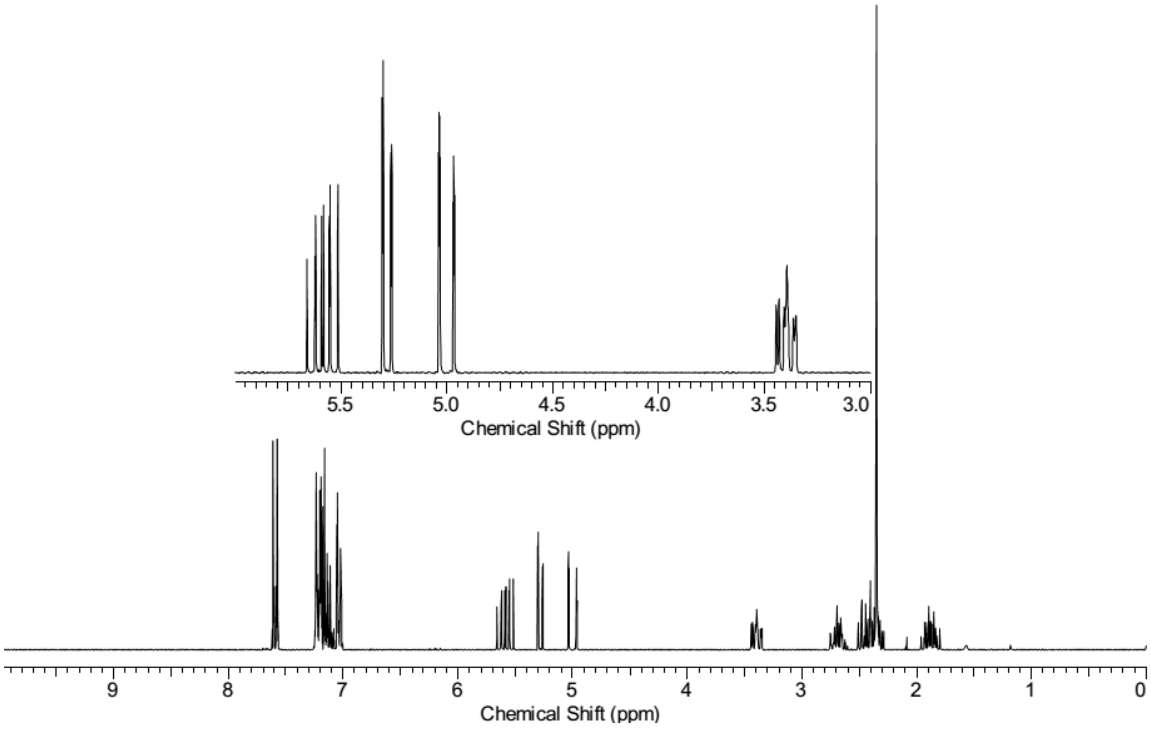
1.15) (1-tosylallyl)cycloheptane (**3o**)

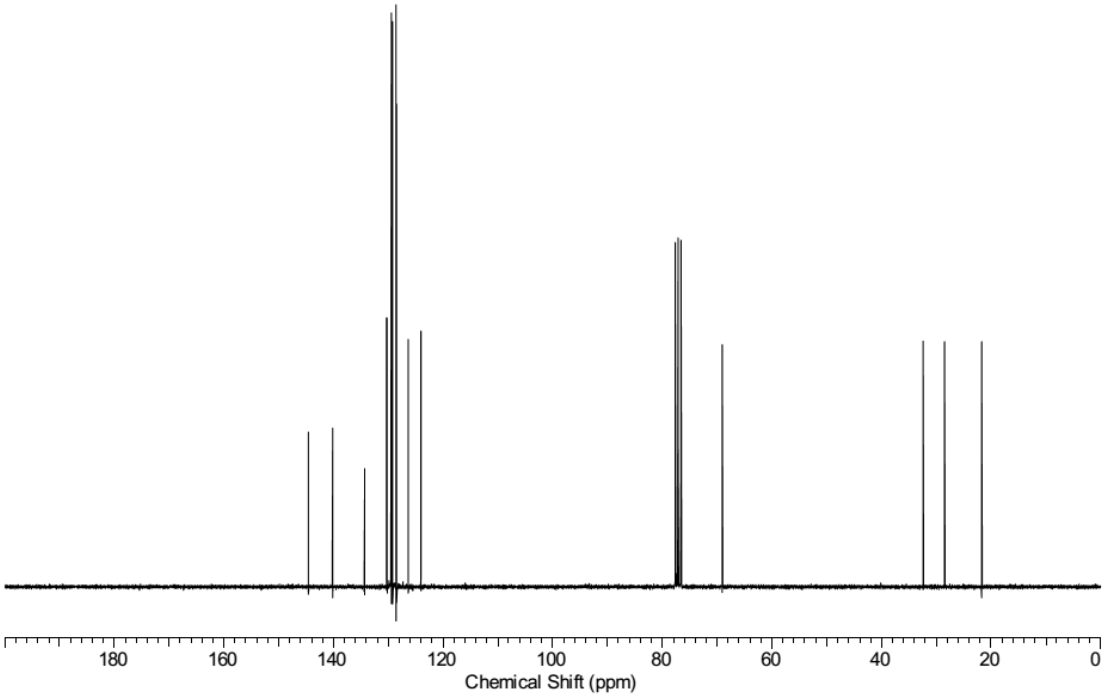




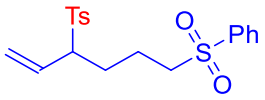
1.16) 1-methyl-4-((5-phenylpent-1-en-3-yl)sulfonyl)benzene (**3p**)

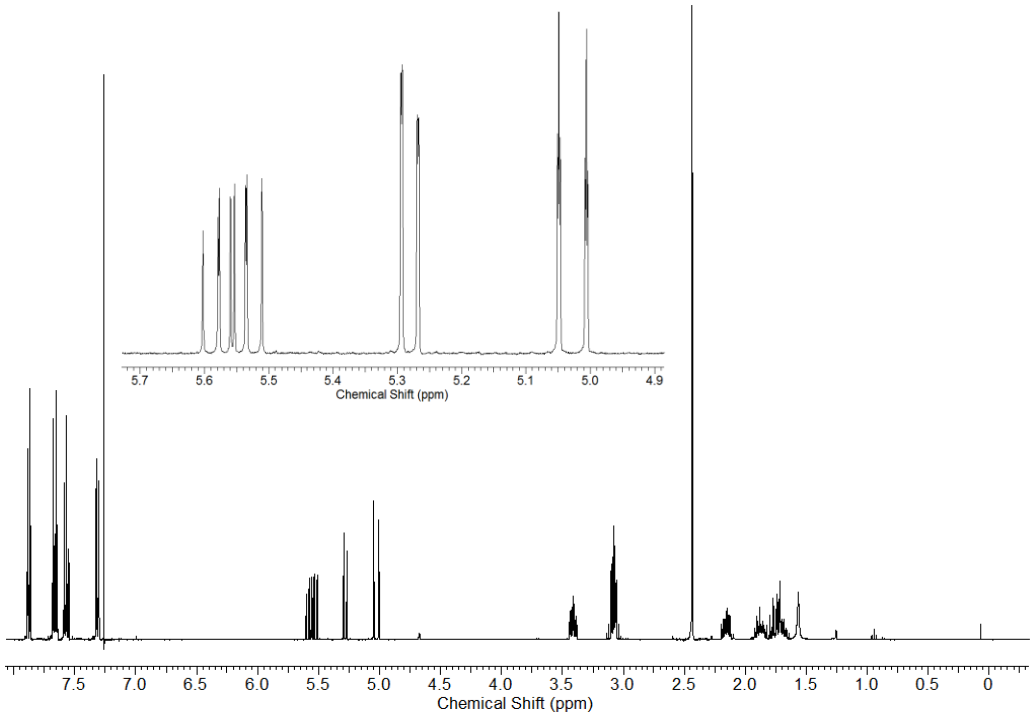


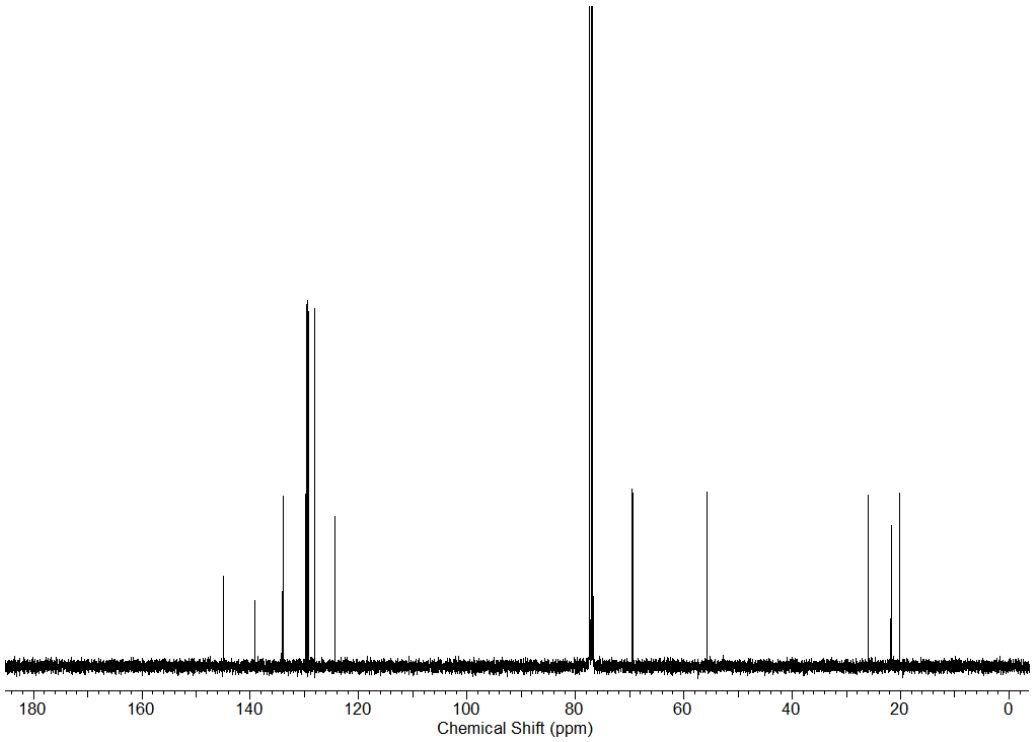




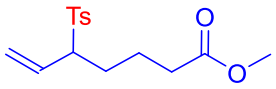
1.17) 1-methyl-4-((6-(phenylsulfonyl)hex-1-en-3-yl)sulfonyl)benzene (**3q**)

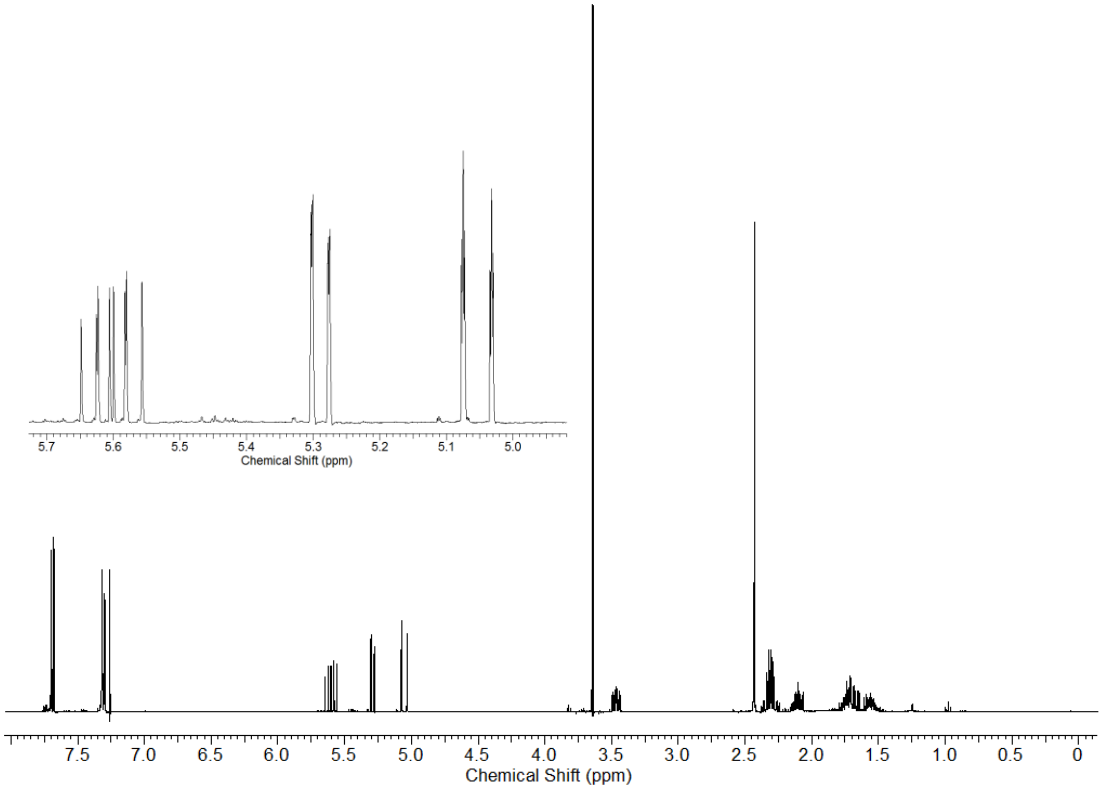


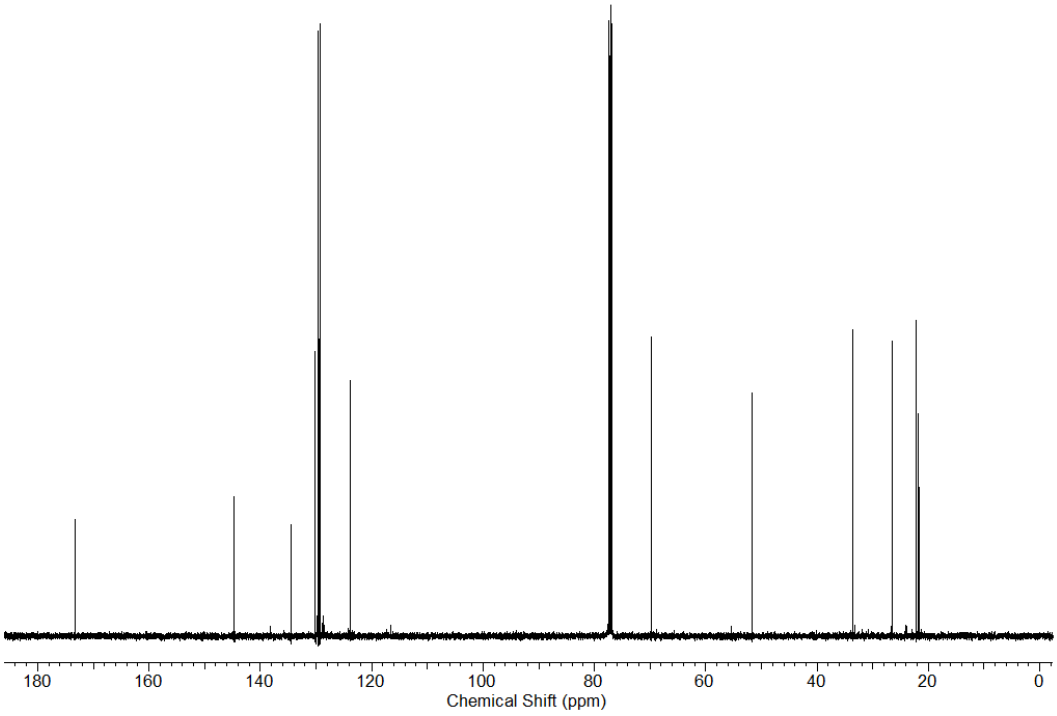




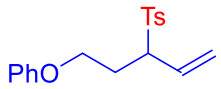
1.18) methyl 5-tosylhept-6-enoate (**3r**)

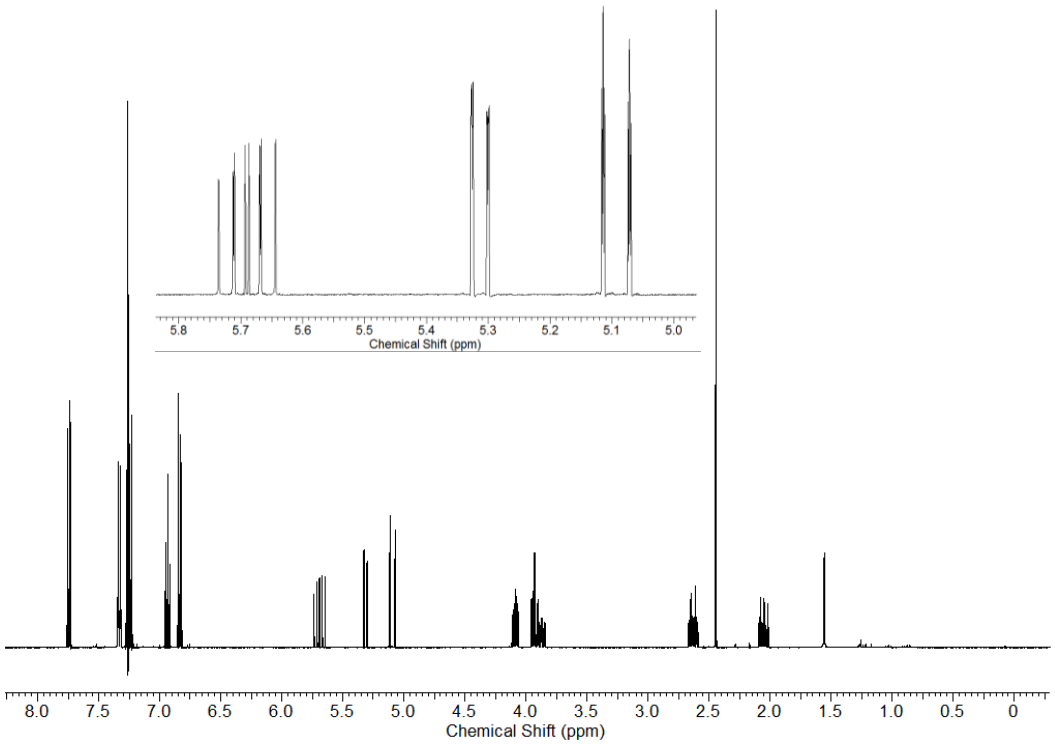


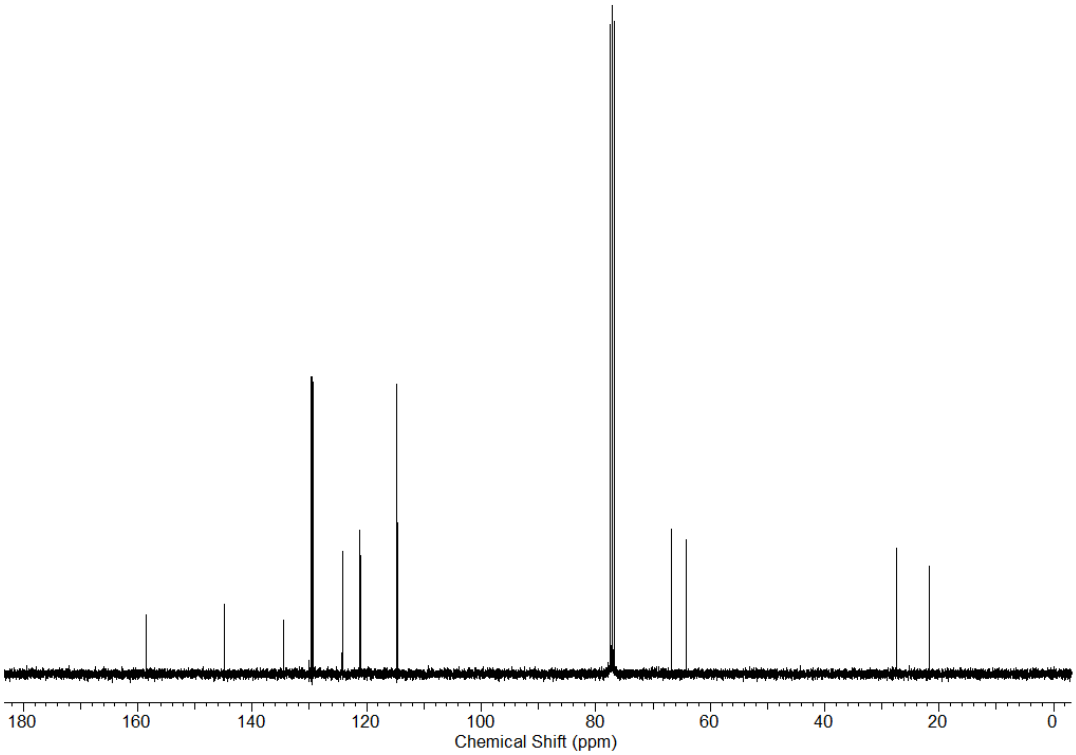




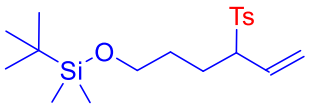
1.19) 1-methyl-4-((5-phenoxypent-1-en-3-yl)sulfonyl)benzene (**3s**)

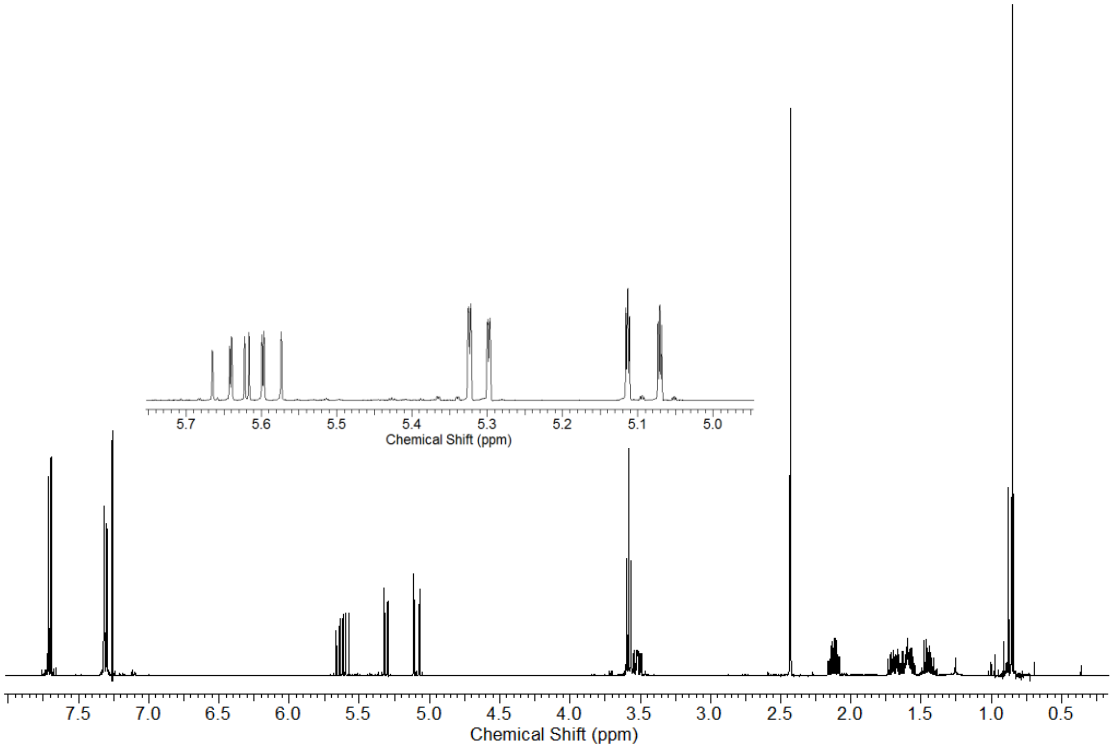


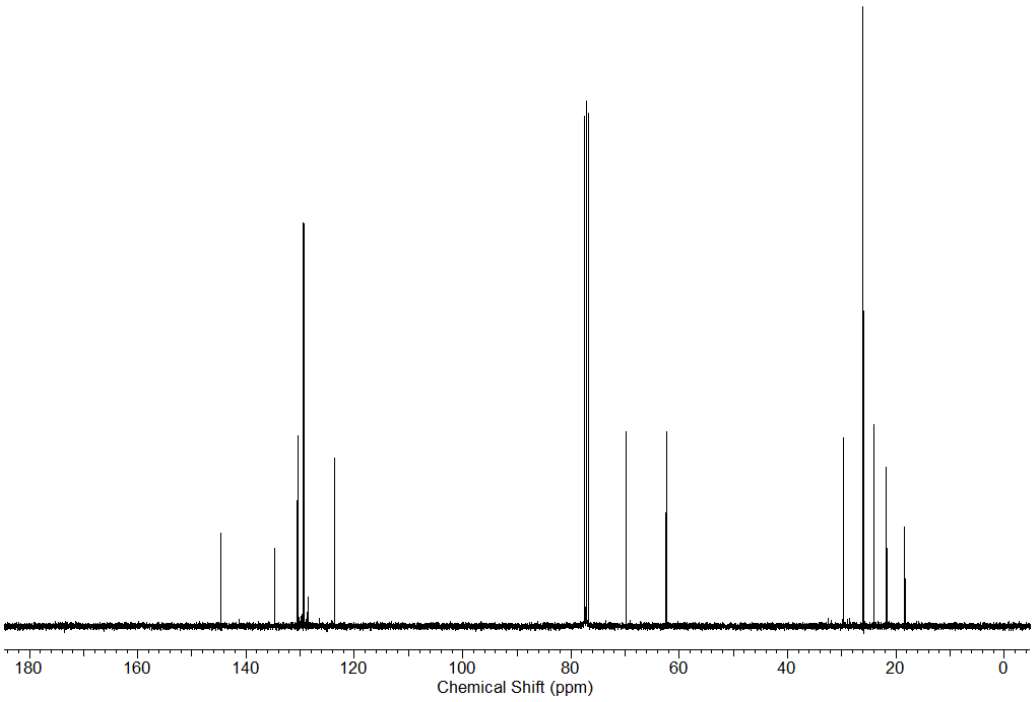




1.20) tert-butyldimethyl((4-tosylhex-5-en-1-yl)oxy)silane (**3t**)

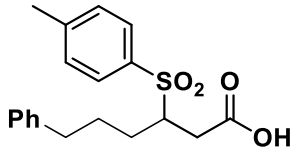


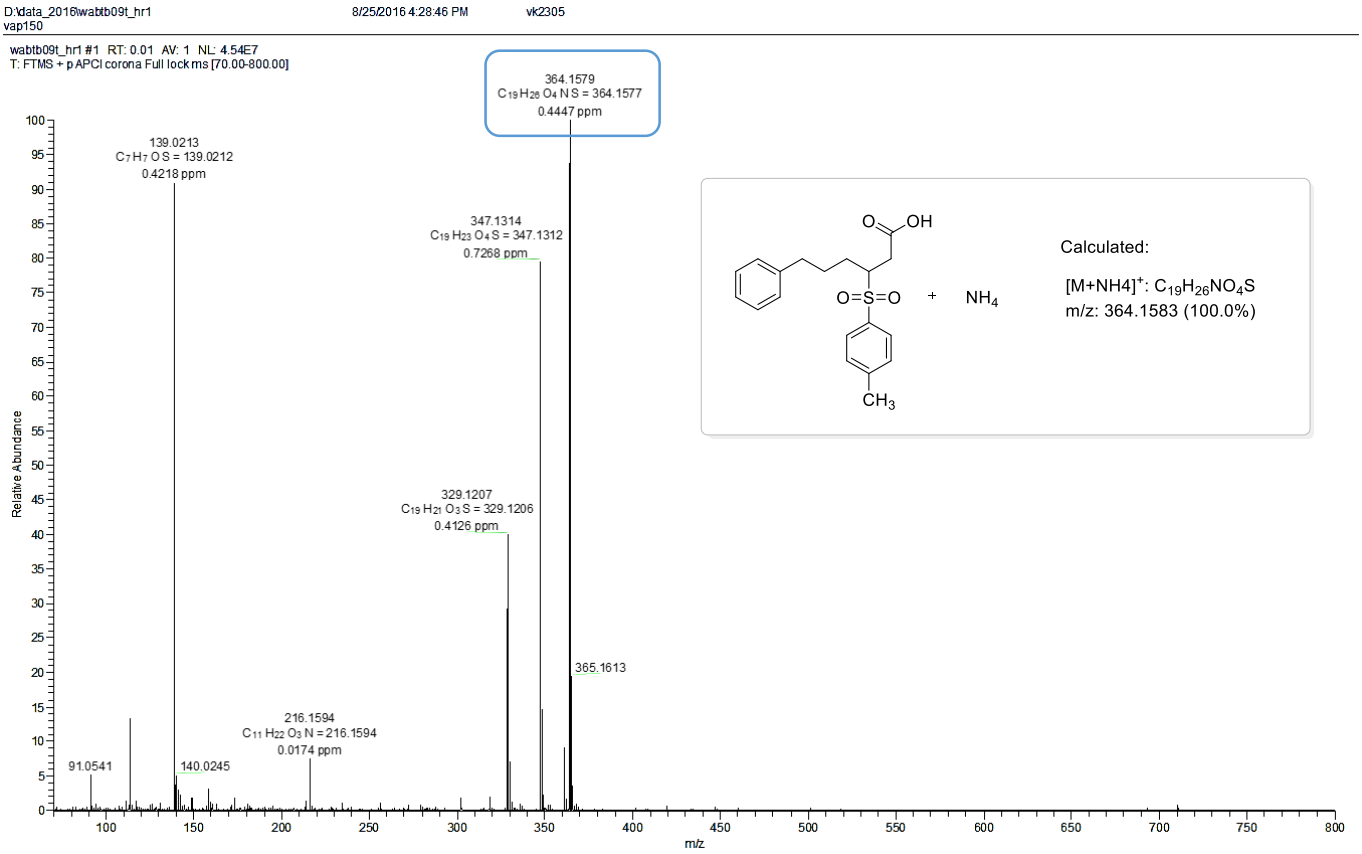


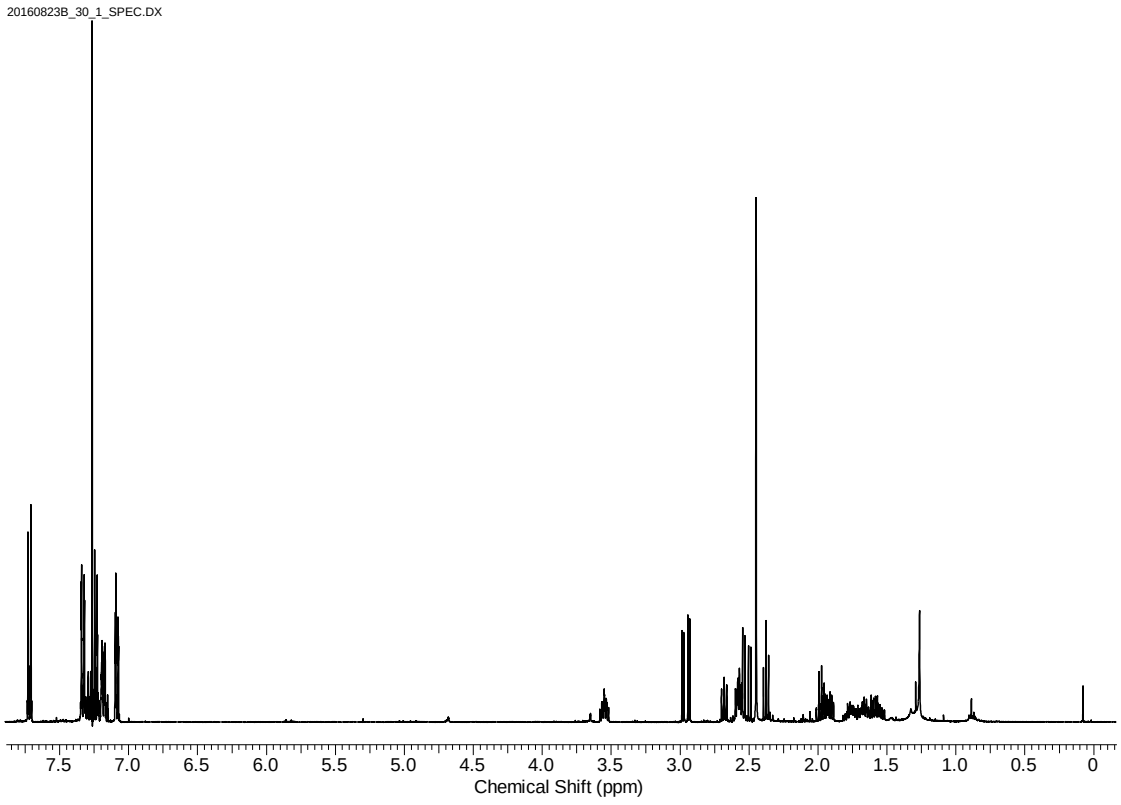


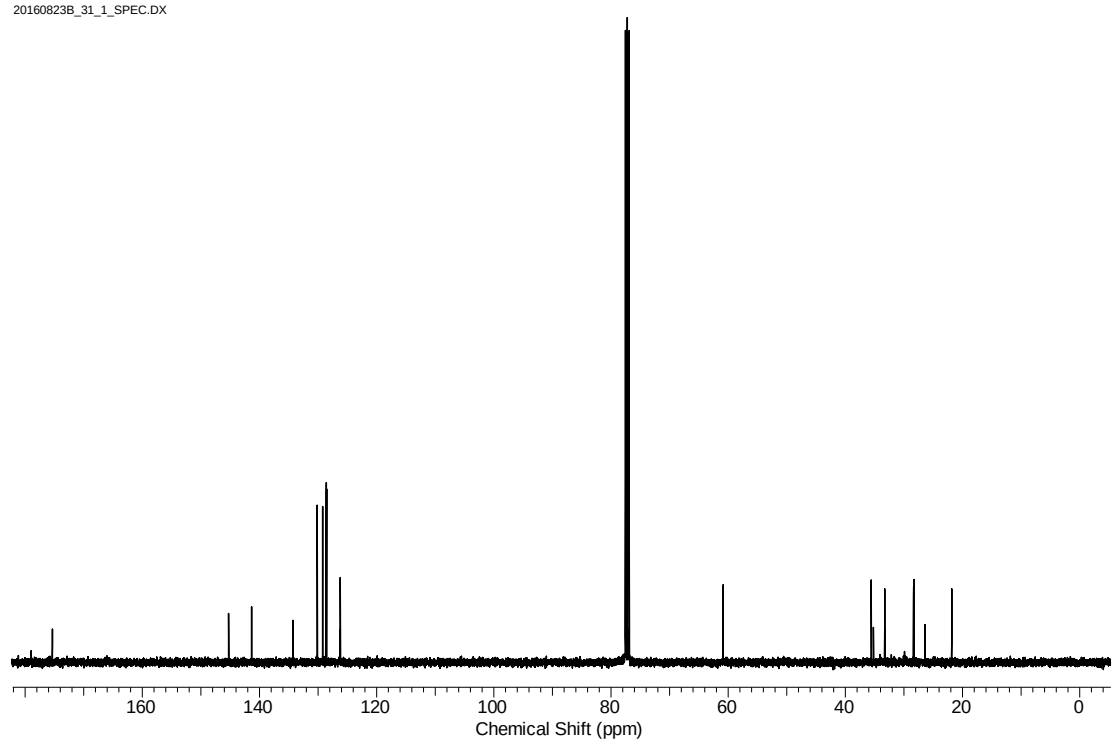
S8 (Derivatization of Branched Allylic Sulfones)

6-phenyl-3-tosylhexanoic acid (**4ac**)

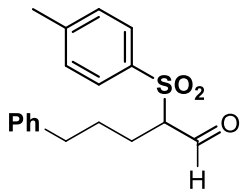


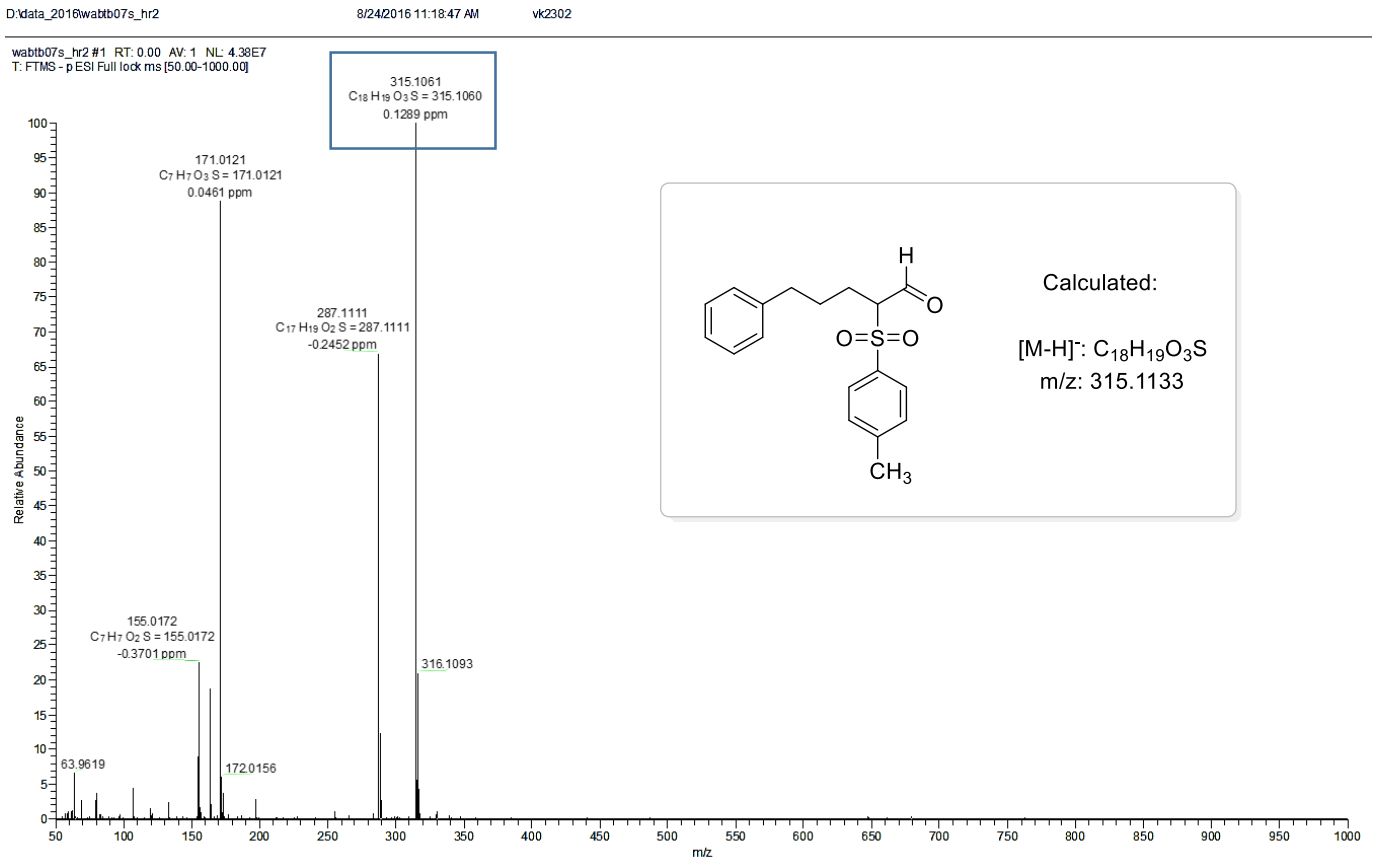



20160823B_30_1_SPEC.DX
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

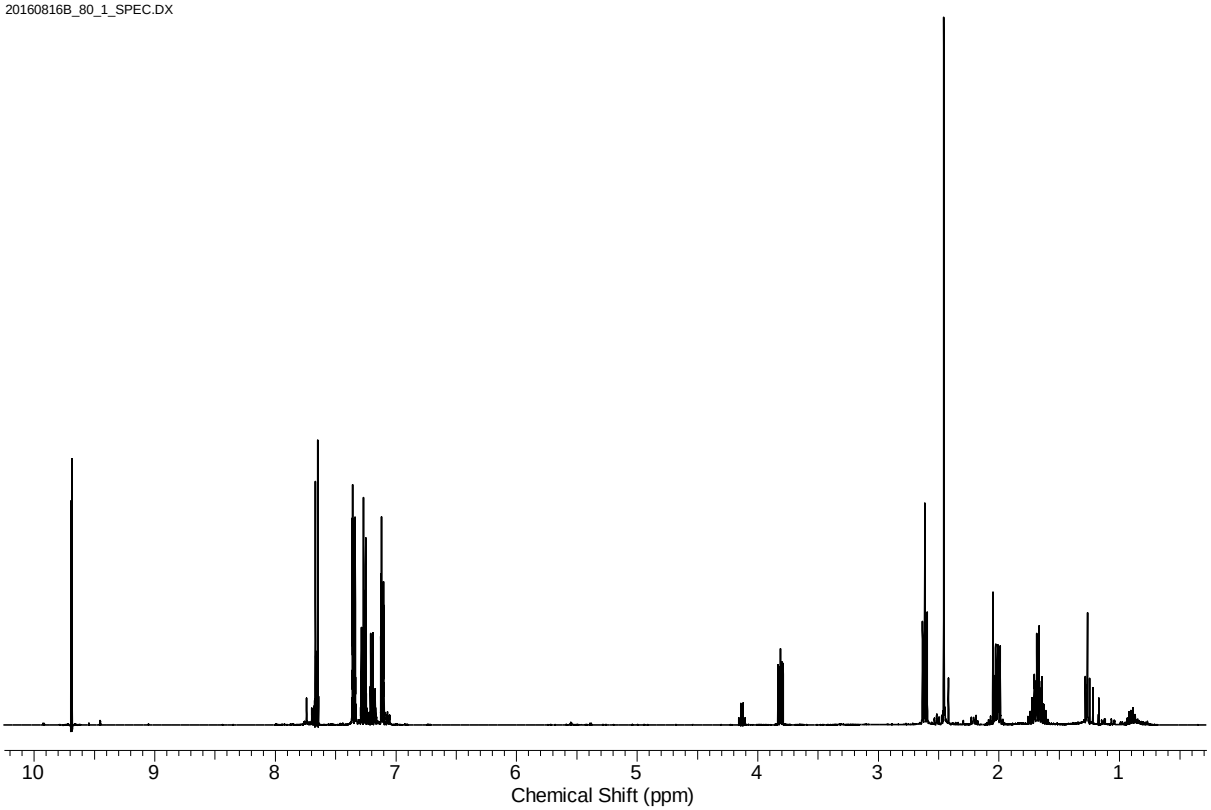

20160823B_31_1_SPEC.DX
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

5-phenyl-2-tosylpentanal (**4ad**)

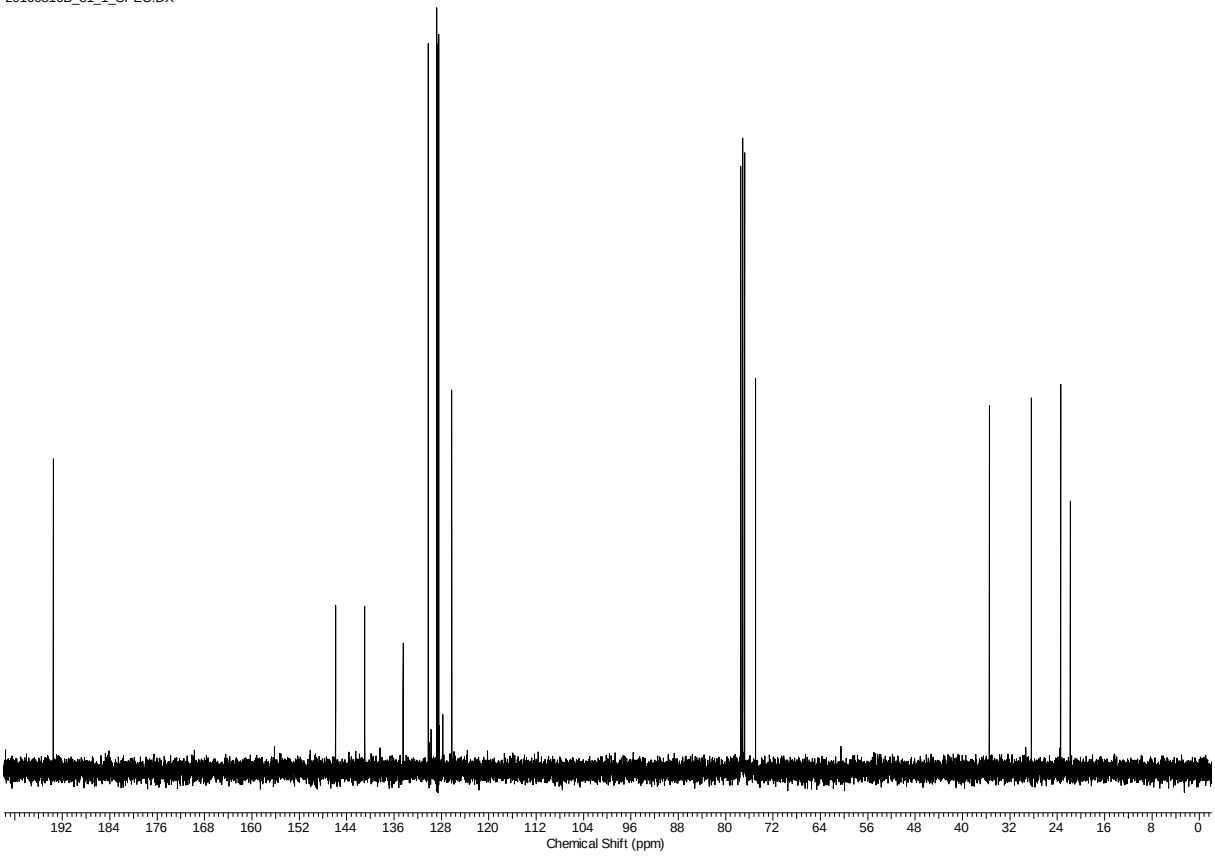




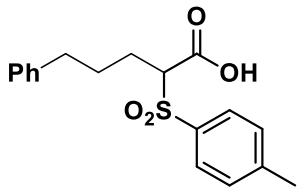
20160816B_80_1_SPEC.DX

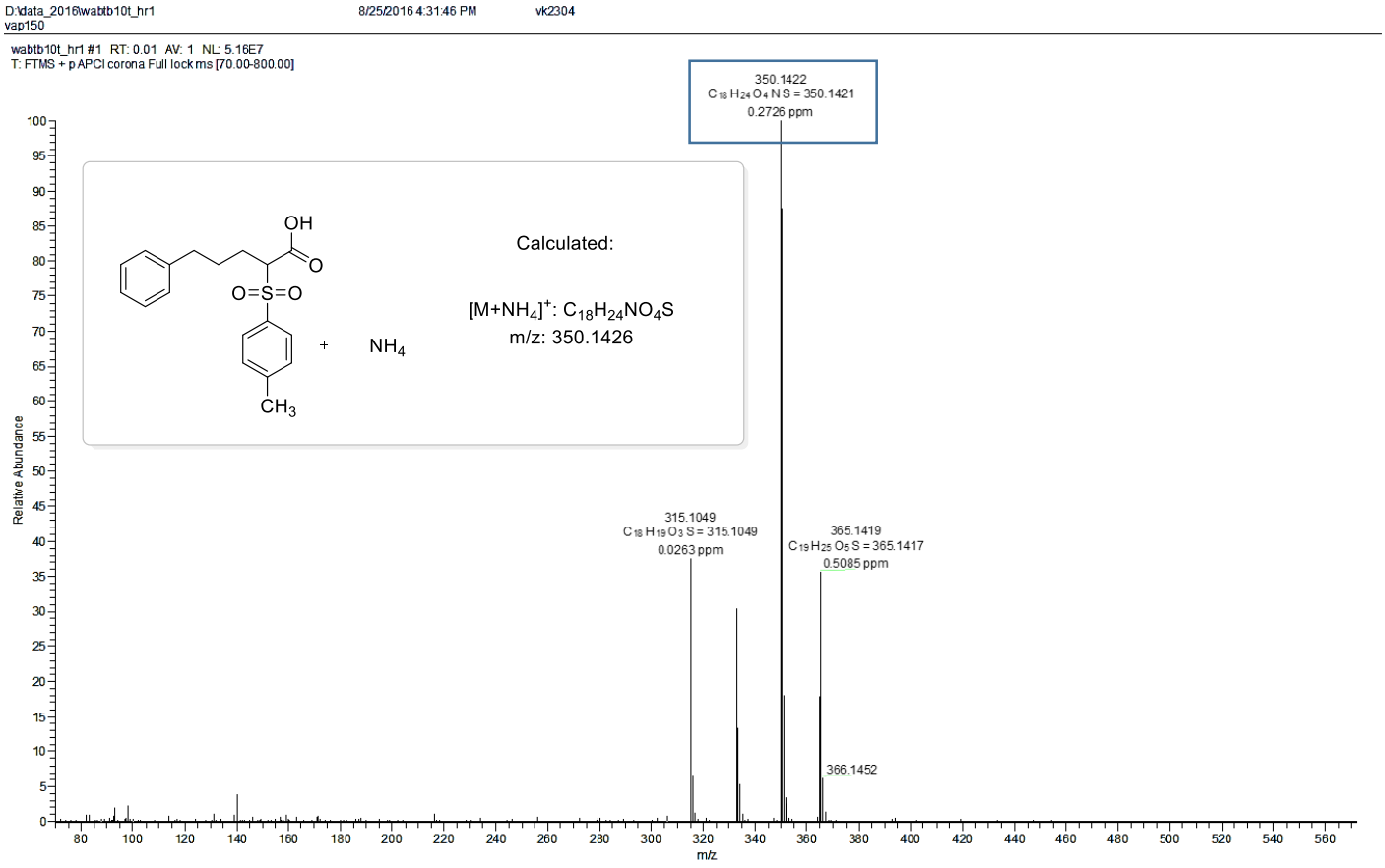


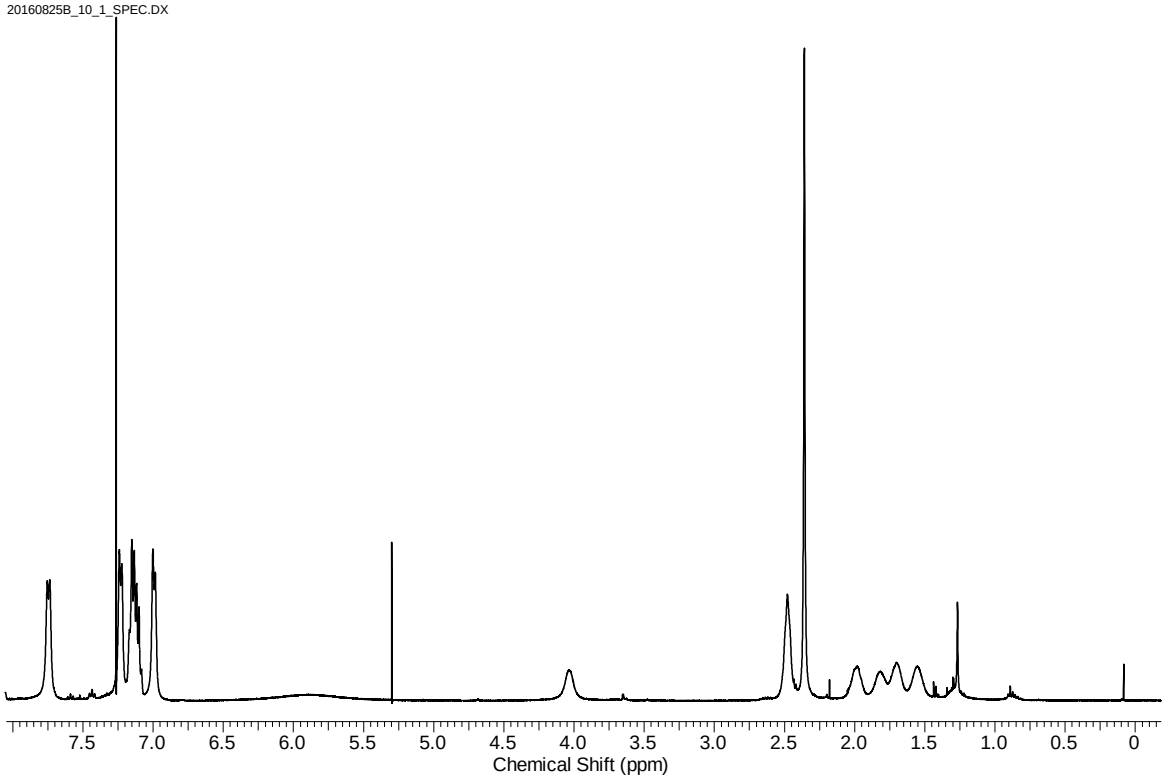
20160816B_81_1_SPEC.DX

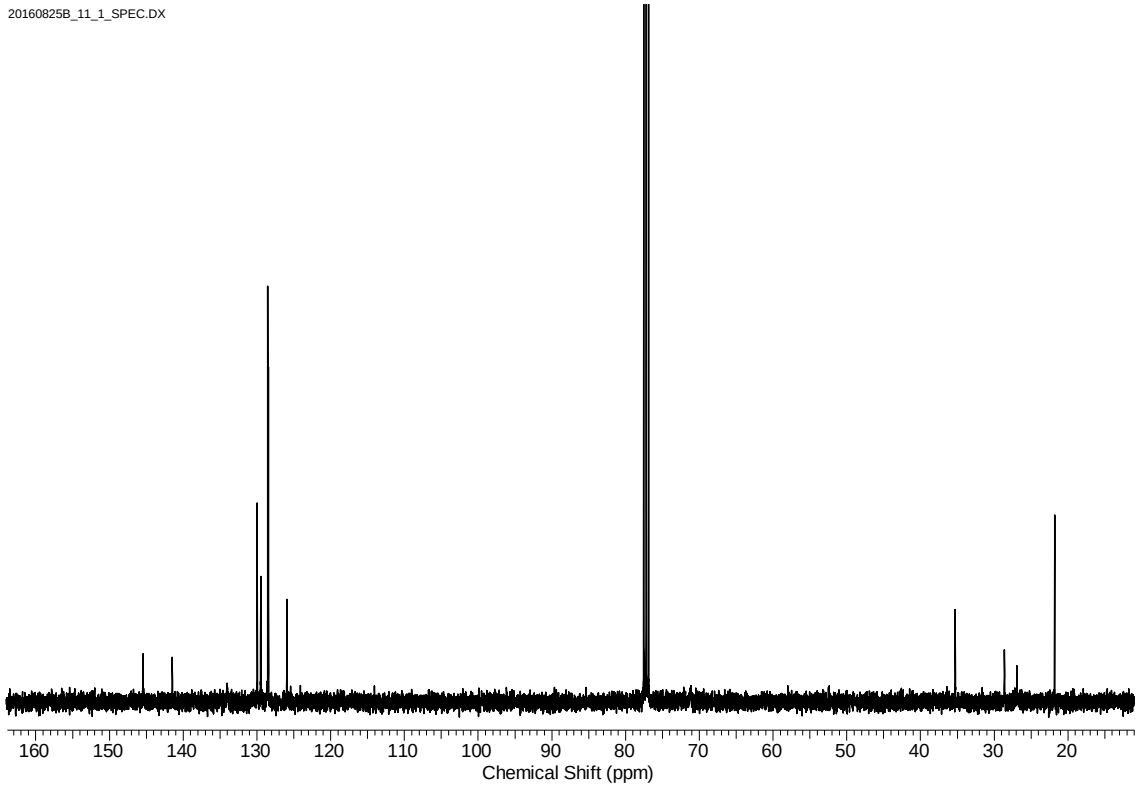


5-phenyl-2-tosylpentanoic acid (**4ae**)

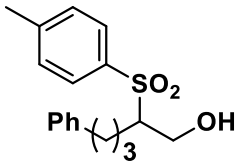




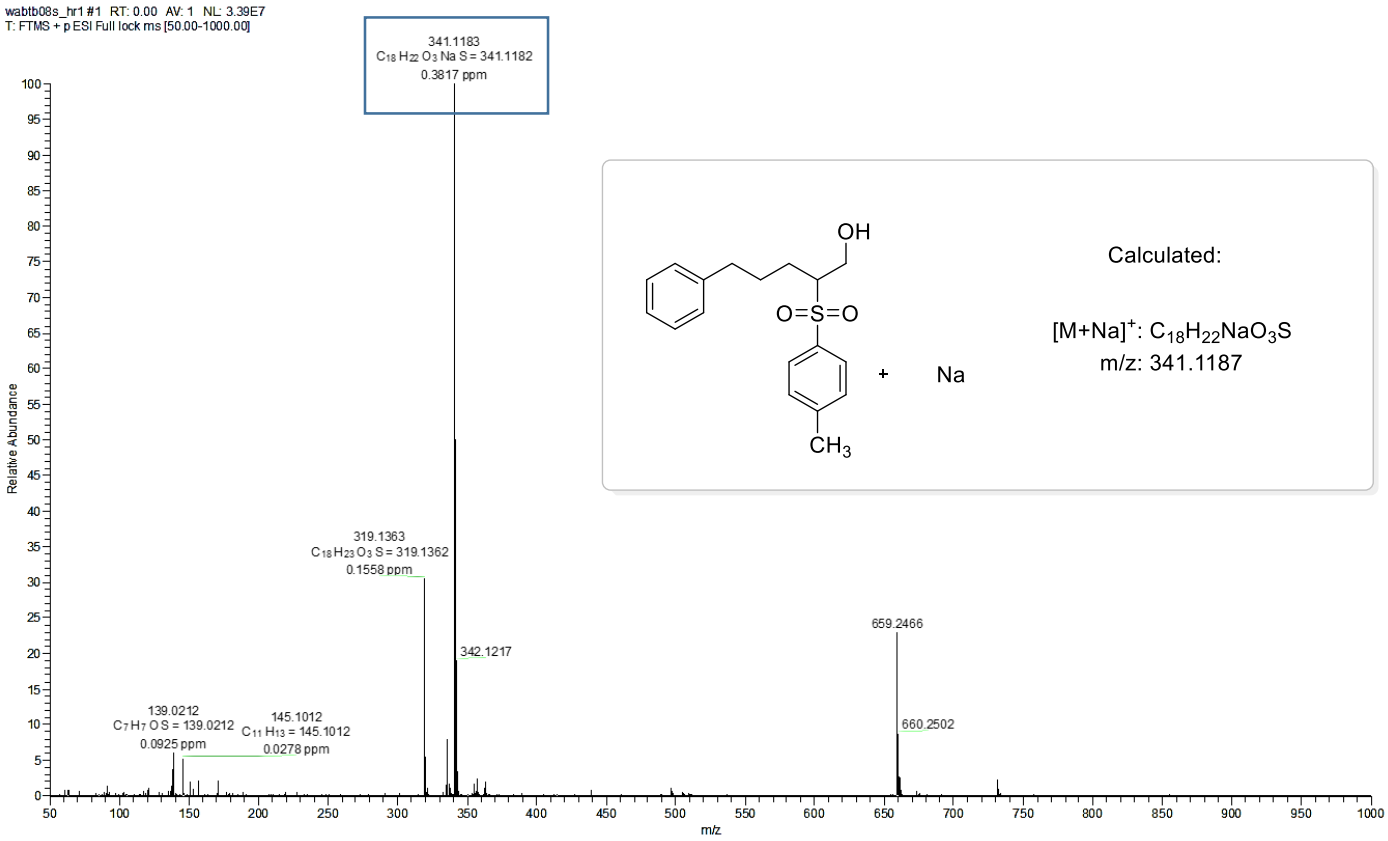




5-phenyl-2-tosylpentan-1-ol (**4af**)

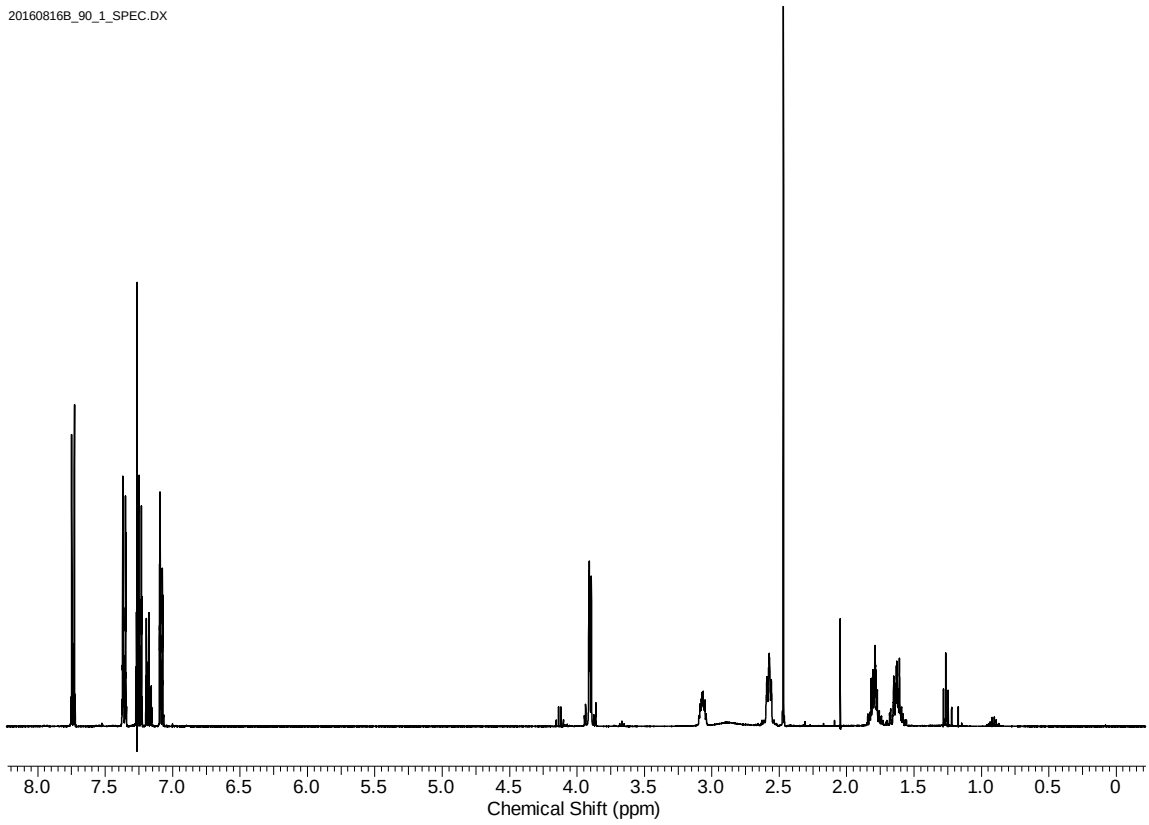


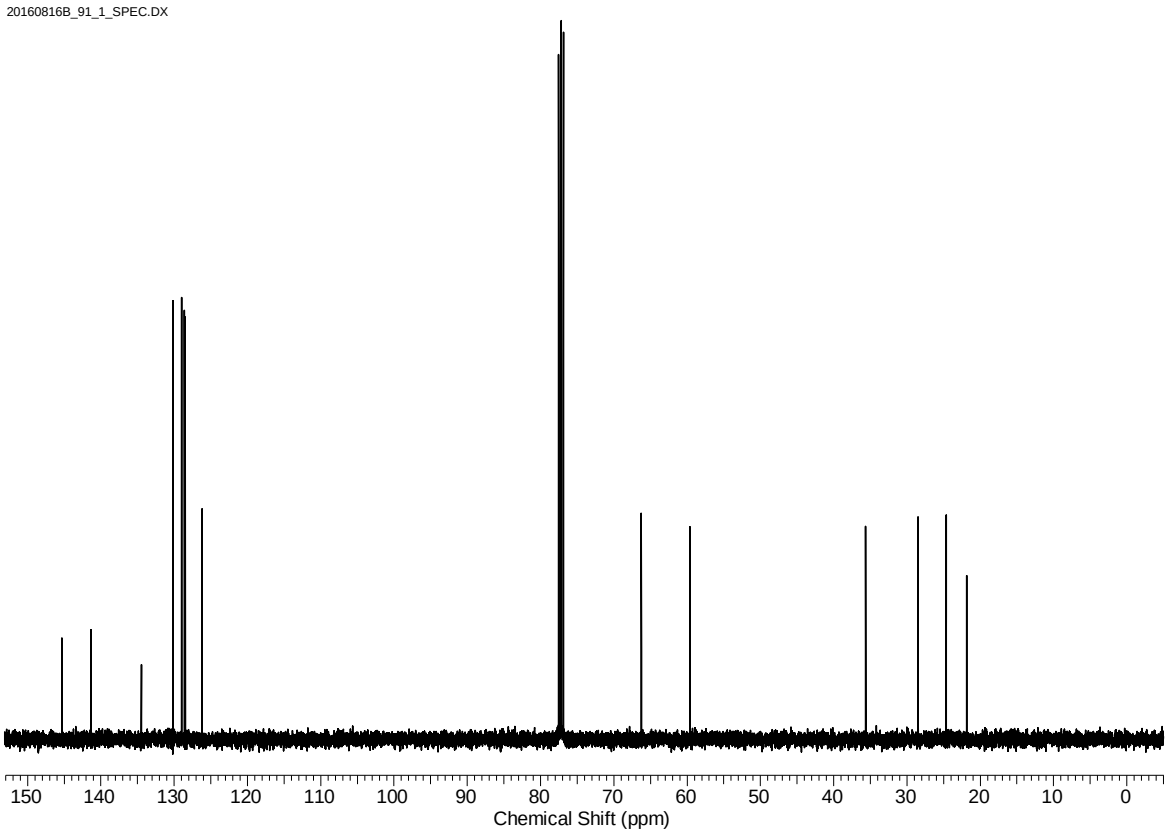
D:\data_2016\wabtb08s_hr1 8/24/2016 11:22:50 AM vk2303



Calculated:

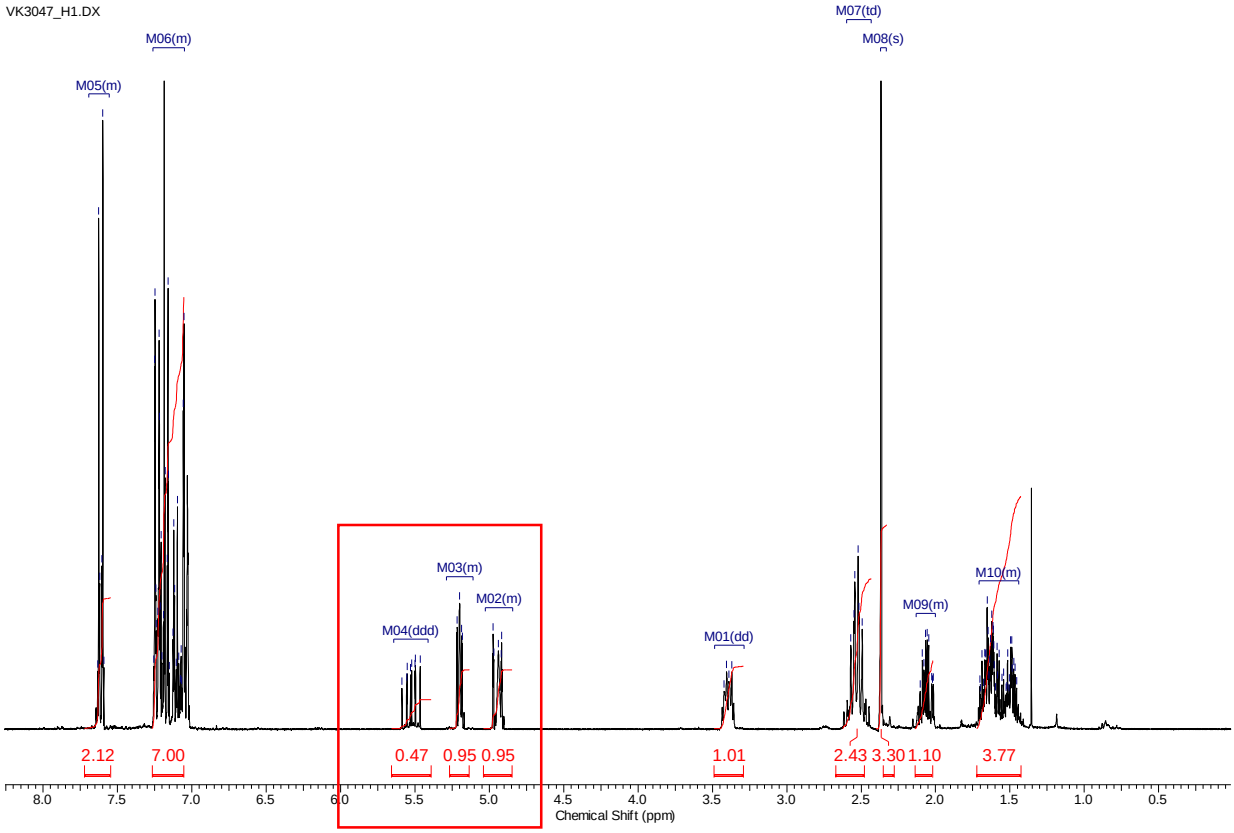
$[M+Na]^+$: $C_{18}H_{22}NaO_3S$
m/z: 341.1187

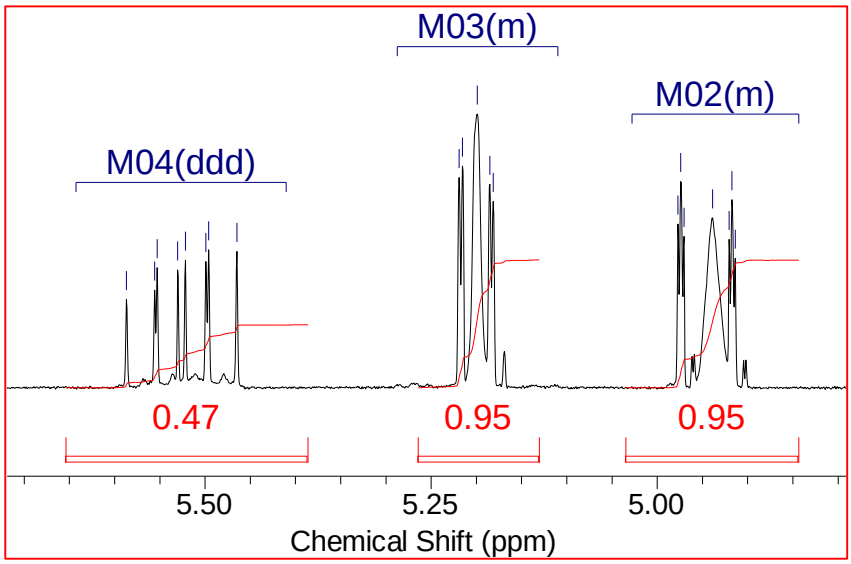

20160816B_90_1_SPEC.DX
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


20160816B_91_1_SPEC.DX
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

S9 (Deuterium-labeling experiment [Set 1])

^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.44 - 1.71 (m, 4 H) 2.00 - 2.13 (m, 1 H) 2.37 (s, 3 H) 2.53 (td, *J*=8.30, 6.51 Hz, 2 H) 3.40 (dd, *J*=9.99, 5.41 Hz, 1 H) 4.84 - 5.03 (m, 1 H) 5.11 - 5.29 (m, 1 H) 5.53 (ddd, *J*=17.06, 10.27, 9.35 Hz, 0 H) 7.05 - 7.26 (m, 7 H) 7.56 - 7.69 (m, 2 H).





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File Title	:	ms3047, pos.ESI
Operator	:	ExactiveUser
Notes	:	Source: D:\data_2015\vhbta14s_hr2.RAW Format: Finnigan

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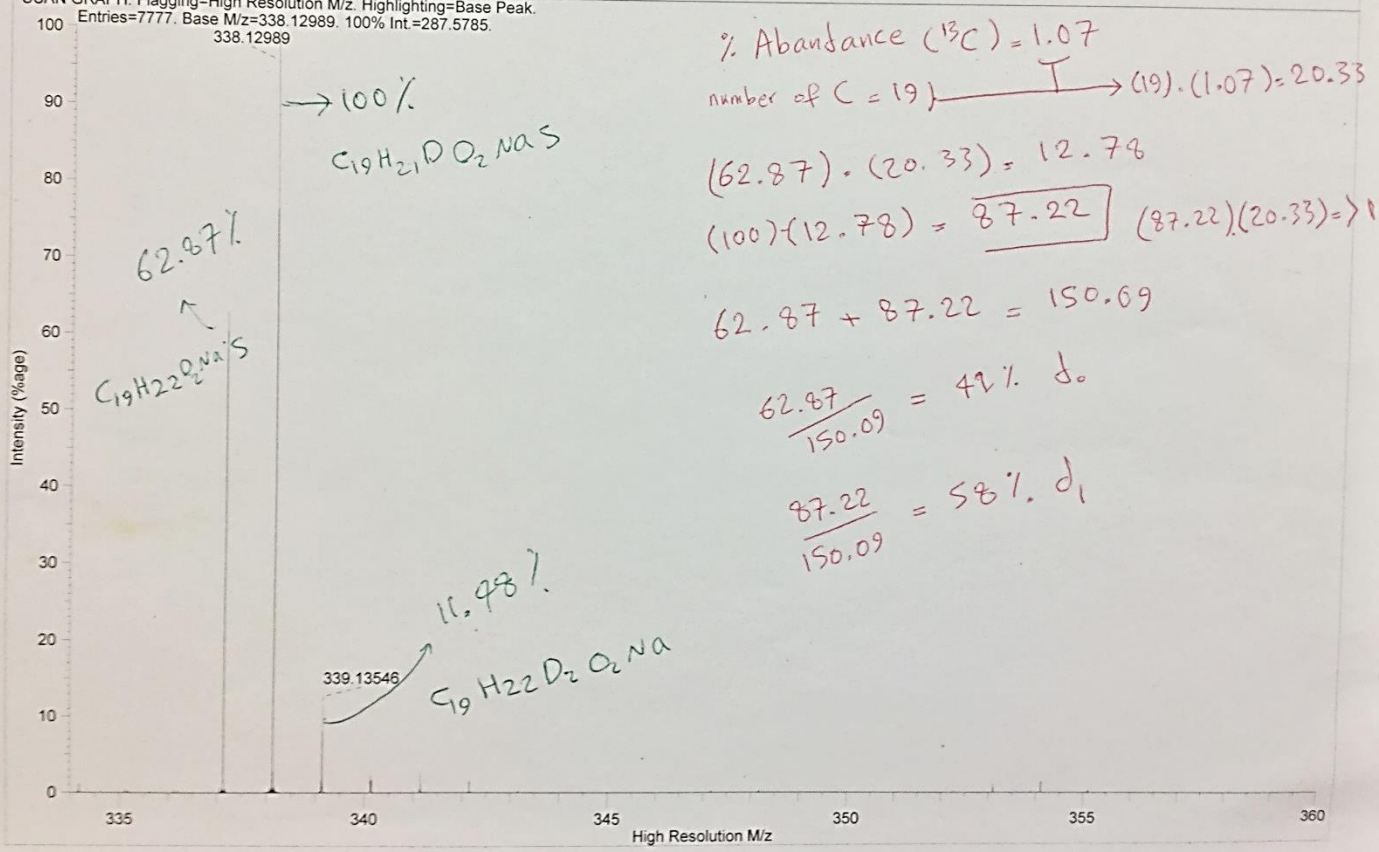
Entries=7777. Base M/z=338.12989. 100% Int.=287.5785.



% Abandance (^{13}C) = 1.07

number of C = 19 → (19).(1.07) = 20.33

(62.87).(20.33) = 12.78

(100) − (12.78) = 87.22 (87.22)(20.33) = >1

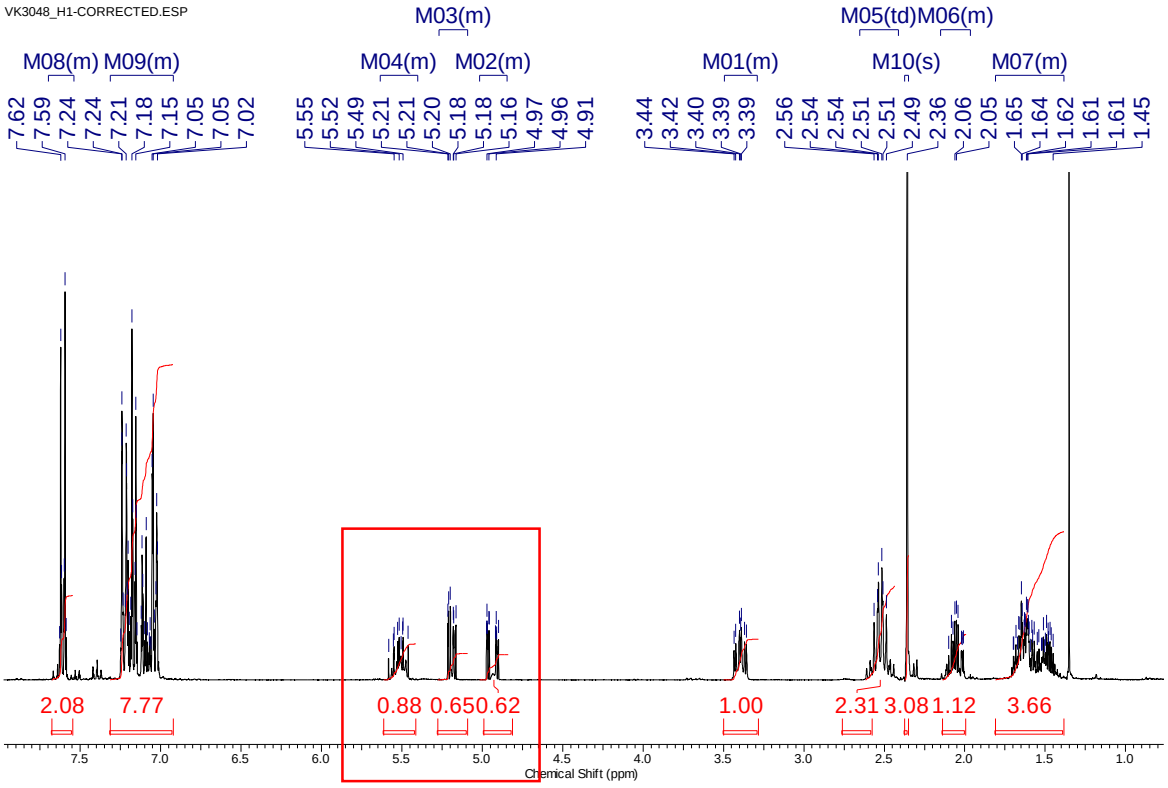
62.87 + 87.22 = 150.09

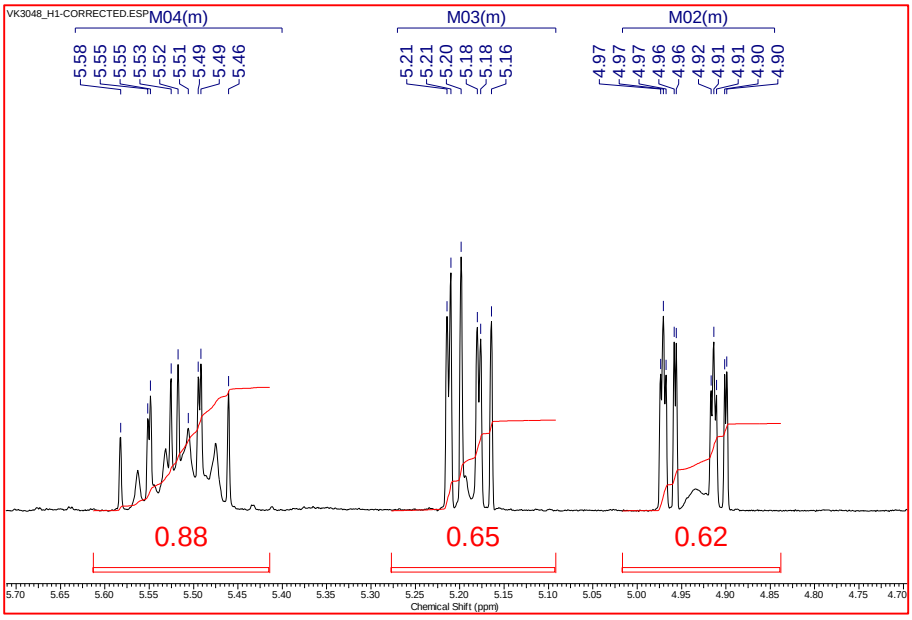
$\frac{62.87}{150.09}$ = 42 % d_0

$\frac{87.22}{150.09}$ = 58 % d_1

Deuterium-labeling experiment (Set 2)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.38 - 1.81 (m, 3 H) 1.97 - 2.15 (m, 1 H) 2.36 (s, 3 H) 2.53 (td, *J*=8.21, 6.51 Hz, 2 H) 3.29 - 3.49 (m, 1 H) 4.85 - 5.02 (m, 1 H) 5.09 - 5.27 (m, 1 H) 5.40 - 5.63 (m, 1 H) 6.92 - 7.31 (m, 6 H) 7.54 - 7.70 (m, 2 H).





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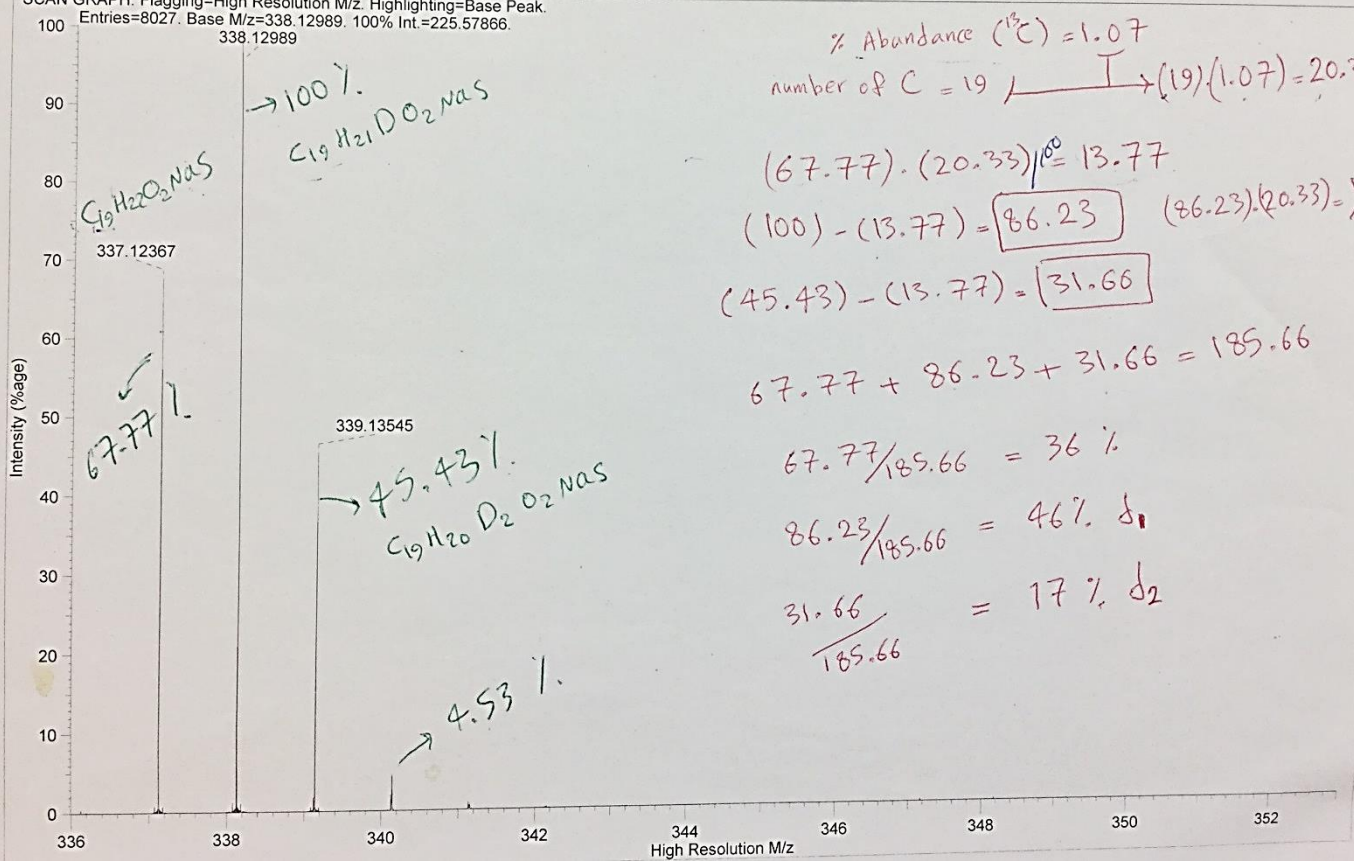
Notes	:	Source: D:\data_2015\vhbta15s_hr2.RAW Format: Finnigan

SCAN GRAPH. Flagging=High Resolution M/z. Highlighting=Base Peak.
Entries=8027. Base M/z=338.12989. 100% Int.=225.57866.



% Abundance (^{13}C) = 1.07

number of C = 19 → (19)(1.07) = 20.33

(67.77)·(20.33)/100 = 13.77

(100) − (13.77) = 86.23 (86.23)·(20.33) = > 17

(45.43) − (13.77) = 31.66

67.77 + 86.23 + 31.66 = 185.66

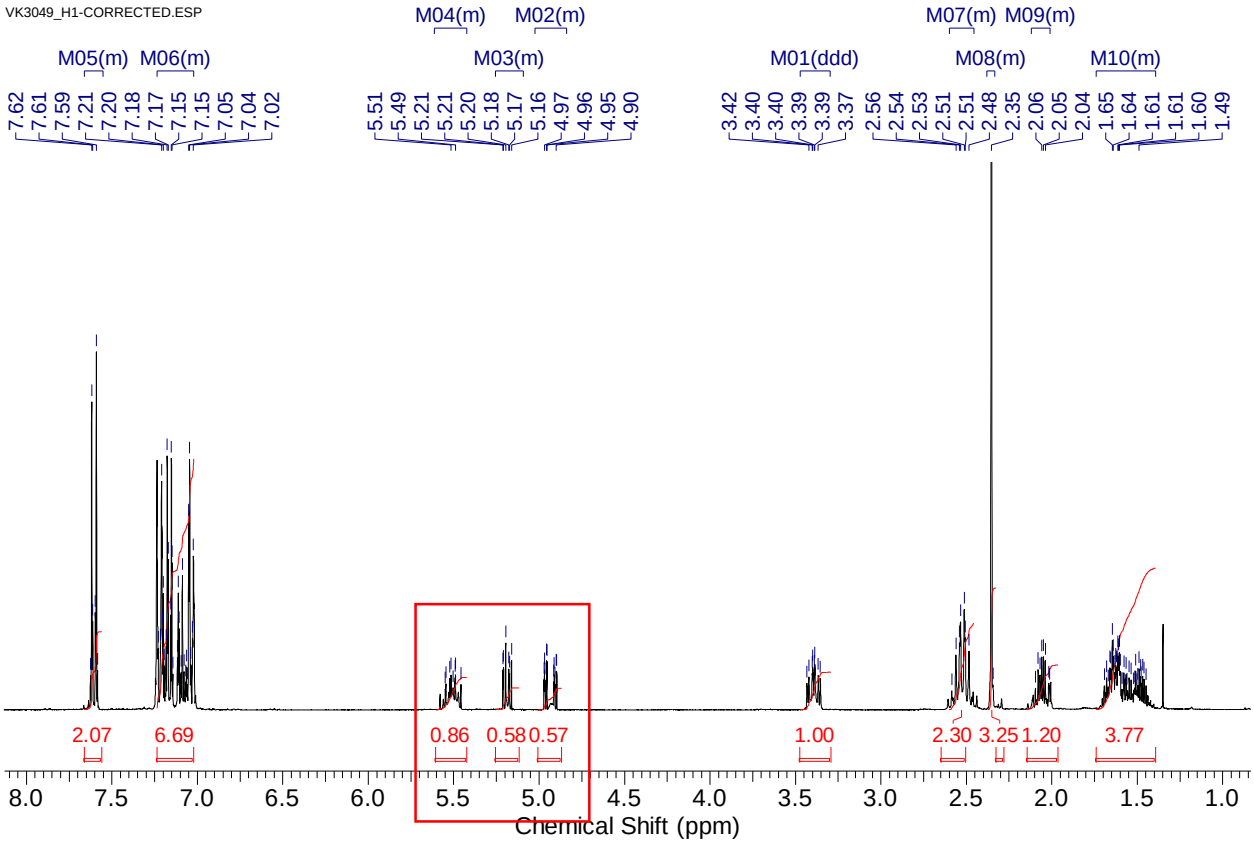
67.77/185.66 = 36 %

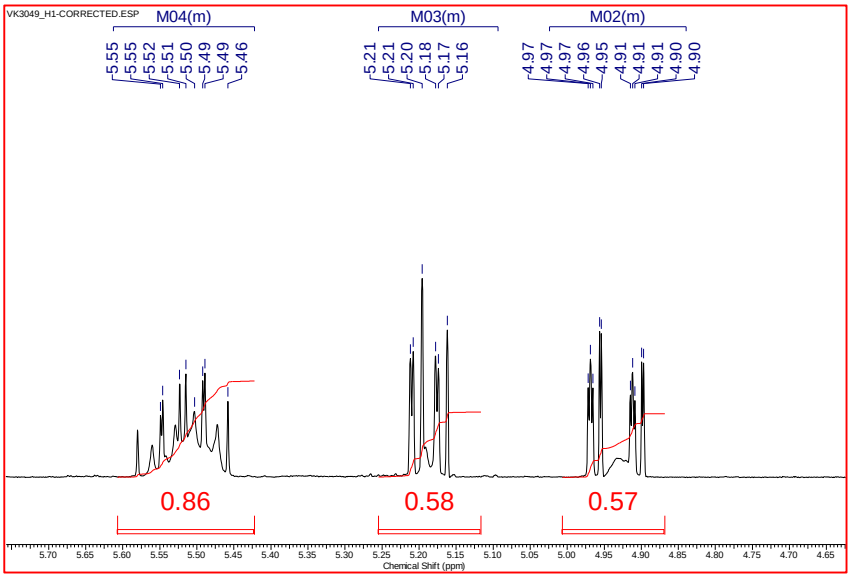
86.23/185.66 = 46 % d_1

31.66/185.66 = 17 % d_2

Deuterium-labeling experiment (Set 3)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.39 - 1.74 (m, 3 H) 2.01 - 2.12 (m, 1 H) 2.33 - 2.38 (m, 3 H) 2.46 - 2.60 (m, 2 H) 3.39 (ddd, *J*=10.45, 9.35, 3.48 Hz, 1 H) 4.84 - 5.02 (m, 1 H) 5.09 - 5.25 (m, 1 H) 5.42 - 5.61 (m, 1 H) 7.02 - 7.23 (m, 7 H) 7.55 - 7.66 (m, 2 H).





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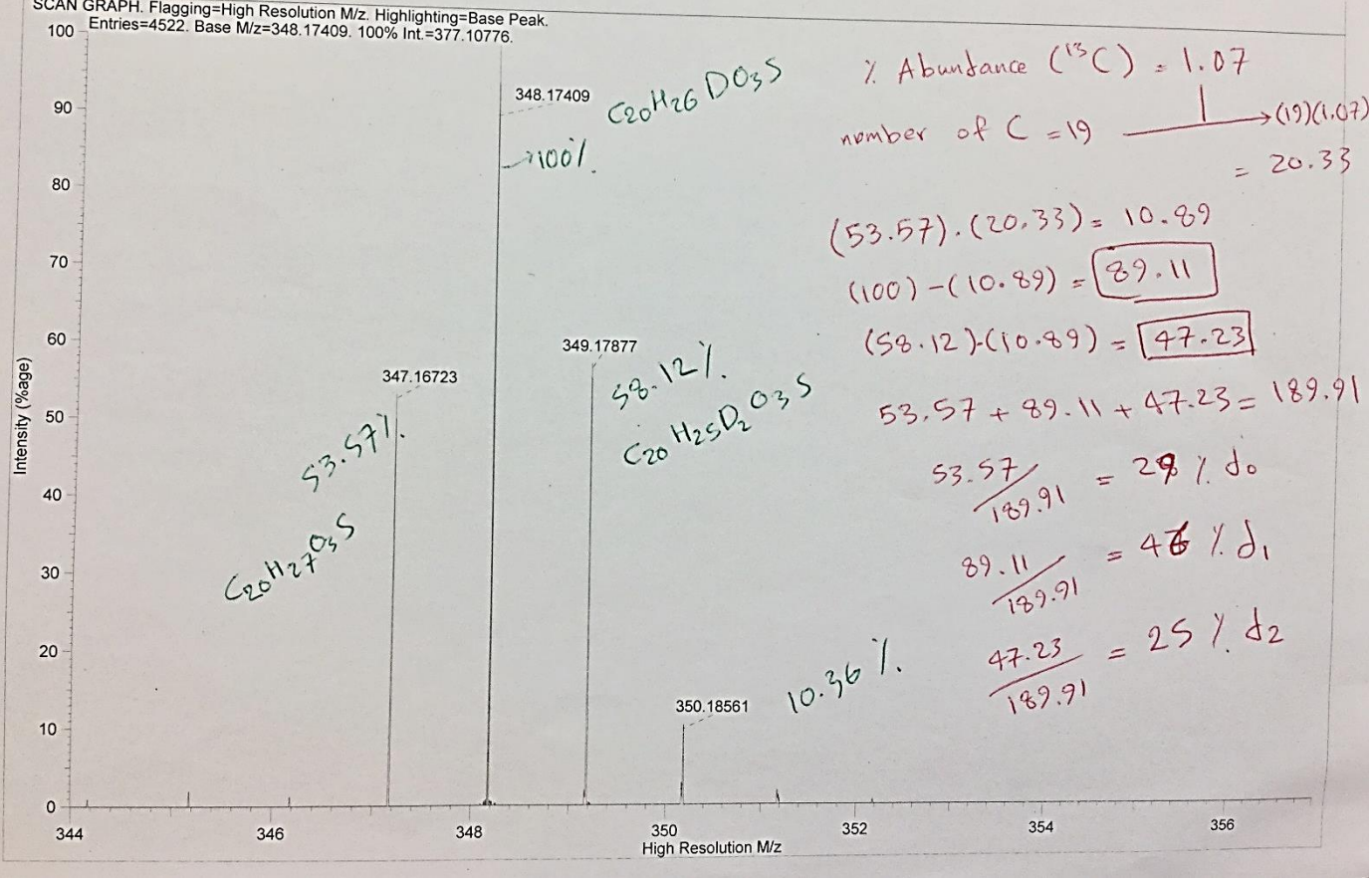
Operator	:	ExactiveUser
Notes	:	Source: D:\data_2015\vhbta16t_hr1.RAW Format: Finnigan



$C_{20}H_{26}DO_3S$

100%

53.57%

$C_{20}H_{27}O_3S$

347.16723

349.17877

58.12%

$C_{20}H_{25}D_2O_3S$

10.36%

350.18561

% Abundance (^{13}C) = 1.07

number of C = 19 → (19)(1.07) = 20.33

(53.57).(20.33) = 10.89

(100) − (10.89) = 89.11

(58.12) − (10.89) = 47.23

53.57 + 89.11 + 47.23 = 189.91

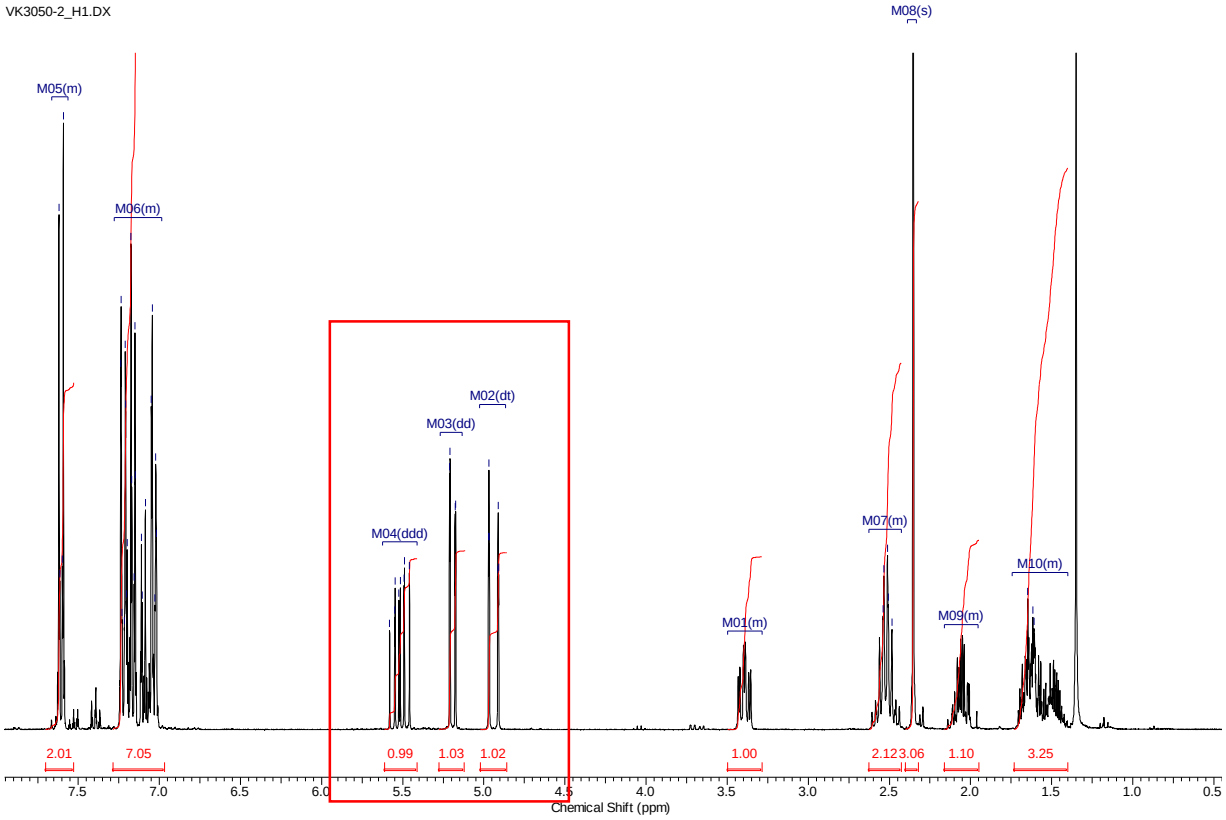
$\frac{53.57}{189.91}$ = 28 % d_0

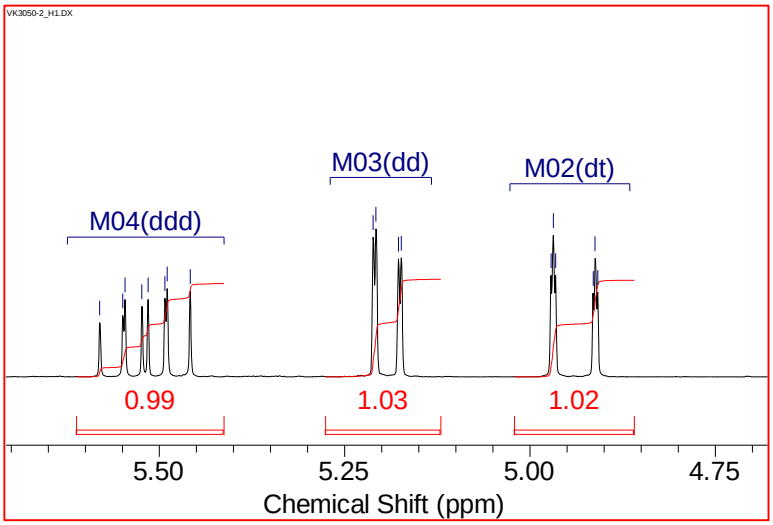
$\frac{89.11}{189.91}$ = 47 % d_1

$\frac{47.23}{189.91}$ = 25 % d_2

Deuterium-labeling experiment (Set 4)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.40 - 1.74 (m, 3 H) 1.95 - 2.16 (m, 1 H) 2.35 (s, 3 H) 2.43 - 2.63 (m, 2 H) 3.29 - 3.50 (m, 1 H) 4.94 (dt, *J*=16.96, 0.96 Hz, 1 H) 5.19 (dd, *J*=10.27, 1.10 Hz, 1 H) 5.52 (ddd, *J*=17.06, 10.27, 9.35 Hz, 1 H) 6.99 - 7.28 (m, 7 H) 7.56 - 7.66 (m, 2 H).





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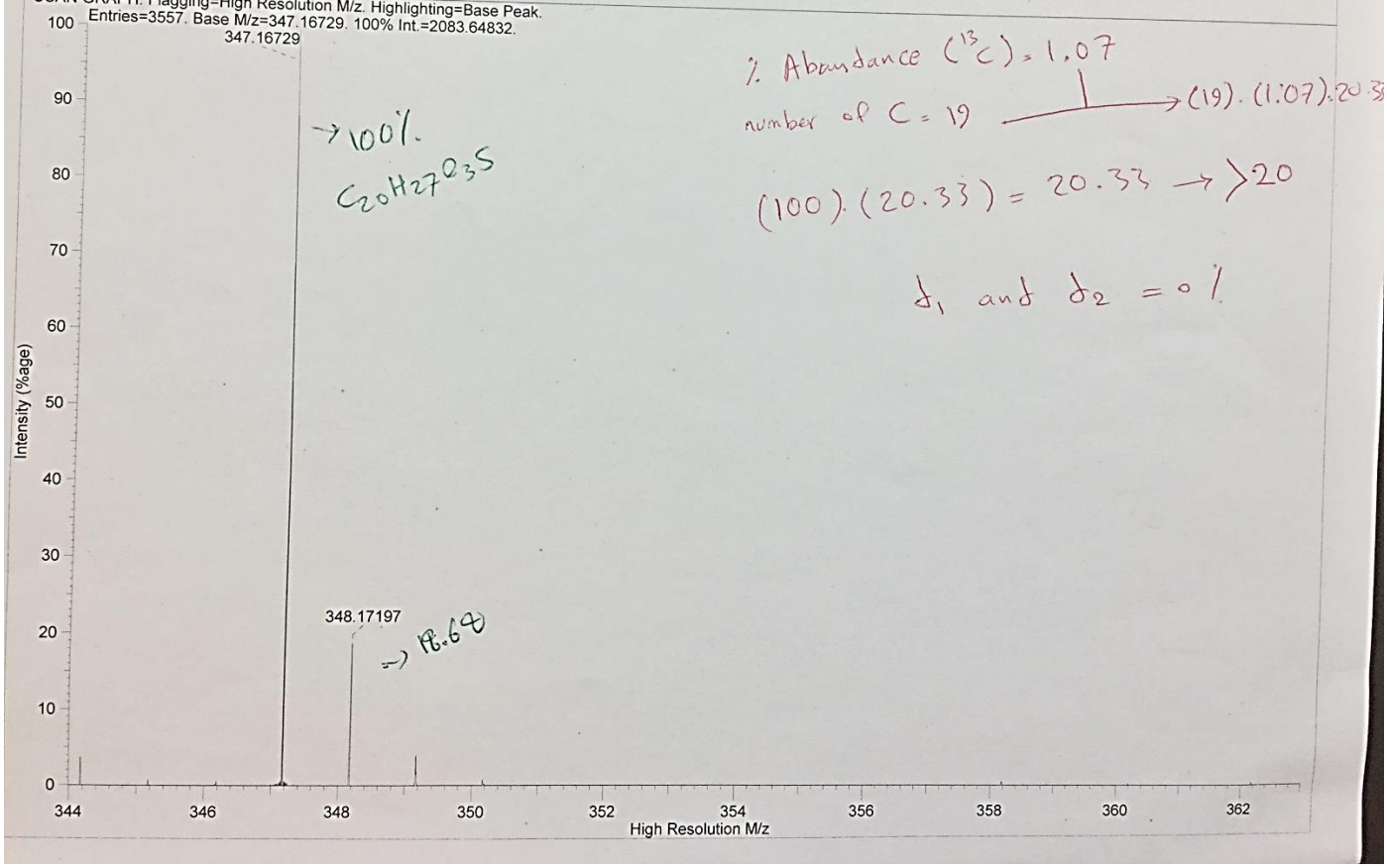

→ 100%.

$C_{20}H_{27}O_3S$

% Abundance (^{13}C) = 1.07

number of C = 19 → (19).(1.07).20.3

(100).(20.33) = 20.33 → >20

δ_1 and δ_2 = 0 !

References

[1] Dion, I.; Vincent-Rocan, J.; Zhang, L.; Cebrowski, P. H.; Lebrun, M.; Pfeiffer, J. Y.; Bédard, A.; Beauchemin, A. M. *J. Org. Chem*. **2013**, 78, 12735-12749.

[2] Schenck, T. G.; Bosnich, B. *J. Am. Chem. Soc*. **1985**, 107, 2058–2066.

[3] Bollans, L.; Bacsa, J.; O'Farrell, D. A.; Waterson, S.; Stachulski, A. V. *Tetrahedron. Lett*. **2010**, 51, 2160-2163.

[4] Xu, K.; Thieme, N.; Breit, B. *Angew. Chem. Int. Ed*. **2014**, 53, 7268-7271.

[5] Synthetic studies on two silicon assisted annulations. By sabin, verity Margaret. From null, No pp., **1994**.