Supporting Information for:

Catalytic Enantioselective Allylic Amination of Unactivated Terminal Olefins via an Ene Reaction/[2,3]-Rearrangement

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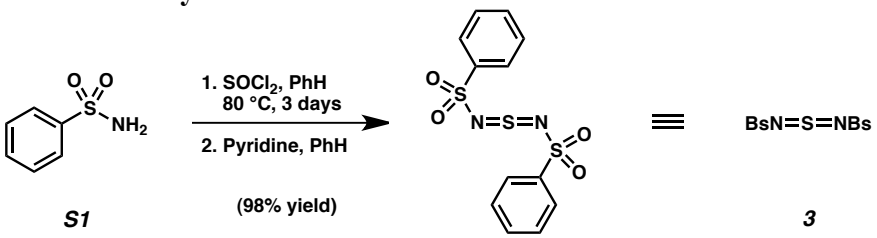
Materials and Methods

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel (particle size 0.032 - 0.063 mm) purchased from SiliCycle was used for flash chromatography. ^{1}H and ^{13}C NMR spectra were recorded on Varian Inova-400 or 500 spectrometers. Data for ^{1}H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to chloroform as an internal standard (77.23 ppm) and are reported in terms of chemical shift (δ ppm). Optical rotations were measured on a JAS DIP-360 digital polarimeter. Infrared spectra were recorded on a Perkin-Elmer 1000 series FTIR. Chiral HPLC analyses were performed on an Agilent 1200 Series system. HRMS data were obtained at The Scripps Center for Mass Spectrometry.

Synthesis of Benzenesulfonyl Sulfurdiimide 3



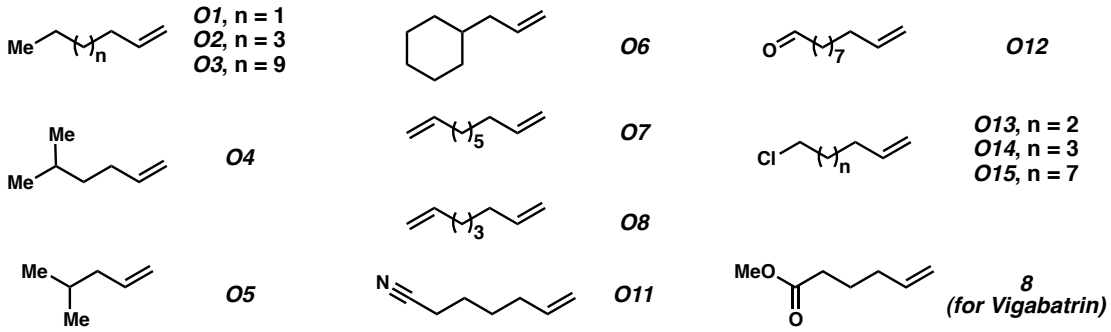
S1 *3*

Our procedure was modified from a method reported in the literature for the synthesis of similar arylsulfonyl sufurdiimides (*1*): A solution of benzenesulfonamide **S1** (50 g, 0.318 mol) and $SOCl_2$ (80 mL, 1.1 mol) in benzene (30 mL) was refluxed at 80 °C for 3 days (over the course of the reaction, the mixture became a clear solution). When the starting material was consumed by ^{1}H NMR analysis of an aliquot, the mixture was concentrated under vacuum to remove benzene and excess $SOCl_2$. Trace amounts of $SOCl_2$ were removed by redissolving the residue in toluene (50 mL), concentrating under reduced pressure, and storing under vacuum at 50 °C for 6 h. The residue was then treated with benzene (70 mL) and heated slightly to ensure all material dissolved in the solvent. Once the solution was cooled to 23 °C, pyridine (0.5 mL) was added, and the mixture was stirred. After 12 h, stirring was ceased, and a yellow precipitate crystallized slowly from the solution. The precipitate was separated be vacuum filtration and stored under vacuum at 50 °C for 8 h. Benzensulfonyl sulfurdiimide **3** was obtained as a yellow solid (53.5 g, 98% yield). *Since benzenesulfonyl sulfurdiimide **3** is sensitive to water, we store it in a dessicator inside a sealed flask that has been purged with N_2. Optimal results for the enantioselective allylic amination were obtained when benzenesulfonyl sulfurdiimide **3** was broken into a fine powder immediately before use.*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 8.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 135.0, 129.6, 128.3. IR (thin film): 3348, 3255, 1557, 1332, 1159 cm^{-1}.

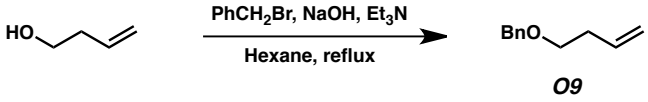
*Although we continue to synthesize benzensulfonyl sulfurdiimide **3** in our lab, Sigma-Aldrich has decided to commercialize this reagent based on conversations with our group about its synthetic utility (Catalog # L511390, $25/gram).*

Synthesis of Terminal Olefins

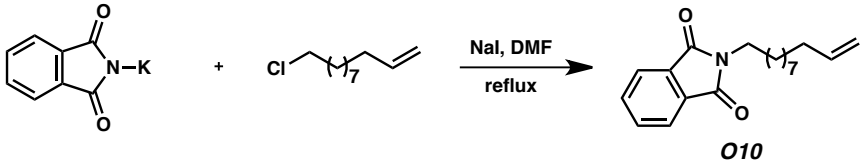
Most terminal olefin substrates were obtained from the following commercial sources: Sigma-Aldrich (for olefins **O1–O3**, **O5–O6**, **O7**, **O8**, **O11, O12**, **O13**, and **O15**, and unsaturated ester **8**), Alfa Aesar (for olefin **O4**), and GFS Chemicals (for olefin **O14**).



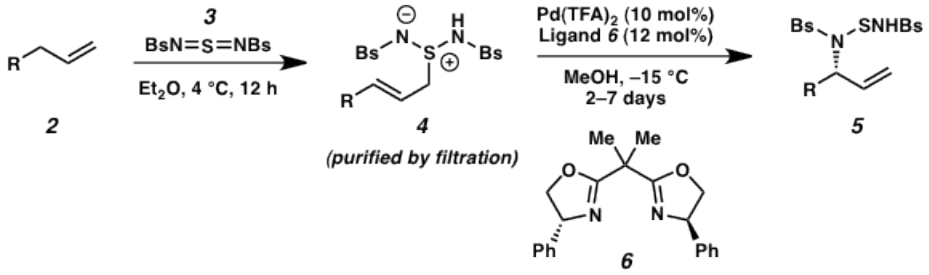
Olefin **O9** was prepared according to a literature procedure (*2*):



Olefin **O10** was prepared according to a literature procedure (*3*):

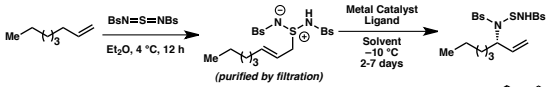


General Procedures for the Catalytic Enantioselective Allylic Amination



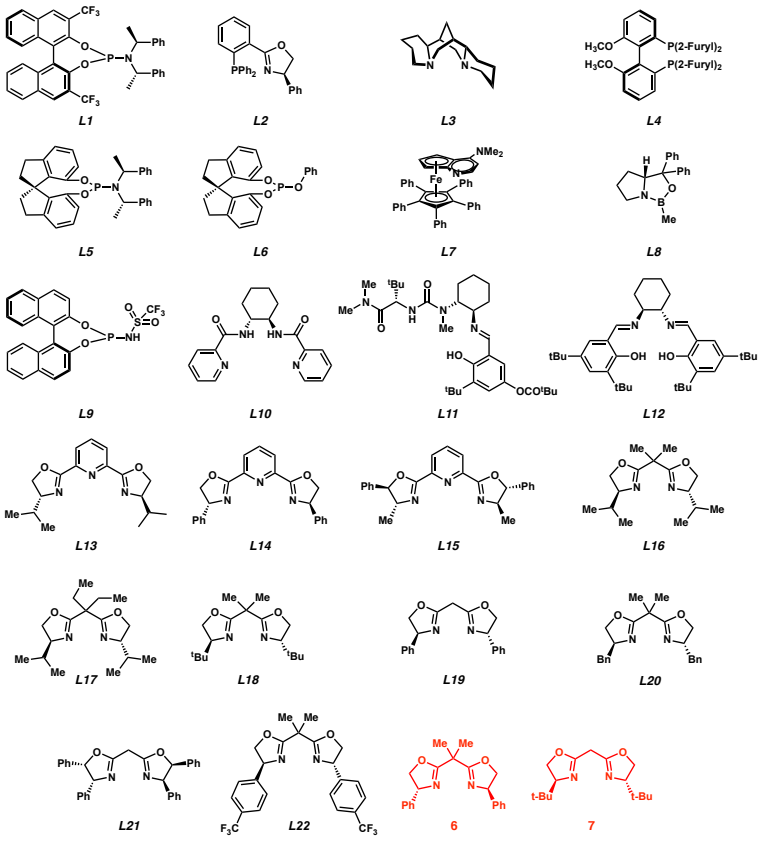
General Procedure for Table 2 (Method A):
A solution of benzenesulfonyl sulfurdiimide **3** (685 mg, 2 mmol) in Et_2O (4 mL, 0.5 M) was cooled to 0 °C and treated with the terminal olefin **2** (6–10 mmol, 3–5 equiv). The reaction was gently stirred at 4 °C for 12 h. The ene adduct **4**, which formed a white precipitate, was purified at room temperature by vacuum filtration, washed with anhydrous Et_2O (20–40 mL), and dried under vacuum. The ene adduct **4** was then suspended in MeOH (5 mL) and cooled to –78 °C. The solution was treated with the palladium-ligand complex in MeOH (10 mL), which was made by premixing $Pd(TFA)_2$ (10 mol%, 66 mg, 0.2 mmol) and ligand **6** (12 mol%, 80 mg, 0.24 mmol) in MeOH (10 mL) and stirring for 20 min at room temperature. The reaction was warmed to –15 °C and stirred for 2-7 days and then concentrated. The residue was purified by flash chromatography.

Table S1. Optimization experiments for the catalytic enantioselective conversion of olefins into chiral allylic amines



Entry	Metal Catalyst (10 mol%)	Ligand (12 mol%)	Solvent (0.13M)	Temp (°C)	Conversion[a]	ee (%)
1	$Pd(OAc)_2$	–	CH_2Cl_2	–10	95	–
2	$Pd(OAc)_2$	L1	DCE	–10	99	3
3	$Pd(TFA)_2$	L1	DCE	–10	99	0
4	$Pd(TFA)_2$	L2	DCE	–10	60	4
5	$Pd(TFA)_2$	*L3*	*DCE*	–10	60	5
6	$Pd(TFA)_2$	*L4*	*DCE*	–10	99	7
7	$Pd(TFA)_2$	*L5*	*DCE*	–10	99	4
8	$Pd(TFA)_2$	*L6*	*DCE*	–10	99	7
9	$Pd(TFA)_2$	*L7*	*DCE*	–10	99	7
10	$Pd(TFA)_2$	*L8*	*DCE*	–10	99	0
11	$Pd(TFA)_2$	*L9*	*DCE*	–10	99	13
12	$Pd(TFA)_2$	*L10*	*DCE*	–10	99	5
13	$Pd(TFA)_2$	*L11*	*DCE*	–10	99	4
14	$Pd(TFA)_2$	*L12*	*DCE*	–10	99	0
15	$Pd(TFA)_2$	*L13*	*DCE*	–10	99	0
16	$Pd(TFA)_2$	*L14*	*DCE*	–10	99	0
17	$Pd(TFA)_2$	*L15*	*DCE*	–10	99	0
18	$Pd(TFA)_2$	*L16*	*DCE*	–10	99	0
19	$Pd(TFA)_2$	*L17*	*DCE*	–10	99	0
20	$Pd(TFA)_2$	*7*	*DCE*	–10	99	17
21	$Pd(TFA)_2$	*L18*	*DCE*	–10	99	8
22	$Pd(TFA)_2$	*L19*	*DCE*	–10	99	13
23	$Pd(TFA)_2$	*L20*	*DCE*	–10	99	0
24	$Pd(TFA)_2$	*L21*	*DCE*	–10	99	15
25	$Pd(TFA)_2$	6	*DCE*	–10	99	31
26	$PdCl_2(MeCN)_2$ $AgBF_4$	6	*DCE*	*–20*	24	22
27	$PdCl_2(MeCN)_2$ $AgSBF_6$	6	*DCE*	*–20*	30	12
28	$Pd(TFA)_2$	6	$PhCF_3$	*–10*	60	59
29	$Pd(TFA)_2$	6	CH_2Cl_2	*–10*	80	29
30	$Pd(TFA)_2$	6	*Dioxane*	*23*	99	9
31	$Pd(TFA)_2$	6	t-BuOMe	*–10*	95	26
32	$Pd(TFA)_2$	6	Et_2O	*–10*	89	22
33	$Pd(TFA)_2$	6	*NMP*	*–10*	75	0
34	$Pd(TFA)_2$	6	*Acetone*	*–10*	63	41
35	$Pd(TFA)_2$	6	DMF	*–10*	59	11
36	$Pd(TFA)_2$	6	*DMAC*	*–10*	90	11
37	$Pd(TFA)_2$	6	MeOH	*–10*	90	93
38	$Pd(TFA)_2$	L22	MeOH	*–10*	82	88
39	$Pd(TFA)_2$	L17	MeOH	*–10*	59	26
40	$Pd(TFA)_2$	L18	MeOH	*–10*	67	53
41	$Pd(TFA)_2$	6	MeOH	*–15*	89[b]	96

[a] Determined by ^{1}HNMR. [b] Isolated yield for 2 steps.



Characterization Data for Ene Adducts 4 and Allylic Amination Products

*Ene adducts **4** undergo facile [2,3]-rearrangement at ambient temperature. Therefore, we assayed the identity and purity of these compounds by rapid NMR spectral analysis. The allylic amination products **5** were then fully characterized after [2,3]-rearrangement (vide infra).*

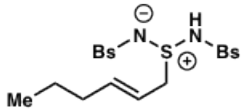


Table 2, entry 1: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.82 (d, J = 7.0 Hz, 4H), 7.59 (t, J = 7.5 Hz, 2H), 7.48 (dd, J = 7.5 Hz, J = 7.0 Hz, 4H), 5.89 (dt, J = 15.0 Hz, J = 6.5 Hz, 1H), 5.23 (dt, J = 15.0 Hz, J = 7.5 Hz, 1H), 4.07 (d, J = 7.5 Hz, 2H), 1.91 (m, 2H), 1.31 (m, 2H), 0.86 (t, J = 7.5 Hz, 3H).

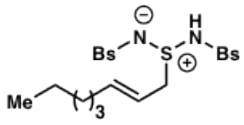


Table 2, entry 2: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.79 (d, *J* = 8.0 Hz, 4H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.45 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 4H), 5.92 (dt, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 5.29 (dt, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 4.13 (d, *J* = 7.0 Hz, 2H), 1.96 (d, *J* = 7.0 Hz, 2H), 1.31-1.23 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 145.11, 141.25, 133.09, 129.29, 129.20, 129.17, 127.96, 127.25, 127.10, 115.03, 57.57, 32.73, 31.46, 31.39, 28.19, 22.58, 14.18.

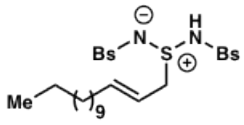


Table 2, entry 3: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.79 (d, *J* = 8.0 Hz, 4H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.45 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 4H), 5.90 (dt, *J* = 15.0 Hz, *J* = 7.0 Hz, 1H), 5.24 (dt, *J* = 15.0 Hz, *J* = 7.5 Hz, 1H), 4.09 (d, *J* = 7.5 Hz, 2H), 1.94 (m, 2H), 1.26 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H).

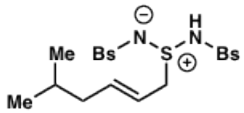


Table 2, entry 4: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.81 (d, *J* = 7.5 Hz, 4H), 7.55 (t, *J* = 7.0 Hz, 2H), 7.45 (dd, *J* = 7.5 Hz, *J* = 7.0 Hz, 4H), 5.88 (dt, *J* = 15.5 Hz, *J* = 7.0 Hz, 1H), 5.22 (dt, *J* = 16.5 Hz, *J* = 7.0 Hz, 1H), 4.07 (d, *J* = 7.0 Hz, 2H), 1.82 (dd, *J* = 7.0 Hz, *J* = 6.5 Hz, 2H), 1.57 (m, 1H), 0.85 (d, *J* = 6.5 Hz, 6H).

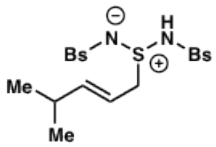


Table 2, entry 5: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O_2) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.84 (d, *J* = 8.0 Hz, 4H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.45 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 4H), 5.87 (dt, *J* = 16.0 Hz, *J* = 6.5 Hz, 1H), 5.14 (dt, *J* = 16.0 Hz, *J* = 7.5 Hz, 1H), 4.02 (d, *J* = 7.5 Hz, 2H), 2.16 (m, 1H), 0.89 (d, *J* = 6.5 Hz, 6H).

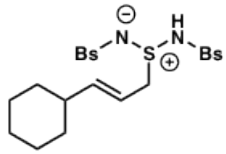


Table 2, entry 6: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.84 (d, *J* = 8.0 Hz, 4H), 7.55 (t, *J* = 7.0 Hz, 2H), 7.45 (dd, *J* = 8.0 Hz, *J* = 7.0 Hz, 4H), 5.80 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 5.14 (dt, *J* = 16.0 Hz, *J* = 7.5 Hz, 1H), 4.01 (d, *J* = 7.0 Hz, 2H), 1.81 (m, 1H), 1.70-1.54 (m, 5H), 1.22-1.09 (m, 3H), 0.97-0.92 (m, 2H).

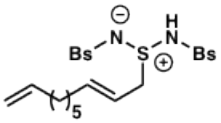


Table 2, entry 7: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.81 (d, *J* = 7.5 Hz, 4H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.45 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 4H), 5.89 (dt, *J* = 15.0 Hz, *J* = 8.0 Hz, 1H), 5.80 (m, 1H), 5.22 (dt, *J* = 15.0 Hz, *J* = 7.0 Hz, 1H), 5.01 (d, *J* = 17.0 Hz, 1H), 4.94 (d, *J* = 10.0 Hz, 1H), 4.06 (t, *J* = 7.0 Hz, 2H), 2.05-2.01 (m, 2H), 1.93 (m, 2H), 1.39-1.22 (m, 6H).

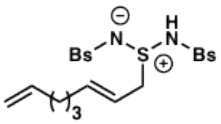


Table 2, entry 8: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O_2) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.81 (d, *J* = 8.0 Hz, 4H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.45 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 4H), 5.90 (dt, *J* = 15.0 Hz, *J* = 7.0 Hz, 1H), 5.76 (m, 1H), 5.25 (dt, *J* = 15.0 Hz, *J* = 7.0 Hz, 1H), 5.01 (d, *J* = 18.5 Hz, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 4.08 (d, *J* = 7.0 Hz, 2H), 2.03-1.94 (m, 4H), 1.38 (tt, *J* = 15.0 Hz, *J* = 7.0 Hz, 2H).

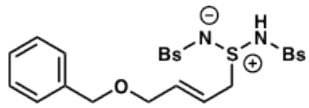


Table 2, entry 9: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.79 (d, *J* = 8.0 Hz, 4H), 7.55 (t, *J* = 7.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, *J* = 7.0 Hz, 4H), 7.36-7.30 (m, 5H), 6.04-6.01(m, 1H), 5.62 (m, 1H), 4.50 (s, 2H), 4.15 (d, *J* = 7.5Hz, 2H), 3.92 (d, *J* = 3.5 Hz, 2H).

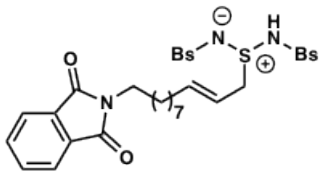


Table 2, entry 10: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.83 (dd, *J* = 7.0 Hz, *J* = 4.0 Hz, 2H), 7.78 (d, *J* = 10.0 Hz, 4H), 7.69 (dd, *J* = 7.0 Hz, *J* = 4.0 Hz, 2H), 7.56 (m, 2H), 7.41 (d, *J* = 10.0 Hz, 4H), 5.89 (dt, *J* = 18.0 Hz, *J* = 8.5 Hz, 1H), 5.26 (m, 1H), 4.10 (d, *J* = 9.0 Hz, 2H), 3.66 (t, *J* = 9.0 Hz, 2H), 1.94 (m, 2H), 1.67 (m, 2H), 1.31-1.18 (m, 10H).

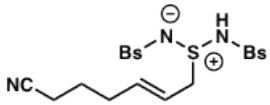


Table 2, entry 11: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.93 (d, *J* = 8.0 Hz, 4H), 7.59 (m, 2H), 7.45 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 4H), 5.90 (dt, *J* = 14.5 Hz, *J* = 7.5 Hz, 1H), 5.39 (dt, *J* = 14.5 Hz, *J* = 7.5 Hz, 1H), 4.10 (d, *J* = 7.5 Hz, 2H), 2.33 (t, *J* = 7.0 Hz, 2H), 2.14 (m, 2H), 1.68 (tt, *J* = 7.5 Hz, *J* = 7.0 Hz).

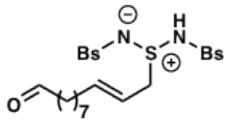


Table 2, entry 12: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 9.76 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 4H), 7.55 (t, *J* = 6.5 Hz, 2H), 7.45 (dd, *J* = 8.5 Hz, *J* = 6.5 Hz, 4H), 5.86 (dt, *J* = 15.0 Hz, *J* = 7.0 Hz, 1H), 5.15 (dt, *J* = 15.0 Hz, *J* = 7.0 Hz, 1H), 3.98 (d, *J* = 7.0 Hz, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 1.87 (m, 2H), 1.61 (m, 2H), 1.28-1.20 (m, 8H).

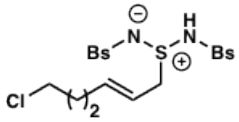


Table 2, entry 13: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.83 (d, *J* = 7.0 Hz, 4H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.46 (dd, *J* = 7.5 Hz, *J* = 7.0 Hz, 4H), 5.89 (dt, *J* = 15.0 Hz, *J* = 6.0 Hz, 1H), 5.26 (dt, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 4.02 (d, *J* = 6.5 Hz, 2H), 3.49 (t, *J* = 6.5 Hz, 2H), 2.09 (m, 2H), 1.75 (m, 2H).

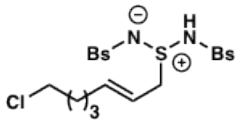


Table 2, entry 14: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.80 (d, *J* = 7.0 Hz, 4H), 7.56 (t, *J* = 7.0 Hz, 2H), 7.46 (t, *J* = 7.0 Hz, 4H), 5.89 (dt, *J* = 15.0 Hz, *J* = 6.0 Hz, 1H), 5.26 (dt, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 4.08 (d, *J* = 6.5 Hz, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 1.99 (m, 2H), 1.73 (m, 2H), 1.46 (m, 2H).

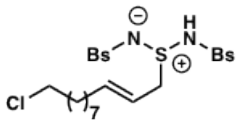


Table 2, entry 15: Following the general procedure for ene adduct formation (in Et_2O at 4 °C for 12 h), purification by vacuum filtration (washing with Et_2O) afforded the product as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.84 (d, *J* = 7.5 Hz, 4H), 7.56 (t, *J* = 7.0 Hz, 2H), 7.45 (dd, *J* = 7.5 Hz, *J* = 7.0 Hz, 4H), 5.87 (dt, *J* = 15.0 Hz, *J* = 7.0 Hz, 1H), 5.17 (dt, *J* = 15.0 Hz, *J* = 7.0 Hz, 1H), 4.01 (d, *J* = 7.0 Hz, 2H), 3.53 (t, *J* = 7.0 Hz, 2H), 1.89 (m, 2H), 1.79-1.73 (m, 2H), 1.43-1.39 (m, 2H), 1.27-1.20 (m, 8H).

Characterization Data for Allylic Amination Products 5

At ambient temperature, most of the allylic amination products ***5*** *yielded ^{1}H NMR spectra with a mixture of rotamers. Therefore, we performed the majority of these ^{1}H NMR experiments at 50 °C to simplify the analysis of the spectra.*

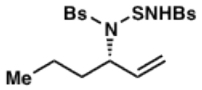
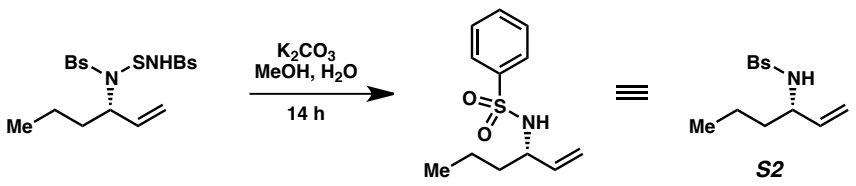


Table 2, entry 1: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –15 °C for 2 d), purification by flash chromatography (20:1 hexanes:ethyl acetate to 5:1 hexanes:ethyl acetate) afforded the product (755 mg, 89 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 97% after conversion to sulfonamide **S2** (see experimental procedure for **S2** and HPLC trace below). $[\alpha]^{23}_D$ = +11.3° (c = 2.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C), δ 7.88 (d, *J* = 7.5 Hz, 4H), 7.59 (t, *J* = 6.0 Hz, 2H), 7.48 (m, 4H), 6.77 (s, 1H), 5.85 (br, 1H), 5.02 (d, *J* = 9.5 Hz, 2H), 4.40 (dt, *J* = 7.5 Hz, *J* = 7.0 Hz, 1H), 1.81-1.67 (m, 2H), 1.14 (m, 2H), 0.85 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 140.2, 139.2, 136.9, 133.2, 129.0, 128.9, 127.7, 127.0, 117.8, 65.9, 34.9, 19.2, 13.5. IR (thin film): 3238, 3068, 2960, 1640, 1448, 1352, 1168, 1088 cm^{-1}. HRMS (ESI) calcd for $[C_{18}H_{22}N_2O_4S_3Na]^+$ ([M+Na]$^+$): 449.0634, found 449.0631.



S2

S2: A solution of the allylic amination product from Table 2, entry 1 (90 mg, 0.2 mmol) in MeOH (1 mL) and H_2O (1.5 mL) was treated with K_2CO_3 (1 mmol, 5 equiv). After stirring for

14 h at 23 °C, the reaction mixture was poured into a mixture of H_2O (10 mL) and ethyl acetate (30 mL). The organic layer was separated, and the aqueous layer was extracted ethyl acetate (2 x 30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by preparative TLC yielded **S2** as a clear oil: $[\alpha]^{23}_D$ = +11.6° (c = 0.53, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.47 (dd, *J* = 7.6 Hz, *J* = 6.8 Hz, 2H), 5.51 (m, 1H), 4.97-4.87 (m, 3H), 3.76 (m, 1H), 1.43 (dt, *J* = 7.6 Hz, *J* = 7.2 Hz, 2H), 1.33-1.18 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 141.0, 137.7, 132.4, 128.8, 127.1, 115.7, 56.1, 37.6, 18.4, 13.6. IR (thin film): 3279, 3068, 2960, 1644, 1447, 1325, 1162 cm^{-1}. HRMS (ESI) calcd for $[C_{12}H_{18}NO_2S]^+$ ($[M+H]^+$): 240.1053, found 240.1061.

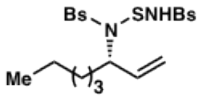


Table 2, entry 2: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –15 °C for 2 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (810 mg, 89 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 96% by comparison to a sample of the racemate (see HPLC trace below). $[\alpha]^{23}_D$ = +28.9° (c = 2.4, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C), δ 7.89 (m, 4H), 7.57 (m, 2H), 7.48 (m, 4H), 7.03 (s, 1H), 5.97 (br, 1H), 5.03 (d, *J* = 10.0 Hz, 2H), 4.37 (m, 1H), 1.83-1.72 (m, 2H), 1.20-1.08 (m, 6H), 0.83 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 140.3, 139.3,133.3, 133.2, 129.1, 128.9, 127.7, 127.0, 117.8, 66.2, 32.8, 31.2, 25.7, 22.4, 13.9. IR (thin film): 3237, 2931, 1654, 1447, 1167, 1088, 811 cm^{-1}. HRMS (ESI) calcd for $[C20H26N2O4S3Na]^+$ ($[M+Na]^+$): 477.0947, found 477.0953.

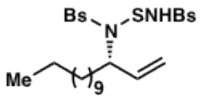


Table 2, entry 3: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –15 °C for 2 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (960 mg, 88 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 98% by comparison to a sample of the racemate (see HPLC trace below). $[\alpha]^{23}_D$ = +26.9° (c = 2.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C), δ 7.89–7.88 (m, 4H), 7.60-7.56(m, 2H), 7.53-7.47 (m, 4H), 6.85 (s, 1H), 5.88 (br, 1H), 5.03 (d, *J* = 10.0 Hz, 2H), 4.37 (dt, *J* = 8.0 Hz, *J* = 7.5 Hz, 1H), 1.84-1.72 (m, 2H), 1.31-1.27 (m, 18H), 0.89 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 140.3, 139.3, 133.3, 133.2, 129.0, 128.9, 127.4, 127.0, 117.8, 66.3, 32.8(br), 31.8, 29.6, 29.5, 29.4, 29.3, 29.0, 26.0. IR (thin film): 3234, 2924, 1447, 1351, 1167, 1088 cm^{-1}. HRMS (ESI) calcd for $[C_{26}H_{38}N_2O_4S_3Na]^+$ ($[M+Na]^+$): 561.1886, found 561.1876.

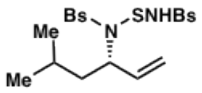


Table 2, entry 4: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –15 °C for 2 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (857 mg, 93 % yield for two steps) as a clear oil.

The enantiomeric excess of the product was determined to be 98% by comparison to a sample of the racemate (see HPLC trace below). $[\alpha]^{23}_{D}$ = +30.0° (c = 2.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 ^{o}C), δ 7.88–7.86 (m, 4H), 7.55 (t, J = 7.5 Hz, 2H), 7.48-7.44 (m, 4H), 7.39 (s, 1H), 5.88 (br, 1H), 4.99 (d, *J* = 10.0 Hz, 2H), 4.46 (dt, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 1.67-1.64 (m, 2H), 0.80 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 50 ^{o}C), δ 140.6, 139.7, 136.8, 133.3, 133.2, 129.1, 128.9, 127.9, 127.1, 117.8, 64.9, 42.2, 24.5, 22.5, 22.0 IR (thin film): 3236, 3068, 2957, 1641, 1448, 1352, 1167, 1088 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{24}N_2O_4S_3Na]^+$ ([M+Na]$^+$): 463.0796, found 463.0778.

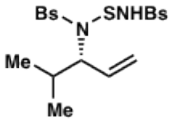


Table 2, entry 5: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –5 °C for 7 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (667 mg, 79 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 91% by comparison to a sample of the racemate (see HPLC trace below). $[\alpha]^{23}_{D}$ = +54.3° (c = 2.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 ^{o}C), δ 7.87 (d, *J* = 7.5 Hz, 4H), 7.56 (m, 2H), 7.46 (m, 4H), 7.09 (s, 1H), 5.95 (br, 1H), 5.02 (d, *J* = 10.0 Hz, 2H), 4.00 (t, *J* = 9.5 Hz, 1H), 2.28 (m, 1H), 0.86 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 50 ^{o}C), δ 140.6, 139.6, 135.9, 133.2, 133.1, 129.1, 128.9, 127.9, 127.0, 118.8, 73.5, 29.7, 20.1, 19.7. IR (thin film): 3236, 3068, 2964, 1637, 1448, 1338, 1166, 1088 cm^{-1}. HRMS (ESI) calcd for $[C_{18}H_{22}N_2O_4S_3Na]^+$ ([M+Na]$^+$): 449.0634, found 449.0630.

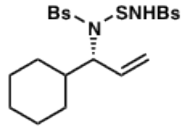


Table 2, entry 6: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –5 °C for 7 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (801 mg, 87 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 94% by comparison to a sample of the racemate (see HPLC trace below). $[\alpha]^{23}_{D}$ = +24.8° (c = 2.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 ^{o}C), δ 7.87 (d, *J* = 7.5 Hz, 4H), 7.60-7.55 (m, 2H), 7.52-7.46 (m, 4H), 6.79 (s, 1H), 5.95 (br, 1H), 5.02 (d, *J* = 9.5 Hz, 2H), 4.11 (t, *J* = 9.5 Hz, 1H), 2.03-1.99 (m, 1H), 1.72-1.56 (m, 5H), 1.27-1.10 (m, 4H), 0.86-0.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 50 ^{o}C), δ 140.7, 139.7, 135.8, 133.3, 129.1, 128.8, 127.9, 127.0, 118.9, 72.4(br), 38.5, 30.2, 30.1, 26.2, 2 5.8, 25.6. IR (thin film): 3236, 3068, 2929, 1639, 1448, 1354, 1168, 1088 cm^{-1}. HRMS (ESI) calcd for $[C_{21}H_{26}N_2O_4S_3Na]^+$ ([M+Na]$^+$): 489.0947, found 489.0949.

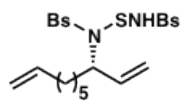


Table 2, entry 7: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –10 °C for 3 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (930 mg, 97 % yield for two steps) as a clear oil.

The enantiomeric excess of the product was determined to be 96% by comparison to a sample of the racemate (see HPLC trace below). $[\alpha]^{23}_D$ = +23.6° (c = 2.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C), δ 7.88 (d, *J* = 8.0 Hz, 4H), 7.60 (m, 2H), 7.48 (m, 4H), 6.86 (s, 1H), 5.85-5.76 (m, 2H), 5.04-4.92 (m, 4H), 4.38 (dt, *J* = 8.0 Hz, *J* = 7.5 Hz, 1H), 2.00 (m, 2H), 1.83-1.74 (m, 2H), 1.31-1.24 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 140.3, 139.3, 138.9, 133.3, 133.2, 129.1, 128.9, 127.7, 127.0, 117.8, 114.2, 66.2, 33.5, 32.8, 28. 6, 28.5, 25.8. IR (thin film): 3234, 2928, 1639, 1447, 1351, 1166, 1088 cm^{-1}. HRMS (ESI) calcd for $[C_{22}H_{29}N_2O_4S_3]^+$ ($[M+H]^+$): 481.1284, found 481.1302.

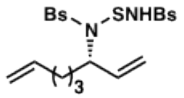
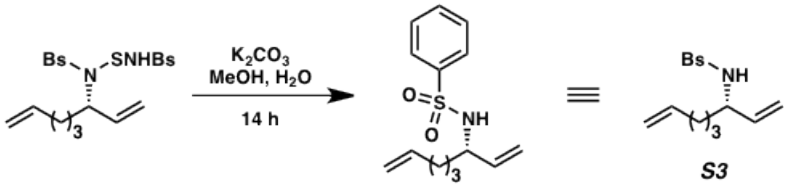


Table 2, entry 8: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –10 °C for 3 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (735 mg, 82 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 96% after conversion to sulfonamide **S3** under the previously described conditions for the synthesis of sulfonamide **S2** (see HPLC trace for **S3** below). $[\alpha]^{23}_D$ = +12.2° (c = 3.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C), δ 7.88 (m, 4H), 7.56 (m, 2H), 7.47 (m, 4H), 7.13 (s, 1H), 5.87 (br, 1H), 5.72 (m, 1H), 5.03-4.91 (m, 4H), 4.39 (dt, *J* = 8.0 Hz, *J* = 7.0 Hz, 1H), 3.5 (m, 2H), 1.98-1.92 (m, 2H), 1.87-1.74 (m, 2H), 1.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 140.2, 139.2, 133.3, 133.2, 129.0, 128.9, 127.7, 126.9, 117.9, 114.7, 66.1, 32.9, 32.3, 25.2. IR (thin film): 3237, 3070, 1639, 1448, 1351, 1167, 1088 cm^{-1}. HRMS (ESI) calcd for $[C_{20}H_{24}N_2O_4S_3Na]^+$ ($[M+Na]^+$): 475.0796, found 475.0769.



S3: $[\alpha]^{23}_D$ = +20.3° (c = 2.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.53 (t, *J* = 8.5 Hz, 1H), 7.46 (t, *J* = 8.5 Hz, 2H), 5.69-5.63 (m, 1H), 5.55-5.46 (m, 1H), 5.26 (d, *J* = 10.0 Hz, 1H), 4.96-4.88 (m, 4H), 3.74 (m, 1H), 1.96-1.90 (m, 2H), 1.48-1.42 (m, 2H), 1.36-1.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 140.9, 138.0, 137.5, 132.3, 128.8, 127.0, 115.8, 114.7, 56.2, 34.8, 33.0, 24.3. IR (thin film): 3297, 3074, 1641, 1447, 1325, 1161 cm^{-1}. HRMS (ESI) calcd for [C14H20NO2S]$^+$ ($[M+H]^+$): 266.1209, found 266.1214.

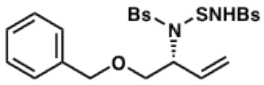


Table 2, entry 9: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –10 °C for 5 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (630 mg, 61 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 91% by comparison to a sample of the racemate (see HPLC trace below). $[\alpha]^{23}_D$ = +144.1° (c = 2.9, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C), δ 7.89 (t, *J* = 8.0 Hz, 4H), 7.62-7.59 (m, 1H), 7.54-7.50 (m, 3H), 7.40 (m, 2H),

7.29 (m, 3H), 7.14 (m, 2H), 6.95 (s, 1H), 5.97 (br, 1H), 5.18 (d, J = 10.5 Hz, 2H), 4.75 (m, 1H), 4.41 (m, 2H), 3.98 (m, 1H), 3.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 50 ^{o}C), δ 140.6, 139.4, 137.7, 133.6, 133.1, 129.1, 128.7, 128.3, 127.9, 127.6, 127.1, 119.2, 72.9, 65.0. IR (thin film): 3239, 3065, 2856, 1448, 1353, 1168, 1089-819 cm^{-1}. HRMS (ESI) calcd for $[C_{23}H_{25}N_2O_5S_3]^+$ ([M+H]$^+$): 505.0926, found 505.0898.

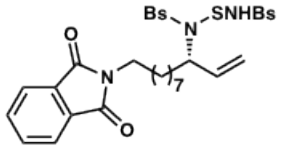
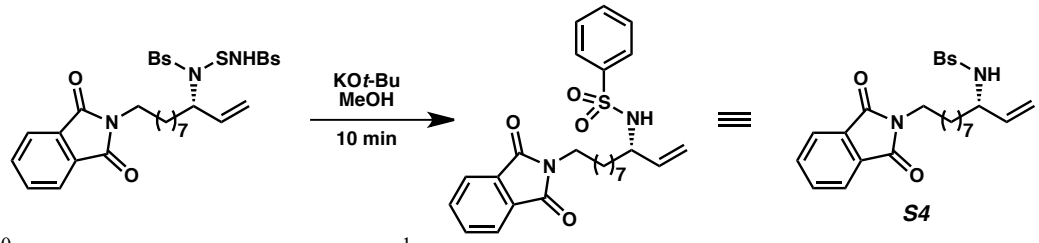


Table 2, entry 10: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –5 °C for 2 d), purification by flash chromatography (20:1 hexanes:ethyl acetate to 1:1 hexanes:ethyl acetate) afforded the product (1.16 g, 82 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 94.3% after conversion to sulfonamide **S4** (see experimental procedure for **S4** and HPLC trace below). $[\alpha]^{20}_D$ = +15.3° (c = 3.2, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 ^{o}C), δ 7.91–7.89 (m, 4H), 7.85-7.84 (m, 2H), 7.71-7.69 (m, 2H), 7.61-7.58 (m, 2H),7.53-7.49 (m, 4H), 7.02 (s, 1H), 5.86 (br, 1H), 5.03 (d, J = 10.0 Hz, 2H), 4.37 (m, 1H), 3.69 (t, J = 7.5 Hz, 2H), 1.81-1.67 (m, 4H), 1.30-1.07 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$, 50°C), δ 168.6, 140.9, 139.9, 134.0, 133.5, 133.4, 132.5, 129.4, 129.2, 128.1, 127.4, 123.3, 118.1, 66.7, 45.0, 38.3, 33.3, 29.2, 29.1, 28.7, 26.9, 26.3. IR (thin film): 3446, 2930, 1771, 1710, 1399, 1357, 1168 cm^{-1}. HRMS (ESI) calcd for $[C_{31}H_{36}N_3O_6S_3]^+$ ([M+H]$^+$): 642.1761, found 642.1758.



S4: $[\alpha]^{20}_D$ = +8.5° (c = 1.7, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.86–7.83 (m, 4H), 7.71-7.69 (m, 2H), 7.55-7.53 (m, 1H), 7.47 (t, J = 7.5 Hz, 2 H), 5.53 (ddd, J = 17.0 Hz, J = 10.5 Hz, J = 6.5 Hz, 1H), 4.97 (d, J = 17.0 Hz, 1H), 4.93 (d, J = 10.5 Hz, 1H), 4.66 (d, J = 7.5 Hz, 1H), 3.74 (m, 1H), 3.65 (t, J = 7.5 Hz, 2H), 1.66-1.61 (m, 2H), 1.44-1.41 (m, 2H), 1.27-1.16 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 168.7, 141.2, 137.9, 134.1, 132.3, 129.1, 127.3, 123.4, 116.0, 56.5, 44.9, 38.1, 35.6, 29.3, 29.1, 29.0, 28.7, 26.9, 25.3. IR (thin film): 3288, 2929, 1771, 1710, 1397, 1160 cm^{-1}. HRMS (ESI) calcd for $[C_{25}H_{31}N_2O_4S]$ ([M+H]$^+$): 455.1999, found 455.1995.

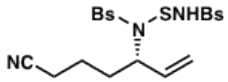


Table 2, entry 11: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –5 °C for 4 d), purification by flash chromatography (20:1 hexanes:ethyl acetate to 1:1 hexanes:ethyl acetate) afforded the product (869 mg, 91 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 97% after conversion to sulfonamide

S4 (see experimental procedure for **S4** and HPLC trace below). $[\alpha]^{20}_D$ = –71.5° (c = 11.3, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C), δ 7.95 (d, *J* = 7.5 Hz, 4H), 7.61 (t, *J* = 7.0 Hz, 2H), 7.52-7.49 (m, 4H), 7.19 (s, 1H), 5.78 (br, 1H), 5.05 (d, *J* = 10.5 Hz, 2H), 4.49 (m, 1H), 2.39-2.23 (m, 3H), 1.94-1.92 (m, 1H), 1.75-1.64 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C), δ 171.2, 140.5, 139.4, 135.9, 133.7, 133.5, 129.4, 129.3, 127.9, 127.2, 126.5, 118.6, 65.5, 31.8, 2 2.4, 16.9. IR (thin film): 3235, 2248, 1449, 1345, 1167 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{22}N_3O_4S_3]^+$ ([M+H]$^+$): 452.0767, found 452.0758.

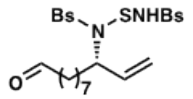
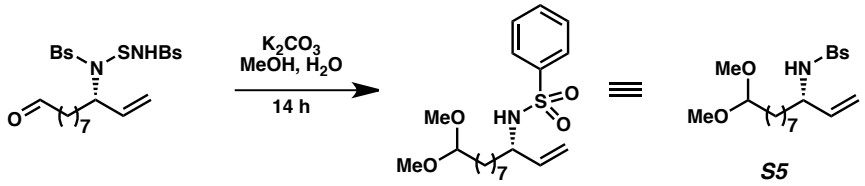


Table 2, entry 12: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –20 °C for 5 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (795 mg, 78 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 97% after conversion to acetal **S5** under the previously described conditions for the synthesis of sulfonamide **S2** (see HPLC trace for **S5** below). $[\alpha]^{23}_D$ = +16.6° (c = 2.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C), δ 9.74 (s, 1H) 7.88 (d, *J* = 6.0 Hz, 4H), 7.57 (m, 2H), 7.51-7.46 (m, 4H), 7.08 (s, 1H), 5.97 (br, 1H), 5.02 (d, *J* = 10.0 Hz, 2H), 4.38 (m, 1H), 2.39 (t, *J* = 7.5 Hz, 2H), 1.85-1.58 (m, 4H), 1.26-1.10 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 203.1, 140.3, 139.3, 133.3, 133.2, 129.7, 128.9, 127.7, 126.9, 117.9, 66.2, 43.7, 32.8, 28.9, 28.8 , 28.7, 25.9, 21.9. IR (thin film): 3234, 2930, 1718, 1447, 1353, 1167 cm^{-1}. HRMS (ESI) calcd for $[C_{23}H_{31}N_2O_5S_3]^+$ ([M+H]$^+$): 511.1395, found 511.1379.



S5: $[\alpha]^{23}_D$ = +11.9° (c = 0.8, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.87–7.84 (m, 2H), 7.54–7.52 (m, 1H), 7.49-7.45 (m, 2H), 5.52 (ddd, *J* = 17.2 Hz, *J* = 10.4 Hz, *J* = 6.8 Hz, 1H), 4.96 (dt, *J* = 17.2 Hz, *J* = 5.2 Hz, 1H), 4.93 (dt, *J* = 10.4 Hz, *J* = 5.2 Hz, 1H), 4.68 (d, *J* = 8.0 Hz, 1H), 4.34 (t, *J* = 5.6 Hz, 2H), 3.76 (m, 1H), 3.30 (s, 6H), 1.58-1.53 (m, 2H), 1.44-1.40 (m, 2H), 1.31-1.17 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 141.0, 137.7, 132.4, 128.8, 127.0, 115.7, 104.5, 56.3, 52.6, 35.5, 32.4, 29.3, 28.9, 25.1, 24.7. IR (thin film): 3276, 3067, 1645, 1447, 1327, 1160, 1094 cm^{-1}. LRMS (ESI) calcd for $[C_{23}H_{31}N_2O_5S_3]^+$ ([M+H]$^+$): 370.2, found 370.2.

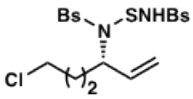


Table 2, entry 13: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –10 °C for 2 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (780 mg, 85 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 97% by comparison to a sample of the racemate (see HPLC trace below). $[\alpha]^{23}_D$ = -48.2° (c = 2.0, CH_2Cl_2). ^{1}H NMR (500 MHz,

$CDCl_3$, 50 °C), δ 7.89 (d, *J* = 7.5 Hz, 4H), 7.59 (m, 2H), 7.50 (m, 4H), 6.94 (s, 1H), 5.83 (br, 1H), 5.05 (d, *J* = 10.0 Hz, 2H), 4.44 (m, 1H), 3.5 (m, 2H), 2.08-2.03 (m, 1H), 1.98-1.92 (m, 1H), 1.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 140.1, 139.1, 133.5, 133.3, 129.2, 129.0, 127.7, 127.0, 118.4, 65.2, 44.5, 30.0, 29.1. IR (thin film): 3238, 3068, 2959, 1448, 1311, 1167, 1088 cm^{-1}. HRMS (ESI) calcd for $[C_{18}H_{21}ClN_2O_4S_3Na]^+$ ($[M+Na]^+$): 483.0244, found 483.0234.

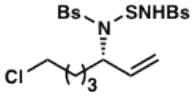


Table 2, entry 14: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –10 °C for 2 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (1.23 g, 87 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 94% by comparison to a sample of the racemate (see HPLC trace below). $[\alpha]^{23}_D$ = -23.5° (c = 2.0, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$, 50 °C), δ 7.81 (d, *J* = 8.0 Hz, 4H), 7.55-7.50 (m, 2H), 7.46-7.41 (m, 4H), 6.69 (br, 1H), 5.76 (br, 1H), 4.98 (d, *J* = 8.0 Hz, 2H), 4.35-4.31 (m, 1H), 3.39 (m, 2H), 1.85-1.67 (m, 4H), 1.24-1.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 140.4, 139.2, 133.6, 133.4, 129.3, 129.2, 127.8, 127.1, 118.3, 65.9, 44.9, 32.2, 32.0, 23.5. IR (thin film): 3238, 1447, 1350, 1167, 1088, 810 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{24}ClN_2O_4S_3]^+$ ($[M+H]^+$): 475.0581, found 475.0570.

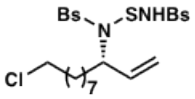
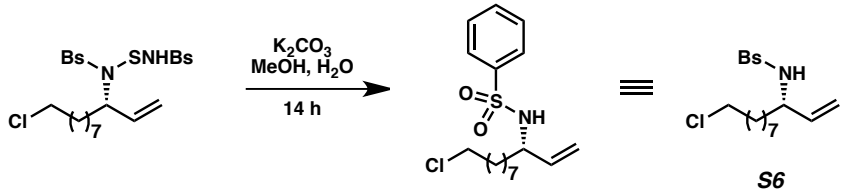


Table 2, entry 15: Following Method A for the catalytic enantioselective allylic amination (in MeOH at –10 °C for 3 d), purification by flash chromatography (20:1 hexanes/ethyl acetate to 5:1 hexanes/ethyl acetate) afforded the product (995 mg, 94 % yield for two steps) as a clear oil. The enantiomeric excess of the product was determined to be 98% after conversion to sulfonamide **S6** under the previously described conditions for the synthesis of sulfonamide **S2** (see HPLC trace for **S6** below). $[\alpha]^{23}_D$ = +17.5° (c = 2.0, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$, 50 °C), δ 7.89 (d, *J* = 7.5 Hz, 4H), 7.59 (m, 2H), 7.53-7.48 (m, 4H), 6.85 (s, 1H), 5.87 (br, 1H), 5.03 (d, *J* = 9.5 Hz, 2H), 4.38 (dt, *J* = 7.5 Hz, *J* = 7.0 Hz, 1H), 3.52 (t, *J* = 6.0 Hz, 2H), 1.83-1.75 (m, 4H), 1.41 (m, 2H), 1.24-1.10 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$), δ139.3, 133.4, 133.3, 129.2, 129.0, 127.7, 127.0, 117.8, 66.3, 45.2,44.7, 32.5, 29.2, 28.9, 28.7, 26 .8, 26.0. IR (thin film): 3278, 3067, 2930, 1644, 1447, 1325, 1161 cm^{-1}. HRMS (ESI) calcd for $[C_{23}H_{31}ClN_2O_4S_3Na]^+$ ($[M+Na]^+$): 553.1027, found 553.1033.

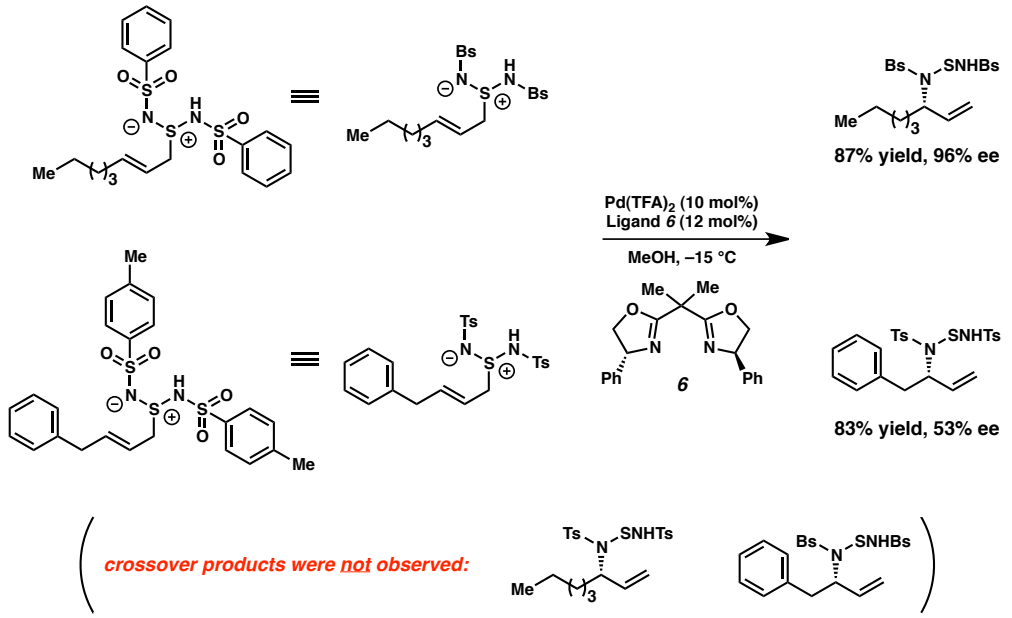


S6

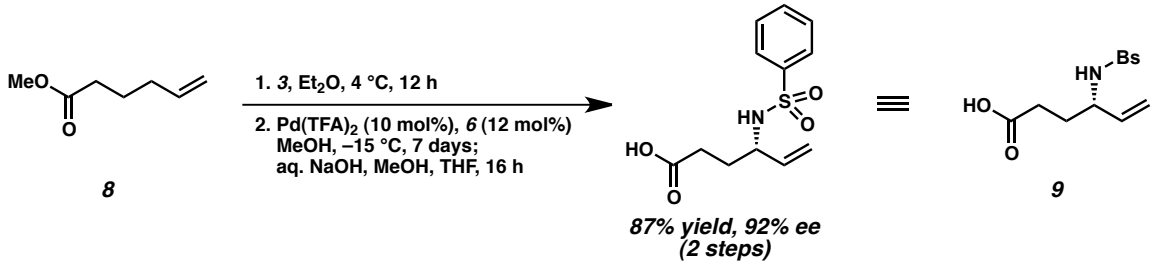
S6: $[\alpha]^{23}_D$ = +12.0° (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$), δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.41 (dd, *J* = 8.0 Hz, *J* = 7.2 Hz, 2H), 5.46 (m, 1H), 4.90 (d, *J* = 17.6 Hz, 1H), 4.86 (d, *J* = 11.2 Hz, 1H), 4.76 (d, *J* = 8.0 Hz, 1H), 3.69 (m, 1H), 3.45 (t, *J* = 6.8 Hz, 2H), 1.67 (m, 2H), 1.38-1.27 (m, 4H), 1.12 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$),

δ 141.0, 137.7, 132.4, 128.8, 127.0, 115.8, 56.3, 45.1, 35.5, 32.5, 29.1, 28.9, 28.7, 26.7, 25.1. IR (thin film): 3239, 3068, 2930, 1447, 1311, 1167 cm^{-1}. HRMS (ESI) calcd for $[C_{17}H_{26}ClNO_2SNa]^+$ ($[M+Na]^+$): 366.1265, found 366.1271.

Crossover Experiment



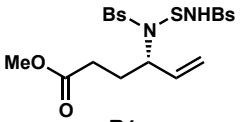
Synthesis of Vigabatrin



Sulfonamide 9: A solution of benzenesulfonyl sulfurdiimide **3** (1.37 g, 4 mmol) in Et_2O (4 mL, 0.5 M) was cooled to 0 °C and treated with unsaturated ester **8** (2.5 mL, 17 mmol, 4.25 equiv). The reaction was stirred at 4 °C for 12 h. The ene adduct, which formed a white precipitate, was purified at room temperature by vacuum filtration, washed with Et_2O (20–40 mL), and dried under vacuum. The ene adduct was then dissolved in MeOH (10 mL) and cooled to –20 °C. The solution was treated with the palladium-ligand complex in MeOH (30 mL), which was made by premixing $Pd(TFA)_2$ (10 mol%, 132 mg, 0.4 mmol) and ligand **6** (12 mol%, 160 mg, 0.48 mmol) in MeOH (30 mL) and stirring for 20 min at room temperature. The reaction was warmed to –15 °C and stirred for 5 days. The solution was then treated with aqueous NaOH (1 N, 14 mL) and THF (10 mL). After stirring for 12 h at 23 °C, the reaction was quenched with aqueous HCl (1 N, 14 mL) and concentrated under reduced pressure to remove THF and MeOH. The resulting solution was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried

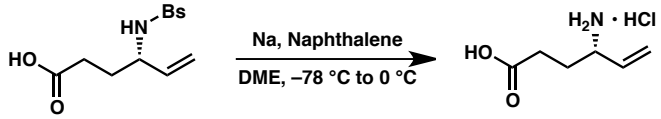
over $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography provided sulfonamide **9** (914 mg, 87% yield from **3**) as a clear oil: $[\alpha]^{23}_D$ = +28.4° (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$), δ 9.6 (br, 1H), 7.85 (d, *J* = 6.8 Hz, 2H), 7.56-7.45 (m, 3H), 5.50 (ddd, *J* = 17.2 Hz, *J* = 10.4 Hz, *J* = 6.8Hz, 1H), 5.38 (br, 1H), 4.94 (d, *J* = 17.2 Hz, 1H), 4.93 (d, *J* = 10.4 Hz, 1H), 3.83 (d, *J* = 6.0 Hz, 1H), 2.4 (t, *J* = 7.6 Hz, 2H), 1.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 140.8, 136.8, 132.8, 127.2, 116.7, 76.9, 55.9, 30.2, 30.1. IR (thin film): 3274, 2935, 1710, 1448, 1325, 1159 cm^{-1}. HRMS (ESI) calcd for $[C_{12}H_{16}NO_4S]^+$ ($[M+H]^+$): 270.0795, found 270.0796.

The enantiomeric excess of the product was determined to be 92% by analysis of the [2,3]-rearrangement product **R1** prior to treatment with aqueous NaOH and THF (see HPLC trace for **R1** below).



R1

R1: $[\alpha]^{23}_D$ = -53.5° (c = 0.9, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C), δ 7.83-7.80 (m, 4H), 7.59-7.57 (m, 2H), 7.51-7.45 (m, 4H), 7.20 (br, 1H), 5.76 (br, 1H), 5.02 (d, *J* = 10 Hz, 2H), 4.50-4.48 (m, 1H), 3.66 (s, 3H), 2.24-2.08 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 50 °C) δ 173.5, 140.6, 139.7, 136.1, 133.6, 133.5, 129.4, 129.3, 128.1, 127.4, 126.6, 118.7, 65.5, 51.8, 30.6, 28.3. IR (thin film): 3226, 1735, 1447, 1353, 1167, 1108 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{23}N_2O_6S_3]^+$ ($[M+H]^+$): 471.0713, found 471.0714.



9 *Vigabatrin (10) (79% yield)*

A solution of sodium naphthalennide in DME (3 mL, 1.0 M) was added dropwise to a solution of sulfonamide **9** (100 mg, 0.37 mmol) in THF (2 mL) at –78 °C. The mixture was warmed to 0 °C and stirred for 2 h. The reaction was then quenched with saturated aqueous $NaHCO_3$ (1 mL) and extracted with ethyl acetate (2 x 10 mL). The aqueous layer was acidified (until pH < 3) with aqueous HCl (1 N) and extracted with ethyl acetate (10 mL). The acidified aqueous layer was concentrated under reduced pressure and diluted with MeOH (5 mL). The mixture was filtered through a plug of cotton to remove NaCl salt. The filtrate was concentrated under reduced pressure to yield the HCl salt of Vigabatrin (**10**) (48 mg, 79% yield) as a white solid: $[\alpha]^{23}_D$ = +11.3° (c = 1.0, D_2O). ^{1}H NMR (500 MHz, D_2O), δ 6.14–6.06 (m, 1H), 5.76–5.73 (m, 2H), 4.18-4.14 (m, 1H), 2.79-2.76 (m, 2H), 2.39-2.35 (m, 1H), 2.25-2.20 (m, 1H). ^{13}C NMR (100 MHz, D_2O) δ 177.2, 132.7, 122.7, 54.0, 30.9, 27.5. HRMS (ESI) calcd for $[C_6H_{11}NO_2Na]^+$ ($[M+Na]^+$): 152.0682, found 152.0683.

Determination of Absolute Stereochemistry of Chiral Allylic Amine Products

The absolute configuration of Vigabatrin (**10**) was determined by comparison to its reported optical rotation in the literature (*4*).

A sample of allylic amine product from Figure 3, entry 6 was recrystallized from hexanes (slow evaporation). The resulting crystals were suitable for X-ray diffraction and the structure was solved (Figure S1). This structure allowed the assignment of absolute configuration as shown. The absolute configurations of all other allylic amine products were assigned by analogy. We thank Dr. Vincent Lynch (Manager of the X-ray Diffraction Lab at UT Austin) for the X-ray structural analysis. The CIF file is available as a separate file in the supporting information.

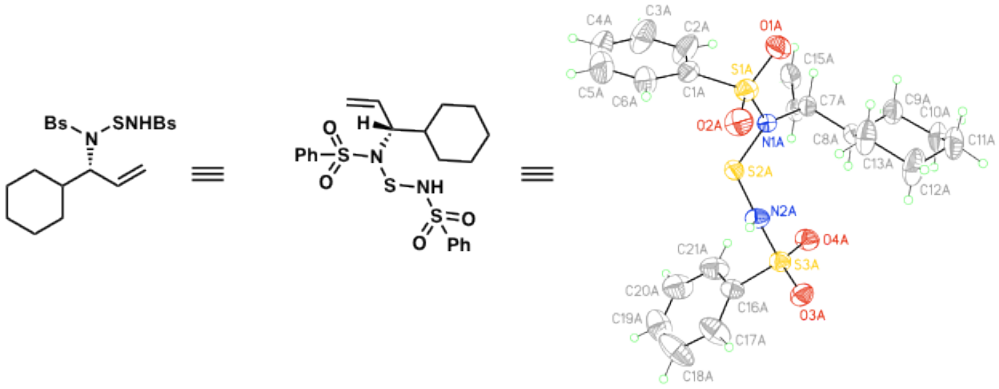


Figure S1

References

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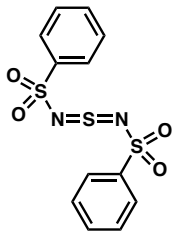
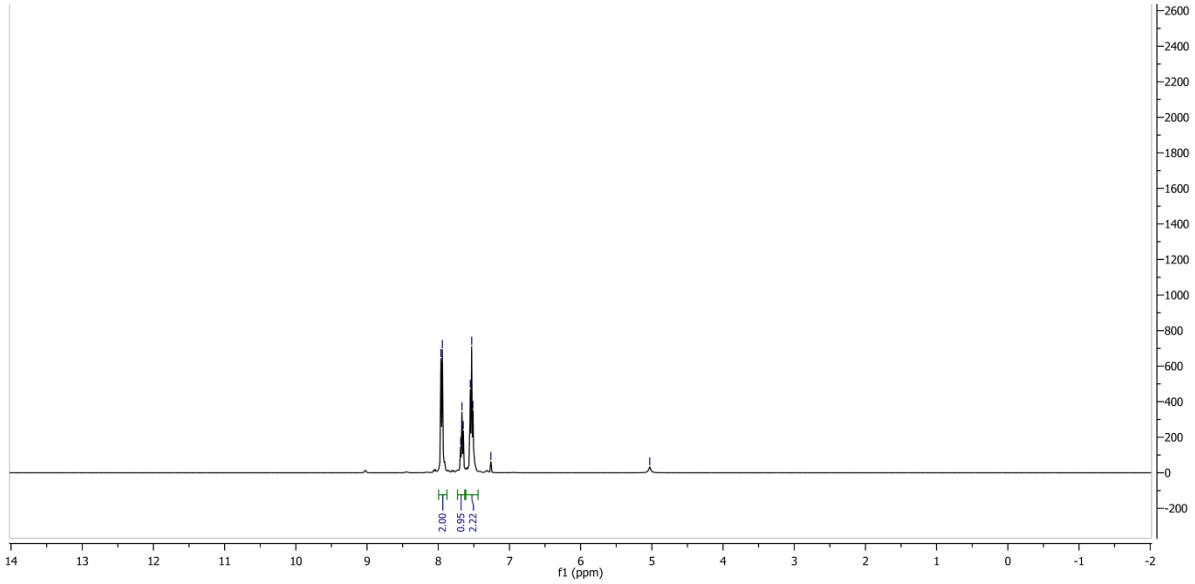
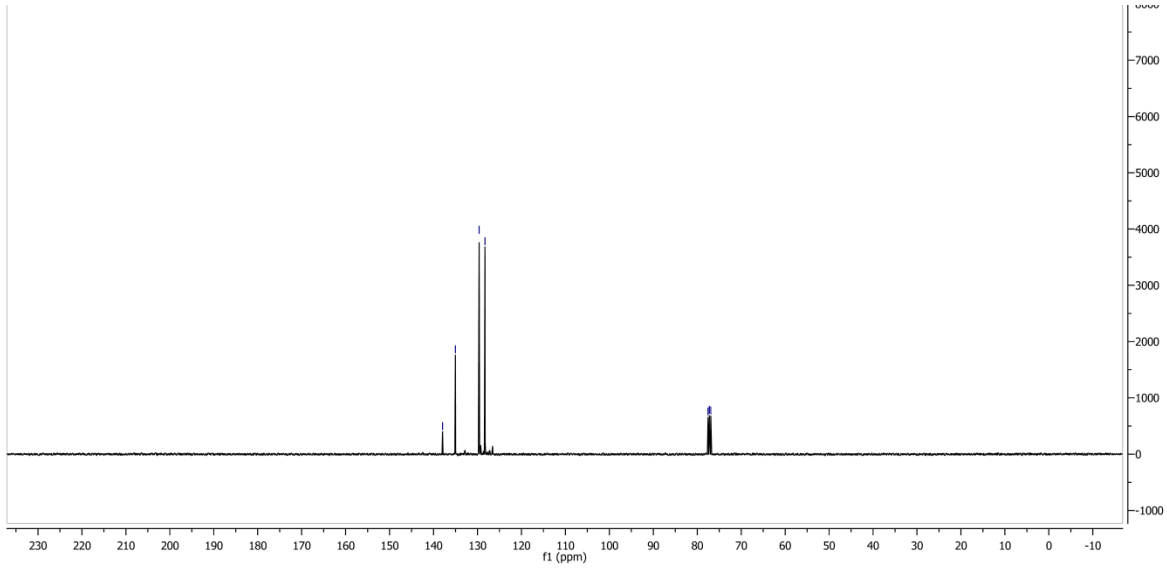
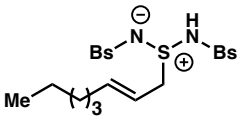
NMR Spectra





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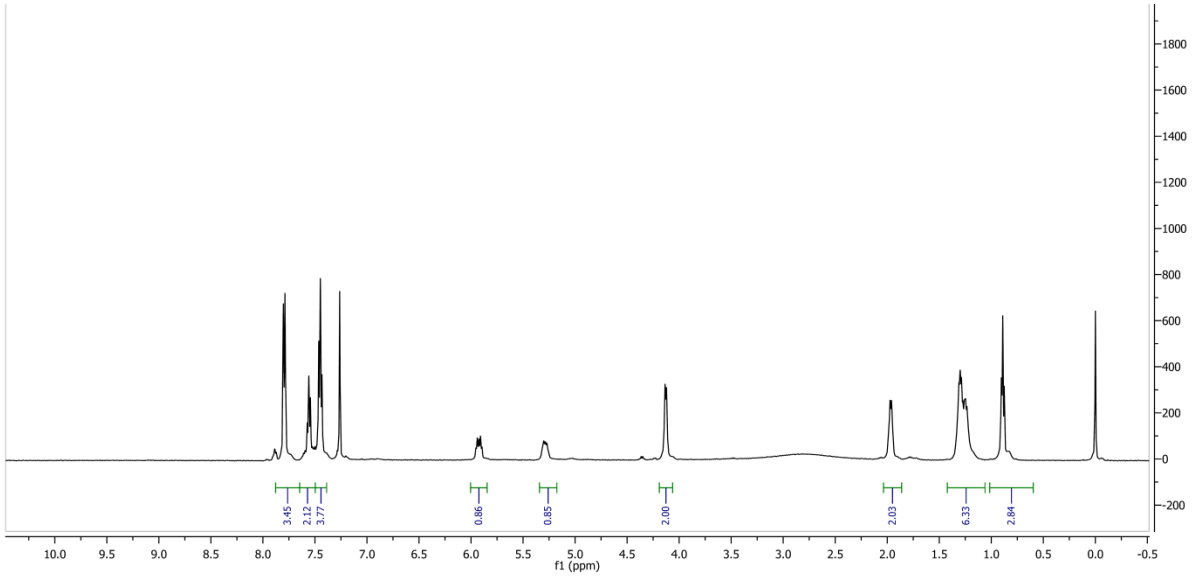
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0.85
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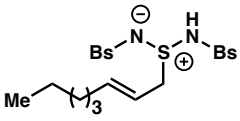
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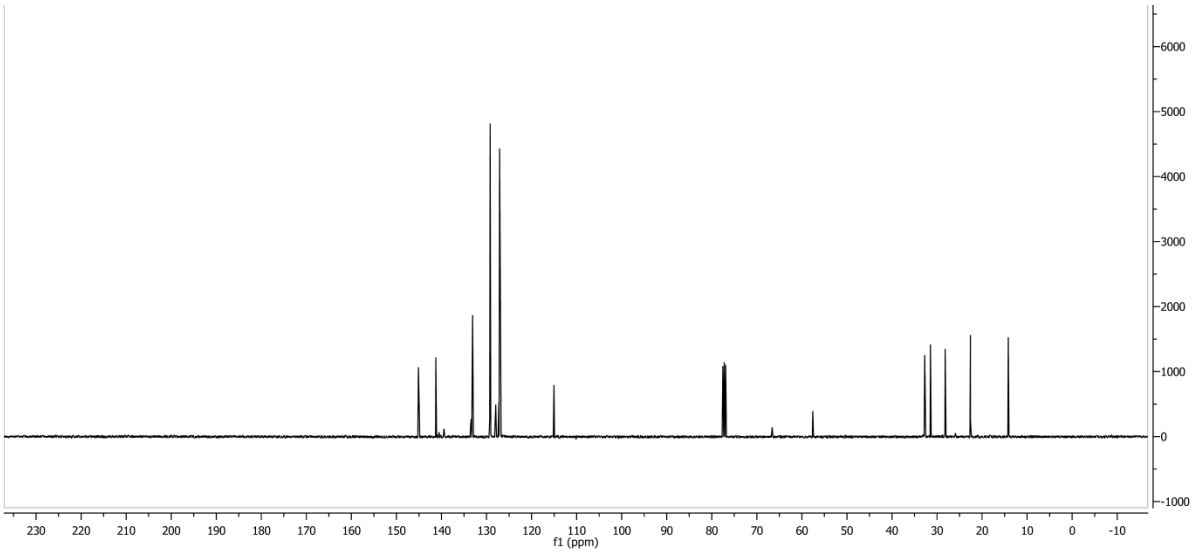
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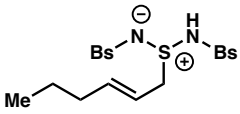
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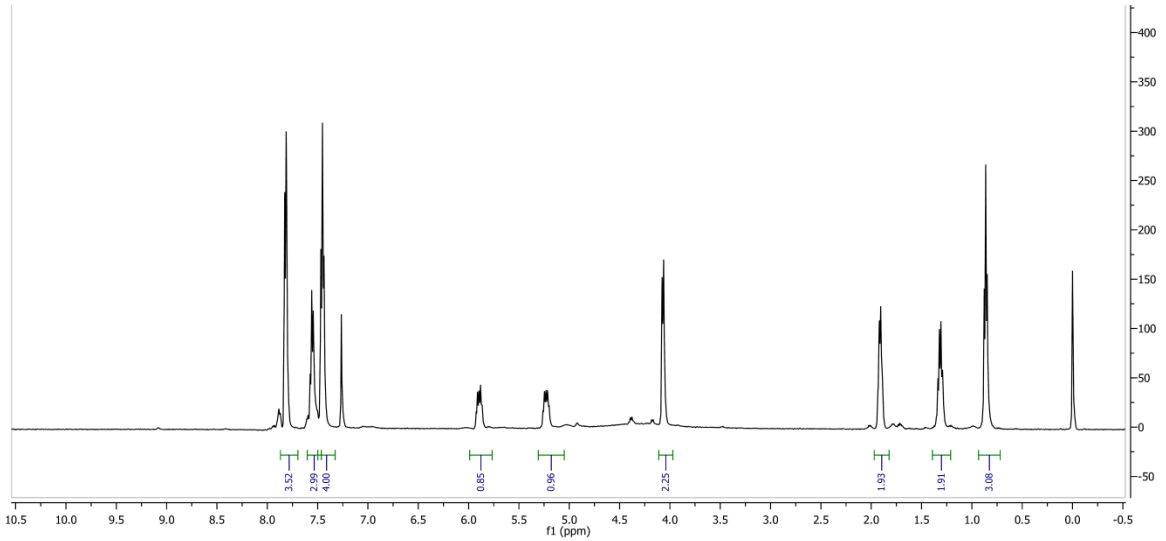
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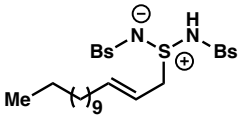
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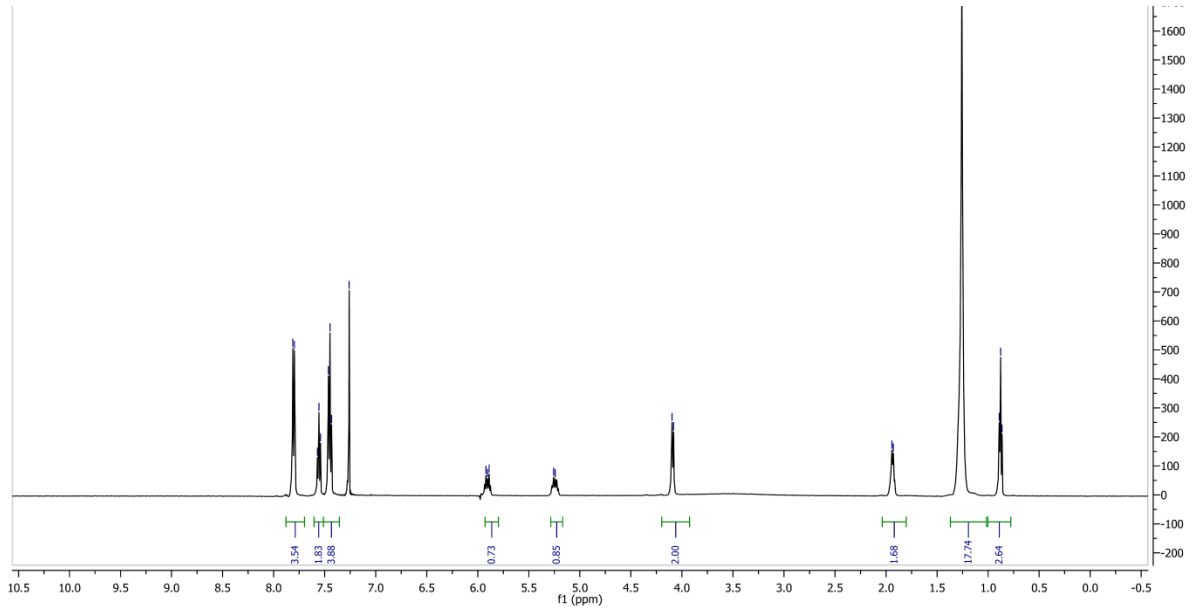
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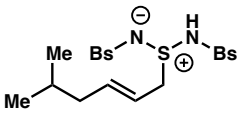
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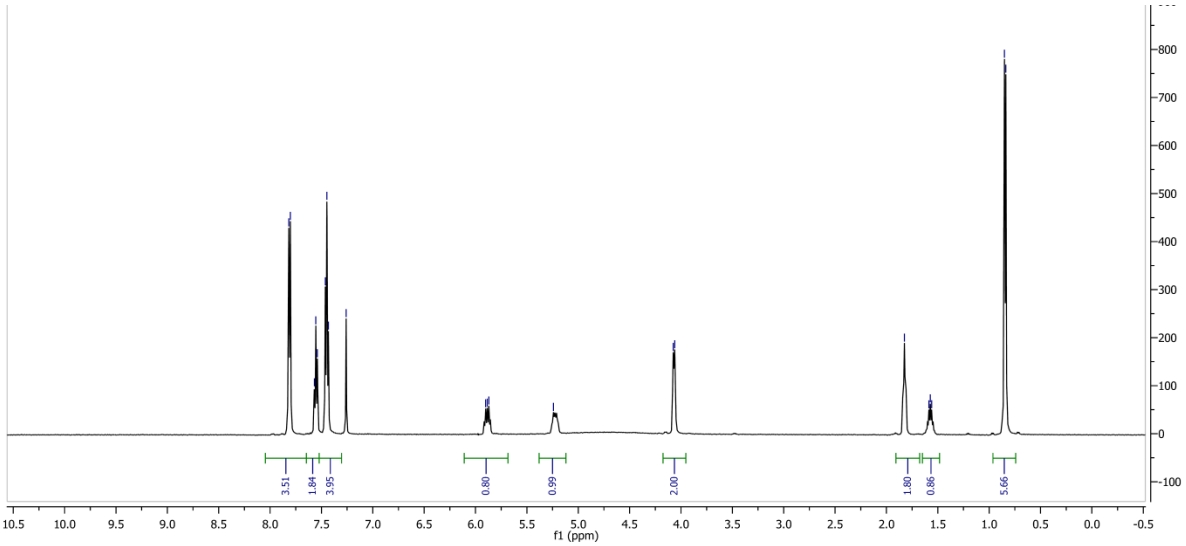
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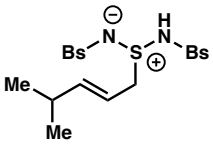
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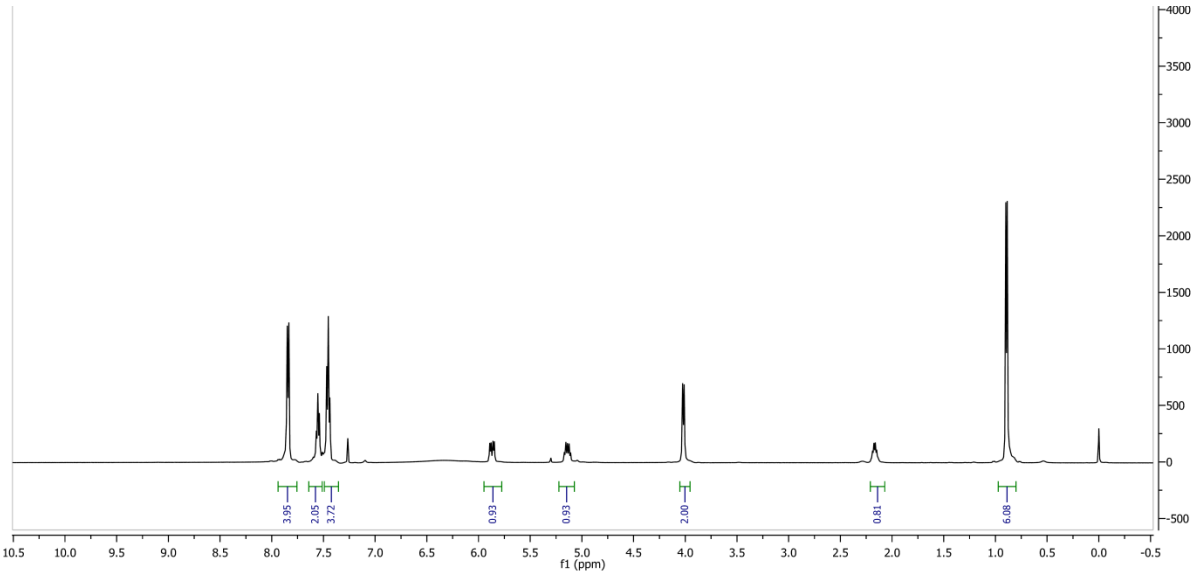
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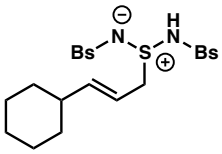
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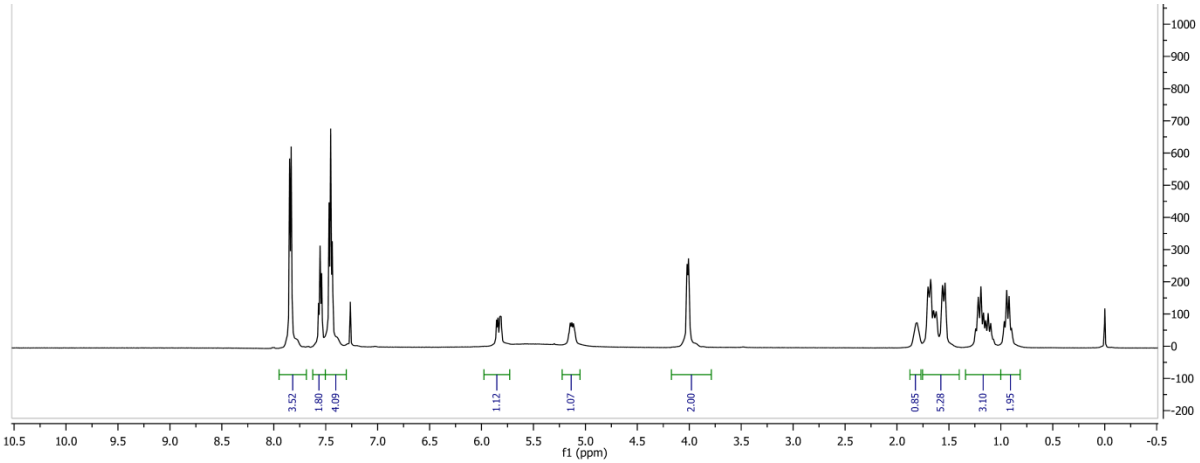
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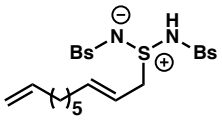
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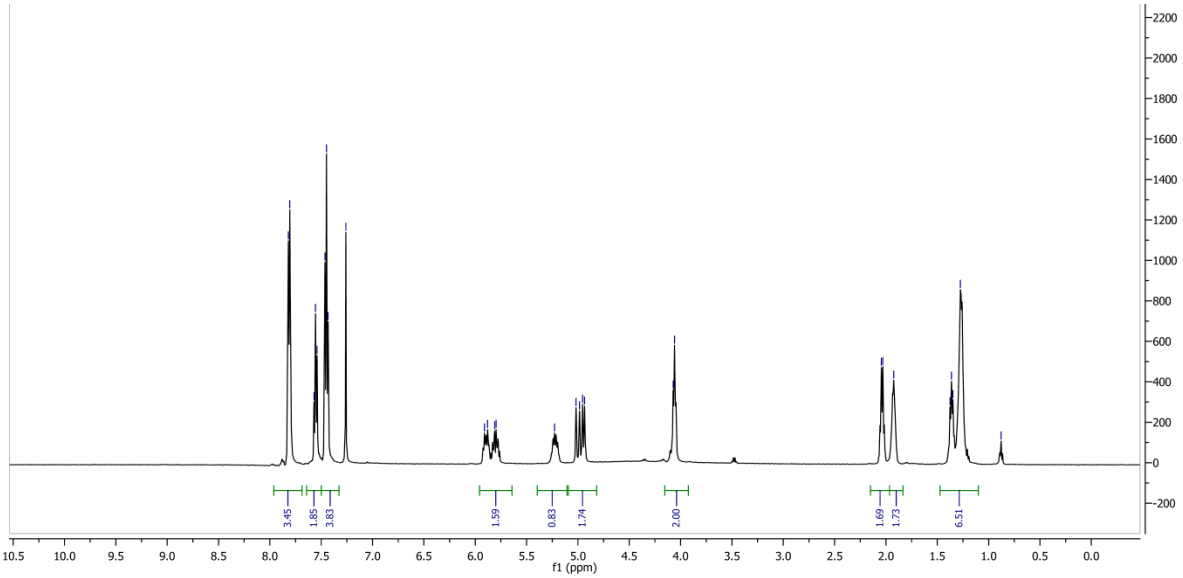
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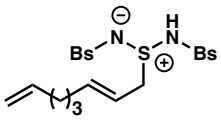
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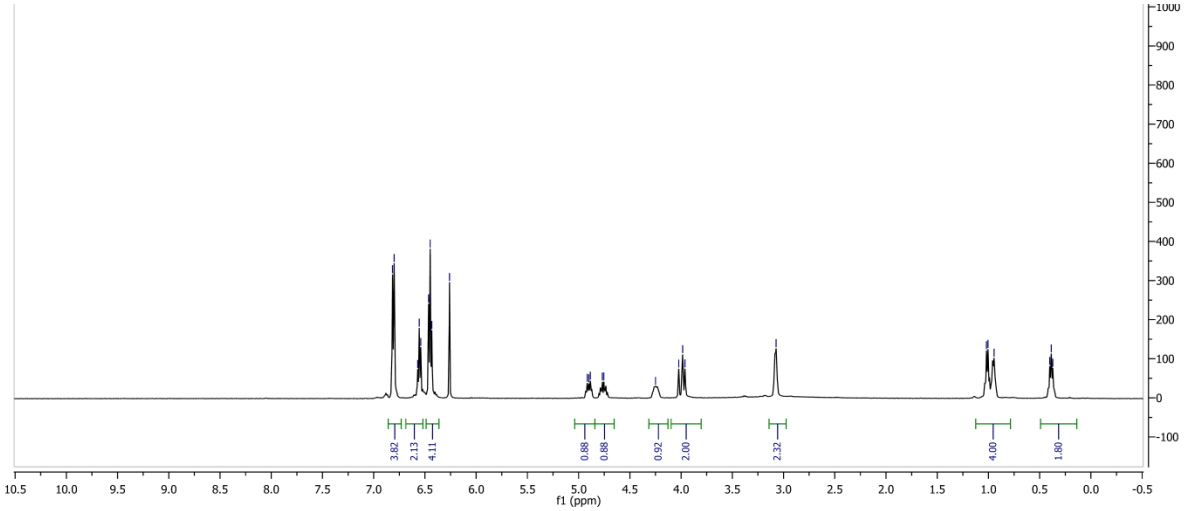
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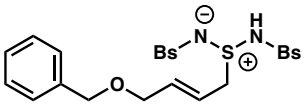
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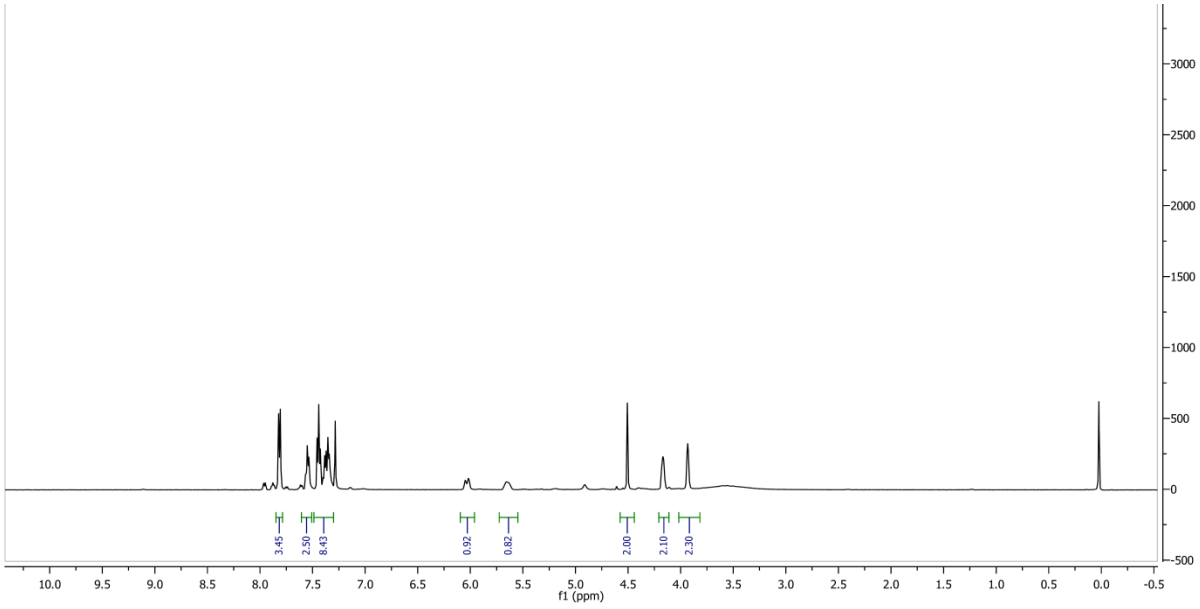
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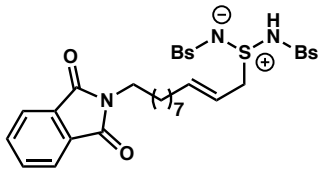
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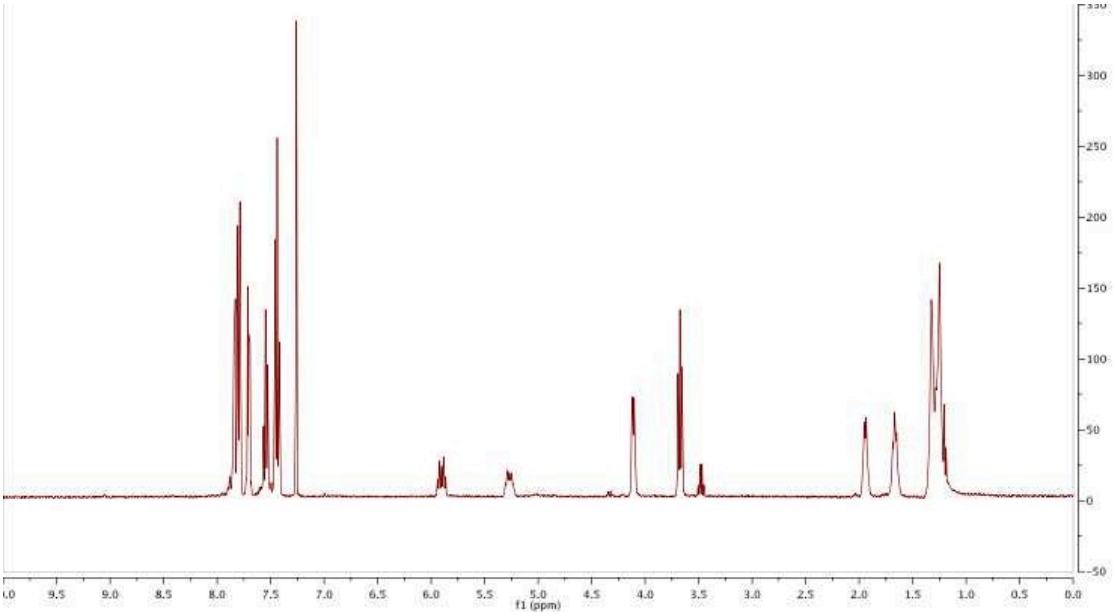
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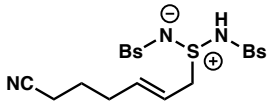
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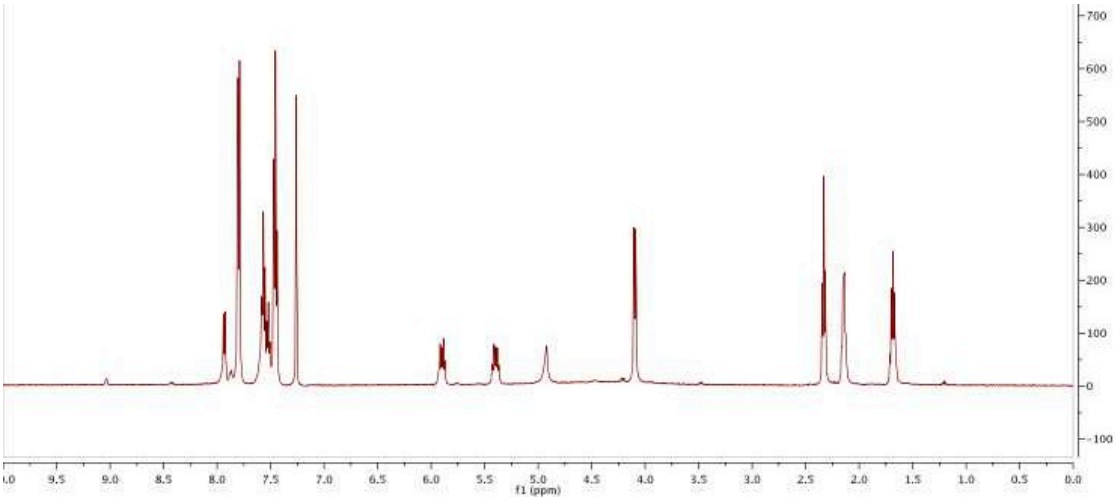
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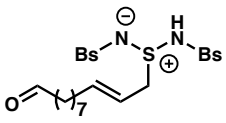
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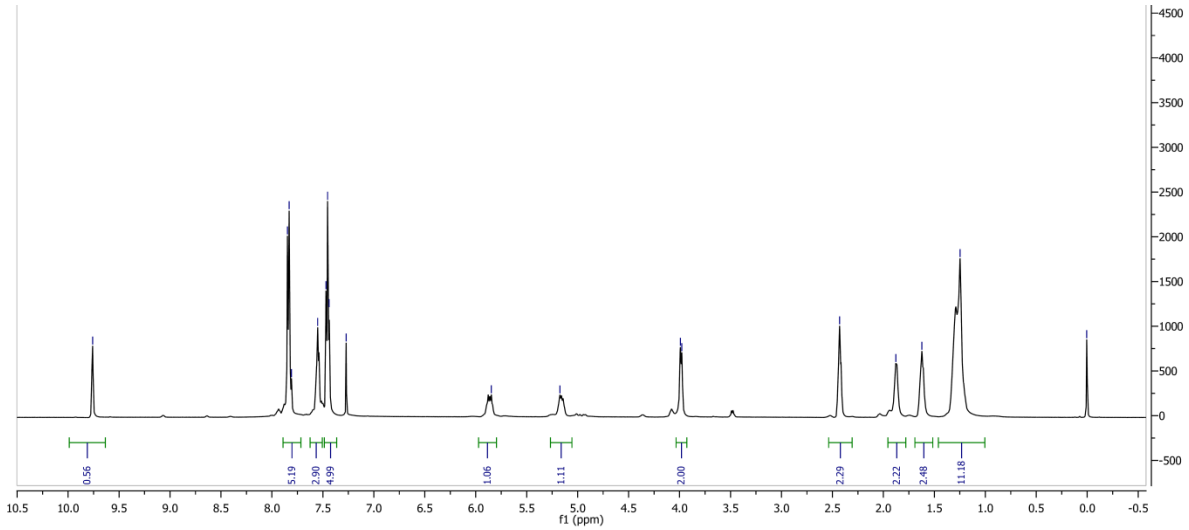
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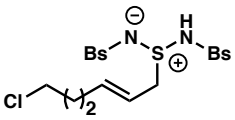
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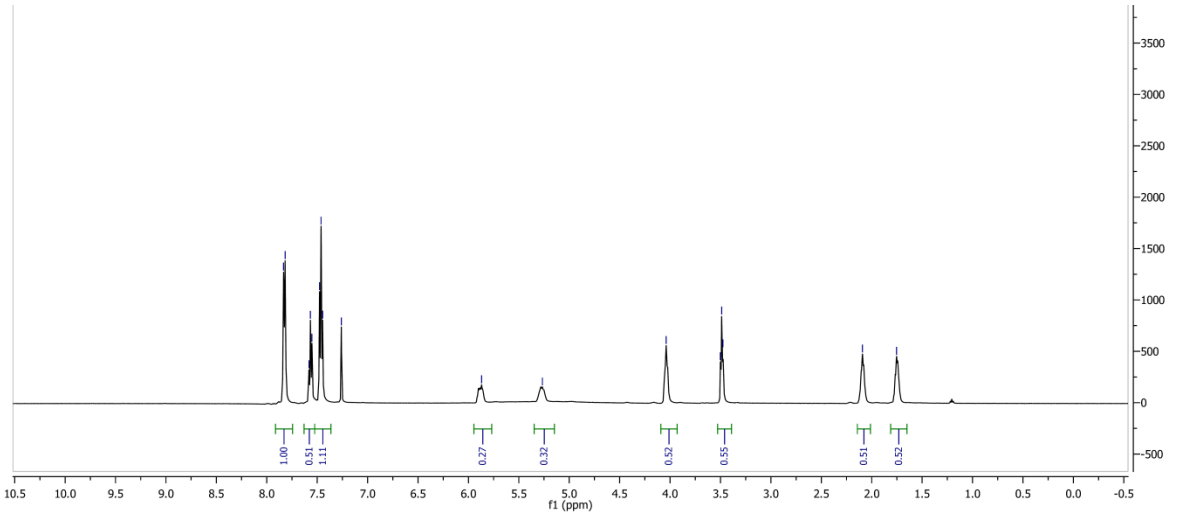
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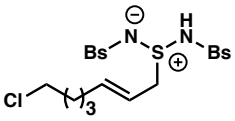
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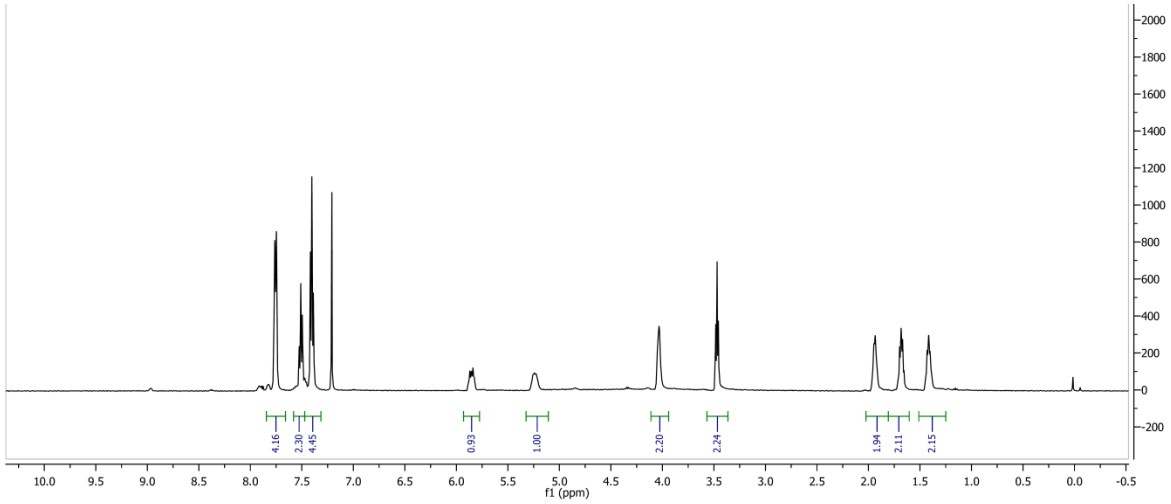
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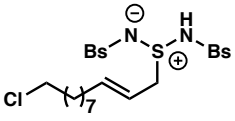
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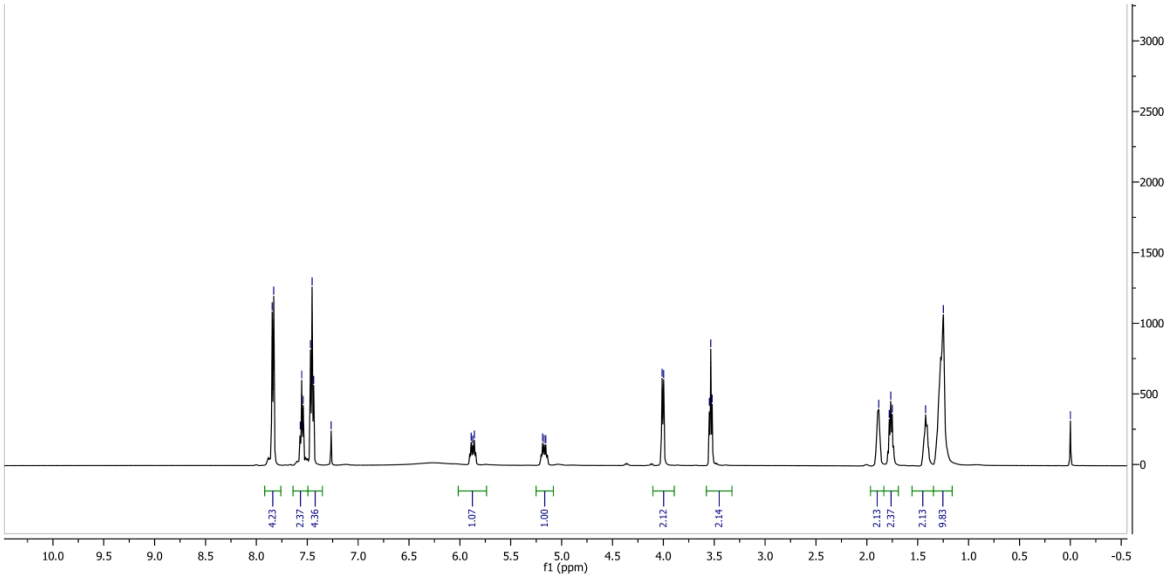
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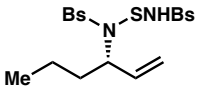
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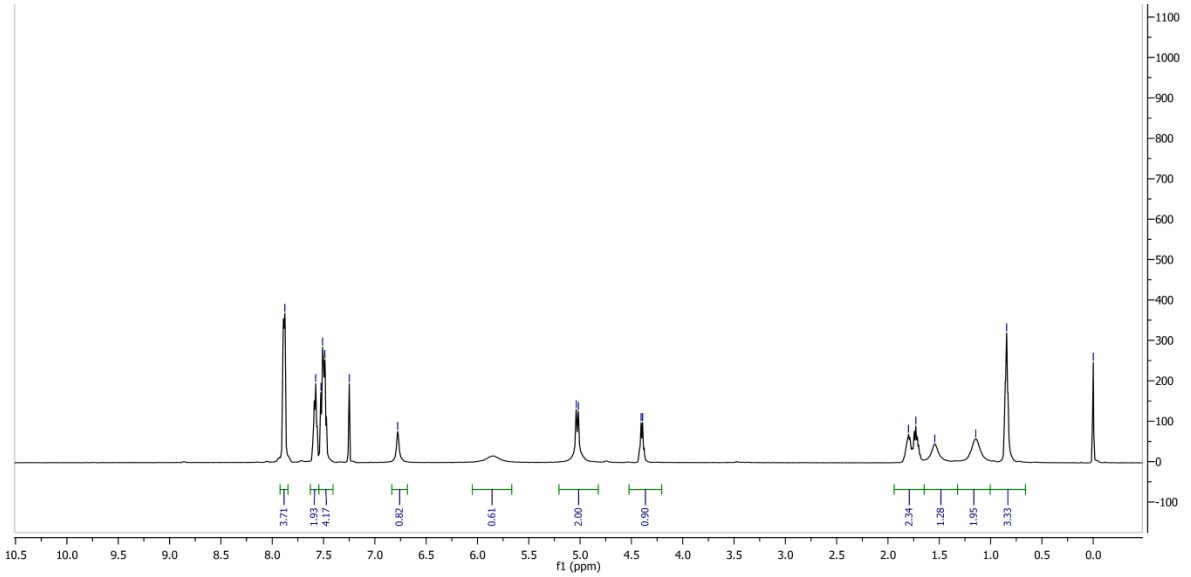
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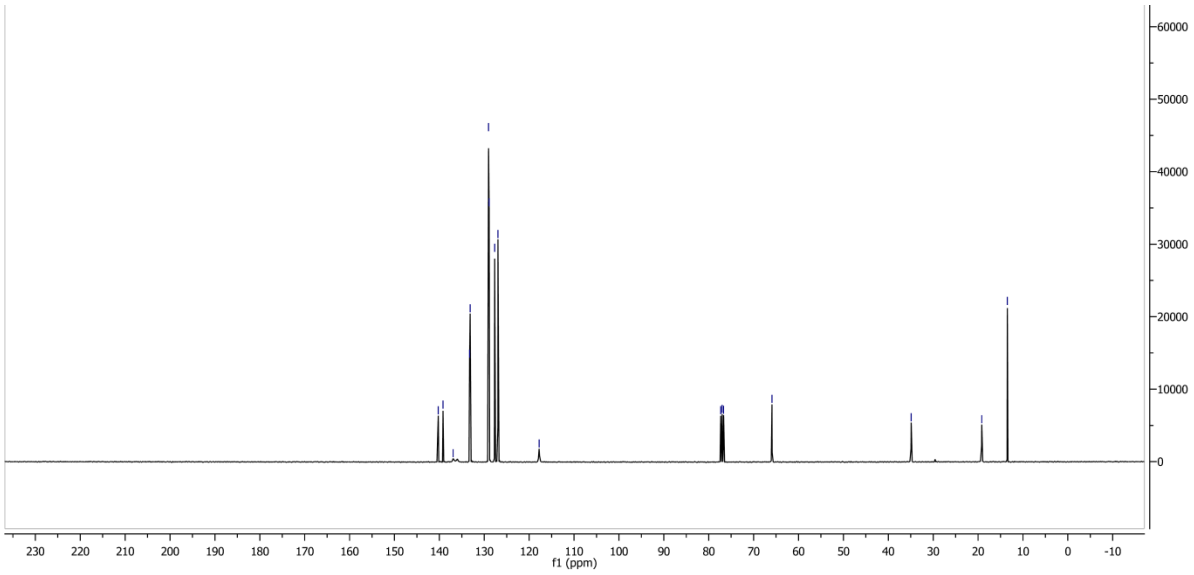
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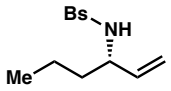

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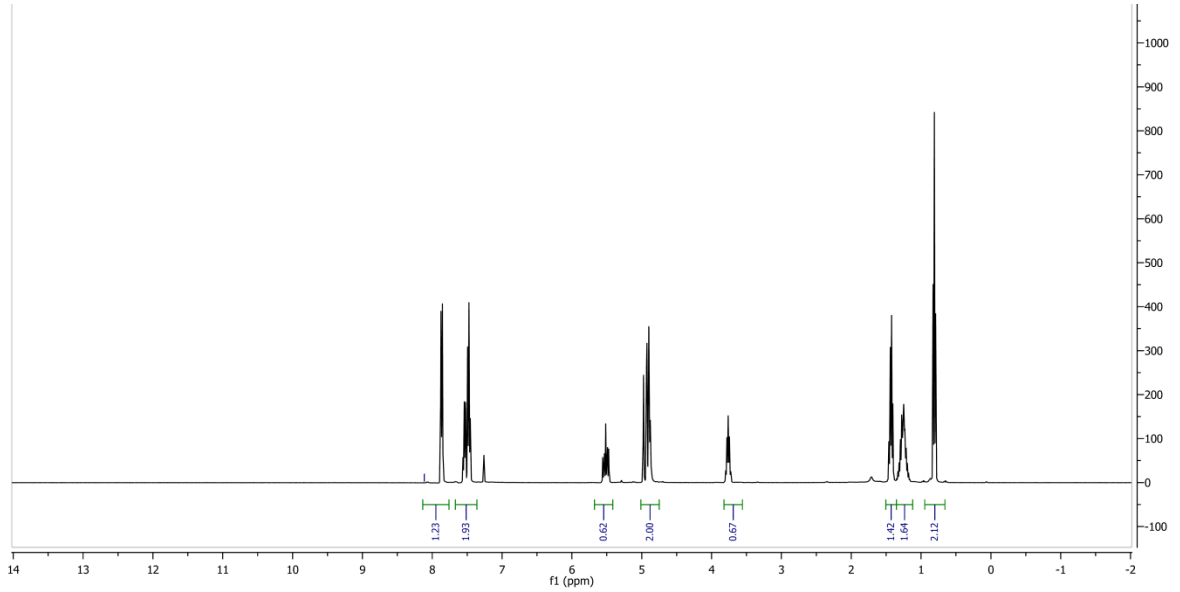

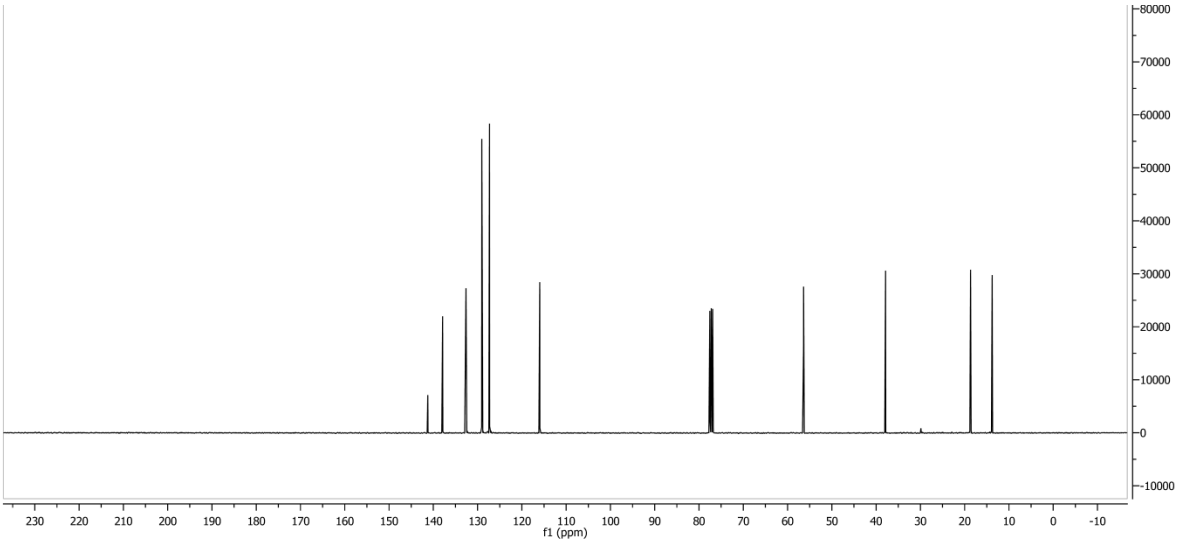

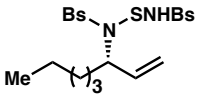
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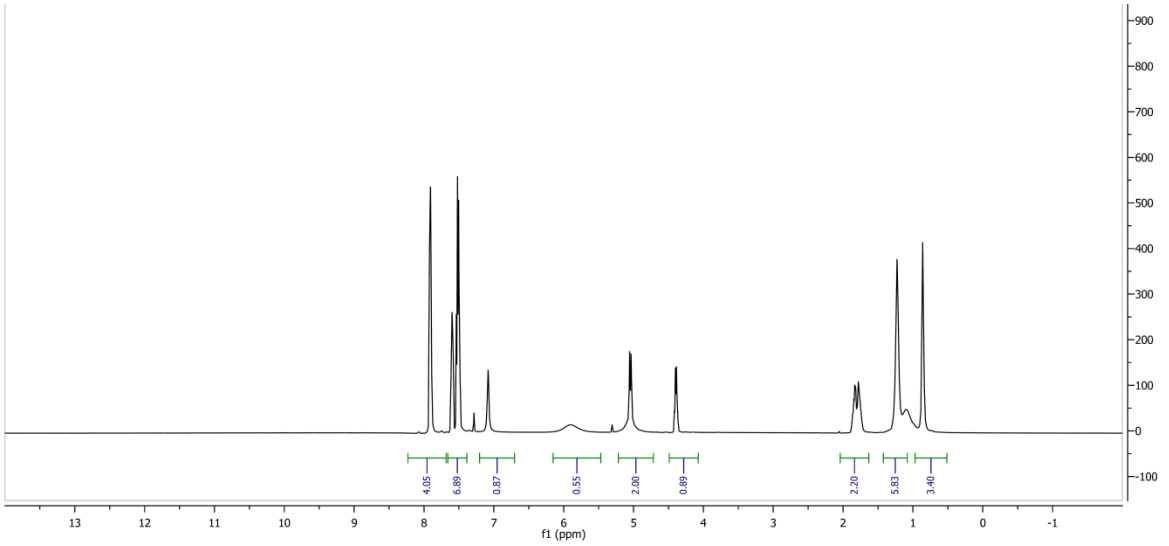
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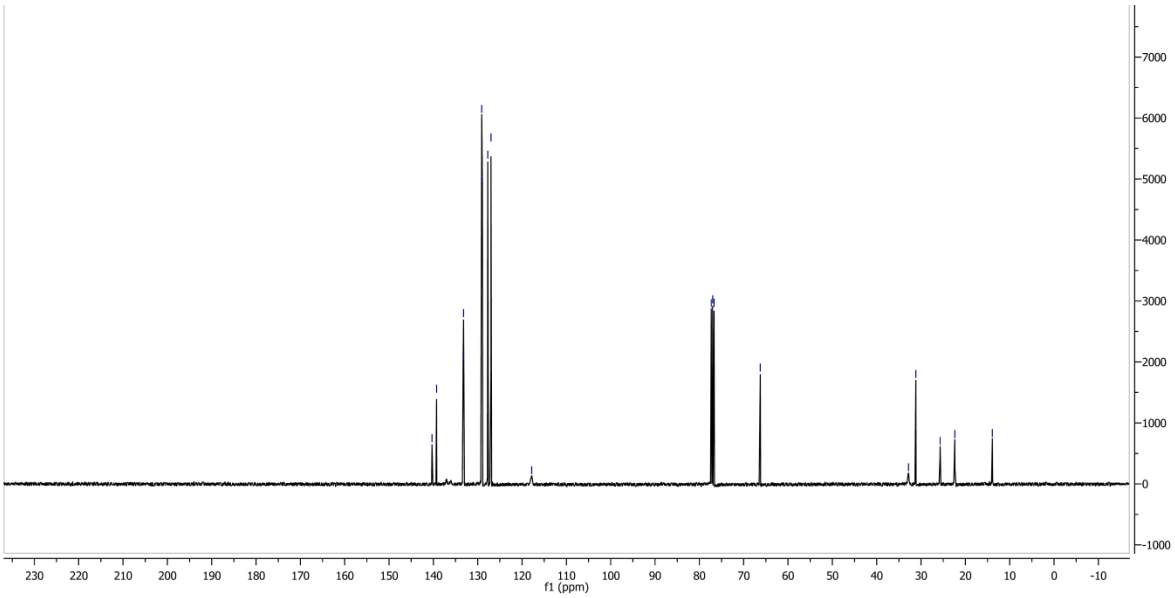
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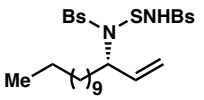
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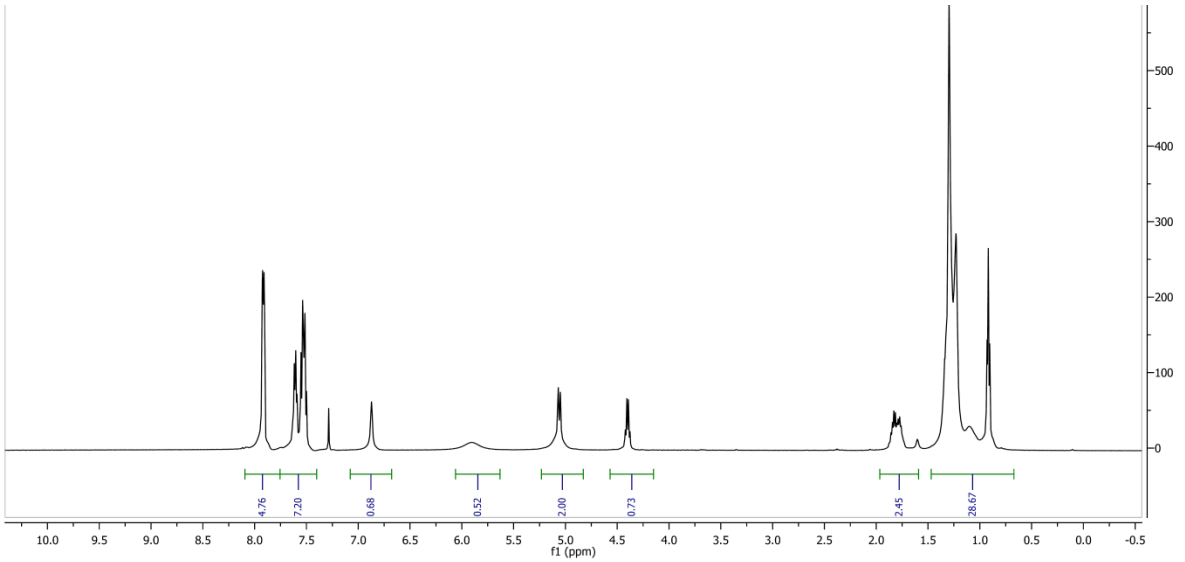
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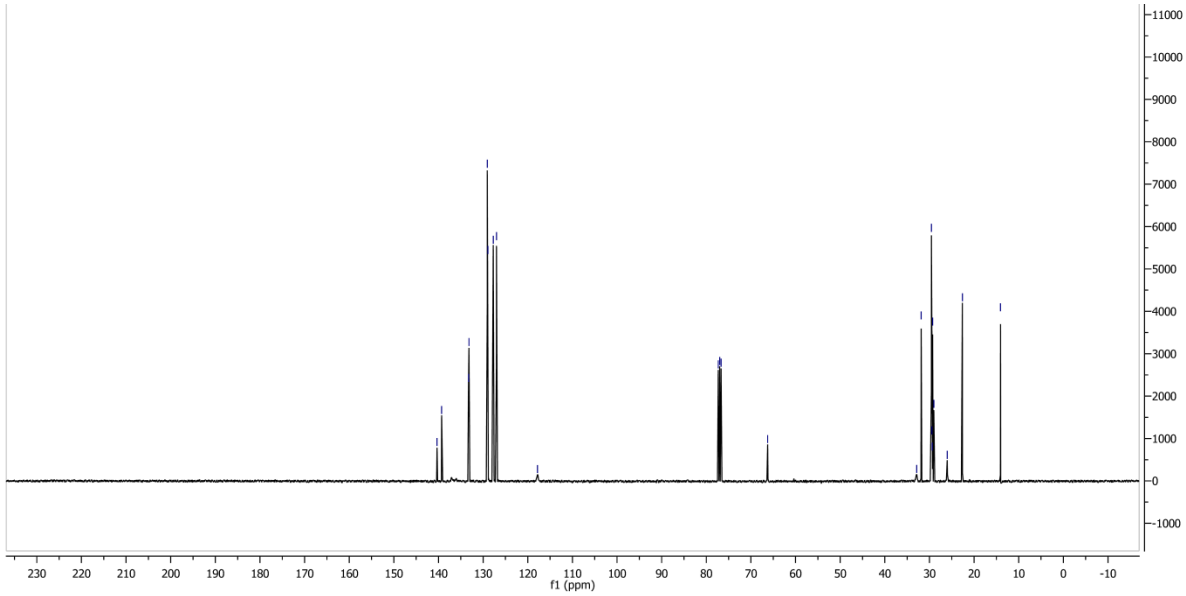
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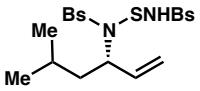
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Me
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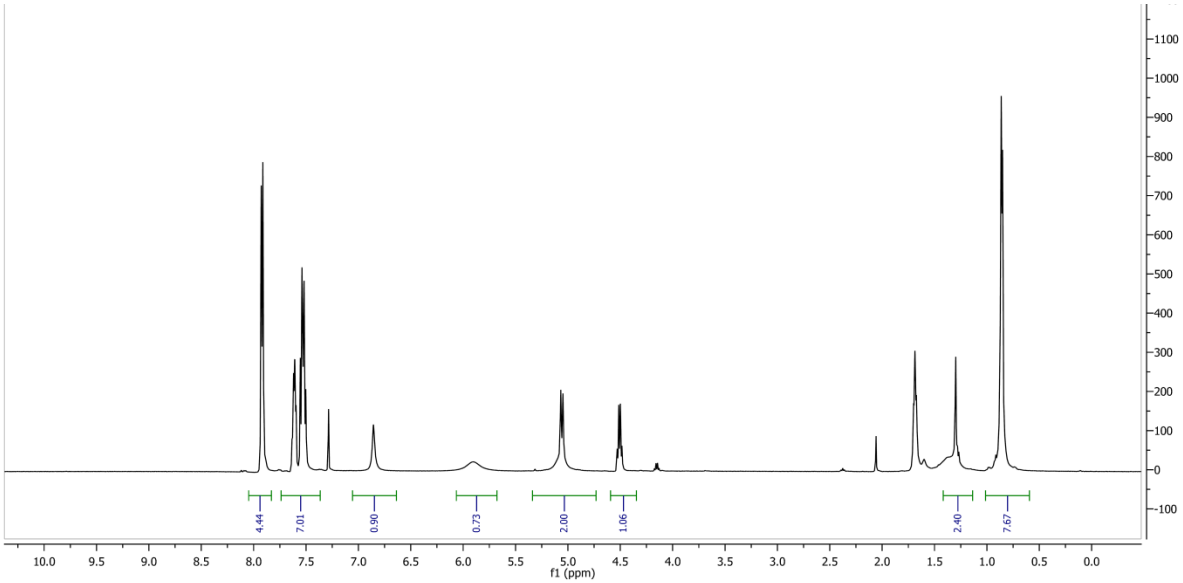
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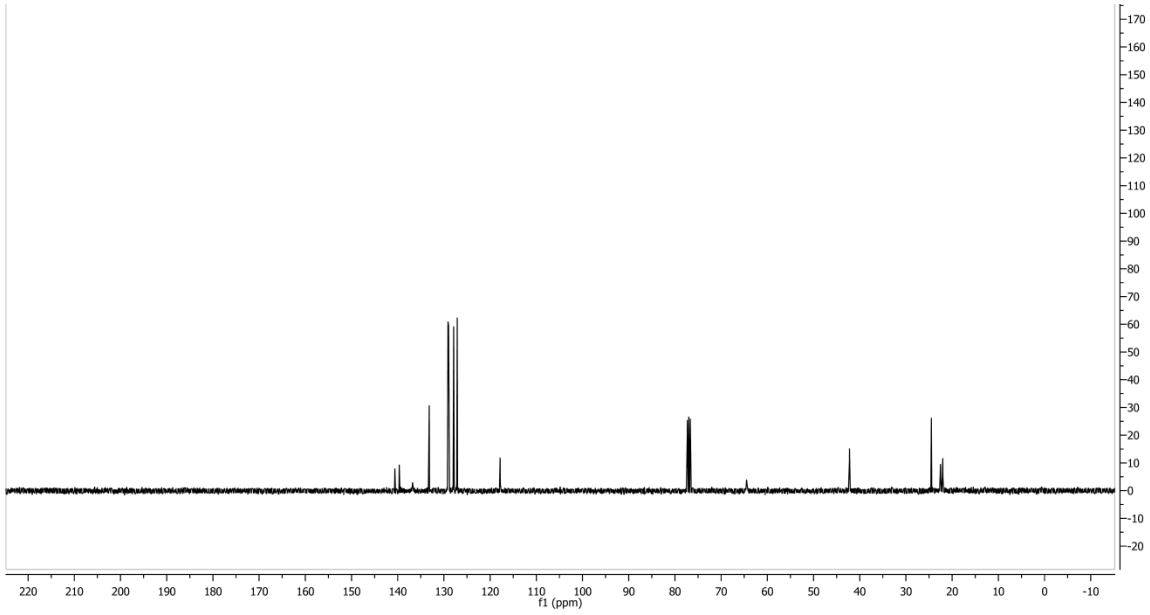
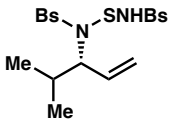
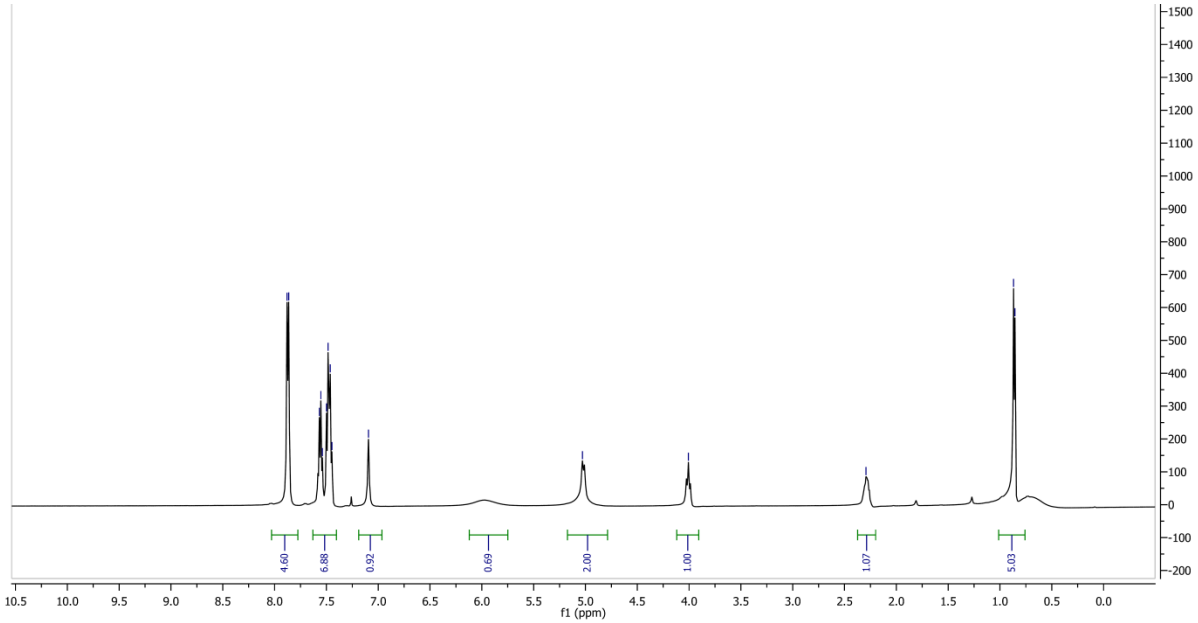
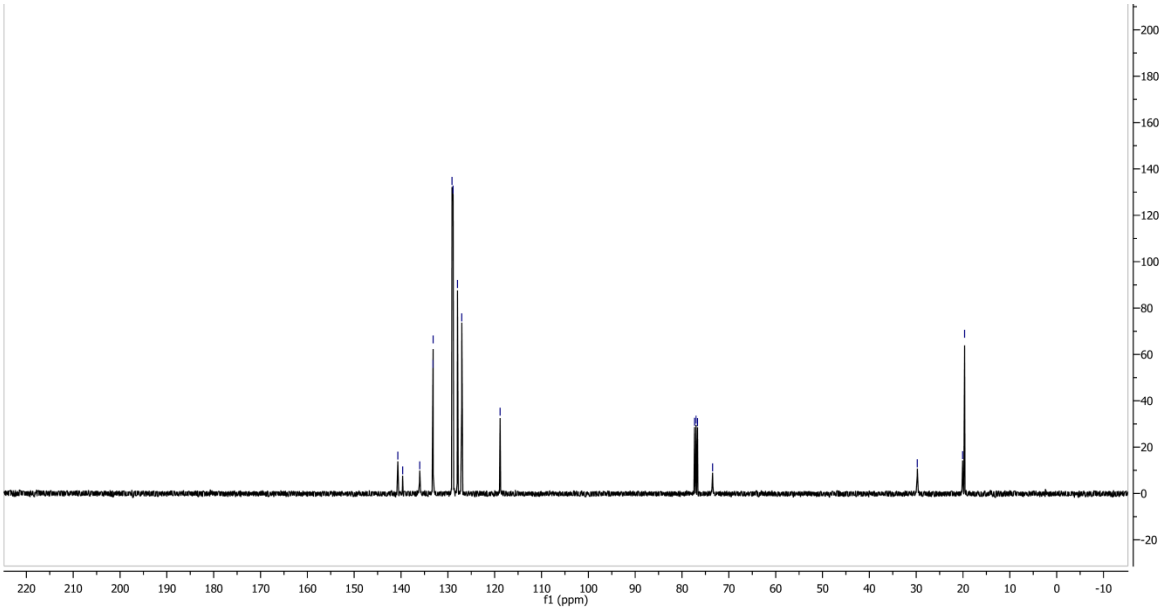
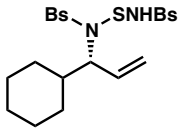
0.73
2.00
1.06
2.40
7.67
f1 (ppm)

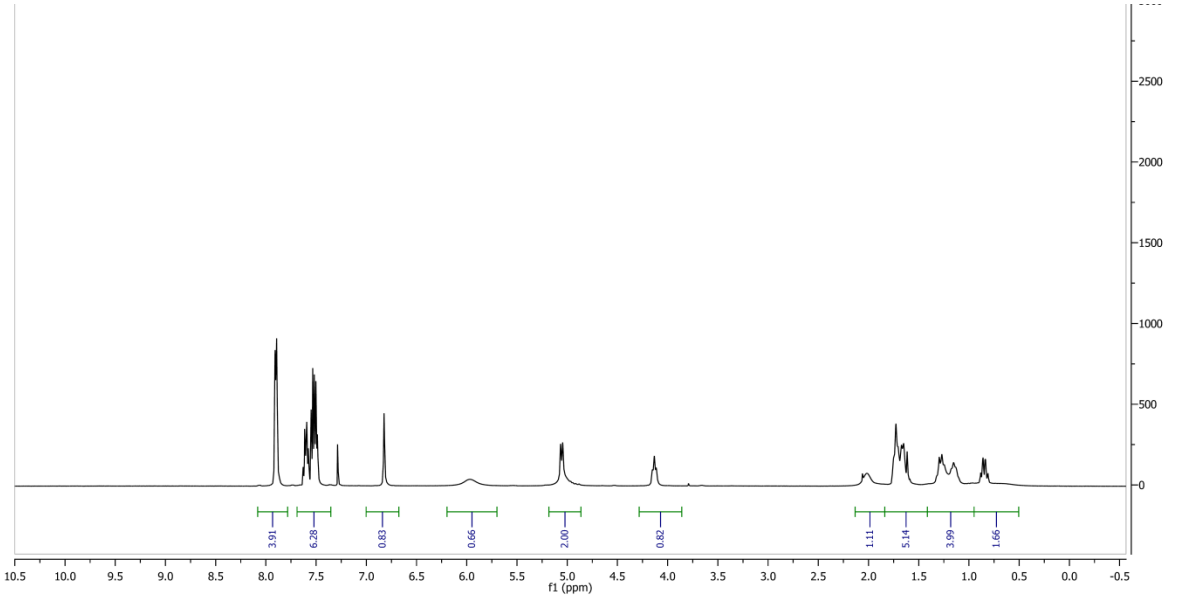

f1 (ppm)

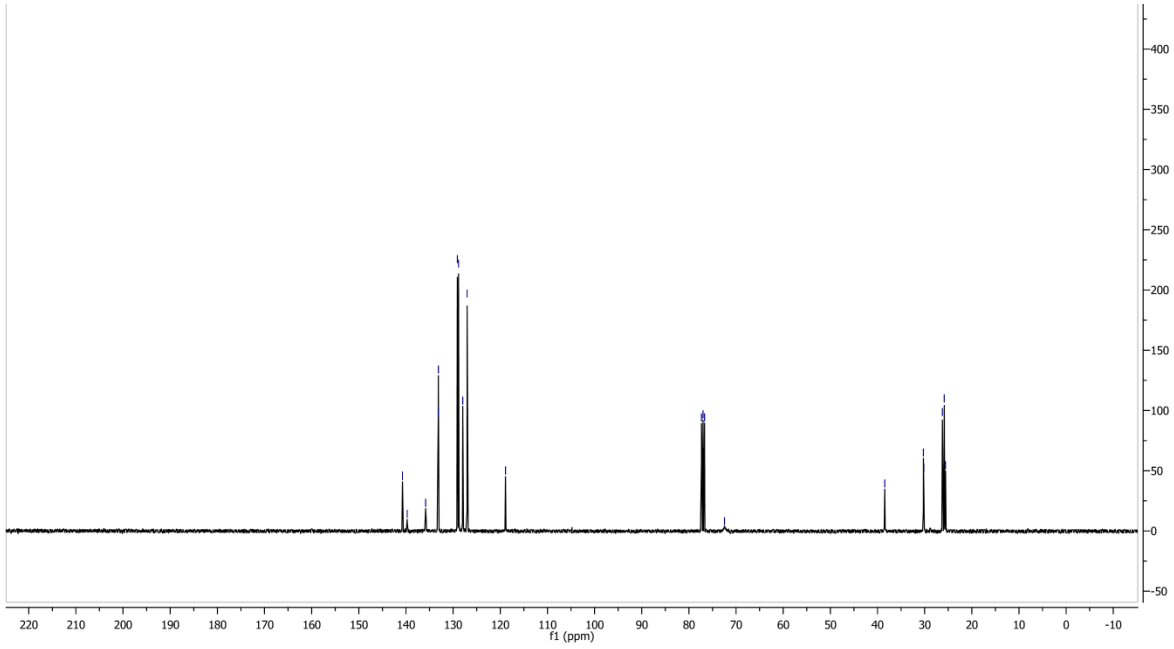

Bs
N
SNHBs
Me
Me

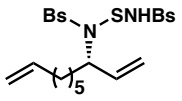

4.60
6.88
0.92
0.69
2.00
1.00
1.07
5.03
f1 (ppm)

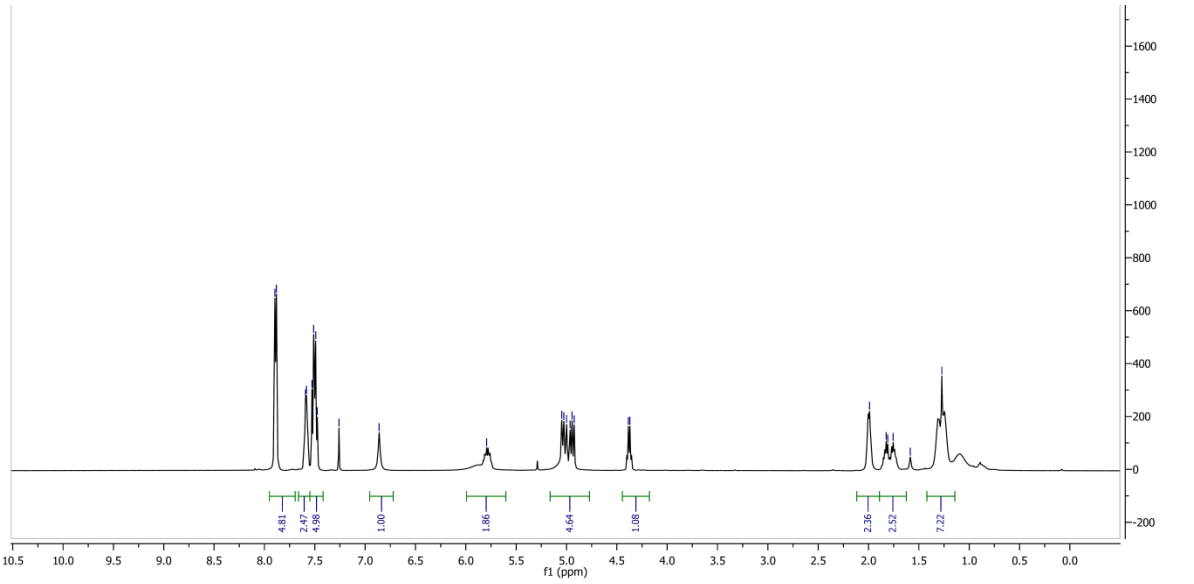

f1 (ppm)

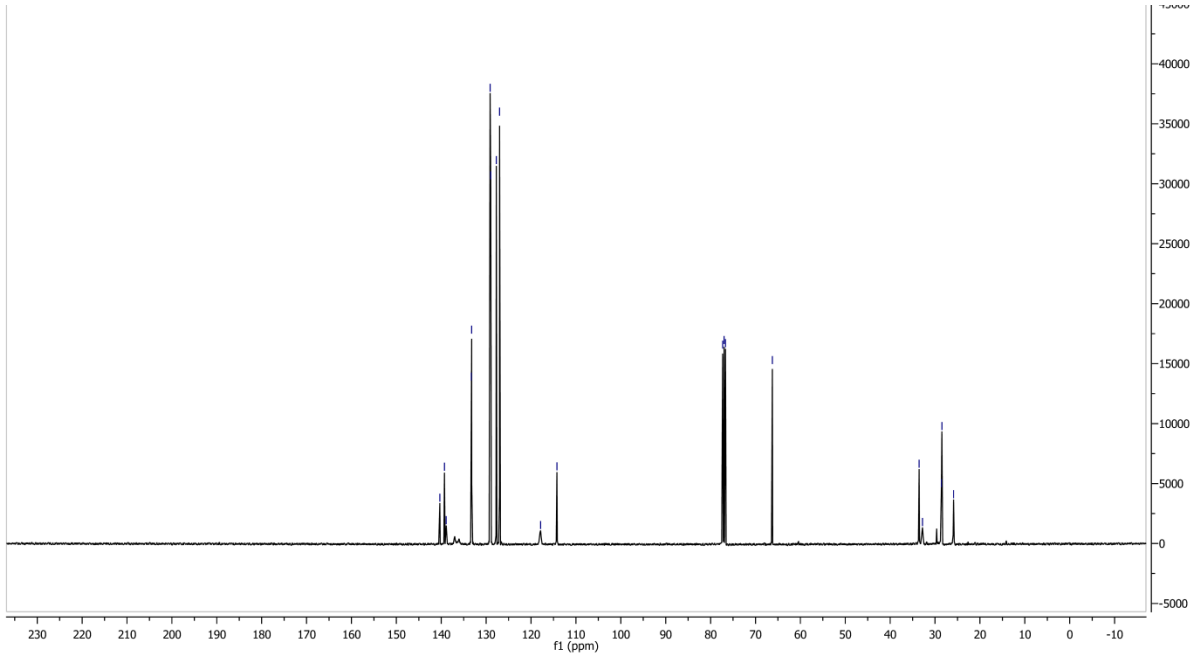

Bs
N
SNHBs


3.91
6.28
0.83
0.66
2.00
0.82
1.11
5.14
3.99
1.66
f1 (ppm)

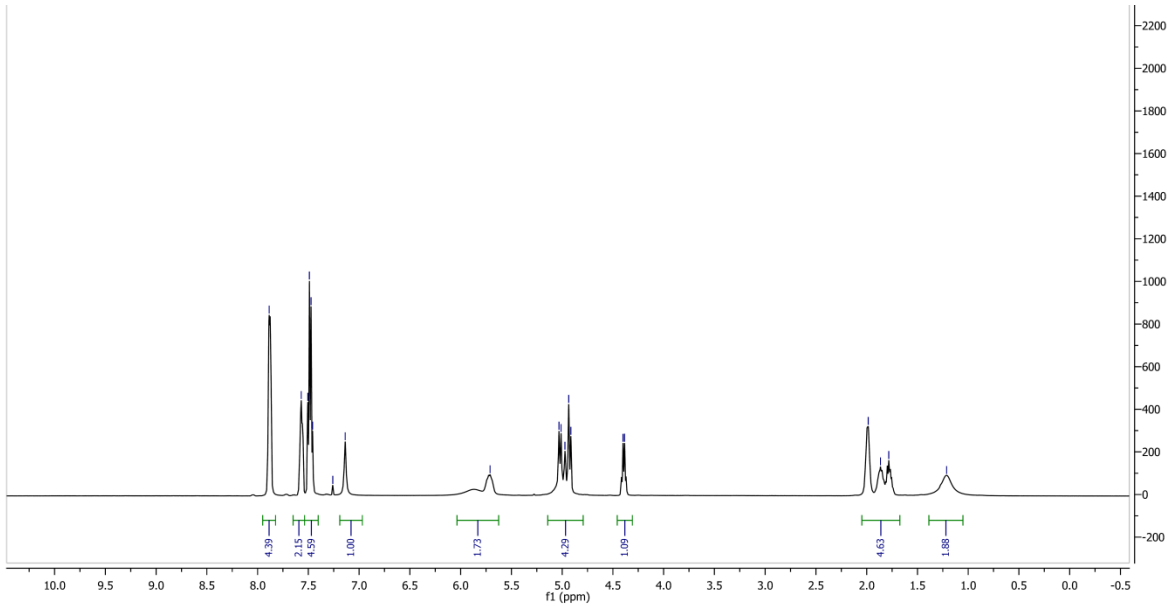

f1 (ppm)

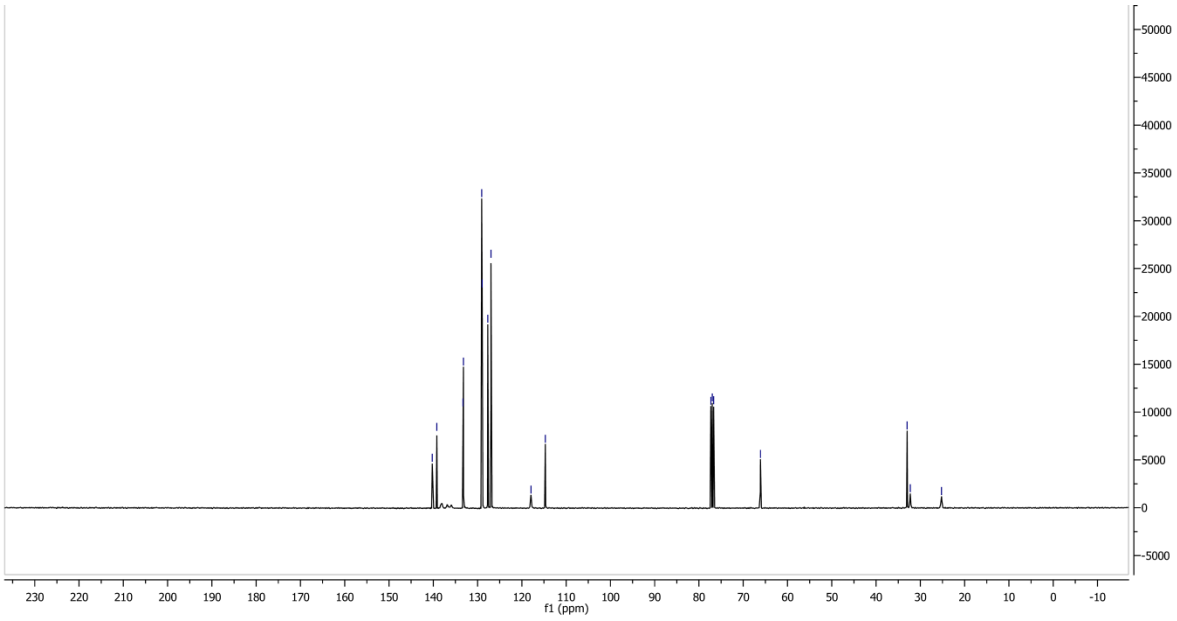

Bs
N
SNHBs
5

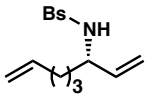

4.81
2.47
4.98
1.00
1.86
4.64
1.08
2.36
2.52
7.22
f1 (ppm)


f1 (ppm)

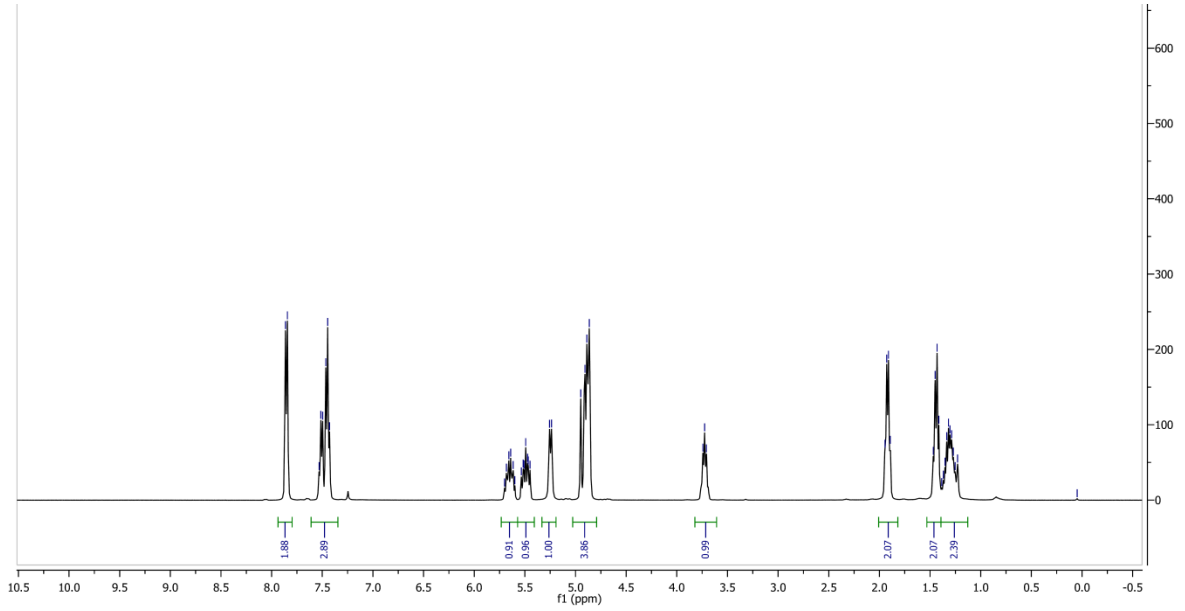

Bs
N
SNHBs
3

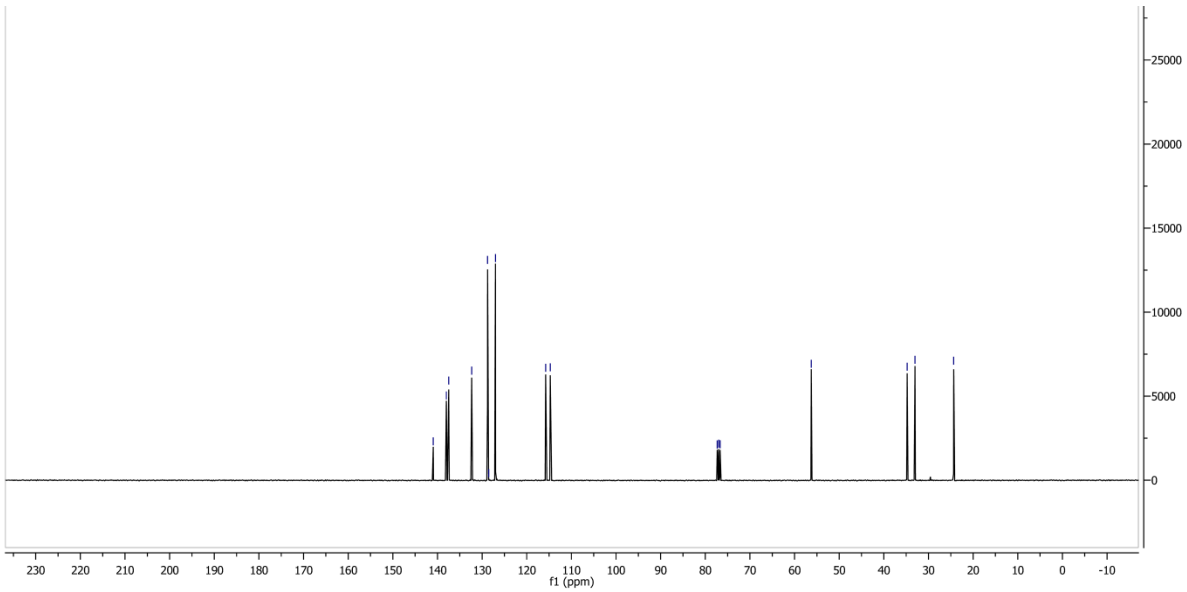

4.39
2.15
4.59
1.00
1.73
4.29
1.09
4.63
1.88
f1 (ppm)

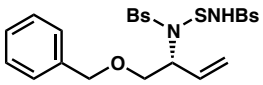

f1 (ppm)

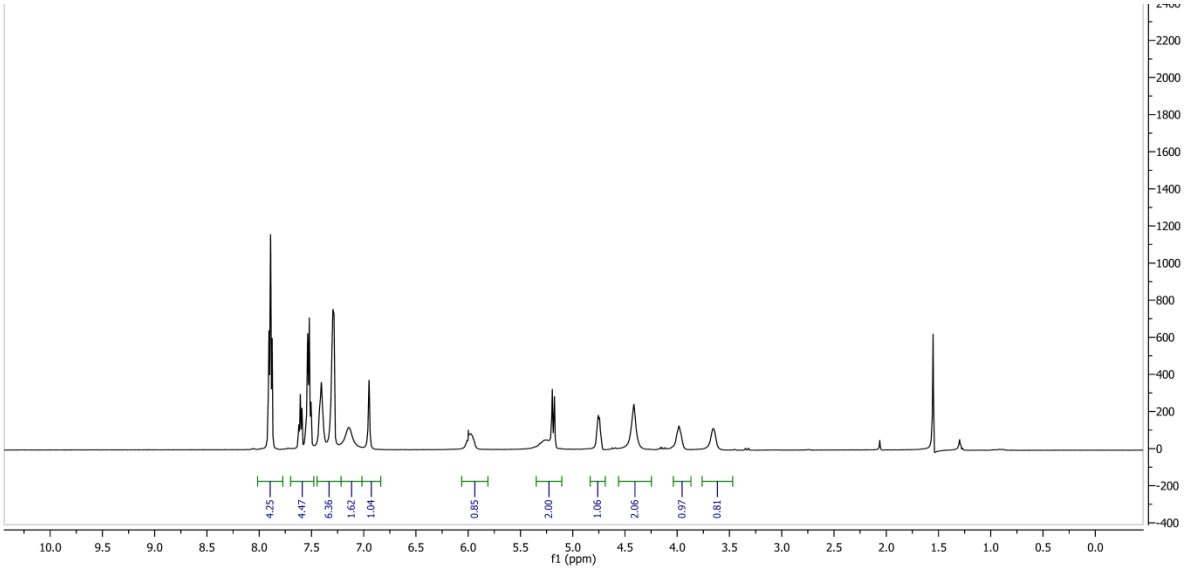


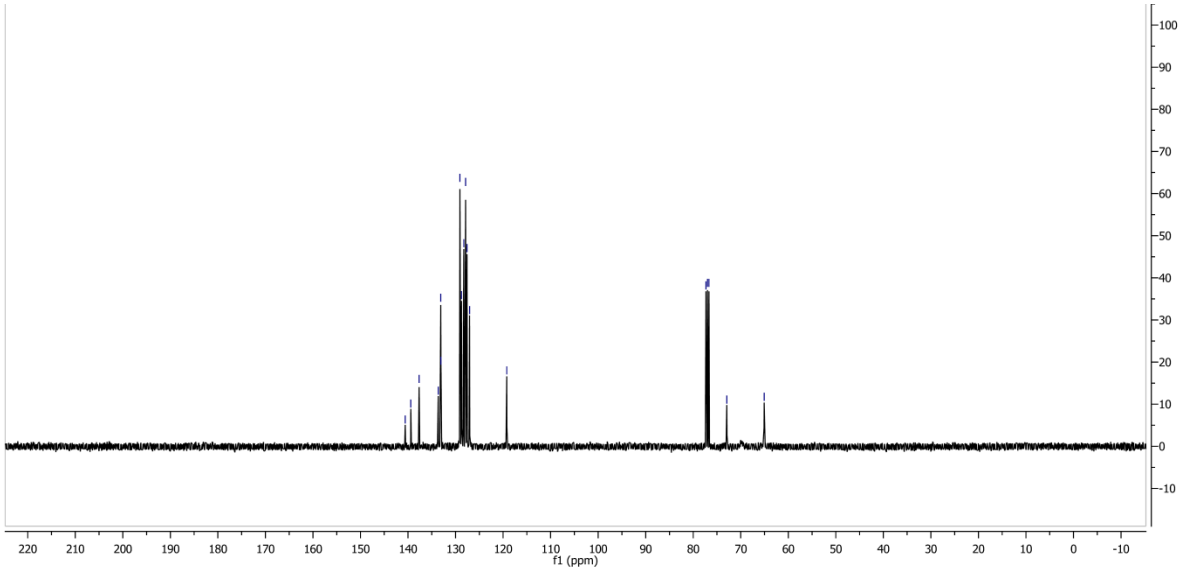
S3

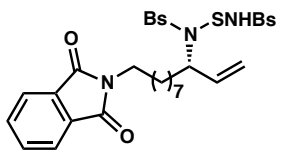


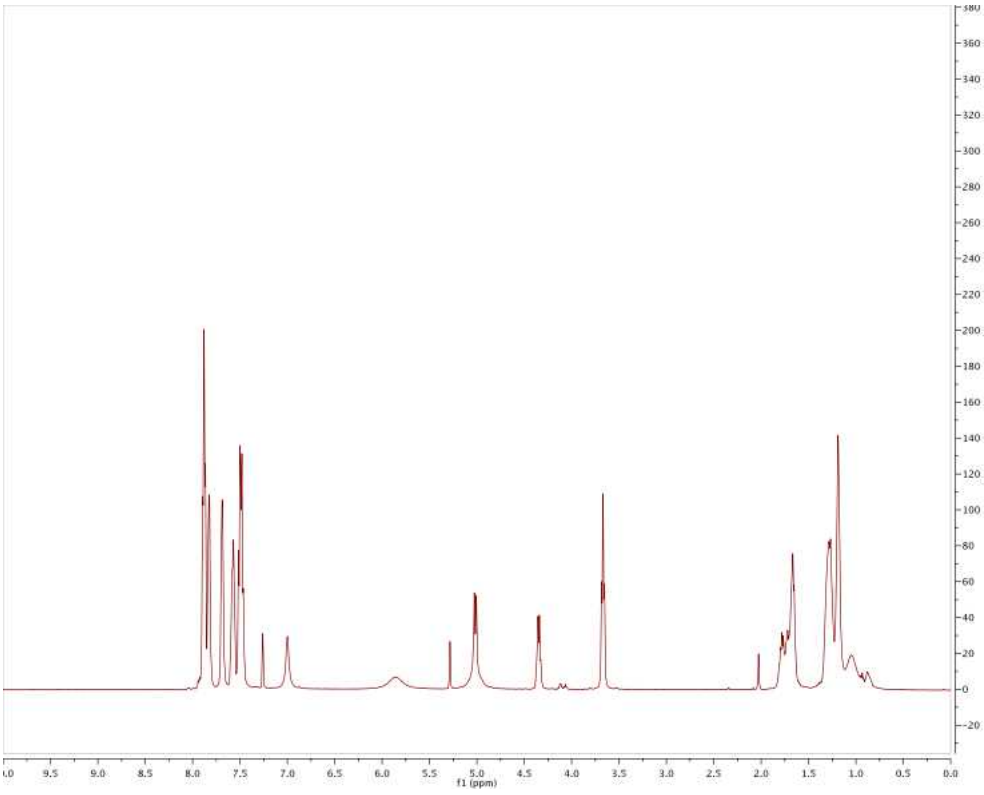


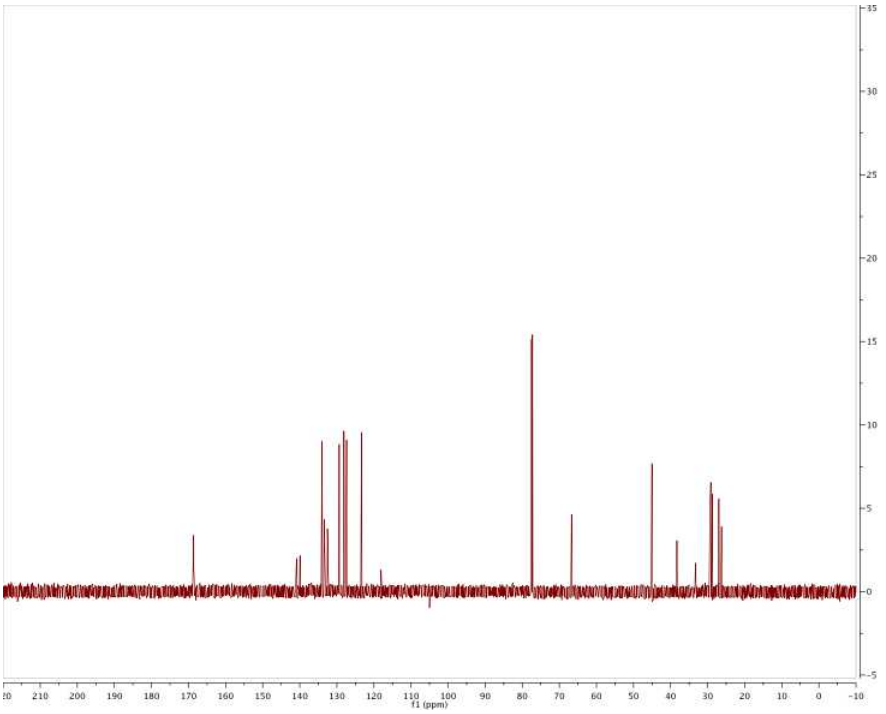

Bs
N
SNHBs
O

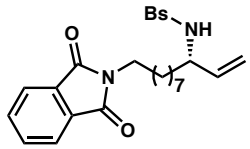

4.25
4.47
6.36
1.62
1.04
0.85
2.00
1.06
2.06
0.97
0.81
f1 (ppm)


f1 (ppm)

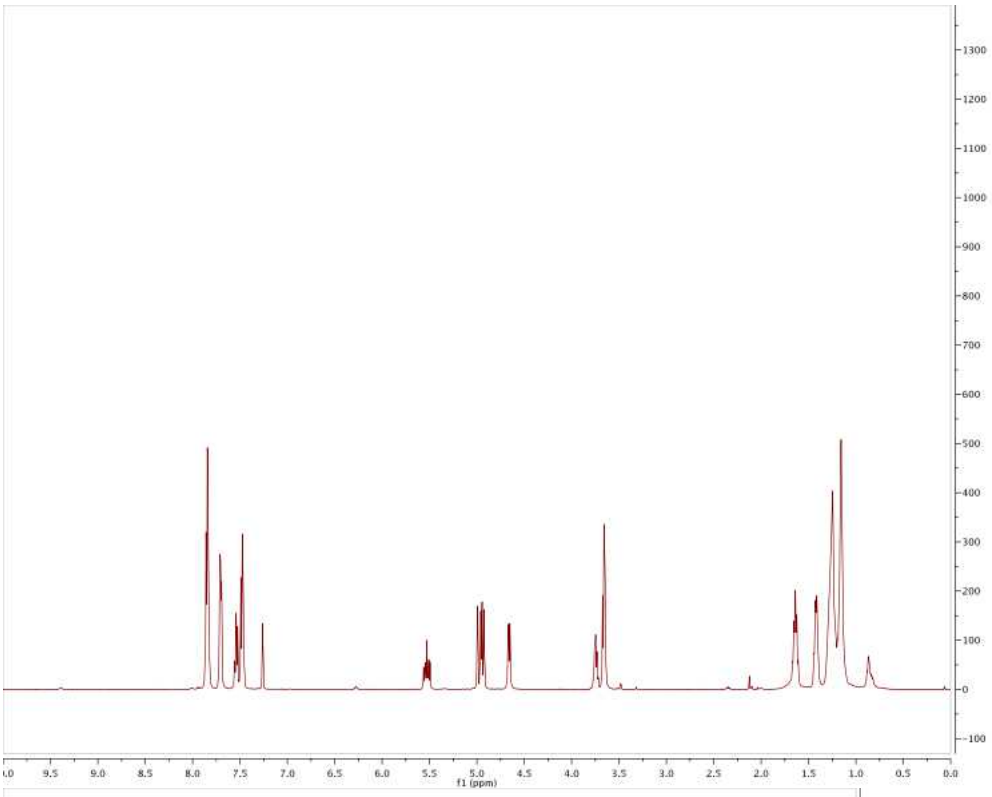

Bs
N
SNHBs
O
N
7
O

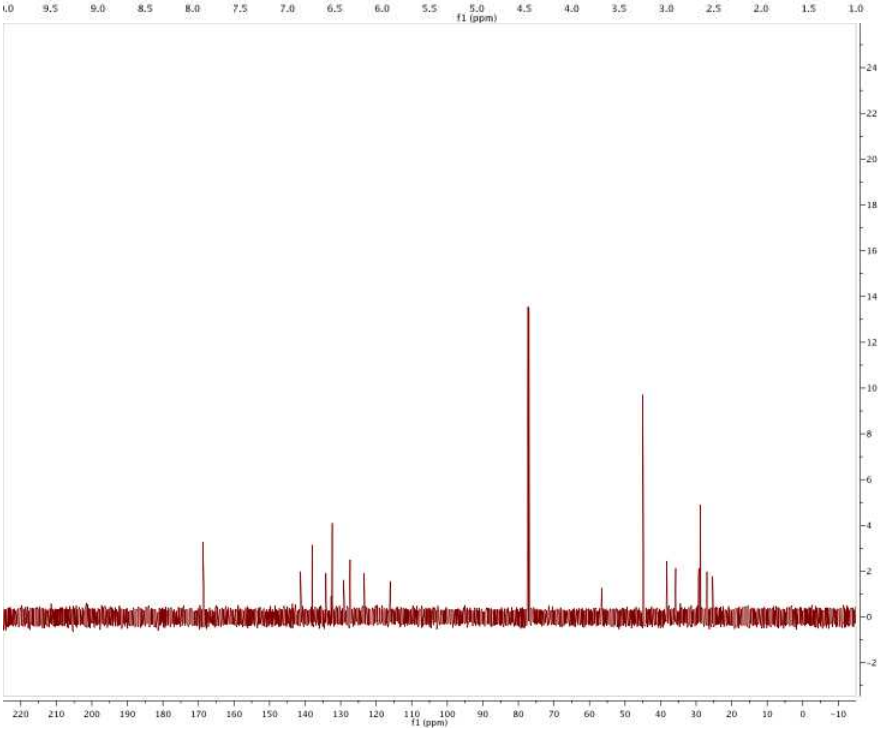

f1 (ppm)

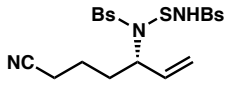

f1 (ppm)

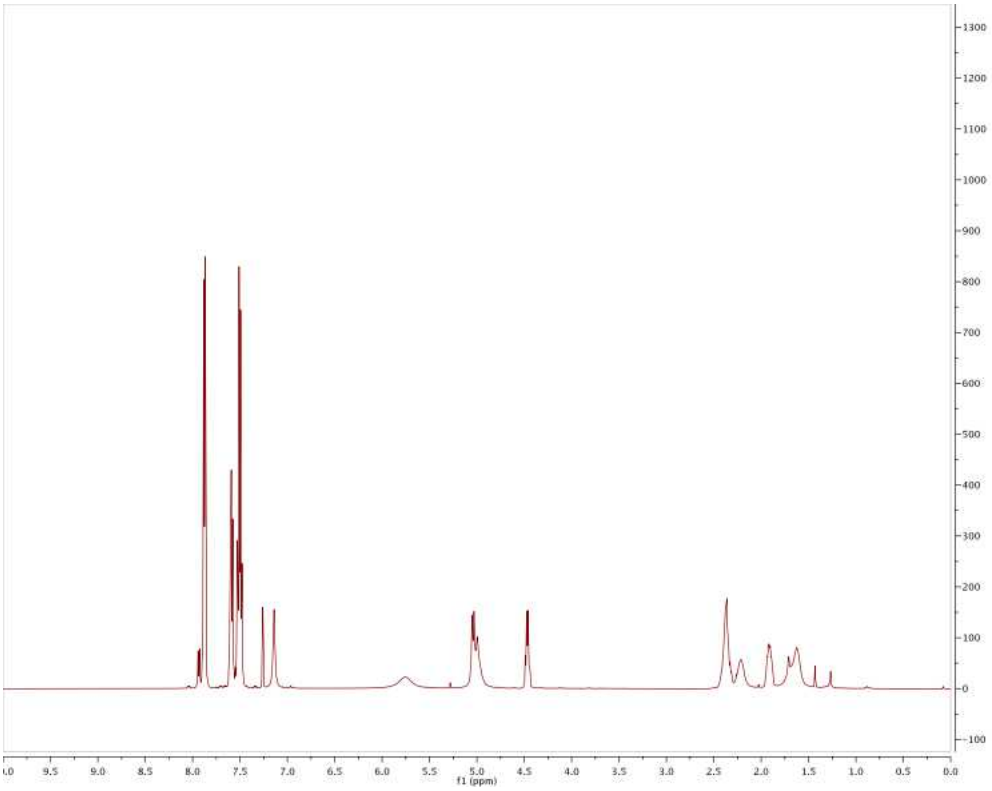


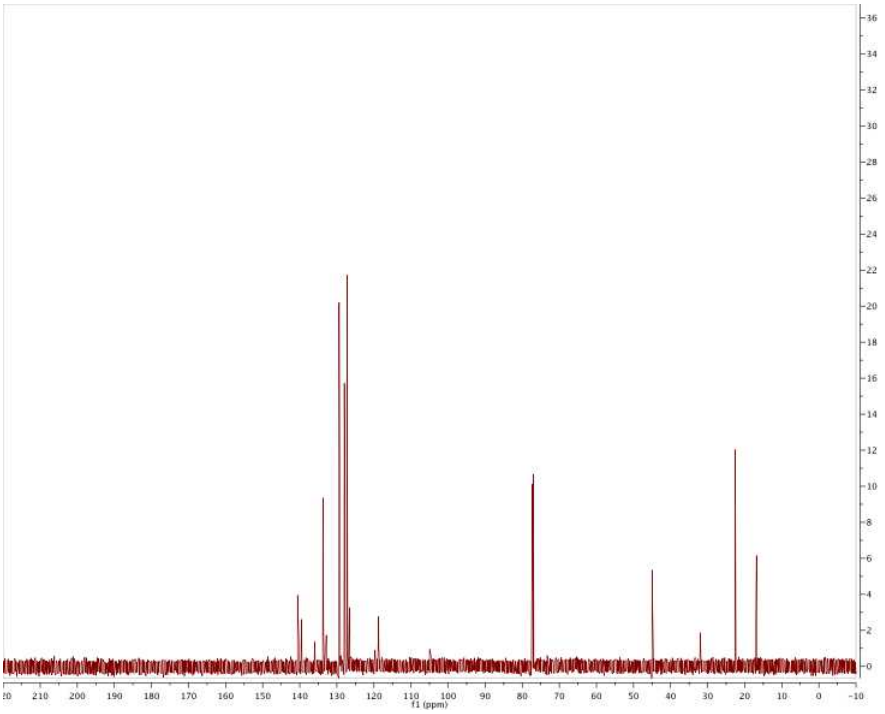
S4

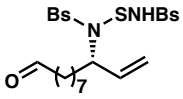


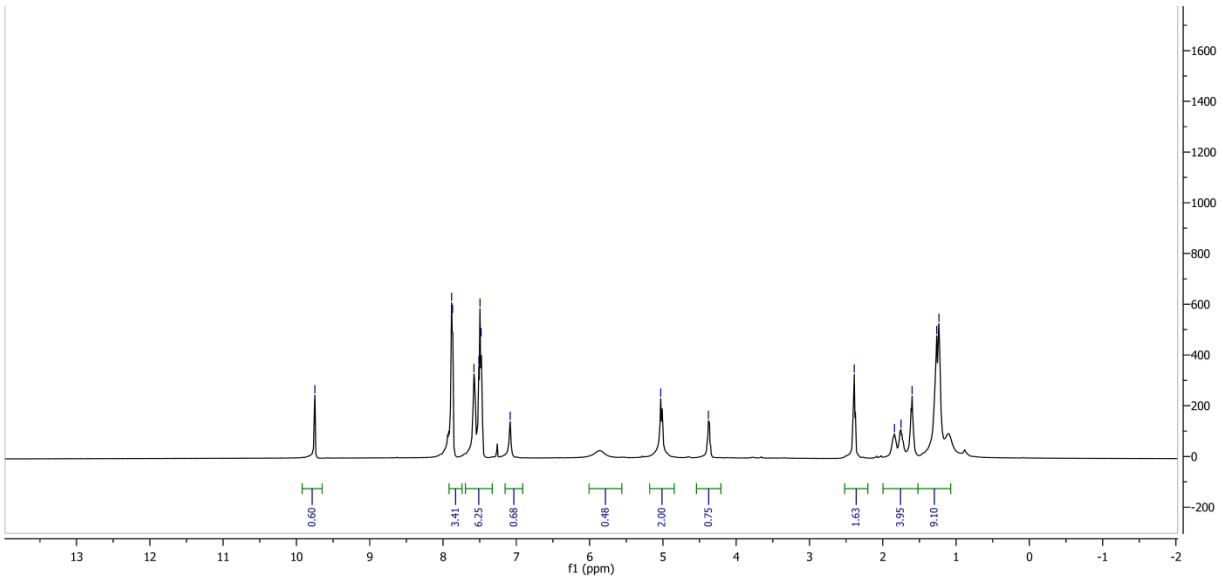


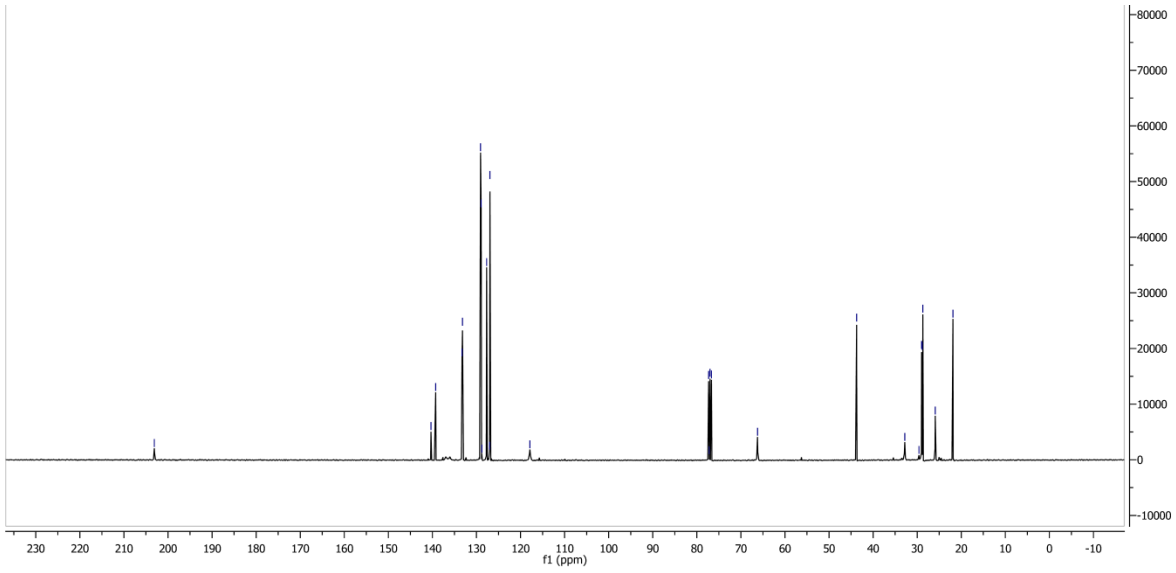

Bs
N
SNHBs
NC

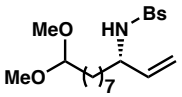

f1 (ppm)


f1 (ppm)

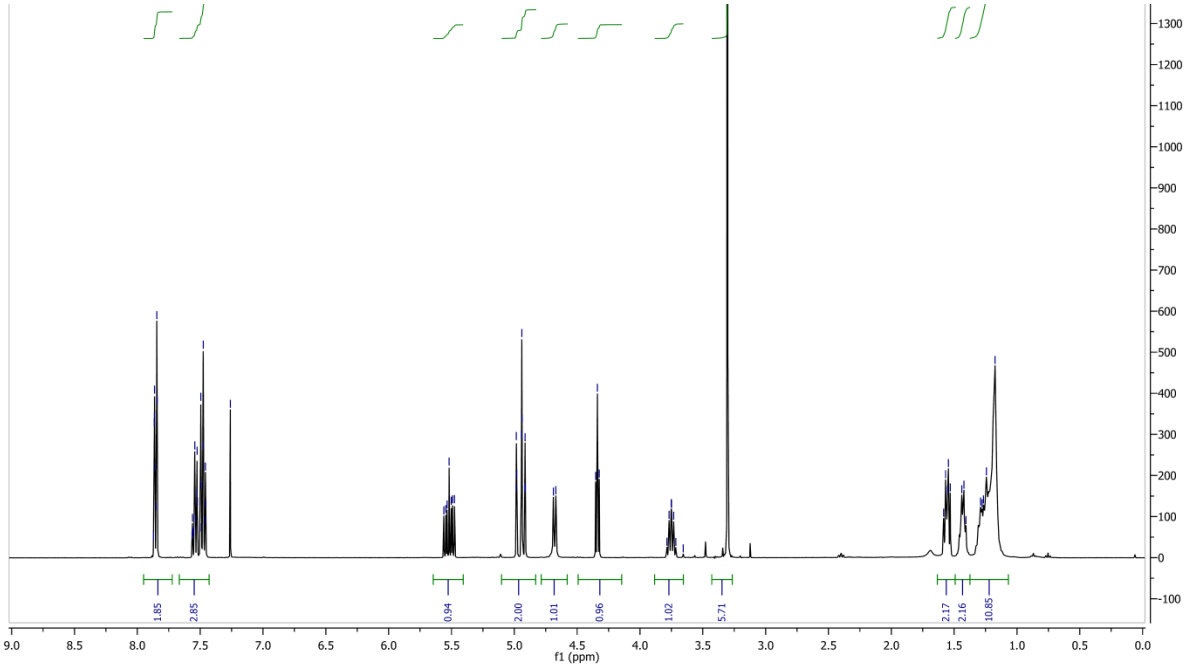

Bs
N
SNHBs
O
7

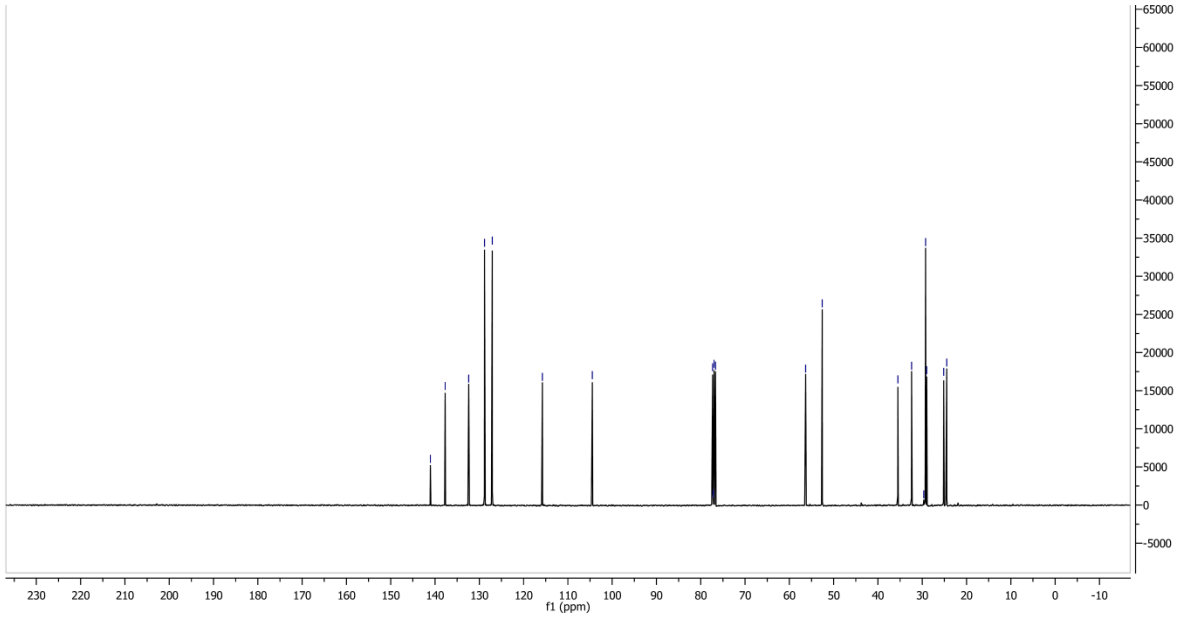

0.60
3.41
6.25
0.68
0.48
2.00
0.75
1.63
3.95
9.10
f1 (ppm)

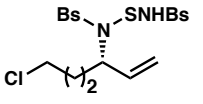

f1 (ppm)

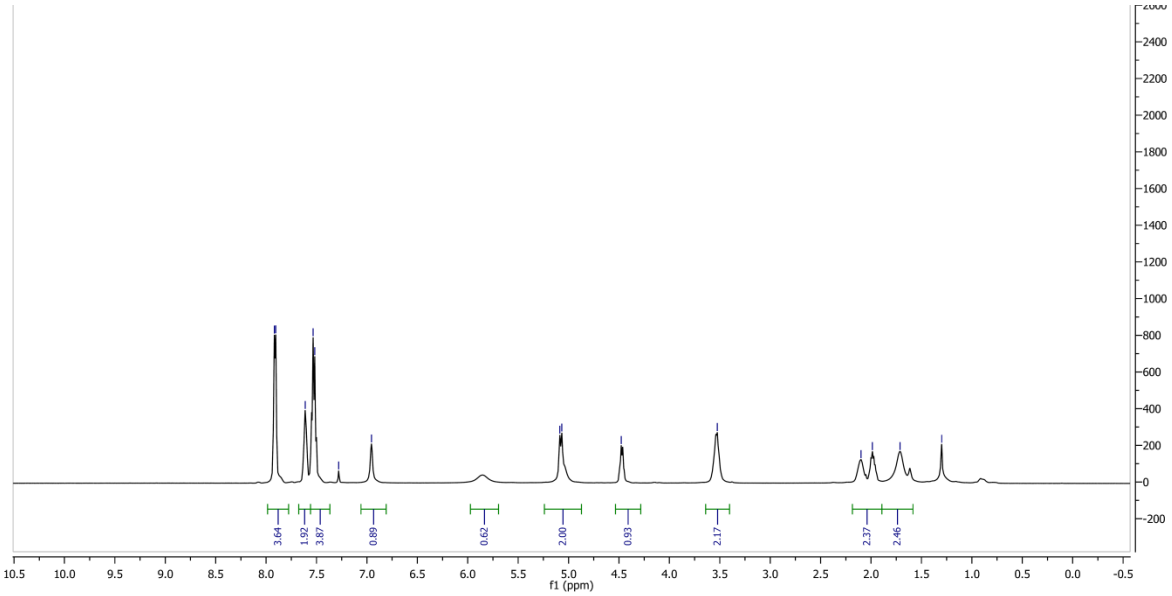

MeO
HN
Bs
MeO
7

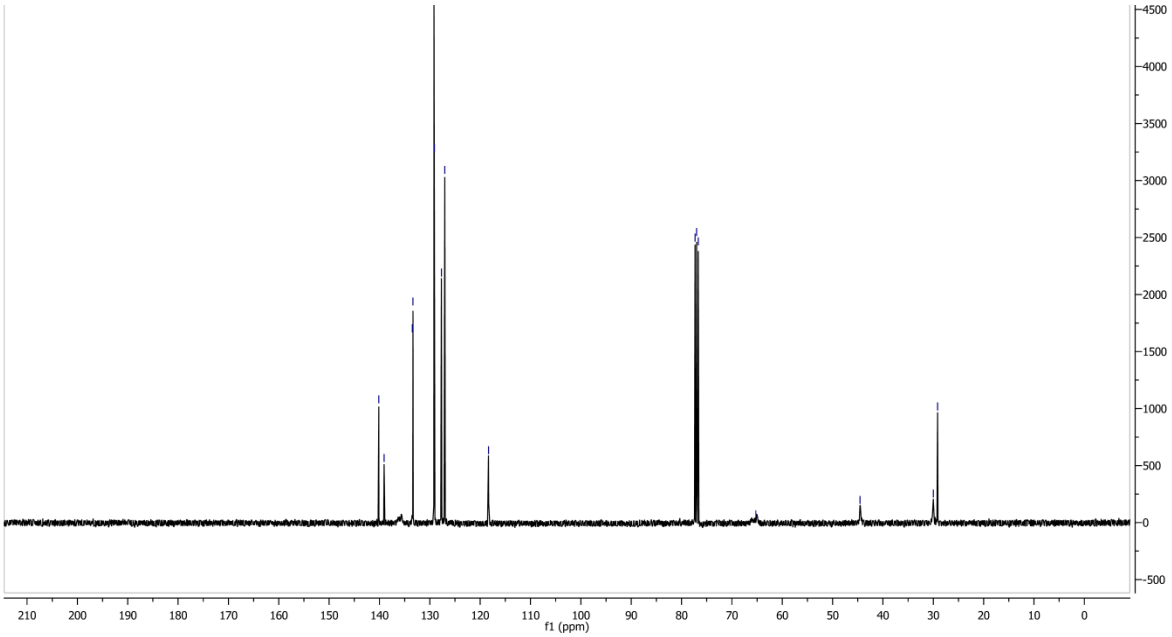
S4

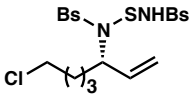

1.85
2.85
0.94
2.00
1.01
0.96
1.02
5.71
2.17
2.16
10.85
f1 (ppm)

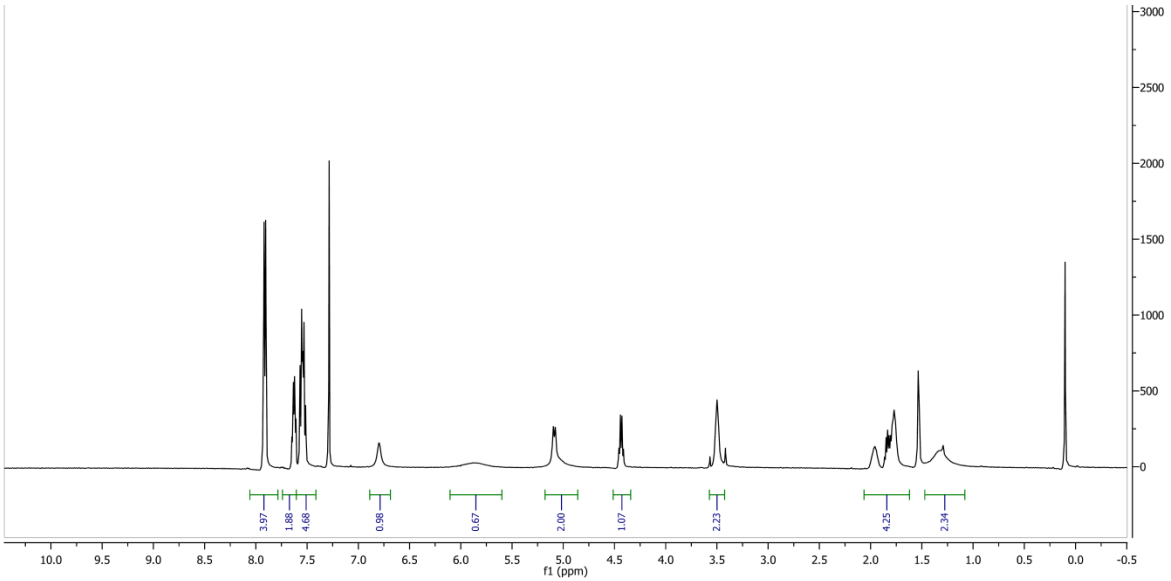

f1 (ppm)

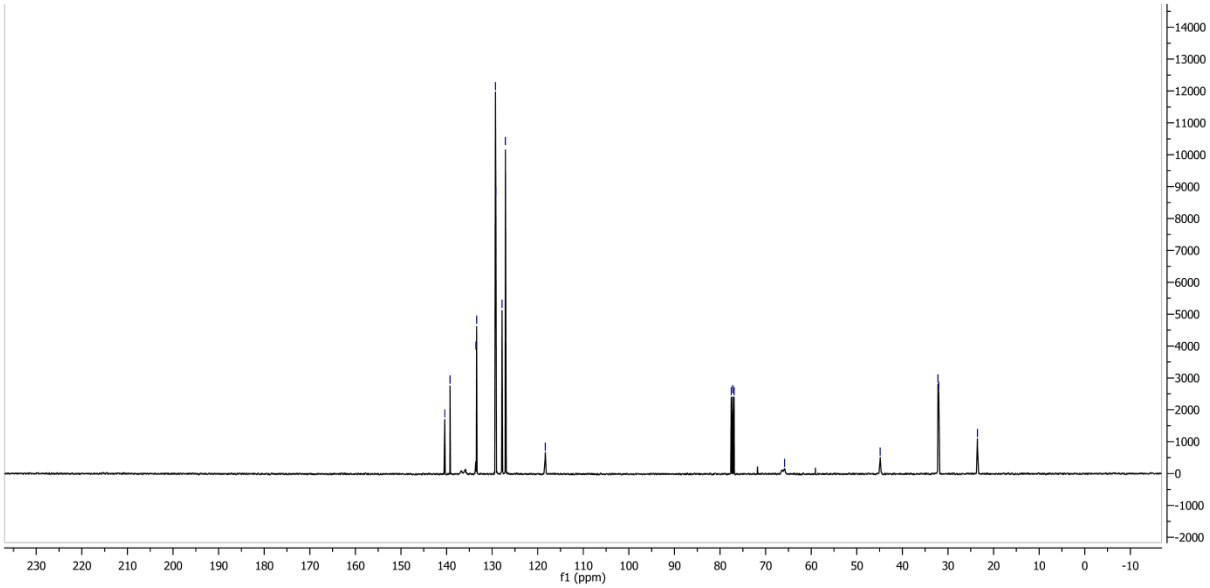

Bs
N
SNHBs
Cl
2

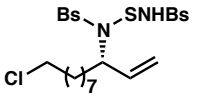

3.64
1.92
3.87
0.89
0.62
2.00
0.93
2.17
2.37
2.46
f1 (ppm)

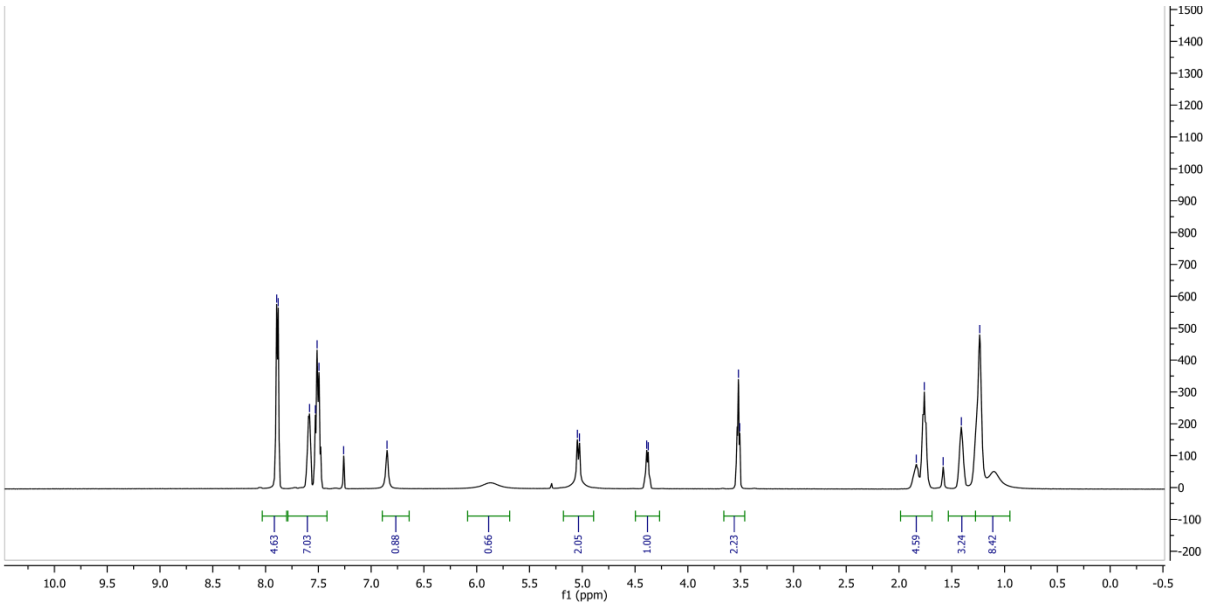

f1 (ppm)

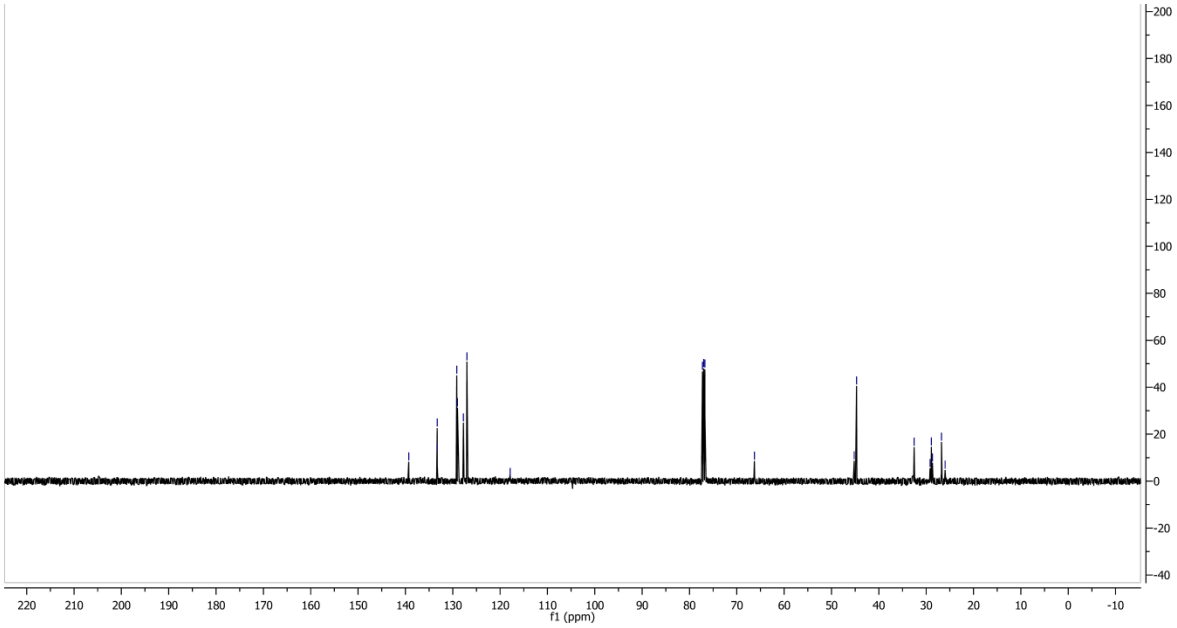

Bs
N
SNHBs
Cl
3

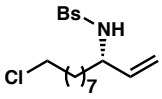

3.97
1.88
4.68
0.98
0.67
2.00
1.07
2.23
4.25
2.34
f1 (ppm)


f1 (ppm)

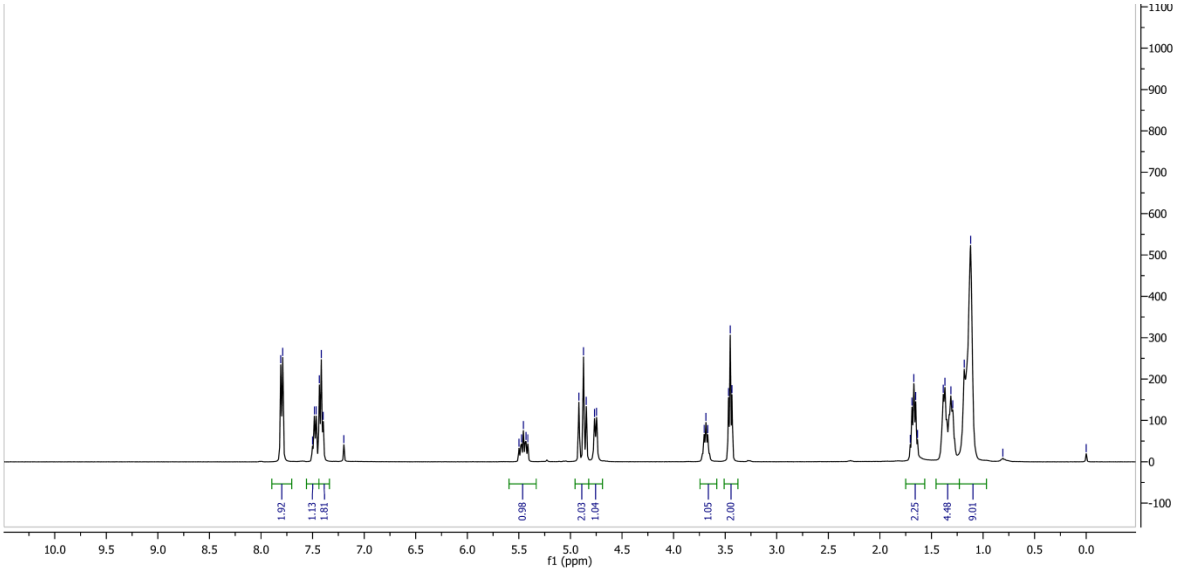

Bs
N
SNHBs
Cl
7

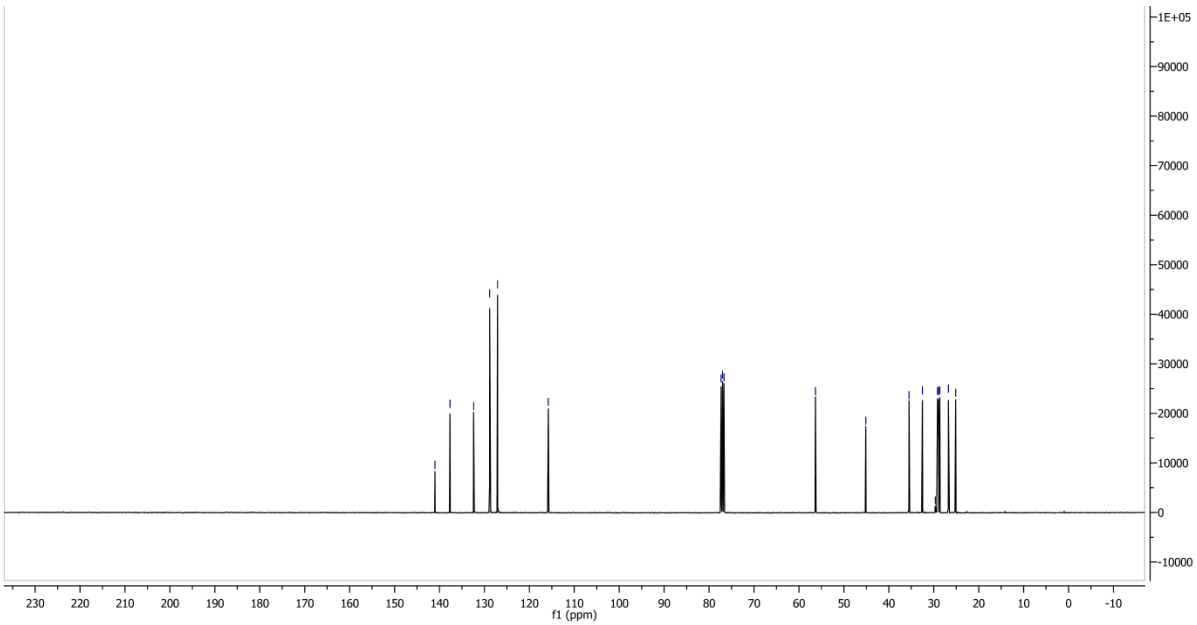

4.63
7.03
0.88
0.66
2.05
1.00
2.23
4.59
3.24
8.42
f1 (ppm)

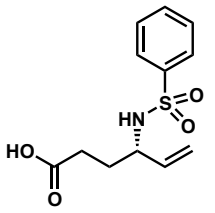

f1 (ppm)


Bs
NH
Cl
7

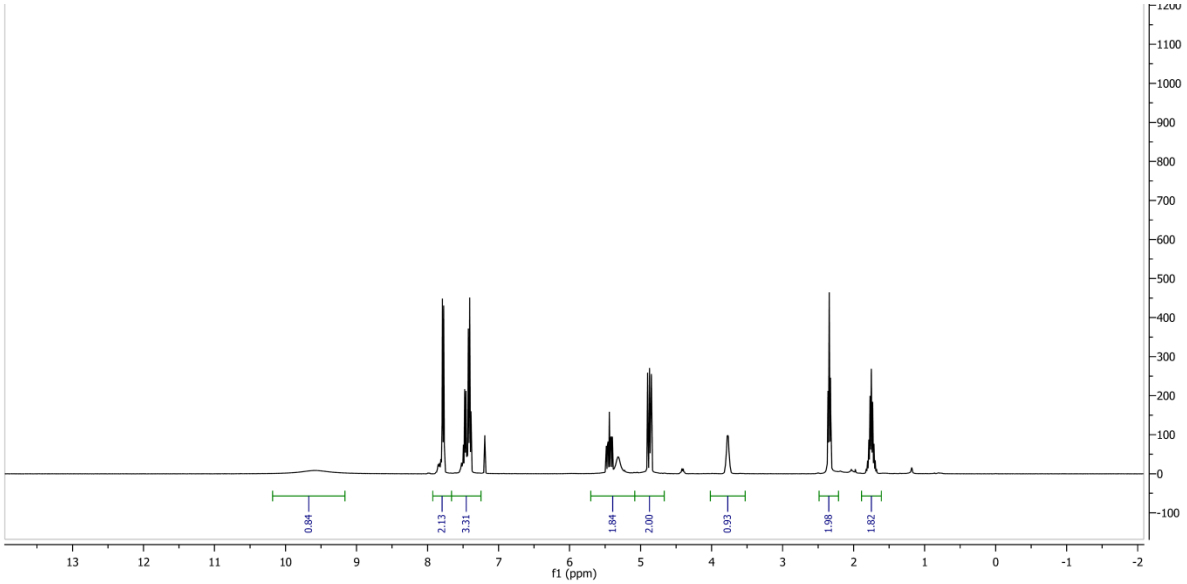
S5

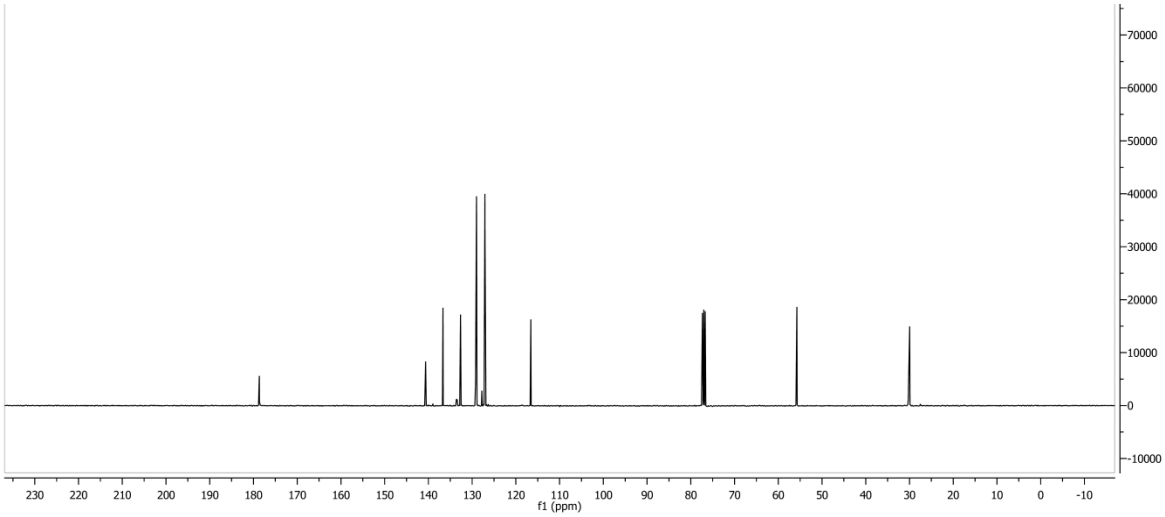

1.92
1.13
1.81
0.98
2.03
1.04
1.05
2.00
2.25
4.48
9.01
f1 (ppm)

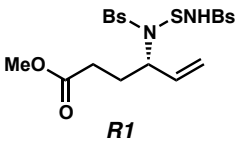

f1 (ppm)



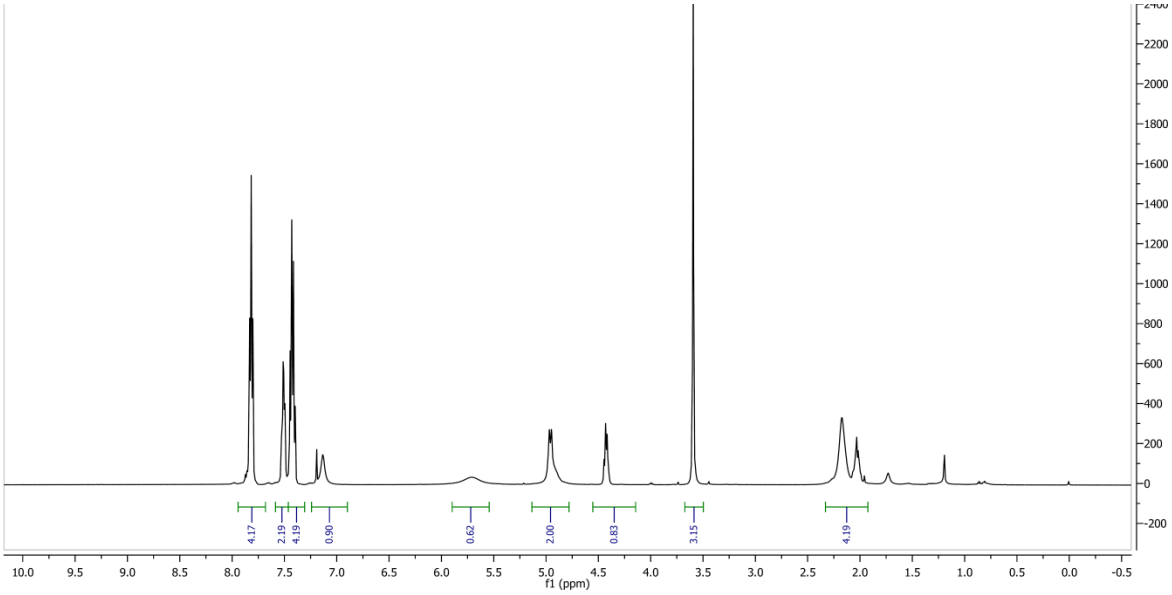
9

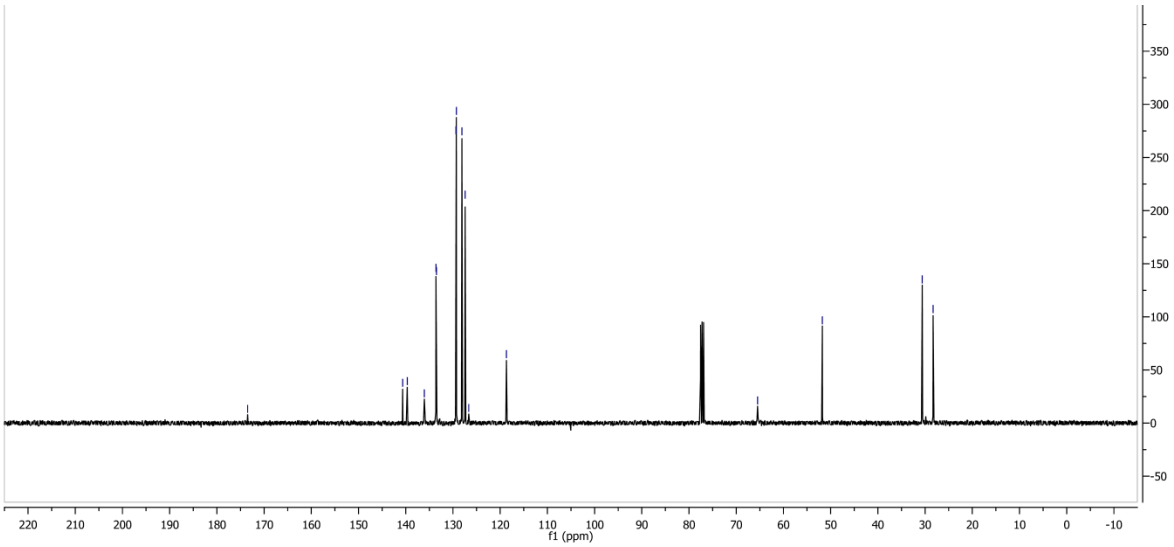


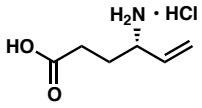




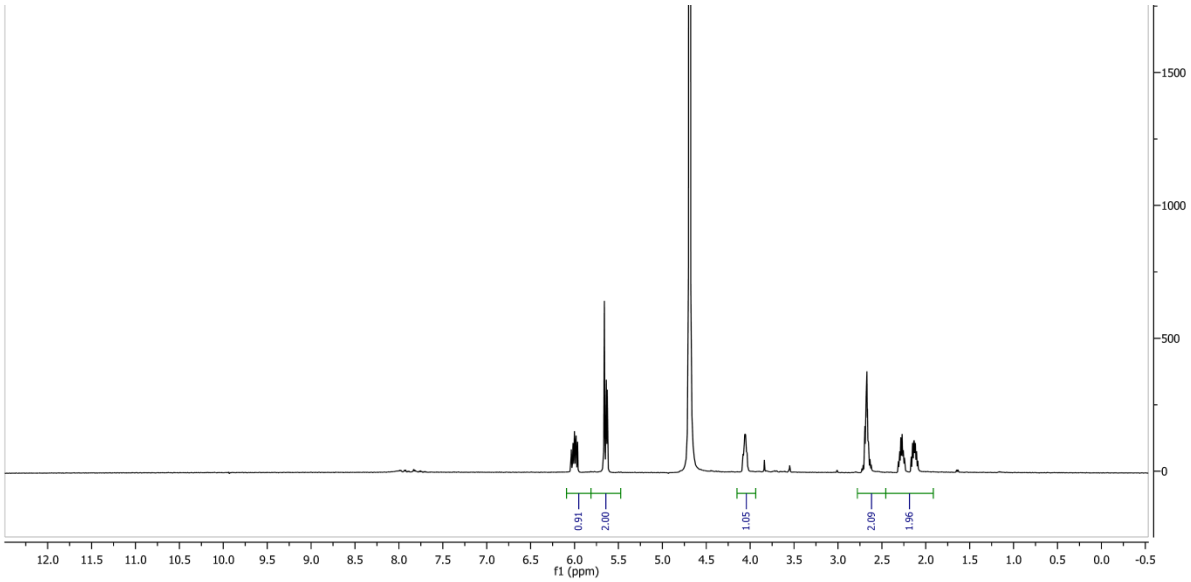
R1

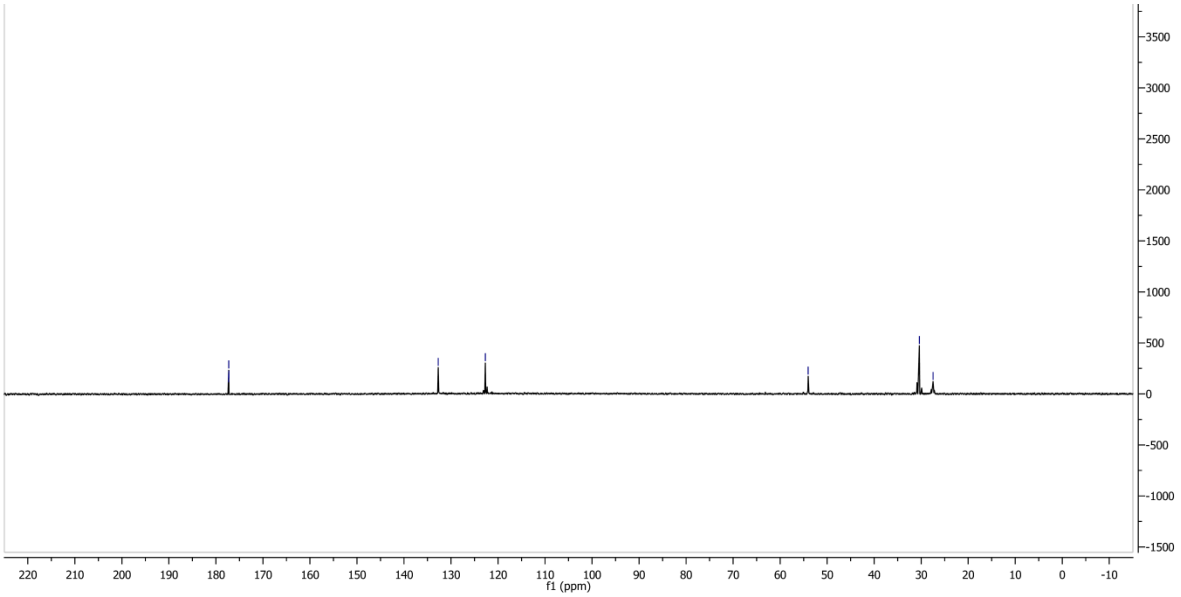




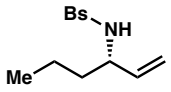


Vigabatrin (10)



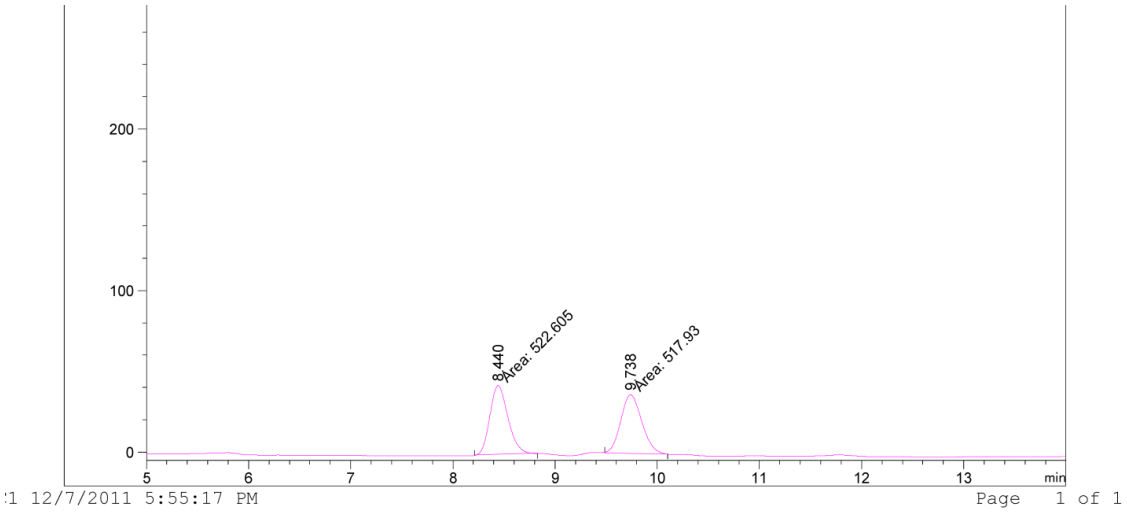


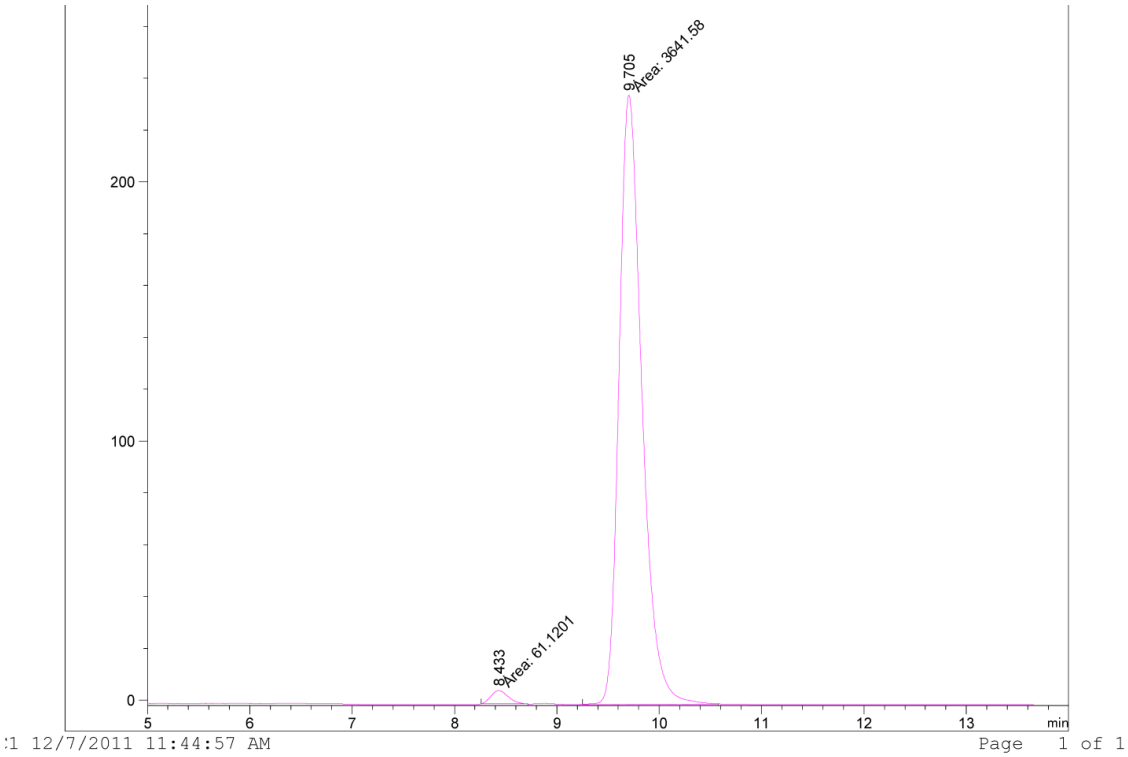
HPLC Traces of Products

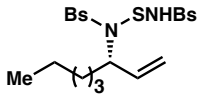


S2

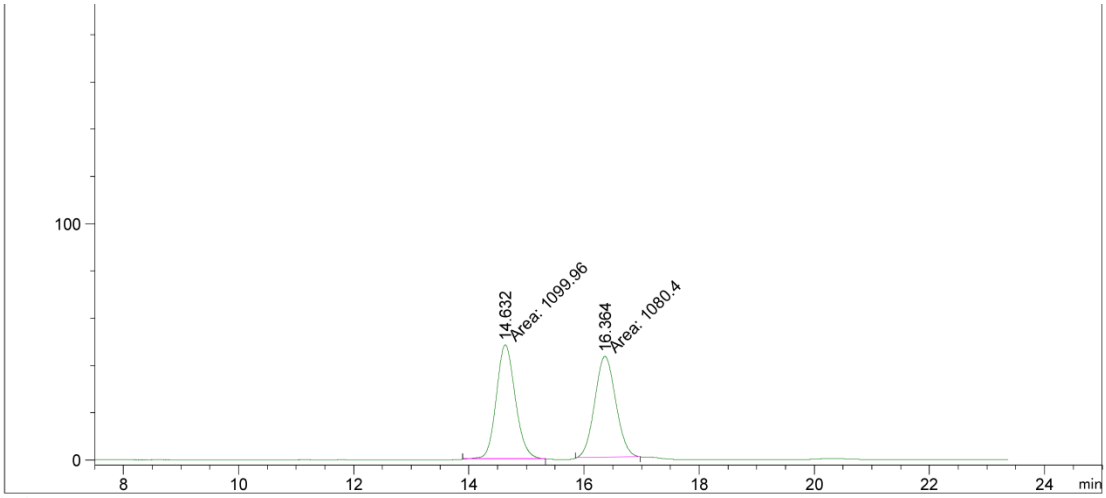
OD-H, 90/10 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 97% ee.







AD-H, 80/20 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 97% ee.



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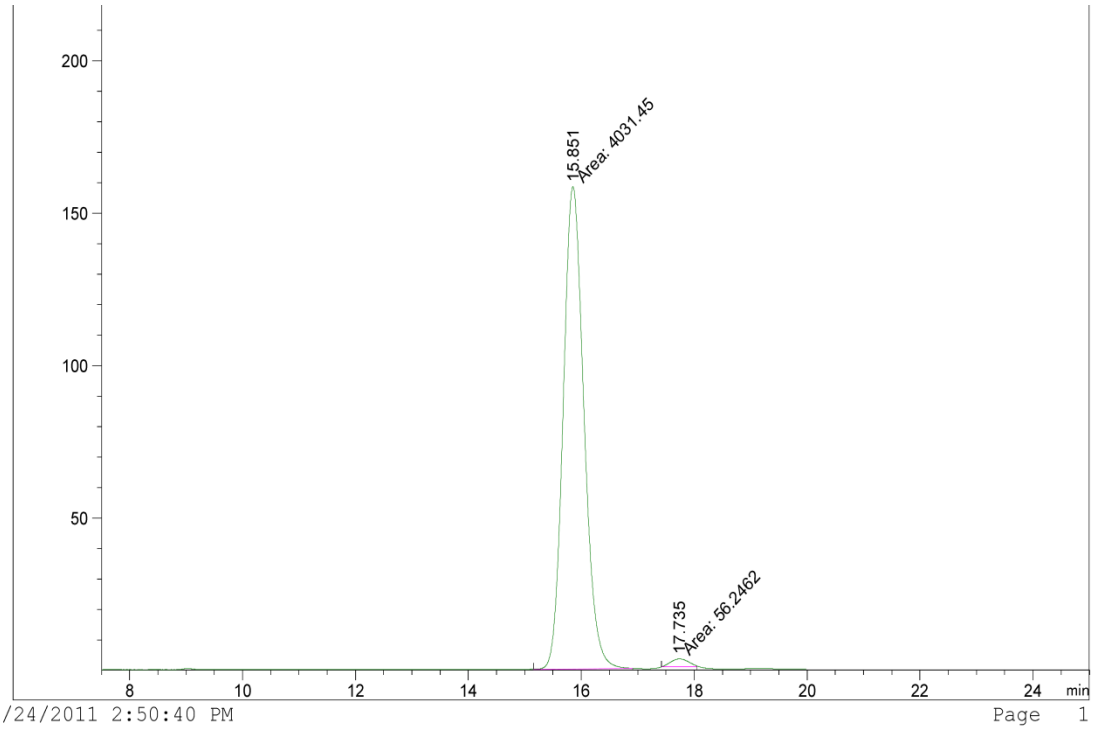

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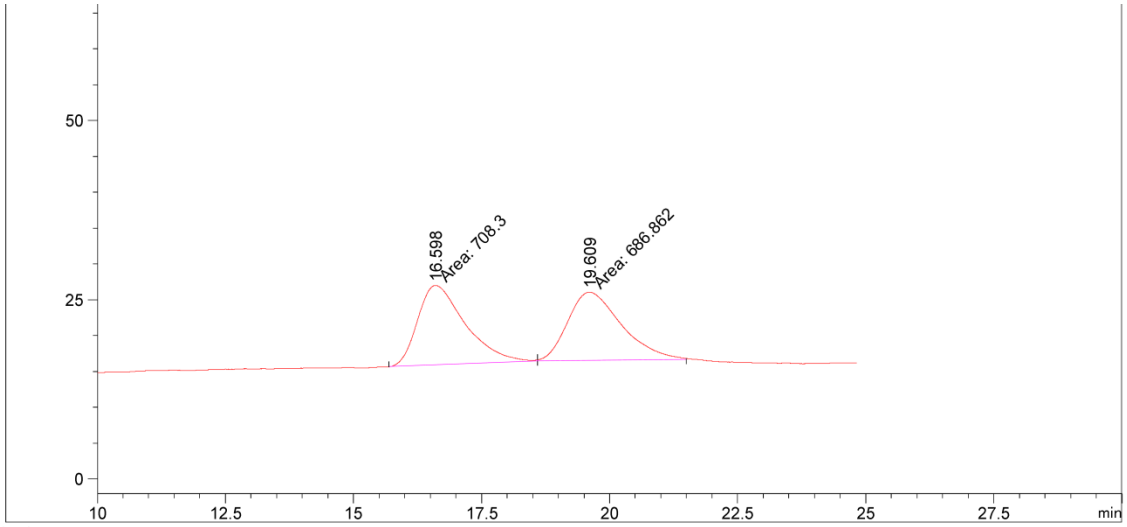
OD-H 96/4 Hx/*i*PrOH, 1.0 mL/min, 230 nm, 98%ee



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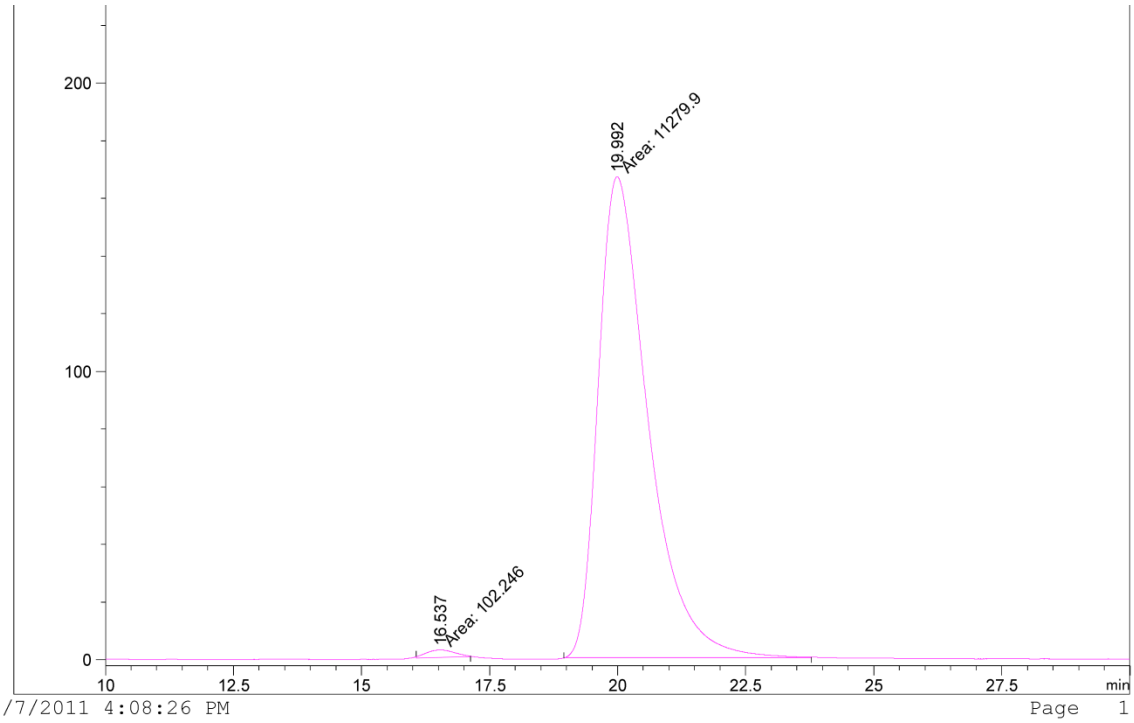

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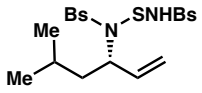
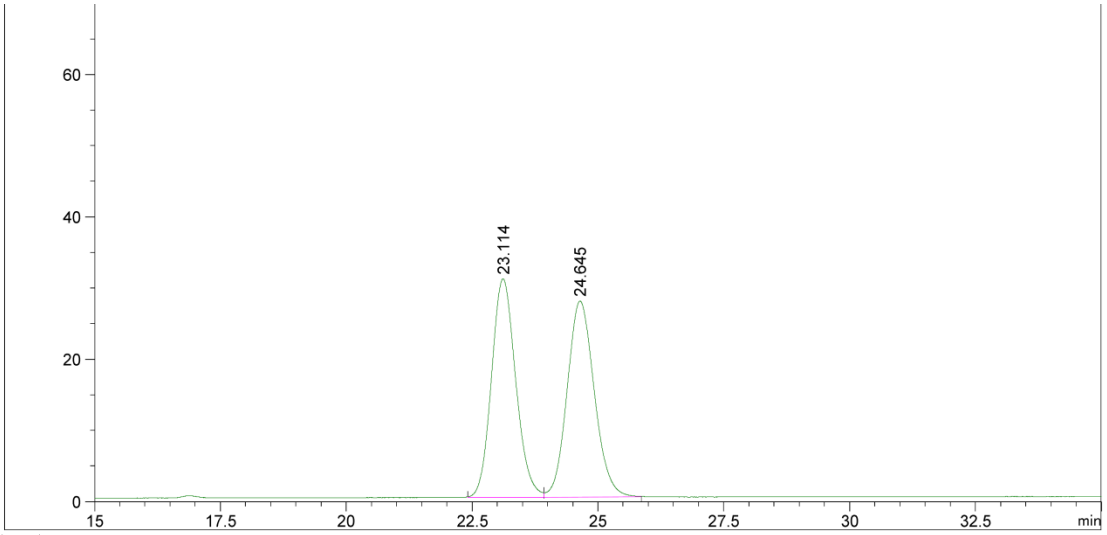


AD-H 90/10 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 98%ee.



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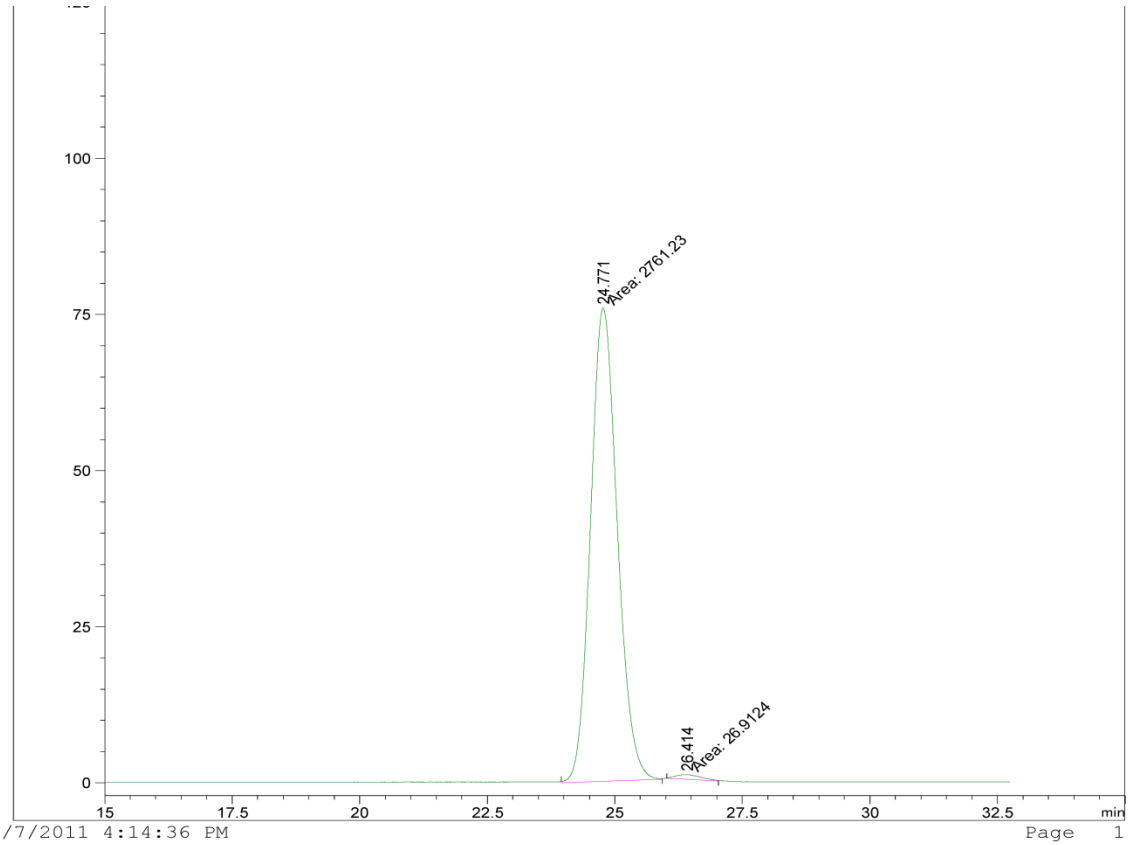

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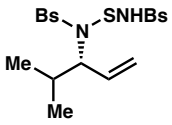
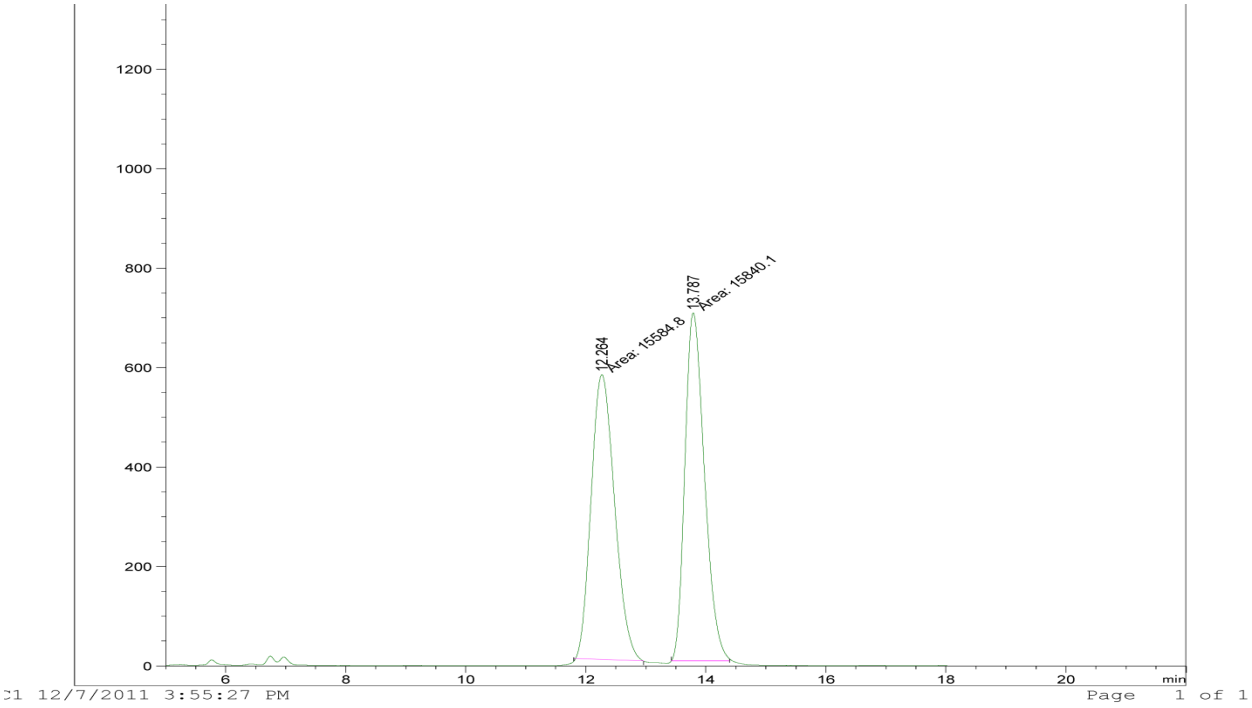
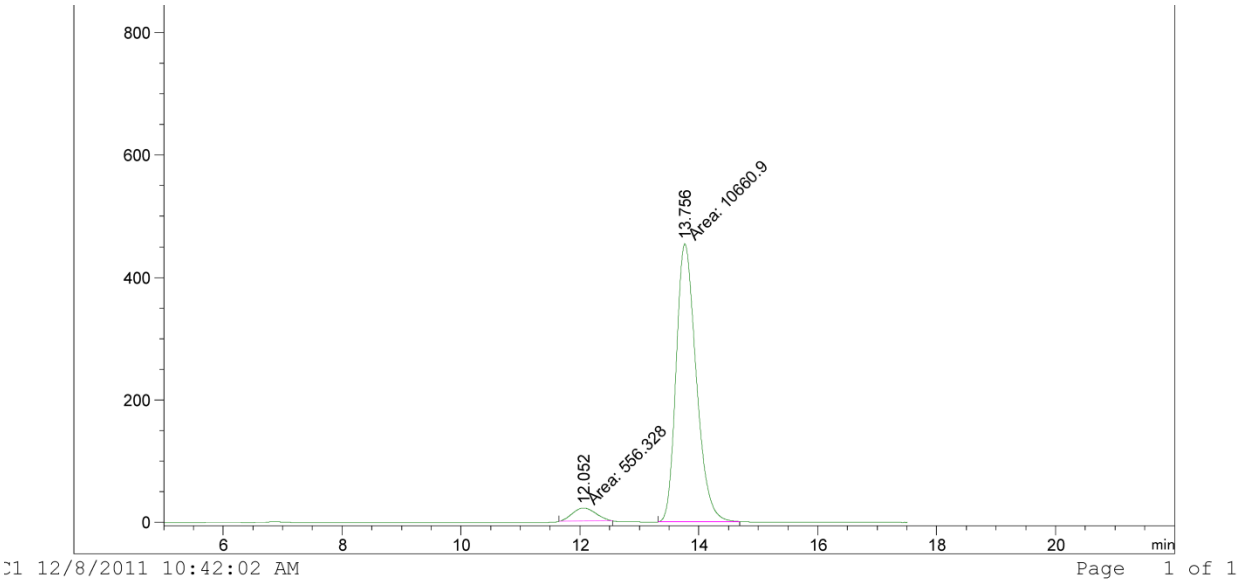
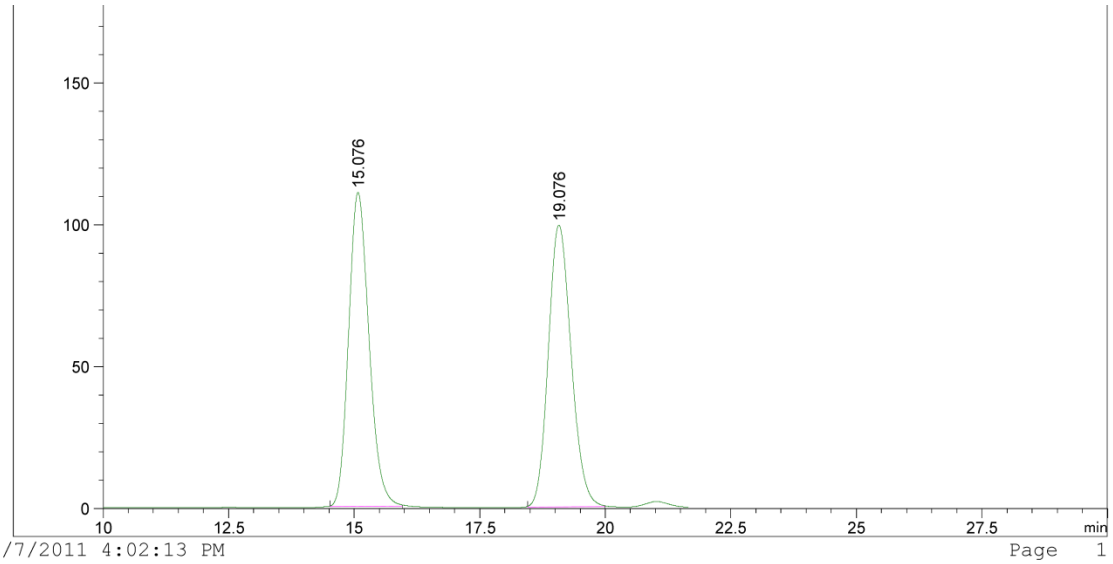


AD-H 75/25 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 91%ee.





AD-H 80/20 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 94%ee.



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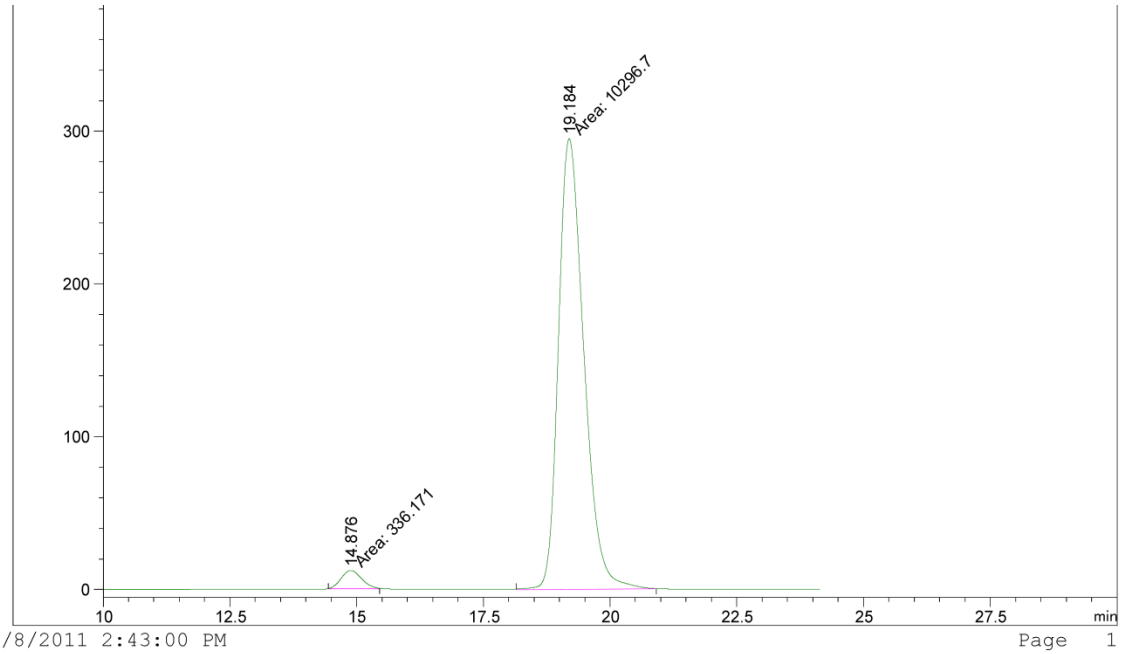

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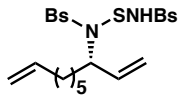
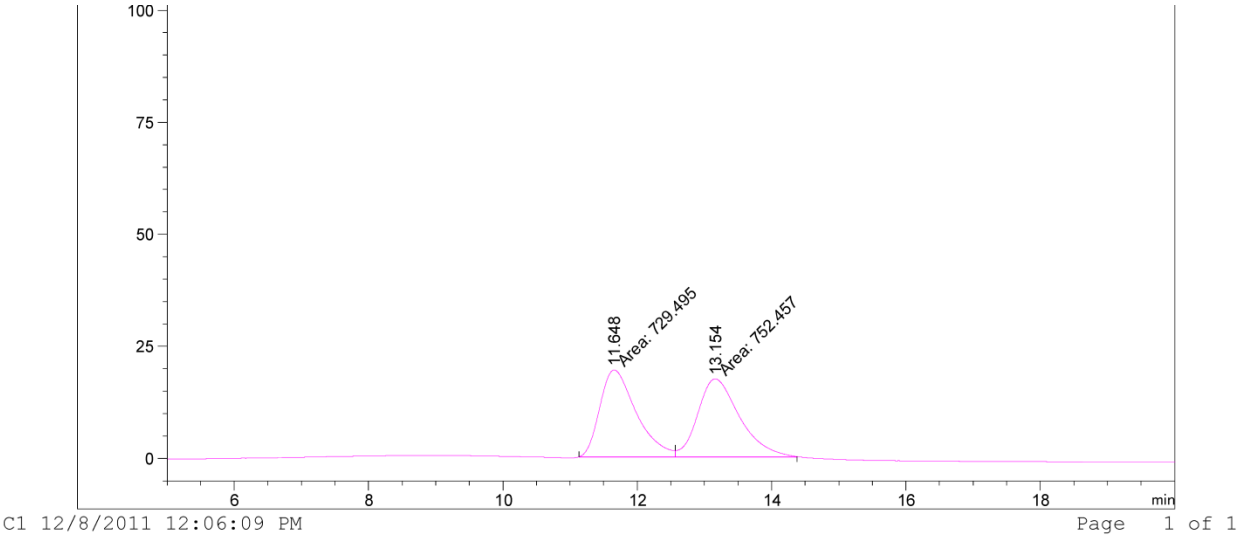
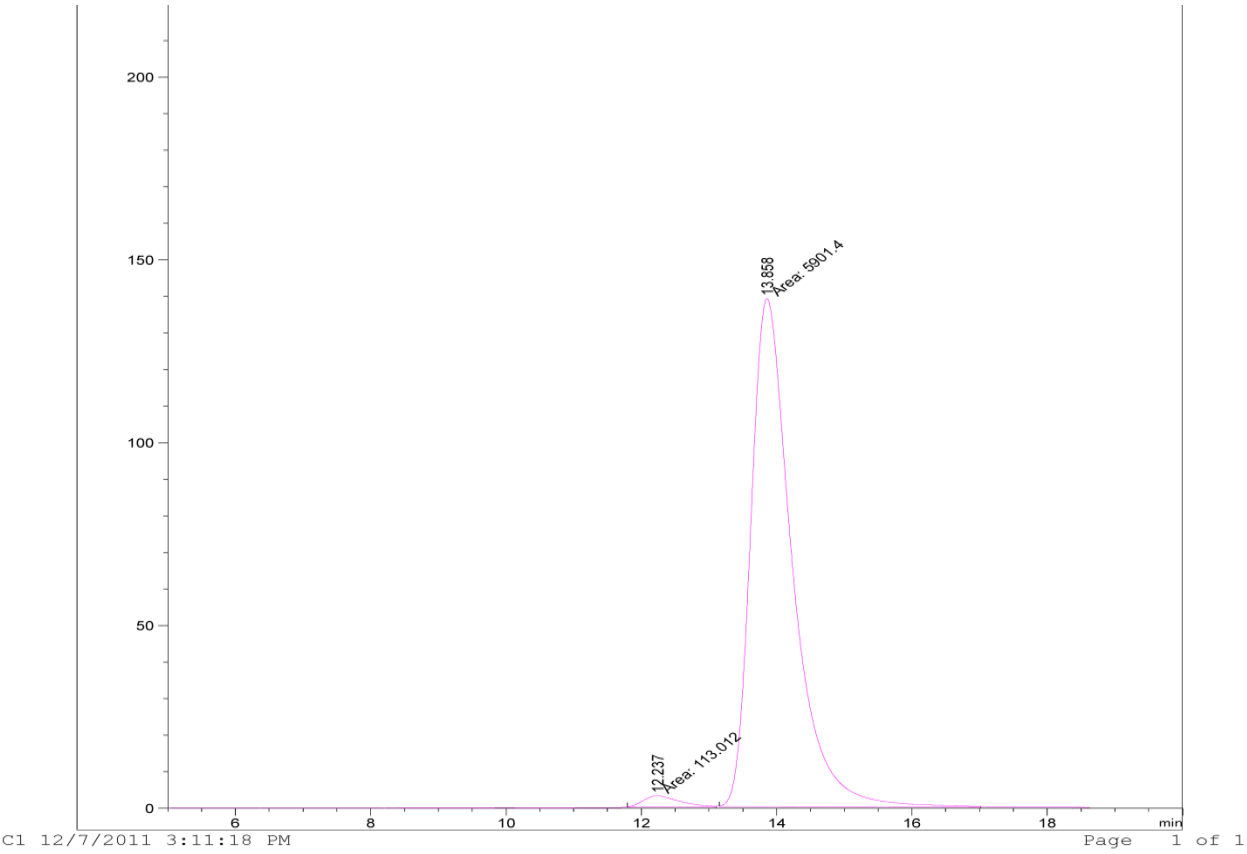
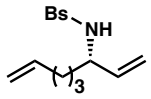


OD-H 90/10 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 97%ee.

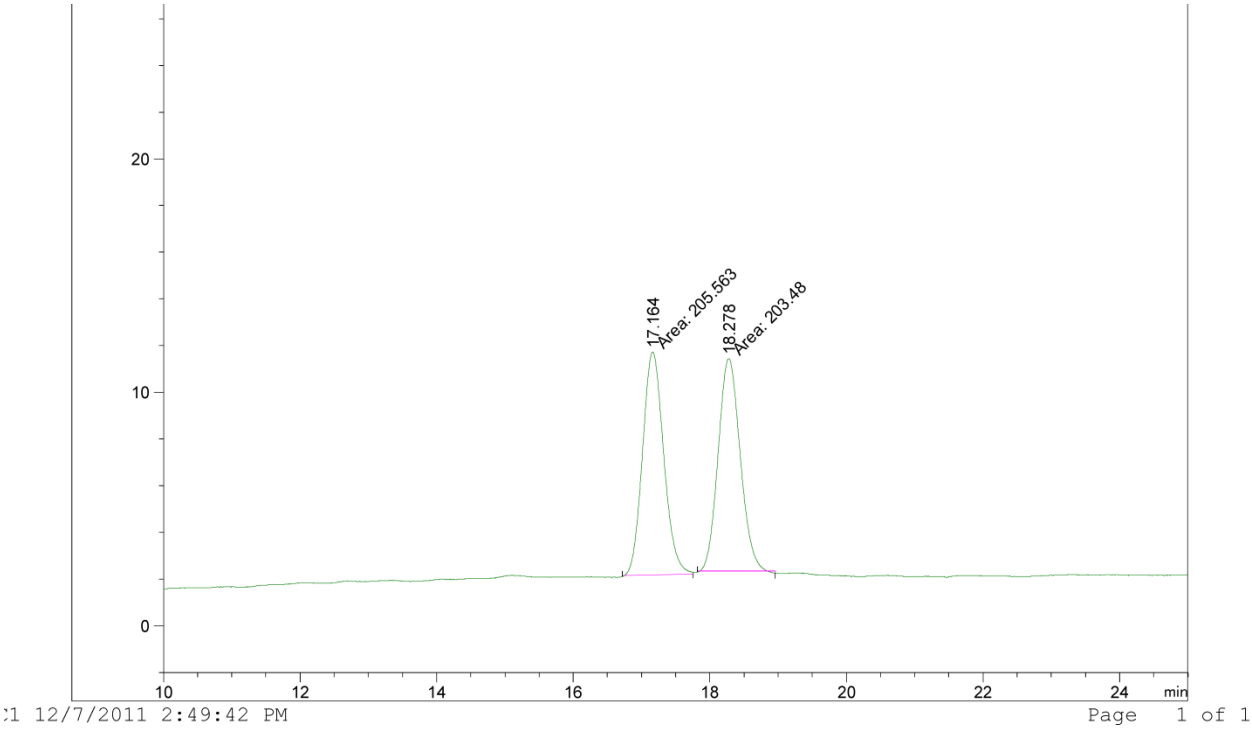






S3

AD-H, 95/5 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 96%ee.



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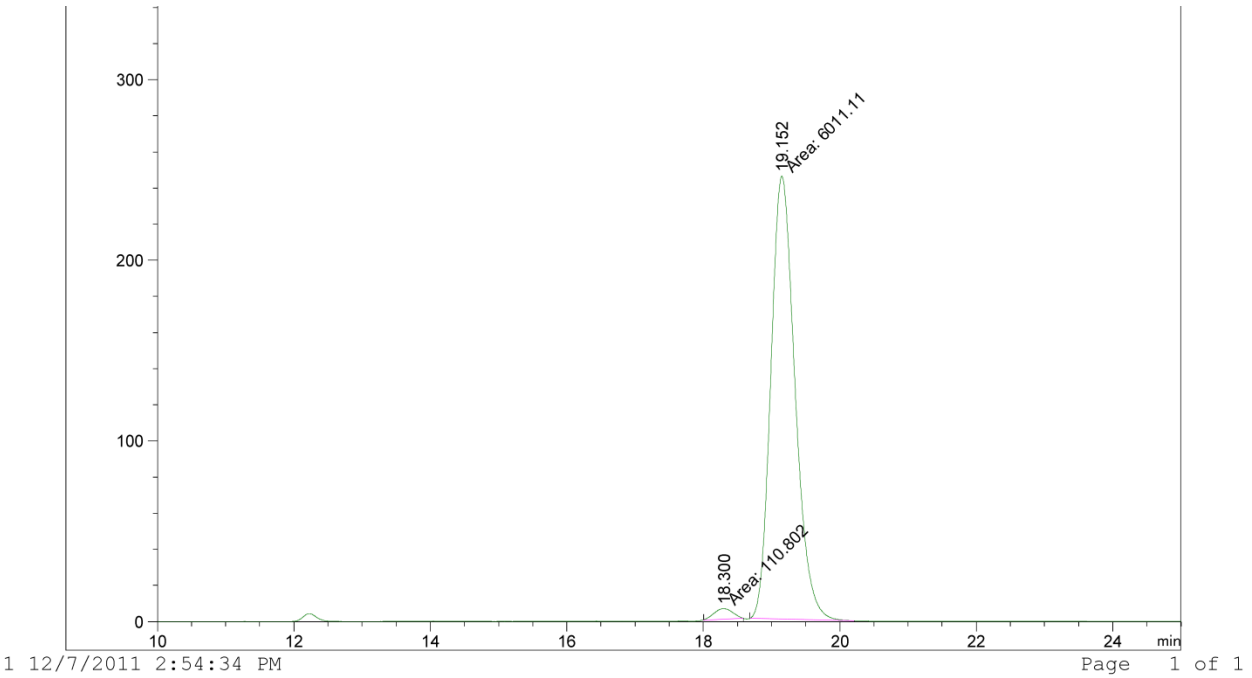

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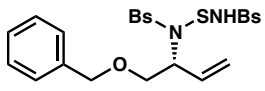
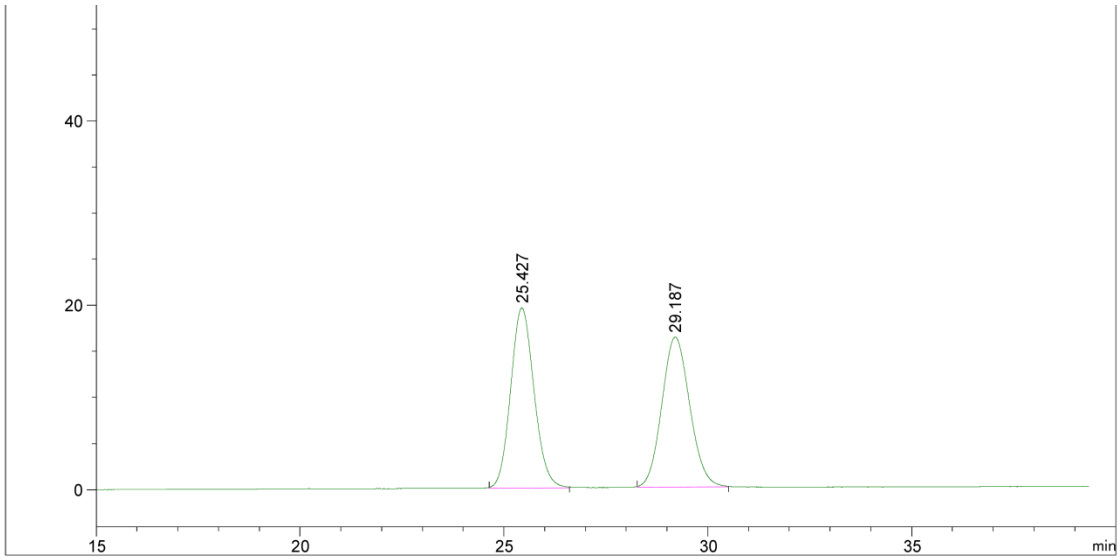


AD-H 80/20 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 91%ee.



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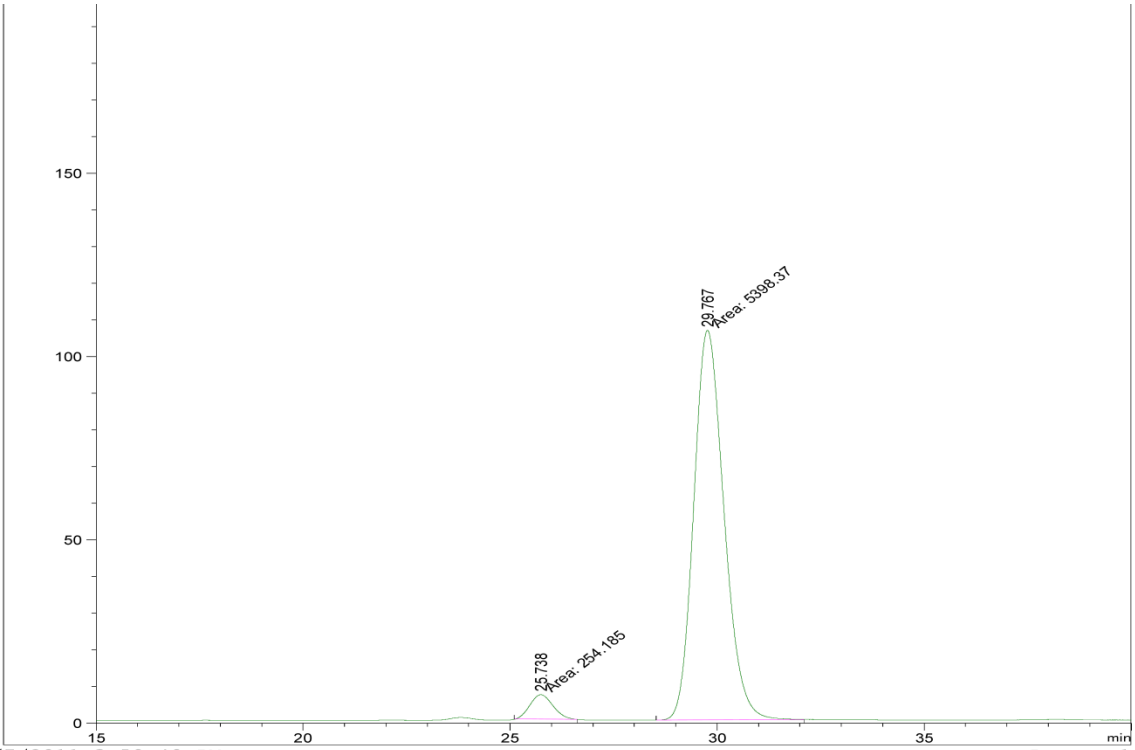
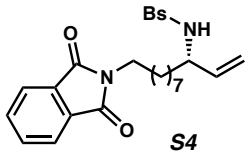
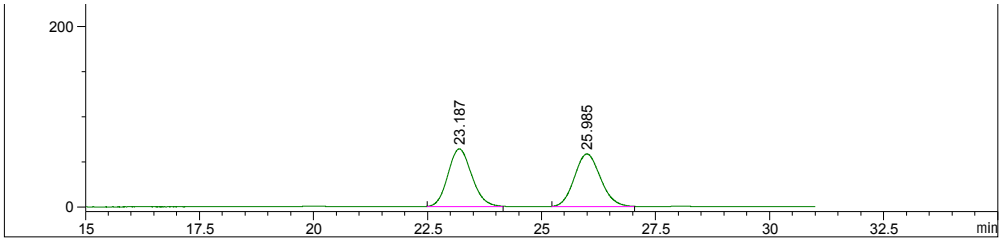


l 12/7/2011 3:50:40 PM Page 1 of 1

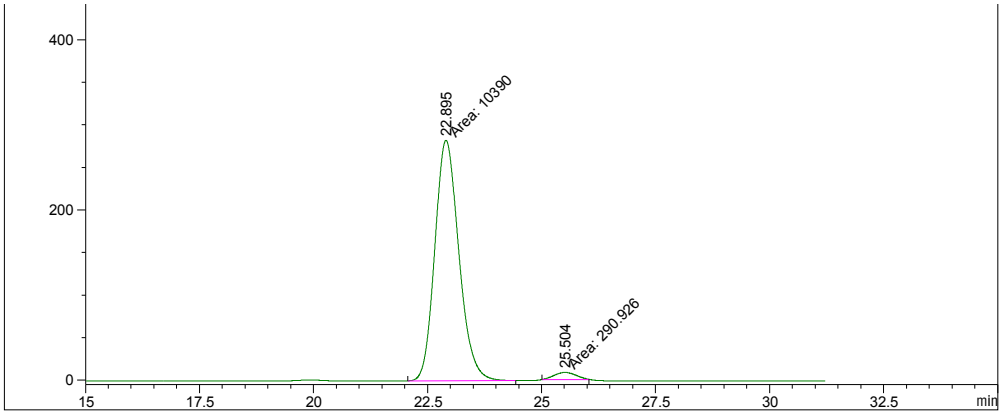


S4

AD-H, 80/20 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 94% ee.



LC1 6/19/2012 4:30:47 PM bao Page 1 of 1



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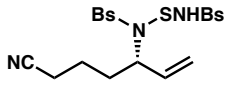
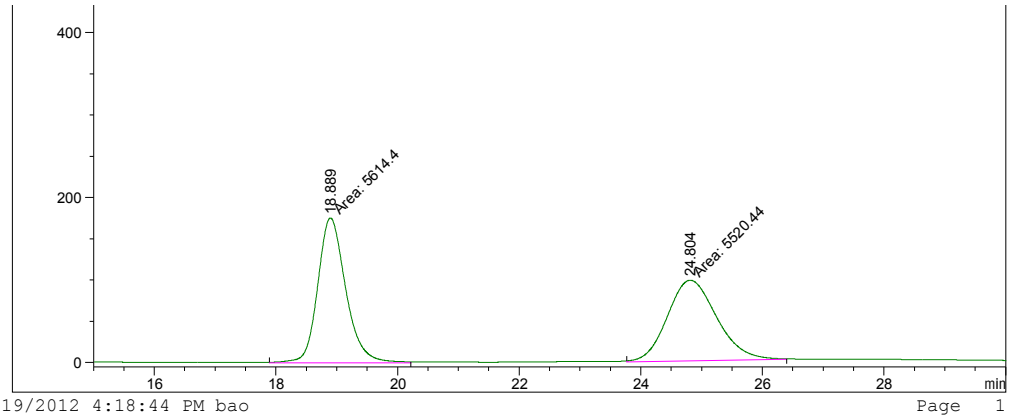


AD-H, 60/40 Hx/*i*PrOH, 0.6 mL/min, 230 nm, 92% ee.



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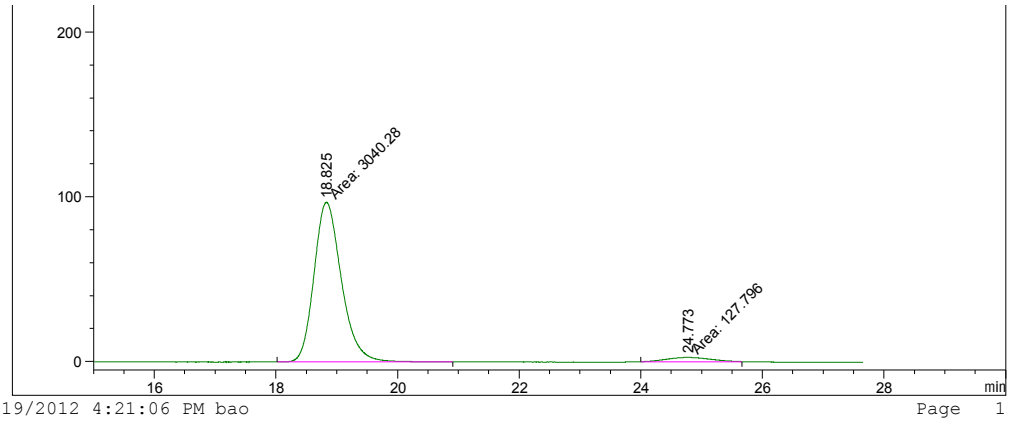

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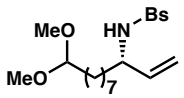
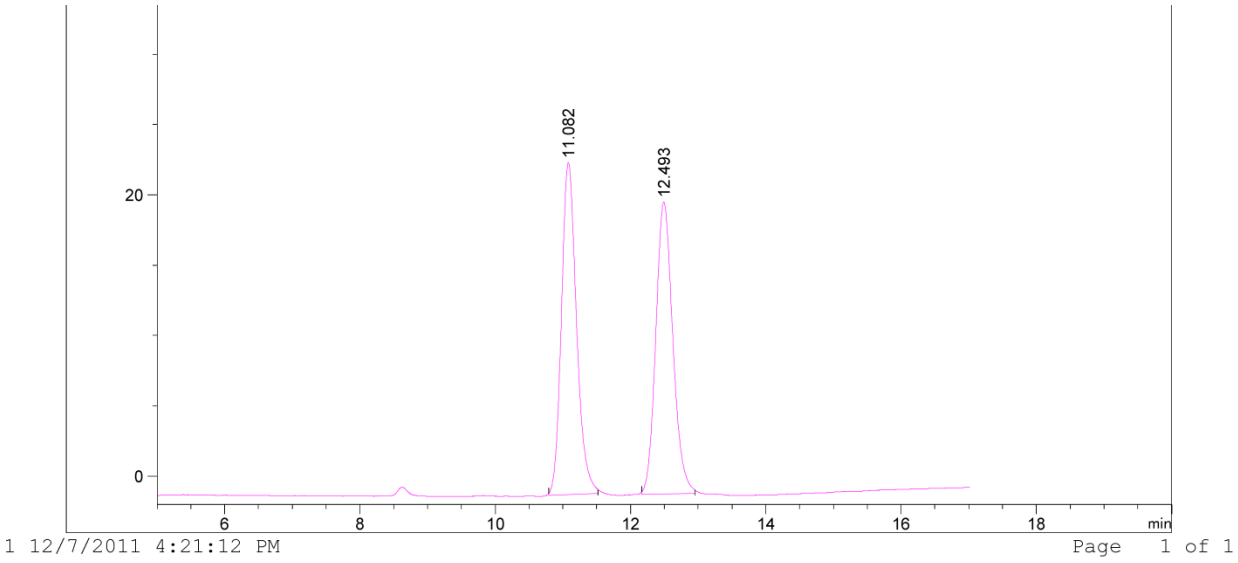
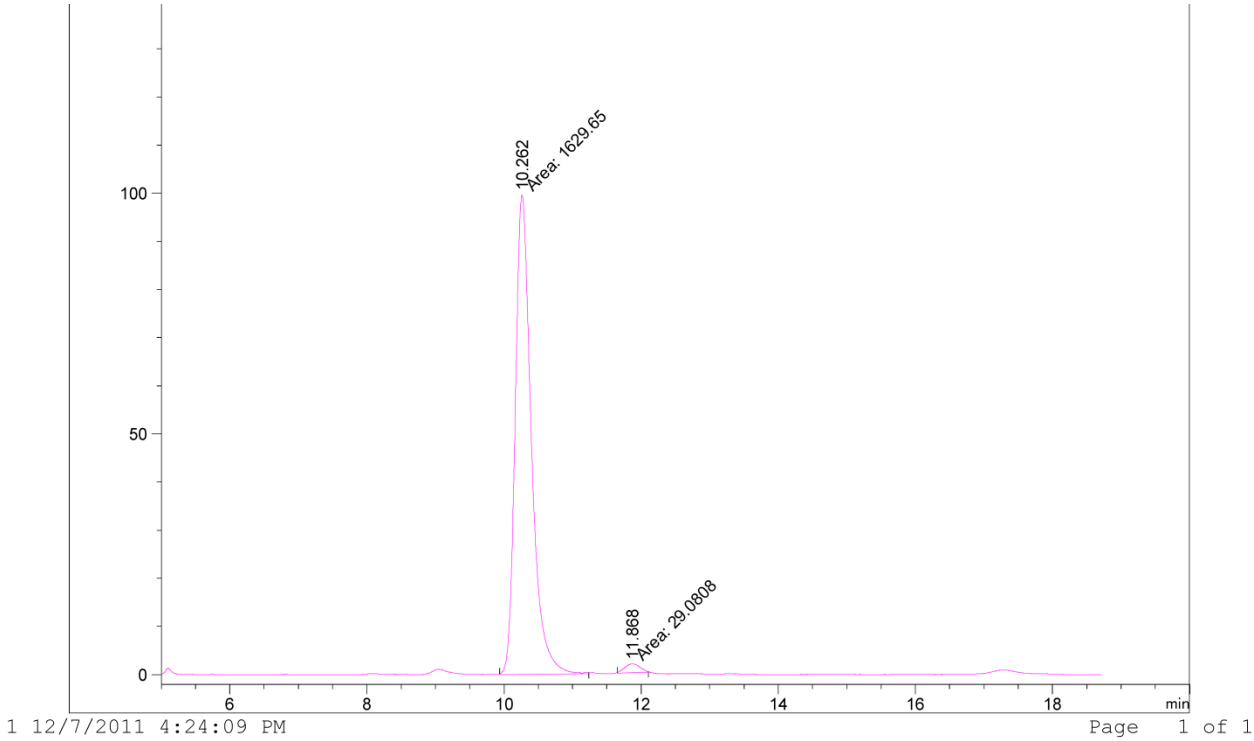
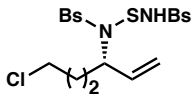


S5

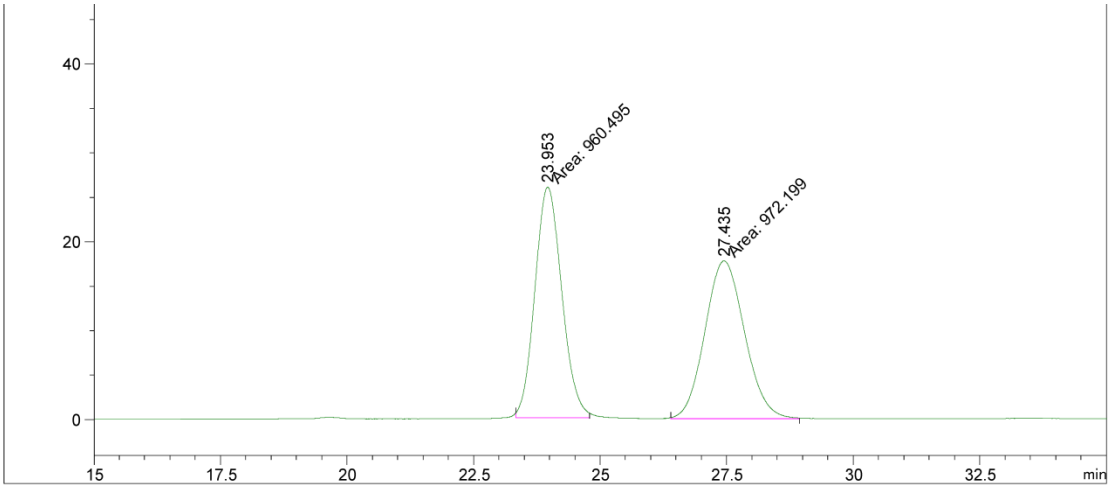
OJ-H 85/15 Hx/*i*PrOH, 1.0 mL/min, 230 nm, 97%ee







AD-H, 80/20 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 97%ee.



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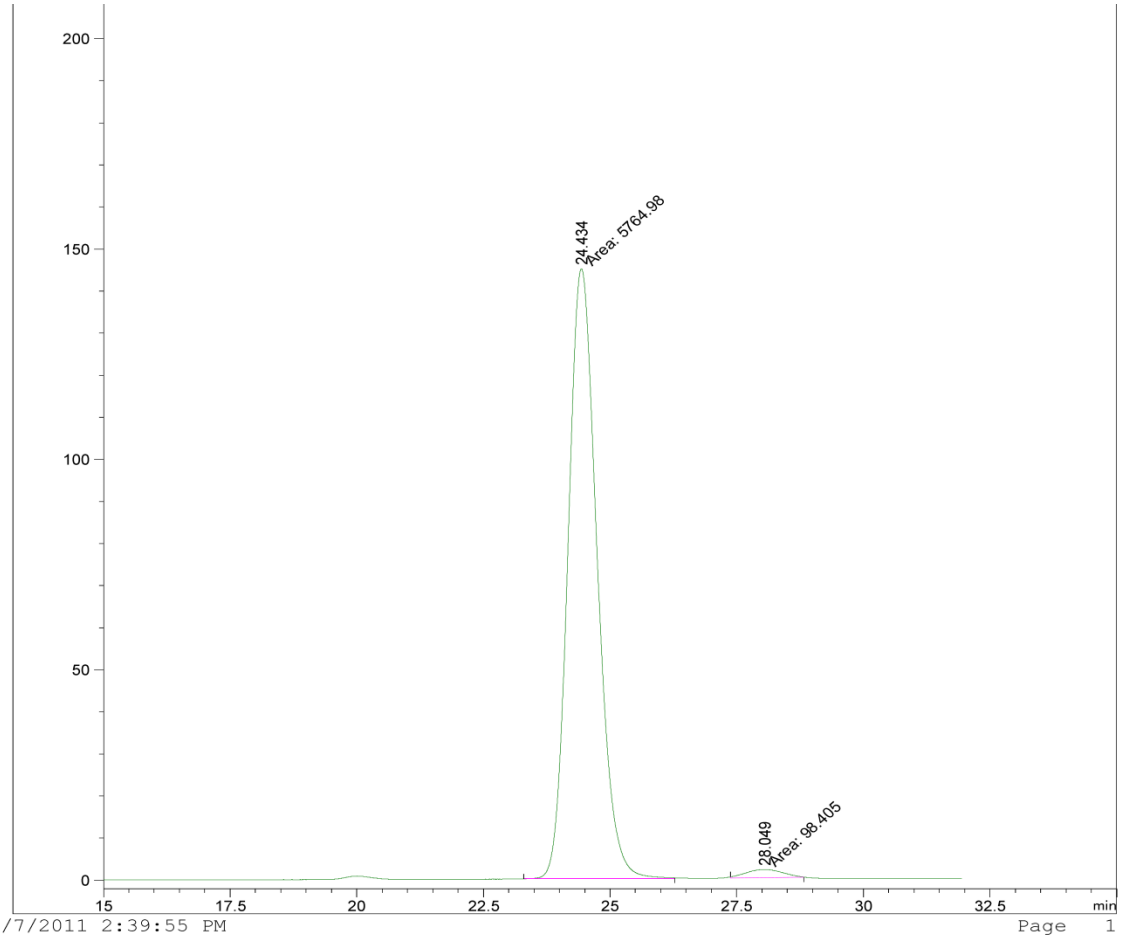

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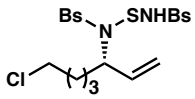
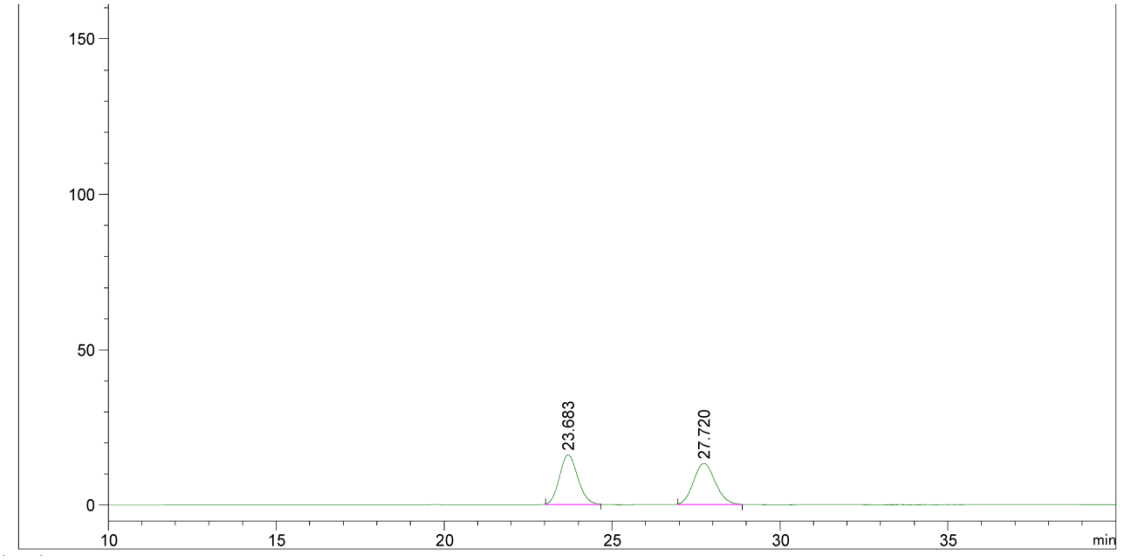
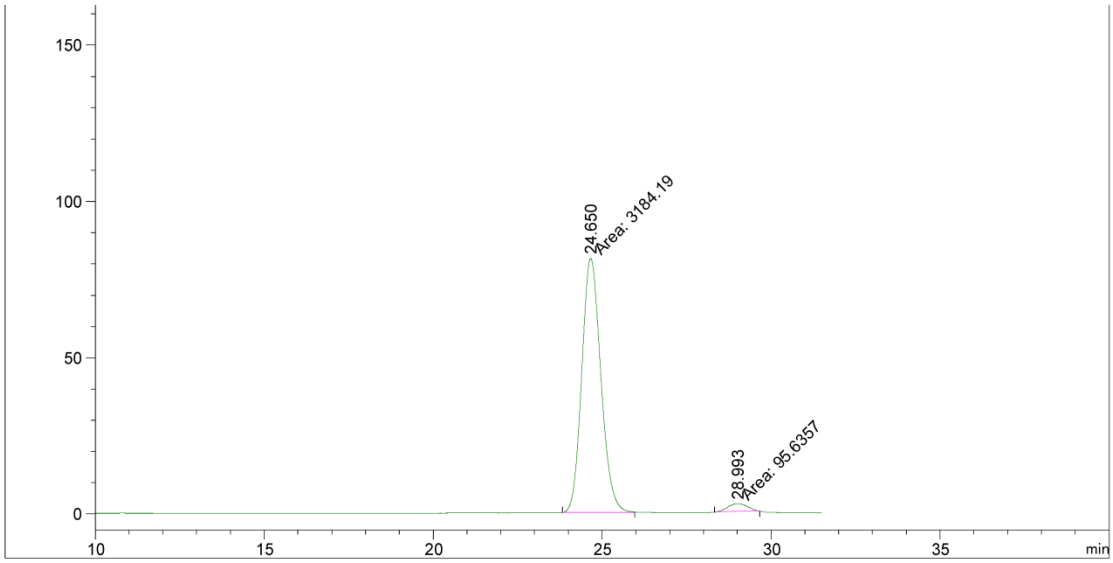
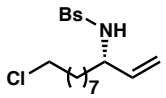


AD-H, 80/20 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 94%ee.

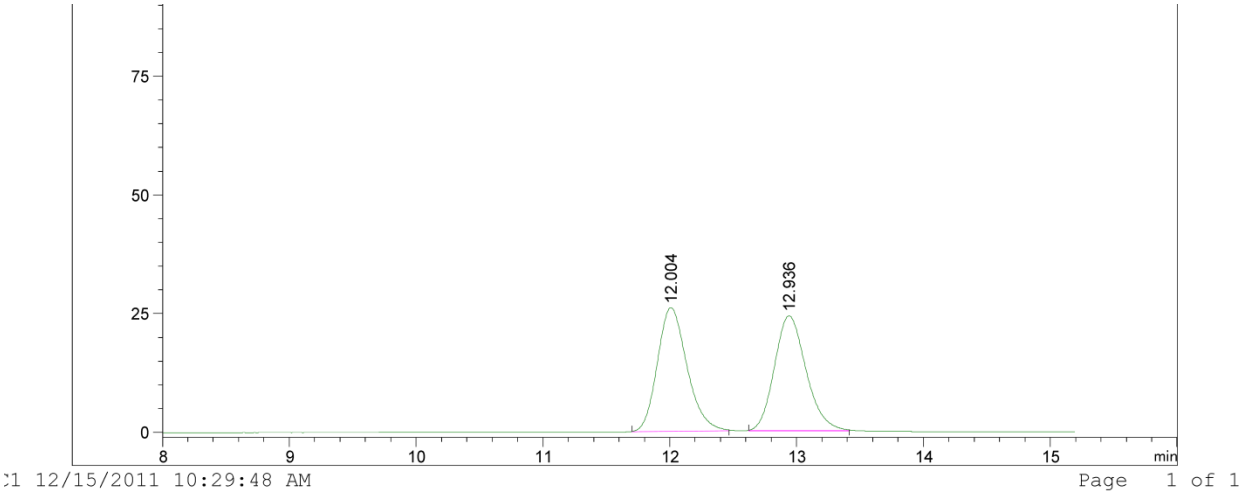


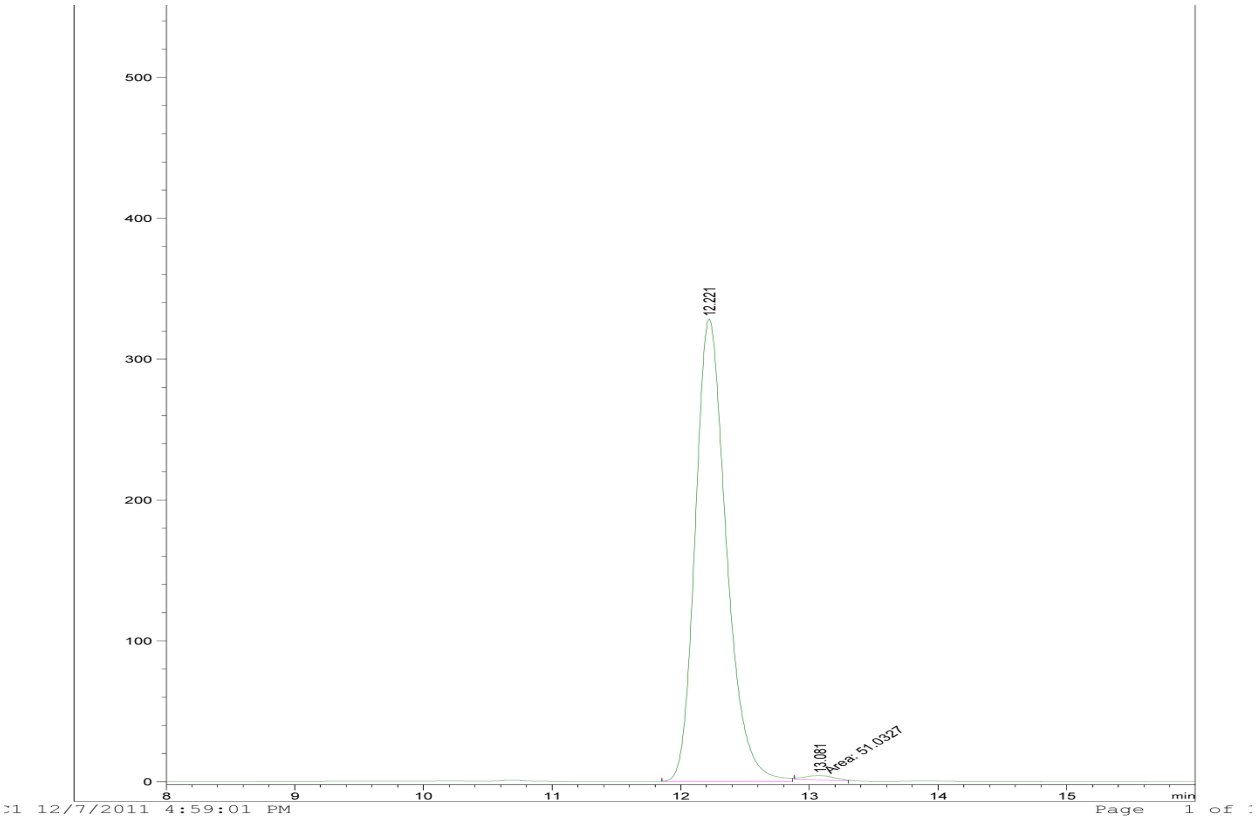


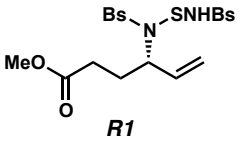


S6

AD-H 90/10 Hx/*i*PrOH, 0.8 mL/min, 230 nm, 98%ee.







R1

OJ-H 80/20 Hx/*i*PrOH, 0.80 mL/min, 230 nm, 92%ee.