Supporting Information

Catalytic Allylic Oxidation of Internal Alkenes to a Multifunctional Chiral Building Block

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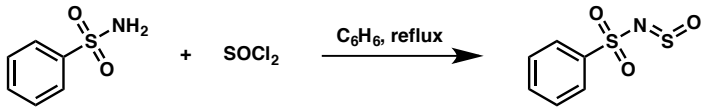
Materials and Methods

All reactions were carried out under an atmosphere of argon 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). All flash chromatography purifications were performed on a Teledyne Isco CombiFlash® Rf unless otherwise indicated. Silica gel (particle size 0.032 - 0.063 mm) purchased from SiliCycle was used for flash chromatography. Reusable RediSep® Rf C18 Reversed Phase columns (40–60 microns) purchased from Teledyne Isco were used for reverse phase 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 (77.16 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. GC analyses were performed on an Agilent 7820A system. HRMS data were obtained at The Scripps Center for Mass Spectrometry and The UT Austin Center for Mass Spectrometry. LRMS data were measured using an AB Sciex QTRAP-4500 LC/MS. X-Ray Diffraction data was obtained Dr. Vincent Lynch at the X-ray Diffraction Lab at University of Texas at Austin.

Synthesis of Benzenesulfonyl Sulfurimide 3d



3d

3d: Our procedure was modified from a method reported in the literature for the synthesis of similar arylsulfonyl sufurimides[33]: A solution of benzenesulfonamide (14.55 g, 92.5 mmol) and $SOCl_2$ (20 mL, 0.275 mol) in benzene (20 mL) was refluxed at 95 °C for 3 days (over the course of the reaction, the mixture became a clear solution). When the starting material was consumed by ^1H NMR analysis of an aliquot, the mixture was concentrated under vacuum to remove benzene and excess $SOCl_2$. To avoid decomposition of the desired product, the crude mixture was transferred quickly to and from the rotavap to avoid exposure to moisture in the atmosphere. Trace amounts of $SOCl_2$ were removed by redissolving the residue in toluene (20 mL) and concentrating under reduced pressure. The residue was redissolved in toluene (8 mL) and stored at 0 ºC until a yellow precipitate crystallized slowly from the solution. The precipitate was obtained by vacuum filtration under an argon atmosphere, washed with cold toluene (3 x 5 mL) and stored under vacuum until dry. Benzensulfonyl sulfurimide **3d** was obtained as a pale yellow solid (15 g, 80% yield). ^1H NMR and ^{13}C NMR spectra were consistent with those reported in literature. *Since benzenesulfonyl sulfurimide **3d** is sensitive to water, we store it in a vacuum desiccator within a sealed flask that has been purged with argon.*

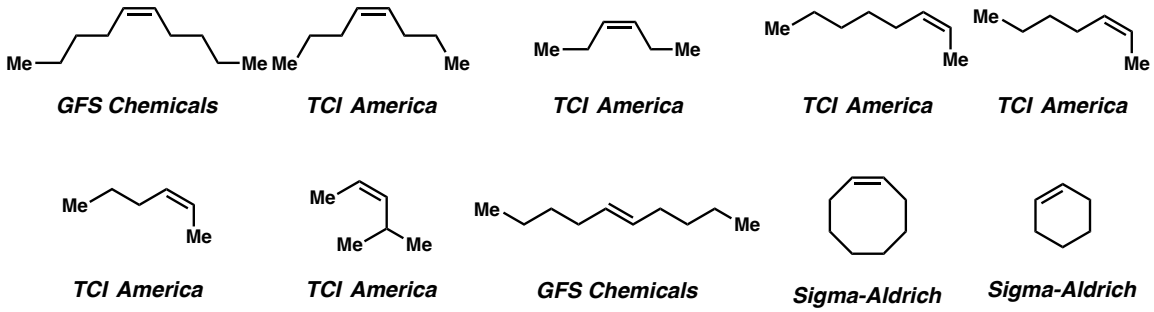
Internal Alkene Starting Materials

Commercially Available Internal Alkenes

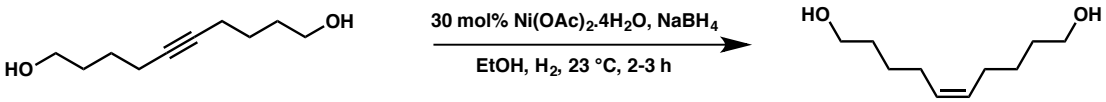
Several internal olefin substrates were obtained from the following commercial sources (Fig. S1): TCI America, GFS Chemicals, and Sigma-Aldrich.

Fig. S1.

Commercially available alkene starting materials.

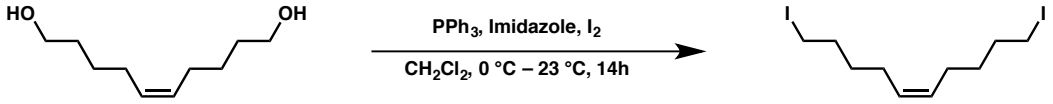


Synthesized Internal Alkenes



S1 *S2*

S2: A flame-dried round-bottom flask was charged with nickel (II) acetate tetrahydrate (0.746 g, 3 mmol, 3 equiv). The flask was then degassed and charged with hydrogen gas from a balloon. Anhydrous ethanol (20 mL) was then added. To a stirred suspension of nickel (II) acetate tetrahydrate in ethanol was added 3.1 mL of a 1 M solution of $NaBH_4$ (3.1 equiv) in ethanol at 23 °C. The solution was stirred for 30 minutes after which an ethanol solution (5 mL) of 1,10-decyne-diol **S1**[34] (1.71g, 10 mmol, 1 equiv) was added. The reaction mixture was then stirred for 2 h. After completion, the reaction was filtered through a celite plug and concentrated to yield the crude product. The crude product was purified by column chromatography (gradient 40-80% EtOAc/hexanes). The product **S2** was obtained as a light yellow oil (1.6 g, 93% yield). The spectra were identical with those reported in the literature[34].

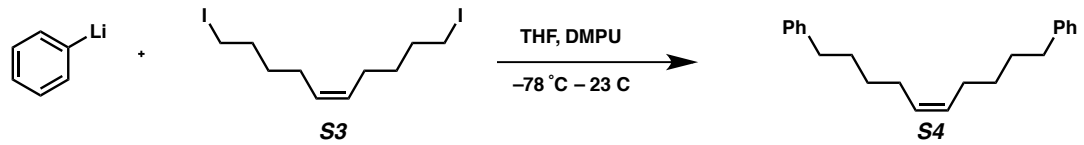


S2 *S3*

S3: Imidazole (0.51 g, 7.5 mmol, 3 equiv) and triphenylphosphine (1.84 g, 7.0 mmol, 2.8 equiv) were added to a stirred solution of *(Z)*-dec-5-ene-1,10-diol **S2** (0.43 g, 2.5 mmol, 1 equiv) in CH_2Cl_2 (10 mL, 0.25 M) at 0 °C. Iodine was then added in portions to the reaction mixture. The resulting solution was stirred for 30 min at 0 °C and 14 h at 23 °C. After completion, the reaction mixture was poured into hexanes (100 mL) and filtered through a silica gel plug. The solid residue was washed with hexanes (5 x 50 mL) and the combined solvent was removed under reduced pressure to give the title compound. The product **S3** was obtained as a clear oil (0.924 g, 94% yield).

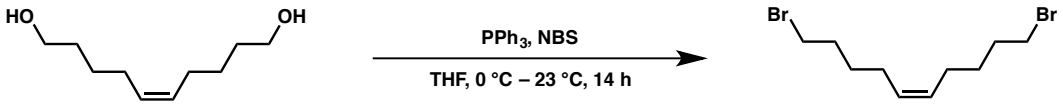
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (t, J = 4.6 Hz, 2H), 3.22 (t, J = 7.0 Hz, 4H), 2.17 – 2.00 (m, 4H), 1.94 – 1.77 (m, 4H), 1.55 – 1.43 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

129.6, 33.0, 30. 5, 26.1, 7.0. IR (thin film): 2929, 2341, 1425, 1207, 720 cm^{-1}. HRMS (CI+) calcd for $[C_{10}H_{18}I_2]^+$ ($[M^+]$): 391.9498, found 391.9508.



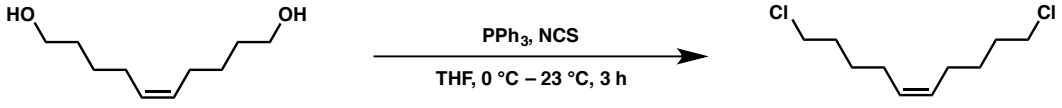
S3 *S4*

S4: A flame-dried round-bottom flask was charged with anhydrous THF (0.5 M), and the flask was cooled to -78 ˚C in a dry ice/acetone bath. *(Z)*-1,10-diiododec-5-ene **S3** (0.784 g, 2.0 mmol, 1 equiv) was then added under an argon atmosphere. Phenyllithium (4.4 mL, 8 mmol, 4 equiv, 1.8 M) was added dropwise to the flask while maintaining the reaction temperature at -78 °C. After 30 minutes at -78 °C, the reaction mixture was allowed to warm to 23 °C and stirred overnight. After completion, a saturated aqueous NH_4Cl solution was added. The reaction mixture was extracted with Et_2O (3x). The organic phases were combined and washed with sodium thiosulfate and brine, dried over anhydrous magnesium sulfate, filtered, and concentrated to yield crude product. The crude product was purified by column chromatography on silica gel using 100% hexanes as an eluent. Olefin **S4** was obtained as a clear oil (0.429 g, 73% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 4H), 7.24 – 7.17 (m, 6H), 5.41 – 5.29 (m, 2H), 2.71 – 2.55 (t, J = 7.7, 4H), 2.08 (td, J = 7.5, 5.2 Hz, 4H), 1.65 (m, 4H), 1.42 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 129.8, 128.4, 128.2, 125.6, 35.8, 31.1, 29.4, 27.1. IR (thin film): 2930, 2855, 1495, 1453, 746 cm^{-1}. HRMS [CI+] calcd for $[C_{22}H_{28}]^+$ ($[M^+]$): 292.2191, found 292.2191.



S2 *S5*

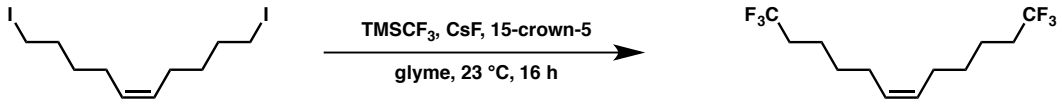
S5: N-Bromosuccinimide (0.62 g, 3.48 mmol, 3 equiv) was added in portions to a stirred solution of *(Z)*-dec-5-ene-1,10-diol **S2** (0.2 g, 1.16 mmol, 1 equiv) and triphenylphosphine (0.852 g, 3.25 mmol, 2.8 equiv) in THF (5 mL) at 0 °C, and the resulting solution was stirred for 30 min at 0 °C and 14 h at 23 °C. After completion, the reaction mixture was poured into hexanes (20 mL) and filtered through a silica gel plug. The solid residue was washed with hexanes (5 x 20 mL) and the combined solvent was removed under reduced pressure to give the title compound. Olefin **S5** was obtained as a clear oil (0.346 g, 99% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (t, J = 4.9 Hz, 2H), 3.41 (t, J = 6.8 Hz, 4H), 2.06 (m, 4H), 1.86 (p, J = 7.2 Hz, 4H), 1.51 (p, J = 7.5 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.6, 33.8, 32.3, 28.1, 26.3. IR (thin film): 2935, 1437, 1248, 740, 645 cm^{-1}. HRMS (CI+) calcd for $[C_{10}H_{17}Br_2]^+$ ($[M\text{-}H]^+$): 294.9697, found 294.9697.



S2 *S6*

S6: N-Chlorosuccinimide (0.6 g, 4.5 mmol, 3 equiv) was added in portions to a stirred solution of *(Z)*-dec-5-ene-1,10-diol **S2** (0.258 g, 1.5 mmol, 1 equiv) and triphenylphosphine (1.1 g, 4.2 mmol, 2.8 equiv) in THF (6 mL) at 0 °C. The resulting solution was stirred for 30 min at 0 °C and 3 h at 23 °C. After completion, the reaction mixture was poured into hexanes (20 mL) and filtered through a silica gel plug. The solid residue was washed with hexanes (5 x 20 mL) and the combined solvent was removed under reduced pressure to give the title compound. Olefin **S6** was obtained as a clear oil (0.289 g, 97% yield).

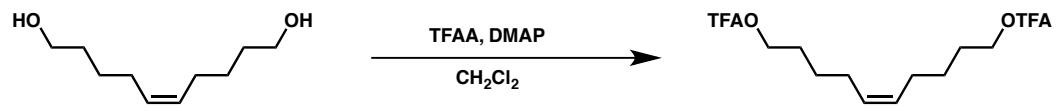
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (t, J = 4.9 Hz, 2H), 3.54 (t, J = 6.7 Hz, 4H), 2.06 (m, 4H), 1.78 (p, J = 6.9 Hz, 4H), 1.61 – 1.39 (p, J = 7.7 Hz 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.7, 45.0, 32.1, 26.8, 26.4. IR (thin film): 2861, 2360, 1445, 1309, 720 cm^{-1}. HRMS (CI+) calcd for $[C_{10}H_{17}Cl_2]^-$ ([M-H]$^-$): 207.0707, found 207.0710.



S3 *S7*

S7: To a solution of *(Z)*-1,10-diiododec-5-ene **S3** (0.392 g, 1.0 mmol, 1 equiv) in monoglyme (5 mL) in a flame-dried round-bottom flask, $TMSCF_3$ (2 mL, 4.0 mmol, 4.0 equiv, 2M in THF) was added. The resulting mixture was then cooled to -10 °C in an ethylene glycol/dry ice bath. CsF (0.607 g, 4 mmol, 4 equiv) and 15-crown-5 (1.5 mL, 8 mmol, 8 equiv) were successively added and the mixture was allowed to warm up to 23 °C and stirred for 14 h. After completion, the reaction mixture was filtered through a celite plug and concentrated. The liquid residue was then washed with pentane (5 x 5 mL) to give a solution of desired product and 15-crown-5. This solution was washed with brine (3x) and water (2x), dried over magnesium sulfate, and concentrated under reduced pressure to give olefin **S7** as a clear oil (0.268 g, 97% yield).

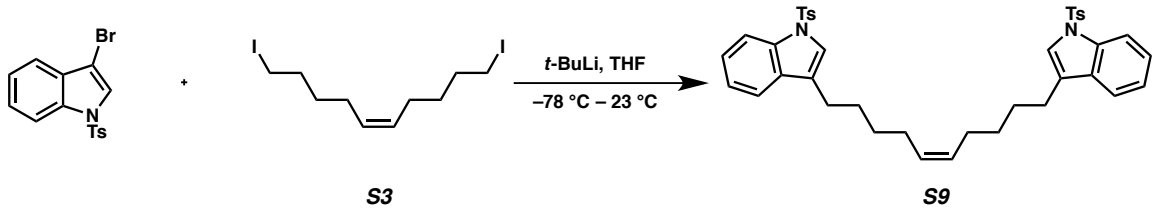
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (t, J = 4.7 Hz, 2H), 2.09 (m, 8H), 1.63 – 1.50 (m, 4H), 1.46 (m, J = 7.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.5, 127.2 (q, J = 276.3 Hz), 33.6 (q, J = 28.4 Hz), 28.6, 26.7, 21.5 (q, J = 2.9 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.39. IR (thin film): 2947, 1389, 1136, 1027, 653 cm^{-1}. HRMS (CI+) calcd for $[C_{12}H_{18}F_6]^+$ ([M$^+$]) : 276.1313, found 276.1311.



S2 *S8*

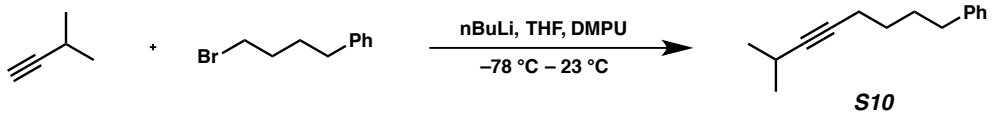
S8: A flame-dried round-bottom flask was charged with anhydrous CH_2Cl_2 (10 mL) and *(Z)*-dec-5-ene-1,10-diol **S2** (0.43 g, 2.5 mmol, 1 equiv). The flask was cooled to 0 °C in an ice bath. 4-Dimethylaminopyridine (0.062 g, 0.5 mmol, 0.2 equiv) was then added under an argon atmosphere. Triflouroacetic anhydride (1.4 mL, 10 mmol, 4 equiv) was added dropwise to the flask while maintaining the reaction temperature at 0 °C. The

reaction mixture was then allowed to warm to 23 °C and stirred overnight. After completion, the reaction mixture was poured into hexanes (100 mL) and filtered through a silica gel plug. The reaction residue on silica gel was washed with hexanes (5 x 30 mL) and the combined solvent was removed under reduced pressure to give the title compound. Olefin **S8** was obtained as a clear oil (0.476 g, 52% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (t, J = 4.4 Hz, 2H), 4.36 (t, J = 6.6 Hz, 4H), 2.08 (td, J = 7.3, 5.3 Hz, 4H), 1.84 – 1.67 (m, 4H), 1.52 – 1.36 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5 (q, *J* = 42.0 Hz), 129.6, 114.5 (q, *J* = 285.7 Hz), 68.0, 27.7, 26.5, 25.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -75.15. IR (thin film): 2943, 1789, 1352, 1222, 777 cm^{-1}. HRMS (CI+) calcd for $[C_{14}H_{19}O_4F_6]^+$ ($[M+H]^+$): 365.1188, found 365.1202.



S3 ***S9***

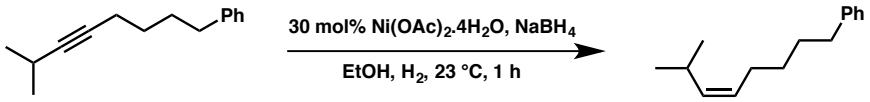
S9: A flame-dried round-bottom flask was charged with anhydrous THF (6 mL) and 3-bromo-1-tosyl-1H-indole[35] (1.314 g, 3.75 mmol, 2.5 equiv). The flask was cooled to -78 ˚C in a dry ice/acetone bath. *t*-BuLi (2.2 mL, 3.75 mmol, 2.5 equiv, 1.7 M) was added dropwise to the flask while maintaining the reaction temperature at -78 °C. After the reaction was stirred for additional 1 h, a solution of *(Z)*-1,10-diiododec-5-ene **S3** (0.588 g, 1.5 mmol, 1 equiv) in THF (3 mL) was added. The reaction mixture was allowed to warm to 23 °C and stirred for 21 h. After completion, a saturated aqueous NH_4Cl solution was added. The reaction mixture was extracted with Et_2O (3x). The organic phases were combined and washed with sodium thiosulfate and brine, dried over anhydrous magnesium sulfate, filtered, and concentrated to yield crude product. The crude product was purified by column chromatography (gradient 0-10% EtOAc/hexanes). Olefin **S9** was obtained as a white solid (0.3 g, 29% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 – 8.18 (d, J = 8.1 Hz,, 2H), 7.65 – 7.58 (d, J = 8.3 Hz, 4H), 7.44 (d, J = 7.6 Hz, 2H), 7.37 – 7.29 (m, 6H), 7.19 (d, J = 8.1 Hz, 4H), 5.39 (d, J = 5.4 Hz, 2H), 3.11 (d, *J* = 7.6 Hz, 4H), 2.35 (s, 6H), 2.17 – 2.04 (m, 4H), 1.82 – 1.69 (m, 4H), 1.53 – 1.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 138. 8, 136.0, 135.6, 129.9, 129.7, 129.2, 126.3, 125.1, 124.1, 119.2, 115.1, 101.9, 29.5, 29.5, 27.4, 27.0, 21. 6. IR (thin film): 2924, 2341, 1448, 1175, 668 cm^{-1}. HRMS (ESI-TOF) calcd for $[C_{40}H_{43}N_2O_4S_2]$ ($[M+H]^+$): 679.2659, found 679.2654.



S10

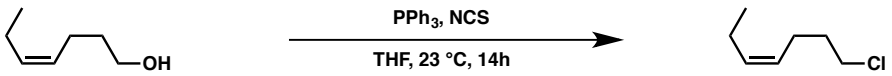
S10: A flame-dried round-bottom flask was charged with anhydrous THF (10 mL) and 3-methylbut-1-yne (0.66 g, 6.5 mmol, 1.3 equiv). The flask was cooled to -78 °C in a dry ice/acetone bath. *n*-BuLi (2.5 mL, 6.25 mmol, 1.25 equiv, 2.5 M) was added dropwise to the flask while maintaining the reaction temperature at -78 °C. After the reaction was stirred for an additional 1 h, (4-bromobutyl)benzene (0.84 mL, 5 mmol, 1 equiv) and 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (5 mL) were sequentially added. The reaction mixture was then allowed to warm to 23 °C and stirred for 17 h. After

completion, a saturated aqueous NH_4Cl solution was added. The reaction mixture was extracted with Et_2O (3x). The organic phases were combined and washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated to yield crude product. The crude product was purified by column chromatography (100% hexanes). Alkyne **S10** was obtained as a clear oil (0.826 g, 88% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 7.18 (d, J = 7.3 Hz, 3H), 2.62 (t, J = 7.7 Hz, 2H), 2.51 (m, 1H), 2.23 – 2.10 (m, 2H), 1.72 (m, 2H), 1.55 – 1.47 (m, 2H), 1.13 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 128.4, 128.2, 125.6, 86.3, 79.0, 35.4, 30.5, 28.7, 23. 5, 20.5, 18.6. IR (thin film): 2935, 2860, 1496, 746, 698 cm^{-1}. HRMS (CI+) calcd for $[C_{15}H_{20}]^+$ ($[M^+]$): 200.1565, found 200.1566.



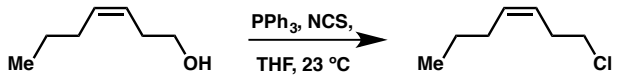
S10 ***S11***

S11: To a flame-dried round-bottom flask was charged with nickel (II) acetate tetrahydrate (0.134 g, 0.54 mmol, 0.27 equiv). The flask was then degassed and charged with hydrogen gas from a balloon. Anhydrous ethanol (4 mL) was then added. To a stirred suspension of nickel (II) acetate tetrahydrate in ethanol was added 0.5 mL of a 1 M solution of $NaBH_4$ (0.25 equiv) in ethanol at 23 °C. The solution was stirred for 30 minutes, and then an ethanol solution (2 mL) of alkyne **S10** (0.4 g, 2 mmol, 1 equiv) was added. The reaction mixture was stirred for 1 h. After completion, the reaction was filtered through a celite plug and concentrated to yield crude product. The crude product was purified by column chromatography (100% hexanes). Olefin **S11** was obtained as a clear oil (0.368 g, 91% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.21 – 7.11 (m, 3H), 5.26 – 5.14 (m, 2H), 2.60 (m, 3H), 2.07 (m, 2H), 1.71 – 1.58 (m, 2H), 1.45 – 1.33 (m, 2H), 0.94 (d, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 137.7, 128.4, 128.2, 127.2, 125.6, 35.8, 31.1, 29.5, 27.1, 26. 5, 23.2. IR (thin film): 2955, 2857, 1496, 1454, 745 cm^{-1}. HRMS (CI+) calcd for $[C_{15}H_{22}]$ ($[M^+]$): 202.1722, found 202.1721.



S12

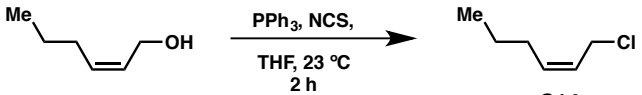
S12: N-Chlorosuccinimide (2.0 g, 15 mmol, 1.5 equiv) was added in portions to a stirred solution of *(Z)*-hept-4-en-1-ol (1.4 g, 10 mmol, 1 equiv) and triphenylphosphine (2.27 g, 14 mmol, 1.4 equiv) in THF (20 mL) at 0 °C. The resulting solution was stirred for 30 min at 0 °C and 14 h at 23 °C. After completion, the reaction mixture was poured into hexanes (100 mL) and filtered through a silica gel plug. The solid residue was washed with hexanes (5 x 30 mL) and the combined solvent was removed under reduced pressure to give the title compound. The product was obtained as a clear oil (0.976 g, 74% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 – 5.37 (m, 1H), 5.36 – 5.20 (m, 1H), 3.54 (t, J = 6.6 Hz, 2H), 2.20 (q, *J* = 7.2 Hz, 2H), 2.12 – 2.00 (m, 2H), 1.82 (p, *J* = 6.8 Hz, 2H), 0.97 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.3, 126.9, 44.5, 32.5, 24.2, 20.5, 14.3. IR (thin film): 2934, 1458, 1308, 726, 654 cm^{-1}. HRMS (CI+) calcd for $[C_7H_{13}Cl]^+$ ($[M^+]$): 132.0706, found 132.0708.



S13

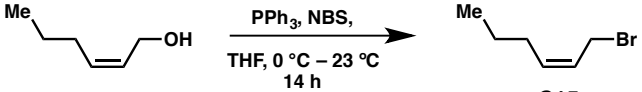
S13: Triphenylphosphine (5.6 mmol, 1.4 equiv) was diluted in THF (8 mL, 0.5 M) within a flame-dried flask set under argon atmosphere. *Cis*-3-hexen-1-ol (4.0 mmol) was added to the solution followed by N-chlorosuccinimide (6.0 mmol, 1.5 equiv) carefully. The reaction was stirred at 23 °C until complete as determined by TLC analysis (2 h). After diluting with pentane (30 mL), the suspension was filtered through a celite plug and purified by flash chromatography (100% pentane) to afford **S13** (92% yield) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 – 5.48 (m, 1H), 5.45 – 5.33 (m, 1H), 3.51 (t, J = 7.1 Hz, 2H), 2.52 (m, 2H), 2.03 (m, 2H), 1.39 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.2, 125.1, 44.4, 30.9, 29.6, 22.8, 13.9. GC-MS calcd for [$C_7H_{13}Cl$] ([M^+]): 132.07, found 132.10.



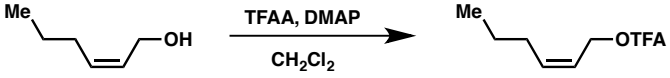
S14

S14: N-Chlorosuccinimide (1.0 g, 7.5 mmol, 1.5 equiv) was added in portions to a stirred solution of *(Z)*-hex-2-en-1-ol (0.59 g, 5 mmol, 1 equiv) and triphenylphosphine (1.84 g, 7 mmol, 1.4 equiv) in THF (10 mL) at 0 °C, and the resulting solution was stirred for 30 min at 0 °C and 2 h at 23 °C. After completion, the reaction mixture was poured into pentane (100 mL) and filtered through a silica gel plug. The solid residue was washed with pentane (5 x 30 mL) and the combined solvent was removed under reduced pressure to give the title compound. Allylic chloride **S14** was obtained as a clear oil (0.358 g, 60% yield). The collected spectra were consistent with those reported in the literature[36].



S15

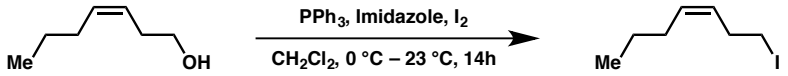
S15: N-Bromosuccinimide (2.67 g, 15 mmol, 1.5 equiv) was added in portions to a stirred solution of *(Z)*-hex-2-en-1-ol (1.2 ml, 10 mmol, 1 equiv) and triphenylphosphine (3.67 g, 14 mmol, 1.4 equiv) in THF (20 mL) at 0 °C, and the resulting solution was stirred for 30 min at 0 °C and 14 h at 23 °C. After completion, the reaction mixture was poured into hexanes (100 mL) and filtered through a silica gel plug. The solid residue was washed with hexanes (5 x 20 mL) and the combined solvent was removed under reduced pressure to give the title compound. Allylic bromide **S15** was obtained as a clear oil (1.55 g, 99% yield). The collected spectra were consistent with those reported in the literature[37].



S16

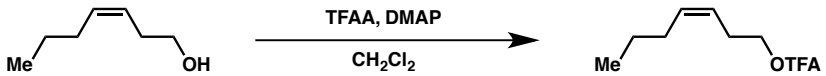
S16: A flame-dried round-bottom flask was charged with anhydrous CH_2Cl_2 (20 mL) and *(Z)*-hex-2-en-1-ol (0.58 ml, 5.0 mmol, 1 equiv). The flask was cooled to 0 °C in an ice bath. 4-Dimethylaminopyridine (0.061 g, 0.5 mmol, 0.1 equiv) was then added under an

argon atmosphere. Trifluoroacetic anhydride (1.4 mL, 10 mmol, 2 equiv) was added dropwise to the flask while maintaining the reaction temperature at 0 °C. The reaction mixture was then allowed to warm to 23 °C and stirred overnight. After completion, the reaction mixture was poured into hexanes (100 mL) and filtered through a silica gel plug. The reaction residue on silica gel was washed with hexanes (5 x 30 mL) and the combined solvent was removed under reduced pressure to give the title compound. Olefin **S16** was obtained as a clear oil (0.88 g, 90% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (m, 1H), 5.69 – 5.55 (m, 1H), 4.91 (d, *J* = 7.2 Hz, 2H), 2.15 (qd, *J* = 7.4, 1.6 Hz, 2H), 1.46 (h, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (q, *J* = 42.2 Hz), 138.2, 120.8, 114.5 (q, *J* = 285.7 Hz), 63.6, 29.6, 22.4, 13.6. ^{19}F NMR (376 MHz, $CDCl_3$) -75.1. IR (thin film): 2966, 1787, 1223, 921, 777 cm^{-1}. LRMS (APCI+) calcd for $[C_8H_{10}F_3O_2]^+$ ($[M-H]^+$): 195.07, found 195.10.



S17

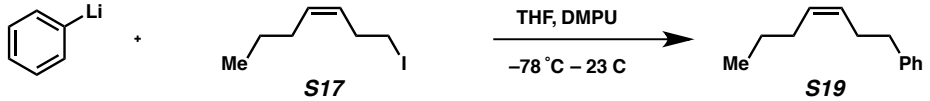
S17: Imidazole (1.021 g, 15 mmol, 1.5 equiv) and triphenylphosphine (3.67 g, 14 mmol, 1.4 equiv) was added to a stirred solution of *cis*-3-hexen-1-ol (1.4 ml, 10 mmol, 1 equiv) in CH_2Cl_2 (20 mL) at 0 °C. Iodine (3.81g, 15 mmol, 1.5 equiv) was then added in portions to the reaction mixture. The resulting solution was stirred for 30 min at 0 °C and 14 h at 23 °C. After completion, the reaction mixture was poured into hexanes (100 mL) and filtered through a silica gel plug. The solid residue was washed with hexanes (5 x 50 mL) and the combined solvent was removed under reduced pressure to give the title compound. The desired product **S17** was obtained as a clear oil (2.3 g, 99% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (m, 1H), 5.39 – 5.26 (m, 1H), 3.14 (t, *J* = 7.3 Hz, 2H), 2.73 – 2.56 (m, 2H), 2.01 (m, 2H), 1.39 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 127.9 , 31.5, 29.5, 22.7, 13.8, 5.6 . IR (thin film): 2929, 2870, 1456, 1241, 1169, 718 cm^{-1}. LRMS (APCI+) calcd for $[C_7H_{13}I]$ [M+]: 224.01, found 224.10.



S18

S18: A flame-dried round-bottom flask was charged with anhydrous CH_2Cl_2 (40 mL) and *cis*-3-hexen-1-ol (1.4ml, 10.0 mmol, 1 equiv). The flask was cooled to 0 °C in an ice bath. 4-Dimethylaminopyridine (0.122 g, 1.0 mmol, 0.1 equiv) was then added under an argon atmosphere. Triflouroacetic anhydride (2.8 mL, 20 mmol, 2 equiv) was added dropwise to the flask while maintaining the reaction temperature at 0 °C. The reaction mixture was then allowed to warm to 23 °C and stirred overnight. After completion, the reaction mixture was poured into hexanes (100 mL) and filtered through a silica gel plug. The reaction residue on silica gel was washed with hexanes (5 x 30 mL) and the combined solvent was removed under reduced pressure to give the title compound. Olefin **S18** was obtained as a clear oil (1.71 g, 81.4% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 – 5.48 (m, 1H), 5.40 – 5.25 (m, 1H), 4.34 (t, *J* = 6.9 Hz, 2H), 2.67 – 2.39 (m, 2H), 2.08 – 1.97 (m, 2H), 1.39 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ157.51 (q, *J* = 42.1 Hz), 134.0, 122.7, 114.5 (q, *J* = 285.9

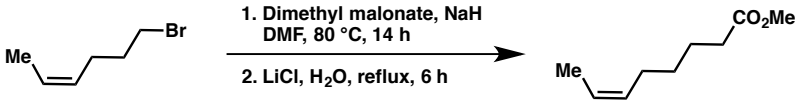
Hz), 67.4, 29.3, 26.4, 22.6, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) -75.13. IR (thin film): 2964, 2935, 1788, 1351, 1223, 776 cm^{-1}. LRMS (APCI+) calcd for $[C_9H_{14}F_3O_2]^+$ ($[M+H]^+$): 211.09, found 211.00.



S17 ***S19***

S19: A flame-dried round-bottom flask was charged with anhydrous THF (0.3 M), DMPU (0.6 M) and the flask was cooled to -78 ˚C in a dry ice/acetone bath. *(Z)*-1-iodohept-3-ene **S17** (1.12 g, 5.0 mmol, 1 equiv) was then added under an argon atmosphere. Phenyllithium (8.3 mL, 15 mmol, 4 equiv, 1.8 M) was added dropwise to the flask while maintaining the reaction temperature at -78 °C. After 30 minutes at -78 °C, the reaction mixture was allowed to warm to 23 °C and stirred overnight. After completion, a saturated aqueous NH_4Cl solution was added. The reaction mixture was extracted with Et_2O (3x). The organic phases were combined and washed with sodium thiosulfate and brine, dried over anhydrous magnesium sulfate, filtered, and concentrated to yield crude product. The crude product was purified by column chromatography on silica gel using 100% hexanes as an eluent. Olefin **S19** was obtained as a clear oil (0.283 g, 32.5% yield).

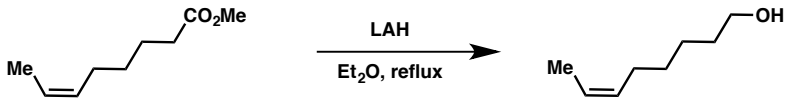
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 5.53 – 5.29 (m, 2H), 2.66 (dd, *J* = 8.8, 6.8 Hz, 2H), 2.36 (m, 2H), 2.03 – 1.89 (m, 2H), 1.32 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.15, 130.5, 128.8, 128.4, 128.2, 125.7, 36.0, 29.3, 29.2, 22.8, 13.8. IR (thin film): 3027, 2958, 1496, 1454, 746 cm^{-1}. HRMS (CI+) calcd for $[C_{13}H_{18}]^+$ ($[M^+]$): 174.1409, found 174.1406.



S20 ***S21***

S21: *(Z)*-6-bromohex-2-ene **S20**[38] (10 mmol) was converted to methyl *(Z)*-oct-6-enoate **S21** under previously described conditions in the literature[39]. Purification by column chromatography on silica gel using 100% hexanes as an eluent furnished the desired ester **S21** as a clear oil (1.006 g, 64% yield).

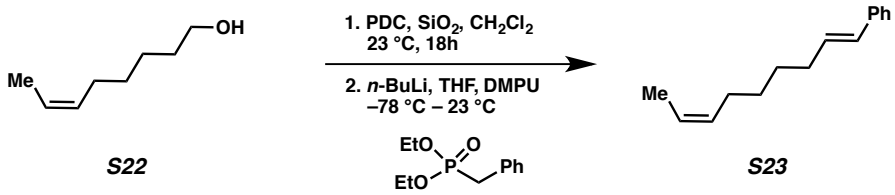
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 – 5.40 (m, 1H), 5.36 (m, 1H), 3.67 (s, 3H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.11 – 1.99 (m, 2H), 1.71 – 1.55 (m, 5H), 1.38 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 130.1, 124.2, 51.5, 34.0, 29.0, 26.4, 24.6, 12.8. IR (thin film): 2935, 2360, 1740, 1158, 668 cm^{-1}. GC-MS (CI+) calcd for $[C_9H_{16}O_2]^+$ ($[M^+]$): 156.11, found 156.00.



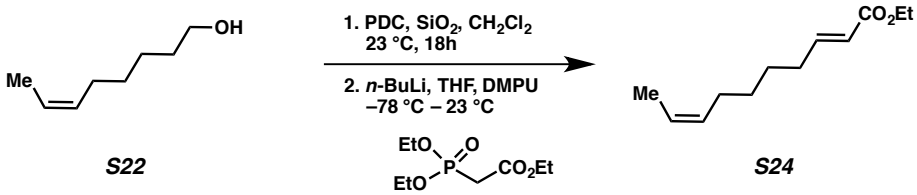
S21 ***S22***

S22: Methyl *(Z)*-oct-6-enoate **S21** (6.4 mmol) was converted to *(Z)*-oct-6-en-1-ol **S22** under the previously described conditions in the literature[39]. Purification by column

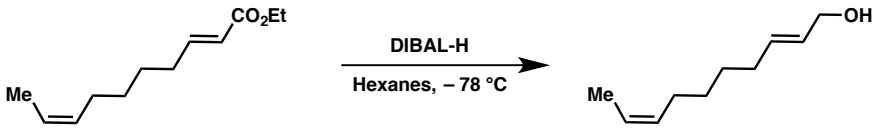
chromatography on silica gel using 5-20% ethyl acetate in hexanes as an eluent yielded alcohol **S22** as a clear oil (0.82 g, 99% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 – 5.32 (m, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.12 – 1.93 (m, 2H), 1.66 – 1.52 (m, 5H), 1.45 – 1.31 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.5, 123.9, 63.0, 32.7, 29.3, 26.8, 25.3, 12.76. IR (thin film): 3336, 2931, 2360, 1457, 1054, 700 cm^{-1}. HRMS (CI+) calcd for $[C_{18}H_{16}O]^+$ ([M$^+$]): 128.1201, found 128.1206.



S23: *(Z)*-oct-6-en-1-ol **S22** (3.0 mmol) was converted to ((1*E*,7*Z*)-nona-1,7-dien-1-yl)benzene **S23** under the previously described conditions in the literature[39]. Purification by column chromatography on silica gel using 100% hexanes as an eluent furnished styrene **S23** was obtained as a clear oil (0.427 g, 71% yield). The *E*-olefin geometry was assigned by the coupling constant at 6.38 ppm (J = 16.0 Hz).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 4H), 7.23 – 7.16 (m, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.23 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.54 – 5.27 (m, 2H), 2.22 (q, *J* = 7.1 Hz, 2H), 2.07 (q, *J* = 7.1 Hz, 2H), 1.61 (d, *J* = 6.2 Hz, 3H), 1.53 – 1.36 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 131.0, 130.6, 129.8, 128.5, 126.8, 125.9, 123.9, 32.9, 29.1, 29.0, 26.7, 12.8. IR (thin film): 3023, 2855, 1448, 963, 691 cm^{-1}. HRMS (CI+) calcd for $[C_{15}H_{20}]^+$ ([M$^+$]): 200.1565, found 200.1572.



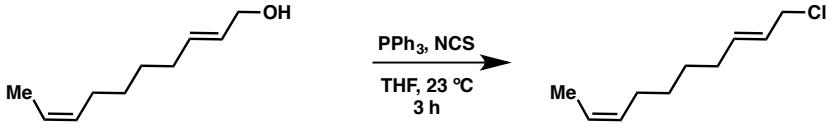
S24: *(Z)*-oct-6-en-1-ol **S22** (8.86 mmol) was converted to ethyl (2*E*,8*Z*)-deca-2,8-dienoate **S24** under the previously described conditions in the literature[39]. Purification by column chromatography on silica gel using 100% hexanes as an eluent. Ester **S24** was obtained as a clear oil (0.9 g, 52% yield). The *E*-olefin geometry was assigned by the coupling constant at 5.81 ppm (J = 15.6 Hz).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.81 (d, *J* = 15.6 Hz, 1H), 5.45 (m, 1H), 5.36 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.20 (m, 2H), 2.05 (m, 2H), 1.60 (d, *J* = 6.6 Hz, 3H), 1.53 – 1.43 (m, 2H), 1.42 – 1.33 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 149.3, 130.2, 124.1, 121.3, 60.1, 32.1, 29.0, 27.6, 26.5, 14.3, 12.8. IR (thin film): 2931, 2360, 1722, 1184, 701 cm^{-1}. HRMS (ESI) calcd for $[C_{12}H_{21}O_2]$ ([M+H]$^+$): 197.1536, found 197.1544.



S24 *S25*

S25: A flame-dried round-bottom flask was charged with ethyl (2*E*,8*Z*)-deca-2,8-dienoate **S24** (0.65 g, 3.31 mmol, 1 equiv) and anhydrous hexanes (0.1 M). The flask was cooled to -78°C. DIBAL-H (11 ml, 1.2 M, 4 equiv) was added dropwise. The reaction was stirred vigorously (~ 1,500 rpm). After 90 min, the reaction was quenched with saturated aqueous ammonium chloride. Following quenching, the crude suspension was stirred vigorously with Rochelle salt for 10 min. Extraction by Et_2O and concentration gave a clear residue, which was purified by flash chromatography (5-20% ethyl acetate in hexanes) to afford **S25** (0.41g, 81% yield) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 – 5.53 (m, 2H), 5.51 – 5.28 (m, 2H), 4.08 (t, J = 5.3 Hz, 2H), 2.04 (m, 4H), 1.59 (d, J = 6.4 Hz, 3H), 1.37 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.4, 130.5, 128.9, 123.8, 63.8, 32.1, 29.0, 28.7, 26.6, 12.8. IR (thin film): 3328, 2927,1438, 969, 700 cm^{-1}. HRMS (CI+) calcd for $[C_{10}H_{18}O]^+$ ($[M^+]$): 154.1358, found 154.1361.



S25 *S26*

S26: N-Chlorosuccinimide (0.51 g, 3.82 mmol, 1.5 equiv) was added in portions to a stirred solution of (2*E*,8*Z*)-deca-2,8-dien-1-ol **S25** (0.394 g, 2.55 mmol, 1 equiv) and triphenylphosphine (0.94 g, 3.57 mmol, 1.4 equiv) in THF (6 mL) at 0 °C. The resulting solution was stirred for 30 min at 0 °C and 3 h at 23 °C. After completion, the reaction mixture was poured into hexanes (100 mL) and filtered through a silica gel plug. The solid residue was washed with hexanes (5 x 30 mL) and the combined solvent was removed under reduced pressure to give the title compound. The desired product **S26** was obtained as a clear oil (0.365 g, 83% yield). The *E*-olefin geometry was assigned by the coupling constant at 5.77 ppm (J = 14.5 Hz).

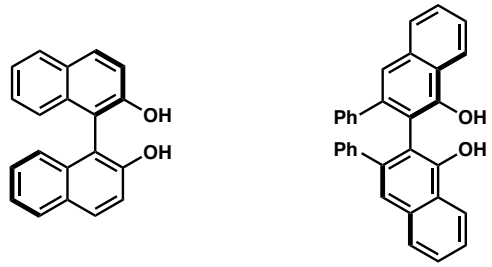
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (dt, J = 14.5, 6.6 Hz, 1H), 5.61 (dt, J = 16.6, 7.1 Hz, 1H), 5.53 – 5.31 (m, 2H), 4.03 (d, J = 7.2 Hz, 2H), 2.05 (m, 4H), 1.60 (d, J = 6.5 Hz, 3H), 1.39 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 130.4, 125.9, 123.9, 45.5, 32.0, 29.0, 28.4, 26.6, 12.8. IR (thin film): 3013, 2857, 1666, 1441, 1250, 966, 679 cm^{-1}. LRMS (APCI+) calcd for $[C_{10}H_{17}Cl]$ ($[M^+]$): 172.10, found 172.10.

Synthesis of BINOL Co-Catalysts

Commercially Available BINOL Co-Catalysts

BINOL 1 and **VANOL** were obtained from Sigma-Aldrich.

Fig. S2.
Commercially available BINOL co-catalysts.

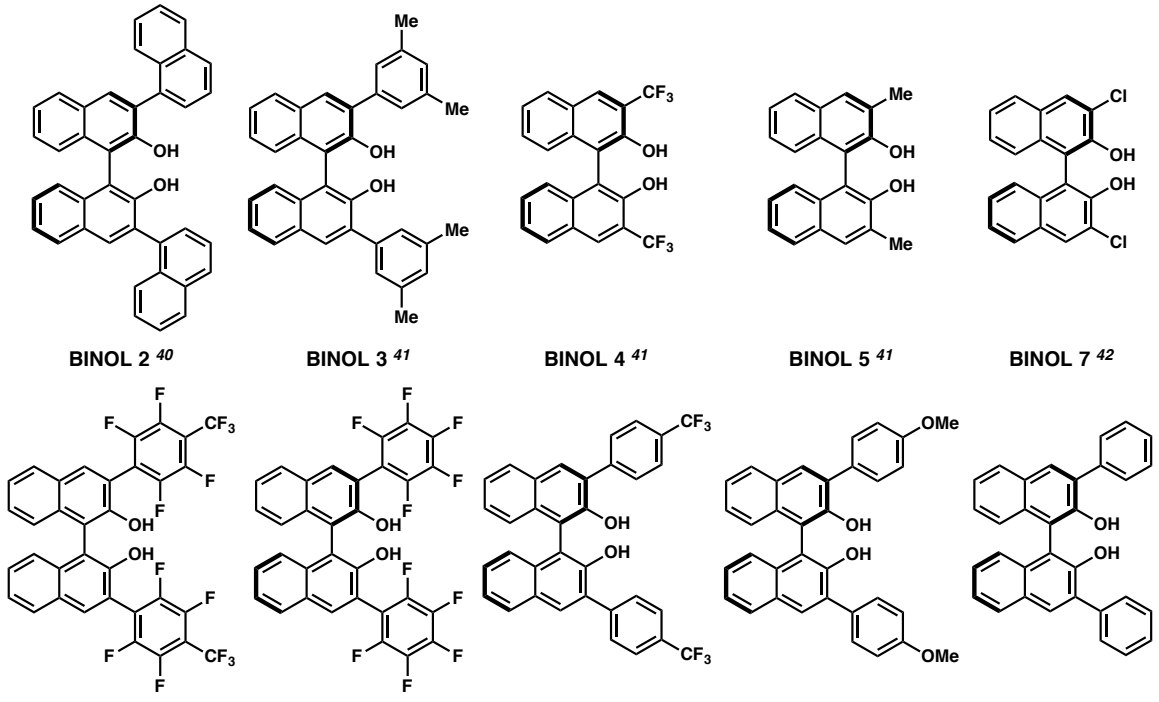


BINOL 1 **VANOL**

Synthesized BINOL Co-Catalysts

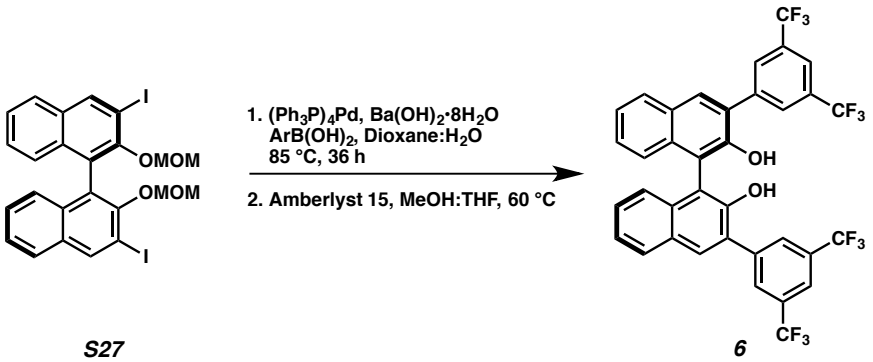
Most other BINOL co-catalysts were synthesized according to the corresponding literature procedures[40–46].

Fig. S3.
Known BINOL co-catalysts synthesized in our laboratory.



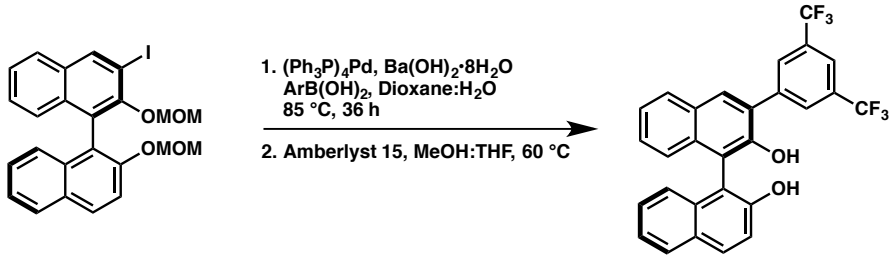
BINOL 2 [40] **BINOL 3** [41] **BINOL 4** [41] **BINOL 5** [41] **BINOL 7** [42]

BINOL 8 [43] **BINOL 9** [44] **BINOL 10** [45] **BINOL 11** [41] **BINOL 12** [41]



S27 *6*

6: A flame-dried round-bottom flask was charged with **S27**[43] (4.38 g, 7 mmol, 1 equiv), 3,5-bis(trifluoromethyl)-phenylboronic acid (5.42 g, 21 mmol, 3 equiv), and barium hydroxide octahydrate (6.63 g, 21 mmol, 3 equiv). The flask was degassed and back-filled with argon (3 times). Tetrakis(triphenylphosphine)palladium(0) (0.81 g, 0.7 mmol, 0.1 equiv) was added and the flask was again degassed and back-filled with argon (3 times). Degassed dioxane and H_2O (60 mL, 3:1) was finally added and the reaction mixture was heated to 85°C with stirring for 36 h. After completion, CH_2Cl_2 was added and the reaction mixture was extracted with CH_2Cl_2 (3x). The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated to yield a crude mixture. Purification by column chromatography (gradient 0-5% EtOAc/ hexanes) afforded the MOM protected intermediate. This material was transferred to a round-bottom flask. A mixture of THF and methanol (20 mL, 1:1) was added, followed by amberlyst 15 (8 g). The reaction mixture was heated to 60 °C and stirred overnight. After completion, the reaction was filtered through a celite plug and concentrated to yield the crude product, which was purified by column chromatography (gradient 0-5% EtOAc/ hexanes). The product was obtained as a white solid (4.15 g, 83% yield). Chiral HPLC analysis indicated the product was obtained with 99:1 enatiomeric ratio. ^{1}H NMR and ^{13}C NMR spectra were consistent with those reported in the literature[41].



S28 *BINOL 6*

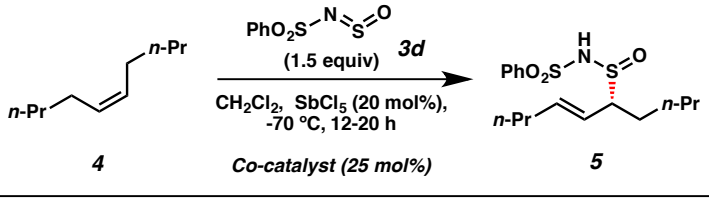
BINOL 6: A flame-dried round-bottom flask was charged with **S28**[46] (2.0 g, 4.0 mmol, 1.0 equiv), 3,5-Bis(trifluoromethyl)phenylboronic acid (2.063 g, 8 mmol, 2.0 equiv), and barium hydroxide octahydrate (2.524 g, 8 mmol, 2.0 equiv). The flask was degassed and back-filled with argon (3 times). Tetrakis(triphenylphosphine)palladium(0) (0.46 g, 0.4 mmol, 0.1 equiv) was added and the flask was again degassed and back-filled with argon (3 times). Degassed dioxane and H_2O (30 mL, 3:1) was finally added and the reaction mixture was heated to 85 °C and stirred for 36 h. After completion, CH_2Cl_2 was added and the reaction mixture was extracted with CH_2Cl_2 (3x). The organic phases were combined and washed with brine, dried over anhydrous magnesium sulfate, filtered, and

concentrated to yield a crude mixture, which was purified by column chromatography on silica gel using 0-5% ethyl acetate in hexanes as an eluent. The MOM protected product was obtained and was quickly transferred to a round bottom flask. THF and methanol (20 mL, 1:1) was then added followed by amberlyst 15 (8 g). The reaction mixture was heated to 60°C and stirred overnight. After completion, the reaction was filtered through a celite plug and concentrated to yield a crude product. The crude product was purified by column chromatography on silica gel using 0-5% ethyl acetate in hexanes as an eluent. The product was obtained as a white solid (1.13 g, 57% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 2H), 8.11 (s, 1H), 8.01 (dd, *J* = 9.0, 2.2 Hz, 2H), 7.99 – 7.90 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.46 – 7.33 (m, 4H), 7.22 (dd, *J* = 13.0, 8.4 Hz, 2H), 5.42 (s, 1H), 5.09 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 149.7, 139.7, 133.5, 133.3, 131.9 (m), 131.5 (q, *J* = 33.1 Hz), 129.9, 129.6, 129.3, 128.7, 128.6, 128.3, 127.8, 127.6, 125.0, 124.6, 124.3, 124.3, 124.0, 122.4, 121.2, 117.9, 112.5, 110.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.68. IR (thin film): 3429, 2928, 1593, 1148, 749 cm^{-1}. HRMS (CI+), calcd for [$C_{28}H_{16}O_2F_6$] ([M^+]): 498.1054, found 498.1057.

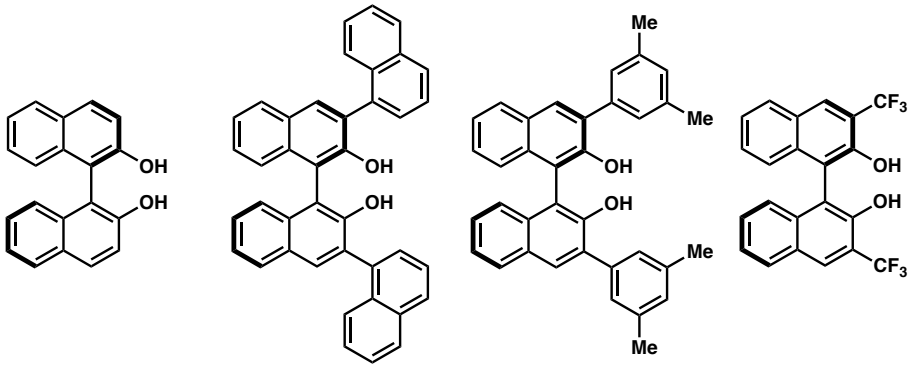
Extended Optimization Tables

Table S1.

Extended screen of BINOL co-catalysts (Part 1)



4 *Co-catalyst (25 mol%)* *5*

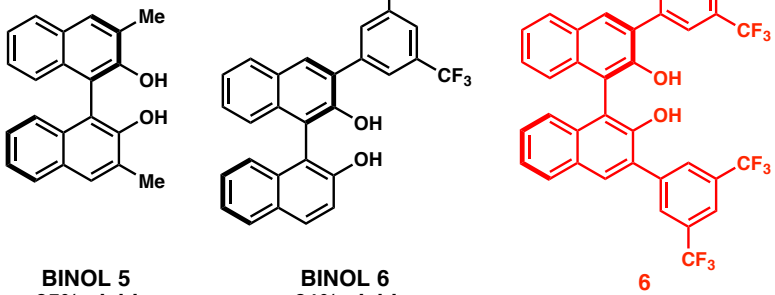


BINOL 1
88% yield
86.5 : 13.5 er

BINOL 2
75% yield
58.5 : 41.5 er

BINOL 3
79% yield
53 : 47 er

BINOL 4
76% yield
61.5 : 38.5 er



BINOL 5
95% yield
86 : 14 er

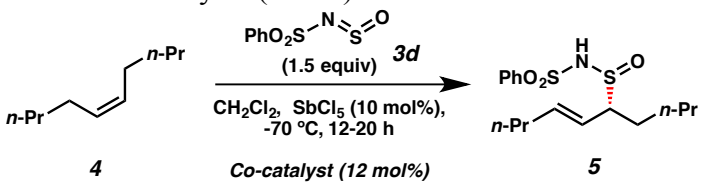
BINOL 6
91% yield
82.5 : 17.5 er

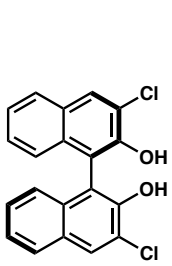
6
89% yield, (84%)[a]
92.5 : 7.5 er

Reaction conditions. *Cis*-5-decene (1 equiv), sulfurimide reagent 3d (1.5 equiv), CH_2Cl_2 (0.13M), $SbCl_5$ (20 mol%), co-catalyst (25 mol%). Yields were determined by ^{1}HNMR using 1,4-dimethoxybenzene as an internal standard. [a] Isolated yield.

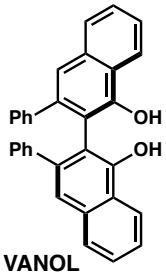
Table S2.

Extended screen of BINOL co-catalysts (Part 2)

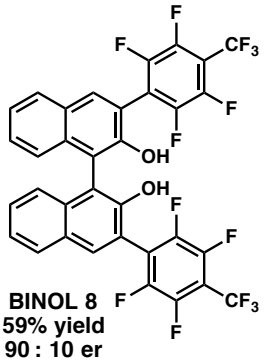




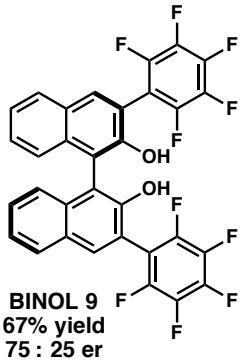
BINOL 7
85% yield
69 : 31 er



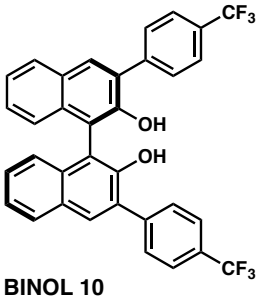
VANOL
20% yield
er ND



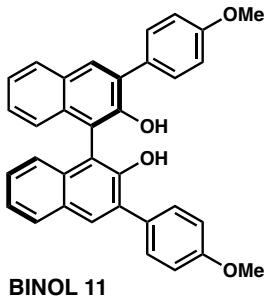
BINOL 8
59% yield
90 : 10 er



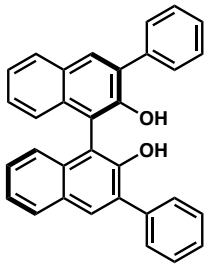
BINOL 9
67% yield
75 : 25 er



BINOL 10
50% yield
77 : 23 er



BINOL 11
23% yield
57.5 : 42.5 er

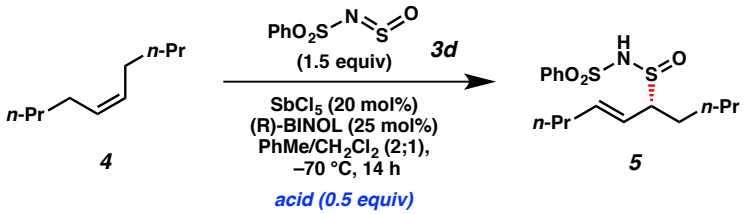


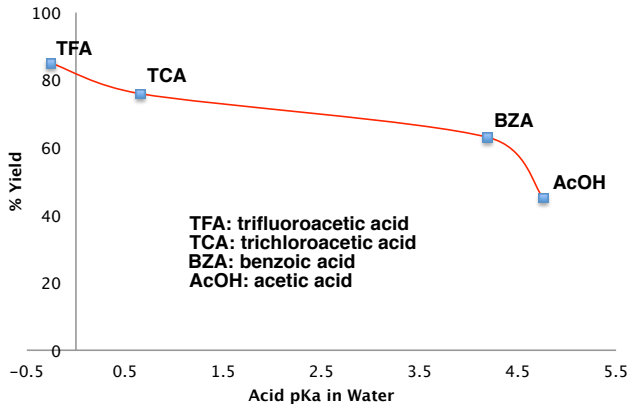
BINOL 112
34% yield
82.5 : 17.5 er

Reaction conditions. *Cis*-5-decene (1 equiv), sulfurimide reagent 3d (1.5 equiv), CH_2Cl_2 (0.13M), $SbCl_5$ (10 mol%), co-catalyst (12 mol%). Yields were determined by ^{1}HNMR using 1,4-dimethoxybenzene as an internal standard.

Fig. S4.

Screen of acid additives.

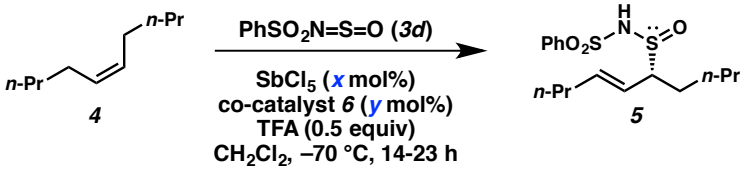




Reaction conditions. *Cis*-5-decene (1 equiv), sulfurimide reagent *3d* (1.5 equiv), solvent (0.13M), $SbCl_5$ (20 mol%), (R)-BINOL (25 mol%), acid (0.5 equiv). Yields were determined by ^{1}HNMR using DMB as an internal standard.

Table S3.

Catalyst loading screen.

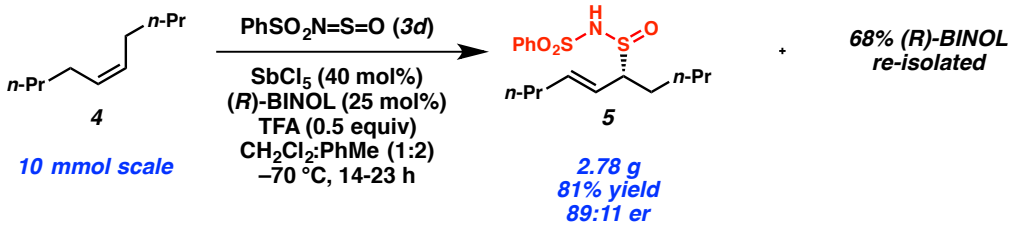


Entry	SbCl5 (*x* mol%)	co-catalyst *6* (*y* mol%)	Yield (%)	Enantiomeric Ratio
1	20	25	89	92.5 : 7.5
2	10	12.5	58	88 : 12
3	20	10	68	86.5 : 13.5
4	50	10	80	84.3 : 15.7
5	100	10	63	60.5 : 39.5

Reaction conditions. *Cis*-5-decene (1 equiv), sulfurimide reagent 3d (1.5 equiv), solvent (0.13M). Yields were determined by ^{1}HNMR using 1,4-dimethoxybenzene as an internal standard.

Fig. S5.

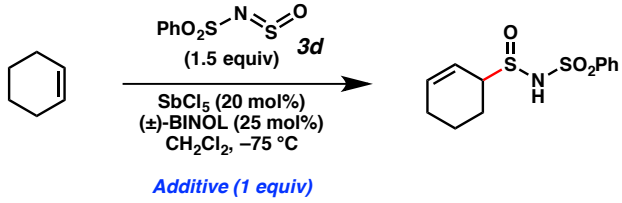
Scale up of enantioselective allylic oxidation on preparative scale (10 mmol).

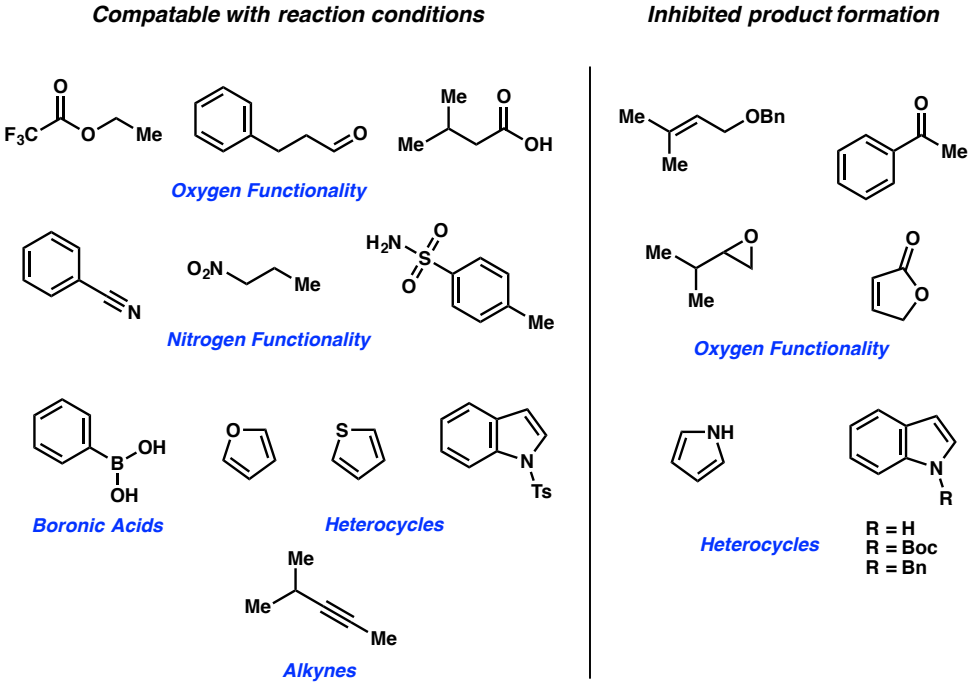


Functional Group Robustness Screen

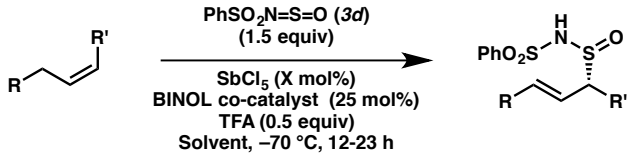
Fig. S6.

Functional group robustness screen.





General Procedures for the Catalytic Enantioselective Allylic Oxidation



General Procedure for the Enantioselective Hetero-Ene Reaction (Method A)

Benzenesulfonyl sulfurimide **3d** (122 mg, 1.5 equiv), and (*R*)-(+)-3,3′-Bis(3,5-bis(trifluoromethyl)phenyl)-1,1′-bi-2-naphthol (**6**) (71 mg, 25 mol%) were set under vacuum in a flame dried flask for approximately 10 minutes before purging with argon. The solids were dissolved in CH_2Cl_2 (1 mL) and cooled to –70 ºC. The resulting yellow solution was then treated with $SbCl_5$ (80 µL, 1 M in CH_2Cl_2, 20 mol%) dropwise while stirring vigorously. After 20 minutes, the alkene substrate (0.4 mmol) was added followed immediately by the addition of 2 mL CH_2Cl_2, washing the sides of the reaction vessel (solvent was added slowly to ensure that the internal reaction temperature did not significantly rise). The resulting black solution was treated with TFA (200 µL, 1 M CH_2Cl_2, 0.5 equiv) and the vessel septum was sealed with wax to prevent contamination by moisture. The solution was stirred at –70 ºC for 14-23 h. The reaction was quenched by addition of water (3 mL) at –70 ºC, and allowed to warm to 23 °C over the span of 1 h while stirring vigorously (~ 1,300 rpm). The resulting organic layer was collected and the aqueous layer was washed with EtOAc (3 x 6 mL, or until the aqueous layer went colorless). The combined organic layers were dried over anyhydrous sodium sulfate and concentrated under reduced pressure.

The resultant crude material was dissolved in a minimal amount of $CHCl_3$. Benzenesulfonamide was precipitated out by trituration with hexanes and removed under vacuum filtration. The filtrate was concentrated under reduced pressure and suspended in Et_2O (20 mL) and NEt_3 (123 µL, 2.2 equiv). The cloudy solution was washed with water (2 x 7 mL), and the combined aqueous extracts were washed with 20 mL Et_2O. The combined organic layers were back extracted with 5 mL water. All combined aqueous washes were acidified with 1N HCl until cloudy (approximately pH = 2), and washed with EtOAc (3 x 20 mL). The combined organic layers were dried over anyhydrous sodium sulfate and concentrated under reduced pressure to afford pure ene adduct.

Modified Procedure for the Enantioselective Hetero-Ene Reaction (Method B)

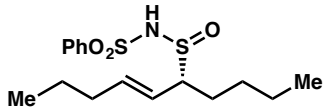
Benzenesulfonyl sulfurimide **3d** (122 mg, 1.5 equiv), and (*R*)-(+)-3,3′-Bis(3,5-bis(trifluoromethyl)phenyl)-1,1′-bi-2-naphthol (**6**) (71 mg, 25 mol%) were set under vacuum in a flame dried flask for approximately 10 minutes before purging with argon. The solids were dissolved in CH_2Cl_2 (1 mL) and cooled to –70 ºC. The resulting yellow solution was then treated with $SbCl_5$ (160 µL, 1 M in CH_2Cl_2, 40 mol%) dropwise while stirring vigorously. After 20 minutes, the alkene substrate (0.4 mmol) was added

followed immediately by the addition of 2 mL CH_2Cl_2, washing the sides of the reaction vessel (solvent was added slowly to ensure that the internal reaction temperature did not significantly rise). The resulting black solution was treated with TFA (200 μL, 1 M CH_2Cl_2, 0.5 equiv) and the vessel septum was sealed with wax to prevent contamination by moisture. The solution was stirred at –70 ºC for 14-23 h. The reaction was quenched by addition of water (3 mL) at –70 ºC, and allowed to warm to 23 °C over the span of 1 h while stirring vigorously (~ 1,300 rpm). The resulting organic layer was collected and the aqueous layer was washed with EtOAc (3 x 6 mL, or until the aqueous layer went colorless). The combined organic layers were dried over anyhydrous sodium sulfate and concentrated under reduced pressure. The product was purified according to Method A.

General Procedure for the Enantioselective Hetero-Ene Reaction (Method C)

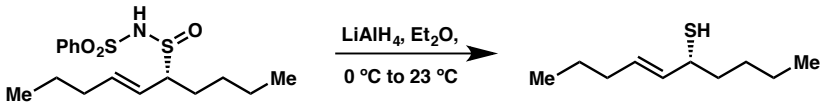
Benzenesulfonyl sulfurimide **3d** (122 mg, 1.5 equiv), and (*R*)-1,1'-Bi-2-naphthol (29 mg, 25 mol%) were set under vacuum in a flame dried flask for approximately 10 minutes before purging with argon. The solids were dissolved in PhMe (1 mL) and cooled to –70 ºC. The resulting yellow solution was then treated with $SbCl_5$ (160 μL, 1 M in CH_2Cl_2, 40 mol%) dropwise while stirring vigorously. After 20 minutes, the alkene substrate (0.4 mmol) was added followed immediately by the addition of 1 mL PhMe and 1 mL CH_2Cl_2, washing the sides of the reaction vessel (solvents were added slowly to ensure that the internal reaction temperature did not significantly rise). The resulting black solution was treated with TFA (200 μL, 1 M CH_2Cl_2, 0.5 equiv) and the vessel septum was sealed with wax to prevent contamination by moisture. The solution was stirred at –70 ºC for 14-23 h. The reaction was quenched by addition of water (3 mL) at –70 ºC, and allowed to warm to 23 °C over the span of 1 h while stirring vigorously (~ 1,300 rpm). The resulting organic layer was collected and the aqueous layer was washed with EtOAc (3 x 6 mL, or until the aqueous layer went colorless). The combined organic layers were dried over anyhydrous sodium sulfate and concentrated under reduced pressure. The product was purified according to Method A.

Characterization Data for Allylic Oxidation Products



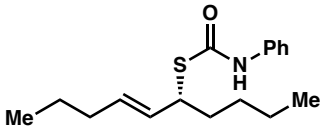
8a: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method A), *cis*-5-decene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 16 h. The product was purified according to the general procedure to afford **8a** (84% yield, 4:1 dr) as an inseparable mixture of diastereomers epimeric at sulfur. The product was a viscous clear oil. The enantiomeric ratio of the product was determined to be 92.5:7.5 after conversion to thiocarbamate **S29** (see experimental procedure for **S29**). The *E*-olefin geometry was assigned by the coupling constant at 5.83 ppm (J = 15.6 Hz). 1D-NOESY experiments also confirmed the *E*-olefin geometry by absence of an NOE interaction between the two olefinic protons.

The following data is representative of a 4:1 mixture of diastereomers: $[\alpha]^{23}_D$ = -39.4° (c = 1.34, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 2H), 7.62 (td, *J* = 7.3, 1.6 Hz, 1H), 7.59 – 7.49 (m, 2H), 5.83 (dt, *J* = 15.6, 7.0 Hz, 1H), 5.40 – 5.23 (m, 1H), 3.43 (td, *J* = 8.8, 5.1 Hz, 0.2H), 3.11 (td, *J* = 9.7, 5.5 Hz, 0.8H), 2.20 – 1.99 (m, 2H), 1.96 – 1.82 (m, 0.8H), 1.79 – 1.62 (m, 1H), 1.61 – 1.49 (m, 0.2H), 1.48 – 1.22 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 141.6, 140.4, 140.4, 133.8, 133.8, 129.5, 129.5, 127.3, 127.3, 120.4, 119.7, 69.1, 69.0, 35.0, 34.8, 29.1, 28.9, 28.9, 27.5, 22.5, 22.4, 22.3, 22.2, 13.9, 13.9, 13.7, 13.7. IR (thin film): 2958, 2360, 1375, 1149, 1071, 856 cm^{-1}. HRMS (ESI-TOF) calcd for $[C_{16}H_{25}NO_3S_2]^+$ ($[M+H]^+$): 344.1349, found 344.1351.

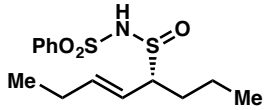


8a ***11***

11: A flame-dried round-bottom flask was charged with $LiAlH_4$ (2.2 equiv) and anhydrous Et_2O (0.1 M). The flask was cooled to 0 °C. Ene adduct **8a** (0.1mmol) was added dropwise. The reaction was warmed to 23 °C and stirred vigorously (~ 1,500 rpm). After 20 min, the reaction was cooled to 0 °C and quenched with 1 mL saturated aqueous ammonium chloride. Following quenching, the crude suspension was stirred vigorously for 1 h. Extraction by Et_2O and concentration gave a grey residue, which was purified by flash chromatography (100% pentane) to afford **11** (72% yield) as a clear oil. The *E*-olefin geometry was assigned by the coupling constant at 5.39 ppm (J = 15.1 Hz).
$[\alpha]^{23}_D$ = -23.2° (c = 0.19, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (dt, *J* = 15.1, 6.4 Hz, 1H), 5.39 (dd, *J* = 15.1, 8.5 Hz, 1H), 3.41 (qd, *J* = 7.4, 4.7 Hz, 1H), 1.98 (q, *J* = 6.8, 6.4 Hz, 2H), 1.64 – 1.53 (m, 2H), 1.44 – 1.24 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 130.4, 42.6, 38.3, 34.3, 29.8, 22.5, 22.5, 14.1, 13.8. IR (thin film): 2958, 2928, 1464, 1378, 964, 730 cm^{-1}. HRMS (CI-) calcd for $[C_{10}H_{19}S]^+$ ($[M-H]^+$): 171.1207, found 171.1212.

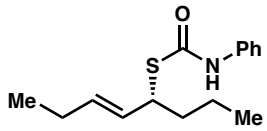


S29: Thiol **11** (0.13 mmol) was suspended in pyridine (200 µL, 0.65 M) and phenyl isothiocyanate (21 µL, 1.4 equiv) was added. The reaction was stirred for 35 minutes. Pyridine was azeotropped off with heptane and the resulting residue was purified by flash chromatography (gradient from 100% hexanes to 10% hexanes/ethyl acetate) to afford **S29** as a white solid (81% yield).
$[\alpha]^{23}_D$ = +69.6° (c = 0.81, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.16 – 7.02 (m, 2H), 5.70 (dt, *J* = 14.3, 6.8 Hz, 1H), 5.42 (dd, *J* = 15.2, 8.7 Hz, 1H), 4.05 (q, *J* = 8.0 Hz, 1H), 2.01 (q, *J* = 7.1 Hz, 2H), 1.81 – 1.62 (m, 2H), 1.47 – 1.28 (m, 6H), 0.89 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 132.9, 130.2, 129.2, 124.4, 119.8, 48.0, 35.0, 34.5, 29.5, 25.5, 22.5, 22.4, 14.1, 13.7. IR (thin film): 2920, 2342, 1440, 1146, 751, 668 cm^{-1}. HRMS (CI+) calcd for $[C_{17}H_{25}NOS]^+$ ($[M^+]$): 291.1657, found 291.1650.



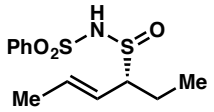
8b: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method A), *cis*-4-octene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 16 h. The product was purified according to the general procedure to afford **8b** (80% yield, 4:1 dr) as an inseparable mixture of diastereomers epimeric at sulfur. The product was a viscous clear oil. The enantiomeric ratio of the product was determined to be 92.5:7.5 after conversion to thiocarbamate **S30** (see experimental procedure for **S30**). The *E*-olefin geometry was assigned by the coupling constant at 5.89 ppm (J = 15.6 Hz).

The following data is representative of a 4:1 mixture of diastereomers: $[\alpha]^{23}_{D}$ = -79.3° (c = 0.30, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 2H), 7.68 – 7.58 (m, 1H), 7.59 – 7.49 (m, 2H), 5.89 (dt, *J* = 15.6, 6.3 Hz, 1H), 5.32 (ddt, *J* = 15.5, 9.8, 1.7 Hz, 1H), 3.45 (td, *J* = 8.9, 5.2 Hz, 0.2H), 3.14 (td, *J* = 9.6, 5.4 Hz, 0.8H), 2.22 – 2.02 (m, 2H), 1.93 – 1.79 (m, 0.8H), 1.76 – 1.30 (m, 3.2H), 1.07 – 0.87 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.3, 140.4, 140.3, 133.9, 133.8, 129.5, 129.5, 127.3, 127.3, 119.1, 118.5, 68.8, 68.7, 31.3, 29.9, 26.0, 26.0, 20.1, 20.0, 13.9, 13.8, 13.6, 13.4. IR (thin film): 2962, 2360, 1374, 1169, 1071, 840 cm^{-1}. HRMS (CI+) calcd for $[C_{14}H_{22}NO_3S_2]^+$ ($[M+H]^+$): 316.1041, found 316.1050.



S30: **8b** (0.2 mmol) was converted to **S30** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S30** as a white solid (13% yield for 2 steps; R_f = 0.43 in 15% EtOAc/Hexanes).

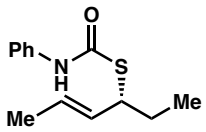
$[\alpha]^{23}_{D}$ = +40.0° (c = 0.18, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.98 (s, 1H), 5.76 (dt, *J* = 13.6, 6.4 Hz, 1H), 5.42 (dd, *J* = 15.2, 8.8 Hz, 1H), 4.06 (q, *J* = 8.4, 7.9 Hz, 1H), 2.05 (m, 2H), 1.80 – 1.59 (m, 2H), 1.42 (m, 2H), 0.96 (m, 6H). IR (thin film): 2959, 1656, 1534, 1309, 1146, 751 cm^{-1}. HRMS (CI+) calcd for $C_{15}H_{21}NOS$ ($[M^+]$): 263.1344, found 263.1347.



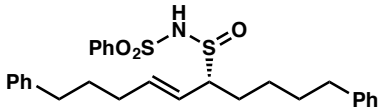
8c: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method A), *cis*-3-hexene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 17 h. The product was purified according to the general procedure to afford **8c** (80% yield, 4:1 dr) as an inseparable mixture of diastereomers epimeric at sulfur. The product was a viscous clear oil. The enantiomeric ratio of the product was determined to be 95:5 after conversion to thiocarbamate **S31** (see experimental procedure for **S31**). The *E*-olefin geometry was assigned by the coupling constant at 5.33 ppm (J = 15.1 Hz).

The following data is representative of a 4:1 mixture of diastereomers: $[\alpha]^{23}_{D}$ = -14.0° (c = 1.30, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 2H), 7.65 – 7.58 (m, 1H),

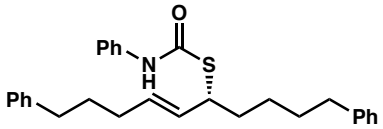
7.57 – 7.48 (m, 2H), 5.91 – 5.70 (m, 1H), 5.33 (ddq, *J* = 15.1, 9.7, 1.7 Hz, 0.8H), 5.20 (ddq, *J* = 15.4, 8.5, 1.7 Hz, 0.2H), 3.36 (td, *J* = 9.3, 4.8 Hz, 0.2H), 3.06 (td, *J* = 9.6, 5.4 Hz, 0.8H), 1.98 – 1.77 (m, 3.4H), 1.73 – 1.52 (m, 1.6H), 0.98 (dt, J = 13.4, 7.4 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 140.4, 140.4, 136.9, 136.2, 133.7, 133.5, 129.5, 129.4, 127.2, 127.2, 121.3, 121.0, 70.5, 70.5, 22.6, 21.5, 18.5, 18.5, 11.4, 11.3. IR (thin film): 2970, 1448, 1373, 1168, 1072, 860 cm^{-1}. HRMS (CI+) calcd for $[C_{12}H_{18}NO_3S_2]^+$ ($[M+H]^+$): 288.0728, found 288.0741.



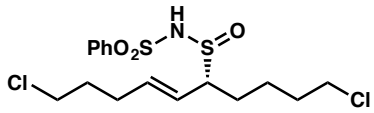
S31: **8c** (0.2 mmol) was converted to **S31** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S31** as a white solid (10% yield for 2 steps; R_f = 0.43 in 15% EtOAc/Hexanes).
$[\alpha]^{23}_D$ = +32.3° (c = 0.16, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.99 (s, 1H), 5.79 – 5.68 (m, 1H), 5.45 (ddd, *J* = 15.2, 8.7, 1.7 Hz, 1H), 3.98 (q, *J* = 7.4 Hz, 1H), 1.84 – 1.66 (m, 5H), 0.99 (t, *J* = 7.3 Hz, 3H). IR (thin film): 2958, 1656, 1440, 1149, 882, 750 cm^{-1}. HRMS (CI+) calcd for $[C_{13}H_{17}NOS]^+$ ($[M^+]$): 235.1031, found 235.1035.



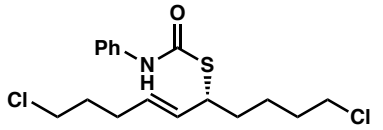
8d: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method A), *cis*-1,10-diphenyl-5-decene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 16 h. The product was purified according to the general procedure to afford **8d** (80% yield, 4:1 dr) as an inseparable mixture of diastereomers epimeric at sulfur. The product was a viscous clear oil. The enantiomeric ratio of the product was determined to be 92.5:7.5 after conversion to thiocarbamate **S32** (see experimental procedure for **S32**). The *E*-olefin geometry was assigned by the coupling constant at 5.29 ppm (J = 15.6 Hz).
The following data is representative of a 4:1 mixture of diastereomers: $[\alpha]^{23}_D$ = -101.7° (c = 0.59, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.87 (m, 2H), 7.66 – 7.44 (m, 3H), 7.35 – 7.10 (m, 10H), 5.89 – 5.73 (m, 1H), 5.29 (dd, J = 15.6, 9.0 Hz, 1H), 3.41 (dt, J = 8.9, 4.9 Hz, 0.5H), 3.11 (dt, J = 9.6, 5.3 Hz, 0.5H), 2.59 (q, J = 7.3 Hz, 4H), 2.22 – 2.00 (m, 2H), 2.00 – 1.83 (m, 0.5H), 1.84 – 1.28 (m, 7.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 142.0, 142.1, 141.9, 141.9, 141.2, 140.4, 140.4, 133.8, 133.7, 129.5, 129.5, 129.0, 128.7, 128.6, 128.5, 128.5, 128.5, 127.3, 127.2, 126.3, 126.2, 126.1, 126.0, 126.0, 125.9, 120.7, 120.0, 69.0, 68.8, 35.6, 35.5, 35.5, 35.5, 32.5, 32.4, 31.1, 31.0, 30.9, 30.7, 29.1, 27.7, 26.4, 26.3. IR (thin film): 2931, 1448, 1375, 1152, 1072, 700 cm^{-1}. HRMS (ESI) calcd for $[C_{28}H_{33}NO_3S_2Na]^+$ ($[M+Na]^+$): 518.1794, found 518.1796.



S32: **8d** (0.1 mmol) was converted to **S32** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S32** as a white solid (16% yield for 2 steps; R_f = 0.48 in 15% EtOAc/Hexanes).
$[\alpha]^{23}_D$ = +45.7° (c = 0.53, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.22 (m, 6H), 7.22 – 7.05 (m, 7H), 6.99 (s, 1H), 5.72 (dt, *J* = 14.2, 6.8 Hz, 1H), 5.43 (dd, *J* = 15.3, 8.8 Hz, 1H), 4.06 (q, *J* = 7.8 Hz, 1H), 2.61 (q, *J* = 7.7 Hz, 4H), 2.07 (q, *J* = 7.2 Hz, 2H), 1.85 – 1.58 (m, 6H), 1.52 – 1.43 (m, 2H). IR (thin film): 2920, 1645, 1439, 1308, 1143, 752 cm^{-1}. HRMS (CI+) calcd for $[C_{29}H_{33}NOS]^+$ ($[M^+]$): 443.2283, found 443.2270.

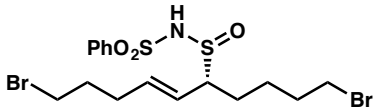


8e: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method B), *cis*-1,10-dichlorodec-5-ene (0.4 mmol, 40 mol% $SbCl_5$) was converted to the desired product. The hetero-ene reaction was stirred for 18.5 h. The product was purified according to the general procedure to afford **8e** (72% yield, 4:1 dr) as an inseparable mixture of diastereomers epimeric at sulfur. The product was a white solid. The enantiomeric ratio of the product was determined to be 93.5:6.5 after conversion to thiocarbamate **S33** (see experimental procedure for **S33**). The *E*-olefin geometry was assigned by the coupling constant at 5.39 ppm (J = 15.4 Hz).
The following data is representative of a 4:1 mixture of diastereomers: $[\alpha]^{23}_D$ = -20.4° (c = 2.11, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.88 (m, 2H), 7.69 – 7.48 (m, 3H), 5.89 – 5.71 (m, 1H), 5.39 (dd, *J* = 15.4, 9.6 Hz, 0.8H), 5.28 (dd, *J* = 15.5, 8.8 Hz, 0.2H), 3.64 – 3.39 (m, 4.2H), 3.22 (dt, *J* = 9.7, 5.0 Hz, 0.8H), 2.30 (q, *J* = 7.1 Hz, 1.6H), 2.21 (q, *J* = 7.4 Hz, 0.4H), 1.95 – 1.41 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 140.2, 139.6, 139.6, 133.8, 133.7, 129.4, 129.4, 127.2, 127.1, 121.3, 121.0, 68.7, 68.5, 44.5, 44.4, 44.2, 44.2, 32.0, 31.9, 31.1, 30.7, 29.8, 29.7, 28.0, 27.3, 24.1, 24.0. IR (thin film): 2956, 1448, 1373, 1072, 855, 688 cm^{-1}. HRMS (CI+) calcd for $[C_{16}H_{24}NO_3S_2Cl_2]^+$ ($[M+H]^+$): 412.0575, found 412.0571.



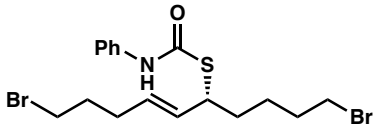
S33: **8e** (0.1 mmol) was converted to **S33** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S33** as a white solid (15% yield for 2 steps; R_f = 0.38 in 20% EtOAc/Hexanes).
$[\alpha]^{23}_D$ = +75.6° (c = 0.59, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.36 – 7.27 (m, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.00 (s, 1H), 5.74 – 5.62 (m, 1H), 5.49 (dd, *J* = 15.2, 8.7 Hz, 1H), 4.05 (q, *J* = 8.2 Hz, 1H), 3.53 (dt, *J* = 8.2, 6.5 Hz, 4H), 2.20 (q, *J* = 7.1, 6.5 Hz, 2H), 1.93 – 1.66 (m, 6H), 1.56 (q, *J* = 7.3 Hz, 2H). IR (thin film): 2919,

1652, 1438, 1308, 1144, 751 cm^{-1}. HRMS (CI+) calcd for $[C_{17}H_{24}NOSCl_2]^+$ ($[M+H]^+$): 360.0956, found 360.0944.



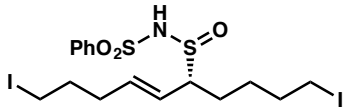
8f: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method A), *cis*-1,10-dibromodec-5-ene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 16.5 h. The product was purified according to the general procedure to afford **8f** (49% yield, 12:1 dr) as an inseparable mixture of diastereomers epimeric at sulfur. The product was a white solid. The enantiomeric ratio of the product was determined to be 93.5:6.5 after conversion to thiocarbamate **S34** (see experimental procedure for **S34**). The *E*-olefin geometry was assigned by the coupling constant at 5.82 ppm (J = 15.5 Hz).

The following data is representative of a 12:1 mixture of diastereomers: $[\alpha]^{23}_D$ = -70.7° (c = 1.8, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 5.82 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.43 (ddt, *J* = 15.6, 9.7, 1.5 Hz, 0.92H), 5.32 (dd, *J* = 15.5, 8.6 Hz, 0.08H), 3.40 (m, 4.07H), 3.20 (td, *J* = 9.6, 5.1 Hz, 0.93H), 2.38 – 2.20 (m, 2H), 2.02 – 1.81 (m, 5H), 1.76 – 1.47 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 140.1, 133.9, 129.5, 127.3, 121.6, 68.6, 33.2, 33.2, 32.2, 31.2, 31.1, 28.1, 25.4. IR (thin film): 2937, 1448, 1371, 1168, 1073, 849 cm^{-1}. HRMS (ESI) calcd for $[C_{16}H_{23}Br_2NO_3S_2Na]^+$ ($[M+Na]^+$): 521.9378, found 521.9375.



S34: **8f** (0.1 mmol) was converted to **S34** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S34** as a white solid (16% yield for 2 steps; R_f = 0.36 in 20% EtOAc/Hexanes).

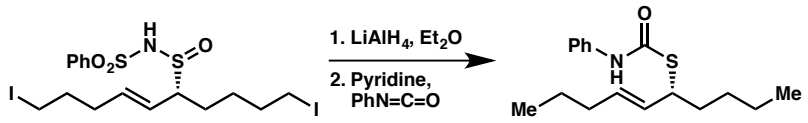
$[\alpha]^{23}_D$ = +40.0° (c = 0.19, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.97 (s, 1H), 5.67 (dt, *J* = 14.0, 6.8 Hz, 1H), 5.50 (dd, *J* = 15.2, 8.7 Hz, 1H), 4.05 (q, *J* = 8.1 Hz, 1H), 3.40 (dt, *J* = 8.5, 6.6 Hz, 4H), 2.21 (q, *J* = 6.7 Hz, 2H), 1.99 – 1.83 (m, 4H), 1.82 – 1.66 (m, 2H), 1.57 (q, *J* = 7.4 Hz, 2H). IR (thin film): 2920, 1652, 1438, 1308, 1142, 751 cm^{-1}. HRMS (CI+) calcd for $[C_{17}H_{24}NOSBr_2]^+$ ($[M+H]^+$): 447.9945, found 447.9926.



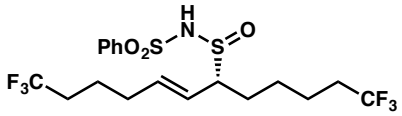
8g: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method B), *cis*-1,10-diiododec-5-ene (0.4 mmol, 40 mol% $SbCl_5$) was converted to the desired product. The hetero-ene reaction was stirred for 16 h. The product was purified according to the general procedure to afford **8g** (84% yield, 9:1 dr) as an inseparable mixture of diastereomers epimeric at sulfur. The product was a white solid. The enantiomeric ratio of the product was determined to be 93.5:6.5 after conversion to

thiocarbamate **S29** (see experimental procedure for **S29**). The *E*-olefin geometry was assigned by the coupling constant at 5.79 ppm (J = 15.5 Hz).

The following data is representative of a 9:1 mixture of diastereomers: $[\alpha]^{23}_D$ = -53.6° (c = 5.29, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.87 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.61 – 7.49 (m, 2H), 5.79 (dt, *J* = 15.5, 6.8 Hz, 0.9H), 5.69 (dt, *J* = 14.6, 7.0 Hz, 0.1H), 5.43 (dd, *J* = 15.5, 9.6 Hz, 0.9H), 5.32 (dd, *J* = 15.4, 8.5 Hz, 0.1H), 3.39 (td, *J* = 9.2, 5.0 Hz, 0.1H), 3.25 – 3.10 (m, 4.9H), 2.35 – 2.14 (m, 2H), 1.96 – 1.77 (m, 5H), 1.75 – 1.60 (m, 1H), 1.60 – 1.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 139.9, 139.5, 139.5, 133.9, 133.8, 129.5, 129.5, 127.2, 127.2, 121.6, 121.2, 68.8, 68.6, 33.4, 33.3, 32.9, 32.7, 31.8, 31.2, 27.7, 27.6, 27.4, 27.1, 7.5, 6.4, 6.4, 6.3. IR (thin film): 2933, 1448, 1372, 1152, 1073, 854 cm^{-1}. LRMS (CI+) calcd for $[C_{16}H_{24}I_2NO_3S_2]^+$ ($[M+H]^+$): 595.92, found 595.91.

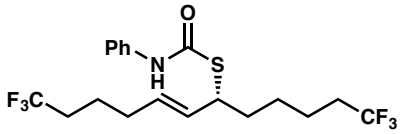


8g (0.15 mmol) was converted to **S29** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S29** as a white solid (19% yield for 2 steps): $[\alpha]^{23}_D$ = +74.2° (c = 0.655, CH_2Cl_2).

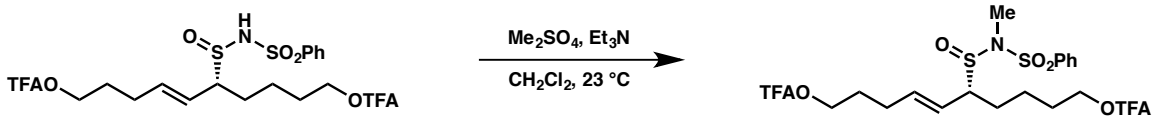


8h: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method B), *cis*-1,1,1,12,12,12-hexafluorododec-6-ene (0.34 mmol, 40 mol% $SbCl_5$) was converted to the desired product. The hetero-ene reaction was stirred for 14 h. The product was purified according to the general procedure to afford **8h** (76% yield, 1:1 dr) as an inseparable mixture of diastereomers epimeric at sulfur. The product was a pale yellow solid. The enantiomeric ratio of the product was determined to be 93.5:6.5 after conversion to thiocarbamate **S35** (see experimental procedure for **S35**). The *E*-olefin geometry was assigned by the coupling constant at 5.34 ppm (J = 15.5 Hz).

The following data is representative of a 1:1 mixture of diastereomers: $[\alpha]^{23}_D$ = -34.0° (c = 2.07, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.86 (m, 2H), 7.68 – 7.58 (m, 1H), 7.58 – 7.49 (m, 2H), 5.78 (ddt, *J* = 22.1, 15.3, 6.7 Hz, 1H), 5.34 (dd, *J* = 15.5, 9.6 Hz, 0.5H), 5.23 (dd, *J* = 15.5, 8.8 Hz, 0.5H), 3.47 (dt, *J* = 9.5, 4.7 Hz, 0.5H), 3.22 (dt, *J* = 9.7, 4.9 Hz, 0.5H), 2.28 – 1.95 (m, 6H), 1.94 – 1.76 (m, 1H), 1.71 – 1.34 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 140.4, 140.3, 139.8, 133.8, 133.6, 129.5, 129.4, 127.2, 127.2 (q, *J* = 275 Hz), 127.1 (q *J* = 275 Hz, 2C), 127.1 (q, *J* = 275 Hz), 127.1, 121.9, 121.4, 68.7, 68.5, 33.4 (q, *J* = 28.5 Hz, 2C), 33.1 (q, *J* = 28.4 Hz), 33.1 (q, *J* = 28.4 Hz), 31.6, 31.6, 28.0, 27.9, 25.9, 25.9, 21.8 (dq, *J* = 8.2, 3.1 Hz; 2C), 21.3 (q, *J* = 2.9 Hz), 21.2 (q, *J* = 2.9 Hz). IR (thin film): 2950, 1449, 1256, 1134, 1031, 838 cm^{-1}. HRMS (CI+) calcd for $[C_{18}H_{24}NO_3F_6S_2]^+$ ($[M+H]^+$): 480.1102, found 480.1097.

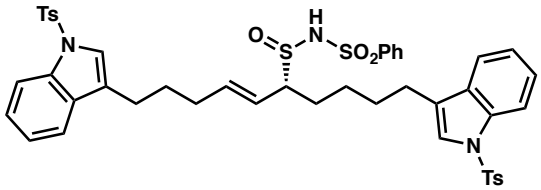


S35: **8h** (0.15 mmol) was converted to **S35** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S35** as a white solid (14% yield for 2 steps; R_f = 0.63 in 20% EtOAc/Hexanes).
$[\alpha]^{23}_D$ = +67.4° (c = 0.78, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 4H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.00 (s, 1H), 5.67 (dt, *J* = 15.1, 6.8 Hz, 1H), 5.46 (dd, *J* = 15.1, 8.8 Hz, 1H), 4.04 (q, *J* = 8.2 Hz, 1H), 2.18 – 1.98 (m, 6H), 1.83 – 1.42 (m, 8H). IR (thin film): 2945, 1655, 1599, 1254, 1029, 752 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{23}F_6NOSNa]^+$ ($[M+Na]^+$): 450.1297, found 450.1305.



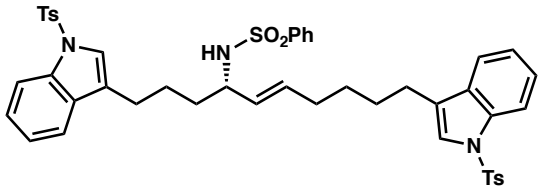
8i ***S36***

8i: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method B), *cis*-1,10-bis(2,2,2-trifluoroacetate)-5-decene (0.4 mmol, 40 mol% $SbCl_5$) was converted to the desired product **8i**. The hetero-ene reaction was stirred for 14.5 h. The product was not stable to the purification procedure for method A, so the crude product mixture was taken directly on to **S36** for analysis (75% yield of **8i** by ^{1}H NMR analysis with 1,4-dimethoxybenzene as internal standard).
S36: Crude **8i** was diluted in CH_2Cl_2 (2 mL, 0.2 M). Dimethylsulfate (2 mmol, 5 equiv) and triethylamine (1.2 mmol, 3 equiv) were added sequentially and the reaction mixture was stirred at 23 °C overnight. Upon completion, the reaction was concentrated under reduced pressure and purified by preparative TLC (R_f = 0.46 in 45% EtOAc/Hexanes) to yield **S36**. The enantiomeric ratio of the product, which was calculated by averaging the enantiomeric ratios of the two diastereomers of **S36**, was determined to be 93.5:6.5 by comparison to a sample of the racemate.
The following data is representative of a 1:1 mixture of diastereomers: $[\alpha]^{23}_D$ = +12.8° (c = 1.56, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) 7.93-7.89 (m, 2H), 7.68 – 7.65 (m, 1H), 7.63-7.55 (m, 2H), 5.91 – 5.77 (m, 1H), 5.49 – 5.41 (m, 0.5H), 5.40 – 5.34 (m, 0.5H), 4.45 – 4.38 (m, 4H), 3.40 – 3.34 (m, 1H), 2.80 (s, 1.5H), 2.79 (s, 1.5H), 2.31 – 2.25 (m, 2H), 1.98 – 1.54 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 157.9, 157.5, 157.5, 138.9, 138.2, 134.1, 134.0, 133.0, 129.7, 129.7, 129.4, 127.7, 127.6, 127.4, 123.6, 123.5, 123.2, 121.9, 121.9, 69.9, 69.1, 67.8, 67.8, 67.5, 67.3, 29.0, 28.9, 28.1, 28.0, 27.5, 27.5, 26.4, 26.1, 23.4, 23.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -75.06. HRMS (ESI-TOF) calcd for $[C_{21}H_{26}F_6NO_7S_2]$ ($[M+H]^+$): 582.1049, found 582.1048.



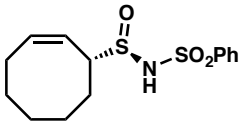
8j: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method B), *cis*-1,10-bis(1-tosyl-1*H*-indol-3-yl)-5-decene (0.2 mmol, 40 mol% $SbCl_5$) was converted to the desired product. The hetero-ene reaction was stirred for 19 h to afford **8j** as a crude mixture (61% yield by ^{1}H NMR analysis with 1,4-dimethoxybenzene as internal standard, 1:1 dr). The enantiomeric ratio of the product was determined to be 90:10 after conversion to amine **S37** (see experimental procedure for **S37**). The *E*-olefin geometry was assigned by the coupling constant at 5.43 ppm (J = 15.8 Hz).

The following data is representative of a 1:1 mixture of diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.2, 3.3 Hz, 2H), 7.97 – 7.86 (m, 2H), 7.62 – 7.07 (m, 19H), 5.91 (ddt, *J* = 16.6, 10.0, 6.7 Hz, 1H), 5.43 (dt, *J* = 15.8, 9.0 Hz, 1H), 3.50 (td, *J* = 8.6, 4.6 Hz, 0.5H), 3.28 – 2.95 (m, 4.5H), 2.35 – 2.14 (m, 7H), 2.06 – 1.41 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 145.2, 145.2, 141.1, 140.4, 140.4, 139.6, 138.4, 138.2, 138.2, 138.2, 136.0, 136.0, 135.6, 135.5, 135.4, 135.3, 133.6, 133.5, 133.4, 132.4, 131.8, 131.5, 130.1, 129.9, 129.9, 129.5, 129.5, 129.4, 129.4, 129.3, 129.2, 129.0, 128.7, 127.8, 127.3, 127.3, 127.2, 126.4, 126.4, 126.4, 126.4, 125.5, 125.5, 125.5, 125.4, 125.3, 124.7, 124.4, 124.4, 124.3, 124.1, 123.4, 121.0, 120.3, 120.3, 119.5, 119.4, 119.4, 115.3, 115.2, 115.2, 114.9, 113.6, 111.9, 109.1, 102.5, 102.4, 102.3, 102.2, 68.7, 68.7, 32.4, 32.3, 31.7, 29.8, 29.2, 29.1, 28.9, 27.2, 27.2, 27.2, 27.1, 26.3, 26.3, 21.7, 14.3; HRMS (ESI-TOF) calcd for $[C_{46}H_{46}N_3O_7S_4]^-$ ($[M\text{-}H]^-$): 880.2224, found 880.9169.

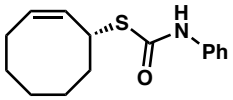


S37: **8j** (0.06 mmol) was converted to **S37** under the allylic amination conditions reported for **13** (*vide infra*). Purification by flash chromatography (gradient from 100% hexanes to 50% hexanes/ethyl acetate) afforded the product (52% yield) as a pale yellow solid.

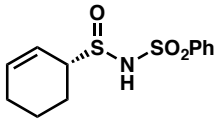
$[\alpha]^{23}_D$ = +8.0° (c = 0.95, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.7 Hz, 2H), 7.80 (ddd, *J* = 5.4, 2.9, 1.5 Hz, 2H), 7.58 (dd, *J* = 8.4, 1.6 Hz, 4H), 7.44 – 7.25 (m, 11H), 7.17 (dd, *J* = 8.2, 3.3 Hz, 4H), 5.33 (dt, *J* = 15.5, 6.5 Hz, 1H), 5.05 (dd, *J* = 15.6, 7.3 Hz, 1H), 4.46 (d, *J* = 8.0 Hz, 1H), 3.78 (p, *J* = 7.1 Hz, 1H), 3.03 (dq, *J* = 7.9, 4.1 Hz, 4H), 2.33 (s, 6H), 1.84 (q, *J* = 7.7 Hz, 2H), 1.71 – 1.50 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 145.2, 141.2, 138.8, 138.1, 136.1, 136.0, 135.6, 135.6, 132.9, 132.4, 130.1, 130.0, 129.3, 129.3, 129.2, 128.9, 127.3, 126.4, 126.4, 125.5, 125.4, 124.4, 124.3, 119.5, 119.4, 115.2, 115.2, 102.3, 102.2, 56.1, 35.5, 31.6, 29.8, 29.3, 28.3, 27.4, 27.1, 25.8, 21.7. IR (thin film): 2926, 1448, 1372, 1175, 1091, 754 cm^{-1}. HRMS (ESI-TOF) calcd for $[C_{46}H_{48}N_3O_6S_3]^+$ ($[M+H]^+$): 834.2700, found 834.0742.



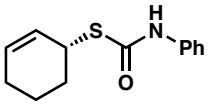
8k: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method A), cyclooctene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 15 h. The product was purified according to the general procedure to afford **8k** (76% yield, >20:1 dr). The product was a white solid. The enantiomeric ratio of the product was determined to be 86:14 after conversion to thiocarbamate **S38** (see experimental procedure for **S38**). The Z-olefin geometry was assigned by the coupling constant at 6.12 ppm (J = 9.6 Hz).
$[\alpha]^{23}_{D}$ = -172.8° (c = 1.6, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.62(t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 6.12 (dt, *J* = 9.6, 7.9 Hz, 1H), 5.68 (ddd, *J* = 10.2, 8.9, 1.3 Hz, 1H), 3.77 (ddd, *J* = 12.5, 8.9, 4.1 Hz, 1H), 2.24 – 2.13 (m, 1H), 2.15 – 2.03 (m,1H), 2.02 – 1.92 (m, 1H), 1.77 – 1.52 (m, 5H), 1.46 – 1.30 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 137.9, 133.8, 129.5, 127.3, 119.1, 62.7, 30.0, 29.0, 27.0, 26.3, 25.2. IR (thin film): 2930, 1448, 1374, 1152, 1073, 840 cm^{-1}. HRMS (CI+) calcd for $[C_{14}H_{20}NO_3S_2]^+$ ($[M+H]^+$): 314.0885, found 314.0885.



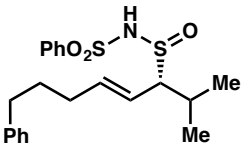
S38: **8k** (0.2 mmol) was converted to **S38** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S38** as a white solid (33% yield for 2 steps; R_f = 0.36 in 10% EtOAc/Hexanes).
$[\alpha]^{23}_{D}$ = -80.0° (c = 0.22, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.02 (s, 1H), 5.77 (q, *J* = 8.8 Hz, 1H), 5.49 (t, *J* = 10.3 Hz, 1H), 4.56 – 4.45 (m, 1H), 2.40 (q, *J* = 12.0, 11.4 Hz, 1H), 2.22 – 2.09 (m, 1H), 2.04 – 1.91 (m, 1H), 1.80 – 1.62 (m, 4H), 1.56 – 1.42 (m, 2H), 1.40 – 1.28 (m, 1H). IR (thin film): 2926, 1599, 1441, 1152, 883, 750 cm^{-1}. HRMS (CI+) calcd for $C_{15}H_{19}NOS$: 261.1187, found 261.1192.



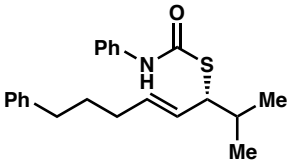
8l: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method A), cyclohexene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 17 h. The product was purified purified by reverse phase column chromatography (acetonitrile/water) to afford **8l** (88% yield, >20:1 dr). The product was a pale yellow solid. The enantiomeric ratio of the product was determined to be 75:25 after conversion to thiocarbamate **S39** (see experimental procedure for **S39**).
$[\alpha]^{23}_{D}$ = +119.5.0° (c = 2.36, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.93 (m, 2H), 7.73 – 7.61 (m, 1H), 7.58 (td, *J* = 8.0, 7.3, 1.7 Hz, 2H), 6.22 (dtd, *J* = 9.8, 3.7, 1.7 Hz, 1H), 5.76 (ddt, *J* = 10.1, 3.9, 2.1 Hz, 1H), 3.62 (m, 1H), 2.11 (m, 2H), 1.95 (m, 1H), 1.79 (m, 2H), 1.63 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 135.9, 133.5, 129.3, 127.0, 119.7, 61.9, 24.7, 22.5, 19.6. IR (thin film): 3065, 2939, 1448, 1167, 854, 687 cm^{-1}. LRMS (ESI) calcd for $[C_{12}H_{16}NO_3S_2]^+$ ($[M+H]^+$): 286.05, found 286.07.



S39: **8l** (0.133 mmol) was converted to **S39** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S39** as a white solid (4.7% yield for 2 steps; R_f = 0.36 in 10% EtOAc/Hexanes).
$[\alpha]^{23}_D$ = +21.4° (c = 0.56, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 10, 2H), 7.35 (t, *J* = 7.5, 2H), 7.14 (t, *J* = 7.5, 1H), 7.00 (s, 1H), 5.92 – 5.88 (m, 1H), 5.78 – 5.75 (m, 1H), 4.30 – 4.28 (m, 1H), 2.13 – 2.06 (m, 3H), 1.97 – 1.92 (m, 1H), 1.79 – 1.73 (m, 2H). IR (thin film): 2934, 1448, 1376, 1168, 854, 687 cm^{-1}. LRMS (ESI) calcd for $[C_{13}H_{16}NOS]^+$ ($[M+H]^+$): 234.09, found 234.13.

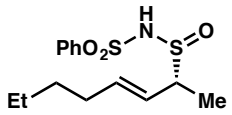


9a: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method A), *cis*-(7-methyl-5-octenyl)benzene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 16 h. The product was purified according to the general procedure to afford **9a** (68% yield, >20:1 rr, 1.5:1 dr) as a viscous clear oil. The enantiomeric ratio of the product was determined to be 96:4 after conversion to **S40** (see experimental procedure for **S40**). The *E*-olefin geometry was assigned by the coupling constant at 5.46 ppm (J = 15.6 Hz). The regioselectivity was assigned by the chemical shift of the methine proton at 1.92 – 2.03 ppm (m, 1H).
The following data is representative of a 1.5:1 mixture of diastereomers: $[\alpha]^{23}_D$ = -5.4° (c = 0.56, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.85 (m, 2H), 7.67 – 7.41 (m, 3H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.12 (m, 3H), 5.80 (ddt, *J* = 30.4, 15.4, 6.8 Hz, 1H), 5.46 (dd, *J* = 15.6, 10.2 Hz, 0.4H), 5.14 (dd, *J* = 15.3, 9.9 Hz, 0.6H), 3.31 (dd, *J* = 9.9, 5.9 Hz, 0.6H), 2.82 – 2.76 (t, *J* = 9.7 Hz, 0.4H), 2.69 – 2.51 (m, 2H), 2.30 – 2.06 (m, 2H), 2.03 – 1.92 (m, 1H), 1.75 (p, *J* = 7.6 Hz, 1H), 1.69 – 1.56 (m, 1H), 1.18 (d, *J* = 6.6 Hz, 1H), 0.99 (td, *J* = 6.9, 4.2 Hz, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 142.3, 142.1, 141.8, 140.4, 140.4, 133.8, 133.6, 129.5, 129.4, 128.6, 128.5, 128.5, 128.4, 127.2, 127.2, 126.0, 125.9, 119.7, 117.9, 76.7, 76.3, 35.5, 35.4, 32.5, 32.4, 31.1, 30.7, 28.8, 27.7, 20.8, 20.6, 20.4, 18.4. IR (thin film): 2930, 1449, 1371, 1169, 1090, 865 cm^{-1}. HRMS (CI+) calcd for $[C_{21}H_{28}NO_3S_2]^+$ ($[M+H]^+$): 406.1511, found 406.1503.

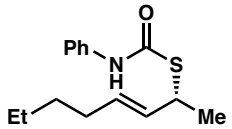


S40: **9a** (0.07 mmol) was converted to **S40** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S40** as a white solid (6% yield for 2 steps; R_f = 0.78 in 20% EtOAc/Hexanes).
$[\alpha]^{23}_D$ = +57.5° (c = 0.08, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.38 – 7.24 (m, 3H), 7.28 – 7.20 (m, 1H), 7.16 (td, *J* = 7.8, 1.3 Hz, 3H), 7.14 – 7.04 (m, 1H), 5.73 (dt, *J* = 14.7, 6.7 Hz, 1H), 5.47 (ddt, *J* = 15.2, 9.3, 1.4 Hz, 1H), 4.01 (dd, *J* =

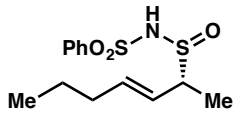
9.3, 5.5 Hz, 1H), 2.64 – 2.55 (m, 2H), 2.08 (q, *J* = 8.2, 7.6 Hz, 2H), 1.99 (dq, *J* = 13.3, 6.7 Hz, 1H), 1.70 (p, *J* = 7.5 Hz, 2H), 1.00 (dd, *J* = 6.7, 1.2 Hz, 6H). IR (thin film): 2926, 1598, 1437, 1308, 1144, 750 cm^{-1}. HRMS (CI) calcd for $[C_{22}H_{27}NOS]$ ($[M^+]$): 353.1813, found 353.1802.



9b: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method C), *cis*-2-octene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 16 h. The product was purified according to the general procedure to afford **9b** (54% yield, >20:1 rr, 12:1 dr) as a viscous clear oil. The enantiomeric ratio of the product was determined to be 90:10 after conversion to thiocarbamate **S41** (see experimental procedure for **S41**). The *E*-olefin geometry was assigned by the coupling constant at 5.53 ppm (J = 15.3 Hz) in **S41**. The regioselectivity was assigned by the chemical shift of the methyl protons at 0.88 (d, *J* = 7.2 Hz, 3H).
The following data is representative of a 12:1 mixture of diastereomers: $[\alpha]^{23}_D$ = -68.3° (c = 0.80, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 7.67 – 7.59 (m, 1H), 7.58 – 7.51 (m, 2H), 5.88 – 5.76 (m, 1H), 5.48 – 5.30 (m, 1H), 3.61 (p, *J* = 7.1 Hz, 0.08H), 3.33 (dp, *J* = 7.1, 3.4 Hz, 0.92H), 2.14 – 2.03 (m, 2H), 1.43 (dd, *J* = 7.0, 2.3 Hz, 3H), 1.40 – 1.25 (m, 4H), 0.88 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 140.4, 133.8, 129.5, 127.3, 121.5, 63.6, 32.5, 31.2, 22.3, 14.4, 14.0. IR (thin film): 2930, 1448, 1376, 1169, 1073, 854 cm^{-1}. HRMS (CI+) calcd for $[C_{14}H_{22}NO_3S_2]^+$ ($[M+H]^+$): 316.1041, found 316.1044.



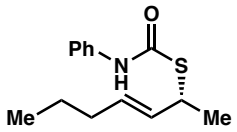
S41: **9b** (0.13 mmol) was converted to **S41** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S41** as a white solid (26% yield for 2 steps; R_f = 0.5 in 15% EtOAc/Hexanes).
$[\alpha]^{23}_D$ = +83.2° (c = 0.375, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.99 (s, 1H), 5.69 (dt, *J* = 14.0, 6.6 Hz, 1H), 5.53 (dd, *J* = 15.3, 7.4 Hz, 1H), 4.19 (p, *J* = 6.9 Hz, 1H), 2.02 (q, *J* = 7.0 Hz, 2H), 1.47 (d, *J* = 7.0 Hz, 3H), 1.36 – 1.27 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H). IR (thin film): 2926, 1655, 1440, 1309, 1149, 751 cm^{-1}. HRMS (CI+) calcd for $[C_{15}H_{21}NOS]$ ($[M^+]$): 263.1344, found 263.1339.



9c: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method C), *cis*-2-heptene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 16 h. The product was purified according to the general procedure to afford **9c** (61% yield, >20:1 rr, 11:1 dr) as a viscous clear oil. The enantiomeric ratio of the product was determined to be 89.5:10.5 after conversion to

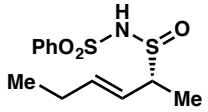
thiocarbamate **S42** (see experimental procedure for **S42**). The *E*-olefin geometry was assigned by the coupling constant at 5.54 ppm (J = 15.3 Hz) in **S42**. The regioselectivity was assigned by the chemical shift and splitting of the methyl protons at 1.45 ppm (d, *J* = 7.1 Hz, 3H).

The following data is representative of a 11:1 mixture of diastereomers: $[\alpha]^{23}_{D}$ = -69.6° (c = 0.75, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 5.87 – 5.74 (m, 1H), 5.45 – 5.30 (m, 1H), 3.62 (m, 0.08H), 3.35 (dq, *J* = 9.4, 7.1 Hz, 0.92H), 2.12 – 1.98 (m, 2H), 1.47 – 1.36 (m, 5H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 140.4, 133.8, 129.5, 127.3, 121.7, 63.6, 34.8, 22.2, 14.4, 13.7. IR (thin film): 2960, 1448, 1373, 1168, 1073, 852 cm^{-1}. HRMS (CI+) calcd for $[C_{13}H_{20}NO_3S_2]^+$ ($[M+H]^+$): 302.0885, found 302.0876.



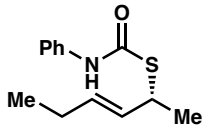
S42: **9c** (0.17 mmol) was converted to **S42** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S42** as a white solid (7% yield for 2 steps; R_f = 0.30 in 15% EtOAc/Hexanes).

$[\alpha]^{23}_{D}$ = +57.6° (c = 0.30, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.6, 1.3 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.96 (s, 1H), 5.69 (dt, *J* = 15.4, 6.8 Hz, 1H), 5.54 (dd, *J* = 15.3, 7.3 Hz, 1H), 4.20 (p, *J* = 6.9 Hz, 1H), 2.00 (q, *J* = 7.4 Hz, 2H), 1.47 (d, *J* = 7.0 Hz, 3H), 1.39 (h, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). IR (thin film): 2920, 1652, 1599, 1440, 1142, 750 cm^{-1}. HRMS (ESI-TOF) calcd for $[C_{14}H_{19}NOS]^-$ ($[M-H]^-$): 248.1115, found 248.0656.

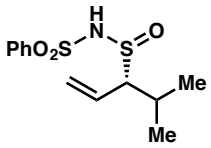


9d: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method C), *cis*-2-hexene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 16.5 h. The product was purified according to the general procedure to afford **9d** (63% yield, >20:1 rr, 7:1 dr) as a viscous clear oil. The enantiomeric ratio of the product was determined to be 88.5:11.5 after conversion to thiocarbamate **S43** (see experimental procedure for **S43**). The *E*-olefin geometry was assigned by the coupling constant at 5.91 ppm (J = 15.5 Hz). The regioselectivity was assigned by the chemical shift and splitting of the methyl protons at 1.46 ppm (d, *J* = 7.0 Hz, 2.64H).

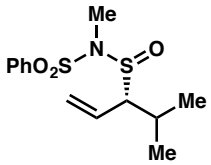
The following data is representative of a 7:1 mixture of diastereomers: $[\alpha]^{23}_{D}$ = -78.0° (c = 1.02, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 2H), 5.91 (dt, *J* = 15.5, 6.3 Hz, 1H), 5.49 – 5.33 (m, 1H), 3.64 (p, *J* = 7.0 Hz, 0.12H), 3.37 (dq, *J* = 9.2, 7.1 Hz, 0.88H), 2.20 – 2.08 (m, 2H), 1.46 (d, *J* = 7.0 Hz, 2.64H), 1.35 (d, *J* = 7.0 Hz, 0.36H), 1.09 – 0.97 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 42.6, 140.4, 133.8, 129.5, 127.3, 120.5, 63.6, 25.9, 14.5, 13.5. IR (thin film): 2967, 1449, 1372, 1168, 1073, 857 cm^{-1}. HRMS (CI+) calcd for $[C_{12}H_{18}NO_3S_2]^+$ ($[M+H]^+$): 288.0728, found 288.0730.



S43: **9d** (0.24 mmol) was converted to **S43** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S43** as a white solid (5% yield for 2 steps; R_f = 0.39 in 15% EtOAc/Hexanes).
$[\alpha]^{23}_D$ = +51.3° (c = 0.16, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.31 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.10 (tt, *J* = 7.3, 1.2 Hz, 1H), 7.02 (s, 1H), 5.74 (dtd, *J* = 15.4, 6.3, 1.2 Hz, 1H), 5.54 (ddt, *J* = 15.3, 7.3, 1.6 Hz, 1H), 4.20 (p, *J* = 7.0 Hz, 1H), 2.10 – 2.00 (m, 2H), 1.47 (d, *J* = 7.0 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H). IR (thin film): 2925, 1599, 1442, 1311, 1238, 751 cm^{-1}. HRMS (CI+) calcd for [$C_{13}H_{17}NOS$] ([M^+]): 235.1031, found 235.1032.



9e: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method A), *cis*-4-methyl-2-pentene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 15 h. The product was purified according to the general procedure to afford **9e** (21% yield, >20:1 rr, 9:1 dr) as a viscous clear oil. The enantiomeric ratio of the product was determined to be 87.5:12.5 after conversion to **S44** (see experimental procedure for **S44**). The *E*-olefin geometry was assigned by the coupling constant at 5.80 ppm (J = 17.1 Hz). The regioselectivity was assigned by the chemical shift and splitting of the methyl protons at 1.19 ppm (d, *J* = 6.6 Hz, 3H).
The following data is representative of a 9:1 mixture of diastereomers: $[\alpha]^{23}_D$ = -70.7° (c = 0.22, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.86 (m, 2H), 7.67 – 7.47 (m, 3H), 5.80 (dt, *J* = 17.1, 10.2 Hz, 0.9H), 5.65 (dd, *J* = 10.2, 1.7 Hz, 0.9H), 5.61 – 5.46 (m, 0.1H), 5.43 – 5.25 (m, 1.1H), 3.26 (dt, *J* = 9.5, 6.2 Hz, 0.1H), 2.80 (t, *J* = 9.7 Hz, 0.9H), 2.29 – 2.06 (m, 1H), 1.19 (d, *J* = 6.6 Hz, 3H), 1.05 – 0.95 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 133.9, 129.5, 128.2, 127.3, 125.7, 77.0, 28.6, 20.6, 20.3. IR (thin film): 3251, 1448, 1370, 1161, 1090, 756 cm^{-1}. HRMS (CI) calcd for [$C_{12}H_{18}NO_3S_2$]$^+$ ([M+H]$^+$): 288.0728, found 288.0734.



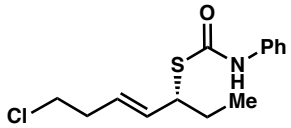
S44: **9e** (0.06 mmol) was converted to **S44** by dissolving the ene adduct in CH_3Cl_2 (0.1 M) and adding NEt_3 (1.2 equiv) and dimethylsulfate (2 equiv) sequentially. After stirring at 23 ºC for 2 h, the reaction was concentrated. Purification by preparative TLC yielded **S44** as a clear oil (49% yield, 9:1 dr; R_f = 0.2 in 15% EtOAc/Hexanes).
The following data is representative of a 9:1 mixture of diastereomers: $[\alpha]^{23}_D$ = -43.9° (c = 0.41, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.83 (m, 2H), 7.60 (dt, *J* = 33.7, 7.2 Hz, 3H), 5.97 – 5.83 (m, 0.9H), 5.79 – 5.64 (m, 0.1H), 5.56 – 5.34 (m, 2H), 3.22 (dd,

J = 10.1, 5.9 Hz, 1H), 2.78 (bs, 3H), 2.41 – 2.18 (m, 1H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 133.8, 129.6, 127.9, 127.7, 124.8, 78.1, 28.4, 26.3, 21.0, 18.9. IR (thin film): 2967, 1447, 1354, 1168, 1087, 804 cm^{-1}. HRMS (CI+) calcd for $[C_{13}H_{20}NO_3S_2]^+$ ($[M+H]^+$): 302.0885, found 302.0874.

(Major) **(Minor)**

9f: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method B), *cis*-7-chloro-3-heptene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 14 h. The product was purified according to the general procedure to afford **9f** (62% yield, 1.2:1 rr, 1:1 dr) as an inseparable mixture of regioisomers and diastereomers epimeric at sulfur. The product was a viscous pale yellow oil. The enantiomeric ratio of the product was determined to be 96:4 after conversion to **S45** (see experimental procedure for **S45**). The *E*-olefin geometry was assigned by the coupling constant at 5.36 ppm (J = 15.1 Hz). The regioselectivity of the major regioisomer was assigned by the chemical shift of the methyl protons of the minor regioisomer at 1.05 ppm.

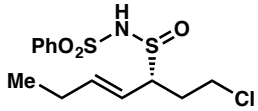
The following data is representative of a 1:1 mixture of diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.87 (m, 2H), 7.70 – 7.58 (m, 1H), 7.60 – 7.49 (m, 2H), 5.96 – 5.70 (m, 1H), 5.59 – 5.45 (m, 0.46H), 5.36 (dd, *J* = 15.1, 9.6 Hz, 0.24H), 5.26 (ddq, *J* = 15.4, 8.3, 1.7 Hz, 0.3H), 3.73 – 3.41 (m, 2.5H), 3.18 (td, *J* = 9.5, 5.4 Hz, 0.25H), 3.10 (td, *J* = 9.5, 5.9 Hz, 0.25H), 2.74 – 2.64 (m, 0.3H), 2.62 – 2.47 (m, 0.7H), 2.10 – 1.58 (m, 4.65H), 1.05 (dt, *J* = 7.5, 7.5 Hz, 1.35H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 140.4, 140.3, 140.2, 137.6, 137.1, 137.0, 135.9, 133.9, 133.8, 133.8, 133.8, 129.6, 129.5, 129.5, 129.5, 127.4, 127.3, 127.3, 127.3, 124.5, 123.5, 120.9, 120.4, 70.3, 70.0, 68.3, 68.2, 44.3, 44.1, 44.1, 43.9, 35.8, 35.5, 29.8, 29.7, 26.8, 25.5, 23.1, 21.0, 18.6, 18.6, 11.5, 11.5. IR (thin film): 2965, 1448, 1372, 1073, 857, 687 cm^{-1}. HRMS (CI+) calcd for $[C_{13}H_{19}NO_3S_2Cl]^+$ ($[M+H]^+$): 336.0495, found 336.0504.



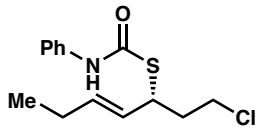
(from minor regioisomer of *9f*)

S45: **9f** (0.15 mmol) was converted to **S45** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded regioisomer **S45** as a white solid (25% yield for 2 steps; R_f = 0.57 in 20% EtOAc/Hexanes).

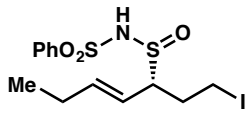
$[\alpha]^{23}_D$ = +11.6° (c = 0.43, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.3 Hz, 2H), 7.31 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.00 (s, 1H), 5.70 (dt, *J* = 15.2, 6.7 Hz, 1H), 5.57 (ddt, *J* = 15.4, 8.5, 1.3 Hz, 1H), 4.00 (q, *J* = 7.6 Hz, 1H), 3.53 (t, *J* = 6.9 Hz, 2H), 2.59 – 2.41 (m, 2H), 1.89 – 1.66 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). IR (thin film): 3293, 1599, 1440, 1309, 1147, 751 cm^{-1}. HRMS (CI+) calcd for $C_{14}H_{18}NOS$ ($[M^+]$): 283.0798, found 283.0795.



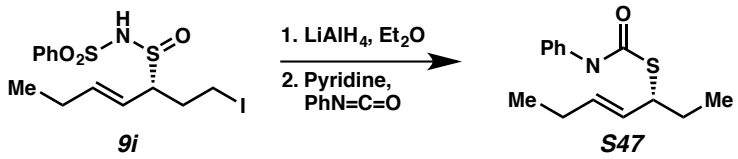
9g: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method B), *cis*-1-chloro-3-heptene (0.4 mmol, 40 mol% $SbCl_5$) was converted to the desired product. The hetero-ene reaction was stirred for 23 h to afford **9g** as a crude mixture (59% ^{1}H NMR yield, >20:1 rr, >20:1 dr). This product was not stable to the purification procedure for Method B, so the crude product mixture was taken directly on to **S46** (see experimental procedure for **S46**). The enantiomeric ratio of the product was determined to be 93:7 after conversion to **S46**.
HRMS (CI) calcd for $[C_{13}H_{19}NO_3S_2Cl]^+$ ($[M+H]^+$): 336.0495, found 336.0493.



S46: Crude **9g** was converted to **S46** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S46** as a white solid (R_f = 0.79 in 20% EtOAc/Hexanes). The *E*-olefin geometry was assigned by the coupling constant at 5.44 ppm (J = 15.4 Hz). The regioselectivity was assigned by the chemical shift and splitting of the methylene protons next to the chlorine atom at 3.60 ppm (qt, *J* = 10.9, 7.1 Hz, 2H).
$[\alpha]^{23}_D$ = +40.0° (c = 0.10, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.03 (s, 1H), 5.82 (dt, *J* = 15.3, 6.3 Hz, 1H), 5.44 (dd, *J* = 15.4, 8.8 Hz, 1H), 4.22 (q, *J* = 7.9 Hz, 1H), 3.60 (qt, *J* = 10.9, 7.1 Hz, 2H), 2.31 – 1.98 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 3H). IR (thin film): 2924, 1600, 1441, 1309, 1146, 751 cm^{-1}. HRMS (CI+) calcd for $[C_{14}H_{19}NOSCl]^+$ ($[M+H]^+$): 284.0876, found 284.0869.

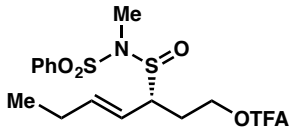


9i: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method B), *cis*-1-iodo-3-heptene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 23 h to afford **9i** as a crude mixture (48% ^{1}H NMR yield, 16:1 rr, 5:1 dr). This product was not stable to the purification procedure for Method B, so the crude product mixture was taken directly on to **S47** (see experimental procedure for **S47**). The enantiomeric ratio of the product was determined to be 90:10 after conversion to **S47**. The *E*-olefin geometry was assigned by the coupling constant at 5.45 ppm (J = 15.2 Hz) in **S47**. The regioselectivity was assigned by the chemical shift and splitting of the methylene protons next to the iodine atom at 3.42 – 3.31 ppm (m, 2H) in the crude ^{1}H NMR of the reaction mixture.



S47: Crude **9i** was converted to **S47** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S47** as a white solid (R_f = 0.36 in 15% EtOAc/Hexanes).

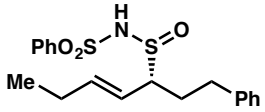
$[\alpha]^{23}_D$ = +34.5° (c = 3.48, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.36 – 7.31 (m, 3H), 5.79 (dt, *J* = 15.3, 6.3 Hz, 1H), 5.45 (dd, *J* = 15.2, 8.6 Hz, 1H), 4.06 – 3.97 (m, 1H), 2.08 (ddd, *J* = 7.7, 5.1, 1.6 Hz, 2H), 1.85 – 1.72 (m, 2H), 1.02 (t, *J* = 7.4, 1.2 Hz, 6H). IR (thin film): 3257, 2964, 1728, 1446, 693 cm^{-1}. HRMS (ESI) calcd for $[C_{14}H_{19}NOSNa]^+$ ($[M+Na]^+$): 272.1080, found 272.1082.



9j: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method A), *(Z)*-hept-3-en-1-yl 2,2,2-trifluoroacetate (0.4 mmol) was converted to the desired allylic oxidation product. The hetero-ene reaction was stirred for 20 h. The product was not stable to the purification procedure for method A, so the crude product mixture was taken directly on to **9j** for analysis (0.097g, 57% yield).

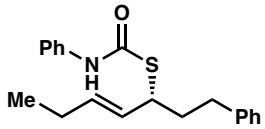
The crude allylic oxidation product was diluted in CH_2Cl_2 (2 mL, 0.2 M). Dimethylsulfate (2 mmol, 5 equiv) and triethylamine (1.2 mmol, 3 equiv) were added sequentially and the reaction mixture was stirred at 23 °C overnight. Upon completion, the reaction was concentrated under reduced pressure and purified by coluum chromatography on silica gel to yield **9j** as an inseparable mixture of diastereomers epimeric at sulfur (2:1 dr, >20:1 rr). The enantiomeric ratio of the product, which was calculated by averaging the enantiomeric ratios of the two diastereomers of **9j**, was determined to be 89:11 by comparison to a sample of the racemate. The *E*-olefin geometry was assigned by the coupling constant at 5.61 ppm (J = 15.1 Hz). The regioselectivity was assigned by the chemical shift and splitting of the methylene protons next to the trifluoroacetoxy group at 4.09 ppm (t, *J* = 6.8 Hz, 4H).

The following data is representative of a 2:1 mixture of diastereomers: $[\alpha]^{23}_D$ = +34.4° (c = 0.64, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.84 – 7.79 (m, 4H), 7.58 (dd, *J* = 9.0, 6.6 Hz, 3H), 7.49 (dt, *J* = 15.2, 7.6 Hz, 6H), 5.71 (dd, *J* = 15.5, 7.5 Hz, 1H), 5.61 (dt, *J* = 15.1, 6.6 Hz, 1H), 5.31 (q, *J* = 8.9, 8.5 Hz, 2H), 5.07 (dq, *J* = 14.7, 7.2 Hz, 2H), 4.51 – 4.39 (m, 3H), 4.36 (t, *J* = 6.7 Hz, 2H), 4.09 (t, *J* = 6.8 Hz, 4H), 3.91 (s, 6H), 3.83 (s, 3H), 2.50 – 2.45 (m, 2H), 2.29 – 2.14 (m, 4H), 1.93 (dt, *J* = 14.6, 7.4 Hz, 2H), 1.72 (dq, *J* = 14.1, 7.2 Hz, 4H), 1.63 – 1.53 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 6H), 0.46 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (q, *J* = 42.0 Hz), 140.1, 134.3, 133.3, 133.1, 132.4, 129.7, 129.0, 128.9, 127.8, 127.7, 126.9, 126.8, 114.4 (q, *J* = 284.9 Hz), 66.9, 66.6, 66.4, 66.3, 65.2, 65.2, 30.8, 29.7, 28.5, 26.3, 10.8, 10.3.^{19}F NMR (376 MHz, $CDCl_3$) δ -75.05. HRMS (ESI) calcd for $[C_{16}H_{20}F_3NO_5S_2Na]$ ([M+Na]+): 450.0627, found 450.0622.



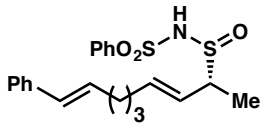
9k: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method A), *(Z)*-hept-3-en-1-ylbenzene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 20 h. The product was purified according to the general procedure to afford **9k** (0.0586 g, 74% yield, 5:1 rr, 1.1:1 dr) as an inseparable mixture of regioisomers and diastereomers epimeric at sulfur and as a viscous clear oil. The enantiomeric ratio of the product was determined to be 7.5:92.5 after conversion to thiocarbamate **S48** (see experimental procedure for **S48**). The regioselectivity was assigned by the chemical shift and splitting of the methylene protons next to the phenyl group at 2.73 ppm (t, J = 8.1 Hz, 2H) in **S48**'s ^{1}H NMR.

The following data is representative of a 5:1 mixture of regioisomers (with each regioisomer existing as two diastereomers): $[\alpha]^{23}_D$ = -34.0° (c = 2.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.67 – 7.63 (m, 1H), 7.59 – 7.54 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.23 (m, 1H), 7.17 (d, J = 10 Hz, 2H), 6.68 (s, 1H), 6.07 – 6.00 (m, 0.17H), 5.96 – 5.89 (m, 0.83H), 5.51 (dt, J = 15, 10 Hz, 0.17H), 5.39 (dt, J = 15, 10 Hz, 0.83H), 3.19 (dt, J = 10, 5 Hz, 0.17H), 3.12 (dt, J = 10, 5 Hz, 0.83H), 2.87 – 2.78 (m, 1H), 2.74 – 2.67 (m, 1H), 2.3 – 2.15 (m, 2.3H), 2.12 – 2.02 (m, 1H), 1.97 – 1.88 (m, 0.6H), 1.08 (t, J = 10 Hz, 1.2H), 0.97 (t, J = 10 Hz, 0.4H), 0.94 (t, J = 10 Hz, 0.3H). ^{13}C NMR (101 MHz, $CDCl_3$) (reported for 2 diastereomers of major regioisomer) δ 144.4, 143.5, 140.50, 140.3, 140.2, 140.1, 139.9, 133.7, 133.6, 129.4, 128.8, 128.6, 128.4, 128.3, 127.1, 126.4, 121.6, 121.1, 118.8, 118.1, 68.3, 67.8, 32.5, 32.4, 30.7, 29.4, 26.0, 25.9, 13.5, 13.3. IR (thin film): 2963, 1448, 1374, 1168, 849, 687 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{23}NO_3S_2]$ ($[M+Na]^+$): 400.1012, found 400.1020.



S48: **9k** (0.20 mmol) was converted to **S48** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S48** as a clear oil (31% yield for 2 steps; R_f = 0.36 in 15% EtOAc/Hexanes).

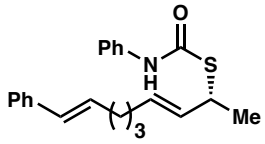
$[\alpha]^{23}_D$ = +27.4° (c = 1.68, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.35 – 7.23 (m, 5H), 7.19 (d, J = 7.2 Hz, 2H), 7.14 – 7.06 (m, 1H), 7.00 (d, J = 3.1 Hz, 1H), 5.79 (dtd, J = 15.3, 6.3, 0.9 Hz, 1H), 5.55 – 5.42 (m, 1H), 4.10 (td, J = 8.2, 6.5 Hz, 1H), 2.73 (t, J = 8.1 Hz, 2H), 2.16 – 1.95 (m, 4H), 1.00 (t, J = 7.4 Hz, 3H). HRMS (ESI) calcd for $[C_{20}H_{23}NOS]$ ($[M+Na]^+$): 348.1393, found 348.1394.



9l: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method C), ((1*E*,7*Z*)-nona-1,7-dien-1-yl)benzene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 20 h. The product was

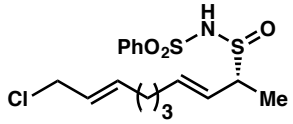
purified according to the general procedure to afford **9l** (0.13 g, 78% yield, >20:1 rr, 9:1 dr) as a viscous clear oil. The enantiomeric ratio of the product was determined to be 89:11 after conversion to thiocarbamate **S49** (see experimental procedure for **S49**). The *E*-olefin geometry was assigned by the coupling constant at 5.89 ppm (J = 15.2 Hz). The regioselectivity was assigned by the chemical shift and splitting of the methyl protons at 1.48 ppm (d, *J* = 7.0 Hz, 3H). The chemoselectivity was assigned by the unchanged styrene protons at 6.41 ppm and 6.21 ppm.

The following data is representative of a 9:1 mixture of diastereomers: $[\alpha]^{23}_{D}$ = -29.8° (c = 2.48, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.68 – 7.60 (m, 1H), 7.58 – 7.52 (m, 2H), 7.40 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.21 (dt, *J* = 15.9, 6.9 Hz, 1H), 5.89 (dt, *J* = 15.2, 6.7 Hz, 1H), 5.43 (dd, *J* = 15.4, 9.2 Hz, 1H), 3.36 (q, *J* = 8.0, 7.4 Hz, 1H), 2.33 – 2.12 (m, 4H), 1.68 – 1.55 (m, 2H), 1.48 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 140.2, 137.6, 133.7, 130.5, 129.9, 129.4, 128.5, 127.2, 127.1, 127.0, 126.0, 125.9, 121.8, 63.4, 32.4, 32.1, 28.6, 14.5. IR (thin film): 2930, 1377, 1279, 1168, 846, 687 cm^{-1}. HRMS (ESI) calcd for $[C_{21}H_{25}NO_3S_2]$ ($[M+Na]^+$): 426.1168, found 426.1176.

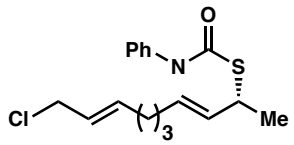


S49: **9l** (0.30 mmol) was converted to **S49** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S49** as a clear oil (92% yield for 2 steps; R_f = 0.56 in 15% EtOAc/Hexanes).

$[\alpha]^{23}_{D}$ = +76.7° (c = 2.32, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.36 – 7.27 (m, 6H), 7.23 – 7.17 (m, 1H), 7.14 – 7.10 (m, 1H), 7.10 – 7.06 (m, 1H), 6.38 (dt, *J* = 15.8, 1.4 Hz, 1H), 6.20 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.81 – 5.66 (m, 1H), 5.58 (ddt, *J* = 15.3, 7.3, 1.3 Hz, 1H), 4.29 – 4.14 (m, 1H), 2.29 – 2.16 (m, 2H), 2.10 (q, *J* = 7.1 Hz, 2H), 1.57 (p, *J* = 7.4 Hz, 2H), 1.49 (d, *J* = 7.0 Hz, 3H). IR (thin film): 3298, 2926, 1774, 1655, 1599, 1498, 1147, 964, 749, 691 cm^{-1}. HRMS (ESI) calcd for $[C_{22}H_{25}NOS]$ ($[M+Na]^+$): 374.1549, found 374.1550.



9m: Following the general procedure for the asymmetric catalytic oxidation of internal alkenes (Method C), (2*E*,8*Z*)-1-chlorodeca-2,8-diene (0.4 mmol) was converted to the desired product. The hetero-ene reaction was stirred for 20 h to afford **9g** as a crude mixture (68% ^{1}H NMR yield, >20:1 rr, 12:1 dr). This product was not stable to the purification procedure for Method C, so the crude product mixture was taken directly on to **S50** (see experimental procedure for **S50**). The enantiomeric ratio of the product was determined to be 90:10 after conversion to **S50**.



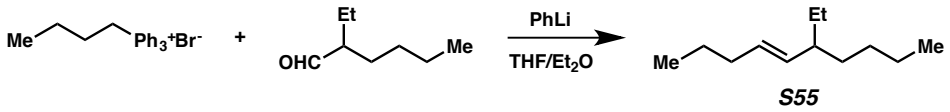
S50: Crude **9m** was converted to **S50** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S50** as a clear oil (R_f = 0.44 in 15% EtOAc/Hexanes). The *E*-olefin geometry was assigned by the coupling constant at 5.89 ppm (J = 15.2 Hz). The regioselectivity was assigned by the chemical shift and splitting of the methyl protons at 1.49 (d, *J* = 7.0 Hz, 3H). The chemoselectivity was assigned by the unchanged methylene protons next to the chlorine at 4.05 ppm (d, *J* = 7.1 Hz, 2H).
$[\alpha]^{23}_D$ = +77.7.0° (c = 3.32, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.38 – 7.32 (m, 2H), 7.14 (td, *J* = 7.3, 3.5 Hz, 1H), 6.99 (d, *J* = 4.1 Hz, 1H), 5.84 – 5.50 (m, 4H), 4.22 (p, *J* = 6.7 Hz, 1H), 4.05 (d, *J* = 7.1 Hz, 2H), 2.15 – 2.00 (m, 4H), 1.53 – 1.45 (m, 2H), 1.49 (d, *J* = 7.0 Hz, 3H). IR (thin film): 3299, 2926, 1655, 1599, 1438, 1146, 965, 751, 691 cm^{-1}. HRMS (ESI) calcd for [$C_{17}H_{22}ClNOS$] ([M+Na]$^+$): 346.1003, found 346.1018.

Synthetic Derivitization of Allylic Oxidation Product 8a (Figure 3)

*Product **10***

(Major) (Minor)

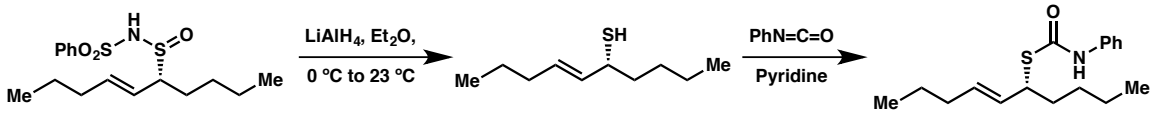
10: Ene adduct **8a** (0.2 mmol, 90:10 er) was diluted in 1,2-dimethoxyethane (2 mL, 0.1 M) within a flame-dried vial set under argon atmosphere. Copper(I) bromide dimethyl sulfide (2.1 mg, 5 mol%) was added at –78 ºC immediately followed by addition of ethylmagnesium chloride (0.4 mL, 2M THF, 4 equiv). The solution was warmed to 0 ºC and stirred vigorously for 3 h. The resulting mixture was then poured onto wet pentane/Et_2O (20:3 mL) and passed through a silica gel plug, which was subsequently washed with pentane. The filtered organics were concentrated under reduced pressure. Purification by flash chromatography (100% hexanes) afforded **10** (73% yield, 3:1 rr, 90:10 er, 100% es) as a clear oil. The major regioisomer was assigned by comparison to an authentic sample of the major regioisomer (see below **S55**).
The following data is representative of a 3:1 mixture of regioisomers: $[\alpha]^{23}_D$ = +0.99° (0.61, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 – 5.26 (m, 1H), 5.08 (dddd, *J* = 15.2, 8.8, 3.0, 1.6 Hz, 1H), 1.97 (dq, *J* = 7.0, 1.4 Hz, 2H), 1.84 – 1.70 (m, 1H), 1.45 – 1.10 (m, 10H), 0.94 – 0.78 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 134.8, 130.4, 130.2, 44.7, 44.5, 37.7, 35.1, 34.9, 32.5, 32.2, 29.9, 29.7, 29.7, 28.4, 23.0, 23.0, 22.3, 20.5, 14.4, 14.3, 14.1, 13.8, 11.9. IR (thin film): 2959, 2926, 2859, 1464, 1378, 968 cm^{-1}. GC-MS calcd for [$C_{12}H_{24}$] ([M$^+$]): 168.19, found 168.20.



S55

S55: *n*-Butyltriphenylphosphonium bromide (1.0 mmol) was diluted in THF (1.75 mL) and Et_2O (1 mL) in a flame-dried flask under argon atmosphere. Phenyl lithium (0.56 mL, 1.8 M in Bu_2O, 1 equiv) was added and the solution was stirred for 15 minutes before cooling to – 78 ºC. 2-Ethylhexanal (0.156 mL, 1 equiv) was added and the reaction was maintained at -78 ºC for 10 minutes before warming to -30 ºC. After 30 minutes, a second equivalent of phenyl lithium as added followed by Et_2O (4 mL). After gradually warming the reaction to – 10 ºC, the reaction was allowed to warm to 23 °C with stirring for 30 minutes. Filtration through celite and purification by flash chromatography (100% pentane) afforded **S55** (43% yield, >20:1 E/Z) as a clear oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (dt, *J* = 15.0, 6.7 Hz, 1H), 5.09 (ddt, *J* = 15.3, 8.8, 1.4 Hz, 1H), 1.97 (qd, *J* = 7.4, 1.4 Hz, 2H), 1.84 – 1.70 (m, 1H), 1.45 – 1.11 (m, 10H), 0.92 – 0.80 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 130.2, 44.8, 35.1, 34.9, 29.7, 28.4, 23.0, 23.0, 14.3, 13.8, 11.9.

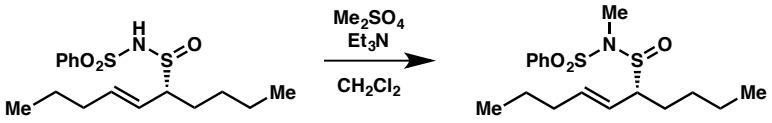
*Product **11***



8a ***11*** ***S29***

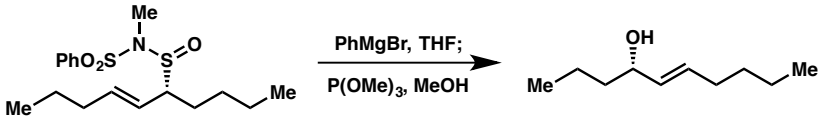
For experimental procedures and characterization data of thiol **11** and its carbamothioate **S29**, see the section "**Characterization Data for Allylic Oxidation Products**."

*Product **12***



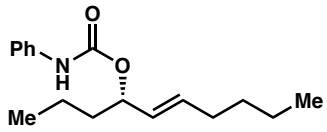
8a ***S51***

S51: Ene adduct **8a** (0.093 mmol, 91.5:8.5 er) was dissolved in CH_2Cl_2. Dimethylsulfate (44 µL, 5 equiv) and triethylamine (39 µl, 3 equiv) were added and the reaction mixture was stirred at 23 °C overnight. Upon completion, CH_2Cl_2 (1 mL) was added and the reaction was concentrated to yield a crude viscous oil which was purified by column chromatography (gradient 0-20% EtOAc/ hexanes) to afford **S51** as a clear oil (87% yield).
The following data is representative of a 1.5:1 mixture of diastereomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 4H), 7.70 – 7.60 (m, 2H), 7.60 – 7.48 (m, 4H), 5.82 (ddt, J = 36.2, 15.2, 6.8 Hz, 2H), 5.39 (ddt, J = 15.3, 9.2, 1.5 Hz, 1H), 5.27 (ddt, J = 15.4, 9.6, 1.5 Hz, 1H), 3.38 – 3.27 (m, 2H), 2.81 (s, 5H), 2.80 (s, 3H), 2.22 – 1.99 (m, 4H), 2.03 – 1.79 (m, 2H), 1.77 – 1.58 (m, 4H), 1.54 – 1.27 (m, 16H), 1.06 – 0.79 (m, 15H). HRMS (ESI-TOF) calcd for [$C_{17}H_{27}NO_3S_2$] 358.1505, found 358.1504.



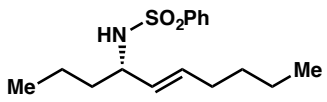
S51 *12*

12: A flame-dried round-bottom flask was charged with anhydrous THF (0.8 mL) and compound **S51** (0.0808 mmol). The flask was cooled to 0 ˚C in an ice bath. PhMgBr (0.24 mmol, 3 equiv) was added dropwise to the flask while maintaining the reaction temperature at 0 °C. After the reaction was stirred for an additional 2 h at 0 °C, trimethyl phosphite (66 μL, 5 equiv) and methanol were added and the reaction mixture was allowed to warm up to 23 °C and stirred overnight. Upon completion, CH_2Cl_2 was added and the reaction was concentrated to yield a crude product. The crude product was purified by column chromatography (gradient 0-20% EtOAc/ hexanes) to afford **12** as clear oil (10.7 mg, 85% yield). The enantiospecificity of this reaction sequence was determined to be 99% after conversion to **S52** (see experimental procedure for **S52**). The *E*-olefin geometry was assigned by the coupling constant at 5.47 ppm (J = 15.4 Hz).
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.65 (dtd, J = 15.3, 6.7, 1.0 Hz, 1H), 5.47 (ddt, J = 15.4, 7.2, 1.4 Hz, 1H), 4.07 (q, J = 6.7 Hz, 1H), 2.05 (q, J = 6.8 Hz, 2H), 1.93 – 1.79 (m, 1H), 1.65 – 1.49 (m, 1H), 1.49 – 1.40 (m, 2H), 1.40 – 1.25 (m, 5H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.9, 132.2, 73.0, 39.5, 31.9, 31.4, 22.2, 18.7, 14.0, 14.0. IR (thin film): 3399, 2930, 1714, 1458, 969 cm^{-1}. HRMS (CI-) calcd for $[C_{10}H_{19}O]^-$ ([M-H]$^-$): 155.1436, found 155.1436.



S52: **12** (0.17 mmol) was converted to **S52** under the previously described conditions for the synthesis of carbamothioate **S29**. Purification by preparative TLC yielded **S52** as a white solid (62% yield; R_f = 0.53 in 15% EtOAc/Hexanes; 91:9 er).
$[\alpha]^{23}_D$ = -17.7° (c = 0.53, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 2H), 7.37 – 7.30 (m, 3H), 6.59 (s, 1H), 5.79 (dt, J = 15.7, 6.8 Hz, 1H), 5.45 (ddt, J = 15.4, 7.5, 1.5 Hz, 1H), 5.22 (q, J = 7.0 Hz, 1H), 2.31 – 1.96 (m, 2H), 1.78 – 1.53 (m, 2H), 1.49 – 1.25 (m, 6H), 0.96 (t, J = 7.4 Hz, 3H), 0.91 (t, J = 7.1 Hz, 3H). IR (thin film): 3320, 2958, 1700, 1539, 1050 cm^{-1}. HR-MS (CI+) calcd for $[C_{17}H_{25}NO_2]^+$ ([M$^+$]): 275.1885, found 275.1884.

*Product **13***



13: Ene adduct **8a** (0.15 mmol, 92.5:7.5 er) was dissolved in anhydrous toluene (0.2M) within a flame-dried vial set under argon atmosphere. Chlorotitanium(IV) triisopropoxide

(30 μL, 1 M hexanes, 20 mol%) was added dropwise, and the solution was heated to 60 ºC. The reaction mixture was stirred at this temperature for 1.5 h or until TLC indicated complete disappearance of **8a**, at which time the reaction was cooled to 23 °C and diluted in MeOH (1.4 mL). Trimethyl phosphite (88 μl, 5 equiv) was added and the solution was stirred for 2 h. The reaction was quenched by addition of water (2 mL) and the crude solution was washed with EtOAc (3 x 7 mL). The combined organic layers were dried over anyhydrous sodium sulfate, filtered and concentrated. Purification by flash chromatography (100% hexanes to 20% EtOAc/Hexanes) afforded **13** (71% yield, 89:11 er, 96% es) as a clear oil. The *E*-olefin geometry was assigned by the coupling constant at 5.02 ppm (J = 15.3Hz).

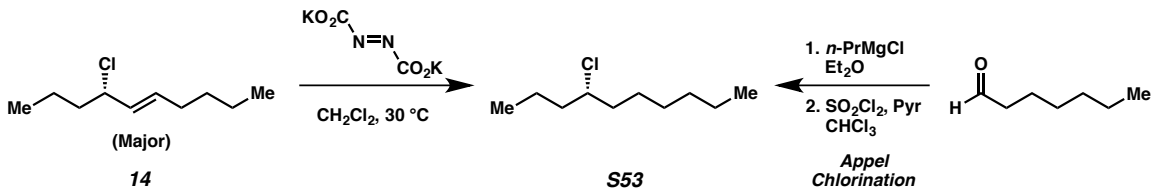
$[\alpha]^{23}_{D}$ = -4.2° (c = 0.53, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.1 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 5.30 (dt, *J* = 14.6, 6.7 Hz, 1H), 5.02 (dd, *J* = 15.3, 7.5 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 3.73 (p, *J* = 7.2 Hz, 1H), 1.78 (q, *J* = 6.6, 6.0 Hz, 2H), 1.53 – 1.32 (m, 2H), 1.34 – 1.06 (m, 6H), 0.83 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 133.0, 132.4, 129.3, 128.9, 127.3, 56.2, 38.4, 31.8, 31.1, 22.2, 18.8, 14.0, 13.8. IR (thin film): 3273, 2959, 1448, 1325, 1163, 689 cm^{-1}. HRMS (CI) calcd for $[C_{16}H_{26}NO_2S]^+$ ($[M+H]^+$): 296.1684, found 296.1683.

*Product **14***

(Major) (Minor)

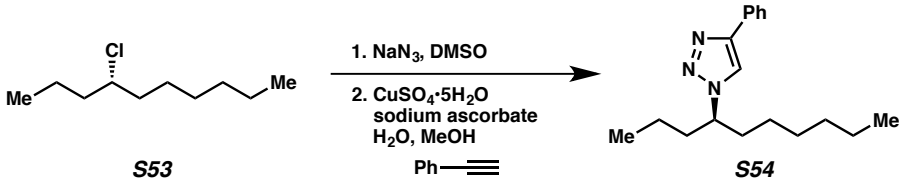
14: Ene adduct **8a** (0.12 mmol, 94:6 er) was diluted in Et_2O (0.6 mL, 0.2 M) within a flame-dried vial set under argon atmosphere. Sulfuryl chloride (11 μL, 1.1 equiv) was added dropwise at –78 ºC and the solution was warmed to –5 ºC. After stirring for 30 minutes, the reaction was quenched by addition of water (0.2 mL). The layers were separated and the aqueous layer was washed with Et_2O (3 x 3 mL). The combined organic extracts were dried over magnesium sulfate and concentrated under reduced pressure. The resulting residue was suspended in pentane (5 mL) and filtered through a celite plug to afford **14** (94% crude yield, 3:1 rr by ^{13}C NMR analysis, 95% es). The major regioisomer was assigned after conversion of **14** to **S53** (see experimental procedure below). The enantiomeric ratio of the product was determined to be 89:11 after conversion to **S54** (see experimental procedure for **S54**). The *E*-olefin geometry was assigned by the coupling constant at 5.51 ppm (J = 15.2 Hz).

The following data is representative of a 3:1 mixture of regioisomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (dtd, *J* = 16.0, 6.8, 2.7 Hz, 1H), 5.51 (ddt, *J* = 15.2, 8.8, 1.5 Hz, 1H), 4.34 (dt, *J* = 13.5, 6.2 Hz, 1H), 2.09 – 1.96 (m, 2H), 1.87 – 1.68 (m, 2H), 1.51 – 1.23 (m, 6H), 0.96 – 0.87 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 133.5, 131.4, 131.1, 64.0, 63.7, 41.1, 38.8, 34.1, 31.8, 31.2, 28.9, 22.3, 22.3, 22.2, 20.0, 14.1, 14.1, 13.8, 13.6.



S53: A flame-dried flask was charged with potassium (*E*)-diazene-1,2-dicarboxylate (254 mg, 12 equiv) and CH_2Cl_2 (2.2 mL, 0.05 M) under argon atmosphere. 4-Chloro-5-decene (**14**) (0.11 mmol) was added to the suspension followed by dropwise addition of acetic acid (0.88 mL, 0.5 M CH_2Cl_2, 4 equiv). The mixture was heated to 30 ºC and stirred vigorously for 13.5 h. The resulting suspension was cooled to 23 °C, filtered through a short silica gel plug and concentrated. Purification by flash chromatography (100% pentane) afforded **S53** (71% yield, 2:1 rr by ^{13}C NMR) as a clear oil. ^1H NMR and ^{13}C NMR spectra were consistent with authentic samples of the corresponding regioisomers prepared by the Appel chlorination.

The following data is representative of a 2:1 mixture of regioisomers: $[\alpha]^{23}_D$ = +1.5° (c = 0.14, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 3.95 – 3.86 (m, 1H), 1.78 – 1.65 (m, 4H), 1.61 – 1.28 (m, 10H), 0.99 – 0.86 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 64.5, 64.2, 40.7, 38.7, 38.6, 38.4, 31.9, 31.5, 29.0, 28.8, 26.6, 26.3, 22.7, 22.7, 22.4, 19.9, 14.2, 14.2, 14.1, 13.8. IR (thin film): 2932, 2873, 2860, 1466, 1380, 725 cm^{-1}. HRMS (ESI-TOF) calcd for $[C_{10}H_{21}ClNa]^+$ ($[M+Na]^+$): 199.1224, found 199.9909.



S54: 4-Chlorodecane **S53** (0.28 mmol) was added to a suspension of sodium azide (28 mg, 1.5 equiv) in DMSO (0.56 mL, 0.5 M) and heated to 50 ºC. After stirring for 2 h, the reaction was diluted with water (10 mL) and washed with Et_2O (3 x 10 mL). Combined organics were dried over magnesium sulfate and concentrated to yield crude 4-azidodecane, which was taken directly on to the next step. $CuSO_4$•$5H_2O$ (7 mg, 10 mol%) and sodium L-ascorbate (11 mg, 20 mol%) were suspended in water/methanol (1:0.5 mL). Phenylacetylene (34 µL, 1.1 equiv) was added followed by crude 4-azidodecane in 0.5 mL methanol. The heterogenous mixture was stirred overnight. The crude mixture was diluted with water (2 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The organic extracts were dried over anyhydrous sodium sulfate and concentrated. Purification by flash chromatography (0-20% EtOAc/hexanes) afforded **S54** as a white solid (18% yield for two steps; R_f = 0.30 in 10% EtOAc/Hexanes, 89:11 er).

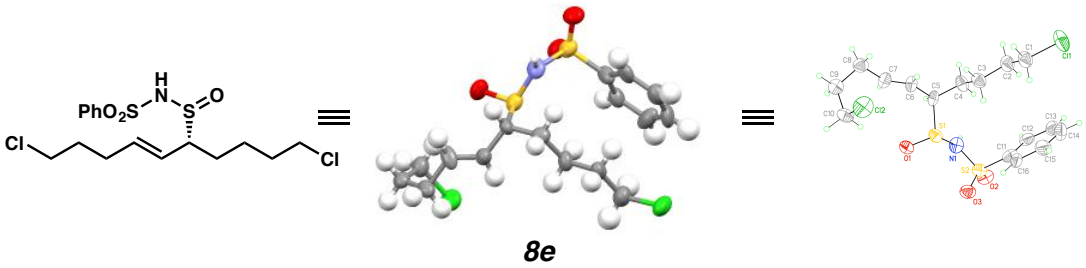
$[\alpha]^{23}_D$ = -5.7° (c = 0.07, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.71 (s, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 4.56 – 4.47 (m, 1H), 1.99 – 1.79 (m, 4H), 1.40 – 1.03 (m, 10H), 0.93 – 0.78 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 131.0, 128.9, 128.1, 125.7, 117.8, 62.5, 35.9, 35.7, 31.5, 28.2, 25.8, 22.5, 22.4, 14.1, 14.0. IR (thin film): 2929, 1463, 1225, 1076, 765, 695 cm^{-1}. HRMS (CI+) calcd for $[C_{18}H_{27}N_3]^{2+}$ ($[M+2H]^{2+}$): 285.2205, found 285.2204.

Determination of Absolute Stereochemistry of Products

A sample of sulfinimide **8e** was recrystallized from hexanes and chloroform (slow diffusion). The resulting crystals were suitable for X-ray diffraction and the structure was solved (Fig. S7). This structure allowed the assignment of absolute configuration as shown. The absolute configurations of all other allylic oxidation 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.

Fig. S7.

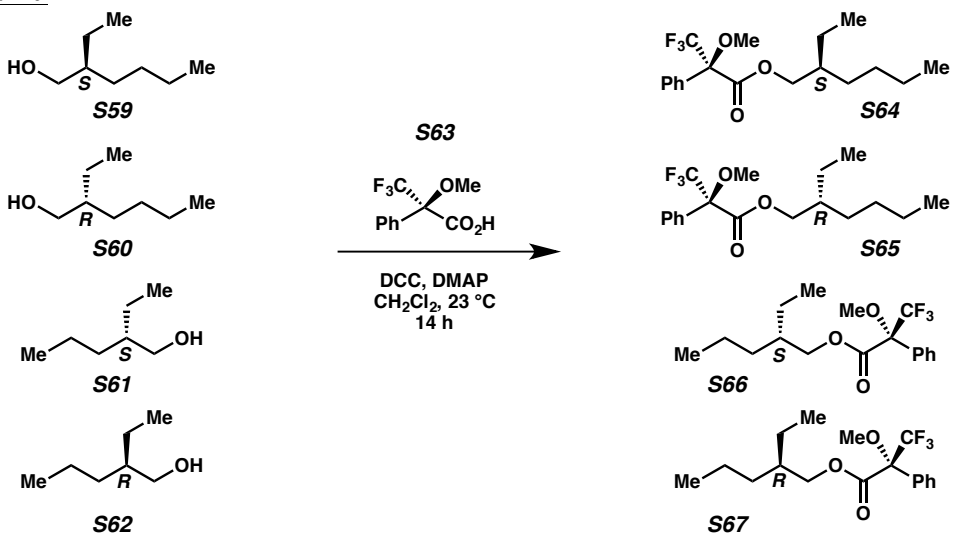
X-ray structural analysis of **8e**. View of **8e** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



8e

Confirmation of Absolute Stereochemistry of Allylic Derivitization Products (Figure 3)

*Product **10***



S59, S60, S61, S62 were synthesized following a procedure in the reported literature[47].

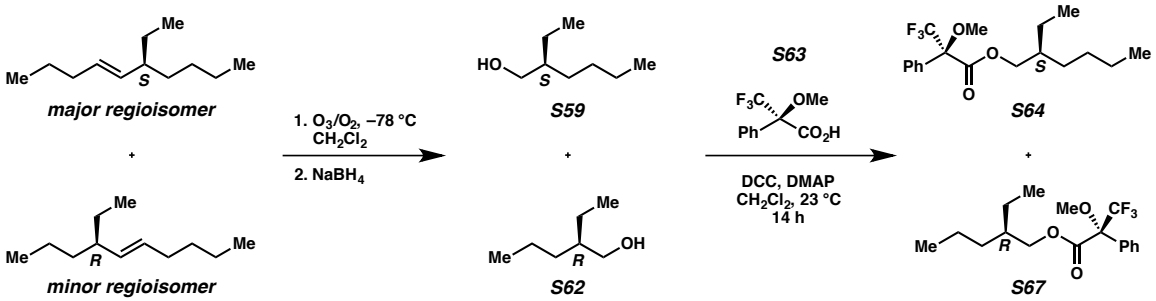
S64: Dicyclohexylcarbodiimide (31 mg, 1.5 equiv) was added to a stirred solution of (*S*)-2-ethylhexan-1-ol **S59** (13 mg, 1 equiv), (*R*)-(+)-α-Methoxy-α-trifluoromethylphenylacetic acid **S63** (35 mg, 1.5 equiv) and DMAP (1.3 mg, 0.1 equiv)

in CH_2Cl_2 (1 mL) at 23 °C. The resulting solution was stirred for 14 h. After completion, a saturated aqueous NH_4Cl solution was added. The reaction mixture was extracted with CH_2Cl_2 (3x). The organic phases were combined, washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 0-10% ethyl acetate in hexanes as an eluent. The product was obtained as a clear oil (31.3 mg, 90% yield). The collected spectra were consistent with those reported in the literature[48].

S65: Following the general procedure for the synthesis of **S64**, the product was purified to afford **S65** (96% yield) as a clear oil. The collected spectra were consistent with those reported in the literature[48].

S66: Following the general procedure for the synthesis of **S64**, the product was purified to afford **S66** (96% yield) as a clear oil.
^{1}H NMR (400 MHz, C_6D_6) δ 7.63 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.11 – 6.93 (m, 3H), 4.06 (dd, *J* = 11.0, 5.5 Hz, 1H), 3.93 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.38 (s, 3H), 1.30 (p, *J* = 6.1 Hz, 1H), 1.15 – 1.04 (m, 2H), 1.04 – 0.96 (m, 4H), 0.75 – 0.67 (m, 3H), 0.64 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 166.3, 132.8, 129.3, 128.2, 123.9 (q, *J* = 288.2 Hz), 84.8 (q, *J* = 27.6 Hz), 67.8, 54.9, 38.2, 32.5, 23.5, 19.6, 14.0, 10.5. LR-MS (ESI+) calcd for [$C_{17}H_{23}F_3O_3$] ([M^+]): 332.16, found 332.20.

S67: Following the general procedure for the synthesis of **S64**, the product was purified to afford **S67** (99% yield) as a clear oil.
^{1}H NMR (400 MHz, C_6D_6) δ 7.64 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.09 – 6.94 (m, 3H), 4.06 (dd, *J* = 10.9, 5.3 Hz, 1H), 3.92 (dd, *J* = 11.0, 5.6 Hz, 1H), 3.38 (s, 3H), 1.38 – 1.23 (m, 1H), 1.16 – 0.96 (m, 6H), 0.77 – 0.67 (m, 3H), 0.63 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 166.3, 132.8, 129.3, 128.2, 123.9 (q, *J* = 288.2 Hz), 84.8 (q, *J* = 27.6 Hz), 67.9, 54.9, 38.2, 32.6, 23.4, 19.5, 14.0, 10.5. LR-MS (ESI+) calcd for [$C_{17}H_{23}F_3O_3$] ([M^+]): 332.16, found 332.20.



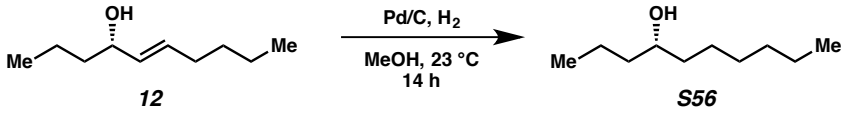
S64: A flame dried flask was charged with a mixture of **10** and CH_2Cl_2 (3 mL), and the flask was cooled to –78 °C in an acetone/dry ice bath. The reaction mixture was purged with ozone gas until the color of the solution turned blue, which is an indication that the reaction was completed. $NaBH_4$ (56 mg, 10 equiv) was then added at –78 °C and the reaction mixture was warmed to 23 °C. After stirring for an additional 2 h, the reaction was quenched with a saturated aqueous NH_4Cl solution. The reaction mixture was extracted with CH_2Cl_2 (3x). The organic phases were combined, washed with brine, dried

over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to yield crude alcohol products **S59** and **S62**.
The above crude product was converted to Mosher esters following the procedure used to synthesize **S64-S67**. The ^{1}H NMR spectra of the crude Mosher esters in C_6D_6 were compared to those of authentic samples of **S64-S67**, which confirmed the formation of **S64** and **S67** as major products from the allylic alkylation.

*Product **11***

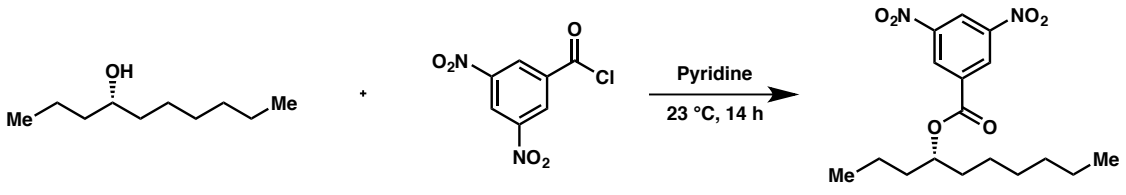
The X-ray crystal structure of sulfinimide **8e** (Fig. S7) allowed the assignment of absolute configuration of this allylic oxidation product. The absolute configuration of thiol **11** was assigned by analogy. For more information, see the section "**Determination of Absolute Stereochemistry of Products**."

*Product **12***



12 ***S56***

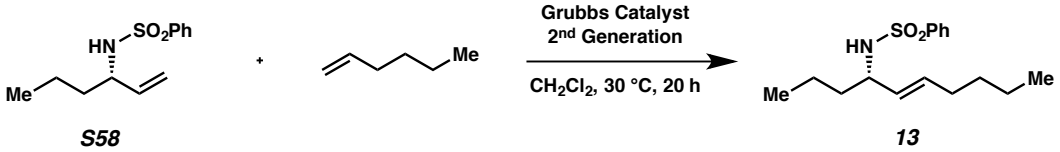
S56: To a flame dried flask was added Pd/C (14 mg, 0.1 eq) and compound ***12*** (90:10 er). The flask was then degassed and purged with hydrogen gas from a balloon. Anhydrous methanol (1.3 mL) was added and the reaction was stirred for 14 h. After completion, the reaction was filtered through a celite plug and concentrated under reduced pressure to yield crude product (18.6 mg), which was used in the next step without further purification.



S56 ***S57***

(*S*)-S57: 3,5-Dinitrobenzoyl chloride (18 mg, 1. 3 eq) was added to a stirred solution of compound **S56** (9.3 mg, 1 equiv) in pyridine (0.2 mL) at 23 °C, and the resulting solution was stirred for 14 min at 0 °C and 14 h at 23 °C. Upon completion, the reaction was concentrated under reduced pressure. The crude product was purified by column chromatography (gradient 0-20% EtOAc/hexanes) to afford **(*S*)-S57** as a white solid (17.3 mg, 73% yield, 2 steps). This product was confirmed to have the same spectral data and sense of optical rotation as reported for the same compound in the literature[49].
(*S*)-S57 from **12**: $[\alpha]^{23}_D$ = +4.1° (c=0.5, EtOH) (90:10 er)
(*S*)-S57 from the literature[49]: $[\alpha]^{20}_D$ = +30.4° (c=0.1, EtOH) (100:0 er)

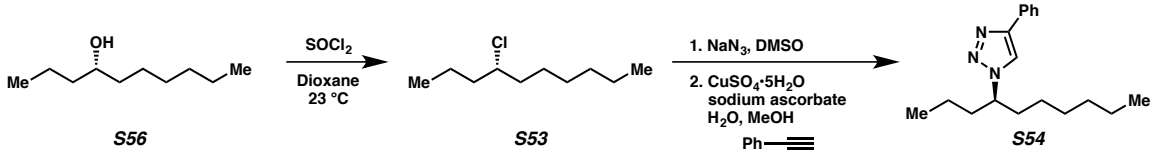
*Product **13***



S58 ***13***

13: A flame dried flask was charged with CH_2Cl_2 (1.0 mL), 1-hexene (0.16 ml, 5 equiv) and (*S*)-N-(hex-1-en-3-yl)benzenesulfonamide **S58**[50] (60 mg, 1 equiv) at 23 °C. Grubbs Second Generation Catalyst (10.6 mg, 0.05 equiv) was then added and the flask was heated to 30 °C for 20 h. Upon completion, the reaction was concentrated under reduced pressure. The crude product was purified by column chromatography (gradient 0-20% EtOAc/ hexanes) to afford **13** as a clear oil (41.8 mg, 57% yield, >20:1 *E/Z*).
13 from **5**: $[\alpha]^{23}_D$ = -4.2° (c = 0.53, CH_2Cl_2) (91.5:8.5 er)
13 from **S58**: $[\alpha]^{23}_D$ = -3.5° (c = 1.3, CH_2Cl_2) (86:14 er)

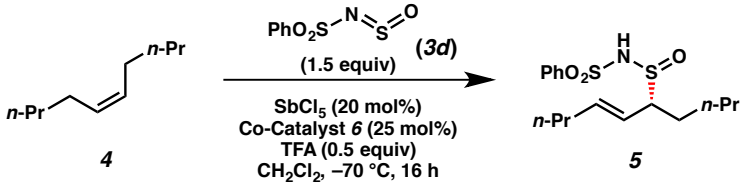
*Product **14***



S56 ***S53*** ***S54***

A flame dried flask was charged with 1,4-dioxane (0.5 mL) and alcohol **S56** (9.4 mg, 1 equiv). The flask was cooled to 10 °C in an ice/water bath. Thionyl chloride(13 μL, 3 equiv) was then added under an argon atmosphere. The reaction mixture was allowed to warm up to 23 °C and stirred for 1 h. After completion, a saturated aqueous NH_4Cl solution was added. The reaction mixture was extracted with Et_2O (3x). The organic phases were combined and washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to yield crude product **S53**.
The crude **S53** was converted to **S54** (4.4 mg, 26% yield, 2 steps) using the procedure to obtain the same compound above. **S54** synthesized by these two methods had the same spectra data and sense of optical rotation.
S54 from **S56**: $[\alpha]^{23}_D$ = -4.5° (c = 0.17, CH_2Cl_2) (80.5:19.5 er)
S54 from **14**: $[\alpha]^{23}_D$ = -5.7° (c = 0.07, CH_2Cl_2) (89:11 er)

Linear Correlation Experiment



4 ***5***

The (*R*)- and (*S*)-enantiomers of co-catalyst **6** were mixed together to obtain the desired enantiomeric ratio, which was confirmed on HPLC by comparison to a sample of the racemate (see HPLC traces below). The ene reactions were run following method A of

the general procedure. The resulting ene adducts were not isolated but directly converted to **S17** for HPLC analysis.

Table S4.

Correlation study between the enantiomeric excess of co-catalyst **6** and the enantiomeric excess of product **5**

Entry	co-catalyst's ee	product's ee
1	4	4
2	10	10
3	22	16
4	52	48
5	90	76
6	98	85

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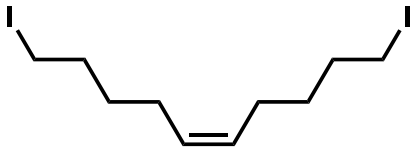
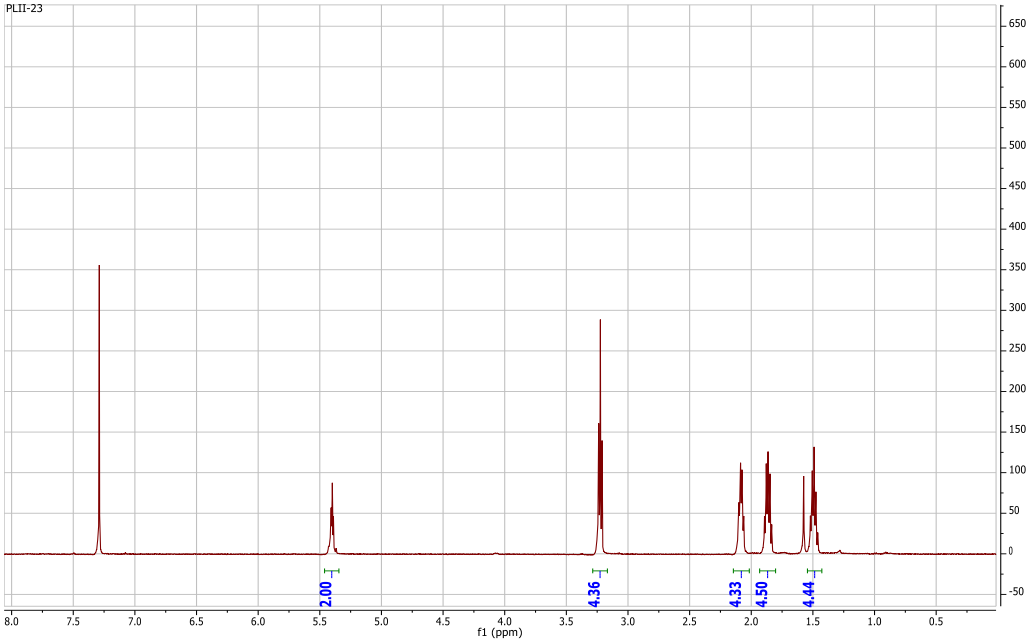
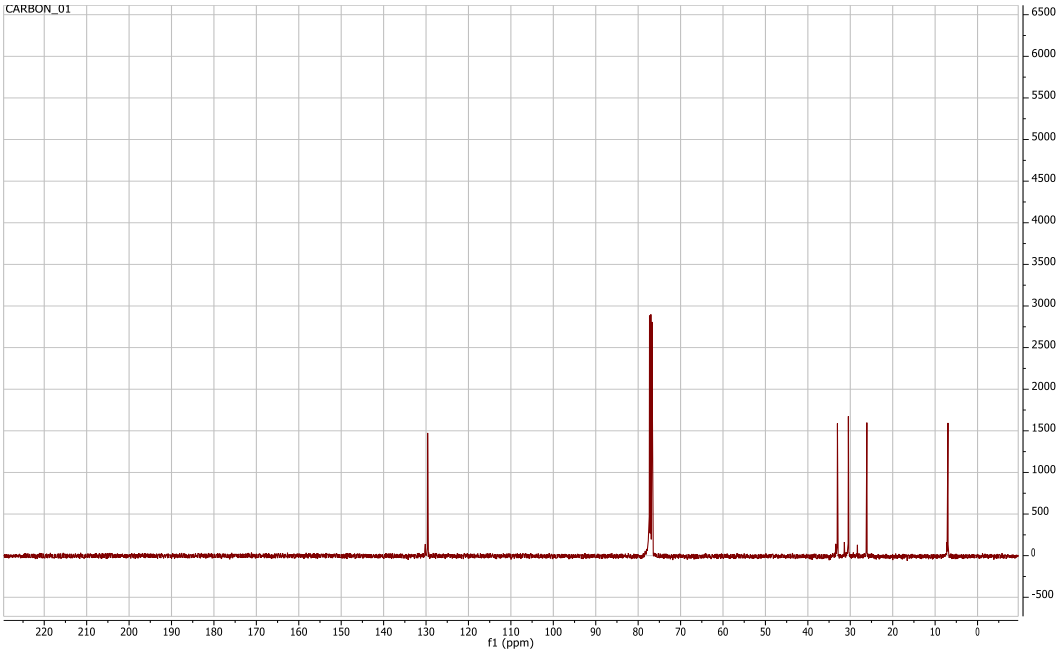
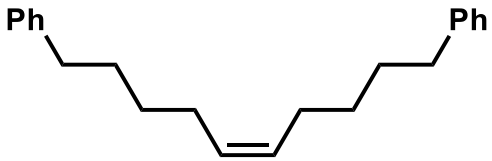
NMR Spectra of New Compounds



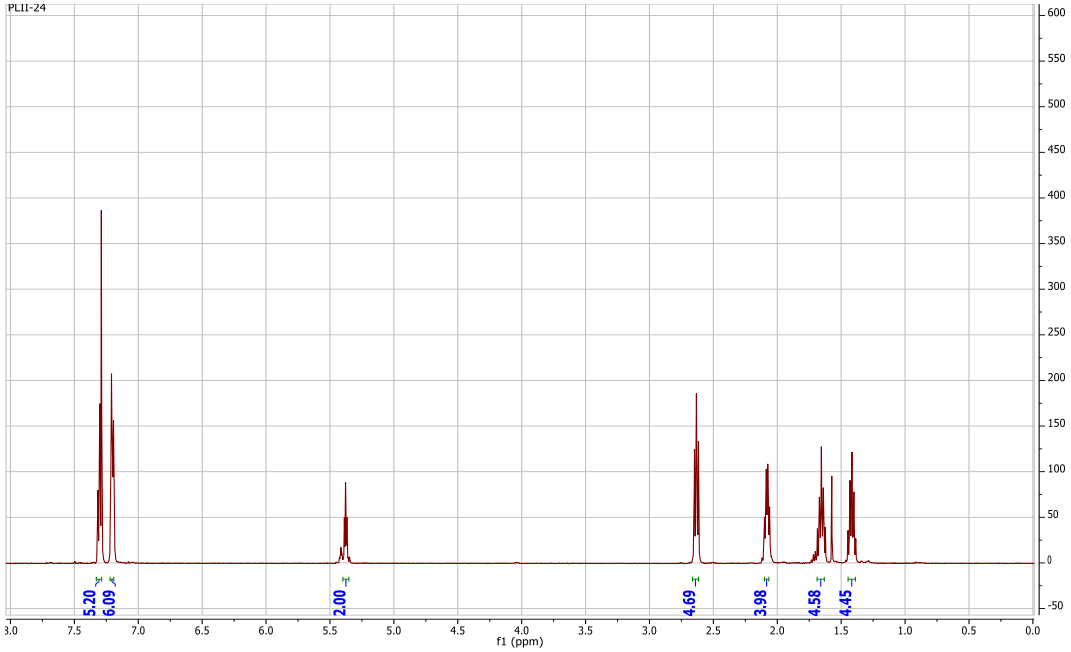
S3 in $CDCl_3$

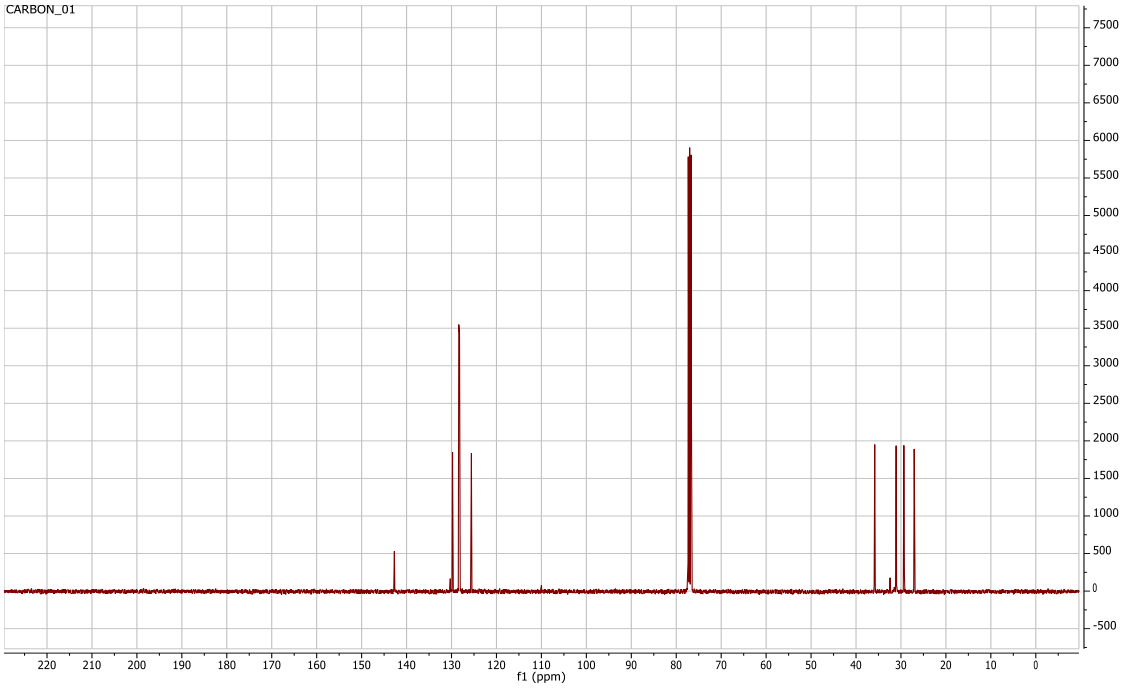


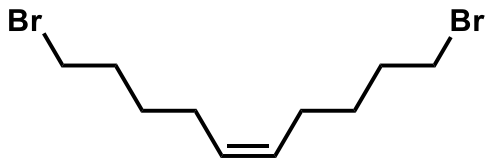




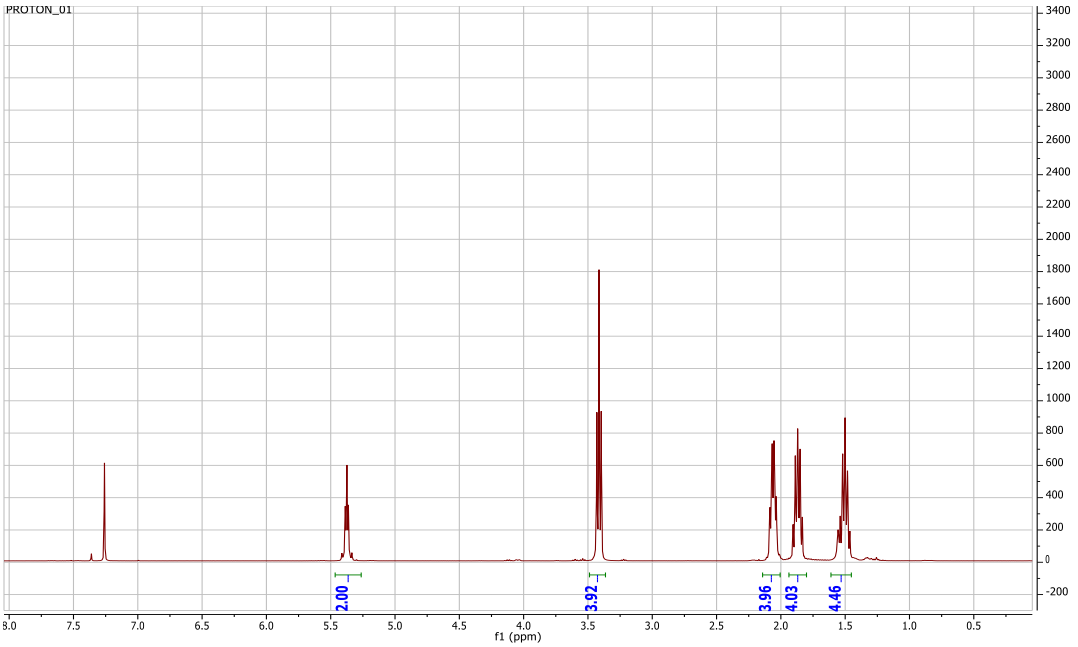
S4 in $CDCl_3$

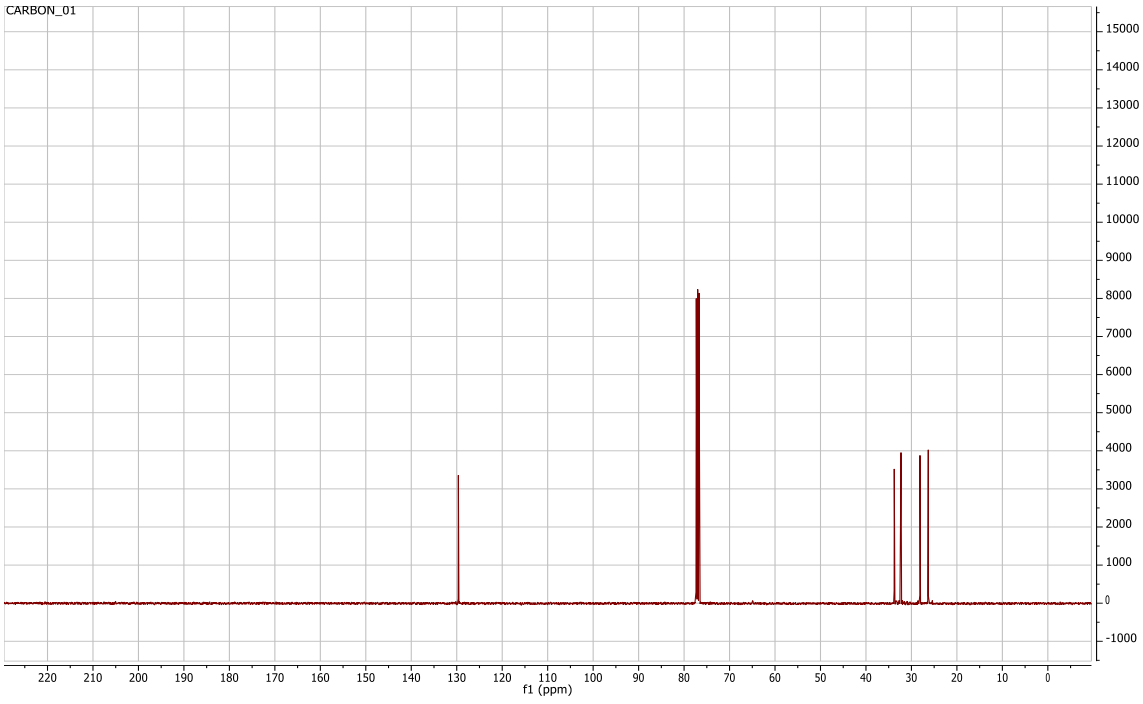


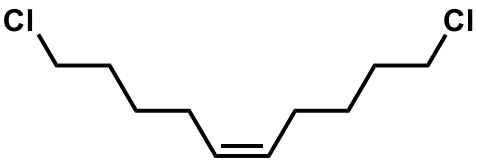




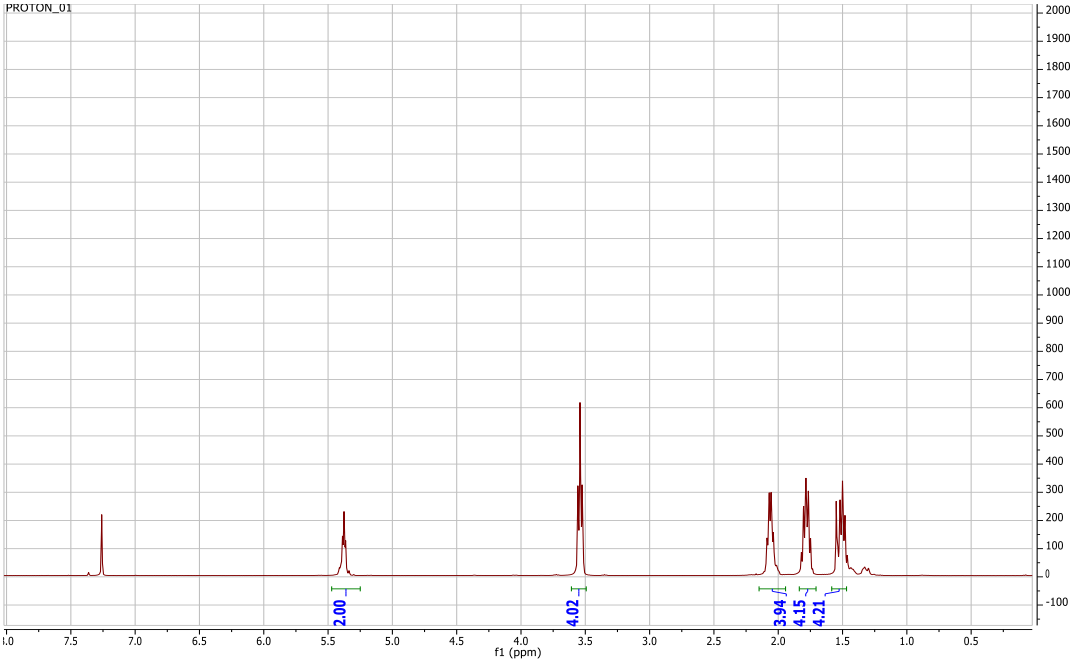
S5 in $CDCl_3$

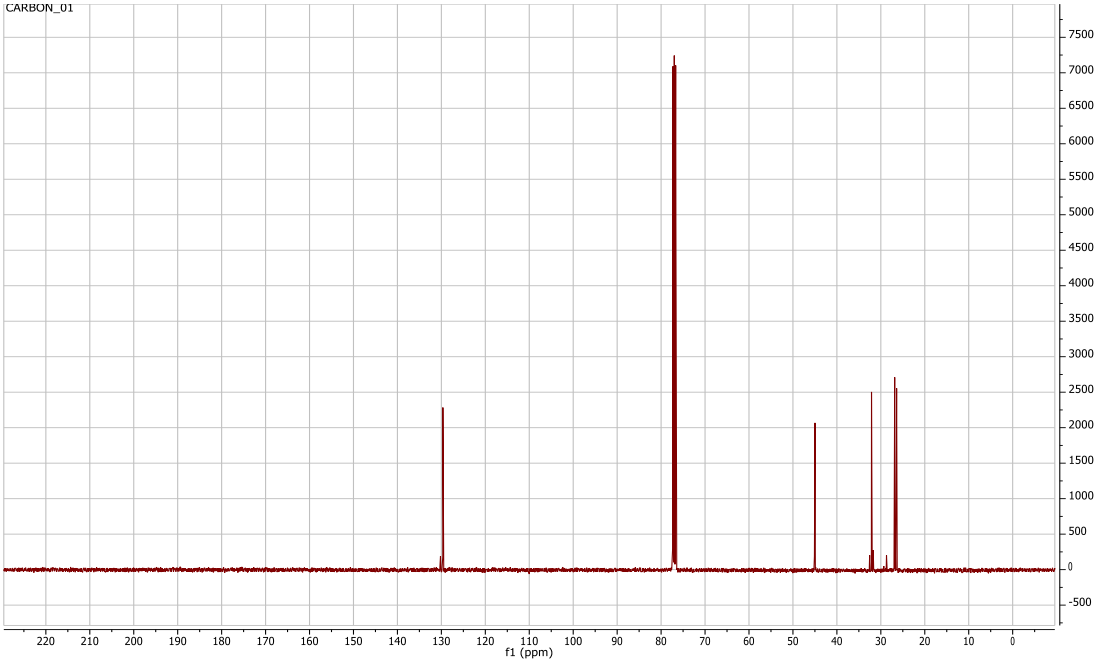


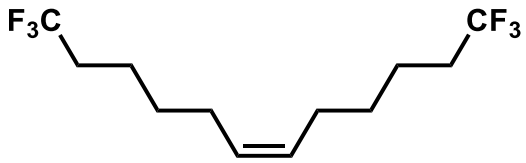




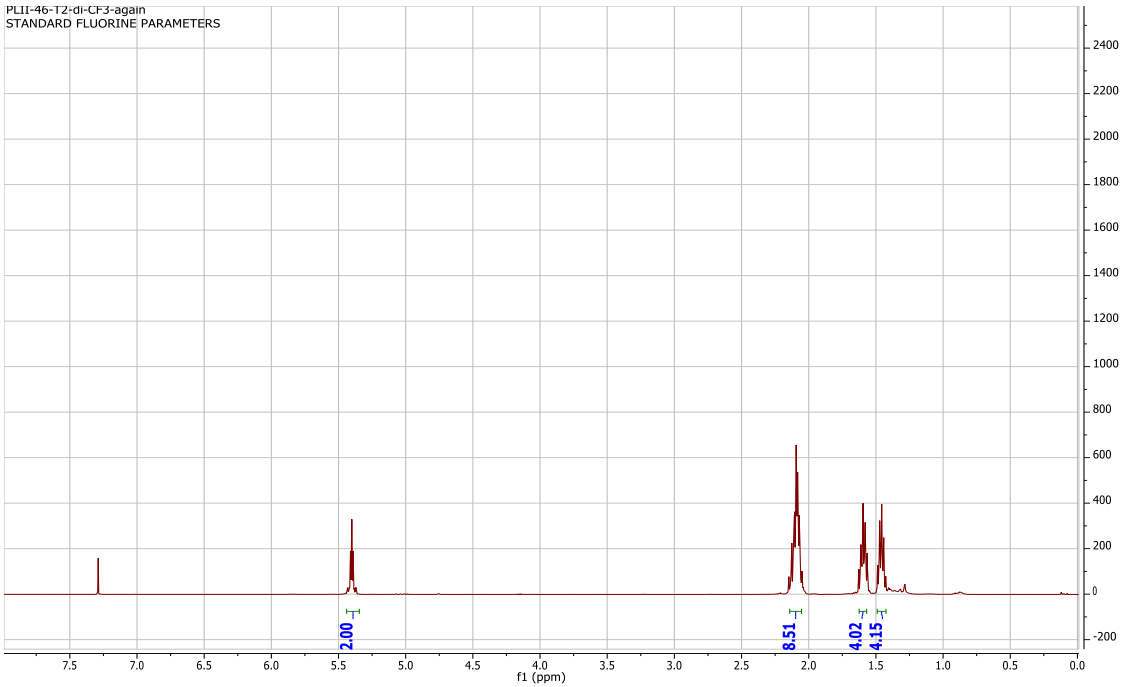
S6 in $CDCl_3$

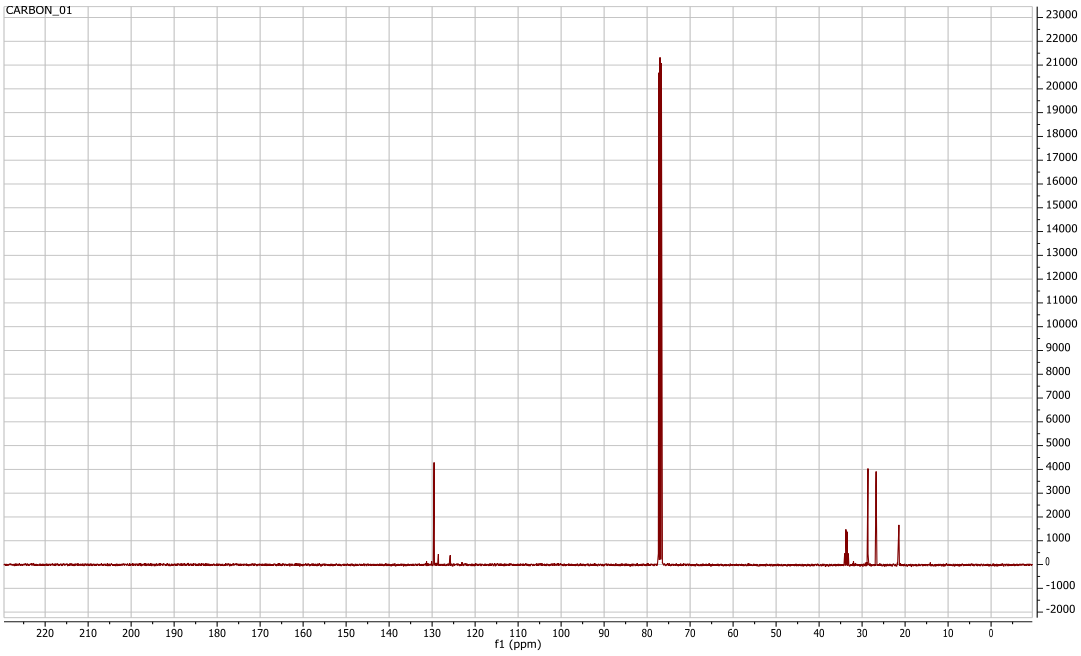


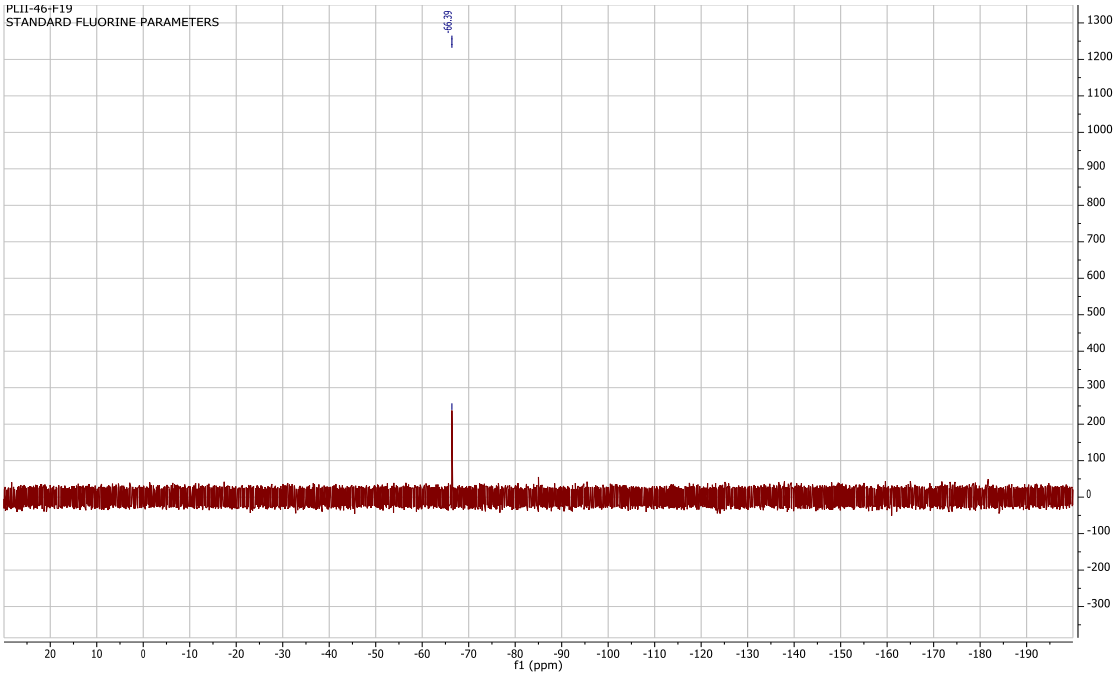


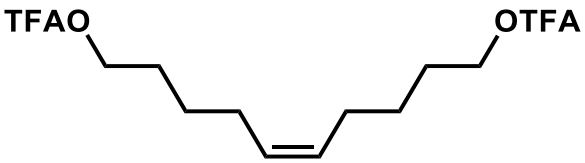

F3C
CF3

S7 in $CDCl_3$

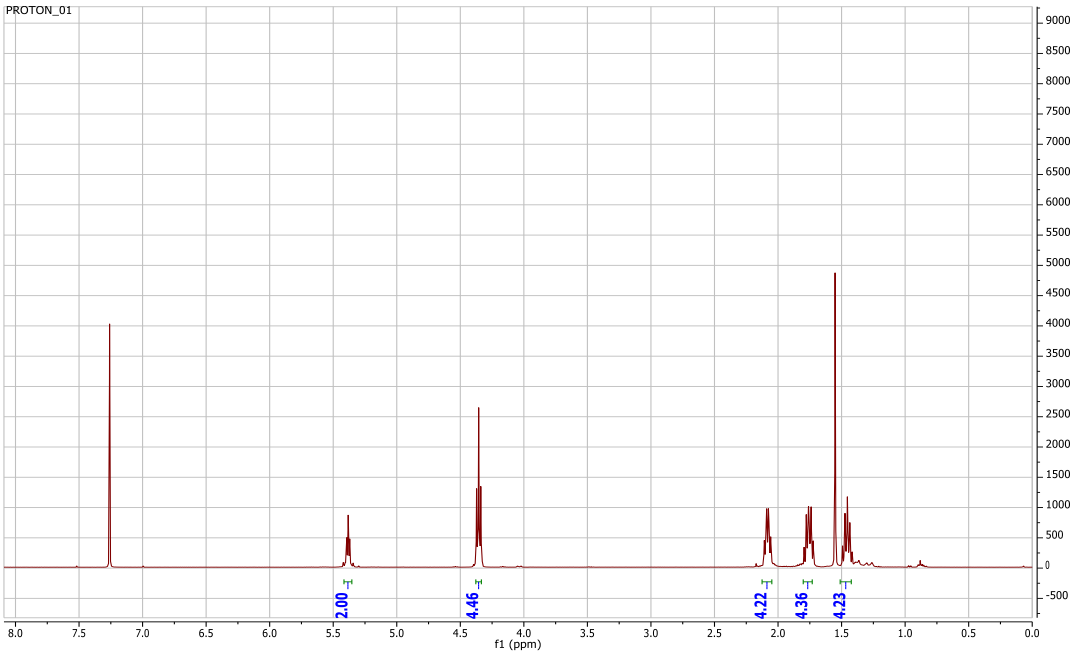

PLII-46-T2-di-CF3-again
STANDARD FLUORINE PARAMETERS
2.00
8.51
4.02
4.15
f1 (ppm)

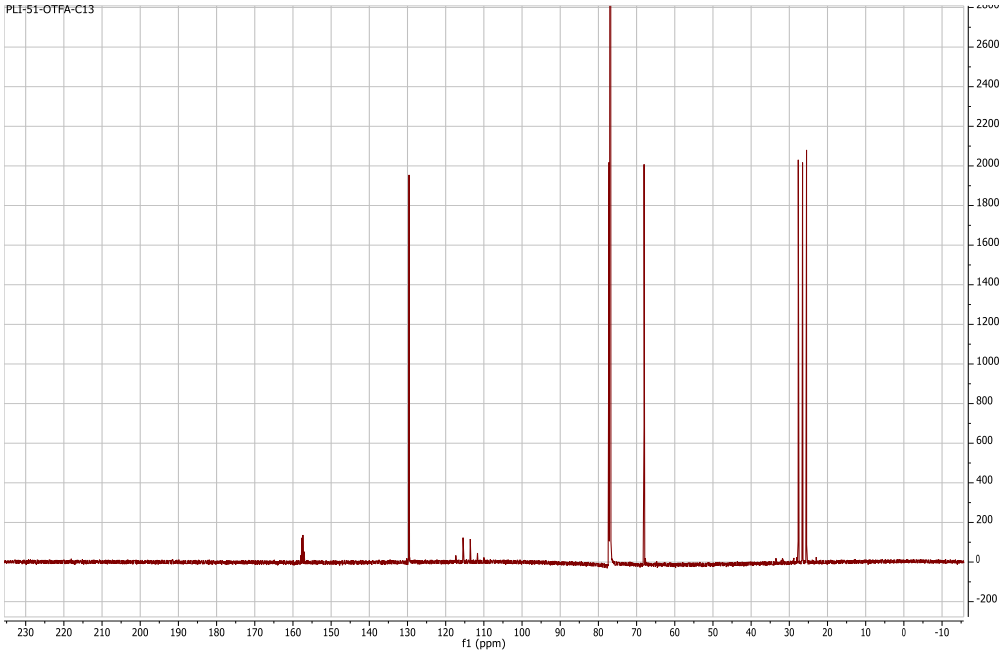

CARBON_01
f1 (ppm)

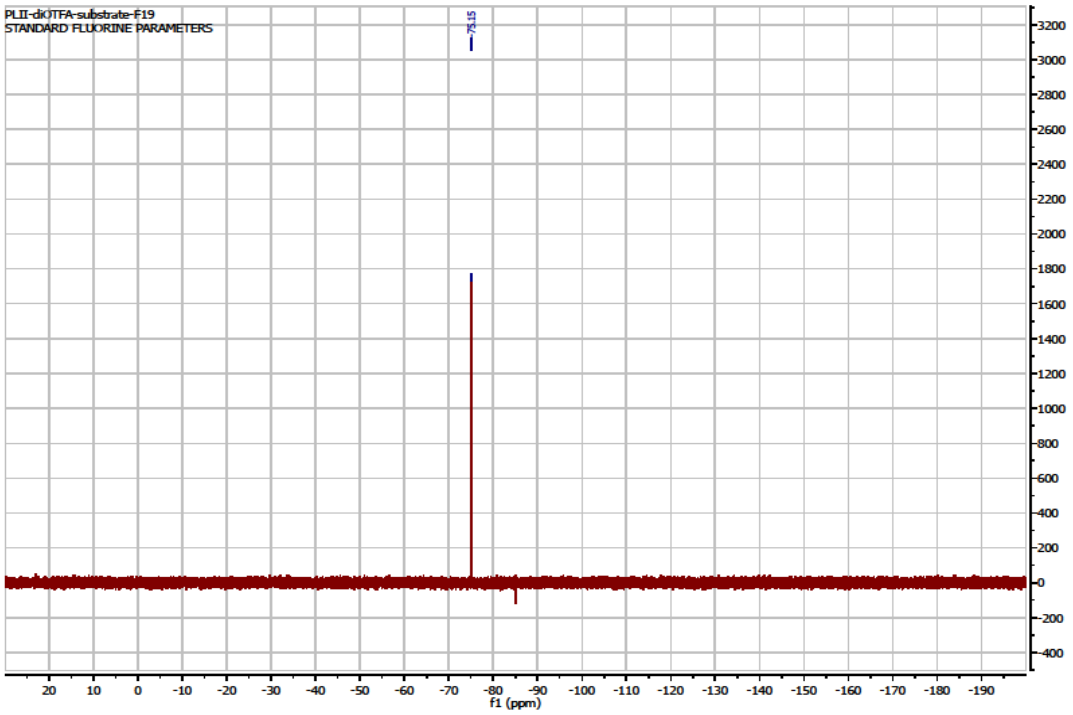

PLII-46-F19
STANDARD FLUORINE PARAMETERS
-66.39
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

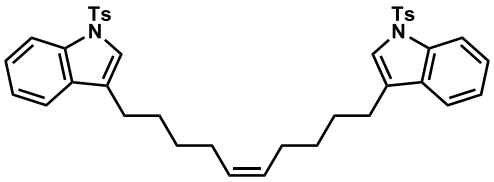

TFAO
OTFA

S8 in $CDCl_3$

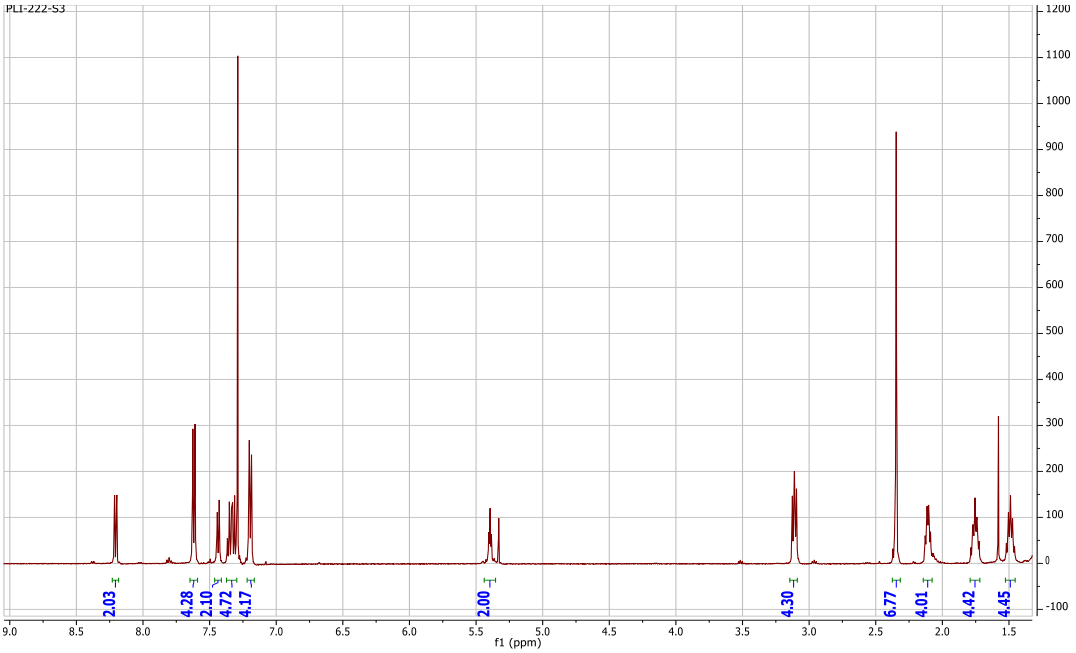

PROTON_01
2.00
4.46
4.22
4.36
4.23
f1 (ppm)

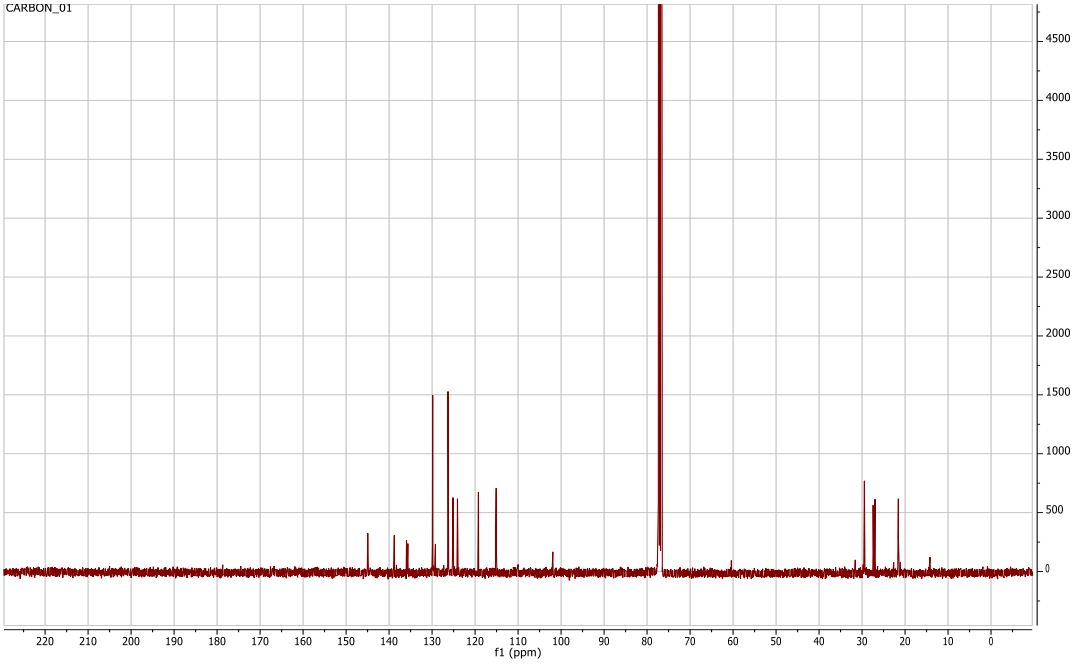

PLI-51-OTFA-C13
f1 (ppm)

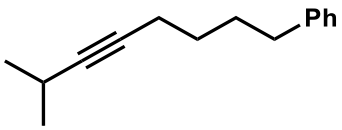

PLII-diOTFA-substrate-F19
STANDARD FLUORINE PARAMETERS
-75.15
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


Ts
N
Ts
N

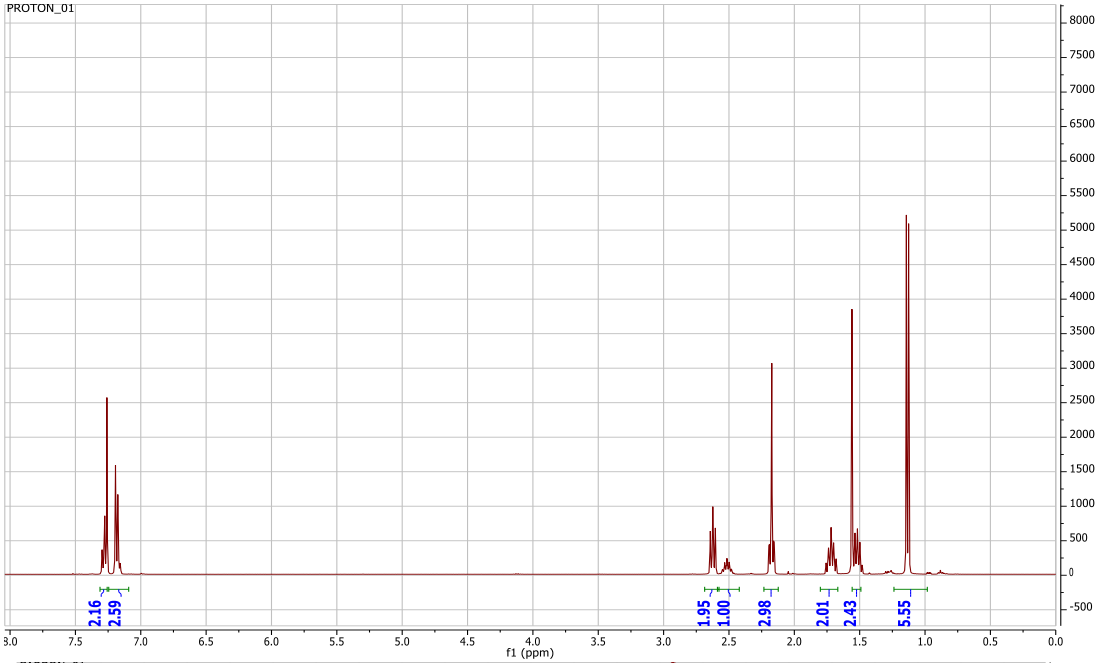
S9 in $CDCl_3$

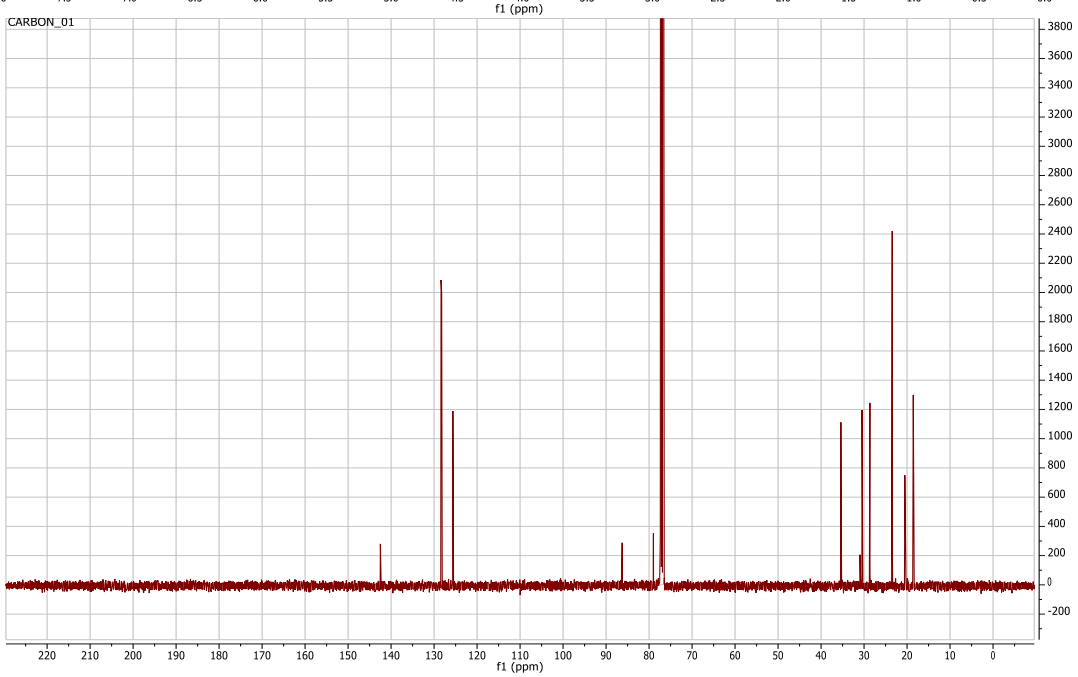

PLI-222-S3
2.03
4.28
2.10
4.72
4.17
2.00
4.30
6.77
4.01
4.42
4.45
f1 (ppm)

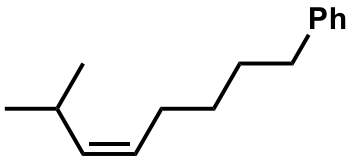

CARBON_01
f1 (ppm)


Ph

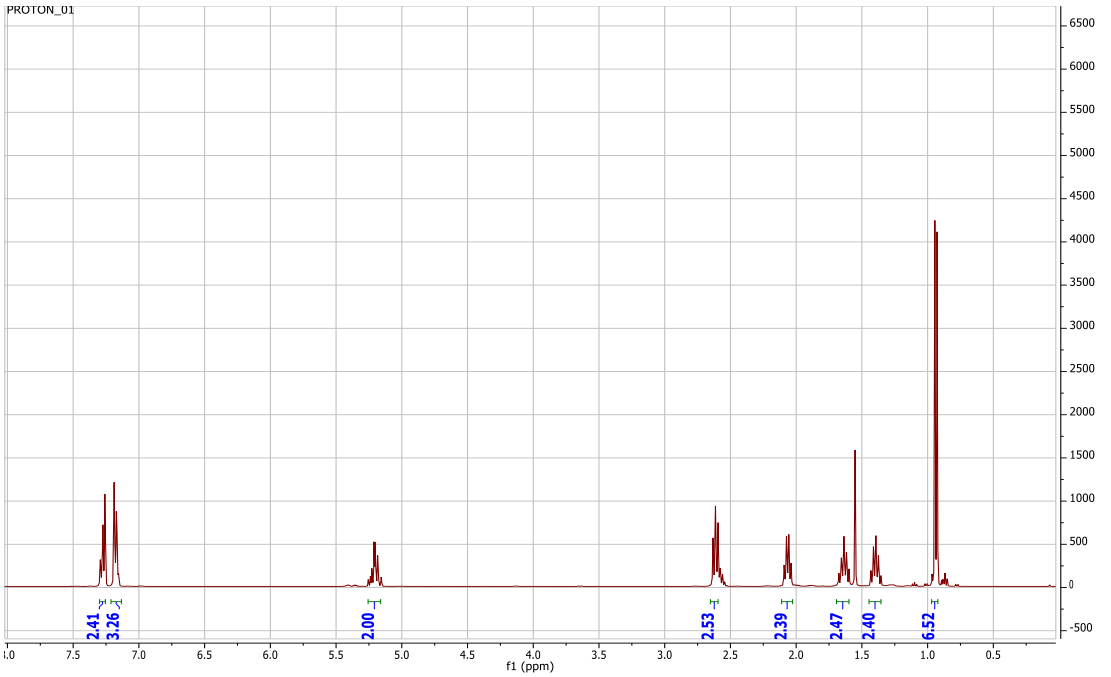
S10 in $CDCl_3$

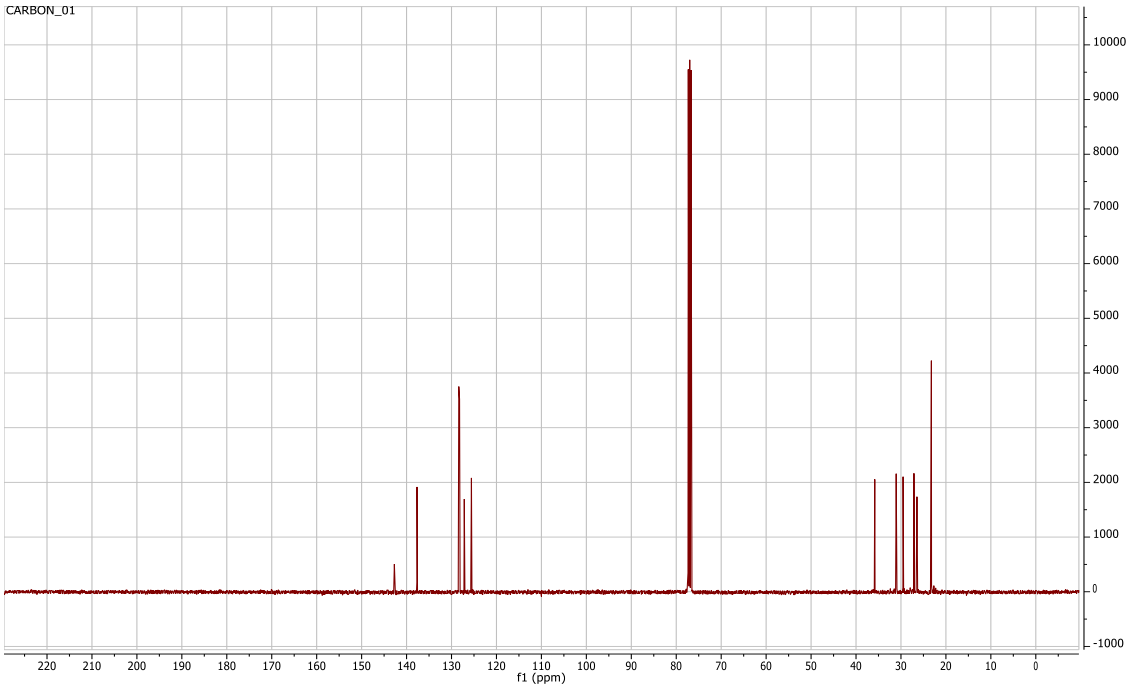

PROTON_01
2.16
2.59
1.95
1.00
2.98
2.01
2.43
5.55
f1 (ppm)

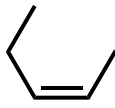

CARBON_01
f1 (ppm)


Ph

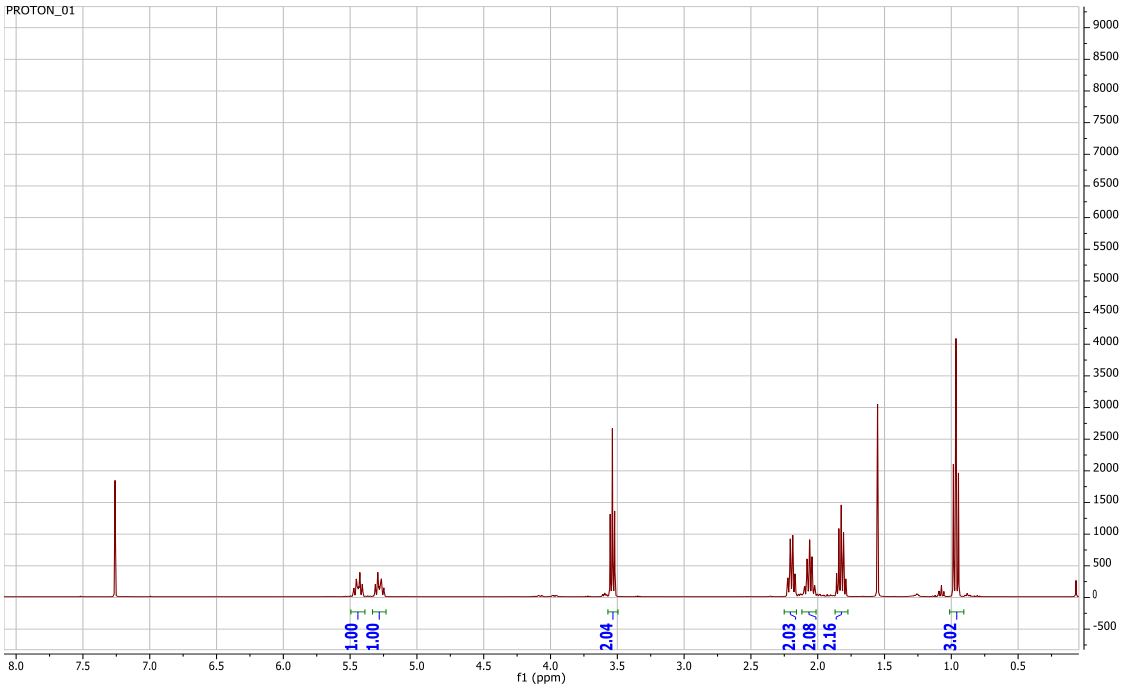
S11 in $CDCl_3$

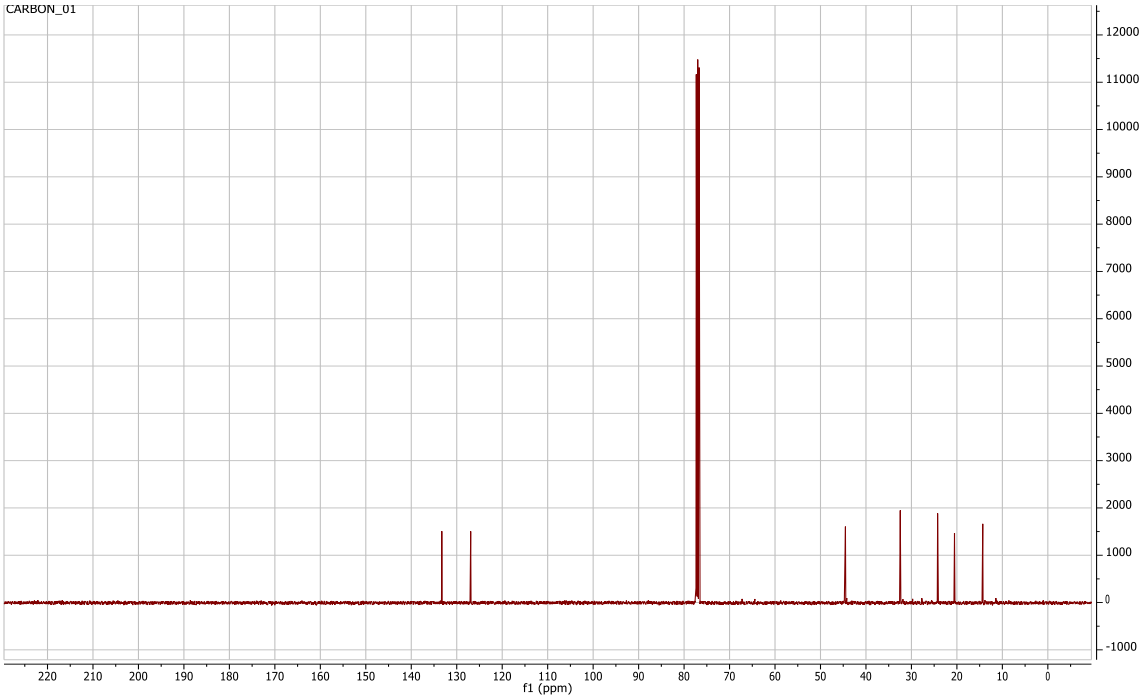

PROTON_01
2.41
3.26
2.00
2.53
2.39
2.47
2.40
6.52
f1 (ppm)

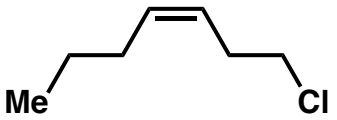

CARBON_01
f1 (ppm)



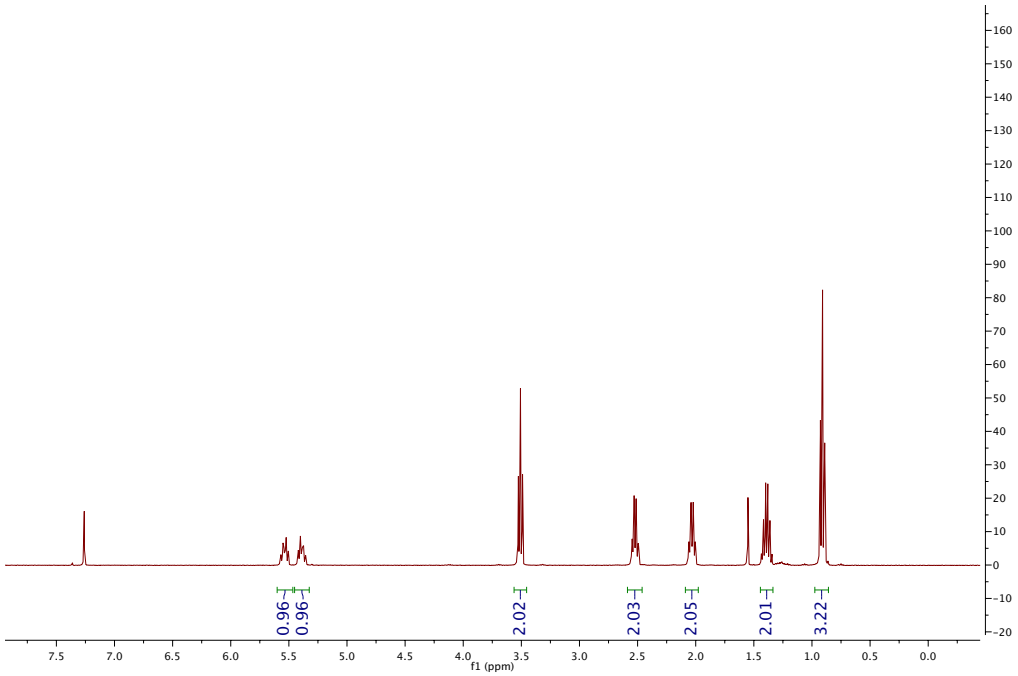
S12 in $CDCl_3$

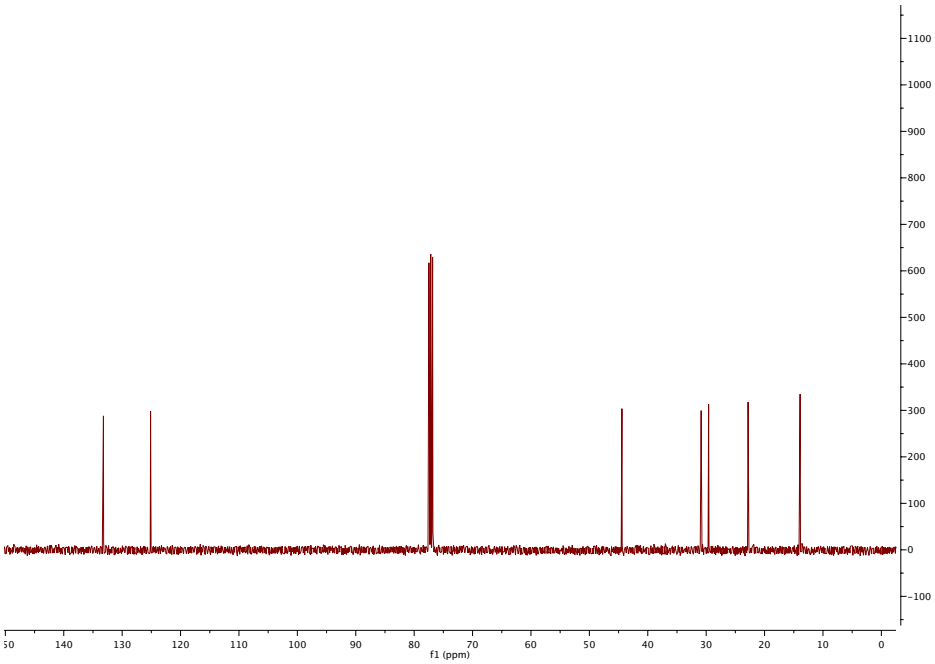


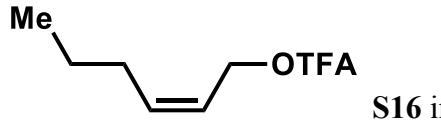




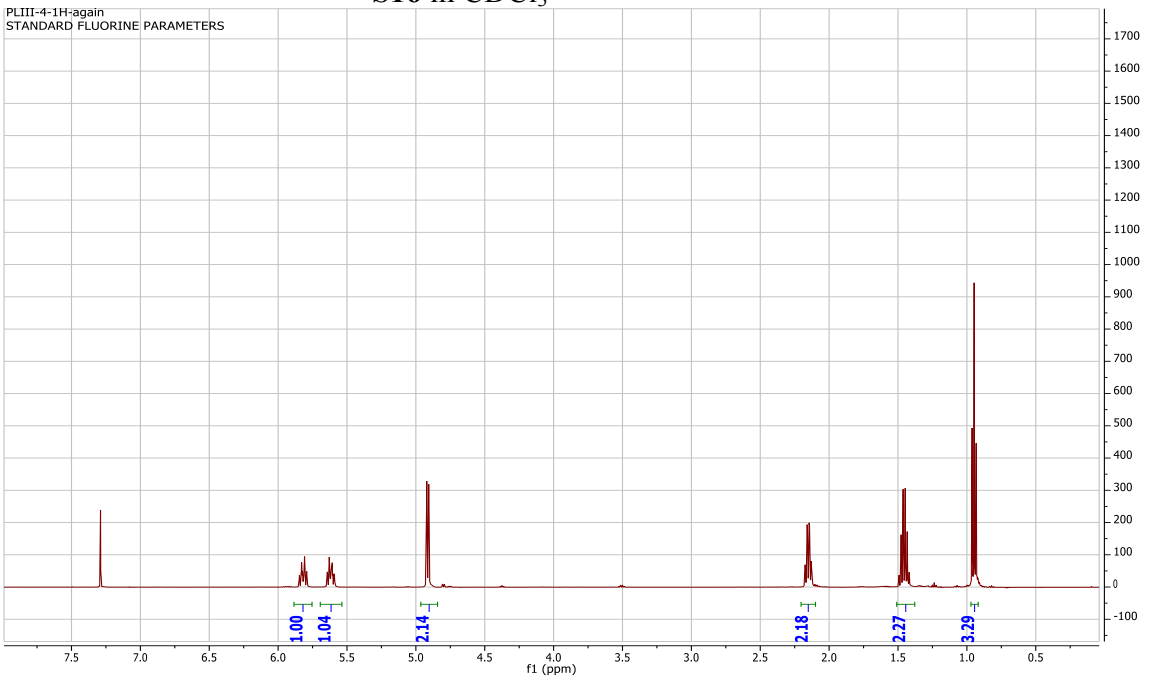
S13 in $CDCl_3$

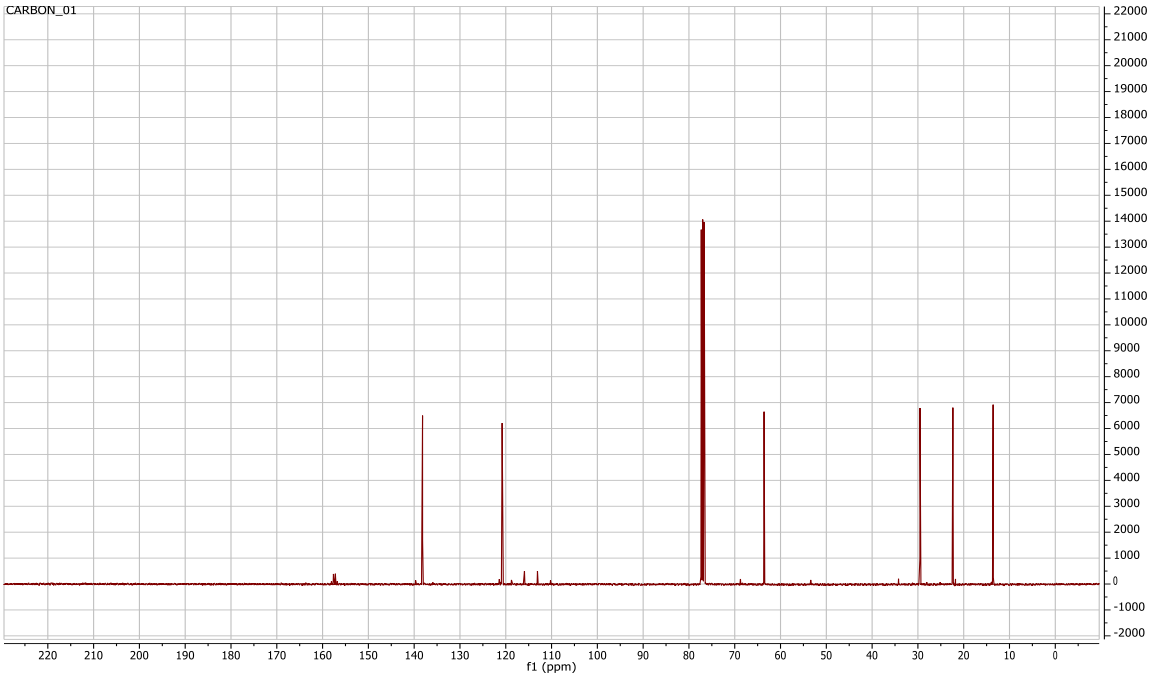


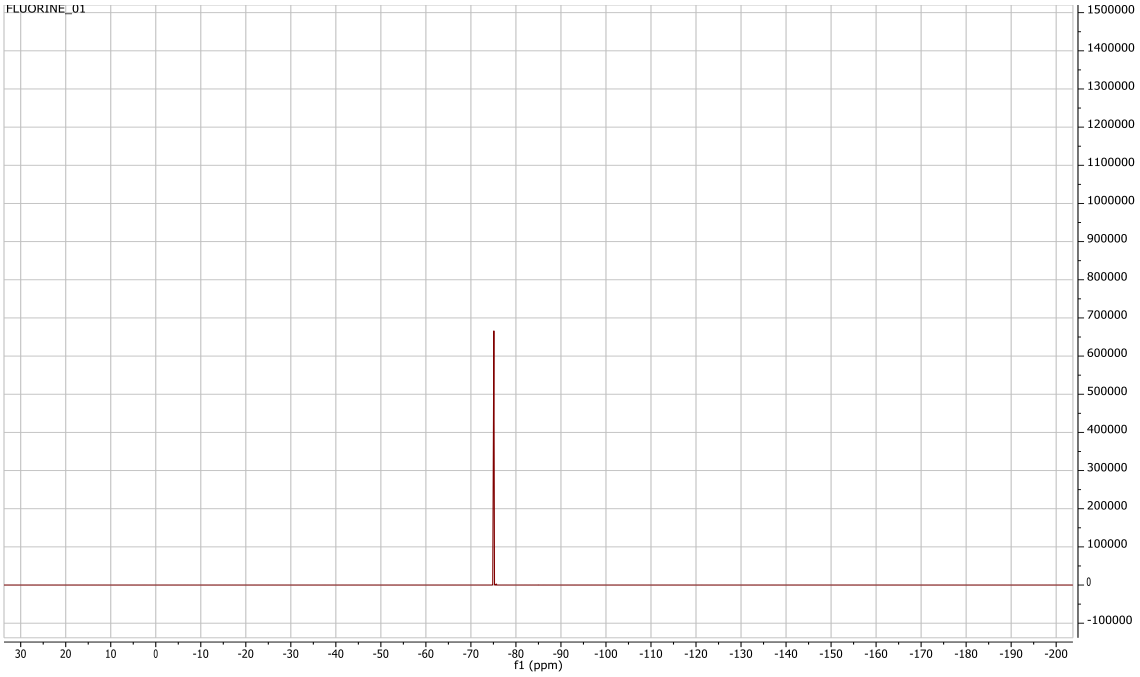


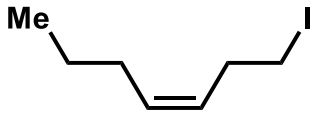

Me
OTFA

S16 in $CDCl_3$

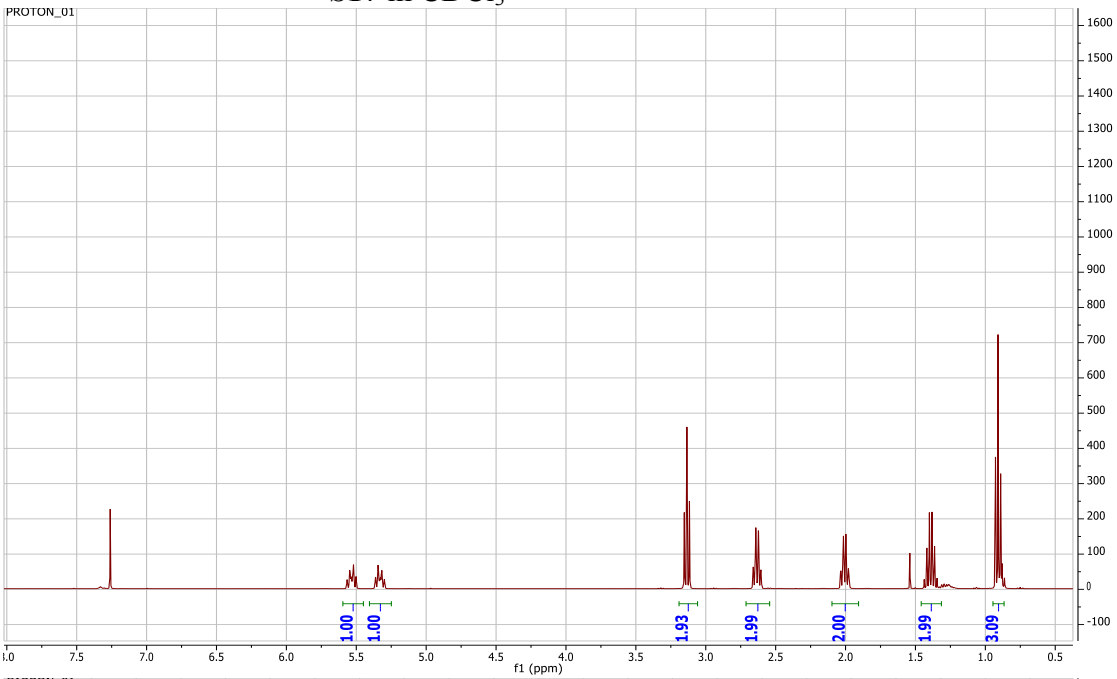

PLIII-4-1H-again
STANDARD FLUORINE PARAMETERS
1.00
1.04
2.14
2.18
2.27
3.29
f1 (ppm)

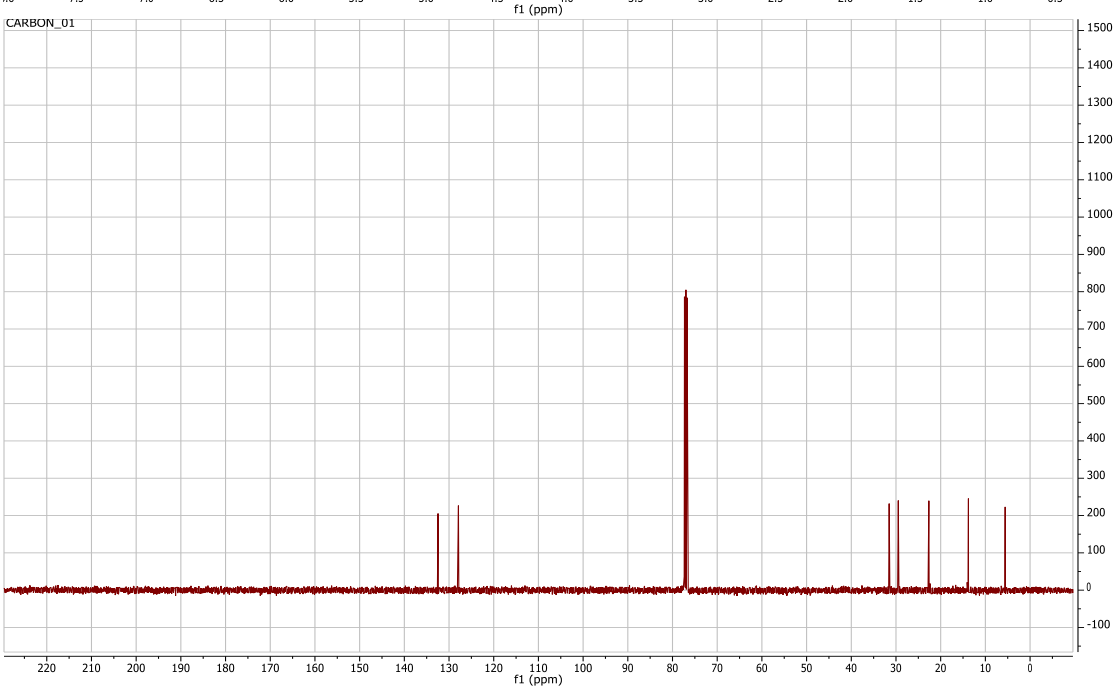

CARBON_01
f1 (ppm)

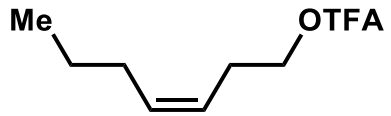

FLUORINE_01
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


Me
I

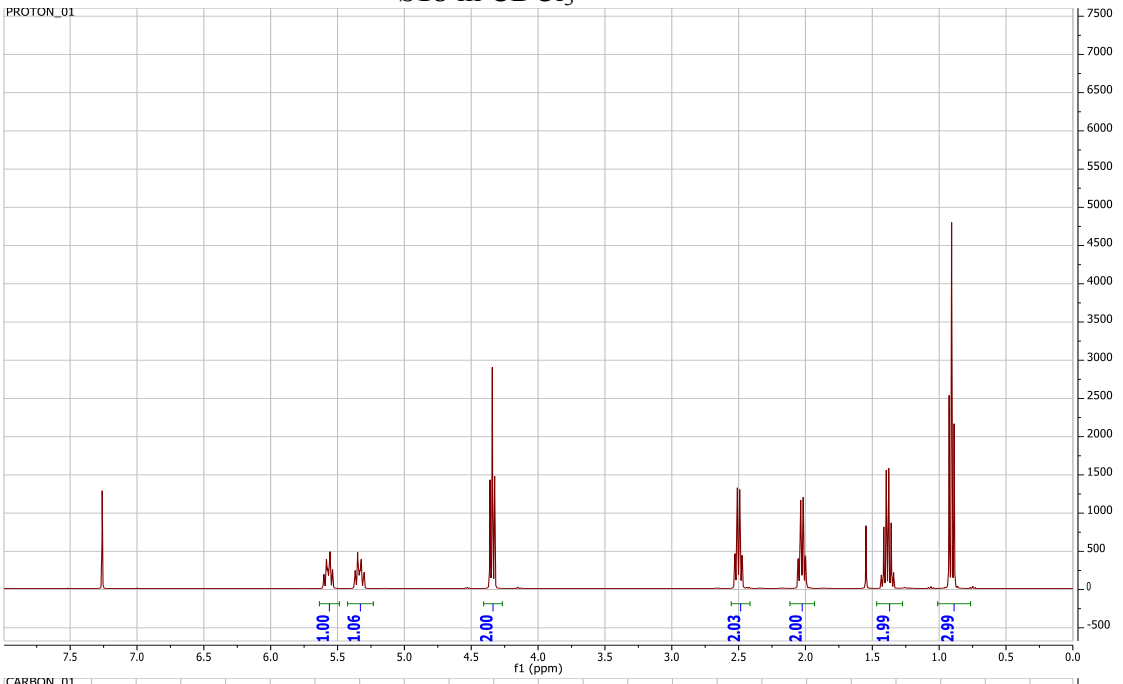
S17 in $CDCl_3$

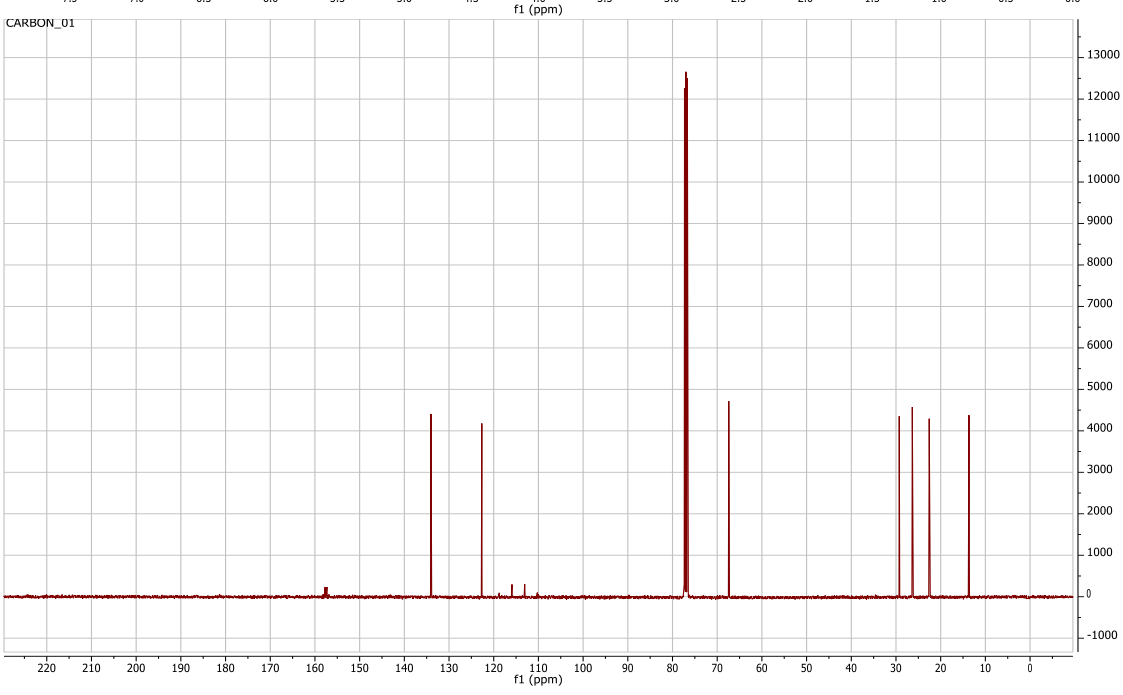

PROTON_01
1.00
1.00
1.93
1.99
2.00
1.99
3.09
f1 (ppm)


CARBON_01
f1 (ppm)

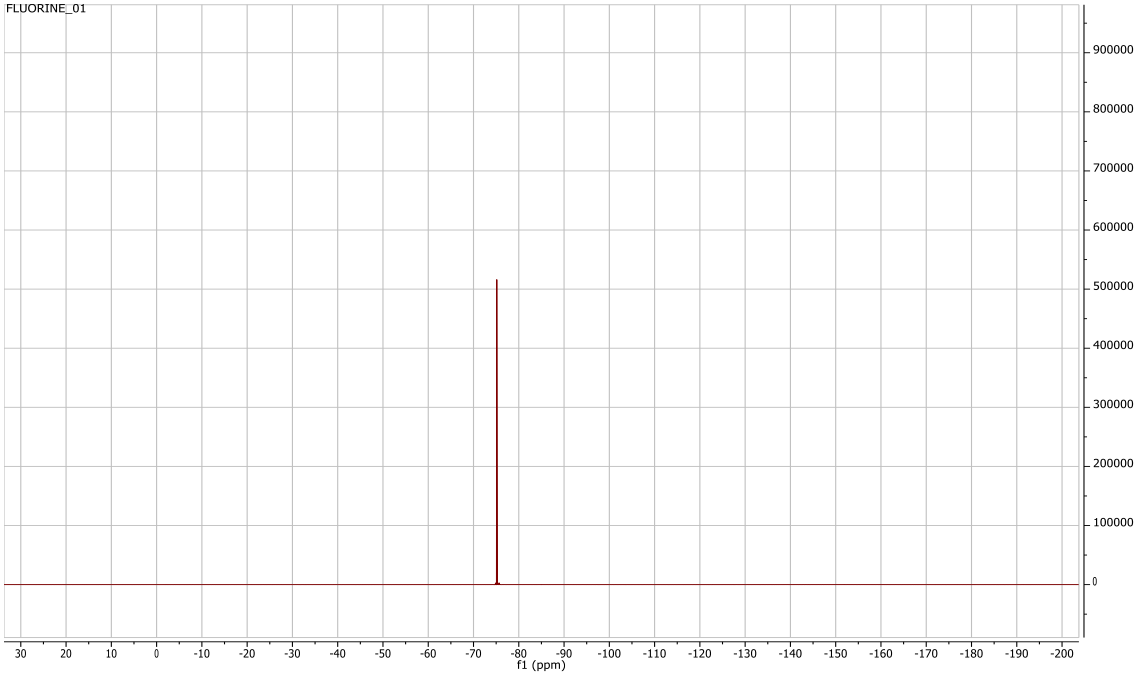

Me
OTFA

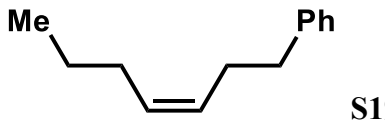
S18 in $CDCl_3$


PROTON_01
1.00
1.06
2.00
2.03
2.00
1.99
2.99
f1 (ppm)

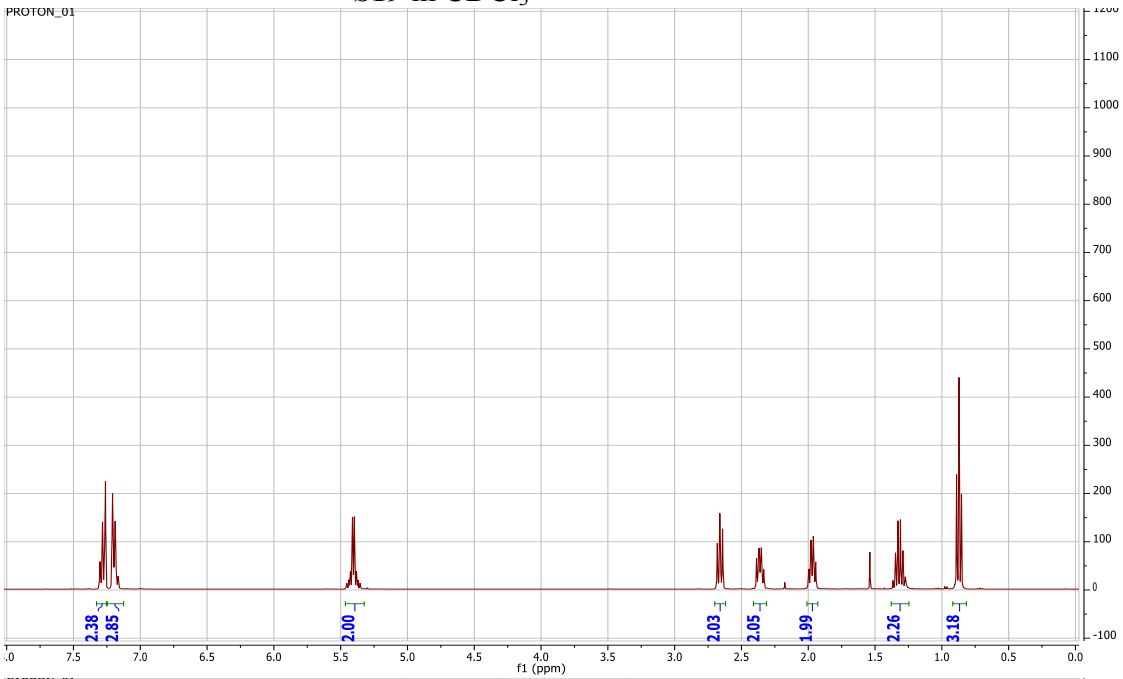

CARBON_01
f1 (ppm)

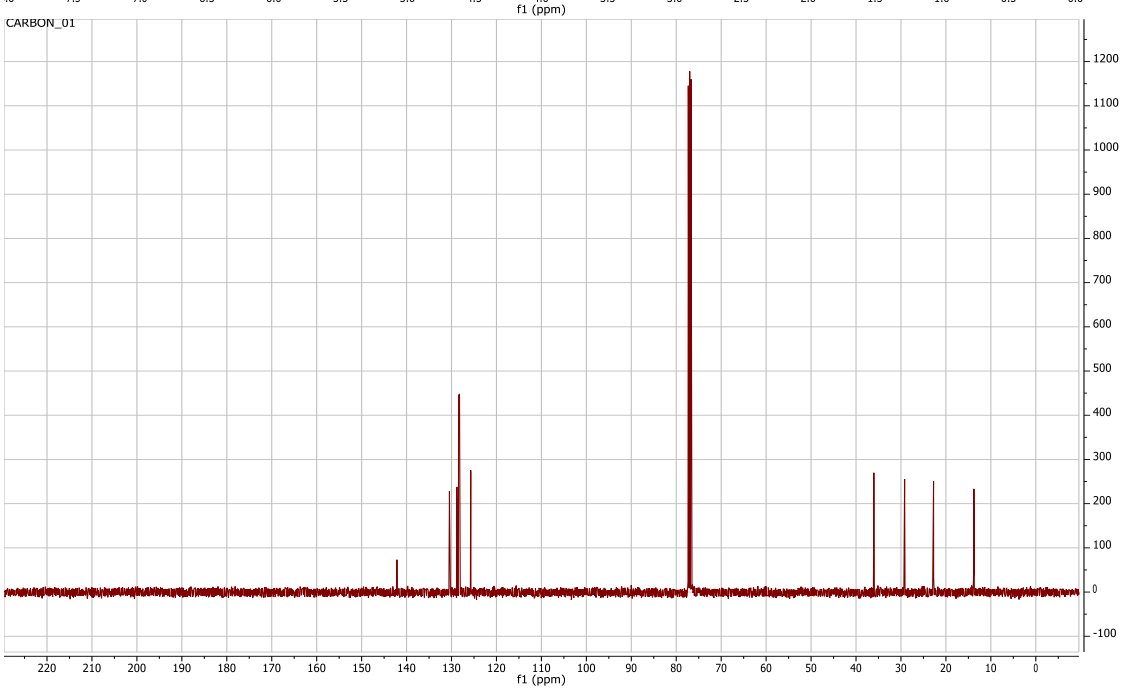
^{19}F NMR

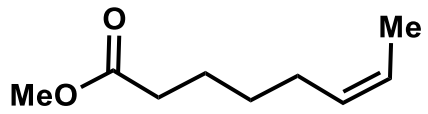

FLUORINE_01
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


Me
Ph

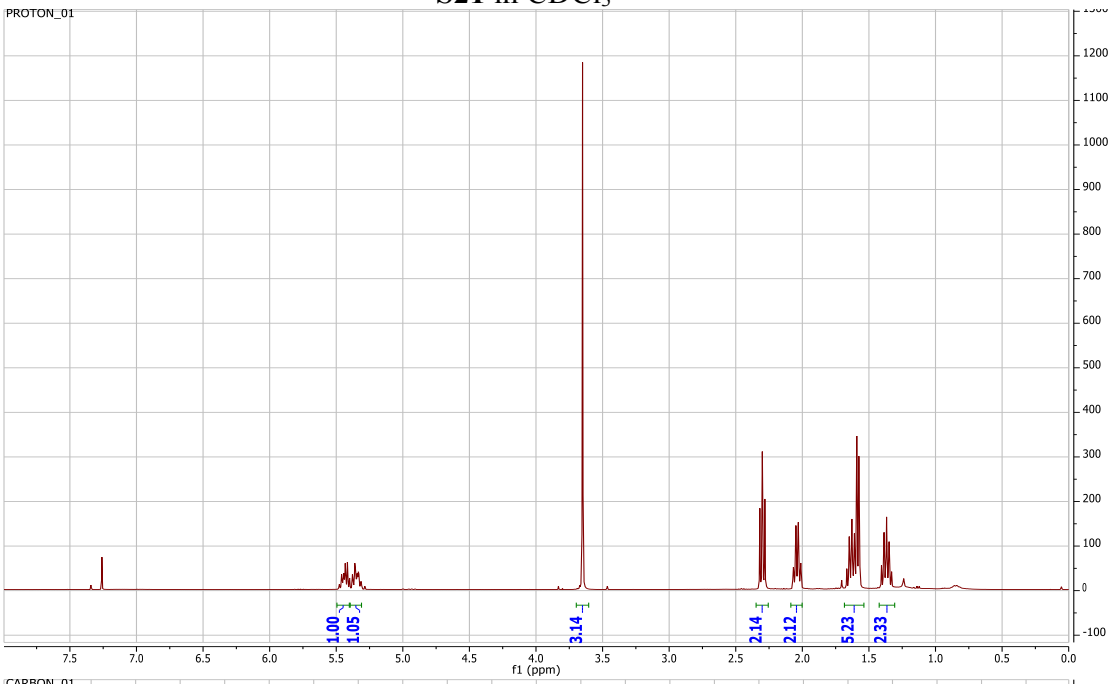
S19 in $CDCl_3$

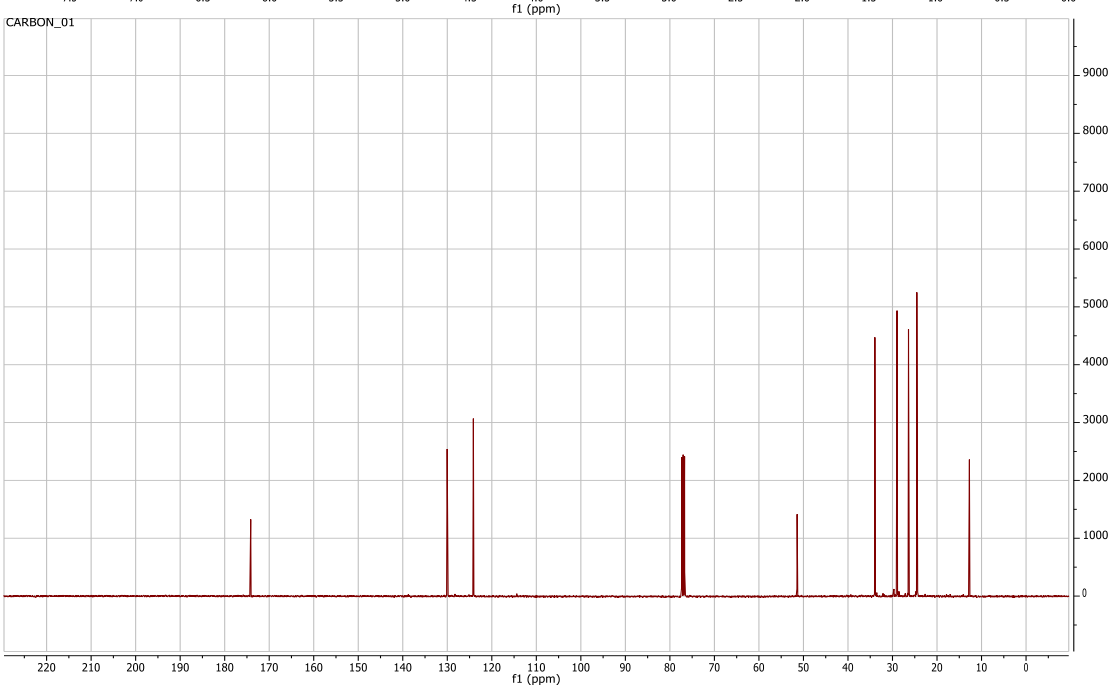

PROTON_01
2.38
2.85
2.00
2.03
2.05
1.99
2.26
3.18
f1 (ppm)

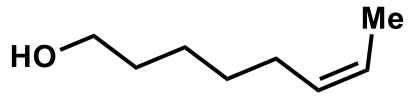

CARBON_01
f1 (ppm)


O
Me
MeO

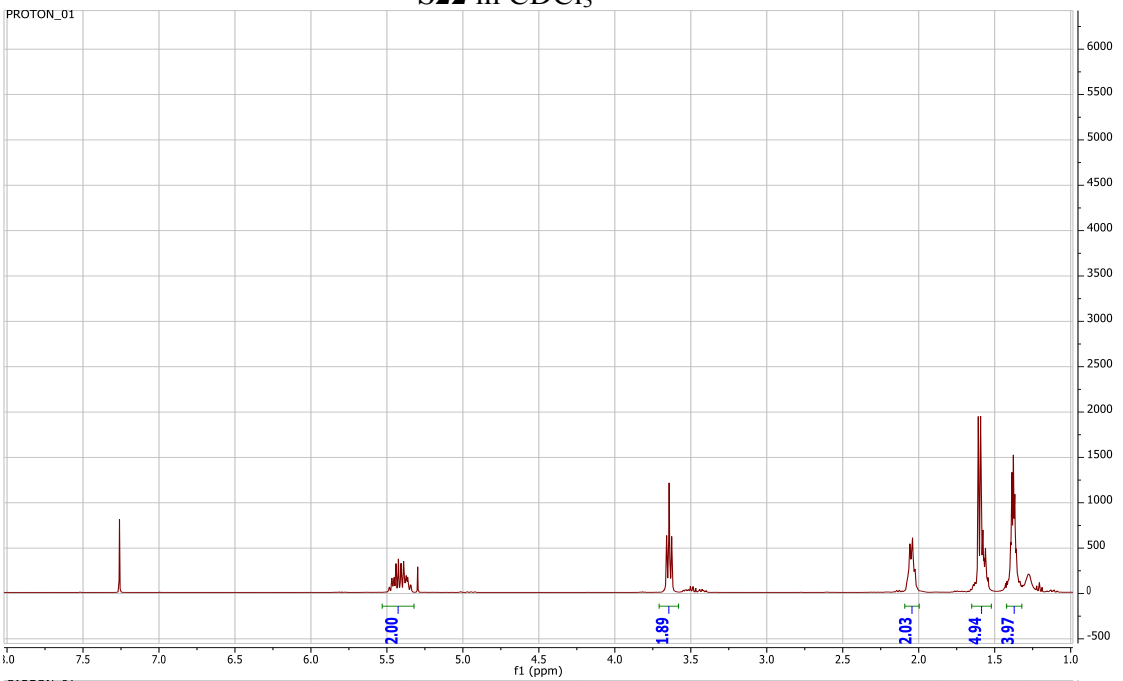
S21 in $CDCl_3$

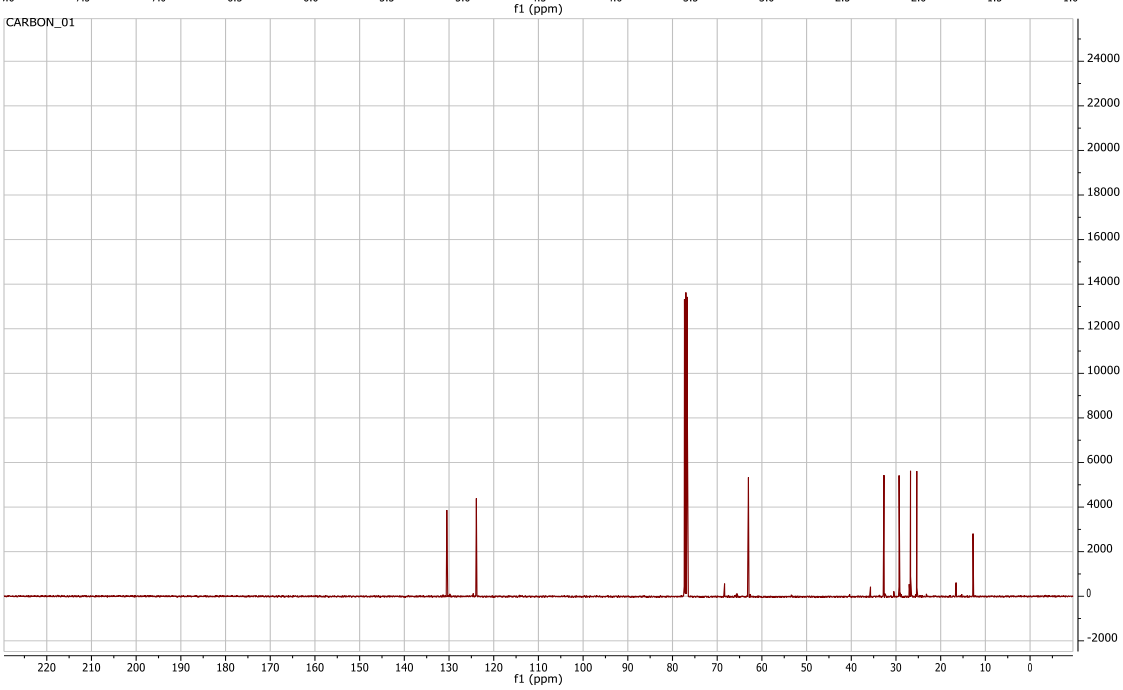

PROTON_01
1.00
1.05
3.14
2.14
2.12
5.23
2.33
f1 (ppm)

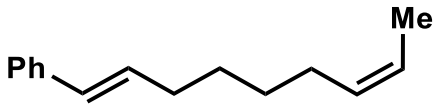

CARBON_01
f1 (ppm)



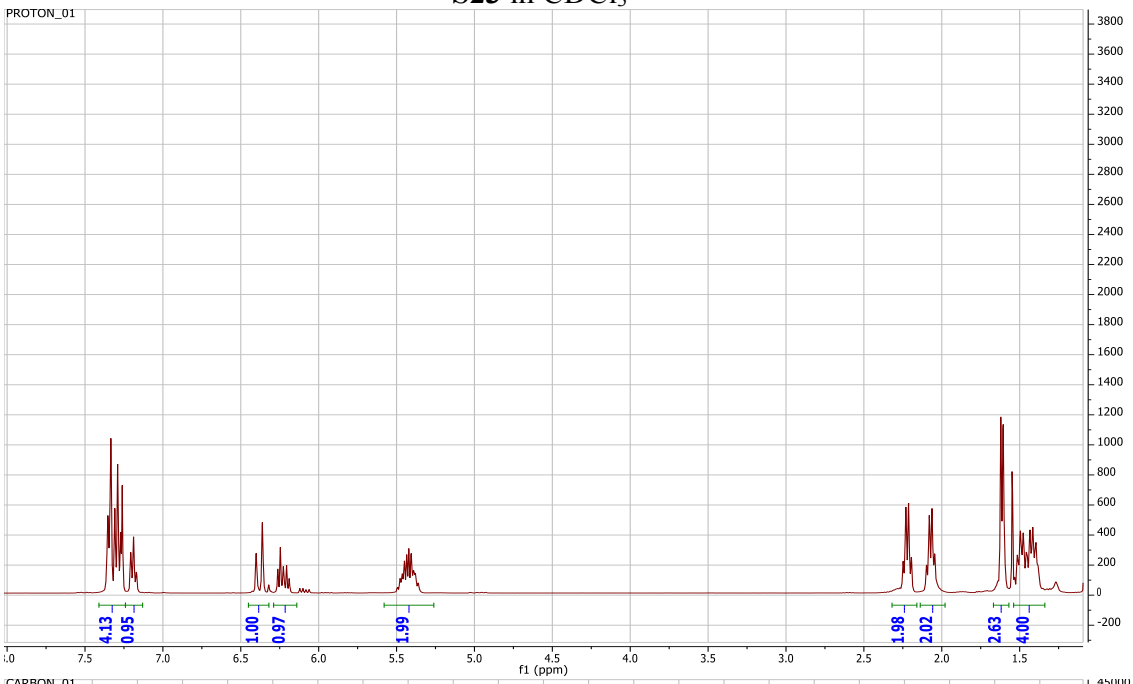
S22 in $CDCl_3$

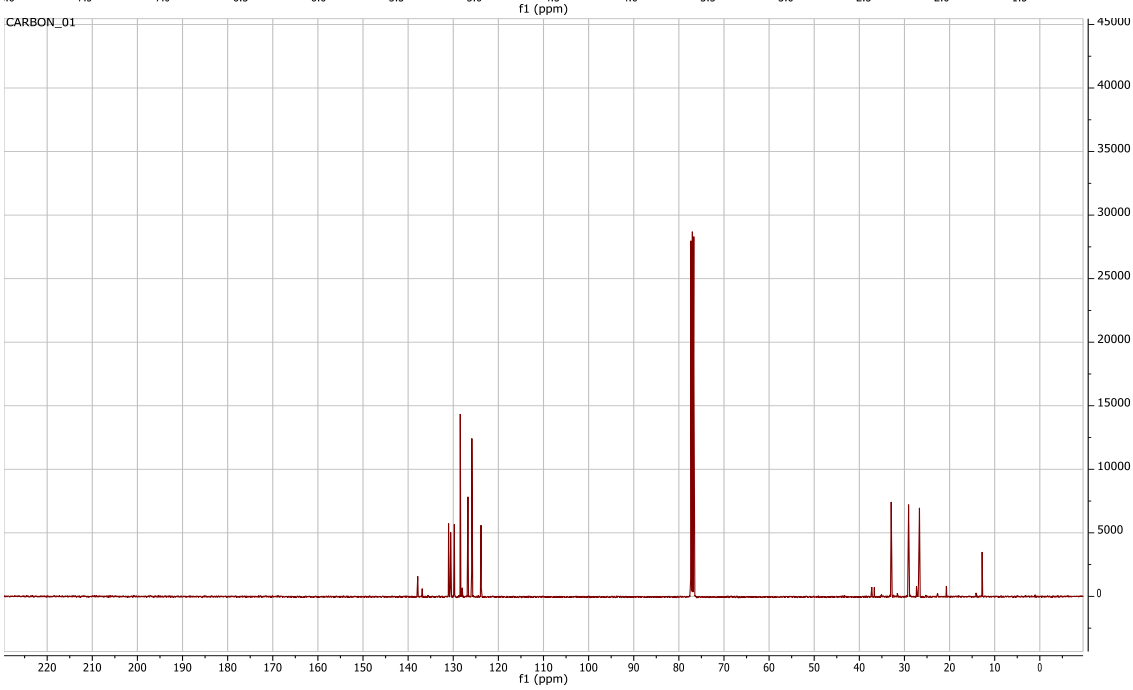


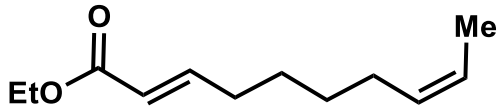



Me
Ph

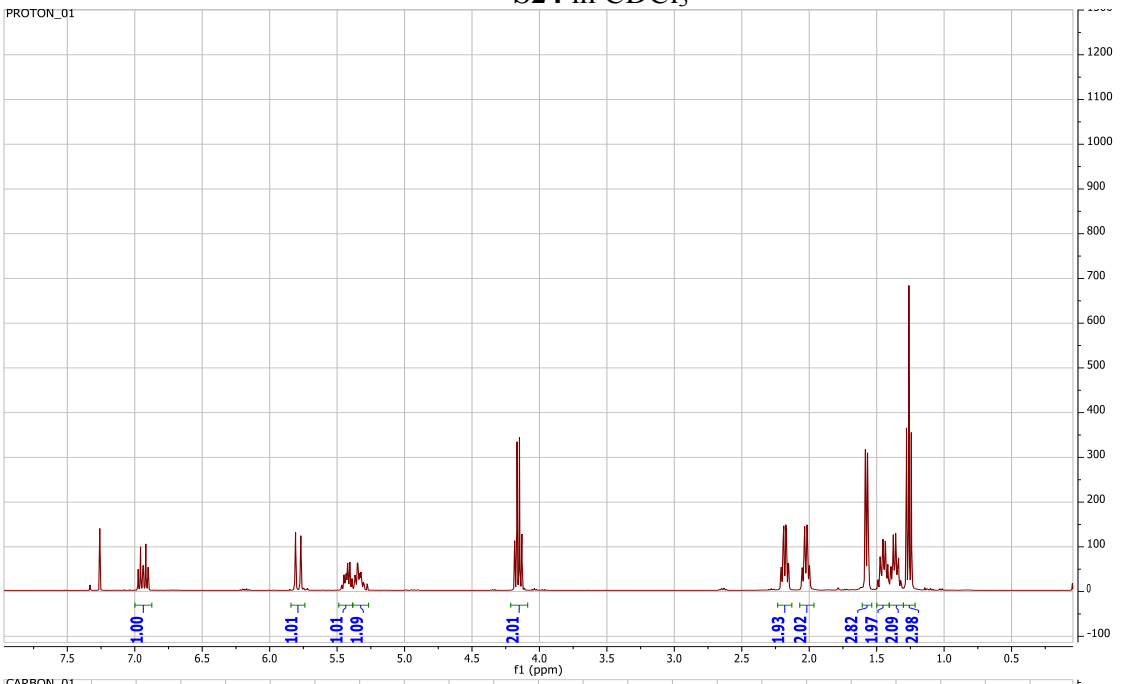
S23 in $CDCl_3$

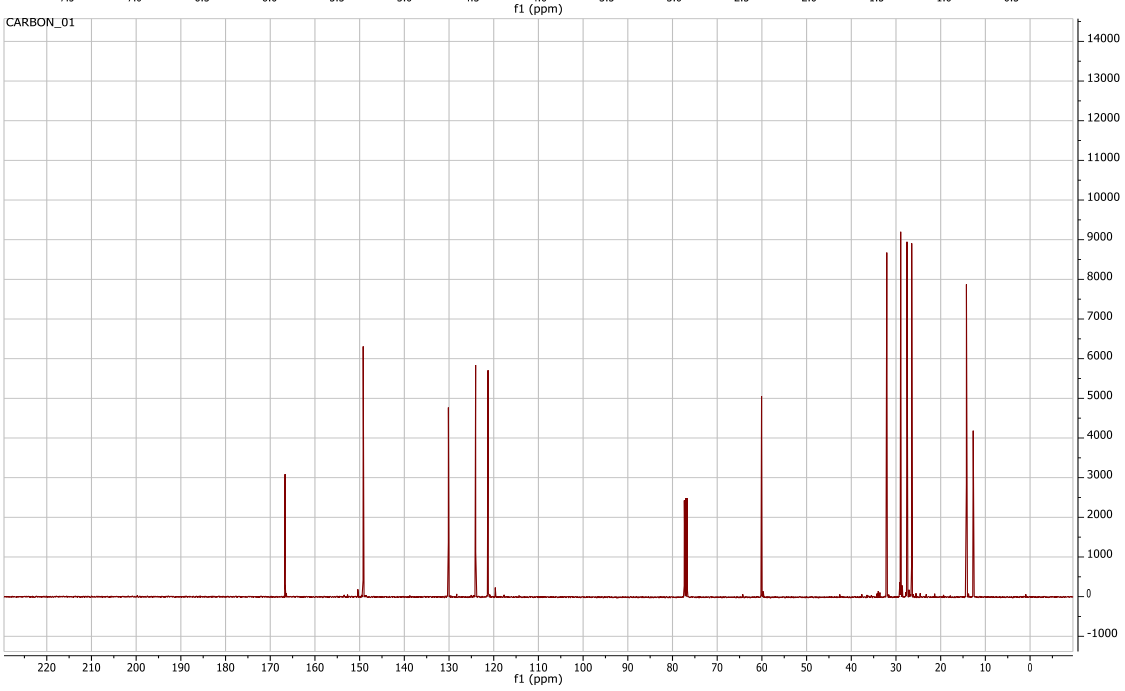

PROTON_01
4.13
0.95
1.00
0.97
1.99
1.98
2.02
2.63
4.00
f1 (ppm)

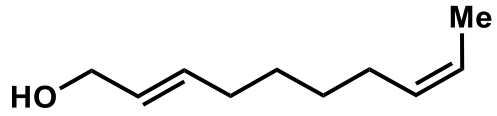

CARBON_01
f1 (ppm)


O
EtO
Me

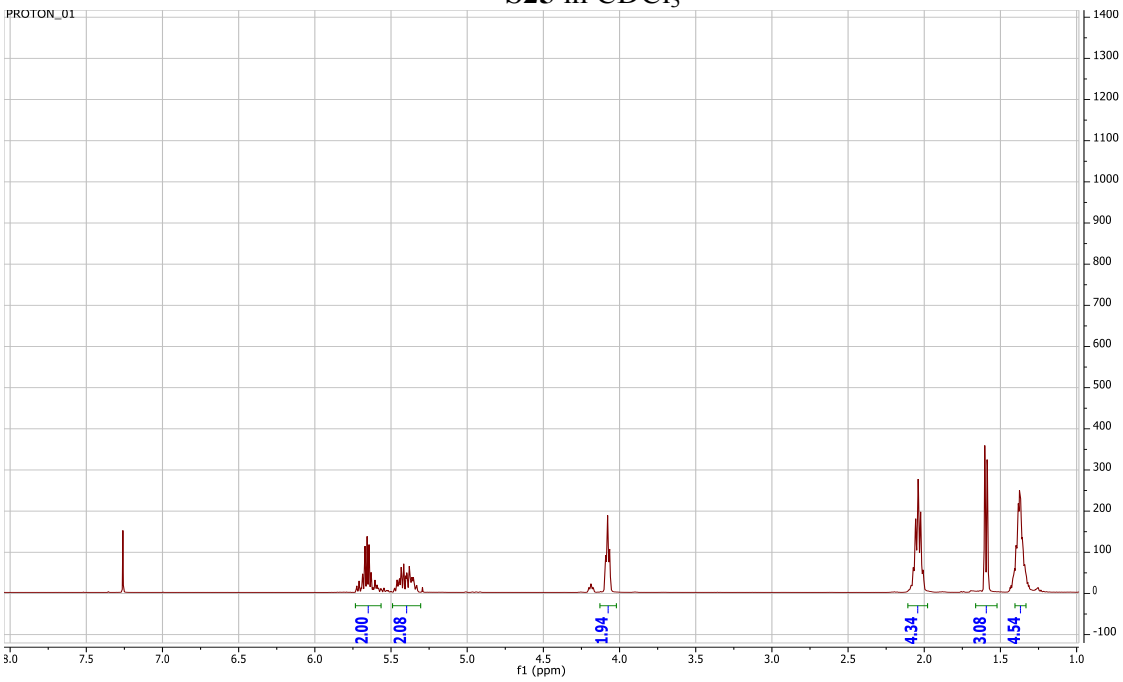
S24 in $CDCl_3$

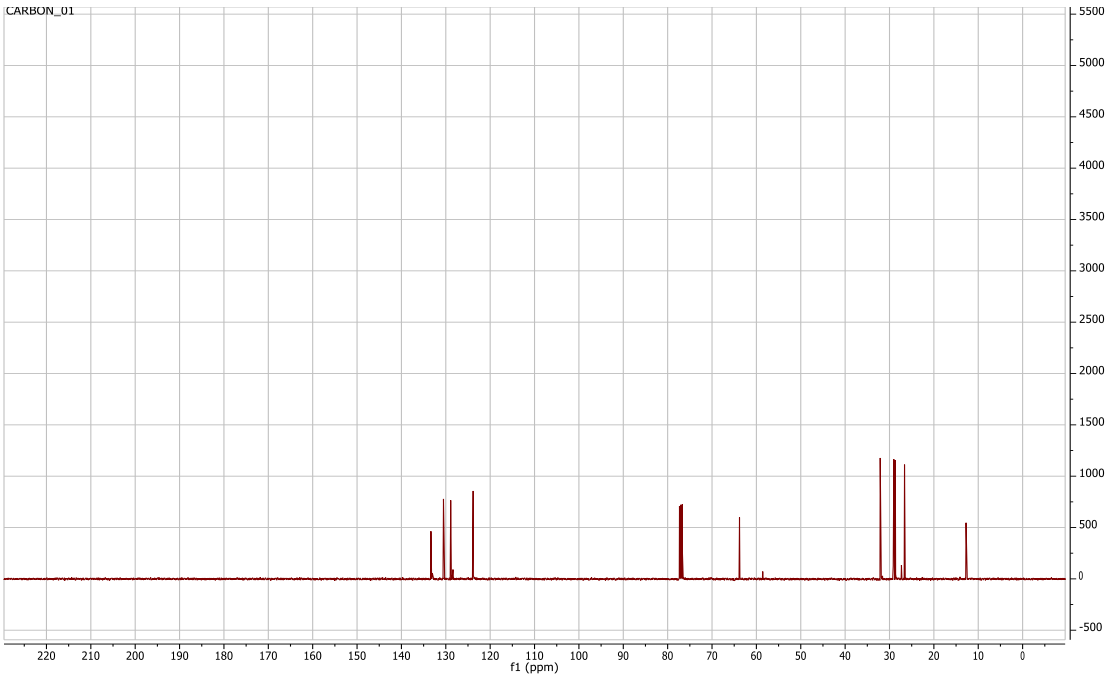

PROTON_01
1.00
1.01
1.01
1.09
2.01
1.93
2.02
2.82
1.97
2.09
2.98
f1 (ppm)

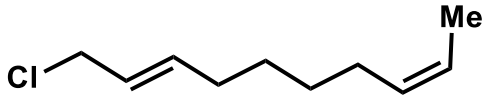

CARBON_01
f1 (ppm)



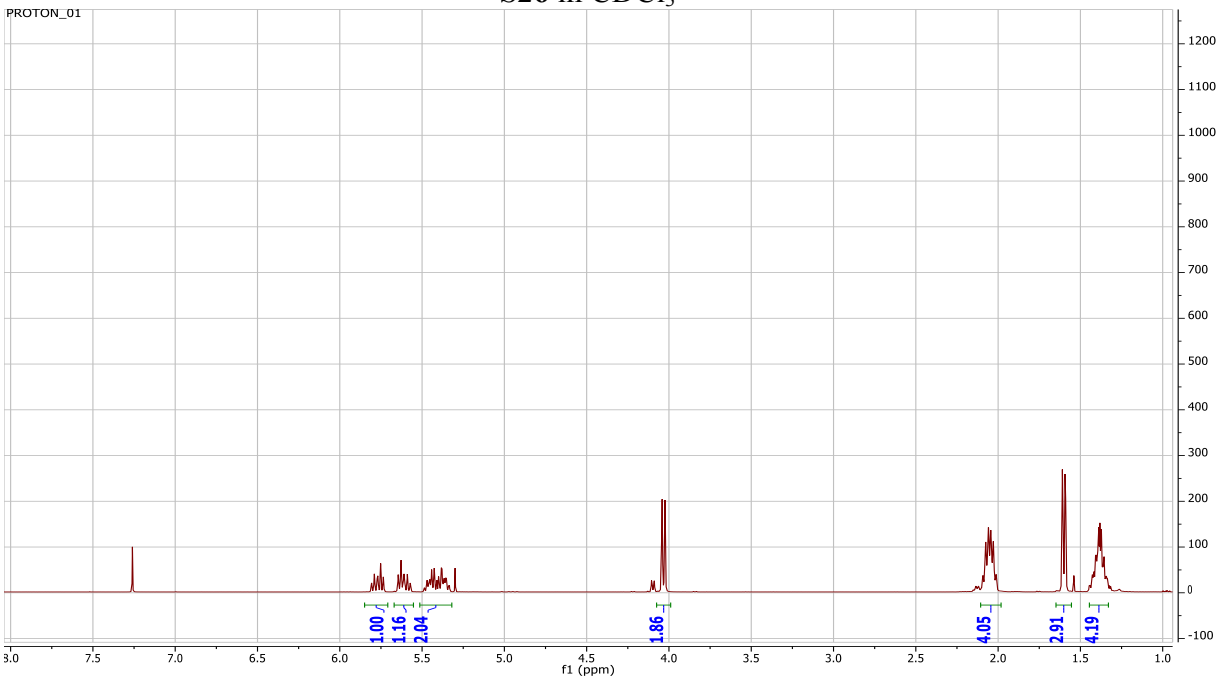
S25 in $CDCl_3$

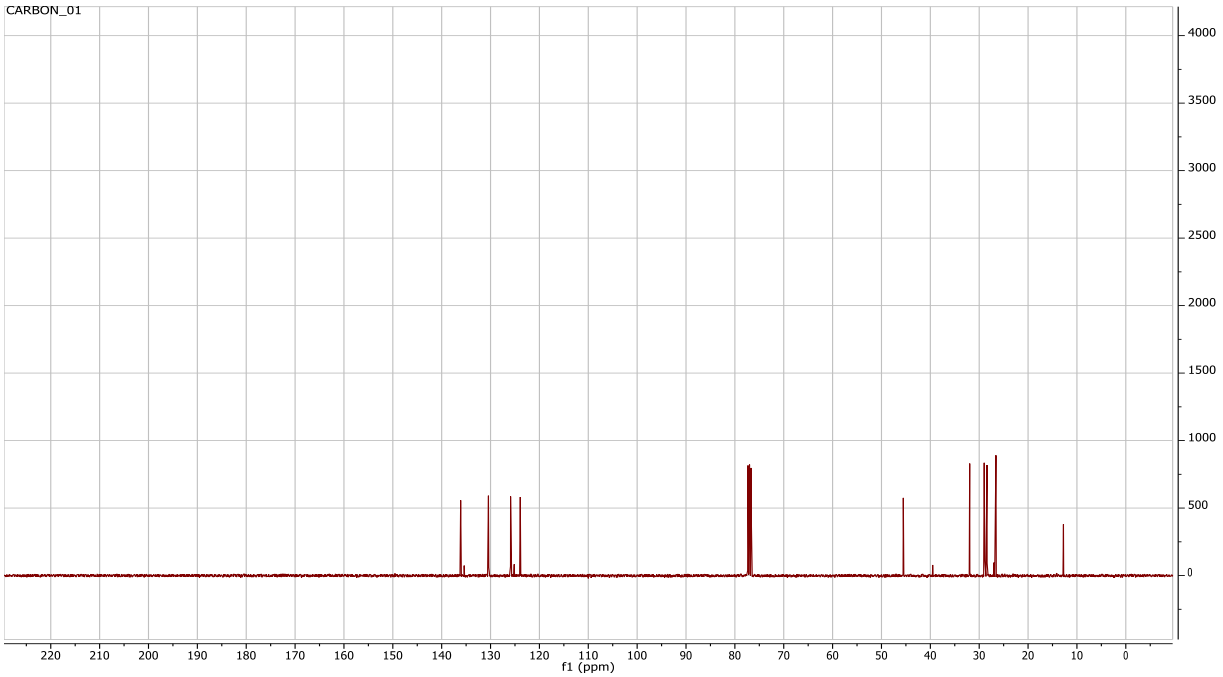


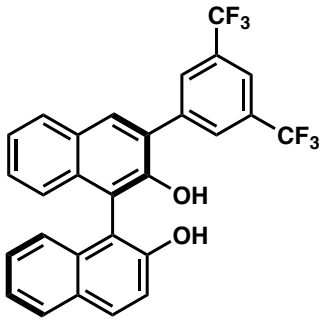



Me
Cl

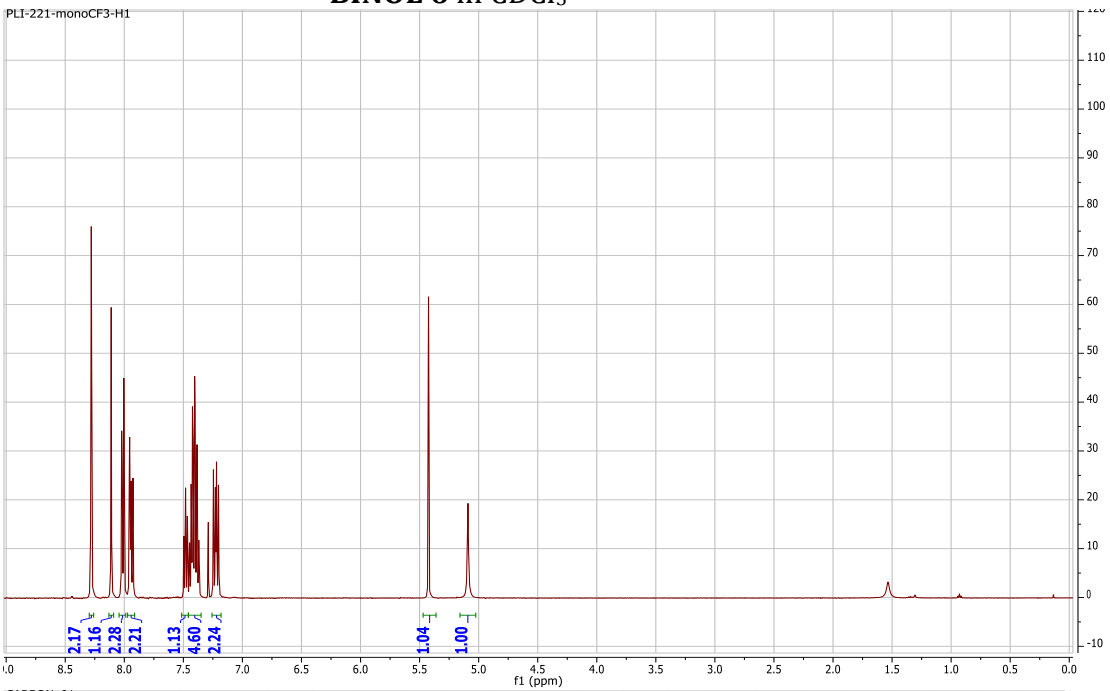
S26 in $CDCl_3$

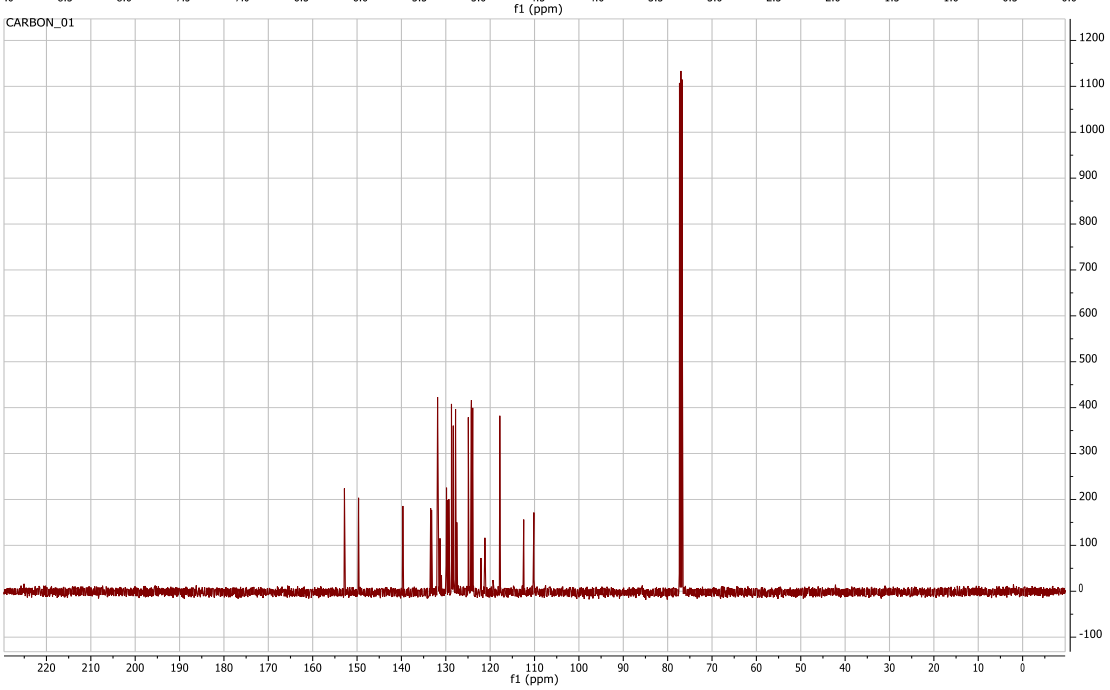

PROTON_01
1.00
1.16
2.04
1.86
4.05
2.91
4.19
f1 (ppm)

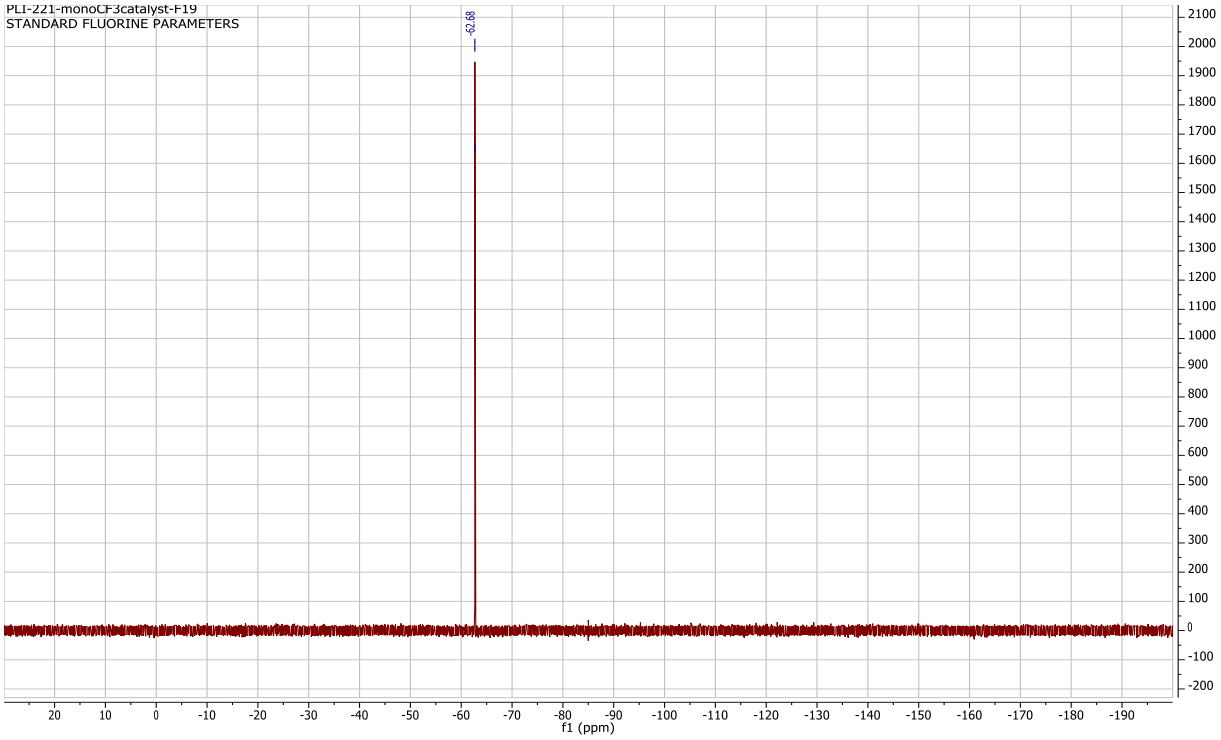

CARBON_01
f1 (ppm)

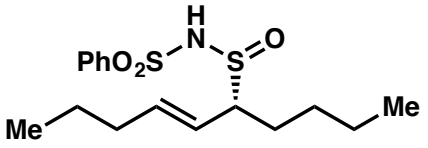


BINOL 6 in $CDCl_3$

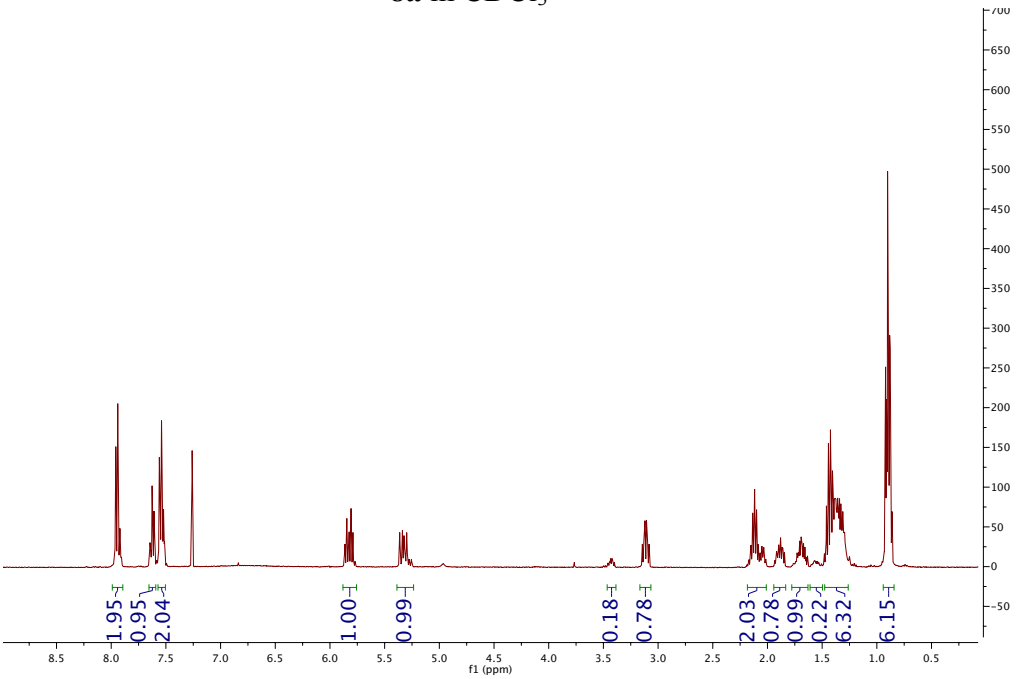


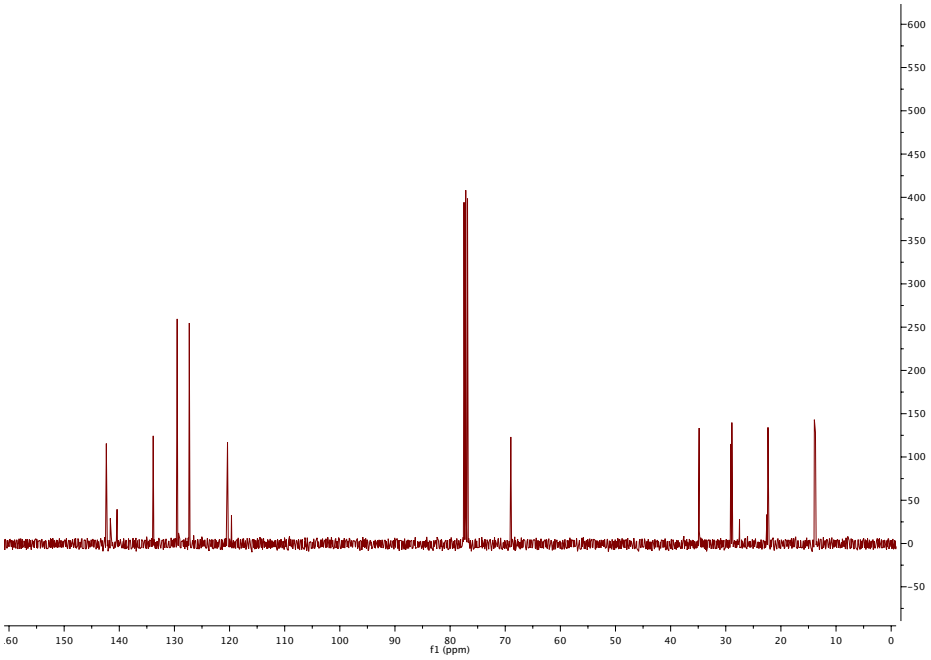


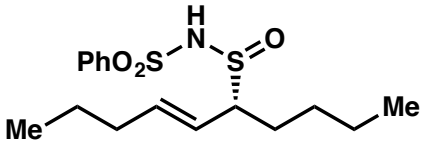

PLI-221-monoCF3catalyst-F19
STANDARD FLUORINE PARAMETERS
-62.68
f1 (ppm)


H
N
PhO2S
S
O
Me
Me

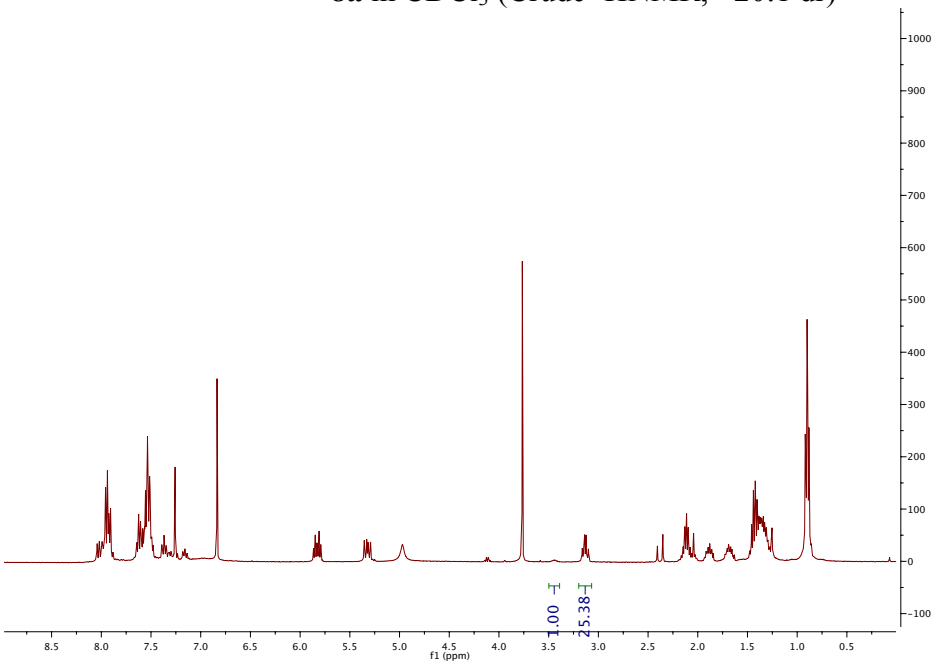
8a in $CDCl_3$


1.95
0.95
2.04
1.00
0.99
0.18
0.78
2.03
0.78
0.99
0.22
6.32
6.15
f1 (ppm)

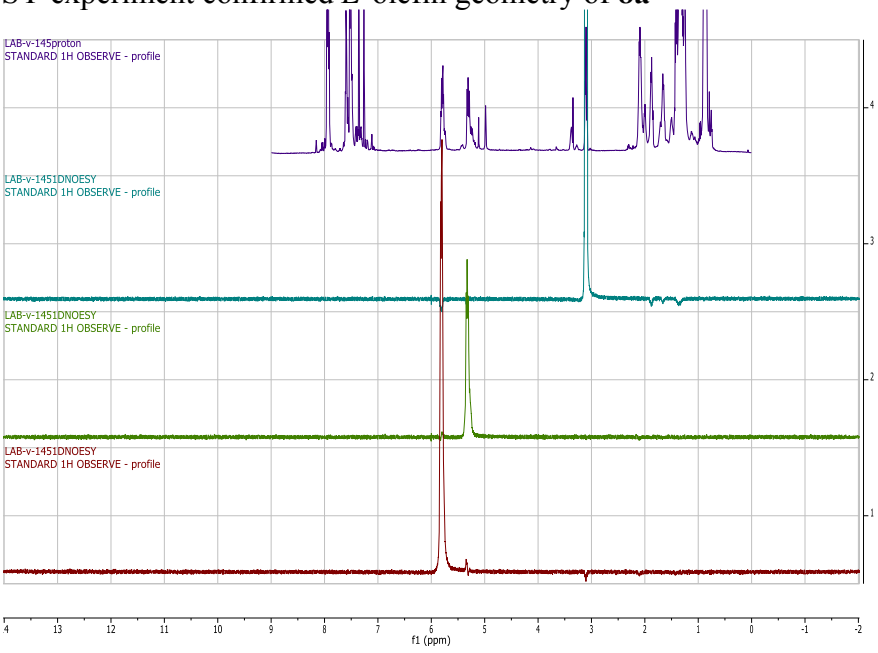

f1 (ppm)

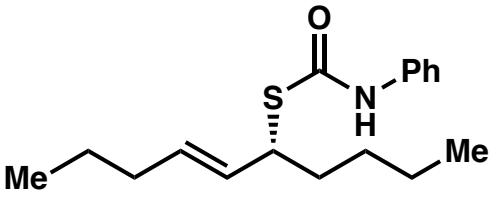


8a in $CDCl_3$ (Crude ^{1}HNMR, >20:1 dr)

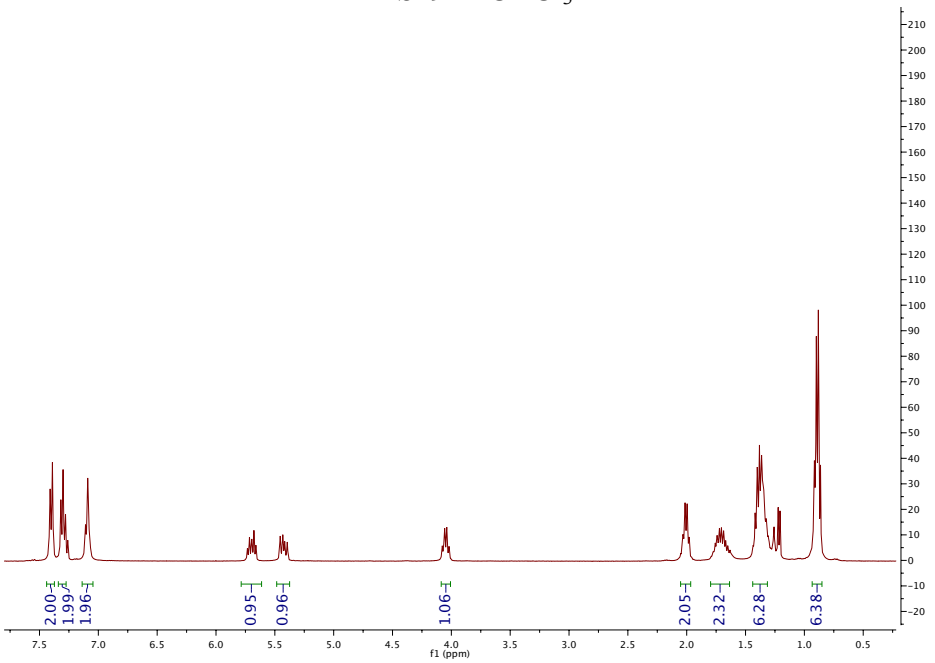


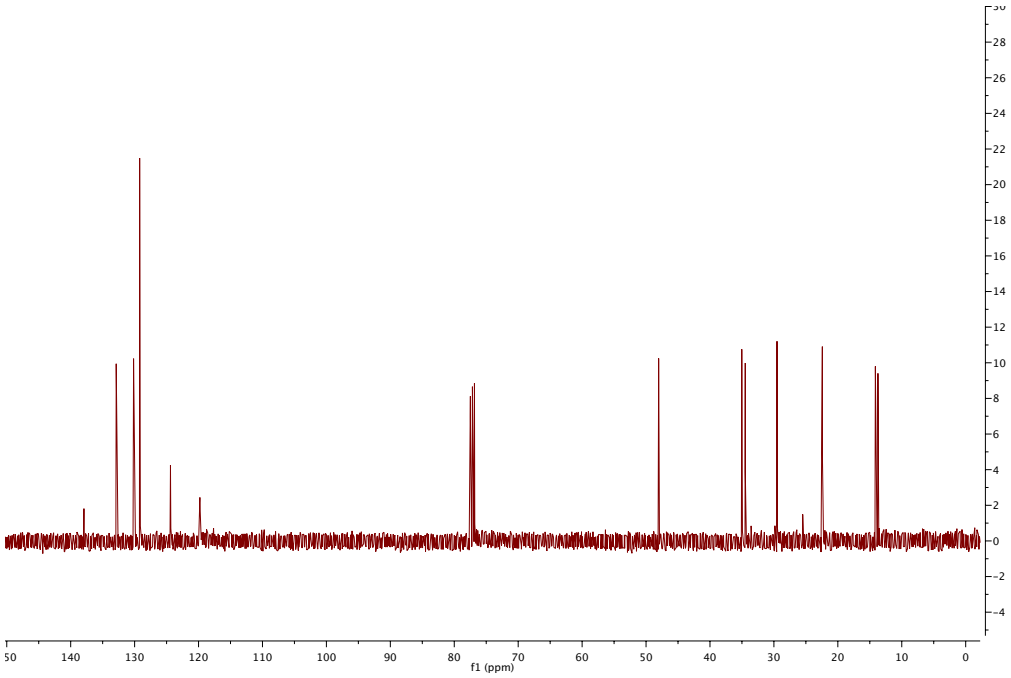
1D-NOESY experiment confirmed *E*-olefin geometry of **8a**

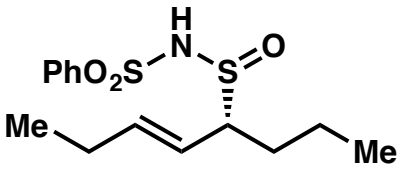



O
Ph
S
N
H
Me
Me

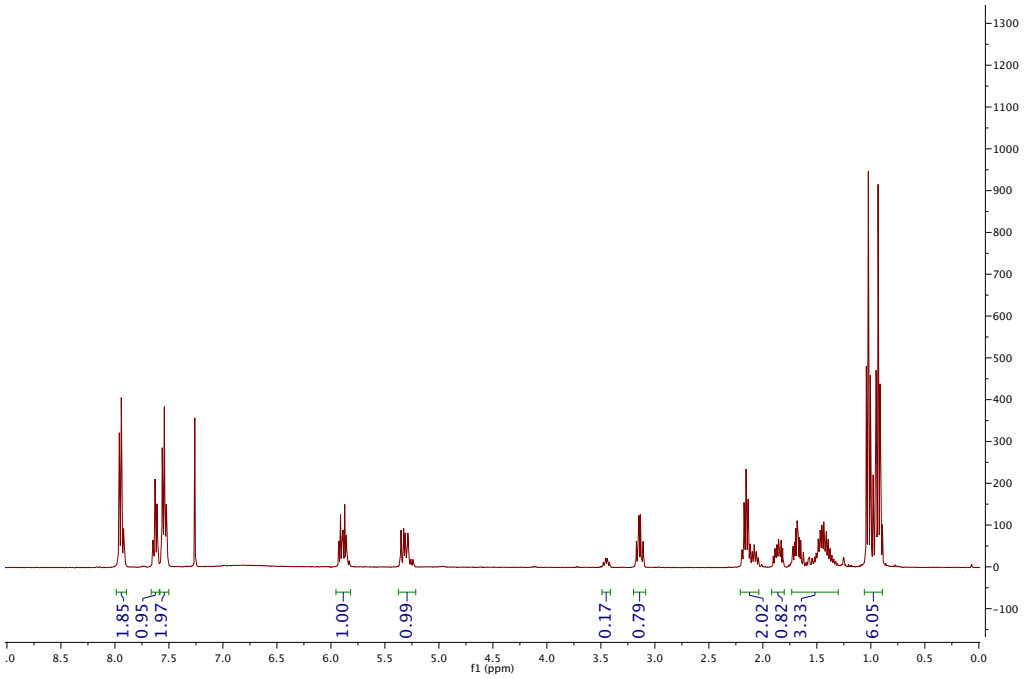
S29 in $CDCl_3$

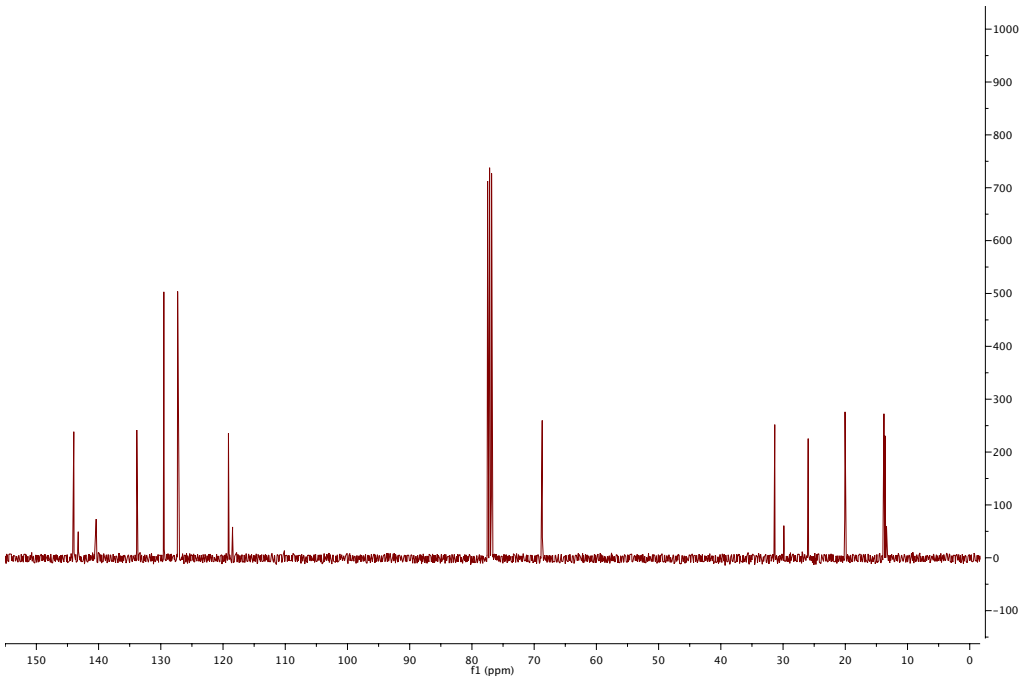

2.00
1.99
1.96
0.95
0.96
1.06
2.05
2.32
6.28
6.38
f1 (ppm)

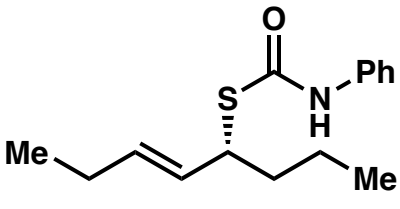

f1 (ppm)


H
N
PhO2S
S
O
Me
Me

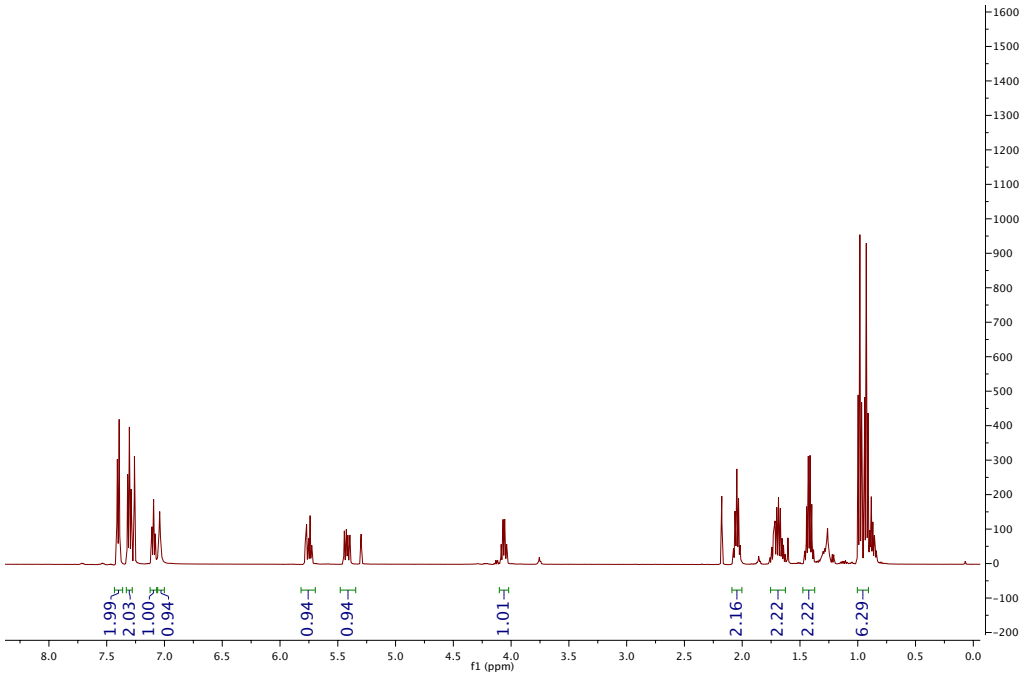
8b in $CDCl_3$

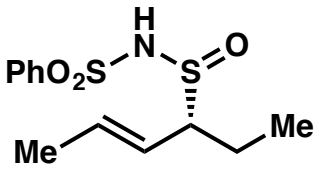

1.85
0.95
1.97
1.00
0.99
0.17
0.79
2.02
0.82
3.33
6.05
f1 (ppm)


f1 (ppm)

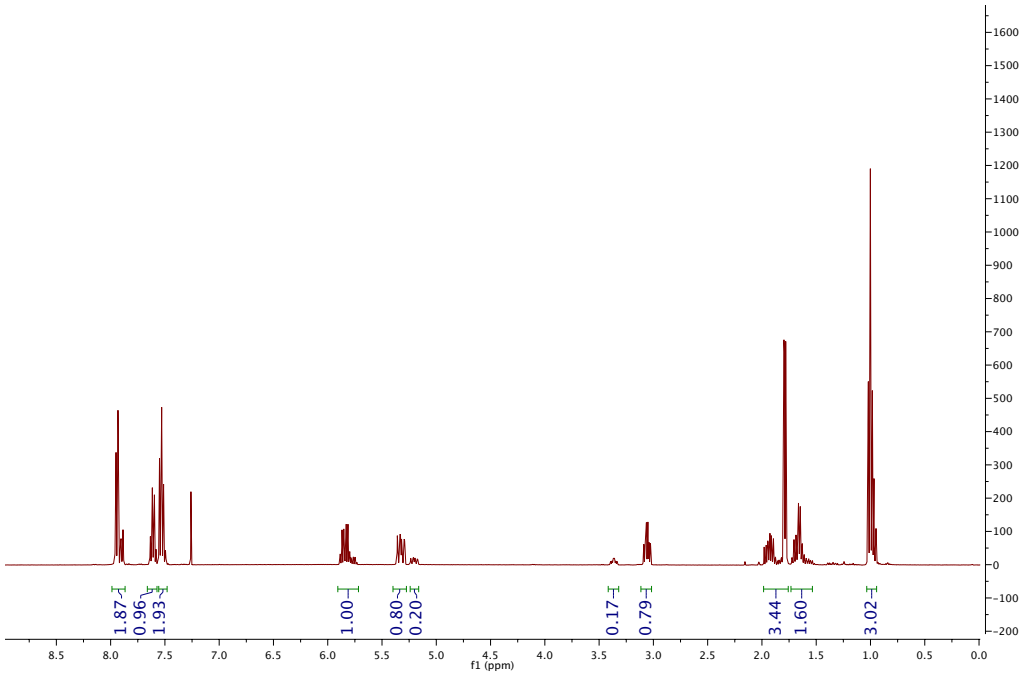


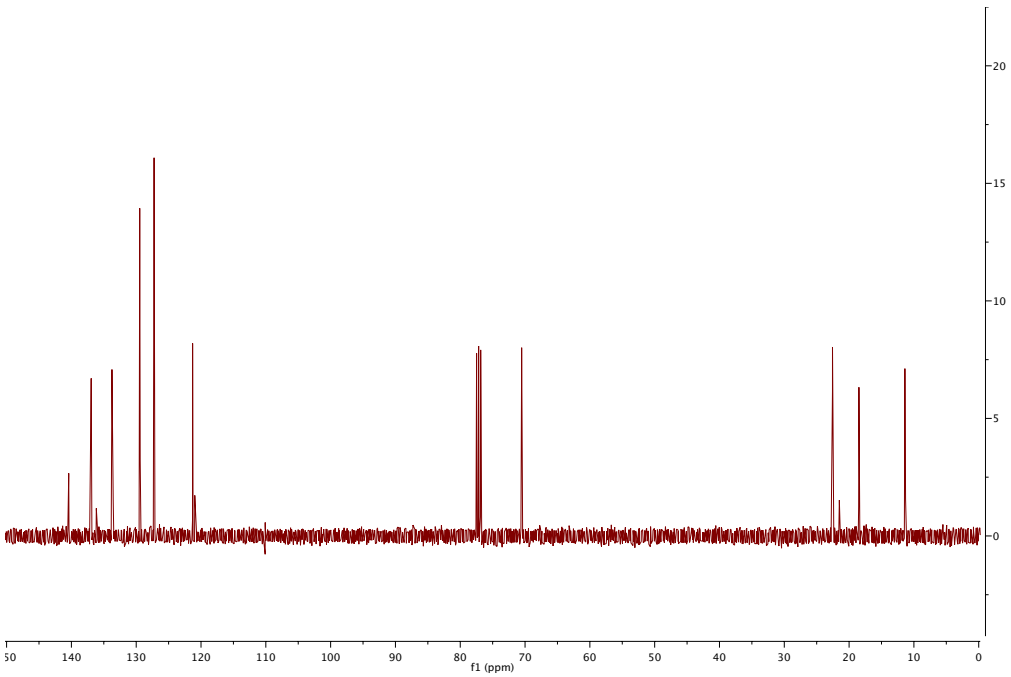
S30 in $CDCl_3$

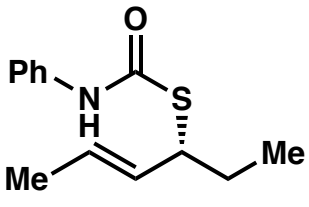



H
N
PhO2S
S
O
Me
Me

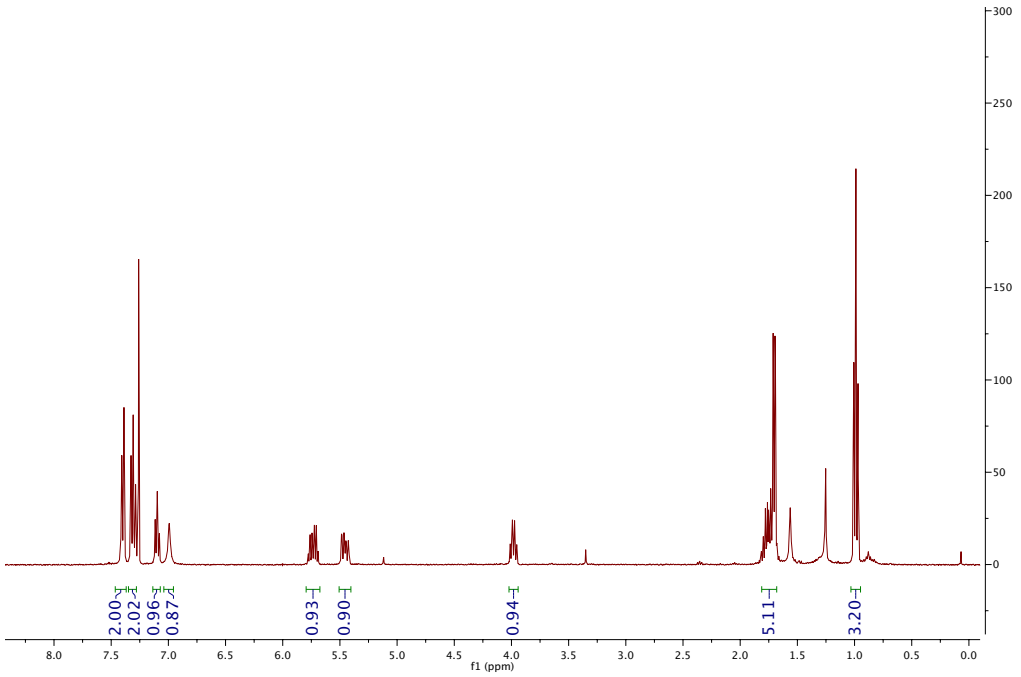
8c in $CDCl_3$

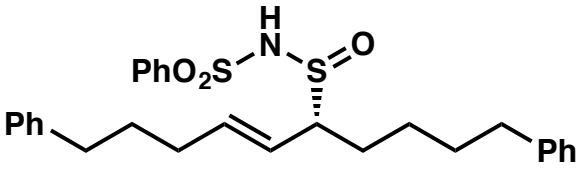

1.87
0.96
1.93
1.00
0.80
0.20
0.17
0.79
3.44
1.60
3.02
f1 (ppm)


f1 (ppm)

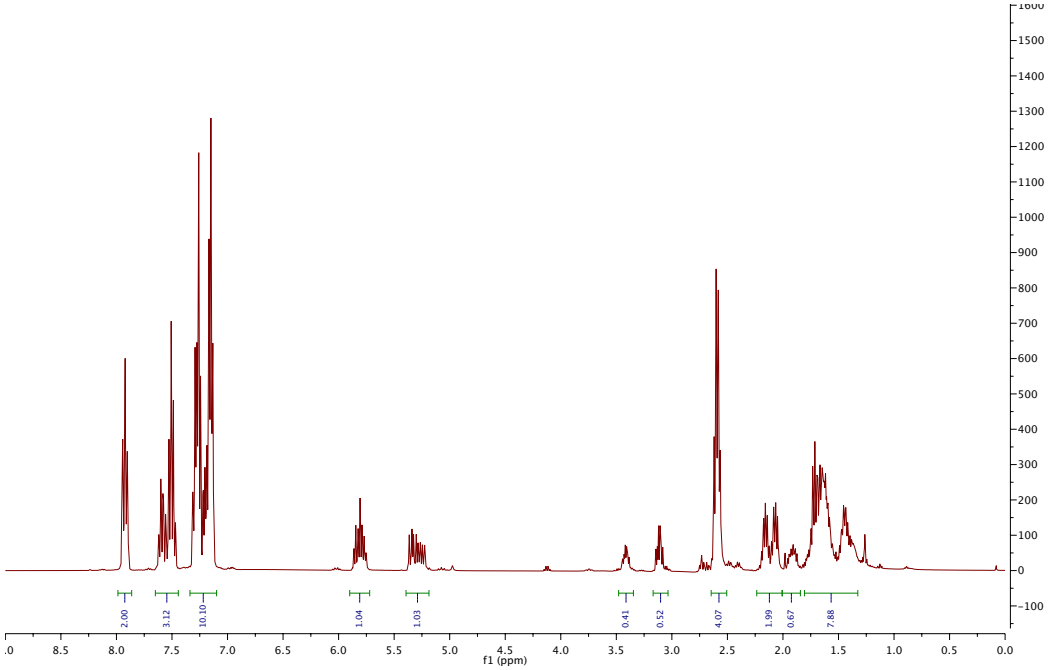


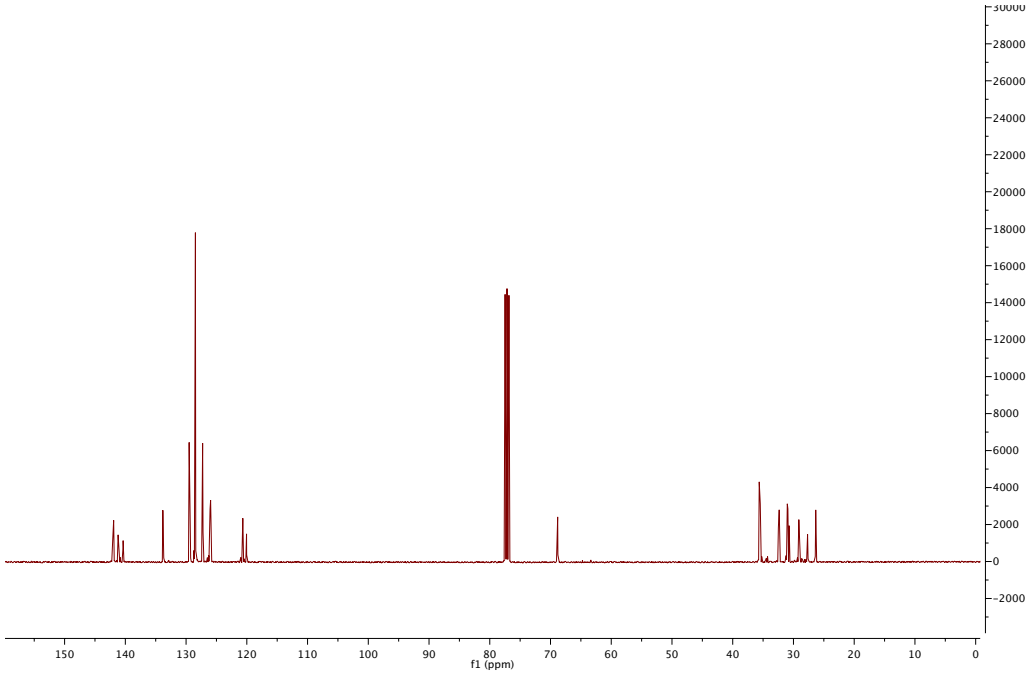
S31 in $CDCl_3$

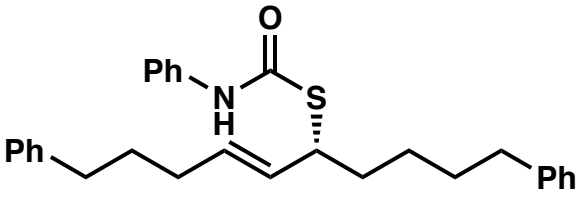



H
N
PhO2S
S
O
Ph
Ph

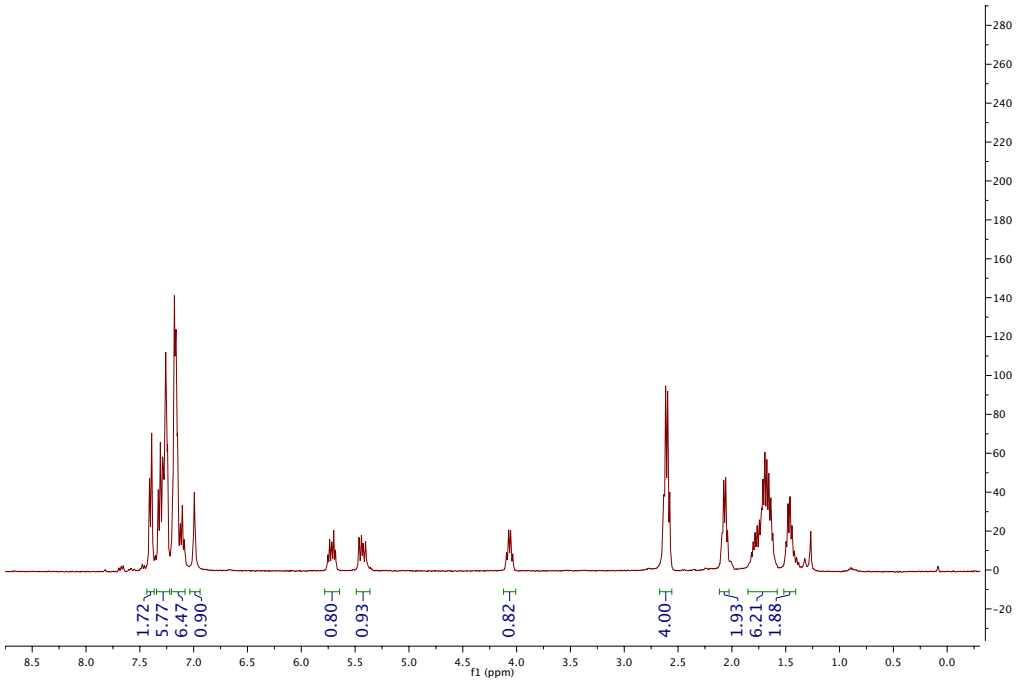
8d in $CDCl_3$

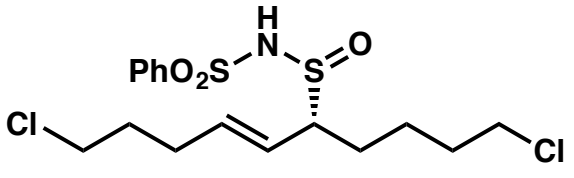

2.00
3.12
10.10
1.04
1.03
0.41
0.52
4.07
1.99
0.67
7.88
f1 (ppm)


f1 (ppm)

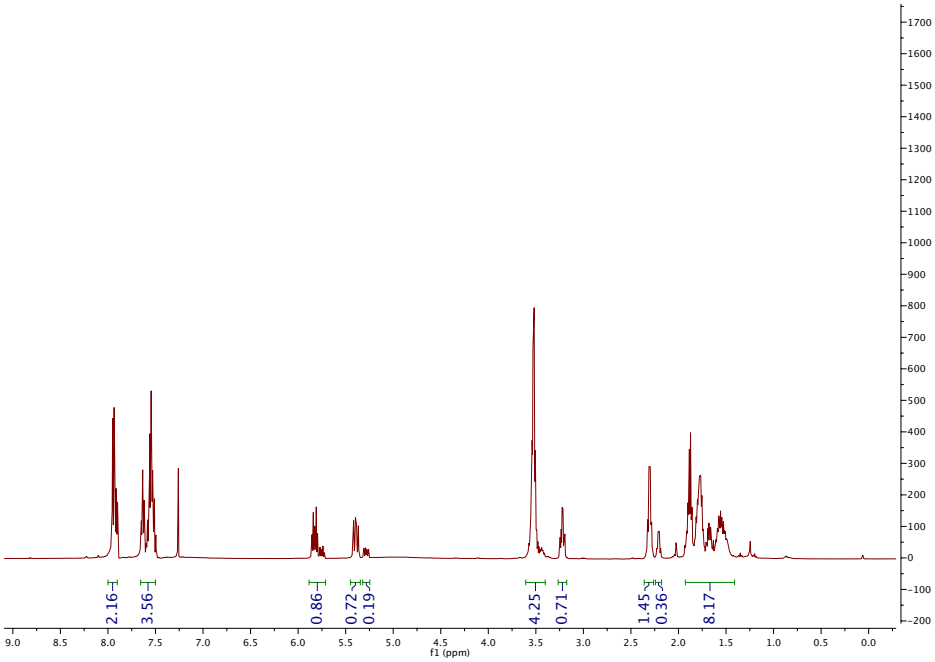


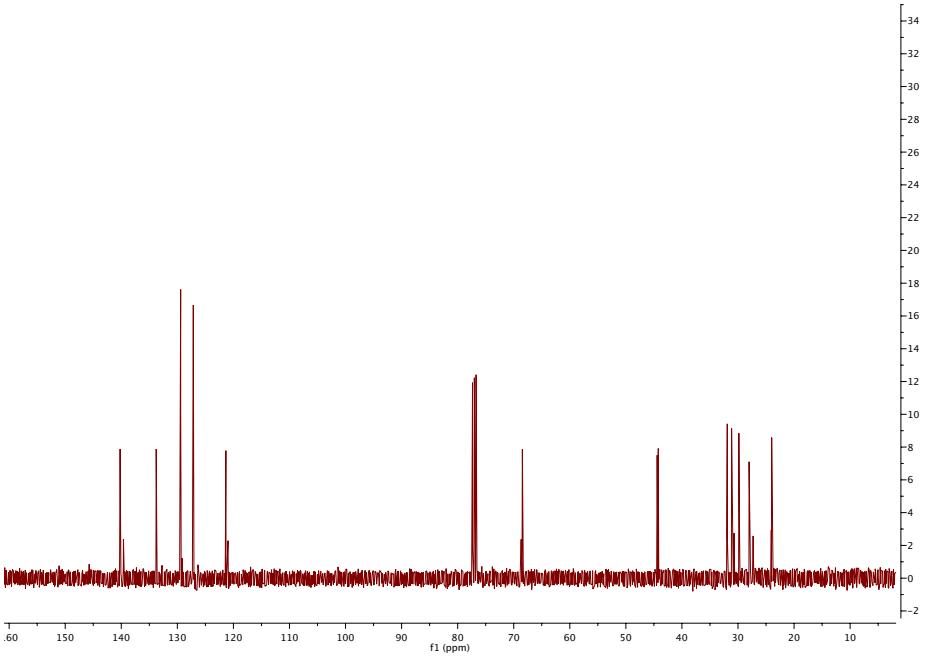
S32 in $CDCl_3$

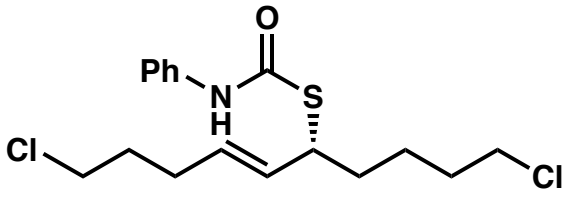



H
N
O
PhO2S
S
Cl
Cl

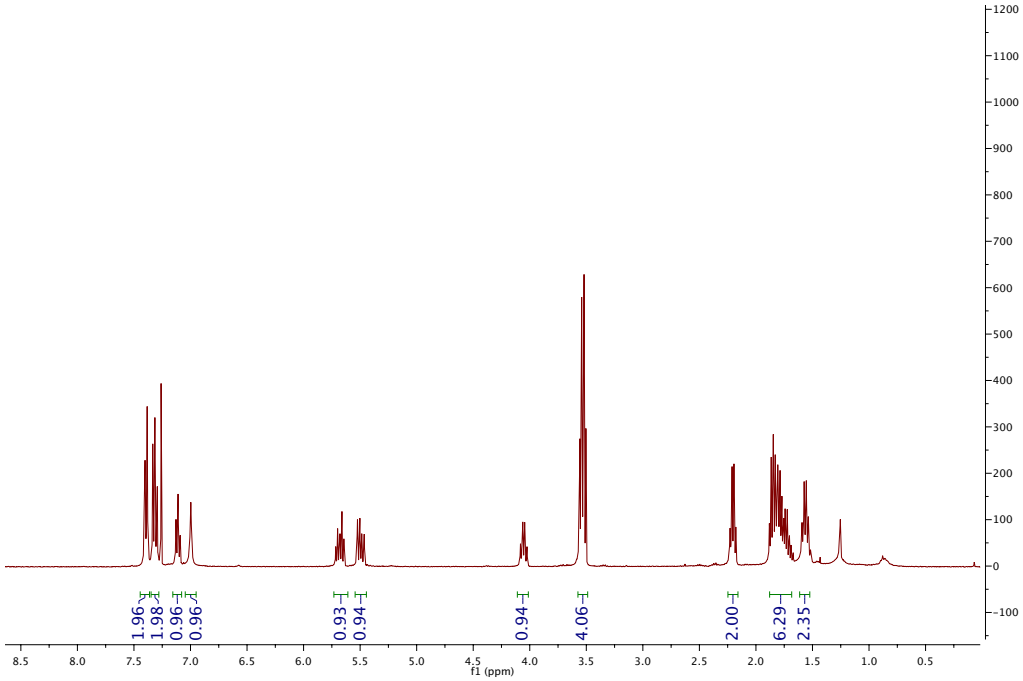
8e in $CDCl_3$

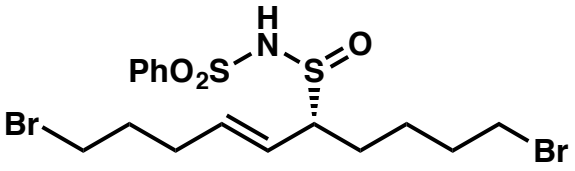

2.16
3.56
0.86
0.72
0.19
4.25
0.71
1.45
0.36
8.17
f1 (ppm)


f1 (ppm)

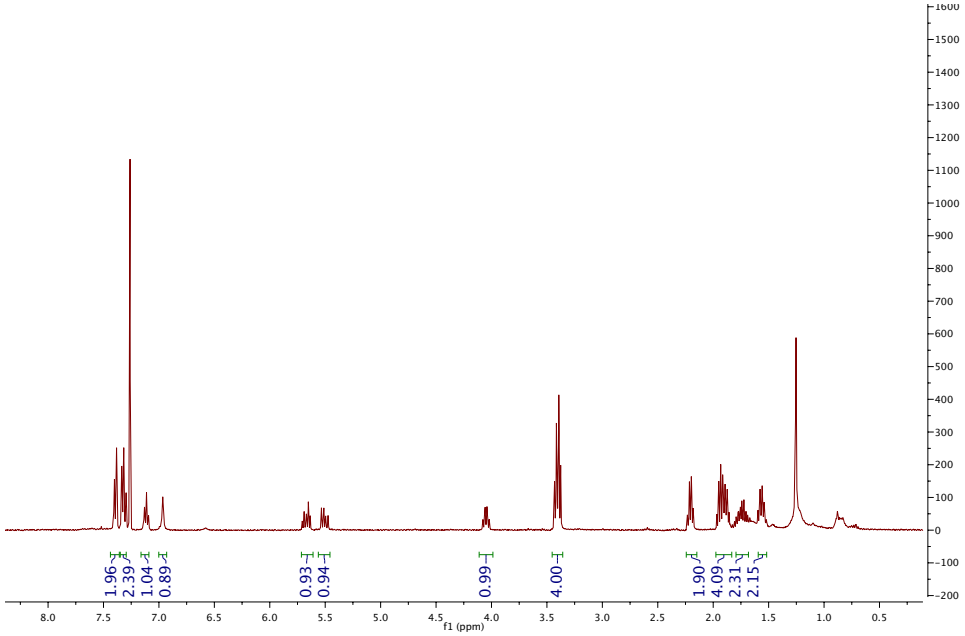


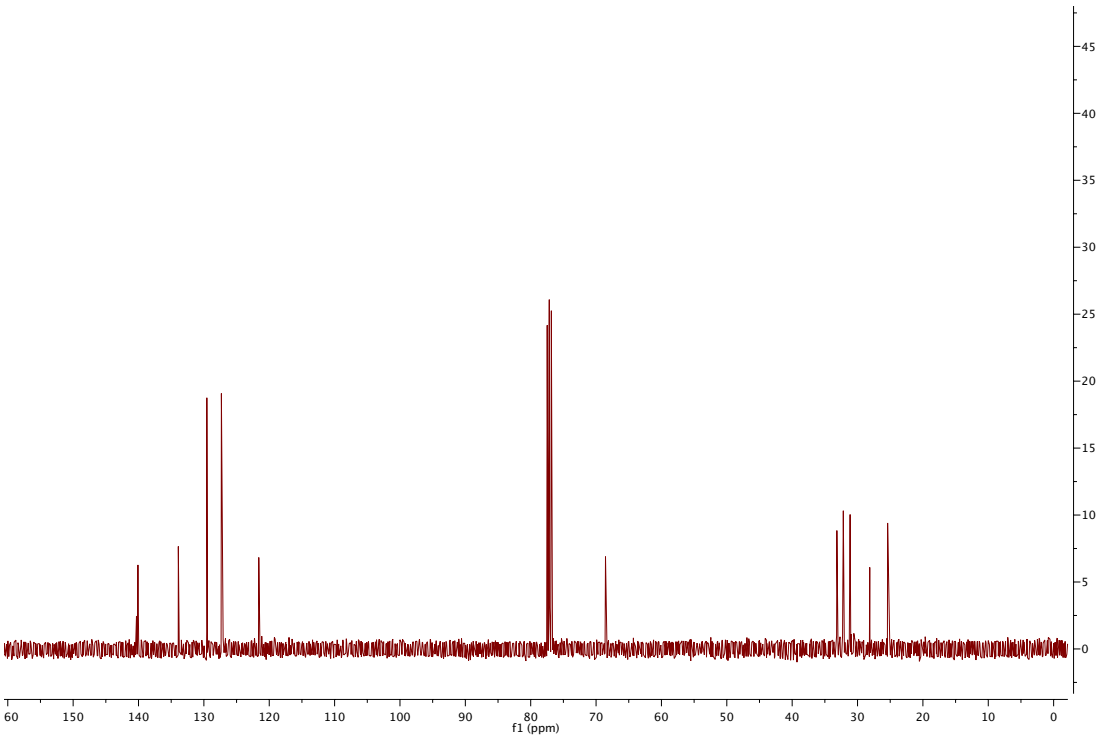
S33 in $CDCl_3$

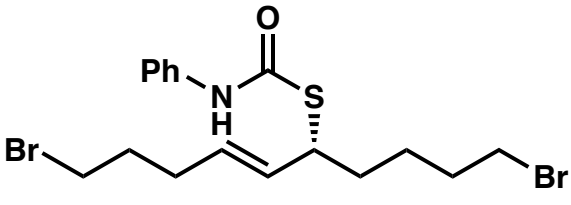



H
N
PhO2S
S
O
Br
Br

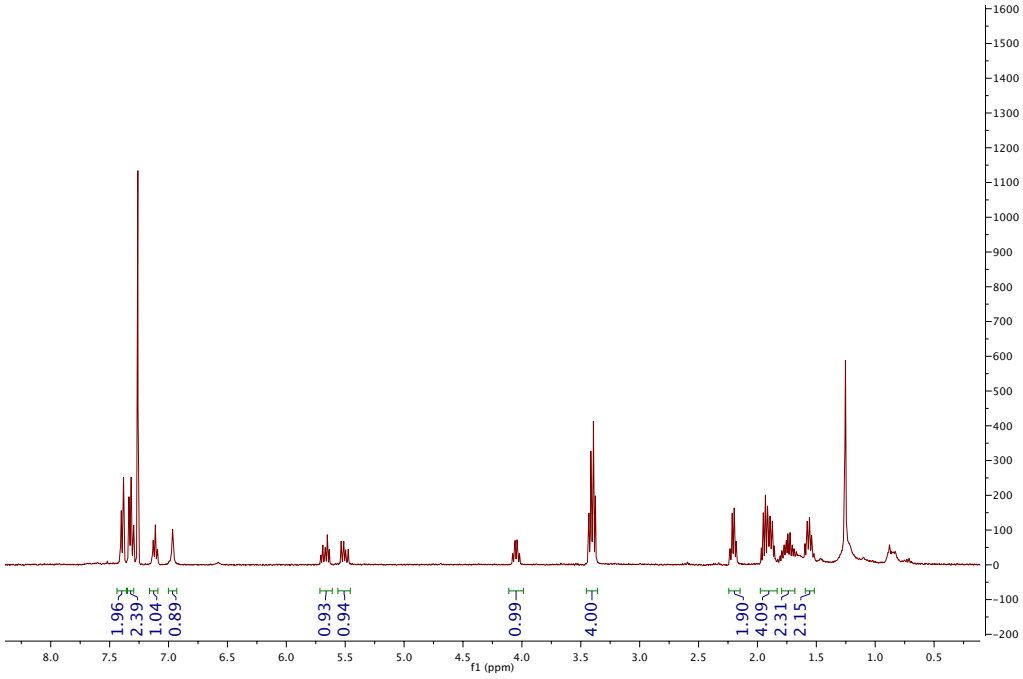
8f in $CDCl_3$

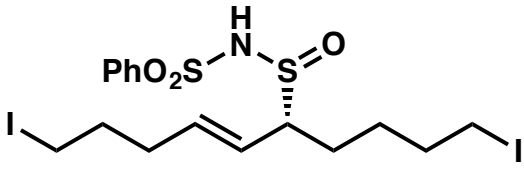

1.96
2.39
1.04
0.89
0.93
0.94
0.99
4.00
1.90
4.09
2.31
2.15
f1 (ppm)


f1 (ppm)

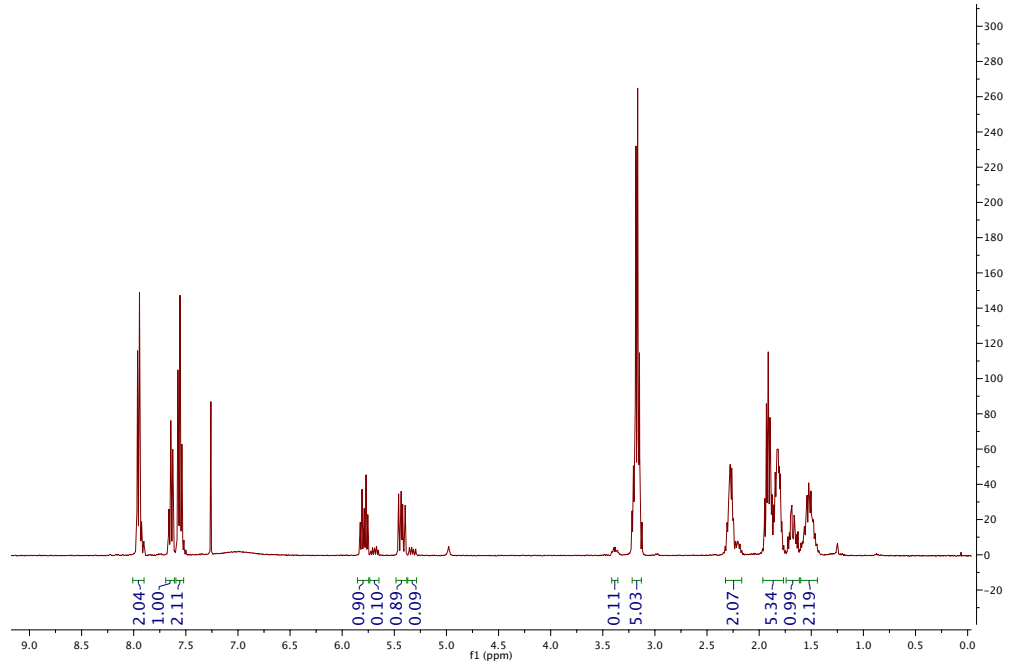

O
Ph
N
H
S
Br
Br

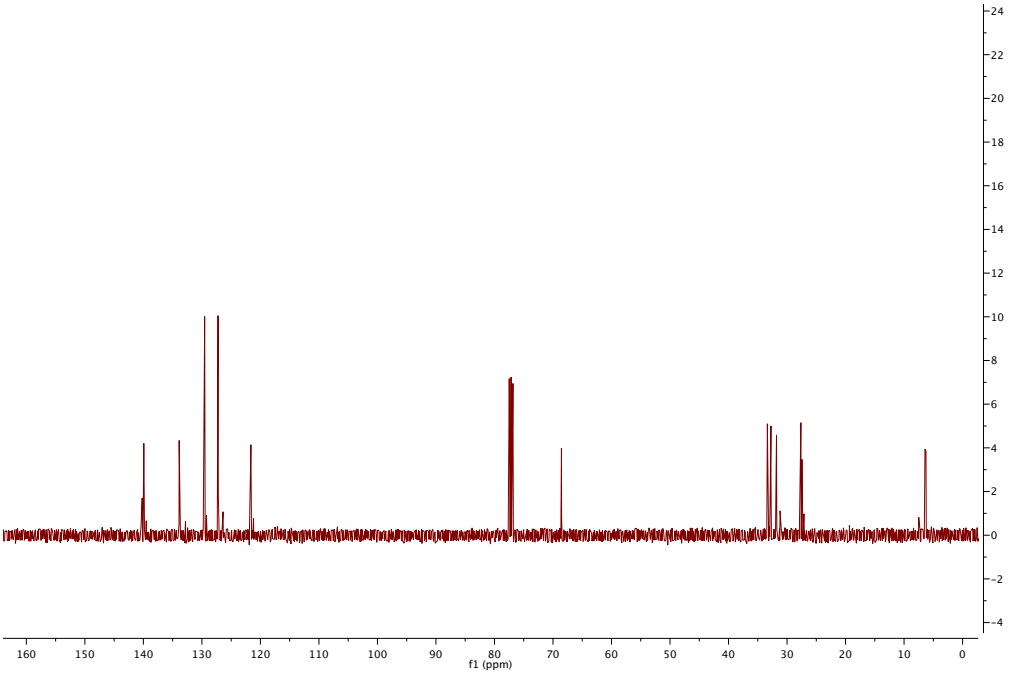
S34 in $CDCl_3$

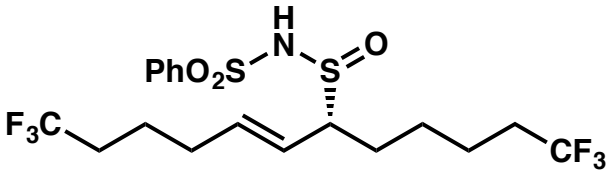

1.96
2.39
1.04
0.89
0.93
0.94
0.99
4.00
1.90
4.09
2.31
2.15
f1 (ppm)


H
N
PhO2S
S
O
I
I

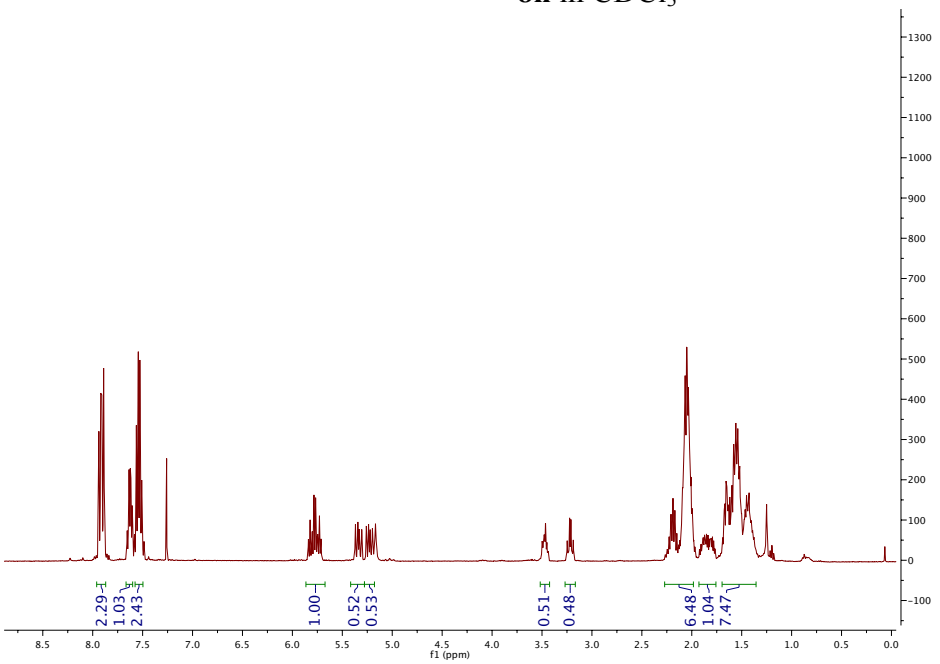
8g in $CDCl_3$

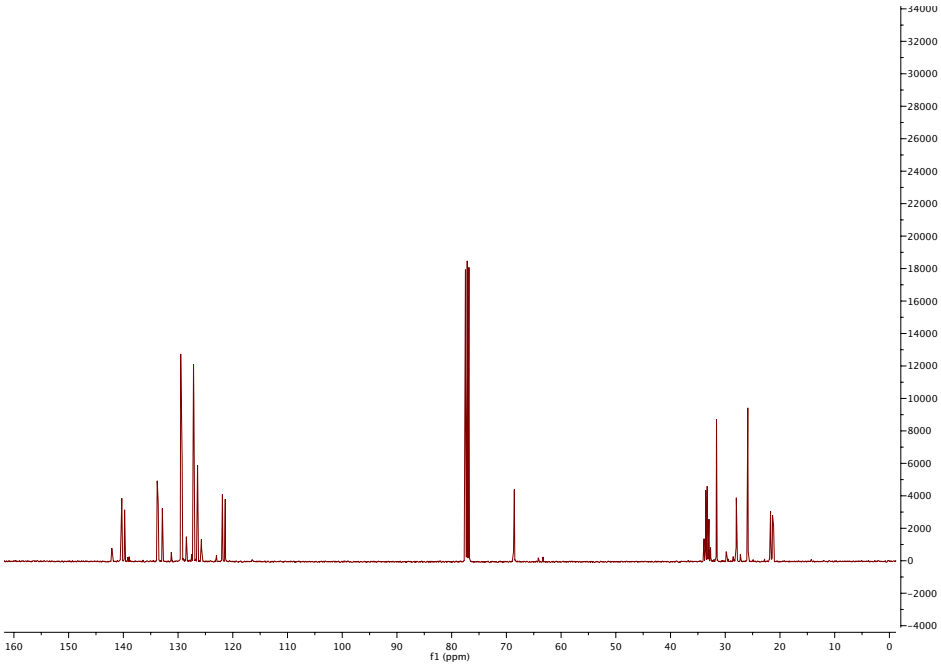

2.04
1.00
2.11
0.90
0.10
0.89
0.09
0.11
5.03
2.07
5.34
0.99
2.19
f1 (ppm)

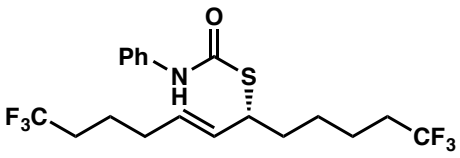

f1 (ppm)


H
N
PhO2S
S
O
F3C
CF3

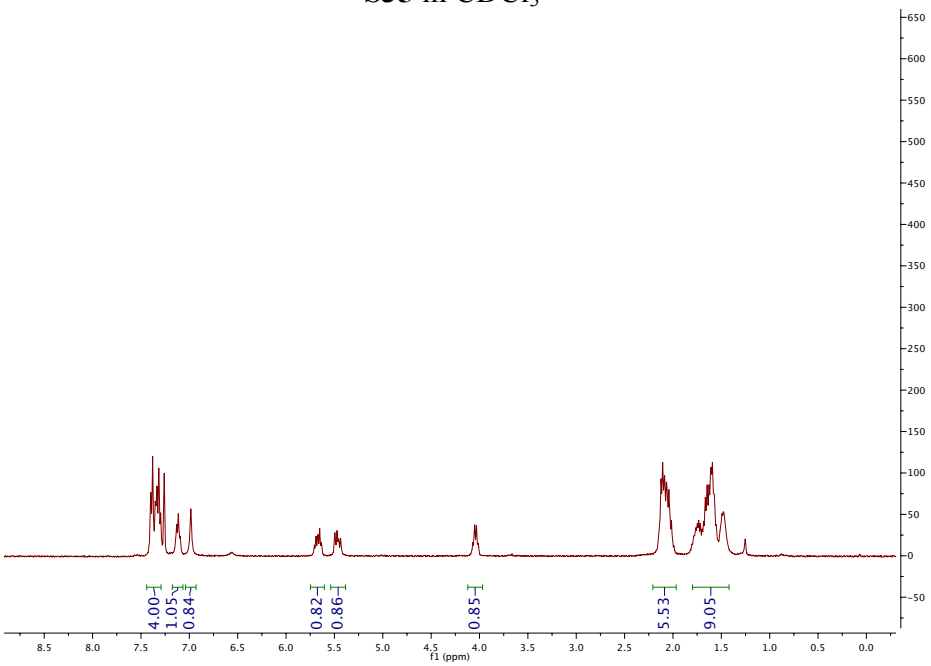
8h in $CDCl_3$

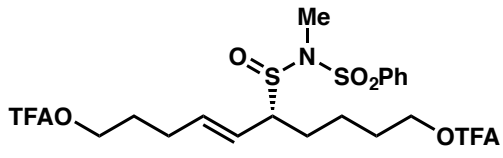

2.29
1.03
2.43
1.00
0.52
0.53
0.51
0.48
6.48
1.04
7.47
f1 (ppm)


f1 (ppm)

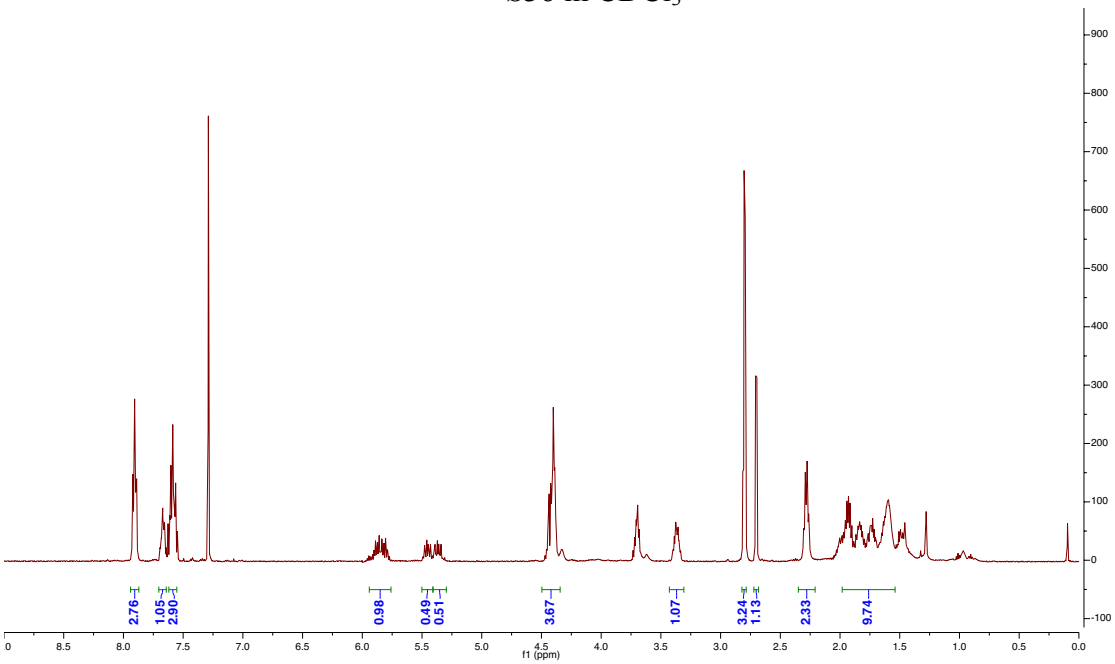


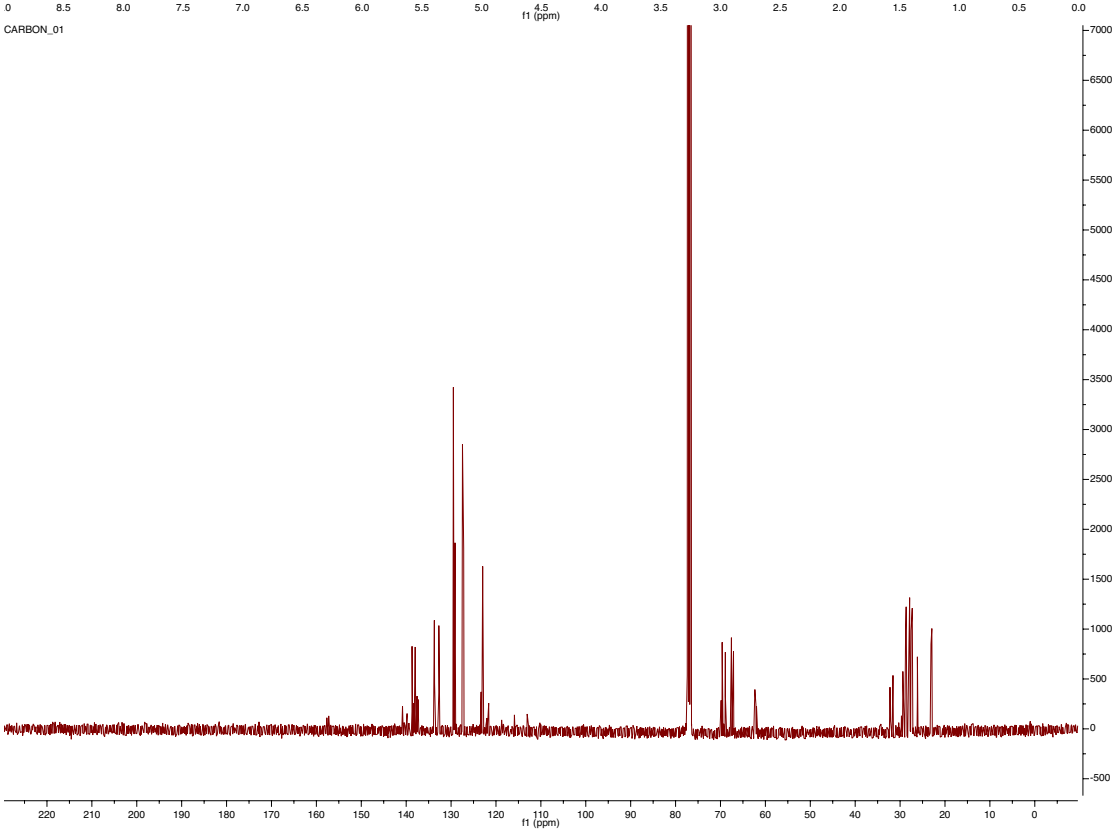
S35 in $CDCl_3$

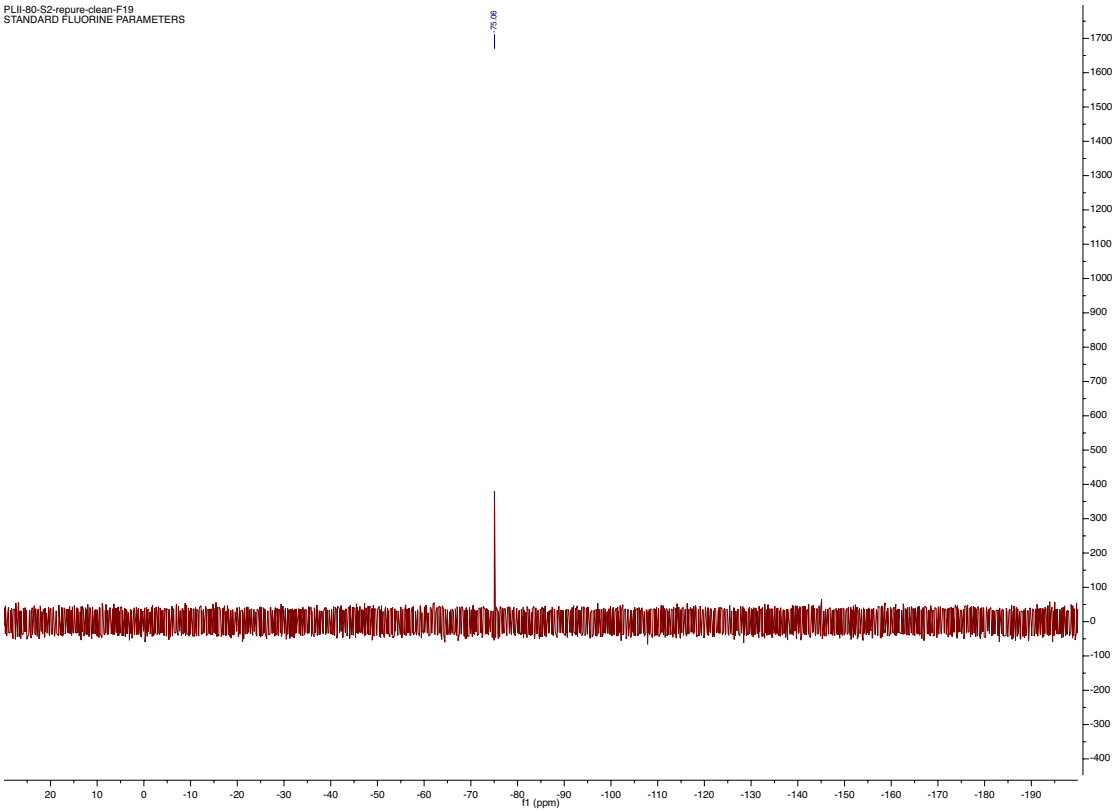


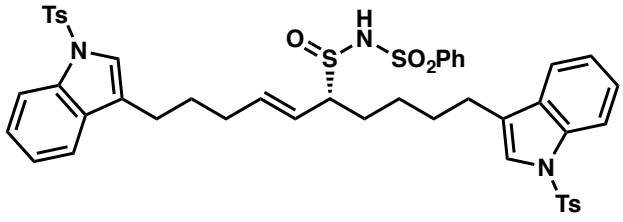

Me
O
S
N
SO2Ph
TFAO
OTFA

S36 in $CDCl_3$

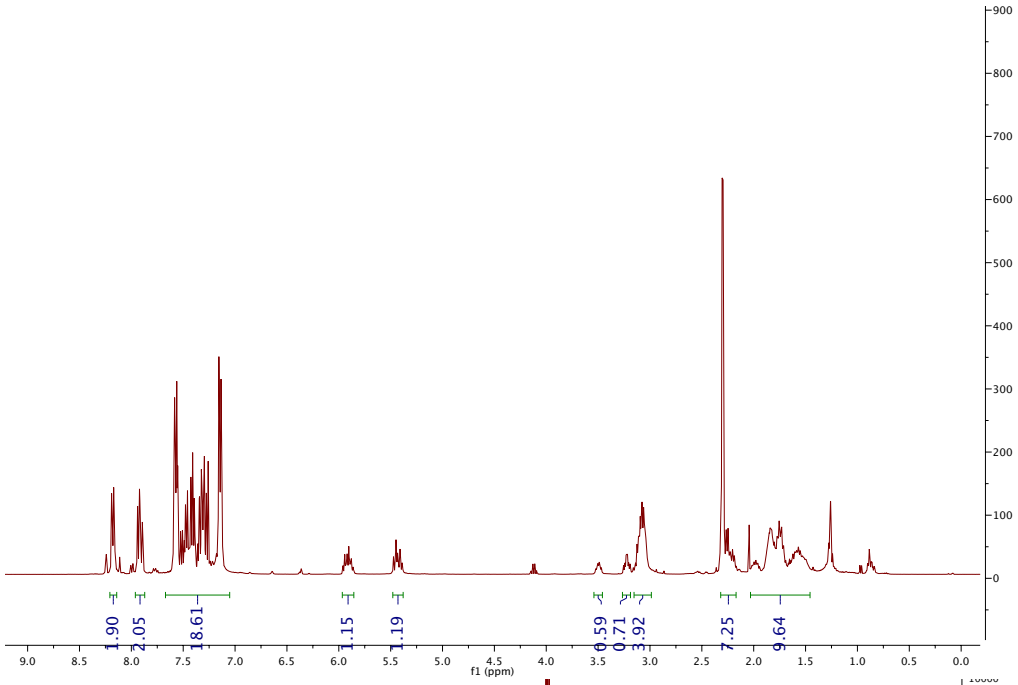

2.76
1.05
2.90
0.98
0.49
0.51
3.67
1.07
3.24
1.13
2.33
9.74
f1 (ppm)

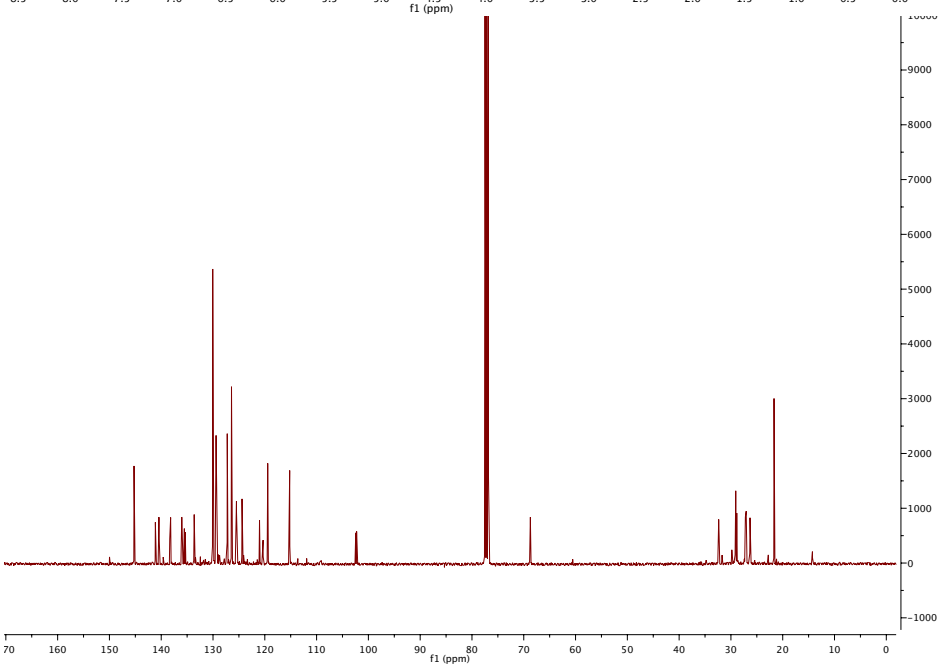

CARBON_01
f1 (ppm)

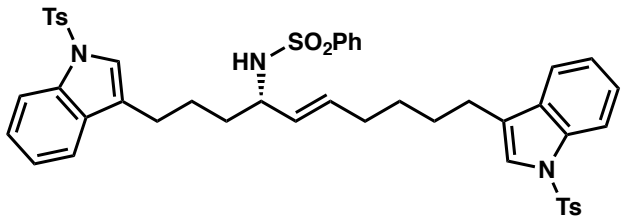

PLII-80-S2-repure-clean-F19
STANDARD FLUORINE PARAMETERS
-75.08
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


Ts
N
O
S
H
N
SO2Ph
N
Ts

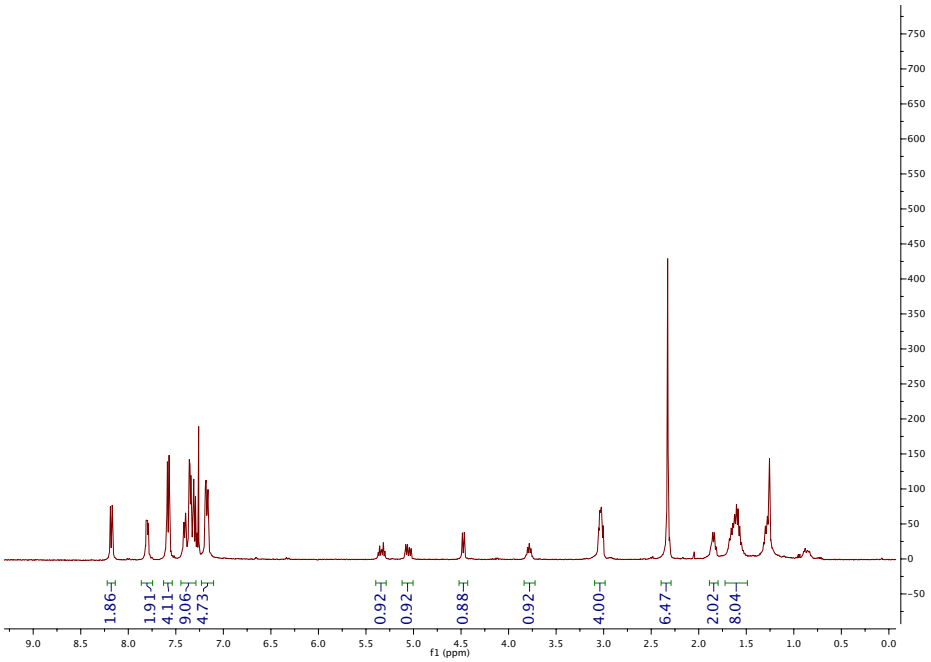
8j in $CDCl_3$

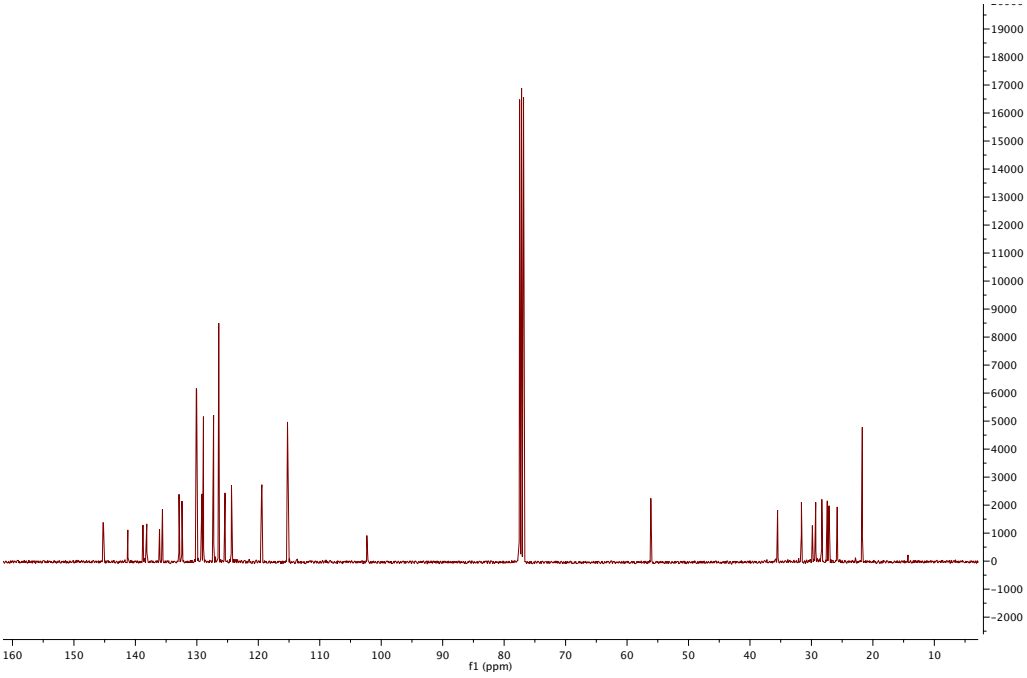

1.90
2.05
18.61
1.15
1.19
0.59
0.71
3.92
7.25
9.64
f1 (ppm)

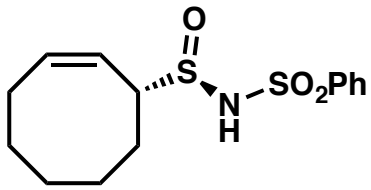

f1 (ppm)


Ts
N
HN
SO2Ph
N
Ts

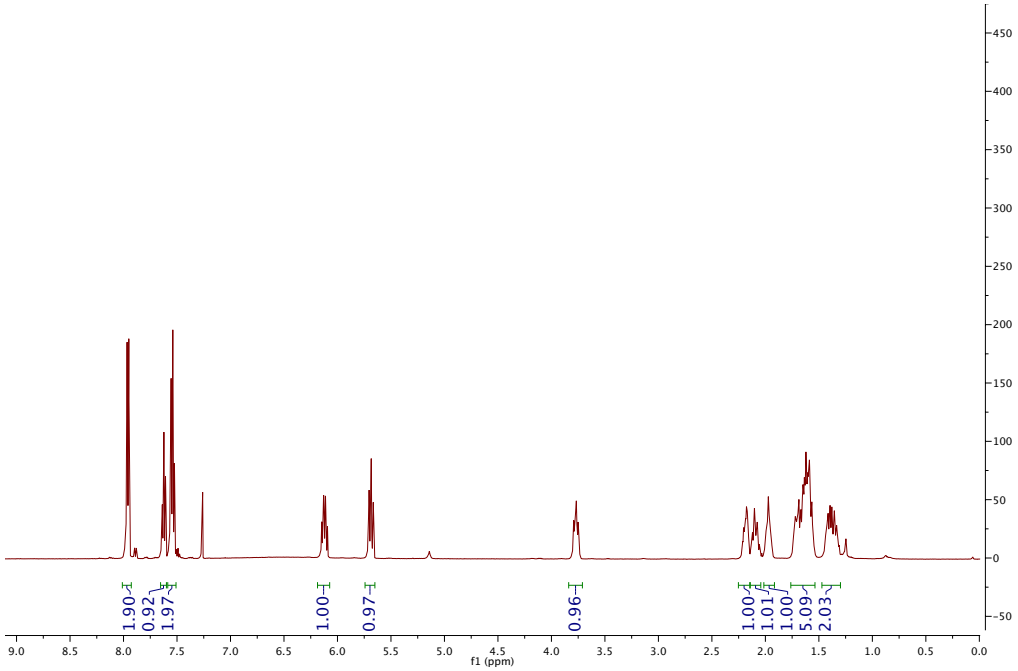
S37 in $CDCl_3$

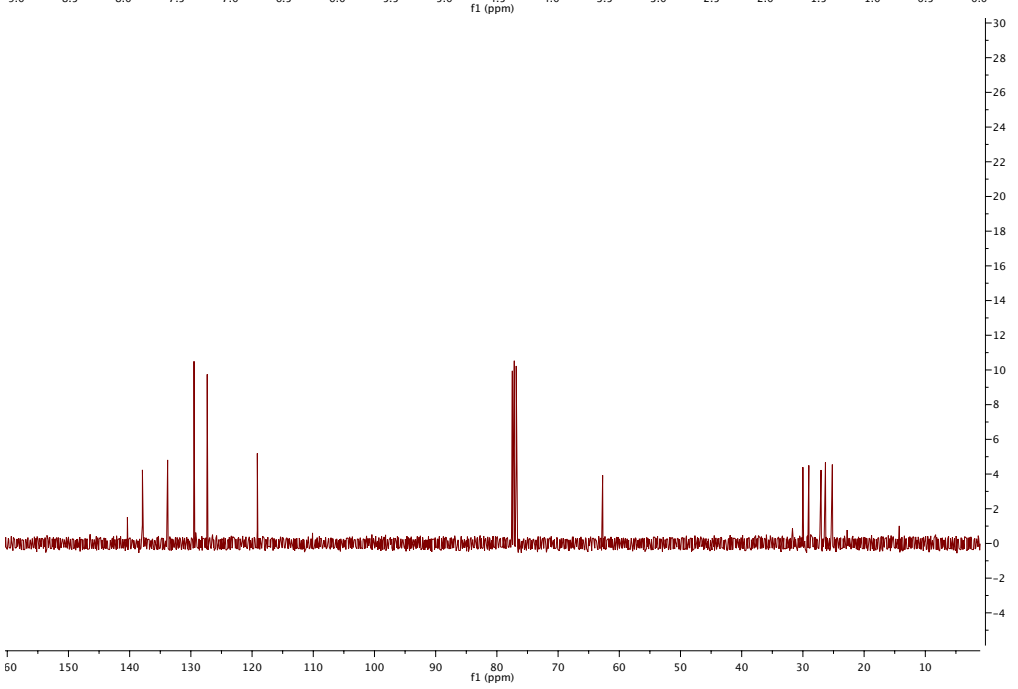

1.86
1.91
4.11
9.06
4.73
0.92
0.92
0.88
0.92
4.00
6.47
2.02
8.04
f1 (ppm)

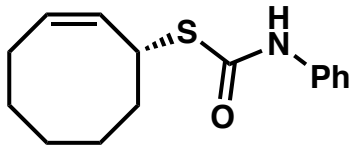

f1 (ppm)


O
S
N
H
SO2Ph

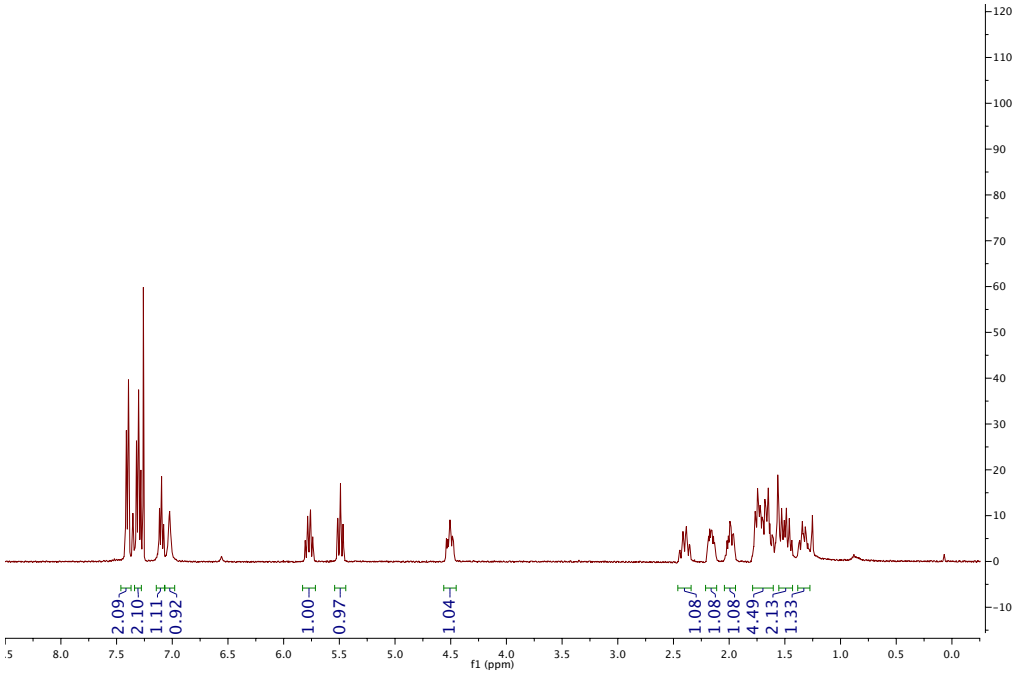
8k in $CDCl_3$

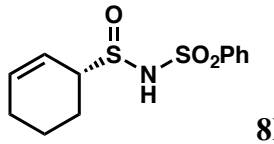

1.90
0.92
1.97
1.00
0.97
0.96
1.00
1.01
1.00
5.09
2.03
f1 (ppm)


f1 (ppm)

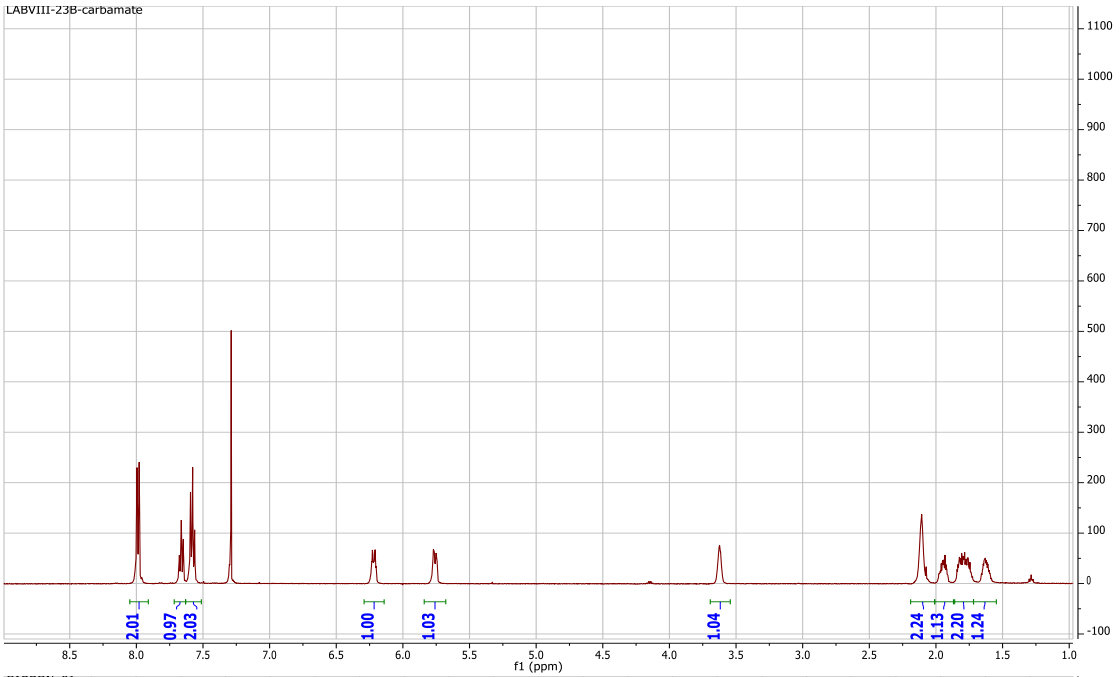

S
H
N
Ph
O

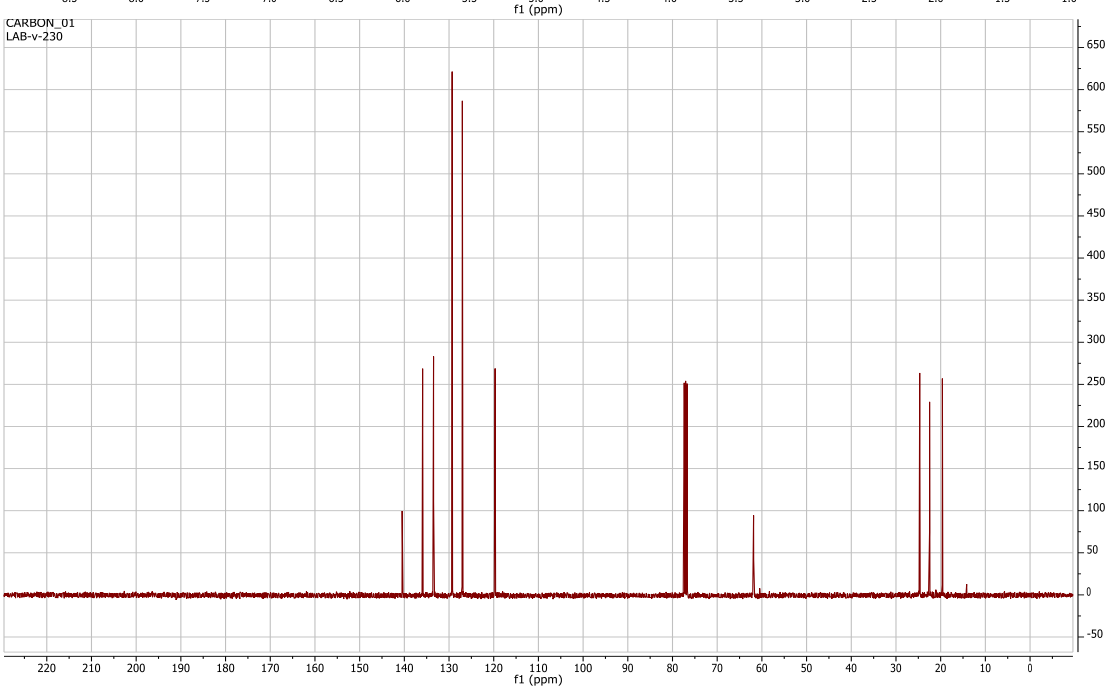
S38 in $CDCl_3$

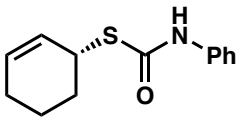

2.09
2.10
1.11
0.92
1.00
0.97
1.04
1.08
1.08
1.08
4.49
2.13
1.33
f1 (ppm)


O
S
N
H
SO2Ph

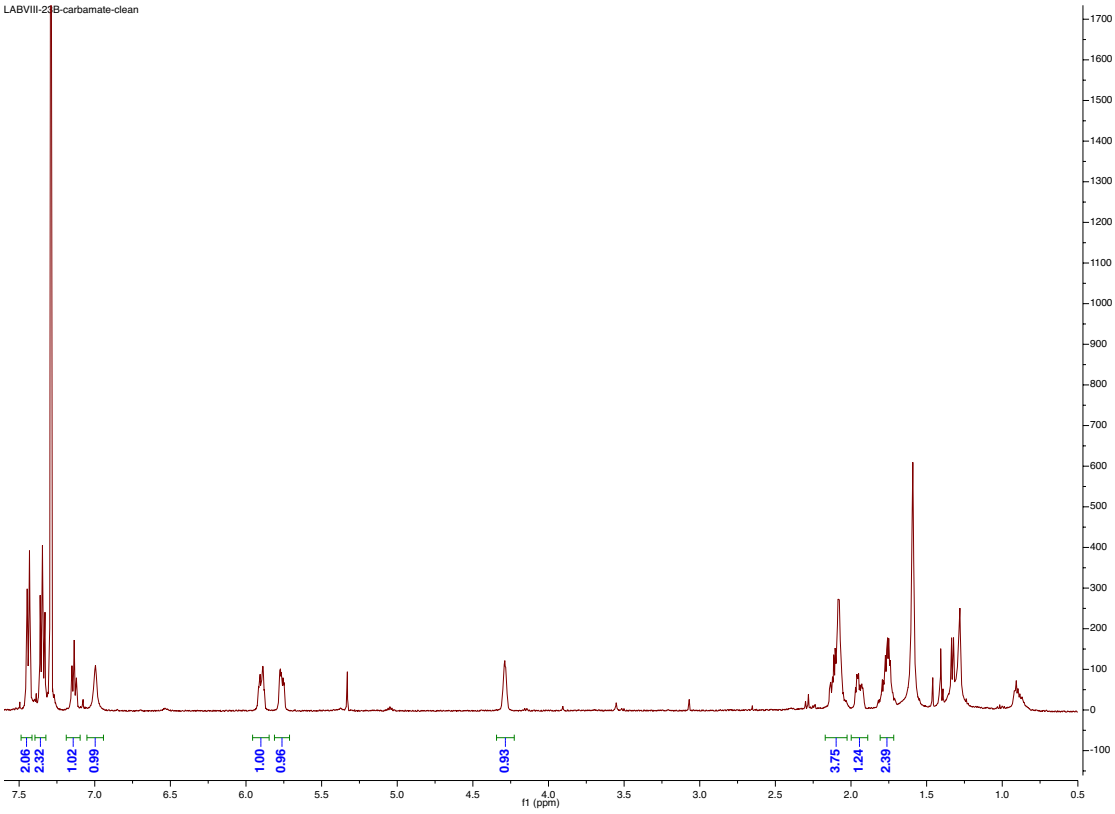
8l

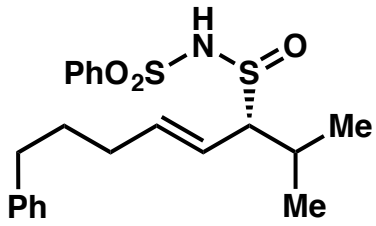

LABVIII-23B-carbamate
2.01
0.97
2.03
1.00
1.03
1.04
2.24
1.13
2.20
1.24
f1 (ppm)


CARBON_01
LAB-v-230
f1 (ppm)

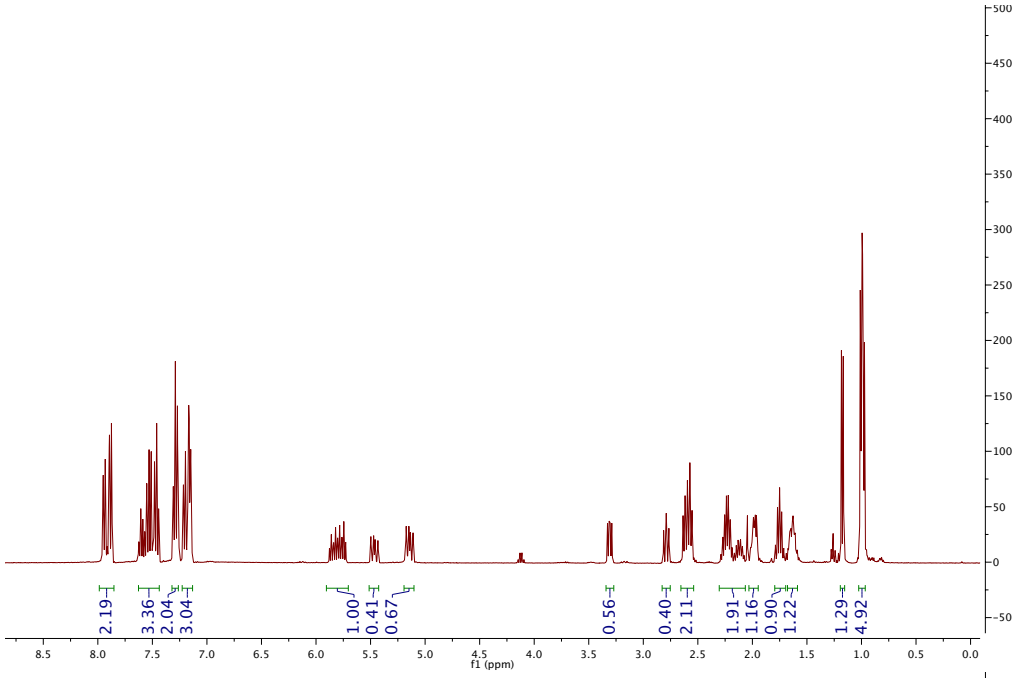

H
N
S
Ph
O

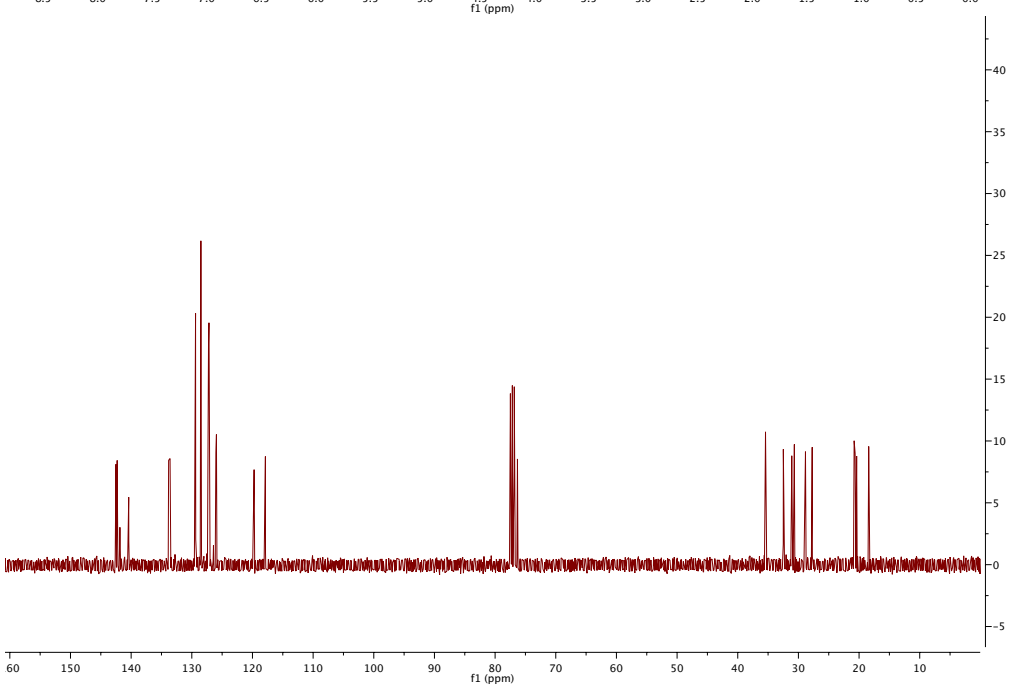
S39 in $CDCl_3$

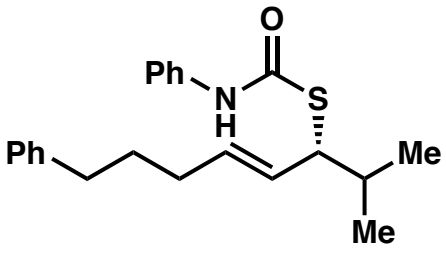

LABVIII-23B-carbamate-clean
2.06
2.32
1.02
0.99
1.00
0.96
0.93
3.75
1.24
2.39
f1 (ppm)


H
N
PhO2S
S
O
Me
Ph
Me

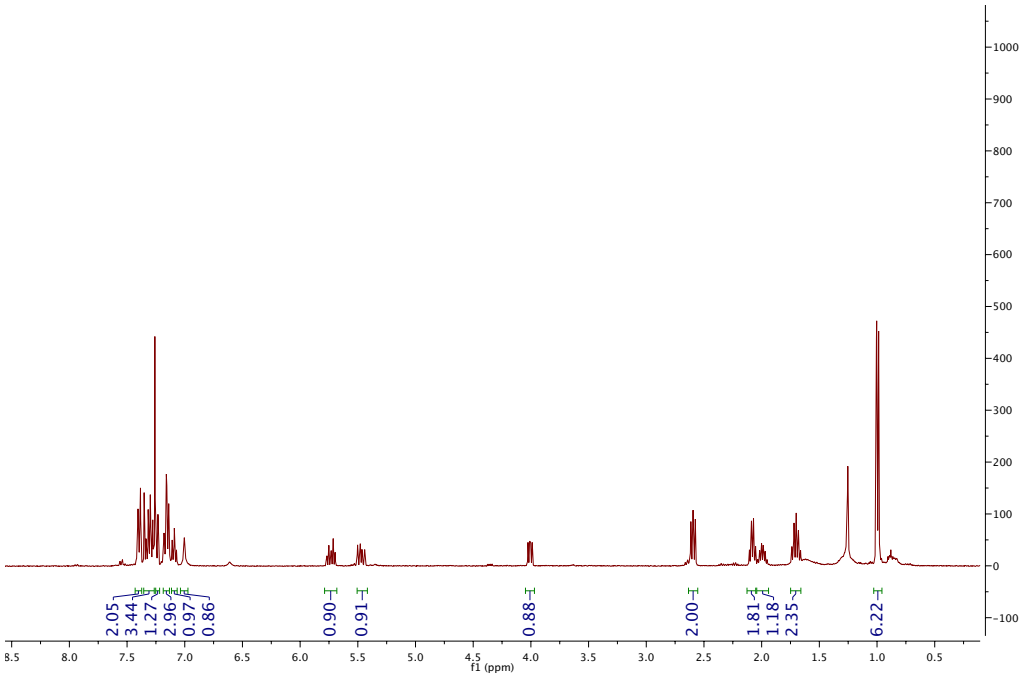
9a in $CDCl_3$

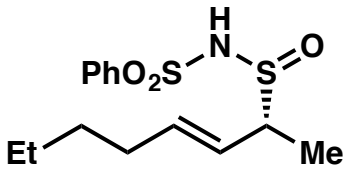

2.19
3.36
2.04
3.04
1.00
0.41
0.67
0.56
0.40
2.11
1.91
1.16
0.90
1.22
1.29
4.92
f1 (ppm)


f1 (ppm)

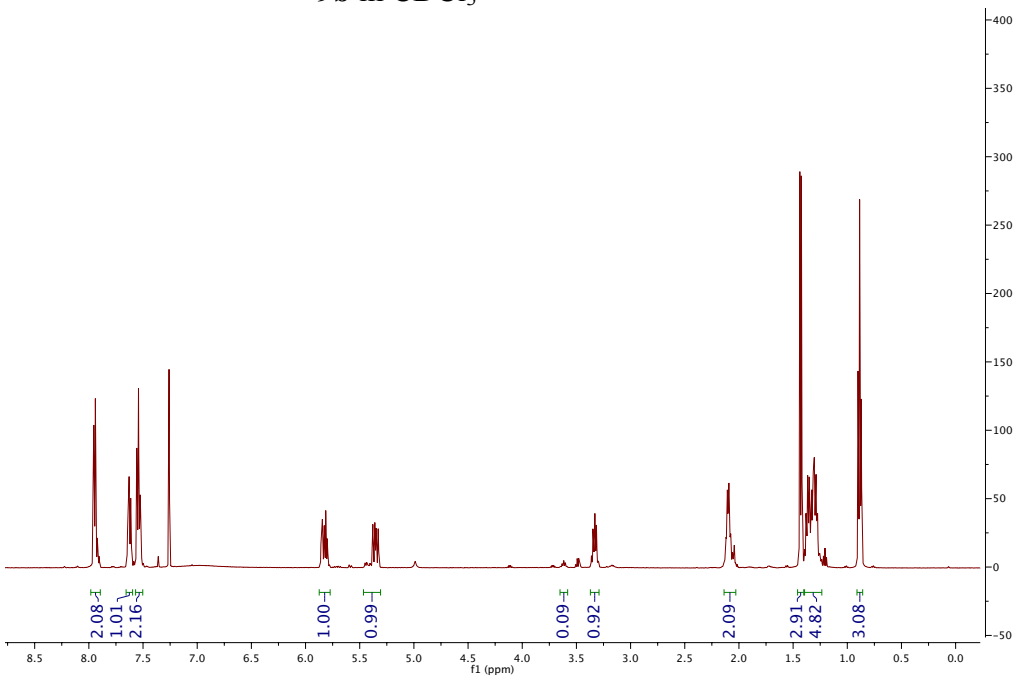

O
Ph
N
H
S
Ph
Me
Me

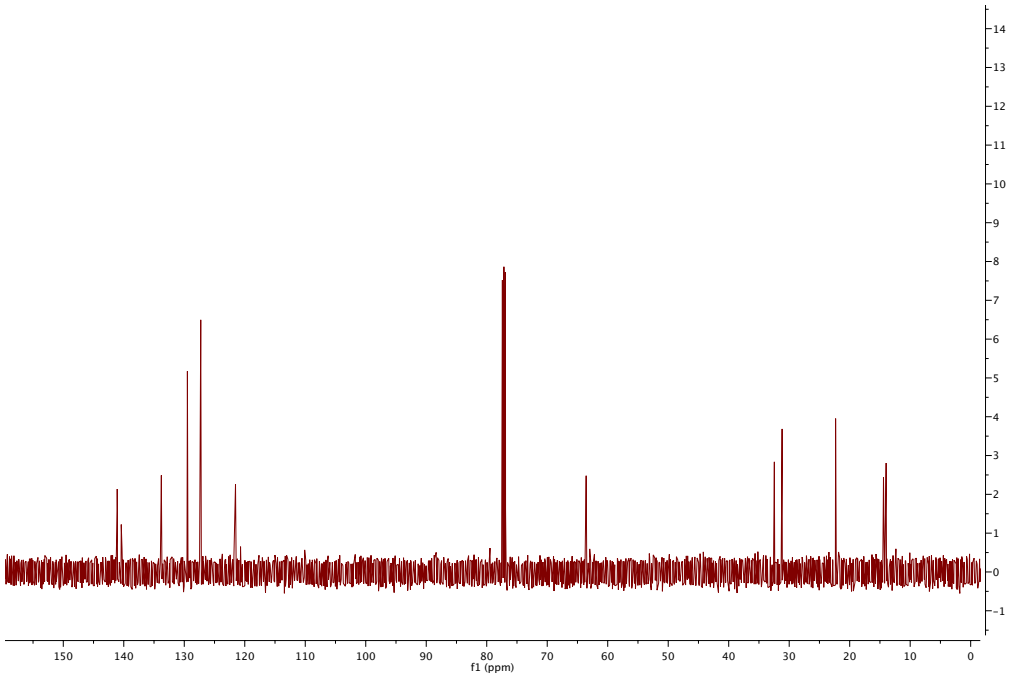
S40 in $CDCl_3$

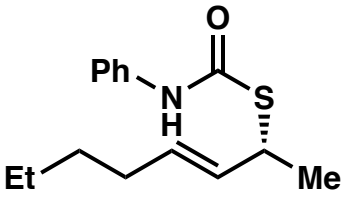

2.05
3.44
1.27
2.96
0.97
0.86
0.90
0.91
0.88
2.00
1.81
1.18
2.35
6.22
f1 (ppm)


H
N
PhO2S
S
O
Et
Me

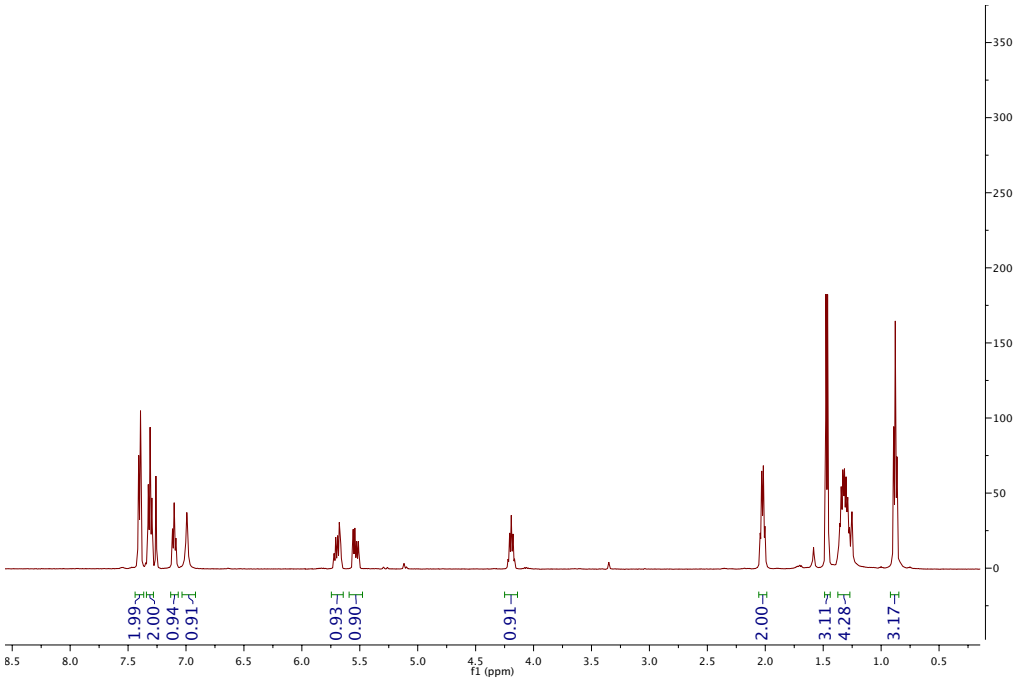
9b in $CDCl_3$

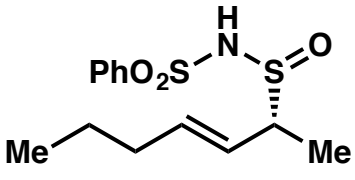

2.08
1.01
2.16
1.00
0.99
0.09
0.92
2.09
2.91
4.82
3.08
f1 (ppm)


f1 (ppm)

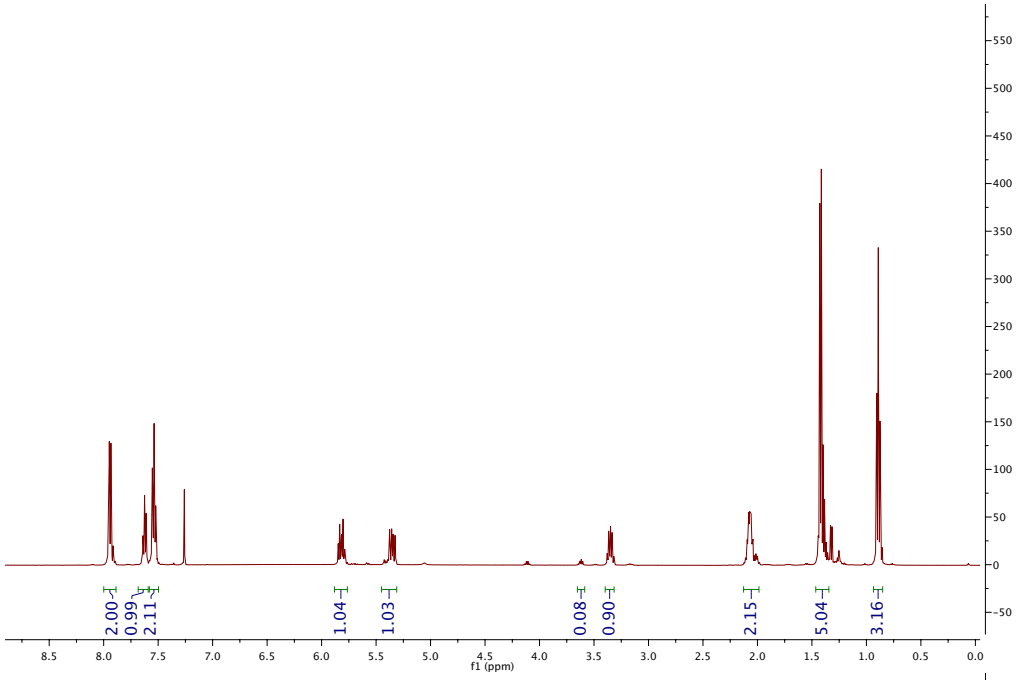


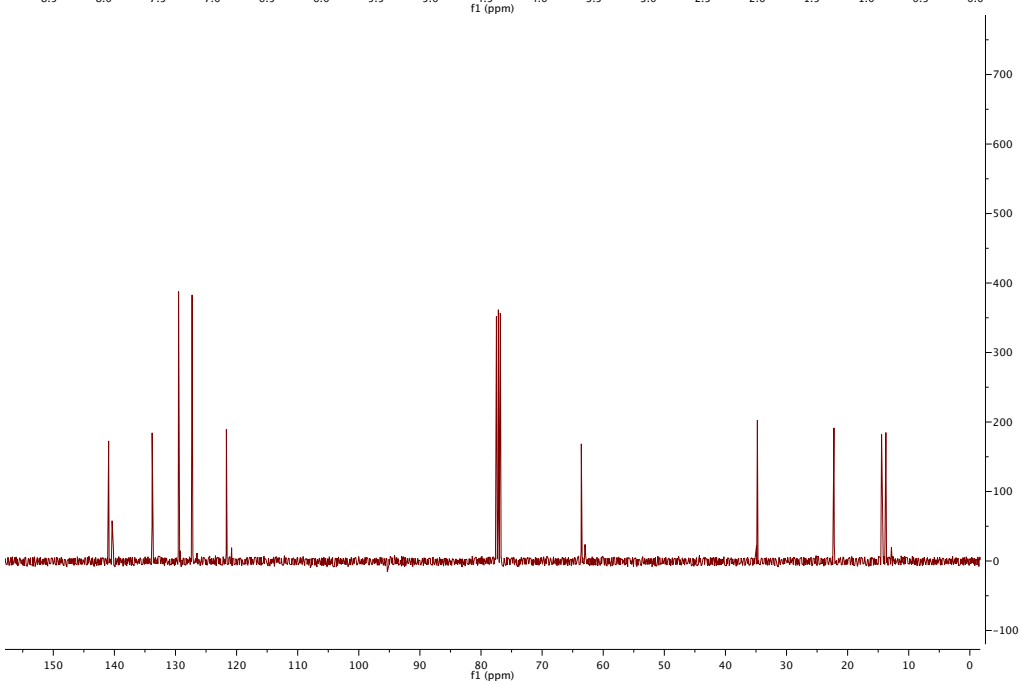
S41 in $CDCl_3$

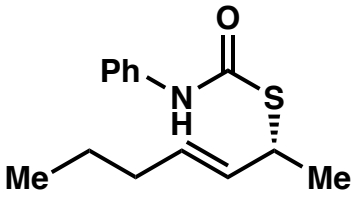



H
N
PhO2S
S
O
Me
Me

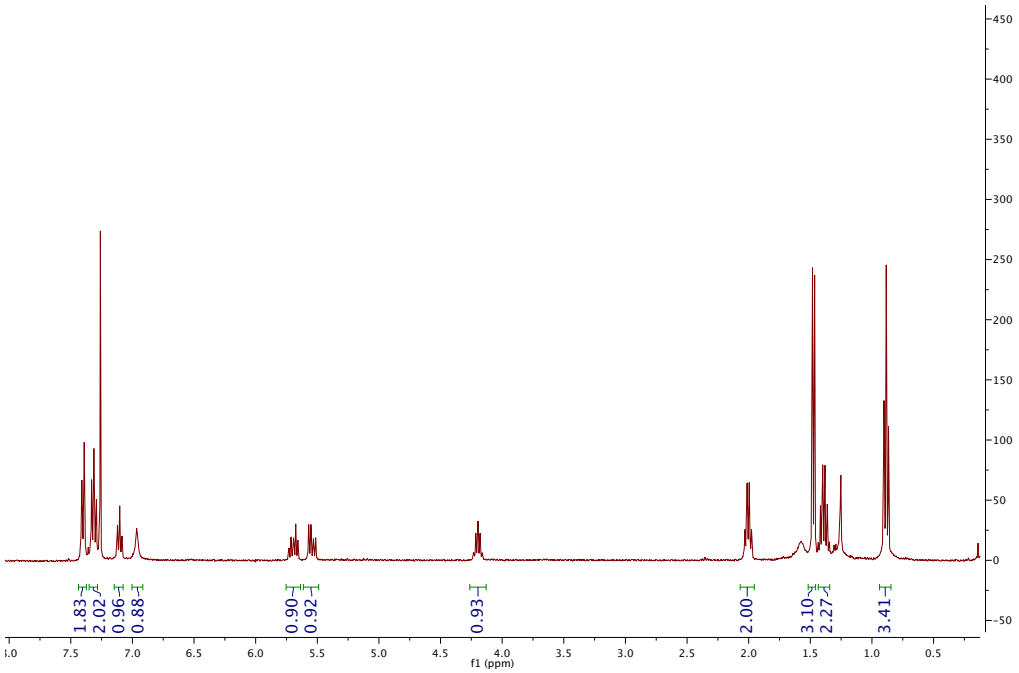
9c in $CDCl_3$

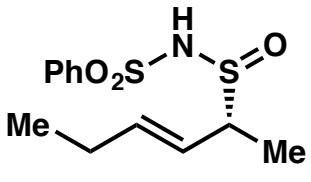

2.00
0.99
2.11
1.04
1.03
0.08
0.90
2.15
5.04
3.16
f1 (ppm)


f1 (ppm)

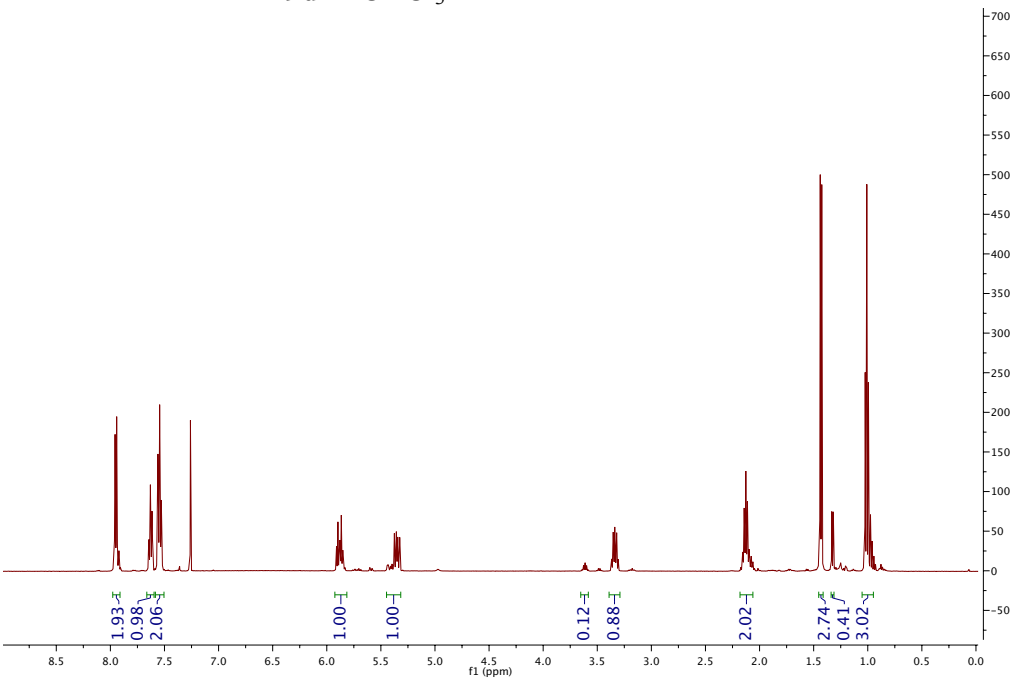


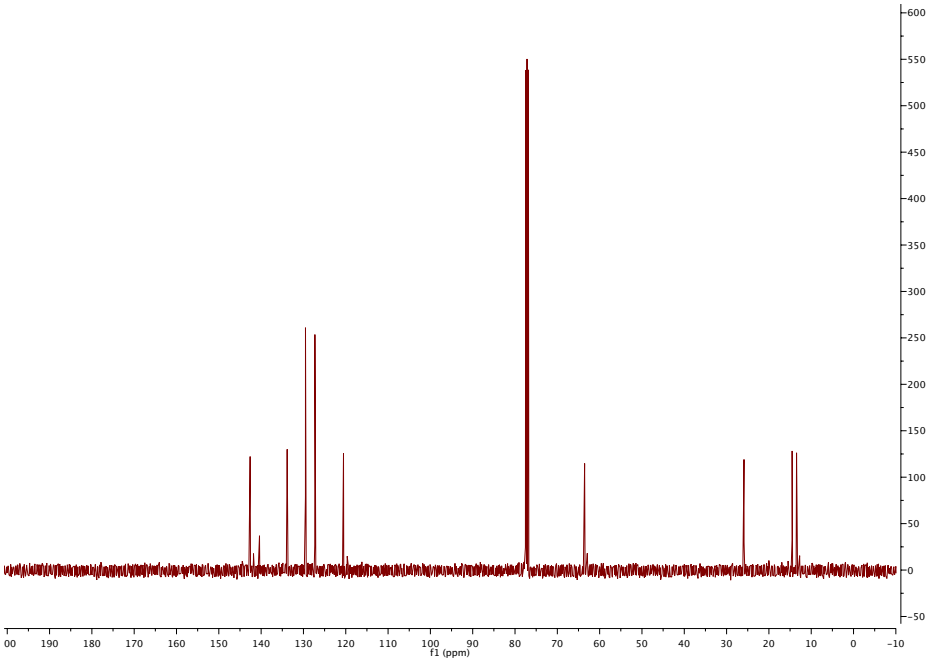
S42 in $CDCl_3$

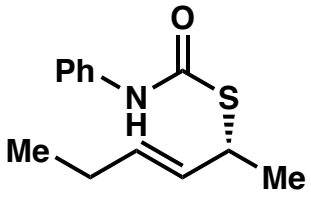



H
N
PhO2S
S
O
Me
Me

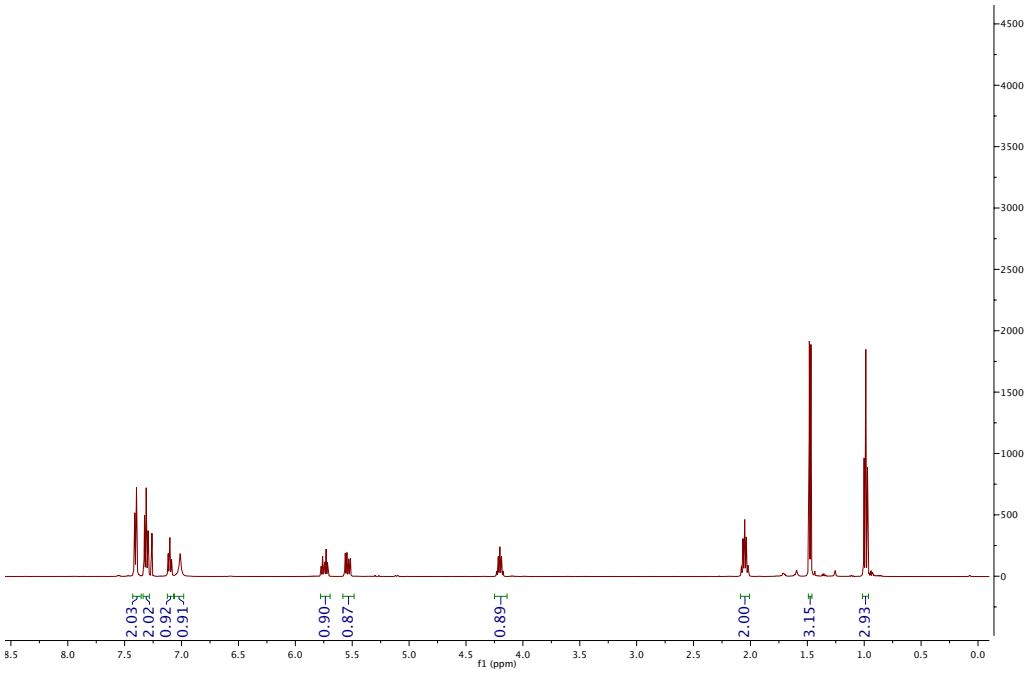
9d in $CDCl_3$

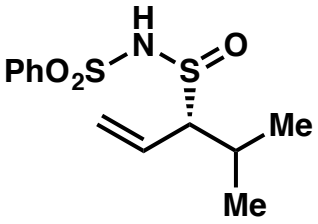

1.93
0.98
2.06
1.00
1.00
0.12
0.88
2.02
2.74
0.41
3.02
f1 (ppm)


f1 (ppm)

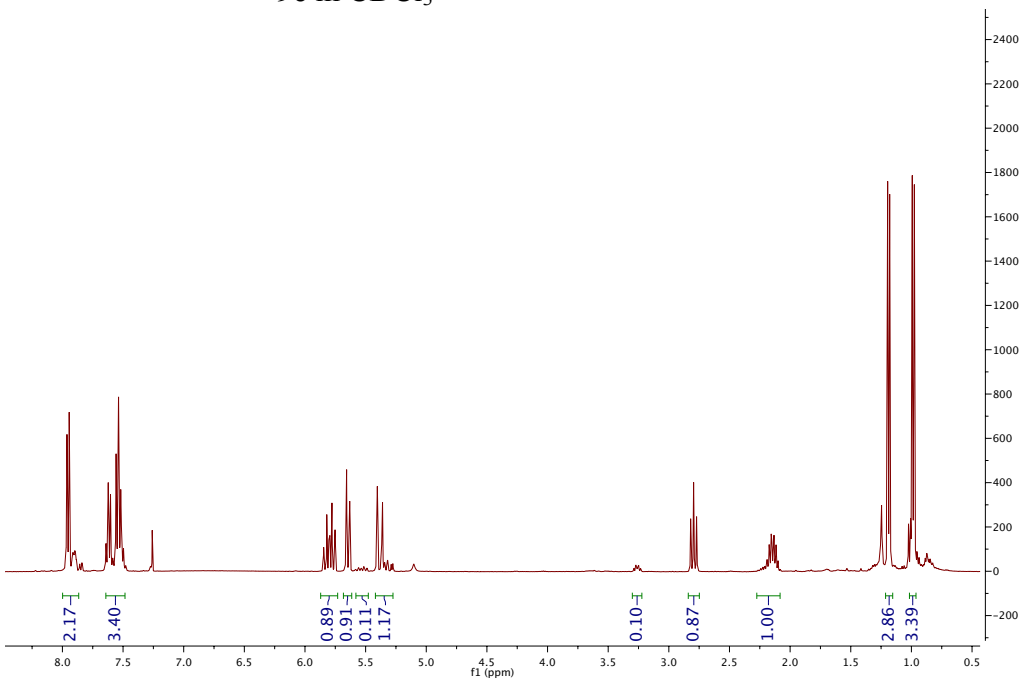

O
Ph
N
H
S
Me
Me

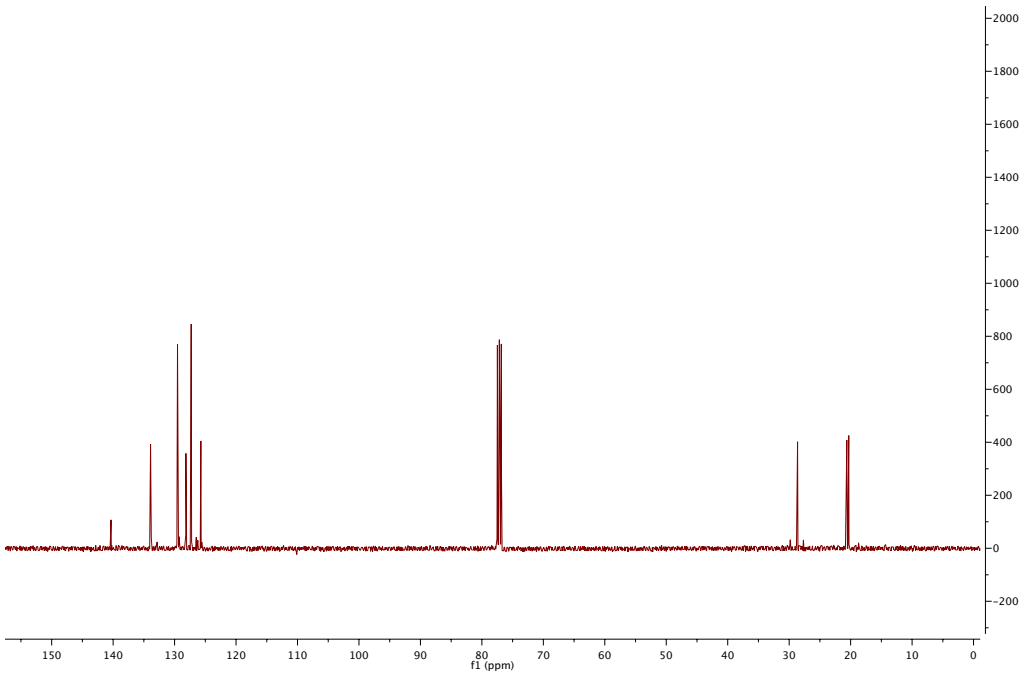
S43 in $CDCl_3$

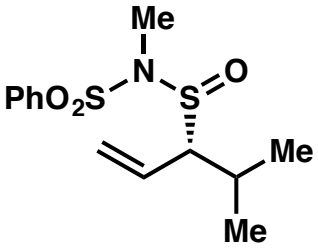

4500
4000
3500
3000
2500
2000
1500
1000
500
0
2.03
2.02
0.92
0.91
0.90
0.87
0.89
2.00
3.15
2.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


H
N
PhO2S
S
O
Me
Me

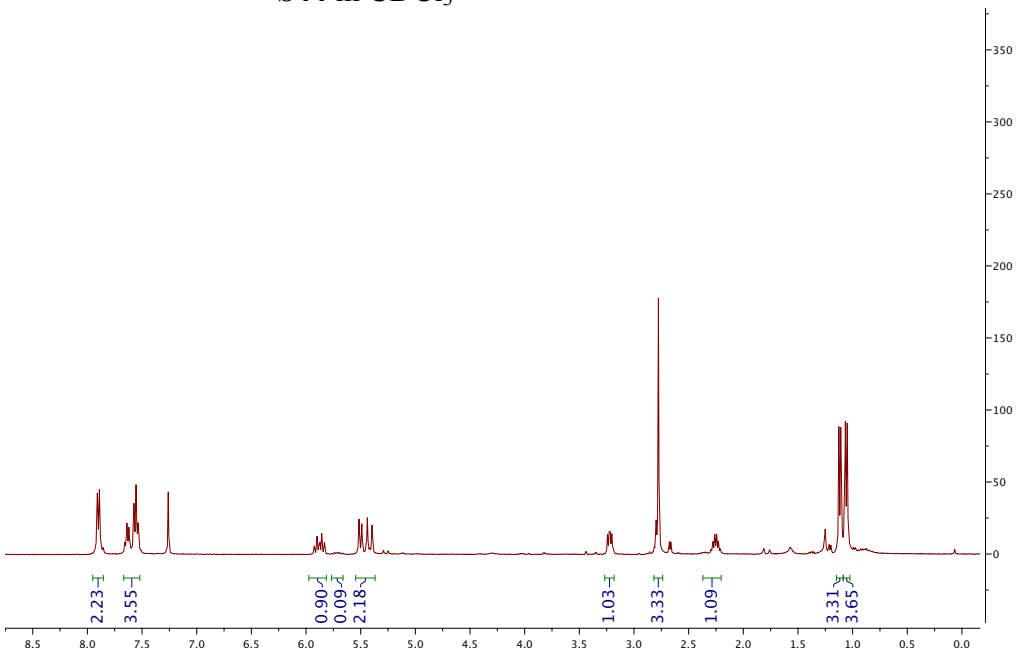
9e in $CDCl_3$

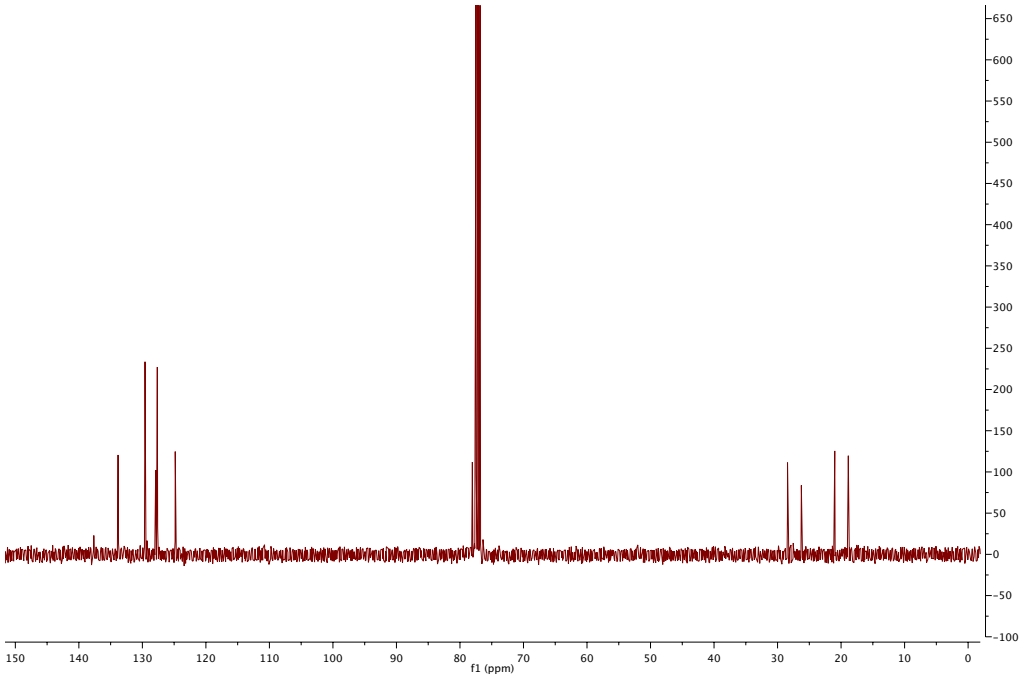

2.17
3.40
0.89
0.91
0.11
1.17
0.10
0.87
1.00
2.86
3.39
f1 (ppm)


f1 (ppm)



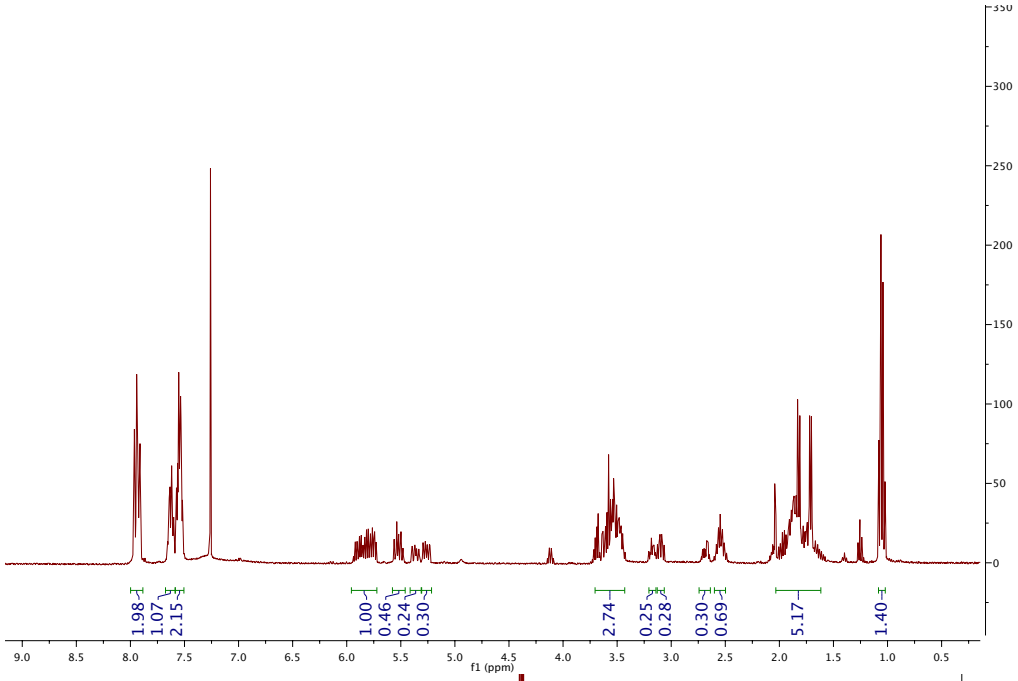
S44 in $CDCl_3$

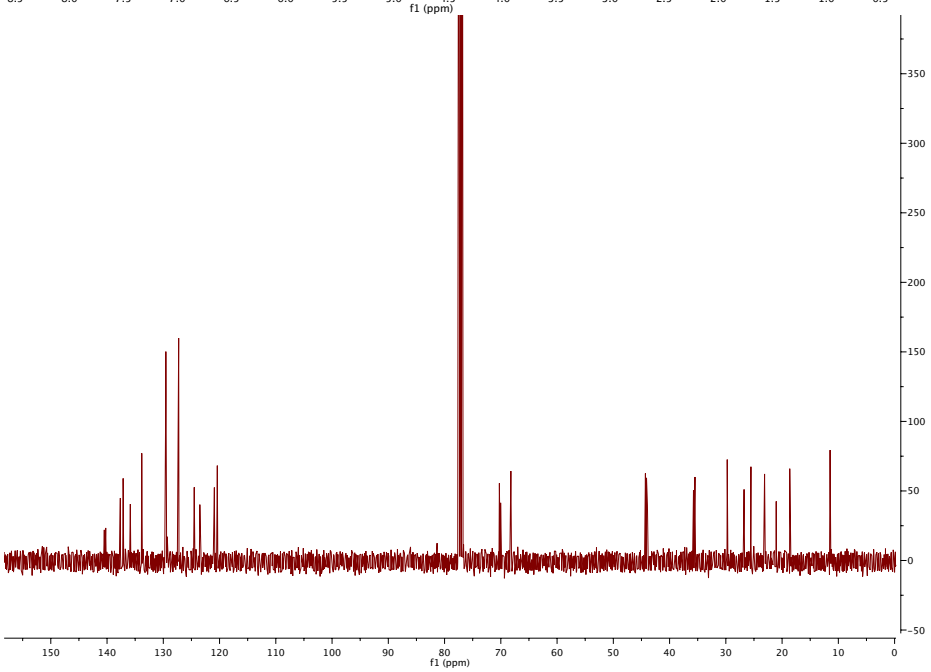


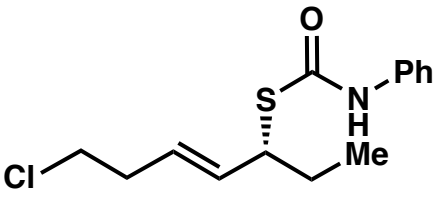


(Major) (Minor)

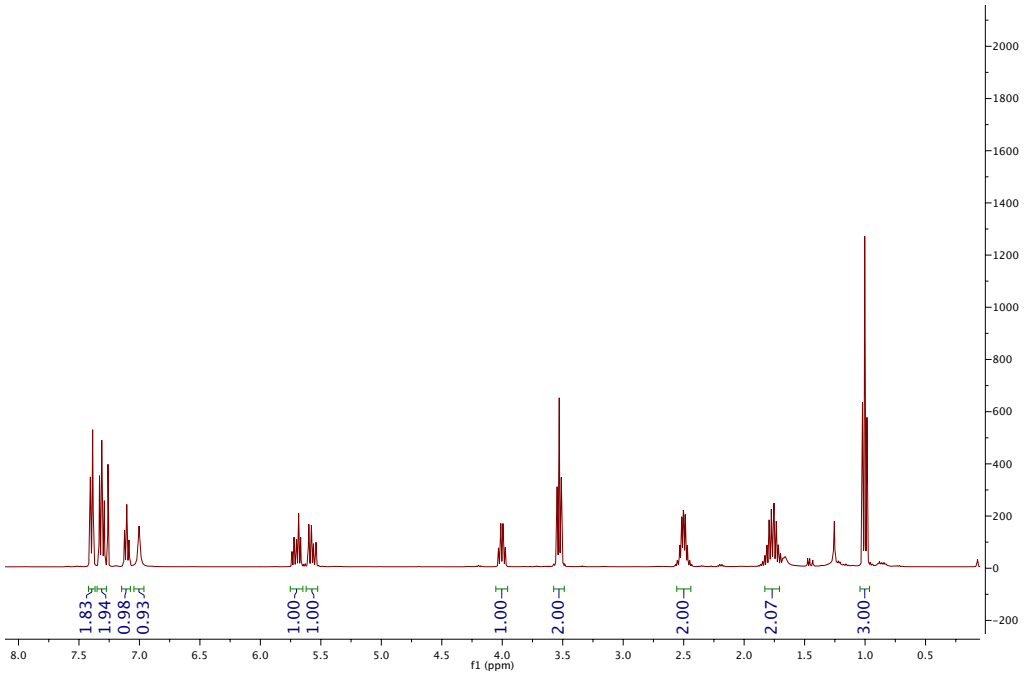
9f in $CDCl_3$

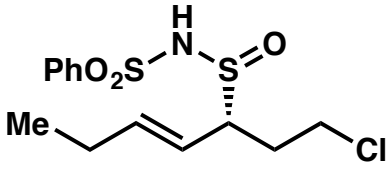




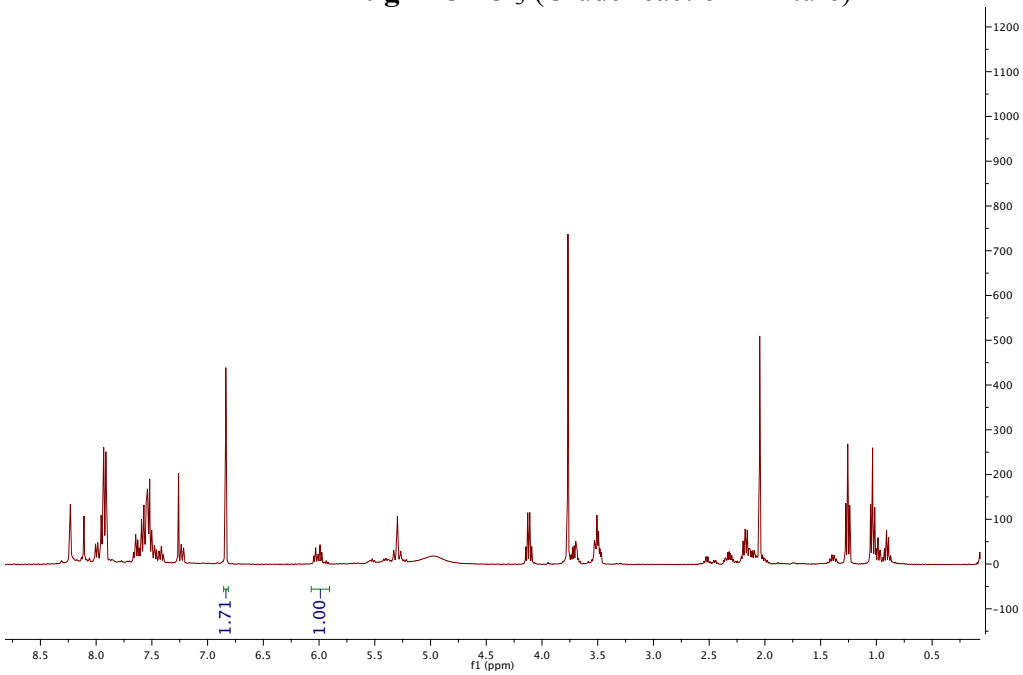

O
Ph
S
N
H
Me
Cl

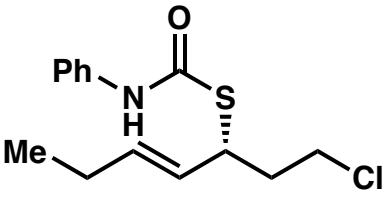
S45 in $CDCl_3$


2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
1.83
1.94
0.98
0.93
1.00
1.00
1.00
2.00
2.00
2.07
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

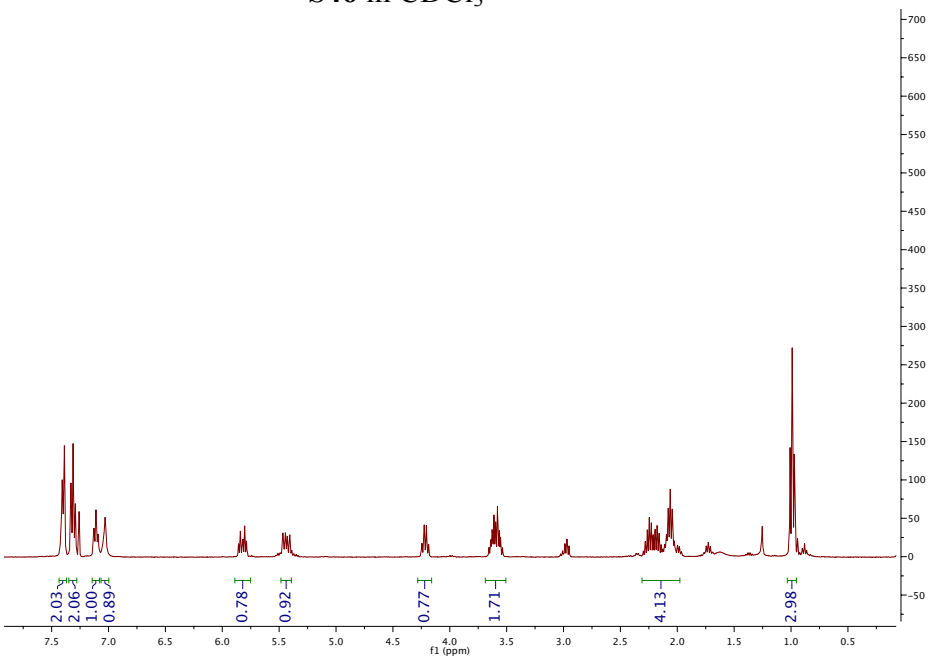


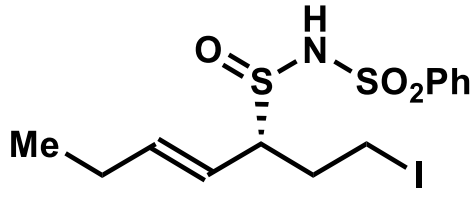
9g in $CDCl_3$ (Crude reaction mixture)



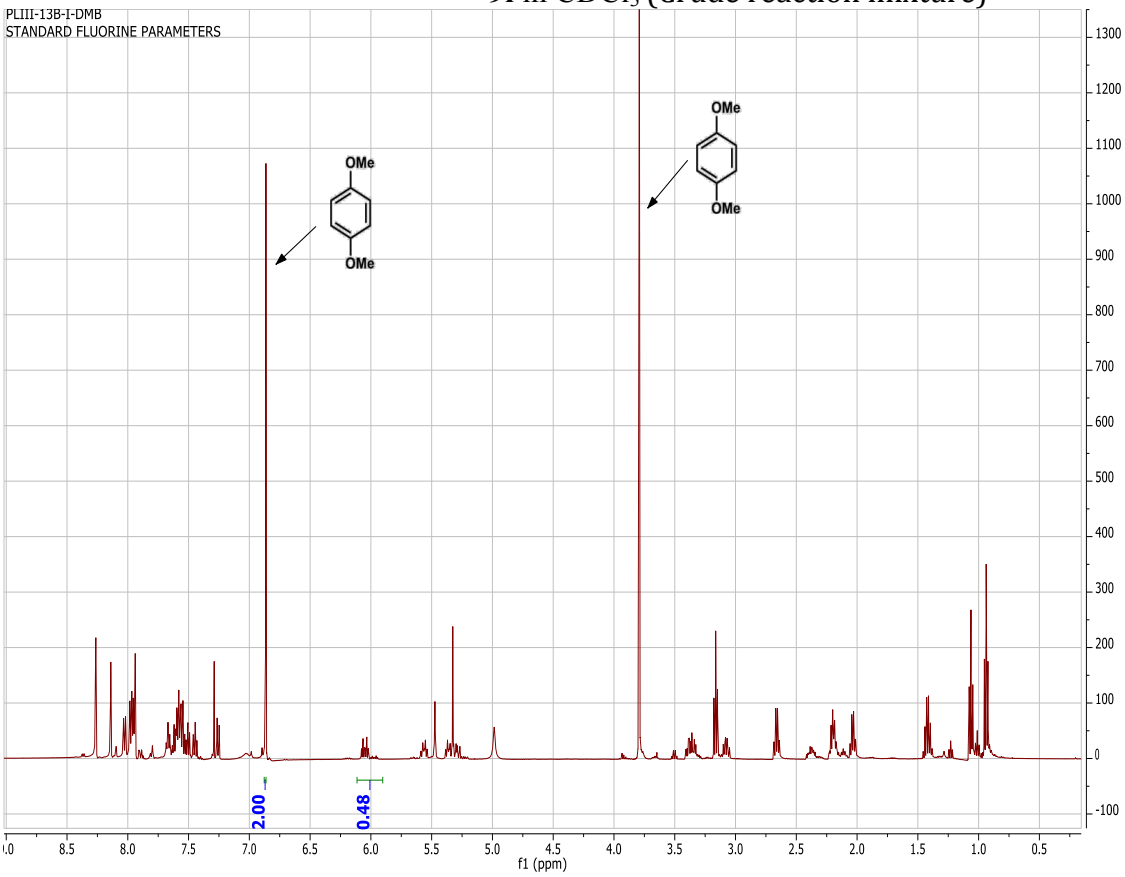


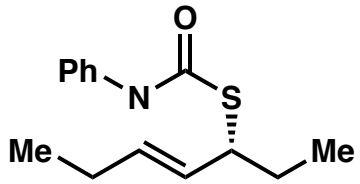
S46 in $CDCl_3$



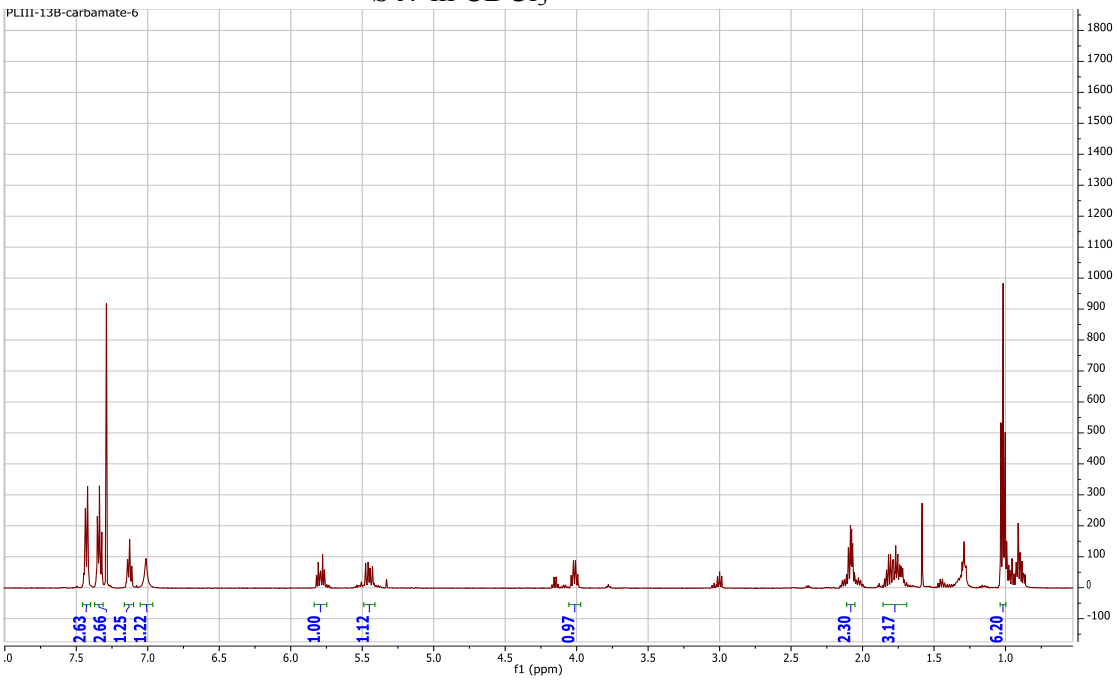


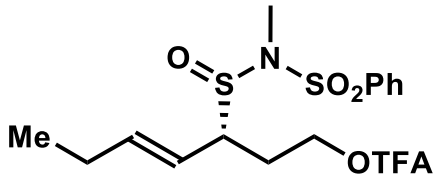
9i in $CDCl_3$ (Crude reaction mixture)



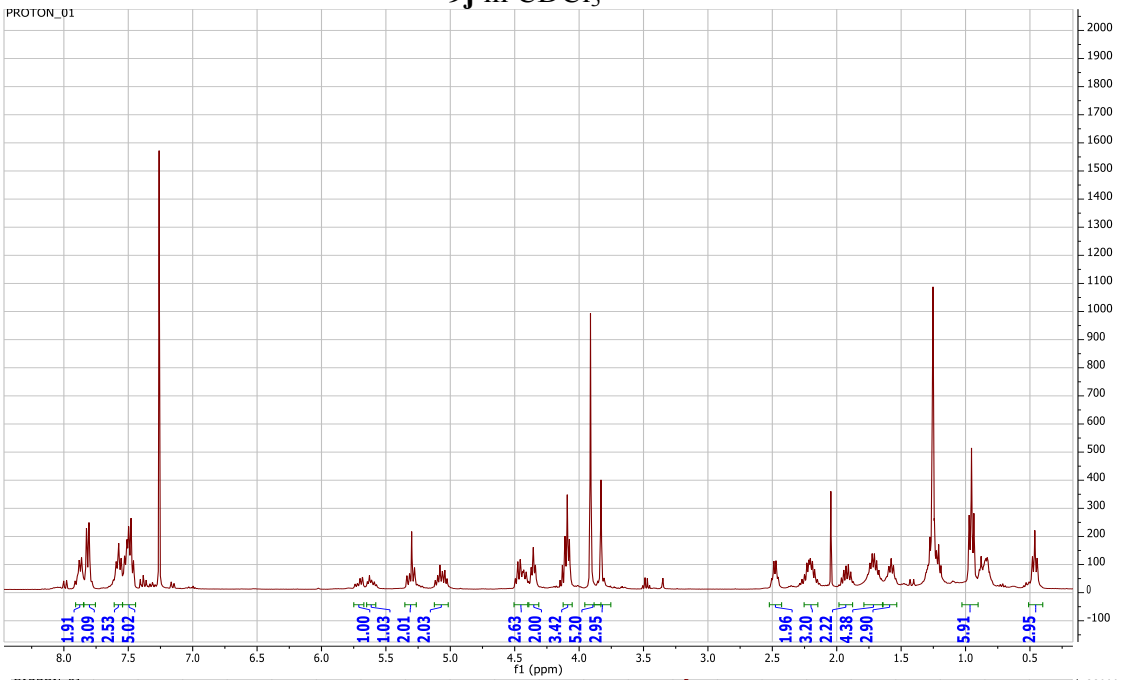

O
Ph
N
S
Me
Me

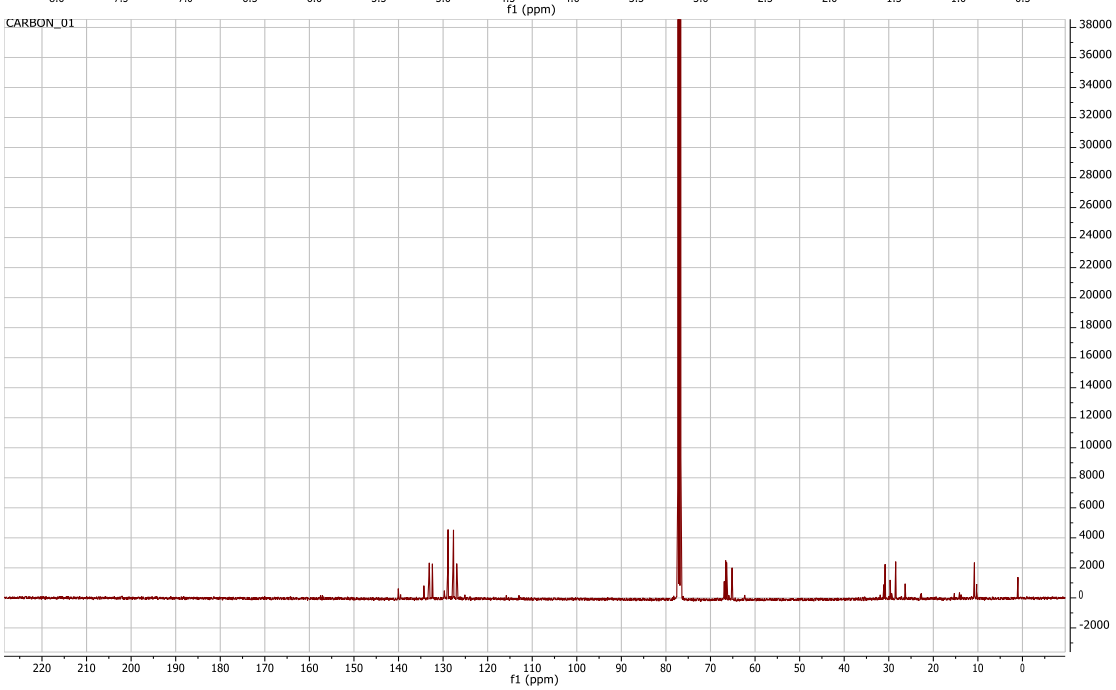
S47 in $CDCl_3$


PLIII-13B-carbamate-6
2.63
2.66
1.25
1.22
1.00
1.12
0.97
2.30
3.17
6.20
f1 (ppm)

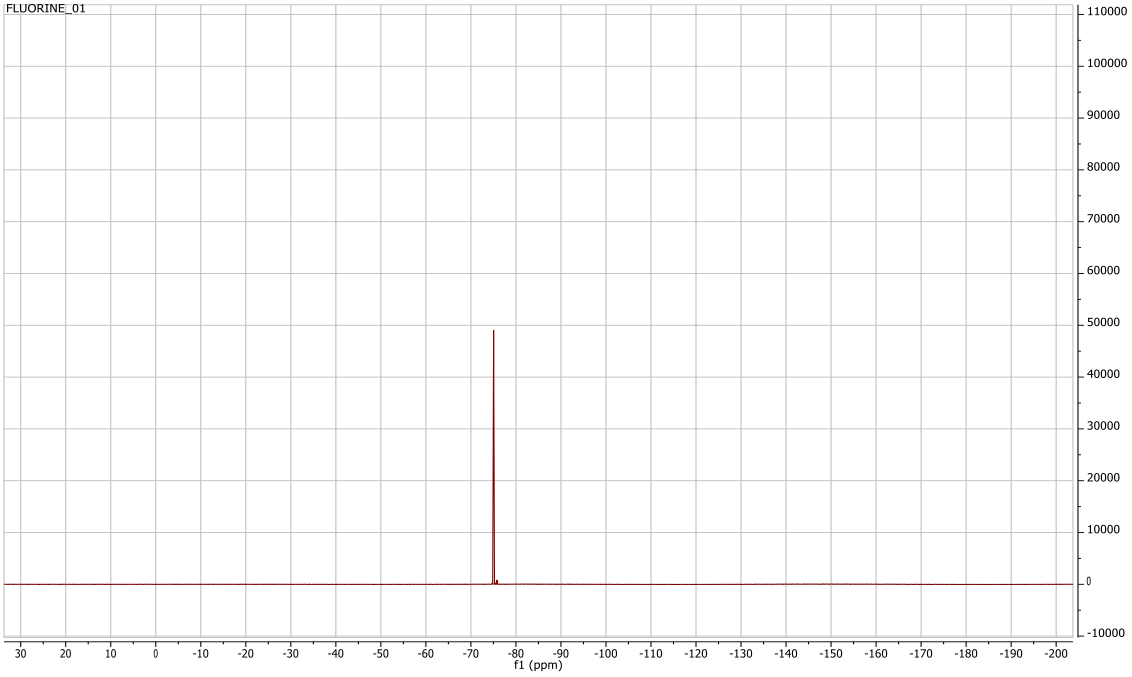

O
S
N
SO2Ph
Me
OTFA

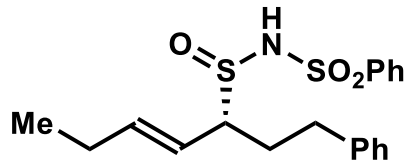
9j in $CDCl_3$


PROTON_01
1.91
3.09
2.53
5.02
1.00
1.03
2.01
2.03
2.63
2.00
3.42
5.20
2.95
1.96
3.20
2.22
4.38
2.90
5.91
2.95
f1 (ppm)

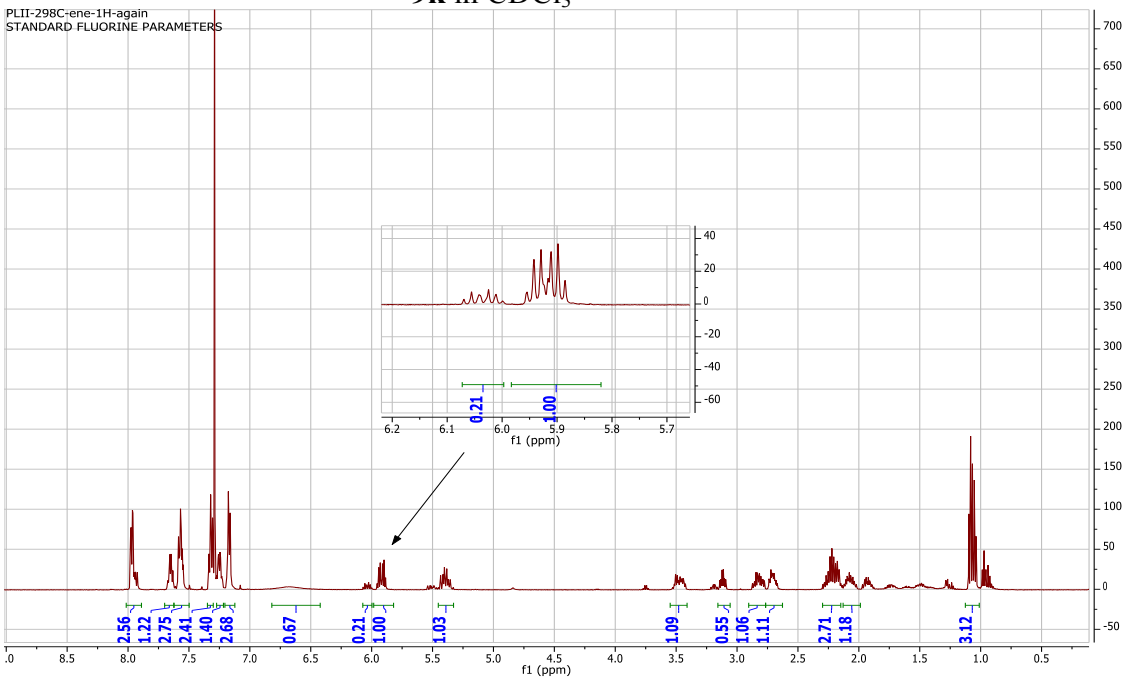

CARBON_01
f1 (ppm)

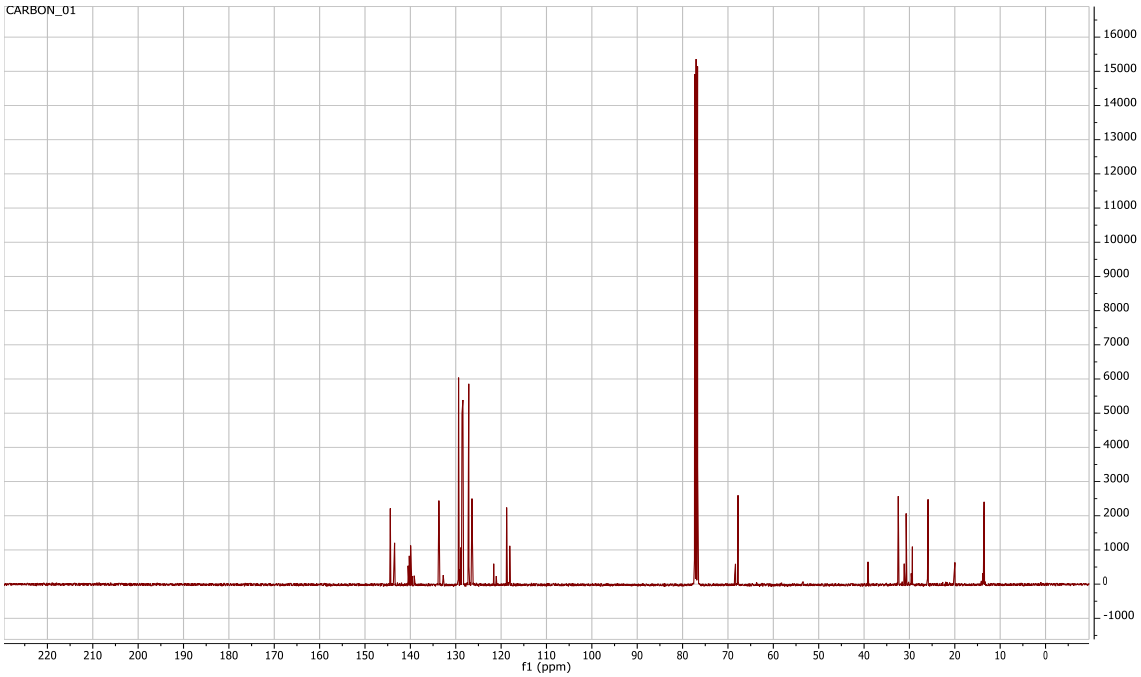
^{19}F NMR

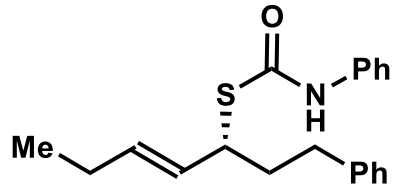

FLUORINE_01
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


H
N
O
S
SO2Ph
Me
Ph

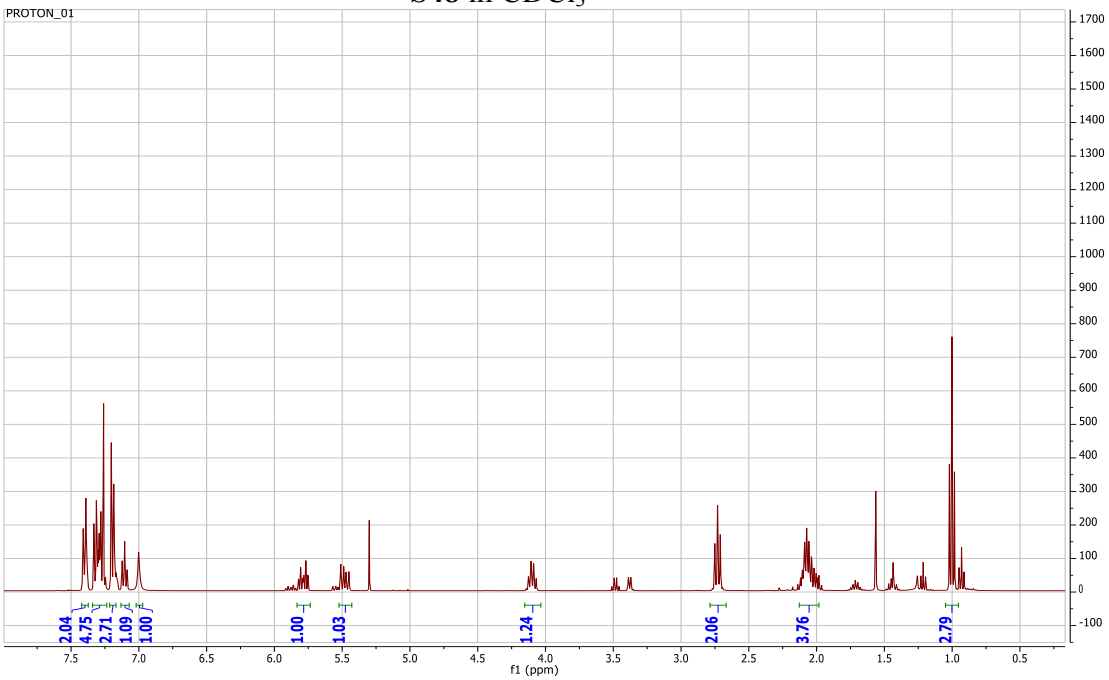
9k in $CDCl_3$

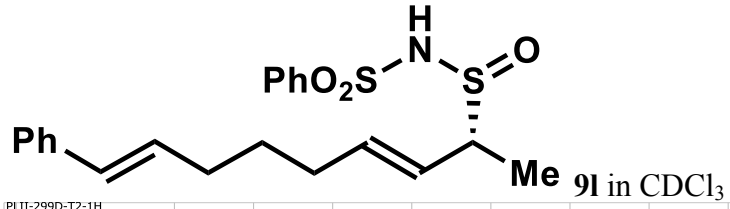

PLII-298C-ene-1H-again
STANDARD FLUORINE PARAMETERS
f1 (ppm)


CARBON_01
f1 (ppm)

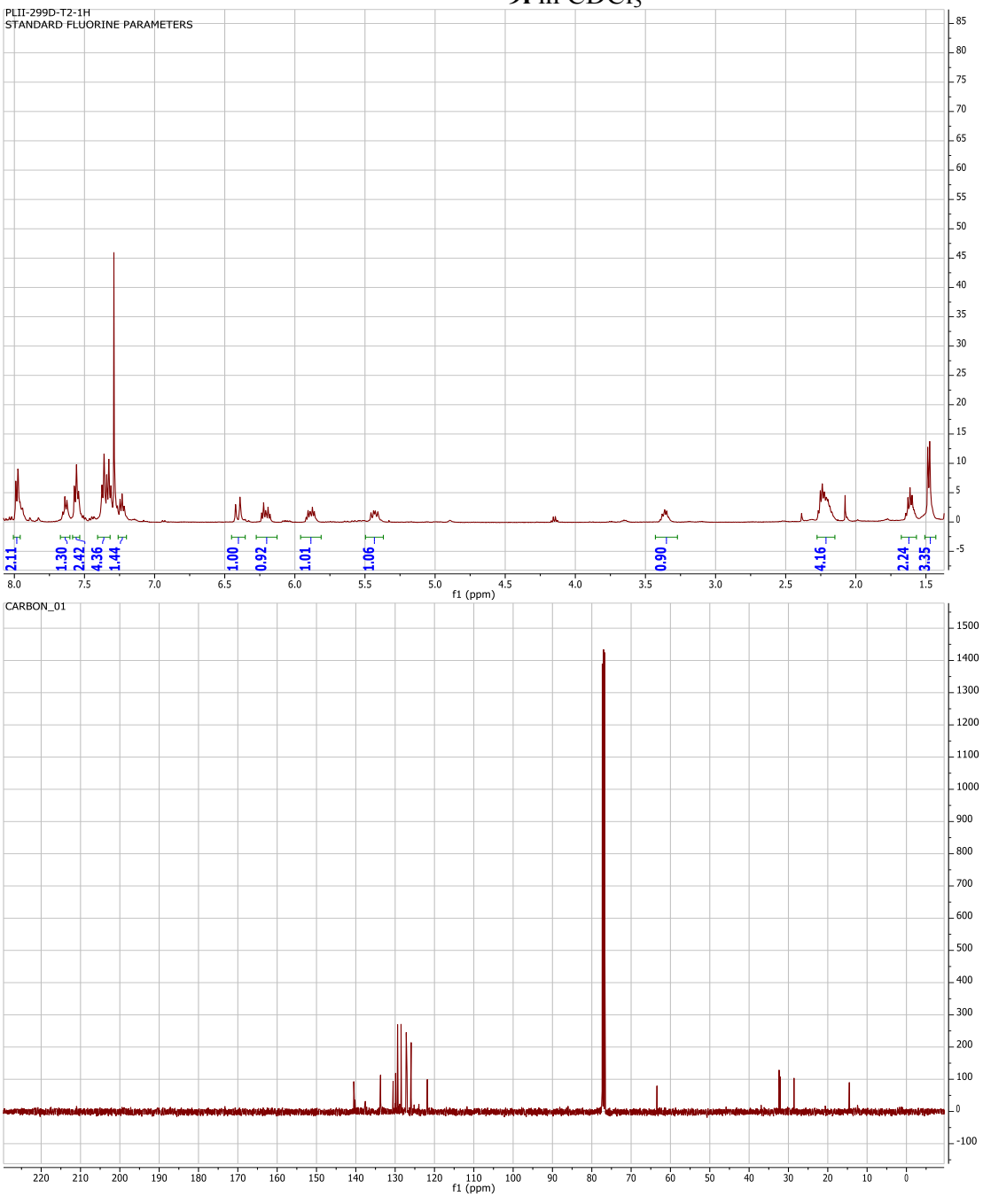

O
S
N
H
Ph
Me
Ph

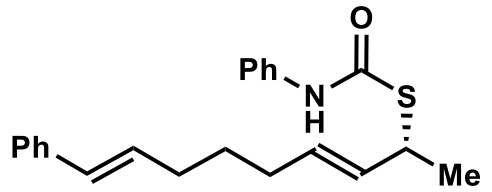
S48 in $CDCl_3$


PROTON_01
2.04
4.75
2.71
1.09
1.00
1.00
1.03
1.24
2.06
3.76
2.79
f1 (ppm)

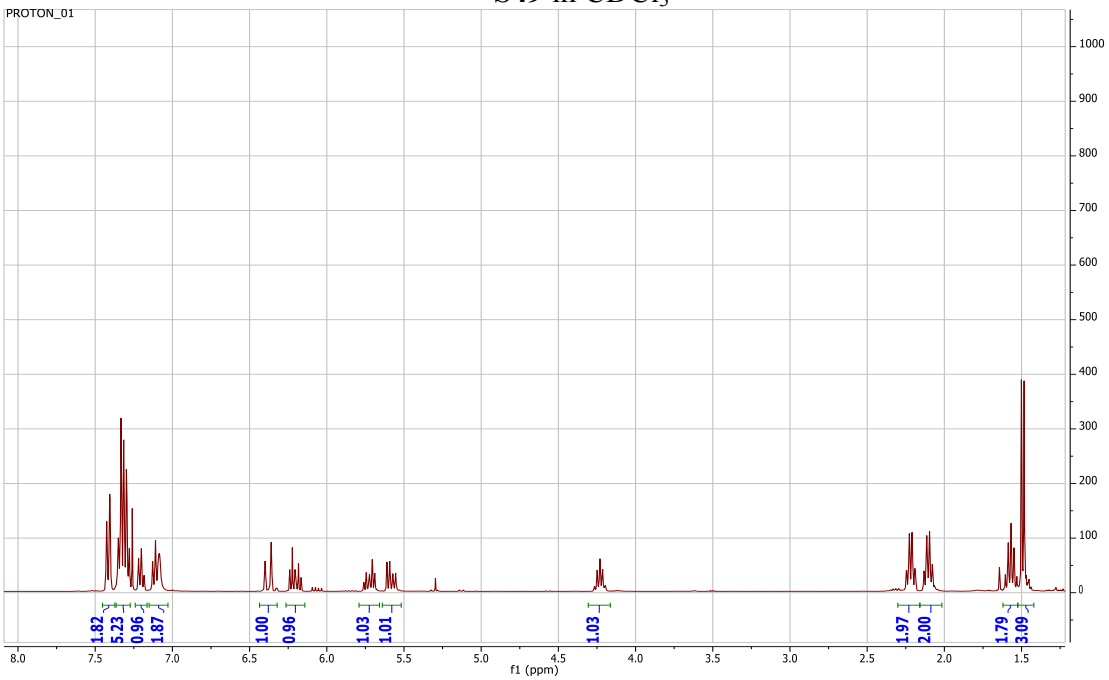

H
N
PhO2S
S
O
Ph
Me

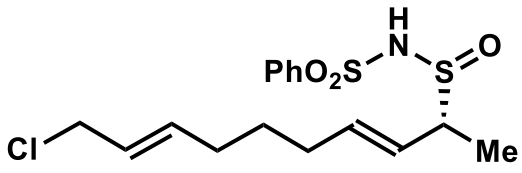
9l in $CDCl_3$


PLII-299D-T2-1H
STANDARD FLUORINE PARAMETERS
2.11
1.30
2.42
4.36
1.44
1.00
0.92
1.01
1.06
0.90
4.16
2.24
3.35
f1 (ppm)
CARBON_01
f1 (ppm)

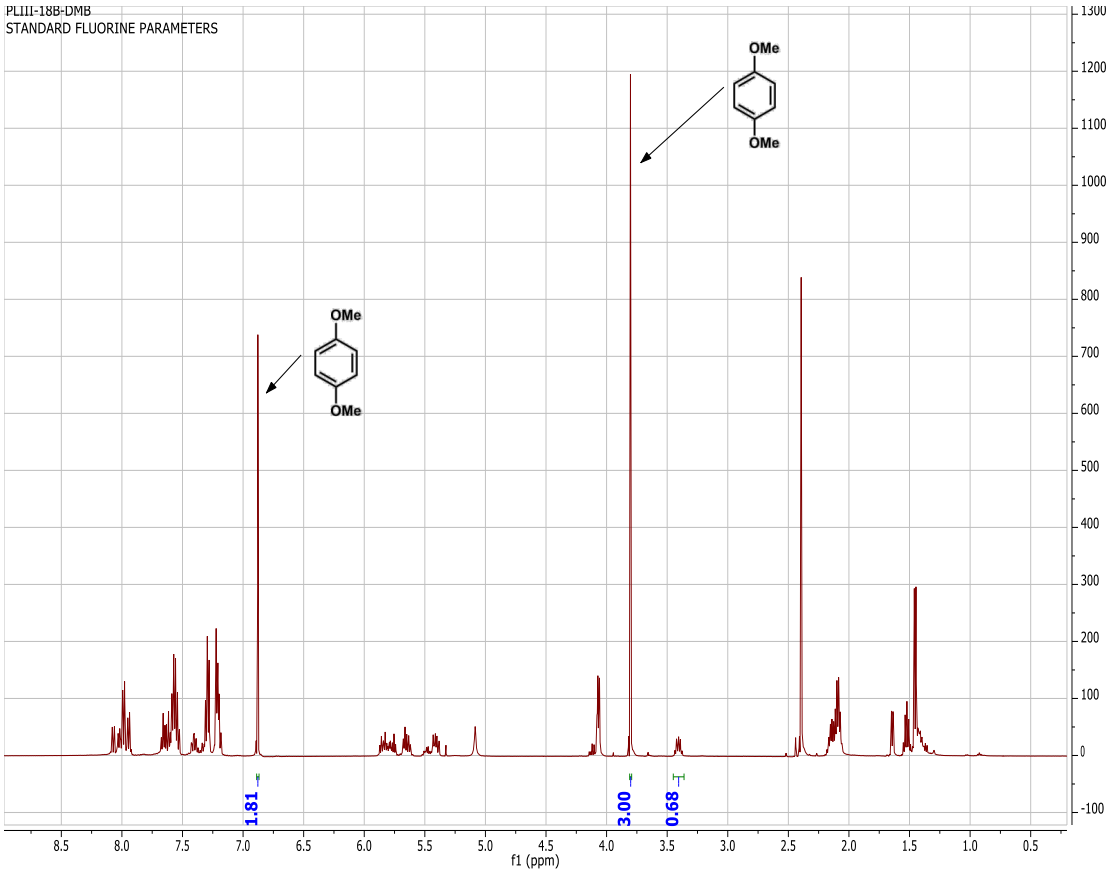

O
Ph
N
H
S
Ph
Me

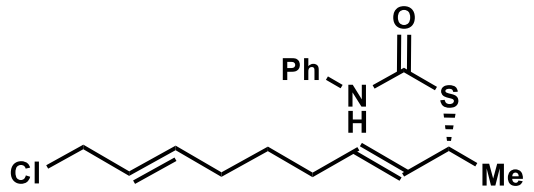
S49 in $CDCl_3$


PROTON_01
1000
900
800
700
600
500
400
300
200
100
0
1.82
5.23
0.96
1.87
1.00
0.96
1.03
1.01
1.03
1.97
2.00
1.79
3.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

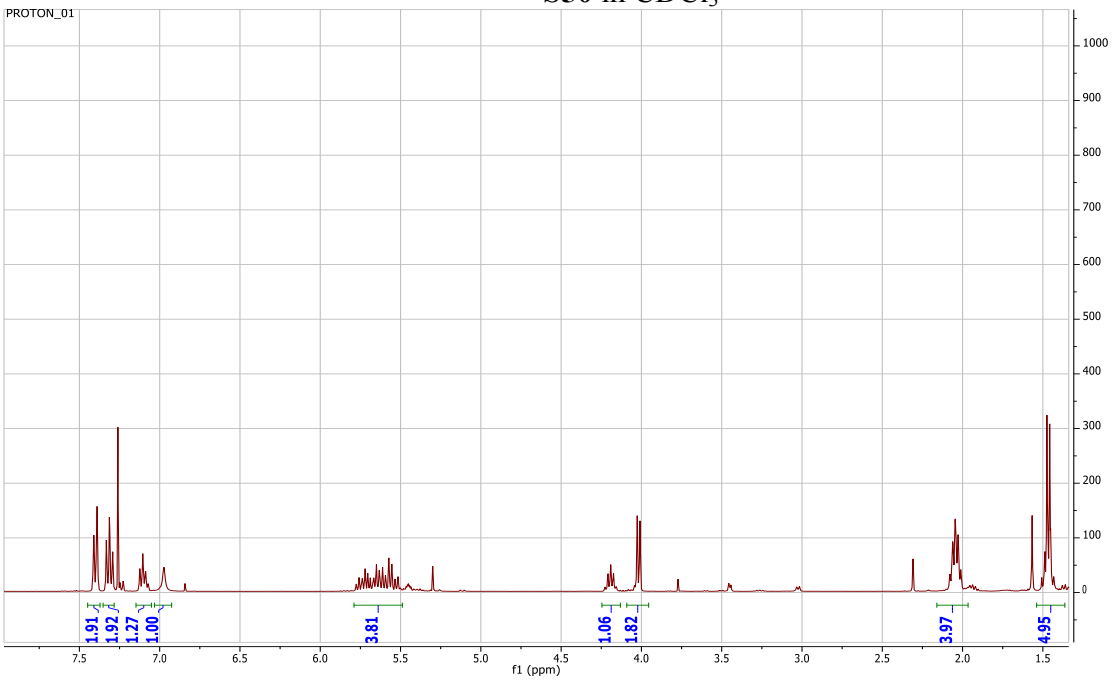


9m in $CDCl_3$ (Crude reaction mixture)



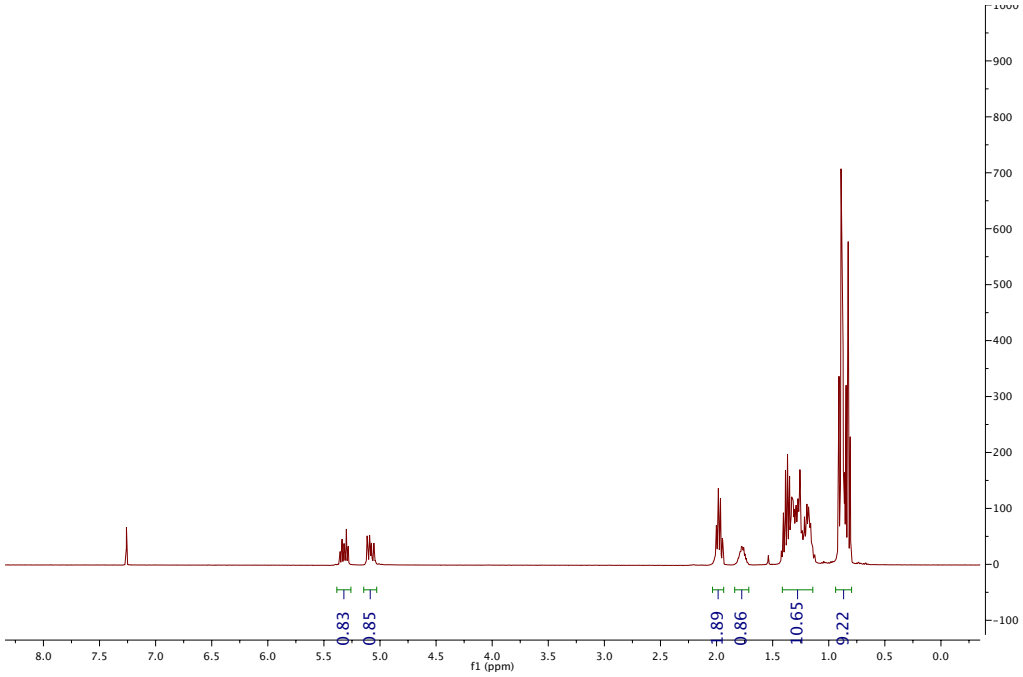

O
Ph
N
H
S
Cl
Me

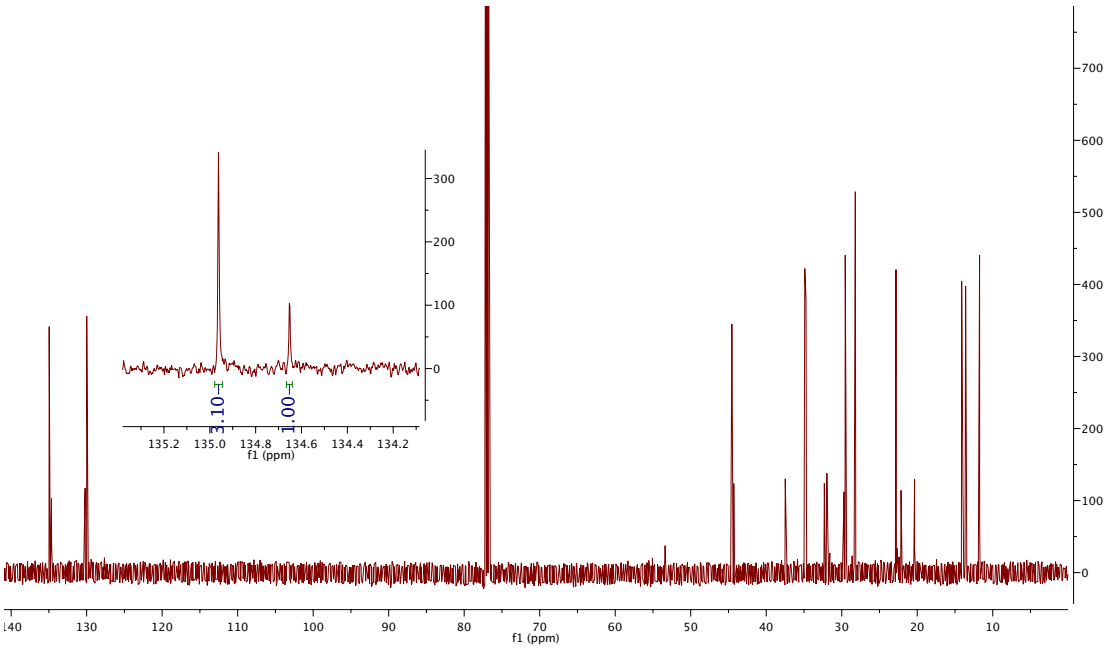
S50 in $CDCl_3$

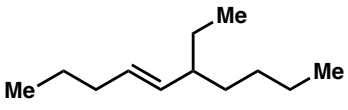

PROTON_01
1000
900
800
700
600
500
400
300
200
100
0
1.91
1.92
1.27
1.00
3.81
1.06
1.82
3.97
4.95
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

major regioisomer + ***minor regioisomer***

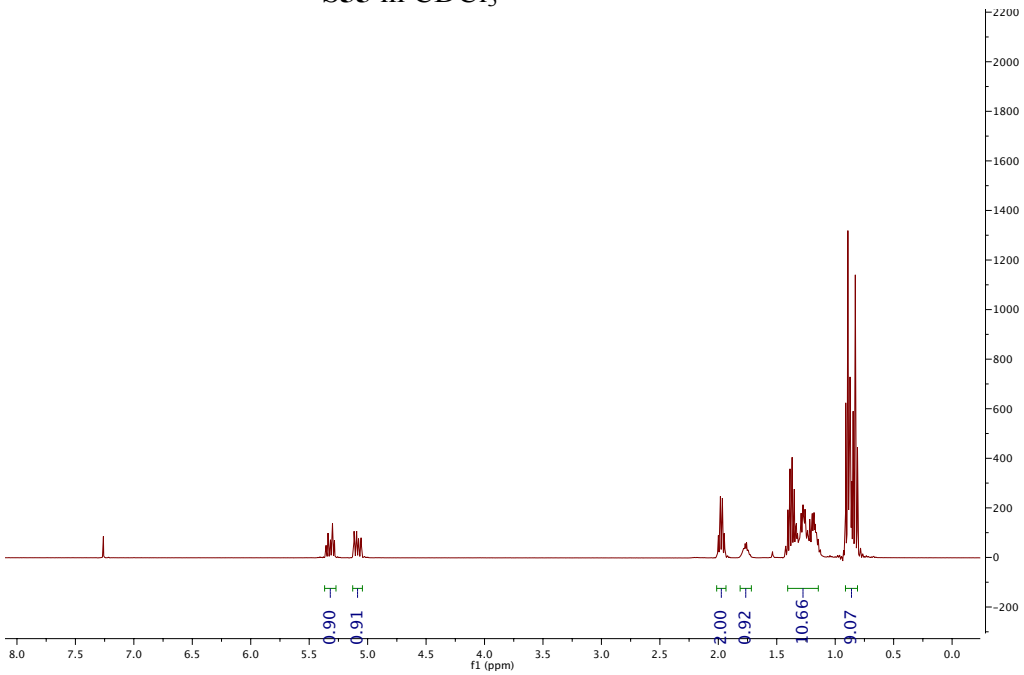
10 in $CDCl_3$

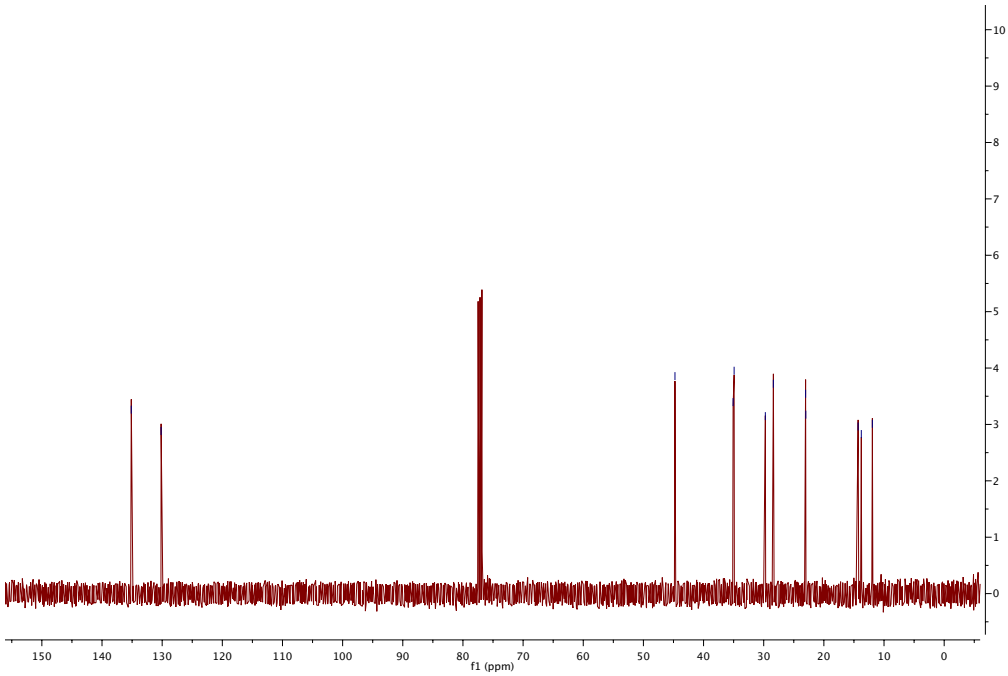


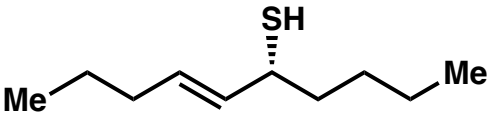




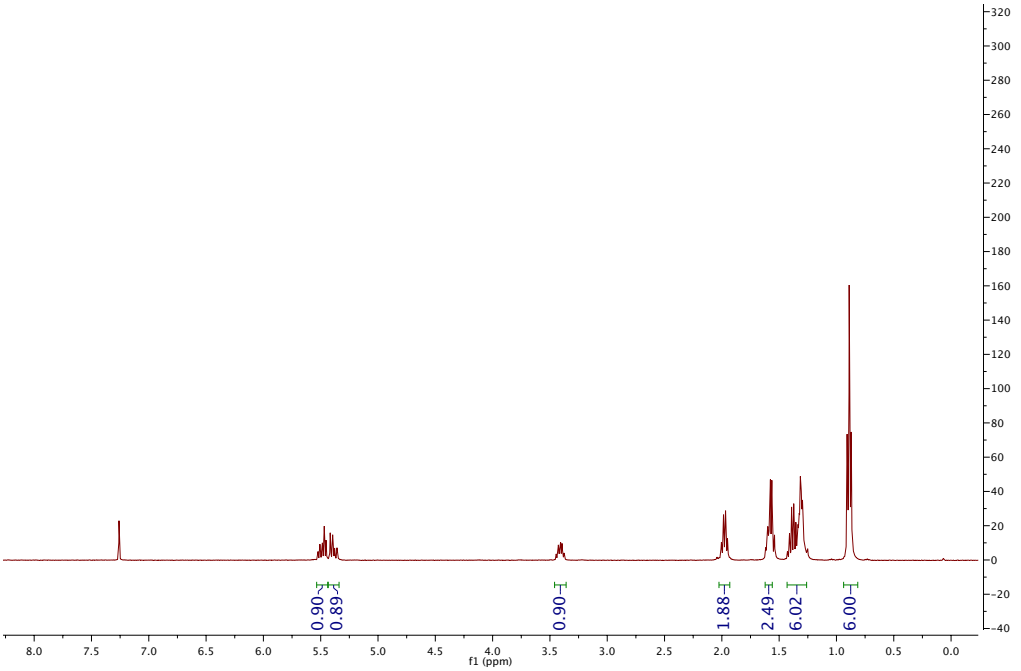
S55 in $CDCl_3$

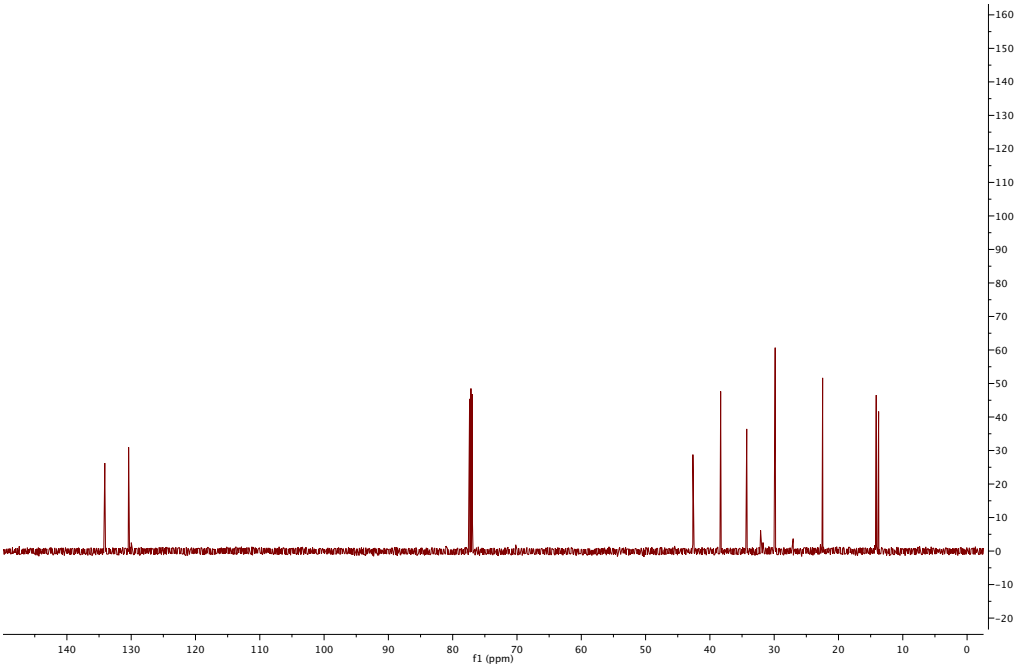


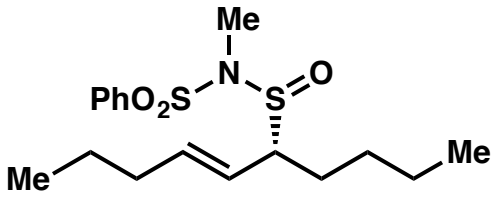




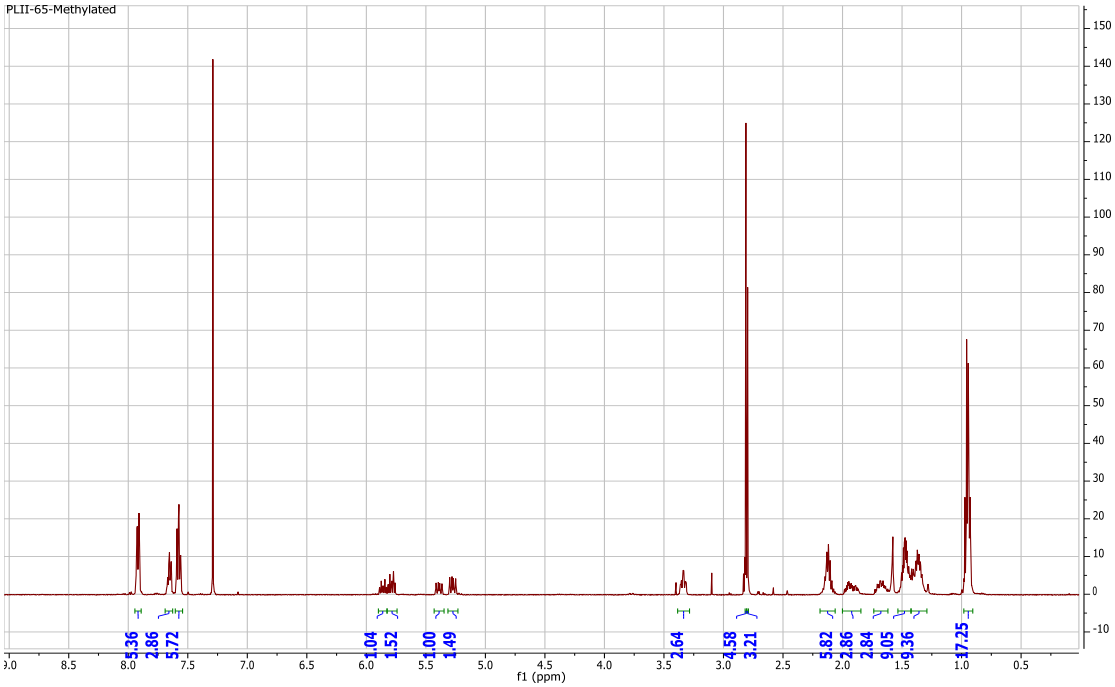
11 in $CDCl_3$

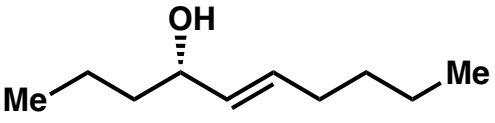




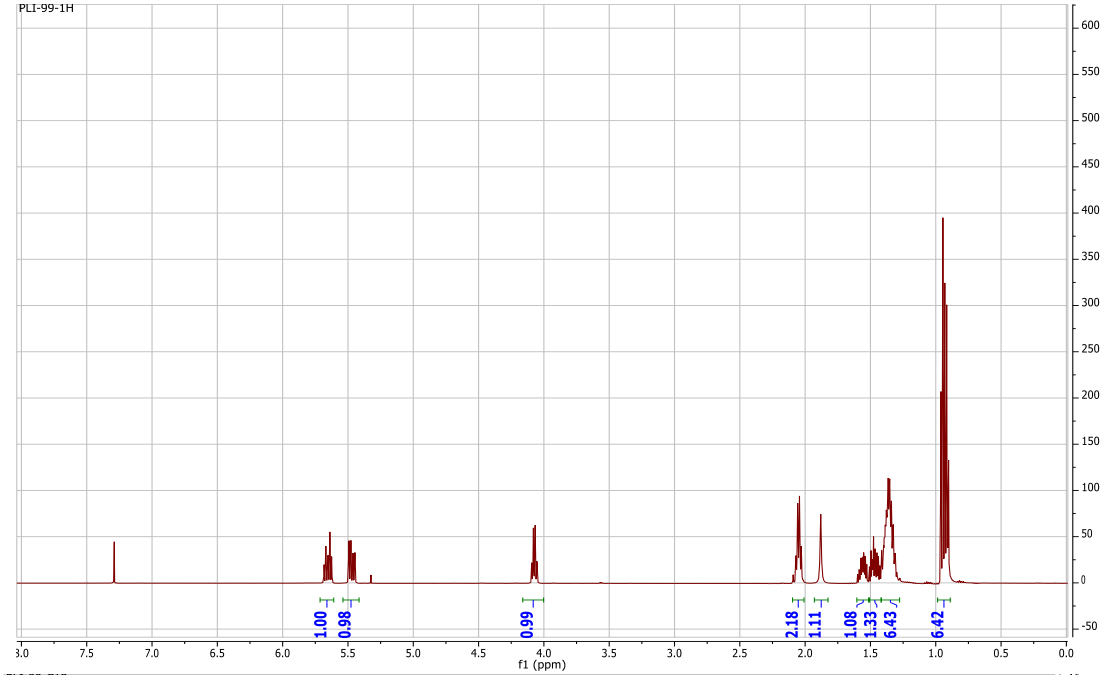

Me
N
PhO2S
S
O
Me
Me

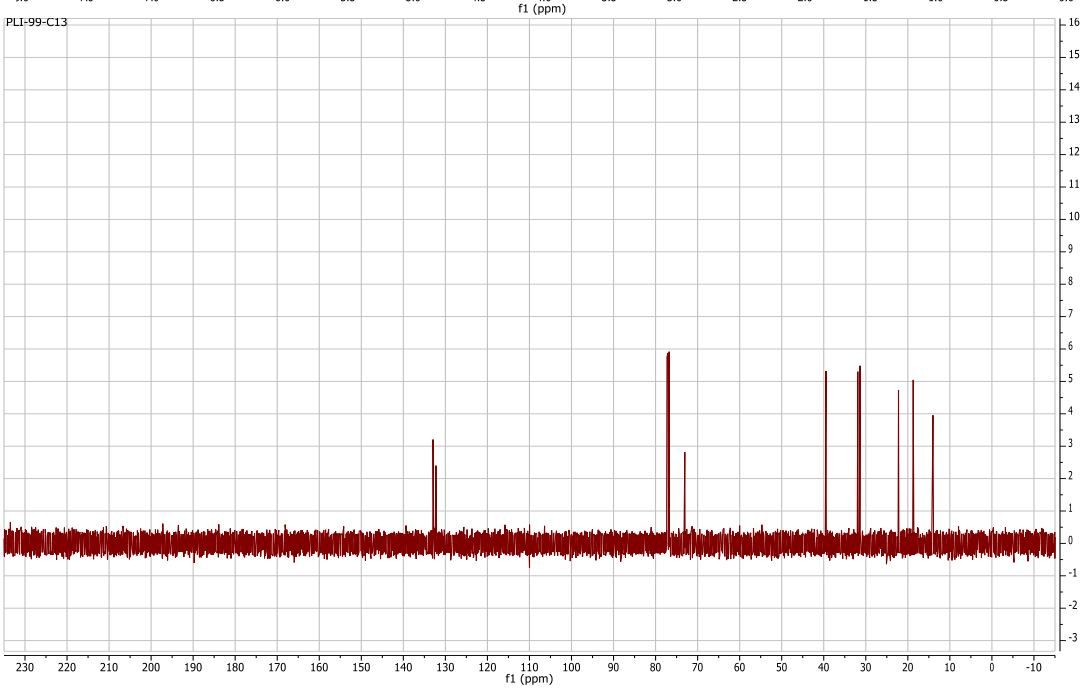
S51 in $CDCl_3$

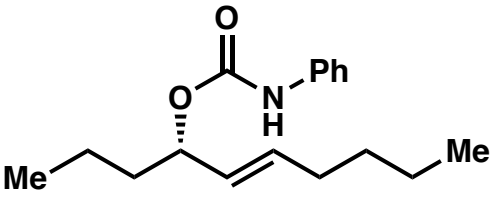

PLII-65-Methylated
f1 (ppm)
5.36
2.86
5.72
1.04
1.52
1.00
1.49
2.64
4.58
3.21
5.82
2.86
2.84
9.05
9.36
17.25


OH
Me
Me

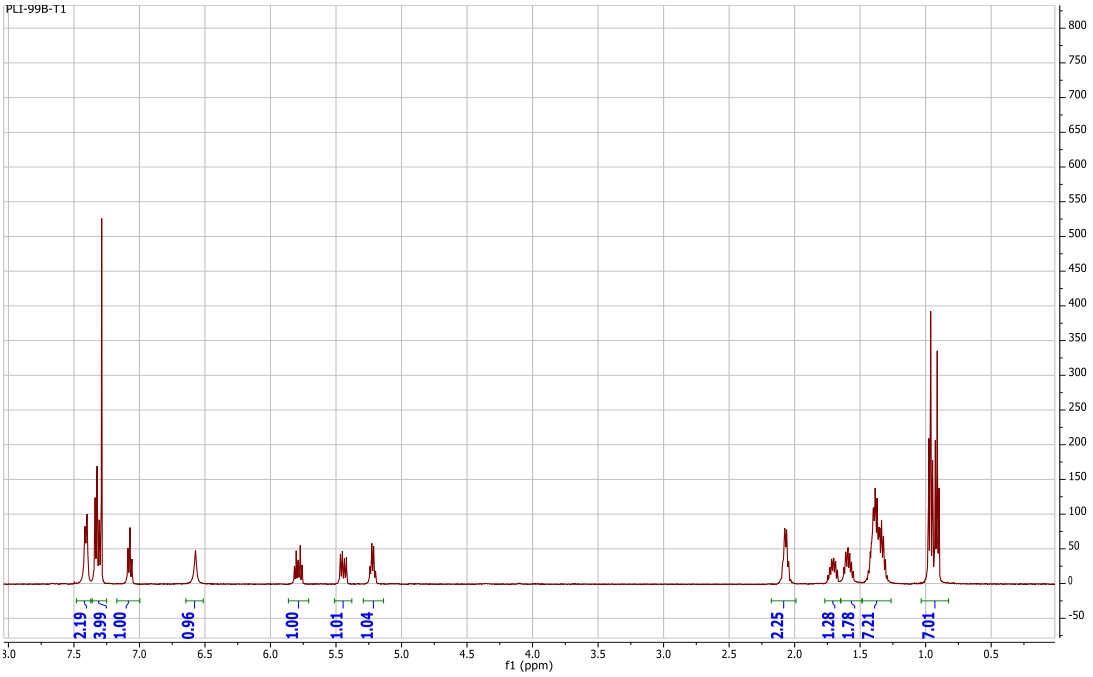
12 in $CDCl_3$

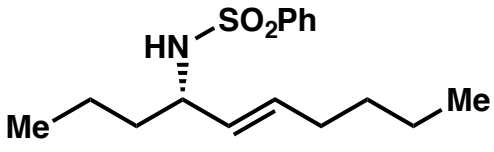

PLI-99-1H
1.00
0.98
0.99
2.18
1.11
1.08
1.33
6.43
6.42
f1 (ppm)


PLI-99-C13
f1 (ppm)

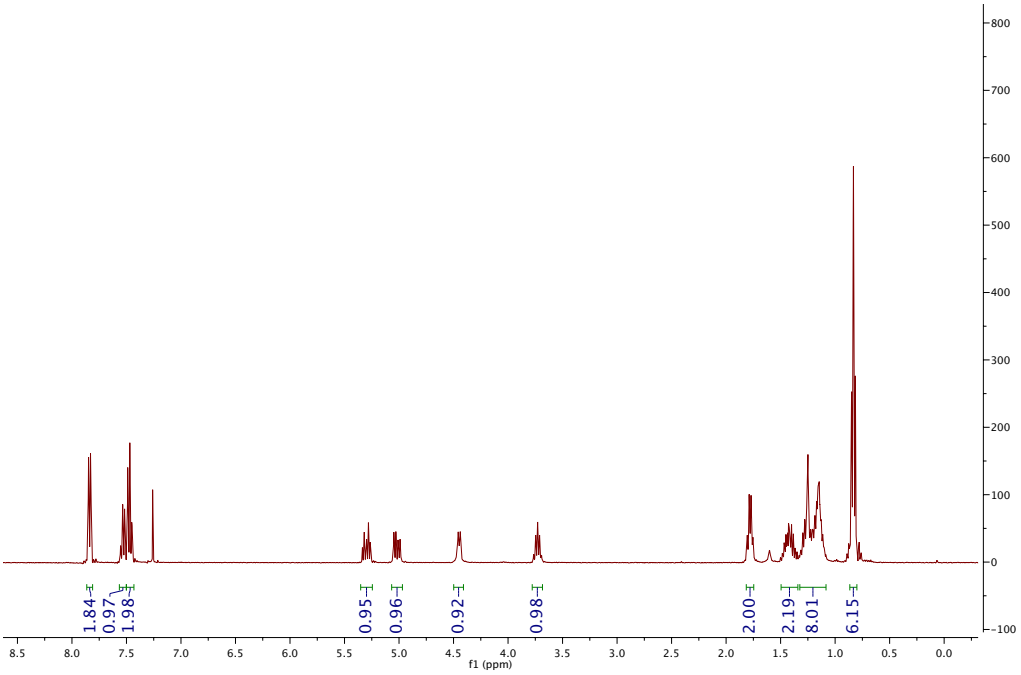

O
O
N
H
Ph
Me
Me

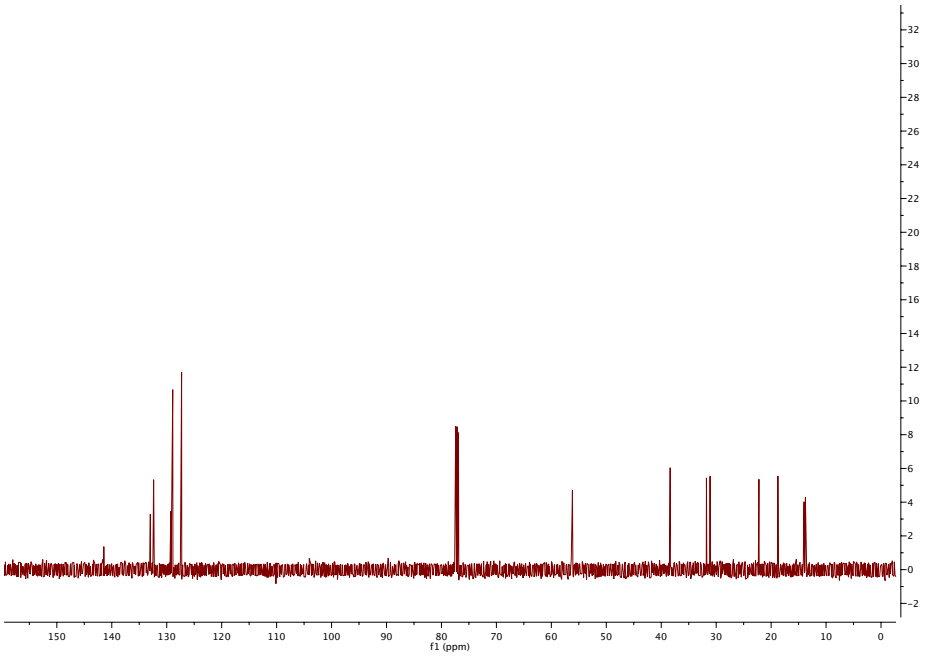
S52 in $CDCl_3$

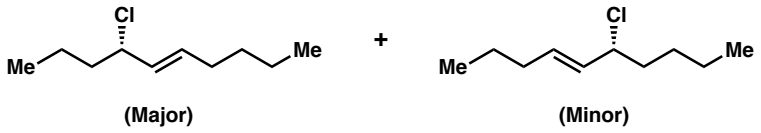

PLI-99B-T1
f1 (ppm)
2.19
3.99
1.00
0.96
1.00
1.01
1.04
2.25
1.28
1.78
7.21
7.01


HN
SO2Ph
Me
Me

13 in $CDCl_3$

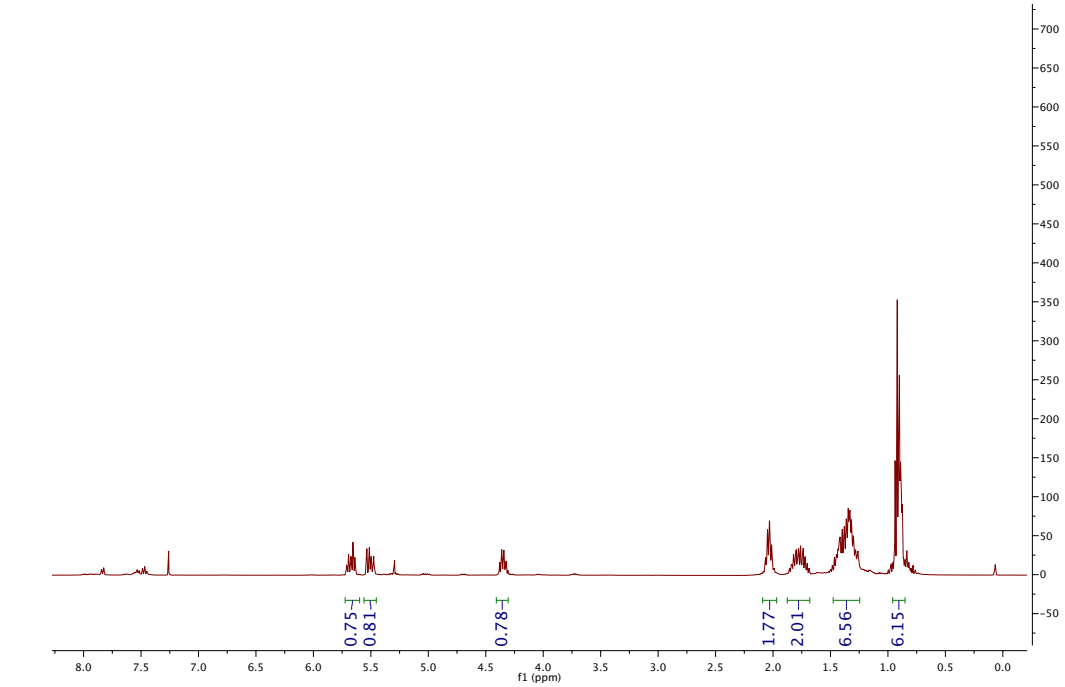

1.84
0.97
1.98
0.95
0.96
0.92
0.98
2.00
2.19
8.01
6.15
f1 (ppm)

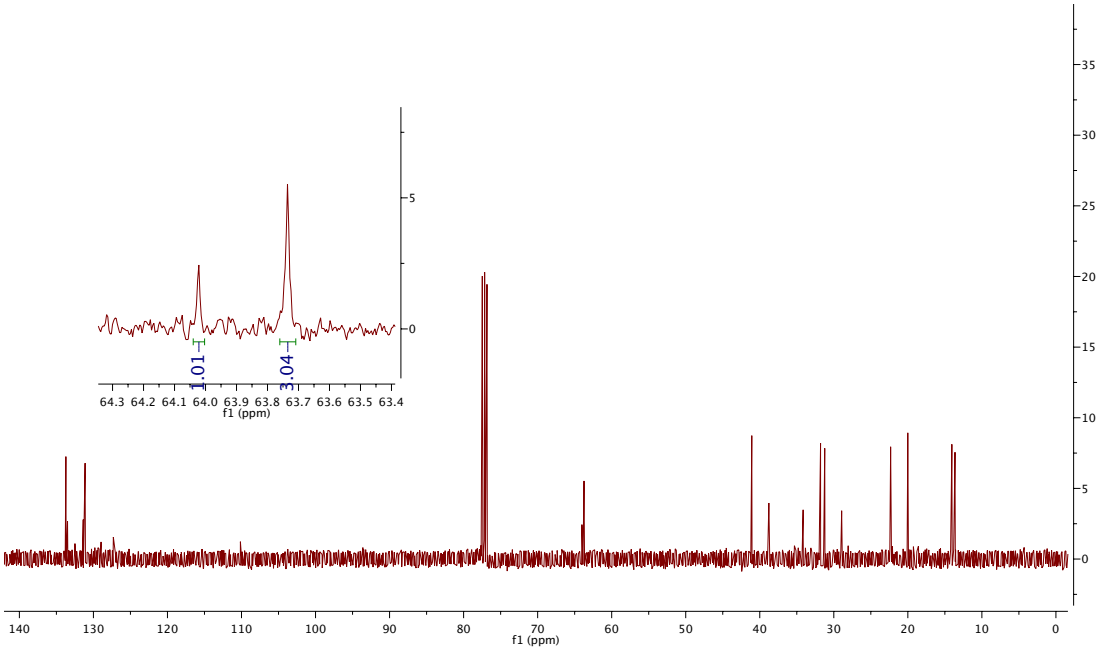

f1 (ppm)

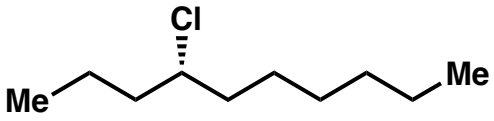


(Major) (Minor)

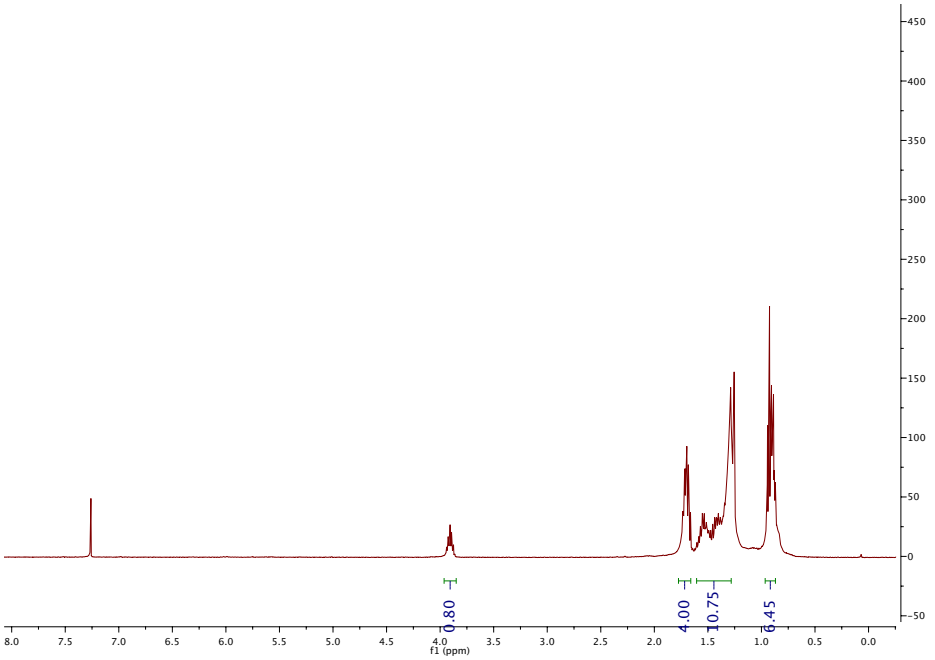
14 in $CDCl_3$

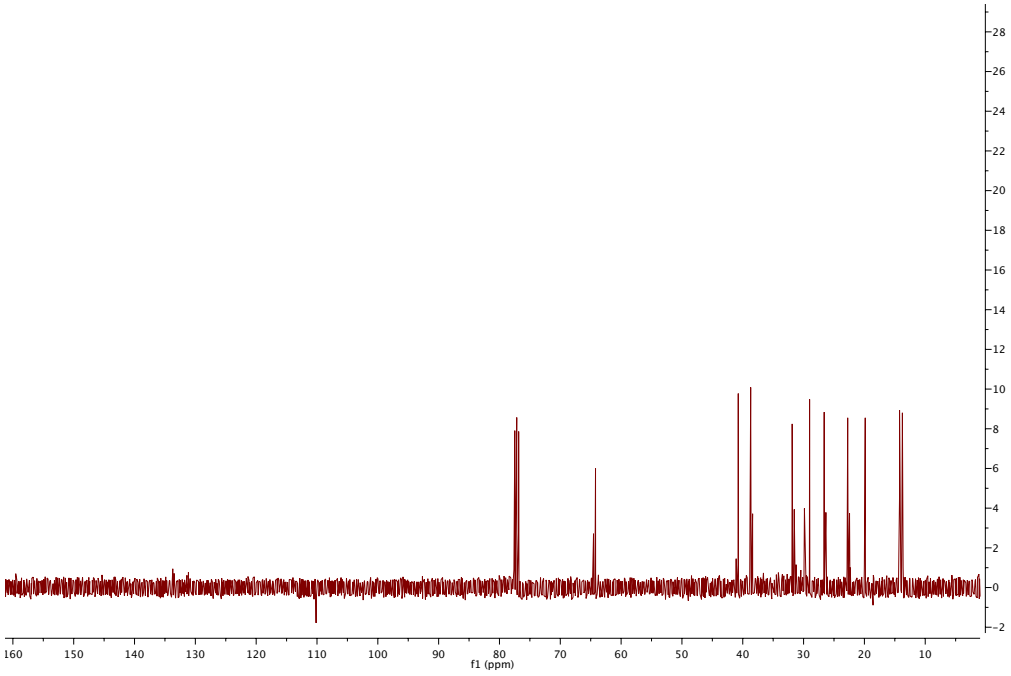


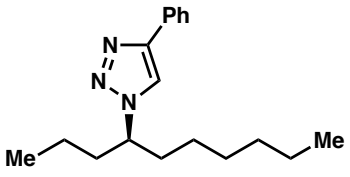




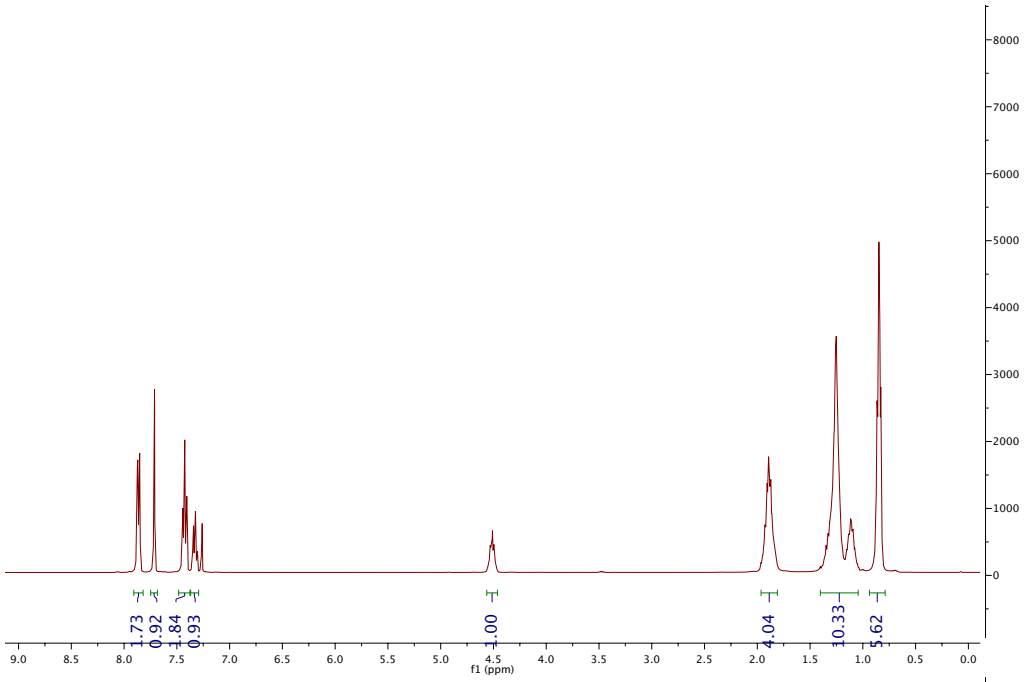
S53 in $CDCl_3$

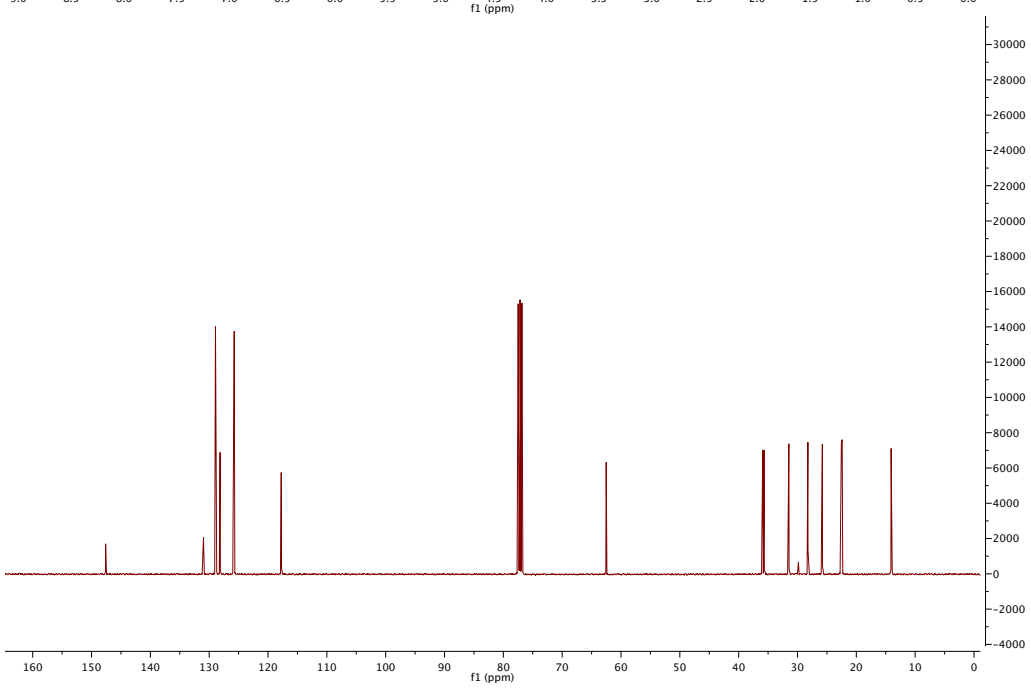


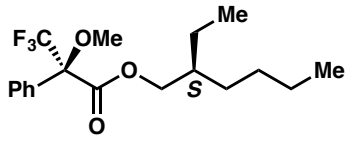




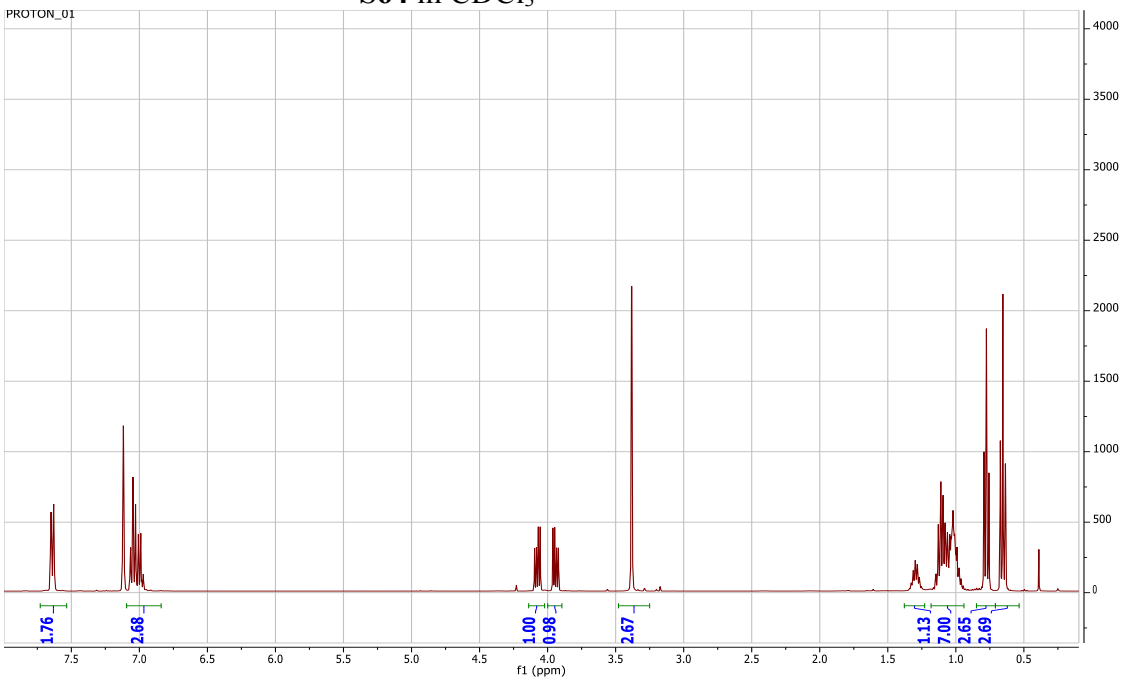
S54 in $CDCl_3$

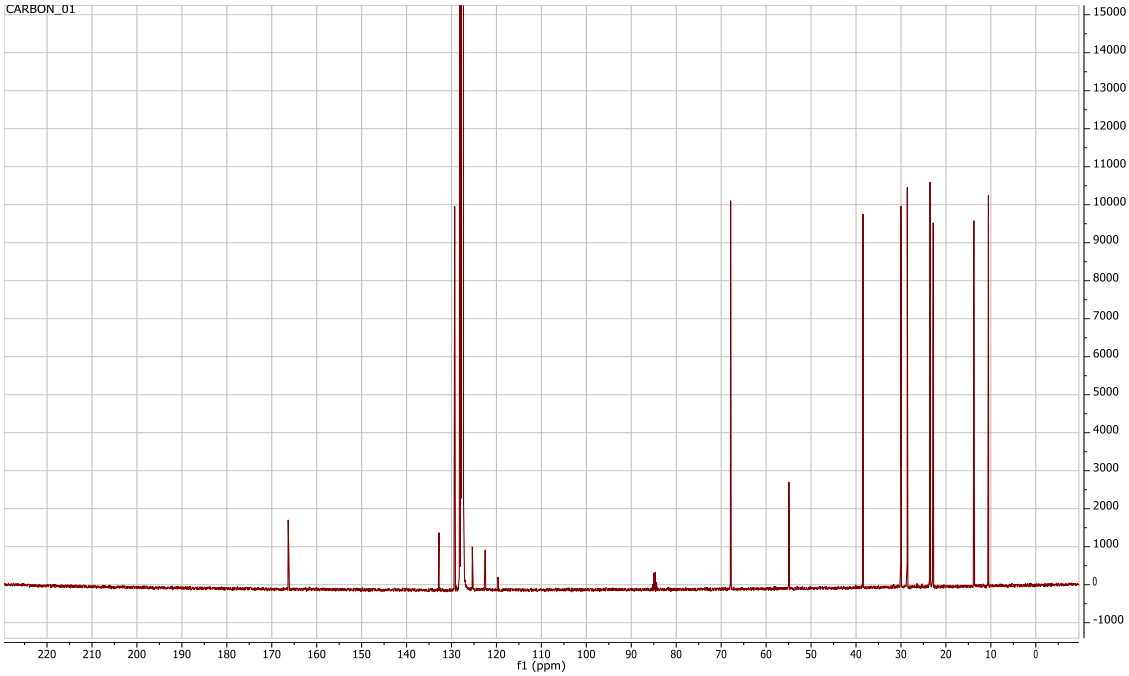


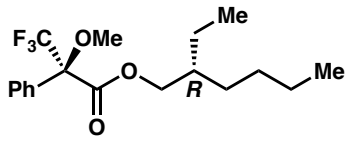



F3C
OMe
Ph
O
O
S
Me
Me

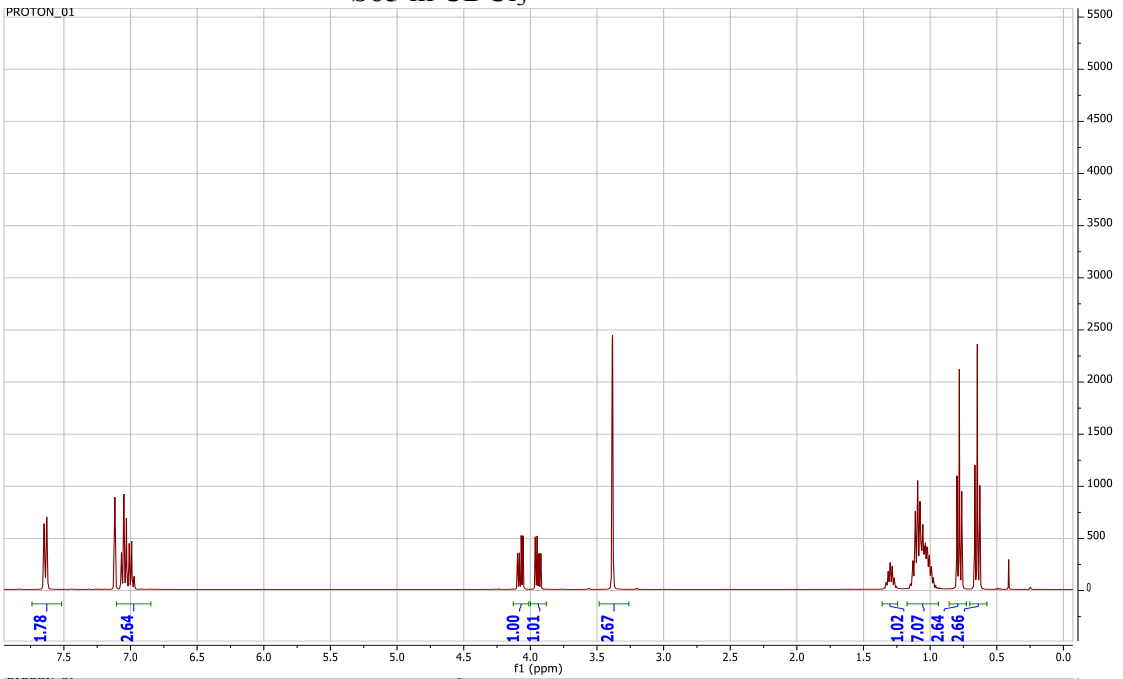
S64 in $CDCl_3$

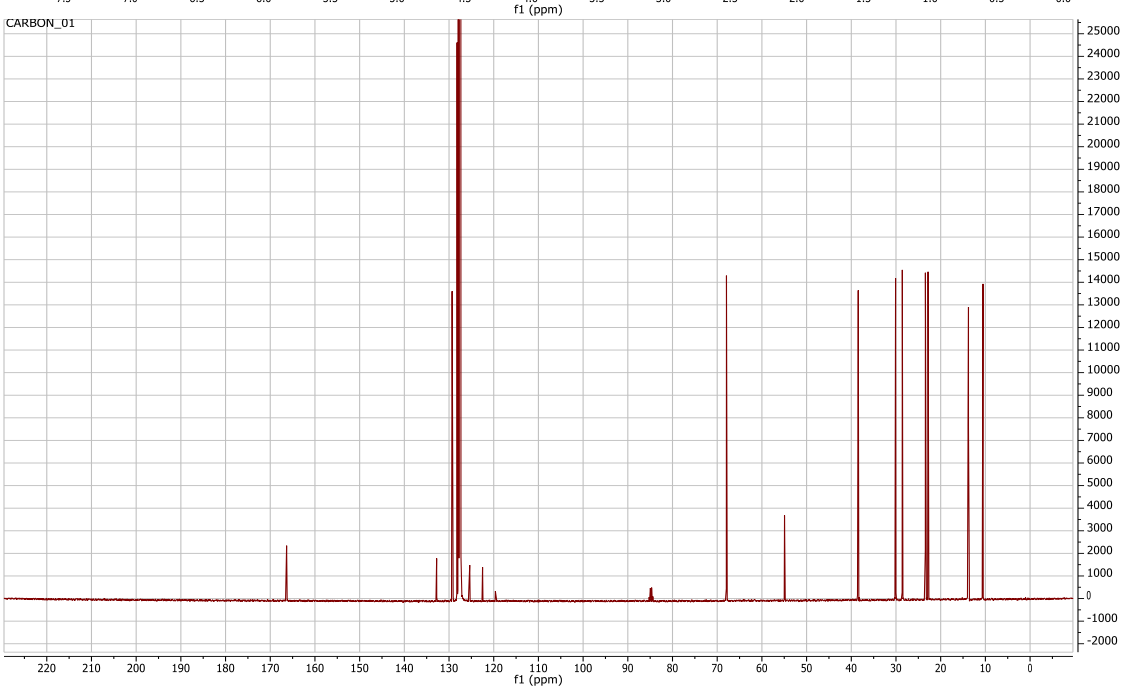

PROTON_01
1.76
2.68
1.00
0.98
2.67
1.13
7.00
2.65
2.69
f1 (ppm)

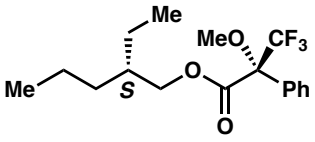

CARBON_01
f1 (ppm)


Me
F3C
OMe
Ph
O
R
Me
O

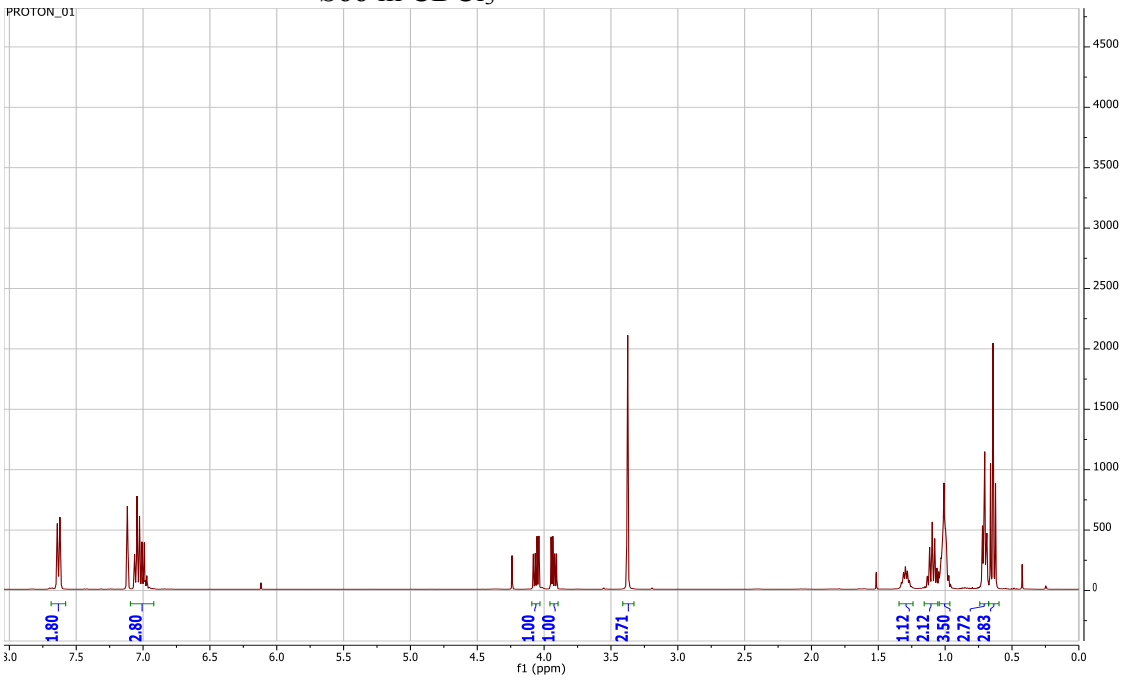
S65 in $CDCl_3$

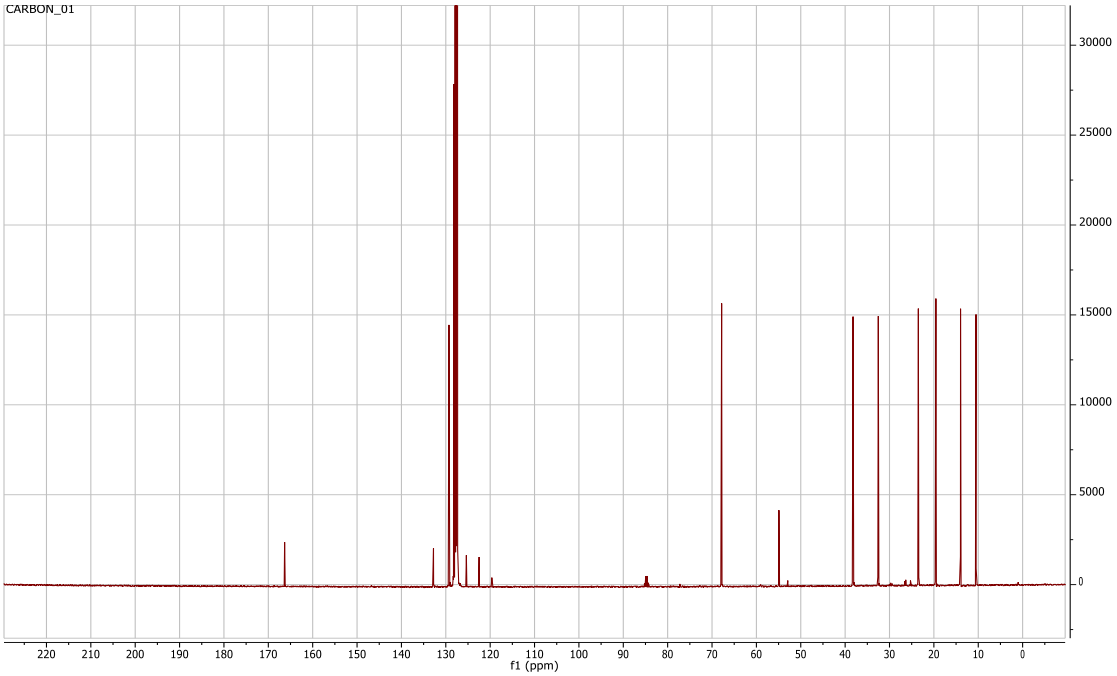

PROTON_01
1.78
2.64
1.00
1.01
2.67
1.02
7.07
2.64
2.66
f1 (ppm)

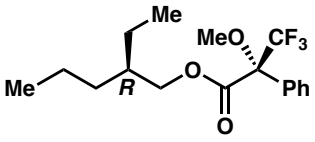

CARBON_01
f1 (ppm)


Me
MeO
CF3
Me
S
O
Ph
O

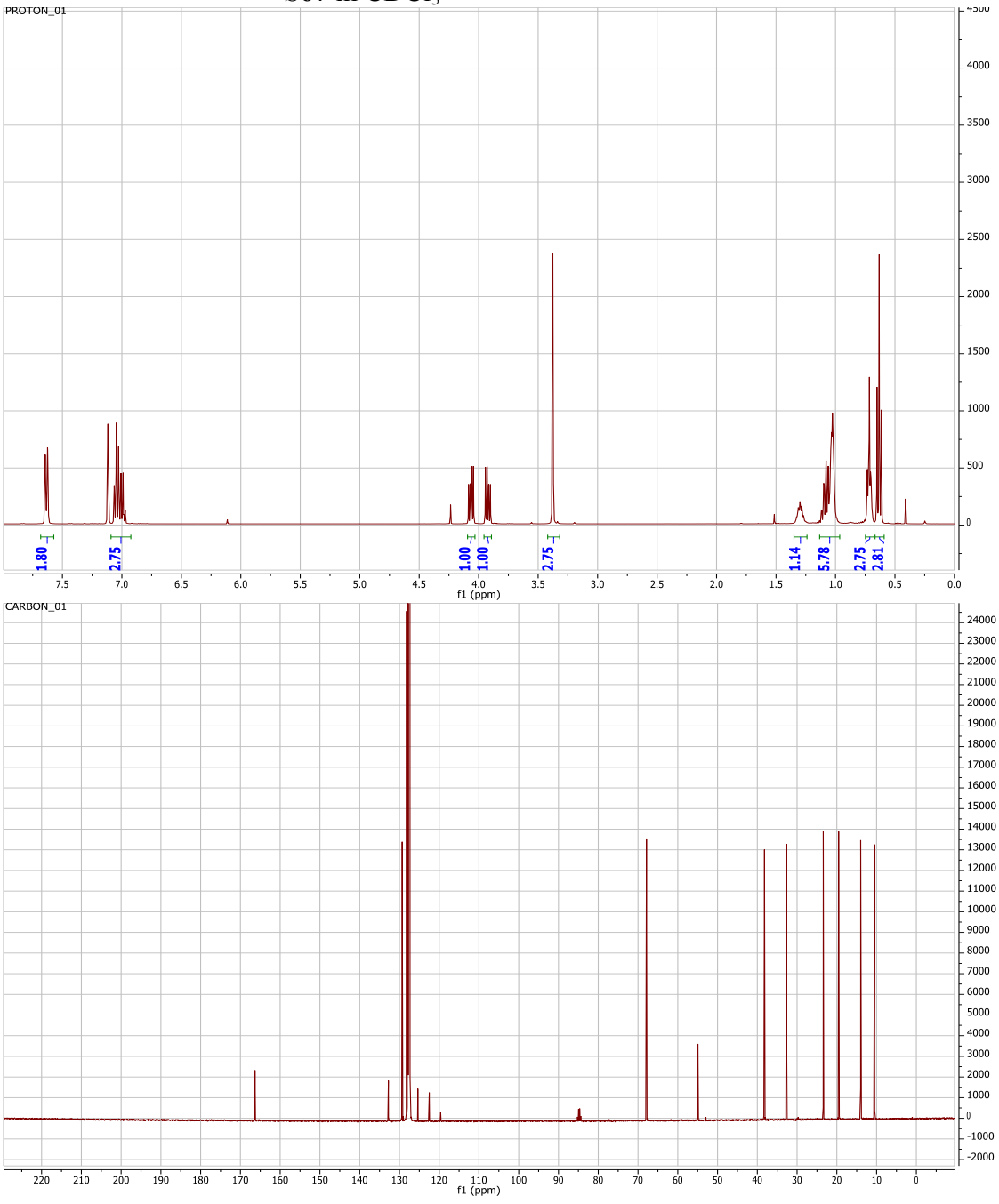
S66 in $CDCl_3$

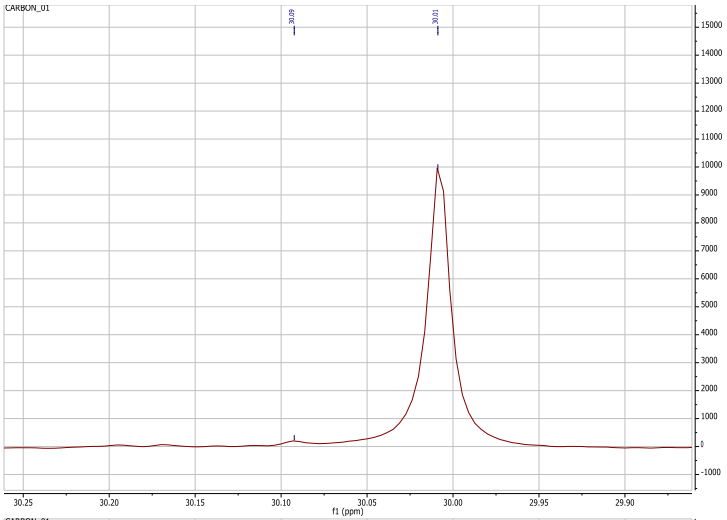

PROTON_01
1.80
2.80
1.00
1.00
2.71
1.12
2.12
3.50
2.72
2.83
f1 (ppm)

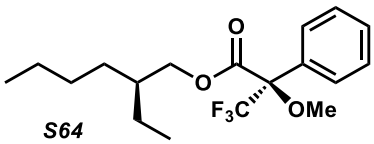

CARBON_01
f1 (ppm)


Me
MeO
CF3
Me
R
O
Ph
O

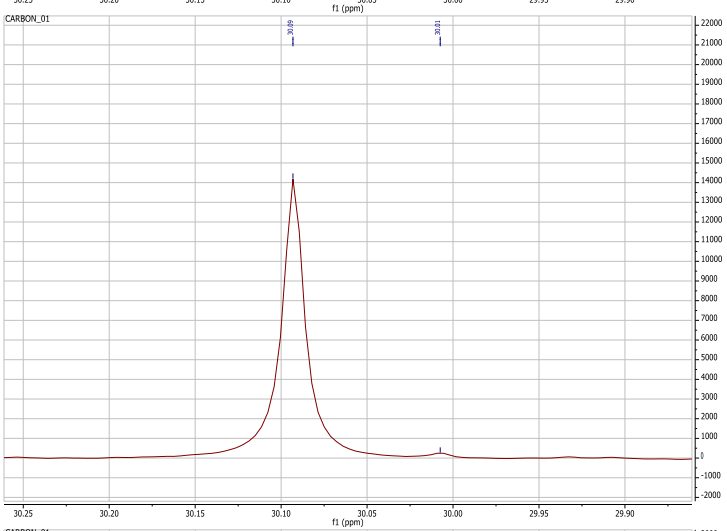
S67 in $CDCl_3$

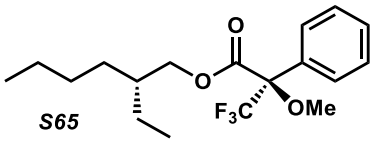

PROTON_01
1.80
2.75
1.00
1.00
2.75
1.14
5.78
2.75
2.81
f1 (ppm)
CARBON_01
f1 (ppm)



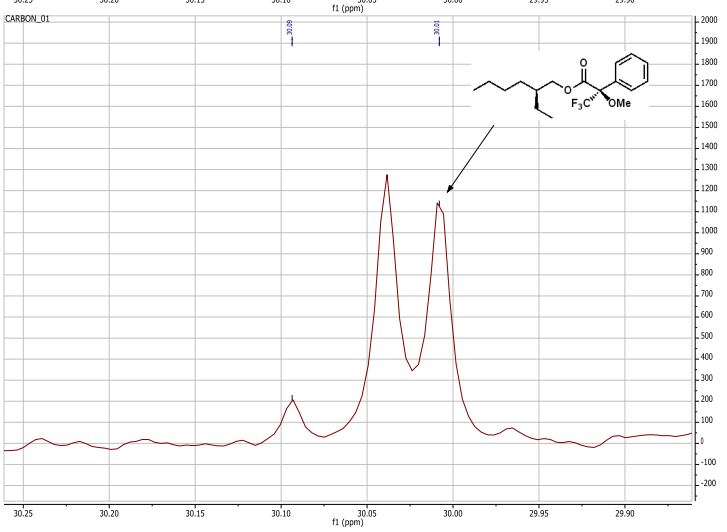


S64

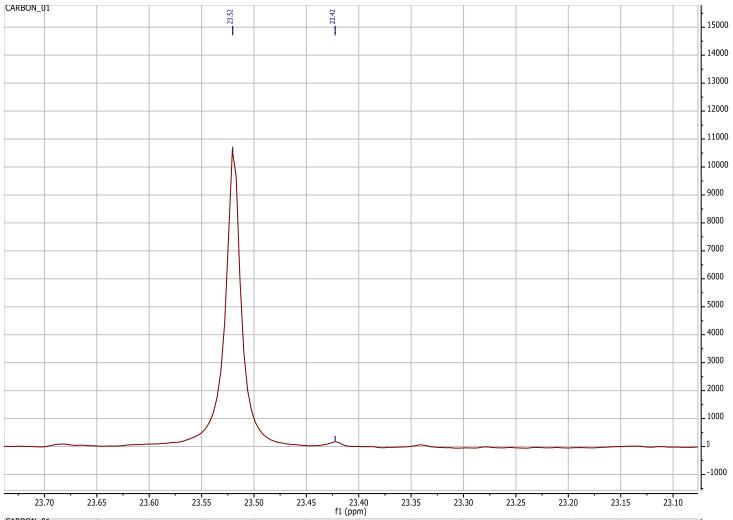


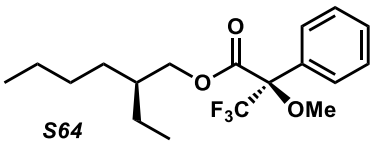


S65

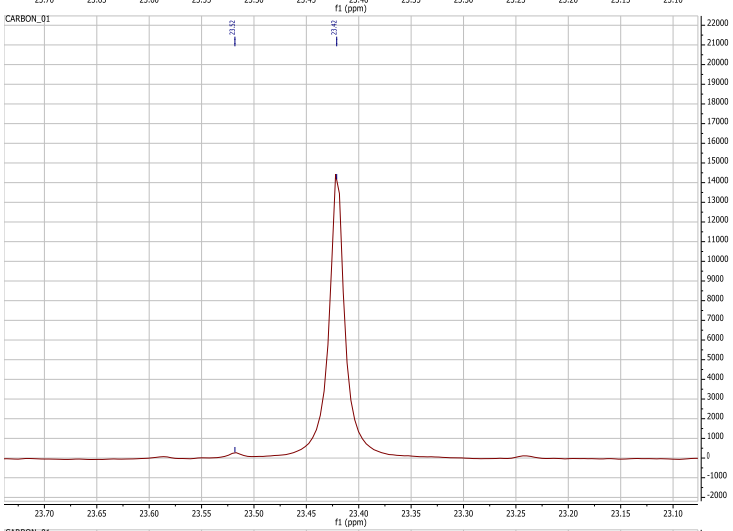


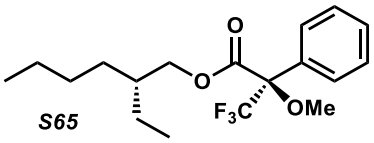
Crude mosher esters from ***10***



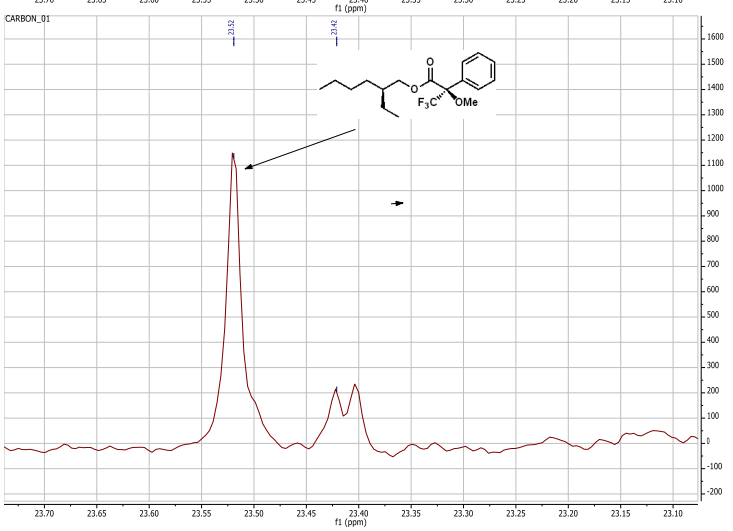


S64

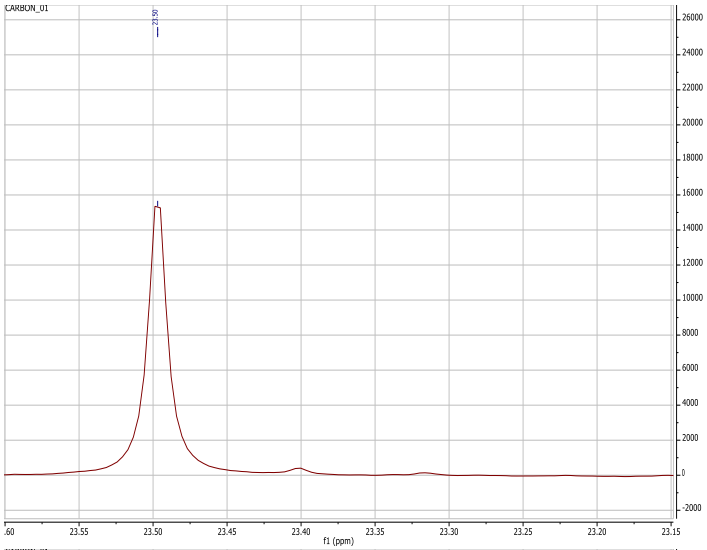


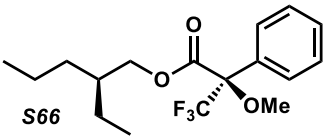


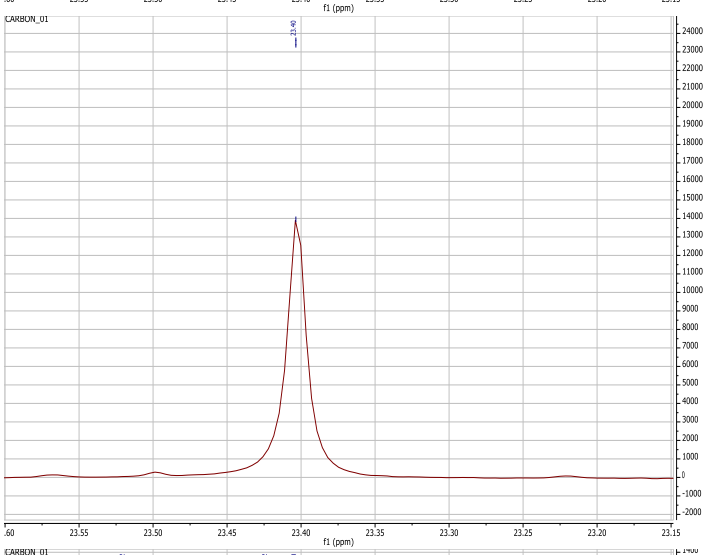
S65

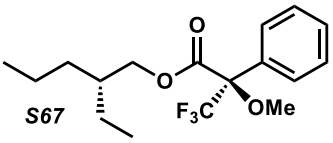


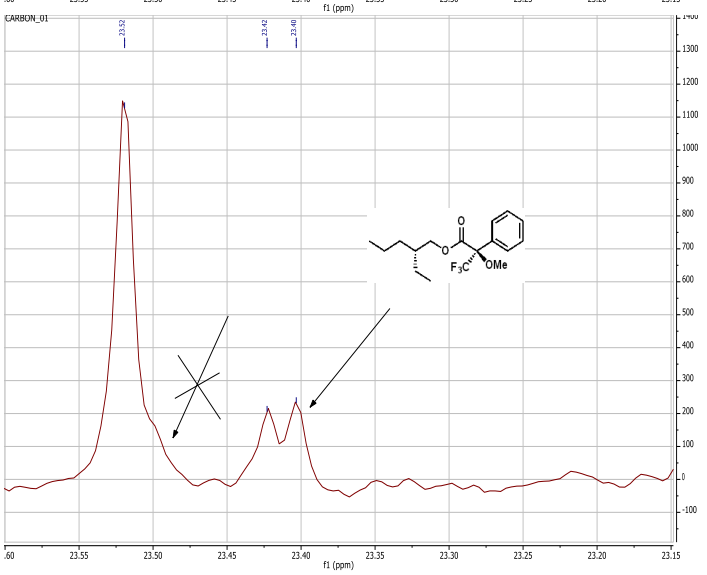
Crude mosher esters from ***10***



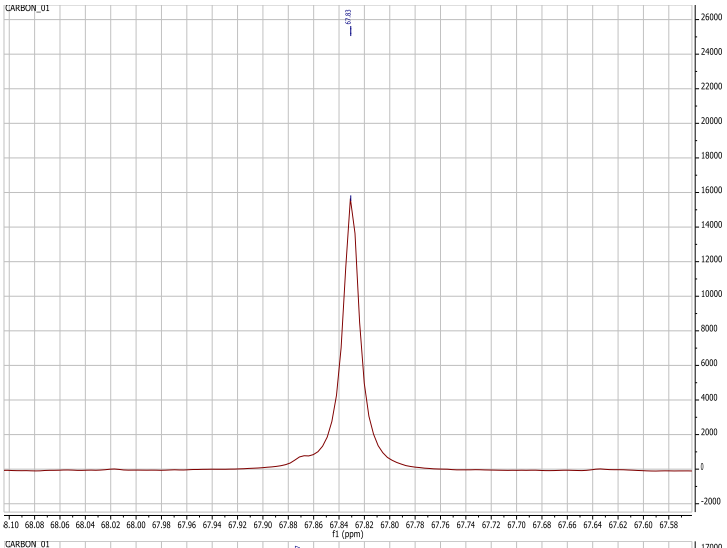


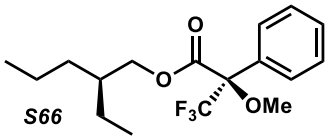


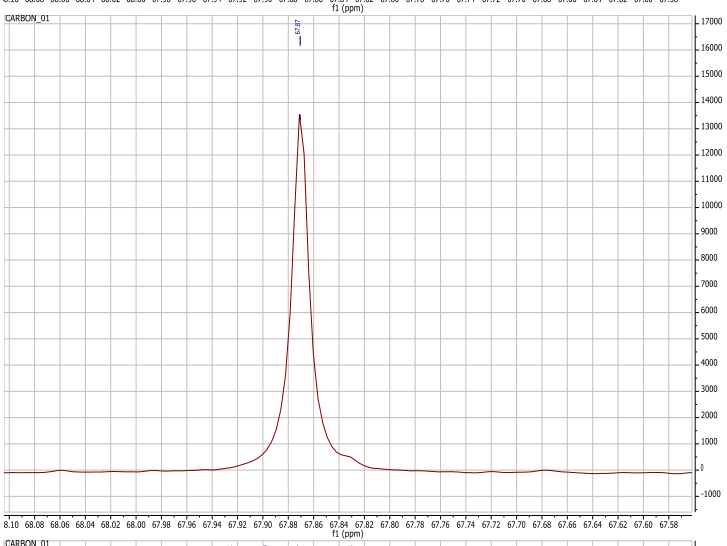


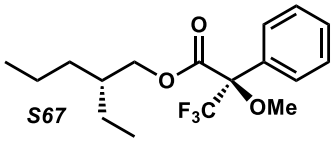


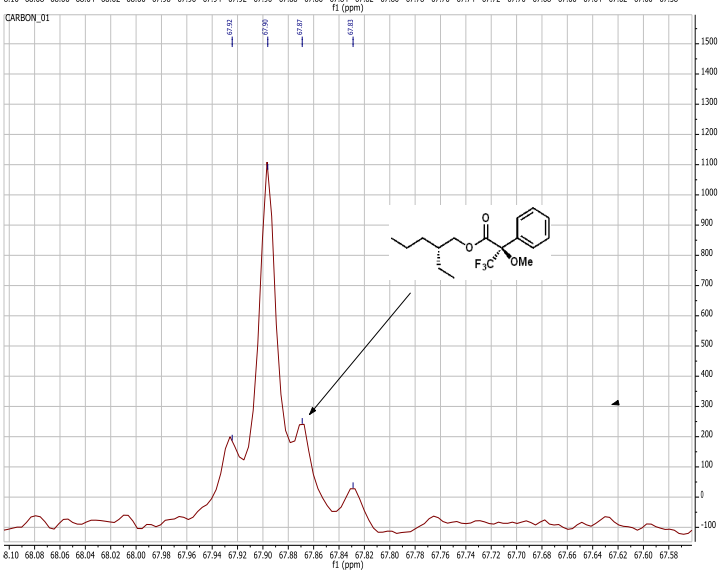
Crude mosher esters from ***10***





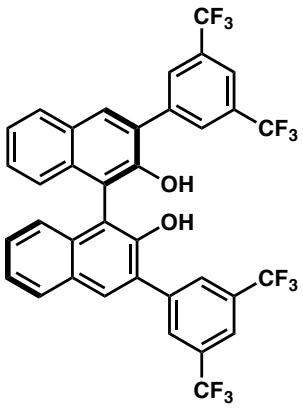






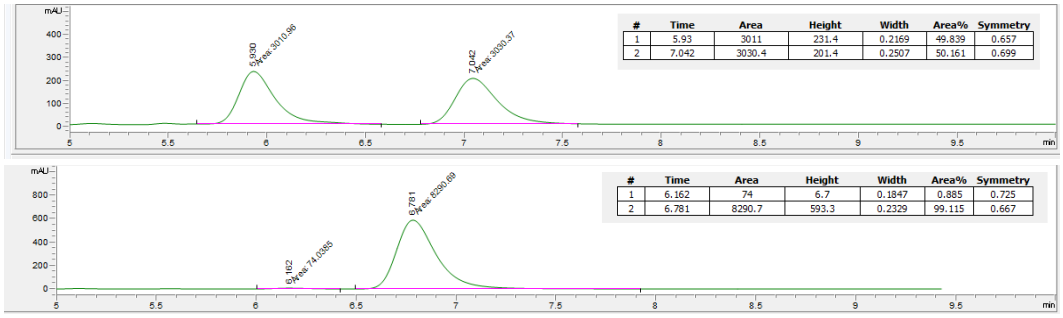
Crude mosher esters from ***10***

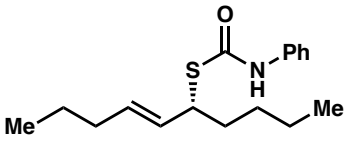
HPLC Data



6

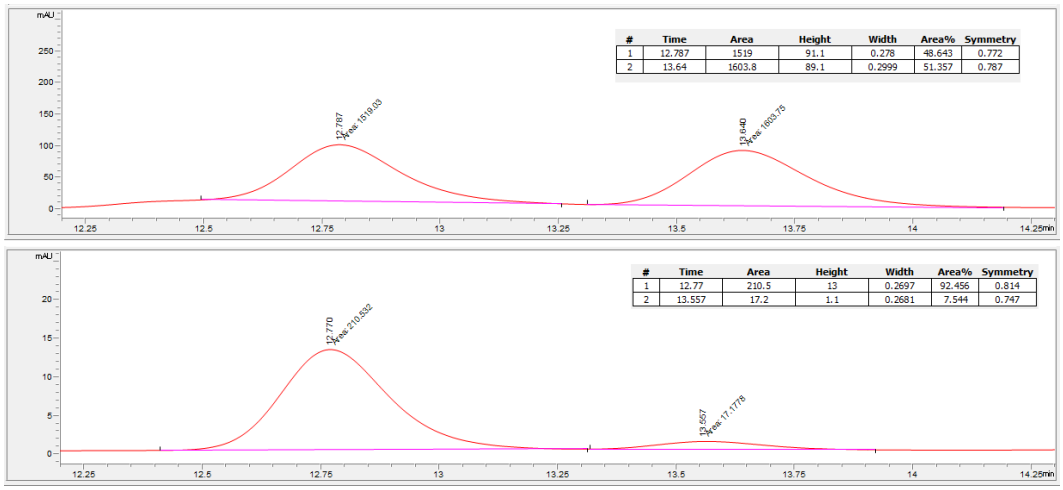
CHIRALCEL OD-H 97:03 IPA:Hexane 0.6 ml/min



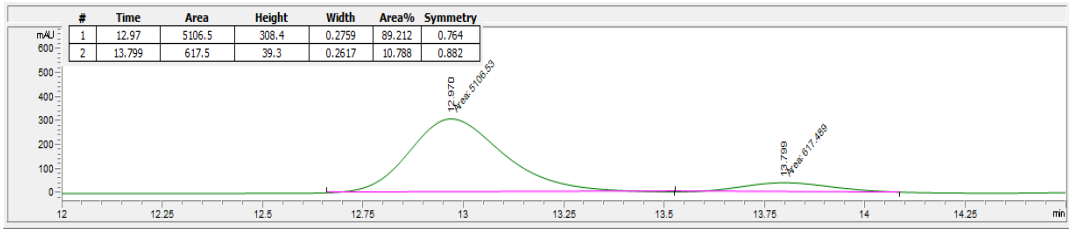


S29

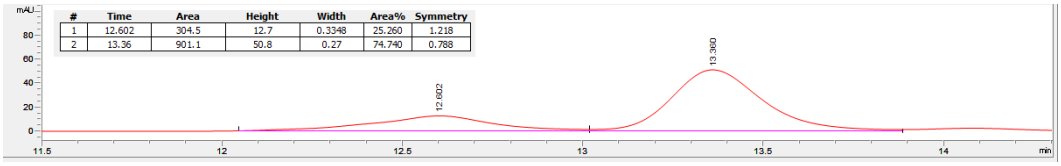
CHIRALCEL OJ-H 95:05 Hex/IPA, 0.5 mL/min, 220 nm

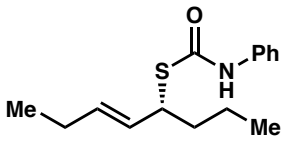


10 mmol scale reaction



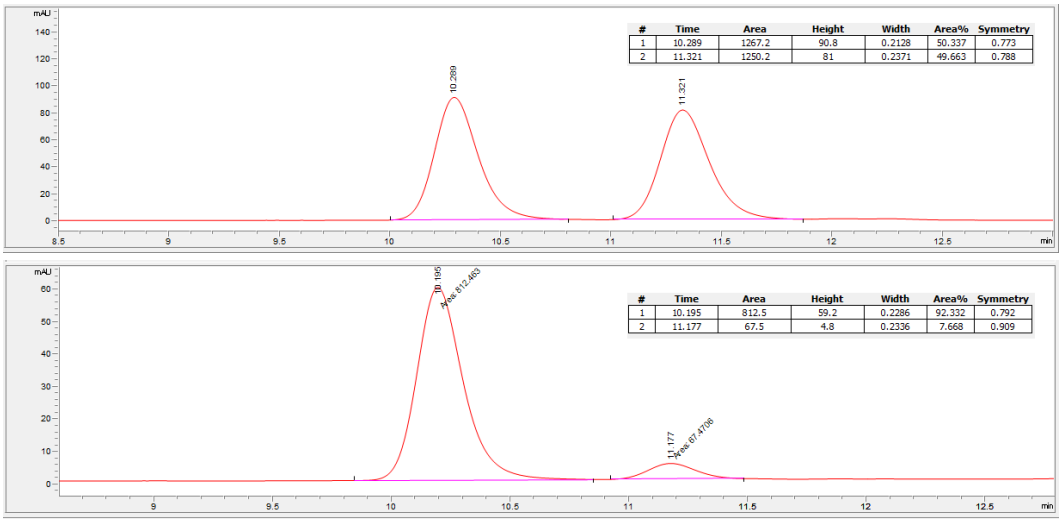
From *trans*-5-decene:

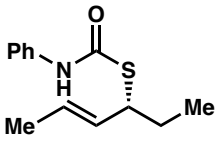




S30

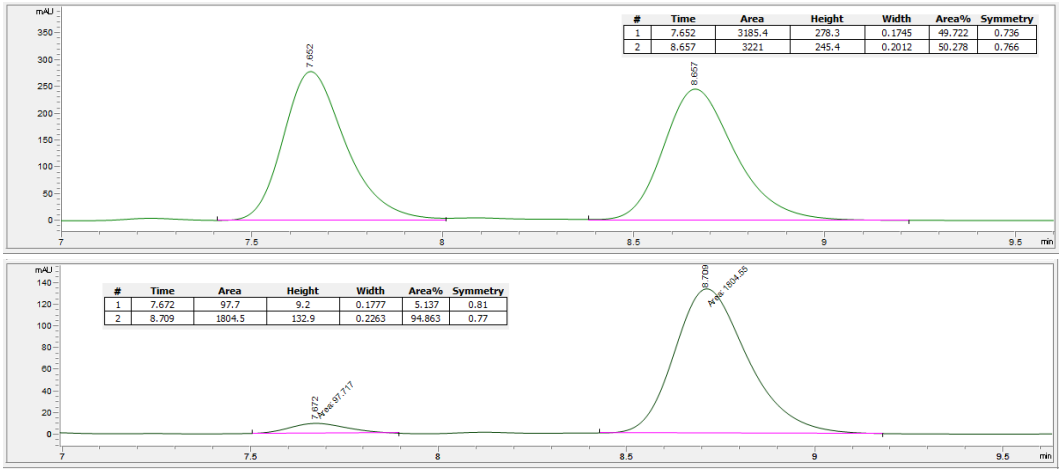
CHIRALCEL OJ-H 95:5 Hex/IPA, 0.5 mL/min, 220 nm

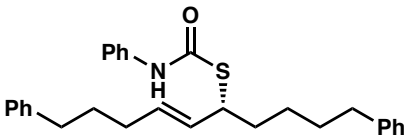




S31

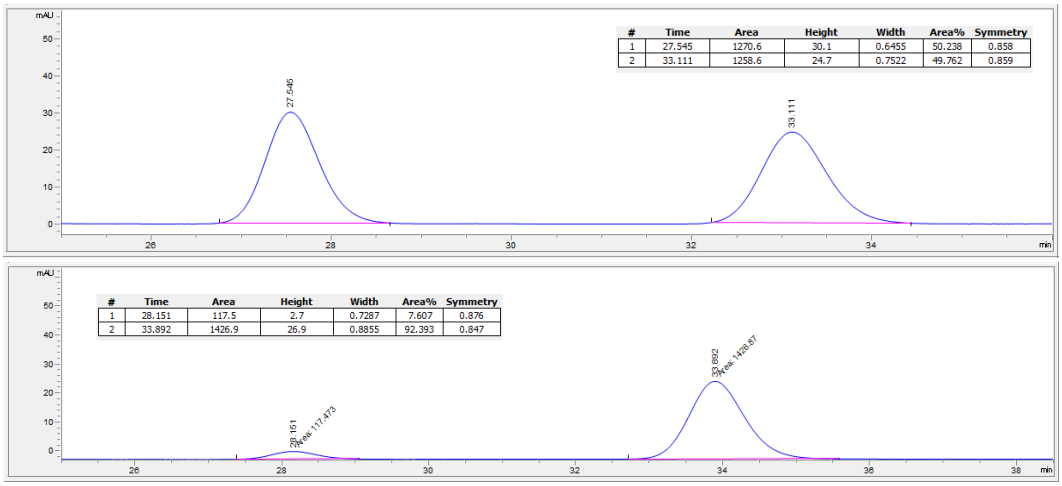
CHIRALCEL OD-H 90:10 Hex/IPA, 0.8 mL/min, 210 nm

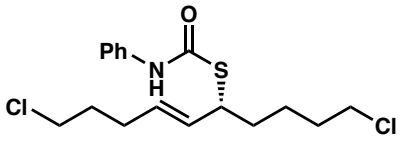




S32

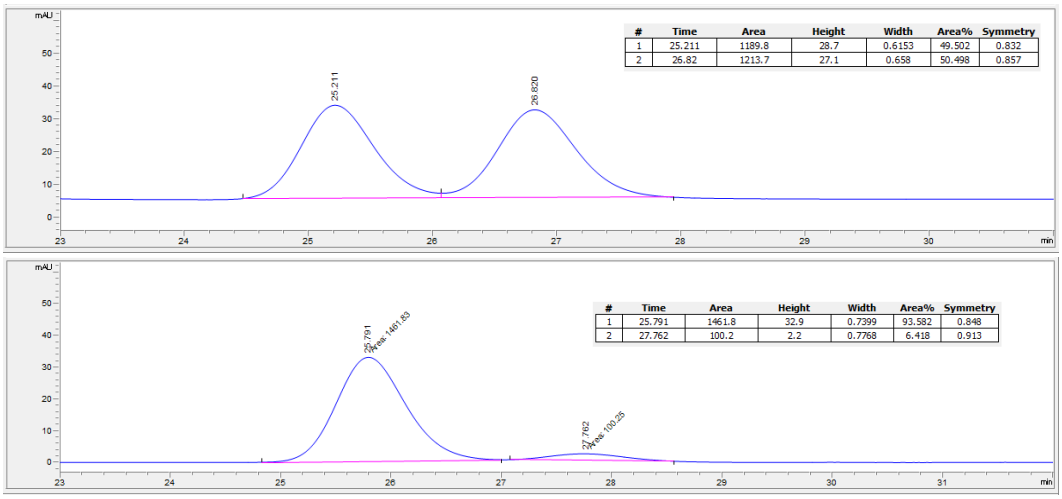
CHIRALPAK AD-H 90:10 Hex/IPA, 0.8 mL/min, 254 nm

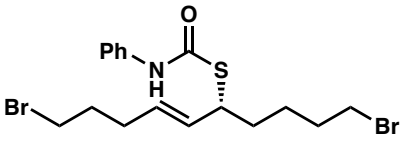




S33

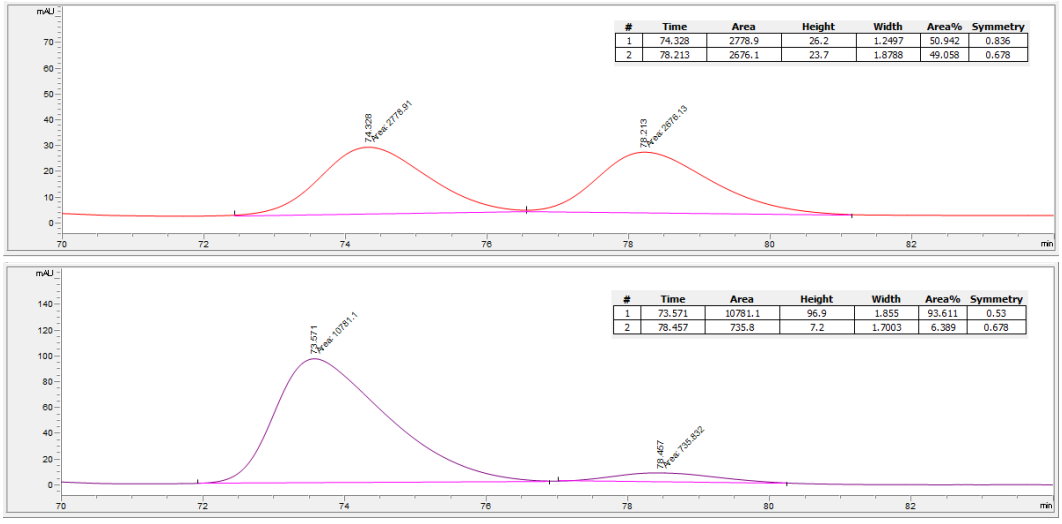
CHIRALCEL OJ-H 90:10 Hex/IPA, 0.8 mL/min, 254 nm

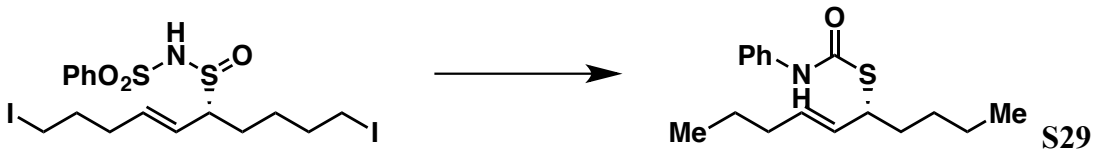




S34

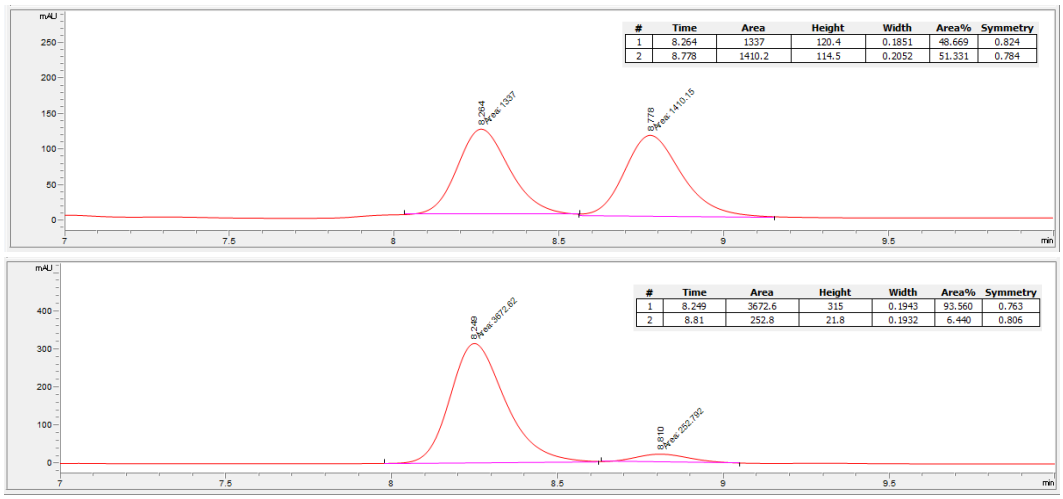
CHIRALPAK AD-H 90:10 Hex/IPA, 0.8 mL/min, 254 nm

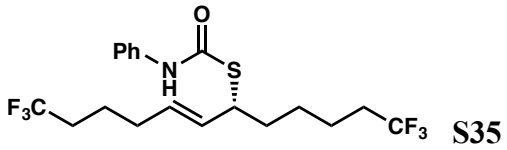




S29

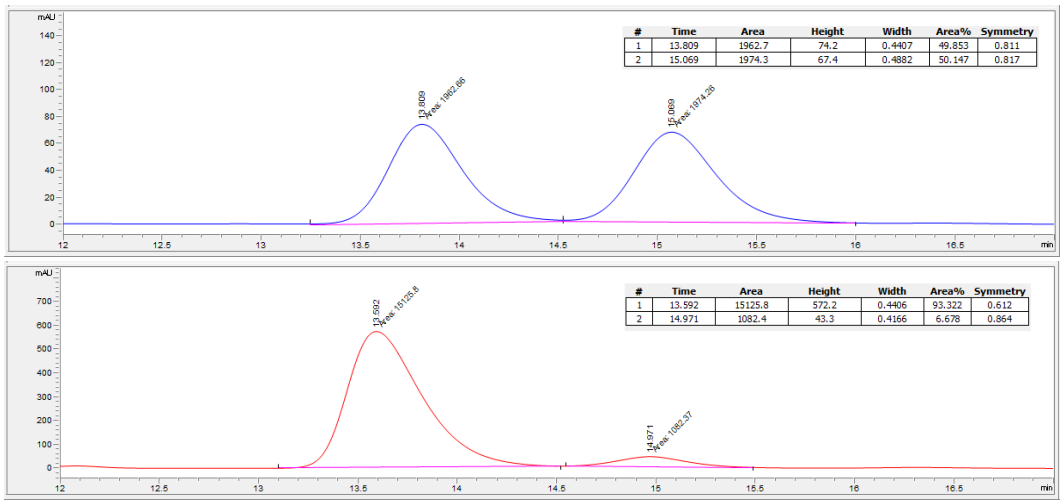
CHIRALCEL OJ-H 95:5 Hex/IPA, 0.8 mL/min, 254 nm





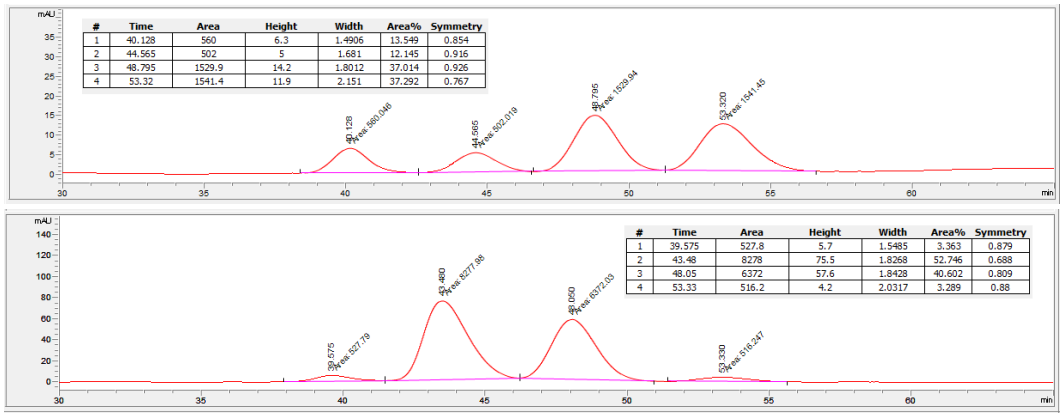
S35

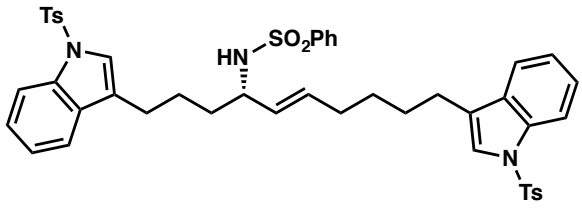
CHIRALCEL OJ-H 90:10 Hex/IPA, 0.6 mL/min, 220 nm



S36

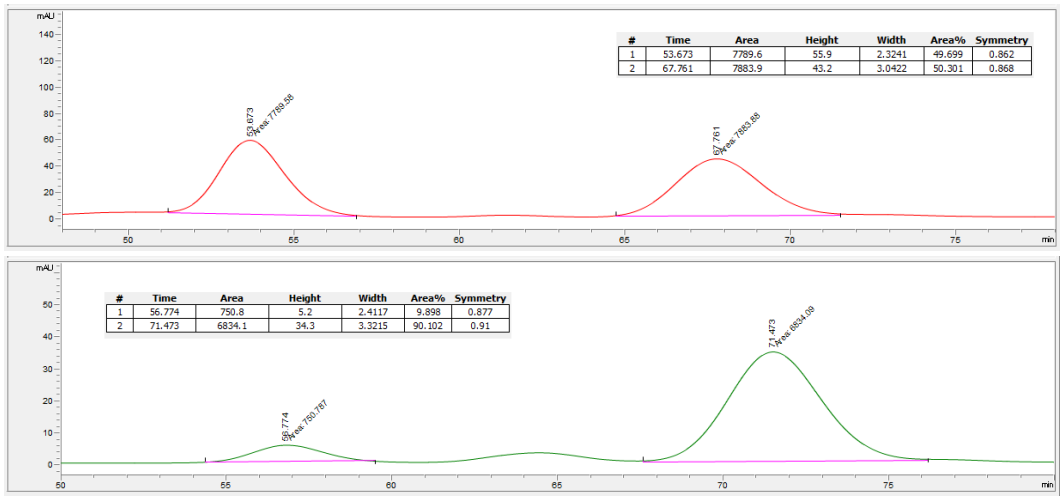
CHIRALPAK AS-H 94:06 Hex/IPA, 0.8 mL/min, 220 nm

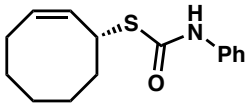




S37

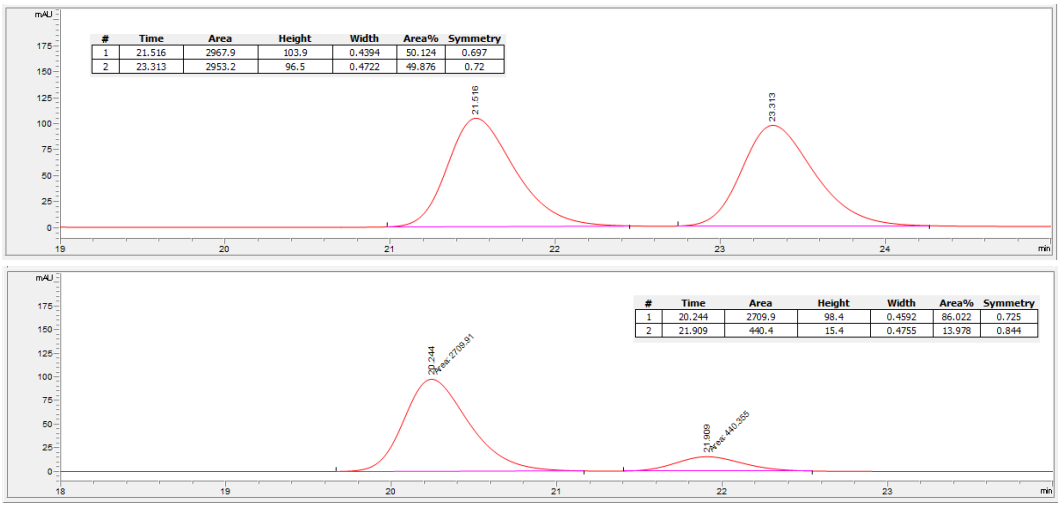
CHIRALPAK AD-H 70:30 Hex/IPA, 0.7 mL/min, 230 nm

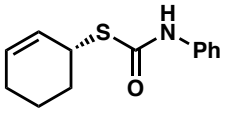




S38

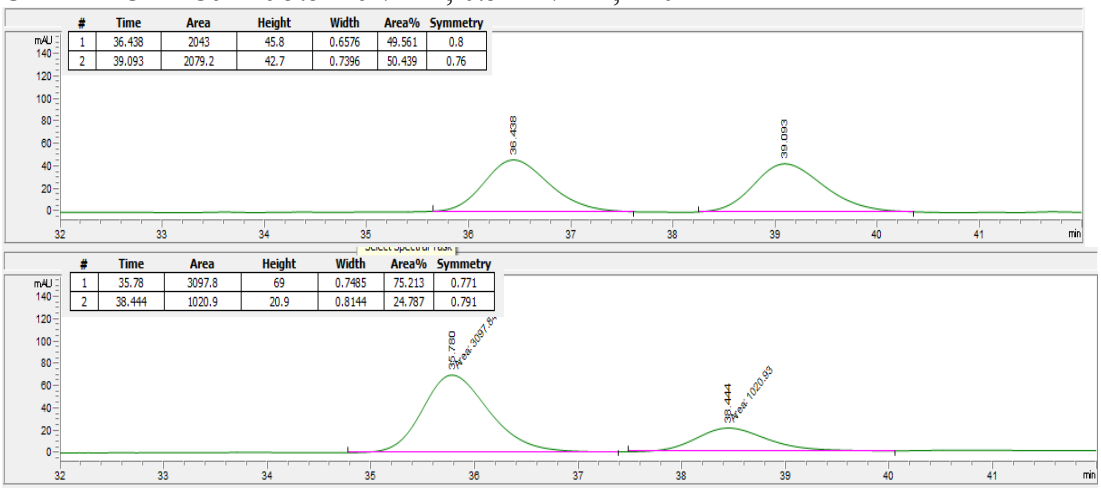
CHIRALCEL OJ-H 95:5 Hex/IPA, 0.8 mL/min, 220 nm

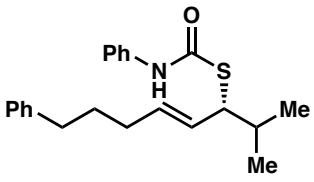




S39

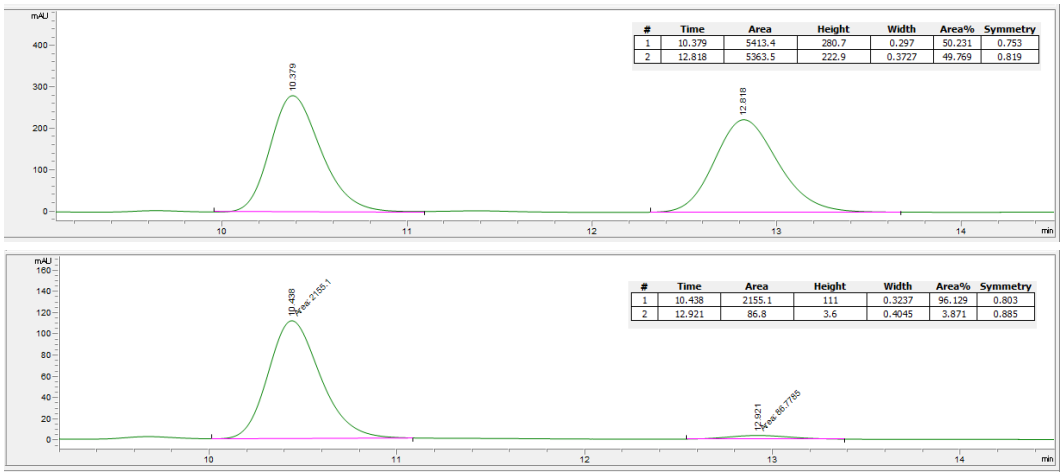
CHIRALCEL OJ-H 95:5 Hex/IPA, 0.5 mL/min, 210 nm

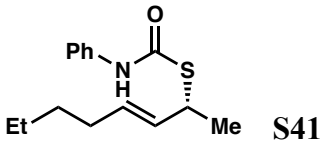




S40

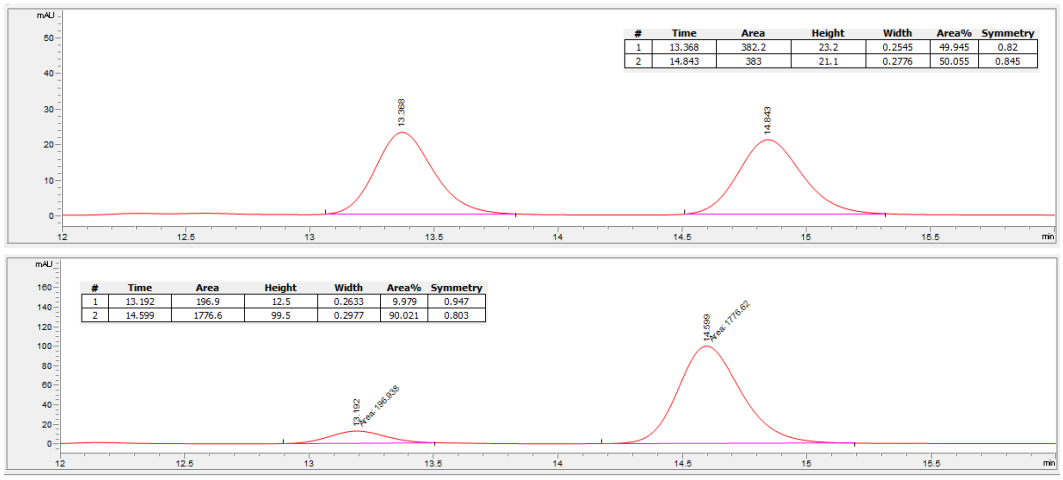
CHIRALCEL OD-H 90:10 Hex/IPA, 0.8 mL/min, 210 nm

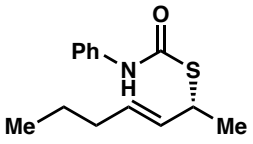




S41

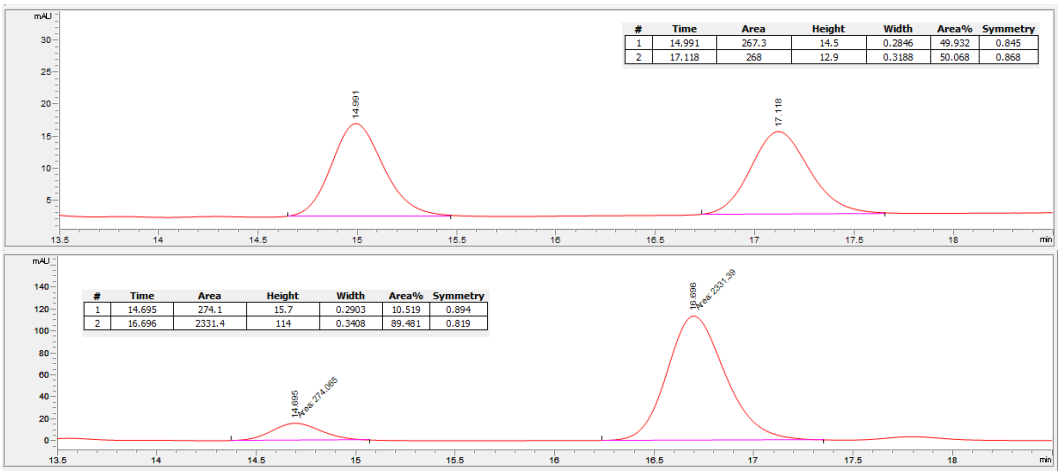
CHIRALCEL OJ-H 95:05 Hex/IPA, 0.8 mL/min, 220 nm





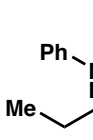
S42

CHIRALCEL OJ-H 95:05 Hex/IPA, 0.8 mL/min, 220 nm



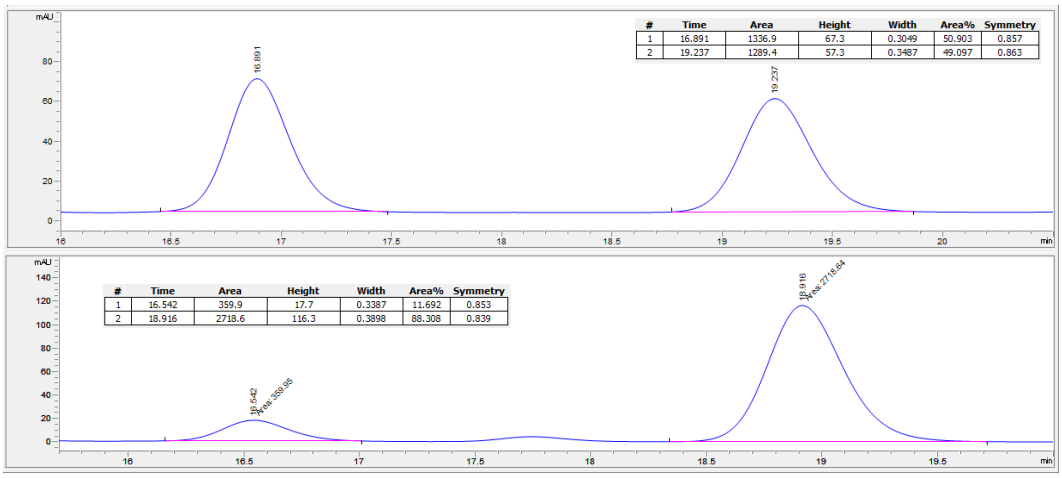
#	Time	Area	Height	Width	Area%	Symmetry
1	14.991	267.3	14.5	0.2846	49.932	0.845
2	17.118	268	12.9	0.3188	50.068	0.868

#	Time	Area	Height	Width	Area%	Symmetry
1	14.695	274.1	15.7	0.2903	10.519	0.894
2	16.696	2331.4	114	0.3408	89.481	0.819



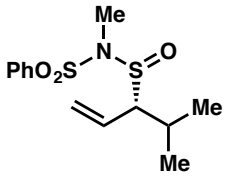
S43

CHIRALCEL OJ-H 95:05 Hex/IPA, 0.8 mL/min, 254 nm



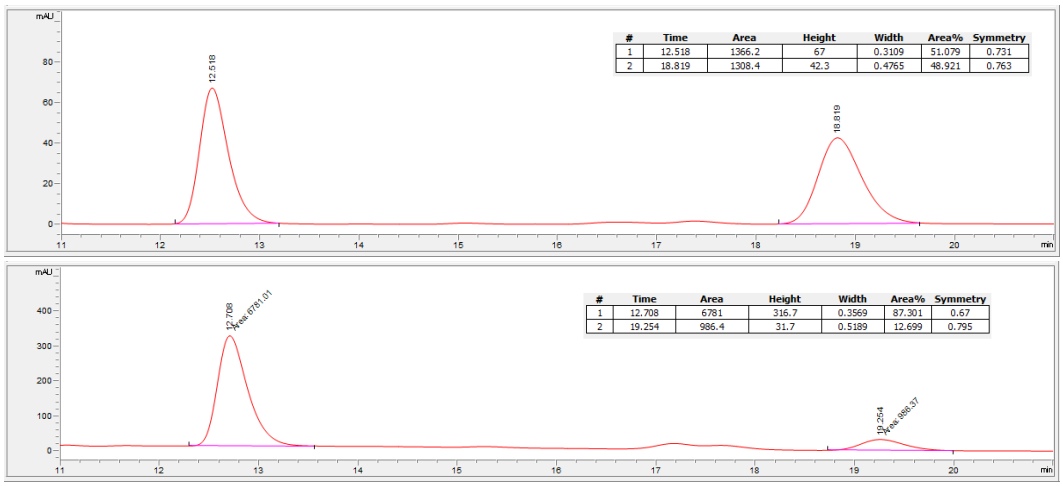
#	Time	Area	Height	Width	Area%	Symmetry
1	16.891	1336.9	67.3	0.3049	50.903	0.857
2	19.237	1289.4	57.3	0.3487	49.097	0.863

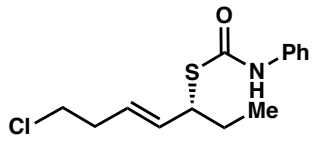
#	Time	Area	Height	Width	Area%	Symmetry
1	16.542	359.9	17.7	0.3387	11.692	0.853
2	18.916	2718.6	116.3	0.3898	88.308	0.839



S44

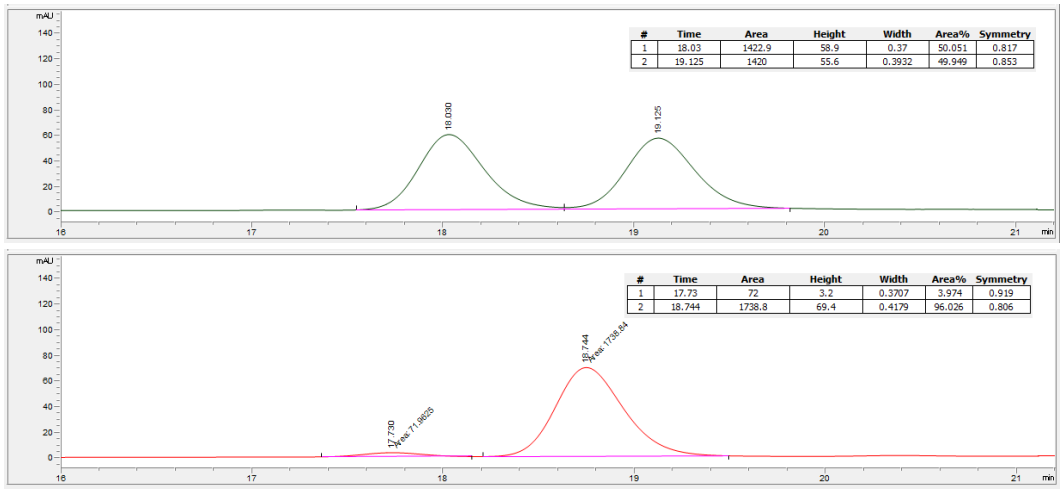
CHIRALCEL OD-H 90:10 Hex/IPA, 0.8 mL/min, 220 nm

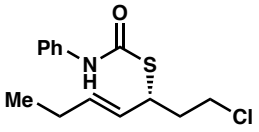




S45 (from minor regioisomer of **9f**)

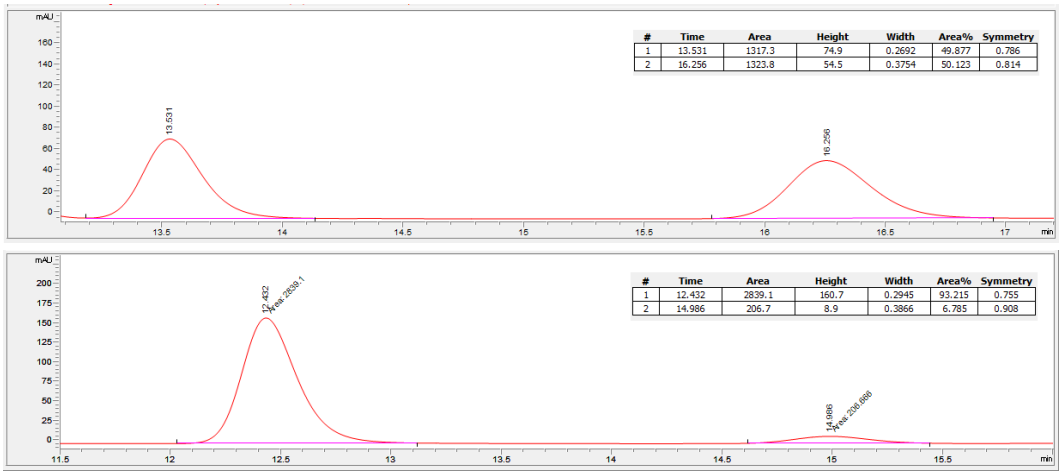
CHIRALCEL OD-H 90:10 Hex/IPA, 0.8 mL/min, 210 nm

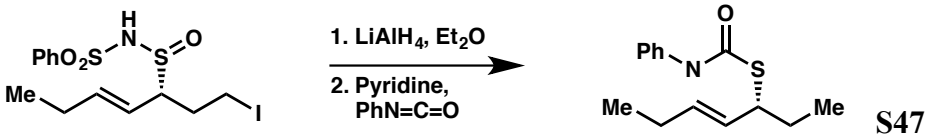




S46

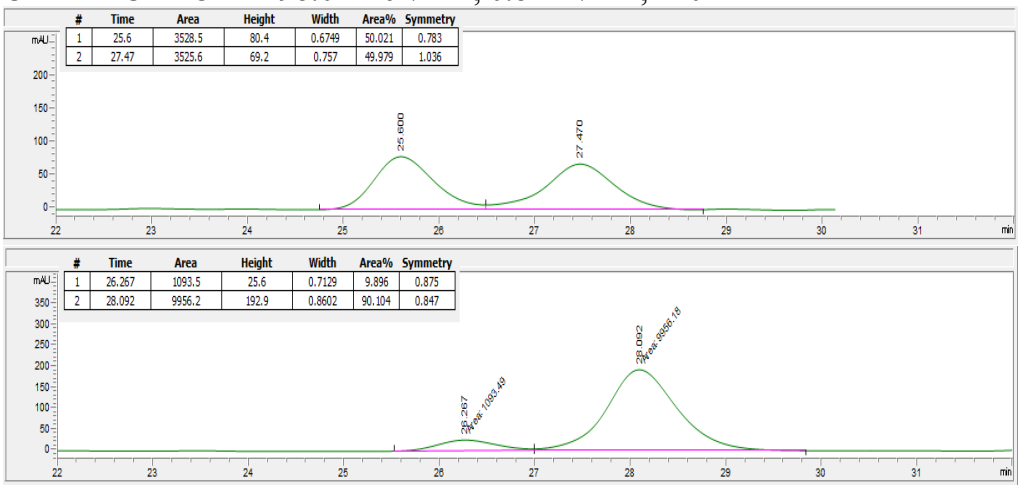
CHIRALCEL OJ-H 90:10 Hex/IPA, 0.8 mL/min, 220 nm

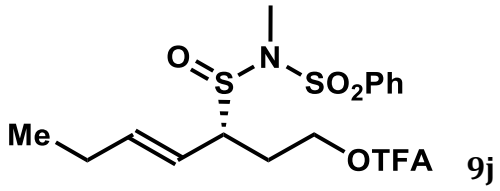




S47

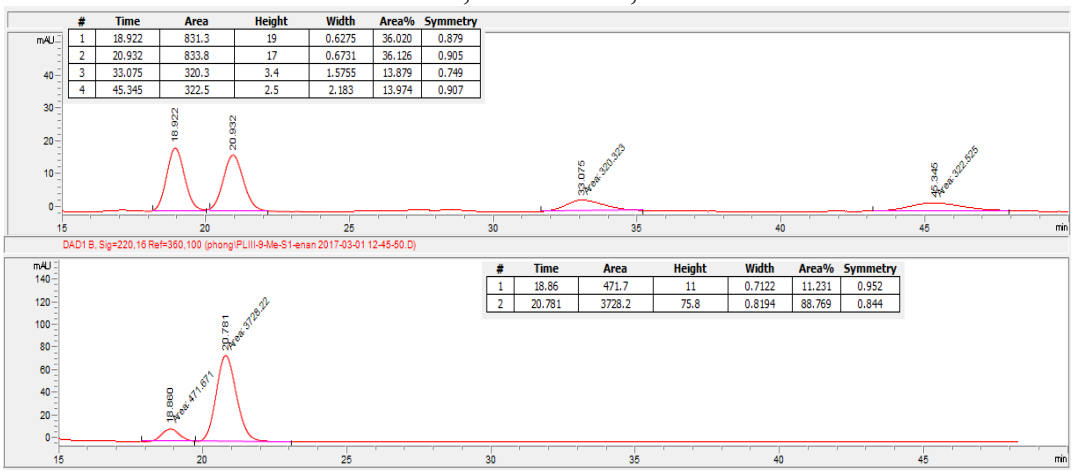
CHIRALCEL OD-H 98:02 Hex/IPA, 0.8 mL/min, 220 nm





9j

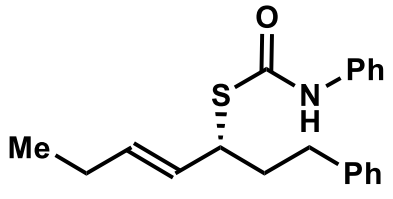
CHIRALCEL OJ-H 90:10 Hex/IPA, 0.8 mL/min, 210 nm



#	Time	Area	Height	Width	Area%	Symmetry
1	18.922	831.3	19	0.6275	36.020	0.879
2	20.932	833.8	17	0.6731	36.126	0.905
3	33.075	320.3	3.4	1.5755	13.879	0.749
4	45.345	322.5	2.5	2.183	13.974	0.907

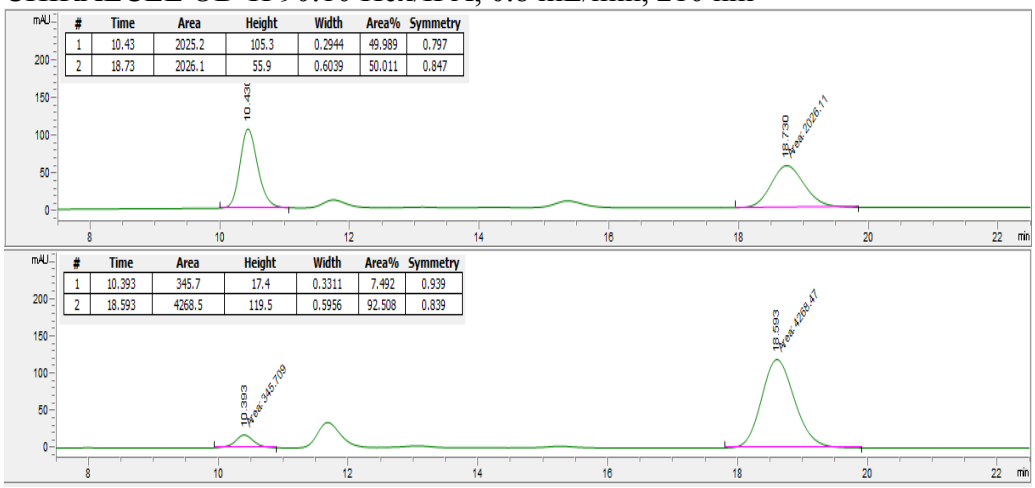
DAD1 B, Sig=220,16 Ref=360,100 (phong\PLIII-9-Me-S1-enan 2017-03-01 12-45-50.D)

#	Time	Area	Height	Width	Area%	Symmetry
1	18.86	471.7	11	0.7122	11.231	0.952
2	20.781	3728.2	75.8	0.8194	88.769	0.844



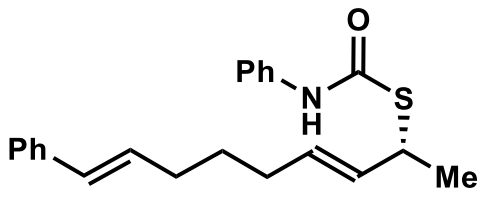
S48

CHIRALCEL OD-H 90:10 Hex/IPA, 0.8 mL/min, 210 nm



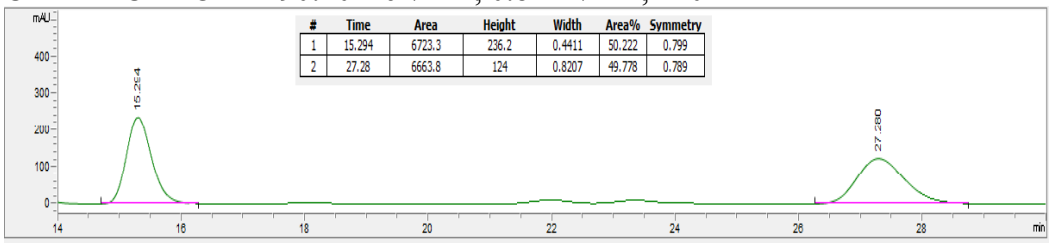
#	Time	Area	Height	Width	Area%	Symmetry
1	10.43	2025.2	105.3	0.2944	49.989	0.797
2	18.73	2026.1	55.9	0.6039	50.011	0.847

#	Time	Area	Height	Width	Area%	Symmetry
1	10.393	345.7	17.4	0.3311	7.492	0.939
2	18.593	4268.5	119.5	0.5956	92.508	0.839

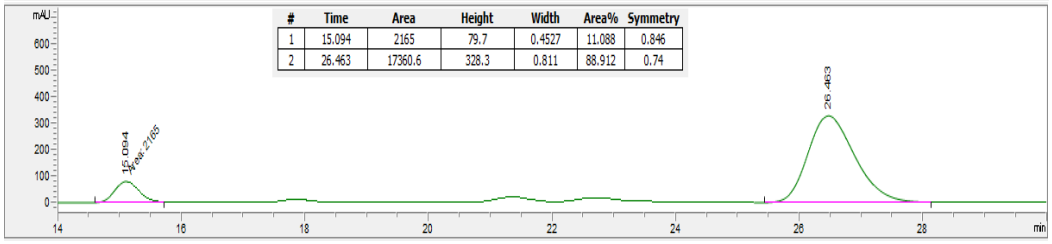


S49

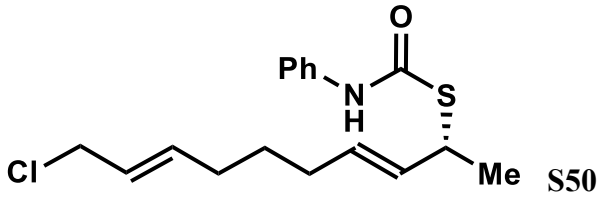
CHIRALCEL OD-H 90:10 Hex/IPA, 0.8 mL/min, 210 nm



#	Time	Area	Height	Width	Area%	Symmetry
1	15.294	6723.3	236.2	0.4411	50.222	0.799
2	27.28	6663.8	124	0.8207	49.778	0.789

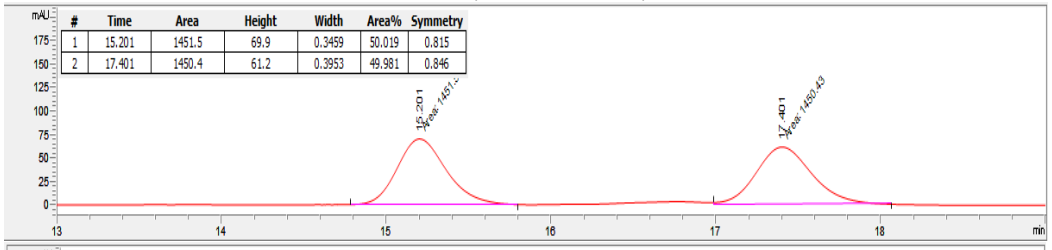


#	Time	Area	Height	Width	Area%	Symmetry
1	15.094	2165	79.7	0.4527	11.088	0.846
2	26.463	17360.6	328.3	0.811	88.912	0.74

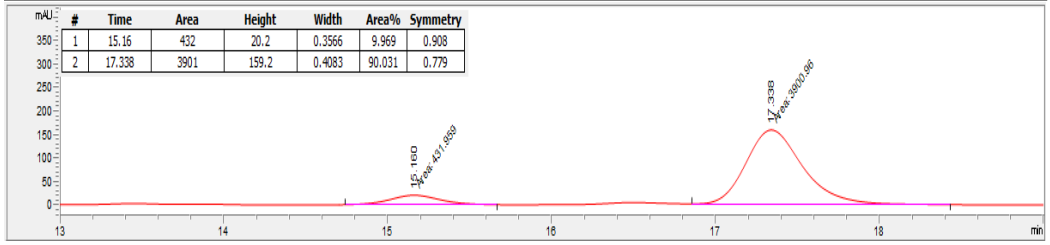


S50

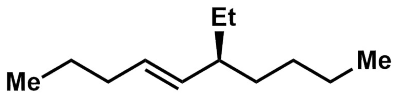
CHIRALCEL AD-H 90:10 Hex/IPA, 0.8 mL/min, 210 nm



#	Time	Area	Height	Width	Area%	Symmetry
1	15.201	1451.5	69.9	0.3459	50.019	0.815
2	17.401	1450.4	61.2	0.3953	49.981	0.846

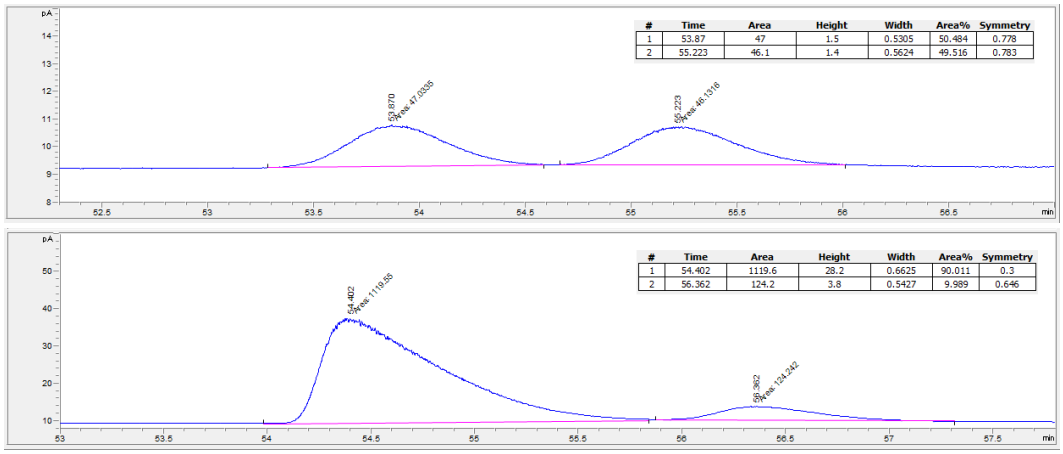


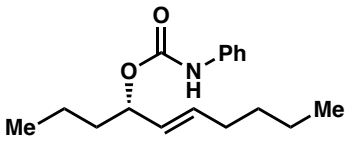
#	Time	Area	Height	Width	Area%	Symmetry
1	15.16	432	20.2	0.3566	9.969	0.908
2	17.338	3901	159.2	0.4083	90.031	0.779



10

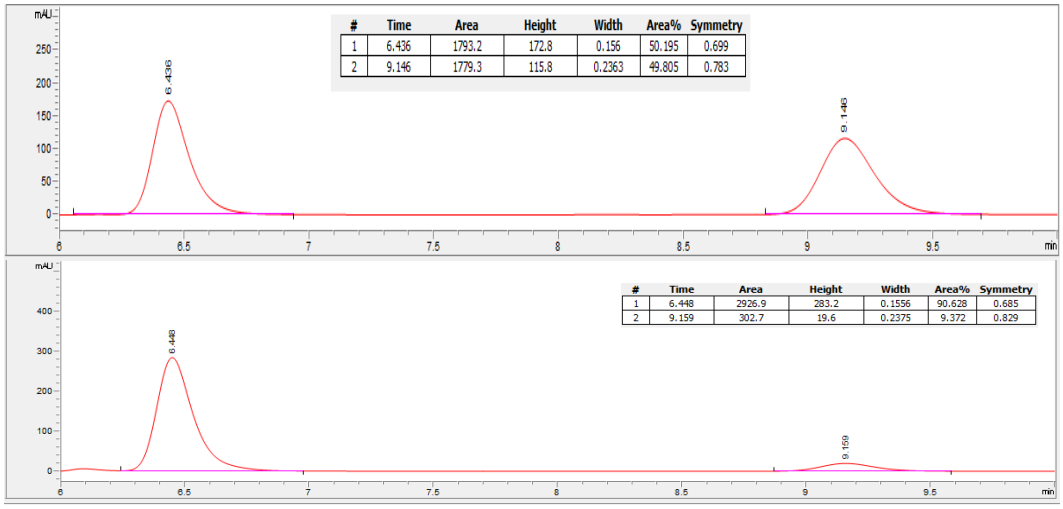
GC Agilent Cyclodex-B (Isothermal, 50 °C; flow rate: 1 mL/min)

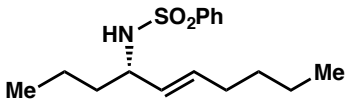




S52

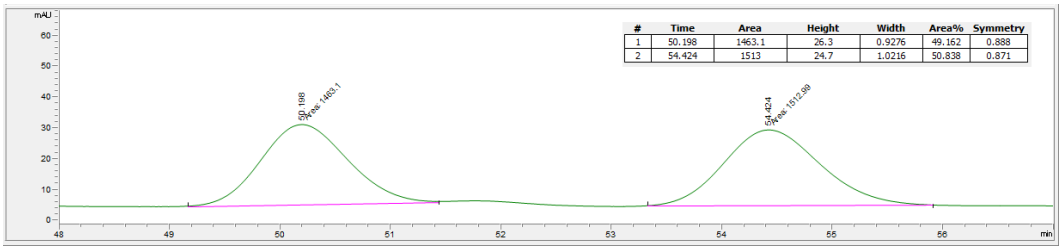
CHIRALCEL OD-H 90:10 IPA/Hexane 0.8 ml/min

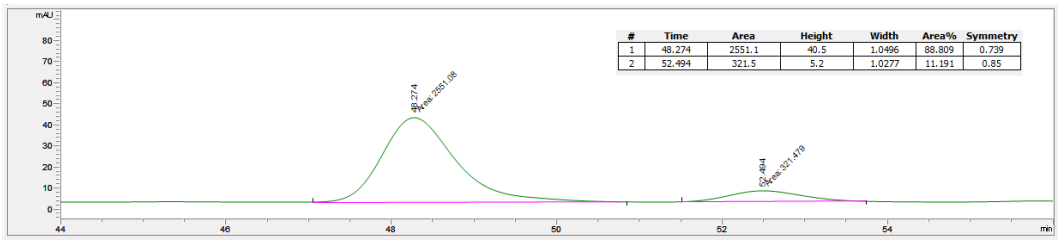


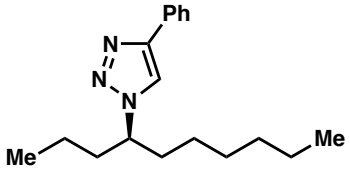


13

CHIRALPAK AD-H 97:03 Hexanes/IPA, 0.25 mL/min, 230 nm

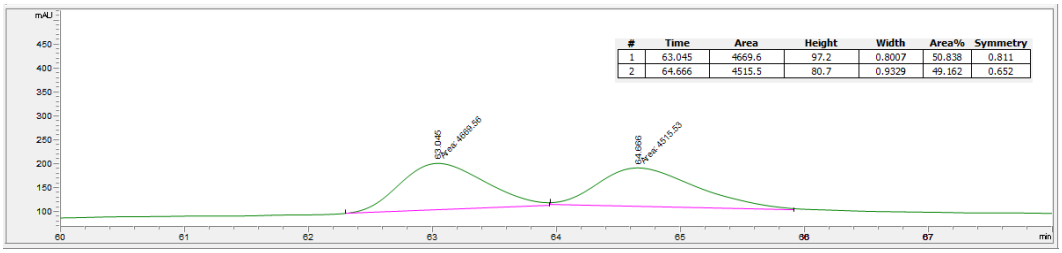


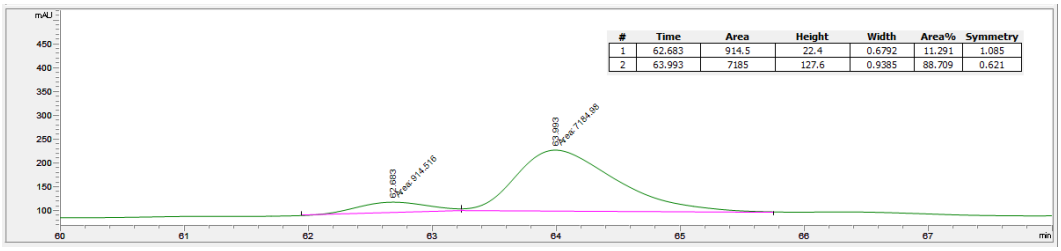




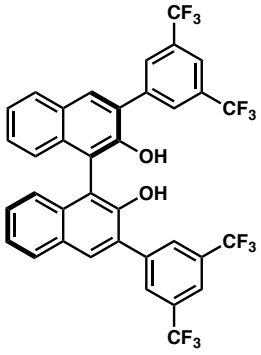
S54

CHIRALCEL OJ-H 100% Hexanes 30 min, gradient to 2% IPA over 20 min, 0.8 mL/min, 210 nm



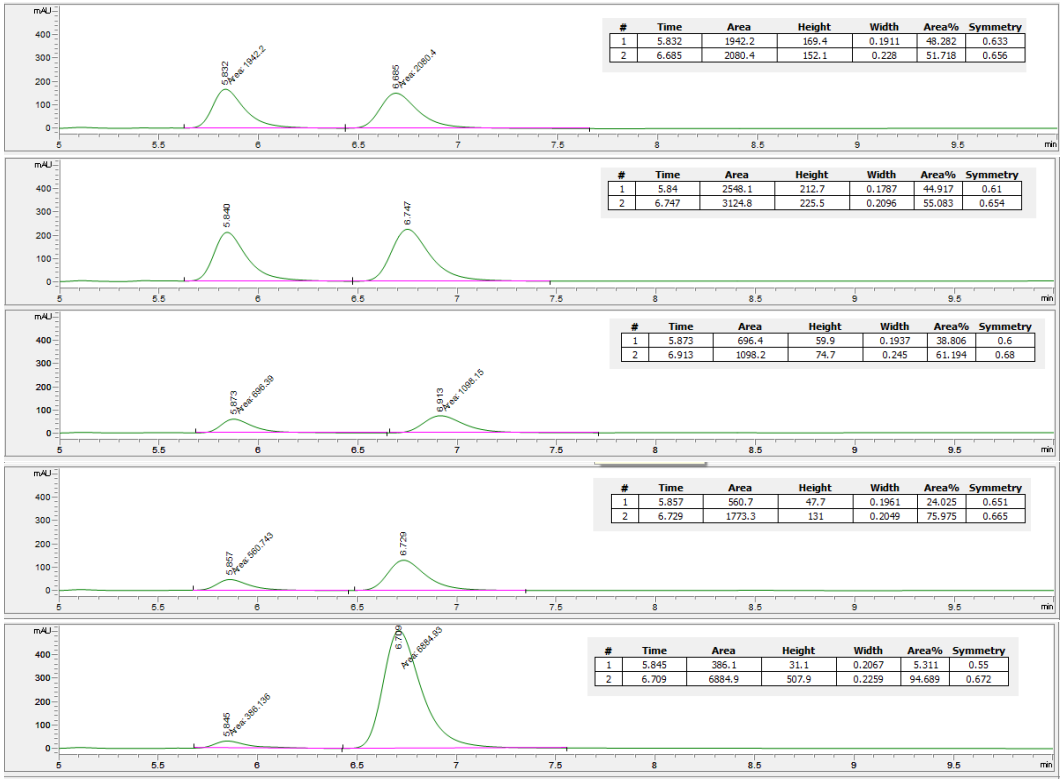


HPLC Traces for Non-Linear Effect Study



6 (R/S mixtures)

CHIRALCEL OD-H 97:03 IPA:Hexane 0.6 ml/min



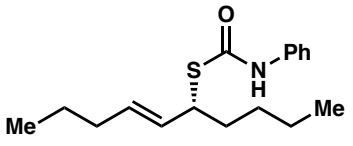
#	Time	Area	Height	Width	Area%	Symmetry
1	5.832	1942.2	169.4	0.1911	48.282	0.633
2	6.685	2080.4	152.1	0.228	51.718	0.656

#	Time	Area	Height	Width	Area%	Symmetry
1	5.84	2548.1	212.7	0.1787	44.917	0.61
2	6.747	3124.8	225.5	0.2096	55.083	0.654

#	Time	Area	Height	Width	Area%	Symmetry
1	5.873	696.4	59.9	0.1937	38.806	0.6
2	6.913	1098.2	74.7	0.245	61.194	0.68

#	Time	Area	Height	Width	Area%	Symmetry
1	5.857	560.7	47.7	0.1961	24.025	0.651
2	6.729	1773.3	131	0.2049	75.975	0.665

#	Time	Area	Height	Width	Area%	Symmetry
1	5.845	386.1	31.1	0.2067	5.311	0.55
2	6.709	6884.9	507.9	0.2259	94.689	0.672



S29

CHIRALCEL OJ-H 95:05 IPA:Hexane 0.5 ml/min

#	Time	Area	Height	Width	Area%	Symmetry
1	12.884	7500.3	429.4	0.2628	52.057	0.691
2	13.804	6907.5	361.2	0.2891	47.943	0.757

#	Time	Area	Height	Width	Area%	Symmetry
1	12.756	3950	220.4	0.2987	55.135	0.704
2	13.673	3214.2	168	0.3188	44.865	0.791

#	Time	Area	Height	Width	Area%	Symmetry
1	12.836	1728.6	98.5	0.2926	58.075	0.738
2	13.776	1247.9	66	0.315	41.925	0.807

#	Time	Area	Height	Width	Area%	Symmetry
1	12.814	2999	173.2	0.2886	73.917	0.755
2	13.756	1058.2	55.5	0.3177	26.083	0.812

#	Time	Area	Height	Width	Area%	Symmetry
1	12.876	3748.4	211.3	0.2956	87.758	0.724
2	13.831	522.9	26.2	0.3323	12.242	0.837