Dynamic Kinetic Resolution of Allylic Sulfoxides by Rh-Catalyzed Hydrogenation: A Combined Theoretical and Experimental Mechanistic Study

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Supporting Information

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1. General Considerations

Commercial reagents were purchased from Sigma Aldrich, Strem or Alfa Aesar and used without further purification. All reactions were carried out under an argon atmosphere unless otherwise indicated. Reactions were monitored using thin-layer chromatography (TLC) on EMD Silica Gel 60 F_{254} plates. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian Mercury 400, VRX-S (Unity) 400, Bruker AV-III 400, Bruker DRX400, Bruker DRX500, Bruker DRX500 with TCI (three channel inverse) cryoprobe or a Bruker AVANCE600 spectrometer. NMR spectra were internally referenced to tetramethylsilane. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm).

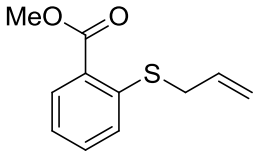
High resolution mass spectra (HRMS) were obtained on a micromass 70S-250 spectrometer (EI), ABI/Sciex QStar Mass Spectrometer (ESI), or a Waters LCT Premier spectrometer (using ESI-TOF). Infrared (IR) spectra were obtained on a Nicolet iS5 FT-IR spectrometer with an iD5 ATR, and are reported in terms of frequency of absorption (cm^{-1}). Enantiomeric excesses (ee's) were ascertained on an Agilent 1200 Series HPLC with an Aurora or Berger SFC system. Optical rotations were measured on a Rudolph Autopol III Automatic Polarimeter. Column chromatography was performed with Silicycle Silia-P Flash Silica Gel, using either glass columns or a Teledyne Isco Combiflash Rf 200 automated purification system. All salts were purchased from Aldrich and used without purification. Solvents were purchased from Caledon and/or Fisher Chemical and were purified according to standard procedures.[1] Solvents used in catalysis were first distilled and then degassed by three 'freeze-pump-thaw' cycles before being taken into a glove box. Chiral diphosphine ligands were purchased from Strem and used as is.

[1] Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: New York, 2003.

2. Preparation of substrates

General procedure A – Oxidation of allyl sulfides

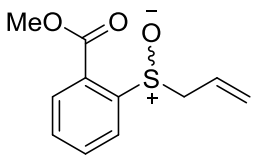
To a solution of allyl aryl sulfide (1 equiv) in glacial acetic acid (0.5 M) was added 35% aqueous H_2O_2 (1.1 equiv). The mixture was stirred at room temperature until complete consumption of starting material. Brine was then added, and the mixture was extracted twice with CH_2Cl_2. The organic extracts were dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The allylic sulfoxide was then purified by column chromatography. *Note:* For the preparation of allyl aryl sulfoxides with electron-withdrawing groups on the aryl ring, acetic acid was found to be the optimal solvent with no over-oxidation to the sulfone observed even with excess oxidant. However, for electron-neutral or electron-rich substrates, which react faster and are more prone to over-oxidation, ethanol was found to be the superior solvent. In this case, the oxidation is slower and more selective for the sulfoxide product than acetic acid.



Methyl 2-(allylthio)benzoate (1a')

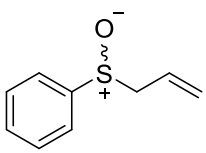
Methyl thiosalicylate (500 mg, 2.97 mmol) was dissolved in dimethylformamide (13.5 mL) under a balloon pressure of argon, cooled to 0 ℃ via an ice/water bath, and added sodium hydride (60% oil dispersion, 178 mg, 4.45 mmol). The yellow reaction mixture was allowed to stir at 0 ℃ for 10 minutes, then added allyl bromide drop-wise (285 μL, 3.29 mmol). The reaction mixture was gradually warmed to rt, and then stirred at rt for 13 h, at which tlc analysis indicated complete conversion of starting material. The reaction mixture was diluted with distilled water (150 mL) and a saturated solution of brine (15 mL) and extracted with diethyl ether (3 × 50 mL). The ethereal layers were combined, washed with brine (50 mL), dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product. Purification by flash chromatography (0–4% ethyl acetate in hexanes) gave the product as a colorless oil (454 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, 1H, J = 1.5 Hz, J = 7.8 Hz), 7.46–7.40 (m, 1H), 7.35–7.31 (m, 1H), 7.19–7.13 (m, 1H), 5.93 (tdd, 1H, J = 6.6 Hz, J = 10.1 Hz, J = 16.8 Hz), 5.33 (ddd, 1H, J = 1.3Hz, J = 2.7 Hz, J = 17.0 Hz), 5.18 (dd, 1H, J = 1.2Hz, J = 10.1 Hz), 3.91 (s, 3H), 3.61 (d, 2H, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 141.3, 132.8, 132.3, 131.4, 127.9, 126.2, 124.1, 118.8, 52.2, 35.5; IR (neat): 3084, 3063, 2950, 2835, 1712, 1637, 1587, 1562, 1463, 1434, 1275,

1249, 1190, 1144, 1108, 1061, 1045, 988, 922, 824, 742 cm^{-1}. HRMS (EI) *m/z* calc'd for $C_{11}H_{12}O_2S$ $[M]^+$: 208.0524; found: 208.0526.



Methyl 2-(allylsulfinyl)benzoate (1a)

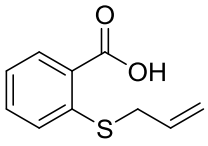
Sulfide **1a'** (434 mg, 2.08 mmol) was dissolved in dichloromethane (20 mL), cooled to 0 °C, and added *m*CPBA (57–86%, 513 mg, *ca.* 2 mmol). The reaction was stirred at 0 °C for 30 min, at which TLC analysis indicated complete conversion of starting material and some formation of over-oxidation product. The reaction mixture was diluted with dH_2O (100 mL), the organic layer separated and the remaining aqueous layer extracted with dichloromethane (2 × 20 mL). The organic layers were combined, washed with brine, dried with anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give the crude product. Purification by flash chromatography (10–60% ethyl acetate in hexanes) gave the product as a pale yellow oil that slowly crystallized to a white solid when cooled (405 mg, 87%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, 1H, *J* = 1.1 Hz, *J* = 8.0 Hz), 8.10 (dd, 1H, *J* = 1.2 Hz, *J* =7.8 Hz), 7.80 (dt, 1H, *J* = 1.3 Hz, *J* = 7.7 Hz), 7.57 (dt, 1H, *J* = 1.2 Hz, *J* = 7.6 Hz), 5.80 (tdd, 1H, *J* = 7.6 Hz, *J* = 10.1 Hz, *J* = 17.4 Hz), 5.34 (d, 1H, *J* = 10.1 Hz), 5.22 (ddd, 1H, *J* = 1.2 Hz, *J* = 2.5 Hz, *J* = 17.0 Hz), 3.96 (s, 3H), 3.87 (dd, 1H, *J* = 7.3 Hz, *J* = 12.9 Hz), 3.51 (ddd, 1H, *J* = 0.5 Hz, *J* = 7.8 Hz, *J* = 12.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 147.6, 133.7, 130.9, 130.3, 126.8, 126.7, 125.8, 123.4, 59.9, 52.8; IR (neat): 3074, 2975, 2956, 2930, 1699, 1587, 1437, 1289, 1256, 1243, 1106, 1084, 1066, 1030, 996, 933, 756, 709, 692 cm^{-1}. HRMS (EI) *m/z* calc'd for $C_{11}H_{12}O_3S$ $[M]^+$: 224.0507; found: 224.0509. SFC analysis: 250 mm CHIRALPAK IA, 8% MeOH, 3.5 mL/min flow rate, 254 nm, 33 °C Column IN, 44 °C Column OUT, nozzle pressure = 200 bar CO_2, t_{R1} = 3.1 min, t_{R2} = 4.2 min.



(±)-allylsulfinyl benzene (1b)

Thiophenol (7.65 mL, 75 mmol) was dissolved in acetone (150 mL) in a round bottom flask equipped with a teflon coated stir bar. Potassium carbonate (15.5 g, 112.5 mmol) was added and the reaction was cooled to 0 °C. Allyl bromide (7.13 mL, 82.5 mmol) was subsequently added to the cooled reaction mixture and this was gradually allowed to warm to room temperature over 9 hours. To the reaction mixture was added a solution of 2M $NaOH_{(aq)}$ (50 mL) and the resulting aqueous mixture was extracted with diethyl ether (3 x 150

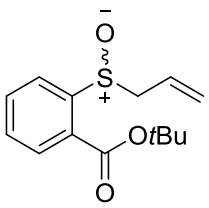
mL). The combined organic extracts were washed with brine (50 mL), dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give the crude allyl sulfide which was used in the next step without further purification. This material was dissolved in 95% ethanol (75 mL) and 35% H_2O_2 (7.1 mL, 82.5 mmol) was added. The reaction was stirred at 35 °C for 36 hours with periodic addition of H_2O_2 (3 x 7.1 mL). The crude mixture was diluted with ethyl acetate (100 mL) and washed with brine (2 x 50 mL). The organic extract was dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography (40─50% ethyl acetate in hexanes) gave the title compound as a colorless liquid (8.55 g, 69%, two steps). The spectroscopic data obtained were in accord with those previously reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 2H), 7.56-7.48 (m, 3H), 5.66 (ddt, *J* = 17.4, 10.2, 7.4 Hz, 1H), 5.34 (d, *J* = 10.1 Hz, 1H), 5.20 (dd, *J* = 17.0, 1.3 Hz, 1H), 3.62-3.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 131.2, 129.2, 125.4, 124.4, 124.0, 61.0; IR(neat): 1443, 1088, 1039, 996, 926, 748, 713, 690; HRMS (ESI+) *m/z* calc'd for $[C_9H_{10}OS+Na]^+$: 189.0350; found: 189.0349.



2-(allylthio)benzoic acid (1c')

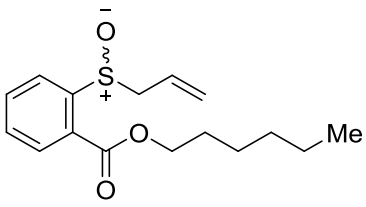
To a mixture of thiosalicylic acid (10.0 g, 64.9 mmol) and K_2CO_3 (17.g, 129.8 mmol) in acetone (130 mL) was added allyl bromide (8.4 mL, 97.3 mmol). The mixture was stirred in a water bath at rt for 45 minutes (a slight exotherm was observed initially). The crude reaction mixture was quenched with a solution of saturated $NH_4Cl_{(aq)}$ and then acidified with 1M $HCl_{(aq)}$. The mixture was then extracted with CH_2Cl_2 (3 x 75 mL) and the combined organic phases were dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The product was isolated by trituration with 1:1 hexanes:ether and then washed with hexanes to obtain a white solid (9.14 g, 73%); m.p. 112─114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.10 (br s, 1H), 8.13 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.48 (ddd, *J* = 8.2, 7.3, 1.6 Hz, 1H), 7.36 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.21 (ddd, *J* = 7.9, 7.4, 1.1 Hz, 1H), 5.95 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.34 (dq, *J* = 17.0, 1.4 Hz, 1H), 5.21 (dq, *J* = 10.2, 1.1 Hz, 1H), 3.63 (dt, *J* = 6.6, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 142.2, 133.0, 132.4, 132.4, 126.4, 126.1, 124.1, 118.8, 35.4; IR (neat): 1672, 1412, 1272, 1253, 1235, 1045, 915, 883, 736 cm^{-1}; HRMS (ESI+) calc'd. for $[C_{10}H_{10}O_2S+H]^+$: 195.04797; found 195.04799.

[2] Bolm, C.; Legros, J. *Chem. Eur. J.* **2005**, *11*, 1086.



tert-butyl 2-(allylsulfinyl)benzoate (1c)

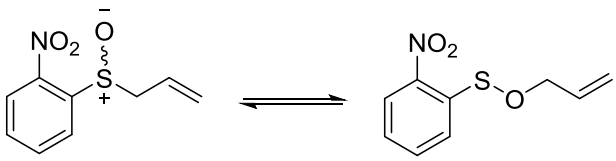
2-(allylthio)benzoic acid **1c'** (500 mg, 2.57 mmol) was dissolved in CH_2Cl_2 and sulfuric acid (30 μL) was added. A separate round bottom flask was equipped with a reflux condenser and a gas outlet connected to a Pasteur pipette dipped in the first reaction vessel. This second flask was charged with *tert*-butanol (17 mL) and anhydrous oxalic acid (6.5 g, 7.2 mmol) and was heated to reflux to generate isobutene gas. Bubbling of the resulting isobutene gas into the main reaction vessel was maintained for 50 minutes, at which point the pipette bubbler was removed, and the reaction was stirred at room temperature for 17 hours. The crude mixture was quenched with a solution of saturated $NaHCO_{3(aq)}$ and the product extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude *tert*-butyl ester was then dissolved in 99% EtOH (8 mL) and 35% H_2O_2 was added (133 μL, 1.55 mmol). The reaction mixture was stirred at rt for 24 hours, at which point an additional aliquot of aqueous 35% H_2O_2 (133 μL, 1.55 mmol) was added. The mixture was stirred for another 12 hours, then diluted with water (5 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The title compound was isolated by column chromatography (30─50% ethyl acetate in hexanes) to yield a clear oil (486 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.03 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.75 (ddd, *J* = 8.0, 7.4, 1.2 Hz, 1H), 7.53 (td, *J* = 7.4, 1.0 Hz, 1H), 5.77 (ddt, *J* = 17.4, 10.1, 7.6 Hz, 1H), 5.32 (dd, *J* = 10.1, 0.8 Hz, 1H), 5.20 (dq, *J* = 17.0, 1.4 Hz, 1H), 3.84 (dd, *J* = 12.9, 7.3 Hz, 1H), 3.50 (dd, *J* = 12.9, 7.8 Hz, 1H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 146.8, 132.8, 130.7, 129.9, 128.7, 126.5, 125.4, 123.1, 82.9, 59.7, 28.1. IR (neat): 2978, 1698, 1294, 1168, 1029, 752 cm^{-1}; HRMS (ESI+) calc'd. for $[C_{14}H_{18}O_3S+H]^+$: 267.10549; found 267.10540.



hexyl 2-(allylsulfinyl)benzoate (1d)

To a flame dried flask under argon was added 2-(allylthio)benzoic acid **1c'** (1g, 5.15 mmol), CH_2Cl_2 (25 mL), and DMF (0.2 mL). The flask was placed in a water bath at rt and oxalyl chloride (0.883 mL, 10.3 mmol, 2.0 equiv) was added dropwise. The solution was stirred at room temperature for 25 minutes at which point the bubbling had ceased.

The mixture was then concentrated *in vacuo* and reconstituted in CH_2Cl_2 (25 mL). Triethylamine (1.44 mL, 10.3 mmol) was added, at which point the solution turned deep red. The appropriate alcohol (10.3 mmol) was then added, and the mixture was stirred at rt for 1 h. The crude mixture was diluted with CH_2Cl_2 (25 mL) and washed with dH_2O (25 mL). The aqueous phase was then re-extracted with CH_2Cl_2 (25 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude sulfide product was subjected to subsequent oxidation without further purification. The sulfide was oxidized to the sulfoxide using general procedure A with a reaction time of 16 h. The title compound was isolated by column chromatography (20─30% ethyl acetate / hexanes) to give a clear oil (701 mg, 46% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, J = 8.0, 1.2 Hz, 1H), 8.10 (dd, J = 7.8, 1.4 Hz, 1H), 7.79 (td, J = 7.7, 1.4 Hz, 1H), 7.56 (td, J = 7.6, 1.3 Hz, 1H), 5.79 (ddt, J = 17.4, 10.1, 7.5 Hz, 1H), 5.34 (dd, J = 10.2, 1.5 Hz, 1H), 5.22 (dq, J = 17.0, 1.3 Hz, 1H), 4.35 (td, J = 6.7, 1.1 Hz, 2H), 3.86 (ddt, J = 12.7, 7.3, 1.0 Hz, 1H), 3.51 (ddd, J = 12.7, 7.8, 1.0 Hz, 1H), 1.79 (dq, J = 8.4, 6.8 Hz, 2H), 1.51–1.40 (m, 2H), 1.38–1.30 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 147.4, 133.3, 130.6, 130.1, 127.0, 126.5, 125.6, 123.2, 66.0, 59.7, 31.3, 28.5, 25.6, 22.5, 13.9; IR(neat): 1707, 1274, 1103, 1032, 752; HRMS (ESI+) calc'd. for $[C_{16}H_{22}O_3S+H]^+$: 295.13679; found 295.13683.



1-(allylsulfinyl)-2-nitrobenzene (1e)

Bis(2-nitrophenyl)disulfide (5.0 g, 16.2 mmol) and $NaBH_4$ (1.53 g, 40.4 mmol) were suspended in anhydrous THF in a flame-dried round-bottom flask equipped with a condenser under an argon atmosphere. The resulting black mixture was heated to 50 °C, at which point the reaction began to reflux. To the refluxing mixture was added anhydrous MeOH (5.5 mL) via syringe pump over 90 min. The reaction mixture was cooled to 0 °C in an ice-water bath and quenched by careful addition of aqueous 1 M HCl (40 mL), followed by 6 M HCl (80 mL). The majority of volatile organic components were removed on the rotary evaporator under reduced pressure and the remaining aqueous solution was extracted with CH_2Cl_2 (4 × 40 mL). The combined organic extract was washed with brine, dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give 2-

nitrothiophenol as a yellow solid (2.8 g). This material decomposes quickly and was used immediately without purification in the subsequent allylation step.

2-Nitrothiophenol (2.8g, ~16.2 mmol) was dissolved in anhydrous dimethylformamide (60 mL) in a flame-dried round bottom flask under an argon atmosphere. The resulting green solution was cooled to 0 °C in an ice-water bath and added K_2CO_3 in one portion, at which point the solution turned dark red. Allyl bromide (1.9 mL, 22 mmol) was subsequently added dropwise via syringe. The reaction mixture gradually turned yellow and was left to stir at rt for 20 h. The crude reaction mixture was diluted with distilled H_2O (400 mL) and brine (50 mL) and extracted with Et_2O (4 × 60 mL). The combined organic extract was washed with brine, dried with anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give allyl(2-(nitrophenyl)sulfane (3.1 g) as a yellow solid which was sufficiently pure by ^{1}H NMR. This material was used without purification in the subsequent oxidation reaction. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.54 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H), 7.43 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.30–7.21 (m, 1H), 5.90 (ddt, *J* = 13.4, 9.9, 6.7 Hz, 1H), 5.45–5.30 (m, 1H), 5.29–5.19 (m, 1H), 3.65 (dt, *J* = 6.5, 1.2 Hz, 2H).

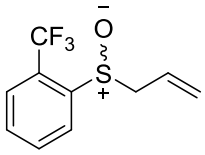
Allyl(2-(nitrophenyl)sulfane (3.1 g) was taken in glacial acetic acid (73 mL) under air and added a solution of aqueous H_2O_2 (35% solution, 6.8 mL, 79 mmol). The resulting greenish-brown solution was stirred at rt for 4 h. The crude reaction mixture was diluted with dH_2O (75 mL) and extracted with CH_2Cl_2 (3 × 40 mL). The combined organic extract was washed with brine, dried with anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give a brown residue consisting of both sulfoxide *and* sulfenate products. Purification by flash column chromatography (35─75% EtOAc in hexanes) and combining only the fractions containing the polar UV-active spots by tlc (40% EtOAc in hexanes, R_f = 0.4) gave a brown solid (1.8 g). Subsequent trituration with cold hexanes gave the product as a golden yellow solid (1.65 g, 7.81 mmol, 24% over 3 steps).

In $CDCl_3$, this compound exists as a 3:1 mixture (thermodynamic ratio) of sulfoxide:sulfenate ester. Major sulfoxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.22 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.95 (td, *J* = 7.8, 1.2 Hz, 1H), 7.73 – 7.68 (m, 1H), 5.85 – 5.71 (m, 1H), 5.36 (d, *J* = 10.0 Hz, 1H), 5.26 – 5.18 (m, 1H), 3.89 (dd, *J* = 12.9, 7.2 Hz, 1H), 3.61 (ddd, *J* = 12.9, 7.9, 0.6 Hz, 1H). Minor sulfenate ester: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.28 (m, 1H), 7.79 – 7.67 (m, 2H), 7.31 (ddd, *J* = 8.4, 6.6, 1.8 Hz, 1H), 6.04 (ddt, *J* = 16.3, 10.4, 5.8 Hz, 1H), 5.46 – 5.36 (m, 1H), 5.36 – 5.30 (m, 1H), 4.39 (dt, *J* = 5.8, 1.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$,

mixture) δ 146.6, 142.5, 135.2, 134.7, 133.1, 131.6, 127.7, 125.9$_1$, 125.9$_0$, 125.5, 125.2, 124.9, 124.2, 122.4, 119.4$_7$, 119.4$_6$, 77.8, 59.6.

In CD_3OD, this compound exists as a 6:1 mixture (thermodynamic ratio) of sulfoxide:sulfenate ester. Major sulfoxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.1 Hz, 1H), 8.15 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.07 (t, *J* = 7.6 Hz, 1H), 7.90 – 7.82 (m, 1H), 5.84 (ddt, *J* = 17.5, 10.1, 7.5 Hz, 1H), 5.39 (d, *J* = 10.2 Hz, 1H), 5.27 (d, *J* = 17.0 Hz, 1H), 4.02 (dd, *J* = 13.1, 7.2 Hz, 1H), 3.67 (dd, *J* = 13.0, 7.9 Hz, 1H).

IR (ATR, solid): 1520, 1344, 1304, 1056, 1032, 990, 934, 852, 791, 745, 727, 711, 680 cm^{-1}. HRMS (ESI+) *m/z* calc'd for $C_9H_9O_3SNNa$ $[M+Na]^+$: 234.0201; found: 234.0205.



1-(allylsulfinyl)-2-(trifluoromethyl)benzene (1f)

(2-Trifluoromethyl)thiophenol (850 mg, 4.77 mmol) was dissolved in dimethylformamide (24 mL) in a flame-dried round bottom flask under a balloon pressure of argon and the reaction vessel was cooled to 0 °C via an ice-water bath. To the cooled reaction mixture was added sodium hydride (60% oil dispersion, 286 mg, 7.15 mmol). The resulting suspension was stirred at 0 °C for 5 minutes and allyl bromide (460 μL, 5.32 mmol) was added dropwise via syringe. The reaction mixture was allowed to gradually warm to rt with stirring over 20 h. The reaction was quenched by pouring the reaction content into a separatory funnel containing dH_2O (100 mL) and saturated brine solution (20 mL). The resulting mixture was then extracted with Et_2O (4 × 25 mL). The combined organic extract was washed with brine, dried with anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give allyl(2-(trifluoromethyl)phenyl)sulfane as a yellow oil which was sufficiently pure by ^{1}H NMR analysis. This material was used without purification in the subsequent oxidation reaction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.41 (m, 2H), 7.33 – 7.26 (m, 1H), 5.88 (ddt, *J* = 16.9, 10.0, 6.8 Hz, 1H), 5.20 – 5.06 (m, 2H), 3.60 (d, *J* = 6.8 Hz, 2H).

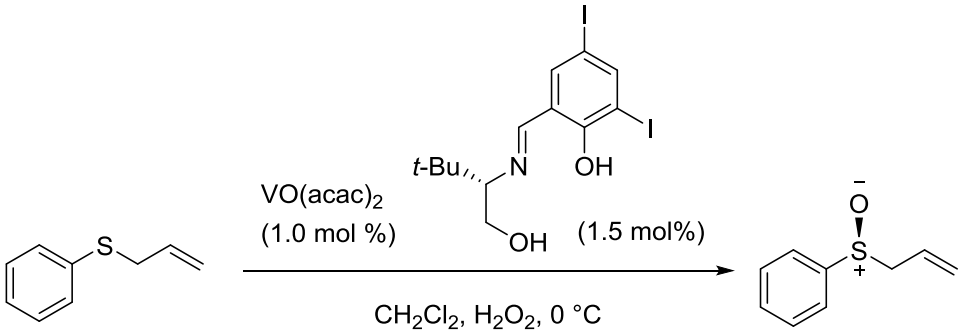
Allyl(2-(trifluoromethyl)phenyl)sulfane was taken in glacial acetic acid (24 mL) with stirring under air and added a solution of aqueous H_2O_2 (35% solution, 820 μL, 9.54 mmol). The resulting solution was stirred at rt for 45 min, at which point an additional portion of aqueous H_2O_2 was added (35% solution, 1.23 mL, 14.3 mmol). The reaction mixture was stirred at rt for an additional 20 h. The reaction was quenched by careful addition of a saturated solution of aqueous $NaHCO_3$ (50 mL), and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic

extract was washed with saturated brine, dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. Purification by flash column chromatography (silica gel) eluting with 0 ─ 25 % EtOAc in hexanes gave the product as a colorless oil (691 mg, 62% over 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.9 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 5.81–5.67 (m, 1H), 5.37 (d, *J* = 10.1 Hz, 1H), 5.22 (dd, *J* = 17.0, 1.1 Hz, 1H), 3.68 (dd, *J* = 13.1, 7.3 Hz, 1H), 3.40 (dd, *J* = 13.1, 7.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 132.9 (q, ~1.1 Hz), 131.2, 127.0 (q, 32.9 Hz), 126.5 (q, 5.3 Hz), 126.2, 125.3, 124.4, 123.6 (q, 274.8 Hz), 60.7; ^{19}F NMR (376.58 MHz, $CDCl_3$) δ ─58.2. IR (neat): 3086, 3058, 3009, 2952, 1635, 1587, 1504, 1343, 1196, 1091, 1060, 1037, 932, 908, 866, 825, 742 cm^{-1}. HRMS (EI) *m/z* calc'd for $C_{10}H_9F_3SO$ $[M+Na]^+$: 257.0224; found: 257.0229.

3. Racemization kinetics

(i) Synthesis of enantioenriched phenyl allyl sulfoxide

Enantioenriched phenyl allyl sulfoxide was synthesized according to Pelotier et al.[3]



To a solution of the chiral ligand (Schiff base of 3,5-diiodosalicylaldehyde and (*S*)-*tert*-leucinol; 28.4 mg, 0.02 mmol, 0.015 eq) in CH_2Cl_2 (2 mL) at 0 °C was added $VO(acac)_3$ (10.6 mg, 0.04 mmol, 0.010 eq) in CH_2Cl_2 (2 mL). The green solution was stirred for 30 minutes, at which time phenyl allyl sulfide (601 mg, 4.0 mmol, 1.0 eq) was added. This solution was stirred at 0 °C for 30 minutes, and then a solution of aqueous 35% H_2O_2 (378 µL, 4.4 mmol, 1.1 eq) was added. The heterogeneous mixture was stirred vigorously at 0 °C for 5 hours, at which point it was quenched with 10% $Na_2S_2O_3$ (10 mL). The mixture was extracted with CH_2Cl_2 (2 x 50 mL), dried with anhydrous Na_2SO_4, and carefully concentrated *in vacuo* while maintaining a water

[3] Pelotier, B.; Anson, M. S.; Campbell, I. B.; Macdonald, S. J. F.; Priem, G.; Jackson, R. F. W. *Synlett* **2002**, *2002*, 1055–1060.

bath temperature of 0 °C. The product was purified by column chromatography (1:1 ethyl acetate:hexanes) to yield a pale yellow oil (395 mg, 59%). SFC analysis: 81% ee (ODH, 15% IPA, 2.5 mL/min, 44 ˚C, nozzle pressure = 200 bar CO_2); $[\alpha]^{25}_D$ = −197 (*c* 1.0, DCE). This substrate was stored neat in a freezer, with no significant loss of optical rotation over a period of several months.

(ii) Kinetics by polarimetry

All kinetic runs were repeated independently three times. The rate constant was taken as the mean value, and the uncertainty is the standard deviation.

For kinetics with $PdCl_2(PhCN)_2$: 2 equivalents of the complex was weighed in order to improve accuracy of the measurement. $PdCl_2(PhCN)_2$ (2.3 mg, 0.006 mmol) was dissolved in 3 mL of 1,2-DCE. 1.5 mL of this solution was then transferred to a vial containing enantioenriched (*S*)-phenyl allyl sulfoxide (24.9 mg, 0.1 mmol). The resulting solution was transferred to a polarimeter cell and sealed with Teflon.

For kinetics without catalyst: (*S*)-phenyl allyl sulfoxide (24.9 mg, 0.1 mmol) was added to the appropriate solvent, and this solution was transferred to a polarimeter cell and sealed with Teflon.

The optical rotation was monitored at periodic time intervals to monitor the loss in optical activity. Least squares linear regression was performed on a plot of the $\ln([\alpha]/[\alpha]_{initial})$ versus time. The rate constant was taken as the negative of the slope of this regression.

(iii) Kinetics by SFC analysis with [Rh(S,S)-PhBPE]BF_4

In a nitrogen-filled glove box, [Rh((*S*,*S*)-PhBPE)(COD)]BF_4 (1.6 mg, 0.002 mmol) was dissolved in methanol (0.5 mL) and stirred for five minutes to ensure dissolution. This solution was transferred to a Schlenk tube, and rinsed with methanol (0.5 mL). On a Schlenk line, the tube is cooled in liquid nitrogen, evacuated, backfilled with H_2, thawed to room temperature and then closed. The reaction was stirred at ambient temperature for 1 hour to hydrogenate the COD ligand. The Schlenk tube was then returned to the glove box, and the activated catalyst solution was added to enantioenriched (*S*)-phenyl allyl sulfoxide **44a** (initially 79% ee). At each time point, a 100 µL aliquot of the reaction was taken. The solvent was removed with a high vacuum pump, which also cools the sample. The solution is then dissolved in CH_2Cl_2 (1 mL) and rapidly transferred to a silica gel plug (height = 1 cm, diameter = 5 mm). The plug was flushed with

CH_2Cl_2 (sulfoxide does not elute), and then flushed with isopropanol (sulfoxide elutes). The isopropanol is then removed with a high vacuum pump. HPLC grade methanol was then added to prepare the sample for SFC analysis. The sample was either analyzed immediately or stored in a -5 °C freezer. Aliquots were taken every 30 minutes for 2 hours. Least squares linear regression was performed on a plot of the $\ln([ee]/[ee]_{initial})$ versus time. The rate constant was taken as the negative of the slope of this regression. All kinetic runs were repeated independently three times. The rate constant was taken as the mean value, and the uncertainty is the standard deviation.

4. Hydrogenation procedures

i) General procedure for ligand screening (atmospheric pressure of H_2)

In a nitrogen-filled glove box, (*S*,*S*)-Ph-BPE (1.2 equiv with respect to Rh) was dissolved in half the required volume of CH_2Cl_2 and added to $[Rh(COD)_2BF_4]$. The remaining volume of CH_2Cl_2 is used to rinse the vial with ligand into the catalyst solution. An appropriate volume of toluene is then added to the catalyst solution, and this is transferred to the substrate in a Schlenk tube. On a Schlenk line, the tube is cooled in liquid nitrogen, evacuated, backfilled with H_2, thawed to room temperature and then closed. The vessel is then stirred at the required temperature for the specified time. Upon completion, the crude reaction mixture is concentrated, loaded directly onto a preparative TLC plate and eluted with 1:1 ethyl acetate:hexanes. The product could not be separated from the starting material by TLC, however an assay of yield in addition to ee could be obtained by SFC analysis.

ii) Optimized procedure for hydrogenations (sub-atmospheric pressures of H_2)

In a nitrogen-filled glove box, $[Rh((S,S)\text{-PhBPE})(COD)]BF_4$ (1.6 mg) was suspended in half the required volume of methanol (0.5 mL) and stirred for five minutes to ensure dissolution. The catalyst solution was transferred to the substrate, and this mixture was added to a Schlenk tube. The remaining volume of methanol (0.5 mL) was used to rinse the vial and this liquid was also transferred to the Schlenk tube. On a Schlenk line, the reaction was pressurized (see below for details) and then stirred at ambient temperature or heated in an oil bath if necessary. After the required time, the reaction was quenched by exposure to air and was concentrated and dissolved in $CDCl_3$ for ^1H NMR analysis to assay the sulfoxide sulfenate ratio. Note: $CDCl_3$ should be treated with K_2CO_3 prior to use in order to quench any traces of HCl. The solution was then

concentrated and purified by preparative TLC in EtOAc:hexanes mixtures to yield the desired product.

iii) General procedure for obtaining reduced pressures of H_2

The following apparatus was assembled on a Schlenk line (see Figure 1): A stopcock connects to a Y-joint, which in turn leads to two Schlenk tubes. One of these tubes is empty, and the other contains the reaction mixture. Schlenk tubes purchased from Chemglass were used (product number AF-0096). The volume inside the tubing and Y-joint which connects the stopcock and the two Schlenk flasks was measured by adding acetone to the apparatus and then pouring into a graduated cylinder. We obtained a volume of 6.5 mL for our apparatus. The reaction flask is degassed with two freeze-pump-thaw cycles, leaving the flask closed, thawed and under vacuum. Meanwhile the empty flask is filled with H_2 (1 atm), and then closed. The space between the flasks is evacuated, and the main stopcock is closed to the Schlenk line. Both flasks are then opened to allow the H_2 to distribute between the two flasks. The reaction flask is then sealed. This procedure can be adapted to obtain any desirable partial pressures, see below for examples. The final pressure in the system is given by the volume of the system that is filled with 1 atm H_2 divided by the total volume of the system, multiplied by 1 atm H_2.

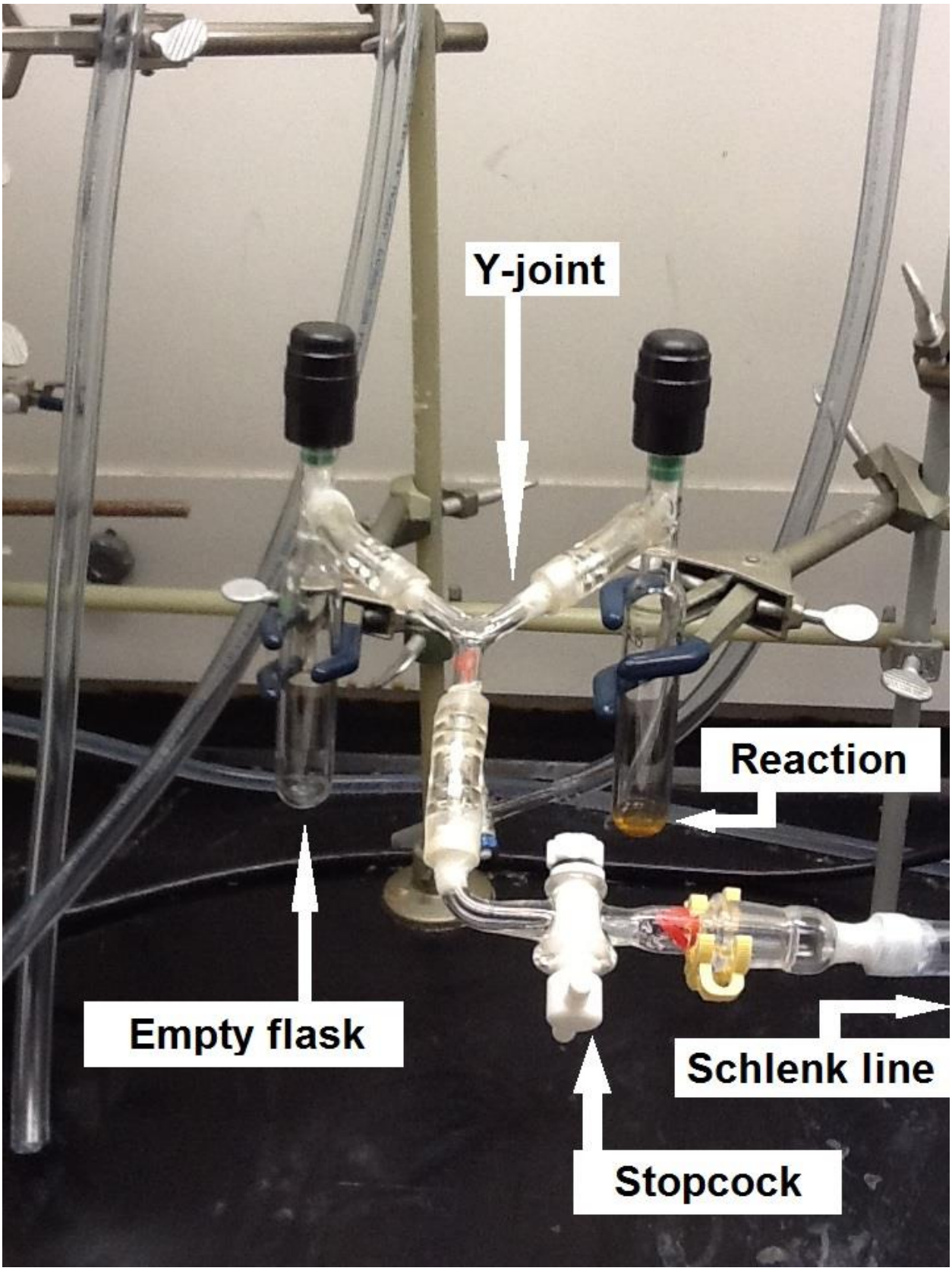


Figure S1. Apparatus for obtaining reduced pressures of H_2.

0.56 atm:

Both the reaction flask and the empty flask are 25 mL Schlenk tubes. Both the empty flask and the tubing between the flasks are filled with H_2 prior to H_2 equilibration. The pressure in the system after opening both flasks is given by:

P = [(25 + 6.5 mL) / (25 + 6.5 + 25 mL)] x 1 atm = 0.56 atm.

0.44 atm:

Both the reaction flask and the empty flask are 25 mL Schlenk tubes. Only the empty 25 mL Schlenk tube is filled with H_2 prior to H_2 equilibration. The pressure in the system after opening both flasks is given by:

P = [(25 mL) / (25 + 6.5 + 25 mL)] x 1 atm = 0.44 atm.

0.31 atm:

The reaction flask is a 50 mL Schlenk tube and the empty flask is a 25 mL Schlenk tube. Only the 25 mL Schlenk tube is filled with H_2 prior to equilibration. The pressure in the system after opening both flasks is given by:

P = [(25 mL) / (25 + 6.5 + 50 mL)] x 1 atm = 0.31 atm.

0.29 atm:

An additional Y joint is added to one of the arms of the original Y joint. The volume of the connecting space is now 10 mL. Three 25 mL Schlenk tubes are attached to the apparatus, one of which contains the reaction. One of the empty tubes is pressurized to 1 atm of H_2, and the reaction flask is evacuated by two 'freeze-pump-thaw' cycles. The third Schlenk tube and the connecting space is evacuated. The stopcock is closed and the three tubes are opened, equilibrating the gas. Note: This procedure has the added benefit that two reactions can be pressurized simultaneously. The pressure is given by:

P = [(25 mL) / (25 + 25 + 25+ 10 mL)] x 1 atm = 0.29 atm.

Figure S2. Apparatus for obtaining 0.29 atm.

0.09 atm:

This pressure can be obtained by performing the procedure for 0.31 atm twice. After this procedure is performed for the first time, the empty flask is sealed at 0.31 atm, and the reaction flask is evacuated by performing one freeze pump thaw cycle. The stopcock is then closed and the two flasks are opened to allow equilibration. The pressure in the system after opening both flasks is given by:

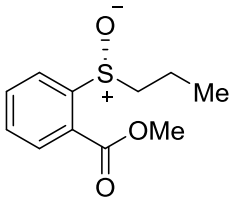
P = [(25 mL) / (25 + 6.5 + 50 mL)] x [(25 mL) / (25 + 6.5 + 50 mL)] x 1 atm = 0.09 atm.

0.06 atm:

The apparatus is setup with an empty 25 mL Schlenk tube and an empty 50 mL Schlenk tube. The 25 mL tube is pressurized to 1 atm H_2. The 50 mL tube and the connecting space is evacuated. Equilibration of the system leads to 0.31 atm. The 25 mL tube is then sealed, and the

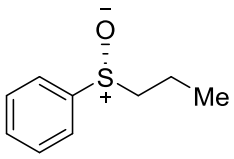
50 mL tube is replaced with a 100 mL Schlenk tube containing the reaction. Two freeze pump thaw cycles are performed on the reaction vessel, leaving the tube closed, evacuated and thawed. With the connecting volume also evacuated, the two tubes are opened, equilibrating to 0.06 atm. Note this vessel is expected to contain 0.24 mmol of H_2. The pressure is given by:

P = [(25 mL) / (25 + 6.5 + 50 mL)] x [(25 mL) / (25 + 6.5 + 100 mL)] x 1 atm = 0.06 atm



Methyl 2-(propylsulfinyl)benzoate (3a)

According to the general procedure for asymmetric hydrogenation, allylic sulfoxide **1a** was hydrogenated under ~0.1 atm H_2 with 2 mol % Rh-catalyst in MeOH (1 mL) solvent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, 1H, *J* = 1.2 Hz, *J* = 7.9 Hz), 8.09 (dd, 1H, *J* = 1.3 Hz, *J* = 7.7 Hz), 7.80 (dt, 1H, *J* = 1.4 Hz, *J* = 7.7 Hz), 7.56 (dt, 1H, *J* = 1.3 Hz, *J* = 7.6 Hz), 3.95 (s, 3H), 3.11 (ddd, 1H, *J* = 6.9 Hz, *J* = 9.6 Hz, *J* = 12.7 Hz), 2.67 (ddd, 1H, *J* = 4.9 Hz, *J* = 9.4 Hz, *J* = 12.7 Hz), 2.09–1.93 (m, 1H), 1.84–1.68 (m, 1H), 1.08 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 148.9, 133.9, 131.0, 130.1, 126.7, 125.0, 59.2, 52.7, 16.8, 13.3; IR (neat): 2960, 2931, 2871, 1713, 1588, 1436, 1300, 1277, 1192, 1140, 1105, 1070, 1033, 961, 827, 754, 694 cm^{-1}. HRMS (EI) *m/z* calc'd for $C_{11}H_{14}O_3S$ $[M]^+$: 226.0664; found: 226.0660. SFC analysis: 88% ee (250 mm CHIRALPAK IA, 6% MeOH, 3.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2), t_{R1} = 4.01 min, t_{R2} = 4.61 min; $[\alpha]^{25}_D$ +225 (*c* = 0.97, $CHCl_3$).

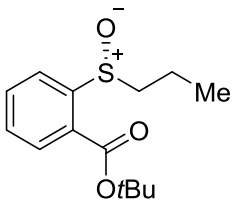


Propylsulfinyl)benzene (3b)

According to the general procedure for asymmetric hydrogenation, allylic sulfoxide **3a** (0.1 mmol, 16.6 mg) was hydrogenated under ~0.1 atm H_2 with 4 mol % Rh-catalyst in MeOH (1 mL) solvent. The title compound was isolated as a clear oil (11.0 mg, 65%, 50% ee). The spectroscopic data obtained were in accord with those previously reported.[4] For ligand screening, the product/starting material ratio and ee's were determined by HPLC analysis (250 mm CHIRALCEL OD-H, 1:19 isopropanol:hexanes, 1.0 mL/min flow rate, 254 nm), $t_{R(P1)}$ = 13.8 min, $t_{R(SM1)}$ = 16.0 min, $t_{R(P2)}$ = 18.1 min, $t_{R(SM2)}$ = 20.8 min. For optimized conditions: $[\alpha]^{25}_D$ = +77 (*c* = 0.73, $CHCl_3$). SFC conditions were also identified: 250 mm CHIRALCEL OD-H, 10% MeOH, 2.5 mL/min, 50 ˚C, nozzle pressure = 200

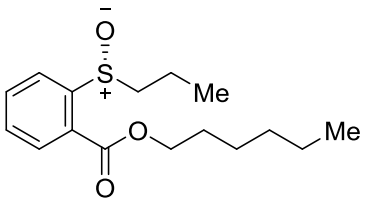
[4] Imada, Y.; Hiroki, I.; Takeshi, N. *J. Am. Chem. Soc.* **2005**, *127*, 14554.

bar, t_{R1} = 2.70 min, t_{R2} = 2.85 min. Absolute configuration was determined by independent synthesis by asymmetric oxidation using Pelotier's method (*vide supra*).[3]



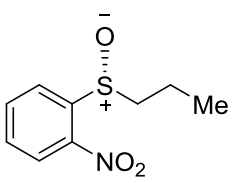
tert-butyl 2-(propylsulfinyl)benzoate (3c)

According to the general procedure for asymmetric hydrogenation, *tert*-butyl 2-(allylsulfinyl)benzoate **1c** (26.6 mg, 0.1 mmol) was hydrogenated under ~0.1 atm H_2 at rt using 2 mol % rhodium catalyst in MeOH (1 mL) solvent. The title compound was isolated as a clear oil (18.4 mg, 69%, 84% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.01 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.76 (td, *J* = 7.7, 1.4 Hz, 1H), 7.52 (td, *J* = 7.6, 1.3 Hz, 1H), 3.10 (ddd, *J* = 12.8, 10.0, 6.4 Hz, 1H), 2.66 (ddd, *J* = 12.8, 9.9, 5.0 Hz, 1H), 2.04─1.94 (m, 1H), 1.77─1.66 (m, 1H), 1.61 (s, 9H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 148.1, 133.0, 130.7, 129.7, 128.6, 124.6, 82.7, 58.7, 28.1, 16.4, 13.1; IR (neat): 2973, 2360, 1700, 1305, 1069, 1024, 752 cm^{-1}; HRMS (ESI+) calc'd. for $[C_{14}H_{20}O_3S+H]^+$: 269.1205; found 269.1196. SFC analysis: 84% ee, 150 mm CHIRALCEL AD-H, 10% IPA, 2.5 mL/min, 254 nm, 44 ℃ , nozzle pressure = 100 bar CO_2, t_{R1} = 4.43 min, t_{R2} = 4.83 min; $[\alpha]^{25}_D$ +167 (*c* = 1.47, $CHCl_3$).



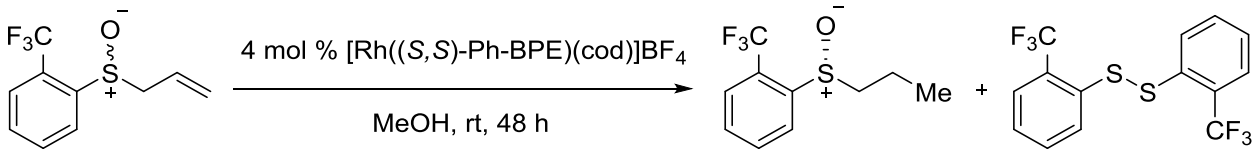
hexyl 2-(propylsulfinyl)benzoate (3d)

According to the general procedure for asymmetric hydrogenation, allylic sulfoxide **1d** was hydrogenated under ~0.1 atm H_2 with 2 mol % Rh-catalyst in MeOH (1 mL) solvent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, J = 7.9, 1.3 Hz, 1H), 8.09 (dd, J = 7.7, 1.2 Hz, 1H), 7.80 (ddd, J = 7.7, 7.4, 1.3 Hz, 1H), 7.55 (td, J = 7.6, 1.4 Hz, 1H), 4.34 (td, J = 6.8, 1.1 Hz, 2H), 3.12 (ddd, J = 12.8, 9.8, 6.7 Hz, 1H), 2.66 (ddd, J = 12.6, 9.7, 4.8 Hz, 1H), 2.00 (tdt, J = 14.3, 9.6, 7.3 Hz, 1H), 1.83–1.69 (m, 3H), 1.50─1.40 (m, 2H), 1.38─1.32 (m, 4H), 1.07 (t, J = 7.4 Hz, 3H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 148.7, 133.5, 130.7, 129.9, 127.0, 124.8, 65.9, 58.9, 31.3, 28.5, 25.6, 22.5, 16.6, 13.9, 13.1; IR (neat): 2930, 1708, 1272, 1103, 1070, 1026, 752; HRMS (ESI+) calc'd. for $[C_{16}H_{24}O_3S+H]^+$: 297.15244; found 297.15266. SFC analysis: 86% ee (250 mm CHIRALCEL IC, 10% MeOH, 3 mL/min, 254 nm, 44 °C , nozzle pressure = 200 bar CO_2), t_{R1} = 5.59 min, t_{R2} = 7.57 min; $[\alpha]^{25}_D$ +175 (*c* = 1.0, $CHCl_3$).

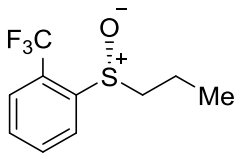


1-nitro-2-(propylsulfinyl)benzene (3e)

According to the general procedure for asymmetric hydrogenation, 1-(allylsulfinyl)-2-nitrobenzene (21.1 mg, 0.1 mmol) was hydrogenated under 0.1 atm H_2 at rt with 2 mol % Rh-catalyst in MeOH (2 mL) solvent for 24 h. The title compound was isolated as a clear oil (11.7 mg, 55%, 72% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.32 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.96 (ddd, *J* = 7.9, 7.4, 1.2 Hz, 1H), 7.70 (ddd, *J* = 8.2, 7.4, 1.4 Hz, 1H), 3.16 (ddd, *J* = 12.8, 9.2, 7.2 Hz, 1H), 2.76 (ddd, *J* = 12.8, 9.0, 5.0 Hz, 1H), 2.11-2.01 (m, 1H), 1.86-1.72 (m, 1H), 1.12 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 143.8, 135.3, 131.2, 126.8, 125.1, 58.9, 16.8, 13.0; IR(neat): 2963, 2360, 2341, 1523, 1341, 1070, 1034, 791, 736 cm^{-1}; HRMS (ESI+) calc'd. for $[C_9H_{11}NO_3S+H]^+$: 214.0532; found 214.0536. SFC analysis: 72% ee (250 mm CHIRALCEL IA, 6% isopropanol, 3 mL/min flow rate, 254 nm, 44 °C), t_{R1} = 6.44 min (minor), t_{R2} = 6.84 min (major); $[\alpha]^{25}_D$ +280 (*c* = 0.02, $CHCl_3$).



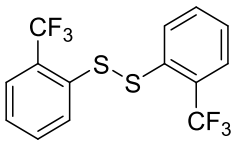
1f **3f** **3ff**



1-(propylsulfinyl)-2-(trifluoromethyl)benzene (3f)

According to the general procedure for asymmetric hydrogenation, allylic sulfoxide **1f** (23.5 mg, 0.1 mmol) was hydrogenated under ~0.1 atm H_2 with 4 mol % Rh-catalyst at rt for 48 h. Purification by prep-tlc (3:7 EtOAc:hexanes) gave the title product as a yellow oil (53% yield, 88% ee, average of 2 reactions). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 2.83 (dt, *J* = 13.5, 8.2 Hz, 1H), 2.71 (td, *J* = 8.6, 4.4 Hz, 1H), 1.93 (tq, *J* = 15.0, 7.6 Hz, 1H), 1.83–1.72 (m, 1H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4 (s), 133.2 (partially resolved quartet, *J* ≈ 0.9 Hz), 131.0 (s), 126.8 (q, *J* = 32.8 Hz), 126.6 (q, *J* = 5.3 Hz), 125.5 (s), 123.6 (q, *J* = 274.8 Hz), 60.1 (s), 16.6 (s), 13.2 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ −52.5. IR (ATR, oil): 2968, 1313, 1260, 1176, 1118, 1087, 1065, 1025, 770, 732, 643, 596 cm^{-1}. HRMS (ESI+) *m/z* calc'd for $[C_{10}H_{11}OSF_3+Na]^+$: 259.0381;

found: 259.0387. SFC analysis: 88% ee (250 mm CHIRALCEL AD-H, 10% isopropanol, 2.5 mL/min flow rate, 254 nm, 50 °C, nozzle pressure = 100 bar CO_2), t_{R1} = 2.21 min (minor), t_{R2} = 2.39 min (major); $[\alpha]^{25}_{D}$ +149 (*c* = 0.83, $CHCl_3$).

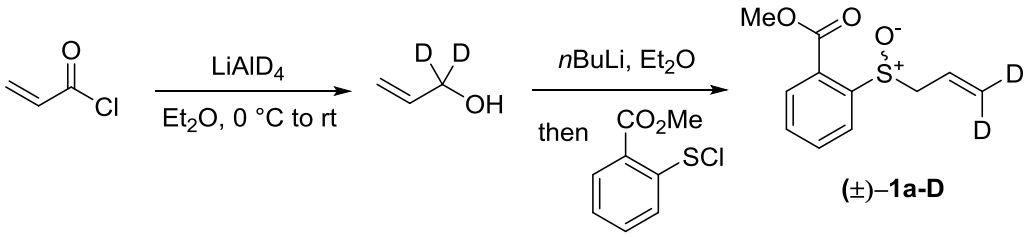


1,2-bis(2-(trifluoromethyl)phenyl)disulfane (3ff)

The disulfide is the major byproduct (6.3─6.5 mg, 36─37%) isolated in the DKR of allylic sulfoxide **1f**. This likely arises from initial hydrogenation of the sulfenate ester **2f** to generate the corresponding thiol which oxidizes to the title compound. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.6 (s), 132.7 (q, *J* ≈ 0.8 Hz), 129.6 (s), 128.6 (q, *J* = 31.2 Hz), 127.3 (s), 126.8 (q, *J* = 5.6 Hz), 123.8 (d, *J* = 274.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ ─60.0. IR (ATR, liquid): 2927, 2855, 1592, 1572, 1469, 1440, 1309, 1259, 1174, 1112, 1088, 1041, 1029, 954, 759, 729, 694, 645, 595 cm^{-1}.

5. Deuterium labeling studies

Preparation of racemic γ-deuterated Methyl 2-(allylsulfinyl)benzoate (±)-1a-D



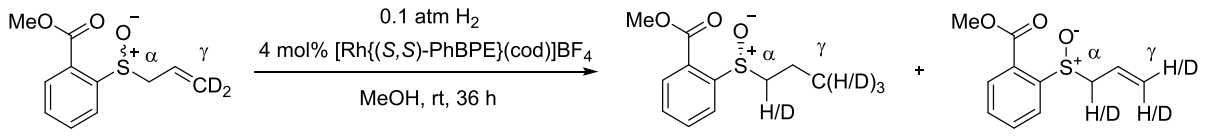
Lithium aluminum deuteride (1.1 g, 26.2 mmol) was suspended in anhydrous Et_2O in a flame-dried round-bottom flask under a nitrogen atmosphere and the mixture was cooled to 0 ˚C in an ice-water bath. To the cooled slurry was added acryloyl chloride (2.1 mL, 26 mmol) dropwise via syringe. The resulting mixture was stirred at 0 ˚C for 10 min, then warmed to rt and stirred at rt for 12 h, at which point the reaction was cooled to 0 ˚C and quenched via Fieser-Fieser workup conditions: sequential addition of 1.1 mL distilled H_2O, 1.1 mL of 15% $NaOH_{(aq)}$ and 3.3 mL distilled H_2O. The resulting suspension was left to stir for approximately 3 h, then filtered through a fritted funnel. Removal of Et_2O under a gentle vacuum (18 ˚C water bath) gave the crude α-d_2-allyl alcohol as a colorless oil. α-d_2-Allyl alcohol was subsequently purified by Kugelrohr distillation between 50─60 ˚C under reduced pressure to give a colorless liquid (837

mg). The ^{1}H NMR data obtained were in accord with those previously reported.[5] ^{1}H NMR analysis of the distilled material indicates a 7:3 mixture of α-d_2-allyl alcohol to diethyl ether (*ca.* 70 % pure, 9.7 mmol, 36 % yield) with >95:5 isotopic purity. This material was used in the subsequent sulfuration/[2,3]-sigmatropic rearrangement without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.00 (dd, J = 17.3, 10.5 Hz, 1H), 5.28 (d, J = 17.2 Hz, 1H), 5.15 (d, J = 10.4 Hz, 1H), alcoholic proton *not* observed; ^{2}H NMR (92 MHz, $CDCl_3$) δ 4.13 (broad signal).

α-d_2-Allyl alcohol (~9 mmol) was taken in anhydrous Et_2O in a flame-dried round-bottom flask under a nitrogen atmosphere, and the solution was cooled to 0 ˚C in an ice-water bath. To the cooled solution was dropwise added a solution of *n*-BuLi in hexanes (1.38 M, 8.1 mL, 11.2 mmol) via syringe. The resulting lithium alkoxide was stirred at 0 ˚C for 5 min and a solution of methyl 2-(chlorothio)benzoate[6] (2.47 g, 12.2 mmol) in Et_2O (4.5 mL) was added dropwise. The resulting suspension was stirred at 0 ˚C for 10 min, then warmed to rt for 5 min. The reaction was quenched by addition of distilled H_2O (30 mL) and the ethereal layer was separated. The aqueous layer was extracted with EtOAc (2 × 25 mL) and the combined organic extract was washed with brine, dried with anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give a yellow oil. Purification by flash silica gel chromatography eluting with 0─90% EtOAc in hexanes, followed by a second flash silica gel chromatography step eluting with 0─10% Et_2O in DCM gave γ-d_2-methyl 2-(allylsulfinyl)benzoate as a pale yellow solid (470 mg, 23%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, J = 7.9 Hz, 1H), 8.10 (d, J = 7.7 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 5.78 (s, 1H), 3.96 (s, 3H), 3.86 (dd, J = 12.9, 7.3 Hz, 1H), 3.50 (dd, J = 12.9, 7.8 Hz, 1H); ^{2}H NMR (61 MHz, $CHCl_3$) δ 5.45 – 5.18 (broad m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 147.7, 133.7, 130.9, 130.3, 126.8, 126.5, 125.8, 59.9, 52.8. IR (ATR, solid film): 3071, 3034, 2983, 2955, 1709, 1434, 1297, 1276, 1139, 1104, 1022, 942, 747, 689. HRMS (ESI+) *m/z* calc'd for $[C_{11}H_{10}O_3D_2S+Na]^+$: 249.0530; found: 249.0524.

[5] Mukherjee, P.; Widenhoefer, R. A. *Org. Lett.* **2010**, *12*, 1184.
[6] Prepared from NCS and methyl thiosalicylate in DCM and used immediately: Chen, C. H.; Fox, J. L. *J. Org. Chem.* **1985**, *50*, 3592.

5.1. Hydrogenation of γ-dideutero-methyl 2-(allylsulfinyl)benzoate in MeOH under 0.1 atm H_2



1a-D

α: 0% D-content
γ: 100% D-content

3a-D

75% yield, 91% ee

α: 37% D-content
γ: 37% D-content

recovered 1a-D

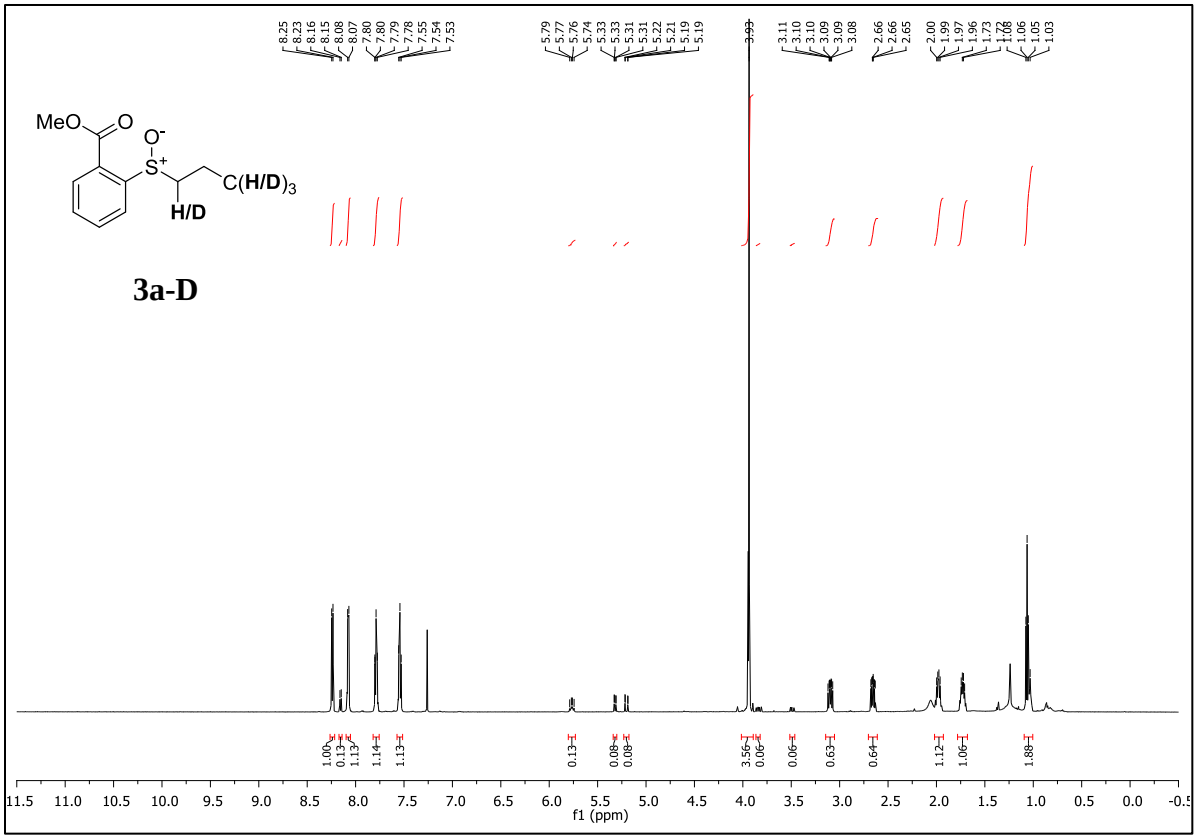
10% yield

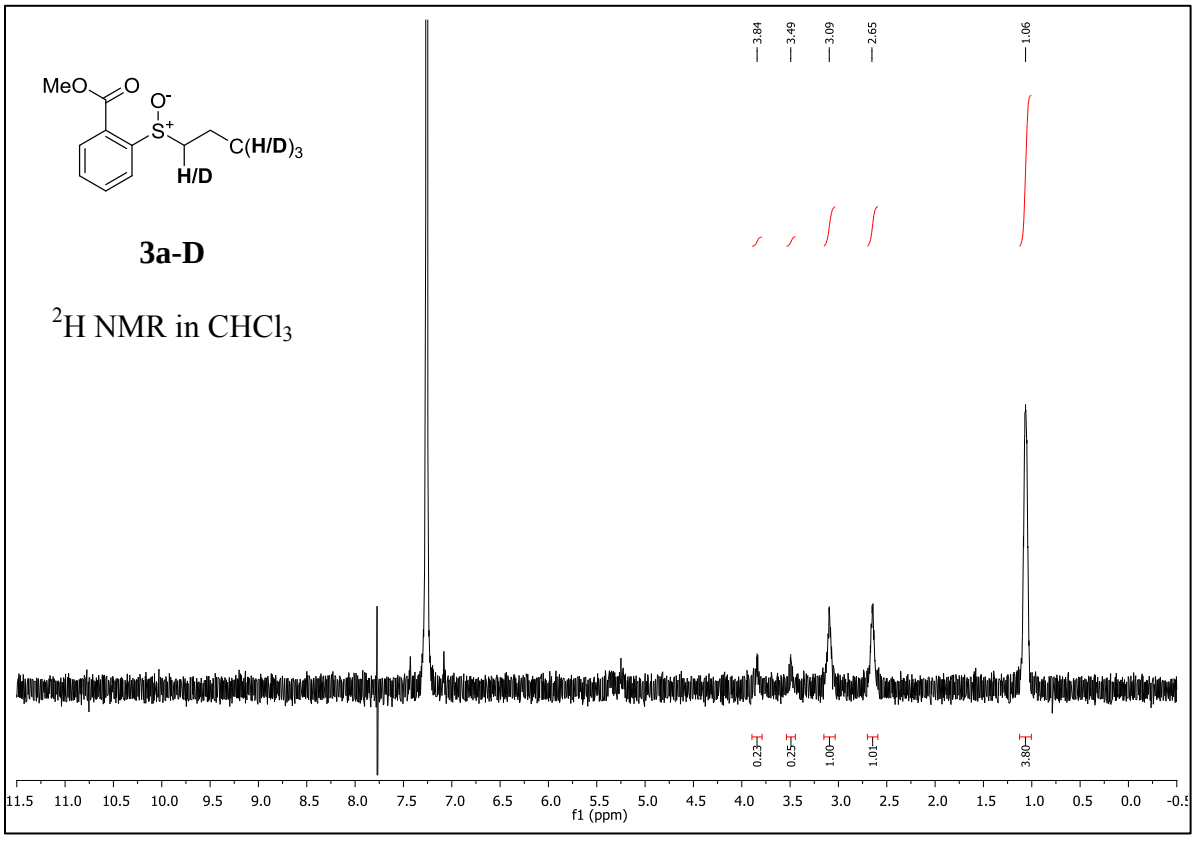
α: 58% D-content
γ: 38% D-content

α_1 proton of **3a-D**, δ 3.09 (ddd, 1H): observed integration = 0.63 H; expected integration = 1 H; therefore, there is 63% protio-content and the remaining 37% is attributed to deutero-content

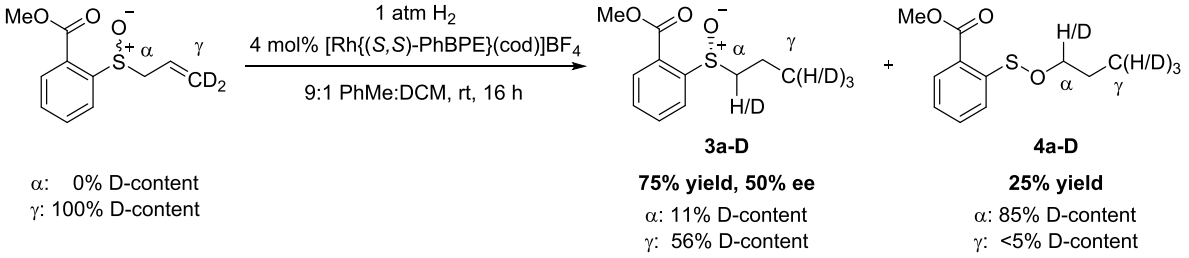
α_2 proton of **3a-D**, δ 2.65 (ddd, 1H): observed integration = 0.64 H; expected integration = 1 H; therefore, there is 64% protio-content and the remaining 36% is attributed to deutero-content

γ protons of **3a-D**, δ 1.09 – 1.00: observed integration = 1.88 H; expected integration = 3 H; therefore, there is 63% protio-content and the remaining 37% is attributed to deutero-content

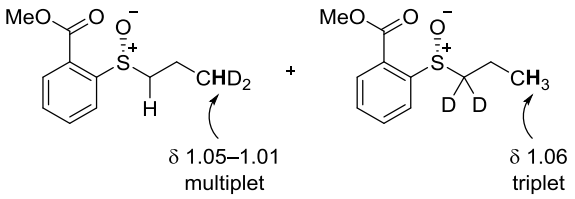

MeO
O
O-
S+
C(H/D)3
H/D
3a-D
f1 (ppm)


MeO
O
O-
S+
C(H/D)3
H/D
3a-D
2H NMR in CHCl3
f1 (ppm)

5.2. Hydrogenation of γ-dideutero-methyl 2-(allylsulfinyl)benzoate in 9:1 PhMe:DCM under 1 atm H_2

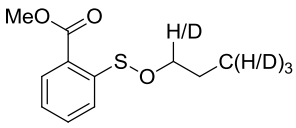


Note: The maximum deuterium content in the γ-position of the hydrogenated sulfoxide product **3a-D** is 66.7% if no scrambling occurs, whereas the maximum deuterium content in the α-position of hydrogenated sulfenate ester **4a-D** is 100% if no scrambling occurs.



d_2-methyl 2-(propylsulfinyl)benzoate (3a-D)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 7.9, 1.0 Hz, 1H), 8.08 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.79 (td, *J* = 7.8, 1.3 Hz, 1H), 7.54 (td, *J* = 7.6, 1.2 Hz, 1H), 3.94 (s, 3H), 3.09 (ddd, *J* = 12.8, 9.6, 6.9 Hz, **0.89H**), 2.65 (ddd, *J* = 12.8, 9.4, 4.9 Hz, **0.89H**), 2.03 – 1.93 (m, 1H), 1.77 – 1.68 (m, 1H), 1.05 – 1.01 (t, *J* = 7.4 Hz, 3H), 1.04 (m, 1H); ^{2}H NMR (92 MHz, $CDCl_3$)[7] δ 3.09 (broad singlet), 2.65 (broad singlet), 1.12 – 1.00 (broad multiplet); ^{13}C NMR (126 MHz, $CDCl_3$)[8] δ 165.8, 148.8, 133.9, 131.0, 130.2, 126.7, 125.0, 59.1, 52.8, 16.7, 16.6 (**α-d_2-3a-D**), 13.2 (**α-d_2-3a-D**), 12.7 (quintet, *J* = 19.4 Hz). IR (ATR, liquid): 2951, 1711, 1588, 1436, 1278, 1105, 1065, 1030, 961, 751, 694. HRMS (ESI+) *m/z* calc'd for $[C_{11}H_{12}O_3D_2S+Na]^+$: 251.0687; found: 251.0689.



d_2-methyl 2-(propoxythio)benzoate (4a-D)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.63 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.58 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.20 – 7.15 (m, 1H), 3.93 (s, 3H), 3.82 (t, *J* = 6.7 Hz, **0.3H**), 1.78 (q, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{2}H NMR (61 MHz, $CDCl_3$) δ 3.81 (broad singlet), 1.00 (broad singlet).

[7] See spectrum for integration
[8] ~1:9 mixture of α-d_2-**3a-D** to γ-d_2-**3a-D**; most carbon atom share the same signal unless otherwise noted.

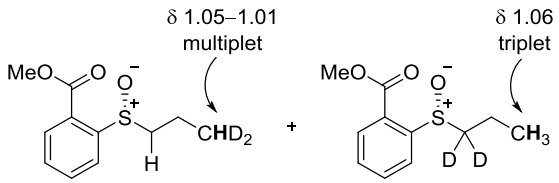
Determination of deuterium content in sulfoxide product **3a-D***:*

The deuterium content was determined by integration of the ^{1}H NMR spectrum (recorded with extended relaxation delay, 25 s):

α_1 proton of **3a-D**, δ 3.09 (ddd, 1H): observed integration = 0.89 H; expected integration = 1 H; therefore, there is 89% protio-content and the remaining 11% is attributed to deutero-content

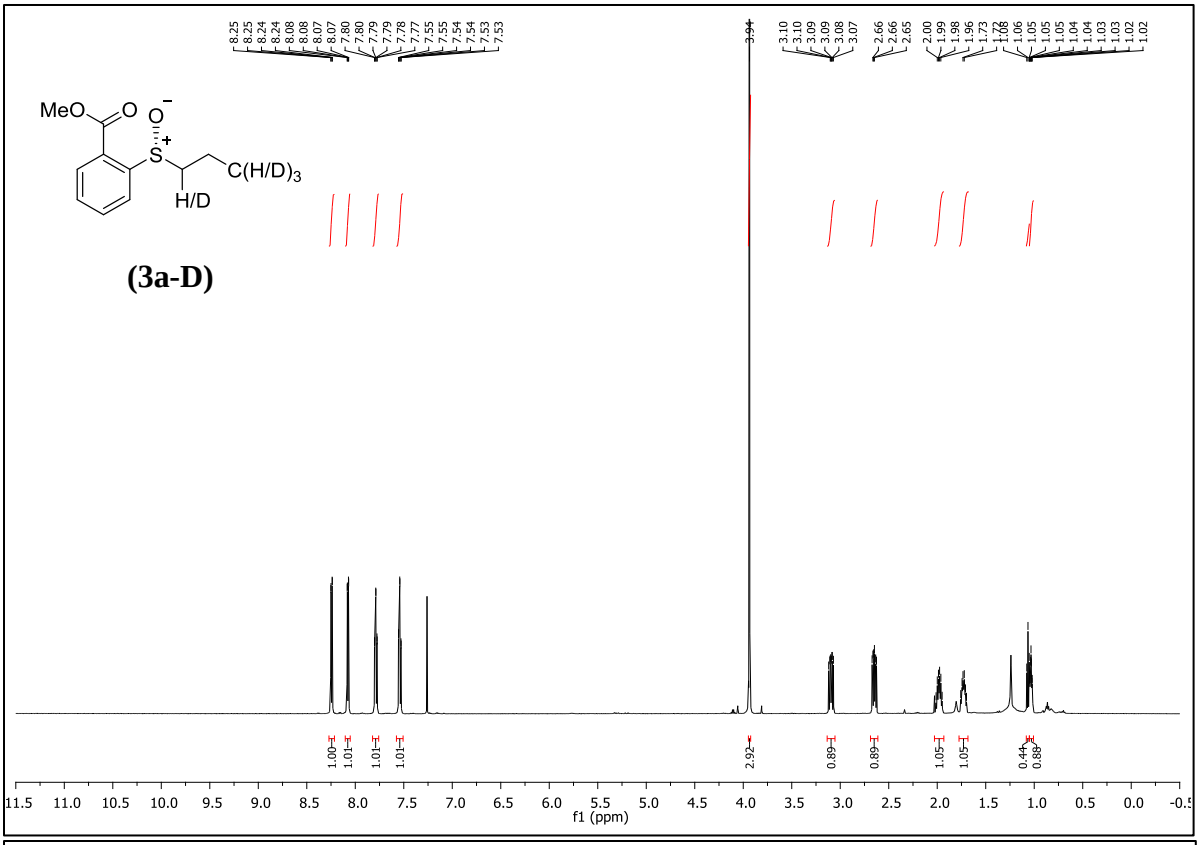
α_2 proton of **3a-D**, δ 2.65 (ddd, 1H): observed integration = 0.89 H; expected integration = 1 H; therefore, there is 89% protio-content and the remaining 11% is attributed to deutero-content

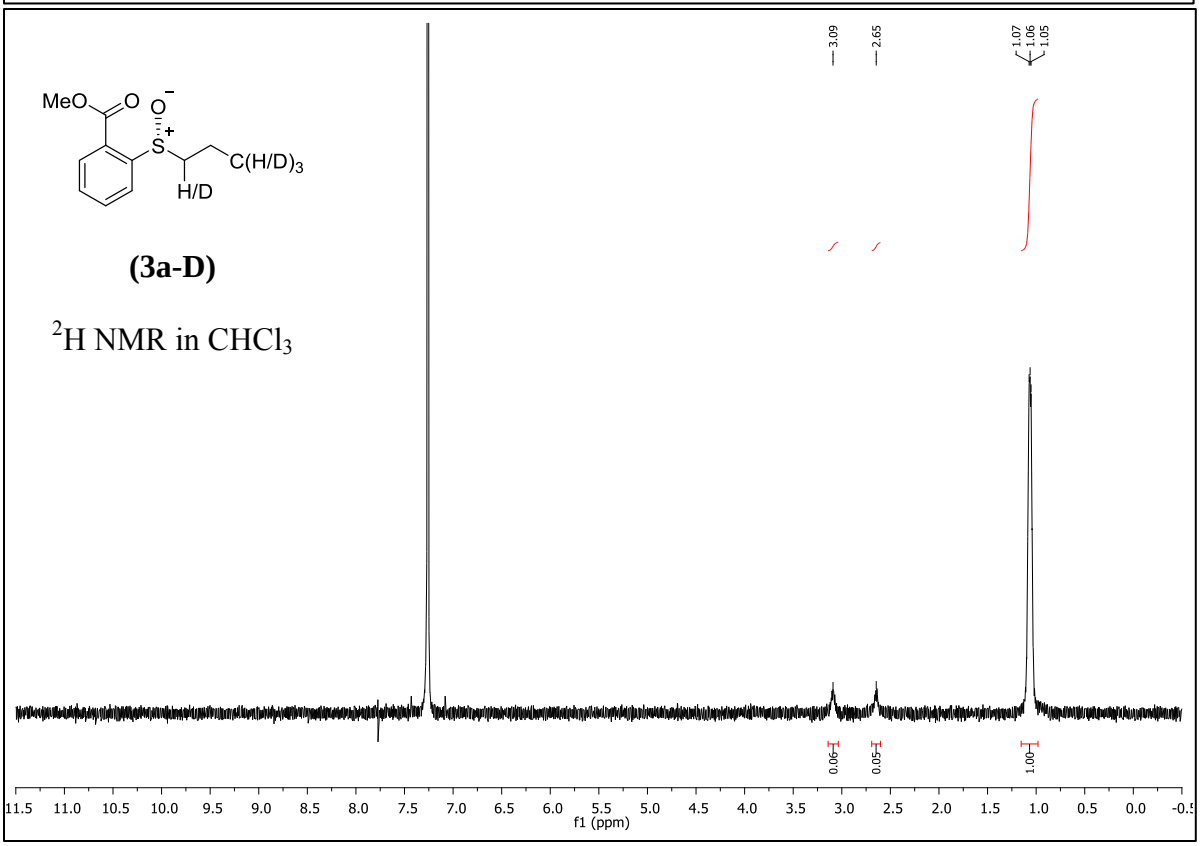
γ protons of **3a-D**, δ 1.09 – 1.00: observed integration = 1.33 H; expected integration = 3 H; therefore, there is 44% protio-content and the remaining 56% is attributed to deutero-content

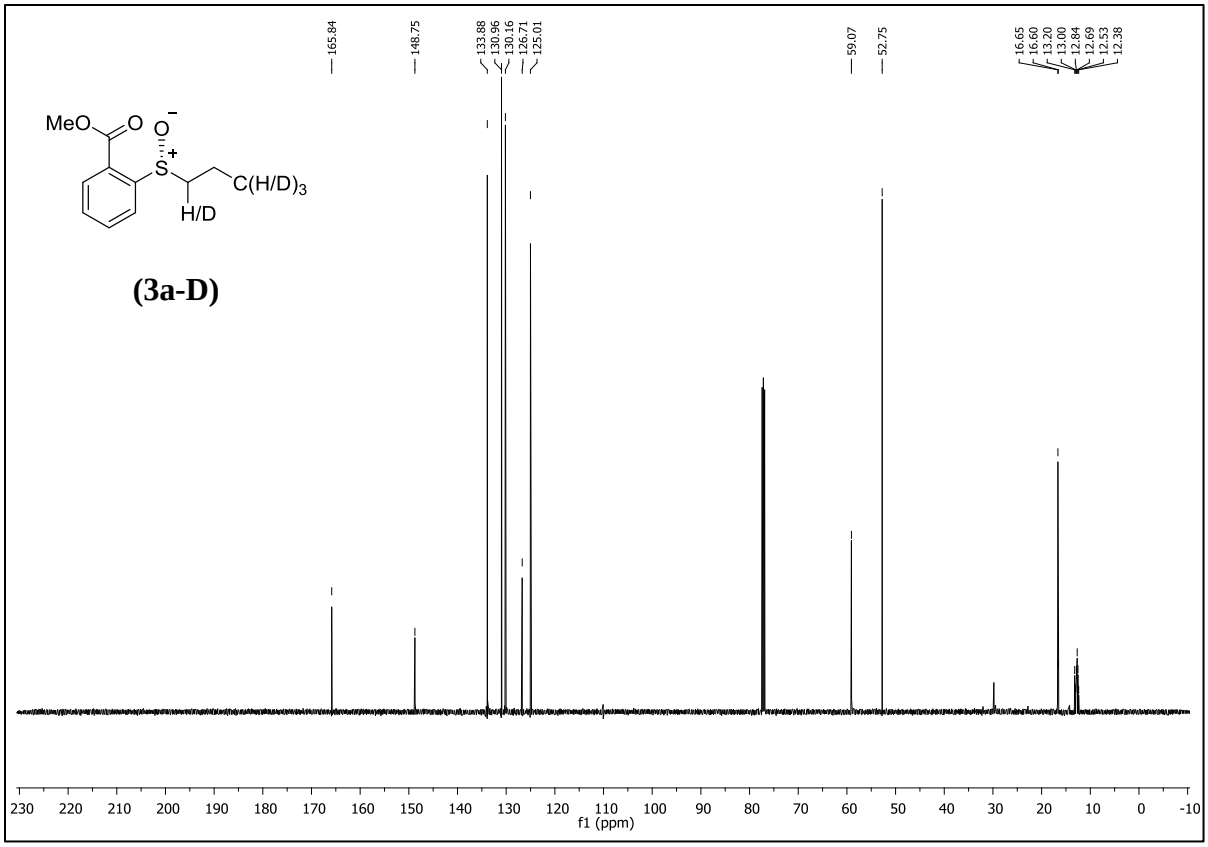


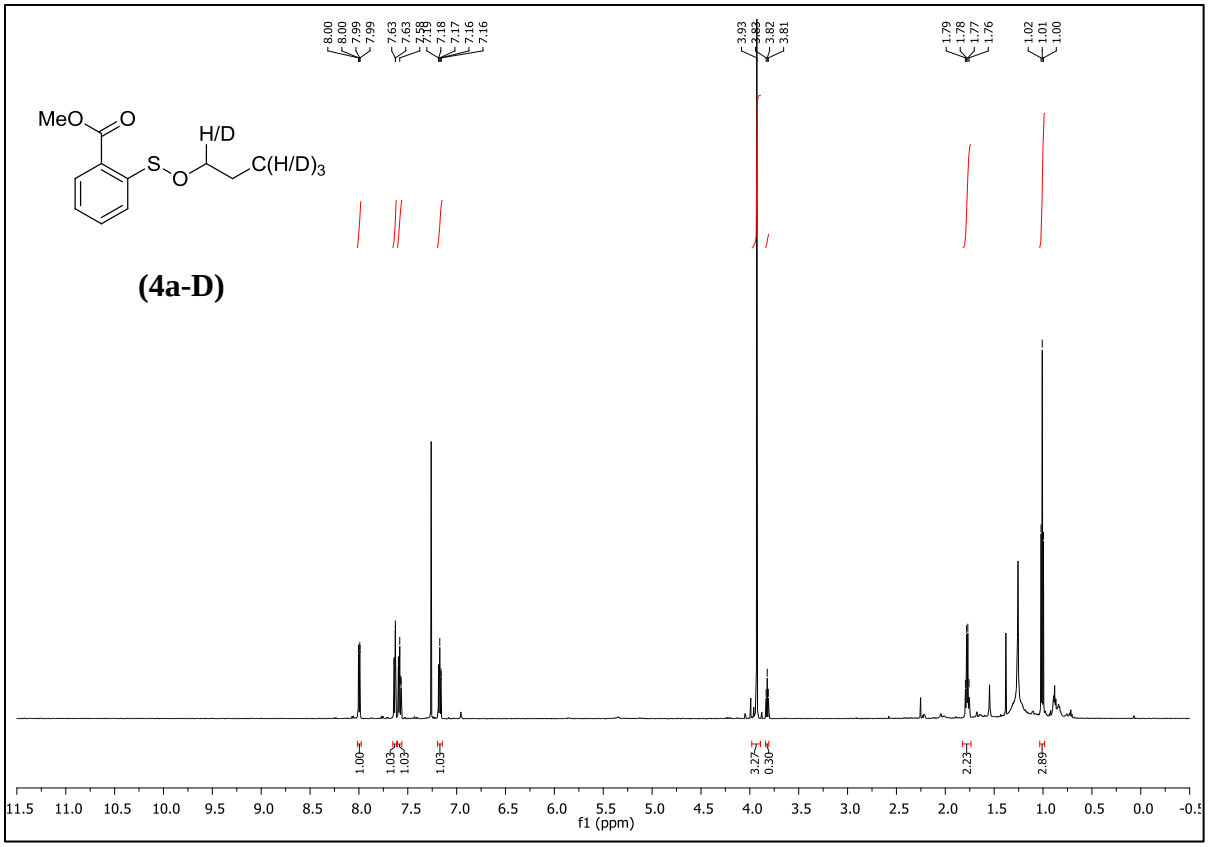
γ–***d*$_2$**–3a-D, 84% α–***d*$_2$**–3a-D, 11%

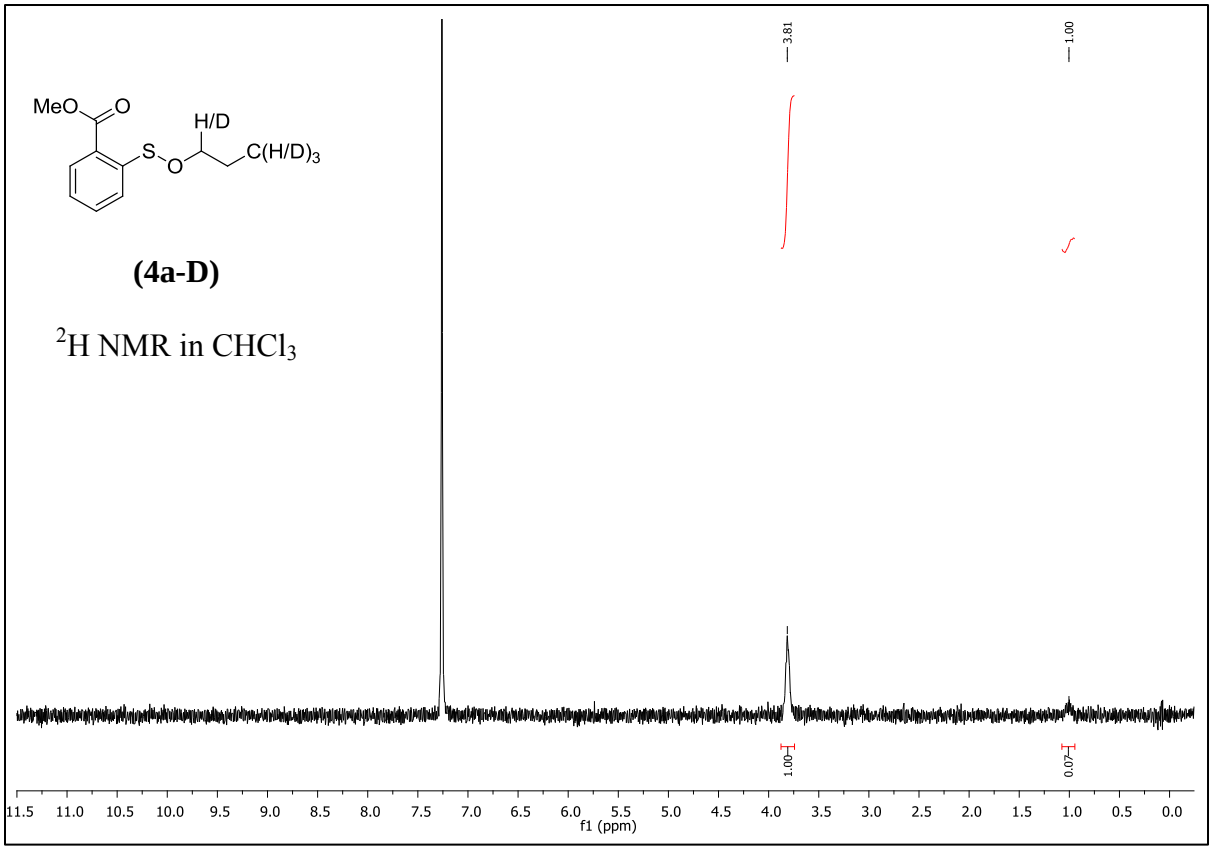
Based on the ^{1}H NMR data, **γ-*d*$_2$-3a-D** accounts for 84% (56% D-content / 66.7% theoretical D-content × 100%) of the starting deuterium content and **α-*d*$_2$-3a-D** accounts for 11% of the starting deuterium content. These values are consistent with the integration obtained from ^{2}H NMR (recorded with extended relaxation delay, 10 s): 90% deutero-content in the γ-position and 10% deutero-content in the α-position.


MeO
O
O
S
C(H/D)3
H/D
(3a-D)
f1 (ppm)


MeO
O
O
S
C(H/D)3
H/D
(3a-D)
2H NMR in CHCl3
f1 (ppm)


MeO
O
O
S
C(H/D)3
H/D
(3a-D)
165.84
148.75
133.88
130.96
130.16
126.71
125.01
59.07
52.75
16.65
16.60
13.20
13.00
12.84
12.69
12.53
12.38
f1 (ppm)


MeO
O
H/D
S
O
C(H/D)3
(4a-D)
8.00
8.00
7.99
7.99
7.63
7.63
7.58
7.58
7.18
7.17
7.16
7.16
3.93
3.83
3.82
3.81
1.79
1.78
1.77
1.76
1.02
1.01
1.00
1.00
1.03
1.03
1.03
3.27
0.30
2.23
2.89
f1 (ppm)


MeO
O
H/D
S
O
C(H/D)3
(4a-D)
2H NMR in CHCl3
3.81
1.00
1.00
0.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

6. DFT Studies

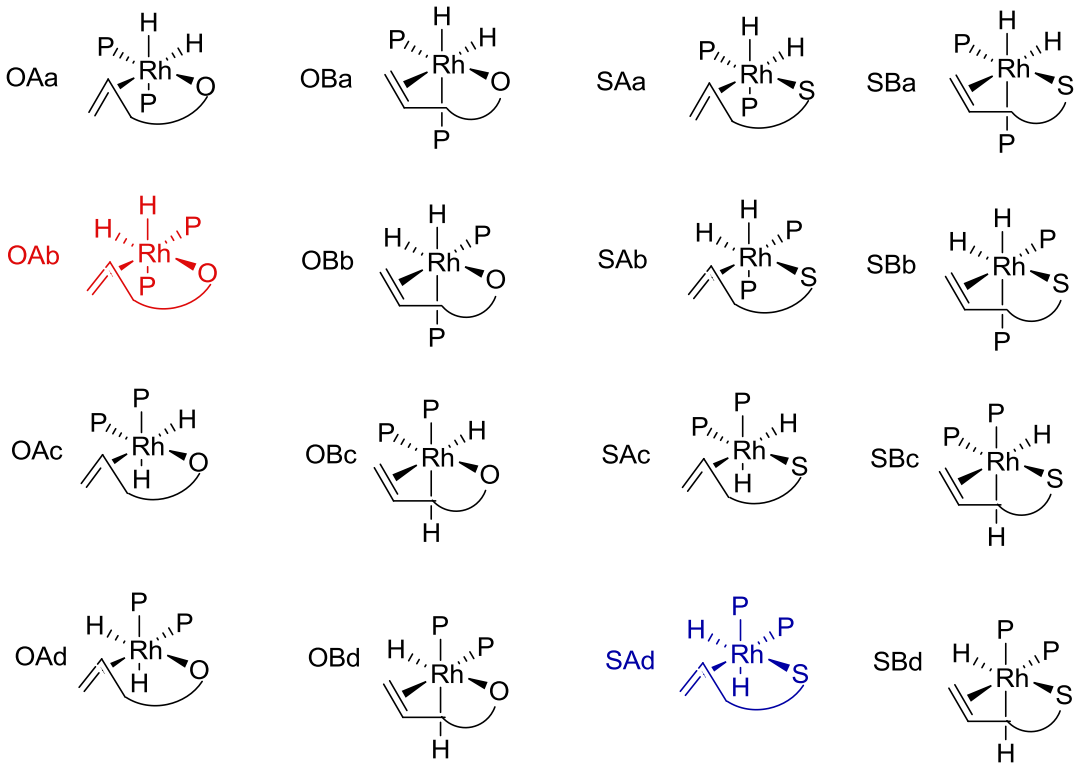
(i) Rhodium catalyzed hydrogenation

16 possible pathways were modeled in the hydrogenation of methyl allyl sulfoxide with $Rh(PMe_2CH_2CH_2PMe_2)^+$. Eight of these are oxygen bound pathways and eight are sulfur bound. The energies of key stationary points are listed in Table 1. OAb is the lowest energy oxygen bound pathway (and lowest pathway overall), while SAd is the lowest energy sulfur bound pathway.

Table 1. Energies of the oxidative addition transition state, the dihydride intermediate and the insertion transition state (relative to the substrate rhodium complex) for each pathway. The dihydride intermediates for each pathway are drawn below for reference.

Pathway	Oxidative addition TS[a]	Dihydride intermediate[a]	Insertion TS[a]
OAa	18.8 (18.7)	13.4 (14.2)	23.6 (24.7)
OAb	18.4 (17.7)	11.3 (11.4)	18.3 (17.6)
OAc	22.5 (23.8)	17.7 (20.0)	23.3 (26.0)
OAd	21.9 (21.4)	14.6 (14.4)	17.0 (15.7)
OBa	18.9 (21.5)	14.5 (18.3)	21.8 (25.1)
OBb	21.6 (20.8)	13.9 (13.8)	16.6 (15.8)
OBc	19.3 (19.6)	13.6 (15.4)	25.3 (27.1)
OBd	18.9 (18.1)	10.3 (10.1)	18.9 (18.0)
SAa	24.5 (31.7)	18.0 (26.6)	29.4 (38.1)
SAb	23.7 (30.3)	17.8 (23.8)	23.8 (28.4)
SAc	21.7 (24.8)	18.1 (21.6)	27.0 (31.1)
SAd	23.3 (26.8)	15.8 (19.5)	22.7 (25.8)
SBa	24.6 (32.3)	19.8 (28.1)	27.9 (37.0)
SBb	23.9 (32.0)	17.6 (24.6)	23.0 (29.0)
SBc	22.5 (25.4)	16.9 (20.7)	27.8 (32.0)
SBd	21.7 (26.3)	15.0 (20.1)	22.9 (27.8)

[a] Free energies with methanol solvent correction. Numbers in parentheses are gas phase values.



Coordinates for pathway OAb (lowest energy pathway)

Rhodium substrate complex (5-O)
M06 SCF Energy: -1661.79953162
M06 Free energy: -1661.525054
M06 Solvent SCF Energy: -1661.87801464

Cartesian coordinates

Atom	X	Y	Z
Rh	0.289810	-0.235801	-0.229545
P	-0.914342	1.725573	-0.134475
P	-1.724219	-1.188102	0.095877
C	-0.677557	2.913273	-1.487342
H	-0.966351	2.457578	-2.437538
H	-1.266854	3.821178	-1.321507
H	0.384368	3.170187	-1.536247
C	-0.546207	2.690402	1.368292
H	-1.132002	3.615736	1.390087
H	-0.768925	2.098667	2.260264
H	0.518862	2.938410	1.371451
C	-1.834453	-2.542489	1.311108
H	-1.435918	-2.205734	2.271903
H	-2.874691	-2.859997	1.442132
H	-1.247704	-3.402894	0.975561
C	-2.594042	-1.856418	-1.365196
H	-3.592896	-2.209640	-1.087302
H	-2.682472	-1.079825	-2.129573
H	-2.032964	-2.689223	-1.796588
S	3.355419	0.432739	0.177729
C	3.171476	-1.319361	-0.327430
H	3.966089	-1.886177	0.170649
H	3.385271	-1.299203	-1.400518
C	1.801931	-1.865028	-0.045567
H	1.654779	-2.326378	0.930466
C	0.936518	-2.184309	-1.074829
H	1.210142	-1.982642	-2.109034
H	0.178879	-2.949975	-0.940656
O	2.037433	1.030351	-0.362923
C	-2.908170	0.080434	0.737032
H	-3.936149	-0.297642	0.685251
H	-2.667368	0.230883	1.797795
C	-2.721727	1.372177	-0.045741
H	-3.084590	1.263405	-1.075909
H	-3.261721	2.214506	0.401172
C	3.084462	0.227878	1.952122
H	2.104327	-0.234878	2.103254
H	3.890921	-0.380293	2.370186
H	3.107440	1.223625	2.398065

Ion-induced dipole complex (13-O)
M06 SCF Energy: -1662.973254
M06 Free energy: -1662.683952
M06 Solvent SCF Energy: -1663.050688

Cartesian coordinates

Atom	X	Y	Z
Rh	0.158540	-0.232962	-0.198605
P	-1.139121	1.672472	-0.172074
P	-1.824266	-1.265011	0.167996
C	-1.496742	2.345891	-1.825747
H	-2.035032	1.608107	-2.426543
H	-2.089232	3.264365	-1.754822
H	-0.546821	2.562851	-2.322879
C	-0.471776	3.094886	0.740639

H	-1.180672	3.929262	0.718003
H	-0.271166	2.814257	1.777896
H	0.466856	3.399294	0.271399
C	-2.433161	-2.593161	-0.929072
H	-1.877858	-3.521511	-0.776055
H	-3.489646	-2.787192	-0.714137
H	-2.328398	-2.289975	-1.974083
C	-3.225154	-0.054043	0.082608
H	-4.084893	-0.446532	0.638728
H	-3.523906	-0.001503	-0.972802
S	3.225579	0.702621	-0.161659
C	3.092292	-1.076426	-0.549454
H	4.000505	-1.565647	-0.177920
H	3.105545	-1.109224	-1.643362
C	1.838683	-1.685683	0.006519
H	1.868407	-1.985325	1.053827
C	0.890333	-2.256715	-0.815260
H	0.991934	-2.219330	-1.898195
H	0.252836	-3.046213	-0.432313
O	1.784150	1.166079	-0.467215
H	-0.075379	0.544881	3.270701
H	0.038889	0.419141	2.534539
C	-1.975986	-2.016548	1.825850
H	-1.189301	-2.766563	1.957850
H	-1.848274	-1.253381	2.597682
H	-2.952699	-2.498028	1.945633
C	-2.779776	1.310056	0.579642
H	-2.639158	1.309565	1.668516
H	-3.503328	2.098524	0.342385
C	3.323459	0.590501	1.637726
H	2.456360	0.044758	2.016061
H	4.261057	0.099301	1.911186
H	3.321426	1.612424	2.020593

Ion-Induced Dipole Transition State (14TS-O)
M06 SCF Energy: -1662.966259
M06 Free energy: -1662.677236
M06 Solvent SCF Energy: -1663.047109
Imaginary Frequency: -90.4662 cm-1

Cartesian coordinates

Atom	X	Y	Z
Rh	0.185859	-0.149688	-0.150191
P	-1.238751	1.686572	-0.202935
P	-1.728659	-1.326382	0.041602
C	-0.918484	2.793375	-1.608254
H	-1.008451	2.231916	-2.541916
H	-1.609754	3.642341	-1.619531
H	0.109338	3.159247	-1.526518
C	-1.258452	2.814066	1.232745
H	-1.906106	3.677714	1.048938
H	-1.610348	2.286789	2.124634
H	-0.238349	3.164650	1.418160
C	-1.764336	-2.546295	1.395540
H	-1.501244	-2.062500	2.340067
H	-2.760393	-2.993571	1.485616
H	-1.037296	-3.338951	1.195645
C	-2.351088	-2.286051	-1.380012
H	-3.331625	-2.710314	-1.140978
H	-2.438431	-1.650126	-2.265314
H	-1.665185	-3.107144	-1.608114
S	3.300848	0.517764	0.100288
C	3.095377	-1.176520	-0.827855
H	3.740253	-1.835561	-0.240116
H	3.523373	-1.091685	-1.831789
C	1.659981	-1.632535	-0.869685
H	1.475247	-2.610805	-0.428848
C	0.826124	-1.167090	-1.901434
H	1.215761	-0.428481	-2.603499
H	0.041093	-1.793010	-2.313152
O	1.901175	1.152723	-0.259962
H	0.185716	0.297183	2.221902
H	0.508023	-0.382321	2.096690
C	-3.123347	-0.177136	0.443627
H	-3.048869	0.036991	1.519239
H	-4.085740	-0.677123	0.281699
C	-2.982924	1.102541	-0.368385
H	-3.163194	0.912955	-1.434660
H	-3.690957	1.875603	-0.049396
C	3.426971	0.019617	1.631458
H	2.689171	-0.753345	1.856422
H	4.441548	-0.349599	1.801759
H	3.252305	0.910705	2.237003

Molecular Hydrogen Complex (15-O)
M06 SCF Energy: -1662.968066
M06 Free energy: -1662.677845
M06 Solvent SCF Energy: -1663.046674

Cartesian coordinates

Atom	X	Y	Z
Rh	0.191971	-0.123555	0.178609
P	-1.220619	1.727418	-0.134593
P	-1.742068	-1.284696	0.329698
C	-0.802659	2.725289	-1.596095
H	-0.805780	2.089286	-2.485749
H	-1.505247	3.553575	-1.734720
H	0.207863	3.123035	-1.464978
C	-1.407538	2.968911	1.189825
H	-2.081353	3.776749	0.885394
H	-1.796200	2.494873	2.095999
H	-0.424420	3.389699	1.420529
C	-1.897763	-2.373751	1.779245
H	-1.706123	-1.806176	2.693834
H	-2.902698	-2.806843	1.826165
H	-1.164225	-3.182116	1.709983
C	-2.230221	-2.366046	-1.054792
H	-3.169508	-2.871332	-0.806924
H	-2.374909	-1.778106	-1.965413
H	-1.464154	-3.123351	-1.244210
S	3.314897	0.444614	-0.059669
C	2.974169	-1.277103	-0.672358
H	3.497492	-1.954134	0.007760
H	3.466176	-1.326344	-1.650272
C	1.499028	-1.573947	-0.770110
H	1.254216	-2.606041	-0.522110
C	0.701297	-0.886990	-1.723460
H	1.155962	-0.097367	-2.322785
H	-0.112378	-1.401075	-2.226012
O	1.931444	1.135042	-0.077636
H	0.211507	0.245838	2.039393
H	0.606190	-0.470554	1.980257
C	-3.159500	-0.106218	0.482044

H	-3.198523	0.204710	1.535122
H	-4.100096	-0.626863	0.264439
C	-2.930606	1.093115	-0.426716
H	-2.987064	0.797056	-1.483040
H	-3.678249	1.878374	-0.267611
C	3.627587	0.046096	1.673189
H	2.848456	-0.621907	2.047843
H	4.612090	-0.423060	1.744028
H	3.627122	0.989312	2.222023

Oxidative Addition Transition State (16TS-O)
M06 SCF Energy: -1662.958655
M06 Free energy: -1662.668847
M06 Solvent SCF Energy: -1663.035824
Imaginary Frequency: -984.8628 cm-1

Cartesian coordinates

Atom	X	Y	Z
Rh	0.092875	-0.145706	-0.835557
P	-0.989086	1.613845	0.376639
P	-1.688122	-1.384073	-0.057674
C	-0.061124	2.767516	1.442416
H	0.563923	3.428489	0.834241
H	-0.751246	3.388615	2.023388
H	0.573190	2.195710	2.124647
C	-2.154569	0.802418	1.555427
H	-2.842761	1.544192	1.978011
H	-1.538600	0.413922	2.376730
C	-2.699258	-2.350477	-1.217594
H	-2.072738	-3.098241	-1.711394
H	-3.511183	-2.858796	-0.686883
H	-3.121449	-1.691503	-1.980567
C	-2.893899	-0.320439	0.846884
H	-3.476968	-0.938619	1.540123
H	-3.596000	0.077779	0.102748
S	2.672415	-0.361370	1.248755
C	2.967340	0.818217	-0.128191
H	4.046758	0.809983	-0.324983
H	2.711597	1.787698	0.312940
C	2.168731	0.552275	-1.369467
H	2.554070	-0.216843	-2.034350
C	1.292679	1.484109	-1.879159
H	1.155519	2.437437	-1.374377
H	0.976709	1.454155	-2.915970
O	1.146395	-0.369457	1.366160
H	-0.221703	-0.737300	-2.292601
H	0.473399	-1.420678	-1.828390
C	-1.112935	-2.595794	1.172489
H	-0.436004	-3.302940	0.683719
H	-0.553464	-2.081902	1.957822
H	-1.961322	-3.142298	1.597982
C	-2.053058	2.722933	-0.609011
H	-1.431710	3.326978	-1.276625
H	-2.730404	2.132065	-1.231006
H	-2.634045	3.390210	0.036672
C	3.097853	-1.893254	0.390873
H	2.381037	-2.046040	-0.422756
H	4.124009	-1.831360	0.019485
H	3.019300	-2.700330	1.120894

Dihydride Intermediate (17-O)
M06 SCF Energy: -1662.972355
M06 Free energy: -1662.678945
M06 Solvent SCF Energy: -1663.050751

Cartesian coordinates

Atom	X	Y	Z
Rh	-0.126725	-0.063866	-0.634532
P	1.621927	-1.317203	0.382021
P	1.146383	1.758715	-0.092946
C	1.282058	-1.889362	2.078634
H	0.454416	-2.604100	2.061440
H	2.165976	-2.367910	2.513110
H	0.971816	-1.046170	2.700879
C	3.042308	-0.153155	0.574362
H	3.543536	-0.097794	-0.401353
H	3.768388	-0.558675	1.289125
C	1.943617	2.649467	-1.461007
H	1.176025	3.011972	-2.149812
H	2.526852	3.495561	-1.083482
H	2.600031	1.971038	-2.012468
C	2.529523	1.212107	1.002934
H	2.119790	1.171696	2.021231
H	3.319781	1.972255	1.003213
S	-2.872371	-0.066022	1.060475
C	-3.159403	-0.936589	-0.554922
H	-3.929015	-0.365160	-1.079672
H	-3.587054	-1.904238	-0.273654
C	-1.924303	-1.132977	-1.399616
H	-2.022512	-0.827423	-2.436449
C	-0.970473	-2.080701	-1.066428
H	-1.070976	-2.649635	-0.142528
H	-0.341419	-2.520509	-1.833356
O	-1.349081	-0.088526	1.259375
H	0.619439	-0.071593	-1.990220
H	-1.002416	1.093858	-1.341536
C	0.305566	3.047257	0.873038
H	-0.441729	3.544189	0.248298
H	-0.195426	2.584377	1.727836
H	1.026834	3.790329	1.229426
C	2.363943	-2.768594	-0.429560
H	1.648298	-3.595341	-0.441196
H	2.626900	-2.520985	-1.461787
H	3.263022	-3.091974	0.105462
C	-3.276312	1.610893	0.522696
H	-2.678557	1.859417	-0.358992
H	-4.346834	1.655995	0.307480
H	-3.042635	2.276066	1.356124

Insertion Transition State (18TS-O)
M06 SCF Energy: -1662.96005
M06 Free energy: -1662.669102
M06 Solvent SCF Energy: -1663.037197
Imaginary Frequency: -675.0043 cm-1

Cartesian coordinates

Atom	X	Y	Z
Rh	-0.040621	-0.094557	-0.647386
P	1.518497	-1.374154	0.509873
P	1.364625	1.695970	-0.173734
C	0.903007	-2.402620	1.879299
H	0.300350	-3.221761	1.476883

H	1.734689	-2.823090	2.454771
H	0.274558	-1.794277	2.535277
C	2.710109	-0.211454	1.312306
H	3.635107	-0.738778	1.574460
H	2.246554	0.113005	2.253967
C	0.842404	2.757920	1.211543
H	0.645698	2.143839	2.094103
H	1.614636	3.500419	1.438692
H	-0.088026	3.267317	0.948650
C	1.858285	2.866077	-1.475596
H	2.617716	3.562102	-1.103944
H	2.257520	2.314426	-2.330827
H	0.985639	3.432940	-1.810028
S	-2.792853	-0.287133	0.984333
C	-3.154527	-0.052115	-0.806030
H	-3.364448	1.010331	-0.965269
H	-4.053996	-0.640533	-1.023648
C	-1.981562	-0.527288	-1.632673
H	-2.106156	-0.314287	-2.693969
C	-1.301021	-1.728724	-1.279749
H	-1.660288	-2.313573	-0.434357
H	-0.844416	-2.316978	-2.069373
O	-1.397917	0.333515	1.165238
H	0.819630	-0.319517	-1.907377
H	-1.089620	0.793900	-1.568399
C	2.969174	0.980590	0.401256
H	3.518025	0.672583	-0.499180
H	3.569193	1.752482	0.898027
C	2.559161	-2.502401	-0.468552
H	1.920066	-3.216196	-0.996303
H	3.118054	-1.932693	-1.216238
H	3.259271	-3.047022	0.173009
C	-3.932408	0.959217	1.614144
H	-3.641291	1.929963	1.206336
H	-4.949584	0.689592	1.318734
H	-3.849865	0.962096	2.701427

Alkyl Hydride Complex (19-O)
M06 SCF Energy: -1662.973936
M06 Free energy: -1662.680868
M06 Solvent SCF Energy: -1663.059398

Cartesian coordinates

Atom	X	Y	Z
Rh	0.144899	-0.380061	-0.280112
P	-0.734755	1.860536	-0.279777
P	-1.968334	-1.001392	0.122723
C	-0.509189	3.078818	-1.618122
H	-0.879149	2.673737	-2.563358
H	-1.034660	4.013435	-1.394894
H	0.558337	3.286724	-1.733195
C	-0.246755	2.802817	1.208469
H	-0.742672	3.778582	1.246570
H	-0.496736	2.234901	2.109266
H	0.836811	2.954908	1.192622
C	-2.321018	-2.288915	1.353277
H	-1.870732	-2.020654	2.312643
H	-3.402310	-2.406341	1.478970
H	-1.897596	-3.241549	1.023667
C	-2.849206	-1.569629	-1.368475
H	-3.897615	-1.782995	-1.133333
H	-2.804941	-0.811271	-2.154922
H	-2.376167	-2.481563	-1.743752
S	3.448956	-0.110620	-0.346643
C	3.201211	-1.770394	0.384661
H	2.795098	-1.644079	1.395312
H	4.207293	-2.197458	0.452904
C	2.263951	-2.587678	-0.492595
H	2.459813	-2.375770	-1.552226
C	0.798593	-2.384077	-0.148611
H	0.176434	-2.948493	-0.860434
H	0.602860	-2.808044	0.845239
O	2.069471	0.340469	-0.868569
H	0.199930	-0.429854	1.243276
H	2.532944	-3.644867	-0.356666
C	-2.919598	0.467972	0.707654
H	-3.992933	0.242767	0.682592
H	-2.645800	0.613238	1.761574
C	-2.572788	1.701649	-0.117263
H	-3.004332	2.610794	0.317628
H	-2.977845	1.611829	-1.133987
C	3.664002	0.813191	1.188821
H	2.738270	0.723838	1.765262
H	4.511427	0.395293	1.738534
H	3.864725	1.854037	0.931809

Reductive Elimination Transition State (20TS-O)
M06 SCF Energy: -1662.968401
M06 Free energy: -1662.675559
M06 Solvent SCF Energy: -1663.048402
Imaginary Frequency: -680.1053 cm-1

Cartesian coordinates

Atom	X	Y	Z
Rh	-0.063387	-0.281501	0.290221
P	0.985304	1.853304	0.258677
P	1.964101	-1.027421	-0.295880
C	0.944515	2.980674	1.689087
H	1.401529	2.503351	2.559477
H	1.470845	3.915750	1.470809
H	-0.099166	3.202686	1.929684
C	0.353397	2.892051	-1.102310
H	0.899892	3.839329	-1.165469
H	0.436190	2.358070	-2.052784
H	-0.704477	3.100238	-0.916302
C	2.126283	-2.348581	-1.534456
H	1.639026	-2.048322	-2.465662
H	3.181416	-2.566226	-1.729845
H	1.641609	-3.256802	-1.164192
C	2.959148	-1.641438	1.106055
H	3.974594	-1.890577	0.778987
H	3.008801	-0.890023	1.898812
H	2.489033	-2.538693	1.519033
S	-3.314728	0.335774	0.517617
C	-3.317778	-1.462915	0.128393
H	-3.071892	-1.593937	-0.931296
H	-4.352626	-1.779478	0.291871
C	-2.332243	-2.191013	1.028976
H	-2.338079	-1.744670	2.030767
C	-0.922065	-2.239550	0.471540
H	-0.214421	-2.605923	1.228557
H	-0.878893	-2.949447	-0.363218
O	-1.875642	0.691820	0.934038
H	-0.582735	-1.109848	-0.907436

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H    -2.702504 -3.216916  1.160225
C     2.959324  0.371653 -0.979261
H     2.590636  0.547639 -1.998409
H     4.011689  0.072947 -1.061705
C     2.780629  1.613522 -0.114937
H     3.293846  1.491831  0.848047
H     3.202126  2.506761 -0.589862
C    -3.477797  0.953060 -1.172034
H    -2.602353  0.624883 -1.740427
H    -4.399632  0.554464 -1.604093
H    -3.530415  2.041757 -1.130012

O-bound Rhodium product complex (21-O)
M06 SCF Energy: -1663.51134593
M06 Free energy: -1663.218081
M06 Solvent SCF Energy:
-1663.59430621

Cartesian coordinates
Atom      X         Y         Z
Rh   -0.039002 -0.106672 -0.103124
P     1.043994  1.800994  0.188598
P     1.985517 -1.077037 -0.076672
C     0.845997  2.563618  1.850869
H     1.195536  1.878348  2.623575
H     1.406803  3.500421  1.913207
H    -0.211366  2.767735  2.026345
C     0.574570  3.148162 -0.964083
H     1.132671  4.061928 -0.742771
H     0.770277  2.840314 -1.991645
H    -0.494240  3.340925 -0.860194
C     2.618397 -1.679093 -1.701767
H     2.637373 -0.858386 -2.420117
H     3.624007 -2.096187 -1.601531
H     1.952289 -2.451213 -2.091534
C     2.257144 -2.528175  1.024301
H     3.305301 -2.838302  1.007241
H     1.972538 -2.276917  2.046838
H     1.643116 -3.366406  0.688691
S    -3.202678  0.149935  0.346895
C    -3.280561 -1.467577 -0.535245
H    -3.313860 -1.229924 -1.600739
H    -4.221958 -1.936047 -0.234061
C    -2.094245 -2.367919 -0.189656
H    -2.127986 -3.213572 -0.883953
C    -2.066138 -2.876820  1.252201
H    -2.974859 -3.442479  1.475552
H    -1.216554 -3.543273  1.410184
O    -1.961956  0.862755 -0.280617
H    -1.987296 -2.062455  1.975720
H    -1.133957 -1.870515 -0.463991
C     3.263921  0.161898  0.479702
H     3.273290  0.142855  1.573252
H     4.261561 -0.129952  0.141210
C     2.875392  1.554195 -0.032944
H     3.079626  1.642529 -1.103806
H     3.434395  2.346643  0.471909
C    -4.606927  0.972422 -0.457802
H    -4.456436  0.964007 -1.537207
H    -5.523447  0.452609 -0.174284
H    -4.629395  1.994742 -0.082619
```

Coordinates for pathway SAd (lowest energy S-bound pathway)

```
Rhodium substrate complex (5-S)
M06 SCF Energy: -1661.78225979
M06 Free energy: -1661.506811
M06 Solvent SCF Energy: -1661.86673151

Cartesian coordinates
Atom      X         Y         Z
Rh   -0.142761 -0.367227  0.151633
P     2.092741 -0.854964 -0.007262
P     0.585769  1.826532  0.027507
C     3.002776  0.654861 -0.560727
H     4.077247  0.536985 -0.375579
H     2.867133  0.727764 -1.647652
C     2.641804 -2.160911 -1.151925
H     3.735162 -2.223606 -1.165760
H     2.242050 -3.128906 -0.835328
H     2.281628 -1.947456 -2.161854
C     2.427446  1.877954  0.138580
H     2.804802  2.814273 -0.288860
H     2.690227  1.879769  1.204455
C    -0.008145  3.059958  1.224302
H     0.473729  4.027494  1.046510
H    -1.089147  3.179357  1.103932
H     0.200735  2.732493  2.245454
S    -2.421754  0.094556 -0.059405
C    -2.554682 -1.516391 -0.950504
H    -2.698051 -1.236150 -1.996823
H    -3.412996 -2.104080 -0.607965
C    -1.207950 -2.152603 -0.700985
H    -0.651799 -2.478521 -1.577758
C    -0.778690 -2.514358  0.551905
H    -1.429792 -2.457766  1.421576
H     0.093423 -3.149989  0.669207
O    -2.930787  1.236335 -0.862678
C     0.178329  2.556078 -1.589670
H     0.621376  1.961498 -2.392894
H    -0.909677  2.546701 -1.712350
H     0.550495  3.584787 -1.647316
C     2.896206 -1.300463  1.569726
H     2.737108 -0.512819  2.310937
H     2.459092 -2.223628  1.960013
H     3.971532 -1.448449  1.422966
C    -3.566853 -0.160993  1.310963
H    -4.565709 -0.286426  0.885578
H    -3.259362 -1.039386  1.882454
H    -3.529675  0.735365  1.931800

Ion-induced dipole complex (13-S)
M06 SCF Energy: -1662.95891890
M06 Free energy: -1662.669565
M06 Solvent SCF Energy: -1663.04380126

Cartesian coordinates
Atom      X         Y         Z
```

Rh	-0.140366	-0.368205	0.104435
P	2.099437	-0.846062	-0.040261
P	0.574501	1.828823	-0.015517
C	3.006642	0.669662	-0.582306
H	4.079776	0.559415	-0.384907
H	2.882330	0.742464	-1.670608
C	2.668201	-2.150298	-1.177092
H	3.762004	-2.205635	-1.181874
H	2.272523	-3.120253	-0.861442
H	2.314263	-1.941671	-2.190193
C	2.414962	1.887877	0.111886
H	2.793593	2.827727	-0.306417
H	2.662828	1.887607	1.181692
C	-0.030297	3.014520	1.223708
H	0.447947	3.990929	1.090551
H	-1.111642	3.134246	1.105085
H	0.176388	2.642591	2.230833
S	-2.415711	0.088161	-0.102506
C	-2.562439	-1.527536	-0.979832
H	-2.721441	-1.253860	-2.025622
H	-3.414135	-2.115226	-0.621383
C	-1.208609	-2.156715	-0.745307
H	-0.656440	-2.474425	-1.627481
C	-0.767572	-2.522971	0.502186
H	-1.411879	-2.476711	1.377905
H	0.109131	-3.154234	0.608552
O	-2.950416	1.224361	-0.895978
H	-0.180792	-0.148100	2.642431
H	-0.085515	-0.040889	3.386086
C	0.162328	2.598959	-1.611468
H	0.617515	2.033689	-2.428933
H	-0.924978	2.576316	-1.738834
H	0.518740	3.634324	-1.638854
C	2.882272	-1.285030	1.548907
H	2.720335	-0.488584	2.280449
H	2.430413	-2.199621	1.943416
H	3.957971	-1.444411	1.418065
C	-3.506086	-0.157161	1.312642
H	-4.526038	-0.262273	0.934476
H	-3.186643	-1.043263	1.865484
H	-3.420584	0.734355	1.936609

Ion-Induced Dipole Transition State (14TS-S)
M06 SCF Energy: -1662.94196758
M06 Free energy: -1662.652978
M06 Solvent SCF Energy: -1663.03186595
Imaginary Frequency: -94.2519 cm-1

Cartesian coordinates

Atom	X	Y	Z
Rh	0.057867	-0.289251	-0.572109
P	-1.865936	-0.986028	0.356993
P	-0.835884	1.817819	-0.164190
C	-2.676177	0.395142	1.272683
H	-3.714038	0.130577	1.508350
H	-2.139151	0.505912	2.223654
C	-1.816283	-2.344636	1.568629
H	-2.822658	-2.521864	1.963185
H	-1.463453	-3.268603	1.101242
H	-1.148273	-2.084086	2.394011
C	-2.572423	1.658763	0.436585
H	-2.864523	2.555769	0.994072
H	-3.220539	1.600232	-0.447261
C	-0.924284	3.024494	-1.524802
H	-1.417649	3.942941	-1.189224
H	0.086645	3.271275	-1.861768
H	-1.478461	2.602566	-2.367275
S	2.490672	0.230404	0.361036
C	2.657988	-1.566814	0.051644
H	3.269319	-1.985710	0.858507
H	3.171075	-1.682291	-0.910173
C	1.260628	-2.112018	0.000746
H	0.844473	-2.457356	0.943446
C	0.640843	-2.404761	-1.187848
H	1.178871	-2.314178	-2.128906
H	-0.257595	-3.013586	-1.221858
O	2.354439	0.459854	1.832130
H	0.454677	0.032379	-2.682646
H	0.998840	0.536304	-2.483427
C	0.031942	2.712648	1.163806
H	0.138083	2.079443	2.048092
H	1.040973	2.971177	0.830703
H	-0.509899	3.631409	1.412801
C	-3.149260	-1.535004	-0.821522
H	-3.368197	-0.741136	-1.540180
H	-2.792771	-2.404769	-1.379866
H	-4.066947	-1.806705	-0.287833
C	4.183190	0.703332	-0.099010
H	4.876071	0.114583	0.508158
H	4.334886	0.529704	-1.166949
H	4.290287	1.763269	0.134929

Molecular Hydrogen Complex (15-S)
M06 SCF Energy: -1662.96058325
M06 Free energy: -1662.668317
M06 Solvent SCF Energy: -1663.04103835

Cartesian coordinates

Atom	X	Y	Z
Rh	-0.231022	-0.043489	1.067138
P	-0.552198	1.566157	-0.603687
P	-1.906580	-1.111985	-0.116035
C	-1.589308	0.875962	-1.957820
H	-2.000071	1.698170	-2.555584
H	-0.911781	0.298847	-2.598155
C	0.750884	2.457946	-1.509591
H	0.277382	3.116383	-2.245866
H	1.349645	3.077590	-0.836522
H	1.385293	1.728260	-2.016782
C	-2.674601	-0.003756	-1.365932
H	-3.186473	-0.604767	-2.126603
H	-3.438678	0.594706	-0.854270
C	-3.302155	-1.843642	0.793713
H	-4.013751	-2.298668	0.096654
H	-2.933116	-2.615890	1.474542
H	-3.811680	-1.075933	1.381545
S	2.294459	-1.086984	-0.484376
C	2.852026	0.394096	0.477967
H	3.245005	1.093176	-0.267923
H	3.684679	0.037164	1.096620
C	1.786459	1.025959	1.329462
H	1.595234	2.078833	1.137194
C	1.382532	0.514490	2.535760
H	1.816876	-0.408187	2.915199
H	0.866708	1.137725	3.260720

```
O     1.420334 -0.570954 -1.609334
H    -0.695442 -0.945850  2.495363
H    -0.222258 -1.501282  2.071319
C    -1.215349 -2.485396 -1.090618
H    -0.412496 -2.097821 -1.726408
H    -0.788977 -3.231650 -0.413497
H    -1.997405 -2.955634 -1.696522
C    -1.554758  2.923005  0.097476
H    -2.461362  2.534275  0.567521
H    -0.973661  3.439254  0.867720
H    -1.826036  3.642239 -0.683356
C     3.904793 -1.397956 -1.258014
H     4.211350 -0.502674 -1.804905
H     4.638736 -1.674290 -0.497450
H     3.762810 -2.224425 -1.955655
```

Oxidative Addition Transition State (16TS-S)
M06 SCF Energy: -1662.94421540
M06 Free energy: -1662.654472
M06 Solvent SCF Energy: -1663.02801450
Imaginary Frequency: -1023.4954 cm-1

Cartesian coordinates

```
Atom      X         Y         Z
Rh   -0.011078 -0.189558 -0.978292
P     0.659603  1.669283  0.395216
P     1.766160 -1.198199  0.058102
C     1.990422  1.100369  1.542153
H     2.579250  1.963427  1.874945
H     1.491445  0.686043  2.427399
C    -0.402543  2.678243  1.482113
H     0.217077  3.397026  2.029078
H    -1.131298  3.239019  0.888847
H    -0.924765  2.026678  2.188459
C     2.849947  0.056276  0.853649
H     3.536640 -0.443630  1.547390
H     3.458877  0.503767  0.057503
C     2.889986 -2.229357 -0.925262
H     3.689704 -2.626947 -0.291715
H     2.335569 -3.061941 -1.365881
H     3.327965 -1.636059 -1.732256
S    -1.897688 -0.716726  0.784127
C    -2.785179  0.658727 -0.084106
H    -2.878890  1.442341  0.672393
H    -3.786148  0.329513 -0.382111
C    -1.934038  1.055837 -1.261445
H    -1.667915  2.105216 -1.361896
C    -1.785393  0.216454 -2.338037
H    -2.329140 -0.724427 -2.388584
H    -1.383099  0.581383 -3.276722
O    -1.582480 -0.304125  2.191391
H     0.809183 -0.337800 -2.357028
H     0.247415 -1.257913 -2.214758
C     1.218570 -2.270604  1.423997
H     0.585032 -1.705582  2.115738
H     0.635581 -3.102571  1.018300
H     2.086585 -2.671778  1.958440
C     1.488792  2.925433 -0.640856
H     2.298703  2.464296 -1.212068
H     0.775203  3.346169 -1.355312
H     1.890362  3.734963 -0.021379
C    -3.241604 -1.926549  0.881870
H    -4.072324 -1.475632  1.430108
H    -3.534509 -2.210153 -0.132568
H    -2.855350 -2.789917  1.425441
```

Dihydride Intermediate (17-S)
M06 SCF Energy: -1662.95816494
M06 Free energy: -1662.666044
M06 Solvent SCF Energy: -1663.04224516

Cartesian coordinates

```
Atom      X         Y         Z
Rh   -0.106596 -0.232517 -0.850148
P     0.704908  1.747467  0.284691
P     1.736289 -1.241507  0.031954
C     2.050061  1.145154  1.396925
H     2.684062  1.986199  1.702655
H     1.558204  0.763185  2.301757
C    -0.282673  2.825164  1.375439
H     0.367038  3.564705  1.855846
H    -1.036414  3.361606  0.790336
H    -0.779830  2.222233  2.141308
C     2.855575  0.054359  0.710343
H     3.578782 -0.413572  1.389208
H     3.423088  0.456713 -0.139035
C     2.789160 -2.251137 -1.042935
H     3.674453 -2.594023 -0.497314
H     2.224713 -3.116865 -1.398286
H     3.098121 -1.661802 -1.909948
S    -1.825260 -0.571697  0.853557
C    -2.858969  0.637260 -0.087381
H    -2.984316  1.484928  0.590725
H    -3.842495  0.215471 -0.318935
C    -2.034629  0.959173 -1.312235
H    -1.763367  1.997468 -1.484889
C    -1.859692  0.032470 -2.307938
H    -2.400374 -0.909598 -2.298288
H    -1.418062  0.310926 -3.257800
O    -1.628385 -0.143340  2.268547
H     0.842443  0.092605 -2.050583
H    -0.213007 -1.639900 -1.605871
C     1.337256 -2.309373  1.450330
H     0.755039 -1.750363  2.190287
H     0.742468 -3.159087  1.102377
H     2.254110 -2.685514  1.916581
C     1.534495  2.932500 -0.826814
H     2.305425  2.423977 -1.411605
H     0.804582  3.348239 -1.528112
H     1.986166  3.751361 -0.257164
C    -2.894937 -2.022511  0.857833
H    -3.816890 -1.769754  1.386970
H    -3.087296 -2.316578 -0.177138
H    -2.360406 -2.813174  1.387198
```

Insertion Transition State (18TS-S)
M06 SCF Energy: -1662.94820268
M06 Free energy: -1662.655961
M06 Solvent SCF Energy: -1663.03141175
Imaginary Frequency: -611.0141 cm-1

Cartesian coordinates

```
Atom      X         Y         Z
Rh   -0.124007 -0.192672 -0.819240
P     0.823919  1.724968  0.191834
```

P	1.696374	-1.313224	0.085282
C	2.090745	1.105133	1.379022
H	2.754198	1.925197	1.679165
H	1.542421	0.785838	2.276005
C	-0.148262	2.916104	1.164315
H	0.517510	3.664625	1.607627
H	-0.862073	3.428185	0.511692
H	-0.693059	2.390303	1.952303
C	2.862365	-0.052971	0.763697
H	3.534413	-0.528721	1.487765
H	3.484192	0.290630	-0.073483
C	2.748947	-2.402902	-0.916393
H	3.600569	-2.764646	-0.330550
H	2.165045	-3.258494	-1.265296
H	3.114457	-1.857049	-1.790117
S	-1.884901	-0.370465	0.911486
C	-2.859875	0.666954	-0.272021
H	-2.934228	1.637745	0.226380
H	-3.868629	0.261542	-0.418012
C	-1.992033	0.700716	-1.508756
H	-1.843824	1.658365	-1.999427
C	-1.826080	-0.490523	-2.258613
H	-2.511593	-1.320689	-2.087592
H	-1.497993	-0.412567	-3.290593
O	-1.768514	0.271544	2.252569
H	0.825270	0.107673	-2.020976
H	-0.630774	-1.448116	-1.760911
C	1.245278	-2.319786	1.538389
H	0.685417	-1.707936	2.253324
H	0.611095	-3.152520	1.220451
H	2.139539	-2.720804	2.027427
C	1.752978	2.786389	-0.962075
H	2.497885	2.199412	-1.504809
H	1.062239	3.214369	-1.694221
H	2.247986	3.599265	-0.420522
C	-2.946176	-1.819090	1.091154
H	-3.900746	-1.491567	1.509771
H	-3.077923	-2.291631	0.114518
H	-2.446270	-2.499410	1.782499

Alkyl Hydride Complex (19-S)
M06 SCF Energy: -1662.94829282
M06 Free energy: -1662.657066
M06 Solvent SCF Energy: -1663.04351920

Cartesian coordinates

Atom	X	Y	Z
Rh	-0.217072	-0.161966	-0.139724
P	1.785828	-1.296393	-0.017668
P	1.153650	1.803150	0.060447
C	3.158728	-0.077844	-0.232044
H	4.103992	-0.527223	0.096374
H	3.252117	0.112747	-1.309916
C	2.123064	-2.605361	-1.234337
H	3.151780	-2.966083	-1.127784
H	1.436418	-3.441011	-1.072341
H	1.979341	-2.228301	-2.250174
C	2.845273	1.210038	0.518906
H	3.591044	1.987827	0.317173
H	2.844805	1.038627	1.603581
C	0.737529	3.049730	1.320590
H	1.522108	3.809756	1.398228
H	-0.201531	3.538466	1.042754
H	0.604349	2.565896	2.292097
S	-2.425956	0.612964	-0.118292
C	-2.820059	-1.038824	-0.820323
H	-2.953376	-0.850922	-1.890070
H	-3.756423	-1.438439	-0.410960
C	-1.539921	-1.806362	-0.476558
H	-1.111979	-2.231201	-1.397123
C	-1.739012	-2.892134	0.555156
H	-2.465790	-3.641366	0.211113
H	-0.807398	-3.426472	0.770136
O	-2.954461	1.776817	-0.867808
H	-0.355139	-0.529080	1.332838
H	-2.112569	-2.500842	1.508708
C	1.427707	2.799592	-1.445729
H	1.830653	2.175081	-2.248169
H	0.474081	3.215380	-1.783959
H	2.125532	3.619705	-1.245643
C	2.138155	-2.082968	1.586457
H	2.106234	-1.336756	2.384978
H	1.383746	-2.844792	1.800161
H	3.127401	-2.552192	1.569812
C	-3.240275	0.533215	1.485151
H	-4.316703	0.571467	1.298986
H	-2.951330	-0.393022	1.985837
H	-2.921450	1.403452	2.060826

Reductive Elimination Transition State (20TS-S)
M06 SCF Energy: -1662.94735504
M06 Free energy: -1662.655292
M06 Solvent SCF Energy: -1663.03345900
Imaginary Frequency: -260.7965 cm-1

Cartesian coordinates

Atom	X	Y	Z
Rh	-0.200718	-0.218522	0.141891
P	1.868476	-1.216546	0.075945
P	1.063792	1.817006	-0.032373
C	3.120512	0.031633	-0.467567
H	4.129680	-0.334506	-0.242492
H	3.042024	0.104161	-1.560622
C	2.129920	-2.628957	-1.040459
H	3.175694	-2.952620	-1.011336
H	1.493448	-3.464338	-0.734731
H	1.869335	-2.350608	-2.065235
C	2.845833	1.380206	0.183595
H	3.484158	2.170256	-0.229302
H	3.039749	1.339478	1.263529
C	0.748240	3.225270	1.071792
H	1.440665	4.046307	0.858084
H	-0.277009	3.571481	0.909530
H	0.854859	2.922697	2.116089
S	-2.372858	0.601978	0.032577
C	-2.664648	-0.885502	-1.018094
H	-2.656390	-0.493282	-2.038909
H	-3.641725	-1.337176	-0.809598
C	-1.460407	-1.762335	-0.688392
H	-0.824815	-1.904511	-1.571763
C	-1.822598	-3.092874	-0.072505
H	-2.403726	-3.692867	-0.785557
H	-0.935300	-3.673120	0.199917
O	-2.768697	1.881143	-0.607339
H	-0.657605	-1.379384	1.075719

H	-2.434275	-2.980476	0.829315
C	0.945699	2.541448	-1.702354
H	1.225557	1.805635	-2.460994
H	-0.091129	2.843340	-1.880438
H	1.597862	3.417264	-1.788537
C	2.481496	-1.804140	1.687013
H	2.454208	-0.990716	2.416879
H	1.831544	-2.605409	2.049974
H	3.505527	-2.181780	1.597544
C	-3.486248	0.266873	1.408334
H	-4.506694	0.331176	1.022237
H	-3.263602	-0.726332	1.804608
H	-3.315250	1.031409	2.166737

O-bound Rhodium product complex (21-S)
M06 SCF Energy: -1663.00050395
M06 Free energy: -1662.704536
M06 Solvent SCF Energy: -1663.08856600

Cartesian coordinates

Atom	X	Y	Z
Rh	-0.063540	-0.365934	0.084563
P	0.760334	1.710676	-0.140782
P	2.152777	-0.982712	0.116408
C	0.166466	3.104424	0.870884
H	0.168139	2.844456	1.932246
H	0.811351	3.975761	0.711259
H	-0.848072	3.372741	0.560733
C	0.497269	2.294814	-1.844902
H	0.885240	3.312805	-1.963691
H	0.996551	1.627028	-2.551657
H	-0.576849	2.278392	-2.057640
C	2.705867	-2.389123	-0.900127
H	2.418339	-2.231318	-1.942896
H	3.793109	-2.505762	-0.838546
H	2.233755	-3.309605	-0.544514
C	2.810617	-1.366182	1.774560
H	3.882539	-1.585748	1.719861
H	2.646345	-0.522397	2.449700
H	2.289612	-2.234940	2.185680
S	-2.291497	0.338516	0.041016
C	-3.273607	-1.203205	0.185420
H	-4.281800	-0.922561	-0.139014
H	-3.289637	-1.444288	1.255644
C	-2.674081	-2.331477	-0.621279
H	-3.285227	-3.223105	-0.445564
C	-1.222664	-2.617282	-0.245729
H	-1.034631	-2.468170	0.832242
H	-0.920850	-3.644782	-0.464533
O	-2.756285	1.127086	-1.132970
H	-0.524330	-2.016203	-0.890191
H	-2.753848	-2.111241	-1.691759
C	3.176775	0.439175	-0.460162
H	4.224787	0.296569	-0.172159
H	3.135590	0.439528	-1.556922
C	2.590084	1.722608	0.103279
H	2.772639	1.800171	1.182763
H	3.016156	2.618489	-0.364018
C	-2.910024	1.150370	1.529117
H	-4.002324	1.159268	1.481434
H	-2.547670	0.612015	2.408391
H	-2.532264	2.172785	1.524582

Catalyst substrate complexes with (S,S)-PhBPE

Coordinates for the two catalyst substrate complexes with Rh[(*S*,*S*)-PhBPE]$^{+}$ and (*R*) or (*S*)-phenyl allyl sulfoxide. Geometry optimization and frequency calculation performed with B3LYP/SDD-6-31G(p), and single point calculation performed with M06/SDD-6-311+G(d,p) and SMD solvent parameters for methanol.

(R)-phenyl allyl sulfoxide complex
(Leads to major product enantiomer)
B3LYP SCF Energy: -2932.80473431
B3LYP Free Energy: -2932.104176
M06 SCF Energy: -2931.97540655

Cartesian coordinates

Atom	X	Y	Z
Rh	-0.178892	0.090396	-0.608441
P	1.189375	-1.309342	0.624466
P	0.496845	1.699973	0.833140
C	2.567569	-2.287959	-0.230003
H	3.475639	-1.697077	-0.065210
C	0.344463	-2.821069	1.423000
H	-0.617577	-2.884483	0.907673
C	-0.720072	2.909044	1.633657
H	-1.245425	2.338737	2.407571
C	1.695351	3.095871	0.385626
H	1.257477	3.496975	-0.535297
S	-2.244817	-1.639807	-2.372173
C	-2.168956	0.079679	-3.073890
H	-3.187759	0.345218	-3.372263
H	-1.562458	-0.050562	-3.975704
C	-1.556747	1.094226	-2.137186
H	-2.252640	1.713578	-1.579072
C	-0.240683	1.514215	-2.305601
H	0.386578	1.069823	-3.077198
H	0.061233	2.499420	-1.971017
O	-0.912586	-1.691130	-1.560649
C	1.239356	0.874919	2.348244
H	1.830289	1.586845	2.933751
H	0.393097	0.561588	2.971673
C	2.077255	-0.346938	1.955325
H	3.035608	-0.030427	1.530661
H	2.283108	-0.973610	2.828216
C	1.219740	-4.040869	1.010529
H	0.734178	-4.533737	0.163343
H	1.258902	-4.776134	1.820028
C	2.637267	-3.587179	0.608723
H	3.169934	-4.373519	0.062910
H	3.224247	-3.381286	1.512539
C	1.526921	4.168236	1.499545
H	1.552036	5.160256	1.036107
H	2.377909	4.140619	2.184063
C	0.208199	3.961141	2.302395
H	-0.331876	4.904873	2.424565

H	0.450664	3.612163	3.311266
C	3.115545	2.678985	0.051770
C	3.488731	2.514247	-1.291721
C	4.090470	2.449955	1.036501
C	4.782626	2.124355	-1.642142
H	2.760243	2.707878	-2.075461
C	5.385356	2.057922	0.690191
H	3.852380	2.590704	2.087182
C	5.736961	1.889958	-0.650573
H	5.047658	2.017967	-2.690483
H	6.123361	1.896601	1.471132
H	6.747023	1.595335	-0.919616
C	-1.765520	3.478819	0.692758
C	-3.073708	2.970441	0.723619
C	-1.490174	4.531752	-0.194804
C	-4.069668	3.480874	-0.110897
H	-3.318750	2.174912	1.423509
C	-2.482498	5.043153	-1.034215
H	-0.501241	4.979867	-0.220653
C	-3.775520	4.517823	-0.999078
H	-5.076998	3.077211	-0.056466
H	-2.245905	5.862996	-1.706675
H	-4.549272	4.924069	-1.643886
C	2.395772	-2.435322	-1.734478
C	1.910243	-3.598735	-2.343737
C	2.770044	-1.361948	-2.559963
C	1.789605	-3.684776	-3.733443
H	1.630162	-4.458385	-1.744661
C	2.651669	-1.444764	-3.946863
H	3.175402	-0.457641	-2.111624
C	2.154749	-2.608200	-4.541147
H	1.418715	-4.602287	-4.182065
H	2.967424	-0.608767	-4.566025
H	2.072992	-2.680844	-5.622056
C	0.069471	-2.648736	2.903663
C	-1.161806	-2.116079	3.319909
C	1.005048	-2.999557	3.890127
C	-1.445879	-1.930143	4.673922
H	-1.913509	-1.869445	2.572750
C	0.722224	-2.816865	5.245517
H	1.959710	-3.434381	3.605068
C	-0.502188	-2.277125	5.643091
H	-2.411203	-1.530488	4.973211
H	1.458889	-3.103569	5.990794
H	-0.723874	-2.141175	6.697541
C	-3.628425	-1.505148	-1.222490
C	-4.805903	-2.160281	-1.597557
C	-3.528097	-0.829631	-0.002666
C	-5.912591	-2.111517	-0.747451
H	-4.857873	-2.708342	-2.534770
C	-4.637272	-0.800308	0.843125
H	-2.593914	-0.340717	0.274376
C	-5.826870	-1.435107	0.470936
H	-6.832167	-2.614369	-1.030664
H	-4.575501	-0.282895	1.796594
H	-6.684687	-1.408985	1.136435

(S)-phenyl allyl sulfoxide complex
(Leads to minor product enantiomer)
B3LYP SCF Energy: -2932.80646557
B3LYP Free Energy: -2932.105550
M06 SCF Energy: -2931.97075178

Cartesian coordinates

Atom	X	Y	Z
Rh	0.167739	0.483875	0.333541
P	-0.357230	-1.568974	-0.615103
P	-2.066431	0.837838	0.323016
C	0.196397	-3.212192	0.152128
H	-0.672185	-3.562205	0.721827
C	0.416355	-1.889477	-2.326608
H	1.209286	-1.140165	-2.393408
C	-2.844296	2.471873	-0.280622
H	-3.103687	2.273546	-1.326378
C	-3.066003	0.755910	1.956093
H	-2.305368	0.805700	2.739584
S	3.029240	1.350822	-0.454973
C	2.589522	2.329121	1.061115
H	3.055356	3.315033	0.961563
H	3.044816	1.790595	1.897483
C	1.090332	2.408702	1.168667
H	0.616651	3.237900	0.653209
C	0.394357	1.725306	2.159727
H	0.921400	1.091900	2.871757
H	-0.568608	2.095851	2.494681
O	2.234835	0.031338	-0.151081
C	-2.850397	-0.375695	-0.870449
H	-3.933684	-0.428446	-0.724769
H	-2.663337	0.031507	-1.871012
C	-2.210151	-1.760447	-0.747484
H	-2.546746	-2.253736	0.170197
H	-2.487268	-2.393339	-1.595871
C	1.059422	-3.302583	-2.219874
H	2.124431	-3.174401	-2.003578
H	0.992101	-3.830068	-3.176363
C	0.395027	-4.112241	-1.090270
H	0.974118	-5.007619	-0.839182
H	-0.589770	-4.463584	-1.421489
C	-3.913725	2.058514	1.982387
H	-3.374497	2.809726	2.569444
H	-4.864563	1.888243	2.497010
C	-4.144554	2.584869	0.552854
H	-4.510653	3.617174	0.562039
H	-4.920993	1.983977	0.064801
C	-3.825822	-0.539672	2.163628
C	-3.238226	-1.570685	2.915371
C	-5.113180	-0.753084	1.645193
C	-3.903065	-2.779678	3.128122
H	-2.256881	-1.413026	3.358249
C	-5.781314	-1.960689	1.856888
H	-5.612132	0.031885	1.083142
C	-5.177440	-2.981083	2.593906
H	-3.432139	-3.556396	3.724454
H	-6.779502	-2.099616	1.451139
H	-5.701021	-3.917360	2.763222
C	-1.925033	3.680267	-0.283276
C	-1.109171	3.903926	-1.405568
C	-1.871430	4.610840	0.764478
C	-0.261485	5.009292	-1.475811
H	-1.148258	3.206333	-2.239382
C	-1.022351	5.719913	0.698697
H	-2.505090	4.492558	1.637374
C	-0.211762	5.922799	-0.418703
H	0.347054	5.166108	-2.362404
H	-1.006070	6.430628	1.520251
H	0.438134	6.791352	-0.474039

C	1.358424	-3.108845	1.129935
C	2.648852	-3.568504	0.840776
C	1.117276	-2.581765	2.410159
C	3.665585	-3.505770	1.799027
H	2.875548	-3.999374	-0.128478
C	2.128014	-2.513280	3.367149
H	0.117326	-2.236852	2.663712
C	3.412067	-2.976707	3.064301
H	4.653279	-3.887171	1.554099
H	1.909780	-2.118915	4.356210
H	4.197581	-2.943423	3.814160
C	-0.540966	-1.657536	-3.478783
C	-0.612282	-0.384717	-4.068956
C	-1.370969	-2.669252	-3.986948
C	-1.486857	-0.128124	-5.126086
H	0.040517	0.406761	-3.705715
C	-2.245643	-2.415673	-5.045846
H	-1.328756	-3.671062	-3.567367
C	-2.310140	-1.143811	-5.617245
H	-1.513787	0.860593	-5.576252
H	-2.872306	-3.216846	-5.427621
H	-2.985821	-0.949331	-6.444969
C	4.754924	0.955959	-0.146575
C	5.720759	1.700400	-0.830008
C	5.100729	-0.067820	0.739923
C	7.069948	1.430743	-0.594233
H	5.428859	2.472460	-1.537408
C	6.453078	-0.332074	0.954620
H	4.329320	-0.656783	1.226172
C	7.433242	0.417667	0.296069
H	7.832933	2.002439	-1.113611
H	6.742678	-1.126828	1.635724
H	8.483784	0.204885	0.470751

(ii) Mechanism of racemization

Rhodium catalyzed racemization

Coordinates for the $Rh(PMe_2CH_2CH_2PMe_2)^+$ catalyzed racemization of methyl allyl sulfoxide

Rhodium substrate complex (5-O)
M06 SCF Energy: -1661.799532
M06 Free energy: -1661.525042
M06 Solvent SCF Energy: -1661.878014

Cartesian coordinates

Atom	X	Y	Z
Rh	-0.193946	-0.210646	-0.188315
P	1.143844	1.664752	-0.196742
P	1.744910	-1.278061	0.224772
C	0.829074	2.744076	1.238811
H	1.001452	2.194801	2.168298
H	1.477626	3.626424	1.212101
H	-0.216132	3.064525	1.211883
C	1.004889	2.779828	-1.623049
H	1.653985	3.653635	-1.503917
H	1.271776	2.247410	-2.539138
H	-0.036017	3.105521	-1.703675
C	2.580696	-2.095411	-1.179300
H	2.731586	-1.376111	-1.988634
H	3.549243	-2.499197	-0.865330
H	1.966930	-2.912456	-1.566819
C	1.747550	-2.557788	1.523114
H	2.761684	-2.937490	1.688752
H	1.363691	-2.134460	2.455206
H	1.105599	-3.394976	1.233031
S	-3.209361	0.693105	0.131044
C	-3.143043	-1.095573	-0.262377
H	-3.980903	-1.573810	0.257308
H	-3.342888	-1.127810	-1.337854
C	-1.818312	-1.716057	0.073759
H	-1.714588	-2.124100	1.078688
C	-0.966228	-2.158954	-0.920325
H	-1.213857	-2.004571	-1.969134
H	-0.266116	-2.965732	-0.727342
O	-1.846848	1.163092	-0.425071
C	3.008254	-0.056955	0.803556
H	2.767578	0.176120	1.849303
H	4.007675	-0.507893	0.790329
C	2.920982	1.192969	-0.060231
H	3.514210	2.022122	0.341553
H	3.285656	0.994916	-1.076361
C	-2.973247	0.581382	1.918631
H	-2.029659	0.062355	2.113262
H	-2.931589	1.602270	2.301963
H	-3.824917	0.057737	2.360785

Oxidative addition (6TS)
M06 SCF Energy: -1661.756152
M06 Free energy: -1661.484207
M06 Solvent SCF Energy: -1661.849284

Cartesian coordinates

Atom	X	Y	Z
Rh	0.709230	-0.213251	0.007834
P	-0.191978	1.812212	0.349553
P	-1.475847	-0.894514	-0.248504
C	0.368283	3.112434	-0.780448
H	0.129249	2.838723	-1.812252
H	-0.113096	4.065425	-0.535537
H	1.453053	3.205236	-0.683089
C	0.217405	2.408810	2.012322
H	-0.144177	3.433298	2.150605
H	-0.233721	1.758307	2.767003
H	1.305544	2.385784	2.125694

C	-2.111157	-2.483808	0.377962
H	-1.896201	-2.600044	1.443390
H	-3.195063	-2.534604	0.230410
H	-1.648094	-3.312050	-0.165492
C	-2.031730	-0.882300	-1.987309
H	-3.106661	-1.082503	-2.055841
H	-1.813061	0.085517	-2.447952
H	-1.491645	-1.650521	-2.548040
S	3.645115	0.025965	-0.942217
C	2.779908	-2.240706	0.769735
H	3.214379	-3.018227	0.151152
H	3.466996	-1.554578	1.250311
C	1.449671	-2.222478	1.076288
H	0.813767	-3.021059	0.696859
C	0.858199	-1.176711	1.864305
H	1.539774	-0.564912	2.458555
H	-0.092179	-1.375412	2.357781
O	2.501372	0.760413	-0.064089
C	-2.532994	0.368736	0.585734
H	-3.586900	0.229082	0.318113
H	-2.444658	0.189219	1.666298
C	-2.030377	1.759256	0.223589
H	-2.287502	2.011226	-0.812899
H	-2.467513	2.538139	0.858610
C	2.738875	-0.477423	-2.429428
H	2.135848	-1.378434	-2.277284
H	2.099850	0.364325	-2.729776
H	3.468038	-0.668571	-3.221946

Allyl rhodium sulfenate (7)
M06 SCF Energy: -1661.788623
M06 Free energy: -1661.515529
M06 Solvent SCF Energy: -1661.873000

Cartesian coordinates

Atom	X	Y	Z
Rh	0.369729	-0.531036	-0.001721
P	-0.522441	1.623183	0.288389
P	-1.804607	-1.116905	-0.417674
C	0.293740	3.116235	-0.363721
H	0.285036	3.119282	-1.455207
H	-0.217873	4.013893	-0.001457
H	1.333976	3.134387	-0.026441
C	-0.841451	2.085744	2.025925
H	-1.394995	3.029490	2.074396
H	-1.416280	1.303281	2.528658
H	0.108818	2.205058	2.553749
C	-2.608324	-2.495594	0.457041
H	-2.624866	-2.304761	1.533545
H	-3.638282	-2.612079	0.103064
H	-2.066941	-3.427674	0.270088
C	-2.087306	-1.514231	-2.175568
H	-3.142427	-1.744436	-2.359110
H	-1.787774	-0.667710	-2.799836
H	-1.474673	-2.376866	-2.452570
S	1.695193	-0.425194	-1.976141
C	1.273335	-2.542322	0.412384
H	0.891735	-3.442853	-0.060471
H	2.315249	-2.299408	0.212724
C	0.658304	-2.057644	1.573996
H	-0.244779	-2.539756	1.941898
C	1.016714	-0.802541	2.092769
H	2.039434	-0.444788	1.983876
H	0.453659	-0.391800	2.924809
O	2.349332	0.103265	-0.638217
C	-2.914555	0.323836	-0.091886
H	-3.853773	0.189671	-0.641838
H	-3.165146	0.303011	0.976990
C	-2.213543	1.623236	-0.457341
H	-2.095248	1.713426	-1.545605
H	-2.779095	2.500410	-0.121502
C	1.320201	1.055849	-2.970513
H	0.287283	1.386133	-2.853173
H	2.020710	1.832181	-2.654191
H	1.509383	0.802811	-4.016446

Sulfenate rotation (8TS)
M06 SCF Energy: -1661.756939
M06 Free energy: -1661.484194
M06 Solvent SCF Energy: -1661.851822

Cartesian coordinates

Atom	X	Y	Z
Rh	0.029878	-0.568462	-0.091449
P	-0.016716	1.705290	0.131559
P	-2.213641	-0.359863	-0.603148
C	1.113036	2.636065	-0.933415
H	0.884676	2.446686	-1.986022
H	1.024061	3.708104	-0.728594
H	2.134064	2.298041	-0.736591
C	0.376101	2.196171	1.830998
H	0.454128	3.285929	1.899374
H	-0.401137	1.848870	2.517829
H	1.331025	1.737025	2.099901
C	-3.507012	-1.512720	-0.043321
H	-3.482030	-1.624954	1.044491
H	-4.492674	-1.133038	-0.332423
H	-3.363237	-2.494541	-0.502492
C	-2.513477	-0.205688	-2.396256
H	-3.547582	0.103542	-2.583200
H	-1.833746	0.529246	-2.837533
H	-2.336121	-1.167000	-2.885468
S	2.997401	-0.483218	-0.887615
C	0.776115	-2.867543	0.277881
H	0.692133	-3.644790	-0.474646
H	1.772146	-2.506296	0.517077
C	-0.313927	-2.492173	1.015200
H	-1.273080	-2.978126	0.852879
C	-0.245100	-1.305253	1.827695
H	0.698131	-1.065511	2.319428
H	-1.140040	-0.981647	2.357535
O	2.001945	-0.151365	0.417161
C	-2.745830	1.265915	0.094121
H	-3.741824	1.526202	-0.284632
H	-2.841244	1.124563	1.179877
C	-1.714714	2.338954	-0.227596
H	-1.745296	2.602223	-1.292263
H	-1.897728	3.262427	0.332922
C	4.545003	0.069976	-0.155002
H	4.486101	1.132139	0.098739
H	4.774475	-0.517619	0.736498
H	5.326827	-0.081508	-0.903998

Allyl rhodium sulfenate (9)

M06 SCF Energy: -1661.793127
M06 Free energy: -1661.519101
M06 Solvent SCF Energy: -1661.876192

Cartesian coordinates

Atom	X	Y	Z
Rh	0.510102	0.005216	0.281340
P	-0.796152	1.928305	0.603262
P	-1.438637	-0.926812	-0.471694
C	-0.146379	3.501838	-0.034831
H	-0.007643	3.439396	-1.117823
H	-0.831522	4.324369	0.193634
H	0.827331	3.698017	0.422541
C	-1.295015	2.327808	2.309576
H	-1.938890	3.213544	2.321326
H	-1.832347	1.485504	2.754346
H	-0.405953	2.526799	2.914161
C	-2.016340	-2.545862	0.124727
H	-2.164835	-2.527654	1.207745
H	-2.966555	-2.800414	-0.356804
H	-1.281971	-3.318675	-0.120901
C	-1.484752	-1.115500	-2.285901
H	-2.447831	-1.525857	-2.608851
H	-1.323714	-0.147017	-2.767763
H	-0.683953	-1.792398	-2.597623
S	1.767432	1.003340	-1.464727
C	1.800485	-1.797738	0.623031
H	1.745422	-2.690982	0.006277
H	2.761971	-1.288323	0.654417
C	0.913241	-1.643573	1.694439
H	0.112158	-2.365861	1.833421
C	0.864542	-0.430000	2.403190
H	1.774572	0.151950	2.542974
H	0.086103	-0.279886	3.144622
O	2.328232	1.185251	0.001577
C	-2.836272	0.217888	-0.093697
H	-3.701756	-0.037035	-0.717177
H	-3.124737	0.033438	0.950061
C	-2.391913	1.660134	-0.284748
H	-2.207749	1.876287	-1.345630
H	-3.149228	2.371591	0.064123
C	2.817780	-0.238785	-2.266464
H	3.725947	0.252336	-2.622256
H	3.062687	-1.041982	-1.573322
H	2.257665	-0.631871	-3.119535

Allyl rotation transition state (10TS)
M06 SCF Energy: -1661.766118
M06 Free energy: -1661.492443
M06 Solvent SCF Energy: -1661.850692

Cartesian coordinates

Atom	X	Y	Z
Rh	0.226251	0.283665	0.584467
P	-1.509176	1.709988	1.143292
P	-1.438561	-0.934569	-0.433079
C	-1.320063	3.365173	0.428502
H	-1.197995	3.276839	-0.654678
H	-2.195678	3.981393	0.658279
H	-0.415861	3.834675	0.822133
C	-1.863972	2.007926	2.906851
H	-2.664507	2.748778	3.007358
H	-2.180693	1.083330	3.397856
H	-0.969575	2.385257	3.409539
C	-1.455025	-2.754694	-0.394280
H	-1.531081	-3.119782	0.632712
H	-2.311680	-3.130114	-0.964431
H	-0.535343	-3.143476	-0.839765
C	-1.680969	-0.558732	-2.201750
H	-2.603814	-1.028568	-2.559795
H	-1.738610	0.521645	-2.361002
H	-0.838918	-0.944314	-2.782569
S	1.478054	1.006809	-1.384784
C	-0.071261	-1.017931	2.261480
H	-0.935114	-0.835742	2.897681
H	0.024470	-2.053340	1.935365
C	1.142136	-0.313355	2.526915
H	1.168635	0.508946	3.237166
C	2.207493	-0.555964	1.690586
H	2.287549	-1.498217	1.154091
H	3.088954	0.074958	1.729542
O	1.337173	1.998839	-0.150210
C	-3.037168	-0.452289	0.347751
H	-3.872960	-0.862536	-0.231748
H	-3.064619	-0.924299	1.339141
C	-3.104465	1.063049	0.460676
H	-3.239102	1.519316	-0.528097
H	-3.945128	1.392390	1.081426
C	3.226569	0.540677	-1.407714
H	3.325167	-0.375145	-1.995828
H	3.790973	1.345301	-1.884613
H	3.583705	0.379097	-0.392025

Allyl rhodium sulfenate (11)
M06 SCF Energy: -1661.791920
M06 Free energy: -1661.518914
M06 Solvent SCF Energy: -1661.875063

Cartesian coordinates

Atom	X	Y	Z
Rh	-0.477592	-0.069811	0.359458
P	1.286541	-1.543232	-0.045102
P	0.947886	1.528682	-0.472729
C	0.929039	-3.113507	-0.885405
H	0.496150	-2.924547	-1.871554
H	1.846987	-3.698715	-1.002758
H	0.206413	-3.683783	-0.295961
C	2.267030	-2.040181	1.407126
H	3.126613	-2.643937	1.097325
H	2.616637	-1.157687	1.949649
H	1.642536	-2.632133	2.081712
C	1.303870	3.095729	0.386148
H	1.603293	2.919453	1.422517
H	2.120170	3.609620	-0.132869
H	0.427016	3.748453	0.378599
C	0.475017	2.077823	-2.145788
H	1.203460	2.792372	-2.544090
H	0.404075	1.216636	-2.815807
H	-0.508003	2.556509	-2.099695
S	-1.923047	-1.095285	-1.244559
C	-0.079357	0.324351	2.486245
H	0.177636	-0.532234	3.102327
H	0.613137	1.160771	2.555378
C	-1.443559	0.562519	2.199687

H	-2.172177	-0.201132	2.467633
C	-1.813592	1.549522	1.286310
H	-1.237984	2.467157	1.212225
H	-2.849129	1.628681	0.971202
O	-1.890267	-1.697872	0.223777
C	2.620326	0.775079	-0.676561
H	3.214765	1.381165	-1.370794
H	3.112749	0.831516	0.304085
C	2.490312	-0.668597	-1.134169
H	2.091434	-0.720680	-2.156077
H	3.454771	-1.189741	-1.134069
C	-3.462416	-0.133852	-1.315398
H	-4.226170	-0.722649	-1.827188
H	-3.772624	0.067490	-0.288986
H	-3.283459	0.799362	-1.854221

Oxidative addition transition state (12TS)
M06 SCF Energy: -1661.756180
M06 Free energy: -1661.485189
M06 Solvent SCF Energy: -1661.848216

Cartesian coordinates

Atom	X	Y	Z
Rh	0.524490	-0.034023	-0.060617
P	-0.818200	1.746280	-0.256043
P	-1.380462	-1.142226	0.600018
C	-0.584854	2.620514	-1.821721
H	-0.804199	1.948679	-2.655682
H	-1.233281	3.501203	-1.877393
H	0.462012	2.931484	-1.883822
C	-0.559416	2.984642	1.045102
H	-1.199080	3.858146	0.879319
H	-0.779713	2.553944	2.025987
H	0.491955	3.284011	1.021855
C	-1.183971	-2.027721	2.179119
H	-0.753737	-1.355184	2.927112
H	-2.144880	-2.407999	2.542152
H	-0.500524	-2.871415	2.040605
C	-2.208137	-2.364933	-0.473395
H	-3.078337	-2.783493	0.042376
H	-2.542175	-1.896921	-1.404072
H	-1.524025	-3.181392	-0.722842
S	3.434671	0.797389	0.554370
C	2.854136	-1.654975	-0.981532
H	3.513809	-2.279381	-0.389276
H	3.318153	-0.882692	-1.583555
C	1.523195	-1.931796	-1.114392
H	1.117185	-2.811485	-0.613587
C	0.636507	-1.091971	-1.870536
H	1.099127	-0.398906	-2.576047
H	-0.301322	-1.515158	-2.222049
O	2.083028	1.274862	-0.195001
C	-2.689411	0.127324	0.910669
H	-3.682656	-0.335426	0.923090
H	-2.509441	0.535099	1.914281
C	-2.577618	1.221859	-0.143193
H	-2.867090	0.848425	-1.134639
H	-3.218350	2.082869	0.079855
C	2.813429	0.149181	2.129393
H	2.376676	-0.851656	2.039755
H	3.652226	0.108530	2.830489
H	2.066363	0.858212	2.511360

Rhodium substrate complex (5-O-ent)
M06 SCF Energy: -1661.799532
M06 Free energy: -1661.525054
M06 Solvent SCF Energy: -1661.878015

Cartesian coordinates

Atom	X	Y	Z
Rh	0.289810	-0.235801	-0.229545
P	-0.914342	1.725573	-0.134475
P	-1.724219	-1.188102	0.095877
C	-0.677557	2.913273	-1.487342
H	-0.966351	2.457578	-2.437538
H	-1.266854	3.821178	-1.321507
H	0.384368	3.170187	-1.536247
C	-0.546207	2.690402	1.368292
H	-1.132002	3.615736	1.390087
H	-0.768925	2.098667	2.260264
H	0.518862	2.938410	1.371451
C	-1.834453	-2.542489	1.311108
H	-1.435918	-2.205734	2.271903
H	-2.874691	-2.859997	1.442132
H	-1.247704	-3.402894	0.975561
C	-2.594042	-1.856418	-1.365196
H	-3.592896	-2.209640	-1.087302
H	-2.682472	-1.079825	-2.129573
H	-2.032964	-2.689223	-1.796588
S	3.355419	0.432739	0.177729
C	3.171476	-1.319361	-0.327430
H	3.966089	-1.886177	0.170649
H	3.385271	-1.299203	-1.400518
C	1.801931	-1.865028	-0.045567
H	1.654779	-2.326378	0.930466
C	0.936518	-2.184309	-1.074829
H	1.210142	-1.982642	-2.109034
H	0.178879	-2.949975	-0.940656
O	2.037433	1.030351	-0.362923
C	-2.908170	0.080434	0.737032
H	-3.936149	-0.297642	0.685251
H	-2.667368	0.230883	1.797795
C	-2.721727	1.372177	-0.045741
H	-3.084590	1.263405	-1.075909
H	-3.261721	2.214506	0.401172
C	3.084462	0.227878	1.952122
H	2.104327	-0.234878	2.103254
H	3.890921	-0.380293	2.370186
H	3.107440	1.223625	2.398065

Uncatalyzed racemization

Coordinates for 2,3-sigmatropic rearrangement of methyl allyl sulfoxide

Methyl allyl sulfoxide (0.0 kcal/mol)
M06 SCF Energy: -630.4737472
M06 Free energy: -630.394
M06 Solvent SCF Energy: -630.492

Cartesian coordinates

Atom	X	Y	Z
S	-1.157540	-0.116811	0.353751
O	-1.438179	-0.880954	-0.906287
C	0.568731	-0.584291	0.871978
H	0.441601	-1.607266	1.242193
H	0.841347	0.067085	1.710463
C	1.526284	-0.515451	-0.252802
H	1.302685	-1.159479	-1.101688
C	2.582157	0.288415	-0.279679
H	2.820600	0.943691	0.556069
H	3.256371	0.314151	-1.129321
C	-0.764714	1.583675	-0.157357
H	-1.693502	2.019454	-0.528441
H	-0.399510	2.151947	0.702703
H	-0.018271	1.552948	-0.954526

Endo Transition state (23.5 kcal/mol)
M06 SCF Energy: -630.4433254
M06 Free energy: -630.363794
M06 Solvent SCF Energy: -630.455248
Imaginary Frequency: -357.2824 cm-1

Cartesian coordinates

Atom	X	Y	Z
S	0.980911	-0.216454	-0.607045
O	0.112532	-1.343355	0.013459
C	-1.000330	1.299629	-0.592777
H	-0.617442	2.312017	-0.498069
H	-1.215785	0.973286	-1.606164
C	-1.539897	0.624373	0.478231
H	-1.433417	1.037861	1.479446
C	-1.763096	-0.736593	0.334975
H	-1.995895	-1.361778	1.189073
H	-2.052439	-1.139317	-0.630060
C	1.784495	0.535726	0.833807
H	2.401440	1.370507	0.489542
H	1.021856	0.891235	1.531232
H	2.409811	-0.212516	1.324633

Exo Transition state (24.1 kcal/mol)
M06 SCF Energy: -630.4418567
M06 Free energy: -630.362223
M06 Solvent SCF Energy: -630.4544224
Imaginary Frequency: -342.8911 cm-1

Cartesian coordinates

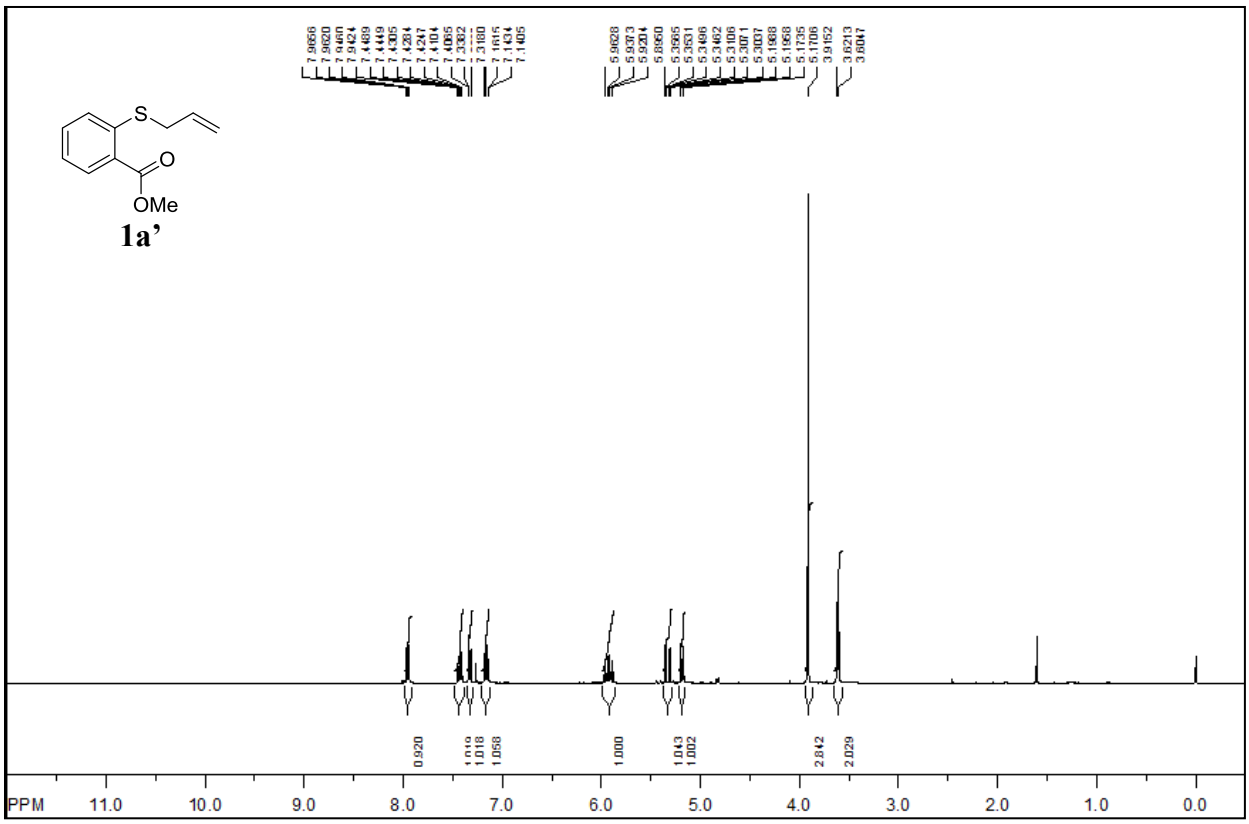
Atom	X	Y	Z
S	0.932913	-0.057363	-0.671325
O	0.127565	-1.301394	-0.220147
C	-0.982798	1.420446	-0.015739
H	-1.008386	2.244835	-0.721230
H	-0.463966	1.620273	0.918700
C	-1.863898	0.366055	-0.106041
H	-2.482120	0.267447	-0.995320
C	-1.608421	-0.760783	0.654890
H	-1.119330	-0.665984	1.619672
H	-2.146571	-1.687309	0.494446
C	1.934858	0.349601	0.790956
H	2.706801	-0.409439	0.930532
H	2.396938	1.328922	0.636966
H	1.291061	0.378294	1.674206

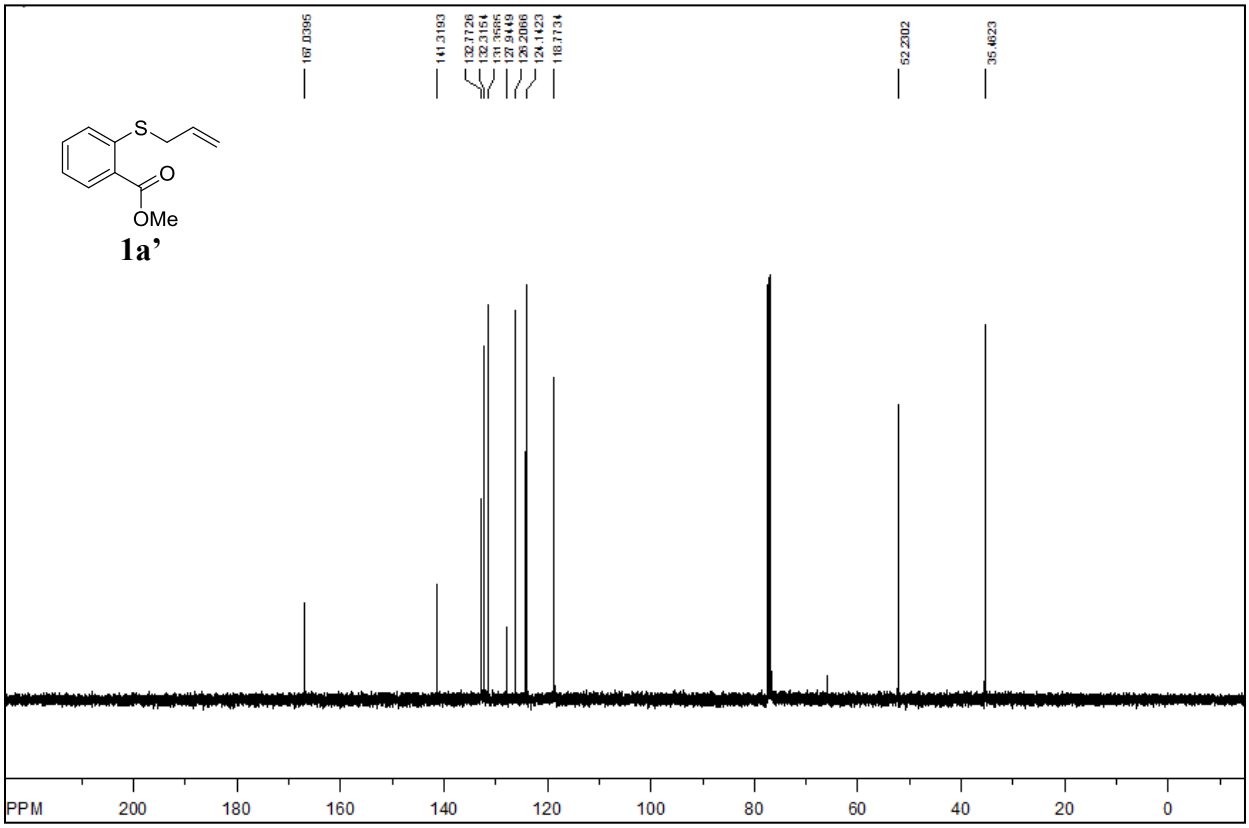
Sulfenate ester (1.3 kcal/mol)
M06 SCF Energy: -630.4812612
M06 Free energy: -630.401638
M06 Solvent SCF Energy: -630.4907567

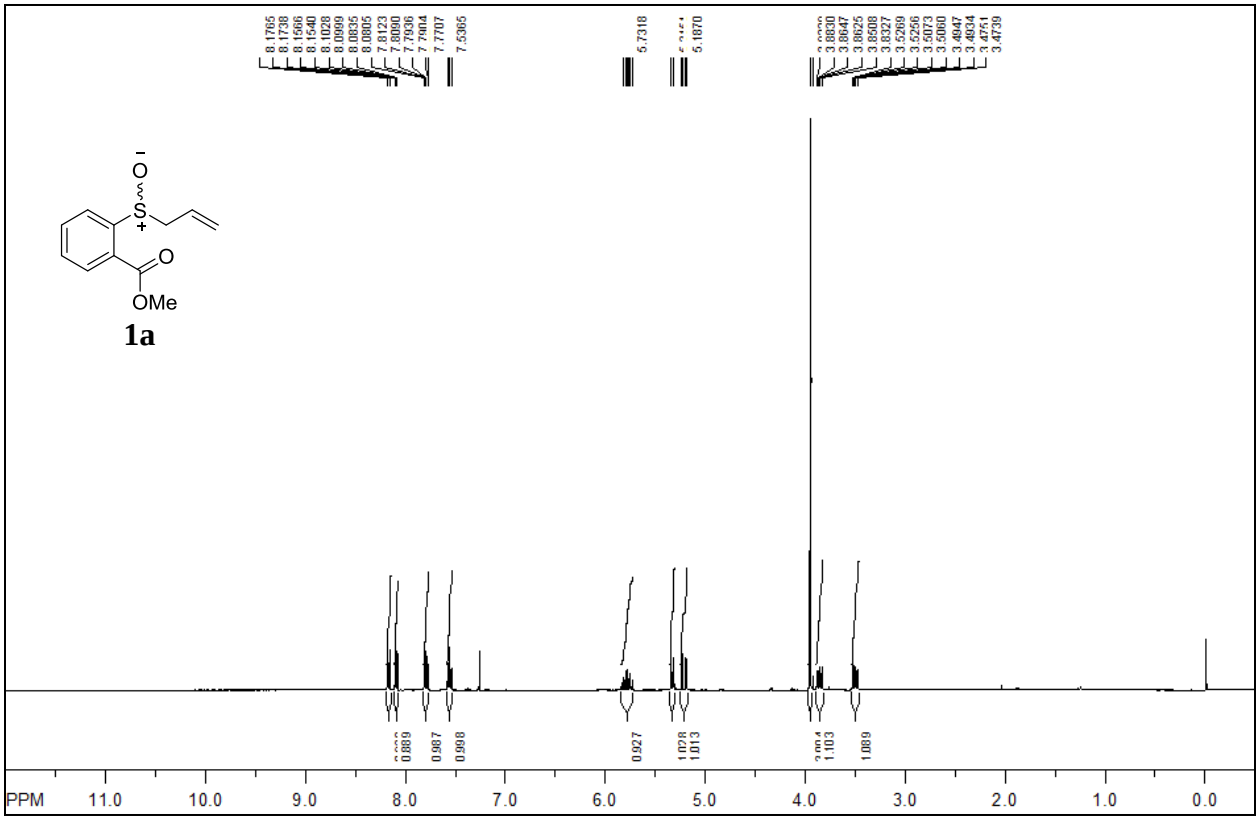
Cartesian coordinates

Atom	X	Y	Z
S	-1.698399	-0.566124	0.073160
O	-0.115067	-0.495299	-0.472782
C	3.140665	0.589264	-0.091794
H	4.127456	0.393323	-0.497919
H	2.962219	1.586640	0.303781
C	2.196256	-0.339435	-0.070212
H	2.380942	-1.330339	-0.482388
C	0.846250	-0.133114	0.515660
H	0.705499	-0.762960	1.407497
H	0.715353	0.916592	0.822112
C	-2.168715	1.165017	-0.106598
H	-3.236824	1.214948	0.125456
H	-1.631767	1.816724	0.587287
H	-2.014695	1.495049	-1.136460

7. NMR Spectra



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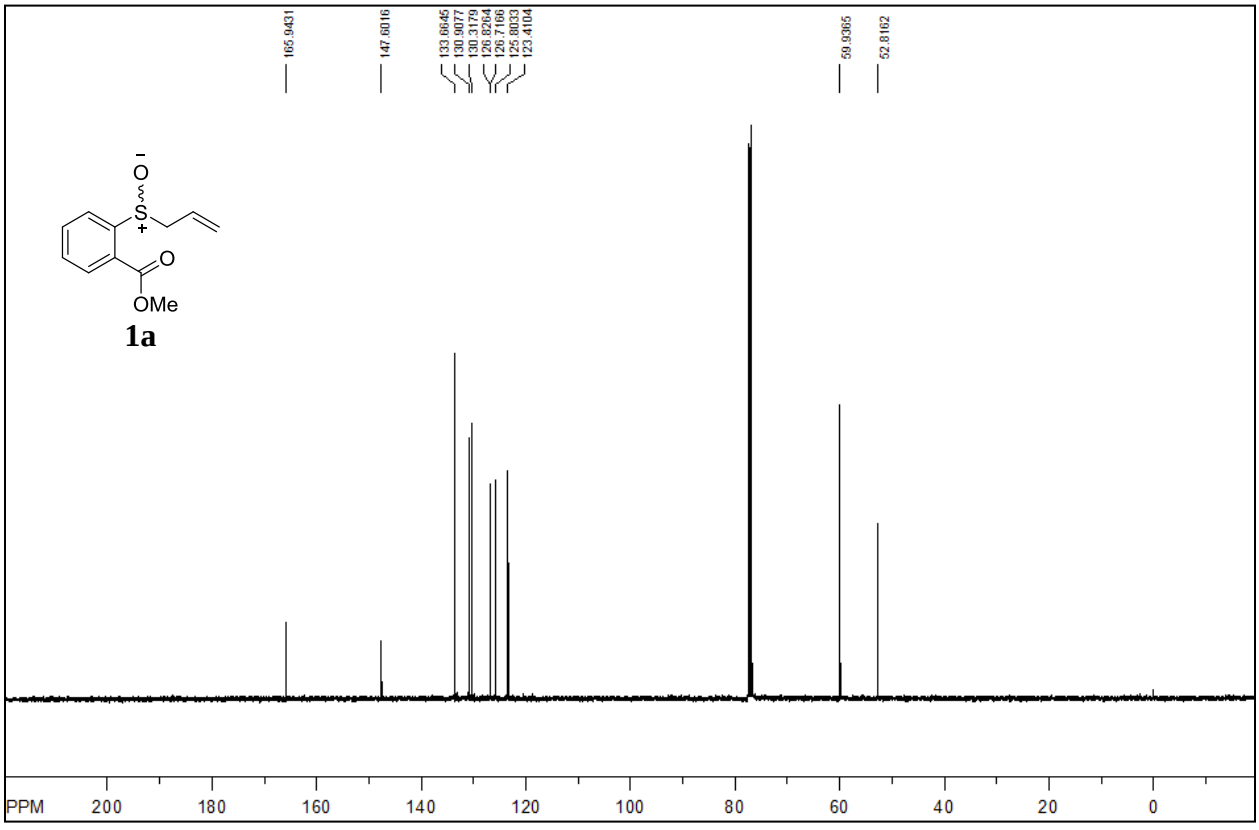
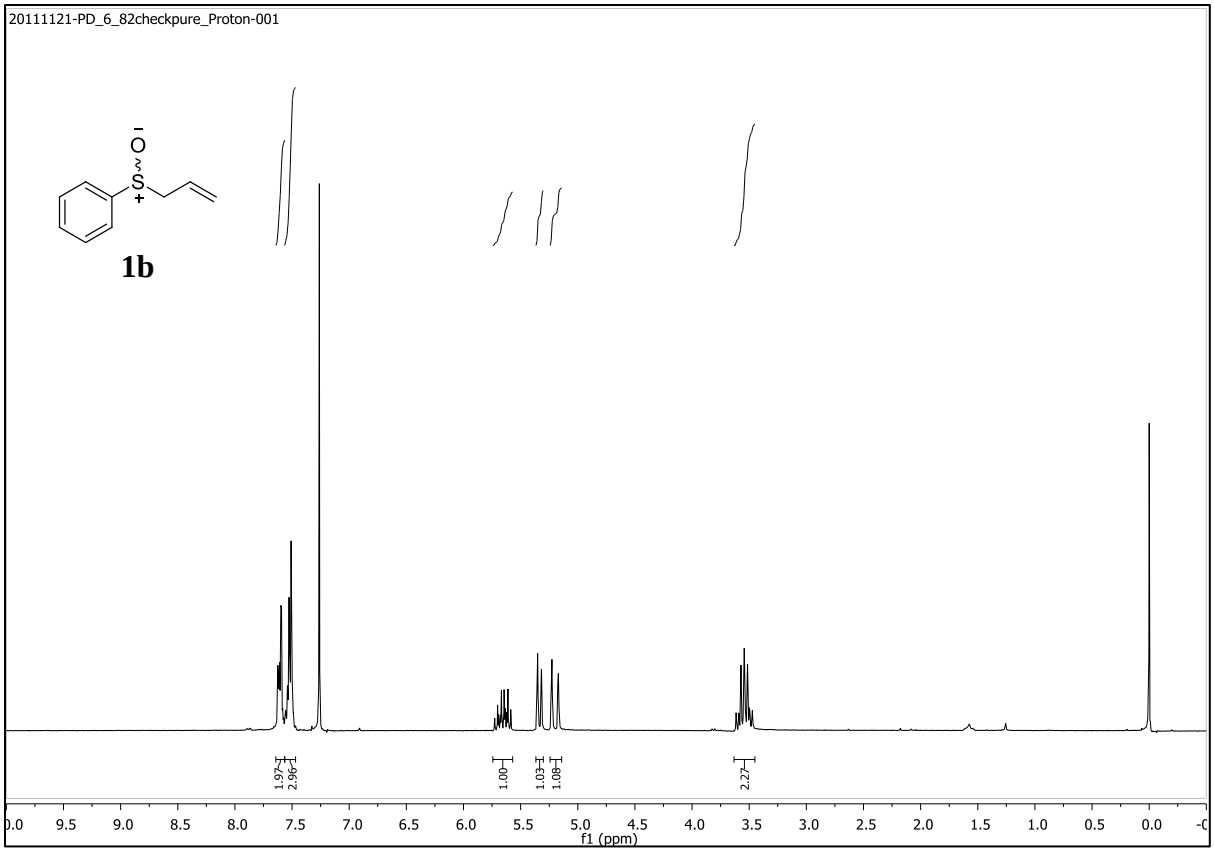
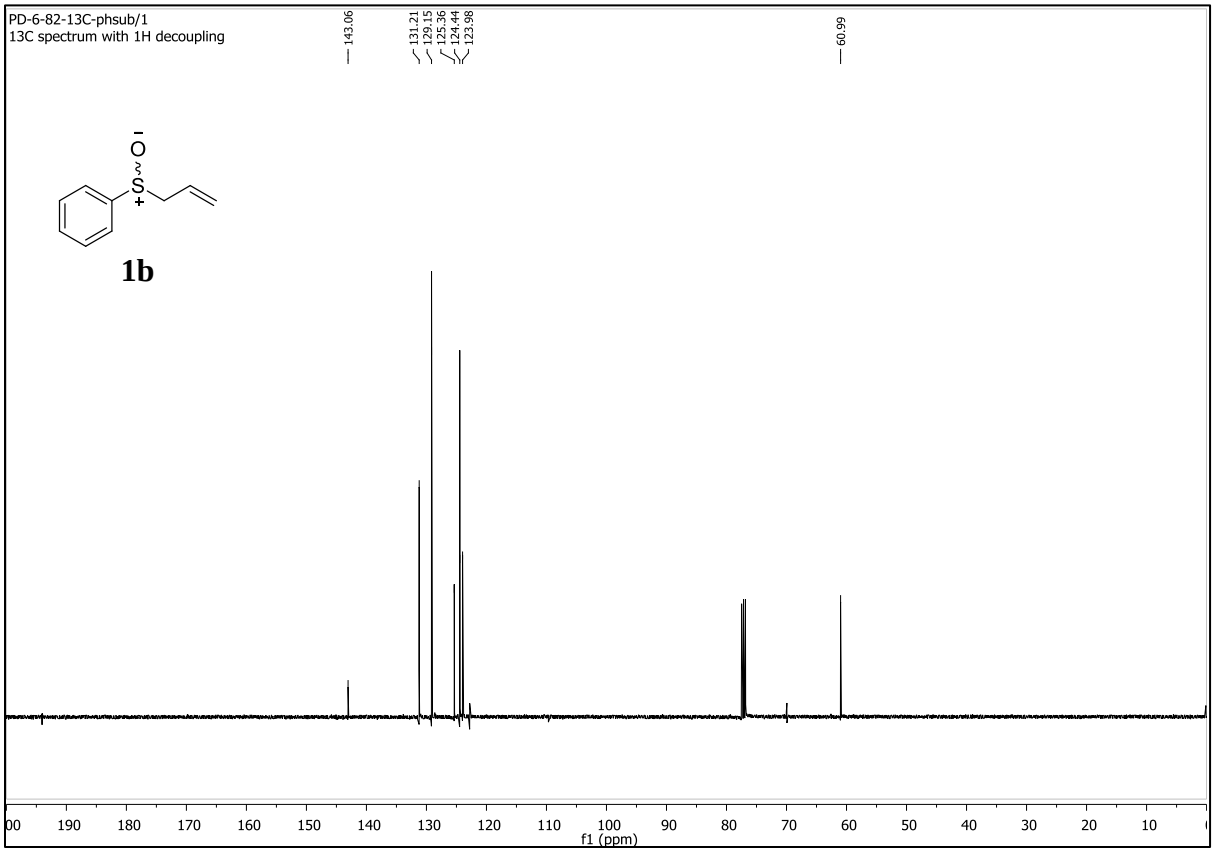
3.8830
3.8647
3.8625
3.8508
3.8327
3.5269
3.5256
3.5073
3.5060
3.4947
3.4934
3.4751
3.4739
0.889
0.987
0.998
0.927
1.028
1.013
1.103
1.089
PPM
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

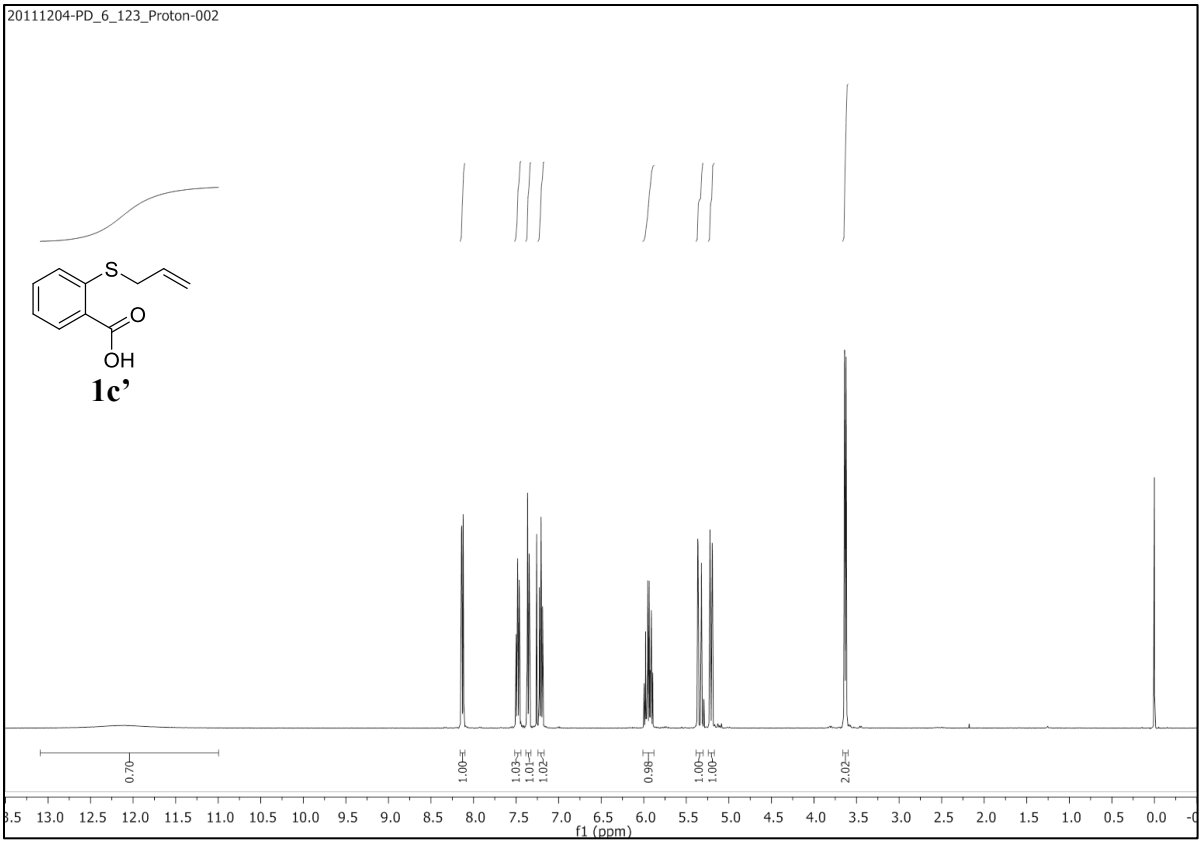
1a

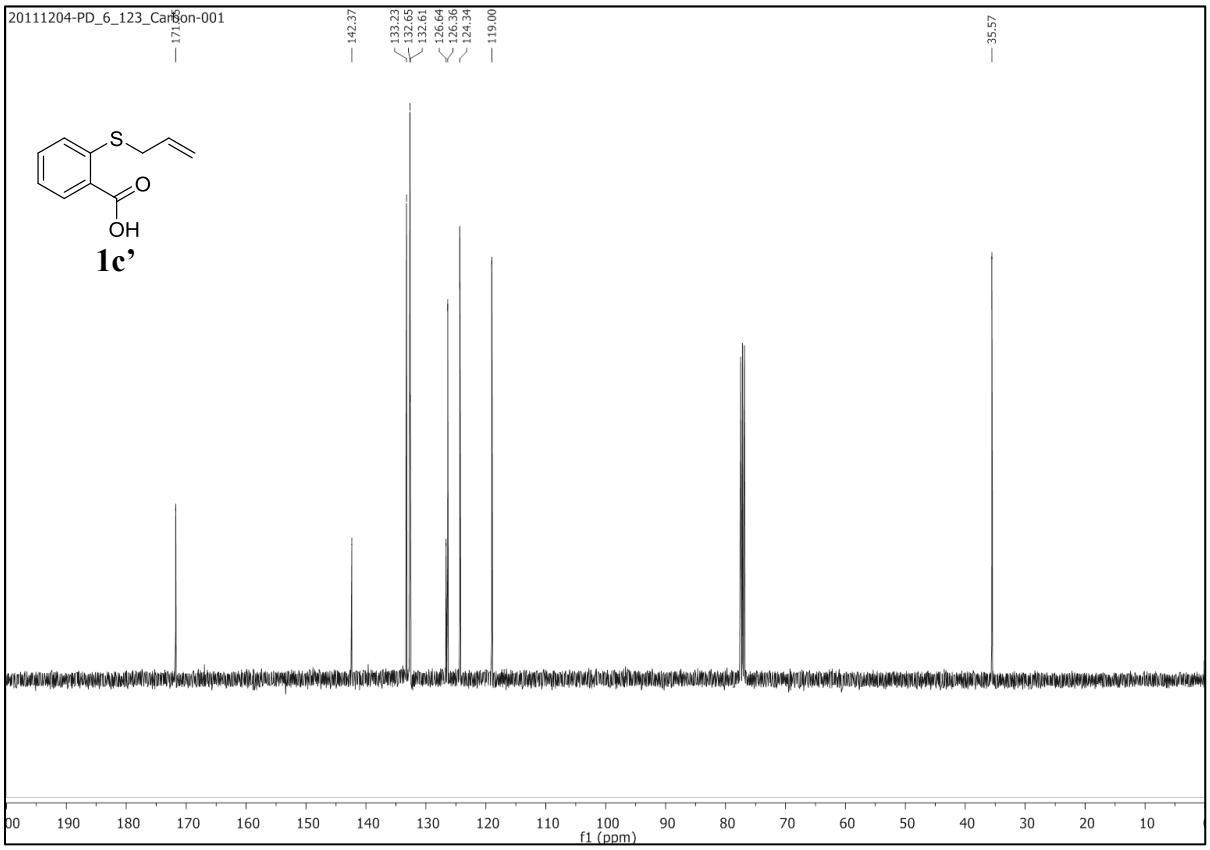

165.9431
147.6016
133.6645
130.9077
130.3179
126.8264
126.7166
125.8033
123.4104
59.9365
52.8162
PPM
200
180
160
140
120
100
80
60
40
20
0

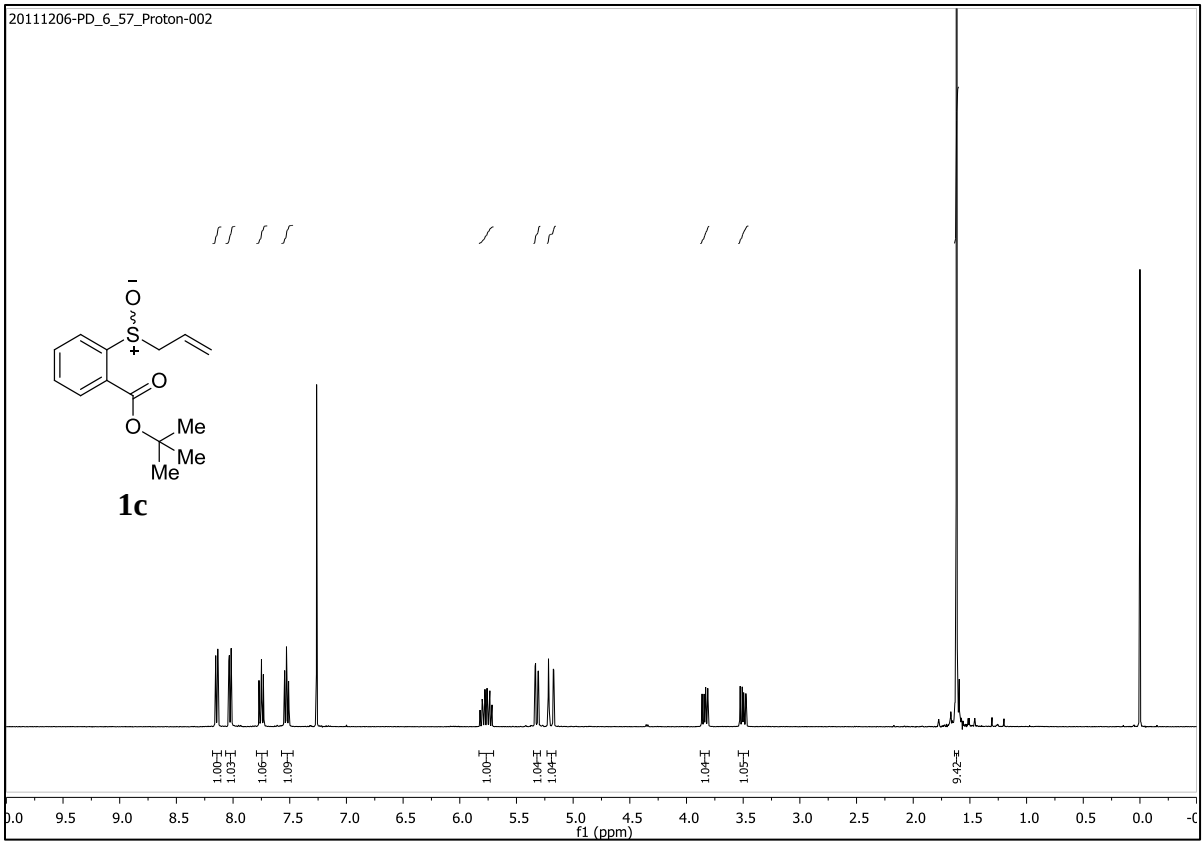
1a


20111121-PD_6_82checkpure_Proton-001
1b
1.97
2.96
1.00
1.03
1.08
2.27
f1 (ppm)

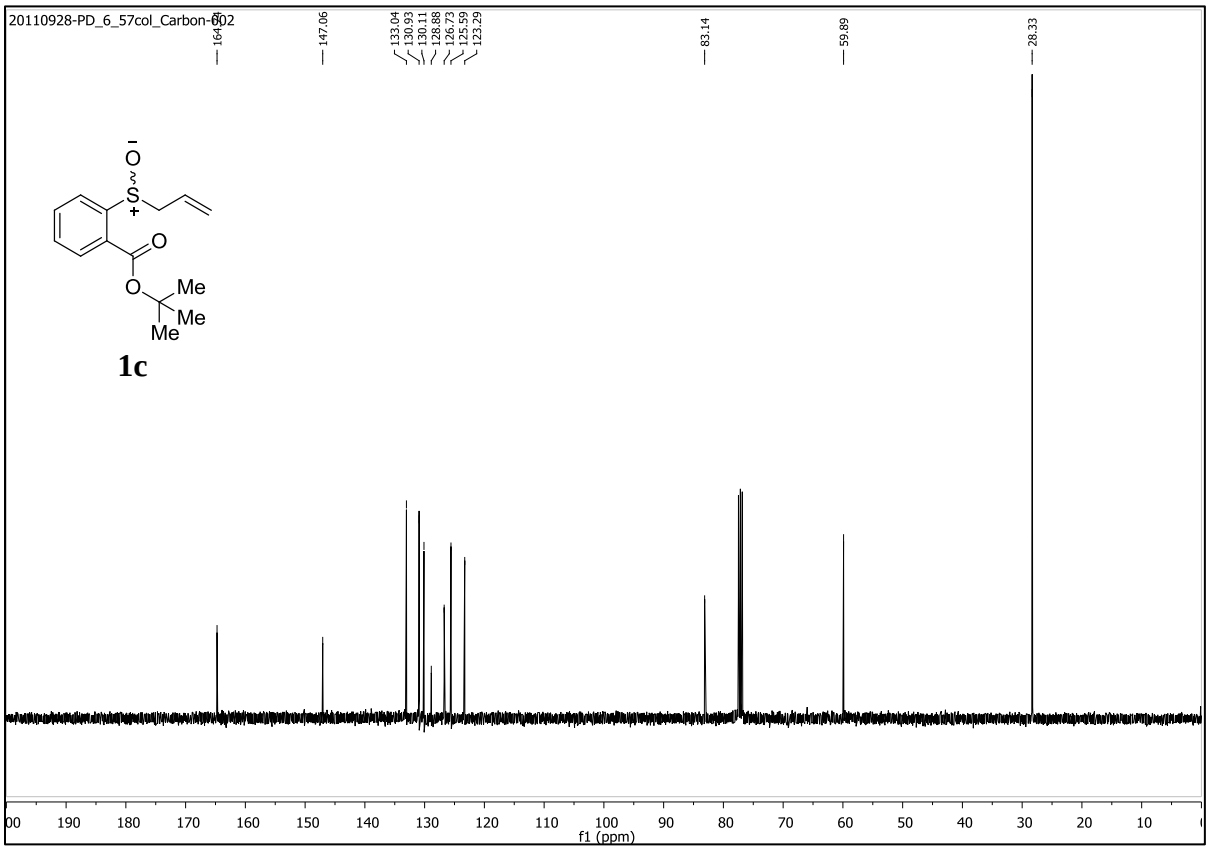

PD-6-82-13C-phsub/1
13C spectrum with 1H decoupling
143.06
131.21
129.15
125.36
124.44
123.98
60.99
1b
f1 (ppm)


20111204-PD_6_123_Proton-002
S
O
OH
1c'
0.70
1.00
1.03
1.01
1.02
0.98
1.00
1.00
2.02
f1 (ppm)

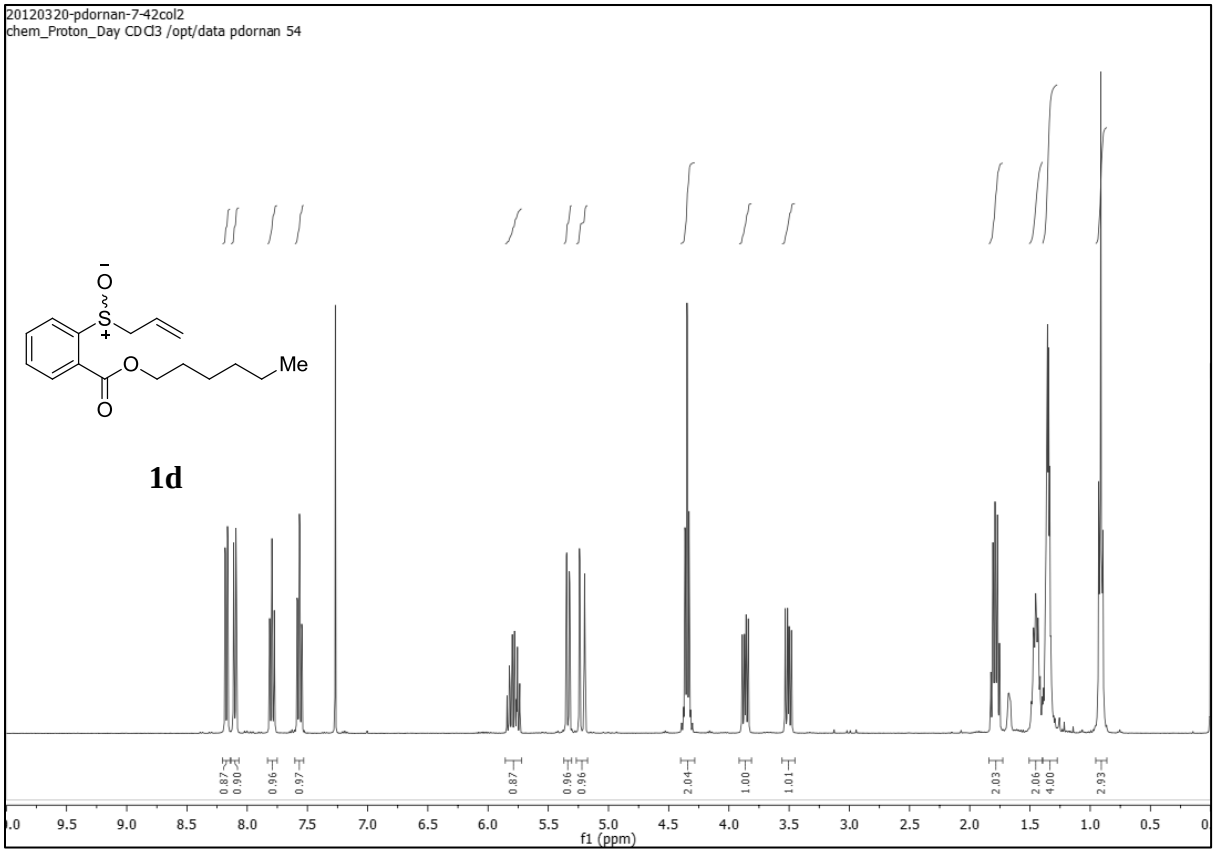

20111204-PD_6_123_Carbon-001
171.45
142.37
133.23
132.65
132.61
126.64
126.36
124.34
119.00
35.57
S
O
OH
1c'
f1 (ppm)

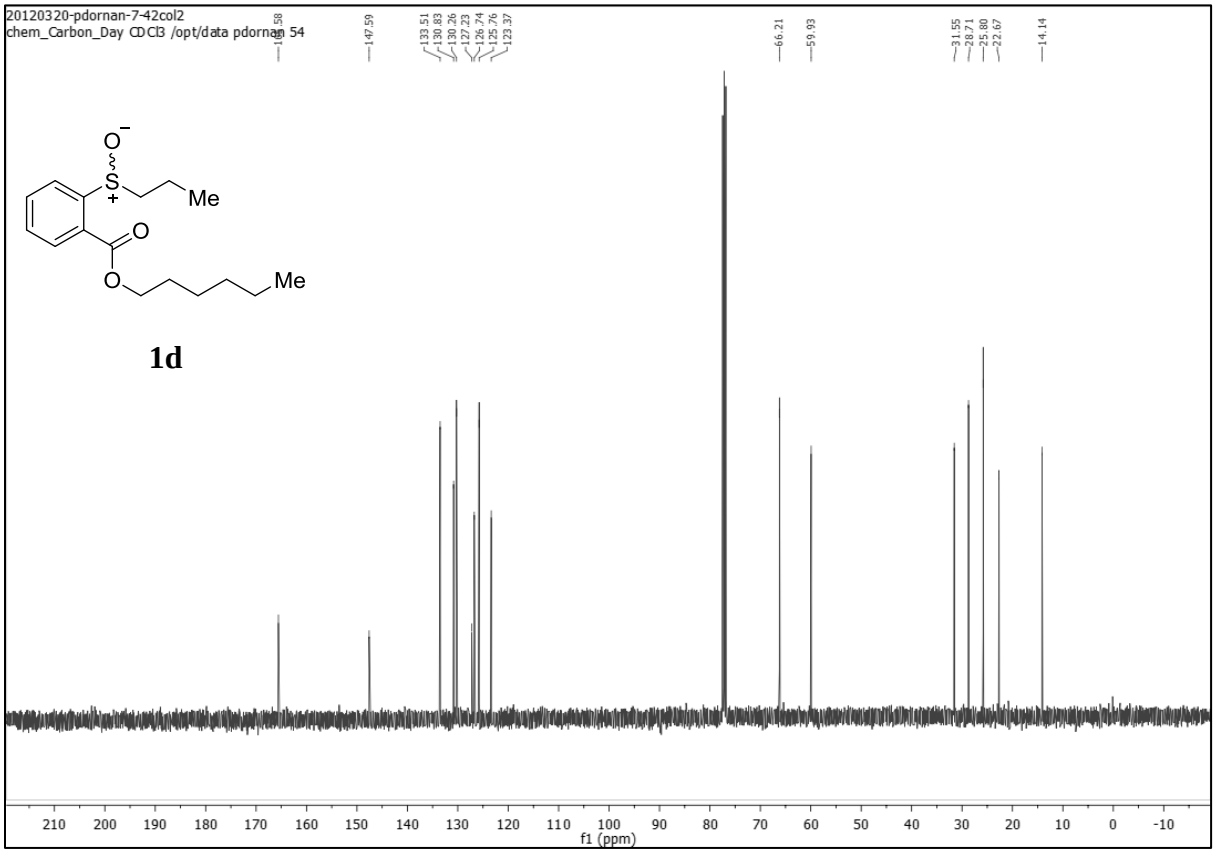

20111206-PD_6_57_Proton-002
1.00
1.03
1.06
1.09
1.00
1.04
1.04
1.04
1.05
9.42
f1 (ppm)

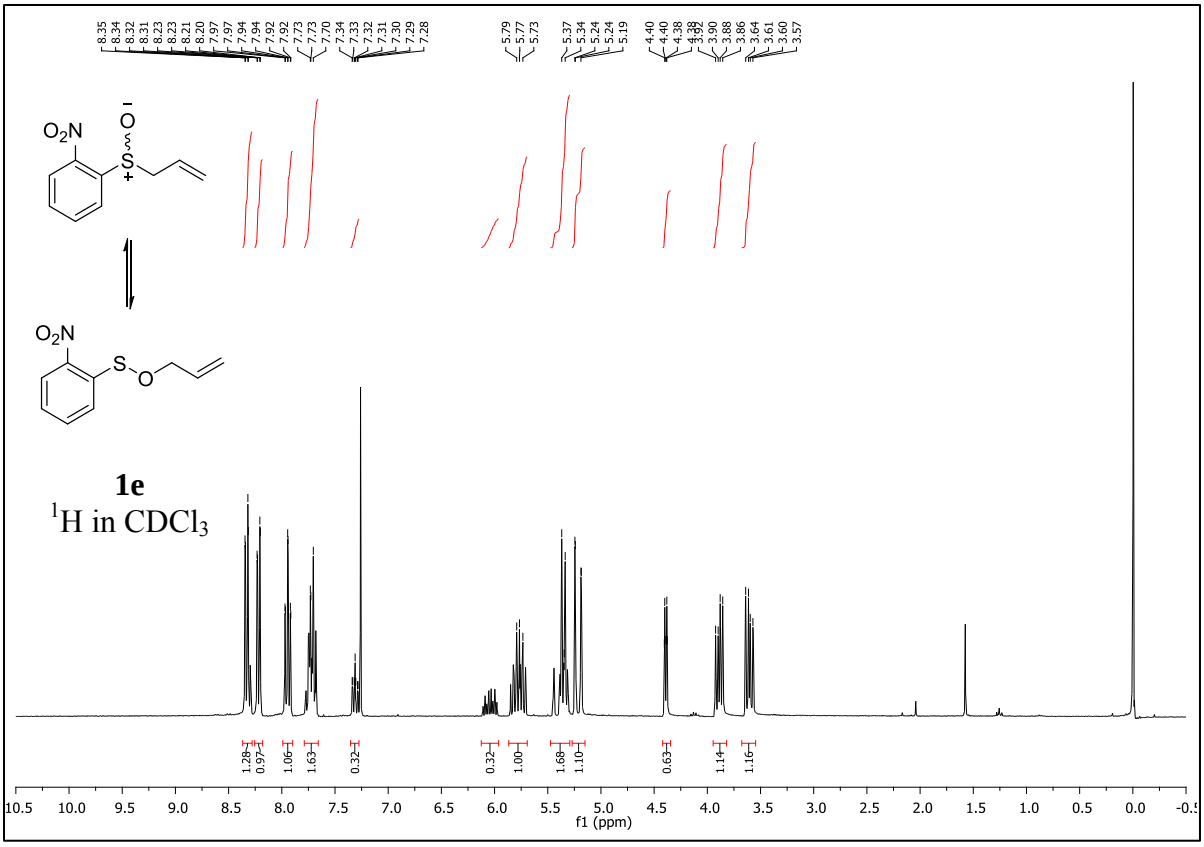
1c

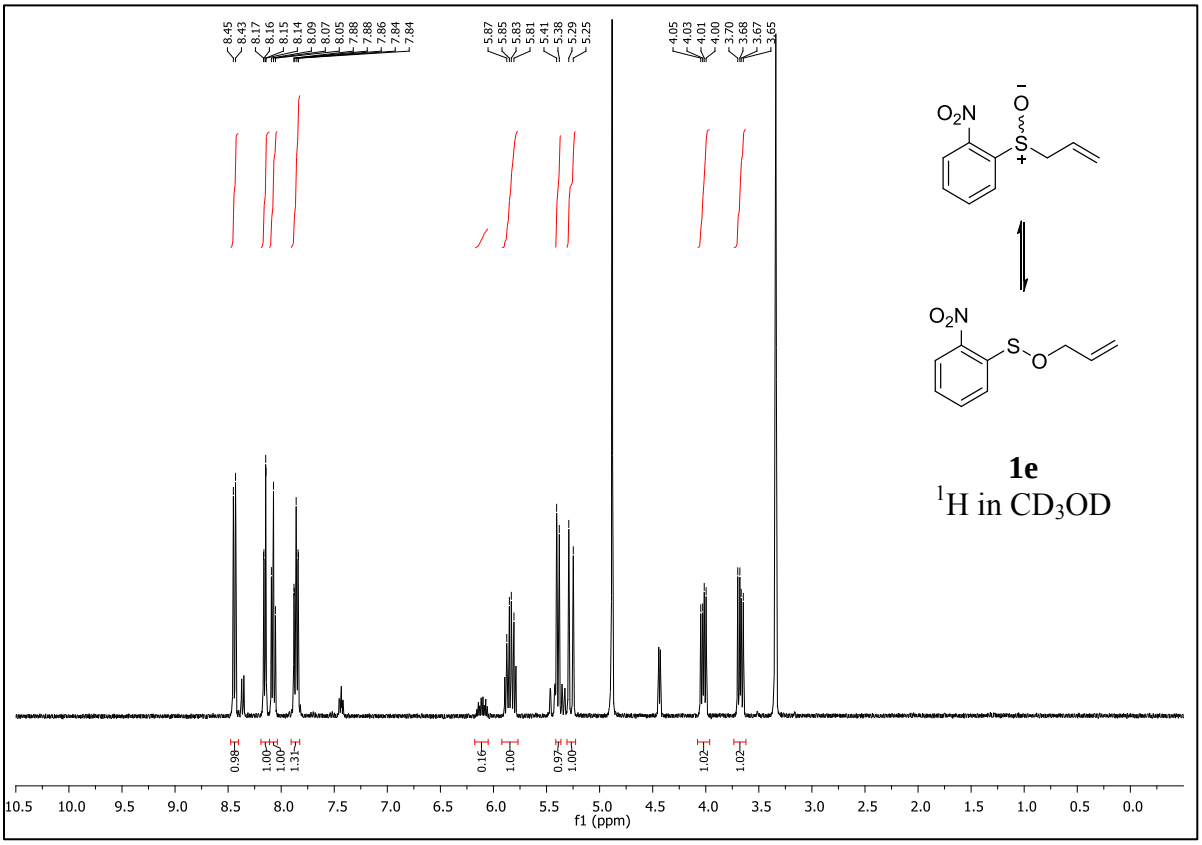

20110928-PD_6_57col_Carbon-002
164.87
147.06
133.04
130.93
130.11
128.88
126.73
125.59
123.29
83.14
59.89
28.33
f1 (ppm)

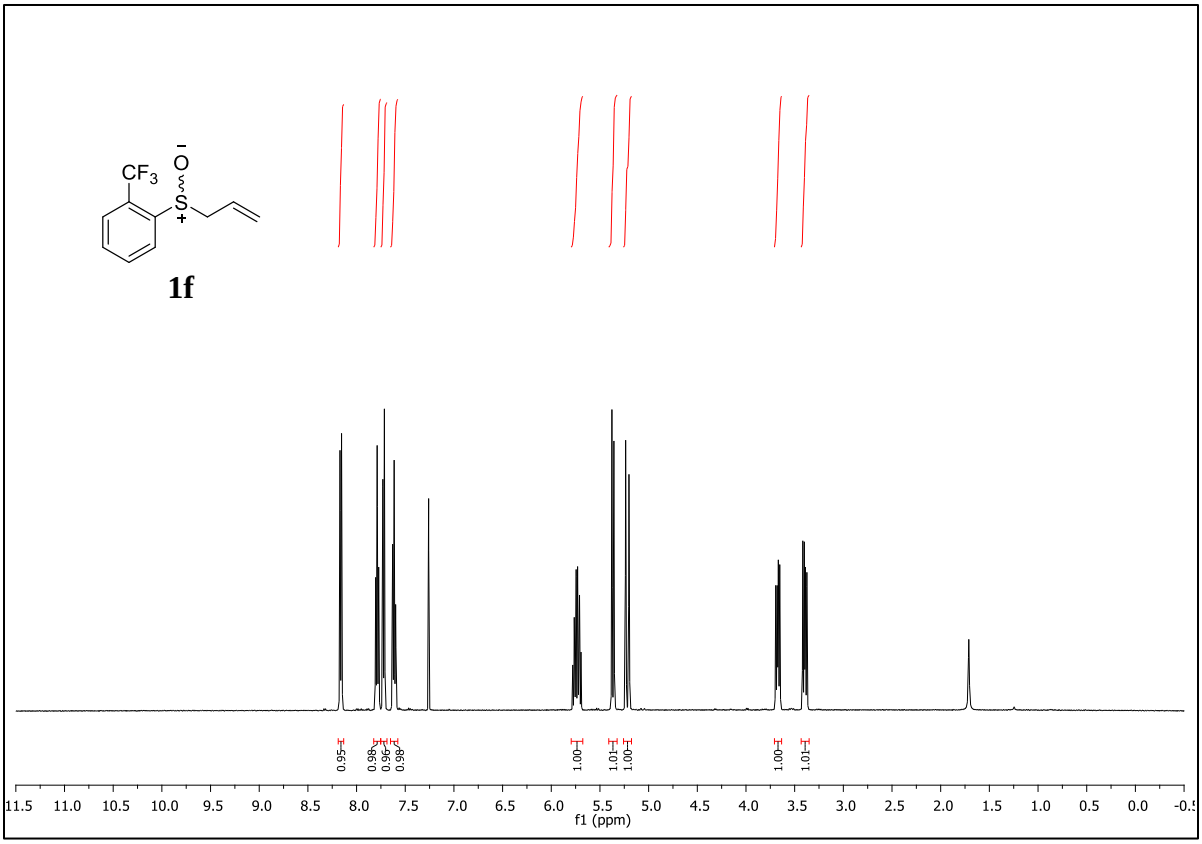
1c

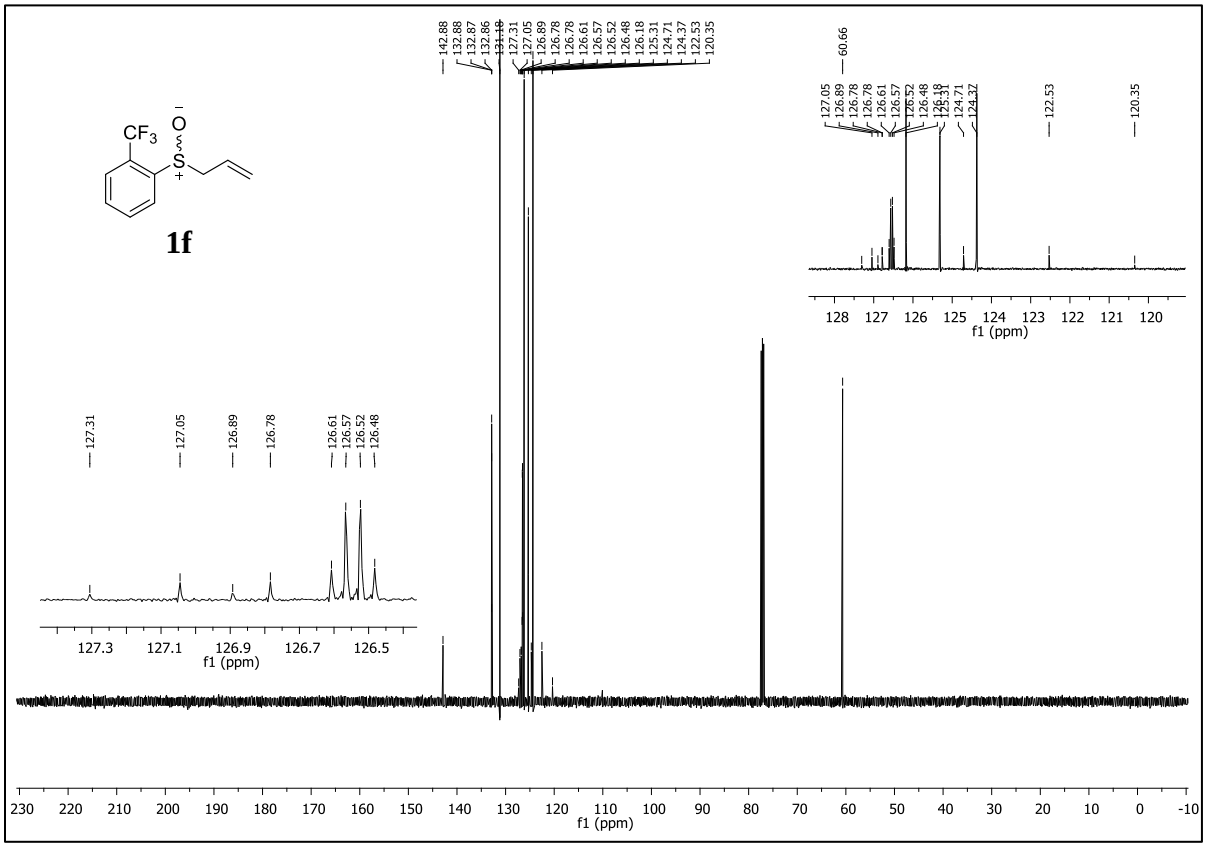

20120320-pdornan-7-42col2
chem_Proton_Day CDCl3 /opt/data pdornan 54
Me
1d
0.87
0.90
0.96
0.97
0.87
0.96
0.96
2.04
1.00
1.01
2.03
2.06
4.00
2.93
f1 (ppm)

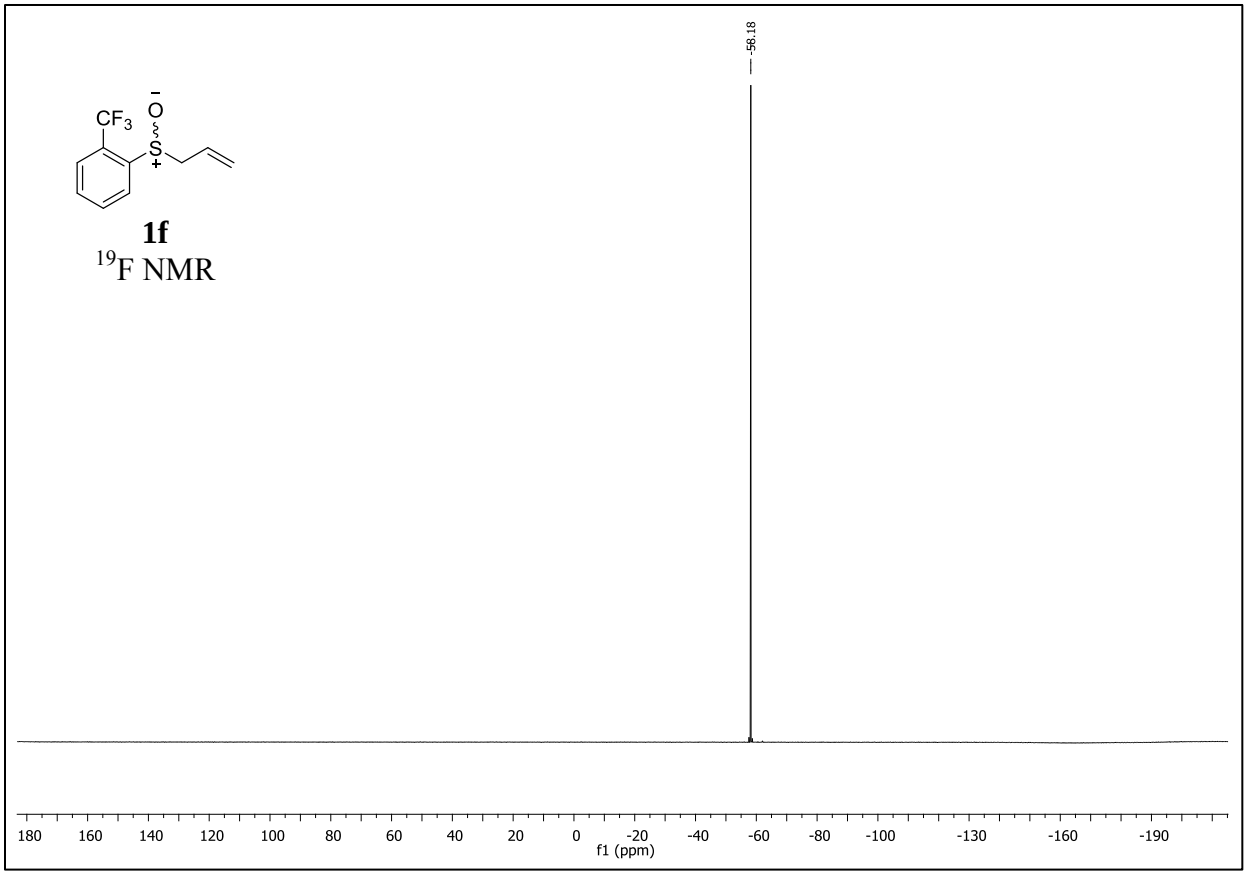

20120320-pdornan-7-42col2
chem_Carbon_Day CDCl3 /opt/data pdornan 54
147.59
133.51
130.83
130.26
127.23
126.74
125.76
123.37
66.21
59.93
31.55
28.71
25.80
22.67
14.14
Me
Me
1d
f1 (ppm)


1e
1H in CDCl3
f1 (ppm)


1e
1H in CD3OD
f1 (ppm)

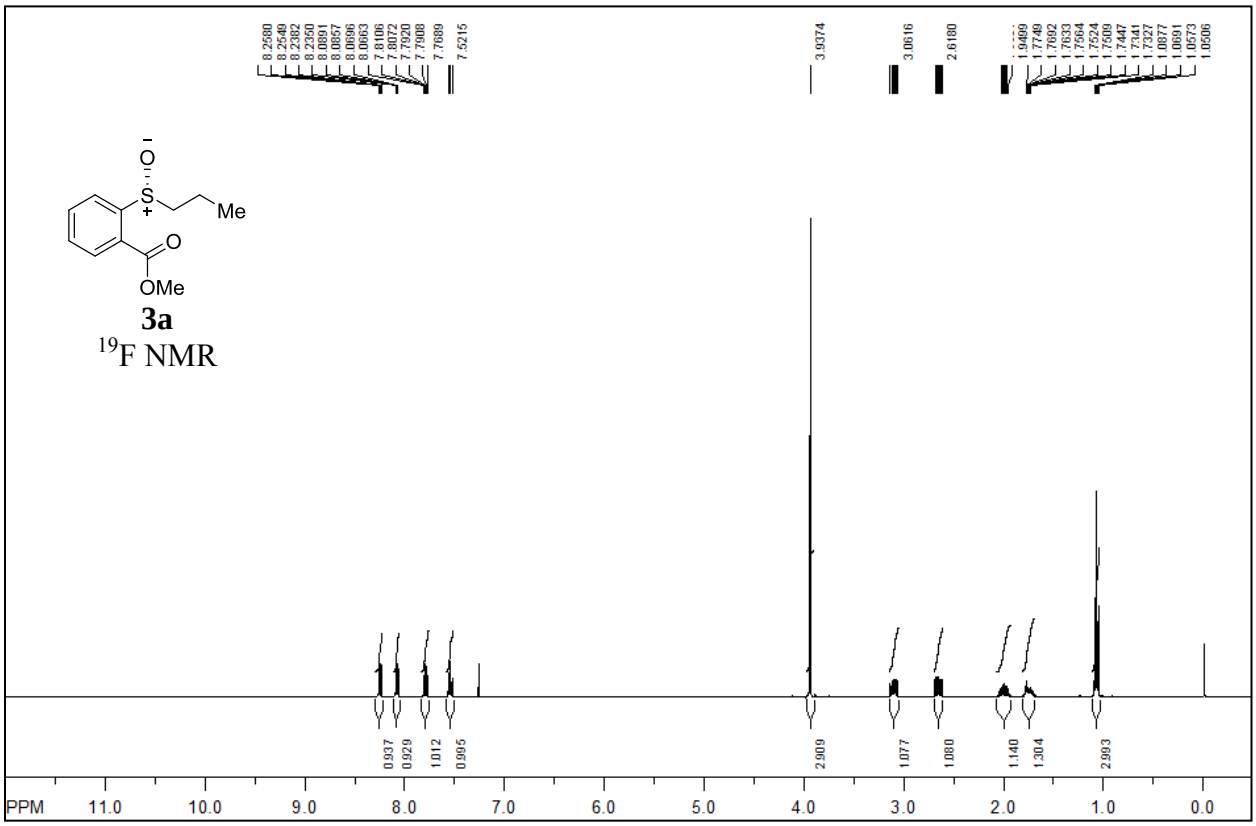

CF3
O
S
1f
0.95
0.98
0.96
0.98
1.00
1.01
1.00
1.00
1.01
f1 (ppm)


CF3
O
S
1f
142.88
132.88
132.87
132.86
127.31
127.05
126.89
126.78
126.78
126.61
126.57
126.52
126.48
126.18
125.31
124.71
124.37
122.53
120.35
60.66
f1 (ppm)



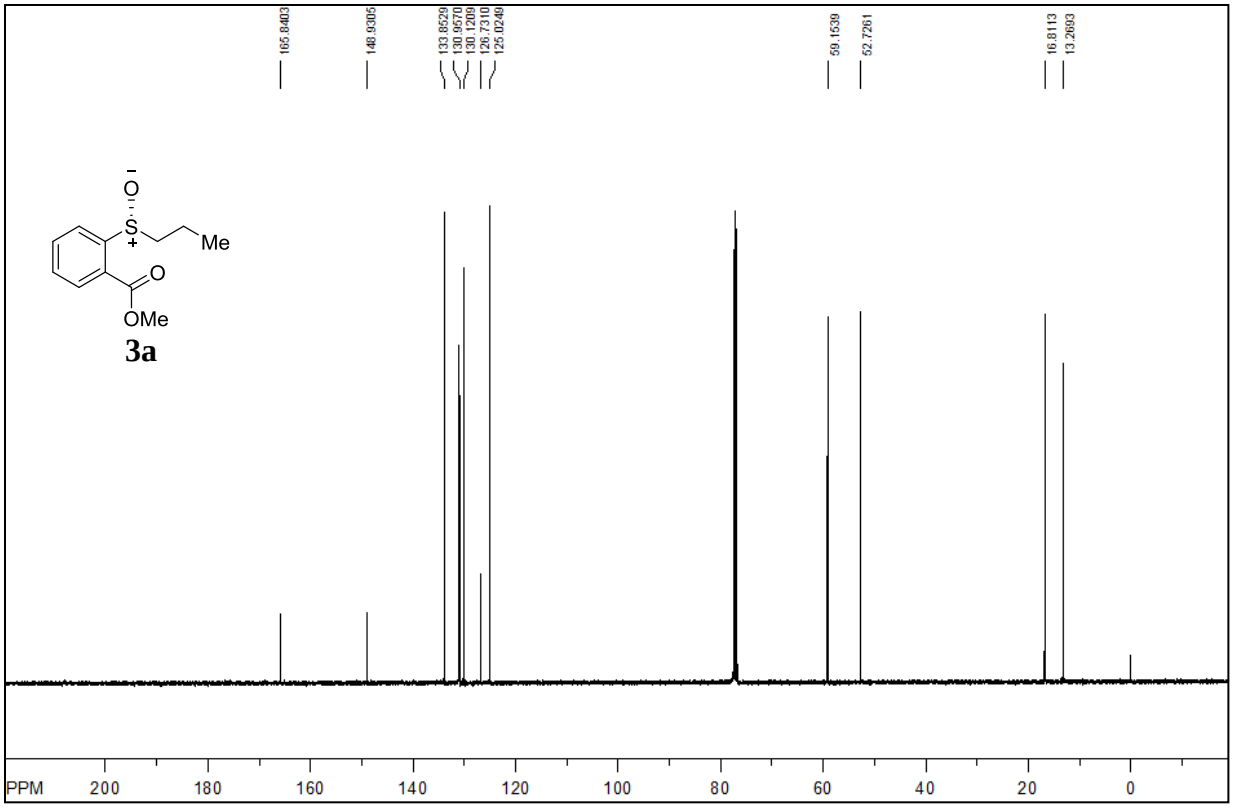
1f

^{19}F NMR

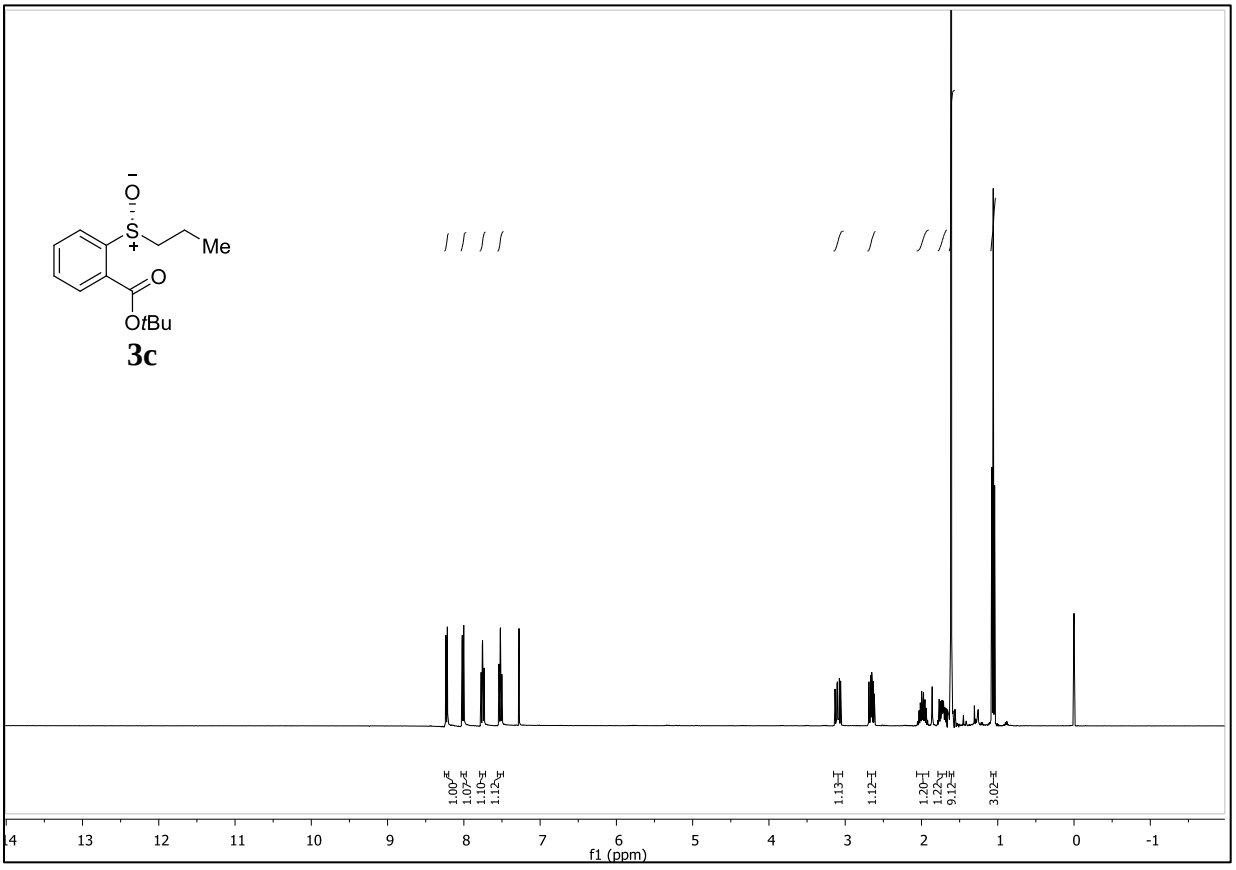


3a

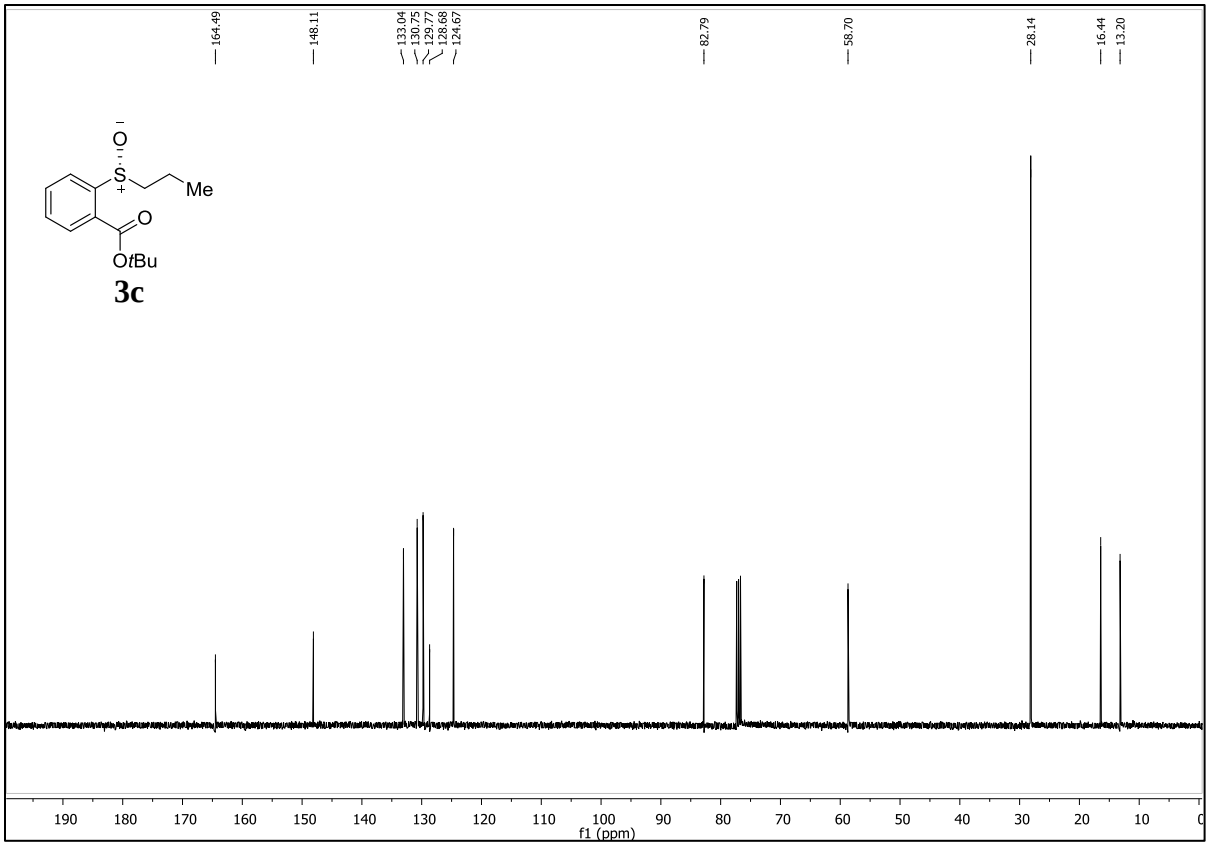
^{19}F NMR

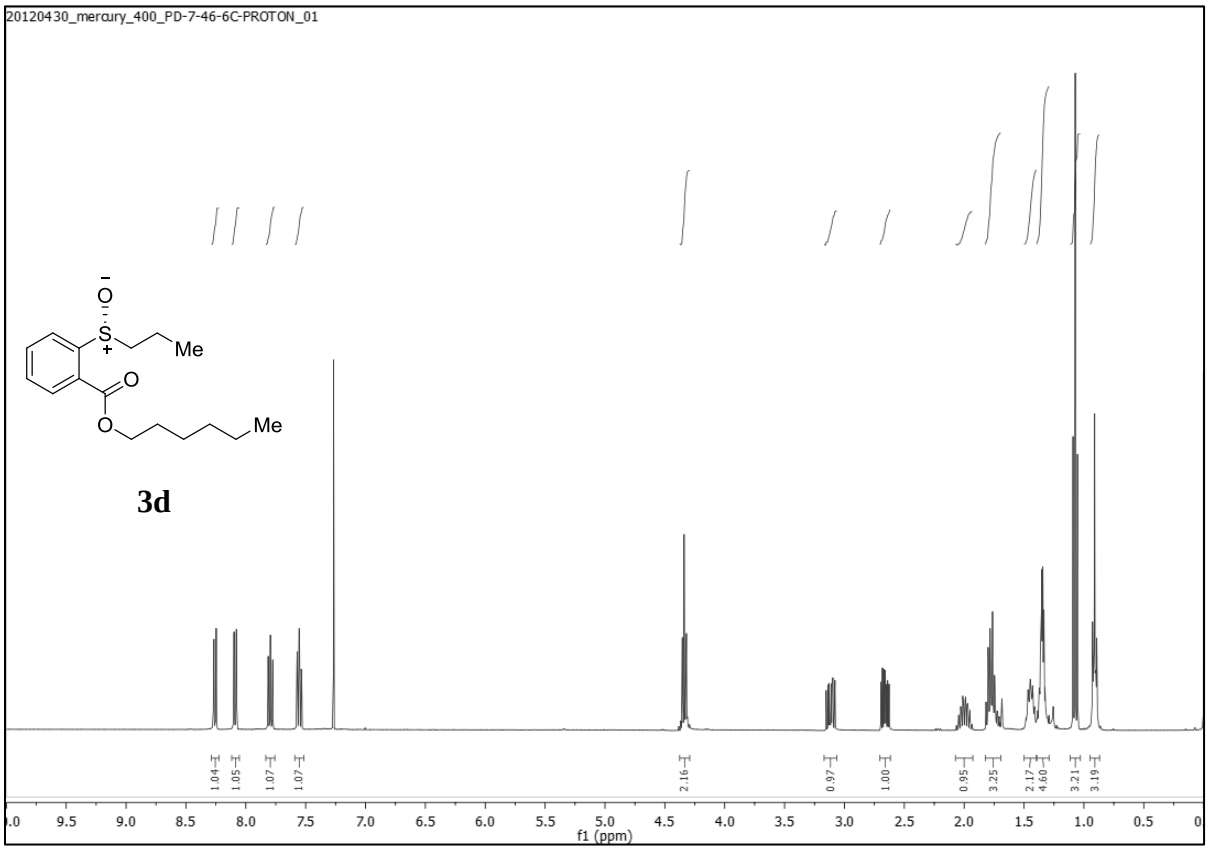

165.8403
148.9305
133.8529
130.9570
130.1209
126.7310
125.0249
59.1539
52.7261
16.8113
13.2693
O
S
Me
O
OMe
PPM
200
180
160
140
120
100
80
60
40
20
0

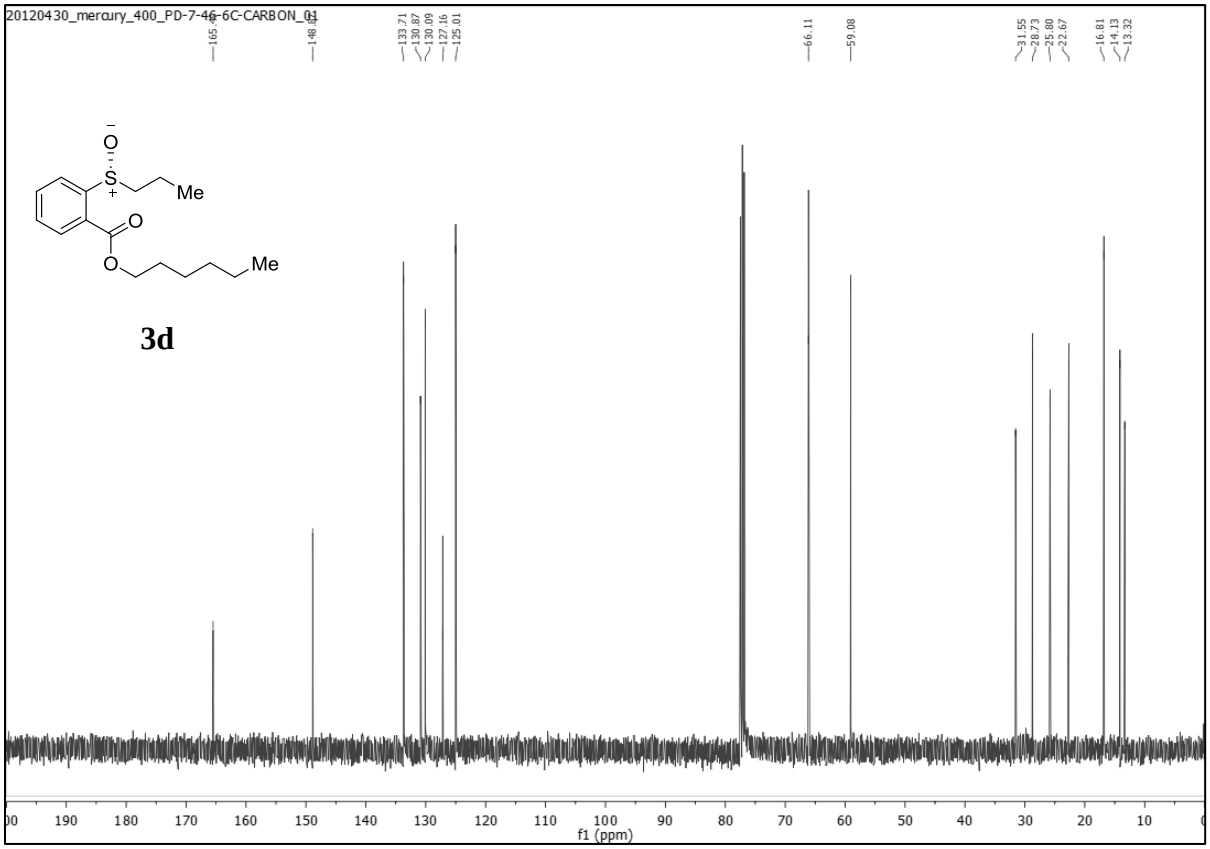
3a


O
S
Me
O
OtBu
1.00
1.07
1.10
1.12
1.13
1.12
1.20
1.22
9.12
3.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

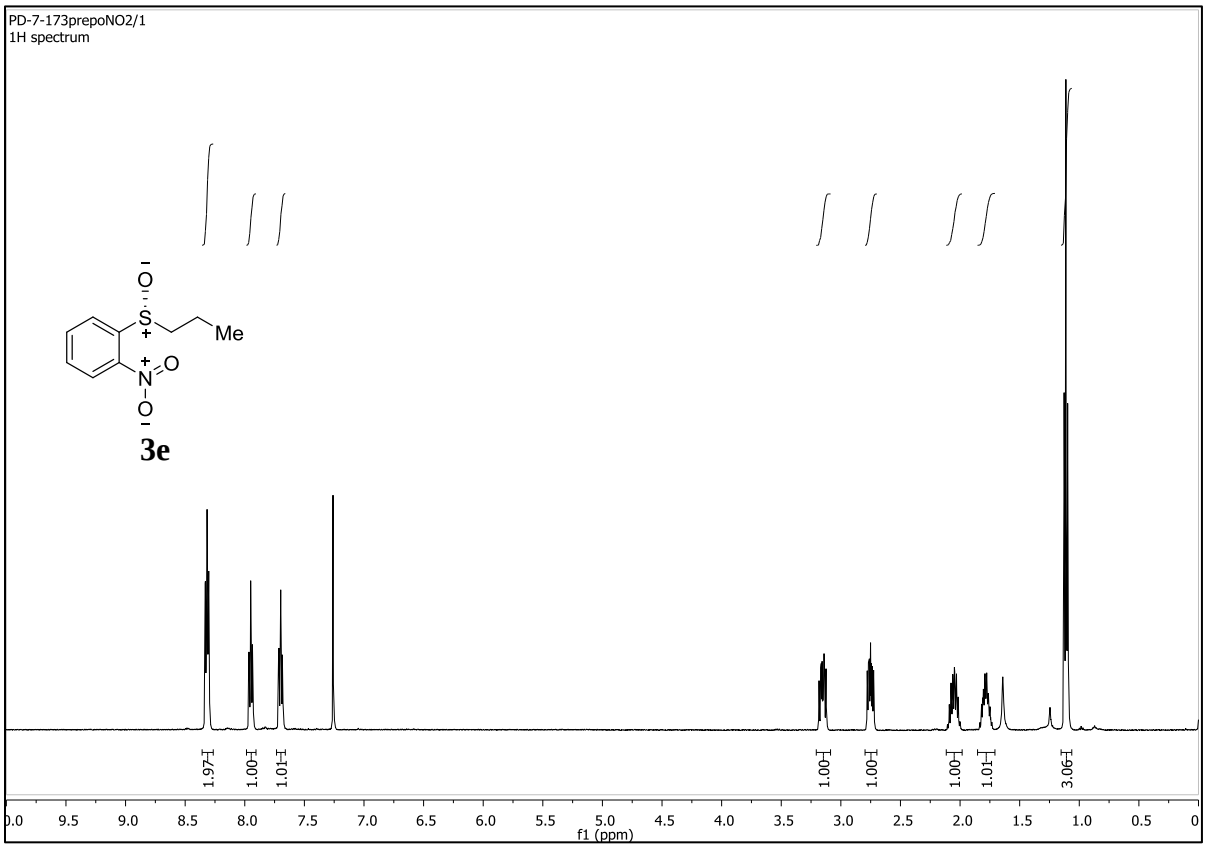
3c


164.49
148.11
133.04
130.75
129.77
128.68
124.67
82.79
58.70
28.14
16.44
13.20
Me
O
OtBu
3c
f1 (ppm)

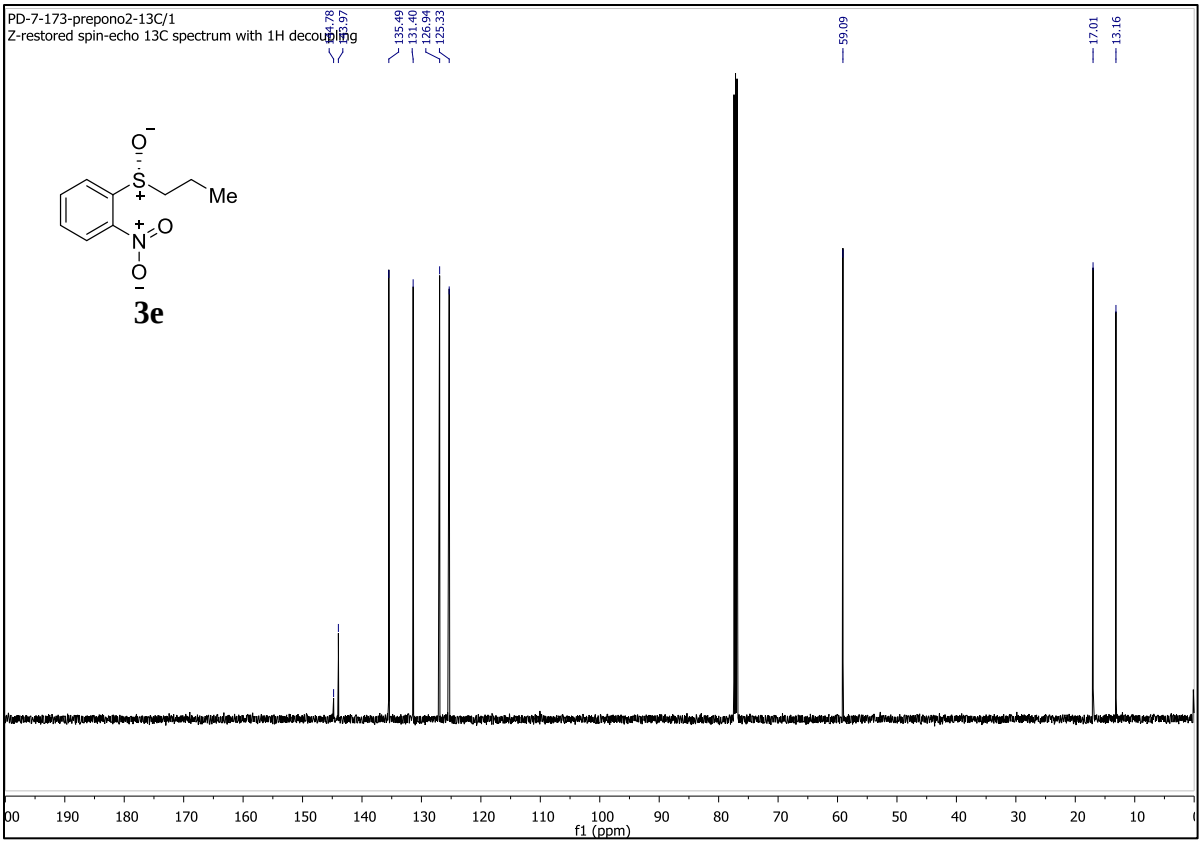

20120430_mercury_400_PD-7-46-6C-PROTON_01
Me
O
Me
3d
1.04
1.05
1.07
1.07
2.16
0.97
1.00
0.95
3.25
2.17
4.60
3.21
3.19
f1 (ppm)

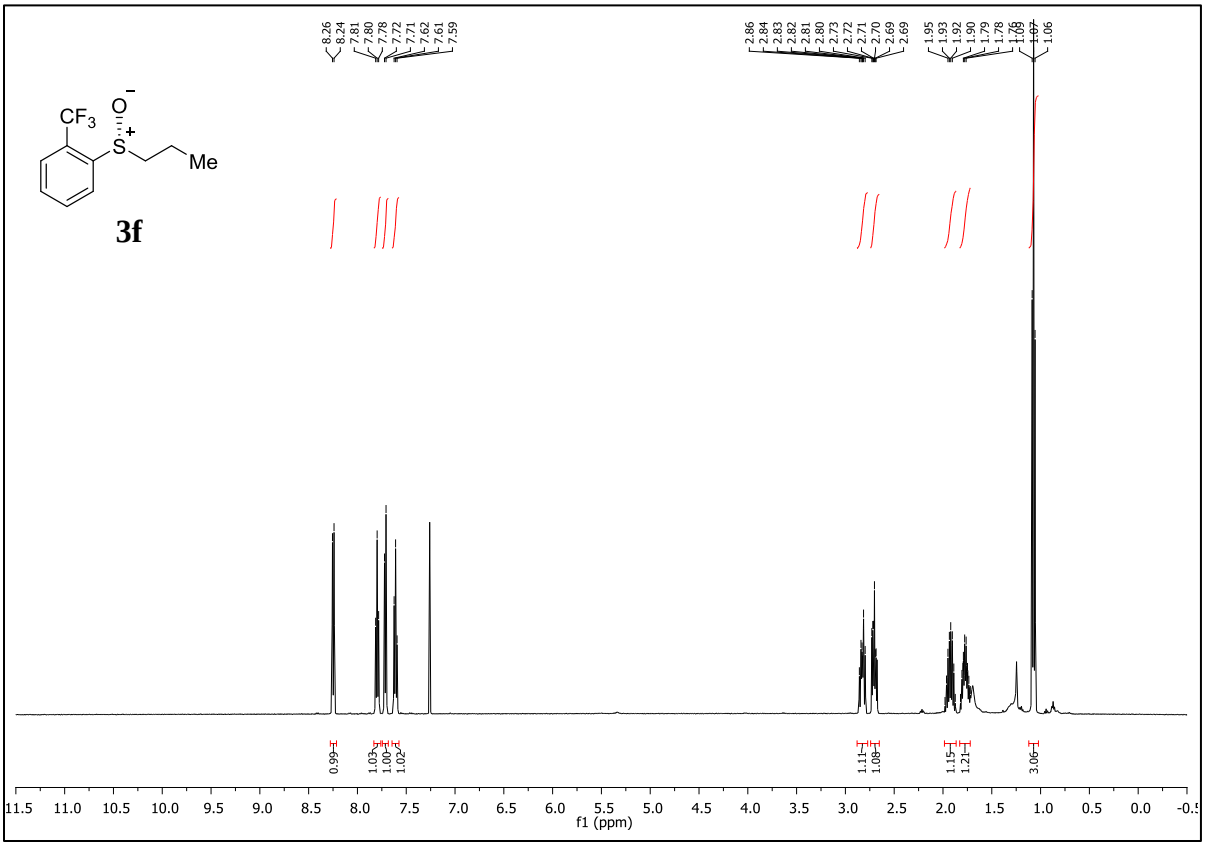

20120430_mercury_400_PD-7-46-6C-CARBON_01
165.58
148.83
133.71
130.87
130.09
127.16
125.01
66.11
59.08
31.55
28.73
25.80
22.67
16.81
14.13
13.32
Me
Me
f1 (ppm)

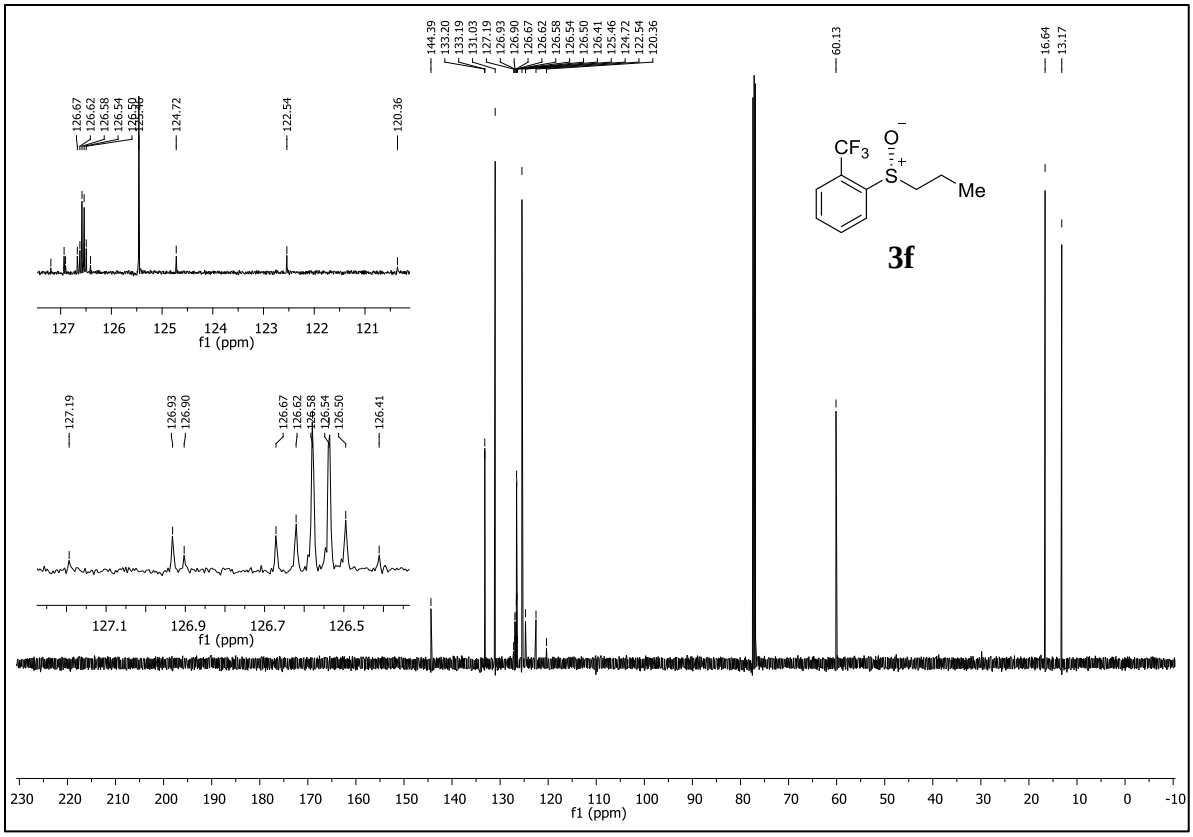
3d

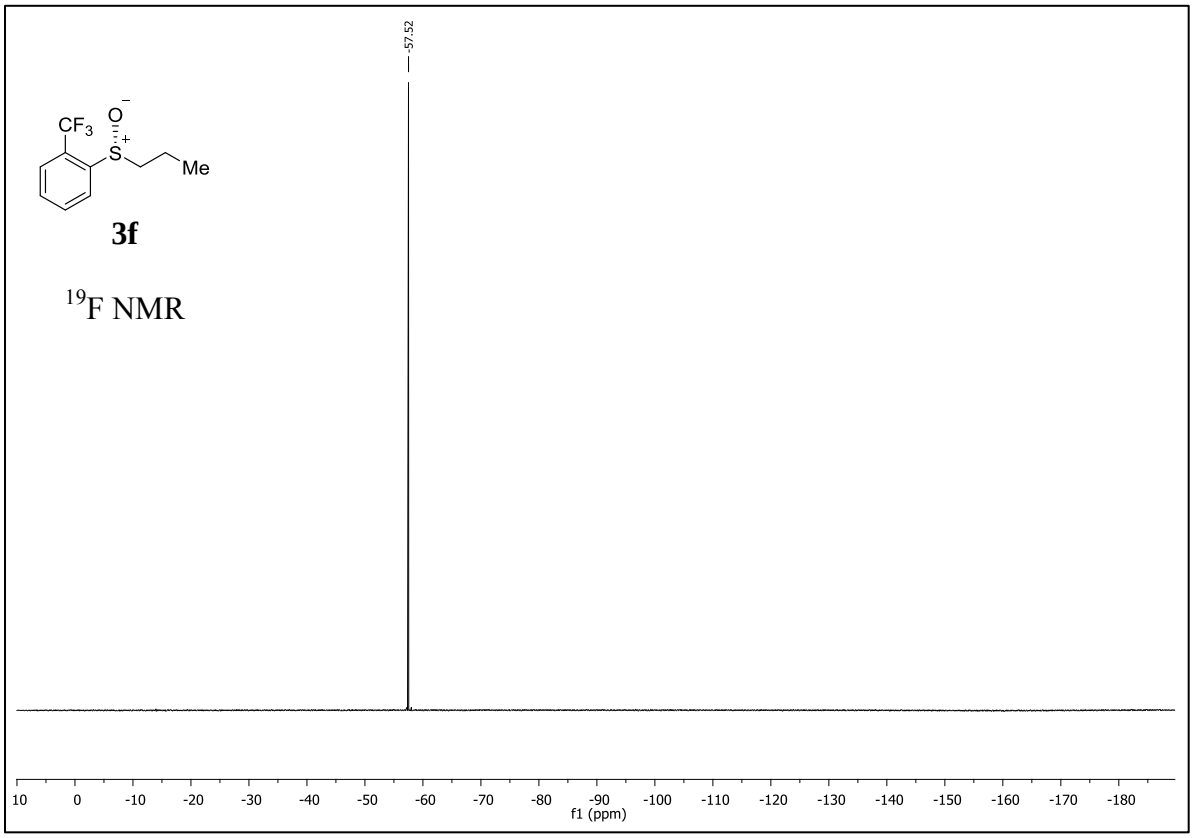

PD-7-173prepoNO2/1
1H spectrum
Me
1.97
1.00
1.01
1.00
1.00
1.00
1.01
3.06
f1 (ppm)

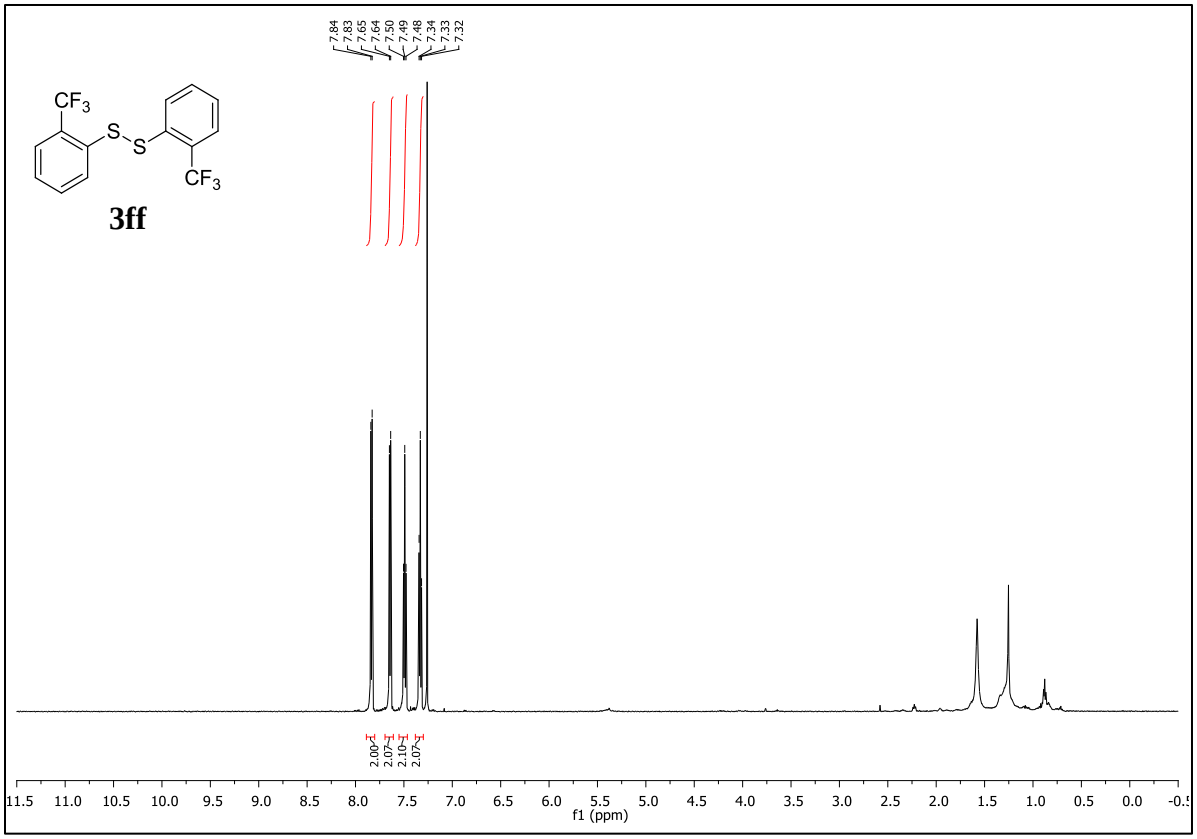
3e

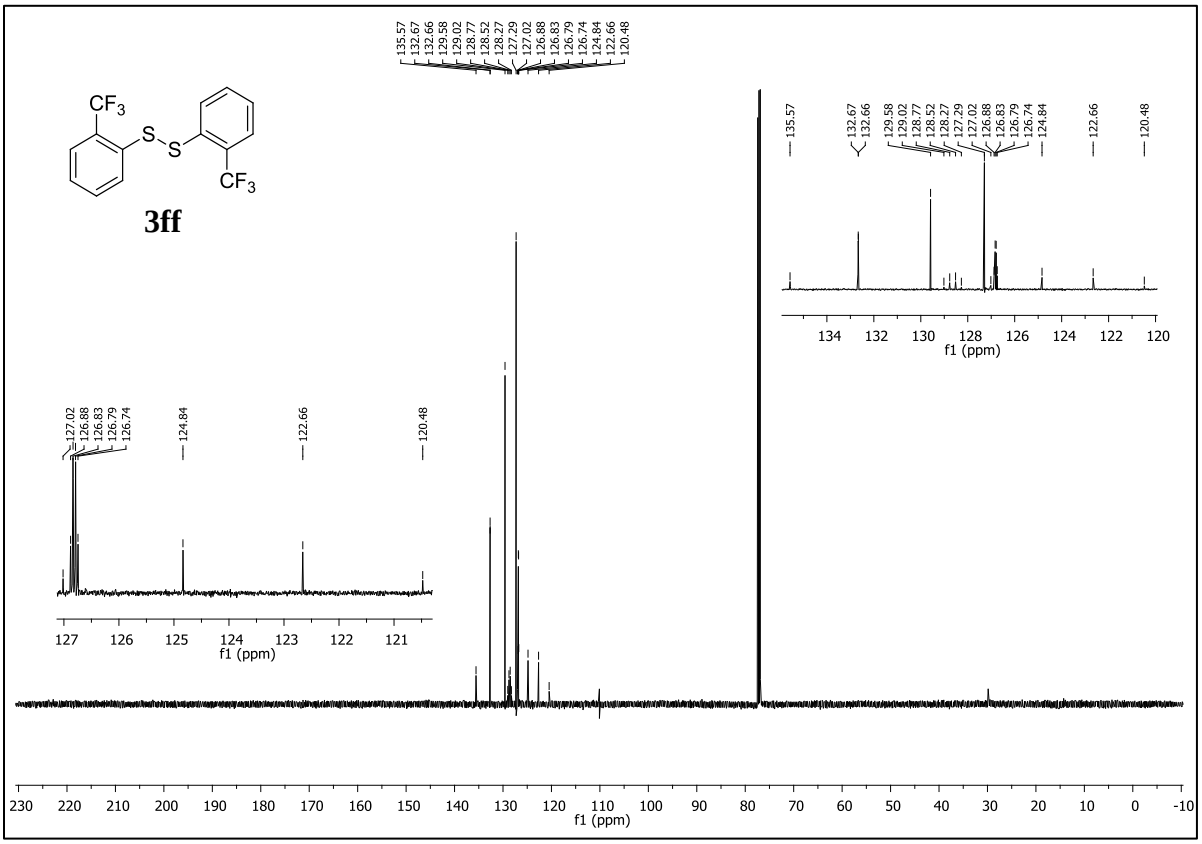

PD-7-173-prepono2-13C/1
Z-restored spin-echo 13C spectrum with 1H decoupling
144.78
143.97
135.49
131.40
126.94
125.33
59.09
17.01
13.16
Me
3e
f1 (ppm)

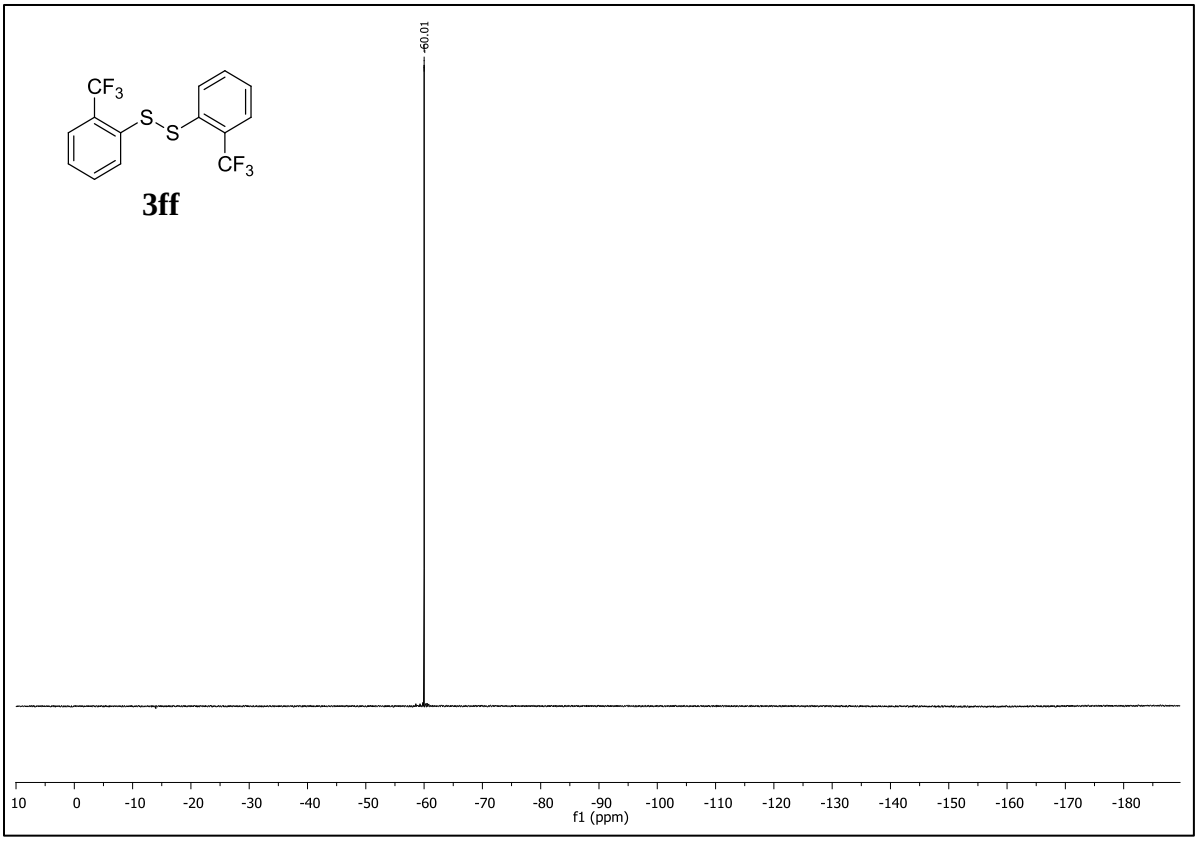

8.26
8.24
7.81
7.80
7.78
7.72
7.71
7.62
7.61
7.59
2.86
2.84
2.83
2.82
2.81
2.80
2.73
2.72
2.71
2.70
2.69
2.69
1.95
1.93
1.92
1.90
1.79
1.78
1.06
CF3
Me
3f
0.99
1.03
1.00
1.02
1.11
1.08
1.15
1.21
3.06
f1 (ppm)


144.39
133.20
133.19
131.03
127.19
126.93
126.90
126.67
126.62
126.58
126.54
126.50
126.41
125.46
124.72
122.54
120.36
60.13
16.64
13.17
CF3
O
S
Me
3f
f1 (ppm)


-57.52
CF3
O
S
Me
3f
19F NMR
f1 (ppm)

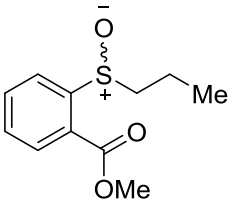

7.84
7.83
7.65
7.64
7.50
7.49
7.48
7.34
7.33
7.32
CF3
S
S
CF3
3ff
2.00
2.07
2.10
2.07
f1 (ppm)


135.57
132.67
132.66
129.58
129.02
128.77
128.52
128.27
127.29
127.02
126.88
126.83
126.79
126.74
124.84
122.66
120.48
CF3
S
S
CF3
3ff
f1 (ppm)

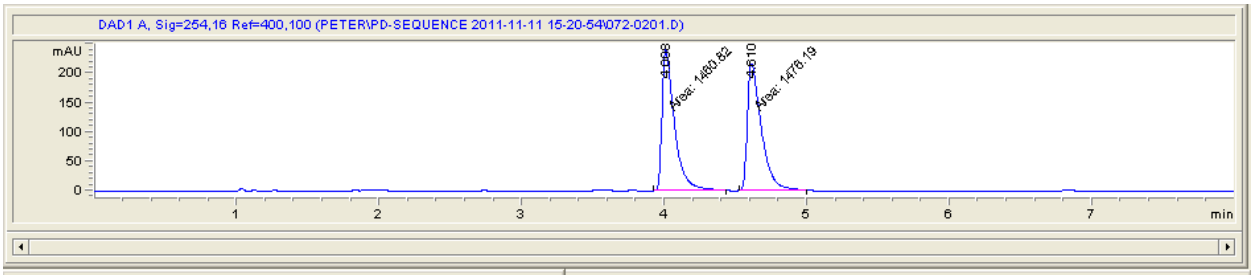

-60.01
CF3
S
S
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

3ff

8. Chiral SFC Chromatograms

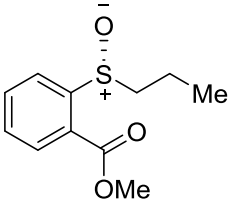


(±)-3a

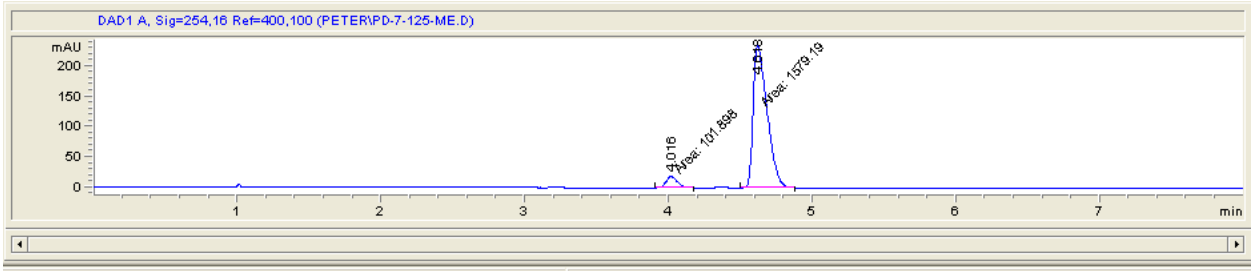


File Information	
LC-File	072-0201.D
File Path	C:\CHEM32\1\DATA\PETER\PD-SEQUENCE 2011-11-11 15-2
Date	11-Nov-11, 15:31:25
Sample	PD-6-103
Sample Info	

#	Time	Area	Height	Width	Area%	Symmetry
1	4.008	1460.8	239.8	0.1015	49.738	0.411
2	4.61	1476.2	216.5	0.1136	50.262	0.413

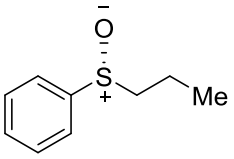


(+)-3a

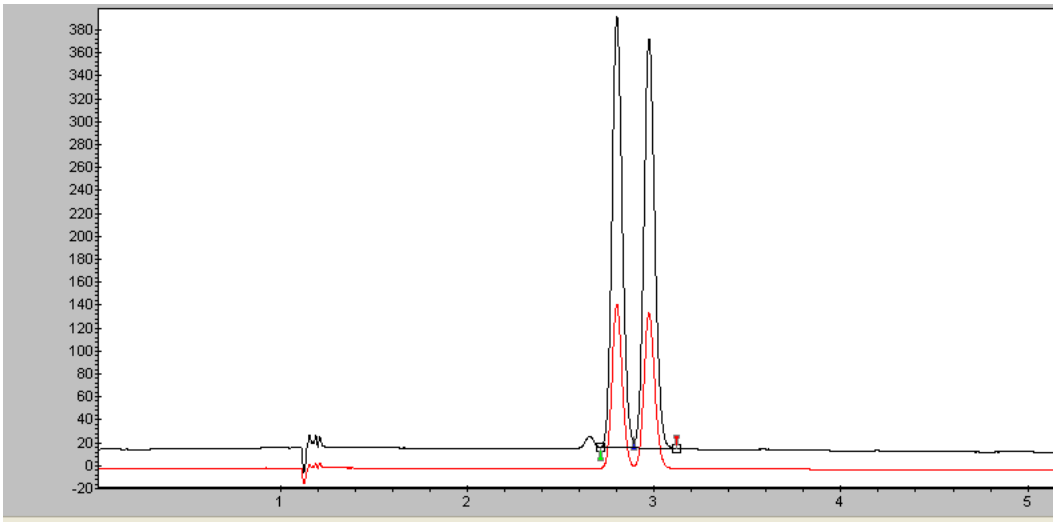


File Information	
LC-File	PD-7-125-ME.D
File Path	C:\CHEM32\1\DATA\PETER\
Date	17-Jul-12, 17:56:38
Sample	PD-7-125-Me
Sample Info	IA 6% 8 min 3ml/min
Barcode	

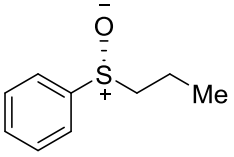
#	Time	Area	Height	Width	Area%	Symmetry
1	4.016	101.9	18.4	0.0924	6.061	0.775
2	4.618	1579.2	234.2	0.1124	93.939	0.466



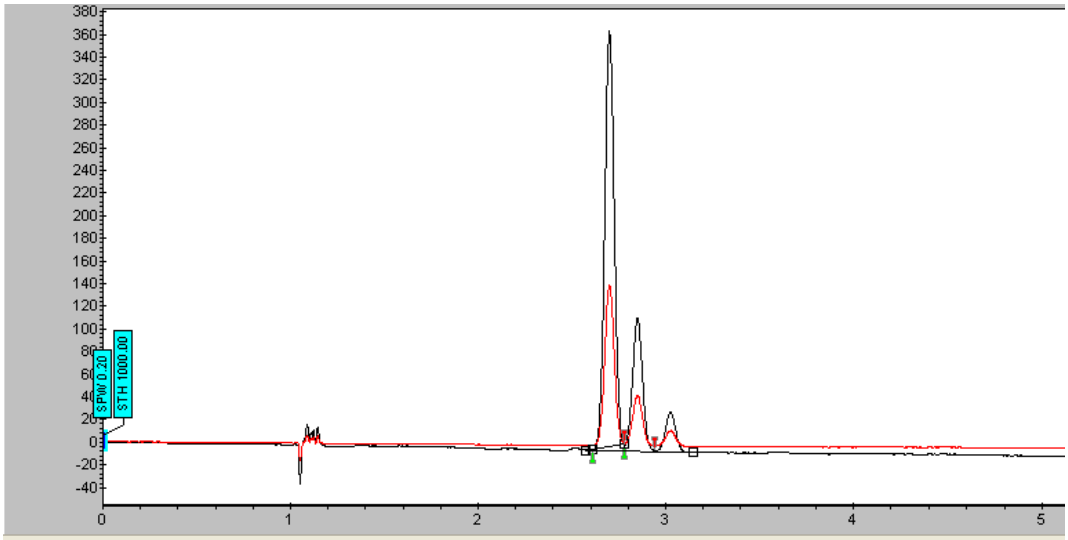
(±)-3b



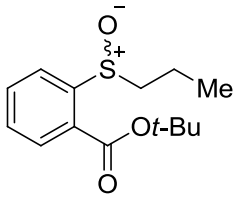
#	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	UNKNOWN	2.71	2.80	2.89	0.00	49.94	376.5	24.1	49.942
2	UNKNOWN	2.89	2.97	3.12	0.00	50.06	356.6	24.1	50.058
Total						100.00	733.1	48.2	100.000



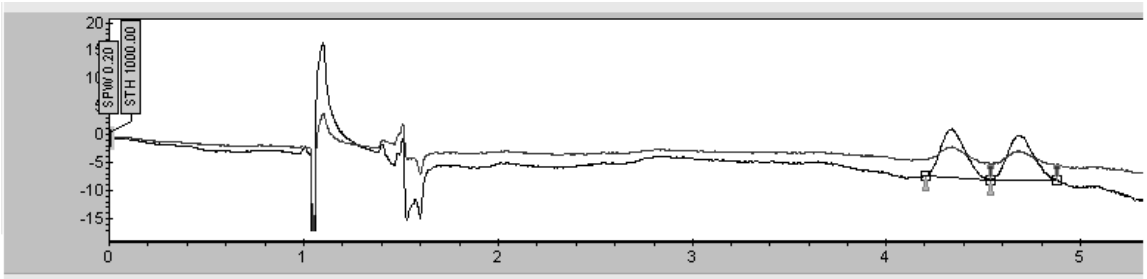
(+)-3b



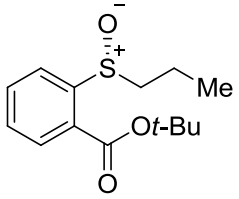
#	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
2	UNKNOWN	2.61	2.70	2.77	0.00	74.64	366.7	21.6	74.644
1	UNKNOWN	2.78	2.85	2.94	0.00	25.36	117.4	7.3	25.356
Total						100.00	484.1	29.0	100.000



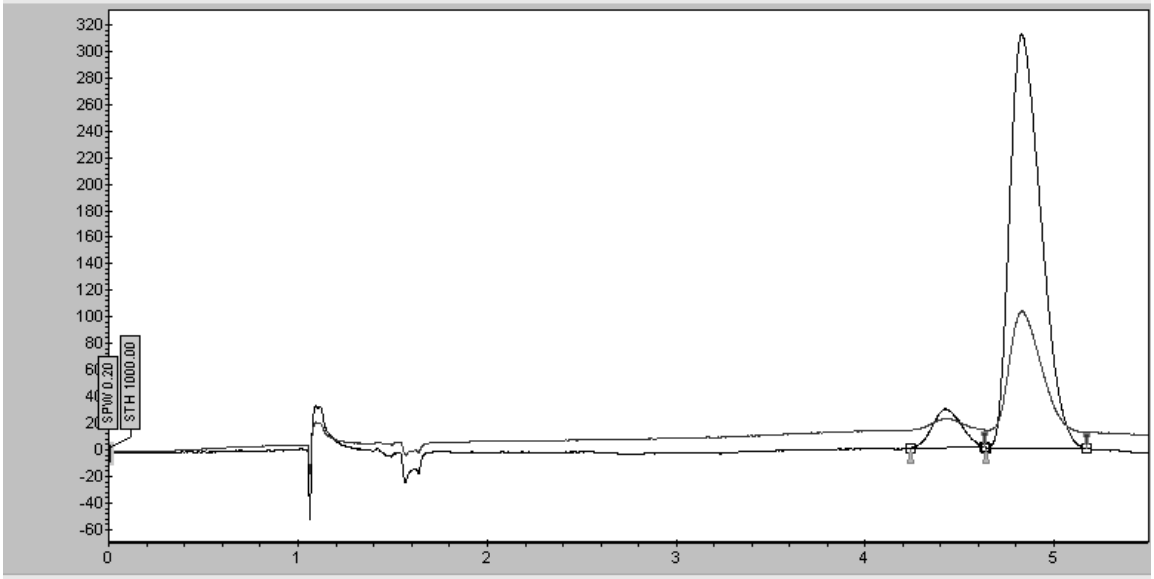
(±)-3c



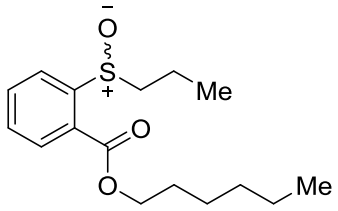
#	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	UNKNOWN	4.20	4.34	4.53	0.00	50.57	8.7	1.3	50.574
2	UNKNOWN	4.53	4.68	4.88	0.00	49.43	8.0	1.2	49.426
Total						100.00	16.7	2.5	100.000



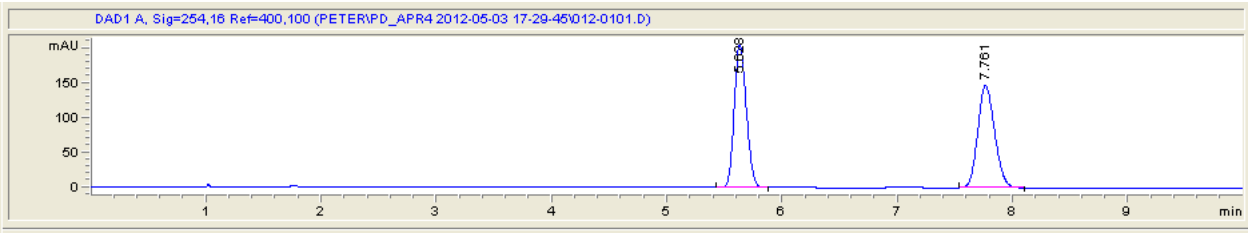
(+)-3c



#	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
2	UNKNOWN	4.24	4.43	4.63	0.00	7.89	29.0	5.1	7.886
1	UNKNOWN	4.64	4.83	5.17	0.00	92.11	311.3	59.9	92.114
Total						100.00	340.3	65.0	100.000

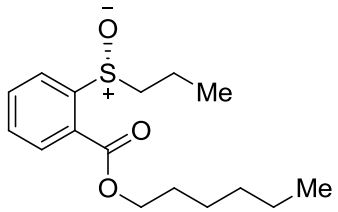


(±)-3d

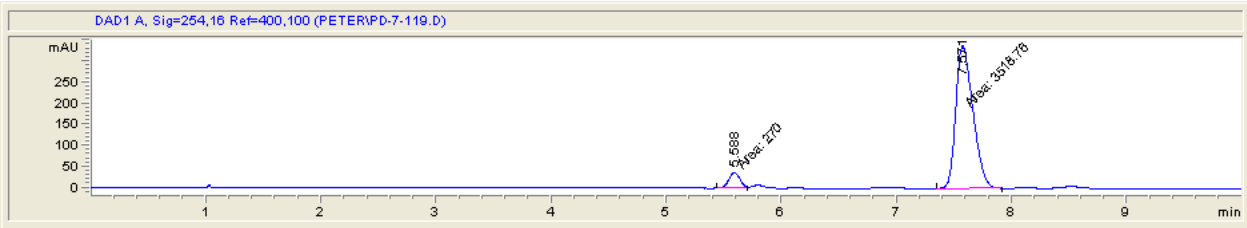


File Information	
LC-File	012-0101.D
File Path	C:\CHEM32\1\DATA\PETER\PD_APR4 2012-05-03 17-29-45\
Date	03-May-12, 17:30:25
Sample	PD-7-46-C6rac

#	Time	Area	Height	Width	Area%	Symmetry
1	5.628	1489.7	205.7	0.1125	49.942	0.782
2	7.761	1493.2	147	0.1585	50.058	0.806

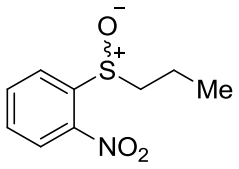


(+)-3d



File Information	
LC-File	PD-7-119.D
File Path	C:\CHEM32\1\DATA\PETER\
Date	03-Jul-12, 15:37:07
Sample	PD-7-119
Sample Info	IC 10% MeOH, 3ml/min, 10 min

#	Time	Area	Height	Width	Area%	Symmetry
1	5.588	270	37.6	0.1198	7.126	0.959
2	7.571	3518.8	338.1	0.1734	92.874	0.637



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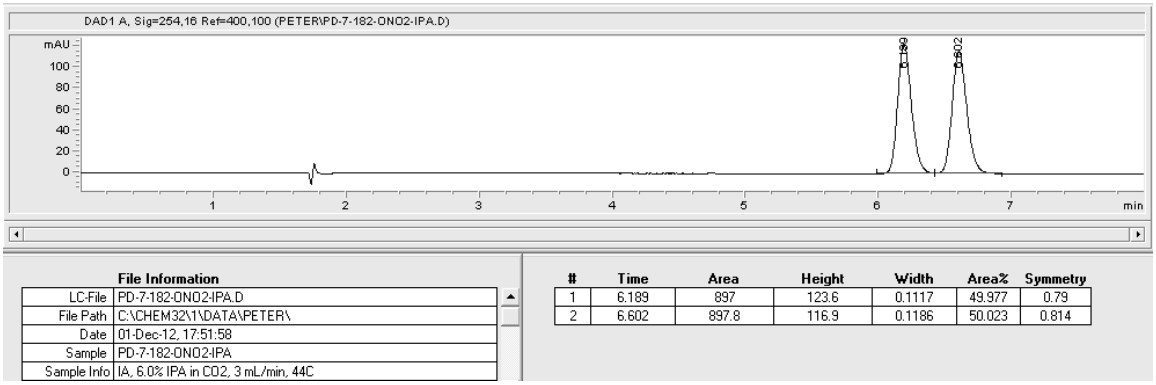
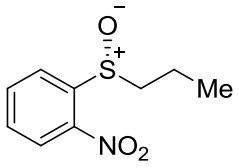


File Information	
LC-File	PD-7-182-ONO2-IPA.D
File Path	C:\CHEM32\1\DATA\PETER\
Date	01-Dec-12, 17:51:58
Sample	PD-7-182-ONO2-IPA
Sample Info	IA, 6.0% IPA in CO2, 3 mL/min, 44C

#	Time	Area	Height	Width	Area%	Symmetry
1	6.189	897	123.6	0.1117	49.977	0.79
2	6.602	897.8	116.9	0.1186	50.023	0.814



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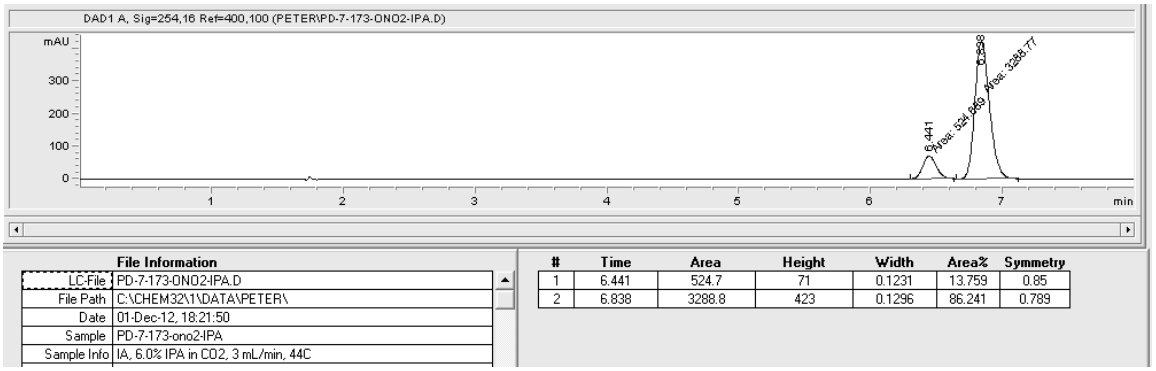
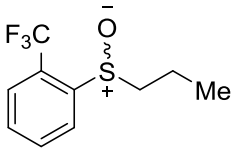
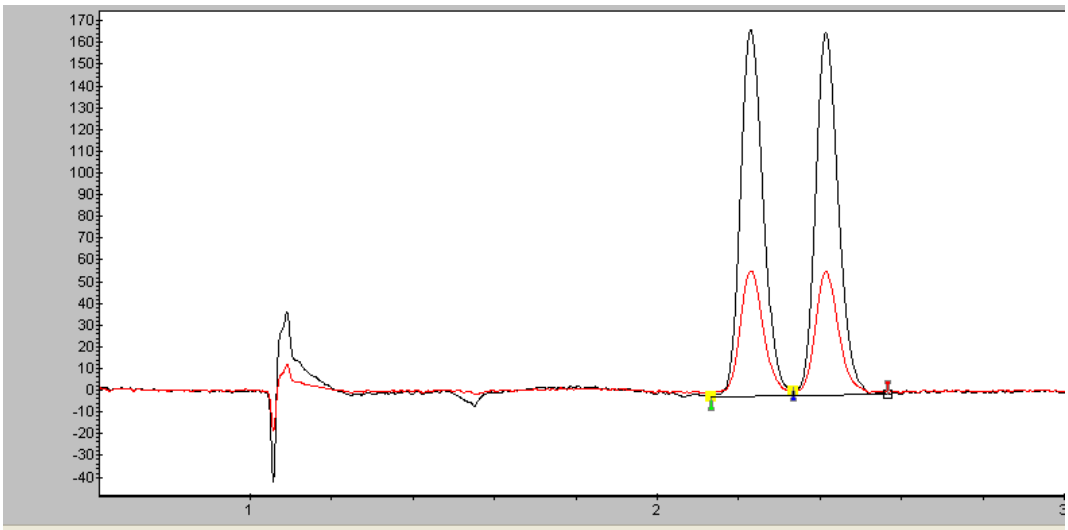


File Information	
LC-File	PD-7-173-ONO2-IPA.D
File Path	C:\CHEM32\1\DATA\PETER\
Date	01-Dec-12, 18:21:50
Sample	PD-7-173-ono2-IPA
Sample Info	IA, 6.0% IPA in CO2, 3 mL/min, 44C

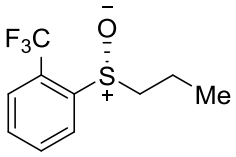
#	Time	Area	Height	Width	Area%	Symmetry
1	6.441	524.7	71	0.1231	13.759	0.85
2	6.838	3288.8	423	0.1296	86.241	0.789



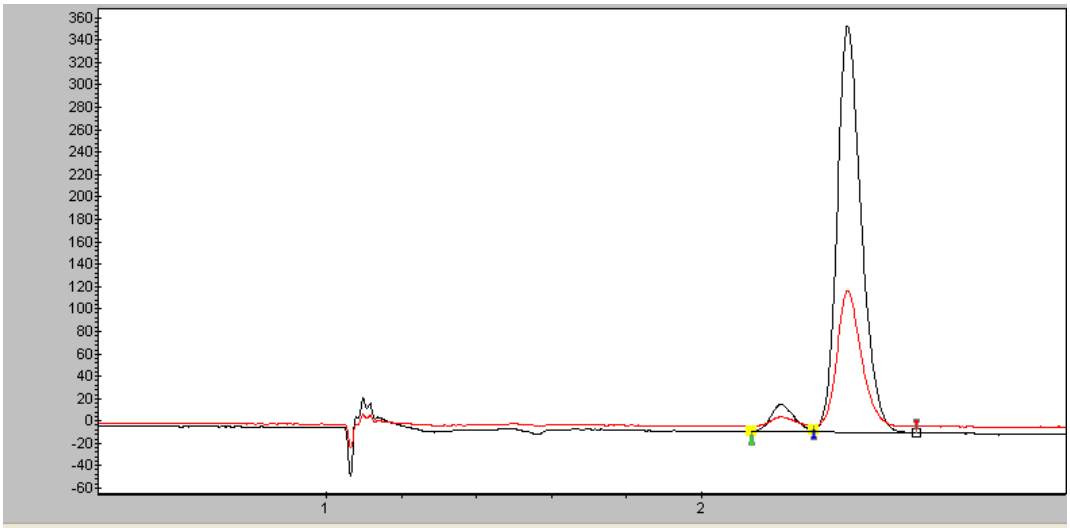
(±)-3f



#	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	UNKNOWN	2.13	2.23	2.33	0.00	49.97	168.8	10.9	49.974
2	UNKNOWN	2.33	2.42	2.57	0.00	50.03	167.1	11.0	50.026
Total						100.00	335.9	21.9	100.000



(±)-3f



#	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	UNKNOWN	2.14	2.21	2.30	0.00	6.10	24.2	1.8	6.097
2	UNKNOWN	2.30	2.39	2.57	0.00	93.90	362.8	27.0	93.903
Total						100.00	386.9	28.8	100.000