Thiophosphonothioates from Oxiranes Supporting Information

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Table of Contents

Materials and Methods

Solvents

The solvents were dried by passing them through drying columns packed with 3 Å molecular sieves (Grubbs apparatus).[1] Alternatively, solvents were dried by stirring with calcium hydride at room temperature overnight, followed by distillation at the corresponding boiling point. Solvents were degassed through five freeze-pump-thaw cycles using liquid nitrogen or dry ice depending on their freezing point.

NMR spectroscopy

The NMR spectra were recorded on Bruker instruments at Larmor frequency of 400 or 500 MHz for proton nuclei, 126 MHz for carbon, and 202 MHz for phosphorus in the indicated solvent.
All deuterated solvents were obtained from Cambridge Isotope Laboratories. The spectra were set to the reference value of the residual proton peak of the solvent. Peak multiplicity is abbreviated as follows: s = singlet, d = doublet, t = triplet, q= quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, bs = broad singlet. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments.

Infrared spectroscopy

Fourier-transform infrared (FT-IR) spectra were recorded using a Shimadzu IRAnity-1S FTIR spectrometer with a wavenumber range from 370 to 4700 cm^{-1} with a standard detector and using 40 scans.

Commercially acquired compounds

Anisole (Oakwood Chemicals), phosphorus(V) sulfide (Oakwood Chemicals), styrene oxide (Oakwood Chemicals), caryophyllene oxide (Sigma Aldrich).

Synthesis

Lawesson's Reagent

Phosphorus pentasulfide (1 g, 4.5 mmol, 1 equiv) was charged to a round-bottom flask along with a magnetic stir bar. Anisole (4.9 mL, 45 mmol, 10 equiv) was then added to the flask using a 1-mL micropipette, portion-wise. The mixture was refluxed at 160 ºC, by heating via a hot plate, and agitated with magnetic stirring for three hours before being allowed to cool to room temperature. Upon cooling, white solid precipitated. Further precipitation was induced by submerging the round-bottom flask in an ice-water bath for an additional 15 minutes. The resultant solid was

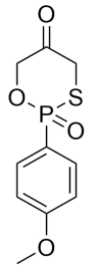
vacuum filtered and washed several times with a 1:1 mixture of diethylether and dichloromethane at room temperature. 1.17 g of a lustrous off-white solid was obtained, representing a 64% yield. A melting point of 224 ºC was obtained using an SRS DigiMelt MPA160 melting point apparatus.

Thiophosphonothioates/Phosphonothioates (TPT/PT)

General procedure

A half-molar equivalent of Lawesson's reagent (LR) in its dimeric form is added to a round-bottom flask along with a magnetic stir bar. Following this, three molar equivalents (unless otherwise stated) of the corresponding epoxide are added to the flask. Dry, degassed xylene is then added to the flask to achieve a concentration of 100 mM (unless otherwise stated) with respect to Lawesson's reagent. The reactants are stirred in heated xylene at 100-145 ºC (the latter is refluxing temperature and requires a condenser) for one to three hours. The mixture is allowed to cool to room temperature before solvent is removed by rotary evaporation under reduced pressure. The crude product is then purified by column chromatography on silica gel using an ethyl acetate/hexane solvent system.

PT-1



Procedure

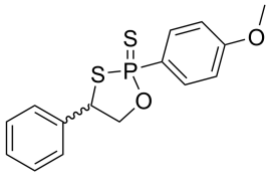
141 mg (348.62 µmol, 0.5 equiv) of LR was charged to a round-bottom flask along with 6.9 mL of xylenes. 250 µL of 3-oxetanone (4.27 mmol, 6.12 equiv) was then added to the flask using a micropipette. The mixture was refluxed at 145 ºC for three hours with stirring via a hotplate. After three hours of heating, the reaction mixture was observed to have turned black. Solvent was removed via rotary evaporation yielding a sulfurous smelling yellow oil. The crude product was purified via silica gel column chromatography using a slow gradient DCM/methanol solvent system (1% increase in methanol every 100 mL). The product eluted as 7.7 mg of colorless oil (4% yield) at 7% methanol concentration. An m/z of 259 was observed through atmospheric solids analysis probing of the pure fractions.

Spectra

^{1}H NMR (500 MHz, CDCl3) δ 7.85 – 7.76 (m, 2H), 7.06 – 6.98 (m, 2H), 4.89 (ddd, J = 17.1, 13.4, 1.1 Hz, 2H), 4.61 (ddd, J = 17.1, 13.2, 1.1 Hz, 2H), 3.88 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, CDCl3) δ 201.57 (d, J = 6.4 Hz), 164.10 (d, J = 3.5 Hz), 134.19 (d, J = 12.1 Hz), 116.76 (d, J = 198.7 Hz), 114.67 (d, J = 16.3 Hz), 70.54, 70.49, 55.65.
^{31}P NMR (202 MHz, CDCl3) δ 18.56 (p, J = 13.1 Hz).

TPT-2



Procedure

200 mg LR (494 µmol, 0.5 equiv) was added to a 20 mL scintillation vial along with a magnetic stir bar. 1.98 mL xylene (500 mM) was added to the vial. Then, 226.4 µL styrene oxide (1.98 mmol, 2 equiv) was added to the vial via micropipette. The vial was sealed, and the lid was wrapped in Teflon tape. The reaction was heated at 100 ºC for 50 mins, dissolution of Lawesson's reagent was noticed within 5 mins of placing the reaction on the hot plate. After 50 mins, the reaction was judged complete by TLC analysis (20% Ethyl Acetate/80% Hexanes). The solvent was removed by rotary evaporation giving the crude product as a yellow oil. The crude was purified by flash chromatography on a 12-g flash column using a slow gradient from 0% to 10% ethyl acetate in hexanes solvent system. Once 10% ethyl acetate was reached, the solvent system was kept isocratic. The product eluted early during the isocratic portion as 64.7 mg (20% yield) of colorless oil. 20.1 mg of this product was able to be isolated as a single isomer while the remaining 44.6 mg contained both isomers.

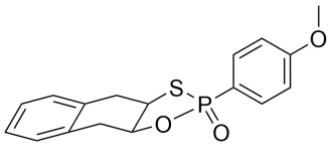
Spectra

***cis*-TPT-2**
^{1}H NMR (500 MHz, CDCl3) δ 8.05 – 7.95 (m, 2H), 7.47 – 7.32 (m, 5H), 7.03 – 6.94 (m, 2H), 5.31 (ddd, J = 8.0, 5.3, 4.4 Hz, 1H), 4.92 – 4.81 (m, 1H), 4.47 (ddd, J = 14.0, 10.0, 8.1 Hz, 1H), 3.87 (s, 3H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, CDCl3) δ 163.43 (d, J = 3.0 Hz), 135.58 (d, J = 5.4 Hz), 133.99 (d, J = 15.3 Hz), 129.29, 129.01, 128.03, 126.50 (d, J = 117.2 Hz), 114.06 (d, J = 16.4 Hz), 76.21 (d, J = 4.5 Hz), 56.88 (d, J = 2.5 Hz), 55.68.
^{31}P NMR (202 MHz, CDCl3) δ 109.40 (p, J = 16.6 Hz)**.**

Mixture of *cis*- and *trans*-TPT-2
^{1}H NMR (500 MHz, CDCl3) δ 8.05 – 7.95 (m, 2H), 7.55 – 7.33 (m, 5H), 7.04 – 6.94 (m, 2H), 5.31 (ddd, J = 8.0, 5.2, 4.4 Hz, 0H), 5.15 (dd, J = 10.7, 5.5 Hz, 0H), 4.99 – 4.79 (m, 1H), 4.77 – 4.64 (m, 0H), 4.56 (ddd, J = 10.7, 10.0, 4.5 Hz, 0H), 4.47 (ddd, J = 13.9, 10.0, 8.0 Hz, 1H), 3.88 (d, J = 4.5 Hz, 3H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, CDCl3) δ 163.42 (t, J = 4.0 Hz), 135.57 (d, J = 5.7 Hz), 133.99 (d, J = 15.3 Hz), 133.78 (d, J = 6.9 Hz), 133.46 (d, J = 14.8 Hz), 129.29, 129.01, 128.51, 128.03,

127.13 (d, J = 122.2 Hz), 126.50 (d, J = 117.1 Hz), 114.07 (dd, J = 16.5, 4.3 Hz), 76.20 (d, J = 4.5 Hz), 75.45 (d, J = 3.7 Hz), 59.05, 56.88 (d, J = 2.5 Hz), 55.68.
IR Characteristic IR vibrations (cm^{-1}): 999 (P-O-C st), 696 (P=S st).

PT-3



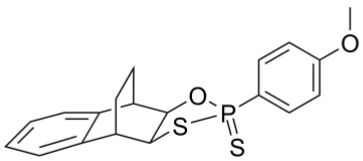
Procedure

90 mg of LR (222.52 µmol, 0.5 equiv) was charged to a round-bottom flask along with a magnetic stir bar. To the flask was added a solution of 195.18 mg of dihydronaphthalene oxide (1.34 mmol, 3 equiv) dissolved in 4.5 mL xylenes (100 mM). The flask was fit with a reflux condenser and set to stir on a hot plate set to 145 ºC for three hours while refluxing. After three hours, solvent was removed via rotary evaporation yielding a sulfurous smelling yellow oil as the crude product. This was purified via flash chromatography on a 12-g silica column using an ethyl acetate/hexanes solvent system set to a stepwise gradient from 0% to 30% ethyl acetate. The product eluted at 30% ethyl acetate and was allowed to dry for several days in a desiccator. After drying, 16.3 mg (11% yield) of white solid was obtained.

Spectra

^{1}H NMR (500 MHz, CDCl3) δ 7.85 – 7.78 (m, 2H), 7.24 – 7.07 (m, 4H), 7.03 – 6.96 (m, 2H), 4.78 (td, J = 10.8, 5.6 Hz, 1H), 4.01 (dddd, J = 11.5, 10.7, 5.7, 0.7 Hz, 1H), 3.87 (s, 3H), 3.53 – 3.39 (m, 1H), 3.34 – 3.09 (m, 3H).
^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 163.47 (d, J = 3.6 Hz), 133.74 (d, J = 12.9 Hz), 132.95, 132.41, 129.87, 128.74, 127.10, 127.06, 123.12 (d, J = 160.8 Hz), 114.26 (d, J = 17.2 Hz), 82.41, 55.50, 54.78, 35.12 (d, J = 8.2 Hz), 34.85 (d, J = 14.1 Hz).
^{31}P NMR (202 MHz, CDCl3) δ 54.29 (t, J = 14.6 Hz).
IR Characteristic IR vibrations (cm^{-1}): 1116 (P=O st), 993 (P-O-C st).

TPT-5



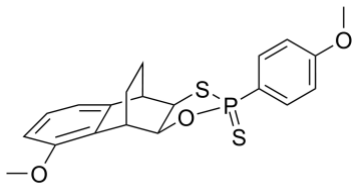
Procedure

192 mg LR (474.72 µmol, 0.5 equiv) was added to a 25 mL round-bottom flask along with a magnetic stir bar. 817 mg EPO-5 (4.75 mmol, 5.0 equiv) was then added to the flask as a solution dissolved in 9.5 mL xylenes (100 mM). The mixture was set to stir on a hotplate set to 145 ºC and allowed to reflux for 3 h. The mixture was allowed to cool to RT before solvent was removed via rotary evaporation. Following solvent evaporation, the crude oil was purified on silica using a 10% ethyl acetate, 90% hexanes solvent system. Solvent was removed from the purified compound using rotary evaporation to give a white crystalline solid in 47.5% yield. This product was crystalized via slow vapor diffusion. The solid was dissolved in a small amount of chloroform in a one-dram vial and placed inside a 20 mL scintillation vial containing 5 mL pentane. After five days, crystals were harvested and analyzed via X-ray diffraction.

Spectra

^{1}H NMR (500 MHz, CDCl3) δ 8.19 – 8.10 (m, 2H), 7.28 – 7.24 (m, 4H), 7.20 (qd, J = 4.8, 2.5 Hz, 1H), 7.07 – 6.98 (m, 2H), 4.87 (ddd, J = 8.7, 3.8, 1.4 Hz, 1H), 4.17 (dq, J = 8.7, 2.3 Hz, 1H), 3.89 (s, 3H), 3.48 (q, J = 3.0 Hz, 1H), 3.15 (q, J = 2.9 Hz, 1H), 2.48 (dddd, J = 12.9, 10.5, 4.9, 2.4 Hz, 1H), 2.28 (ddt, J = 13.6, 10.6, 3.3 Hz, 1H), 1.50 – 1.29 (m, 2H).
^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 163.84 (d, J = 3.5 Hz), 141.96, 139.42, 134.81 (d, J = 15.3 Hz), 127.72, 127.49, 125.69, 124.49, 123.75 (d, J = 118.6 Hz), 114.18 (d, J = 16.4 Hz), 79.43 (d, J = 3.5 Hz), 55.71, 53.67, 39.56 – 39.19 (m), 19.25 (d, J = 15.3 Hz).
^{31}P NMR (202 MHz, CDCl3) δ 108.18 (t, J = 14.9 Hz).
IR Characteristic IR vibrations (cm^{-1}): 987 (P-O-C st), 689 (P=S st)

TPT-6



Procedure

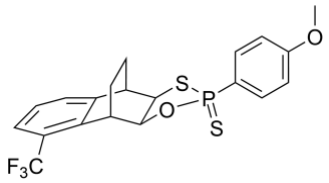
133.0 mg Lawesson’s reagent (328.84 µmol, 0.5 equiv) was added to a round-bottom flask along with a magnetic stir bar. 399.05 mg EPO-6 (1.97 mmol, 3.0 equiv) was dissolved in 6.58 mL xylenes (100 mM). The xylene solution was then added to the round-bottom flask containing LR. The mixture was refluxed at 145 ºC for three hours before being allowed to cool to room temperature. Solvent was removed via rotary evaporation. Following solvent evaporation, a sulfurous smelling yellow oil was obtained as a crude product. The crude was loaded onto a 12-g silica gel column and purified via an isocratic 10% ethyl acetate, 90% hexanes solvent system. 112.8 mg pure product was obtained in 42% yield as a white solid.

Spectra

^{1}H NMR (500 MHz, CDCl3) δ 8.23 – 8.11 (m, 2H), 7.23 (td, J = 8.0, 1.3 Hz, 1H), 7.11 – 7.00 (m, 2H), 6.90 (d, J = 7.4 Hz, 1H), 6.84 (dt, J = 8.7, 2.0 Hz, 1H), 4.91 – 4.82 (m, 1H), 4.15 (tq, J = 8.7, 2.3 Hz, 1H), 3.89 (s, 3H), 3.84 (d, J = 1.9 Hz, 3H), 3.68 (p, J = 3.3 Hz, 1H), 3.48 (q, J = 3.0 Hz, 1H), 2.48 (dddt, J = 13.2, 10.0, 5.4, 2.7 Hz, 1H), 2.34 – 2.24 (m, 1H), 1.52 – 1.23 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 163.72 (d, J = 3.5 Hz), 154.24, 141.11, 134.76, 134.64, 129.40, 127.93, 123.79 (d, J = 4.6 Hz), 118.01, 114.16, 114.03, 109.63, 79.38 (d, J = 3.5 Hz), 55.65, 55.58, 53.41, 39.39, 39.31, 31.46 (d, J = 3.7 Hz), 19.19, 18.50.
^{31}P NMR (162 MHz, CDCl3) δ 108.57 – 107.76 (m).
IR Characteristic IR signals (cm^{-1}): 975 (P-O-C st), 691 (P=S st)

TPT-7



Procedure

160 mg LR (395 µmol, 0.5 equiv) was charged to a round-bottom flask along with a magnetic stir bar. 508.4 mg of EPO-7 (2.37 mmol, 3 equiv) was dissolved in 7.9 mL of xylene (100 mM) and added to the flask. A condenser was assembled above the flask and then mixture was set to reflux for 3h. After 3 h the crude liquid was kept in the freezer overnight and then removed via rotary evaporation giving a sulfurous smelling yellow oil as the crude product. The product was purified via flash chromatography using a 12-g silica gel column. A slow gradient from 0% to 10% EtOAc in hexanes for 6 column volumes followed by an isocratic hold for the rest of the purification. Solvent was removed via rotary evaporation revealing the product as 111.6 mg of colorless oil (32%).

Spectra

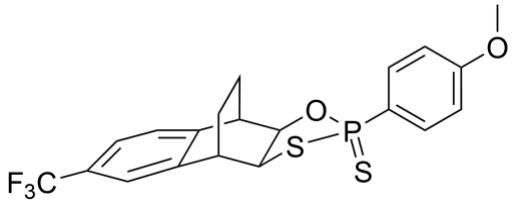
Major Isomer
^{1}H NMR (500 MHz, CDCl3) δ 8.17 – 8.09 (m, 2H), 7.62 – 7.53 (m, 1H), 7.50 – 7.32 (m, 2H), 7.07 – 7.01 (m, 2H), 4.87 (ddd, J = 8.7, 3.8, 1.4 Hz, 1H), 4.17 (dq, J = 8.7, 2.4 Hz, 1H), 3.99 – 3.94 (m, 1H), 3.90 (s, 3H), 3.25 (q, J = 3.1 Hz, 1H), 2.61 – 2.49 (m, 1H), 2.33 (ddq, J = 13.9, 10.5, 3.4 Hz, 1H), 1.50 – 1.29 (m, 2H).
^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 163.95 (d, J = 3.1 Hz), 143.85, 141.37, 134.77 (d, J = 14.8 Hz), 128.21, 127.43, 125.89 (q, J = 30.6 Hz), 124.29 (q, J = 5.3 Hz), 123.89 (d, J = 118.6 Hz), 123.04 (q, J = 273.3 Hz), 114.25 (d, J = 16.4 Hz), 78.46 – 78.33 (m), 55.72, 52.91, 39.27 (d, J = 3.8 Hz), 35.94 (d, J = 11.7 Hz), 18.80, 18.46.

Minor Isomer

^{1}H NMR (500 MHz, CDCl3) δ 8.17 – 8.09 (m, 2H), 7.62 – 7.53 (m, 1H), 7.50 – 7.32 (m, 2H), 7.07 – 7.01 (m, 2H), 4.87 (ddd, J = 8.7, 3.8, 1.4 Hz, 1H), 4.17 (dq, J = 8.7, 2.4 Hz, 1H), 3.90 (s, 3H), 3.61 (s, 0H), 3.58 (q, J = 3.1 Hz, 0H), 2.61 – 2.49 (m, 1H), 2.33 (ddq, J = 13.9, 10.5, 3.4 Hz, 1H), 1.50 – 1.29 (m, 2H).
^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 163.95 (d, J = 3.1 Hz), 140.29, 137.72, 134.91 (d, J = 15.2 Hz), 129.41, 127.21, 127.00 (q, J = 30.6 Hz), 124.48 (t, J = 5.1 Hz), 123.79 (d, J = 118.8 Hz), 123.08 (q, J = 273.3 Hz), 114.25 (d, J = 16.4 Hz), 78.46 – 78.33 (m), 55.72, 52.50, 39.45 (d, J = 11.1 Hz), 35.72, 18.72, 18.41.

Mixture of isomers
^{31}P NMR (202 MHz, CDCl3) δ 108.26 (t, J = 14.0 Hz).
IR Characteristic IR vibrations (cm^{-1}): 970 (P-O-C st), 692 (P=S st)

TPT-8



Procedure

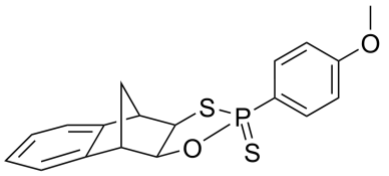
26 mg LR (64.28 μmol, 0.5 equiv) was charged to a round-bottom flask along with a magnetic stir bar. To this flask was added a solution of EPO-8 (92.7 mg, 385 μmol, 3 equiv) in 1.29 mL xylenes (100 mM). The mixture was set to stir on a hot plate and a reflux condenser was inserted into the flask. The hot plate was then set to 145 ºC and the mixture was allowed to reflux for three hours. After three hours, the mixture was allowed to cool to rt, and solvent was removed via rotary evaporation yielding a sulfurous smelling yellow oil as a crude product. The crude product was purified by column chromatography using a 4g silica column to which a gradient 5%-10% ethyl acetate in hexanes solvent system was applied. 17 mg of pure product was isolated as a colorless oil (30%).

Spectra

^{1}H NMR (500 MHz, CDCl3) δ 8.20 – 8.09 (m, 2H), 7.55 (dd, J = 7.6, 2.0 Hz, 1H), 7.48 (d, J = 1.8 Hz, 1H), 7.41 (d, J = 7.7 Hz, 1H), 7.09 – 7.02 (m, 2H), 4.87 (ddt, J = 8.6, 3.9, 2.0 Hz, 1H), 4.15 (dp, J = 9.2, 2.4 Hz, 1H), 3.90 (s, 3H), 3.59 (q, J = 3.1 Hz, 1H), 3.25 (q, J = 2.9 Hz, 1H), 2.54 (dddd, J = 13.0, 10.5, 5.0, 2.3 Hz, 1H), 2.34 (ddt, J = 13.6, 10.6, 3.3 Hz, 1H), 1.48 (ttt, J = 10.7, 3.5, 1.8 Hz, 1H), 1.39 – 1.30 (m, 1H).
^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 163.90 (d, J = 3.2 Hz), 143.40, 142.62, 134.83 (d, J = 15.4 Hz), 130.30 – 129.46 (m), 126.08, 125.30 (q, J = 272.1 Hz), 124.50 (q, J = 3.9 Hz), 123.66 (d, J = 118.5 Hz), 121.41 (q, J = 3.7 Hz), 114.21 (d, J = 17.0 Hz), 78.62 (d, J = 3.2 Hz), 55.73, 53.11, 39.43 – 39.06 (m), 18.97, 18.82.

^{31}P NMR (202 MHz, CDCl3) δ 108.35 (t, J = 15.5 Hz).
IR Characteristic IR vibrations (cm^{-1}): 993 (P-O-C st), 694 (P=S st)**.**

TPT-9



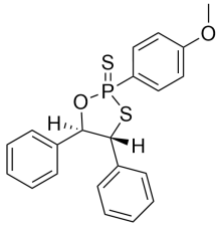
Procedure

225 mg LR (556.31 µmol, 0.5 equiv) was added to a round-bottom flask along with a magnetic stir bar. 528 mg of EPO-9 (3.34 mmol, 3 equiv) as a yellow oil was diluted with 11.13 mL xylenes (100 mM). The oxirane solution was added to the flask containing LR and the mixture was refluxed at 145 °C for three hours before being allowed to cool to room temperature. Solvent was removed via rotary evaporation giving a yellow oil as the crude product. The crude was purified via column chromatography on silica gel using a gradient solvent system. First the column was equilibrated with 50 mL of 5% ethyl acetate, 95% hexanes solution. As fractions eluted, the eluent was gradually replaced with 150 mL of a solution containing 10% ethyl acetate, 90% hexanes. 135.34 mg of product was obtained as an off-white wax (34%).

Spectra

^{1}H NMR (500 MHz, CDCl3) δ 8.17 – 8.06 (m, 2H), 7.29 (dd, J = 5.5, 2.9 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.18 – 7.14 (m, 2H), 7.05 – 6.99 (m, 2H), 4.92 (dt, J = 6.1, 1.0 Hz, 1H), 4.10 (dt, J = 5.9, 2.1 Hz, 1H), 3.88 (s, 3H), 3.67 – 3.63 (m, 1H), 3.43 – 3.40 (m, 1H), 2.63 – 2.56 (m, 1H), 2.17 – 2.11 (m, 1H).
^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 163.87 (d, J = 3.5 Hz), 146.25, 142.46, 134.59 (d, J = 14.9 Hz), 127.62, 127.34, 124.03 (d, J = 117.2 Hz), 123.28, 123.09, 121.83, 114.10 (d, J = 16.3 Hz), 85.51 (d, J = 4.3 Hz), 56.61, 55.68, 49.79 (d, J = 3.1 Hz), 49.54 (d, J = 9.2 Hz), 43.85.
^{31}P NMR (202 MHz, CDCl3) δ 113.25 (t, J = 14.9 Hz).
IR Characteristic IR vibrations (cm^{-1}): 997 (P-O-C st), 692 (P=S st)**.**

TPT-10



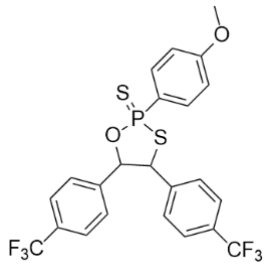
Procedure

50 mg LR (123.62 µmol, 0.5 equiv) and 97 mg stilbene oxide (494.5 µmol, 2 equiv) were charged to a 1-dram vial along with a magnetic stir bar, 494.5 µL of xylene (500 mM) was added to the vial to dissolve the solids. The vial was sealed and wrapped in Teflon and then placed on a hot plate with stirring at 100 ºC for 1.5 h. The reaction was monitored every 15 mins during the process. After 15 mins, the reaction mixture turned green. The reaction was kept in the freezer for five days before purification in which time, it turned from green to yellow. Solvent was removed via rotary evaporation yielding a sulfurous smelling yellow oil as the crude. This was loaded onto a 4-g silica flash column to which a gradient 0-15% EtOAc/hexanes solvent system was applied. The product eluted at 11% EtOAc. After evaporation of the solvent, the product was obtained as a colorless oil (28.3 mg, 29% yield).

Spectra

^{1}H NMR (500 MHz, CDCl3) δ 8.18 – 8.12 (m, 2H), 7.41 – 7.20 (m, 11H), 7.10 – 7.04 (m, 3H), 5.78 (dd, J = 10.2, 1.5 Hz, 1H), 5.07 (d, J = 10.2 Hz, 1H), 3.90 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 163.47 (d, J = 3.6 Hz), 134.93, 134.82, 133.82, 133.69, 129.21 – 128.93 (m), 128.59, 127.77 (d, J = 125.3 Hz), 126.72, 114.18 (d, J = 16.9 Hz), 88.57 (d, J = 3.2 Hz), 65.51, 55.70.
^{31}P NMR (202 MHz, CDCl3) δ 98.60 (t, J = 15.0 Hz).
IR Characteristic IR vibrations (cm^{-1}): 972 (P-O-C st), 692 (P=S st)**.**

TPT-11



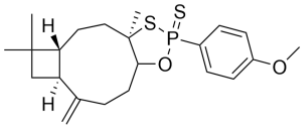
Procedure

15 mg LR (37.09 µmol, 0.5 equiv) was placed in a 5 mL round-bottom flask along with a magnetic stir bar. Then 73.93 mg of bis *p*-trifluoromethyl stilbene oxide (222.52 µmol, 3 equiv) was dissolved in 750 µL xylene (100 mM). The stilbene solution was transferred to the 5 mL round-bottom flask, and a reflux condenser was fitted to the flask. The reaction mixture was set to stir on a hot plate set at 145 ºC. After 3h of reflux, the flask was taken off and allowed to cool to rt before being kept in the freezer overnight. Solvent was removed yielding a sulfurous smelling yellow oil as the crude. The reaction mixture was purified via column chromatography using a 2-g silica column. An isocratic 10% solvent system was applied to the column yielding 11.2 mg of pure product as a colorless oil (29% yield).

Spectra

^{1}H NMR (400 MHz, CDCl3) δ 8.17 – 8.07 (m, 2H), 7.64 – 7.59 (m, 2H), 7.52 (dd, J = 11.9, 8.1 Hz, 4H), 7.22 – 7.17 (m, 2H), 7.11 – 7.06 (m, 3H), 5.82 (dd, J = 10.2, 1.7 Hz, 1H), 5.05 (d, J = 10.2 Hz, 1H), 3.92 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 163.85 (d, J = 3.6 Hz), 133.98 (d, J = 15.3 Hz), 131.66 (q, J = 33.7 Hz), 129.61, 129.43, 127.36 (q, J = 42.6 Hz), 127.31, 126.96, 126.63 (d, J = 122.5 Hz), 126.31 (q, J = 4.0 Hz), 125.84 (q, J = 4.0 Hz), 123.79 (d, J = 269.8 Hz), 114.38 (d, J = 17.1 Hz), 87.13, 64.67, 55.79.
^{31}P NMR (202 MHz, CDCl3) δ 99.25 (t, J = 15.1 Hz).
IR Characteristic IR vibrations (cm^{-1}): 1016 (P-O-C st), 696 (P=S st)**.**

TPT-12



Procedure

200 mg LR (494.5 µmol, 0.5 equiv) was added to a round-bottom flask along with a magnetic stir bar and 653 mg caryophyllene oxide (2.97 mmol, 3 equiv). 9.89 mL of xylene (100 mM) was added to the round-bottom flask. The mixture was placed on a hot plate set to 100 ºC and heated for 2.5 h. After heating, solvent was removed via rotary evaporation giving a yellow oil as the crude product. The crude product was loaded onto a 12-g silica gel column packed with 5% EtOAc and hexanes. An isocratic hold at 5% EtOAc eluted the product as 67.2 mg of yellow oil (16% yield).

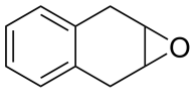
Spectra

^{1}H NMR (500 MHz, CDCl3) δ 8.05 – 7.94 (m, 2H), 7.01 – 6.91 (m, 3H), 5.09 – 5.00 (m, 2H), 4.73 (ddd, J = 6.5, 4.2, 2.5 Hz, 1H), 3.85 (s, 3H), 2.49 (td, J = 9.9, 4.8 Hz, 1H), 2.41 (td, J = 9.8, 7.6 Hz, 1H), 2.23 – 2.11 (m, 2H), 2.07 (ddd, J = 15.1, 9.3, 1.5 Hz, 1H), 2.02 – 1.87 (m, 2H), 1.83 (t, J = 10.5 Hz, 1H), 1.80 – 1.69 (m, 1H), 1.62 (dd, J = 10.4, 7.4 Hz, 1H), 1.55 (s, 3H), 1.47 – 1.38 (m, 1H), 1.04 (s, 3H), 0.99 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 163.06 (d, J = 3.5 Hz), 150.11, 133.57 (d, J = 14.6 Hz), 127.21 (d, J = 121.6 Hz), 113.92 (d, J = 16.8 Hz), 112.38, 84.47 (d, J = 2.6 Hz), 69.04, 58.06, 55.61, 42.40, 41.56, 36.12, 34.68, 34.53, 29.99, 29.41 (d, J = 14.3 Hz), 24.40, 22.17.
^{31}P NMR (202 MHz, CDCl3) δ 99.05 (t, J = 14.9 Hz).
IR Characteristic IR vibrations (cm^{-1}): 952 (P-O-C st), 689 (P=S st)**.**

Precursor Synthesis

1,4-Dihydronapthalene Oxide (EPO-2)



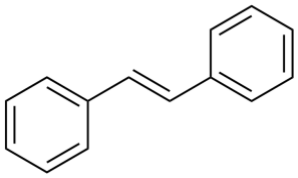
Procedure

446 mg of 1,4-dihydronaphthalene (3.43 mmol, 1 equiv) was dissolved in 34.26 mL DCM (100 mM) in a round-bottom flask. A magnetic stir bar was added to the flask. While stirring, 1.58 g (6.85 mmol, 2 equiv) of 75% *meta*-chloroperbenzoic acid (mCPBA) was added slowly to the flask. The flask was sealed with a rubber septum and allowed to stir at room temperature for 24 h. After 24 h, the flask was placed in an ice bath for 20 mins while stirring to precipitate *meta*-chloro benzoic acid. The precipitate was filtered out via gravity filtration. 15 mL of saturated sodium thiosulfate solution (aq) was added to the filtrate and the layers were stirred vigorously for 1 h. The mixture was added to a separatory funnel and the DCM layer was filtered off. The aqueous layer was decanted, and the DCM layer was returned to the funnel. The organic layer was washed three times with 10 mL portions of saturated sodium bicarbonate solution (aq) and once with a 10 mL portion of brine. The combined organic layers were dried with sodium sulfate overnight and then gravity filtered. Solvent was removed via rotary evaporation yielding a colorless oil as a crude product. The crude was purified via flash chromatography using a gradient 0-20% EtOAc in hexanes solvent system giving 208 mg of pure product as a cloudy white solid (42% yield).

Spectra

^{1}H NMR (400 MHz, CDCl3) δ 7.18 – 7.11 (m, 2H), 7.05 (dd, J = 5.5, 3.5 Hz, 2H), 3.49 (p, J = 1.3 Hz, 2H), 3.32 (d, J = 1.3 Hz, 2H), 3.20 (d, J = 17.8 Hz, 2H). Spectrum matched a previously published one.[2]

E-Stilbene



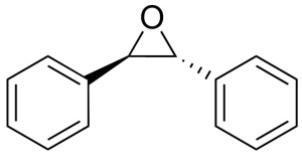
Sequentially to a round-bottom flask was added, iodobenzene (1.09 mL, 9.8 mmol, 1 equiv), a magnetic stir bar, palladium(II) chloride (52.2 mg, 294 umol, 0.03 equiv, styrene (2.25 mL, 19.6 mmol, 2 equiv), and anhydrous DMF as a solvent (19.61 mL, 500 mM). The reaction vessel was set on a hot plate open to air and allowed to stir at room temperature while sodium acetate was weighed (2.09 g, 25.49 mmol, 2.6 equiv). Sodium acetate was slowly added to the stirred mixture,

upon complete addition a rubber septum was used to cap the flask, and a nitrogen-filled balloon was inserted into the septum. The hot plate was set to 140 ºC and allowed to react overnight. Upon returning, the reaction mixture was grey with noticeable white precipitate at the bottom. The mixture was gravity filtered then the precipitate was washed with several portions of ether. Deionized water was then added to the filtrate causing *E*-stilbene to precipitate out of solution. 1.22 g of *E*-Stilbene was isolated via gravity filtration and washed several times with deionized water. The product was a shiny white solid, no further purification was needed.

Spectra

^{1}H NMR (400 MHz, CDCl3) δ 7.55 – 7.50 (m, 4H), 7.39 – 7.34 (m, 4H), 7.30 – 7.24 (m, 3H), 7.12 (s, 2H). Spectrum matched a previously published one.[3]

EPO-10 (stilbene oxide)



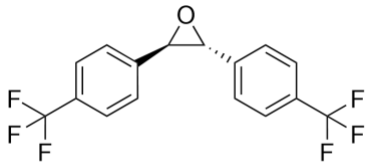
Procedure

500 mg stilbene (2.77 mmol, 1 equiv) and 957.7 mg mCPBA (5.55 mmol, 2 equiv) were charged to a 50 mL round-bottom flask along with a magnetic stir bar, DCM was then added (27.3 mL, 100 mM) causing the mixture to instantly turn pink. The reaction was set to stir at room temperature overnight, a color change from pink to yellow was observed. Upon returning, a white precipitate was observed in the flask, this was gravity filtered and the filter cake was washed 3x with small portions of DCM. The filtrate was transferred to a separatory funnel, and 7 mL of aqueous saturated sodium thiosulfate solution was added to the funnel. The organic layer was extracted, and the aqueous layer was decanted before the org layer was returned to the funnel. This was repeated a total of 3 times. The same protocol was followed using a saturated sodium bicarbonate (3 times with 7 mL each time) Finally, the mixture was washed one time with 7 mL brine, then allowed to dry overnight using sodium sulfate. The combined organic layers were gravity filtered and solvent was removed by rotary evaporation. Upon solvent removal, the product was obtained as an off-white solid which was used without further purification.

Spectra

^{1}H NMR (400 MHz, CDCl3) δ 7.43 – 7.31 (m, 10H), 3.88 (s, 2H). Spectrum matched a previously published one.[4]

EPO-11



Procedure

150 mg (*E*)-bis(*p*-trifluoromethyl)stilbene was charged to a 10 mL round-bottom flask along with a magnetic stir bar and 4.5 mL DCM was added to the flask and stirring was started until dissolution was observed. Then 163.7 mg *m*-CPBA was added to the flask. Then, the flask was sealed with a rubber septum and allowed to stir overnight. The reaction was cooled at 0 ºC for one hour to precipitate meta-chlorobenzoic acid and benzoic acid salts. Then the mixture was diluted to 10 mL with DCM and transferred to a separatory funnel. 10 mL of a 20% sodium thiosulfate solution was added to the flask; the DCM layer was extracted and the aqueous layer was decanted off. This was repeated 3 more times. The combined organic layers were washed once with 40 mL of saturated sodium carbonate solution. Extracted, then washed again with a 40 mL brine. The DCM layer was dried with sodium sulfate and gravity filtered into an RBF and allowed to sit in the freezer overnight. DCM was removed via rotary evaporation yielding a colorless oil. The oil was loaded onto a 2-g silica column and eluted using a 10% ethyl acetate in hexanes solvent system. The product eluted as 73.93 mg of colorless oil (47% yield).

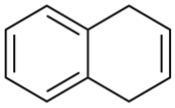
Spectra

^{1}H NMR (400 MHz, CDCl3) δ 7.68 – 7.64 (m, 4H), 7.50 – 7.45 (m, 4H), 3.91 (s, 2H).

Other compound sources

The following compounds have been prepared by researchers at the University of Kansas, primarily in groups of Prof. Grunewald and Prof. Hanzlik. We purified and characterized the compounds before using them.

1,4-Dihydronaphthalene

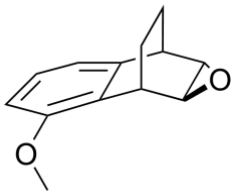


^{1}H NMR (400 MHz, CDCl3) δ 7.20 – 7.06 (m, 4H), 5.93 (m, 2H), 3.40 (d, J = 1.3 Hz, 4H). Spectrum matched a previously published one.[5]

EPO-5

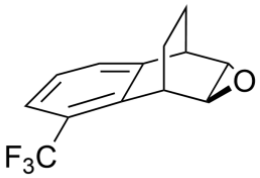
^{1}H NMR (400 MHz, CDCl3) δ 7.25 – 7.18 (m, 4H), 3.41 – 3.33 (m, 4H), 2.11 – 2.01 (m, 2H), 1.13 – 1.02 (m, 2H). Spectrum matched a previously published one.[6]

EPO-6



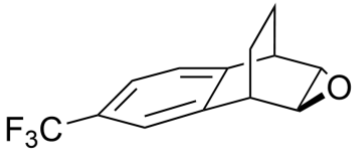
^{1}H NMR (400 MHz, CDCl3) δ 7.16 (dd, J = 8.3, 7.3 Hz, 1H), 6.89 (dt, J = 7.3, 0.8 Hz, 1H), 6.80 (dd, J = 8.3, 0.9 Hz, 1H), 3.89 (p, J = 2.8 Hz, 1H), 3.85 (s, 3H), 3.40 – 3.30 (m, 3H), 2.10 – 1.96 (m, 2H), 1.11 – 0.97 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 155.07, 145.48, 130.98, 126.85, 118.08, 109.06, 58.18 (d, J = 2.3 Hz), 55.62, 38.11, 30.43, 23.49, 22.89.

EPO-7



^{1}H NMR (400 MHz, CDCl3) δ 7.50 (dd, J = 7.9, 1.2 Hz, 1H), 7.45 – 7.34 (m, 2H), 7.28 (d, J = 7.9 Hz, 1H), 3.86 (d, J = 4.0 Hz, 1H), 3.43 (tq, J = 3.1, 1.5 Hz, 1H), 3.39 – 3.33 (m, 2H), 2.15 – 2.06 (m, 2H), 1.16 – 0.98 (m, 2H). Spectrum matched a previously published one.[7]

EPO-8

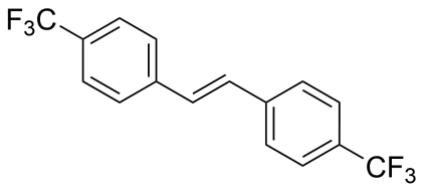


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 3.45 (dt, *J* = 3.5, 1.7 Hz, 2H), 3.36 (t, *J* = 3.7 Hz, 2H), 2.15 – 2.04 (m, 2H), 1.06 (dt, *J* = 9.3, 2.1 Hz, 2H). Spectrum matched a previously published one.[7]

EPO-9

^{1}H NMR (400 MHz, CDCl3) δ 7.28 – 7.19 (m, 2H), 7.07 (dd, J = 5.2, 3.1 Hz, 2H), 3.41 (s, 2H), 3.39 (s, 2H), 2.02 – 1.47 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 148.50, 125.85, 122.72, 56.59, 44.64, 39.42.

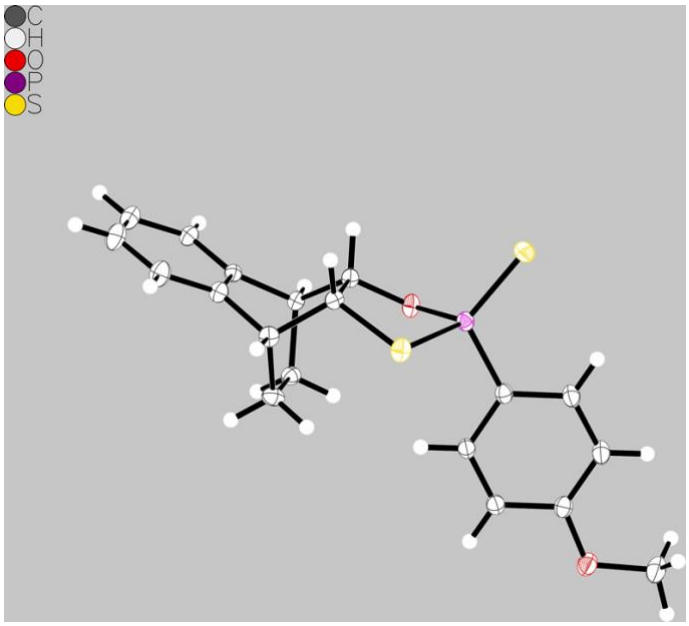
(E)-*bis*(*p*-trifluoromethyl)stilbene



^{1}H NMR (400 MHz, CDCl3) δ 7.63 (s, 8H), 7.20 (s, 2H). Spectrum matched a previously published one.[8]

Crystallographic data of TPT-5

The structure of TPT-5 was confirmed by X-ray crystallography and deposited to CCDC deposit number 2434451. TPT-5 was dissolved in chloroform at room temperature in a clean 1-dram vial. This vial was then placed inside a 20 mL scintillation vial containing pentane. The 20 mL scintillation vial was sealed and the lid was wrapped in parafilm. The system of vials was then placed in a stable location for five days and pentane was allowed to slowly diffuse into chloroform. After five days of development, long clear crystals were observed to form in the one-dram vial. A single crystal was harvested and analyzed via a Bruker D8-Venture with graphite-monochromated MoKα radiation. Unit-cell parameters refinement, integration, and data reduction were carried out with SAINT V8.40B (2016) program. SADABS-2016/2 (Bruker,2016) was used for absorption correction. Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement.



Thermal ellipsoid plot of TPT-5. Thermal ellipsoids are drawn to a 50% probability level.

Crystal data and structure refinement for mo_IS_3_75_0m.

Identification code	mo_IS_3_75_0m
Empirical formula	$C_{19}H_{19}O_2PS_2$
Formula weight	374.43
Temperature/K	101.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.0164(3)
b/Å	7.4894(2)
c/Å	21.0540(7)
α/°	90
β/°	97.4350(10)
γ/°	90
Volume/Å^3	1722.48(9)
Z	4
ρ_{calc}g/cm^3	1.444
μ/mm^{-1}	0.411
F(000)	784.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.736 to 66.408
Index ranges	-16 ≤ h ≤ 16, -11 ≤ k ≤ 11, -32 ≤ l ≤ 32
Reflections collected	65549
Independent reflections	6600 [R_{int} = 0.0404, R_{sigma} = 0.0219]
Data/restraints/parameters	6600/0/218
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.1089

Final R indexes [all data] $R_1 = 0.0423$, $wR_2 = 0.1129$
Largest diff. peak/hole / e $Å^{-3}$ 1.59/-0.32

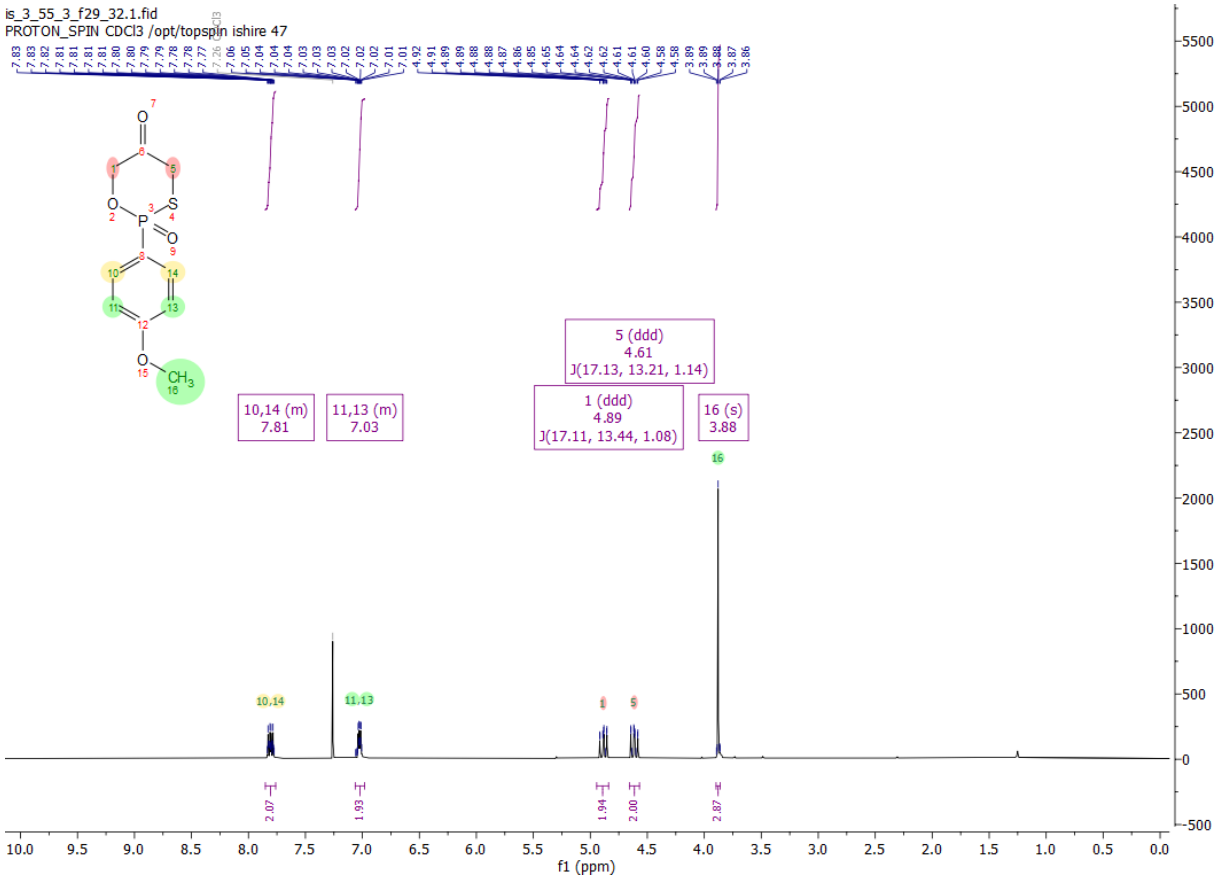
Number	Label	Charge	SybylType	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD
1	S001	0	S.2	0.87413(3)	-0.10321(4)	0.39779(2)
2	P002	0	P.3	0.74621(3)	0.04344(4)	0.42461(2)
3	S003	0	S.3	0.69521(3)	-0.01589(4)	0.51432(2)
4	O004	0	O.3	0.77806(8)	0.24914(11)	0.43923(4)
5	O005	0	O.3	0.28349(9)	0.07870(13)	0.24584(4)
6	C006	0	C.2	0.60052(12)	-0.03668(16)	0.31054(6)
7	H006	0	H	0.668864	-0.101953	0.299693
8	C007	0	C.3	0.60868(10)	0.05171(14)	0.36914(5)
9	C008	0	C.3	0.79236(10)	0.48310(14)	0.51822(5)
10	H008	0	H	0.819033	0.57102	0.487065
11	C009	0	C.2	0.84734(10)	0.52625(14)	0.58557(5)
12	C00A	0	C.2	0.50706(10)	0.14859(15)	0.38410(5)
13	H00A	0	H	0.511858	0.209716	0.423879
14	C00B	0	C.3	0.65184(10)	0.48455(15)	0.51668(5)
15	H00B	0	H	0.612613	0.446584	0.473843
16	H00C	0	H	0.623923	0.607262	0.524574
17	C00C	0	C.3	0.83302(10)	0.29334(15)	0.50361(5)
18	H00D	0	H	0.924181	0.2905	0.505563
19	C00D	0	C.2	0.39254(11)	0.06529(15)	0.28338(5)
20	C00E	0	C.2	0.40019(10)	0.15647(15)	0.34190(5)
21	H00E	0	H	0.3323	0.223286	0.352477

22	C00F	0	C.2	0.49309(12)	-0.03029(16)	0.26768(6)
23	H00F	0	H	0.488362	-0.09096	0.227805
24	C00G	0	C.2	0.81279(10)	0.40705(15)	0.63110(5)
25	C00H	0	C.2	0.91929(10)	0.67383(15)	0.60455(5)
26	H00H	0	H	0.943204	0.754195	0.573538
27	C00I	0	C.3	0.79276(10)	0.15984(14)	0.55435(5)
28	H00I	0	H	0.867766	0.102898	0.577619
29	C00J	0	C.3	0.72699(10)	0.26266(15)	0.60314(5)
30	H00J	0	H	0.704373	0.181224	0.637371
31	C00K	0	C.3	0.26970(14)	-0.01208(19)	0.18558(6)
32	H00G	0	H	0.328562	0.035813	0.158847
33	H00K	0	H	0.186334	0.005669	0.163951
34	H00L	0	H	0.284773	-0.139948	0.192658
35	C00L	0	C.3	0.61314(10)	0.35691(16)	0.56836(6)
36	H00M	0	H	0.571889	0.425511	0.599585
37	H00N	0	H	0.554759	0.266968	0.547978
38	C00M	0	C.2	0.95606(12)	0.70284(17)	0.66962(6)
39	H00O	0	H	1.005204	0.803612	0.682989
40	C00N	0	C.2	0.85005(13)	0.43649(18)	0.69603(6)
41	H00P	0	H	0.827003	0.355634	0.72712
42	C00O	0	C.2	0.92133(14)	0.5854(2)	0.71499(6)
43	H00Q	0	H	0.946333	0.606739	0.759232

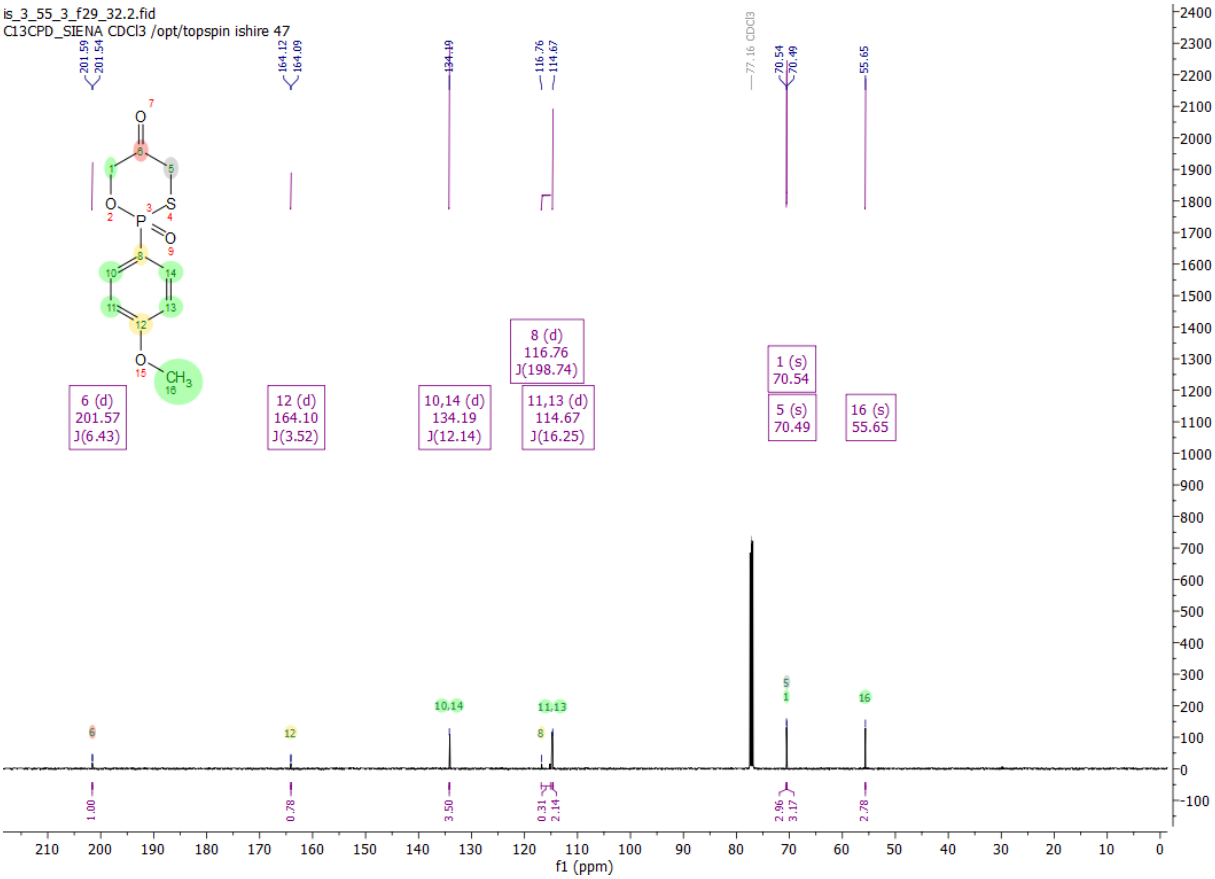
NMR Figures

PT-1

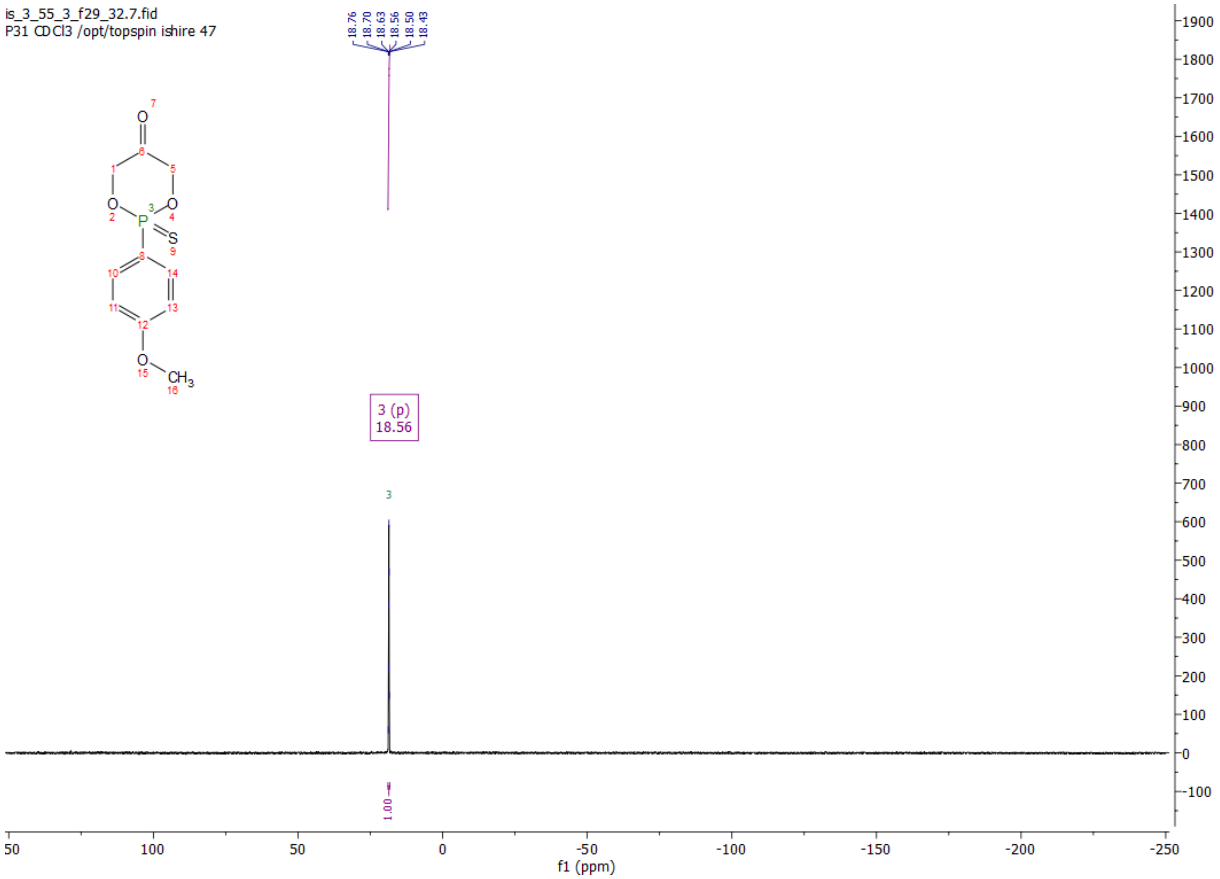
^{1}H NMR:



^{13}C NMR:

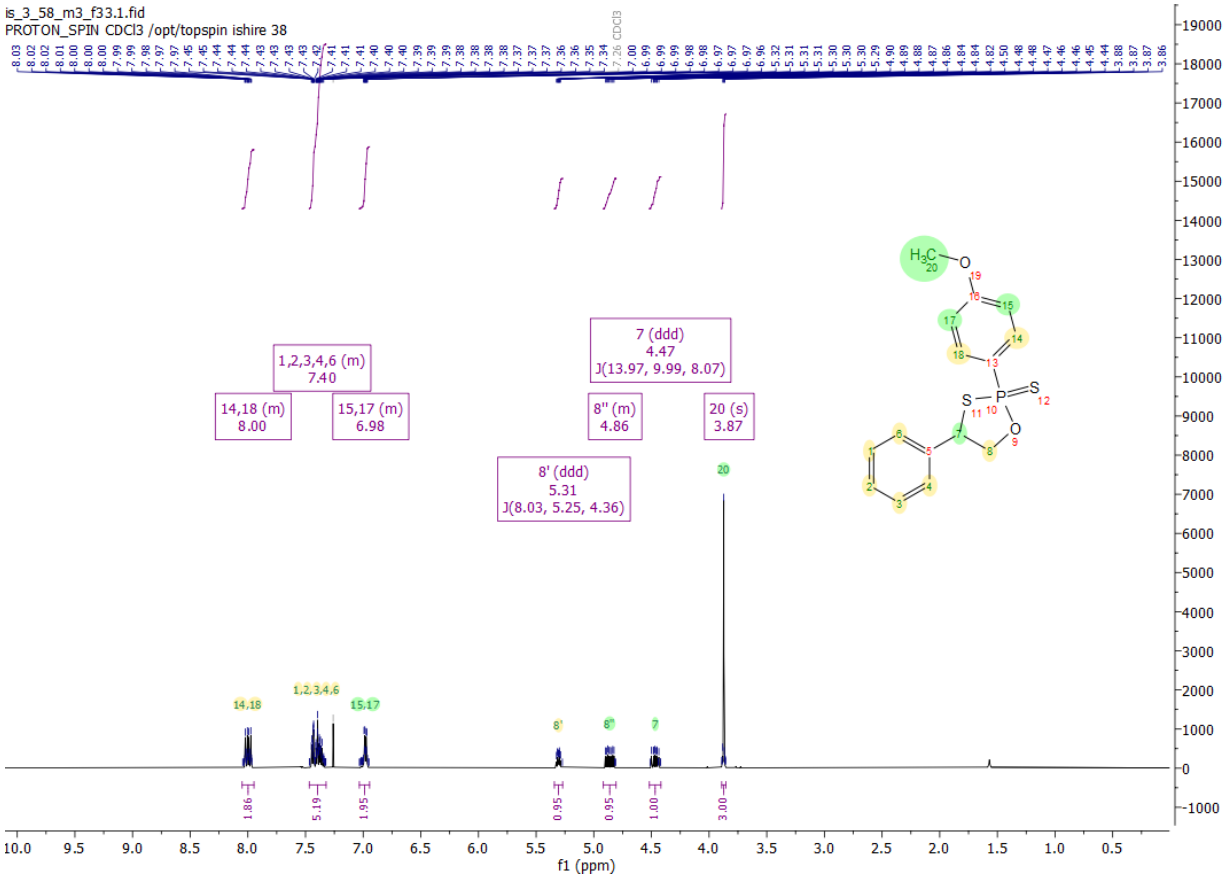

is_3_55_3_f29_32.2.fid
C13CPD_SIENA CDCl3 /opt/topspin ishire 47
201.59
201.54
164.12
164.09
134.49
116.76
114.67
77.16 CDCl3
70.54
70.49
55.65
6 (d)
201.57
J(6.43)
12 (d)
164.10
J(3.52)
10,14 (d)
134.19
J(12.14)
8 (d)
116.76
J(198.74)
11,13 (d)
114.67
J(16.25)
1 (s)
70.54
5 (s)
70.49
16 (s)
55.65
f1 (ppm)

^{31}P NMR:

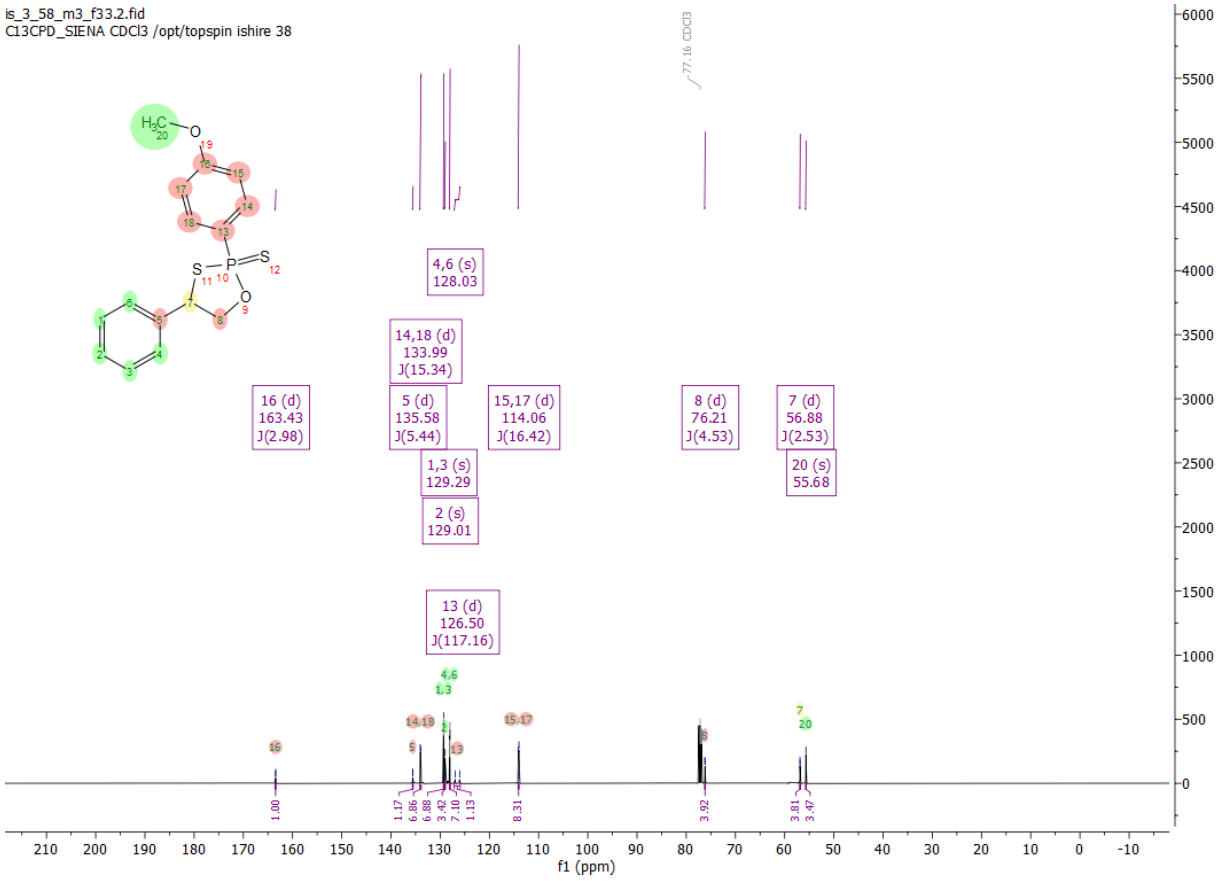

is_3_55_3_f29_32.7.fid
P31 CDCl3 /opt/topspin ishire 47
18.76
18.70
18.63
18.56
18.50
18.43
3 (p)
18.56
1.00
f1 (ppm)

Cis-TPT-2

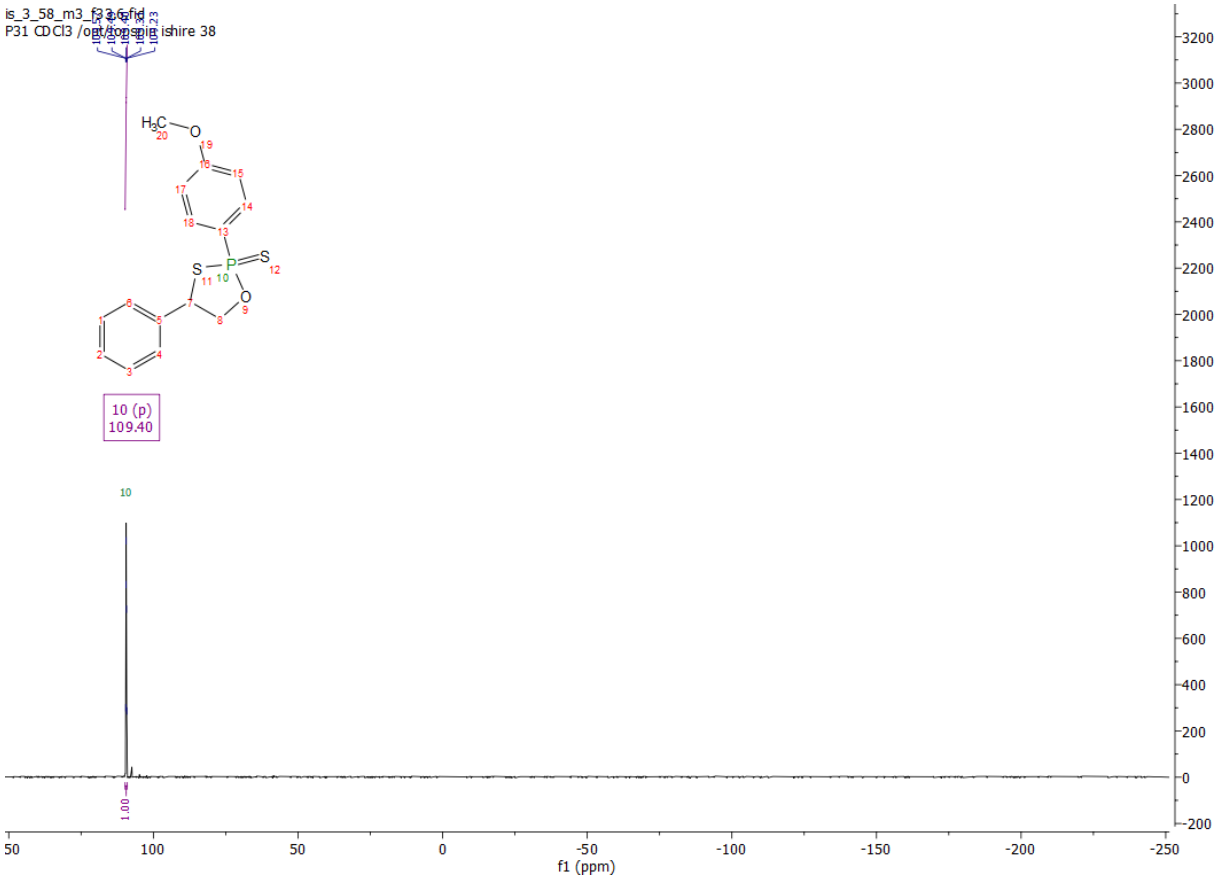
^{1}H NMR:



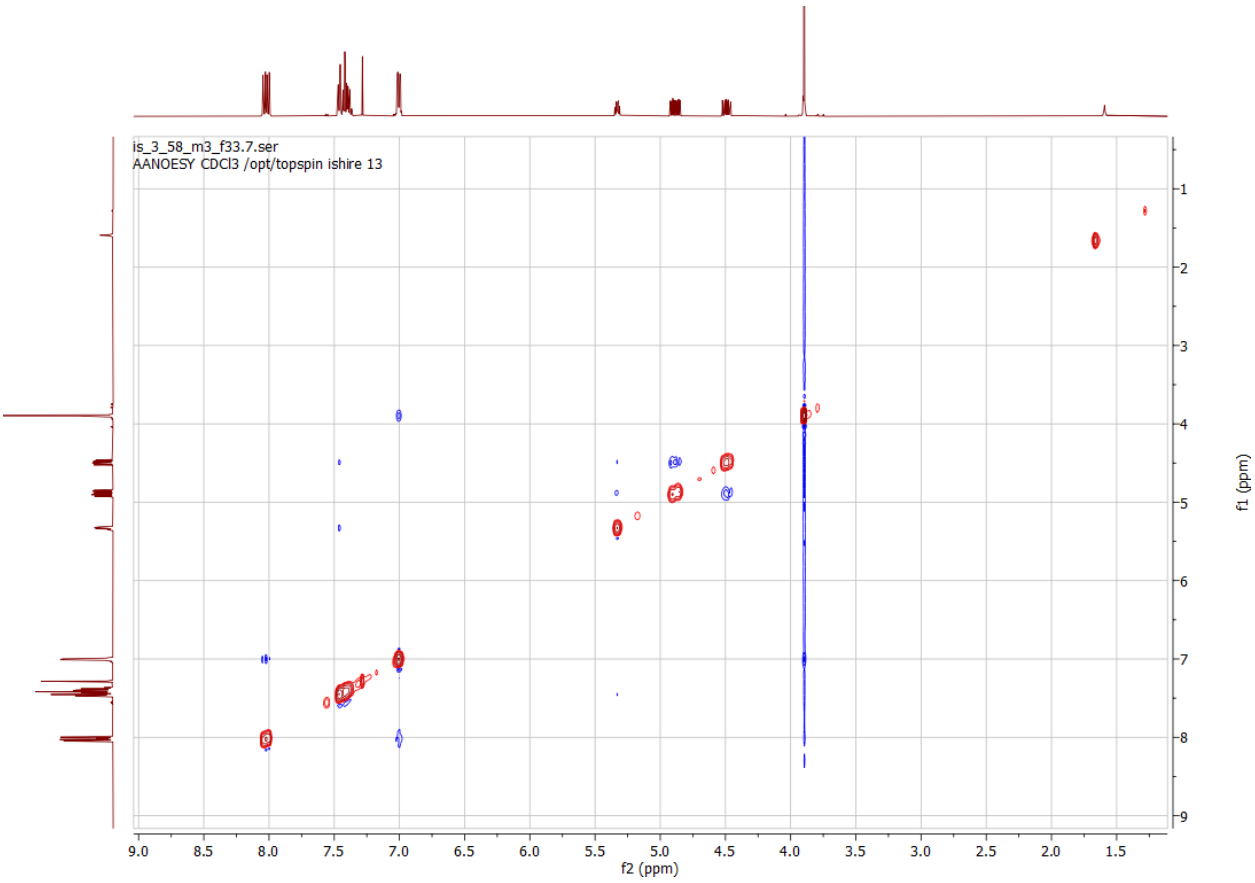
^{13}C NMR:


is_3_58_m3_f33.2.fid
C13CPD_SIENA CDCl3 /opt/topspin ishire 38
77.16 CDCl3
4,6 (s)
128.03
14,18 (d)
133.99
J(15.34)
16 (d)
163.43
J(2.98)
5 (d)
135.58
J(5.44)
15,17 (d)
114.06
J(16.42)
8 (d)
76.21
J(4.53)
7 (d)
56.88
J(2.53)
1,3 (s)
129.29
20 (s)
55.68
2 (s)
129.01
13 (d)
126.50
J(117.16)
f1 (ppm)

^{31}P NMR:

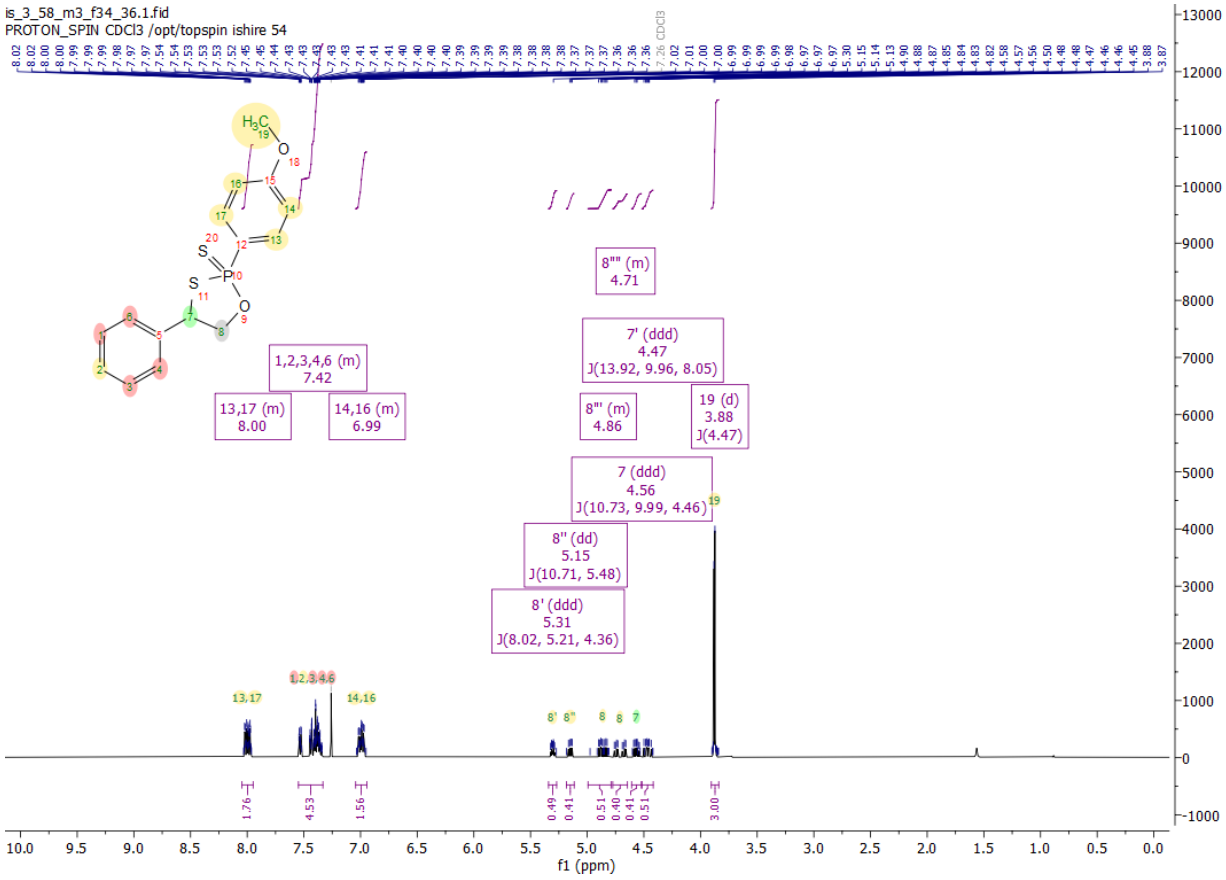

is_3_58_m3_f23.6.fid
P31 CDCl3 /opt/topspin ishire 38
10 (p)
109.40
10
1.00
f1 (ppm)

NOESY 2D NMR

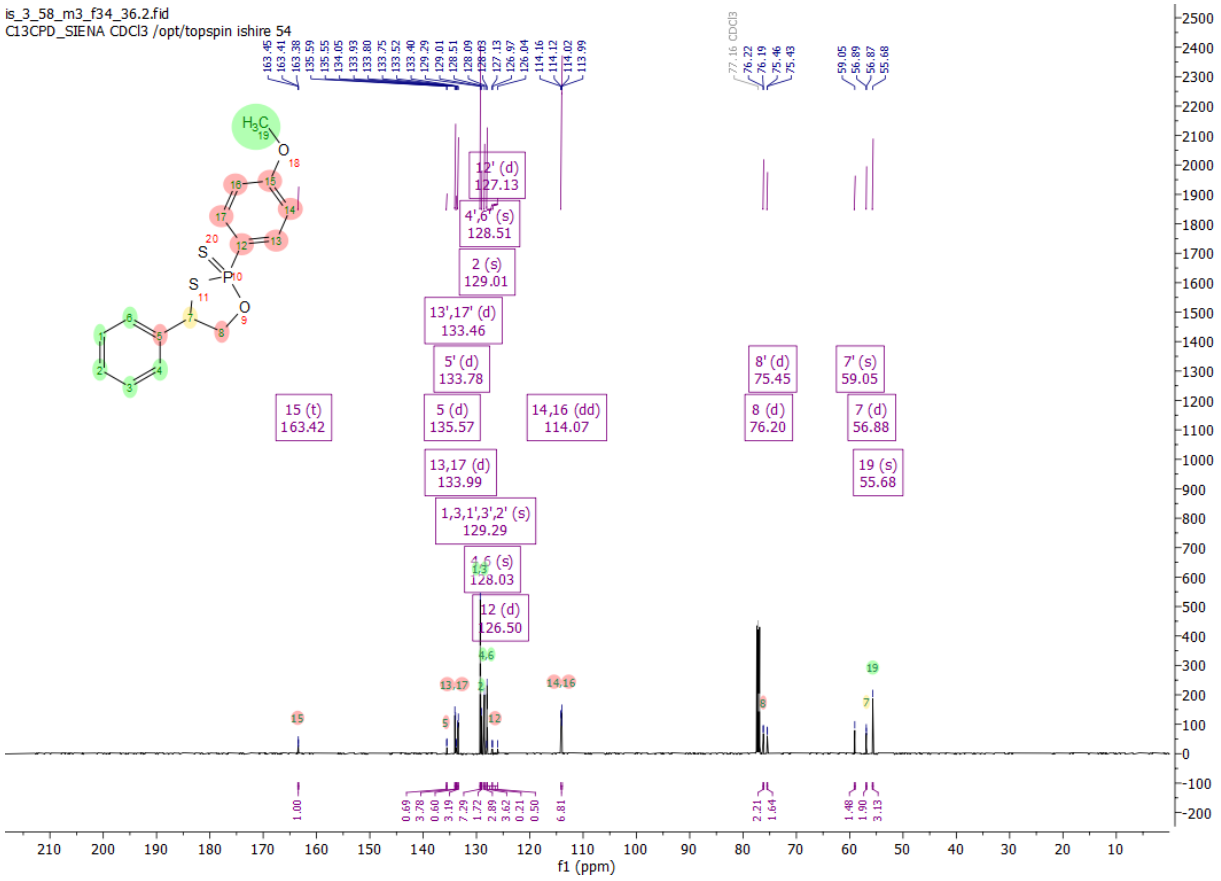

is_3_58_m3_f33.7.ser
AANOESY CDCl3 /opt/topspin ishire 13
f2 (ppm)
f1 (ppm)

Cis- and trans-TPT-2

^{1}H NMR:

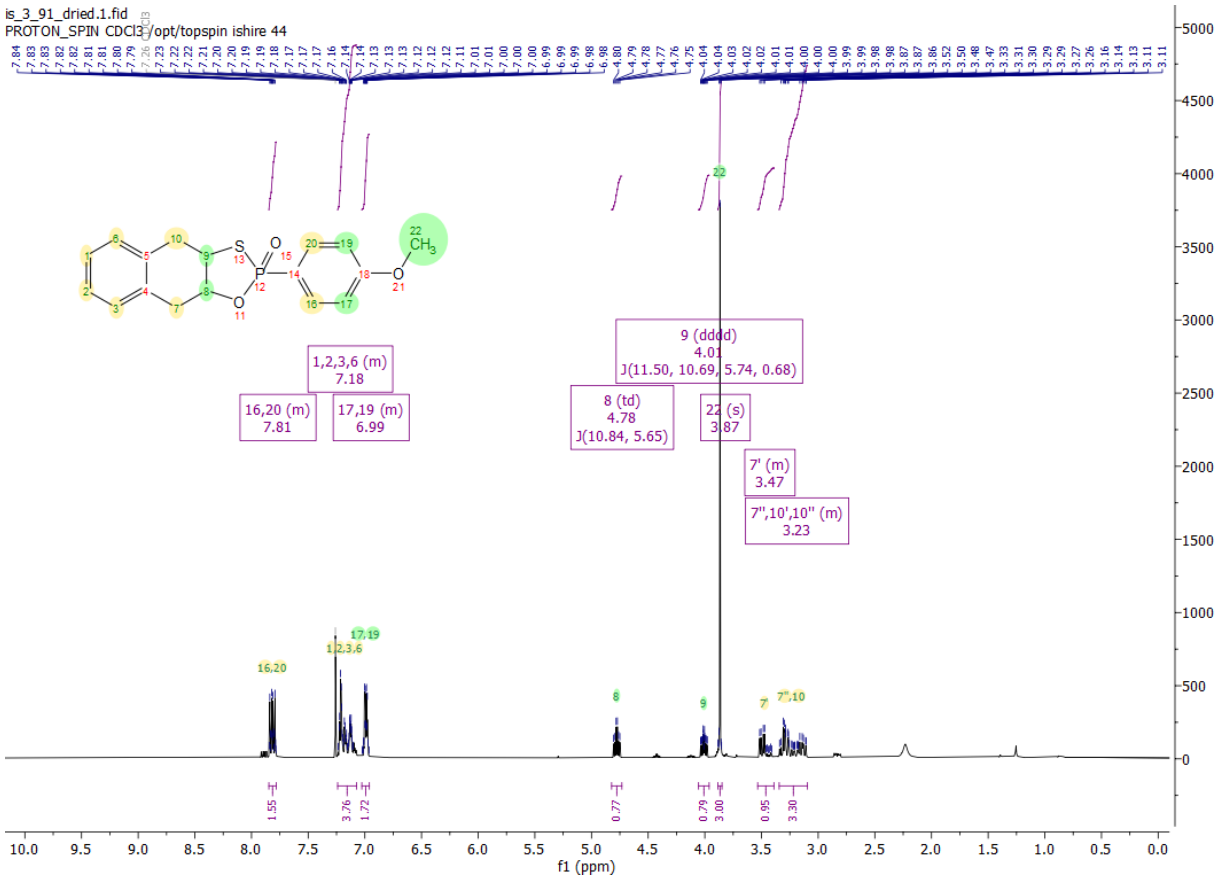


^{13}C NMR:

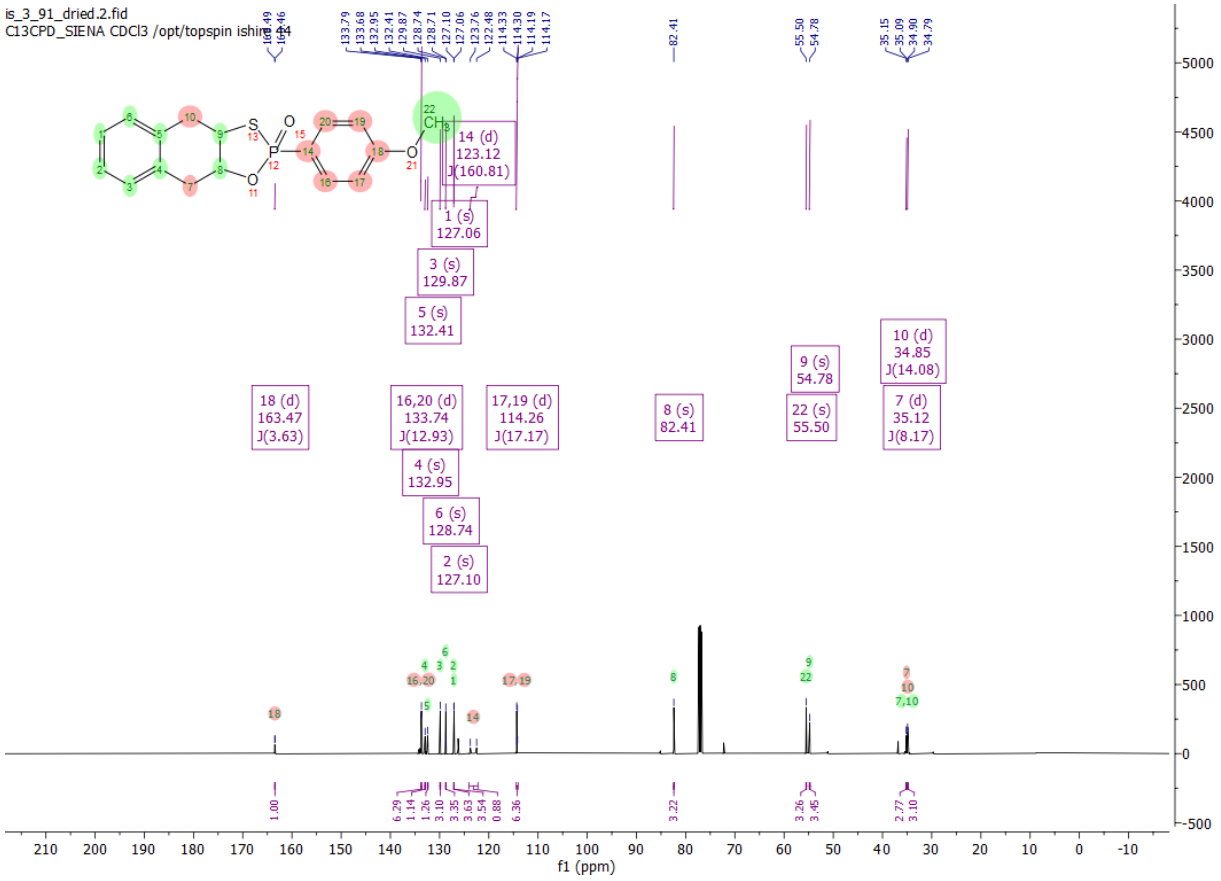

is_3_58_m3_f34_36.2.fid
C13CPD_SIENA CDCl3 /opt/topspin ishire 54
12' (d) 127.13
4',6' (s) 128.51
2 (s) 129.01
13',17' (d) 133.46
5' (d) 133.78
15 (t) 163.42
5 (d) 135.57
14,16 (dd) 114.07
8' (d) 75.45
8 (d) 76.20
7' (s) 59.05
7 (d) 56.88
19 (s) 55.68
13,17 (d) 133.99
1,3,1',3',2' (s) 129.29
4,6 (s) 128.03
12 (d) 126.50
f1 (ppm)

PT-3

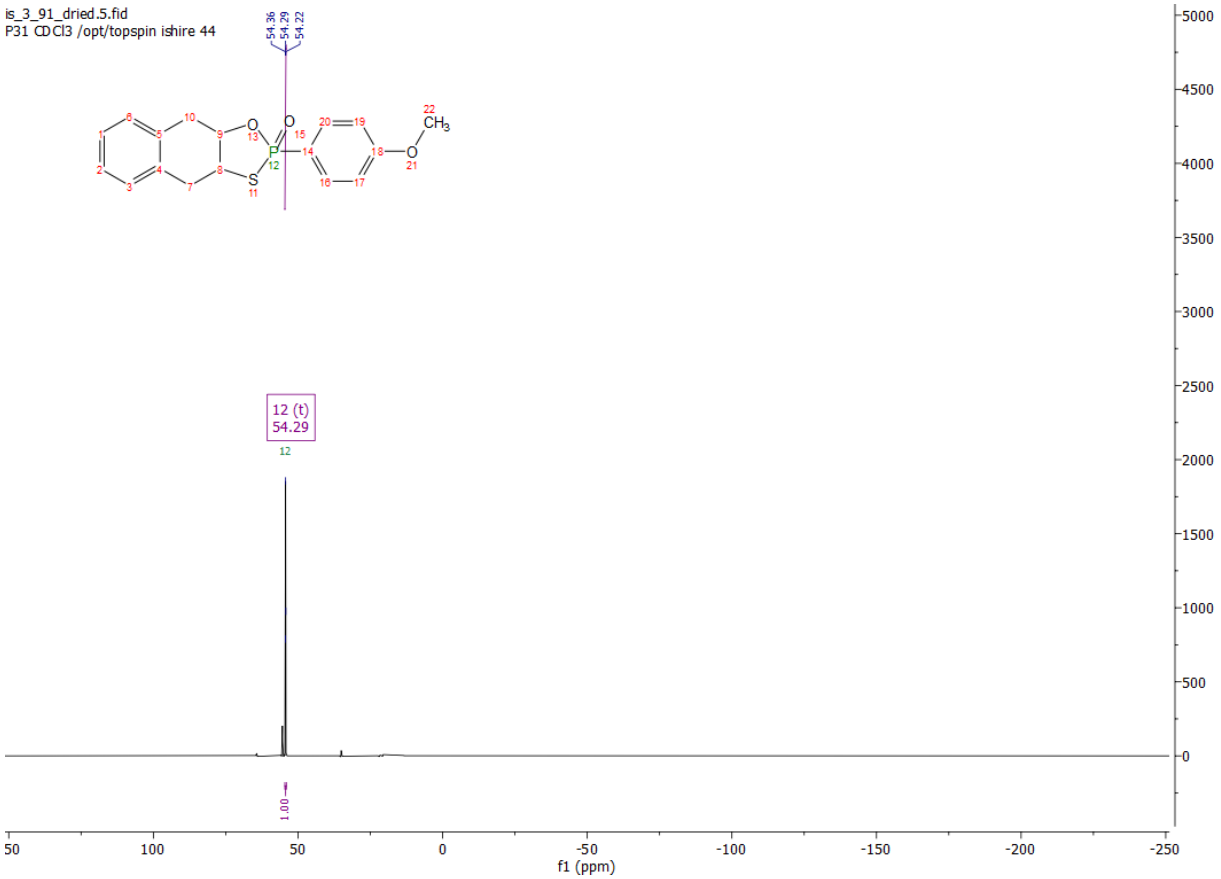
^{1}H NMR:


is_3_91_dried.1.fid
PROTON_SPIN CDCl3 /opt/topspin ishire 44
1,2,3,6 (m)
7.18
16,20 (m)
7.81
17,19 (m)
6.99
9 (dddd)
4.01
J(11.50, 10.69, 5.74, 0.68)
8 (td)
4.78
J(10.84, 5.65)
22 (s)
3.87
7' (m)
3.47
7'',10',10'' (m)
3.23
f1 (ppm)

^{13}C NMR:

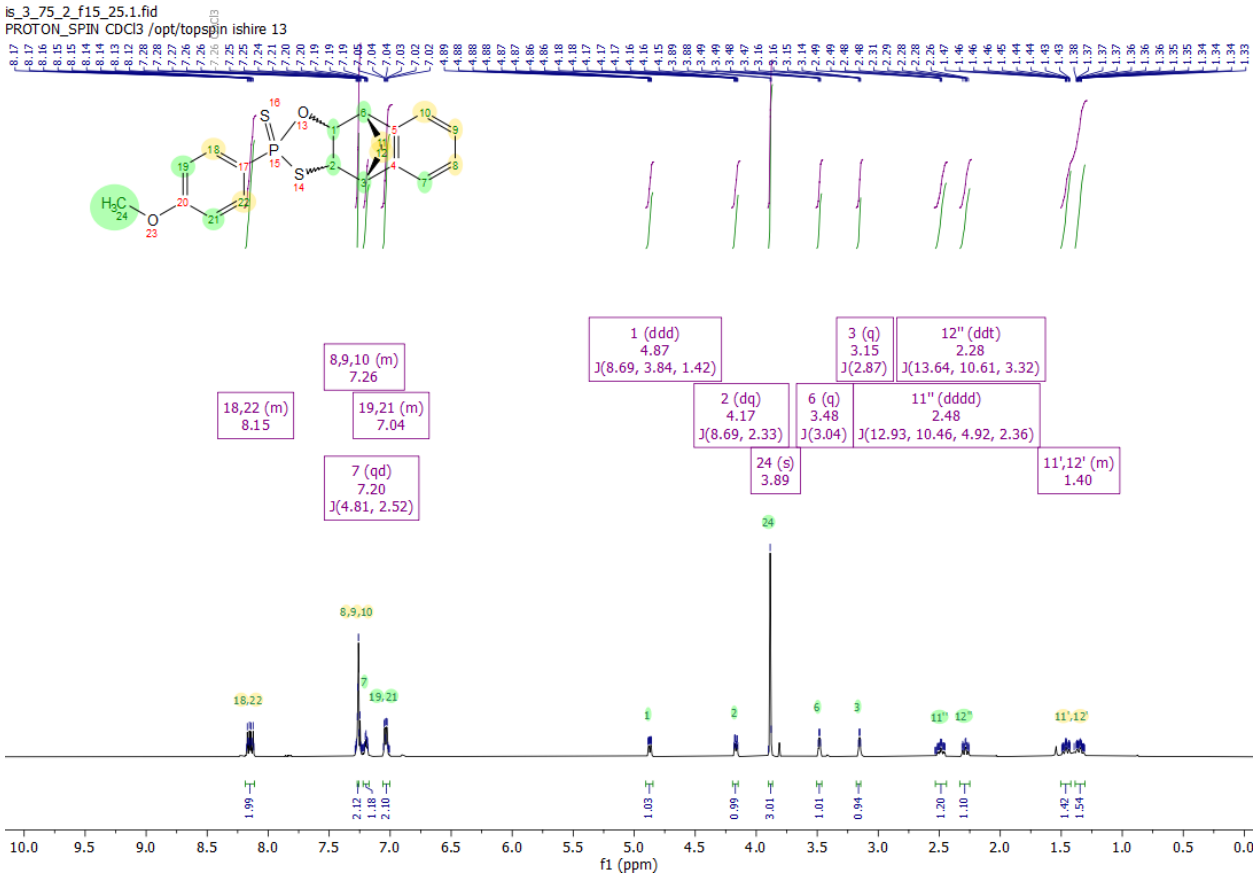

is_3_91_dried.2.fid
C13CPD_SIENA CDCl3 /opt/topspin ishira 44
14 (d)
123.12
J(160.81)
1 (s)
127.06
3 (s)
129.87
5 (s)
132.41
18 (d)
163.47
J(3.63)
16,20 (d)
133.74
J(12.93)
17,19 (d)
114.26
J(17.17)
8 (s)
82.41
9 (s)
54.78
22 (s)
55.50
10 (d)
34.85
J(14.08)
7 (d)
35.12
J(8.17)
4 (s)
132.95
6 (s)
128.74
2 (s)
127.10
f1 (ppm)

^{31}P NMR

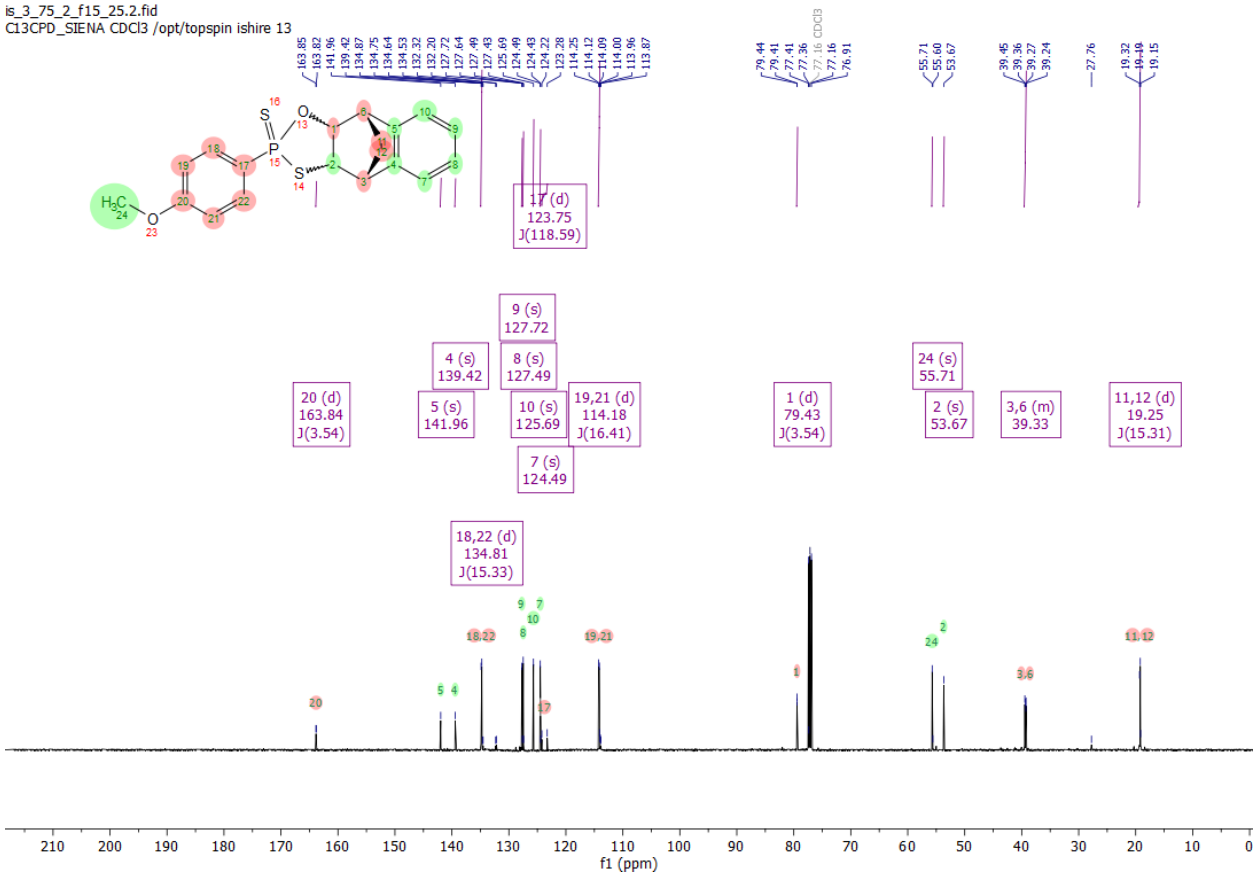

is_3_91_dried.5.fid
P31 CDCl3 /opt/topspin ishire 44
54.36
54.29
54.22
12 (t)
54.29
12
1.00
f1 (ppm)

TPT-5

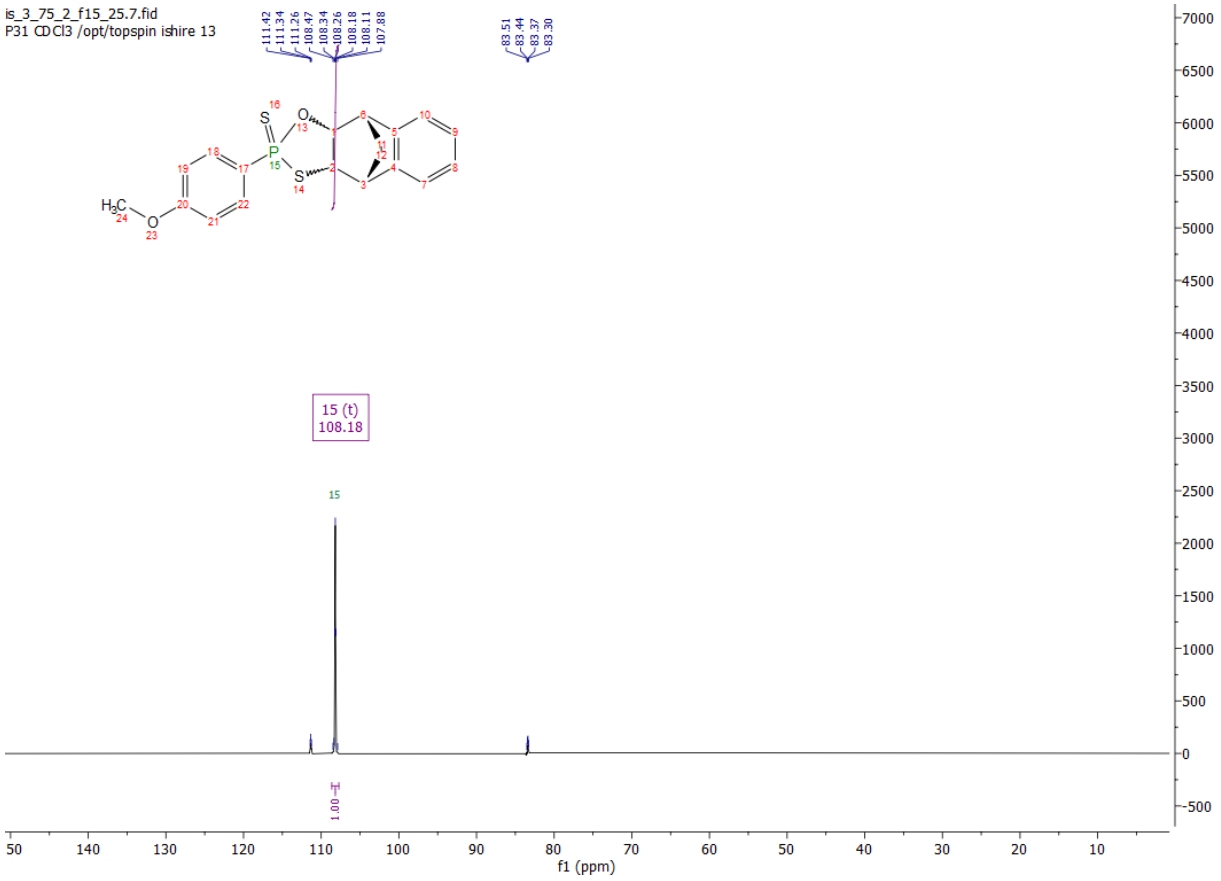
^{1}H NMR:


is_3_75_2_f15_25.1.fid
PROTON_SPIN CDCl3 /opt/topspin ishire 13
8,9,10 (m)
7.26
18,22 (m)
8.15
19,21 (m)
7.04
7 (qd)
7.20
J(4.81, 2.52)
1 (ddd)
4.87
J(8.69, 3.84, 1.42)
2 (dq)
4.17
J(8.69, 2.33)
24 (s)
3.89
6 (q)
3.48
J(3.04)
3 (q)
3.15
J(2.87)
11" (dddd)
2.48
J(12.93, 10.46, 4.92, 2.36)
12" (ddt)
2.28
J(13.64, 10.61, 3.32)
11',12' (m)
1.40
f1 (ppm)

^{13}C NMR:

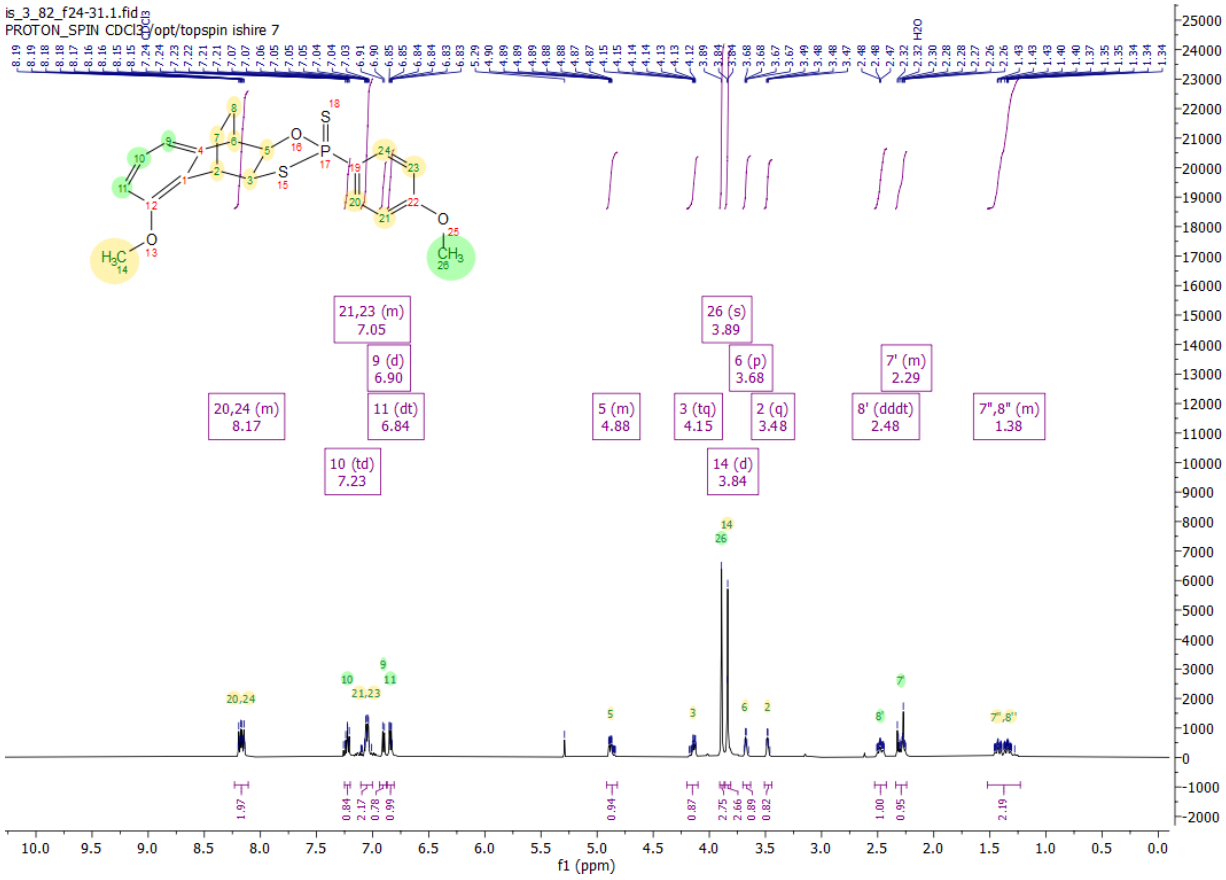

is_3_75_2_f15_25.2.fid
C13CPD_SIENA CDCl3 /opt/topspin ishire 13
17 (d)
123.75
J(118.59)
9 (s)
127.72
4 (s)
139.42
8 (s)
127.49
24 (s)
55.71
20 (d)
163.84
J(3.54)
5 (s)
141.96
10 (s)
125.69
19,21 (d)
114.18
J(16.41)
1 (d)
79.43
J(3.54)
2 (s)
53.67
3,6 (m)
39.33
11,12 (d)
19.25
J(15.31)
7 (s)
124.49
18,22 (d)
134.81
J(15.33)
f1 (ppm)

^{31}P NMR:

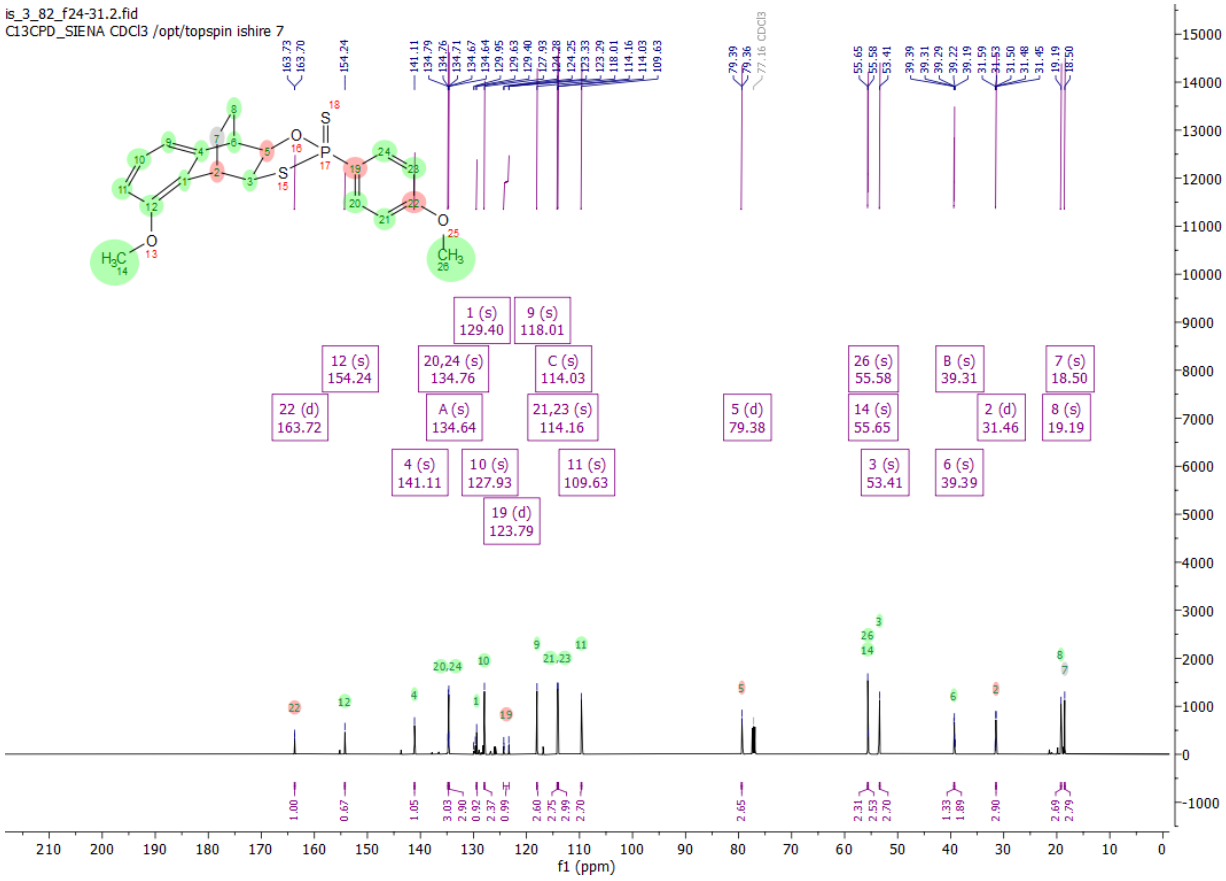

is_3_75_2_f15_25.7.fid
P31 CDCl3 /opt/topspin ishire 13
111.42
111.34
111.26
108.47
108.34
108.26
108.18
108.11
107.88
83.51
83.44
83.37
83.30
15 (t)
108.18
15
1.00
f1 (ppm)

TPT-6

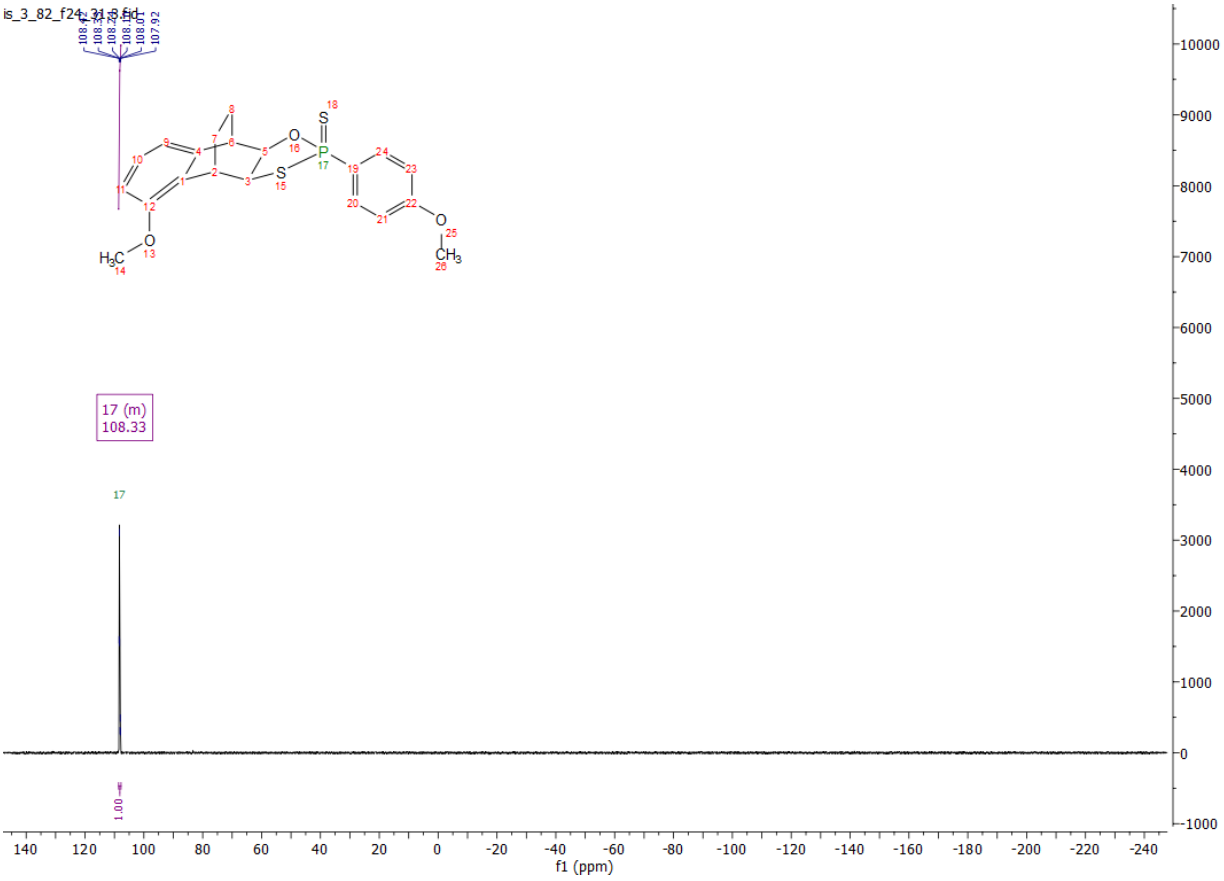
^{1}H NMR:


is_3_82_f24-31.1.fid
PROTON_SPIN CDCl3 /opt/topspin ishire 7
21,23 (m) 7.05
9 (d) 6.90
20,24 (m) 8.17
11 (dt) 6.84
10 (td) 7.23
5 (m) 4.88
26 (s) 3.89
6 (p) 3.68
3 (tq) 4.15
2 (q) 3.48
14 (d) 3.84
7' (m) 2.29
8' (dddt) 2.48
7",8" (m) 1.38
f1 (ppm)

^{13}C NMR:

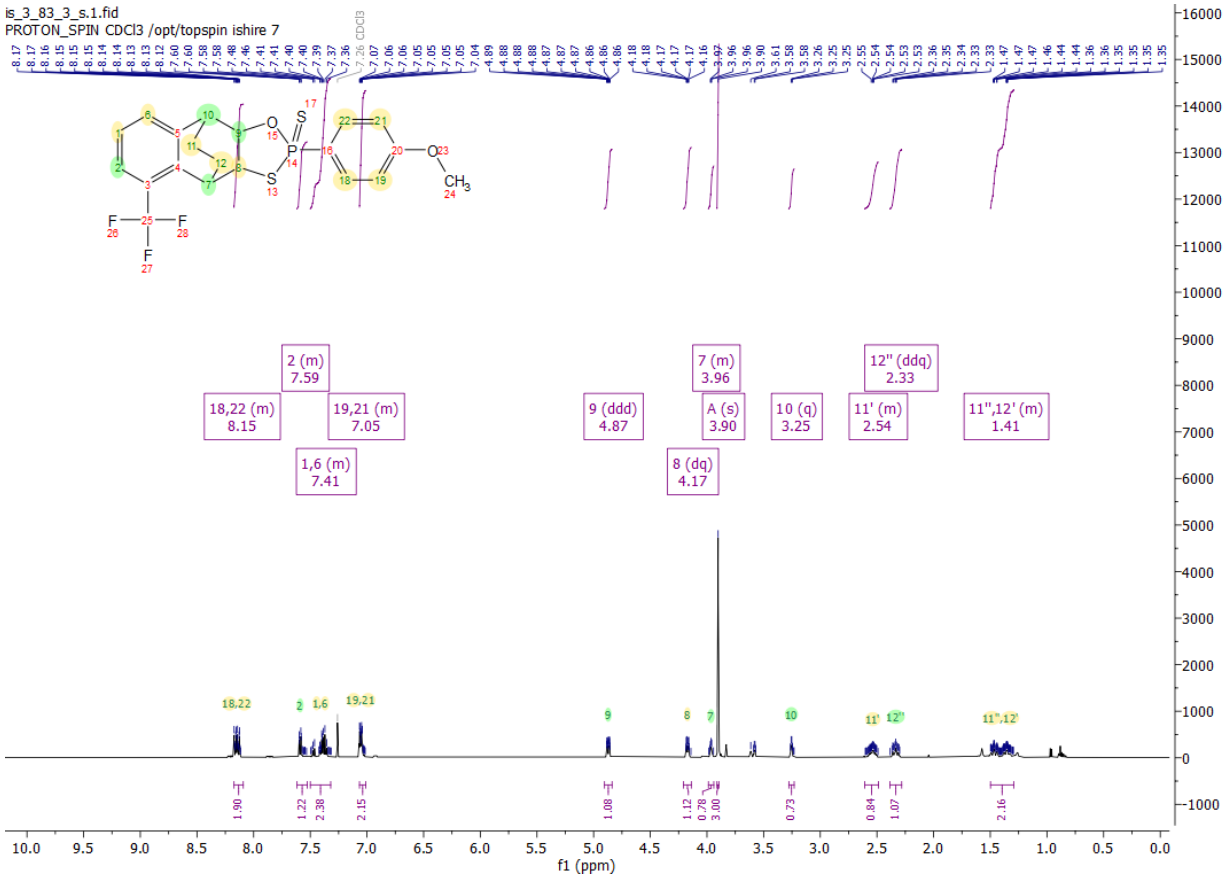

is_3_82_f24-31.2.fid
C13CPD_SIENA CDCl3 /opt/topspin ishire 7
1 (s) 129.40
9 (s) 118.01
12 (s) 154.24
20,24 (s) 134.76
C (s) 114.03
26 (s) 55.58
B (s) 39.31
7 (s) 18.50
22 (d) 163.72
A (s) 134.64
21,23 (s) 114.16
5 (d) 79.38
14 (s) 55.65
2 (d) 31.46
8 (s) 19.19
4 (s) 141.11
10 (s) 127.93
11 (s) 109.63
3 (s) 53.41
6 (s) 39.39
19 (d) 123.79
f1 (ppm)

^{31}P NMR:

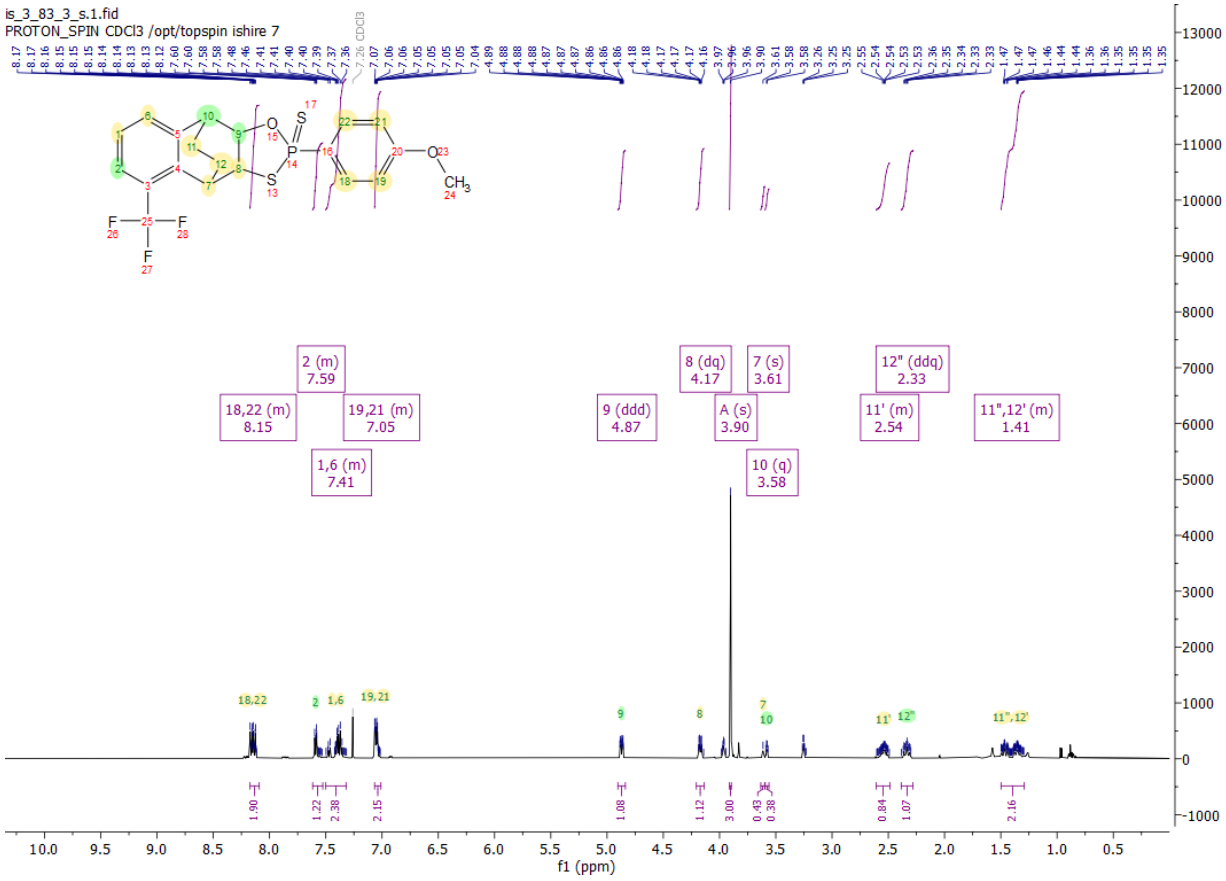

is_3_82_f24_31_8.fid
108.47
108.33
108.20
108.10
108.07
107.92
17 (m)
108.33
17
1.00
f1 (ppm)

TPT-7

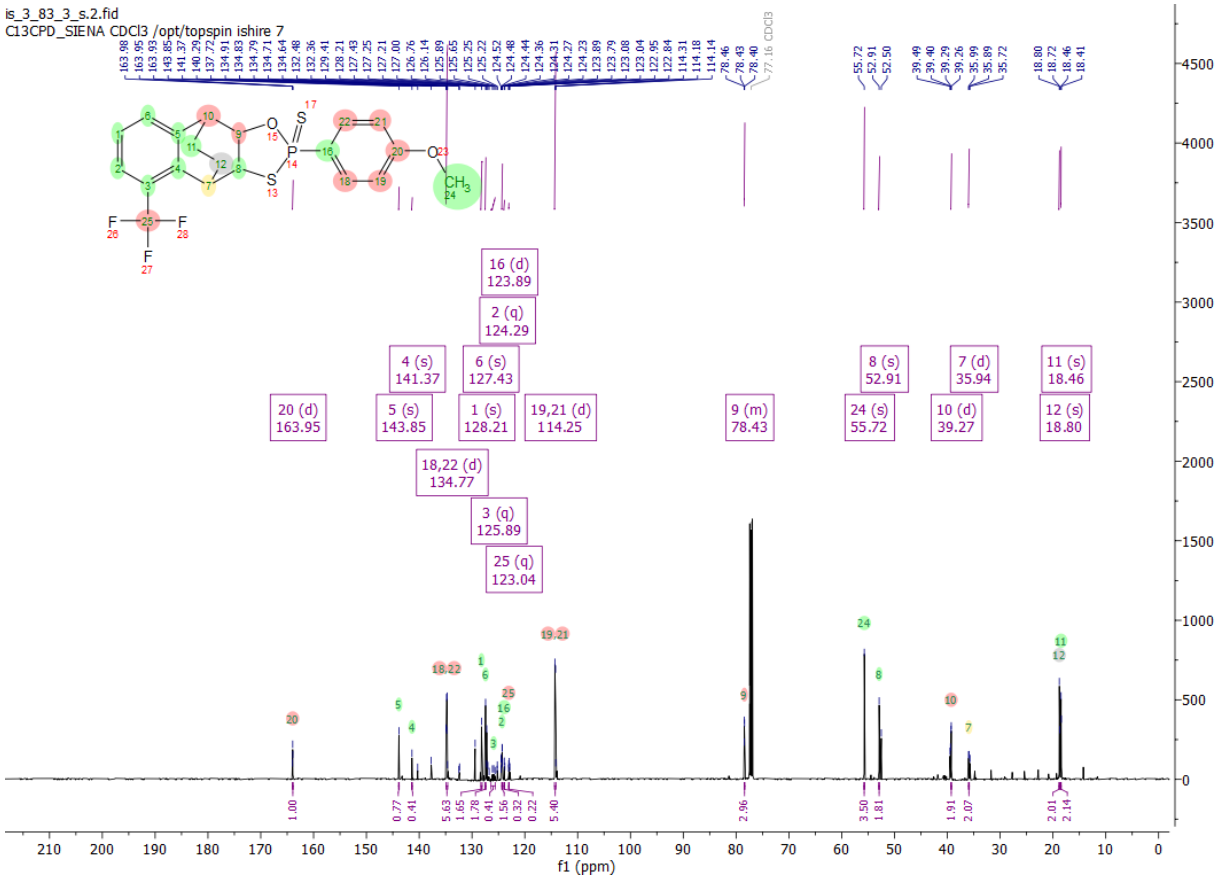
^{1}H NMR (Major):



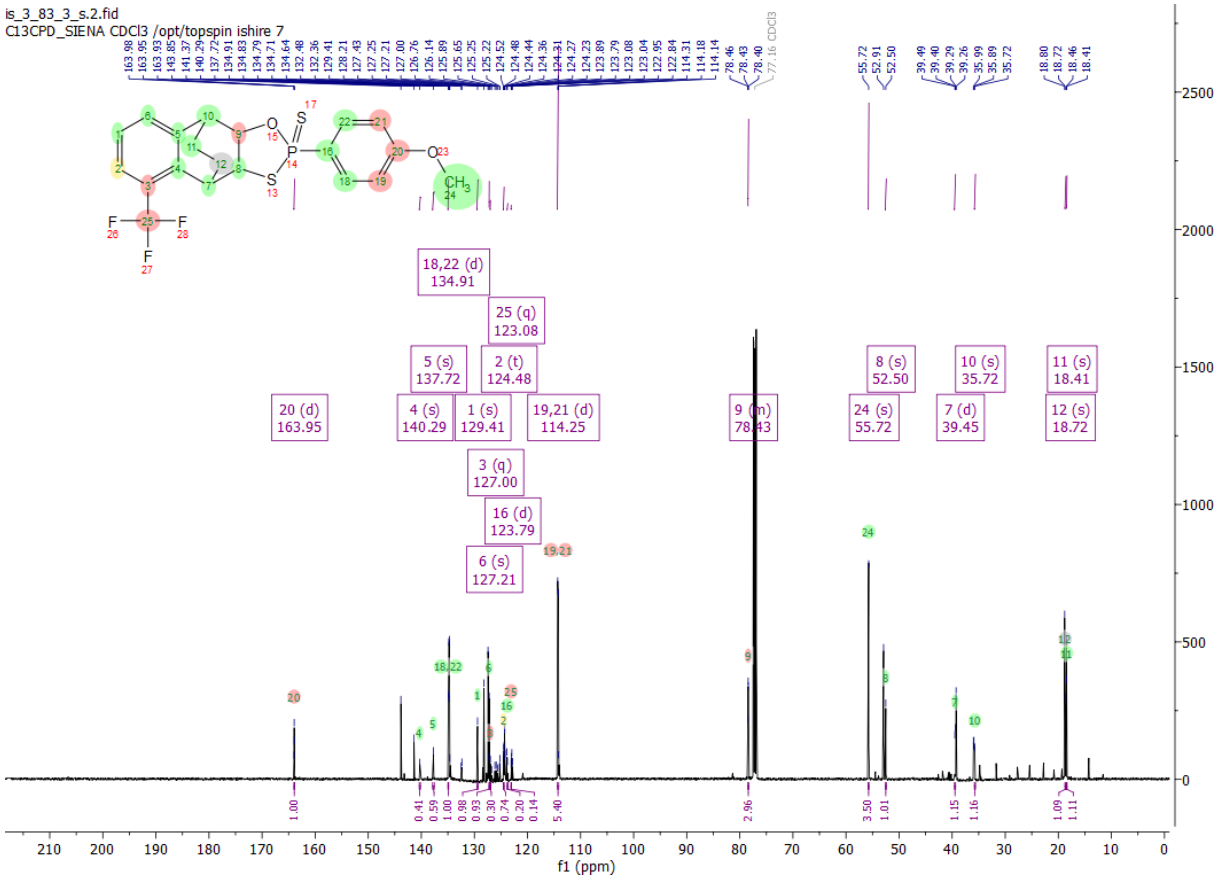
^{1}H NMR (minor):


is_3_83_3_s.1.fid
PROTON_SPIN CDCl3 /opt/topspin ishire 7
2 (m) 7.59
18,22 (m) 8.15
19,21 (m) 7.05
1,6 (m) 7.41
9 (ddd) 4.87
8 (dq) 4.17
7 (s) 3.61
A (s) 3.90
10 (q) 3.58
12" (ddq) 2.33
11' (m) 2.54
11",12' (m) 1.41
f1 (ppm)

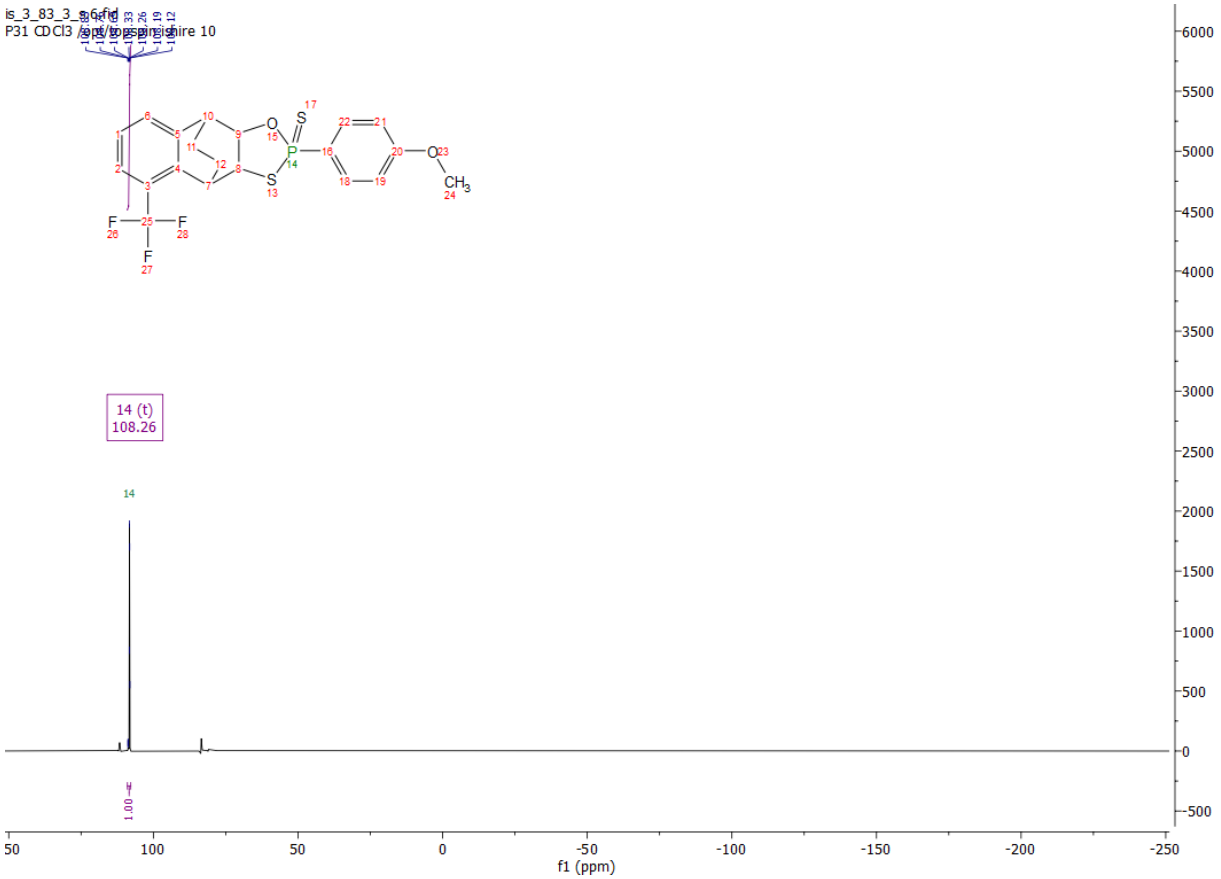
^{13}C NMR (major):



^{13}C NMR (minor):

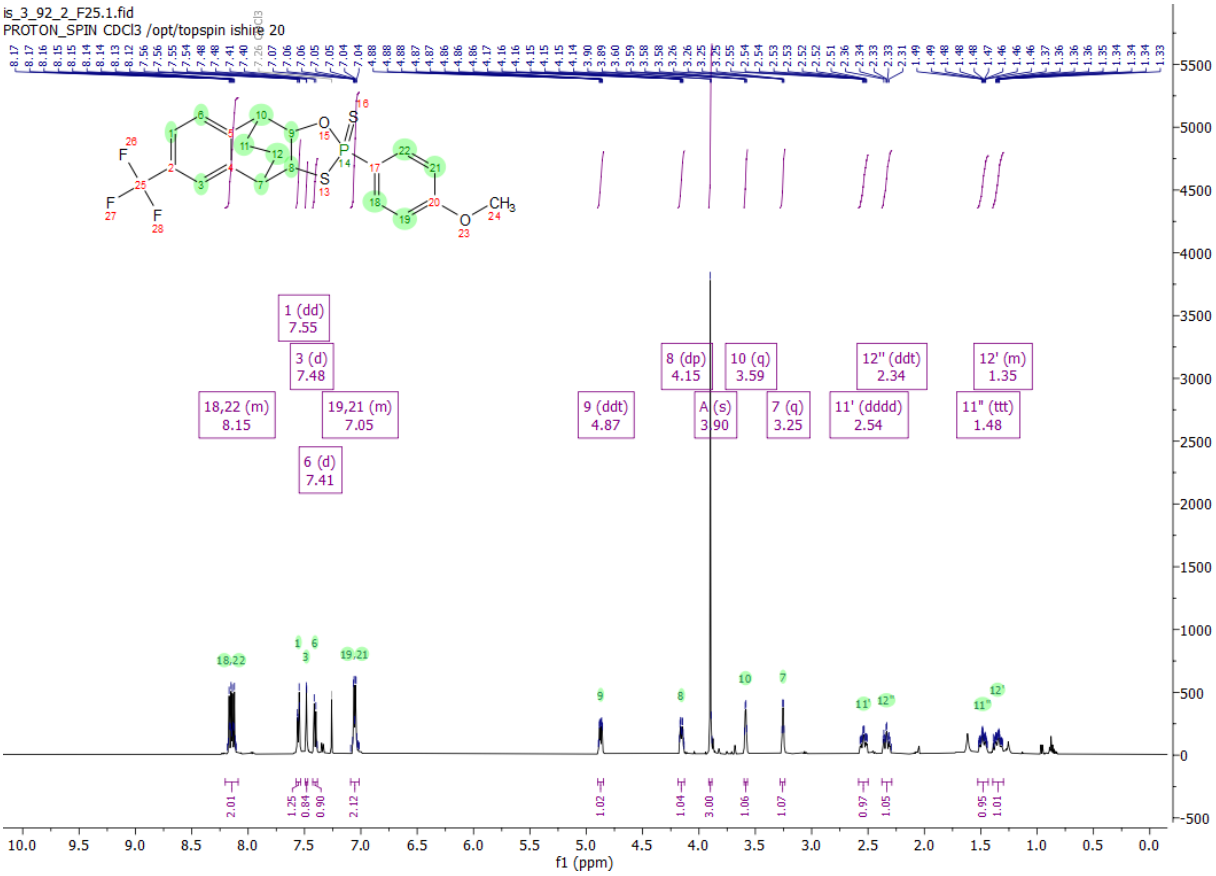


^{31}P NMR:

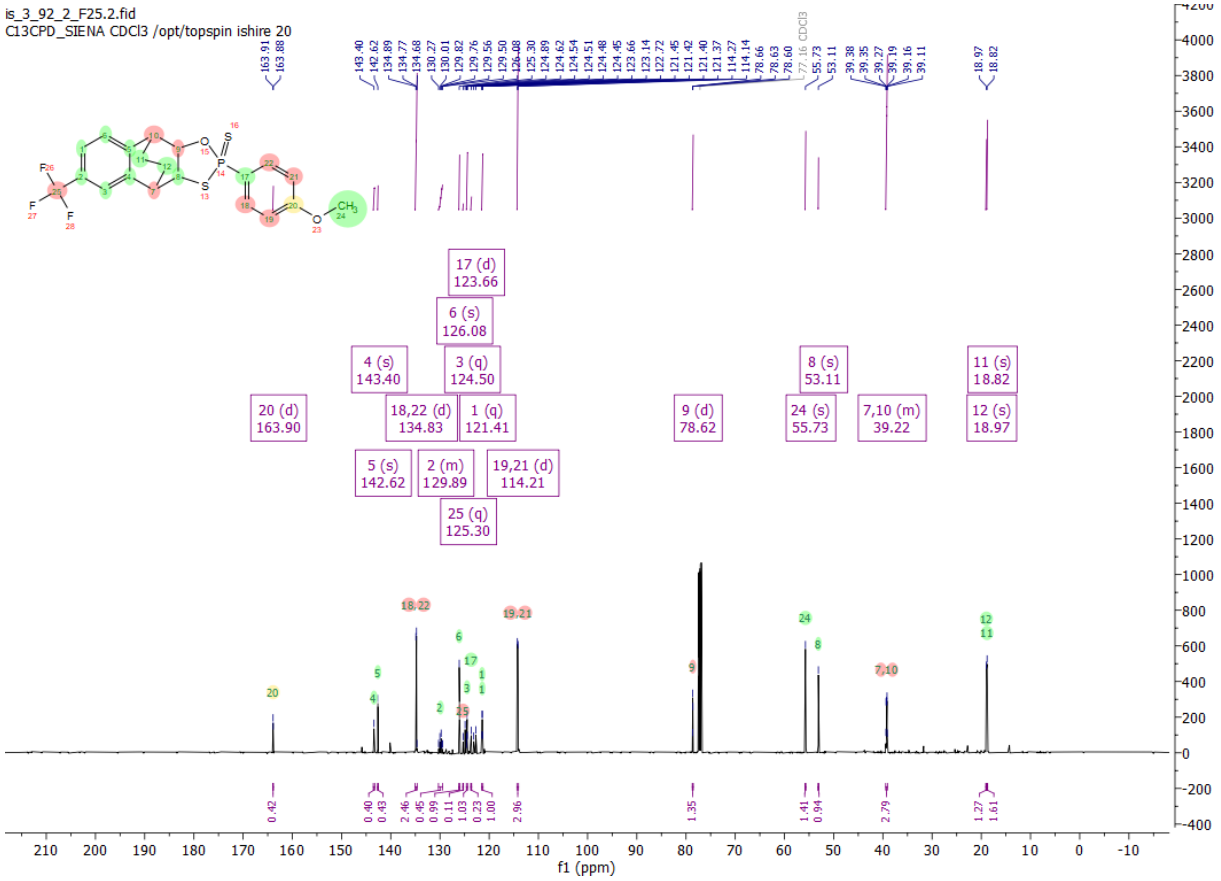

is_3_83_3_a6.fid
P31 CDCl3 /opt/topspin4/shire 10
14 (t)
108.26
14
1.00
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
50
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

TPT-8

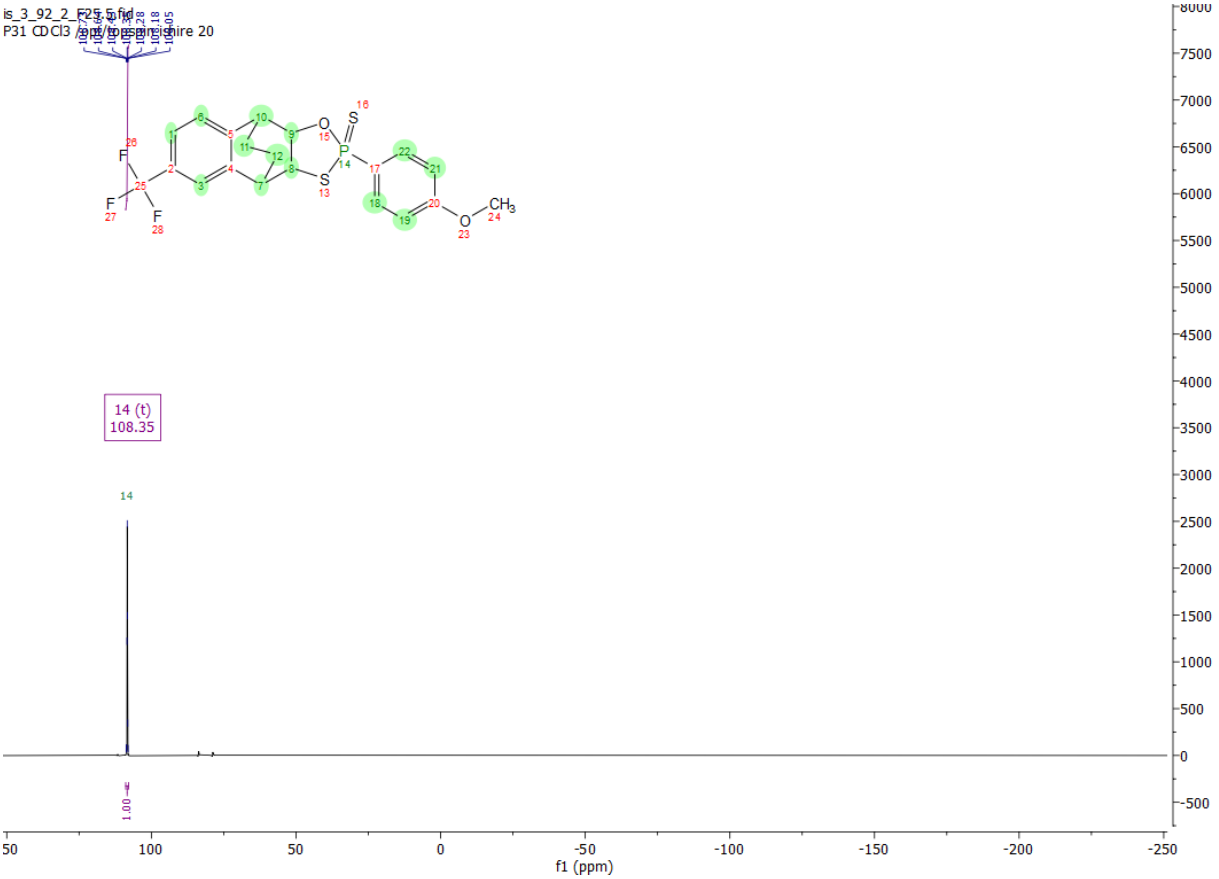
^{1}H NMR:


is_3_92_2_F25.1.fid
PROTON_SPIN CDCl3 /opt/topspin ishire 20
1 (dd) 7.55
3 (d) 7.48
18,22 (m) 8.15
19,21 (m) 7.05
6 (d) 7.41
9 (ddt) 4.87
8 (dp) 4.15
10 (q) 3.59
A (s) 3.90
7 (q) 3.25
12'' (ddt) 2.34
11' (dddd) 2.54
12' (m) 1.35
11'' (ttt) 1.48
f1 (ppm)

^{13}C NMR:

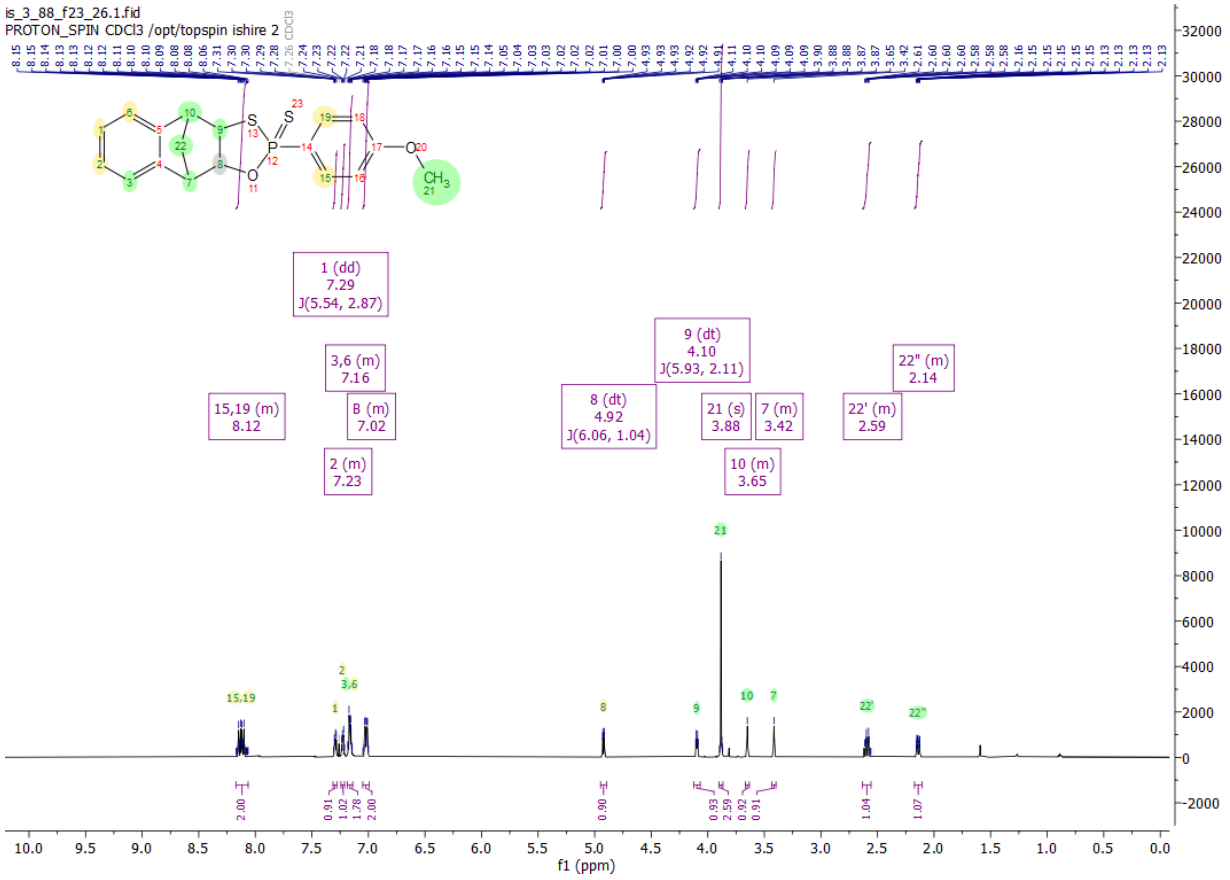

is_3_92_2_F25.2.fid
C13CPD_SIENA CDCl3 /opt/topspin ishire 20
17 (d) 123.66
6 (s) 126.08
4 (s) 143.40
3 (q) 124.50
8 (s) 53.11
11 (s) 18.82
20 (d) 163.90
18,22 (d) 134.83
1 (q) 121.41
9 (d) 78.62
24 (s) 55.73
7,10 (m) 39.22
12 (s) 18.97
5 (s) 142.62
2 (m) 129.89
19,21 (d) 114.21
25 (q) 125.30
f1 (ppm)

^{31}P NMR:

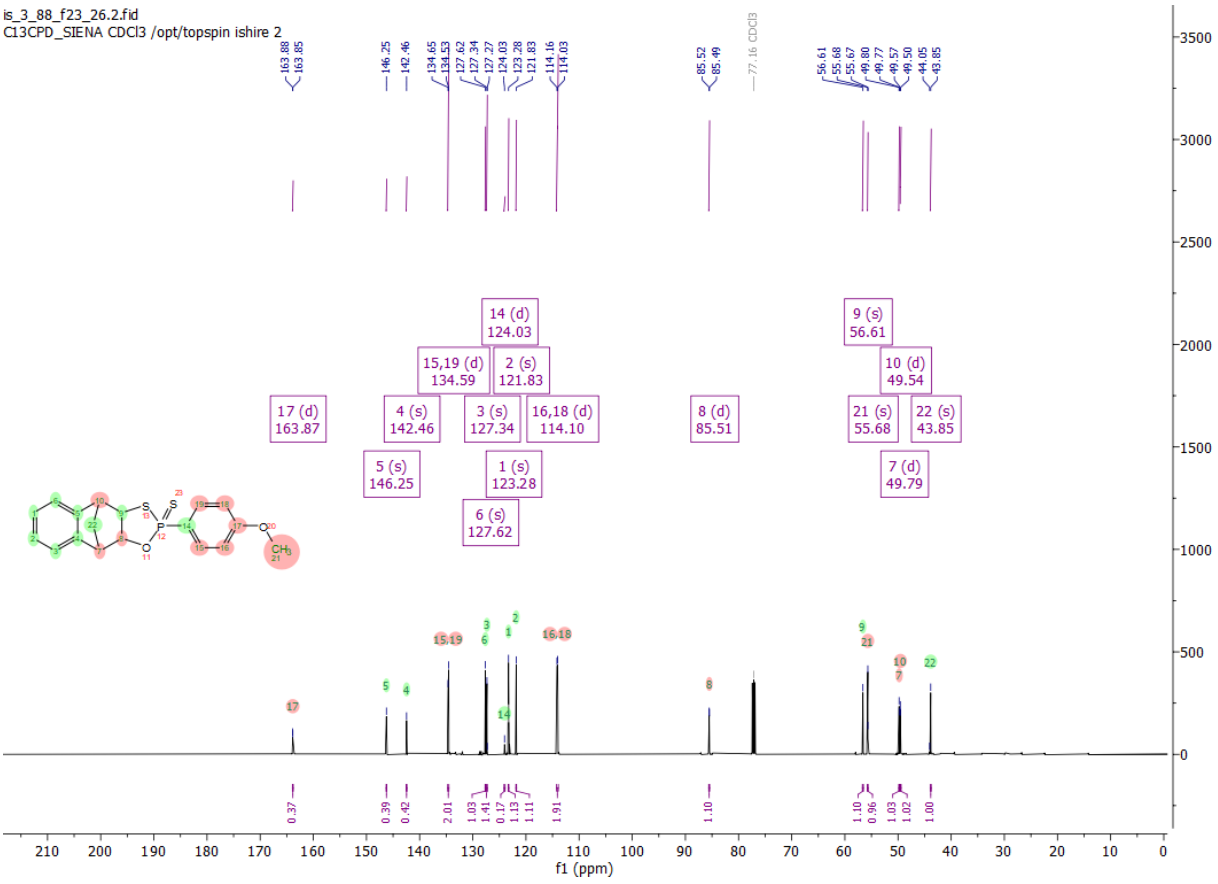

is_3_92_2_F25.5.fid
P31 CDCl3 /opt/topspin/shire 20
14 (t)
108.35
14
1.00
f1 (ppm)

TPT-9

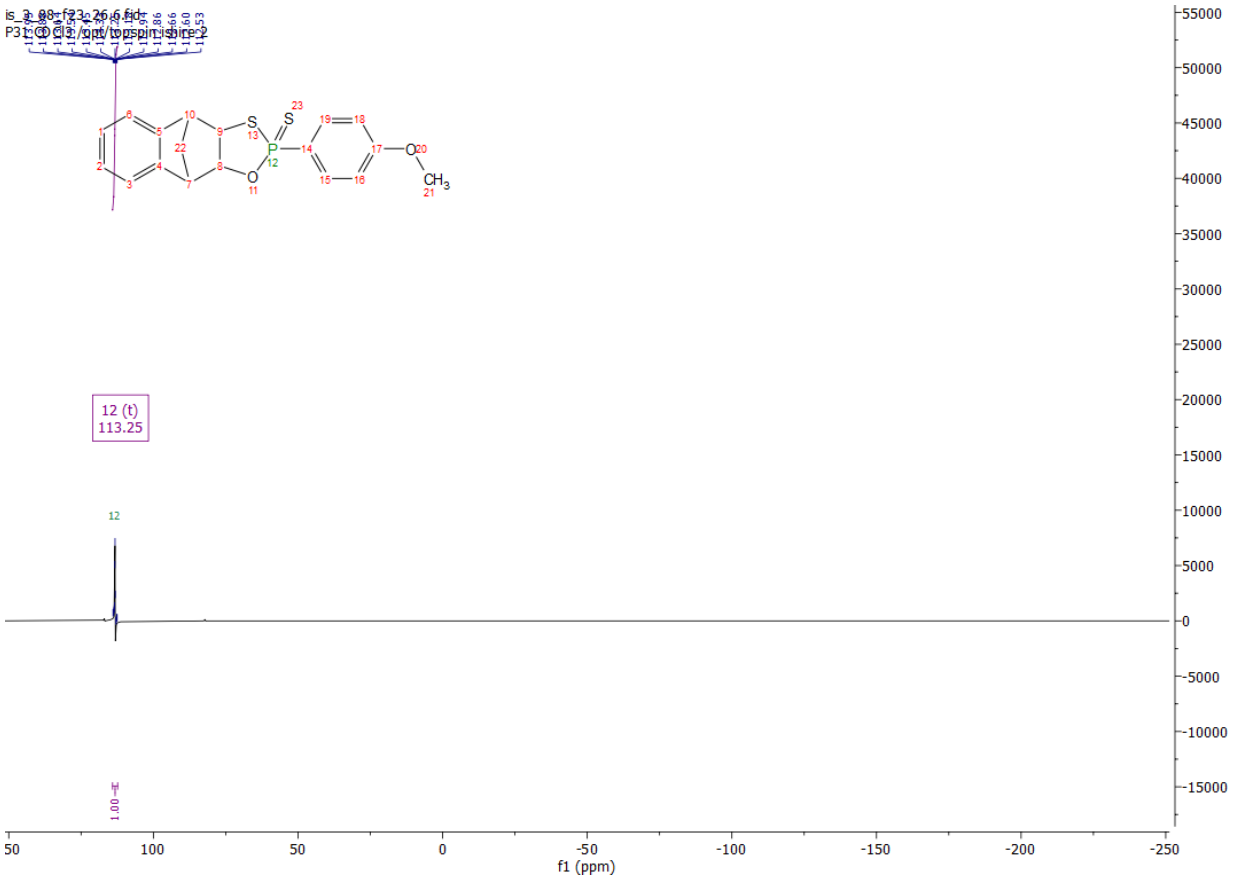
^{1}H NMR:


is_3_88_f23_26.1.fid
PROTON_SPIN CDCl3 /opt/topspin ishire 2
1 (dd)
7.29
J(5.54, 2.87)
3,6 (m)
7.16
B (m)
7.02
2 (m)
7.23
15,19 (m)
8.12
9 (dt)
4.10
J(5.93, 2.11)
8 (dt)
4.92
J(6.06, 1.04)
21 (s)
3.88
7 (m)
3.42
10 (m)
3.65
22" (m)
2.14
22' (m)
2.59
f1 (ppm)

^{13}C NMR:

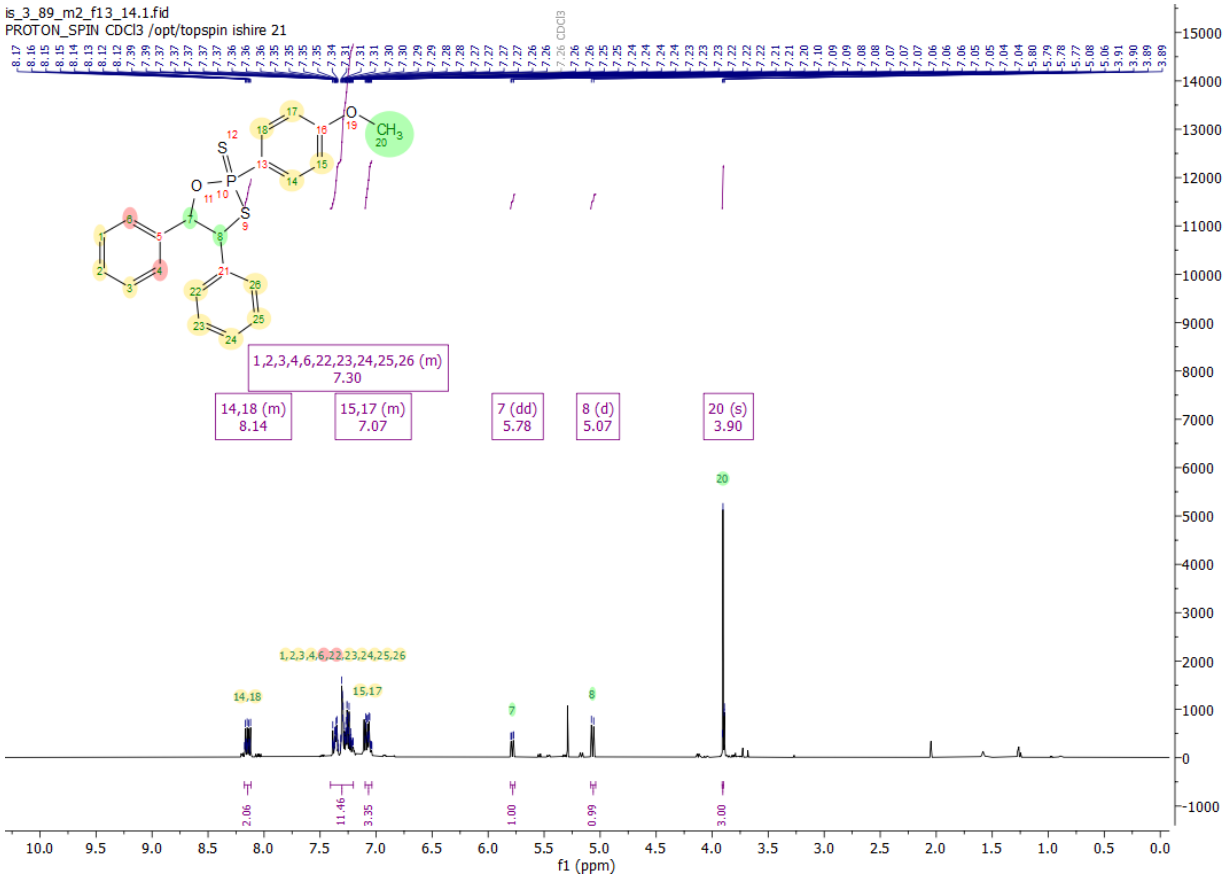

is_3_88_f23_26.2.fid
C13CPD_SIENA CDCl3 /opt/topspin ishire 2
f1 (ppm)

^{31}P NMR:

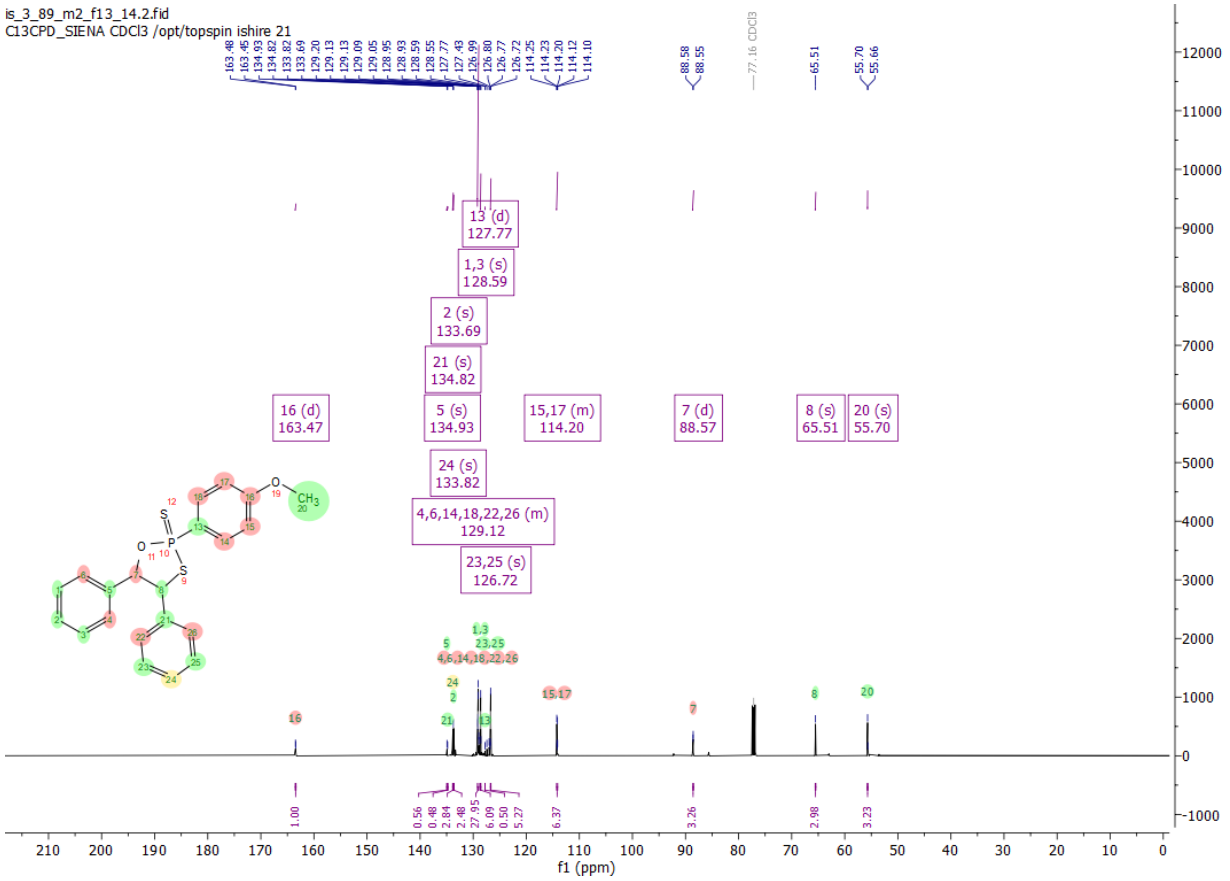

12 (t)
113.25
12
1.00
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
50
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

TPT-10

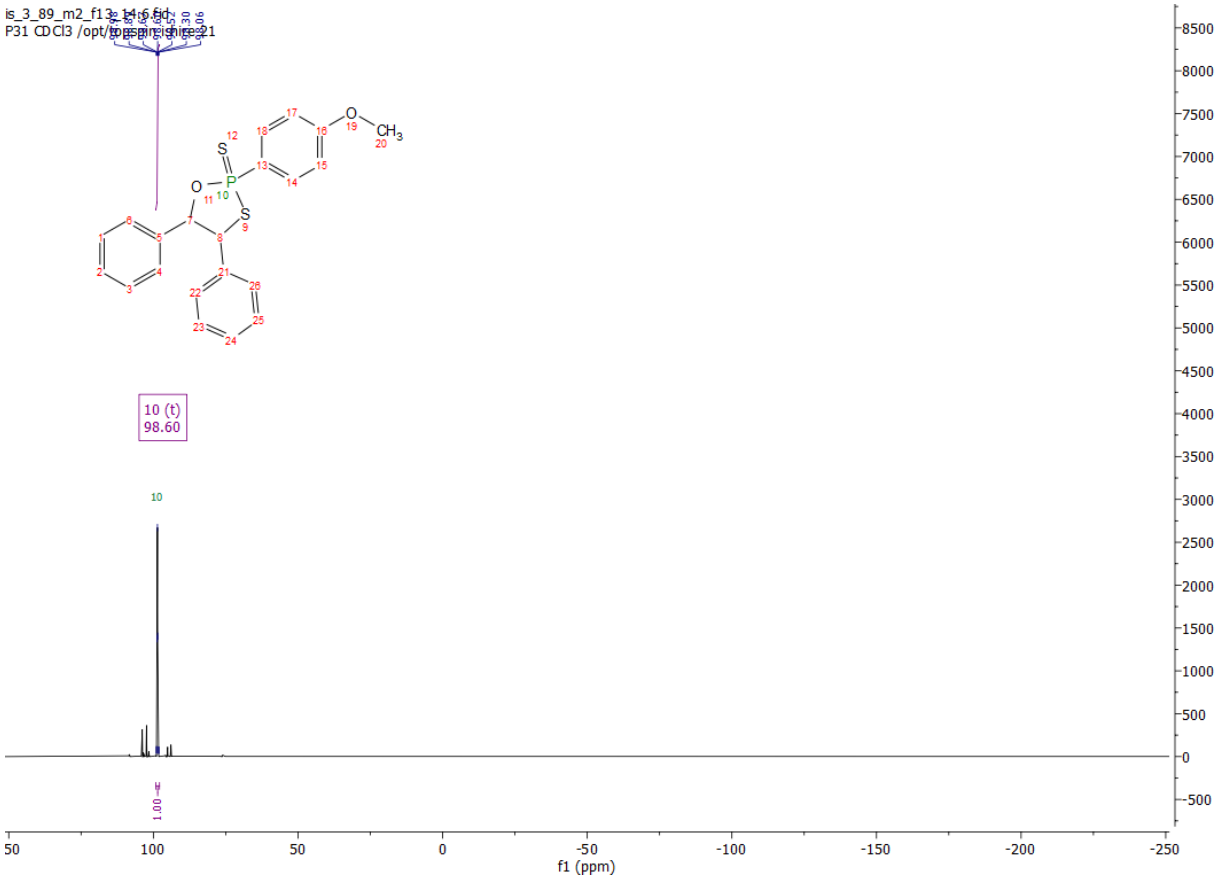
^{1}H NMR:


is_3_89_m2_f13_14.1.fid
PROTON_SPIN CDCl3 /opt/topspin ishire 21
1,2,3,4,6,22,23,24,25,26 (m)
7.30
14,18 (m)
8.14
15,17 (m)
7.07
7 (dd)
5.78
8 (d)
5.07
20 (s)
3.90
f1 (ppm)

^{13}C NMR:

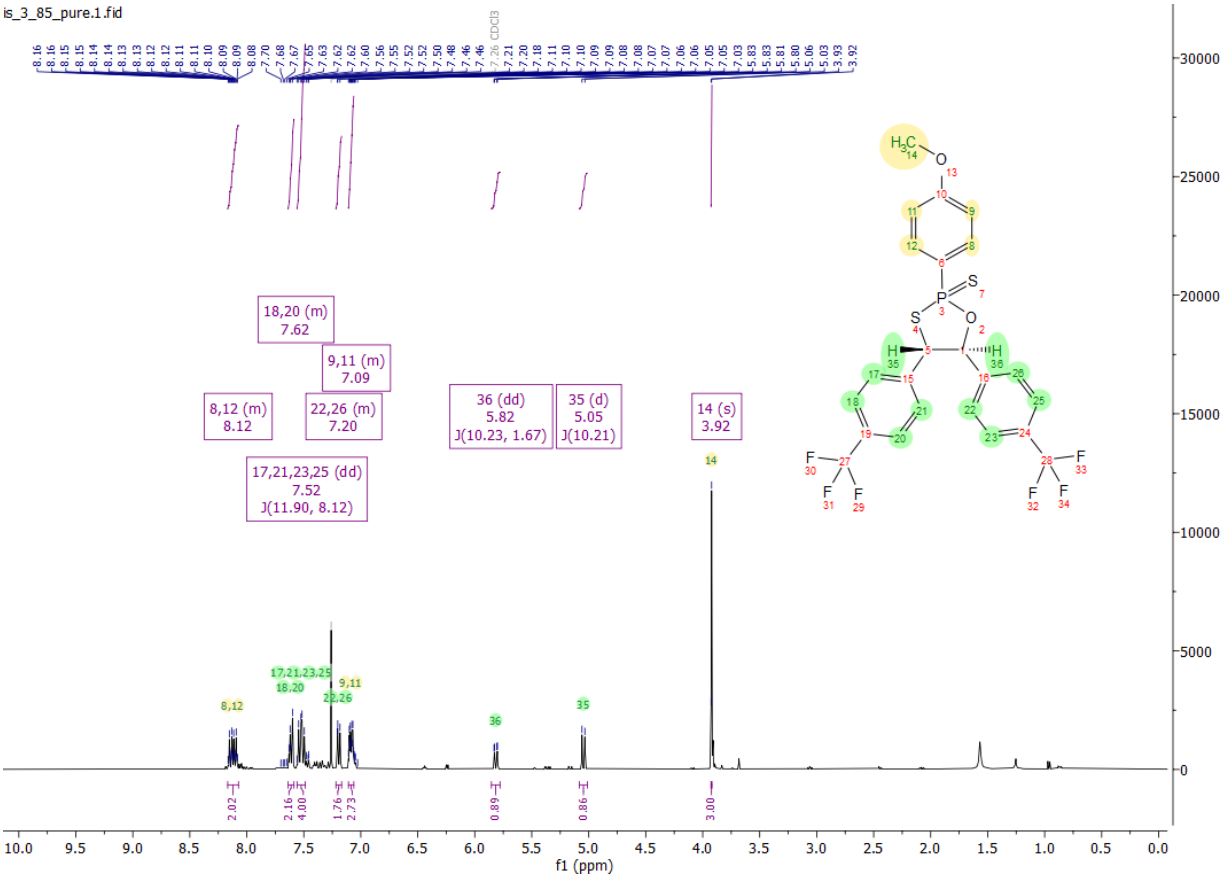

is_3_89_m2_f13_14.2.fid
C13CPD_SIENA CDCl3 /opt/topspin ishire 21
13 (d)
127.77
1,3 (s)
128.59
2 (s)
133.69
21 (s)
134.82
16 (d)
163.47
5 (s)
134.93
15,17 (m)
114.20
7 (d)
88.57
8 (s)
65.51
20 (s)
55.70
24 (s)
133.82
4,6,14,18,22,26 (m)
129.12
23,25 (s)
126.72
f1 (ppm)

^{31}P NMR:

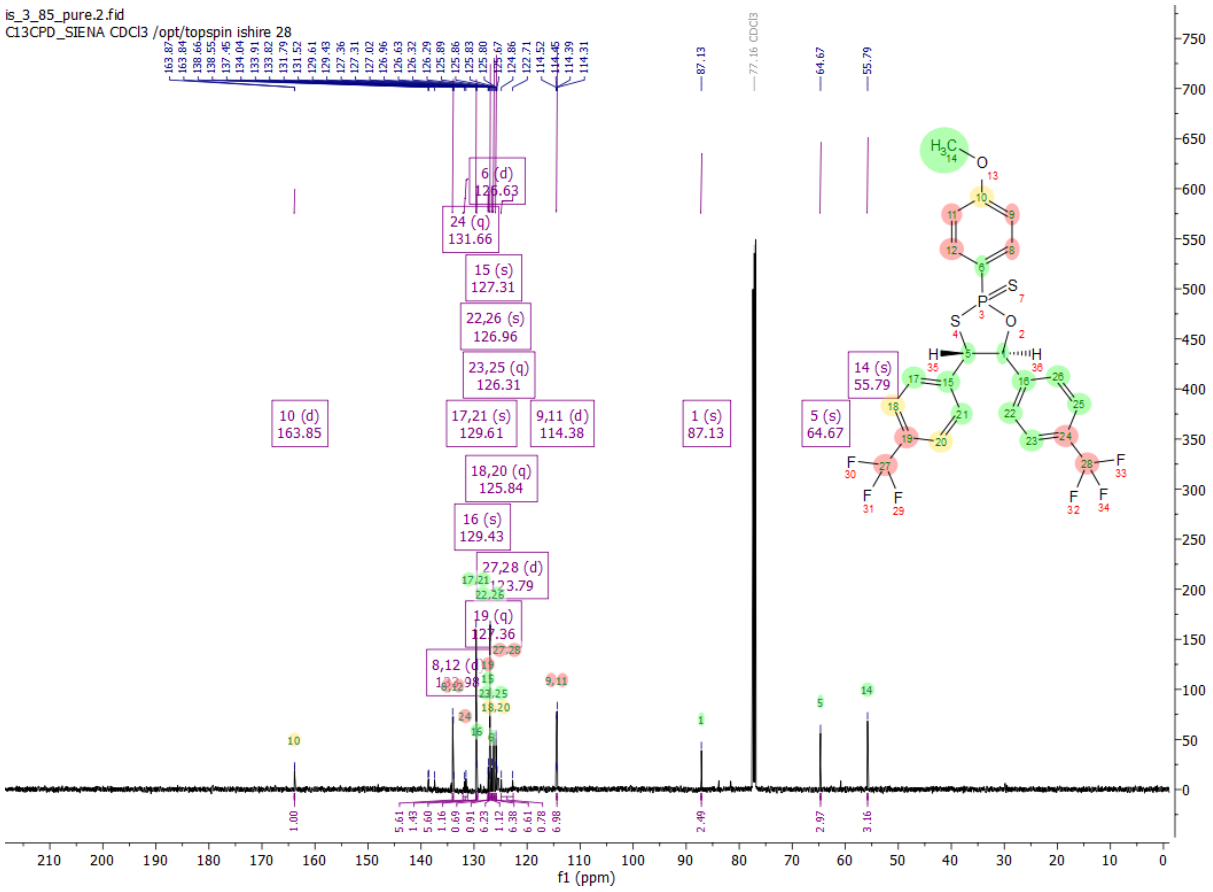

is_3_89_m2_f13_14.6.fid
P31 CDCl3 /opt/topspin/exp/stan/nmr/lists/pp/standard_pp 21
10 (t)
98.60
10
1.00
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
50
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

TPT-11

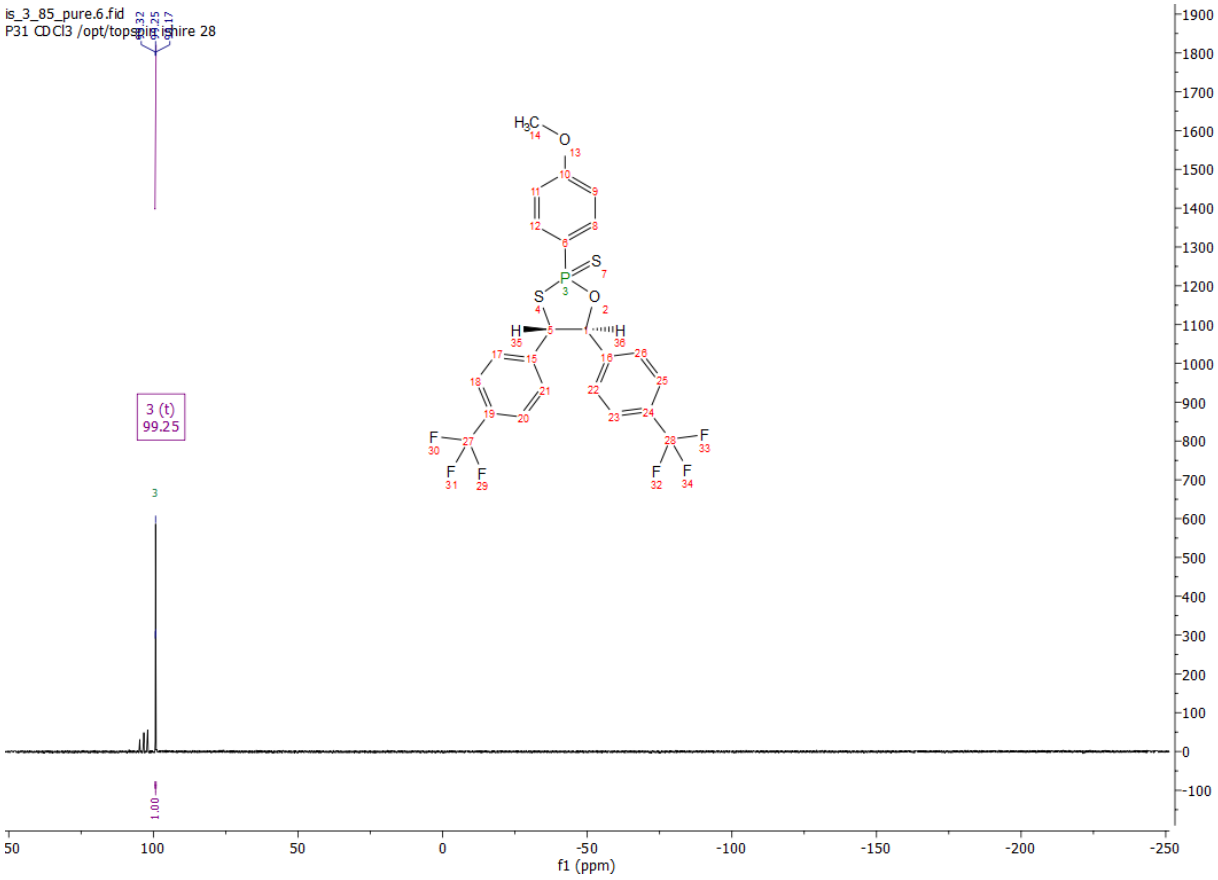
^{1}H NMR:


is_3_85_pure.1.fid
18,20 (m)
7.62
9,11 (m)
7.09
8,12 (m)
8.12
22,26 (m)
7.20
17,21,23,25 (dd)
7.52
J(11.90, 8.12)
36 (dd)
5.82
J(10.23, 1.67)
35 (d)
5.05
J(10.21)
14 (s)
3.92
f1 (ppm)

^{13}C NMR:

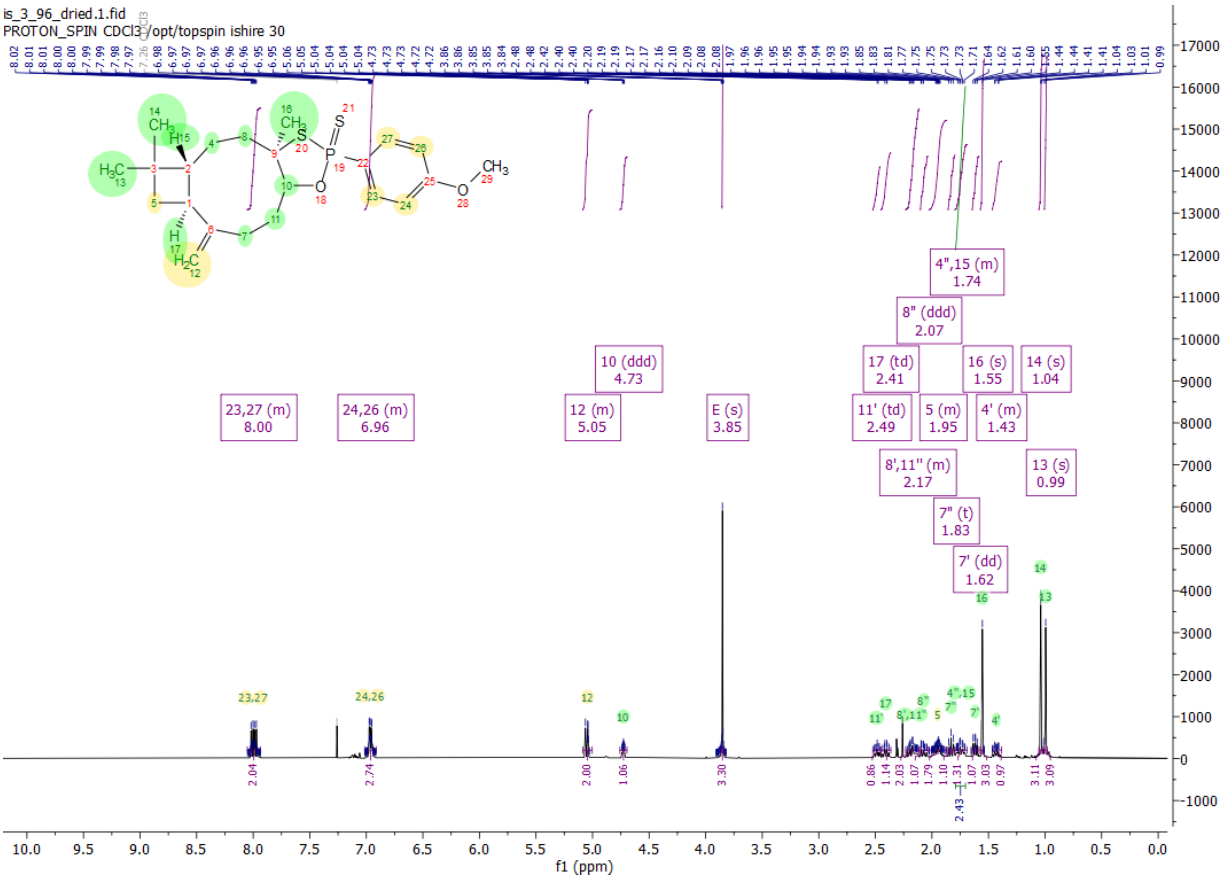

is_3_85_pure.2.fid
C13CPD_SIENA CDCl3 /opt/topspin ishire 28
77.16 CDCl3
87.13
64.67
55.79
6 (d)
126.63
24 (q)
131.66
15 (s)
127.31
22,26 (s)
126.96
23,25 (q)
126.31
10 (d)
163.85
17,21 (s)
129.61
9,11 (d)
114.38
1 (s)
87.13
5 (s)
64.67
14 (s)
55.79
18,20 (q)
125.84
16 (s)
129.43
27,28 (d)
123.79
19 (q)
127.36
8,12 (d)
f1 (ppm)

^{31}P NMR

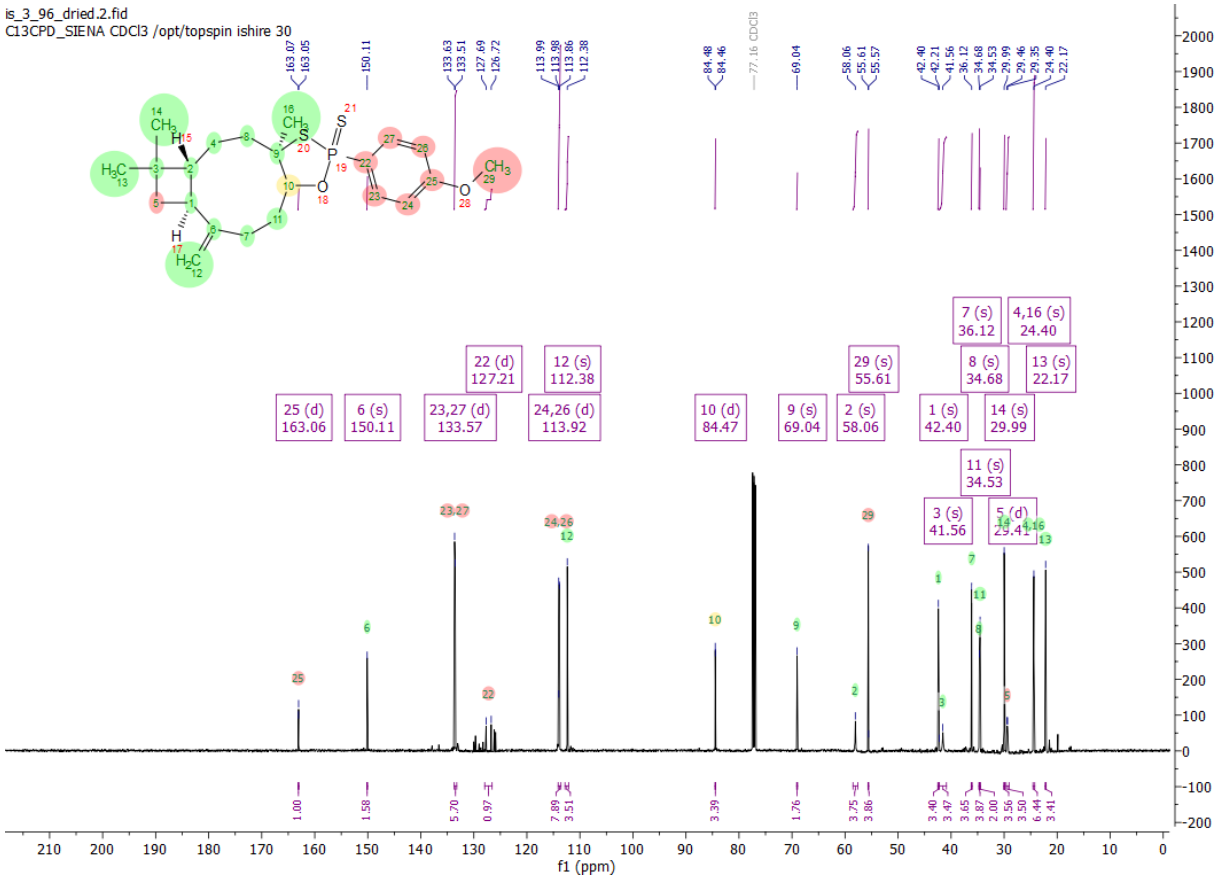

is_3_85_pure.6.fid
P31 CDCl3 /opt/topspin/exshire 28
99.32
99.25
99.17
3 (t)
99.25
3
1.00
50
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

TPT-12

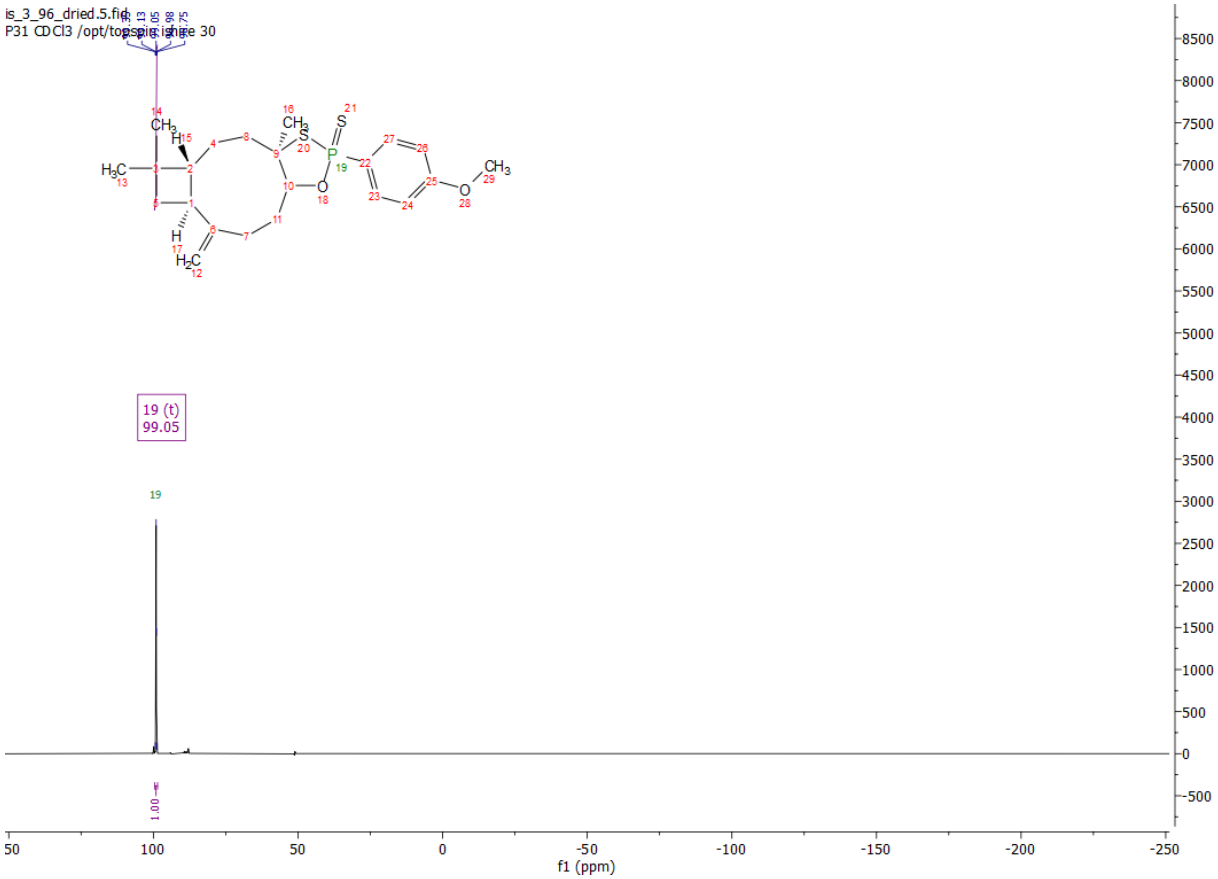
^{1}H NMR:


is_3_96_dried.1.fid
PROTON_SPIN CDCl3 /opt/topspin ishire 30
4",15 (m) 1.74
8" (ddd) 2.07
10 (ddd) 4.73
17 (td) 2.41
16 (s) 1.55
14 (s) 1.04
23,27 (m) 8.00
24,26 (m) 6.96
12 (m) 5.05
E (s) 3.85
11' (td) 2.49
5 (m) 1.95
4' (m) 1.43
8',11'' (m) 2.17
13 (s) 0.99
7'' (t) 1.83
7' (dd) 1.62
f1 (ppm)

^{13}C NMR:

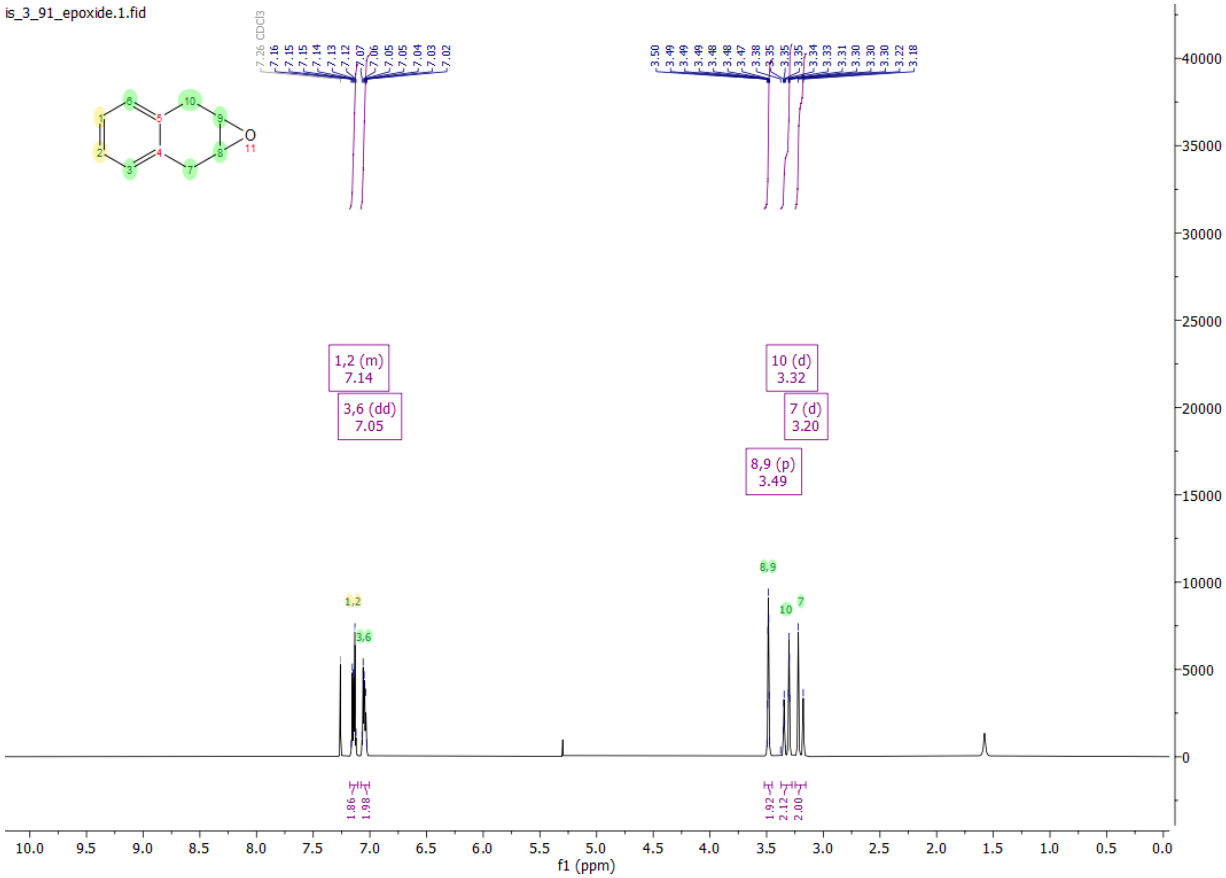

is_3_96_dried.2.fid
C13CPD_SIENA CDCl3 /opt/topspin ishire 30
25 (d) 163.06
6 (s) 150.11
23,27 (d) 133.57
22 (d) 127.21
24,26 (d) 113.92
12 (s) 112.38
10 (d) 84.47
9 (s) 69.04
2 (s) 58.06
29 (s) 55.61
1 (s) 42.40
3 (s) 41.56
7 (s) 36.12
8 (s) 34.68
14 (s) 29.99
11 (s) 34.53
5 (d) 29.41
4,16 (s) 24.40
13 (s) 22.17
f1 (ppm)

^{31}P NMR:



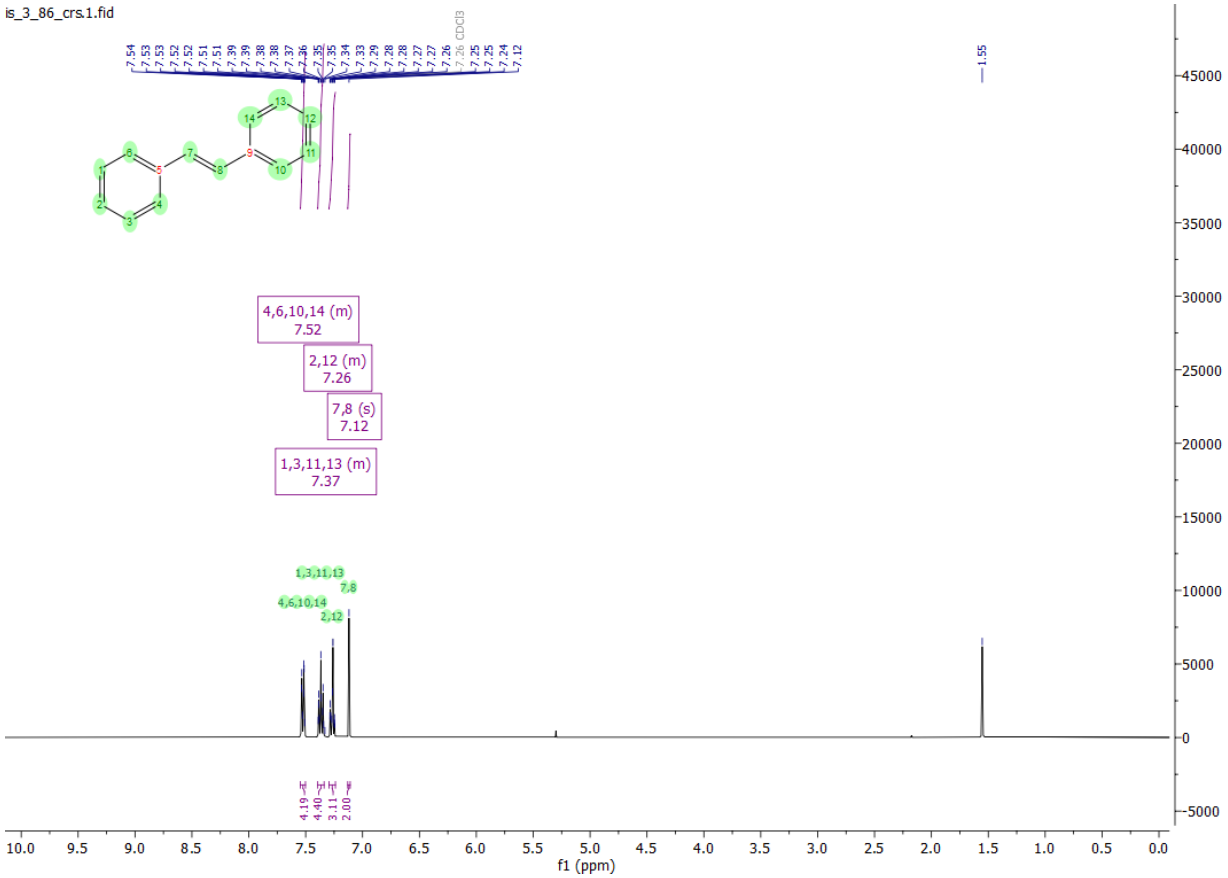
EPO-2 (dihydronaphthalene oxide)

^{1}H NMR:



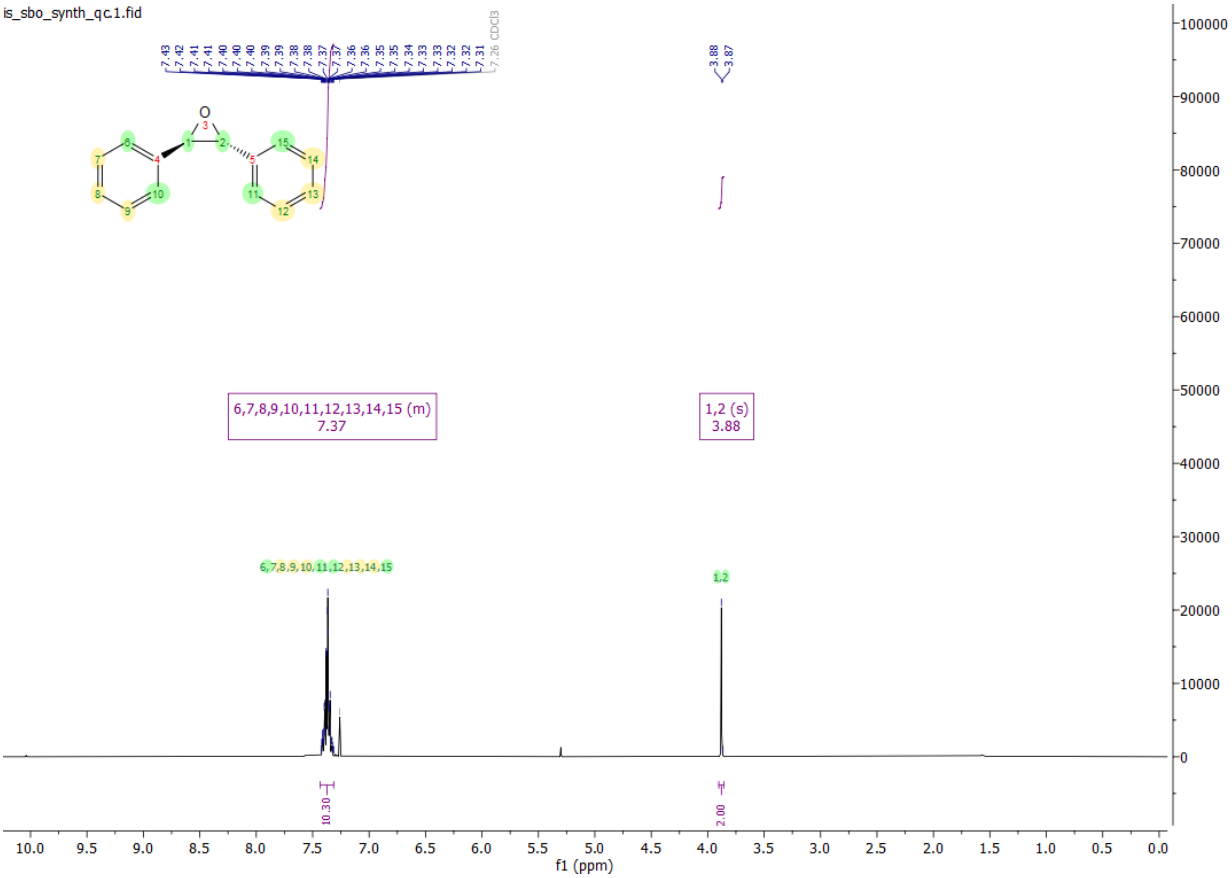
E-Stilbene

^{1}H NMR:



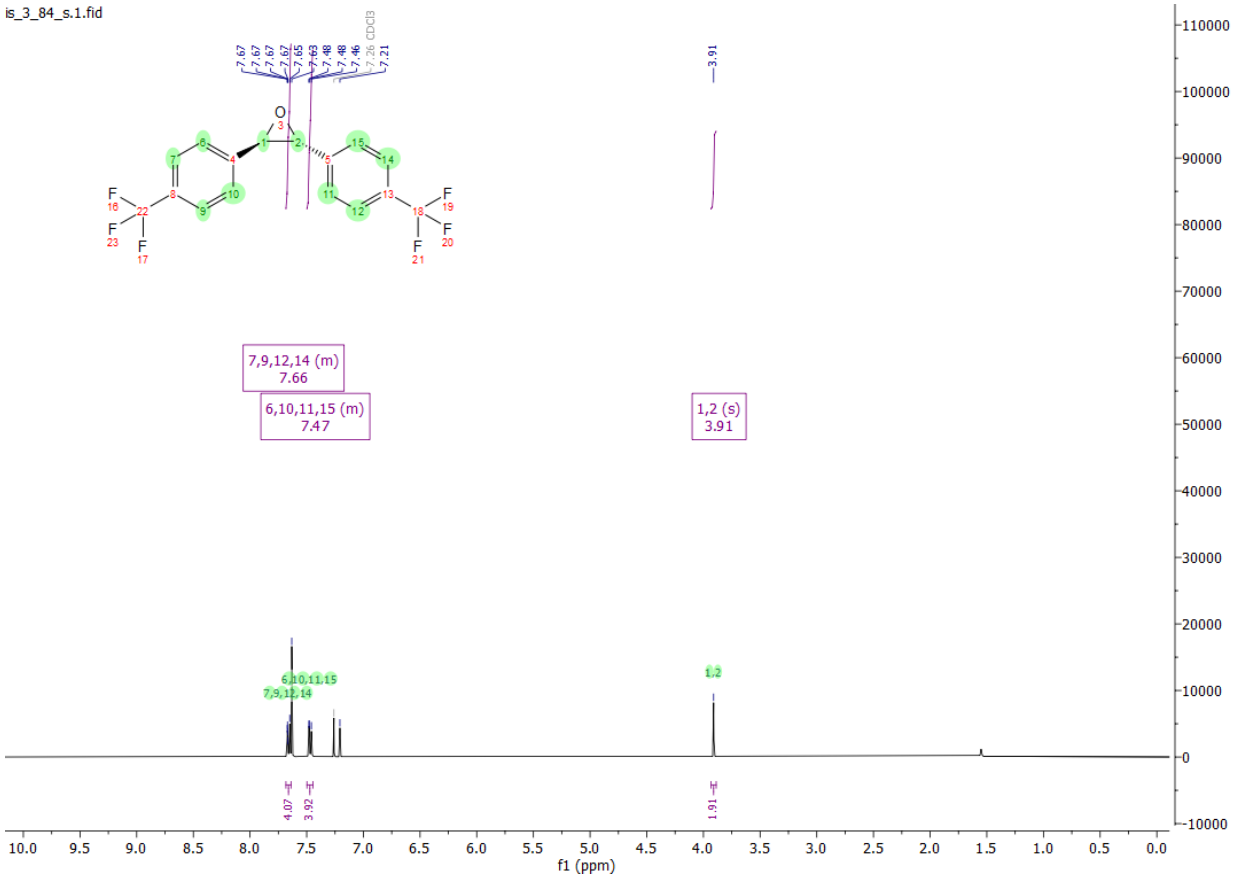
EPO-10

^{1}H NMR


is_sbo_synth_qc.1.fid
7.26 CDCl3
6,7,8,9,10,11,12,13,14,15 (m)
7.37
1,2 (s)
3.88
6,7,8,9,10,11,12,13,14,15
1,2
10.30
2.00
f1 (ppm)

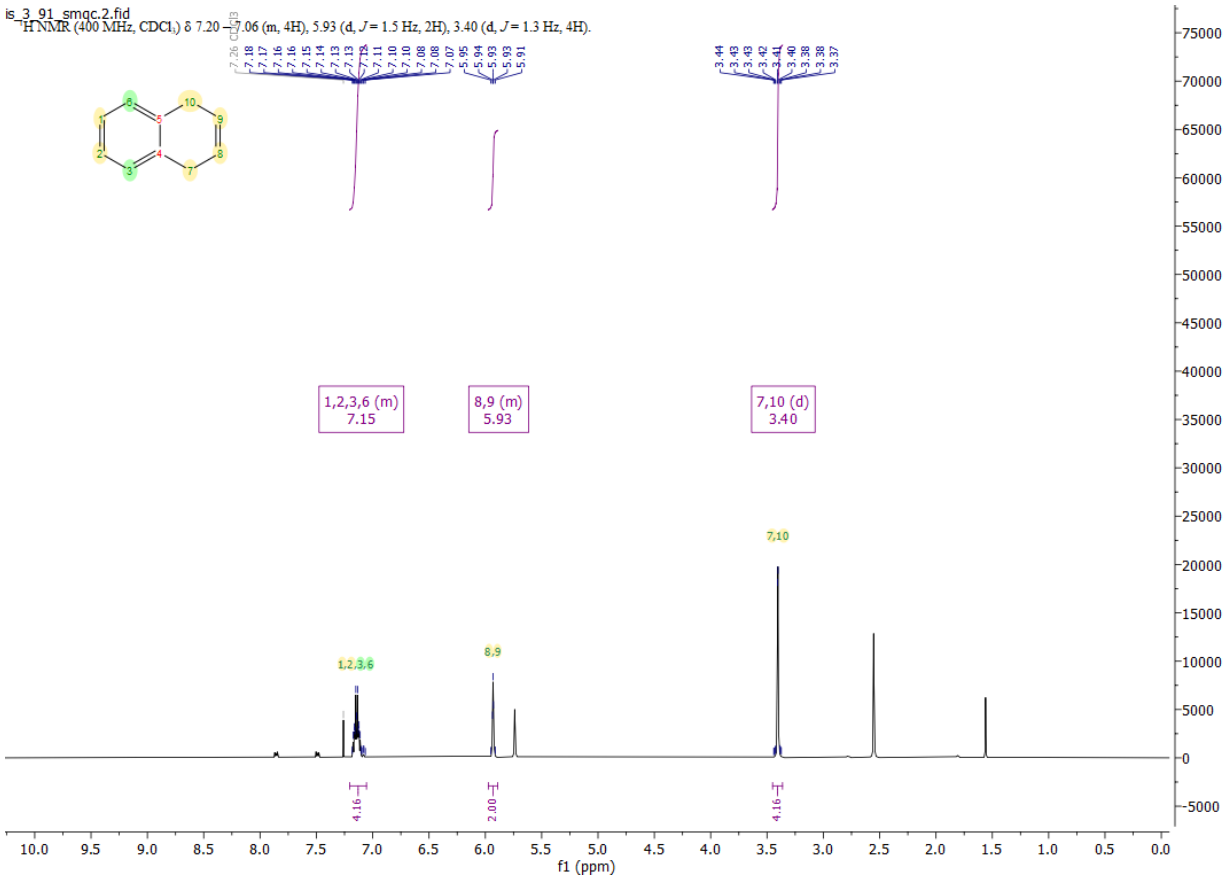
EPO-11

^{1}H NMR



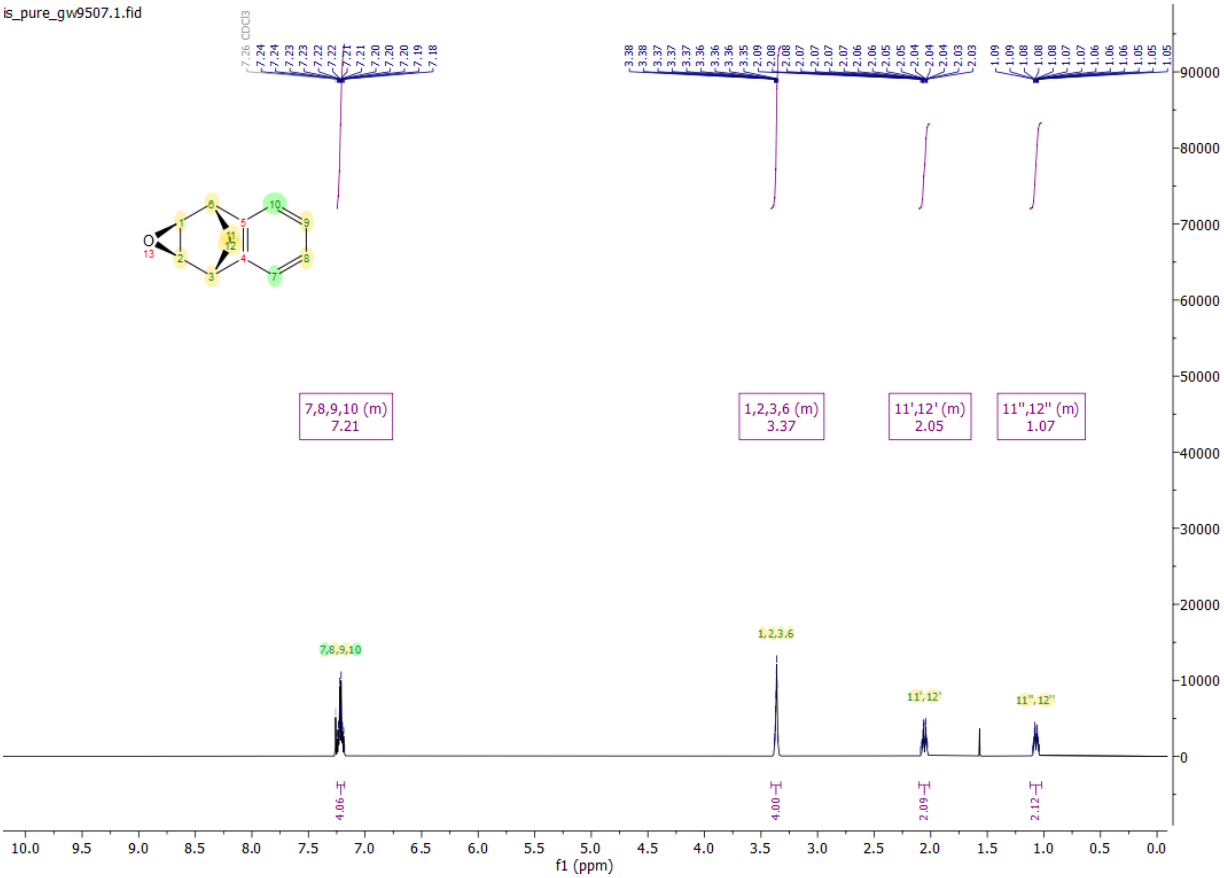
1,4-Dihydronaphthalene

^{1}H NMR:



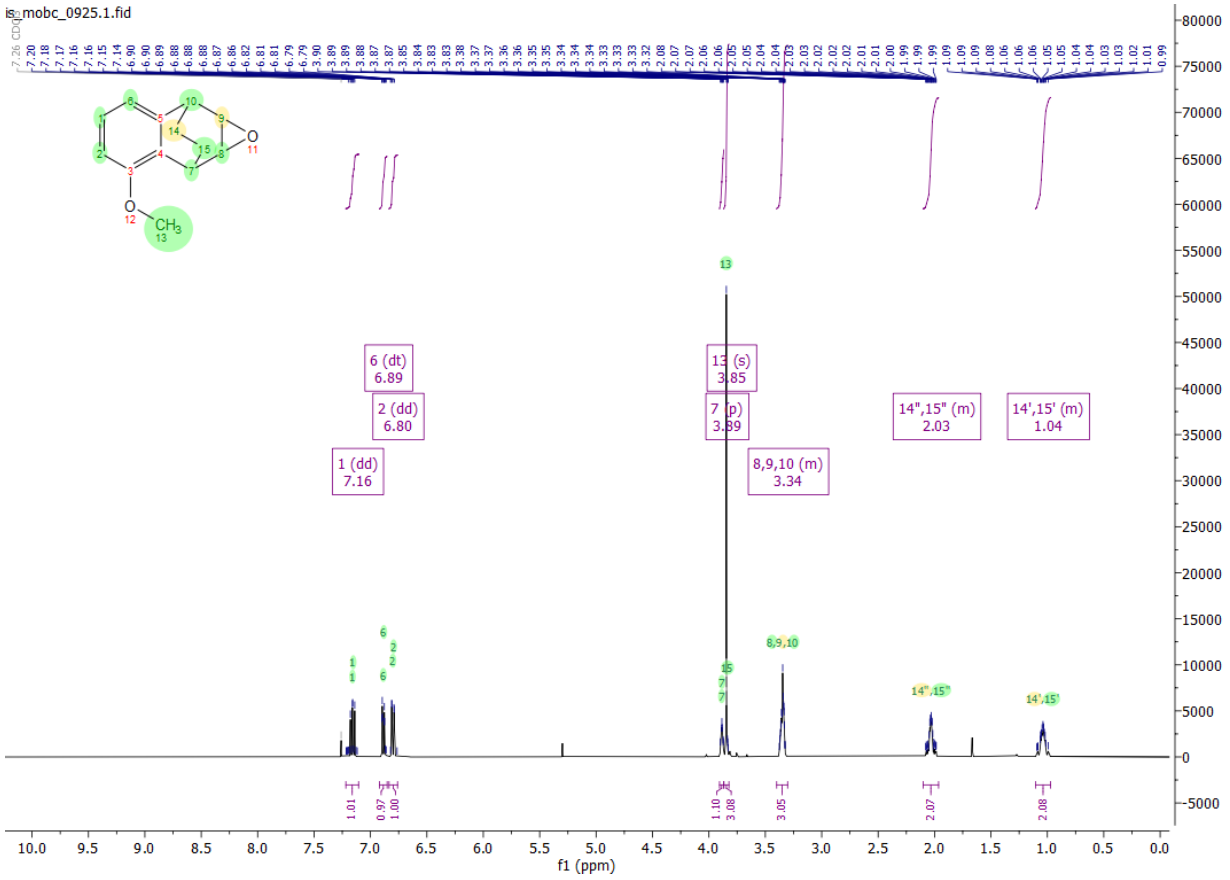
EPO-5

^{1}H NMR

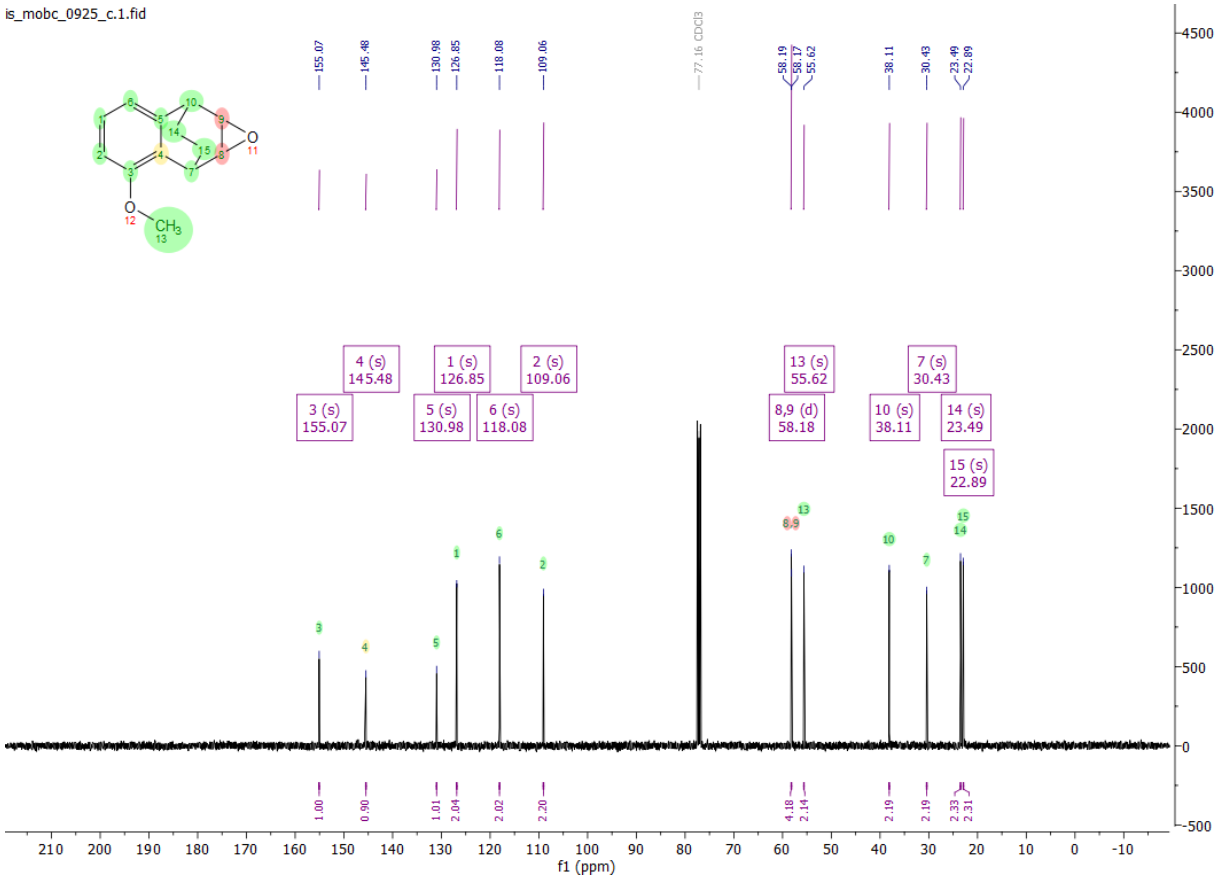

is_pure_gw9507.1.fid
7,8,9,10 (m)
7.21
1,2,3,6 (m)
3.37
11',12' (m)
2.05
11'',12'' (m)
1.07
7,8,9,10
1,2,3,6
11',12'
11'',12''
4.06
4.00
2.09
2.12
f1 (ppm)

EPO-6

^{1}H NMR

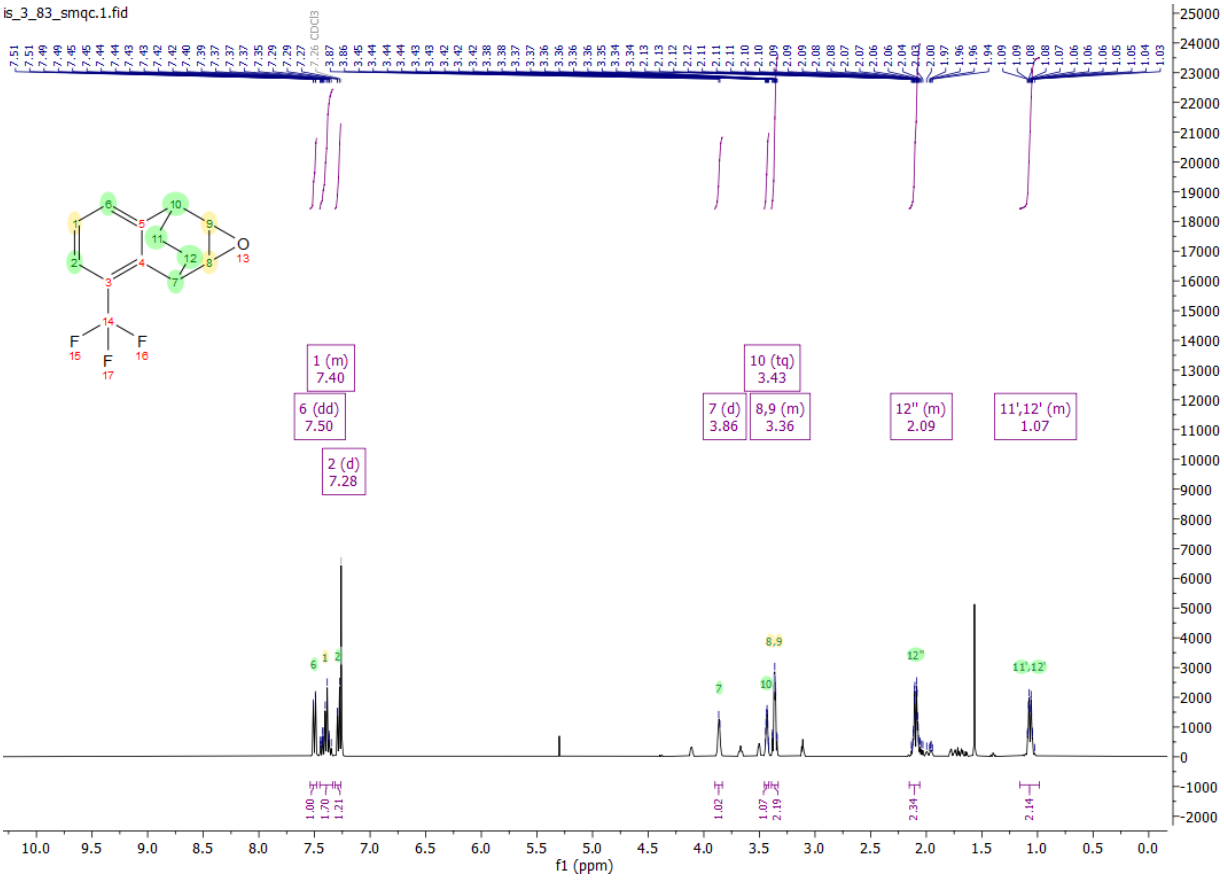

is_mobc_0925.1.fid
6 (dt)
6.89
2 (dd)
6.80
1 (dd)
7.16
13 (s)
3.85
7 (p)
3.39
8,9,10 (m)
3.34
14",15" (m)
2.03
14',15' (m)
1.04
f1 (ppm)

^{13}C NMR


is_mobc_0925_c.1.fid
155.07
145.48
130.98
126.85
118.08
109.06
77.16 CDCl3
58.19
58.17
55.62
38.11
30.43
23.49
22.89
4 (s) 145.48
1 (s) 126.85
2 (s) 109.06
13 (s) 55.62
7 (s) 30.43
3 (s) 155.07
5 (s) 130.98
6 (s) 118.08
8,9 (d) 58.18
10 (s) 38.11
14 (s) 23.49
15 (s) 22.89
f1 (ppm)

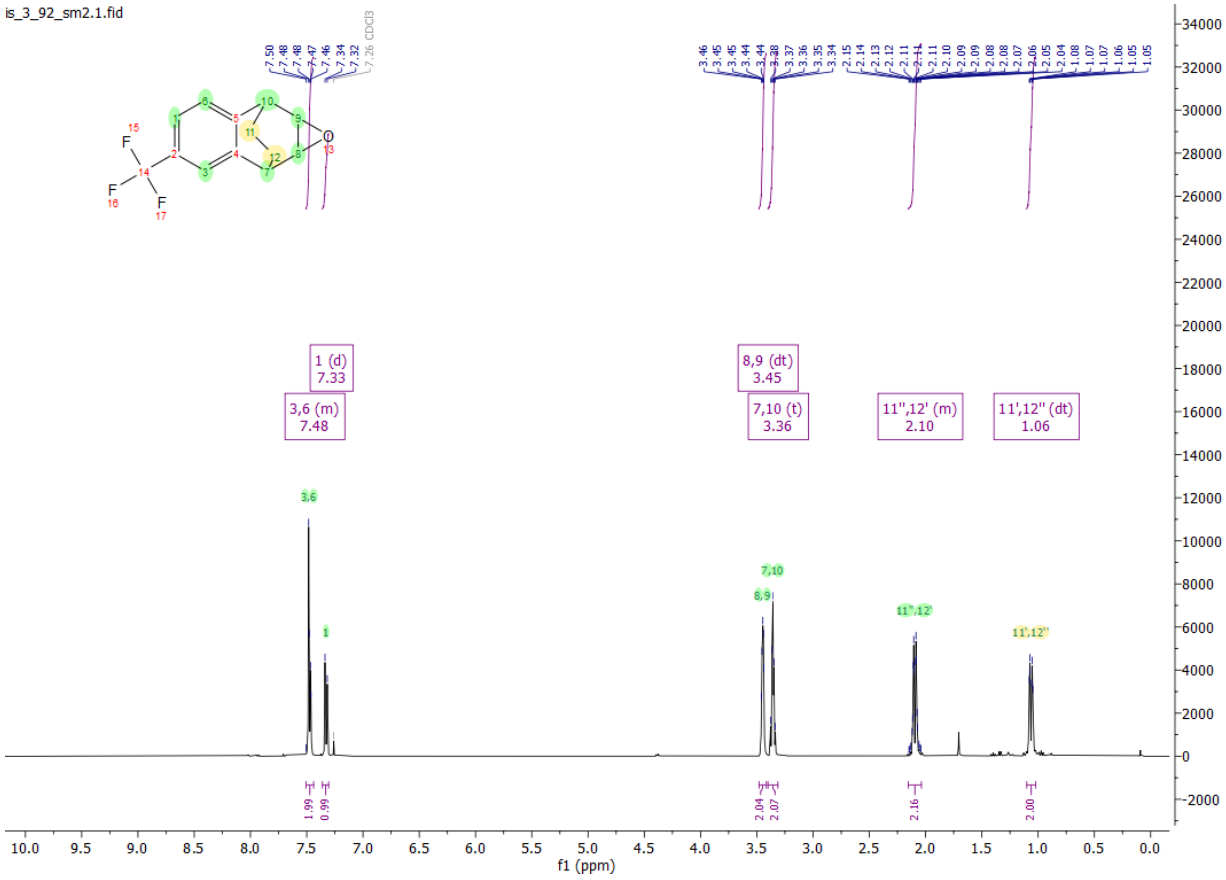
EPO-7

^{1}H NMR


is_3_83_smqc.1.fid
1 (m)
7.40
6 (dd)
7.50
2 (d)
7.28
10 (tq)
3.43
7 (d)
3.86
8,9 (m)
3.36
12'' (m)
2.09
11',12' (m)
1.07
f1 (ppm)

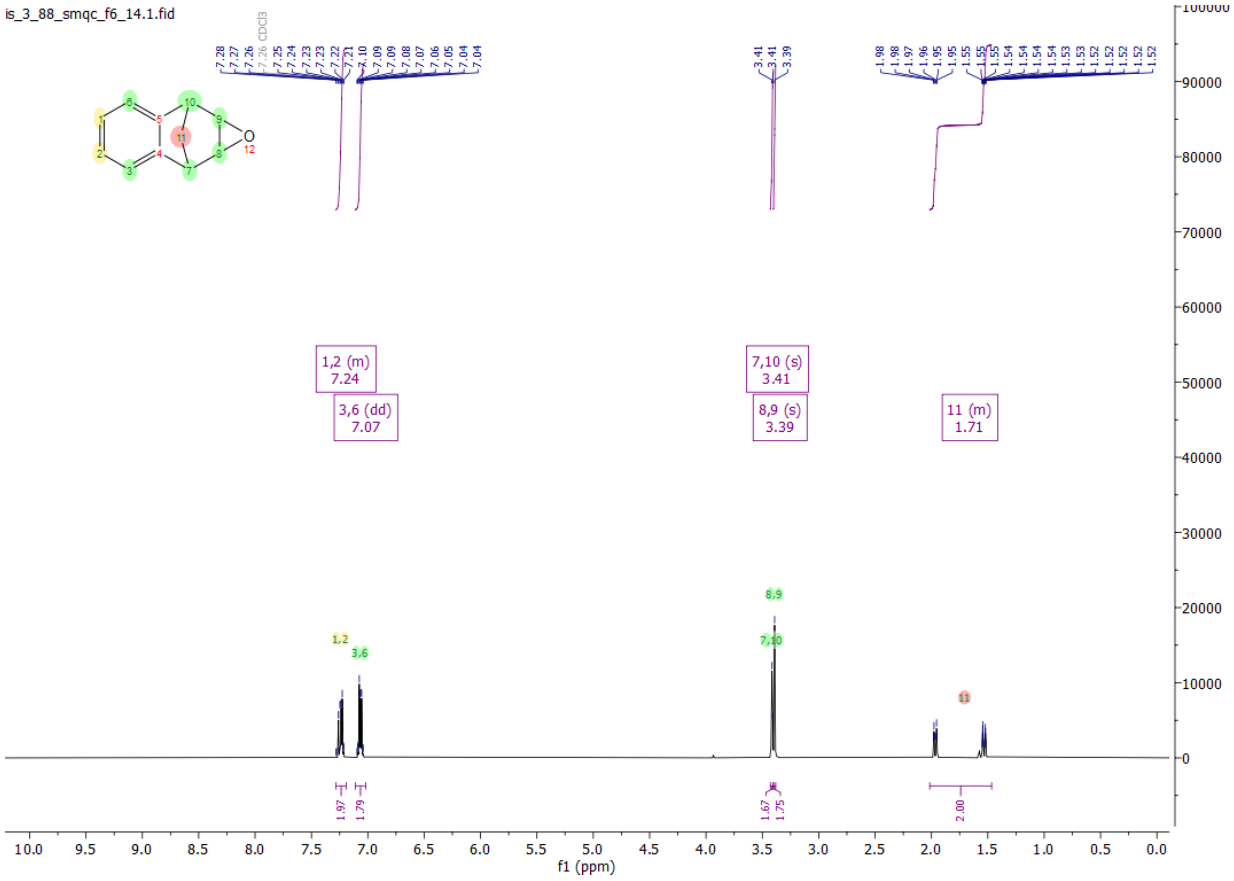
EPO-8

^{1}H NMR

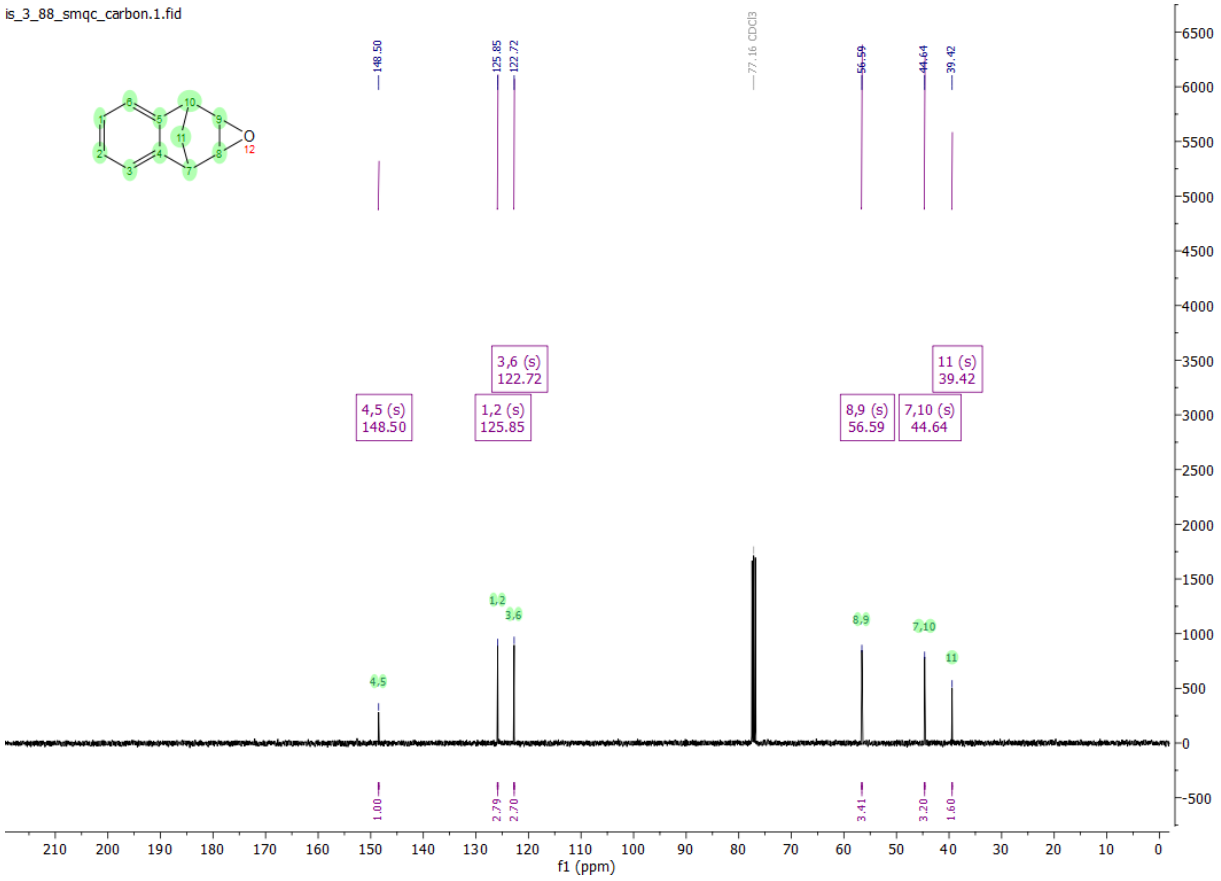

is_3_92_sm2.1.fid
1 (d)
7.33
3,6 (m)
7.48
8,9 (dt)
3.45
7,10 (t)
3.36
11'',12' (m)
2.10
11',12'' (dt)
1.06
f1 (ppm)

EPO-9

^{1}H NMR


is_3_88_smqc_f6_14.1.fid
1,2 (m)
7.24
3,6 (dd)
7.07
7,10 (s)
3.41
8,9 (s)
3.39
11 (m)
1.71
f1 (ppm)

^{13}C NMR


is_3_88_smqc_carbon.1.fid
148.50
125.85
122.72
77.16 CDCl3
56.59
44.64
39.42
4,5 (s)
148.50
1,2 (s)
125.85
3,6 (s)
122.72
8,9 (s)
56.59
7,10 (s)
44.64
11 (s)
39.42
1,2
3,6
4,5
8,9
7,10
11
1.00
2.79
2.70
3.41
3.20
1.60
f1 (ppm)

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