Supporting Information

Visible-Light Mediated Alkyl Sulfonylative Cascade using Hantzsch Esters *via* SO_2 Insertion

Indranil Halder, Akshay M. Nair and Chandra M. R. Volla*

Department of Chemistry, Indian Institute of Technology Bombay, Powai,

Mumbai 400076, India;

E–mail: chandra.volla@chem.iitb.ac.in

Table of contents

1. General Information:

All reactions were carried out under air atmosphere in screw cap reaction tubes and the workups were performed under air. All the solvents used for the reactions were dried by following the reported procedures. Unless otherwise noted, all materials were purchased from commercial suppliers and used as received. Reactions were monitored using thin-layer chromatography (SiO2). A gradient elution using petroleum ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel 60F254). TLC plates were visualized with UV light (254 nm) or KMnO4 stain. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. NMR studies were performed on Bruker Avance DPX at 400 MHz (1H) or 500 MHz (1H) and at 101 MHz (13C) or 126 MHz (13C), respectively. Chemical shifts (d) are reported in ppm, using the residual solvent peak in CDCl3 (δH = 7.26 and δC = 77.16) ppm as internal standards. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, b = broad. Fluorescence quenching study was recorded in Horiba Fluoromax Plus instrument. The high-resolution mass spectra (HRMS) were recorded with Agilent Advance Bio 6454XT LC/Q-TOF mass spectrometer. X-ray diffraction studies were carried out using Bruker D8 QUEST (APEX-II CCD) diffractometer. Alkynyl-cyclohexadienones[1] and 4-substituted Hantzsch esters[2], DABSO[3] and 4-CzIPN[4] were synthesized as per the pervious literature. 456 nm 40W Blue-LEDs were purchased from Kessil.

2. Fluorescence quenching studies:

The fluorescence emission intensities were recorded on a Horiba Fluormax-4 spectrofluorometer and the excitation wavelength was fixed at 450nm. The samples were prepared by mixing 4-CzIPN (2.0×10^{-5} mol/L) stock solution and increasing concentration of the appropriate quencher **1** or **2** in MeCN in a light path quartz fluorescence cuvette. Then the emission intensity was collected and the results were presented considering the emission at 531 nm.

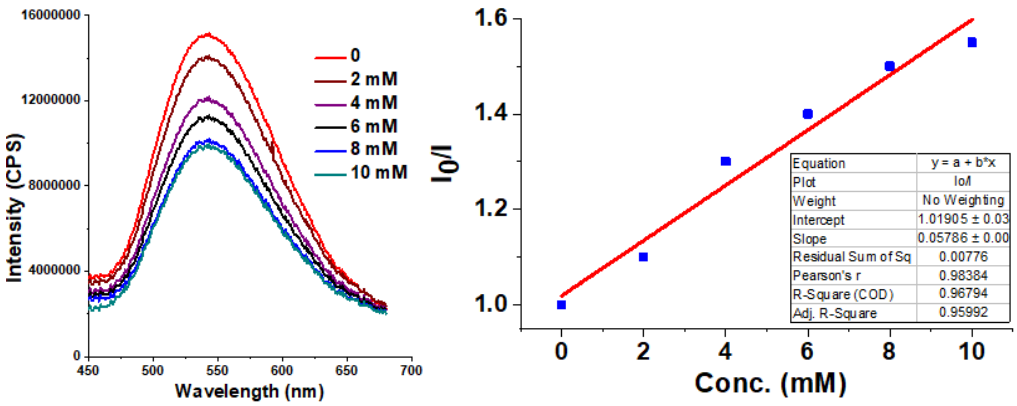


Figure 1: Fluorescence quenching of 4-CzIPN with Hantzsch ester 2 and the respective Stern-Volmer plot.

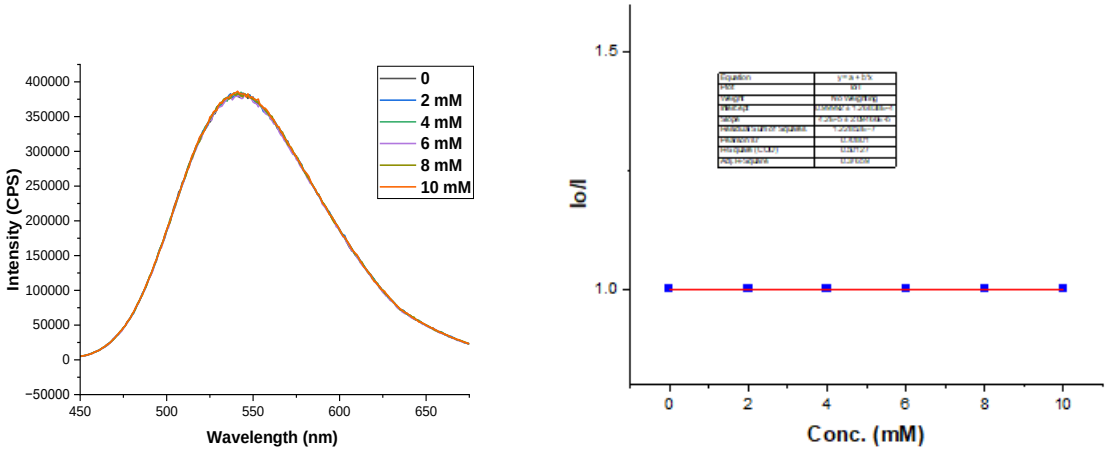
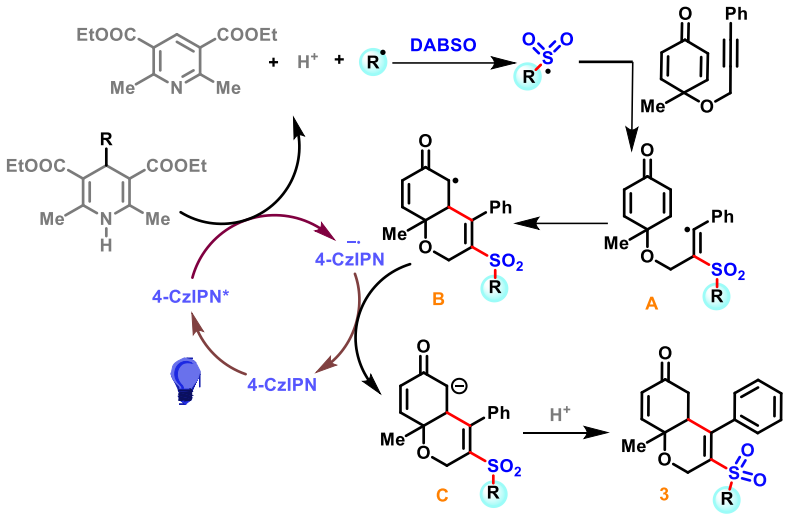


Figure 2: Fluorescence quenching of 4-CzIPN with cyclohexadienone **1** and the respective Stern-Volmer plot.

3. <u>Proposed Mechanism:</u>

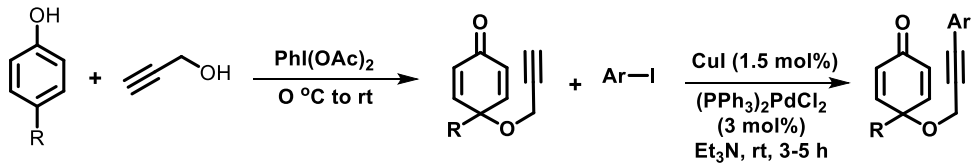
On the basis of the radical quenching studies and literature reports, we propose the following plausible reaction mechanism. 4-CzIPN upon photoexcitation undergoes single electron transfer with 4-alkyl-DHPs to generate an alkyl radical and pyridine *via* a reductive quenching cycle. The generated alkyl radical then forms alkyl sulfonyl radical by combining with sulfur dioxide, which subsequently adds onto the alkyne **1** forming the radical intermediate **A**. This vinyl radical on further Giese cyclization forms the α-carbonyl radical **B,** which gets reduced

by 4-CzIPN$^{\bullet-}$ forming the anion intermediate **C** which on subsequent protonation affords the desired product **3**.

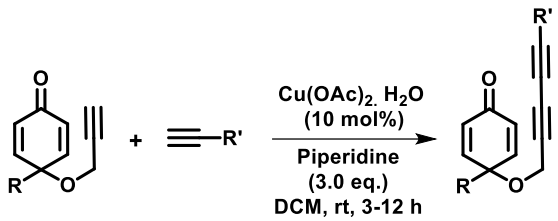


4. Experimental procedures:

4.1. General procedure for preparation of starting materials:

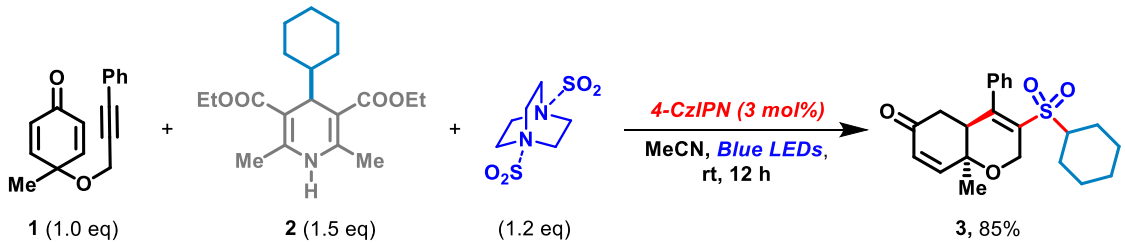


To a solution of 4-substituted phenol (10 mmol) in 10 mL of propargyl alcohol was added phenyliodine(III) diacetate (15 mmol) in several portions at 0 °C. This reaction mixture was stirred at room temperature overnight. Then the reaction was quenched with saturated aqueous sodium bicarbonate (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layer was washed with brine (20 mL), dried over Na2SO4, filtered, and concentrated in vacuo. The crude reaction mixture was purified by silica gel (100−200 mesh) column chromatography (EtOAc/hexane) to give the alkyne-tethered cyclohexadienone. For the next step, to a solution of alkyne-tethered cyclohexadienone (1.0 mmol) in degassed Et_3N (1 M, 1 mL) was added $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (1.5 mol%) and aryl iodide (1.2 mmol). The mixture was stirred at room temperature for 3-5 hours. Water (10 mL) was added, and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic solvent was washed with 10% aqueous HCl (5 mL), dried (Na_2SO4), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (EtOAc/hexane) to give aryl substituted alkynes in good yields.



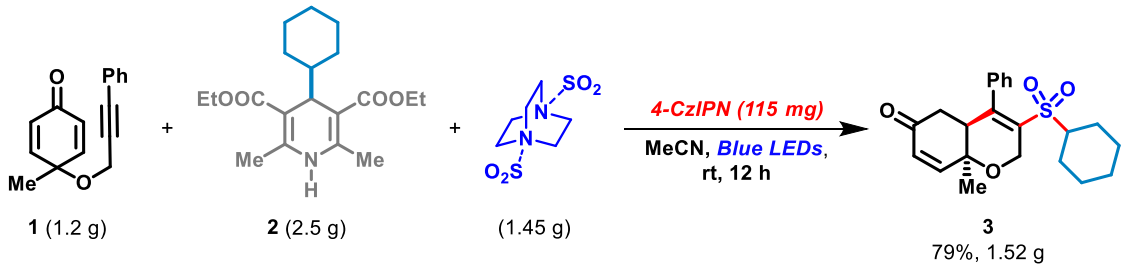
A mixture of alkyne-tethered cyclohexadienone (1.0 mmol), terminal alkyne (5 mmol), piperidine (3 mmol), and $Cu(OAc)_2 \cdot H_2O$ (10 mol%) in DCM (2 mL) was stirred under open atmospheric air at 25°C for 3–12 h. After completion of reaction (monitored by TLC), the mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to afford 1,3- diyne-tethered cyclohexadienone.

4.2. General procedure for the cascade cyclization with 4-alkyl-DHP:



In a reaction vial equipped with magnetic stirring bar, was added alkynylcyclohexadienones **1** (24 mg, 0.1 mmol), 4-Cyclohexyl Hantzsch ester **2** (50.2 mg, 0.15 mmol), DABSO (33.6 mg, 0.12 mmol), 4CzIPN (2.4 mg, 0.003 mmol) followed by MeCN (1.5 mL). The reaction was then kept under stirring for 12 hrs under the irradiation of 40 W blue-LED. The reaction mass was then diluted with water (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic layer was dried over Na_2SO_4, evaporated under reduced pressure and chromatographed with EtOAc in Petroleum ether (3:7) to give 32.8 mg, 85% yield of the desired product **3**.

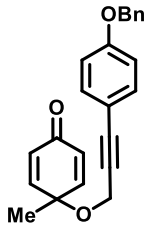
4.3. Gram-scale synthesis of sulfonylated chromenone:



In a 50 mL round, bottomed flask equipped with a magnetic stirring bar added alkynylcyclohexadienones **1** (1.2 g, 5.0 mmol), 4-substituted Hantzsch ester **2** (2.5 g, 7.5 mmol), DABSO (1.45 g, 6.0 mmol), 4CzIPN (115 mg, 0.003 mmol) followed by MeCN (10.0 mL). The reaction was then kept under stirring for 12 hrs under the irradiation of 40 W blue-LED. The reaction mass was then diluted with water (10 mL) and extracted with ethyl acetate (3 x 12 mL). Organic layer was dried over Na_2SO_4, evaporated under reduced pressure and chromatographed with EtOAc in Petroleum ether (3:7) to give 1.52 g, 79% yield of the desired product **3**.

5. Characterization data of new starting materials:

4-((3-(4-(benzyloxy)phenyl)prop-2-yn-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one:



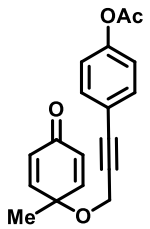
Yellow solid, 213 mg 62% yield, 0.5 Rf in 20 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.32 (m, 7H), 6.94 – 6.84 (m, 4H), 6.37 – 6.29 (m, 2H), 5.06 (s, 2H), 4.21 (s, 2H), 1.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 185.3, 159.2, 151.3, 136.6, 133.4, 130.5, 128.8, 128.3, 127.6, 114.98, 114.89, 86.9, 84.6, 73.3, 70.2, 54.8, 26.6.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{21}O_3$ = 345.1485; found = 345.1502.

4-(3-((1-methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)phenyl acetate:



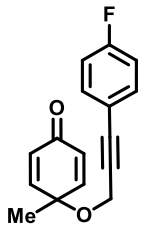
Brown solid, 160 mg 54% yield, 0.3 Rf in 20 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 10.3 Hz, 2H), 6.33 (d, *J* = 10.3 Hz, 2H), 4.21 (s, 2H), 2.29 (s, 3H), 1.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 185.2, 169.2, 151.1, 150.9, 133.0, 130.5, 121.8, 120.2, 86.1, 86.0, 73.4, 54.7, 26.5, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{17}O_4$ = 297.1121; found = 297.1106.

4-((3-(4-fluorophenyl)prop-2-yn-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one:



Yellow solid, 176 mg 69% yield, 0.5 Rf in 30 % EtOAc in pet ether.

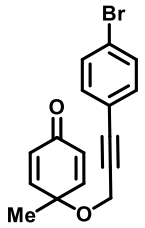
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.36 (m, 2H), 7.03 – 6.96 (m, 2H), 6.91 – 6.84 (m, 2H), 6.39 – 6.28 (m, 2H), 4.21 (s, 2H), 1.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 185.2, 162.8 (d, *J* = 250.1 Hz), 151.0, 133.8 (d, *J* = 8.5 Hz), 130.6, 118.6 (d, *J* = 3.8 Hz), 115.8 (d, *J* = 22.0 Hz), 85.9, 85.6 (d, *J* = 1.7 Hz), 73.4, 54.6, 26.5.

^{19}F NMR (377 MHz, $CDCl_3$): δ -110.31.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{14}FO_2$ = 257.0972; found = 257.0950.

4-((3-(4-bromophenyl)prop-2-yn-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one



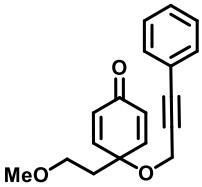
Brown solid, 196 mg 62% yield, 0.5 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.40 (m, 2H), 7.30 – 7.22 (m, 2H), 6.90 – 6.83 (m, 2H), 6.39 – 6.29 (m, 2H), 4.19 (s, 2H), 1.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 185.1, 150.9, 133.2, 131.7, 130.6, 123.1, 121.4, 86.9, 85.8, 73.4, 54.6, 26.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{14}BrO_2$ = 317.0172; found = 317.0190.

4-(2-methoxyethyl)-4-((3-phenylprop-2-yn-1-yl)oxy)cyclohexa-2,5-dien-1-one



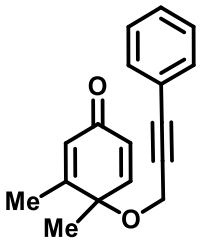
Yellow solid, 127.05 mg 45% yield, 0.4 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.38 (m, 2H), 7.34 – 7.29 (m, 3H), 6.95 – 6.88 (m, 2H), 6.43 – 6.32 (m, 2H), 4.24 (s, 2H), 3.45 (t, *J* = 6.2 Hz, 2H), 3.26 (s, 3H), 2.07 (t, *J* = 6.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 185.5, 150.2, 131.8, 131.0, 128.8, 128.4, 122.5, 87.0, 86.0, 75.1, 67.4, 58.7, 54.4, 39.7.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{19}O_3$ = 283.1329; found =283.1324.

3,4-dimethyl-4-((3-phenylprop-2-yn-1-yl)oxy)cyclohexa-2,5-dien-1-one:



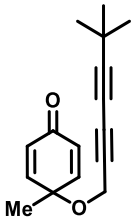
Yellow solid, 161 mg 64% yield, 0.5 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.38 (m, 2H), 7.33 – 7.27 (m, 3H), 6.87 (dd, *J* = 10.1, 1.1 Hz, 1H), 6.34 – 6.28 (m, 1H), 6.23 – 6.17 (m, 1H), 4.12 (dd, *J* = 15.3, 0.8 Hz, 1H), 4.03 (dd, *J* = 15.3, 0.8 Hz, 1H), 2.06 (s, 3H), 1.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 185.50, 160.01, 151.45, 131.83, 130.24, 129.38, 128.71, 128.40, 122.49, 86.69, 85.21, 75.15, 54.27, 25.75, 18.22.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{17}O_2$ = 253.1223; found = 253.1245.

4-((6,6-dimethylhepta-2,4-diyn-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one:



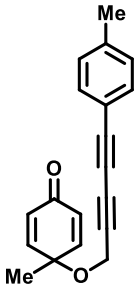
Dark brown oil, 162 mg 67% yield, 0.6 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (d, *J* = 10.1 Hz, 2H), 6.28 (d, *J* = 10.3 Hz, 2H), 4.01 (s, 2H), 1.43 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 185.0, 150.7, 130.6, 89.6, 73.4, 73.3, 71.9, 63.2, 54.4, 30.5, 28.1, 26.3.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{19}O_2$ = 243.1380; found = 243.1381.

4-methyl-4-((5-(p-tolyl)penta-2,4-diyn-1-yl)oxy)cyclohexa-2,5-dien-1-one:



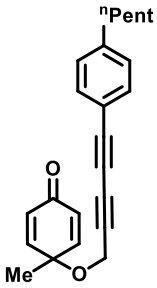
Brown solid, 163 mg 59% yield, 0.5 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.34 (m, 2H), 7.18 – 7.01 (m, 2H), 6.96 – 6.75 (m, 2H), 6.33 (d, *J* = 10.3 Hz, 2H), 4.12 (s, 2H), 2.35 (s, 3H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 185.07, 150.62, 132.74, 132.63, 130.70, 129.33, 128.14, 79.29, 78.80, 73.55, 72.69, 71.82, 54.59, 26.38, 21.73.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{17}O_2$ = 277.1223; found = 277.1231.

4-methyl-4-((5-(4-pentylphenyl)penta-2,4-diyn-1-yl)oxy)cyclohexa-2,5-dien-1-one:



Dark yellowish oil, 206 mg 62% yield, 0.65 Rf in 30 % EtOAc in pet ether.

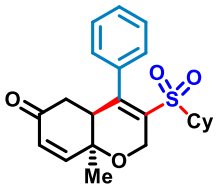
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 10.1 Hz, 2H), 6.34 (d, *J* = 10.1 Hz, 2H), 4.13 (s, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.49 (s, 3H), 1.36 – 1.25 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 185.1, 150.6, 145.0, 132.7, 130.7, 128.7, 118.5, 79.4, 78.8, 73.6, 72.7, 71.9, 54.6, 36.1, 31.5, 30.9, 26.4, 22.6, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{25}O_2$ = 333.1849; found = 333.1863.

6. Characterization data of final products:

3-(cyclohexylsulfonyl)-8a-methyl-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (3)



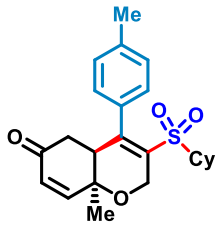
Dark yellowish sticky solid, 32.8 mg 85% yield, 0.4 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (q, *J* = 3.4 Hz, 3H), 7.17 (d, *J* = 6.0 Hz, 2H), 6.75 (dd, *J* = 10.3, 4.3 Hz, 1H), 6.07 (dd, *J* = 10.4, 4.3 Hz, 1H), 4.65 – 4.57 (m, 1H), 4.56 – 4.47 (m, 1H), 2.89 – 2.79 (m, 1H), 2.52 – 2.35 (m, 2H), 2.09 – 2.01 (m, 1H), 1.88 – 1.74 (m, 4H), 1.58 (s, 3H), 1.44 – 1.32 (m, 2H), 1.29 – 1.20 (m, 1H), 1.15 – 1.02 (m, 1H), 1.00 – 0.90 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.8, 150.4, 147.9, 135.6, 134.3, 130.6, 129.1, 129.0, 128.5, 70.7, 61.9, 61.7, 46.1, 38.3, 25.5, 25.12, 25.08, 25.01, 24.0, 23.3.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{27}O_4S$ = 387.1625; found = 387.1629.

3-(cyclohexylsulfonyl)-8a-methyl-4-(p-tolyl)-4a,8a-dihydro-2H-chromen-6(5H)-one: (4)



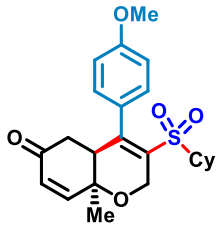
Brown sticky solid, 37.0 mg 92% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.74 (d, *J* = 10.2 Hz, 1H), 6.07 (d, *J* = 10.1 Hz, 1H), 4.58 (d, *J* = 17.5 Hz, 1H), 4.51 (d, *J* = 17.7 Hz, 1H), 2.89 – 2.75 (m, 1H), 2.45 (dd, *J* = 16.4, 5.3 Hz, 1H), 2.40 (d, *J* = 6.9 Hz, 1H), 2.38 (s, 3H), 2.15 – 2.08 (m, 1H), 1.87 – 1.77 (m, 4H), 1.57 (s, 3H), 1.44 – 1.34 (m, 2H), 1.30 – 1.23 (m, 1H), 1.12 – 1.06 (m, 1H), 1.01 – 0.93 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.9, 150.5, 148.2, 139.1, 134.1, 133.5, 132.6, 130.6, 129.16, 70.8, 61.8, 61.7, 46.1, 38.4, 25.52, 25.14, 25.10, 25.02, 24.0, 23.3, 21.4.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{28}NaO_4S$ = 423.1601; found = 423.1599.

3-(cyclohexylsulfonyl)-4-(4-methoxyphenyl)-8a-methyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (5)



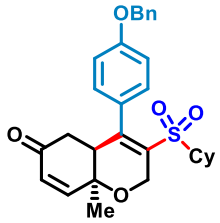
Brown sticky solid, 37.4 mg 90% yield, 0.3 Rf in 40 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 10.2 Hz, 1H), 6.06 (d, *J* = 10.2 Hz, 1H), 4.58 (dd, *J* = 17.7, 2.2 Hz, 1H), 4.50 (dd, *J* = 17.6, 2.2 Hz, 1H), 3.83 (s, 3H), 2.84 – 2.77 (m, 1H), 2.49 – 2.33 (m, 2H), 2.14 – 2.06 (m, 1H), 1.89 – 1.75 (m, 4H), 1.56 (s, 3H), 1.44 – 1.33 (m, 2H), 1.26 – 1.22 (m, 1H), 1.13 – 1.05 (m, 1H), 1.01 – 0.90 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.9, 160.0, 150.5, 147.9, 134.3, 130.6, 130.5, 127.5, 114.0, 70.8, 61.7, 55.3, 46.3, 46.1, 38.4, 25.6, 25.1, 24.1, 23.9, 23.2.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{29}O_5S$ = 417.1730; found = 417.1721.

4-(4-(benzyloxy)phenyl)-3-(cyclohexylsulfonyl)-8a-methyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (6)



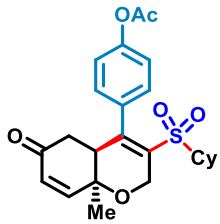
Pale yellow sticky solid, 41.4 mg 84% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.33 (m, 5H), 7.18 – 7.08 (m, 2H), 7.06 – 6.97 (m, 2H), 6.74 (d, *J* = 10.3 Hz, 1H), 6.07 (d, *J* = 10.3 Hz, 1H), 5.10 (s, 2H), 4.59 (dd, *J* = 17.7, 2.2 Hz, 1H), 4.50 (dd, *J* = 17.6, 2.2 Hz, 1H), 2.89 – 2.71 (m, 1H), 2.60 – 2.36 (m, 2H), 2.22 – 2.07 (m, 1H), 1.89 – 1.75 (m, 4H), 1.56 (s, 3H), 1.42 – 1.36 (m, 2H), 1.25 (d, *J* = 1.2 Hz, 1H), 1.03 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.8, 159.2, 150.3, 147.6, 136.5, 134.2, 130.5, 129.6, 128.7, 128.2, 127.7, 127.5, 114.7, 70.7, 70.05, 61.63, 61.61, 46.0, 38.4, 25.5, 25.0, 24.99, 24.9, 23.9, 23.1.

HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{29}H_{33}O_5S$ = 493.2048; found = 493.1998.

4-(3-(cyclohexylsulfonyl)-8a-methyl-6-oxo-4a,5,6,8a-tetrahydro-2H-chromen-4-yl)phenyl acetate: (7)



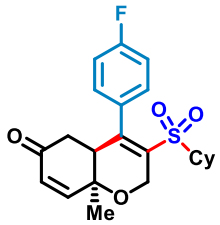
Yellow sticky solid, 37.0 mg 83% yield, 0.3 Rf in 40 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.12 (m, 4H), 6.74 (d, *J* = 10.1 Hz, 1H), 6.08 (d, *J* = 10.1 Hz, 1H), 4.59 (dd, *J* = 17.8, 2.2 Hz, 1H), 4.51 (dd, *J* = 17.8, 2.2 Hz, 1H), 2.88 – 2.82 (m, 1H), 2.49 (dd, *J* = 16.3, 5.3 Hz, 1H), 2.41 (dd, *J* = 16.4, 7.7 Hz, 1H), 2.31 (s, 3H), 2.05 – 1.97 (m, 1H), 1.88 – 1.75 (m, 4H), 1.70 – 1.65 (m, 1H), 1.57 (s, 3H), 1.44 – 1.33 (m, 2H), 1.12 – 0.93 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.4, 168.9, 151.1, 150.2, 146.8, 135.1, 132.8, 130.5, 121.7, 70.7, 61.8, 61.6, 45.9, 38.2, 25.5, 25.0, 24.9, 23.9, 23.2, 21.1.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{24}H_{28}O_6SNa$= 467.1499; found = 467.1517.

3-(cyclohexylsulfonyl)-4-(4-fluorophenyl)-8a-methyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (8)



Brownish white sticky solid, 32.8 mg 81% yield, 0.3 Rf in 30 % EtOAc in pet ether.

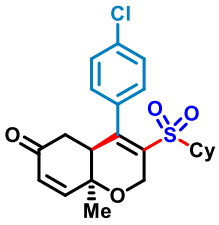
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 – 7.08 (m, 4H), 6.75 (d, *J* = 10.2 Hz, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 4.57 (dd, *J* = 17.7, 2.3 Hz, 1H), 4.51 (dd, *J* = 17.7, 2.2 Hz, 1H), 2.89 – 2.78 (m, 1H), 2.47 (dd, *J* = 16.4, 5.2 Hz, 1H), 2.36 (dd, *J* = 16.3, 7.4 Hz, 1H), 2.18 – 2.09 (m, 1H), 1.89 – 1.77 (m, 4H), 1.58 (s, 3H), 1.45 – 1.35 (m, 2H), 1.25 (d, *J* = 2.2 Hz, 1H), 1.15 – 1.09 (m, 1H), 1.07 – 0.93 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.6, 162.8 (d, *J* = 249.7 Hz), 150.5, 147.4, 135.0, 133.3 (d, *J* = 8.1 Hz), 131.3 (d, *J* = 3.4 Hz), 130.7, 115.7 (d, *J* = 21.6 Hz), 71.0, 62.1, 61.8, 46.3, 38.3, 25.4, 25.1, 25.1, 24.1, 23.4.

HRMS (ESI) m/z: $[M+K]^+$ calculated for $C_{22}H_{25}KFO_4S$ =443.1089; found = 443.1089.

^{19}F NMR (376 MHz, $CDCl_3$): δ -111.55.

4-(4-chlorophenyl)-3-(cyclohexylsulfonyl)-8a-methyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (9)



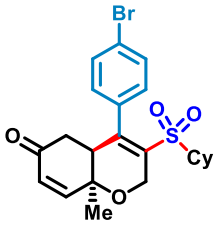
Brownish sticky solid, 35.3 mg 84% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.65 (m, 1H), 7.60 – 7.53 (m, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.34 (s, 1H), 6.76 (d, *J* = 10.5 Hz, 1H), 6.10 (d, *J* = 10.1 Hz, 1H), 4.58 (dd, *J* = 17.8, 2.4 Hz, 1H), 4.53 (dd, *J* = 17.8, 2.3 Hz, 1H), 2.91 – 2.81 (m, 1H), 2.50 (dd, *J* = 16.4, 5.3 Hz, 1H), 2.36 (dd, *J* = 16.3, 7.4 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.92 – 1.76 (m, 4H), 1.60 (s, 3H), 1.45 – 1.34 (m, 2H), 1.28 – 1.23 (m, 1H), 1.16 – 0.99 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.2, 150.4, 147.1, 136.4, 135.7, 130.7, 129.0, 125.8, 122.5, 71.1, 62.7, 61.9, 46.2, 38.2, 25.3, 25.11, 25.07, 24.9, 24.1, 23.7.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{26}ClO_4S$= 421.1235; found = 421.1255.

4-(4-bromophenyl)-3-(cyclohexylsulfonyl)-8a-methyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (10)



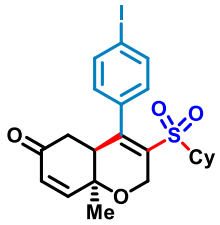
Brownish sticky solid, 38.6 mg 83% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 10.2 Hz, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 4.59 – 4.47 (m, 2H), 2.86 – 2.77 (m, 1H), 2.55 (q, *J* = 7.2 Hz, 1H), 2.47 (dd, *J* = 16.4, 5.3 Hz, 1H), 2.34 (dd, *J* = 16.3, 7.2 Hz, 1H), 2.26 – 2.18 (m, 1H), 1.90 – 1.79 (m, 4H), 1.57 (s, 3H), 1.45 – 1.34 (m, 2H), 1.08 – 1.01 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.3, 150.5, 147.3, 135.0, 134.4, 131.7, 130.7, 130.0, 123.3, 71.1, 62.3, 61.8, 46.2, 38.3, 25.3, 25.10, 25.07, 25.05, 24.1, 23.6.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{26}BrO_4S$= 465.0730; found = 465.0722.

3-(cyclohexylsulfonyl)-4-(4-iodophenyl)-8a-methyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (11)



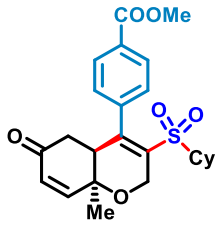
Pale yellow sticky solid, 42.0 mg 82% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 10.2, 0.6 Hz, 1H), 6.08 (d, *J* = 10.3 Hz, 1H), 4.52 (t, *J* = 2.4 Hz, 2H), 2.85 – 2.77 (m, 1H), 2.47 (dd, *J* = 16.4, 5.3 Hz, 1H), 2.34 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.27 – 2.17 (m, 1H), 1.93 – 1.79 (m, 4H), 1.65 – 1.61 (m, 1H), 1.57 (s, 3H), 1.46 – 1.36 (m, 2H), 1.15 – 1.00 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.4, 150.5, 147.4, 137.6, 135.0, 134.8, 130.7, 95.0, 71.1, 62.3, 61.8, 46.2, 38.3, 25.3, 25.10, 25.06, 24.2, 23.6.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{26}IO_4S$= 513.0591; found =513.0604.

Methyl-4-(3-(cyclohexylsulfonyl)-8a-methyl-6-oxo-4a,5,6,8a-tetrahydro-2H-chromen-4-yl)benzoate: (12)



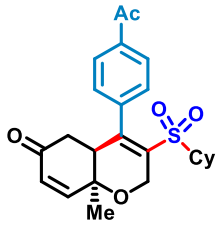
Brownish yellow sticky solid, 38.2 mg 86% yield, 0.3 Rf in 40 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 – 8.04 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 10.2 Hz, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 4.54 (t, *J* = 2.4 Hz, 2H), 3.93 (s, 3H), 2.89 – 2.80 (m, 1H), 2.47 (dd, *J* = 16.4, 5.3 Hz, 1H), 2.32 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.26 – 2.18 (m, 1H), 1.90 – 1.74 (m, 4H), 1.68 – 1.62 (m, 1H), 1.58 (s, 3H), 1.46 – 1.32 (m, 2H), 1.15 – 0.97 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.2, 166.4, 150.5, 147.7, 140.4, 134.9, 130.7, 130.6, 129.6, 71.0, 62.4, 61.8, 52.4, 46.1, 38.2, 25.2, 25.07, 25.03, 24.1, 23.7.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{28}NaO_6S$= 467.1499; found = 467.1494.

4-(4-acetylphenyl)-3-(cyclohexylsulfonyl)-8a-methyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (13)



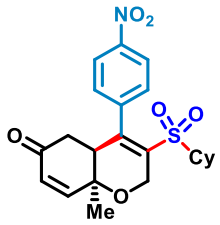
Yellow sticky solid, 37.3 mg 87% yield, 0.3 Rf in 40 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 10.2 Hz, 1H), 6.12 (d, *J* = 10.2 Hz, 1H), 4.57 (d, *J* = 2.1 Hz, 2H), 2.90 (t, *J* = 6.3 Hz, 1H), 2.65 (s, 3H), 2.54 – 2.46 (m, 1H), 2.42 – 2.21 (m, 2H), 1.92 – 1.80 (m, 4H), 1.62 (s, 3H), 1.47 – 1.35 (m, 2H), 1.31 – 1.24 (m, 1H), 1.17 – 1.01 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.4, 196.2, 150.6, 147.8, 140.5, 137.1, 134.8, 130.8, 128.3, 71.2, 62.5, 61.8, 46.2, 38.2, 26.8, 25.2, 25.05, 25.02, 25.00, 24.2, 23.8.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{29}O_5S$= 429.1730; found = 429.1727.

3-(cyclohexylsulfonyl)-8a-methyl-4-(4-nitrophenyl)-4a,8a-dihydro-2H-chromen-6(5H)-one: (14)



Brownish yellow sticky solid, 37.9 mg 88% yield, 0.3 Rf in 30 % EtOAc in pet ether.

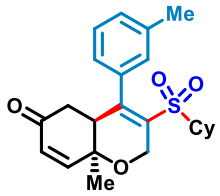
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 – 7.99 (m, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 10.2 Hz, 1H), 6.12 (d, *J* = 10.3 Hz, 1H), 4.67 – 4.48 (m, 2H), 2.91 – 2.86 (m, 1H), 2.52 (dd, *J* =

16.4, 5.3 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.29 (dd, *J* = 16.4, 6.6 Hz, 1H), 1.96 – 1.82 (m, 4H), 1.68 – 1.65 (m, 1H), 1.61 (s, 3H), 1.13 (t, *J* = 8.0 Hz, 2H), 0.93 – 0.76 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 195.8, 150.5, 148.0, 147.0, 142.5, 135.5, 130.9, 123.5, 71.4, 62.7, 61.8, 46.4, 38.2, 32.1, 25.08, 25.03, 25.01, 24.3, 24.1.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{25}NaNO_6S$= 454.1295; found = 454.1299.

3-(cyclohexylsulfonyl)-8a-methyl-4-(m-tolyl)-4a,8a-dihydro-2H-chromen-6(5H)-one: (15)



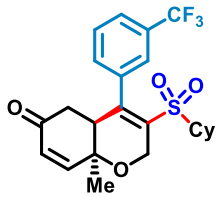
Brown sticky solid, 34.8 mg 87% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.96 (b, 2H), 6.74 (d, *J* = 10.2 Hz, 1H), 6.07 (d, *J* = 10.1 Hz, 1H), 4.59 (dd, *J* = 17.5, 2.1 Hz, 1H), 4.52 (dd, *J* = 17.7, 2.3 Hz, 1H), 2.86 – 2.76 (m, 1H), 2.50 – 2.43 (m, 2H), 2.37 (s, 3H), 1.90 – 1.76 (m, 4H), 1.57 (s, 3H), 1.44 – 1.34 (m, 2H), 1.28 – 1.23 (m, 1H), 1.15 – 1.07 (m, 1H), 0.98 – 0.91 (m, 2H), 0.89 – 0.86 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.9, 150.4, 148.0, 138.3, 135.7, 134.0, 130.5, 129.8, 128.4, 70.6, 61.9, 61.7, 46.0, 38.4, 25.6, 25.19, 25.17, 25.08, 23.9, 23.4, 21.6.

HRMS (ESI) m/z: $[M+K]^+$ calculated for $C_{23}H_{28}O_4SK$ =439.1340; found = 439.1341.

3-(cyclohexylsulfonyl)-8a-methyl-4-(3-(trifluoromethyl)phenyl)-4a,8a-dihydro-2H-chromen-6(5H)-one: (16)



Pale yellow sticky solid, 38.2 mg 84% yield, 0.3 Rf in 30 % EtOAc in pet ether.

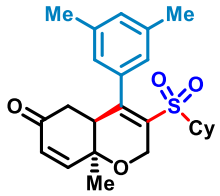
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.36 (m, 2H), 7.21 – 7.04 (m, 2H), 6.77 (dd, *J* = 10.1, 0.7 Hz, 1H), 6.11 (d, *J* = 10.1 Hz, 1H), 4.62 – 4.48 (m, 2H), 2.89 – 2.80 (m, 1H), 2.50 (dd, *J* = 16.4, 5.3 Hz, 1H), 2.36 (dd, *J* = 16.3, 7.2 Hz, 1H), 2.30 – 2.17 (m, 1H), 1.93 – 1.80 (m, 4H), 1.60 (s, 3H), 1.47 – 1.36 (m, 2H), 1.27 (d, *J* = 2.0 Hz, 1H), 1.17 – 1.13 (m, 1H), 1.11 – 1.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.3, 150.4, 147.1, 136.4, 135.7, 131.1, 130.7, 129.0, 125.6 (q, *J* = 3.8 Hz), 125.2, 122.4, 71.0, 62.7, 61.9, 46.2, 38.2, 25.3, 25.1, 25.1, 25.0, 24.1, 23.7.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{25}F_3NaO_4S$= 477.1318; found = 455.1345.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.66.

3-(cyclohexylsulfonyl)-4-(3,5-dimethylphenyl)-8a-methyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (17)



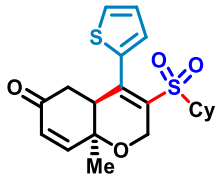
Brown sticky solid, 34.4 mg 83% yield, 0.2 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (s, 1H), 7.01 (s, 1H), 6.75 (s, 1H), 6.72 (s, 1H), 6.07 (d, *J* = 10.1 Hz, 1H), 4.60 (dd, *J* = 17.6, 2.0 Hz, 1H), 4.51 (dd, *J* = 17.6, 2.2 Hz, 1H), 2.81 – 2.73 (m, 1H), 2.44 (dd, *J* = 6.8, 3.9 Hz, 2H), 2.33 (s, 6H), 2.15 – 2.07 (m, 1H), 1.88 – 1.76 (m, 4H), 1.60 (b, 1H), 1.57 (s, 3H), 1.44 – 1.35 (m, 2H), 1.14 – 1.06 (m, 1H), 1.01 – 0.87 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.0, 150.3, 148.1, 138.1, 135.7, 133.7, 131.1, 130.6, 130.4, 70.4, 62.0, 61.6, 45.9, 38.4, 25.6, 25.3, 25.2, 25.1, 23.9, 23.4, 21.4.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{24}H_{30}NaO_4S$ =437.1757; found = 437.1758.

3-(cyclohexylsulfonyl)-8a-methyl-4-(thiophen-2-yl)-4a,8a-dihydro-2H-chromen-6(5H)-one: (18)



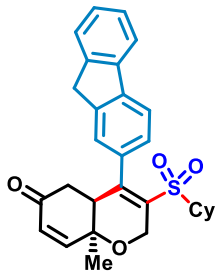
Yellow sticky solid, 31.7 mg 81% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.23 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.06 (dd, *J* = 5.3, 3.4 Hz, 1H), 6.71 (d, *J* = 10.3 Hz, 1H), 6.06 (d, *J* = 10.2 Hz, 1H), 4.66 – 4.58 (m, 1H), 4.57 – 4.47 (m, 1H), 2.90 – 2.77 (m, 1H), 2.55 – 2.36 (m, 2H), 2.26 – 2.11 (m, 1H), 1.91 (d, *J* = 12.5 Hz, 1H), 1.85 – 1.73 (m, 3H), 1.60 (d, *J* = 3.5 Hz, 1H), 1.55 (s, 3H), 1.48 – 1.36 (m, 2H), 1.15 – 1.05 (m, 1H), 1.03 – 0.93 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.7, 149.9, 140.8, 136.9, 135.3, 131.3, 130.5, 127.8, 127.7, 70.6, 62.0, 61.2, 46.8, 38.8, 26.1, 25.16, 25.08, 24.9, 23.8, 22.9.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{24}NaO_4S_2$= 415.1008; found = 415.1007.

3-(cyclohexylsulfonyl)-4-(9H-fluoren-2-yl)-8a-methyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (19)



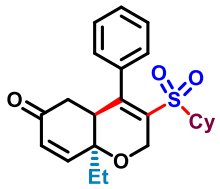
Brown sticky solid, 40.3 mg 85% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.47 – 7.31 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 10.2 Hz, 1H), 6.09 (d, *J* = 10.1 Hz, 1H), 4.63 (dd, *J* = 17.7, 2.3 Hz, 1H), 4.55 (dd, *J* = 17.7, 2.3 Hz, 1H), 3.94 (s, 2H), 3.05 – 2.87 (m, 1H), 2.53 – 2.40 (m, 2H), 2.22 – 2.15 (m, 1H), 1.90 – 1.71 (m, 4H), 1.60 (s, 3H), 1.45 – 1.34 (m, 2H), 1.28 – 1.22 (m, 1H), 1.13 – 1.04 (m, 1H), 1.01 – 0.82 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.7, 150.5, 148.4, 143.6, 143.4, 142.59, 140.9, 134.3, 133.8, 130.6, 127.5, 127.1, 125.3, 120.4, 119.8, 70.8, 62.0, 61.8, 46.3, 38.5, 37.1, 25.6, 25.12, 25.09, 25.06, 24.1, 23.3.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{31}O_4S$= 475.1938; found = 475.1943.

3-(cyclohexylsulfonyl)-8a-ethyl-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (20)



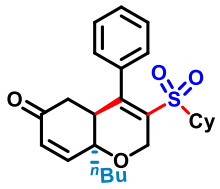
Pale white solid, 33.6 mg 84% yield, 0.4 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.20 – 7.07 (m, 2H), 6.91 – 6.79 (m, 1H), 6.13 (d, *J* = 10.3 Hz, 1H), 4.54 (d, *J* = 2.2 Hz, 2H), 2.94 – 2.89 (m, 1H), 2.48 (dd, *J* = 16.4, 5.4 Hz, 1H), 2.38 (dd, *J* = 16.5, 7.3 Hz, 1H), 2.00 – 1.89 (m, 2H), 1.85 – 1.75 (m, 4H), 1.60 (s, 3H), 1.44 – 1.34 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), 1.01 – 0.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.8, 149.6, 148.2, 136.0, 134.5, 131.5, 129.04, 129.00, 128.5, 73.1, 62.0, 61.7, 44.1, 38.3, 29.7, 25.5, 25.16, 25.11, 25.0, 23.4, 7.9.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{28}NaO_4S$= 423.1601; found = 423.1596.

8a-butyl-3-(cyclohexylsulfonyl)-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (21)



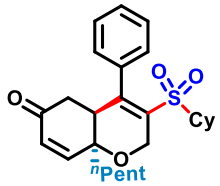
Brown solid, 31.0 mg 72% yield, 0.4 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.41 (m, 3H), 7.22 – 7.14 (m, 2H), 6.86 (d, *J* = 10.5 Hz, 1H), 6.14 (d, *J* = 10.4 Hz, 1H), 4.56 (dd, *J* = 2.3, 1.2 Hz, 2H), 2.96 – 2.91 (m, 1H), 2.56 – 2.35 (m, 2H), 2.32 – 2.21 (m, 1H), 2.04 – 1.99 (m, 1H), 1.89 – 1.79 (m, 5H), 1.62 (t, *J* = 6.8 Hz, 3H), 1.48 – 1.38 (m, 6H), 1.03 – 0.95 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.8, 149.9, 148.3, 135.7, 134.4, 131.6, 131.3, 129.0, 128.5, 73.0, 67.0, 61.9, 61.8, 44.4, 38.3, 36.7, 34.1, 26.6, 26.0, 25.7, 25.0, 23.2, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{25}H_{32}NaO_4S$= 451.1914; found = 451.1916.

3-(cyclohexylsulfonyl)-8a-pentyl-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (22)



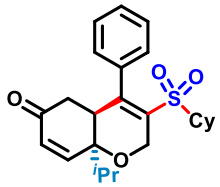
Brownish yellow solid, 37.2 mg 84% yield, 0.4 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 5.4, 1.8 Hz, 3H), 7.19 – 7.11 (m, 2H), 6.83 (d, *J* = 10.4 Hz, 1H), 6.12 (d, *J* = 10.3 Hz, 1H), 4.54 (dd, *J* = 2.3, 1.1 Hz, 2H), 2.98 – 2.89 (m, 1H), 2.48 (dd, *J* = 16.5, 5.3 Hz, 1H), 2.38 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.06 (d, *J* = 12.8 Hz, 2H), 1.88 – 1.76 (m, 5H), 1.58 (d, *J* = 4.5 Hz, 4H), 1.39 – 1.33 (m, 5H), 1.26 – 1.23 (m, 2H), 0.95 – 0.90 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.8, 149.9, 148.3, 135.7, 134.4, 131.3, 129.0, 128.5, 73.1, 62.0, 61.8, 44.5, 38.3, 37.0, 32.4, 25.5, 25.15, 25.10, 25.0, 23.4, 23.2, 22.6, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{26}H_{35}O_4S$= 443.2251; found = 443.2237.

3-(cyclohexylsulfonyl)-8a-isopropyl-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (23)



Brownish yellow sticky solid, 31.5 mg 76% yield, 0.3 Rf in 30 % EtOAc in pet ether.

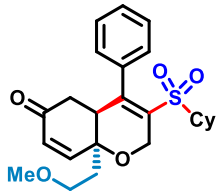
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.20 – 7.10 (m, 2H), 6.88 (d, *J* = 10.5 Hz, 1H), 6.17 (d, *J* = 10.4 Hz, 1H), 4.57 (dd, *J* = 17.8, 2.0 Hz, 1H), 4.51 (dd, *J* = 17.8, 2.1 Hz, 1H), 3.14 – 3.02 (m, 1H), 2.56 – 2.39 (m, 2H), 2.32 (q, *J* = 6.8 Hz, 1H), 1.86 – 1.75

(m, 4H), 1.62 – 1.56 (m, 3H), 1.43 – 1.33 (m, 3H), 1.17 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.97 – 0.93 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.9, 148.2, 148.2, 136.0, 134.2, 132.0, 129.0, 128.6, 74.6, 62.0, 61.6, 42.3, 38.4, 32.1, 25.4, 25.15, 25.12, 25.0, 23.5, 17.9, 16.8.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{24}H_{30}NaO_4S$= 437.1757; found = 437.1752.

3-(cyclohexylsulfonyl)-8a-(2-methoxyethyl)-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (24)



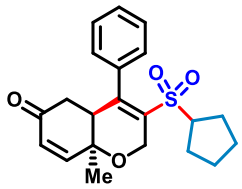
Pale white sticky solid, 32.3 mg 75% yield, 0.3 Rf in 40 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.22 – 7.14 (m, 2H), 6.81 (d, *J* = 10.4 Hz, 1H), 6.12 (d, *J* = 10.3 Hz, 1H), 4.55 (d, *J* = 2.4 Hz, 2H), 3.66 – 3.55 (m, 2H), 3.33 (s, 3H), 3.18 – 3.12 (m, 1H), 2.49 (dd, *J* = 16.5, 5.3 Hz, 1H), 2.36 (dd, *J* = 16.4, 7.3 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.10 – 1.99 (m, 2H), 1.85 – 1.75 (m, 4H), 1.67 – 1.60 (m, 1H), 1.43 – 1.33 (m, 2H), 1.12 – 1.03 (m, 1H), 0.99 – 0.89 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.9, 149.8, 148.3, 135.7, 134.1, 131.4, 129.0, 128.4, 72.6, 67.7, 61.9, 61.7, 58.9, 44.5, 38.2, 36.8, 25.5, 25.14, 25.09, 25.0, 23.3.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{30}NaO_5S$= 453.1706; found = 453.1707.

3-(cyclopentylsulfonyl)-8a-methyl-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (25)



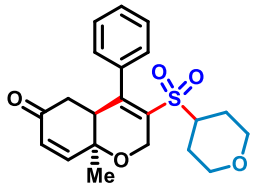
Brown sticky solid, 30.5 mg 82% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 5.3, 1.8 Hz, 3H), 7.26 – 7.17 (m, 2H), 6.77 (d, *J* = 10.1 Hz, 1H), 6.10 (d, *J* = 10.1 Hz, 1H), 4.68 (dd, *J* = 17.6, 2.1 Hz, 1H), 4.59 (dd, *J* = 17.8, 2.2 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.78 – 2.69 (m, 1H), 2.45 (dd, *J* = 6.8, 3.7 Hz, 2H), 2.00 – 1.91 (m, 1H), 1.89 – 1.80 (m, 1H), 1.76 – 1.67 (m, 4H), 1.60 (s, 3H), 1.55 – 1.48 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.9, 150.3, 147.9, 135.7, 135.7, 130.7, 130.5, 129.1, 128.5, 70.5, 62.5, 62.0, 46.1, 38.3, 27.4, 26.1, 25.9, 25.8, 23.8.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{25}O_4S$= 373.1468; found = 373.1480.

8a-methyl-4-phenyl-3-((tetrahydro-2H-pyran-4-yl)sulfonyl)-4a,8a-dihydro-2H-chromen-6(5H)-one: (26)



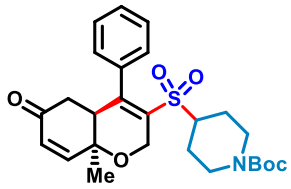
Brown sticky solid, 32.2 mg 83% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.42 (m, 3H), 7.18 (s, 2H), 6.81 – 6.71 (m, 1H), 6.09 (d, *J* = 10.2 Hz, 1H), 4.60 (dd, *J* = 17.7, 2.4 Hz, 1H), 4.53 (dd, *J* = 17.8, 2.2 Hz, 1H), 4.01 – 3.94 (m, 2H), 3.09 – 3.01 (m, 2H), 2.95 – 2.83 (m, 1H), 2.48 (dd, *J* = 16.3, 5.3 Hz, 1H), 2.39 (dd, *J* = 16.4, 7.5 Hz, 1H), 1.82 – 1.74 (m, 2H), 1.67 – 1.61 (m, 3H), 1.58 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.5, 150.4, 148.8, 135.4, 134.1, 130.7, 129.7, 129.3, 128.6, 70.9, 66.6, 66.3, 61.7, 59.1, 46.2, 38.3, 25.6, 24.1, 23.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{25}O_5S$= 389.1417; found = 389.1404.

***tert*-butyl-4-((8a-methyl-6-oxo-4-phenyl-4a,5,6,8a-tetrahydro-2H-chromen-3-yl)sulfonyl)piperidine-1-carboxylate: (27)**



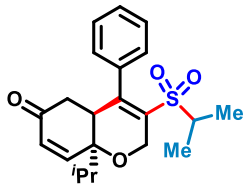
Brownish yellow sticky solid, 41.4 mg 85% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 4.7, 2.1 Hz, 3H), 7.16 (d, *J* = 4.7 Hz, 2H), 6.74 (d, *J* = 10.3 Hz, 1H), 6.07 (d, *J* = 10.1 Hz, 1H), 4.57 (dd, *J* = 17.8, 2.4 Hz, 1H), 4.50 (dd, *J* = 17.8, 2.2 Hz, 1H), 4.20 – 4.09 (m, 2H), 2.94 – 2.83 (m, 1H), 2.47 (dd, *J* = 16.4, 5.3 Hz, 1H), 2.41 – 2.31 (m, 2H), 1.77 – 1.66 (m, 3H), 1.57 (s, 3H), 1.46 – 1.42 (m, 2H), 1.40 (s, 9H), 1.26 – 1.21 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.5, 154.3, 150.3, 148.7, 135.3, 134.1, 130.7, 129.4, 129.3, 128.6, 80.2, 70.9, 61.5, 60.0, 46.1, 38.3, 28.4, 25.0, 24.0, 22.9.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{26}H_{34}NO_6S$= 488.2101; found = 488.2114.

8a-isopropyl-3-(isopropylsulfonyl)-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (28)



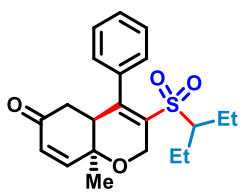
White sticky solid, 31.8 mg 85% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 6.3 Hz, 3H), 7.19 – 7.12 (m, 2H), 6.88 (d, *J* = 10.4 Hz, 1H), 6.17 (d, *J* = 10.4 Hz, 1H), 4.69 – 4.43 (m, 2H), 3.15 – 3.01 (m, 1H), 2.55 – 2.37 (m, 3H), 2.36 – 2.27 (m, 1H), 1.26 – 1.12 (m, 9H), 1.04 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.9, 148.9, 148.2, 136.0, 134.1, 132.0, 129.0, 128.5, 74.6, 61.8, 54.2, 42.5, 38.4, 32.2, 17.9, 16.7, 15.5, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{27}O_4S$= 375.1625; found = 375.1633.

8a-methyl-3-(pentan-3-ylsulfonyl)-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (29)



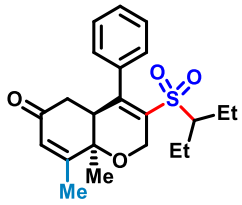
Yellow sticky solid, 29.5 mg 79% yield, 0.4 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.37 (m, 3H), 7.21 – 7.16 (m, 2H), 6.75 (d, *J* = 10.2 Hz, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 4.61 (dd, *J* = 17.7, 2.1 Hz, 1H), 4.54 (dd, *J* = 17.7, 2.3 Hz, 1H), 2.95 – 2.79 (m, 1H), 2.50 – 2.33 (m, 2H), 2.05 – 1.95 (m, 1H), 1.74 – 1.63 (m, 3H), 1.58 (s, 3H), 1.54 – 1.46 (m, 2H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.80 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.8, 150.5, 147.6, 135.5, 131.6, 130.6, 129.1, 129.0, 128.4, 70.8, 65.1, 61.8, 46.1, 38.3, 24.0, 20.8, 18.7, 11.7, 11.0.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{27}O_4S$= 375.1625; found = 375.1645.

8,8a-dimethyl-3-(pentan-3-ylsulfonyl)-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (30)



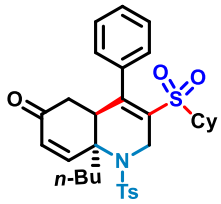
Brown sticky solid, 31.5 mg 81% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.33 (m, 3H), 7.18 – 7.12 (m, 2H), 6.04 – 5.99 (m, 1H), 4.53 (dd, *J* = 17.6, 2.8 Hz, 1H), 4.43 (dd, *J* = 17.7, 2.6 Hz, 1H), 2.93 – 2.84 (m, 1H), 2.53 – 2.39 (m, 2H), 2.33 (dd, *J* = 16.2, 6.9 Hz, 1H), 2.07 (s, 3H), 1.65 (b, 2H), 1.59 (s, 3H), 1.24 – 1.08 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 195.8, 160.1, 148.4, 135.5, 134.5, 129.6, 129.1, 129.0, 128.4, 73.4, 61.8, 54.1, 46.9, 38.2, 23.1, 18.1, 15.5, 13.9.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{28}NaO_4S$= 411.1601; found = 411.1598.

8a-butyl-3-(cyclohexylsulfonyl)-4-phenyl-1-tosyl-1,4a,5,8a-tetrahydroquinolin-6(2H)-one: (31)



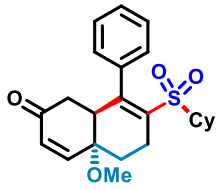
Brownish sticky solid, 48.3 mg 83% yield, 0.3 Rf in 40 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.41 (dd, *J* = 4.3, 2.1 Hz, 3H), 7.32 – 7.28 (m, 2H), 7.26 (d, *J* = 10.2 Hz, 1H), 7.14 (b, 2H), 6.02 (d, *J* = 10.2 Hz, 1H), 4.93 – 4.71 (m, 1H), 4.25 – 4.01 (m, 1H), 2.86 – 2.75 (m, 1H), 2.44 (s, 3H), 2.24 (dd, *J* = 16.6, 3.7 Hz, 1H), 2.18 – 2.11 (m, 1H), 2.07 – 1.95 (m, 2H), 1.92 – 1.79 (m, 5H), 1.65 (s, 2H), 1.49 – 1.40 (m, 6H), 1.17 – 1.10 (m, 1H), 1.01 – 0.94 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.5, 148.9, 147.8, 144.3, 138.3, 136.0, 131.7, 130.0, 129.5, 129.3, 128.5, 127.2, 61.8, 58.7, 48.8, 44.5, 38.2, 35.8, 26.0, 25.6, 25.12, 25.1, 24.9, 23.5, 23.1, 21.7, 13.9.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{32}H_{40}NO_5S_2$= 582.2342; found = 582.2346.

3-(cyclohexylsulfonyl)-8a-methoxy-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (32)



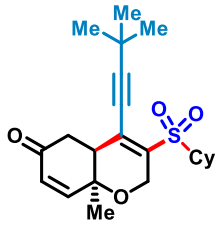
Brownish sticky solid, 32.0 mg 80% yield, 0.3 Rf in 40 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.36 (m, 2H), 7.32 – 7.28 (m, 1H), 7.10 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.87 (dd, *J* = 10.3, 4.1 Hz, 1H), 6.28 – 6.21 (m, 1H), 6.10 (dd, *J* = 10.3, 1.1 Hz, 1H), 3.38 (s, 3H), 3.21 – 3.11 (m, 1H), 2.87 – 2.79 (m, 1H), 2.64 – 2.56 (m, 1H), 2.55 – 2.47 (m, 1H), 2.34 (t, *J* = 7.2 Hz, 1H), 2.23 – 2.18 (m, 1H), 2.16 – 2.07 (m, 1H), 1.90 – 1.79 (m, 4H), 1.61 (b, 2H), 1.45 – 1.36 (m, 2H), 1.11 – 0.95 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.6, 153.0, 149.4, 147.1, 137.5, 135.3, 131.2, 130.2, 127.7, 73.9, 60.85, 60.83, 50.6, 44.9, 40.7, 34.9, 27.2, 25.2, 24.5, 24.2, 23.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{28}NaO_4S$= 423.1601; found = 423.1598.

3-(cyclohexylsulfonyl)-4-(3,3-dimethylbut-1-yn-1-yl)-8a-methyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (33)



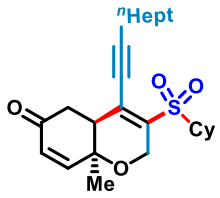
Brownish yellow sticky solid, 33.2 mg 85% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 – 6.63 (m, 1H), 6.03 (d, *J* = 10.3 Hz, 1H), 4.63 – 4.44 (m, 1H), 4.40 – 4.26 (m, 1H), 3.52 – 3.43 (m, 1H), 3.03 – 2.95 (m, 1H), 2.83 – 2.74 (m, 2H), 2.17 – 2.07 (m, 1H), 1.91 (d, *J* = 13.6 Hz, 4H), 1.73 – 1.65 (m, 2H), 1.51 (s, 3H), 1.31 (s, 9H), 1.23 (b, *J* = 14.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.0, 150.8, 139.8, 130.9, 130.6, 114.1, 74.3, 71.4, 62.2, 61.2, 43.9, 39.5, 30.3, 28.8, 25.4, 25.3, 25.3, 25.2, 24.6, 24.1.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{31}O_4S$= 391.1938; found = 391.1944.

3-(cyclohexylsulfonyl)-8a-methyl-4-(non-1-yn-1-yl)-4a,8a-dihydro-2H-chromen-6(5H)-one: (34)



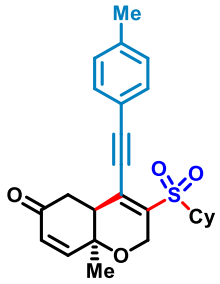
Brown sticky solid, 36.3 mg 84% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (d, *J* = 10.3 Hz, 1H), 6.03 (d, *J* = 10.3 Hz, 1H), 4.62 – 4.49 (m, 1H), 4.41 – 4.28 (m, 1H), 3.43 – 3.34 (m, 1H), 3.06 – 2.94 (m, 1H), 2.84 – 2.68 (m, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.13 – 2.05 (m, 1H), 2.00 (s, 1H), 1.95 – 1.83 (m, 3H), 1.74 – 1.67 (m, 1H), 1.63 – 1.55 (m, 3H), 1.51 (s, 3H), 1.46 – 1.39 (m, 3H), 1.33 – 1.20 (m, 8H), 0.92 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 195.9, 150.8, 139.6, 130.8, 106.7, 75.5, 71.4, 62.2, 61.6, 44.4, 39.5, 31.5, 28.8, 28.3, 25.5, 25.35, 25.31, 25.28, 25.2, 24.6, 24.3, 22.6, 20.1, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{25}H_{37}O_4S$= 433.2407; found = 433.2415.

3-(cyclohexylsulfonyl)-8a-methyl-4-(*p*-tolylethynyl)-4a,8a-dihydro-2H-chromen-6(5H)-one: (35)



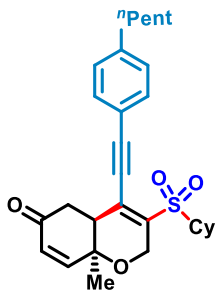
Brown sticky solid, 36.9 mg 87% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 13.1, 8.2 Hz, 2H), 7.19 (dd, *J* = 12.5, 8.1 Hz, 2H), 6.74 (d, *J* = 10.4 Hz, 1H), 6.06 (d, *J* = 10.2 Hz, 1H), 4.84 – 4.57 (m, 1H), 4.46 – 4.26 (m, 1H), 3.45 – 3.35 (m, 1H), 3.20 – 3.04 (m, 1H), 2.96 – 2.88 (m, 2H), 2.67 (q, *J* = 7.6 Hz, 1H), 2.38 (s, 3H), 2.14 (dd, *J* = 11.0, 1.7 Hz, 1H), 2.00 – 1.85 (m, 4H), 1.67 (d, *J* = 7.8 Hz, 1H), 1.55 (s, 3H), 1.27 – 1.21 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 195.9, 150.8, 140.6, 139.9, 132.0, 130.9, 129.5, 128.4, 118.5, 104.2, 83.3, 71.4, 62.4, 62.0, 43.9, 39.5, 25.4, 25.3, 25.2, 24.6, 24.3, 21.8, 15.4.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{25}H_{29}O_4S$= 425.1781; found = 425.1786.

3-(cyclohexylsulfonyl)-8a-methyl-4-((4-pentylphenyl)ethynyl)-4a,8a-dihydro-2H-chromen-6(5H)-one: (36)



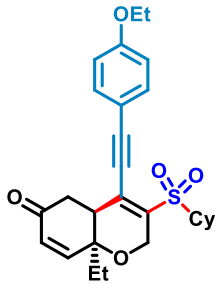
Brownish yellow sticky solid, 39.4 mg 82% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 10.2 Hz, 1H), 6.06 (d, *J* = 10.4 Hz, 1H), 4.68 – 4.58 (m, 1H), 4.49 – 4.35 (m, 1H), 3.44 – 3.38 (m, 1H), 3.10 (dd, *J* = 15.0, 4.3 Hz, 1H), 2.95 – 2.87 (m, 1H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.00 (s, 4H), 1.91 – 1.85 (m, 2H), 1.70 – 1.66 (m, 1H), 1.65 – 1.58 (m, 3H), 1.55 (s, 3H), 1.36 – 1.28 (m, 6H), 1.23 – 1.19 (m, 1H), 0.94 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 195.9, 150.8, 145.6, 139.8, 132.0, 130.9, 130.5, 128.9, 118.7, 104.3, 83.3, 71.4, 62.4, 62.0, 43.9, 39.5, 36.1, 31.7, 31.5, 30.9, 25.4, 25.3, 25.1, 24.6, 24.3, 22.6, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{37}O_4S$= 481.2407; found = 481.2413.

(4aS,8aS)-3-(cyclohexylsulfonyl)-4-((4-ethoxyphenyl)ethynyl)-8a-methyl-4a,8a-dihydro-2H-chromen-6(5H)-one: (37)



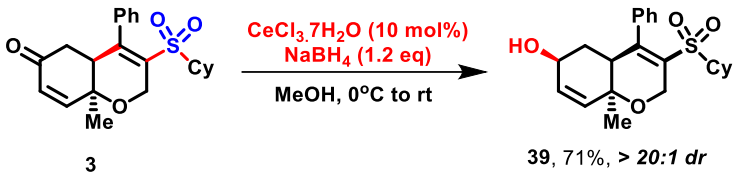
Brownish yellow sticky solid, 39.8 mg 85% yield, 0.3 Rf in 30 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.41 (m, 2H), 6.94 – 6.85 (m, 2H), 6.80 (d, *J* = 10.5 Hz, 1H), 6.09 (d, *J* = 10.4 Hz, 1H), 4.73 – 4.57 (m, 1H), 4.46 – 4.23 (m, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 3.53 – 3.31 (m, 1H), 3.14 (dd, *J* = 16.6, 5.1 Hz, 1H), 2.97 (s, 1H), 2.85 (dd, *J* = 16.6, 5.6 Hz, 1H), 2.15 (d, *J* = 13.3 Hz, 1H), 1.97 – 1.74 (m, 4H), 1.70 – 1.63 (m, 2H), 1.61 – 1.49 (m, 3H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.21 (s, 2H), 1.06 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 195.9, 160.5, 150.4, 139.3, 133.8, 131.6, 130.9, 114.9, 113.5, 104.6, 83.1, 73.6, 63.8, 62.4, 62.0, 41.7, 39.4, 30.6, 25.6, 25.3, 25.2, 24.3, 14.8, 7.8.

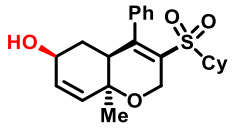
HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{27}H_{33}NO_5S$= 469.2043; found = 469.2037.

Procedure: Reduction of keto group *via* Luche reduction:



Procedure: To a solution of **3** (38.6 mg, 0.1 mmol) in 1.2 mL MeOH was added 0.1 eq. of $CeCl_3.7H_2O$ followed by 1.2 eq of $NaBH_4$ slowly. The reaction was stirred at rt for 1 h then quenched with water then the organic layer was collected and purified by column chromatography to give 27.5 mg, 71% of the desired compound **39** as a white sticky solid.

3-(cyclohexylsulfonyl)-8a-methyl-4-phenyl-4a,5,6,8a-tetrahydro-2H-chromen-6-ol: (39)



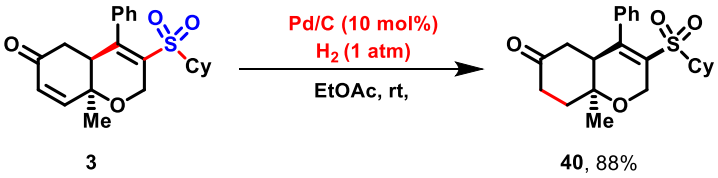
White sticky solid, 27.5 mg 71% yield, 0.3 Rf in 50 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 5.3, 1.8 Hz, 3H), 7.25 (b, 2H), 5.86 (dt, *J* = 10.0, 1.6 Hz, 1H), 5.67 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.66 (dd, *J* = 17.6, 0.9 Hz, 1H), 4.37 (dd, *J* = 17.7, 2.4 Hz, 1H), 4.05 (b, 1H), 2.16 (dt, *J* = 12.4, 2.4 Hz, 1H), 2.03 (h, *J* = 3.2 Hz, 1H), 1.99 – 1.86 (m, 2H), 1.81 – 1.72 (m, 5H), 1.63 – 1.50 (m, 2H), 1.41 (s, 3H), 1.38 – 1.32 (m, 1H), 1.12 – 1.04 (m, 1H), 0.99 – 0.89 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.8, 137.1, 134.1, 132.9, 132.0, 128.7, 128.2, 68.8, 67.5, 61.5, 61.2, 45.5, 33.3, 25.5, 25.0, 24.9, 23.1, 22.6.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{22}H_{28}NaO_4S$= 411.1601; found = 411.1586.

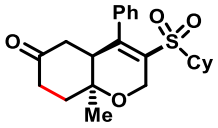
Procedure: Synthesis of tetrahydrochromenone 40 *via* catalytic hydrogenation:



38.6 mg, 0.1 mmol of **3** was dissolved in 2 mL of dry EtOAc in a 10 mL round bottomed flask, then 14 mg of 10% Pd/C (10 mol%) was added and the reaction mixture was flushed with

hydrogen gas and stirred overnight at rt. The reaction mass was then filtered through a celite plug and the filtrate evaporated under reduced pressure and chromatographed with EtOAc in Petroleum ether (4:6) to give 34.2 mg, 88% yield of the desired product **40**.

3-(cyclohexylsulfonyl)-8a-methyl-4-phenyl-4a,7,8,8a-tetrahydro-2H-chromen-6(5H)-one: (40)



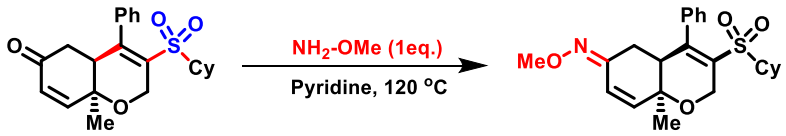
White sticky solid, 34.2 mg 88% yield, 0.2 Rf in 40 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.22 – 7.13 (m, 2H), 4.77 (d, *J* = 17.9 Hz, 1H), 4.49 (dd, *J* = 17.9, 2.0 Hz, 1H), 2.77 – 2.65 (m, 1H), 2.48 – 2.43 (m, 2H), 2.31 – 2.18 (m, 3H), 2.04 – 1.95 (m, 1H), 1.94 – 1.86 (m, 2H), 1.83 – 1.73 (m, 3H), 1.61 – 1.54 (m, 1H), 1.44 (s, 3H), 1.42 – 1.35 (m, 2H), 1.13 – 1.03 (m, 1H), 0.97 – 0.86 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 209.6, 148.7, 136.9, 132.4, 129.0, 128.5, 128.1, 69.8, 61.6, 61.3, 48.7, 41.9, 37.5, 36.5, 25.6, 25.1, 25.1, 24.9, 23.1, 22.7.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{28}NaO_4S$= 411.1601; found = 411.1592.

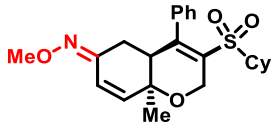
Procedure: Synthesis of oxime 41:



3 **41**, 75%

38.6 mg, 0.1 mmol of **3** was dissolved in 2 mL of pyridine in a 10 mL reaction tube, then 31.3 mg of $NH_2OMe.HCl$ was added and the reaction mixture was stirred overnight at 120 °C. The reaction was then evaporated under reduced pressure and chromatographed with EtOAc in Petroleum ether (1:1) to give 31.2 mg, 75% yield of the desired product **41**.

(Z)-3-(cyclohexylsulfonyl)-8a-methyl-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one O-methyl oxime: (41)



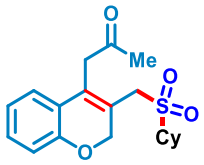
Brownish yellow sticky solid, 31.2 mg 75% yield, 0.3 Rf in 50 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 4.5, 2.2 Hz, 3H), 7.19 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.27 (d, *J* = 10.1 Hz, 1H), 6.04 (d, *J* = 10.1 Hz, 1H), 4.58 (dd, *J* = 17.5, 2.2 Hz, 1H), 4.49 (dd, *J* = 17.5, 2.1 Hz, 1H), 3.83 (s, 3H), 2.69 – 2.59 (m, 1H), 2.58 – 2.51 (m, 1H), 2.15 – 2.06 (m, 1H), 1.95 – 1.75 (m, 4H), 1.63 – 1.57 (m, 1H), 1.51 (s, 3H), 1.46 – 1.36 (m, 2H), 1.33 – 1.24 (m, 1H), 1.18 – 1.07 (m, 1H), 1.07 – 0.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.0, 149.1, 139.8, 136.9, 136.2, 134.2, 128.7, 128.2, 127.0, 71.4, 62.0, 61.9, 61.5, 44.6, 25.4, 25.16, 25.13, 25.0, 24.8, 23.7, 23.4.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{30}NO_4S$= 416.1890; found = 416.1897.

1-(3-((cyclohexylsulfonyl)methyl)-2H-chromen-4-yl)propan-2-one: (43)



Brown sticky solid, 21.2 mg 61% yield, 0.3 Rf in 50 % EtOAc in pet ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.18 (m, 1H), 7.10 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.90 (dd, *J* = 8.0, 1.3 Hz, 1H), 4.82 (s, 2H), 3.85 (s, 2H), 3.75 (s, 2H), 3.01 – 2.90 (m, 1H), 2.23 (s, 3H), 2.01 – 1.93 (m, 2H), 1.83 – 1.73 (m, 1H), 1.68 – 1.54 (m, 3H), 1.40 – 1.24 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 205.2, 154.3, 131.3, 130.0, 123.9, 123.2, 121.7, 119.0, 116.5, 68.5, 62.1, 51.6, 42.9, 29.7, 25.4, 25.08, 25.03.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{25}O_4S$= 349.1468; found = 349.1454.

7. References:

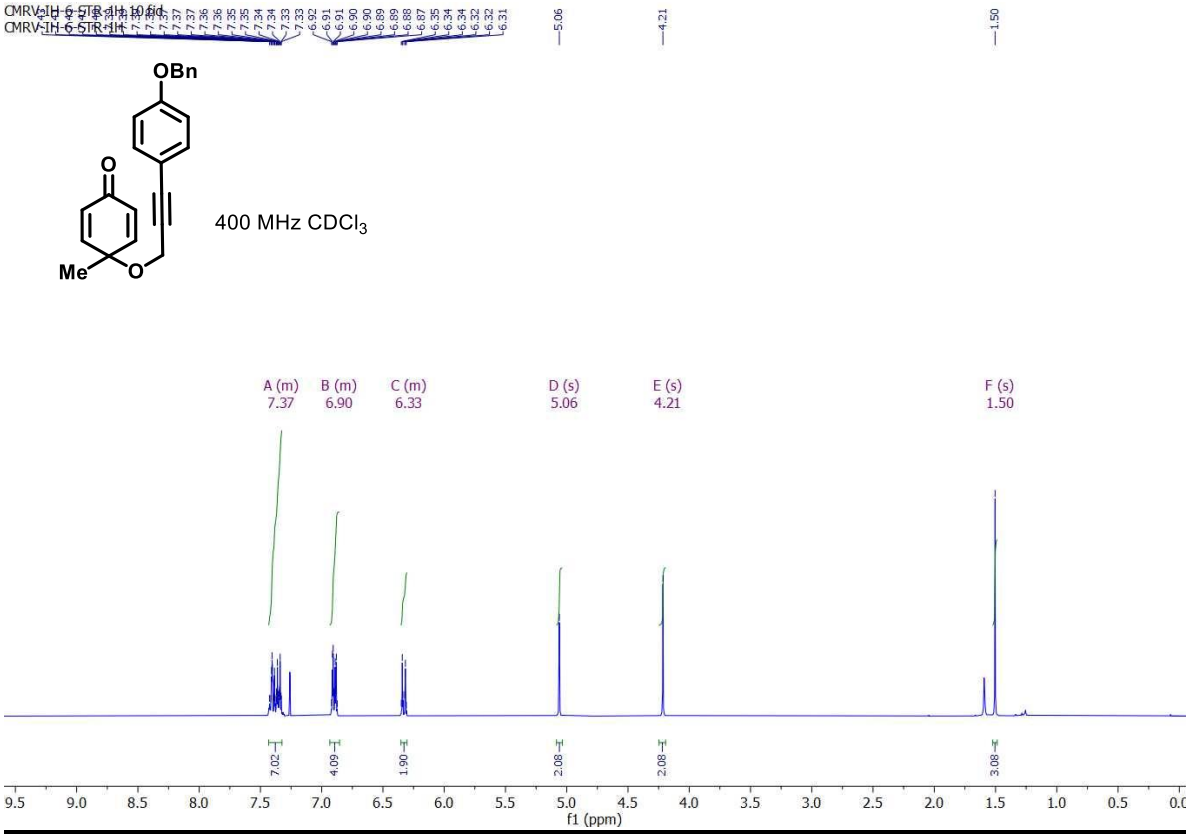
1) (a) R. Tello-Aburto and A. M. Harned, *Org. Lett*. 2009, **11**, 3998; (b) K. K. Gollapelli, S. Donikela, N. Manjula and R. Chegondi, *ACS Catal*. 2018, **8**, 1440; (c) A. Munakala and R. Chegondi, *Org. Lett.*, 2020, **23**, 317; (d) A. Munakala, K. K. Gollapelli, J. B. Nanubolu and R. Chegondi, *Org. Lett.*, 2020, **22**, 7019; (e) R. K. Mallick, S. Dutta, R. Vanjari, A. Voituriez and A. K. Sahoo, *J. Org. Chem.*, 2019, **84**, 10509; (f) R. K. Mallick, S. Vangara, N. Kommu, T. Guntreddi and A. K. Sahoo, *J. Org. Chem*., 2021, **86**, 7059; (g) J. K. Hexum, R. Tello-Aburto, N. B. Struntz, A. M. Harned and D. A. Harki, *ACS Med. Chem. Lett*., 2012, **3**, 459.

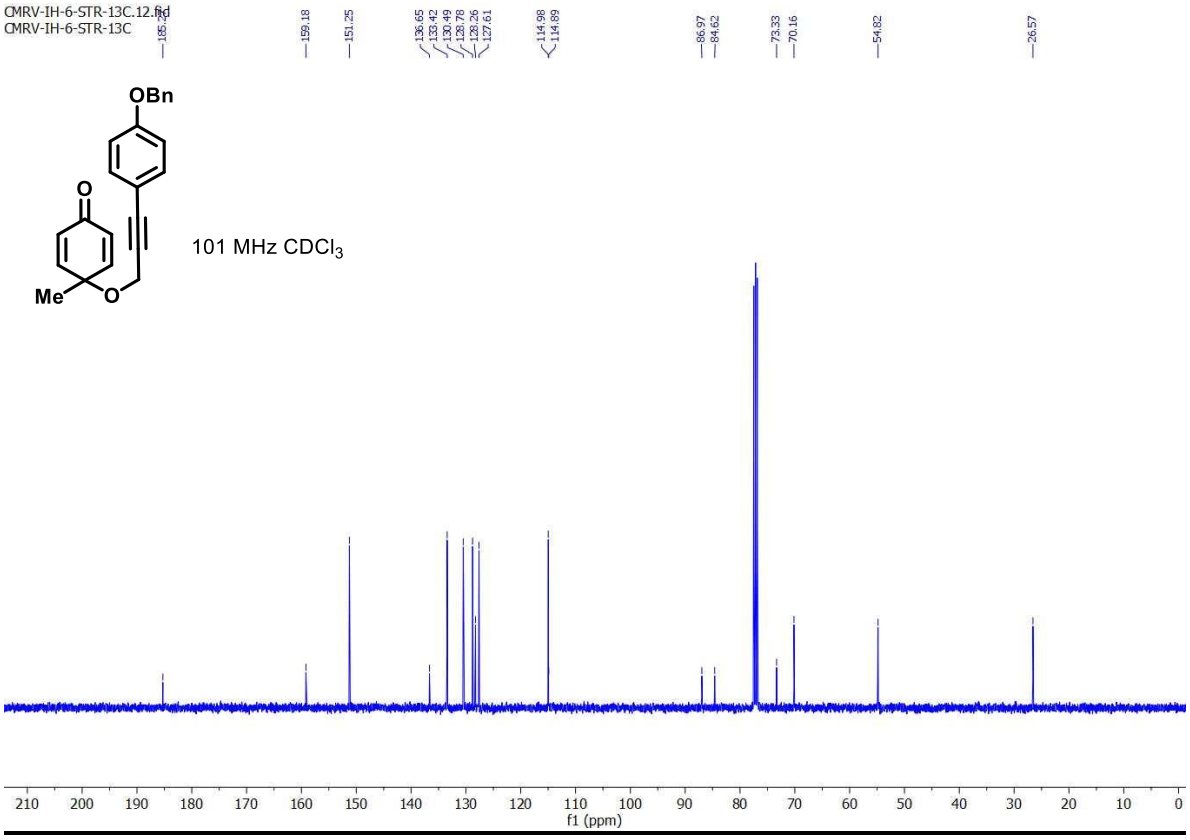
2) (a) L. Li, S.-qi Zhang, Y. Chen, X. Cui, G. Zhao, Z. Tang and G.-xun Li, *ACS Catal*. 2022, **12**, 15334; (b) X. Wang, Y. Tang, S. Ye, J. Zhang, Y. Kuang and J. Wu, *Org. Lett*. 2022, **24**, 2059.

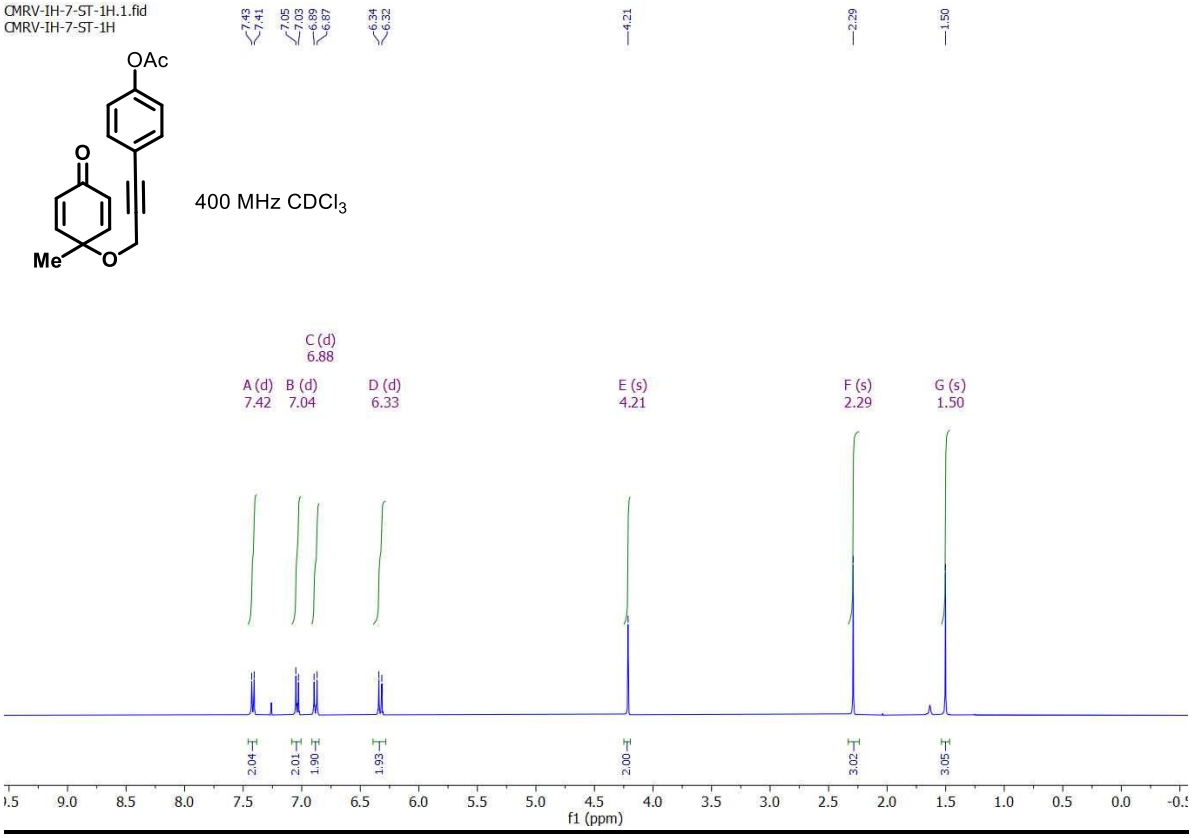
3) S. Van Mileghem and W. M. De Borggraeve, *Org. Process Res. Dev*. 2017, **21**, 785.

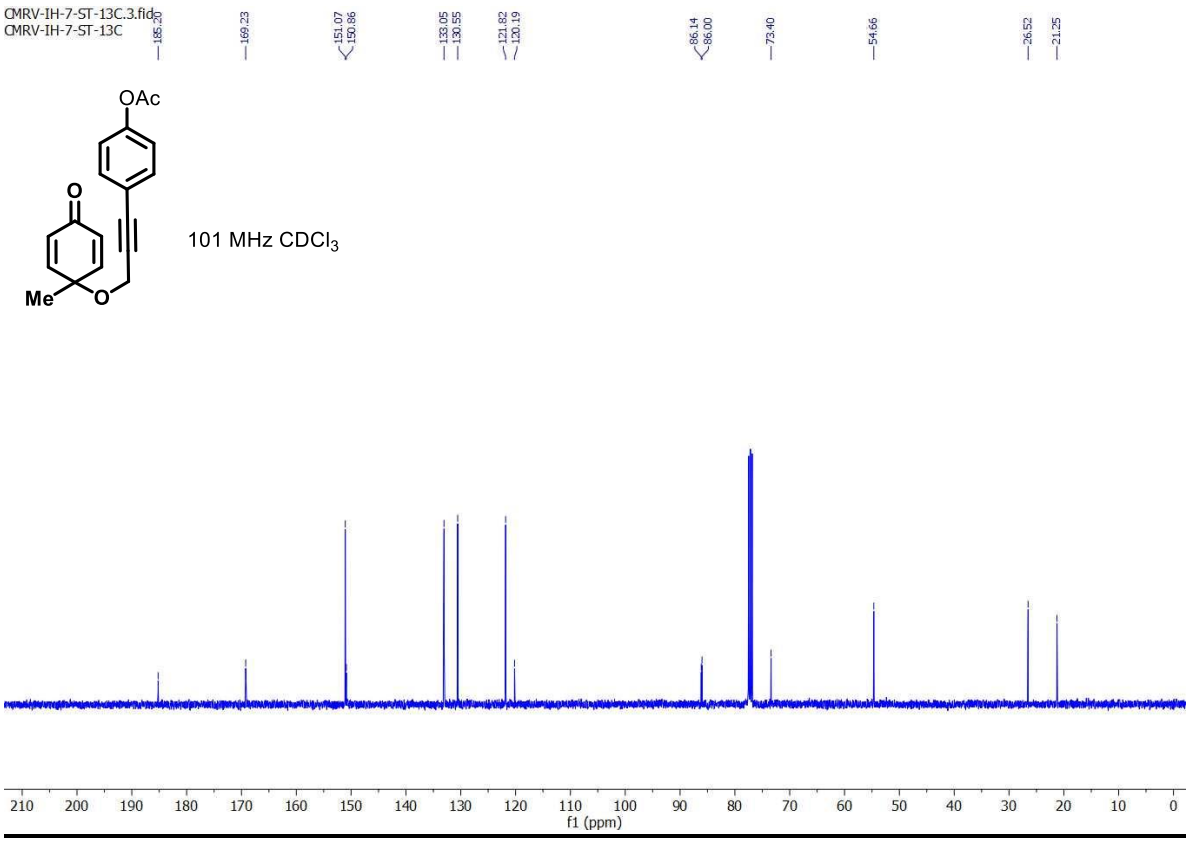
4) (a) S. Engle, *Org. Synth*. 2019, **96**, 455; (b) Y. Liu, X.-L. Chen, X.-Y. Li, S.-S. Zhu, S.-J. Li, Y. Song, L.-B. Qu and B. Yu, *J. Am Chem Soc*. 2020, **143**, 964.

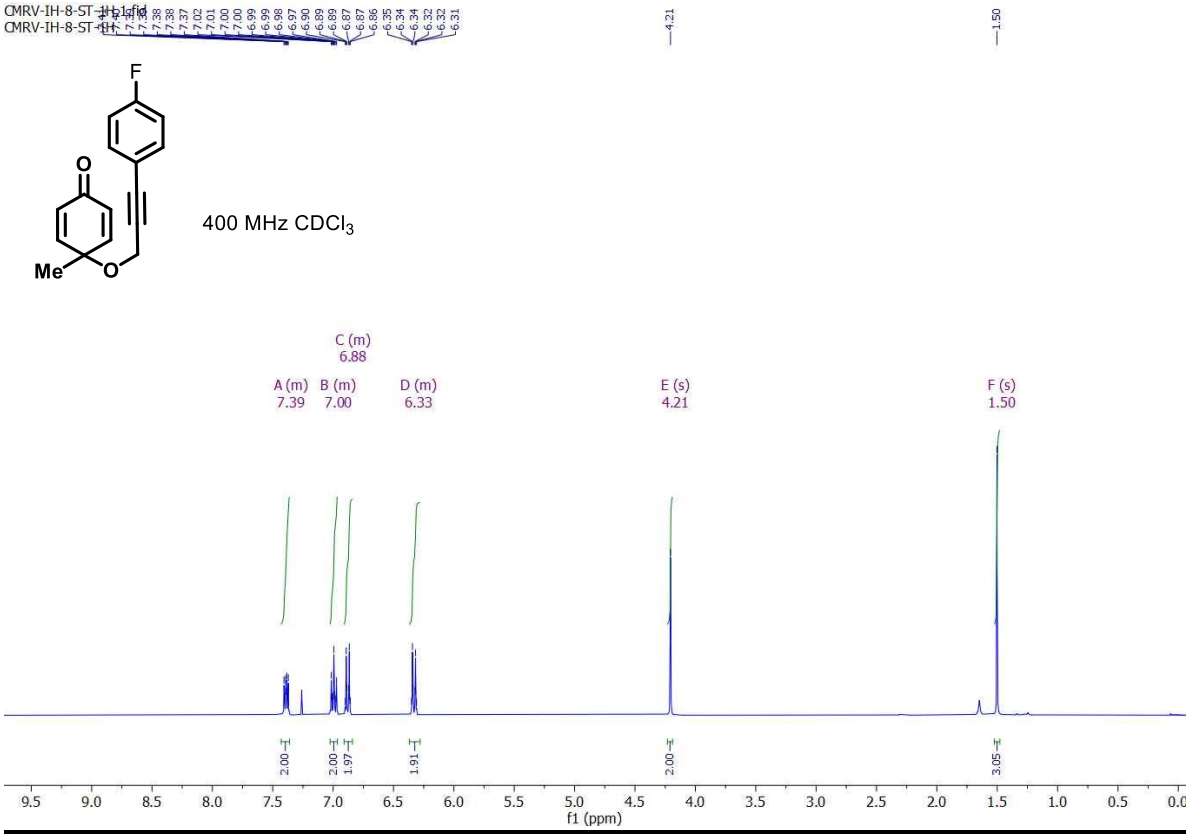
8. ^{1}H and ^{13}C Spectra:

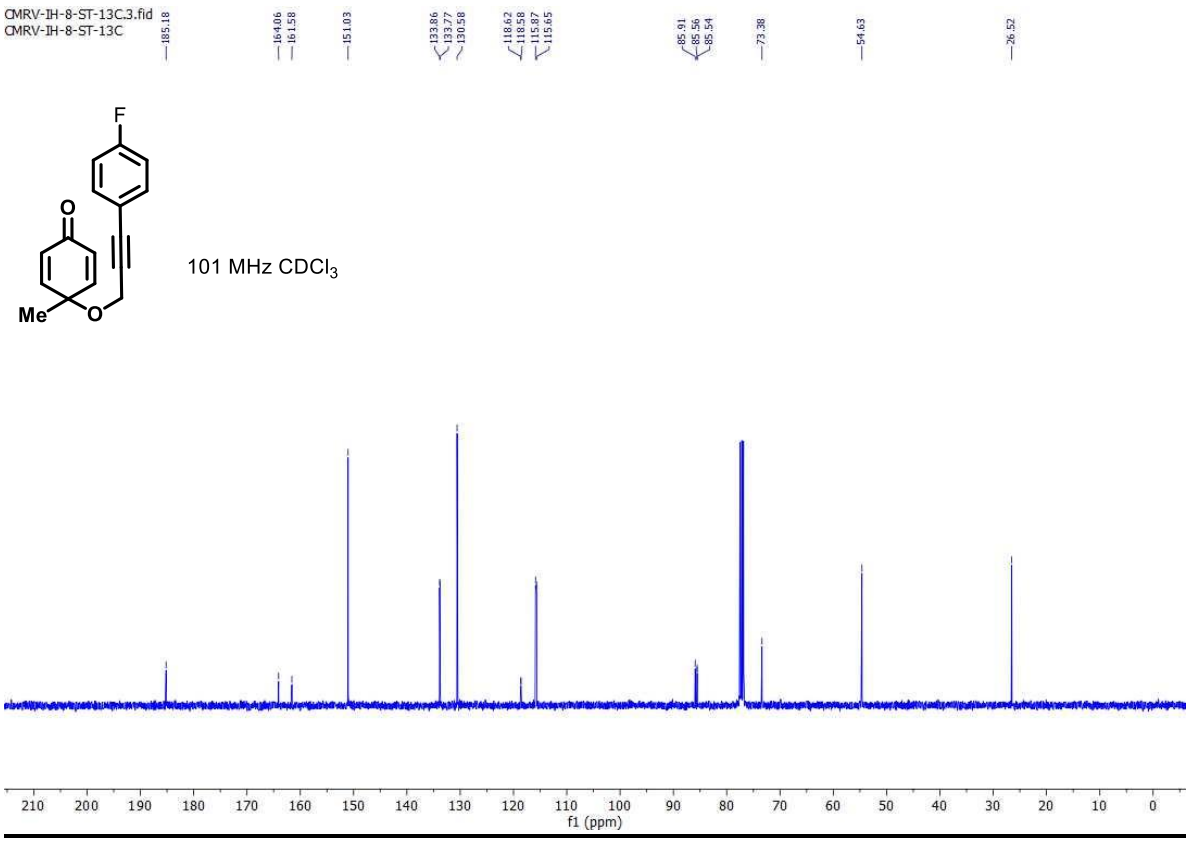




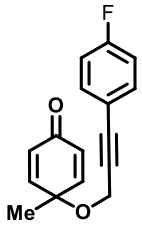

CMRV-IH-7-ST-1H.1.fid
CMRV-IH-7-ST-1H
7.43
7.41
7.05
7.03
6.89
6.87
6.34
6.32
4.21
2.29
1.50
OAc
O
Me
O
400 MHz CDCl3
C (d)
6.88
A (d)
7.42
B (d)
7.04
D (d)
6.33
E (s)
4.21
F (s)
2.29
G (s)
1.50
2.04
2.01
1.90
1.93
2.00
3.02
3.05
f1 (ppm)


CMRV-IH-7-ST-13C.3.fid
CMRV-IH-7-ST-13C
185.20
169.23
151.07
150.86
133.05
130.55
121.82
120.19
86.14
86.00
73.40
54.66
26.52
21.25
OAc
O
Me
O
101 MHz CDCl3
f1 (ppm)

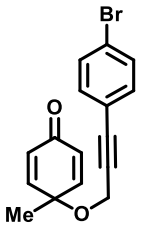

CMRV-IH-8-ST-1H.1.fid
CMRV-IH-8-ST-1H
4.21
1.50
F
O
Me
O
400 MHz CDCl3
C (m)
6.88
A (m)
7.39
B (m)
7.00
D (m)
6.33
E (s)
4.21
F (s)
1.50
2.00
2.00
1.97
1.91
2.00
3.05
f1 (ppm)


CMRV-IH-8-ST-13C.3.fid
CMRV-IH-8-ST-13C
185.18
164.06
161.58
151.03
133.86
133.77
130.58
118.62
118.58
115.87
115.65
85.91
85.56
85.54
73.38
54.63
26.52
F
O
Me
O
101 MHz CDCl3
f1 (ppm)

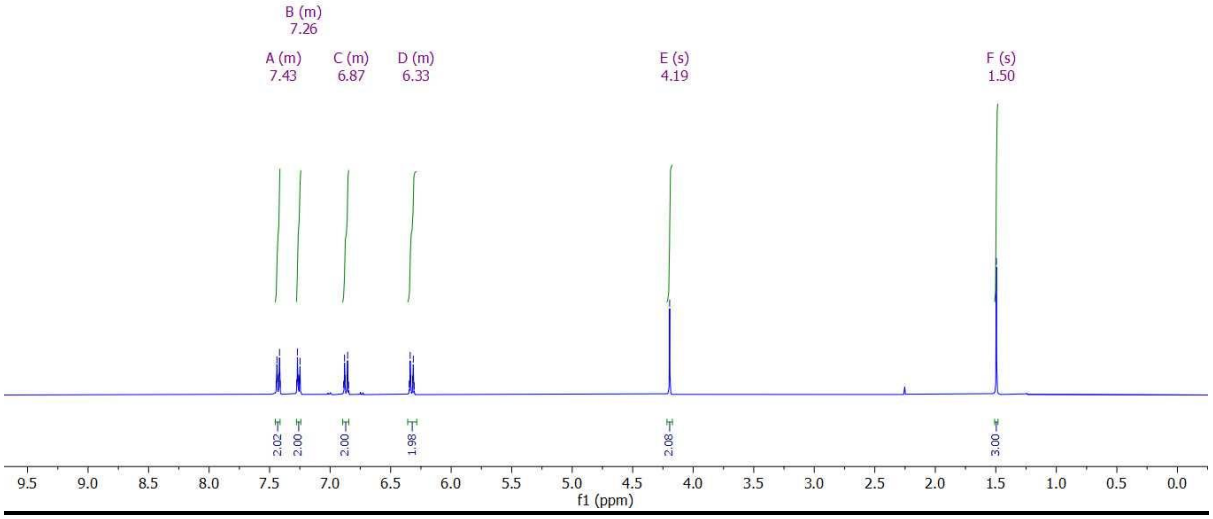
CMRV-IH-8-ST-19F.5.fid
CMRV-IH-8-ST-19F

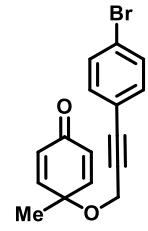


377 MHz $CDCl_3$

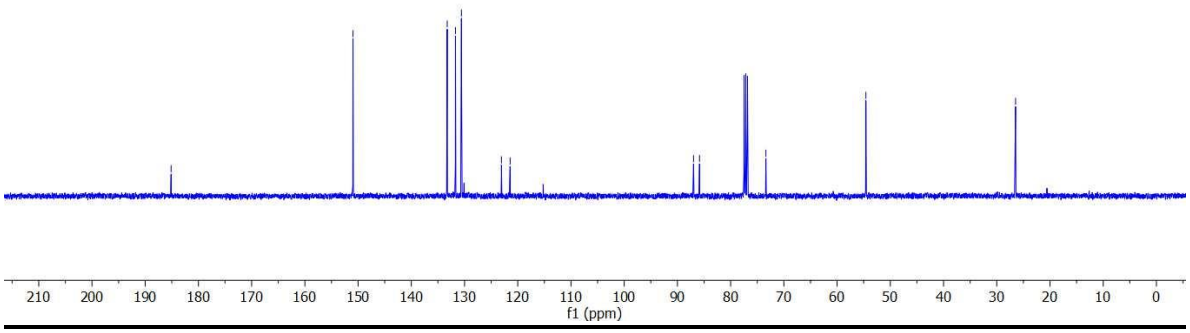


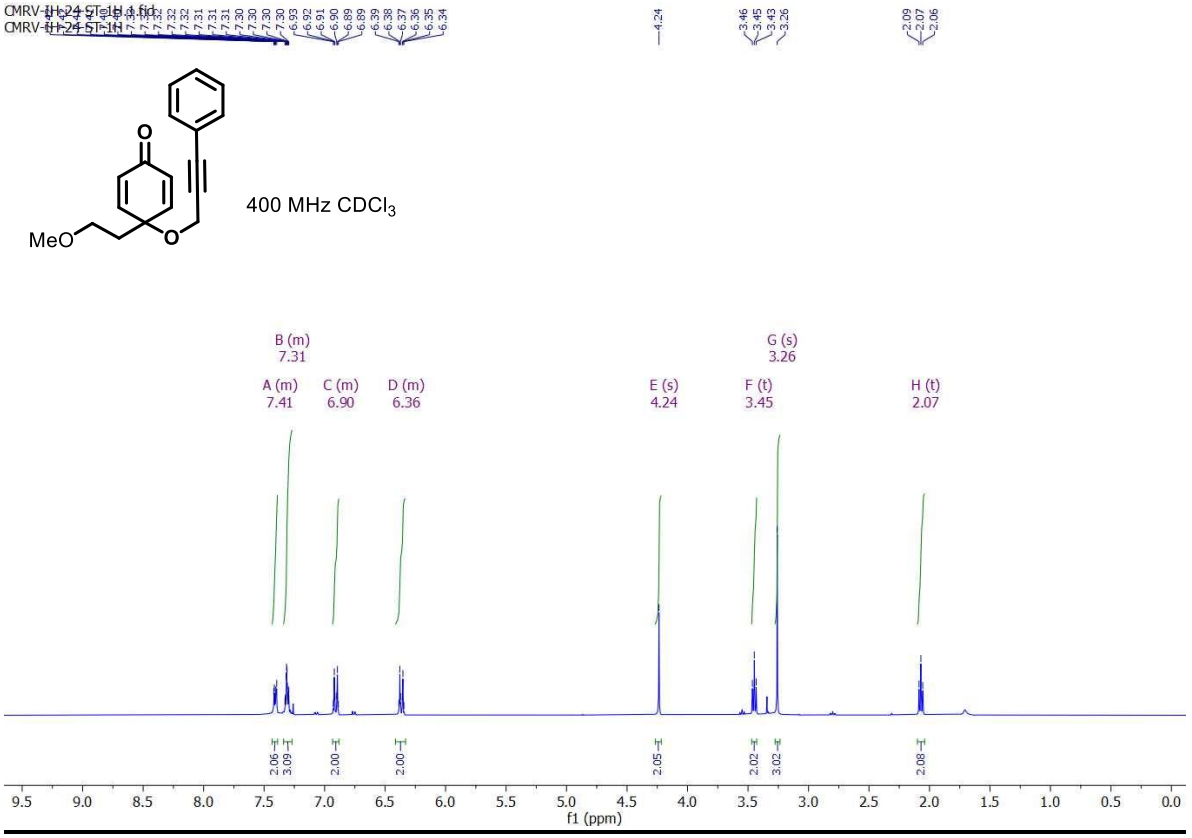
400 MHz $CDCl_3$

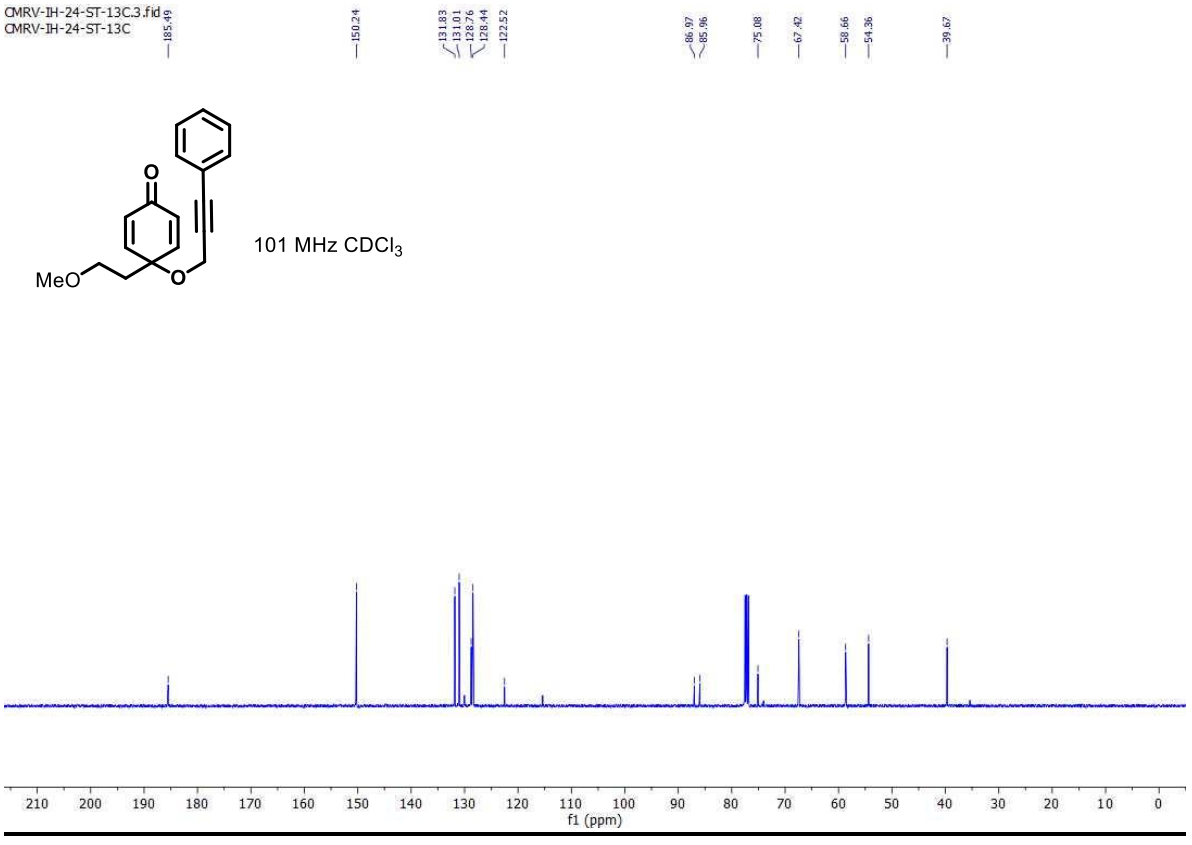


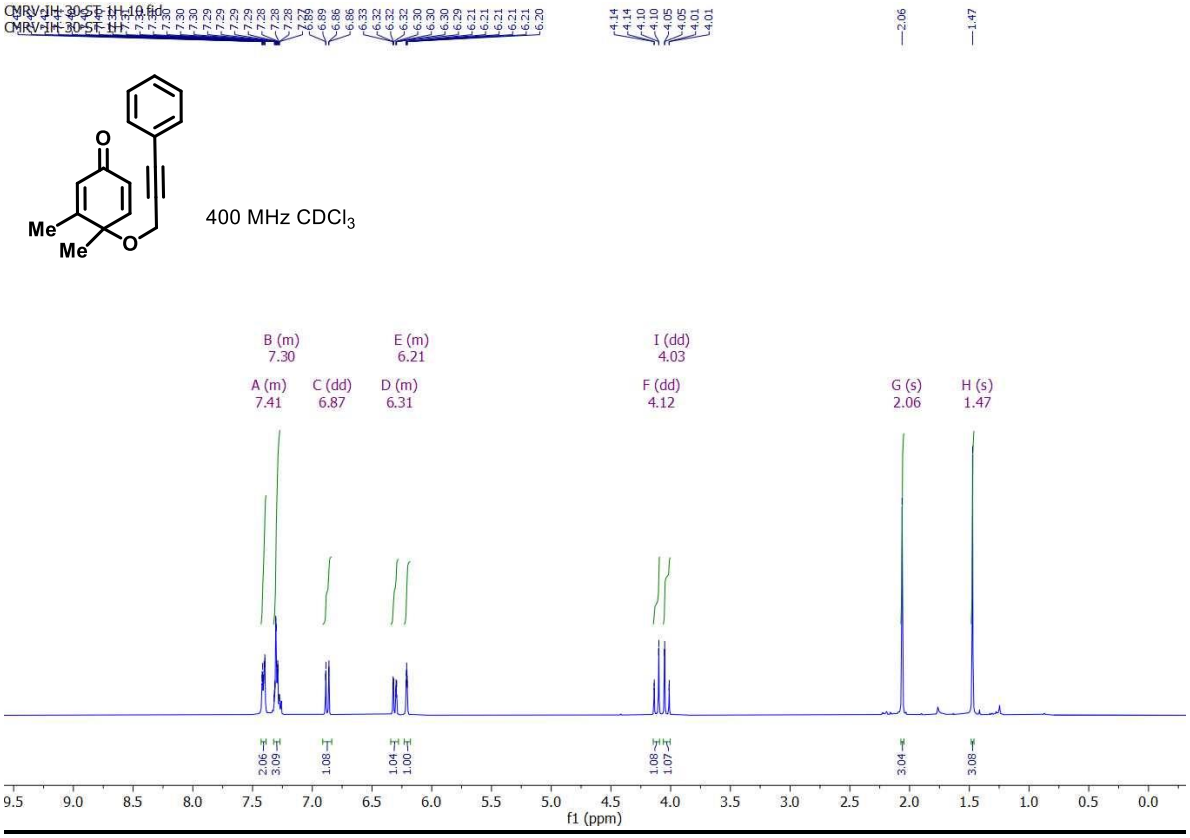


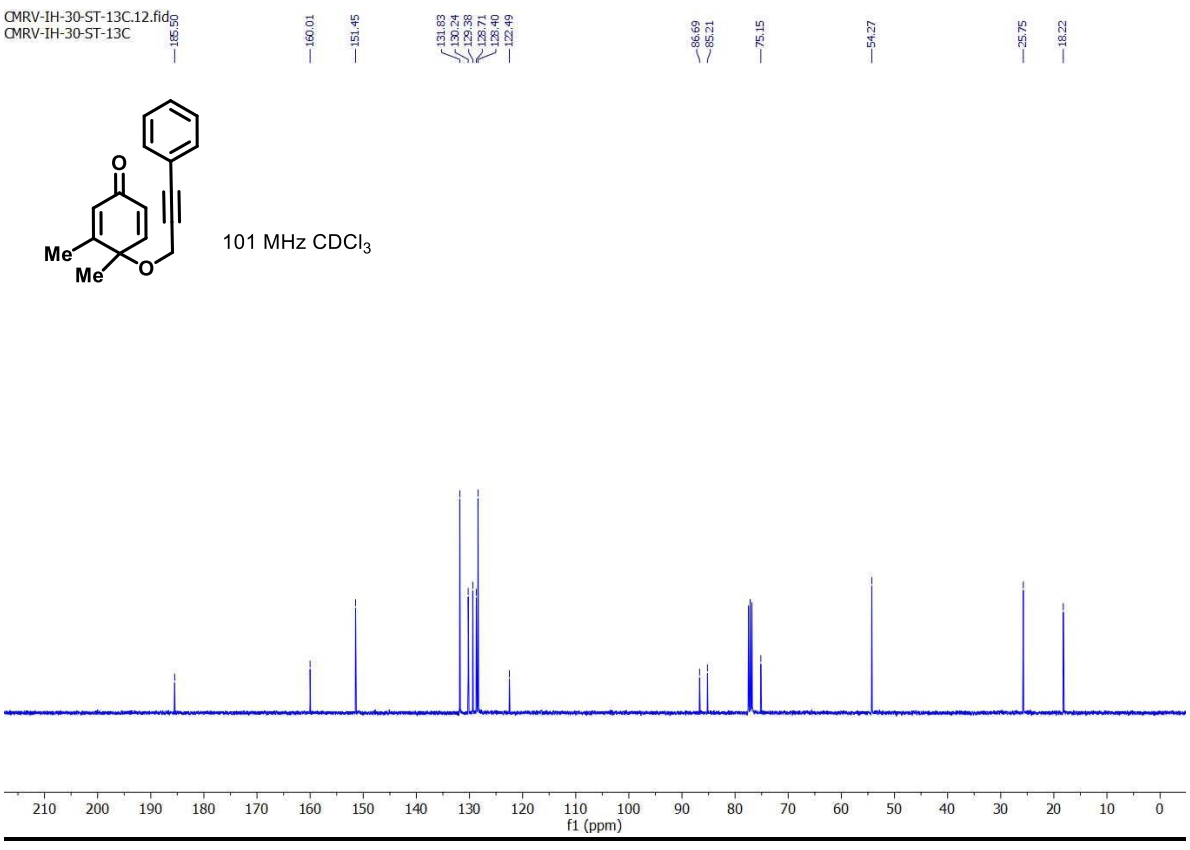
101 MHz $CDCl_3$

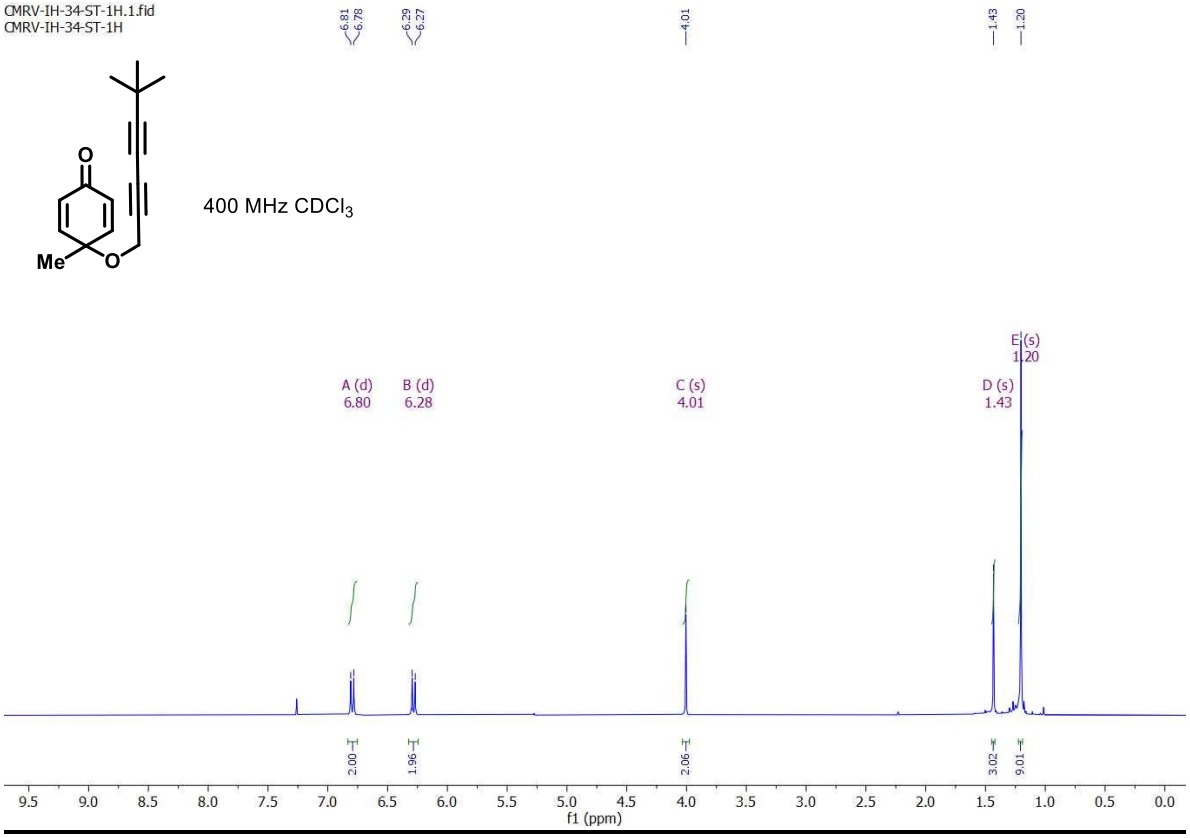


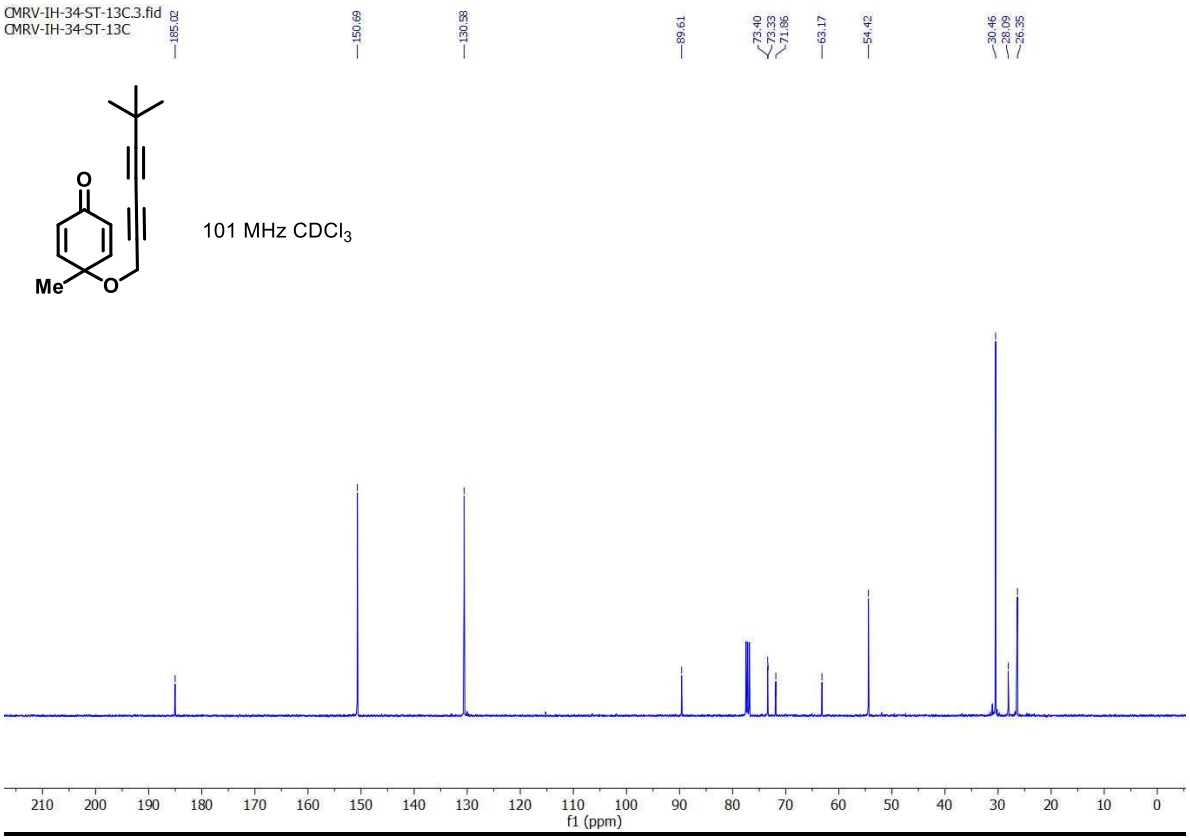

CMRV-1H-24-ST-1H.4.fid
CMRV-1H-24-ST-1H
7.41
7.32
7.31
7.30
6.93
6.92
6.91
6.90
6.89
6.39
6.38
6.37
6.36
6.35
6.34
4.24
3.46
3.45
3.43
3.26
2.09
2.07
2.06
O
MeO
O
400 MHz CDCl3
B (m)
7.31
G (s)
3.26
A (m)
7.41
C (m)
6.90
D (m)
6.36
E (s)
4.24
F (t)
3.45
H (t)
2.07
2.06
3.09
2.00
2.00
2.05
2.02
3.02
2.08
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)

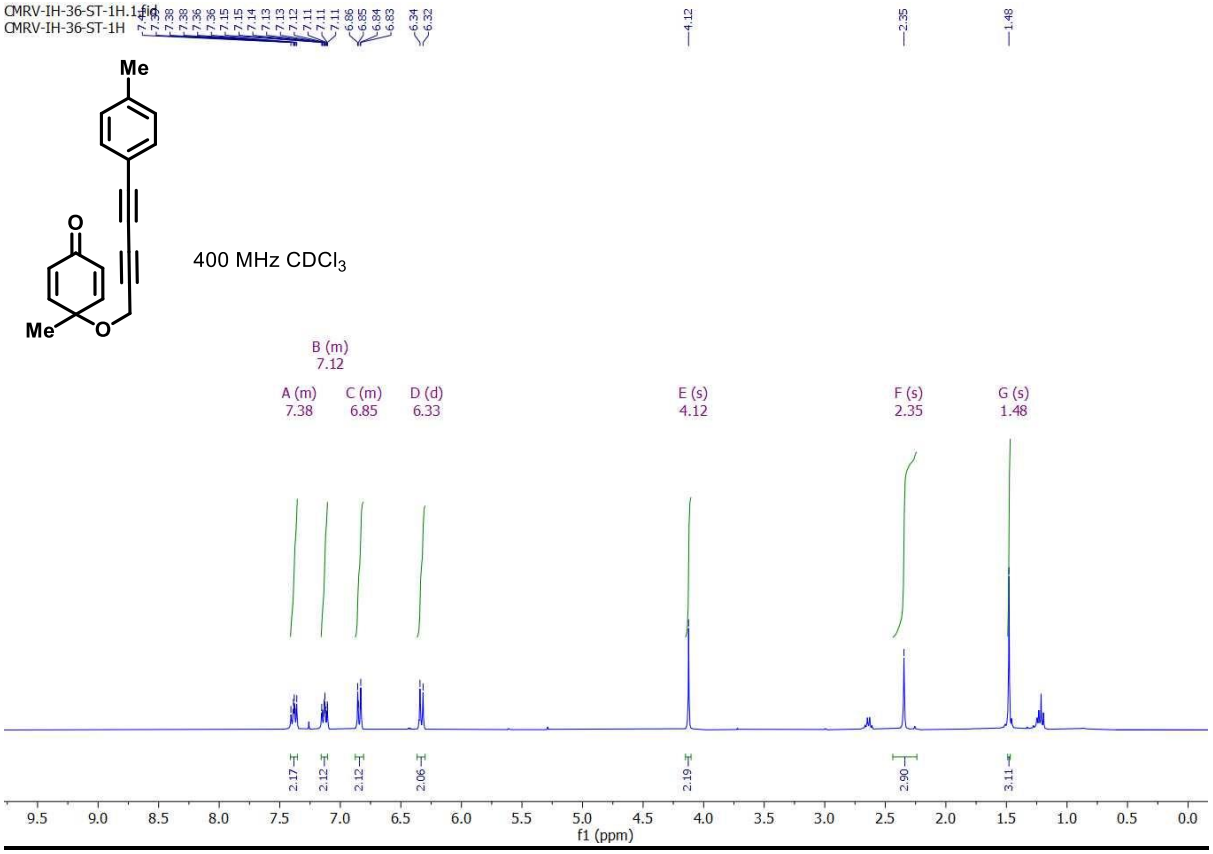

CMRV-1H-24-ST-13C.3.fid
CMRV-1H-24-ST-13C
185.49
150.24
131.83
131.01
128.26
128.44
122.52
86.97
85.96
75.08
67.42
58.66
54.36
39.67
O
MeO
O
101 MHz CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

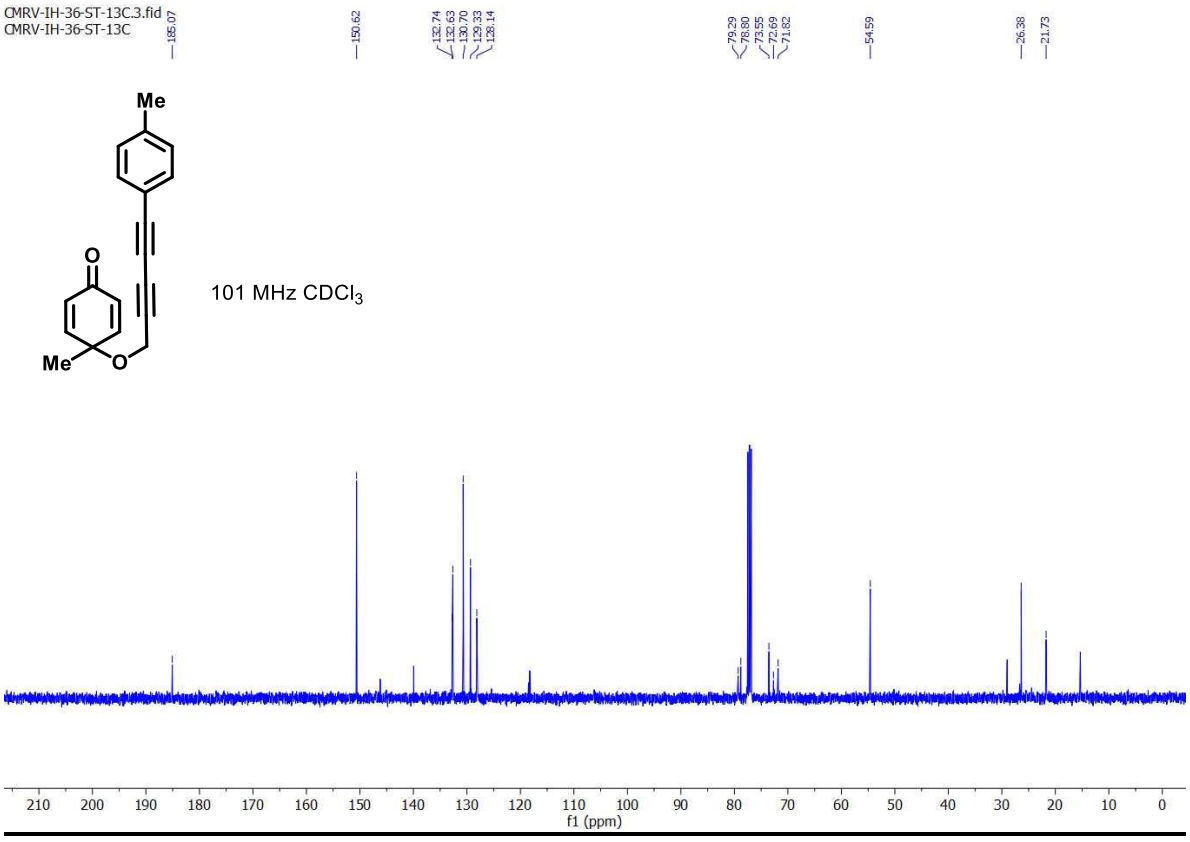

CMRV-IH-30-ST-1H.10.fid
CMRV-IH-30-ST-1H
7.41
7.30
7.29
7.28
6.89
6.87
6.33
6.32
6.31
6.30
6.29
6.21
6.20
4.14
4.10
4.05
4.01
2.06
1.47
O
Me
Me
O
400 MHz CDCl3
B (m)
7.30
E (m)
6.21
I (dd)
4.03
A (m)
7.41
C (dd)
6.87
D (m)
6.31
F (dd)
4.12
G (s)
2.06
H (s)
1.47
2.06
3.09
1.08
1.04
1.00
1.08
1.07
3.04
3.08
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)

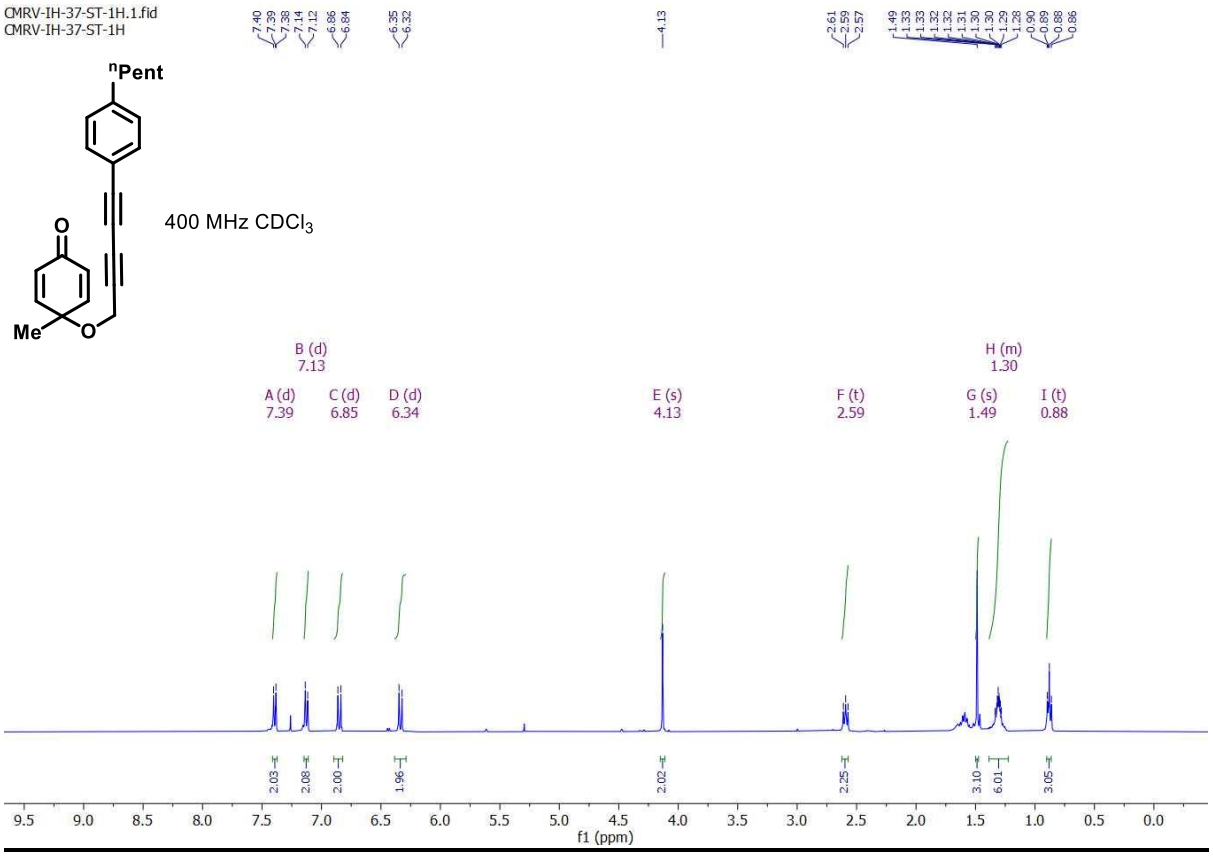

CMRV-IH-30-ST-13C.12.fid
CMRV-IH-30-ST-13C
185.50
160.01
151.45
131.83
130.24
129.38
128.71
128.40
122.49
86.69
85.21
75.15
54.27
25.75
18.22
O
Me
Me
O
101 MHz CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

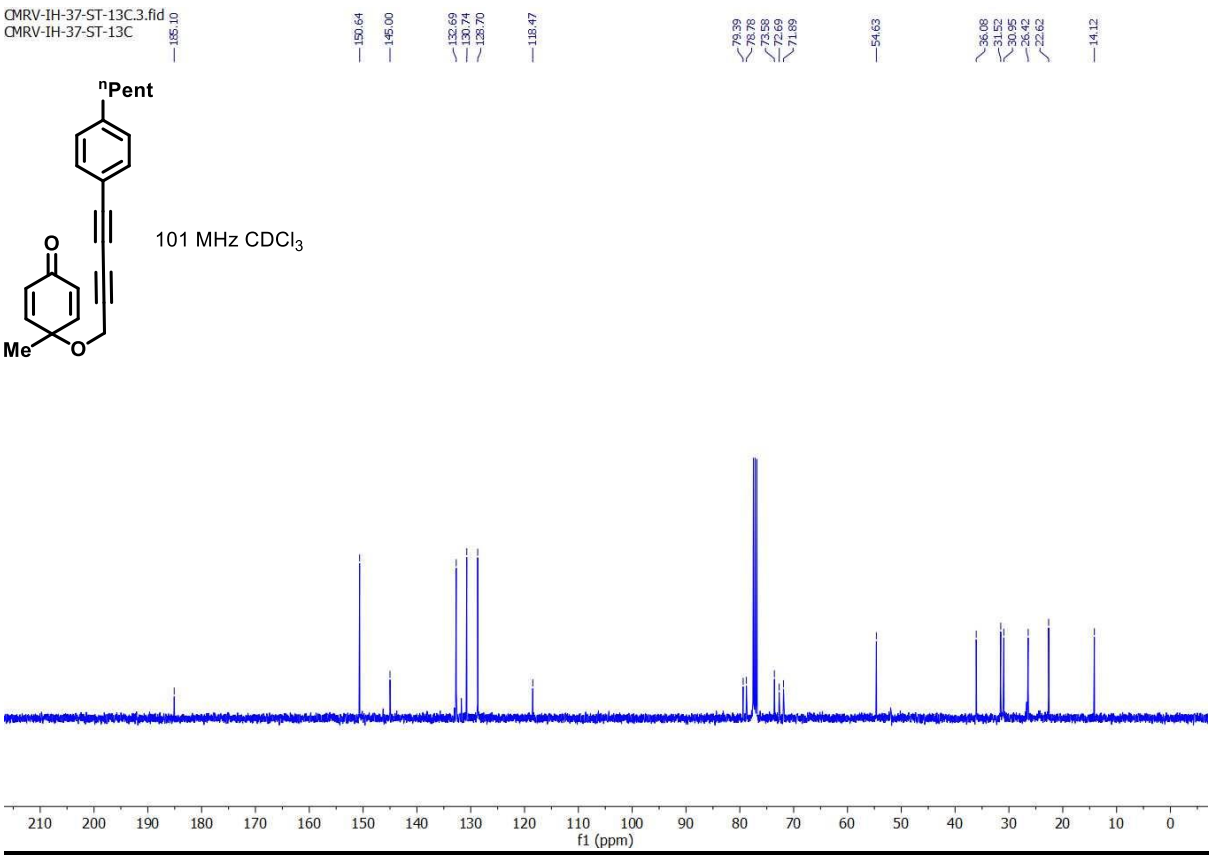

CMRV-IH-34-ST-1H.1.fid
CMRV-IH-34-ST-1H
6.81
6.78
6.29
6.27
4.01
1.43
1.20
O
Me
O
400 MHz CDCl3
A (d)
6.80
B (d)
6.28
C (s)
4.01
D (s)
1.43
E (s)
1.20
2.00
1.96
2.06
3.02
9.01
f1 (ppm)


CMRV-IH-34-ST-13C.3.fid
CMRV-IH-34-ST-13C
185.02
150.69
130.58
89.61
73.40
73.33
71.86
63.17
54.42
30.46
28.09
26.35
O
Me
O
101 MHz CDCl3
f1 (ppm)

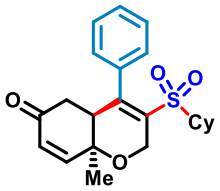

CMRV-IH-36-ST-1H.1.fid
CMRV-IH-36-ST-1H
Me
O
Me
O
400 MHz CDCl3
B (m)
7.12
A (m)
7.38
C (m)
6.85
D (d)
6.33
E (s)
4.12
F (s)
2.35
G (s)
1.48
f1 (ppm)


CMRV-IH-36-ST-13C.3.fid
CMRV-IH-36-ST-13C
Me
O
Me
O
101 MHz CDCl3
f1 (ppm)


CMRV-IH-37-ST-1H.1.fid
CMRV-IH-37-ST-1H
nPent
O
Me
O
400 MHz CDCl3
B (d)
7.13
H (m)
1.30
A (d)
7.39
C (d)
6.85
D (d)
6.34
E (s)
4.13
F (t)
2.59
G (s)
1.49
I (t)
0.88
f1 (ppm)

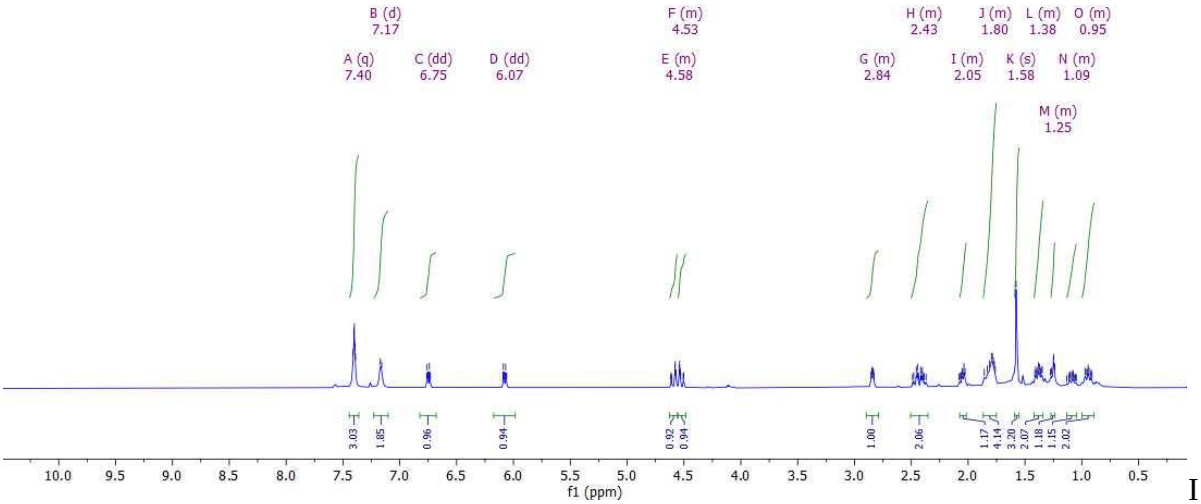

CMRV-IH-37-ST-13C.3.fid
CMRV-IH-37-ST-13C
nPent
O
Me
O
101 MHz CDCl3
f1 (ppm)

CMRV-IH-362-1H.1.fid
CMRV-IH-362-1H



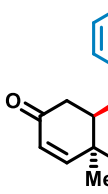
3

500 MHz $CDCl_3$



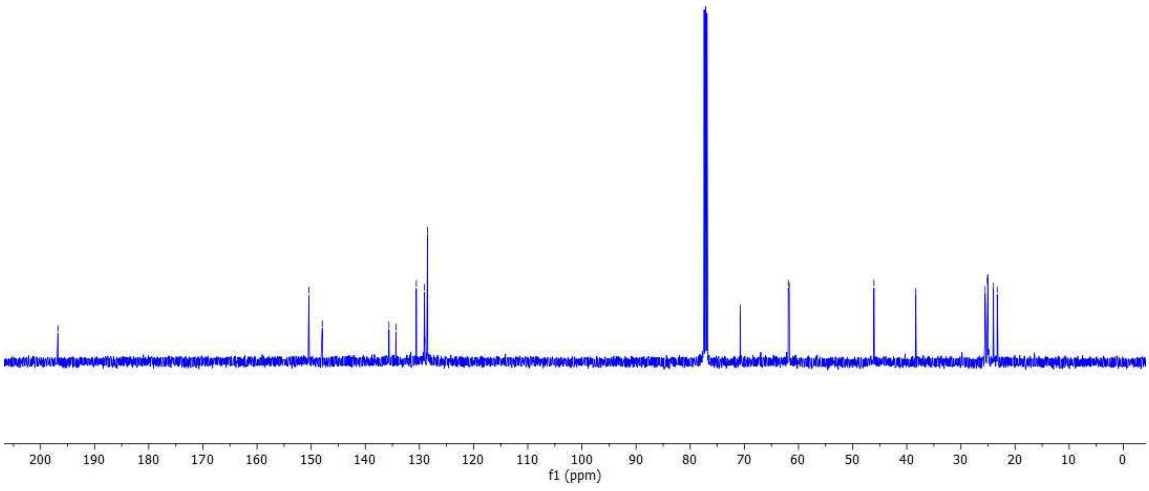
I

CMRV-IH-362-13C.2.fid
CMRV-IH-362-13C

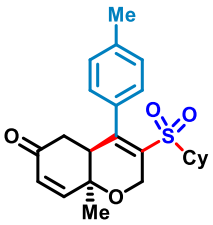


3

126 MHz $CDCl_3$

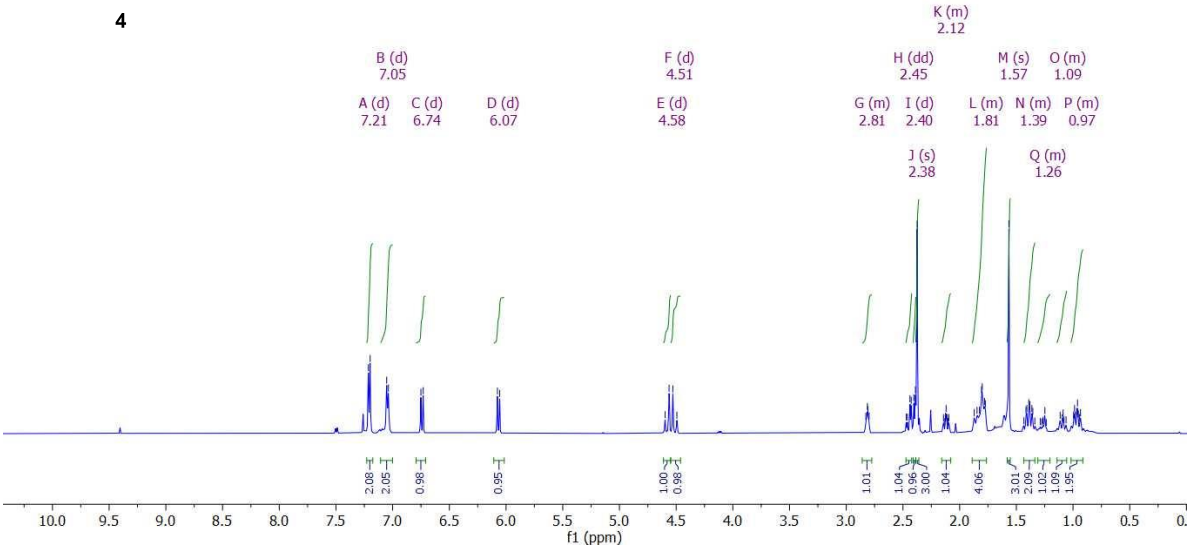


CMRV-IH-736-A-II-1H.2.fid
CMRV-IH-736-A-II-1H

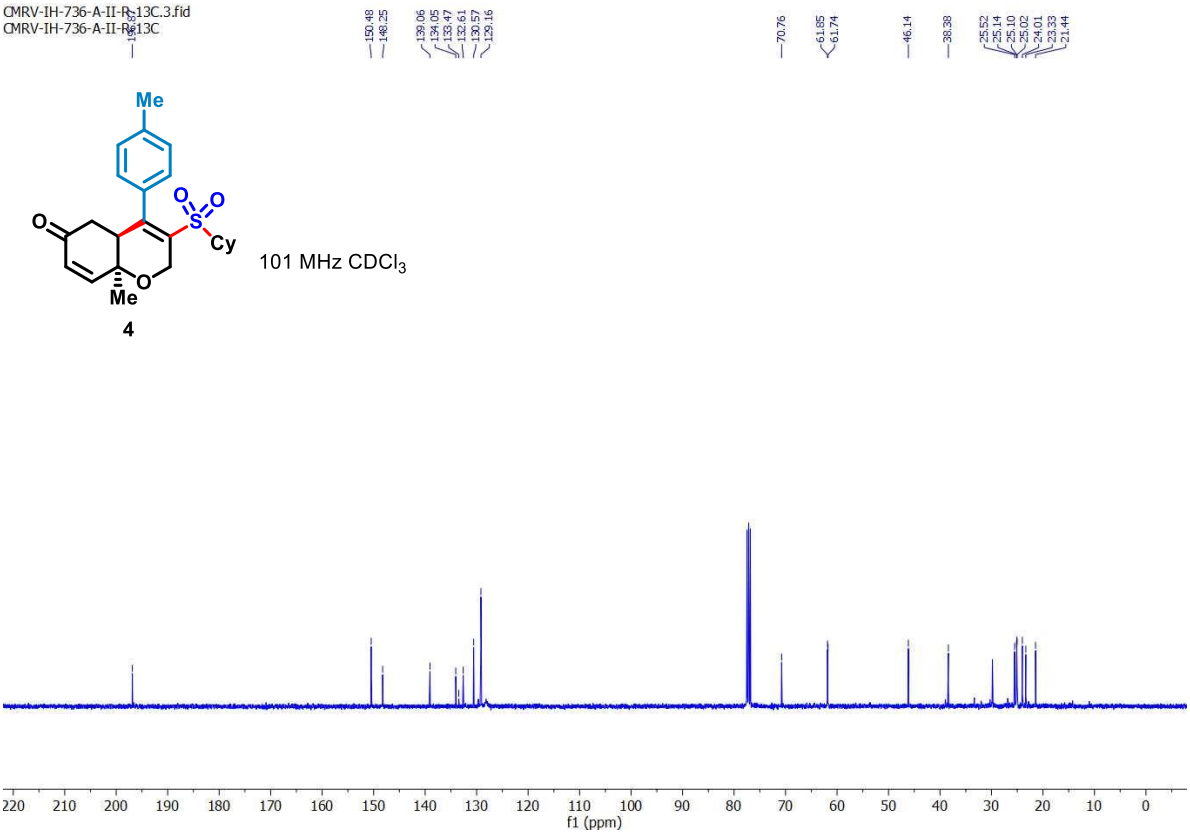


4

500 MHz $CDCl_3$



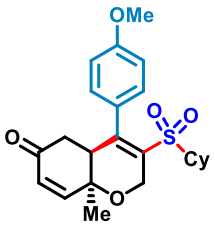
CMRV-IH-736-A-II-R-13C.3.fid
CMRV-IH-736-A-II-R-13C



4

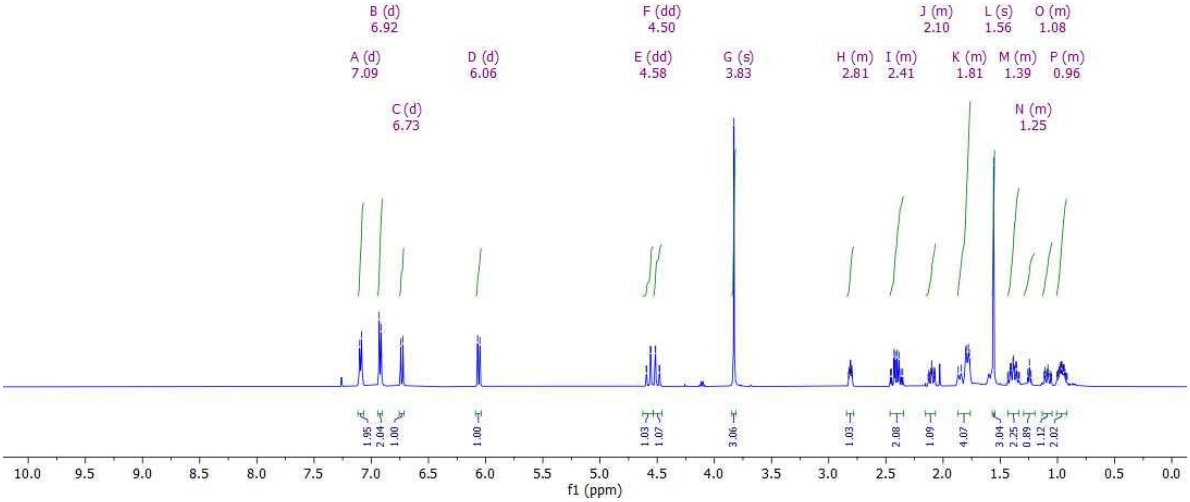
101 MHz $CDCl_3$

CMRV-IH-376-1H.3.fid
CMRV-IH-376-1H

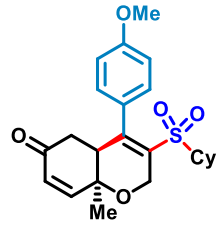


500 MHz $CDCl_3$

5

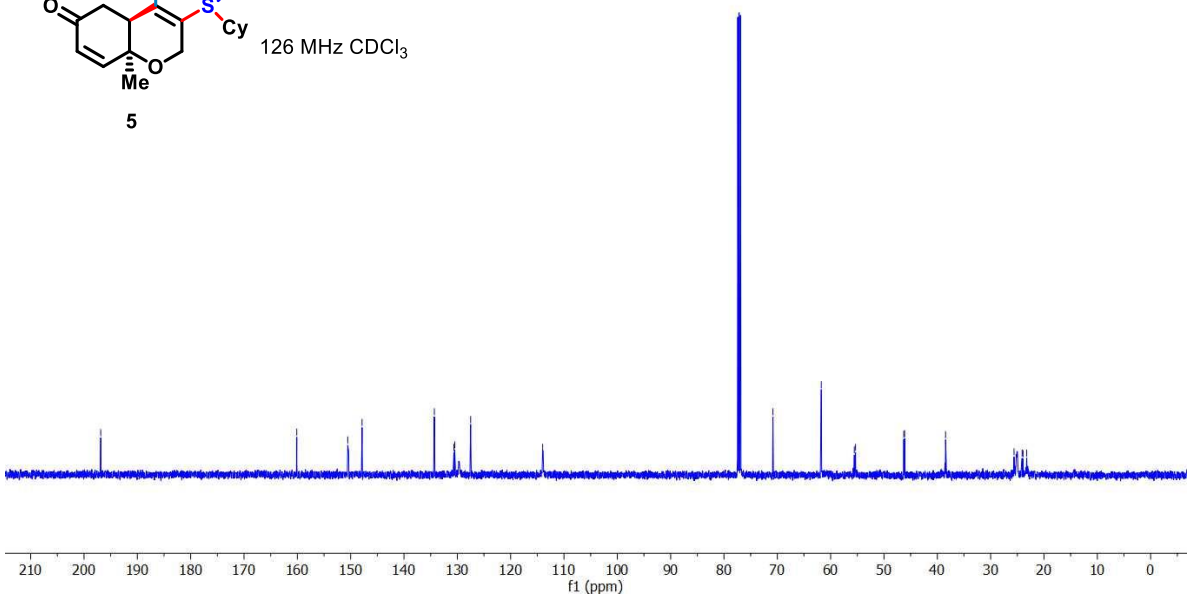


CMRV-IH-376-13C.4.fid
CMRV-IH-376-13C

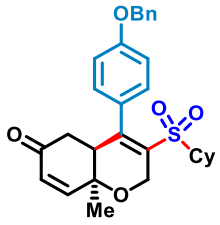


126 MHz $CDCl_3$

5

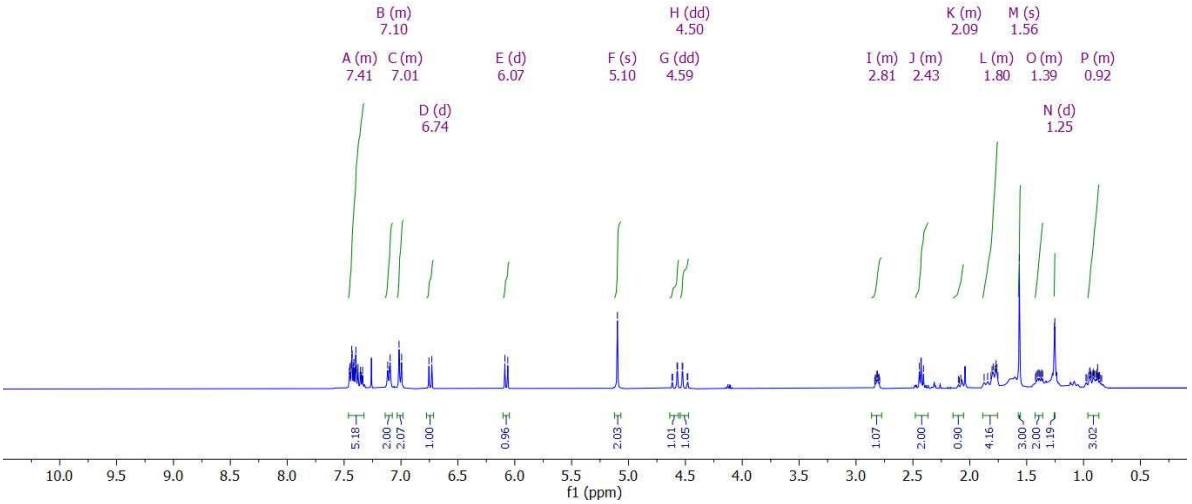


CMRV-IH-497-B-1H.14.fid
CMRV-IH-497-B-1H

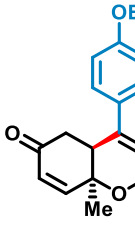


400 MHz $CDCl_3$

6

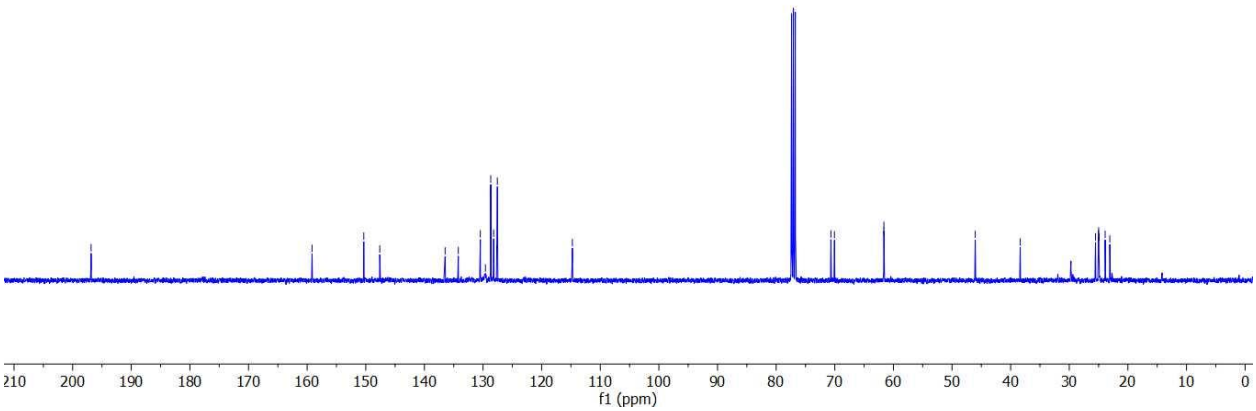


CMRV-IH-497-B-13C.16.fid
CMRV-IH-497-B-13C

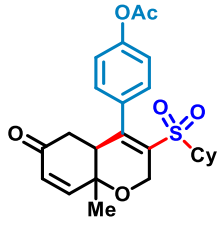


101 MHz $CDCl_3$

6

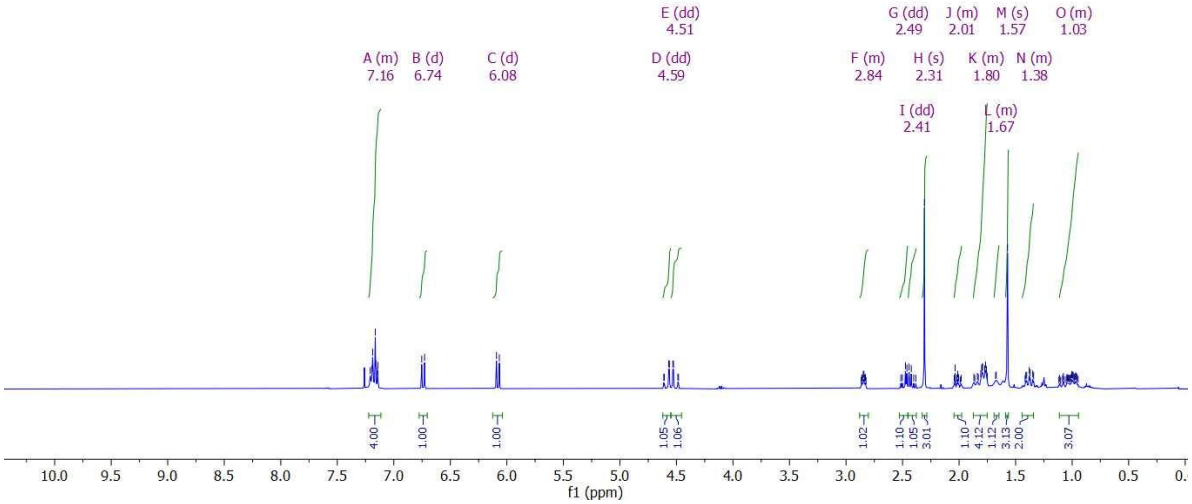


CMRV-IH-473-B-1H.6.fid
CMRV-IH-473-B-1H

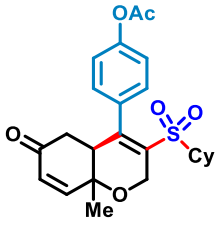


400 MHz $CDCl_3$

7

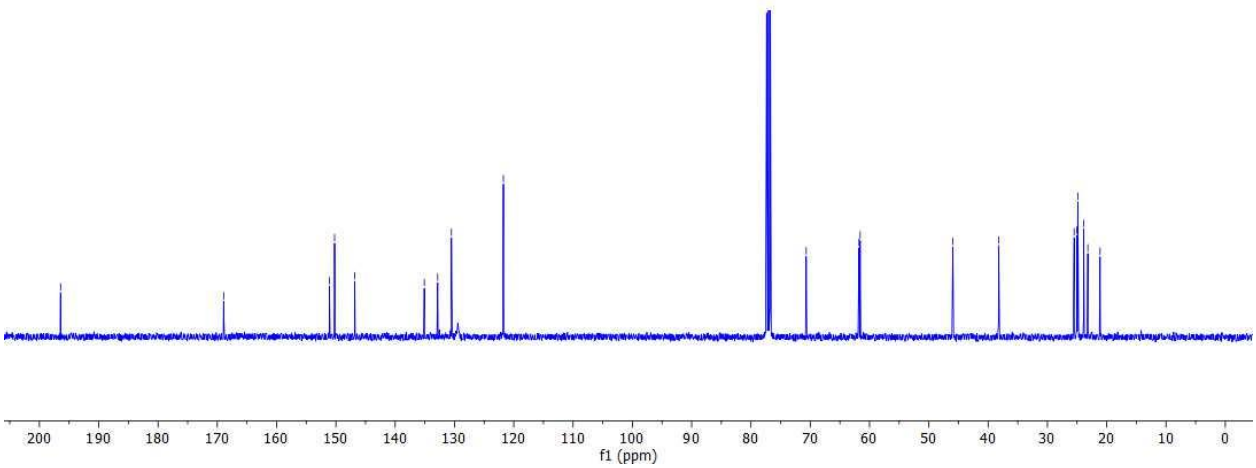


CMRV-IH-473-B-13C.3.fid
CMRV-IH-473-B-13C

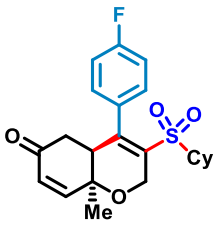


101 MHz $CDCl_3$

7

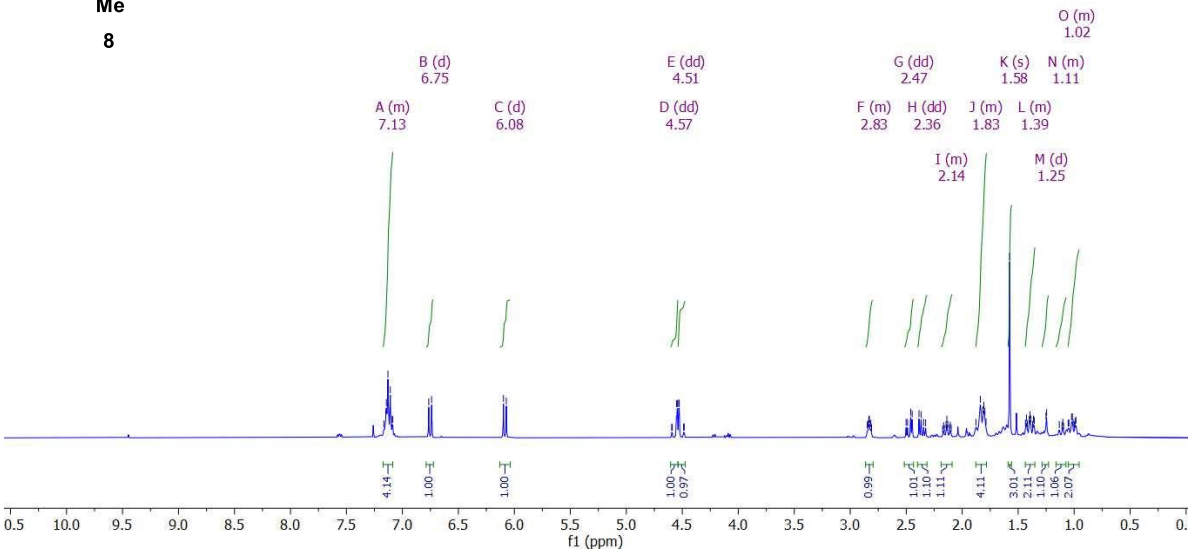


CMRVIH-423-A-1H.1.fid
CMRVIH-423-A-1H

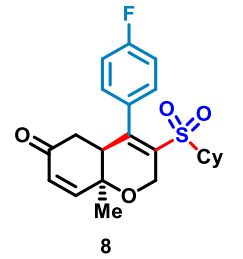


8

400 MHz $CDCl_3$

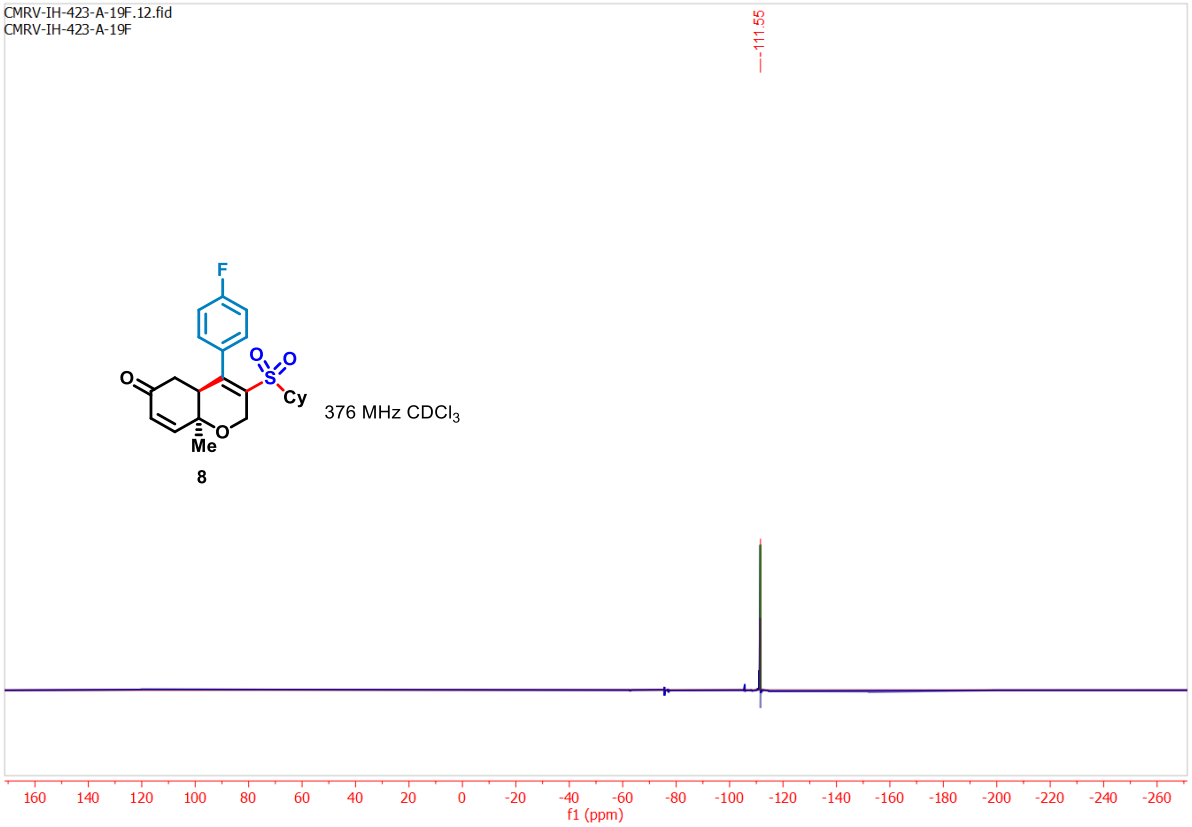


CMRVIH-423-A-13C.2.fid
CMRVIH-423-A-13C

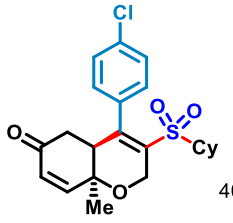


8

101 MHz $CDCl_3$

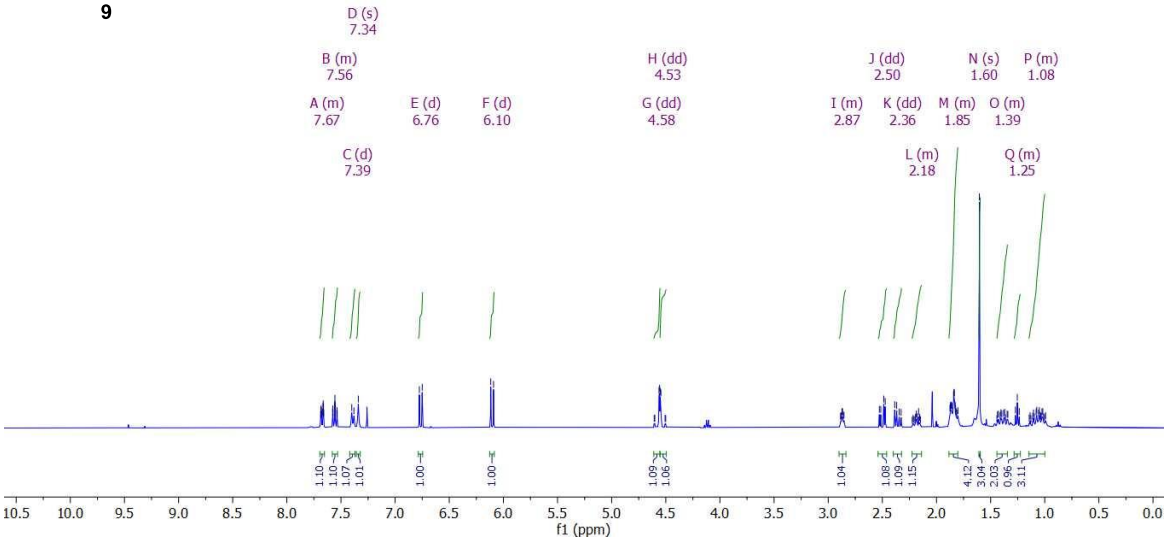

CMRV-IH-423-A-19F.12.fid
CMRV-IH-423-A-19F
-111.55
F
O
O
S
O
Cy
Me
O
376 MHz CDCl3
8
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

CMRV-418-A-1H.20.fid
CMRV-418-A-1H

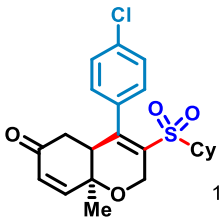


400 MHz $CDCl_3$

9

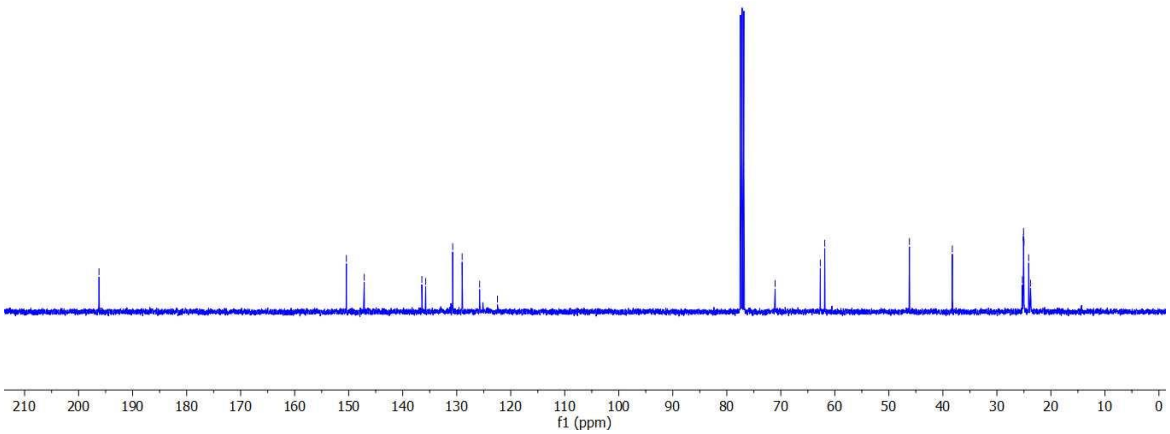


CMRV-418-A-13C.21.fid
CMRV-418-A-13C

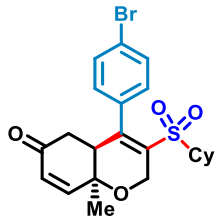


101 MHz $CDCl_3$

9

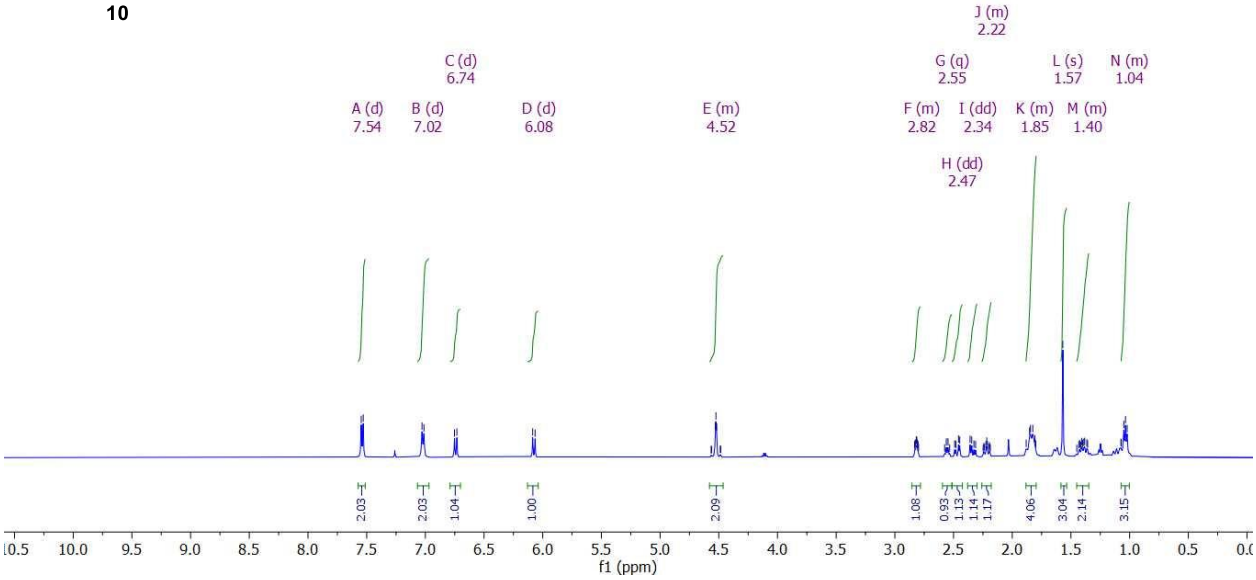


CMRV-IH-382-1H.3.fid
CMRV-IH-382-1H

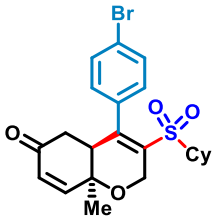


10

500 MHz $CDCl_3$

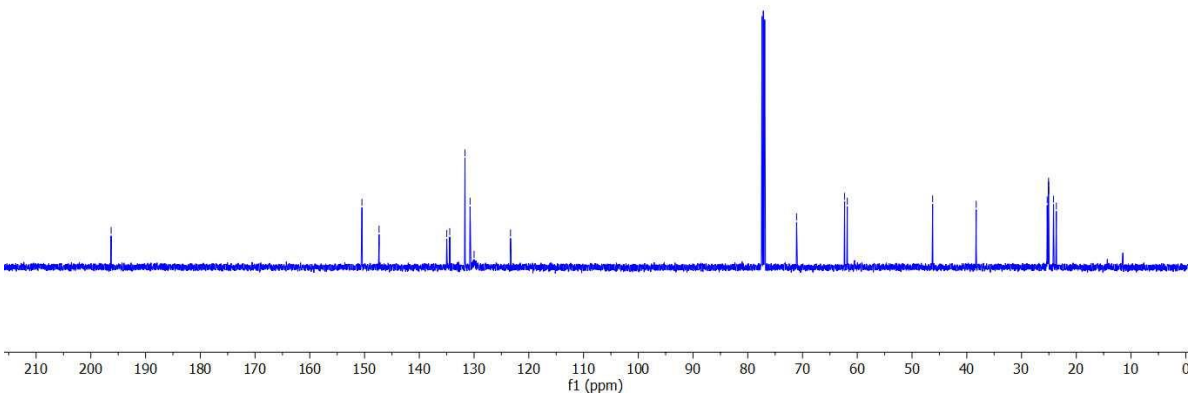


CMRV-IH-382-13C.4.fid
CMRV-IH-382-13C

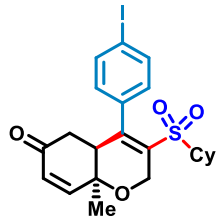


10

126 MHz $CDCl_3$

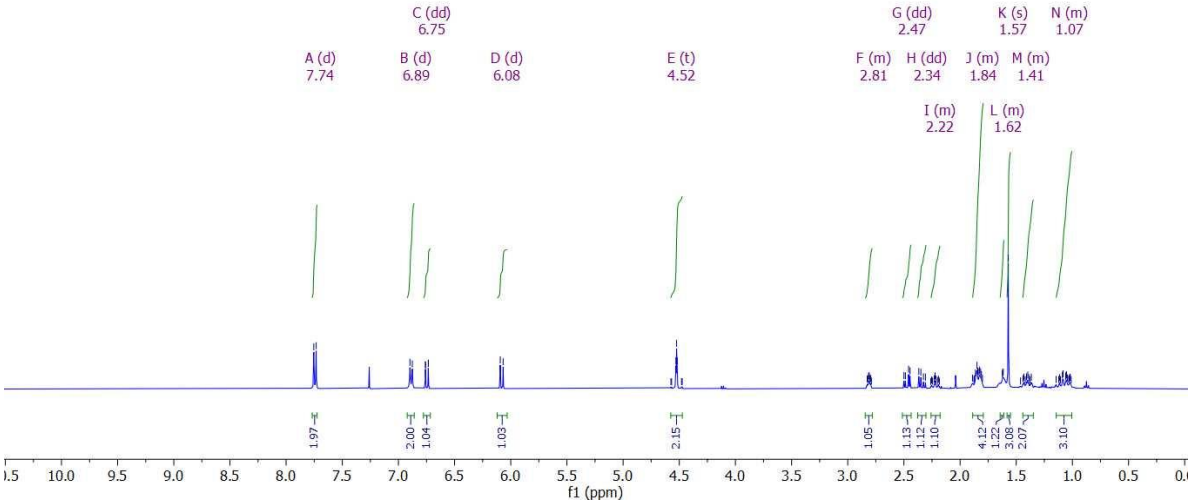


CMRV-IH-425-1H.10.fid
CMRV-IH-425-1H

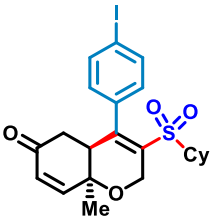


400 MHz $CDCl_3$

11

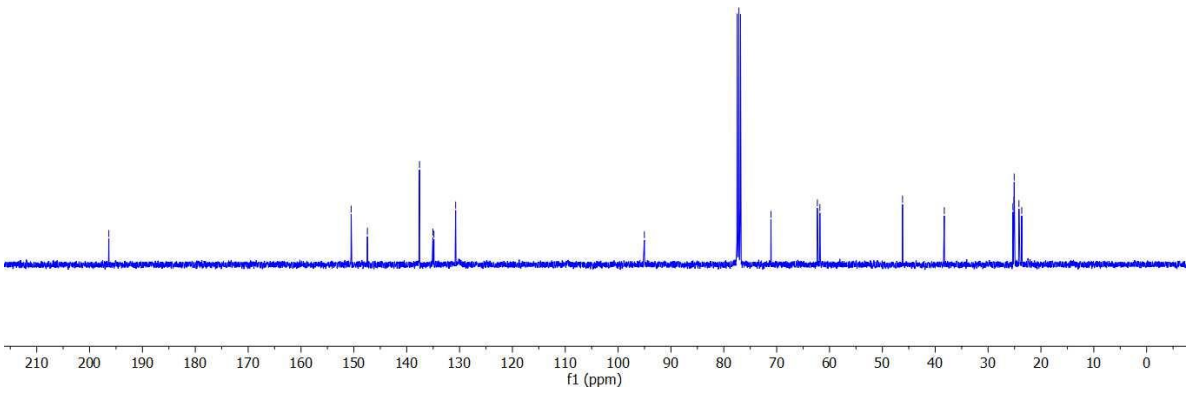


CMRV-IH-425-13C.12.fid
CMRV-IH-425-13C

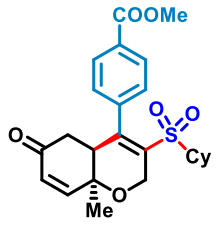


126 MHz $CDCl_3$

11

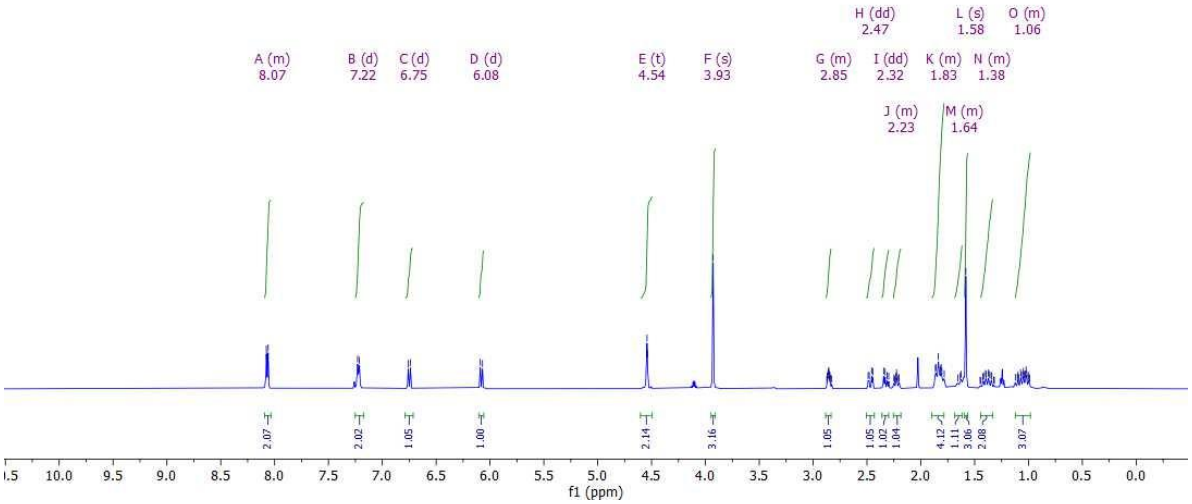


CMRV-IH-397-1H.10.fid
CMRV-IH-397-1H

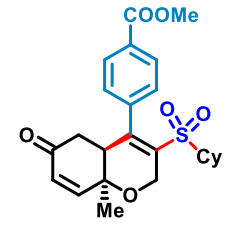


500 MHz $CDCl_3$

12

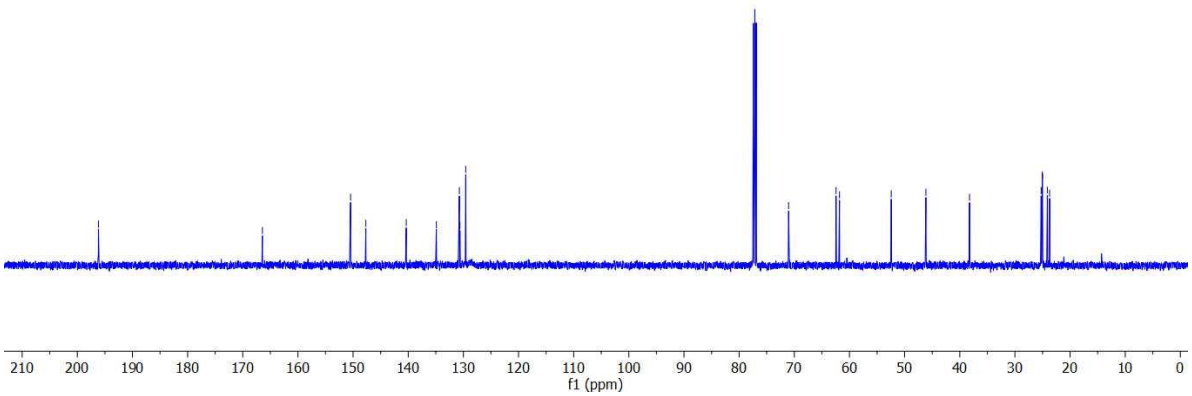


CMRV-IH-397-13C.11.fid
CMRV-IH-397-13C

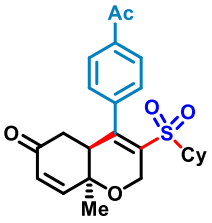


126 MHz $CDCl_3$

12

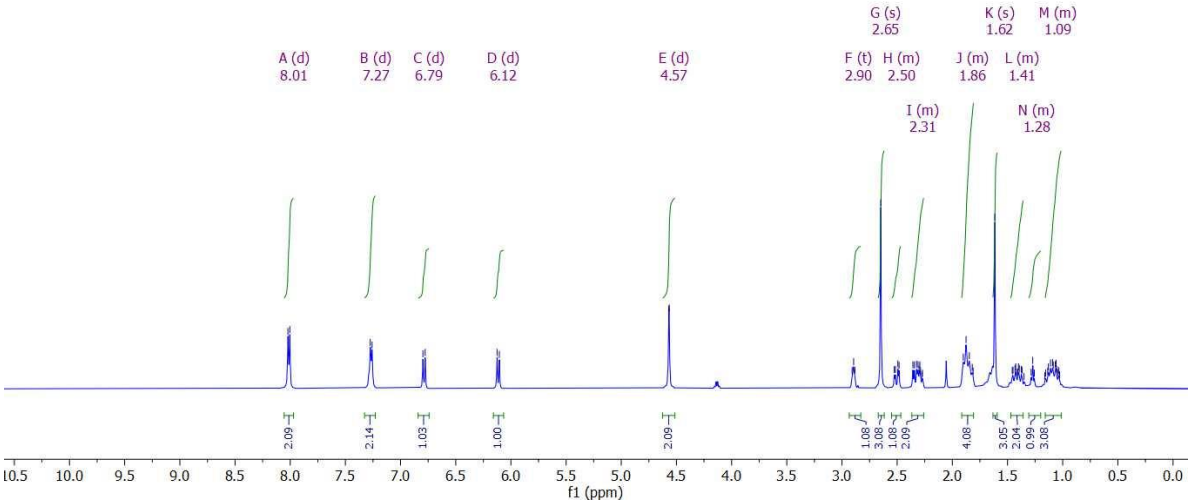


CMRV-IH-383-1H.1.fid
CMRV-IH-383-1H

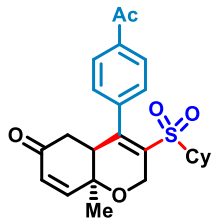


500 MHz $CDCl_3$

13

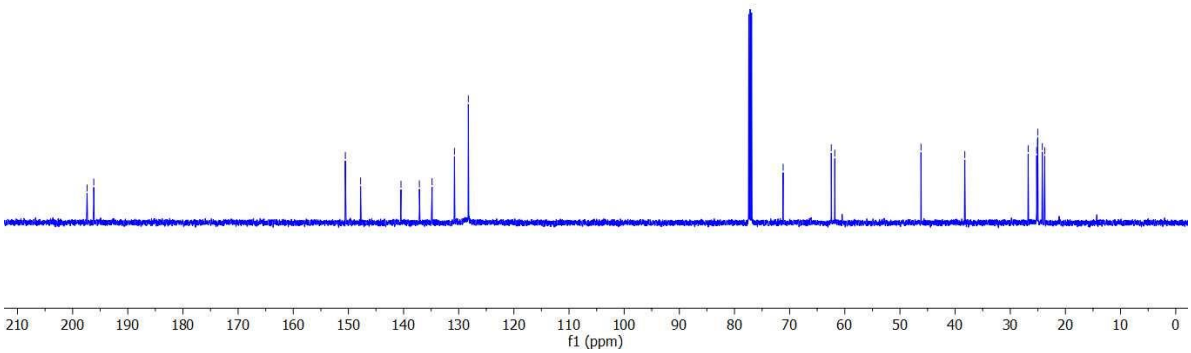


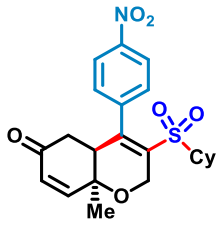
CMRV-IH-383-13C.2.fid
CMRV-IH-383-13C



126 MHz $CDCl_3$

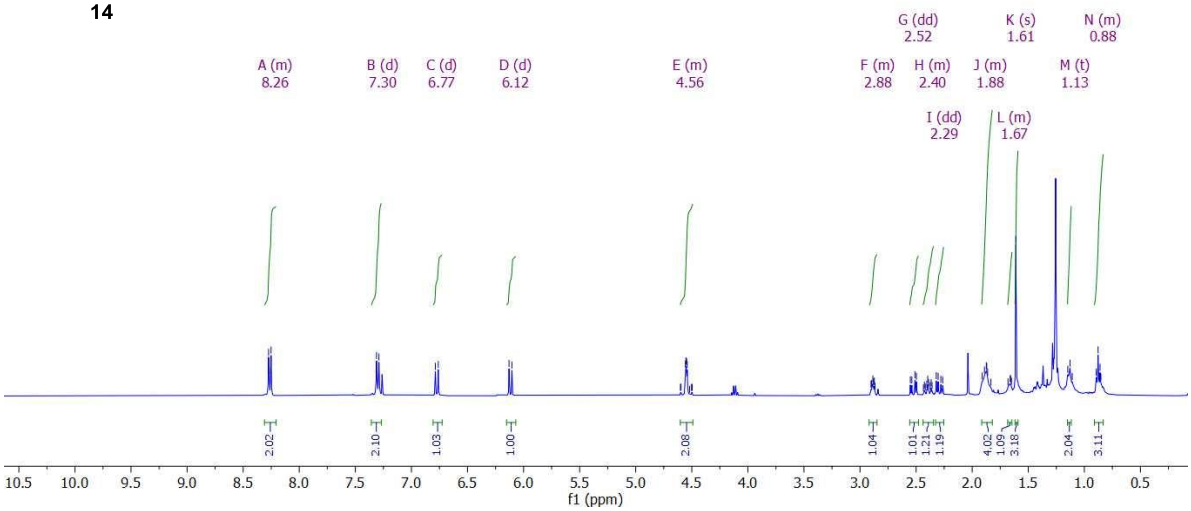
13

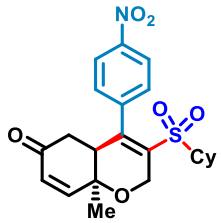




14

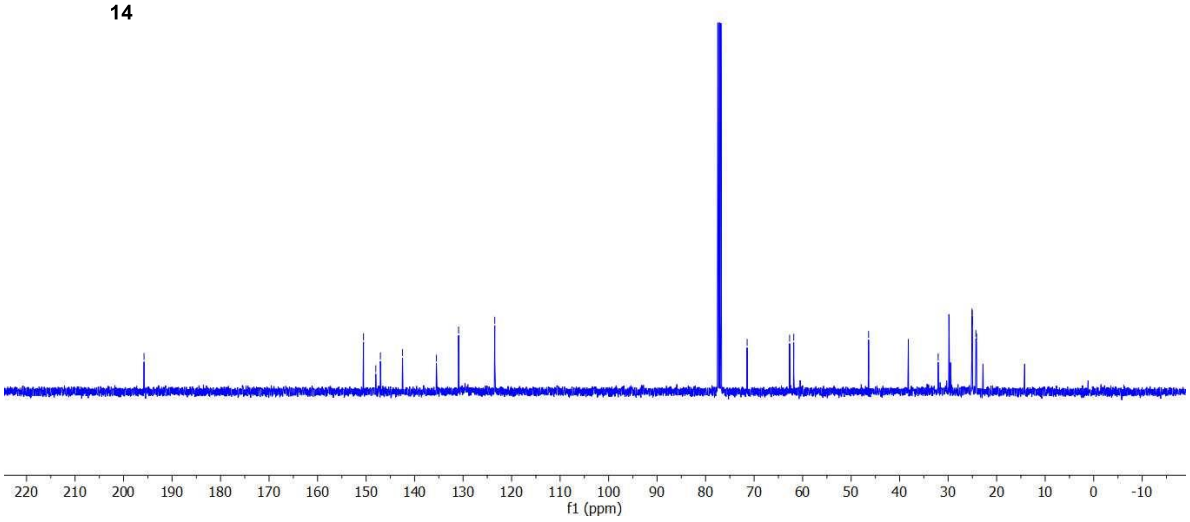
400 MHz $CDCl_3$

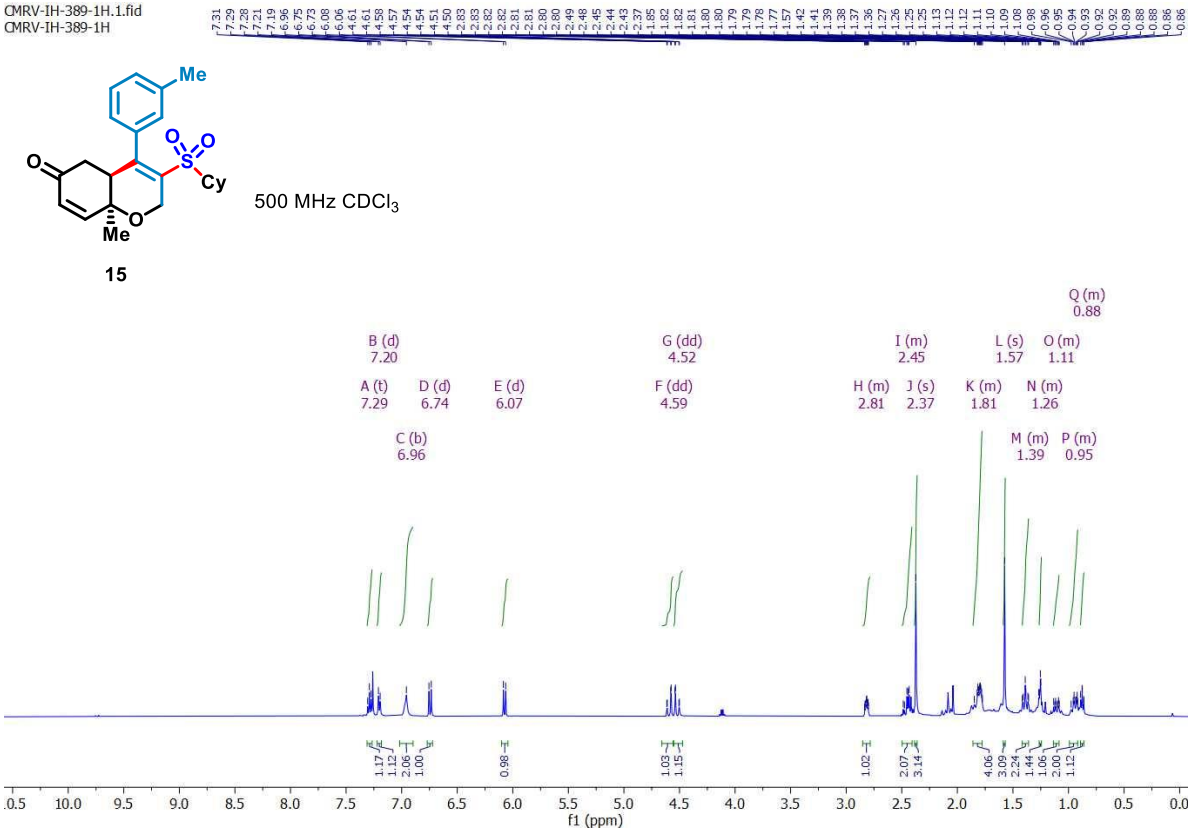


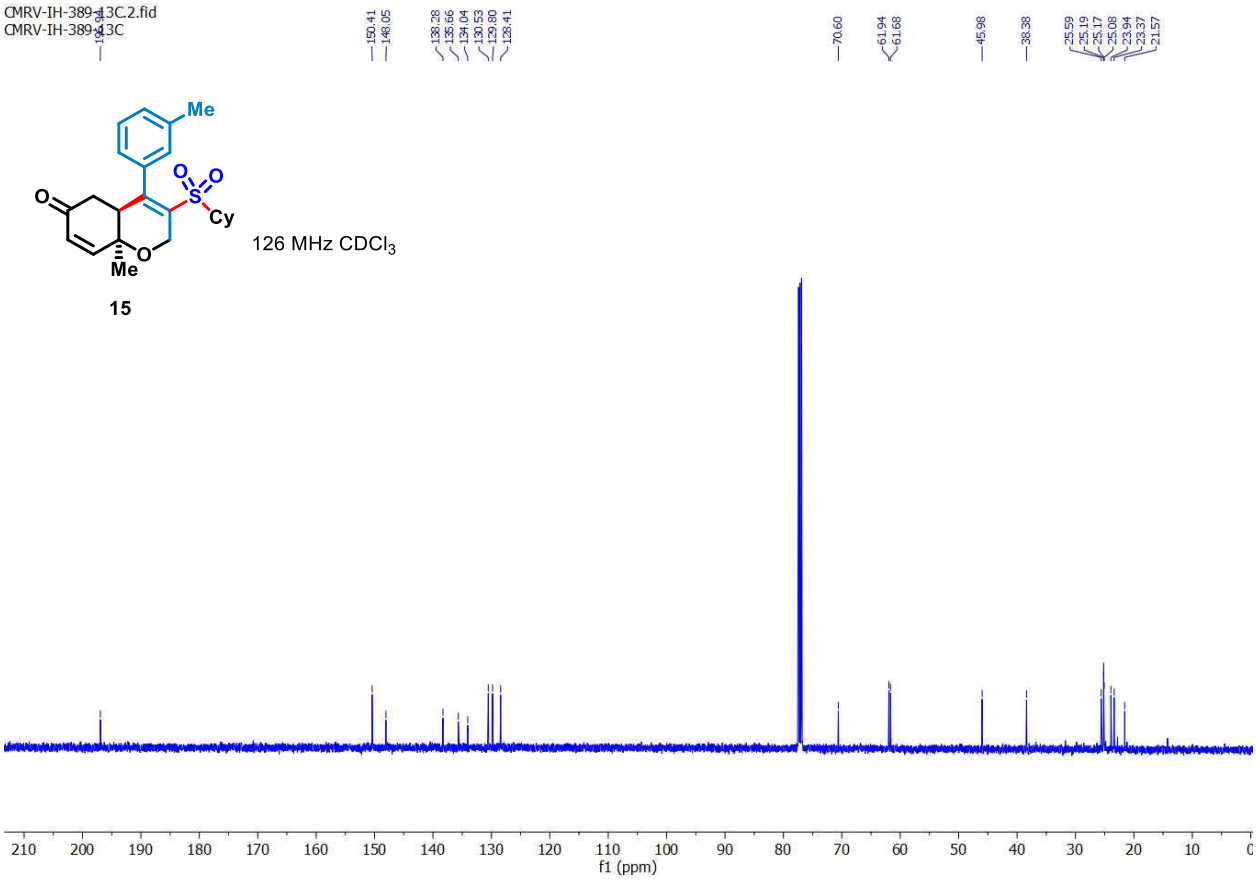


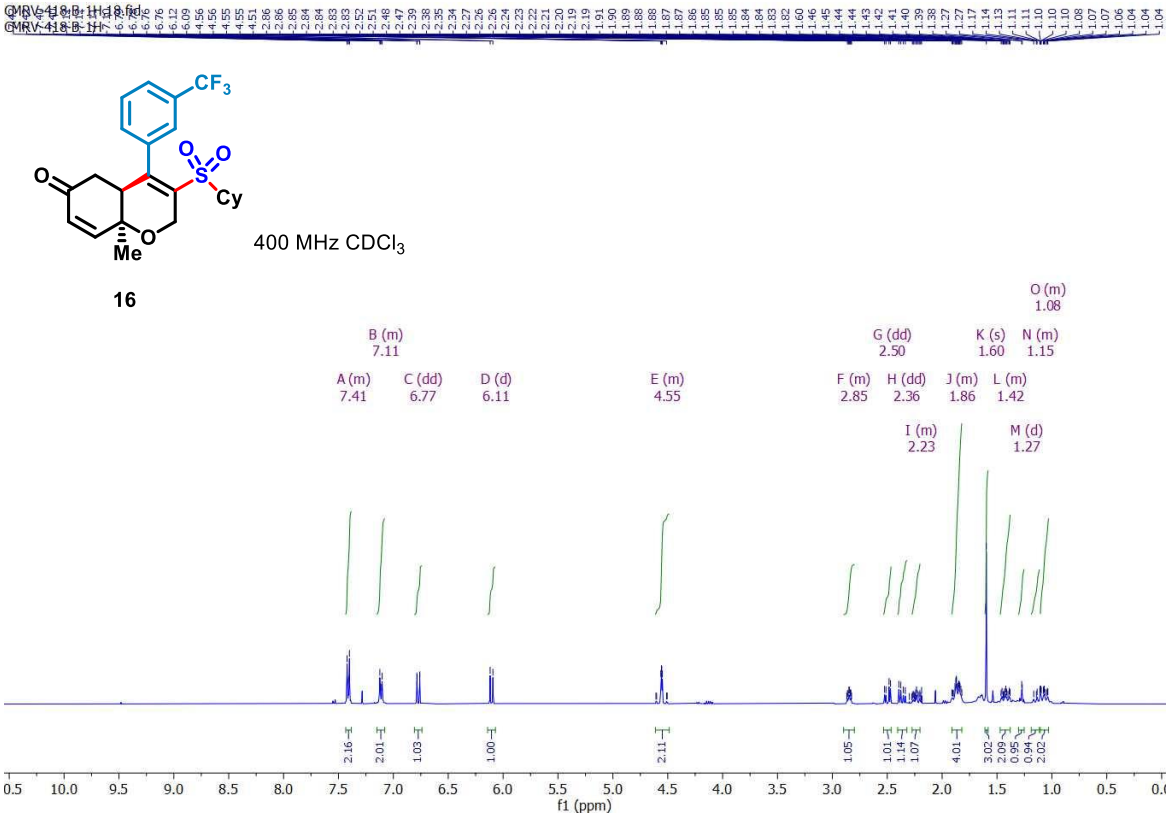
14

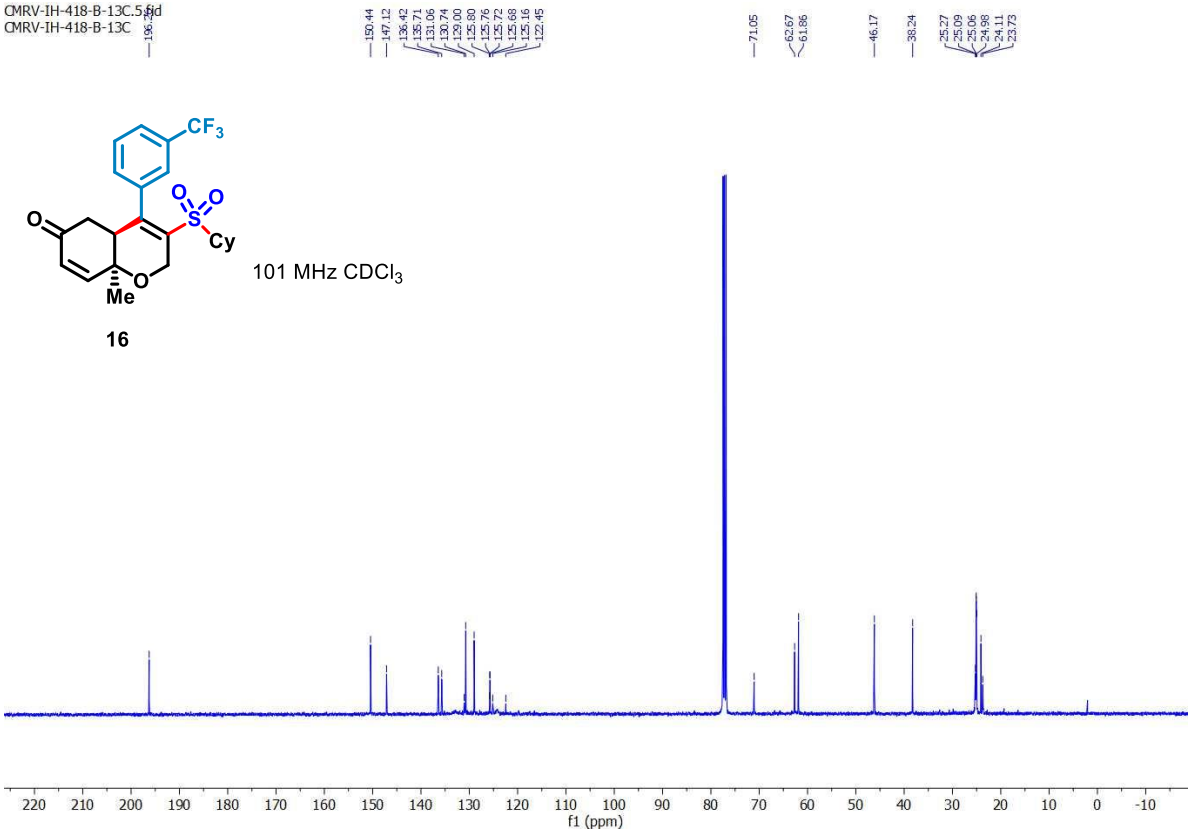
101 MHz $CDCl_3$

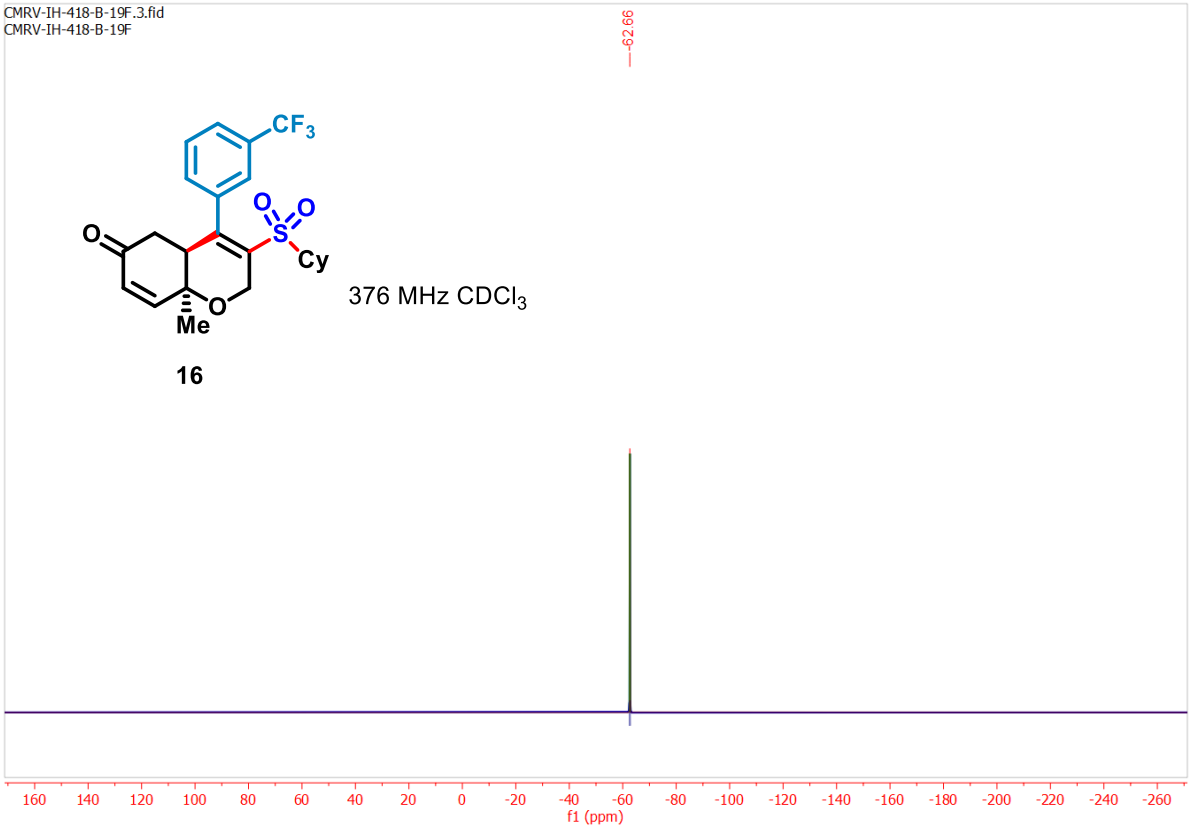



CMRV-IH-389-1H.1.fid
CMRV-IH-389-1H
Me
O
O
S
O
Cy
O
Me
500 MHz CDCl3
15
Q (m) 0.88
B (d) 7.20
G (dd) 4.52
I (m) 2.45
L (s) 1.57
O (m) 1.11
A (t) 7.29
D (d) 6.74
E (d) 6.07
F (dd) 4.59
H (m) 2.81
J (s) 2.37
K (m) 1.81
N (m) 1.26
C (b) 6.96
M (m) 1.39
P (m) 0.95
f1 (ppm)


CMRV-IH-389-13C.2.fid
CMRV-IH-389-13C
Me
O
O
S
O
Cy
O
Me
126 MHz CDCl3
15
f1 (ppm)

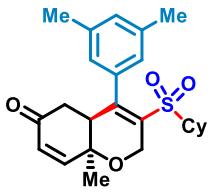

CMRV-418-B-1H-18.fid
CMRV-418-B-1H
CF3
O
O
S
O
Cy
O
Me
400 MHz CDCl3
16
O (m) 1.08
B (m) 7.11
G (dd) 2.50
K (s) 1.60
N (m) 1.15
A (m) 7.41
C (dd) 6.77
D (d) 6.11
E (m) 4.55
F (m) 2.85
H (dd) 2.36
J (m) 1.86
L (m) 1.42
I (m) 2.23
M (d) 1.27
2.16
2.01
1.03
1.00
2.11
1.05
1.01
1.14
1.07
4.01
3.02
2.05
0.95
0.94
2.02
f1 (ppm)


CMRV-IH-418-B-13C.5.fid
CMRV-IH-418-B-13C
150.44
147.12
136.42
135.71
131.06
130.74
129.00
125.80
125.76
125.72
125.68
125.46
122.45
71.05
62.67
61.86
46.17
38.24
25.27
25.09
25.06
24.98
24.11
23.73
CF3
O
O
S
O
Cy
O
Me
101 MHz CDCl3
16
f1 (ppm)


CMRV-IH-418-B-19F.3.fid
CMRV-IH-418-B-19F
62.66
CF3
O
O
O
S
Cy
Me
376 MHz CDCl3
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

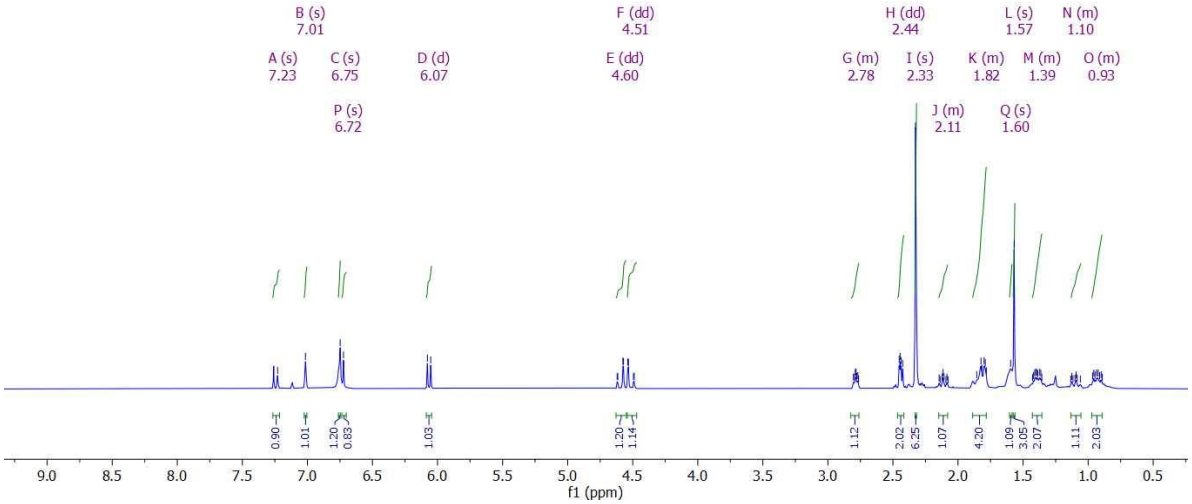
16

CMRV-IH-736-B-II-1H.1.fid
CMRV-IH-736-B-II-1H

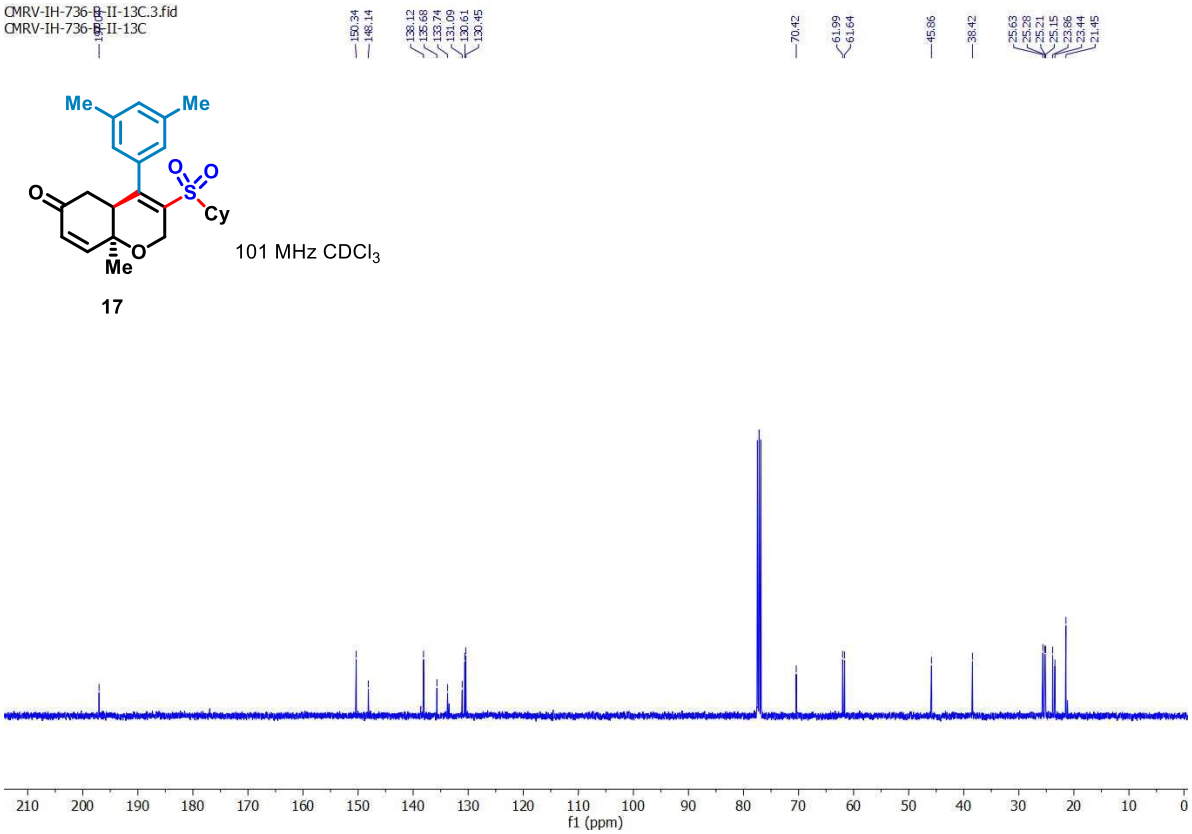


400 MHz $CDCl_3$

17



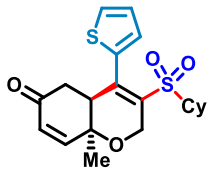
CMRV-IH-736-B-II-13C.3.fid
CMRV-IH-736-B-II-13C



101 MHz $CDCl_3$

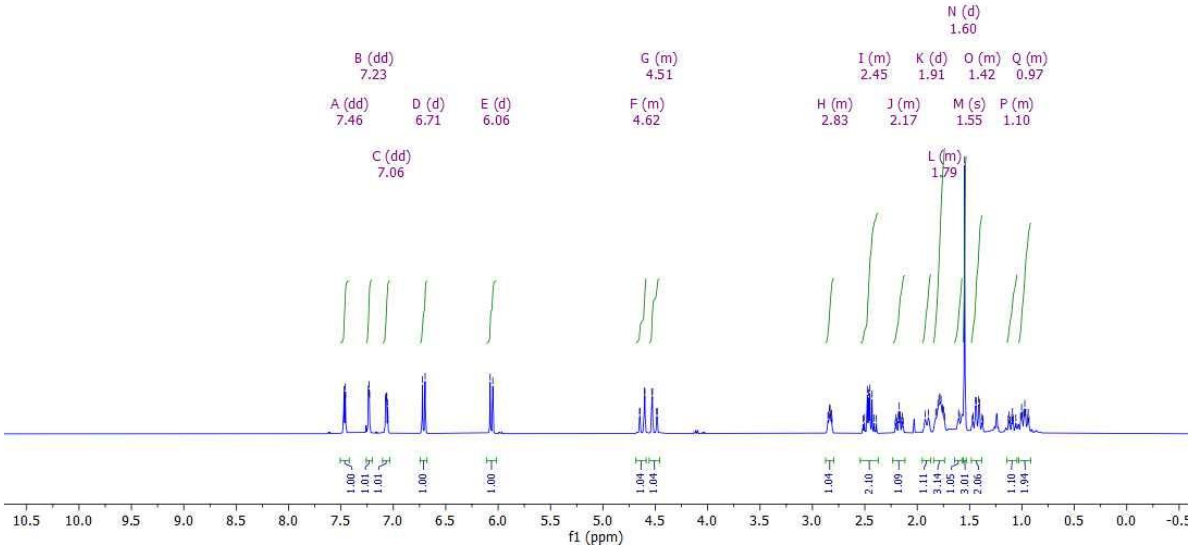
17

CMRV-IH-415-B-1H.3.fid
CMRV-IH-415-B-1H

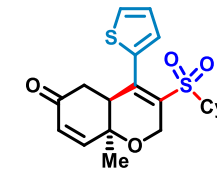


400 MHz $CDCl_3$

18

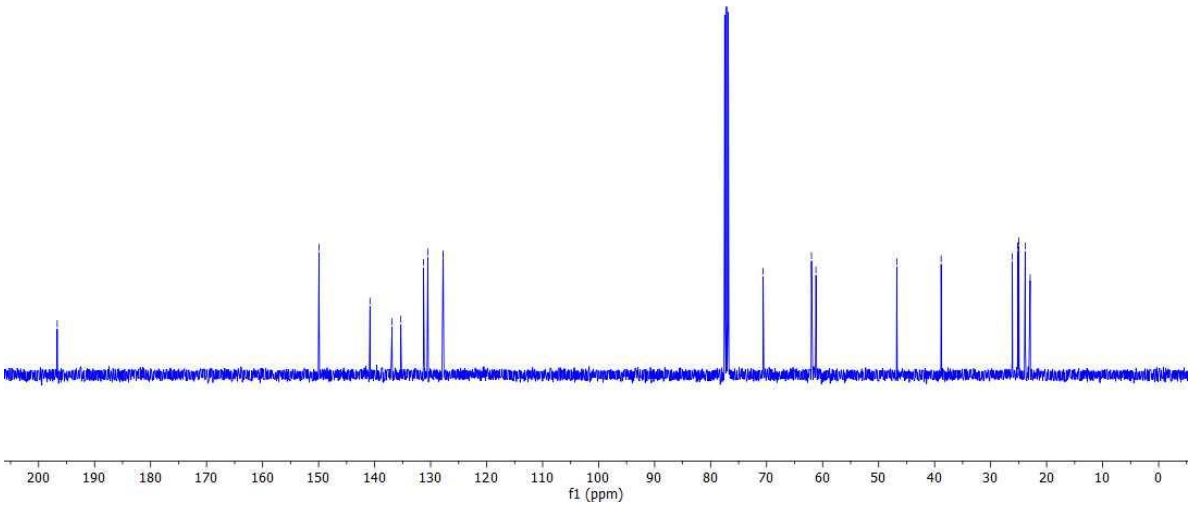


CMRV-IH-415-B-13C.5.fid
CMRV-IH-415-B-13C

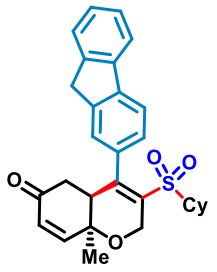


101 MHz $CDCl_3$

18

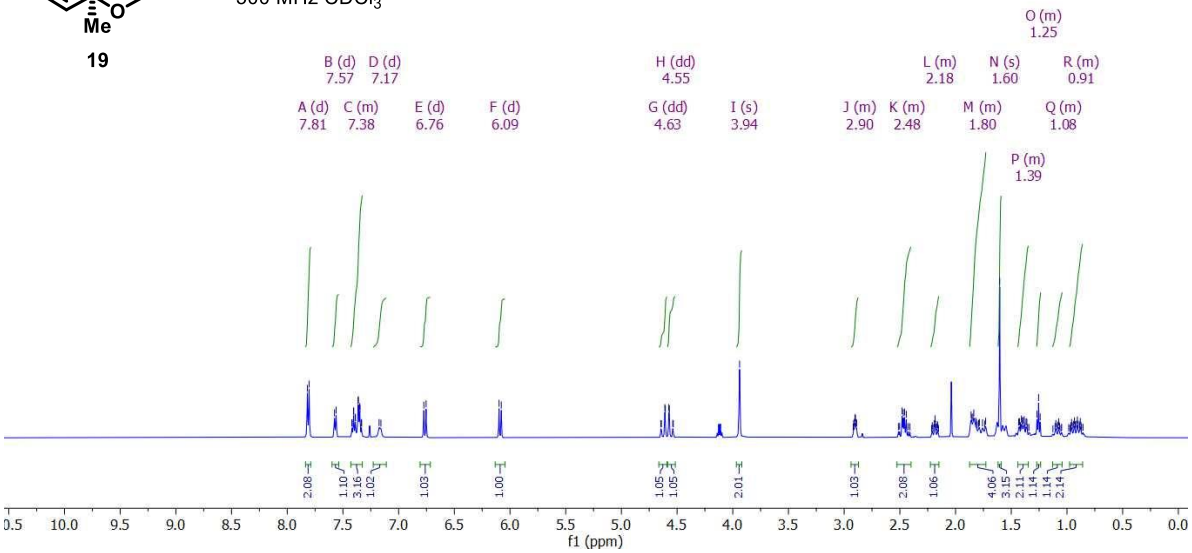


CMRV-IH-396-1H.13.fid
CMRV-IH-396-1H

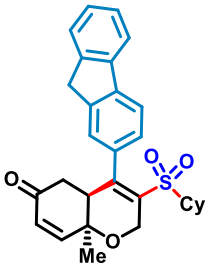


19

500 MHz $CDCl_3$

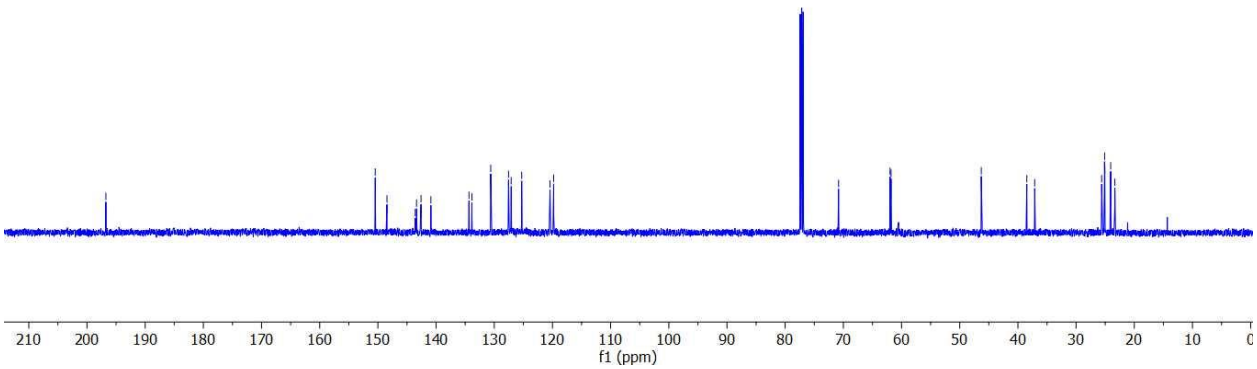


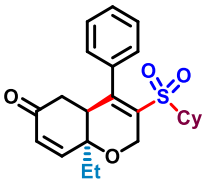
CMRV-IH-396-13C.14.fid
CMRV-IH-396-13C



19

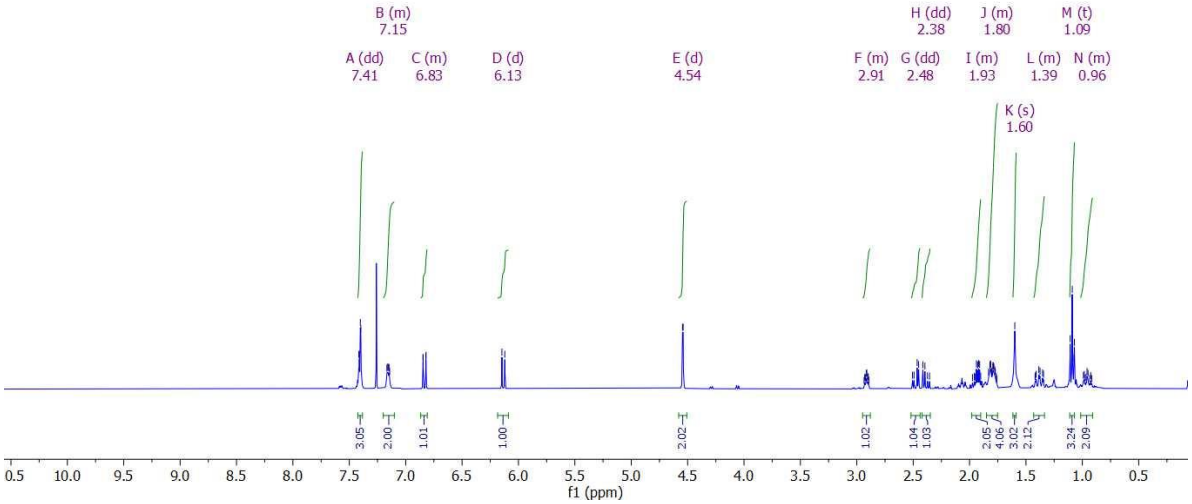
126 MHz $CDCl_3$

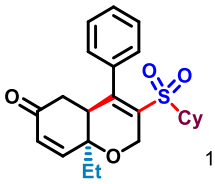




400 MHzCDCl$_3$

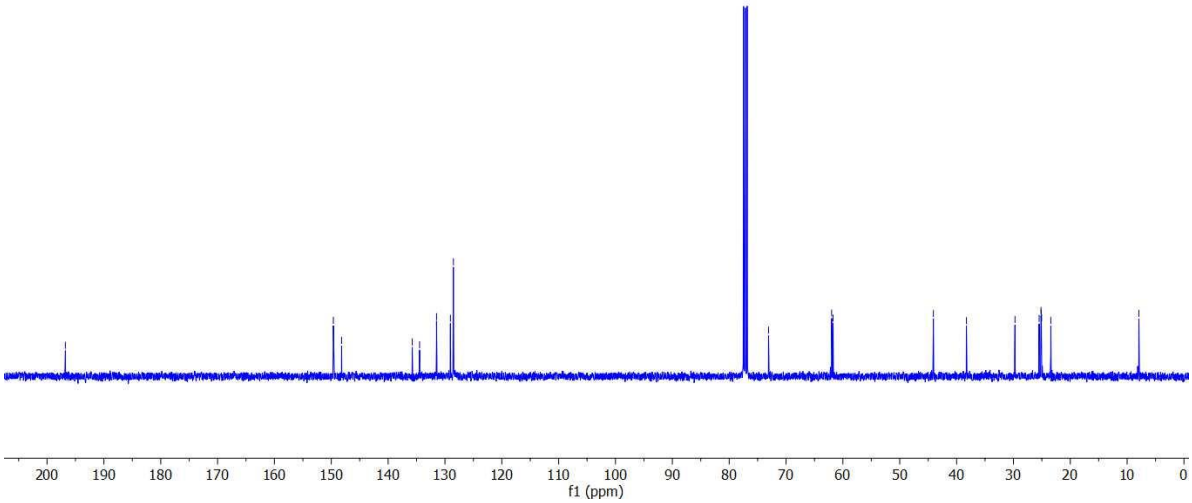
20

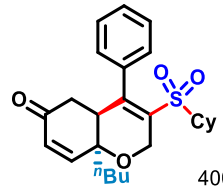




101 MHz CDCl$_3$

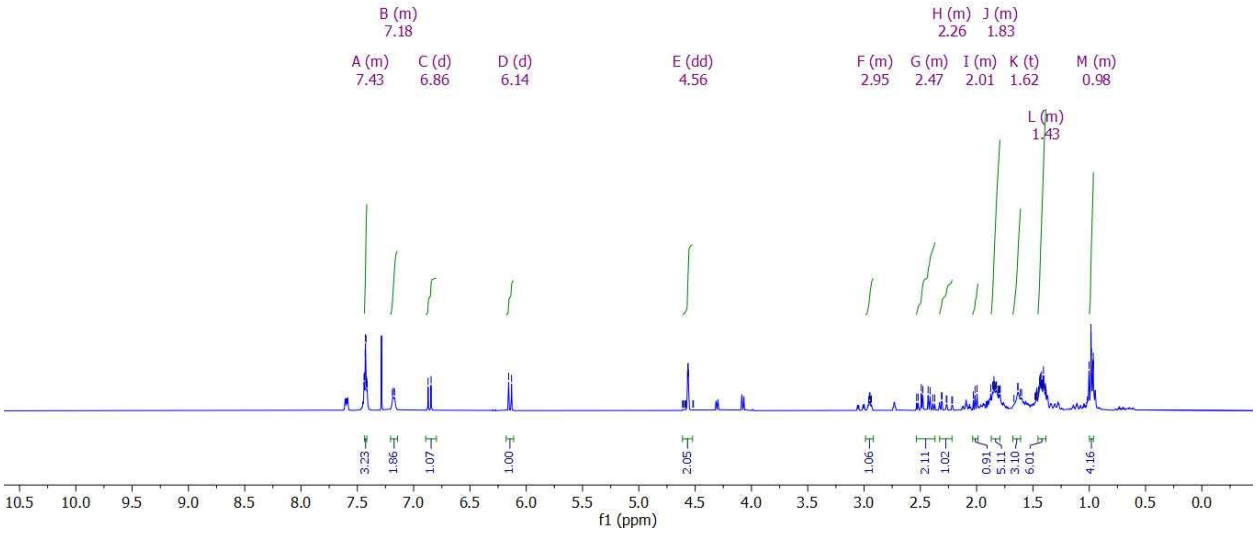
20

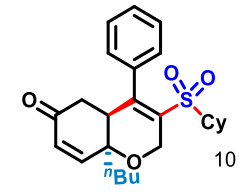




400 MHz $CDCl_3$

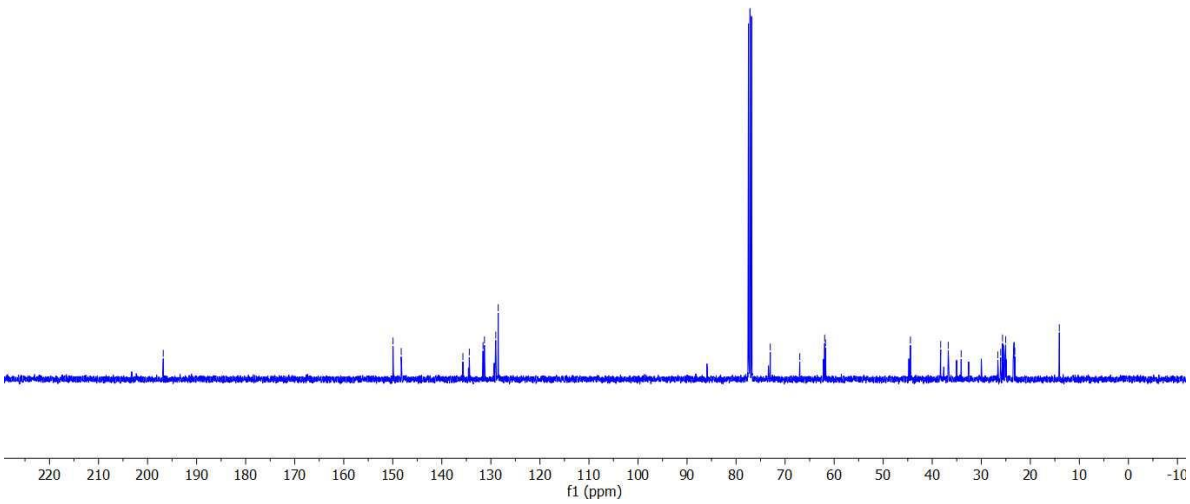
21

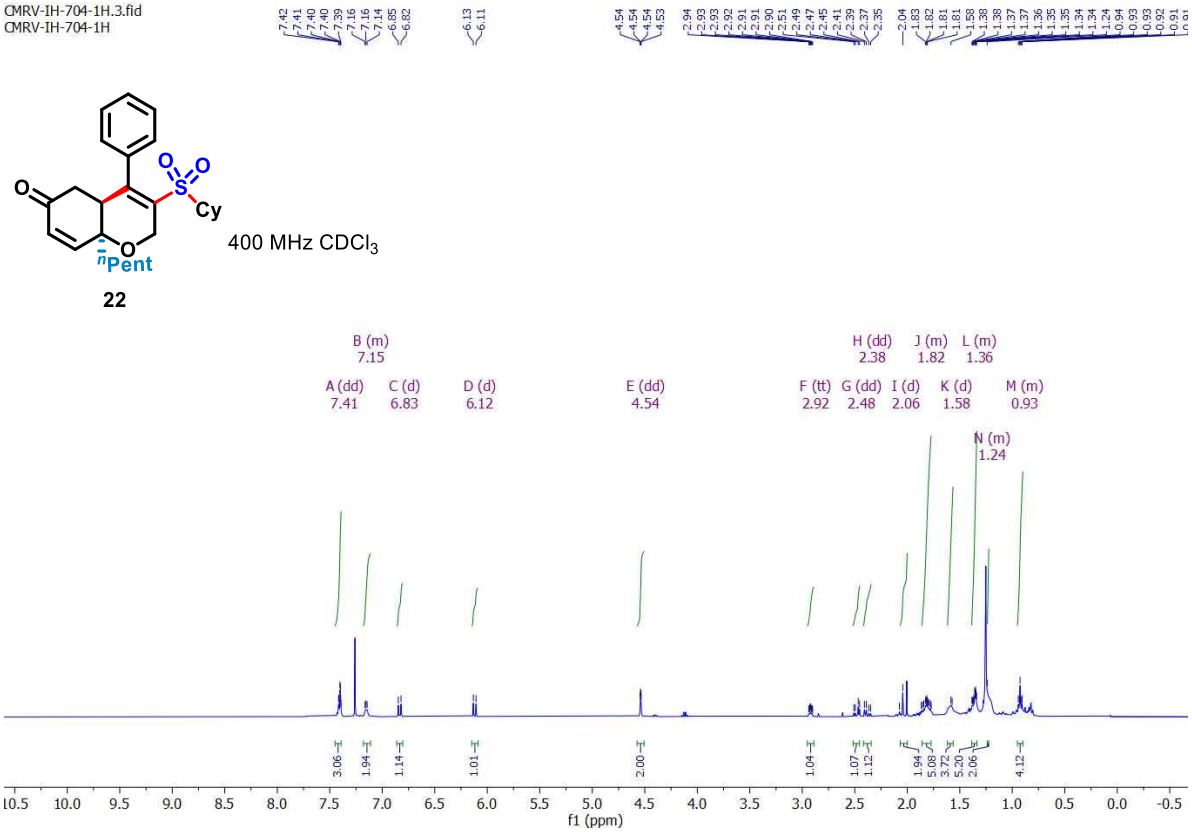


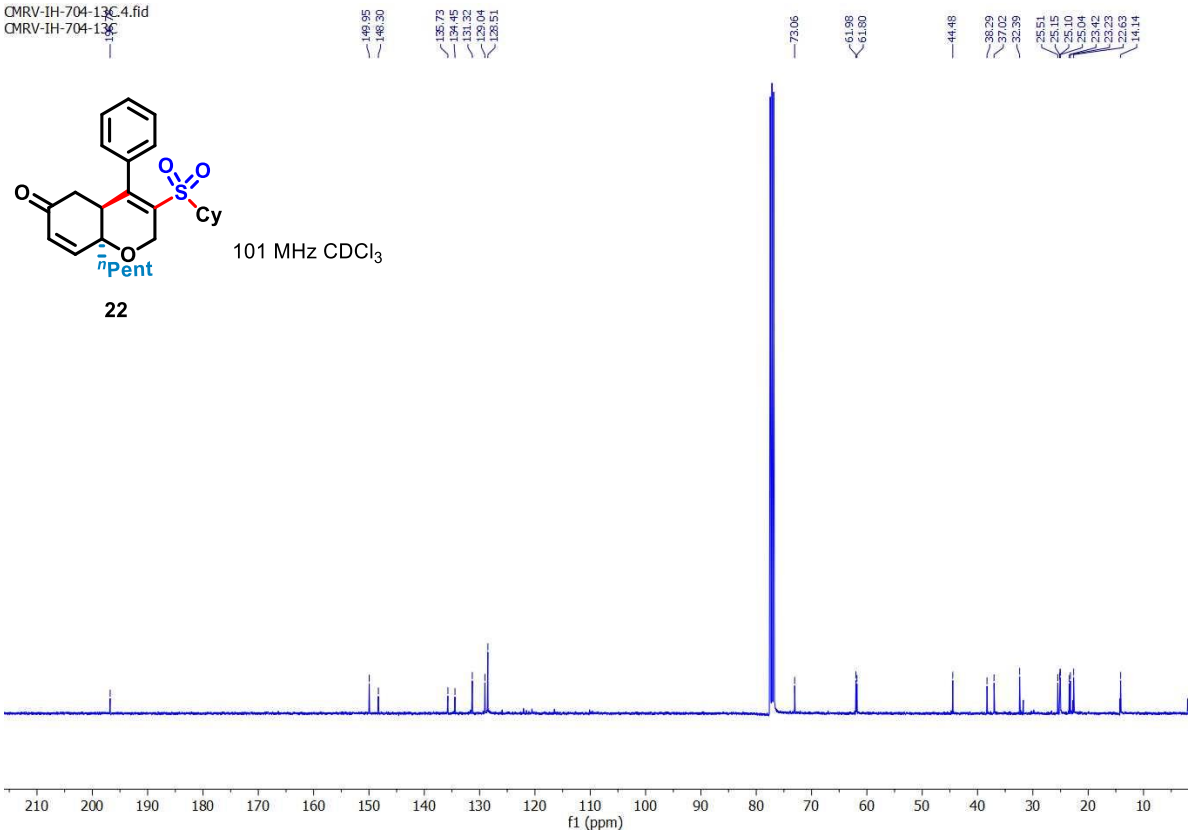


101 MHz $CDCl_3$

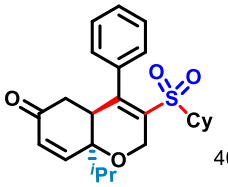
21




CMRV-IH-704-1H.3.fid
CMRV-IH-704-1H
7.42 7.41 7.40 7.40 7.39 7.16 7.16 7.14 6.85 6.82 6.13 6.11
4.54 4.54 4.54 4.53 2.94 2.93 2.93 2.92 2.91 2.91 2.90 2.51 2.49 2.47 2.45 2.41 2.39 2.37 2.35 2.04 1.83 1.82 1.81 1.81 1.58 1.38 1.38 1.37 1.37 1.36 1.35 1.35 1.34 1.34 1.24 0.94 0.93 0.93 0.92 0.91
O
O
O
S
Cy
O
nPent
400 MHz CDCl3
22
B (m) 7.15
A (dd) 7.41
C (d) 6.83
D (d) 6.12
E (dd) 4.54
F (tt) 2.92
G (dd) 2.48
H (dd) 2.38
I (d) 2.06
J (m) 1.82
K (d) 1.58
L (m) 1.36
M (m) 0.93
N (m) 1.24
3.06 1.94 1.14 1.01 2.00 1.04 1.07 1.12 1.94 5.08 3.72 5.26 2.06 4.12
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 -0.5
f1 (ppm)

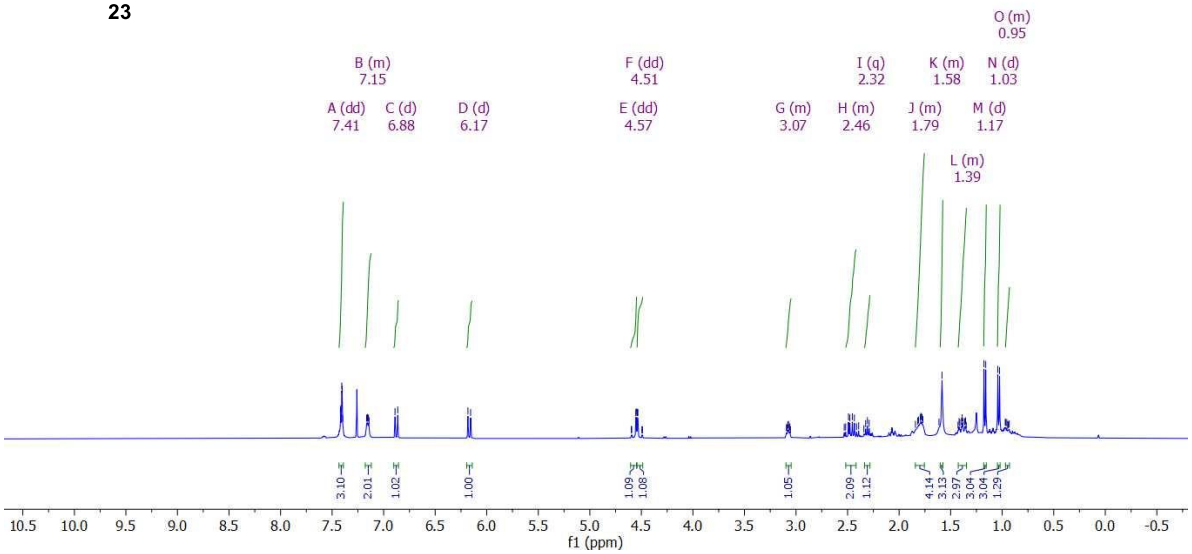

CMRV-IH-704-13C.4.fid
CMRV-IH-704-13C
149.95 148.30 135.73 134.45 131.32 129.04 128.51 73.06 61.98 61.80 44.48 38.29 37.02 32.39 25.51 25.15 25.10 25.04 23.42 23.23 22.63 14.14
O
O
O
S
Cy
O
nPent
101 MHz CDCl3
22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

CMRV-IH-407-II-RE-1H.10.fid
CMRV-IH-407-II-RE-1H

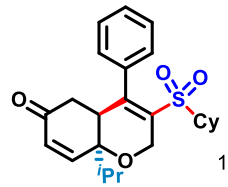


400 MHz $CDCl_3$

23



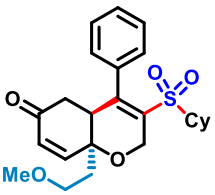
CMRV-IH-407-II-RE-13C.12.fid
CMRV-IH-407-II-RE-13C



101 MHz $CDCl_3$

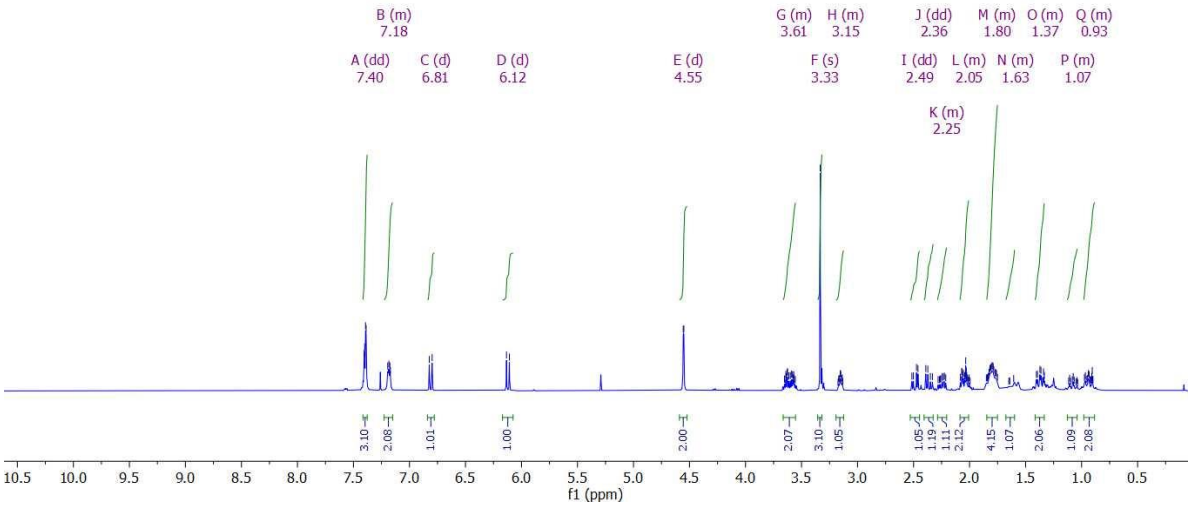
23

CMRV-IH-381-1h.7.fid
CMRV-IH-381-1H

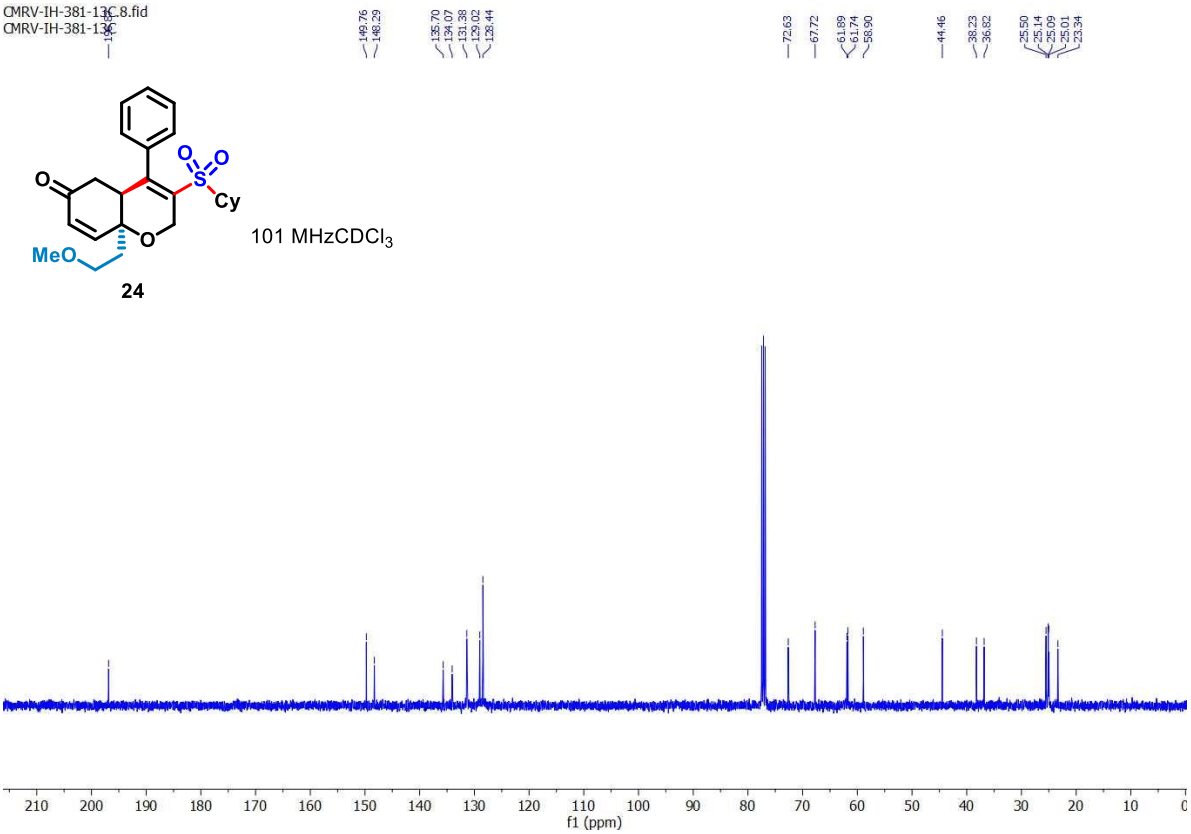


400 MHz $CDCl_3$

24



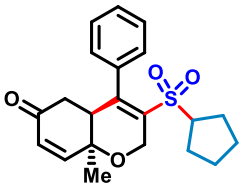
CMRV-IH-381-13C.8.fid
CMRV-IH-381-13C



101 MHzCDCl$_3$

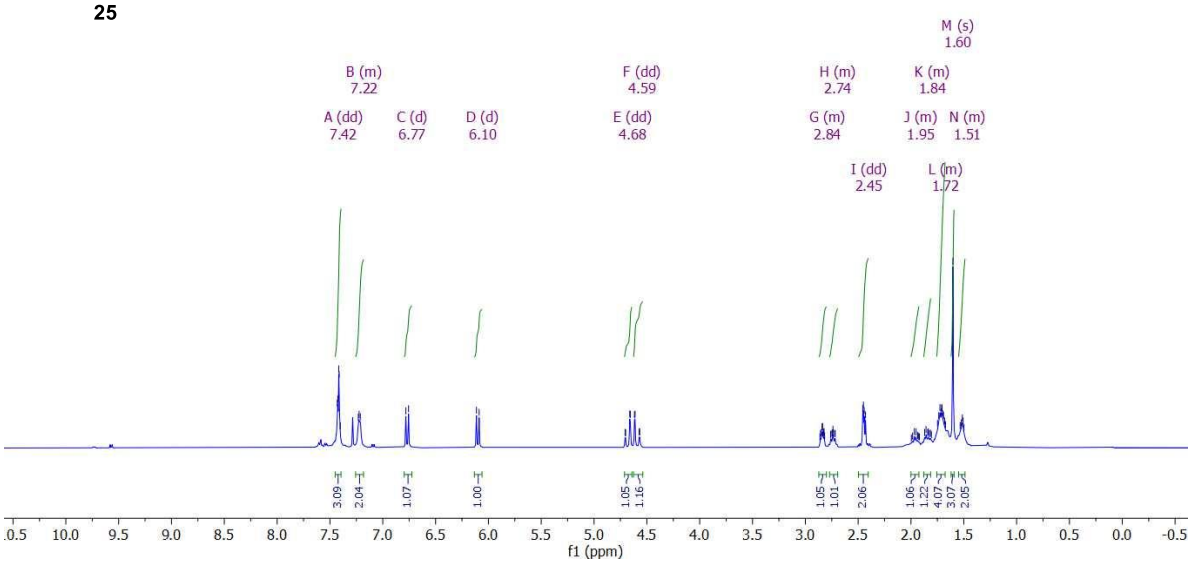
24

CMRV-IH-697-1H.1.fid
CMRV-IH-697-1H

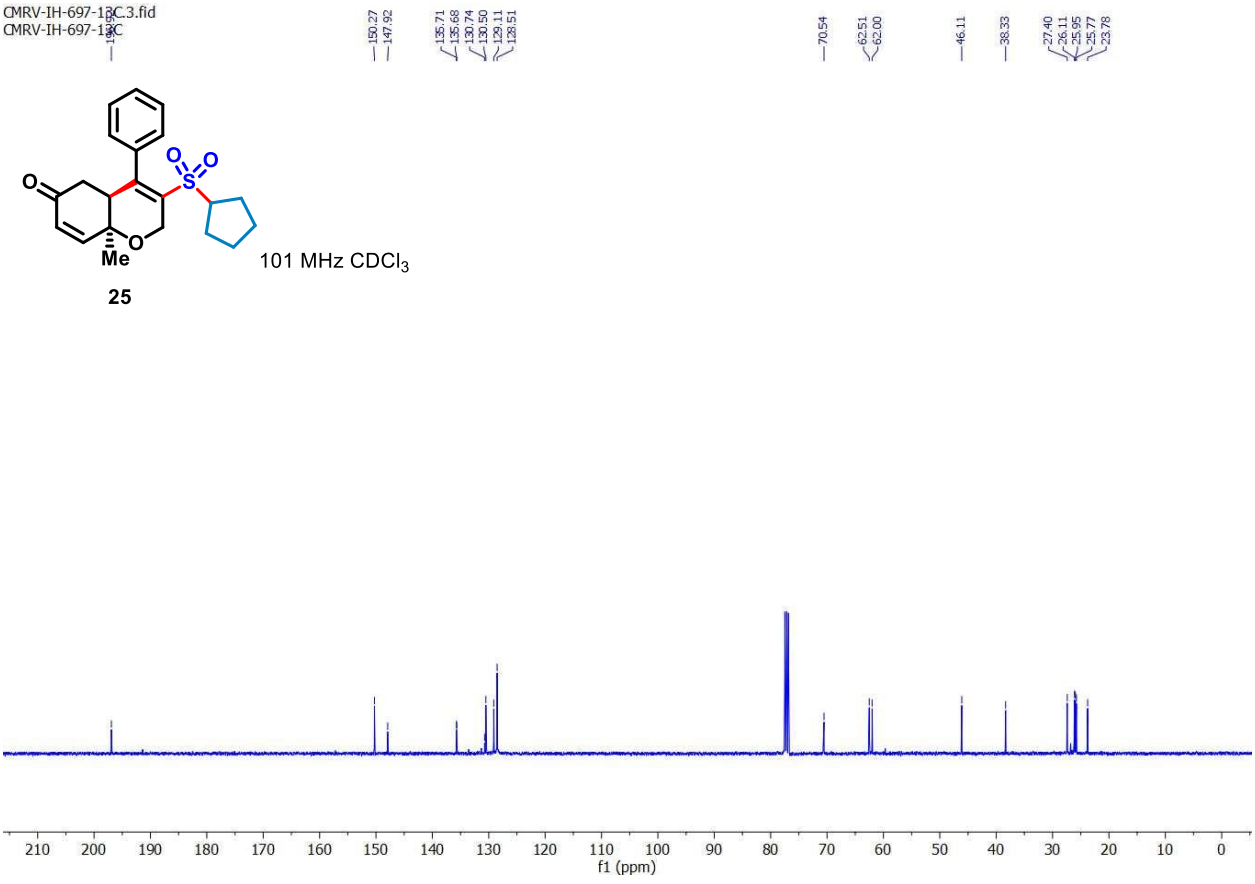


25

400 MHz $CDCl_3$



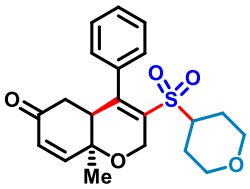
CMRV-IH-697-13C.3.fid
CMRV-IH-697-13C



25

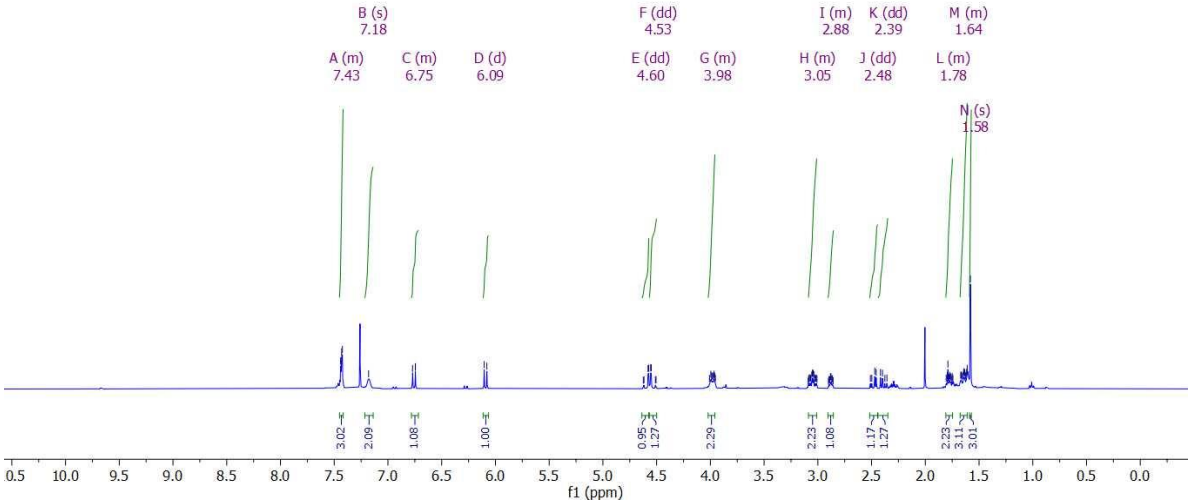
101 MHz $CDCl_3$

CMRV-IH-696-B-1H.1.fid
CMRV-IH-696-B-1H

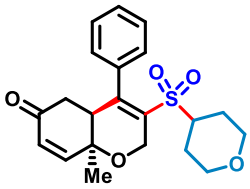


400 MHz $CDCl_3$

26

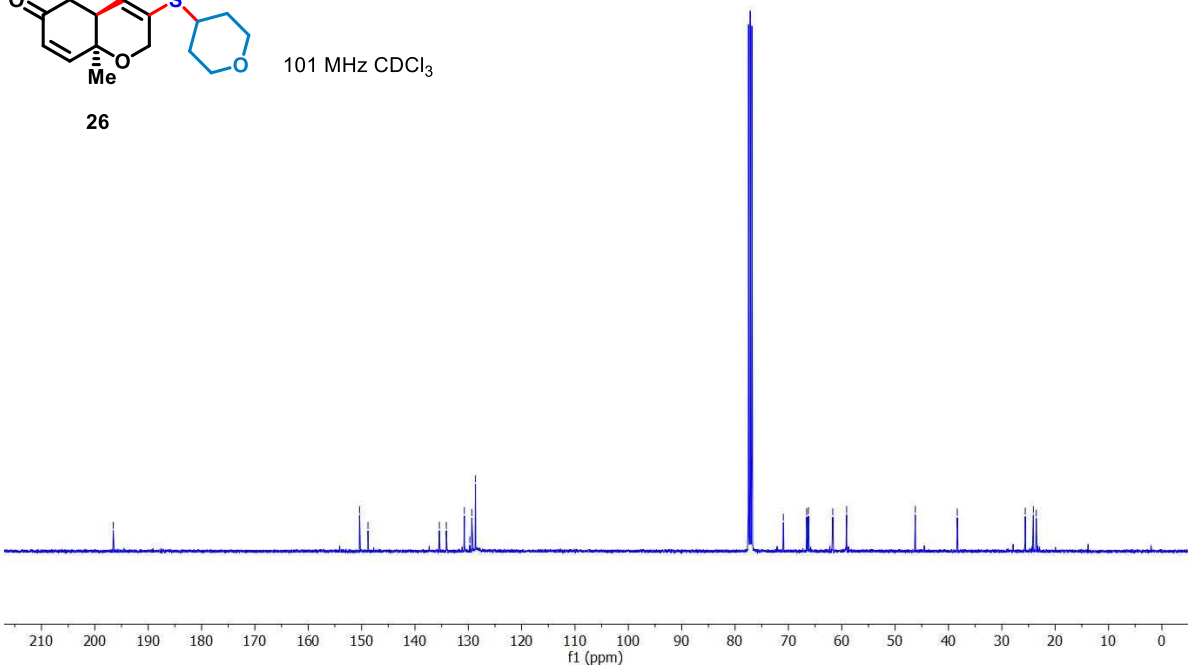


CMRV-IH-696-B-13C.2.fid
CMRV-IH-696-B-13C

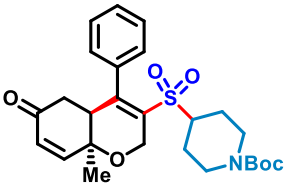


101 MHz $CDCl_3$

26

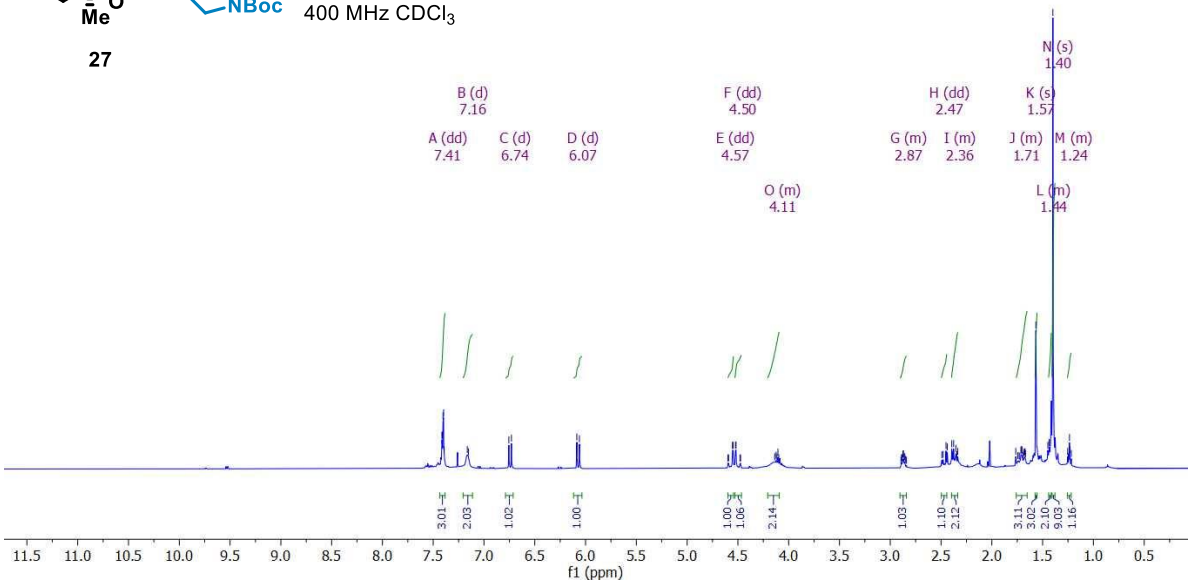


CMRV-IH-695-1H.1.fid
CMRV-IH-695-1H

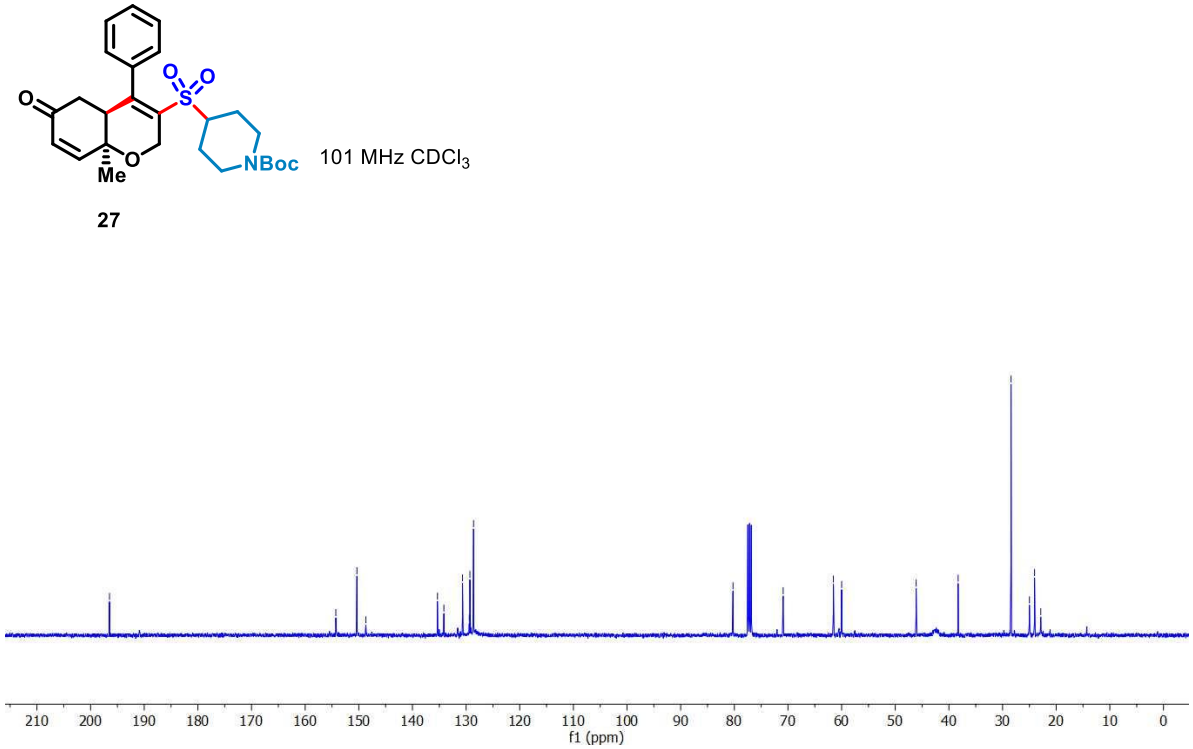


27

400 MHz $CDCl_3$

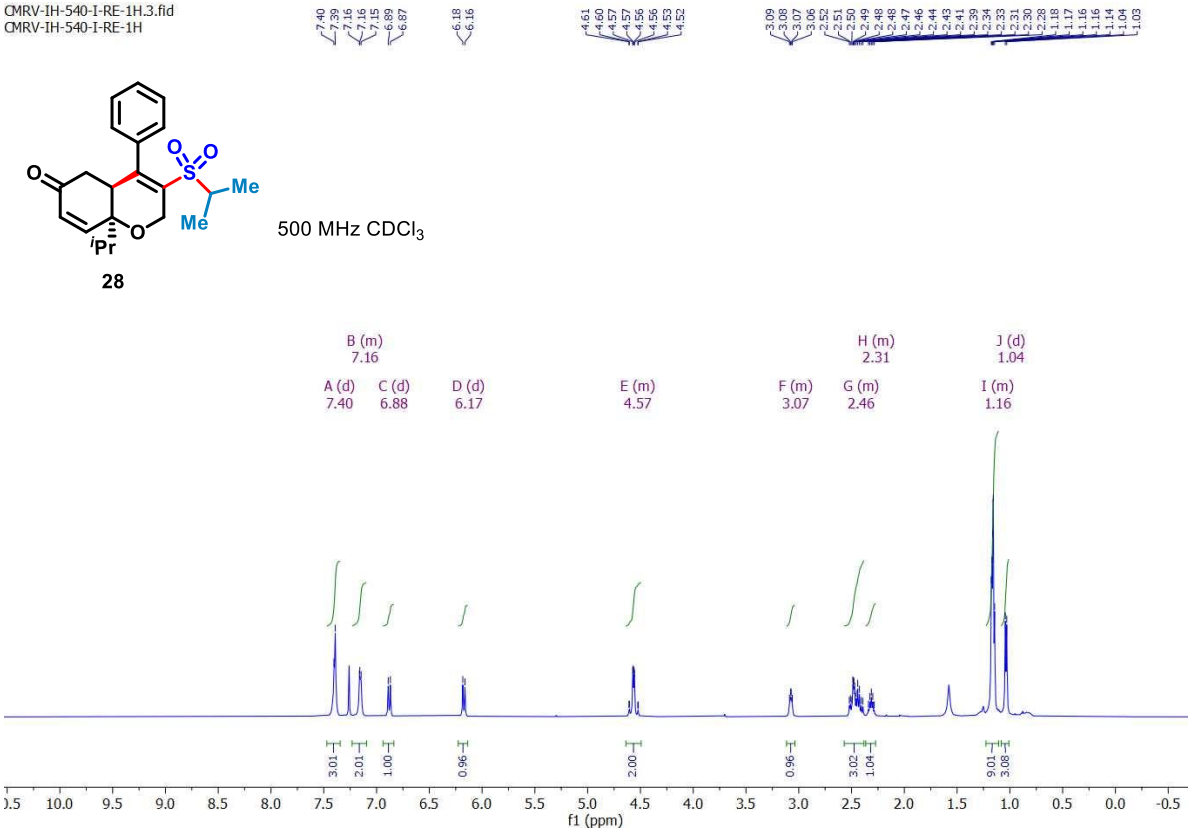


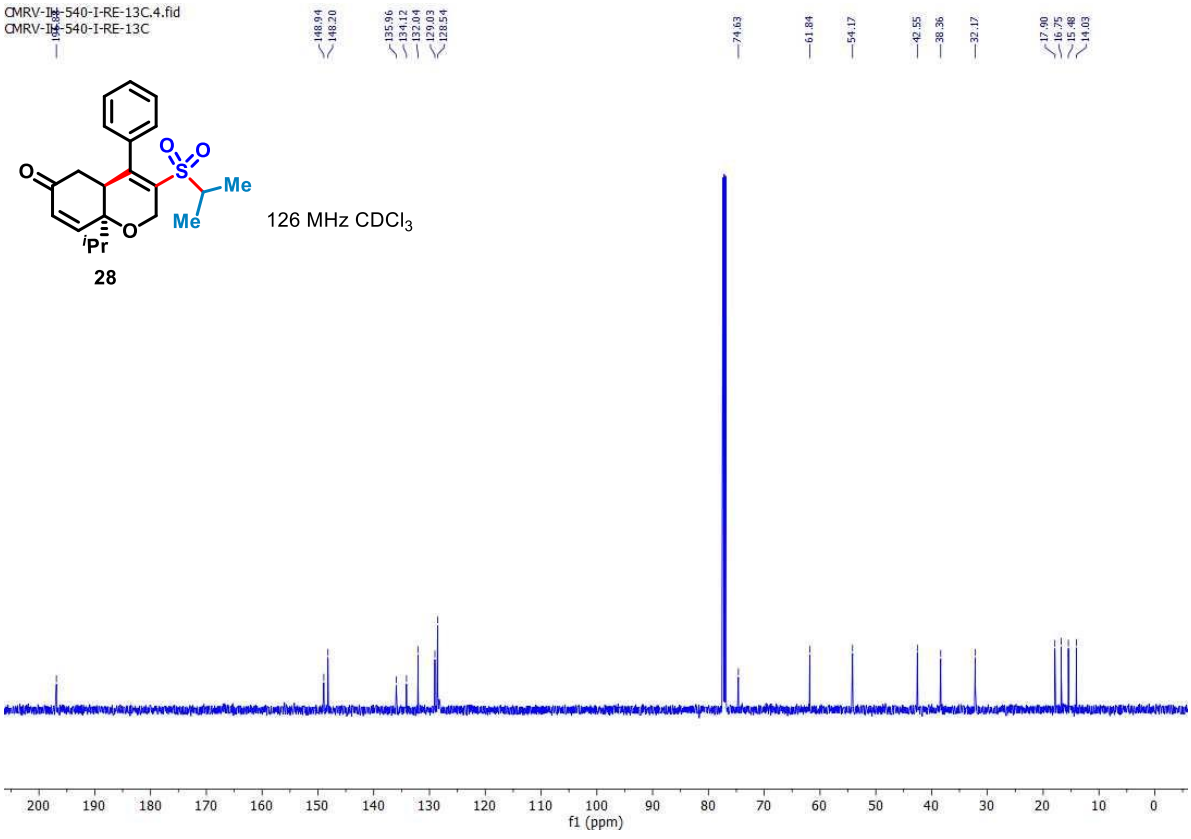
CMRV-IH-695-13C.3.fid
CMRV-IH-695-13C

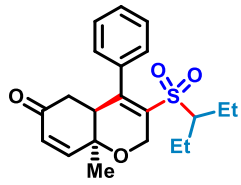


27

101 MHz $CDCl_3$

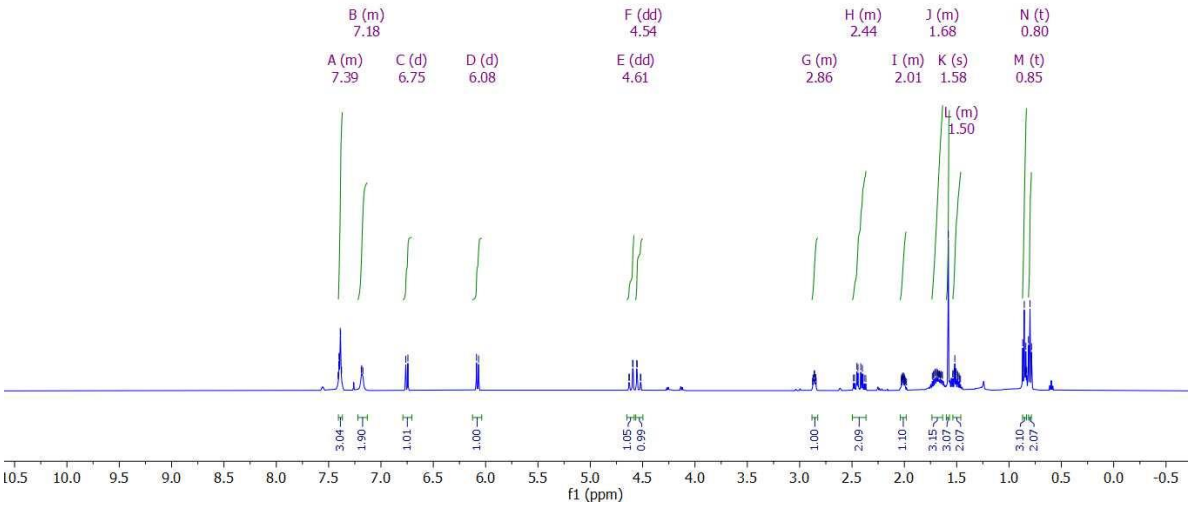

CMRV-IH-540-I-RE-1H.3.fid
CMRV-IH-540-I-RE-1H
Me
Me
iPr
28
500 MHz CDCl3
B (m) 7.16
A (d) 7.40
C (d) 6.88
D (d) 6.17
E (m) 4.57
F (m) 3.07
G (m) 2.46
H (m) 2.31
I (m) 1.16
J (d) 1.04
f1 (ppm)

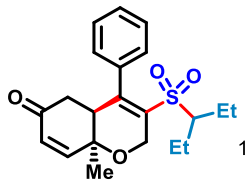

CMRV-IH-540-I-RE-13C.4.fid
CMRV-IH-540-I-RE-13C
Me
Me
iPr
28
126 MHz CDCl3
f1 (ppm)



500 MHz $CDCl_3$

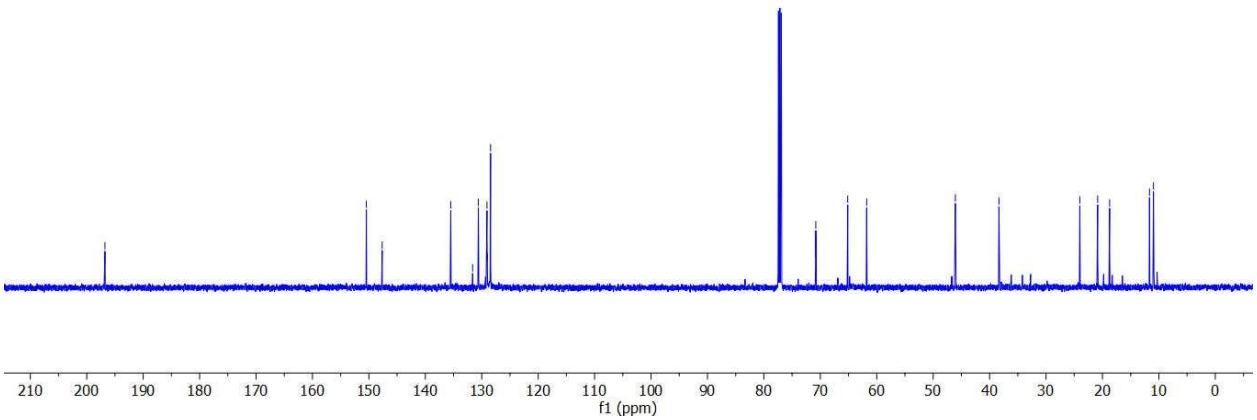
29



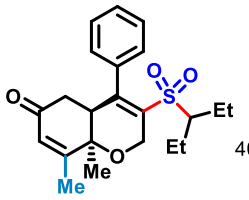


126 MHz $CDCl_3$

29

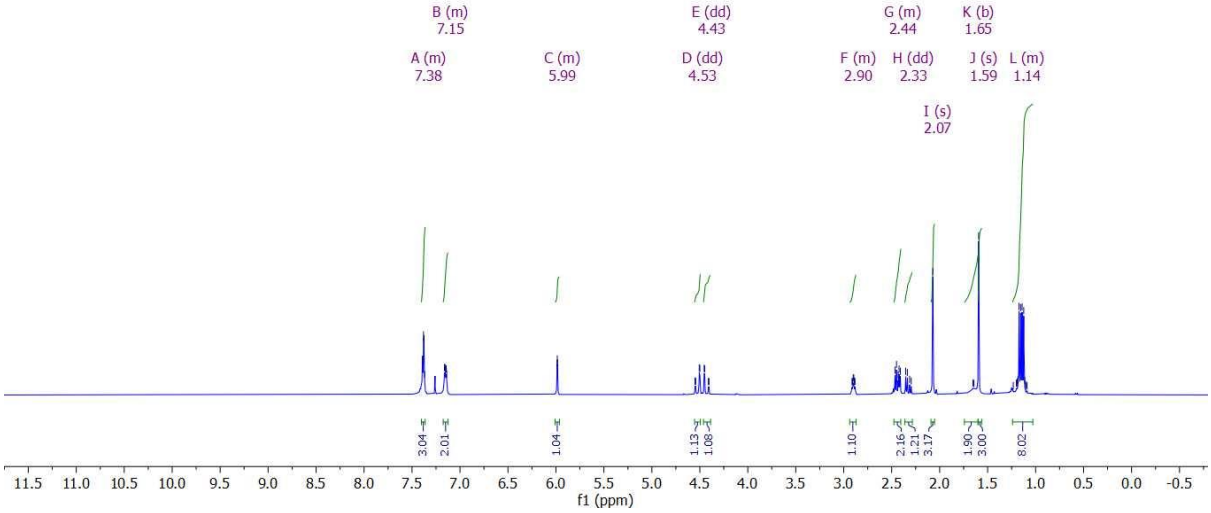


CMRV-IH-452-B-1H.1.fid
CMRV-IH-452-B-1H

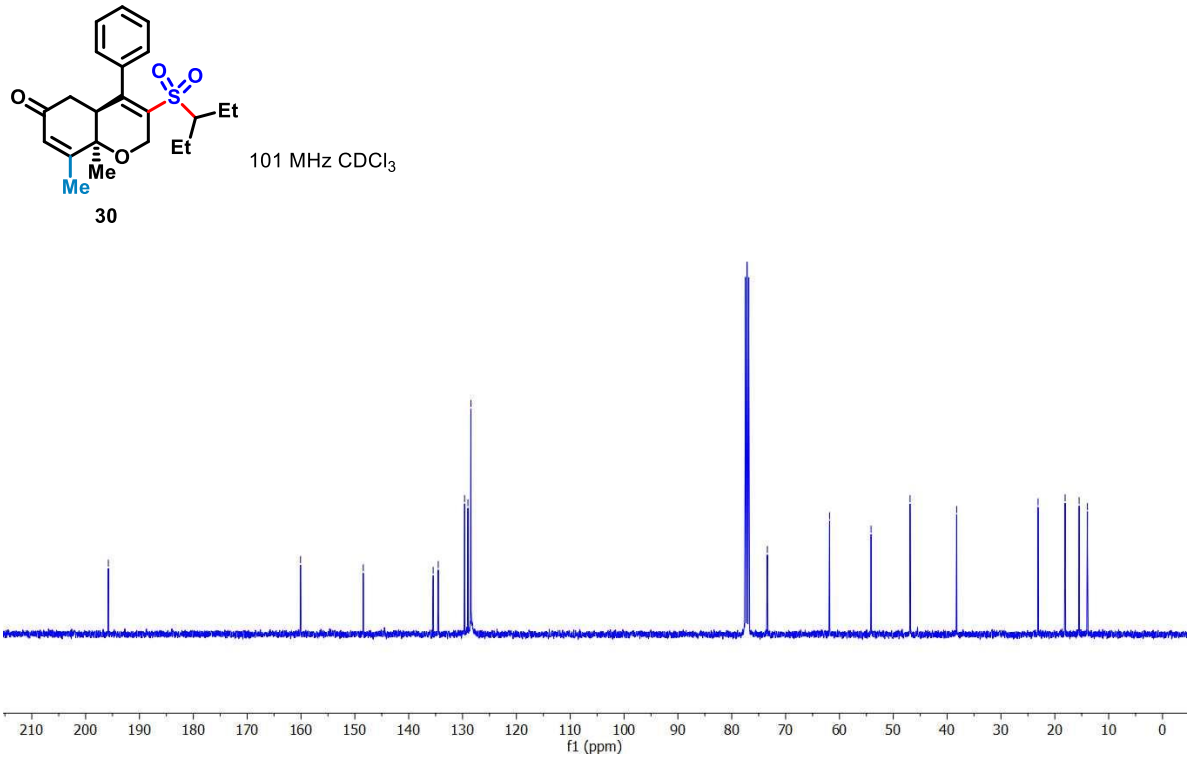


400 MHz $CDCl_3$

30



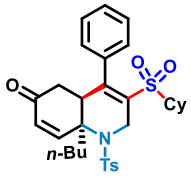
CMRV-IH-452-B-13C.3.fid
CMRV-IH-452-B-13C



101 MHz $CDCl_3$

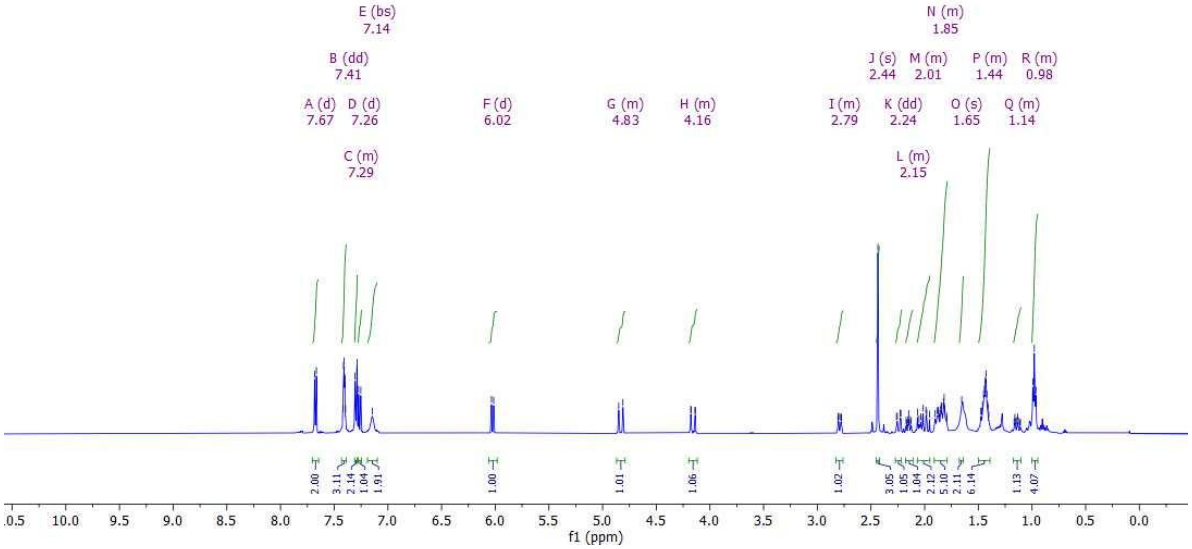
30

CMRV-IH-451-C-2-1H.24.fid
CMRV-IH-451-C-2-1H

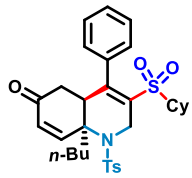


500 MHz $CDCl_3$

31

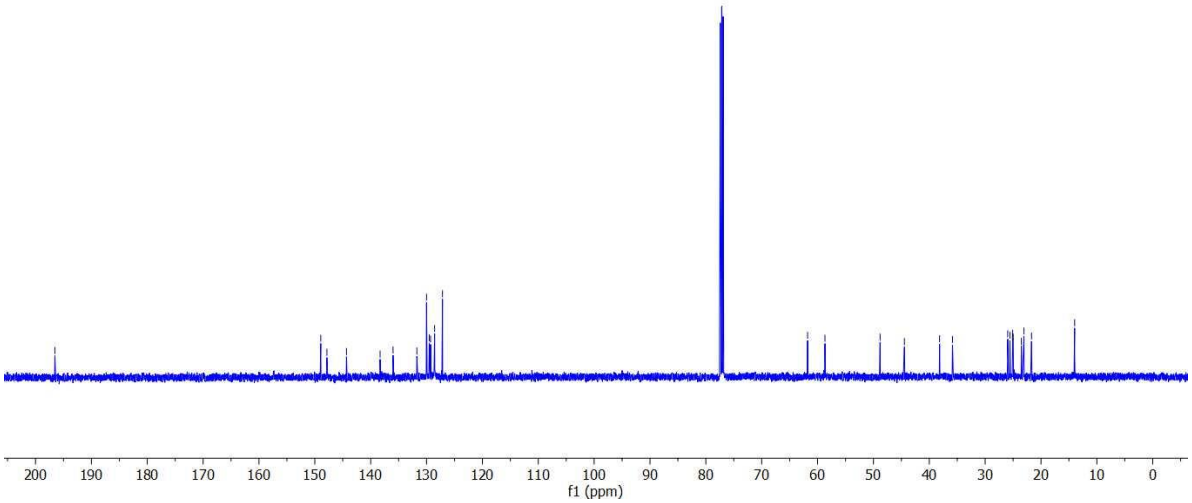


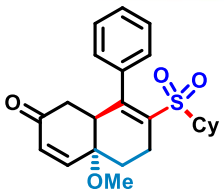
CMRV-IH-451-C-2-13C.24.fid
CMRV-IH-451-C-2-13C



126 MHz $CDCl_3$

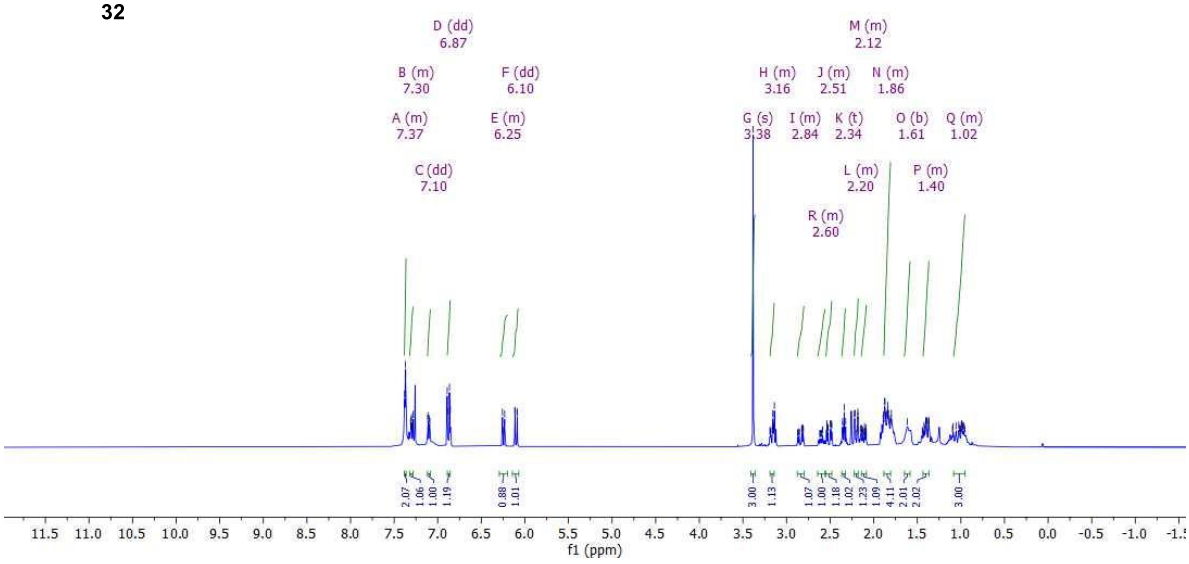
31

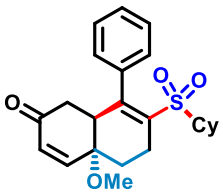




400 MHz $CDCl_3$

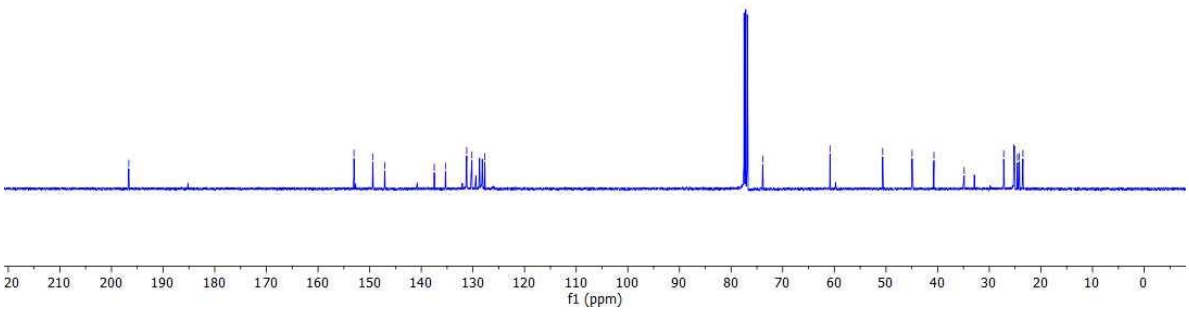
32

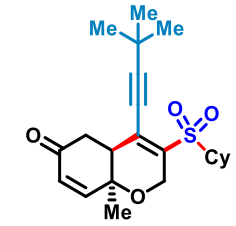




101 MHz $CDCl_3$

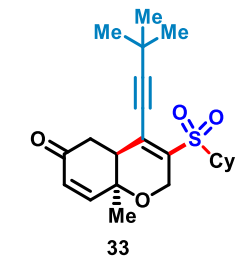
32





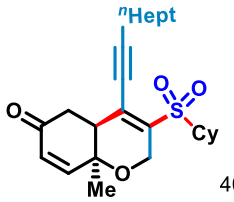
33

400 MHz $CDCl_3$



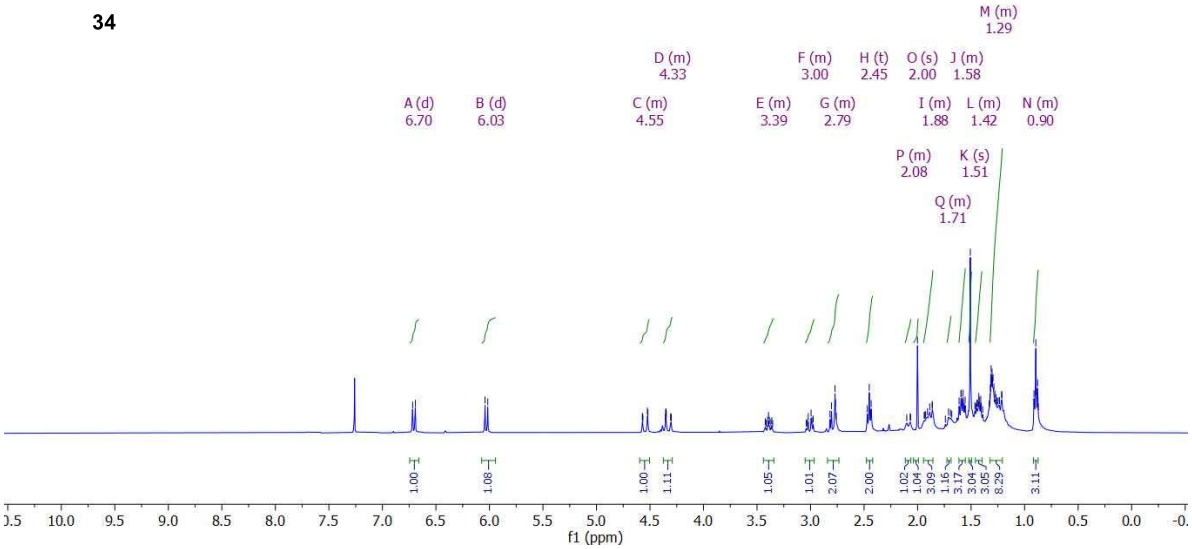
33

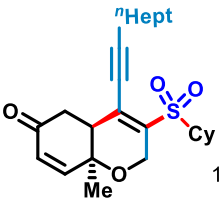
101 MHz $CDCl_3$



400 MHz $CDCl_3$

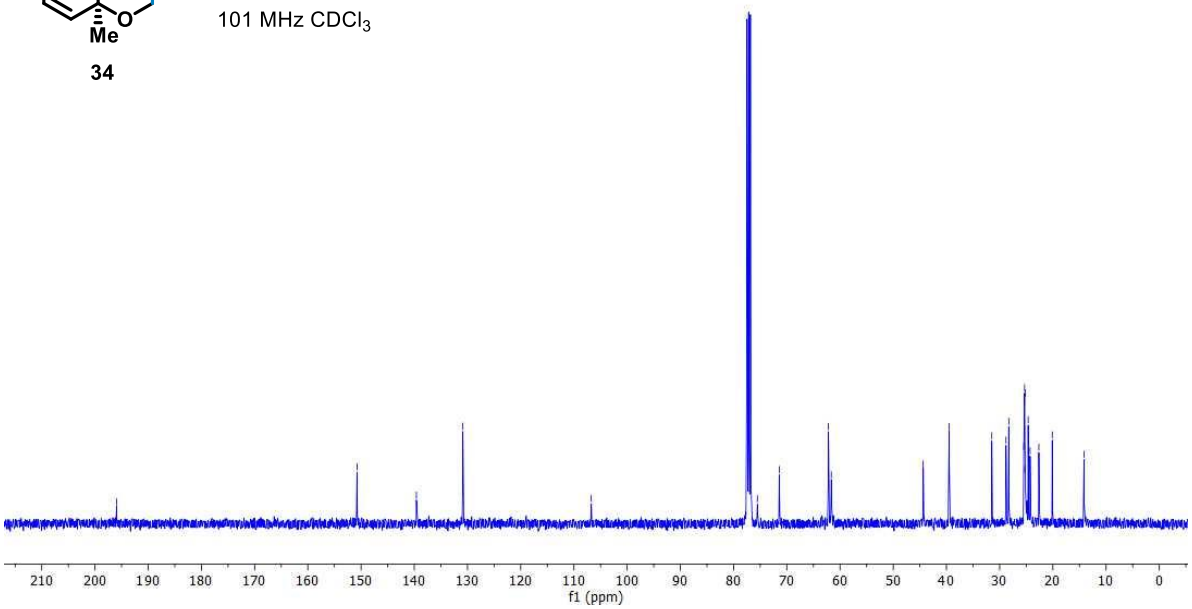
34

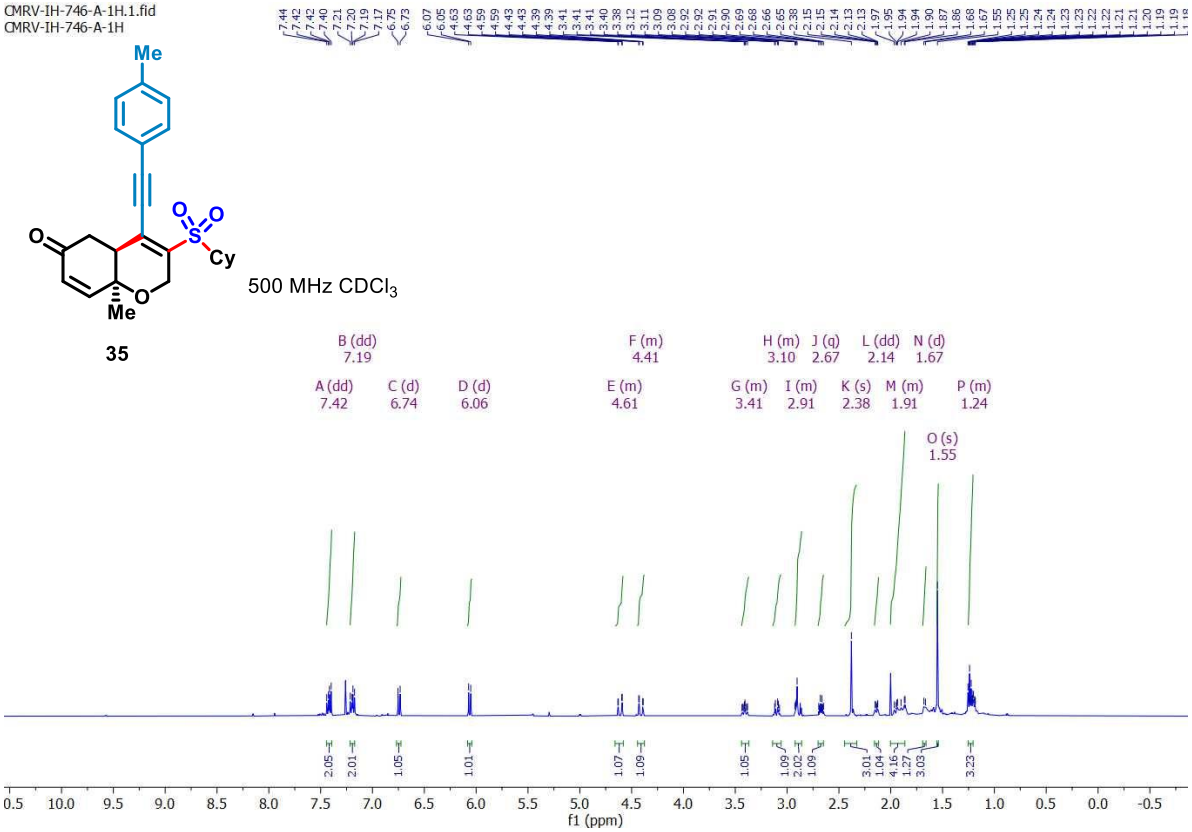


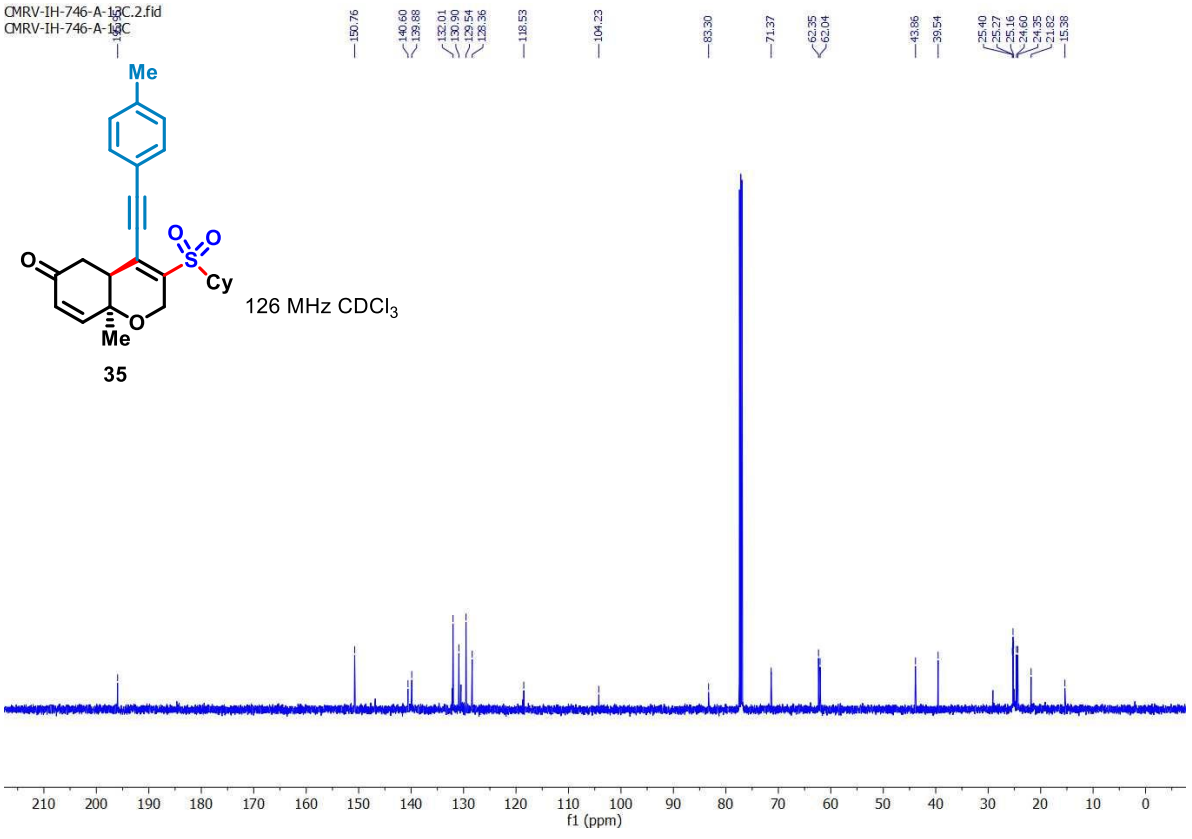


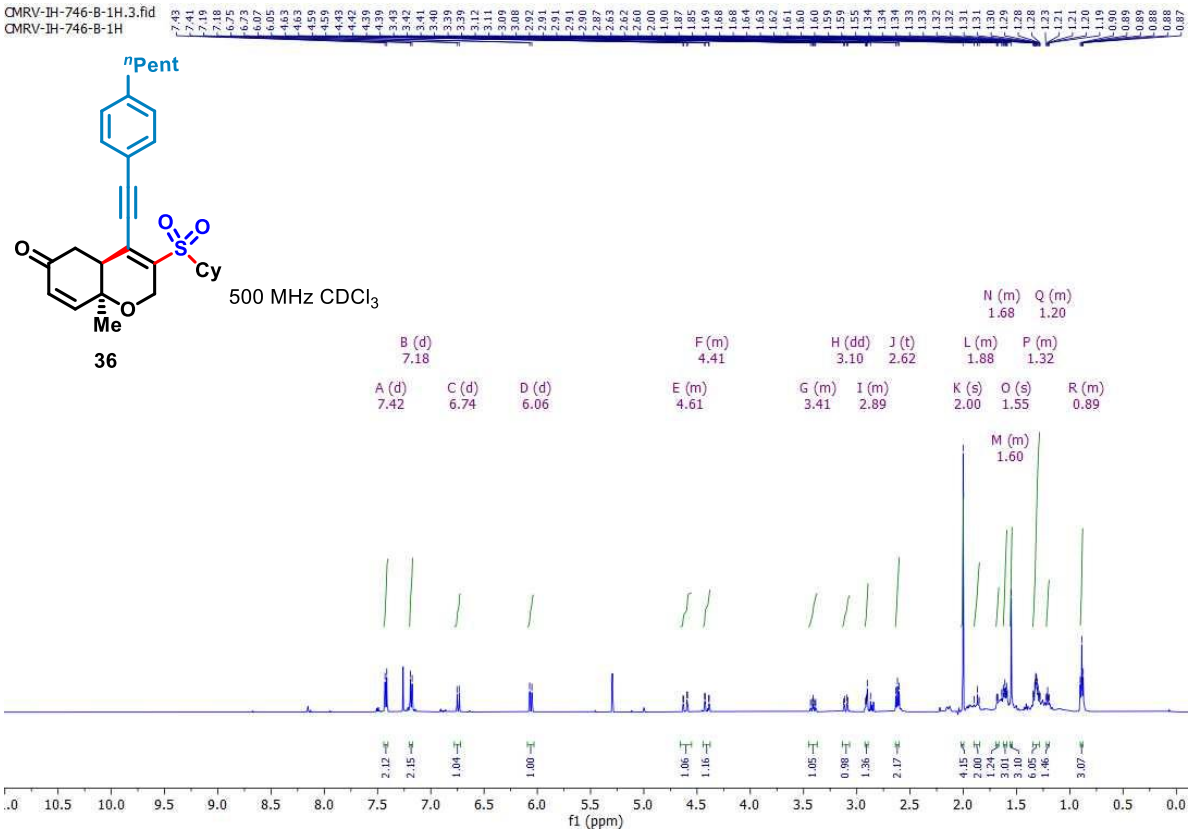
101 MHz $CDCl_3$

34

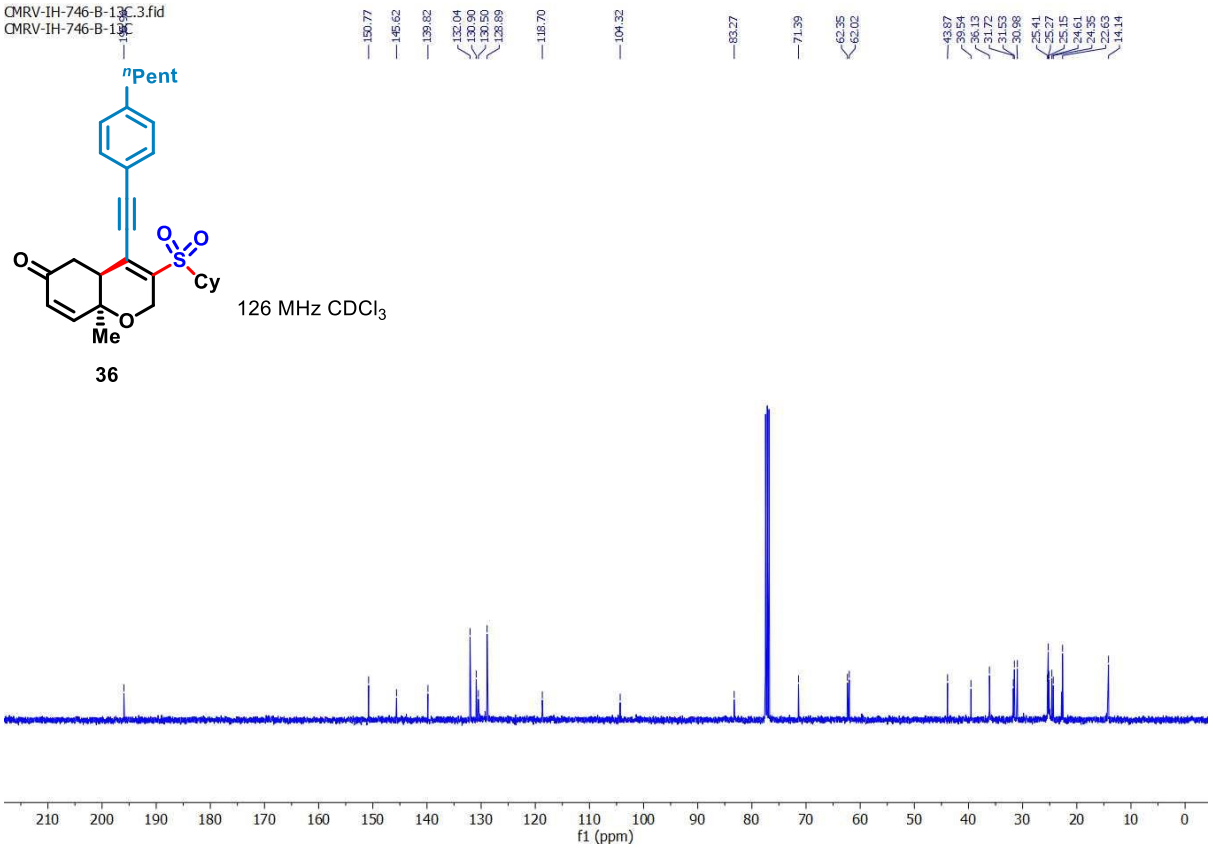



CMRV-IH-746-A-1H.1.fid
CMRV-IH-746-A-1H
Me
O
O
S
O
Cy
O
Me
35
500 MHz CDCl3
B (dd) 7.19
F (m) 4.41
H (m) 3.10
J (q) 2.67
L (dd) 2.14
N (d) 1.67
A (dd) 7.42
C (d) 6.74
D (d) 6.06
E (m) 4.61
G (m) 3.41
I (m) 2.91
K (s) 2.38
M (m) 1.91
P (m) 1.24
O (s) 1.55
f1 (ppm)


CMRV-IH-746-A-13C.2.fid
CMRV-IH-746-A-13C
Me
O
O
S
O
Cy
O
Me
35
126 MHz CDCl3
f1 (ppm)

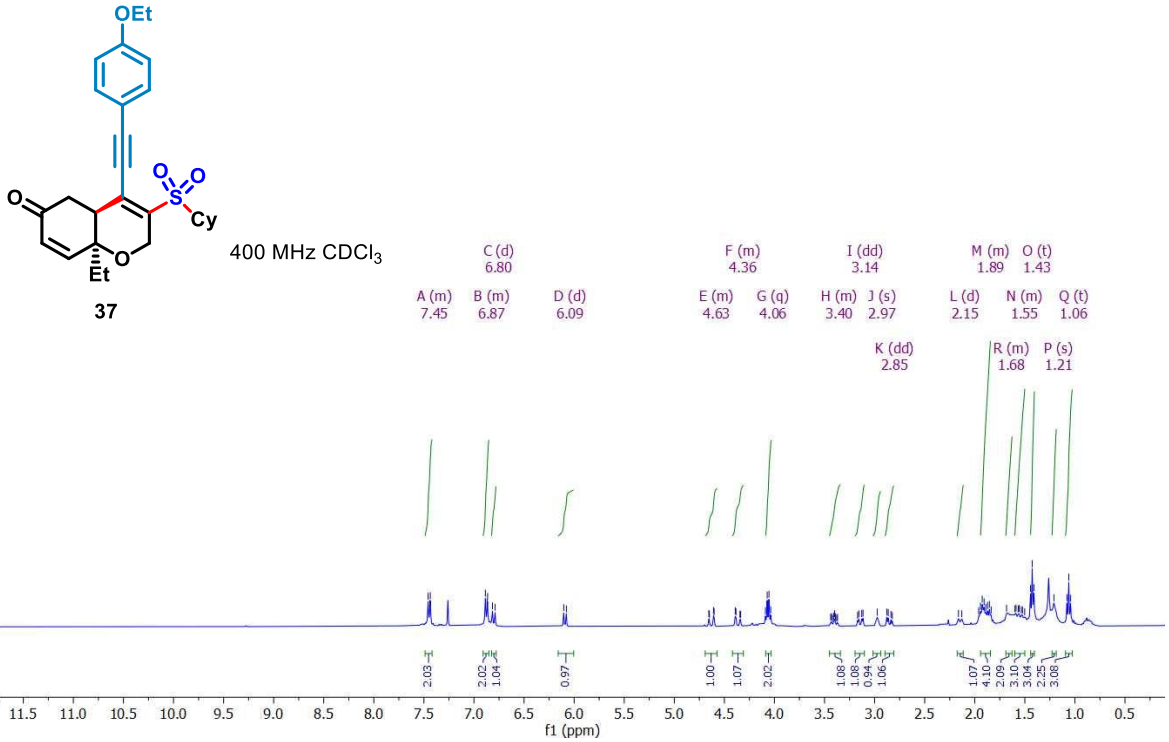

CMRV-IH-746-B-1H.3.fid
CMRV-IH-746-B-1H
nPent
O
O
S
O
Cy
O
Me
500 MHz CDCl3
B (d) 7.18
F (m) 4.41
H (dd) 3.10
J (t) 2.62
N (m) 1.68
Q (m) 1.20
L (m) 1.88
P (m) 1.32
A (d) 7.42
C (d) 6.74
D (d) 6.06
E (m) 4.61
G (m) 3.41
I (m) 2.89
K (s) 2.00
O (s) 1.55
R (m) 0.89
M (m) 1.60
f1 (ppm)

36

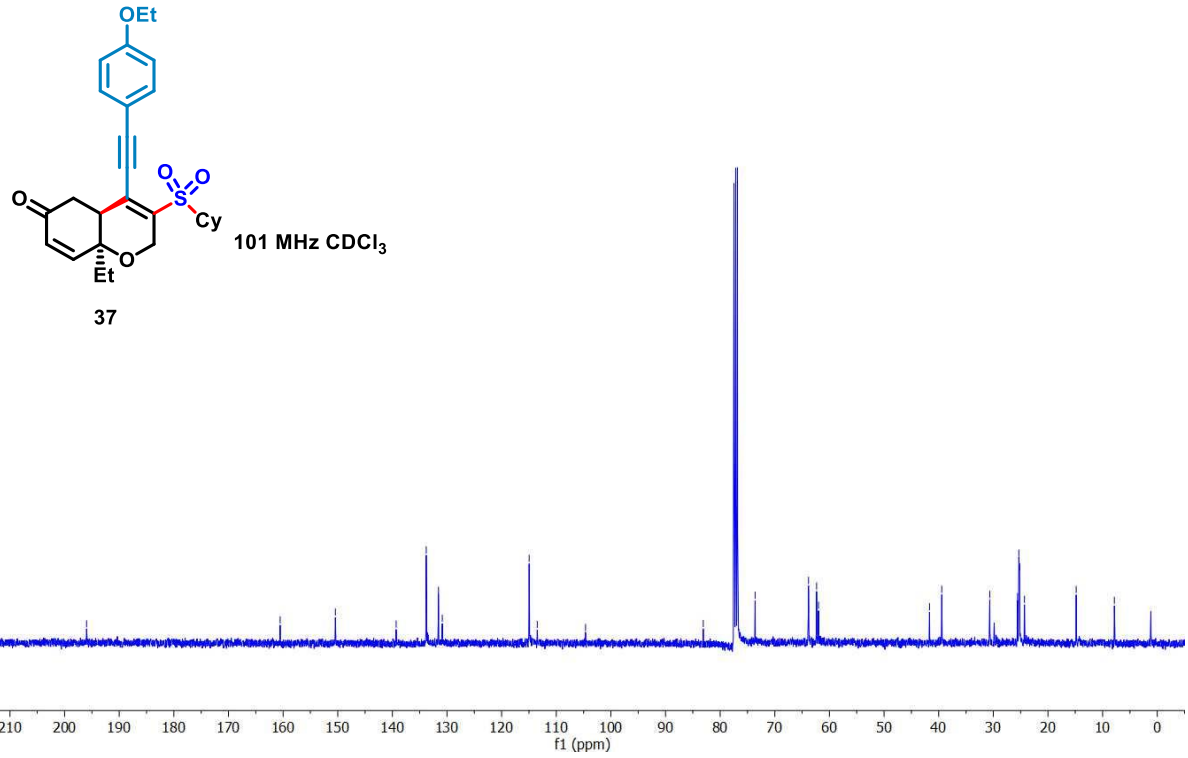

CMRV-IH-746-B-13C.3.fid
CMRV-IH-746-B-13C
nPent
O
O
S
O
Cy
O
Me
126 MHz CDCl3
f1 (ppm)

36

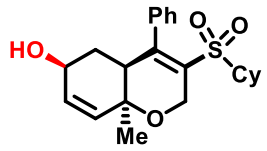
CMRV-IH-737-RE--1H.1.fid
CMRV-IH-737-RE--1H



CMRV-IH-737-RE--13C.3.fid
CMRV-IH-737-RE--13C

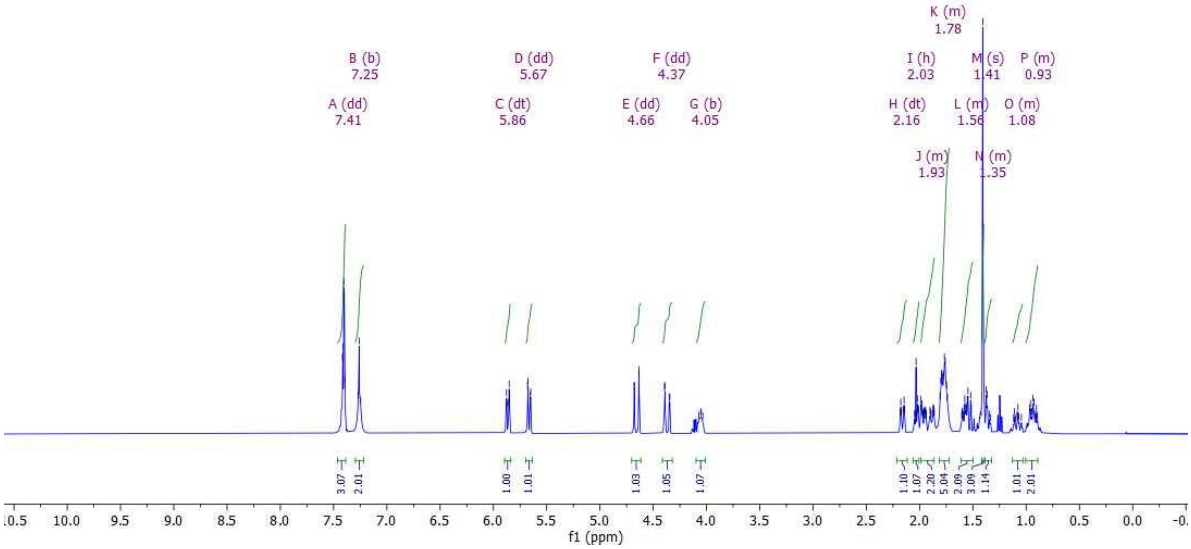


CMRV-IH-468-B-1H.1.fid
CMRV-IH-468-B-1H

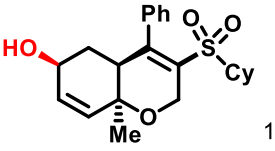


400 MHz $CDCl_3$

39

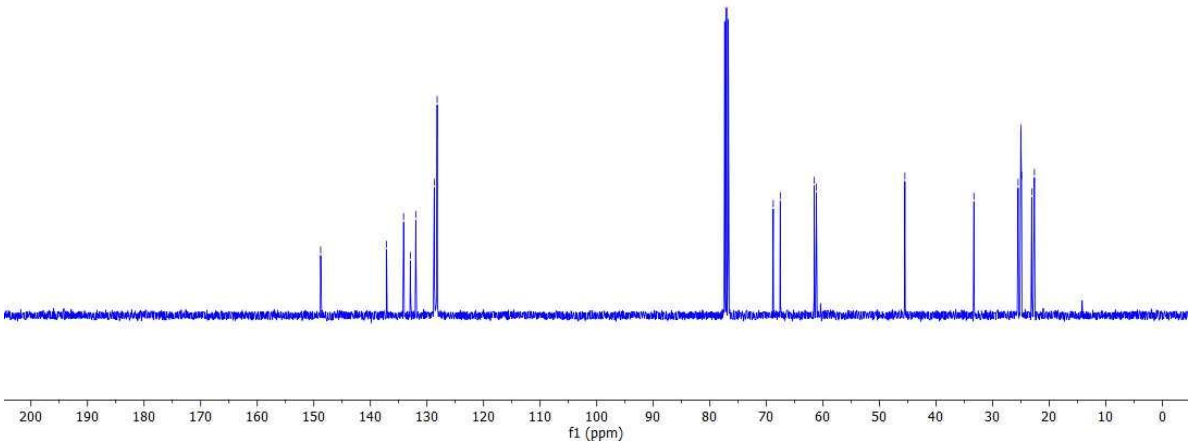


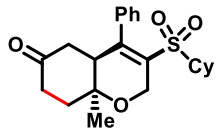
CMRV-IH-468-B-13C.3.fid
CMRV-IH-468-B-13C



101 MHz $CDCl_3$

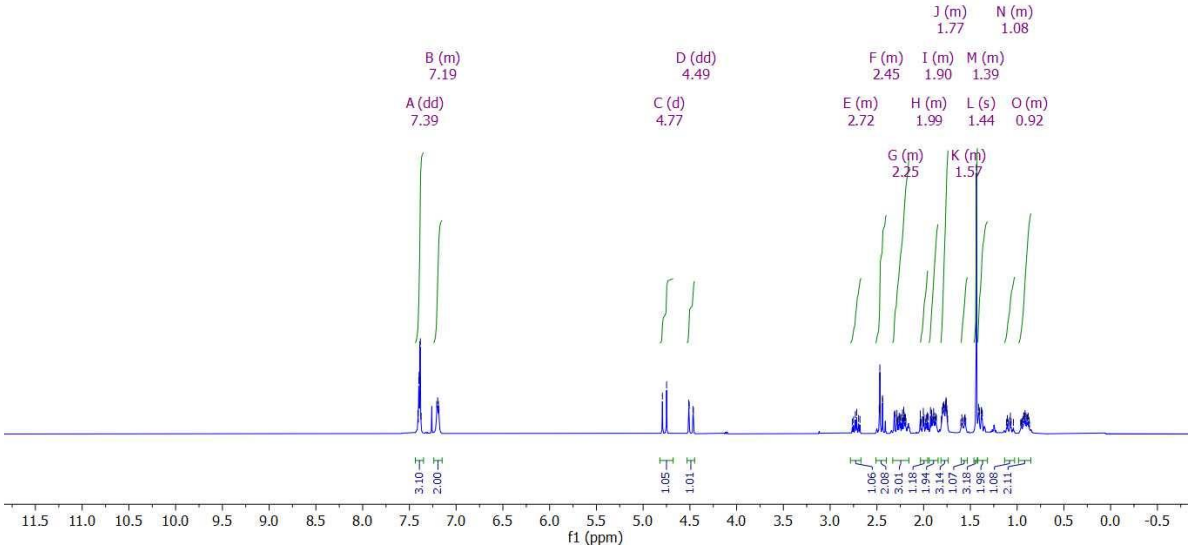
39

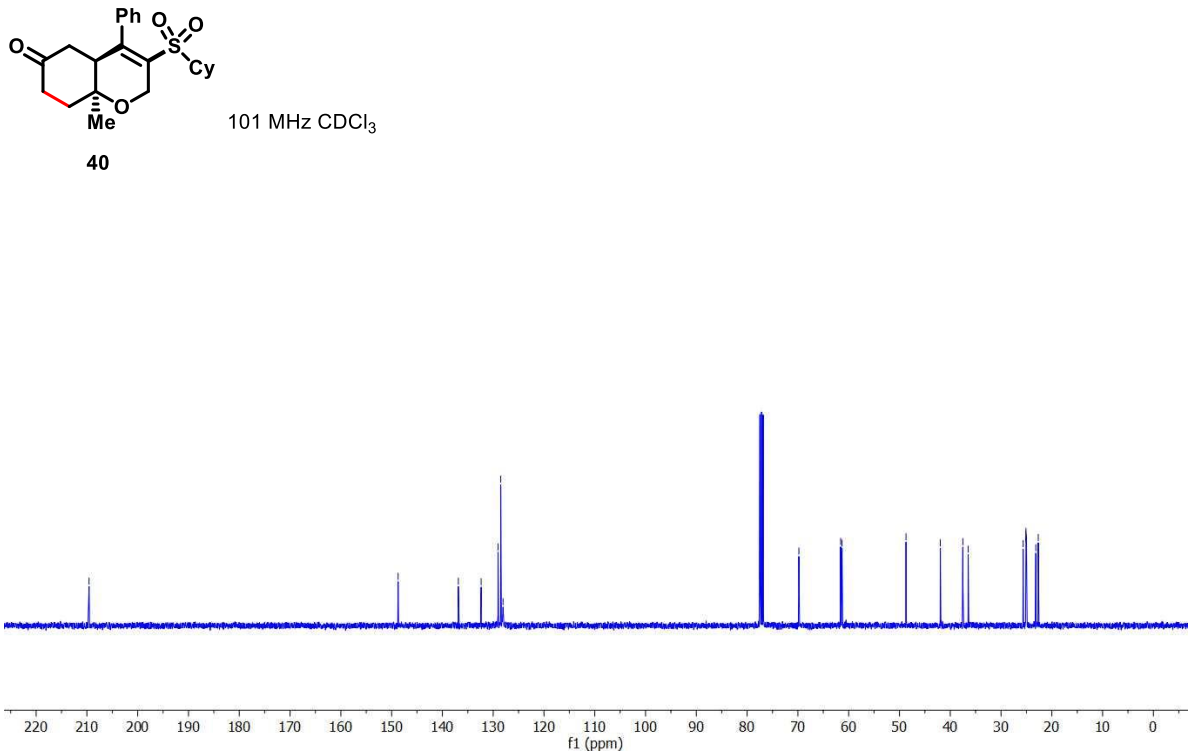




400 MHz $CDCl_3$

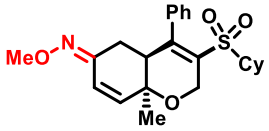
40





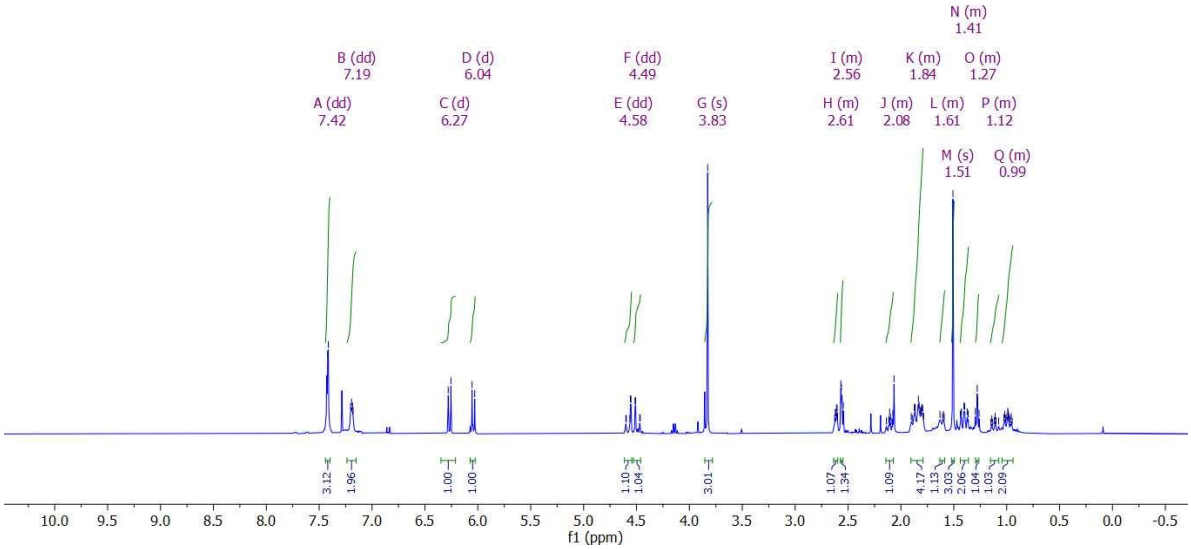
101 MHz $CDCl_3$

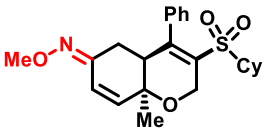
40



400 MHz $CDCl_3$

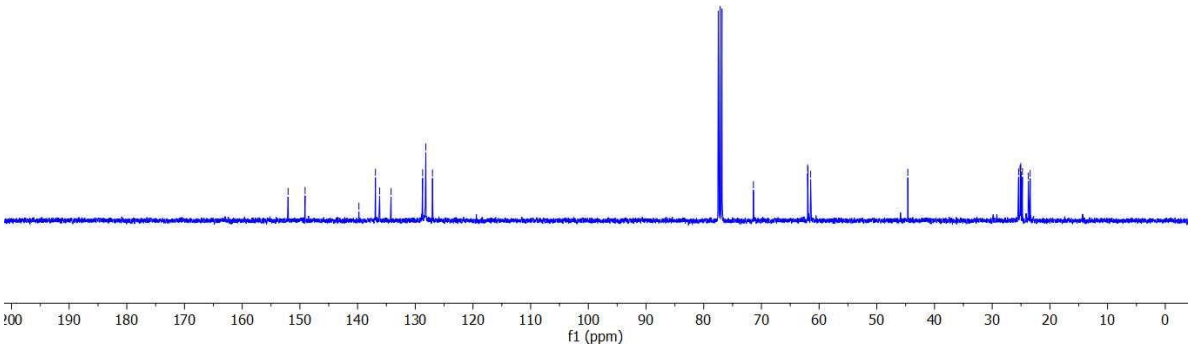
41



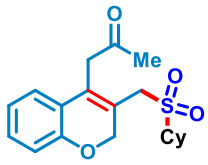


101 MHz $CDCl_3$

41

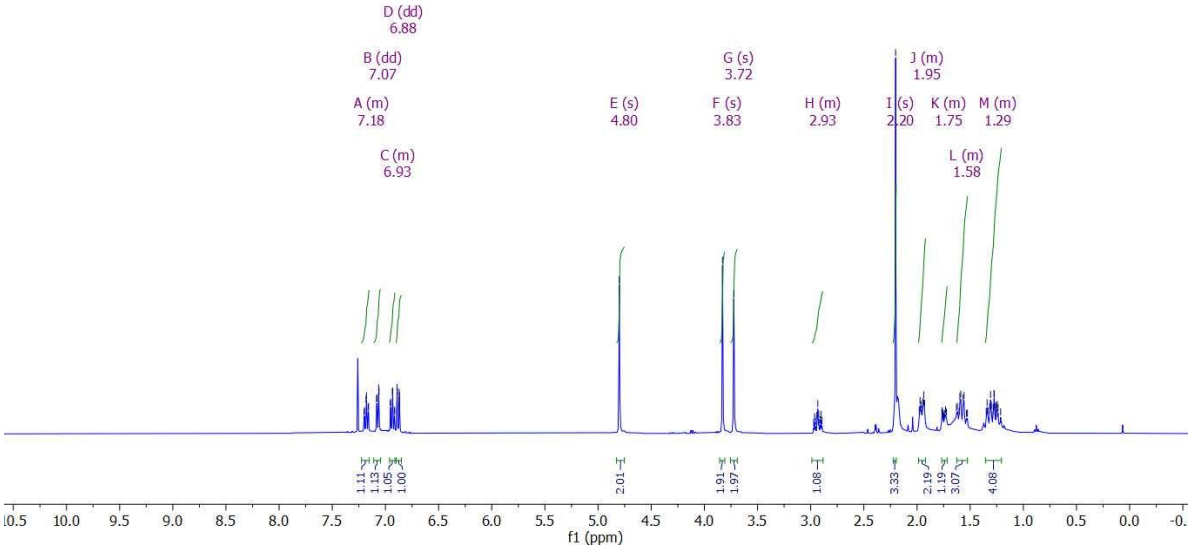


CMRV-IH-632-C-II-1H.10.fid
CMRV-IH-632-C-II-1H

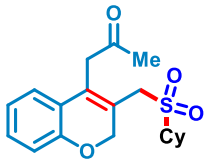


43

400 MHz $CDCl_3$

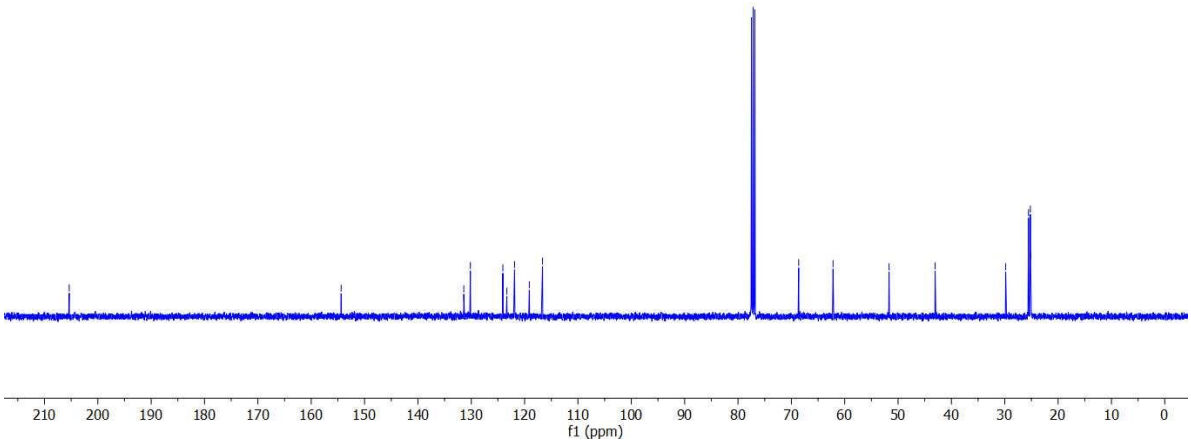


CMRV-IH-632-C-II-13C.12.fid
CMRV-IH-632-C-II-13C



43

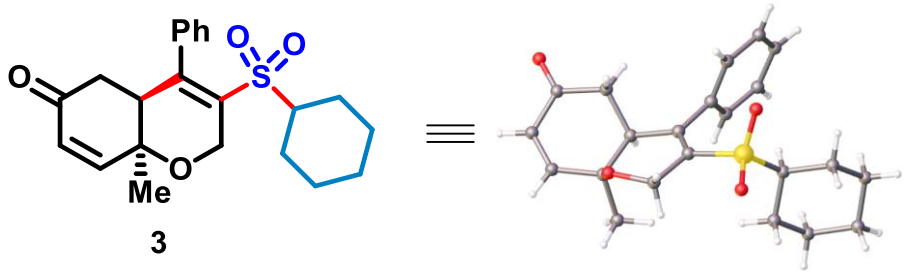
101MHz $CDCl_3$



9) <u>X-ray Crystallography data:</u>

a) <u>X-ray Crystallography data for the compound 3:</u>

10–20 mg of compound **3** was taken in a 4–8 mL of glass vial. To this was added DMSO: Acetone: DCM (1:1:1). The vial was then plugged with cotton lightly and kept on the work bench until crystals appeared in and around the walls of vial. Further the X-ray diffraction data were collected on a Bruker D8 QUEST (APEX-II CCD) diffractometer by using Mo Kα (λ =0.71073). Molecular structure of **3** with 50% ellipsoid probability is provided below.



3

CCDC: 2245728

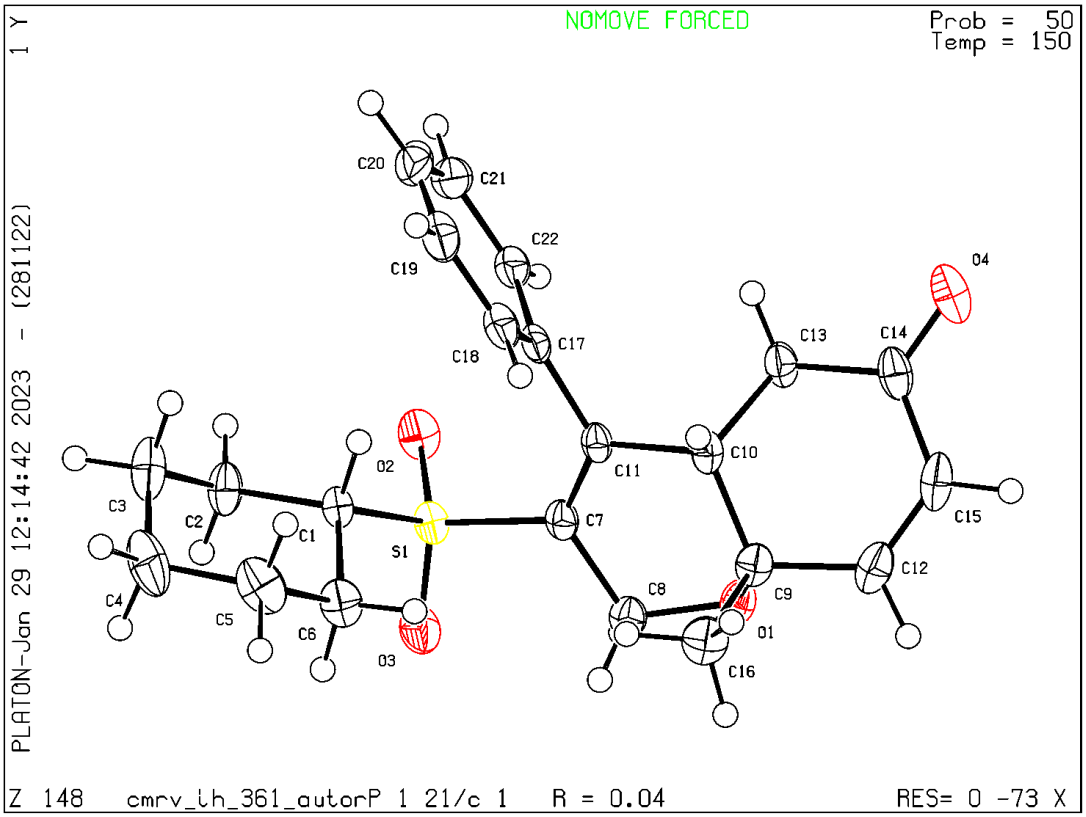
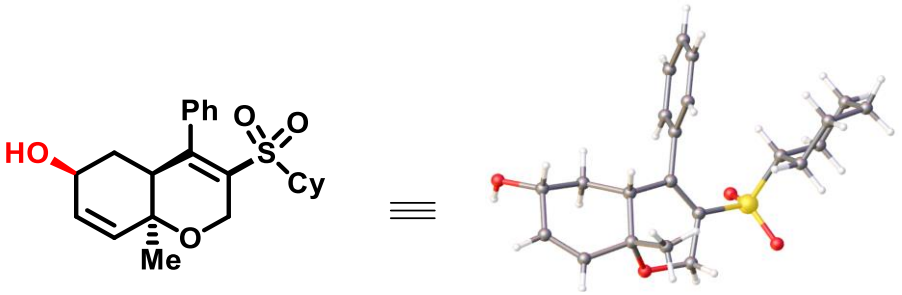


Table 1 Crystal data and structure refinement for 3	
Identification code	3
Empirical formula	$C_{22}H_{26}O_4S$
Formula weight	386.49
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.4337(5)
b/Å	6.53480(10)
c/Å	17.2542(6)
α/°	90
β/°	114.748(4)
γ/°	90
Volume/Å^3	1989.96(11)
Z	4
ρ_{calc}g/cm^3	1.290
μ/mm^{-1}	0.187
F(000)	824.0
Crystal size/mm^3	0.268 × 0.168 × 0.046
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.724 to 50
Index ranges	$-23 \leq h \leq 23$, $-7 \leq k \leq 7$, $-20 \leq l \leq 20$
Reflections collected	23710
Independent reflections	3477 [R_{int} = 0.1032, R_{sigma} = 0.0469]
Data/restraints/parameters	3477/0/245
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0449, wR_2 = 0.1160
Final R indexes [all data]	R_1 = 0.0502, wR_2 = 0.1223
Largest diff. peak/hole / e Å^{-3}	0.36/-0.45

b) <u>X-ray Crystallography data for the compound 39:</u>

10–20 mg of compound **39** was taken in a 4–8 mL of glass vial. To this was added DMSO: Acetone: DCM (1:1:1). The vial was then plugged with cotton lightly and kept on the work bench until crystals appeared in and around the walls of vial. Further the X-ray diffraction data were collected on a Bruker D8 QUEST (APEX-II CCD) diffractometer by using Mo Kα (λ =0.71073). Molecular structure of **39** with 50% ellipsoid probability is provided below.



39 **CCDC: 2250720**

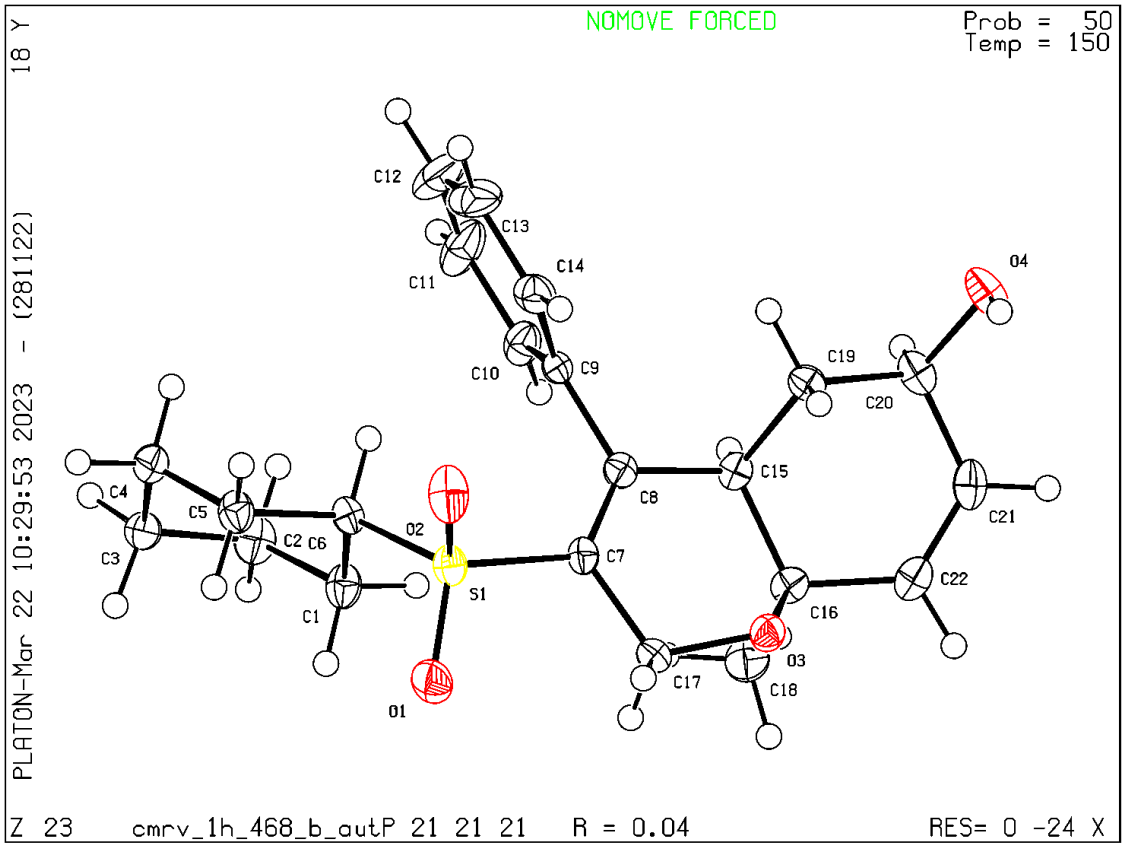


Table 1 Crystal data and structure refinement for 39	
Identification code	39
Empirical formula	$C_{22}H_{28}O_4S$
Formula weight	388.50
Temperature/K	150.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.5572(2)
b/Å	12.2026(2)
c/Å	15.4049(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1984.54(6)
Z	4
ρ_{calc}g/cm^3	1.300
μ/mm^{-1}	0.188
F(000)	832.0
Crystal size/mm^3	0.214 × 0.12 × 0.089
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.258 to 49.998
Index ranges	$-11 \leq h \leq 12$, $-14 \leq k \leq 14$, $-18 \leq l \leq 18$
Reflections collected	31354
Independent reflections	3508 [R_{int} = 0.1701, R_{sigma} = 0.0636]
Data/restraints/parameters	3508/0/246
Goodness-of-fit on F^2	1.115
Final R indexes [I>=2σ (I)]	R_1 = 0.0365, wR_2 = 0.0878
Final R indexes [all data]	R_1 = 0.0379, wR_2 = 0.0883
Largest diff. peak/hole / e Å^{-3}	0.28/-0.59
Flack parameter	0.03(3)