Electronic Supplementary Material (ESI) for Chemical Science.

Supporting information

Visible-Light-Driven Radical Opening of Epoxides via the Combination of Titanocene and Photoredox Catalysis

Contents

S1 General Information

Unless otherwise noted, all reactions of substrates preparation were conducted in flame-dried glassware under a nitrogen atmosphere using anhydrous solvent passed through an activated alumina column (Innovative Technology). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using Huanghai TLC silica gel plates HSG F254 and visualized using UV light, anisaldehyde or potassium permanganate. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020L) with 10W LED. 1H and 13C NMR spectra were recorded in $CDCl_3$ on a Bruker 400M spectrometer. Chemical shifts in ^1H NMR spectra were reported in parts per million (ppm) on the δ scale from an internal standard of residual $CDCl_3$ (7.26 ppm). Data for ^1H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz) and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift in ppm from the central peak of CDCl3 (77.00 ppm). IR spectra were recorded on a Thermo Scientific Nicolet 6700 Flex FT-IR spectrometer. ESI mass spectra were obtained from an HPLC-Q-Tof mass spectrometer using acetonitrile as the mobile phase. UV-vis spectra were collected on an HP 8453 spectrometer. The fluorescence emission spectra were collected on an Edinburgh FS920. The electrochemical measurements were carried out in a sealed electrolytic cell by using an electrochemical workstation (CHI 660E) in a three-electrode system devised of a glass carbon electrode, a saturated calomel electrode (SCE) and a Pt wire as working, counter and reference electrodes, respectively.

S2 UV-vis experiments

In a N_2-filled glovebox, an oven-dried 8 mL culture tube equipped with a magnetic stir bar was charged with Cp_2TiCl_2 (12.4 mg, 0.05 mmol, 1.0 equiv, 1.0 x10^{-2} M), $[Ir(dtbbpy)(ppy)_2]PF_6$ (9.2 mg, 0.01 mmol, 0.2 equiv, 2x10^{-3} M) and HE (25.3 mg, 0.1 mmol, 2 equiv, 2.0 x10^{-2} M) in 5 ml THF. The mixture was stirred for 1 min in the dark until the components were fully dissolved. Then the mixture was irradiated under 23w compact fluorescent lamp (CFL). UV-Vis spectrum is taken from 300 to 800 nm to track the decay of absorbance at 515 nm for every 5 min.

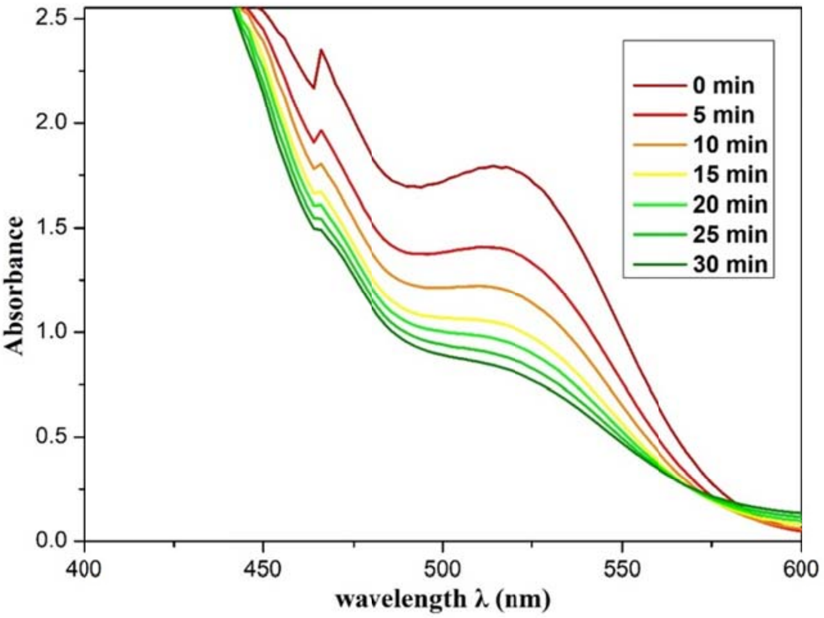


Figure S1 UV-Vis trace for detecting the decay of Ti^{IV} (515 nm).

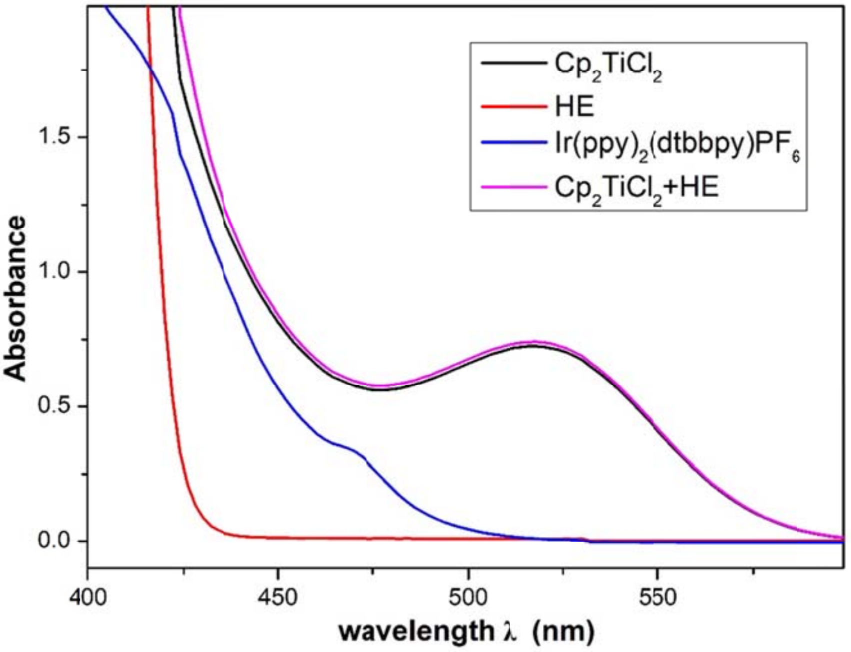


Figure S2 UV-Vis spectra of Cp$_2$TiCl$_2$ (5.0 x10^{-3} M), HE (1.0 x10^{-2} M), [Ir(dtbbpy)(ppy)$_2$]PF$_6$ (5.0 x10^{-4} M) and the mixture of Cp$_2$TiCl$_2$ (5.0 x10^{-3} M) and HE (1.0 x10^{-2} M).

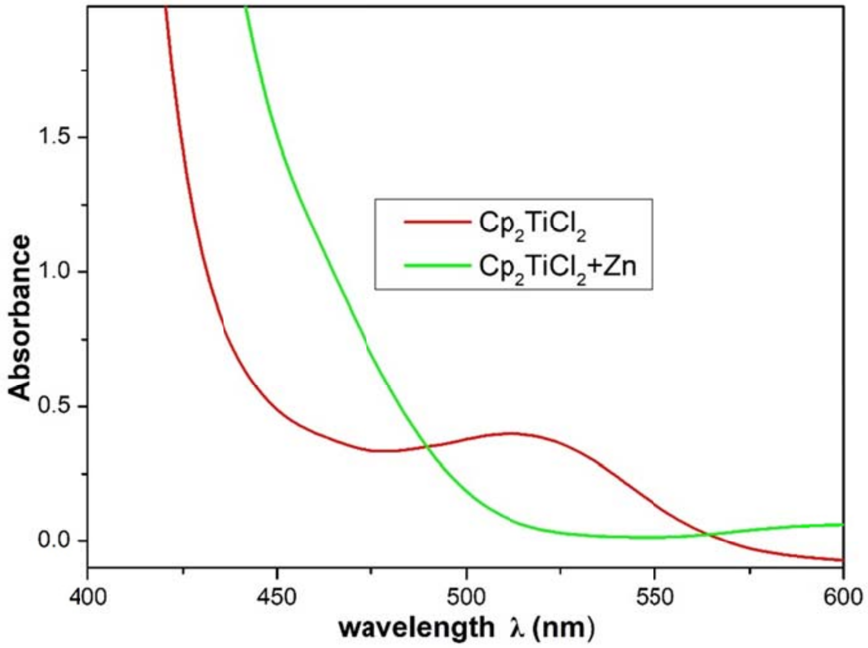
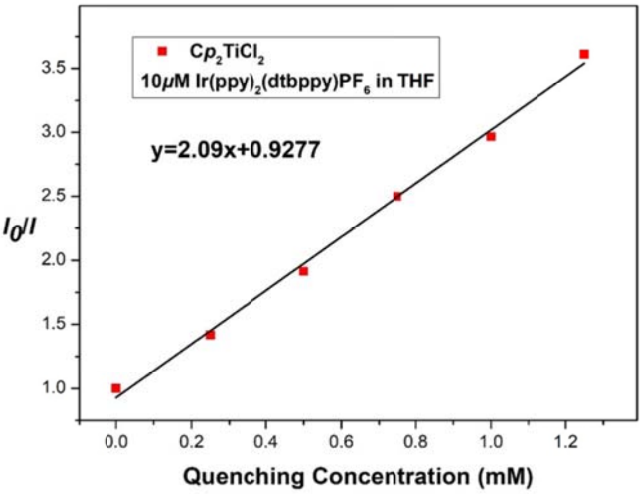


Figure S3 UV-Vis spectra of Cp$_2$TiCl$_2$ (1.0 x10^{-4} M) and Cp$_2$Ti^{III}Cl (reduction by Zn, 1.0 x10^{-4} M)

S3 Luminescence Quenching Experiments

Emission intensities were recorded using Edinburgh FS920 Fluorescence Spectrophotometer for all experiments. All Ir(ppy)$_2$(dtbbpy)PF$_6$ solutions were excited at 468 nm and the emission intensity was collected at 500-800 nm. In a typical experiment, the THF solution of Ir(ppy)$_2$(dtbbpy)PF$_6$ (10 M) was added the appropriate amount of quencher in a screw-top 4.5 cm quartz cuvette. After degassing with nitrogen for 15 min, the emission spectra of the samples were collected. The results showed that Cp$_2$TiCl$_2$ and Hantzsch ester (HE) quenched the photoexcited Ir(III)* effectively, while the epoxides didn't quench.

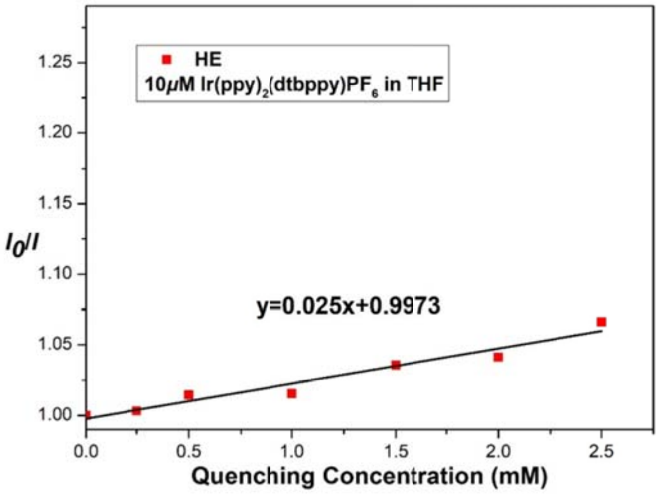


Kq 0 = 2.09L•mol^{-1}

0 = 557ns

Kq = 3.8x10^9 L•mol^{-1}•S^{-1}

Figure S4 [Ir(dtbbpy)(ppy)$_2$]PF$_6$ Emission Quenching by Cp$_2$TiCl$_2$.



Kq 0 = 0.025L•mol^{-1}

0 = 557ns

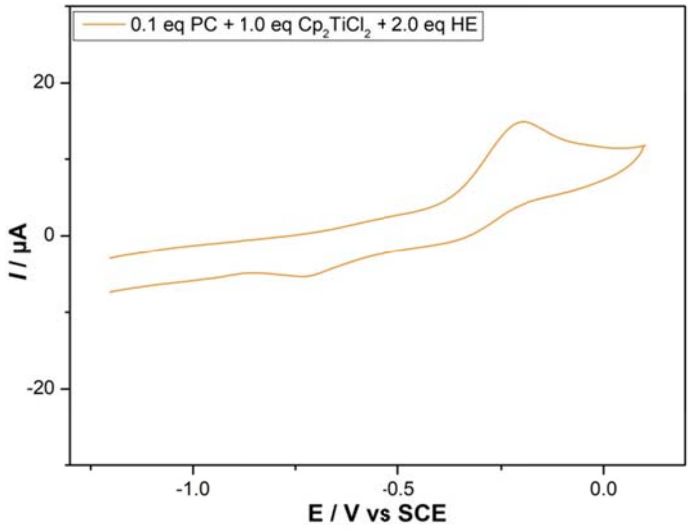
Kq = 4.5x10^7 L•mol^{-1}• S^{-1}

Figure S5 [Ir(dtbbpy)(ppy)$_2$]PF$_6$ Emission Quenching by HE.

S4 Cyclic Voltammetry Experiments

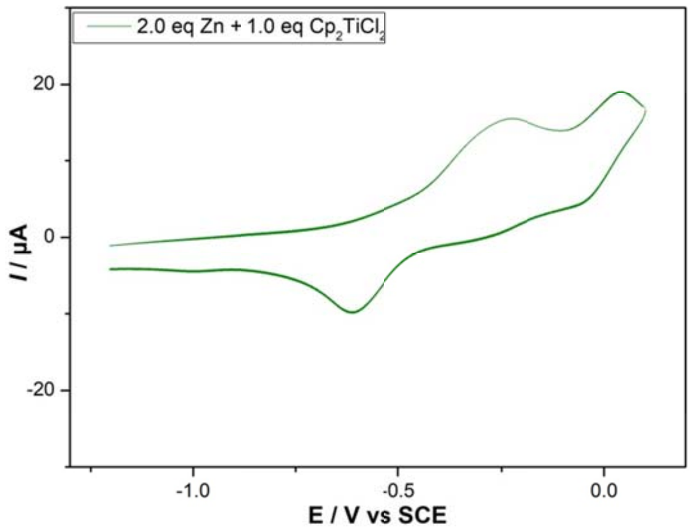
The working electrode was a glassy carbon disk of diameter 1 mm. The electrode surface was polished using 0.25 µm diamond paste, followed by cleaning in an ethanol bath. The counter electrode consisted of a platinum coil melted into glass, while a SCE (saturated calomel electrode) served as the reference electrode. All potentials were reported against the SCE. All handling of chemicals was performed on a vacuum line, and at no point during the different operations was the interference of oxygen allowed. The ohmic drop was compensated with a positive feedback system incorporated in the potentiostat. The kinetic traces were recorded by means of a fiber-optic spectrometer, model S1000 (dip-probe), from Ocean Optics, using a light path length of 1 cm.

Procedure A: In the glove box, mixture of 10 mg titanocene, 20mg HE and 5mg PC **1a** was dissolved in 20 ml of fresh distilled THF. After irradiation with 23w CFL for 1h, 15ml THF and 1.16g Bu_4NPF_6 were transferred to an electrochemical cell. Cyclic voltammetry experiments were performed at 0.1V/S.



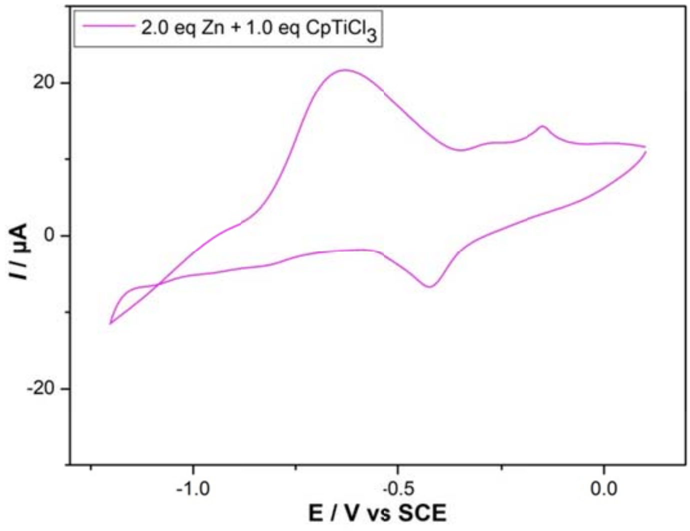
Cyclic voltammetry of 2 mM Cp_2TiCl_2/[Ir(dtbbpy)(ppy)$_2$]PF_6/HE

Procedure B: In the glove box, mixture of 10 mg titanocene and 10mg Zn was dissolved in 20ml of fresh distilled THF. The mixture was sired for 30 min. 15ml THF and 1.16g Bu_4NPF_6 were transferred to an electrochemical cell. Cyclic voltammetry experiments were performed at 0.1V/S.



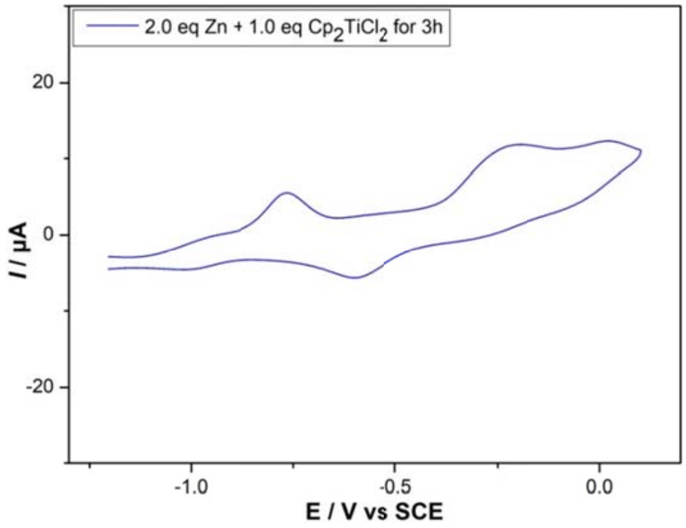
Cyclic voltammetry of 2 mM Cp_2TiCl_2/Zn

Procedure C: In the glove box, mixture of 8.6 mg $CpTiCl_3$ and 8.6mg Zn was dissolved in 20ml of fresh distilled THF. The mixture was sired for 30 min. 15ml THF and 1.16g Bu_4NPF_6 were transferred to an electrochemical cell. Cyclic voltammetry experiments were performed at 0.1V/S.



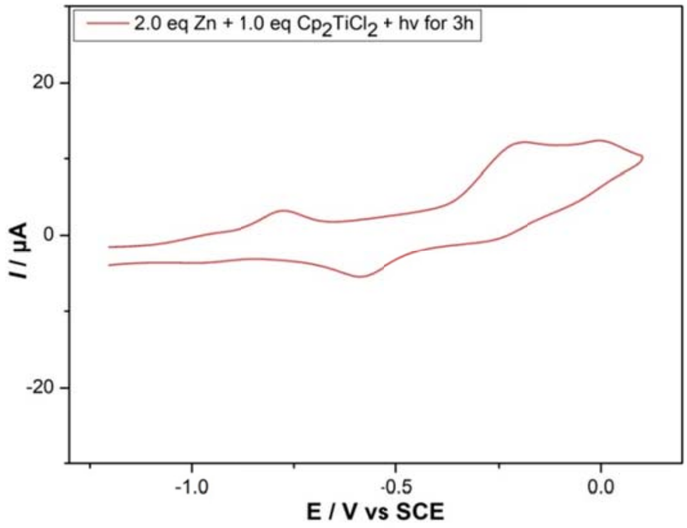
Cyclic voltammetry of 2 mM $CpTiCl_3$/Zn

Procedure D: In the glove box, mixture of 10 mg titanocene and 10mg Zn was dissolved in 20ml of fresh distilled THF. The mixture was sired for 30 min and shielded from light for further 3 h. 15ml THF and 1.16g Bu_4NPF_6 were transferred to an electrochemical cell. Cyclic voltammetry experiments were performed at 0.1V/S.



Cyclic voltammetry of 2 mM Cp_2TiCl_2/Zn shielded from light for 3 hours

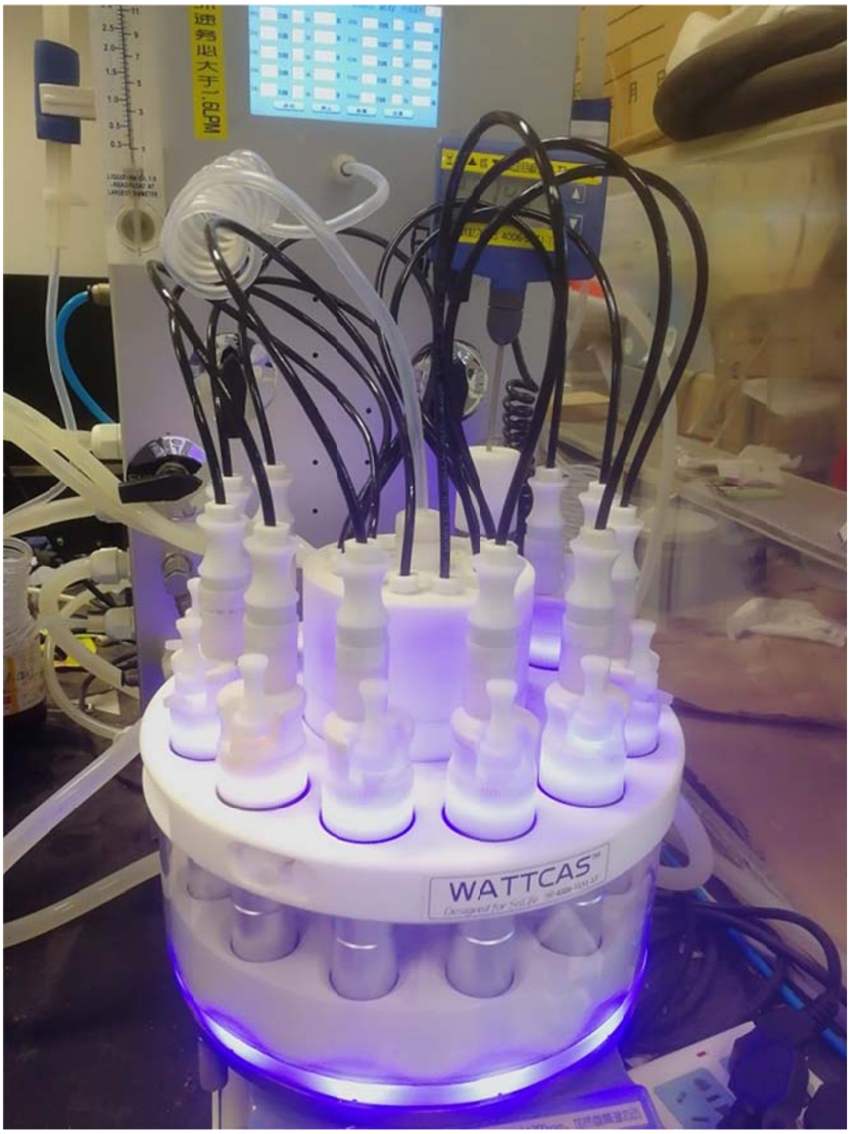
Procedure E: In the glove box, mixture of 10 mg titanocene and 10mg Zn was dissolved in 20ml of fresh distilled THF. The mixture was sired for 30 min then irradiated with 23 w CFL for further 3 h. 15ml THF and 1.16g Bu_4NPF_6 were transferred to an electrochemical cell. Cyclic voltammetry experiments were performed at 0.1V/S.



Cyclic voltammetry of 2 mM Cp_2TiCl_2/Zn irradiation with 23w CFL for 3 hours

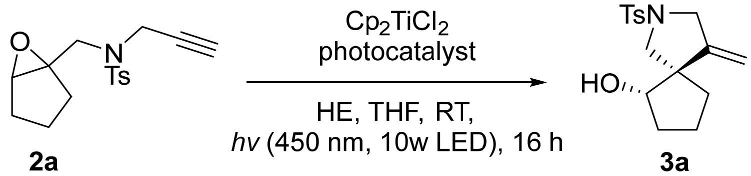
S5 Picture of Reaction Set-Up

The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020L) with 10 W 450-nm LED.



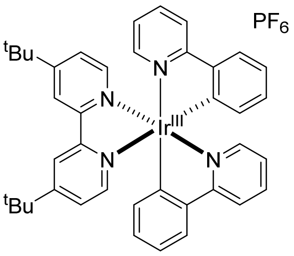
S6 Reaction Optimizations

General procedure for experiment of opening/spirocyclization of epoxides reaction.

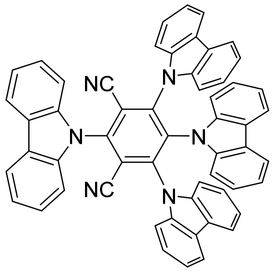


2a **3a**

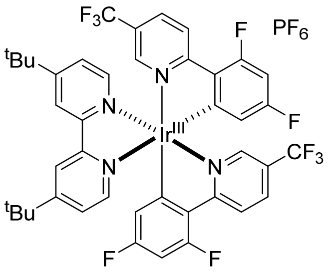
2a, Cp_2TiCl_2, photocatalyst and Hantzsch ester were added to solvent in tube under nitrogen. The reaction mixture was stirred and irradiated using 10 W 450nm blue LED lamps for 16 hours. After the reaction finished, the mixture was concentrated in vacuo and the residue was analyzed by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard.



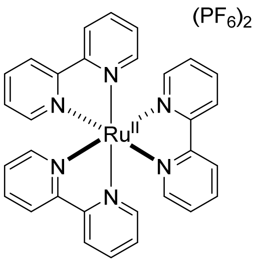
$Ir(ppy)_2(dtbbpy)PF_6$ **1a**



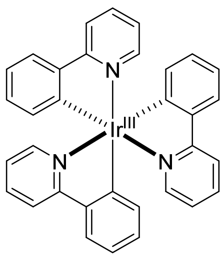
4CzIPN **1b**



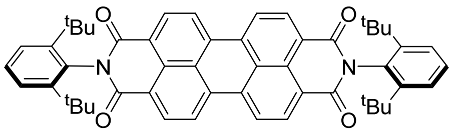
$Ir[dF(CF_3)ppy_2](dtbbpy)PF_6$ **1c**



$Ru(bpy)_3(PF_6)_2$ **1d**

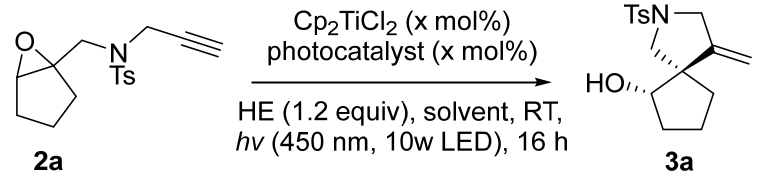


fac-$Ir(ppy)_3$ **1e**



PDI **1f**

Table S1 Screen of conditions

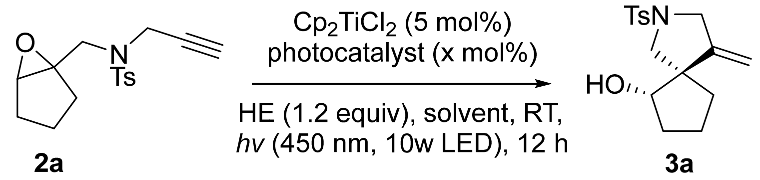


Entry	conditions	yield(%)
		3a
1	Ti 20.0 mol%, **1a** 1.0 mol%, He 1.2 eq, THF	76
2	Ti 10.0 mol%, **1a** 1.0 mol%, He 1.2 eq, THF	94
3	Ti 5.0 mol%, **1a** 1.0 mol%, He 1.2 eq, THF	96
4	Ti 5.0 mol%, **1a** 1.0 mol%, He 1.2 eq, DCE	93
5	Ti 5.0 mol%, **1a** 5.0 mol%, He 1.2 eq, THF	95
6	Ti 2.0 mol%, **1a** 1.0 mol%, He 1.2 eq, THF	94
7	Ti 1.0 mol%, **1a** 1.0 mol%, He 1.2 eq, THF	67
8	no titanocene	0
9	no photocatalyst	0
10	no HE	0
11	no *hv*	0

Table S2 Screen of bases additives

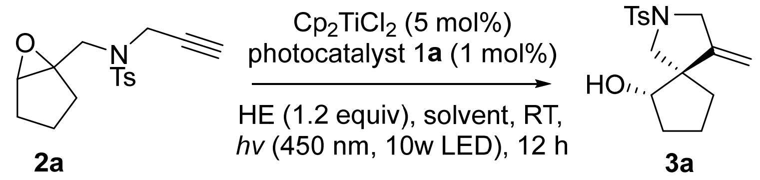
Entry	additives	yield(%)
		3a
1	Na_2CO_3 1 equiv	3
2	Na_2CO_3 0.5 equiv	2
3	$NaHCO_3$ 0.5 equiv	44
4	DMAP 0.5 equiv	24
5	Collidine 0.5 equiv	94
6	Collidine 0.2 equiv	95

Table S3 Screen of photocatalysts



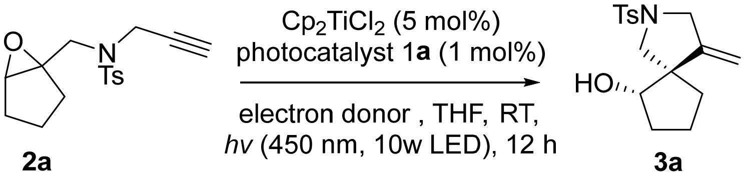
Entry	conditions	yield(%)
		3a
1	**1a** 1 mol%	95
2	**1b** 1 mol%	94
3	**1c** 1 mol%	94
4	**1d** 1 mol%	24
5	**1e** 1 mol%	45
6	**1f** 1 mol%	0

Table S4 Screen of solvents



Entry	conditions	yield(%)
		3a
1	DMF	16
2	DCE	93
3	DMSO	trace
4	CH_3OH	trace
5	CH_3CN	23
6	1,4-dioxane	9

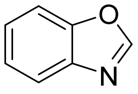
Table S5 Screen of electron donors



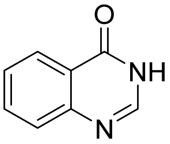
Entry	conditions	yield(%)
		3a
1	Trimethylamine 1.2 equiv	trace
2	Triethanolamine 1.2 equiv	trace
3	ascorbic acid 1.2 equiv	5
4	HE 1.2 equiv	95
5	Et_3N 1.2 equiv	9

S7 Additive Effect

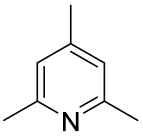
Additive Effect on the Ti-catalyzed cyclization



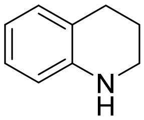
S6a
A:96% B:81%



S6b
A:95% B:92%

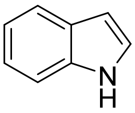


S6c
A:94% B:95%

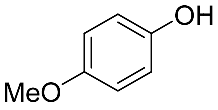


S6d
A:84% B:86%

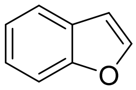
S6e
A:96% B:95%



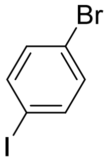
S6f
A:78% B:81%



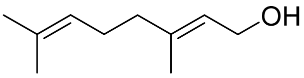
S6g
A:92% B:95%



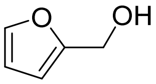
S6h
A:92% B:83%



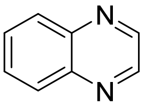
S6i
A:88% B:89%



S6j
A:95% B:94%



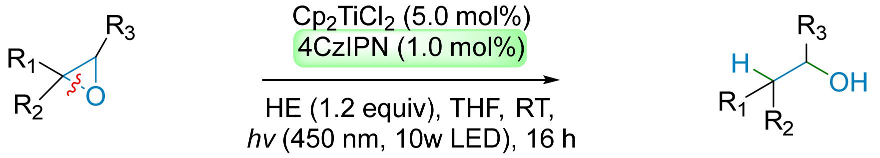
S6k
A:95% B:67%



S6l
A:23% B:49%

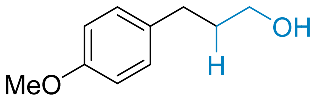
[a] In all cases **2l** was used as substrate and the yield of **3l** were determined with 1H NMR. [b] Values in parentheses are recovery yields of the additives determined with 1H NMR.

S8 Hydrogen transfer reaction

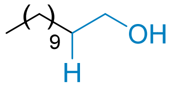


Cp_2TiCl_2 (5.0 mol%)
4CzIPN (1.0 mol%)
HE (1.2 equiv), THF, RT,
hv (450 nm, 10w LED), 16 h
4-methoxybenzenethiol (10 mol%)

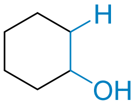
S7 **S8**



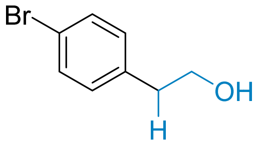
S8a: 86% yield



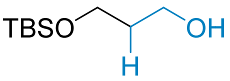
S8b: 88% yield



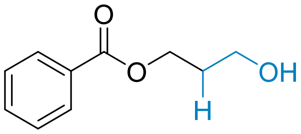
S8c:83% yield



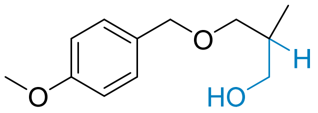
S8d: 76% yield



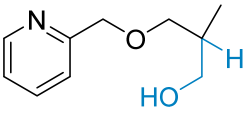
S8e: 81% yield



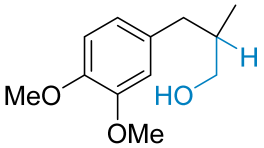
S8f: 79% yield



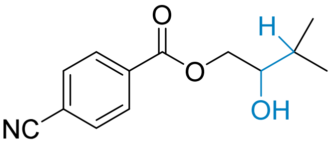
S8g: 93% yield



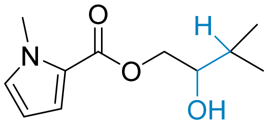
S8h: 90% yield



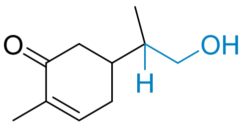
S8i: 89% yield



S8j: 78% yield



S8k: 86% yield



S8l: 92% yield

[a] Reaction conditions: **7** (100 mg, 0.1 M in THF). [b] Isolated yield.

S9 Photo-stability tests of $Cp_2Ti^{III}Cl$ and Cp_2TiCl_2

The $Cp_2Ti^{III}Cl$ species exhibits special stability under photo conditions and this can be demonstrated in the parallel experiments showed in figure below. Two newly prepared $Cp_2Ti^{III}Cl$ solutions, one shielded from light and the other irradiated with 23w CFL for 5 hours, were then used to catalyze cyclization of epoxide **2l** to afford **3l** in 78% and 71% yield respectively (a and b). On the contrary, a Cp_2TiCl_2 solution was irradiated for 5 hours before being treated with Zn (c). The $Cp_2Ti^{III}Cl$ obtained by this way showed lower catalytic activity and produced **3l** in 19% yield only.

$$\textbf{2l} \longrightarrow \textbf{3l}$$

$$\text{a) } Cp_2TiCl_2 \xrightarrow{\text{Zn}} Cp_2Ti^{III}Cl \xrightarrow{\text{no irradiation}} \text{Cat-a} \qquad \text{78\% yield}$$

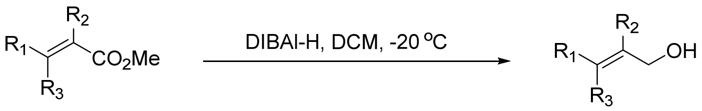
$$\text{b) } Cp_2TiCl_2 \xrightarrow{\text{Zn}} Cp_2Ti^{III}Cl \xrightarrow{\text{irradiation for 5h}} \text{Cat-b} \qquad \text{71\% yield}$$

$$\text{c) } Cp_2TiCl_2 \xrightarrow{\text{irradiation for 5h}} \text{then} \xrightarrow{\text{Zn}} \text{Cat-c} \qquad \text{19\% yield}$$

Photo-stability tests of $Cp_2Ti^{III}Cl$ and Cp_2TiCl_2. [a] Conditions: 23 w CFL, Cp_2TiCl_2 (0.36 mmol, 0.1 M in THF), Zn (0.72 mmol, 2 eq), **2l** (0.36 mmol, 1 eq). [b] The yield of **3l** was determined with 1H NMR. [c] Cyclic voltammetry experiments are found in **SI, S4 Cyclic Voltammetry Experiments**

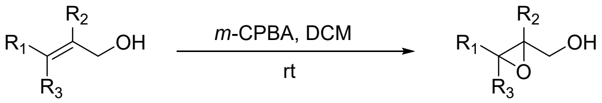
S10 Substrates Preparation

Procedure A



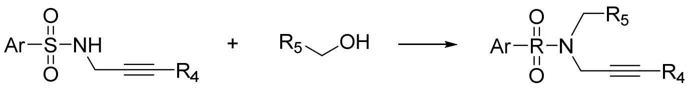
The ester (2.0 g, 8.3 mmol) was dissolved in DCM (50 mL).The mixture was cooled to -20 °C and slowly added DIBAL-H solution (14mL, 1.5M hexane solution). The mixture was stirred at -20 ° C for 30 min. Then at -20 ° C, the reaction was quenched by dropwise addition of 5 ml of methanol over 30 minutes. The reaction solution was allowed to rise to room temperature. Add 50 ml of sodium potassium tartrate solution, extracted with DCM, washed with brine, dried over anhydrous sodium sulfate. The crude residue was purified by flash column chromatography to afford the product.

Procedure B



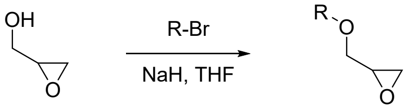
A solution of alkene (1 mmol, 1.0eq) in DCM (5 ml) in a round bottom flask was cooled to 0 ℃ with an ice bath. Then an m-chloroperbenzoic acid (<85 % purity, 2.0 eq) was added portion wise over 10 minutes. The mixture was allowed to warm to ambient temperature and then stirred until TLC indicated the complete consumption of the starting material (approximately 3 h). After completion, saturated aq. Na_2CO_3 was slowly added and the mixture was stirred vigorously until gas evolution had ceased. The organic layer was separated and washed with 1M aq. sodium sulfite, once with brine, and then dried over Na_2SO_4. The filtrate was concentrated in vacuo and the crude product was purified by column chromatography on silica gel to afford the product.

Procedure C

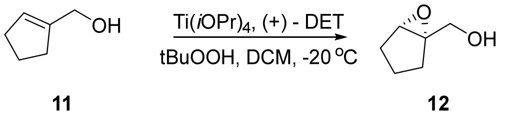


the corresponding sulfonamide and triphenylphosphine were dissolved in THF and cooled to 0 ℃. DIAD and alcohol were added sequentially. The mixture was warmed to room temperature and stirred until TLC indicated the complete consumption of the starting material. The organic layer was separated and washed with 1M aq. sodium sulfite, once with brine, and then dried over Na_2SO_4. The filtrate was concentrated in vacuo and the crude product was purified by column chromatography on silica gel to afford the product.

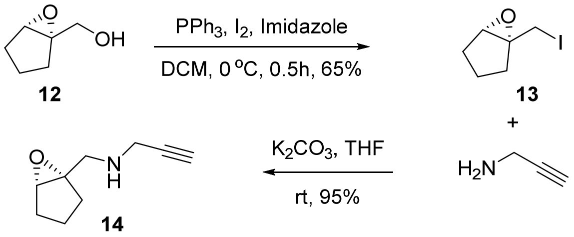
Procedure D



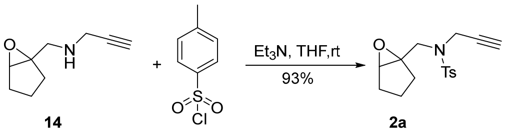
To a solution of the epoxide (1 mmol, 1.0eq) in dry THF was slowly added NaH (1.2eq) at 0 ℃. The mixture was stirred at 0 ℃ for 30min. Then the alkyl bromide (1.2eq) was added and the mixture was stirred at room temperature overnight. The reaction was quenched with the saturated solution of NH_4Cl then extracted with 50 mL of EtOAc. The filtrate was concentrated in vacuo and the crude product was purified by column chromatography on silica gel to afford the product.



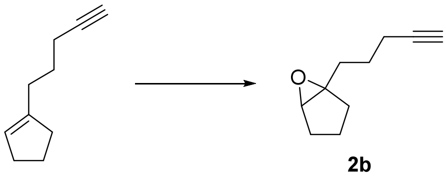
An ovendried 100 mL three-necked round-bottomed flask equipped with a magnetic stirbar, pressure equalizing addition funnel, thermometer, nitrogen inlet, and bubbler was charged with 150 mg of 4A powdered, activated molecular sieves and 15 mL of dry DCM. The flask was cooled to -20 °C L-(+)-Diethyl tartrate (0.67 g, 3.3 mmol) and Ti(o*i*Pr)$_4$ (0.8 mL, 0.77 g, 2.7 mmol, via syringe) were added sequentially with stirring. The reaction mixture was stirred at -20 °C as TBHP (2.2 mL, 10.8 mmol, 5 M in decane) was added through the addition funnel at a moderate rate (over ca. 5 min). The resulting mixture was stirred at -20 °C for 30 min.1 (0.53 g, 5.4 mmol,), dissolved in 10 mL of DCM, was then added dropwise through the same addition funnel over a period of 20 min, being careful to maintain the reaction temperature between -20 and -15 °C. The mixture was stirred for an additional 3.5 h at -20 to -15 °C. Workup was then performed, the crude product was purified by column chromatography on silica gel to afford the product epoxide alcohol and all data were in accordance with those previously reported: J. Am. Chem. Soc. 1987, 109, 5765.



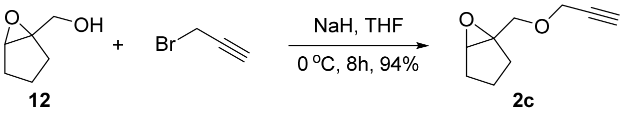
To a solution of **12** (1.7 g, 14.5 mmol, 1.0 equiv) in DCM (20 mL) at 0 ℃ was added imidazole (2.0 g, 29.1 mmol, 2.0 eq.), PPh_3 (4.9 g, 18.9 mmol, 1.3 eq.) and iodine (4.4g, 17.4 mmol, 1.2 eq.). The mixture was vigorously stirred at rt for 30 min. After this time the solvent was evaporated under reduced pressure and the crude residue was purified by flash column chromatography to obtain **13** as pale yellow oil. **13** (1.3g, 5.8mmol, 1 eq.) solution of 30ml dry THF was added dropwise to vigorously stirred 2-Propynylamine (1 ml, 17.3mmol, 3 eq.) and K_2CO_3 (1.6g, 11.5mmol, 2 eq.) in dry 10 mL THF at 0°C. The mixture was then allowed to warm to room temperature for 8 hours. The organic layer was then extracted from EA (50mL x 3), The organic phases were then combined and dried followed by removal of the solvent in vacuo to afford the crude product as a yellow oil **14**.



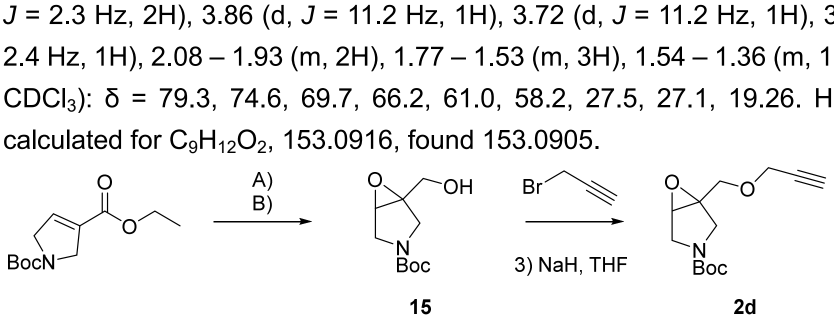
To a solution of **14** (0.2 g, 1.3 mmol, 1.0 equiv) in THF (20 mL) at 0 ℃ was added Tosyl chloride (0.5 g, 2.6 mmol, 2.0 eq.) and Et_3N (0.4mL, 2.6 mmol, 2.0 eq.). The mixture was vigorously stirred at rt for 8 hours. After this time the solvent was evaporated under reduced pressure and the crude residue was purified by flash column chromatography to obtain **2a** as colorless oil (0.34g, 1.1 mmol, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.27 (m, 2H), 4.23 (t, *J* = 2.6 Hz, 2H), 3.63 (d, *J* = 14.6 Hz, 1H), 3.48 (d, *J* = 14.6 Hz, 1H), 3.39 (s, 1H), 2.43 (s, 3H), 2.04 – 1.92 (m, 3H), 1.80 – 1.59 (m, 3H), 1.48 – 1.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6 , 135.8 , 129.4 , 127.6 , 73.9 , 66.2 , 61.2 , 47.5 , 37.6 , 27.8 , 27.1 , 21.5 , 19.3 . HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{19}NO_3S$, 306.1164, found 306.1160



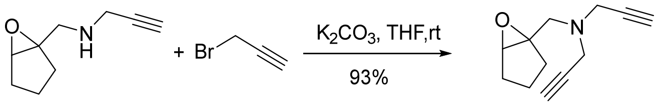
Following the general procedure B, **2b** was obtained as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.86 (t, J = 6.2 Hz, 1H), 2.38 (q, J = 7.8 Hz, 2H), 2.01 (d, J = 2.9 Hz, 1H), 1.78 (ddt, J = 27.2, 13.4, 7.1 Hz, 4H), 1.55 (td, J = 14.9, 12.7, 5.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 83.3, 68.8, 63.3, 63.0, 35.5, 29.3, 27.2, 25.6, 24.8, 24.7, 15.8. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{10}H_{14}O$, 151.1123, found 151.1125.



To a solution of **12** (0.6 g, 5.1 mmol, 1.0 equiv) in THF (20 mL) was added 3-bromopropyne (1.8 g, 15.3 mmol, 3.0 eq.) and sodium hydride (0.4g, 10.2 mmol, 2.0 eq.) at 0 ℃. The mixture was vigorously stirred at rt for 8 hours. After this time the solvent was evaporated under reduced pressure and the crude residue was purified by flash column chromatography to obtain **2c** as colorless oil (0.73g, 4.8 mmol, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 4.20 (t, *J* = 2.3 Hz, 2H), 3.86 (d, *J* = 11.2 Hz, 1H), 3.72 (d, *J* = 11.2 Hz, 1H), 3.39 (s, 1H), 2.43 (t, *J* = 2.4 Hz, 1H), 2.08 – 1.93 (m, 2H), 1.77 – 1.53 (m, 3H), 1.54 – 1.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.3, 74.6, 69.7, 66.2, 61.0, 58.2, 27.5, 27.1, 19.26. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_9H_{12}O_2$, 153.0916, found 153.0905.

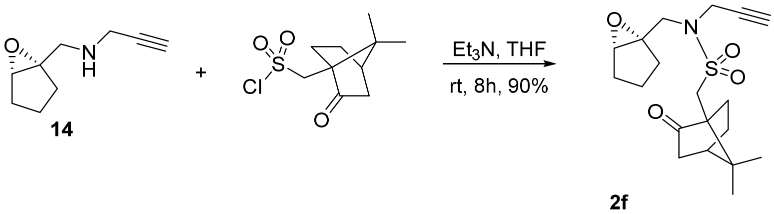


Following the general procedure A and B, **15** was obtained as oil. Then To a solution of epoxide **15** (1.1 g, 5.1 mmol, 1.0 equiv) in THF (20 mL) at 0 ^{o}C was added 3-Bromopropyne (1.8 g, 15.3 mmol, 3.0 eq.) and sodium hydride (0.4g, 10.2 mmol, 2.0 eq.) at 0 ℃. The mixture was vigorously stirred at rt for 8 hours. After this time the solvent was evaporated under reduced pressure and the crude residue was purified by flash column chromatography to obtain **2d** as colorless oil (1.17g, 4.6 mmol, 55% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.16 (dt, *J* = 4.6, 2.3 Hz, 2H), 3.87 (ddd, *J* = 11.4, 5.7, 2.1 Hz, 1H), 3.75 – 3.63 (m, 3H), 3.55 (t, *J* = 1.7 Hz, 1H), 3.32 (ddt, *J* = 19.8, 13.0, 2.0 Hz, 2H), 2.47 – 2.42 (m, 1H), 1.37 (d, *J* = 2.6 Hz, 9H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 154.5, 154.4, 79.7, 79.6, 78.8, 78.7, 75.2, 75.1, 67.9, 67.4, 64.9, 64.5, 58.8, 58.4, 58.4, 58.3, 47.8, 47.3, 47.3, 46.8, 28.2. HRMS-ESI (m/z) [M+Na]$^+$ calculated for $C_{13}H_{19}NO_4$, 276.1212, found 276.1215.



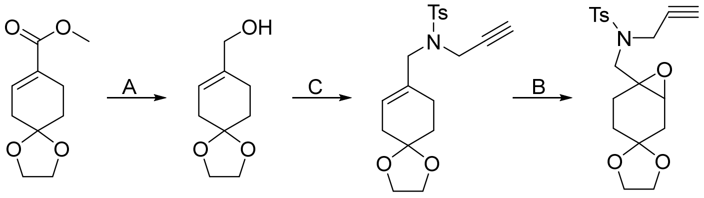
14 **2e**

To a solution of **14** (0.2 g, 1.3 mmol, 1.0 equiv) in THF (20 mL) at 0 ℃ was added 3-bromopropyne (0.4 g, 3.9 mmol, 3.0 eq.) and K_2CO_3 (0.36g, 2.6 mmol, 2.0 eq.). The mixture was vigorously stirred at rt for 8 hours. After this time the solvent was evaporated under reduced pressure and the crude residue was purified by flash column chromatography to obtain **2e** as colorless oil (0.23g, 1.1 mmol, 93% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.44 (d, *J* = 2.6 Hz, 4H), 3.25 (s, 1H), 2.90 (d, *J* = 13.3 Hz, 1H), 2.72 (d, *J* = 13.3 Hz, 1H), 2.20 (t, *J* = 2.5 Hz, 2H), 1.93 (ddd, *J* = 13.8, 8.2, 3.5 Hz, 2H), 1.72 – 1.49 (m, 3H), 1.43 – 1.30 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 78.6, 73.1, 66.1, 60.91, 54.4, 42.6, 28.2, 27.2, 19.2. HRMS-ESI (m/z) [M+H]$^+$ calculated for $C_{12}H_{15}NO$, 190.1232, found 190.1225.



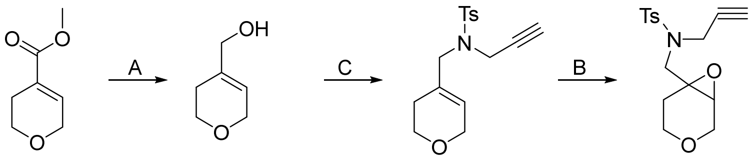
14 **2f**

To a solution of **14** (0.2 g, 1.3 mmol, 1.0 equiv) in THF (20 mL) at 0 ℃ was added D(+)-10-Camphorsulfonyl chloride (0.65 g, 2.6 mmol, 2.0 eq.) and Et_3N (0.4mL, 2.6 mmol, 2.0 eq.). The mixture was vigorously stirred at rt for 8 hours. After this time the solvent was evaporated under reduced pressure and the crude residue was purified by flash column chromatography to obtain **2f** as colorless oil (0.43g, 1.1 mmol, 90% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.24 (qdd, *J* = 18.6, 2.4, 0.9 Hz, 2H), 3.91 (dd, *J* = 14.7, 1.1 Hz, 1H), 3.51 – 3.30 (m, 2H), 3.00 (d, *J* = 14.6 Hz, 1H), 2.55 – 2.43 (m, 1H), 2.43 – 2.30 (m, 2H), 2.08 (dt, *J* = 17.0, 4.1 Hz, 2H), 2.03 – 1.90 (m, 3H), 1.79 – 1.55 (m, 5H), 1.43 (tdd, *J* = 9.4, 4.6, 2.7 Hz, 2H), 1.13 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 214.8, 77.8, 74.3, 66.6, 60.8, 58.4 , 48.1, 47.9, 47.8, 42.8, 42.6, 37.4, 27.9, 27.3, 26.9, 25.4, 20.0, 19.8, 19.4. RMS-ESI (m/z) [M+H]$^+$ calculated for $C_{19}H_{27}NO_4S$, 366.1739, found 366.1736.



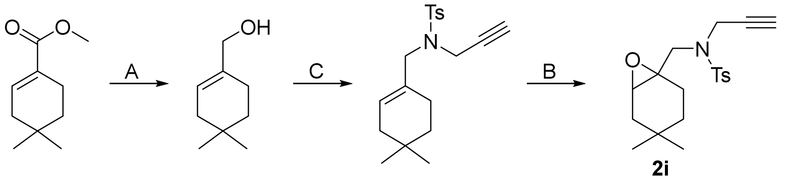
2g

Following the general procedure A, C and B, **2g** was obtained as colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.66 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.20 (dd, *J* = 31.8, 2.3 Hz, 2H), 3.96 – 3.78 (m, 4H), 3.33 (d, *J* = 14.0 Hz, 1H), 3.21 (d, *J* = 14.0 Hz, 1H), 3.08 – 3.02 (m, 1H), 2.36 (s, 3H), 2.13 – 2.00 (m, 2H), 1.94 (t, *J* = 2.4 Hz, 1H), 1.64 – 1.50 (m, 1H), 1.51 – 1.38 (m, 1H), 1.21 (t, *J* = 5.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.5, 135.5, 129.3, 127.6, 106.5, 76.0, 74.1, 64.3, 63.9, 57.8, 55.6, 50.0, 36.9, 34.4, 27.4, 23.1, 21.3. HRMS-ESI calculated for $C_{19}H_{23}NO_5S$ [M+H]$^+$ 378.1375, found 378.1377.



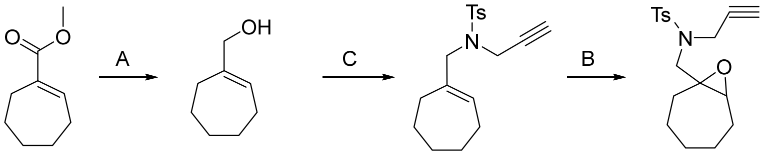
2h

Following the general procedure A, C and B, **2h** was obtained as colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 4.32 – 4.13 (m, 2H), 4.05 – 3.88 (m, 2H), 3.56 – 3.45 (m, 2H), 3.45 (d, *J* = 8.5 Hz, 1H), 3.32 (d, *J* = 14.4 Hz, 1H), 3.17 (d, *J* = 2.7 Hz, 1H), 2.42 (s, 3H), 2.14 – 2.03 (m,1H), 2.01 – 1.92 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.8, 135.6, 129.5, 127.7, 76.3, 74.1, 64.7, 61.5, 56.7, 54.5, 50.7, 37.8, 26.1, 21.5. HRMS (ESI$^+$) calculated for $C_{16}H_{19}NO_4S$ [M+H]$^+$ 322.1113, found 332.1107.



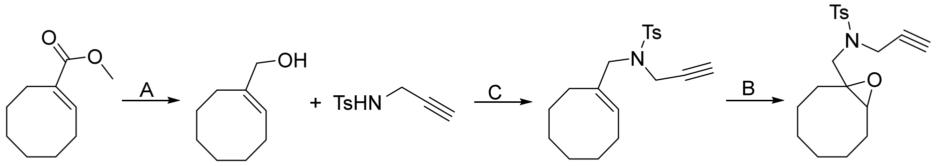
2i

Following the general procedure A, C and B, **2i** was obtained as colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.71 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 4.22 (d, *J* = 3.2 Hz, 2H), 3.43 (d, *J* = 14.5 Hz, 1H), 3.22 (d, *J* = 14.3 Hz, 1H), 3.05 (d, *J* = 4.9 Hz, 1H), 2.41 (s, 3H), 1.98 – 1.87 (m, 3H), 1.69 – 1.53 (m, 2H), 1.37 – 1.23 (m, 1H), 1.15 – 1.04 (m, 1H), 0.87 (d, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.6, 135.8, 129.4, 127.7, 76.4, 73.9, 58.2, 55.5, 51.3, 37.7, 31.7, 30.9, 27.8, 26.7, 22.5, 21.5. HRMS (ESI$^+$) calculated for $C_{19}H_{25}NO_3S$ [M+H]$^+$ 348.1633, found 348.1629.



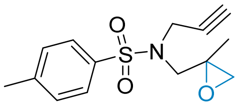
2j

Following the general procedure A, C and B, **2j** was obtained as colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.21 (d, *J* = 1.9 Hz, 2H), 3.45 (d, *J* = 14.4 Hz, 1H), 3.14 (d, *J* = 14.4 Hz, 1H), 3.02 (dd, *J* = 6.7, 3.3 Hz, 1H), 2.41 (s, 3H), 2.02 – 1.91 (m, 3H), 1.90 – 1.80 (m, 2H), 1.64 (d, *J* = 3.7 Hz, 1H), 1.59 – 1.43 (m, 5H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.5, 135.8, 129.3, 127.5, 76.4, 73.7, 61.9, 59.3, 51.2, 37.6, 30.9, 29.7, 28.5, 24.3, 24.06, 21.39. HRMS (ESI$^+$) calculated for $C_{18}H_{23}NO_3S$ [M+H]$^+$ 334.1477, found 334.1472.



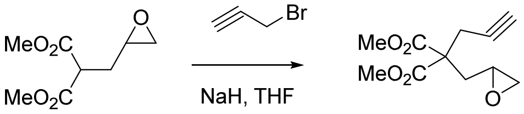
2k

Following the general procedure A, C and B, **2k** was obtained as colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.71 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 6.2 Hz, 1H), 4.32 (d, *J* = 18.4 Hz, 1H), 4.16 (d, *J* = 18.5 Hz, 1H), 3.82 (d, *J* = 14.5 Hz, 1H), 2.90 (d, *J* = 14.5 Hz, 1H), 2.80 (dd, *J* = 10.2, 4.3 Hz, 1H), 2.40 (s, 2H), 2.26 – 2.07 (m, 1H), 1.92 (t, *J* = 2.4 Hz, 0H), 1.69 – 1.19 (m, 5H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.5, 135.8, 129.3, 127.7, 76.5, 73.6, 61.3, 58.6, 48.8, 37.7, 27.0, 26.9, 26.5, 25.9, 25.3, 24.9, 21.4. HRMS (ESI$^+$) calculated for $C_{19}H_{25}NO_3S$ [M+H]$^+$ 348.1633, found 348.1633.



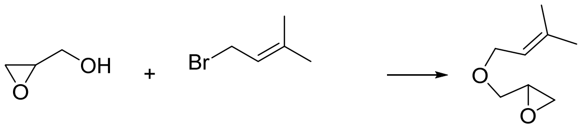
2l

The compound **2l** was prepared and all data were in accordance with those previously reported: *J. Am. Chem. Soc.* **2011**, 133, 417. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.69 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.29 – 4.11 (m, 2H), 3.37 (d, *J* = 14.3 Hz, 1H), 3.23 (d, *J* = 14.4 Hz, 1H), 2.73 (d, *J* = 4.6 Hz, 1H), 2.60 (d, *J* = 4.7 Hz, 1H), 2.38 (s, 3H), 1.96 (s, 1H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.6, 135.6, 129.3, 127.5, 76.2, 73.9, 55.4, 51.3, 50.7, 37.5, 21.4, 18.6.



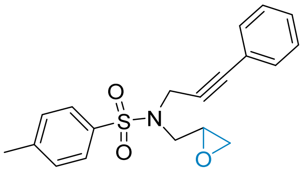
2m

The compound **2m** was prepared and all data were in accordance with those previously reported: *J. Am. Chem Soc*, **2010**, 132, 12748. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 3.77 (s, ,3H), 3.76 (s, 3H), 3.00 – 2.97 (m, 1H), 2.95 (d, *J* = 2.7 Hz, 2H), 2.78 – 2.73 (m, 1H), 2.49 (dd, *J* = 5.1, 2.6 Hz, 1H), 2.44 (dd, *J* = 14.6, 4.5 Hz, 1H), 2.10 (dd, *J* = 14.6, 7.4 Hz, 1H), 2.04 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 170.0, 169.9, 78.3, 71.7, 55.5, 52.8, 52.8, 48.0, 46.4, 35.7, 23.5.



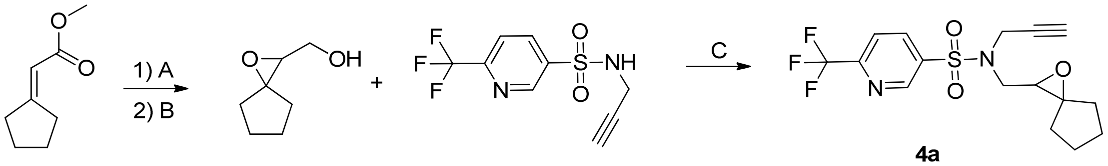
2n

Similar to general procedure D, oxiran was treated with 1-bromo-3-methylbut-2-ene and NaH in dry THF at 0 ℃ then warmed to room temperature overnight. The crude product was purified by SiO$_2$ chromatography to give **2n** as a colorless oil. All data were in accordance with those previously reported: *Org. Lett.* **2018**, 20, 2253. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 5.35 – 5.25 (m, 1H), 4.10 – 3.93 (m, 2H), 3.64 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.35 (ddd, *J* = 11.4, 5.8, 1.5 Hz, 1H), 3.17 – 3.07 (m, 1H), 2.75 (t, *J* = 4.5 Hz, 1H), 2.56 (dt, *J* = 4.8, 2.0 Hz, 1H), 1.71 (s, 3H), 1.64 (s, 3H). 13C NMR (100 MHz, CDCl$_3$): δ = 137.2, 120.6, 70.5, 67.5, 50.7, 44.2, 25.6, 17.8.



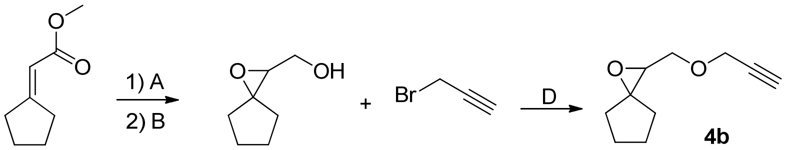
2o

The compound **2o** was prepared and all data were in accordance with those previously reported: *ACS Catal*. **2018**, 8, 8993. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.80 – 7.78 (m, 2H), 7.37 – 7.21 (m, 5H), 7.09 – 7.08 (m, 2H), 4.48 (s, 2H), 3.58 (dd, *J* = 14.6, 4.0 Hz, 1H), 3.38 (dd, *J* = 14.6, 5.5 Hz, 1H), 3.23 (d, *J* = 4.4 Hz, 1H), 2.83 (t, *J* = 4.5 Hz, 1H), 2.74 – 2.65 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 135.8, 131.4, 129.5, 128.4, 128.0, 127.7, 122.0, 85.7, 81.7, 50.5, 48.3, 45.0, 38.8, 21.3.HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{19}H_{20}NO_3S$, 342.1158, found 342.1160.



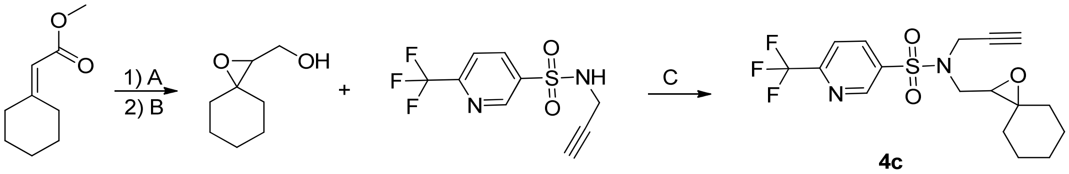
4a

Following the general procedure A, B and C, the reactions afforded **4a** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.14 (d, *J* = 2.2 Hz, 1H), 8.34 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.83 (dd, *J* = 8.2, 0.8 Hz, 1H), 4.62 – 4.02 (m, 2H), 3.69 (ddd, *J* = 14.3, 3.3, 1.1 Hz, 1H), 3.20 (dd, *J* = 7.4, 3.3 Hz, 1H), 3.09 (dd, *J* = 14.3, 7.4 Hz, 1H), 2.05 (t, *J* = 2.5 Hz, 1H), 1.97 – 1.75 (m, 5H), 1.70 – 1.53 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3 (q, $J_{C,F}$ = 35.0 Hz), 148.6, 138.3, 137.1, 122.0 (q, $J_{C,F}$ = 273 Hz), 120.5 (q, $J_{C,F}$ = 3.0 Hz), 75.9, 74.7, 68.4, 58.9, 47.5, 37.6, 33.2, 29.1, 24.9, 24.7. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{18}F_3N_2O_3S$, 375.0990, found 375.0995.



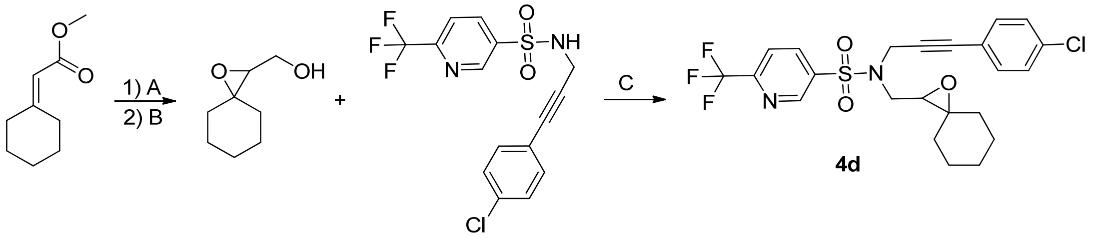
4b

Following the general procedure A, B and D, **4b** was obtained as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ =4.21 (qd, *J* = 15.8, 2.4 Hz, 2H), 3.72 (dd, *J* = 10.9, 4.4 Hz, 1H), 3.52 (dd, *J* = 10.9, 6.3 Hz, 1H), 3.20 (dd, *J* = 6.3, 4.4 Hz, 1H), 2.45 (t, *J* = 2.4 Hz, 1H), 2.01 – 1.75 (m, 4H), 1.70 – 1.56 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =79.3, 74.7, 69.6, 68.3, 59.1, 58.3, 33.4, 29.1, 25.1, 24.8. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{10}H_{14}O_2$, 167.1072, found 167.1061.

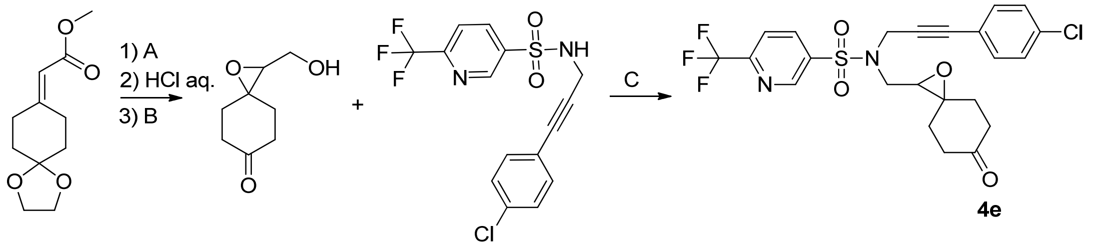


4c

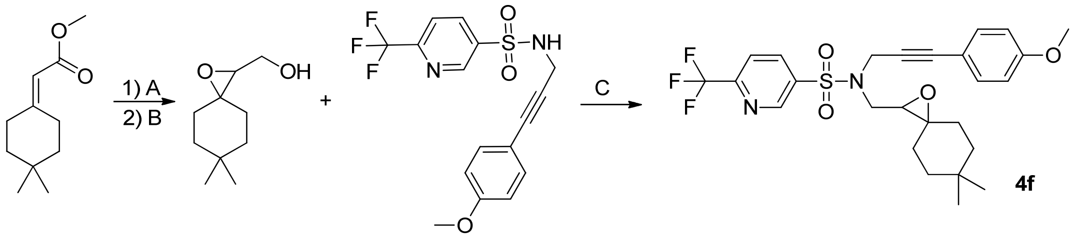
Following the general procedure A, B and C, the reactions afforded **4c** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.14 (d, *J* = 2.2 Hz, 1H), 8.34 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 4.55 – 3.96 (m, 2H), 3.67 (ddd, *J* = 14.5, 3.9, 1.1 Hz, 1H), 3.21 (dd, *J* = 14.5, 7.3 Hz, 1H), 2.95 (dd, *J* = 7.3, 3.9 Hz, 1H), 2.05 (t, 1H), 1.68 (ddd, *J* = 14.1, 10.8, 6.5 Hz, 2H), 1.61 – 1.38 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =151.3 (q, $J_{C,F}$ = 35.0 Hz), 148.6, 138.2, 137.2, 122.1 (q, $J_{C,F}$ = 272 Hz), 120.5 (q, $J_{C,F}$ = 3.0 Hz), 75.8, 74.8, 62.3, 61.6, 45.7, 37.5, 34.9, 29.3, 25.3, 24.6, 24.6. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{20}F_3N_2O_3S$, 389.1147, found 389.1149.



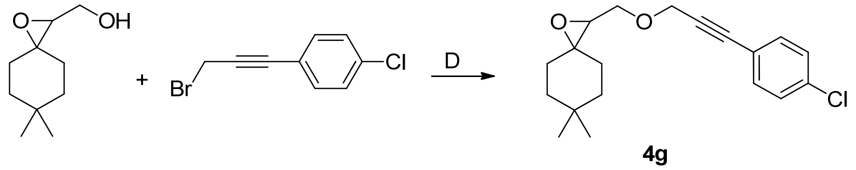
Following the general procedure A, B and C, the reactions afforded **4d** as a white semi-solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.19 (d, *J* = 2.1 Hz, 1H), 8.34 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.11 (m, 2H), 7.06 – 6.90 (m, 2H), 4.69 – 4.41 (m, 2H), 3.72 (dd, *J* = 14.3, 4.0 Hz, 1H), 3.27 (dd, *J* = 14.3, 7.2 Hz, 1H), 3.00 (dd, *J* = 7.2, 4.0 Hz, 1H), 1.78 – 1.42 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2 (q, $J_{C,F}$ = 35.0 Hz), 148.7, 138.3, 137.1, 135.1, 132.5, 128.6, 122.0 (q, $J_{C,F}$ = 273 Hz), 120.5 (q, $J_{C,F}$ = 3.0 Hz), 119.2, 85.6, 81.7, 76.6, 62.4, 61.7, 45.9, 38.4, 34.9, 29.3, 25.3, 24.67, 24.63. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{23}H_{23}ClF_3N_2O_3S$, 499.1070, found 499.1070.



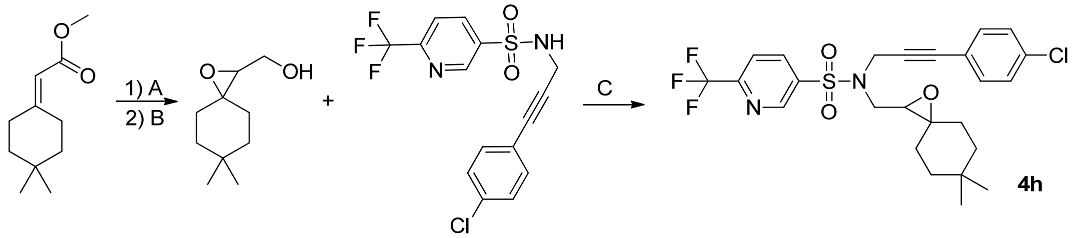
Following the general procedure A, B and C, the reactions afforded **4e** as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.20 (d, *J* = 2.1 Hz, 1H), 8.35 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 4.76 – 4.36 (m, 2H), 3.75 (dd, *J* = 14.3, 3.9 Hz, 1H), 3.56 – 3.20 (m, 2H), 2.78 – 2.55 (m, 2H), 2.46 (dq, *J* = 14.7, 4.9 Hz, 2H), 2.25 – 2.09 (m, 2H), 1.92 – 1.80 (m, 1H), 1.80 – 1.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 208.9, 151.5 (q, $J_{C,F}$ = 35.0 Hz), 148.7, 138.1, 137.1, 135.3, 132.5, 132.5, 128.7, 122.0 (q, $J_{C,F}$ = 273 Hz), 120.6 (q, $J_{C,F}$ = 3.0 Hz), 85.8, 81.4, 61.9, 60.2, 46.2, 38.7, 38.4, 38.3, 33.1, 27.9. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{23}H_{21}ClF_3N_2O_4S$, 513.0863, found 513.0852.



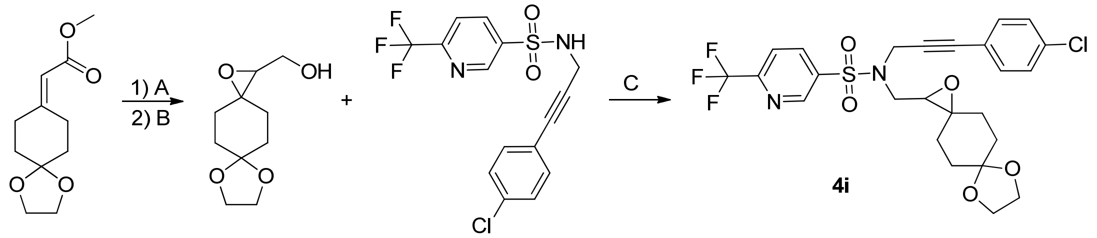
Following the general procedure A, B and C, the reactions afforded **4f** as a white semi-solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.20 (d, *J* = 2.2 Hz, 1H), 8.35 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.08 – 6.86 (m, 2H), 6.82 – 6.64 (m, 2H), 4.70 – 4.38 (m, 2H), 3.78 (s, 3H), 3.69 (dd, *J* = 14.3, 4.3 Hz, 1H), 3.32 (dd, *J* = 14.3, 7.0 Hz, 1H), 3.03 (dd, *J* = 7.0, 4.2 Hz, 1H), 1.78 – 1.59 (m, 3H), 1.56 – 1.31 (m, 5H), 0.96 (d, *J* = 4.6 Hz, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 151.2 (q, $J_{C,F}$ = 35.0 Hz), 148.7, 138.3, 137.2, 132.9, 122.1 (q, $J_{C,F}$ = 273 Hz), 120.5 (q, $J_{C,F}$ = 2.0 Hz), 113.9, 113.1, 86.9, 79.3, 62.3, 61.7, 55.3, 45.9, 38.7, 37.1, 37.0, 30.8, 29.9, 29.2, 26.5, 25.3. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{26}H_{30}F_3N_2O_4S$, 523.1878, found 523.1879.



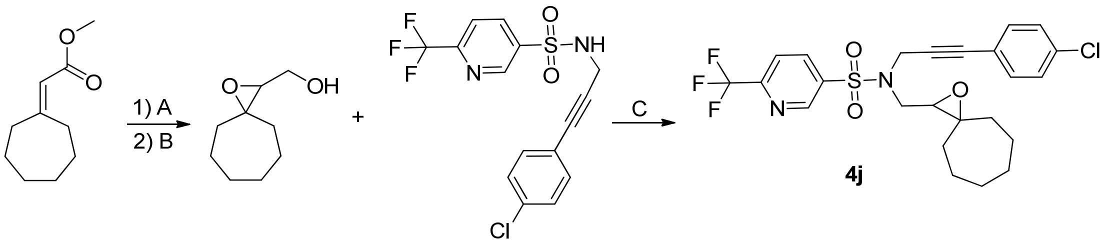
Following the general procedure D, the reaction afforded **4g** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.27 (dd, *J* = 8.7, 2.2 Hz, 2H), 4.41 (qd, *J* = 15.9, 2.3 Hz, 2H), 3.80 (ddd, *J* = 11.0, 4.8, 2.2 Hz, 1H), 3.65 (ddd, *J* = 10.9, 6.1, 2.2 Hz, 1H), 2.99 (td, *J* = 5.9, 4.8, 2.3 Hz, 1H), 1.80 – 1.28 (m, 8H), 0.95 (dd, *J* = 9.3, 2.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4, 132.8, 128.5, 120.9, 85.7, 68.0, 62.1, 61.6, 58.9, 37.1, 37.1, 31.0, 29.8, 28.7, 26.9, 25.2. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{19}H_{24}ClO_2$, 319.1465, found 319.1467.



Following the general procedure A, B and C, the reactions afforded **4h** as a white semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.20 (d, *J* = 2.2 Hz, 1H), 8.35 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.02 – 6.80 (m, 2H), 4.76 – 4.23 (m, 2H), 3.73 (dd, *J* = 14.3, 4.0 Hz, 1H), 3.27 (dd, *J* = 14.3, 7.2 Hz, 1H), 3.02 (dd, *J* = 7.2, 3.9 Hz, 1H), 1.89 – 1.30 (m, 7H), 0.96 (d, *J* = 4.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2 (q, $J_{C,F}$ = 36.0 Hz), 148.7, 138.3, 137.1, 135.1, 132.5, 128.6, 122.0 (q, $J_{C,F}$ = 273 Hz), 120.5 (q, $J_{C,F}$ = 2.0 Hz), 85.6, 81.7, 62.2, 61.5, 46.0, 38.4, 37.0, 36.9, 30.8, 29.8, 29.1, 26.4, 25.2. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{25}H_{27}ClF_3N_2O_3S$, 527.1383, found 527.1379.

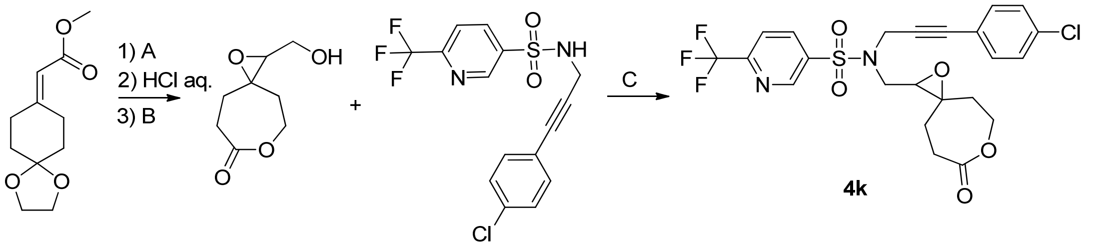


Following the general procedure A, B and C, the reactions afforded **4i** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.20 (d, *J* = 2.3 Hz, 1H), 8.34 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.51 (q, *J* = 18.7 Hz, 2H), 3.96 (d, *J* = 3.3 Hz, 4H), 3.68 (dd, *J* = 14.4, 4.3 Hz, 1H), 3.32 (dd, *J* = 14.4, 6.9 Hz, 1H), 3.10 (dd, *J* = 7.0, 4.3 Hz, 1H), 1.99 – 1.72 (m, 6H), 1.64 – 1.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4 (q, $J_{C,F}$ = 36.0 Hz), 148.7, 138.3, 137.1, 135.2, 132.6, 128.7, 122.0 (q, $J_{C,F}$ = 273 Hz), 120.5 (q, $J_{C,F}$ = 3.0 Hz), 107.9, 85.7, 81.6, 64.4, 64.4, 61.4, 61.1, 46.0, 38.5, 32.6, 32.5, 31.7, 26.2. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{25}H_{25}ClF_3N_2O_5S$, 557.1125, found 557.1125.



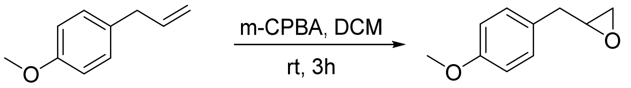
4j

Following the general procedure A, B and C, the reactions afforded **4j** as a white semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.20 (d, *J* = 2.1 Hz, 1H), 8.35 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.16 (m, 2H), 6.99 – 6.91 (m, 2H), 4.76 – 4.38 (m, 2H), 3.75 (dd, *J* = 14.3, 3.6 Hz, 1H), 3.20 (dd, *J* = 14.3, 7.4 Hz, 1H), 3.00 (dd, *J* = 7.4, 3.6 Hz, 1H), 1.87 – 1.43 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4 (q, $J_{C,F}$ = 36.0 Hz), 148.7, 143.0, 138.4, 137.1, 135.1, 132.6, 129.7, 128.6, 122.0 (q, $J_{C,F}$ = 273 Hz), 120.5 (q, $J_{C,F}$ = 3.0 Hz), 85.3, 82.1, 76.0, 51.1, 38.9, 32.3, 28.5, 28.1, 27.0, 26.6. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{24}H_{25}ClF_3N_2O_3S$, 513.1227, found 513.1228.



4k

Following the general procedure A, B and C, the reactions afforded **4k** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.20 (d, *J* = 2.1 Hz, 1H), 8.35 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.08 – 6.70 (m, 2H), 4.66 – 4.38 (m, 3H), 4.29 (ddd, *J* = 13.3, 5.9, 2.0 Hz, 1H), 3.68 (dd, *J* = 14.6, 4.5 Hz, 1H), 3.34 (dd, *J* = 14.5, 6.6 Hz, 1H), 3.21 (dd, *J* = 6.6, 4.5 Hz, 1H), 2.96 (ddd, *J* = 14.5, 12.4, 2.1 Hz, 1H), 2.66 (ddd, *J* = 14.5, 7.7, 1.8 Hz, 1H), 2.34 – 2.11 (m, 2H), 1.78 – 1.67 (m, 1H), 1.60 – 1.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.4, 151.5 (q, $J_{C,F}$ = 35.0 Hz), 148.6, 138.0, 137.1, 137.1, 135.4, 132.7, 132.5, 128.7, 121.9 (q, $J_{C,F}$ = 273 Hz), 120.6 (q, $J_{C,F}$ = 3.0 Hz), 85.9, 81.3, 64.8, 63.3, 63.0, 61.8, 61.8, 45.7, 45.6, 38.7, 38.7, 38.3, 32.7, 32.0, 29.9, 29.8, 26.4. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{23}H_{21}ClF_3N_2O_5S$, 529.0812, found 529.0781.

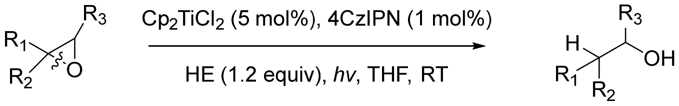


1a

Following the general procedure C, the reaction afforded 1a as colorless oil. All data were in accordance with those previously reported: J. Am. Chem. Soc. 2014, 136, 11145. ^{1}H-NMR (400 MHz, CDCl3): δ = 7.17 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 3.16 – 3.09 (m, 1H), 2.91 – 2.83 (m, 1H), 2.81 – 2.74 (m, 2H), 2.53 (dd, J = 5.0, 2.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3): δ = 158.1, 129.7, 128.9, 113.6, 54.9, 52.3, 46.5, 37.5.

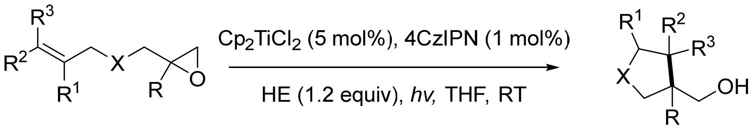
S8 Characterization of Products

Procedure 1: General procedure for reductive opening of epoxides.

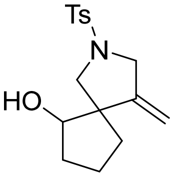


Epoxide (100.0 mg, 1.0 equiv.), Cp_2TiCl_2 (5.0 mol%), 4CzIPN (1.0 mol%), Hantzsch ester (HE, 1.2 equiv.), 4-Methoxybenzenethiol (10 mol%) were added in THF (0.1 M) under nitrogen. The reaction mixture was stirred and irradiated using 10 W 450nm blue LED lamps for 16 hours. After the reaction finished, the mixture was concentrated in vacuo and the residue was purified by flash column chromatography to afford the products.

Procedure 2: General procedure for cyclization reaction.

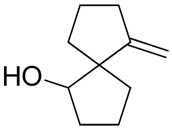


Epoxide (100.0 mg, 1.0 equiv.), Cp_2TiCl_2 (5.0 mol%), 4CzIPN (1.0 mol%) and Hantzsch ester (HE, 1.2 equiv.) were added in THF (0.1 M) under nitrogen. The reaction mixture was stirred and irradiated using 10 W 450nm blue LED lamps for 16 hours. After the reaction finished, the mixture was concentrated in vacuo and the residue was purified by flash column chromatography to afford the products.



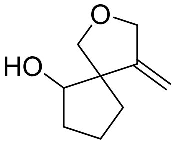
3a

Following the general procedure 2, the reaction of **2a** (100 mg, 0.33 mmol) afforded **3a** as a colorless oil (95 mg, 95% yield, d.r, = 13:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.23 (m, 2H), 4.91 (t, *J* = 2.1 Hz, 1H), 4.83 (t, *J* = 2.4 Hz, 1H), 3.97 – 3.87 (m, 2H), 3.80 (dt, *J* = 13.9, 2.2 Hz, 1H), 3.62 (d, *J* = 9.4 Hz, 1H), 2.92 (d, *J* = 9.4 Hz, 1H), 2.42 (s, 3H), 2.14 (s, 1H), 2.06 – 1.95 (m, 1H), 1.81 – 1.72 (m, 2H), 1.71 – 1.54 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.59 , 143.69 , 132.48 , 129.65 , 127.87 , 105.73 , 77.57 , 57.37 , 53.25 , 52.61 , 33.93 , 32.36 , 21.52 , 20.42 . HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{21}NO_3S$, 308.1320, found 308.1312.



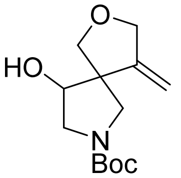
3b

Following the general procedure 2, the reaction of **2a** (100 mg, 0.66 mmol) afforded **3a** as a colorless oil (86 mg, 86% yield). ^{1}H NMR (400 MHz, Chloroform-d): δ = 4.92 (d, J = 2.2 Hz, 1H), 4.78 (d, J = 2.5 Hz, 1H), 4.03 (td, J = 7.3, 3.4 Hz, 1H), 2.37 (dddd, J = 16.4, 10.8, 8.3, 5.8 Hz, 2H), 2.13 – 1.87 (m, 2H), 1.77 – 1.63 (m, 4H), 1.62 – 1.49 (m, 2H), 1.45 (dd, J = 12.3, 6.1 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3): δ = 158.5, 103.5, 79.3, 77.3, 56.8, 37.5, 34.1, 32.0, 31.6, 23.1, 19.6, 14.1. HRMS-ESI (m/z) [M+H]+ calculated for $C_{10}H_{17}O$, 153.1279, found 153.1279



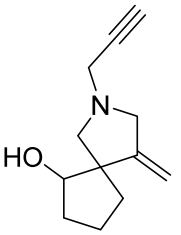
3c

Following the general procedure 2, the reaction of **2c** (100 mg, 0.66 mmol) afforded **3c** as a colorless oil (92 mg, 91% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.92 (dt, *J* = 20.2, 2.3 Hz, 2H), 4.43 (dt, *J* = 13.3, 2.3 Hz, 1H), 4.38 – 4.31 (m, 1H), 4.26 (d, *J* = 8.8 Hz, 1H), 4.02 (t, *J* = 6.2 Hz, 1H), 3.53 (d, *J* = 8.7 Hz, 1H), 2.13 – 2.05 (m, 1H), 2.01 (s, 1H) ,1.84 – 1.69 (m, 4H), 1.64 – 1.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8 , 102.6 , 79.3 , 74.2 , 72.1 , 57.2 , 33.5 , 32.9 , 20.7 . HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_9H_{14}O_2$, 155.1072, found 155.1055



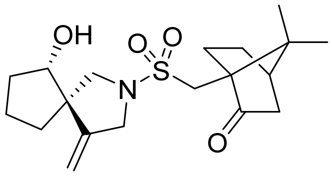
3d

Following the general procedure 2, the reaction of **2d** (100 mg, 0.39 mmol) afforded **3d** as a colorless oil (81 mg, 81% yield, d.r. = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.06 – 4.87 (m, 2H), 4.52 – 4.25 (m, 2H), 4.13 – 4.01 (m, 1H), 3.66 (d, *J* = 6.2 Hz, 1H), 3.59 (d, *J* = 9.2 Hz, 1H), 3.50 – 3.26 (m, 4H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7, 154.6 , 151.6 , 151.5 , 104.6 , 79.9 , 79.8 , 74.2 , 73.1 , 72.0 , 71.9, 71.5 , 71.1 , 56.8 , 56.1 , 52.7 , 52.6 , 51.7 , 50.9 , 28.5 . HRMS-ESI (m/z) $[M-H]^-$ calculated for $C_{13}H_{21}NO_4$, 254.1392, found 254.1402.



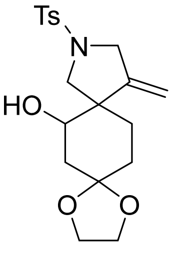
3e

Following the general procedure 2, the reaction of **2e** (100 mg, 0.53 mmol) afforded **3e** as a colorless oil (78 mg, 78% yield)^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.01 – 4.88 (m, 2H), 3.92 (dd, *J* = 8.2, 7.1 Hz, 1H), 3.72 – 3.54 (m, 1H), 3.45 (dd, *J* = 2.4, 0.8 Hz, 2H), 3.34 – 3.14 (m, 2H), 2.39 (d, *J* = 8.7 Hz, 1H), 2.25 (t, *J* = 2.4 Hz, 1H), 2.15 – 2.03 (m, 1H), 1.90 – 1.80 (m, 1H), 1.70 – 1.52 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4 , 104.0 , 83.1 , 77.7 , 73.6 , 59.8 , 57.1 , 55.5 , 42.1 , 34.4 , 33.06 , 21.00 . HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{12}H_{17}NO$, 192.1388, found 192.1387.



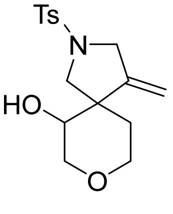
3f

Following the general procedure 2, the reaction of **2f** (100 mg, 0.27 mmol) afforded **3f** as a colorless oil (92 mg, 92% yield, d.r, > 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.95 (dt, *J* = 28.7, 2.2 Hz, 2H), 4.08 (dt, *J* = 5.5, 2.2 Hz, 2H), 3.95 (dd, *J* = 5.9, 4.6 Hz, 1H), 3.87 (d, *J* = 9.9 Hz, 1H), 3.46 (d, *J* = 14.9 Hz, 1H), 3.16 (d, *J* = 9.8 Hz, 1H), 2.86 (d, *J* = 14.9 Hz, 1H), 2.52 (ddd, *J* = 14.8, 11.8, 3.9 Hz, 1H), 2.36 (ddd, *J* = 18.5, 4.8, 3.3 Hz, 1H), 2.09 (t, *J* = 4.6 Hz, 1H), 2.03 (tdd, *J* = 7.2, 3.2, 1.4 Hz, 2H), 1.92 (d, *J* = 18.5 Hz, 1H), 1.87 – 1.80 (m, 2H), 1.77 – 1.69 (m, 2H), 1.66 – 1.57 (m, 2H), 1.41 (ddd, *J* = 13.0, 9.3, 3.9 Hz, 1H), 1.09 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 216.1 , 150.9 , 105.8 , 77.3 , 58.3 , 58.0 , 52.9 , 52.3 , 48.1 , 45.7 , 42.6, 42.5, 32.9, 32.2 , 26.9 , 24.8 , 20.6 , 19.8 , 19.7 . RMS-ESI (m/z) $[M+H]^+$ calculated for $C_{19}H_{29}NO_4S$, 368.1896, found 368.1891.



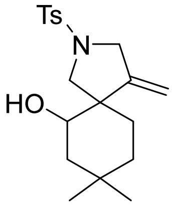
3g

Following the general procedure 2, the reaction of **2g** (100 mg, 0.27 mmol) afforded **3g** as a colorless oil (82 mg, 82% yield, d.r, = 3:1). ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.70 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.18 – 4.93 (m, 2H), 4.03 (d, *J* = 13.9 Hz, 1H), 4.00 – 3.88 (m, 4H), 3.88 – 3.75 (m, 1H), 3.66 (d, *J* = 13.8 Hz, 1H), 3.51 (d, *J* = 7.3 Hz, 0.3H), 3.39 – 3.23 (m, 2H), 3.00 (d, *J* = 10.0 Hz, 0.3H), 2.42 (d, *J* = 3.2 Hz, 3H), 2.06 – 1.86 (m, 2H), 1.74 – 1.60 (m, 2H), 1.59 – 1.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 147.2, 143.8, 143.7, 132.4, 132.2, 129.7, 129.6, 127.8, 127.6, 109.8, 108.2, 107.9, 106.3, 71.3, 69.3, 64.5, 64.3, 64.2, 64.0, 56.0, 52., 52.2, 51.1, 50.7, 49.4, 39.8, 36.7, 32.1, 31.5, 31.4, 26.8, 21.4. HRMS (ESI^+) calculated for $C_{19}H_{25}NO_5S$ $[M+H]^+$ 380.1532, found 380.1538.



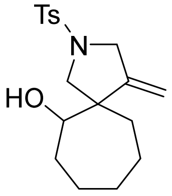
3h

Following the general procedure 2, the reaction of **2h** (100 mg, 0.31 mmol) afforded **3h** as a colorless oil (63 mg, 63% yield, d.r. = 5 :1). Major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.72 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.10 (t, *J* = 2.1 Hz, 1H), 5.04 (t, *J* = 2.1 Hz, 1H), 4.04 – 3.94 (m, 1H), 3.85 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.82 – 3.76 (m, 1H), 3.76 – 3.67 (m, 2H), 3.45 (d, *J* = 9.6 Hz, 1H), 3.43 – 3.37 (m, 1H), 3.34 (d, *J* = 9.6 Hz, 1H), 3.14 (dd, *J* = 11.3, 9.8 Hz, 1H), 2.43 (s, 3H), 1.72 (s, 1H), 1.68 – 1.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7, 143.8, 132.0, 129.7, 127.8, 106.9, 70.2, 68.8, 64.6, 52.8, 50.8, 49.6, 35.7, 21.5. HRMS (ESI$^+$) calculated for $C_{16}H_{21}NO_4S$ [M+H]$^+$ 324.1270, found 324.1260.



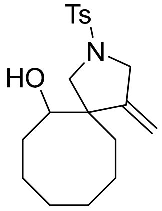
3i

Following the general procedure 2, the reaction of **2i** (100 mg, 0.29 mmol) afforded **3i** as a colorless oil (81 mg, 81% yield, d.r, = 8:1). ^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.72 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 5.14 – 4.85 (m, 2H), 4.01 (d, *J* = 13.7 Hz, 1H), 3.82 (d, *J* = 11.9 Hz, 1H), 3.66 (d, *J* = 13.6 Hz, 1H), 3.42 – 3.20 (m, 2H), 2.43 (s, 3H), 1.72 (s, 1H), 1.56 (d, *J* = 14.4 Hz, 2H), 1.38 (t, *J* = 13.4 Hz, 1H), 1.23 (t, *J* = 12.3 Hz, 2H), 1.09 (t, *J* = 12.4 Hz, 1H), 0.96 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4, 143.6, 132.2, 129.6, 127.8, 105.5, 70.7, 52.9, 52.1, 49.9, 44.1, 35.3, 32.7, 32.5, 31.6, 24.9, 21.5. HRMS (ESI$^+$) calculated for $C_{19}H_{27}NO_3S$ [M+H]$^+$ 350.1790, found 350.1781.



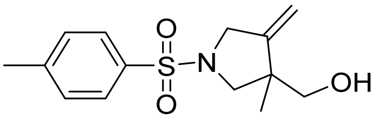
3j

Following the general procedure 2, the reaction of **2j** (100 mg, 0.30 mmol) afforded **3j** as a colorless oil (67 mg, 67% yield, d.r, = 11:1). ^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.03 (t, *J* = 2.0 Hz, 1H), 4.93 (t, *J* = 2.3 Hz, 1H), 4.07 – 3.98 (m, 1H), 3.70 (dd, *J* = 10.1, 2.7 Hz, 1H), 3.66 – 3.58 (m, 1H), δ 3.34 (d, *J* = 9.4 Hz, 1H), 3.28 (d, *J* = 9.4 Hz, 1H), 2.43 (s, 3H), 1.92 – 1.77 (m, 1H), 1.78 – 1.32 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 143.6, 132.1, 129.6, 127.8, 105.5, 75.8, 54.5, 52.8, 51.5, 36.9, 32.6, 26.5, 22.6, 22.5, 21.5. HRMS (ESI$^+$) calculated for $C_{18}H_{25}NO_3S$ [M+H]$^+$ 336.1633, found 336.1630.



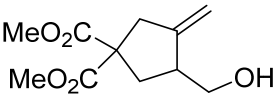
3k

Following the general procedure 2, the reaction of **2k** (100 mg, 0.29 mmol) afforded **3k** as a colorless oil (71 mg, 71% yield, d.r. = 2:1). ^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.07 (t, *J* = 2.3 Hz, 1H), 4.95 (t, *J* = 2.3 Hz, 1H), 4.14 – 3.96 (m,2H), 3.68 – 3.56 (m, 1H), 3.41 (d, *J* = 9.1 Hz, 1H), 3.24 (d, *J* = 9.1 Hz, 1H), 2.42 (s, 3H), 1.84 – 1.39 (m, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 150.5, 143.6, 132.5, 129.6, 127.8, 106.0, 76.6, 71.5, 54.7, 53.6, 52.8, 33.6, 32.6, 27.8, 26.9, 24.5, 21.6, 21.5. HRMS (ESI$^+$) calculated for $C_{19}H_{27}NO_3S$ [M+H]$^+$ 350.1790, found 350.1790.



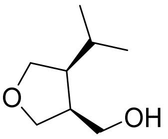
3l

Following the general procedure 2, the reaction of **9g** (100 mg, 0.36 mmol) afforded **10g** as pale yellow oil (95 mg, 94% yield). All data were in accordance with those previously reported: *J. Am. Chem. Soc.* **2011**, 133, 417. IR (neat): 667,818, 1030, 1160, 1340, 1730, 1590, 1660, 2870, 2930, 3510 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.68 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.98 (s, 1H), 4.87 (s, 1H), 3.91 (d, *J* = 14.1 Hz, 1H), 3.75 (d, *J* = 14.1 Hz, 1H), 3.42 (d, *J* = 9.9 Hz, 2H), 3.29 (d, *J* = 11.0 Hz, 1H), 2.81 (d, *J* = 9.5 Hz, 1H), 2.41 (s, 3H), 2.21 (s, 1H), 1.08 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 149.3, 143.7, 132.2, 129.6, 127.7, 107.1, 67.3, 56.2, 52.3, 47.6, 21.4, 20.6. HRMS-ESI (m/z) [M+H]$^+$ calculated for $C_{14}H_{20}NO_3S$, 282.1158, found 282.1129.



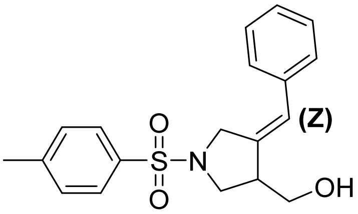
3m

Following the general procedure 2, the reaction of **9c** (100 mg, 0.53 mmol) afforded **10c** as a colorless oil (88 mg, 88% yield). All data were in accordance with those previously reported: *J. Am. Chem. Soc.* **2010**, 132, 6163. IR (neat): 1041, 1255, 1376, 1425, 1726, 2880, 2956, 3357 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 5.04 (d, *J* = 2.2 Hz, 1H), 4.91 (d, *J* = 2.3 Hz, 1H), 3.71 (s, 6 H), 3.64 (dd, *J* = 5.6, 1.5 Hz, 2H), 3.00 – 2.90 (m, 2H), 2.83 – 2.73(m, 1H), 2.58 (dd, *J* = 13.3, 8.9 Hz, 1H), 2.10 (dd, *J* = 13.3, 8.9 Hz, 1H), 1.83 (s, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 172.0, 172.0, 148.7, 107.9, 64.4, 58.6, 52.8, 52.8, 44.7, 41.4, 36.7. HRMS-ESI (m/z) [M+H]$^+$ calculated for $C_{11}H_{17}O_5$, 229.1071, found 229.1066.



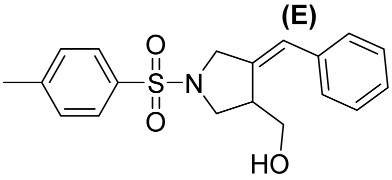
3n

Following the general procedure 2, the reaction of **9e** (100 mg, 0.69 mmol) afforded **10e** as a colorless oil (74 mg, 75% yield)**.** 1H-NMR (400 MHz, $CDCl_3$): δ = 3.96 (dd, J = 8.8, 7.4 Hz, 1H), 3.81 – 3.77 (m, 2H), 3.67 (dd, J = 10.3, 5.1 Hz, 1H), 3.53 – 3.42 (m, 2H), 2.21 – 2.12 (m, 1H), 1.86 (s, 1H), 1.67 – 1.56 (m, 2H), 0.97 (d, J = 6.3 Hz, 3H), 0.89 (d, J = 6.3 Hz, 3H). 13C NMR (100 MHz, CDCl3): δ = 72.1, 71.3, 65.6, 48.7, 45.5, 31.0, 21.2, 20.6. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_8H_{17}O_2$, 145.1223, found 145.1198.



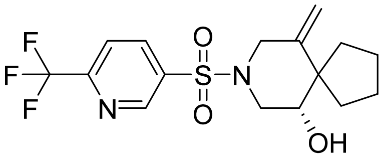
3o (Z)

Following the general procedure 2, the reaction of **9h** (100 mg, 0.53 mmol) afforded **10h** (Z) as a white solid (48 mg, 48% yield) and **10h** (E) 46 mg, 46% yield. All data were in accordance with those previously reported: *ACS Catal.* **2017**, 7, 1181. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.38 (m, 4H), 7.25 (d, *J* = 6.4 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.36 (s, 1H), 4.17 – 4.24 (m, 1H), 4.01 (dd, *J* = 14.8, 2.0 Hz, 1H), 3.57– 3.67 (m, 2H), 3.38 (dd, *J* = 9.6, 4.0 Hz, 1H), 3.28 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.94 – 3.03 (m, 1H), 2.42 (s, 3H), 1.80(s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 136.8, 136.1, 132.4, 129.7, 128.6, 128.1, 127.7, 127.3, 124.6, 63.8, 50.6, 49.2, 47.4, 21.5. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{19}H_{22}NO_3S$, 344.1315, found 344.1331.



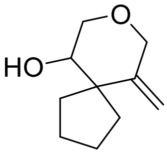
3o (E)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.17 (m, 7H), 6.37 (s, 1H), 4.12 – 4.08 (m, 1H), 3.75 (d, *J* = 15.6 Hz, 1H), 3.68 (d, *J* = 9.7 Hz, 1H), 3.60 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.44 (t, *J* = 9.9 Hz, 1H), 3.40 – 3.31 (m, 1H), 3.12 (dd, *J* = 9.7, 6.1 Hz, 1H), 2.43 (s, 3H), 1.73(s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 136.7, 135.9, 132.3, 129.7, 128.6, 127.9, 127.8, 127.3, 124.9, 61.9, 53.4, 50.9, 43.4, 21.5. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{19}H_{22}NO_3S$, 344.1315, found 344.1321.



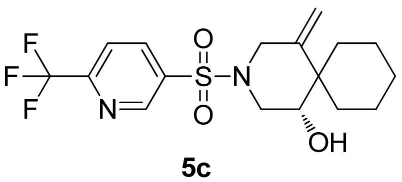
5a

Following the general procedure 2, the reaction of **4a** (100 mg, 0.27 mmol) afforded **5a** as a colorless oil (80 mg, 80% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.10 (d, *J* = 2.1 Hz, 1H), 8.28 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 5.17 (s, 1H), 5.02 (s, 1H), 4.05 (dd, *J* = 12.8, 1.8 Hz, 1H), 3.69 (ddd, *J* = 12.5, 4.1, 1.8 Hz, 1H), 3.55 – 3.36 (m, 2H), 3.05 (dd, *J* = 12.5, 1.9 Hz, 1H), 1.90 (t, 1H), 1.72 – 1.47 (m, 7H), 1.42 (dd, *J* = 5.0, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 151.1 (q, $J_{C,F}$ = 36.0 Hz), 148.6, 138.3, 137.2, 122.1 (q, $J_{C,F}$ = 273.0 Hz), 120.5 (q, $J_{C,F}$ = 2.0 Hz), 75.9, 74.7, 68.4, 59.0, 47.5, 37.6, 33.3, 29.2, 25.0, 24.7. HRMS-ESI (m/z) [M-H]$^-$ calculated for $C_{16}H_{18}F_3N_2O_3S$, 375.0996, found 375.1002.



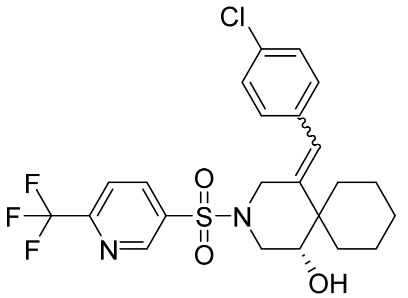
5b

Following the general procedure 2, the reaction of **4b** (100 mg, 0.53 mmol) afforded **5b** as a colorless oil (86 mg, 86% yield)^{1}H NMR (400 MHz, CDCl$_3$): δ = 5.02 (s, 1H), 4.95 (s, 1H), 4.19 – 3.98 (m, 2H), 3.89 – 3.66 (m, 2H), 3.32 (t, *J* = 2.2 Hz, 1H), 2.14 (s, 1H), 2.06 – 1.93 (m, 1H), 1.77 – 1.71 (m, 1H), 1.69 – 1.52 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 147.1, 111.8, 74.9, 71.1, 70.2, 52.5, 34.7, 33.9, 24.6, 24.0. HRMS-ESI (m/z) [M+Na]$^+$ calculated for $C_{10}H_{16}O_2$, 191.1047, found 191.1046.



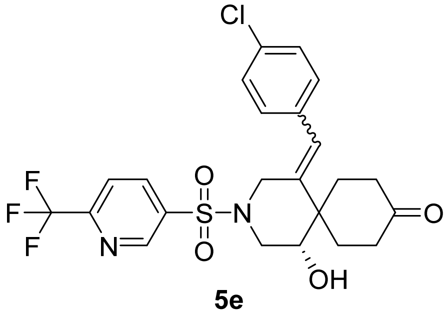
5c

Following the general procedure 2, the reaction of **4c** (100 mg, 0.26 mmol) afforded **5c** as a colorless oil (41 mg, 41% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.09 (d, *J* = 2.5 Hz, 1H), 8.28 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 5.29 (s, 1H), 5.09 (s, 1H), 3.99 (dd, *J* = 12.6, 1.7 Hz, 1H), 3.76 – 3.64 (m, 2H), 3.48 (d, *J* = 12.6 Hz, 1H), 3.13 (dd, *J* = 12.5, 1.8 Hz, 1H), 1.89 (s, 1H), 1.79 – 1.64 (m, 1H), 1.63 – 1.23 (m, 9H). ^{13}C NMR (101 MHz, CDCl$_3$): δ= 151.3 (q, $J_{C,F}$ = 36.0 Hz), 148.5, 148.1, 143.1, 138.1, 137.0, 136.8, 136.6, 124.6, 122.1 (q, $J_{C,F}$ = 273.0 Hz), 120.7 (q, $J_{C,F}$ = 2.0 Hz), 117.0, 74.2, 70.4, 51.0, 49.2, 47.5, 46.0, 44.1, 42.9, 35.4, 33.4, 32.3, 30.2, 26.0, 25.6, 21.9, 21.5, 21.4, 21.3. HRMS-ESI (m/z) [M+H]$^+$ calculated for $C_{17}H_{22}F_3N_2O_3S$, 391.1303, found 391.1305.



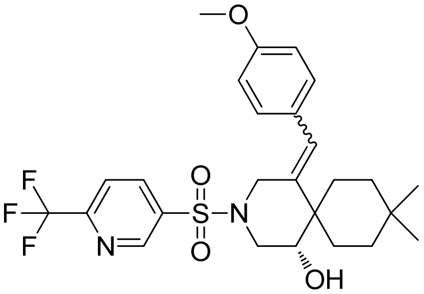
5d

Following the general procedure 2, the reaction of **4d** (100 mg, 0.20 mmol) afforded **5d** as a colorless oil (89 mg, 90% yield, Z/E = 5:4). **Isomer 1**: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.16 (d, *J* = 6.2 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.73 (s, 1H), 4.06 (d, *J* = 13.3 Hz, 2H), 3.78 (dd, *J* = 33.8, 13.0 Hz, 2H), 3.16 (d, *J* = 12.9 Hz, 1H), 1.79 – 1.60 (m, 3H), 1.42 (td, *J* = 14.9, 13.4, 5.4 Hz, 4H), 1.21 – 1.14 (m, 3H), 1.07 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$): δ = 151.1 (q, $J_{C,F}$ = 35.0 Hz), 148.7, 137.7, 137.1, 136.5, 132.7, 131.5, 129.6, 127.8, 122.1 (q, $J_{C,F}$ = 272.0 Hz), 120.7 (q, $J_{C,F}$ = 3.0 Hz), 77.3, 76.6, 67.4, 51.7, 47.6, 45.0, 33.5, 32.9, 25.5, 21.4, 20.7. HRMS-ESI (m/z) [M+H]$^+$ calculated for $C_{23}H_{25}ClF_3N_2O_3S$, 501.1227, found 501.1227. **Isomer 2**: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.98 (d, *J* = 2.1 Hz, 1H), 8.10 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.75 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.41 – 7.30 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.55 (s, 1H), 4.44 (dd, *J* = 13.2, 1.7 Hz, 1H), 3.86 (dd, *J* = 3.5, 1.9 Hz, 1H), 3.77 (ddd, *J* = 12.7, 3.5, 1.7 Hz, 1H), 3.42 (d, *J* = 13.2 Hz, 1H), 3.25 (dd, *J* = 12.7, 1.9 Hz, 1H), 1.86 – 1.65 (m, 4H), 1.63 – 1.53 (m, 4H), 1.53 – 1.35 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ =151.2 (q, $J_{C,F}$ = 35.0 Hz), 148.5, 136.9, 136.9, 134.6, 133.2, 130.0, 129.5, 128.71, 122.1 (q, $J_{C,F}$ = 273.0 Hz), 120.5 (q, $J_{C,F}$ = 3.0 Hz), 70.5, 60.3, 47.4, 43.2, 42.3, 32.8, 30.5, 26.1, 21.5, 21.3, 14.1. HRMS-ESI (m/z) [M+H]$^+$ calculated for $C_{23}H_{25}ClF_3N_2O_3S$, 501.1227, found 501.1227.



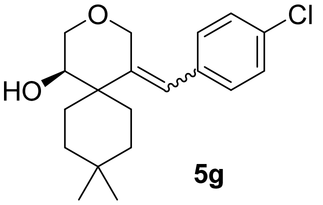
5e

Following the general procedure 2, the reaction of **4e** (100 mg, 0.19 mmol) afforded **5e** as a white solid (79 mg, 80% yield, Z/E = 3:2). Major isomer: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.98 (s, 1H), 8.11 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 1H), 4.37 (d, *J* = 13.3 Hz, 1H), 3.93 (d, *J* = 36.8 Hz, 1H), 3.72 (d, *J* = 12.6 Hz, 1H), 3.55 (d, *J* = 13.3 Hz, 1H), 3.36 (d, *J* = 12.7 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.33 (t, 2H), 2.20 (d, *J* = 6.8 Hz, 1H), 2.04 (q, *J* = 27.1, 23.2 Hz, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 210.2, 151.4 (q, $J_{C,F}$ = 35.0 Hz), 148.4, 136.9, 135.0, 134.0, 133.6, 130.0, 128.8, 122.0 (q, $J_{C,F}$ = 273.0 Hz), 120.7 (q, $J_{C,F}$ = 3.0 Hz), 70.5, 47.8, 42.8, 42.7, 36.8, 36.5, 30.9, 29.3. HRMS-ESI (m/z) [M+H]$^+$ calculated for $C_{23}H_{23}ClF_3N_2O_4S$, 515.1019, found 515.1020.



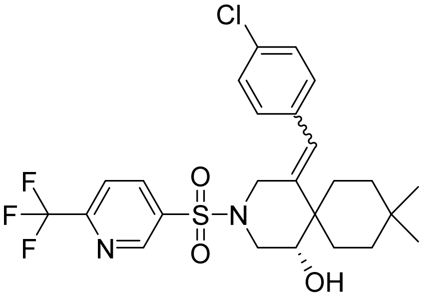
5f

Following the general procedure 2, the reaction of **4f** (100 mg, 0.19 mmol) afforded **5f** as a white semi-solid (40 mg, 40% yield, Z/E =1:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.15 (d, *J* = 2.1 Hz, 1H), 8.33 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.86 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.80 – 6.69 (m, 3H), 4.55 (dd, *J* = 13.3, 1.5 Hz, 1H), 4.05 (d, *J* = 1.7 Hz, 1H), 3.79 (s, 3H), 3.50 (d, *J* = 13.3 Hz, 1H), 3.16 (dd, *J* = 12.8, 1.8 Hz, 1H), 2.00 (s, 1H), 1.86 – 1.79 (m, 1H), 1.69 – 1.62 (m, 1H), 1.60 – 1.53 (m, 3H), 1.38 (t, *J* = 6.2 Hz, 1H), 1.31 – 1.22 (m, 5H), 0.72 (d, *J* = 47.7 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ =158.3, 151.1 (q, $J_{C,F}$ = 35.0 Hz), 148.7, 137.1, 129.9, 129.2, 122.1 (q, $J_{C,F}$ = 273.0 Hz), 120.6 (q, $J_{C,F}$ = 3.0 Hz), 113.9, 113.0, 55.1, 51.9, 47.6, 44.4, 42.3, 34.3, 33.7, 29.8, 29.4, 27.6. HRMS-ESI (m/z) [M+H]$^+$ calculated for $C_{27}H_{33}F_3NO_4S$, 524.2082, found 524.2082.



5g

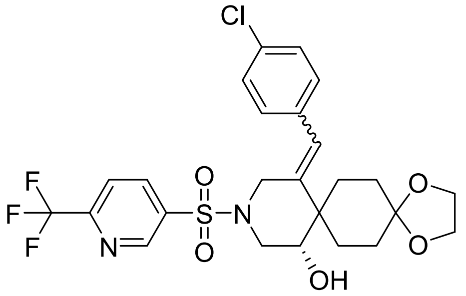
Following the general procedure 2, the reaction of **4g** (100 mg, 0.31 mmol) afforded **5g** as a colorless oil (82 mg, 83% yield, Z/E > 20：1). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.31 – 7.27 (m, 1H), 7.13 – 6.78 (m, 1H), 6.58 (s, 1H), 4.46 (d, *J* = 12.7 Hz, 0H), 4.14 (d, *J* = 12.8 Hz, 0H), 4.05 – 3.94 (m, 0H), 3.80 – 3.67 (m, 1H), 2.09 (s, 1H), 2.00 – 1.85 (m, 2H), 1.82 – 1.67 (m, 2H), 1.48 – 1.24 (m, 5H), 0.94 (d, *J* = 10.0 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ =141.9, 135.3, 132.6, 130.3, 128.3, 127.1, 68.1, 63.1, 42.8, 34.7, 34.2, 29.9, 29.5, 27.7, 26.5. HRMS-ESI (m/z) [M+H]$^+$ calculated for $C_{19}H_{26}ClO_2$, 321.1621, found 321.1604.



5h

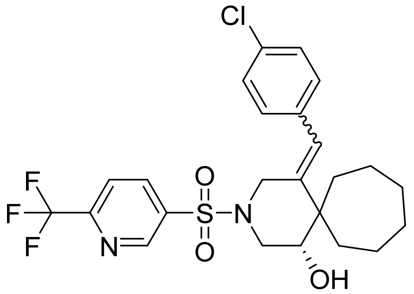
Following the general procedure 2, the reaction of **4h** (100 mg, 0.19 mmol) afforded **5h** as a white solid (80 mg, 80% yield, Z/E =17:1). Major isomer: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.98 (d, *J* = 2.1 Hz, 1H), 8.09 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.29 (m, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 4.44 (dd, *J* = 13.2, 1.7 Hz, 1H), 4.01 – 3.67 (m, 2H), 3.44 (d, *J* = 13.2

Hz, 1H), 3.26 (dd, J = 12.7, 1.9 Hz, 1H), 2.33 – 2.10 (m, 1H), 1.87 (dd, J = 43.8, 7.8 Hz, 2H), 1.68 (q, 3H), 1.59 – 1.49 (m, 1H), 1.46 – 1.36 (m, 2H), 1.35 – 1.17 (m, 4H), 0.91 (d, J = 11.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2 (q, $J_{C,F}$ = 36.0 Hz), 148.5, 136.9, 134.6, 133.3, 130.1, 129.4, 128.7, 122.1 (q, $J_{C,F}$ = 276.0 Hz), 120.5 (q, $J_{C,F}$ = 3.0 Hz), 47.4, 43.0, 42.3, 34.4, 34.2, 29.9, 29.6, 28.6, 26.2. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{25}H_{29}ClF_3N_2O_3S$, 529.1540, found 529.1541.



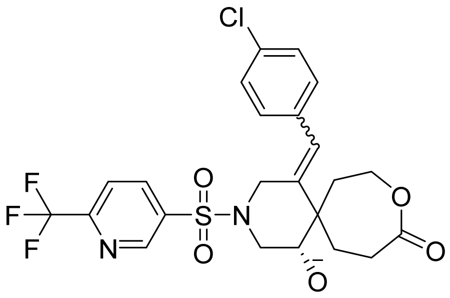
5i

Following the general procedure 2, the reaction of **4i** (100 mg, 0.18 mmol) afforded **5i** as a white solid (82 mg, 82% yield, Z/E =1.2：1). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (d, J = 2.1 Hz, 1H), 8.10 (dd, J = 8.2, 2.1 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 6.60 (s, 1H), 4.43 (dd, J = 13.3, 1.5 Hz, 1H), 3.96 – 3.91 (m, 4H), 3.81 (t, J = 2.4 Hz, 1H), 3.76 (dd, J = 12.5, 3.6 Hz, 1H), 3.42 (d, J = 13.2 Hz, 1H), 3.26 (dd, J = 12.7, 1.8 Hz, 1H), 2.08 – 1.99 (m, 1H), 1.82 (td, J = 13.5, 13.1, 5.7 Hz, 4H), 1.74 (t, J = 6.4 Hz, 3H), 1.59 (td, J = 8.1, 7.5, 4.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3 (q, $J_{C,F}$ = 36.0 Hz), 148.5, 137.0, 136.7, 135.5, 134.4, 133.4, 130.0, 129.7, 128.7, 122.1 (q, $J_{C,F}$ = 273.0 Hz), 120.5 (q, $J_{C,F}$ = 3.0 Hz), 108.2, 70.4, 64.3, 64.2, 47.7, 42.6, 42.4, 30.5, 2.7, 27.9. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{25}H_{27}ClF_3N_2O_5S$, 559.1281, found 559.1283.



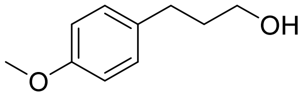
5j

Following the general procedure 2, the reaction of **4j** (100 mg, 0.19 mmol) afforded **5j** as a colorless oil (81 mg, 81% yield， Z/E =13/1). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (s, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.3 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.2 Hz, 2H), 6.53 (s, 1H), 4.38 (d, J = 13.2 Hz, 1H), 3.83 – 3.62 (m, 2H), 3.37 (dd, J = 58.7, 12.9 Hz, 2H), 2.11 – 1.84 (m, 2H), 1.76 (dd, J = 15.5, 6.7 Hz, 1H), 1.68 – 1.40 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3 (q, $J_{C,F}$ = 36.0 Hz), 148.5, 137.8, 137.0, 136.8, 134.7, 133.2, 130.1, 128.7, 128.3, 122.1 (q, $J_{C,F}$ = 273.0 Hz), 120.5 (q, $J_{C,F}$ = 2.0 Hz), 72.0, 47.8, 46.4, 43.0, 34.5, 32.3, 30.4, 30.4, 22.4, 22.3. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{24}H_{27}ClF_3N_2O_3S$, 515.1383, found 515.1386.



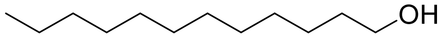
5k

Following the general procedure 2, the reaction of **4k** (100 mg, 0.19 mmol) afforded **5k** as a white semi-solid (46 mg, 46% yield, Z/E = 9/1). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.96 (d, *J* = 2.0 Hz, 1H), 8.15 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.34 (m, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.48 (s, 1H), 4.70 (dd, *J* = 14.0, 1.6 Hz, 1H), 4.26 (dd, *J* = 11.1, 5.2 Hz, 1H), 4.01 (ddd, *J* = 12.1, 5.1, 1.6 Hz, 1H), 3.63 (tt, *J* = 6.0, 3.7 Hz, 2H), 3.29 (d, *J* = 13.9 Hz, 1H), 2.96 (t, *J* = 11.6 Hz, 1H), 2.81 (dd, *J* = 9.5, 5.2 Hz, 2H), 2.34 (dt, *J* = 13.4, 5.5 Hz, 1H), 2.06 – 1.92 (m, 1H), 1.88 (dt, *J* = 13.2, 5.5 Hz, 1H), 1.71 (dt, *J* = 14.4, 6.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.9, 151.8 (q, $J_{C,F}$ = 36.0 Hz), 148.2, 136.8, 136.7, 135.1, 134.0, 133.5, 130.0, 129.0, 128.8, 122.0 (q, $J_{C,F}$ = 273.0 Hz), 120.9 (q, $J_{C,F}$ = 3.0 Hz), 79.4, 77.2, 57.9, 43.7, 43.0, 40.4, 27.1, 27.1. HRMS-ESI (m/z) $[M-H]^-$ calculated for $C_{23}H_{21}ClF_3N_2O_5S$, 529.0817, found 529.0820.



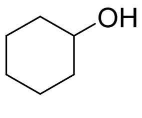
S8a

Following the general procedure 1, the reaction of 7a (100 mg, 0.61 mmol) afforded 8a as a colorless oil (87 mg, 86% yield). All data were in accordance with those previously reported: Org. Lett., 2012, 14. ^{1}H-NMR (400 MHz, CDCl3): δ = 7.14 – 7.10 (m, 2H), 6.85 – 6.82 (m, 2H), 3.79 (s, 3H), 3.67 (t, J = 6.4 Hz, 2 H), 2.67 – 2.63 (m, 2 H), 1.90 – 1.83 (m, 2H). ^{13}C NMR (100 MHz, CDCl3): δ = 157.5, 133.7, 129.1, 113.5, 61.9, 55.0, 34.2, 30.9.



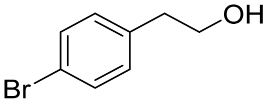
S8b

Following the general procedure 1, the reaction of **7b** (83.9 mg, 0.46 mmol) afforded **8b** as a colorless oil (73 mg, 88% yield). All data matched that reported in the literature: *Green Chem.*, **2014**, 16, 4081. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.64 (t, *J* = 6.6 Hz, 2H), 1.56 (p, *J* = 6.7 Hz, 2H), 1.27 (m, 19H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.1, 32.8, 31.9, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 25.7, 22.6, 14.1.



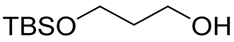
S8c

Following the general procedure 1, the reaction of **7c** (91.1 mg, 0.93 mmol) afforded **8c** as a colorless oil (76 mg, 83% yield). All data were in accordance with those previously reported: *Chem. Commun.*, **2013**, 49, 1005—1007. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.63 – 3.57 (m, 1H), 1.92 – 1.86 (m, 2H), 1.74 – 1.71 (m, 2H), 1.56 – 1.53 (m, 2H), 1.33 – 1.13 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.1, 35.4, 25.3, 24.0.



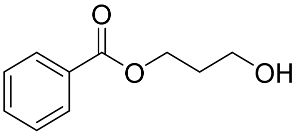
S8d

Following the general procedure 1, the reaction of **7d** (103 mg, 0.52mmol) afforded **8d** as a colorless oil (78 mg, 76% yield). All data were in accordance with those previously reported: *Chem. Eur. J.* **2015**, 21, 14737. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 3.82 (t, *J* = 6.5 Hz, 2H), 2.81 (t, *J* = 6.5 Hz, 2H), 1.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 137.5, 131.5, 130.7, 120.2, 63.3, 38.4.



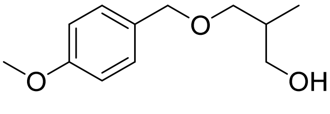
S8e

Following the general procedure 1, the reaction of **7e** (100 mg, 0.53 mmol) afforded **8e** as a colorless oil (80 mg, 81% yield). All data were in accordance with those previously reported: *Chem. Commun.*, **2012**, 48, 6163–6165. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.84 – 3.82 (m, 2H), 3.80 (t, *J* = 5.5 Hz, 2H), 1.77 (p, *J* = 5.6 Hz, 1H), 0.89 (s, 9H), 0.07 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 62.9, 62.4, 34.1, 25.8, 18.1, -5.5.



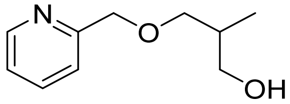
S8f

Following the general procedure 1, the reaction of **7f** (105 mg, 0.53 mmol) afforded **8f** as a colorless oil (83 mg, 79% yield). IR (neat): 3423,2960,1723,1610,1455,1320,1278,1125,720 cm^{-1}, ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.05 – 8.03 (m, 2H), 7.59 – 7.54 (m, 1H), 7.46 – 7.42 (m, 2H), 4.49 (t, *J* = 6.1 Hz, 2H), 3.78 (t, *J* = 6.1 Hz, 2H), 2.01 (p, *J* = 6.1 Hz, 2H), 1.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 133.0, 130.0, 129.5, 128.3, 61.7, 59.0, 31.8. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{10}H_{13}O_3$, 181.0859, found 181.0859.

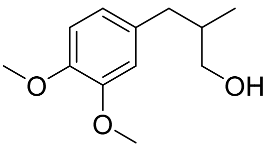


S8g

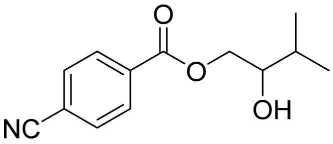
Following the general procedure 1, the reaction of **7g** (108 mg, 0.52 mmol) afforded **8g** as a colorless oil (100 mg, 93% yield). IR (neat): 3420,2927,1517,1460,1250,1080,1030,820 cm^{-1}, ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.47 (s, 2H), 3.83 (s, 3H), 3.66 – 3.59 (m, 2H), 3.58 – 3.53 (m, 1H), 3.44 – 3.39 (m, 1H), 2.12 – 2.05 (m, 1H), 0.89 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 130.0, 129.1, 113.7, 75.0, 72.9, 67.6, 55.2, 35.5, 13.4. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{12}H_{19}O_3$, 211.1329, found 211.1316.


S8h

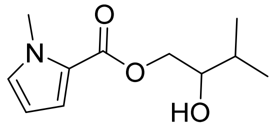
Following the general procedure 1, the reaction of **7h** (106 mg, 0.59 mmol) afforded **8h** as a colorless oil (95 mg, 90% yield). IR (neat): 3362,2925,1594,1436,1361,1123,1050,760cm^{-1}, ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 4.6 Hz, 1H), 7.71 (td, *J* = 7.7, 1.5 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.23 – 7.20 (m, 1H), 4.67 (d, *J* = 2.7 Hz, 2H), 3.72 – 3.60 (m, 3H), 3.55 – 3.50 (m, 1H), 2.14 – 2.05 (m, 1H), 0.92 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 148.8, 136.6, 122.3, 121.1, 74.7, 73.3, 66.1, 35.6, 13.5. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{10}H_{16}NO_2$, 182.1176, found 182.1174.


S8i

Following the general procedure 1, the reaction of **7i** (100 mg, 0.48 mmol) afforded **8i** as a colorless oil (88 mg, 89% yield). IR (neat): 3425,2930,1516,1470,1261,1142,1030,770 cm^{-1}, ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.80 – 6.78 (m, 1H), 6.72 – 6.70 (m, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.55 – 3.46 (m, 2H), 2.70 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.37 (dd, *J* = 13.5, 8.0 Hz, 1H), 1.96 – 1.88 (m, 1H), 0.91 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4, 147.0, 133.1, 120.8, 112.1, 110.9, 67.3, 55.7, 55.6, 39.1, 37.7, 16.3. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{12}H_{19}O_3$, 211.1329, found 211.1321.

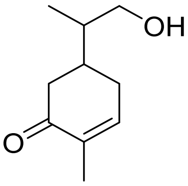

S8j

Following the general procedure 1, the reaction of **7j** (104 mg, 0.45 mmol) afforded **8j** as a colorless oil (81 mg, 78% yield). IR (neat): 3518, 2967, 2238, 1730, 1585, 1408, 1275, 1121, 1015, 763 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 4.48 (dd, *J* = 11.5, 3.0 Hz, 1H), 4.34 (dd, *J* = 11.5, 7.5 Hz, 1H), 3.75 (ddd, *J* = 7.4, 6.0, 2.9 Hz, 1H), 1.86 (dq, *J* = 13.4, 6.7 Hz, 2H), 1.03 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 133.7, 132.2, 130.1, 117.8, 116.5, 74.6, 68.3, 31.2, 18.7, 17.6. HRMS-EI (m/z) $[M]^+$ calculated for $C_{13}H_{15}NO_3$, 233.1052, found 233.1049.



S8k

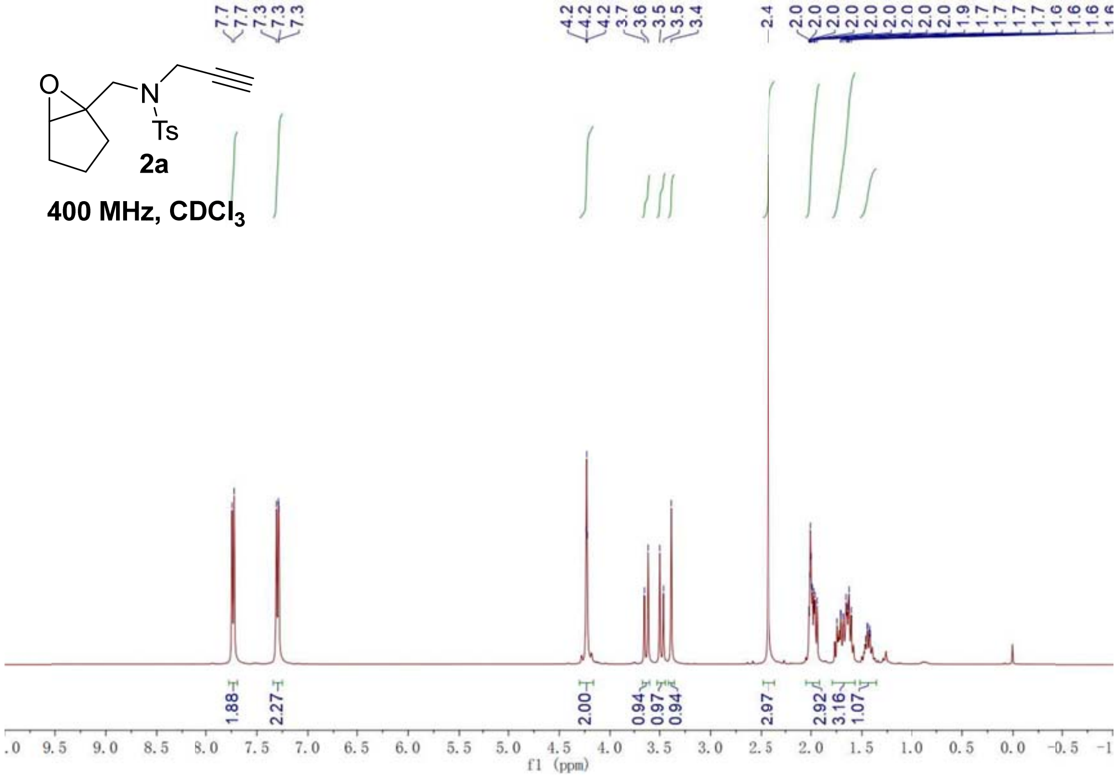
Following the general procedure 1, the reaction of **7k** (96 mg, 0.46 mmol) afforded **8k** as a colorless oil (83 mg, 86% yield). I (neat): 3462, 3118, 2958, 1718, 1531, 1417, 1321, 1249, 1117, 748 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 6.96 (dd, *J* = 4.0, 1.8 Hz, 1H), 6.81 (t, *J* = 2.0 Hz, 1H), 6.12 (dd, *J* = 3.9, 2.5 Hz, 1H), 4.36 (dd, *J* = 11.5, 2.9 Hz, 1H), 4.19 (dd, *J* = 11.5, 7.5 Hz, 1H), 3.93 (s, 3H), 3.69 – 3.65 (m, 1H), 1.82 – 1.78 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 161.3, 129.7, 121.9, 118.0, 107.8, 74.8, 66.6, 36.7, 31.0, 18.6, 17.7. HRMS-ESI (m/z) [M+Na]$^+$ calculated for $C_{11}H_{17}NNaO_3$, 234.1101, found 234.1099.



S8l

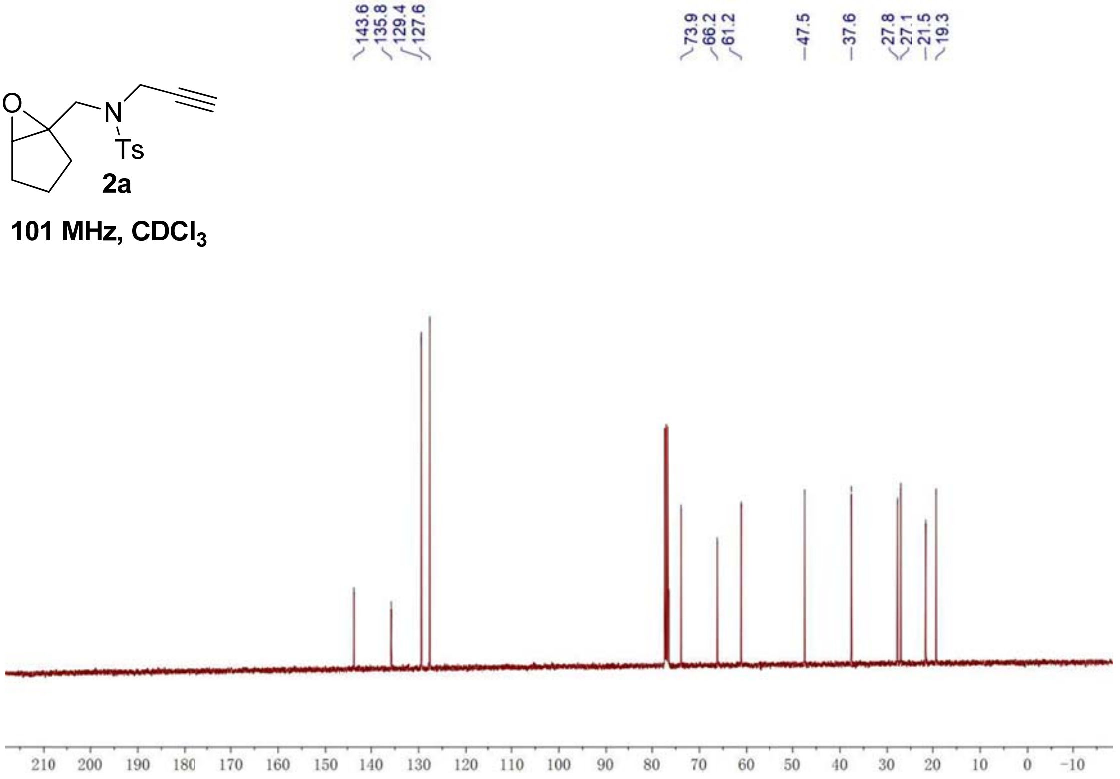
Following the general procedure 1, the reaction of **7l** (107 mg, 0.64 mmol) afforded **8l** as a colorless oil (99 mg, 92% yield). IR (neat): 3458, 3105, 2958, 1733, 1464, 1148, 1075 cm-1. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 6.75 (d, *J* = 6.0 Hz, 2H), 3.65 – 3.59 (m, 2H), 3.57 – 3.52 (m, 2H), 2.53 – 2.52 (m, 1H), 2.49 – 2.49 (m, 1H), 2.39 – 2.32 (m, 2H), 2.25 – 2.12 (m, 6H), 1.77 (s, 6H), 1.69 – 1.62 (m, 2H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 200.3, 200.3, 145.2, 145.1, 135.3, 65.4, 65.3, 42.5, 40.9, 39.3, 37.0, 37.0, 30.5, 28.7, 15.6, 15.6, 13.3, 13.3. HRMS-ESI (m/z) [M+H]$^+$ calculated for $C_{10}H_{17}O_2$, 169.1223, found 169.1223.

9 Spectra of Compounds



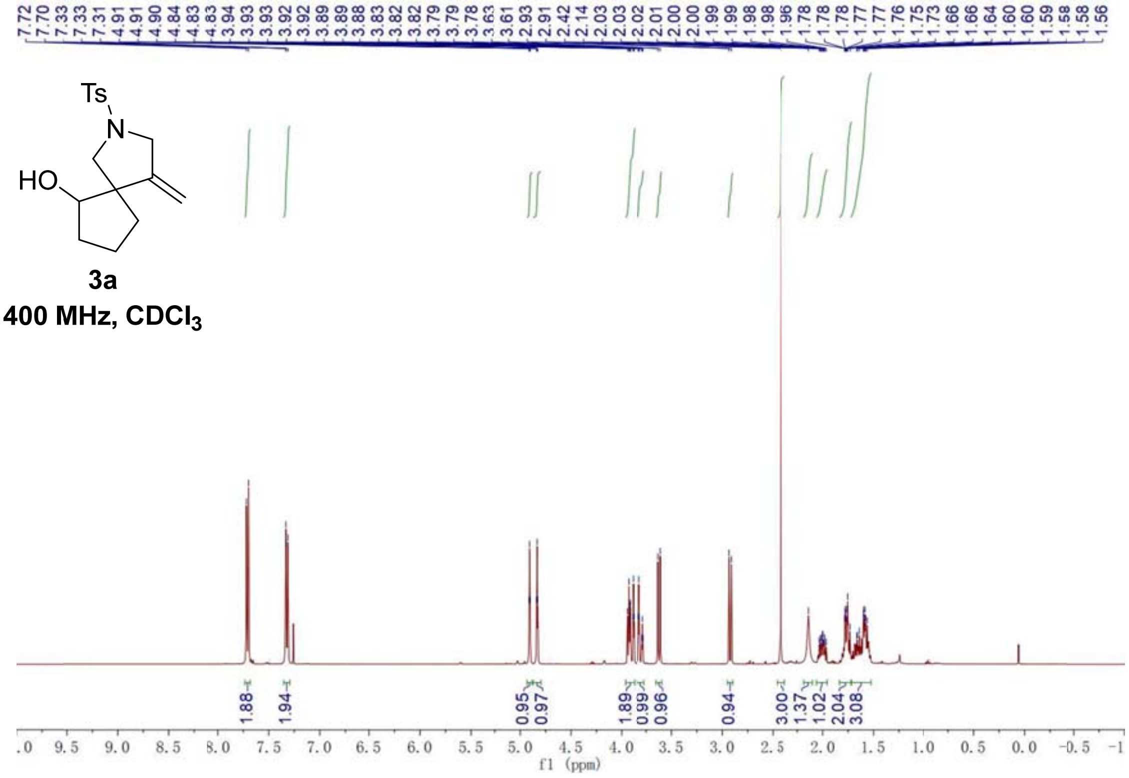
2a

400 MHz, $CDCl_3$

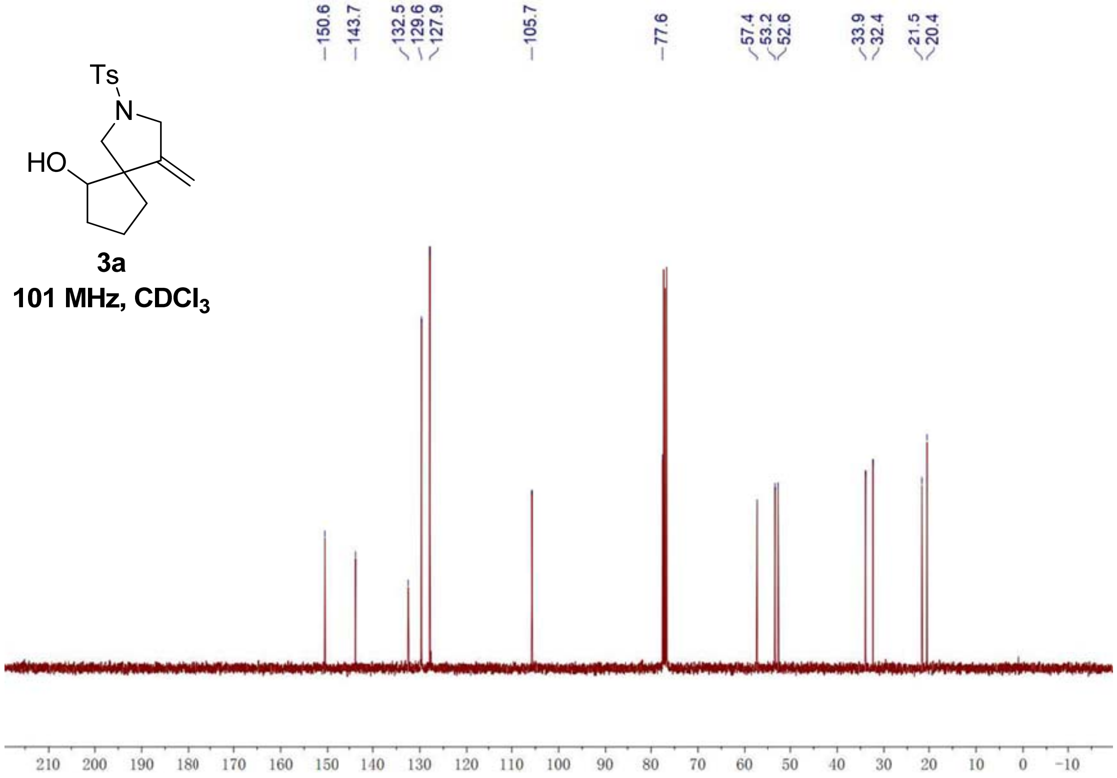


2a

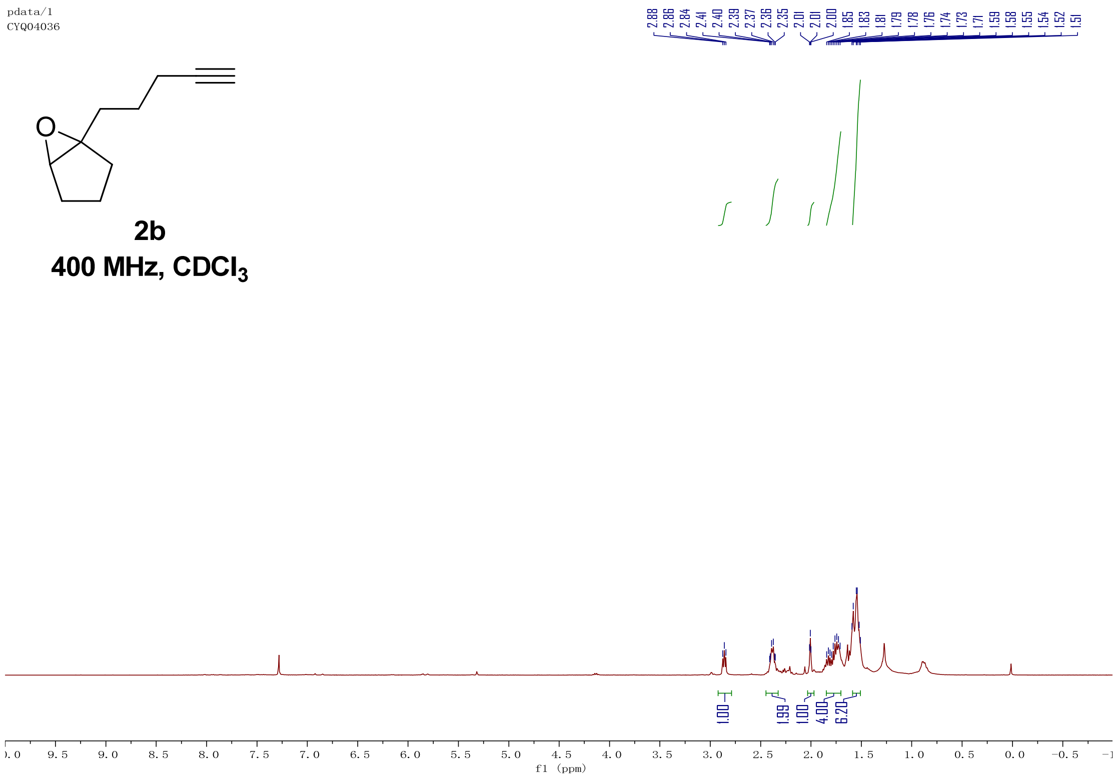
101 MHz, $CDCl_3$

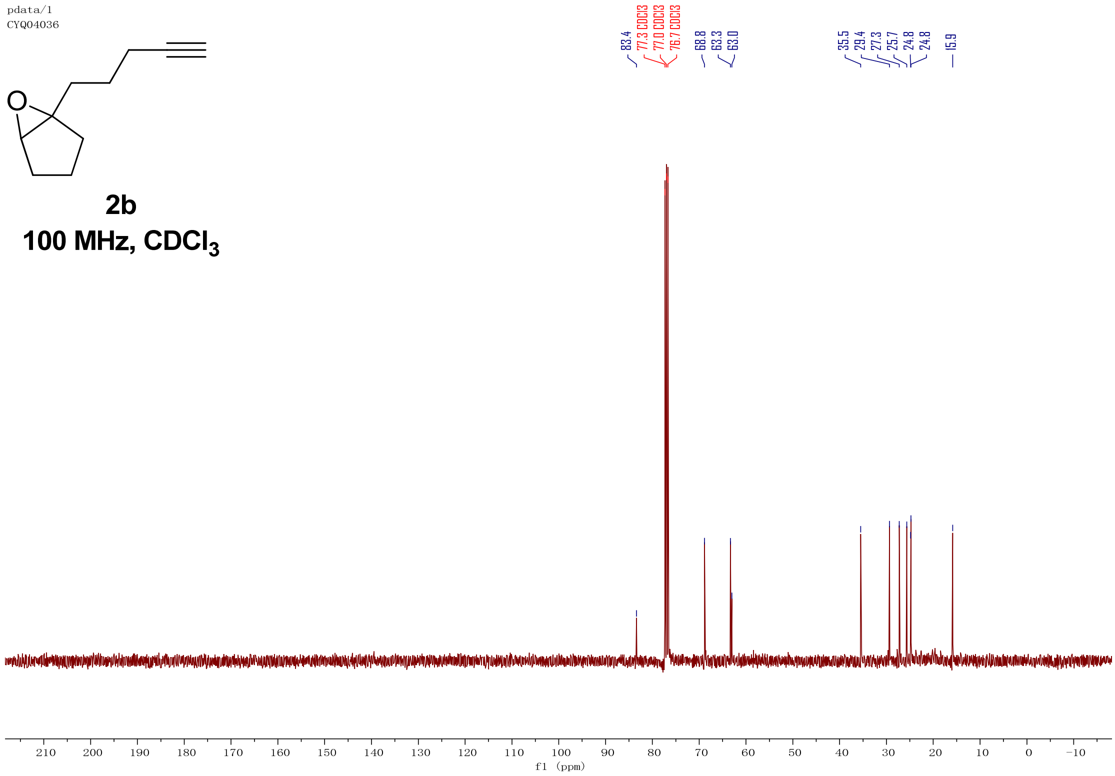


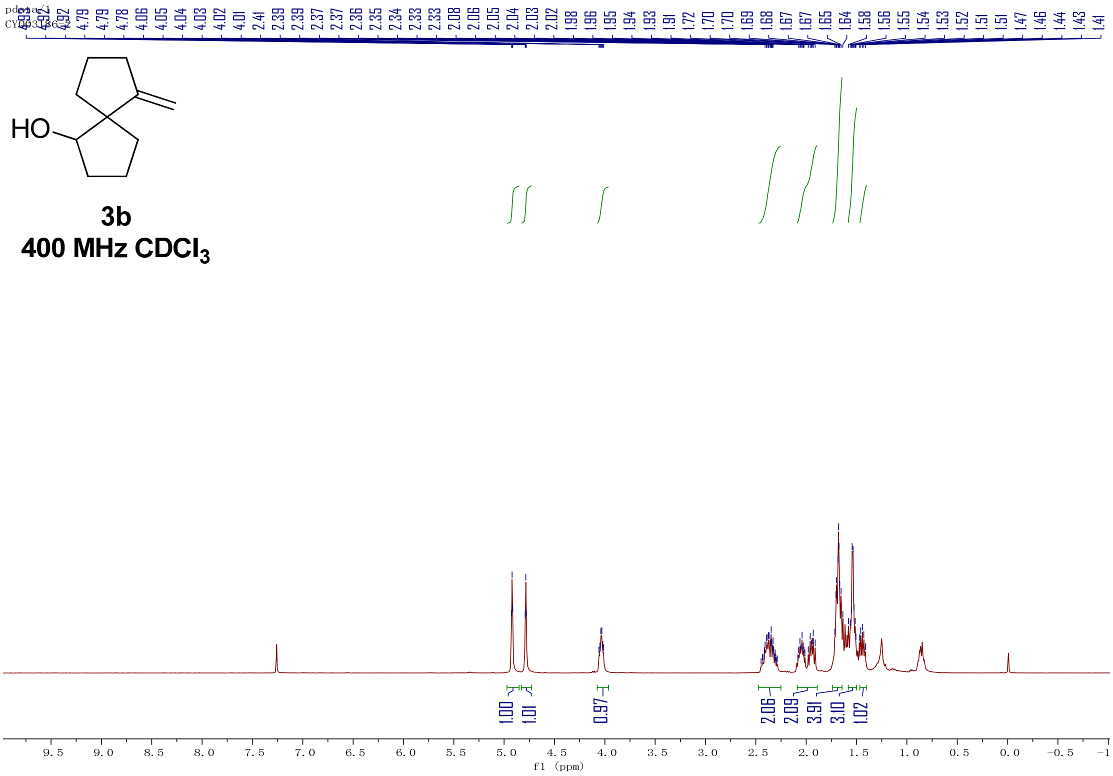
3a
400 MHz, $CDCl_3$



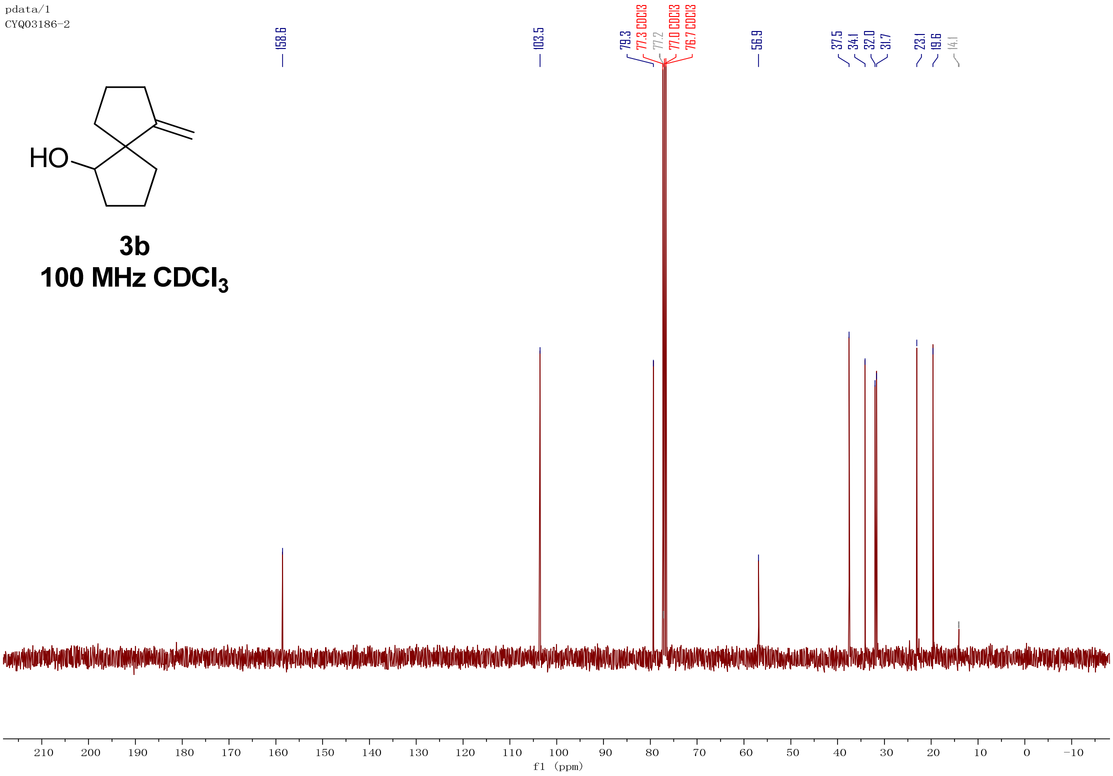
3a
101 MHz, $CDCl_3$


pdata/1
CYQ04036
O
2b
400 MHz, CDCl$_3$
2.88 2.86 2.84 2.41 2.40 2.39 2.37 2.36 2.35 2.01 2.01 2.00 1.85 1.83 1.81 1.79 1.78 1.76 1.74 1.73 1.71 1.59 1.58 1.55 1.54 1.52 1.51
1.00
1.99
1.00
4.00
6.20
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 −1
f1 (ppm)

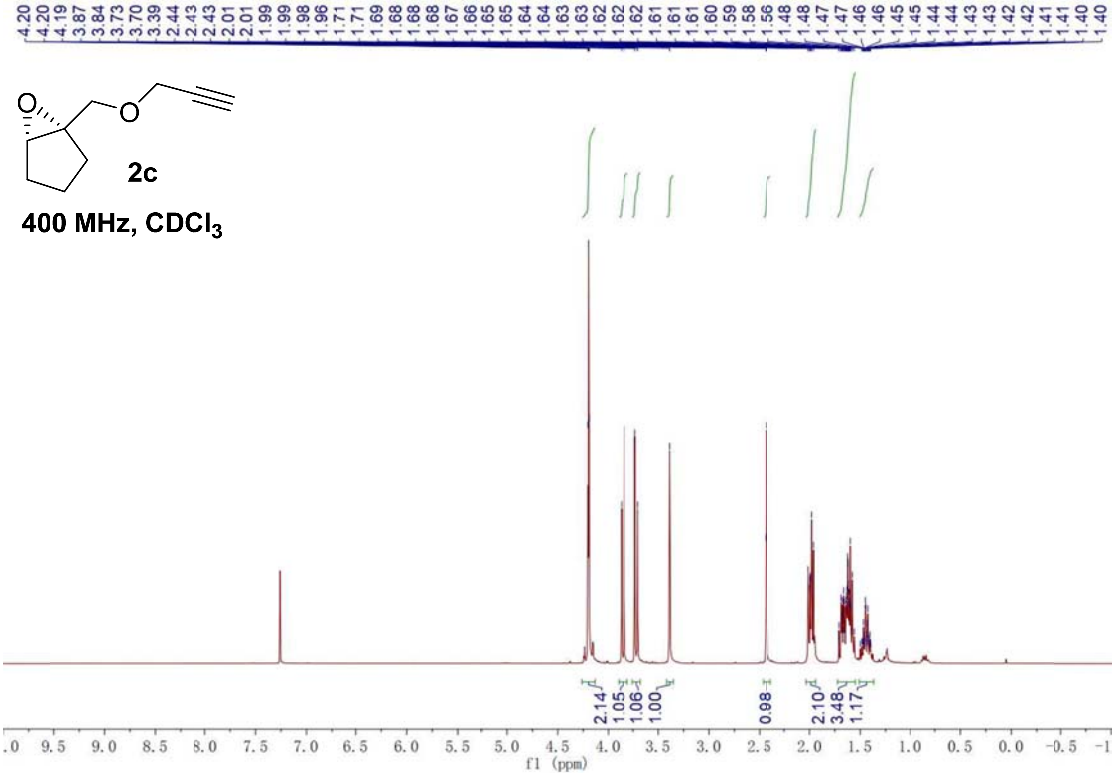

pdata/1
CYQ04036
O
2b
100 MHz, CDCl$_3$
83.4
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
68.8
63.3
63.0
35.5
29.4
27.3
25.7
24.8
24.8
15.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



3b
400 MHz CDCl$_3$



3b
100 MHz CDCl$_3$


4.20
4.20
4.19
3.87
3.84
3.73
3.70
3.39
2.44
2.43
2.43
2.01
1.99
1.98
1.96
1.71
1.69
1.68
1.68
1.68
1.67
1.66
1.65
1.65
1.64
1.64
1.63
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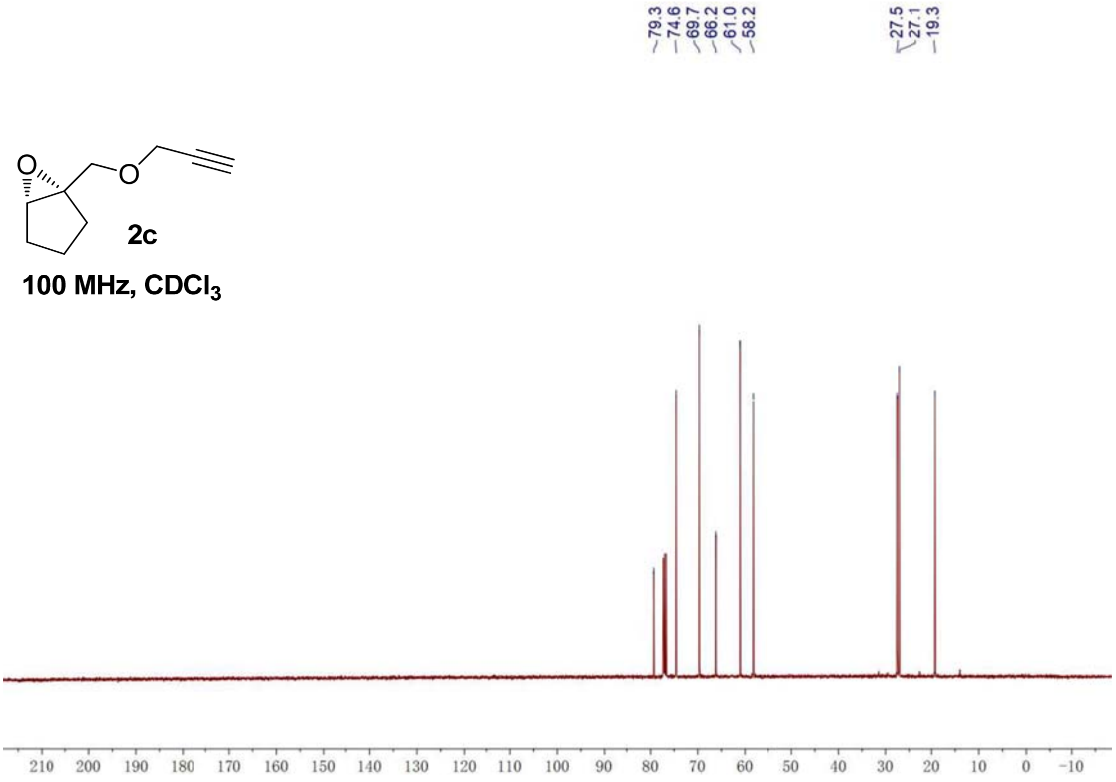
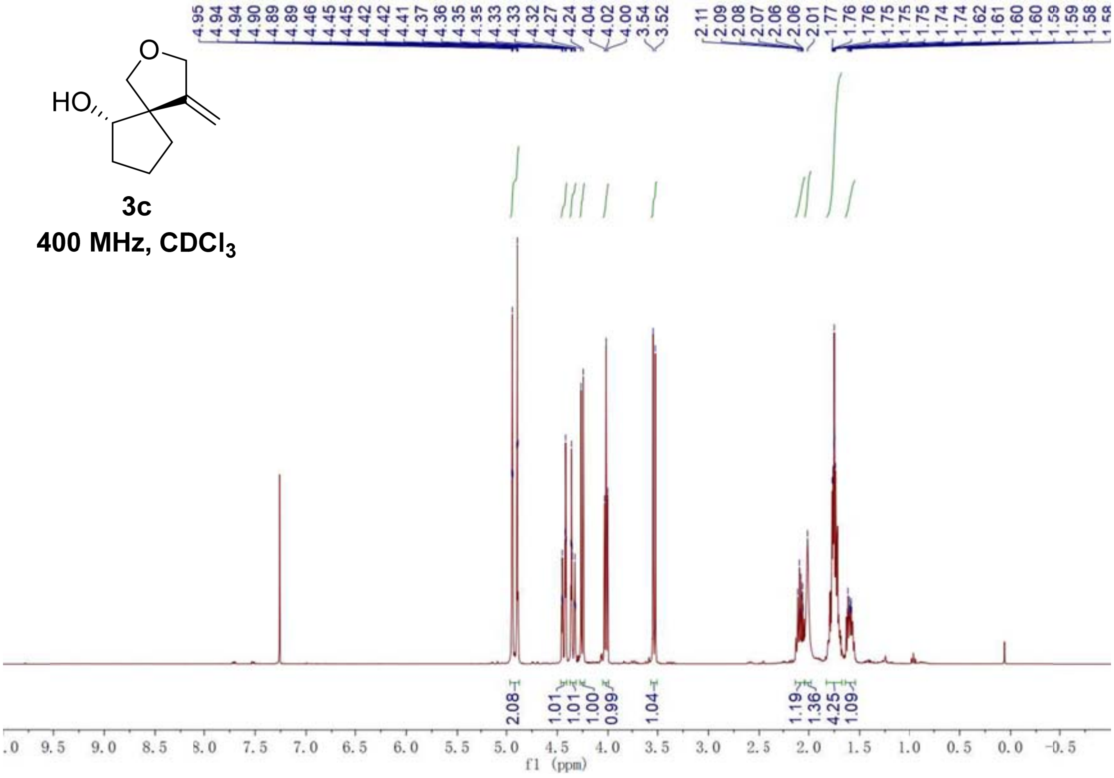
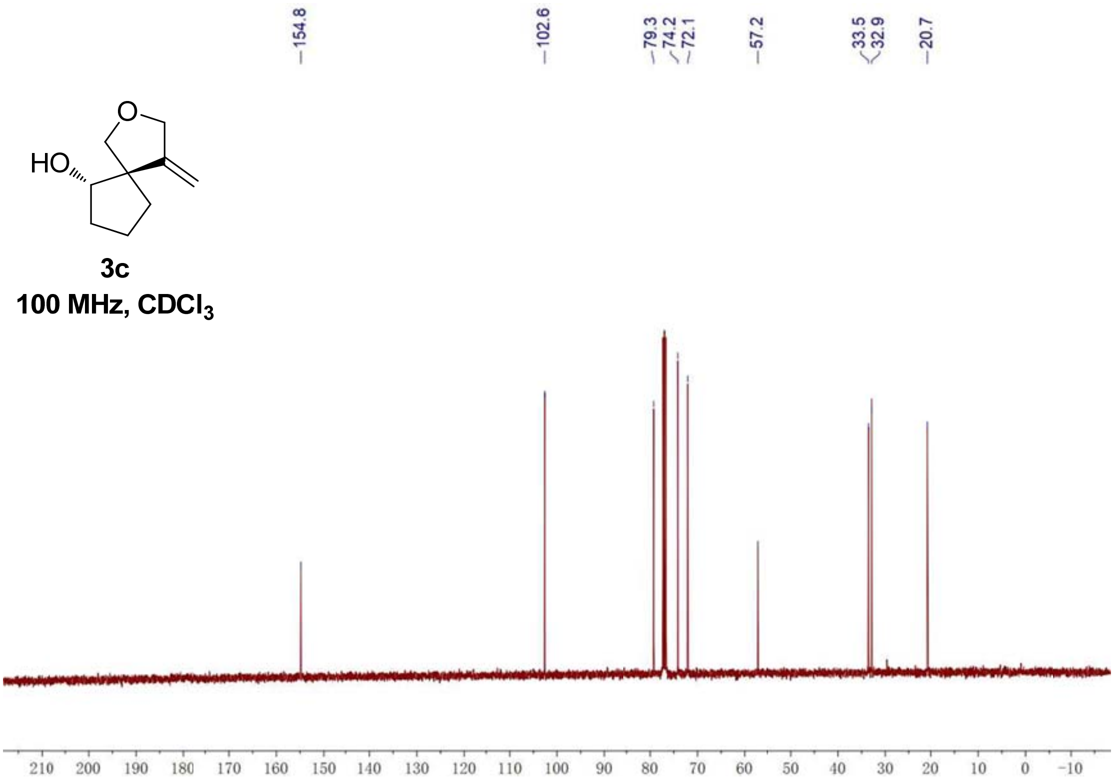
1.59
1.58
1.56
1.48
1.48
1.47
1.47
1.46
1.46
1.45
1.45
1.44
1.44
1.43
1.42
1.42
1.41
1.41
1.40
1.40
2c
400 MHz, CDCl3
2.14
1.05
1.06
1.00
0.98
2.10
3.48
1.17
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

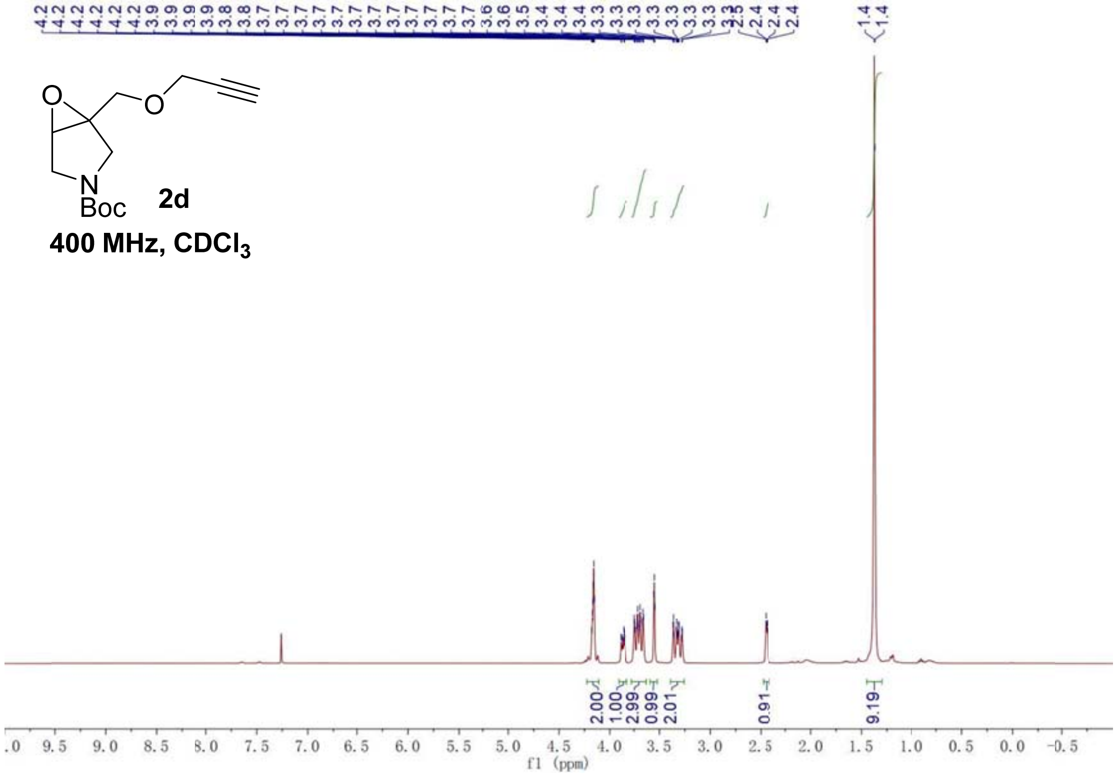

79.3
74.6
69.7
66.2
61.0
58.2
27.5
27.1
19.3
2c
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



3c
400 MHz, $CDCl_3$

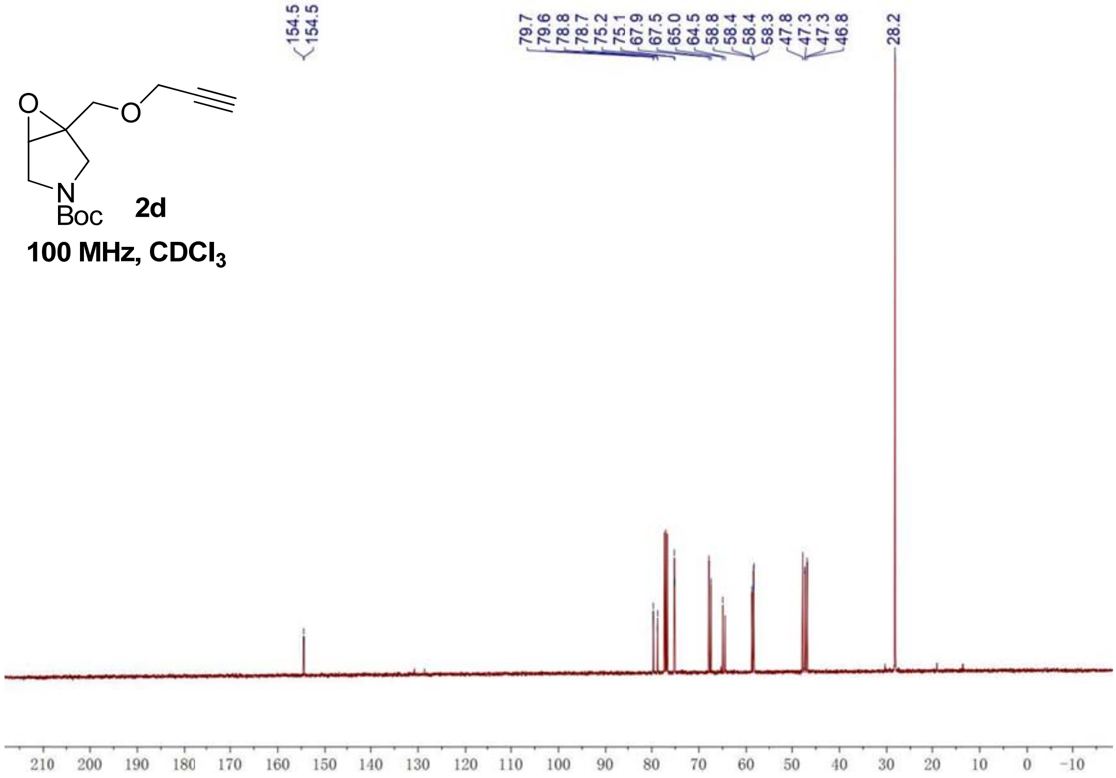


3c
100 MHz, $CDCl_3$



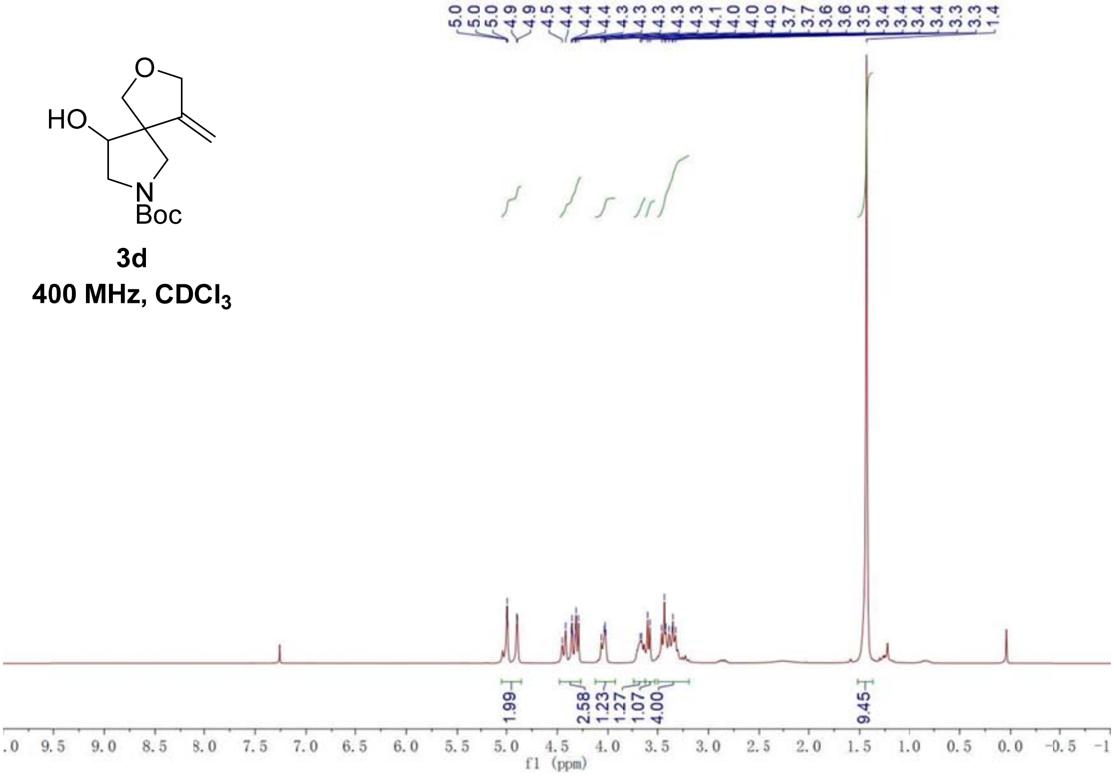
2d

400 MHz, $CDCl_3$



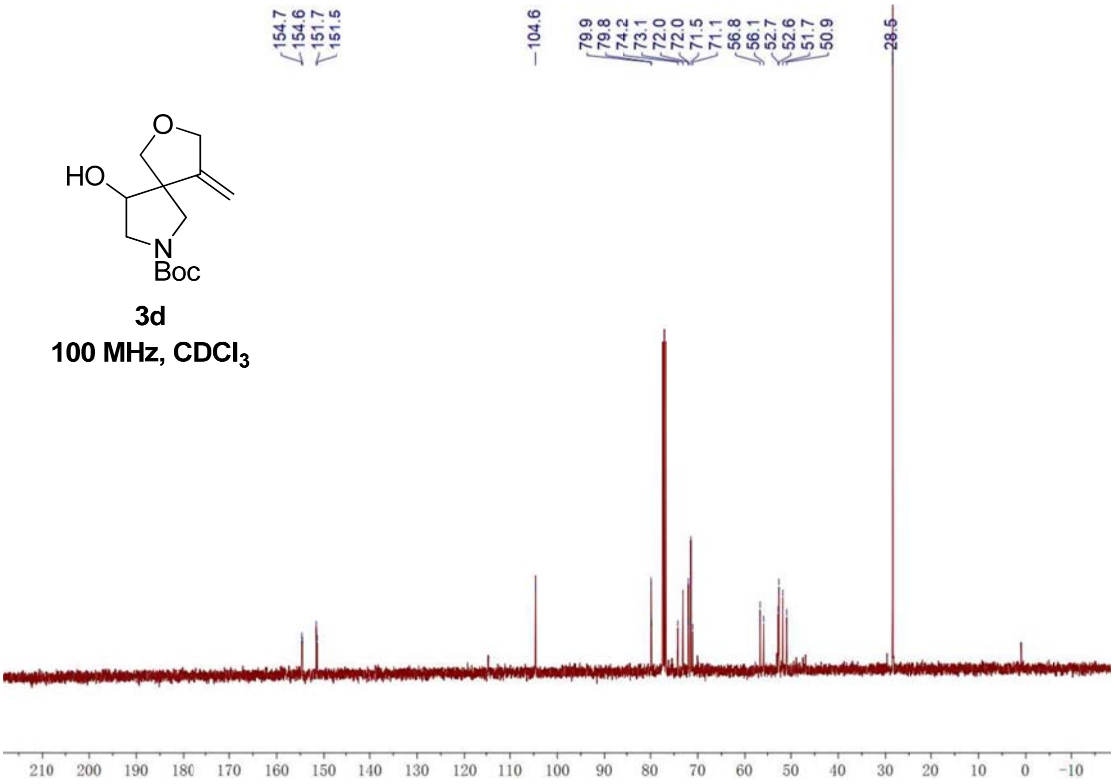
2d

100 MHz, $CDCl_3$



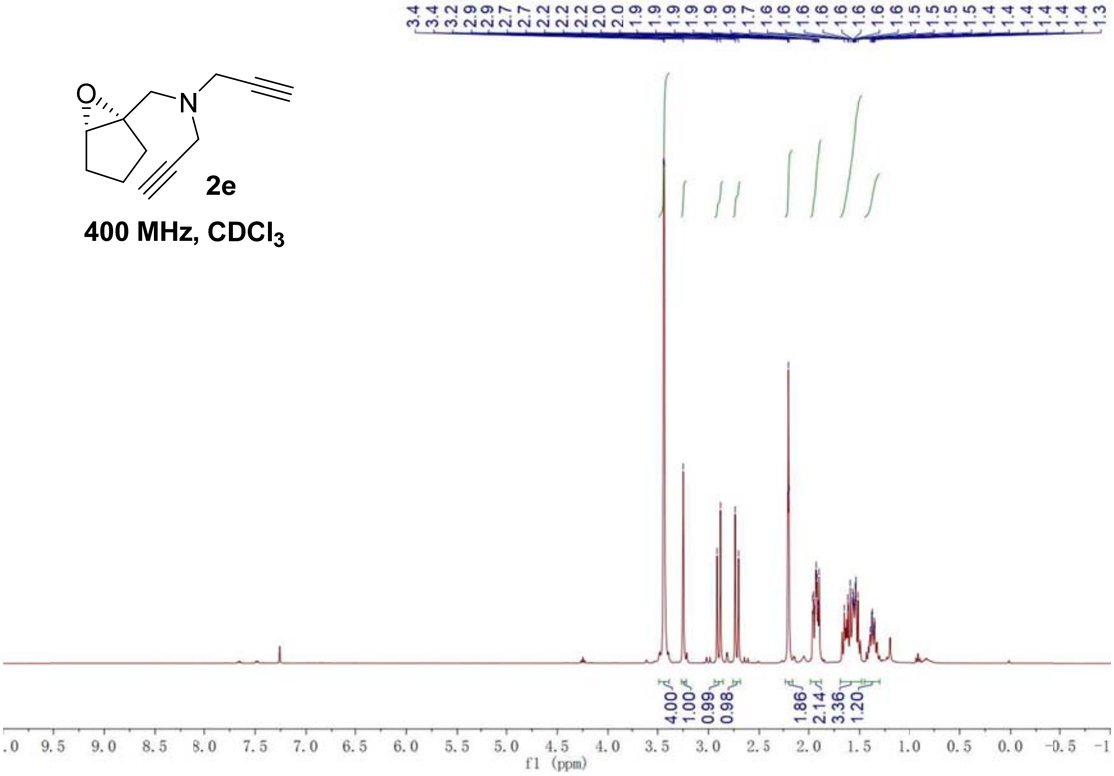
3d

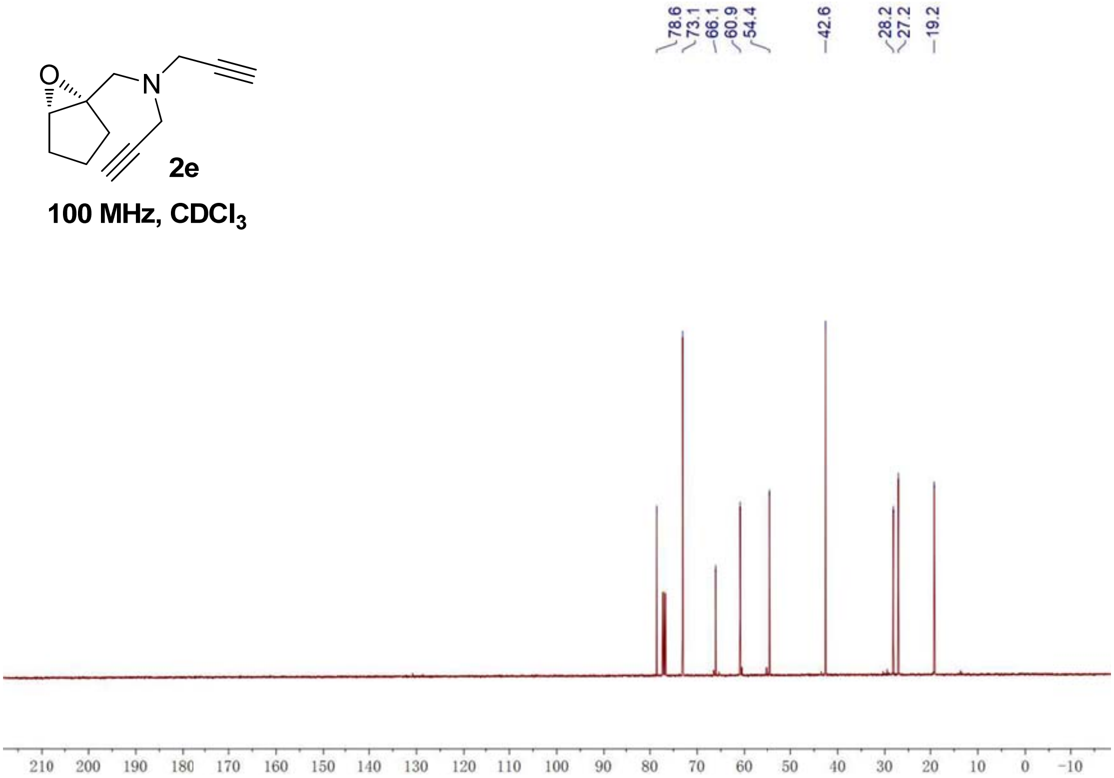
400 MHz, $CDCl_3$

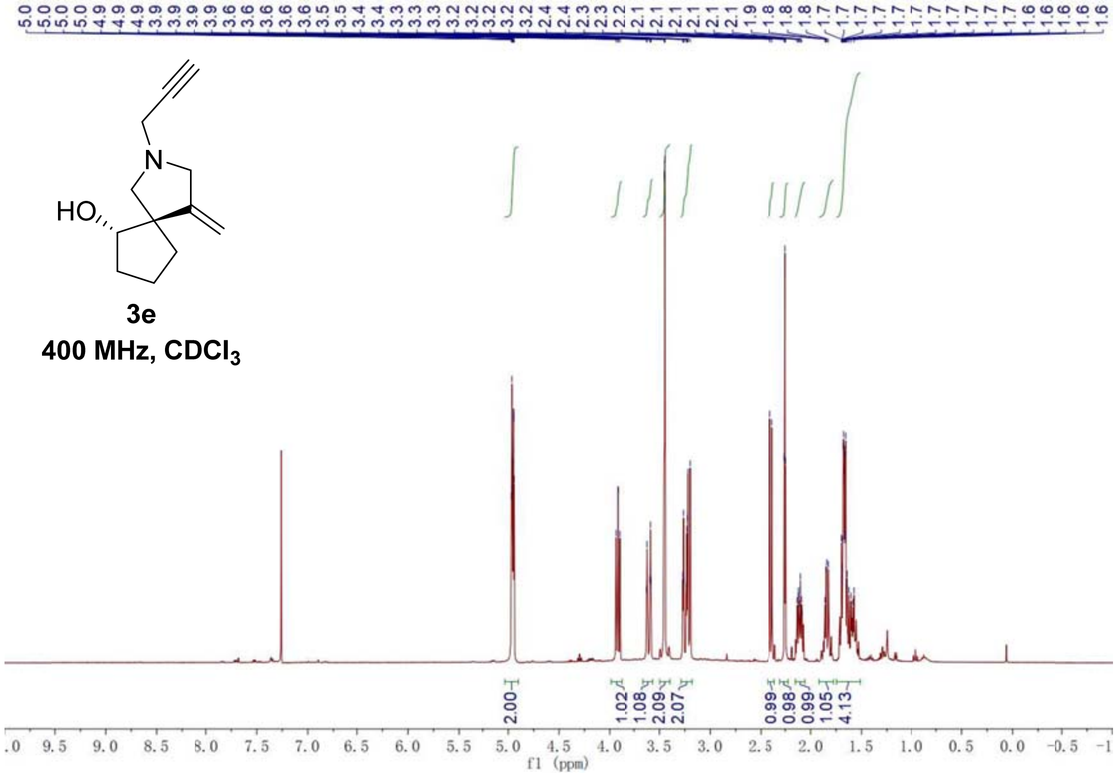


3d

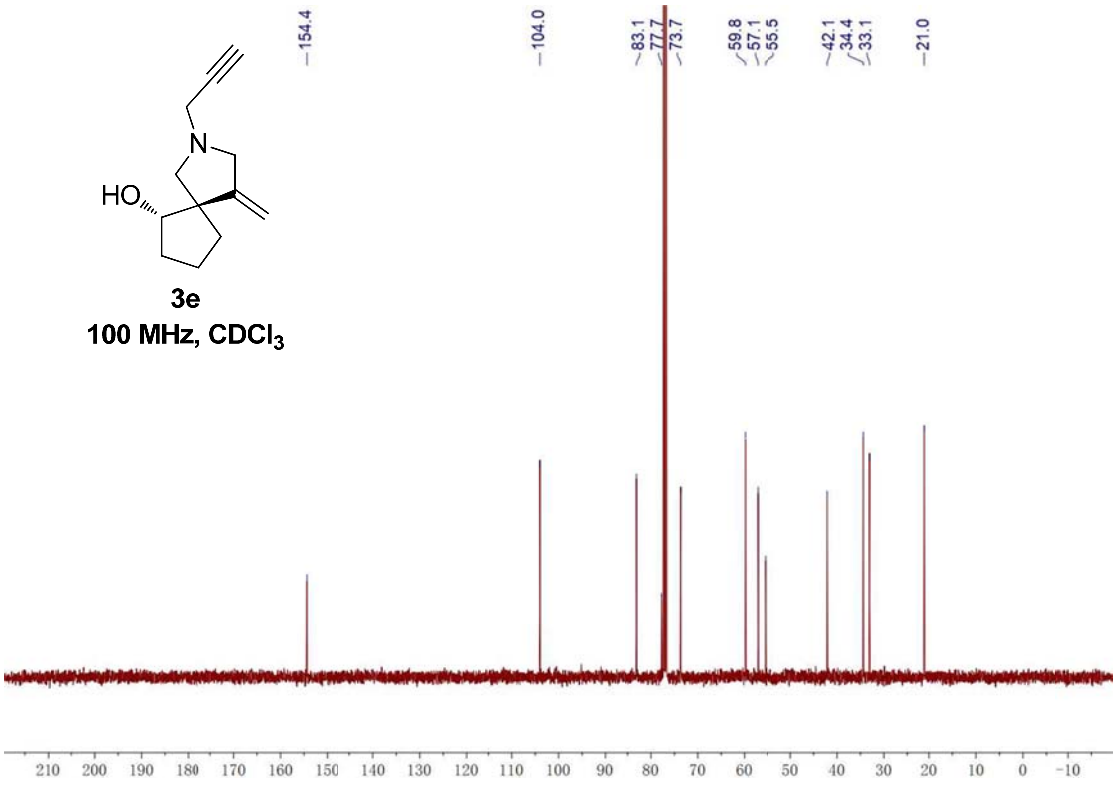
100 MHz, $CDCl_3$


2e
400 MHz, CDCl$_3$
3.4 3.4 3.2 2.9 2.9 2.7 2.7 2.2 2.2 2.2 2.0 2.0 1.9 1.9 1.9 1.9 1.9 1.9 1.7 1.6 1.6 1.6 1.6 1.6 1.6 1.6 1.6 1.5 1.5 1.5 1.5 1.4 1.4 1.4 1.4 1.4 1.4 1.3
4.00 1.00 0.99 0.98 1.86 2.14 3.36 1.20
.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 -1
f1 (ppm)

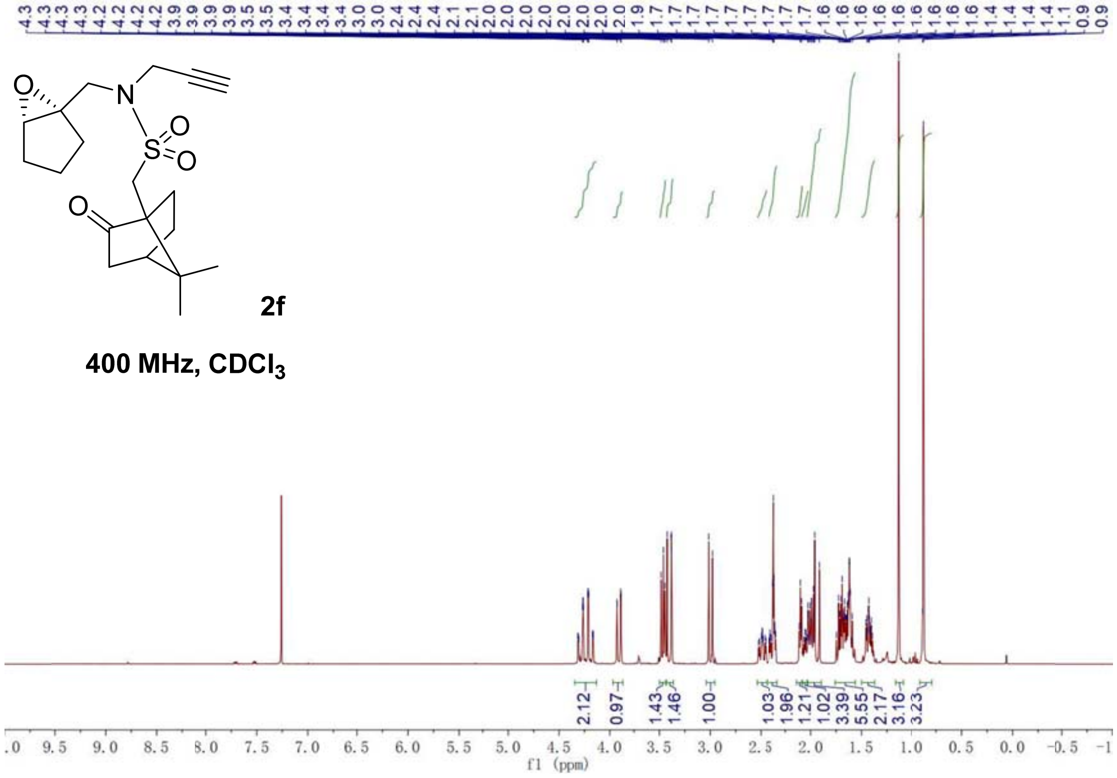

78.6 73.1 66.1 60.9 54.4 42.6 28.2 27.2 19.2
2e
100 MHz, CDCl$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


3e

400 MHz, $CDCl_3$

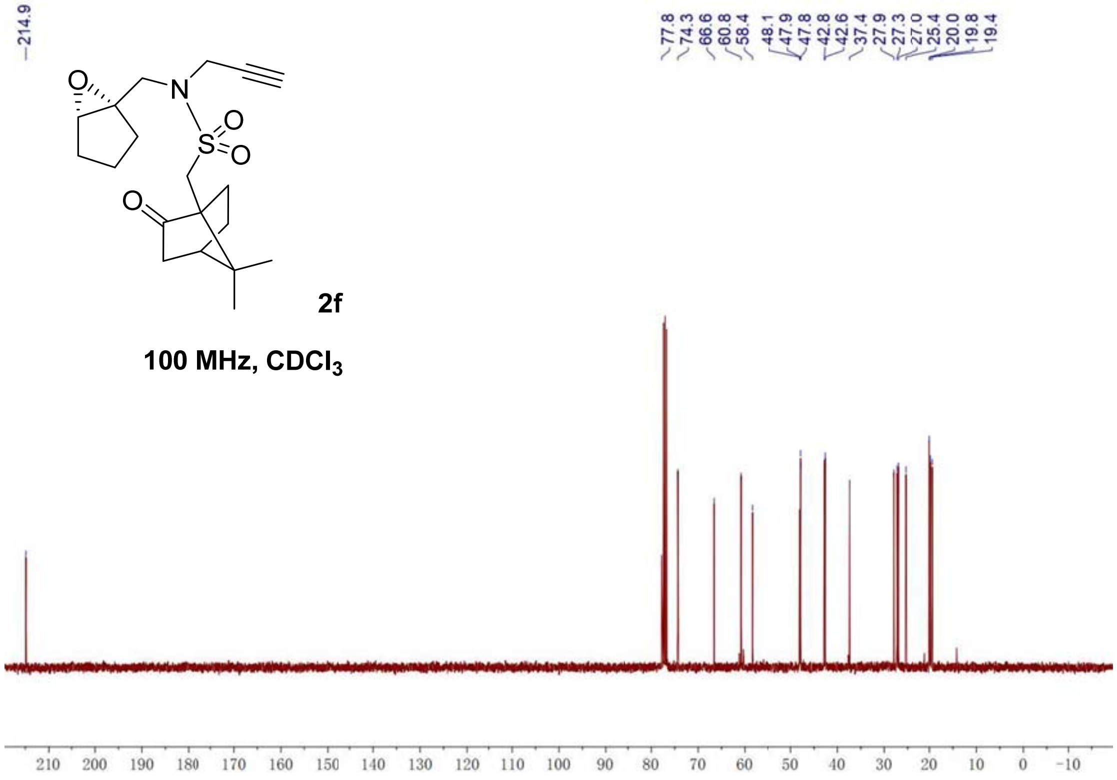

3e

100 MHz, $CDCl_3$



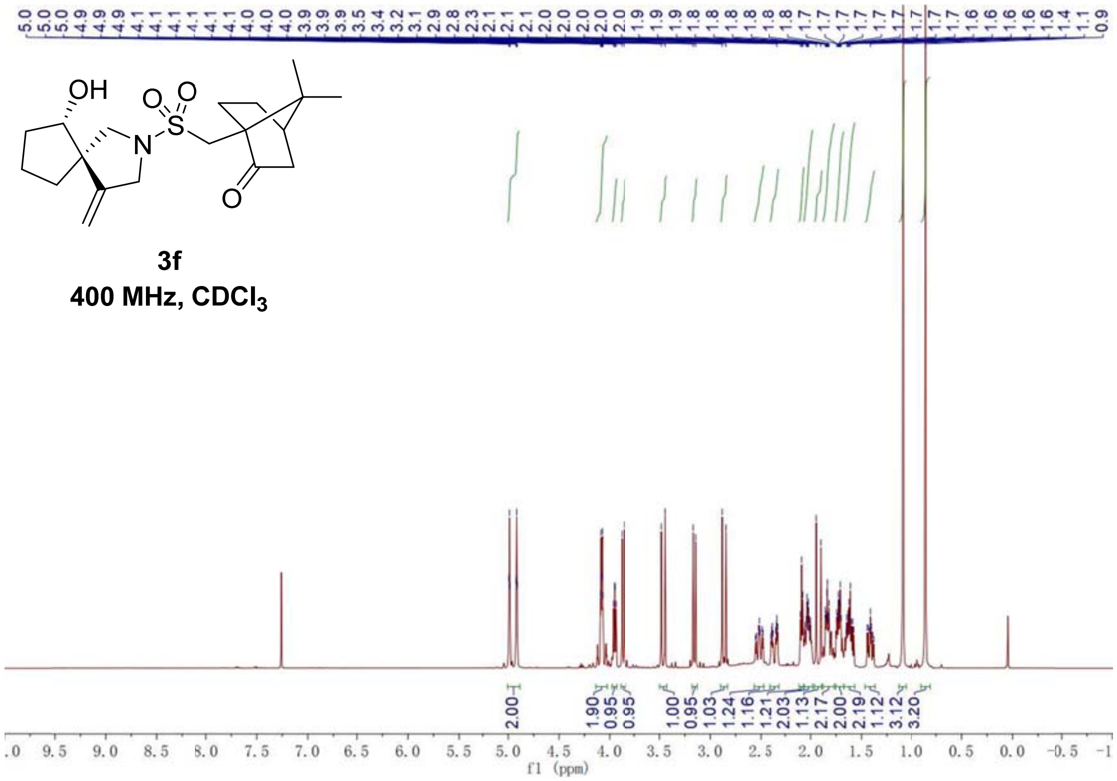
2f

400 MHz, CDCl$_3$

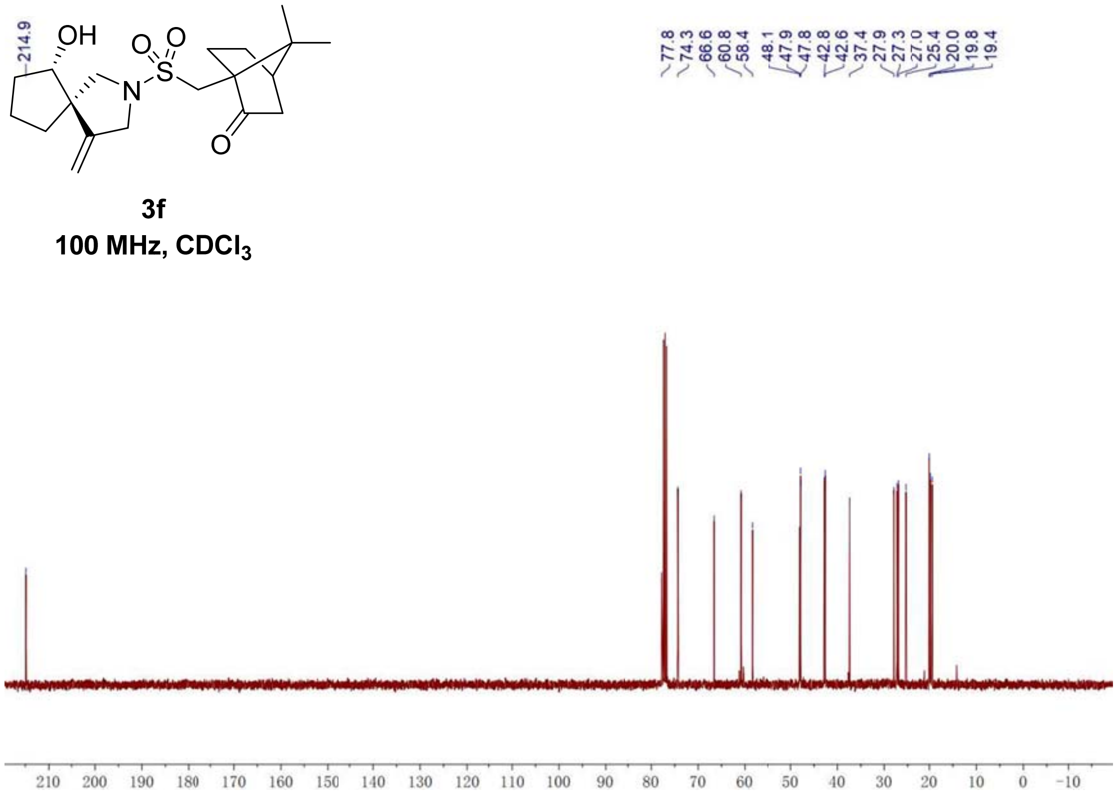


2f

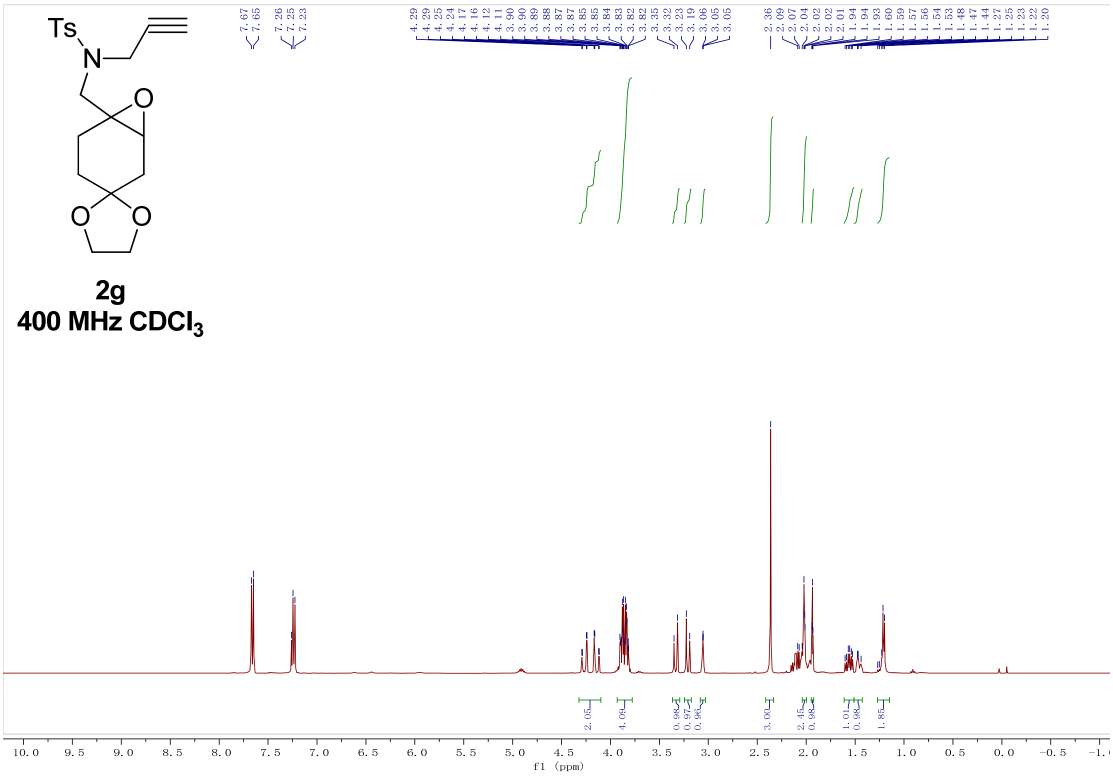
100 MHz, CDCl$_3$

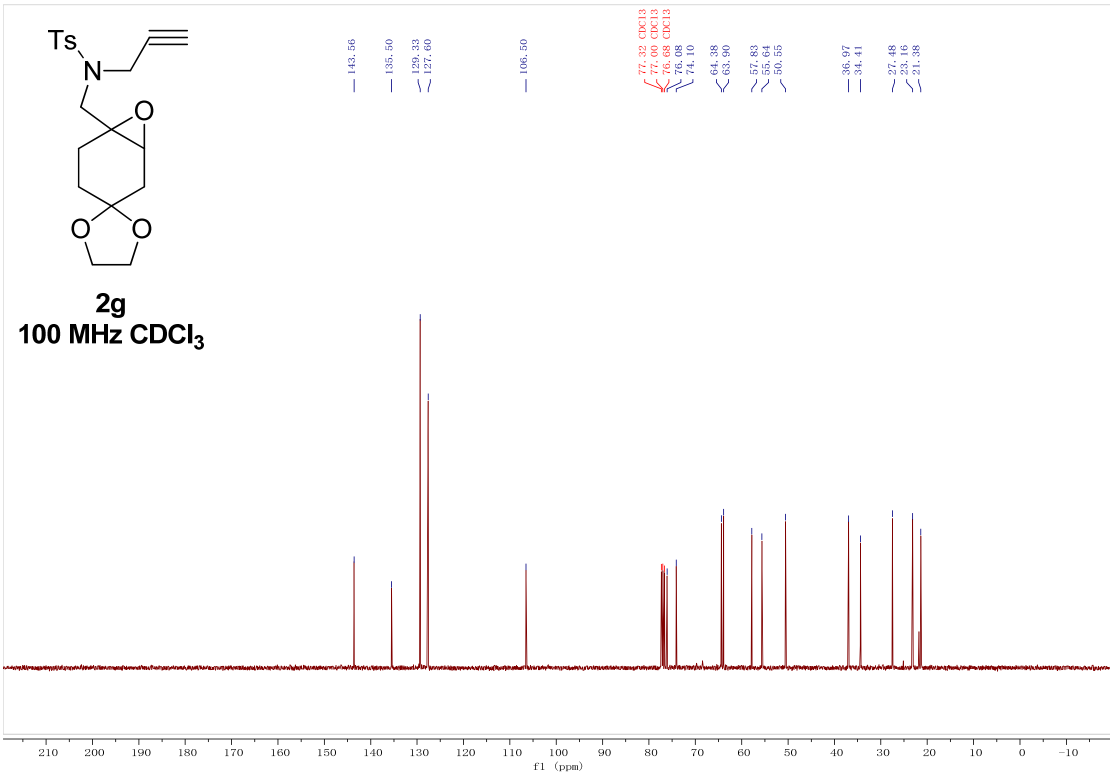


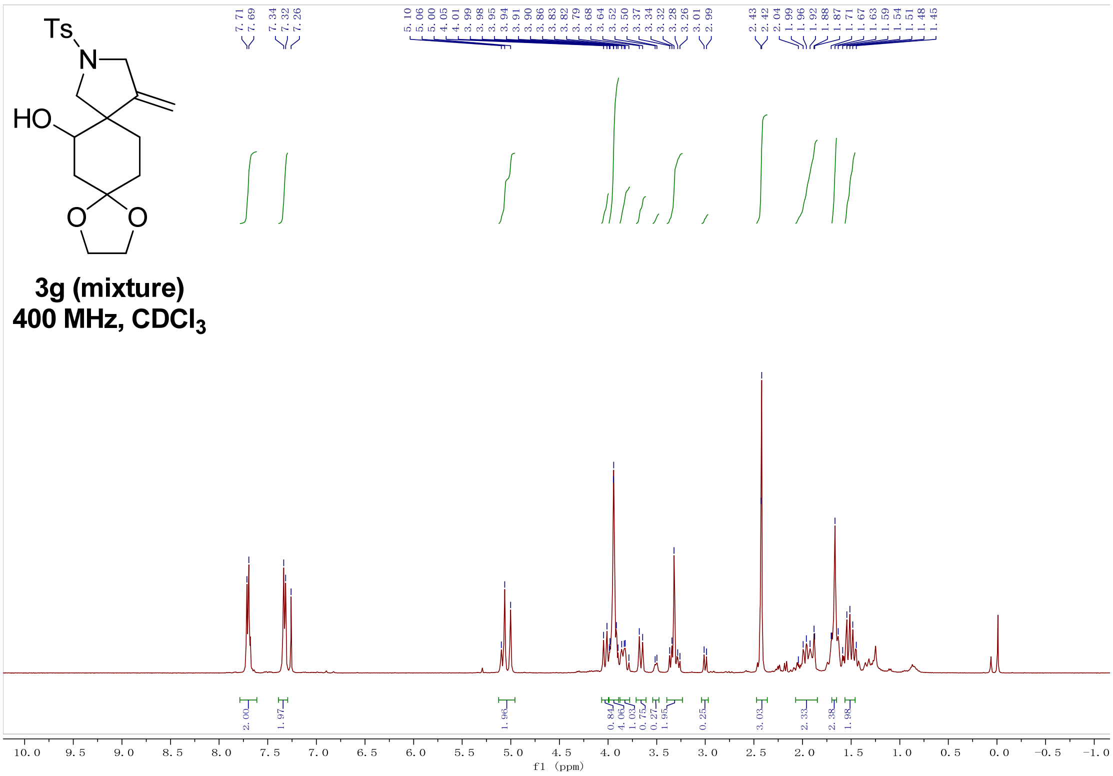
3f
400 MHz, $CDCl_3$

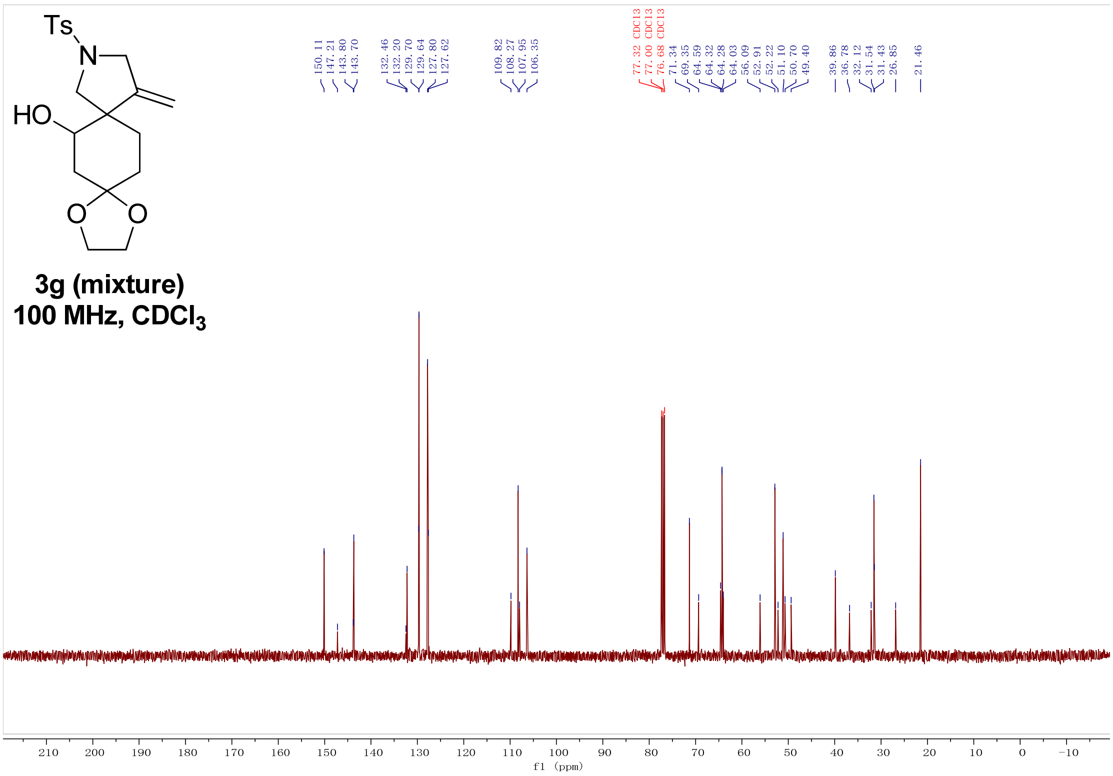


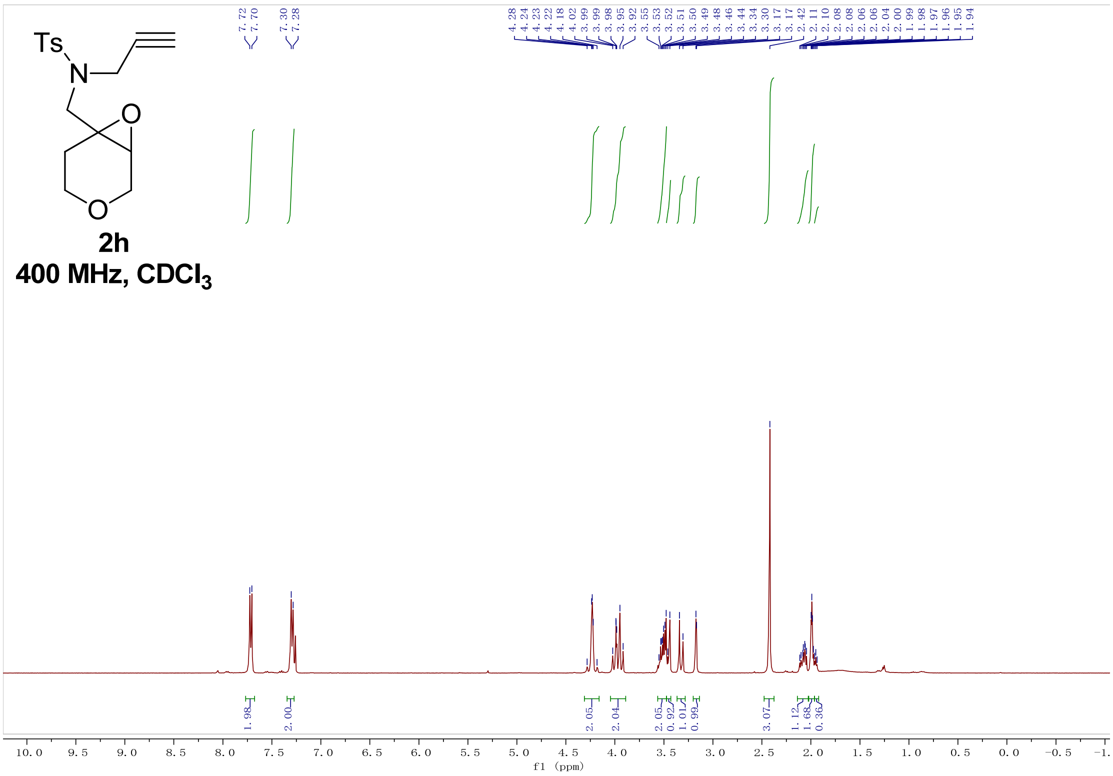
3f
100 MHz, $CDCl_3$


Ts
N
O
O
O
2g
400 MHz CDCl3
7.67
7.65
7.26
7.25
7.23
4.29
4.29
4.25
4.24
4.17
4.16
4.12
4.11
3.90
3.90
3.89
3.88
3.87
3.85
3.85
3.84
3.83
3.82
3.82
3.35
3.32
3.23
3.19
3.06
3.05
3.05
2.36
2.09
2.07
2.04
2.02
2.02
2.01
1.94
1.94
1.93
1.60
1.59
1.57
1.56
1.54
1.53
1.48
1.47
1.44
1.27
1.25
1.23
1.22
1.20
2.05
4.09
0.98
0.97
0.96
3.00
2.45
0.98
1.01
0.98
1.85
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
-1.0
f1 (ppm)

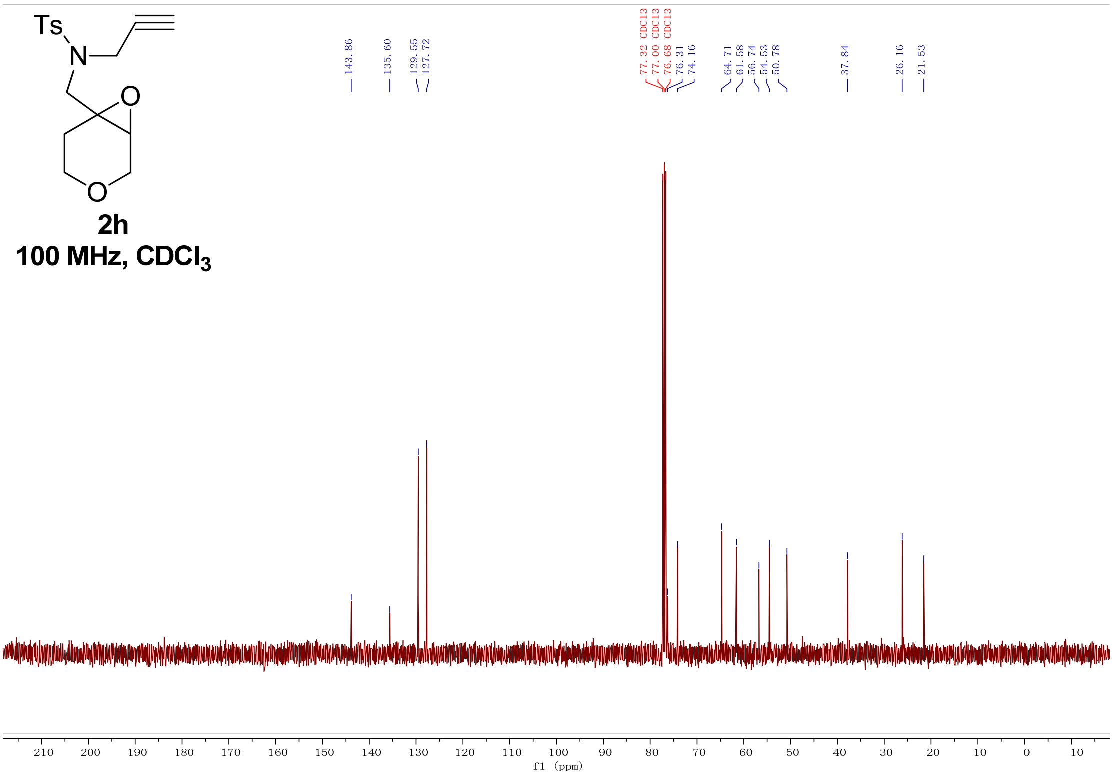

Ts
N
O
O
O
2g
100 MHz CDCl3
143.56
135.50
129.33
127.60
106.50
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.08
74.10
64.38
63.90
57.83
55.64
50.55
36.97
34.41
27.48
23.16
21.38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ts
N
HO
O
O
3g (mixture)
400 MHz, CDCl$_3$
7.71
7.69
7.34
7.32
7.26
5.10
5.06
5.00
4.05
4.01
3.99
3.98
3.95
3.94
3.91
3.90
3.86
3.83
3.82
3.79
3.68
3.64
3.52
3.50
3.37
3.34
3.32
3.28
3.26
3.01
2.99
2.43
2.42
2.04
1.99
1.96
1.92
1.88
1.87
1.71
1.67
1.63
1.59
1.54
1.51
1.48
1.45
2.00
1.97
1.96
0.84
4.06
1.03
0.75
0.27
1.95
0.25
3.03
2.33
2.38
1.98
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
−1.0
f1 (ppm)

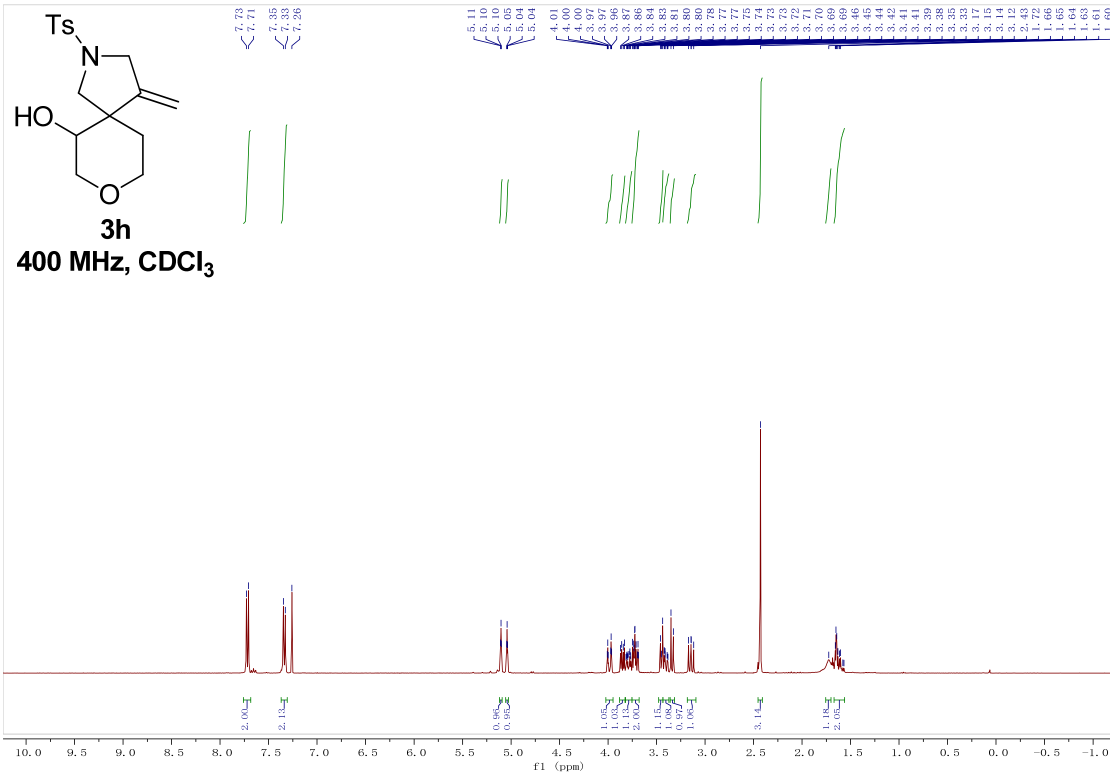

Ts
N
HO
O
O
3g (mixture)
100 MHz, CDCl$_3$
150.11
147.21
143.80
143.70
132.46
132.20
129.70
129.64
127.80
127.62
109.82
108.27
107.95
106.35
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
71.34
69.35
64.59
64.32
64.28
64.03
56.09
52.91
52.22
51.10
50.70
49.40
39.86
36.78
32.12
31.54
31.43
26.85
21.46
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

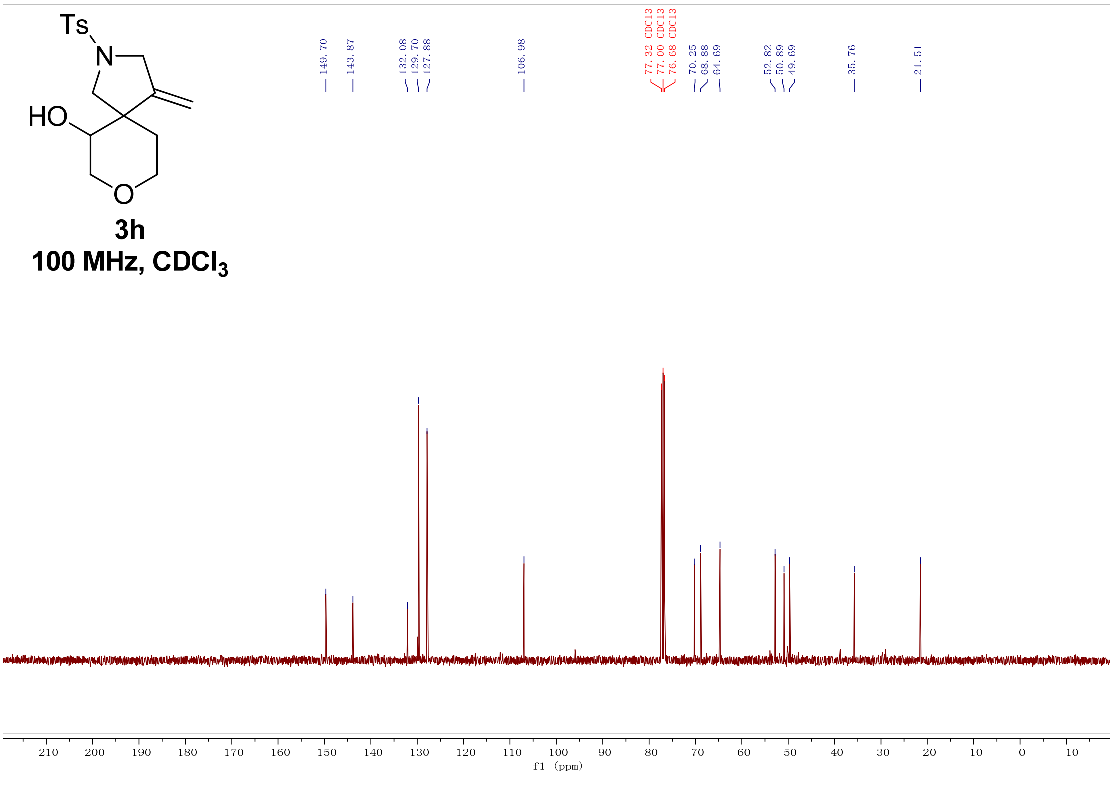


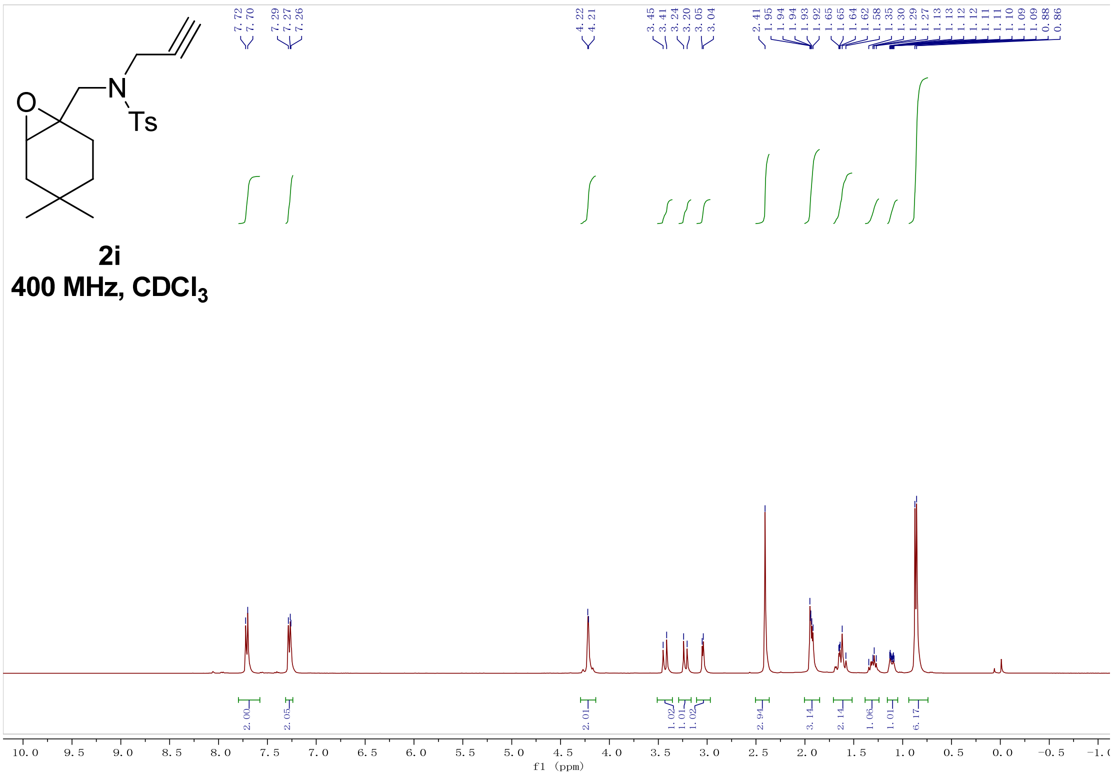
Ts
N
O
O
2h
400 MHz, CDCl$_3$
7.72
7.70
7.30
7.28
4.28
4.24
4.23
4.22
4.18
4.02
3.99
3.99
3.98
3.95
3.92
3.55
3.53
3.52
3.51
3.50
3.49
3.48
3.46
3.44
3.34
3.30
3.17
3.17
2.42
2.11
2.10
2.08
2.08
2.06
2.06
2.04
2.00
1.99
1.98
1.97
1.96
1.95
1.94
1.98
2.00
2.05
2.04
2.05
0.92
1.01
0.99
3.07
1.12
1.68
0.36
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
-1.
f1 (ppm)

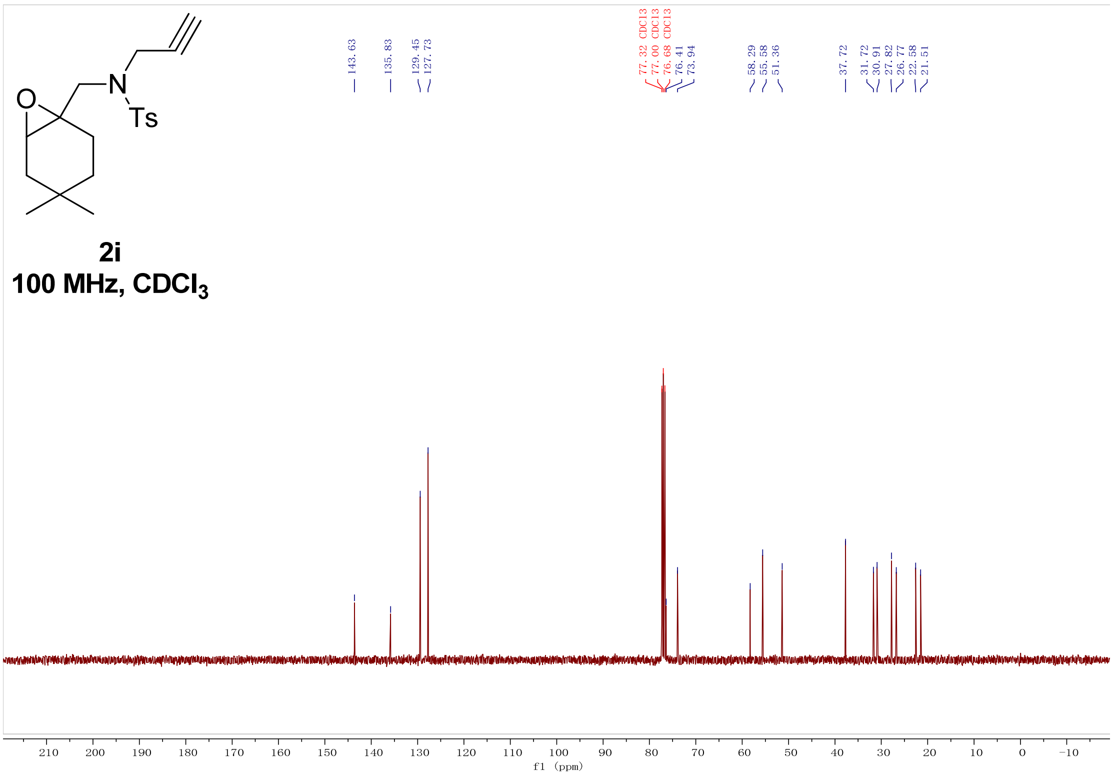


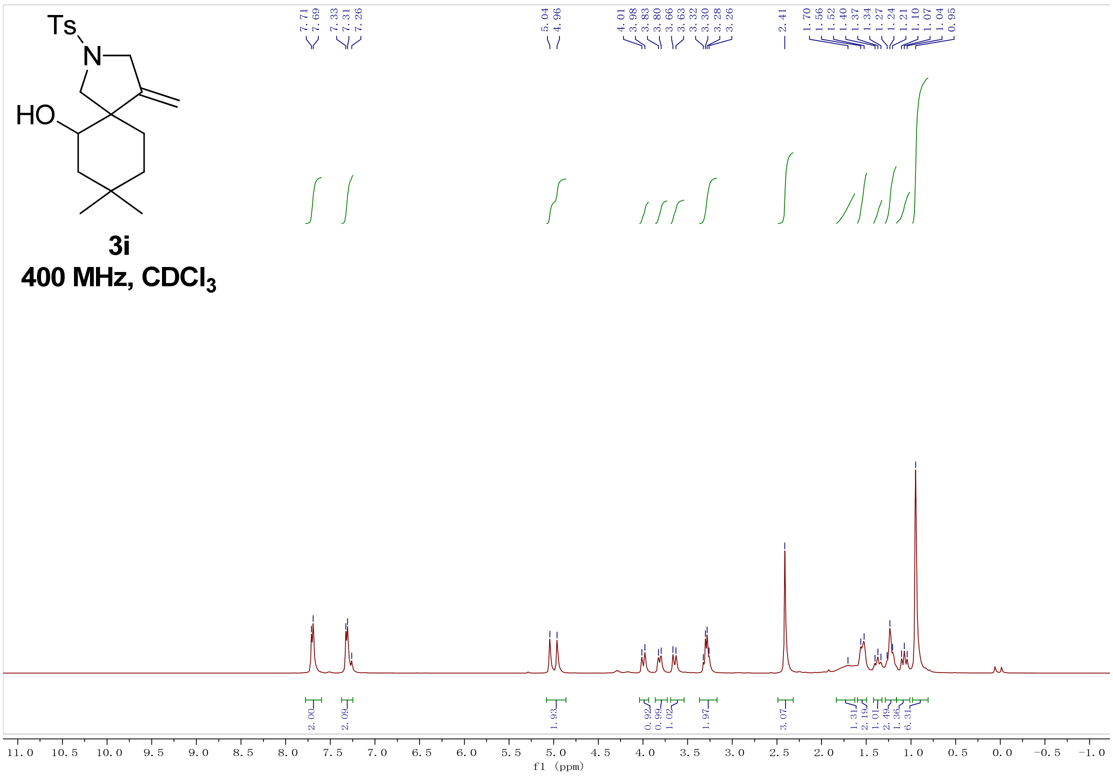
Ts
N
O
O
2h
100 MHz, CDCl$_3$
143.86
135.60
129.55
127.72
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.31
74.16
64.71
61.58
56.74
54.53
50.78
37.84
26.16
21.53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ts
N
HO
O
3h
400 MHz, CDCl$_3$
7.73
7.71
7.35
7.33
7.26
5.11
5.10
5.10
5.05
5.04
5.04
4.01
4.00
4.00
3.97
3.97
3.96
3.87
3.86
3.84
3.83
3.81
3.80
3.80
3.78
3.77
3.77
3.75
3.74
3.73
3.73
3.72
3.71
3.70
3.69
3.69
3.46
3.45
3.44
3.42
3.41
3.41
3.39
3.38
3.35
3.33
3.17
3.15
3.14
3.12
2.43
1.72
1.66
1.65
1.64
1.63
1.61
2.00
2.13
0.96
0.95
1.05
1.03
1.13
2.00
1.15
1.08
0.97
1.06
3.14
1.18
2.05
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
-1.0
f1 (ppm)


Ts
N
HO
O
3h
100 MHz, CDCl$_3$
149.70
143.87
132.08
129.70
127.88
106.98
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
70.25
68.88
64.69
52.82
50.89
49.69
35.76
21.51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

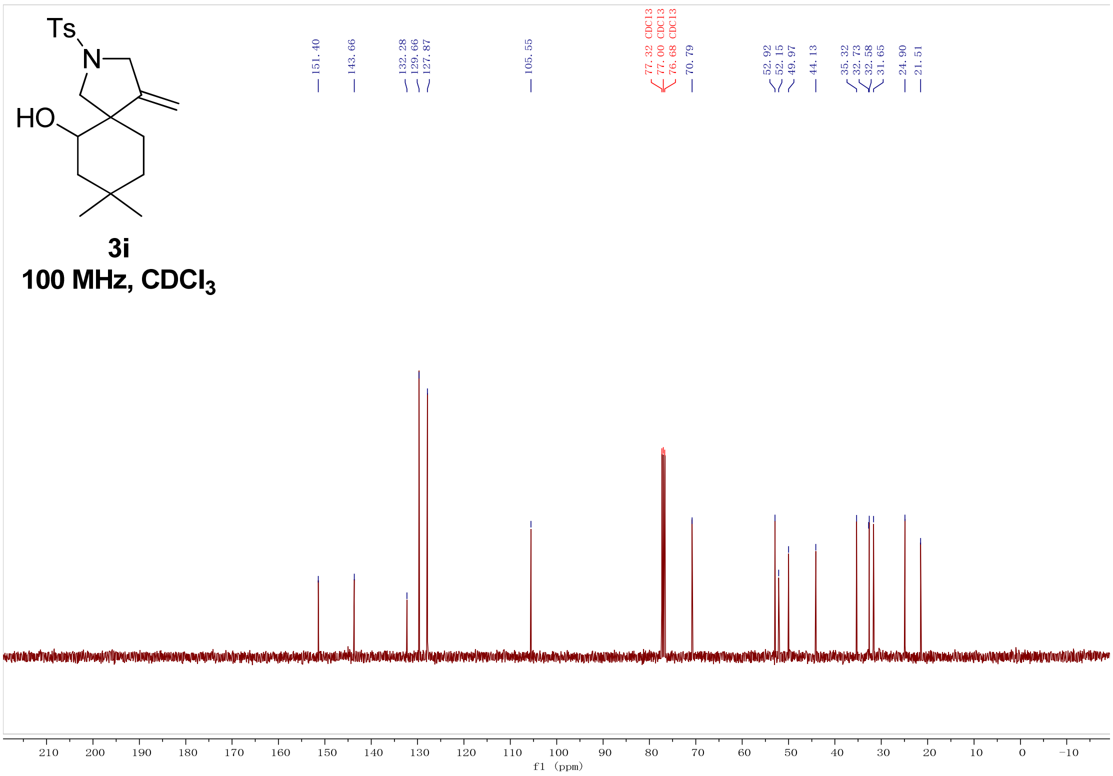

O
N
Ts
2i
400 MHz, CDCl$_3$
7.72
7.70
7.29
7.27
7.26
4.22
4.21
3.45
3.41
3.24
3.20
3.05
3.04
2.41
1.95
1.94
1.94
1.93
1.92
1.65
1.65
1.64
1.62
1.58
1.35
1.30
1.29
1.27
1.13
1.13
1.12
1.11
1.11
1.10
1.09
1.09
0.88
0.86
2.00
2.05
2.01
1.02
1.01
1.02
2.94
3.14
2.14
1.06
1.01
6.17
10.0
9.5
9.0
8.5
8.0
7.5
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
-1.0
f1 (ppm)


O
N
Ts
2i
100 MHz, CDCl$_3$
143.63
135.83
129.45
127.73
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.41
73.94
58.29
55.58
51.36
37.72
31.72
30.91
27.82
26.77
22.58
21.51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



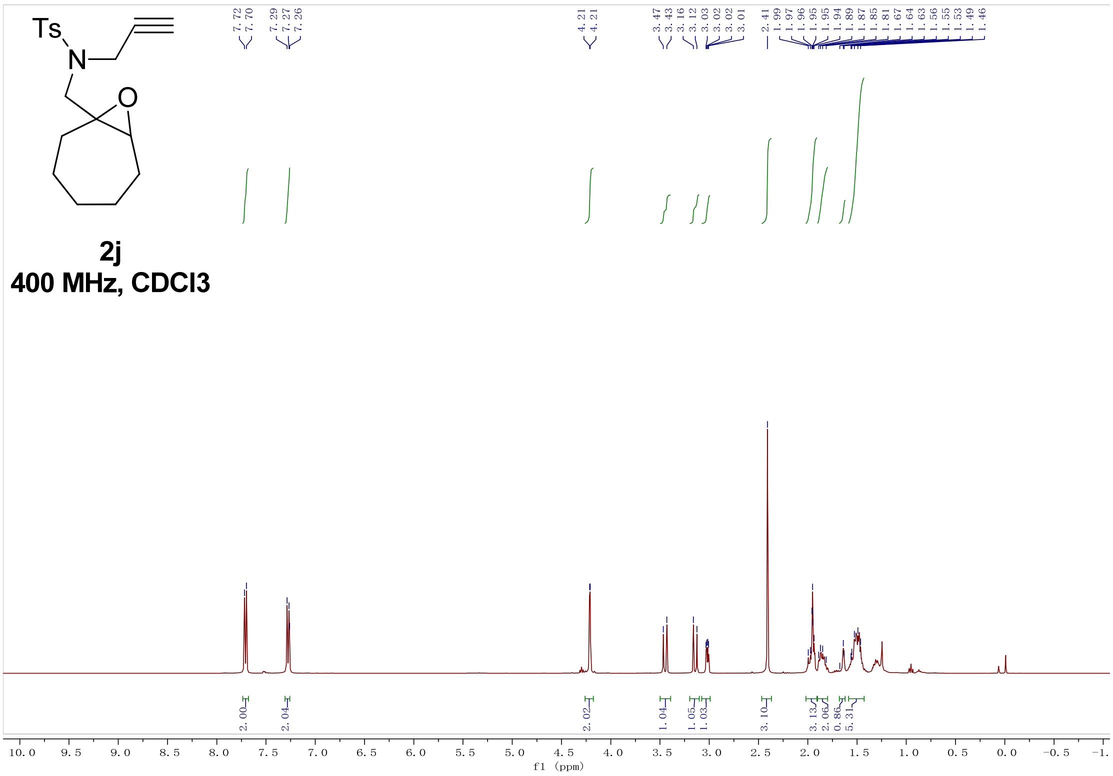
3i

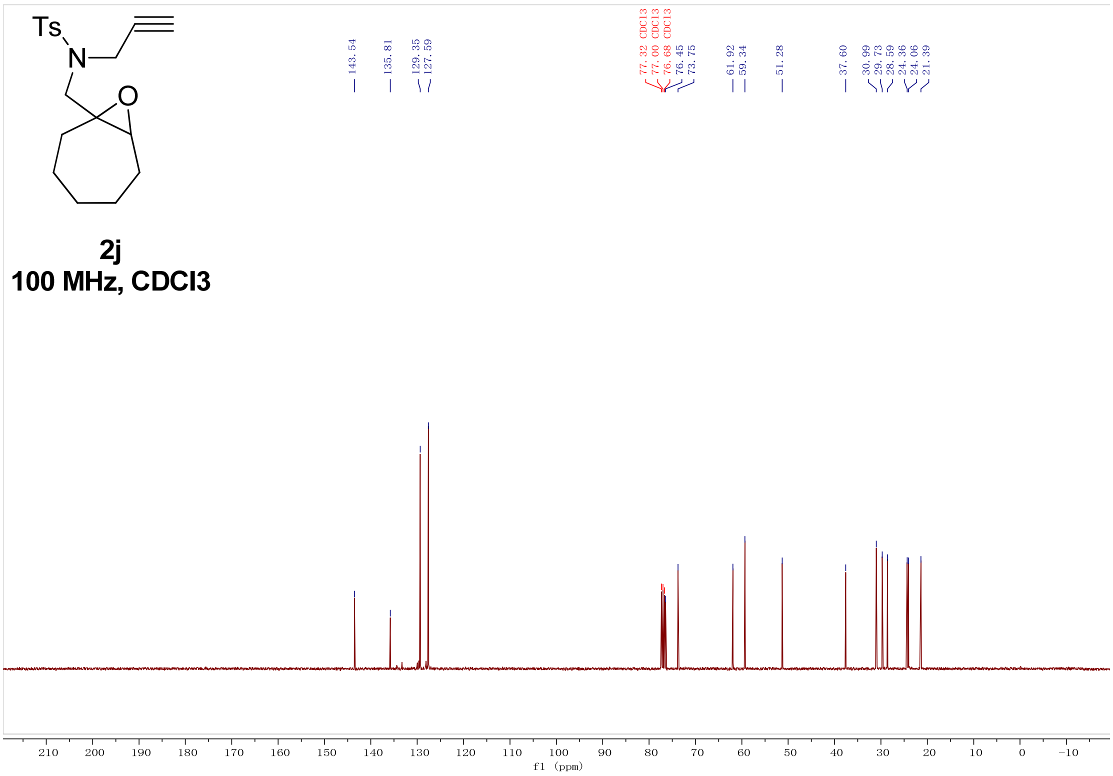
400 MHz, $CDCl_3$

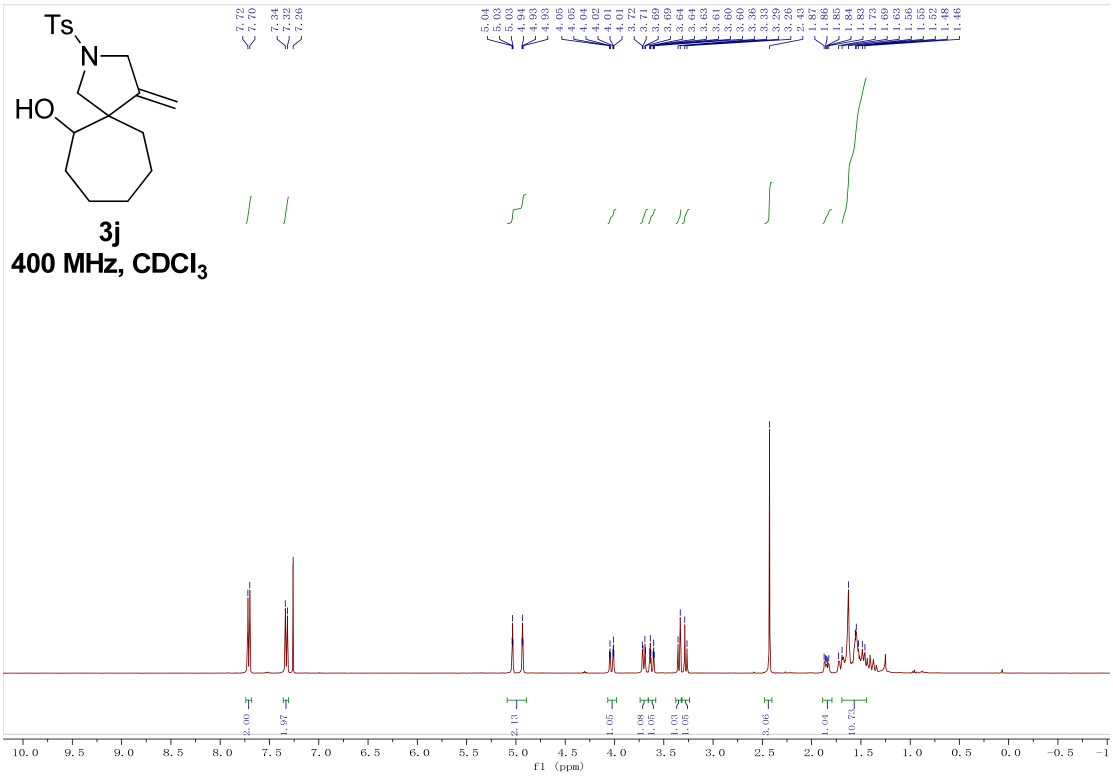


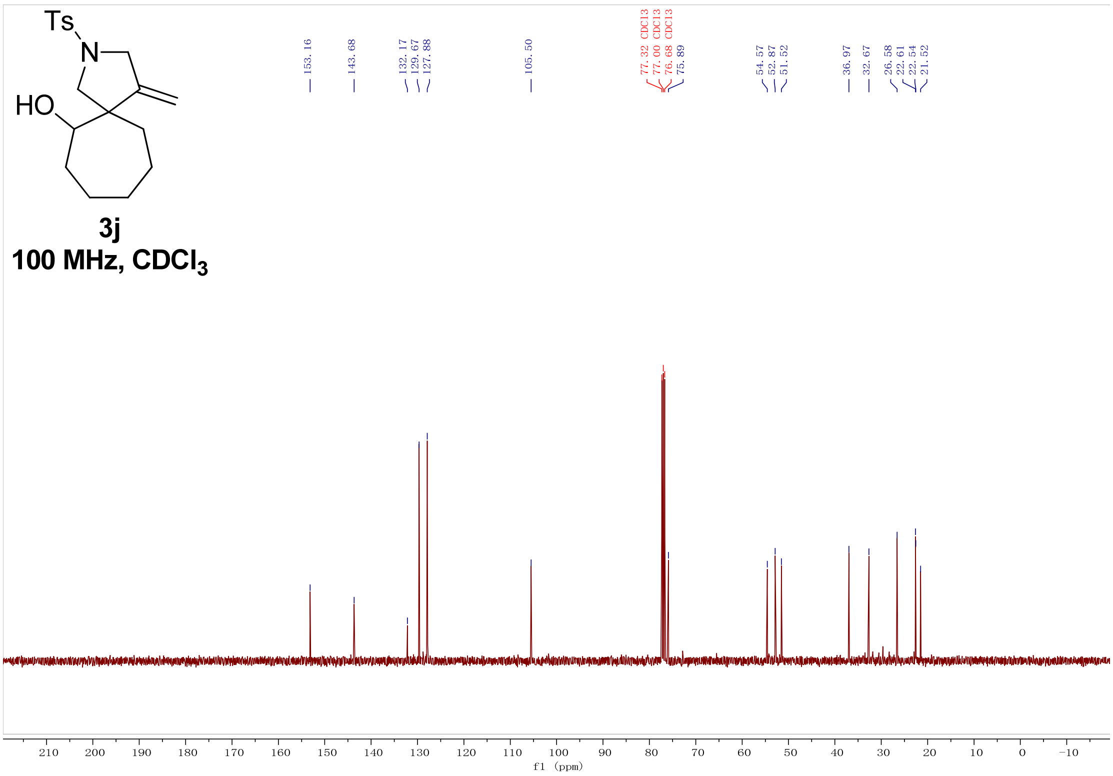
3i

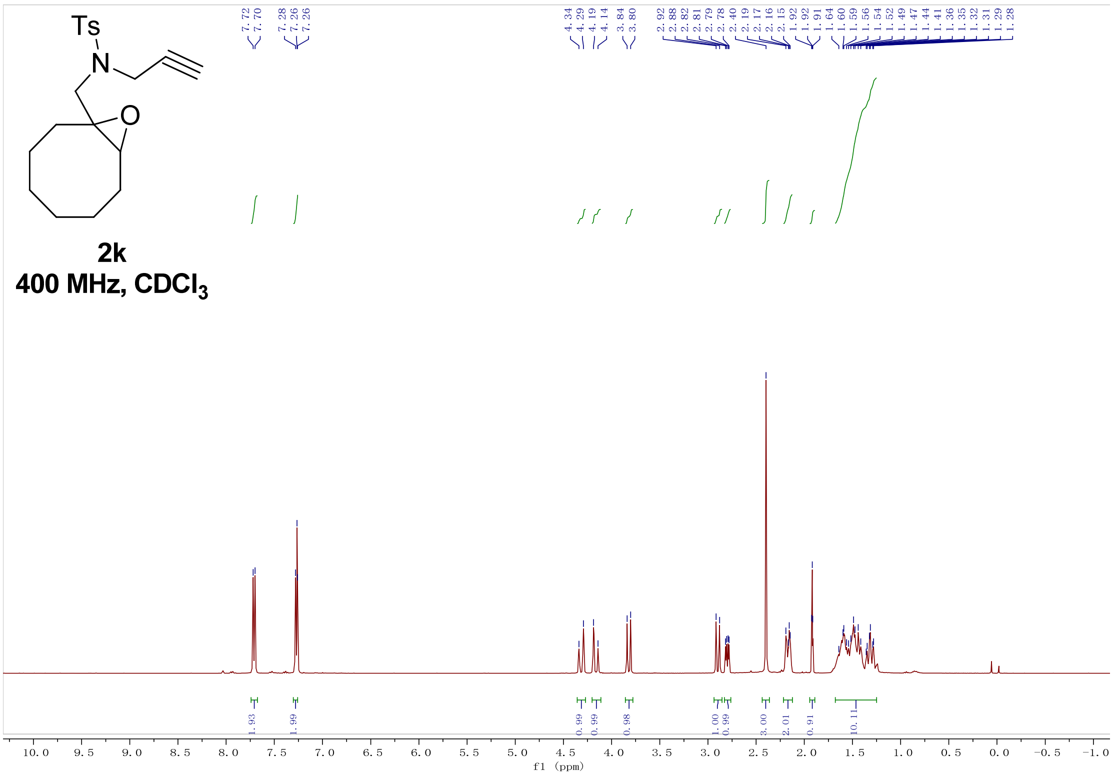
100 MHz, $CDCl_3$

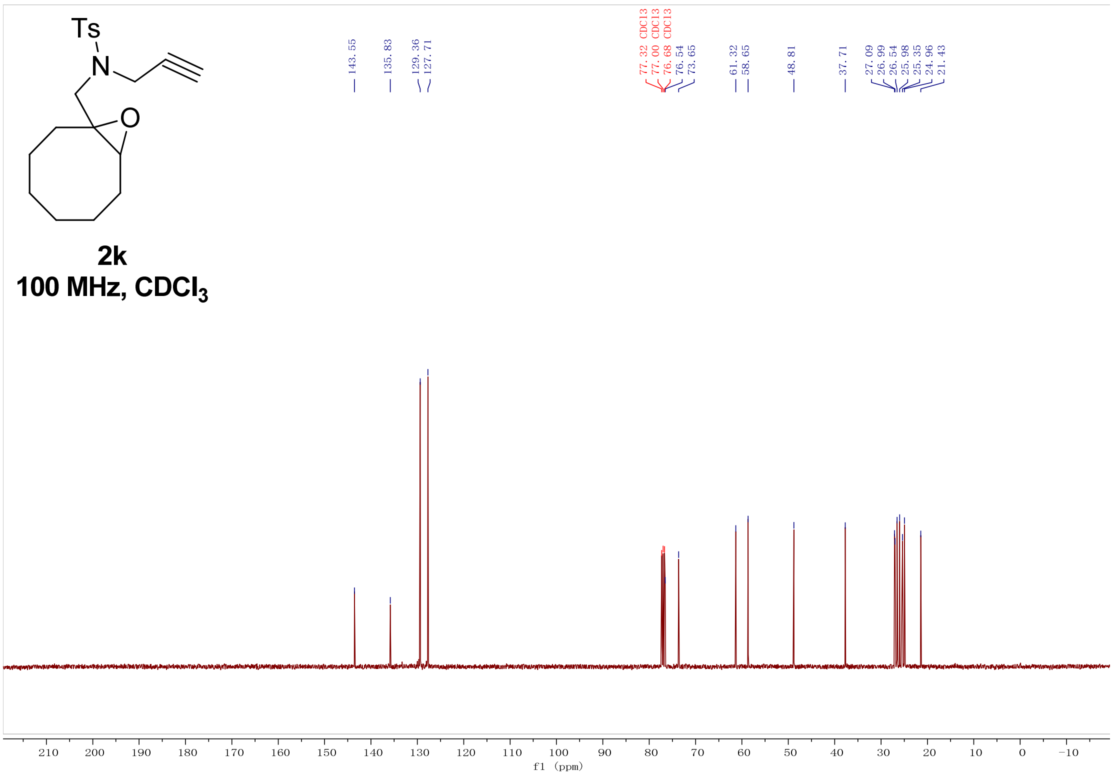

Ts
N
O
2j
400 MHz, CDCl3
7.72
7.70
7.29
7.27
7.26
4.21
4.21
3.47
3.43
3.16
3.12
3.03
3.02
3.02
3.01
2.41
1.99
1.97
1.96
1.95
1.95
1.94
1.89
1.87
1.85
1.81
1.67
1.64
1.63
1.56
1.55
1.53
1.49
1.46
2.00
2.04
2.02
1.04
1.05
1.03
3.10
3.13
2.06
0.86
5.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

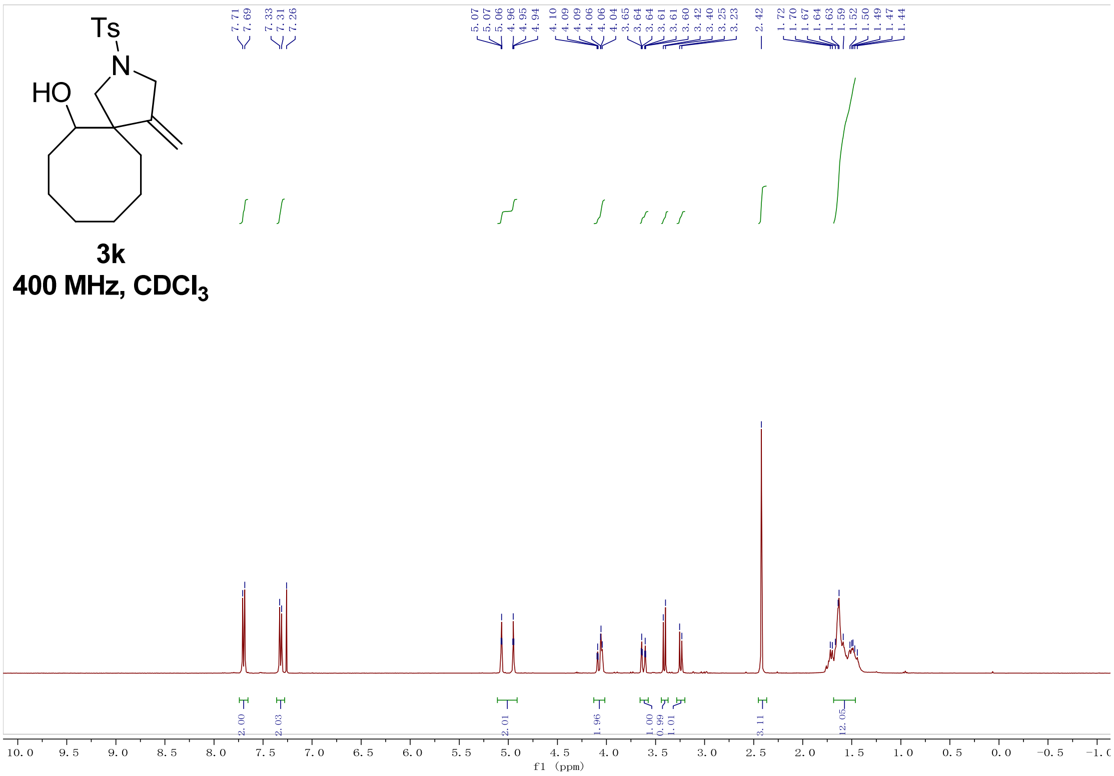

Ts
N
O
2j
100 MHz, CDCl3
143.54
135.81
129.35
127.59
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.45
73.75
61.92
59.34
51.28
37.60
30.99
29.73
28.59
24.36
24.06
21.39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

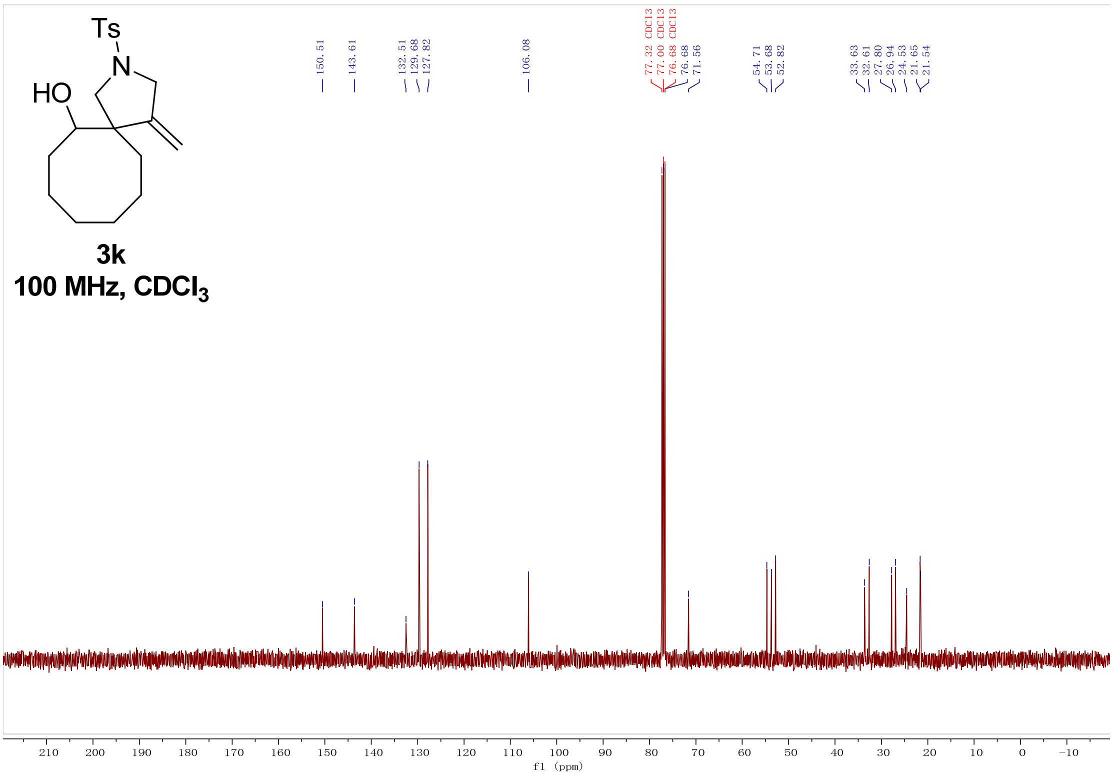

Ts
N
HO
3j
400 MHz, CDCl$_3$
7.72
7.70
7.34
7.32
7.26
5.04
5.03
5.03
4.94
4.93
4.93
4.05
4.05
4.04
4.02
4.01
4.01
3.72
3.71
3.69
3.69
3.64
3.64
3.63
3.61
3.60
3.60
3.36
3.33
3.29
3.26
2.43
1.87
1.86
1.85
1.84
1.83
1.73
1.69
1.63
1.56
1.55
1.52
1.48
1.46
2.00
1.97
2.13
1.05
1.08
1.05
1.03
1.05
3.06
1.04
10.73
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 −1
f1 (ppm)

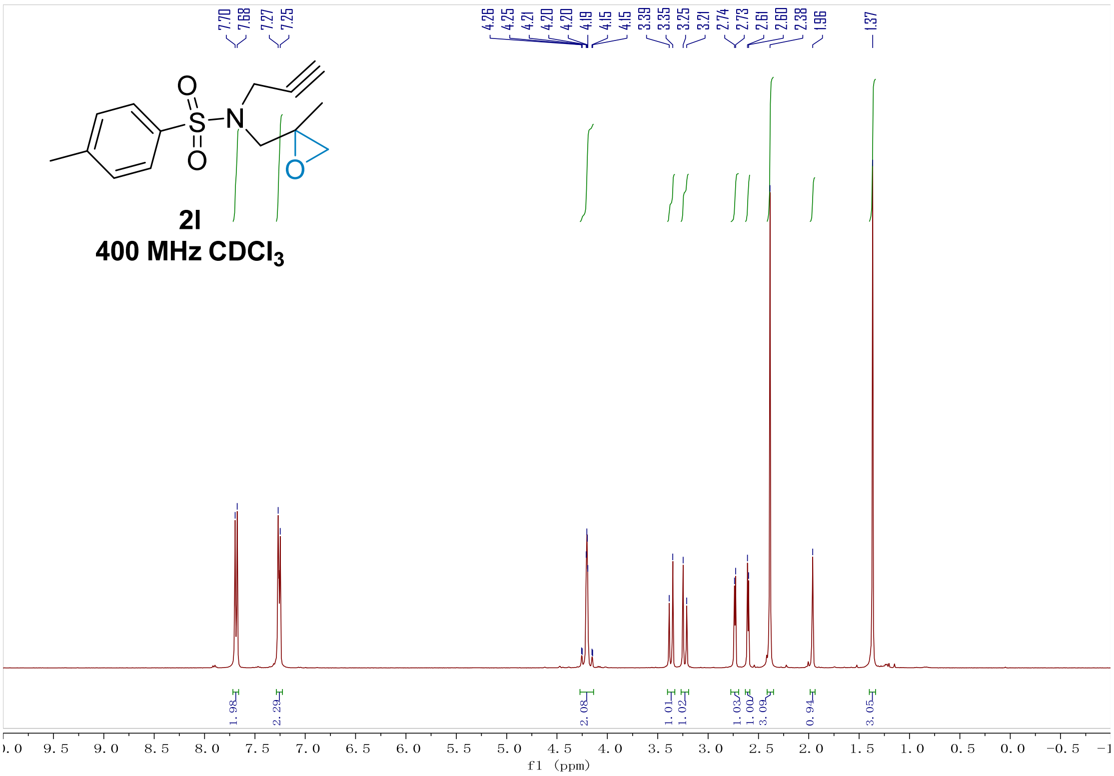

Ts
N
HO
3j
100 MHz, CDCl$_3$
153.16
143.68
132.17
129.67
127.88
105.50
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
75.89
54.57
52.87
51.52
36.97
32.67
26.58
22.61
22.54
21.52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


Ts
N
O
2k
400 MHz, CDCl3
7.72
7.70
7.28
7.26
7.26
4.34
4.29
4.19
4.14
3.84
3.80
2.92
2.88
2.82
2.81
2.79
2.78
2.40
2.19
2.17
2.16
2.15
1.92
1.92
1.91
1.64
1.60
1.59
1.56
1.54
1.52
1.49
1.47
1.44
1.41
1.36
1.35
1.32
1.31
1.29
1.28
1.93
1.99
0.99
0.99
0.98
1.00
0.99
3.00
2.01
0.91
10.11
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
-1.0
f1 (ppm)

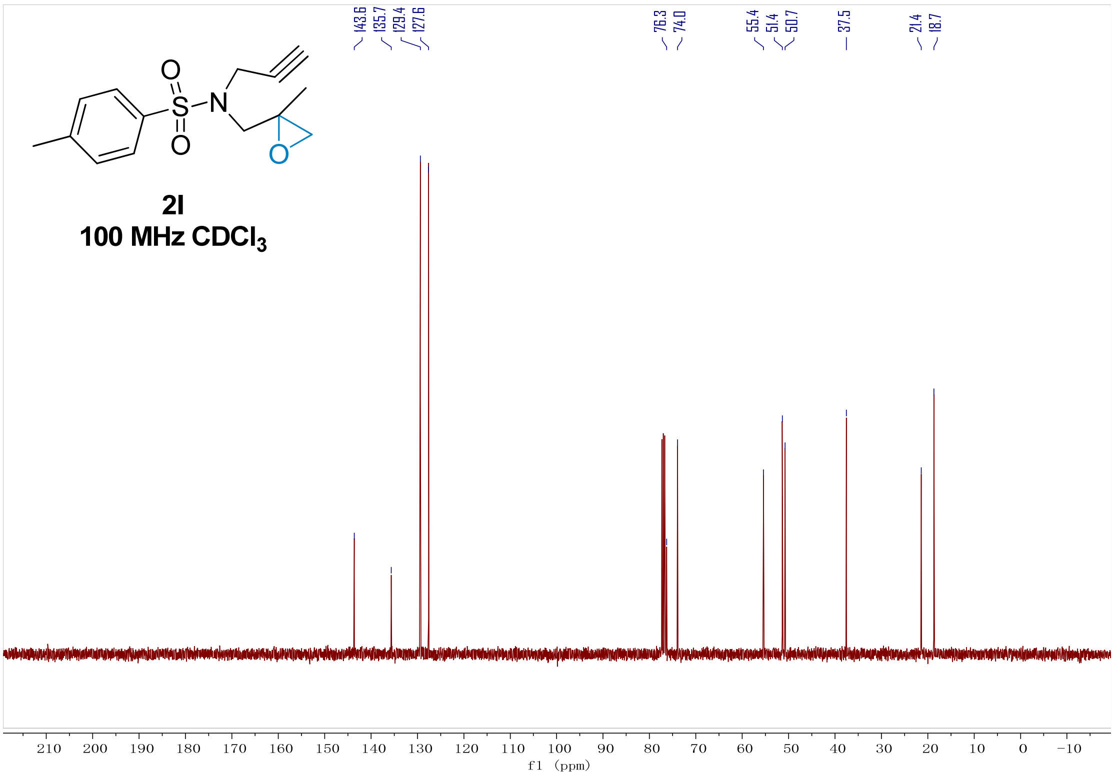

Ts
N
O
2k
100 MHz, CDCl3
143.55
135.83
129.36
127.71
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.54
73.65
61.32
58.65
48.81
37.71
27.09
26.99
26.54
25.98
25.35
24.96
21.43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


3k
400 MHz, CDCl$_3$

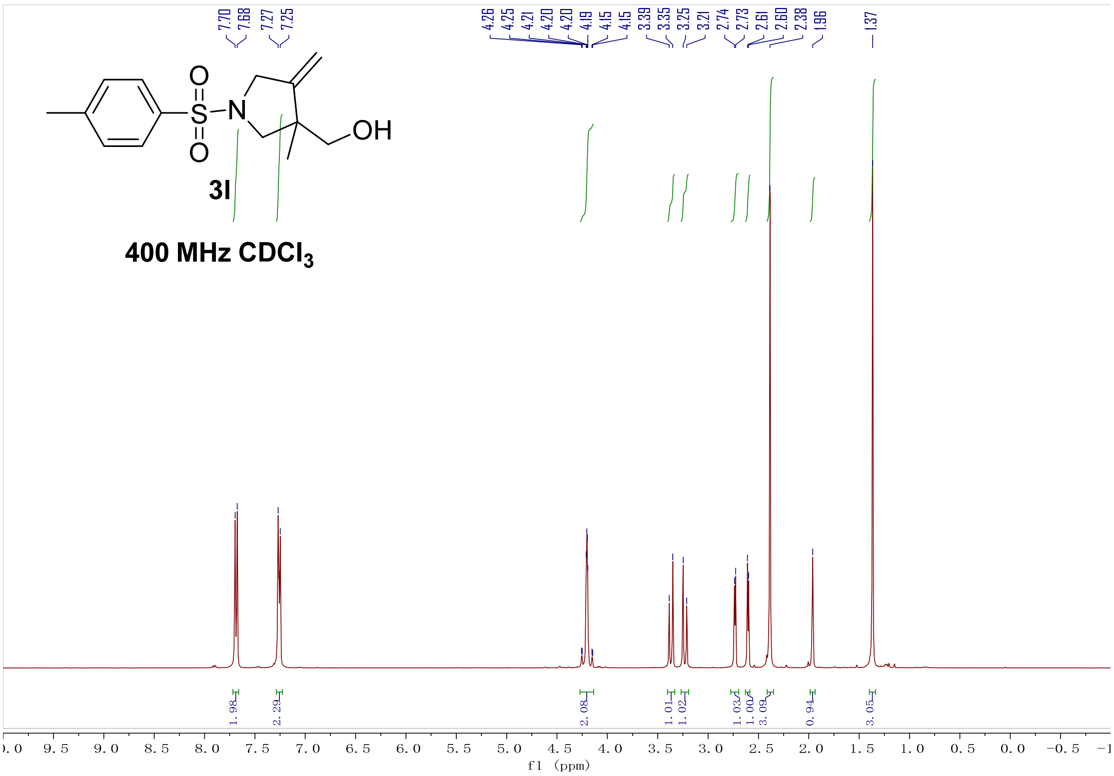

3k
100 MHz, CDCl$_3$

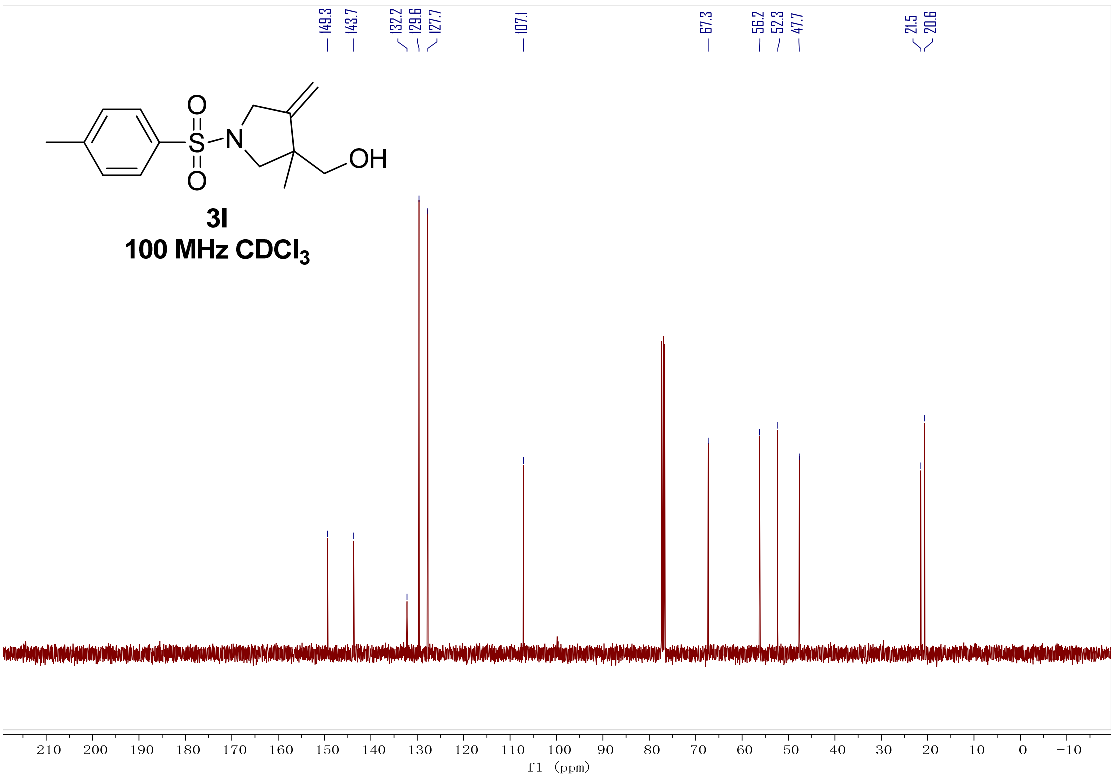


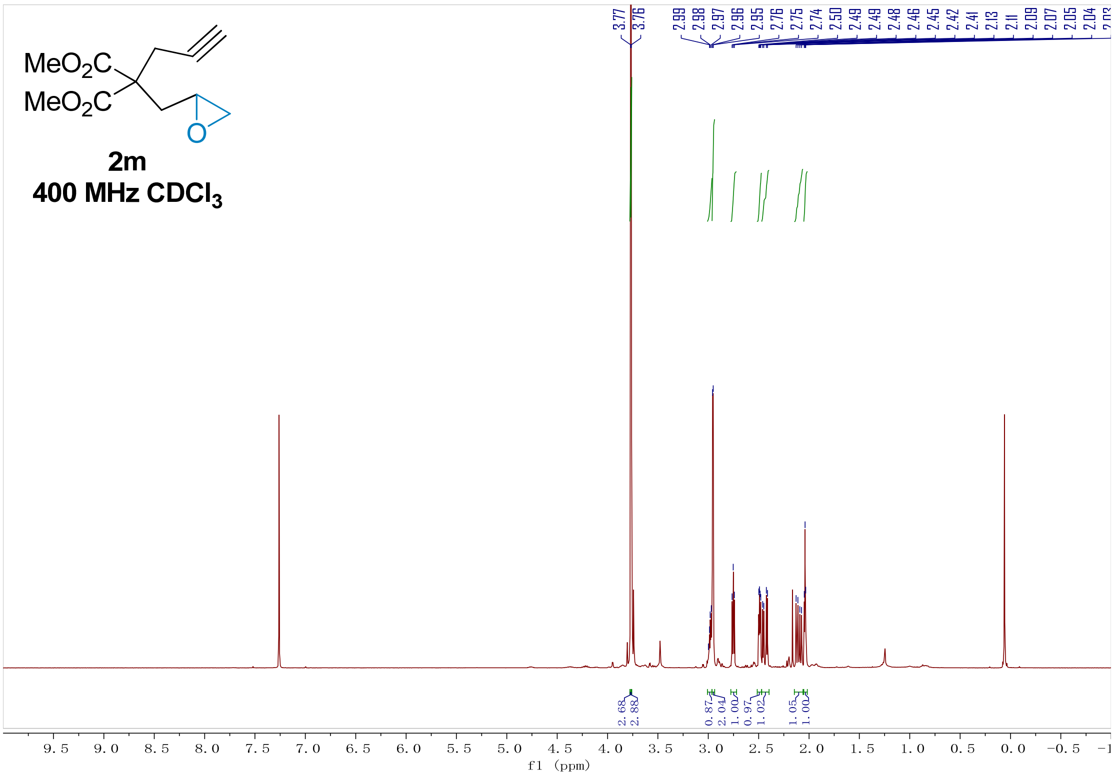
2l
400 MHz $CDCl_3$

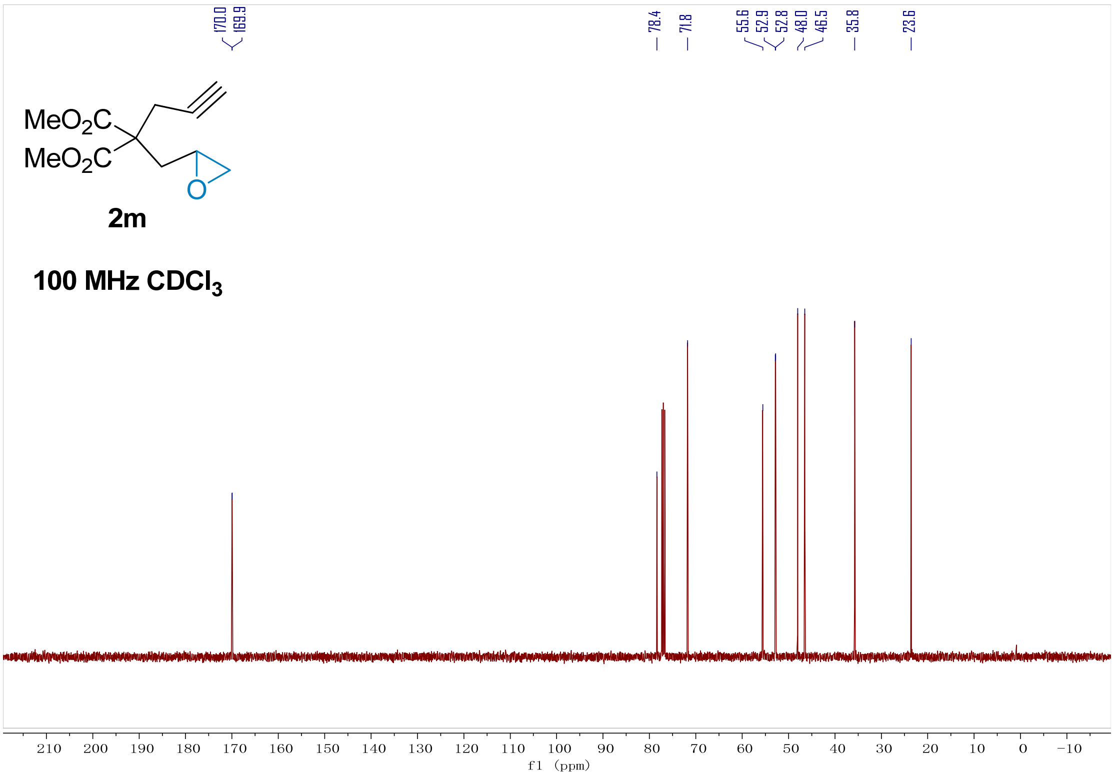


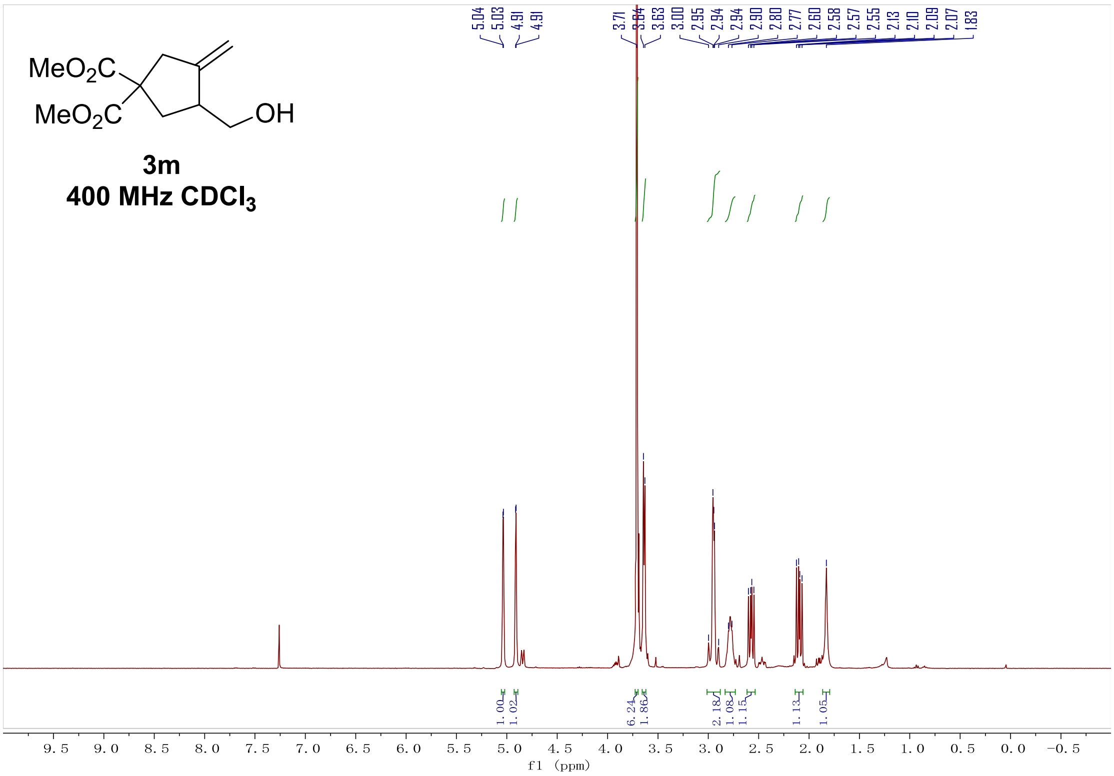
2l
100 MHz $CDCl_3$

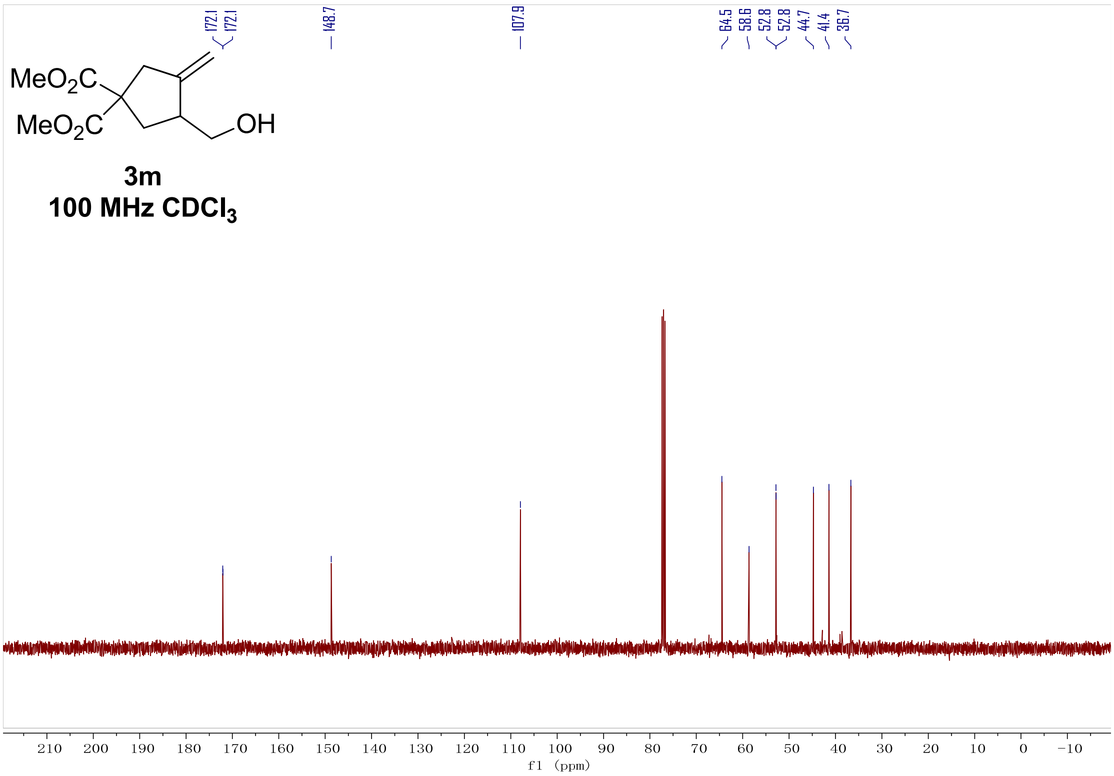

7.70
7.68
7.27
7.25
4.26
4.25
4.21
4.20
4.20
4.19
4.15
4.15
3.39
3.35
3.25
3.21
2.74
2.73
2.61
2.60
2.38
1.96
1.37
O
S
O
N
OH
3l
400 MHz CDCl$_3$
1.98
2.29
2.08
1.01
1.02
1.03
1.00
3.09
0.94
3.05
f1 (ppm)

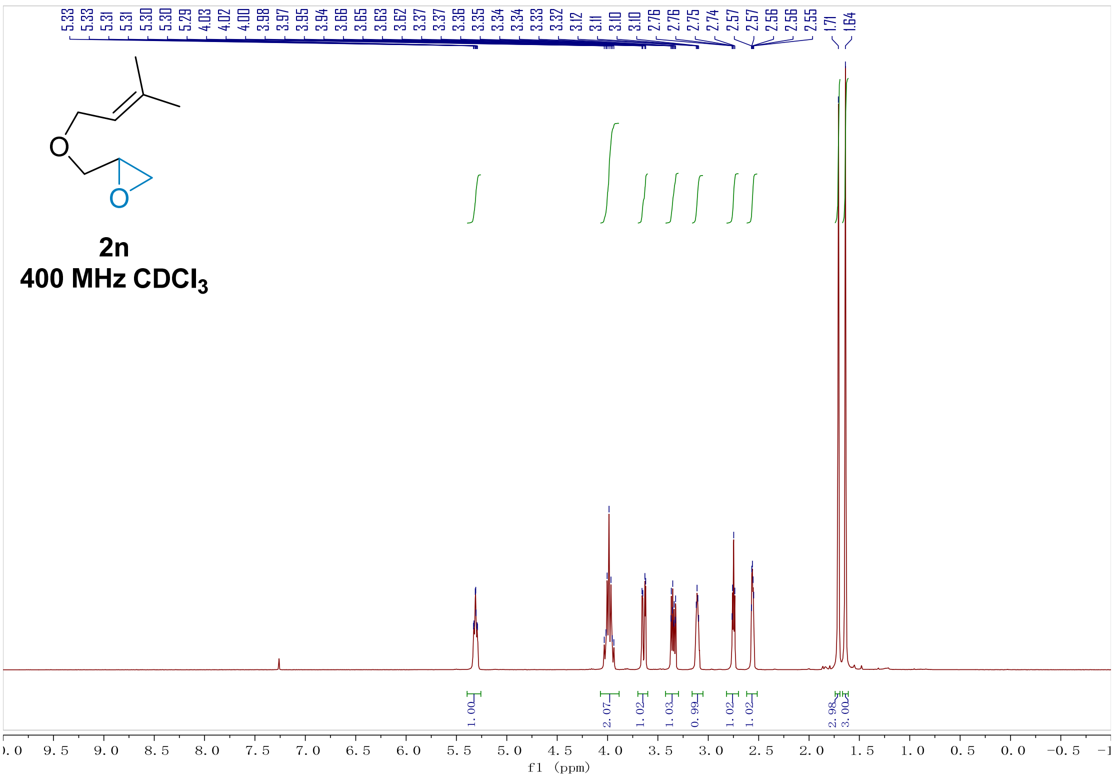

149.3
143.7
132.2
129.6
127.7
107.1
67.3
56.2
52.3
47.7
21.5
20.6
O
S
O
N
OH
3l
100 MHz CDCl$_3$
f1 (ppm)

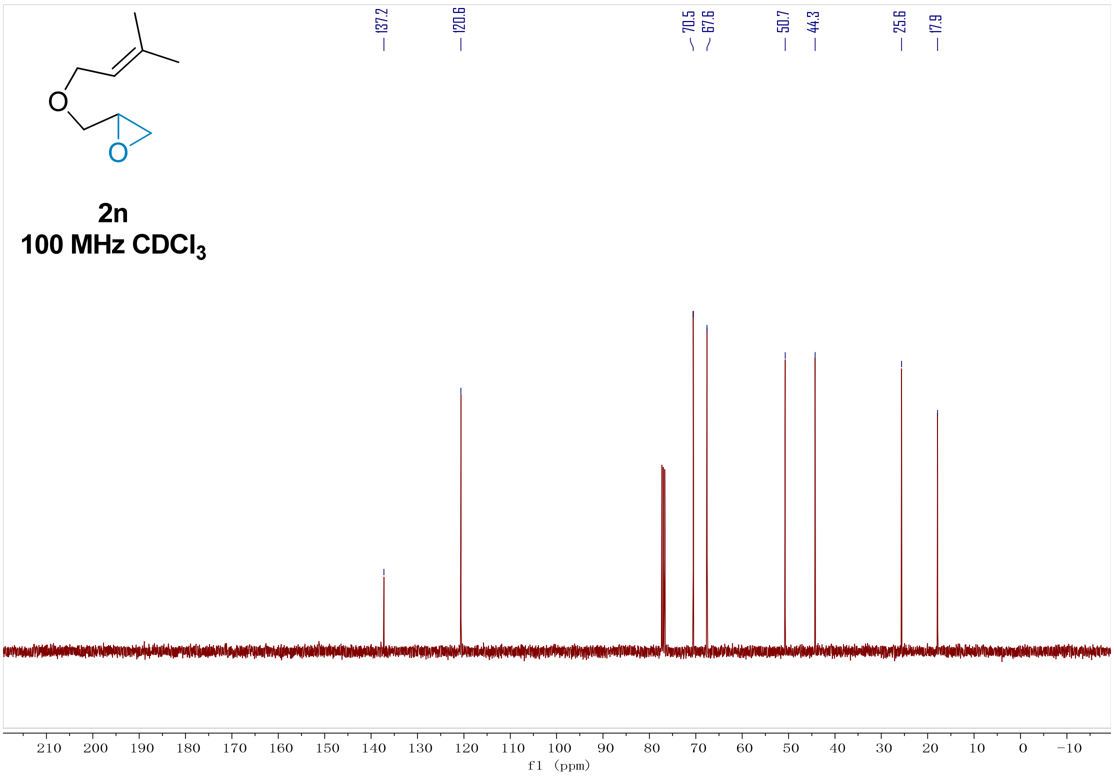

MeO$_2$C
MeO$_2$C
O
2m
400 MHz CDCl$_3$
3.77
3.76
2.99
2.98
2.97
2.96
2.95
2.76
2.75
2.74
2.50
2.49
2.49
2.48
2.46
2.45
2.42
2.41
2.13
2.11
2.09
2.07
2.05
2.04
2.68
2.88
0.87
2.04
1.00
0.97
1.02
1.05
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

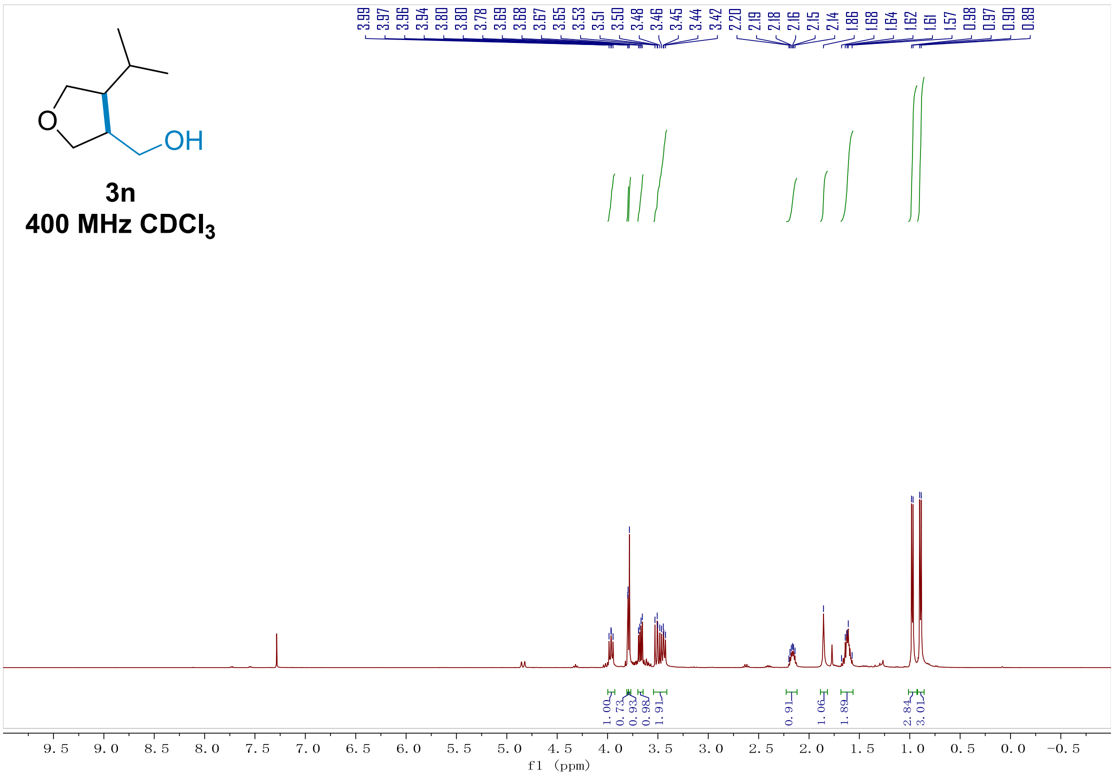

170.0
169.9
78.4
71.8
55.6
52.9
52.8
48.0
46.5
35.8
23.6
MeO$_2$C
MeO$_2$C
O
2m
100 MHz CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

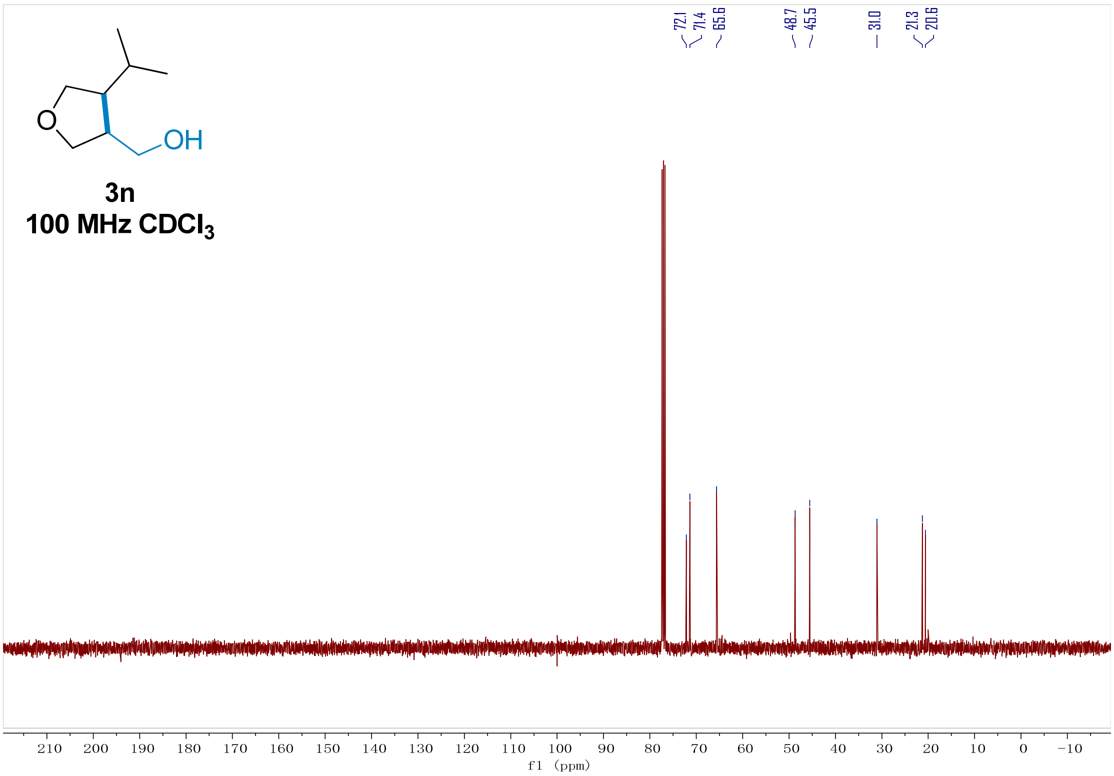

MeO2C
MeO2C
OH
3m
400 MHz CDCl3
5.04
5.03
4.91
4.91
3.71
3.64
3.63
3.00
2.95
2.94
2.94
2.90
2.80
2.77
2.60
2.58
2.57
2.55
2.13
2.10
2.09
2.07
1.83
1.00
1.02
6.24
1.86
2.18
1.08
1.15
1.13
1.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

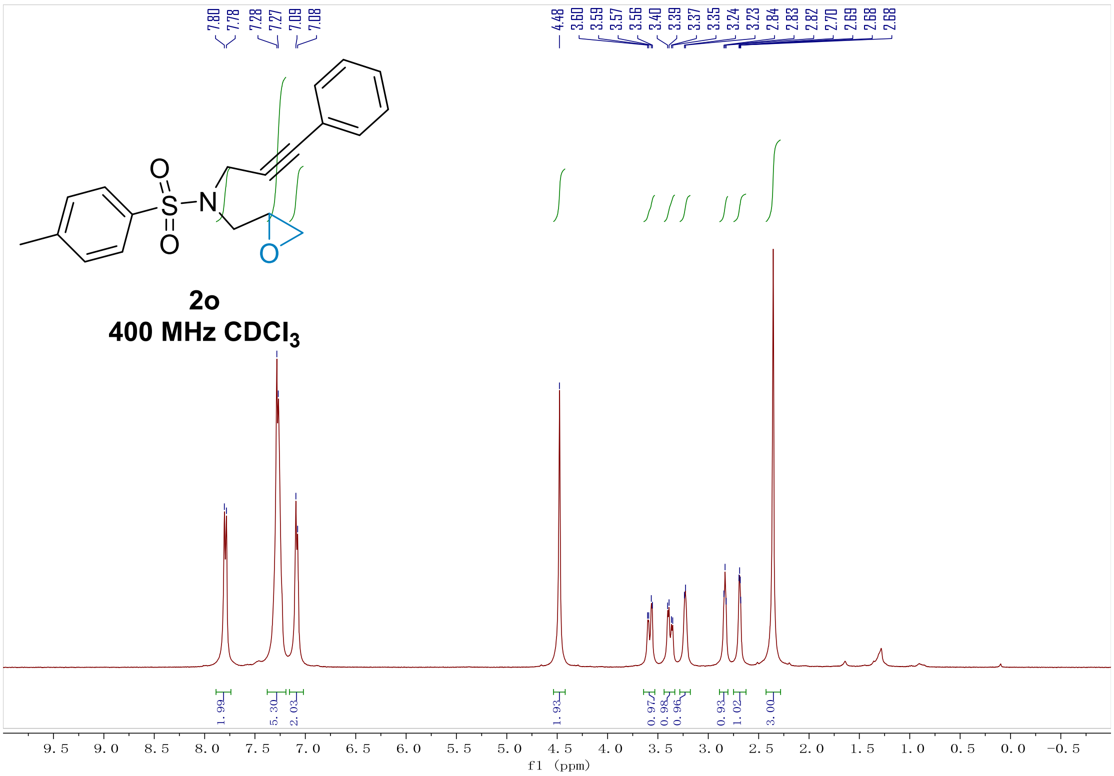

MeO2C
MeO2C
OH
3m
100 MHz CDCl3
172.1
172.1
148.7
107.9
64.5
58.6
52.8
52.8
44.7
41.4
36.7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

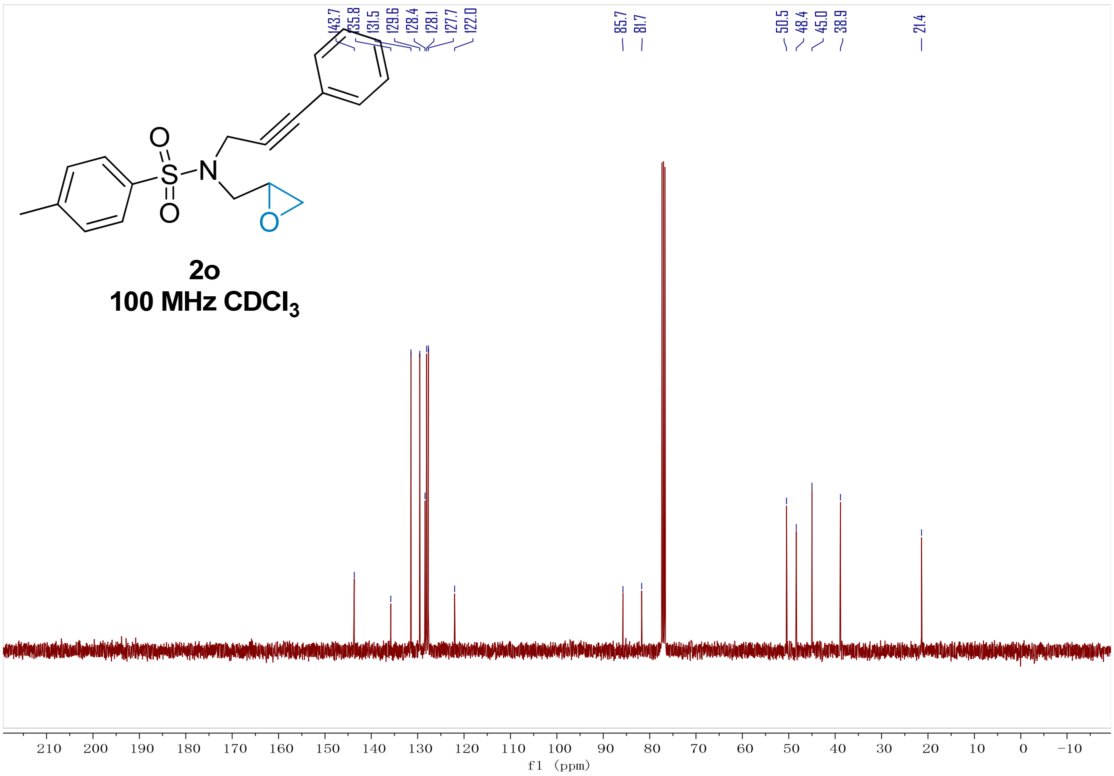

5.33
5.33
5.31
5.31
5.30
5.30
5.29
4.03
4.02
4.00
3.98
3.97
3.95
3.94
3.66
3.65
3.63
3.62
3.37
3.37
3.36
3.35
3.34
3.34
3.33
3.32
3.12
3.11
3.10
3.10
2.76
2.76
2.75
2.74
2.57
2.57
2.56
2.56
2.55
1.71
1.64
O
O
2n
400 MHz CDCl3
1.00
2.07
1.02
1.03
0.99
1.02
1.02
2.98
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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)

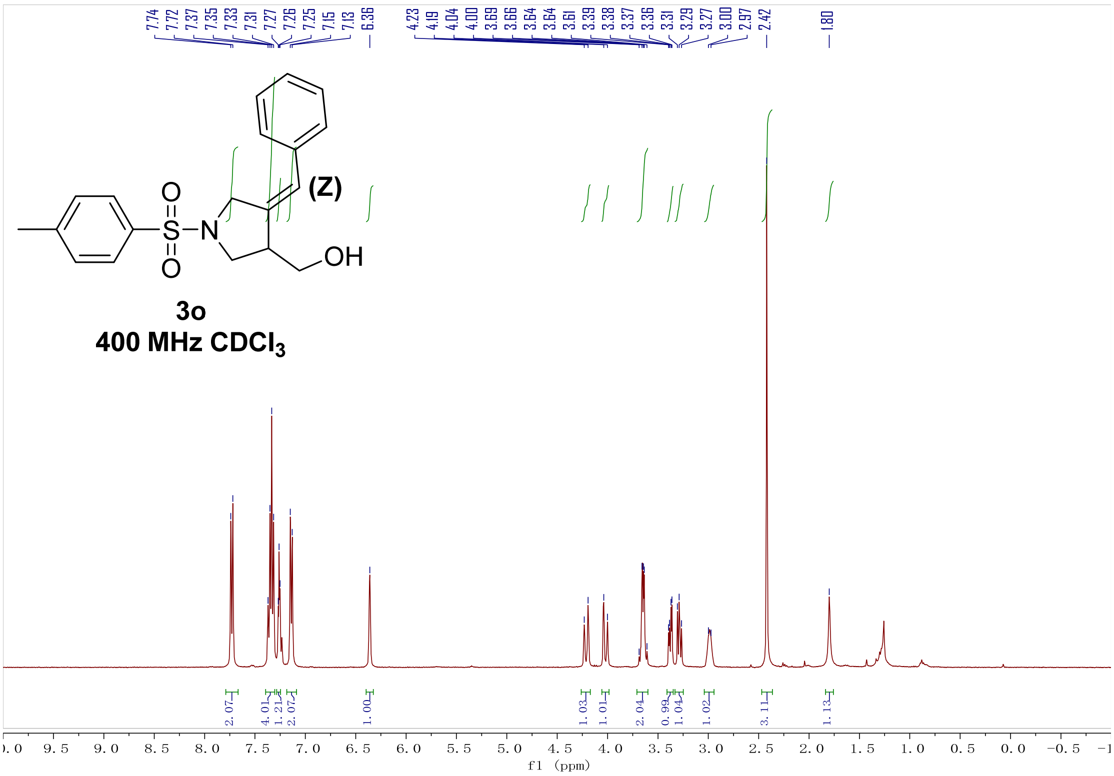

137.2
120.6
70.5
67.6
50.7
44.3
25.6
17.9
O
O
2n
100 MHz CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

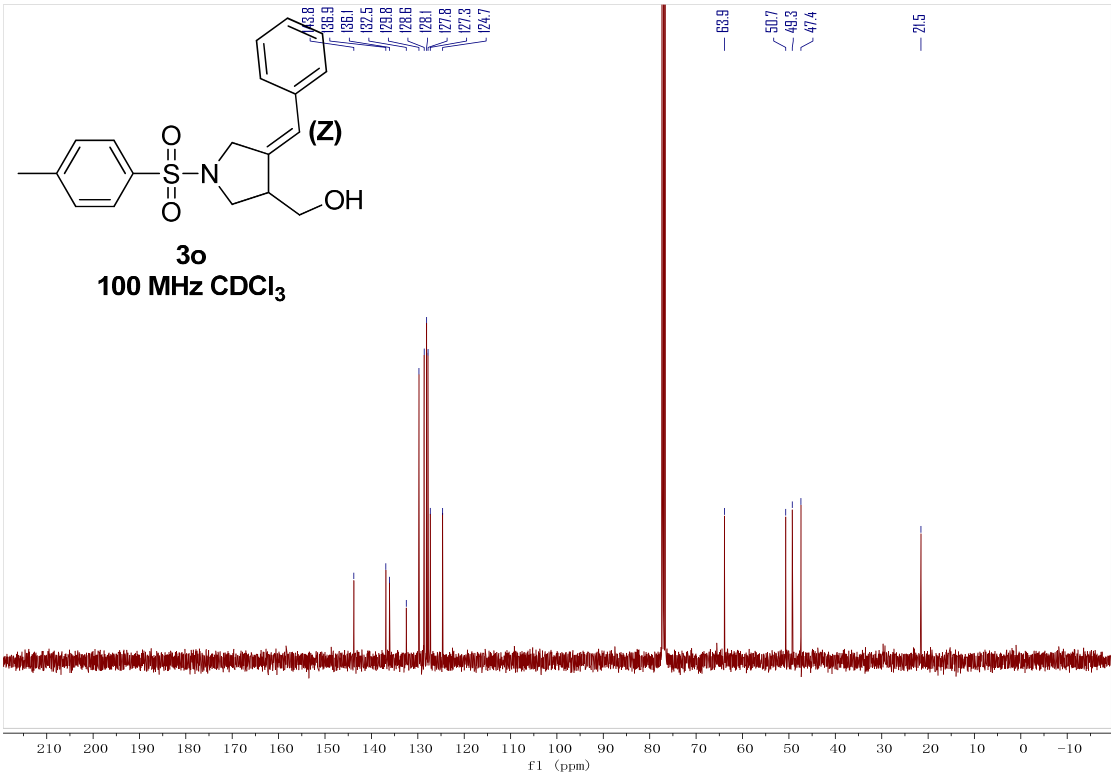

OH
O
3n
400 MHz CDCl$_3$
3.99
3.97
3.96
3.94
3.80
3.80
3.78
3.69
3.68
3.67
3.65
3.53
3.51
3.50
3.48
3.46
3.45
3.44
3.42
2.20
2.19
2.18
2.16
2.15
2.14
1.86
1.68
1.64
1.62
1.61
1.57
0.98
0.97
0.90
0.89
1.00
0.73
0.93
0.98
1.91
0.91
1.06
1.89
2.84
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

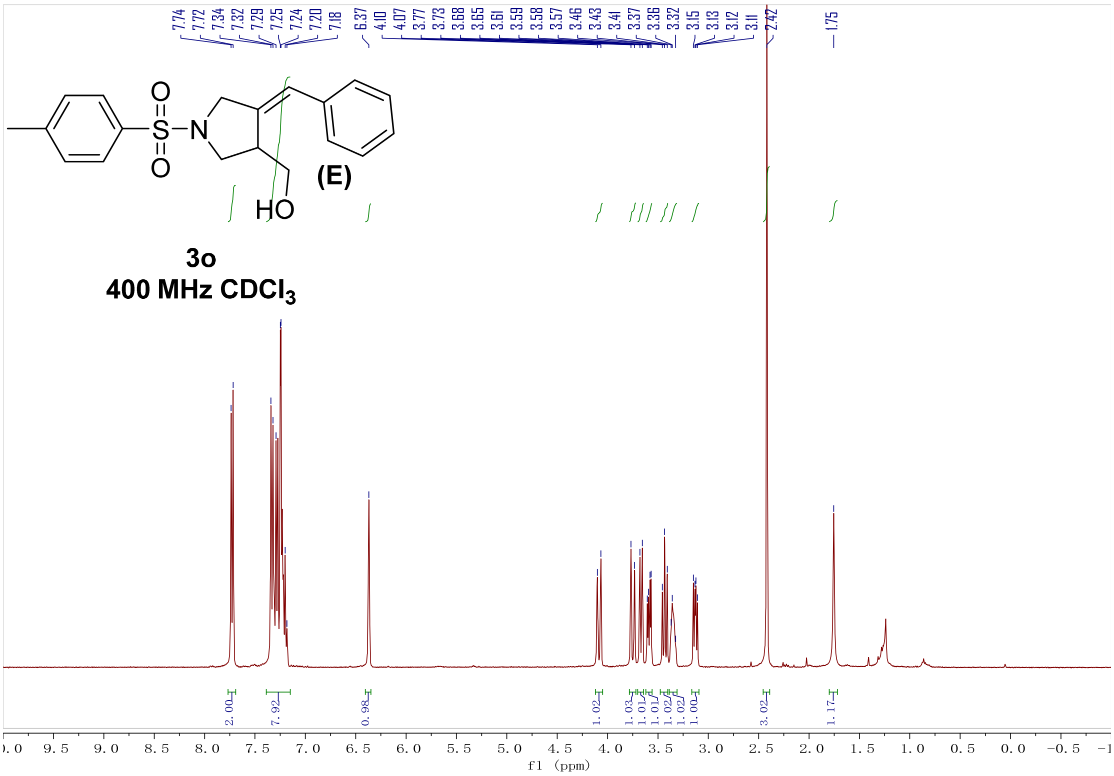

OH
O
3n
100 MHz CDCl$_3$
72.1
71.4
65.6
48.7
45.5
31.0
21.3
20.6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

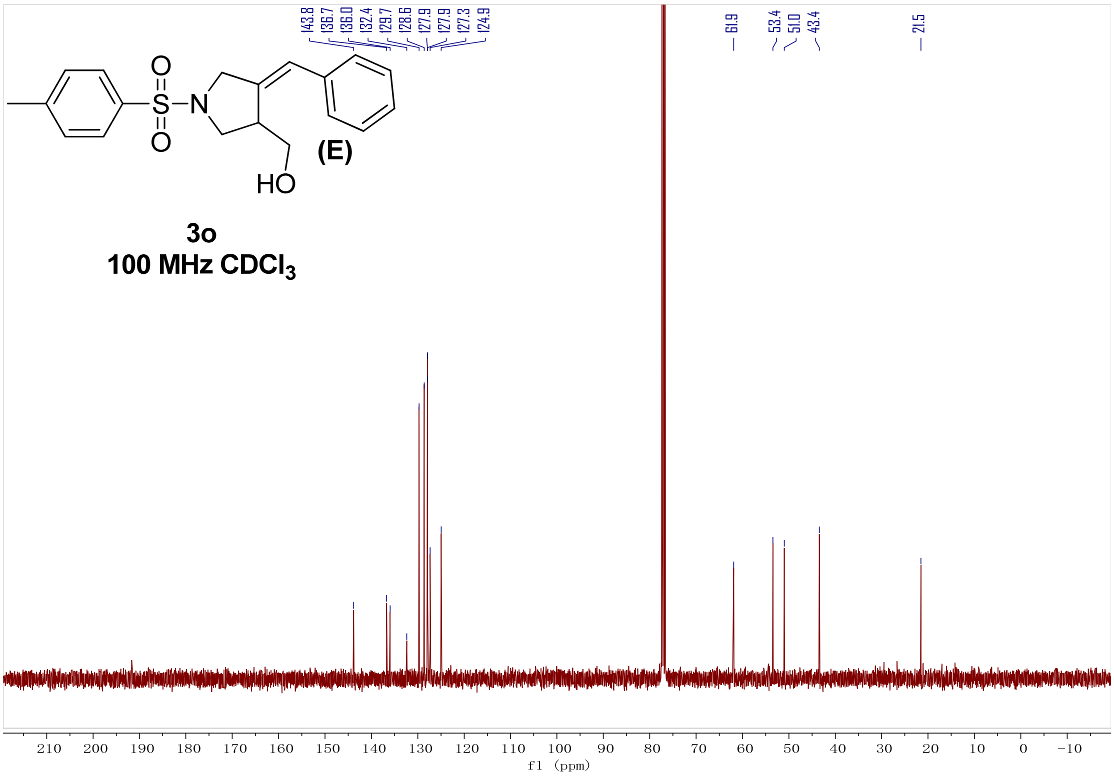

2o
400 MHz $CDCl_3$

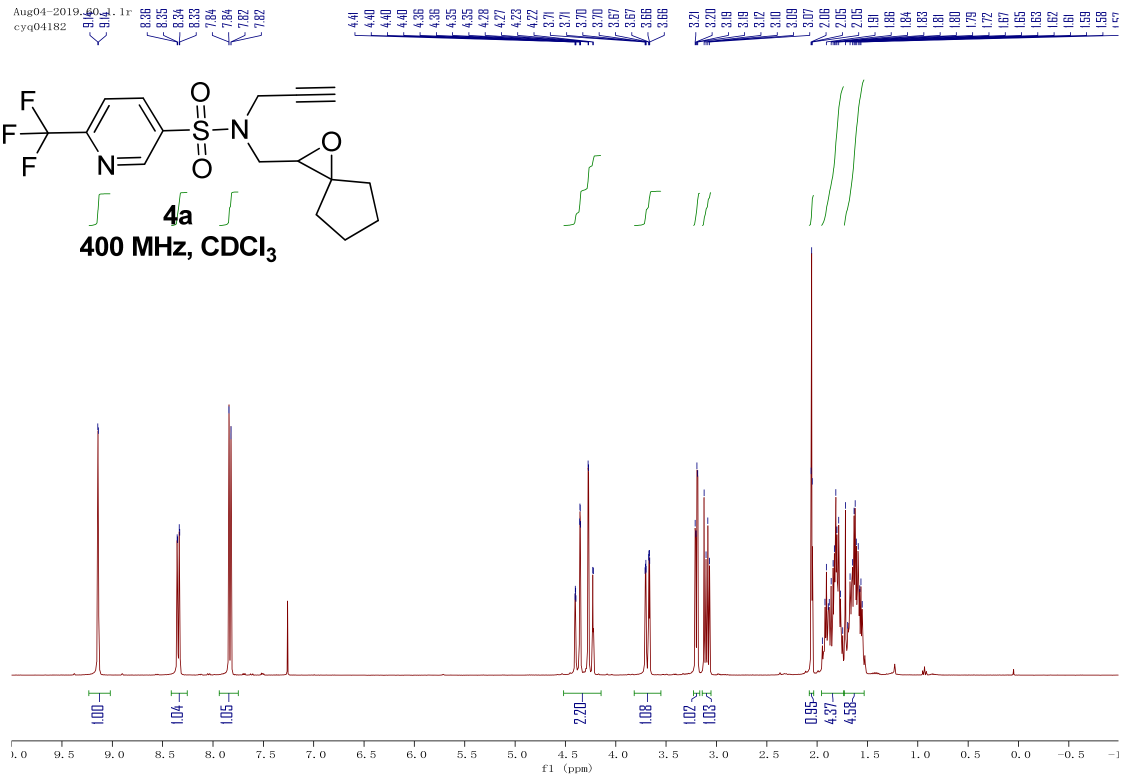

2o
100 MHz $CDCl_3$


7.74
7.72
7.37
7.35
7.33
7.31
7.27
7.26
7.25
7.15
7.13
6.36
4.23
4.19
4.04
4.00
3.69
3.66
3.64
3.64
3.61
3.39
3.38
3.37
3.36
3.31
3.29
3.27
3.00
2.97
2.42
1.80
(Z)
O
S
N
O
OH
3o
400 MHz CDCl3
2.07
4.01
1.21
2.07
1.00
1.03
1.01
2.04
0.99
1.04
1.02
3.11
1.13
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
−1
f1 (ppm)

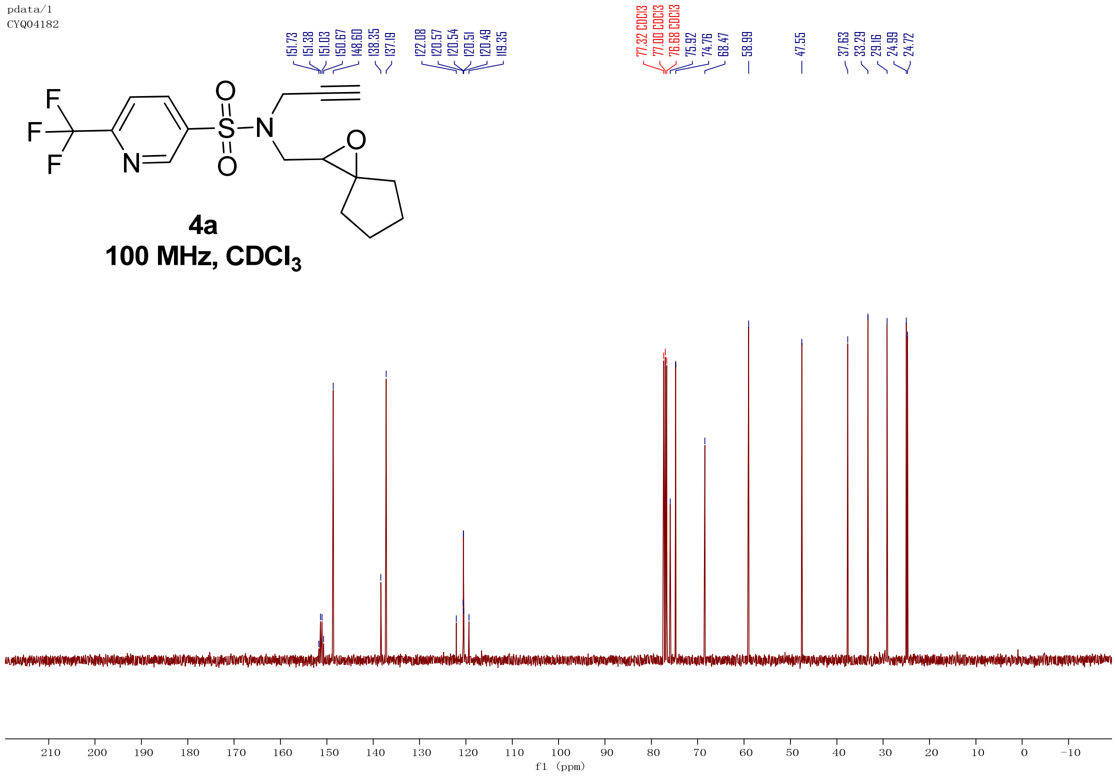

143.8
136.9
136.1
132.5
129.8
128.6
128.1
127.8
127.3
124.7
63.9
50.7
49.3
47.4
21.5
(Z)
O
S
N
O
OH
3o
100 MHz CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.74
7.72
7.34
7.32
7.29
7.25
7.24
7.20
7.18
6.37
4.10
4.07
3.77
3.73
3.68
3.65
3.61
3.59
3.58
3.57
3.46
3.43
3.41
3.37
3.36
3.32
3.15
3.13
3.12
3.11
2.42
1.75
(E)
HO
3o
400 MHz CDCl3
2.00
7.92
0.98
1.02
1.03
1.01
1.01
1.02
1.02
1.00
3.02
1.17
f1 (ppm)

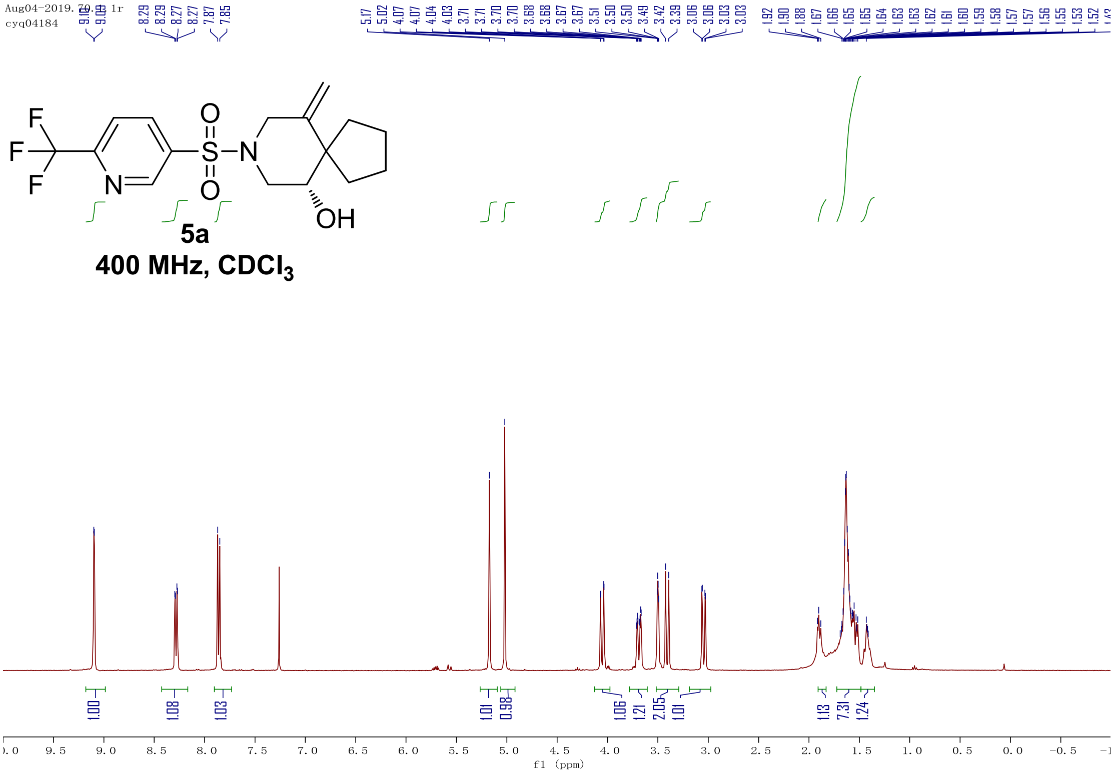

143.8
136.7
136.0
132.4
129.7
128.6
127.9
127.9
127.3
124.9
61.9
53.4
51.0
43.4
21.5
(E)
HO
3o
100 MHz CDCl3
f1 (ppm)



4a
400 MHz, $CDCl_3$

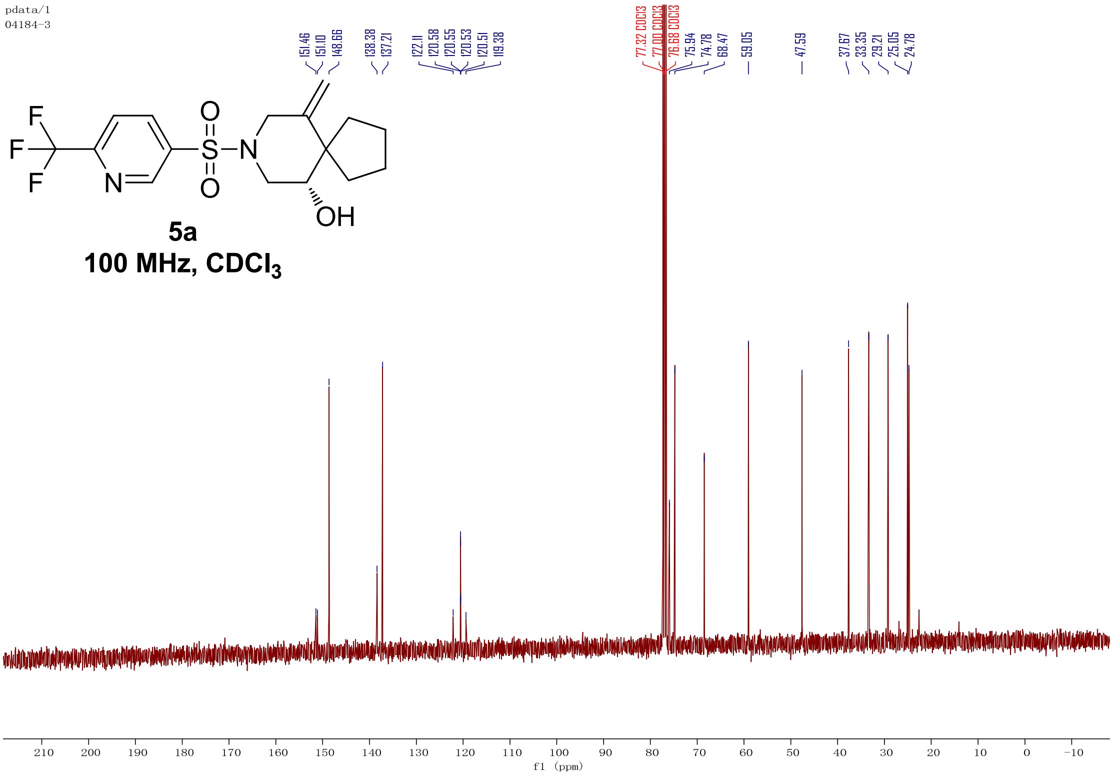


4a
100 MHz, $CDCl_3$



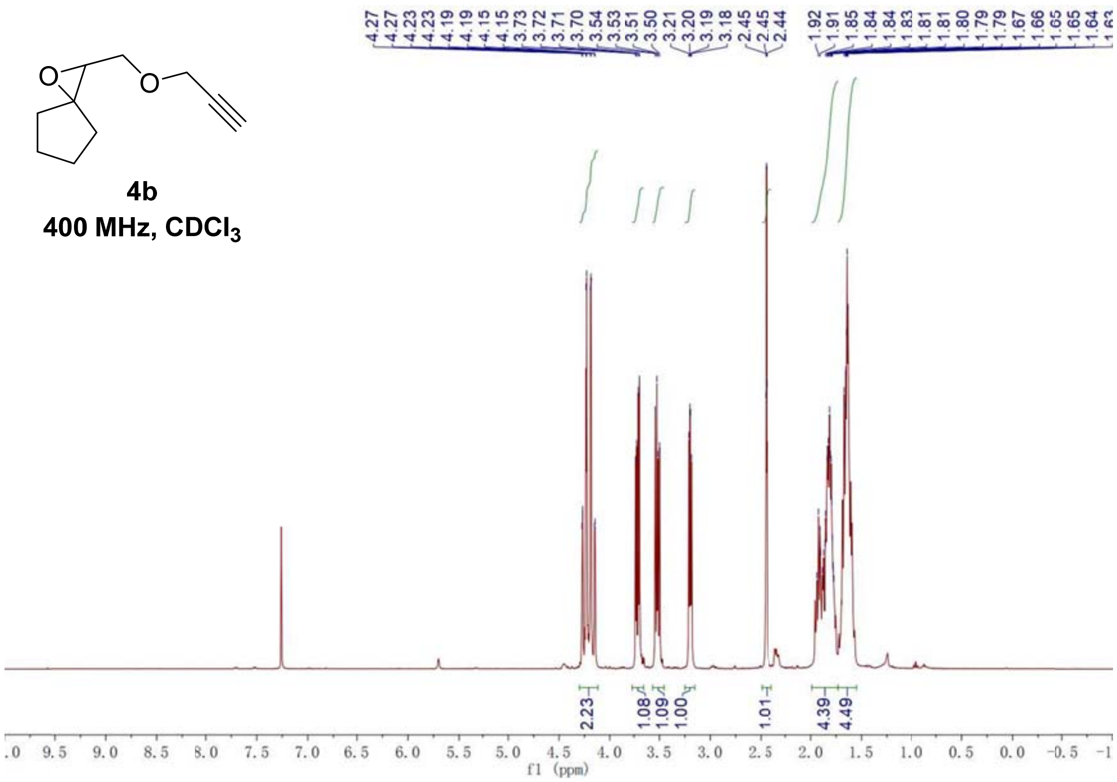
5a

400 MHz, $CDCl_3$

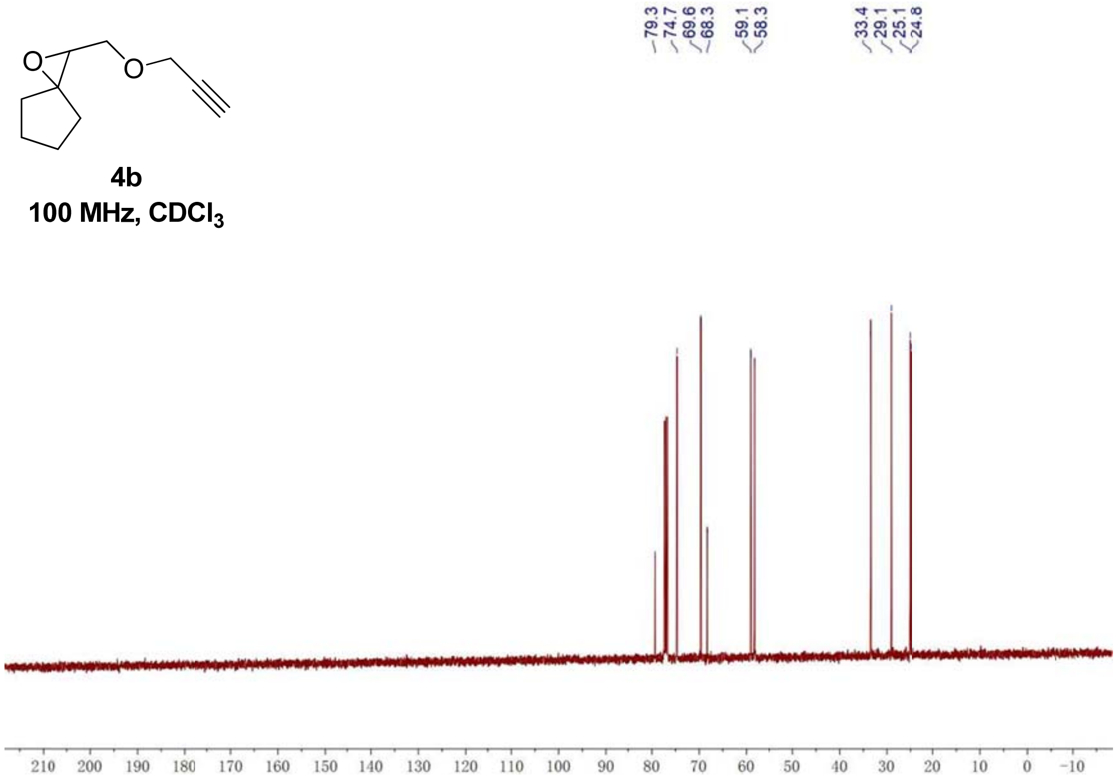


5a

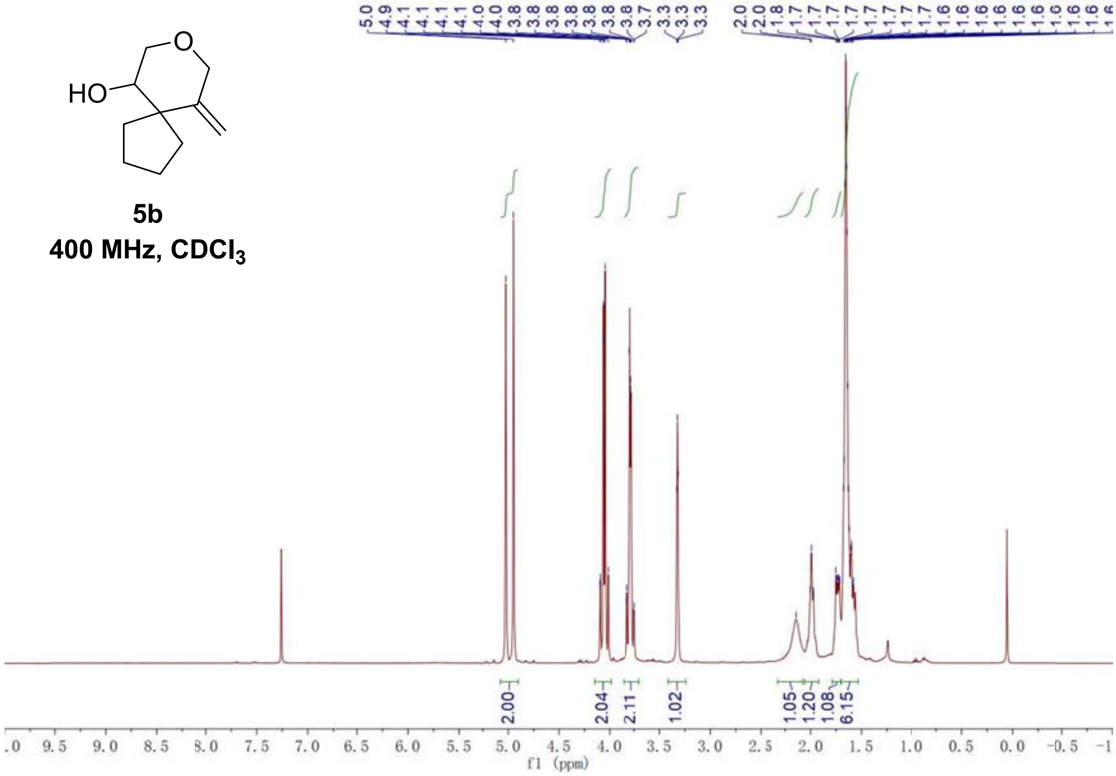
100 MHz, $CDCl_3$



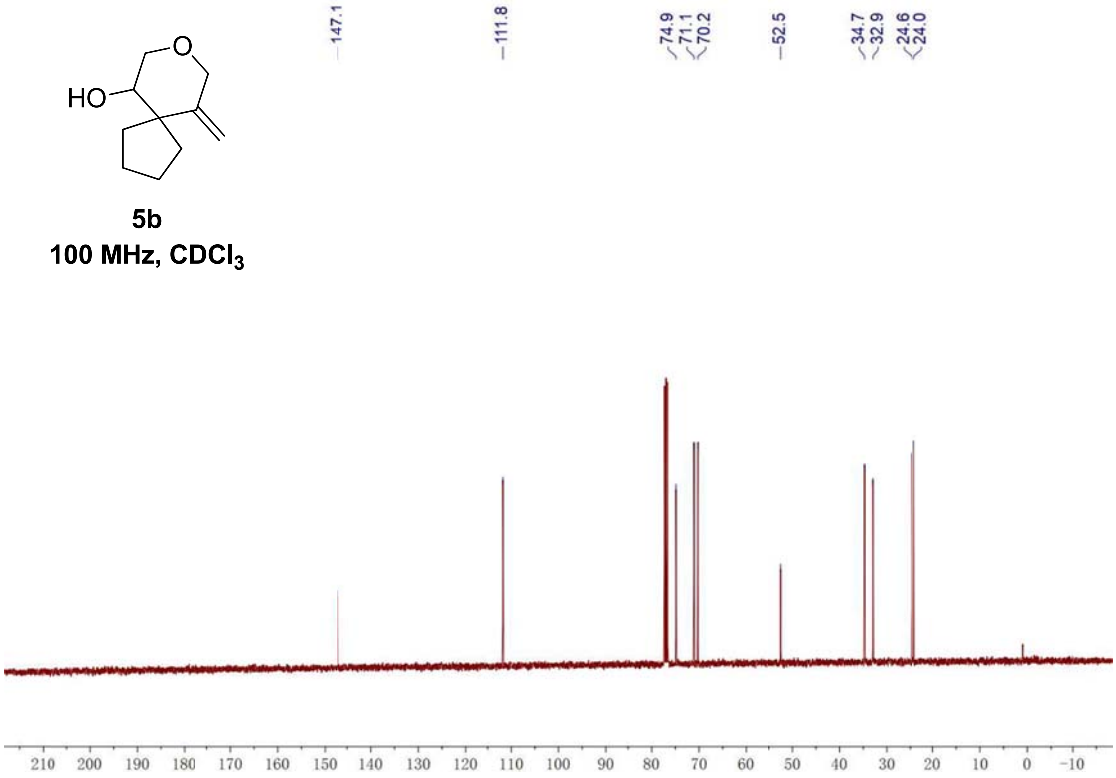
4b
400 MHz, $CDCl_3$



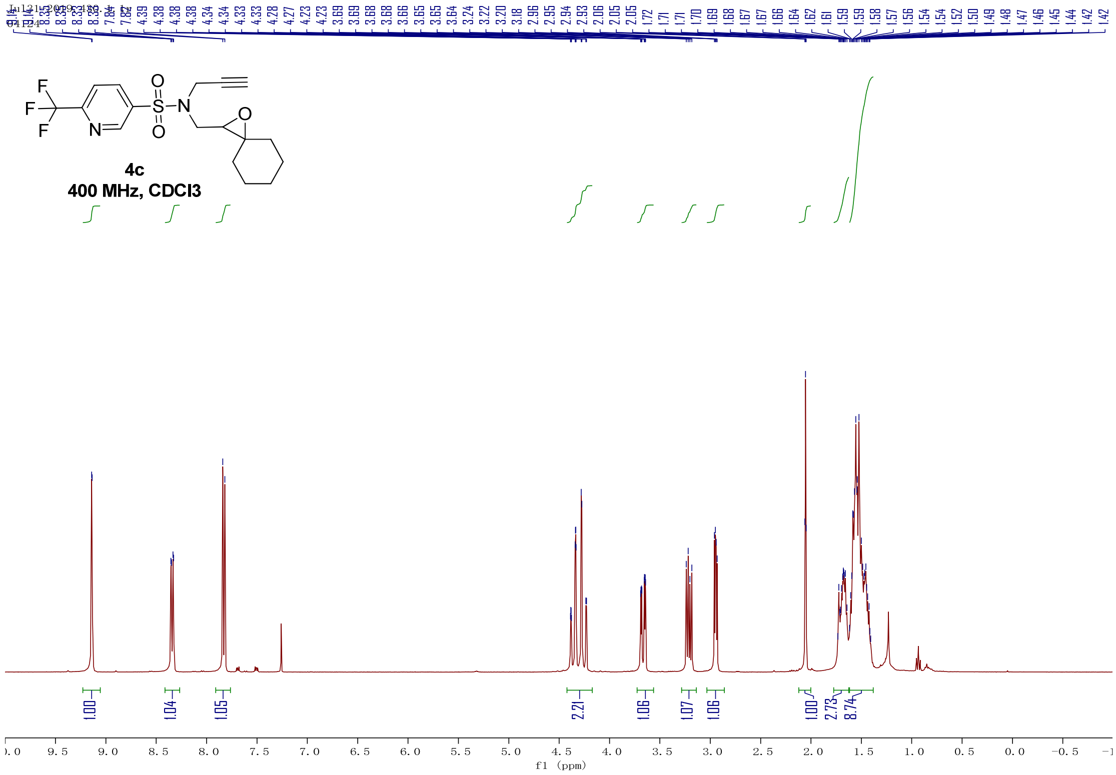
4b
100 MHz, $CDCl_3$

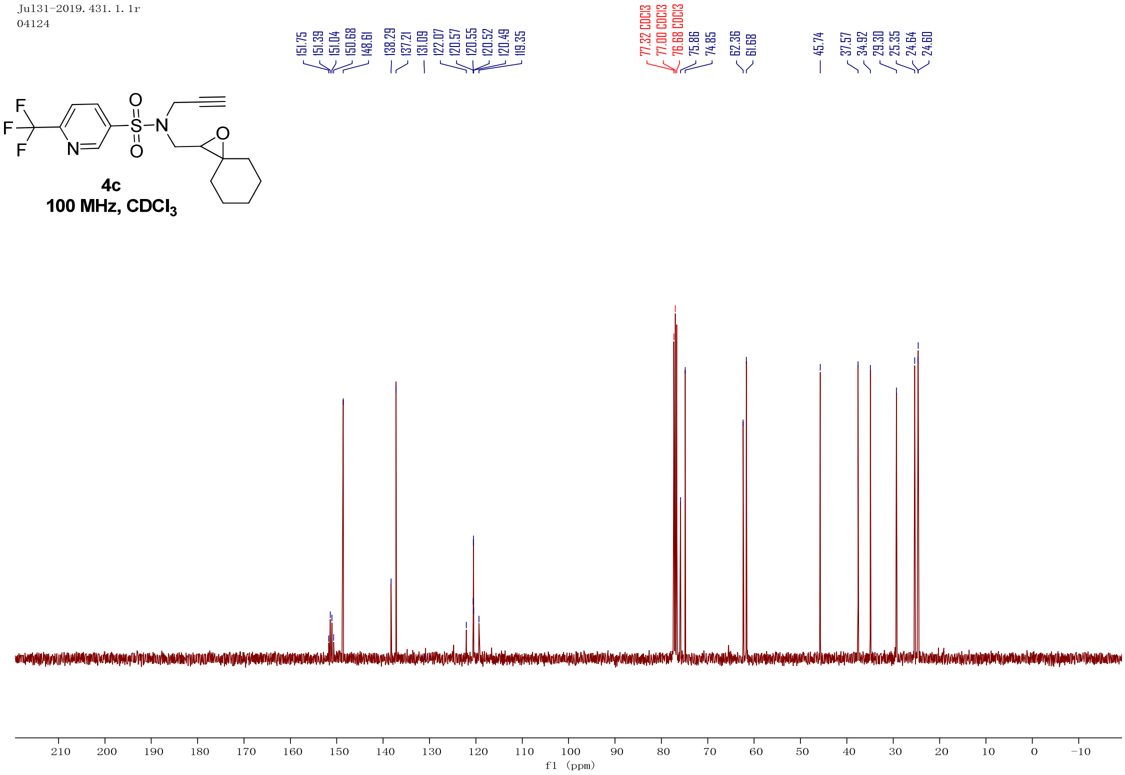


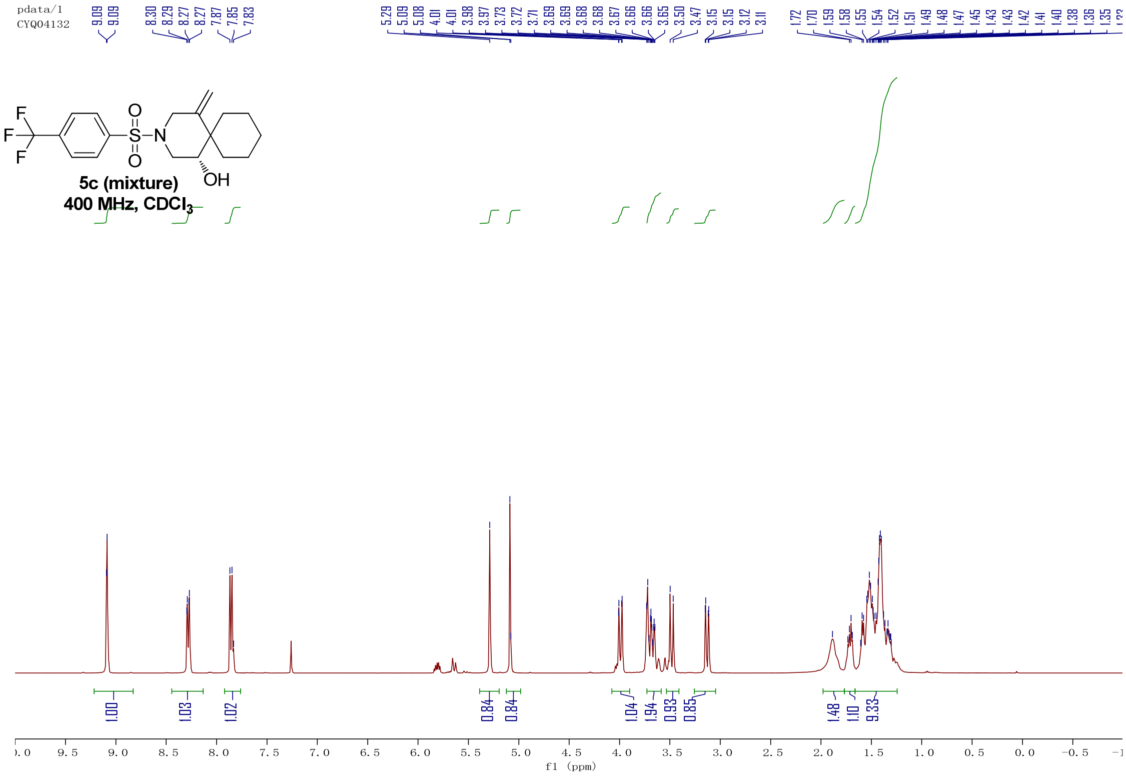
5b
400 MHz, CDCl$_3$

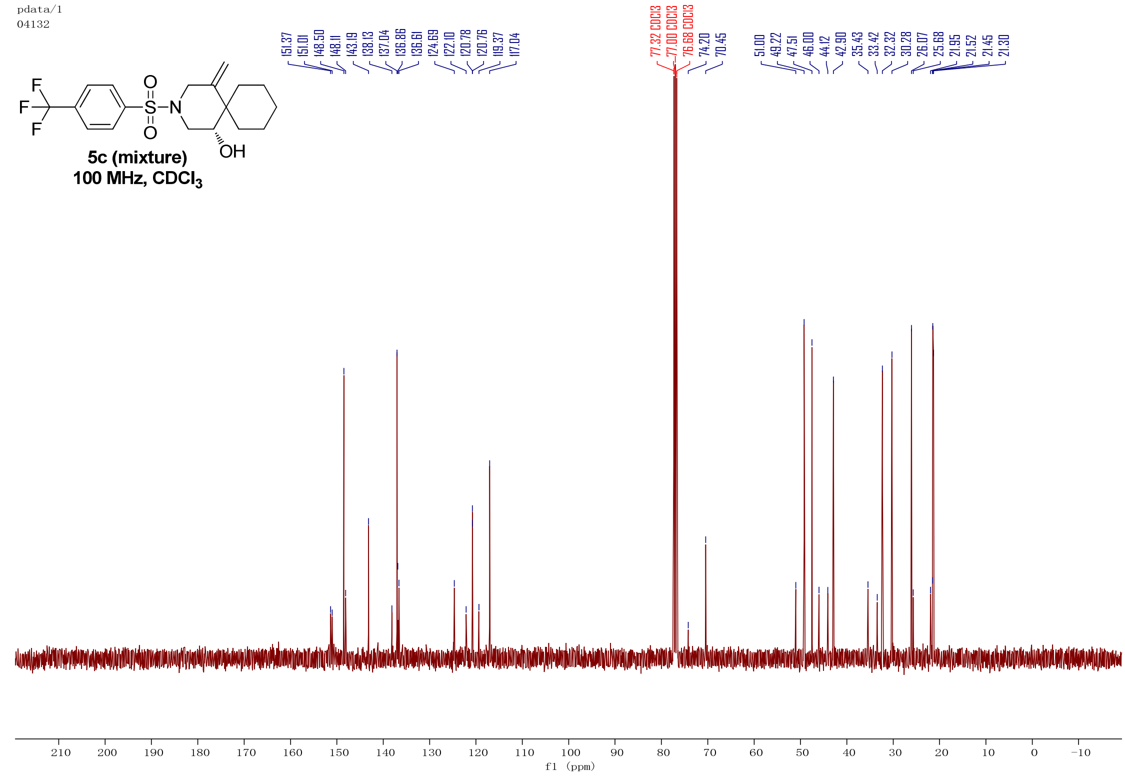


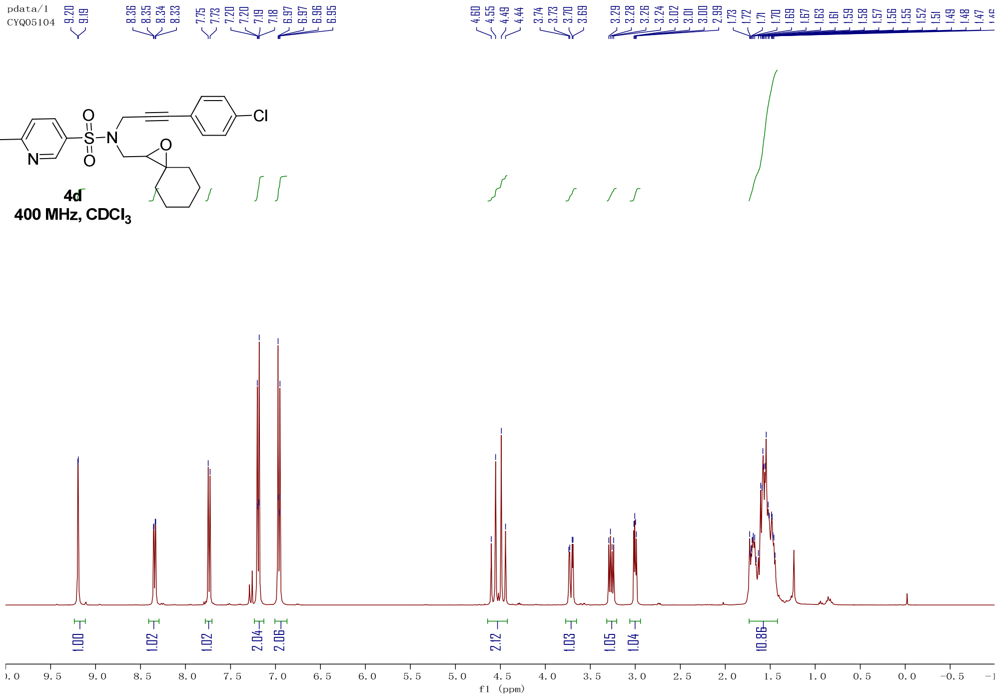
5b
100 MHz, CDCl$_3$

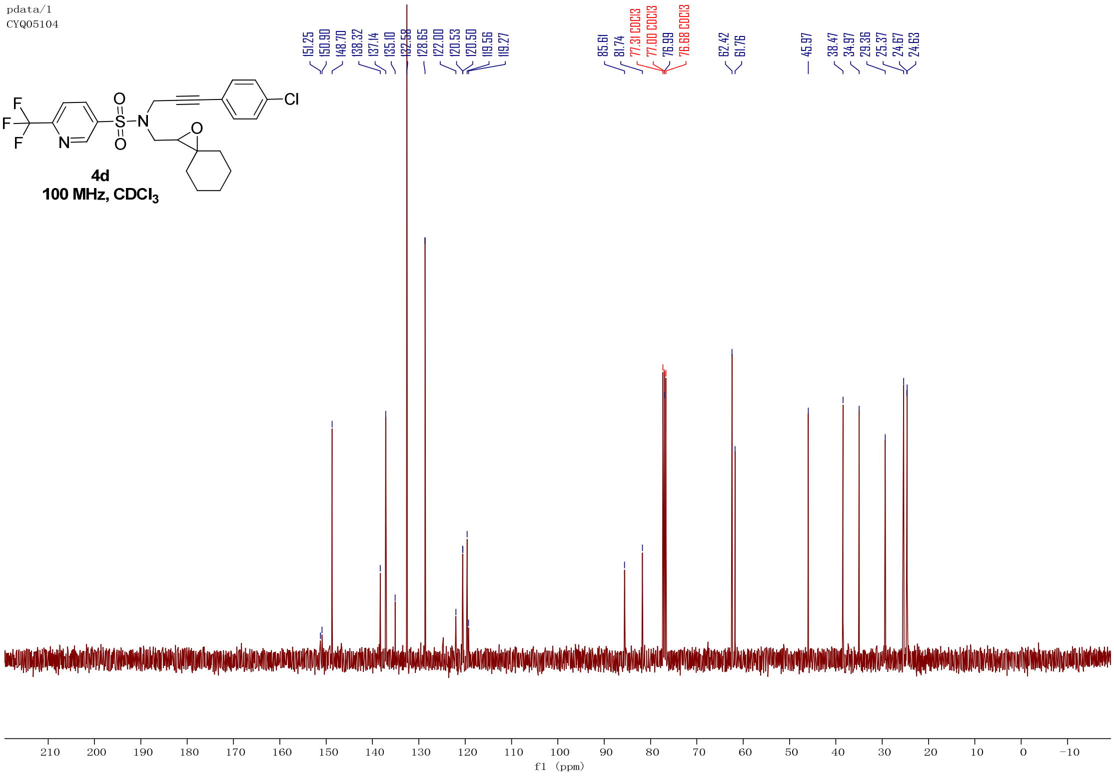

9.14
9.14
8.35
8.35
8.33
8.33
7.84
7.82
4.39
4.38
4.38
4.38
4.34
4.34
4.33
4.33
4.28
4.27
4.23
4.23
3.69
3.69
3.68
3.68
3.66
3.65
3.65
3.64
3.24
3.22
3.20
3.18
2.96
2.95
2.94
2.93
2.06
2.05
2.05
1.72
1.71
1.71
1.70
1.69
1.68
1.67
1.67
1.66
1.64
1.62
1.61
1.59
1.59
1.58
1.57
1.56
1.54
1.54
1.52
1.50
1.49
1.48
1.47
1.46
1.45
1.44
1.42
1.42
F
F
F
N
O
S
O
N
O
4c
400 MHz, CDCl3
1.00
1.04
1.05
2.21
1.06
1.07
1.06
1.00
2.73
8.74
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)

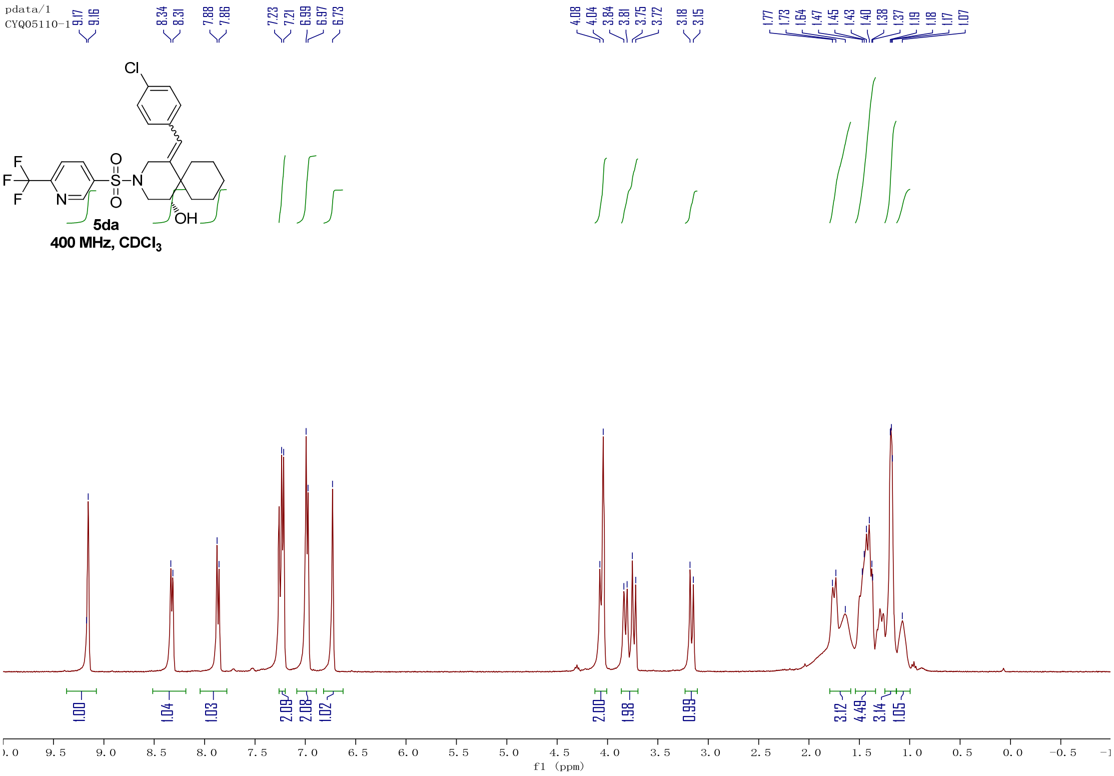

Jul31-2019.431.1.1r
04124
151.75
151.39
151.04
150.68
148.61
138.29
137.21
131.09
122.07
120.57
120.55
120.52
120.49
119.35
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
75.86
74.85
62.36
61.68
45.74
37.57
34.92
29.30
25.35
24.64
24.60
F
F
F
N
O
S
O
N
O
4c
100 MHz, CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

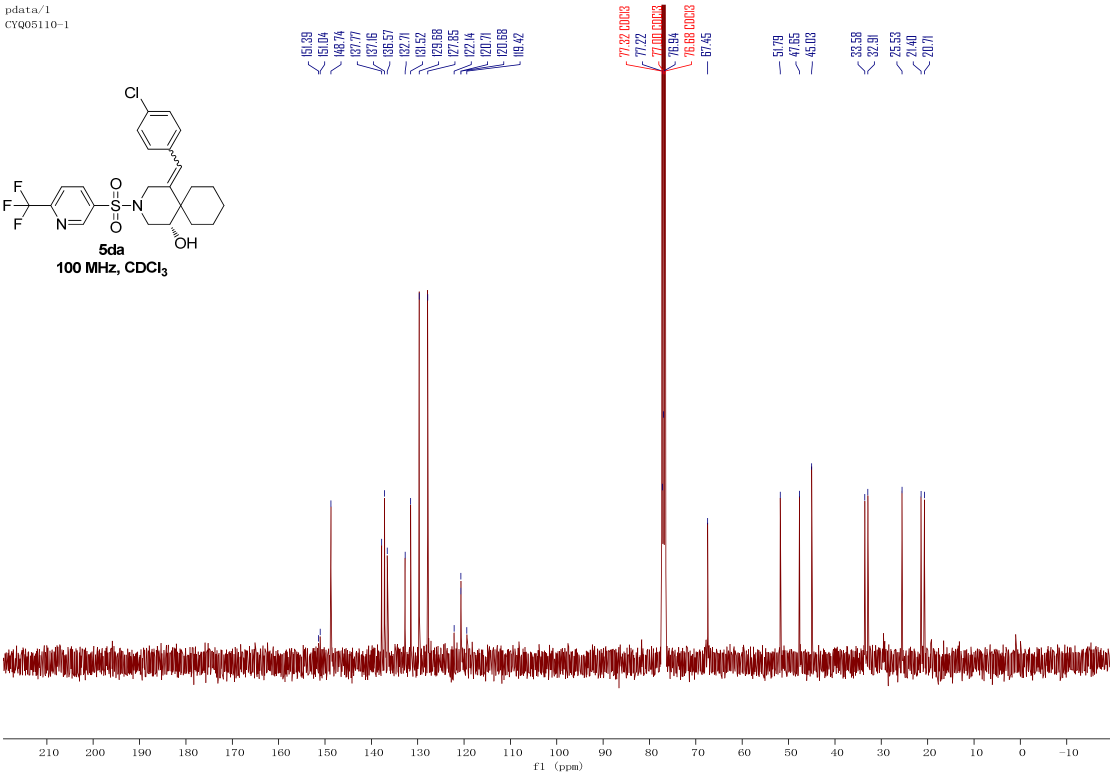

pdata/1
CYQ04132
9.09
9.09
8.30
8.29
8.27
8.27
7.87
7.85
7.83
5.29
5.09
5.08
4.01
4.01
3.98
3.97
3.73
3.72
3.71
3.69
3.69
3.68
3.68
3.67
3.66
3.66
3.65
3.50
3.47
3.15
3.15
3.12
3.11
1.72
1.70
1.59
1.58
1.55
1.54
1.52
1.51
1.49
1.48
1.47
1.45
1.43
1.43
1.42
1.41
1.40
1.38
1.36
1.35
F
F
F
O
S
O
N
OH
5c (mixture)
400 MHz, CDCl3
1.00
1.03
1.02
0.84
0.84
1.04
1.94
0.93
0.85
1.48
1.10
9.33
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)

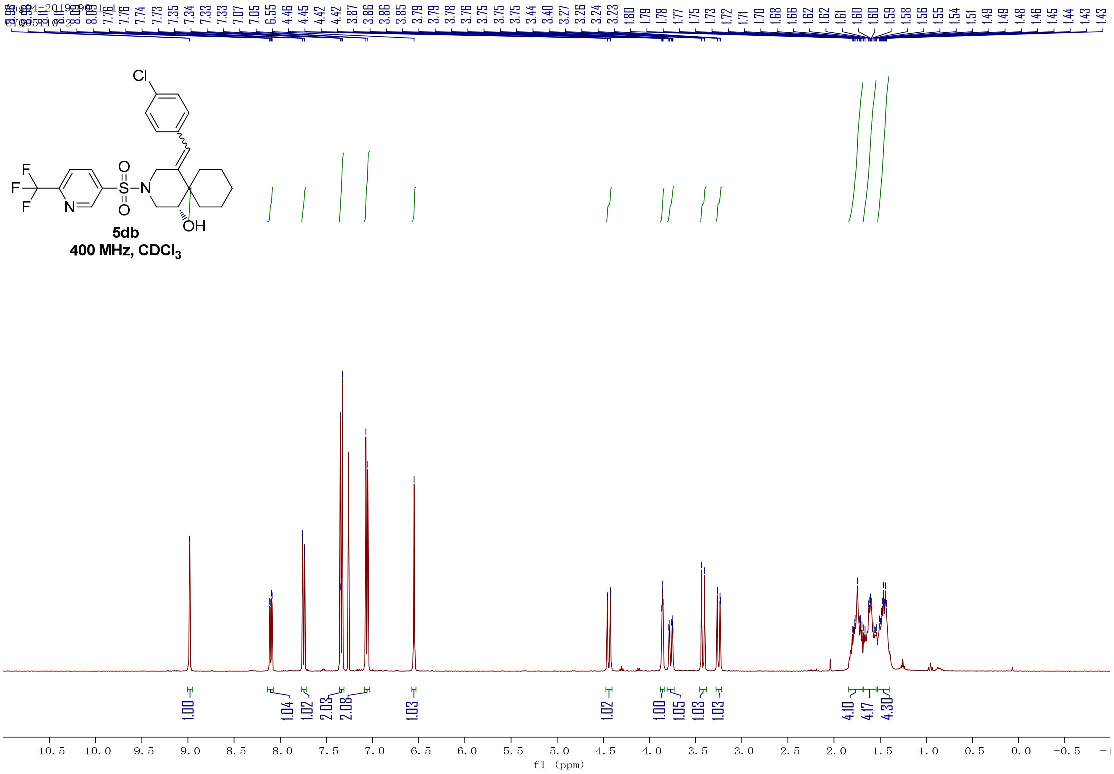

pdata/1
04132
151.37
151.01
148.50
148.11
143.19
138.13
137.04
136.86
136.61
124.69
122.10
120.78
120.76
119.37
117.04
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
74.20
70.45
51.00
49.22
47.51
46.00
44.12
42.90
35.43
33.42
32.32
30.28
26.07
25.68
21.95
21.52
21.45
21.30
F
F
F
O
S
O
N
OH
5c (mixture)
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

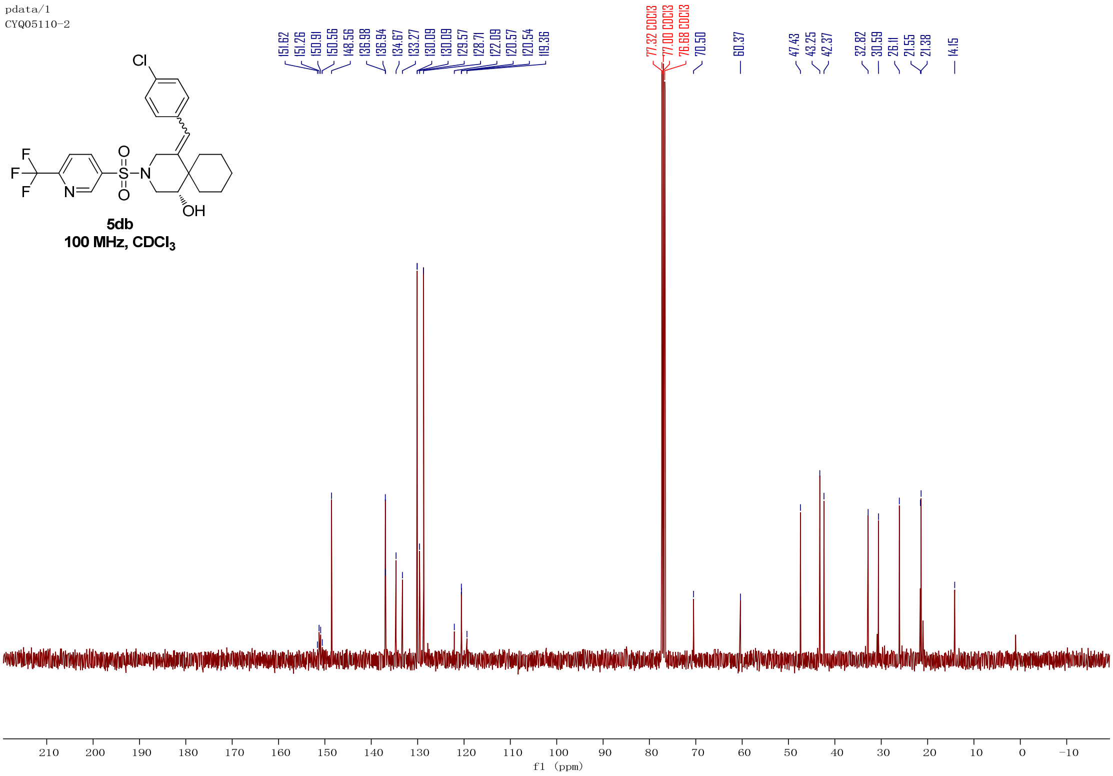

pdata/1
CYQ05104
9.20
9.19
8.36
8.35
8.34
8.33
7.75
7.73
7.20
7.20
7.19
7.18
6.97
6.97
6.96
6.95
4.60
4.55
4.49
4.44
3.74
3.73
3.70
3.69
3.29
3.28
3.26
3.24
3.02
3.01
3.00
2.99
1.73
1.72
1.71
1.70
1.69
1.67
1.63
1.61
1.59
1.58
1.57
1.56
1.55
1.52
1.51
1.49
1.48
1.47
F
F
F
N
O
S
O
N
O
Cl
4d
400 MHz, CDCl3
1.00
1.02
1.02
2.04
2.06
2.12
1.03
1.05
1.04
10.86
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)

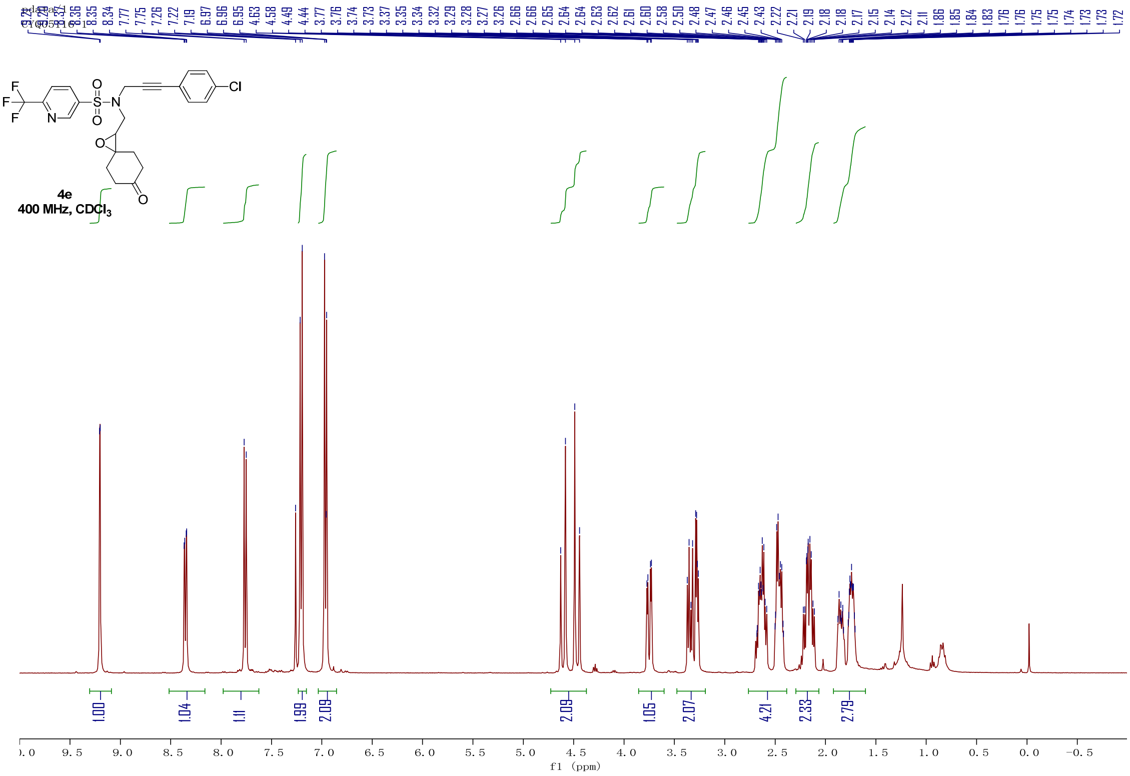

pdata/1
CYQ05104
151.25
150.90
148.70
138.32
137.14
135.10
132.58
128.65
122.00
120.53
120.50
119.56
119.27
85.61
81.74
77.31 CDCl3
77.00 CDCl3
76.99
76.68 CDCl3
62.42
61.76
45.97
38.47
34.97
29.36
25.37
24.67
24.63
F
F
F
N
O
S
O
N
O
Cl
4d
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

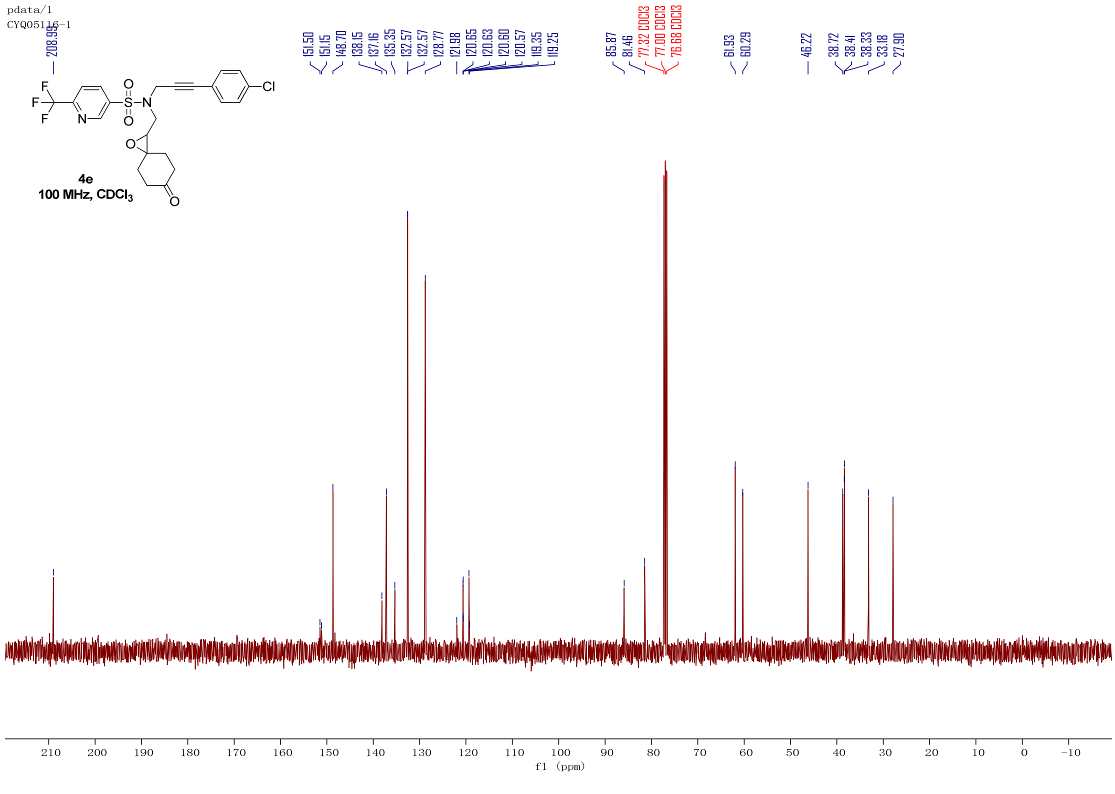

pdata/1
CYQ05110-1
9.17 9.16 8.34 8.31 7.88 7.86 7.23 7.21 6.99 6.97 6.73
4.08 4.04 3.84 3.81 3.75 3.72 3.18 3.15
1.77 1.73 1.64 1.47 1.45 1.43 1.40 1.38 1.37 1.19 1.18 1.17 1.07
Cl
F
F
F
N
O
S
O
N
OH
5da
400 MHz, CDCl3
1.00 1.04 1.03 2.09 2.08 1.02 2.00 1.98 0.99 3.12 4.49 3.14 1.05
9.5 9.0 8.5 8.0 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)

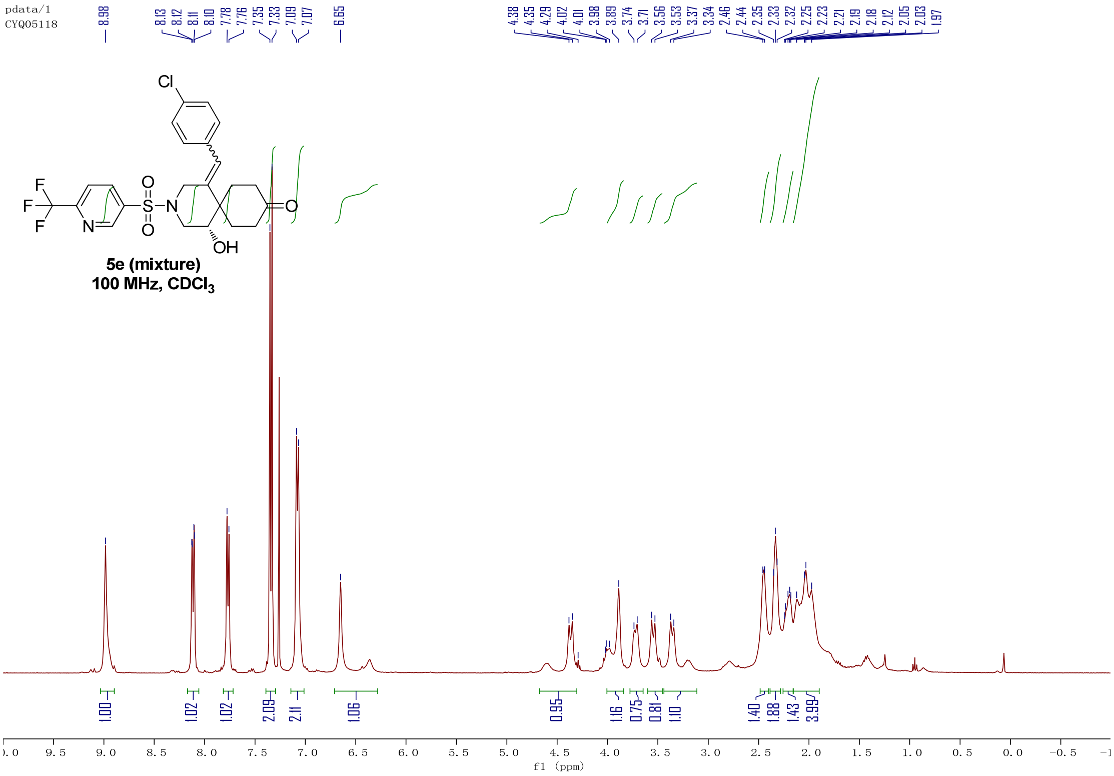

pdata/1
CYQ05110-1
151.39 151.04 148.74 137.77 137.16 136.57 132.71 131.52 129.68 127.85 122.14 120.71 120.68 119.42
77.32 CDCl3 77.22 77.00 CDCl3 76.94 76.68 CDCl3 67.45
51.79 47.65 45.03 33.58 32.91 25.53 21.40 20.71
Cl
F
F
F
N
O
S
O
N
OH
5da
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

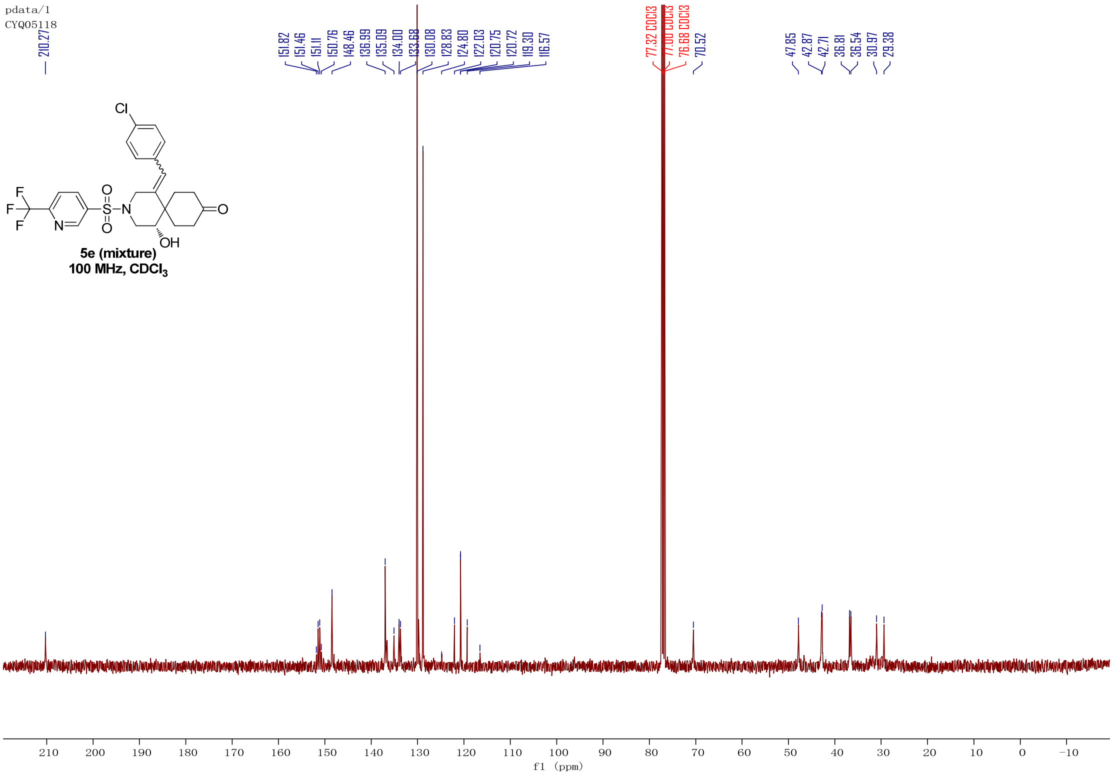

Aug04-2019.90.1.1r
CYQ05110-2
8.99
8.99
8.11
8.11
8.09
8.09
7.76
7.76
7.74
7.73
7.35
7.34
7.33
7.33
7.07
7.05
6.55
4.46
4.45
4.42
4.42
3.87
3.86
3.86
3.85
3.79
3.79
3.78
3.76
3.75
3.75
3.75
3.44
3.40
3.27
3.26
3.24
3.23
1.80
1.79
1.78
1.77
1.75
1.73
1.72
1.71
1.70
1.68
1.66
1.62
1.62
1.61
1.60
1.60
1.59
1.58
1.56
1.55
1.54
1.51
1.49
1.49
1.48
1.46
1.45
1.44
1.43
1.43
Cl
F
F
F
N
O
S
O
N
OH
5db
400 MHz, CDCl3
1.00
1.04
1.02
2.03
2.08
1.03
1.02
1.00
1.05
1.03
1.03
4.10
4.17
4.30
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)

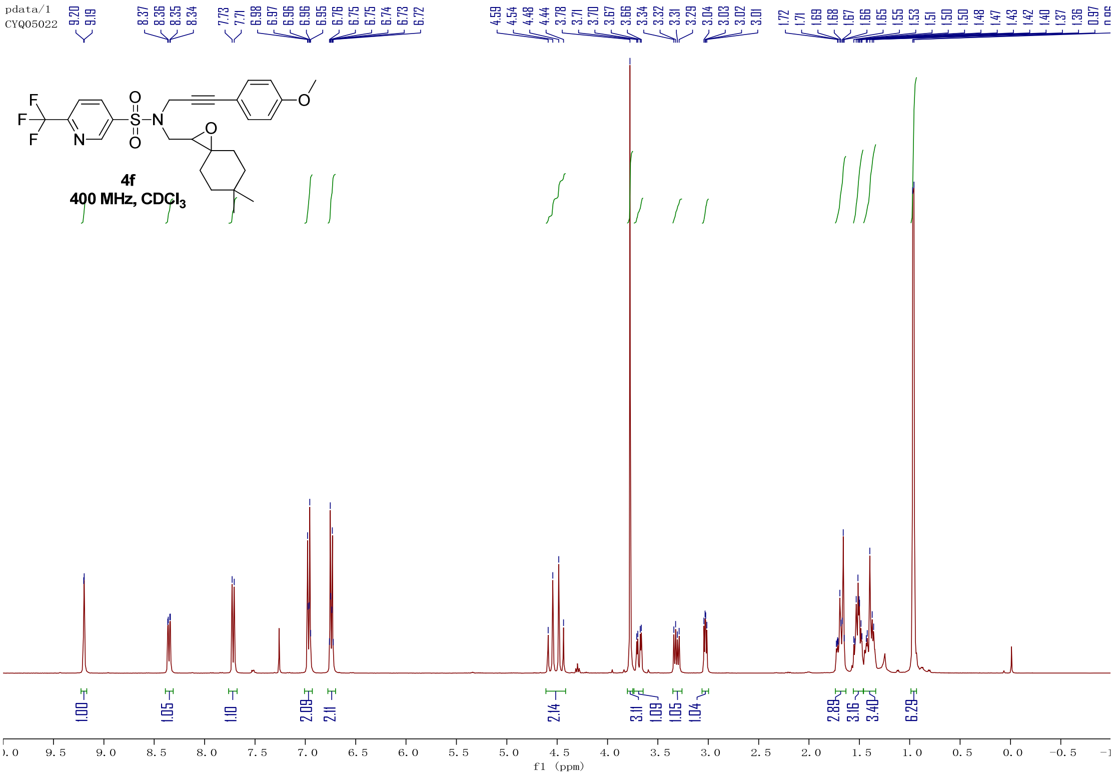

pdata/1
CYQ05110-2
151.62
151.26
150.91
150.56
148.56
136.98
136.94
134.67
133.27
130.09
130.09
129.57
128.71
122.09
120.57
120.54
119.36
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
70.50
60.37
47.43
43.25
42.37
32.82
30.59
26.11
21.55
21.38
14.15
Cl
F
F
F
N
O
S
O
N
OH
5db
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

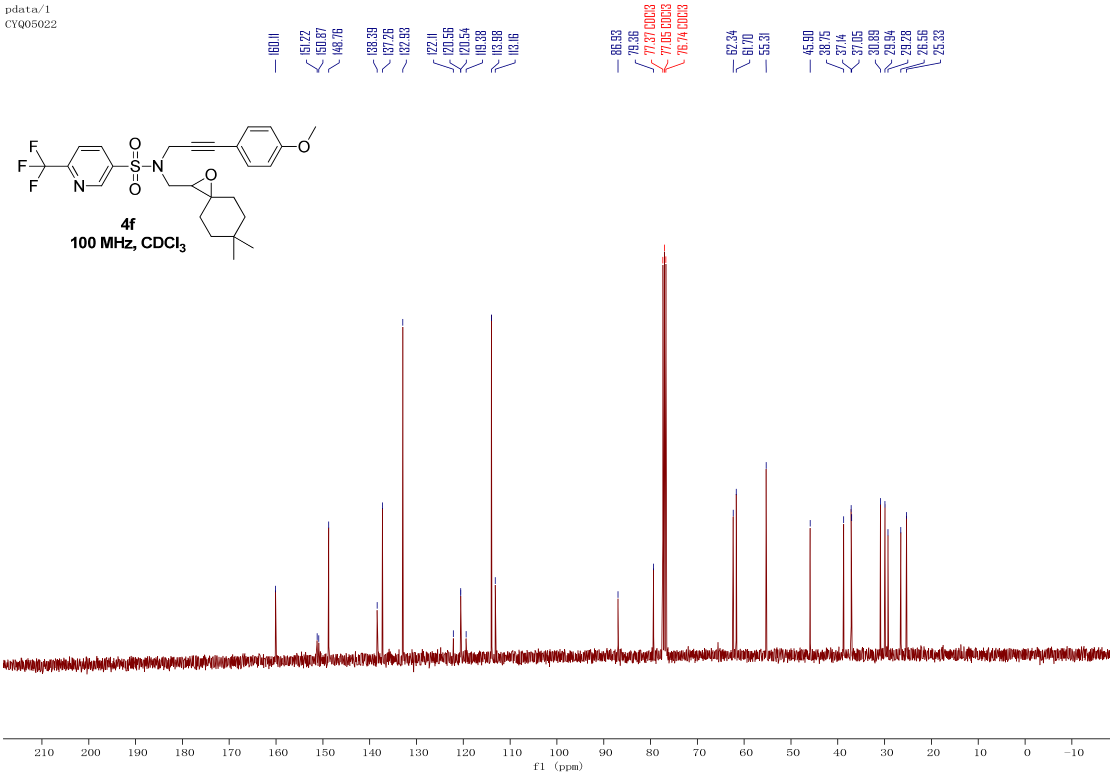

pdata/1
CYQ05116-1
9.21 9.20 8.37 8.36 8.35 8.34 7.77 7.75 7.26 7.22 7.19 6.97 6.96 6.95 4.63 4.58 4.49 4.44 3.77 3.76 3.74 3.73 3.37 3.35 3.34 3.32 3.29 3.28 3.27 3.26 2.66 2.66 2.65 2.64 2.64 2.63 2.62 2.61 2.60 2.58 2.50 2.48 2.47 2.46 2.45 2.43 2.22 2.21 2.19 2.18 2.18 2.17 2.15 2.14 2.12 2.11 1.86 1.85 1.84 1.83 1.76 1.76 1.75 1.75 1.74 1.73 1.73 1.72
F
F
F
N
O
S
O
N
Cl
O
O
4e
400 MHz, CDCl3
1.00
1.04
1.11
1.99
2.09
2.09
1.05
2.07
4.21
2.33
2.79
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)

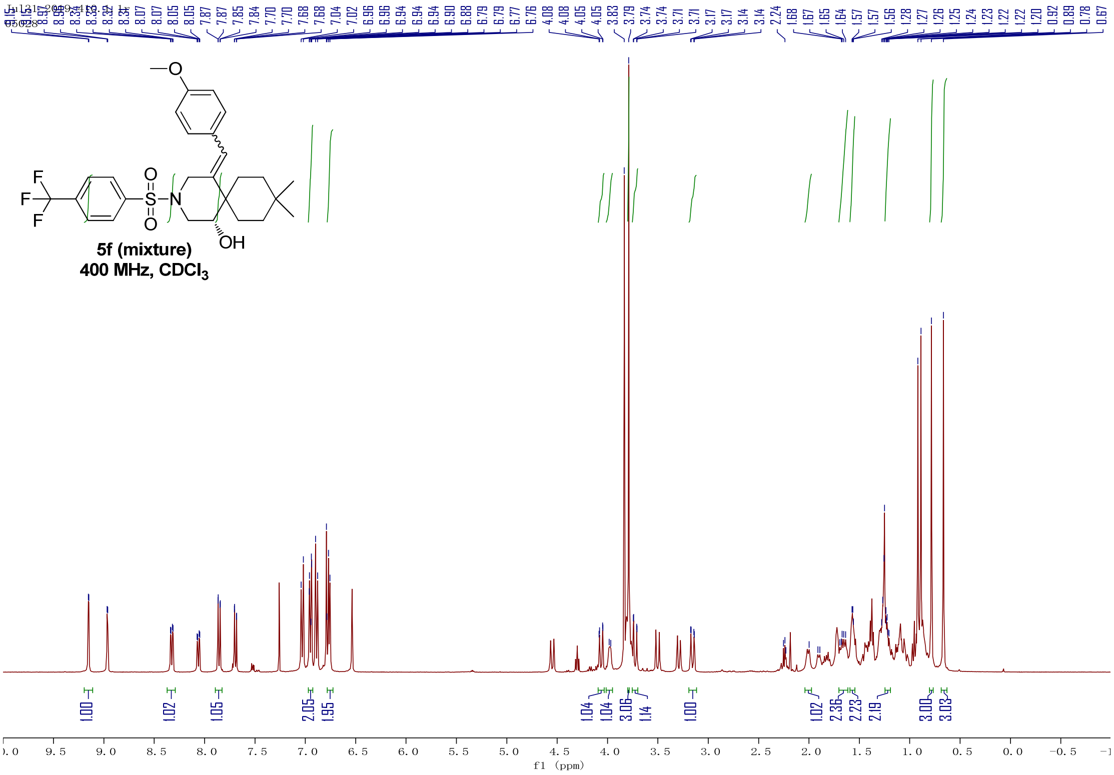

pdata/1
CYQ05116-1
208.95
151.50 151.15 148.70 138.15 137.16 135.35 132.57 132.57 128.77 121.98 120.65 120.63 120.60 120.57 119.35 119.25
85.87 81.46 77.32 CDCl3 77.00 CDCl3 76.68 CDCl3
61.93 60.29
46.22
38.72 38.41 38.33 33.18 27.90
F
F
F
N
O
S
O
N
Cl
O
O
4e
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

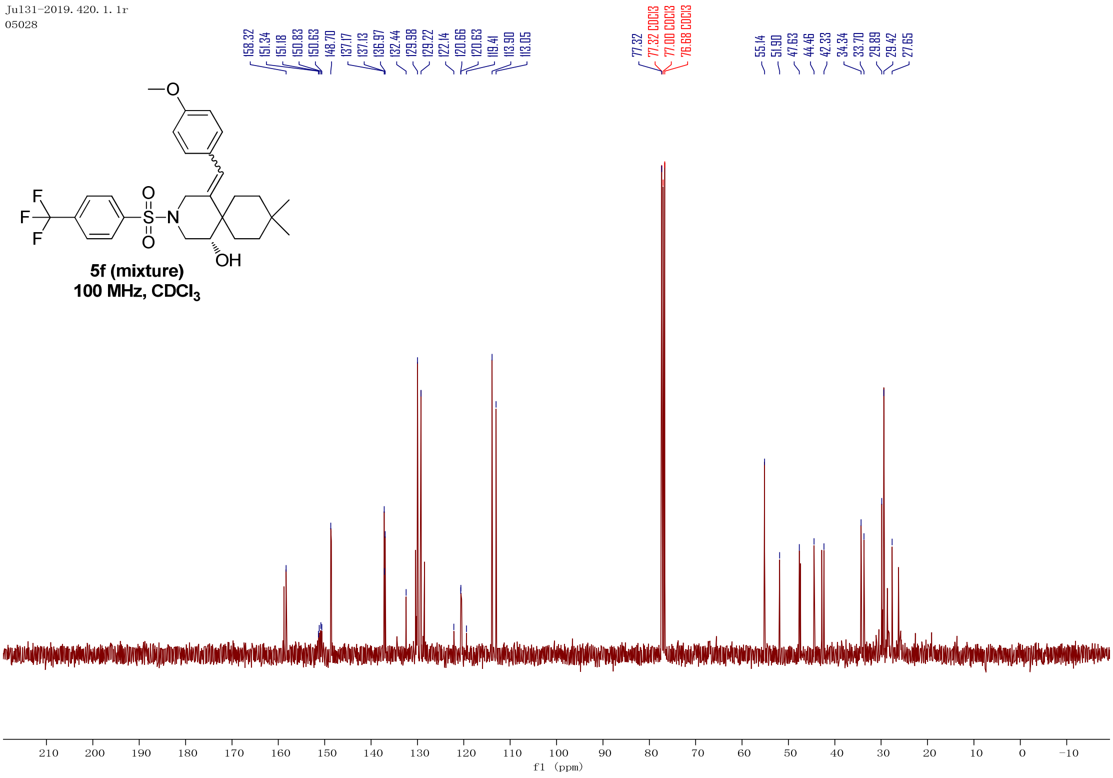

pdata/1
CYQ05118
8.98
8.13
8.12
8.11
8.10
7.78
7.76
7.35
7.33
7.09
7.07
6.65
4.38
4.35
4.29
4.02
4.01
3.98
3.89
3.74
3.71
3.56
3.53
3.37
3.34
2.46
2.44
2.35
2.33
2.32
2.25
2.23
2.21
2.19
2.18
2.12
2.05
2.03
1.97
Cl
F
F
F
N
O
S
O
N
O
OH
5e (mixture)
100 MHz, CDCl3
1.00
1.02
1.02
2.09
2.11
1.06
0.95
1.16
0.75
0.81
1.10
1.40
1.88
1.43
3.99
f1 (ppm)

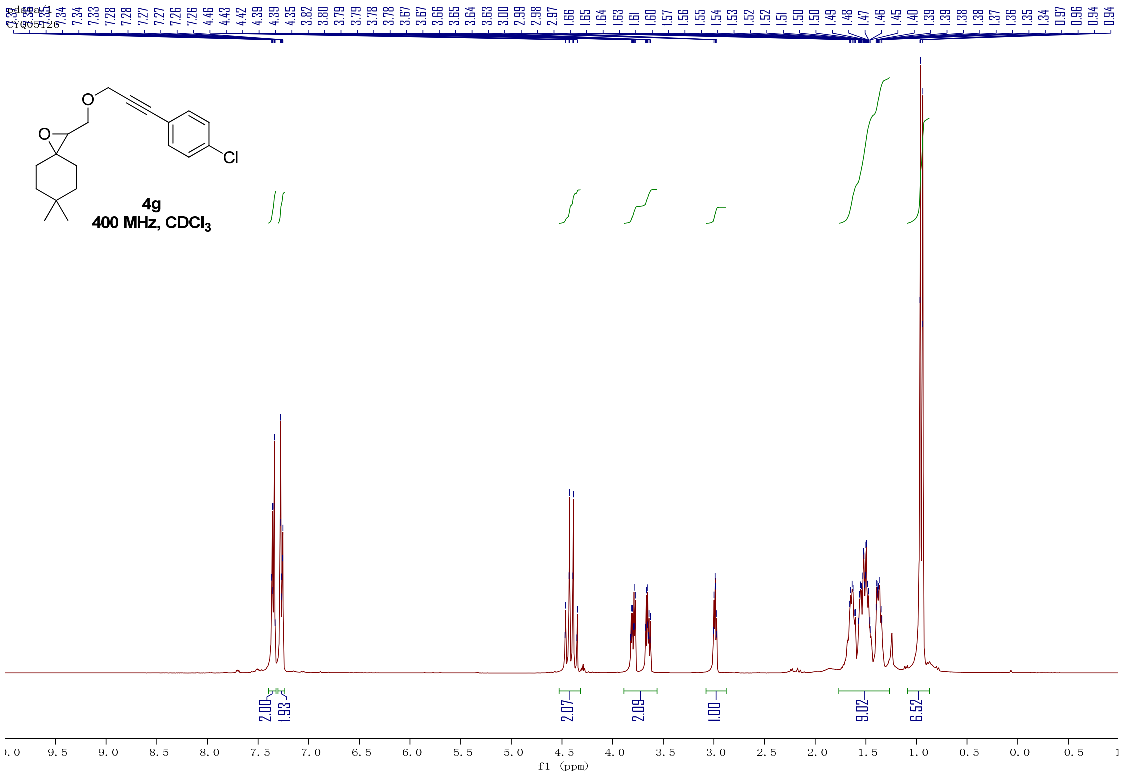

pdata/1
CYQ05118
210.27
151.82
151.46
151.11
150.76
148.46
136.99
135.09
134.00
133.68
130.08
128.83
124.80
122.03
120.75
120.72
119.30
116.57
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
70.52
47.85
42.87
42.71
36.81
36.54
30.97
29.38
Cl
F
F
F
N
O
S
O
N
O
OH
5e (mixture)
100 MHz, CDCl3
f1 (ppm)

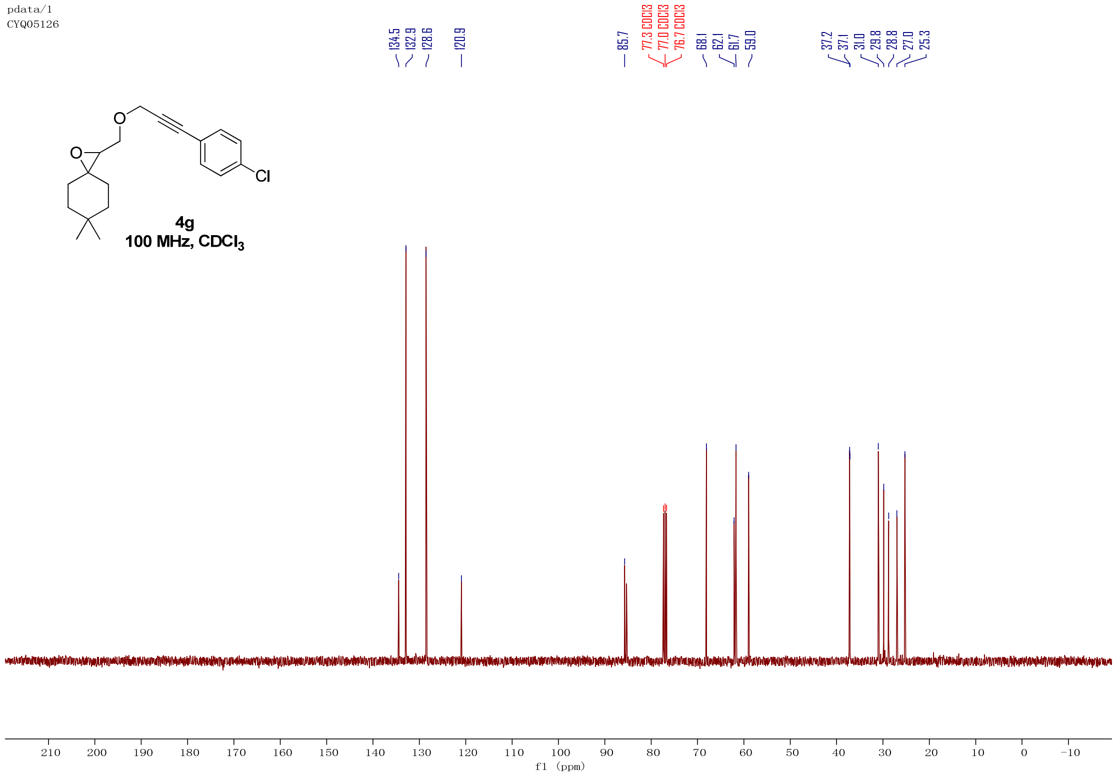

pdata/1
CYQ05022
9.20
9.19
8.37
8.36
8.35
8.34
7.73
7.71
6.98
6.97
6.96
6.96
6.95
6.76
6.75
6.75
6.74
6.73
6.72
4.59
4.54
4.48
4.44
3.78
3.71
3.70
3.67
3.66
3.34
3.32
3.31
3.29
3.04
3.03
3.02
3.01
1.72
1.71
1.69
1.68
1.67
1.66
1.65
1.55
1.53
1.51
1.50
1.50
1.48
1.47
1.43
1.42
1.40
1.37
1.36
0.97
F
F
F
N
O
S
O
N
O
O
4f
400 MHz, CDCl3
1.00
1.05
1.10
2.09
2.11
2.14
3.11
1.09
1.05
1.04
2.89
3.16
3.40
6.29
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)

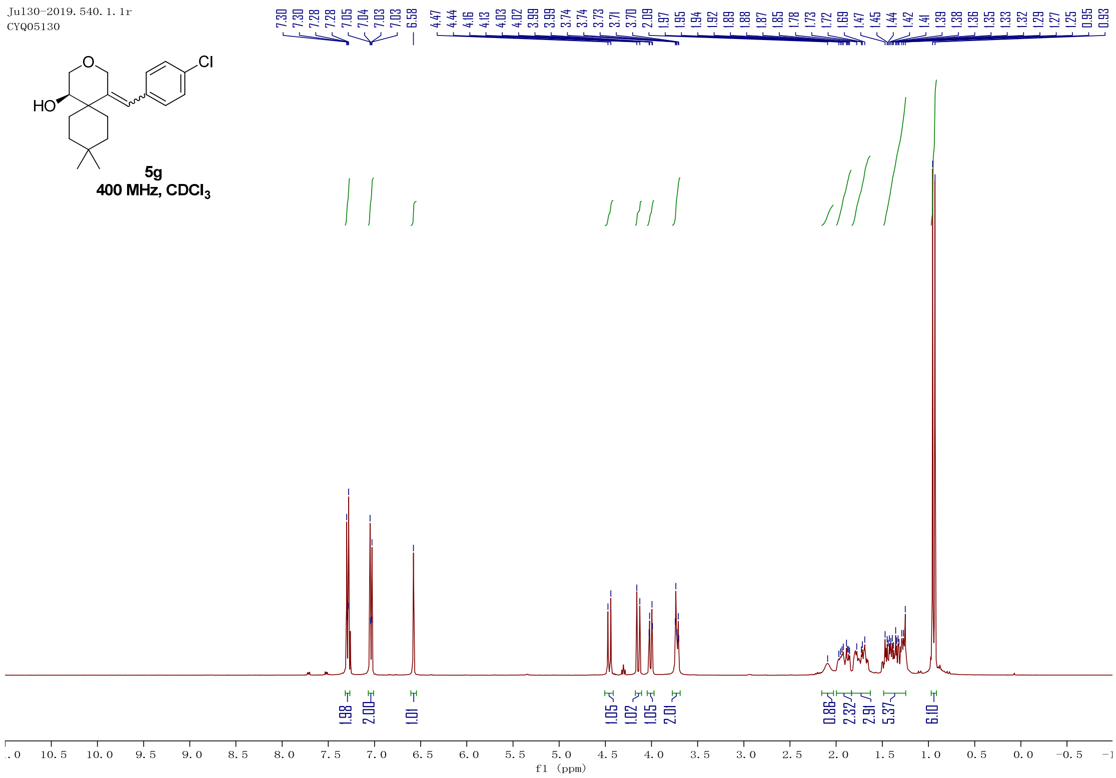

pdata/1
CYQ05022
160.11
151.22
150.87
148.76
138.39
137.26
132.93
122.11
120.56
120.54
119.38
113.98
113.16
86.93
79.36
77.37 CDCl3
77.05 CDCl3
76.74 CDCl3
62.34
61.70
55.31
45.90
38.75
37.14
37.05
30.89
29.94
29.28
26.56
25.33
F
F
F
N
O
S
O
N
O
O
4f
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

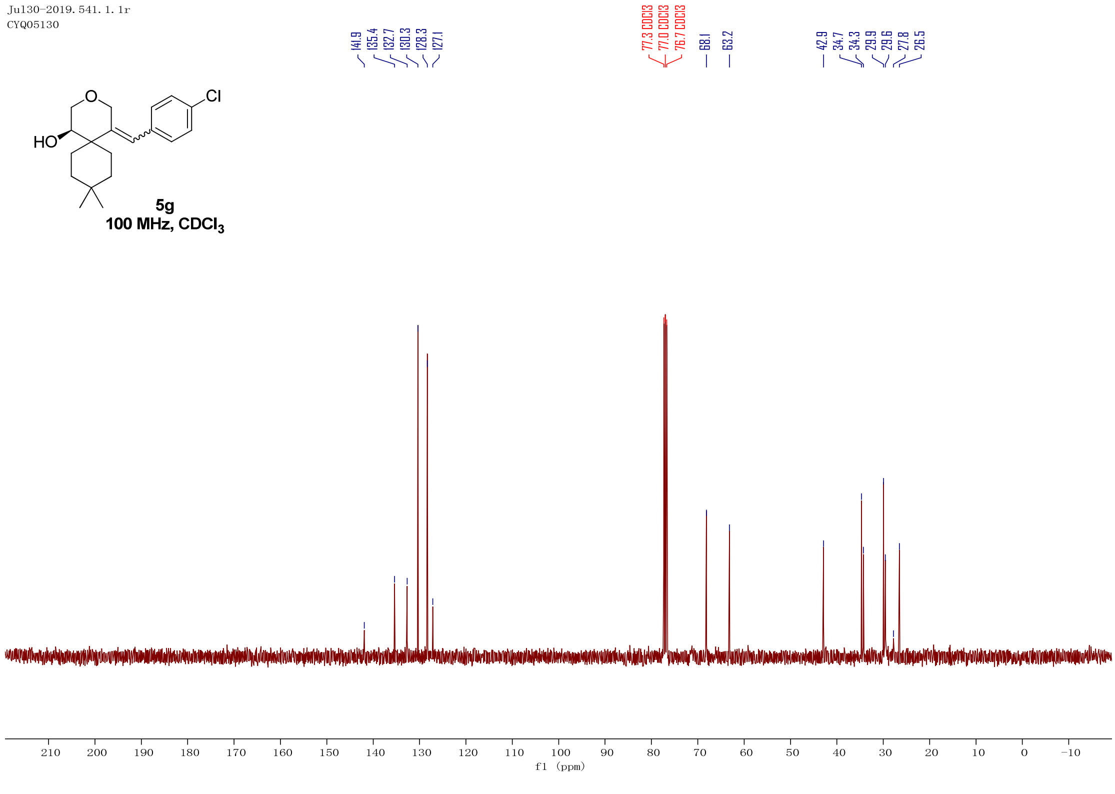

Jul31-2019.410.1.1r
05028
9.15 9.15 8.97 8.95 8.34 8.33 8.32 8.31 8.07 8.07 8.05 8.05 7.87 7.87 7.85 7.84 7.70 7.70 7.68 7.68 7.04 7.02 6.96 6.96 6.94 6.94 6.94 6.90 6.88 6.79 6.79 6.77 6.76 4.08 4.08 4.05 4.05 3.83 3.79 3.74 3.74 3.71 3.71 3.17 3.17 3.14 3.14 2.24 1.68 1.67 1.65 1.64 1.57 1.57 1.56 1.28 1.27 1.26 1.25 1.24 1.23 1.22 1.22 1.20 0.92 0.89 0.78 0.67
F
F
F
O
S
O
N
OH
O
5f (mixture)
400 MHz, CDCl3
1.00 1.02 1.05 2.05 1.95 1.04 1.04 3.06 1.14 1.00 1.02 2.36 2.23 2.19 3.00 3.03
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 −1
f1 (ppm)

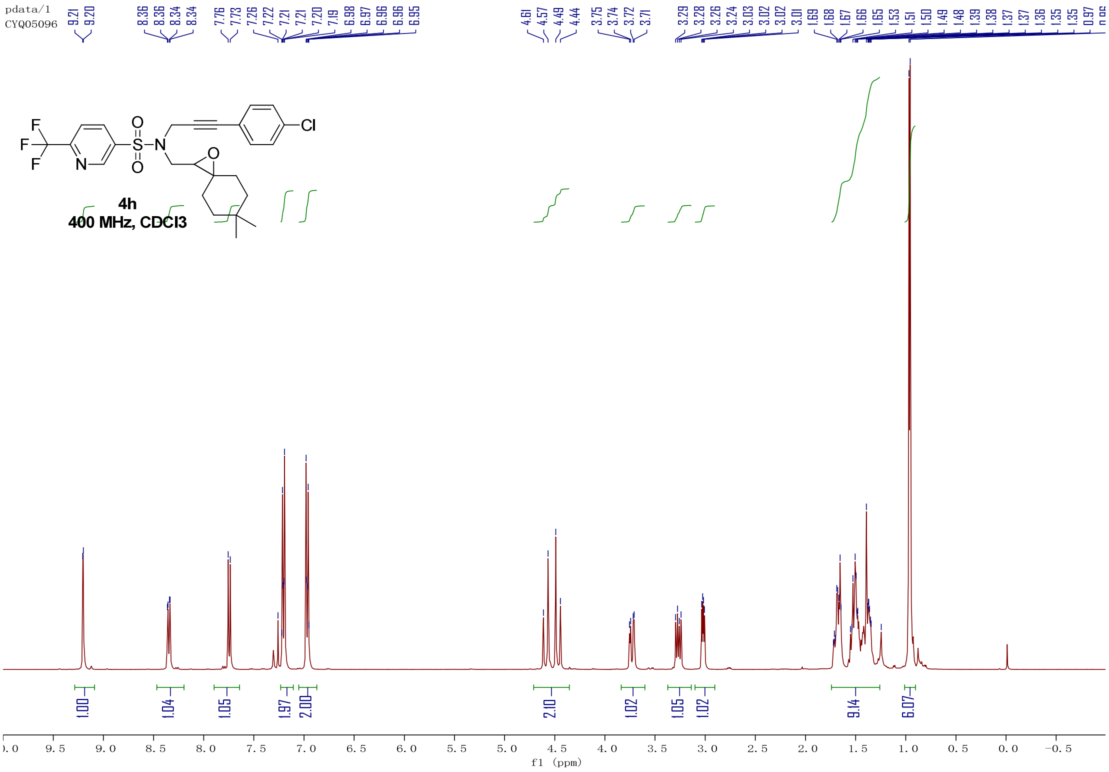

Jul31-2019.420.1.1r
05028
158.32 151.34 151.18 150.83 150.63 148.70 137.17 137.13 136.97 132.44 129.98 129.22 122.14 120.66 120.63 119.41 113.90 113.05
77.32 77.32 CDCl3 77.00 CDCl3 76.68 CDCl3
55.14 51.90 47.63 44.46 42.33 34.34 33.70 29.89 29.42 27.65
F
F
F
O
S
O
N
OH
O
5f (mixture)
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

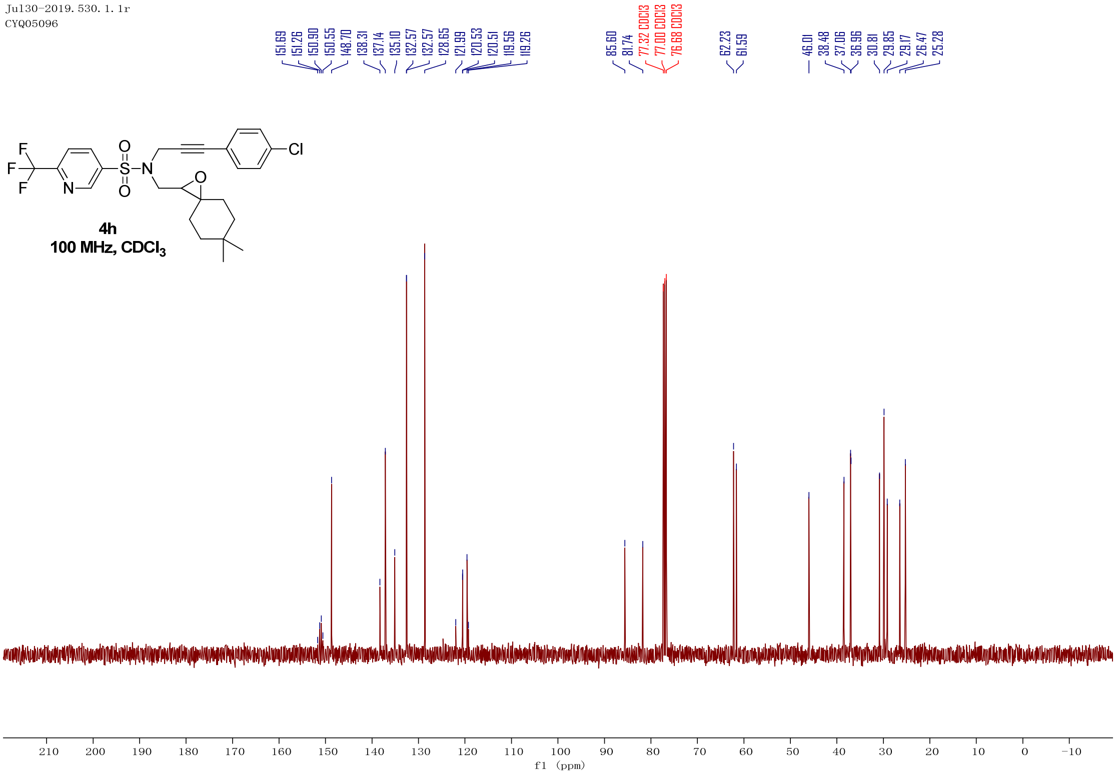

pdata/1
CYQ05126
7.34
7.34
7.33
7.28
7.28
7.27
7.27
7.26
7.26
4.46
4.43
4.42
4.39
4.39
4.35
3.82
3.80
3.79
3.79
3.78
3.78
3.67
3.67
3.66
3.65
3.64
3.63
3.00
2.99
2.98
2.97
1.66
1.65
1.64
1.63
1.61
1.60
1.57
1.56
1.55
1.54
1.53
1.52
1.52
1.51
1.50
1.50
1.49
1.48
1.47
1.46
1.45
1.40
1.39
1.39
1.38
1.38
1.37
1.36
1.35
1.34
0.97
0.96
0.94
0.94
Cl
O
O
4g
400 MHz, CDCl3
2.00
1.93
2.07
2.09
1.00
9.02
6.52
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)

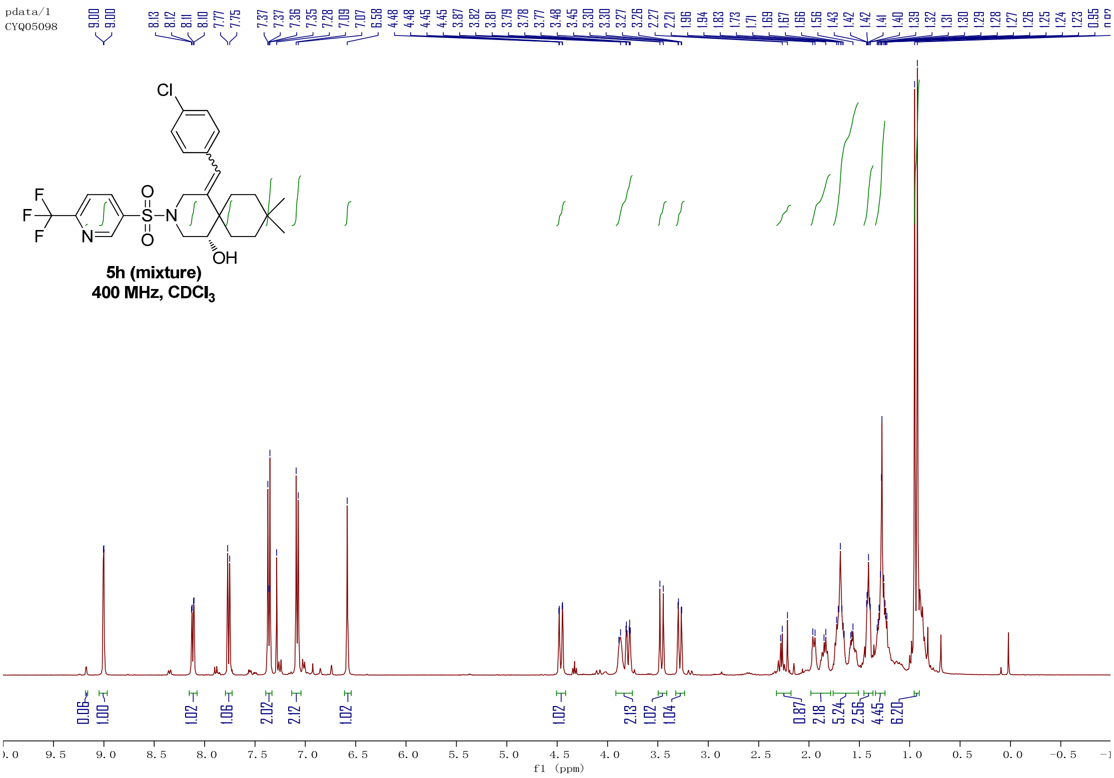

pdata/1
CYQ05126
134.5
132.9
128.6
120.9
85.7
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
68.1
62.1
61.7
59.0
37.2
37.1
31.0
29.8
28.8
27.0
25.3
Cl
O
O
4g
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

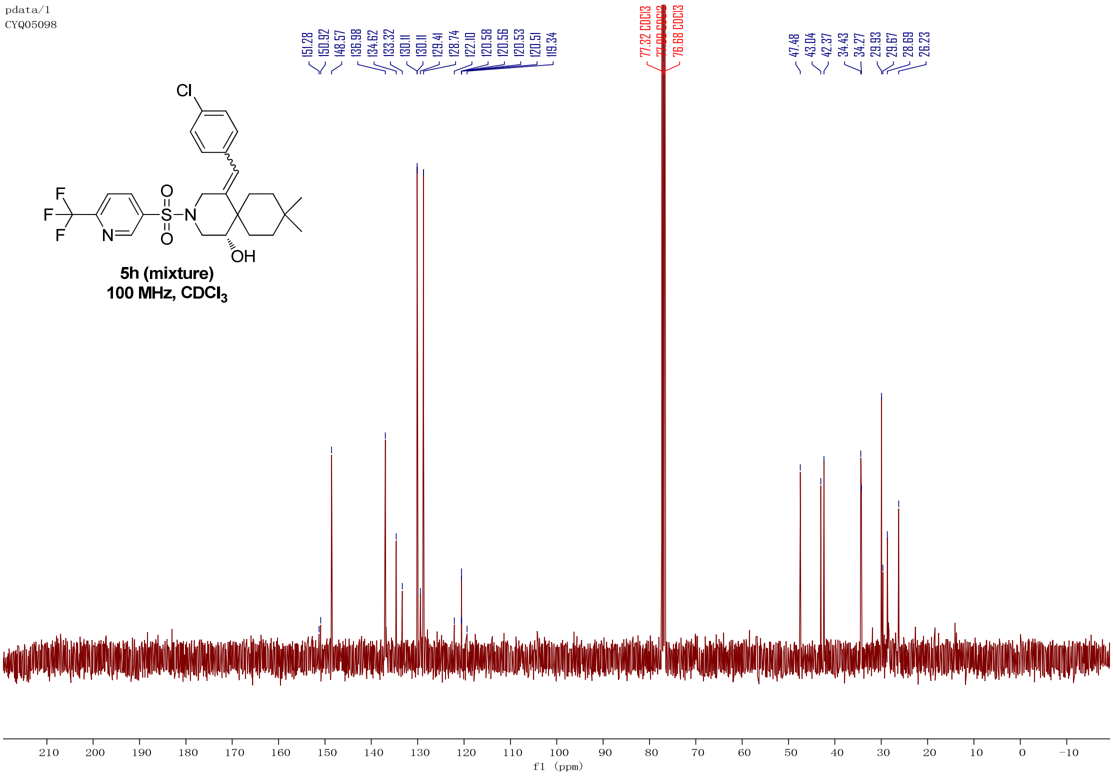

Jul30-2019.540.1.1r
CYQ05130
5g
400 MHz, CDCl$_3$
Cl
HO
O
7.30
7.30
7.28
7.28
7.05
7.04
7.03
7.03
6.58
4.47
4.44
4.16
4.13
4.03
4.02
3.99
3.99
3.74
3.74
3.73
3.71
3.70
2.09
1.97
1.95
1.94
1.92
1.89
1.88
1.87
1.85
1.78
1.73
1.72
1.69
1.47
1.45
1.44
1.42
1.41
1.39
1.38
1.36
1.35
1.33
1.32
1.29
1.27
1.25
0.95
0.93
1.98
2.00
1.01
1.05
1.02
1.05
2.01
0.86
2.32
2.91
5.37
6.10
f1 (ppm)

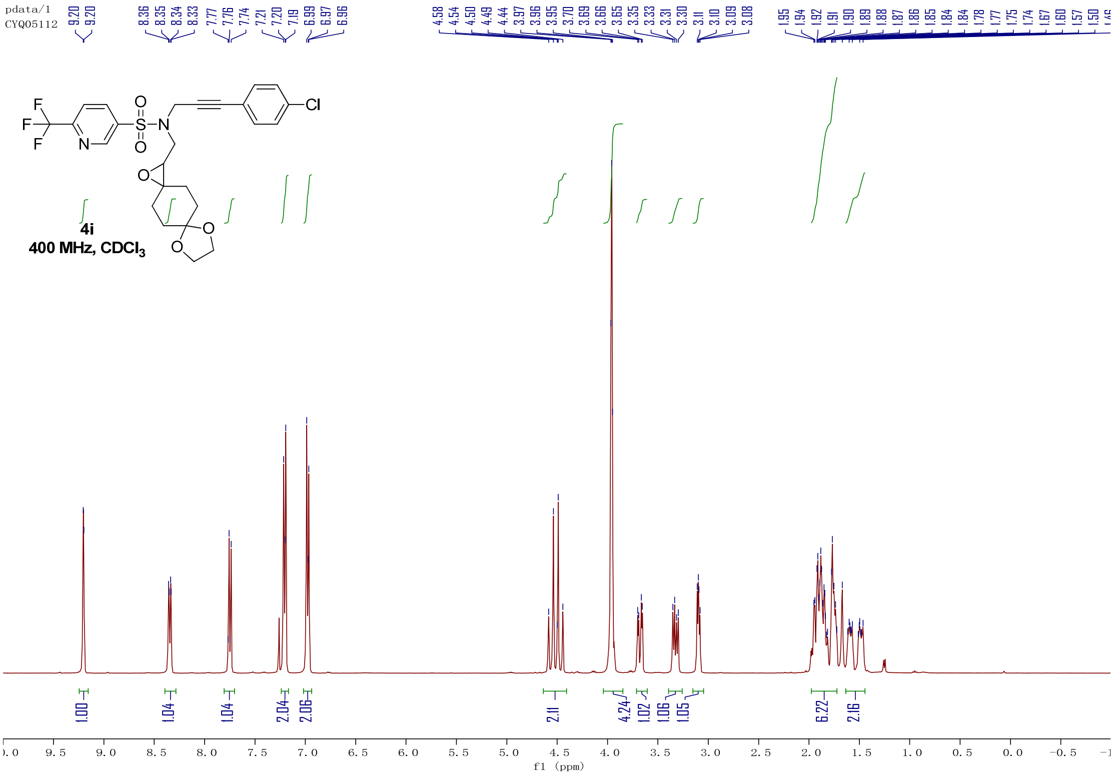

Jul30-2019.541.1.1r
CYQ05130
5g
100 MHz, CDCl$_3$
Cl
HO
O
141.9
135.4
132.7
130.3
128.3
127.1
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
68.1
63.2
42.9
34.7
34.3
29.9
29.6
27.8
26.5
f1 (ppm)

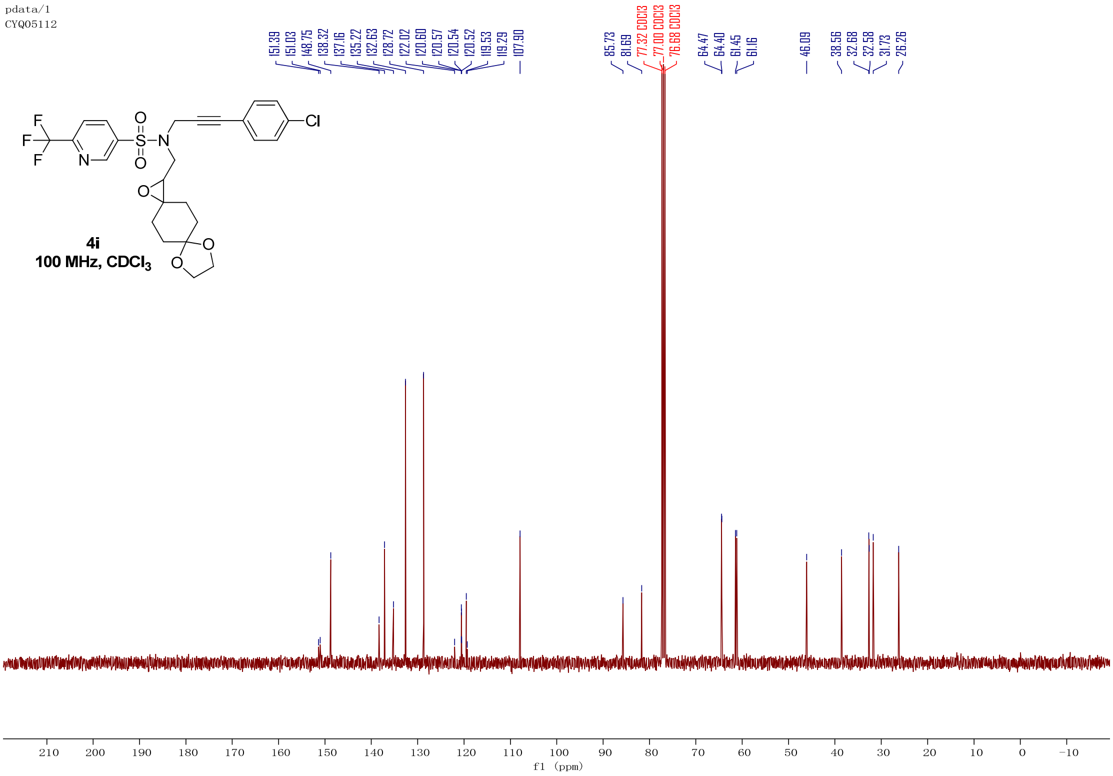

pdata/1
CYQ05096
9.21
9.20
8.36
8.36
8.34
8.34
7.76
7.73
7.26
7.22
7.21
7.21
7.20
7.19
6.98
6.97
6.96
6.96
6.95
4.61
4.57
4.49
4.44
3.75
3.74
3.72
3.71
3.29
3.28
3.26
3.24
3.03
3.02
3.02
3.01
1.69
1.68
1.67
1.66
1.65
1.53
1.51
1.50
1.49
1.48
1.39
1.38
1.37
1.37
1.36
1.35
0.97
F
F
F
N
O
S
O
N
O
Cl
4h
400 MHz, CDCl3
1.00
1.04
1.05
1.97
2.00
2.10
1.02
1.05
1.02
9.14
6.07
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)

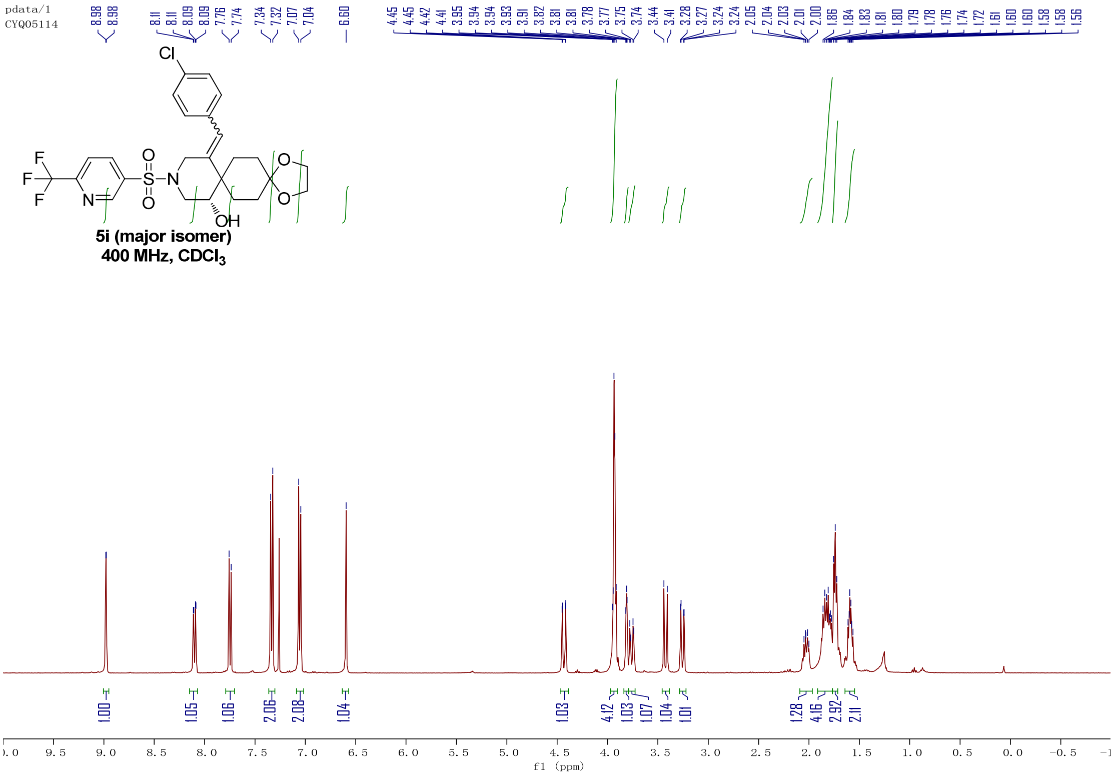

Jul30-2019.530.1.1r
CYQ05096
151.69
151.26
150.90
150.55
148.70
138.31
137.14
135.10
132.57
132.57
128.65
121.99
120.53
120.51
119.56
119.26
85.60
81.74
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
62.23
61.59
46.01
38.48
37.06
36.96
30.81
29.85
29.17
26.47
25.28
F
F
F
N
O
S
O
N
O
Cl
4h
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

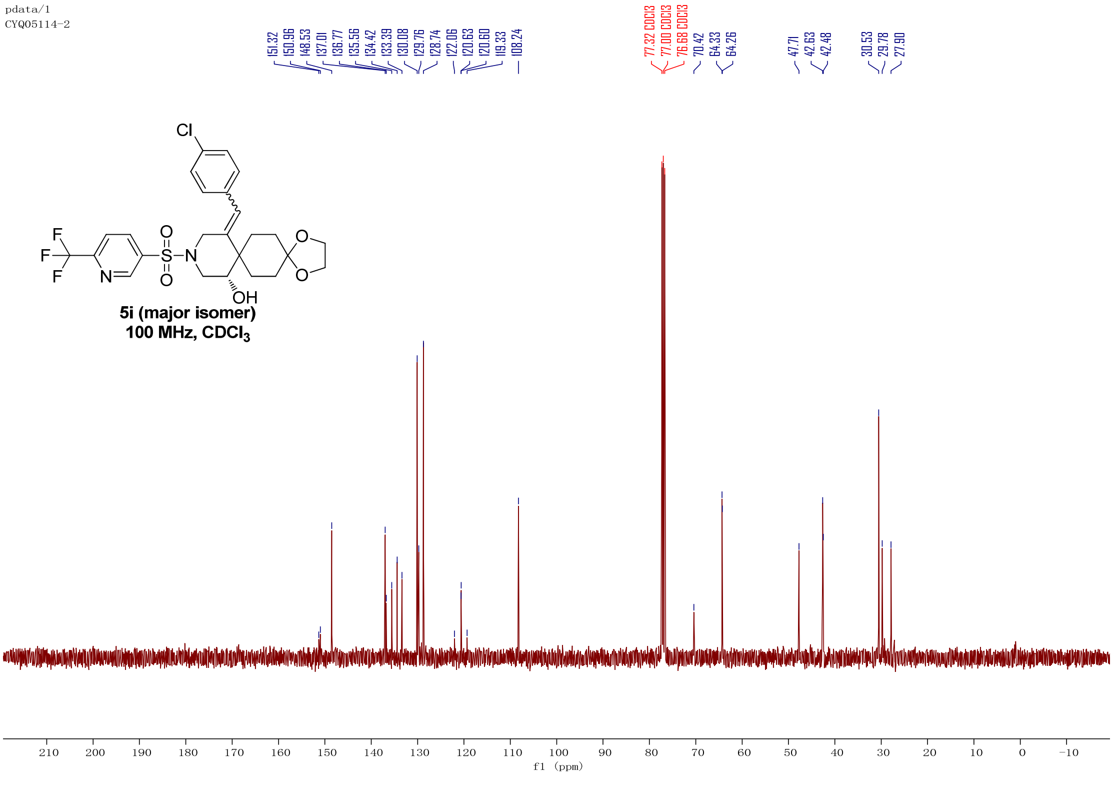

pdata/1
CYQ05098
9.00
9.00
8.13
8.12
8.11
8.10
7.77
7.75
7.37
7.37
7.36
7.35
7.28
7.09
7.07
6.58
4.48
4.48
4.45
4.45
3.87
3.82
3.81
3.79
3.78
3.77
3.48
3.45
3.30
3.30
3.27
3.26
2.27
2.21
1.96
1.94
1.83
1.73
1.71
1.69
1.67
1.66
1.56
1.43
1.42
1.42
1.41
1.40
1.39
1.32
1.31
1.30
1.29
1.28
1.27
1.26
1.25
1.24
1.23
0.95
Cl
F
F
F
N
O
S
O
N
OH
5h (mixture)
400 MHz, CDCl$_3$
0.06
1.00
1.02
1.06
2.02
2.12
1.02
1.02
2.13
1.02
1.04
0.87
2.18
5.24
2.56
4.45
6.20
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)

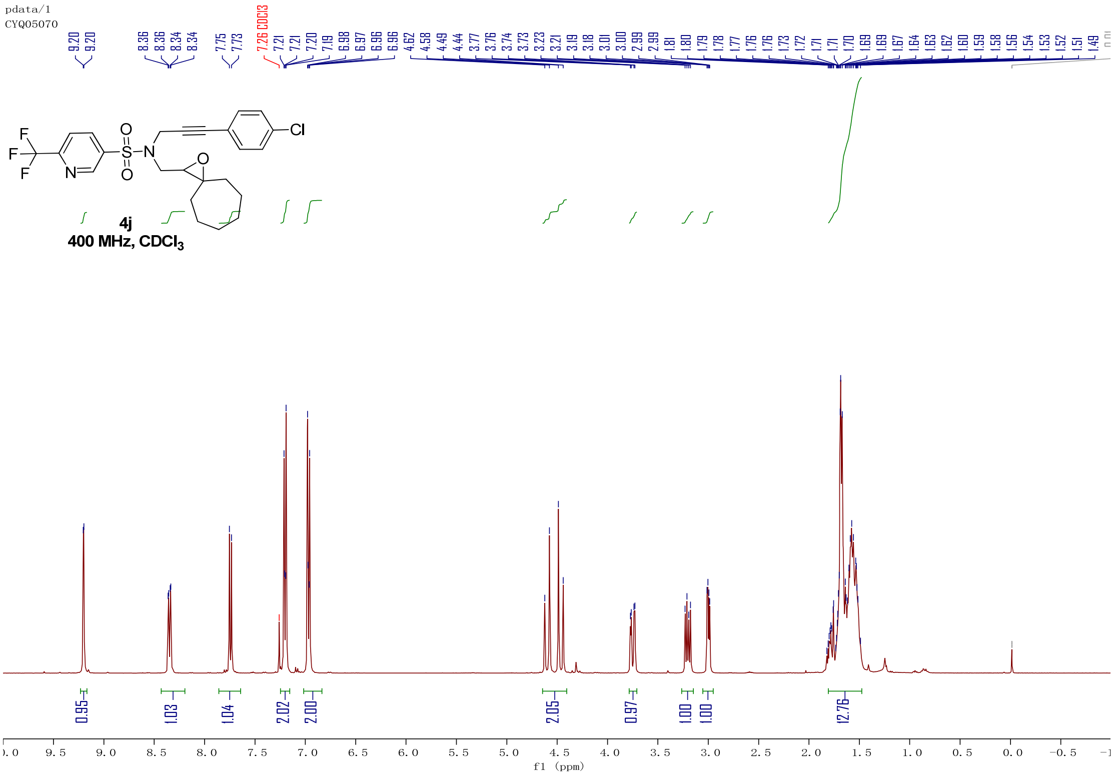

pdata/1
CYQ05098
151.28
150.92
148.57
136.98
134.62
133.32
130.11
130.11
129.41
128.74
122.10
120.58
120.56
120.53
120.51
119.34
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
47.48
43.04
42.37
34.43
34.27
29.93
29.67
28.69
26.23
Cl
F
F
F
N
O
S
O
N
OH
5h (mixture)
100 MHz, CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

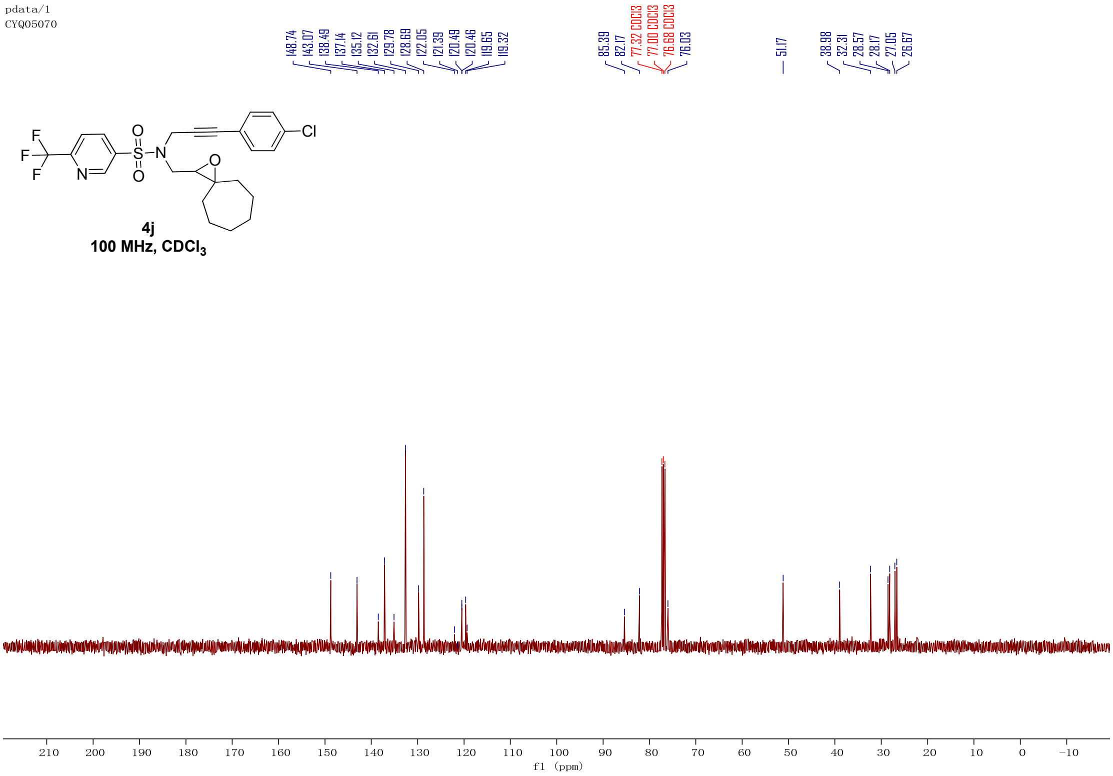

pdata/1
CYQ05112
9.20
9.20
8.36
8.35
8.34
8.33
7.77
7.76
7.74
7.21
7.20
7.19
6.99
6.97
6.96
4.58
4.54
4.50
4.49
4.44
3.97
3.96
3.95
3.70
3.69
3.66
3.65
3.35
3.33
3.31
3.30
3.11
3.10
3.09
3.08
1.95
1.94
1.92
1.91
1.90
1.89
1.88
1.87
1.86
1.85
1.84
1.84
1.78
1.77
1.75
1.74
1.67
1.60
1.57
1.50
F
F
F
N
O
S
O
N
Cl
O
O
O
4i
400 MHz, CDCl$_3$
1.00
1.04
1.04
2.04
2.06
2.11
4.24
1.02
1.06
1.05
6.22
2.16
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)

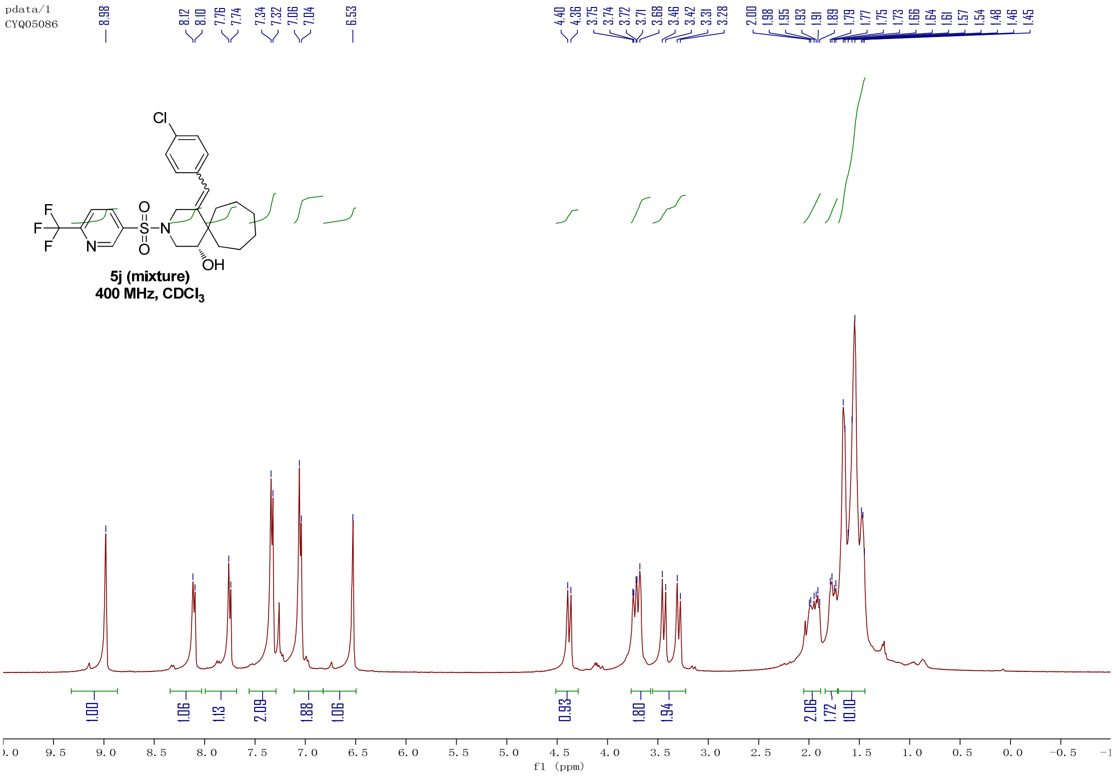

pdata/1
CYQ05112
151.39
151.03
148.75
138.32
137.16
135.22
132.63
128.72
122.02
120.60
120.57
120.54
120.52
119.53
119.29
107.90
85.73
81.69
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
64.47
64.40
61.45
61.16
46.09
38.56
32.68
32.58
31.73
26.26
F
F
F
N
O
S
O
N
Cl
O
O
O
4i
100 MHz, CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


pdata/1
CYQ05114
8.98
8.98
8.11
8.11
8.09
8.09
7.76
7.74
7.34
7.32
7.07
7.04
6.60
4.45
4.45
4.42
4.41
3.95
3.94
3.94
3.93
3.91
3.82
3.81
3.81
3.78
3.77
3.75
3.74
3.44
3.41
3.28
3.27
3.24
3.24
2.05
2.04
2.03
2.01
2.00
1.86
1.84
1.83
1.81
1.80
1.79
1.78
1.76
1.74
1.72
1.61
1.60
1.60
1.58
1.58
1.56
Cl
F
F
F
N
O
S
O
N
O
O
OH
5i (major isomer)
400 MHz, CDCl$_3$
1.00
1.05
1.06
2.06
2.08
1.04
1.03
4.12
1.03
1.07
1.04
1.01
1.28
4.16
2.92
2.11
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
-1
f1 (ppm)

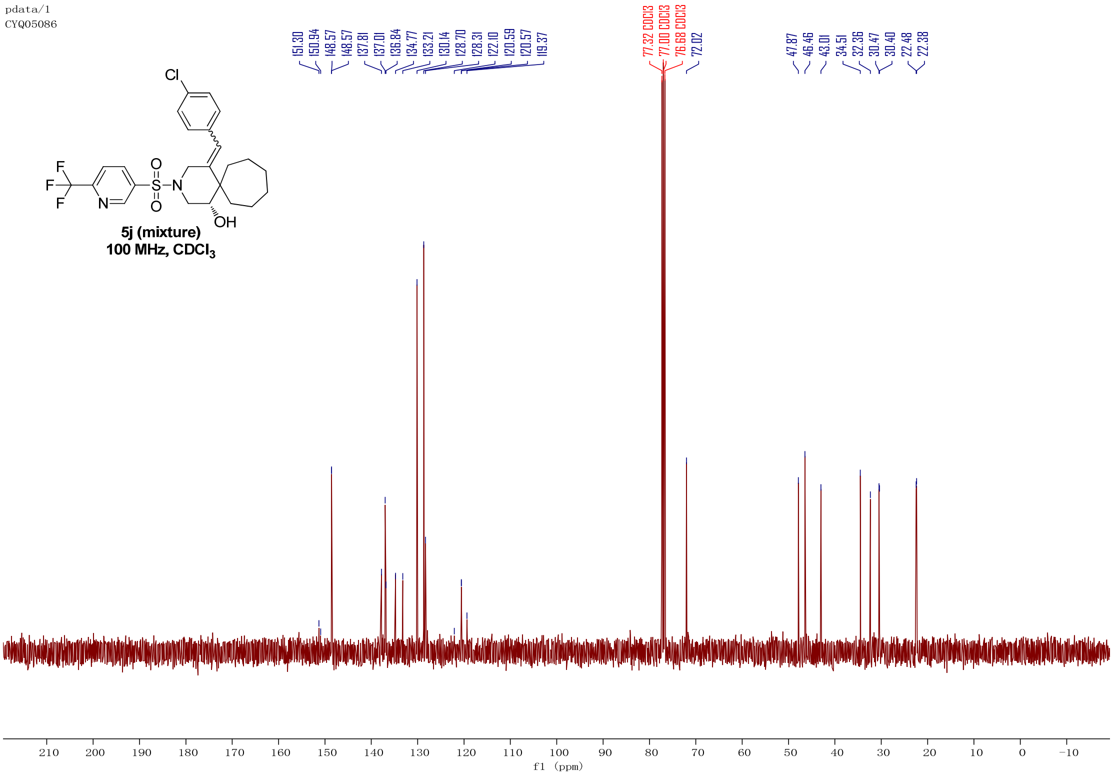

pdata/1
CYQ05114-2
151.32
150.96
148.53
137.01
136.77
135.56
134.42
133.39
130.08
129.76
128.74
122.06
120.63
120.60
119.33
108.24
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
70.42
64.33
64.26
47.71
42.63
42.48
30.53
29.78
27.90
Cl
F
F
F
N
O
S
O
N
O
O
OH
5i (major isomer)
100 MHz, CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


pdata/1
CYQ05070
9.20
9.20
8.36
8.36
8.34
8.34
7.75
7.73
7.26 CDCl3
7.21
7.21
7.20
7.19
6.98
6.97
6.96
6.96
4.62
4.58
4.49
4.44
3.77
3.76
3.74
3.73
3.23
3.21
3.19
3.18
3.01
3.00
2.99
2.99
1.81
1.80
1.79
1.78
1.77
1.76
1.76
1.73
1.72
1.71
1.71
1.70
1.69
1.69
1.67
1.64
1.63
1.62
1.60
1.59
1.58
1.56
1.54
1.53
1.52
1.51
1.49
F
F
F
N
O
S
O
N
O
Cl
4j
400 MHz, CDCl$_3$
0.95
1.03
1.04
2.02
2.00
2.05
0.97
1.00
1.00
12.76
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)

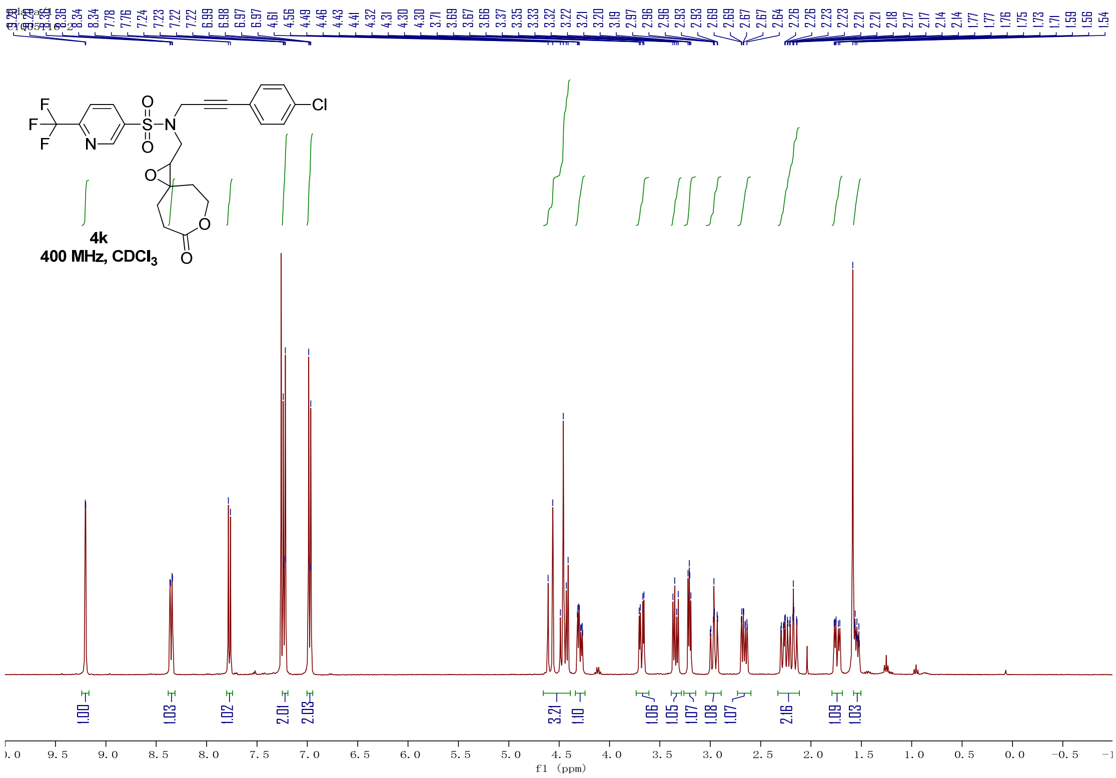

pdata/1
CYQ05070
148.74
143.07
138.49
137.14
135.12
132.61
129.78
128.69
122.05
121.39
120.49
120.46
119.65
119.32
85.39
82.17
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.03
51.17
38.98
32.31
28.57
28.17
27.05
26.67
F
F
F
N
O
S
O
N
O
Cl
4j
100 MHz, CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

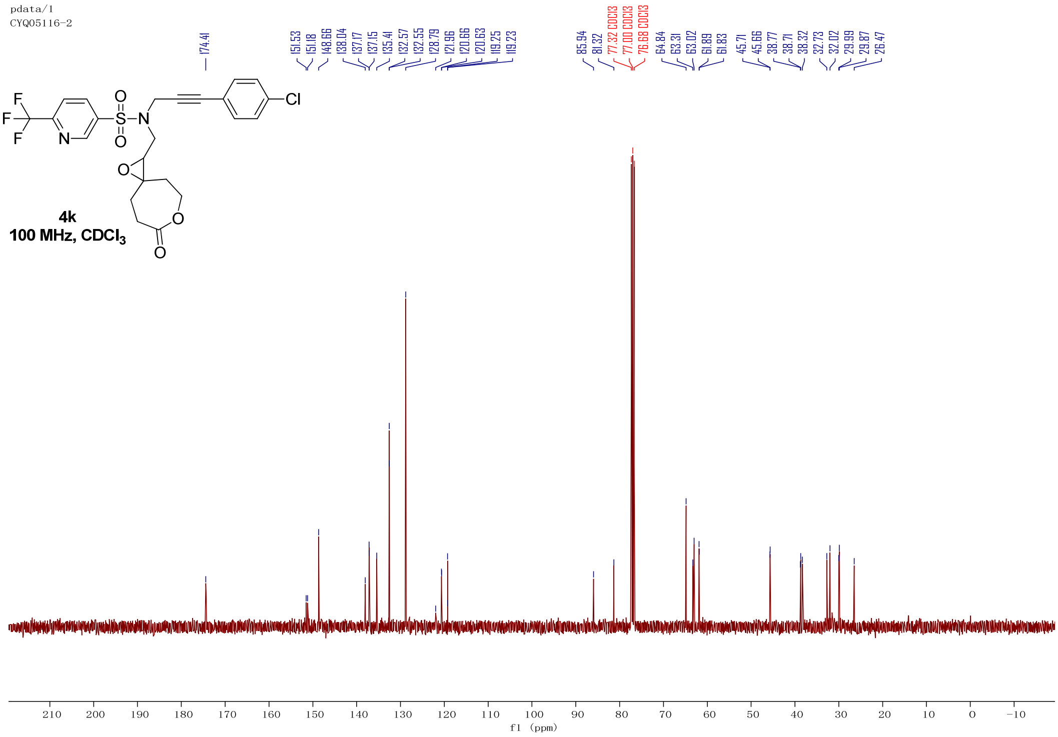


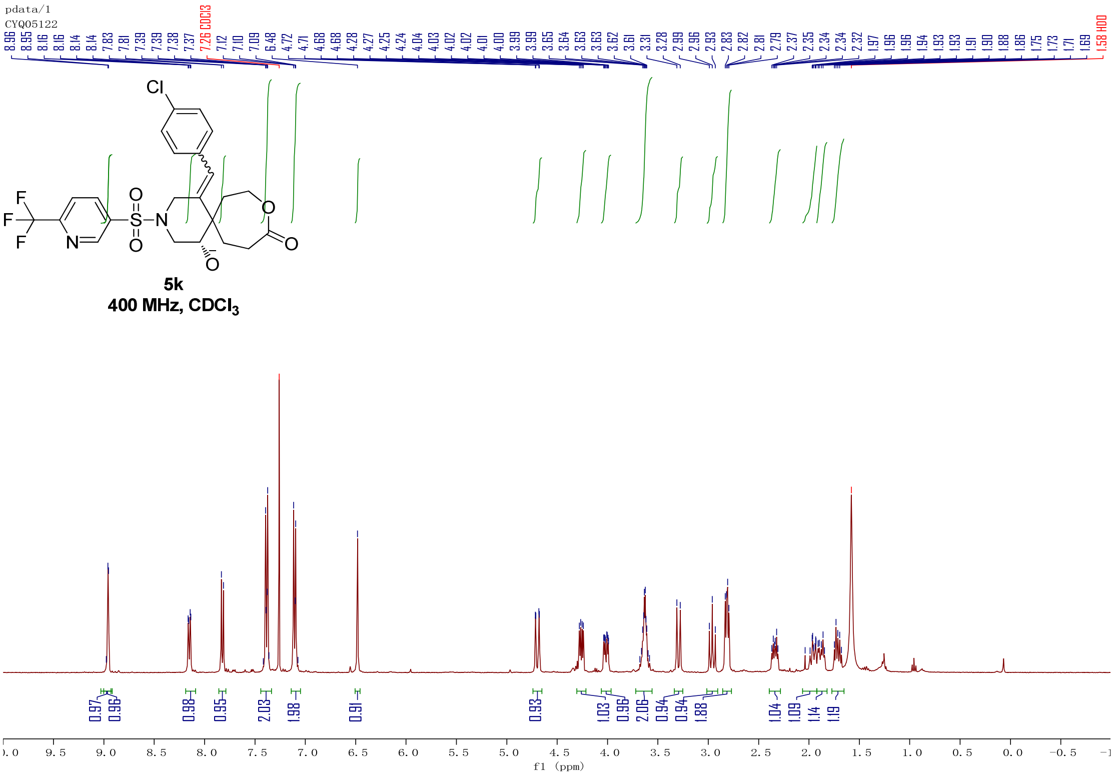
5j (mixture)
400 MHz, CDCl$_3$



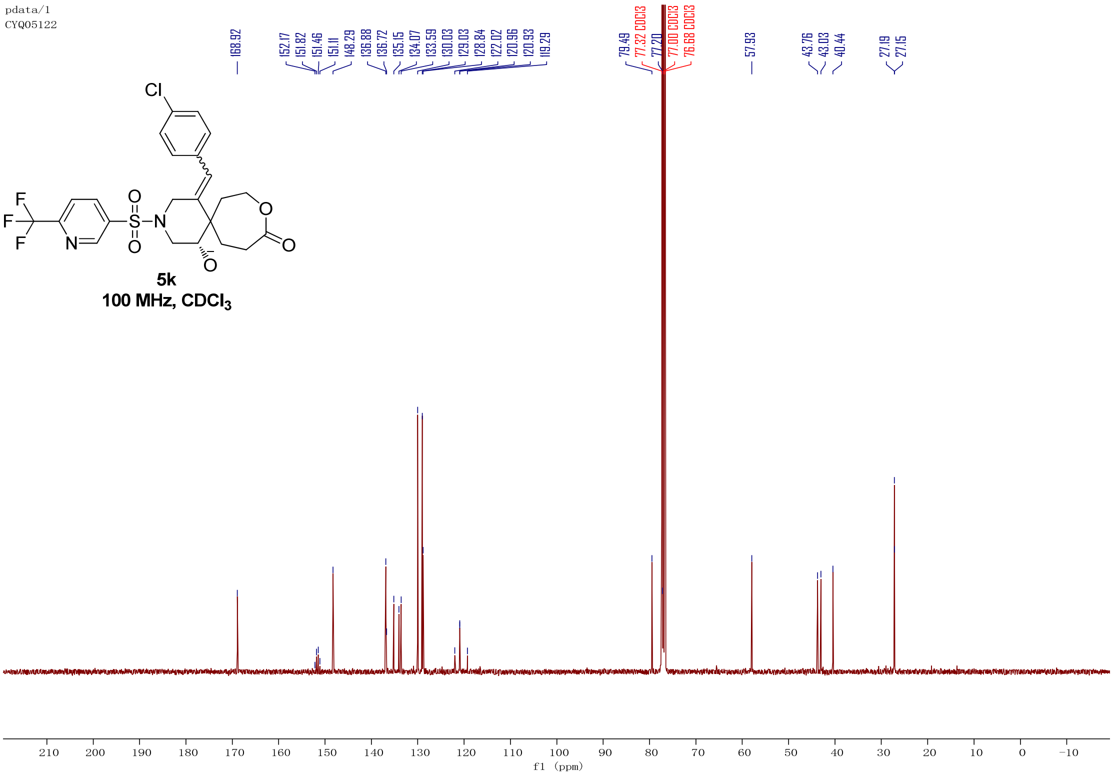
5j (mixture)
100 MHz, CDCl$_3$


pdata/1
CYQ05116-2
9.20
9.20
8.36
8.36
8.34
8.34
7.78
7.76
7.24
7.23
7.22
7.22
6.99
6.98
6.97
6.97
4.61
4.56
4.49
4.46
4.43
4.41
4.32
4.31
4.30
4.30
3.71
3.69
3.67
3.66
3.37
3.35
3.33
3.32
3.22
3.21
3.20
3.19
2.97
2.96
2.96
2.93
2.93
2.69
2.69
2.67
2.67
2.64
2.26
2.26
2.23
2.23
2.21
2.21
2.18
2.17
2.17
2.14
2.14
1.77
1.77
1.76
1.75
1.73
1.71
1.59
1.56
1.54
F
F
F
N
O
S
O
N
Cl
O
O
O
4k
400 MHz, CDCl$_3$
1.00
1.03
1.02
2.01
2.03
3.21
1.10
1.06
1.05
1.07
1.08
1.07
2.16
1.09
1.03
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
−1
f1 (ppm)

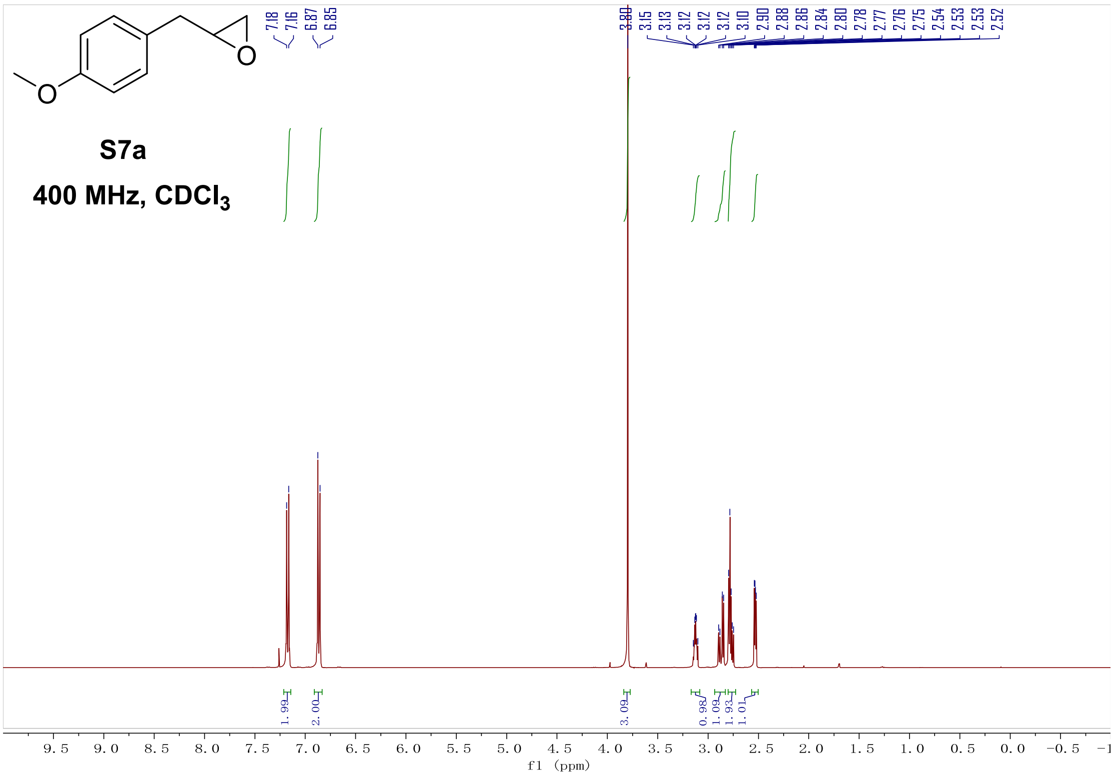

pdata/1
CYQ05116-2
174.41
151.53
151.18
148.66
138.04
137.17
137.15
135.41
132.57
132.55
128.79
121.96
120.66
120.63
119.25
119.23
85.94
81.32
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
64.84
63.31
63.02
61.89
61.83
45.71
45.66
38.77
38.71
38.32
32.73
32.02
29.99
29.87
26.47
F
F
F
N
O
S
O
N
Cl
O
O
O
4k
100 MHz, CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

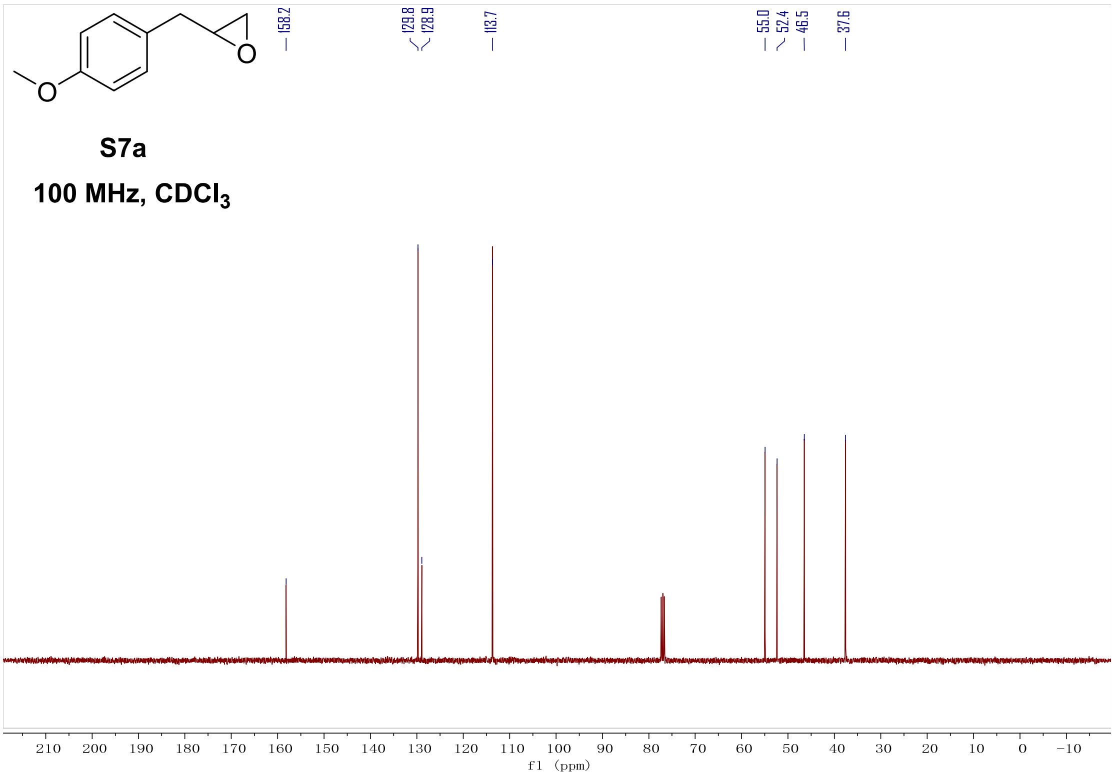


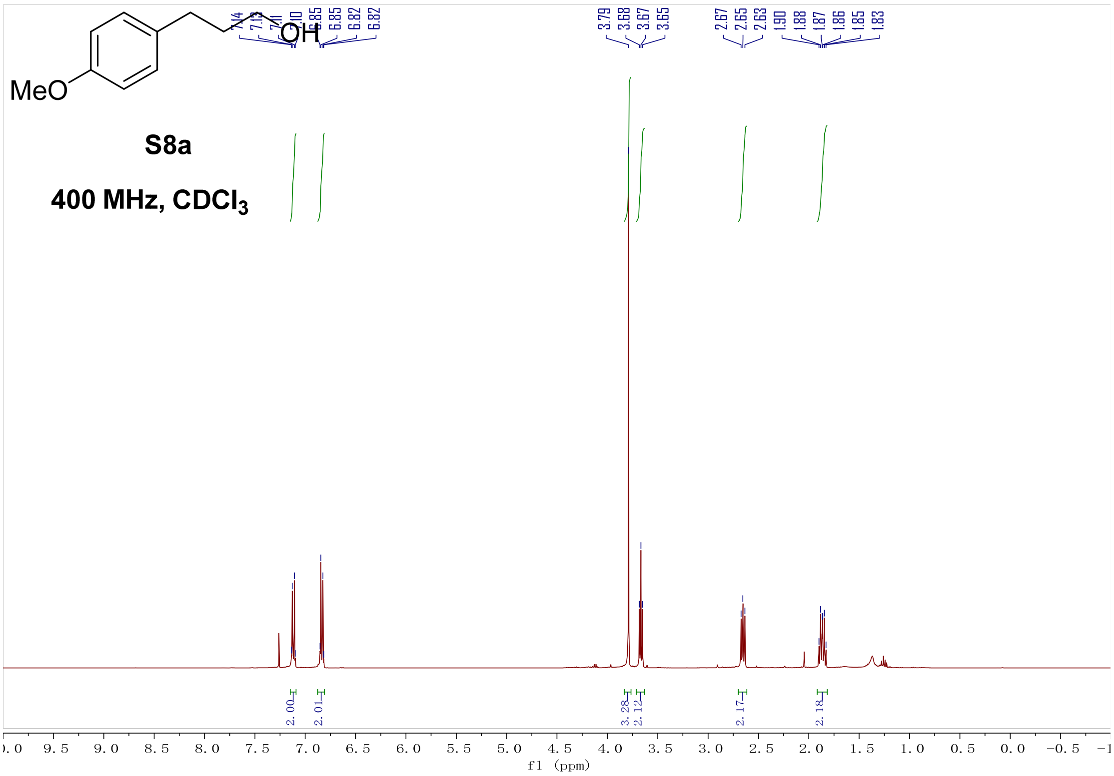
5k
400 MHz, CDCl$_3$

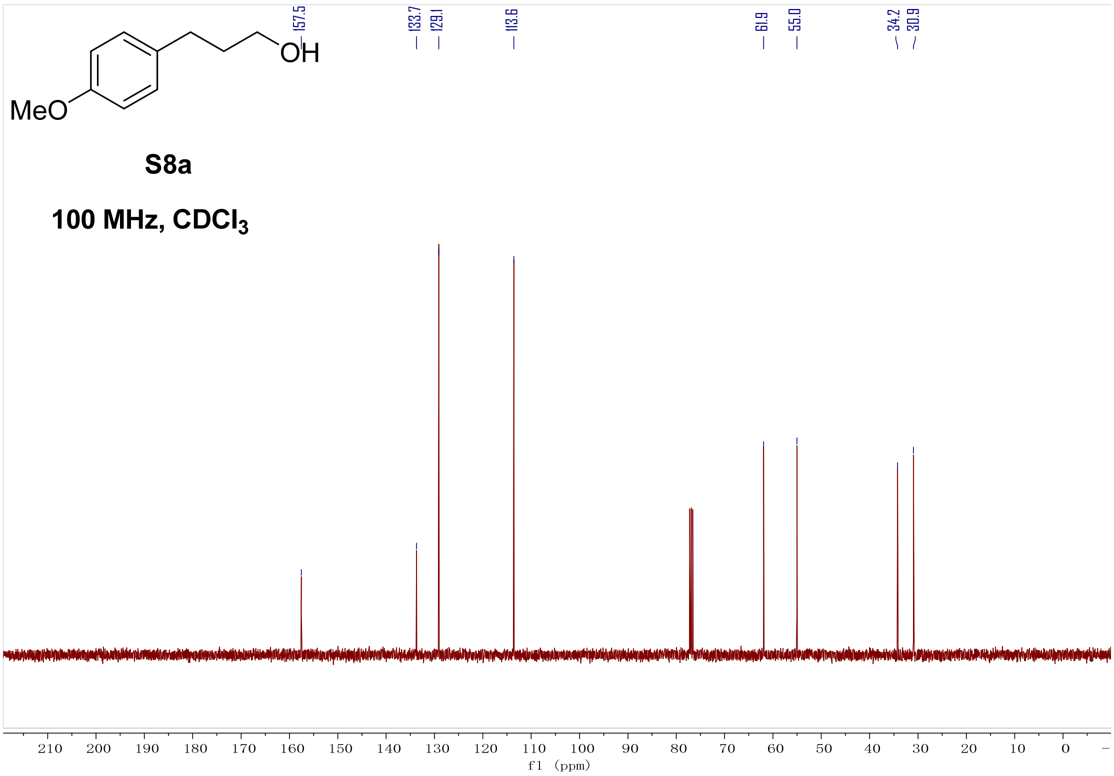


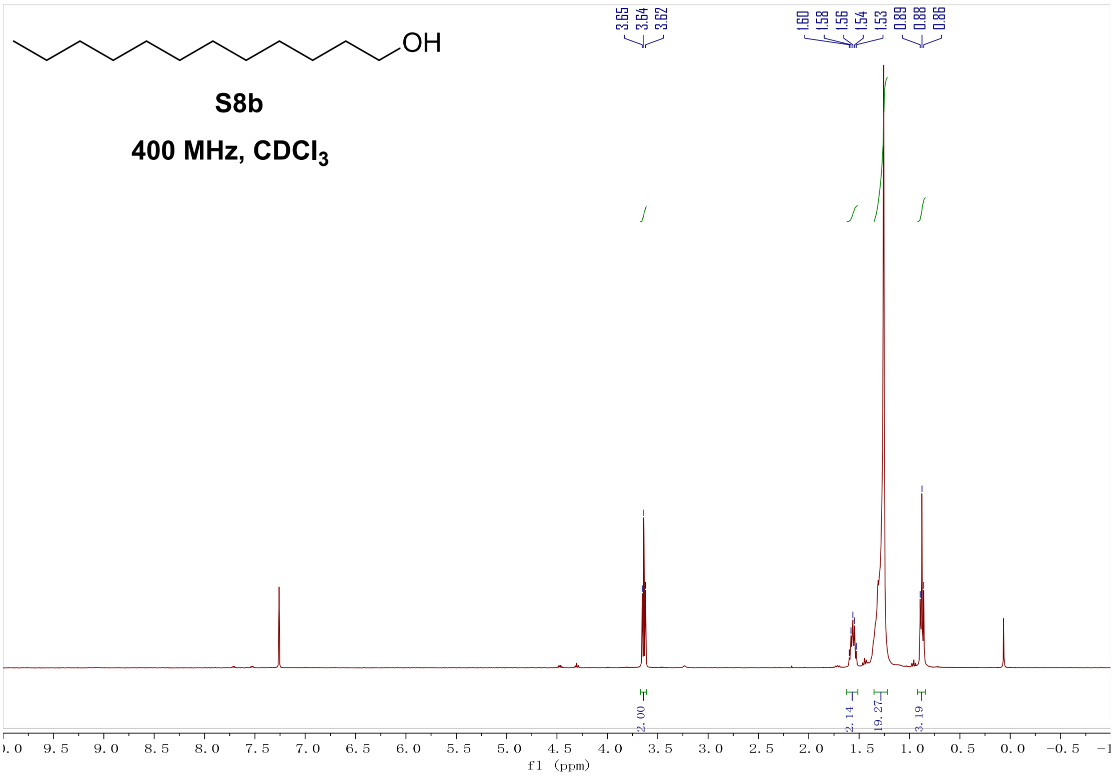
5k
100 MHz, CDCl$_3$


S7a
400 MHz, CDCl$_3$
7.18
7.16
6.87
6.85
3.80
3.15
3.13
3.12
3.12
3.12
3.10
2.90
2.88
2.86
2.84
2.80
2.78
2.77
2.76
2.75
2.54
2.53
2.53
2.52
1.99
2.00
3.09
0.98
1.09
1.93
1.01
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 −1
f1 (ppm)

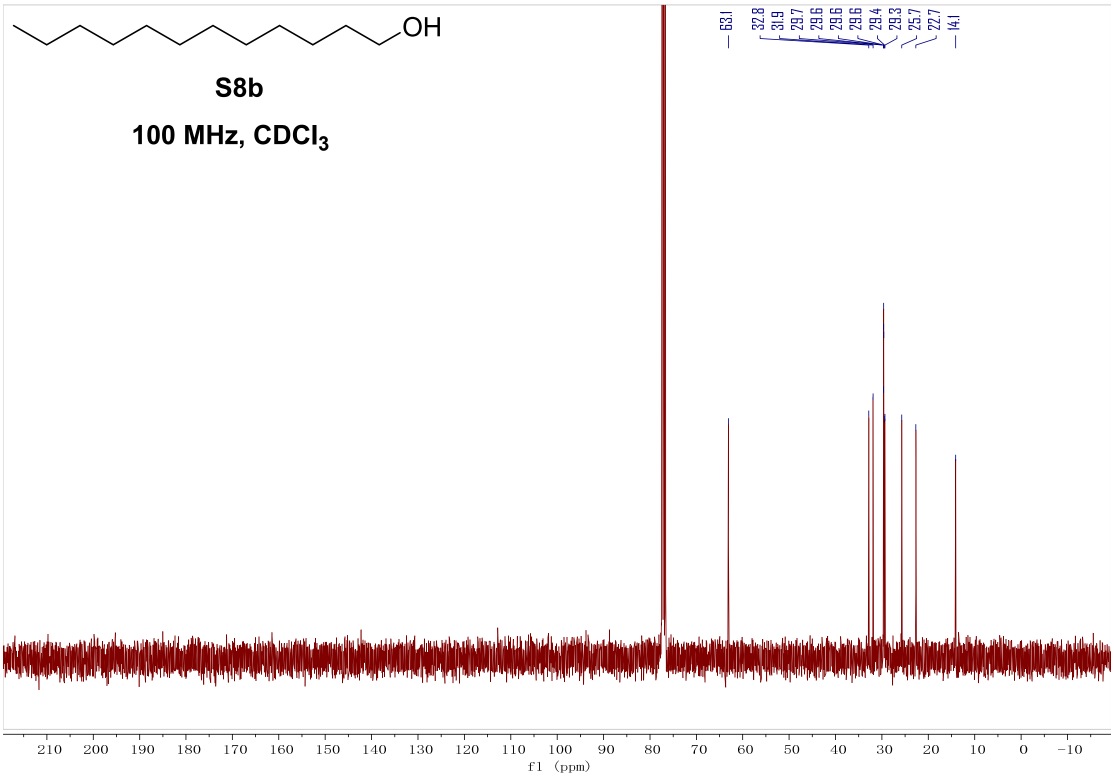

S7a
100 MHz, CDCl$_3$
158.2
129.8
128.9
113.7
55.0
52.4
46.5
37.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


MeO
OH
S8a
400 MHz, CDCl3
7.14
7.13
7.11
7.10
6.85
6.85
6.82
6.82
3.79
3.68
3.67
3.65
2.67
2.65
2.63
1.90
1.88
1.87
1.86
1.85
1.83
2.00
2.01
3.28
2.12
2.17
2.18
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)

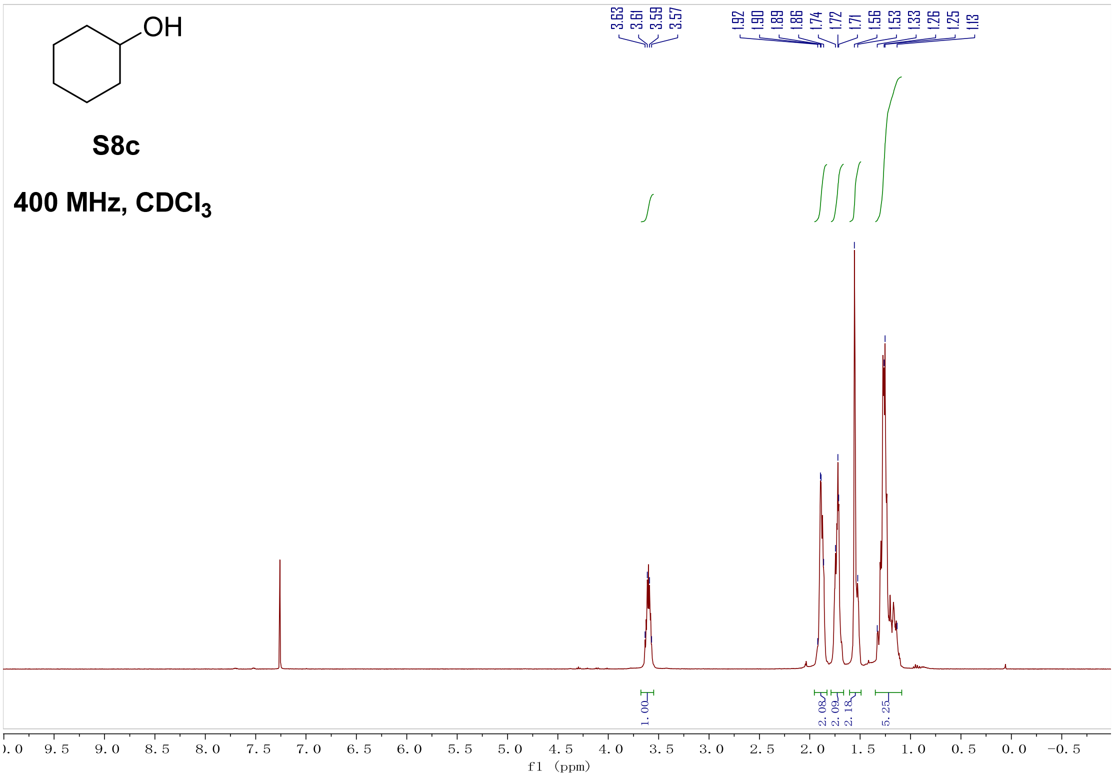

MeO
OH
S8a
100 MHz, CDCl3
157.5
133.7
129.1
113.6
61.9
55.0
34.2
30.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S8b

400 MHz, $CDCl_3$

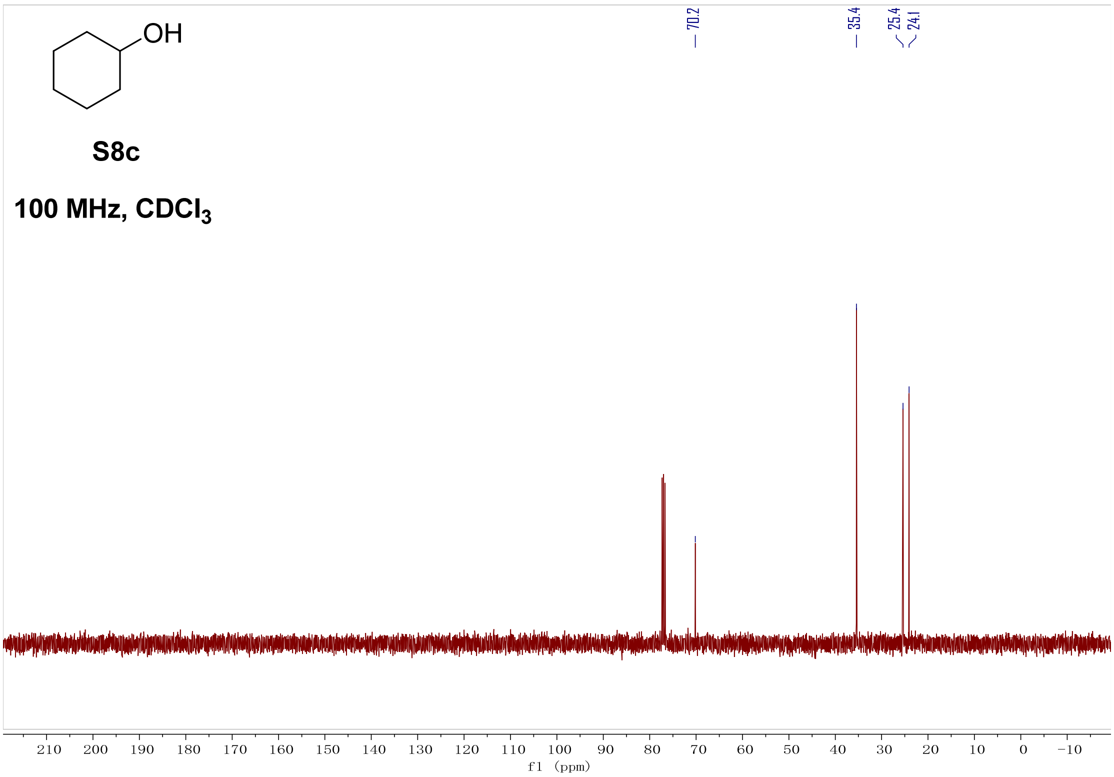

S8b

100 MHz, $CDCl_3$



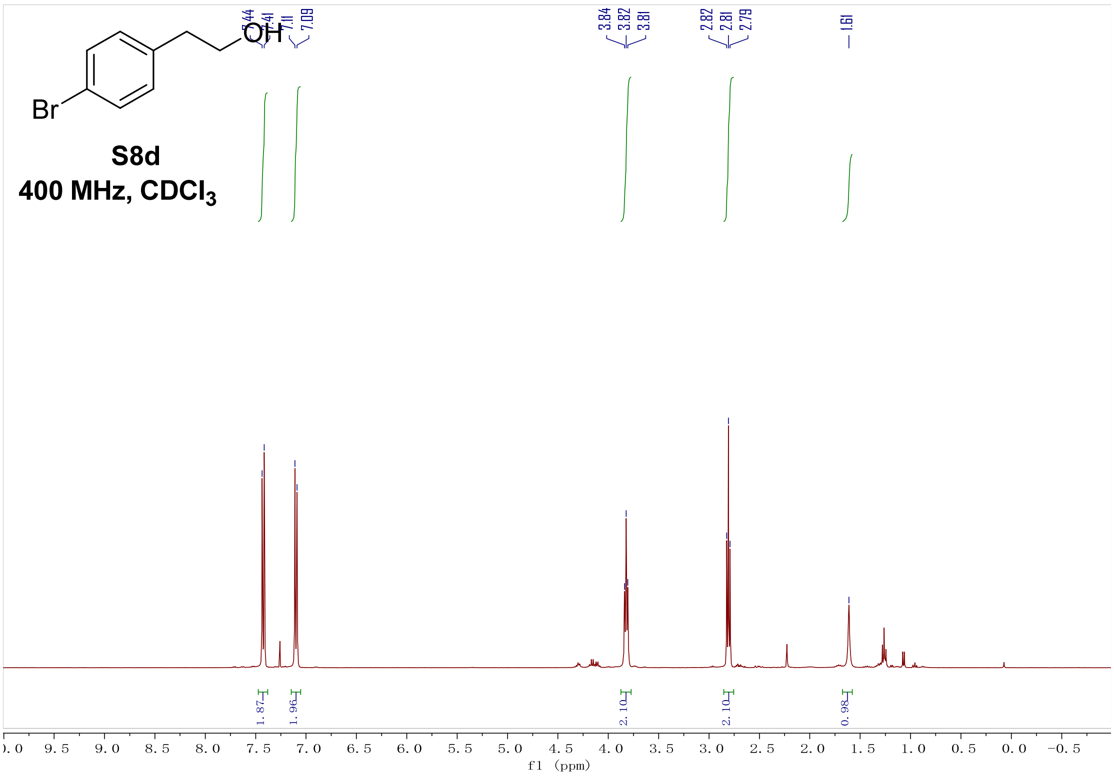
S8c

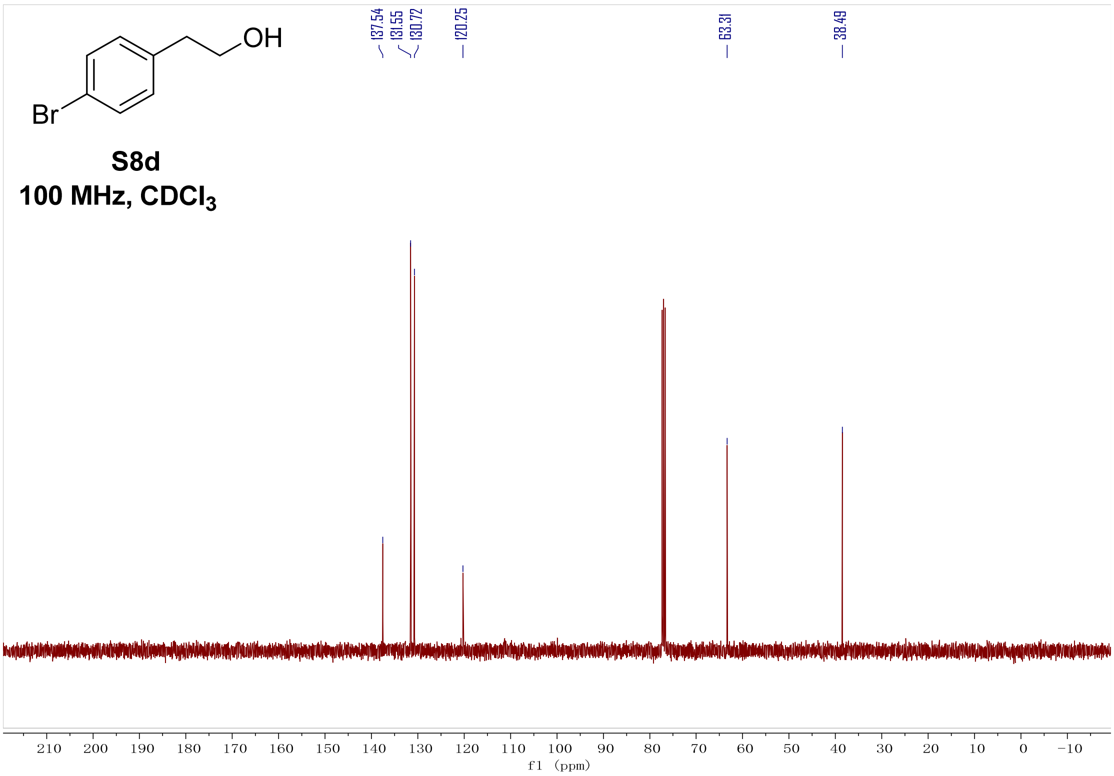
400 MHz, CDCl$_3$

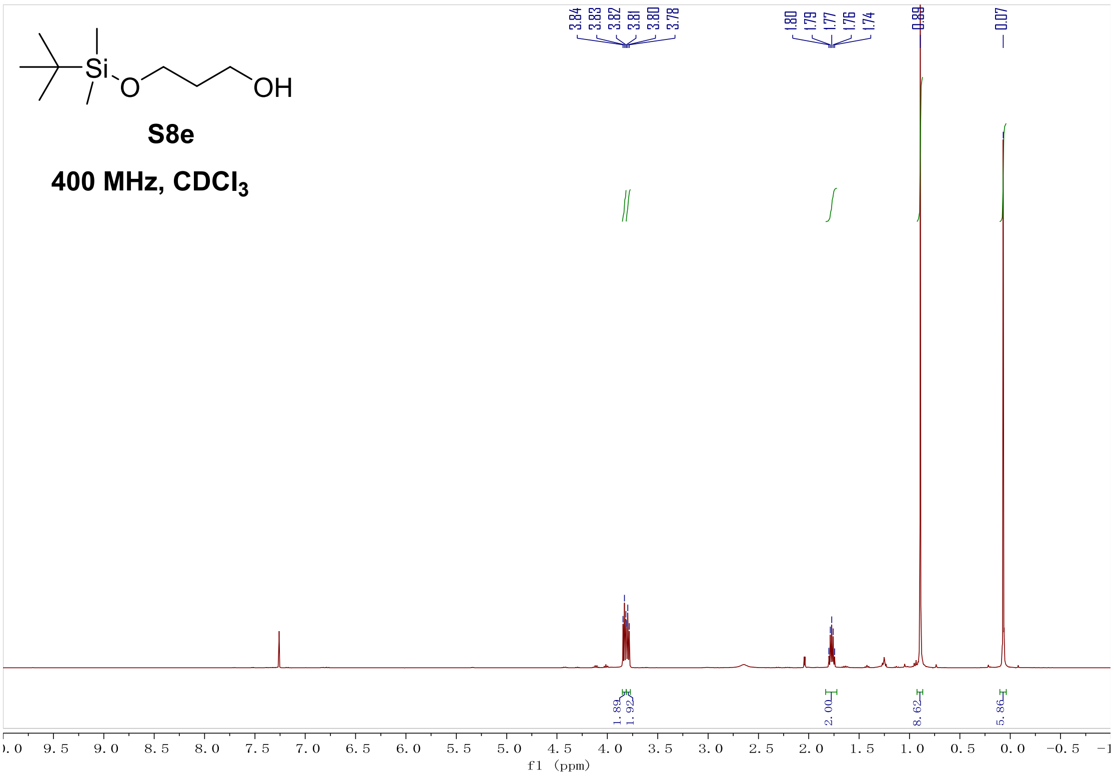


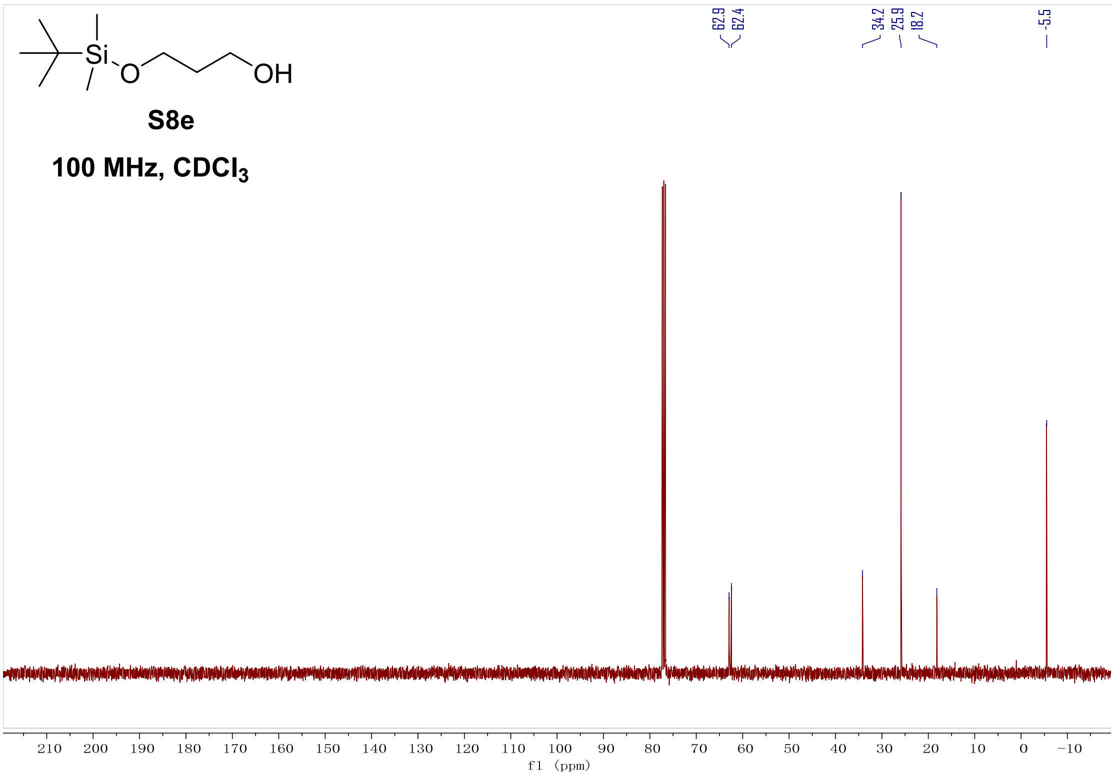
S8c

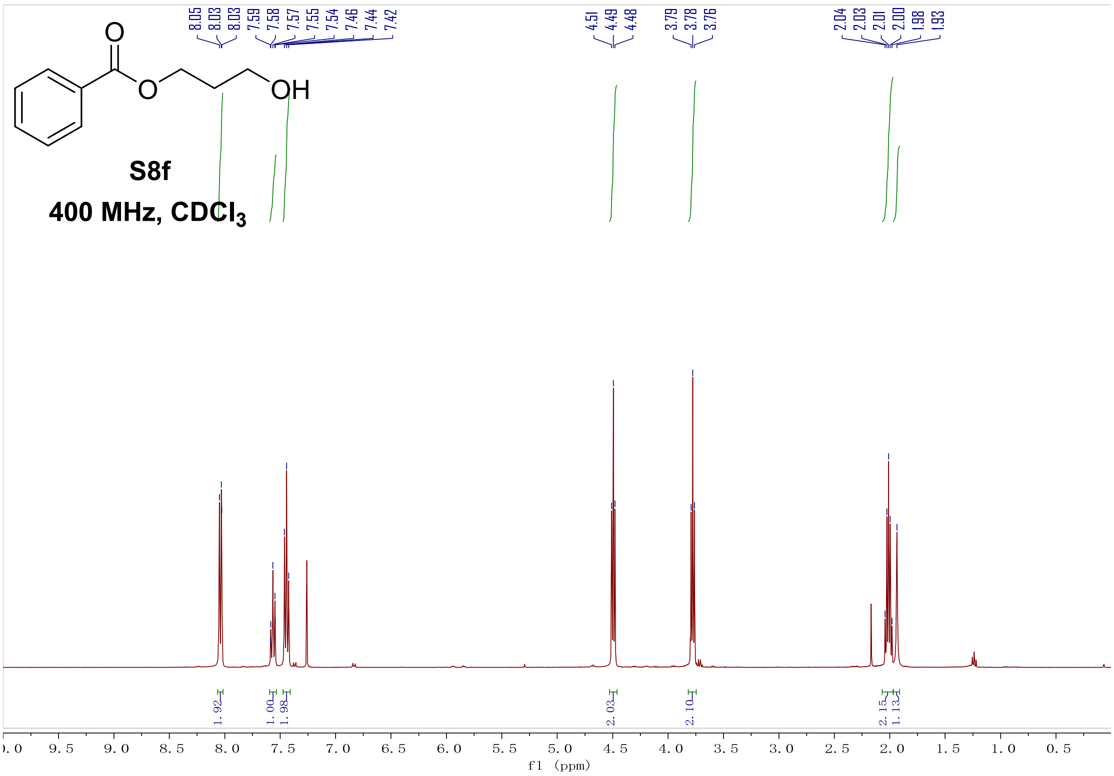
100 MHz, CDCl$_3$

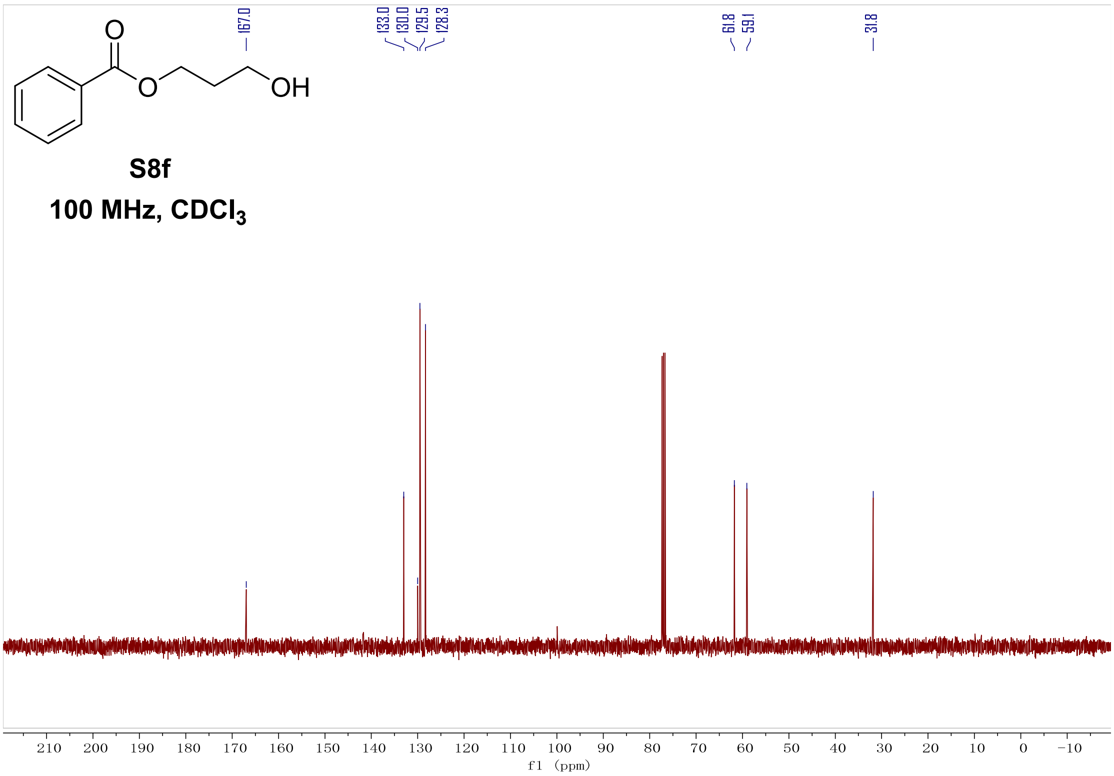

7.44
7.41
7.11
7.09
3.84
3.82
3.81
2.82
2.81
2.79
1.61
OH
Br
S8d
400 MHz, CDCl$_3$
1.87
1.96
2.10
2.10
0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

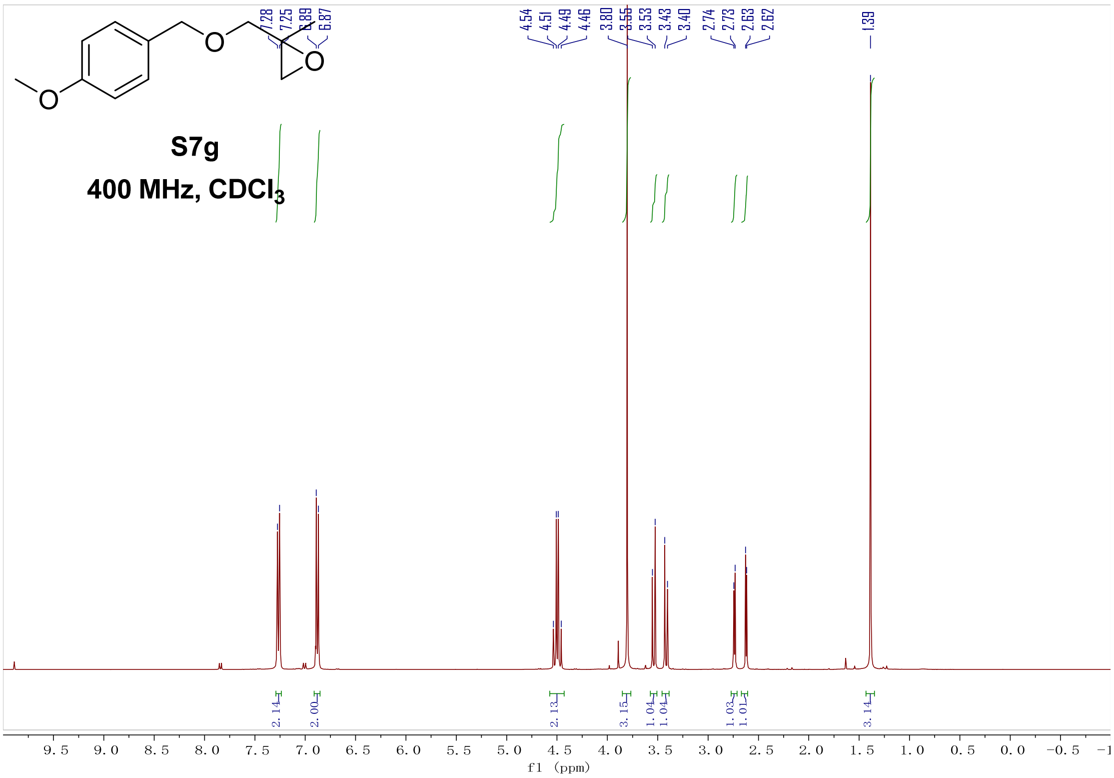

137.54
131.55
130.72
120.25
63.31
38.49
OH
Br
S8d
100 MHz, CDCl$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

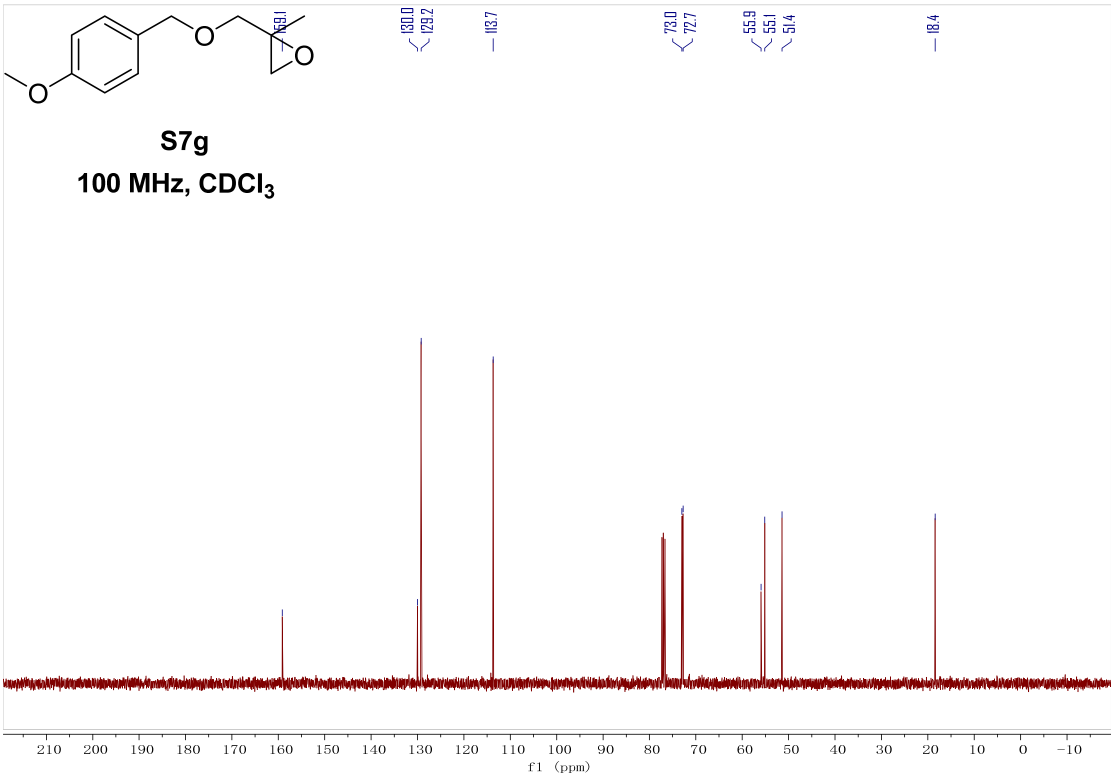

S8e
400 MHz, CDCl3
3.84
3.83
3.82
3.81
3.80
3.78
1.80
1.79
1.77
1.76
1.74
0.89
0.07
1.89
1.92
2.00
8.62
5.86
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)
Si
O
OH

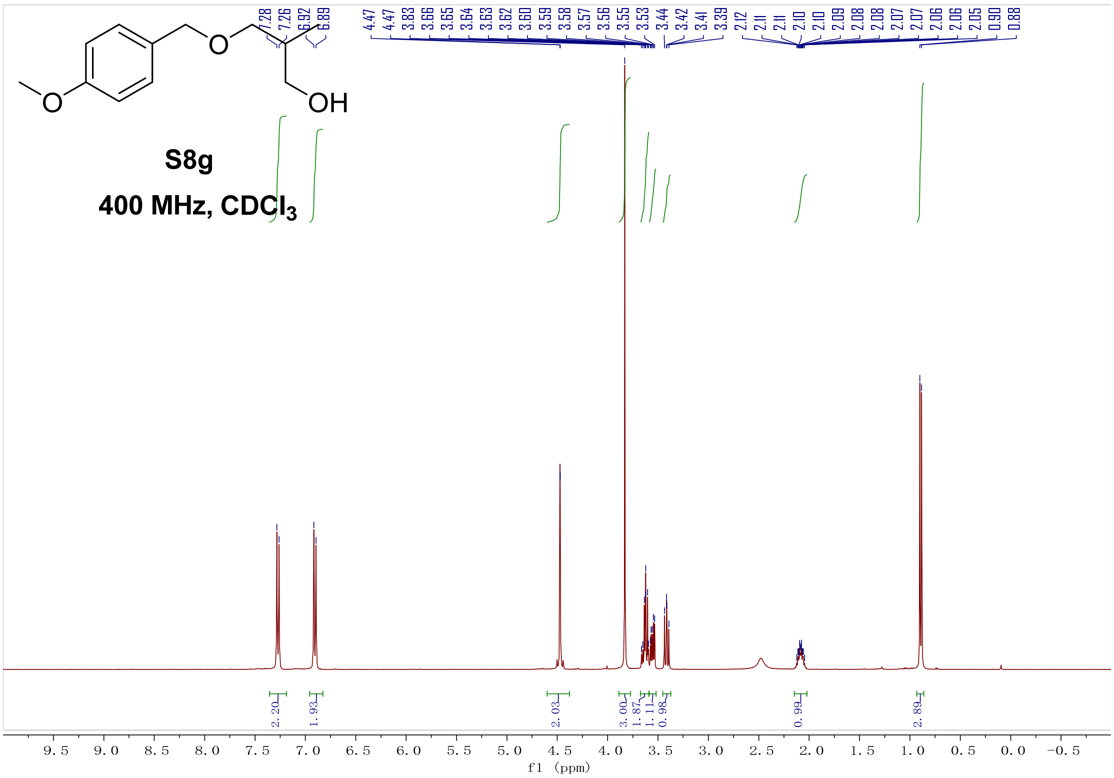

S8e
100 MHz, CDCl3
62.9
62.4
34.2
25.9
18.2
-5.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
Si
O
OH

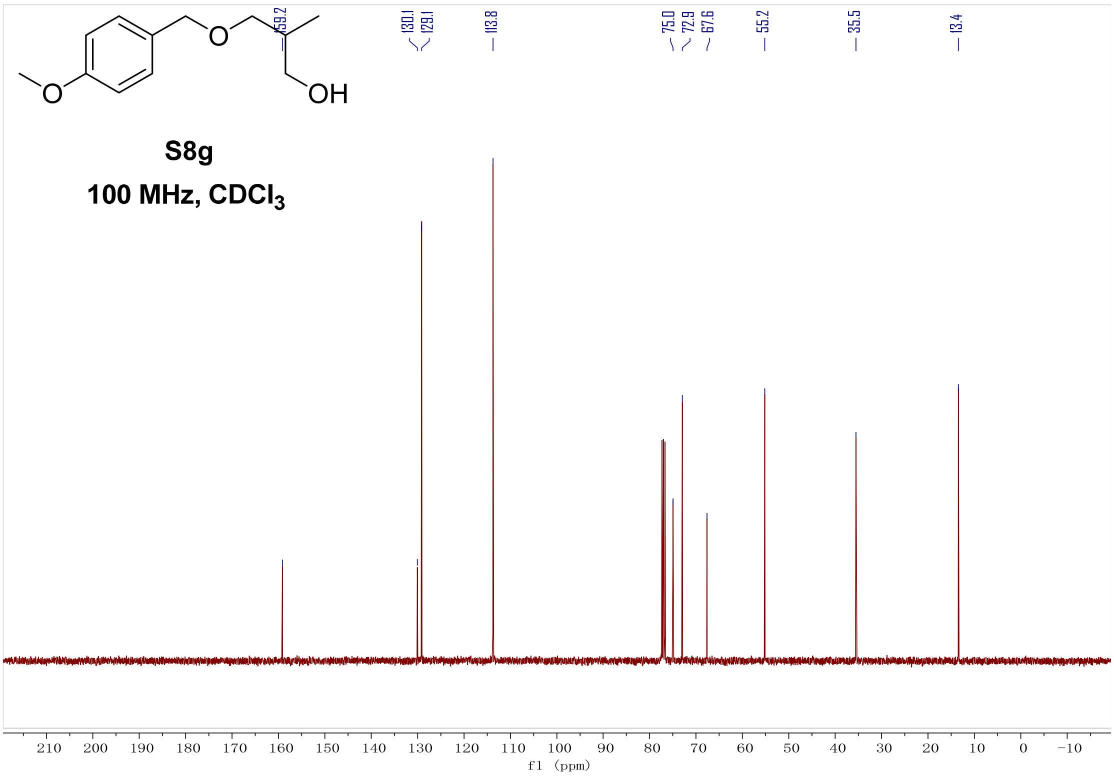

8.05
8.03
8.03
7.59
7.58
7.57
7.55
7.54
7.46
7.44
7.42
4.51
4.49
4.48
3.79
3.78
3.76
2.04
2.03
2.01
2.00
1.98
1.93
O
O
OH
S8f
400 MHz, CDCl3
1.92
1.00
1.98
2.03
2.10
2.15
1.13
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

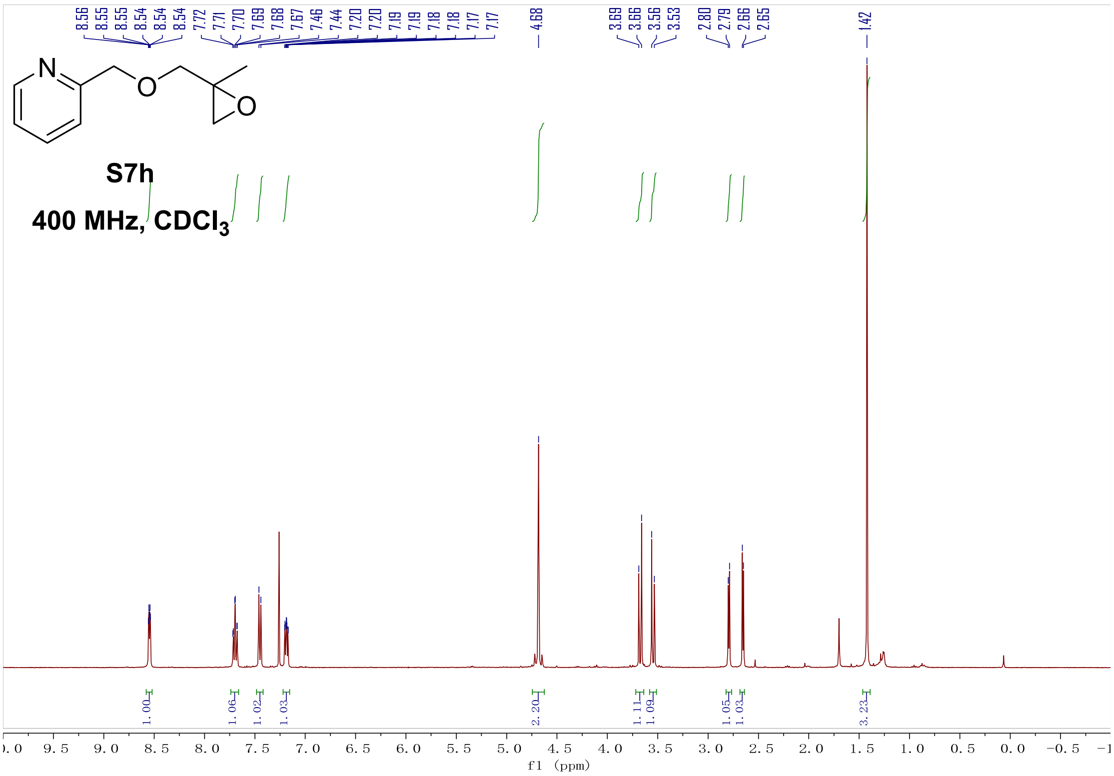

167.0
133.0
130.0
129.5
128.3
61.8
59.1
31.8
O
O
OH
S8f
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

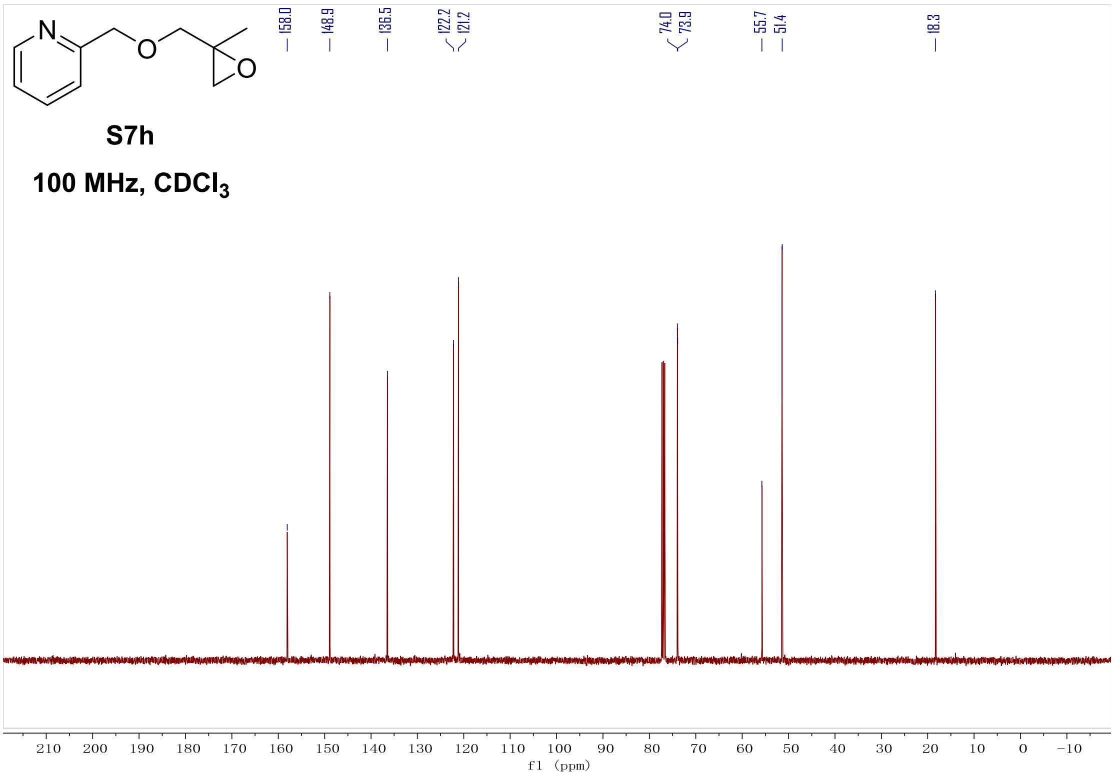

S7g
400 MHz, CDCl3
7.28
7.25
6.89
6.87
4.54
4.51
4.49
4.46
3.80
3.55
3.53
3.43
3.40
2.74
2.73
2.63
2.62
1.39
2.14
2.00
2.13
3.15
1.04
1.04
1.03
1.01
3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

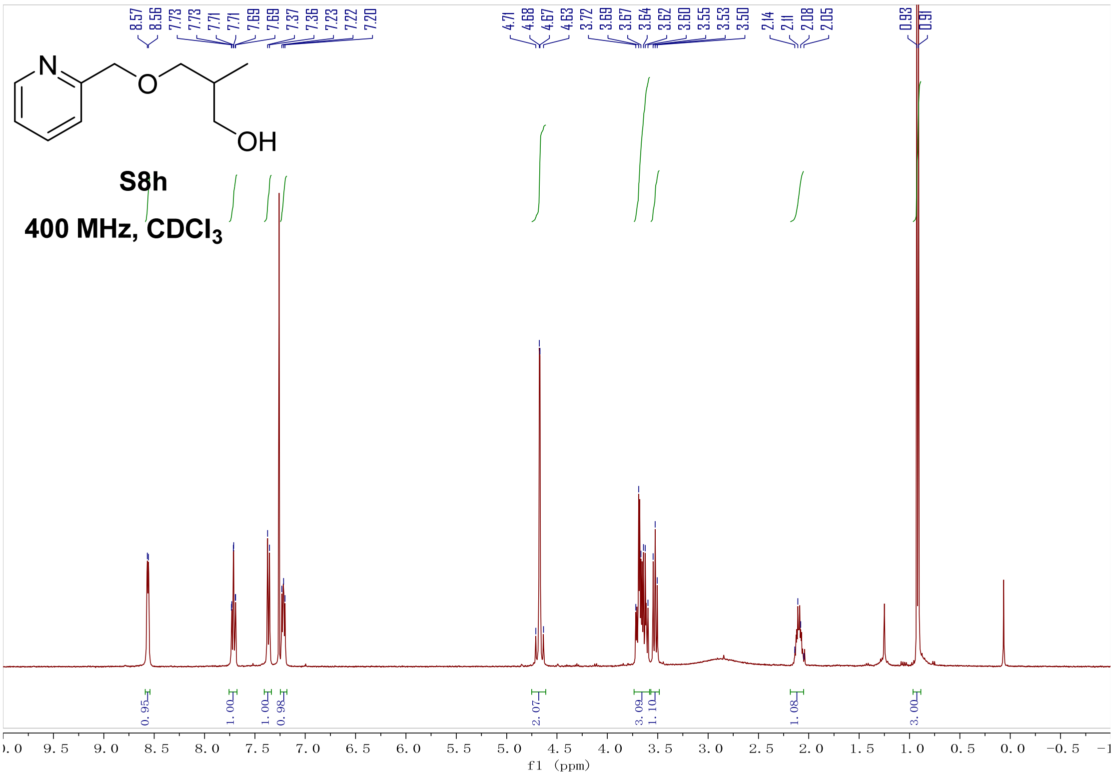

S7g
100 MHz, CDCl3
159.1
130.0
129.2
113.7
73.0
72.7
55.9
55.1
51.4
18.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

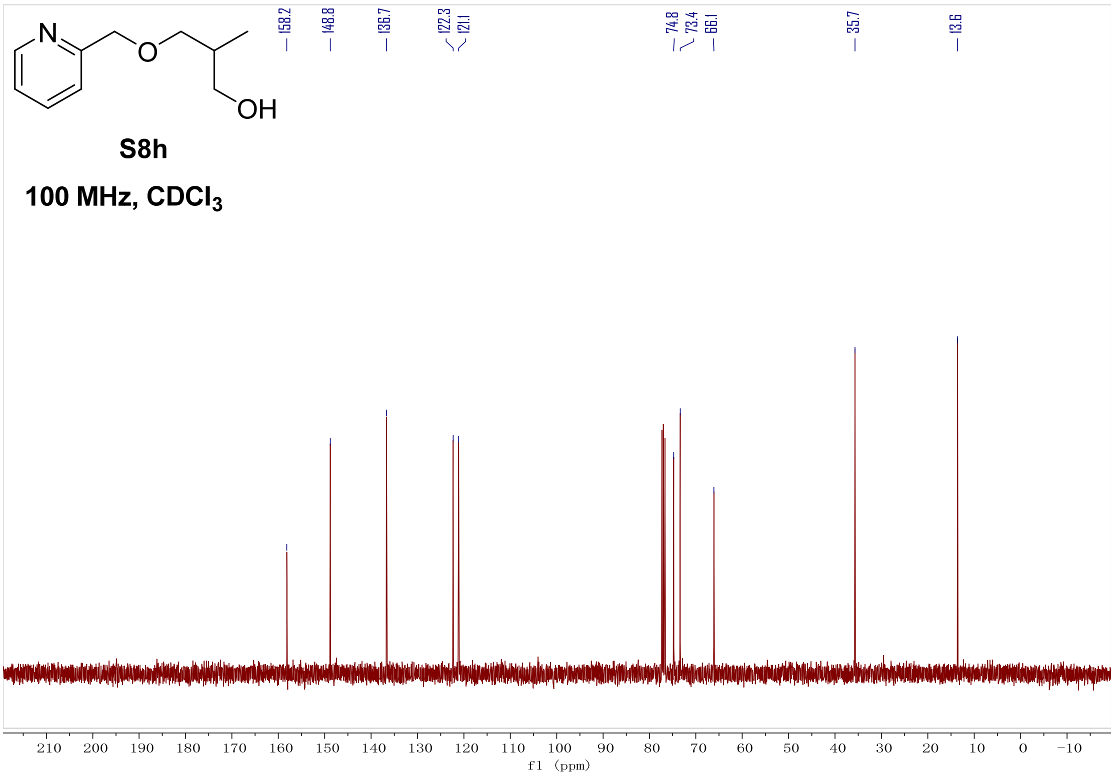

S8g
400 MHz, CDCl$_3$
OH
O
O
7.28
7.26
6.92
6.89
4.47
4.47
3.83
3.66
3.65
3.64
3.63
3.62
3.60
3.59
3.58
3.57
3.56
3.55
3.53
3.44
3.42
3.41
3.39
2.12
2.11
2.11
2.10
2.10
2.09
2.08
2.08
2.07
2.07
2.06
2.06
2.05
0.90
0.88
2.20
1.93
2.03
3.00
1.87
1.11
0.98
0.99
2.89
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

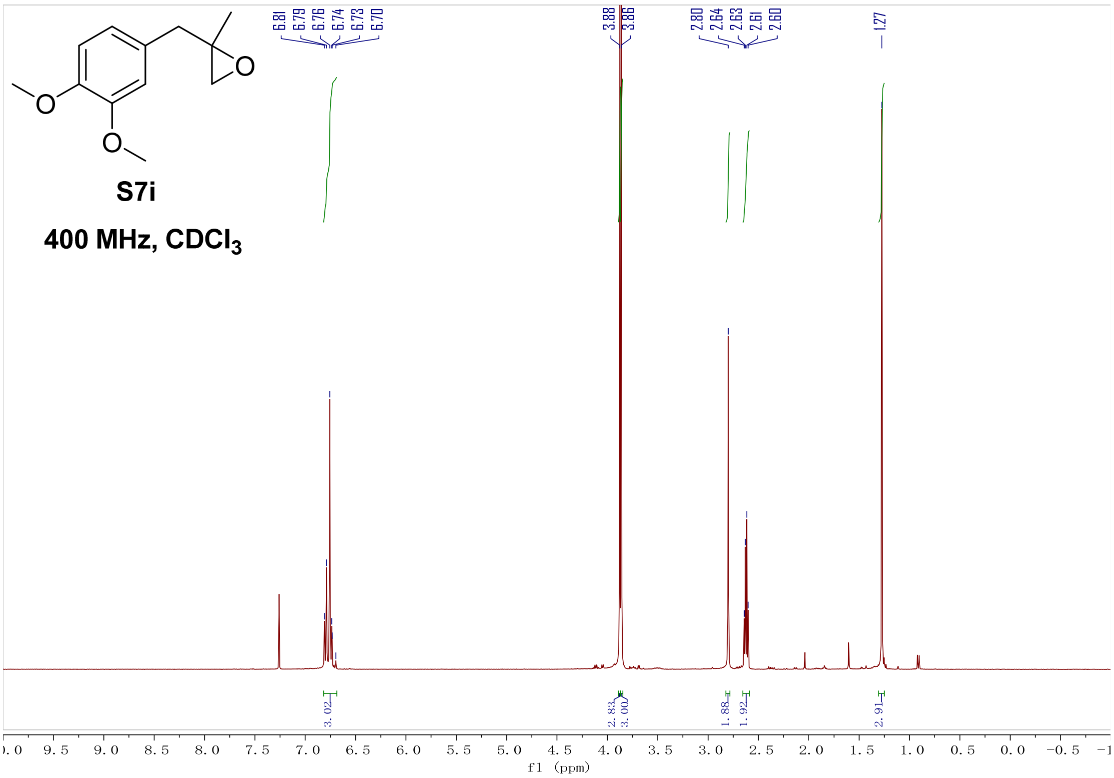

S8g
100 MHz, CDCl$_3$
OH
O
O
159.2
130.1
129.1
113.8
75.0
72.9
67.6
55.2
35.5
13.4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

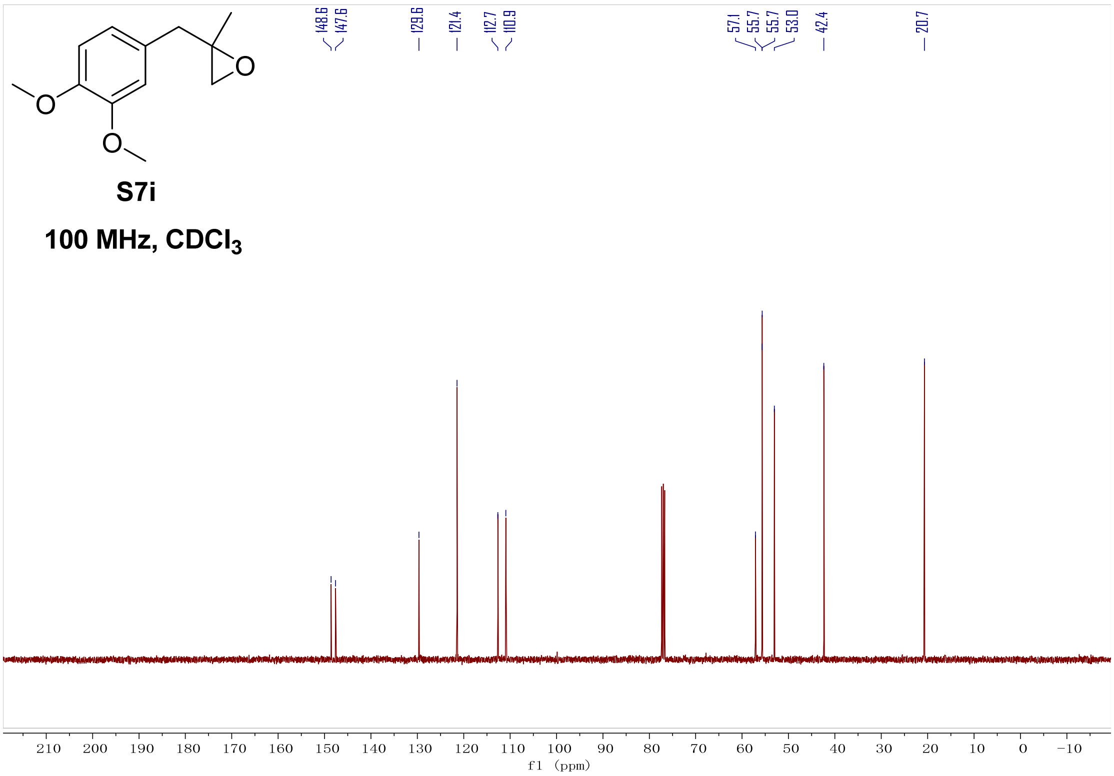

8.56
8.55
8.55
8.54
8.54
8.54
7.72
7.71
7.70
7.69
7.68
7.67
7.46
7.44
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.17
4.68
3.69
3.66
3.56
3.53
2.80
2.79
2.66
2.65
1.42
N
O
O
S7h
400 MHz, CDCl$_3$
1.00
1.06
1.02
1.03
2.20
1.11
1.09
1.05
1.03
3.23
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

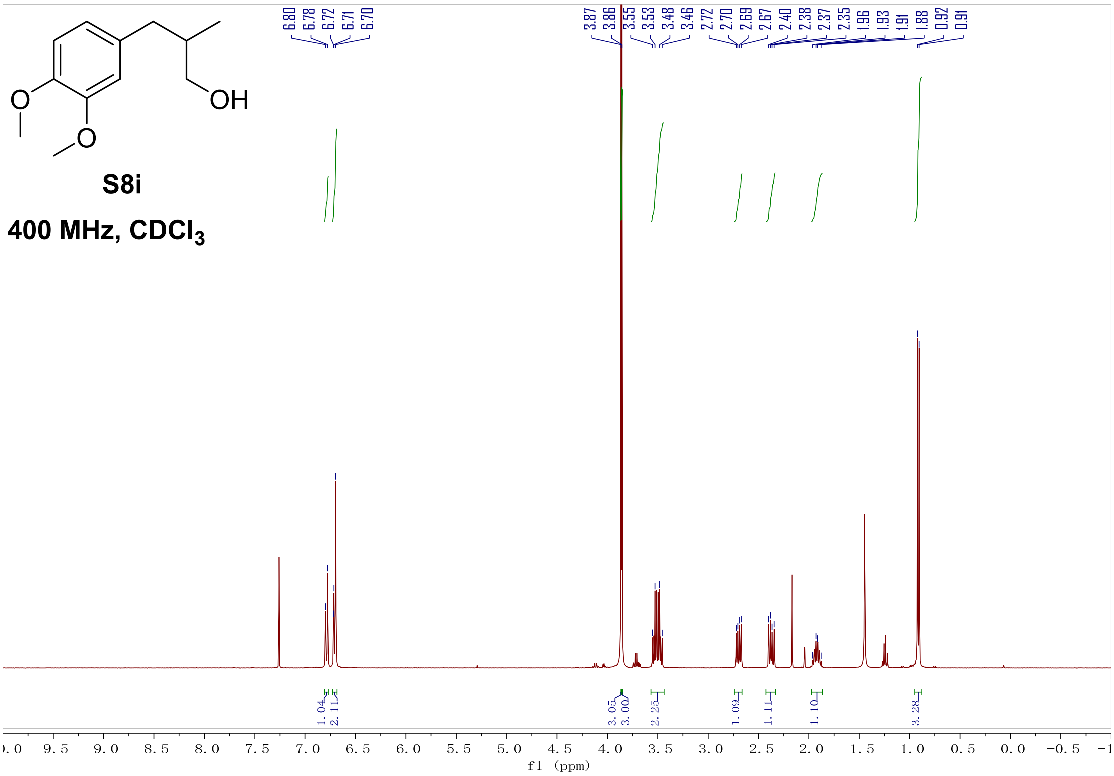

158.0
148.9
136.5
122.2
121.2
74.0
73.9
55.7
51.4
18.3
N
O
O
S7h
100 MHz, CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

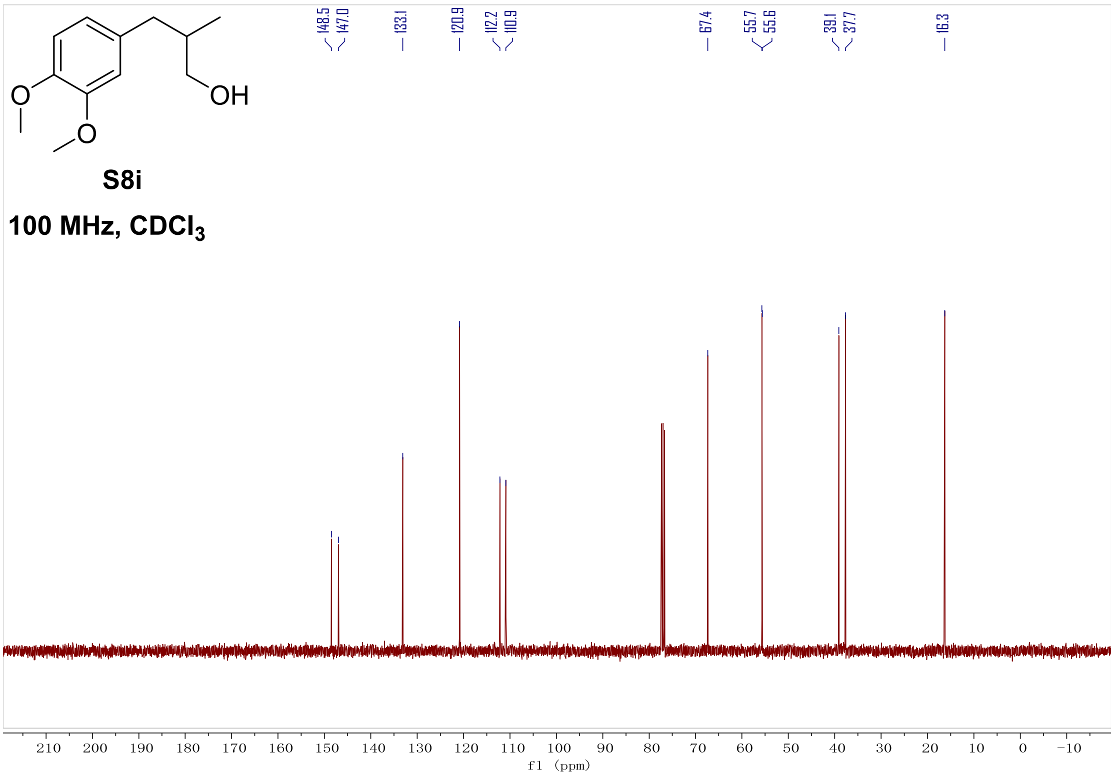

N
O
OH
S8h
400 MHz, CDCl$_3$
8.57
8.56
7.73
7.73
7.71
7.71
7.69
7.69
7.37
7.36
7.23
7.22
7.20
4.71
4.68
4.67
4.63
3.72
3.69
3.67
3.64
3.62
3.60
3.55
3.53
3.50
2.14
2.11
2.08
2.05
0.93
0.91
0.95
1.00
1.00
0.98
2.07
3.09
1.10
1.08
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

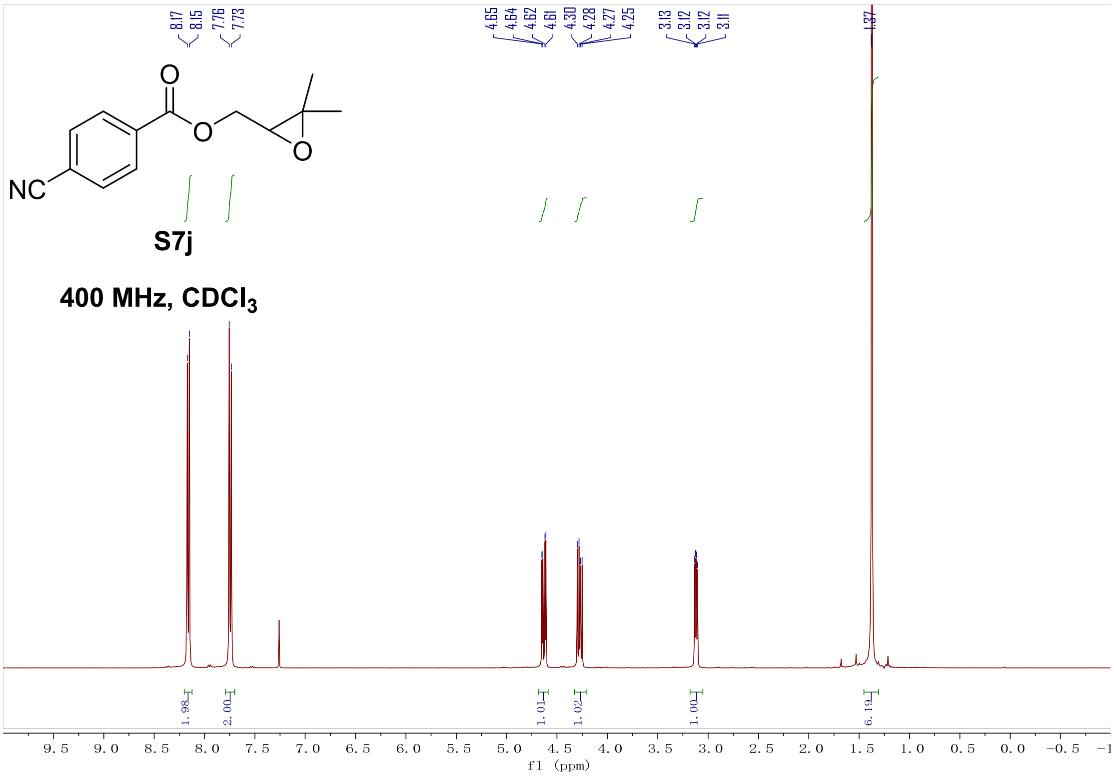

N
O
OH
S8h
100 MHz, CDCl$_3$
158.2
148.8
136.7
122.3
121.1
74.8
73.4
66.1
35.7
13.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

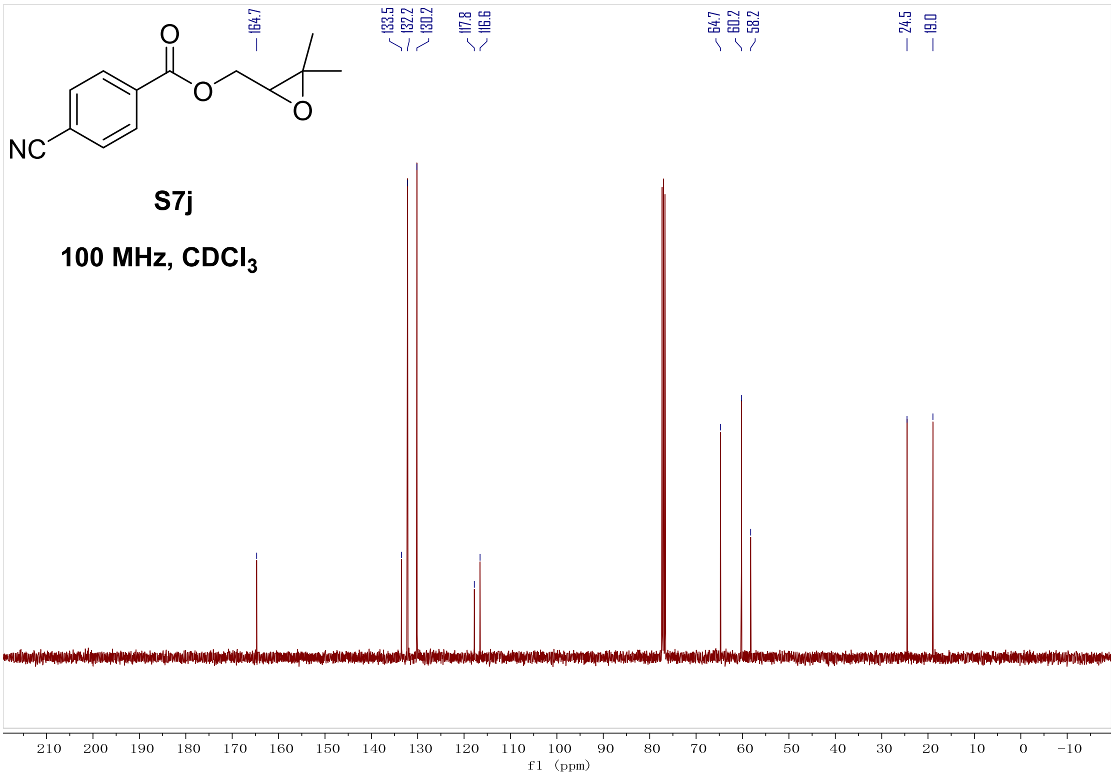

S7i
400 MHz, CDCl$_3$
O
O
O
6.81
6.79
6.76
6.74
6.73
6.70
3.88
3.86
2.80
2.64
2.63
2.61
2.60
1.27
3.02
2.83
3.00
1.88
1.92
2.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

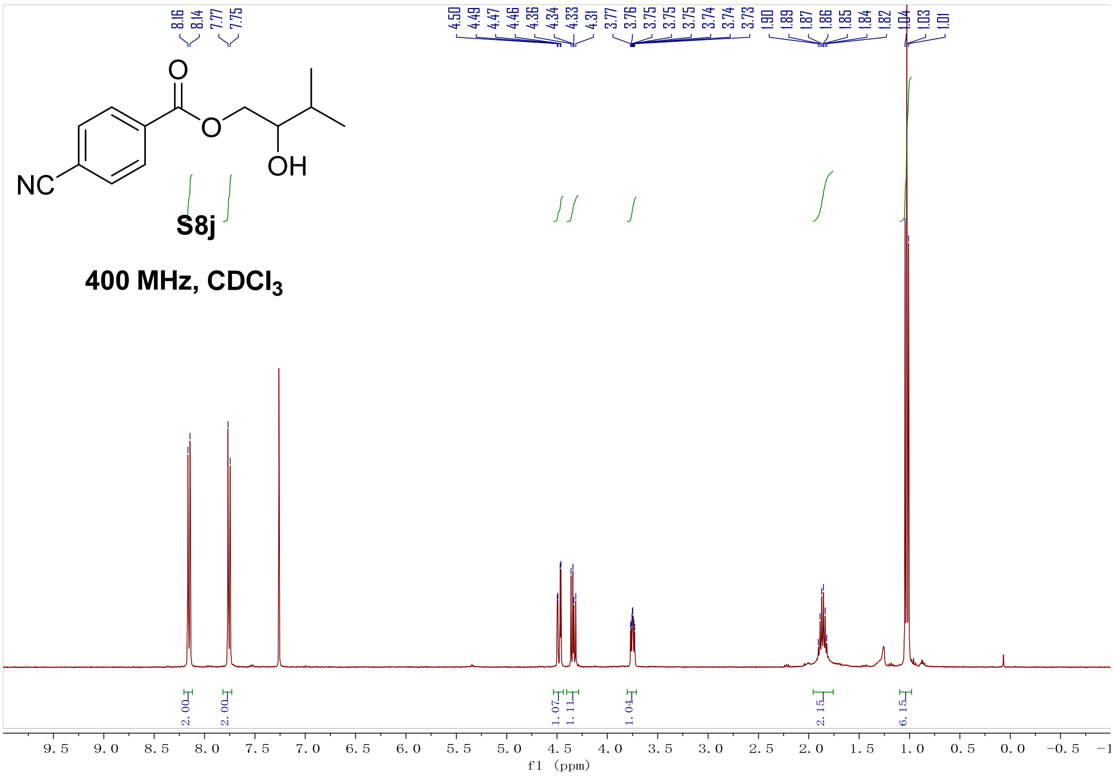

S7i
100 MHz, CDCl$_3$
O
O
O
148.6
147.6
129.6
121.4
112.7
110.9
57.1
55.7
55.7
53.0
42.4
20.7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

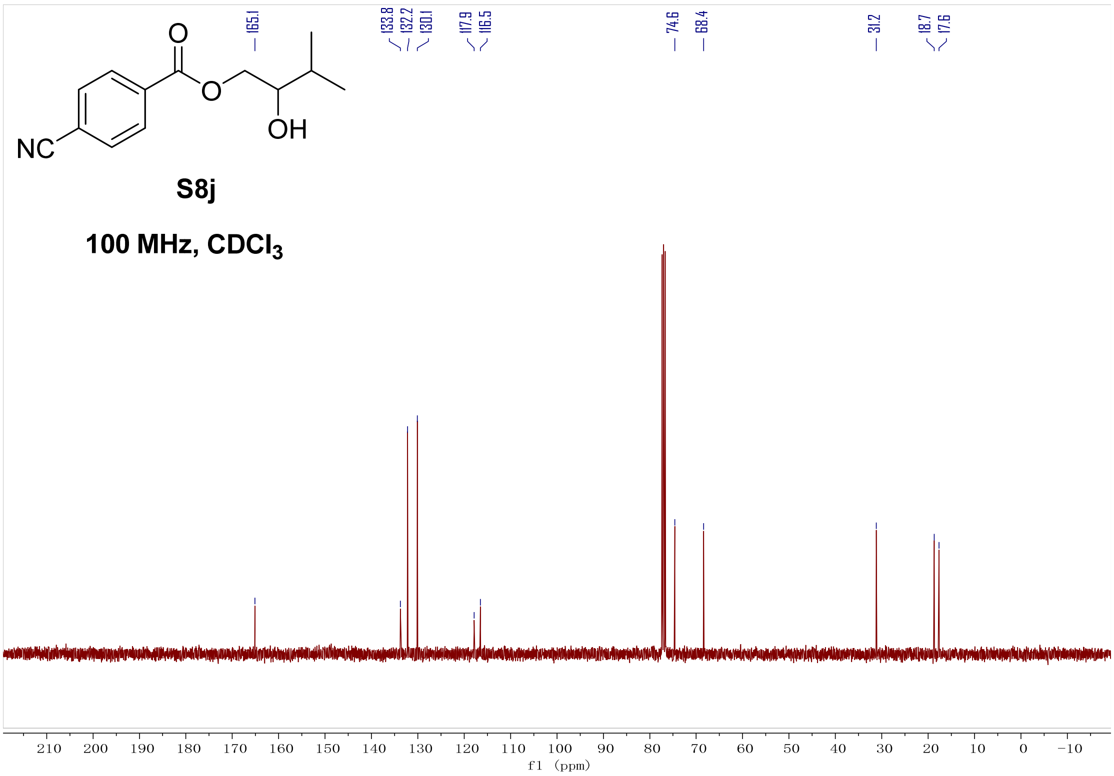

S8i
400 MHz, CDCl$_3$
OH
O
O
6.80
6.78
6.72
6.71
6.70
3.87
3.86
3.55
3.53
3.48
3.46
2.72
2.70
2.69
2.67
2.40
2.38
2.37
2.35
1.96
1.93
1.91
1.88
0.92
0.91
1.04
2.11
3.05
3.00
2.25
1.09
1.11
1.10
3.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

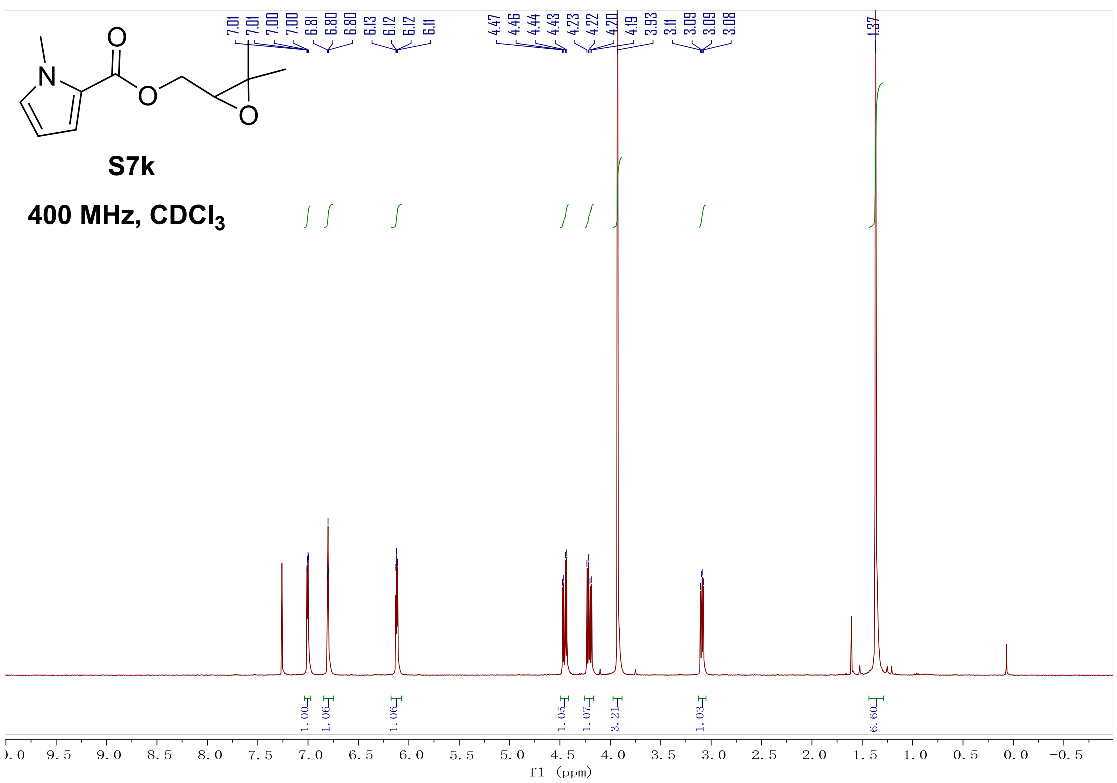

S8i
100 MHz, CDCl$_3$
OH
O
O
148.5
147.0
133.1
120.9
112.2
110.9
67.4
55.7
55.6
39.1
37.7
16.3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

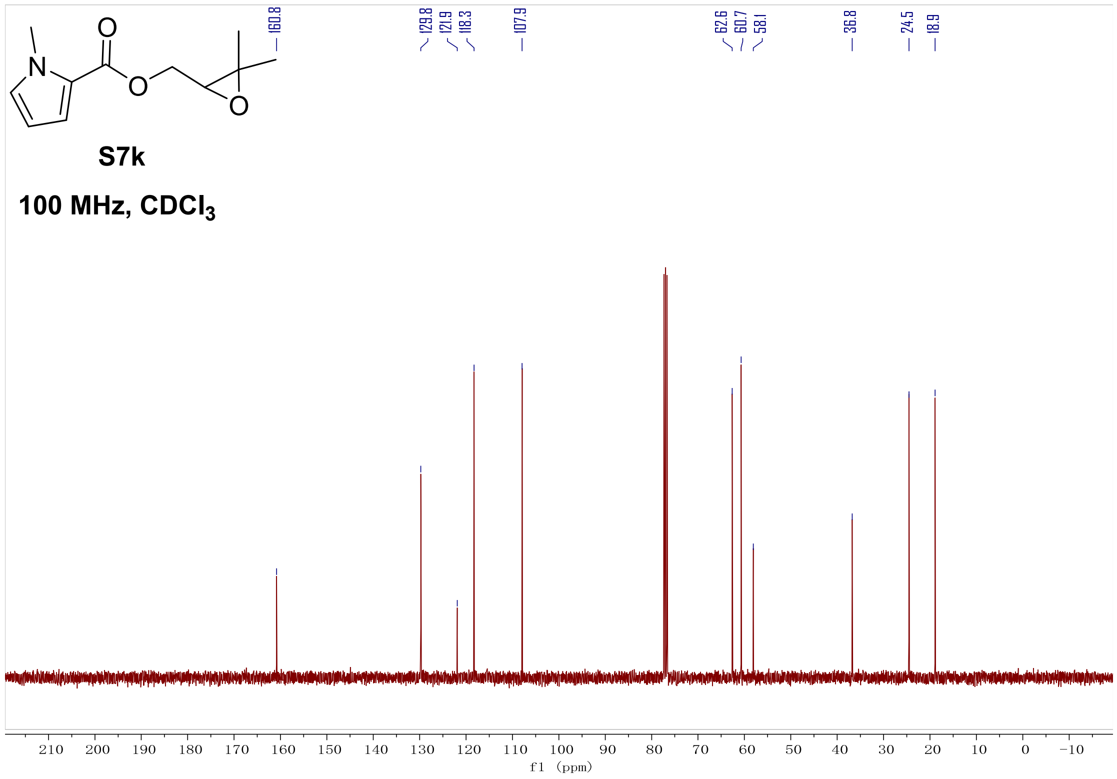

8.17
8.15
7.76
7.73
4.65
4.64
4.62
4.61
4.30
4.28
4.27
4.25
3.13
3.12
3.12
3.11
1.37
O
O
O
NC
S7j
400 MHz, CDCl$_3$
1.98
2.00
1.01
1.02
1.00
6.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

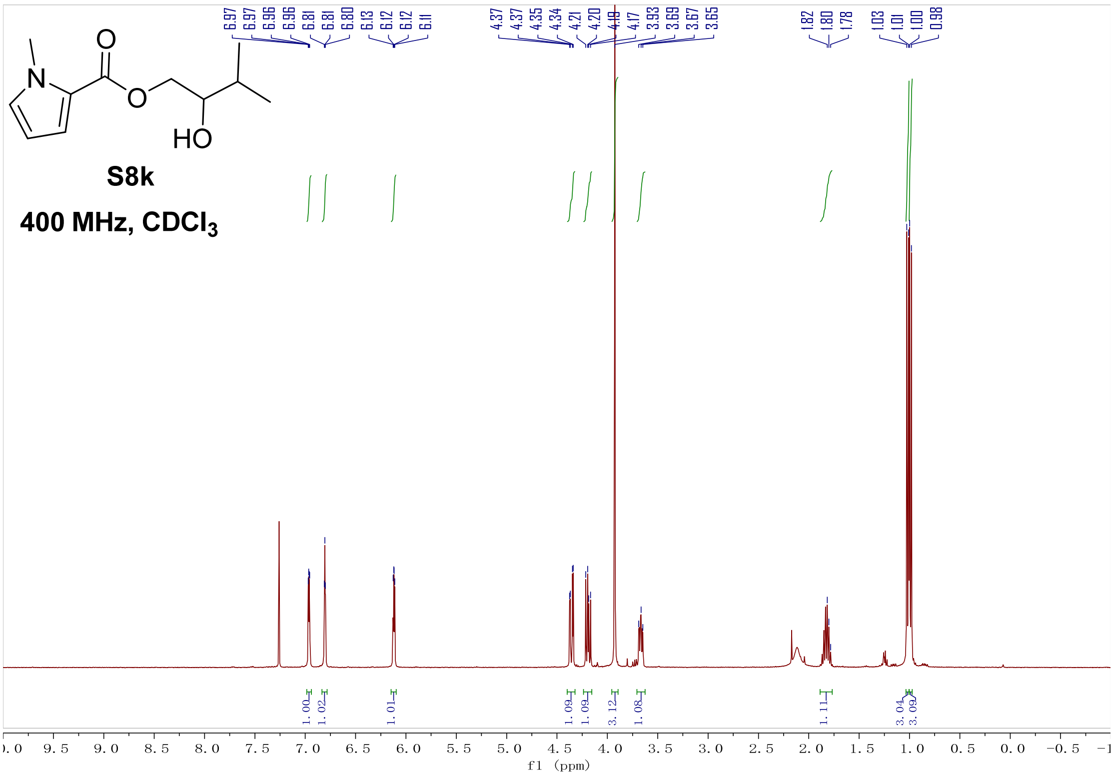

164.7
133.5
132.2
130.2
117.8
116.6
64.7
60.2
58.2
24.5
19.0
O
O
O
NC
S7j
100 MHz, CDCl$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

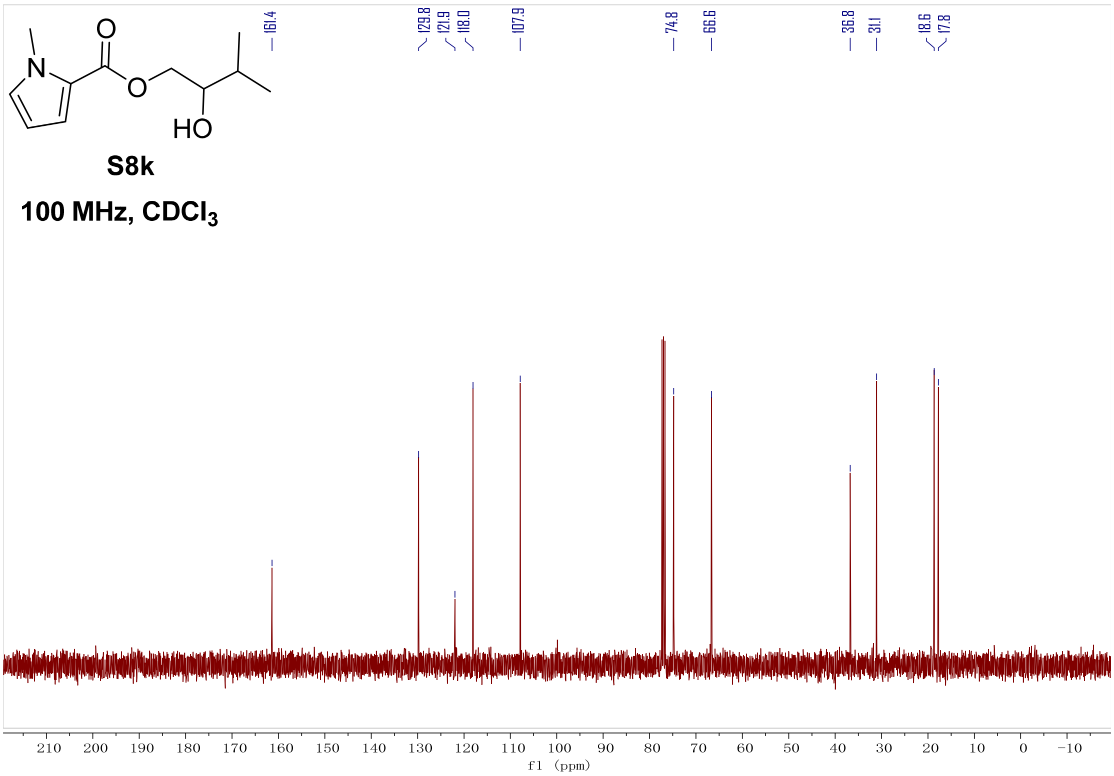

8.16
8.14
7.77
7.75
4.50
4.49
4.47
4.46
4.36
4.34
4.33
4.31
3.77
3.76
3.75
3.75
3.75
3.74
3.74
3.73
1.90
1.89
1.87
1.86
1.85
1.84
1.82
1.04
1.03
1.01
O
O
OH
NC
S8j
400 MHz, CDCl$_3$
2.00
2.00
1.07
1.11
1.04
2.15
6.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

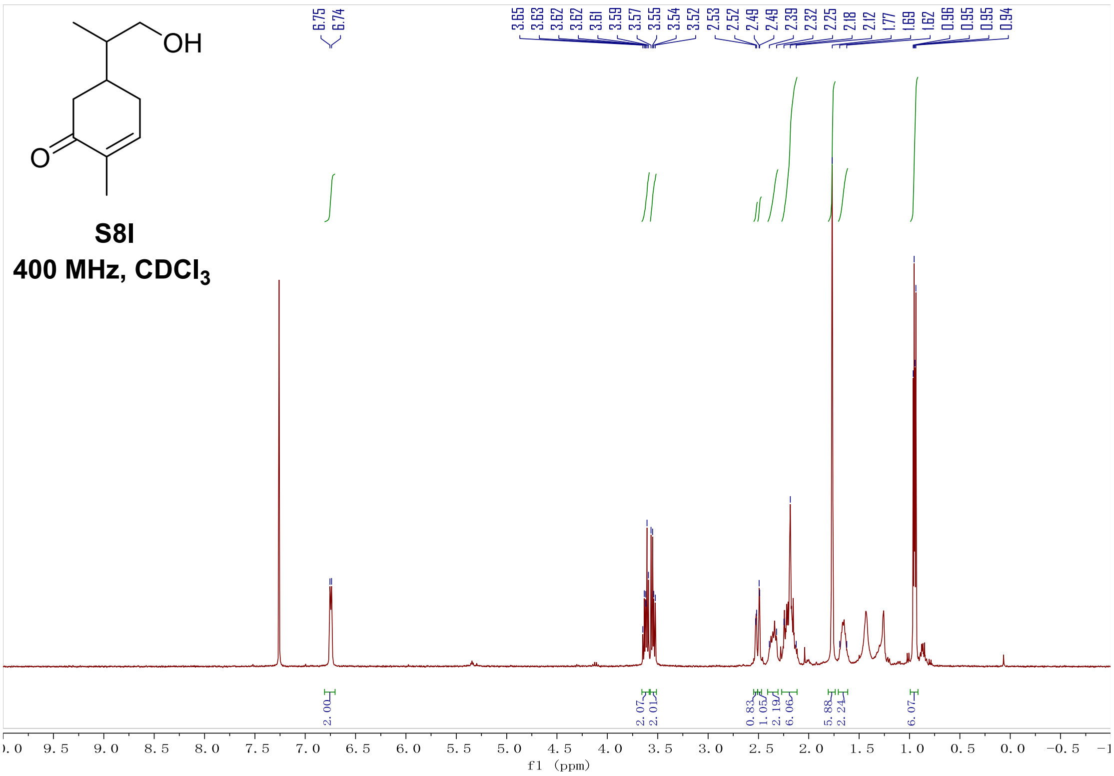

165.1
133.8
132.2
130.1
117.9
116.5
74.6
68.4
31.2
18.7
17.6
O
O
OH
NC
S8j
100 MHz, CDCl$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


O
N
O
O
S7k
400 MHz, $CDCl_3$
7.01
7.01
7.00
7.00
6.81
6.80
6.80
6.13
6.12
6.12
6.11
4.47
4.46
4.44
4.43
4.23
4.22
4.20
4.19
3.93
3.11
3.09
3.09
3.08
1.37
1.00
1.06
1.06
1.05
1.07
3.21
1.03
6.60
).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)

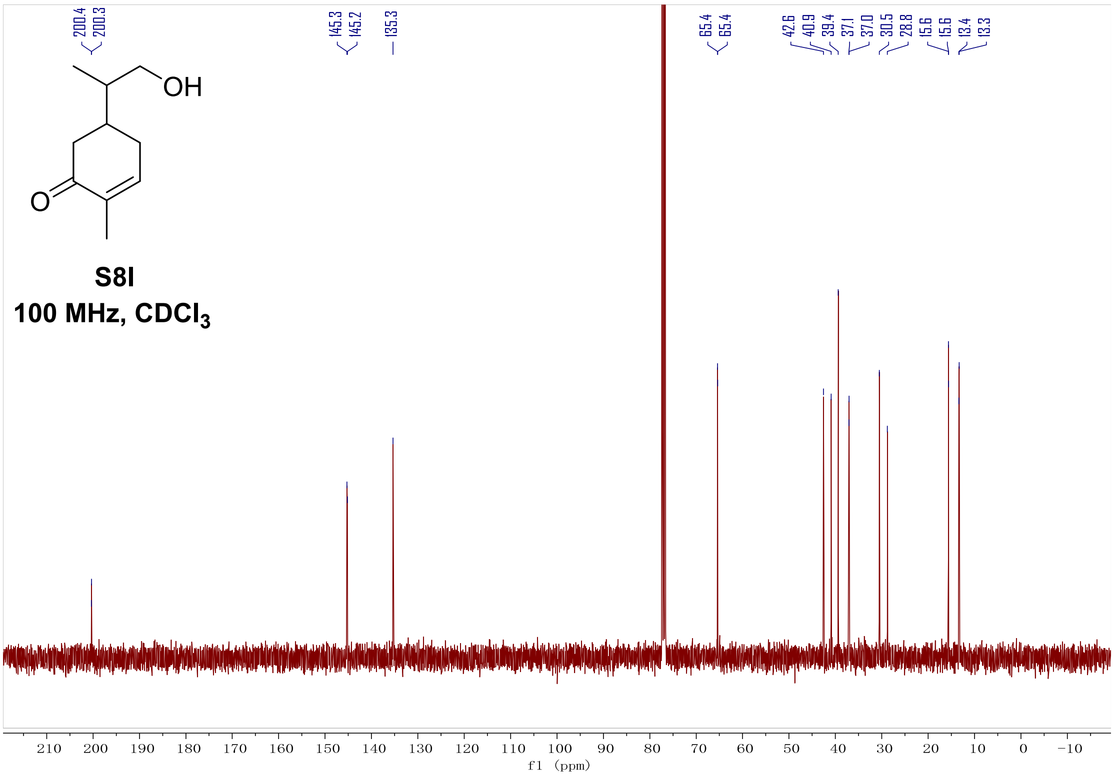

O
N
O
O
S7k
100 MHz, $CDCl_3$
160.8
129.8
121.9
118.3
107.9
62.6
60.7
58.1
36.8
24.5
18.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
S8k
400 MHz, CDCl$_3$
6.97
6.97
6.96
6.96
6.81
6.81
6.80
6.13
6.12
6.12
6.11
4.37
4.37
4.35
4.34
4.21
4.20
4.19
4.17
3.93
3.69
3.67
3.65
1.82
1.80
1.78
1.03
1.01
1.00
0.98
1.00
1.02
1.01
1.09
1.09
3.12
1.08
1.11
3.04
3.09
f1 (ppm)


HO
S8k
100 MHz, CDCl$_3$
161.4
129.8
121.9
118.0
107.9
74.8
66.6
36.8
31.1
18.6
17.8
f1 (ppm)



S8l
400 MHz, $CDCl_3$



S8l
100 MHz, $CDCl_3$