Supporting Information

Highly Enantioselective Epoxidation of Trisubstituted Vinyl Sulfones with H_2O_2 Catalyzed by a Bioinspired Manganese Catalyst

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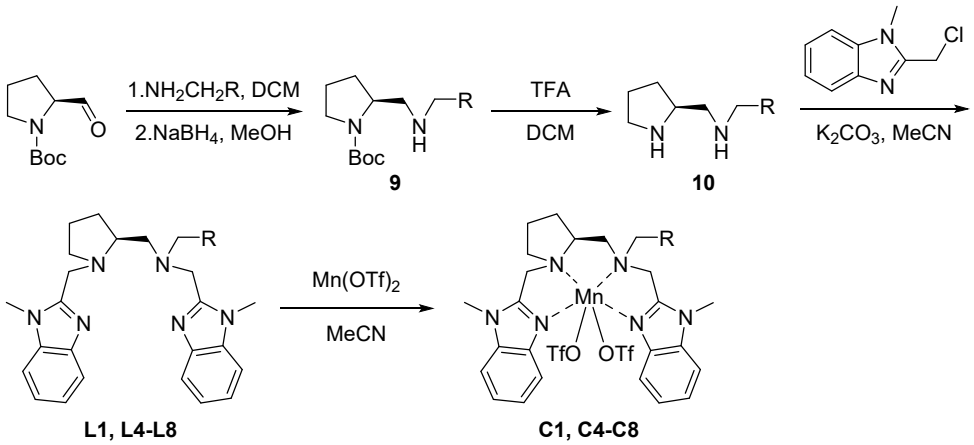
1. General information

Commercial reagents were purchased from Adamas-beta, Aladdin, Bidepharm, Energy Chemical and TCI. All air-sensitive manipulations were carried out with standard Schlenk techniques under an inert atmosphere (Ar). NMR spectra were recorded on 400 MHz Bruker spectrometers. Chemical shifts were reported in δ (ppm) referenced to the residual solvent peak of $CDCl_3$ (δ 7.26 for ^1H NMR and δ 77.1 for ^{13}C NMR). Coupling constants (*J*) are reported in Hz with the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br s (broad singlet), dd (doublet of doublets), dt (doublet of triplets). High-resolution mass spectra (HRMS) were obtained on an Agilent 1200HPLC-6210TOFMS using ESI as an ion source. Thin-layer chromatography (TLC) was performed on pre-coated silica-gel 60 F_{254} plates. Spots were visualized under UV light (254 nm and 365 nm) and by staining with $KMnO_4$ or phosphomolybdic acid (PMA) solutions. Flash column chromatography was carried out using silica gel (200-300 mesh) with ethyl acetate, petroleum ether, dichloromethane and methanol. Melting points were determined using a Büchi B-540 capillary melting point apparatus. Optical rotations were determined using an AUTOPOL® V polarimeter. HPLC analyses were performed on Agilent 1100 or Waters e2695 systems equipped with the following chiral columns thermostatted at 25 °C: OD-H, AD-H, OJ-H, IA-H and IC-H.

2. General procedure for catalysts synthesis

2.1 The procedure for the synthesis of C1, C4-C8



L1: R = Me, **L4**: R = Ph, **L5**: R = 1,3,5-$(Me)_3C_6H_2$, **L6**: R = 2-naphthyl, **L7**: R = 4-$OMeC_6H_4$, **L8**: R = 4-BrC_6H_4

The catalysts **C1, C4-C8** were synthesized according to literature procedures[1-3].

Step 1: A solution of ethylamine (5.0 mmol, 1.0 equiv.) and *N*-Boc-*L*-Prolinal (5.0 mmol, 1.0 equiv.) in DCM (10 mL) was stirred under an argon atmosphere at 25 °C for 8 h. Upon complete consumption of the aldehyde (monitored by TLC), the solvent was removed in vacuo to afford the crude imine, which was used directly in the next step without further purification. The residue was dissolved in MeOH (10.0 mL), cooled to 0 °C, and treated with $NaBH_4$ (12.5 mmol, 2.5 equiv.) portionwise. The resulting mixture was warmed to room temperature, stirred for 8 h, quenched with H_2O (30 mL) at 0 °C, and extracted with DCM (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 10:1) to afford compound **9** as a yellow oil in 72-88% yield.

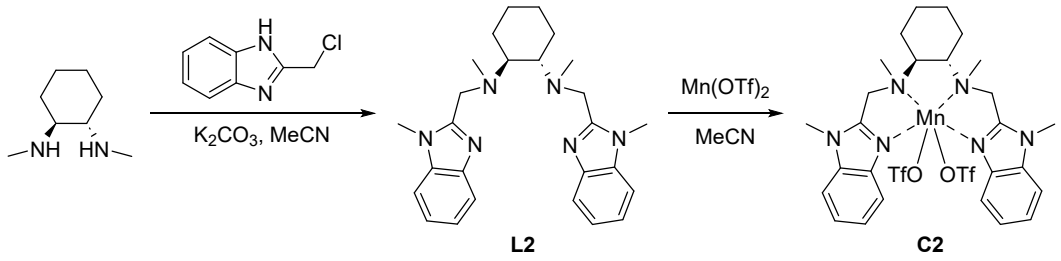
Step 2: A solution of **9** (4.0 mmol) in DCM (20 mL) was cooled to 0 °C; TFA (2.0 mL) was added dropwise. The mixture was stirred at room temperature for 12 h, then diluted with DCM (50 mL) and washed with sat. $NaHCO_3$ (2 × 20 mL) and brine. After drying (Na_2SO_4) and concentration, crude amine **10** was obtained and used immediately without further purification.

Step 3: A mixture of amine **10** (2.0 mmol, 1.0 equiv.), 2-(chloromethyl)-1-methyl-1*H*-benzimidazole (5.0 mmol, 2.5 equiv.), and K_2CO_3 (6.0 mmol, 3.0 equiv.) in MeCN (30 mL) was stirred at 60 °C under an argon atmosphere for 8 h. Upon completion (monitored by TLC), the

mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The crude residue was purified by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 5:1) to afford the corresponding ligands **L1** or **L4-L8** as a white solid in 60-90% yield.

Step 4: The corresponding ligand **L1 (or L4-L8)** (1.5 mmol, 1.0 equiv.) and $Mn(OTf)_2$ (1.65 mmol, 1.1 equiv.) was dissolved in MeCN (30 mL) under Ar and stirred at 60 °C for 6 h. The solvent was removed in vacuo; the residue was triturated with *n*-pentane (3 × 20 mL) and dried under vacuum to afford **C1 (or C4-C8)** as a yellow solid in 90-98% yield.

2.2 The procedure for the synthesis of C2



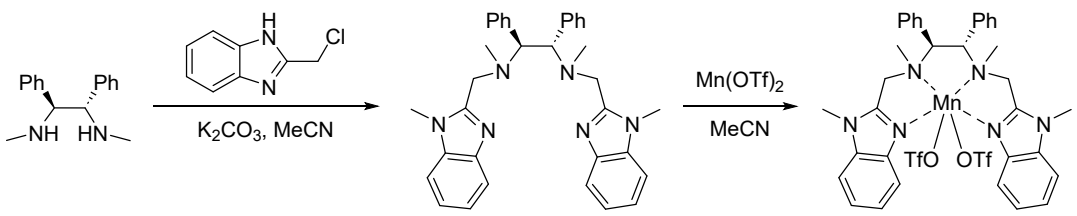
L2 **C2**

The catalyst **C2** was synthesized according to literature procedures[2].

Step 1: A mixture of (1*S*,2*S*)-cyclohexane-1,2-diamine (2.0 mmol, 1.0 equiv.), 2-(chloromethyl)-1-methyl-1*H*-benzimidazole (5.0 mmol, 2.5 equiv.), and K_2CO_3 (6.0 mmol, 3.0 equiv.) in MeCN (30 mL) was stirred at 60 °C under Ar for 8 h. Upon completion (monitored by TLC), the mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The crude residue was purified by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 5:1) to afford the ligand **L2** as a white solid in 86% yield.

Step 2: The corresponding ligand **L2** (1.5 mmol, 1.0 equiv.) and $Mn(OTf)_2$ (1.65 mmol, 1.1 equiv.) was dissolved in MeCN (30 mL) under Ar. The solution was stirred at 60 °C for 6 h, during which the colour changed from colourless to deep yellow. After completion, the solvent was removed in vacuo; the residue was triturated with *n*-pentane (3 × 20 mL) and dried under vacuum to afford **C2** as a yellow solid in 95% yield.

2.3 The procedure for the synthesis of C3.



L3 **C3**

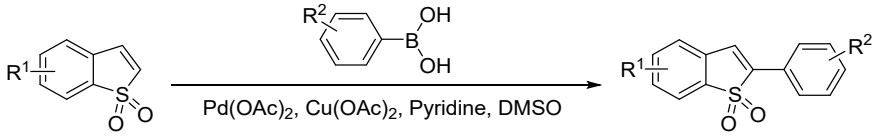
The catalyst **C3** was synthesized according to literature procedures[4].

Step 1: A mixture of (1*S*,2*S*)-*N*1,*N*2-dimethyl-1,2-diphenylethane-1,2-diamine (2.0 mmol, 1.0 equiv.), 2-(chloromethyl)-1-methyl-1*H*-benzimidazole (5.0 mmol, 2.5 equiv.), and K_2CO_3 (6.0 mmol, 3.0 equiv.) in MeCN (30 mL) was stirred at 60 °C under Ar for 8 h. Upon completion (monitored by TLC), the mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The crude residue was purified by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 5:1) to afford the ligand **L3** as a white solid in 78% yield.

Step 2: The corresponding ligand **L3** (1.5 mmol, 1.0 equiv.) and $Mn(OTf)_2$ (1.65 mmol, 1.1 equiv.) was dissolved in MeCN (30 mL) under Ar. The solution was stirred at 60 °C for 6 h, during which the colour changed from colourless to deep yellow. After completion, the solvent was removed in vacuo; the residue was triturated with *n*-pentane (3 × 20 mL) and dried under vacuum to afford **C3** as a yellow solid in 98% yield.

3. General procedure for substrates synthesis

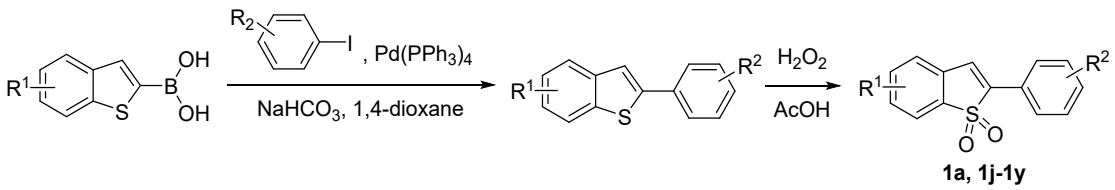
3.1 The procedure for the synthesis of substrate 1.



1b-1i, 1z

Substrates **1b-1i, 1z** were synthesized according to the reference literature[5].

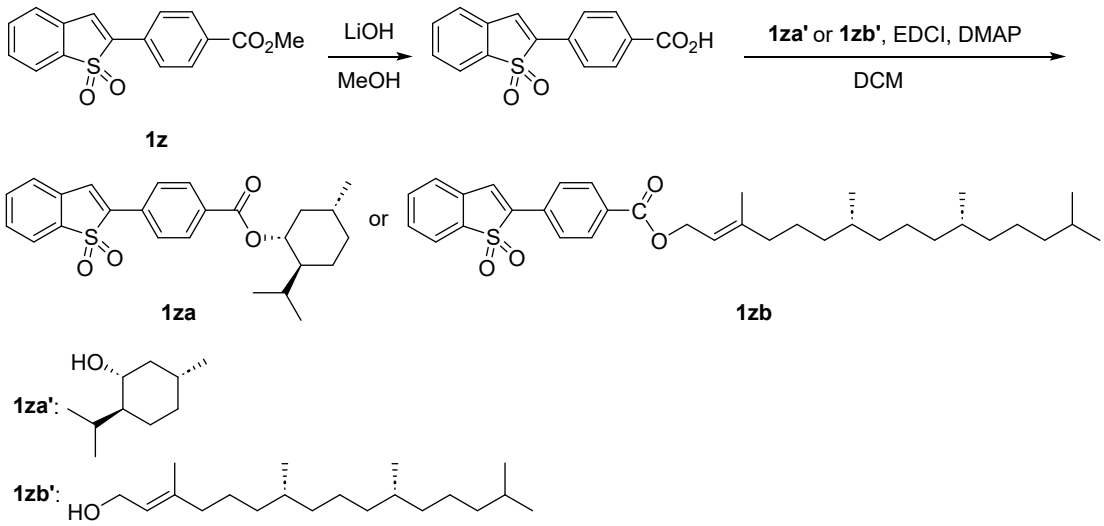
A mixture of benzo[*b*]thiophene 1,1-dioxide (2.0 mmol, 1.0 equiv.), phenylboronic acid (6.0 mmol, 3.0 equiv.), $Pd(OAc)_2$ (0.2 mmol, 0.1 equiv.), $Cu(OAc)_2$ (6.0 mmol, 3.0 equiv.) and pyridine (6.0 mmol, 3.0 equiv.) in anhydrous DMSO (30 mL) was stirred at 100 °C under Ar for 20 h. After cooling to room temperature, the reaction mixture was diluted with H_2O (60 mL), and extracted with EA (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 5:1) to afford substrates **1b-1i** and **1z** as yellow solids in 60-80% isolated yield.



Substrates **1a, 1j-1y** were synthesized according to the reference literature[6-8].

Step 1: To a solution of $Pd(PPh_3)_4$ (0.05 mmol, 0.005 equiv.) in dry 1,4-dioxane (50 mL) under an argon atmosphere was added the aromatic iodide (10.00 mmol, 1.0 equiv.). The mixture was stirred at room temperature for 20 min. Then, a saturated aqueous solution of $NaHCO_3$ (14 mL) and 1-benzothiophen-2-ylboronic acid (11.0 mmol, 1.1 equiv.) were added sequentially. The resulting reaction mixture was heated at reflux overnight. After completion, the reaction mixture was cooled to room temperature, diluted with water (80 mL), and extracted with DCM (3 × 60 mL). The combined organic layers were washed with 1 M aqueous NaOH (40 mL), followed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford a brown crystalline solid. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 5:1) to yield 2-phenylbenzo[*b*]thiophene in 50-80% yield.

Step 2: The relevant 2-phenylbenzo[*b*]thiophene (1.0 equiv.) was suspended in glacial AcOH (15 mL) under an argon atmosphere. A 30% aqueous solution of H_2O_2 (30% aq. solution, 6.5 equiv.) was added slowly via syringe. The mixture was heated to 100 °C, at which temperature it gradually became a clear solution. The reaction was stirred at 100 °C for 3 h. After cooling to room temperature, the mixture was partitioned between DCM and a saturated aqueous solution of $NaHCO_3$ (adjusted to pH $\approx$ 9). The layers were separated, and the aqueous phase was extracted with DCM (3 × 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford the crude product. Purification by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 5:1) yielded the desired sulfoxide product **1a** and **1j-1y** in 70-90% yield.

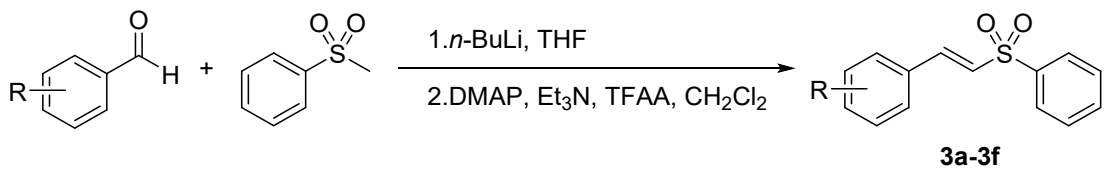


Substrates **1za**, **1zb** were synthesized according to the reference literature[9-10].

Step 1: To a solution of **1z** (1.0 mmol, 1.0 equiv.) in MeOH (5 mL) was added a solution of $LiOH·H_2O$ (2.0 mmol, 2.0 equiv.) at 0 °C. The resulting mixture was stirred as it was allowed to warm gradually to room temperature over 5 h (monitored by TLC). After completion, the reaction mixture was diluted with H_2O (10 mL) and extracted with EA (3 × 10 mL). The aqueous layer was separated, acidified to pH 2-3 with 2 M HCl, and the resulting precipitate was collected by filtration. The solid was washed with H_2O and dried under vacuum to afford the crude carboxylic acid as a white solid. The crude carboxylic acid was used directly in the next step without further purification.

Step 2: Under an argon atmosphere, carboxylic acid (1.0 mmol, 1.0 equiv.), alcohol (1.2 mmol, 1.2 equiv.), EDCI (1.3 mmol, 1.3 equiv.), and DMAP (0.1 mmol, 0.1 equiv.) were dissolved in anhydrous DCM (5 mL). The mixture was stirred at room temperature for 16 h (monitored by TLC). Upon completion, the reaction mixture was diluted with DCM and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 5:1) afforded the desired ester product **1za, 1zb** in 60-80% yield.

3.2 The procedure for the synthesis of substrate 3.

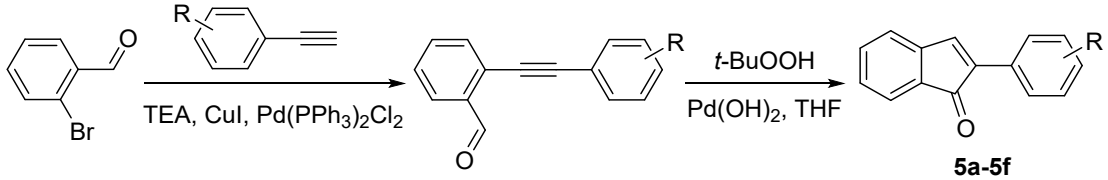


Substrates **3** (**3a-3f**) were synthesized according to the reference literature[8].

Step 1: To an oven-dried 250 mL three-neck round-bottom flask under an argon atmosphere was added methyl phenyl sulfone (1.0 mmol, 1.0 equiv.). Anhydrous THF (6 mL) was added, and the mixture was cooled to -78 °C. A solution of *n*-BuLi (1.1 mmol, 1.1 equiv., 2.5 M in hexanes) was added dropwise with stirring, and the reaction was stirred at -78 °C for 30 min. The corresponding ketone (1.1 mmol, 1.1 equiv.) was then added dropwise, and the resulting solution was stirred at -78 °C for 1 h, during which time TLC analysis indicated complete consumption of the starting material. The reaction was quenched with saturated aqueous NH_4Cl solution and extracted with EA (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford the crude alcohol (used directly in Step 2).

Step 2: The residue was dissolved in anhydrous DCM (30 mL) and cooled to 0 °C. To this solution were added DMAP (0.1 equiv.) and Et_3N (2.0 equiv.), followed by dropwise addition of TFAA (1.2 equiv.). The reaction mixture was stirred at 0 °C for 30 min, then allowed to warm to room temperature and stirred overnight. After completion, the mixture was quenched with saturated aqueous NH_4Cl solution and extracted with DCM (3 × 30 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 20:1) afforded the corresponding products **3a-3f**.

3.3 The procedure for the synthesis of substrate 5.



5a-5f

Substrates **5** (**5a-5f**) were synthesized according to the reference literature[11,12].

Step 1: A 50 mL three-neck round-bottom flask, equipped with a magnetic stirrer and Ar inlet, was charged with the appropriate brominated aldehyde (1.0 mmol, 1.0 equiv.), Pd $(PPh_3)_2Cl_2$ (0.05 mmol, 0.05 equiv.), CuI (0.1 mmol, 0.1 equiv.) and triethylamine (3.3 mL). The terminal alkyne derivative (1.20 mmol, 1.2 equiv.) was then added dropwise. The resulting suspension was stirred under a nitrogen atmosphere at 50 °C for 16 h. After cooling to room temperature, the reaction mixture was diluted with EA (50 mL) and filtered through a pad of Celite. The filtrate was washed with saturated aqueous NH_4Cl solution until the aqueous layer reached neutral pH. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The

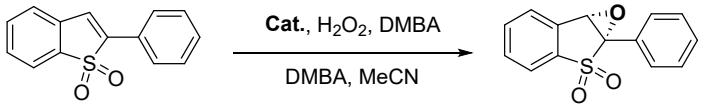
combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford the crude product. Purification by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 50:1) yielded the Internal acetylene as a yellow solid in 60-90% yield.

Step 2: A screw-cap pressure tube (10 mL) was charged with the above internal alkyne (0.3 mmol, 1.0 equiv.), TBHP (70% aq. solution, 2.1 mmol, 7.0 equiv.), $Pd(OAc)_2$ (0.03 mmol, 0.1 equiv.), and dry THF (4 mL). The reaction mixture was stirred magnetically at 60 °C for 12 h. After cooling to room temperature, the residue was purified directly by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 25:1) to afford substrates **5a-5f** as a white solid in 60-90% yield.

4. Optimization of asymmetric epoxidation

4.1 Evaluation of axial ligand for 1a

Table S1 Design and optimization of catalysts for **1a**[a]



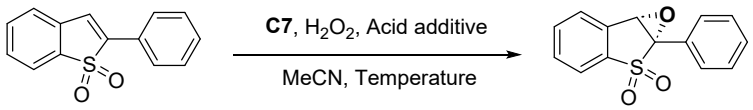
1a **2a**

Entry	Cat.	Conv. (%)	Yield (%)	*ee* (%)
1	**C1**	100	85	86.3
2	**C2**	90	73	82.1
3	**C3**	86	69	80.0
4	**C4**	100	93	96.4
5	**C5**	95	87	95.5
6	**C6**	84	79	96.2
7	**C7**	**100**	**95**	**98.0**
8	**C8**	100	84	98.0
9[b]	**C7**	100	96	98.0
10[c]	C7	100	87	96.8
11[d]	C7	83	72	96.4
12[e]	C7	69	56	93.8

[a]Standard reaction conditions: **1a** (0.5 mmol), **Cat**. (10 μmol, 2 mol%), and DMBA (6 equiv.) were dissolved in 2 mL of MeCN, then H_2O_2 (3.0 equiv., 30% aqueous solution was diluted in 0.5 mL MeCN) was added to the solution dropwise at -40 °C, using a syringe pump over 2.5 h and stirred for an additional 0.5 h. Isolated yields. Determined by chiral HPLC analysis. [b]**C7** (15 μmol, 3 mol%). [c]**C7** (5 μmol, 1 mol%). [d]**C7** (2.5 μmol, 0.5 mol%). [e]**C7** (0.5 μmol, 0.1 mol%).

4.2 Evaluation of acid additive and temperature for 1a

Table S2 Evaluation of acid additive and temperature for **1a**[a]



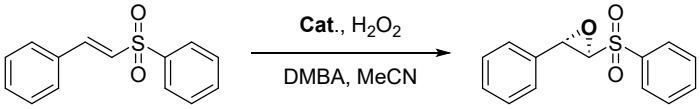
1a **2a**

Entry	Acid	Temperature (°C)	Usage (equiv.)	Yield (%)	*ee* (%)
1	EHA (2-Ethylhexanoic acid)	-40	6	60	93.1
2	PBA (4-Phenylbutyric acid)	-40	6	/	/
3	**DMBA (2,2-Dimethylbutyric acid)**	**-40**	**6**	**95**	**98.0**
4	PA (Pivalic acid)	-40	6	39	93.0
5	AcOH	-40	6	81	91.4
6	DMBA	-30	6	91	93.8
7	DMBA	-20	6	87	87.7
8	DMBA	-40	4	45	97.8
9	DMBA	-40	10	94	98.0

[a]Standard reaction conditions: **1a** (0.5 mmol), **C7** (2 mol%), and acid were dissolved in 2 mL of MeCN, then H_2O_2 (3.0 equiv., 30% aqueous solution was diluted in 0.5 mL MeCN) was added to the solution dropwise using a syringe pump over 2.5 h and stirred for an additional 0.5 h. Isolated yields. Determined by chiral HPLC analysis.

4.2 Evaluation of acid additive and temperature for 3a

Table S3 Evaluation of acid additive and temperature for **3a**[a]



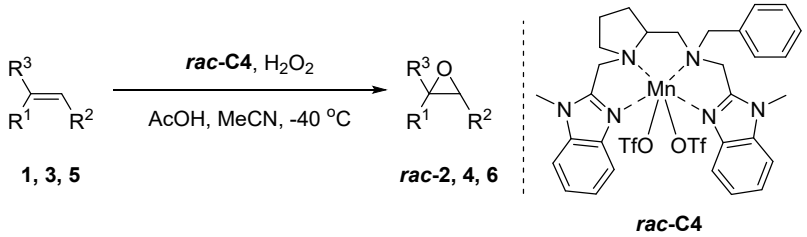
3a **4a**

Entry	**Cat.**	Conv. (%)	Yield (%)	*ee* (%)
1	**C4**	64	53	83.2
2	**C5**	30	18	82.1
3	**C6**	63	51	79.5
4	**C7**	75	66	84.4
5	**C8**	**78**	**68**	**91.6**
6[b]	**C8**	78	69	91.6
7[c]	**C8**	51	41	90.0

[a]Standard reaction conditions: **3a** (0.5 mmol), **Cat.** (10 μmol, 2 mol%), and DMBA (6 equiv.) were dissolved in 2 mL of MeCN, then H_2O_2 (3.0 equiv., 30% aqueous solution was diluted in 0.5 mL MeCN) was added to the solution dropwise at -40 °C, using a syringe pump over 2.5 h and stirred for an additional 0.5 h. [b]**C8** (15 μmol, 3 mol%). [c]**C8** (5 μmol, 1 mol%). Isolated yields. Determined by chiral HPLC analysis.

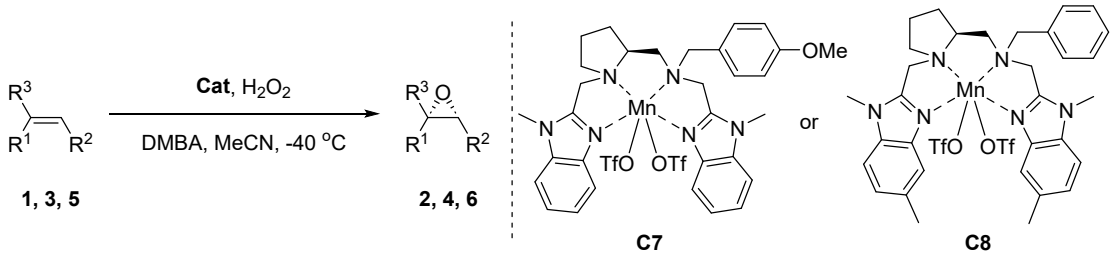
5. General procedure for epoxidation

5.1 General procedure for racemic epoxidation



To a Schlenk flask charged with Substrate **1** (**3** or **5**) (0.5 mmol, 1.0 equiv.), the corresponding catalyst ***rac*-C4** (10 μmol, 2 mol%), and AcOH (5.0 mmol, 10.0 equiv.) in MeCN (2 mL) at -40 °C was added a solution of H_2O_2 (2.5 mmol, 5.0 equiv., 30% aqueous solution, diluted in 0.5 mL MeCN) via syringe pump over 2 h and stirred for an additional 1 h (monitored by TLC). Upon completion, the mixture was quenched with a saturated Na_2SO_3 aqueous solution and then extracted with DCM. The combined organic layers were washed twice with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the racemic epoxides **2**, **4** and **6**.

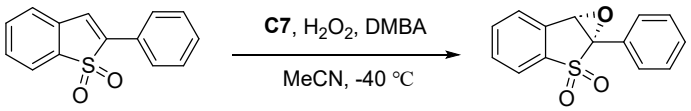
5.2 General procedure for asymmetric epoxidation of 2, 4 and 6.



To a Schlenk flask charged with Substrate **1** (**3** or **5**) (0.5 mmol, 1.0 equiv.), the corresponding catalyst (**C7** for **1** or **5**, **C8** for **3**, 10 μmol, 2 mol%), and DMBA (3.0 mmol, 6.0 equiv.) in MeCN (2 mL) at -40 °C was added a solution of H_2O_2 (1.5 mmol, 3.0 equiv., 30% aqueous solution, diluted in 0.5 mL MeCN) via syringe pump over 2 h and stirred for an additional 1 h (monitored by TLC). Upon completion, the mixture was quenched with a saturated Na_2SO_3 aqueous solution and then extracted with DCM. The combined organic layers were washed twice with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the asymmetric epoxides. Purification by flash column chromatography on silica gel (eluent: petroleum

ether-ethyl acetate, 5:1) to afford the asymmetric products **2**, **4** and **6**. The *ee* were determined using chiral HPLC analysis.

6. Gram-scale asymmetric epoxidation



1a

970 mg

2a

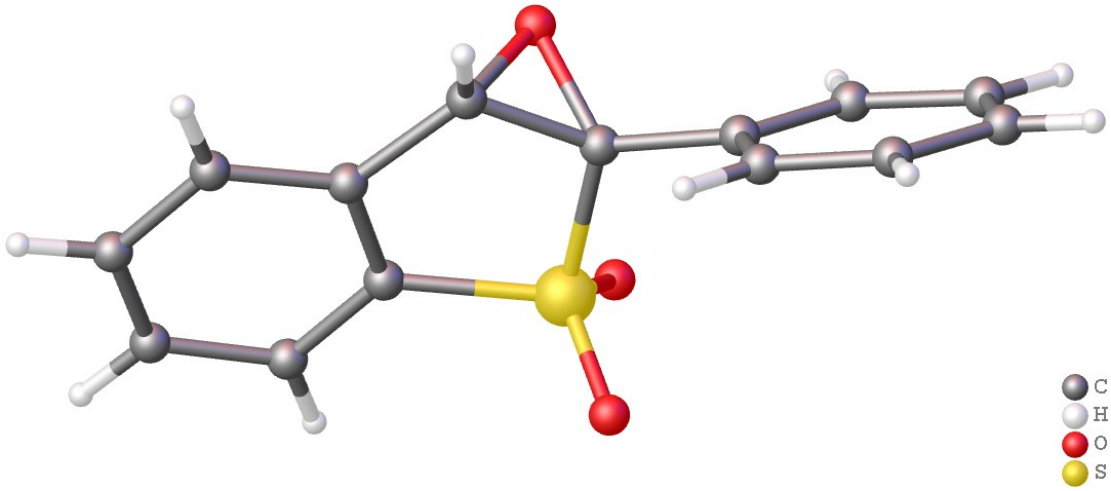
951 mg, 92% yield, 91.0% *ee*
837 mg, 81% yield, 99.9% *ee* after recrystallization

To a Schlenk flask charged with Substrate **1a** (970 mg, 4.0 mmol, 1.0 equiv.), catalyst **C7** (69 mg, 2 mol%), and DMBA (2.79 g, 24.0 mmol, 6.0 equiv.) in MeCN (30 mL) at -40 °C was added a solution of H_2O_2 (1.36 g, 24.0 mmol, 3.0 equiv., 30% aqueous solution, diluted in 2.0 mL MeCN) via syringe pump over 3 h and stirred for an additional 1 h (monitored by TLC). Upon completion, the reaction was quenched with a saturated Na_2SO_3, diluted with DCM, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford the crude epoxide. Purification by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 5:1) to afford the asymmetric products **2a** (951mg, 92% yield, 91.0% *ee*). This material was recrystallized from MeOH (10 mL g^{-1}) to afford the pure compound as a white solid **2a** (837mg, 81% yield, 99.9% *ee*).

7. X-ray crystallographic data for 2a (CCDC 2484440)

Table S4 Crystal data and structure refinement for A.

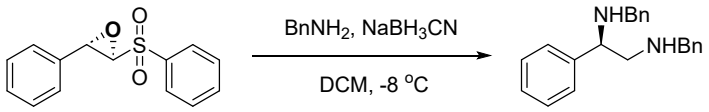
Identification code	A
Empirical formula	$C_{14}H_{10}O_3S$
Formula weight	258.28
Temperature/K	193.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	14.9751(5)
b/Å	6.1259(2)
c/Å	12.9261(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1185.79(7)
Z	4
ρ_{calc}g/cm^3	1.447
μ/mm^{-1}	2.411
F(000)	536.0
Crystal size/mm^3	0.13 × 0.12 × 0.09
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.038 to 158.95
Index ranges	$-19 \leq h \leq 19$, $-7 \leq k \leq 7$, $-16 \leq l \leq 16$
Reflections collected	25602
Independent reflections	2549 [R_{int} = 0.0527, R_{sigma} = 0.0307]
Data/restraints/parameters	2549/0/163
Goodness-of-fit on F^2	1.111
Final R indexes [I>=2σ (I)]	R_1 = 0.0389, wR_2 = 0.1054
Final R indexes [all data]	R_1 = 0.0393, wR_2 = 0.1058
Largest diff. peak/hole / e Å^{-3}	0.56/-0.34
Flack parameter	0.050(6)



Supplementary Fig. 1 Structure drawing of **2a** (CCDC 2484440)

8. Substrate derivatization

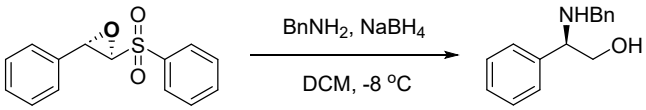
8.1 Synthesis of vicinal diamine[13]



4a **4ab**

To a Schlenk flask charged with **4a** (1.0 mmol, 1.0 equiv.) in DCM (5 mL) was added $BnNH_2$ (3.0 mmol, 3.0 equiv.) at 0 °C. The mixture was stirred at -8°C for 16 h. Then, $NaBH_3CN$ (6 mmol, 6 equiv.) was added portionwise over 10 min,, and the resulting mixture was stirred for additional 8 h (monitored by TLC). Finally, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (10 mL) and extracted with DCM (3 × 30 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 2:1) afforded the product **4ab** (54% yield, 95.0% *ee*).

8.2 Synthesis of chiral *β*-amino alcohol[13]

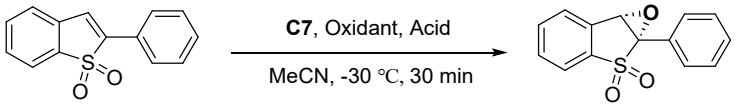


4a **4ac**

To a Schlenk flask charged with **4a** (1.0 mmol, 1.0 equiv.) in DCM (5 mL) was added $BnNH_2$ (3.0 mmol, 3.0 equiv.) at 0 °C. The mixture was stirred at -8°C for 16 h. Then, $NaBH_4$ (8 mmol, 8 equiv.) was added portionwise over 10 min, and the resulting mixture was stirred for additional 8 h (monitored by TLC). Finally, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (10 mL) and extracted with DCM (3 × 30 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica gel (eluent: petroleum ether-ethyl acetate, 2:1) afforded the product **4ac** (62% yield, 91.1% *ee*).

9. Mechanistic studies

9.1 Comparison of Oxidants for Epoxidation of 1a[a]



1a **2a**

Entry	Condition	Yield (%)	*ee* (%)
1	H_2O_2, DMBA	91	94
2	H_2O_2, DMBA, without **C7**	N.R.	-
3	H_2O_2, AcOH	79	87
4	*t*-BuOOH, AcOH	80	86
5	AcOOH, AcOH	45	87

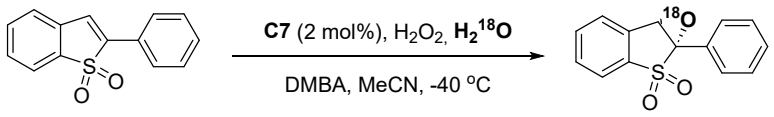
[a]Standard reaction conditions: **1a** (0.5 mmol), **C7** (10 μmol, 2 mol%), and Acid (6 equiv.) were dissolved in 2 mL of MeCN, then Oxidant (3.0 equiv., 30% aqueous solution was diluted in 0.5 mL MeCN) was added to the solution dropwise at -30 °C, using a syringe pump over 0.5 h. Isolated yields. Determined by chiral HPLC analysis.

9.2 ^{18}O-Labeling experiment

To a Schlenk flask charged with Substrate **1a** (24.23 mg, 0.1 mmol, 1.0 equiv.), **C7** (1.7 mg, 2 mol%), DMBA (69.7 mg, 0.6 mmol, 6.0 equiv.) and $H_2{}^{18}O$ (1.5 equiv., 98 atom %) in MeCN (2 mL) was added H_2O_2 (30% aq., 3.0 equiv., pre-diluted in 0.5 mL MeCN) via syringe pump over 2 h at 0 **°C** (or -40 °C for the low-temperature set). After an additional 1 h at the same temperature, the reaction was quenched with sat. Na_2SO_3 and analysed by GC-MS (Supplementary Fig. 2 and 3).

At 0 °C, ^{18}O-incorporation into the epoxide was 0.76%, while at -40 °C it dropped to 0.03%. Lowering the temperature from 0 °C to -40 °C reduces ^{18}O-incorporation to within experimental error, indicating negligible O-atom exchange with bulk water under cryogenic conditions.

$H_2{}^{18}O/H_2{}^{16}O_2$ labeling experiment

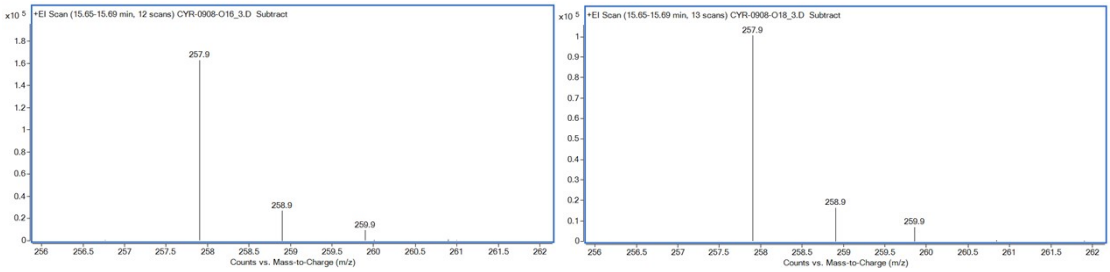


1a **2a**

0 °C: 0.76% ^{18}O-incorporation

-40 °C: 0.03% ^{18}O-incorporation

a. Regular epoxide at 0 °C b. Epoxide obtained from the $H_2{}^{18}O$ experiment at 0 °C

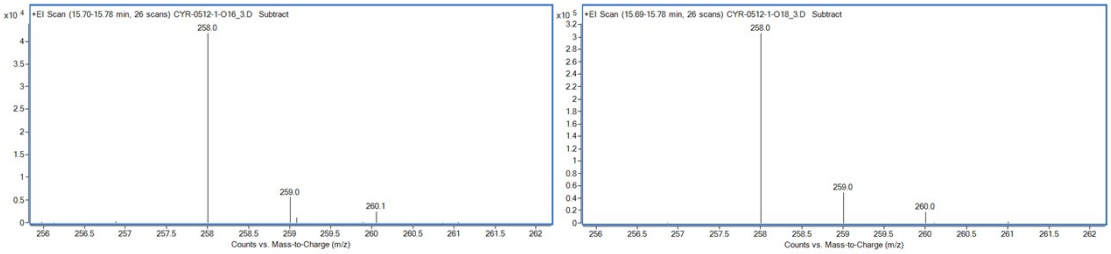


m/z	Abund	Abund%
257.9	163511	81.68
258.9	27022	13.50
259.9	9642	4.82

m/z	Abund	Abund%
257.9	100715	81.13
258.9	16502	13.29
259.9	6930	5.58

Supplementary Fig. 2 ^{18}O-Labeling experiment at 0 °C

a. Regular epoxide at -40 °C b. Epoxide obtained from the $H_2{}^{18}O$ experiment at -40 °C

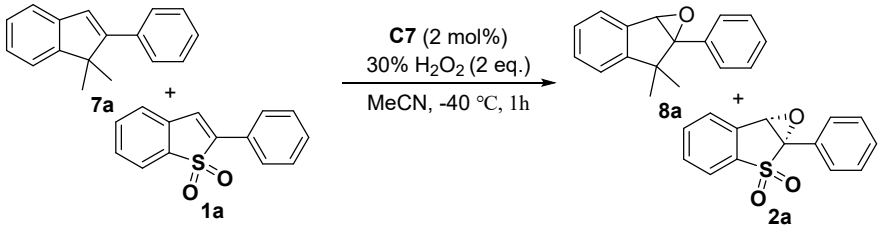


m/z	Abund	Abund %
258	61924.91	82.22
259	9724.32	12.91
260	3666.3	4.87

m/z	Abund	Abund %
258	629796.38	81.95
259	101012.76	13.14
260	37670.21	4.90

Supplementary Fig. 3 ^{18}O-Labeling experiment at -40 °C

9.3 Competitive epoxidation experiment

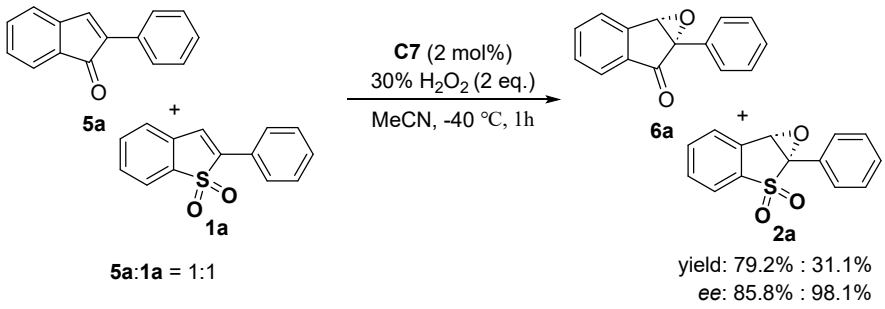


7a:**1a** = 1:1

yield: 91.9% : 24.9%

ee: 0% : 98.0%

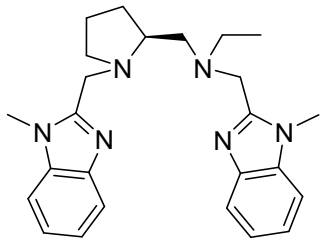
An MeCN solution (2.0 mL) containing **7a** (0.04 mmol, 1.0 equiv.), **1a** (0.04 mmol, 1.0 equiv.), **C7** (1.0 mg, 2 mol %) and DMBA (0.25 mmol, 6.0 equiv.) was prepared in a 10 mL vial equipped with a stir bar and cooled at -40 ºC. Then a solution of H_2O_2 (30% aq., 2.0 equiv., pre-diluted in 0.5 mL MeCN) was added via syringe pump over 30 min. The solution was further stirred at -30 ºC for 30 minutes. At this point, biphenyl (0.04 mmol, internal standard) was added; the solution was immediately passed through a basic alumina plug (200 mg, rinsed with 2 × 1 mL EtOAc). GC analysis of the solution provided substrate conversions and product yields relative to the internal standard integration; products were identified by comparison with authentic samples.



An MeCN solution (2.0 mL) containing **5a** (0.04 mmol, 1.0 equiv.), **1a** (0.04 mmol, 1.0 equiv.), **C7** (1.0 mg, 2 mol %) and DMBA (0.25 mmol, 6.0 equiv.) was prepared in a 10 mL vial equipped with a stir bar and cooled at -40 ºC. Then a solution of H_2O_2 (30% aq., 2.0 equiv., pre-diluted in 0.5 mL MeCN) was added via syringe pump over 30 min. The solution was further stirred at -30 ºC for 30 minutes. At this point, biphenyl (0.04 mmol, internal standard) was added; the solution was immediately passed through a basic alumina plug (200 mg, rinsed with 2 × 1 mL EtOAc). GC analysis of the solution provided substrate conversions and product yields relative to the internal standard integration; products were identified by comparison with authentic samples.

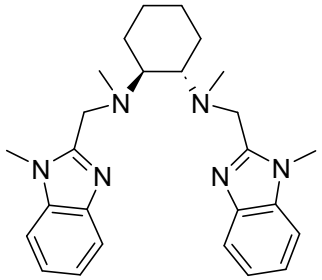
10. Spectra data

(*S*)-*N*-((1-methyl-1H-benzo[d]imidazol-2-yl)methyl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)ethanamine (L1)



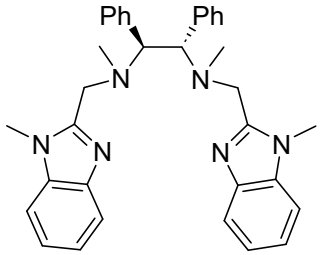
Yellow solid, m.p.= 79.3-80.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.64 (m, 2H), 7.28 – 7.19 (m, 6H), 4.20 (d, *J* = 13.2 Hz, 1H), 3.86 – 3.79 (m, 4H), 3.72 (d, *J* = 13.6 Hz, 1H), 3.65 – 3.55 (m, 4H), 2.76 – 2.70 (m, 1H), 2.63 – 2.49 (m, 4H), 2.40 (dd, *J* = 12.8, 8.0 Hz, 1H), 2.28 (q, *J* = 7.2 Hz, 1H), 1.94 – 1.88 (m, 1H), 1.62 – 1.49 (m, 2H), 1.45 – 1.37 (m, 1H), 1.04 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 152.2, 142.1, 142.1, 136.3, 136.2, 122.6, 122.4, 121.9, 121.8, 119.5, 119.4, 109.1, 62.3, 58.8, 54.9, 52.4, 52.3, 48.8, 30.4, 30.1, 29.9, 22.5, 11.6. HRMS-ESI (m/z): calcd for $C_{25}H_{33}N_6$ $[M + H]^+$: 417.2762, found: 417.2763.

(1*S*,2*S*)-*N*^{1},*N*^{2}-dimethyl-*N*^{1},*N*^{2}-bis((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)cyclohexane-1,2-diamine (L2)



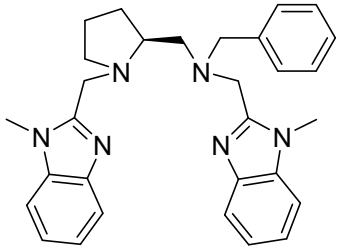
White solid, m.p.= 165.1-165.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 2H), 7.27 – 7.24 (m, 6H), 3.97 (s, 4H), 3.80 (s, 6H), 2.72 (s, 2H), 2.16 (s, 6H), 2.00 (d, *J* = 10.8 Hz, 2H), 1.80 (d, *J* = 7.2 Hz, 2H), 1.29 – 1.16 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 142.2, 136.3, 122.5, 121.8, 119.6, 109.1, 62.8, 51.7, 35.9, 29.9, 25.6, 24.0. HRMS-ESI (m/z): calcd for $C_{26}H_{35}N_6$ $[M + H]^+$: 431.2918, found: 431.2919.

(1*S*,2*S*)-*N*^{1},*N*^{2}-dimethyl-*N*^{1},*N*^{2}-bis((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)-1,2-diphenylethane-1,2-diamine (L3)



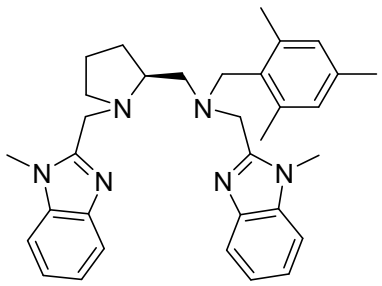
White solid, m.p.= 234.3-234.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H), 7.31 – 7.24 (m, 6H), 7.21 – 7.05 (m, 10H), 4.53 (s, 2H), 3.87 – 3.84 (m, 8H), 3.75 (d, *J* = 13.6 Hz, 2H), 2.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 142.4, 136.3, 133.4, 129.9, 127.8, 127.1, 122.6, 121.9, 119.8, 109.1, 65.4, 51.9, 36.4, 29.9. HRMS-ESI (m/z): calcd for $C_{34}H_{37}N_6$ $[M + H]^+$: 529.3075, found: 529.3079.

(*S*)-*N*-benzyl-1-(1-methyl-1*H*-benzo[d]imidazol-2-yl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (L4)



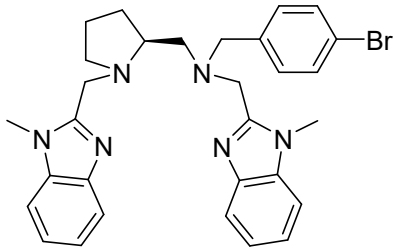
White solid, m.p.= 136.3-137.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 2H), 7.35 – 7.26 (m, 4H), 7.27 – 7.17 (m, 7H), 4.20 (d, *J* = 13.2 Hz, 1H), 3.75 (q, *J* = 10.8 Hz, 2H), 3.61 (t, *J* = 11.2 Hz, 3H), 3.55 (s, 3H), 3.46 (s, 3H), 2.75 – 2.64 (m, 3H), 2.56 – 2.46 (m, 1H), 2.28 (q, *J* = 7.6 Hz, 1H), 2.02 – 1.90 (m, 1H), 1.64 – 1.55 (m, 1H), 1.52 – 1.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 151.7, 142.2, 142.2, 138.4, 136.2, 129.6, 128.3, 127.5, 122.6, 122.4, 121.9, 121.8, 119.5, 119.5, 109.1, 109.1, 62.4, 60.2, 59.4, 54.8, 52.4, 52.1, 30.5, 29.9, 29.7, 22.4. HRMS-ESI (m/z): calcd for $C_{30}H_{35}N_6$ $[M + H]^+$: 479.2918, found: 479.2916.

(*S*)-1-mesityl-*N*-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (L5)



White solid, m.p.= 135.3-136.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 2H), 7.26 – 7.17 (m, 6H), 6.84 (s, 2H), 4.08 (d, *J* = 13.2 Hz, 1H), 3.81 – 3.68 (m, 2H), 3.69 – 3.60 (m, 2H), 3.55 (s, 3H), 3.49 (s, 3H), 2.80 – 2.68 (m, 2H), 2.63 – 2.51 (m, 2H), 2.32 (s, 6H), 2.25 (s, 3H), 2.07 – 1.86 (m, 3H), 1.47 – 1.39 (m, 1H), 1.32 – 1.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 149.7, 142.1, 142.1, 138.0, 137.0, 136.2, 136.1, 131.3, 129.3, 122.6, 122.4, 121.9, 121.8, 119.4, 109.1, 109.1, 62.2, 60.0, 54.7, 53.7, 52.0, 51.3, 30.9, 29.8, 29.6, 22.5, 20.9, 20.2. HRMS-ESI (m/z): calcd for $C_{33}H_{41}N_6$ $[M + H]^+$: 521.3388, found: 521.3383.

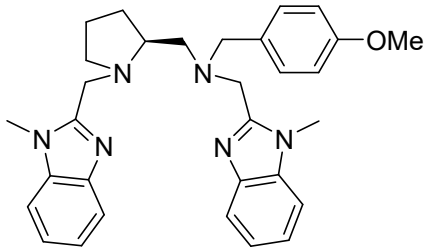
(*S*)-*N*-(4-bromobenzyl)-1-(1-methyl-1H-benzo[d]imidazol-2-yl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (L6)



Yellow solid, m.p.= 131.7-133.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.21 (m, 6H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.17 (d, *J* = 13.2 Hz, 1H), 3.82 – 3.78 (m, 1H), 3.68 (d, *J* = 13.6 Hz, 2H), 3.61 (s, 3H), 3.54 (s, 3H), 3.45 (d, *J* = 13.2 Hz, 1H), 2.76 (s, 2H), 2.59 – 2.55 (m, 1H), 2.51 – 2.46 (m, 1H), 2.32 (d, *J* = 10.8 Hz, 1H), 2.05 – 1.88 (m, 2H), 1.51 – 1.40 (m, 1H), 1.30 – 1.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 142.1, 137.4, 136.1, 131.4, 131.1, 122.7, 122.5, 122.1, 121.9, 121.2, 119.6, 119.5, 109.1, 62.3, 59.3, 54.9, 52.4, 52.1, 31.6, 30.5, 30.0, 29.8, 22.5. HRMS-ESI (m/z): calcd for $C_{30}H_{34}BrN_6$ $[M + H]^+$: 557.2023, found:

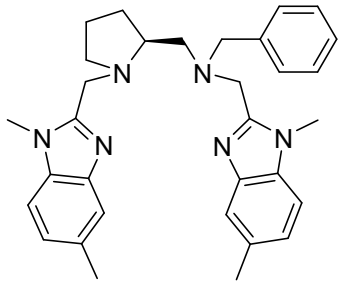
557.2021.

(*S*)-*N*-(4-methoxybenzyl)-1-(1-methyl-1*H*-benzo[d]imidazol-2-yl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (L7)



White solid, m.p.= 53.9-55.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 2H), 7.27 – 7.17 (m, 8H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.23 (d, *J* = 13.2 Hz, 1H), 3.78 (s, 3H), 3.76 – 3.66 (m, 2H), 3.64 – 3.49 (m, 6H), 3.43 (s, 3H), 2.74 – 2.62 (m, 3H), 2.54 – 2.42 (m, 1H), 2.31 – 2.20 (m, 1H), 2.02 – 1.89 (m, 1H), 1.64 – 1.52 (m, 1H), 1.53 – 1.42 (m, 1H), 1.44 – 1.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 152.3, 151.9, 142.1, 142.1, 136.2, 136.2, 130.8, 130.3, 122.6, 122.4, 122.0, 121.8, 119.5, 119.4, 113.6, 109.1, 62.3, 59.4, 59.3, 55.3, 54.9, 52.4, 51.9, 30.5, 30.0, 29.7, 22.3. HRMS-ESI (m/z): calcd for $C_{31}H_{37}N_6O$ $[M + H]^+$: 509.3024, found: 509.3025.

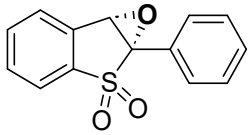
(*S*)-*N*-benzyl-1-(1,5-dimethyl-1H-benzo[d]imidazol-2-yl)-*N*-((1-((1,5-dimethyl-1H-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (L8)



Yellow solid, m.p.= 135.4-136.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.25 – 7.23 (d, *J* = 4.9 Hz, 1H), 7.15 – 7.01 (m, 4H), 4.18 (d, *J* = 13.2 Hz, 1H), 3.81 – 3.66 (m, 2H), 3.61 – 2.53 (d, *J* = 23.2 Hz, 6H), 3.46 (s, 3H), 2.74 – 2.62 (m, 3H), 2.46 (s, 6H), 2.26 (q, *J* = 8.4 Hz, 1H), 2.01 – 1.91 (m, 2H), 1.63 – 1.52 (m, 1H), 1.42 – 1.35 (m, 1H), 1.29 – 1.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 151.7, 142.5, 142.4, 138.5, 134.3, 134.3, 131.5, 131.4, 129.6, 128.3, 127.4,

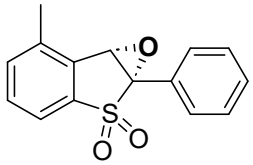
124.0, 123.8, 119.3, 119.2, 108.6, 108.6, 62.4, 60.2, 59.4, 54.8, 52.3, 52.2, 30.5, 30.0, 29.8, 22.4, 21.6. HRMS-ESI (m/z): calcd for $C_{32}H_{39}N_6$ $[M + H]^+$: 507.3231, found: 557.3232.

(1a*R*,6b*S*)-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2a)



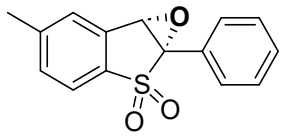
White solid, m.p.= 147.8-149.1 °C. 95% yield, 98.0% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 1H), 7.78 – 7.75 (m, 2H), 7.71 – 7.63 (m, 3H), 7.54 – 7.47 (m, 3H), 4.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 133.7, 133.3, 132.1, 131.3, 129.7, 129.4, 128.2, 125.5, 124.1, 75.6, 60.1. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 16.837 min, t (minor) = 22.351 min. HRMS-ESI (m/z): calcd for $C_{14}H_{11}O_3S$ $[M + H]^+$: 259.0424, found: 259.0425.

(1a*R*,6b*S*)-6-methyl-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2b)



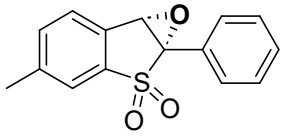
White solid, m.p.= 169.2-172.1 °C. 89% yield, 99.7% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.54 – 7.43 (m, 5H), 4.66 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 137.7, 134.5, 131.4, 130.9, 130.6, 129.1, 128.8, 125.2, 120.9, 74.8, 58.0, 17.4. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 12.654 min, t (minor) = 24.917 min. HRMS-ESI (m/z): calcd for $C_{15}H_{13}O_3S$ $[M + H]^+$: 273.0580, found: 273.0581.

(1a*R*,6b*S*)-5-methyl-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2c)



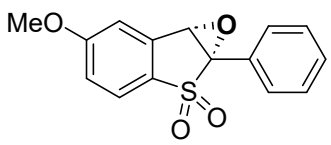
White solid, m.p.= 187.1-187.6 °C. 85% yield, 90.0% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 3H), 7.53 – 7.46 (m, 4H), 7.43 (d, *J* = 7.8 Hz, 1H), 4.53 (s, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 136.6, 133.0, 132.2, 130.6, 129.2, 128.8, 128.1, 125.1, 123.3, 75.2, 59.6, 21.7. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 25.751 min, t (minor) = 45.070 min. HRMS-ESI (m/z): calcd for $C_{15}H_{13}O_3S$ $[M + H]^+$: 273.0580, found: 273.0588.

(1a*R*,6b*S*)-4-methyl-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2d)



White solid, m.p.= 154.5-157.1 °C. 90% yield, 95.5% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.62 (s, 1H), 7.58 – 7.41 (m, 5H), 4.55 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 139.5, 133.9, 130.6, 129.9, 129.1, 128.8, 127.4, 125.2, 123.7, 75.3, 59.5, 21.6. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 15.662 min, t (minor) = 22.342 min. HRMS-ESI (m/z): calcd for $C_{15}H_{13}O_3S$ $[M + H]^+$: 273.0580, found: 273.0584.

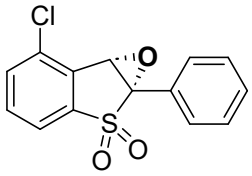
(1a*R*,6b*S*)-5-methoxy-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2e)



White solid, m.p.= 159.7-160.3 °C. 88% yield, 98.2% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 3H), 7.50 – 7.49 (d, *J* = 7.6 Hz, 3H), 7.15 – 7.09 (m, 2H), 4.52 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 135.1, 130.9, 130.7, 129.2, 128.8, 125.2, 125.1, 116.8, 113.0, 75.4, 59.3, 56.0. Chiral HPLC: The ee was

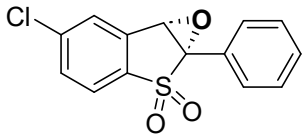
determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 30.706 min, t (minor) = 48.341 min. HRMS-ESI (m/z): calcd for $C_{15}H_{13}O_4S$ $[M + H]^+$: 289.0530, found: 289.0535.

(1a*R*,6b*S*)-6-chloro-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2f)



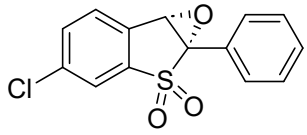
White solid, m.p.= 149.3-151.3 ºC. 89% yield, 98.8% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 1.6 Hz, 1H), 7.75 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.68 – 7.58 (m, 2H), 7.55 – 7.48 (m, 3H), 4.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 137.9, 133.4, 131.1, 130.9, 129.1, 128.9, 128.7, 124.5, 124.0, 75.8, 58.9. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 15.190 min, t (minor) = 19.252 min. HRMS-ESI (m/z): calcd for $C_{14}H_{10}ClO_3S$ $[M + H]^+$: 293.0034, found: 293.0035.

(1a*R*,6b*S*)-5-chloro-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2g)



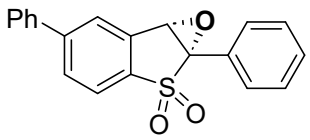
White solid, m.p.= 198.8-201.2 ºC. 95% yield, 96.8% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 3H), 7.68 (d, *J* = 1.6 Hz, 1H), 7.61 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.56 – 7.48 (m, 3H), 4.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 137.8, 134.7, 131.8, 130.9, 129.2, 128.9, 127.9, 124.9, 124.4, 75.4, 58.8. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 20.815 min, t (minor) = 27.713 min. HRMS-ESI (m/z): calcd for $C_{14}H_{10}ClO_3S$ $[M + H]^+$: 293.0034, found: 293.0031.

(1a*R*,6b*S*)-4-chloro-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2h)



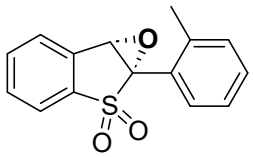
White solid, m.p.= 177.5-179.2 °C. 91% yield, 99.1% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 2H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.65 – 7.48 (m, 5H), 4.85 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 133.9, 133.6, 132.8, 130.9, 129.2, 128.9, 124.4, 121.8, 75.2, 57.5. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 10.823 min, t (minor) = 13.483 min. HRMS-ESI (m/z): calcd for $C_{14}H_{10}ClO_3S$ $[M + H]^+$: 293.0034, found: 293.0033.

(1a*R*,6b*S*)-1a,5-diphenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2i)



White solid, m.p.= 142.4-143.5 °C. 75% yield, 99.6% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.75 (m, 5H), 7.64 – 7.57 (m, 2H), 7.56 – 7.44 (m, 6H), 4.64 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 138.8, 137.9, 133.5, 130.7, 130.3, 129.3, 129.2, 129.0, 128.9, 127.4, 126.2, 125.0, 123.9, 75.4, 59.6. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 37.900 min, t (minor) = 52.057 min. HRMS-ESI (m/z): calcd for $C_{20}H_{15}O_3S$ $[M + H]^+$: 335.0737, found: 335.0738.

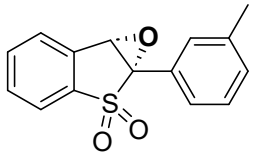
(1aR,6bS)-1a-(o-tolyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-b]oxirene 2,2-dioxide (2j)



White solid, m.p.= 186.7-188.1 °C. 86% yield, 92.0% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.54 (m, 5H), 7.45 – 7.40 (m, 1H), 7.34 – 7.26 (m, 2H), 4.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 139.5, 133.2, 132.7, 131.6, 131.0, 130.9, 127.8, 126.1, 123.8, 123.6, 75.4, 59.0, 19.9. Chiral HPLC: The ee was determined by Daicel Chiralcel

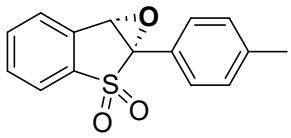
AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 13.778 min, t (minor) = 18.705 min. HRMS-ESI (m/z): calcd for $C_{15}H_{13}O_3S$ $[M + H]^+$: 273.0580, found: 273.0582.

(1a*R*,6b*S*)-1a-(m-tolyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2k)



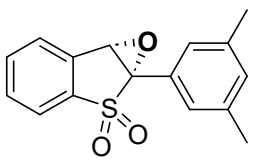
White solid, m.p.= 145.3-146.3 °C. 96% yield, 93.5% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.28 (m, 1H), 7.70 – 7.61 (m, 3H), 7.58 – 7.54 (m, 2H), 7.40 – 7.32 (m, 2H), 4.59 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 138.8, 133.1, 132.8, 131.6, 131.5, 129.7, 128.8, 127.6, 126.3, 124.8, 123.5, 75.2, 59.4, 21.4. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 14.735 min, t (minor) = 19.483 min. HRMS-ESI (m/z): calcd for $C_{15}H_{13}O_3S$ $[M + H]^+$: 273.0580, found: 273.0587.

(1a*R*,6b*S*)-1a-(p-tolyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2l)



White solid, m.p.= 184.6-186.3 °C. 94% yield, 96.1% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 1H), 7.70 – 7.62 (m, 5H), 7.30 (d, *J* = 7.6 Hz, 2H), 4.57 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 139.5, 133.1, 132.9, 131.5, 129.6, 129.1, 127.6, 123.5, 121.8, 75.1, 59.4, 21.5. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 20.969 min, t (minor) = 30.829 min. HRMS-ESI (m/z): calcd for $C_{15}H_{13}O_3S$ $[M + H]^+$: 273.0580, found: 273.0583.

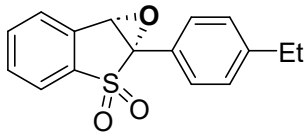
(1a*R*,6b*S*)-1a-(3,5-dimethylphenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2m)



White solid, m.p.= 162.3-163.5 °C. 95% yield, 98.4% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 1H), 7.70 – 7.59 (m, 3H), 7.36 (s, 2H), 7.15 (s, 1H), 4.58 (s, 1H), 2.37

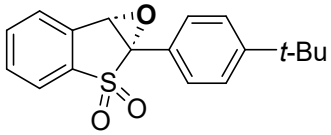
(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 138.7, 133.1, 132.9, 132.6, 131.5, 127.6, 126.9, 124.6, 123.5, 75.3, 59.2, 21.3. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 12.096 min, t (minor) = 16.875 min. HRMS-ESI (m/z): calcd for $C_{16}H_{15}O_3S$ $[M + H]^+$: 287.0737, found: 287.0736.

(1a*R*,6b*S*)-1a-(4-ethylphenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2n)



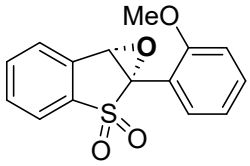
White solid, m.p.= 139.2-141.3 °C. 65% yield, 96.8% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 1H), 7.70 – 7.63 (m, 5H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.57 (s, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 139.5, 133.1, 132.9, 131.5, 129.2, 128.4, 127.6, 123.6, 122.0, 75.2, 59.4, 28.8, 15.4. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 19.833 min, t (minor) = 29.821 min. HRMS-ESI (m/z): calcd for $C_{16}H_{15}O_3S$ $[M + H]^+$: 287.0737, found: 287.0739.

(1a*R*,6b*S*)-1a-(4-(tert-butyl)phenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2o)



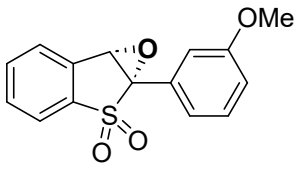
White solid, m.p.= 140.5-142.2 °C. 96% yield, 97.0% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 1H), 7.70 – 7.63 (m, 5H), 7.53 – 7.50 (m, 2H), 4.57 (s, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 139.5, 133.1, 132.9, 131.5, 128.9, 127.6, 125.9, 123.6, 121.8, 75.1, 59.4, 34.9, 31.2. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 16.469 min, t (minor) = 21.876 min. HRMS-ESI (m/z): calcd for $C_{18}H_{19}O_3S$ $[M + H]^+$: 315.1050, found: 315.1055.

(1a*R*,6b*S*)-1a-(2-methoxyphenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2p)



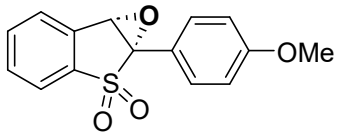
White solid, m.p.= 120.6-122.2 °C. 90% yield, 99.9% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 1H), 7.75 – 7.70 (m, 1H), 7.67 – 7.61 (m, 3H), 7.53 – 7.48 (m, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 4.70 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 139.7, 133.1, 133.0, 132.6, 131.5, 131.4, 127.8, 123.6, 121.0, 113.8, 111.5, 73.2, 58.8, 56.0. Chiral HPLC: The ee was determined by Daicel Chiralcel OD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 19.880 min, t (minor) = 24.016 min. HRMS-ESI (m/z): calcd for $C_{15}H_{13}O_4S$ $[M + H]^+$: 289.0530, found: 289.0533.

(1a*R*,6b*S*)-1a-(3-methoxyphenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2q)



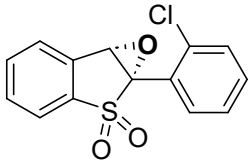
White solid, m.p.= 128.4-130.0 °C. 77% yield, 97.4% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.82 (m, 1H), 7.72 – 7.64 (m, 3H), 7.43 – 7.33 (m, 2H), 7.28 – 7.27 (m, 1H), 7.07 – 7.04 (m, 1H), 4.58 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 139.6, 133.1, 132.7, 131.6, 130.0, 127.6, 126.2, 123.6, 121.4, 117.0, 114.1, 75.0, 59.6, 55.5. Chiral HPLC: The ee was determined by Daicel Chiralcel OD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 24.311 min, t (minor) = 26.781 min. HRMS-ESI (m/z): calcd for $C_{15}H_{13}O_4S$ $[M + H]^+$: 289.0530, found: 289.0532.

(1a*R*,6b*S*)-1a-(4-methoxyphenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2r)



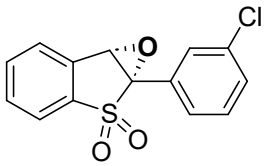
White solid, m.p.= 112.7-114.2 °C. 95% yield, 81.1% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 1H), 7.70 – 7.61 (m, 5H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.56 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 139.5, 133.1, 132.9, 131.5, 130.7, 127.6, 123.5, 116.5, 114.4, 75.1, 59.4, 55.4. Chiral HPLC: The ee was determined by Daicel Chiralcel AS, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 75.875 min, t (minor) = 92.333 min. HRMS-ESI (m/z): calcd for $C_{15}H_{13}O_4S$ $[M + H]^+$: 289.0530, found: 289.0538.

(1a*R*,6b*S*)-1a-(2-chlorophenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2s)



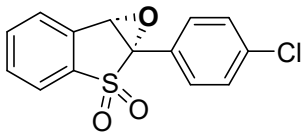
White solid, m.p.= 178.6-181.0 °C. 82% yield, 99.1% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 1H), 7.78 – 7.73 (m, 2H), 7.70 – 7.63 (m, 2H), 7.53 – 7.40 (m, 3H), 4.76 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 135.2, 133.2, 132.4, 132.3, 132.2, 131.7, 130.1, 128.0, 127.4, 124.2, 123.6, 74.1, 59.5. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 14.402 min, t (minor) = 19.674 min. HRMS-ESI (m/z): calcd for $C_{14}H_{10}ClO_3S$ $[M + H]^+$: 293.0034, found: 293.0037.

(1a*R*,6b*S*)-1a-(3-chlorophenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2t)



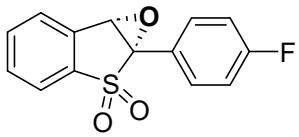
White solid, m.p.= 153.4-155.1 °C. 85% yield, 99.7% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 1H), 7.77 – 7.62 (m, 5H), 7.51 – 7.48 (m, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 4.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 134.9, 133.3, 132.4, 131.7, 130.9, 130.2, 129.2, 127.7, 127.3, 127.0, 123.5, 74.2, 59.8. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 11.670 min, t (minor) = 16.018 min. HRMS-ESI (m/z): calcd for $C_{14}H_{10}ClO_3S$ $[M + H]^+$: 293.0034, found: 293.0034.

(1a*R*,6b*S*)-1a-(4-chlorophenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2u)



White solid, m.p.= 157.4-158.5 °C. 95% yield, 99.9% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 1H), 7.72 – 7.63 (m, 5H), 7.49 – 7.45 (m, 2H), 4.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 137.1, 133.3, 132.5, 131.7, 130.5, 129.2, 127.7, 123.6, 123.5, 74.4, 59.8. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 23.831 min, t (minor) = 33.725 min. HRMS-ESI (m/z): calcd for $C_{14}H_{10}ClO_3S$ $[M + H]^+$: 293.0034, found: 293.0038.

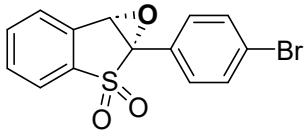
(1a*R*,6b*S*)-1a-(4-fluorophenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2v)



White solid, m.p.= 149.5-150.8 °C. 96% yield, 93.1% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 1H), 7.78 – 7.73 (m, 2H), 7.71 – 7.63 (m, 3H), 7.18 (t, *J* = 8.4 Hz, 2H), 4.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2 (d, $^1J_{C\text{-}F}$ = 249.5 Hz), 139.2, 133.2, 132.6, 131.7, 131.3 (d, $^3J_{C\text{-}F}$ = 8.8 Hz), 127.7, 123.6, 120.8(d, $^4J_{C\text{-}F}$ = 3.3 Hz), 116.2 (d, $^2J_{C\text{-}F}$ = 22.1 Hz), 74.5, 59.7. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) =

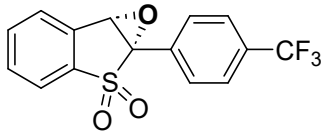
20.046 min, t (minor) = 26.975 min. HRMS-ESI (m/z): calcd for $C_{14}H_{10}FO_3S$ $[M + H]^+$: 277.0330, found: 277.0333.

(1a*R*,6b*S*)-1a-(4-bromophenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2w)



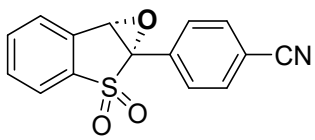
Yellow solid, m.p.= 168.4-170.3 °C. 85% yield, 98.0% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 1H), 7.71 – 7.64 (m, 7H), 4.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 133.3, 132.5, 132.1, 131.7, 130.7, 127.7, 125.4, 124.0, 123.6, 74.5, 59.8. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 24.797 min, t (minor) = 39.397 min. HRMS-ESI (m/z): calcd for $C_{14}H_{10}BrO_3S$ $[M + H]^+$: 336.9529, found: 336.9535.

(1a*R*,6b*S*)-1a-(4-(trifluoromethyl)phenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2x)



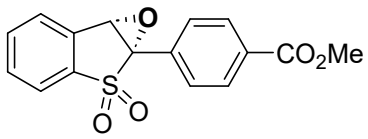
White solid, m.p.= 121.8-122.2 °C. 86% yield, 99.0% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 2H), 7.85 – 7.810 (m, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.73 – 7.66 (m, 3H), 4.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 133.4, 132.7 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 132.3, 131.8, 129.6, 129.1, 127.7, 125.8 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.7 (q, $^1J_{C\text{-}F}$ = 270.9 Hz), 123.6, 74.2, 60.0. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 16.990 min, t (minor) = 29.899 min. HRMS-ESI (m/z): calcd for $C_{15}H_{10}F_3O_3S$ $[M + H]^+$: 327.0298, found: 327.0299.

4-((1a*R*,6b*S*)-2,2-dioxidobenzo[4,5]thieno[2,3-*b*]oxiren-1a(6b*H*)-yl)benzonitrile (2y)



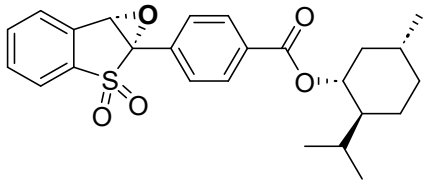
Yellow solid, m.p.= 166.2-168.3 °C. 78% yield, 99.1% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.85 – 7.80 (m, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.73 – 7.67 (m, 3H), 4.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 133.5, 132.5, 132.1, 132.0, 130.3, 129.8, 127.8, 123.6, 118.0, 114.5, 74.0, 60.3. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 42.414 min, t (minor) = 63.261 min. HRMS-ESI (m/z): calcd for $C_{15}H_{10}NO_3S$ $[M + H]^+$: 284.0376, found: 284.0380.

methyl 4-((1a*R*,6b*S*)-2,2-dioxidobenzo[4,5]thieno[2,3-*b*]oxiren-1a(6b*H*)-yl) benzoate (2z)



Yellow solid, m.p.= 178.8-179.5 °C. 93% yield, 99.5% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.88 – 7.79 (m, 3H), 7.71 – 7.64 (m, 3H), 4.60 (s, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 139.3, 133.3, 132.4, 132.2, 131.8, 129.9, 129.8, 129.2, 127.7, 123.6, 74.5, 60.0, 52.4. Chiral HPLC: The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 27.137 min, t (minor) = 46.817 min. HRMS-ESI (m/z): calcd for $C_{16}H_{12}O_5S$ $[M + H]^+$: 316.0405, found: 316.0406.

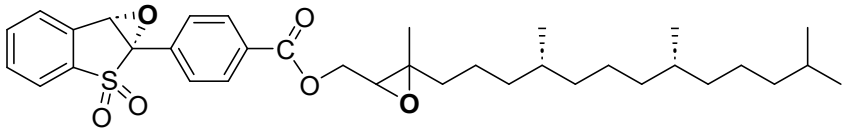
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-((1a*R*,6b*S*)-2,2-dioxidobenzo[4,5] thieno [2,3-*b*]oxiren-1a(6b*H*)-yl)benzoate (2za)



Colorless oil. 75% yield, 99.3% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 3H), 7.74 – 7.63 (m, 3H), 4.96 (td, *J* = 10.8, 4.4 Hz, 1H), 4.60 (s, 1H), 2.13 (d, *J* = 12.4 Hz, 1H), 2.02 – 1.88 (m, 1H), 1.78 – 1.70 (m, 2H), 1.64 – 1.56 (m, 2H), 1.27 (d, *J* = 11.2 Hz, 1H), 1.19 – 1.16 (m, 2H), 0.93 (t, *J* = 6.8 Hz, 6H), 0.80 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 139.4, 133.3, 132.9, 132.4, 131.7, 129.9, 129.5, 129.2, 127.7, 123.6, 75.4, 74.6, 59.9, 47.3, 40.9, 34.3, 31.5, 26.6,

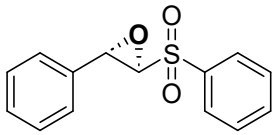
23.7, 22.1, 20.8, 16.5. Chiral HPLC: The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 16.679 min, t (minor) = 22.629 min. HRMS-ESI (m/z): calcd for $C_{25}H_{29}O_5S$ $[M + H]^+$: 441.1731, found: 441.1734.

(3-methyl-3-((4*R*,8*R*)-4,8,12-trimethyltridecyl)-2l3-oxiran-2-yl)methyl 4-((1a*R*,6b*S*)-2,2-dioxidobenzo[4,5]thieno[2,3-*b*]oxiren-1a(6b*H*)-yl)benzoate (2zb)



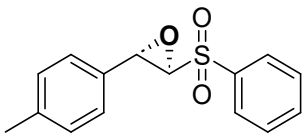
Yellow oil. 35% yield, 98.3% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 2H), 7.89 – 7.82 (m, 3H), 7.73 – 7.64(m, 3H), 4.66 – 4.58 (m, 2H), 4.33 (dd, *J* = 12.0, 6.8 Hz, 1H), 3.14 (dd, *J* = 7.2, 4.4 Hz, 1H), 1.37 (s, 6H), 1.31 – 1.19 (m, 10H), 1.16 – 1.01 (m, 8H), 0.89 – 0.82 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 139.4, 133.3, 132.4, 131.8, 131.8, 130.1, 130.1, 129.2, 127.7, 123.6, 74.5, 64.4, 60.9, 60.0, 59.6, 39.4, 38.6, 37.4, 37.4, 37.3, 36.9, 32.8, 32.8, 32.7, 28.0, 24.8, 24.5, 22.7, 22.6, 22.5, 22.5, 19.7, 19.6, 17.0. Chiral HPLC: The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 13.013 min, t (minor) = 15.407 min. HRMS-ESI (m/z): calcd for $C_{35}H_{49}O_6S$ $[M + H]^+$: 597.3245, found: 597.3247.

(2*S*,3*S*)-2-phenyl-3-(phenylsulfonyl)oxirane (4a)



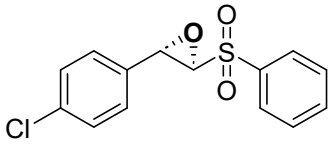
White solid, m.p.= 120.1-122.5 ℃. 68% yield, 91.6% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.0 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.30 – 7.23 (m, 2H), 4.59 (d, *J* = 1.6 Hz, 1H), 4.18 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 134.6, 132.7, 129.6, 129.5, 128.9, 128.8, 126.1, 71.1, 57.5. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (minor) = 22.056 min, t (major) = 23.208 min. HRMS-ESI (m/z): calcd for $C_{14}H_{13}O_3S$ $[M + H]^+$: 261.0580, found: 261.0586.

(2*S*,3*S*)-2-(phenylsulfonyl)-3-(*p*-tolyl)oxirane (4b)



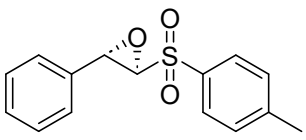
White solid, m.p.= 132.5-134.1 °C. 62% yield, 88.9% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 2H), 7.20 – 7.10 (m, 4H), 4.55 (d, *J* = 1.2 Hz, 1H), 4.18 (d, *J* = 1.6 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.0, 134.6, 129.6, 129.5, 129.5, 128.9, 126.1, 71.0, 57.6, 21.3. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (minor) = 24.382 min, t (major) = 31.109 min. HRMS-ESI (m/z): calcd for $C_{15}H_{15}O_3S$ $[M + H]^+$: 275.0737, found: 275.0733.

(2*S*,3*S*)-2-(4-chlorophenyl)-3-(phenylsulfonyl)oxirane (4c)



White solid, m.p.= 123.1-124.6 °C. 81% yield, 84.0% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.57 (d, *J* = 1.6 Hz, 1H), 4.14 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.6, 134.7, 131.3, 129.6, 129.1, 128.9, 127.4, 71.0, 56.9. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (minor) = 13.386 min, t (major) = 15.910 min. HRMS-ESI (m/z): calcd for $C_{14}H_{12}ClO_3S$ $[M + H]^+$: 295.0191, found: 295.0193.

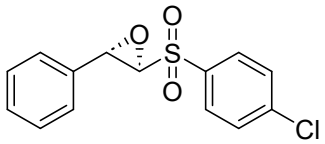
(2*S*,3*S*)-2-phenyl-3-tosyloxirane (4d)



White solid, m.p.= 118.1-120.6 °C. 69% yield, 90.1% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.26 – 7.23 (m, 2H), 4.56 (d, *J* = 1.6 Hz, 1H), 4.16 (d, *J* = 1.6 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 133.9, 132.8, 130.2, 129.6, 128.9, 128.8, 126.1, 71.2, 57.5, 21.8.

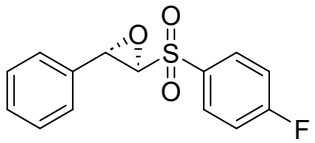
Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 21.257 min, t (minor) = 24.297 min. HRMS-ESI (m/z): calcd for $C_{15}H_{15}O_3S$ $[M + H]^+$: 275.0736, found: 275.0731.

(2*S*,3*S*)-2-((4-chlorophenyl)sulfonyl)-3-phenyloxirane (4e)



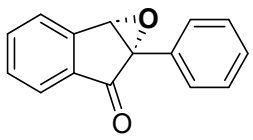
White solid, m.p.= 125.1-127.5 ºC. 65% yield, 91.6% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.36 (m, 3H), 7.29 – 7.22 (m, 2H), 4.59 (d, *J* = 1.5 Hz, 1H), 4.17 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$)) δ 141.6, 135.3, 132.5, 130.4, 129.9, 129.7, 128.9, 126.1, 71.0, 57.7. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 20.597 min, t (minor) = 22.583 min. HRMS-ESI (m/z): calcd for $C_{14}H_{12}ClO_3S$ $[M + H]^+$: 295.0190, found: 295.0191.

(2*S*,3*S*)-2-((4-fluorophenyl)sulfonyl)-3-phenyloxirane (4f)



White solid, m.p.= 135.2-136.9 ºC. 65% yield, 90.0% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.41 – 7.34 (m, 3H), 7.34 – 7.29 (m, 2H), 7.28 – 7.26 (m, 2H), 4.59 (d, *J* = 1.6 Hz, 1H), 4.17 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5 (d, $^1J_{C\text{-}F}$ = 260.0 Hz), 132.9 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 132.5, 131.9 (d, $^3J_{C\text{-}F}$ = 9.7 Hz), 129.7, 128.9, 126.1, 117.0 (d, $^2J_{C\text{-}F}$ = 22.6 Hz), 71.1, 57.7. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 20.681 min, t (minor) = 23.214 min. HRMS-ESI (m/z): calcd for $C_{14}H_{12}FO_3S$ $[M + H]^+$: 279.0486, found: 279.0488.

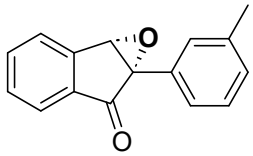
(1a*S*,6a*S*)-6a-phenyl-1a,6a-dihydro-6*H*-indeno[1,2-*b*]oxiren-6-one (6a)



White solid, m.p.= 86.4-87.2 ºC. 80% yield, 85.7% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ

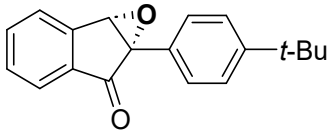
8.31 (d, *J* = 7.2 Hz, 1H), 7.74 – 7.59 (m, 5H), 7.51 – 7.42 (m, 3H), 4.22 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 136.4, 134.3, 133.3, 131.6, 130.7, 129.7, 129.5, 128.7, 126.0, 123.0, 85.7, 58.8. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (minor) = 14.177 min, t (major) = 20.847 min. HRMS-ESI (m/z): calcd for $C_{15}H_{11}O_2$ $[M + H]^+$: 223.0754, found: 223.0756.

(1a*S*,6a*S*)-6a-(m-tolyl)-1a,6a-dihydro-6*H*-indeno[1,2-*b*]oxiren-6-one (6b)



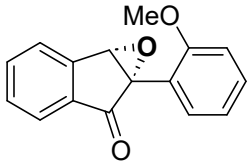
White solid, m.p.= 88.1-89.6 ºC. 68% yield, 85.8% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.61 (m, 3H), 7.46 – 7.32 (m, 3H), 7.29 – 7.22 (m, 1H), 4.21 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 138.6, 136.4, 134.3, 133.2, 131.6, 130.6, 130.5, 129.5, 128.6, 126.6, 123.0, 123.0, 85.8, 58.8, 21.4. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (minor) = 12.431 min, t (major) = 14.240 min. HRMS-ESI (m/z): calcd for $C_{16}H_{13}O_2$ $[M + H]^+$: 237.0911, found: 237.0915.

(1a*S*,6a*S*)-6a-(4-(tert-butyl)phenyl)-1a,6a-dihydro-6*H*-indeno[1,2-*b*]oxiren-6-one (6c)



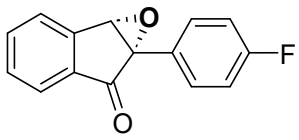
Colorless oil. 61% yield, 73.0% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.6 Hz, 1H), 7.72 – 7.61 (m, 3H), 7.56 – 7.47 (m, 4H), 4.21 (s, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 153.0, 136.5, 134.3, 131.6, 130.6, 130.3, 129.4, 125.7, 125.7, 123.1, 85.8, 58.8, 34.8, 31.3. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (minor) = 11.386 min, t (major) = 31.964 min. HRMS-ESI (m/z): calcd for $C_{19}H_{19}O_2$ $[M + H]^+$: 279.1380, found: 279.1389.

(1a*S*,6a*S*)-6a-(2-methoxyphenyl)-1a,6a-dihydro-6H-indeno[1,2-*b*]oxiren-6-one (6d)



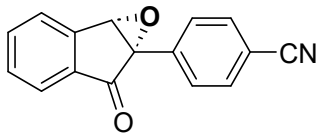
White solid, m.p.= 107.2-108.2 °C. 73% yield, 88.4% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.59 (m, 4H), 7.45 – 7.40 (m, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 4.19 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 157.6, 136.5, 134.1, 131.5, 131.5, 130.5, 129.7, 128.1, 123.1, 122.0, 120.4, 111.0, 85.0, 56.5, 55.7. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 °C, t (major) = 17.038 min, t (minor) = 20.951 min. HRMS-ESI (m/z): calcd for $C_{16}H_{13}O_3$ $[M + H]^+$: 253.0860, found: 253.0861.

(1a*S*,6a*S*)-6a-(4-fluorophenyl)-1a,6a-dihydro-6*H*-indeno[1,2-*b*]oxiren-6-one (6e)



White solid, m.p.= 133.7-134.4 °C. 89% yield, 83.1% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.56 (m, 5H), 7.15 – 7.56 (m, 2H), 4.21 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, $^{1}J_{C\text{-}F}$ = 247.6 Hz), 161.4, 136.2, 134.4, 131.7, 130.8, 129.5, 129.3 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 128.1(d, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 122.9, 115.8 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 85.5, 58.8. Chiral HPLC: The ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 °C, t (minor) = 14.672 min, t (major) = 28.171 min. HRMS-ESI (m/z): calcd for $C_{15}H_{10}FO_2$ $[M + H]^+$: 241.0660, found: 241.0665.

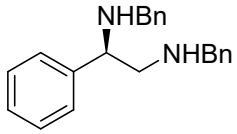
4-((1a*S*,6a*S*)-6-oxo-1a,6-dihydro-6a*H*-indeno[1,2-*b*]oxiren-6a-yl)benzonitrile (6f)



White solid, m.p.= 129.3-131.3 °C. 69% yield, 89.6% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$)

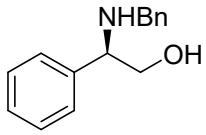
δ 8.31 (d, *J* = 7.6 Hz, 1H), 7.80 – 7.63 (m, 7H), 4.25 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 138.3, 135.7, 134.6, 132.6, 131.8, 131.1, 129.6, 126.9, 122.7, 118.1, 113.8, 84.9, 58.9. Chiral HPLC: The ee was determined by Daicel Chiralcel OD, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 220 nm, T =25 ℃, t (major) = 29.243 min, t (minor) = 32.256 min. HRMS-ESI (m/z): calcd for $C_{16}H_{10}NO_2$ $[M + H]^+$: 248.0707, found: 248.0708.

(*R*)-*N*^{1},*N*^{2}-dibenzyl-1-phenylethane-1,2-diamine (4ab)



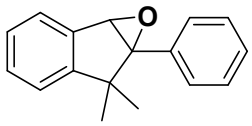
Colourless oil. 54% yield, 95.0% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 7.32 – 7.22 (m, 11H), 3.80 – 3.69 (m, 4H), 3.53 (d, *J* = 13.2 Hz, 1H), 2.86 – 2.75 (m, 2H), 1.88 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 140.7, 140.4, 128.6, 128.4, 128.4, 128.2, 128.1, 127.4, 127.3, 126.9, 126.9, 61.8, 56.2, 53.8, 51.4. Chiral HPLC: The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 90/10, 0.5 mL/min, λ = 220 nm, T =25 ℃, t (minor) = 13.037 min, t (major) = 14.470 min. HRMS-ESI (m/z): calcd for $C_{22}H_{25}N_2$ $[M + H]^+$: 317.2012, found: 317.2011.

(*R*)-2-(benzylamino)-2-phenylethan-1-ol (4ac)



White solid, m.p.= 68.7-69.2 ºC. 62% yield, 91.1% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.35 – 7.28 (m, 7H), 7.28 – 7.22 (m, 1H), 3.83 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.76 (d, *J* = 13.2 Hz, 1H), 3.72 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.63 – 3.54 (m, 2H), 2.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 140.1, 128.7, 128.5, 128.3, 127.7, 127.3, 127.1, 66.8, 63.8, 51.2. Chiral HPLC: The ee was determined by Daicel Chiralcel OD, Hexanes/IPA = 90/10, 0.5 mL/min, λ = 220 nm, T =25 ℃, t (major) = 17.093 min, t (minor) = 21.892 min. HRMS-ESI (m/z): calcd for $C_{15}H_{18}NO$ $[M + H]^+$: 228.1383, found: 228.1385.

6,6-dimethyl-6a-phenyl-1a,6a-dihydro-6*H*-indeno[1,2-*b*]oxirene (8a)



White solid, m.p.= 93.7-95.2 °C. 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 3H), 7.43 – 7.35 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.20 (m, 2H), 4.38 (s, 1H), 1.51 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 139.4, 134.9, 128.8, 128.6, 128.2, 128.1, 126.2, 124.8, 123.9, 74.6, 63.9, 47.2, 27.8, 22.4. HRMS-ESI (m/z): calcd for $C_{17}H_{17}O_7$ $[M + H]^+$: 237.1274, found: 237.1277.

11. References

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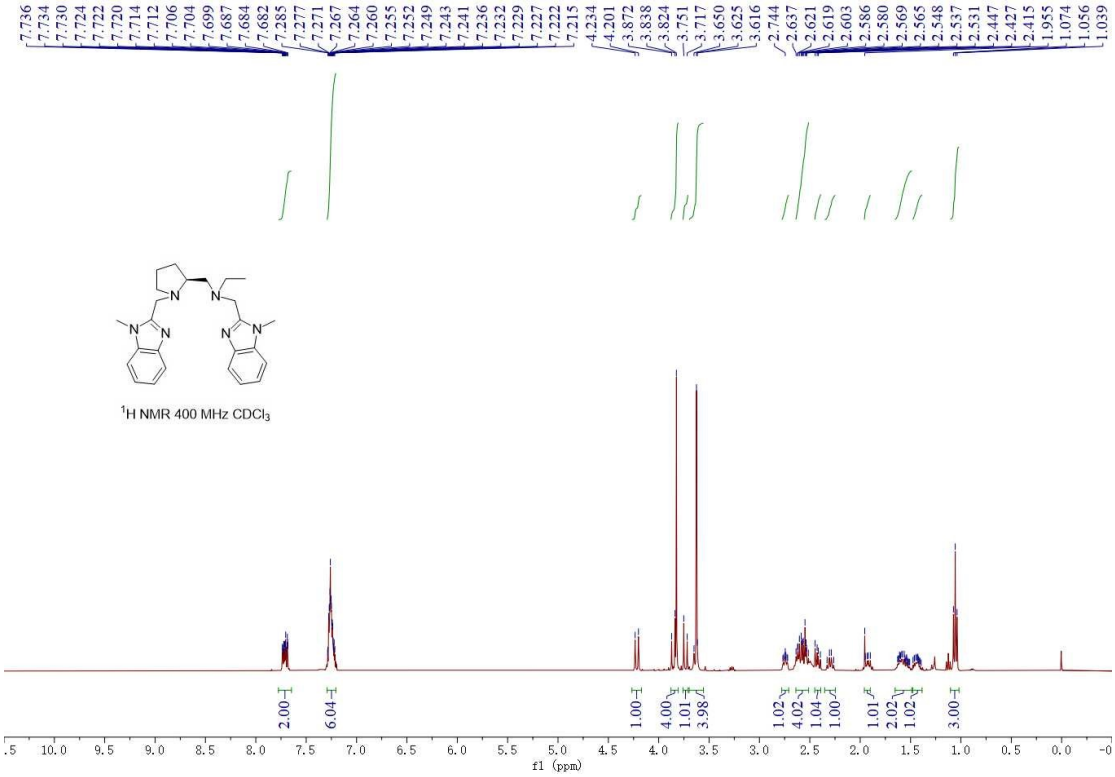
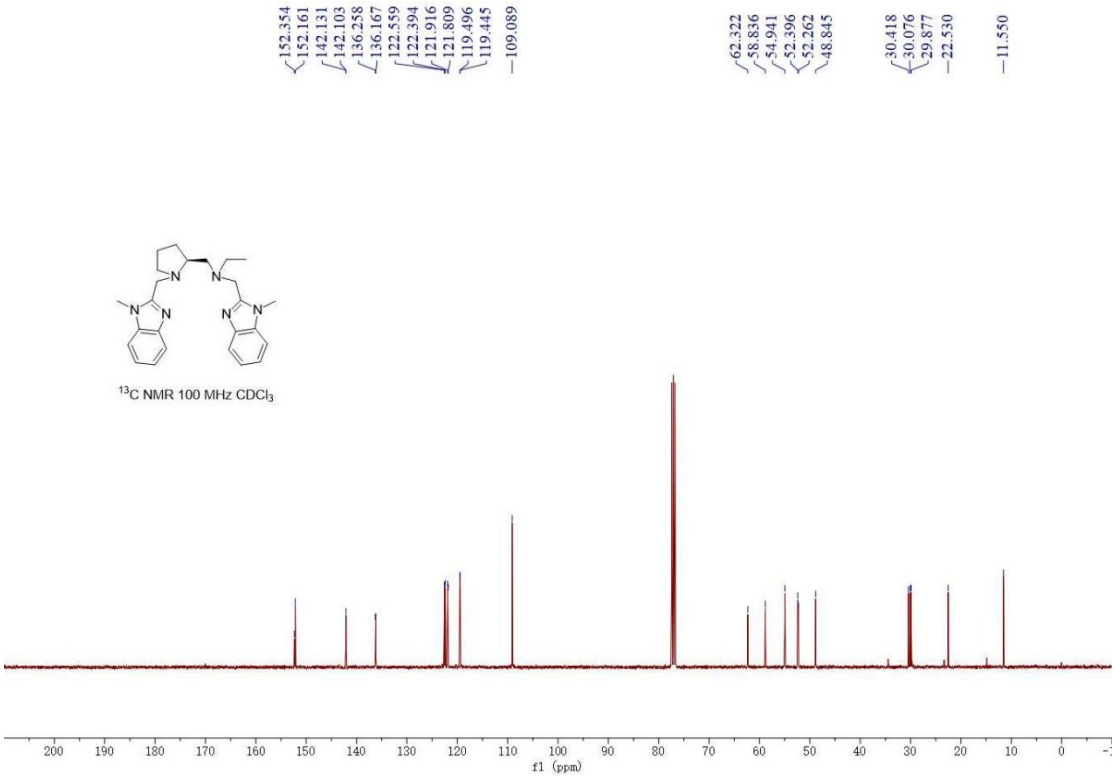
12. NMR spectra and HPLC chromatograms

(*S*)-*N*-((1-methyl-1H-benzo[d]imidazol-2-yl)methyl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)ethanamine (L1)

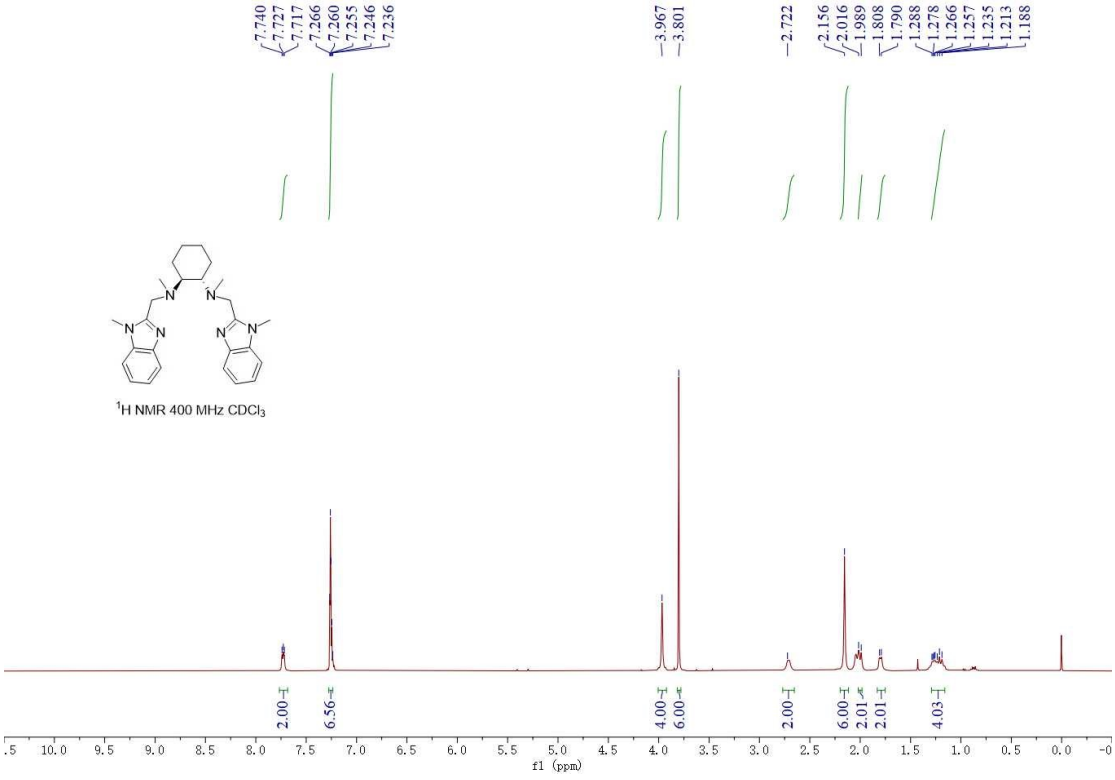


^{1}H NMR of **L1**

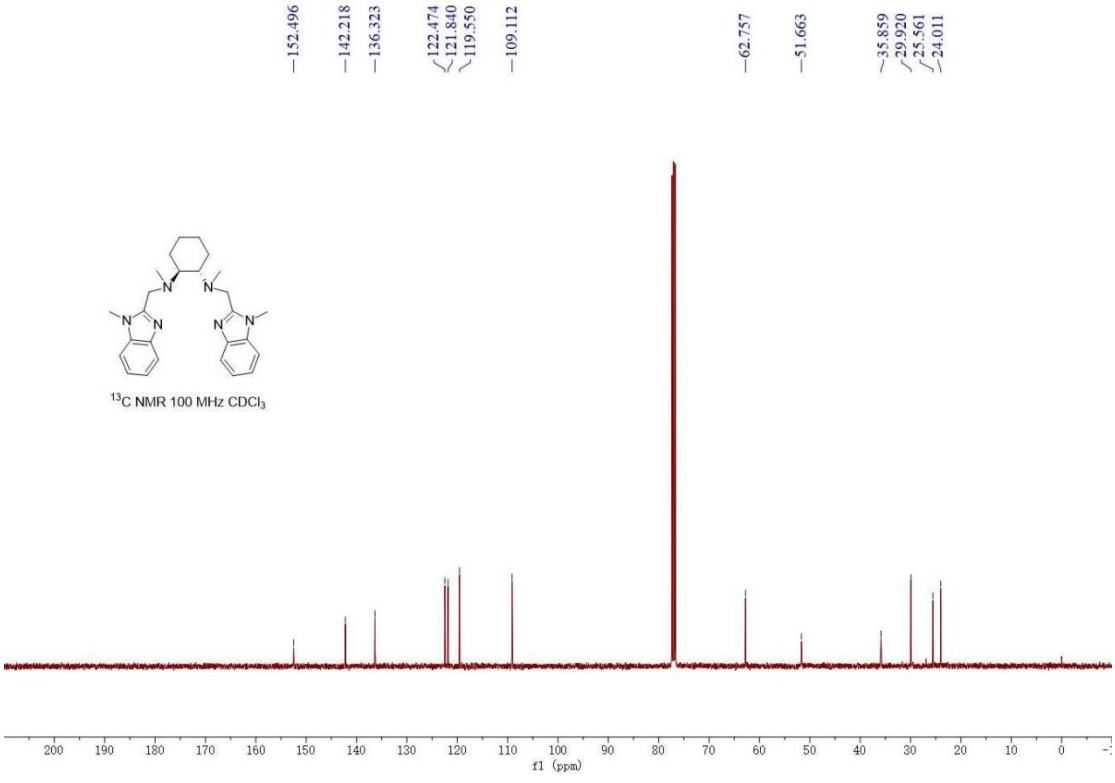


^{13}C NMR of **L1**

(1*S*,2*S*)-N^1,N^2-dimethyl-N^1,N^2-bis((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)cyclohexane-1,2-diamine (L2)

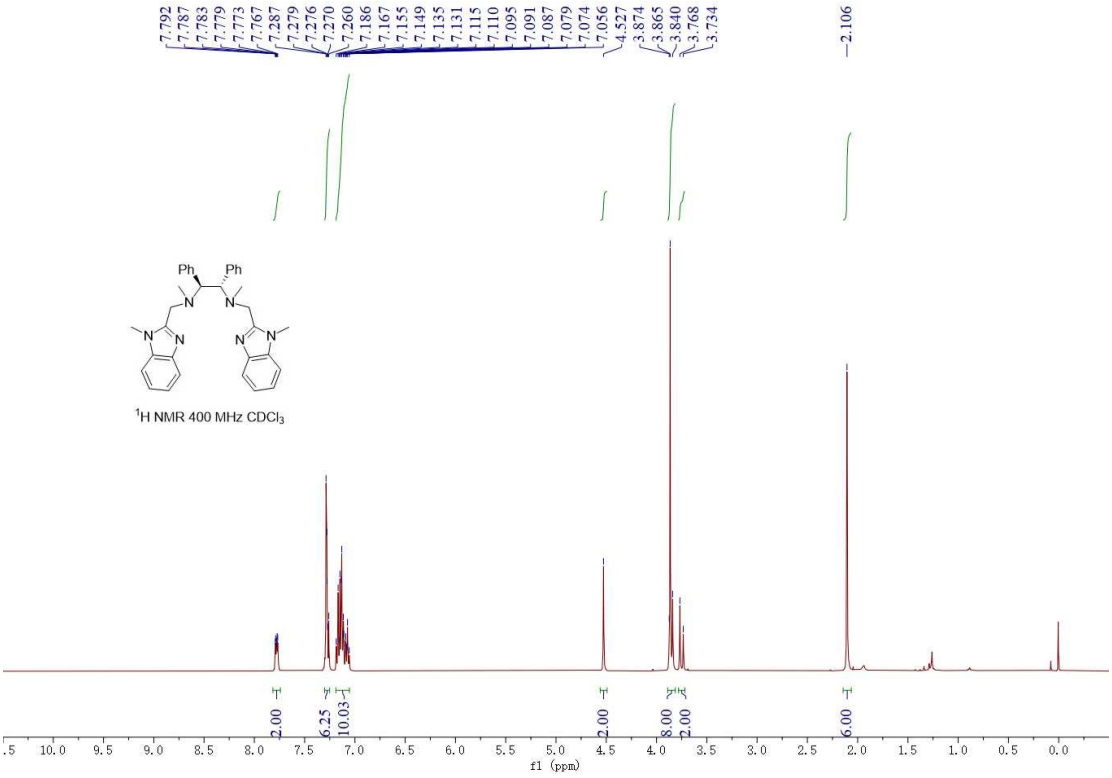


^{1}H NMR of **L2**

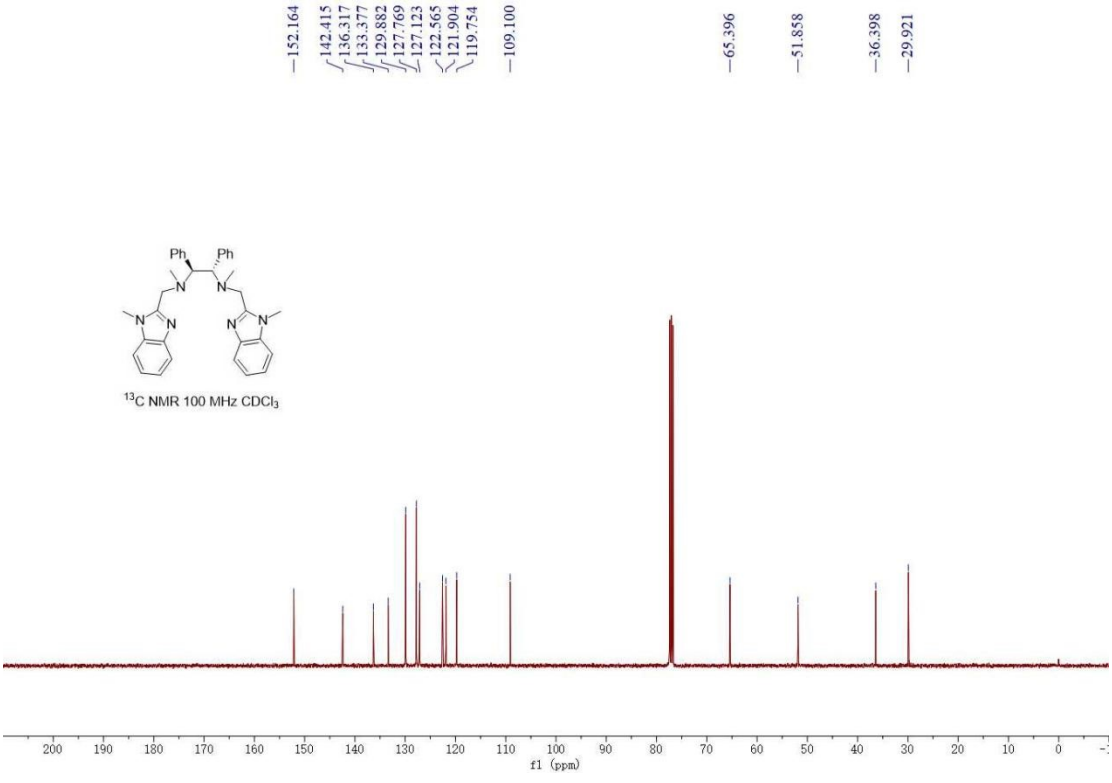


^{13}C NMR of **L2**

(1*S*,2*S*)-N^1,N^2-dimethyl-N^1,N^2-bis((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)-1,2-diphenylethane-1,2-diamine (L3)

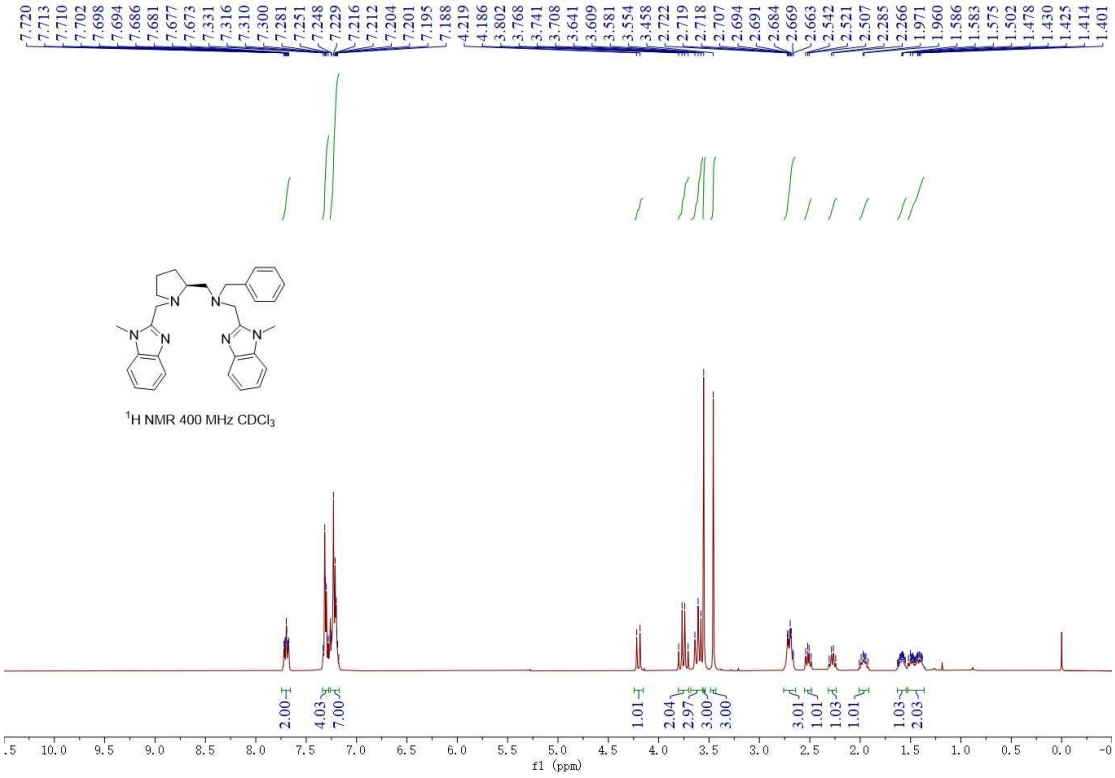


^{1}H NMR of **L3**

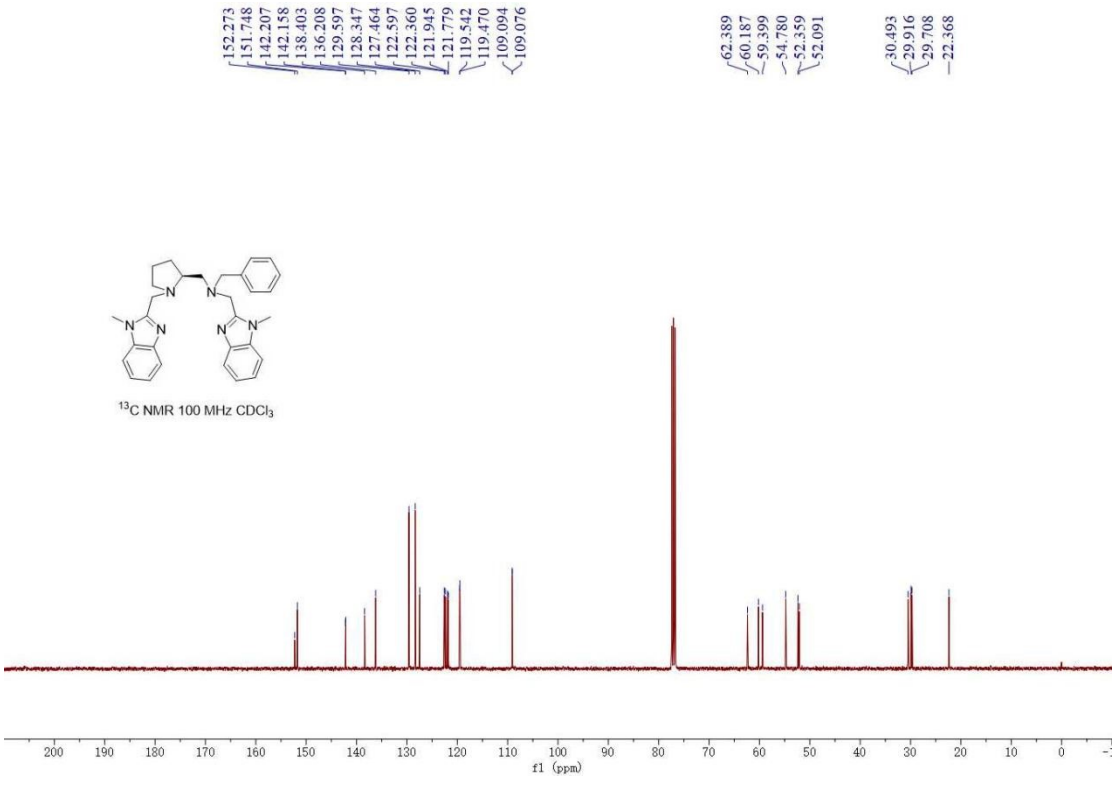


^{13}C NMR of **L3**

(*S*)-*N*-benzyl-1-(1-methyl-1*H*-benzo[d]imidazol-2-yl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (L4)

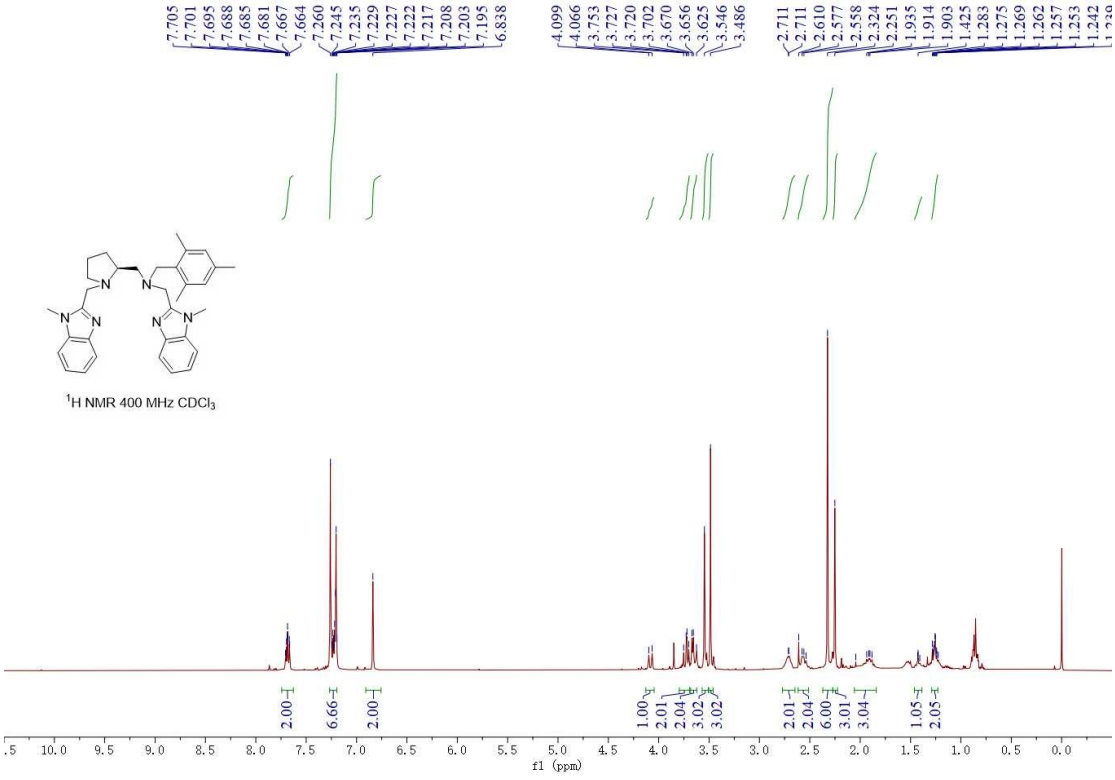


^{1}H NMR of **L4**



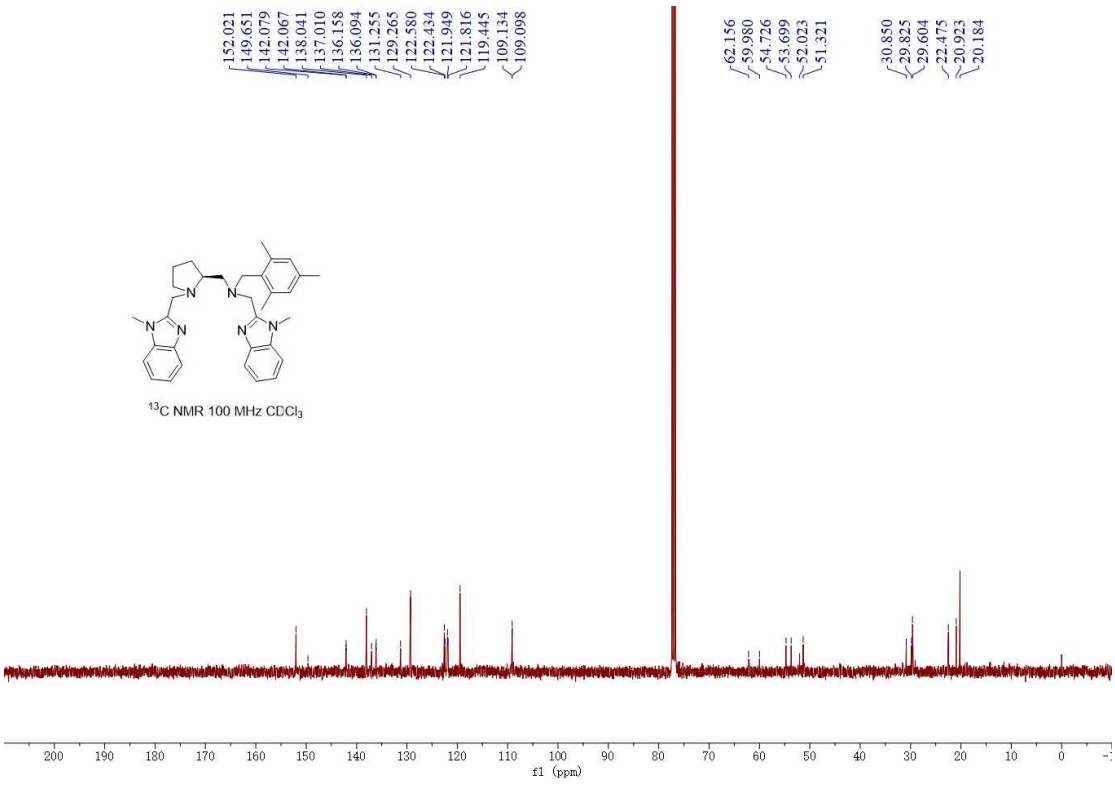
^{13}C NMR of **L4**

(*S*)-1-mesityl-*N*-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (L5)



^{1}H NMR 400 MHz $CDCl_3$

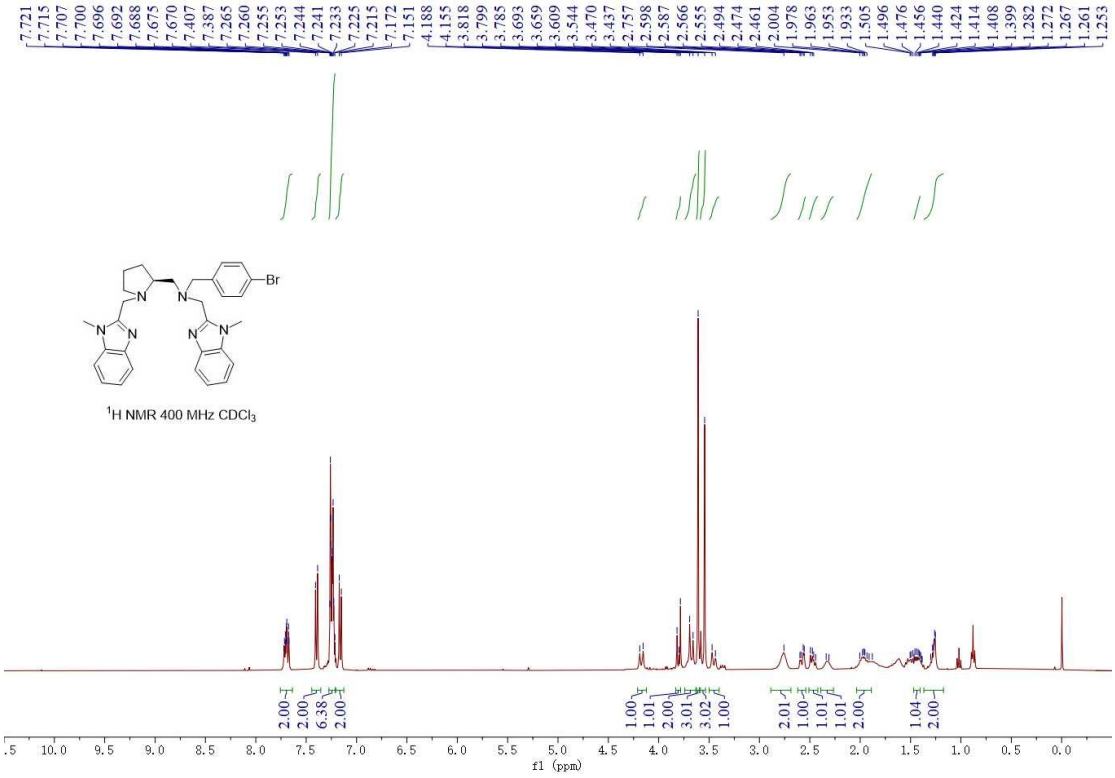
^{1}H NMR of **L5**



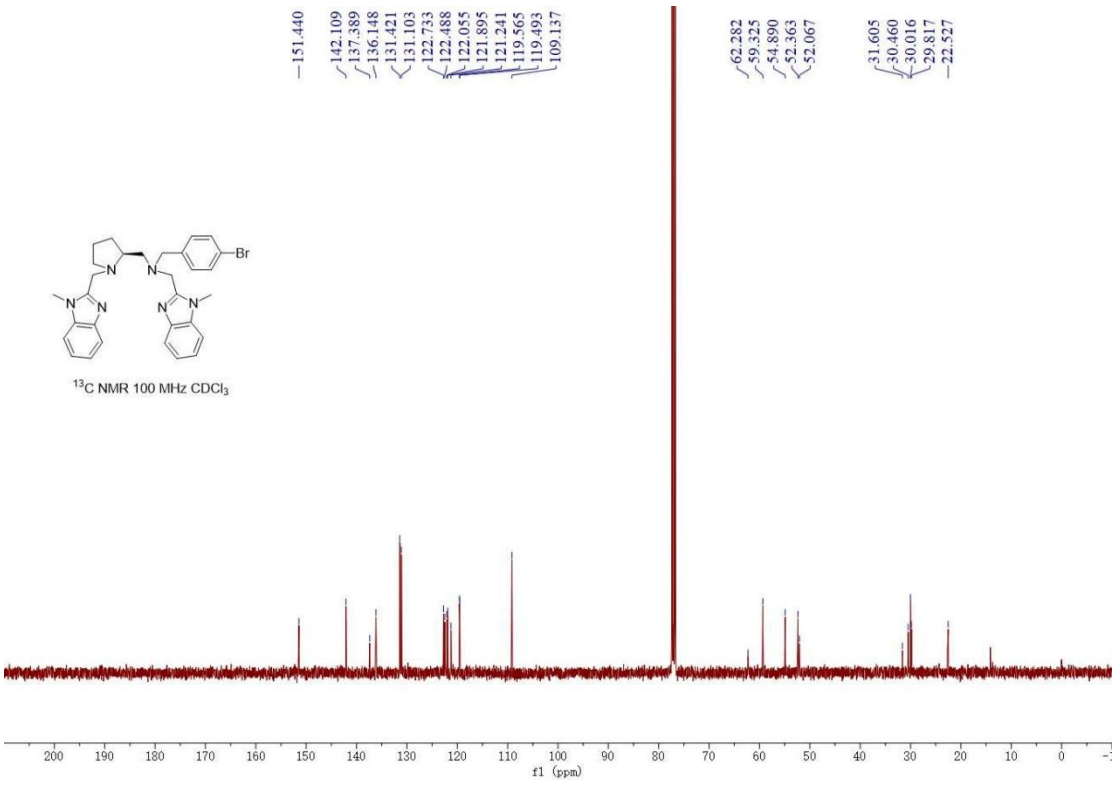
^{13}C NMR 100 MHz $CDCl_3$

^{13}C NMR of **L5**

(*S*)-*N*-(4-bromobenzyl)-1-(1-methyl-1H-benzo[d]imidazol-2-yl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (L68)

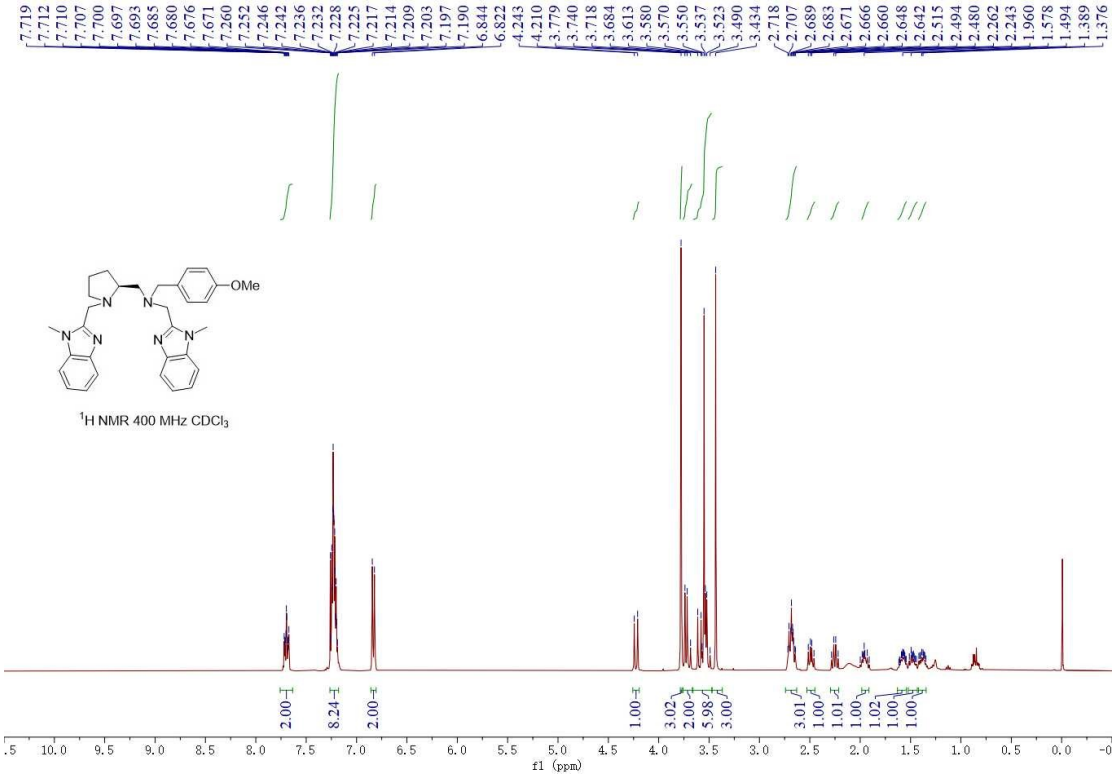


^{1}H NMR of **L6**

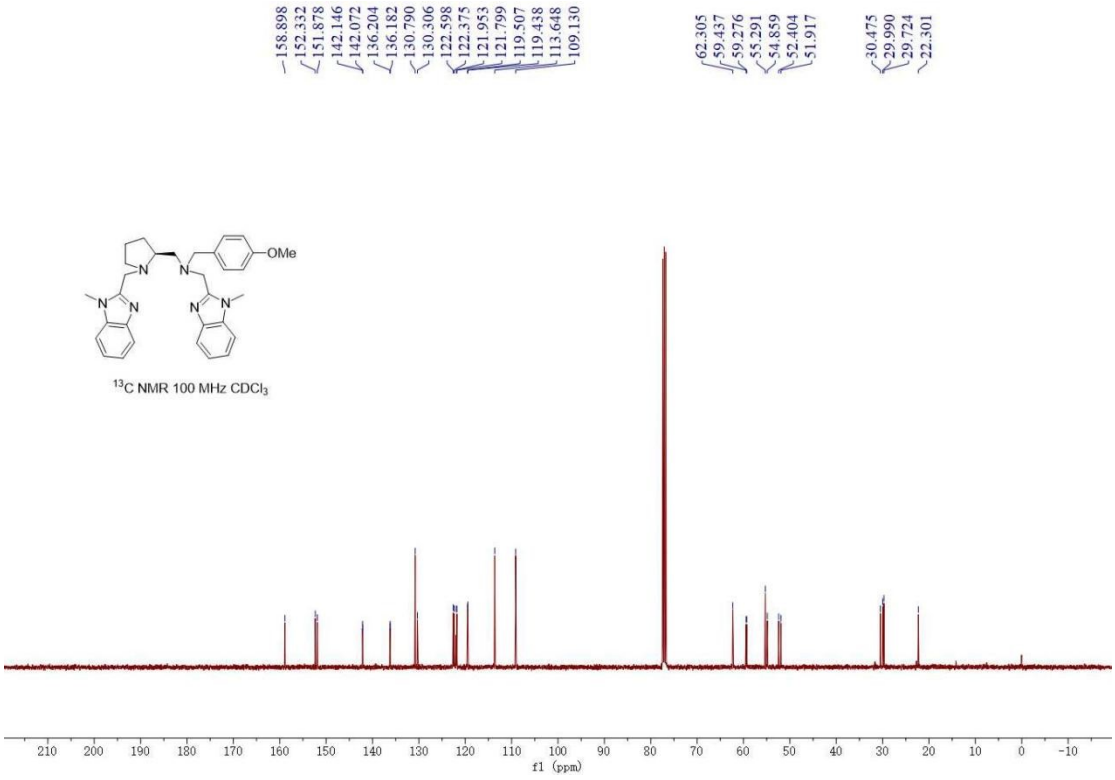


^{13}C NMR of **L6**

(*S*)-*N*-(4-methoxybenzyl)-1-(1-methyl-1*H*-benzo[d]imidazol-2-yl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (L7)

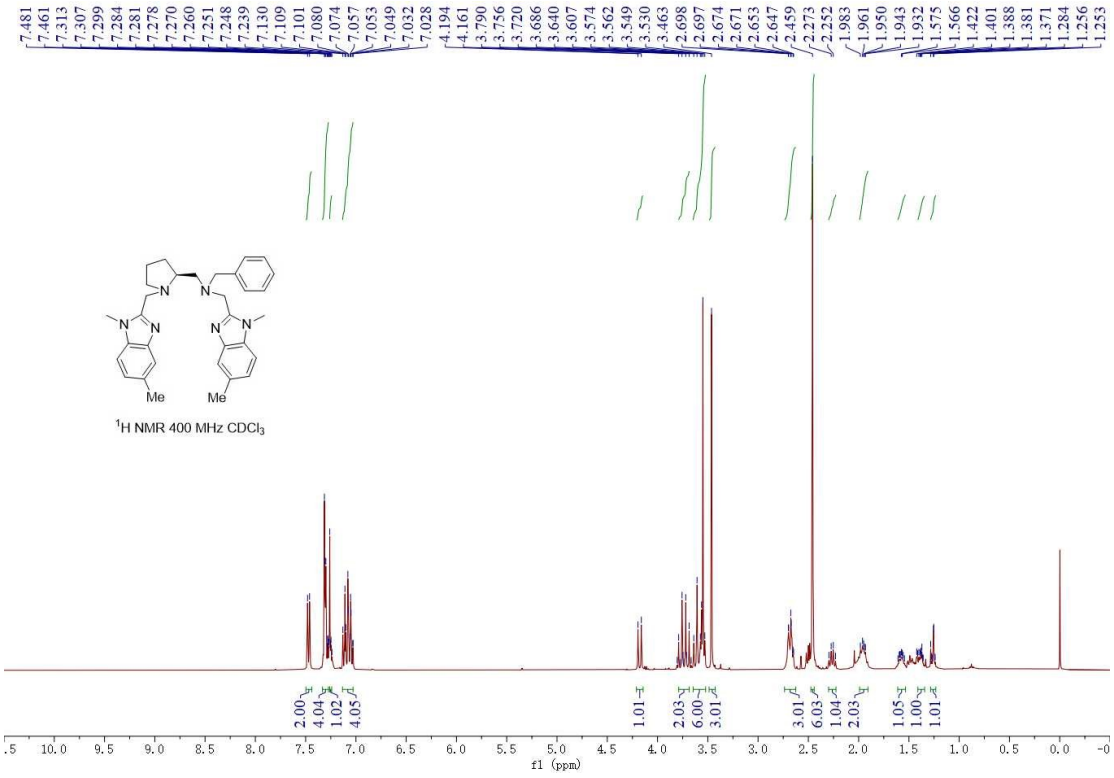


^{1}H NMR of **L7**

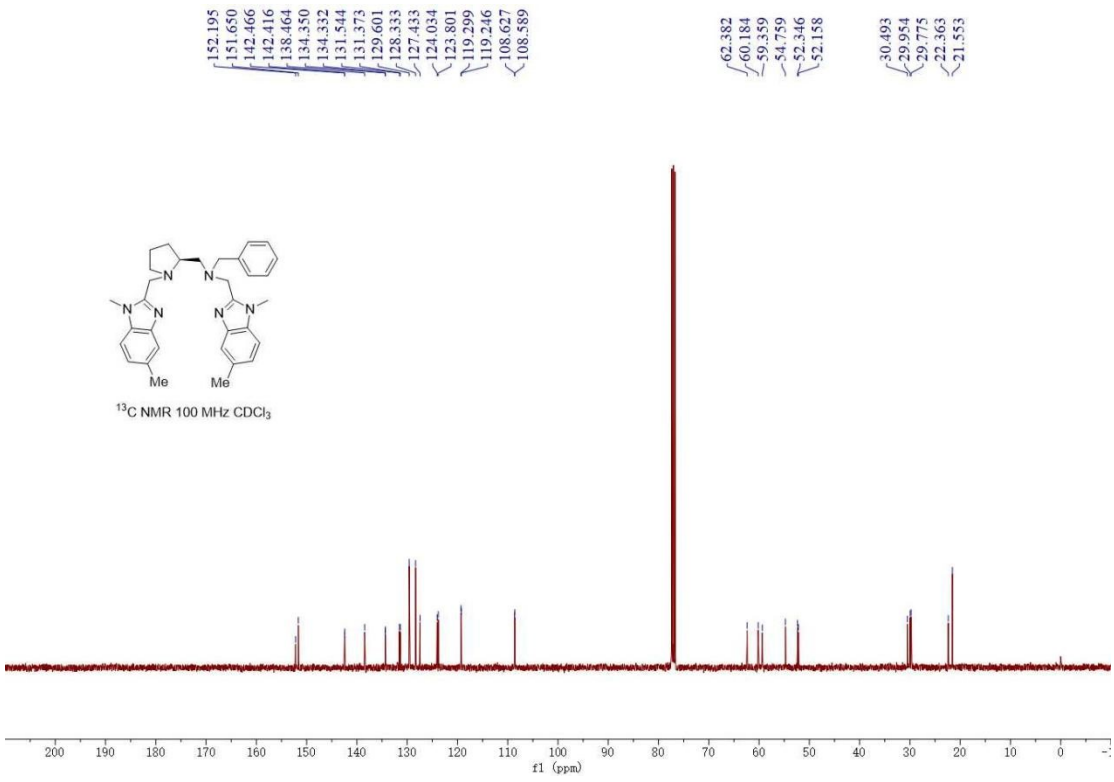


^{13}C NMR of **L7**

(*S*)-*N*-benzyl-1-(1,5-dimethyl-1H-benzo[d]imidazol-2-yl)-*N*-((1-((1,5-dimethyl-1H-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (L8)

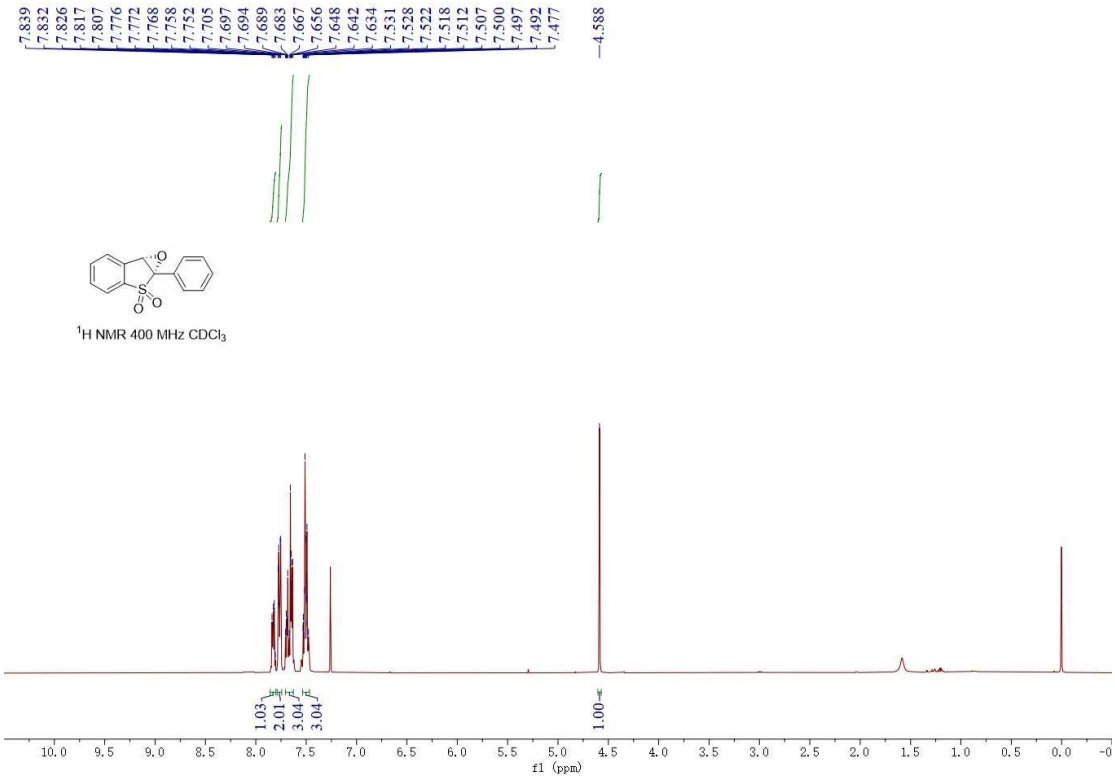


^{1}H NMR of **L8**

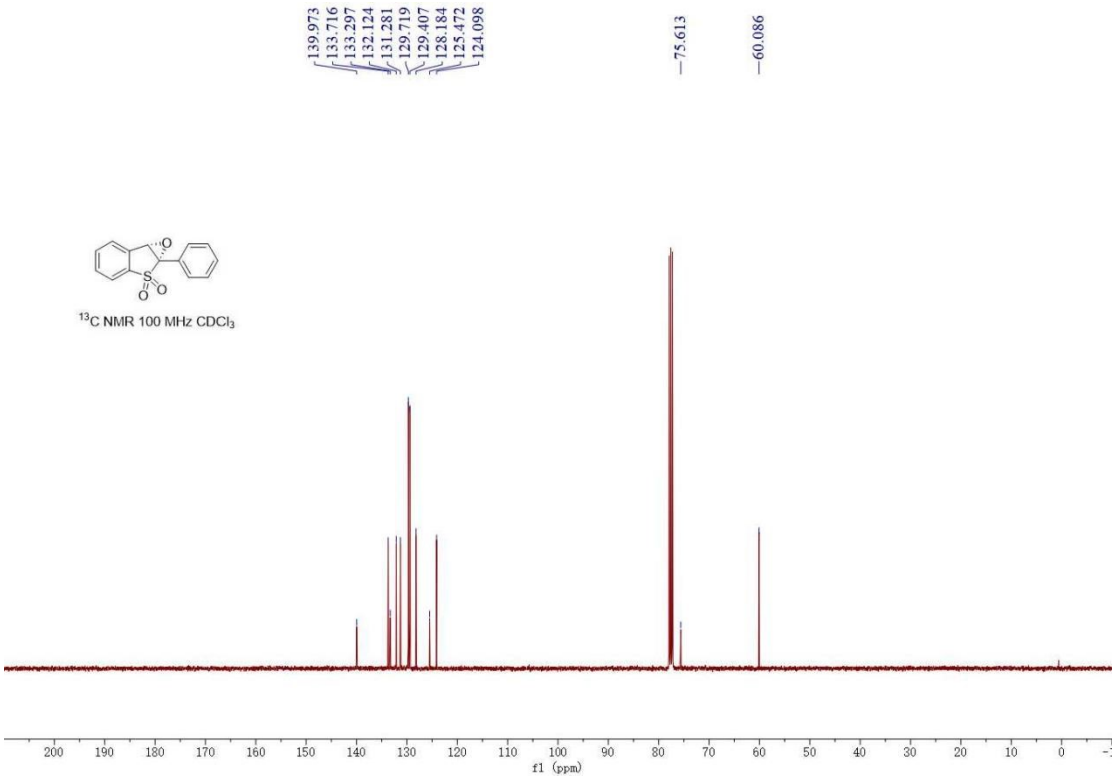


^{13}C NMR of **L8**

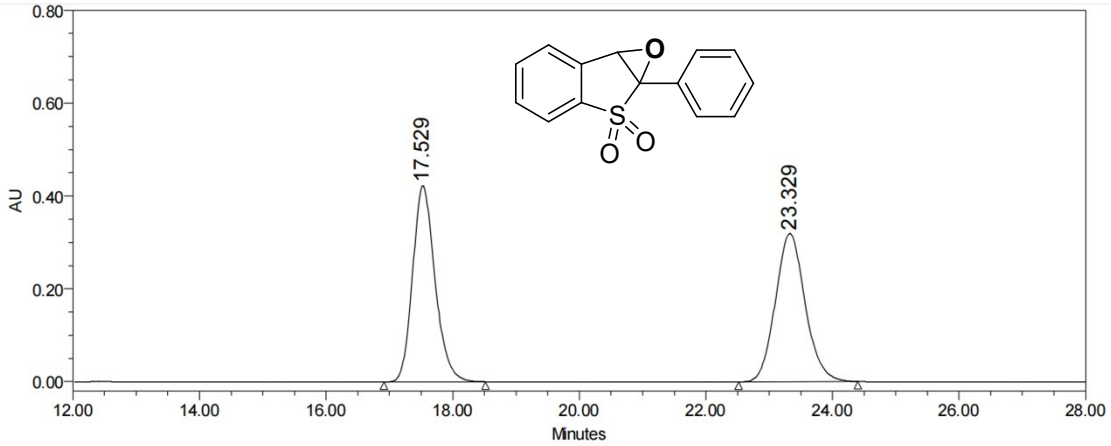
(1a*R*,6b*S*)-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2a)



^{1}H NMR of **2a**



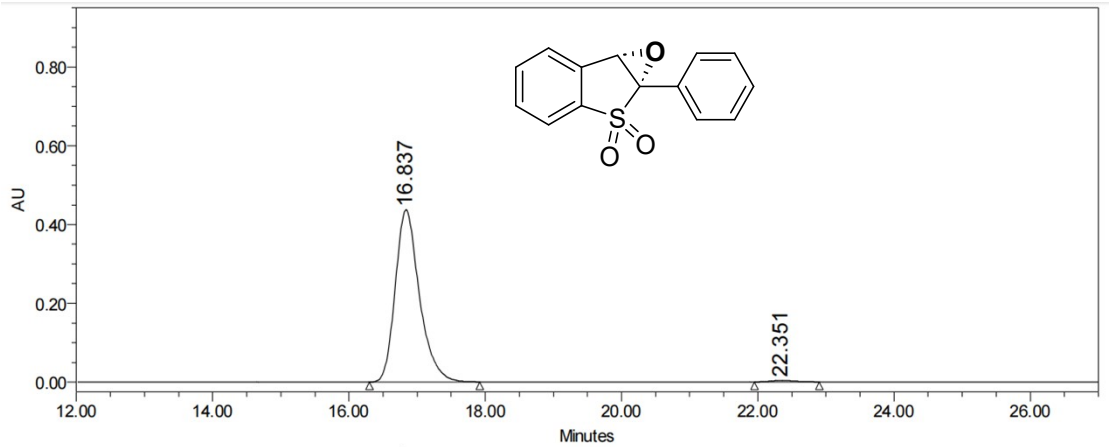
^{13}C NMR of **2a**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 11058; Processing Method: 1

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	17.529	10438633	49.97	422438
2	W2489 ChB 220nm	23.329	10450460	50.03	319293

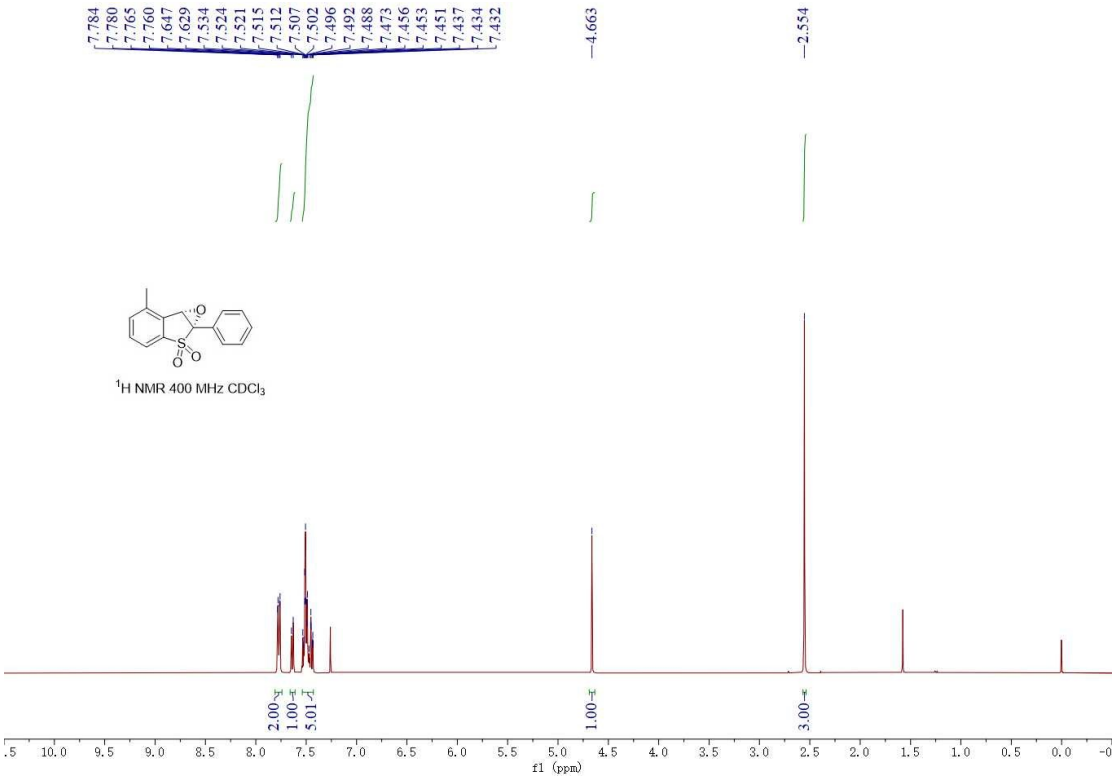


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12177; Processing Method: 1

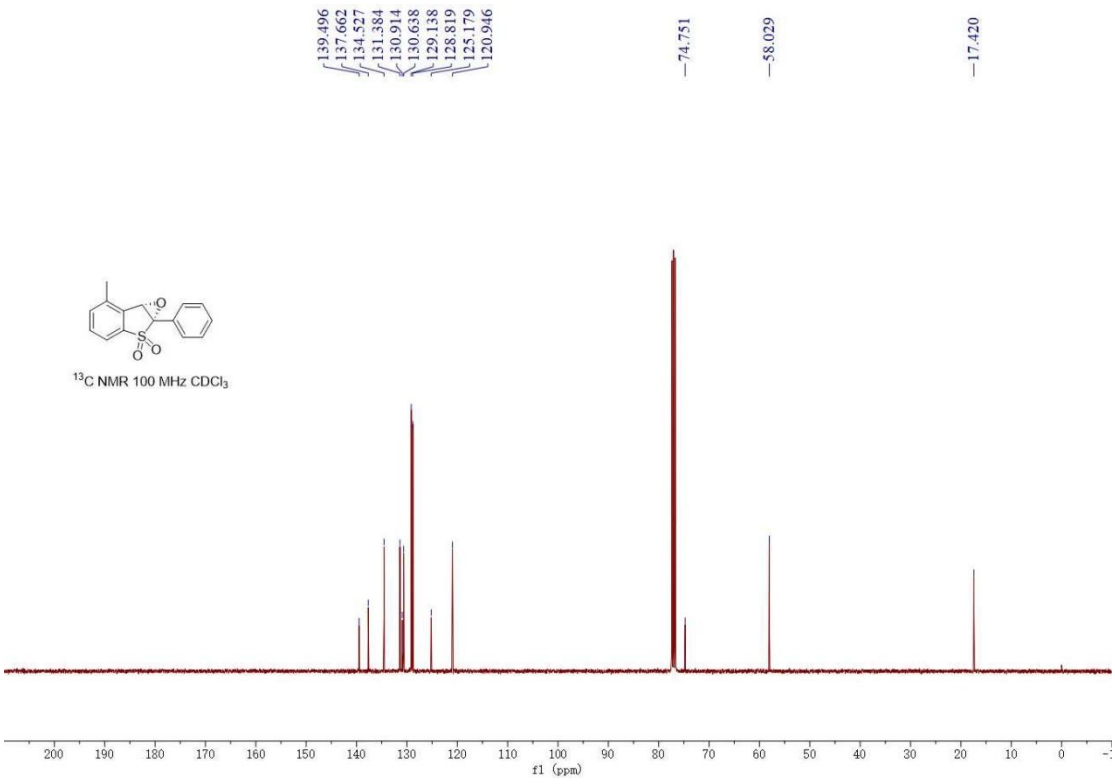
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	16.837	10776894	99.01	437214
2	W2489 ChB 220nm	22.351	107522	0.99	3821

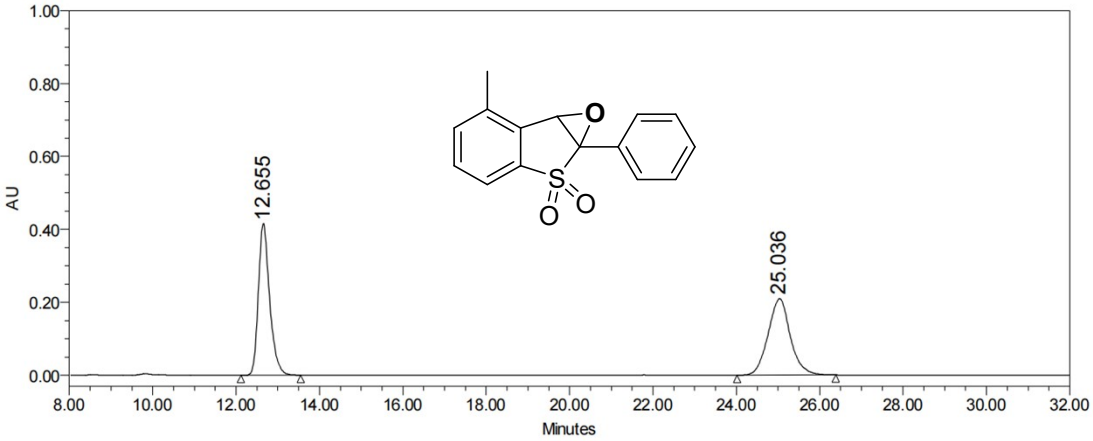
(1a*R*,6b*S*)-6-methyl-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2b)



^{1}H NMR of **2b**



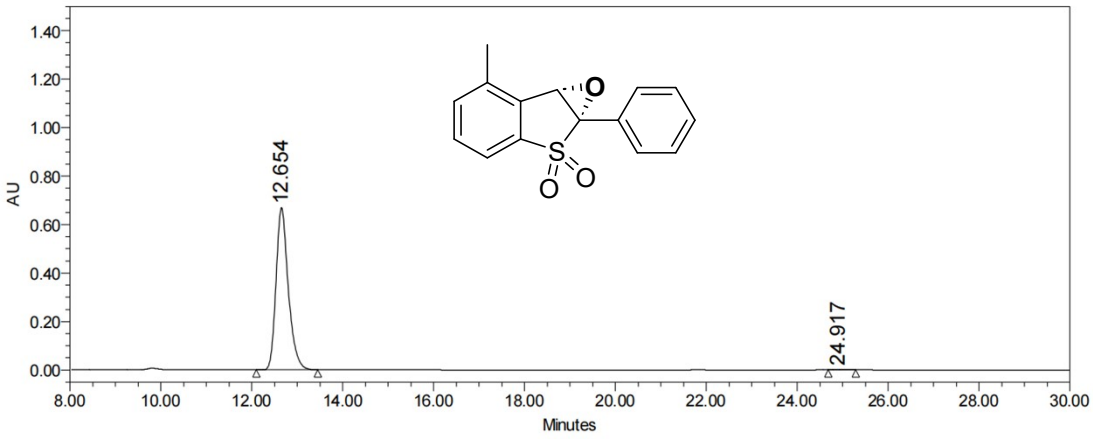
^{13}C NMR of **2b**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14032; Processing Method: 129345

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	12.655	7795570	50.17	415650
2	W2489 ChB 220nm	25.036	7742443	49.83	209348

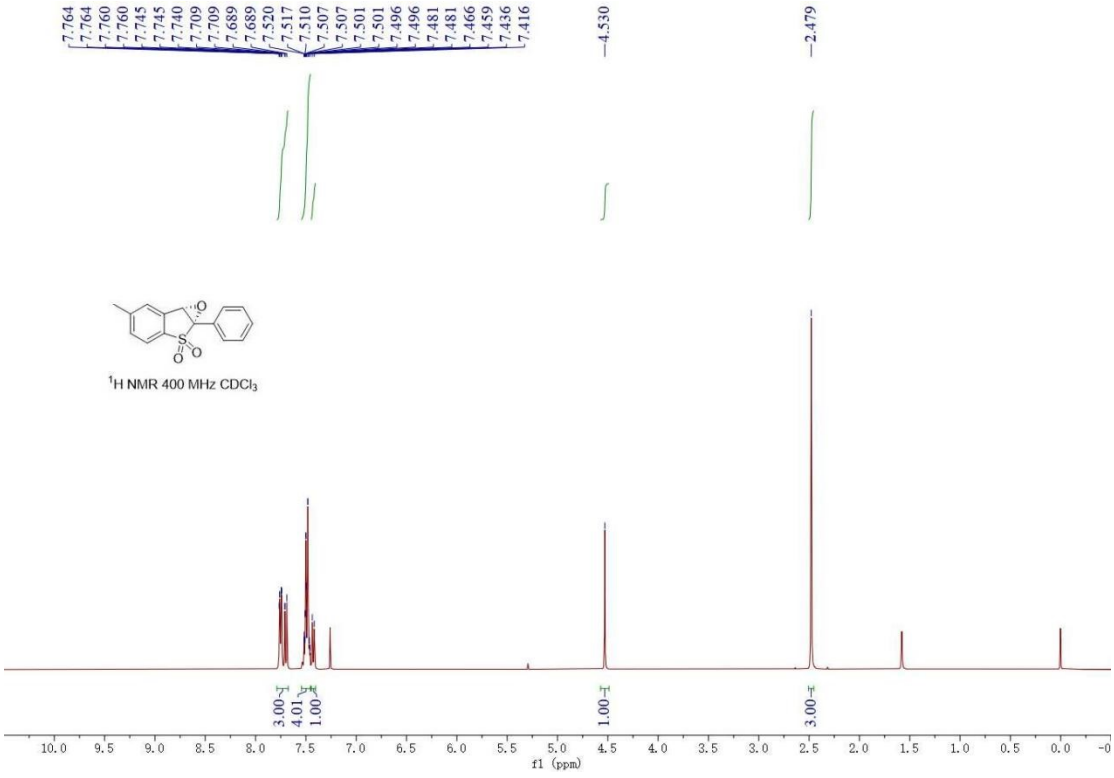


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14035; Processing Method: 123464

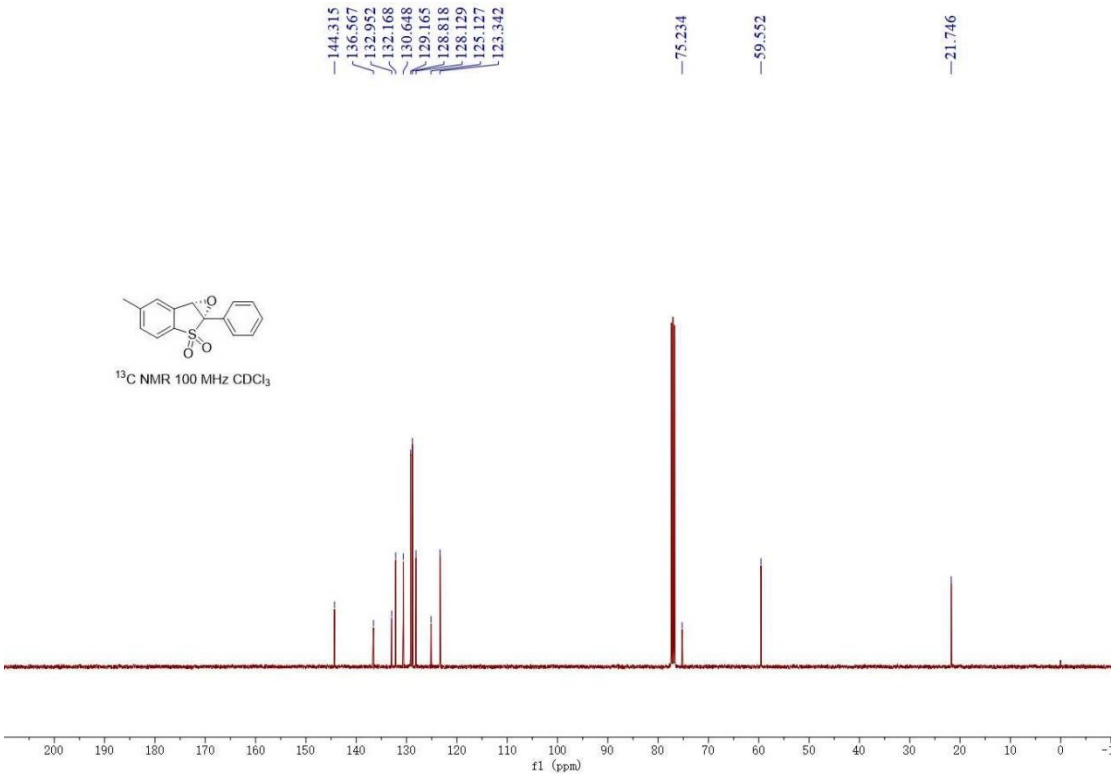
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	12.654	12588489	99.84	668881
2	W2489 ChB 220nm	24.917	19879	0.16	947

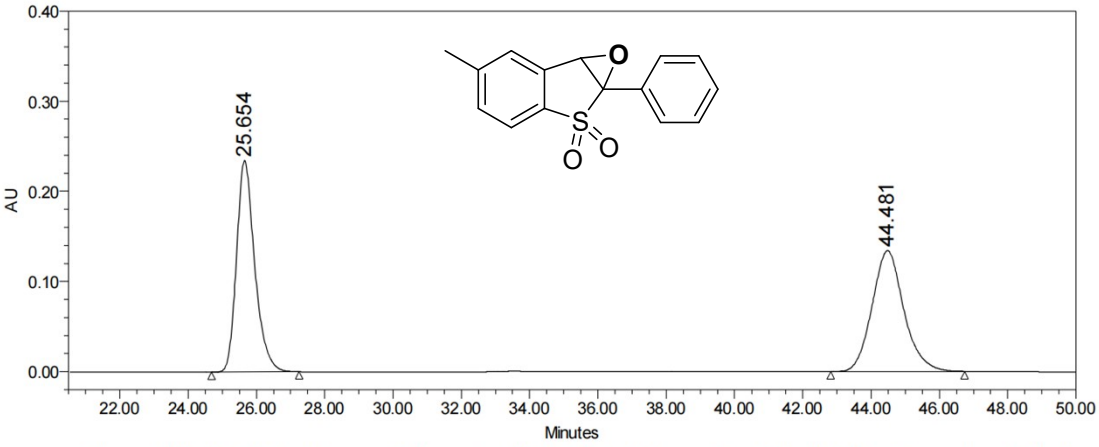
(1a*R*,6b*S*)-5-methyl-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2c)



^{1}H NMR of **2c**



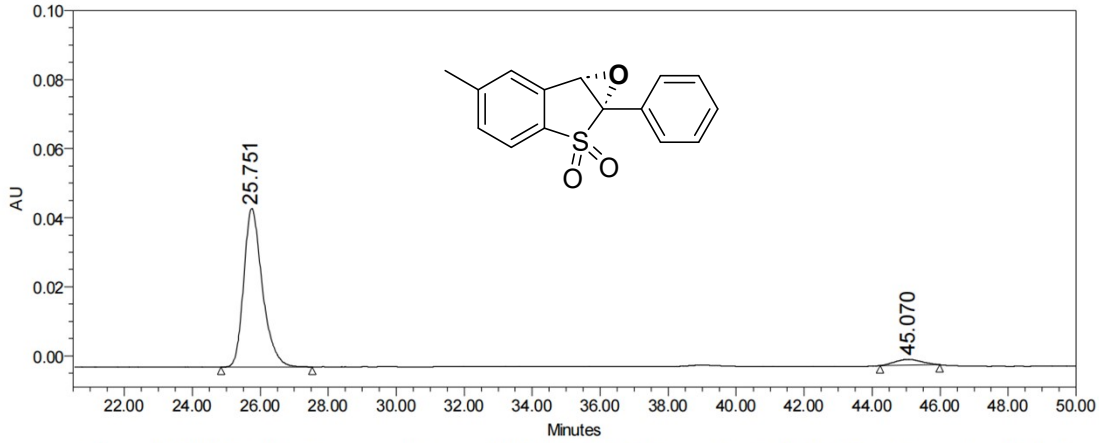
^{13}C NMR of **2c**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12912; Processing Method: VDXSZF

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	25.654	8678147	50.00	234587
2	W2489 ChB 220nm	44.481	8677649	50.00	134143

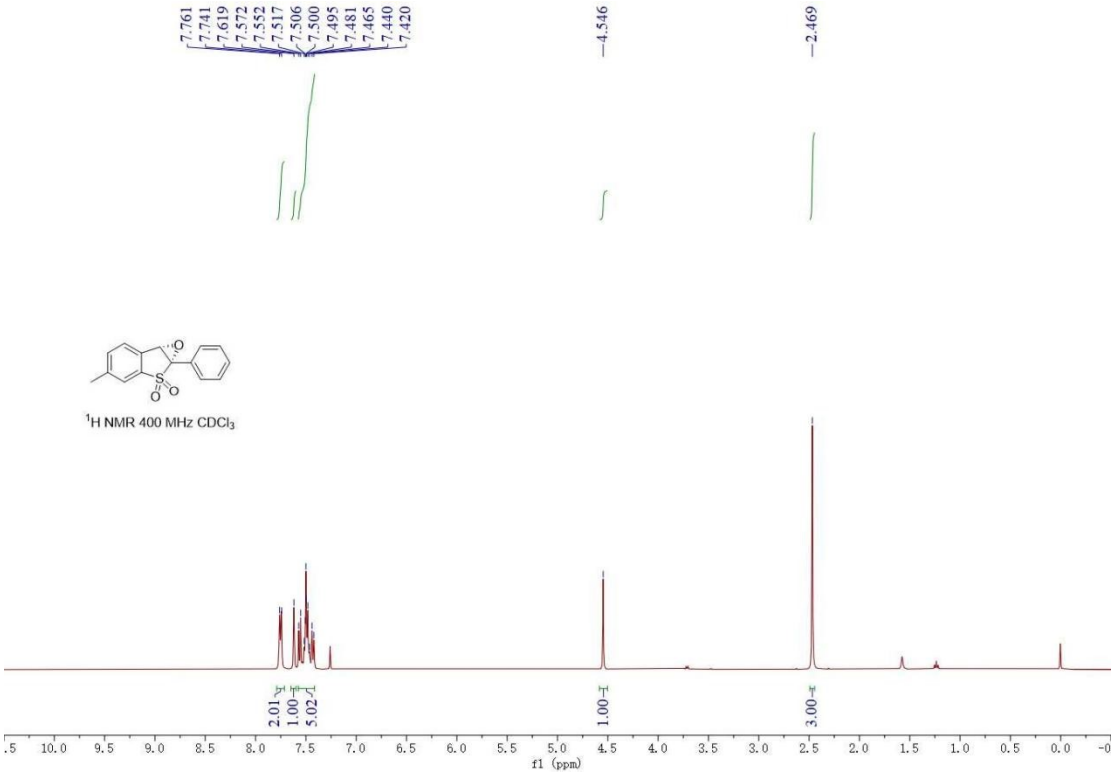


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12928; Processing Method: gbfds

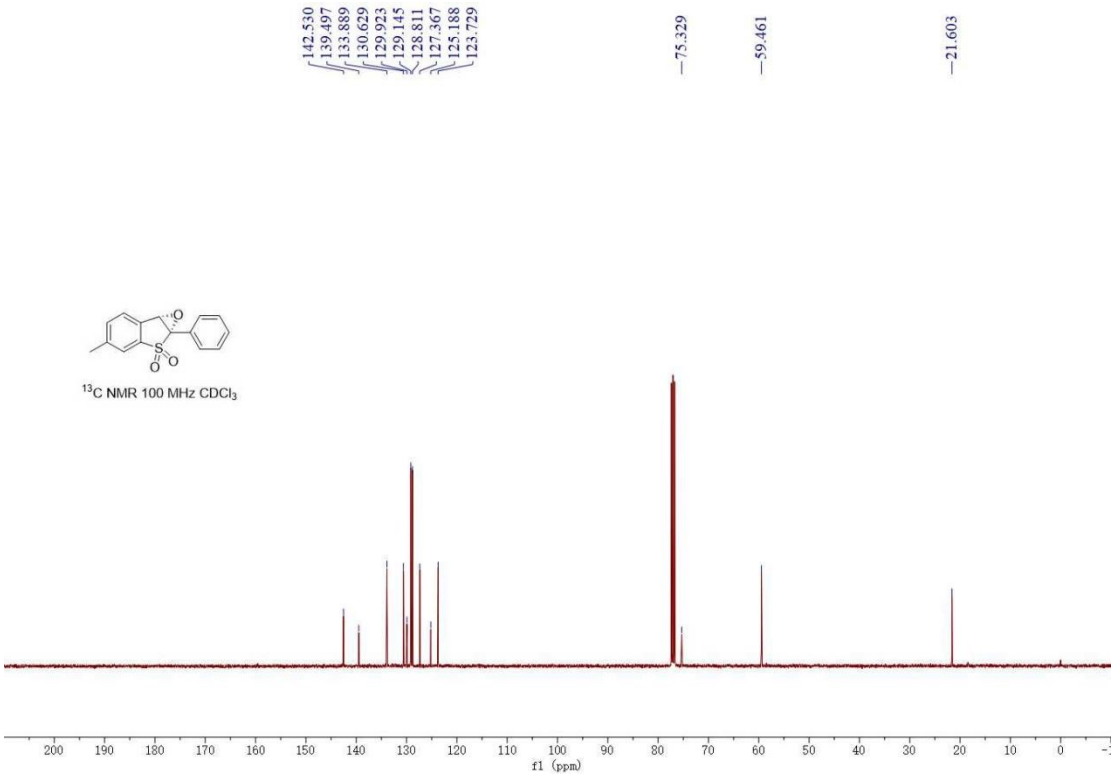
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	25.751	1747912	95.01	45877
2	W2489 ChB 220nm	45.070	91767	4.99	1666

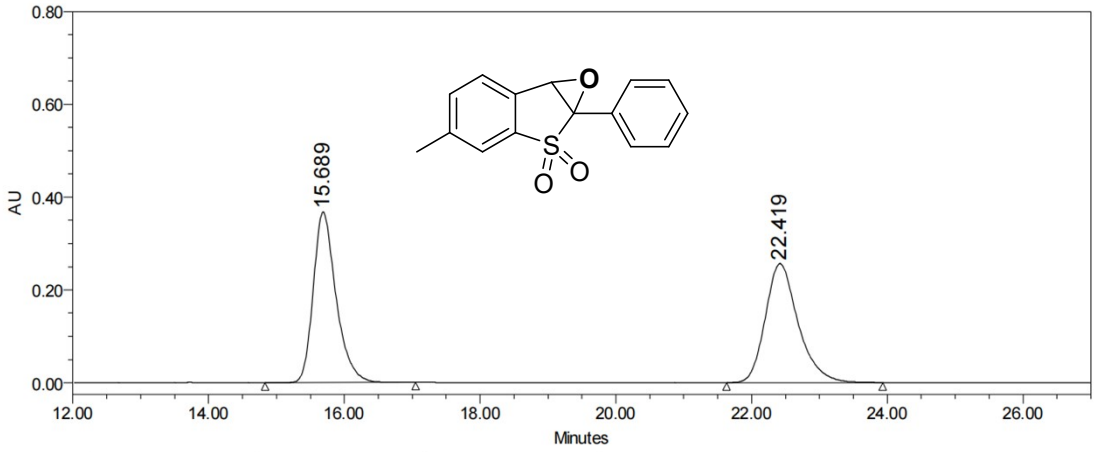
(1a*R*,6b*S*)-4-methyl-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2d)



^{1}H NMR of **2d**



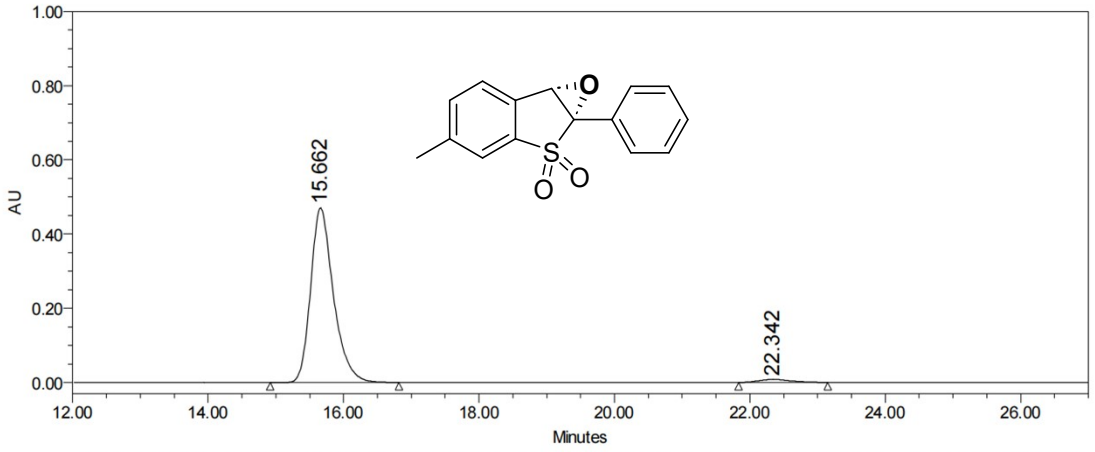
^{13}C NMR of **2d**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14053; Processing Method: 4464

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	15.689	8554591	49.85	367211
2	W2489 ChB 220nm	22.419	8604796	50.15	256411

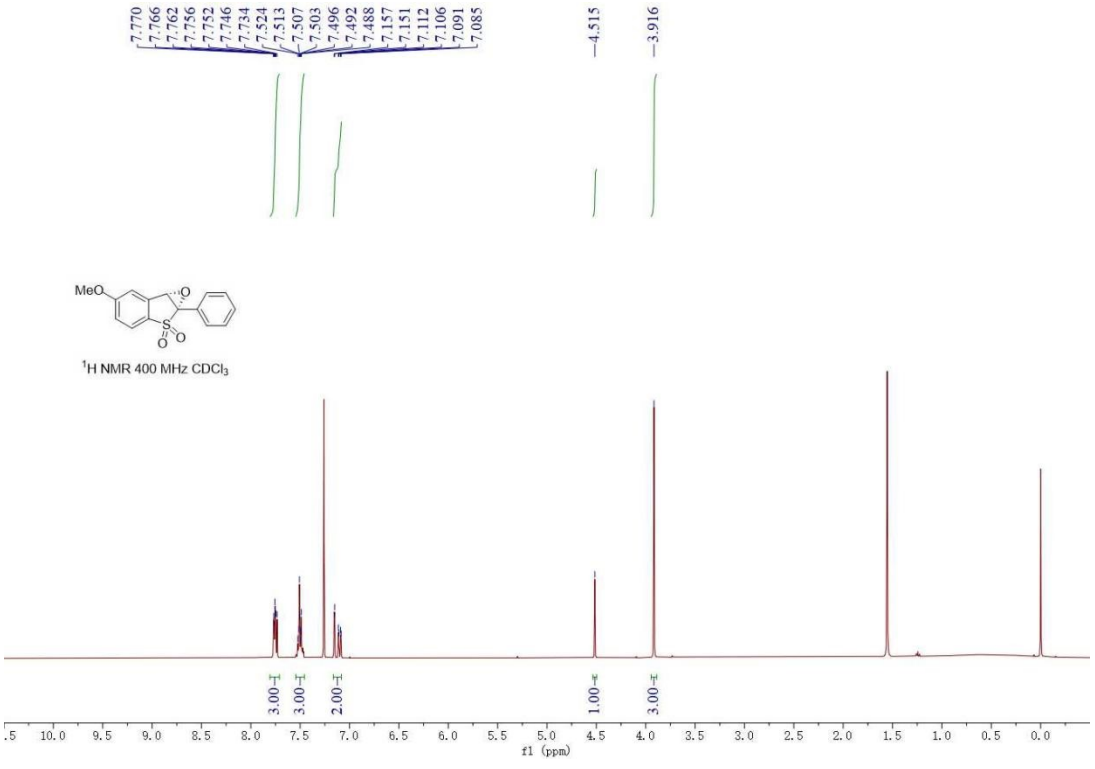


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14056; Processing Method: 84646

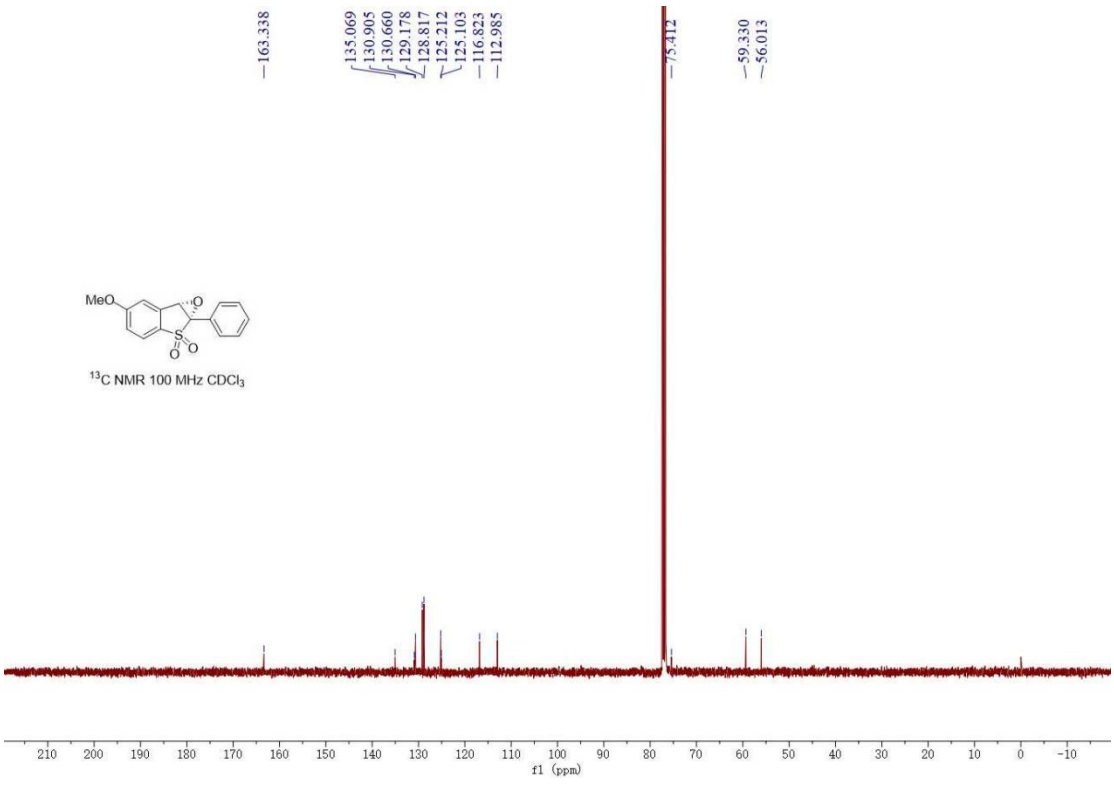
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	15.662	11010031	97.76	470423
2	W2489 ChB 220nm	22.342	252465	2.24	7882

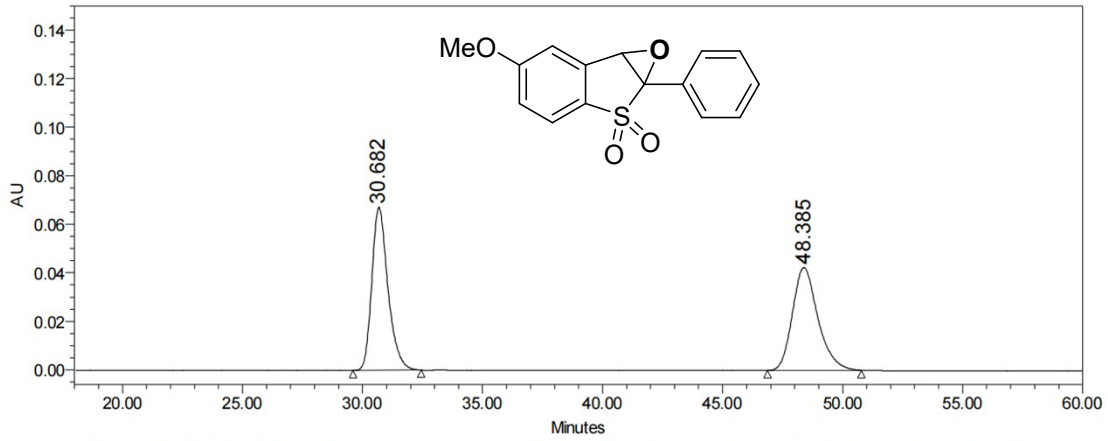
(1a*R*,6b*S*)-5-methoxy-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2e)



^{1}H NMR of **2e**



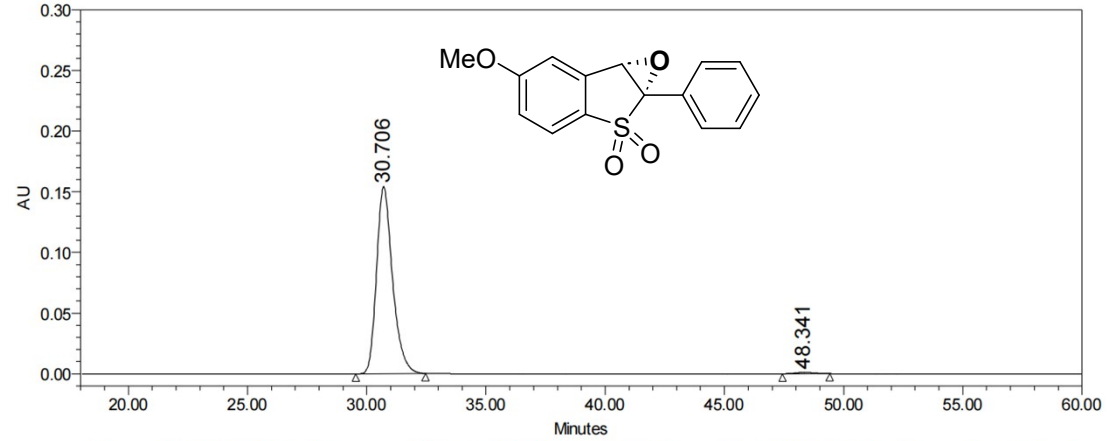
^{13}C NMR of **2e**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14215; Processing Method: 98656

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	30.682	3135590	49.99	67157
2	W2489 ChB 220nm	48.385	3136760	50.01	42364

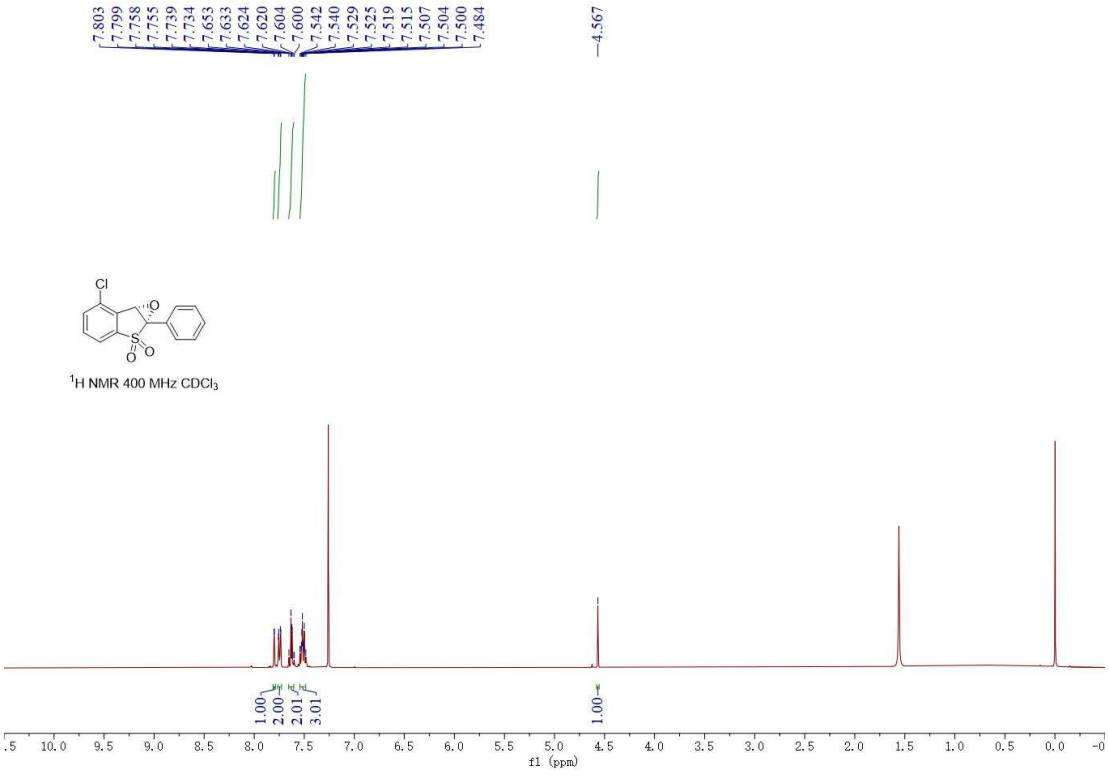


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14218; Processing Method: 9664646

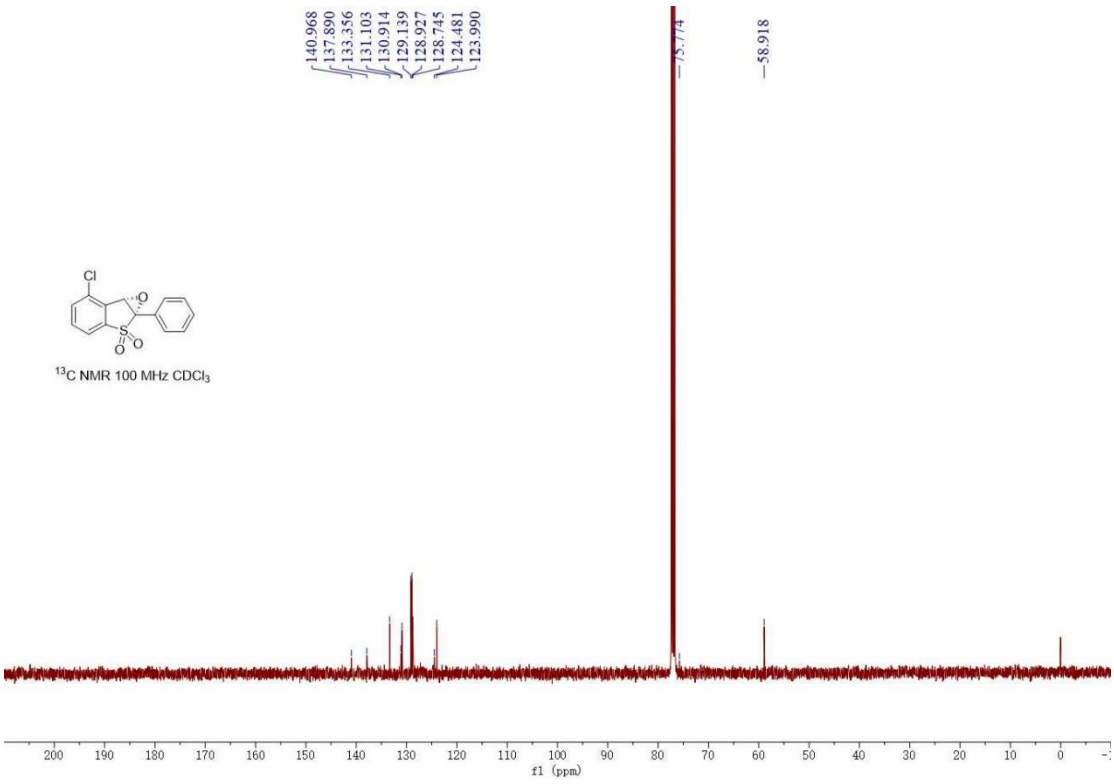
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	30.706	7192200	99.09	154092
2	W2489 ChB 220nm	48.341	65862	0.91	1089

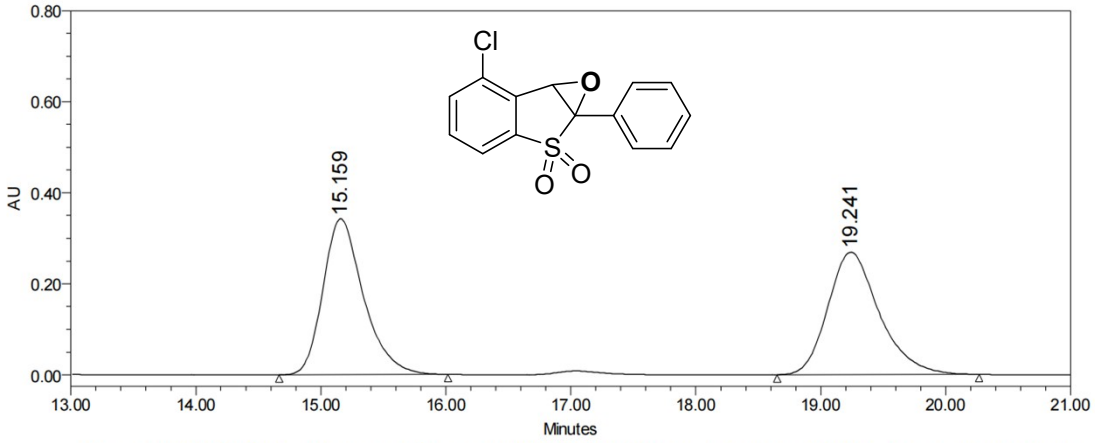
(1a*R*,6b*S*)-6-chloro-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2f)



^{1}H NMR of **2f**



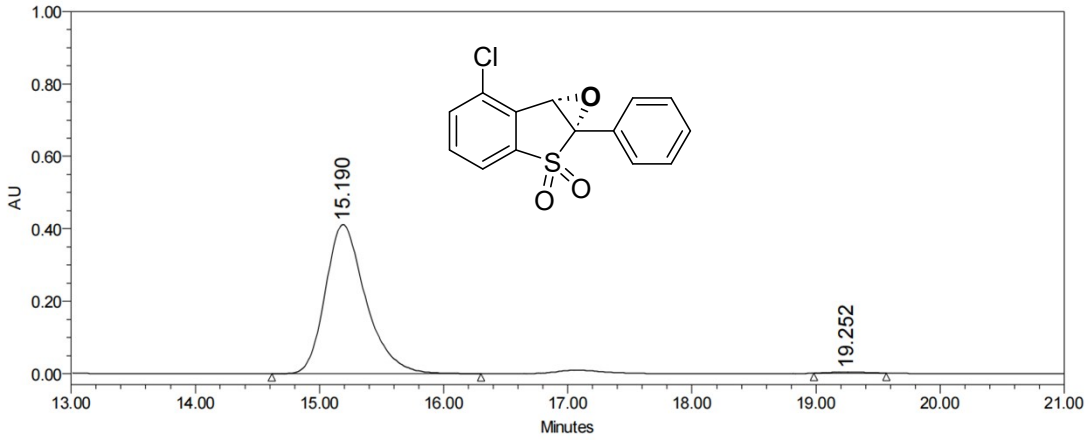
^{13}C NMR of **2f**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 13418; Processing Method: 15981

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	15.159	7704750	50.05	342607
2	W2489 ChB 220nm	19.241	7690717	49.95	269202

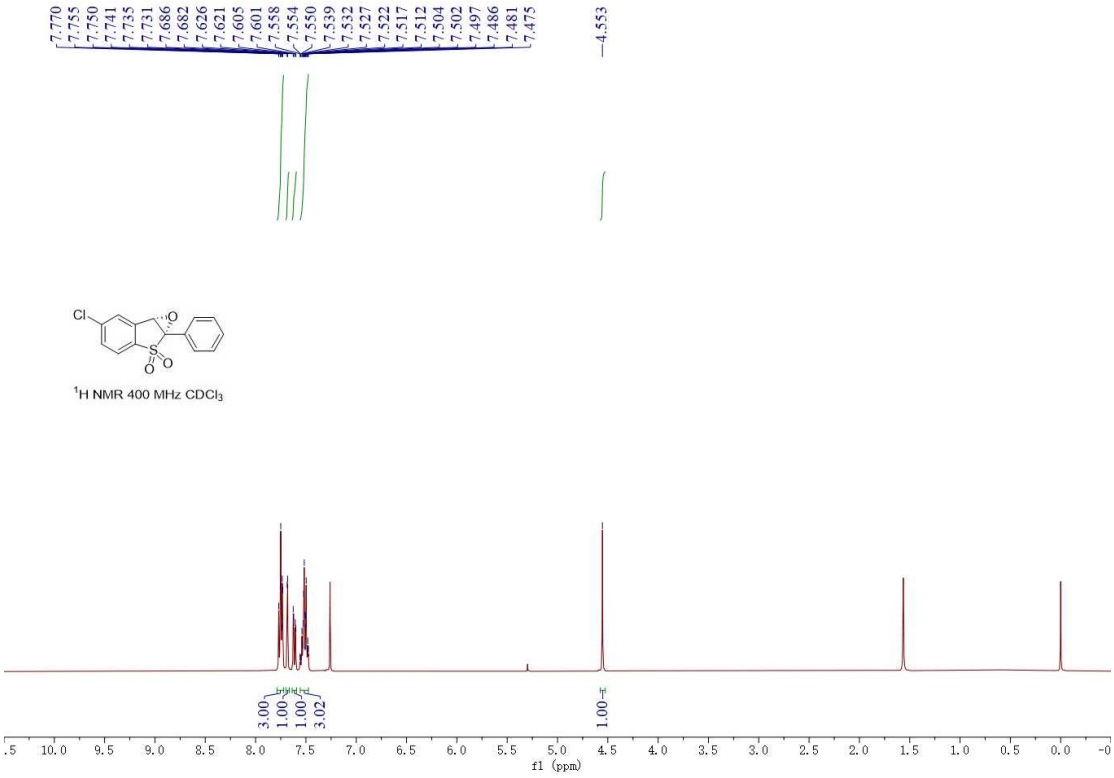


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 13415; Processing Method: 15976

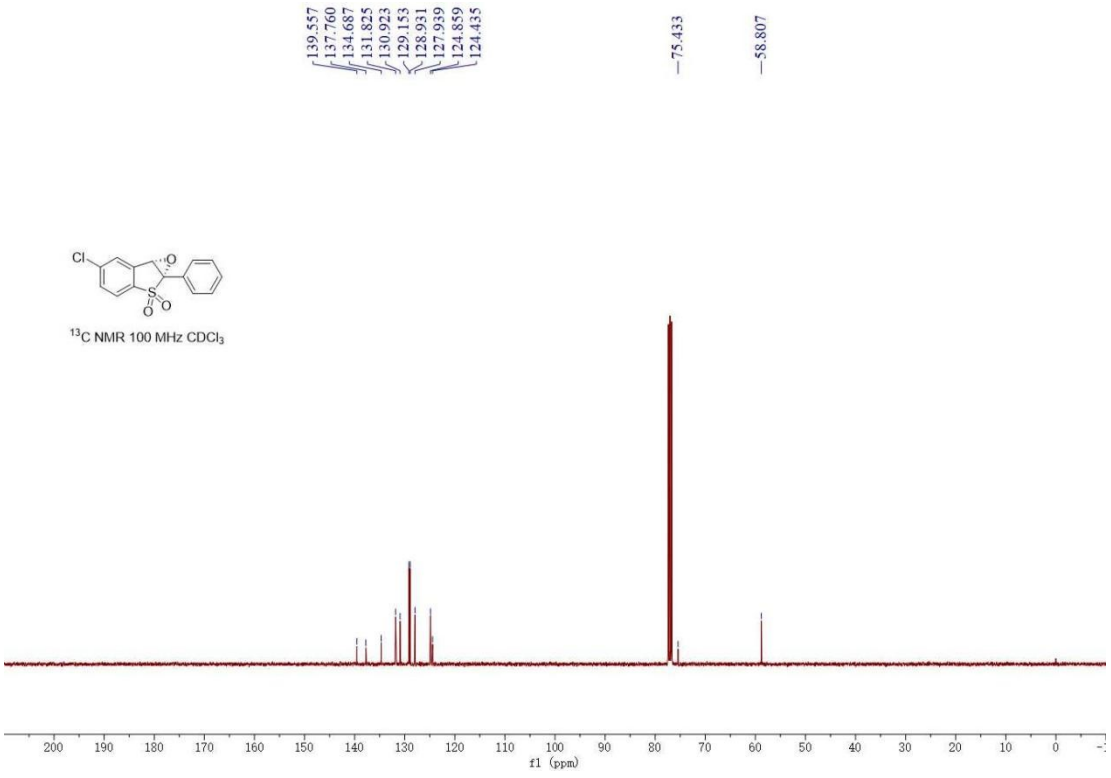
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	15.190	9289458	99.40	411816
2	W2489 ChB 220nm	19.252	56082	0.60	2839

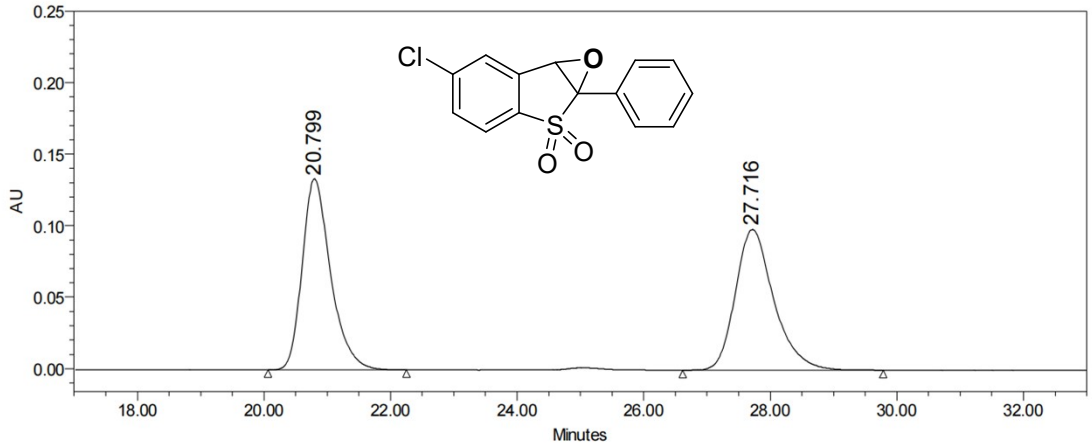
(1a*R*,6b*S*)-5-chloro-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2g)



^{1}H NMR of **2g**



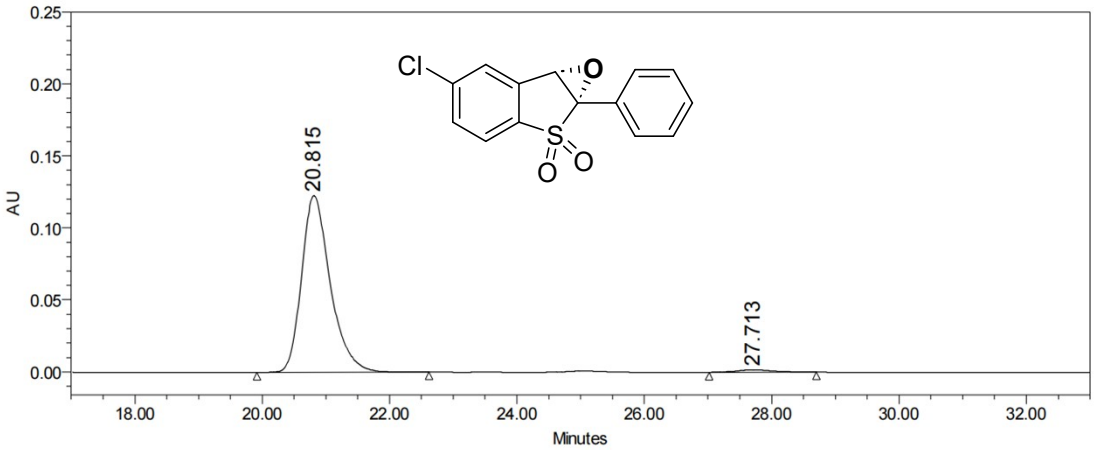
^{13}C NMR of **2g**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12972; Processing Method: SDFAF

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	20.799	4174340	50.18	133506
2	W2489 ChB 220nm	27.716	4145188	49.82	98341

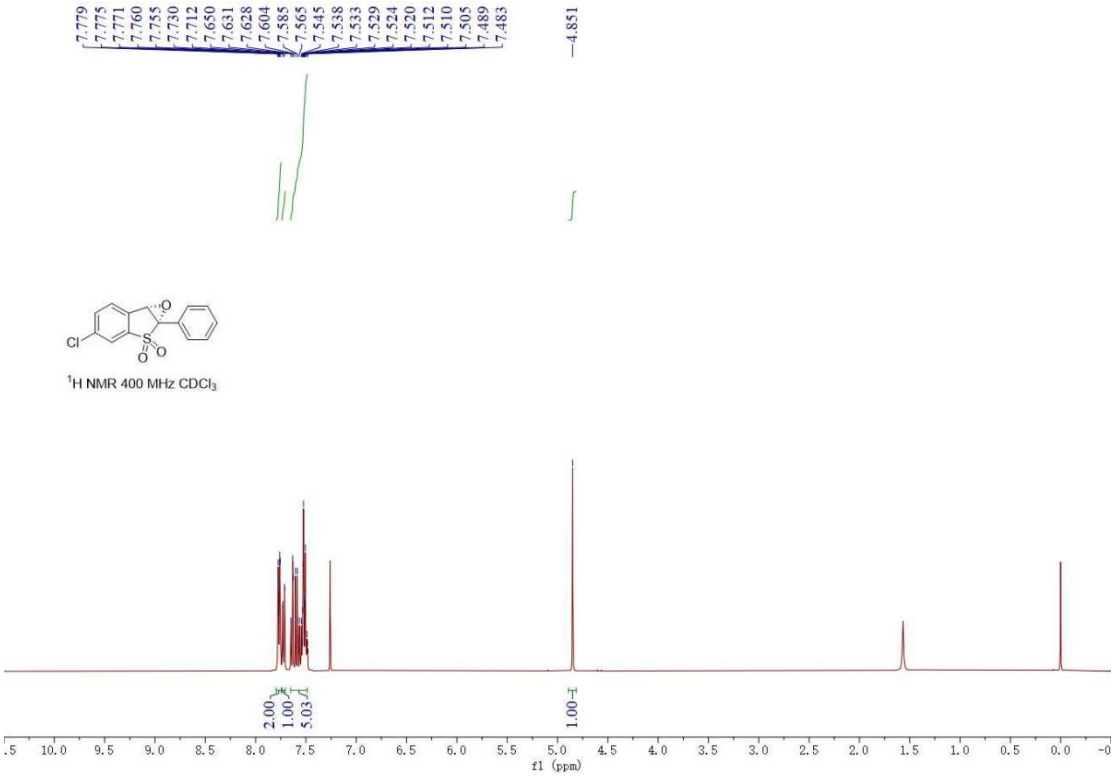


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12983; Processing Method: 1

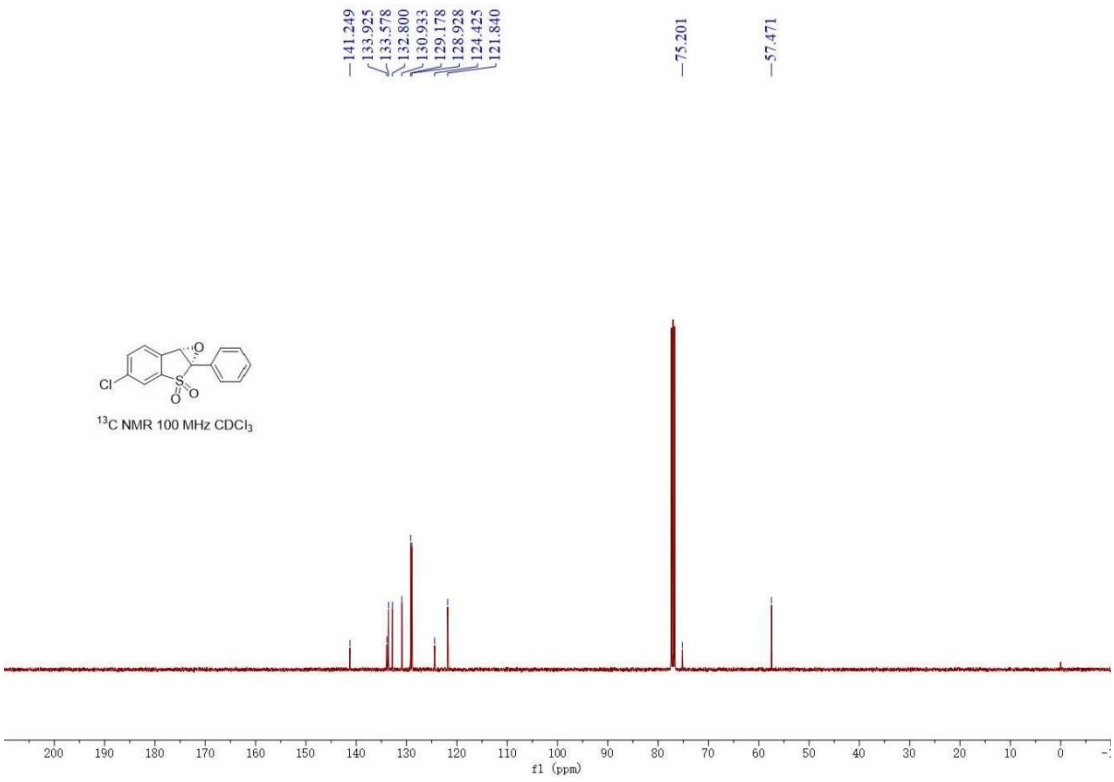
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	20.815	3838301	98.39	122767
2	W2489 ChB 220nm	27.713	62879	1.61	1590

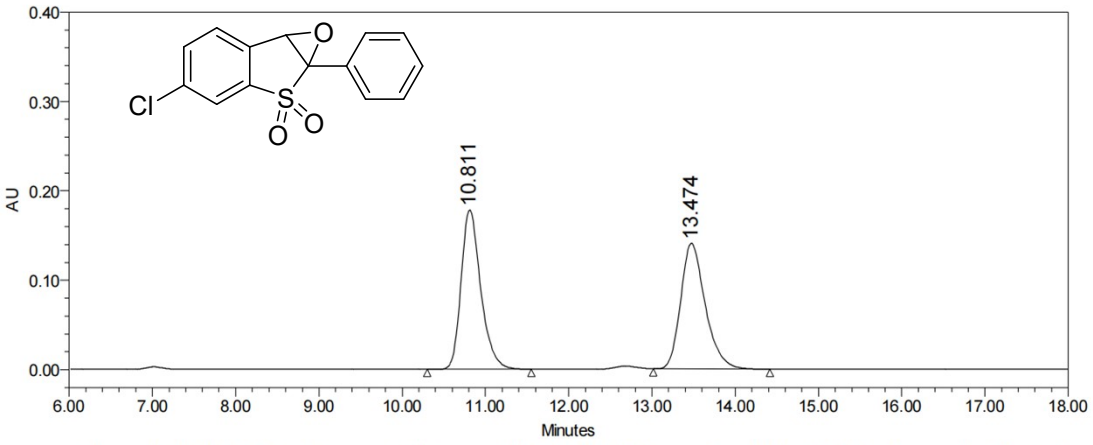
(1a*R*,6b*S*)-4-chloro-1a-phenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2h)



^{1}H NMR of **2h**



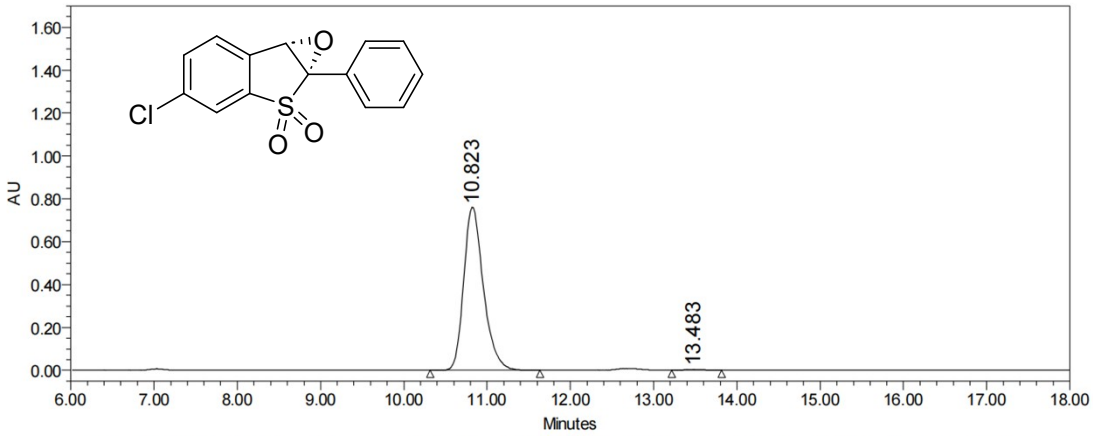
^{13}C NMR of **2h**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14065; Processing Method: 4646

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	10.811	2908633	50.29	178339
2	W2489 ChB 220nm	13.474	2875458	49.71	140863

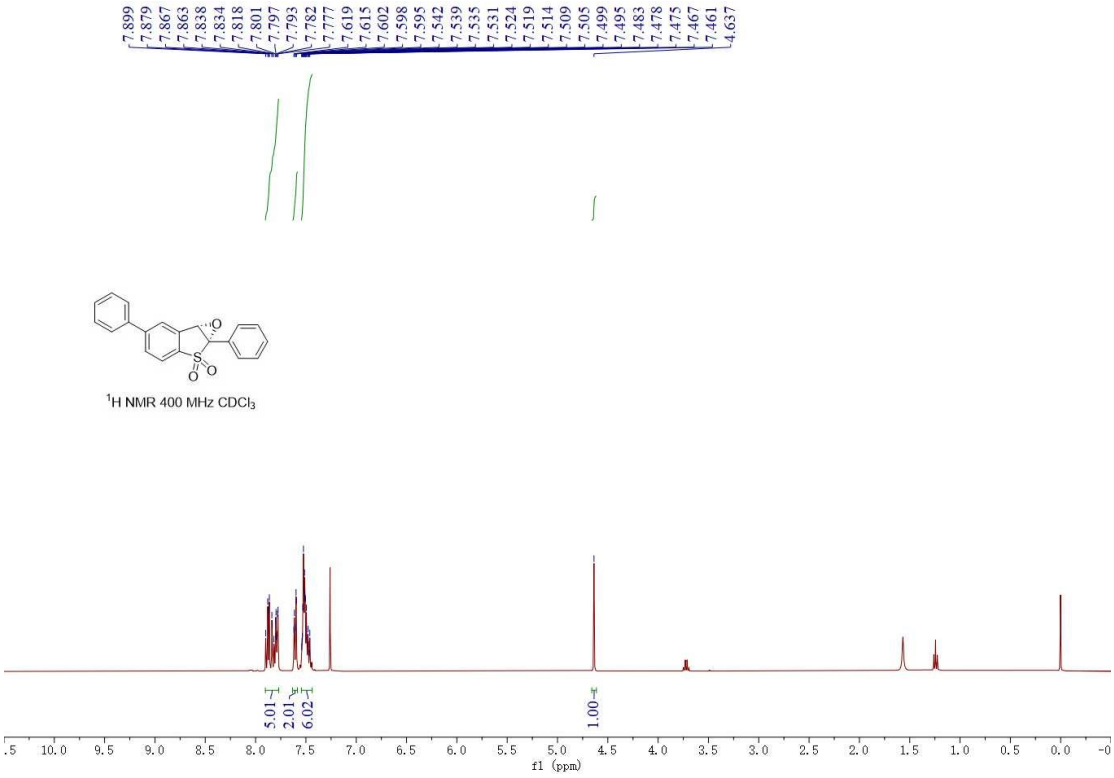


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14068; Processing Method: 46464

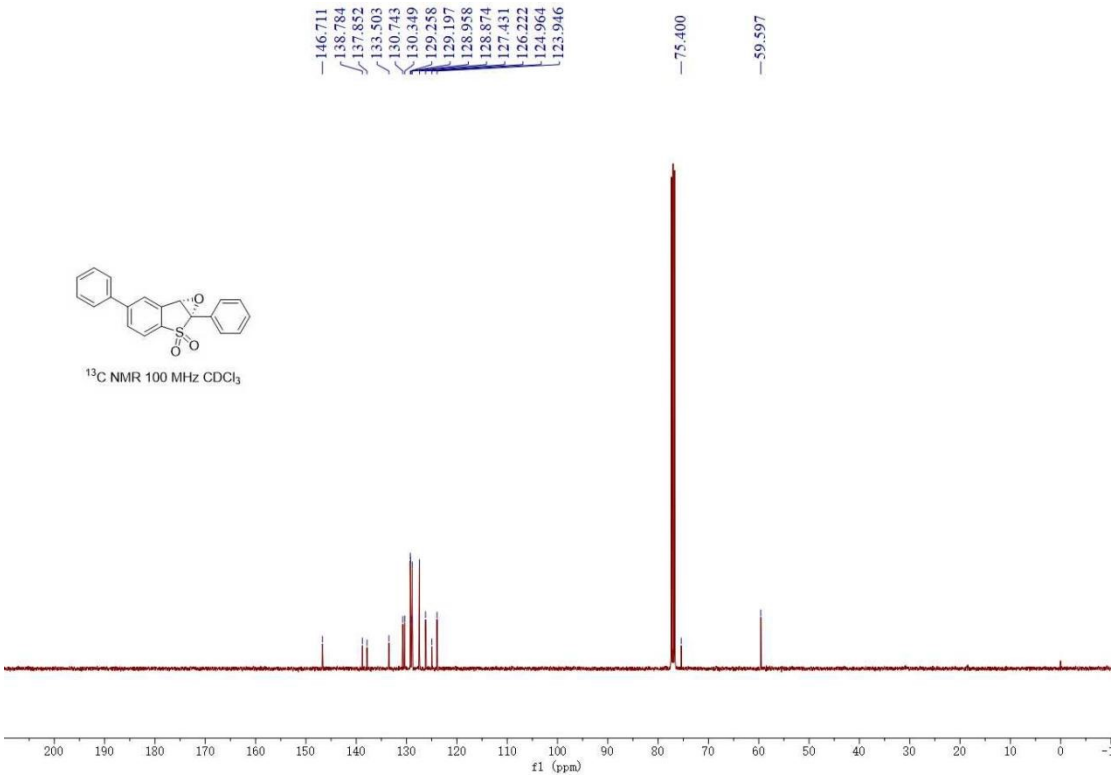
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	10.823	12462755	99.57	761804
2	W2489 ChB 220nm	13.483	53761	0.43	3145

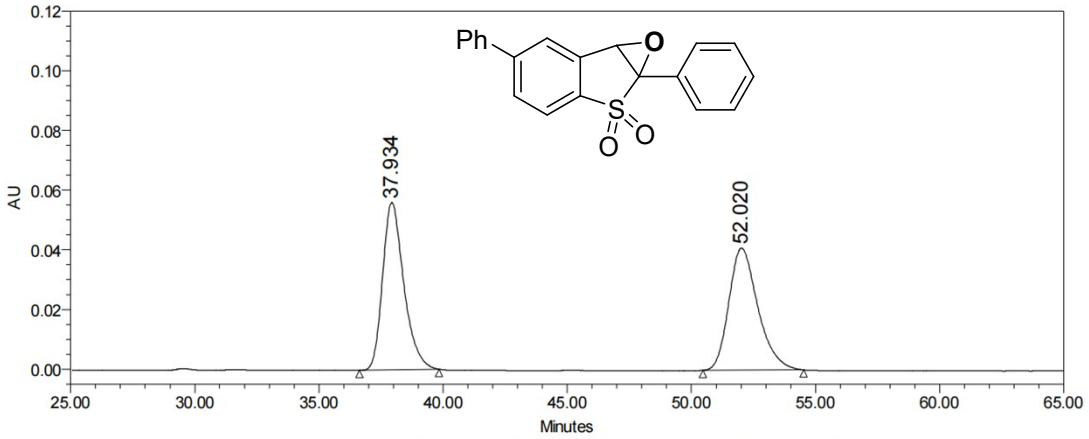
(1a*R*,6b*S*)-1a,5-diphenyl-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2i)



^{1}H NMR of **2i**



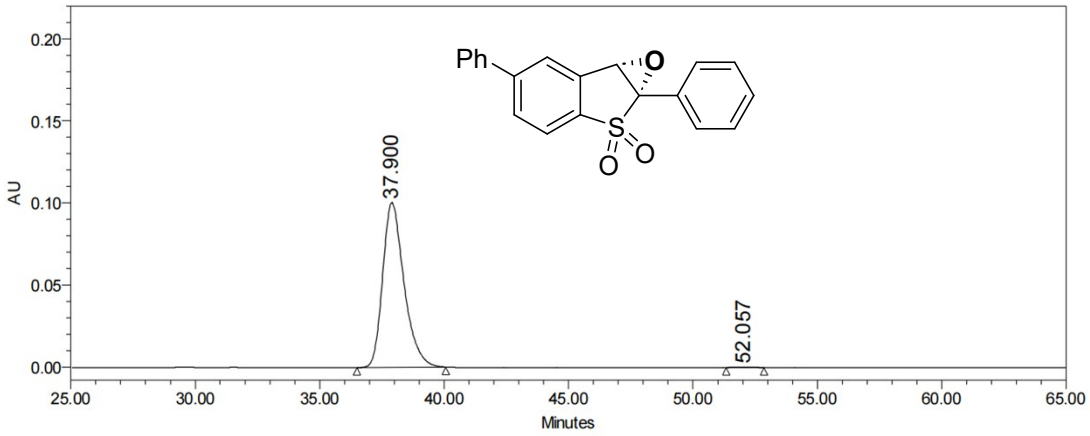
^{13}C NMR of **2i**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14227; Processing Method: 66461

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	37.934	3333210	50.04	56101
2	W2489 ChB 220nm	52.020	3327424	49.96	40903

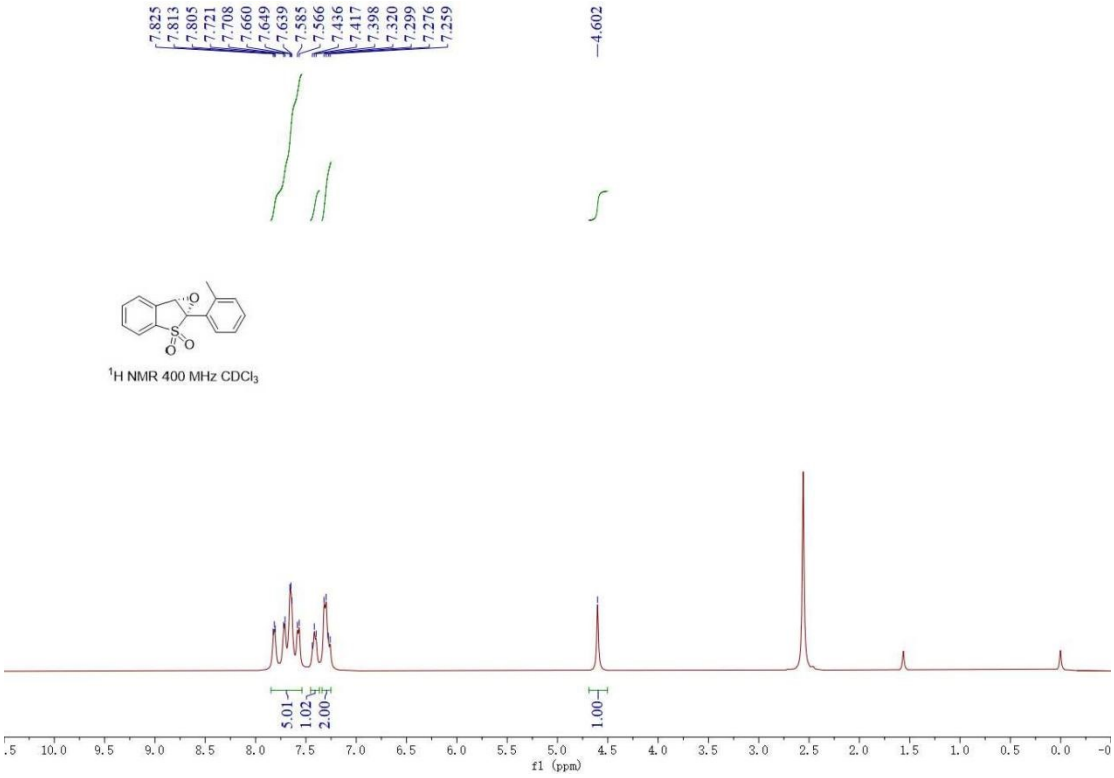


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14230; Processing Method: 964646

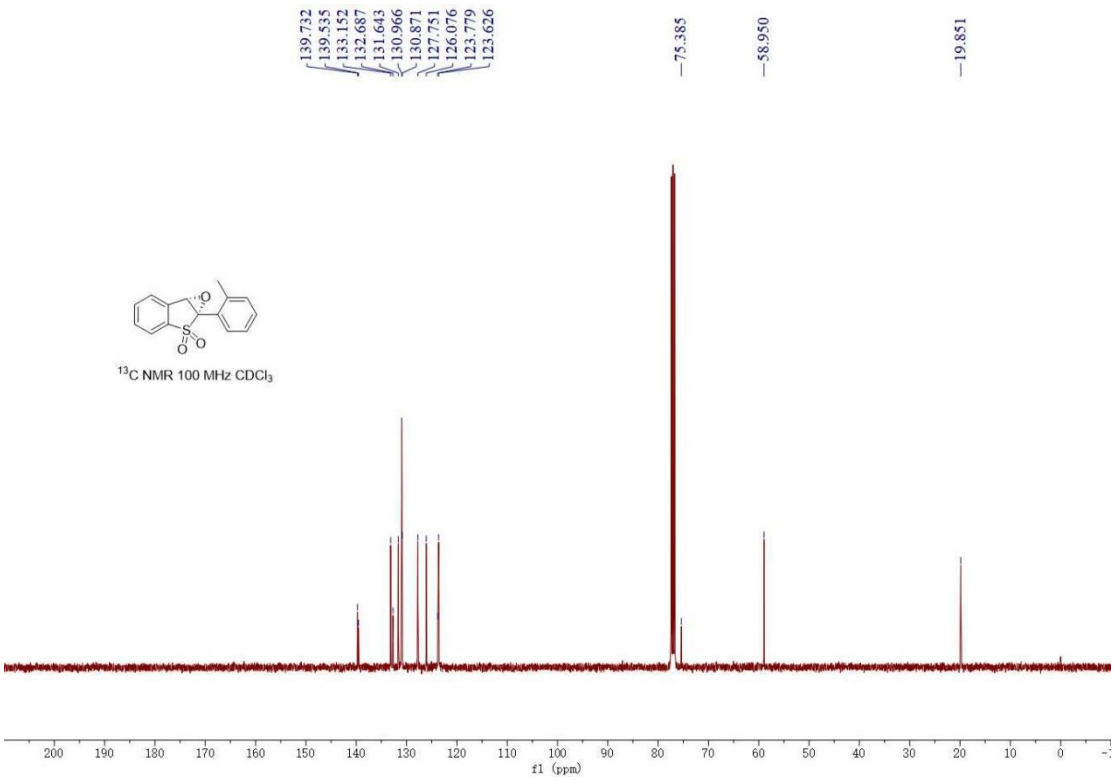
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	37.900	5990076	99.80	100414
2	W2489 ChB 220nm	52.057	11723	0.20	228

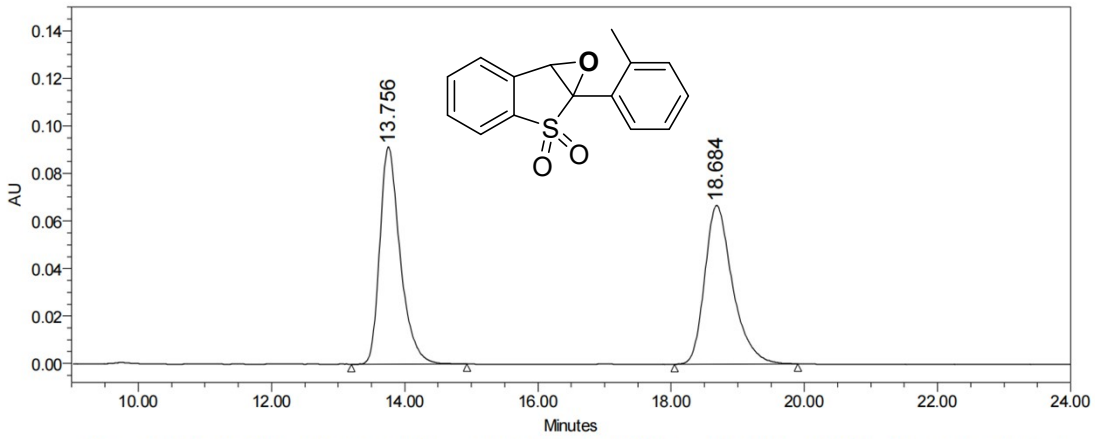
(1aR,6bS)-1a-(o-tolyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-b]oxirene 2,2-dioxide (2j)



^{1}H NMR of **2j**



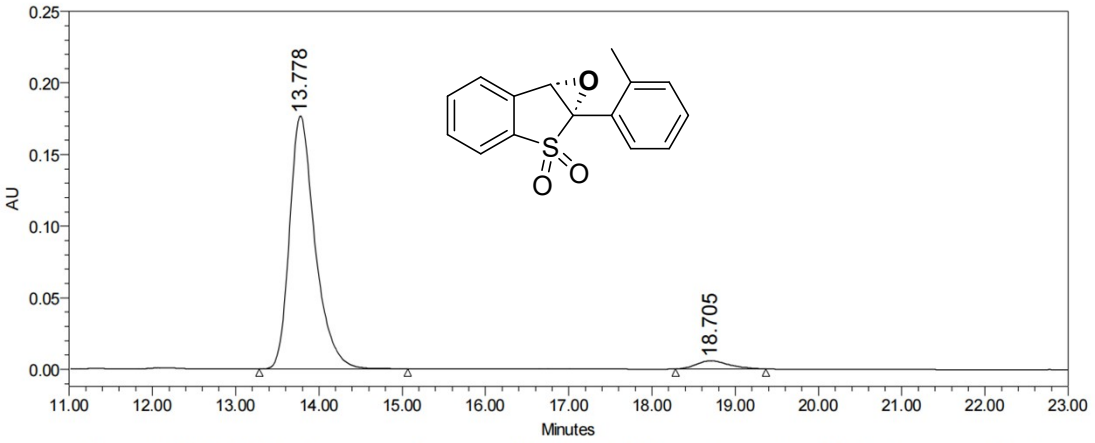
^{13}C NMR of **2j**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12388; Processing Method: dfgsdfg

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	13.756	1940303	50.01	91415
2	W2489 ChB 220nm	18.684	1939287	49.99	66782

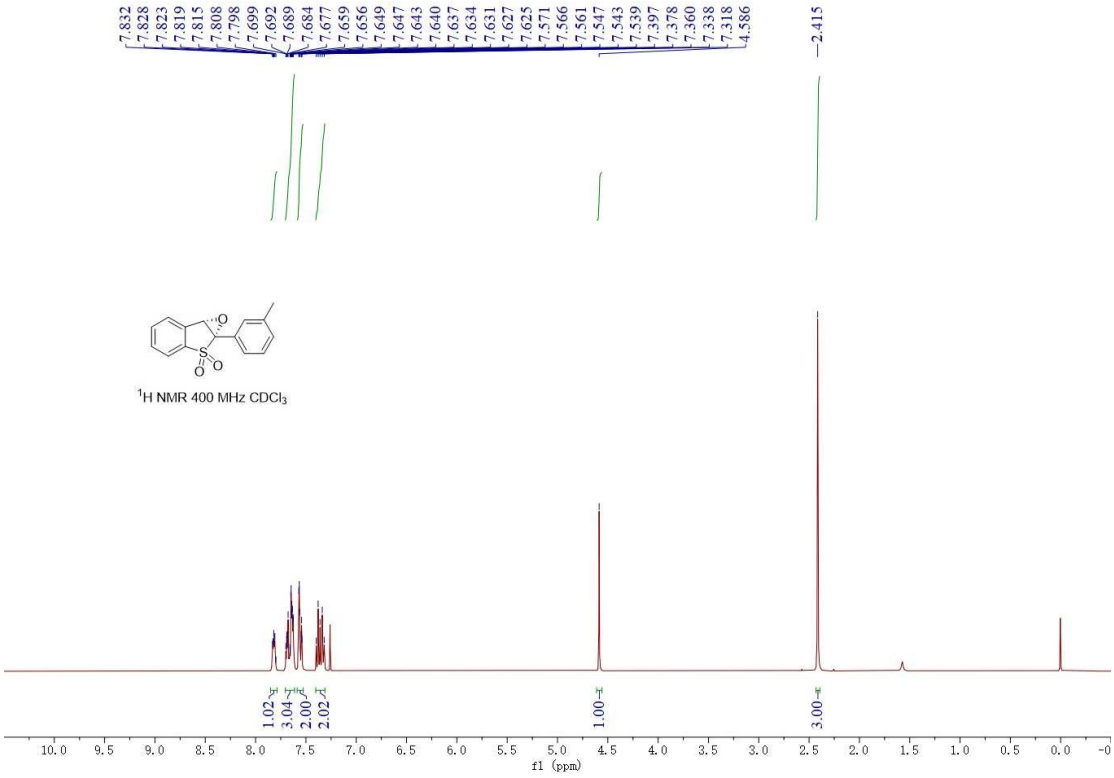


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12391; Processing Method: sadfa

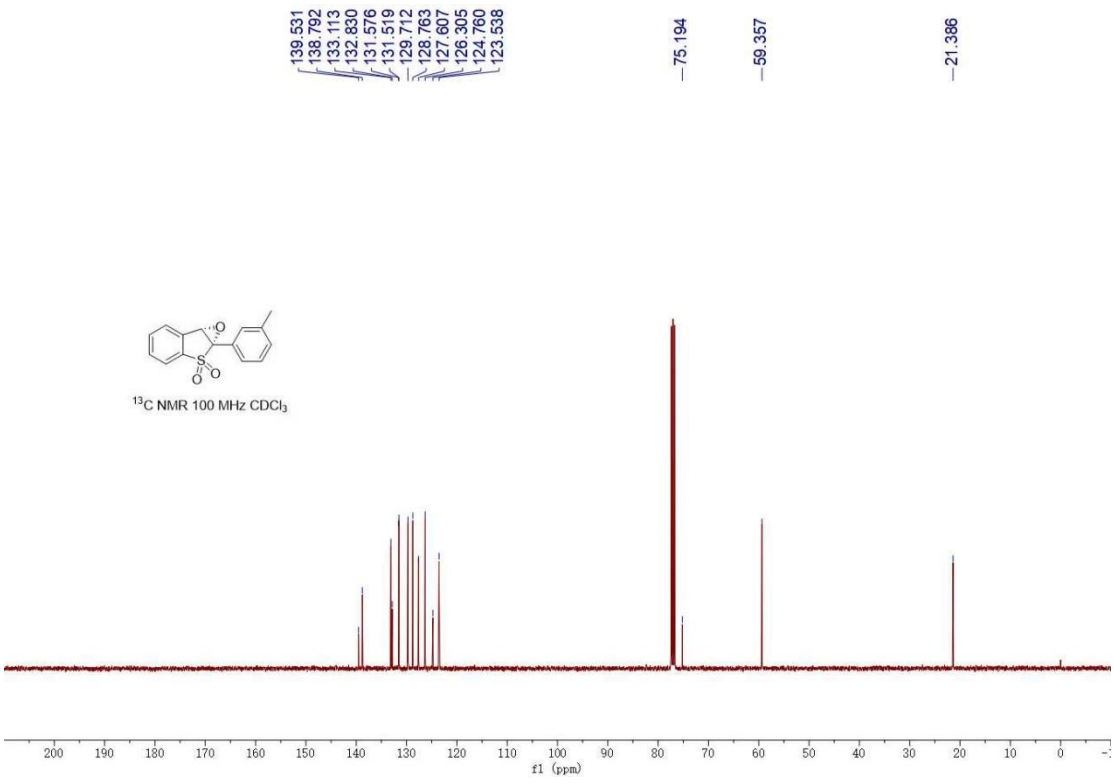
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	13.778	3751971	96.01	176791
2	W2489 ChB 220nm	18.705	155846	3.99	5710

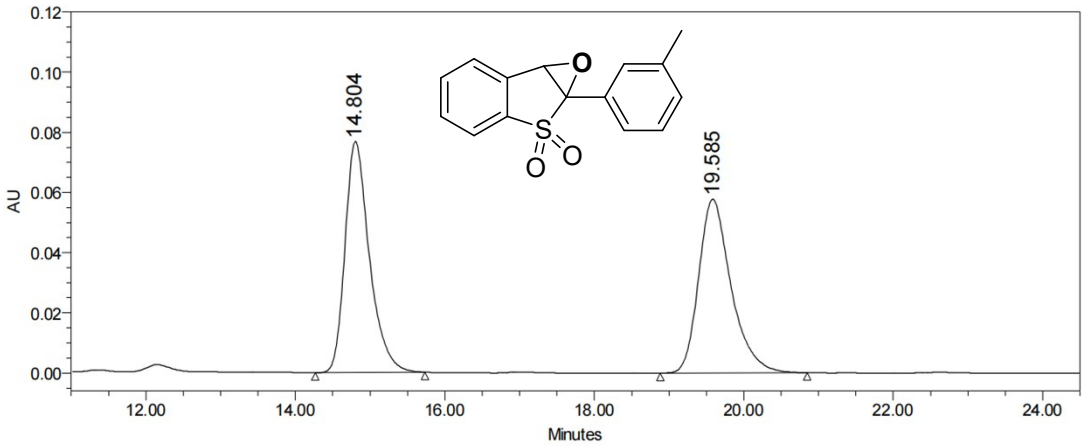
(1a*R*,6b*S*)-1a-(m-tolyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2k)



^{1}H NMR of **2k**



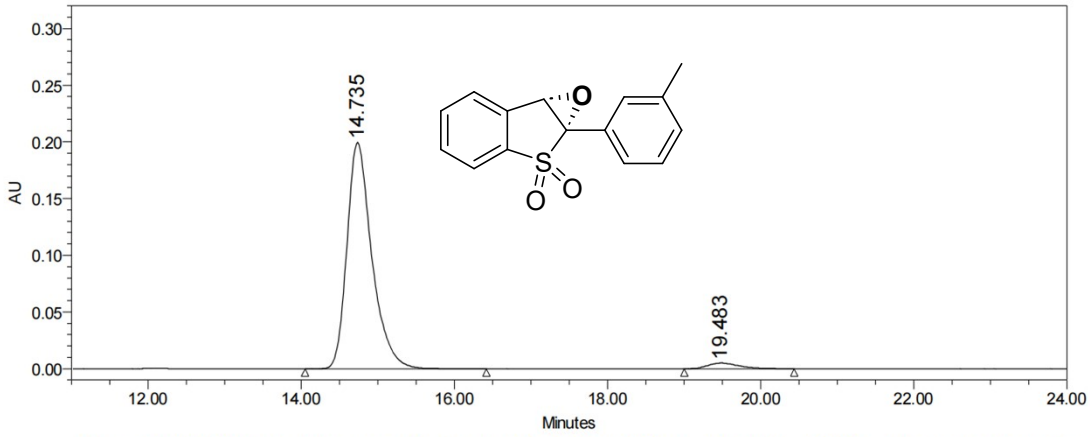
^{13}C NMR of **2k**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12381; Processing Method: sdffd

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	14.804	1741795	50.04	76835
2	W2489 ChB 220nm	19.585	1738860	49.96	57745

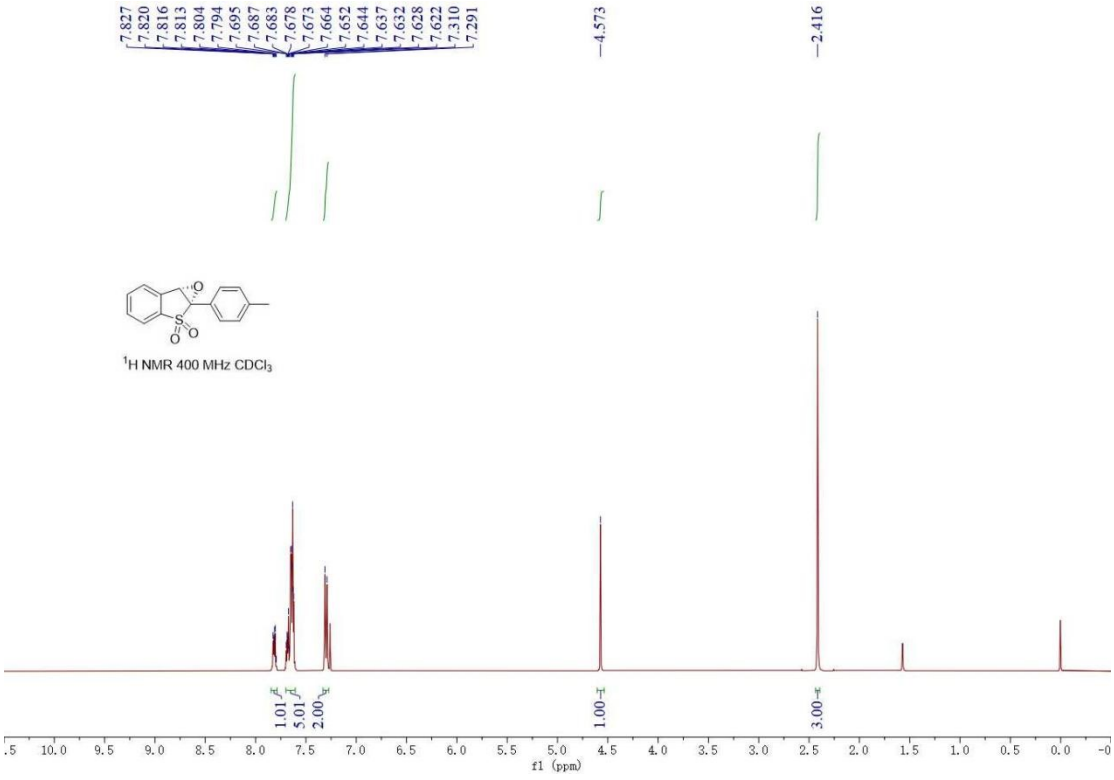


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12385; Processing Method: sdfasdf

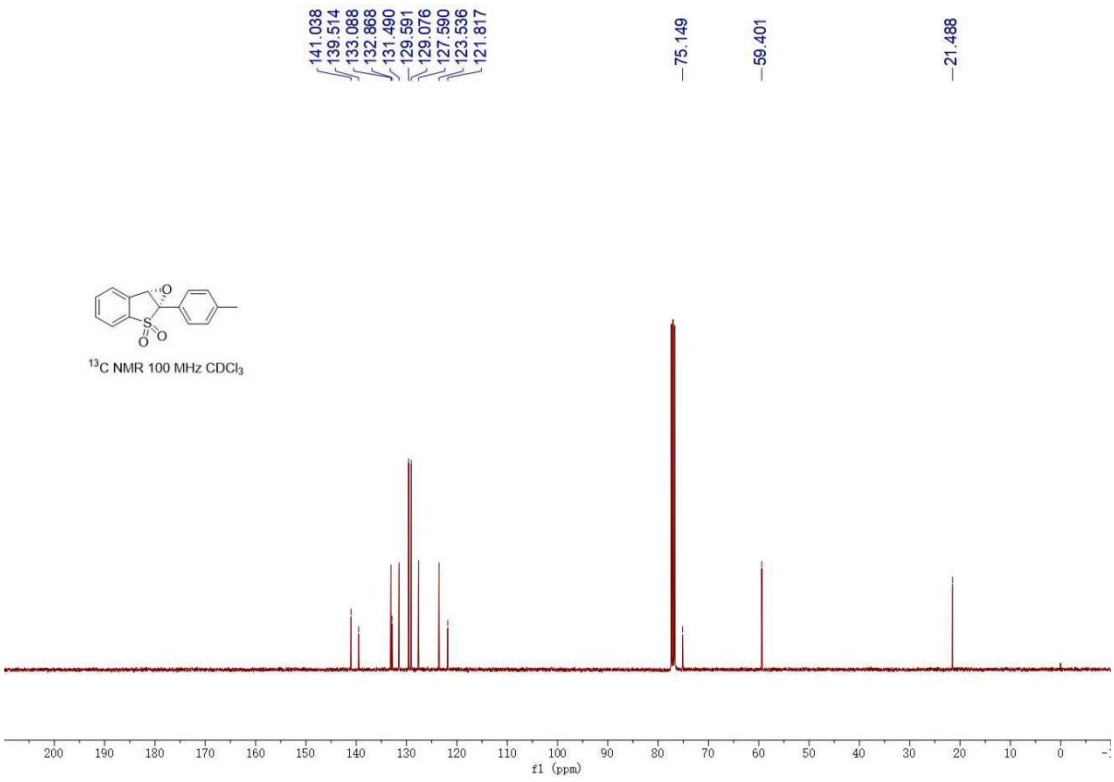
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	14.735	4522600	96.75	199880
2	W2489 ChB 220nm	19.483	151690	3.25	5133

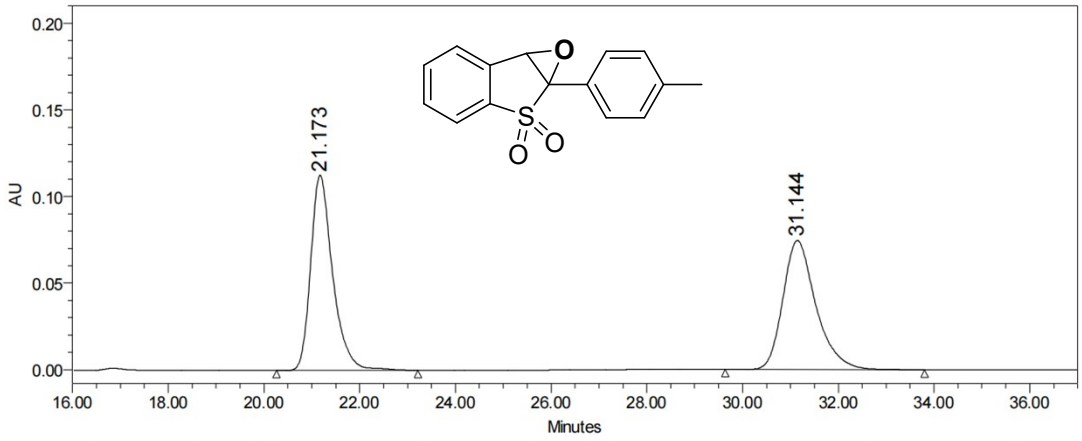
(1a*R*,6b*S*)-1a-(p-tolyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2l)



^{1}H NMR of **2l**



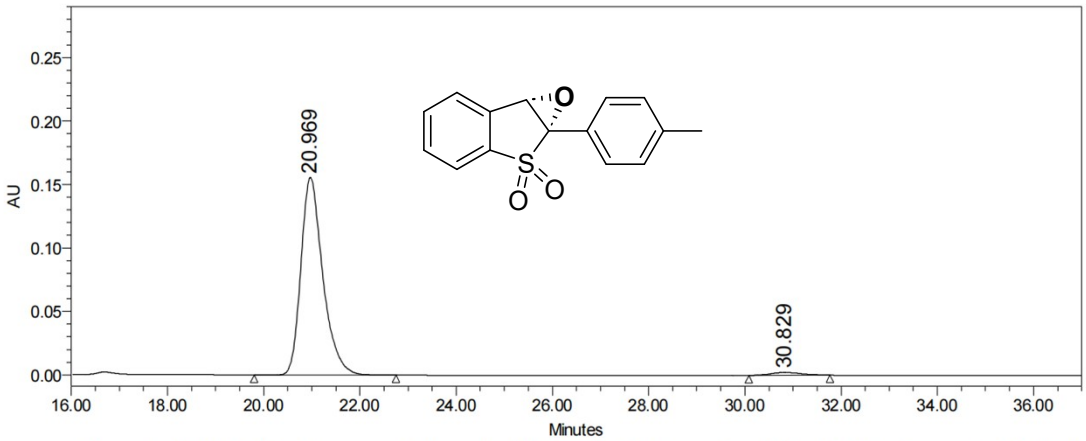
^{13}C NMR of **2l**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12646; Processing Method: 1

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	21.173	3594107	50.15	112608
2	W2489 ChB 220nm	31.144	3572071	49.85	74556

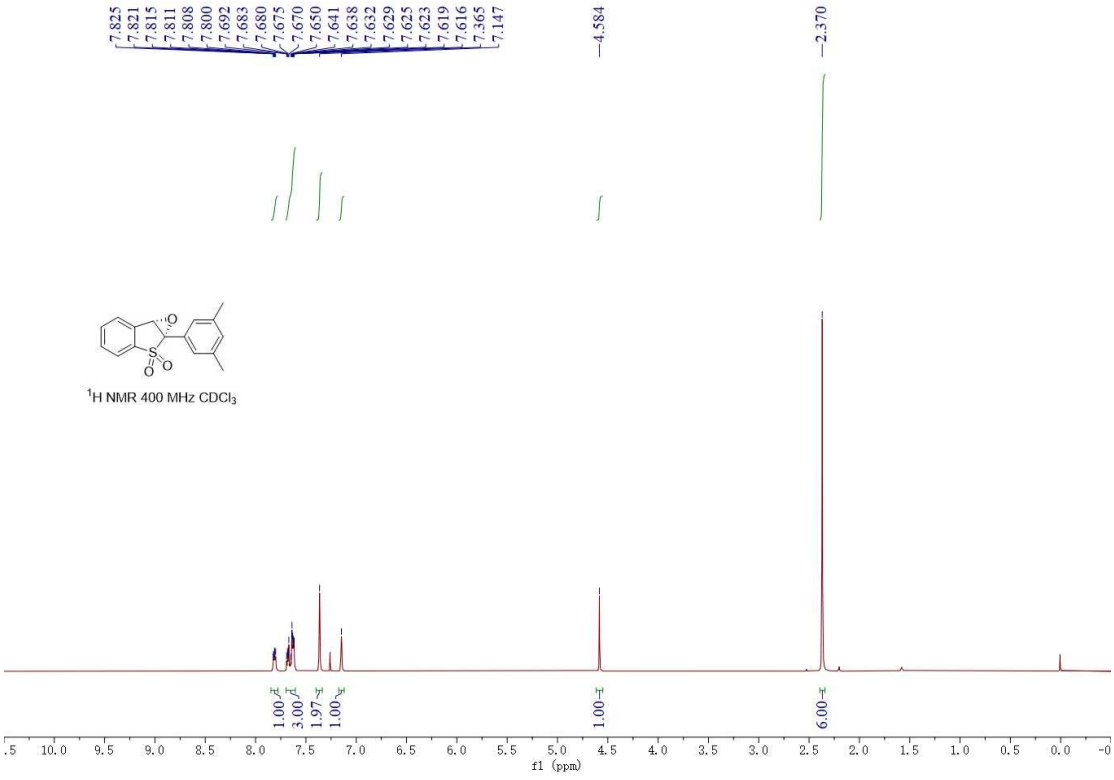


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12649; Processing Method: 1

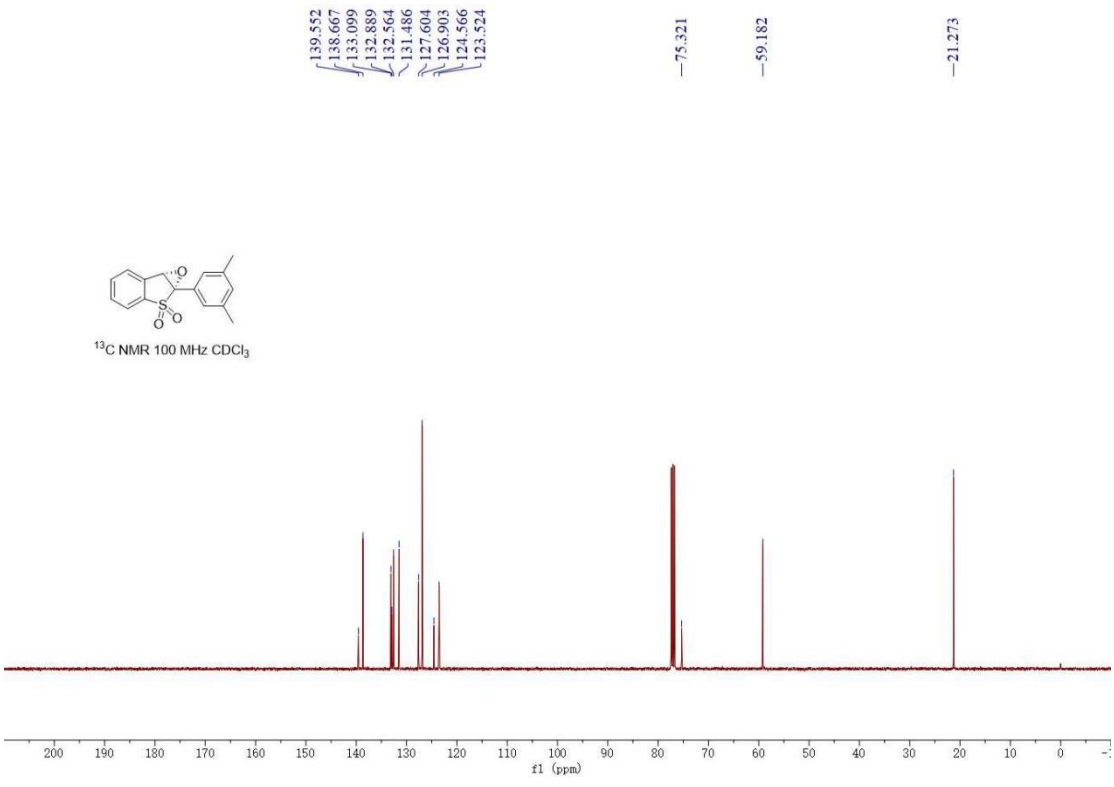
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	20.969	4933787	98.04	155839
2	W2489 ChB 220nm	30.829	98552	1.96	2287

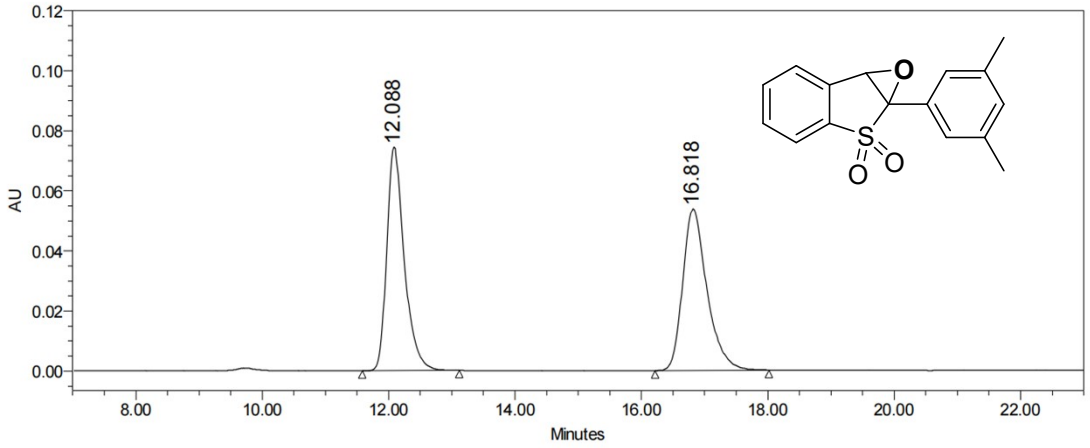
(1a*R*,6b*S*)-1a-(3,5-dimethylphenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2m)



^{1}H NMR of **2m**



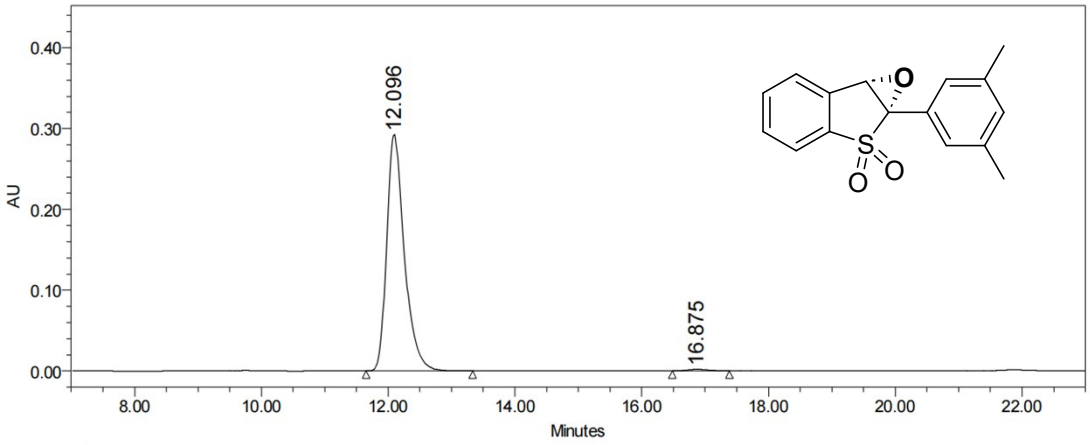
^{13}C NMR of **2m**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12394; Processing Method: asdfasdf

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	12.088	1428343	49.94	74416
2	W2489 ChB 220nm	16.818	1431786	50.06	53675

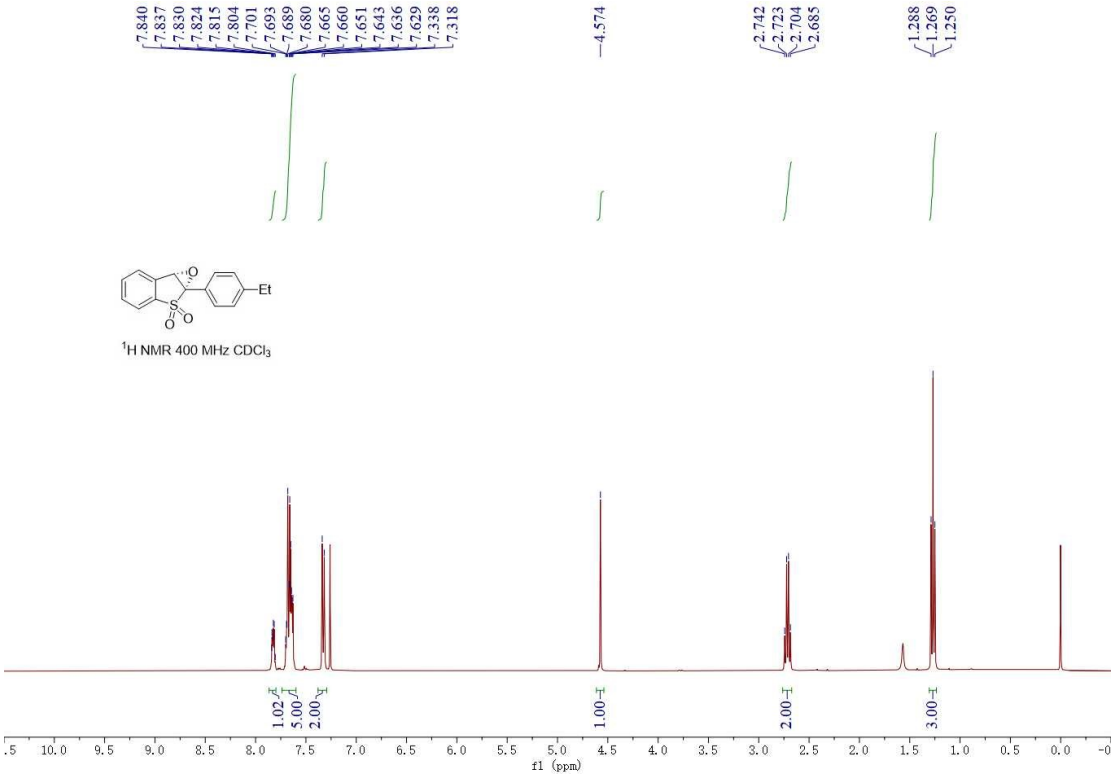


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12397; Processing Method: asdfasdfasdf

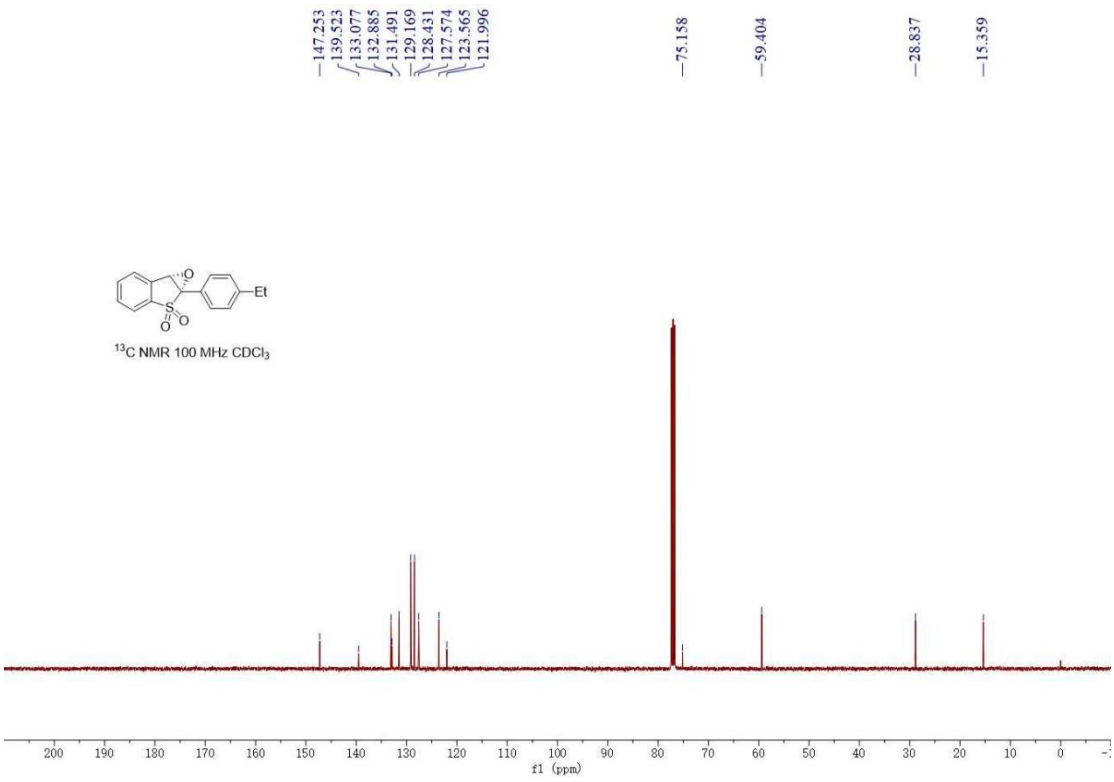
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	12.096	5663017	99.19	292853
2	W2489 ChB 220nm	16.875	46336	0.81	1841

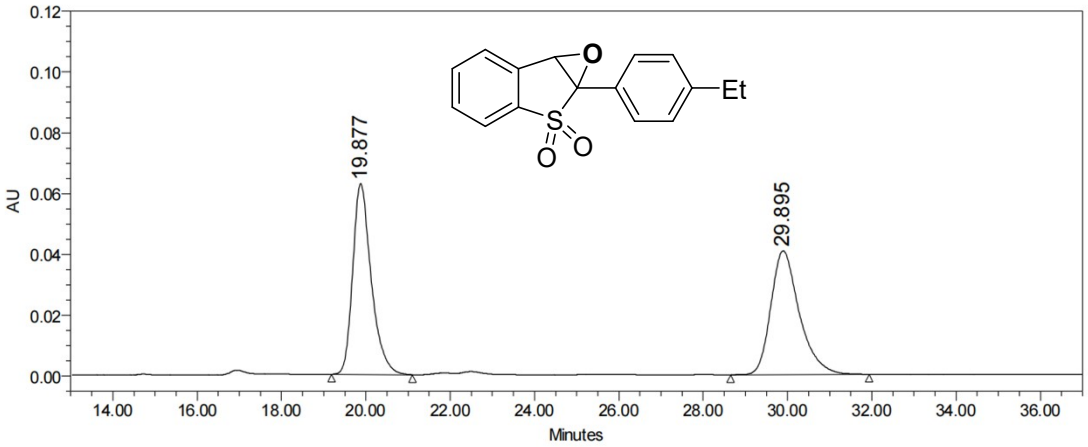
(1a*R*,6b*S*)-1a-(4-ethylphenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2n)



^{1}H NMR of **2n**



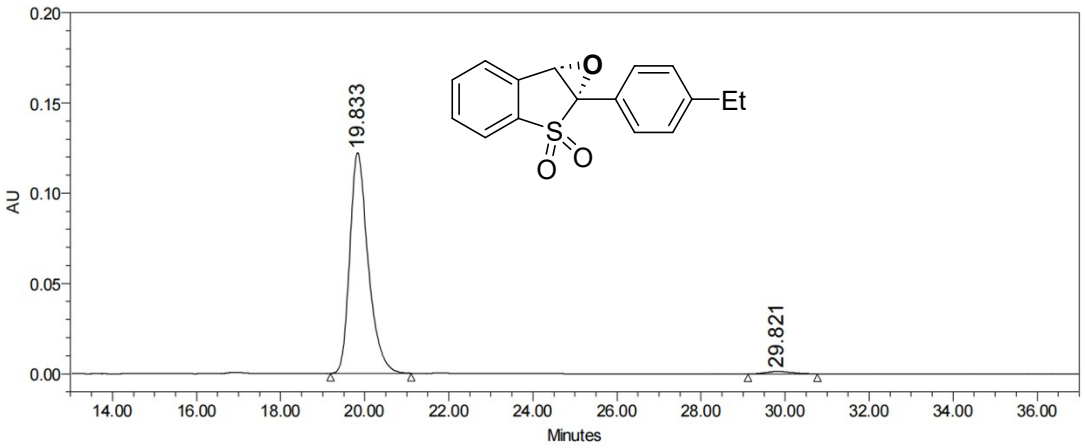
^{13}C NMR of **2n**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12400; Processing Method: qwer

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	19.877	1912862	50.05	62733
2	W2489 ChB 220nm	29.895	1909328	49.95	40700

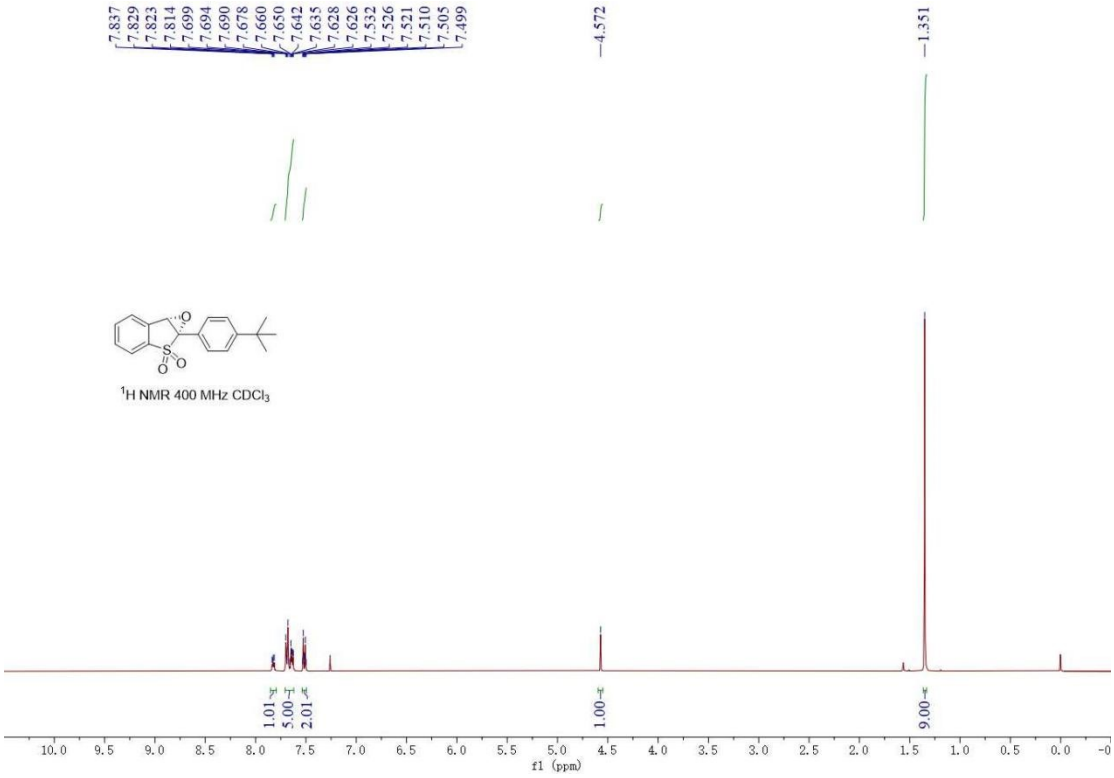


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12403; Processing Method: qwe

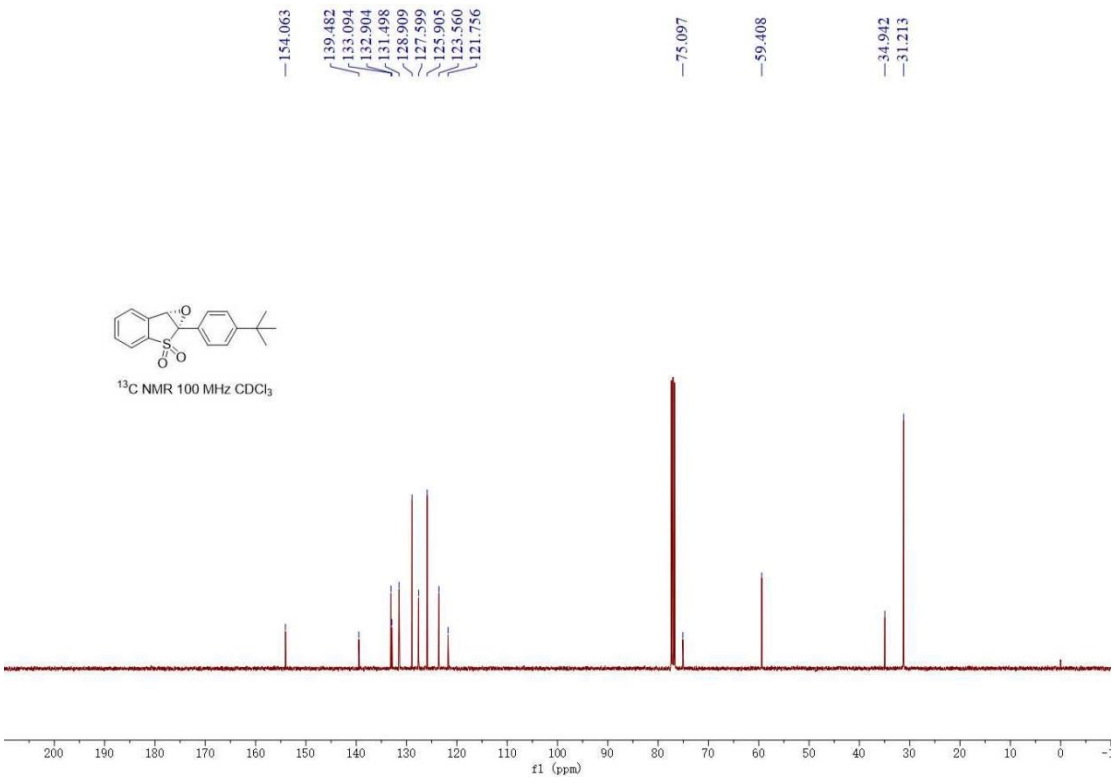
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	19.833	3709428	98.40	122228
2	W2489 ChB 220nm	29.821	60254	1.60	1371

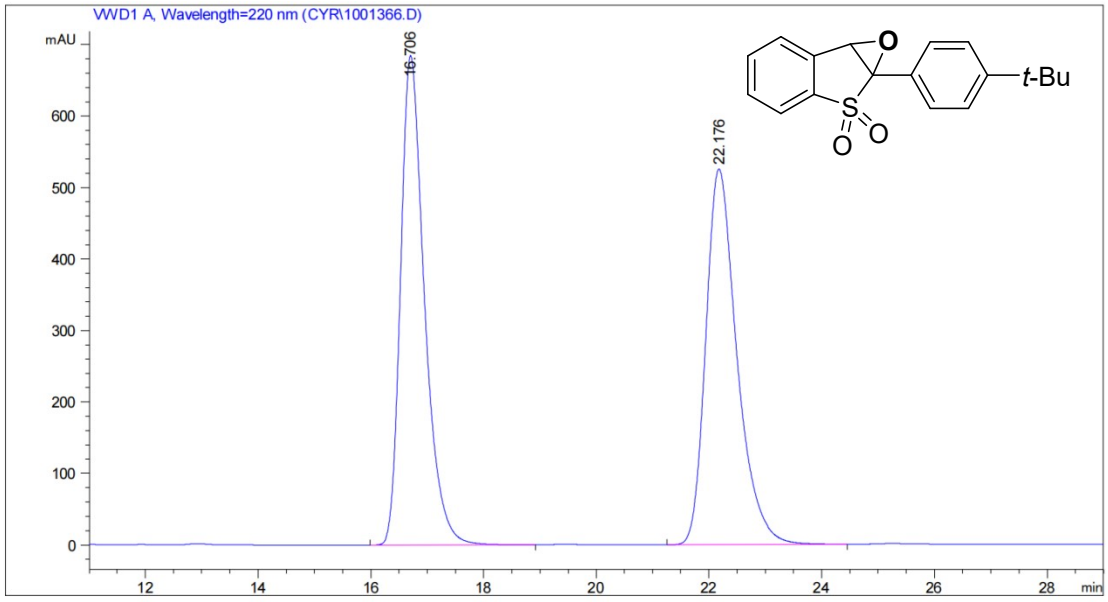
(1a*R*,6b*S*)-1a-(4-(tert-butyl)phenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2o)



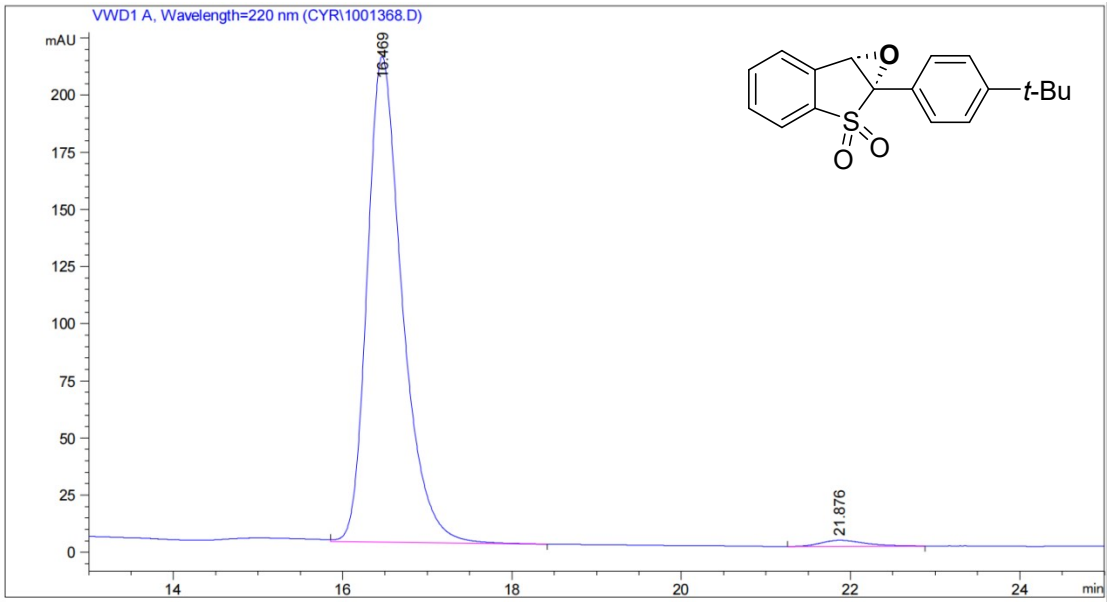
^{1}H NMR of **2o**



^{13}C NMR of **2o**

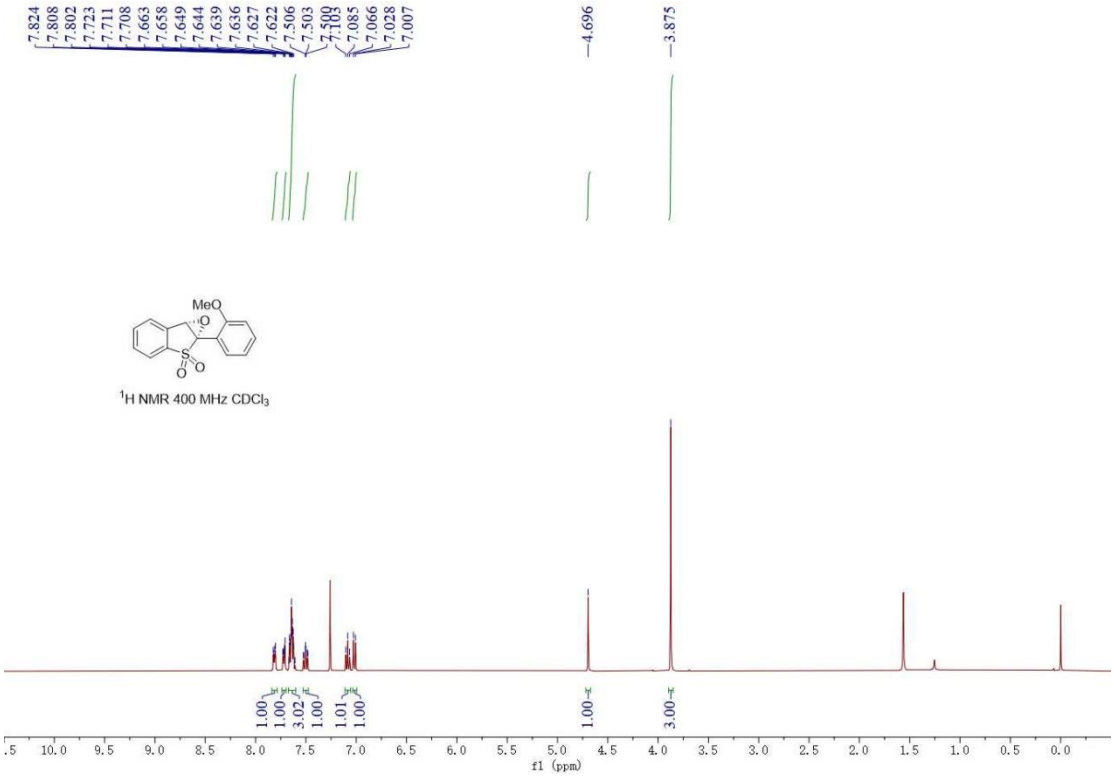


#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.706	BB	0.4406	2.00379e4	684.44714	49.9385
2	22.176	BB	0.5769	2.00872e4	525.57928	50.0615

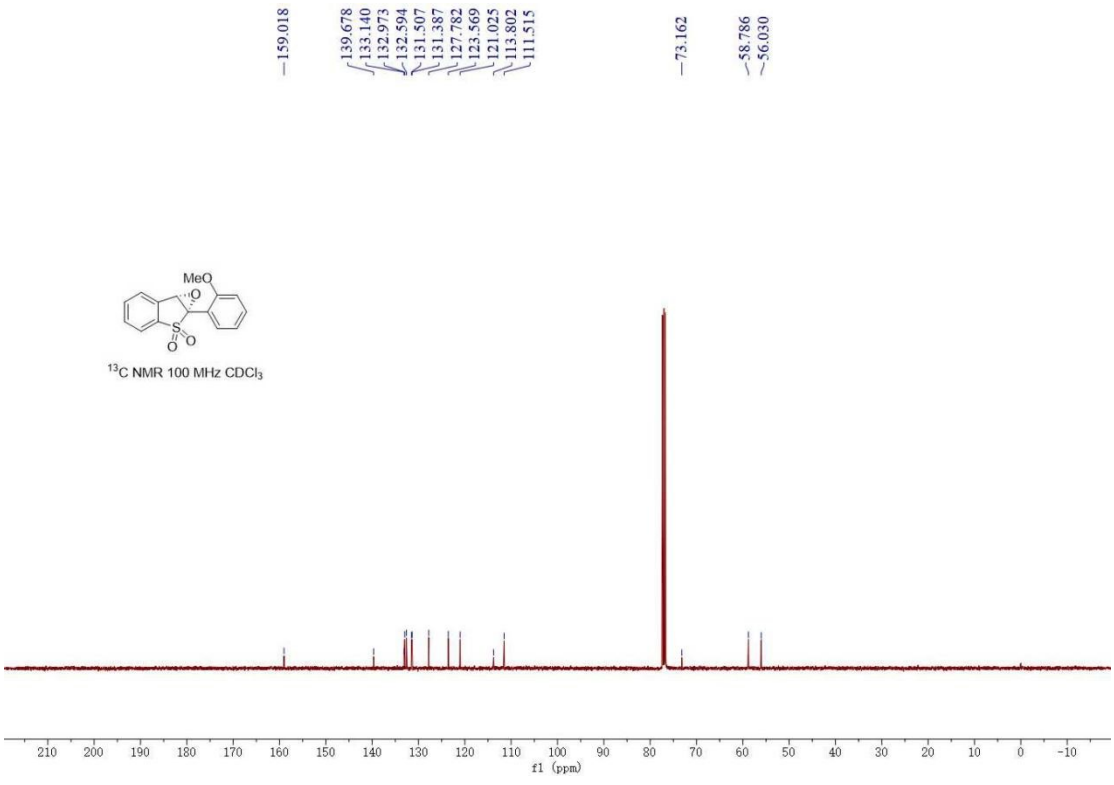


#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.469	VB	0.4349	6114.85010	212.36327	98.4944
2	21.876	BB	0.5307	93.47150	2.63272	1.5056

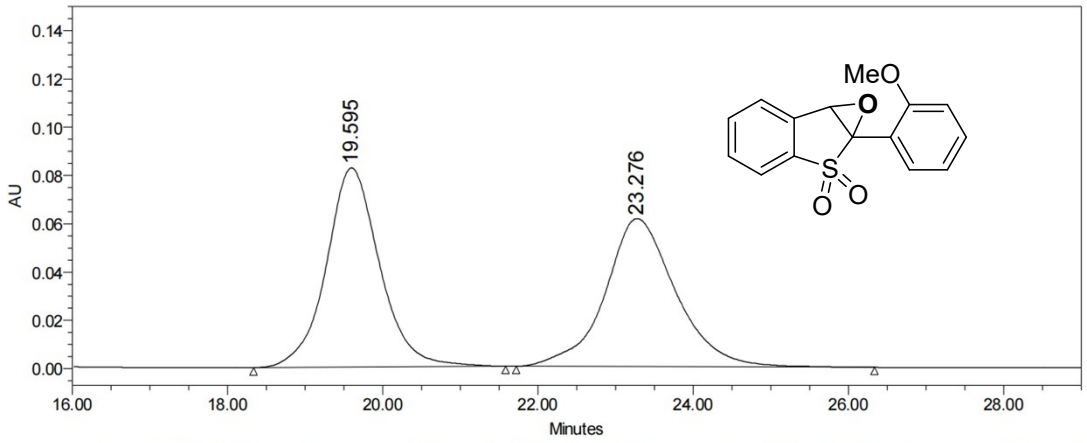
(1a*R*,6b*S*)-1a-(2-methoxyphenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2p)



^{1}H NMR of **2p**



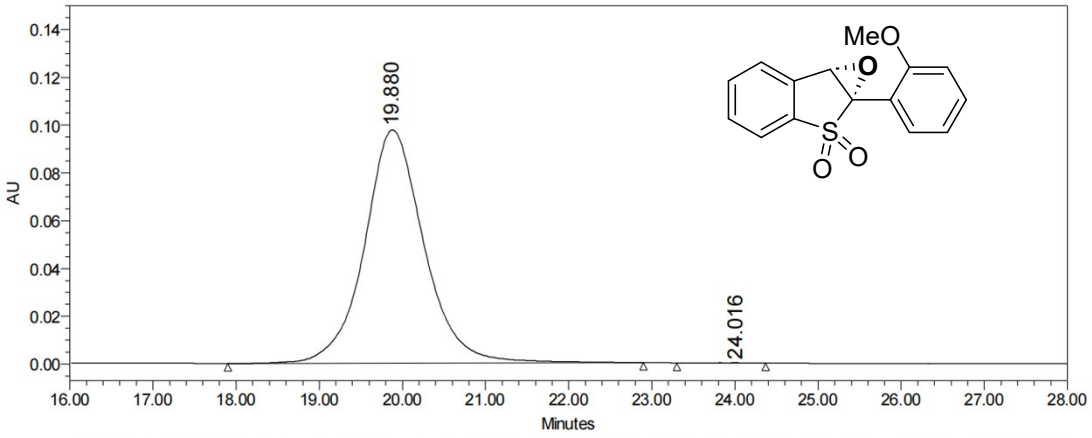
^{13}C NMR of **2p**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12515; Processing Method: SDF

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	19.595	3946276	50.42	82554
2	W2489 ChB 220nm	23.276	3880222	49.58	61307

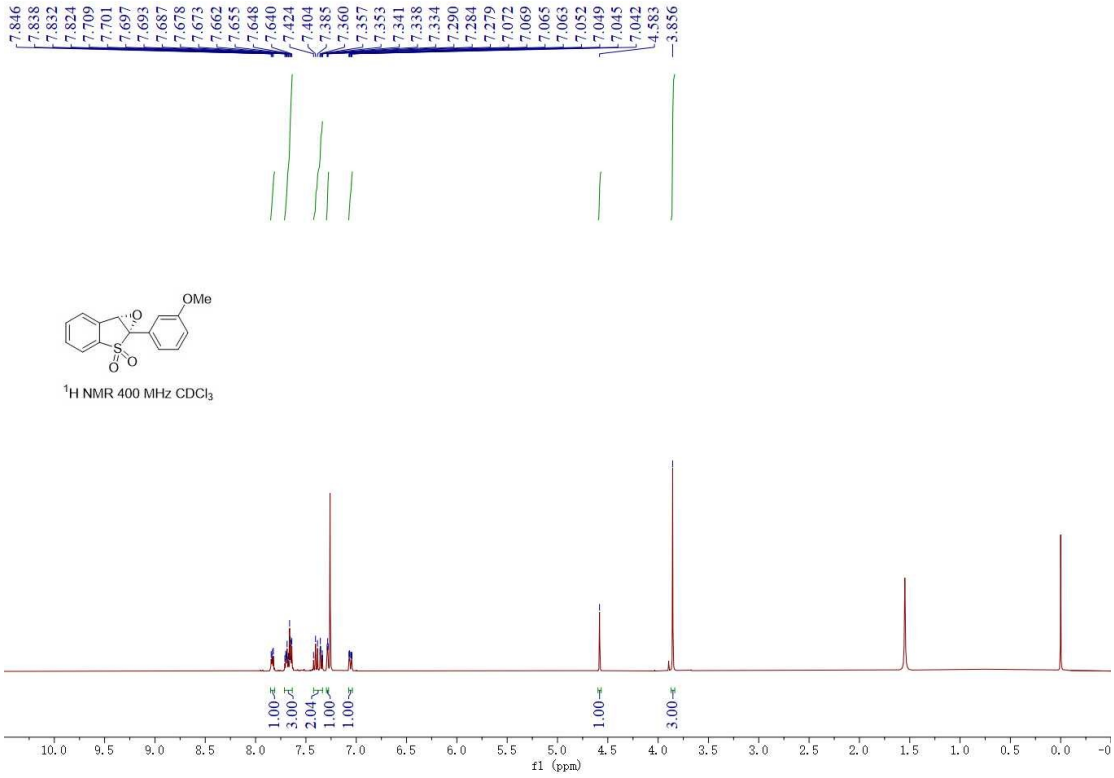


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12518; Processing Method: SDFASDF

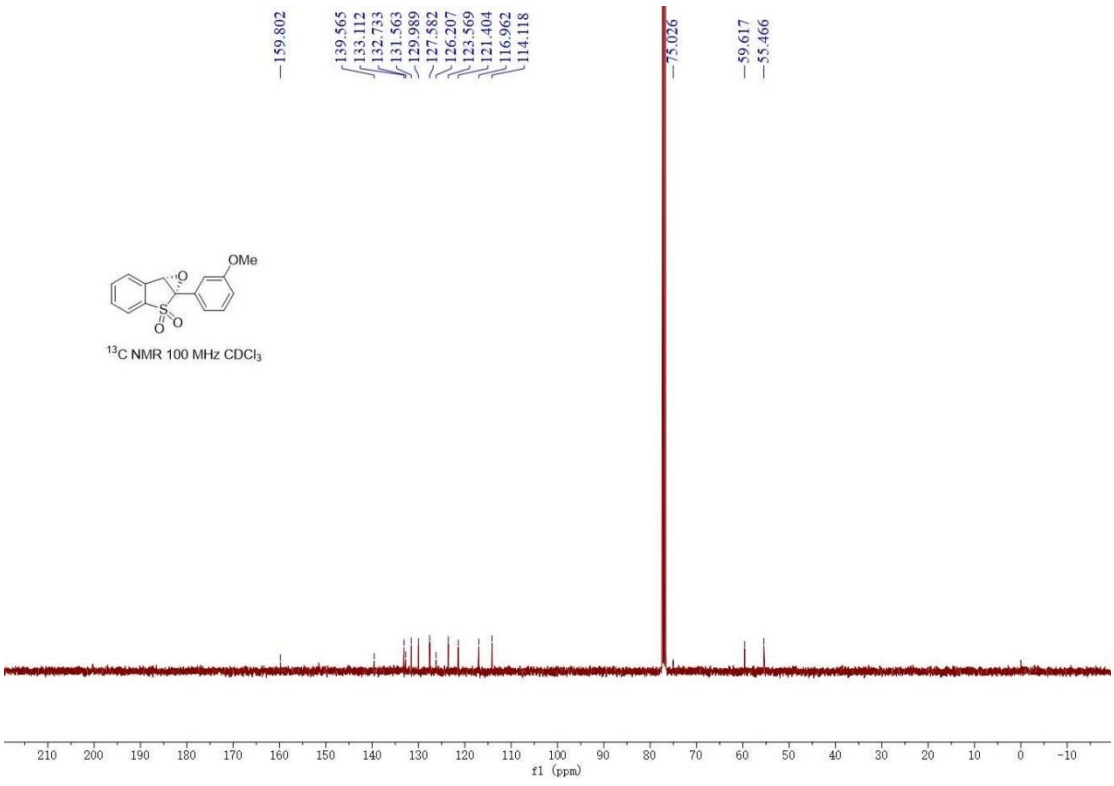
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	19.880	4880771	99.95	97706
2	W2489 ChB 220nm	24.016	2287	0.05	75

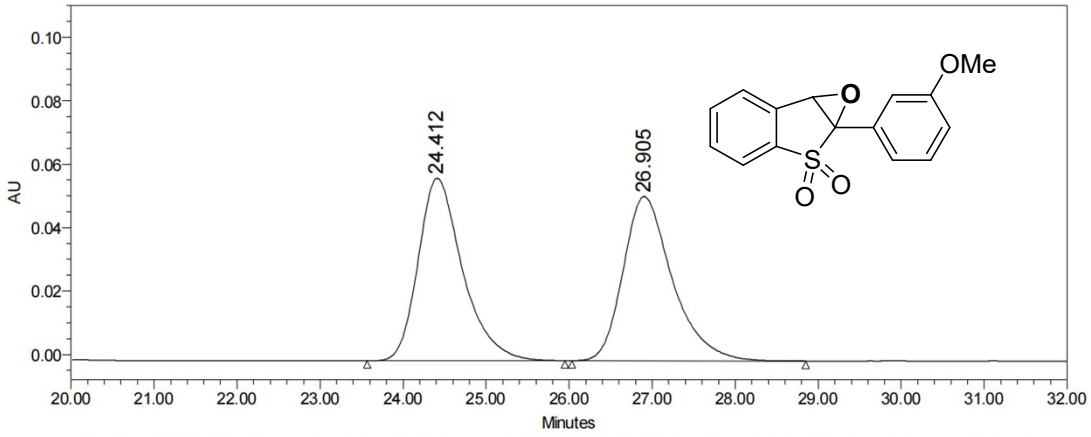
(1a*R*,6b*S*)-1a-(3-methoxyphenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2q)



^{1}H NMR of **2q**



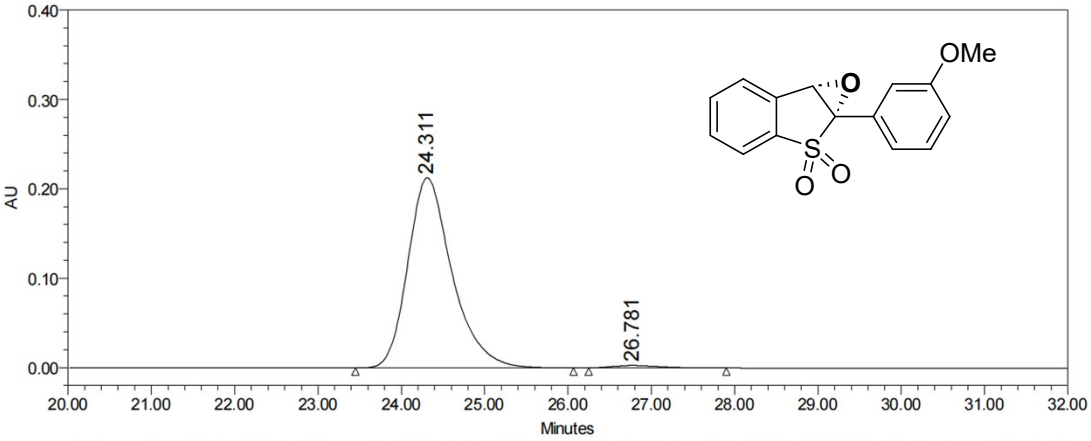
^{13}C NMR of **2q**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12752; Processing Method: XZCVZXCV

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	24.412	2135787	50.03	57598
2	W2489 ChB 220nm	26.905	2132864	49.97	51798

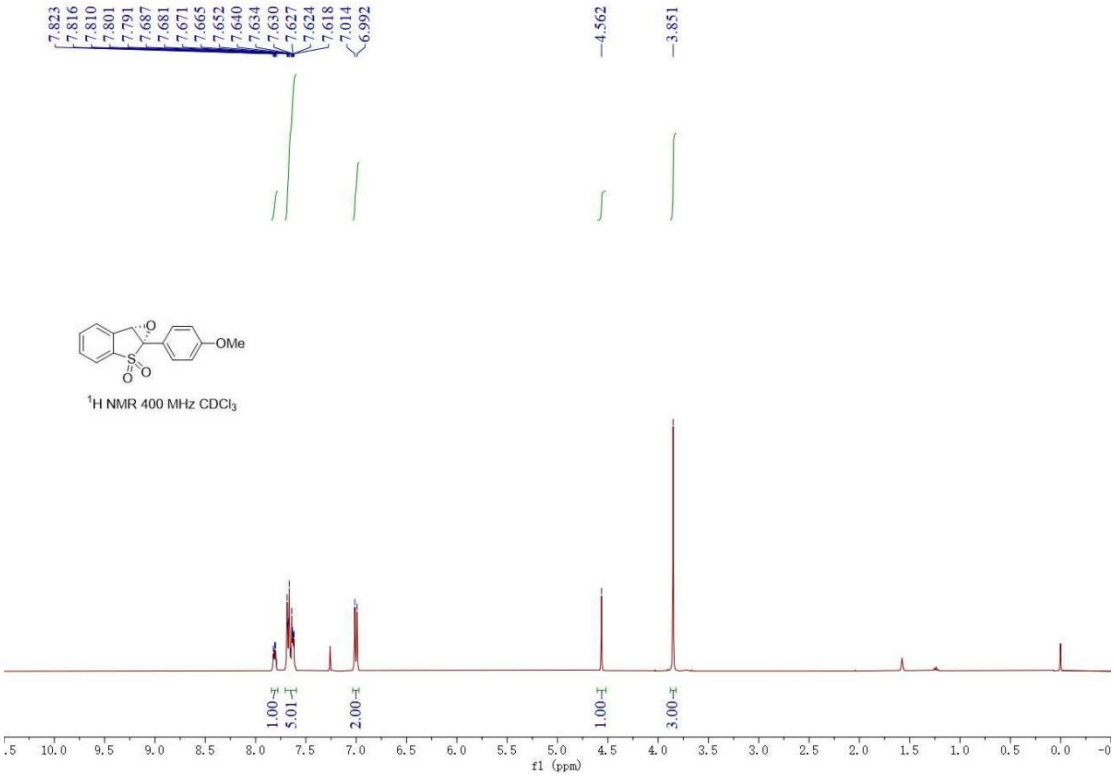


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12764; Processing Method: DFSFD

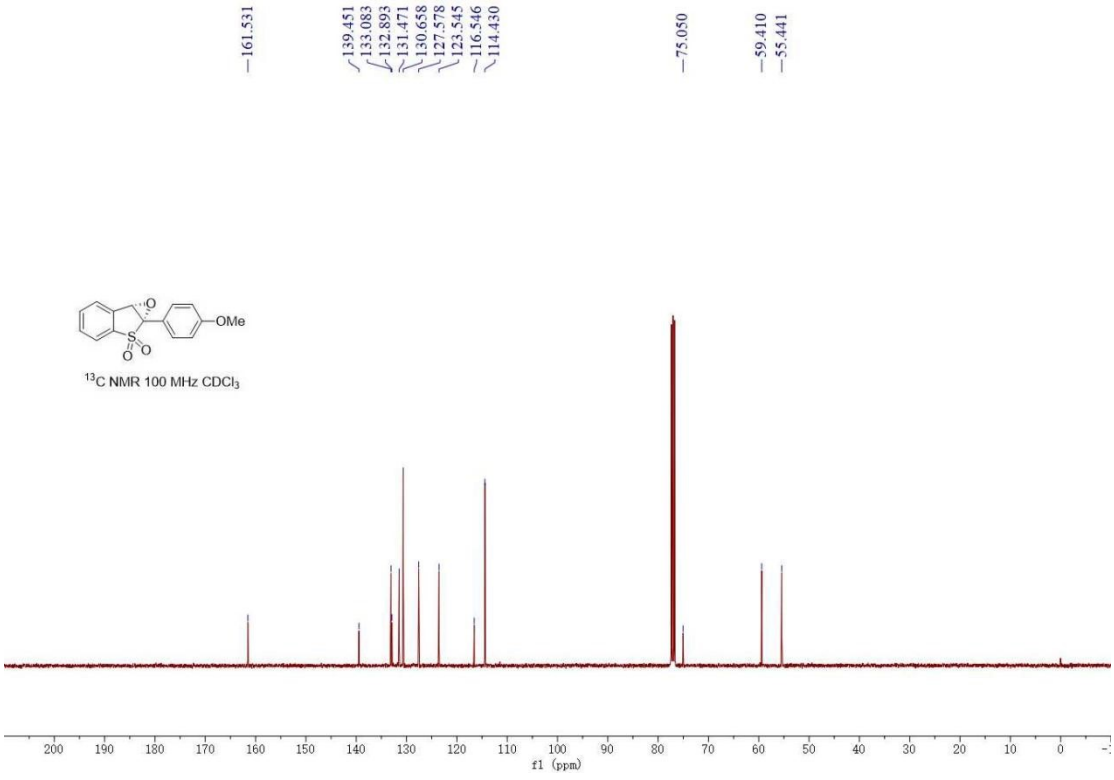
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	24.311	7854167	98.69	212735
2	W2489 ChB 220nm	26.781	103859	1.31	2696

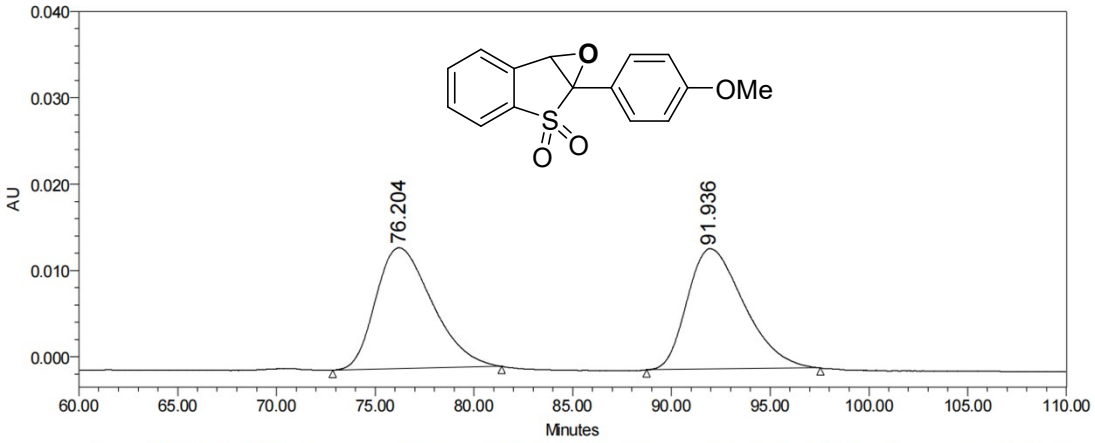
(1a*R*,6b*S*)-1a-(4-methoxyphenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2r)



^{1}H NMR of **2r**



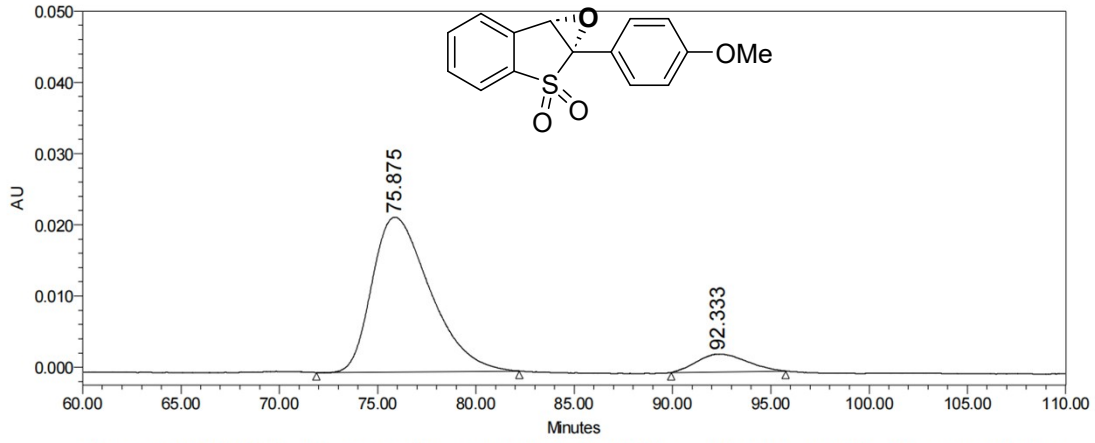
^{13}C NMR of **2r**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14010; Processing Method: 123456

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	76.204	2785299	50.00	13990
2	W2489 ChB 220nm	91.936	2784767	50.00	13937

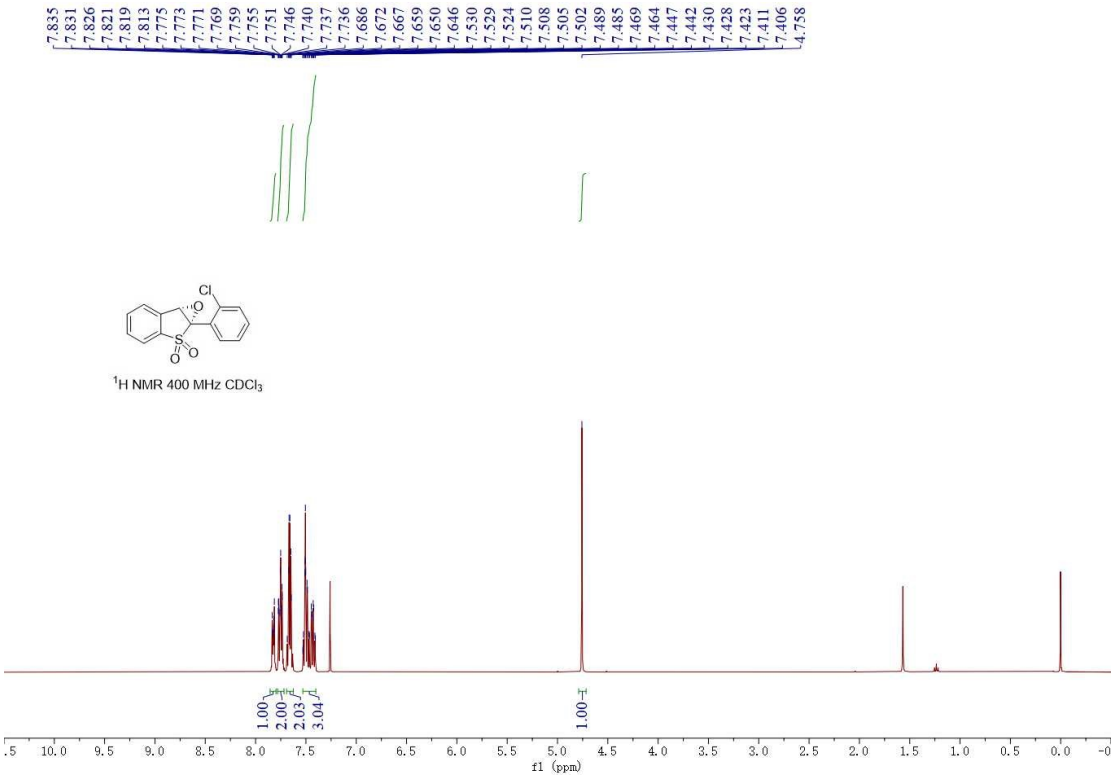


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14013; Processing Method: 12345

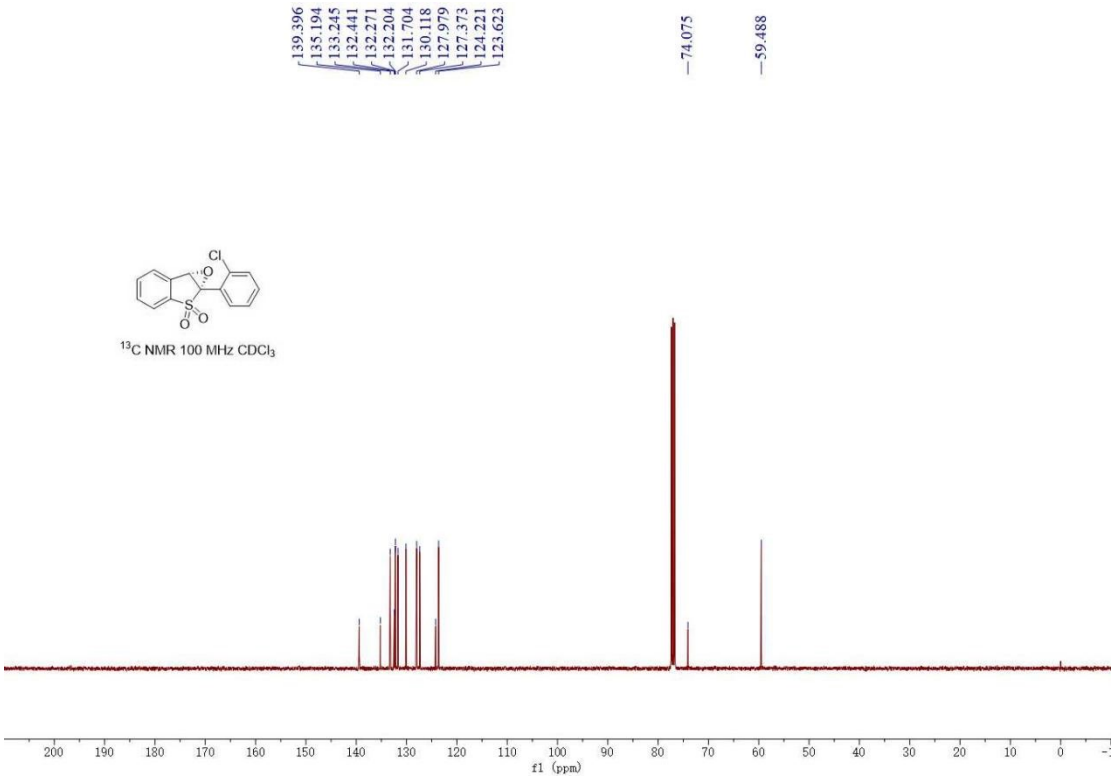
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	75.875	4444314	91.03	21729
2	W2489 ChB 220nm	92.333	438092	8.97	2504

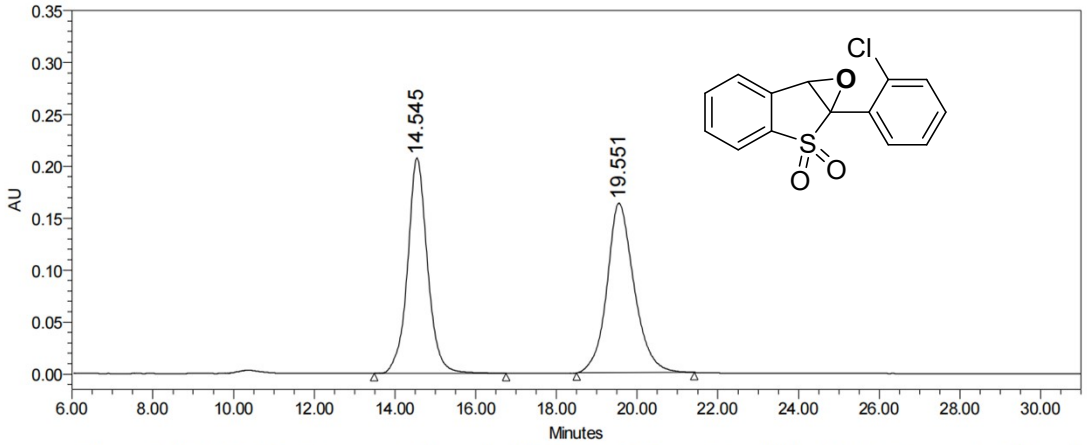
(1a*R*,6b*S*)-1a-(2-chlorophenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2s)



^{1}H NMR of **2s**



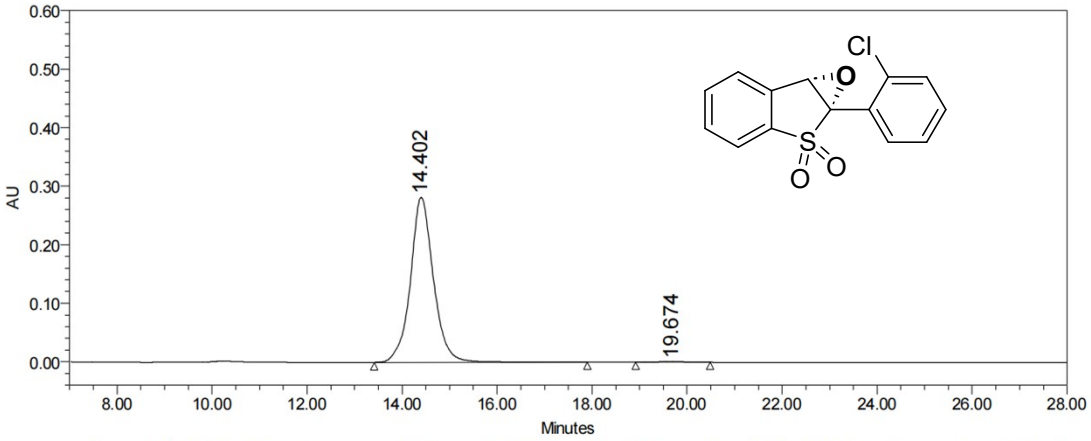
^{13}C NMR of **2s**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12774; Processing Method: fgdgggg

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	14.545	7102600	48.13	207541
2	W2489 ChB 220nm	19.551	7654985	51.87	163469

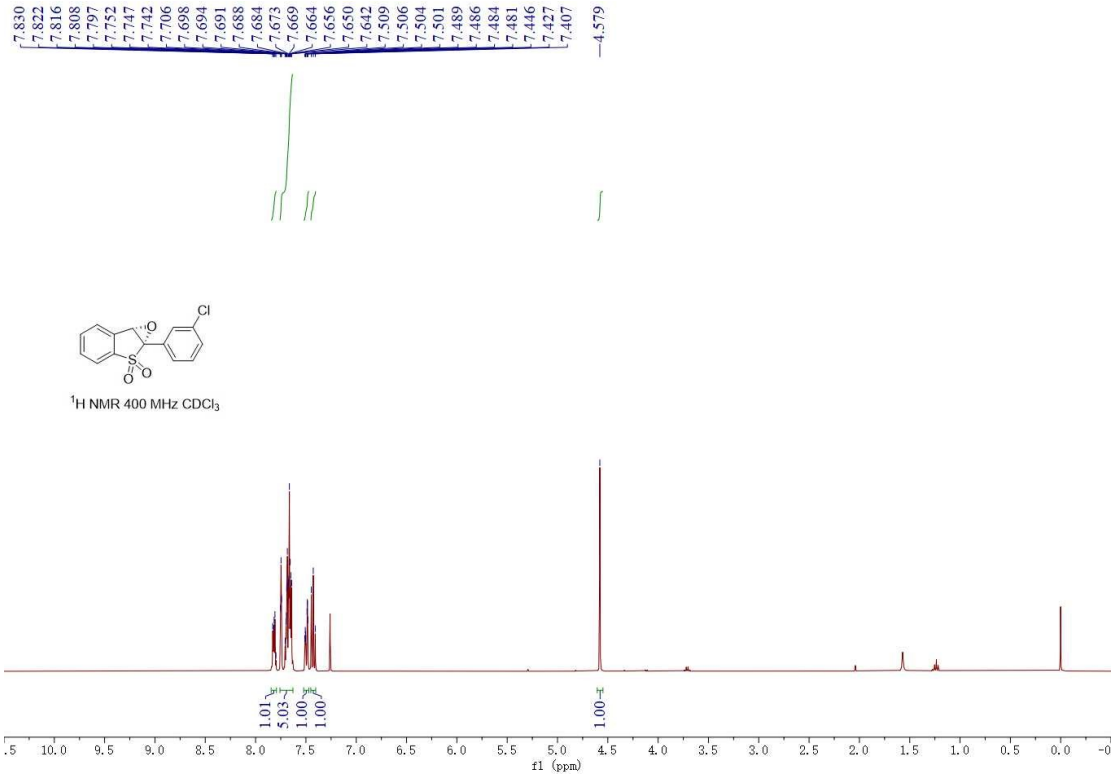


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12777; Processing Method: sdfasdf

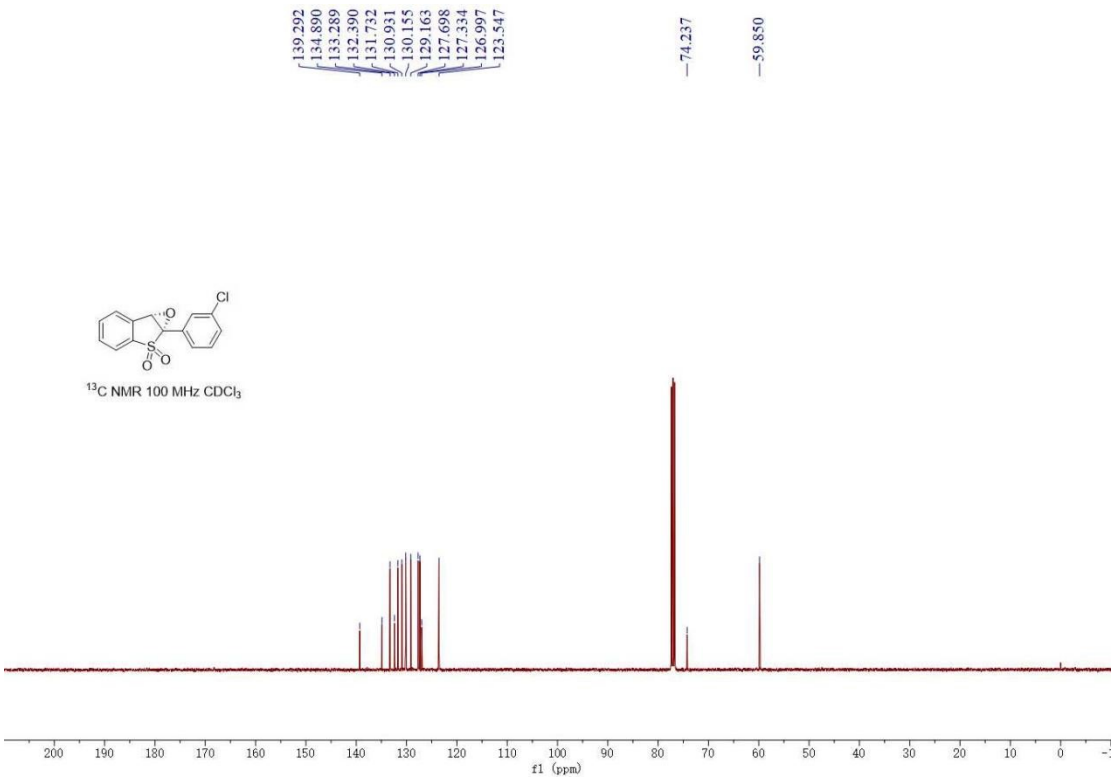
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	14.402	9503249	99.54	281789
2	W2489 ChB 220nm	19.674	43777	0.46	1020

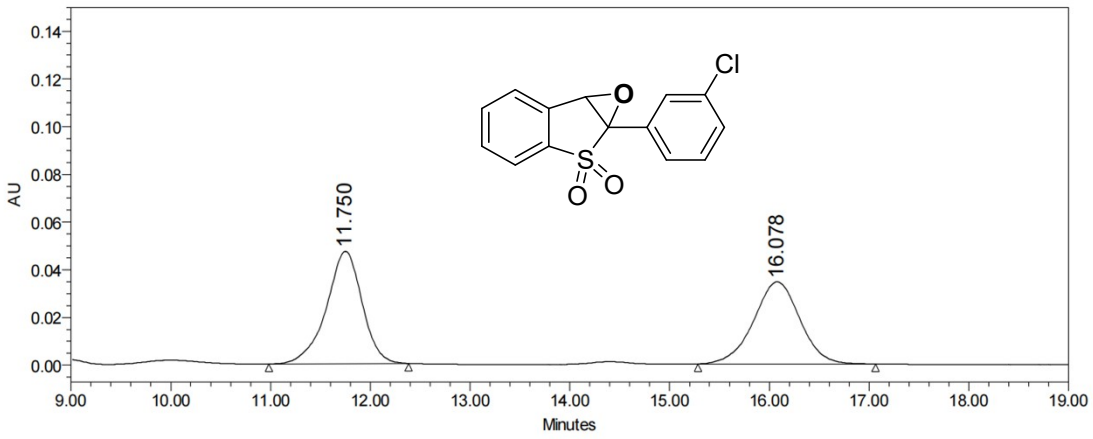
(1a*R*,6b*S*)-1a-(3-chlorophenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2t)



^{1}H NMR of **2t**



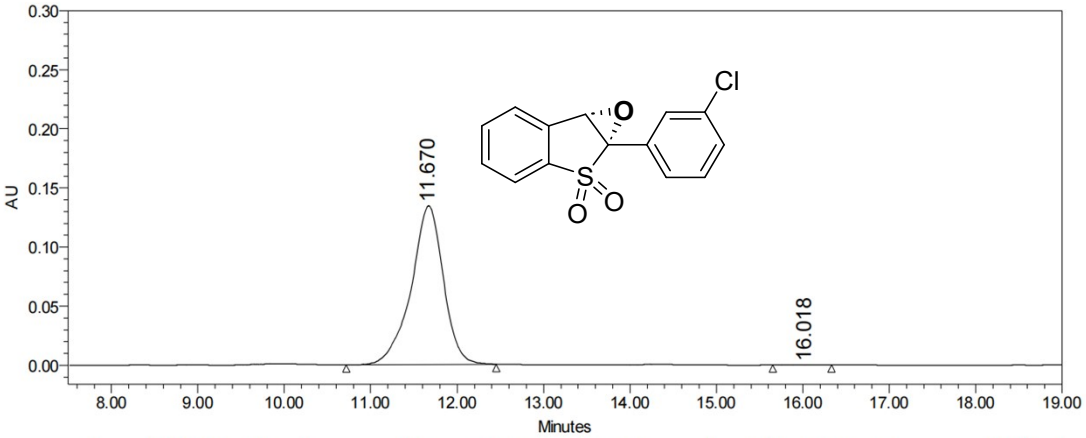
^{13}C NMR of **2t**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12847; Processing Method: dscav

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	11.750	1175324	51.26	47180
2	W2489 ChB 220nm	16.078	1117716	48.74	34500

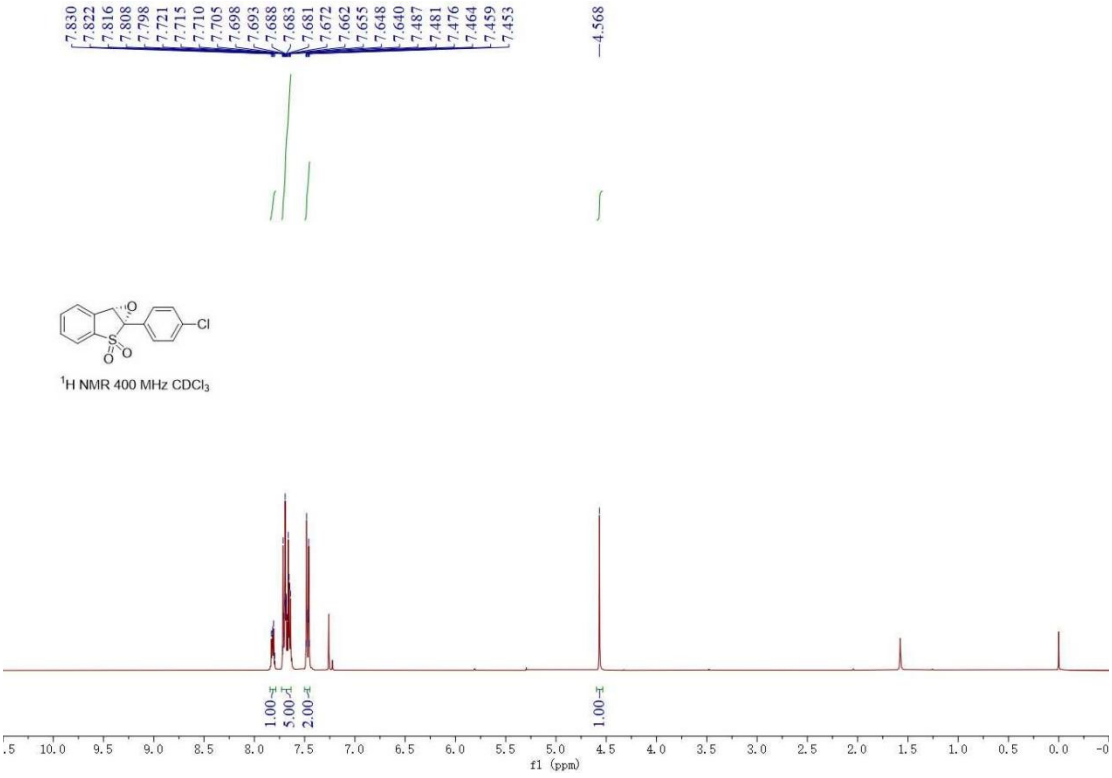


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12844; Processing Method: fgffgewrwr

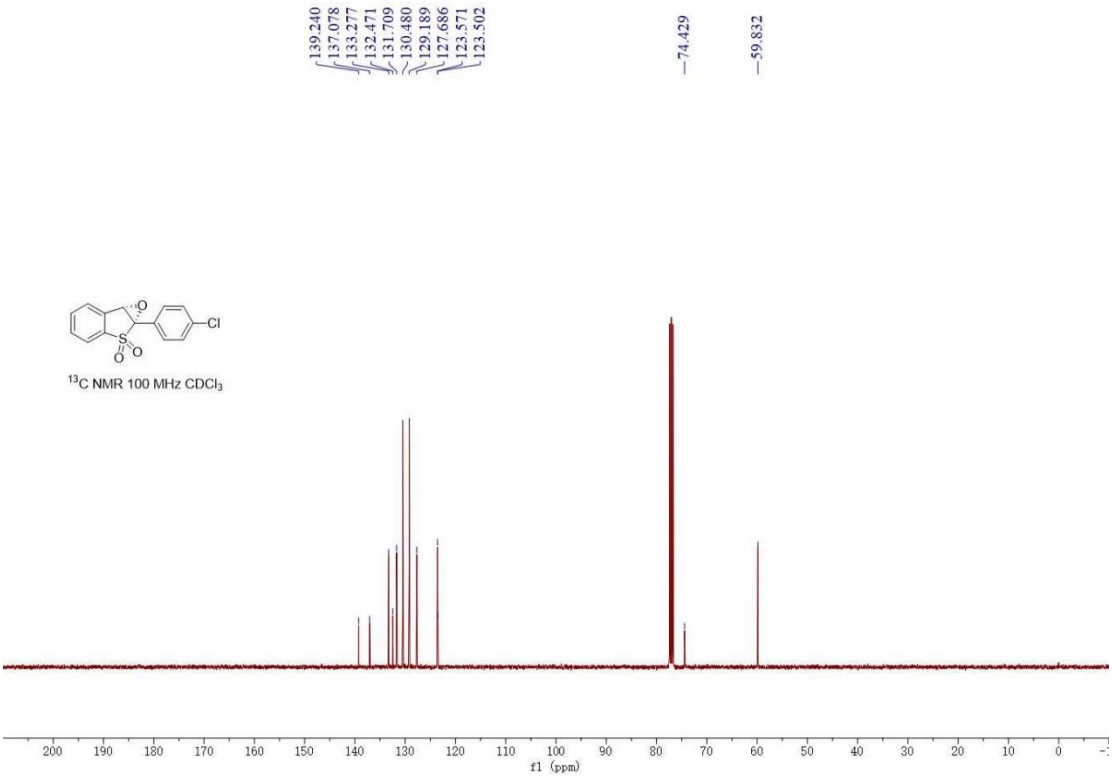
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	11.670	3476885	99.85	134295
2	W2489 ChB 220nm	16.018	5056	0.15	223

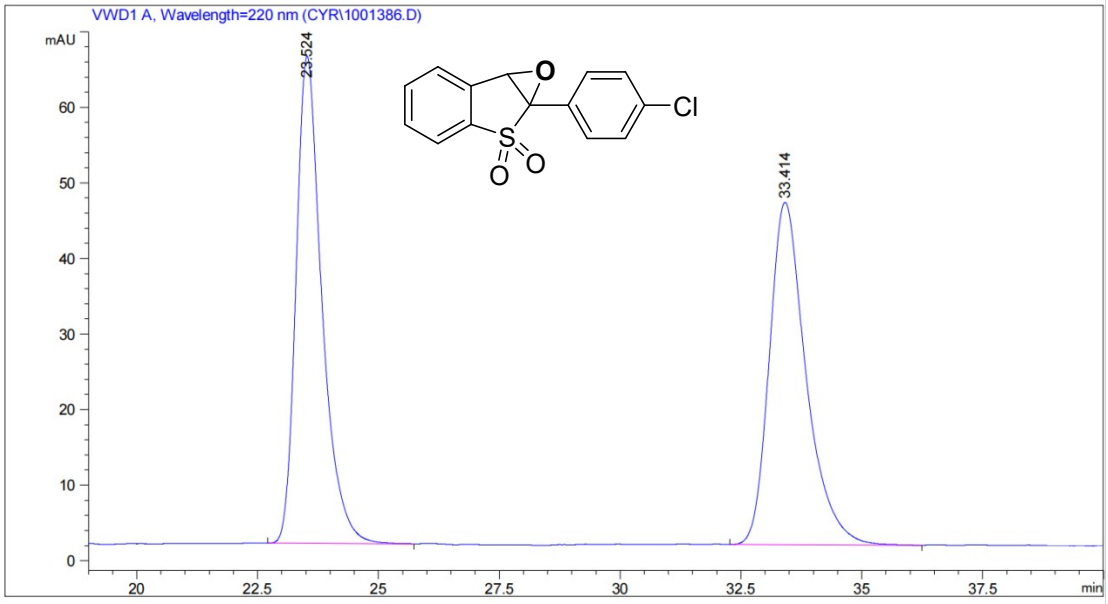
(1a*R*,6b*S*)-1a-(4-chlorophenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2u)



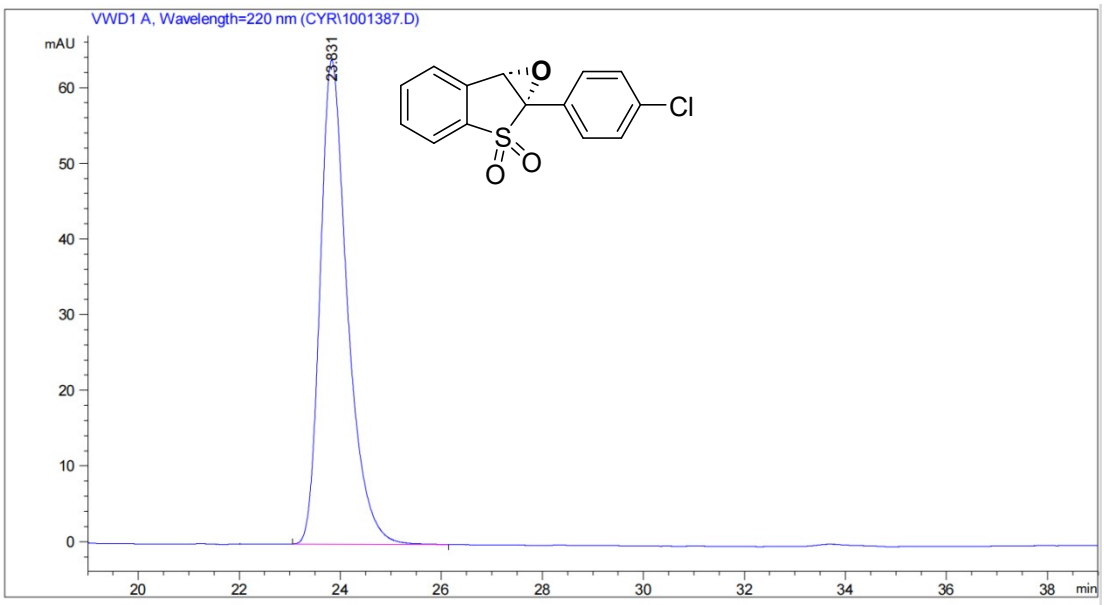
^{1}H NMR of **2u**



^{13}C NMR of **2u**

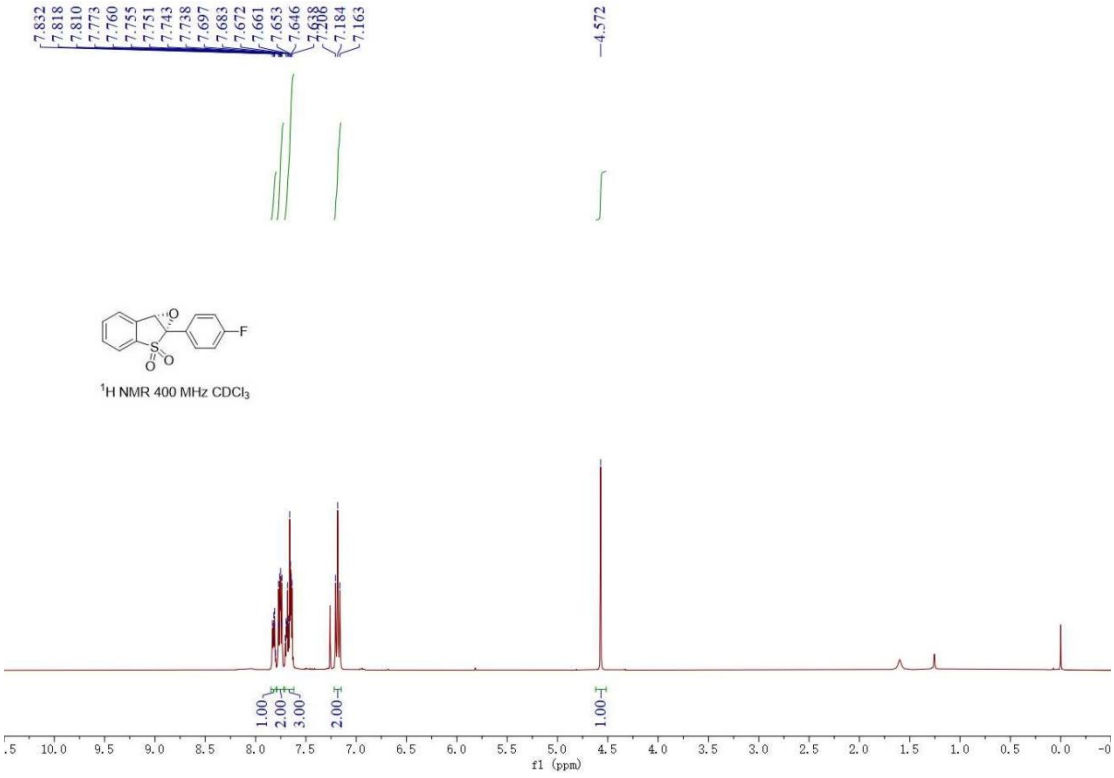


#	[min]		[min]	[mAU*s]	[mAU]	%
1	23.524	BB	0.5624	2400.07690	64.47083	50.0287
2	33.414	BB	0.7981	2397.32153	45.29262	49.9713

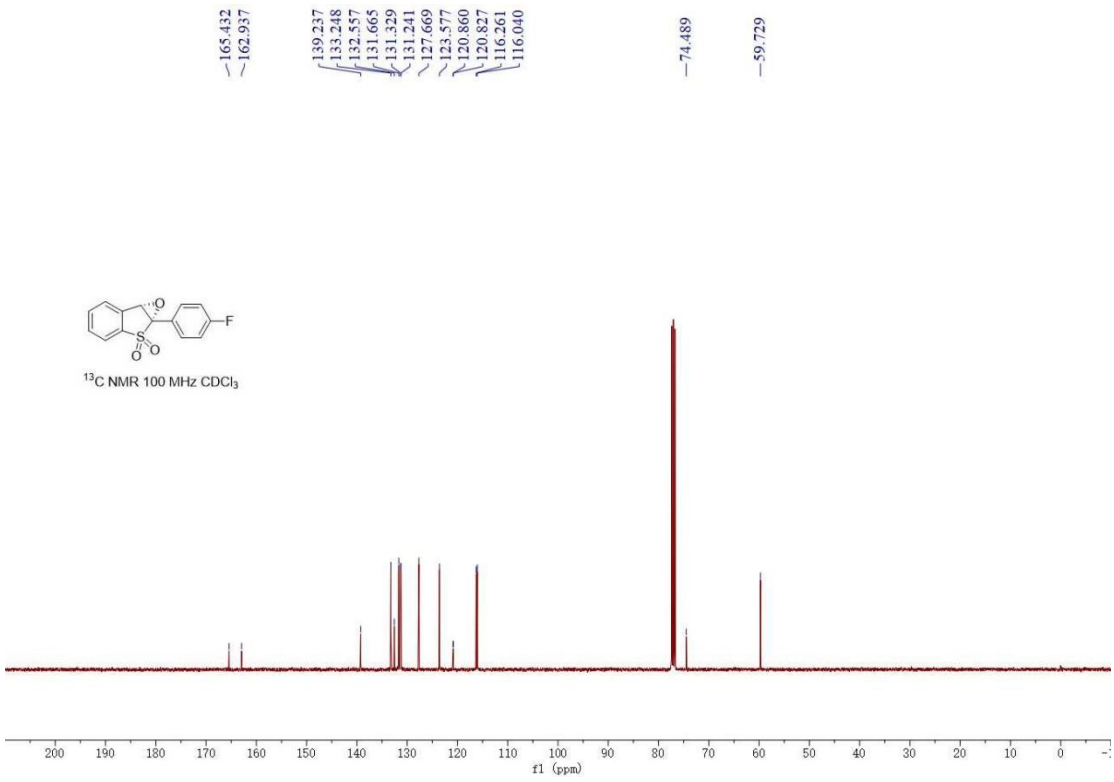


#	[min]		[min]	[mAU*s]	[mAU]	%
1	23.831	BB	0.5661	2402.49268	63.99822	100.0000

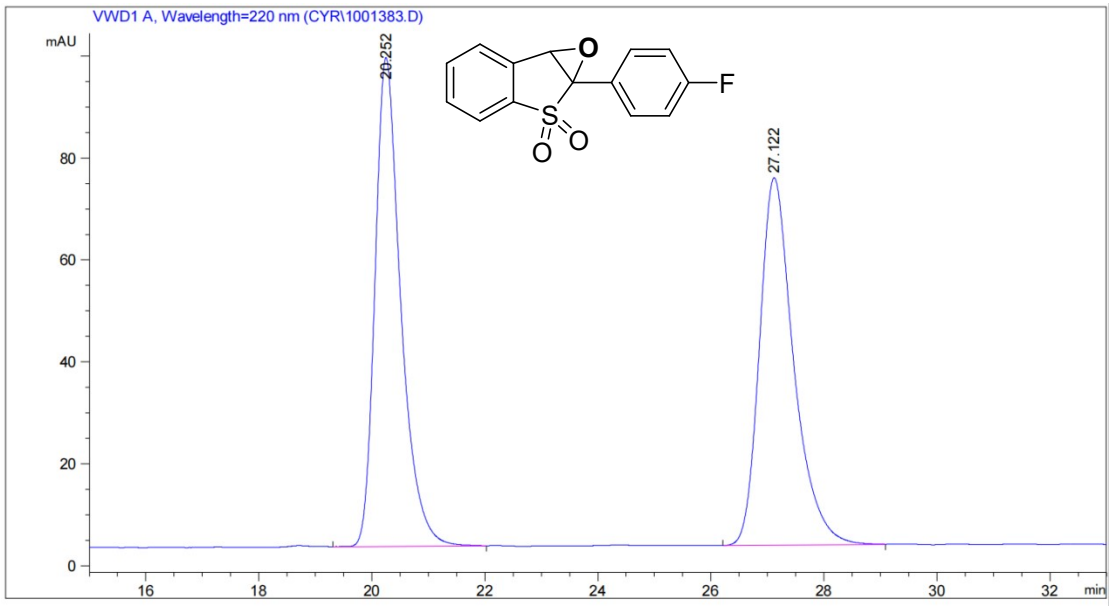
(1a*R*,6b*S*)-1a-(4-fluorophenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2v)



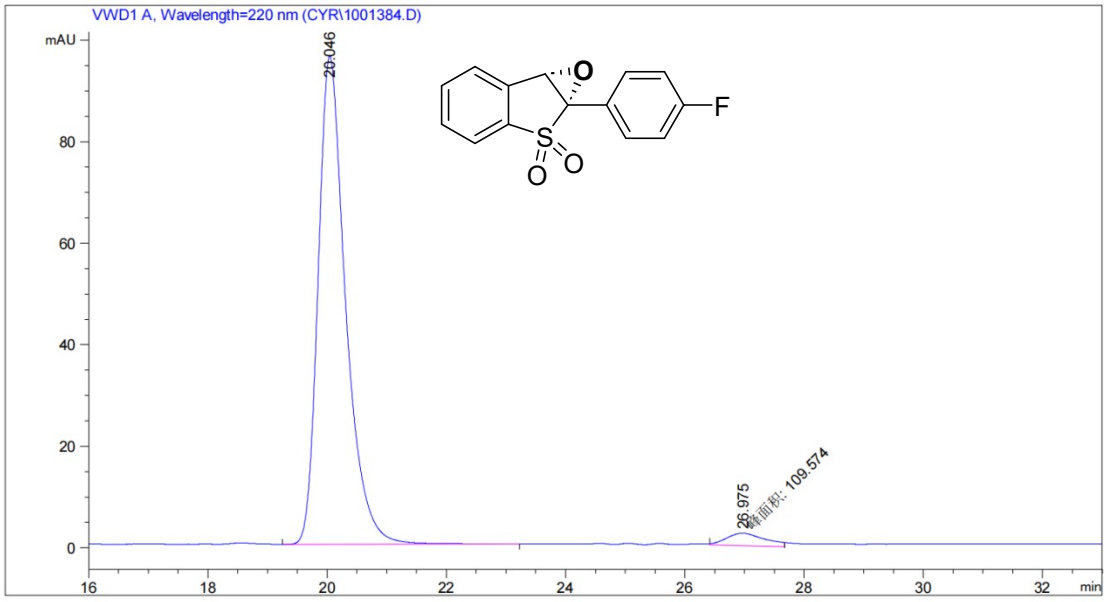
^{1}H NMR of **2v**



^{13}C NMR of **2v**

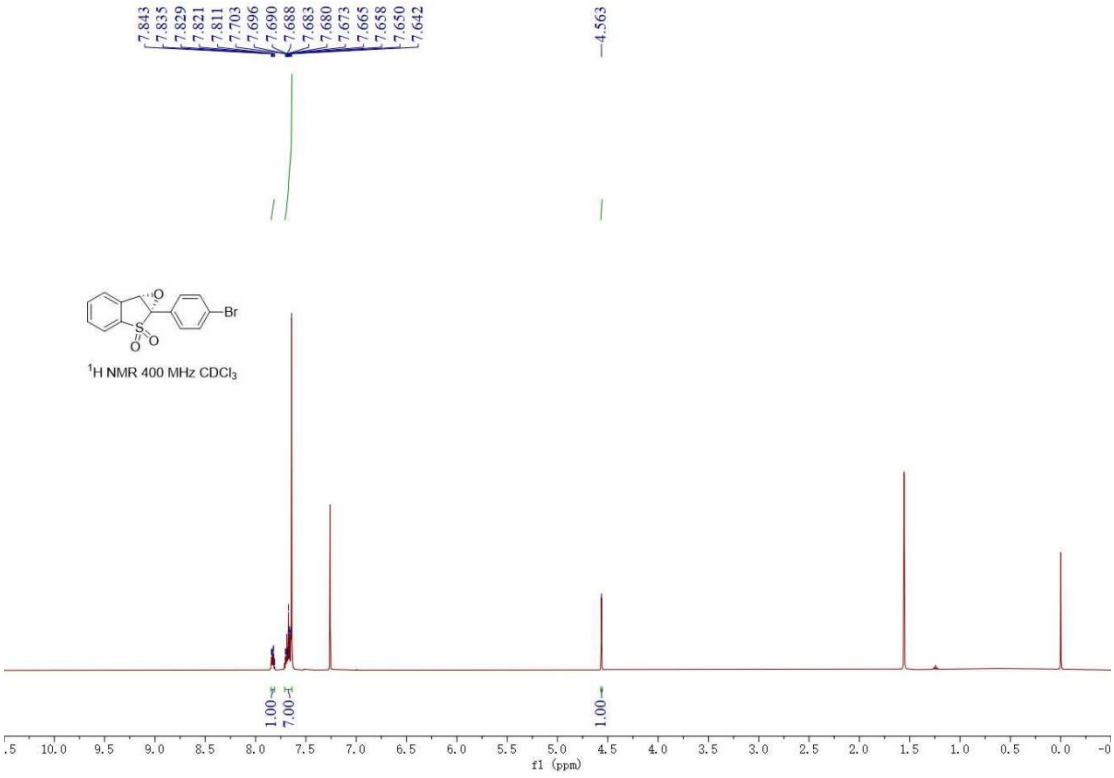


#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.252	BB	0.4743	3037.46460	95.91372	50.0621
2	27.122	BB	0.6329	3029.92285	72.11133	49.9379

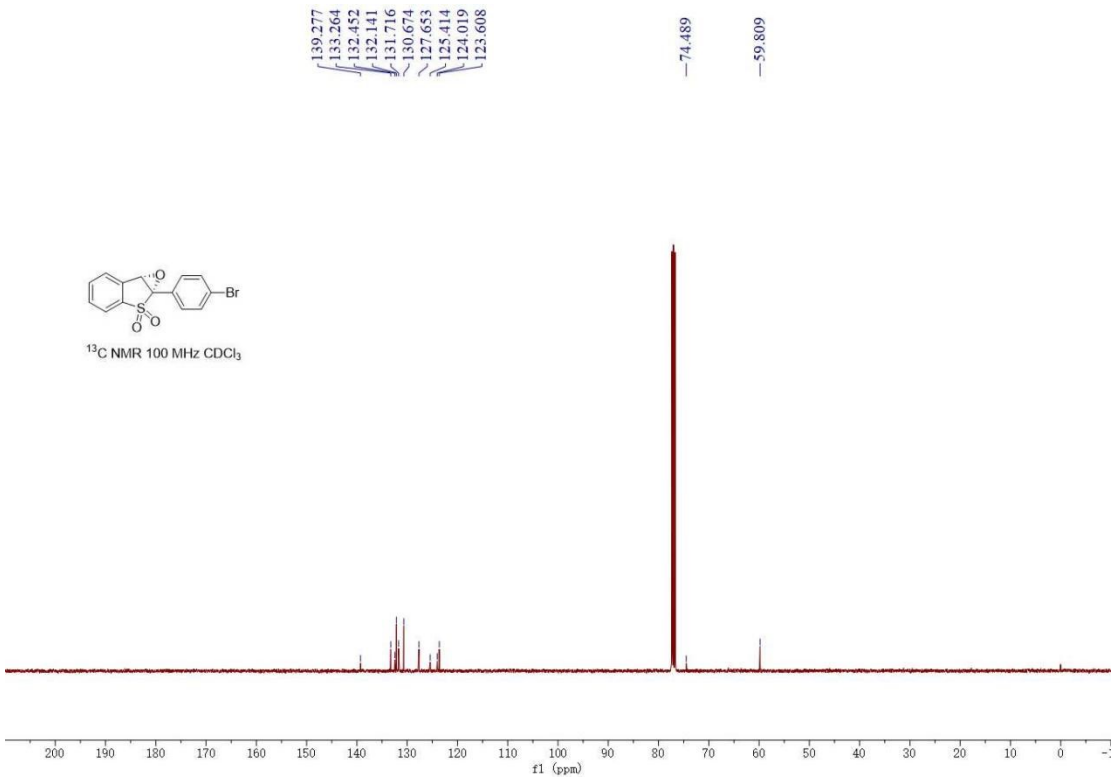


#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.046	BB	0.4820	3086.28027	96.20559	96.5714
2	26.975	MM	0.7501	109.57420	2.43470	3.4286

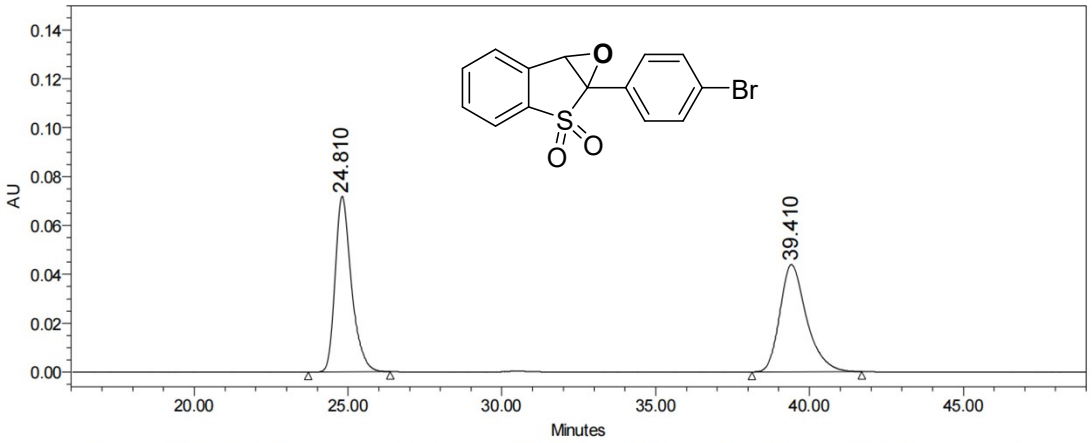
(1a*R*,6b*S*)-1a-(4-bromophenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2w)



^{1}H NMR of **2w**



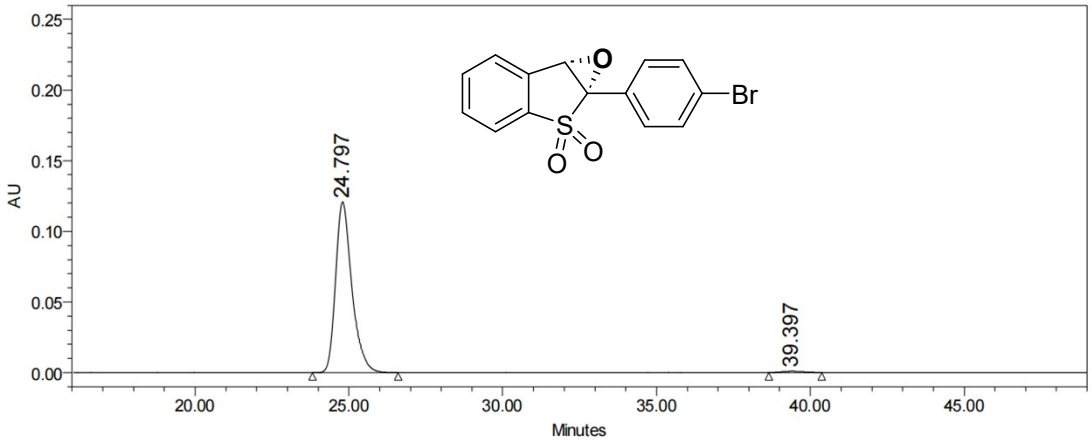
^{13}C NMR of **2w**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 13032; Processing Method: 123

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	24.810	2659212	49.98	71798
2	W2489 ChB 220nm	39.410	2661860	50.02	43896

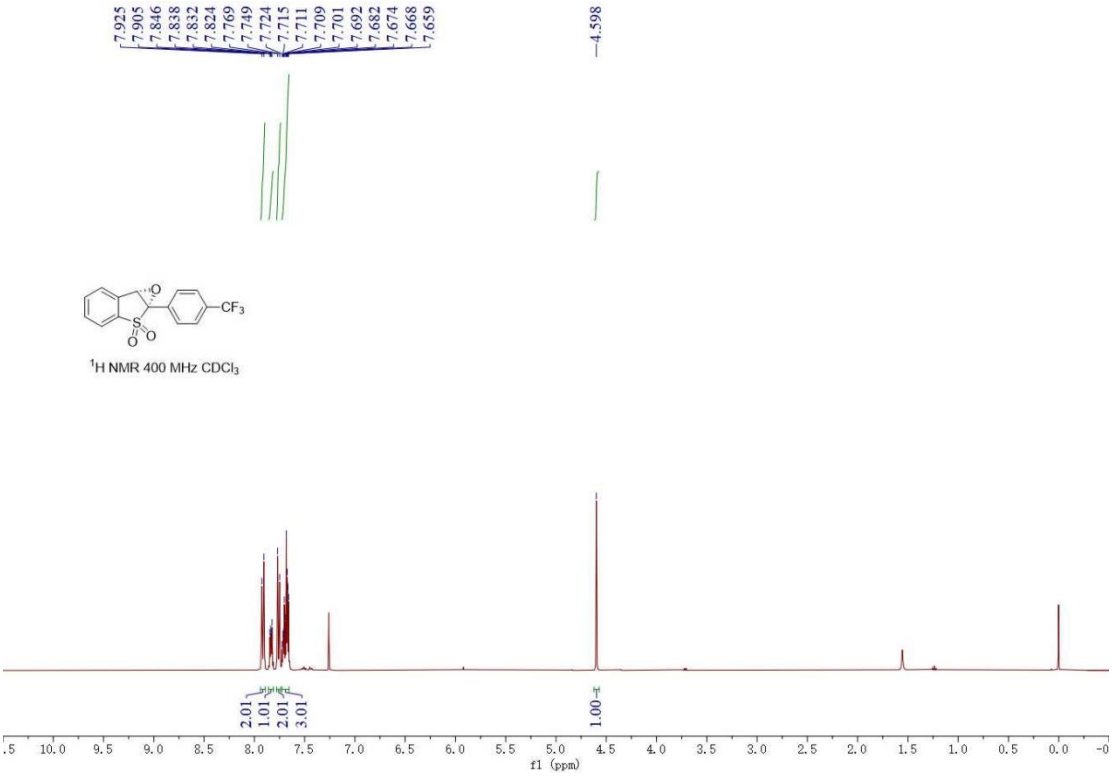


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 13036; Processing Method: 123

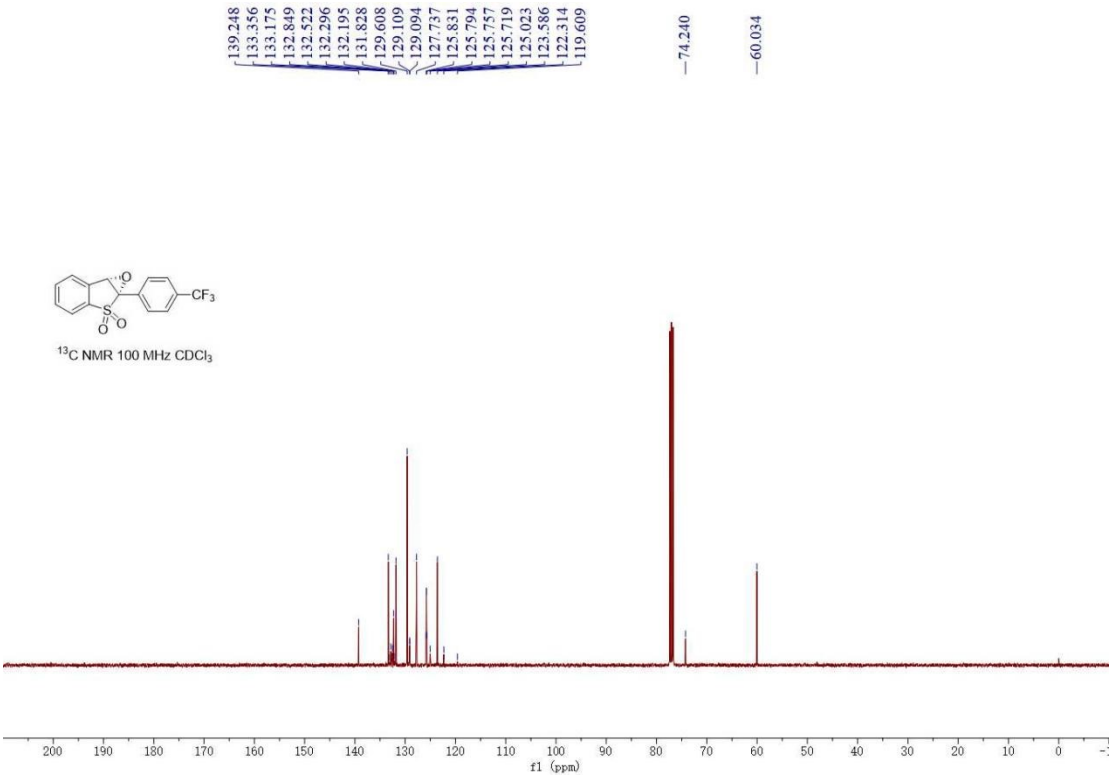
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	24.797	4478166	99.02	120687
2	W2489 ChB 220nm	39.397	44233	0.98	863

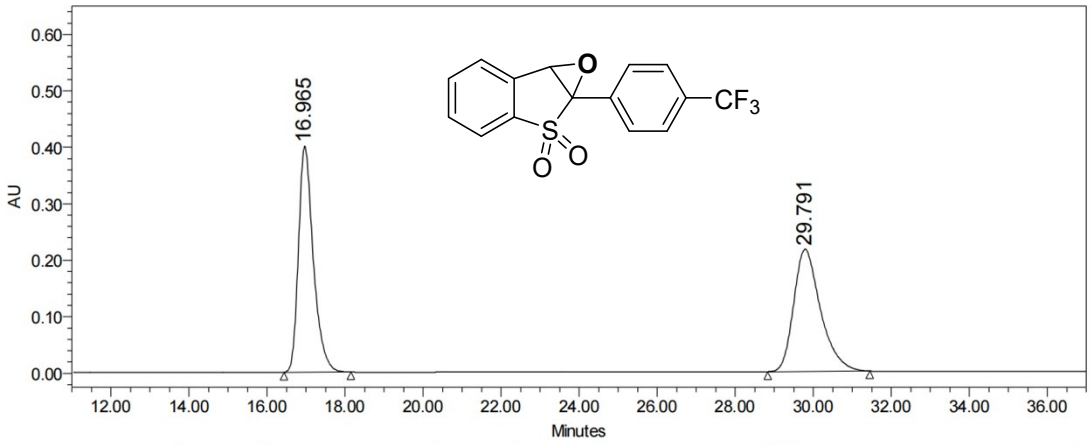
(1a*R*,6b*S*)-1a-(4-(trifluoromethyl)phenyl)-1a,6b-dihydrobenzo[4,5]thieno[2,3-*b*]oxirene 2,2-dioxide (2x)



^{1}H NMR of **2x**



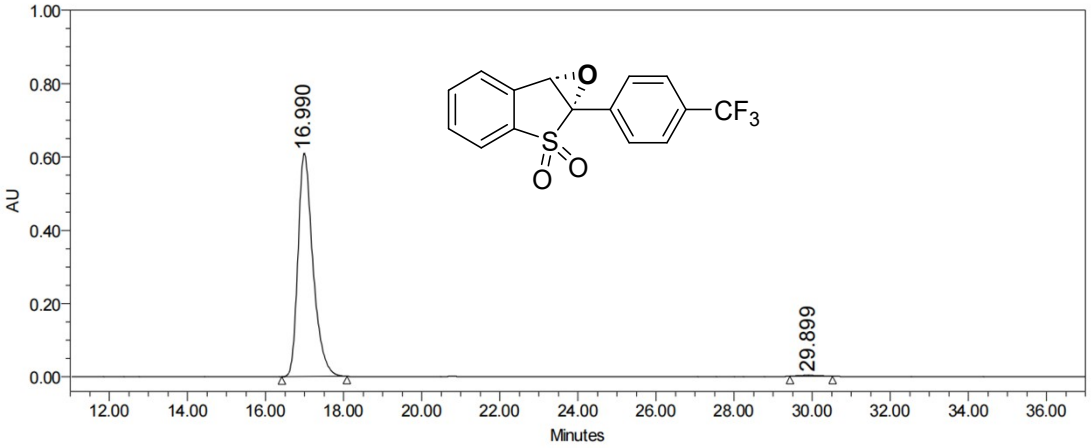
^{13}C NMR of **2x**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12554; Processing Method: GFH

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	16.965	10565793	50.50	400263
2	W2489 ChB 220nm	29.791	10358125	49.50	216331

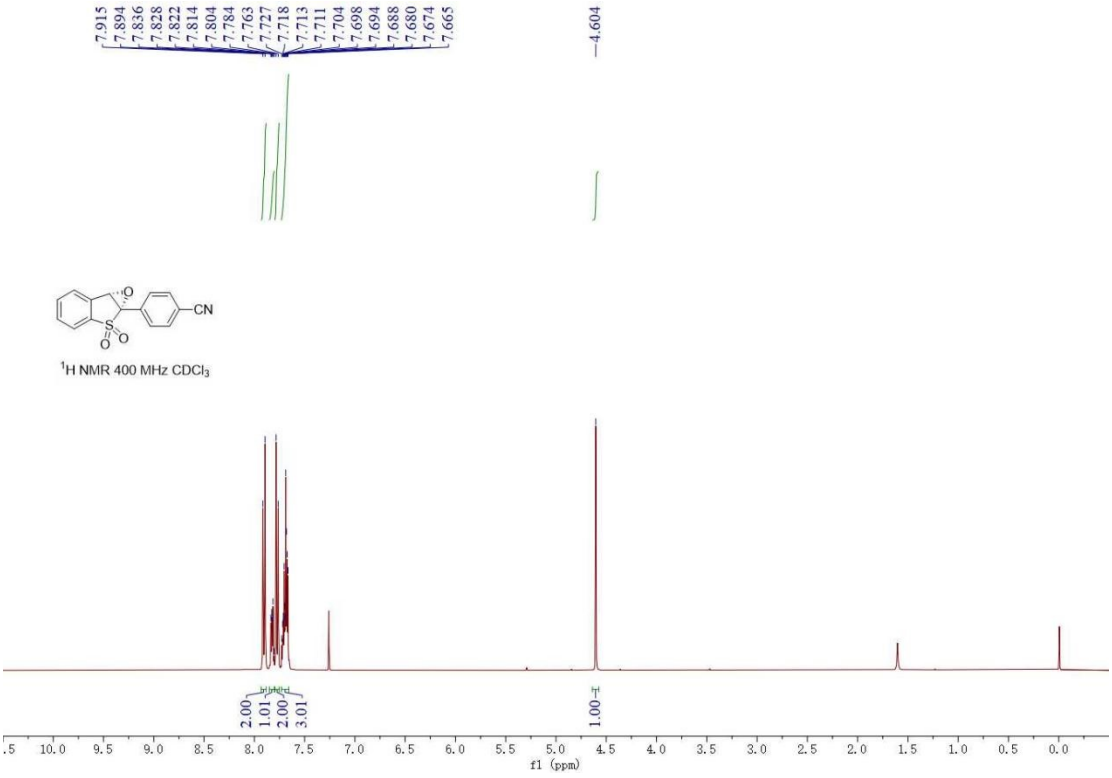


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 12561; Processing Method: GGGGG

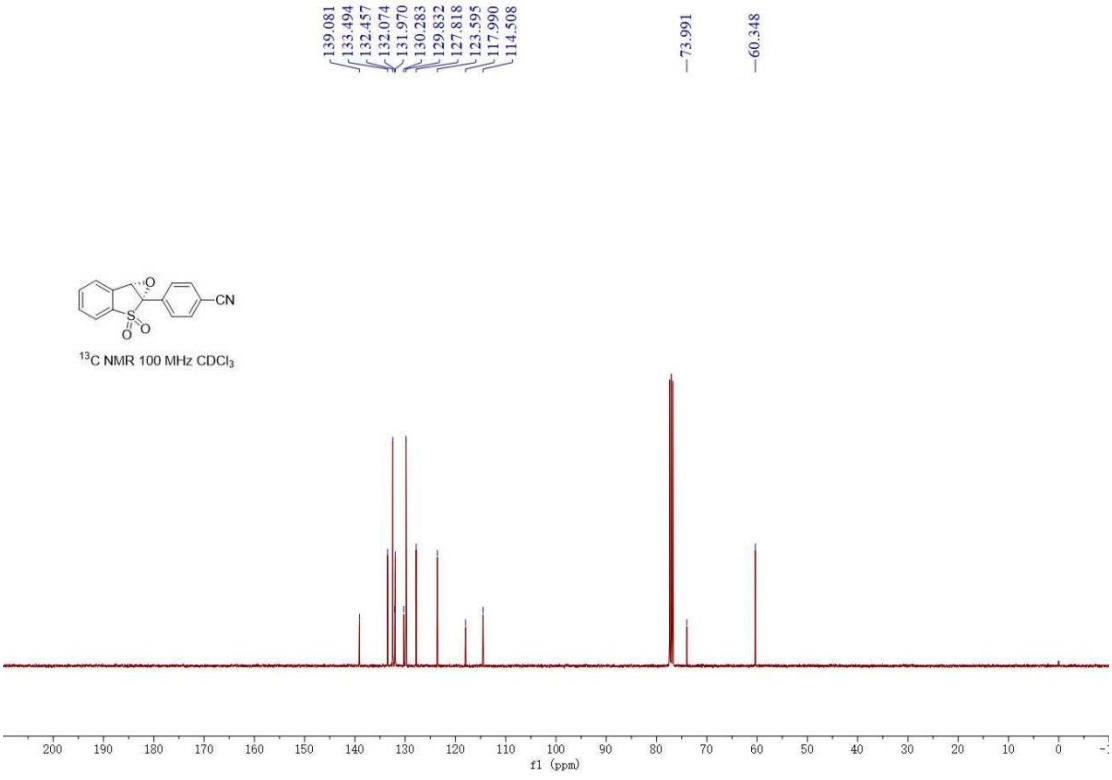
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	16.990	16217855	99.48	609303
2	W2489 ChB 220nm	29.899	84041	0.52	2358

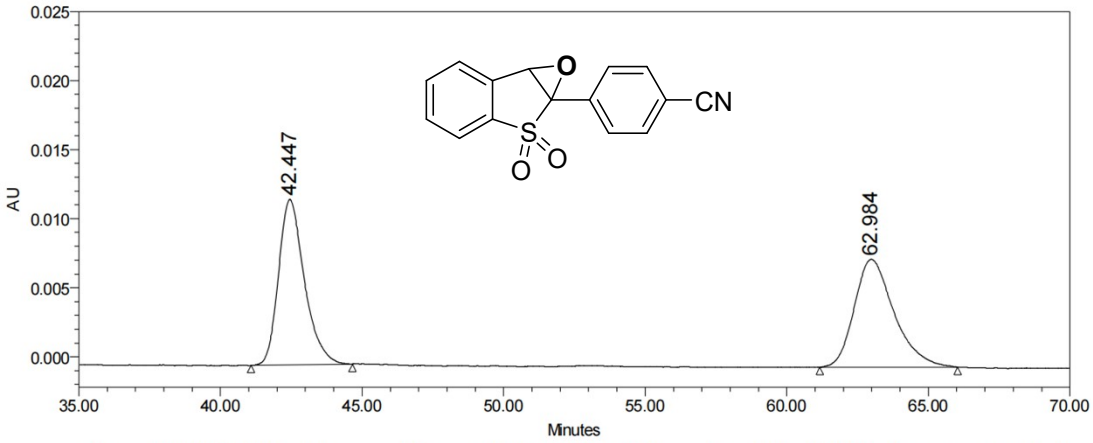
4-((1a*R*,6b*S*)-2,2-dioxidobenzo[4,5]thieno[2,3-*b*]oxiren-1a(6b*H*)-yl)benzonitrile (2y)



^{1}H NMR of **2y**



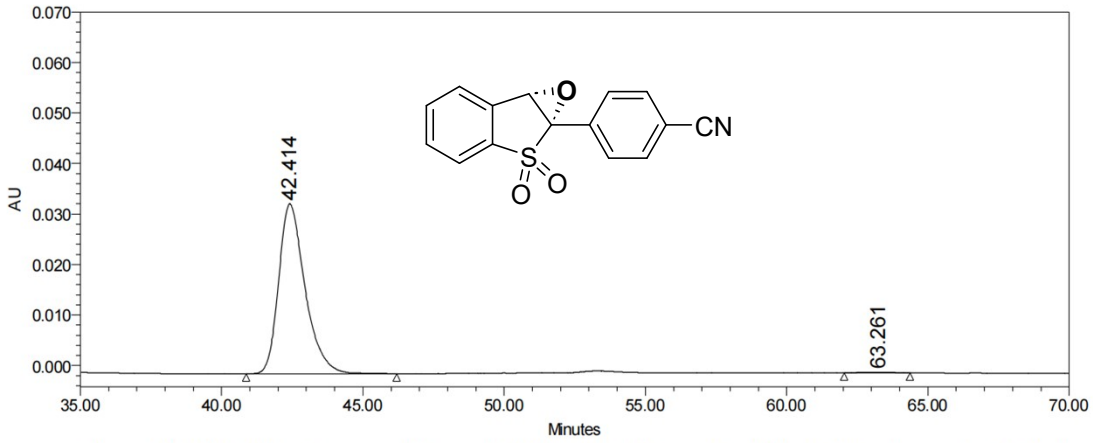
^{13}C NMR of **2y**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 13114; Processing Method: gfrew

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	42.447	759797	49.92	11975
2	W2489 ChB 220nm	62.984	762367	50.08	7797

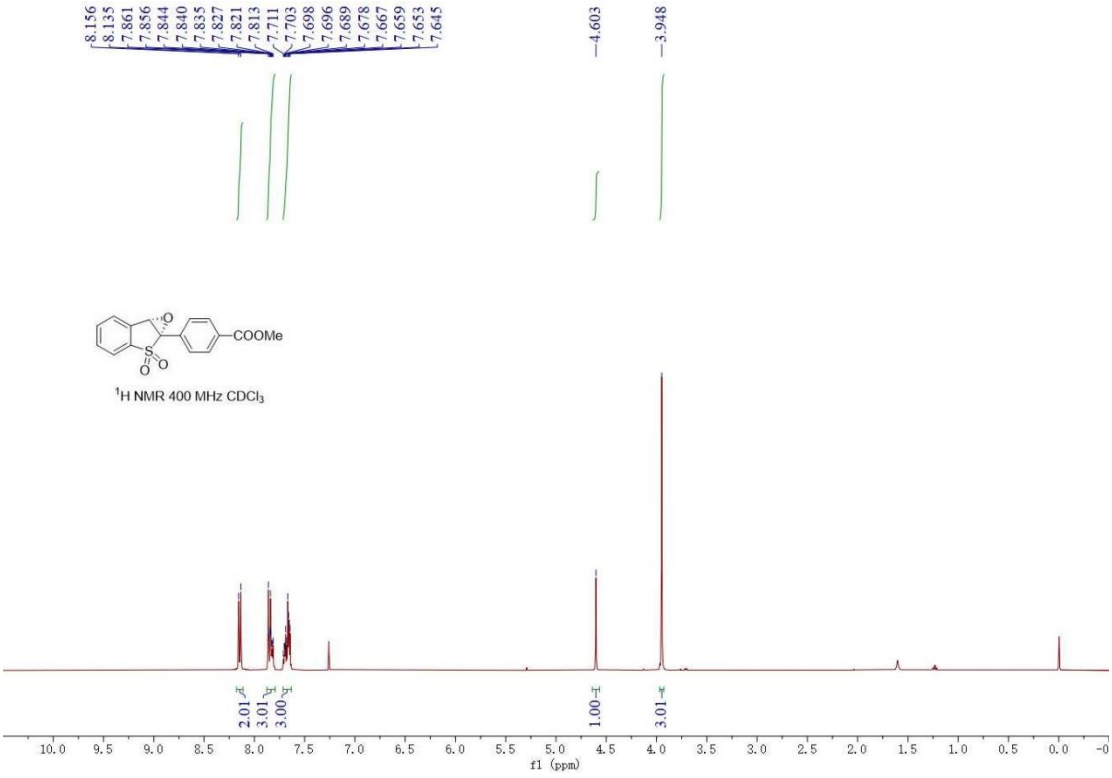


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 13173; Processing Method: FDGDFS

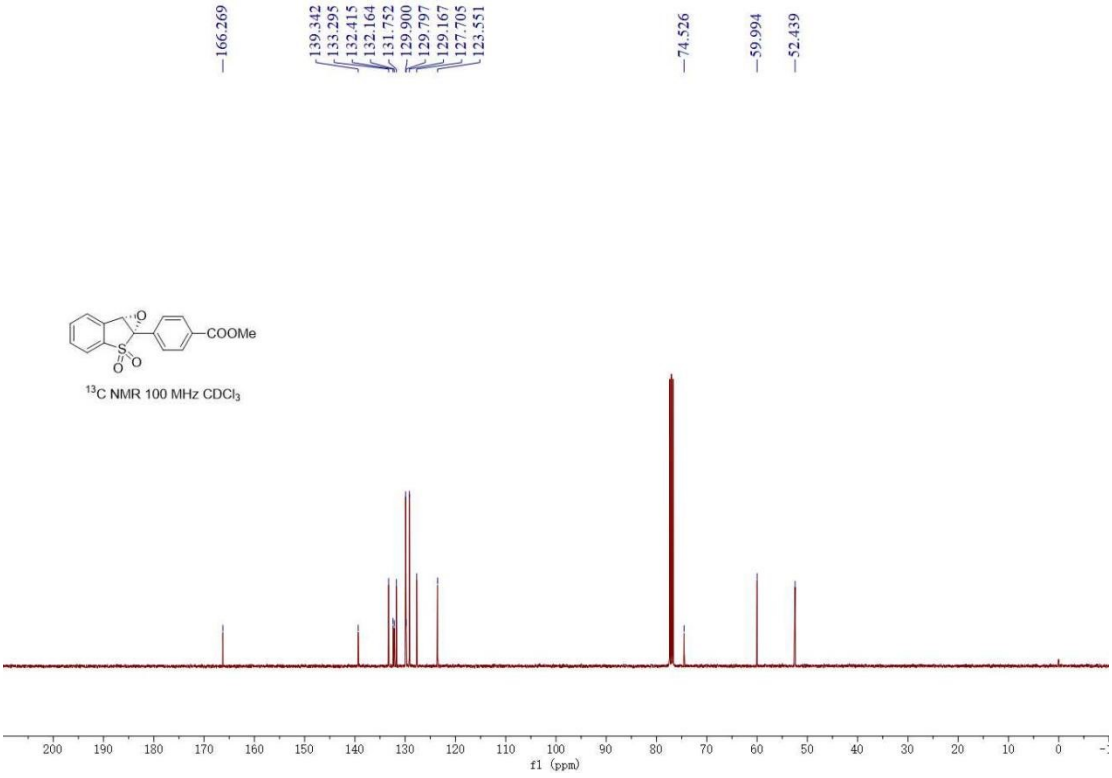
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	42.414	2189209	99.53	33650
2	W2489 ChB 220nm	63.261	10264	0.47	136

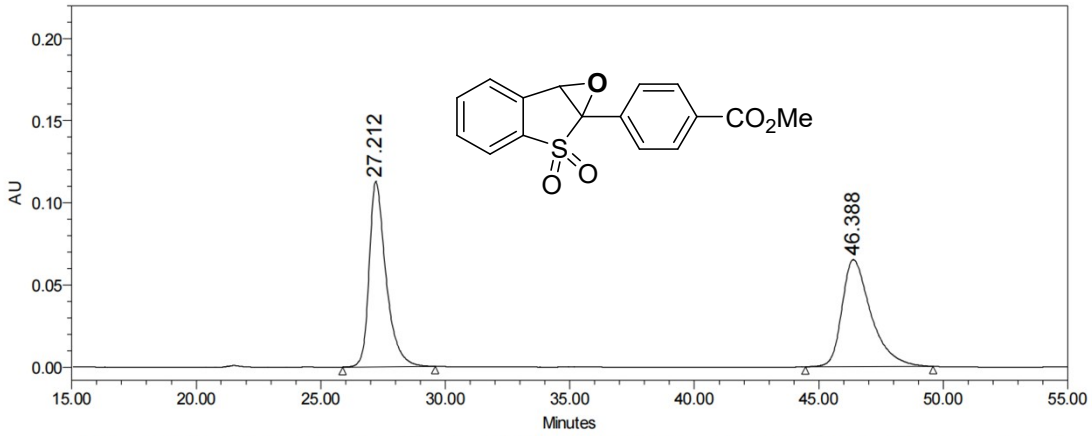
methyl 4-((1a*R*,6b*S*)-2,2-dioxidobenzo[4,5]thieno[2,3-*b*]oxiren-1a(6b*H*)-yl) benzoate (2z)



^{1}H NMR of **2z**



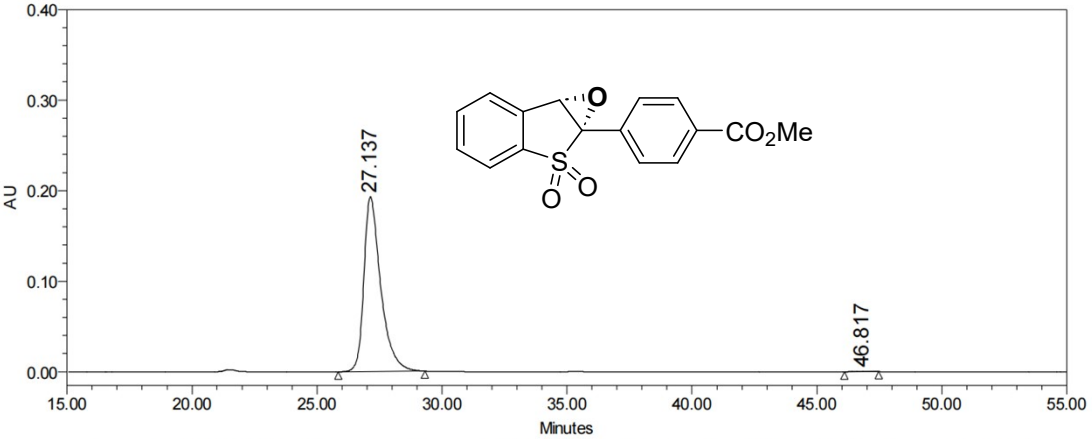
^{13}C NMR of **2z**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14243; Processing Method: 3315616

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	27.212	5303697	50.05	112821
2	W2489 ChB 220nm	46.388	5293279	49.95	65144

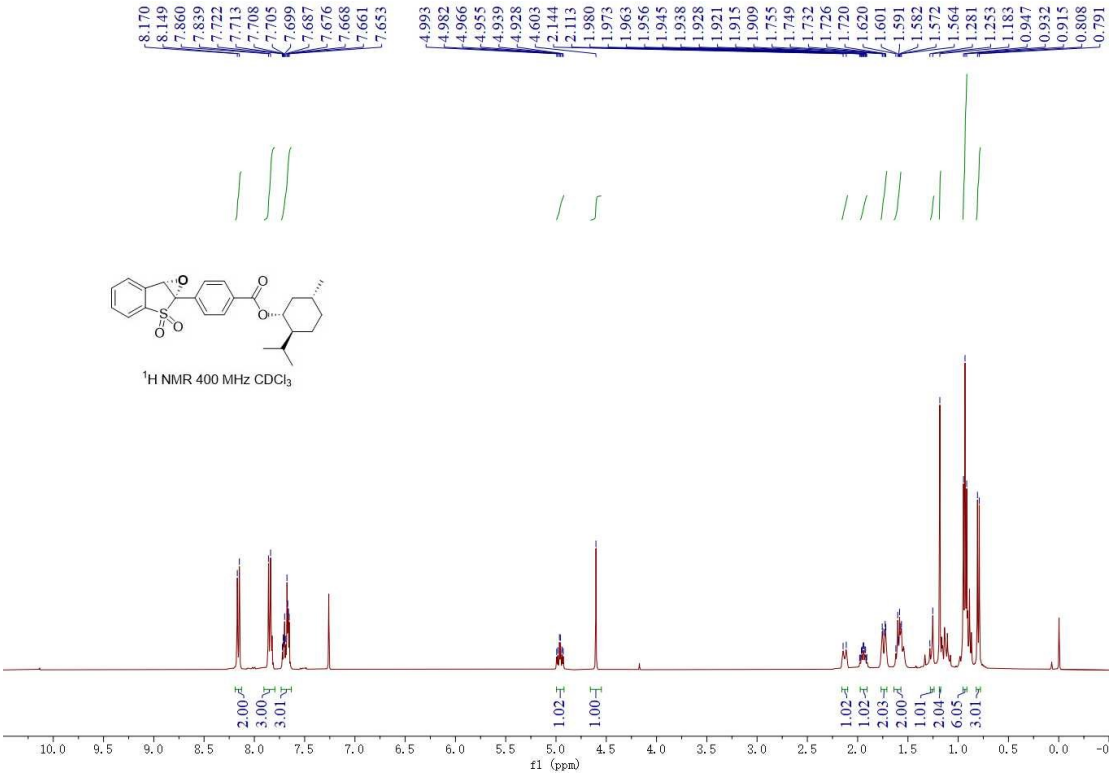


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14246; Processing Method: 326646

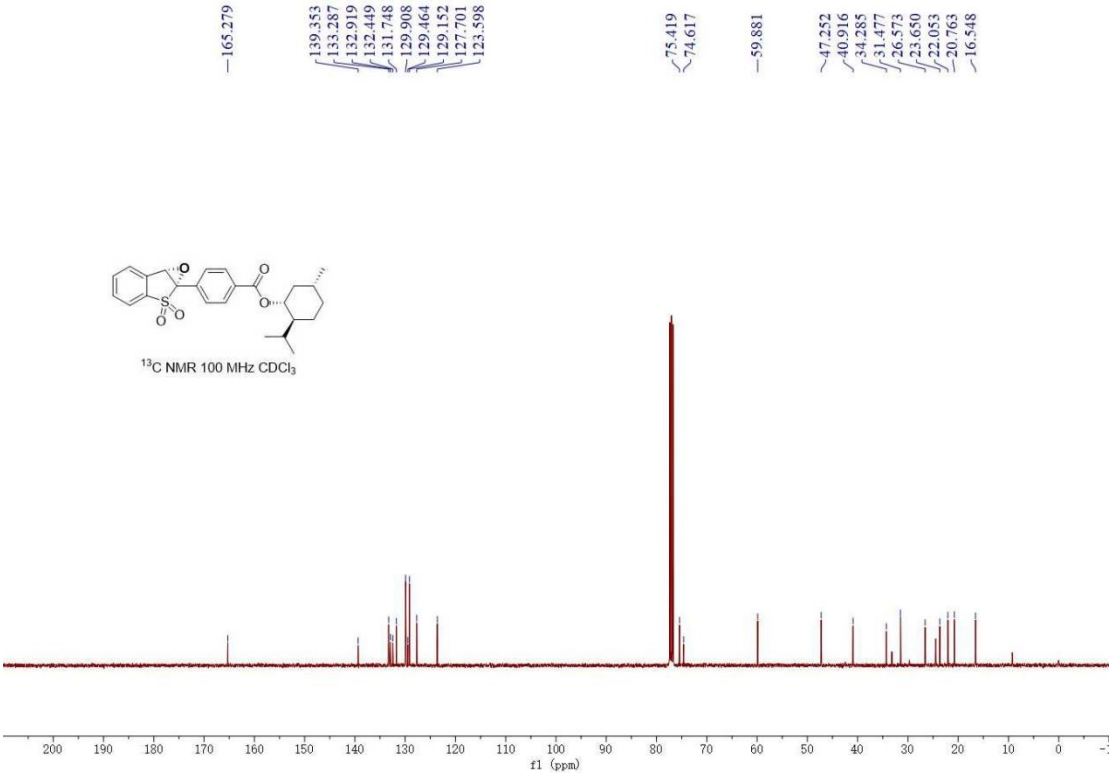
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	27.137	9039703	99.76	192958
2	W2489 ChB 220nm	46.817	22008	0.24	448

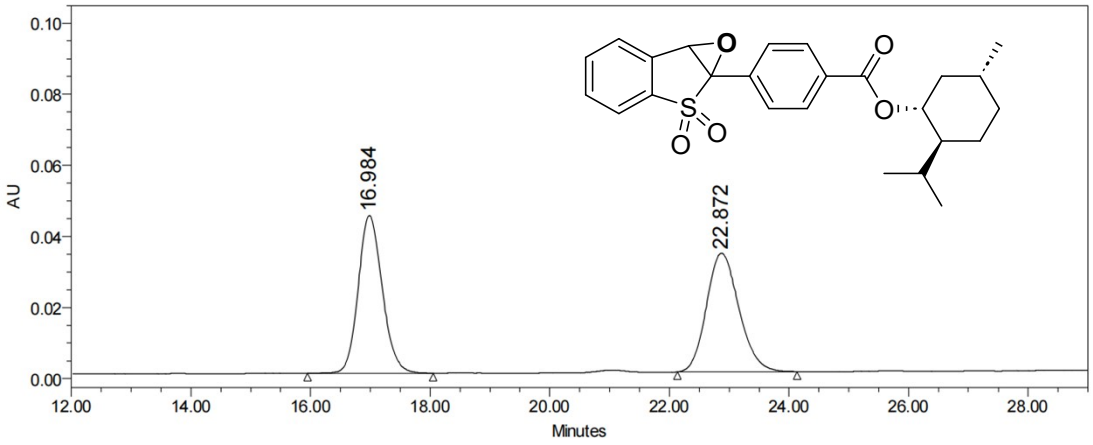
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-((1a*R*,6b*S*)-2,2-dioxidobenzo[4,5] thieno [2,3-*b*]oxiren-1a(6b*H*)-yl)benzoate (2za)



^{1}H NMR of **2za**



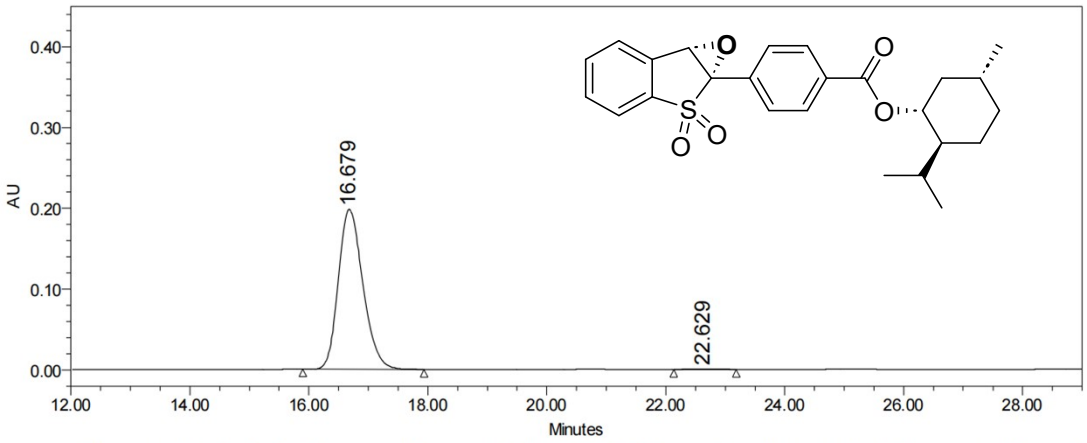
^{13}C NMR of **2za**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14412; Processing Method: 4646131

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	16.984	1239219	49.58	44317
2	W2489 ChB 220nm	22.872	1260101	50.42	33405

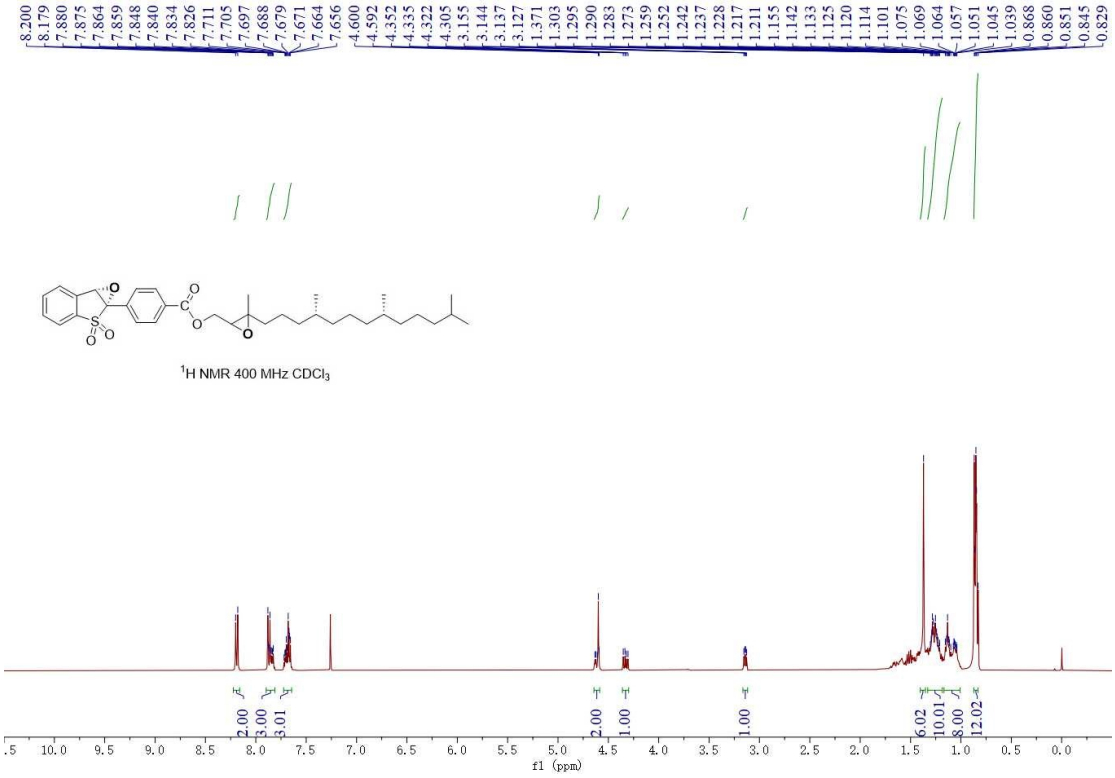


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14417; Processing Method: 6364661

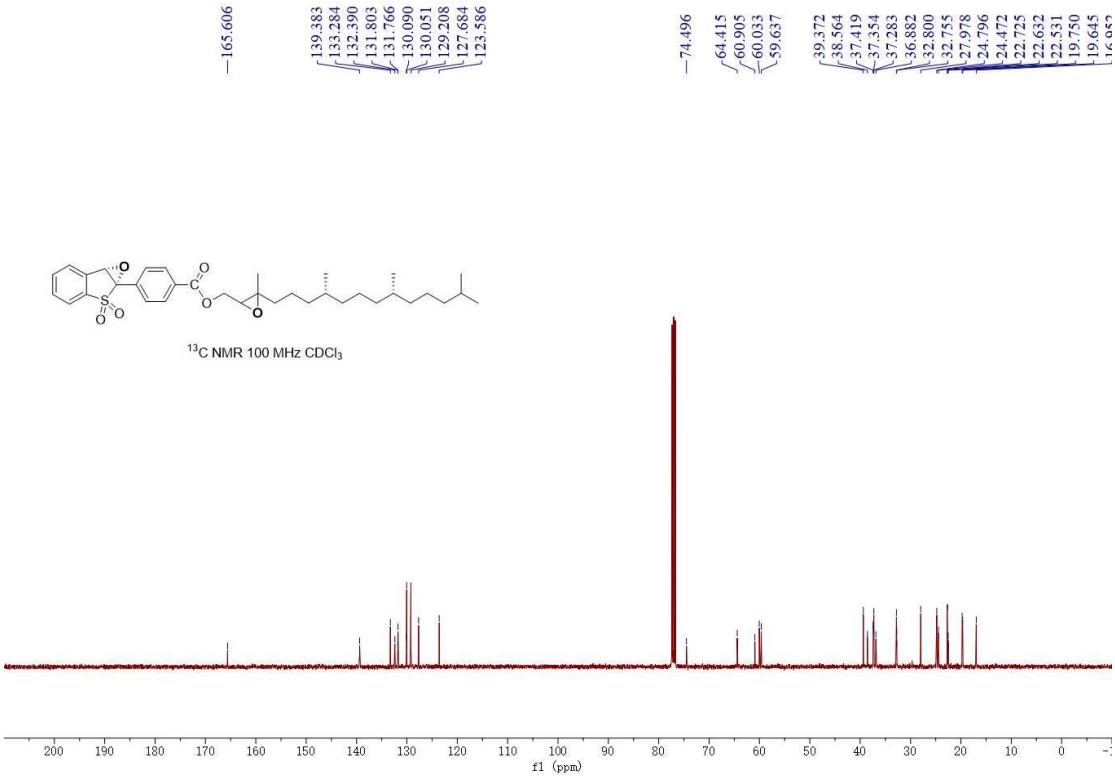
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	16.679	5670738	99.65	197828
2	W2489 ChB 220nm	22.629	20099	0.35	612

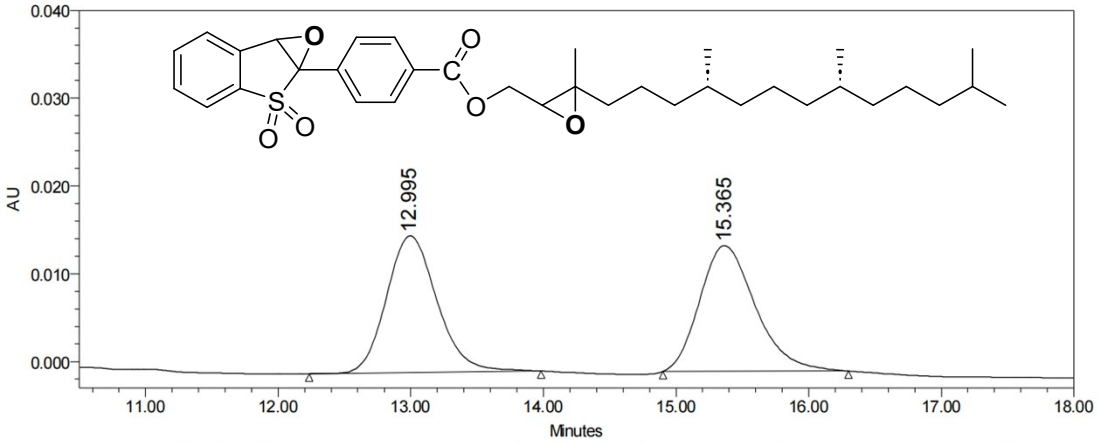
(3-methyl-3-((4*R*,8*R*)-4,8,12-trimethyltridecyl)-2l3-oxiran-2-yl)methyl 4-((1a*R*,6b*S*)-2,2-dioxidobenzo[4,5]thieno[2,3-*b*]oxiren-1a(6b*H*)-yl)benzoate (2zb)



^{1}H NMR of **2zb**



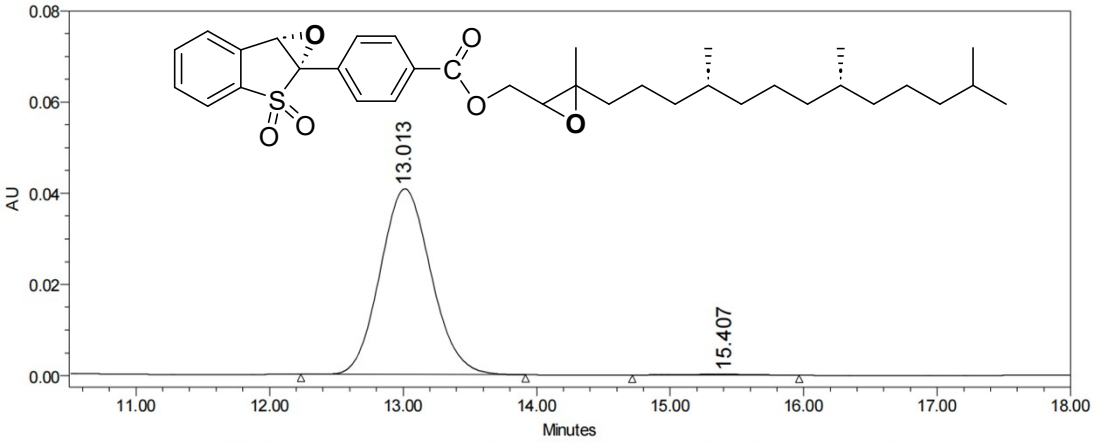
^{13}C NMR of **2zb**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14733; Processing Method: 169562

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	12.995	410747	49.59	15565
2	W2489 ChB 220nm	15.365	417486	50.41	14310

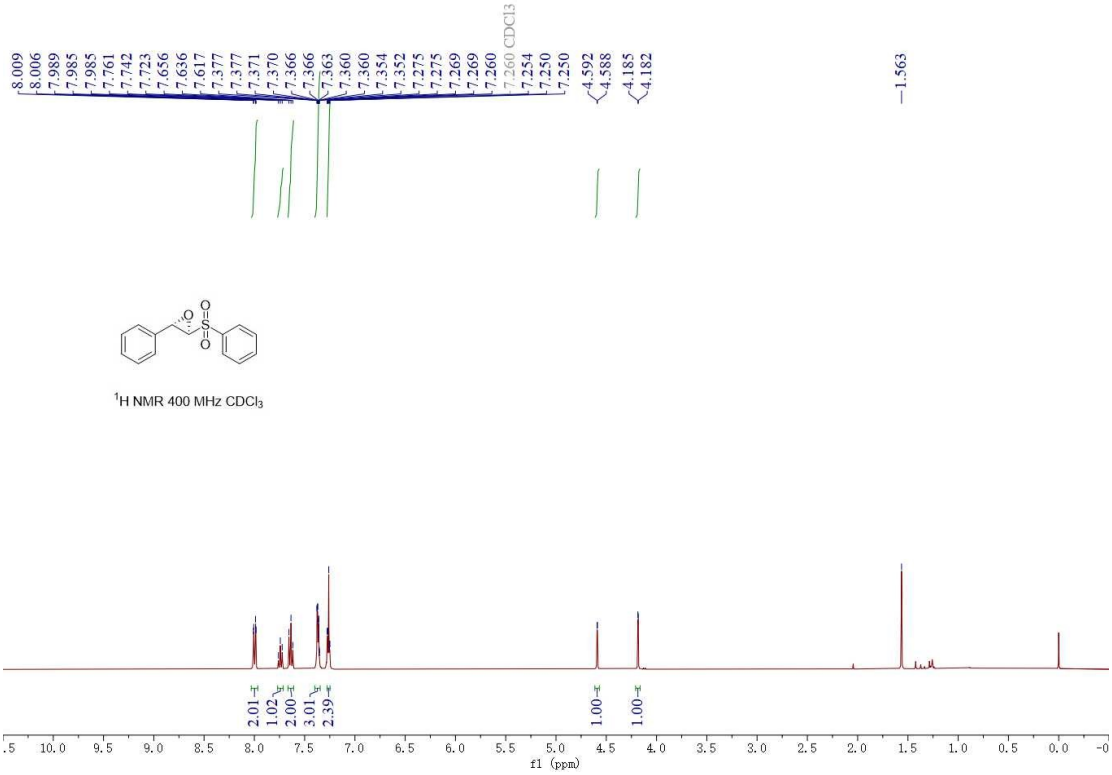


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14736; Processing Method: 65139

Processed Channel Descr.: W2489 ChB 220nm

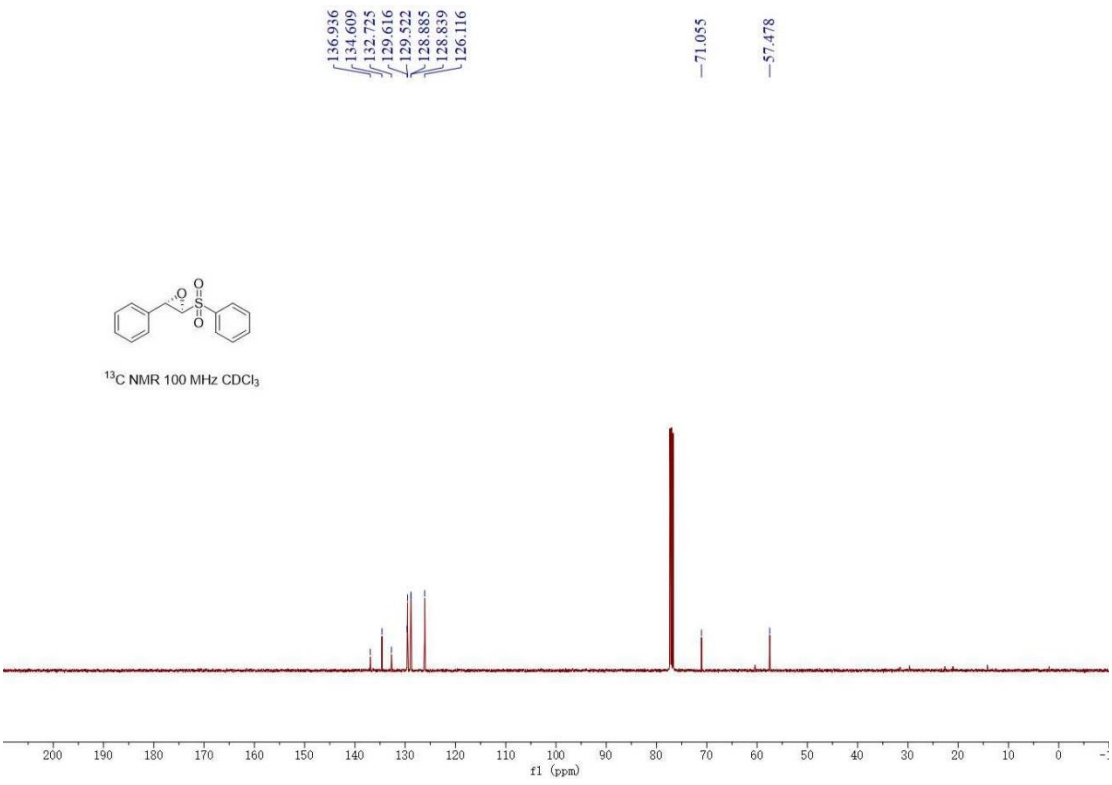
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	13.013	1075177	99.13	40704
2	W2489 ChB 220nm	15.407	9405	0.87	239

(2*S*,3*S*)-2-phenyl-3-(phenylsulfonyl)oxirane (4a)



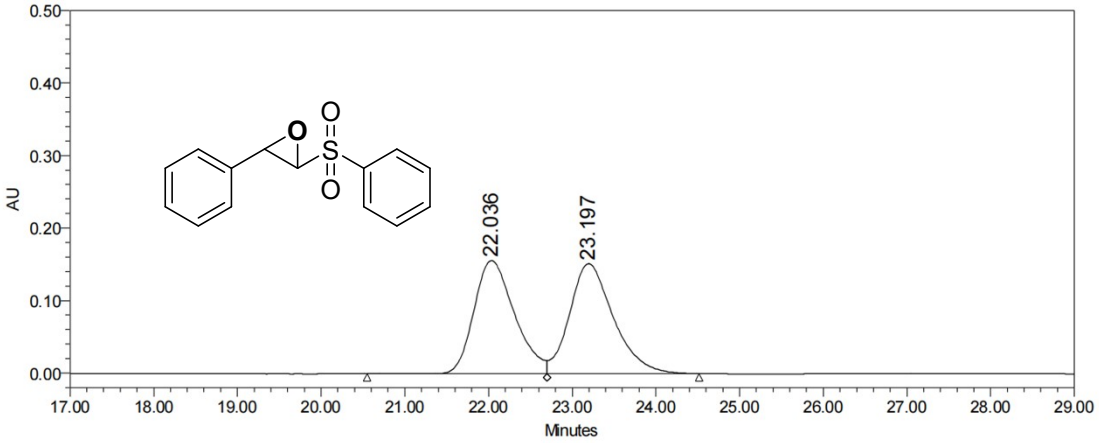
^{1}H NMR 400 MHz $CDCl_3$

^{1}H NMR of **4a**



^{13}C NMR 100 MHz $CDCl_3$

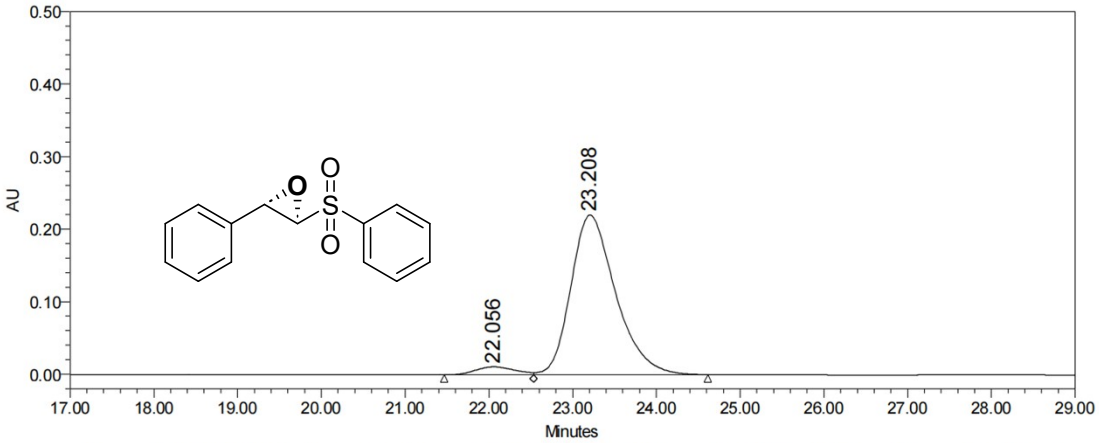
^{13}C NMR of **4a**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 16000; Processing Method: 47582

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	22.036	5250917	48.75	156026
2	W2489 ChB 220nm	23.197	5520344	51.25	151521

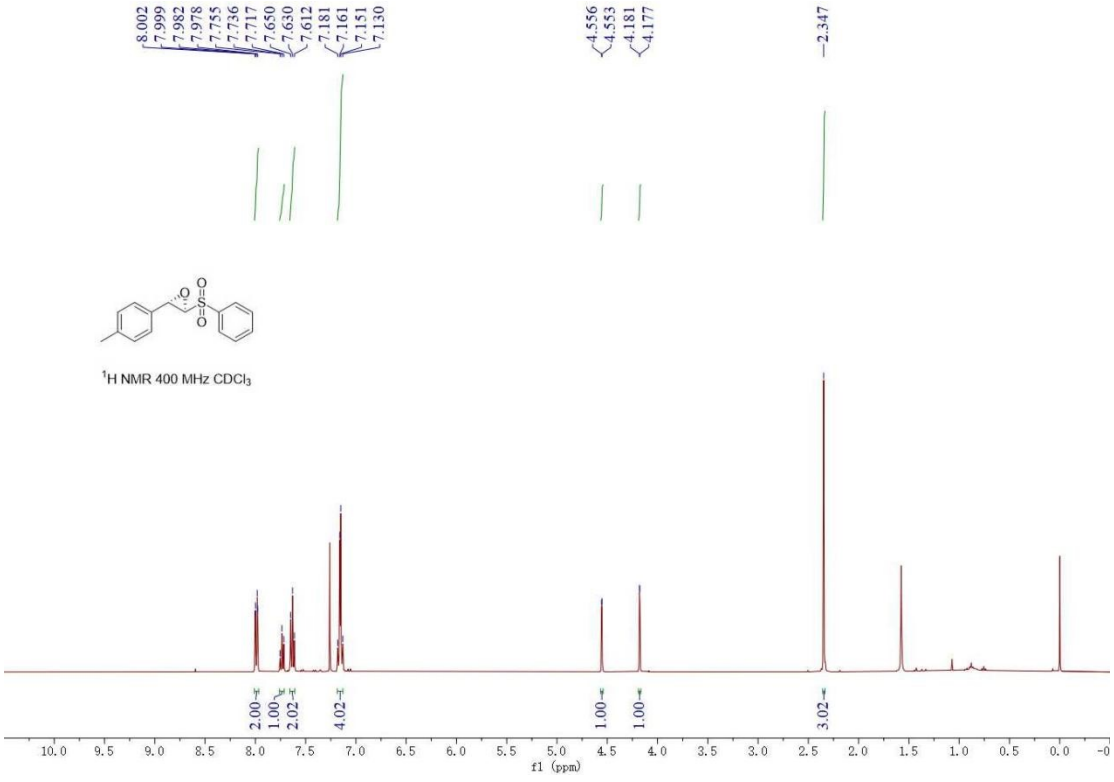


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15995; Processing Method: 52424

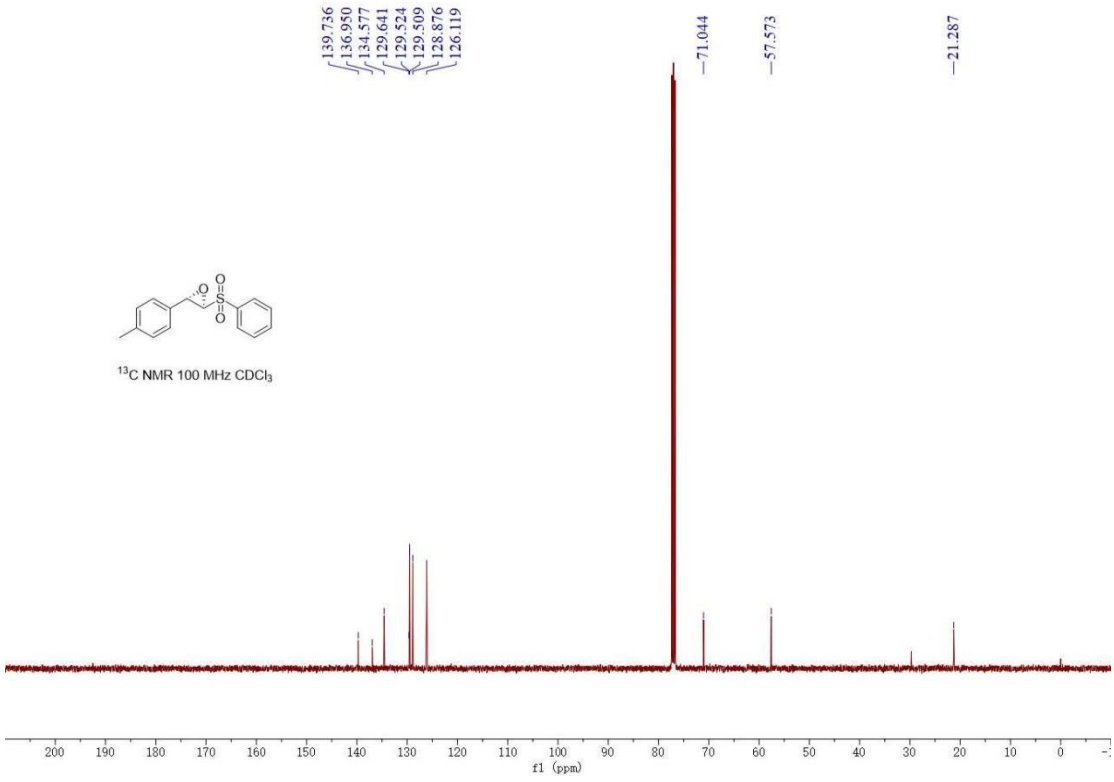
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	22.056	359711	4.22	11021
2	W2489 ChB 220nm	23.208	8169147	95.78	219973

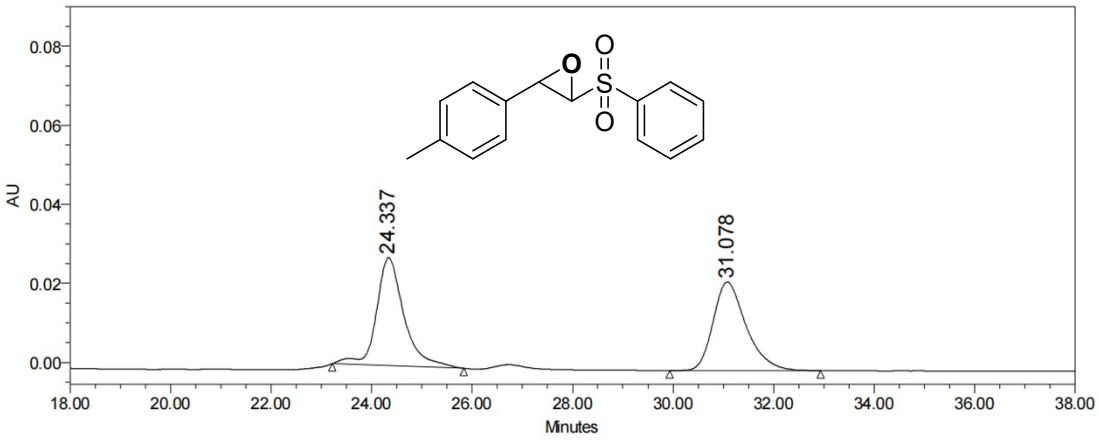
(2*S*,3*S*)-2-(phenylsulfonyl)-3-(*p*-tolyl)oxirane (4b)



^{1}H NMR of **4b**



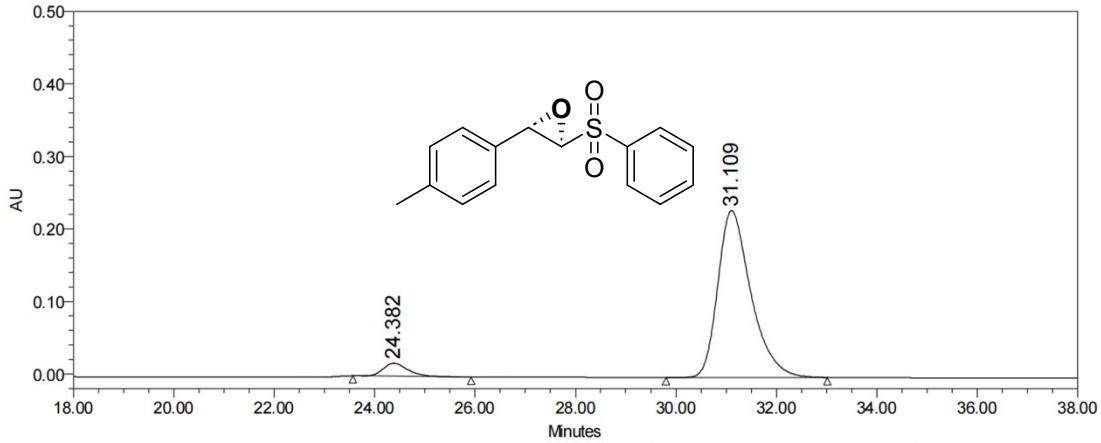
^{13}C NMR of **4b**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 16002; Processing Method: 4464

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	24.337	1043113	50.51	27300
2	W2489 ChB 220nm	31.078	1022177	49.49	22382

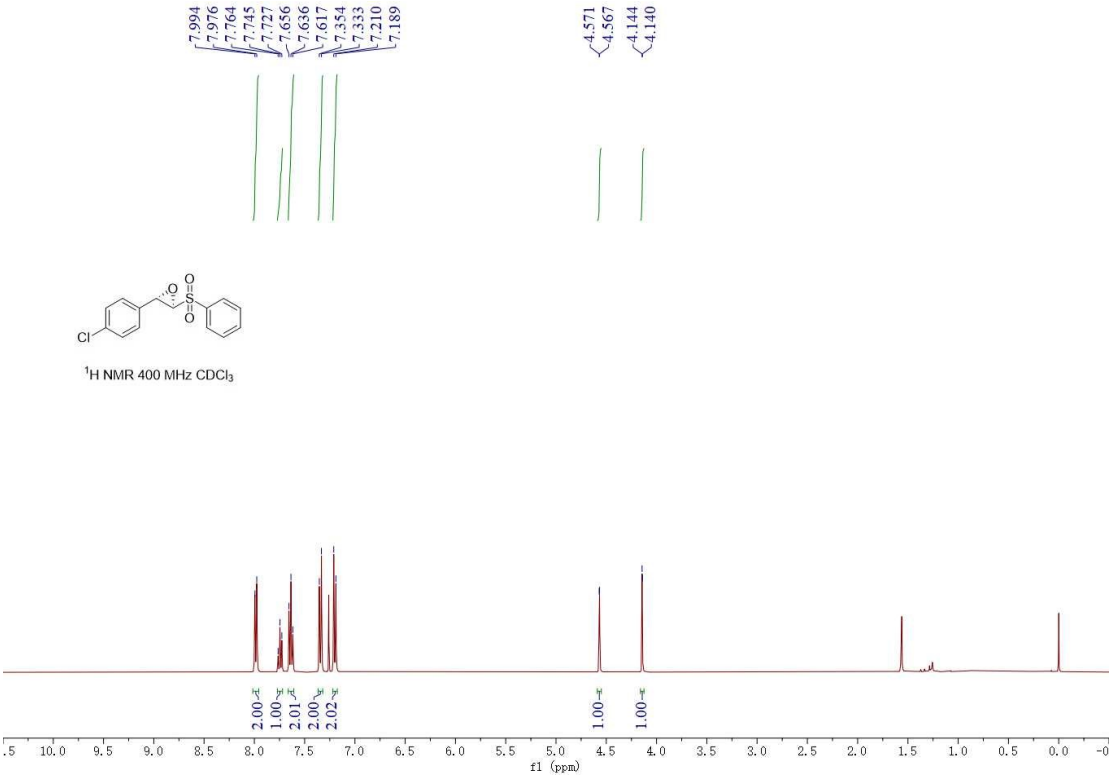


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 16005; Processing Method: 54121

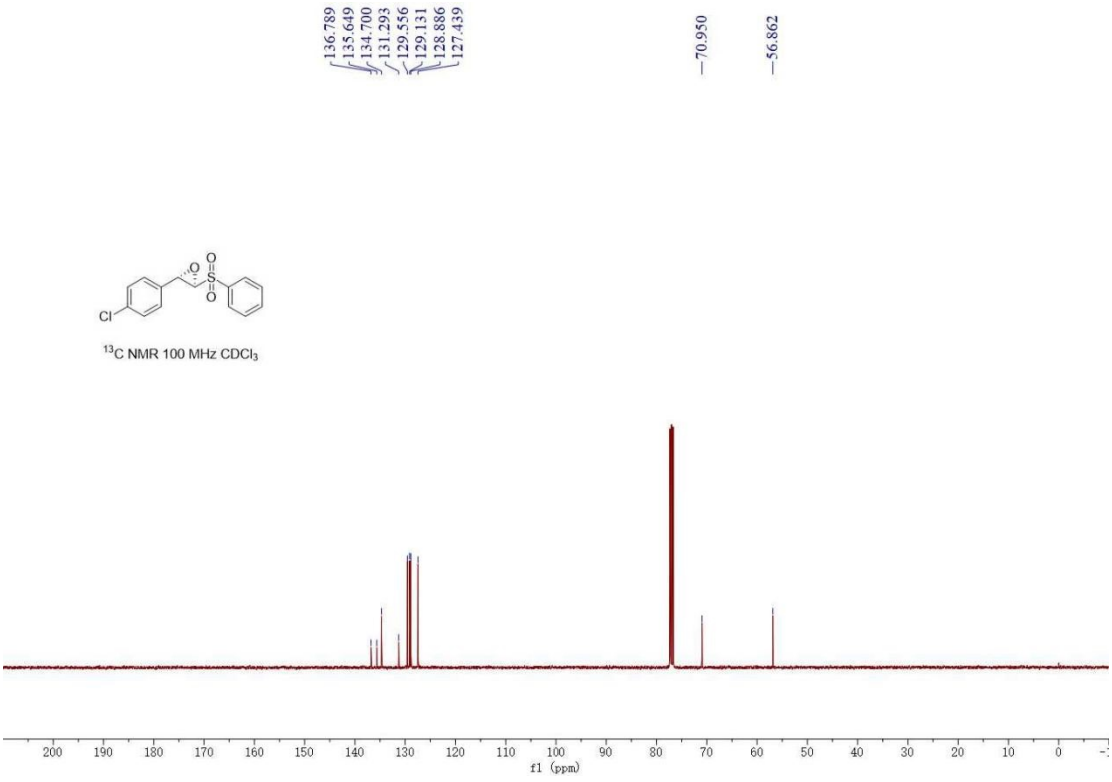
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	24.382	617594	5.54	17928
2	W2489 ChB 220nm	31.109	10530617	94.46	229832

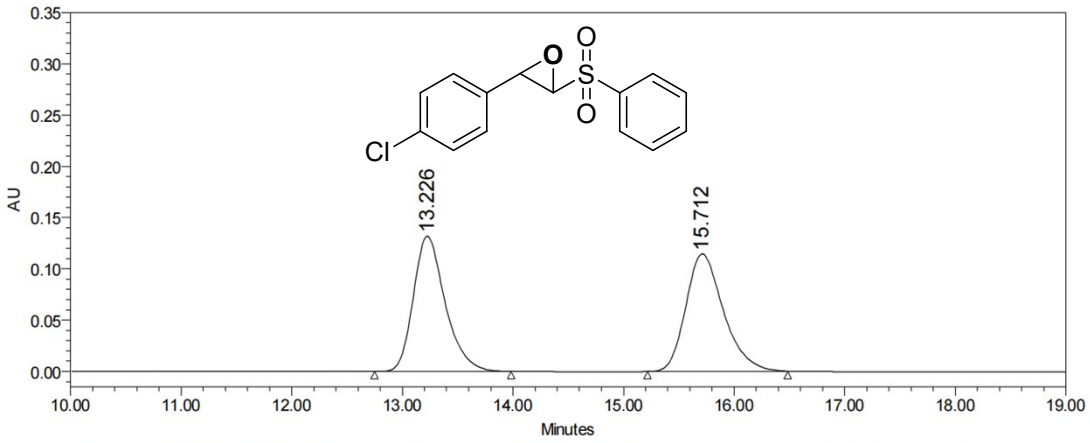
(2*S*,3*S*)-2-(4-chlorophenyl)-3-(phenylsulfonyl)oxirane (4c)



^{1}H NMR of **4c**



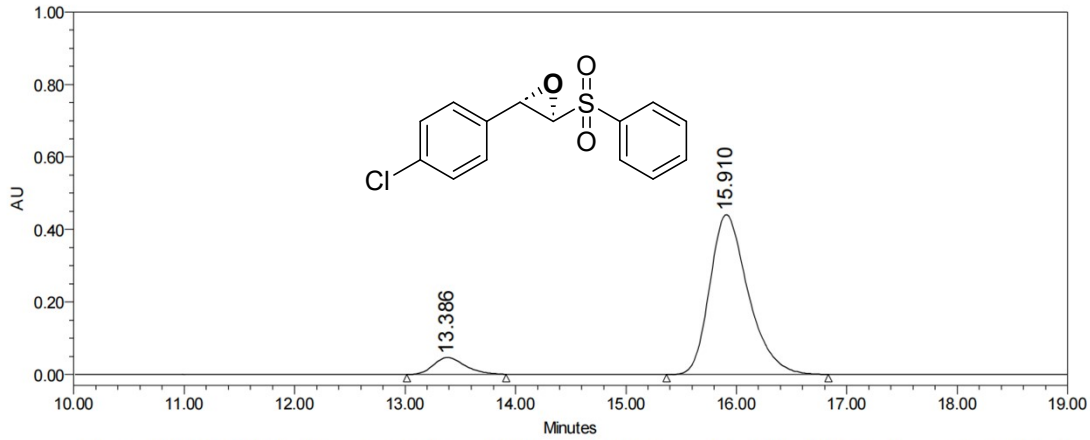
^{13}C NMR of **4c**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14201; Processing Method: 446565

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	13.226	2633681	49.22	131891
2	W2489 ChB 220nm	15.712	2716933	50.78	114783

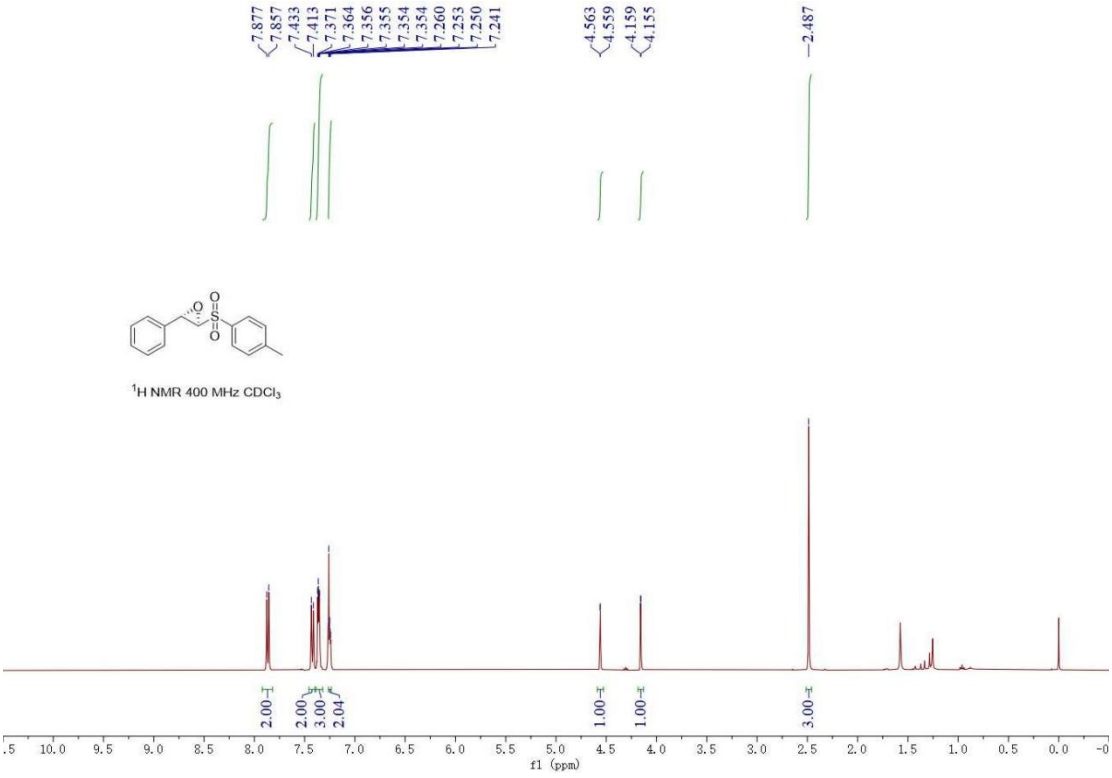


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 14204; Processing Method: 99464

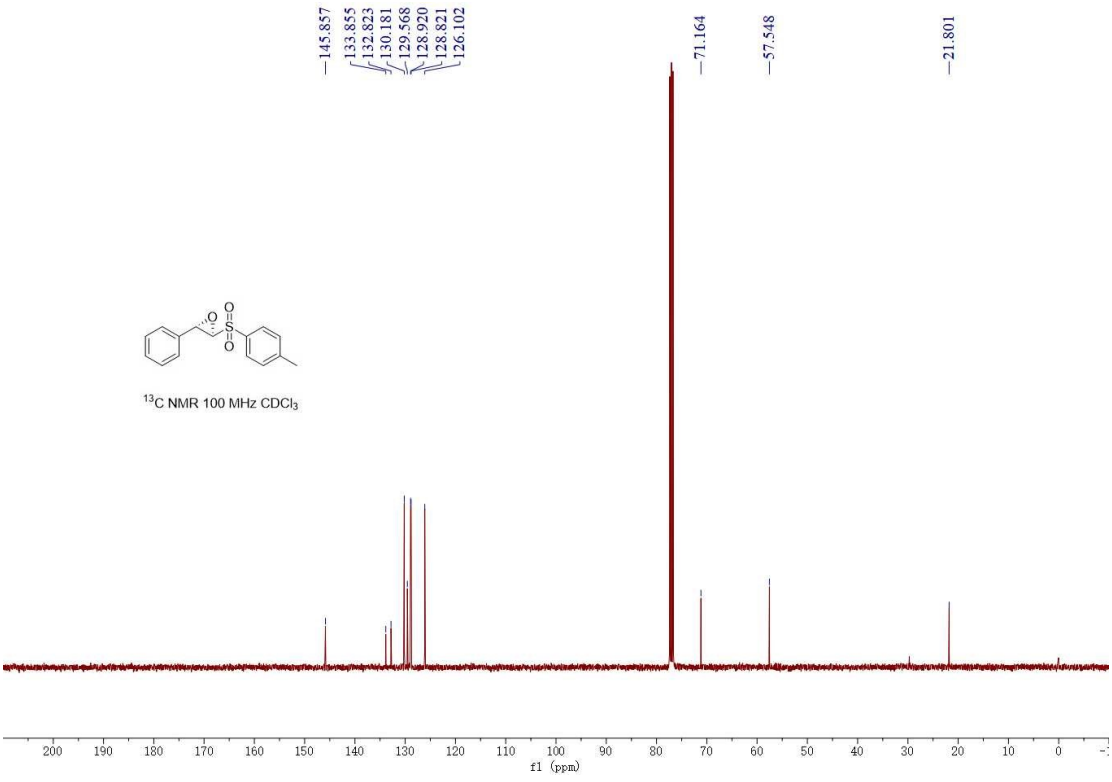
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	13.386	925820	7.99	46876
2	W2489 ChB 220nm	15.910	10661846	92.01	440947

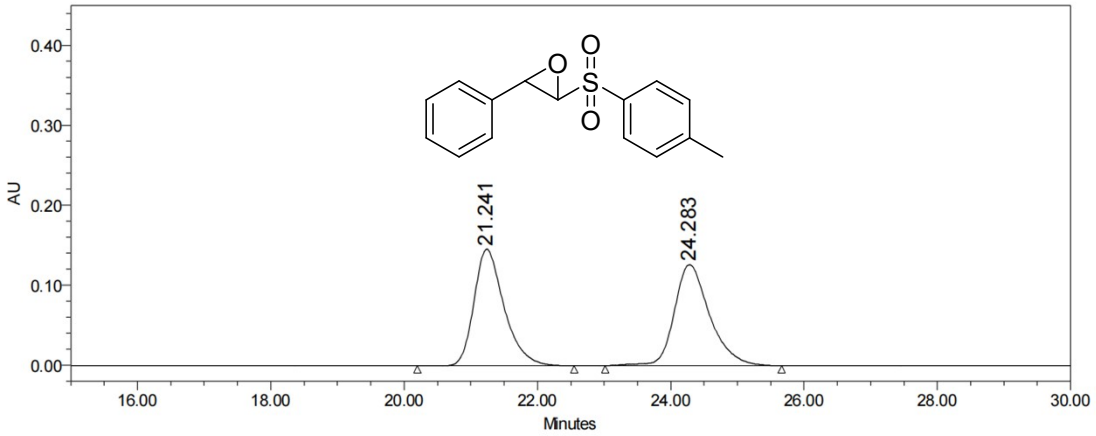
(2*S*,3*S*)-2-phenyl-3-tosyloxirane (4d)



^{1}H NMR of **4d**



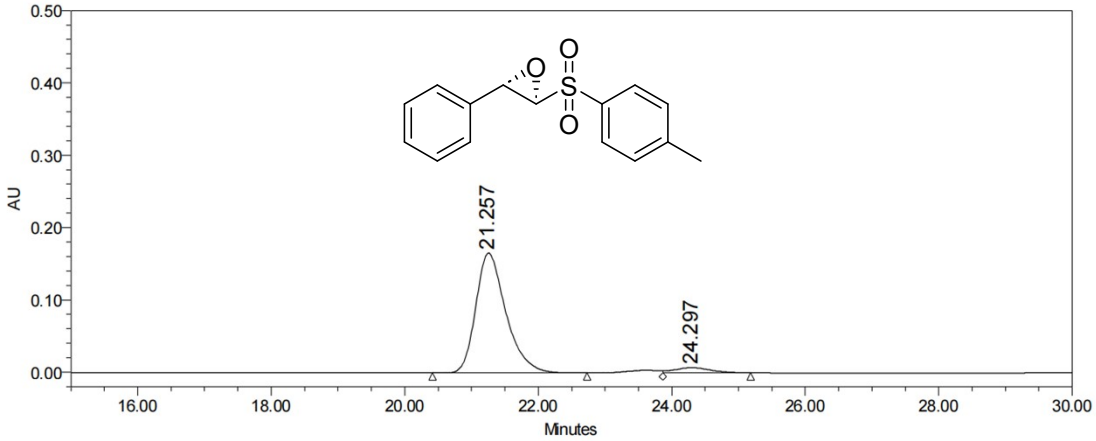
^{13}C NMR of **4d**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 16024; Processing Method: 574254

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	21.241	4564037	49.55	145750
2	W2489 ChB 220nm	24.283	4646145	50.45	126353

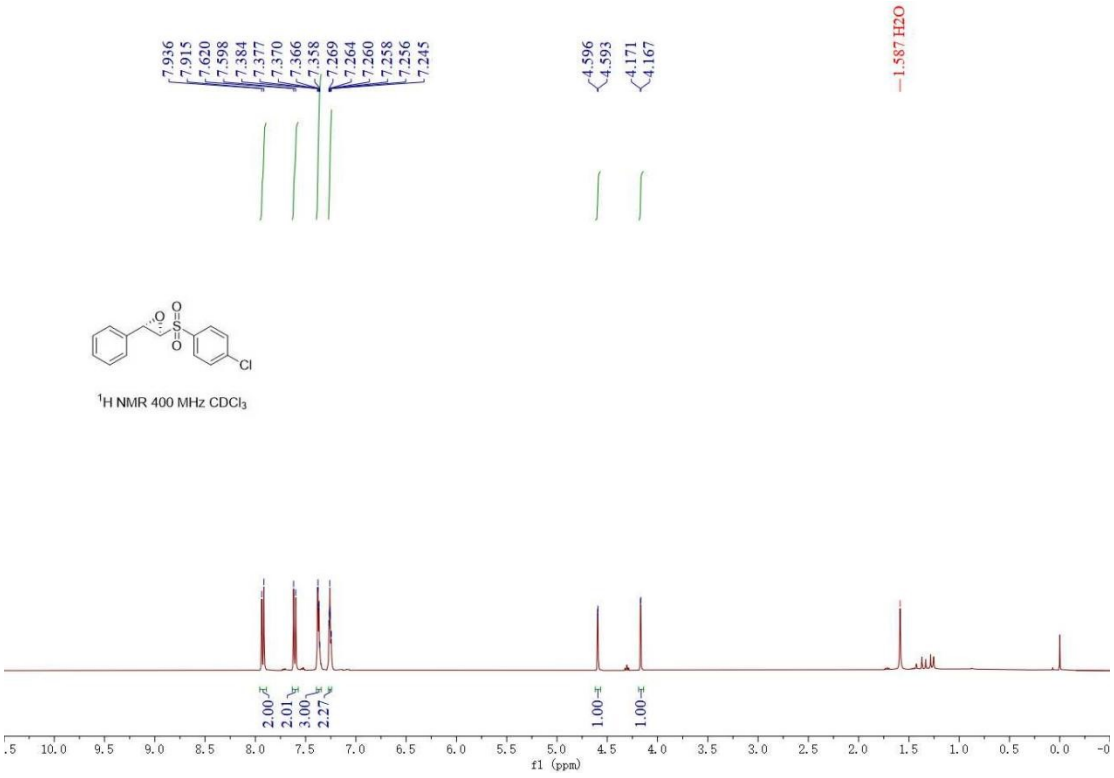


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 16021; Processing Method: 31316161

Processed Channel Descr.: W2489 ChB 220nm

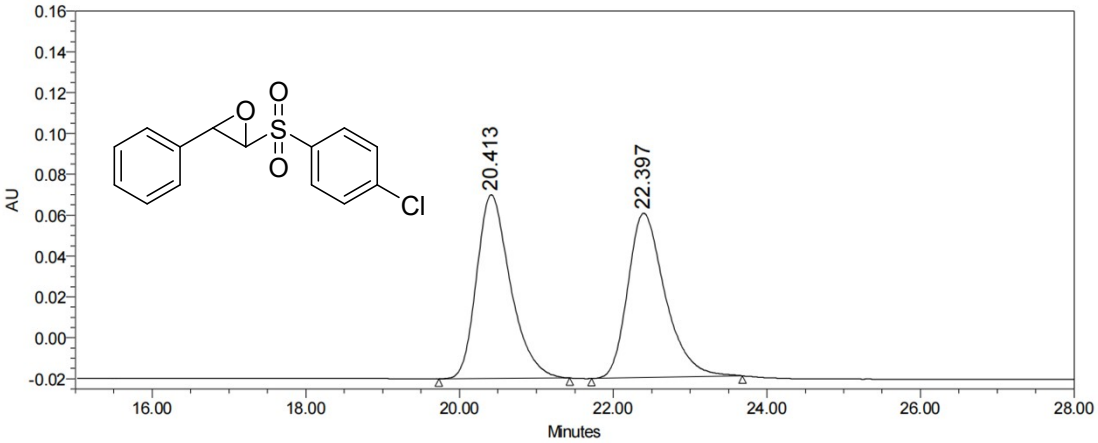
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	21.257	5196097	95.04	165762
2	W2489 ChB 220nm	24.297	270916	4.96	7211

(2*S*,3*S*)-2-((4-chlorophenyl)sulfonyl)-3-phenyloxirane (4e)



^{1}H NMR of **4e**

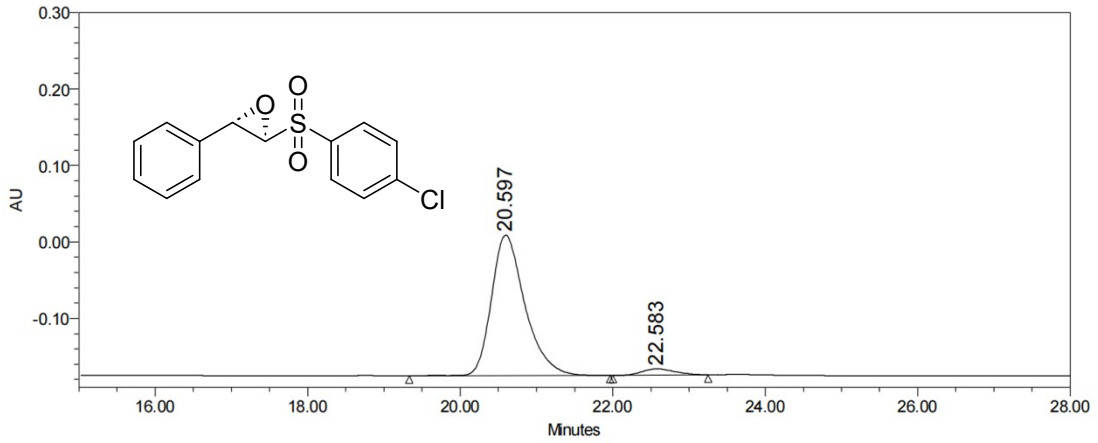
^{13}C NMR of **4e**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15921; Processing Method: 4646515

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	20.413	2751091	50.30	89928
2	W2489 ChB 220nm	22.397	2718263	49.70	80540

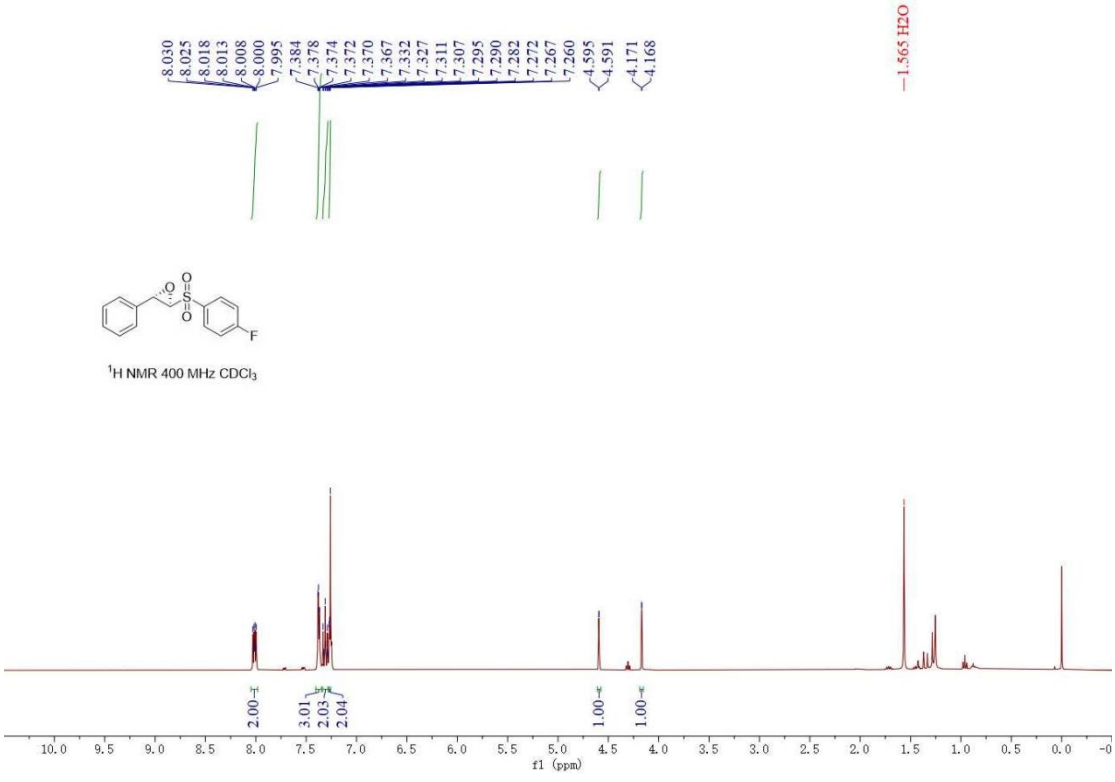


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 16061; Processing Method: 16616

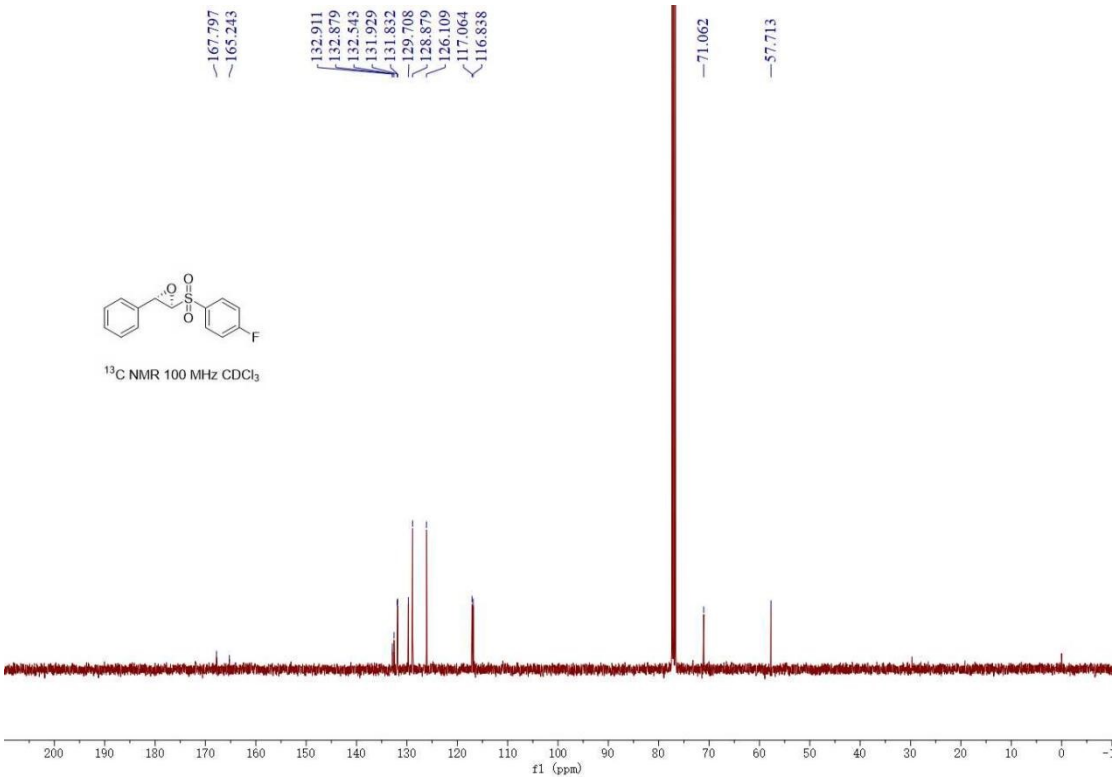
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	20.597	5605082	95.81	183627
2	W2489 ChB 220nm	22.583	245338	4.19	8173

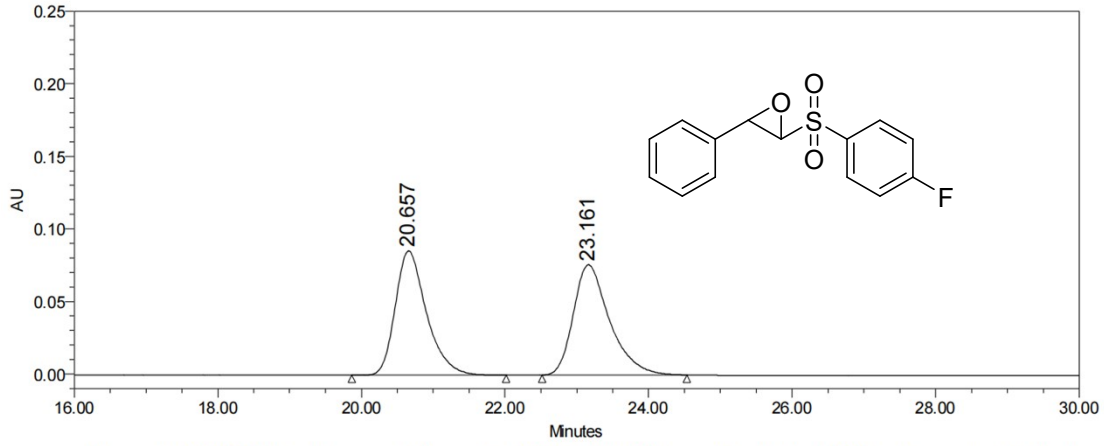
(2*S*,3*S*)-2-((4-fluorophenyl)sulfonyl)-3-phenyloxirane (4f)



^{1}H NMR of **4f**



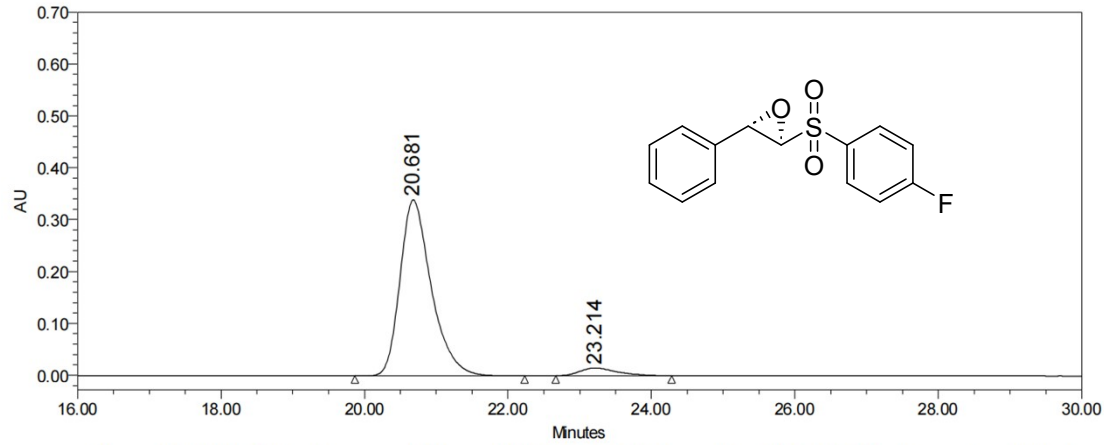
^{13}C NMR of **4f**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 16030; Processing Method: 3165464646

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	20.657	2591269	49.26	85804
2	W2489 ChB 220nm	23.161	2669560	50.74	75986

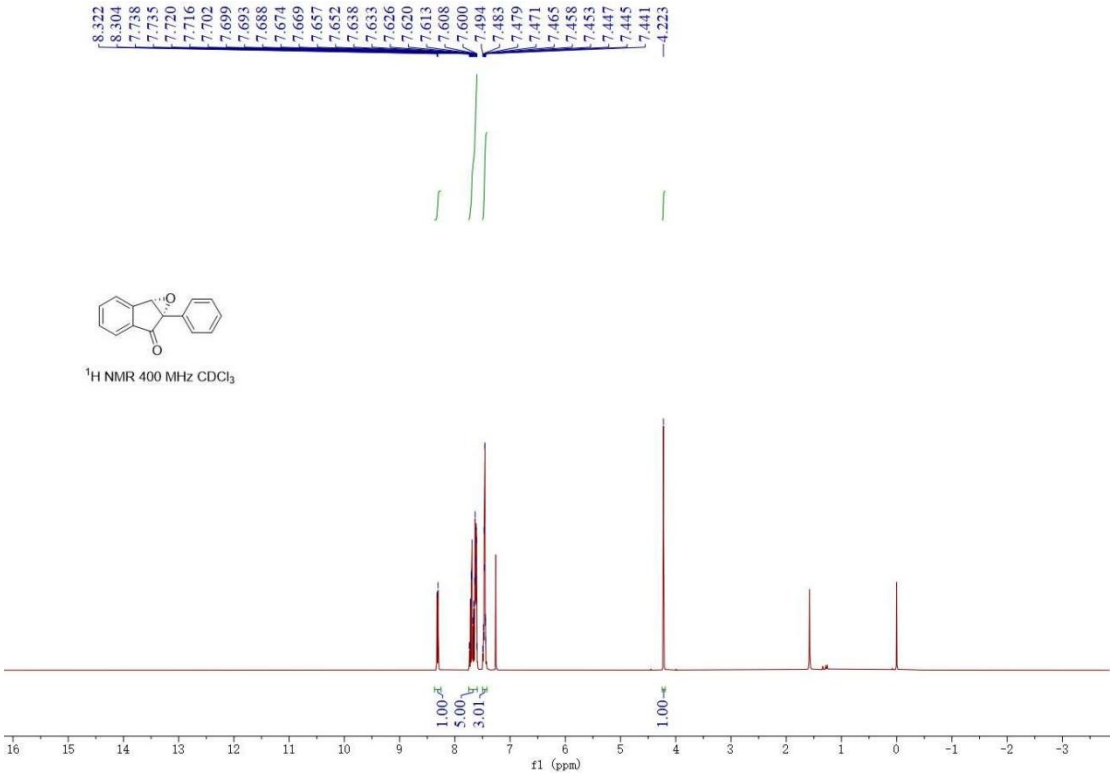


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 16033; Processing Method: 242524542

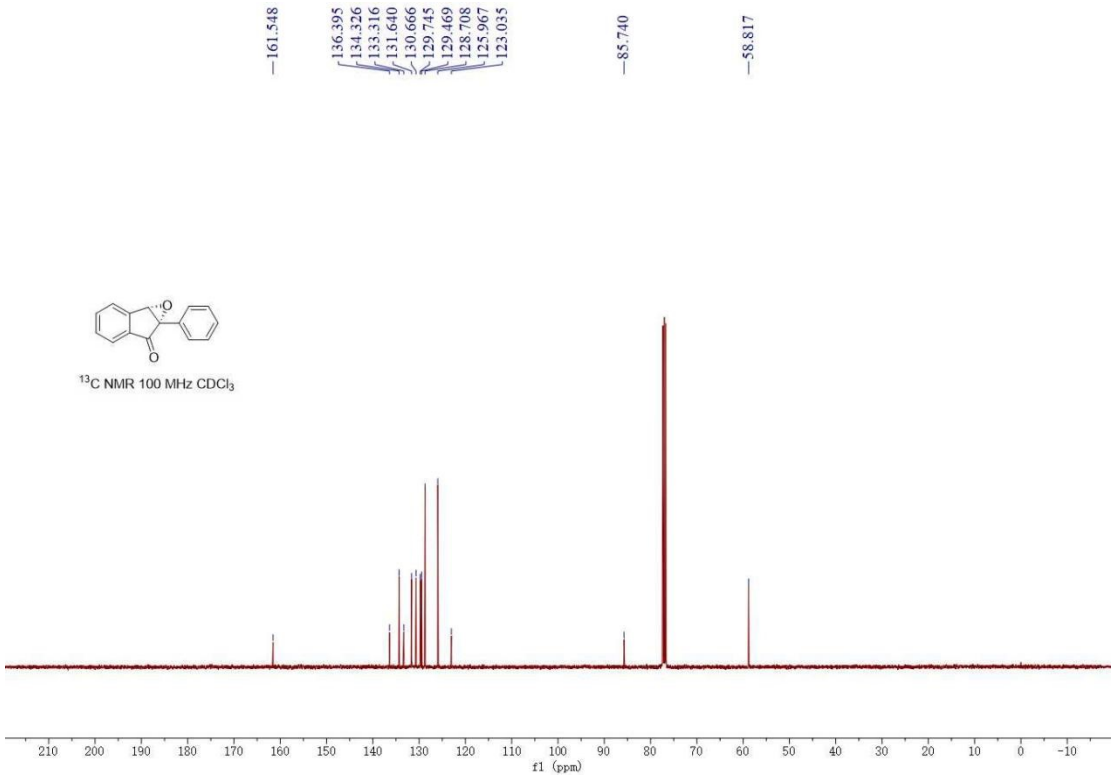
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	20.681	10279406	94.98	339473
2	W2489 ChB 220nm	23.214	542747	5.02	15124

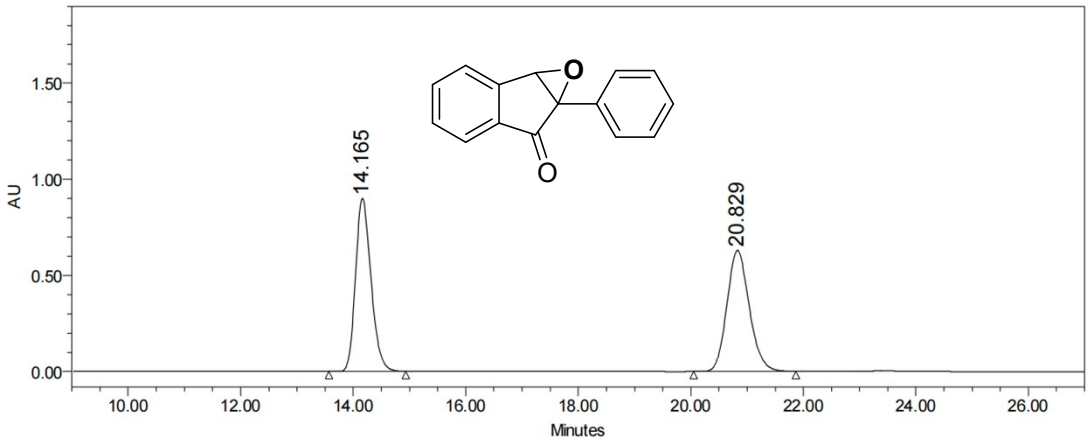
(1a*S*,6a*S*)-6a-phenyl-1a,6a-dihydro-6*H*-indeno[1,2-*b*]oxiren-6-one (6a)



^{1}H NMR of **6a**



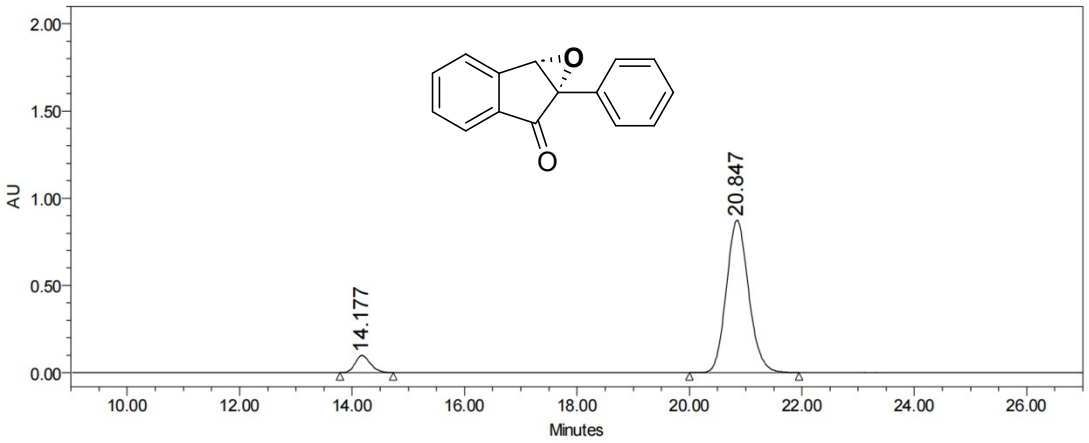
^{13}C NMR of **6a**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15101; Processing Method: 2313

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	14.165	17186501	49.71	899575
2	W2489 ChB 220nm	20.829	17389473	50.29	630220

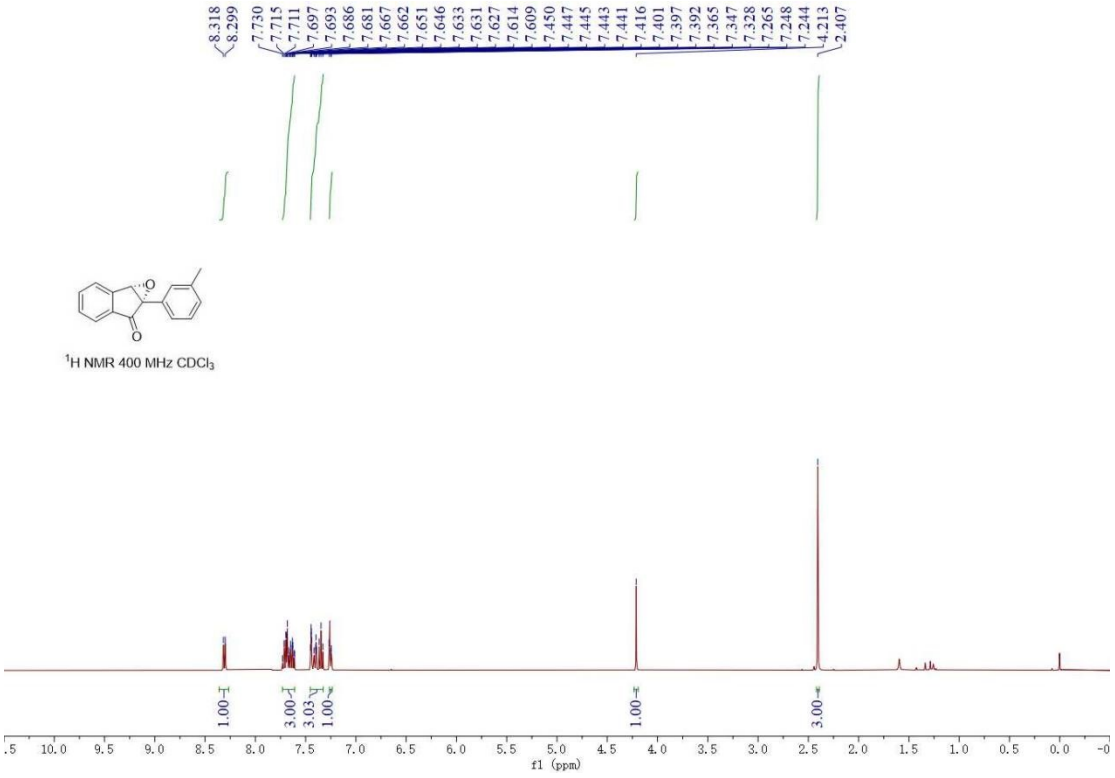


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15104; Processing Method: 656231

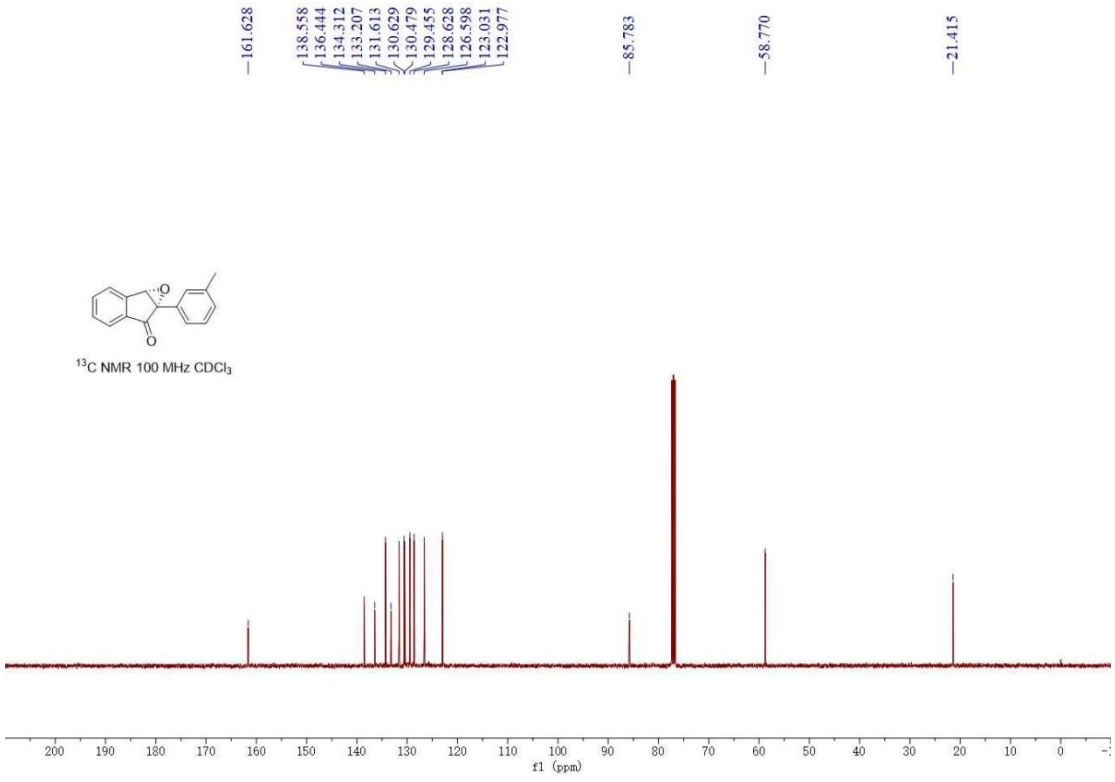
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	14.177	1852109	7.13	98577
2	W2489 ChB 220nm	20.847	24111619	92.87	873486

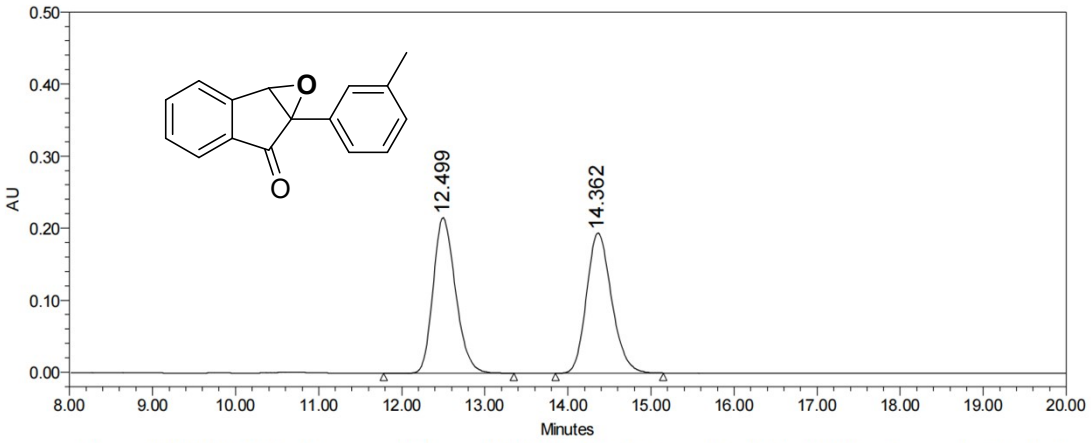
(1a*S*,6a*S*)-6a-(m-tolyl)-1a,6a-dihydro-6*H*-indeno[1,2-*b*]oxiren-6-one (6b)



^{1}H NMR of **6b**



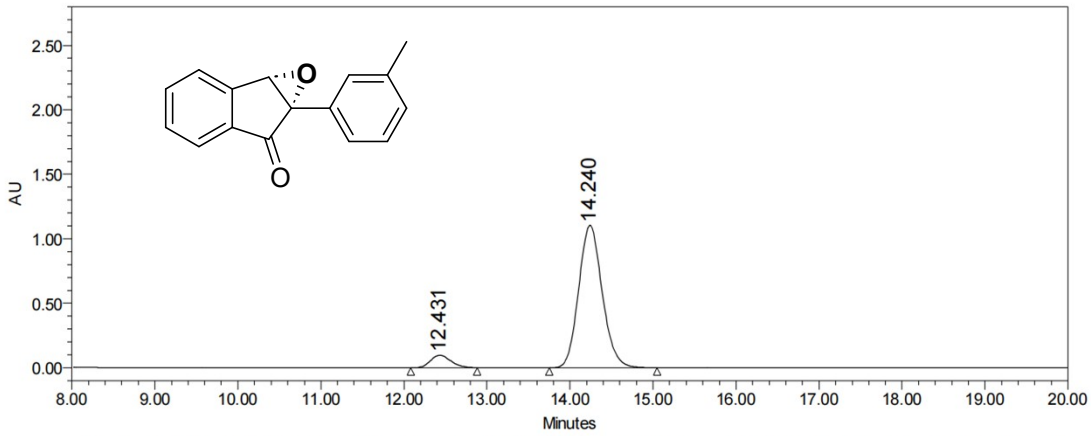
^{13}C NMR of **6b**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15113; Processing Method: 6436413

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	12.499	4039792	49.73	215852
2	W2489 ChB 220nm	14.362	4083850	50.27	194482

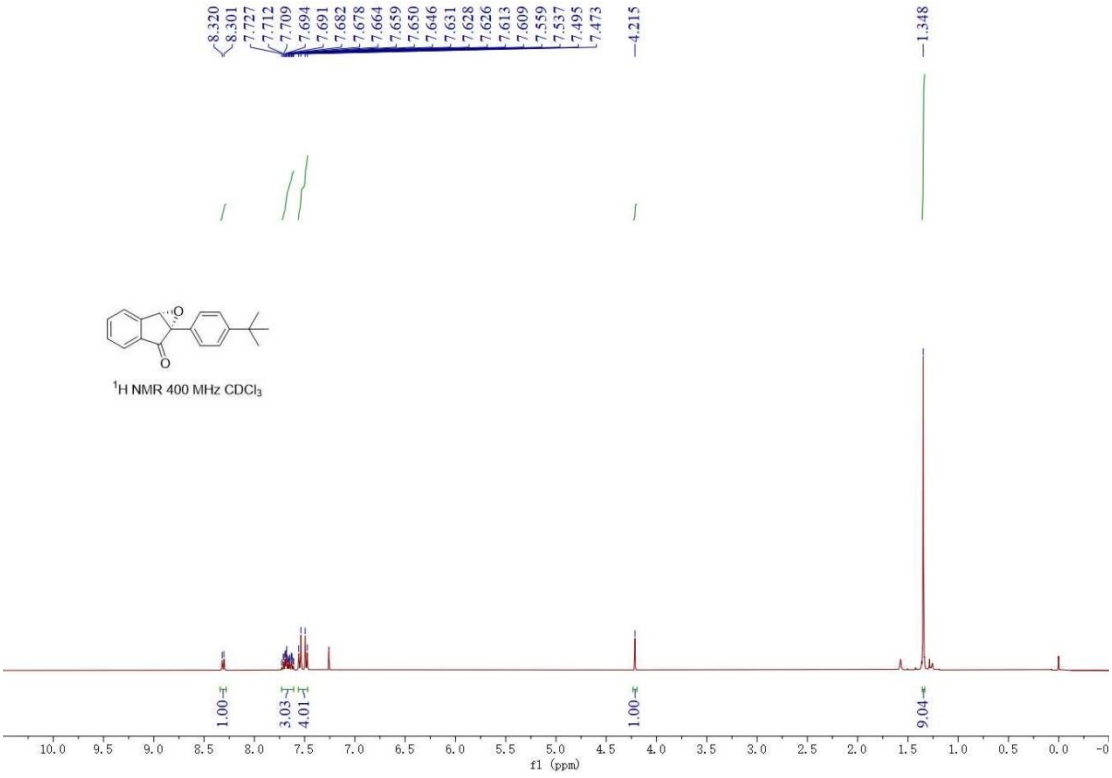


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15116; Processing Method: 9746496464

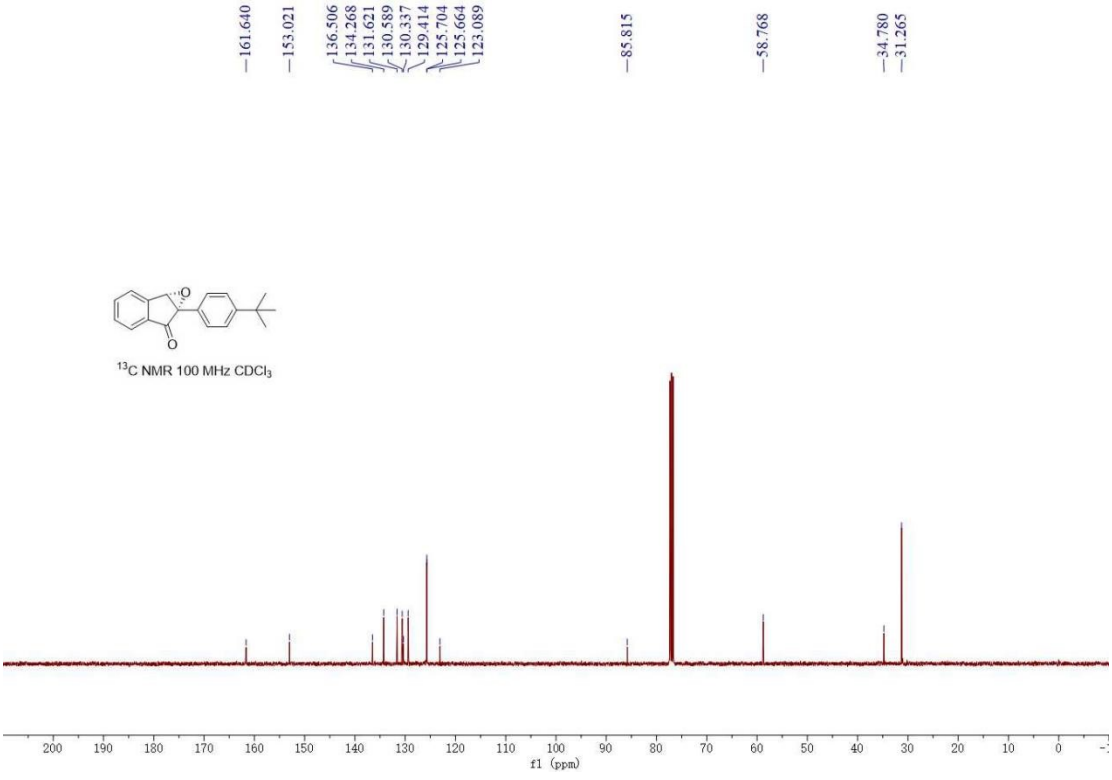
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	12.431	1666915	7.11	97214
2	W2489 ChB 220nm	14.240	21788563	92.89	1105828

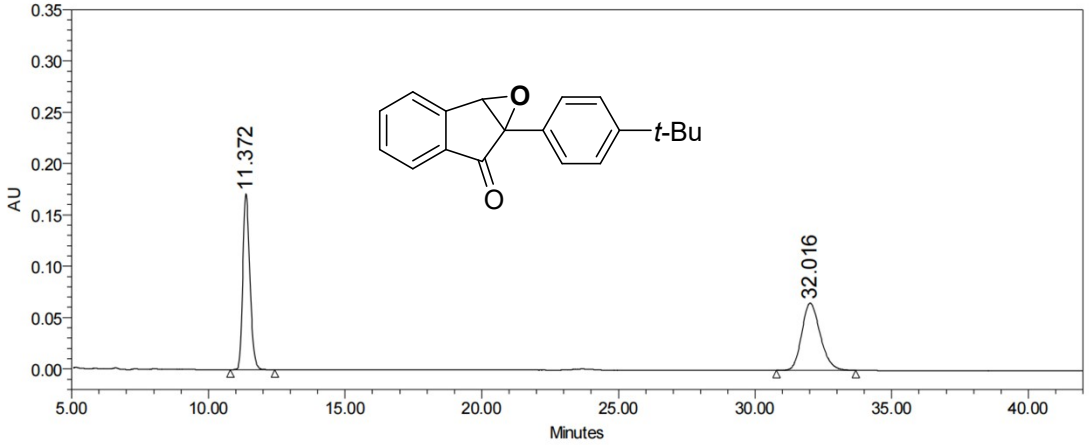
(1a*S*,6a*S*)-6a-(4-(tert-butyl)phenyl)-1a,6a-dihydro-6*H*-indeno[1,2-*b*]oxiren-6-one (6c)



^{1}H NMR of **6c**



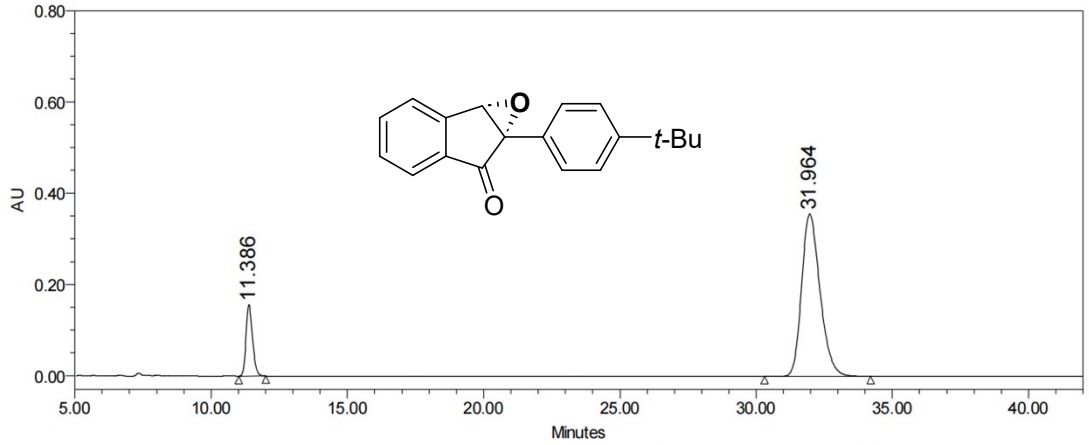
^{13}C NMR of **6c**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15119; Processing Method: 764845

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	11.372	3083063	49.99	171334
2	W2489 ChB 220nm	32.016	3084836	50.01	65680

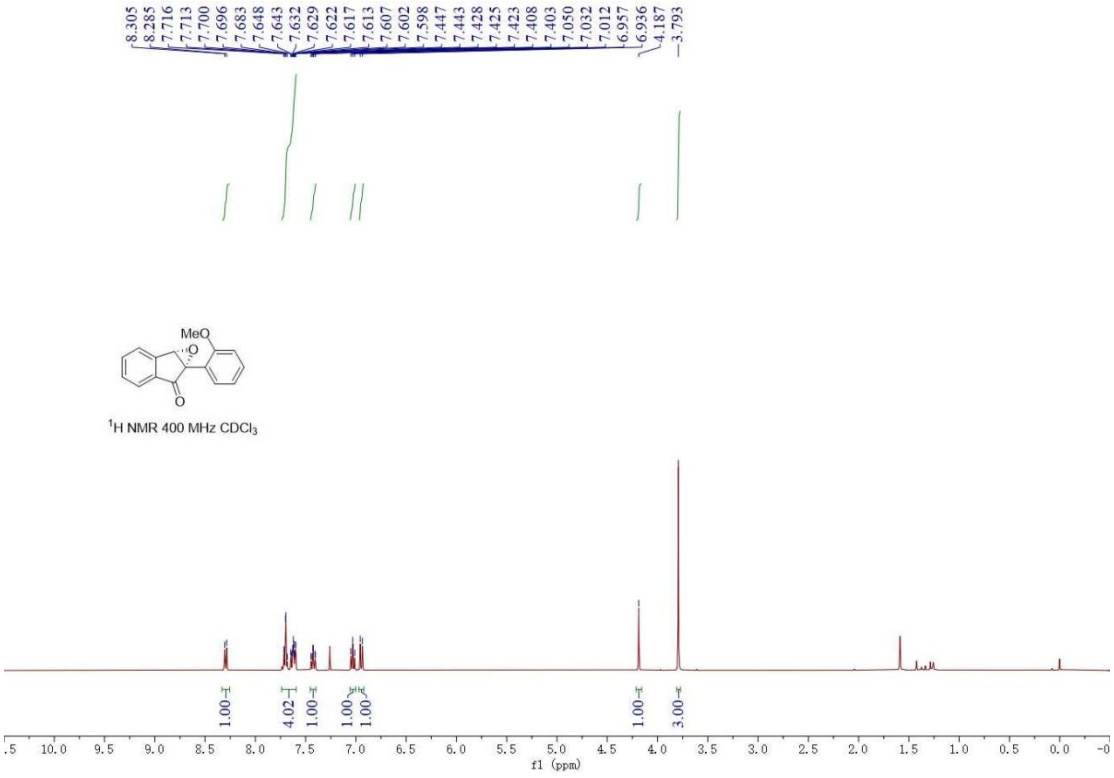


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15122; Processing Method: 9664845

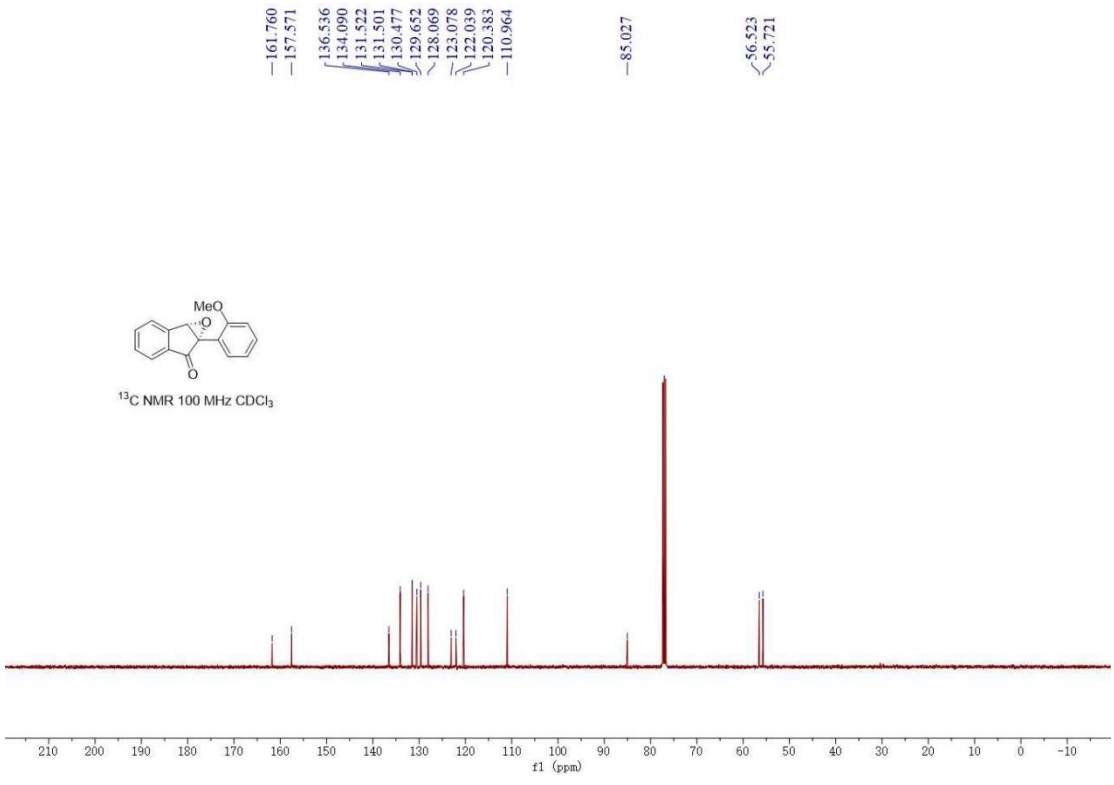
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	11.386	2612616	13.49	156600
2	W2489 ChB 220nm	31.964	16749238	86.51	356114

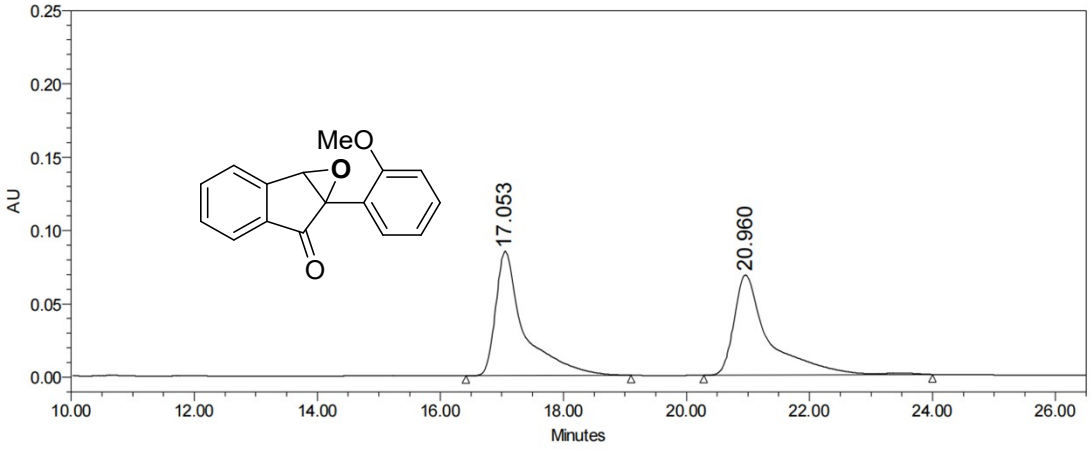
(1a*S*,6a*S*)-6a-(2-methoxyphenyl)-1a,6a-dihydro-6H-indeno[1,2-*b*]oxiren-6-one (6d)



^{1}H NMR of **6d**



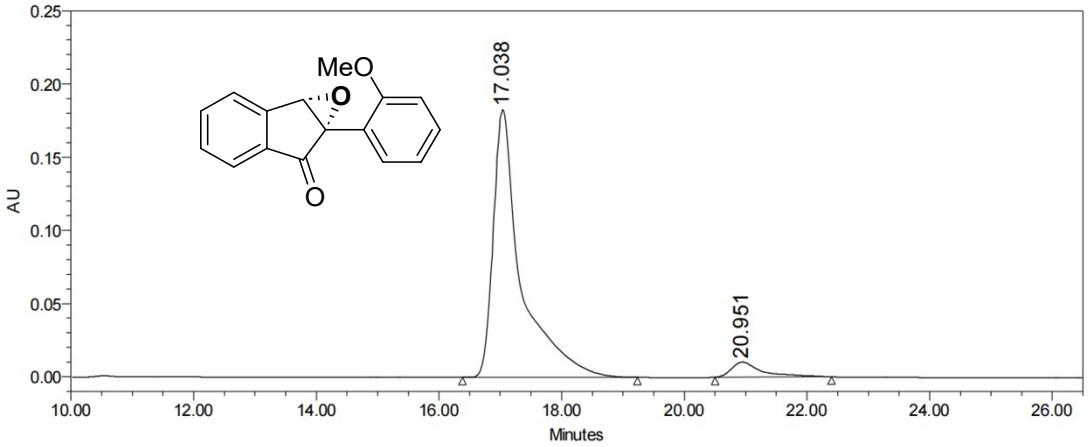
^{13}C NMR of **6d**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15131; Processing Method: 46464

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	17.053	2716005	50.04	84641
2	W2489 ChB 220nm	20.960	2712043	49.96	68379

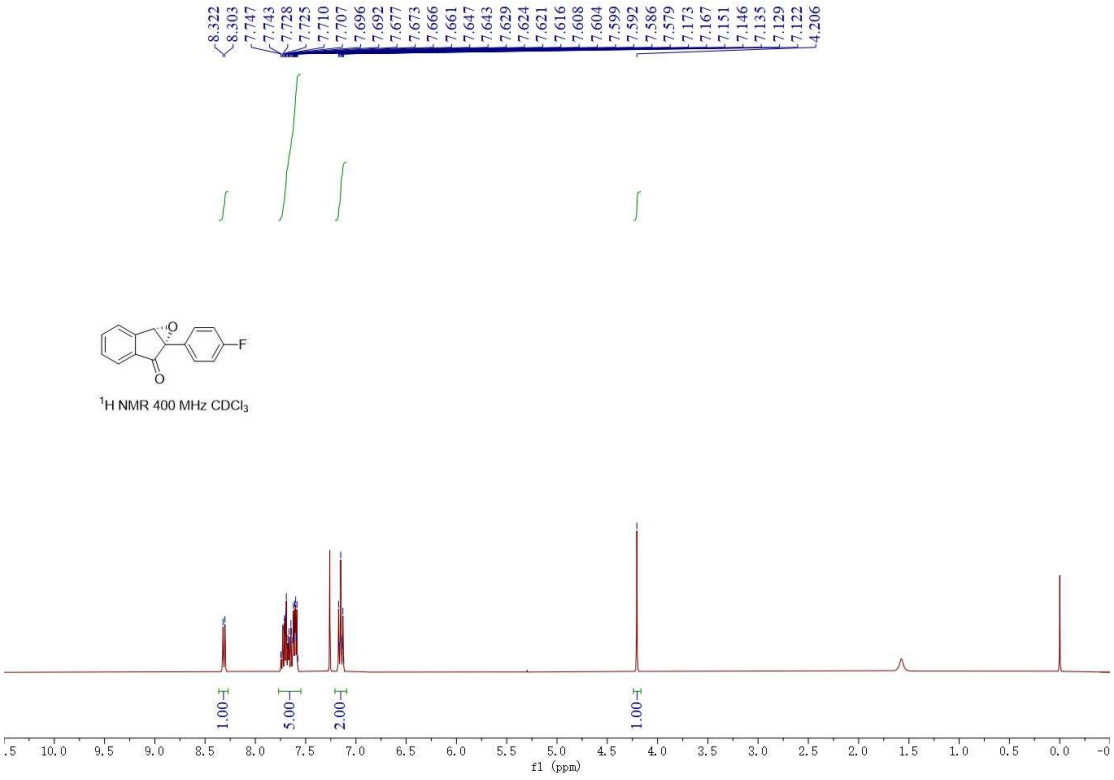


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15128; Processing Method: 966461

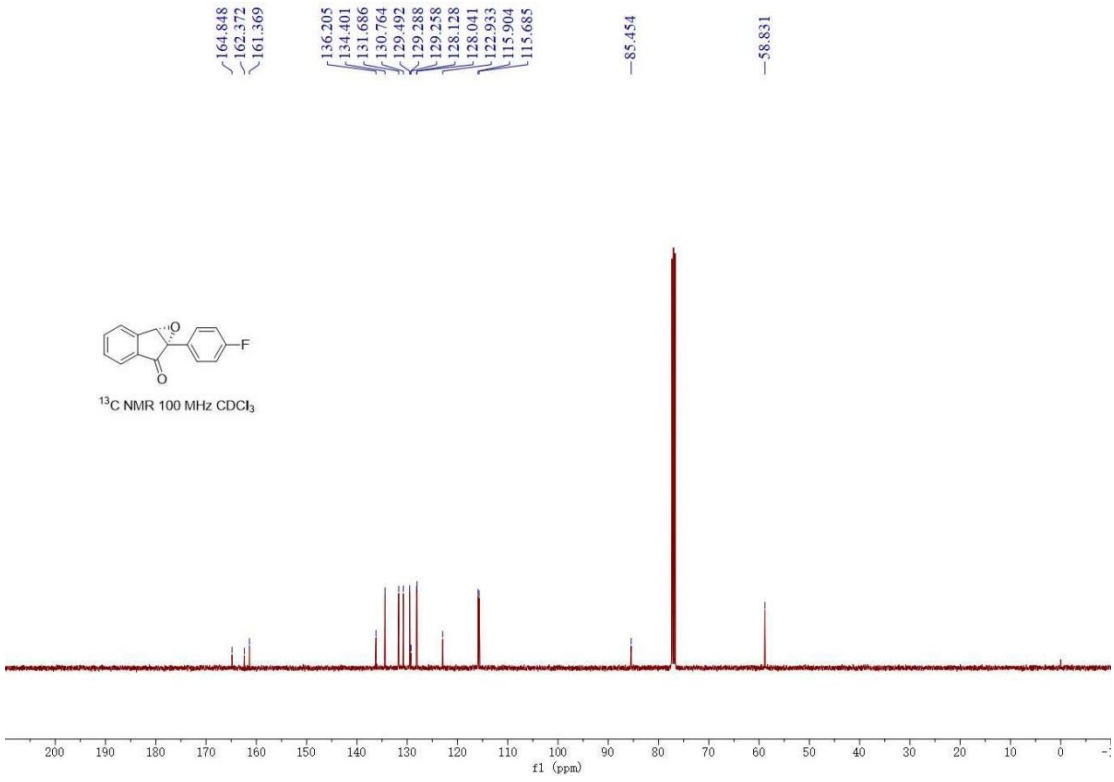
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	17.038	5752371	94.19	182953
2	W2489 ChB 220nm	20.951	354764	5.81	10245

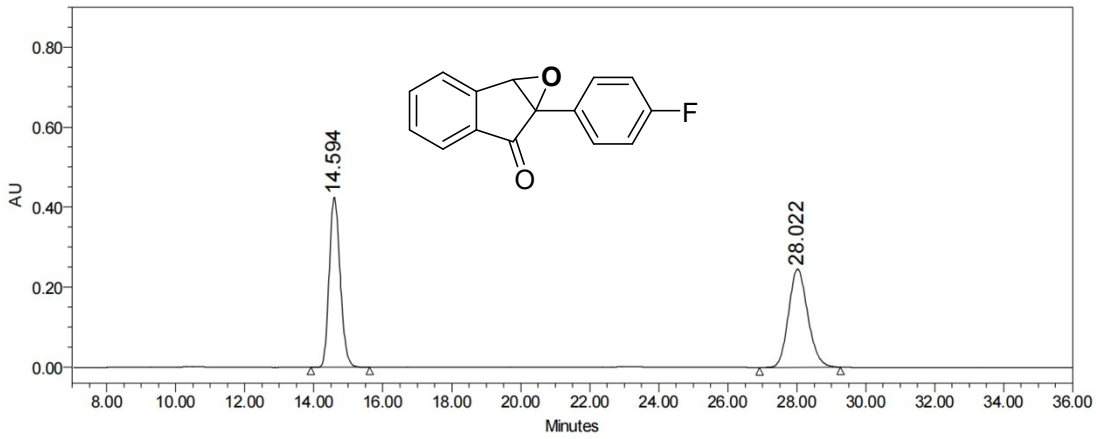
(1a*S*,6a*S*)-6a-(4-fluorophenyl)-1a,6a-dihydro-6*H*-indeno[1,2-*b*]oxiren-6-one (6e)



^{1}H NMR of **6e**



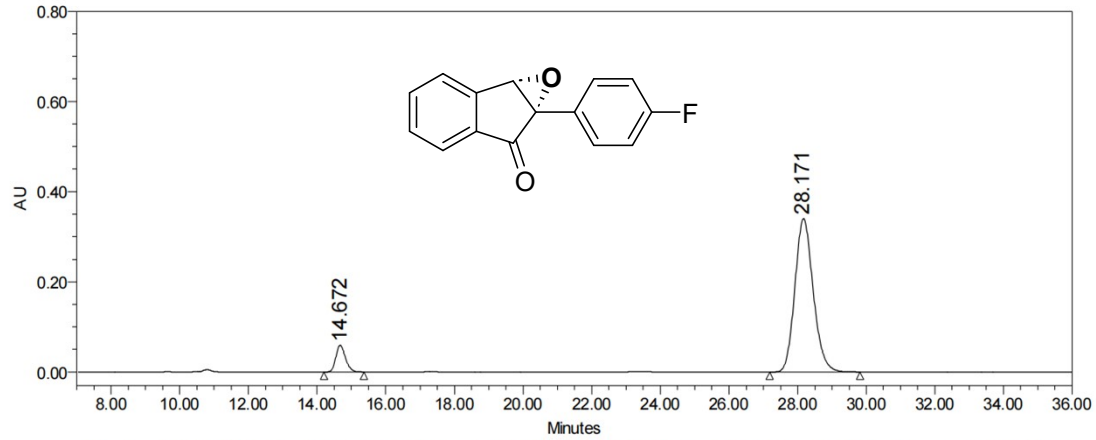
^{13}C NMR of **6e**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15107; Processing Method: 64465623

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	14.594	9407414	49.77	425105
2	W2489 ChB 220nm	28.022	9492816	50.23	245261

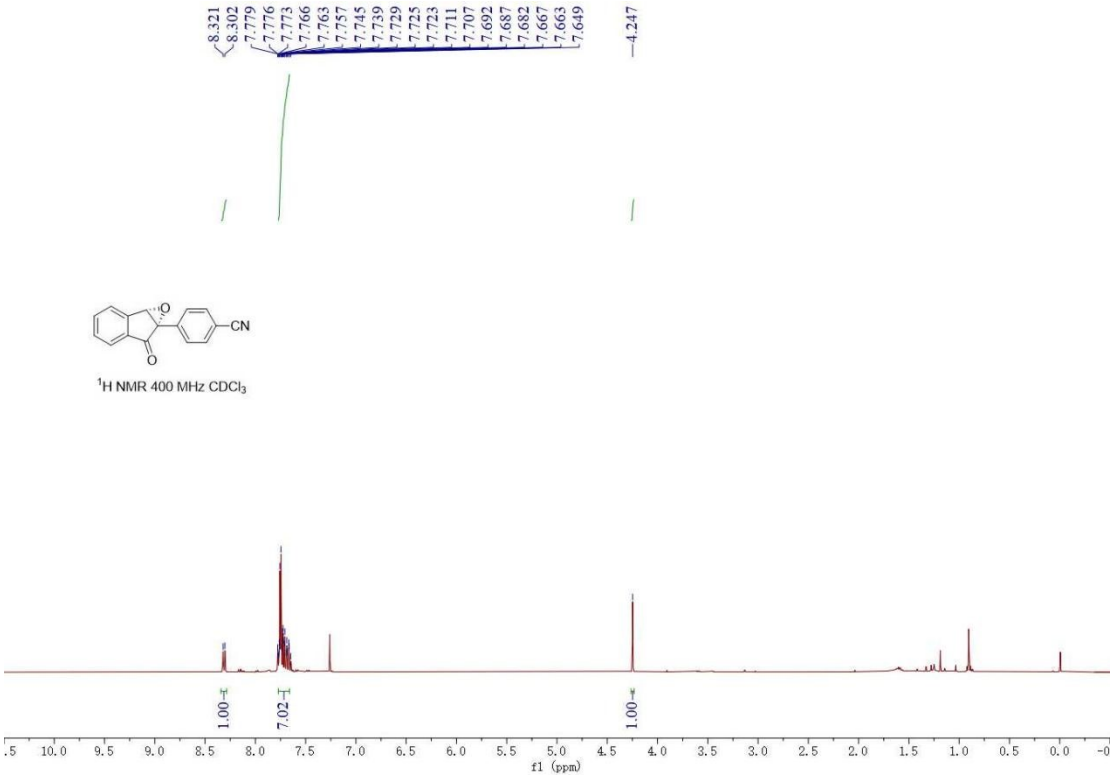


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15110; Processing Method: 9661464

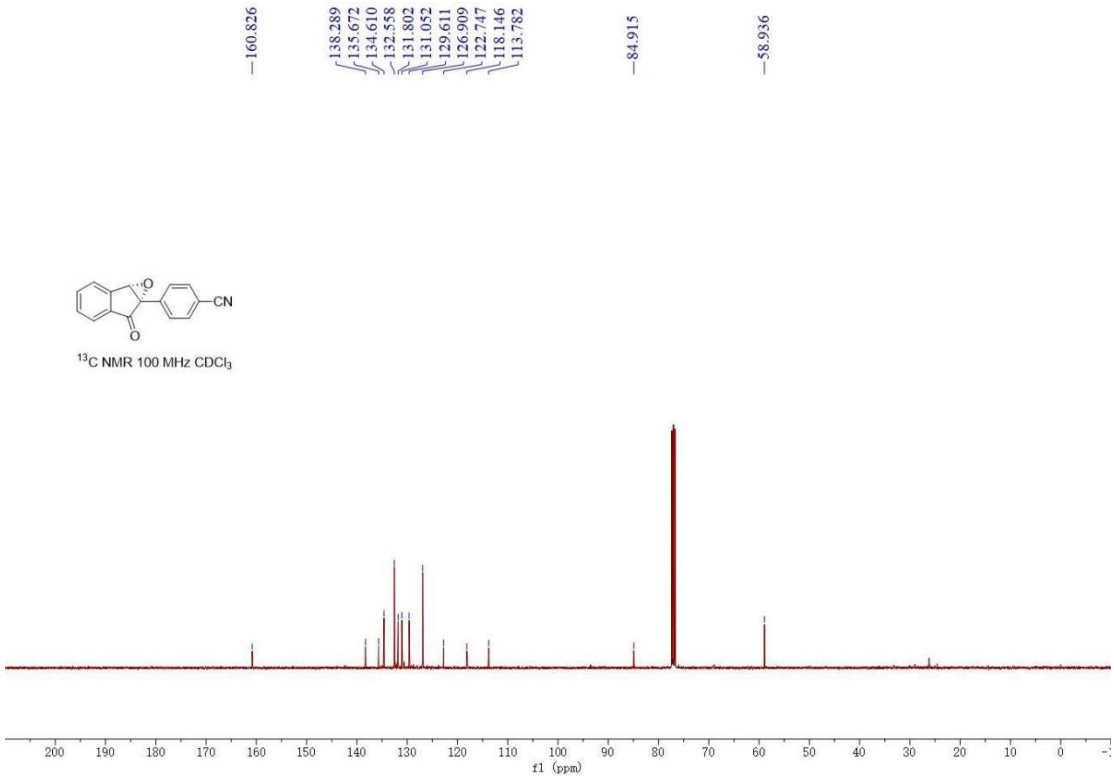
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	14.672	1164920	8.45	59823
2	W2489 ChB 220nm	28.171	12627327	91.55	340427

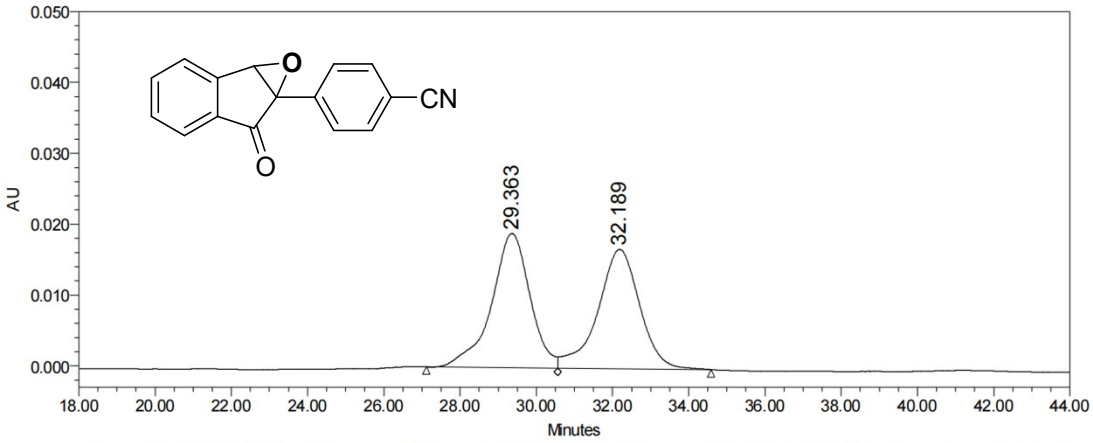
4-((1a*S*,6a*S*)-6-oxo-1a,6-dihydro-6a*H*-indeno[1,2-*b*]oxiren-6a-yl)benzonitrile (6f)



^{1}H NMR of **6f**



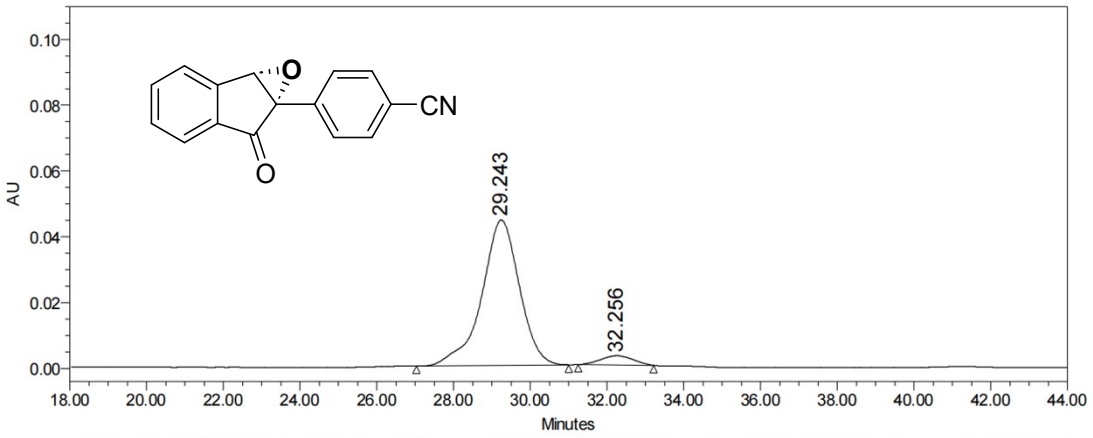
^{13}C NMR of **6f**



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15140; Processing Method: 94641316

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	29.363	1327253	50.81	18943
2	W2489 ChB 220nm	32.189	1285055	49.19	16830

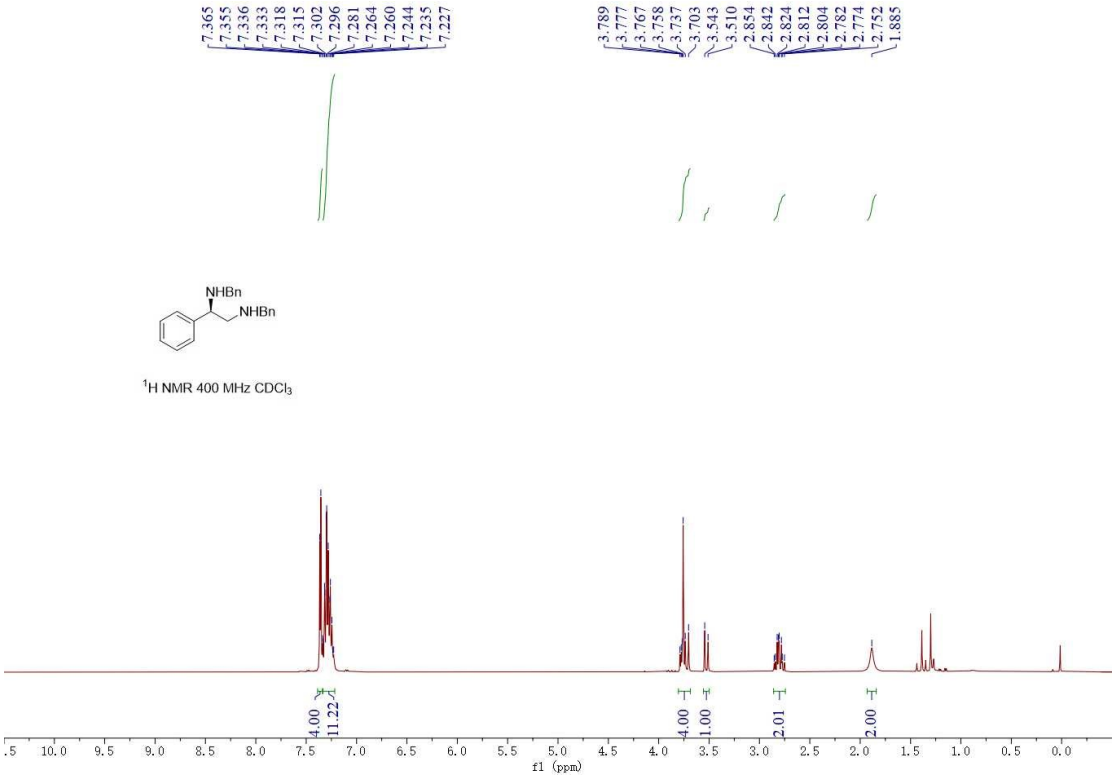


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 15137; Processing Method: 6513646

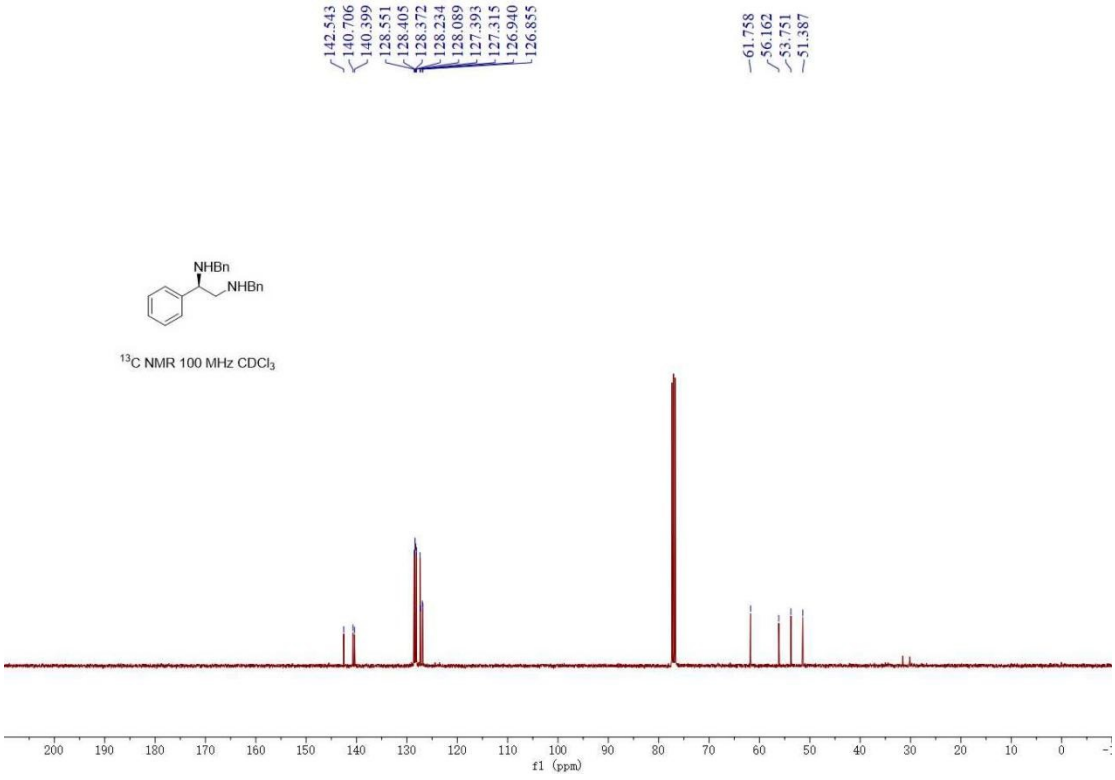
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	29.243	3019303	94.81	44241
2	W2489 ChB 220nm	32.256	165423	5.19	2796

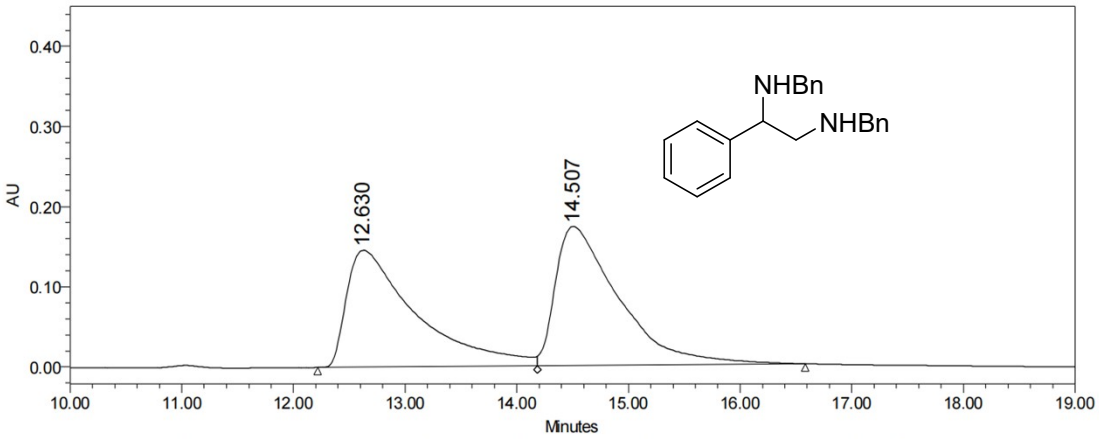
(*R*)-N^1,N^2-dibenzyl-1-phenylethane-1,2-diamine (4ab)



^{1}H NMR of **4ab**



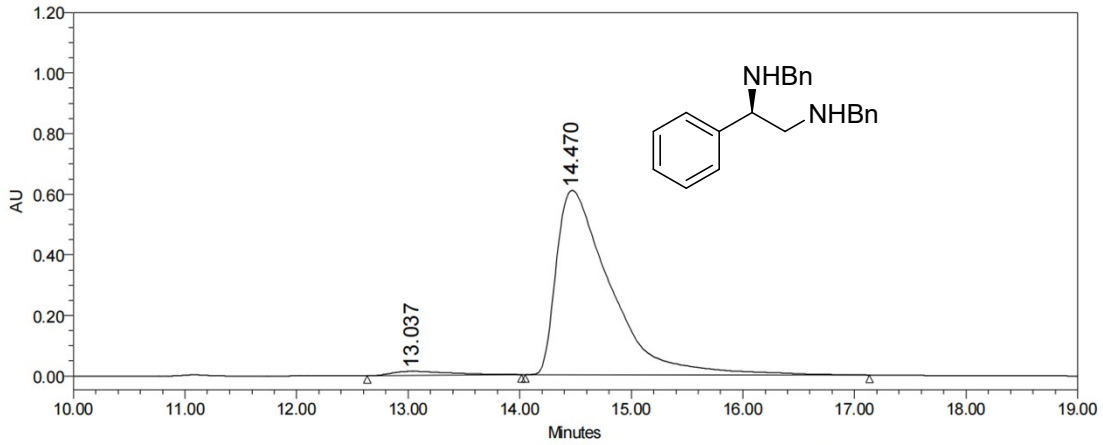
^{13}C NMR of **4ab**



Channel: W2489 ChA; Processed Channel: W2489 ChA 220nm; Result Id: 16235; Processing Method: 656436

Processed Channel Descr.: W2489 ChA 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 220nm	12.630	6301459	48.05	145784
2	W2489 ChA 220nm	14.507	6812596	51.95	173673

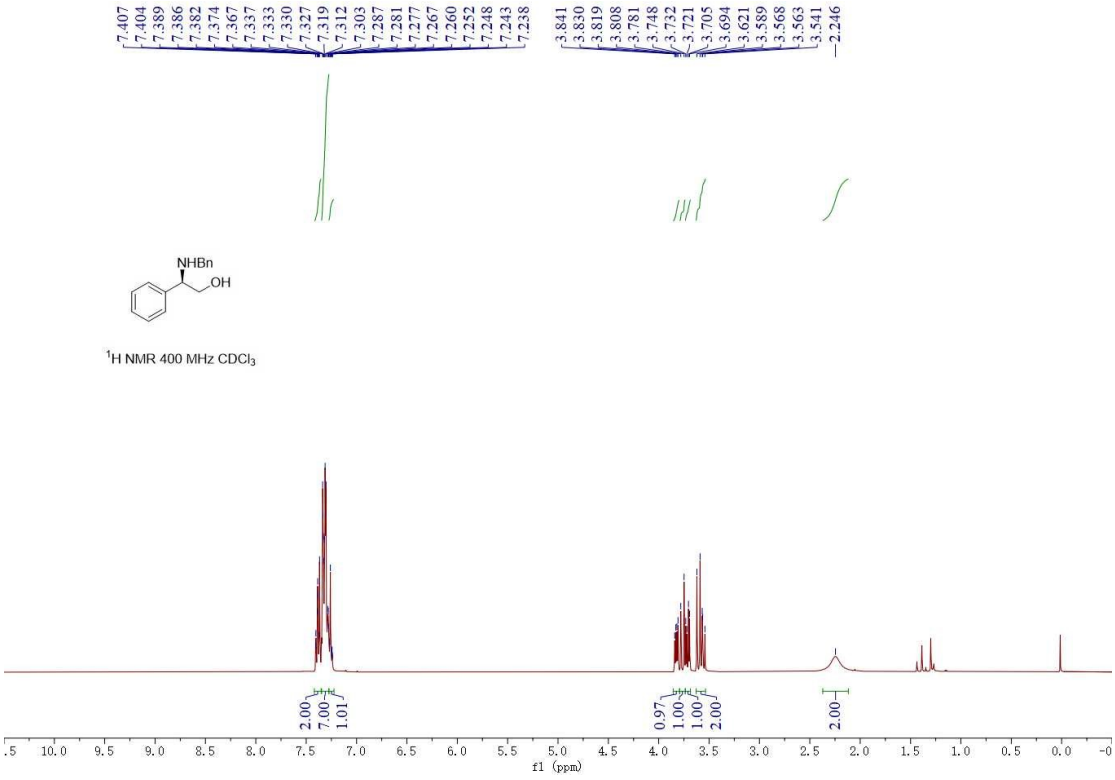


Channel: W2489 ChA; Processed Channel: W2489 ChA 220nm; Result Id: 16232; Processing Method: 164364646

Processed Channel Descr.: W2489 ChA 220nm

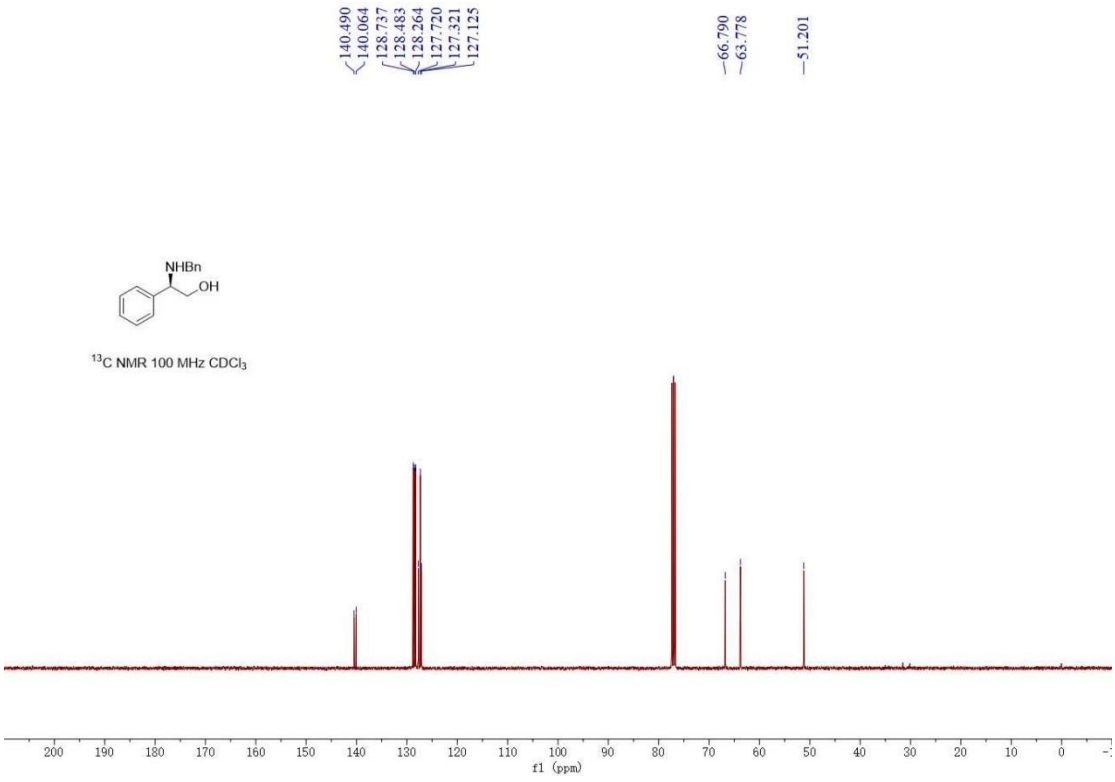
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 220nm	13.037	524639	2.49	13781
2	W2489 ChA 220nm	14.470	20544448	97.51	608490

(*R*)-2-(benzylamino)-2-phenylethan-1-ol (4ac)



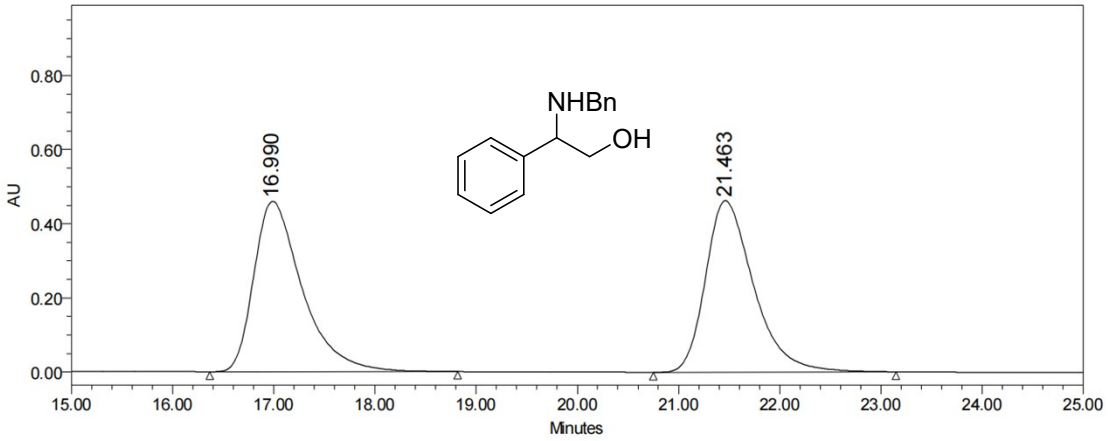
^{1}H NMR 400 MHz $CDCl_3$

^{1}H NMR of **4ac**



^{13}C NMR 100 MHz $CDCl_3$

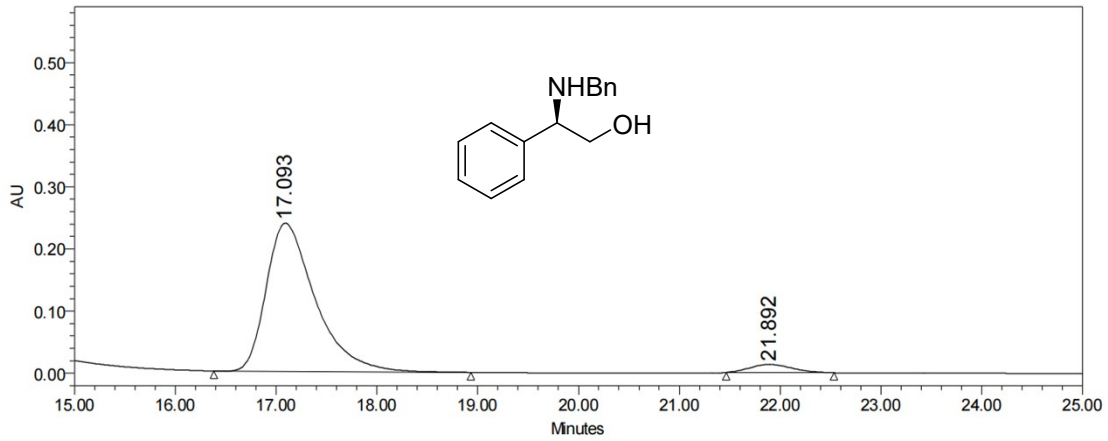
^{13}C NMR of **4ac**



Channel: W2489 ChA; Processed Channel: W2489 ChA 220nm; Result Id: 16139; Processing Method: 646565

Processed Channel Descr.: W2489 ChA 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 220nm	16.990	15290709	50.03	459922
2	W2489 ChA 220nm	21.463	15272428	49.97	462742

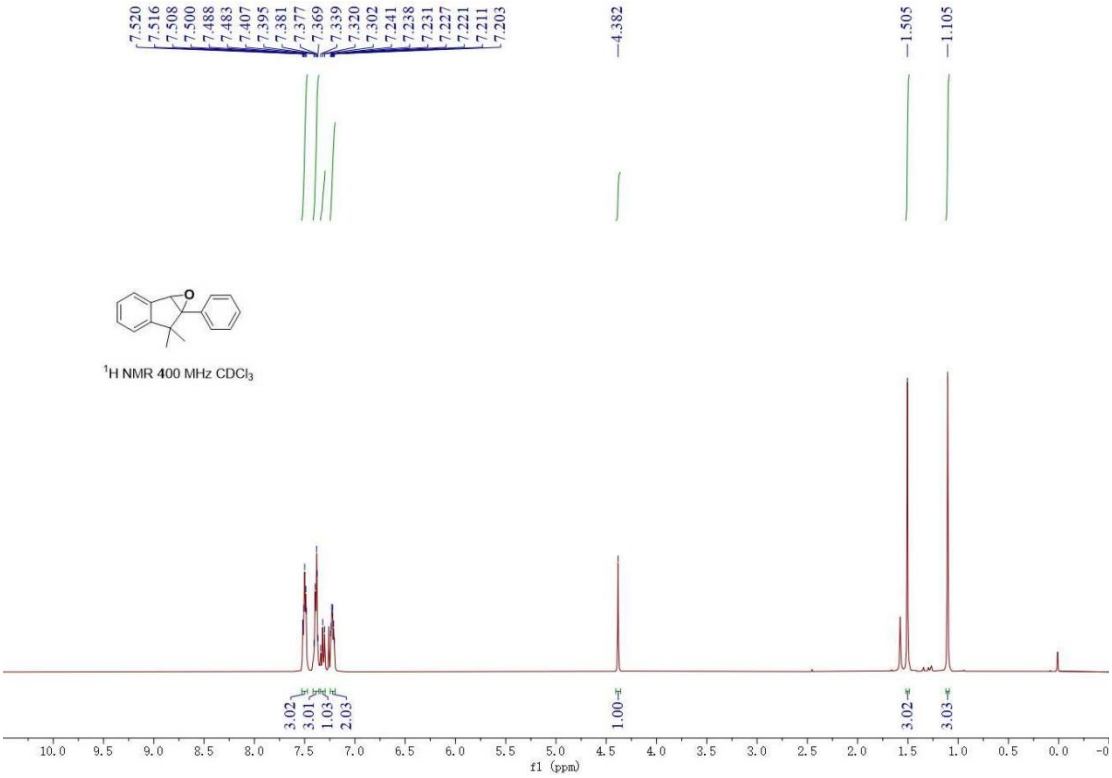


Channel: W2489 ChA; Processed Channel: W2489 ChA 220nm; Result Id: 16136; Processing Method: 641445

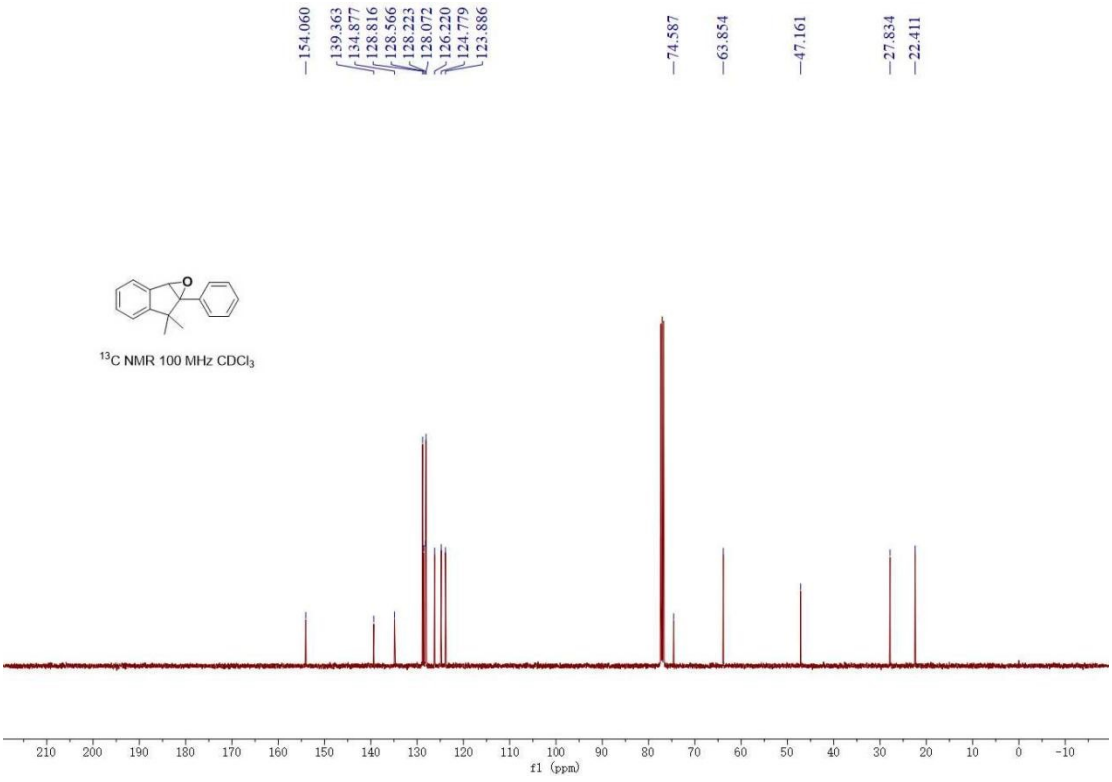
Processed Channel Descr.: W2489 ChA 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 220nm	17.093	8047926	95.53	238578
2	W2489 ChA 220nm	21.892	376276	4.47	13031

6,6-dimethyl-6a-phenyl-1a,6a-dihydro-6*H*-indeno[1,2-*b*]oxirene (8a)



^{1}H NMR of **8a**



^{13}C NMR of **8a**