Supporting Information

Visible-light-induced chemo-, diastereo- and enantioselective α-C(sp^3)−H functionalization of alkyl silanes

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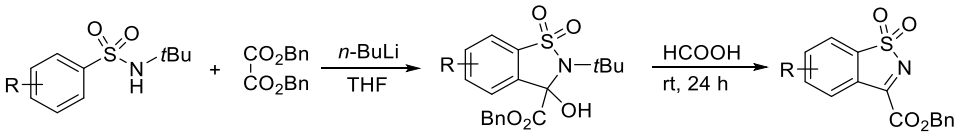
1. General remarks

10 W or 20 W blue LEDs (Chinese Taobao, https://shop112050379.taobao.com) were used as light sources. ^{1}H NMR spectra were recorded on Bruker ASCEND^{TM} 400M (400 MHz) or 600M (600 MHz). ^{13}C{^{1}H} NMR data were collected on Bruker ASCEND^{TM} 400M (101 MHz) or 600M (151 MHz) with complete proton decoupling. Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26) for ^{1}H NMR and ($CDCl_3$, δ = 77.0) for ^{13}C{^{1}H} NMR. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{19}F{^{1}H} NMR spectra were collected on Bruker ASCEND^{TM} 400M (376 MHz) with complete proton decoupling. Chemical shifts δ are given relative to $CFCl_3$ (external reference, δ ^{19}F($CFCl_3$) = 0). Enantiomeric excesses were determined by chiral HPLC analysis on Daicel Chiralcel AD-H or chiral UPC^2 analysis on Phenomenex Chiralcel Lux 5u Cellulose at 35 ºC with UV detector at 220 nm in comparison with the authentic racemates. Optical rotations were determined after flash column chromatography purification and reported as follows: $[\lambda]_D^T$ (*c*: g/100 mL, in CH_2Cl_2). HRMS were recorded on Thermo Q-Exactive Focus (FTMS+*c* ESI). IR spectra were recorded on SHIMADZU IR Tracer-100 FT-IR spectrophotometer. Emission intensities were recorded using a F-7000 FL Spectrophotometer. EPR spectra were recorded at room temperature on a Bruker EPR A300. All reactions were performed in sealed oven-dried glass tubes under an atmosphere of nitrogen unless otherwise noted. $CHCl_3$ was distilled over CaH_2. All the solvents were purified by usual methods before use. Chromatography: Qingdao Haiyang silica gel, HG/T2354-92, HCP. The chiral *N,N′*-dioxides were prepared according to methods reported in the literature.[1-3]

2. The synthesis of substrates

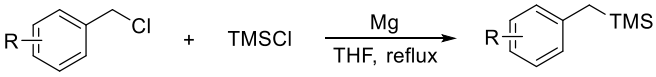
2.1 General procedure for the synthesis of *N*-sulfonyl cyclic ketimines



Butyllithium (30.75 mmol, 2 M in THF) was added dropwise over a 20 minutes period to a cold (0 ºC), mechanically stirred solution of aryl sulfonamide (15 mmol) in anhydrous tetrahydrofuran (80 mL) under a dry nitrogen atmosphere. The mixture was stirred for an additional 25 min at 0 ºC and a precipitate was formed. The suspension was cooled to -78 ºC and dibenzyl oxalate (45 mmol) in THF (20 mL) was added dropwise over 10 minutes. The cooling bath was removed and the suspension was stirred at ambient temperature for 2 h. The reaction was quenched with 5% HCl (40 mL) and added to water (200 mL). The organic phase was extracted with ether (3×50 mL). The ether phase was washed with brine (200 mL). The solvent was removed and the crude product was obtained used directly in the next step without further purification. To the crude product obtained above, formic acid (25 mL) was added and the suspension was stirred at room temperature under a dry nitrogen atmosphere. After 5 min dissolution occurred. After 24 h the solution was concentrated and the resultant solid was dissolved in CH_2Cl_2 and concentrated to remove traces of formic acid. This afforded the title compound as a solid which was further purified by flash chromatography (DCM/PE = 1/2 - DCM).[4]

2.2 General procedure for the synthesis of alkyl silanes

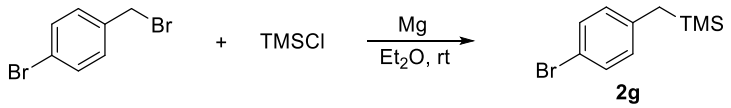
General procedure I (for **2a**, **2b**, **2c**, **2d**, **2f**, **2h, 2i)**[5]



2a: R = H; **2b**: R = 3-Me; **2c**: R = 4-Me
2d: R = 4-MeO; **2e**: R = 4-F; **2f**: R = 4-Cl
2h: R = 2-F; **2i**: R = 3-F

A flame-dried, three-neck, round-bottom flask, equipped with a mechanical stirrer, reflux condenser, N_2 inlet, and addition funnel, was charged with dry magnesium turnings (0.528 g, 22 mmol), dry tetrahydrofuran (20 mL), and chlorotrimethylsilane (3.26 mL, 30 mmol). The appropriate benzyl chloride (20 mmol) in dry tetrahydrofuran (20 mL) was added slowly, at a rate to maintain gentle reflux. After addition was complete, the mixture was heated under reflux 2 h, cooled, and poured into cold water. Pentane (15 mL) was added and the pentane layer washed three times with cold water (30 mL) and once with saturated NaCl solution (30 mL), dried ($MgSO_4$), and then rotary evaporated to yield the crude benzyl trimethylsilanes, which was purified by column chromatography to yield the silane derivatives as colorless oils.

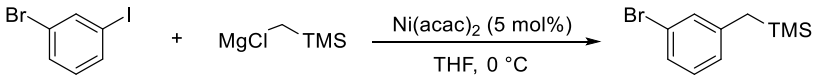
General procedure II (for **2g**)[6]



2g

To a suspension of Mg-tunings (0.3 g) in Et_2O (10 mL) was added a solution of (2.9 g, 12 mmol) of *p*-bromobenzyl bromide (Aldrich) in Et_2O (20 mL). To the resulting Grignard reagent was added (3.0 mL, 24 mmol) of chlorotrimethylsilane (Aldrich), and the resulting mixture was stirred at 25 ºC for 12 h. Addition of ice-water followed by separation, drying, and concentration of the mixture gave an oil which was subjected to molecular distillation (0.05 mm, 40 °C) to the silylbromoarene **2g** as an oil.

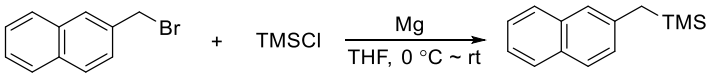
General procedure III (for **2j**)[7]



2j

A solution of haloarene (1.0 equiv) and $Ni(acac)_2$ (0.05 equiv) in dry THF (0.24 M) was stirred for 5 min at room temperature and then cooled to 0 ºC. A solution Me_3SiCH_2MgCl of in Et_2O (1.5 equiv) was added *via* a cannula, and the mixture was allowed to stir at the indicated temperature for 2 h. At this point, the reaction was quenched with water and extracted with Et_2O three times. The combined organic layers were washed with water, brine, dried over Na_2SO_4 (anhydrous) and then concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography afforded benzyltrimentylsilane.

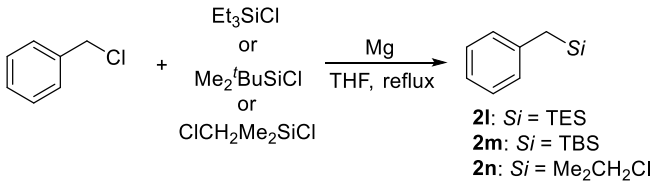
General procedure IV (for **2k**)[8]



2k

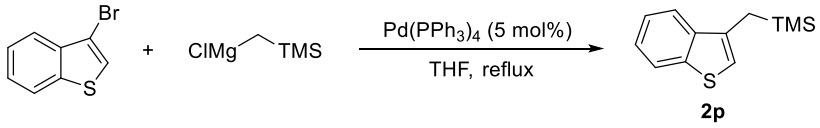
Dry magnesium turnings (0.85 g, 35 mmol) and TMSCl (5.7 mL, 44. mmol) was added as a single portion into THF (21 mL). The mixture was cooled to 0 °C and maintained for 15 min. 2-Naphthylbromide (7.00 g, 31.7 mmol) was dissolved in THF (56 mL) and added dropwise *via* syringe pump. The mixture was maintained for 5 h, and then it was allowed to warm to ambient temperature and maintained for 12 h. The mixture was then cooled to 0 ºC, quenched and worked up as described in the general procedure I. Flash chromatography (2% Et_2O/petroleum ether) afforded 6.10 g (90%) of **2k** as a white solid.

General procedure V (for **2l**, **2m, 2n**)[8]



Activated Mg powder (1.1 equiv) was added as a single portion into a solution of aryl chloride in THF (0.8 M). The suspension was cooled to 0 ºC and 1 h later, the mixture was allowed to warm to ambient temperature and was maintained for another l h. The reaction was then heated to reflux and the indicated chlorosilane (1.4 equiv) was added dropwise. After 12 h, the mixture was cooled to 0 ºC and the reaction was quenched with saturated aqueous NH_4Cl. The mixture was allowed to warm to ambient temperature, concentrated in vacuo, then taken up in Et_2O and washed three times with brine. The combined aqueous phases were extracted twice with Et_2O and the combined organic layers were dried over $MgSO_4$ and then concentrated in vacuo. The arylsilanes products were purified by flash chromatography.

General procedure VI (for **2p**)[9]



An oven-dried, argon purged two neck round-bottomed flask fitted with a condenser and septum was added magnesium turnings (750 mg, 2.2 equiv) and anhydrous TFH (8 mL). Chloromethyl trimethylsilane (20 mmol, 2.8 mL, 3 equiv) was added dropwise to maintain reflux. The mixture was cooled to ambient temperature and transferred by cannula into a 50 mL sealable Schlenk tube containing a solution of 3-bromobenzothiophene (1.41 g, 6.65 mmol) and palladium tetrakis-(triphenylphosphine)-palladium (384 mg, 5 mol%) in anhydrous THF (10 mL). The mixture was heated to 80 ºC for 48 hours. After the completion of this reaction, the mixture was cooled to room temperature and pour the solution into cold HCl solution (1 M, 50 mL), and then extracted the aqueous phase twice with pentane, the combined organic phase was dried over magnesium sulfate and concentrate in vacuo. The crude product was purified by flash chromatography (hexane 100%) to afford (benzo[b]thiophen-3-ylmethyl)trimethylsilane **2p**.

3. General procedure for the preparation of the racemic products

An oven-dried reaction tube was charged with *N*-sulfonyl cyclic ketimines **1** (0.1 mmol), benzyl silanes **2** (0.1 mmol), [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ (1 mol%) and CHCl$_3$ (1.0 mL).The reaction mixture was positioned in four 20 W blue LEDs lamp under N_2 atmosphere at room temperature After being stirred for the 0.5–24 h (monitored by TLC analysis), the reaction mixture was concentrated and then purified by flash chromatography on silica gel (eluted with PE/EtOAc/DCM = 8:1:1, v/v/v) to afford racemic product *rac*-**3**.

4. General procedure for the catalytic asymmetric reactions

An oven-dried reaction tube was charged with *N*-sulfonyl cyclic ketimines **1** (0.1 mmol), alkyl silanes **2** (0.1 mmol), [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ (1 mol%), **L$_3$-RaPr$_2$Ad** (10 mol%), Ni(OTf)$_2$ (10 mol%), 4 Å MS (20 mg) and CHCl$_3$ (1.0 mL). The reaction mixture was positioned in four 20 W blue LEDs lamp under N_2 atmosphere at room temperature. After being stirred for the 0.5–72 h (monitored by TLC analysis), the reaction mixture was concentrated and then purified by flash chromatography on silica gel (eluted with PE/EtOAc/DCM = 8:1:1, v/v/v). *The reported isolated yields represented the total yield of the two diastereomers.*

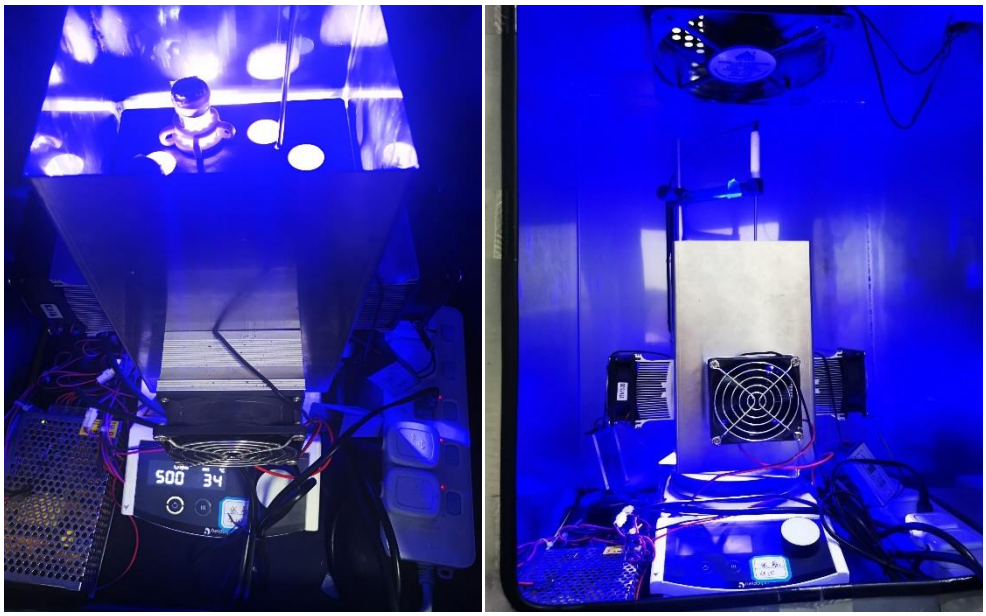
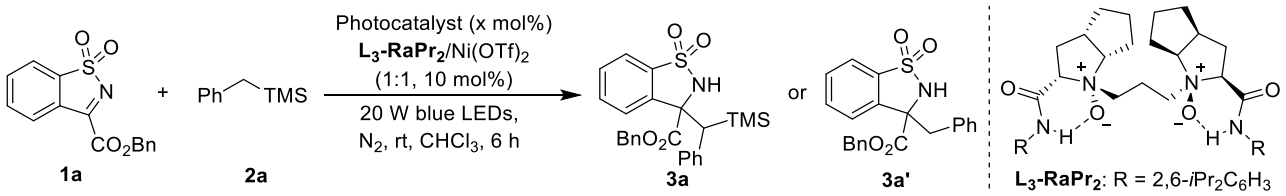


Figure S1. Photochemical setup with blue LEDs

5. Optimization of the reaction conditions

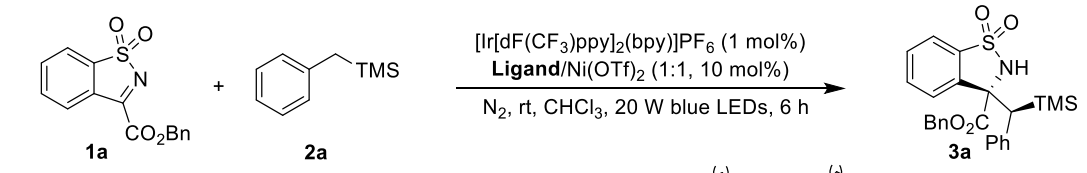
Table S1. Screening of the photocatalysts

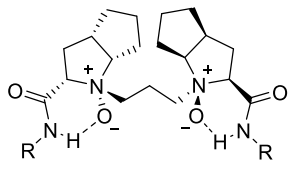


Entry[a]	photocatalyst (x mol%)	yield/%[b]	ee/%[c]	dr[c]
1	xanthone (4 mol%)	0	/	/
2	*fac*-Ir(dFppy)$_3$ (1 mol%)	0	/	/
3	4CzIPN (1 mol%)	0	/	/
4	[Ir[d(Me)ppy]$_2$(dtbbpy)]PF$_6$ (1 mol%)	12	2/-3	54:46
5	[Ir[dF(CF$_3$)ppy]$_2$(bpy)]PF$_6$ (1 mol%)	69	63/15	66:34
6	[Ir[dF(Me)ppy]$_2$(dtbbpy)]PF$_6$ (1 mol%)	32	32/-6	55:45
7[d]	[Ir[dF(CF$_3$)ppy]$_2$(5,5'-dCF$_3$-bpy)]PF$_6$ (1 mol%)	30(38)	62/11(29)[d]	64:36
8	Ru(bpz)$_3$PF$_6$ (1 mol%)	0	/	/
9	Mes-Acr-Me-ClO$_4$ (2 mol%)	0(95)	/(17)	/
10	Anthraquinone (2 mol%)	33	18/-8	55:45
11	Eosin Y (1 mol%)	0	/	/
12	$Na_4W_{10}O_{24}$ (1 mol%)	0	/	/
13	Rhodamine B (1 mol%)	0	/	/

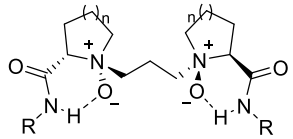
[a]All the reactions were performed with Ni(OTf)$_2$ (10 mol%), **L$_3$-RaPr$_2$** (10 mol%), **1a** (0.10 mmol), **2a** (0.10 mmol) and photocatalyst (x mol%) in CHCl$_3$ (1.0 mL) at rt under the irradiation of 20 W blue LEDs for 6 h. [b]Yield of isolated product. [c]The ee and dr values were determined by UPC^2 analysis. [d]Data of desilylation product **3a′** in parenthesis.

Table S2. Screening of the ligands





L$_3$-RaEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$
L$_3$-RaPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$
L$_3$-RaMe$_2$: R = 2,6-Me$_2$C$_6$H$_3$
L$_3$-RaPr$_3$: R = 2,4,6-*i*Pr$_3$C$_6$H$_2$
L$_3$-RaPr$_2$Ad: R = 2,6-*i*Pr$_2$-4-adamantyl-C$_6$H$_2$
L$_3$-RaBn: R = benzyl
L$_3$-RaCy: R = cyclohexyl



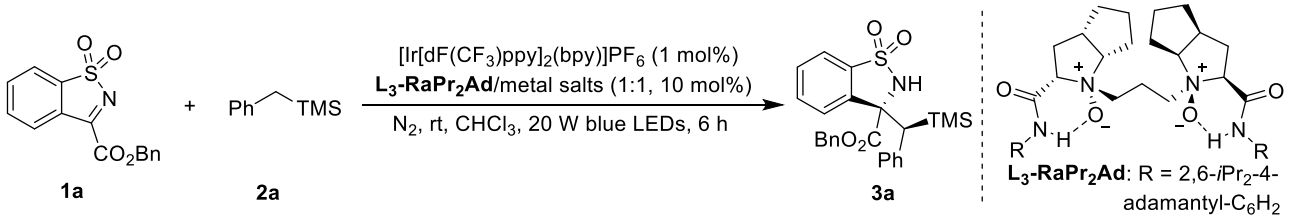
L$_3$-PrPr$_2$: R =2,6-*i*Pr$_2$C$_6$H$_3$, n = 1
L$_3$-PiPr$_2$: R =2,6-*i*Pr$_2$C$_6$H$_3$, n = 2
L$_3$-PiPr$_3$: R =2,4,6-*i*Pr$_3$C$_6$H$_2$, n = 2
L$_3$-PiPr$_2$Ad: R = 2,6-*i*Pr$_2$-4-adamantyl-C$_6$H$_2$, n = 2

entry[a]	ligand	yield/%[b]	ee/%[c]	dr[c]
1	**L$_3$-RaPr$_2$**	69	62/13	66:34
2	**L$_3$-PiPr$_2$**	73	91/44	73:27
3	**L$_3$-PrPr$_2$**	51	57/31	60:40
4	**L$_3$-RaEt$_2$**	50	38/19	60:40
5	**L$_3$-RaMe$_2$**	32	7/-8	52:48
6	**L$_3$-RaPr$_3$**	86	91/44	81:19

7	**L_3-PiPr$_3$**	56	92/55	78:22
8	**L_3-RaPr$_2$Ad**	75	94/47	86:14
9	**L_3-PiPr$_2$Ad**	79	93/57	77:23
10	**L_3-RaBn**	52	26/-17	55:45
11	**L_3-RaCy**	64	-32/-39	47:53

[a]All the reactions were performed with $Ni(OTf)_2$ (10 mol %), **ligand** (10 mol %), **1a** (0.10 mmol), **2a** (0.10 mmol) and $[Ir[dF(CF_3)ppy]_2(bpy)]PF_6$ (1 mol %) in $CHCl_3$ (1.0 mL) at rt under the irradiation of 20 W blue LEDs for 6 h. [b]Yield of isolated product. [c]The ee and dr values were determined by UPC^2 analysis.

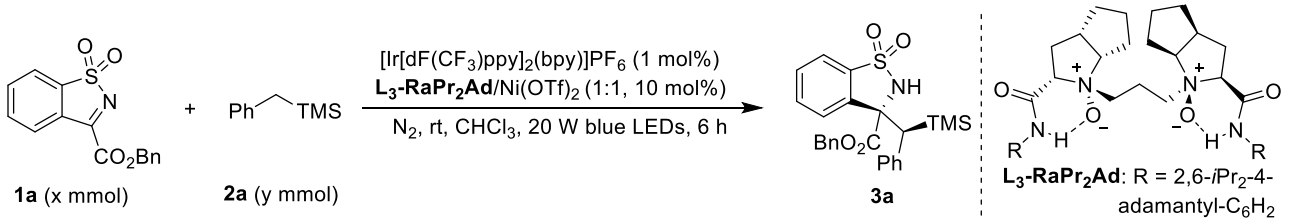
Table S3. Screening of the metal salts



entry[a]	metal salts	yield/%[b]	ee/%[c]	dr[c]
1	$Ni(OTf)_2$	76	94/48	86:14
2	$Mg(OTf)_2$	46	-3/-10	50:50
3	$Sc(OTf)_3$	36	11/0	50:50
4	$Y(OTf)_3$	41	-13/-13	49:51
5	$Fe(OTf)_2$	37	7/-3	54:46
6	$Zn(OTf)_2$	71	61/63	63:37
7	$Co(OTf)_2$	58	70/6	69:31
8	$Cu(OTf)_2$	49	2/-8	48:52
9	$Ni(NTf_2)_2$	73	90/37	82:18
10	$Ni(acac)_2$	71	37/5	68:32
11	$Ni(ClO_4)_2·6H_2O$	39	-6/-10	51:49
12	$Ni(BF_4)_2·6H_2O$	56	-37/-10	58:42
13	$NiCl_2$	57	-8/-2	49:51

[a]All the reactions were performed with metal salt (10 mol%), **L_3-RaPr$_2$Ad** (10 mol%), **1a** (0.10 mmol), **2a** (0.10 mmol) and $[Ir[dF(CF_3)ppy]_2(bpy)]PF_6$ (1 mol%) in $CHCl_3$ (1.0 mL) at rt under the irradiation of 20 W blue LEDs for 6 h. [b]Yield of isolated product. [c]The ee and dr values were determined by UPC^2 analysis.

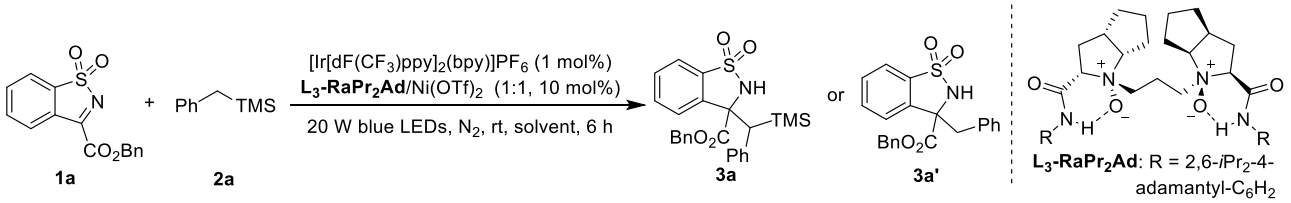
Table S4. Screening of the ratio between **1a** and **2a**



entry[a]	x:y	yield/%[b]	ee/%[c]	dr[c]
1	0.12:0.10	94	94/48	86:14
2	0.10:0.10	76	94/50	86:14
3	0.10:0.12	80	95/52	86:14

[a]All the reactions were performed with $Ni(OTf)_2$ (10 mol%), **L_3-RaPr$_2$Ad** (10 mol%), **1a** (x mmol), **2a** (y mmol) and $[Ir[dF(CF_3)ppy_2](bpy)]PF_6$ (1 mol%) in $CHCl_3$ (1.0 mL) at rt under the irradiation of 20 W blue LEDs for 6 h. [b]Yield of isolated product. [c]The ee and d.r. values were determined by UPC^2 analysis.

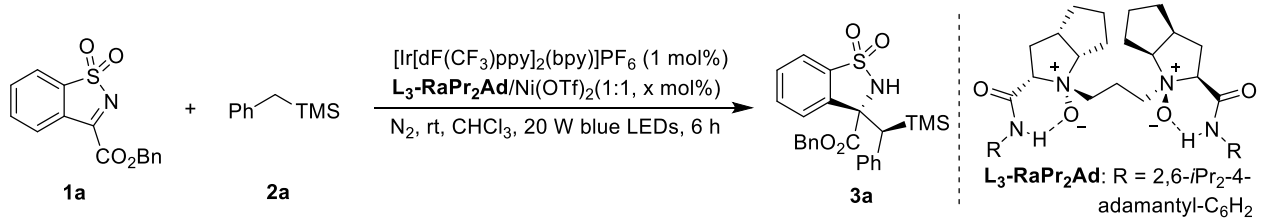
Table S5. Screening of the solvents and concentration.



entry[a]	solvents	yield/%[b]	ee/%[c]	dr[c]
1	$CHCl_3$	94	94/48	86:14
2	THF	0(11)	n.a.	n.a.
3[d]	Toluene	23(75)	92/35(47)	85:15
4	CH_3CN	0(99)	n.a.(36)	n.a.
5	CH_3OH	0(98)	n.a.(7)	n.a.
6	Et_2O	0	n.a.	n.a.
7[e]	$CHCl_3$	66	91/37	83.5:16.5
8[f]	$CHCl_3$	85	92/42	84:16

[a]All the reactions were performed with $Ni(OTf)_2$ (10 mol%), **L_3-RaPr$_2$Ad** (10 mol%), **1a** (0.12 mmol), **2a** (0.10 mmol) and $[Ir[dF(CF_3)ppy]_2(bpy)]PF_6$ (1 mol%) in corresponding solvents (1.0 mL) at rt under the irradiation of 20 W blue LEDs for 6 h. [b]Yield of isolated product. [c]The ee and dr values were determined by UPC^2 analysis. [d]Data of desilylation product **3a′** in parenthesis. [e]$CHCl_3$ (0.5 mL). [f]$CHCl_3$ (2.0 mL).

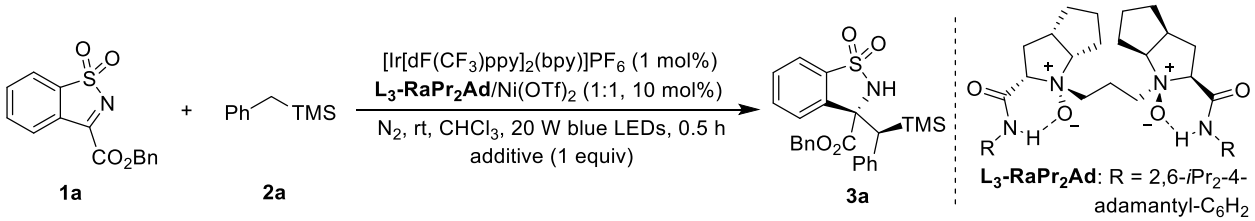
Table S6. Screening of the amount of chiral catalyst, reaction temperature and time



entry[a]	x	yield/%[b]	ee/%[c]	dr[c]
1	10	94	94/48	86:14
2	5	87	92/42	84:16
3	1	43	41/0	61:39
4[d]	10	87	93/56	85:15
5[e]	10	74	90/49	84:16
6[f]	10	92	93/46	86:14

[a]All the reactions were performed with $Ni(OTf)_2$ (x mol%), **L_3-RaPr$_2$Ad** (x mol%), **1a** (0.12 mmol), **2a** (0.10 mmol) and $[Ir[dF(CF_3)ppy]_2(bpy)]PF_6$ (1 mol%) in $CHCl_3$ (1.0 mL) at rt under the irradiation of 20 W blue LEDs for 6 h. [b]Yield of isolated product. [c]The ee and dr values were determined by UPC^2 analysis. [d]At 10 °C. [e]At -10 °C. [f]For 0.5 h.

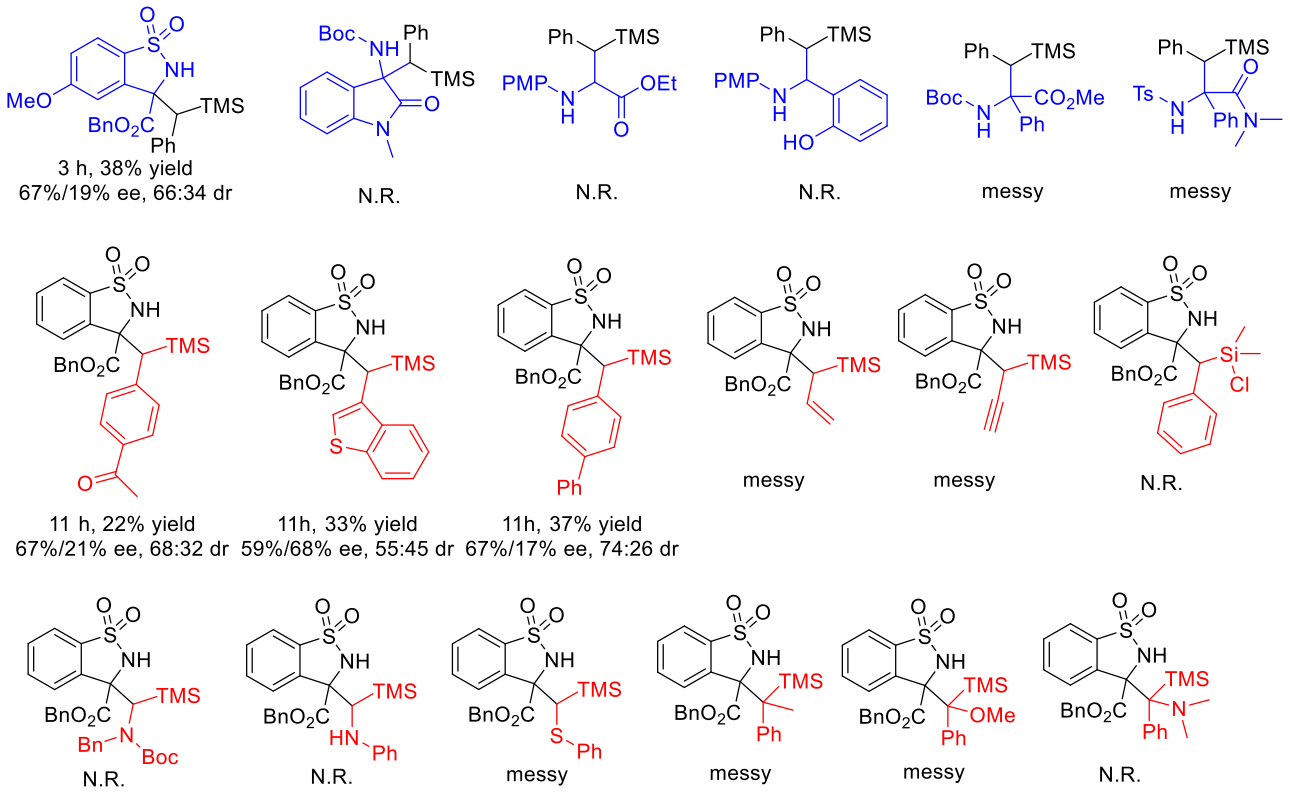
Table S7. Screening of the additives



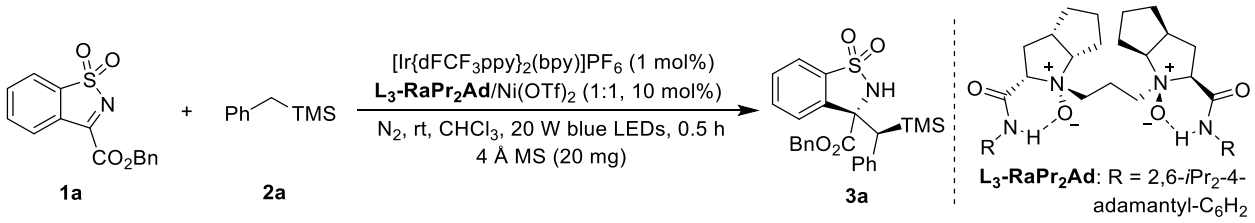
entry[a]	additives	yield/%[b]	ee/%[c]	dr[c]
1	-	94	94/48	86:14
2	NaBr	83	91/35	83:17
3	LiBr	27	83/33	78:22
4	$MgSO_4$	70	87/27	80:20
5	Na_2SO_4	78	89/34	82:18
6	LiCl	79	93/45	85:15
7[d]	3 Å MS	93	95/43	86:14
8[d]	4 Å MS	95	95/40	86:14
9[d]	5 Å MS	94	93/45	86:14
10	H_2O	67	84/0	76:24

[a]All the reactions were performed with $Ni(OTf)_2$ (10 mol%), **L_3-RaPr$_2$Ad** (10 mol%), **1a** (0.12 mmol), **2a** (0.10 mmol) and $[Ir[dF(CF_3)ppy]_2(bpy)]PF_6$ (1 mol%) in $CHCl_3$ (1.0 mL) at rt under the irradiation of 20 W blue LEDs for 0.5 h. [b]Yield of isolated product. [c]The ee and dr values were determined by UPC^2 analysis. [d]20 mg.

6. The limited substrate scope



7. Control experiments

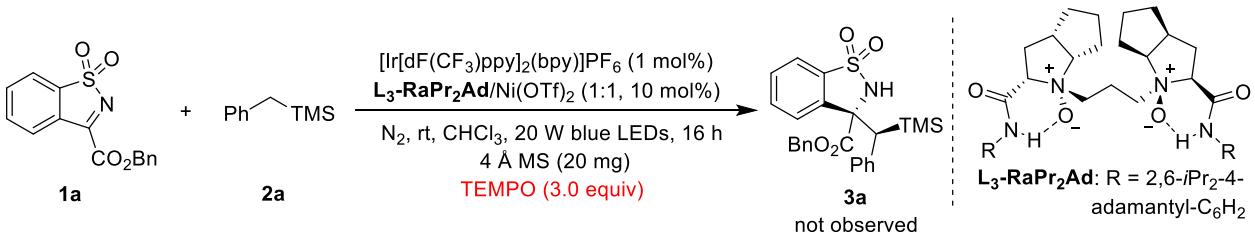


Entry[a]	variation of conditions	yield/%[b]	ee/%[c]	d.r.[c]
1	none	95	95	86:14
2	without light	0	/	/
3	without Ir	0	/	/
4	without **L3-RaPr2Ad**/Ni(OTf)2	48	/	52:48
5	without **L3-RaPr2Ad**	28	/	47:53
6	without Ni(OTf)2	48	/	51:49
7	in air	0	/	/

[a]All the reactions were performed with Ni(OTf)2 (10 mol%), **L3-RaPr2Ad** (10 mol%), **1a** (0.12 mmol), **2a** (0.10 mmol) and [Ir{dFCF3ppy}2(bpy)]PF6 (1 mol%) in $CHCl_3$ (1.0 mL) at rt under the irradiation of 20 W blue LEDs for 0.5 h. [b]Yield of isolated product. [c]The ee and dr values were determined by UPC[2] analysis.

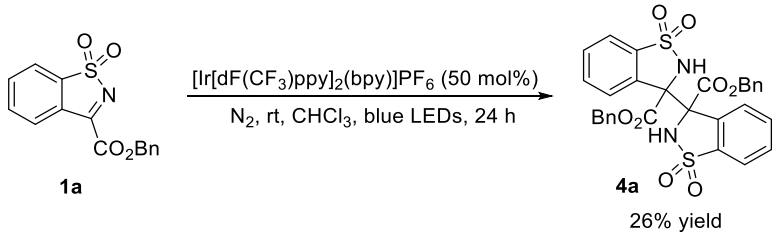
8. Mechanistic investigations

8.1 Catalytic reaction interfered with a radical quencher



The reaction was performed with Ni(OTf)2 (10 mol%), **L3-RaPr2Ad** (10 mol%), **1a** (0.12 mmol), **2a** (0.10 mmol), [Ir{dFCF3ppy}2(bpy)]PF6 (1 mol%), 4 Å MS (20 mg) and TEMPO (3 equiv) in $CHCl_3$ (1.0 mL) at rt under the irradiation of 20 W blue LEDs for 16 h. No desired product **3a** was observed.

8.2 Detection of the homocoupling product 4a



The reaction was performed with **1a** (0.10 mmol) and [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ (50 mol%) in CHCl$_3$ (1.0 mL) at rt under the irradiation of 20 W blue LEDs for 24 h. Then the reaction mixture was concentrated and purified by flash chromatography on silica gel (eluted with PE:EtOAc = 4:1 to 2:1) to afford product **4a** as a white solid (15.8 mg, 26% yield).

8.3 EPR studies

The reactions were performed with Ni(OTf)$_2$ (10 mol%), **L$_3$-RaPr$_2$Ad** (10 mol%), **1a** (0.12 mmol), **2a** (0.10 mmol), [Ir[dF(CF$_3$)ppy]$_2$(bpy)]PF$_6$ (1 mol%), 4Å MS (20 mg) in CHCl$_3$ (1.0 mL) under the irradiation of 20 W blue LEDs. After being stirred at rt for 15 min, DMPO (5,5-dimethyl-1-pyrroline *N*-oxide, 11.3 mg, 0.10 mmol) was added. The reaction mixture was analyzed by electron paramagnetic resonance (EPR). The existence of radical **6** was further established by HRMS.

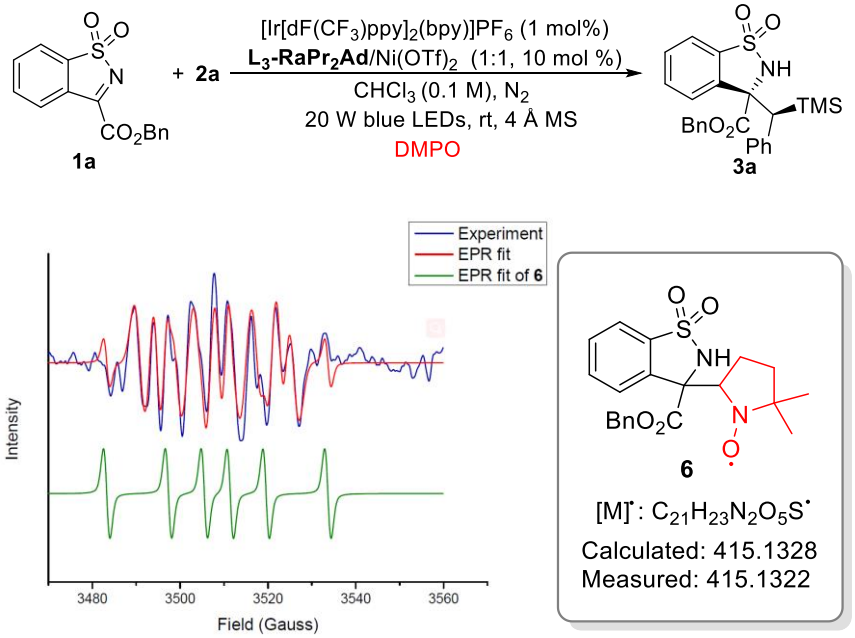


Figure S2. EPR spectra of the reaction mixture and **6**

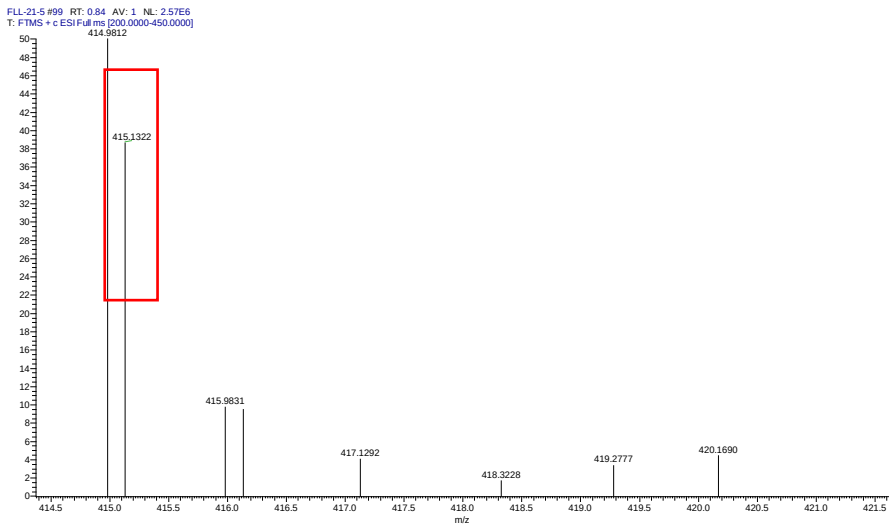


Figure S3. HRMS spectra of **6**

8.4 Stern-Volmer emission quenching experiments

All [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ solutions were excited at 370 nm and the emission intensity was collected at 420-600 nm. Stern-Volmer quenching experiments were carried out using a 0.1 mM solution of [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ and variable concentrations (1, 2, 4, 6, 8 mM) of imine **1a** or benzyltrimethylsilane **2a**. The samples were prepared in 2 mL quartz cuvettes. The intensity of the emission peak at 468 nm (λ_{ex} = 370 nm) for [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ expressed as the ratio I_0/I, where I_0 is the emission intensity of [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ at 468 nm in the absence of a quencher and I is the observed intensity, as a function of the quencher concentration was measured.

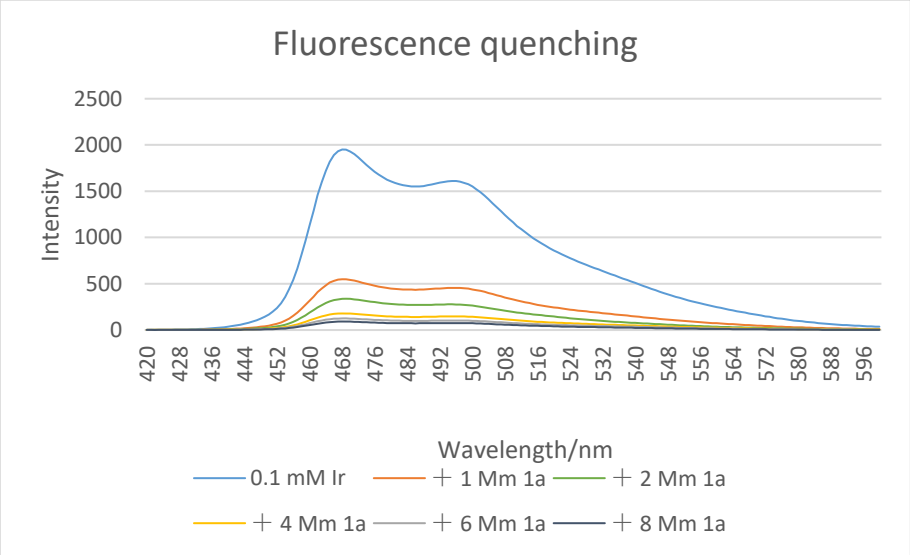


Figure S4. Fluorescence quenching spectra of **1a**

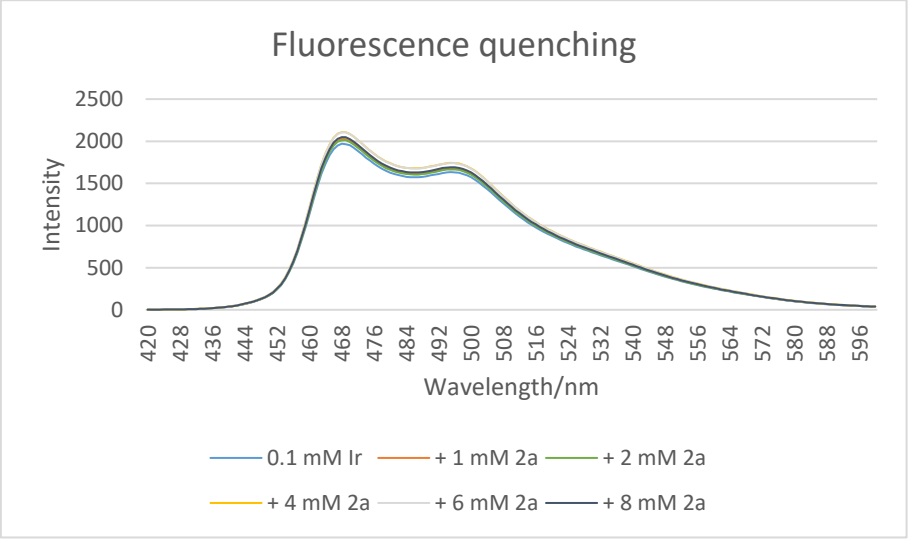


Figure S5. Fluorescence quenching spectra of **2a**

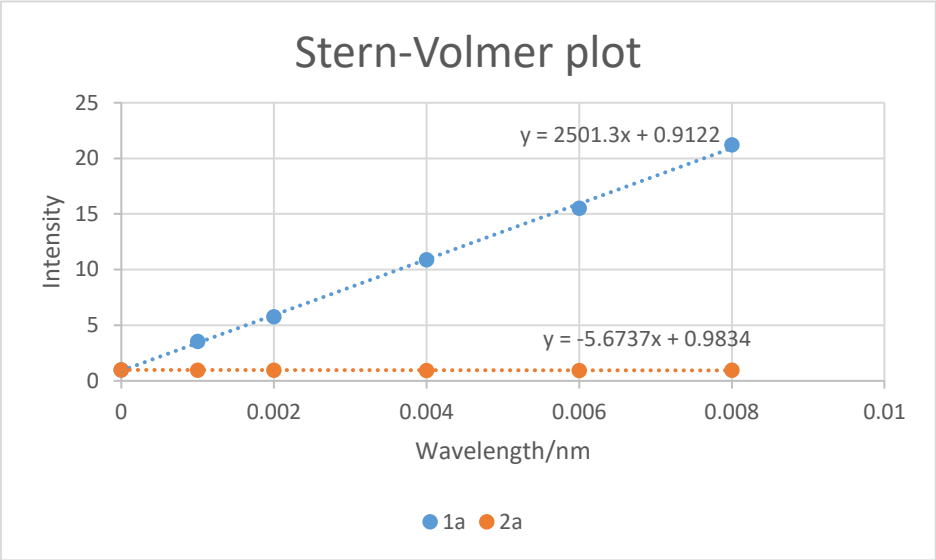


Figure S6. Stern-Volmer quenching study of **1a** and **2a**

All [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ solutions were excited at 370 nm and the emission intensity was collected at 420-600 nm. Stern-Volmer quenching experiments were carried out using a 0.1 mM solution of [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ and variable concentrations (0.5, 1.0, 1.5, 2.0 mM) of imine **1a** or **1a**/Ni(OTf)$_2$/**L$_3$-RaPr$_2$Ad**. The samples were prepared in 2 mL quartz cuvettes. The intensity of the emission peak at 470 nm (λ_{ex} = 370 nm) for [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ expressed as the ratio I_0/I, where I_0 is the emission intensity of [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ at 470 nm in the absence of a quencher and I is the observed intensity, as a function of the quencher concentration was measured.

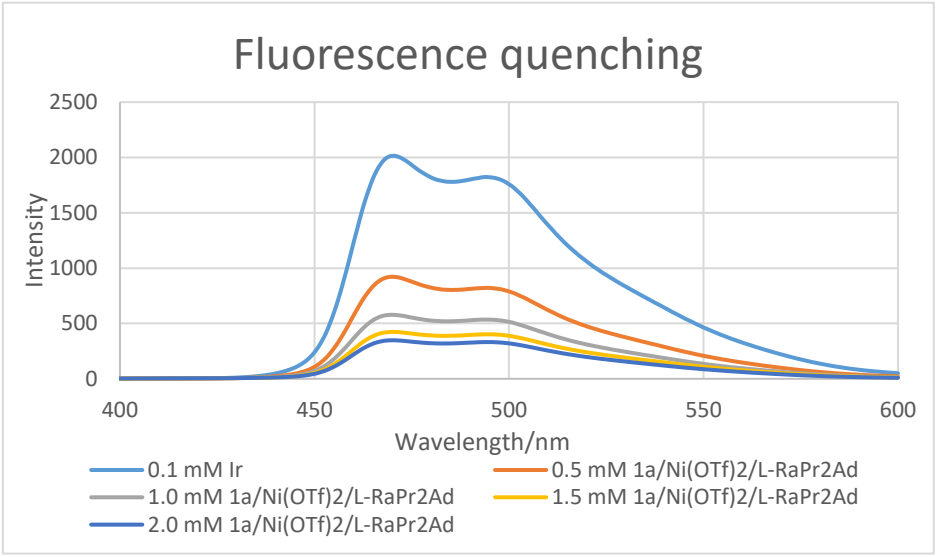


Figure S7. Fluorescence quenching spectra of **1a**/Ni(OTf)$_2$/L-RaPr$_2$Ad

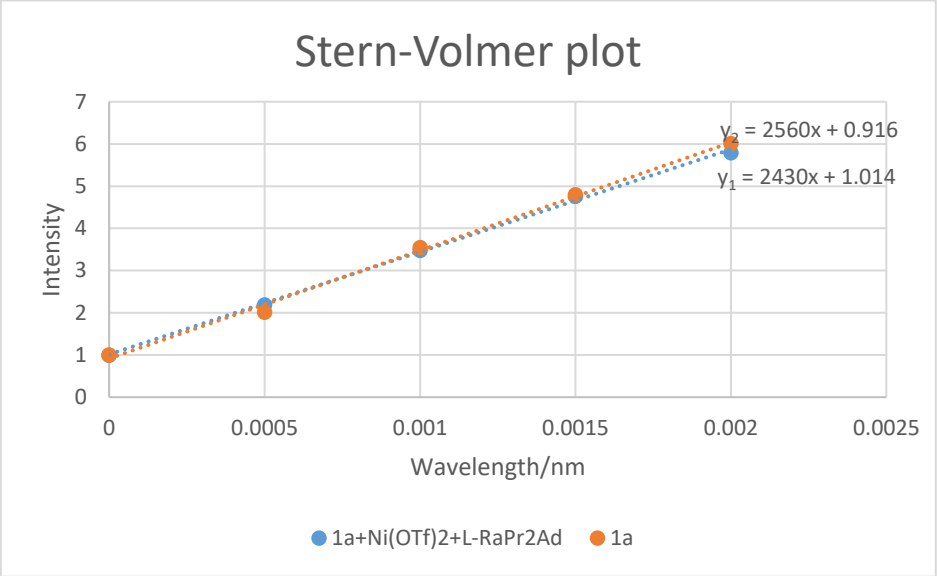
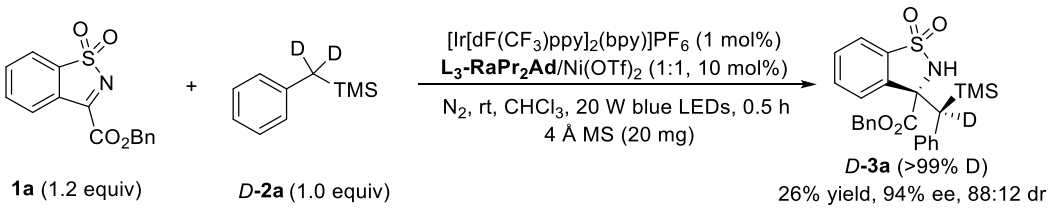
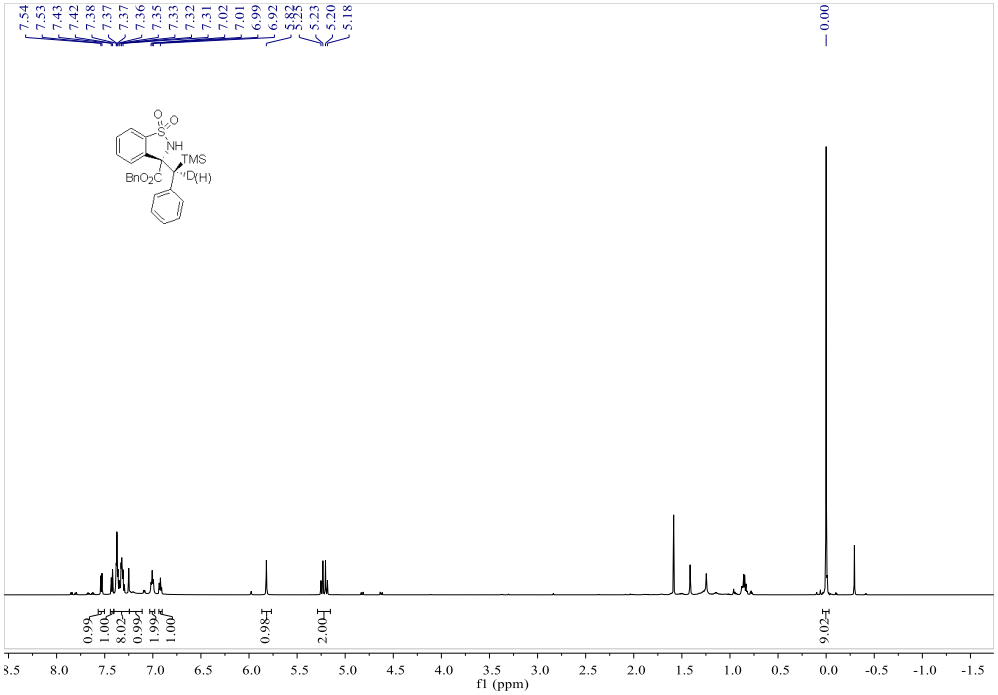


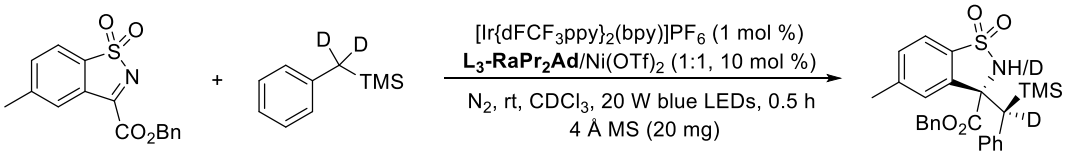
Figure S8. Stern-Volmer quenching study of **1a** and **1a**/Ni(OTf)$_2$/**L$_3$-RaPr$_2$Ad**

8.5 Deuterium experiment



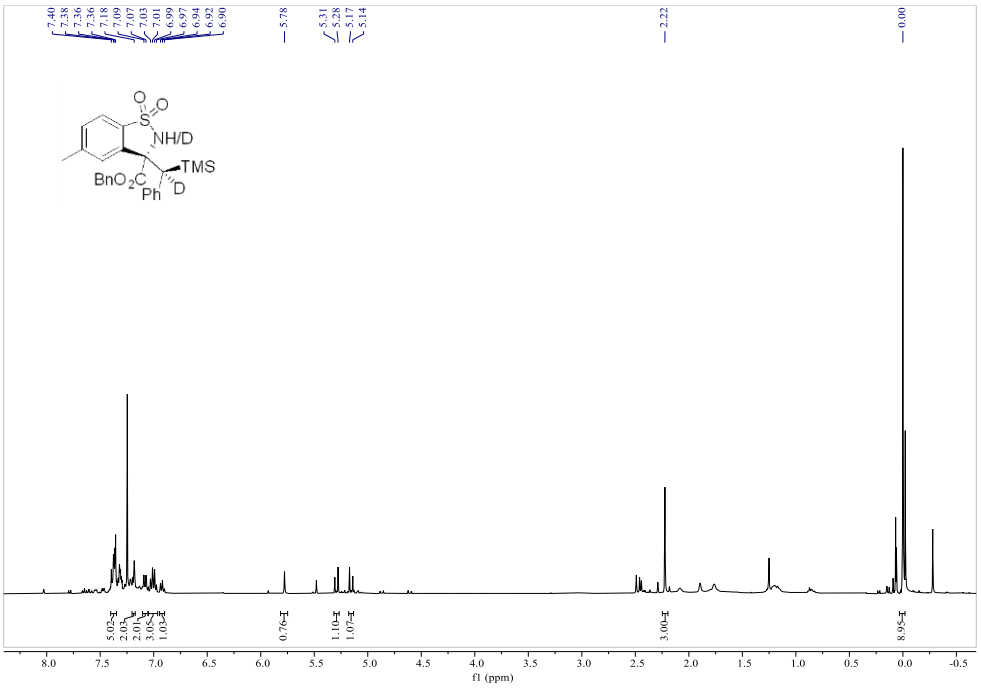
The reaction was performed according to the typical procedure by using deuterated benzyl trimethyl silicon *D*-**2a**. The deuterated ratio was determined by ^{1}H NMR spectrum after chromatography with silica gel column. The peak of H at 3.31 ppm is not observed, which indicates full deuteration of H.

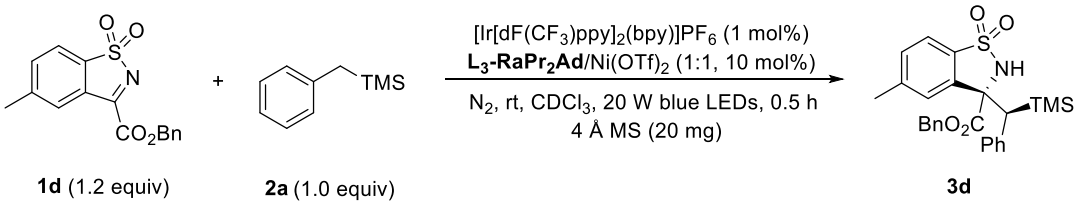




1d (1.2 equiv) *D*-**2a** (1.0 equiv) *D*-**3d** (24% D)

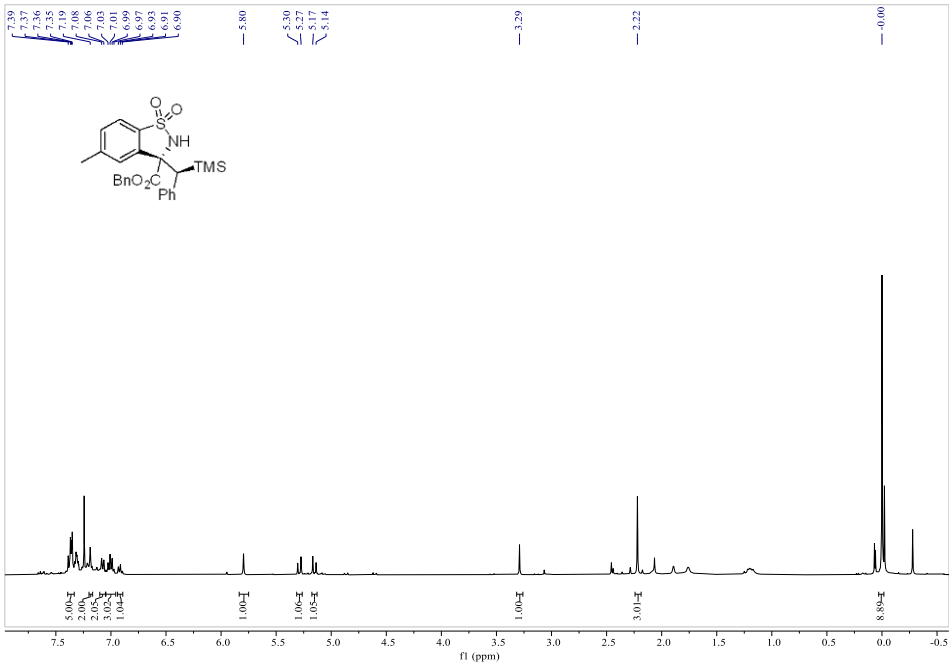
The reaction was performed according to the typical procedure by using deuterated benzyl trimethyl silicon *D*-**2a**. The deuterated ratio was determined by ^{1}H NMR spectrum after filtration under nitrogen atmosphere. The peak integral at 5.78 is 0.76 and the deuteration rate is 0.24, suggesting the N-H comes from *D*-**2a**.





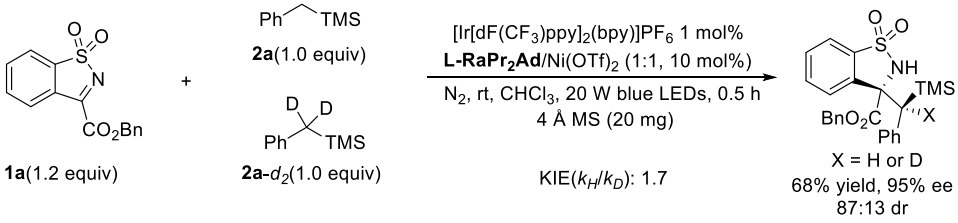
1d (1.2 equiv) **2a** (1.0 equiv) **3d**

The deuterated ratio was determined by 1H NMR spectrum after filtration under nitrogen atmosphere. The peak integral at 5.80 is 1.00.

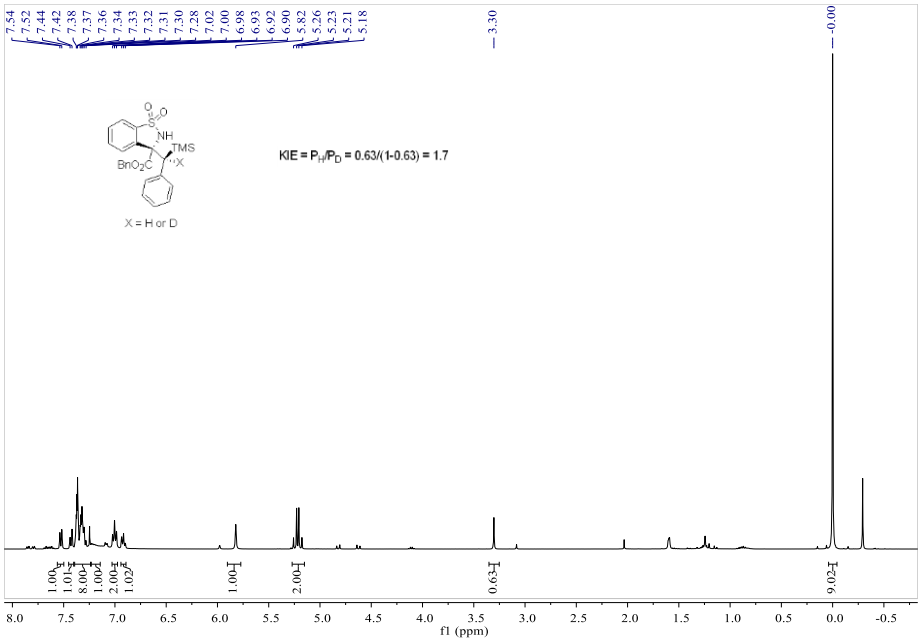


8.6 KIE experiment

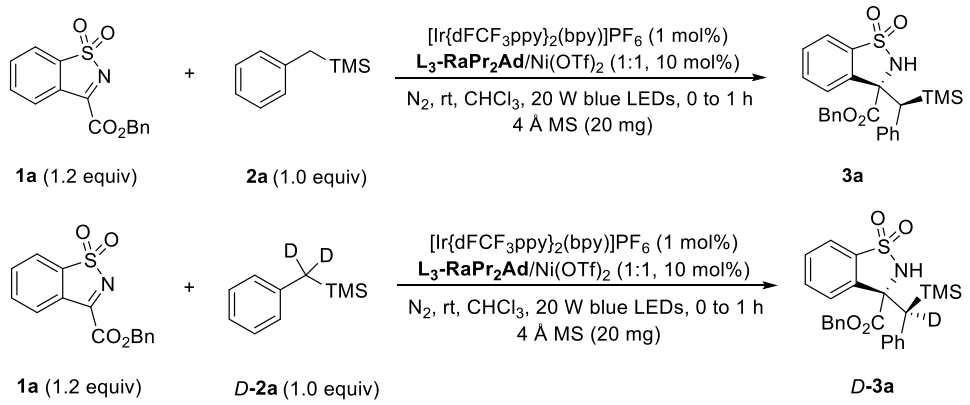
Competitive KIE experiments



The reaction was performed according to the typical procedure by using a mixture of **2a** (0.10 mmol) and deuterated borane adduct *D*-**2a** (0.10 mmol). The deuterated ratio was determined by ^{1}H NMR spectrum after chromatography with silica gel column.



Parallel KIE experiments



The reaction progress of benzyltrimethylsilane **2a** and *D*-benzyltrimethylsilane **2a** with benzosultam **1a** was monitored in parallel at six distinct periods (10 min, 20 min, 30 min, 40 min, 50 min and 1 h). [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ (1 mol%), Ni(OTf)$_2$/**L$_3$-RaPr$_2$Ad** (1:1, 10 mol%), **1a** (0.12 mmol), **2a** or *D*-**2a** (0.10 mmol), and 4 Å MS (20 mg) in $CHCl_3$ (1.0 mL) at rt under the irradiation of 20 W blue LEDs for 0−1 h. After the reaction was completed, the suspension was filtered through a sand core funnel, and the filtrate was concentrated under vacuum. The residue was detected by ^{1}H NMR analysis (CH_2Br_2 as the internal standard). The KIE of the reaction, which was calculated by dividing the rate constant of the reaction of benzyltrimethylsilane (Y1:k_H = 1.47) by that of *D*-benzyltrimethylsilane (Y2:k_D = 1.01), was determined to be 1.46.

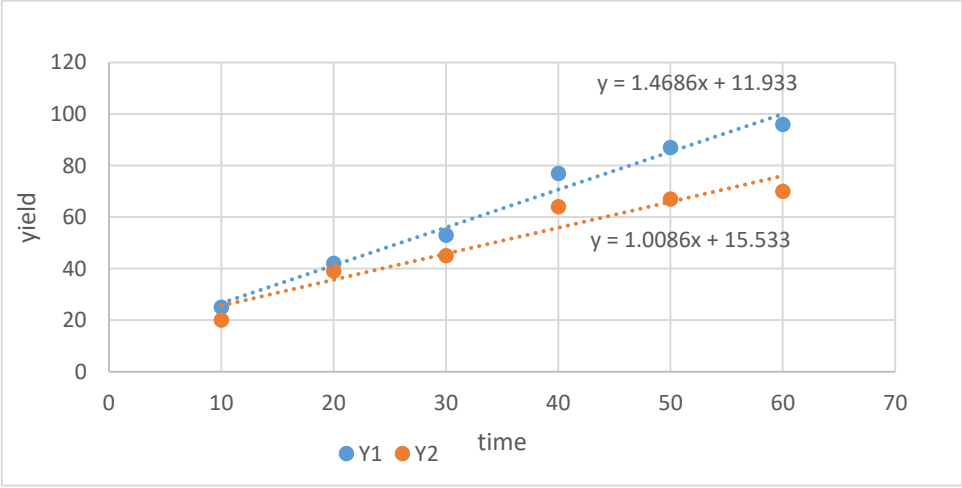


Figure S9. Parallel KIE experiments

8.7 Cyclic voltammetry analysis

Cyclic voltammograms for mechanistic analysis were carried out with a μStat-i 400s potentiostat by a three-electrode cell with a glassy carbon working electrode, a platinum mesh counter electrode, and an Ag/AgNO$_3$ reference electrode at room temperature in CH_3CN. *n*-Bu$_4$NPF$_6$ (0.1 M) was used as the supporting electrolyte, and a Glass Carbon electrode was used as the working electrode. The scan rate was 100 mV s^{-1}. The experimental setup was calibrated using ferrocene (Fc/Fc+) prior to each experiment. Samples were prepared with 0.3 mmol substrate in 10 mL *n*-Bu$_4$NPF$_6$ electrolyte

(0.03 M in CH_3CN) and degassed by sparging with nitrogen gas for 10 min prior to use. The potential ($E_{p/2}$) was determined and converted to SCE as described by Nicewicz[10].

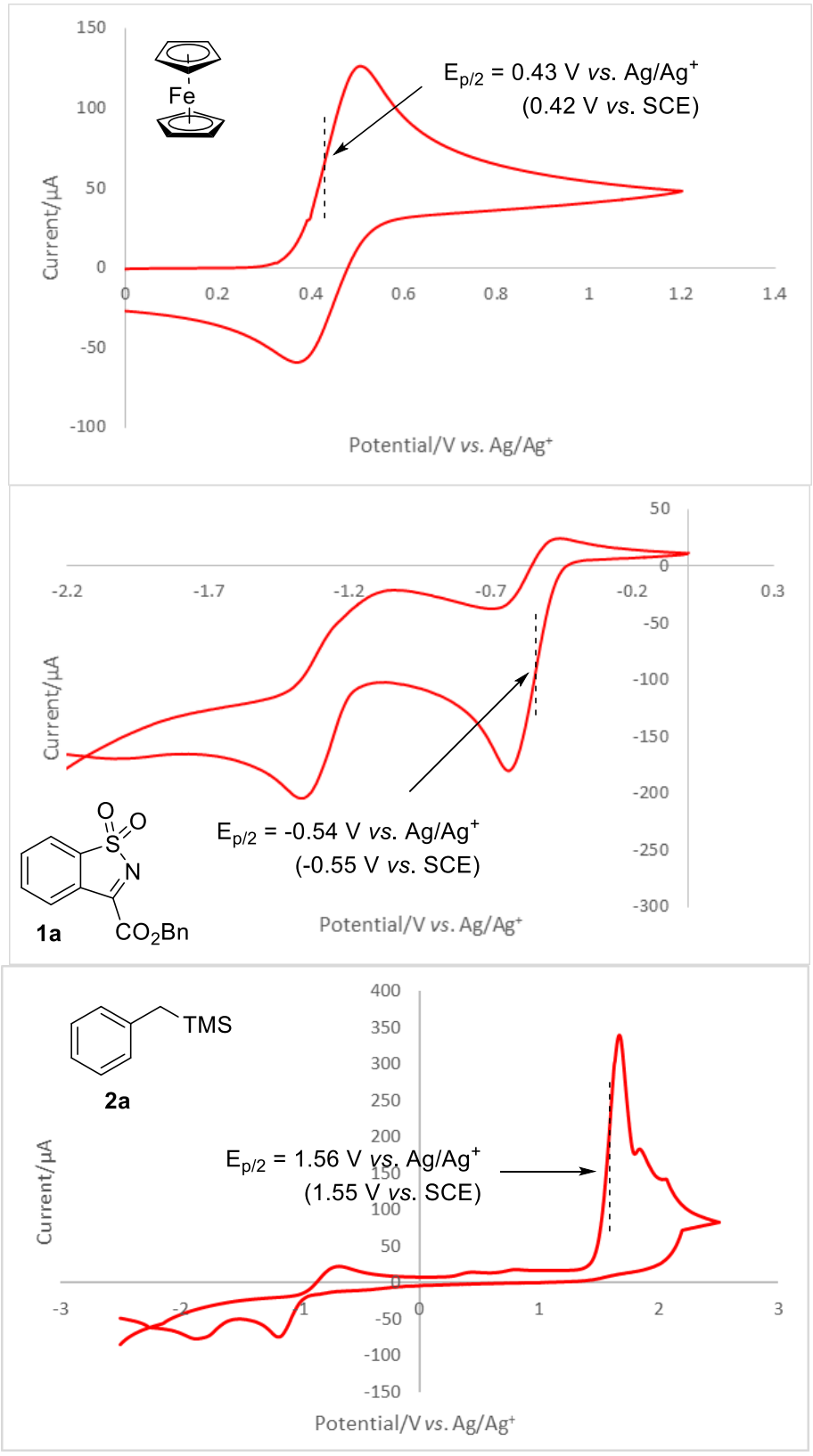


Figure S10. Cyclic voltammogram of **1a** and **2a**

8.8 Quantum yield measurement

General Protocol to assess the photon flux of LED:

The photon flux set by the LED (λ = 420 nm, 20 W) was determined using the standard potassium ferric oxalate photometric method, following a modified literature procedure[11].

A 0.018 M potassium ferric oxalate solution was prepared by dissolving 178 mg of potassium ferric oxalate trihydrate and 84 μL of H_2SO_4 (95–98%) in 20 mL of water. This solution was kept in an amber bottle in the dark. Then a buffer solution was prepared by dissolving 2.5 g of sodium acetate and 0.50 mL of H_2SO_4 (95–98%) in 50 mL of water.

1.0 mL of the 0.018 M potassium ferric oxalate solution was added to a flask containing a stirring bar. Then, the solution was irradiated for 0 s, 30 s, 60 s. Immediately after irradiation, 100 μL of the solution was transferred to a foil-covered 10 mL volumetric flask in which containing 15 mg of 1,10-phenanthroline dissolved in 3.0 mL of the buffer solution. Then add water to the flask to bring the total volume to 10 ml. The flask was shaken to ensure efficient mixing and the solution was stored in the dark for approximately 20 min. 2.0 mL of the solution was transferred to a quartz cuvette (1.0 mL path length) and the absorbance at λ = 510 nm was measured by UV/Vis spectroscopy (**Figure S11**). This process was repeated for 30 s, 60 s, and the absorbance of a unirradiated sample was also measured.

Caution: minimizing exposure to background light!

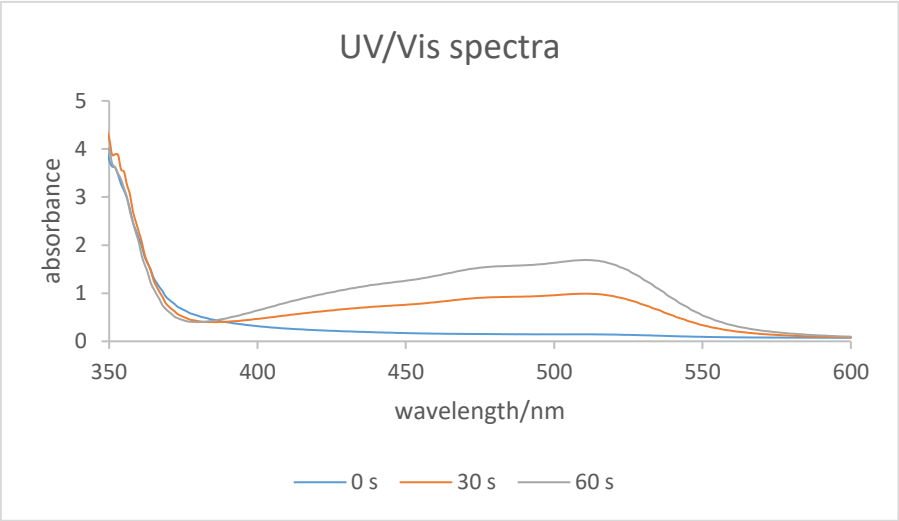


Figure S11. UV/Vis spectra of potassium ferric oxalate/1,10-phenanthroline solutions

The number of moles of Fe^{2+} produced by light irradiation was calculated using:

$$mol\ Fe^{2+} = \frac{V_1 V_3 \Delta A\ (510\ nm)}{V_2 l \varepsilon\ (510\ nm)}$$

Where

V_1 = the volume of potassium ferric oxalate solution irradiated (1.0×10^{-3} L).

V_2 = the volume of the solution taken for measurement of the Fe^{2+} ions (1.0×10^{-4} L).

V_3 = the final volume of solution after complexation with 1,10-phenanthroline (1.0×10^{-2} L).

ΔA (510 nm) = the absorbance difference at λ = 510 nm between the irradiated solution and the solution kept in dark.

l = the optical path length of the cuvette (1.0 cm).

ε (510 nm) = the molar absorption coefficient of the $Fe(phen)_3^{2+}$ complex at λ = 510 nm (1.11×10^4 L mol^{-1} cm^{-1}).

The moles of Fe^{2+} were plotted as a function of time (**Figure. S12**)

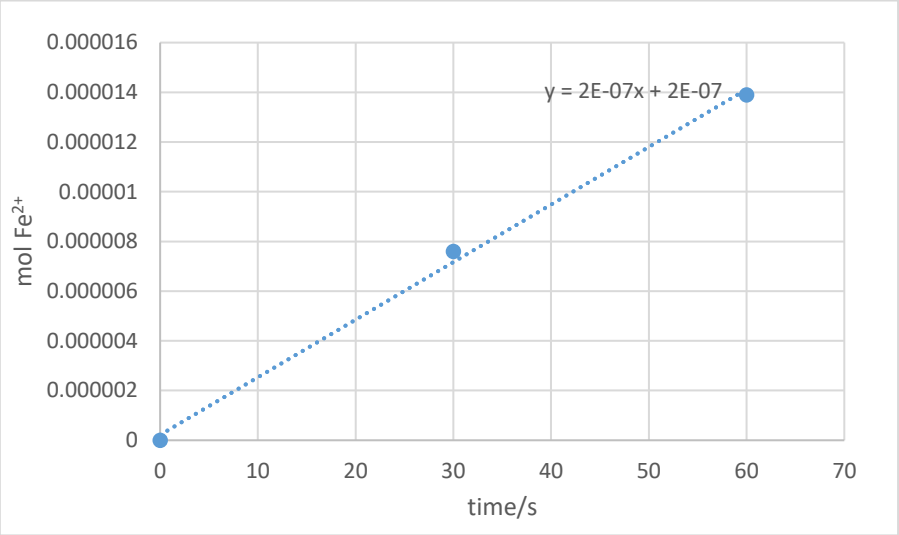


Figure S12. The molar number of Fe^{2+} as a function of time

The photon flux was then calculated using:

$$photon\ flux = \frac{mol\ Fe^{2+}}{\phi t(1-10^{-A})}$$

Where

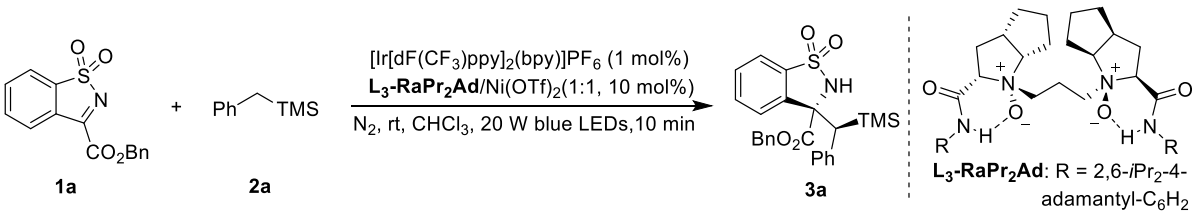
Φ = the quantum yield of the potassium ferric oxalate in room temperature at 420 nm is 1.13.[12]

t = the irradiated time(s).

A = the potassium ferric oxalate absorbance at 420 nm, which was measured placing 1 mL of the solution in a cuvette which path length is 1 cm by UV/Vis spectrophotometry. We obtained an absorbance value of 1.706.

$$photon\ flux = \frac{2.0 \times 10^{-7}}{1.13 \times (1-10^{-1.706})} = 1.81 \times 10^{-7}$$

Quantum yield of radical reaction:



An oven-dried reaction tube was charged with *N*-sulfonyl cyclic ketimines **1a** (0.12 mmol), alkyl silanes **2a** (0.10 mmol), [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ (1 mol%), **L$_3$-RaPr$_2$Ad** (10 mol%), Ni(OTf)$_2$ (10 mol%), 4 Å MS (20 mg) and $CHCl_3$ (1.0 mL). The mixture was stirred under 420 nm 20 W blue LED irradiation at room temperature. After 10 minutes, the yield of **3a** was determined by ^{1}HNMR, using

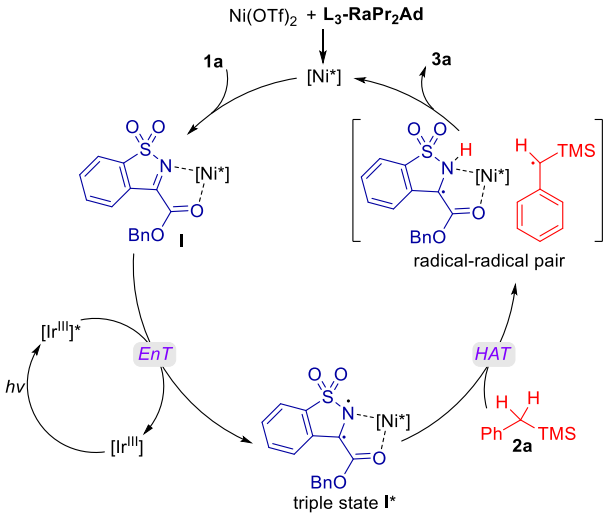
dibromaethan as an internal standard. And 2.5×10^{-5} mol **3a** was produced. The quantum yield (ϕ) of this reaction was calculated using the following equation:

$$\phi = \frac{mol\ product}{photon\ flux\ \times\ t\ \times (1-10^{-A})}$$

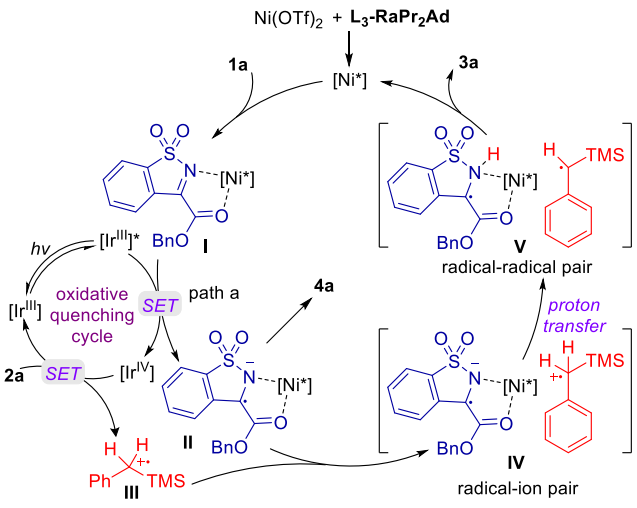
Where
Φ = the quantum yield of the catalytic reaction in room temperature at 420 nm.
t = the reaction time(s).
A = the catalytic reaction absorbance at 420 nm, which was measured placing 1 mL of the solution in a cuvette which path length is 1 cm by UV/Vis spectrophotometry. We obtained an absorbance value of 1.954

$$\phi = \frac{2.5\times10^{-5}}{1.81\times10^{-7}\ \times 600\ \times\ (1-10^{-1.954})} = 2.30\times10^{-1}$$

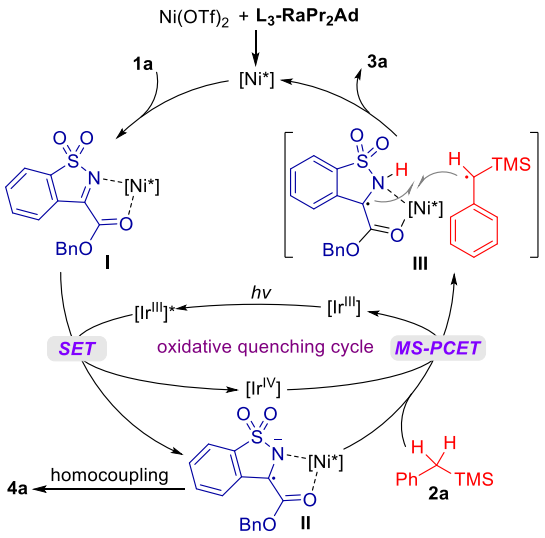
8.9 Catalytic cycle



HAT mechanism

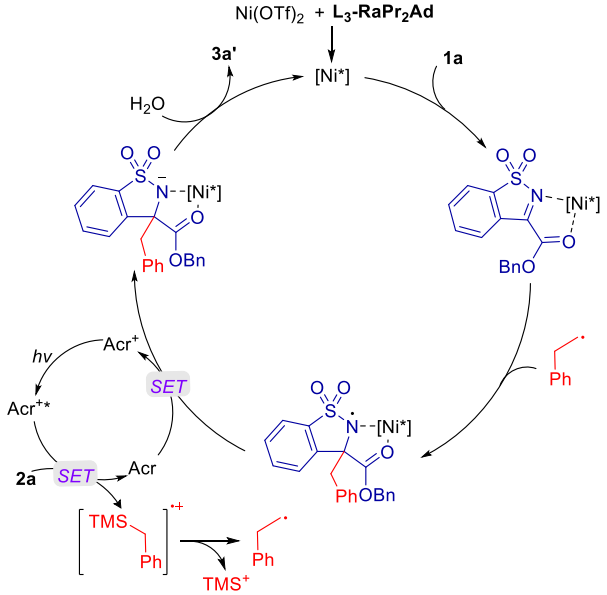


SET/PT mechanism



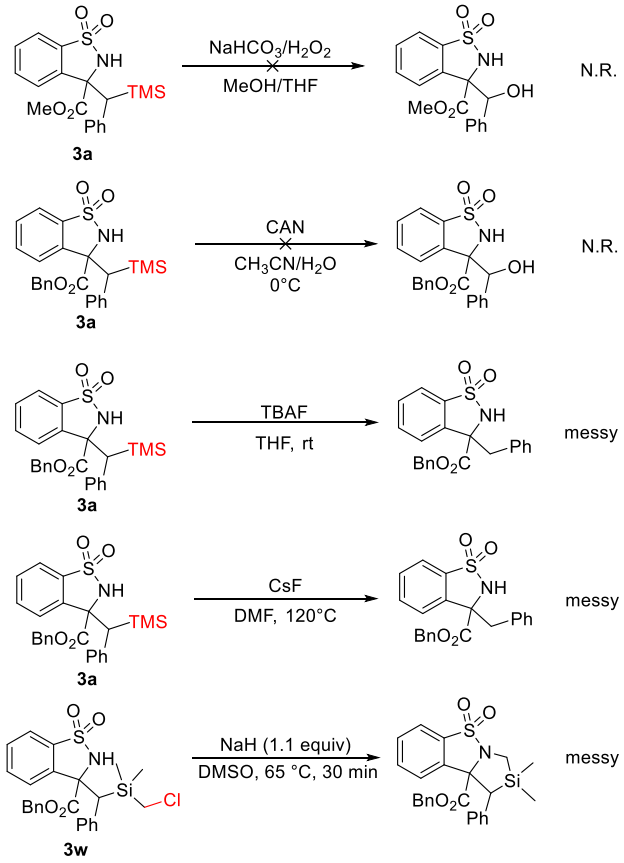
MS-PCET mechanism

Figure S12. Three possible cycle of reaction



SET oxidation-triggered radical addition mechanism with Acr$^+$ as photocatalyst

9. Product derivation

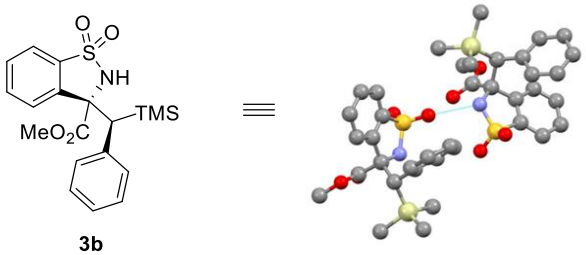


10. Single-crystal data

Crystallographic Data for $C_{38}H_{46}N_2O_8S_2Si_2$	
Formula	$2(C_{38}H_{46}N_2O_8S_2Si_2)$
Formula mass (amu)	779.07
Space group	P 21 21 21
a (Å)	11.6468(8)
b (Å)	16.5589(12)
c (Å)	21.0550(17)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	4060.6(5)
Z	4
λ (Å)	0.71073
T (K)	173 K
ρ_{calcd} (g cm^{-3})	1.274
μ (mm^{-1})	0.241
Transmission factors	0.878,0.981
θ_{max} (deg)	25.368
No. of unique data, including $F_o^2 < 0$	7419
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	7187
No. of variables	485
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0328
$R_w(F_o^2)$ [b]	0.0759
Goodness of fit	1.103

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.



3b

11. References

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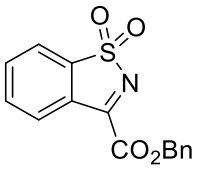
12. Characterization of typical substrates 1a-1h

benzyl benzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(1a)

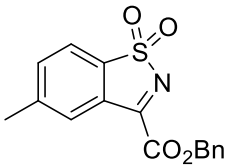


White solid, m.p. 130 – 131 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 4.0 Hz, 1H), 7.79-7.72 (m, 2H), 7.49-7.47 (m, 2H), 7.44-7.37 (m, 3H), 5.49 (s, 2H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.3, 156.0, 140.2, 134.3, 134.2, 133.8, 129.1, 128.8, 128.2, 127.6, 123.0, 69.2.

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{11}NNaO_4S^+$ ([M+Na$^+$]) = 324.0301, Found 324.0299.

IR (film, cm^{-1}) : 3035, 1736, 1348, 1202, 1178, 1028, 763, 700, 579, 532.

benzyl 5-methylbenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(1b)

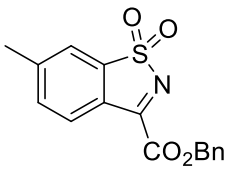


White solid, m.p. 106 – 108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.50-7.47 (m, 2H), 7.44 – 7.37 (m, 3H), 5.49 (s, 2H), 2.51 (s, 3H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.4, 160.1, 145.7, 137.4, 134.6, 133.9, 129.1, 128.8, 128.7, 127.9, 122.8, 69.1, 21.8.

HRMS (ESI$^+$) m/z calcd for $C_{16}H_{13}NNaO_4S^+$ ([M+Na$^+$]) = 338.0458, Found 338.0457.

IR (film, cm^{-1}) : 3270, 1743, 1310, 1238, 1186, 1147, 1102, 896, 822, 736, 699, 572.

benzyl 6-methylbenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(1c)

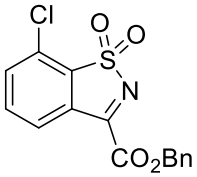


White solid, m.p. 107 – 108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H), 7.66 (s, 1H), 7.46 – 7.40 (m, 3H), 7.36-7.29 (m, 3H), 5.41 (s, 2H), 2.46 (s, 3H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.4, 160.0, 146.3, 140.7, 134.9, 133.9, 129.1, 128.8, 127.23, 125.9, 123.7, 69.1, 21.8.

HRMS (ESI$^+$) m/z calcd for $C_{16}H_{13}NNaO_4S^+$ ([M+Na$^+$]) = 338.0458, Found 338.0454.

IR (film, cm^{-1}) : 2963, 1735, 1345, 1206, 1170, 1022, 837, 804, 698, 572.

benzyl 7-chlorobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(1d)



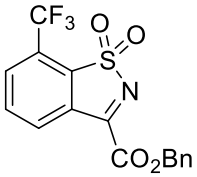
White solid, m.p. 129 – 130 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 8.09 (m, 1H), 7.63 – 7.59 (m, 2H), 7.42 – 7.40 (m, 2H), 7.38 – 7.33 (m, 3H), 5.42 (s, 2H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 158.6, 137.6, 135.78, 134.8, 133.6, 131.2, 130.3, 129.2, 128.9, 125.7, 69.3.

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{10}{}^{35}ClNNaO_4S^+$ ([M+Na$^+$]) = 357.9912, Found 357.9911.

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{10}{}^{37}ClNNaO_4S^+$ ([M+Na$^+$]) = 359.9882, Found 359.9884.

IR (film, cm^{-1}) : 2963, 1736, 1356, 1179, 1060, 794, 699, 580.

benzyl 7-(trifluoromethyl)benzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(1e)

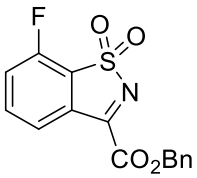


White solid, m.p. 101 – 102 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 6.0 Hz, 1H), 7.99 (d, *J* = 12.0 Hz, 1H), 7.92 (t, *J* = 6.0 Hz, 1H), 7.49 (d, *J* = 6.4 Hz, 2H), 7.50 – 7.48(m, 3H), 5.51 (s, 2H).; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.0, 158.4, 137.9, 135.3, 133.6, 131.1 (q, *J* = 3.7 Hz), 130.8, 129.5, 129.3, 128.9, 128.9, 127.8 (q, *J* = 36.9 Hz), 122.8, 121.0, 69.5; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -60.0. (s, 3F).

HRMS (ESI$^+$) m/z calcd for $C_{16}H_{10}F_3NNaO_4S^+$ ([M+Na$^+$]) = 392.0175, Found 392.0180.

IR (film, cm^{-1}) : 3093, 1739, 1365, 1321, 1180, 1140, 825, 806, 702, 574.

benzyl 7-fluorobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(1f)

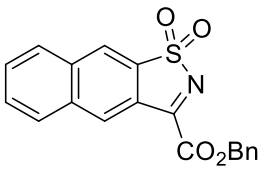


White solid, m.p. 123 – 124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.48 – 7.40 (m, 6H), 5.49 (s, 2H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 158.8, 157.2 (d, *J* = 262.2 Hz), 137.5 (d, *J* = 6.9 Hz), 133.7, 130.9, 129.2, 128.9, 128.9, 126.3 (d, *J* = 21.0 Hz), 123.5 (d, *J* = 3.4 Hz), 122.2 (d, *J* = 19.6 Hz), 69.4; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.0. (s, 1F)

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{10}FNNaO_4S^+$ ([M+Na$^+$]) = 342.0207, Found 342.0207.

IR (film, cm^{-1}) : 3087, 1737, 1498, 1358, 1261, 1222, 1180, 1108, 841, 755, 700, 522.

benzyl naphtho[2,3-*d*]isothiazole-3-carboxylate 1,1-dioxide(1g)



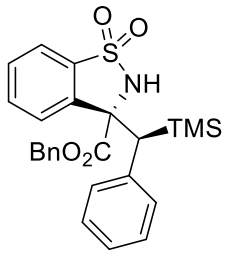
White solid, m.p. 207 – 208 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.39 (s, 1H), 8.05 (t, *J* = 8.0 Hz, 2H), 7.82 – 7.74 (m, 2H), 7.54 – 7.51 (m, 2H), 7.45 – 7.40 (m, 3H), 5.54 (s, 2H).; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.5, 160.0, 134.8, 134.6, 134.1, 133.9, 131.2, 131.0, 123.0, 129.9, 129.8, 129.1, 128.9, 125.0, 124.5, 69.1.

HRMS (FTMS+*c* ESI, m/z) calcd for $C_{19}H_{13}NNaO_4S^+$ ([M+Na$^+$]) = 374.0458, Found 374.0455.

IR (neat): (cm^{-1}) 3066, 1740, 1340, 1171, 754, 602, 471.

12. Characterization of the products

benzyl 3-(phenyl(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3a)



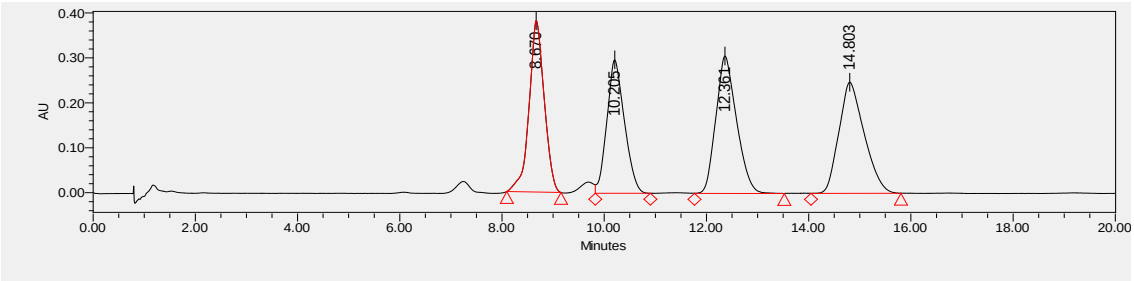
White amorphous solid, 44.2 mg, 95% yield, 95% ee, 88:12 dr, m.p. 150–152 °C. $[\alpha]_D^{20}$ = -57.5 (*c* = 0.74, CH_2Cl_2); **SFC** Chiralcel OX-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 220 nm, t_1 = 9.11 min, t_2 = 10.70 min, t_3 = 13.06 min, t_4 = 15.62 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 6.0 Hz ,1H), 7.43 (d, *J* = 6.0 Hz ,1H), 7.38 – 7.35 (m, 3H), 7.34 – 7.30 (m, 3H), 7.29 – 7.27 (m, 3H), 7.24 – 7.23 (m, 1H), 7.20 – 7.16 (m, 1H), 7.00 (t, *J* = 6.0 Hz, 2H), 6.91 (t, *J* = 6.0 Hz, 1H), 5.83 (s, 1H), 5.22 (dd, J_1 = 12.0, J_2 = 30.0 Hz, 2H), 3.31 (s, 1H), 0.00 (s, 9H).

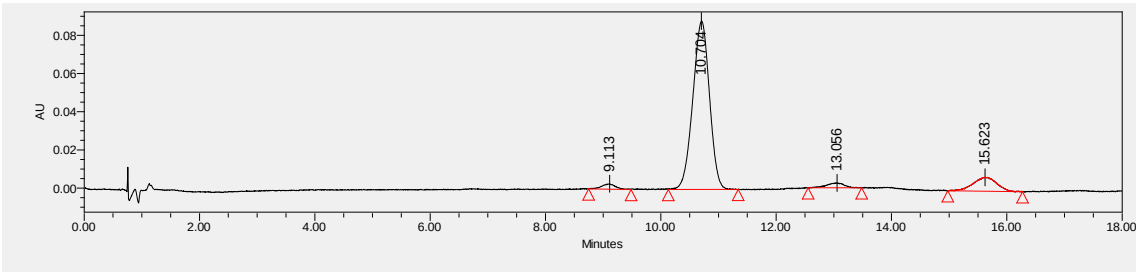
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 166.6, 164.0, 140.1, 140.0, 136.8, 133.9, 130.7, 129.3, 129.0, 128.9, 128.2, 126.3, 123.4, 123.3, 118.3, 118.1, 113.4, 113.2, 72.0, 70.0, 44.7, 0.9.

IR (film, cm^{-1}) : 3280, 2956, 1734, 1307, 1249, 1220, 1169, 845, 754, 703;

HRMS (ESI$^+$) m/z calcd for $C_{25}H_{27}NNaO_4SSi^+$ ([M]+Na^+) = 488.1323, found 488.1324.

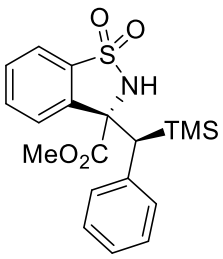


	Retention Time	Area	% Area
1	8.670	7105578	22.73
2	10.205	7076041	22.63
3	12.361	8585482	27.46
4	14.803	8500149	27.19



	Retention Time	Area	% Area
1	9.113	45460	2.19
2	10.704	1767611	85.16
3	13.056	54764	2.64
4	15.623	207921	10.02

methyl 3-(phenyl(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3b)



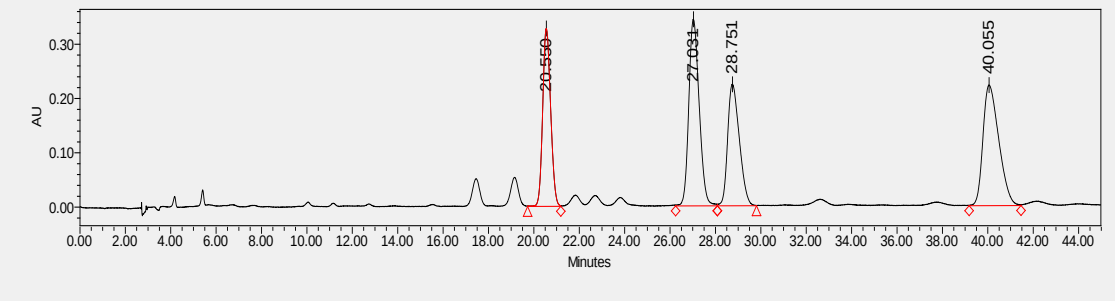
White amorphous solid, 38.1 mg, 98% yield, 96% ee, 83:17 dr, m.p. 181–183 °C. $[\alpha]_D^{20}$ = -27.6 (*c* = 0.56, CH_2Cl_2); **SFC** Chiralcel OXH, CO_2/MeOH = 90/10, 1.0 mL/min, λ = 220 nm, t_1 = 20.59min, t_2 = 26.98 min, t_3 = 27.92 min, t_4 = 39.92 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.18 – 7.14 (m, 1H), 6.98 (t, *J* = 8.0 Hz, 2H), 6.89 (t, *J* = 8.0 Hz, 1H), 5.79 (s, 1H), 3.82 (s, 3H), 3.27 (s, 1H), 0.00 (s, 9H).

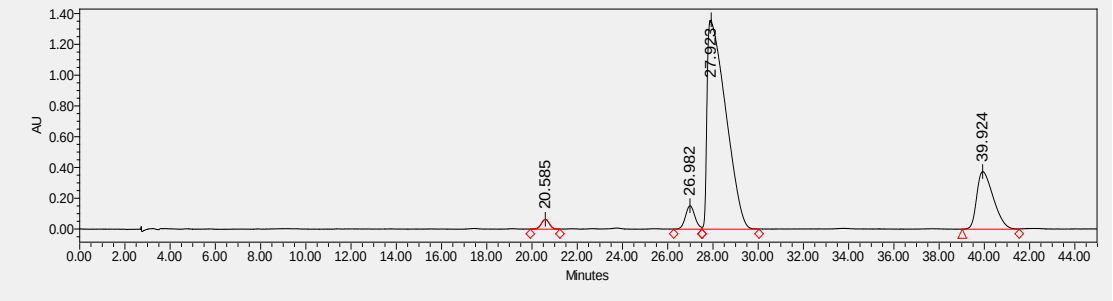
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 137.0, 136.6, 134.2, 133.0, 129.9, 127.9, 126.1, 125.9, 120.9, 72.2, 54.3, 44.5, -1.1.

IR (film, cm^{-1}) : 3276, 2956, 1736, 1306, 1246, 1206, 1169, 845, 756, 707;

HRMS (ESI^+) m/z calcd for $C_{19}H_{23}NNaO_4SSi^+$ ([M]+Na^+) = 412.1010, found 412.1010.

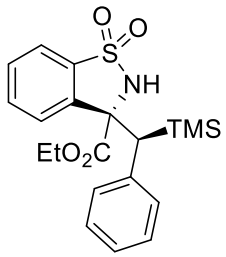


	Retention Time	Area	% Area
1	20.550	7962780	21.16
2	27.031	10912453	29.00
3	28.751	7982324	21.22
4	40.055	10767036	28.62



	Retention Time	Area	% Area
1	20.585	1628302	1.59
2	26.982	4454558	4.35
3	27.923	77398824	75.50
4	39.924	19038359	18.57

ethyl 3-(phenyl(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3c)



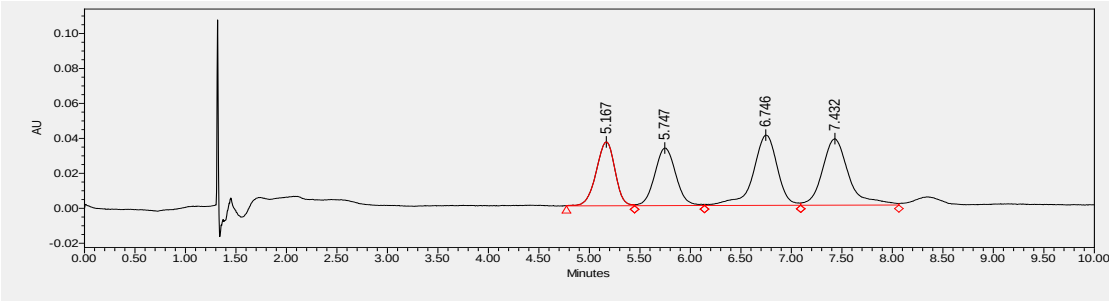
Colorless oil, 39.1 mg, 97% yield, 90% ee, 86:14 dr, $[\alpha]_D^{20}$ = -18.5 (*c* = 0.60, CH_2Cl_2); **SFC** Chiralcel ID-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 220 nm, t_1 = 5.05 min, t_2 = 5.41 min, t_3 = 6.57 min, t_4 = 7.23 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz,, 1H), 7.21 (s, 1H), 7.17 – 7.14 (m, 1H), 6.97 (t, *J* = 8.0 Hz, 2H), 6.88 (t, *J* = 8.0 Hz, 1H), 5.79 (s, 1H), 4.31 – 4.18 (m, 2H), 3.27 (s, 1H), 3.06 (s, 0H), 1.29 (t, *J* = 8.0 Hz, 3H), 0.00 (s, 9H).

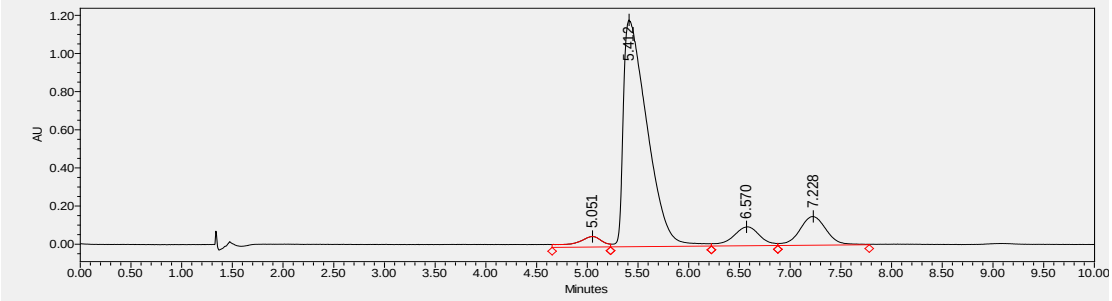
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 137.1, 136.9, 134.3, 132.9, 129.8, 127.8, 126.1, 125.9, 120.9, 72.2, 63.8, 44.5, 13.9, -1.0.

IR (film, cm^{-1}) : 3275, 2959, 1730, 1306, 1240, 1206, 1169, 844, 756, 707;

HRMS (ESI^+) m/z calcd for $C_{20}H_{25}NNaO_4SSi^+$ ([M]+Na^+) = 426.1166, found 426.1162.

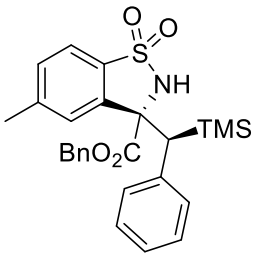


	Retention Time	Area	% Area
1	5.167	471587	20.49
2	5.747	476634	20.71
3	6.746	667927	29.02
4	7.432	685445	29.78



	Retention Time	Area	% Area
1	5.051	987860	3.96
2	5.412	19367332	77.67
3	6.570	1818022	7.29
4	7.228	2761707	11.08

benzyl 5-methyl-3-(phenyl(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3d)



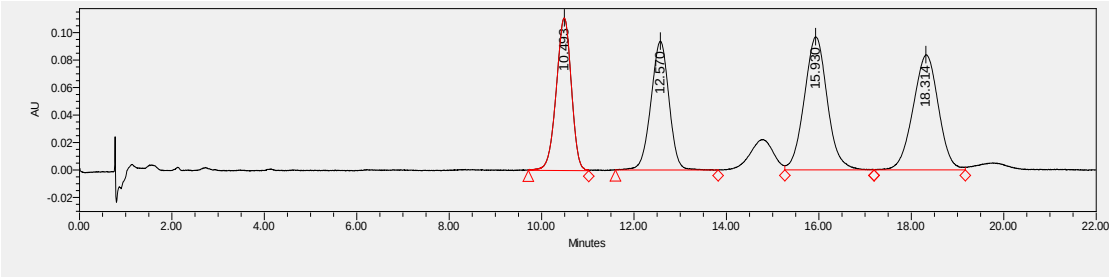
Colorless oil, 44.5mg, 93% yield, 88% ee, 88:12 dr, $[\alpha]_D^{20}$ = -66.9 (*c* = 0.73, CH_2Cl_2); **SFC** Chiralcel OX-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 220 nm, t_1 = 10.31 min, t_2 = 12.32 min, t_3 = 15.67 min, t_4 = 17.98 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 1H), 7.38 – 7.34 (m, 3H), 7.32 – 7.30 (m, 2H), 7.23 – 7.19 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 8.0 Hz, 1H), 5.79 (s, 1H), 5.23 (dd, J_1 = 12.0 Hz, J_2 = 16.0 Hz, 2H), 3.29 (s, 1H), 2.23 (s, 3H), 0.00 (s, 9H).

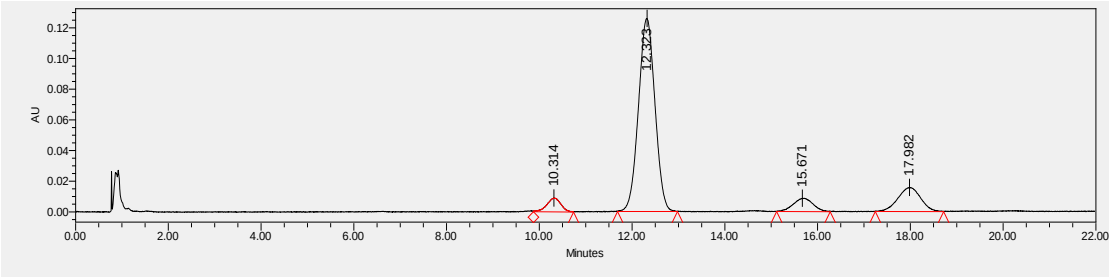
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 143.8, 137.1, 136.9, 134.0, 131.7, 130.8, 128.9, 128.7, 128.6, 127.8, 126.3, 125.8, 120.6, 72.0, 69.3, 44.3, 21.6, -1.1.

IR (film, cm^{-1}) : 3282, 2956, 1734, 1306, 1240, 1222, 1186, 1143, 843, 753, 701;

HRMS (ESI^+) m/z calcd for $C_{26}H_{29}NNaO_4SSi^+$ ([M]+Na^+) = 502.1479, found 502.1479.

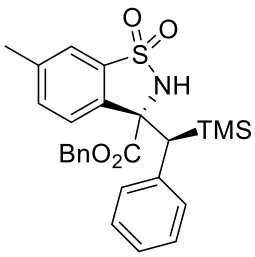


	Retention Time	Area	% Area
1	10.493	2511445	21.68
2	12.570	2537643	21.91
3	15.930	3345712	28.88
4	18.314	3188898	27.53



	Retention Time	Area	% Area
1	10.314	190461	4.66
2	12.323	3104158	75.87
3	15.671	257505	6.29
4	17.982	539352	13.18

benzyl 6-methyl-3-(phenyl(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3e)



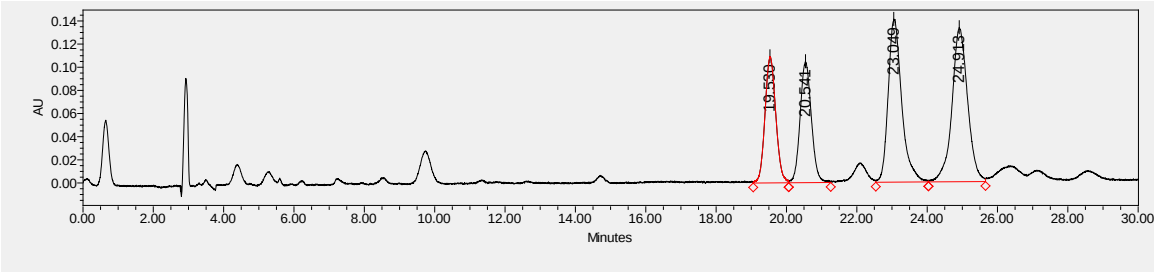
White amorphous solid, 27.8 mg, 58% yield, 84% ee, 80:20 dr, m.p. 75–78 °C. $[\alpha]_D^{20}$ = -72.9 (*c* = 0.14, CH_2Cl_2); **SFC** Chiralcel ODH, CO_2/MeOH = 93/7, 1.0 mL/min, λ = 220 nm, t_1 = 19.40 min, t_2 = 20.54 min, t_3 = 23.07 min, t_4 = 24.90 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.35 – 7.32 (m, 4H), 7.30 (s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.10 – 7.08 (m, 1H), 7.03 (t, J = 8.0 Hz, 2H), 6.94 (t, J = 8.0 Hz, 1H), 5.80 (s, 1H), 5.21 (dd, J_1 = 12.0 Hz, J_2 = 20.0 Hz, 2H), 3.29 (s, 1H), 2.27 (s, 3H), 0.00 (s, 9H).

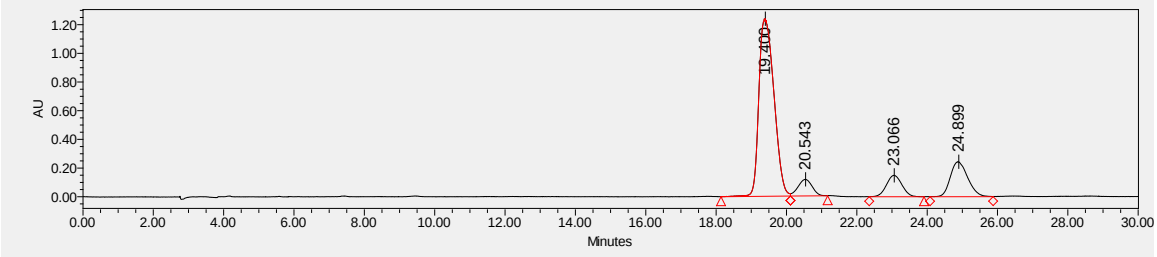
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 140.6, 137.2, 134.4, 134.1, 133.8, 128.9, 128.8, 128.6, 127.9, 125.9, 125.8, 120.8, 72.1, 69.4, 44.2, 21.1, -1.0.

IR (film, cm^{-1}) : 3279, 2955, 1735, 1307, 1250, 1223, 1161, 1143, 844, 750, 703;

HRMS (ESI^+) m/z calcd for $C_{26}H_{29}NNaO_4SSi^+$ ([M]+Na^+) = 502.1479, found 502.1476.

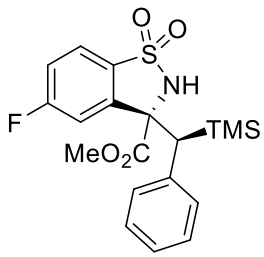


	Retention Time	Area	% Area
1	19.530	2317628	18.51
2	20.541	2324535	18.57
3	23.049	3768440	30.10
4	24.913	4109191	32.82



	Retention Time	Area	% Area
1	19.400	36810085	69.48
2	20.543	3206524	6.05
3	23.066	4591198	8.67
4	24.899	8369467	15.80

methyl (S)-5-fluoro-3-((S)-phenyl(trimethylsilyl)methyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide(3f)



White amorphous solid, 26.8 mg, 66% yield, 96% ee, 94:6 dr, m.p. 186–188 °C $[\alpha]_D^{20}$ = -35.1 (*c* = 0.51, CH_2Cl_2); **HPLC** Daicel chiralcel IA, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 220 nm, t_1 = 17.56 min, t_2 = 23.14 min, t_3 = 52.82 min, t_4 = 57.37 min**;**

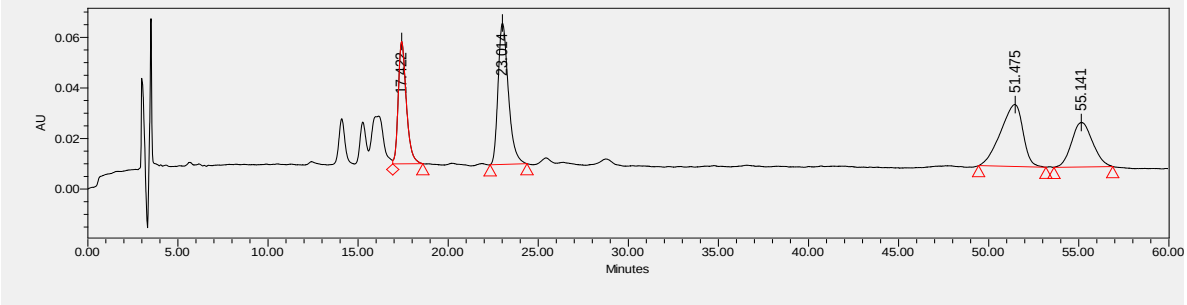
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.47 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.15 (dd, J_1 = 2.2 Hz, J_2 = 8.0 Hz Hz, 1H), 7.04 – 6.92 (m, 5H), 5.84 (s, 1H), 3.85 (s, 3H), 3.17 (s, 1H), -0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 171.4, 165.3 (d, *J* = 254.0 Hz), 140.0 (d, *J* = 10.0 Hz), 136.6, 130.4 (d, *J* = 2.0 Hz), 128.1, 126.2, 123.2 (d, *J* = 10.0 Hz), 118.1 (d, *J* = 24.0 Hz), 113.2 (d, *J* = 24.0 Hz), 71.7, 54.5, 44.8, -1.1.

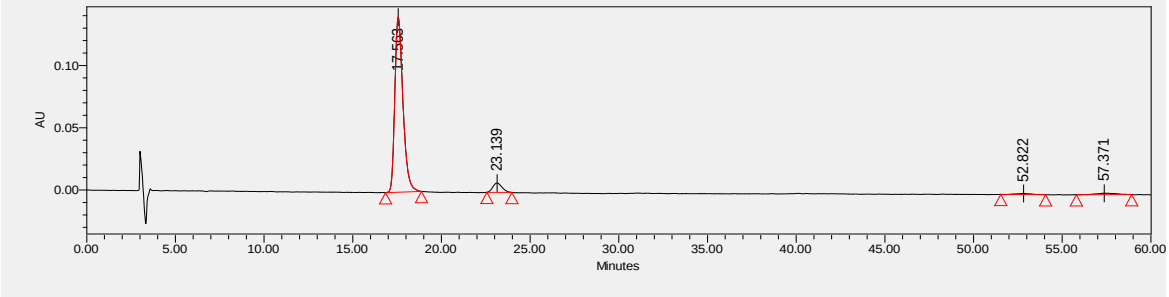
^{19}F NMR (377 MHz, $CDCl_3$) *δ* -103.8. (s, 1F).

IR (film, cm^{-1}) : 3279, 2954, 1739, 1302, 1245, 1203, 1173, 851, 754, 710;

HRMS (ESI^+) m/z calcd for $C_{19}H_{22}FNNaO_4SSi^+$ ([M]+Na^+) = 430.0916, found 430.0918.

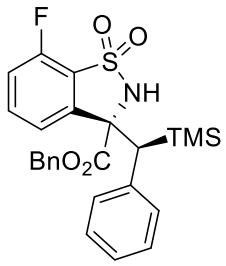


	Retention Time	Area	% Area
1	17.422	1508518	20.71
2	23.014	2216745	30.43
3	51.475	2123246	29.15
4	55.141	1435188	19.70



	Retention Time	Area	% Area
1	17.563	4477207	91.52
2	23.139	272720	5.57
3	52.822	52248	1.07
4	57.371	89841	1.84

benzyl 7-fluoro-3-(phenyl(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3g)



Colorless oil, 37.1 mg, 77% yield, 96% ee, 81:19 dr, $[\alpha]_D^{20}$ = -50.0 (*c* = 0.55, CH_2Cl_2); **HPLC** Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 220 nm, t_1 = 19.14 min, t_2 = 21.54 min, t_3 = 23.36 min, t_4 = 33.57 min**;**

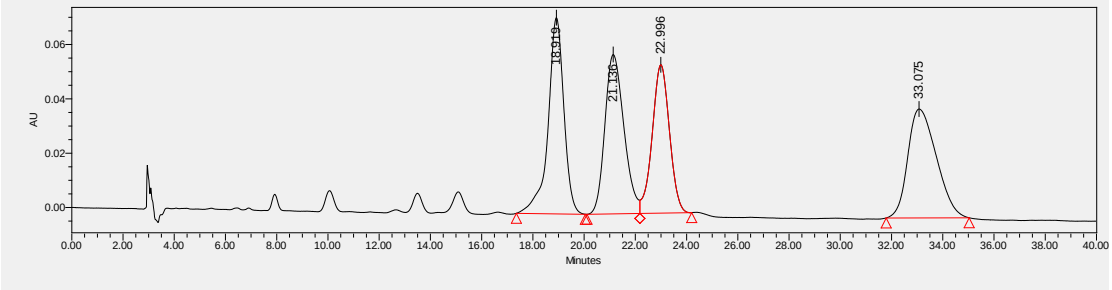
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 3H), 7.35 – 7.32 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 2H), 6.97 – 6.92 (m, 2H), 5.92 (s, 1H), 5.24 (dd, J_1 = 12.0 Hz, J_2 = 24.0 Hz, 2H), 3.29 (s, 1H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 155.8 (d, *J* = 259.0 Hz), 139.7, 136.7, 135.1 (d, *J* = 7.2 Hz), 133.8, 129.1, 128.8, 128.7, 128.0, 126.1, 122.7 (d, *J* = 19.0 Hz), 121.9 (d, *J* = 3.9 Hz), 116.5 (d, *J* = 18.3 Hz), 72.5, 69.8, 44.5, -1.1.

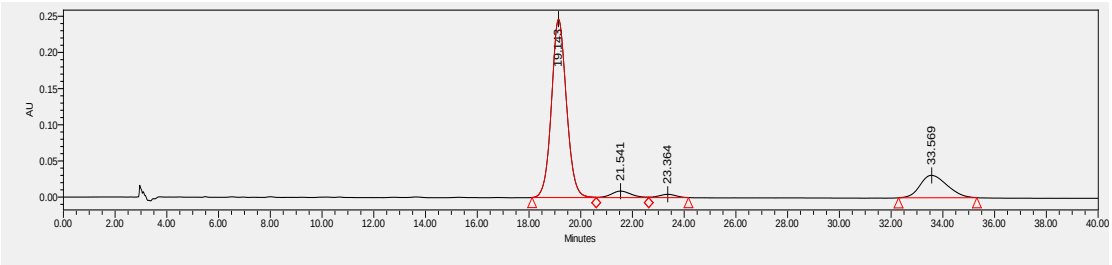
^{19}F NMR (377 MHz, $CDCl_3$) δ -115.3. (s, 1F)

IR (film, cm^{-1}) : 3272, 2957, 1736, 1317, 1253, 1219, 1176, 1143, 844, 755, 701;

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}NNaO_4SSi^+$ ($[M]+Na^+$) = 506.1229, found 506.1227.

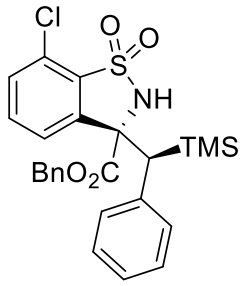


	Retention Time	Area	% Area
1	18.919	2578566	22.95
2	21.136	3022449	26.91
3	22.996	2531615	22.54
4	33.075	3100860	27.60



	Retention Time	Area	% Area
1	19.143	9906889	77.16
2	21.541	470026	3.66
3	23.364	203815	1.59
4	33.569	2258964	17.59

benzyl 7-chloro-3-(phenyl(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3h)



Colorless oil, 41.2 mg, 82% yield, 96% ee, 80:20 dr, $[\alpha]_D^{20}$ = -34.7 (*c* = 0.64, CH_2Cl_2);

SFC Chiralcel IH-3, CO_2/MeOH = 96/4, 1.0 mL/min, λ = 220 nm, t_1 = 18.31 min, t_2 = 20.63 min, t_3 = 23.42 min, t_2 = 26.54 min;

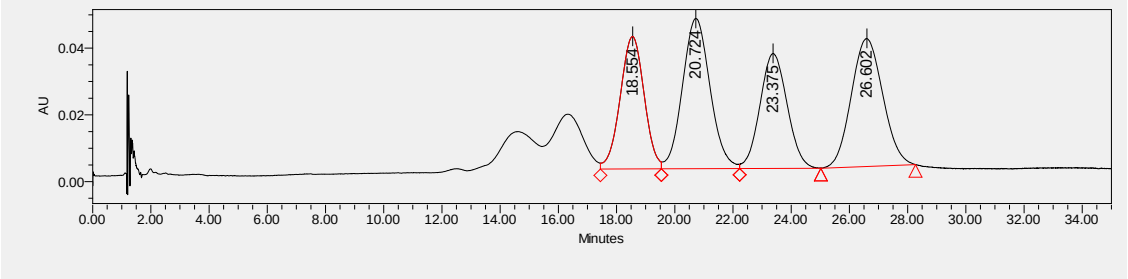
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 3H), 7.35 – 7.31 (m, 3H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.23 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H), 7.10 – 7.06 (m, 1H), 7.04 (t, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 8.0 Hz, 1H), 5.92 (s, 1H), 5.22 (dd, J_1 = 12.0 Hz, J_2 = 24.0 Hz, 2H), 3.29 (s, 1H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 139.0, 136.7, 133.8, 133.8, 132.4, 130.6, 129.1, 128.8, 128.7, 128.0, 126.1, 124.5, 71.4, 69.8, 44.2, -1.1.

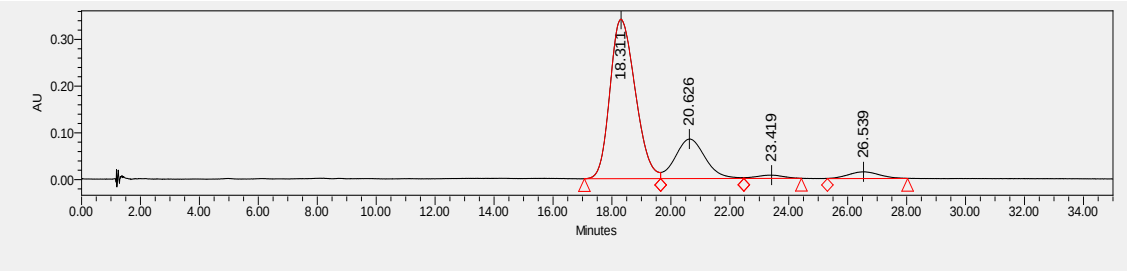
IR (film, cm^{-1}) : 3273, 2957, 1735, 1317, 1250, 1218, 1170, 1143, 847, 754, 701;

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}{}^{35}ClNNaO_4SSi^+$ ([M]+Na^+) = 522.0933, found 522.0930.

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}{}^{37}ClNNaO_4SSi^+$ ([M]+Na^+) = 524.0904, found 524.0904.

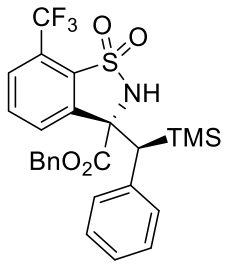


	Retention Time	Area	% Area
1	18.554	2261164	21.62
2	20.724	2964948	28.34
3	23.375	2233061	21.35
4	26.602	3001791	28.70



	Retention Time	Area	% Area
1	18.311	20320916	73.25
2	20.626	5932726	21.38
3	23.419	443677	1.60
4	26.539	1045813	3.77

benzyl 3-(phenyl(trimethylsilyl)methyl)-7-(trifluoromethyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3i)



Colorless oil, 40.9 mg, 77% yield, 99% ee, 83:17 dr, $[\alpha]_D^{20}$ = -43.3 (*c* = 0.45, CH_2Cl_2); **HPLC** Daicel chiralcel IC, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 220 nm, t_1 = 12.27 min, t_2 = 17.66 min, t_3 = 23.46 min, t_2 = 40.59 min;

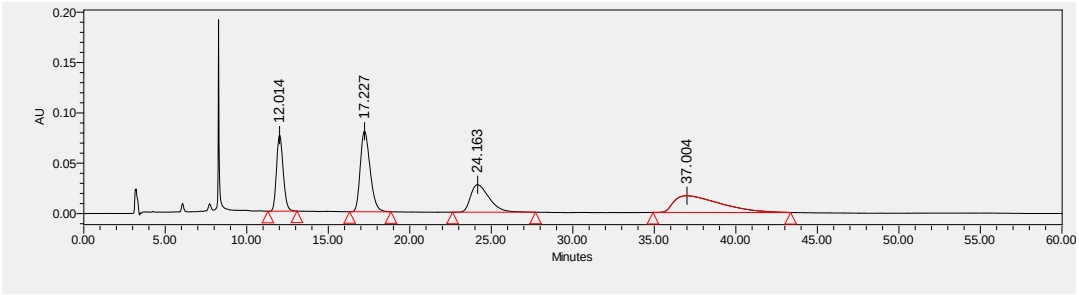
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.38 – 7.36 (m, 3H), 7.33 – 7.31 (m, 2H), 7.23-7.21 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 2H), 6.93 (t, *J* = 8.0 Hz, 1H), 5.96 (s, 1H), 5.23 (dd, J_1 = 12.0 Hz, J_2 = 16.0 Hz, 2H), 3.32 (s, 1H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 138.9, 136.7, 133.7, 132.9, 130.2, 129.1, 128.8, 128.7, 128.1, 127.8 (d, *J* = 4.8 Hz), 126.1, 71.7, 69.9, 44.6, -1.1.

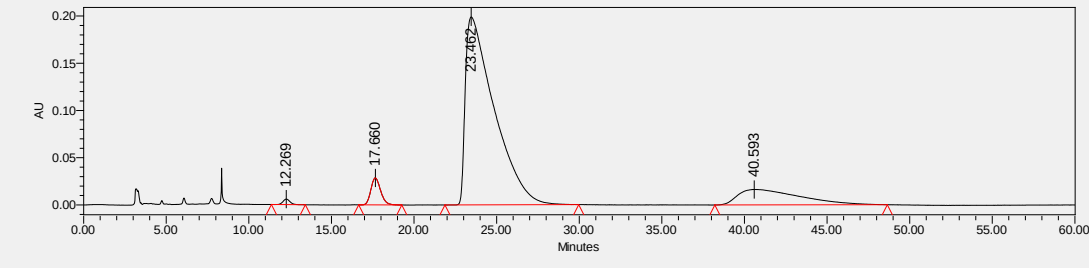
^{19}F NMR (377 MHz, $CDCl_3$) δ -59.6. (s, 3F)

IR (film, cm^{-1}) : 3269, 2958, 1736, 1322, 1251, 1219, 1175, 1142, 842, 754, 703;

HRMS (ESI$^+$) m/z calcd for $C_{26}H_{26}F_3NNaO_4SSi^+$ ([M]+Na^+) = 556.1197, found 556.1197.

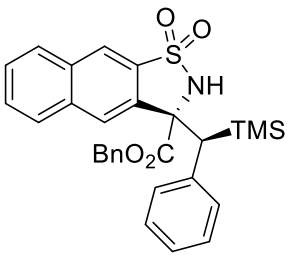


	Retention Time	Area	% Area
1	12.014	2157086	19.71
2	17.227	3344408	30.56
3	24.163	2169981	19.83
4	37.004	3270850	29.89



	Retention Time	Area	% Area
1	12.269	174298	0.59
2	17.660	1169531	3.94
3	23.462	24098945	81.16
4	40.593	4249749	14.31

benzyl 3-(phenyl(trimethylsilyl)methyl)-2,3-dihydronaphtho[2,3-*d*]isothiazole-3-carboxylate 1,1-dioxide(3j)

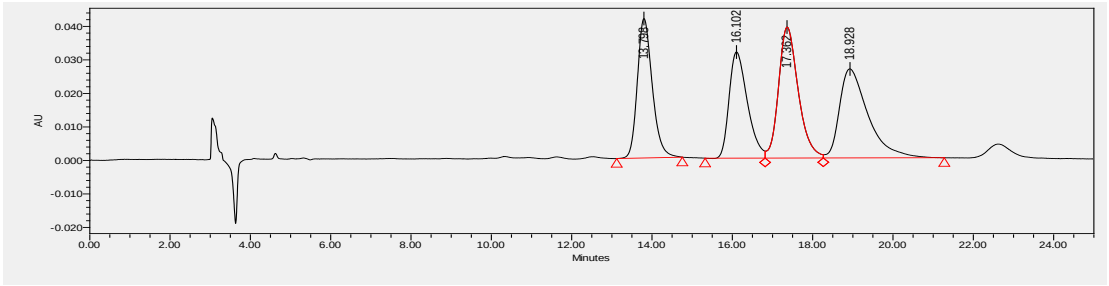


White amorphous solid, 15.4 mg, 30% yield, 82% ee, 80:20 dr, m.p. 79–83 °C. $[\alpha]_D^{20}$ = -73.8 (*c* = 0.20, CH_2Cl_2); **HPLC** Daicel chiralcel IG, *n*-hexane/*i*-PrOH 93/7, 1.0 mL/min, λ = 235 nm, t_1 = 13.70 min, t_2 = 16.12 min, t_3 = 17.40 min, t_2 = 18.85 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.86 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.31 – 7.26 (m, 5H), 7.19 – 7.16 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 2H), 6.79 (t, *J* = 8.0 Hz, 1H), 5.83 (s, 1H), 5.19 (dd, J_1 = 12.0 Hz, J_2 = 44.0 Hz, 2H), 3.41 (s, 1H), 0.00 (s, 9H).

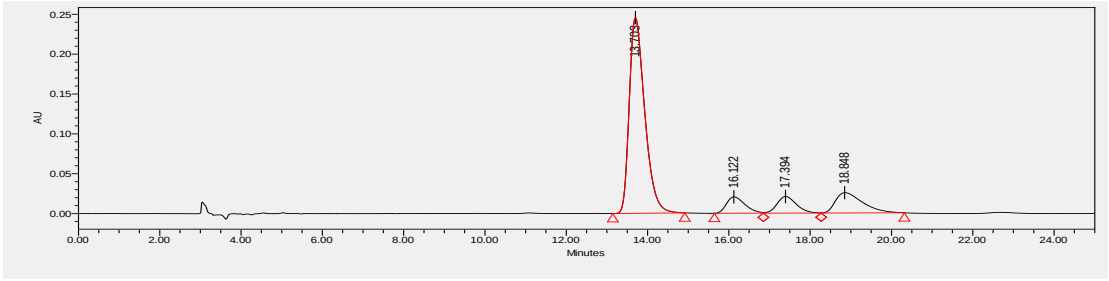
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 137.2, 135.0, 134.0, 132.8, 132.3, 132.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.3, 127.9, 127.7, 126.0, 125.8, 121.7, 72.3, 69.5, 45.0, -0.9.

IR (film, cm^{-1}) : 3278, 2957, 1735, 1308, 1249, 1219, 1170, 1152, 844, 752, 701;

HRMS (ESI^+) m/z calcd for $C_{29}H_{29}NNaO_4SSi^+$ ([M]+Na^+) = 538.1479, found 538.1480.

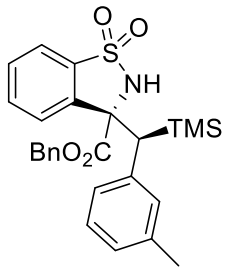


	Retention Time	Area	% Area
1	13.798	1009260	21.70
2	16.102	1002391	21.55
3	17.362	1328568	28.56
4	18.928	1311009	28.19



	Retention Time	Area	% Area
1	13.703	6485840	72.01
2	16.122	648127	7.20
3	17.394	687998	7.64
4	18.848	1184836	13.15

benzyl 3-(m-tolyl(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (3k)



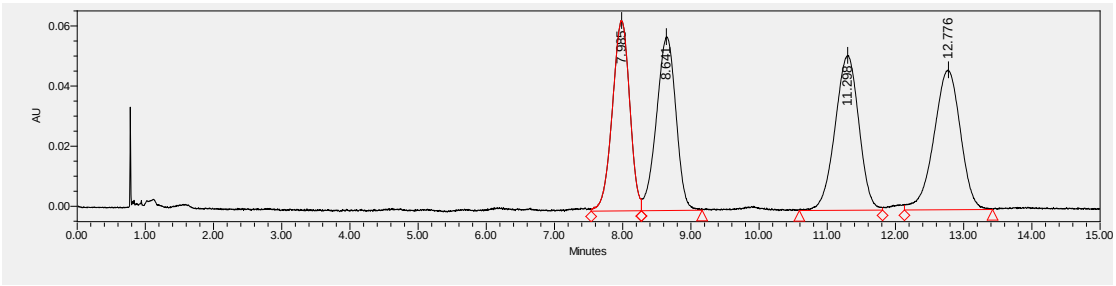
Colorless oil, 34.7 mg, 72% yield, 95% ee, 87:13 dr, $[\alpha]_D^{20}$ = -53.5 (*c* = 0.52, CH_2Cl_2); **SFC** Chiralcel OX-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 220 nm, t_1 = 8.02 min, t_2 = 8.67 min, t_3 = 11.37 min, t_4 = 12.86 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 4.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.36 (m, 3H), 7.34 – 7.28 (m, 4H), 7.25 (s, 2H), 6.87 (t, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.82 (s, 1H), 5.21 (dd, J_1 = 12.0, J_2 = 20.0 Hz, 2H), 3.25 (s, 1H), 2.13 (s, 3H), 0.00 (s, 9H).

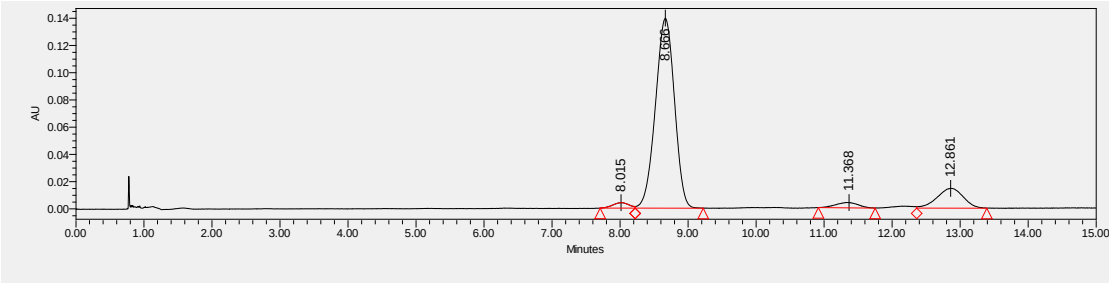
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 136.8, 136.6, 134.4, 134.0, 132.8, 129.8, 128.9, 128.8, 128.6, 127.6, 126.6, 126.2, 120.9, 72.3, 69.5, 44.2, 21.2, -1.0.

IR (film, cm^{-1}) :3280, 2955, 1734, 1307, 1249, 1219, 1170, 842, 754, 701;

HRMS (ESI^+) m/z calcd for $C_{26}H_{29}NNaO_4SSi^+$ ([M]+Na^+) = 502.1479, found 502.1478.

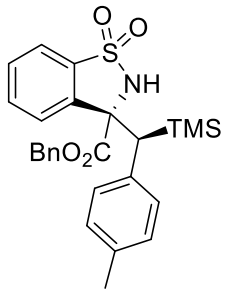


	Retention Time	Area	% Area
1	7.985	1120200	23.46
2	8.641	1145218	23.99
3	11.298	1251204	26.21
4	12.776	1257959	26.35



	Retention Time	Area	% Area
1	8.015	67402	2.07
2	8.666	2709466	83.16
3	11.368	90023	2.76
4	12.861	391063	12.00

benzyl 3-(p-tolyl(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (3l)



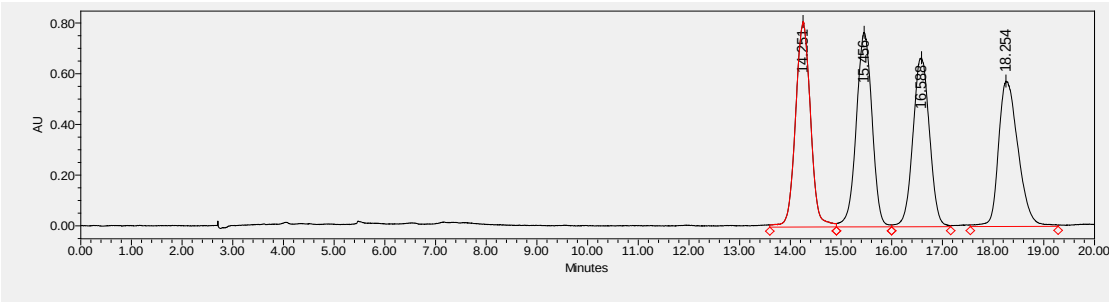
Colorless oil, 30.2 mg, 63% yield, 93% ee, 87:13 dr, $[\alpha]_D^{20}$ = -50.0 (*c* = 0.46, CH_2Cl_2); **SFC** Chiralcel ODH, CO_2/MeOH = 90/10, 1.0 mL/min, λ = 220 nm, t_1 = 14.02 min, t_2 = 15.47 min, t_3 = 16.59 min, t_4 = 18.19 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 6.0 Hz, 1H), 7.46 (d, *J* = 6.0 Hz, 1H), 7.40 – 7.38 (m, 4H), 7.33 – 7.32 (m, 4H), 7.05 (d, *J* = 6.0 Hz, 1H), 6.82 (d, *J* = 6.0 Hz, 2H), 5.81 (s, 1H), 5.22 (dd, J_1 = 12.0, J_2 = 30.0 Hz, 2H), 3.26 (s, 1H), 2.10 (s, 3H), 0.00 (s, 9H).

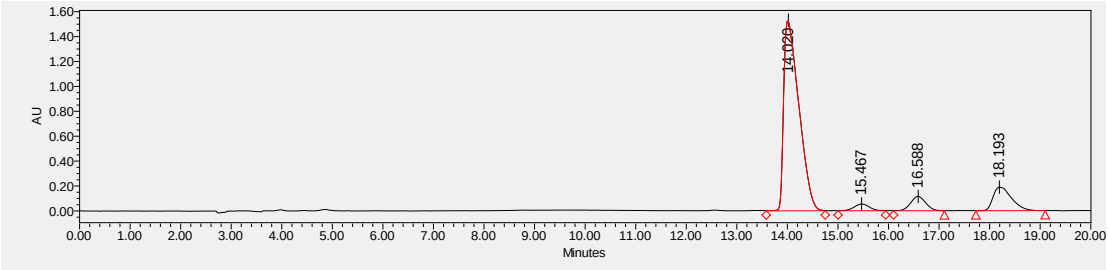
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 136.7, 135.3, 134.3, 133.7, 132.9, 129.8, 128.9, 128.8, 128.6, 126.1, 121.0, 72.4, 69.5, 43.8, 20.8, -1.0.

IR (film, cm^{-1}) :3282, 2955, 1735, 1308, 1250, 1220, 1169, 848, 754, 698;

HRMS (ESI^+) m/z calcd for $C_{26}H_{29}NNaO_4SSi^+$ ([M]+Na^+) = 502.1479, found 502.1480.

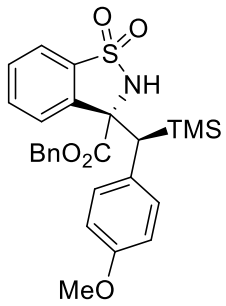


	Retention Time	Area	% Area
1	14.251	16641400	26.10
2	15.456	16544271	25.95
3	16.588	15152490	23.76
4	18.254	15423329	24.19



	Retention Time	Area	% Area
1	14.020	31793044	79.15
2	15.467	1167989	2.91
3	16.588	2402958	5.98
4	18.193	4803895	11.96

benzyl 3-((4-methoxyphenyl)(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3m)



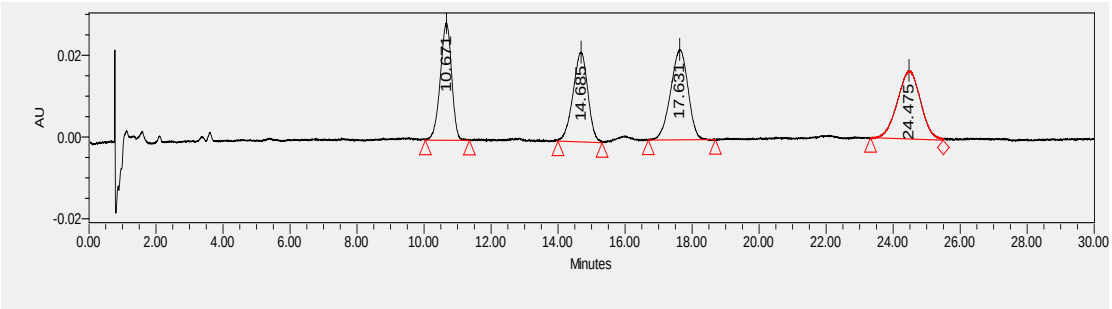
Colorless oil, 10.6 mg, 21% yield, 87% ee, 86:14 dr, $[\alpha]_D^{20}$ = -40.4 (*c* = 0.39, CH_2Cl_2); **SFC** Chiralcel OX-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 220 nm, t_1 = 10.64 min, t_2 = 14.58 min, t_3 = 17.59 min, t_4 = 24.38 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.44 (m, 1H), 7.41 – 7.36 (m, 4H), 7.36 – 7.30 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 5.80 (s, 1H), 5.22 (dd, J_1 = 12.0, J_2 = 24.0 Hz, 2H), 3.63 (s, 3H), 3.24 (s, 1H), 0.00 (s, 9H).

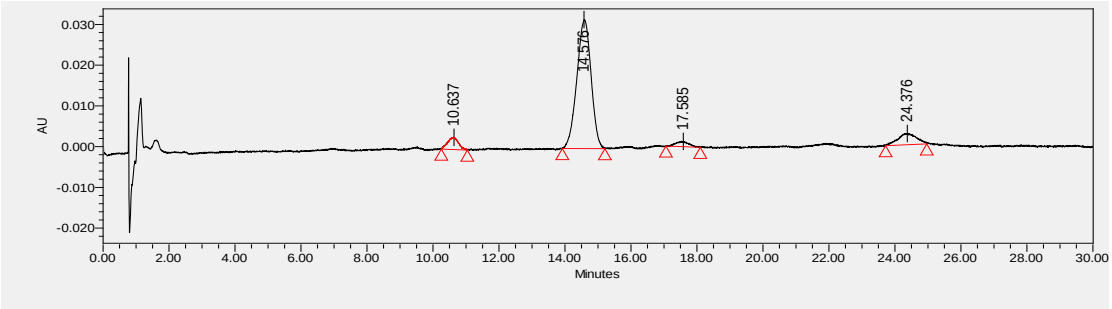
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 157.6, 136.7, 134.4, 134.0, 132.9, 129.9, 128.9, 128.8, 128.6, 126.2, 121.0, 113.2, 72.5, 69.5, 54.9, 43.4, -1.0.

IR (film, cm^{-1}) :3279, 2956, 1735, 1306, 1248, 1221, 1173, 848, 755, 698;

HRMS (ESI^+) m/z calcd for $C_{26}H_{29}NNaO_5SSi^+$ ([M]+Na^+) = 518.1428, found 518.1430.

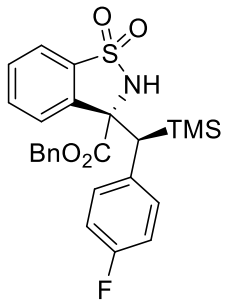


	Retention Time	Area	% Area
1	10.671	676406	22.94
2	14.685	677179	22.96
3	17.631	796829	27.02
4	24.475	798419	27.08



	Retention Time	Area	% Area
1	10.637	68254	5.88
2	14.576	949378	81.81
3	17.585	34601	2.98
4	24.376	108267	9.33

benzyl 3-((4-fluorophenyl)(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3n)



Colorless oil, 44.9 mg, 93% yield, 96% ee, 86:14 dr, $[\alpha]_D^{20}$ = -56.7 (*c* = 0.60, CH_2Cl_2); **SFC** Chiralcel OX-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 220 nm, t_1 = 6.14 min, t_2 = 7.29 min, t_3 = 11.51 min, t_4 = 13.34 min;

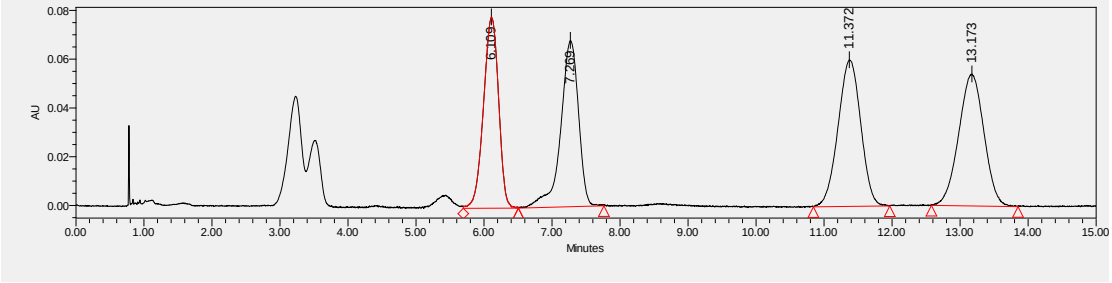
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.40 – 7.35 (m, 4H), 7.33 – 7.30 (m, 3H), 7.14 – 7.08 (m, 1H), 6.87 – 6.82 (m, 1H), 6.77 – 6.72 (m, 1H), 5.85 (s, 1H), 5.23 (dd, J_1 = 12.0, J_2 = 20.0 Hz, 2H), 3.89 (s, 1H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 161.1 (d, *J* = 244.5 Hz), 139.7, 139.7, 136.3, 134.4, 133.8, 133.0, 132.8 (d, *J* = 3.3 Hz), 130.1, 129.0, 128.8, 128.7, 126.0, 121.1, 115.2 (d, *J* = 21.3 Hz), 72.0, 69.7, 44.3, -1.1.

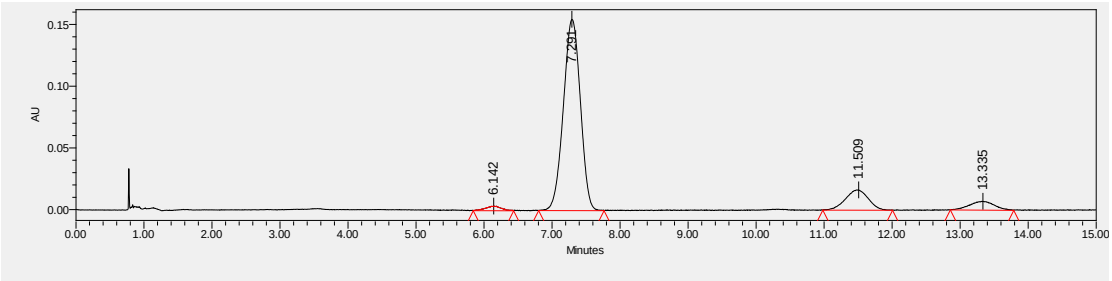
^{19}F NMR (565 MHz, $CDCl_3$) δ -116.8. (s, 1F)

IR (film, cm^{-1}) :3279, 2957, 1735, 1307, 1222, 1220, 1166, 849, 755, 698;

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}FNNaO_4SSi^+$ ([M]+Na^+) = 506.1229, found 506.1230.

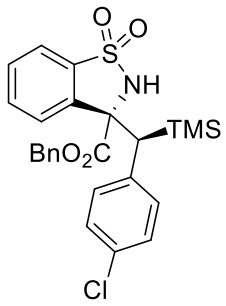


	Retention Time	Area	% Area
1	6.109	1207385	23.06
2	7.269	1238600	23.66
3	11.372	1393905	26.62
4	13.173	1395782	26.66



	Retention Time	Area	% Area
1	6.142	59619	1.80
2	7.291	2687164	80.94
3	11.509	387532	11.67
4	13.335	185580	5.59

benzyl 3-((4-chlorophenyl)(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3o)



Colorless oil, 46.7 mg, 93% yield, 96% ee, 86:14 dr, $[\alpha]_D^{20}$ = -55.6 (*c* = 0.61, CH_2Cl_2); **SFC** Chiralcel OX-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 235 nm, t_1 = 9.01 min, t_2 = 11.17 min, t_3 = 17.05 min, t_4 = 20.64 min;

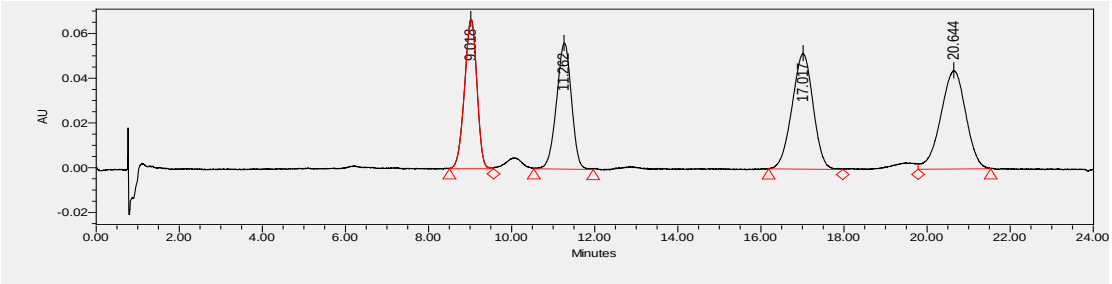
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.56 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.40 (m, 3H), 7.38 – 7.35 (m, 3H), 7.33 – 7.30 (m, 3H), 7.21 – 7.11 (m, 1H), 6.99 (d, J = 8.0 Hz, 2H), 5.83 (s, 1H), 5.22 (dd, J_1 = 12.0, J_2 = 24.0 Hz, 2H), 3.30 (s, 1H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 171.1, 136.3, 135.7, 134.3, 133.8, 133.1, 131.8, 130.1, 129.0, 128.8, 128.7, 128.1, 125.9, 121.2, 72.0, 69.7, 43.9, -1.1.

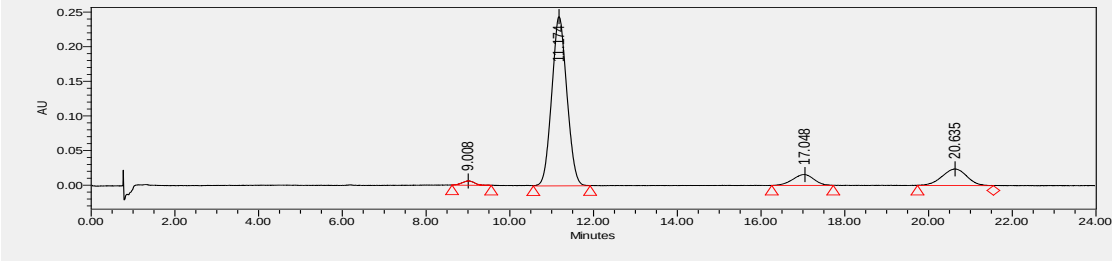
IR (film, cm^{-1}) :3278, 2956, 1736, 1308, 1251, 1220, 1169, 848, 755, 698;

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}{}^{35}ClNNaO_4SSi^+$ ([M]+Na^+) = 522.0933, found 522.0931.

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}{}^{37}ClNNaO_4SSi^+$ ([M]+Na^+) = 524.0904, found 524.0900

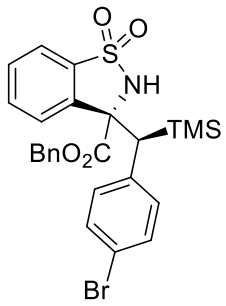


	Retention Time	Area	% Area
1	9.018	1386664	21.47
2	11.262	1408641	21.81
3	17.017	1817129	28.14
4	20.644	1845628	28.58



	Retention Time	Area	% Area
1	9.008	131729	1.69
2	11.174	6132089	78.55
3	17.048	556076	7.12
4	20.635	986582	12.64

benzyl 3-((4-bromophenyl)(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3p)



Colorless oil, 47.1 mg, 86% yield, 96% ee, 84:16 dr, $[\alpha]_D^{20}$ = -51.1 (*c* = 0.70, CH_2Cl_2); **SFC** Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 240 nm, t_1 = 4.53 min, t_2 = 5.25 min, t_3 = 6.03 min, t_4 = 8.54 min;

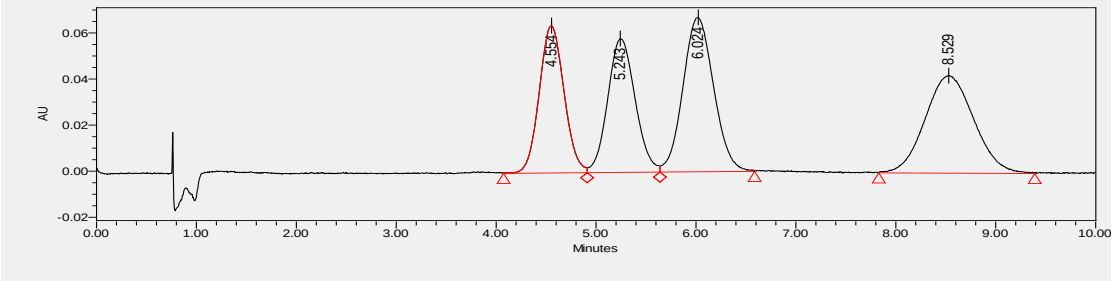
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 6.0 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.38 – 7.35 (m, 4H), 7.32 (s, 3H), 7.14 (d, *J* = 6.0 Hz, 2H), 7.08 (d, *J* = 6.0 Hz, 1H), 5.85 (s, 1H), 5.23 (dd, J_1 = 12.0, J_2 = 36.0 Hz, 2H) 3.29 (s, 1H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 137.4, 137.4, 135.5, 135.0, 134.3, 132.1, 131.3, 130.2, 123.0, 129.8, 127.1, 122.3, 121.1, 73.1, 70.8, 45.0, 0.0.

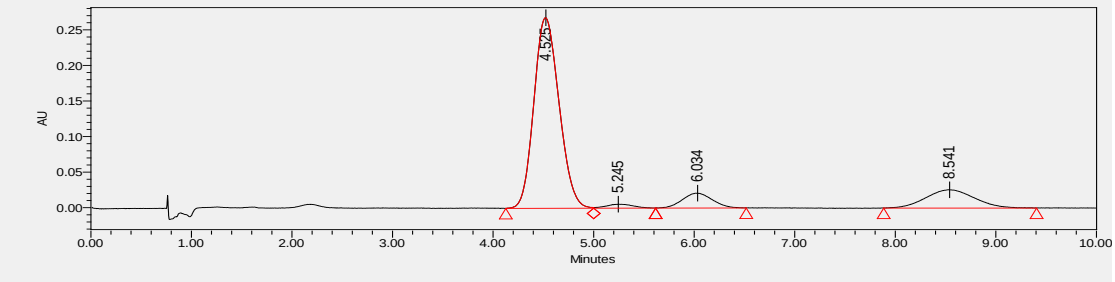
IR (film, cm^{-1}) :3276, 2956, 1735, 1307, 1250, 1218, 1169, 847, 755, 698;

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}{}^{79}BrNNaO_4SSi^+$ ([M]+Na^+) = 566.0428, found 566.0428.

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}{}^{81}BrNNaO_4SSi^+$ ([M]+Na^+) = 568.0407, found 568.0399.

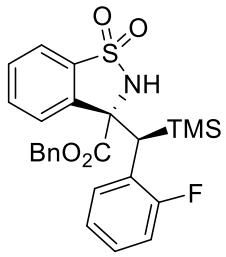


	Retention Time	Area	% Area
1	4.554	1101684	21.70
2	5.243	1107601	21.82
3	6.024	1432255	28.21
4	8.529	1434678	28.26



	Retention Time	Area	% Area
1	4.525	4655471	76.68
2	5.245	104778	1.73
3	6.034	437560	7.21
4	8.541	873695	14.39

benzyl 3-((2-fluorophenyl)(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3q)



Colorless oil, 22.1 mg, 46% yield, 86% ee, 83:17 dr, $[\alpha]_D^{20}$ = -42.4 (*c* = 0.29, CH_2Cl_2); **SFC** Chiralcel OX-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 220 nm, t_1 = 5.81 min, t_2 = 7.10 min, t_3 = 9.08 min, t_4 = 11.21 min;

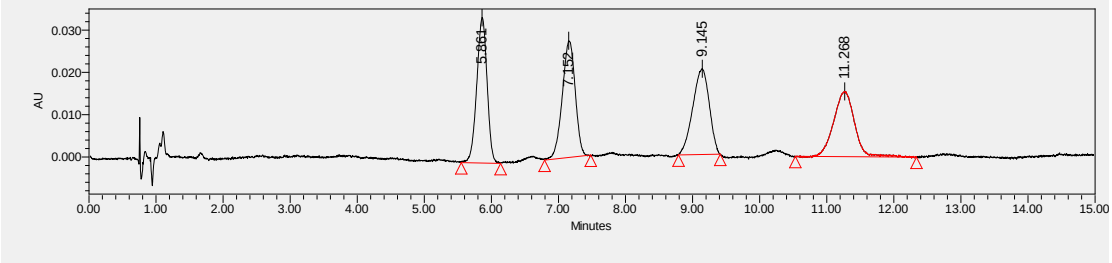
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.60 – 7.55 (m, 1H), 7.52 (t, J = 8.0 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.33 – 7.30 (m, 3H), 7.14 – 7.08 (m, 1H), 6.86 – 6.82 (m, 1H), 6.77 – 6.72 (m, 1H), 5.85 (s, 1H), 5.23 (dd, J_1 = 12.0, J_2 = 20.0 Hz, 2H), 3.89 (s, 1H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 171.1, 139.7 (d, *J* = 7.4 Hz), 135.3 (d, *J* = 191.2 Hz), 133.8, 133.1, 130.1, 129.0, 128.8, 128.7, 125.9, 121.1, 112.9 (d, *J* = 20.6 Hz), 72.0, 69.7, 44.3, -1.1.

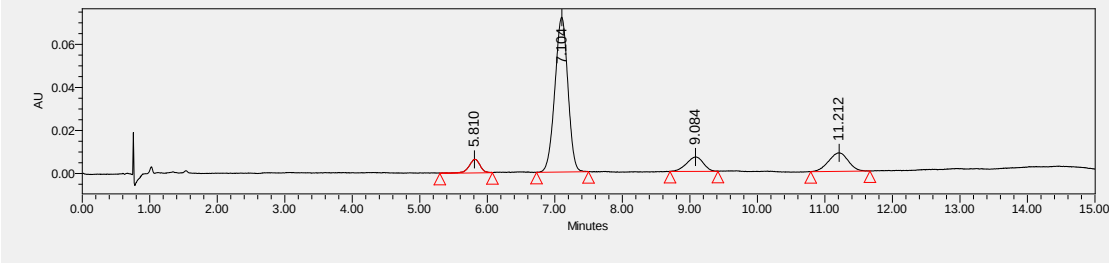
^{19}F NMR (377 MHz, $CDCl_3$) *δ* -117.3. (s, 1F)

IR (film, cm^{-1}) :3281, 2958, 1736, 1308, 1262, 1222, 1166, 844, 734, 700;

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}FNNaO_4SSi^+$ ($[M]+Na^+$) = 506.1229, found 506.1229.

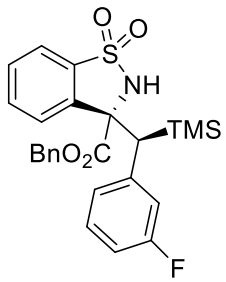


	Retention Time	Area	% Area
1	5.861	369595	26.03
2	7.152	369302	26.01
3	9.145	346008	24.37
4	11.268	334968	23.59



	Retention Time	Area	% Area
1	5.810	73028	5.51
2	7.104	963238	72.63
3	9.084	115520	8.71
4	11.212	174458	13.15

benzyl 3-((3-fluorophenyl)(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3r)



Colorless oil, 33.1 mg, 68% yield, 89% ee, 82:18 dr, $[\alpha]_D^{20}$ = -23.4 (*c* = 0.53, CH_2Cl_2); **SFC** Chiralcel AD-3, CO_2/MeOH = 92/8, 1.5 mL/min, λ = 220 nm, t_1 = 3.50 min, t_2 = 4.12 min, t_3 = 4.87 min, t_4 = 6.85 min;

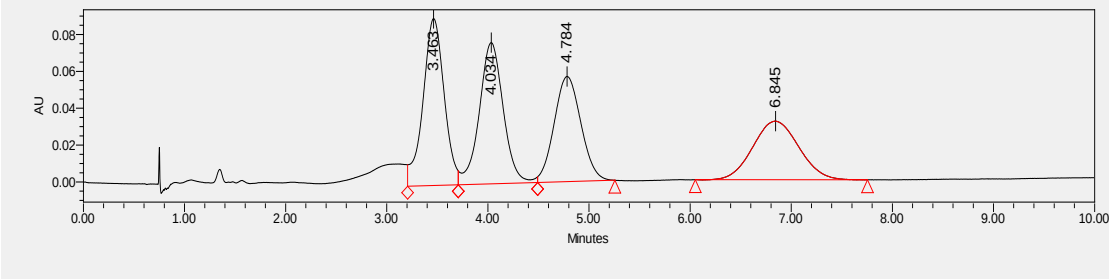
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 1H), 7.43-7.38 (m, 2H), 7.37 – 7.35 (m, 3H), 7.33 – 7.31 (m, 3H), 7.11 – 7.09 (m, 1H), 6.99 – 6.86 (m, 2H), 6.64 – 6.60 (m, 1H), 5.83 (s, 1H), 5.21 (dd, J_1 = 12.0, J_2 = 24.0 Hz, 2H), 3.29 (s, 1H), 0.00 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 137.9 (d, J = 336.8 Hz), 133.8, 133.1, 130.1, 129.1, 128.8, 128.7, 125.9, 121.2, 72.0, 69.7, 44.3, -1.10;

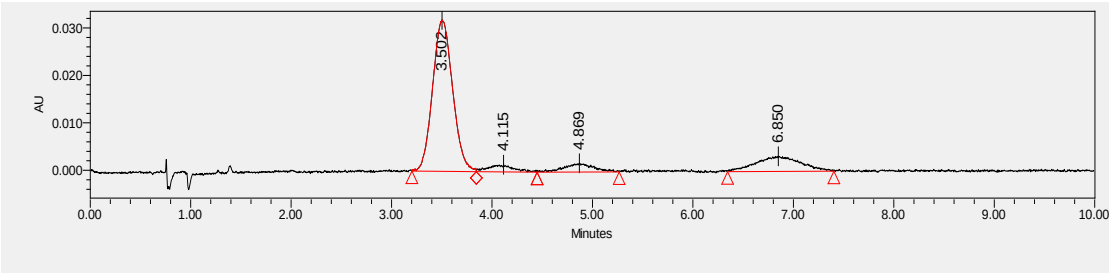
^{19}F NMR (565 MHz, $CDCl_3$) δ -112.2. (s, 1F)

IR (film, cm^{-1}) :3278, 2957, 1735, 1308, 1250, 1220, 1170, 823, 755, 701;

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}FNNaO_4SSi^+$ ([M]+Na^+) = 506.1229, found 506.1229.

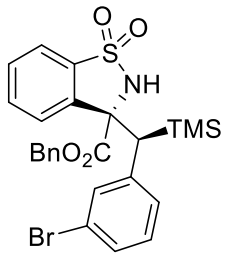


	Retention Time	Area	% Area
1	3.463	1311938	28.33
2	4.034	1267104	27.36
3	4.784	1047830	22.63
4	6.845	1004107	21.68



	Retention Time	Area	% Area
1	3.502	441524	73.31
2	4.115	25736	4.27
3	4.869	37461	6.22
4	6.850	97511	16.19

benzyl 3-((3-bromophenyl)(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3s)



Colorless oil, 27.1 mg, 50% yield, 83% ee/32%, 78:22 dr, $[\alpha]_D^{20}$ = -35.9 (*c* = 0.42, CH_2Cl_2); **HPLC** Daicel chiralcel IF, *n*-hexane/*i*-PrOH 93/7, 1.0 mL/min, λ = 220 nm, t_1 = 30.79 min, t_2 = 35.09 min, t_3 = 37.15 min, t_4 = 43.12 min;

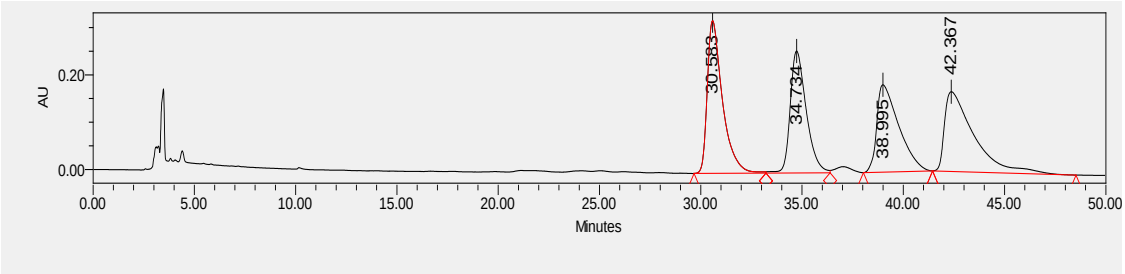
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.41 (m, 2H), 7.38 – 7.34 (m, 5H), 7.32 – 7.29 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.88 (t, *J* = 8.0 Hz, 1H), 5.83 (s, 1H), 5.21 (dd, J_1 = 12.0, J_2 = 24.0 Hz, 2H), 3.24 (s, 1H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 139.6, 136.2, 133.8, 133.1, 130.1, 129.1, 128.8, 128.7, 125.9, 121.2, 72.0, 69.7, 44.3, -1.1.

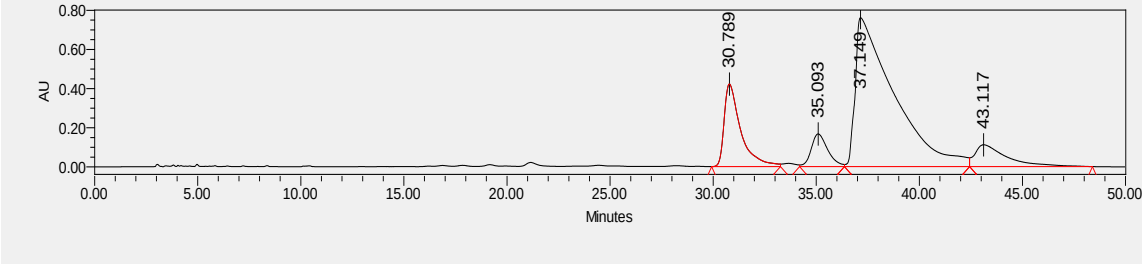
IR (film, cm^{-1}) :3276, 2956, 1735, 1308, 1251, 1221, 1169, 845, 755, 696;

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}{}^{79}BrNNaO_4SSi^+$ ([M]+Na^+) = 566.0428, found 566.0428.

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}{}^{81}BrNNaO_4SSi^+$ ([M]+Na^+) = 568.0407, found 568.0399.

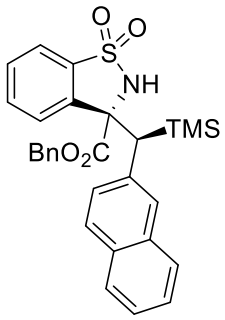


	Retention Time	Area	% Area
1	30.583	16802551	27.13
2	34.734	14199210	22.93
3	38.995	13954848	22.53
4	42.367	16975034	27.41



	Retention Time	Area	% Area
1	30.789	23631657	16.37
2	35.093	9315881	6.45
3	37.149	99340194	68.80
4	43.117	12093581	8.38

benzyl 3-(naphthalen-2-yl(trimethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3t)



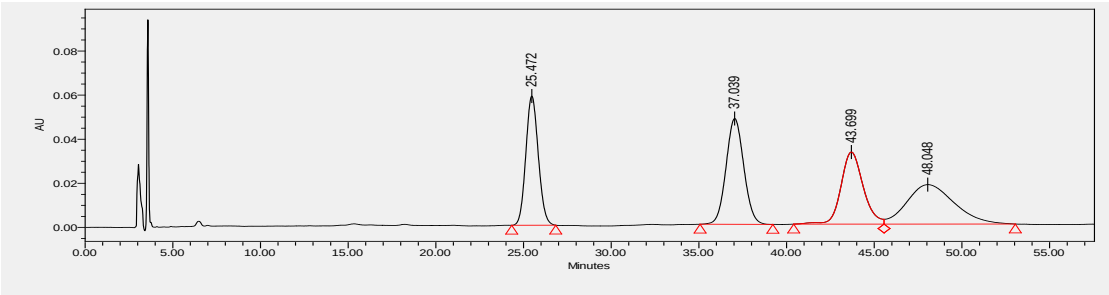
White amorphous solid, 26.3mg, 51% yield, 94% ee, 83:17 dr, m.p. 76–78 °C. $[\alpha]_D^{20}$ = -44.6 (*c* = 0.66, CH_2Cl_2); **HPLC** Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 220 nm, t_1 = 25.49 min, t_2 = 37.13 min, t_3 = 43.81 min, t_4 = 48.08 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 2H), 7.58 (d, J = 6.0 Hz, 1H), 7.48 – 7.44 (m, 4H), 7.37 – 7.36 (m, 3H), 7.33 – 7.31 (m, 2H), 7.30 – 7.25 (m, 3H), 7.20 – 7.17 (m, 1H), 5.88 (s, 1H), 5.22 (dd, J_1 = 8.0, J_2 = 16.0 Hz, 2H), 3.48 (s, 1H), 0.00 (s, 9H).

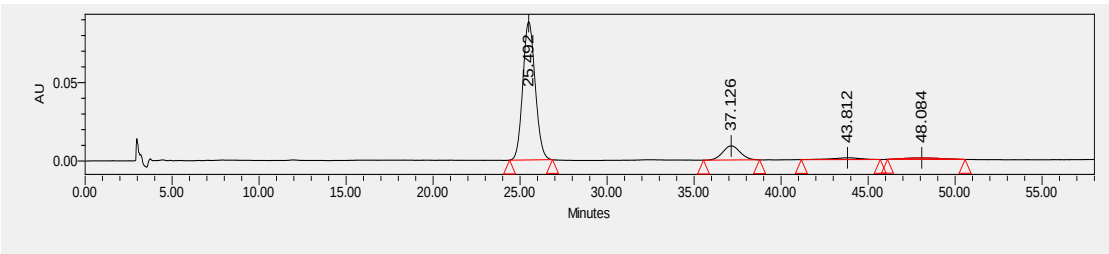
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 136.6, 134.9, 134.4, 134.0, 132.9, 131.7, 129.9, 129.0, 128.8, 128.6, 125.6, 125.1, 121.0, 72.4, 69.6, 44.4, -1.0.

IR (film, cm^{-1}) :3279, 2956, 1735, 1308, 1250, 1221, 1169, 843, 752, 698;

HRMS (ESI^+) m/z calcd for $C_{29}H_{29}NNaO_4SSi^+$ ([M]+Na^+) = 538.1479, found 538.1479.

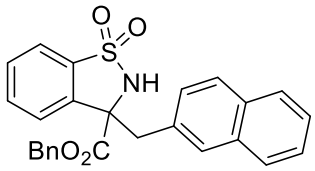


	Retention Time	Area	% Area
1	25.472	2893704	23.16
2	37.039	3369963	26.97
3	43.699	2870355	22.98
4	48.048	3358901	26.89



	Retention Time	Area	% Area
1	25.492	4361901	82.95
2	37.126	627637	11.94
3	43.812	125832	2.39
4	48.084	142976	2.72

benzyl 3-(naphthalen-2-ylmethyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide(3t′)



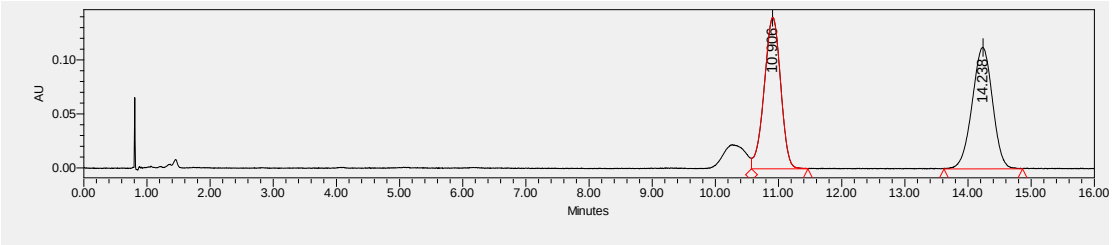
Colorless oil, 18.3 mg, 41% yield, 47% ee, $[\alpha]_D^{20}$ = -9.2 (*c* = 0.34, CH_2Cl_2); **SFC** Chiralcel IB-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 220 nm, t_1 = 10.85 min, t_2 = 14.19 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 6.0Hz, 1H), 7.81 (d, *J* = 12.0 Hz, 2H), 7.77 – 7.68 (m, 4H), 7.64 – 7.61 (m, 1H), 7.49 – 7.46 (m, 2H), 7.39 – 7.36 (m, 2H), 7.32 (t, *J* = 6.0 Hz, 2H), 7.23 (d, *J* = 6.0 Hz, 2H), 5.62 (s, 1H), 5.15 (q, *J* = 12.0 Hz, 2H), 3.72 (d, *J* = 12.0 Hz, 1H), 3.34 (d, *J* = 12.0 Hz, 1H).

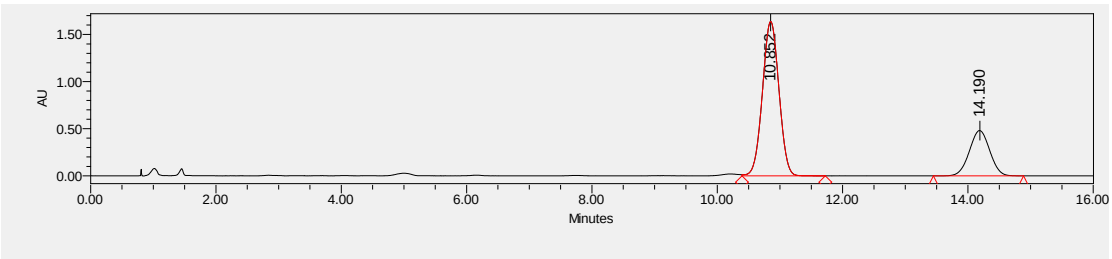
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 138.0, 135.5, 133.9, 133.5, 133.2, 132.7, 131.8, 130.7, 129.4, 129.0, 128.8, 128.8, 128.28, 128.0, 127.8, 127.6, 126.1, 126.0, 125.1, 121.6, 69.8, 69.2, 46.3.

IR (film, cm^{-1}) : 3288, 2928, 1738, 1304, 1168, 1222, 1186, 898, 754, 698;

HRMS (ESI^+) m/z calcd for $C_{26}H_{21}NNaO_4S^+$ ([M]+Na^+) = 466.1084, found 466.1077.

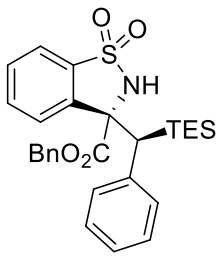


	Retention Time	Area	% Area
1	10.906	2534158	50.04
2	14.238	2530219	49.96



	Retention Time	Area	% Area
1	10.852	29962516	73.37
2	14.190	10873810	26.63

benzyl 3-(phenyl(triethylsilyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3u)



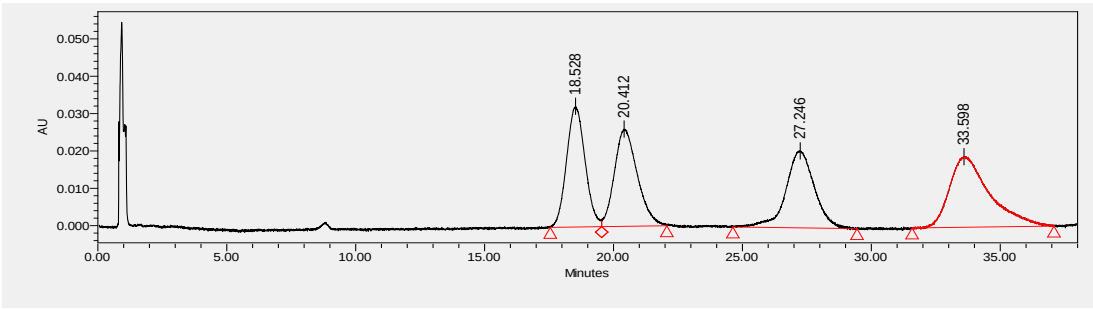
Colorless oil, 29.5 mg, 58% yield, 94% ee, 92:8 dr, $[\alpha]_D^{20}$ = -31.5 (*c* = 0.47, CH_2Cl_2); **SFC** Chiralcel ID-3, CO_2/MeOH = 95/5, 1.5 mL/min, λ = 211 nm, t_1 = 17.78 min, t_2 = 18.87 min, t_3 = 26.33 min, t_4 = 32.58 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 6.0 Hz, 1H), 7.42 (d, *J* = 12.0 Hz, 1H), 7.39 – 7.36 (m, 4H), 7.35 – 7.29 (m, 4H), 7.23 – 7.19 (m, 1H), 7.00 (s, 2H), 6.93 – 6.90 (m, 1H), 5.79 (s, 1H), 5.23 (dd, J_1 = 12.0, J_2 = 42.0 Hz, 2H), 3.45 (s, 1H), 0.86 (t, J = 12.0 Hz, 9H), 0.56 – 0.49 (m, 6H).

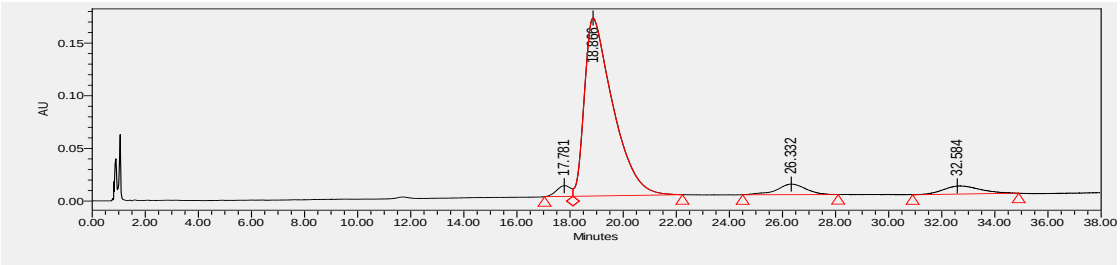
^{13}C NMR (150 MHz, $CDCl_3$) δ 171.4, 137.2, 136.7, 134.4, 133.9, 132.8, 129.8, 129.0, 128.8, 128.7, 126.3, 125.8, 120.9, 72.3, 69.6, 41.6, 7.5, 3.3.

IR (film, cm^{-1}) :3283, 3030, 2954, 2877, 1735, 1309, 1219, 1170, 809, 754, 705;

HRMS (ESI^+) m/z calcd for $C_{28}H_{33}NNaO_4SSi^+$ ([M]+Na^+) = 530.1792, found 530.1792.

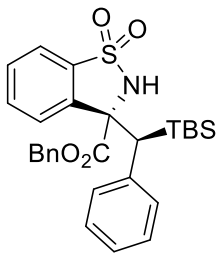


	Retention Time	Area	% Area
1	18.528	1567248	27.11
2	20.412	1561962	27.02
3	27.246	1321966	22.87
4	33.598	1328918	22.99



	Retention Time	Area	% Area
1	17.781	377085	2.62
2	18.866	12517996	86.81
3	26.332	771702	5.35
4	32.584	752424	5.22

benzyl 3-((tert-butyldimethylsilyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide(3v)



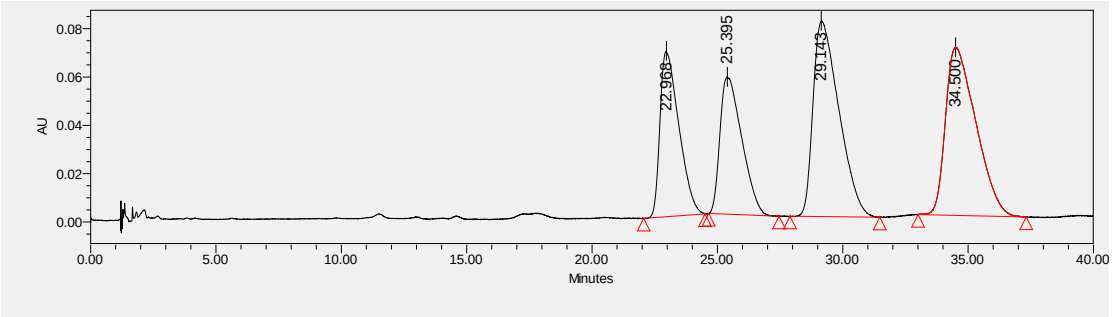
Colorless oil, 34.5 mg, 68% yield, 96% ee, 92:8 dr, $[\alpha]_D^{20}$ = -73.5 (*c* = 0.59, CH_2Cl_2); **SFC** Chiralcel OZ-3, CO_2/MeOH = 95/5, 1.0 mL/min, λ = 220 nm, t_1 = 23.69 min, t_2 = 26.00 min, t_3 = 30.04 min, t_4 = 35.47 min;

^{1}H NMR (400 MHz, CDCl3) *δ* 7.47 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.32 (m, 6H), 7.27 – 7.24 (m, 2H), 6.98 (s, 2H), 6.90 – 6.86 (m, 2H), 5.80 (s, 1H), 5.21 (s, 2H), 3.59 (s, 1H), 0.63 (s, 9H), 0.22 (s, 3H), 0.00 (s, 3H).

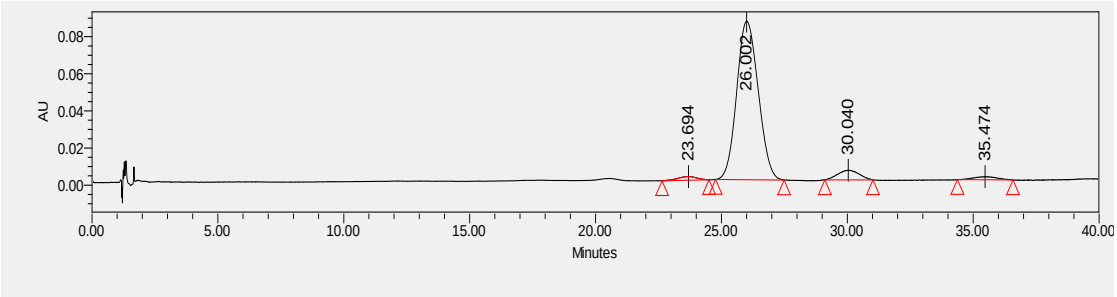
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 171.5, 137.4, 136.5, 134.4, 133.9, 132.7, 129.8, 129.0, 128.8, 128.7, 126.2, 126.1, 121.0, 73.3, 69.6, 40.4, 26.7, 17.7, -4.6, -4.8.

IR (film, cm^{-1}) :3279, 3030, 2957, 2931, 2857, 1736, 1309, 1255, 1220, 1169, 828, 756, 705;

HRMS (ESI^+) m/z calcd for $C_{28}H_{33}NNaO_4SSi^+$ ([M]+Na^+) = 530.1792, found 530.1792.

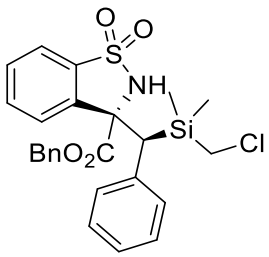


	Retention Time	Area	% Area
1	22.968	3579551	19.16
2	25.395	3438259	18.40
3	29.143	5794111	31.01
4	34.500	5874028	31.44



	Retention Time	Area	% Area
1	23.694	100544	1.77
2	26.002	5100039	89.99
3	30.040	348371	6.15
4	35.474	118129	2.08

benzyl (S)-3-((S)-((chloromethyl)dimethylsilyl)(phenyl)methyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide(3w)



Colorless oil, 33.6 mg, 67% yield, 88% ee, 81:19 dr, $[\alpha]_D^{20}$ = -36.2 (*c* = 0.39, CH_2Cl_2); **SFC** Chiralcel IG-3, CO_2/MeOH = 93/7, 1.5 mL/min, λ = 220 nm, t_1 = 14.74 min, t_2 = 17.19 min, t_3 = 18.85 min, t_4 = 21.60 min;

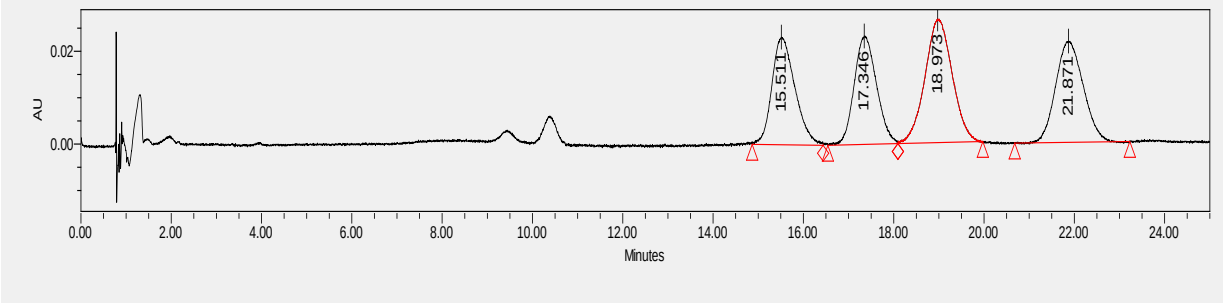
^{1}H NMR (400 MHz, CDCl3) δ 7.41 (dd, J_1 = 4.0, J_2 = 8.0 Hz, 1H), 7.27 – 7.17 (m, 9H), 7.11 – 7.08 (m, 1H), 6.90 – 6.87 (m, 2H), 6.81 (t, *J* = 4.0 Hz, 1H), 5.83 (s, 1H), 5.11 (s, 2H), 3.46 (s, 1H), 2.47 (dd, J_1 = 12.0, J_2 = 36.0 Hz, 2H), 0.01 (d, *J* = 12.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 136.2, 136.0, 134.5, 133.8, 133.0, 130.0, 129.0, 128.8, 128.7, 128.2, 126.4, 126.2, 121.0, 72.0, 69.8, 42.0, 29.6, -4.1.

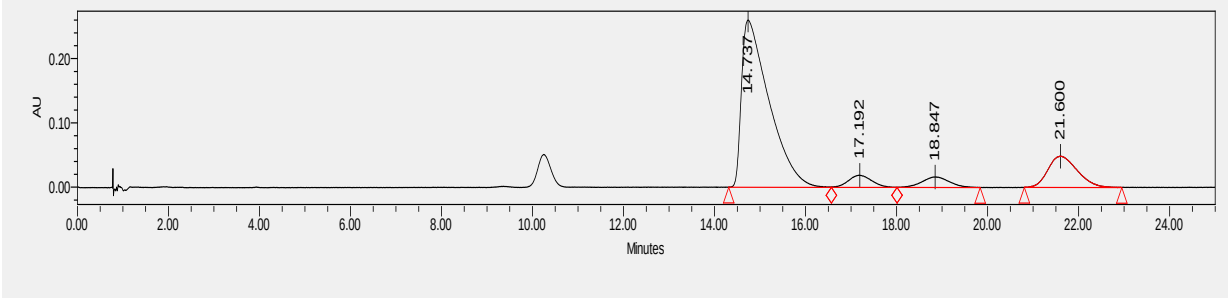
IR (film, cm^{-1}) :3276, 3032, 2956, 2932, 2854, 1735, 1311, 1255, 1222, 1170, 816, 749, 700;

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}{}^{35}ClNNaO_4SSi^+$ ([M]+Na^+) = 522.0933, found 522.0935;

HRMS (ESI^+) m/z calcd for $C_{25}H_{26}{}^{37}ClNNaO_4SSi^+$ ([M]+Na^+) = 524.0904, found 524.0903.

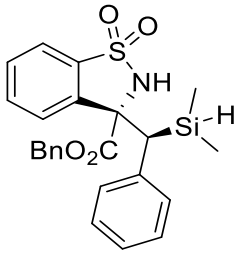


	Retention Time	Area	% Area
1	15.511	748493	22.36
2	17.346	736586	22.00
3	18.973	930335	27.79
4	21.871	932683	27.86



	Retention Time	Area	% Area
1	14.737	10914629	75.48
2	17.192	674325	4.66
3	18.847	693571	4.80
4	21.600	2178479	15.06

benzyl (S)-3-((S)-(dimethylsilyl)(phenyl)methyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide(3x)



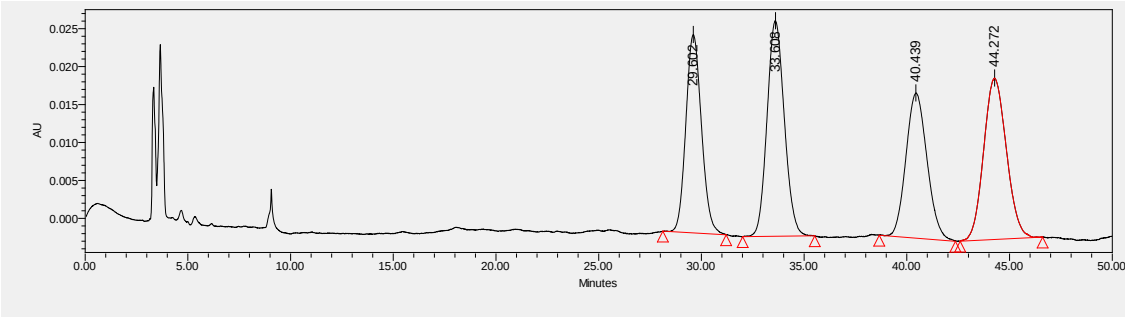
Colorless oil, 25.2 mg, 56% yield, 80%/43% ee, 73:27 dr, $[\alpha]_D^{20}$ = -58.4 (*c* = 0.25, CH_2Cl_2); **HPLC** Daicel chiralcel IC, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 220 nm, t_1 = 29.81 min, t_2 = 33.91 min, t_3 = 40.66 min, t_4 = 44.80 min;

^{1}H NMR (400 MHz, CDCl3) *δ* 7.54 (dd, J_1 = 7.8, J_2 = 8.0 Hz, 2H), 7.45 – 7.33 (m, 8H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 8.0 Hz, 2H), 5.89 (s, 1H), 5.26 (dd, J_1 = 12.0, J_2 = 16.0 Hz,, 2H), 4.06 – 4.02 (m, 1H), 3.30 (d, *J* = 4.0 Hz, 1H), 0.07 (d, *J* = 4.0 Hz, 3H), -0.00 (d, *J* = 4.0 Hz, 3H).

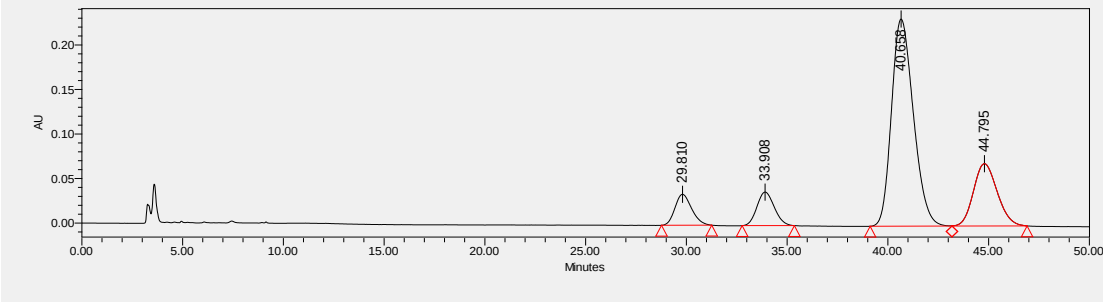
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.8, 137.7, 136.2, 136.0, 134.6, 134.1, 133.6, 133.0, 130.0, 129.0, 129.0, 128.7, 128.1, 126.3, 125.9, 121.1, 72.3, 69.5, 42.8, -4.4, -4.7.

IR (film, cm^{-1}) :3276, 3035, 2955, 2929, 2855, 1733, 1305, 1259, 1222, 1172, 829, 757, 706;

HRMS (ESI^+) m/z calcd for $C_{24}H_{25}NNaO_4SSi^+$ ([M]+Na^+) = 474.1166, found 474.1164.

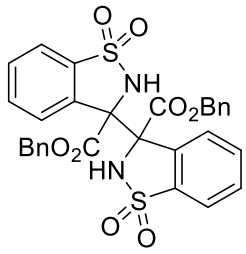


	Retention Time	Area	% Area
1	29.602	1378761	22.83
2	33.608	1659117	27.48
3	40.439	1364798	22.60
4	44.272	1635899	27.09



	Retention Time	Area	% Area
1	29.810	1993913	7.24
2	33.908	2251016	8.18
3	40.658	17555608	63.78
4	44.795	5726485	20.80

dibenzyl [3,3'-bibenzo[d]isothiazole]-3,3'(2H,2'H)-dicarboxylate 1,1,1',1'-tetraoxide (4a)

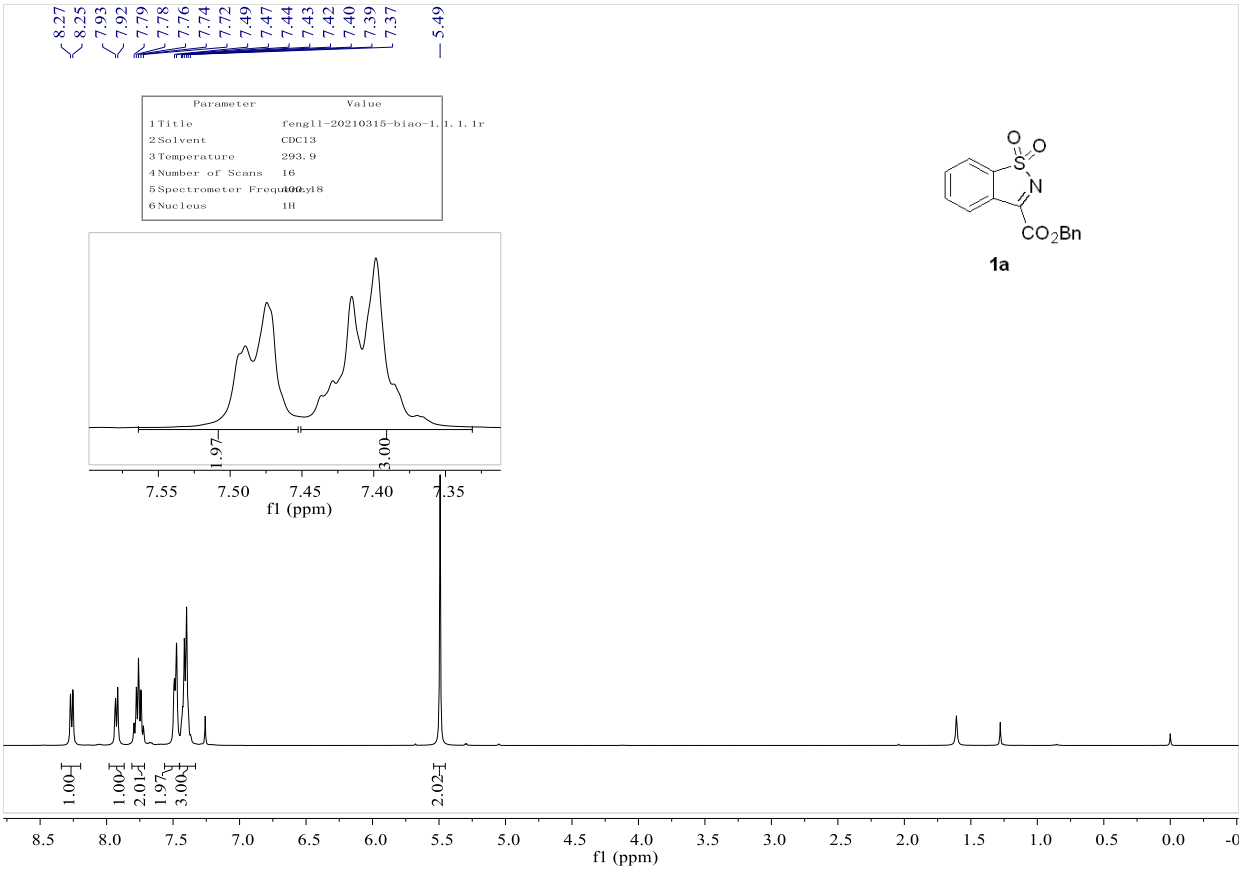


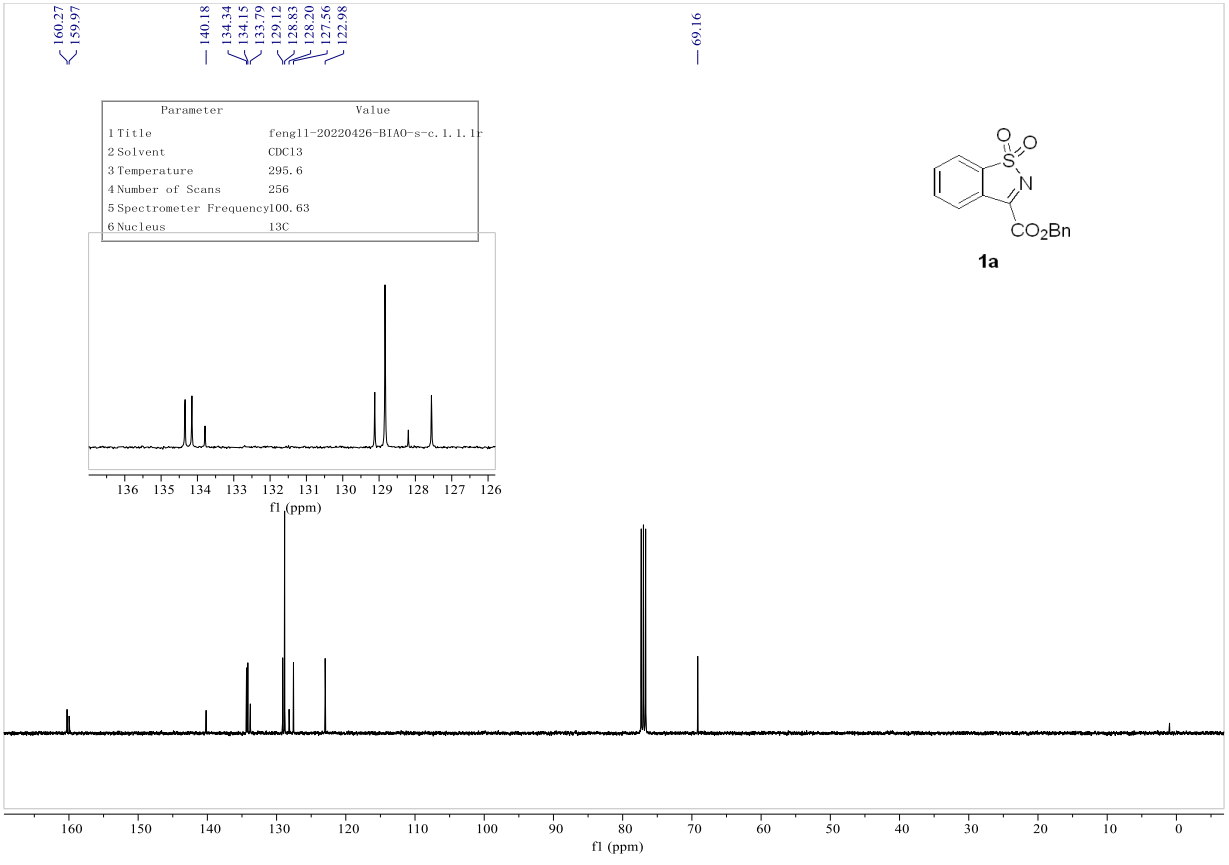
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.24 (s, 2H), 7.89 – 7.87 (m, 2H), 7.68 – 7.66 (m, 2H), 7.54 – 7.51 (m, 4H), 7.29 – 7.27 (m, 6H), 7.20 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 4H), 5.14 – 5.08 (m, 4H).

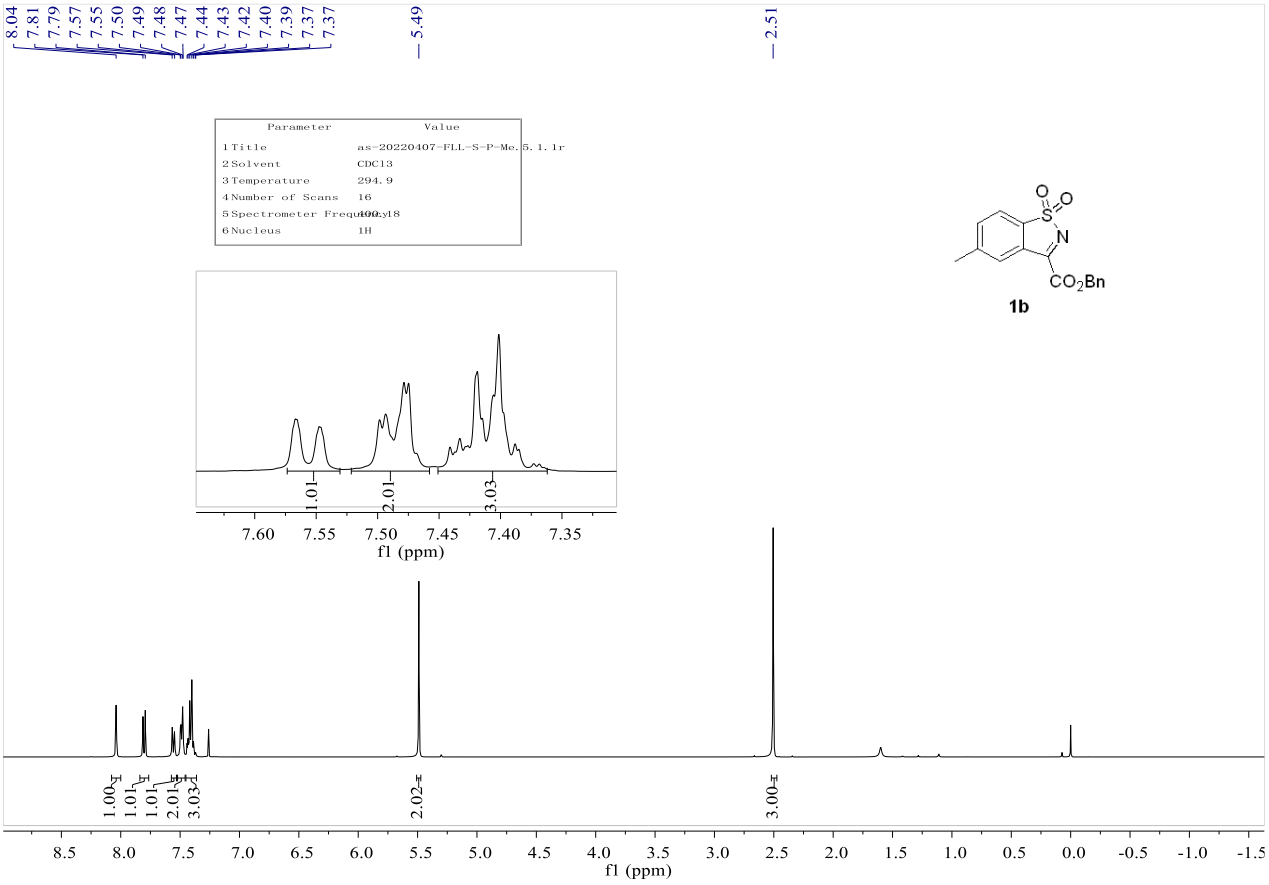
^{13}C NMR (101 MHz, DMSO-d_6) δ 168.1, 135.8, 135.2, 133.0, 131.8, 131.3, 128.8, 128.7, 128.6, 128.4, 128.2, 127.8, 121.2, 71.9, 68.5.

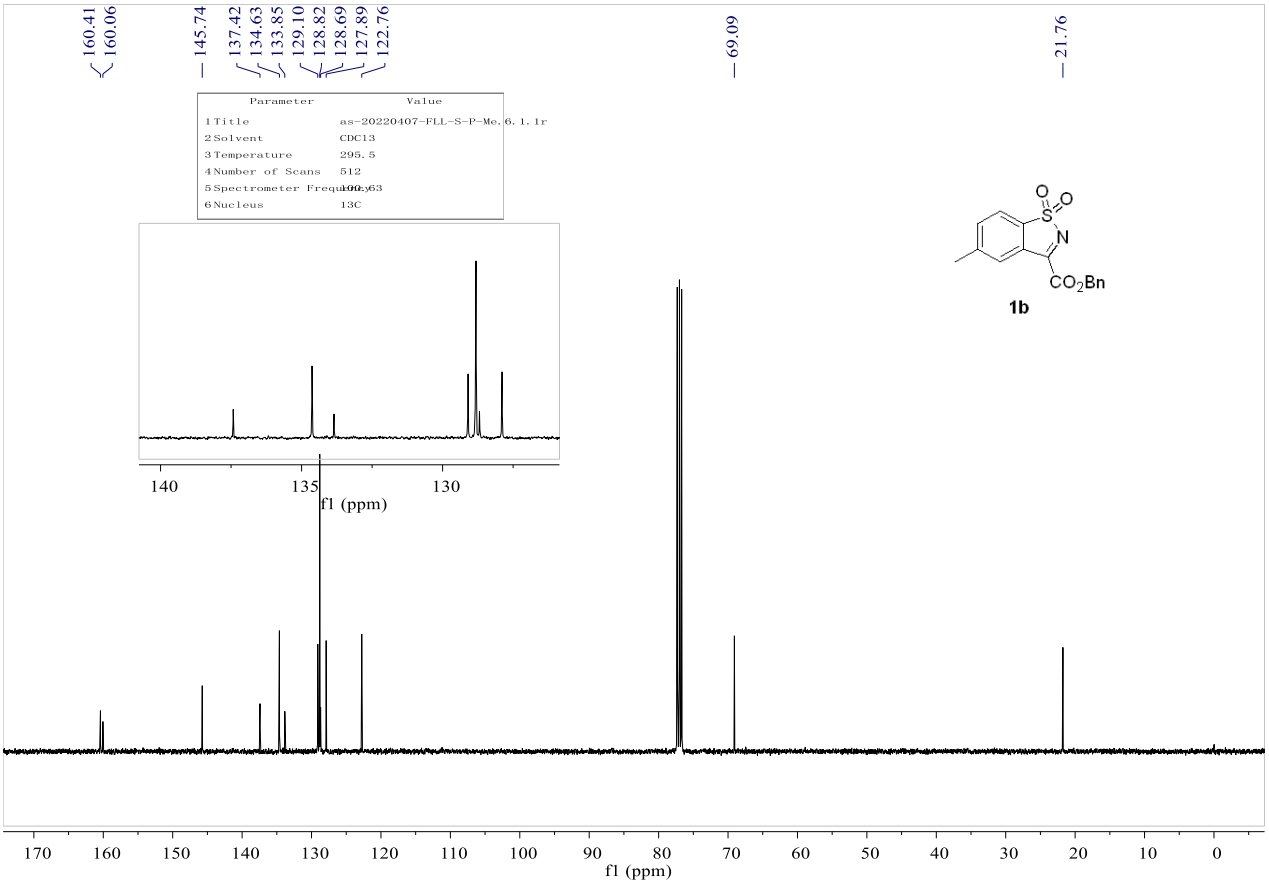
HRMS (ESI$^+$) m/z calcd for $C_{30}H_{24}N_2NaO_8S_2^+$ ([M]+Na$^+$) = 627.0867, found 627.0866.

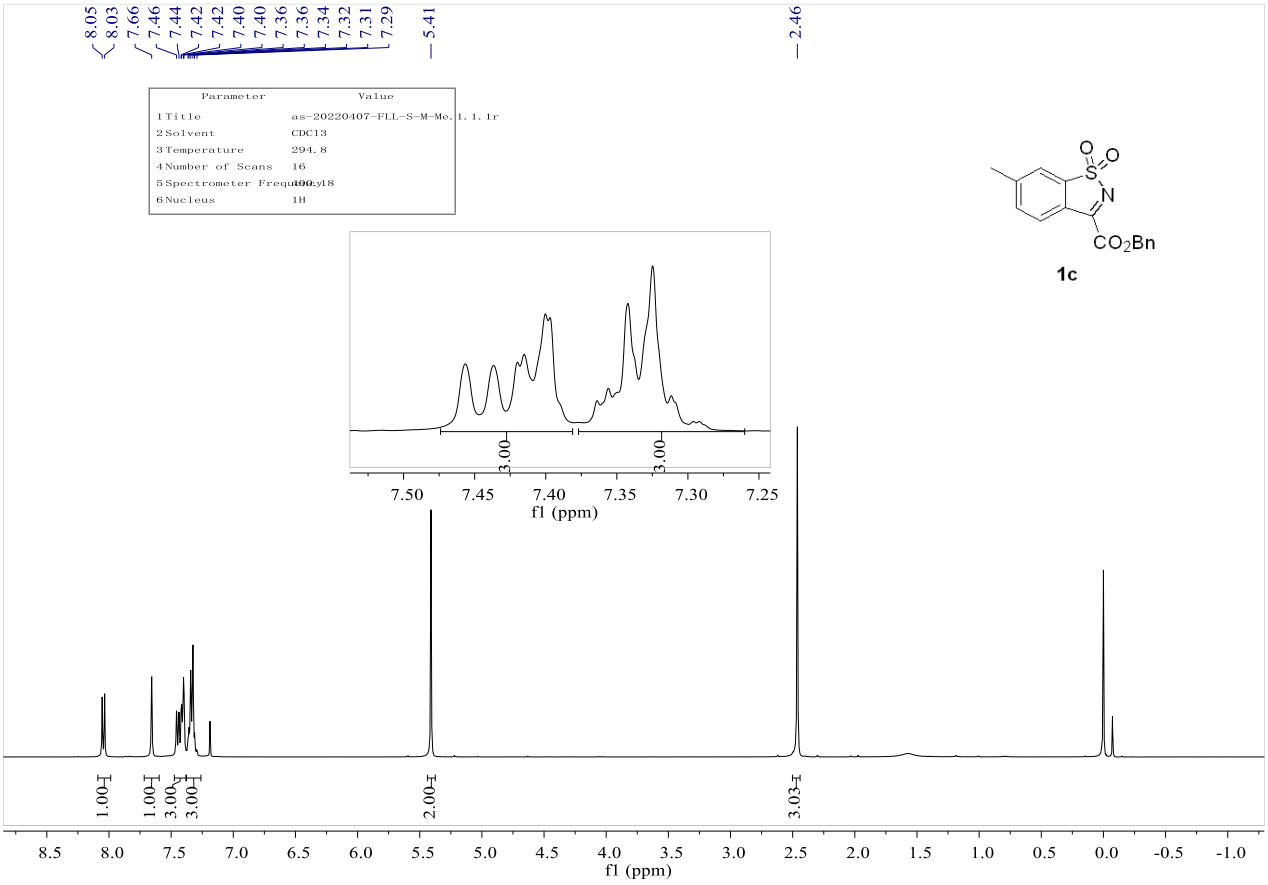
13. Copies of NMR spectra and CD spectra for the reaction substrates and products

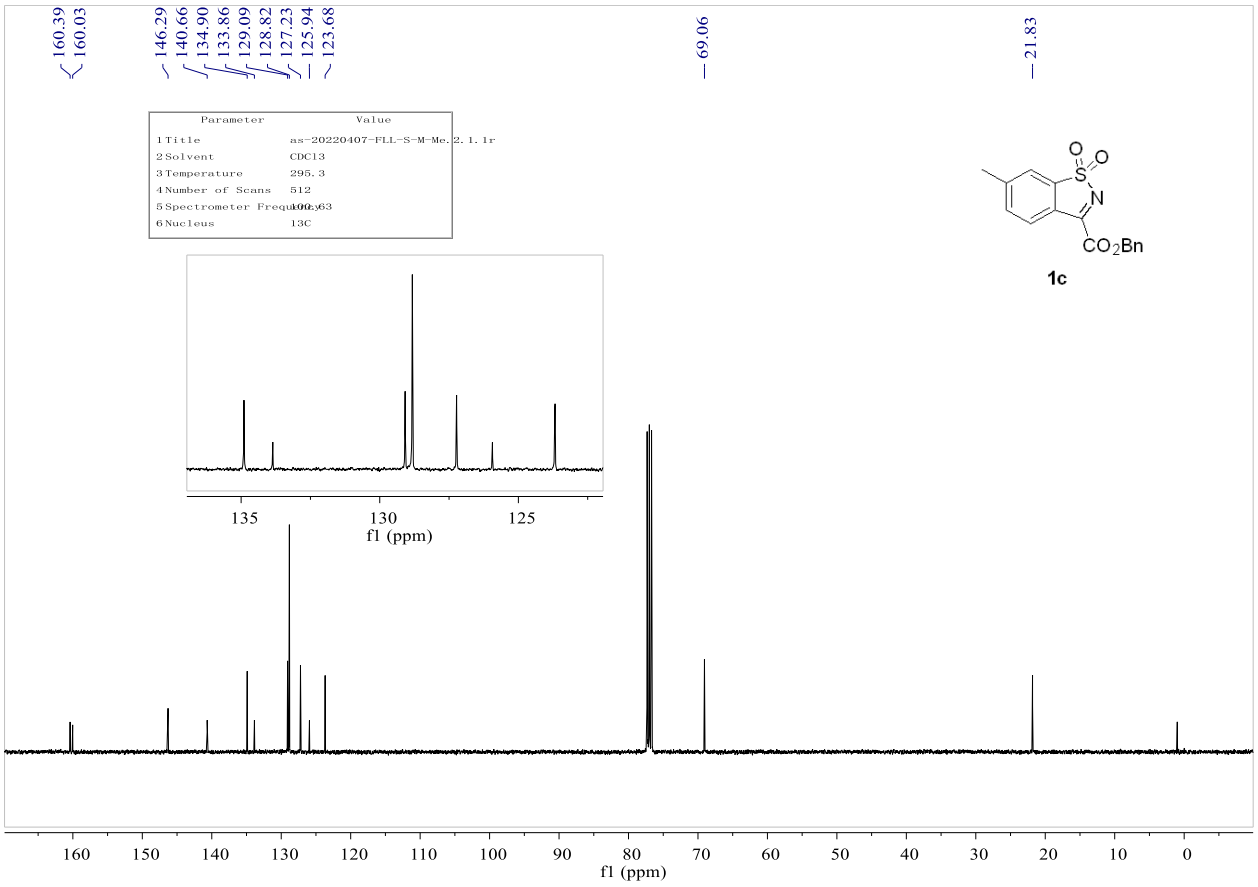


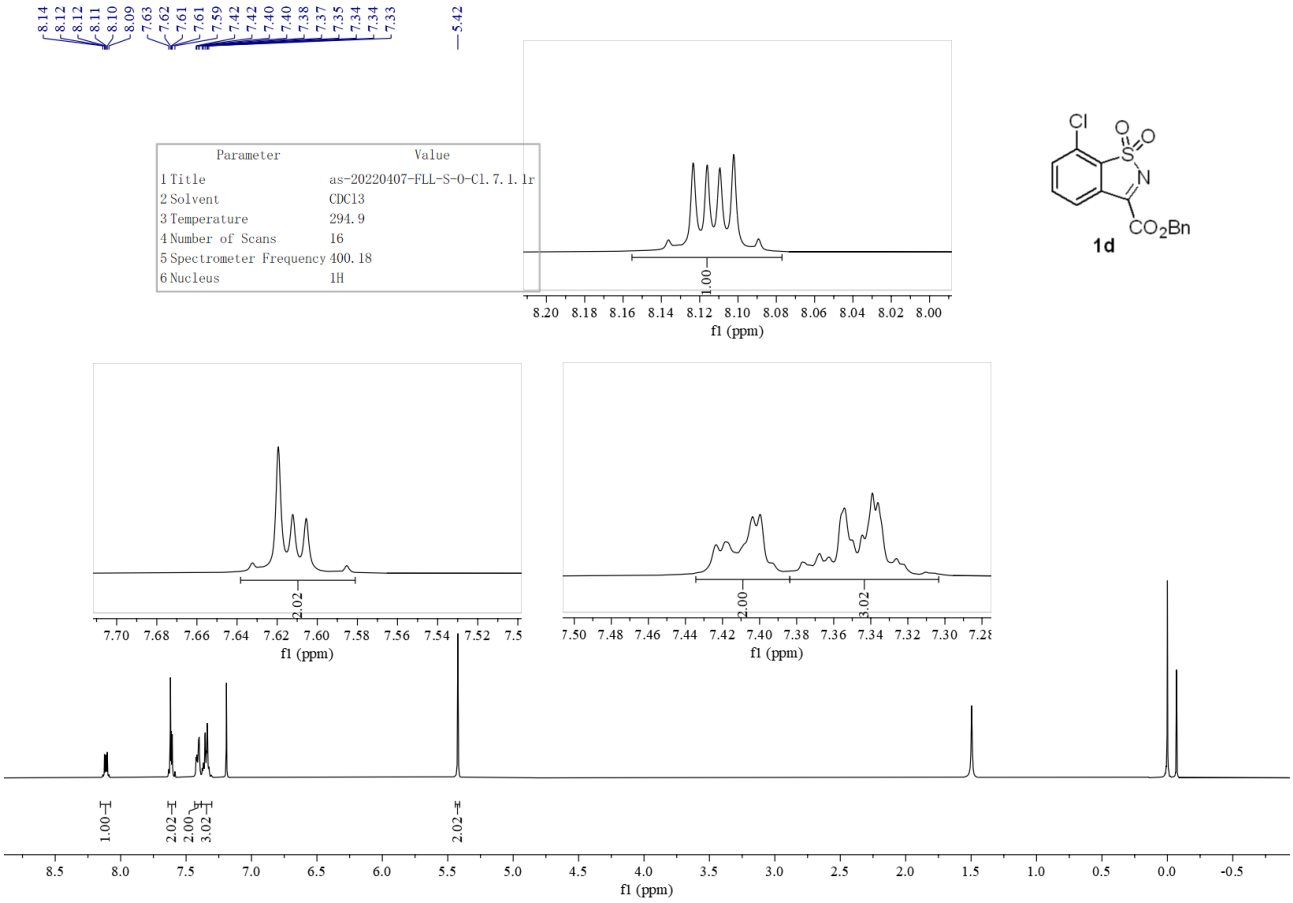


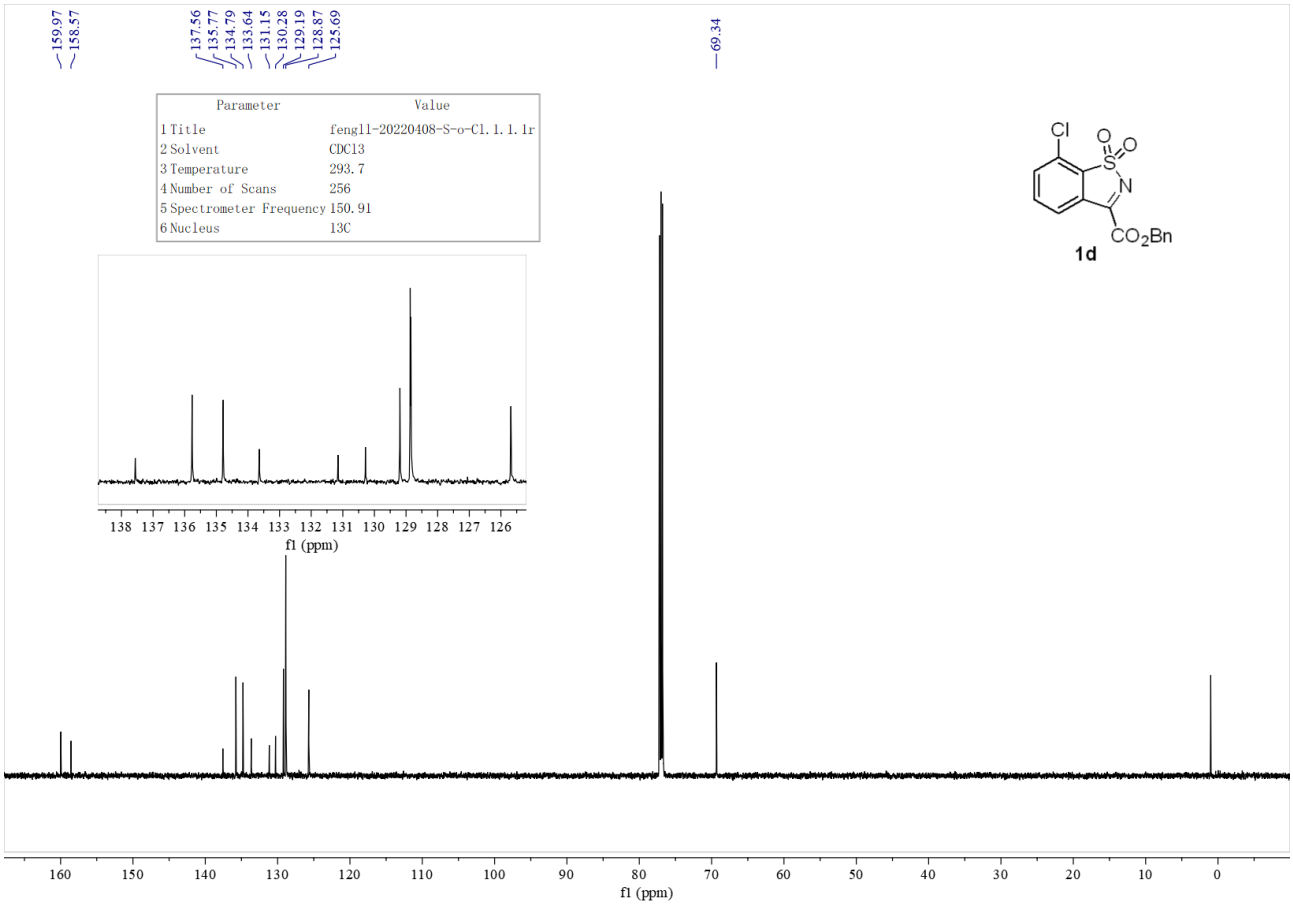

8.04
7.81
7.79
7.57
7.55
7.50
7.49
7.48
7.47
7.44
7.43
7.42
7.40
7.39
7.37
7.37
5.49
2.51
Parameter Value
1 Title as-20220407-FLL-S-P-Me.5.1.1r
2 Solvent CDCl3
3 Temperature 294.9
4 Number of Scans 16
5 Spectrometer Frequency
6 Nucleus 1H
1.01
2.01
3.03
7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
1.00
1.01
1.01
2.01
3.03
2.02
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)
O
S
O
N
CO2Bn
1b

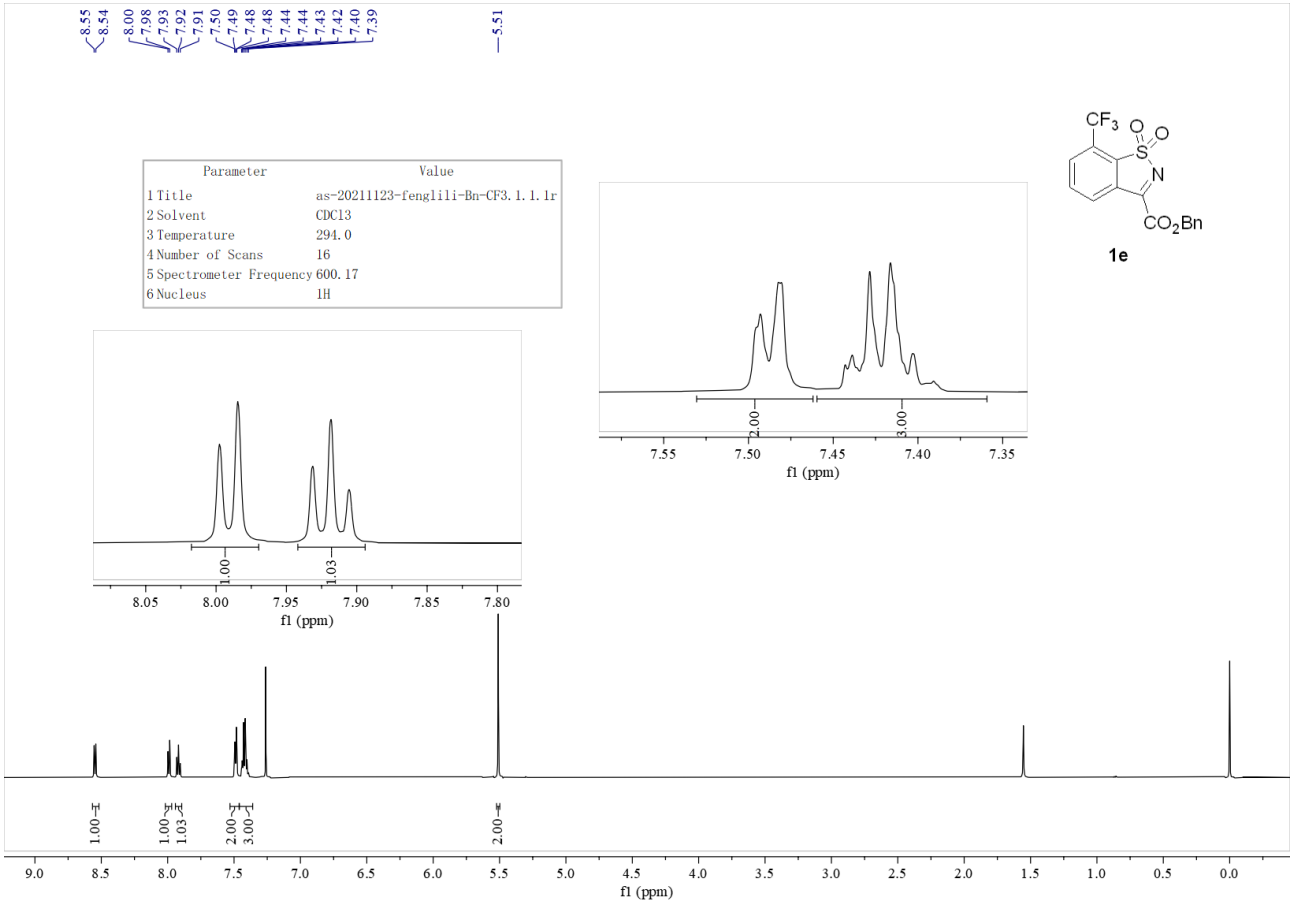

160.41
160.06
145.74
137.42
134.63
133.85
129.10
128.82
128.69
127.89
122.76
69.09
21.76
Parameter Value
1 Title as-20220407-FLL-S-P-Me.6.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 512
5 Spectrometer Frequency
6 Nucleus 13C
140 135 130
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
S
O
N
CO2Bn
1b

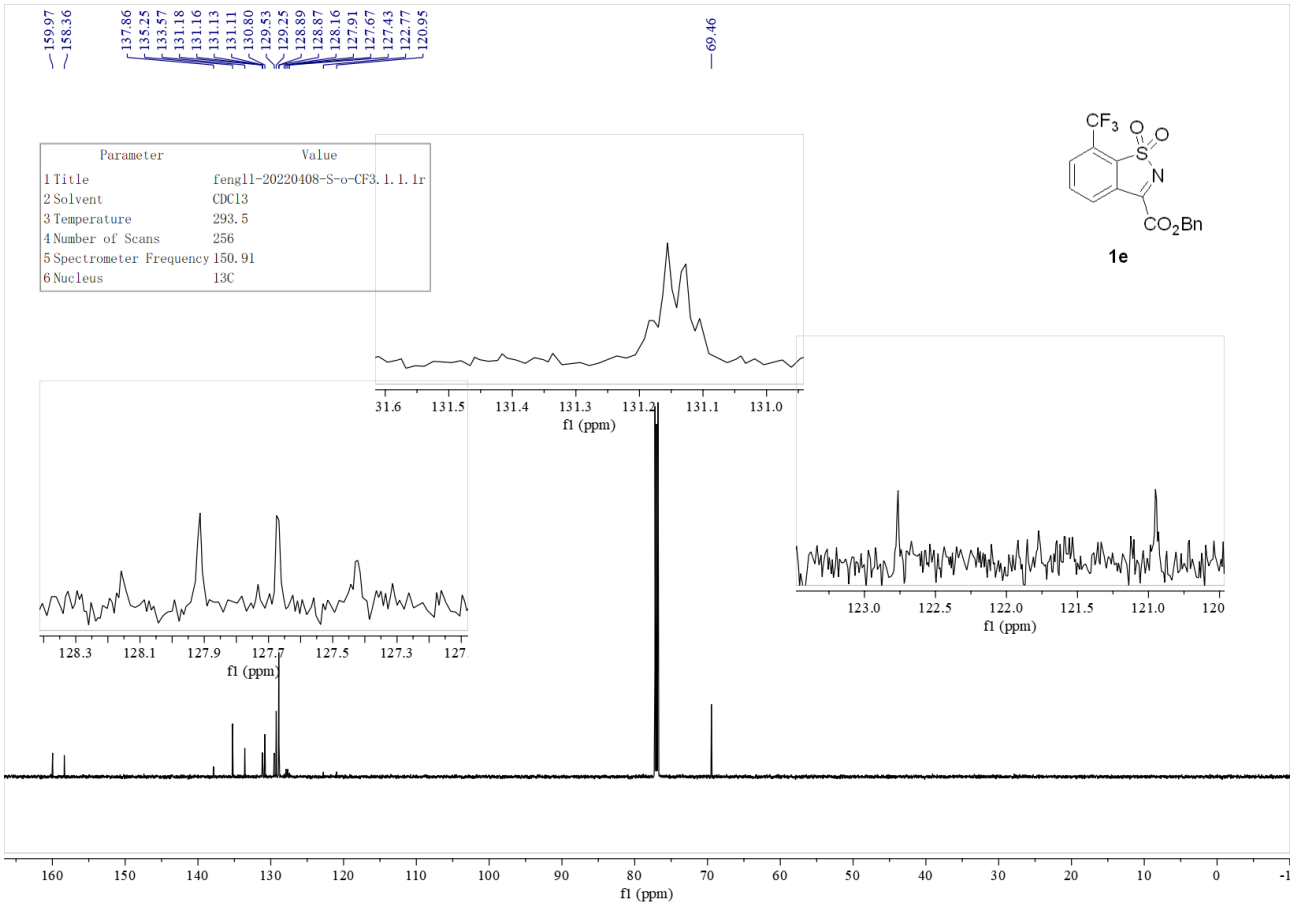

8.05
8.03
7.66
7.46
7.44
7.42
7.42
7.40
7.40
7.36
7.36
7.34
7.32
7.31
7.29
5.41
2.46
Parameter Value
1 Title as-20220407-FLL-S-M-Me.1.1.1r
2 Solvent CDCl3
3 Temperature 294.8
4 Number of Scans 16
5 Spectrometer Frequency
6 Nucleus 1H
CO2Bn
1c
3.00
3.00
7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)
1.00
1.00
3.00
3.00
2.00
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

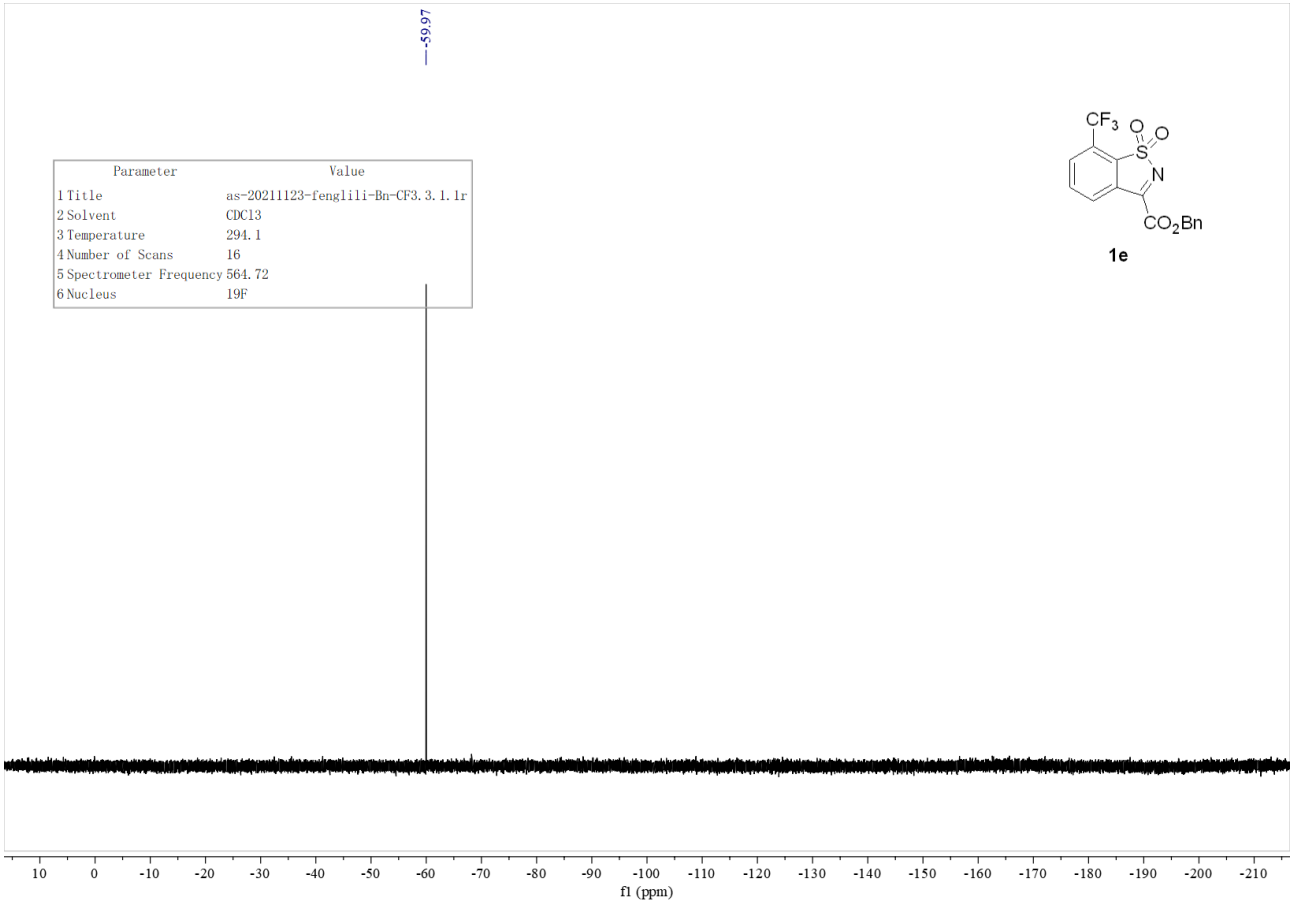

160.39
160.03
146.29
140.66
134.90
133.86
129.09
128.82
127.23
125.94
123.68
69.06
21.83
Parameter Value
1 Title as-20220407-FLL-S-M-Me.2.1.1r
2 Solvent CDCl3
3 Temperature 295.3
4 Number of Scans 512
5 Spectrometer Frequency
6 Nucleus 13C
CO2Bn
1c
135 130 125
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

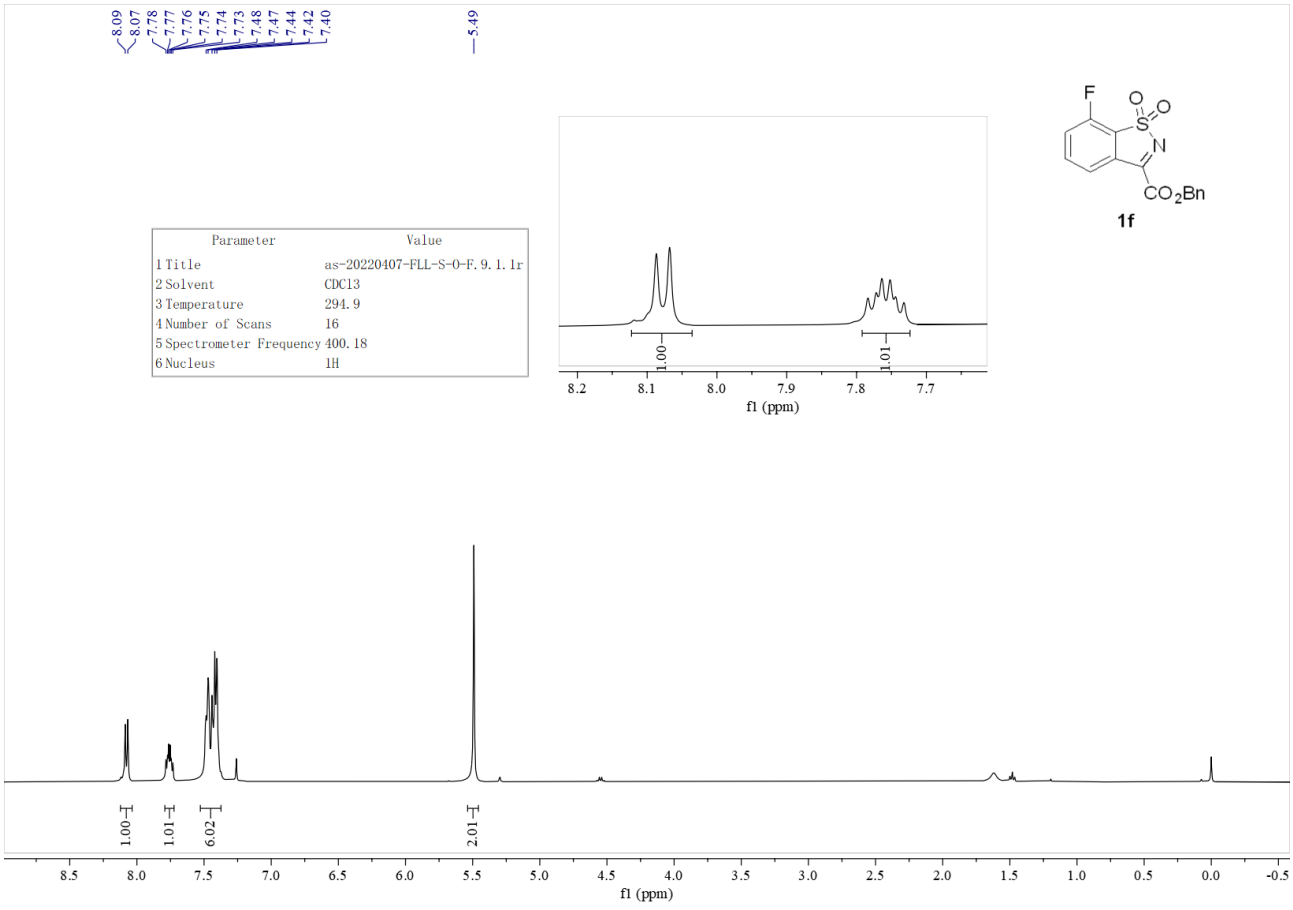

8.14
8.12
8.12
8.11
8.10
8.09
7.63
7.62
7.61
7.61
7.59
7.42
7.42
7.40
7.40
7.38
7.37
7.35
7.34
7.34
7.33
5.42
Parameter Value
1 Title as-20220407-FLL-S-O-Cl.7.1.1r
2 Solvent CDCl3
3 Temperature 294.9
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
1.00
f1 (ppm)
Cl
O
O
S
N
CO2Bn
1d
2.02
2.00
3.02
f1 (ppm)
1.00
2.02
2.00
3.02
2.02
f1 (ppm)

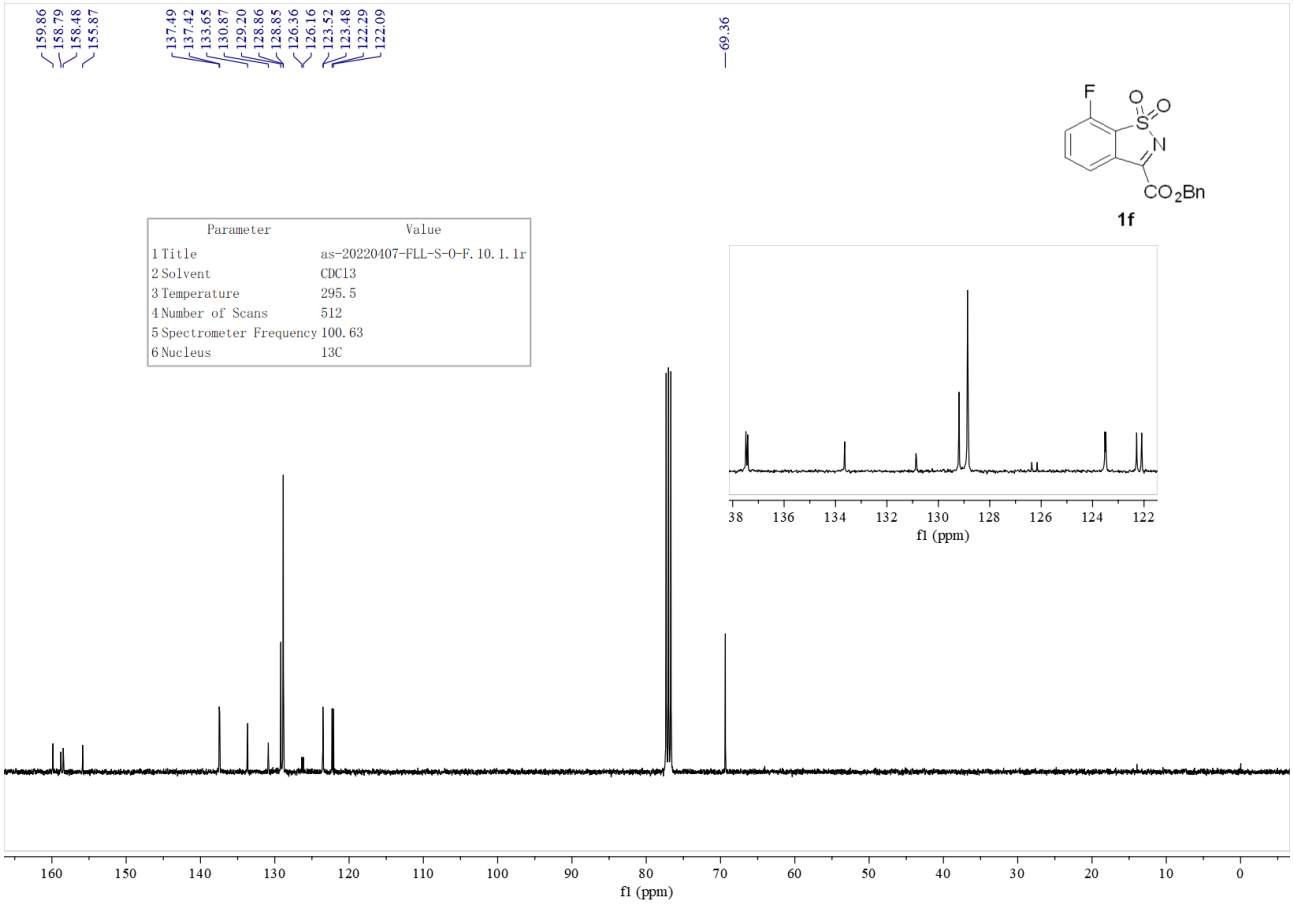

159.97
158.57
137.56
135.77
134.79
133.64
131.15
130.28
129.19
128.87
125.69
69.34
Parameter Value
1 Title fengll-20220408-S-o-Cl.1.1.1r
2 Solvent CDCl3
3 Temperature 293.7
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
f1 (ppm)
Cl
O
O
S
N
CO2Bn
1d
f1 (ppm)

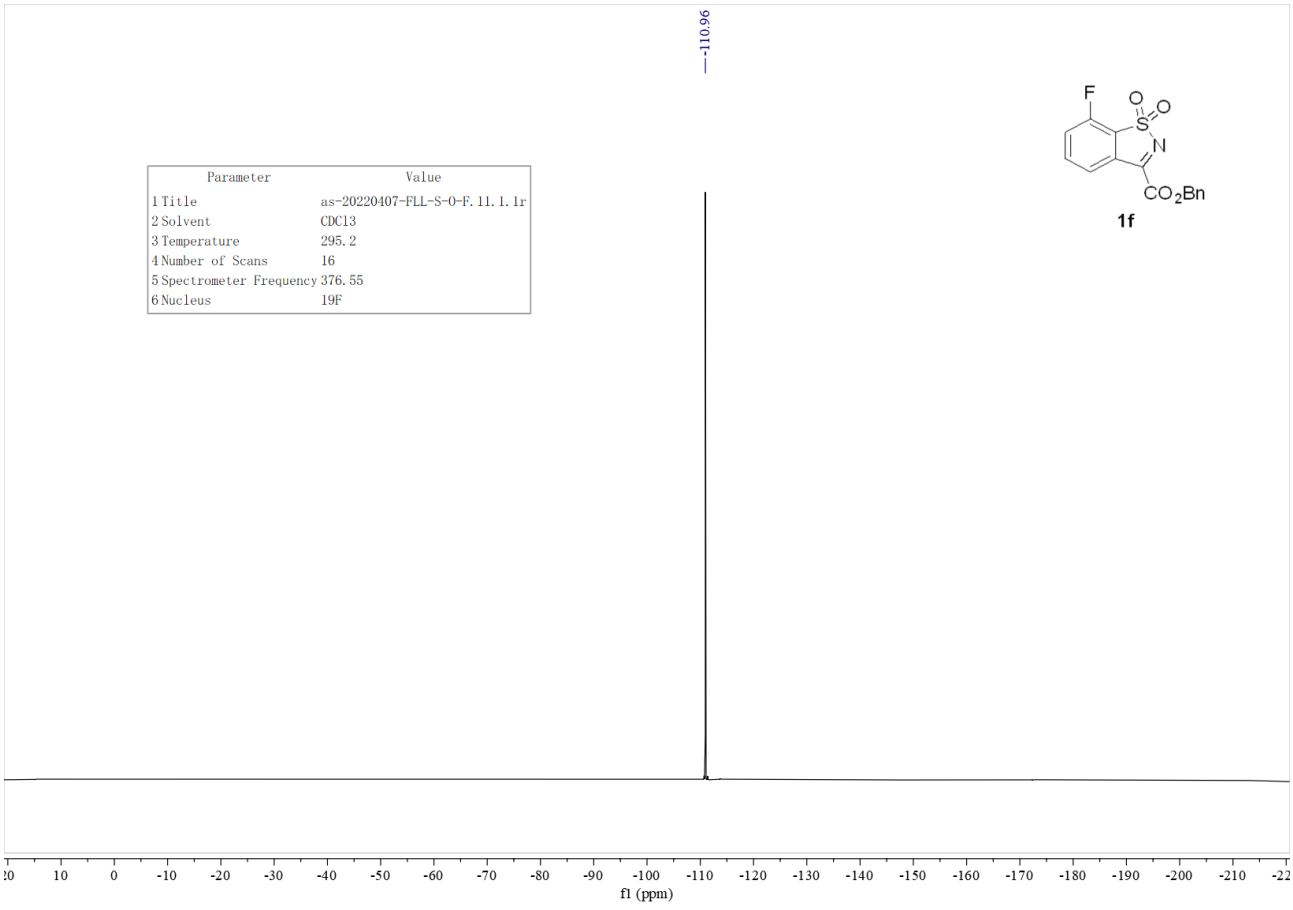

8.55
8.54
8.00
7.98
7.93
7.92
7.91
7.50
7.49
7.48
7.48
7.44
7.44
7.43
7.42
7.40
7.39
5.51
Parameter Value
1 Title as-20211123-fenglili-Bn-CF3.1.1.1r
2 Solvent CDCl3
3 Temperature 294.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
CF3
O
O
S
N
CO2Bn
1e
2.00
3.00
7.55
7.50
7.45
7.40
7.35
f1 (ppm)
1.00
1.03
8.05
8.00
7.95
7.90
7.85
7.80
f1 (ppm)
1.00
1.00
1.03
2.00
3.00
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

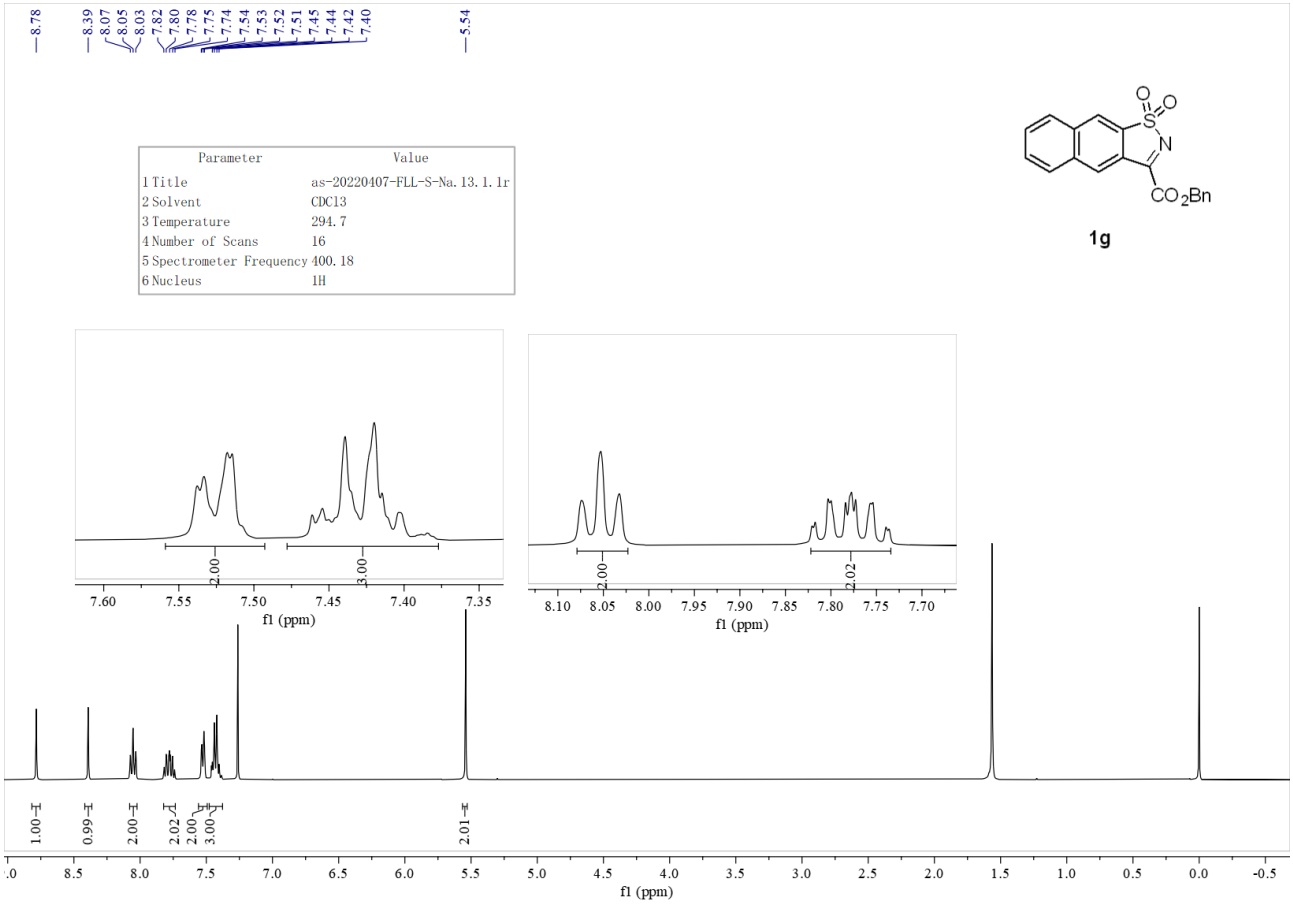

159.97
158.36
137.86
135.25
133.57
131.18
131.16
131.13
131.11
130.80
129.53
129.25
128.89
128.87
128.16
127.91
127.67
127.43
122.77
120.95
69.46
Parameter Value
1 Title fengli1-20220408-S-o-CF3.1.1.1r
2 Solvent CDCl3
3 Temperature 293.5
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
CF3
O
O
S
N
CO2Bn
1e
31.6
131.5
131.4
131.3
131.2
131.1
131.0
f1 (ppm)
123.0
122.5
122.0
121.5
121.0
120
f1 (ppm)
128.3
128.1
127.9
127.7
127.5
127.3
127
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

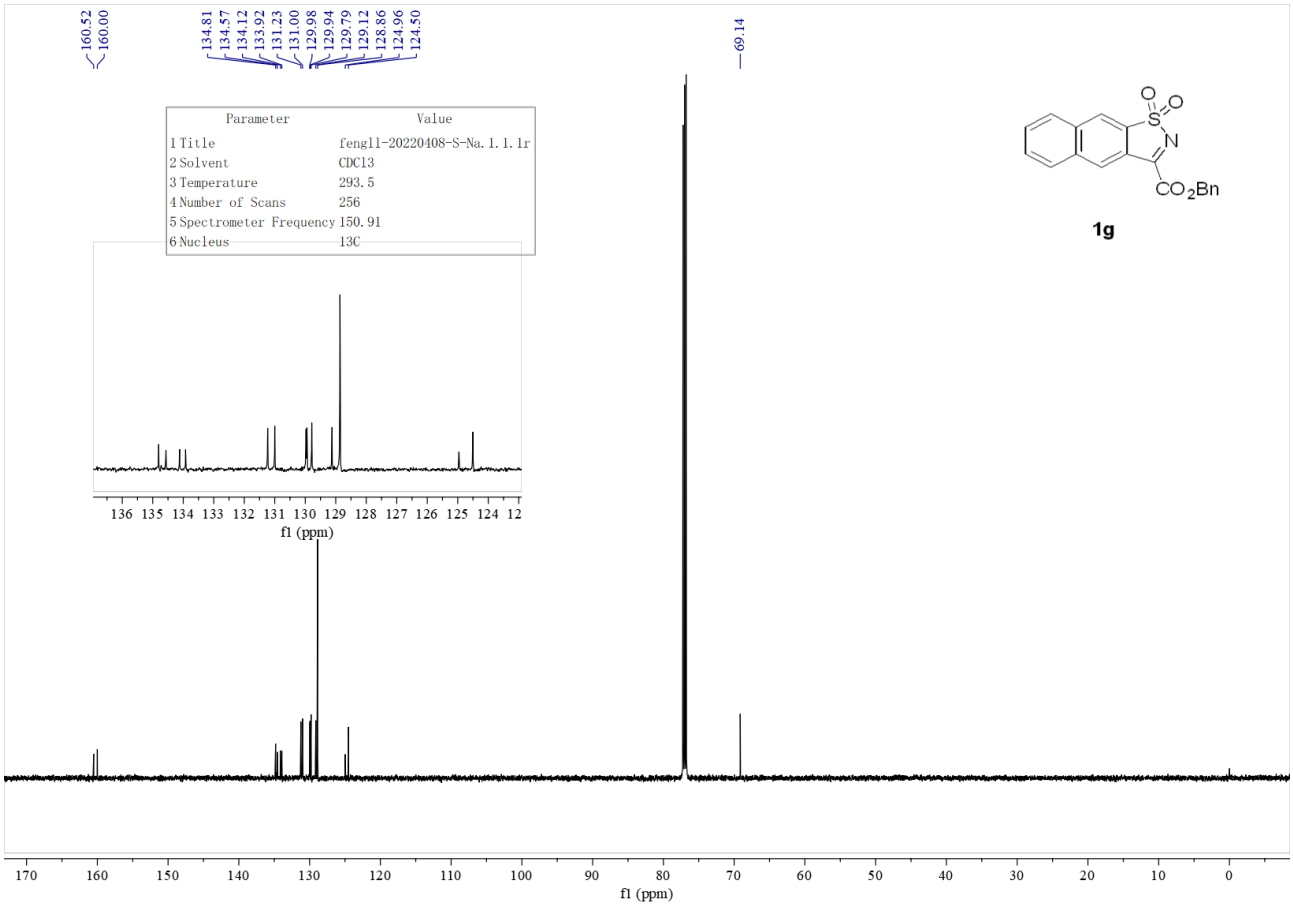

-59.97
Parameter Value
1 Title as-20211123-fenglili-Bn-CF3.3.1.1r
2 Solvent CDCl3
3 Temperature 294.1
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
CF3
O
O
S
N
CO2Bn
1e
f1 (ppm)

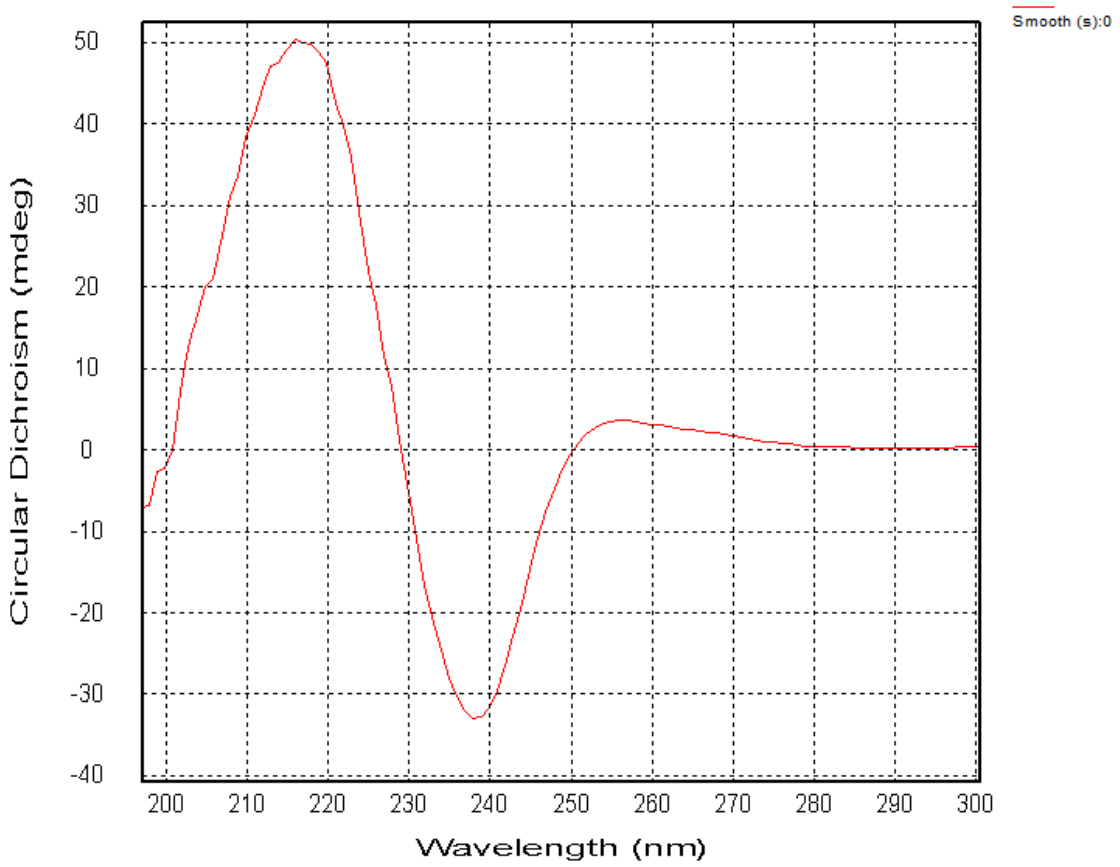

8.09
8.07
7.78
7.77
7.76
7.75
7.74
7.73
7.48
7.47
7.44
7.42
7.40
5.49
Parameter Value
1 Title as-20220407-FLL-S-O-F.9.1.1r
2 Solvent CDCl3
3 Temperature 294.9
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
1.00
1.01
6.02
2.01
F
O
O
S
N
CO2Bn
1f
f1 (ppm)


159.86
158.79
158.48
155.87
137.49
137.42
133.65
130.87
129.20
128.86
128.85
126.36
126.16
123.52
123.48
122.29
122.09
69.36
F
O
O
S
N
CO2Bn
1f
Parameter Value
1 Title as-20220407-FLL-S-O-F.10.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
38 136 134 132 130 128 126 124 122
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

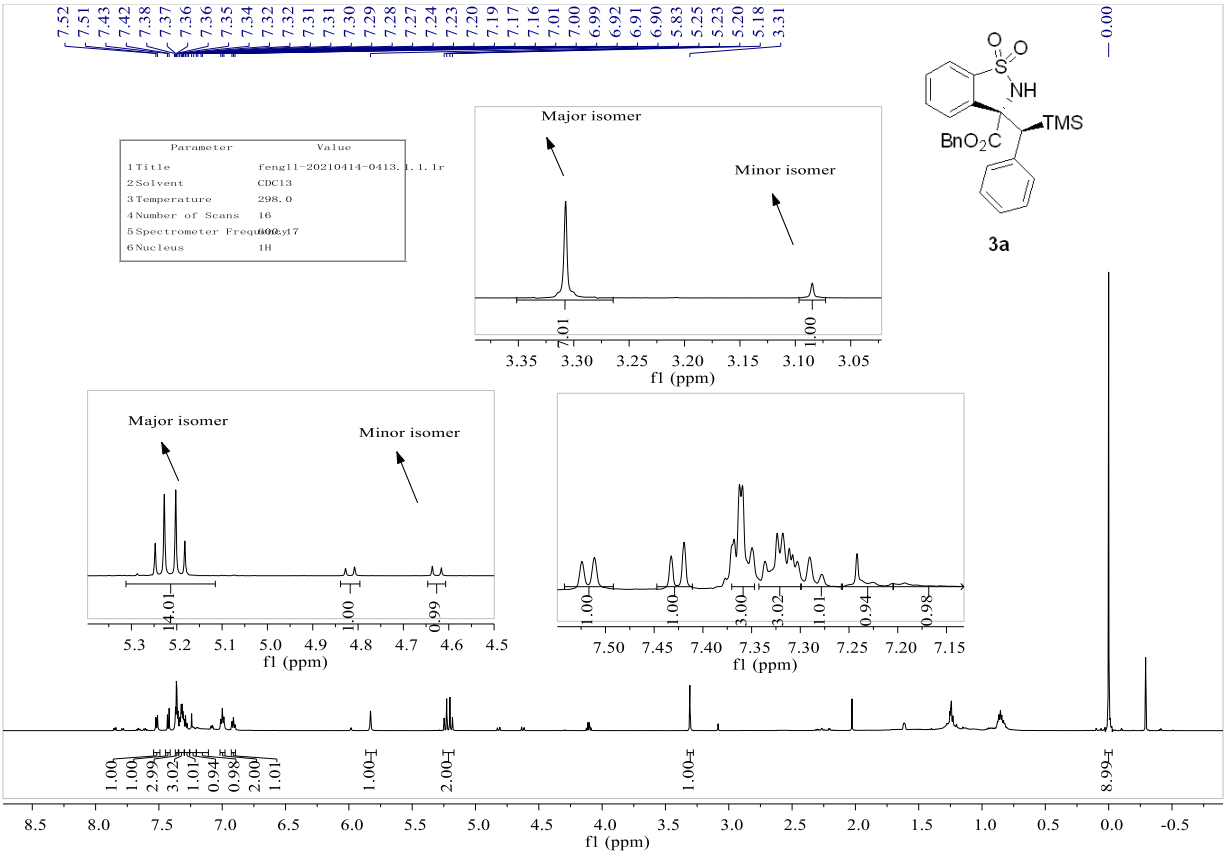

-110.96
F
O
O
S
N
CO2Bn
1f
Parameter Value
1 Title as-20220407-FLL-S-O-F.11.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

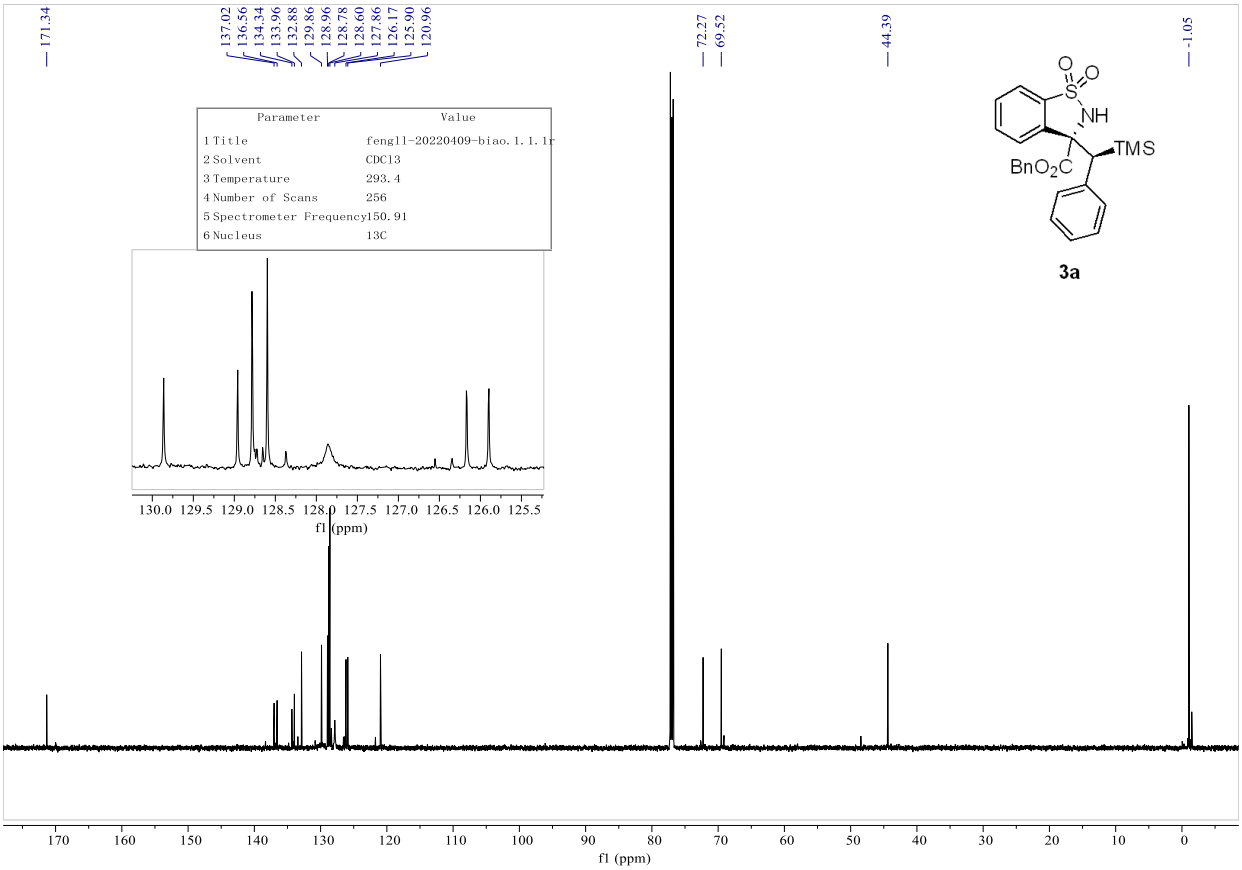

8.78
8.39
8.07
8.05
8.03
7.82
7.80
7.78
7.75
7.74
7.54
7.53
7.52
7.51
7.45
7.44
7.42
7.40
5.54
Parameter Value
1 Title as-20220407-FLL-S-Na.13.1.1r
2 Solvent CDCl3
3 Temperature 294.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
1g
f1 (ppm)
1.00
0.99
2.00
2.02
2.00
3.00
2.01


160.52
160.00
134.81
134.57
134.12
133.92
131.23
131.00
129.98
129.94
129.79
129.12
128.86
124.96
124.50
69.14
Parameter Value
1 Title fengll-20220408-S-Na.1.1.1r
2 Solvent CDCl3
3 Temperature 293.5
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
1g
f1 (ppm)

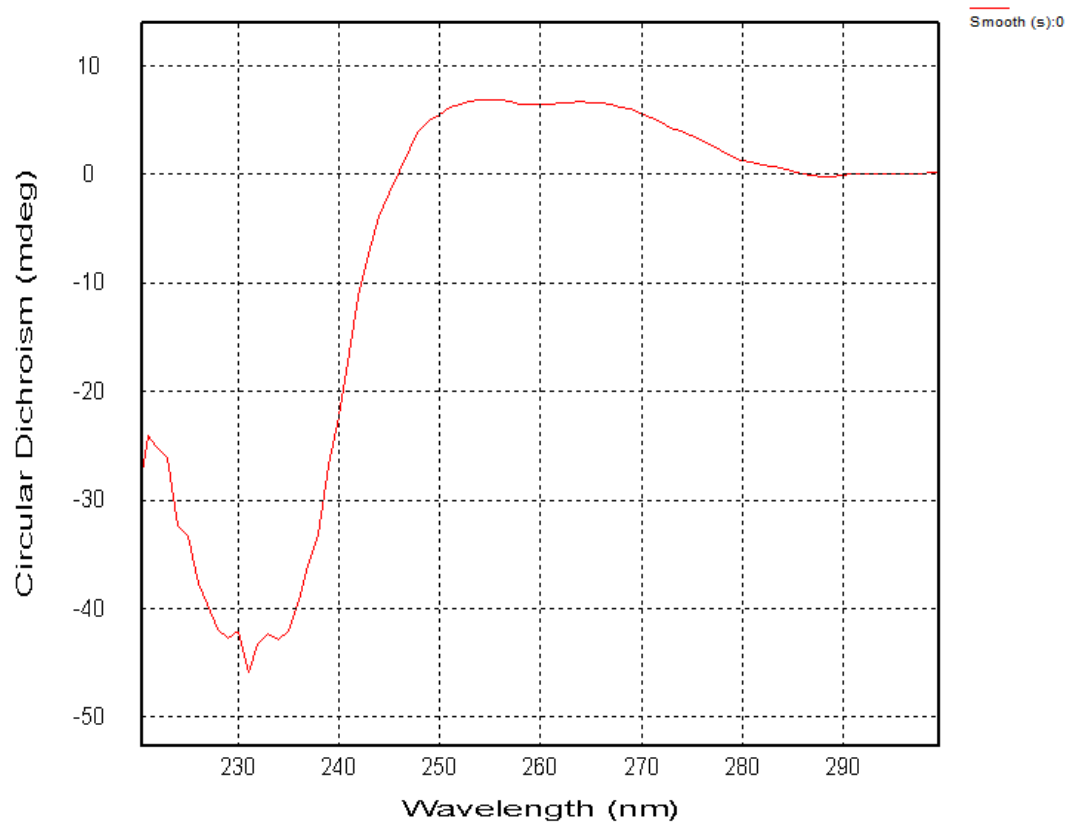

Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)

3a

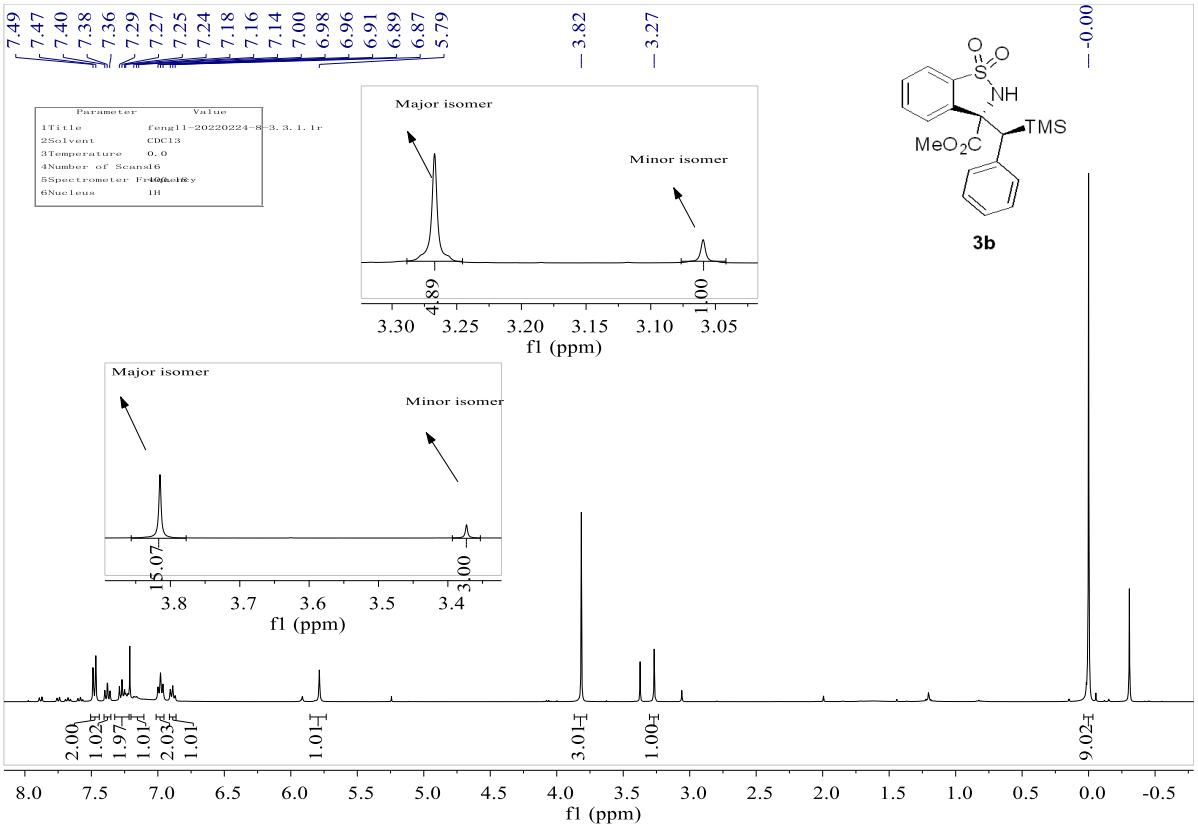

Major isomer
Minor isomer
3a
f1 (ppm)

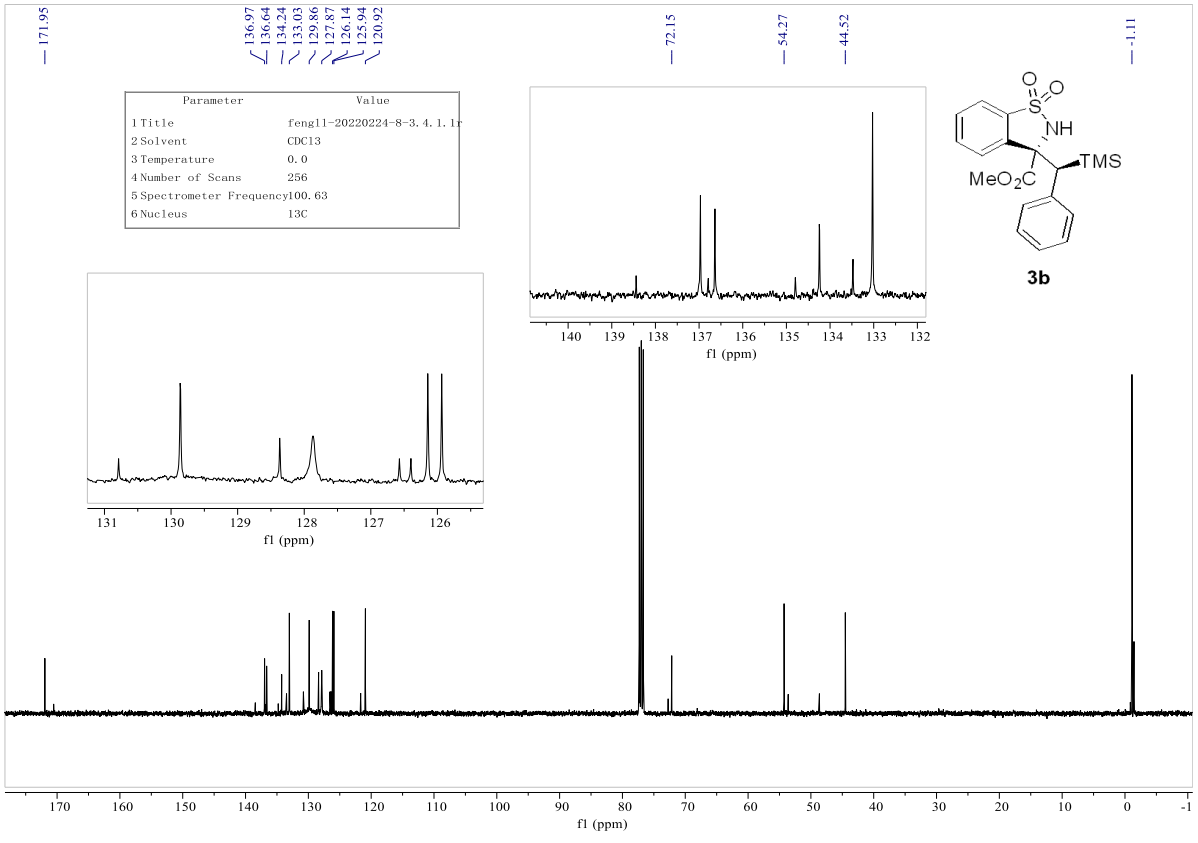

171.34
137.02
136.56
134.34
133.96
132.88
129.86
128.96
128.78
128.60
127.86
126.17
125.90
120.96
72.27
69.52
44.39
-1.05
Parameter Value
1 Title fengll-20220409-biao.1.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
f1 (ppm)
f1 (ppm)
NH
TMS
BnO2C

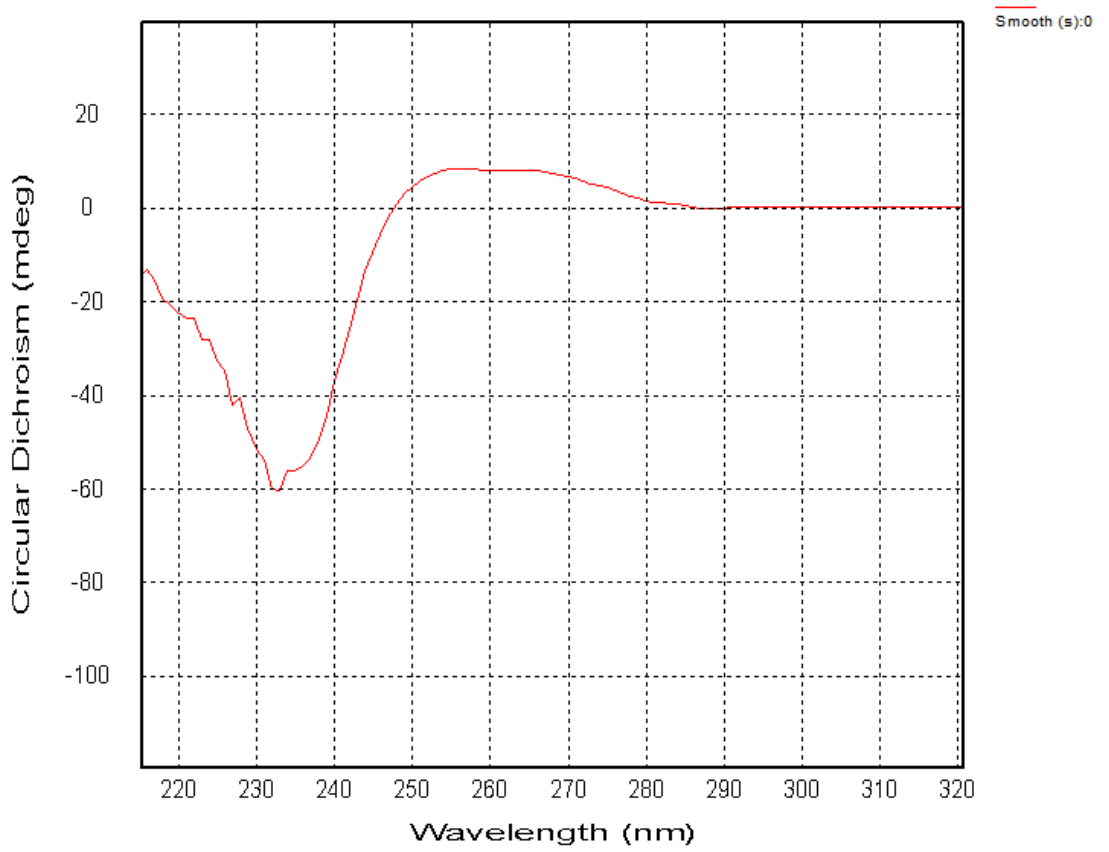
3a


Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)

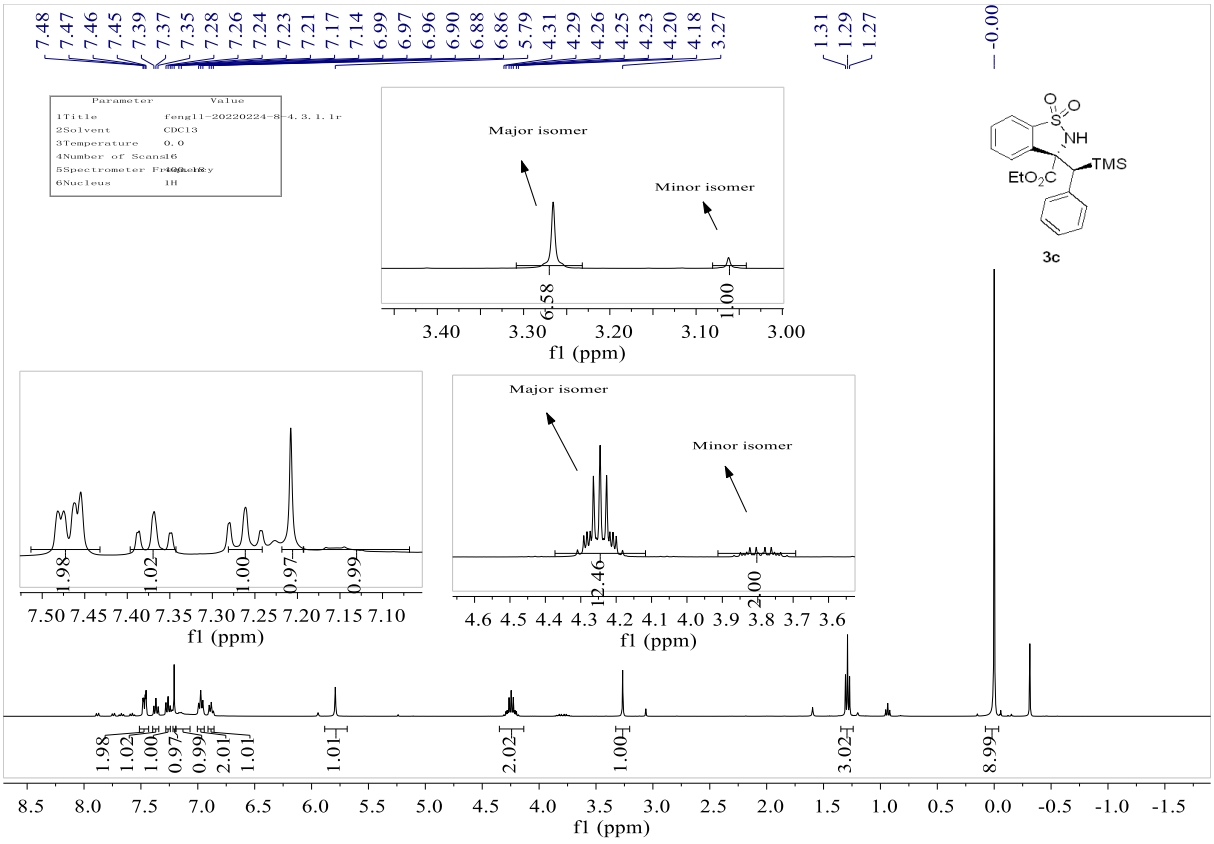
3b

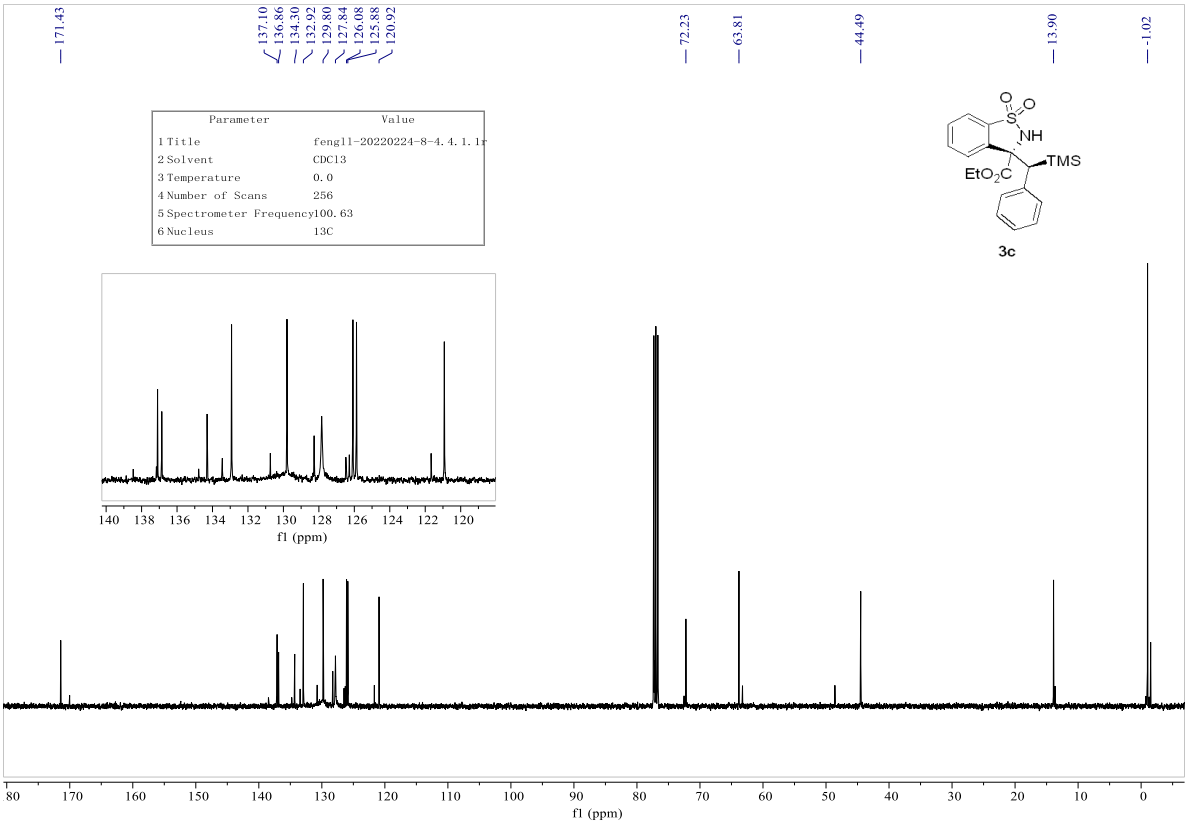

7.49
7.47
7.40
7.38
7.36
7.29
7.27
7.25
7.24
7.18
7.16
7.14
7.00
6.98
6.96
6.91
6.89
6.87
5.79
3.82
3.27
-0.00
Parameter Value
1Title fengll-20220224-8-3.3.1.1r
2Solvent CDCl3
3Temperature 0.0
4Number of Scans 16
5Spectrometer Frequency
6Nucleus 1H
Major isomer
Minor isomer
4.89
1.00
3.30 3.25 3.20 3.15 3.10 3.05
f1 (ppm)
Major isomer
Minor isomer
15.07
3.00
3.8 3.7 3.6 3.5 3.4
f1 (ppm)
NH
TMS
MeO2C
3b
2.00
1.02
1.97
1.01
2.03
1.01
1.01
3.01
1.00
9.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

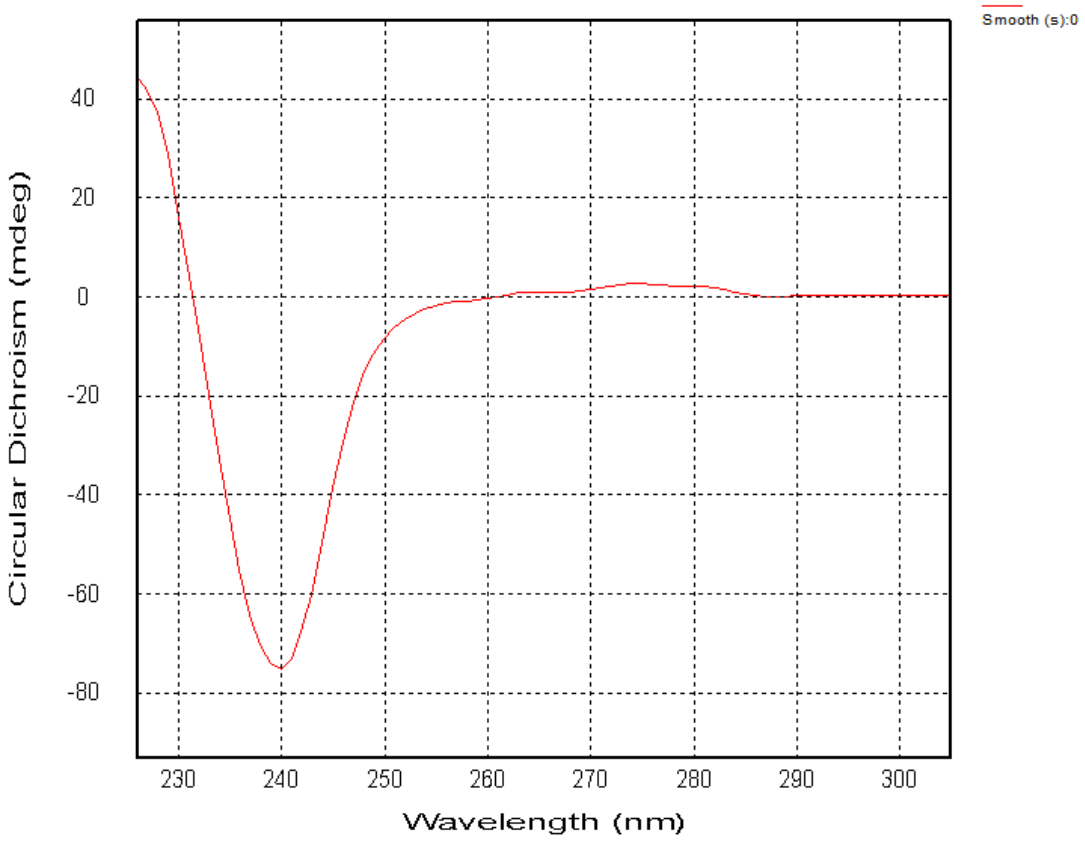

171.95
136.97
136.64
134.24
133.03
129.86
127.87
126.14
125.94
120.92
72.15
54.27
44.52
-1.11
Parameter Value
1 Title fengll-20220224-8-3.4.1.1r
2 Solvent CDCl3
3 Temperature 0.0
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
140 139 138 137 136 135 134 133 132
f1 (ppm)
131 130 129 128 127 126
f1 (ppm)
NH
TMS
MeO2C
3b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
220 230 240 250 260 270 280 290 300 310 320
Wavelength (nm)

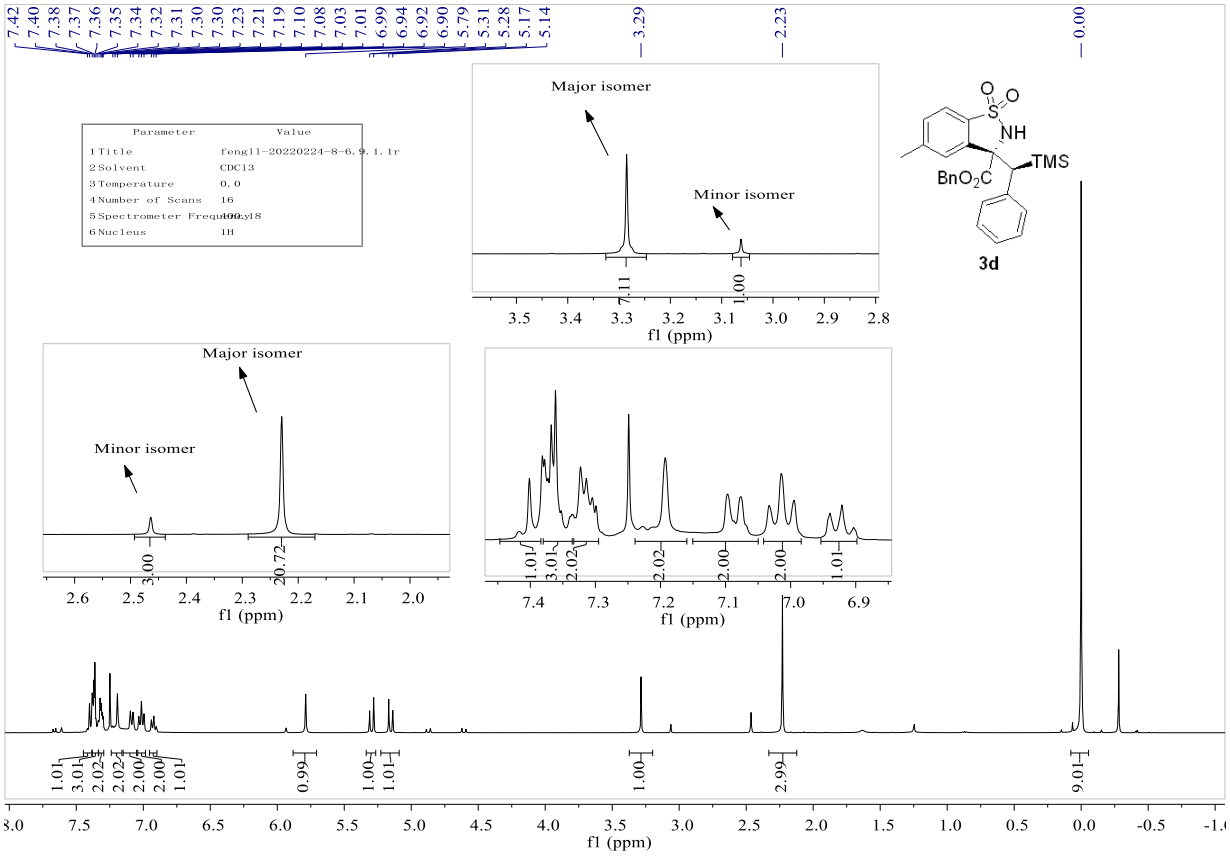
3c

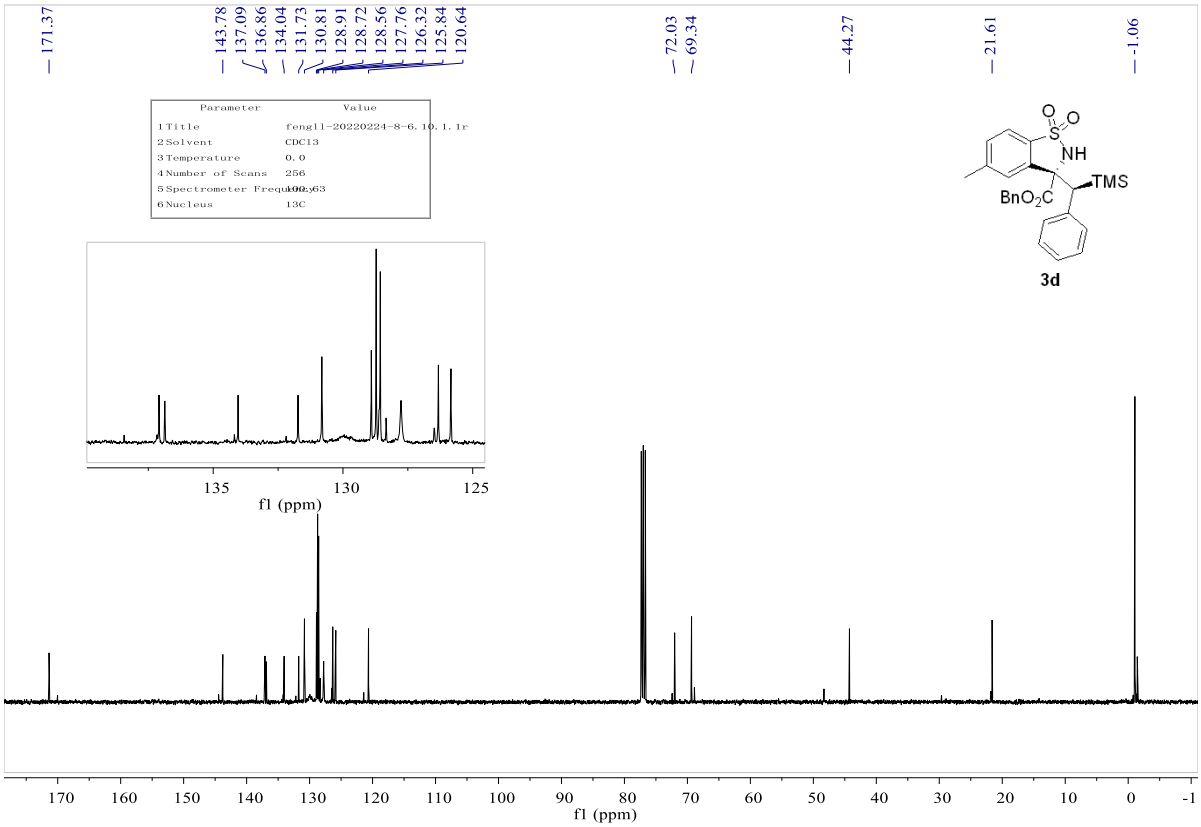

Major isomer
Minor isomer
fl (ppm)
3c
Major isomer
Minor isomer
fl (ppm)
fl (ppm)

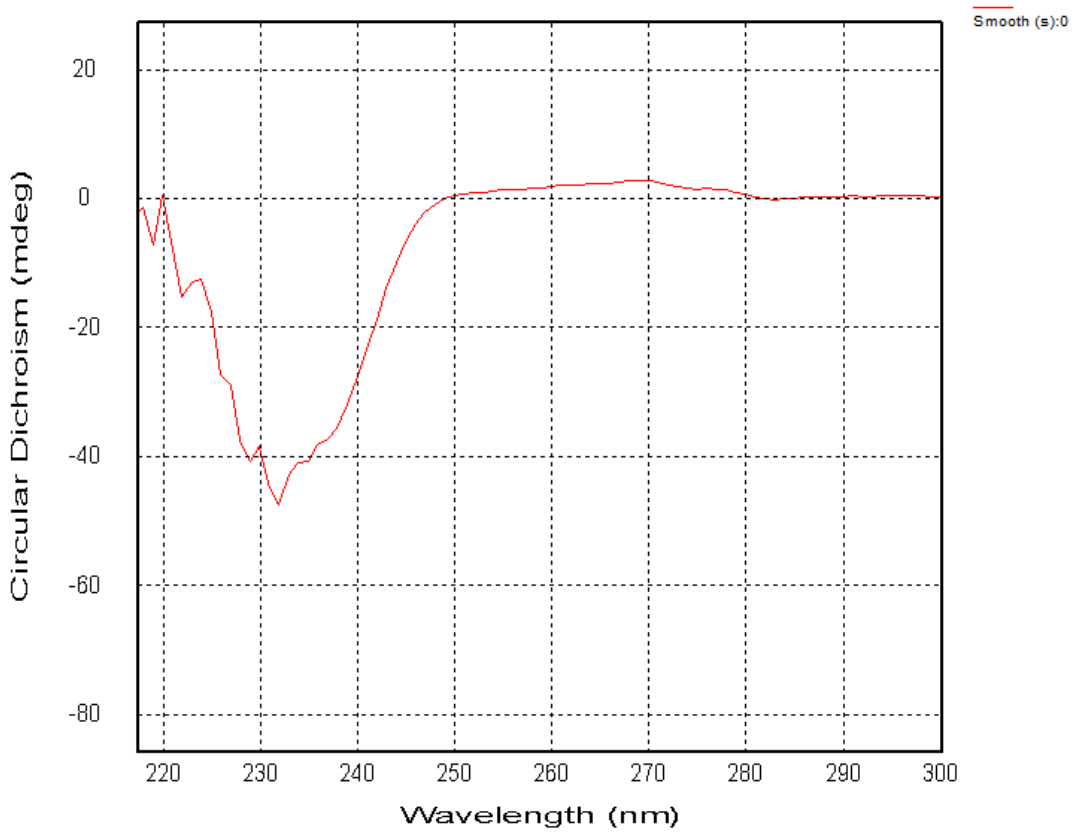

171.43
137.10
136.86
134.30
132.92
129.80
127.84
126.08
125.88
120.92
72.23
63.81
44.49
13.90
-1.02
Parameter Value
1 Title fengll-20220224-8-4.4.1.1r
2 Solvent CDCl3
3 Temperature 0.0
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
NH
TMS
EtO2C
3c
f1 (ppm)
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)

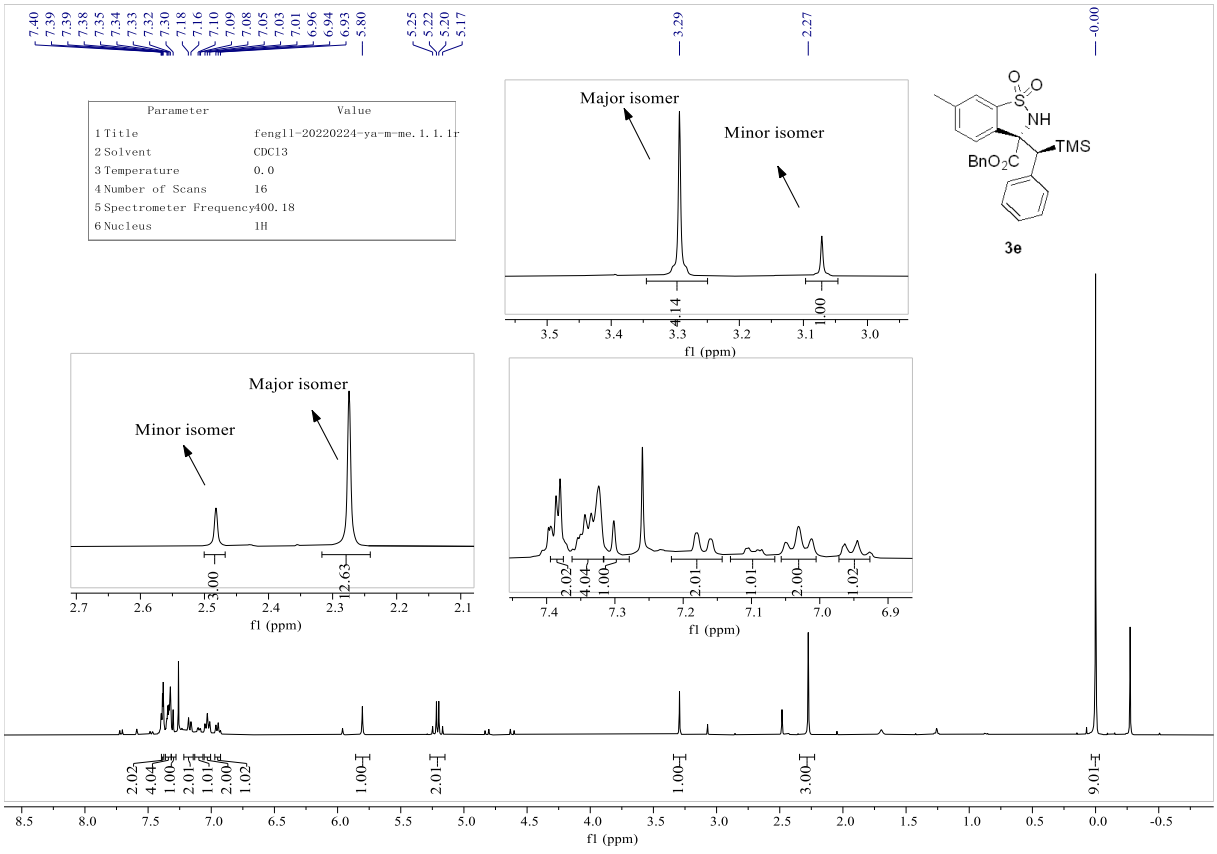
3d

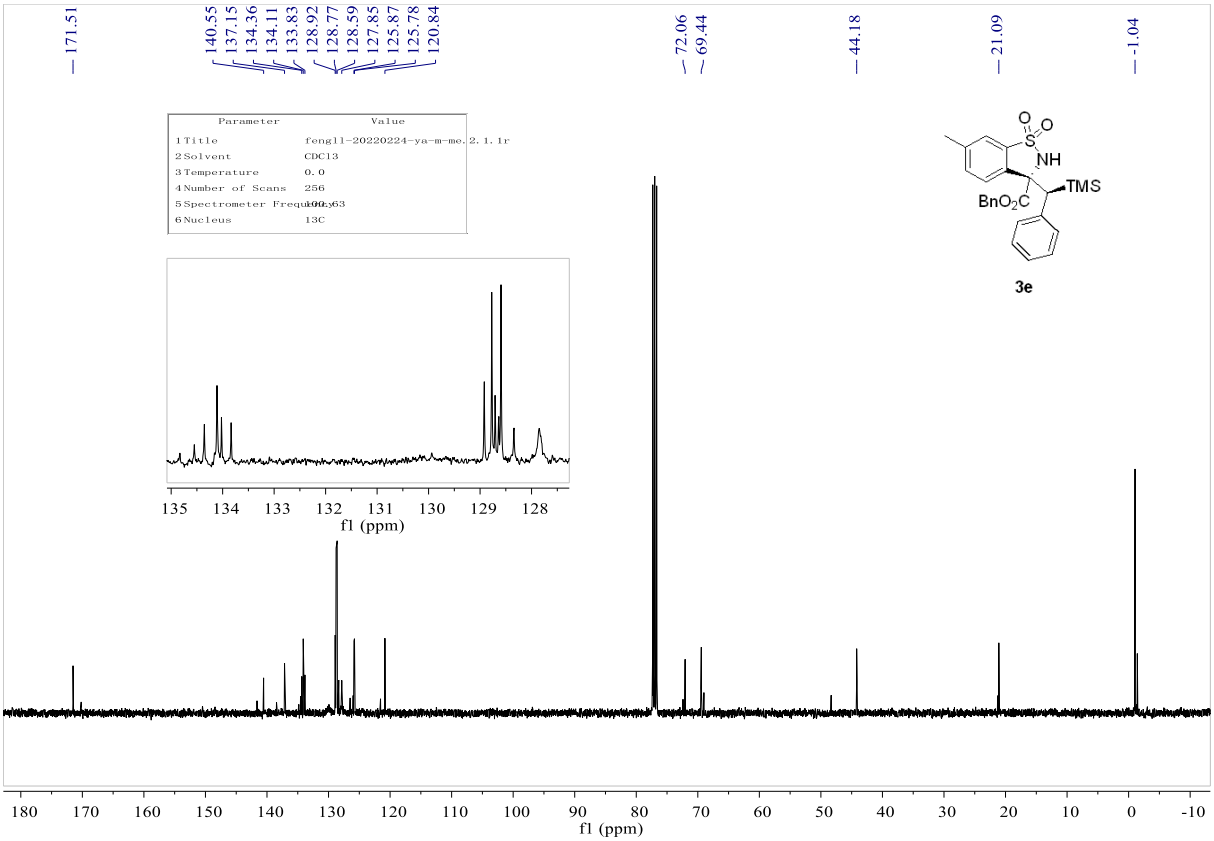

Major isomer
Minor isomer
Major isomer
Minor isomer
3d
fl (ppm)

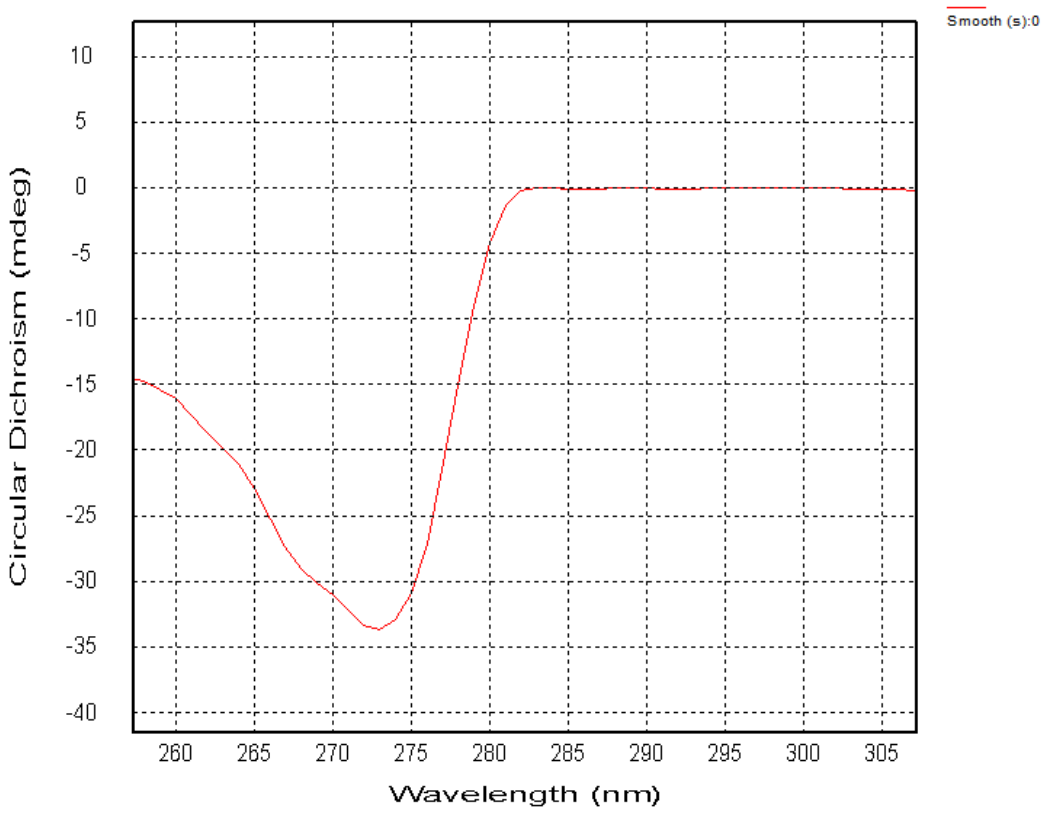

3d
fl (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
220
230
240
250
260
270
280
290
300
Wavelength (nm)

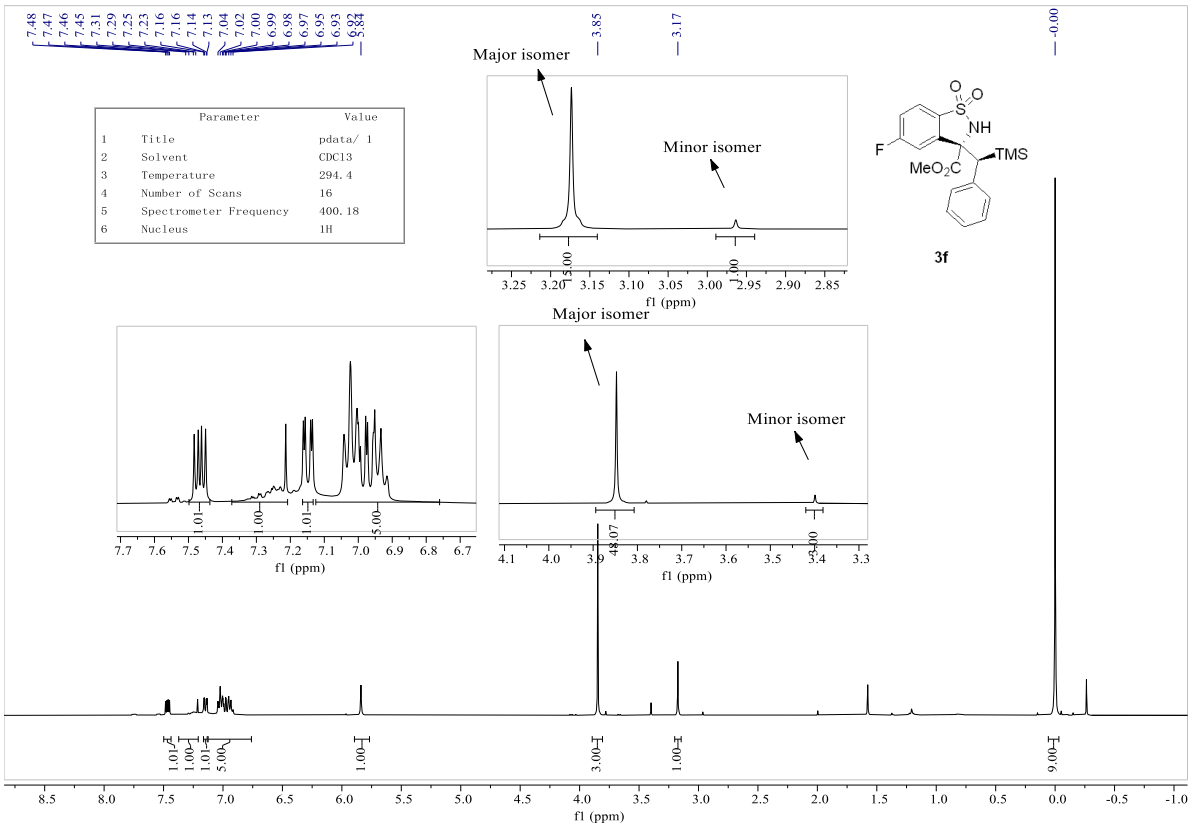
3e

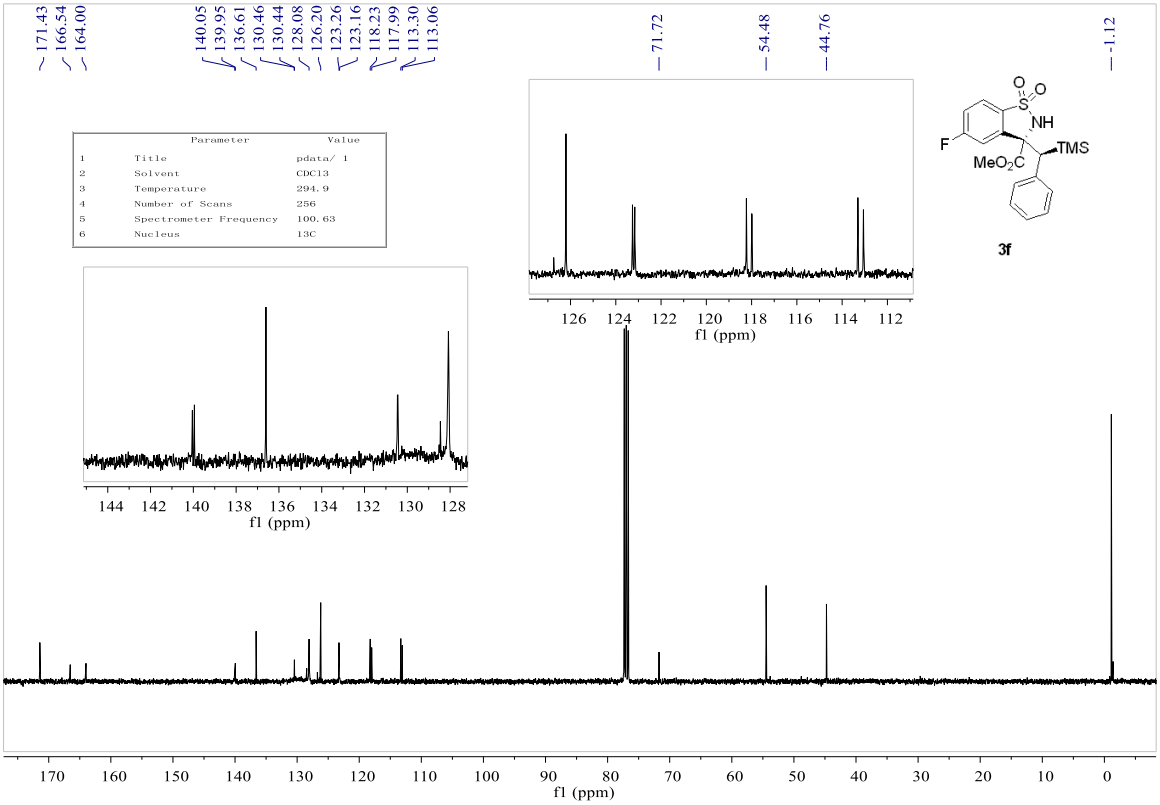

Parameter Value
1 Title fengll-20220224-ya-m-me. 1. 1. 1r
2 Solvent CDCl3
3 Temperature 0. 0
4 Number of Scans 16
5 Spectrometer Frequency 400. 18
6 Nucleus 1H
Major isomer
Minor isomer
3e
f1 (ppm)
Major isomer
Minor isomer
f1 (ppm)
f1 (ppm)
f1 (ppm)

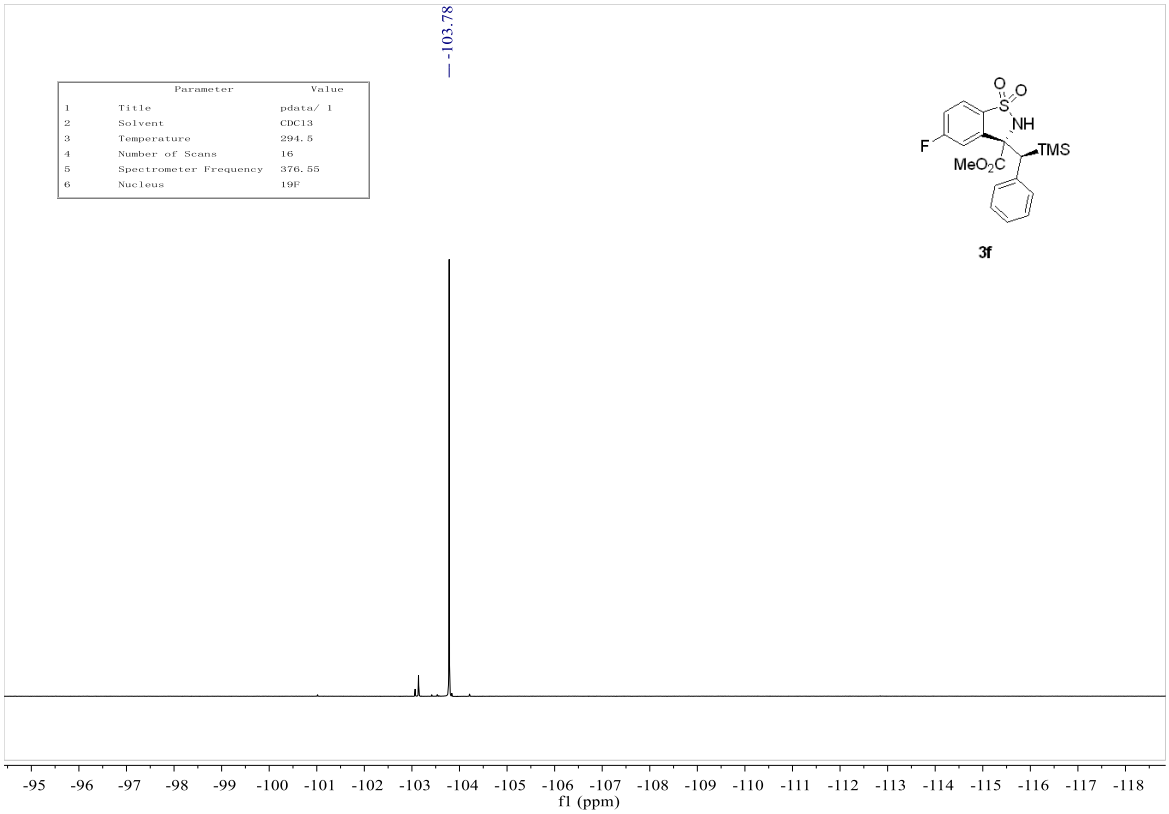

171.51
140.55
137.15
134.36
134.11
133.83
128.92
128.77
128.59
127.85
125.87
125.78
120.84
72.06
69.44
44.18
21.09
-1.04
Parameter Value
1 Title fengll-20220224-ya-m-me.2.1.1r
2 Solvent CDCl3
3 Temperature 0.0
4 Number of Scans 256
5 Spectrometer Frequency
6 Nucleus 13C
NH
TMS
BnO2C
3e
f1 (ppm)
f1 (ppm)

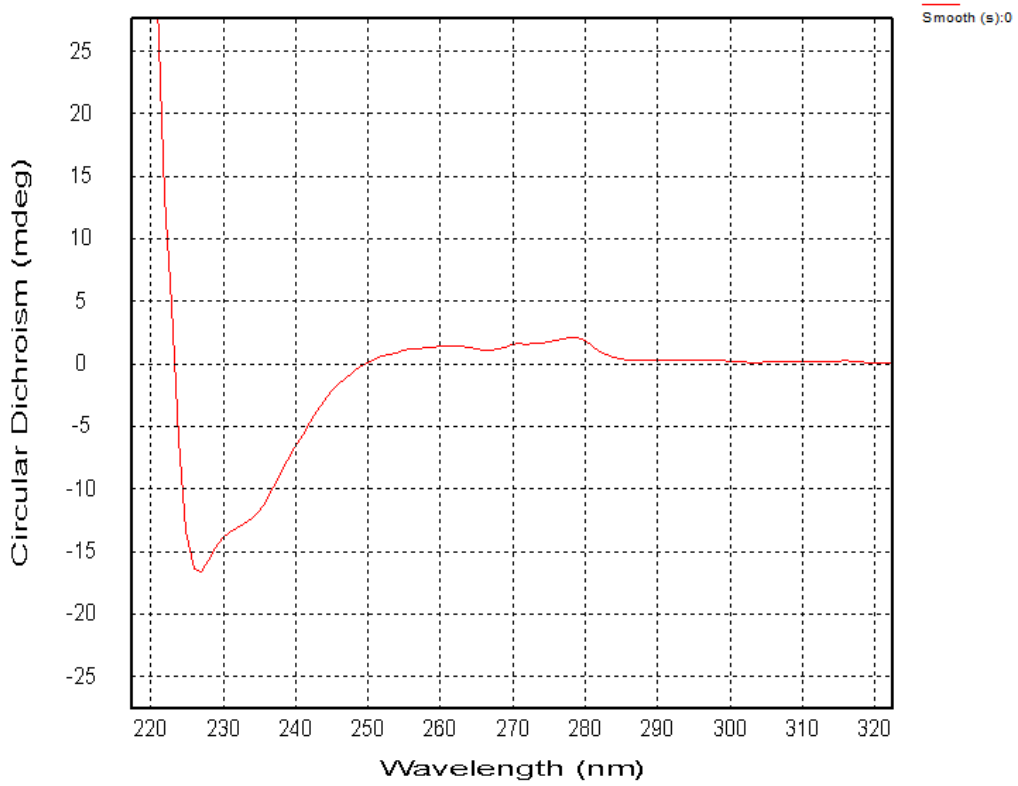

Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)

3f

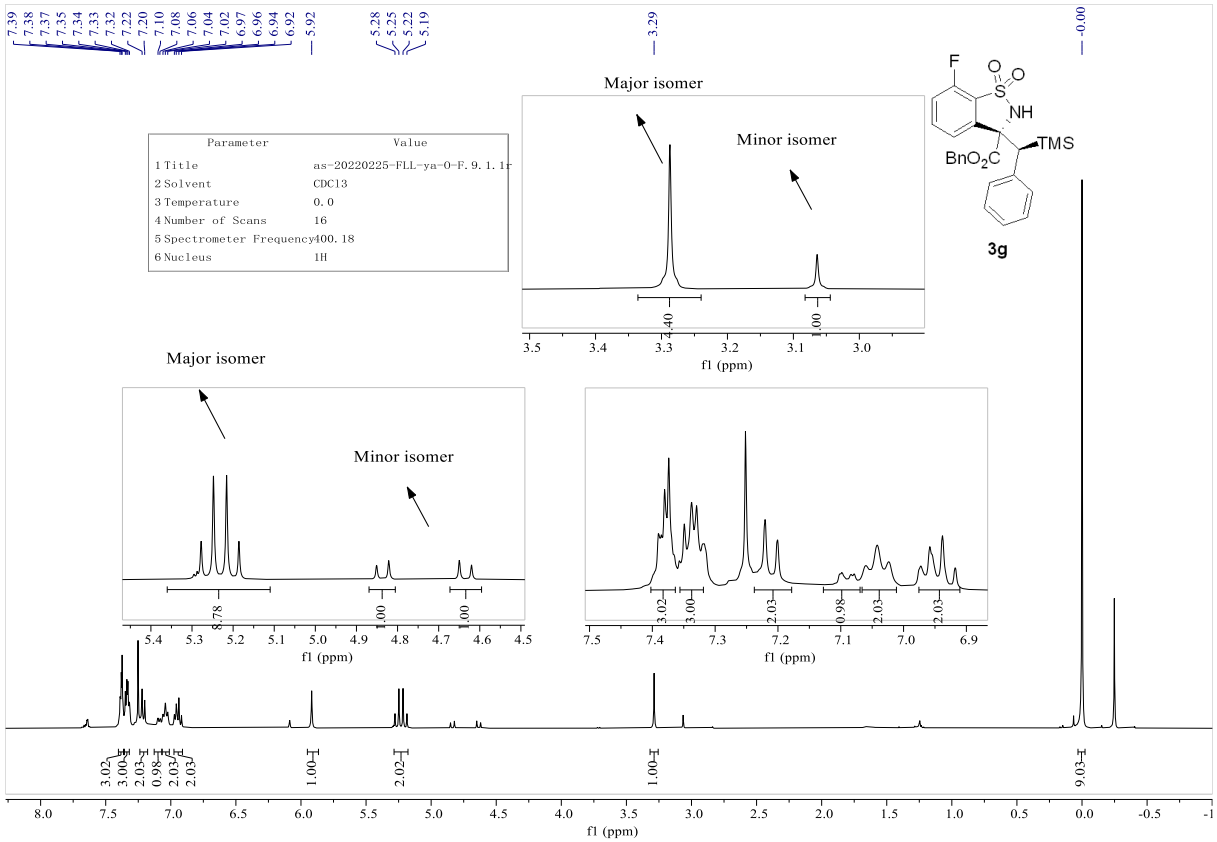

Major isomer
Minor isomer
Major isomer
Minor isomer
3f
f1 (ppm)


3f
f1 (ppm)

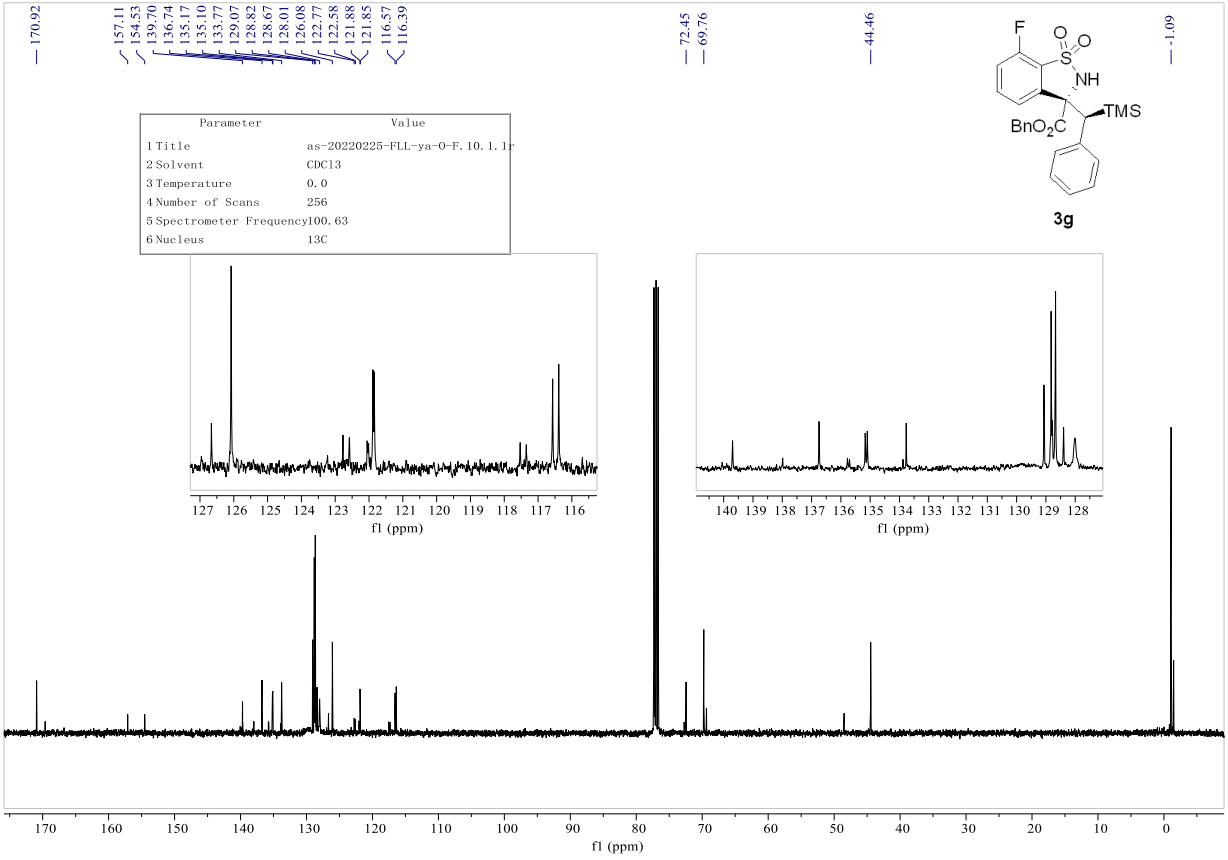

-103.78
Parameter Value
1 Title pdata/ 1
2 Solvent CDCl3
3 Temperature 294.5
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
F
NH
TMS
MeO2C
3f
-95 -96 -97 -98 -99 -100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
25 20 15 10 5 0 -5 -10 -15 -20 -25
220 230 240 250 260 270 280 290 300 310 320
Wavelength (nm)

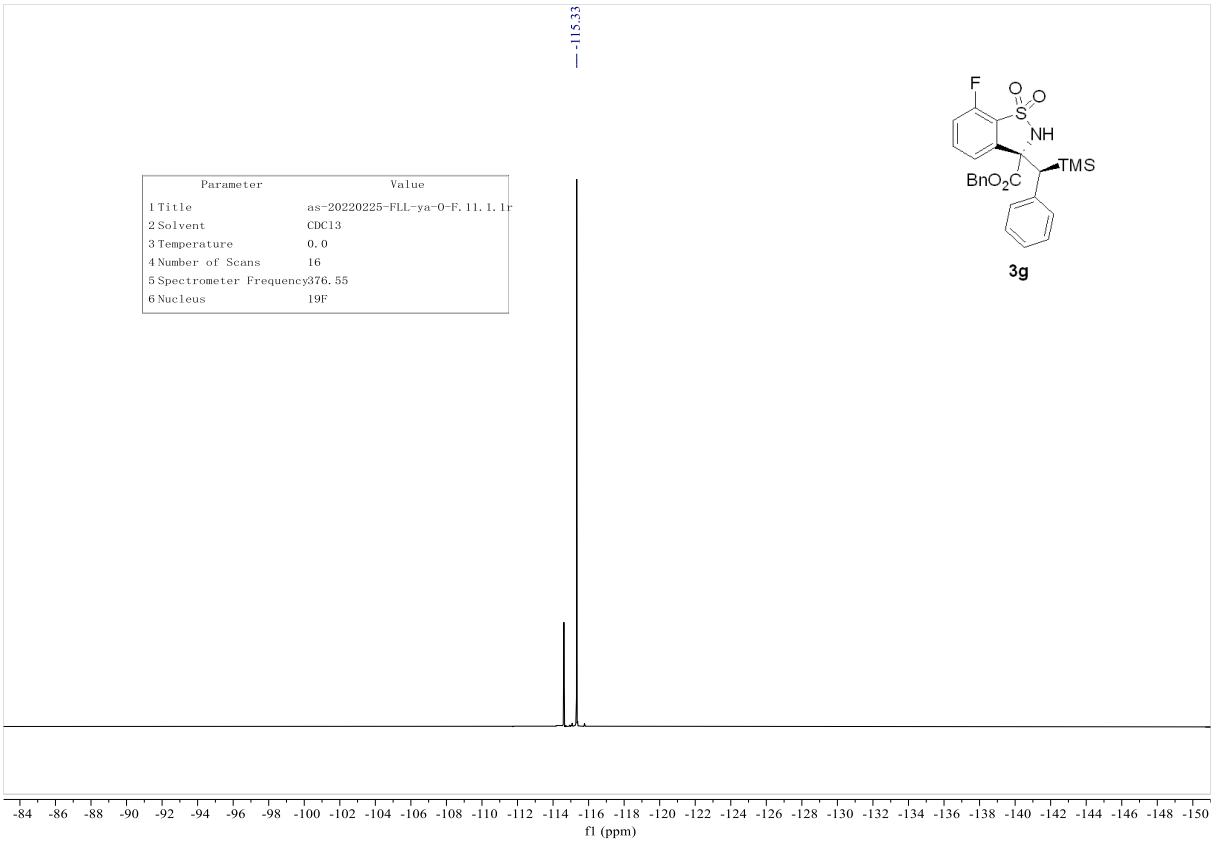
3g

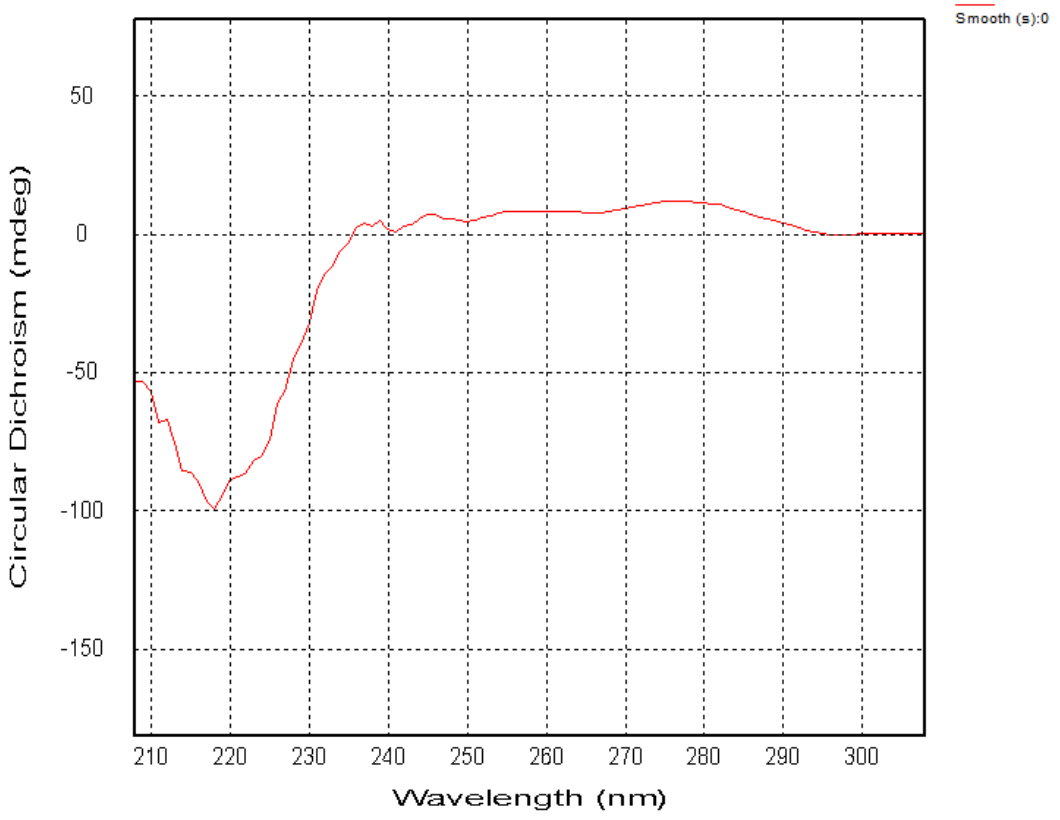


Parameter	Value
1 Title	as-20220225-FLL-ya-0-F. 9. 1. 1r
2 Solvent	CDCl3
3 Temperature	0. 0
4 Number of Scans	16
5 Spectrometer Frequency	400. 18
6 Nucleus	1H

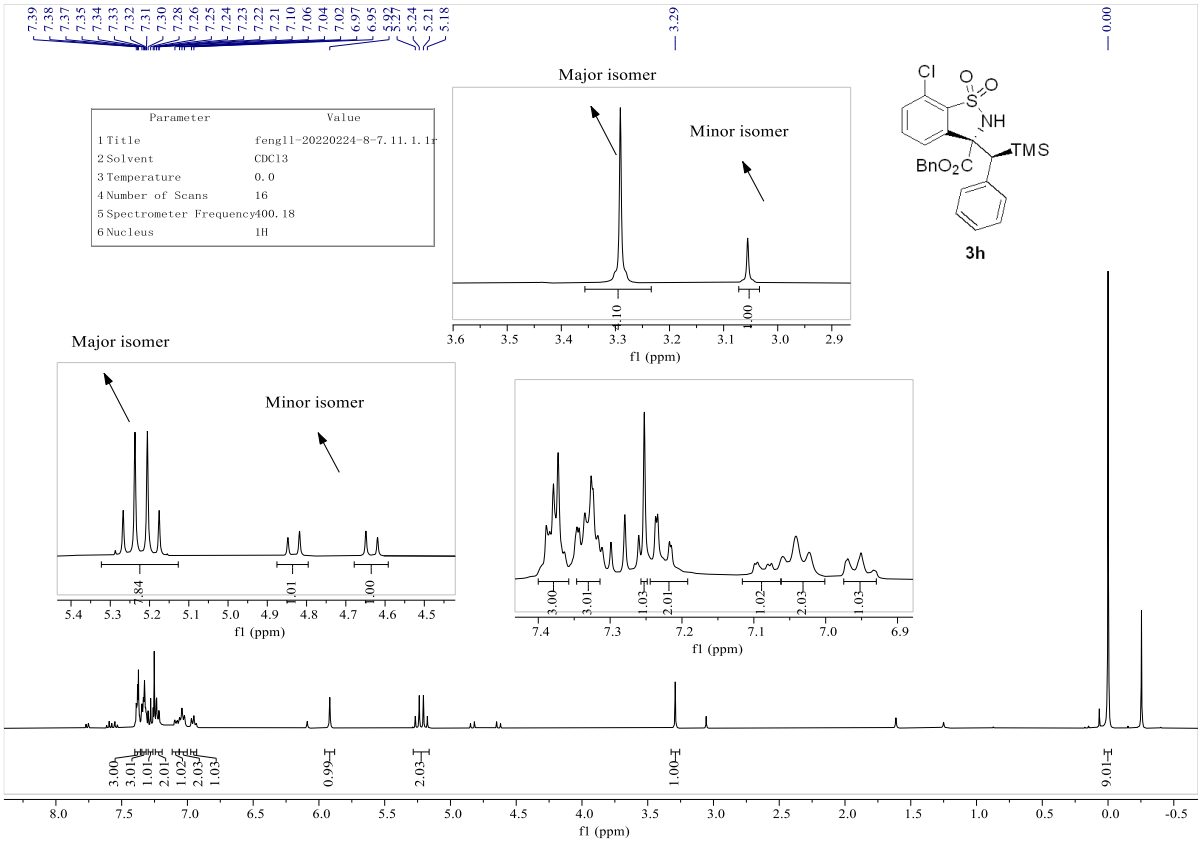


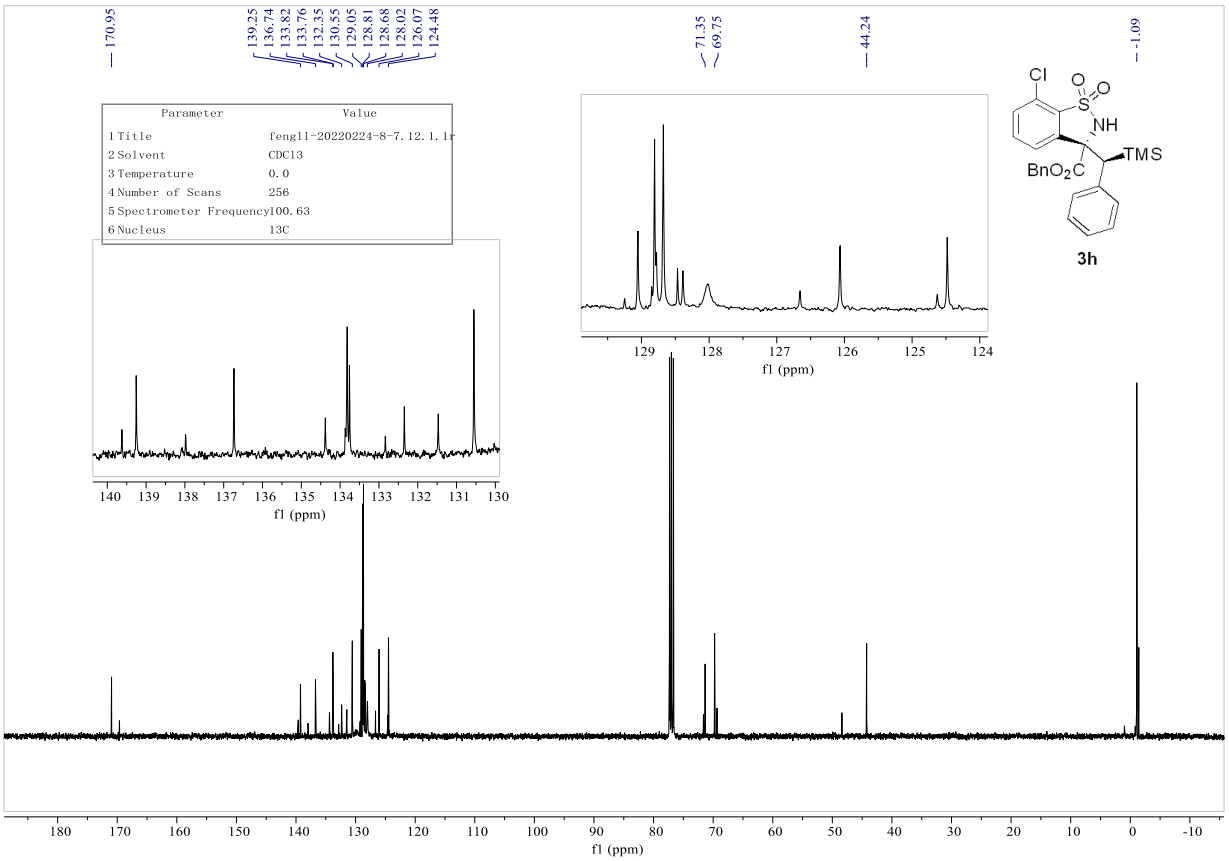
Parameter	Value
1 Title	as-20220225-FLL-ya-0-F. 10. 1. 1r
2 Solvent	CDCl3
3 Temperature	0. 0
4 Number of Scans	256
5 Spectrometer Frequency	100. 63
6 Nucleus	13C

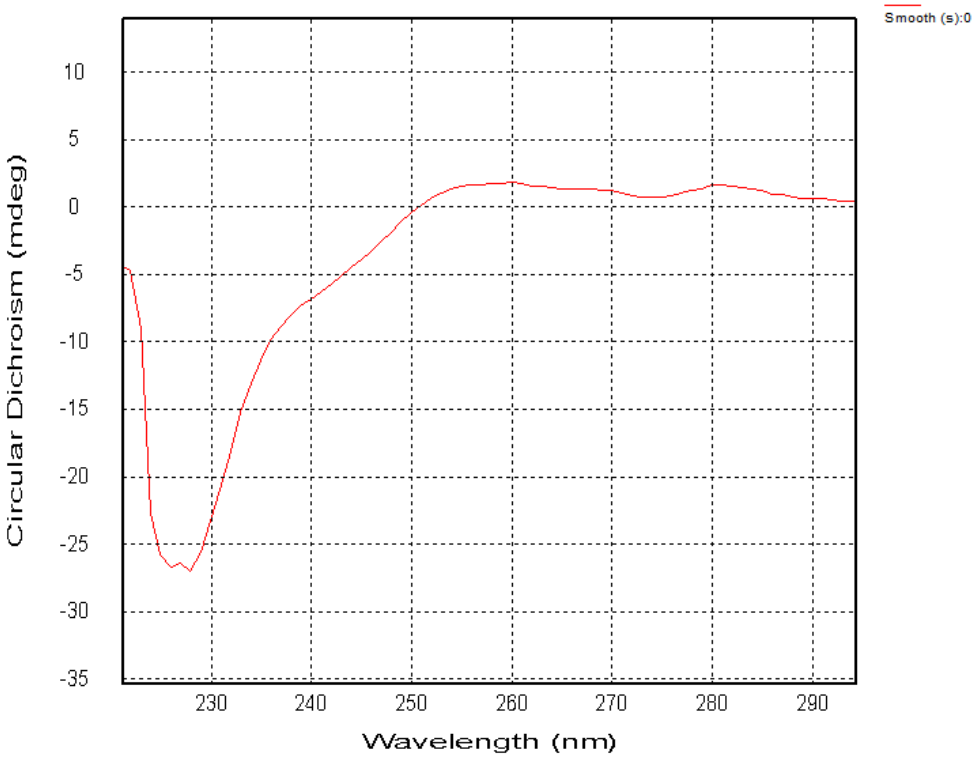

-115.33
F
O
O
S
NH
TMS
BnO2C
3g
Parameter Value
1 Title as-20220225-FLL-ya-0-F. 11. 1. 1r
2 Solvent CDC13
3 Temperature 0. 0
4 Number of Scans 16
5 Spectrometer Frequency 376. 55
6 Nucleus 19F
-84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
50
0
-50
-100
-150
210 220 230 240 250 260 270 280 290 300
Wavelength (nm)

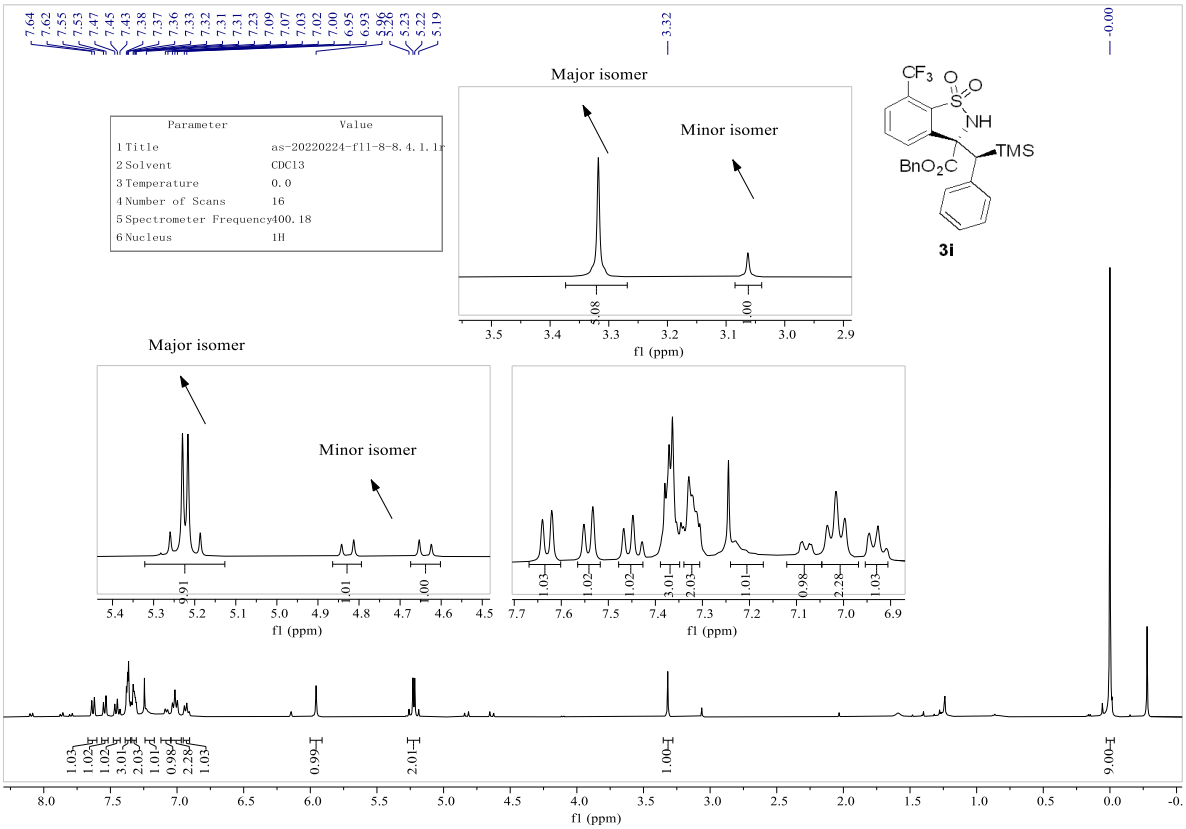
3h

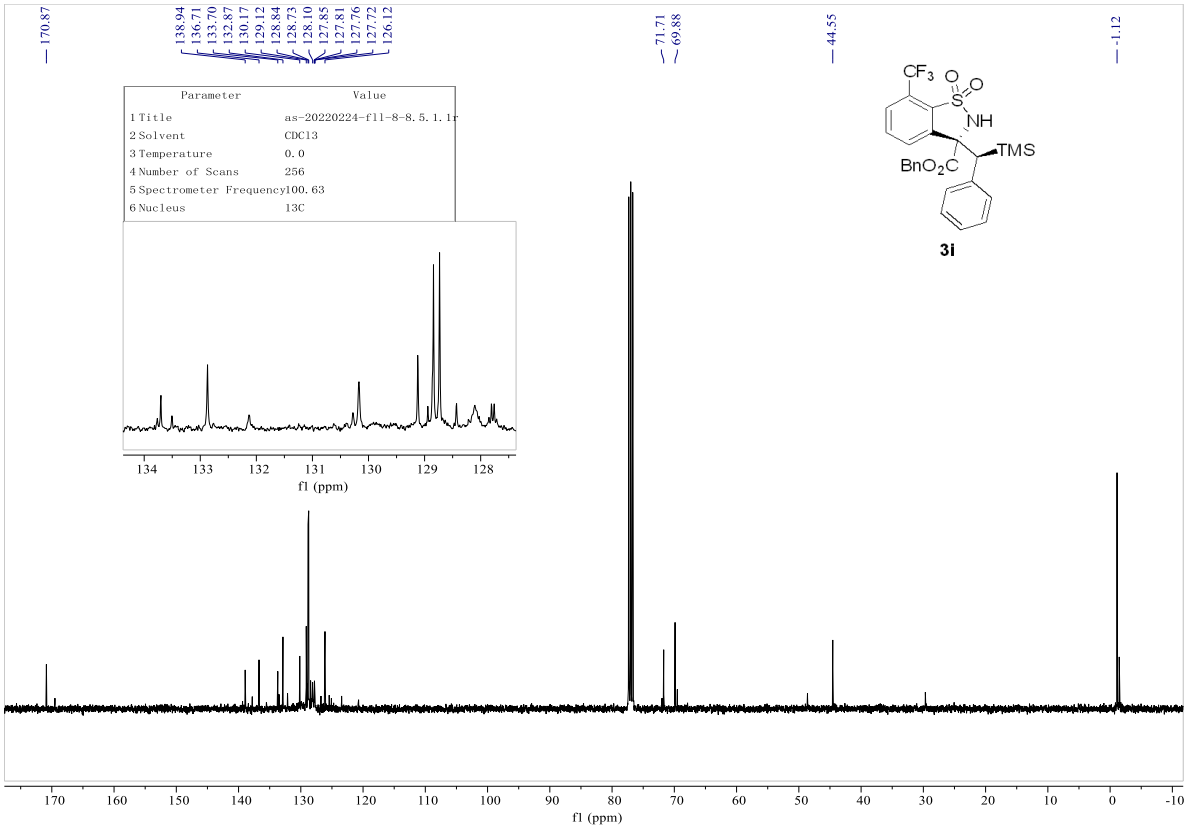

Major isomer
Minor isomer
Major isomer
Minor isomer
3h
f1 (ppm)

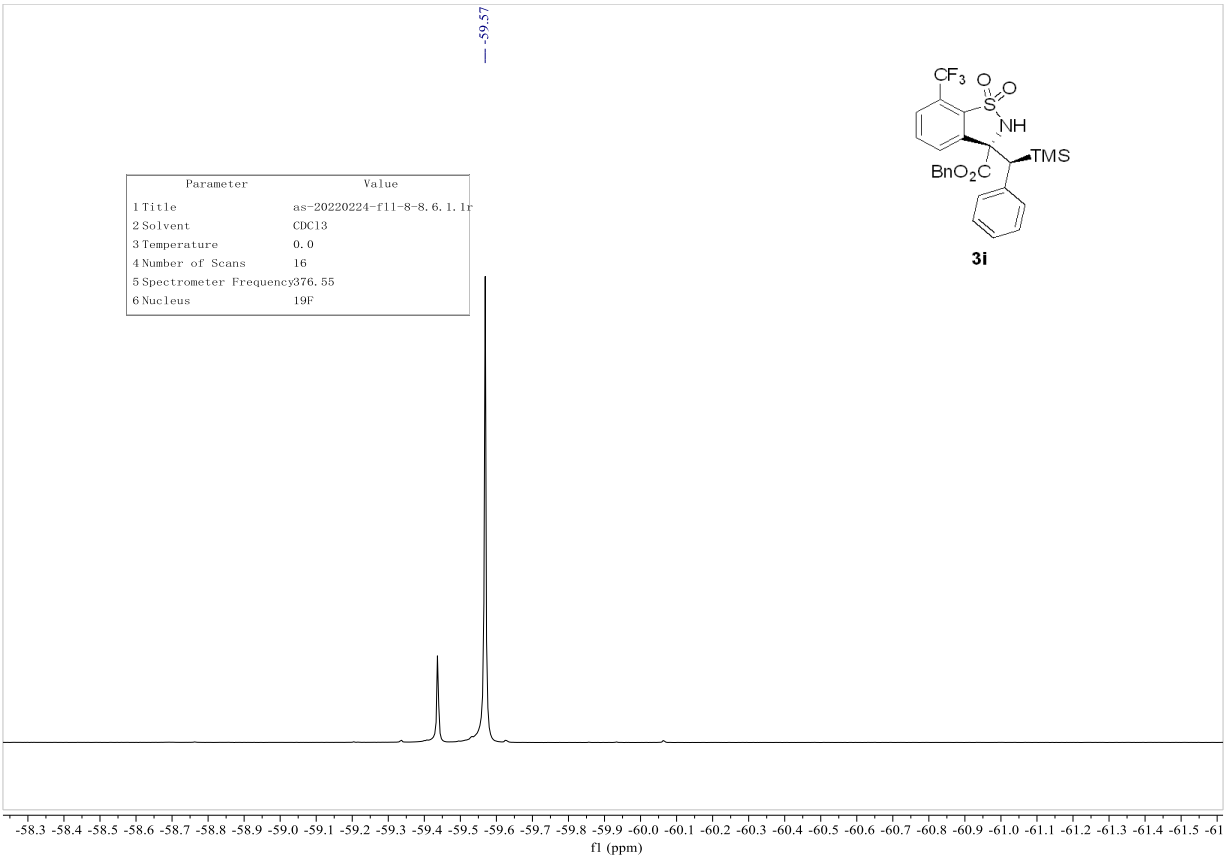

3h
f1 (ppm)

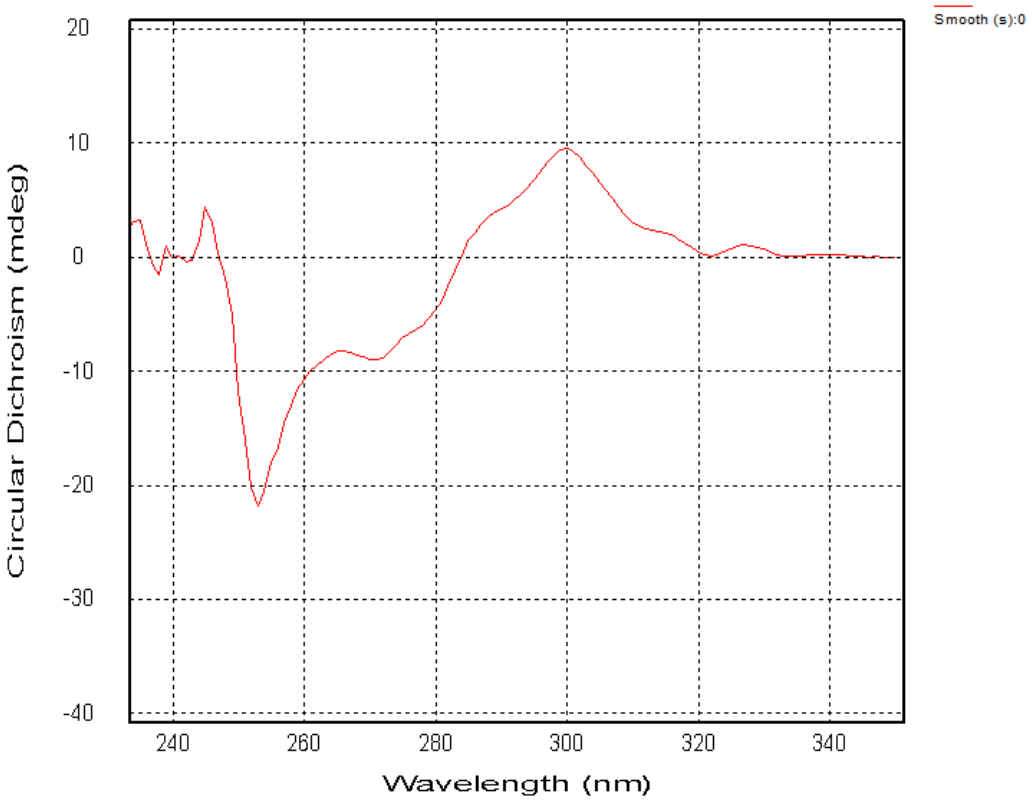

Smooth (s):0
Circular Dichroism (mdeg)
10
5
0
-5
-10
-15
-20
-25
-30
-35
230
240
250
260
270
280
290
Wavelength (nm)

3i

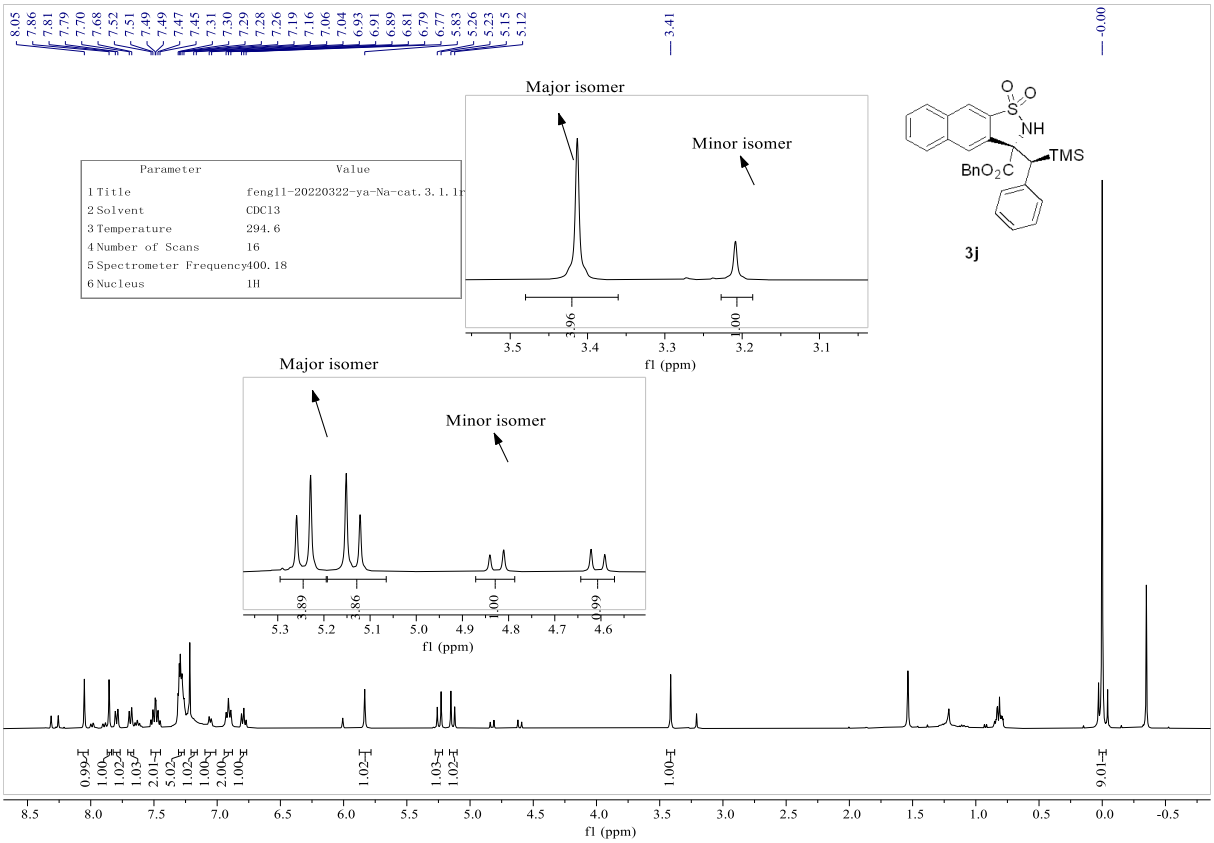

Parameter Value
1 Title as-20220224-f11-8-8.4.1.1r
2 Solvent CDCl3
3 Temperature 0.0
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
Major isomer
Minor isomer
f1 (ppm)
CF3
NH
TMS
BnO2C
3i

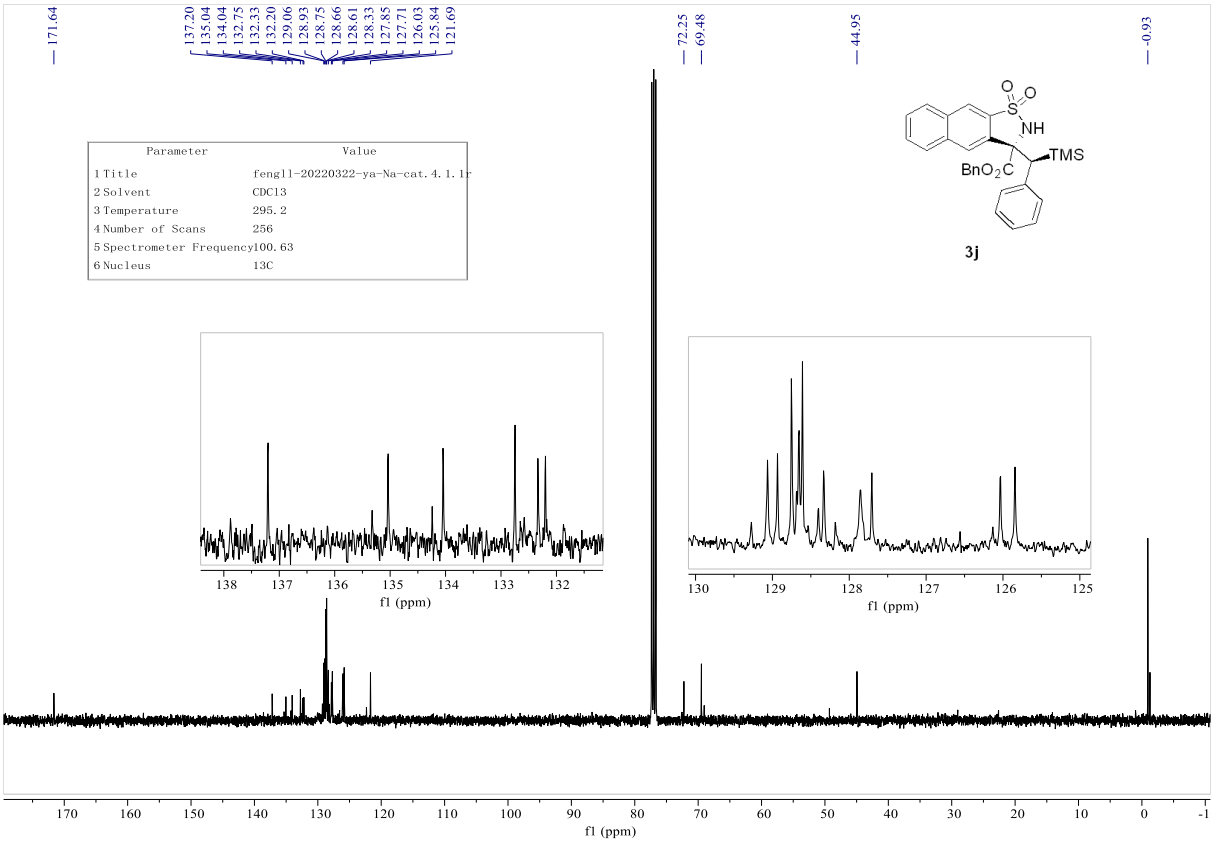

170.87
138.94
136.71
133.70
132.87
130.17
129.12
128.84
128.73
128.10
127.85
127.81
127.76
127.72
126.12
71.71
69.88
44.55
-1.12
Parameter Value
1 Title as-20220224-f11-8-8.5.1.1r
2 Solvent CDCl3
3 Temperature 0.0
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
134 133 132 131 130 129 128
f1 (ppm)
CF3
O
O
S
NH
TMS
BnO2C
3i
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

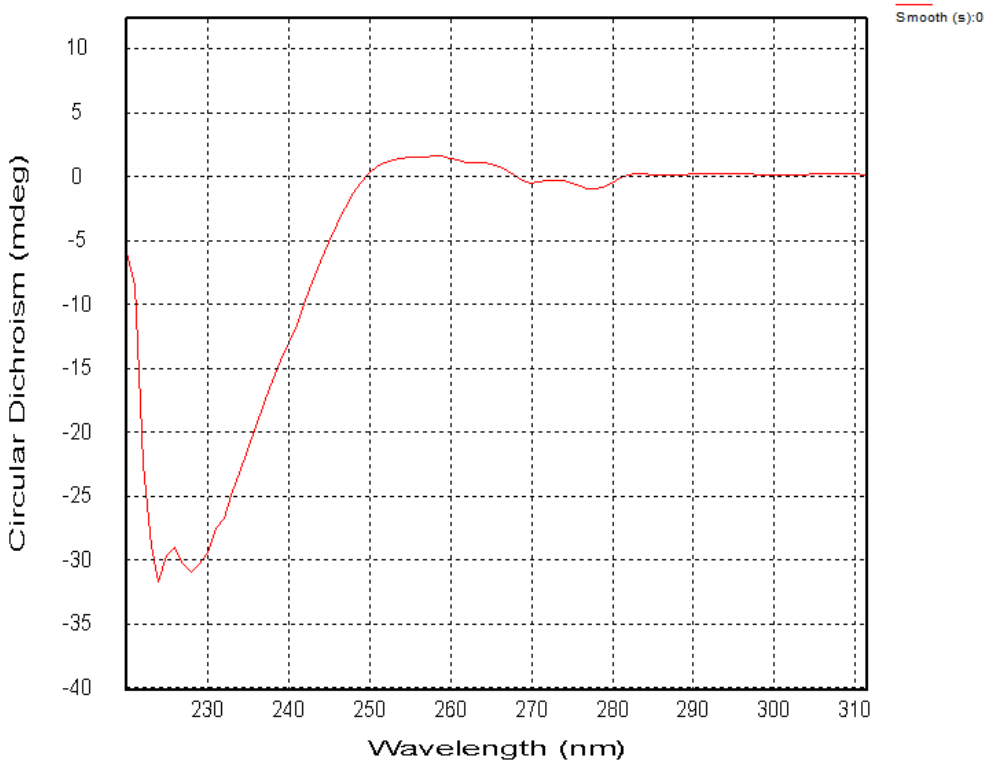

-59.57
Parameter Value
1 Title as-20220224-f11-8-8.6.1.1r
2 Solvent CDCl3
3 Temperature 0.0
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
CF3
O
O
S
NH
TMS
BnO2C
3i
-58.3 -58.4 -58.5 -58.6 -58.7 -58.8 -58.9 -59.0 -59.1 -59.2 -59.3 -59.4 -59.5 -59.6 -59.7 -59.8 -59.9 -60.0 -60.1 -60.2 -60.3 -60.4 -60.5 -60.6 -60.7 -60.8 -60.9 -61.0 -61.1 -61.2 -61.3 -61.4 -61.5 -61
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)
20
10
0
-10
-20
-30
-40
240
260
280
300
320
340

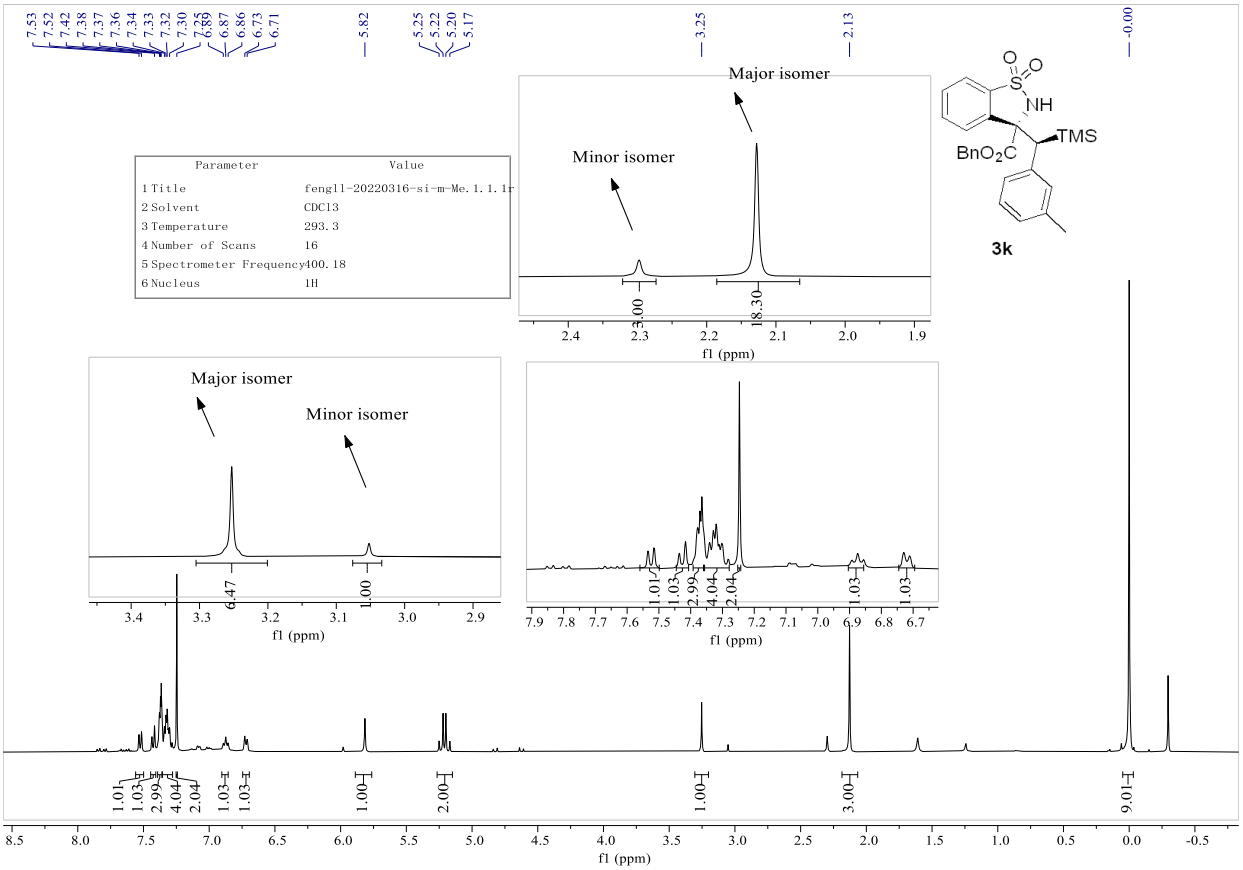
3j

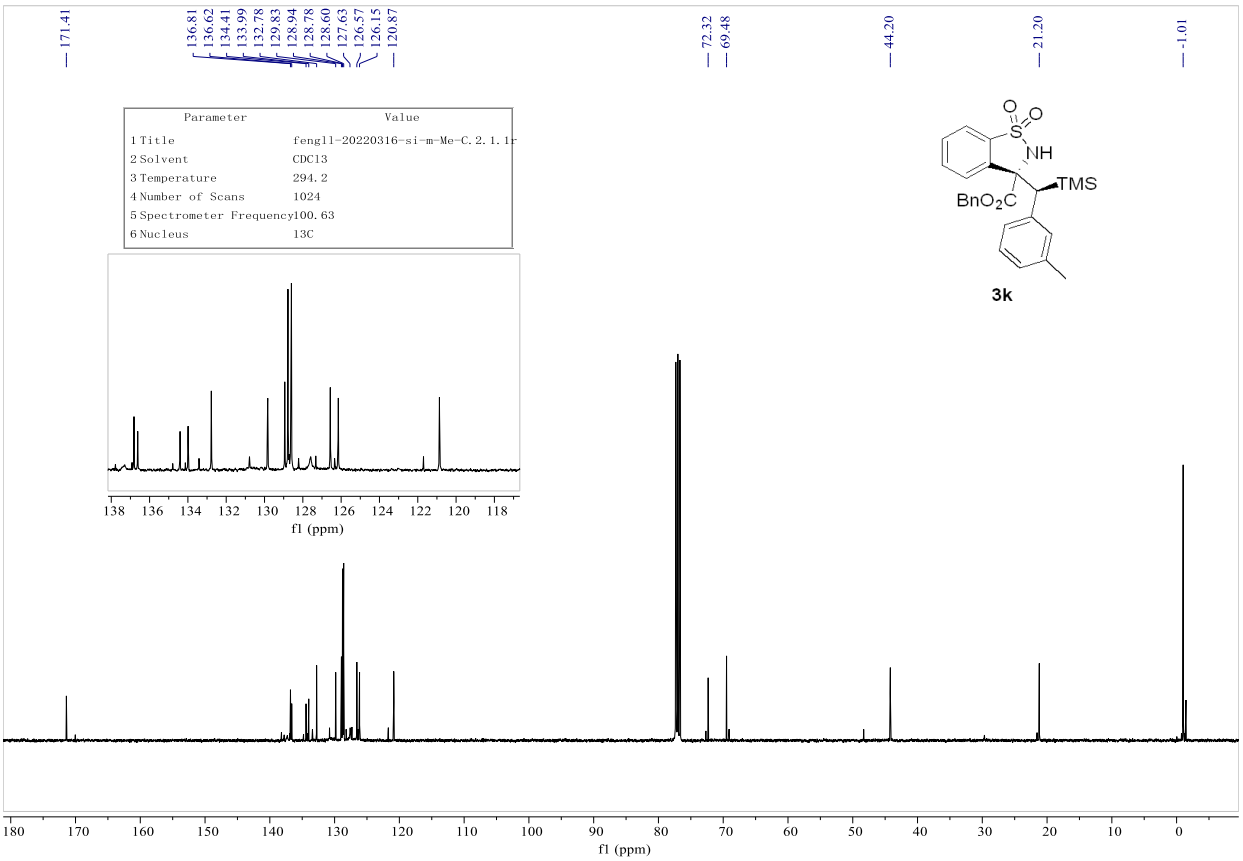

Major isomer
Minor isomer
Major isomer
Minor isomer
Parameter
Value
1 Title
2 Solvent
CDCl3
3 Temperature
294.6
4 Number of Scans
16
5 Spectrometer Frequency
400.18
6 Nucleus
1H
NH
TMS
3j
f1 (ppm)
f1 (ppm)
f1 (ppm)

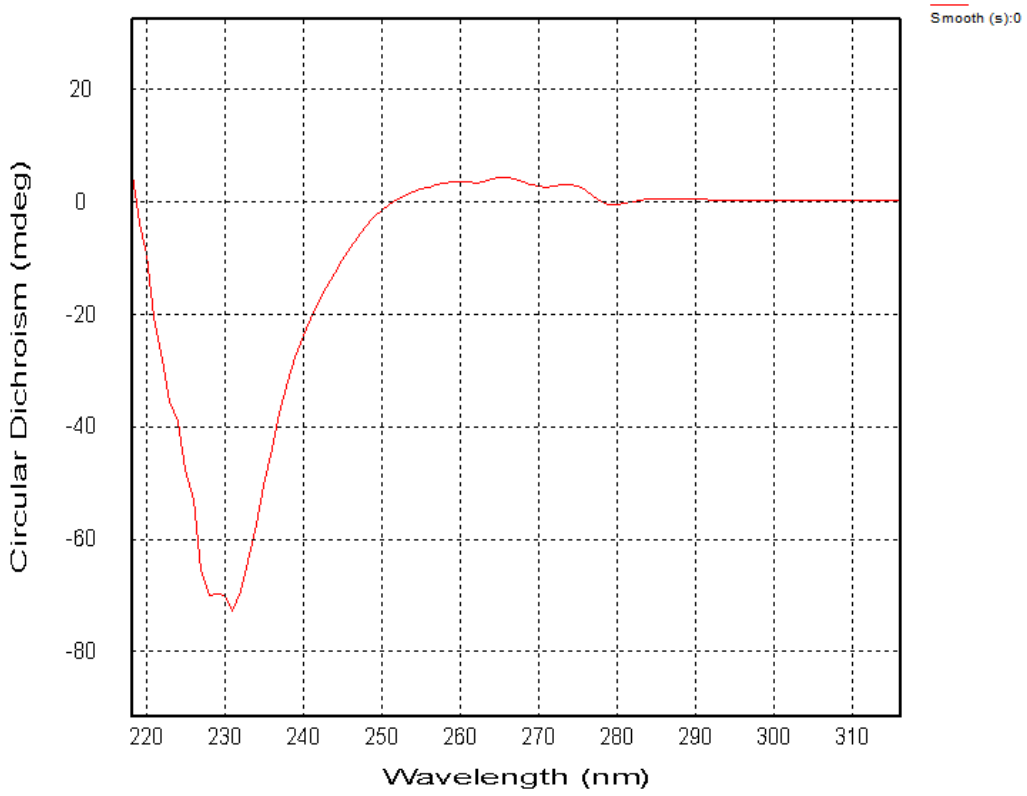

171.64
137.20
135.04
134.04
132.75
132.33
132.20
129.06
128.93
128.75
128.66
128.61
128.33
127.85
127.71
126.03
125.84
121.69
72.25
69.48
44.95
-0.93
Parameter Value
1 Title fengll-20220322-ya-Na-cat.4.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
NH
TMS
BnO2C
3j
f1 (ppm)
f1 (ppm)
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)

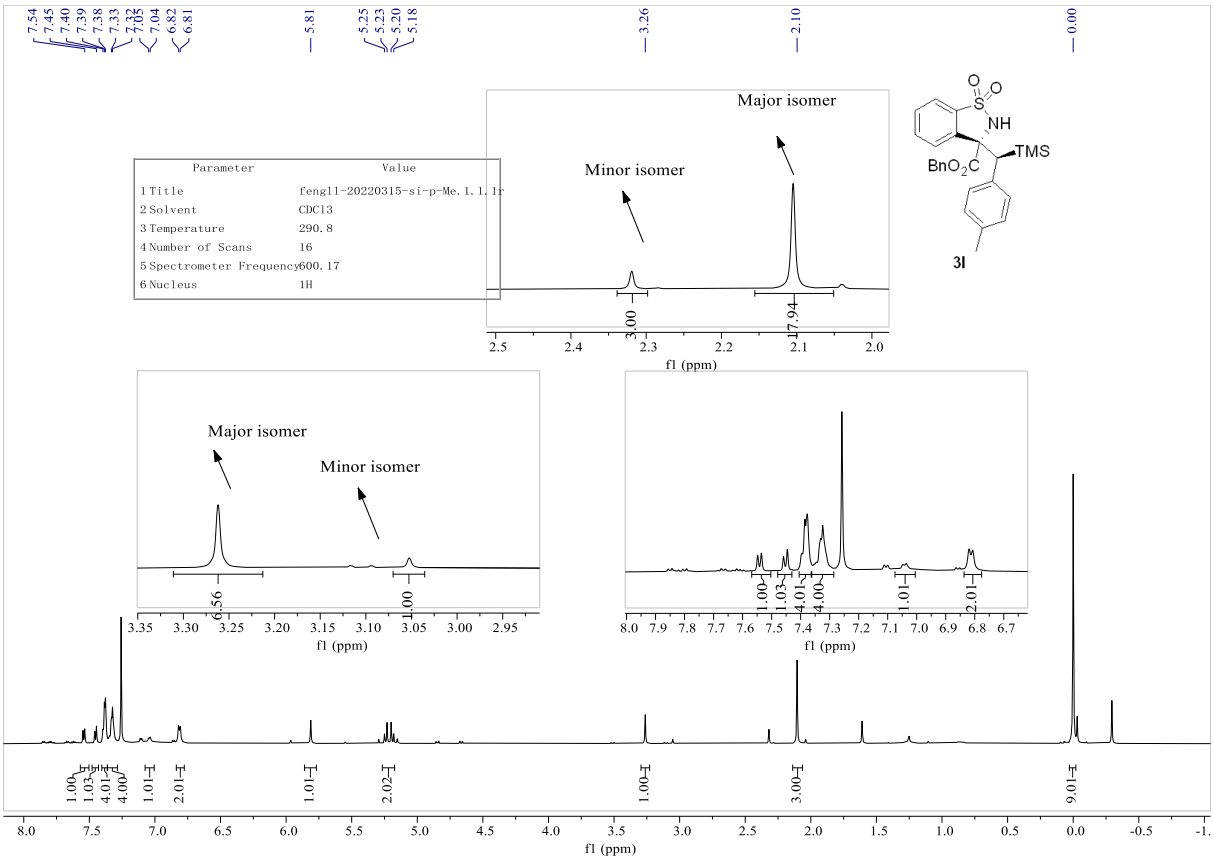
3k

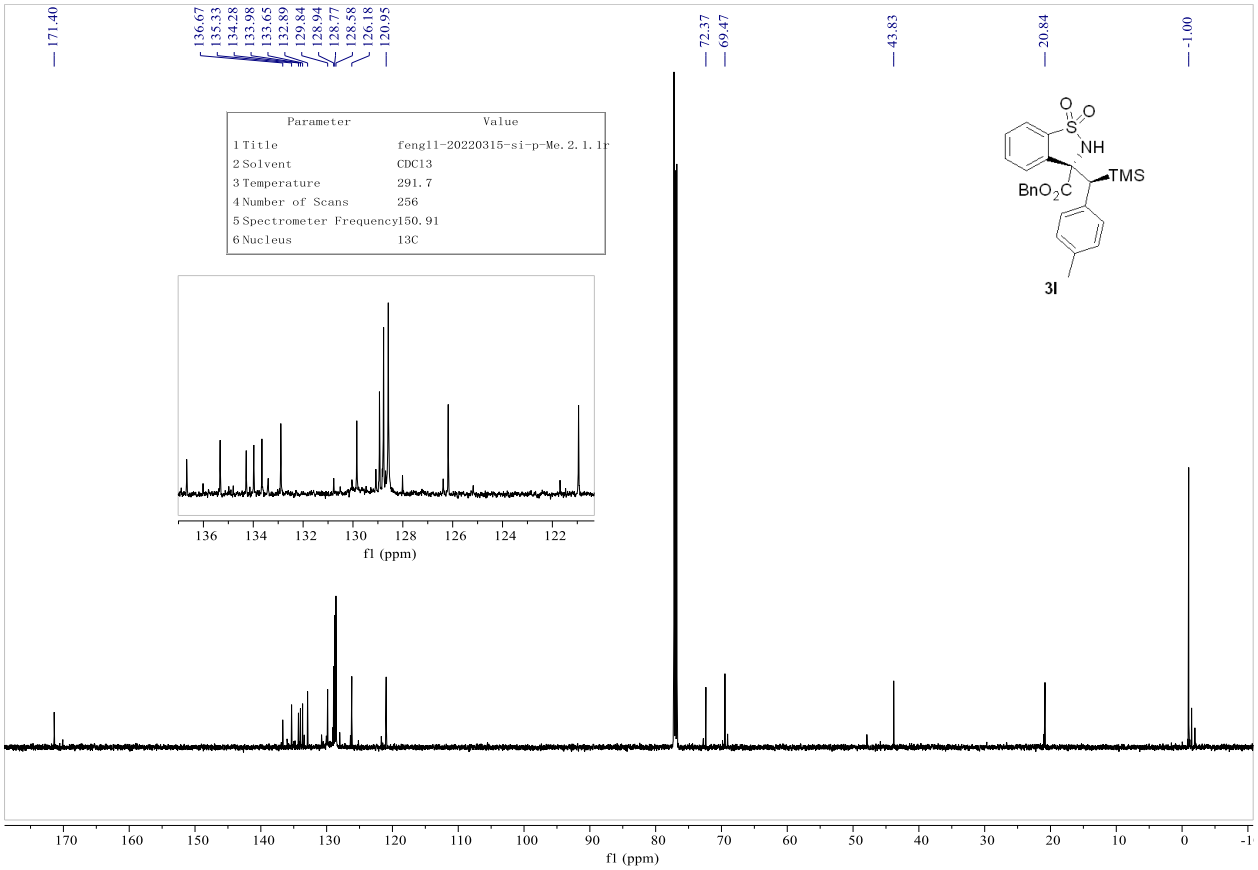

Major isomer
Minor isomer
Parameter Value
1 Title fengll-20220316-si-m-Me. 1. 1. 1r
2 Solvent CDCl3
3 Temperature 293. 3
4 Number of Scans 16
5 Spectrometer Frequency 400. 18
6 Nucleus 1H
3k
f1 (ppm)

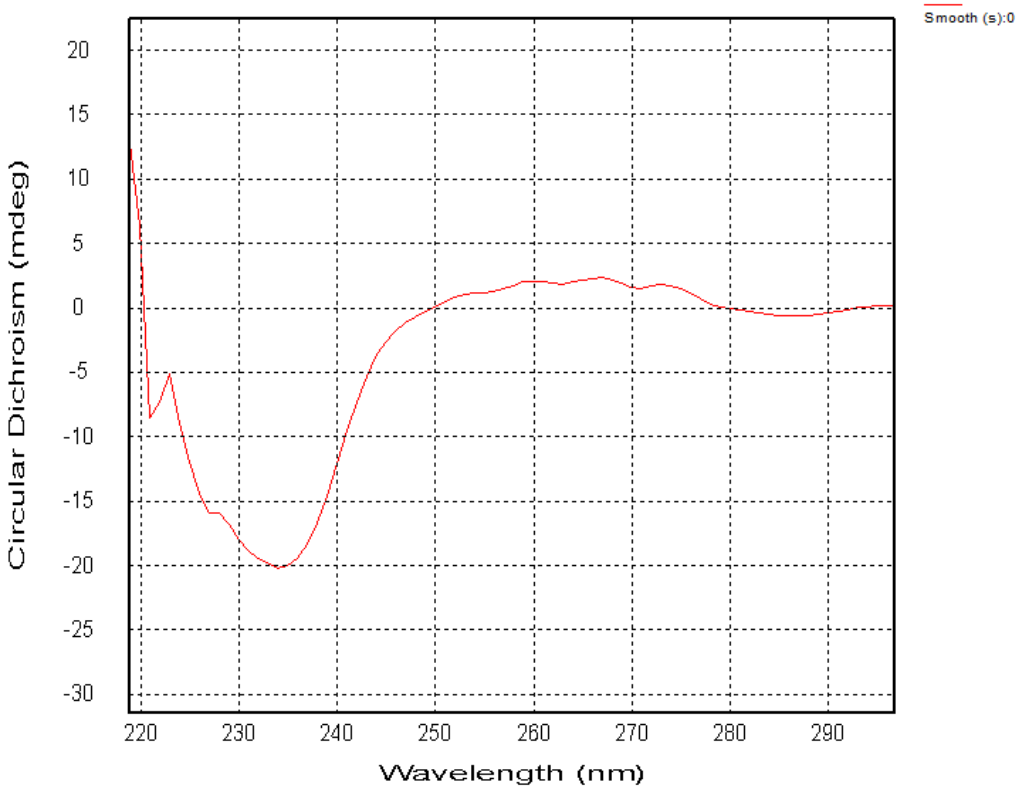

Parameter Value
1 Title fengll-20220316-si-m-Me-C. 2. 1. 1r
2 Solvent CDCl3
3 Temperature 294. 2
4 Number of Scans 1024
5 Spectrometer Frequency 100. 63
6 Nucleus 13C
3k
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
220
230
240
250
260
270
280
290
300
310
Wavelength (nm)

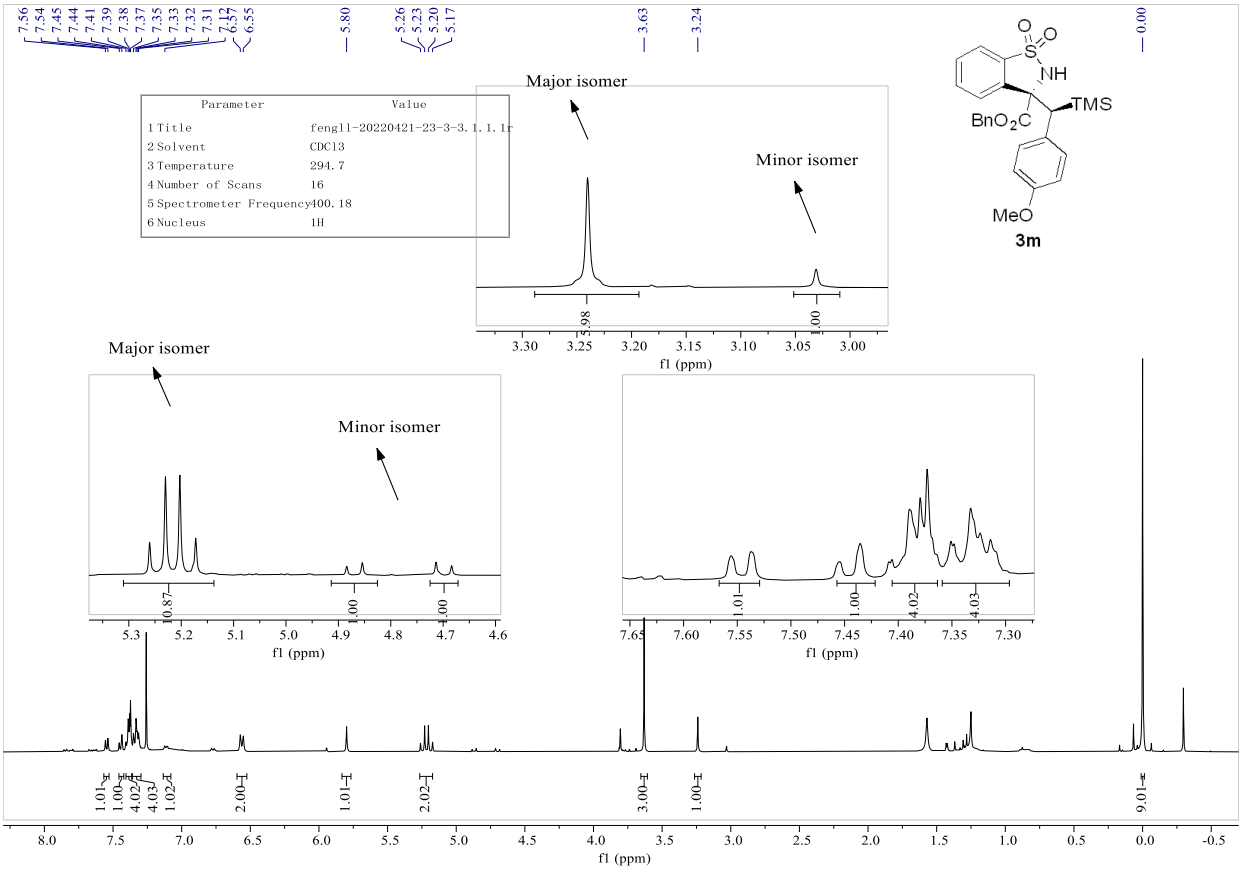
3l

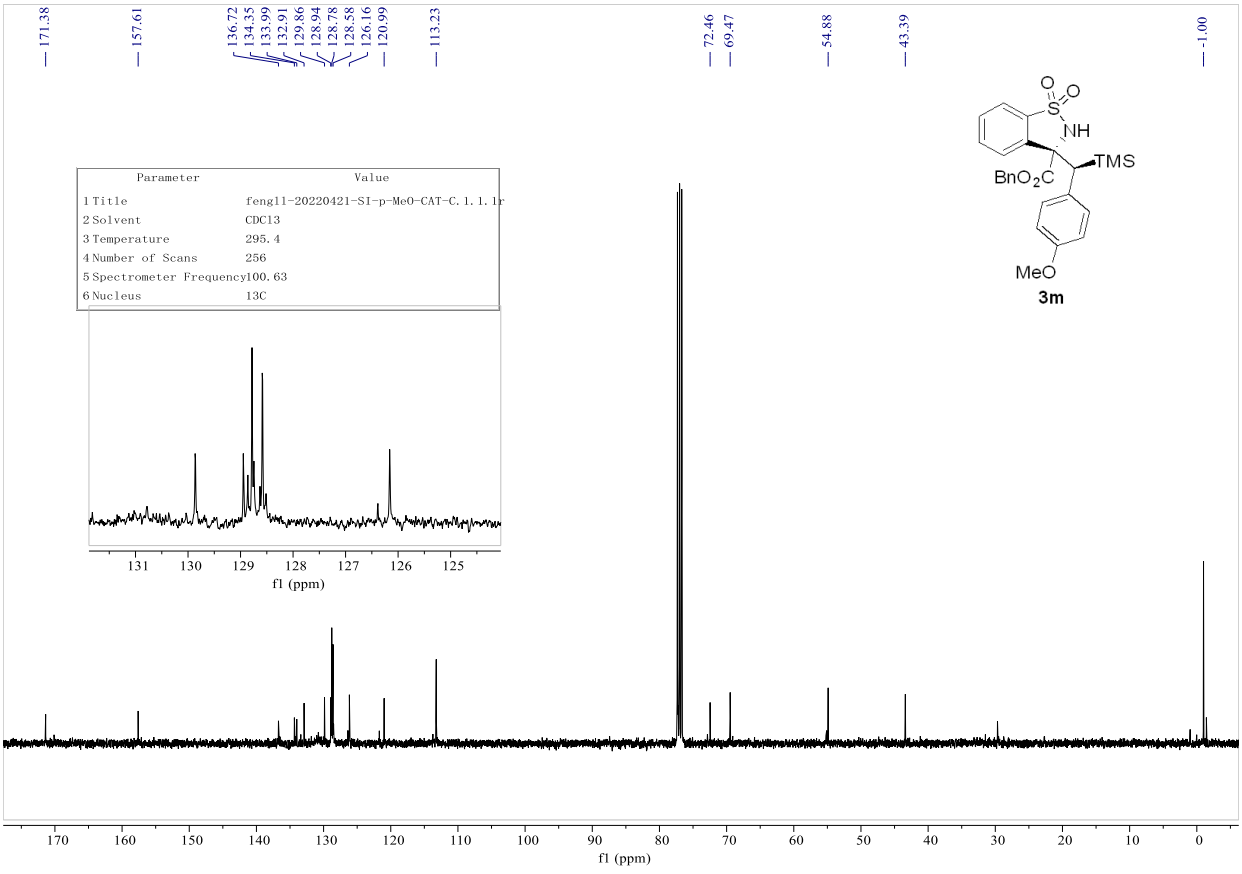

Parameter Value
1 Title fengll-20220315-si-p-Me. 1. 1. 1r
2 Solvent CDCl3
3 Temperature 290. 8
4 Number of Scans 16
5 Spectrometer Frequency 600. 17
6 Nucleus 1H
Major isomer
Minor isomer
3l
f1 (ppm)
Major isomer
Minor isomer
f1 (ppm)
f1 (ppm)

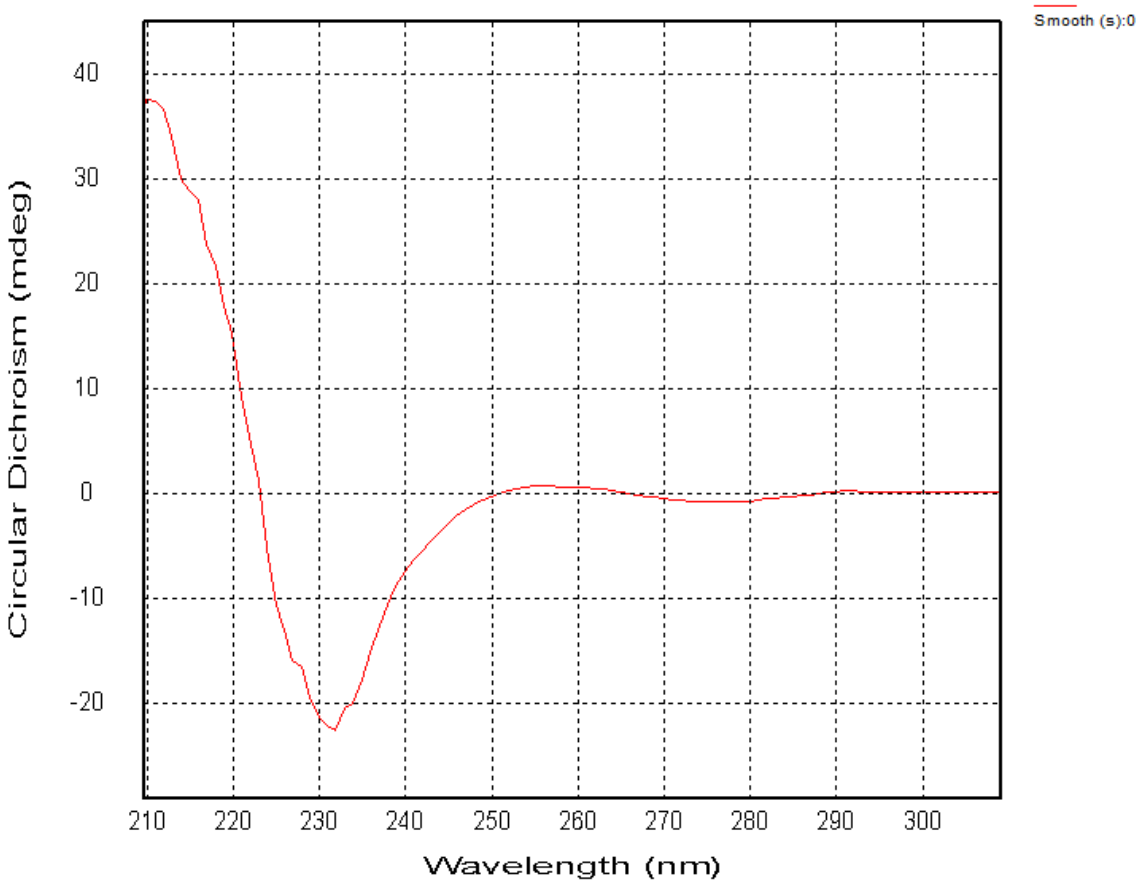

171.40
136.67
135.33
134.28
133.98
133.65
132.89
129.84
128.94
128.77
128.58
126.18
120.95
72.37
69.47
43.83
20.84
-1.00
Parameter Value
1 Title fengll-20220315-si-p-Me.2.1.1r
2 Solvent CDCl3
3 Temperature 291.7
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
NH
TMS
BnO2C
3l
f1 (ppm)
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)

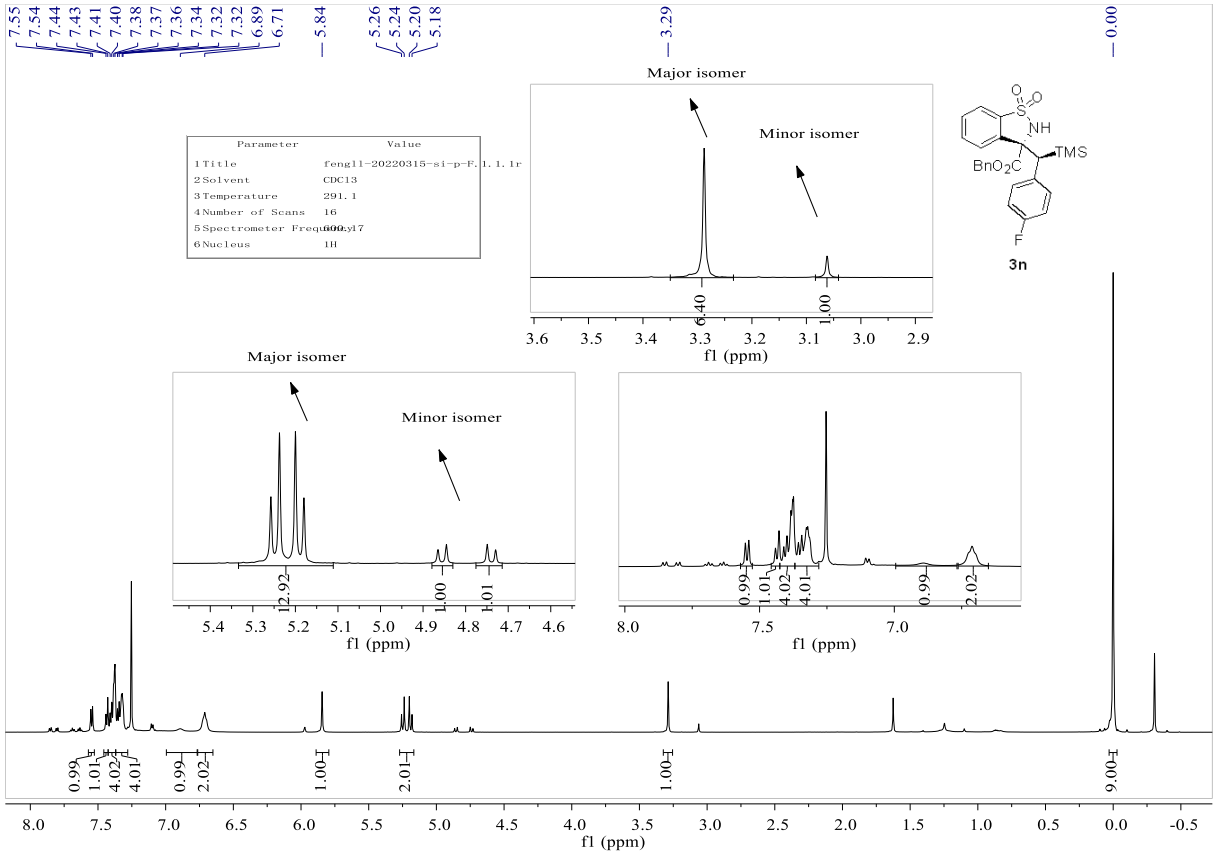
3m

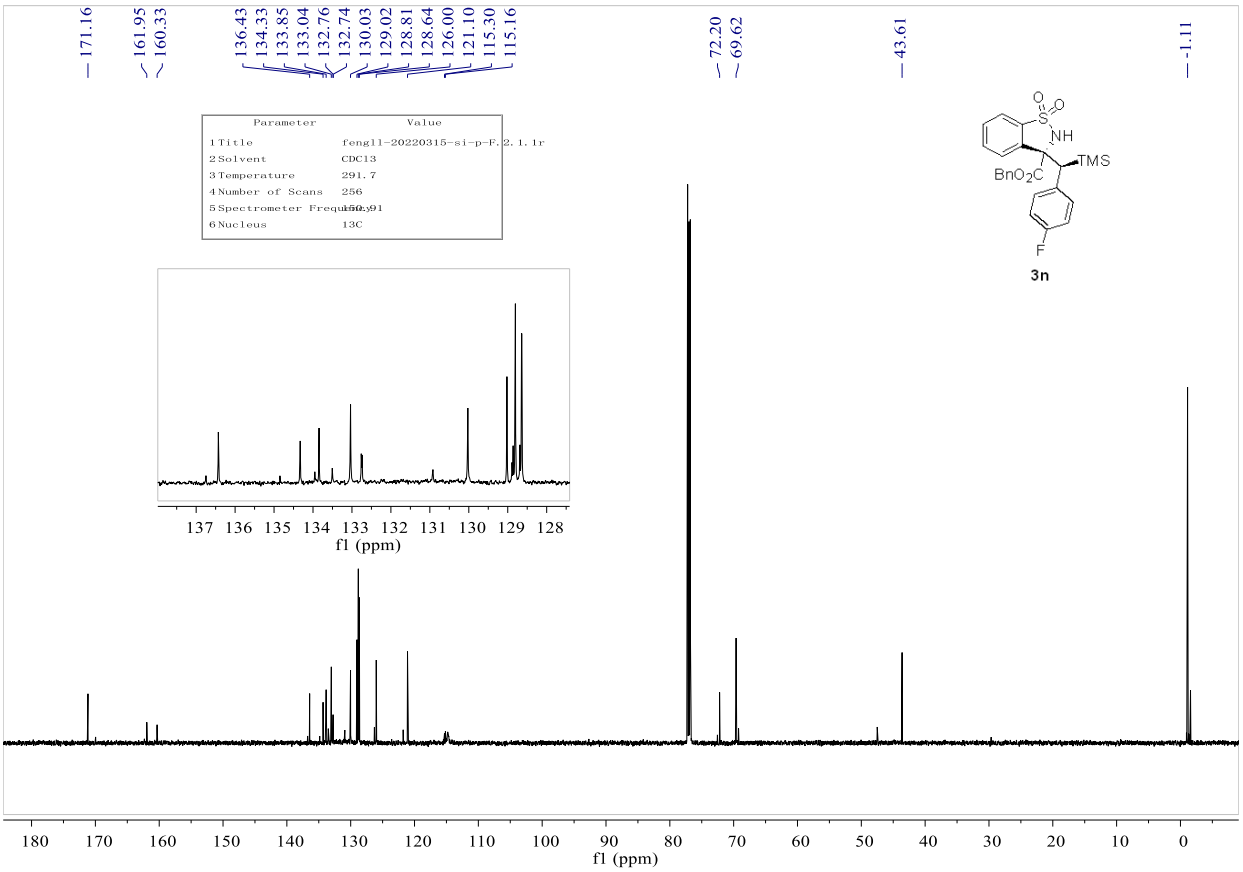

Parameter Value
1 Title fengll-20220421-23-3-3.1.1.1r
2 Solvent CDCl3
3 Temperature 294.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
Major isomer
Minor isomer
3m
f1 (ppm)

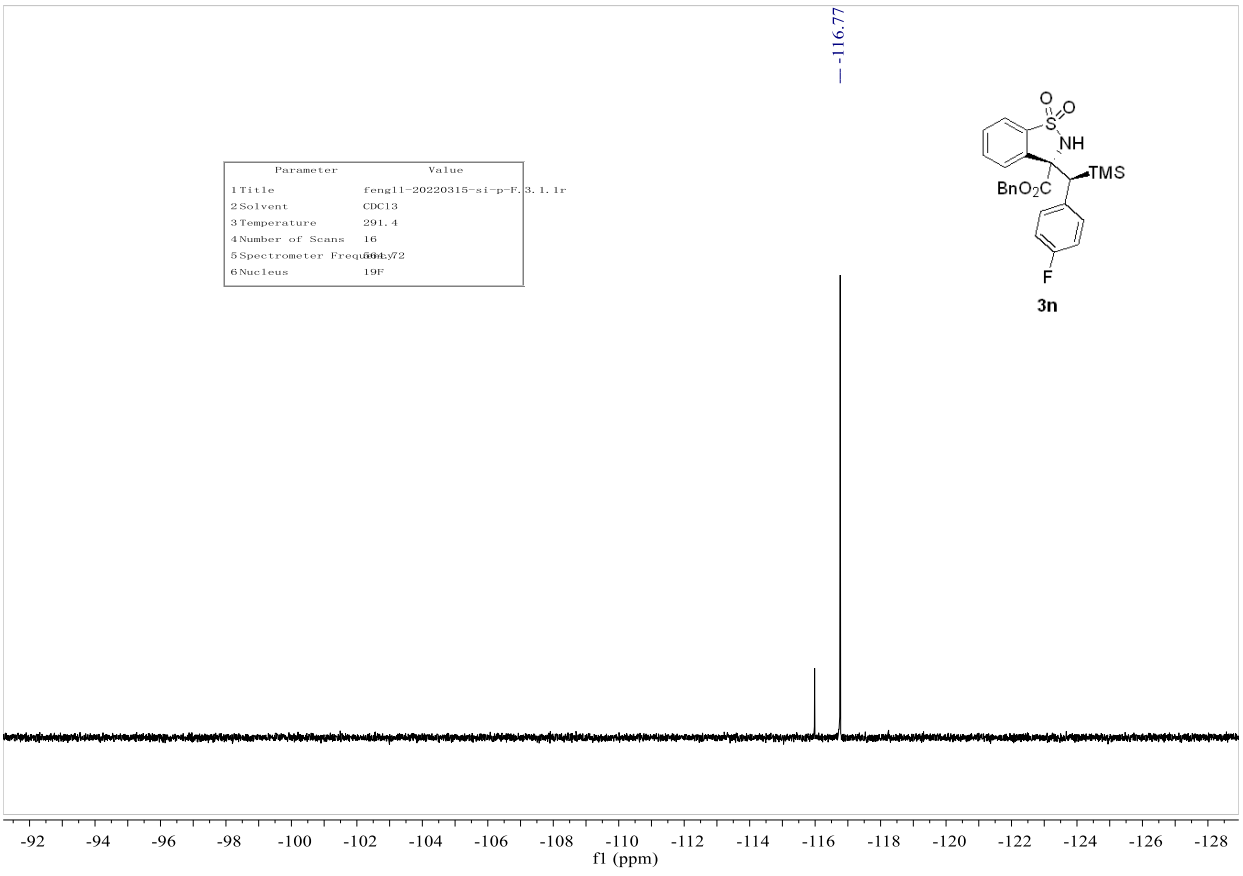

Parameter Value
1 Title fengll-20220421-SI-p-MeO-CAT-C.1.1.1r
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
3m
f1 (ppm)

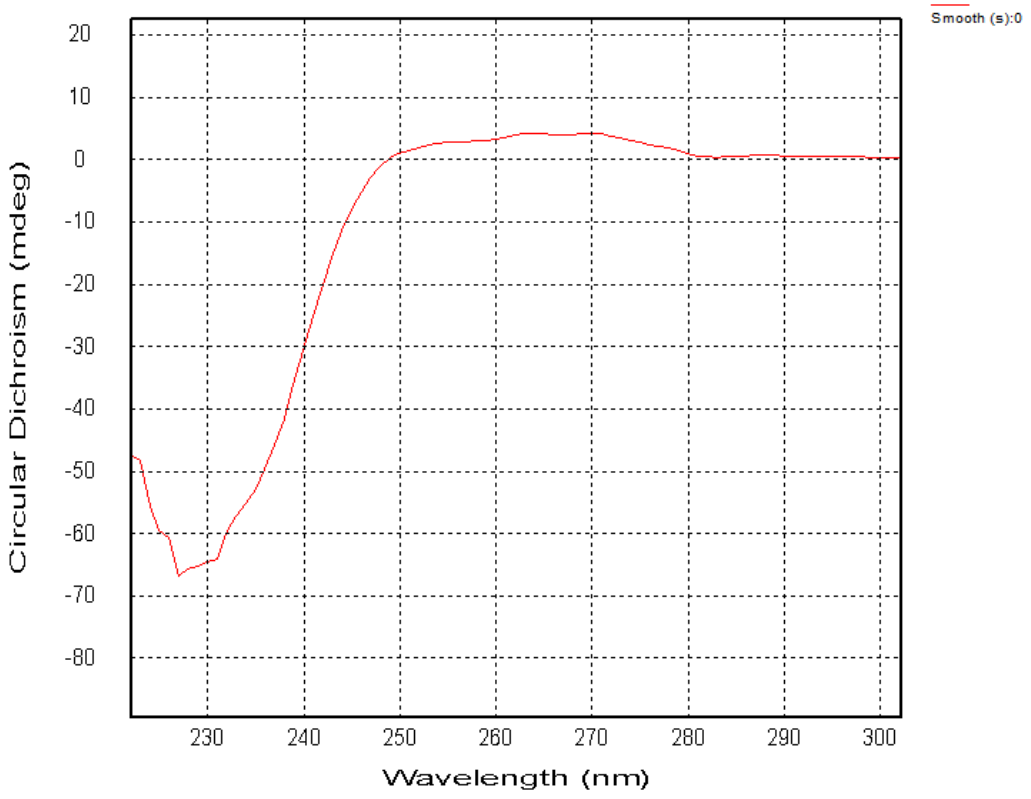

Smooth (s):0
Circular Dichroism (mdeg)
40
30
20
10
0
-10
-20
210
220
230
240
250
260
270
280
290
300
Wavelength (nm)

3n

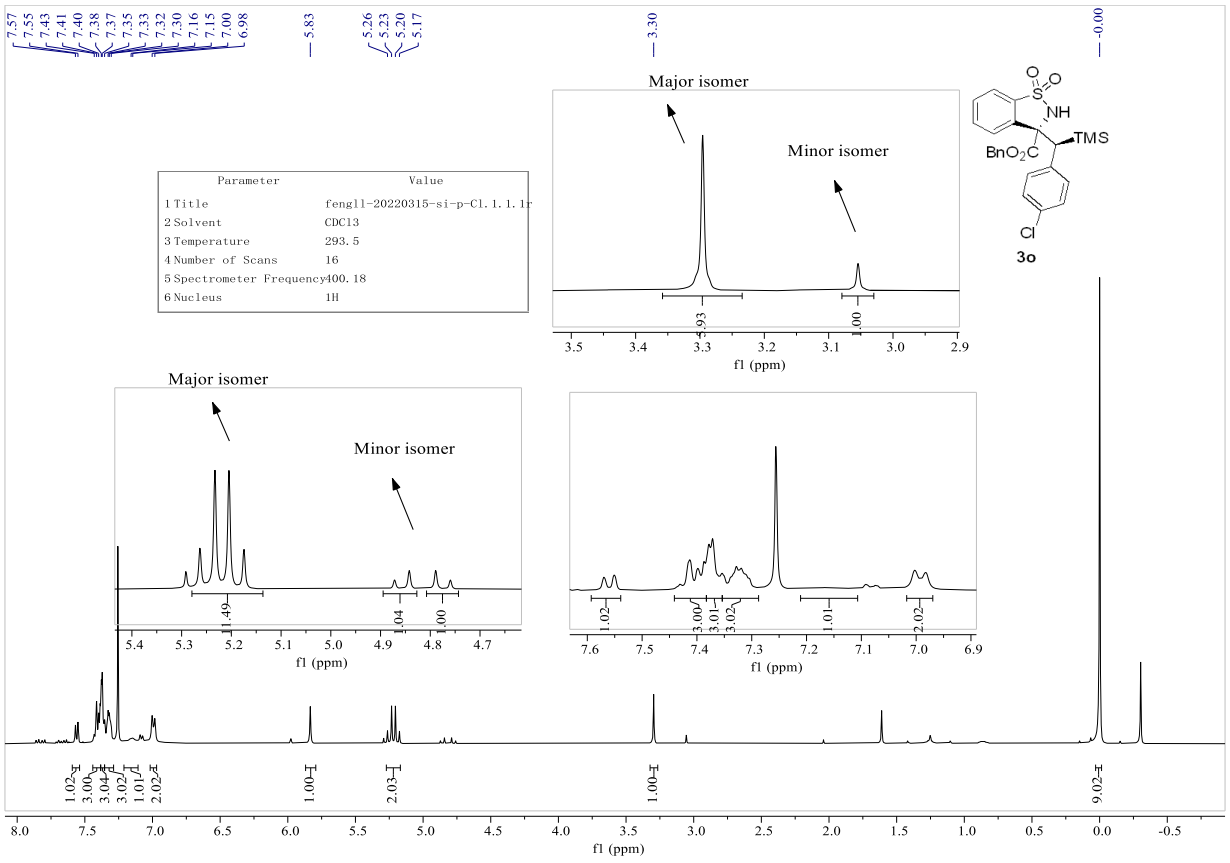

Major isomer
Minor isomer
NH
TMS
BnO2C
F
3n
f1 (ppm)

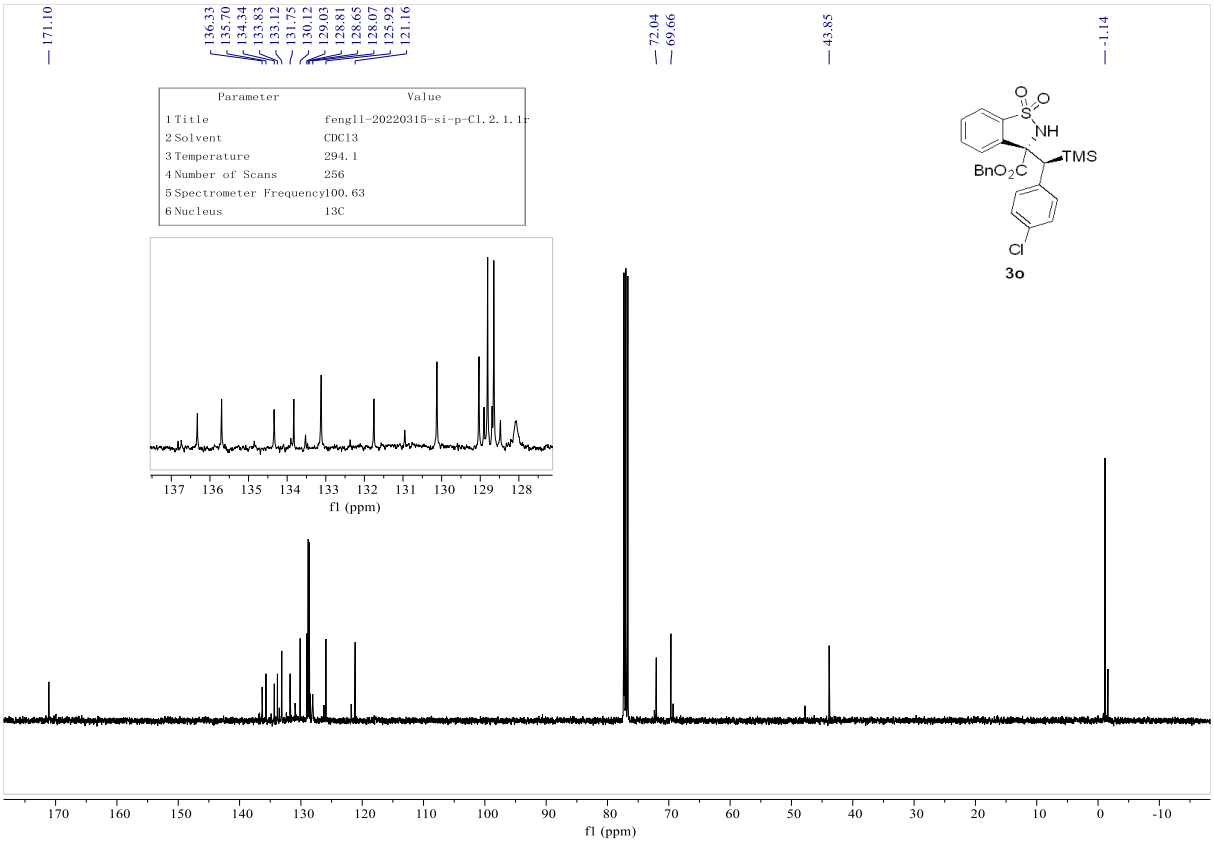

171.16
161.95
160.33
136.43
134.33
133.85
133.04
132.76
132.74
130.03
129.02
128.81
128.64
126.00
121.10
115.30
115.16
72.20
69.62
43.61
-1.11
Parameter Value
1 Title fengll-20220315-si-p-F.2.1.1r
2 Solvent CDCl3
3 Temperature 291.7
4 Number of Scans 256
5 Spectrometer Frequency
6 Nucleus 13C
137 136 135 134 133 132 131 130 129 128
f1 (ppm)
NH
TMS
BnO2C
F
3n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

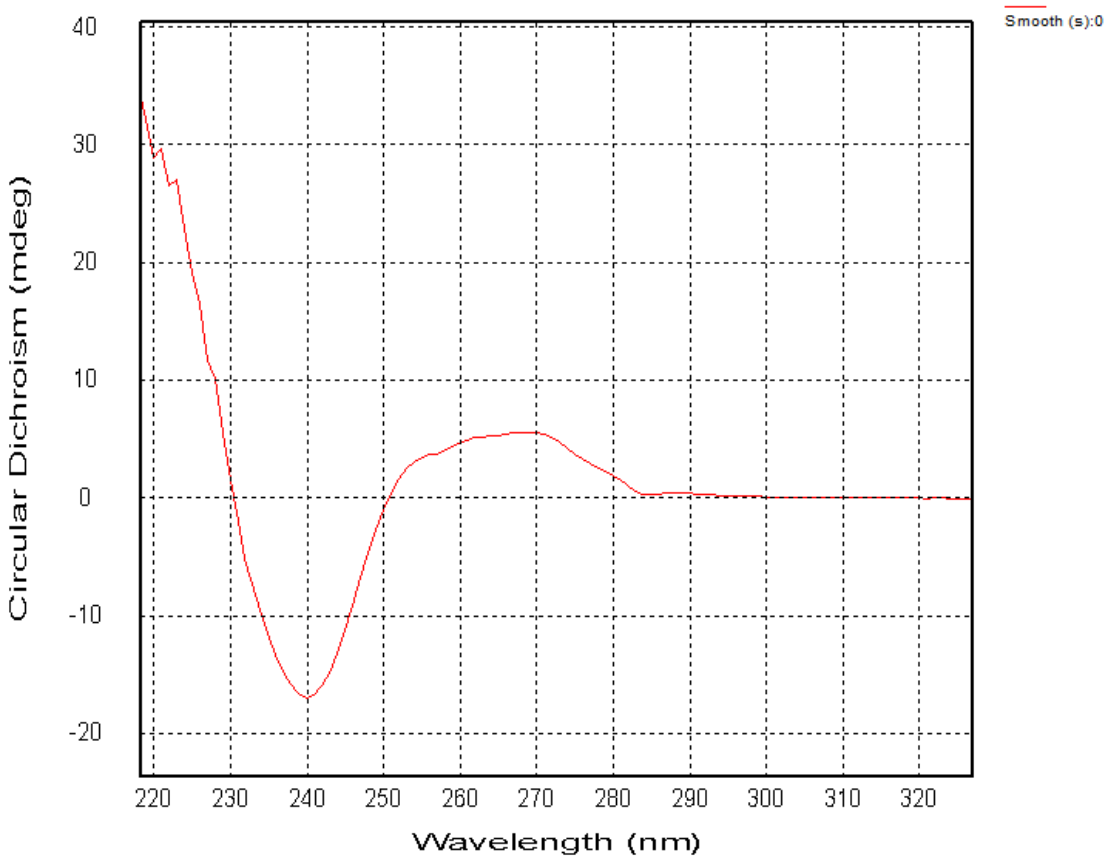

-116.77
Parameter Value
1 Title fengll-20220315-si-p-F.3.1.1r
2 Solvent CDCl3
3 Temperature 291.4
4 Number of Scans 16
5 Spectrometer Frequency
6 Nucleus 19F
NH
TMS
BnO2C
F
3n
-92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)

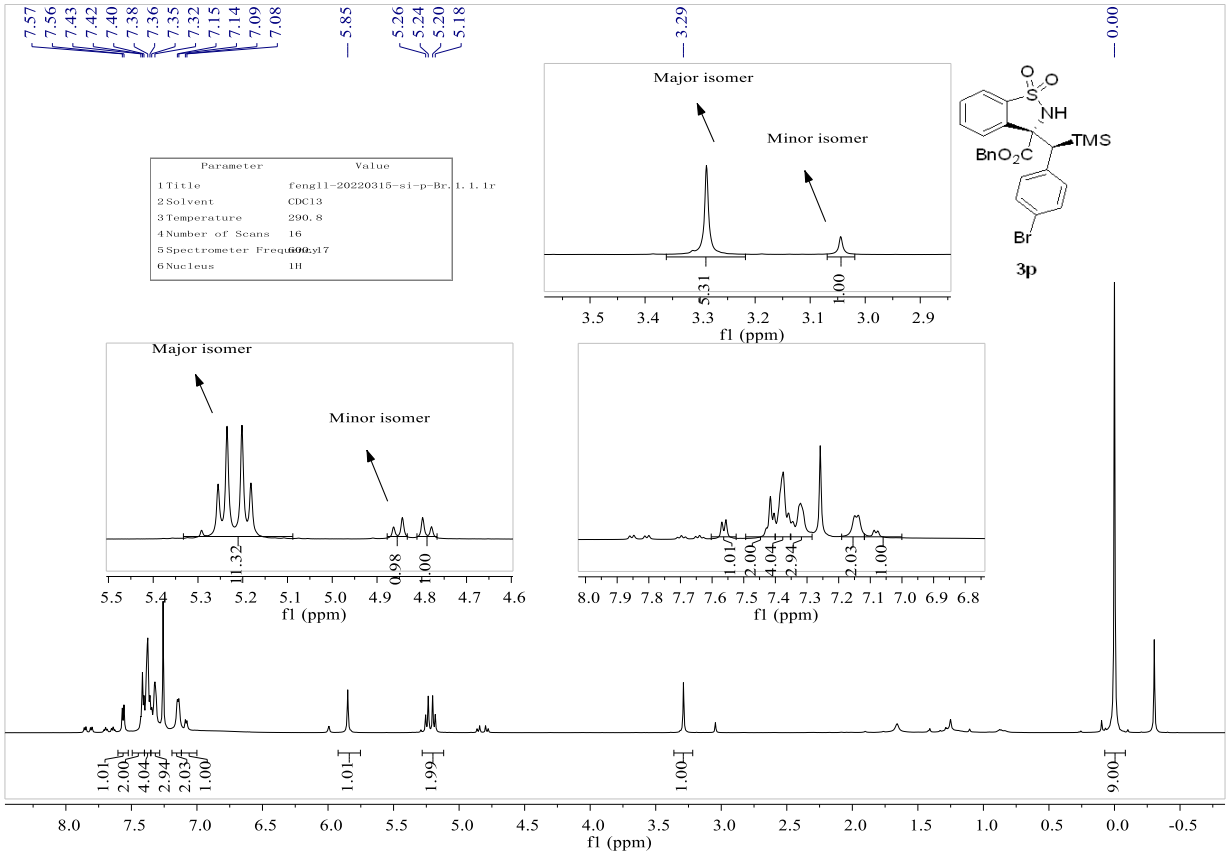
3o

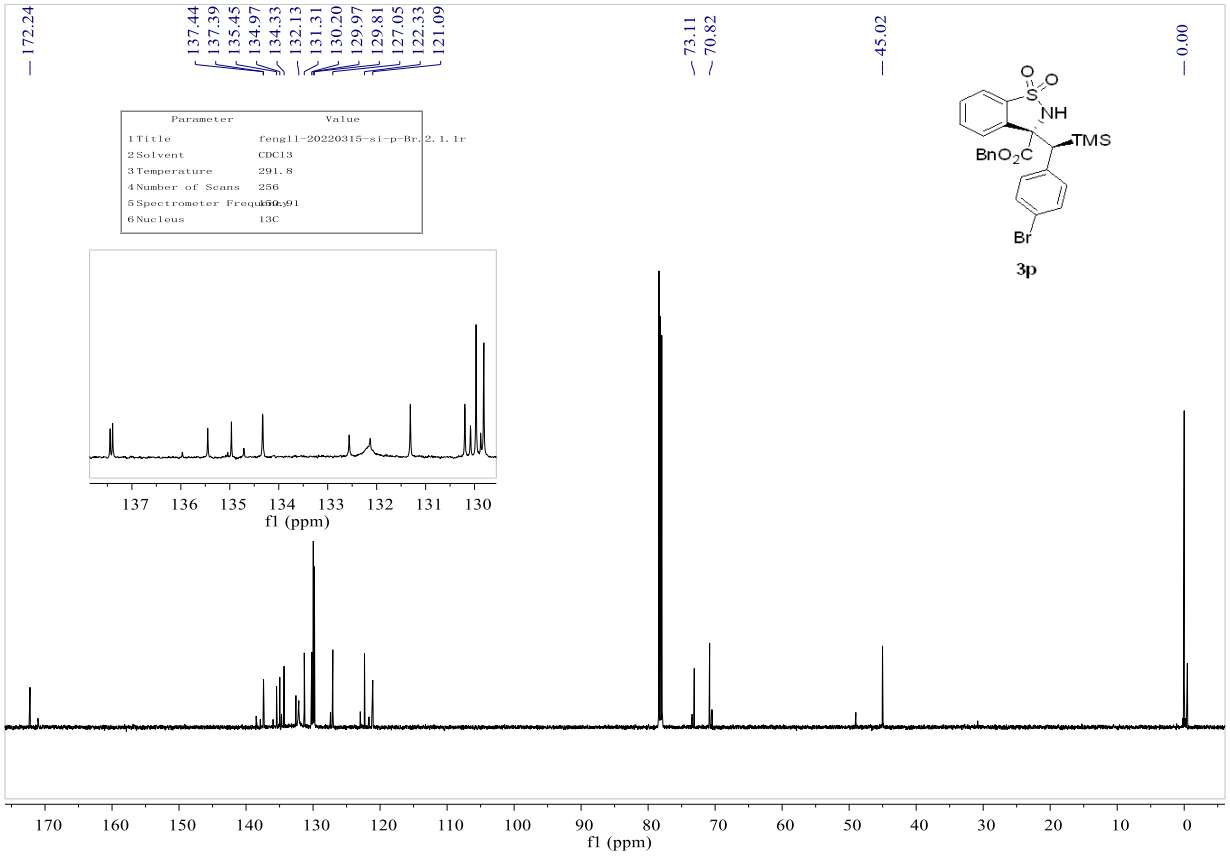

Major isomer
Minor isomer
Major isomer
Minor isomer
Parameter Value
1 Title fengll-20220315-si-p-Cl.1.1.1.1r
2 Solvent CDCl3
3 Temperature 293.5
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
fl (ppm)
3o

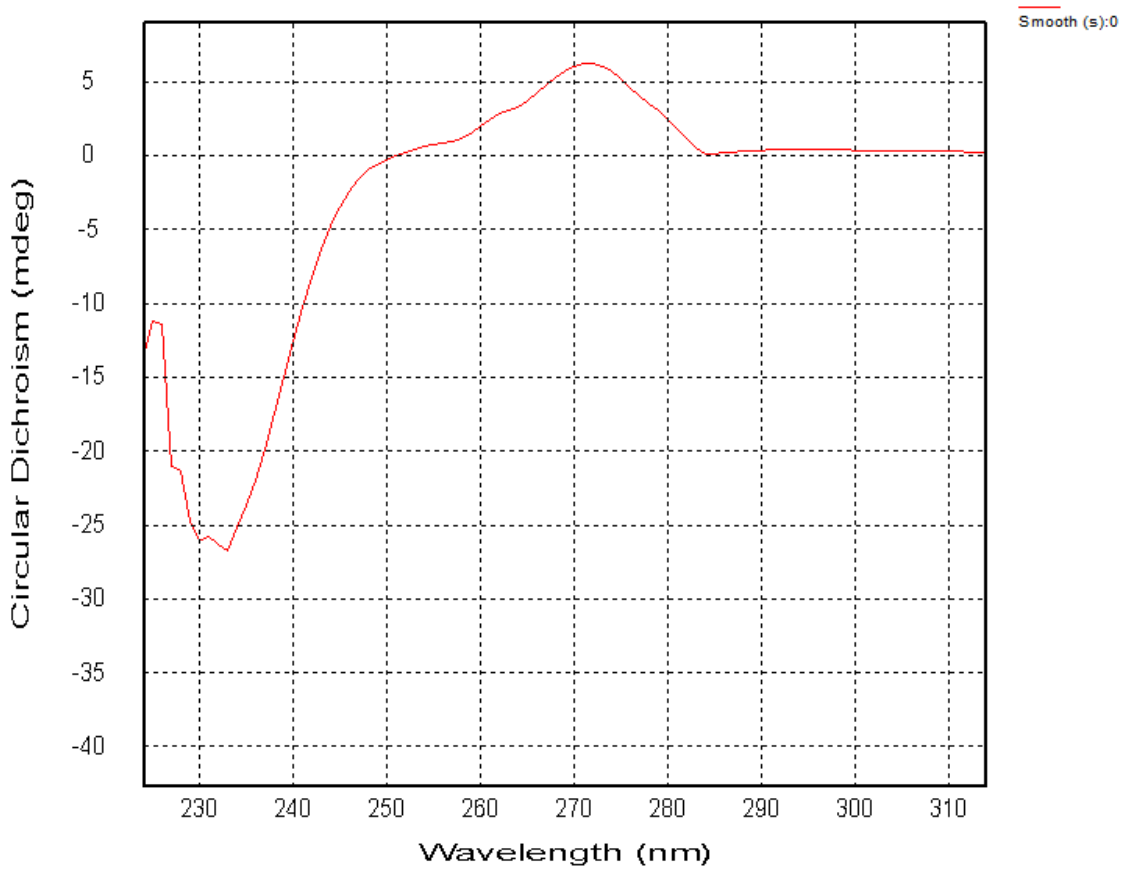

171.10
136.33
135.70
134.34
133.83
133.12
131.75
130.12
129.03
128.81
128.65
128.07
125.92
121.16
72.04
69.66
43.85
-1.14
Parameter Value
1 Title fengll-20220315-si-p-Cl.2.1.1r
2 Solvent CDCl3
3 Temperature 294.1
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
NH
TMS
BnO2C
Cl
3o
f1 (ppm)
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)

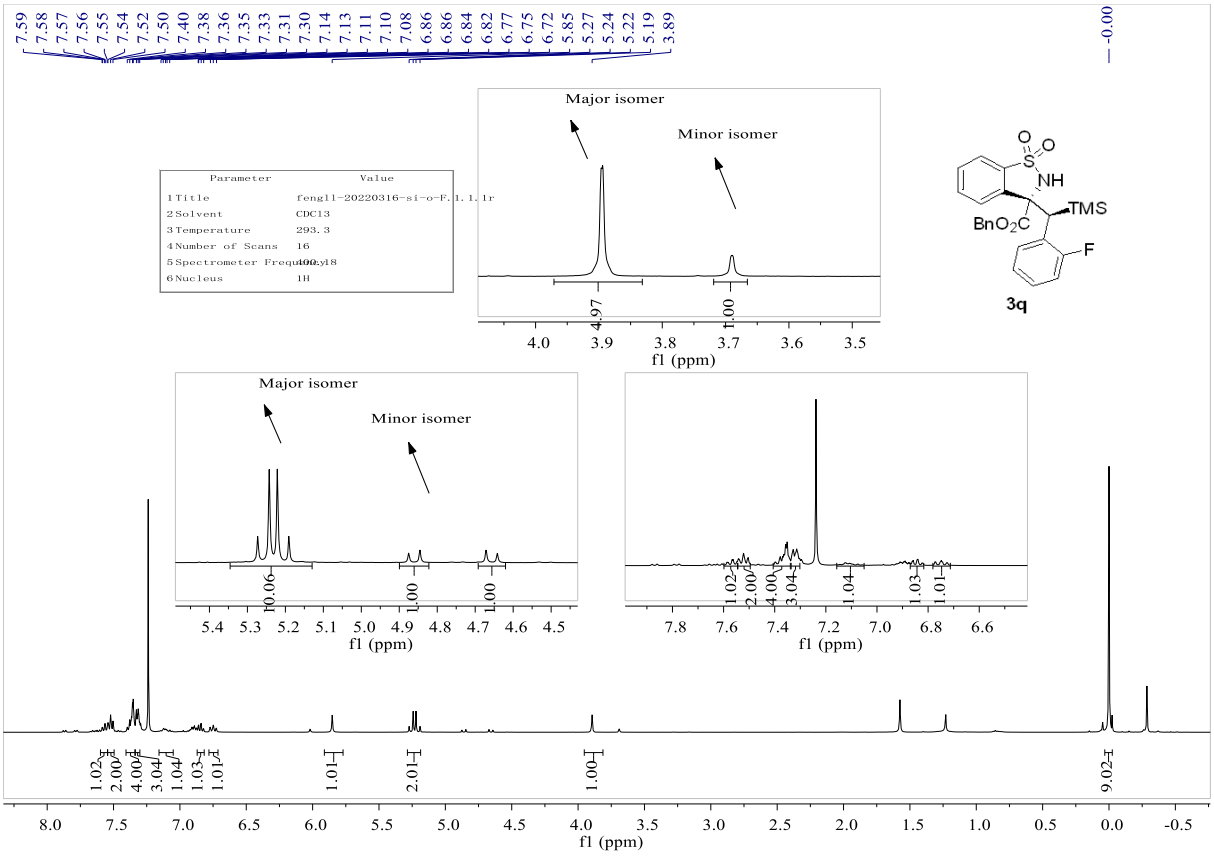
3p

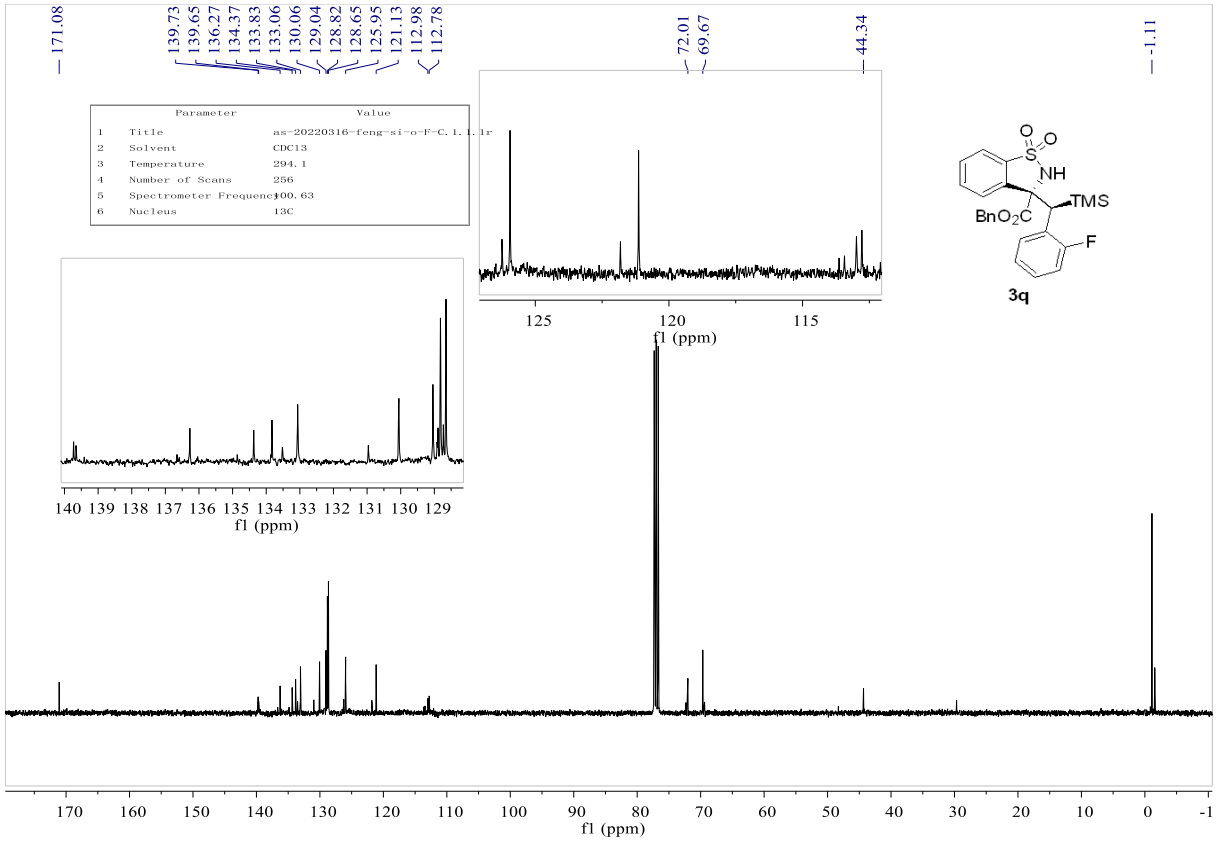

7.57 7.56 7.43 7.42 7.40 7.38 7.36 7.35 7.32 7.15 7.14 7.09 7.08
5.85
5.26 5.24 5.20 5.18
3.29
0.00
Major isomer
Minor isomer
Parameter Value
1 Title fengll-20220315-si-p-Br.1.1.1r
2 Solvent CDCl3
3 Temperature 290.8
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
NH
TMS
BnO2C
Br
3p
5.31
1.00
f1 (ppm)
11.32
0.98
1.00
1.01
2.00
4.04
2.94
2.03
1.00
1.01
1.99
1.00
9.00

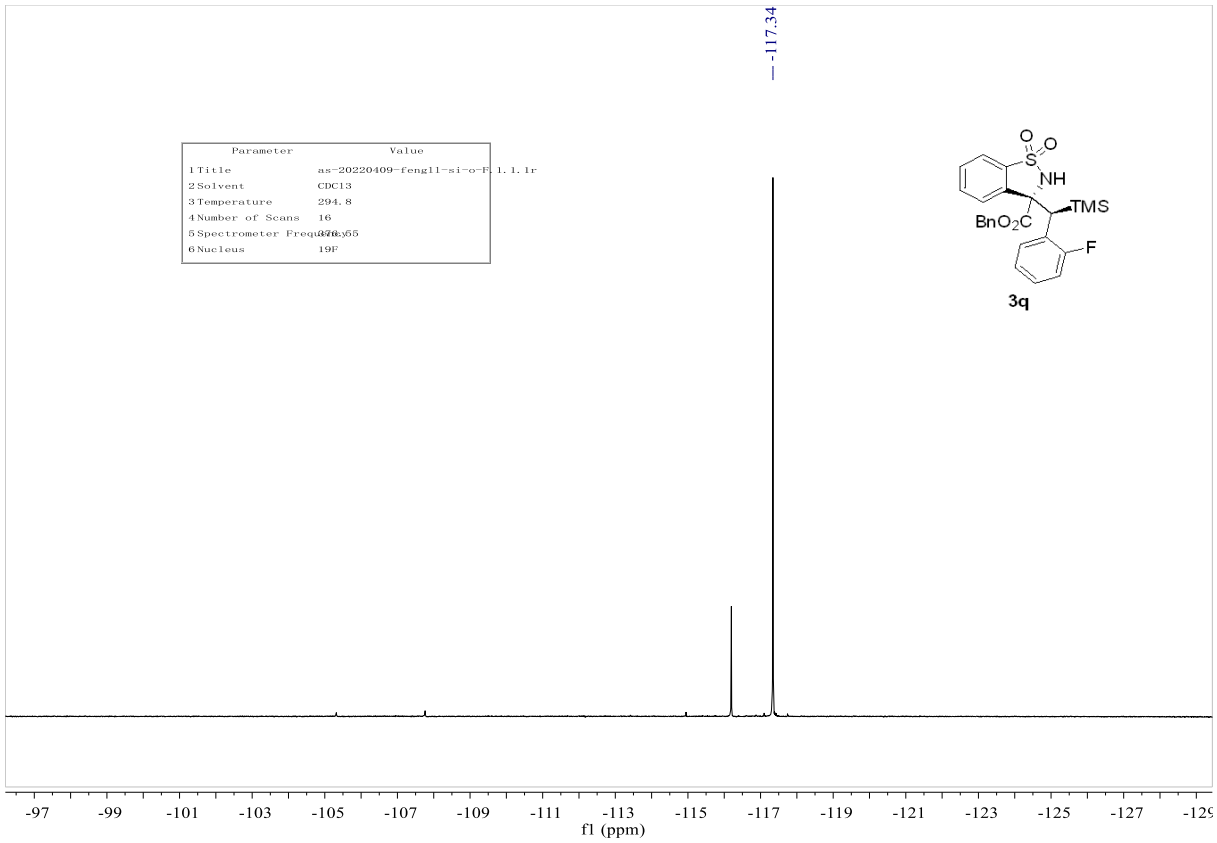

172.24
137.44 137.39 135.45 134.97 134.33 132.13 131.31 130.20 129.97 129.81 127.05 122.33 121.09
73.11
70.82
45.02
0.00
Parameter Value
1 Title fengll-20220315-si-p-Br.2.1.1r
2 Solvent CDCl3
3 Temperature 291.8
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
NH
TMS
BnO2C
Br
3p
f1 (ppm)

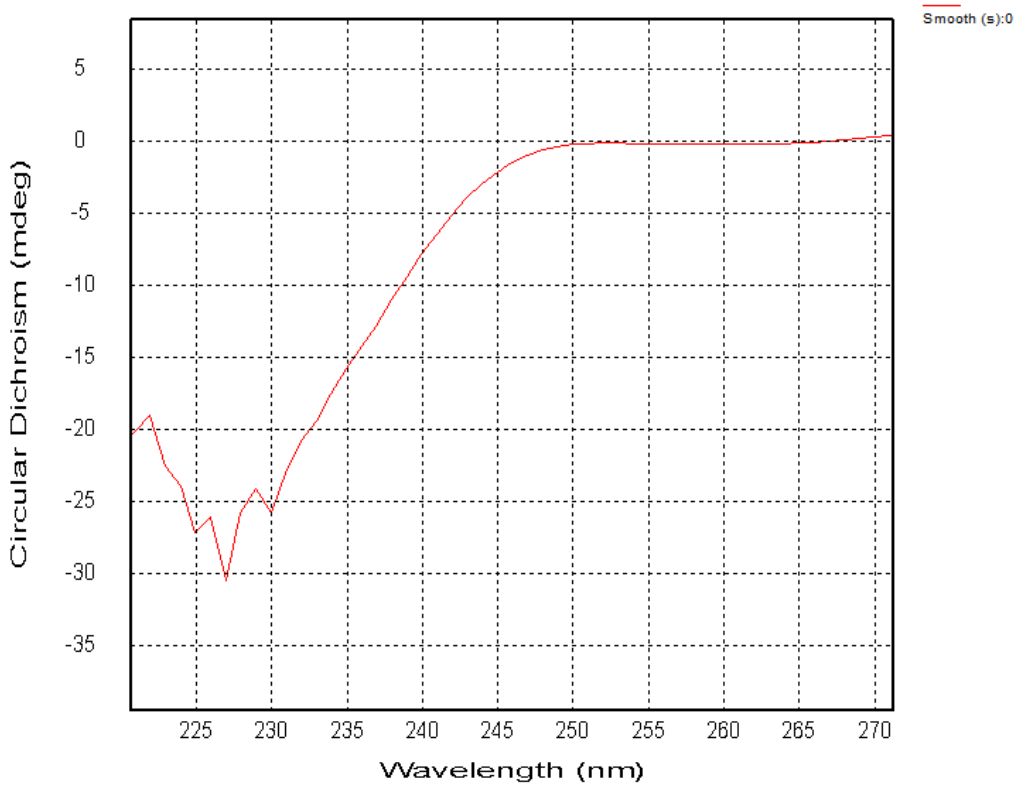

Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)

3q

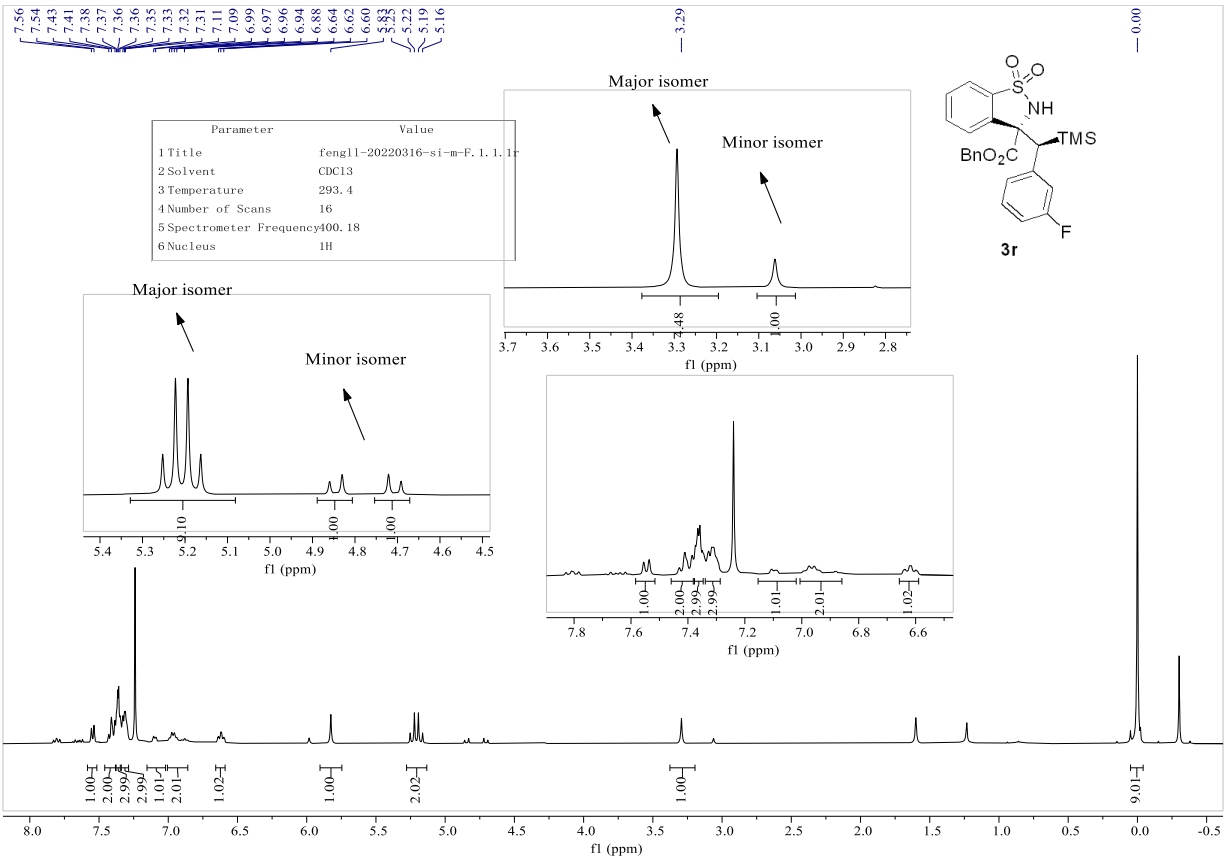

Major isomer
Minor isomer
f1 (ppm)
NH
TMS
BnO2C
F
3q

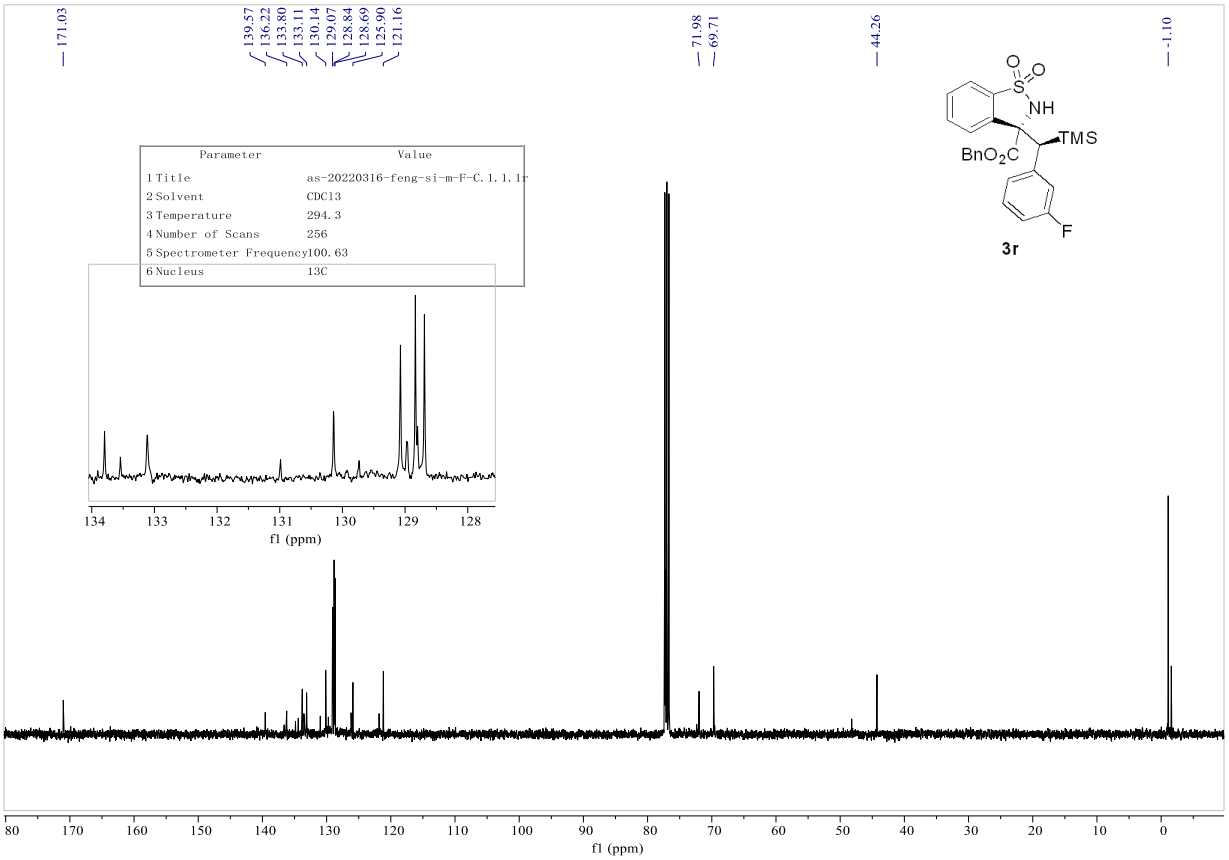

171.08
139.73
139.65
136.27
134.37
133.83
133.06
130.06
129.04
128.82
128.65
125.95
121.13
112.98
112.78
72.01
69.67
44.34
-1.11
Parameter Value
1 Title as-20220316-feng-si-o-F-C.1.1.1r
2 Solvent CDCl3
3 Temperature 294.1
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
125 120 115
f1 (ppm)
140 139 138 137 136 135 134 133 132 131 130 129
f1 (ppm)
O
O
S
NH
TMS
BnO2C
F
3q
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

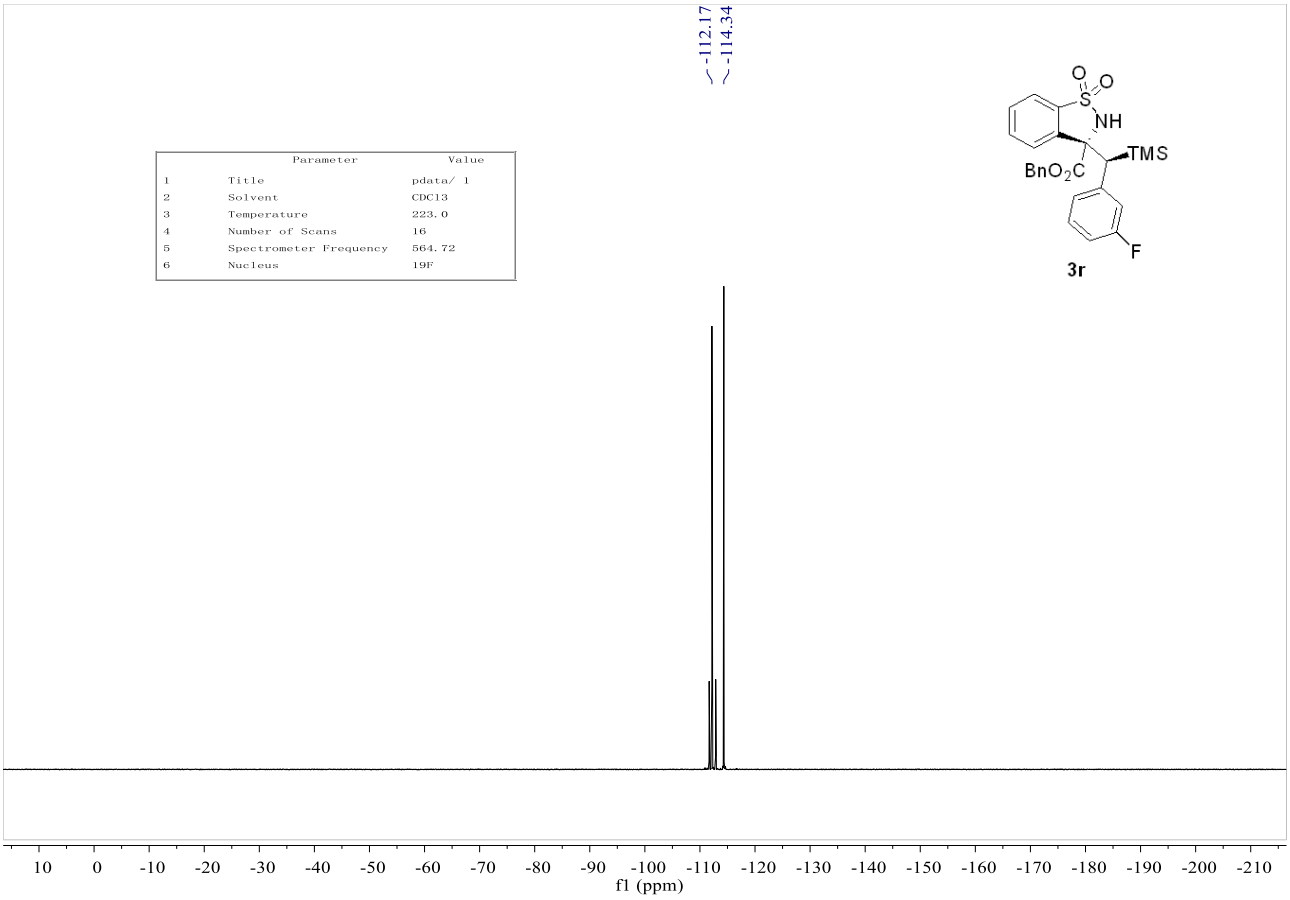

-117.34
Parameter Value
1 Title as-20220409-feng11-si-o-F.1.1.1r
2 Solvent CDCl3
3 Temperature 294.8
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
O
O
S
NH
TMS
BnO2C
F
3q
-97 -99 -101 -103 -105 -107 -109 -111 -113 -115 -117 -119 -121 -123 -125 -127 -129
f1 (ppm)

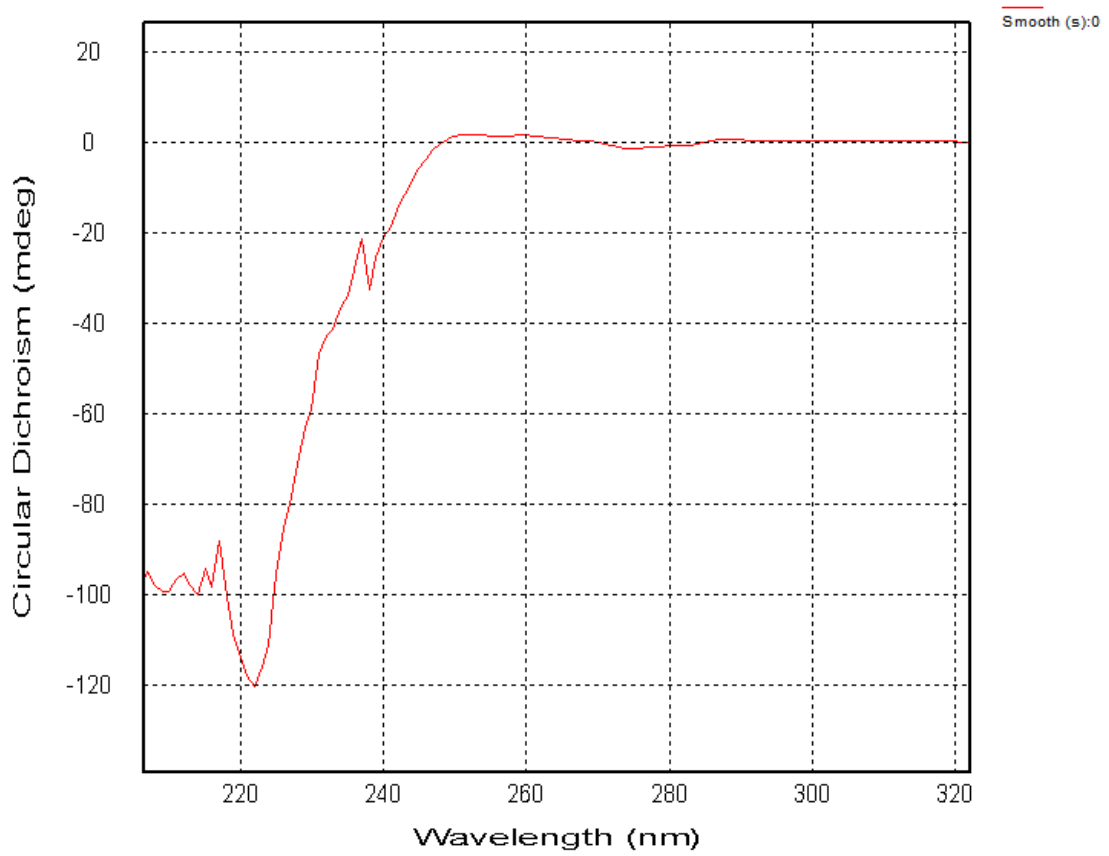

Smooth (s):0
Circular Dichroism (mdeg)
5
0
-5
-10
-15
-20
-25
-30
-35
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)

3r

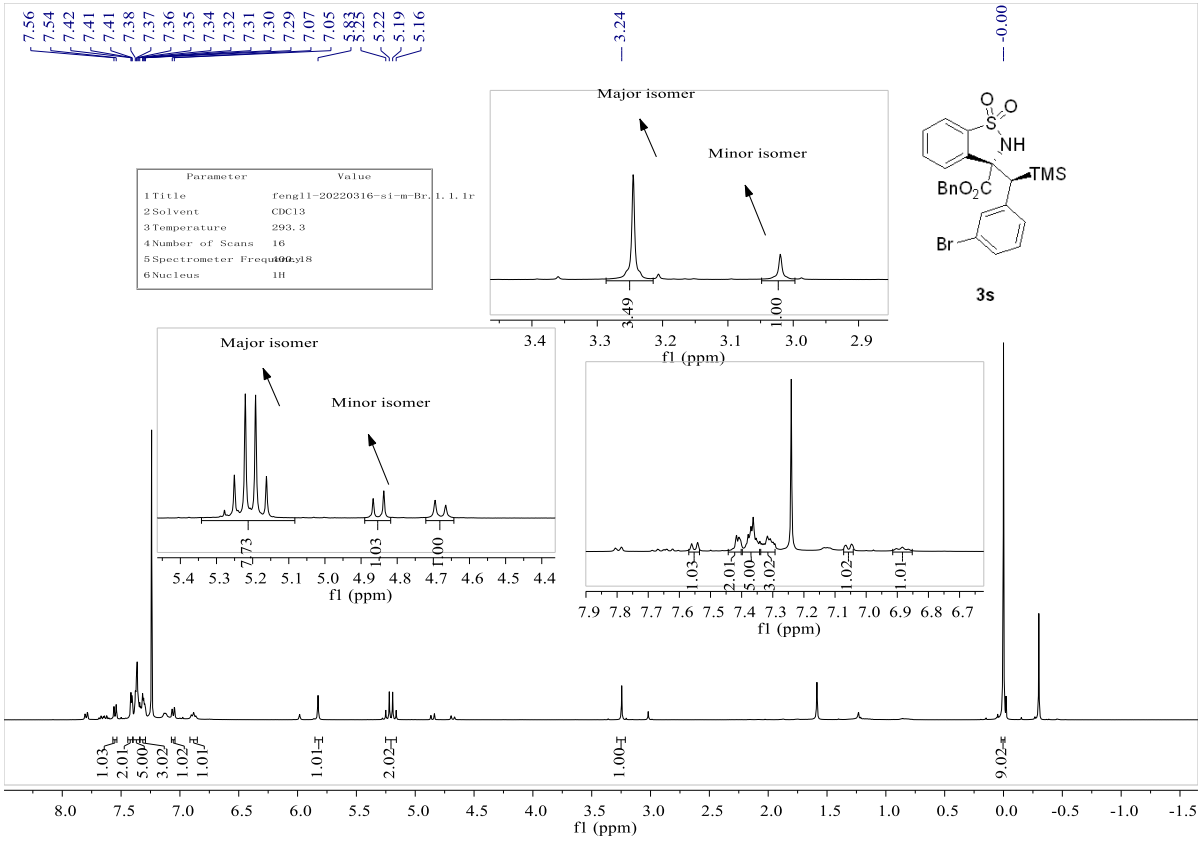

Major isomer
Minor isomer
Major isomer
Minor isomer
Parameter Value
1 Title fengll-20220316-si-m-F.1.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
NH
TMS
BnO2C
F
3r
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)

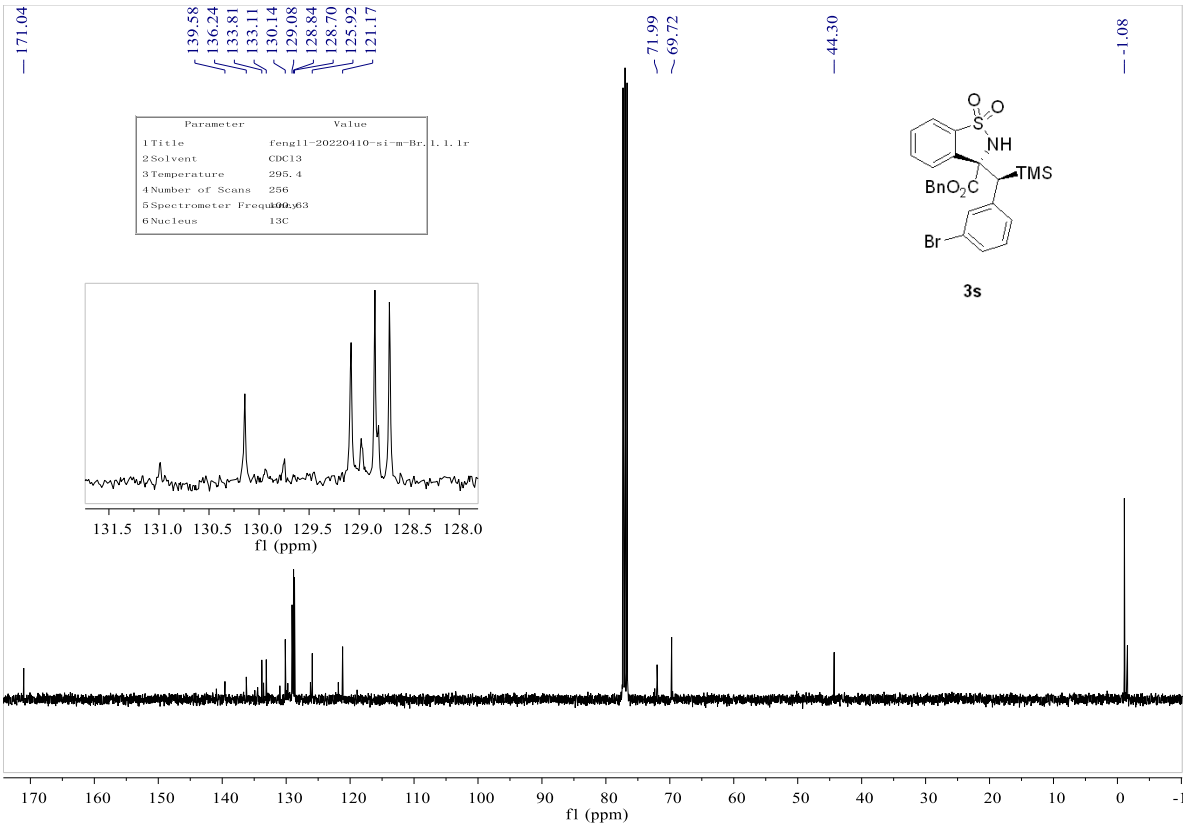

171.03
139.57
136.22
133.80
133.11
130.14
129.07
128.84
128.69
125.90
121.16
71.98
69.71
44.26
-1.10
Parameter Value
1 Title as-20220316-feng-si-m-F-C.1.1.1r
2 Solvent CDCl3
3 Temperature 294.3
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
134 133 132 131 130 129 128
f1 (ppm)
NH
TMS
BnO2C
F
3r
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-112.17
-114.34
Parameter Value
1 Title pdata/ 1
2 Solvent CDCl3
3 Temperature 223.0
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
NH
TMS
BnO2C
F
3r
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

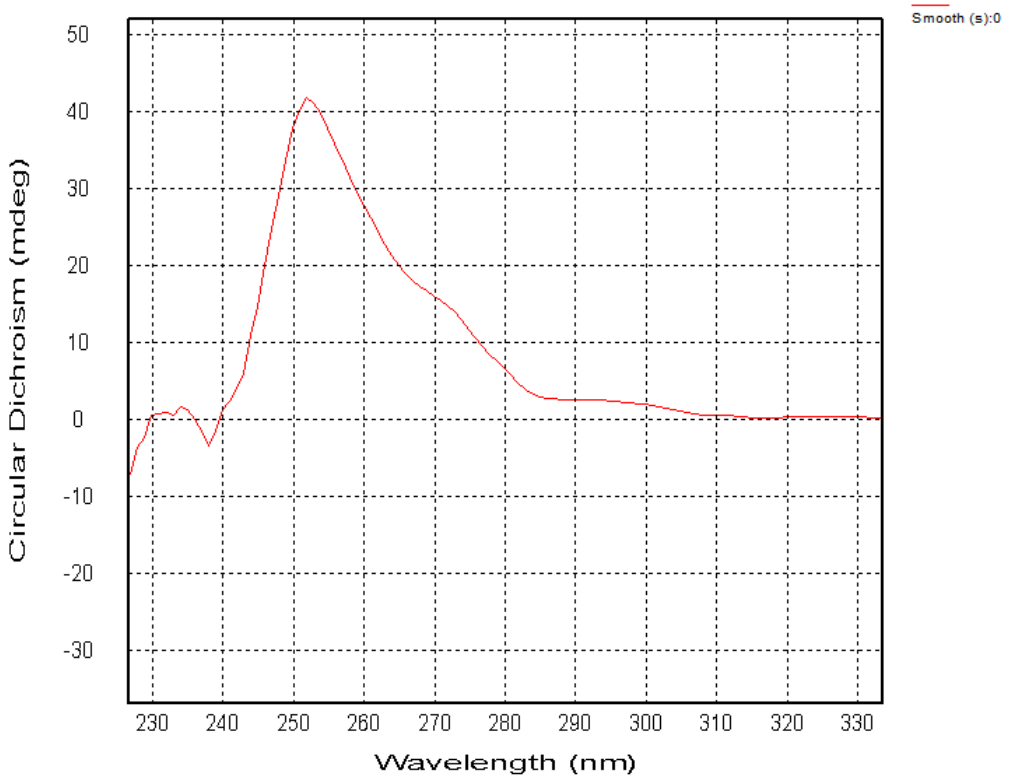

Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
-120
220
240
260
280
300
320
Wavelength (nm)

3s

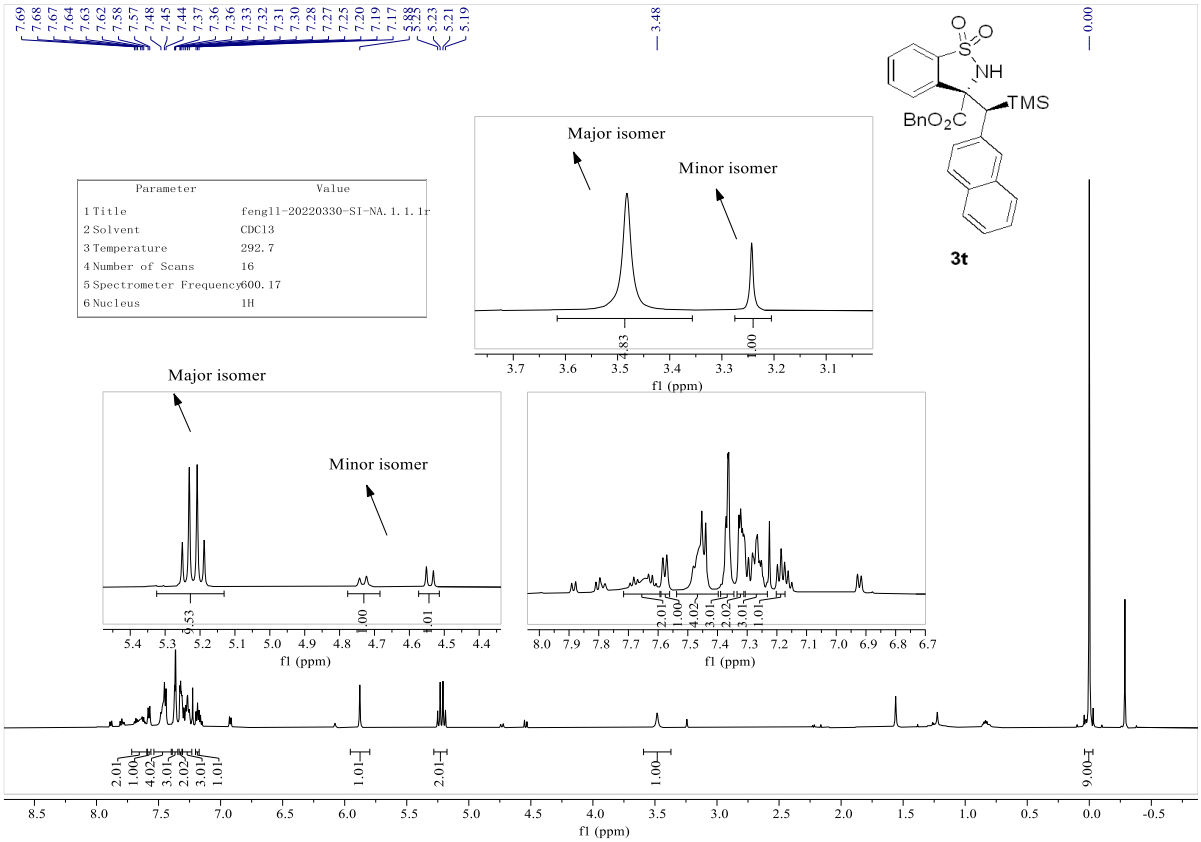

Major isomer
Minor isomer
3s
fl (ppm)

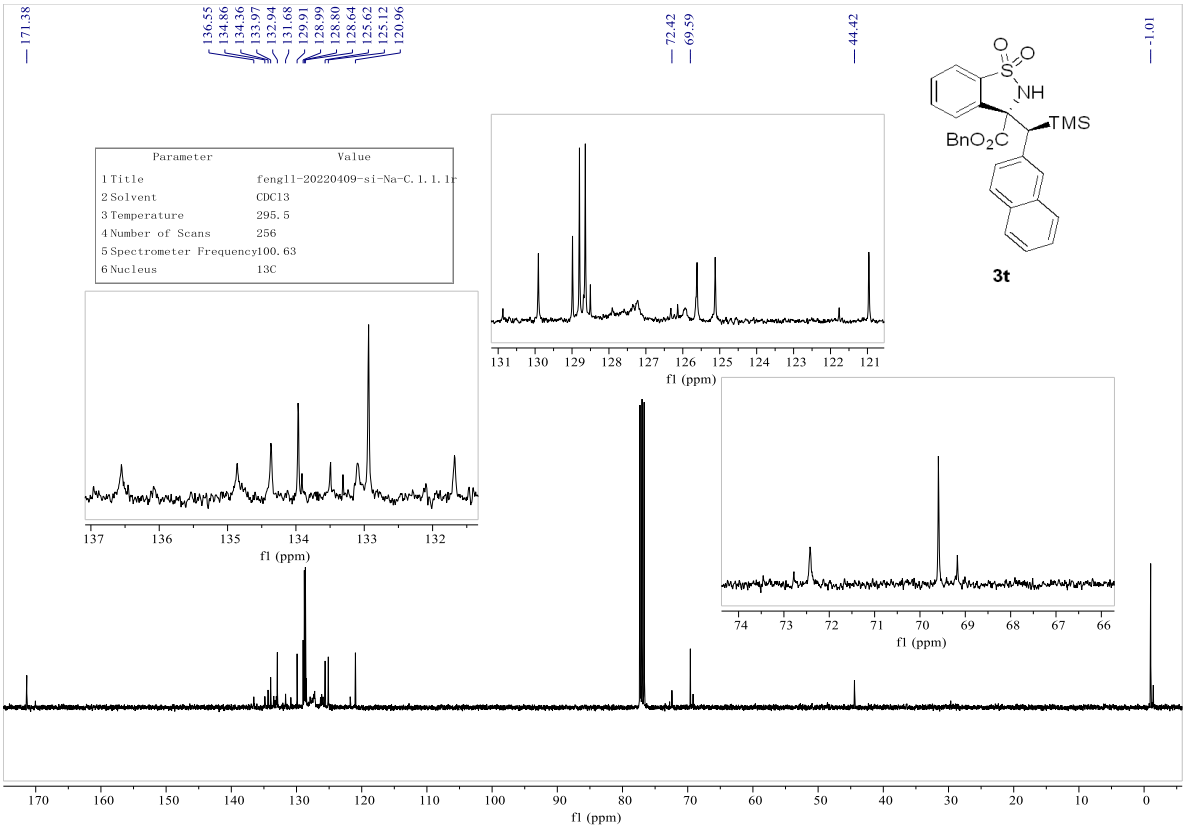

171.04
139.58
136.24
133.81
133.11
130.14
129.08
128.84
128.70
125.92
121.17
71.99
69.72
44.30
-1.08
Parameter Value
1Title fengll-20220410-si-m-Br.1.1.1r
2Solvent CDCl3
3Temperature 295.4
4Number of Scans 256
5Spectrometer Frequency
6Nucleus 13C
131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
O
S
NH
TMS
BnO2C
Br

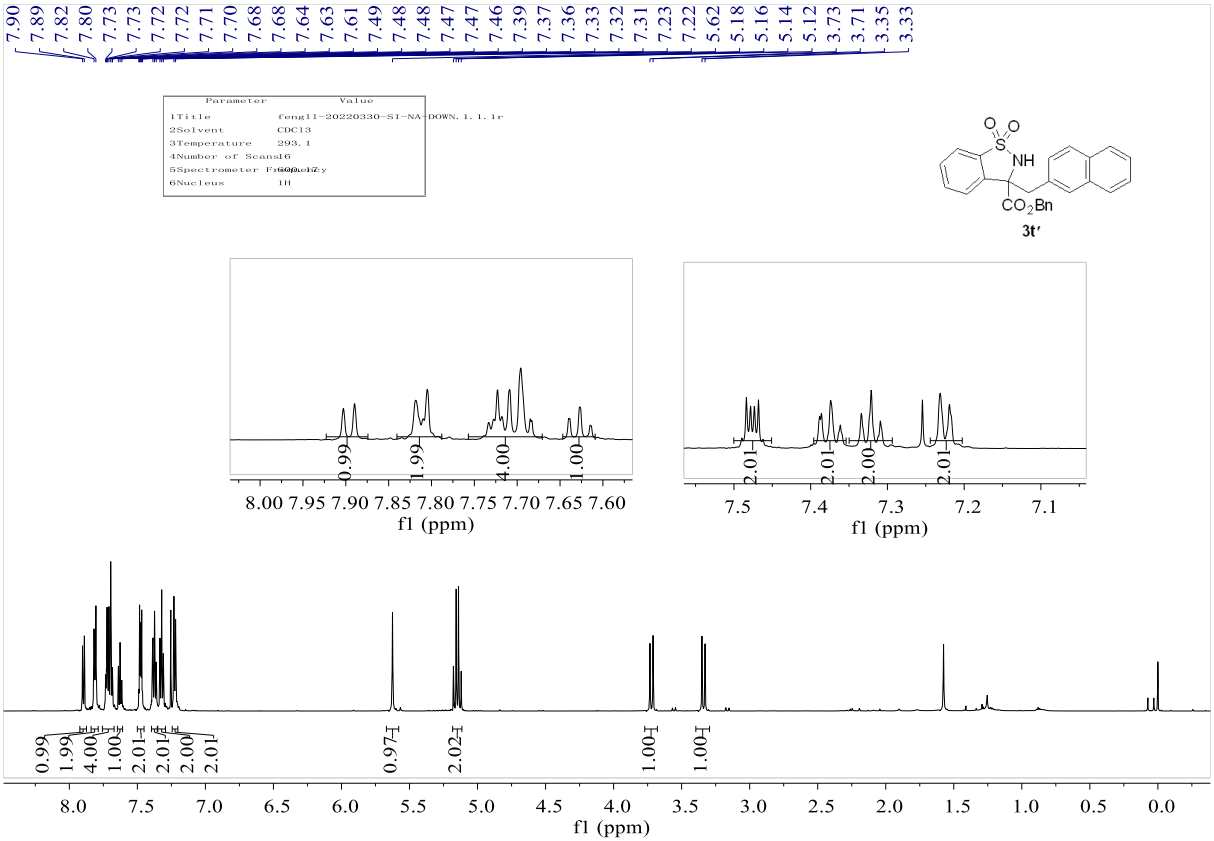
3s

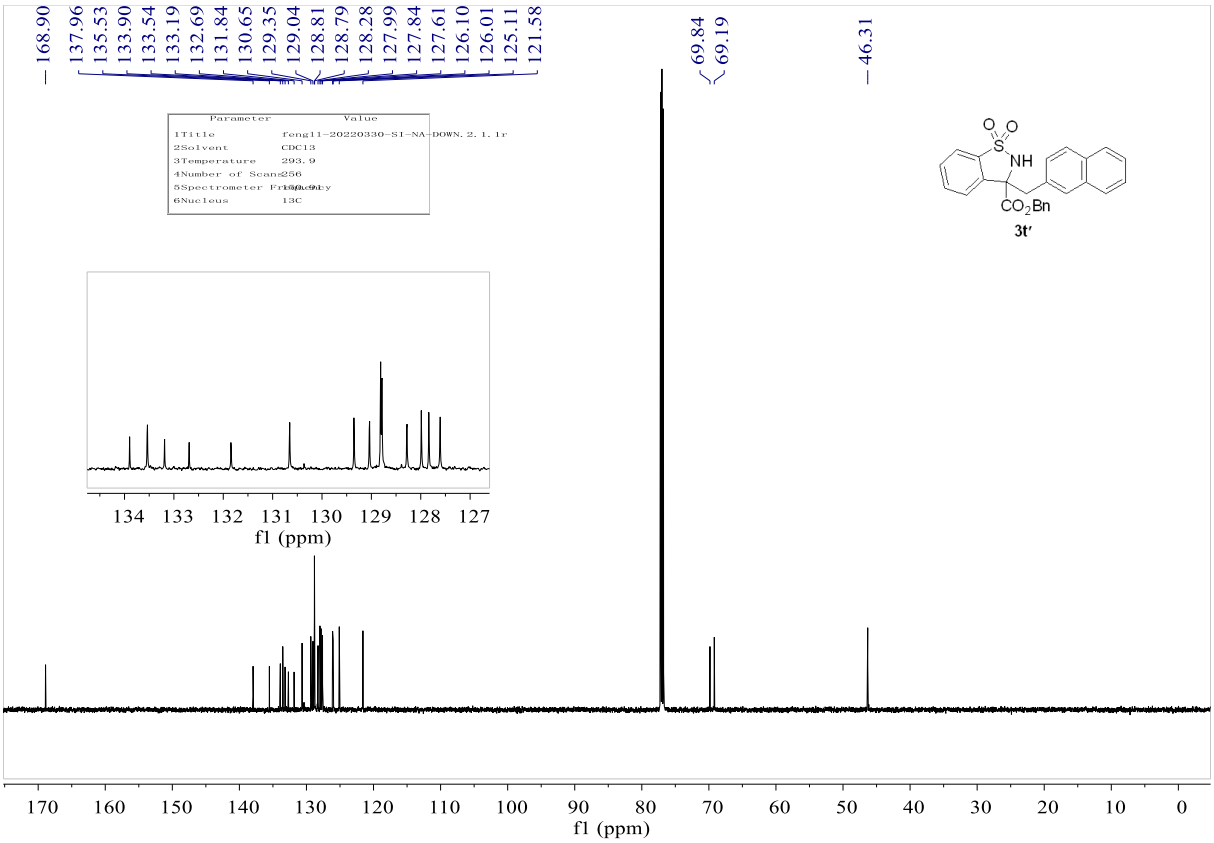

Smooth (s):0
Circular Dichroism (mdeg)
50
40
30
20
10
0
-10
-20
-30
230 240 250 260 270 280 290 300 310 320 330
Wavelength (nm)

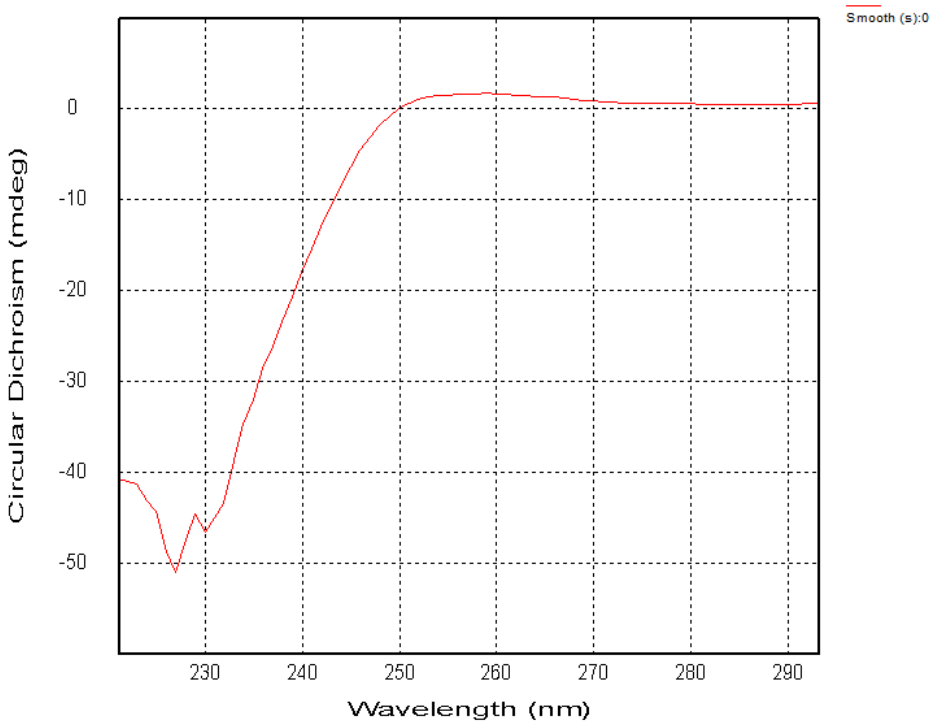
3t


Major isomer
Minor isomer
3t
f1 (ppm)

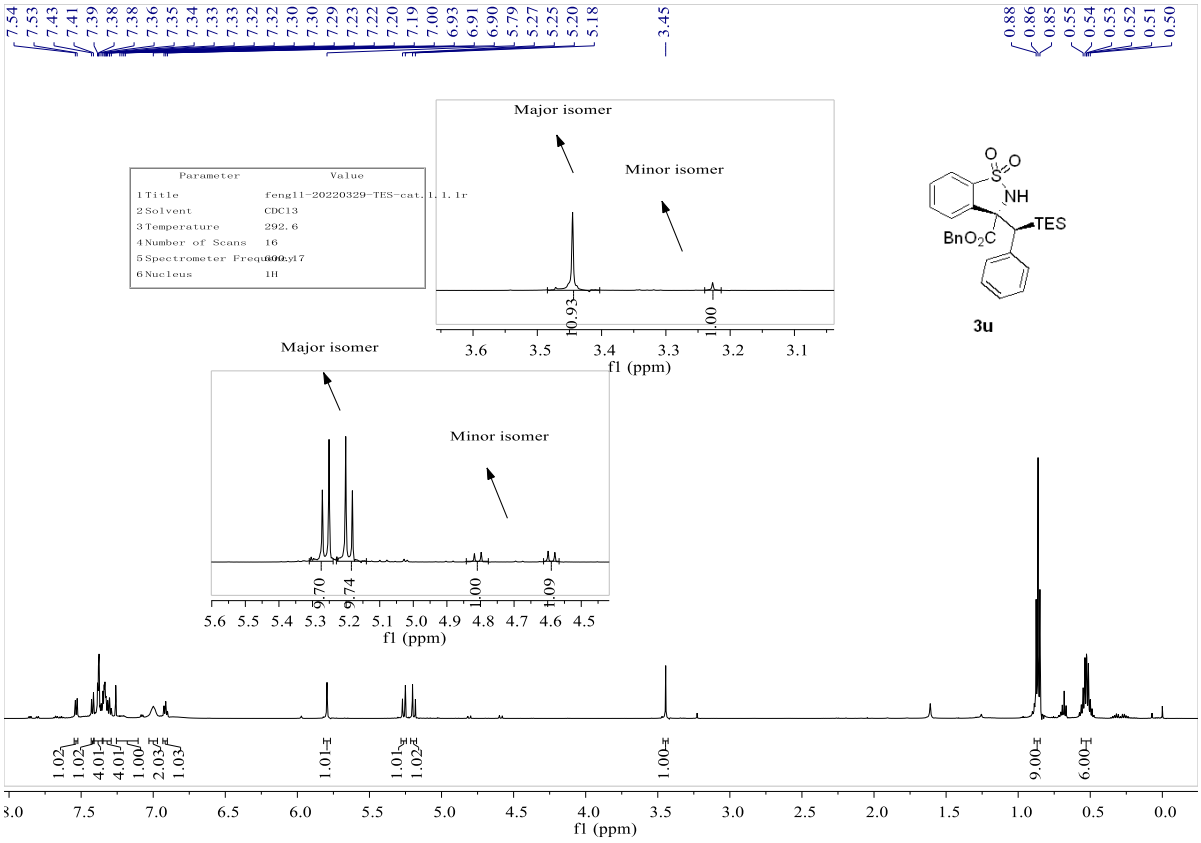

Major isomer
Minor isomer
3t
f1 (ppm)

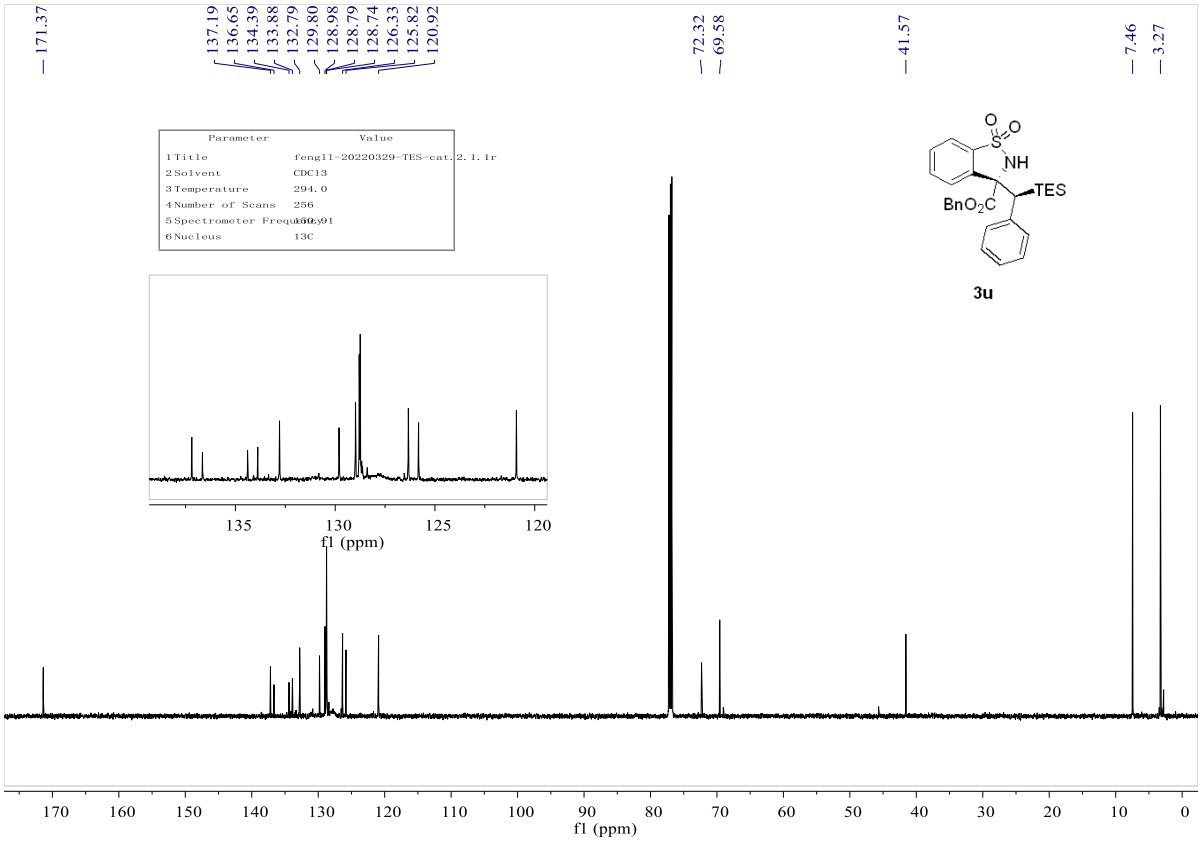

7.90 7.89 7.82 7.80 7.73 7.73 7.72 7.72 7.71 7.70 7.68 7.68 7.64 7.63 7.61 7.49 7.48 7.48 7.47 7.47 7.46 7.39 7.37 7.36 7.33 7.32 7.31 7.23 7.22 5.62 5.18 5.16 5.14 5.12 3.73 3.71 3.35 3.33
Parameter Value
1Title fengll-20220330-S1-NA-DOWN. 1. 1. 1r
2Solvent CDCl3
3Temperature 293. 1
4Number of Scans 16
5Spectrometer Frequency
6Nucleus 1H
NH
CO2Bn
3t'
0.99 1.99 4.00 1.00
8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60
f1 (ppm)
2.01 2.01 2.00 2.01
7.5 7.4 7.3 7.2 7.1
f1 (ppm)
0.99 1.99 4.00 1.00 2.01 2.01 2.00 2.01 0.97 2.02 1.00 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

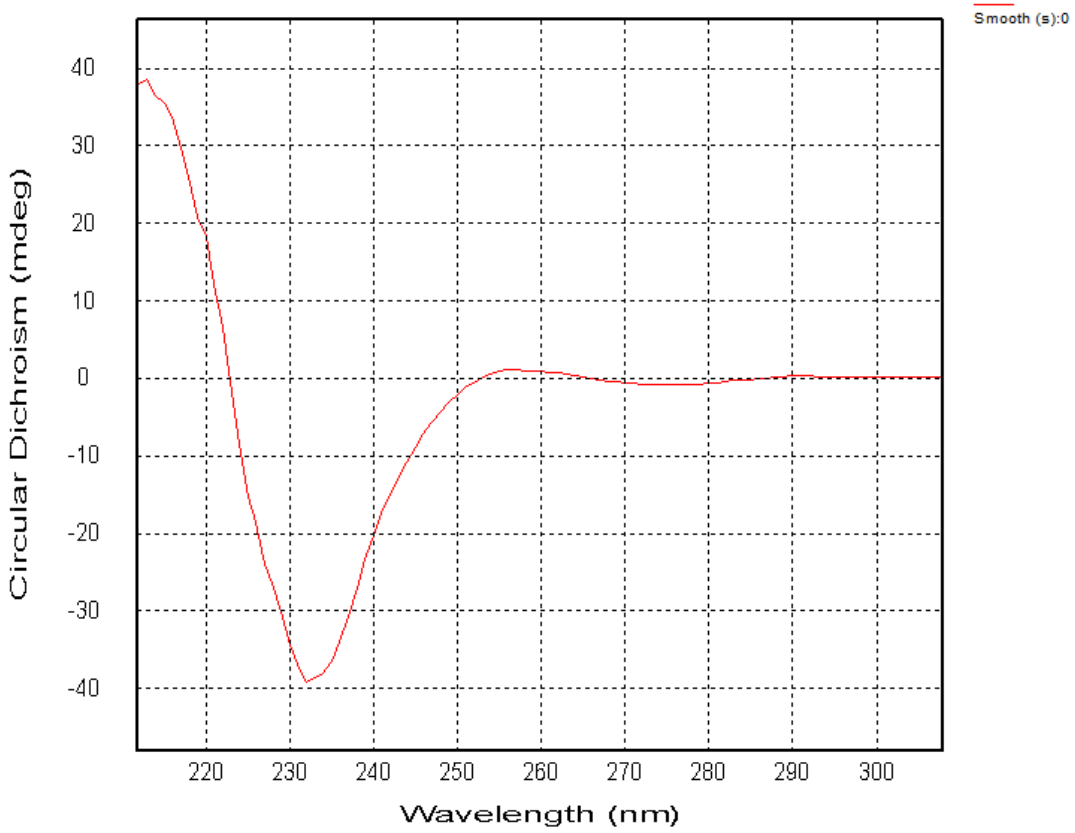

168.90 137.96 135.53 133.90 133.54 133.19 132.69 131.84 130.65 129.35 129.04 128.81 128.79 128.28 127.99 127.84 127.61 126.10 126.01 125.11 121.58
69.84 69.19
46.31
Parameter Value
1Title fengll-20220330-S1-NA-DOWN. 2. 1. 1r
2Solvent CDCl3
3Temperature 293. 9
4Number of Scans 256
5Spectrometer Frequency
6Nucleus 13C
NH
CO2Bn
3t'
134 133 132 131 130 129 128 127
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
0
-10
-20
-30
-40
-50
230
240
250
260
270
280
290
Wavelength (nm)

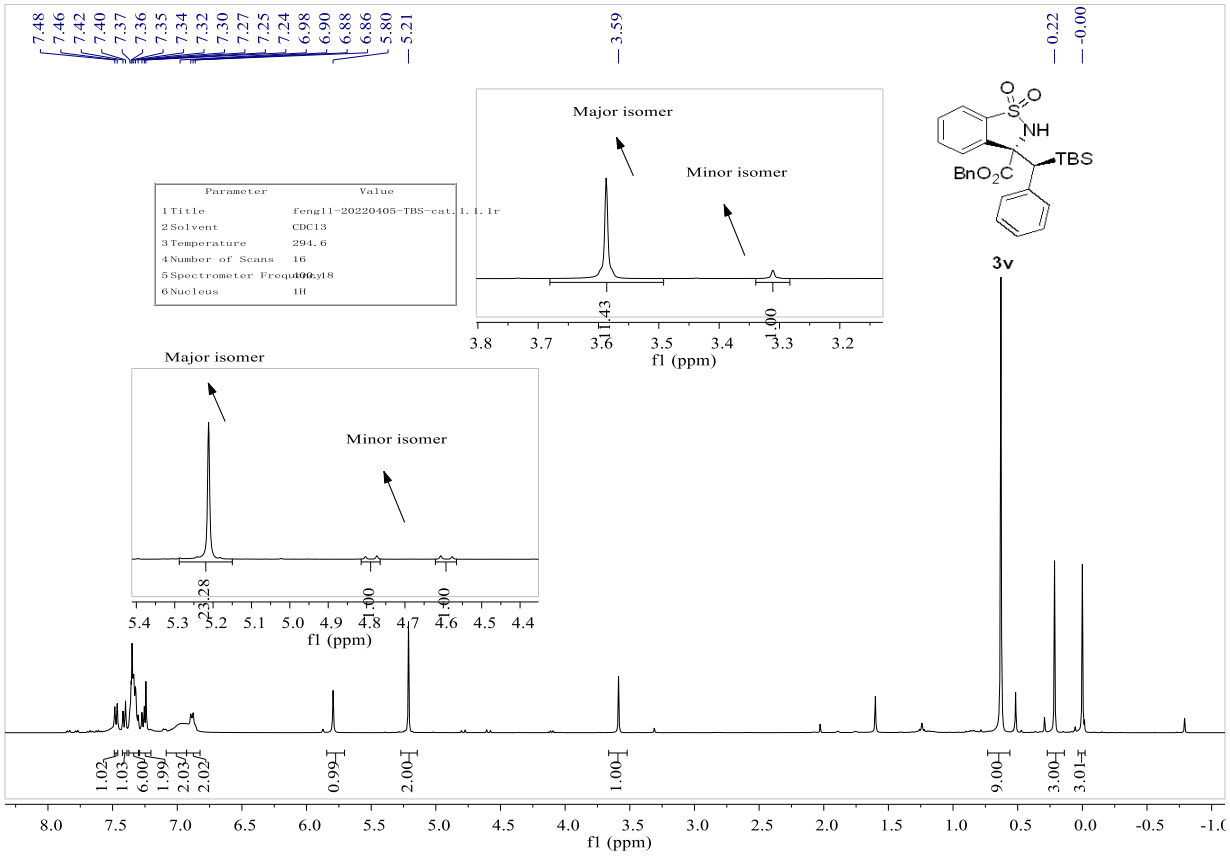
3u

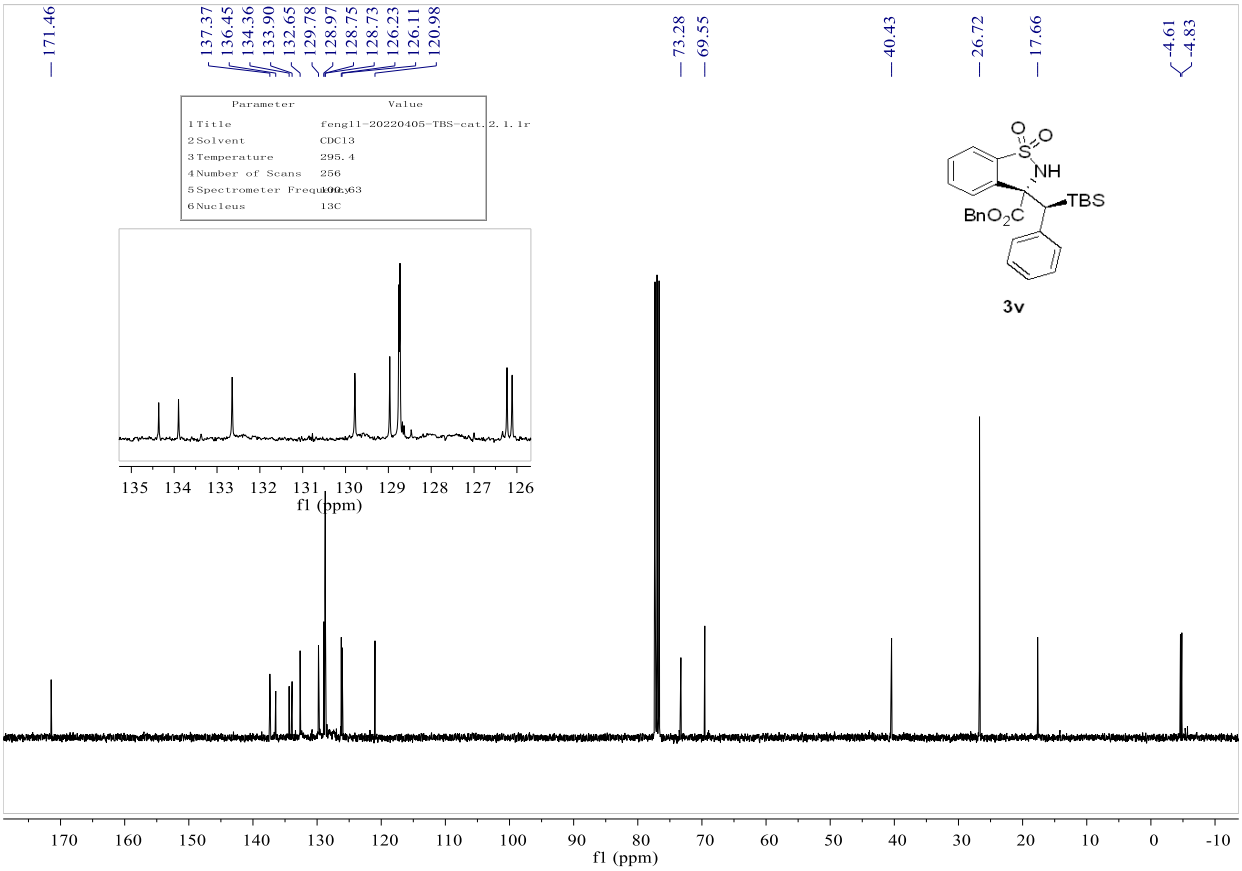

Major isomer
Minor isomer
Major isomer
Minor isomer
3u
fl (ppm)

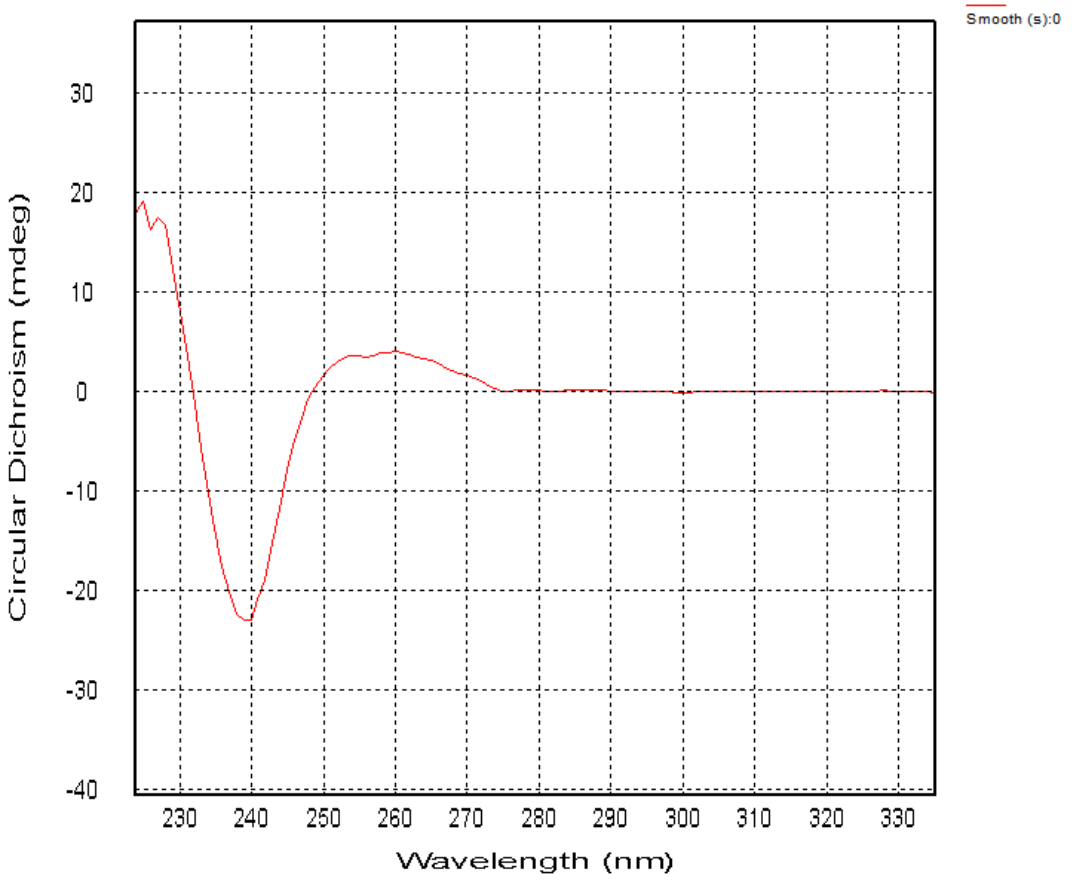

171.37
137.19
136.65
134.39
133.88
132.79
129.80
128.98
128.79
128.74
126.33
125.82
120.92
72.32
69.58
41.57
7.46
3.27
Parameter Value
1 Title fengll-20220329-TES-cat.2.1.1r
2 Solvent CDCl3
3 Temperature 294.0
4 Number of Scans 256
5 Spectrometer Frequency
6 Nucleus 13C
NH
TES
BnO2C
3u
f1 (ppm)
f1 (ppm)


Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)

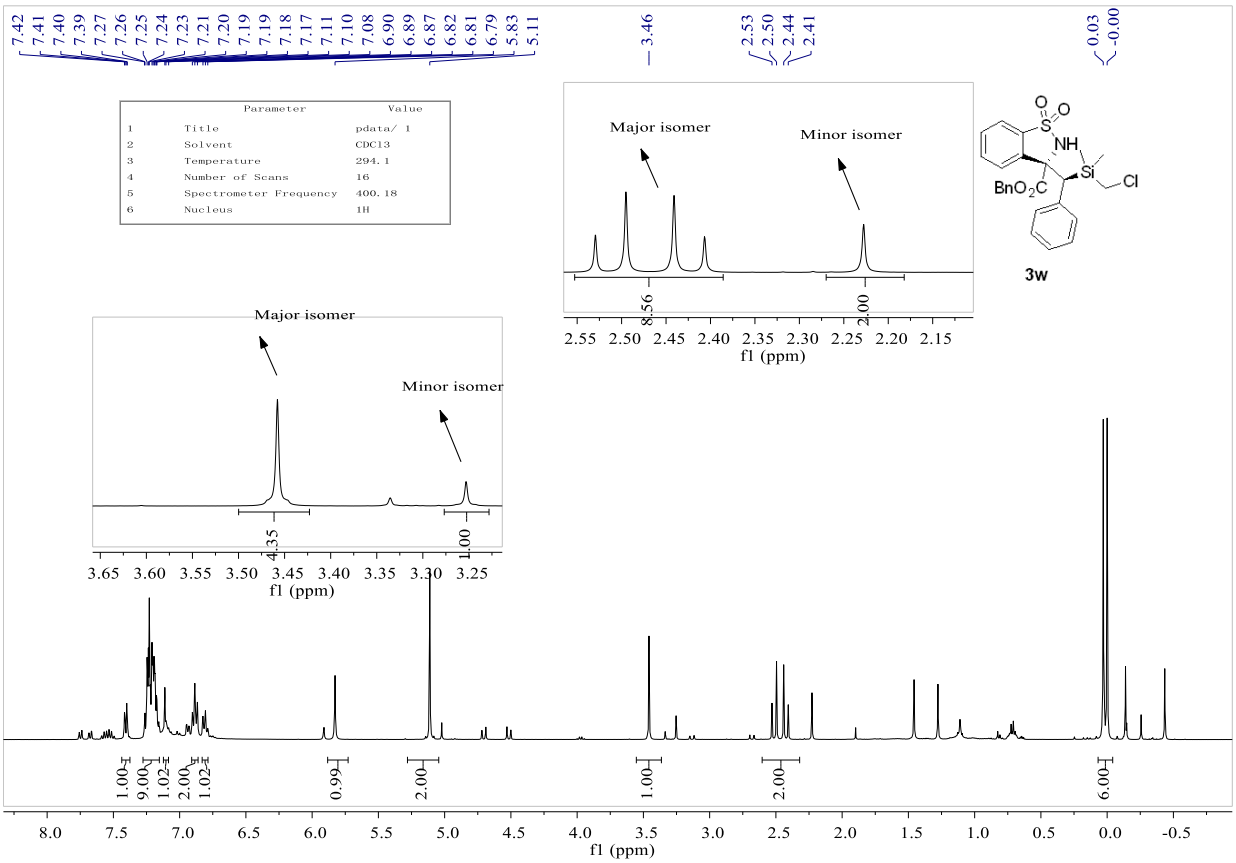
3v

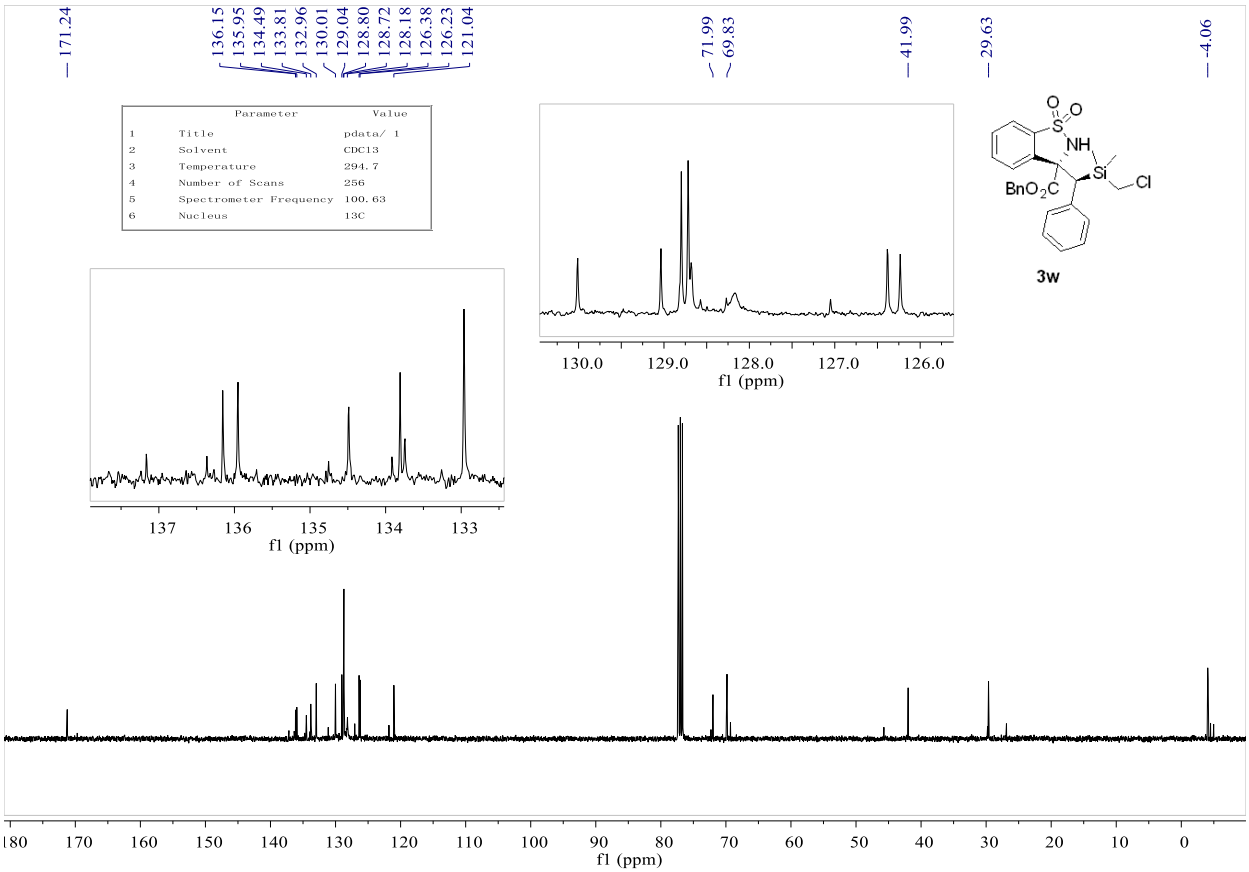

Major isomer
Minor isomer
3v

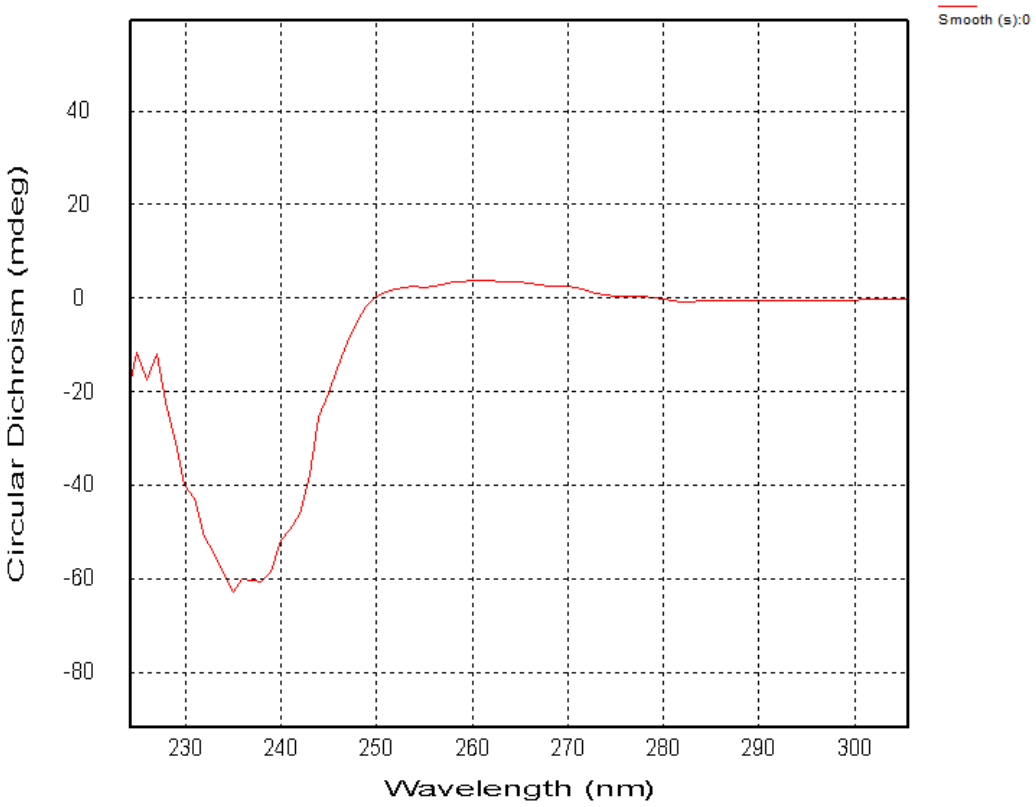

Major isomer
Minor isomer
3v


Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
-40
230
240
250
260
270
280
290
300
310
320
330
Wavelength (nm)

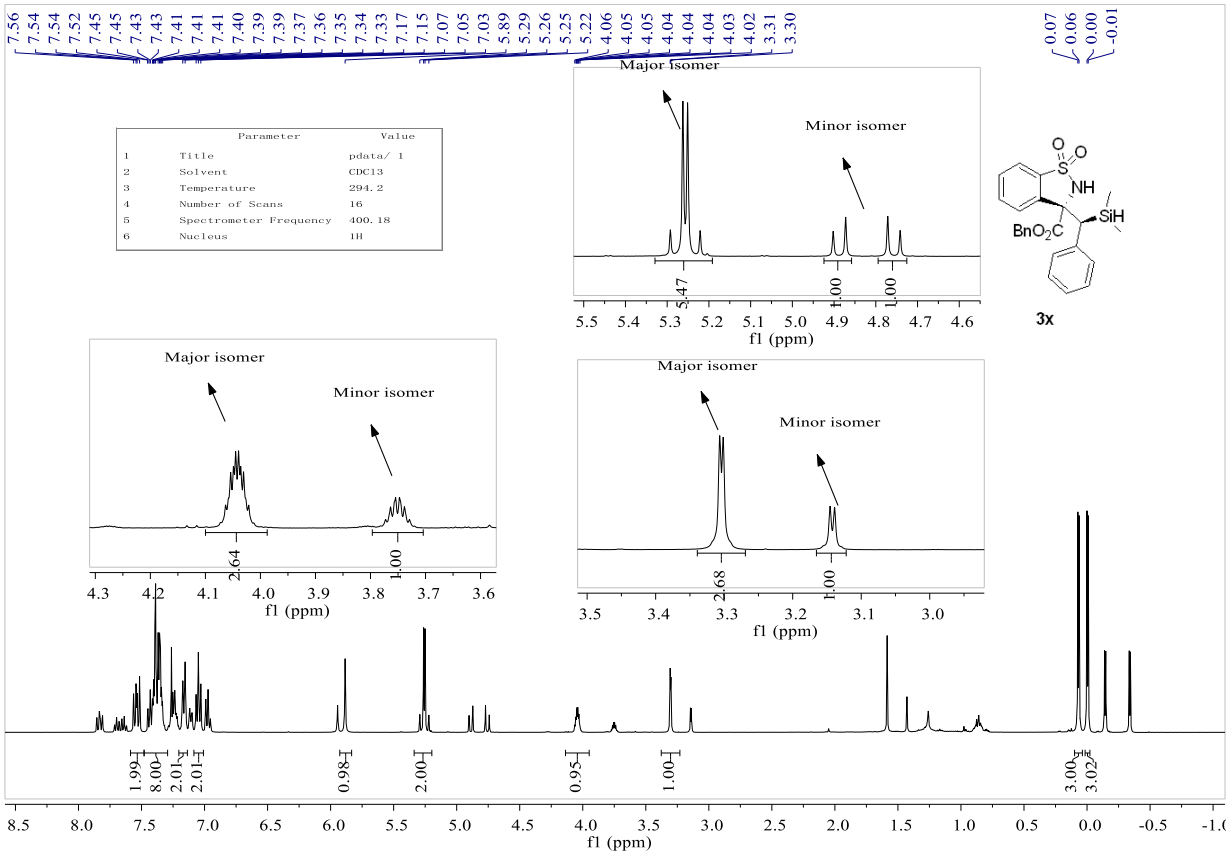
3w

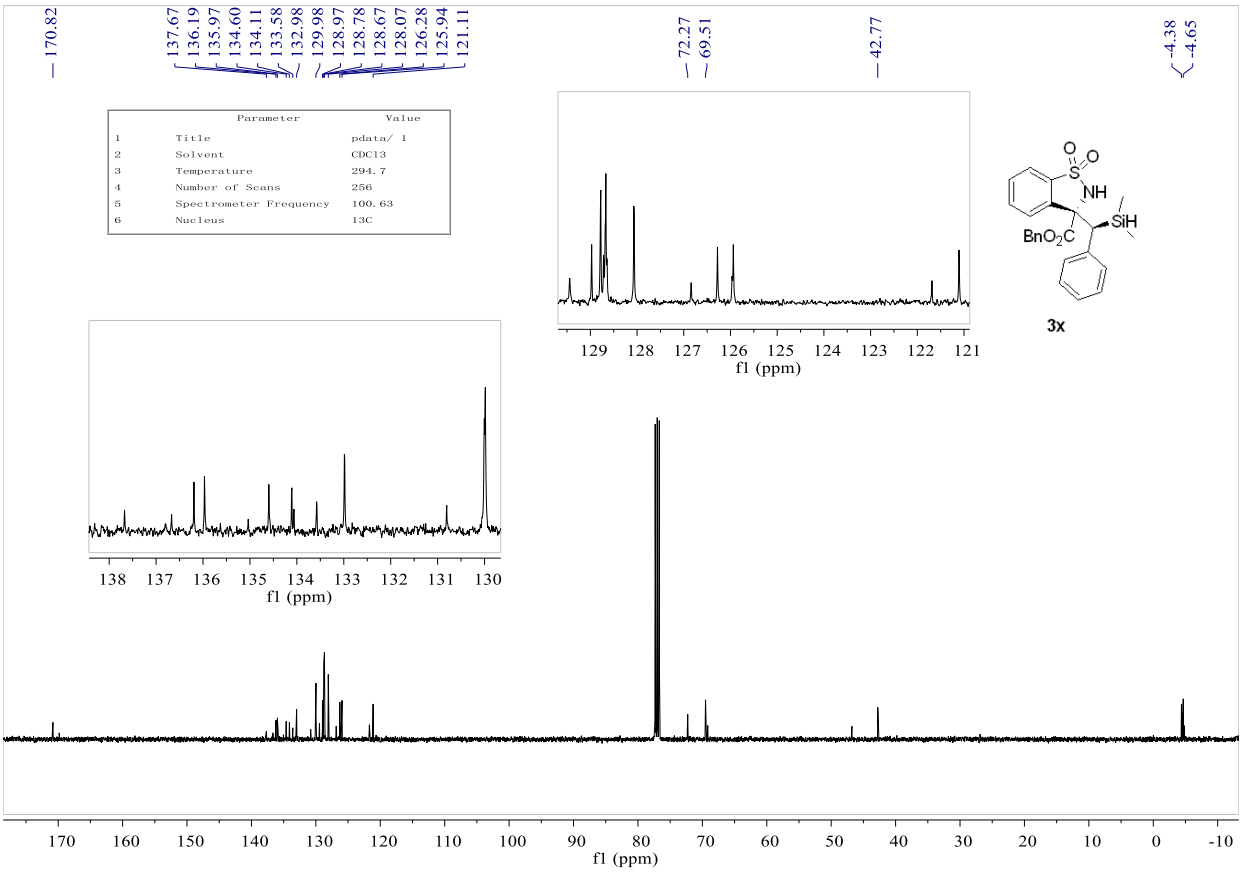

Parameter Value
1 Title pdata/ 1
2 Solvent CDCl3
3 Temperature 294.1
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
Major isomer
Minor isomer
8.56
2.00
f1 (ppm)
3w
Major isomer
Minor isomer
4.35
1.00
f1 (ppm)
f1 (ppm)

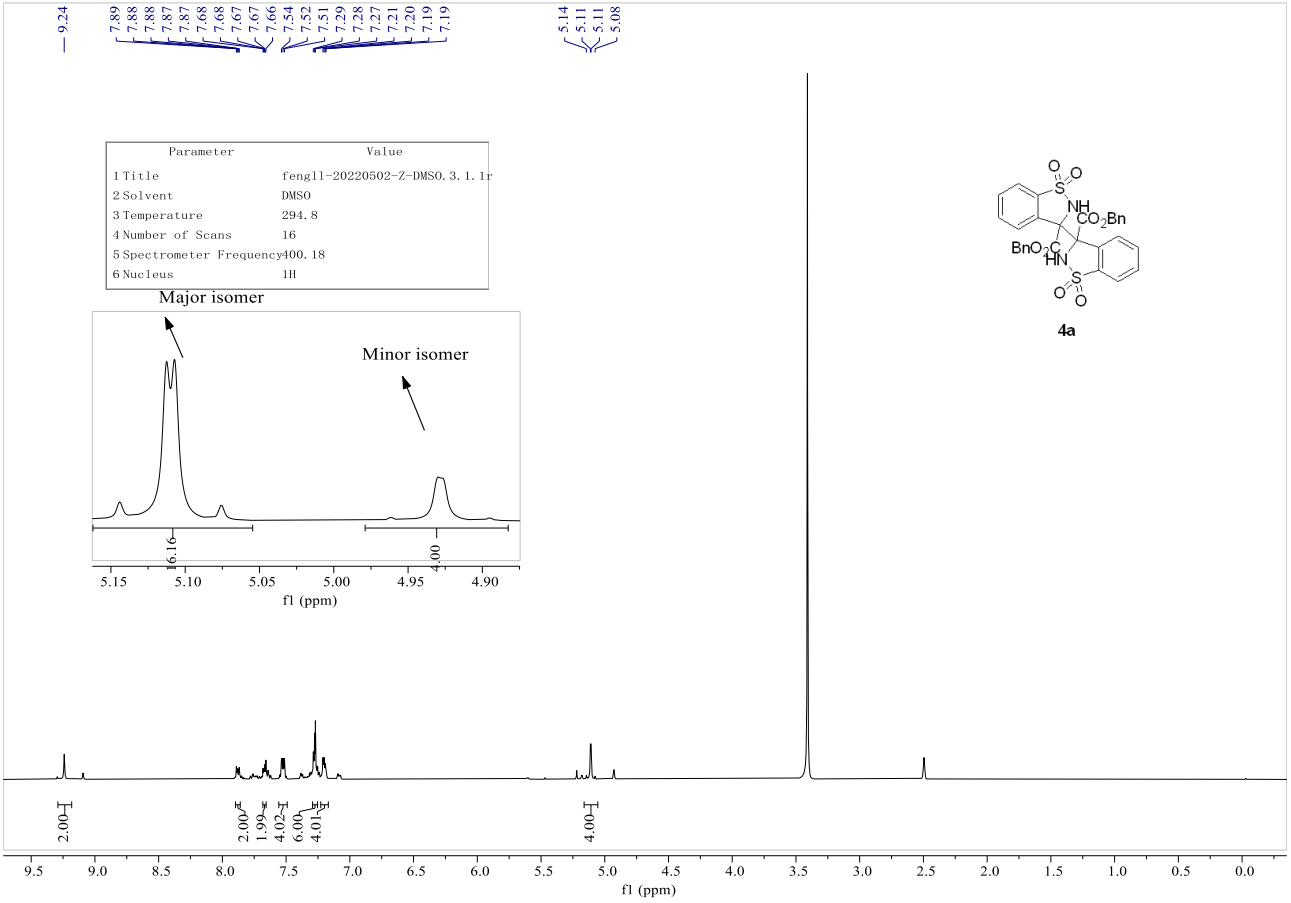

171.24
136.15
135.95
134.49
133.81
132.96
130.01
129.04
128.80
128.72
128.18
126.38
126.23
121.04
71.99
69.83
41.99
29.63
-4.06
Parameter Value
1 Title pdata/ 1
2 Solvent CDCl3
3 Temperature 294.7
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
137 136 135 134 133
f1 (ppm)
130.0 129.0 128.0 127.0 126.0
f1 (ppm)
O
O
S
NH
Si
Cl
BnO2C
3w
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

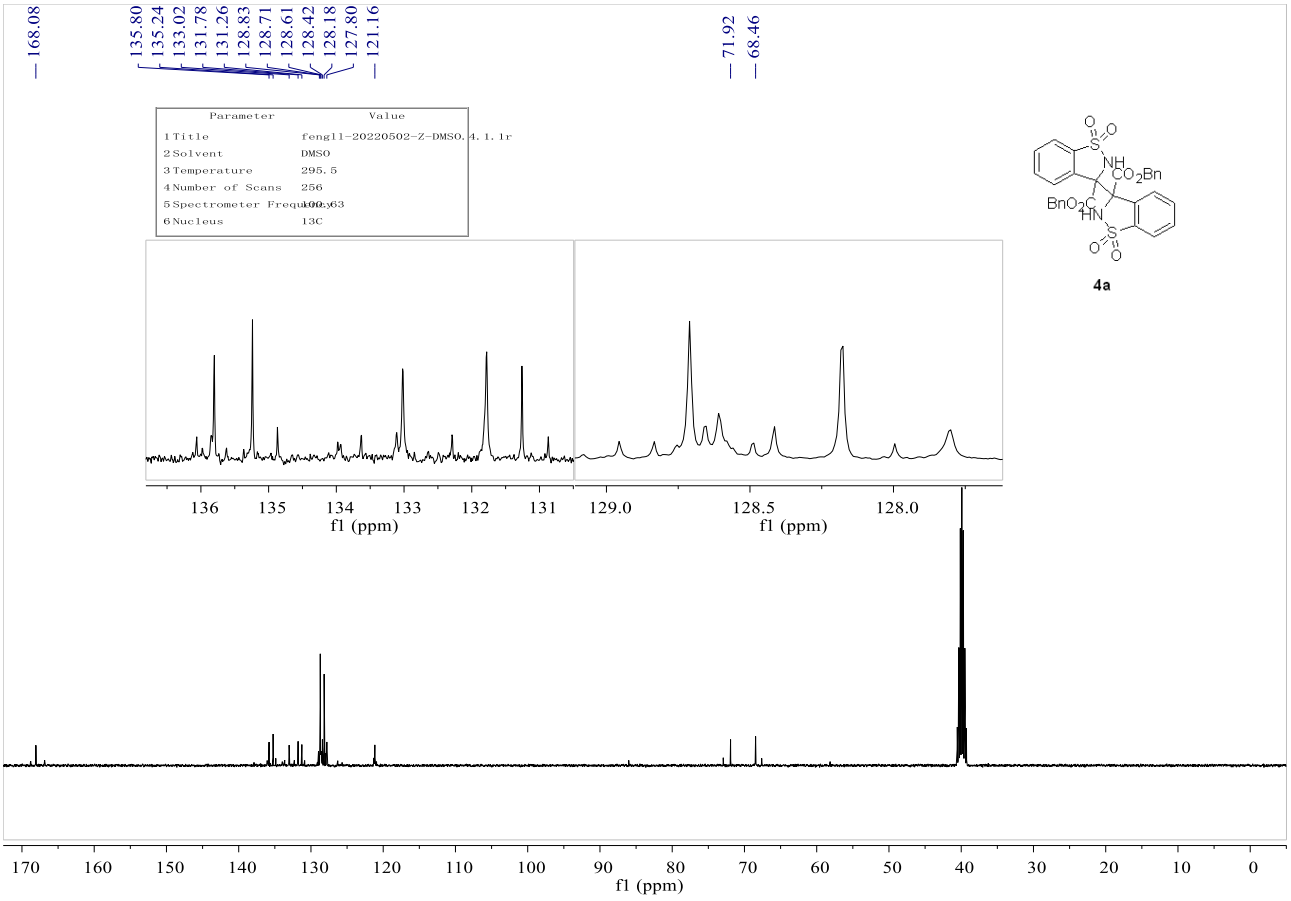

Smooth (s):0
Circular Dichroism (mdeg)
40
20
0
-20
-40
-60
-80
230 240 250 260 270 280 290 300
Wavelength (nm)

3x


Major isomer
Minor isomer
Parameter Value
1 Title pdata/ 1
2 Solvent CDCl3
3 Temperature 294.2
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
3x
f1 (ppm)


Parameter Value
1 Title pdata/ 1
2 Solvent CDCl3
3 Temperature 294.7
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
3x
f1 (ppm)


9.24
7.89
7.88
7.88
7.87
7.87
7.68
7.68
7.67
7.67
7.66
7.54
7.52
7.51
7.29
7.28
7.27
7.21
7.20
7.19
7.19
5.14
5.11
5.11
5.08
Parameter Value
1 Title fengll-20220502-Z-DMSO. 3. 1. 1r
2 Solvent DMSO
3 Temperature 294. 8
4 Number of Scans 16
5 Spectrometer Frequency 400. 18
6 Nucleus 1H
Major isomer
Minor isomer
16.16
4.00
5.15 5.10 5.05 5.00 4.95 4.90
f1 (ppm)
4a
2.00
2.00
1.99
4.02
6.00
4.01
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.08
135.80
135.24
133.02
131.78
131.26
128.83
128.71
128.61
128.42
128.18
127.80
121.16
71.92
68.46
Parameter Value
1 Title fengll-20220502-Z-DMSO. 4. 1. 1r
2 Solvent DMSO
3 Temperature 295. 5
4 Number of Scans 256
5 Spectrometer Frequ 100. 63
6 Nucleus 13C
136 135 134 133 132 131
f1 (ppm)
129.0 128.5 128.0
f1 (ppm)
4a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)