Electronic Supplementary Material (ESI) for Chemical Science.

Cu(II)-mediated direct intramolecular cyclopropanation of distal olefinic acetate: access to cyclopropane-fused γ-lactone

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Supplementary Information

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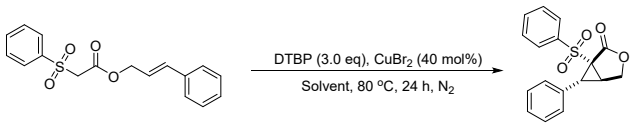
1. General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance and JEOL III–400 spectrometer at 25 ^{o}C in solvents as indicated. Chemical shift values are reported in ppm with the solvent resonance refereed to the standard position ($CDCl_3$: ^{1}H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.16$). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and dd, doublet of doublets. The coupling constants *J* are reported in Hertz (Hz). HRMS were obtained on a QTOF micro spectrometer. Melting points were measured using open glass capillaries in SGW® X-4A apparatus. The fluorescent quenching experiment was conducted on a FL970 Plus Fluorescence Spectrometer.

All reactions were carried out in oven–dried Schlenk–tubes under an atmosphere of nitrogen. Unless otherwise stated, all the reagents were purchased from commercial sources and used without further purification. Conversion of the reactions was monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254. Compounds were visualized by UV light at 254 nm and by dipping the plates in an ethanolic phosphomolybdic acid solution followed by heating. Flash column chromatography was performed over silica gel (230-400 mesh). All the compounds were prepared according to reported method.

2. Optimization of the reaction conditions

Table S1. Solvents Screening[a]

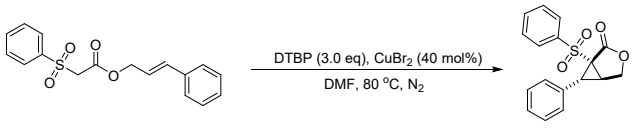


1aa 2aa

Entry	Solvent	Yield of **2aa**[b] （%）	d.r.
1	MeCN	83	> 20:1
2	THF	N.D.	-
3	1,2-DCE	N.D.	-
4	DMSO	58	> 20:1
5	DMF	86	> 20:1
6	Toluene	N.D.	-

[a]Reaction conditions: **1aa** (0.2 mmol), DTBP (0.6 mmol) and $CuBr_2$ (40 mol%) in solvent (1.0 mL) under N_2 at 80 °C for 24 h. [b]Yield of isolated product. N.D. = Not Detected. 1,2-DCE = 1,2-dichloroethane. d.r. was determined by crude ^{1}HNMR spectroscopy.

Table S2. Effect of reaction time[a]

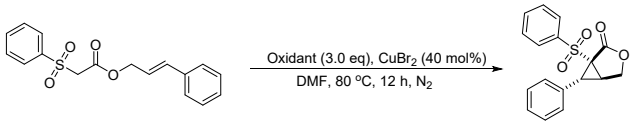


1aa 2aa

Entry	Time	Yield of **2aa**[b] （%）	d.r.
1	6	72	> 20:1
2	12	87	> 20:1
3	18	87	> 20:1
4	24	86	> 20:1

[a]Reaction conditions: **1aa** (0.2 mmol), DTBP (0.6 mmol) and $CuBr_2$ (40 mol%) in DMF (1.0 mL) under N_2 at 80 °C. [b]Yield of isolated product. d.r. was determined by crude ^{1}HNMR spectroscopy.

Table S3. Effect of oxidants on the reaction[a]

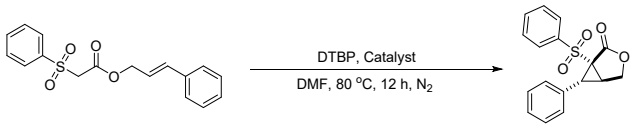


1aa 2aa

Entry	Oxidant	Yield of **2aa**[b] （%）	d.r.
1	TBPB	Trace	-
2	BPO	N.D.	-
3	LPO	N.R.	-
4	TBHP	Trace	-
5	DCP	80	> 20:1
6	DTBP	87	> 20:1

[a]Reaction conditions: **1aa** (0.2 mmol), Oxidant (0.6 mmol) and $CuBr_2$ (40 mol%) in DMF (1.0 mL) under N_2 at 80 °C for 12 h. [b]Yield of isolated product. TBPB = *tert*-butyl peroxybenzoate; BPO = benzoyl peroxide; LPO = lauroyl peroxide; TBHP = tert-butyl hydroperoxide; DCP = dicumyl peroxide; N.D. = not detected. N.R. = no reaction. d.r. was determined by crude ^{1}HNMR spectroscopy.

Table S4. Effect of catalysts on the reaction

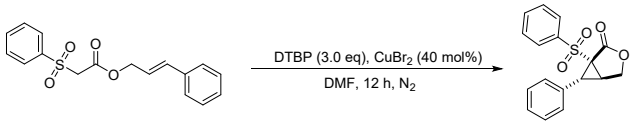


1aa 2aa

Entry[a]	Catalyst	Yield of **2aa**[b] （%）	d.r.
1	$Cu(acac)_2$	8	-
2	$Cu(OTf)_2$	N.D.	-
3	$Cu(OAc)_2$	N.R.	-
4	$CuCl_2$	16	> 20:1
5	$CuBr_2$	87	> 20:1
6	CuBr	64	> 20:1
7	CuI	71	> 20:1
8	CuSCN	Trace	-
9	Cu_2O	Trace	-
10	$Fe(acac)_2$	N.R.	-
11	$Fe(OTf)_2$	N.R.	-
12	$Fe(OAc)_2$	N.R.	-
13	$FeCl_2$	N.R.	-
14	$FeBr_2$	N.R.	-
15	$Fe(acac)_3$	N.R.	-
16	$Fe(OTf)_3$	N.R.	-
17	$Fe(OTs)_3$	N.R.	-

[a]Reaction conditions: **1aa** (0.2 mmol), DTBP (0.6 mmol) and Copper salt (40 mol%) in DMF (1.0 mL) under N_2 at 80 °C for 12 h. [b]Yield of isolated product. [c]Reaction conditions: **1aa** (0.2 mmol), DTBP (0.4 mmol) and Ferric salt (20 mol%) in DMF (1.0 mL) under N_2 at 80 °C for 12 h. d.r. was determined by crude ^{1}HNMR spectroscopy.

Table S5. Effect of temperature on the reaction[a]

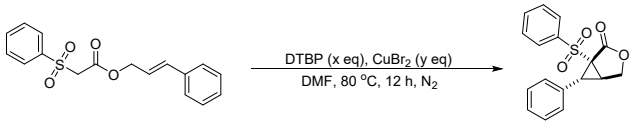


1aa 2aa

Entry	Temperature (℃)	Yield of **2aa**[b] （%）	d.r.
1	40	N.D.	-
2	60	81	> 20:1
3	80	87	> 20:1
4	100	87	> 20:1

[a]Reaction conditions: **1aa** (0.2 mmol), DTBP (0.6 mmol) and $CuBr_2$ (40 mol%) in DMF (1.0 mL) under N_2 for 12h. [b]Yield of isolated product. d.r. was determined by crude ^{1}HNMR spectroscopy.

Table S6. Reaction optimization[a]



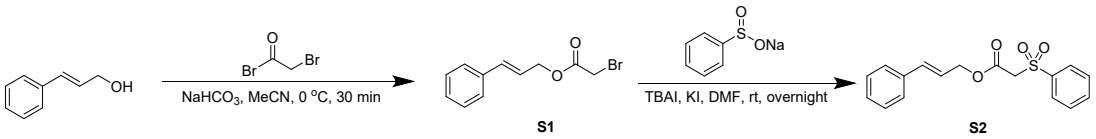
1aa 2aa

Entry	DTBP (x eq)	$CuBr_2$ (y eq)	Yield of **2aa**[b] （%）	d.r.
1	-	0.4	N.R.	-
2	1.5	0.4	71	> 20:1
3	2.0	0.4	89	> 20:1
4	2.5	0.4	88	> 20:1
5	3.0	0.4	87	> 20:1
6	3.5	0.4	87	> 20:1
7	2.0	-	N.R.	-
8	2.0	0.1	22	> 20:1
9	2.0	0.2	61	> 20:1
10	2.0	0.3	87	> 20:1

[a]Reaction conditions: **1aa** (0.2 mmol), DTBP (x eq) and $CuBr_2$ (y eq) in DMF (1.0 mL) under N_2 at 80 ℃ for 12 h. [b]Yield of isolated product. d.r. was determined by crude ^{1}HNMR spectroscopy.

3. General procedure for the synthesis of starting materials

3.1 Compound 1aa was prepared according to the general procedure 1 (GP1)

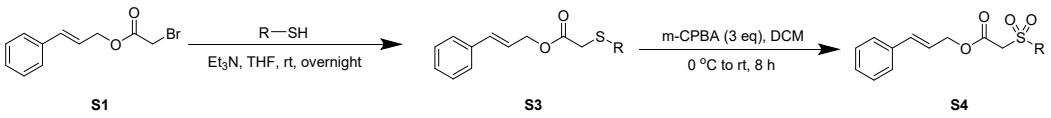


S1 S2

(1) Following the reported procedure,[1] to a solution of cinnamyl alcohol (10 mmol, 1.0 equiv) in acetonitrile (0.3 M) was added $NaHCO_3$ (15 mmol, 1.5 equiv) followed by the slowly addition of bromoacetyl bromide (12 mmol, 1.2 equiv) at 0 °C. After stirring 30 min at this temperature, the reaction was quenched with H_2O. The mixture was extracted with ethyl acetate (20 mL × 3). The combined organic layer was washed with brine (15 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **S1**.

(2) Following the reported procedure,[2] to a solution of **S1** (5 mmol, 1.0 equiv) in *N,N*-dimethylformamide (0.3 M) was added sodium benzenesulfinate (6 mmol, 1.2 equiv), tetrabutylammonium iodide (0.5 mmol, 0.1 equiv), potassium iodide (6 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature overnight and then quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **S2**.

3.2 Compounds 1ab - 1aq were prepared according to the general procedure 2 (GP2)



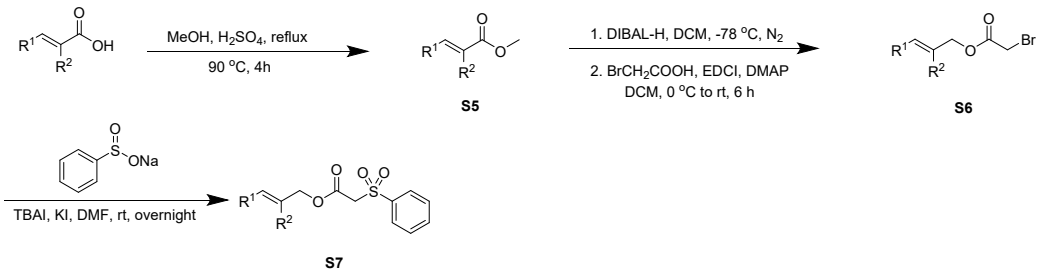
S1 S3 S4

(1) Following the reported procedure,[3] to a solution of **S1** (5 mmol, 1.0 equiv) in tetrahydrofuran (0.3 M) was added thiophenol (5.0 mmol, 1.0 equiv) and triethylamine (10 mmol, 2.0 equiv). The reaction mixture was stirred at room temperature overnight and then quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layer was washed with brine (15 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **S3**.

(2) Following the reported procedure,[4] to a solution of **S3** (5 mmol, 1.0 equiv) in dichloromethane (0.3 M) was added slowly 3-chloroperoxybenzoic acid (15 mmol, 3.0 equiv). Then the solution was allowed to warm to room temperature and stirred for 8 h.After completion, the reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). And the mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (15 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column

chromatography (petroleum ether / ethyl acetate) to afford **S4**.[4]

3.3 Compounds 1ba - 1bh, 1bl were prepared according to the general procedure 3 (GP3)



(1) Following the reported procedure,[5] to a solution of α,β-unsaturated carboxylic acid (5 mmol, 1.0 equiv) in methanol (0.5 M) was added H_2SO_4 (cat.). The reaction was stirred at 90 °C for 4 h then cooled to room temperature. And the reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layer was washed with brine (15 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to afford **S5**, which was used without further purification unless stated.

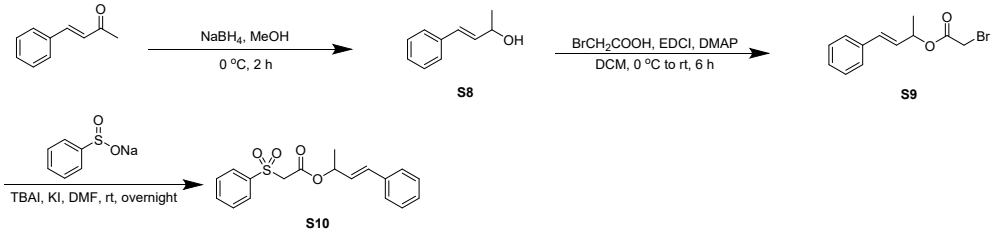
(2) Following the reported procedure,[6] to a solution of methyl cinnamate (5 mmol, 1.0 eq.) in dry dichloromethane (0.5 M) was added DIBAL-H (10 mL, 10 mmol, 1.0 M solution in hexane, 2.0 eq.) at - 78°C dropwise. The reaction mixture was stirred for 2 h at - 78 °C and allowed to warm up gradually. Then the reaction mixture was cooled to 0 °C, and carefully quenched with saturated aqueous NH_4Cl (10 mL). The reaction mixture was stirred at room temperature for 1 h, and the resulting white precipitate was filtered through a pad of Celite®. The filtrate was extracted three times with dichloromethane (5 ml × 3). The organic phase was directly used for the next step.

Following the reported procedure,[7] to a solution of cinnamyl alcohol (5 mmol, 1.0 equiv) in dichloromethane (0.3 M) was added slowly bromoacetic acid (6 mmol, 1.2 equiv), EDCI HCl (6 mmol, 1.2 mmol) and 4-(dimethylamino)pyridine (0.5 mmol, 0.1 equiv) at 0 °C. Then the solution was allowed to warm to room temperature and stirred for 6 h. After completion, the reaction was quenched with saturated aqueous $NaHCO_3$ (15 mL) and the aqueous layer was extracted with dichloromethane (10 mL × 3). The combined organic extract was washed with brine (15 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography (petroleum ether / ethyl acetate) to afford **S6**.

(3) To a solution of **S6** (5 mmol, 1.0 equiv) in N,N-dimethylformamide (0.3 M) was added sodium benzenesulfinate (6 mmol, 1.2 equiv), tetrabutylammonium iodide (0.5 mmol, 0.1 equiv) and potassium iodide (6 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature overnight and then quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layer

was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **S7**.

3.4 Compound 1bk was prepared according to the general procedure 4 (GP4)

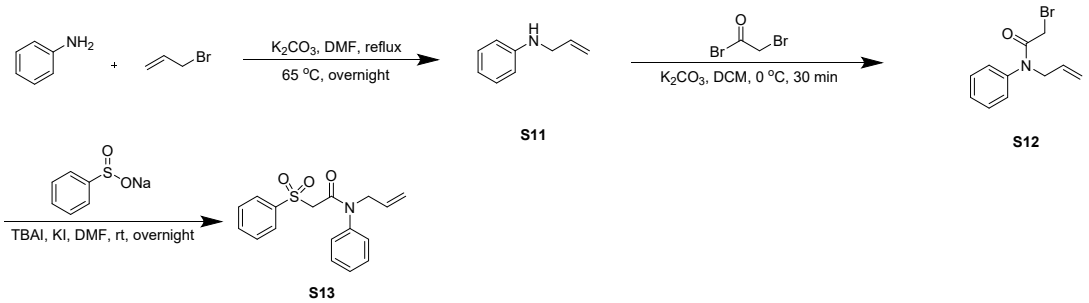


(1) Following the reported procedure,[8] to a solution of (*E*)-4-phenyl-3-buten-2-one (10 mmol, 1.0 equiv) in methanol (0.3 M) was added slowly sodium borohydride (15 mmol, 1.5 equiv) at 0 °C. After stirring 2 h at this temperature, the reaction was quenched with saturated aqueous NH_4Cl (20 mL). The mixture was extracted with ethyl acetate (20 mL × 3). The combined organic layer was washed with brine (15 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **S8**.

(2) To a solution of **S8** (8 mmol, 1.0 equiv) in dichloromethane (0.4 M) was added bromoacetic acid (9.6 mmol, 1.2 equiv), EDCI HCl (9.6 mmol, 1.2 mmol), and 4-(dimethylamino)pyridine (0.8 mmol, 0.1 equiv) at 0 °C. Then the solution was allowed to warm to room temperature and stirred for 6 h. After completion, the reaction was quenched with saturated aqueous $NaHCO_3$ (20 mL) and the mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (15 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography (petroleum ether / ethyl acetate) to afford **S9**.

(3) To a solution of **S9** (5 mmol, 1.0 equiv) in N,N-dimethylformamide (0.3 M) was added sodium benzenesulfinate (6 mmol, 1.2 equiv), tetrabutylammonium iodide (0.5 mmol, 0.1 equiv) and potassium iodide (6 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature overnight and then quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **S10**.

3.5 Compound 1bk was prepared according to the general procedure 5 (GP5)

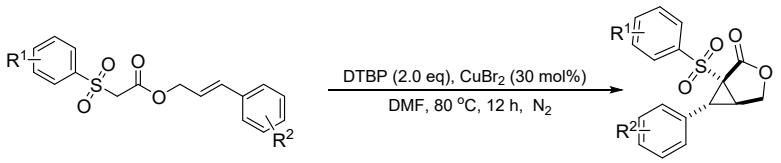


(1) To a solution of aniline (5 mmol, 1.0 equiv) in N,N-dimethylformamide (15 mL) was added potassium carbonate (6 mmol, 1.2 equiv) and allyl bromide (5 mmol, 1.0 equiv). The reaction mixture was stirred at 65 °C overnight and then cooled to room temperature. The reaction was quenched with H_2O (10 mL). The mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layer was washed with brine (15 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **S11**.

(2) Following the reported procedure,[9] to a solution of **S11** (3 mmol, 1.0 eq) in dichloromethane (0.3 M) was added slowly K_2CO_3 (4.5 mmol, 1.5 eq), bromoacetyl bromide (3.6 mmol, 1.2 eq) at 0 °C and stirred for 30 min. The reaction was quenched with H_2O (10 mL). The mixture was extracted with dichloromethane (10 mL × 3). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **S12**.

(3) To a solution of **S12** (5 mmol, 1.0 equiv) in N,N-dimethylformamide (0.3 M) was added sodium benzenesulfinate (6 mmol, 1.2 equiv), tetrabutylammonium iodide (0.5 mmol, 0.1 equiv) and potassium iodide (6 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature overnight and then quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **S13**.

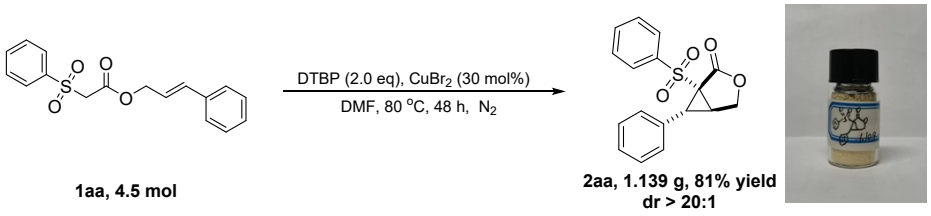
4. The general procedure 6 (GP6) for the synthesis of cyclopropanation product 2



1 **2**

An oven-dried 5 mL Schlenk tube equipped with a PTFE-coated stir bar was charged with **1** (63.3 mg, 0.2 mmol, 1.0 equiv) and $CuBr_2$ (13.4 mg, 0.06 mmol, 30 mol%), then the tube was evacuated and backfilled with N_2 for three times. DMF (1.0 mL) and DTBP (58.5 mg, 0.40 mmol, 2.0 equiv) were successively added via syringe under N_2 atmosphere. The sealed tube was placed into a preheated oil bath at 80 °C with stirring for 12 h. After cooling to room temperature, the mixture was diluted with water (10 mL). The layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was rinsed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether / ethyl acetate) on silica gel to afford **2.**

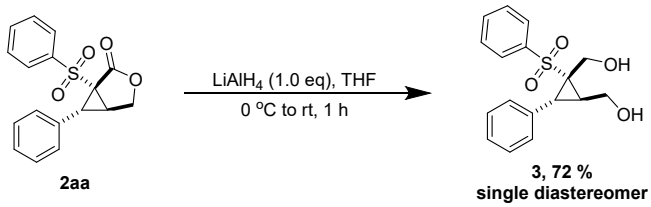
5. Scale-up synthesis of product 2aa



An oven-dried 50 mL Schlenk tube equipped with a PTFE-coated stir bar was charged with **1aa** (1.42 g, 4.5 mmol, 1.0 equiv) and $CuBr_2$ (301.5 mg, 1.35 mmol, 30 mol%), then the tube was evacuated and backfilled with N_2 for three times. DMF (25 mL) and DTBP (1.32 g, 9.0 mmol, 2.0 equiv) were successively added via syringe under N_2 atmosphere. The sealed tube was placed into a preheated oil bath at 80 °C with stirring for 48 h. After cooling to room temperature, the mixture was diluted with water (50 mL). The layer was separated and the aqueous layer was extracted with ethyl acetate (30 mL × 3). The combined organic layer was rinsed with brine (30 mL), dried over Na_2SO_4, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether / ethyl acetate) on silica gel to afford **2aa** (1.14 g, 3.62 mmol, 81%).

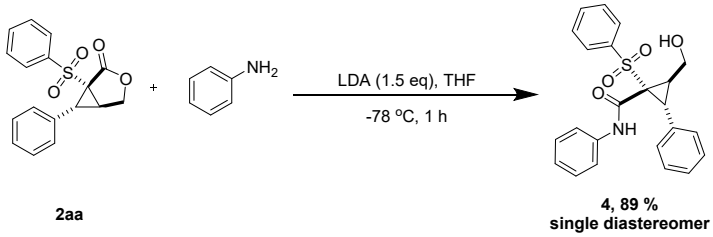
6. Derivatization reactions of product 2aa

6.1 Synthesis of compound 3



An oven-dried 5 mL Schlenk tube equipped with a PTFE-coated stir bar was charged with **2aa** (62.9 mg, 0.2 mmol, 1.0 equiv), then the tube was evacuated and backfilled with N_2 for three times. Dry THF (2 ml) and $LiAlH_4$ (200 µl 1.0 M solution in tetrahydrofuran, 0.2 mmol, 1.0 eq) were successively added via syringe under N_2 atmosphere at 0 °C. After stirring 1 h at this temperature, carefully quenched with 5 mL of a saturated solution of NH_4Cl. The reaction mixture was stirred at room temperature for 1 h, and the resulting white precipitate was filtered through a pad of Celite®. The filtrate was extracted three times with ethyl acetate (5 ml × 3) and concentrated in vacuo. The crude product was purified by flash chromatography to afford **3**.[10]

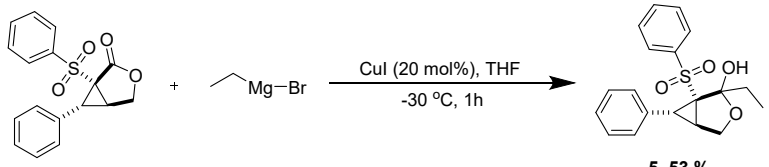
6.2 Synthesis of compound 4



An oven-dried 5 mL Schlenk tube equipped with a PTFE-coated stir bar was charged with **2aa** (62.9 mg, 0.2 mmol,

1.0 equiv), then the tube was evacuated and backfilled with N_2 for three times. Dry THF (2 ml) and aniline (22.4 mg, 0.24 mmol, 1.2 equiv) were successively added via syringe under N_2 atmosphere. Then the LDA (150 µl 2.0 M solution in tetrahydrofuran, 0.3 mmol, 1.5 eq) was added dropwise to the solution of **2aa** under - 78 °C. After stirring 1 h at this temperature, the solution was allowed to warm to room temperature and quenched with saturated aqueous NH_4Cl (10 mL). The mixture was extracted with ethyl acetate (5 mL × 3). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **4.**[11]

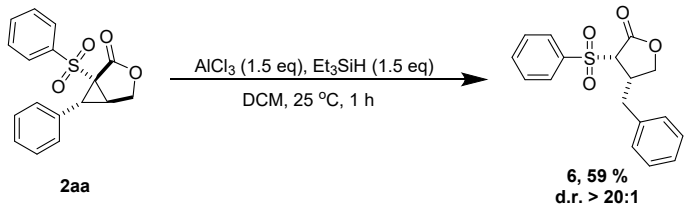
6.3 Synthesis of compound 5



2aa **5, 53 %**
d.r. = 7:1

An oven-dried 5 mL Schlenk tube equipped with a PTFE-coated stir bar was charged with **2aa** (62.9 mg, 0.2 mmol, 1.0 equiv) and cuprous iodide (7.6 mg, 0.04 mmol, 0.2 eq), then the tube was evacuated and backfilled with N_2 for three times. Dry THF (2 ml) and ethylmagnesium bromide (240 µl 1.0 M solution in tetrahydrofuran, 0.24 mmol, 1.2 eq) were successively added via syringe under N_2 atmosphere at - 30 °C. After stirring 1 h at this temperature, the reaction was quenched with saturated aqueous NH_4Cl (5 mL). The mixture was extracted with ethyl acetate (5 mL × 3). The combined organic layer was washed with brine (15 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **5.**

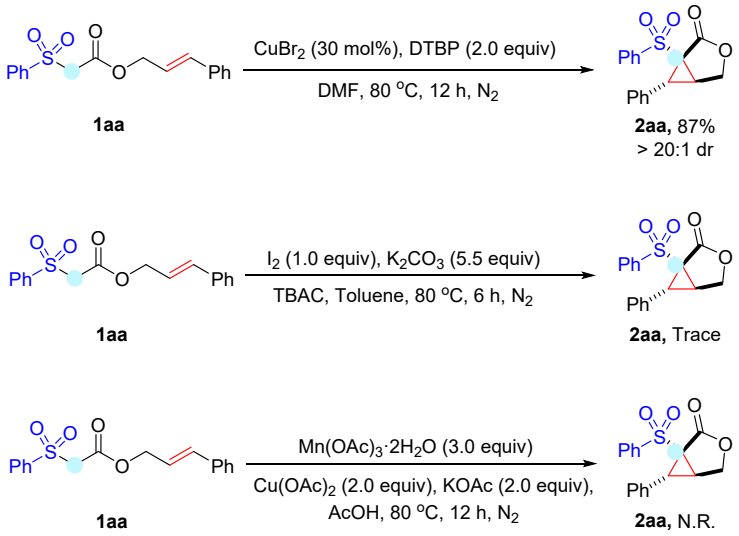
6.3 Synthesis of compound 6



An oven-dried 5 mL Schlenk tube equipped with a PTFE-coated stir bar was charged with **2aa** (62.9 mg, 0.2 mmol, 1.0 equiv) and $AlCl_3$ (40.0 mg, 0.3 mmol, 1.5 eq), then the tube was evacuated and backfilled with N_2 for three times. DCM (2.0 mL) and Et_3SiH (47.9 µl, 0.3 mmol, 1.5 equiv) were successively added via syringe under N_2 atmosphere.The reaction mixture was stirred at room temperature for 1 h and then quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with DCM. The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford **6.**[12]

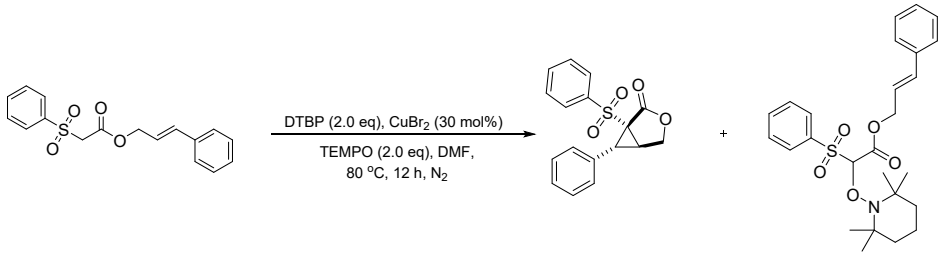
7. Control experiments

7.1 Comparing of this method with reported ones



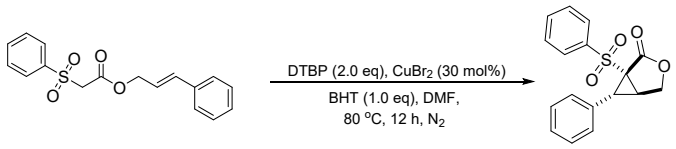
Followed the reported procedure for the intramolecular cyclopropanation reactions, both the halocyclization and $Mn(OAc)_3$ mediated cyclization protocols were evaluated.[13] Neither the $Mn(OAc)_3$ mediated oxidative annulation nor the halocyclization protocol could efficiently produce the expected cyclopropane-fused γ-lactone.

7.2 Radical trapping experiments



1aa **2aa, trace** **7, 22% yield**

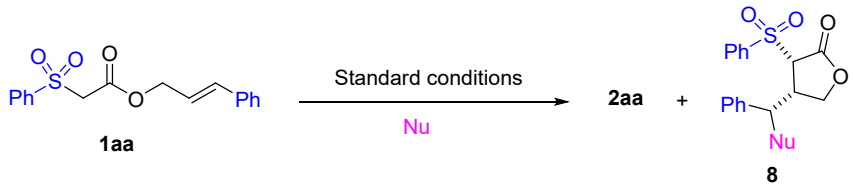
An oven-dried 5 mL Schlenk tube equipped with a PTFE-coated stir bar was charged with **1aa** (63.3 mg, 0.2 mmol, 1.0 equiv), $CuBr_2$ (13.4 mg, 0.06 mmol, 30 mol%) and 2,2,6,6-tetramethylpiperidine N-oxide (TEMPO, 62.5 mg, 0.4 mmol, 2.0 equiv), then the tube was evacuated and backfilled with N_2 for thrree times. DMF (1.0 mL) and DTBP (58.5 mg, 0.4 mmol, 2.0 equiv) were successively added via syringe under N_2 atmosphere. The mixture was stirred at 80 °C for 12 h under N_2 atmosphere. After cooling to room temperature, the mixture was diluted with water (10 mL). The layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was rinsed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Traces of the product 2aa were observed by TLC analysis. The resultant residue was purified by flash column chromatography (petroleum ether / ethyl acetate) on silica gel to afford **7** (21.1 mg, 0.045 mmol, 22%).



1aa **2aa, trace**

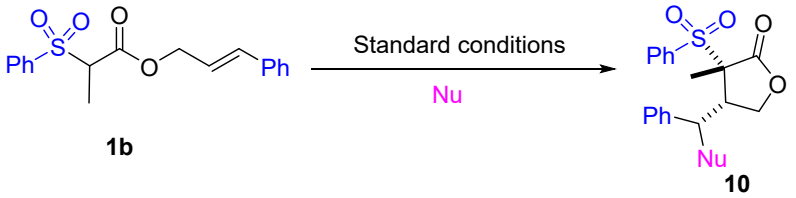
An oven-dried 5 mL Schlenk tube equipped with a PTFE-coated stir bar was charged with **1aa** (63.3 mg, 0.2 mmol, 1.0 equiv), $CuBr_2$ (13.4 mg, 0.06 mmol, 30 mol%) and 2,6-di-*tert*-butyl-4-methylphenol (BHT, 44.1 mg, 0.2 mmol, 1.0 equiv), then the tube was evacuated and backfilled with N_2 for three times. DMF (1.0 mL) and DTBP (58.5 mg,0.4 mmol, 2.0 equiv) were successively added via syringe under N_2 atmosphere. The mixture was stirred at 80 °C for 12 h under N_2 atmosphere. After cooling to room temperature, the mixture was diluted with water (10 mL). The layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was rinsed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Traces of the product **2aa** were observed by TLC analysis.

7.3 Carbocation trapping



1aa　　8

Entry	Nucleophile	Yield of **2aa** （%）	Yield of **8** （%）
1	H_2O (30 equiv)	Trace	-
2	MeOH (3.0 equiv)	Trace	-
3	TMSCN (1.5 equiv)	-	-
4	Aniline (1.5 equiv)	-	-
5	Indole (3.0 equiv)	-	-
6	$Et_3N \cdot 3HF$ (3.0 equiv)	-	-
7	TFE (3.0 equiv)	58	-
8	CH_3ONa (3.0 equiv)	-	-
9	NaOH (3.0 equiv)	Trace	-
10	CH_3COONa (3.0 equiv)	Trace	-
11	KBr (3.0 equiv)	69	-
12	1,3,5-Trimethoxybenzene (3.0 equiv)	60	-

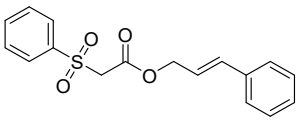


1b　　10

Entry	Nucleophile	Yield of **10** （%）
1	H_2O (30 equiv)	-.
2	MeOH (3.0 equiv)	-
3	TMSCN (1.5 equiv)	-
4	Indole (3.0 equiv)	-
5	1,3,5-Trimethoxybenzene (3.0 equiv)	-

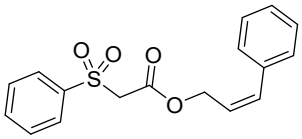
8. Characterization of products

Cinnamyl 2-(phenylsulfonyl)acetate (1aa)



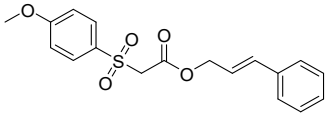
The title compound was prepared according to GP1 and isolated as a white solid. 81% yield, 1.281 g. mp 89 - 91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.65 – 7.61 (m, 1H), 7.54 – 7.50 (m, 2H), 7.38 – 7.28 (m, 5H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.13 (dt, *J* = 16.0, 6.6 Hz, 1H), 4.73 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.16 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 138.6, 135.9, 135.6, 134.4, 129.3, 128.8, 128.7, 128.5, 126.8, 121.6, 66.9, 61.1. HRMS (ESI, m/z): calcd. for $C_{17}H_{16}O_4S + Na^+$ [M + Na] $^+$: 339.0662; found: 339.0669.

(*Z*)-3-Phenylallyl 2-(phenylsulfonyl)acetate (1aa')



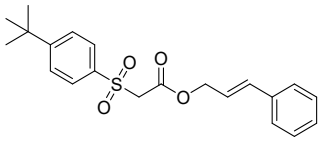
The title compound was prepared according to literature reports[14] and isolated as a colorless oil. 60% yield, 65 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H), 7.69 – 7.65 (m, 1H), 7.58 – 7.53 (m, 2H), 7.37 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 7.18 – 7.16 (m, 2H), 6.68 (d, *J* = 11.6 Hz, 1H), 5.68 (dt, *J* = 11.6, 6.8 Hz, 1H), 4.84 (dd, *J* = 6.8, 1.6 Hz, 2H), 4.15 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 138.7, 135.7, 134.4, 134.2, 129.4, 128.8, 128.7, 128.6, 127.9, 124.2, 63.3, 61.1. HRMS (ESI, m/z): calcd. for $C_{17}H_{16}O_4S + Na^+$ [M + Na] $^+$: 339.0662; found: 339.0665.

Cinnamyl 2-((4-methoxyphenyl)sulfonyl)acetate (1ac)



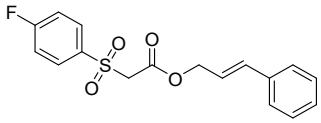
The title compound was prepared according to GP2 and isolated as a white solid. 66% yield, 1.142 g, mp 86 - 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.38 – 7.27 (m, 5H), 6.97 – 6.93 (m, 2H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.15 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.74 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.13 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 162.6, 135.9, 135.5, 131.0, 130.0, 128.8, 128.5, 126.8, 121.7, 114.5, 66.8, 61.4, 55.7. HRMS (ESI, m/z): calcd. for $C_{18}H_{18}O_5S + Na^+$ [M + Na] $^+$: 369.0767; found: 369.0766.

Cinnamyl 2-((4-(*tert*-butyl)phenyl)sulfonyl)acetate (1ad)



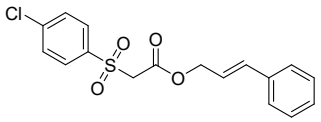
The title compound was prepared according to GP2 and isolated as a colorless oil. 45% yield, 838.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.53 – 7.51 (m, 2H), 7.39 – 7.27 (m, 5H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.18 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.76 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.15 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 158.5, 135.9, 135.7, 135.6, 128.8, 128.6, 128.5, 126.8, 126.3, 121.7, 66.9, 61.1, 35.4, 31.1. HRMS (ESI, m/z): calcd. for $C_{21}H_{24}O_4S + Na^+$ [M + Na]$^+$: 395.1288; found: 395.1289.

Cinnamyl 2-((4-fluorophenyl)sulfonyl)acetate (1ae)



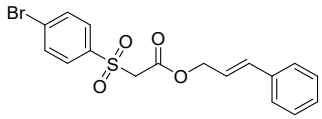
The title compound was prepared according to GP2 and isolated as a white solid. 40% yield, 668.8 mg, mp 59 - 63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.39 – 7.27 (m, 5H), 7.22 – 7.14 (m, 2H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.15 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.75 (dd, *J* = 6.6, 0.8 Hz, 2H), 4.16 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.6 – -102.8 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3 (d, J_{C-F} = 256.0 Hz), 162.3, 135.9, 135.8, 134.6 (d, J_{C-F} = 3.5 Hz), 131.8 (d, J_{C-F} = 9.7 Hz), 128.8, 128.6, 126.8, 121.5, 116.7 (d, J_{C-F} = 22.9 Hz), 67.0, 61.1. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}FO_4S + Na^+$ [M + Na]$^+$: 357.0567; found: 357.0566.

Cinnamyl 2-((4-chlorophenyl)sulfonyl)acetate (1af)



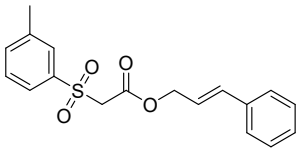
The title compound was prepared according to GP2 and isolated as a white solid. 50% yield, 877.1 mg, mp 76 - 80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.50 – 7.45 (m, 2H), 7.40 – 7.27 (m, 5H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.14 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.74 (dd, *J* = 6.7, 1.3 Hz, 2H), 4.16 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 141.3, 137.0, 135.9, 135.8, 130.3, 129.7, 128.9, 128.6, 126.8, 121.5, 67.0, 61.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}{}^{35}ClO_4S + Na^+$ [M + Na]$^+$: 37.0272; found: 373.0289.

Cinnamyl 2-((4-bromophenyl)sulfonyl)acetate (1ag)



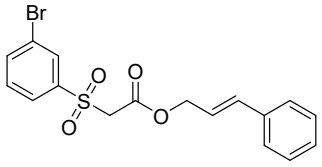
The title compound was prepared according to GP2 and isolated as a white solid. 55% yield, 1.089 g, mp 89 - 95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.66 – 7.63 (m, 2H), 7.39 – 7.28 (m, 5H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.14 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.75 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.15 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 137.5, 135.9, 135.8, 132.7, 130.3, 130.0, 128.9, 128.6, 126.8, 121.4, 67.0, 61.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}{}^{79}BrO_4S + Na^+$ [M + Na] $^+$: 416.9767; found: 416.9768.

Cinnamyl 2-(*m*-tolylsulfonyl)acetate (1ah)



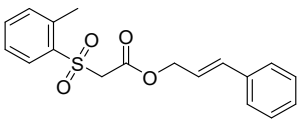
The title compound was prepared according to GP2 and isolated as a colorless oil. 56% yield, 925.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.39 – 7.27 (m, 7H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.13 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.73 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.16 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 139.7, 138.5, 135.9, 135.4, 135.2, 129.2, 128.9, 128.8, 128.5, 126.8, 125.8, 121.7, 66.8, 61.1, 21.4. HRMS (ESI, m/z): calcd. for $C_{18}H_{18}O_4S + Na^+$ [M + Na] $^+$: 353.0818; found: 353.0821.

Cinnamyl 2-((3-bromophenyl)sulfonyl)acetate (1ai)



The title compound was prepared according to GP2 and isolated as a colorless oil. 45% yield, 889.4 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (t, *J* = 1.9 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.27 (m, 6H), 6.63 (d, *J* = 15.8 Hz, 1H), 6.15 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.75 (d, *J* = 6.6 Hz, 2H), 4.17 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 140.4, 137.5, 135.9, 135.8, 131.6, 130.8, 128.8, 128.6, 127.4, 126.9, 123.3, 121.3, 67.1, 61.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}{}^{79}BrO_4S + Na^+$ [M + Na] $^+$: 416.9767; found: 416.9771.

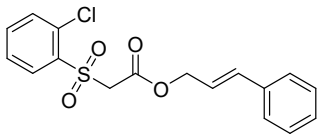
Cinnamyl 2-(*o*-tolylsulfonyl)acetate (1aj)



The title compound was prepared according to GP2 and isolated as a colorless oil. 64% yield, 1.056 g.

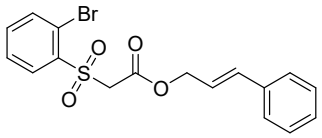
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.48 (td, *J* = 7.4, 1.4 Hz, 1H), 7.36 – 7.27 (m, 7H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.07 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.69 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.19 (s, 2H), 2.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 138.3, 136.8, 135.9, 135.5, 134.4, 132.9, 130.9, 128.8, 128.5, 126.8, 126.7, 121.6, 66.9, 60.4, 20.5. HRMS (ESI, m/z): calcd. for $C_{18}H_{18}O_4S + Na^+$ $[M + Na]^+$: 353.0818; found: 353.0826.

Cinnamyl 2-((2-chlorophenyl)sulfonyl)acetate (1ak)



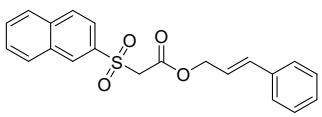
The title compound was prepared according to GP2 and isolated as a colorless oil. 57% yield, 999.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.37 – 7.27 (m, 6H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.05 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.69 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.49 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 136.2, 135.9, 135.6, 135.3, 132.8, 132.3, 131.9, 128.8, 128.5, 127.5, 126.8, 121.5, 66.9, 58.8. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}{}^{35}ClO_4S + Na^+$ $[M + Na]^+$: 373.0272; found: 373.0276.

Cinnamyl 2-((2-bromophenyl)sulfonyl)acetate (1al)



The title compound was prepared according to GP2 and isolated as a colorless oil. 53% yield, 1.047 g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.12 (m, 1H), 7.76 – 7.74 (m, 1H), 7.43 – 7.38 (m, 2H), 7.36 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 6.56 (dt, *J* = 15.8, 1.3 Hz, 1H), 6.06 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.69 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.53 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 137.8, 135.9, 135.6, 135.5, 135.3, 132.7, 128.8, 128.5, 128.1, 126.8, 121.5, 120.9, 66.9, 58.4. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}{}^{79}BrO_4S + Na^+$ $[M + Na]^+$: 416.9767; found: 416.9778.

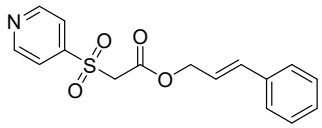
Cinnamyl 2-(naphthalen-2-ylsulfonyl)acetate (1am)



The title compound was prepared according to GP2 and isolated as a colorless oil. 76% yield, 1.392 g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 1.8 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.92 – 7.88 (m, 3H),

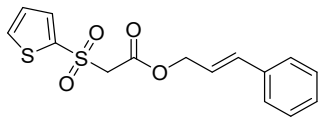
7.68 – 7.63 (m, 1H), 7.60 – 7.56 (m, 1H), 7.34 – 7.27 (m, 5H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.05 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.71 (dd, *J* = 6.7, 1.3 Hz, 2H), 4.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 148.8, 135.8, 135.6, 135.6, 135.5, 132.1, 130.9, 129.7, 129.6, 128.7, 128.5, 128.1, 127.9, 126.8, 123.0, 121.5, 66.9, 61.2. HRMS (ESI, m/z): calcd. for $C_{21}H_{18}O_4S + Na^+$ $[M + Na]^+$: 389.0818; found: 389.0821.

Cinnamyl 2-(pyridin-4-ylsulfonyl)acetatev (1an)



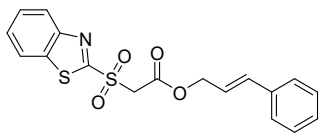
The title compound was prepared according to GP2 and isolated as a white solid. 35% yield, 555.4 mg. mp 57 - 61 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 – 8.86 (m, 2H), 7.81 – 7.78 (m, 2H), 7.39 – 7.28 (m, 5H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.15 (dt, *J* = 15.9, 6.8 Hz, 1H), 4.76 (dd, *J* = 6.8, 1.3 Hz, 2H), 4.20 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 151.1, 146.8, 136.2, 135.7, 128.9, 128.7, 126.8, 121.9, 121.2, 67.3, 60.4. HRMS (ESI, m/z): calcd. for $C_{16}H_{15}NO_4S + H^+$ $[M + H]^+$: 318.0795; found: 318.0795.

Cinnamyl 2-(thiophen-2-ylsulfonyl)acetate (1ao)



The title compound was prepared according to GP2 and isolated as a white solid. 41% yield, 660.9 mg. mp 45 - 48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.75 (m, 1H), 7.72 – 7.70 (m, 1H), 7.39 – 7.26 (m, 5H), 7.12 – 7.09 (m, 1H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.19 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.79 (dd, *J* = 6.7, 1.3 Hz, 2H), 4.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 139.3, 135.9, 135.7, 135.6, 135.2, 128.8, 128.5, 128.1, 126.8, 121.7, 67.0, 62.1. HRMS (ESI, m/z): calcd. for $C_{15}H_{14}O_4S_2$+Na^+ $[M + Na]^+$: 345.0226; found: 345.0226.

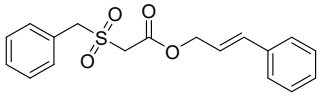
Cinnamyl 2-(benzo[d]thiazol-2-ylsulfonyl)acetate (1ap)



The title compound was prepared according to GP2 and isolated as a white solid. 30% yield, 560.2 mg. mp 71 - 76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.18 (m, 1H), 7.91 – 7.88 (m, 1H), 7.62 – 7.58 (m, 1H), 7.54 – 7.53 (m, 1H), 7.33 – 7.27 (m, 3H), 7.26 – 7.23 (m, 2H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.04 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.74 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.62 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9,

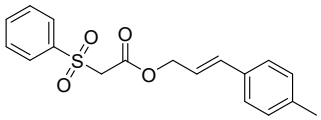
161.5, 152.5, 137.0, 135.8, 135.7, 128.7, 128.5, 128.3, 127.9, 126.8, 125.6, 122.5, 121.3, 67.2, 58.9. HRMS (ESI, m/z): calcd. for $C_{18}H_{15}NO_4S_2 + Na^+$ $[M + Na]^+$: 396.0335; found: 396.0338.

Cinnamyl 2-(benzylsulfonyl)acetate (1aq)



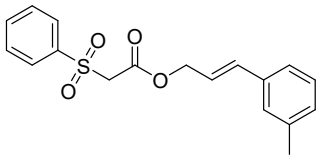
The title compound was prepared according to GP2 and isolated as a colorless oil. 50% yield, 826.0 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 2H), 7.43 – 7.38 (m, 5H), 7.37 – 7.28 (m, 3H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.90 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.53 (s, 2H), 3.82 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 135.9, 131.1, 129.5, 129.3, 128.8, 128.7, 128.6, 127.8, 126.9, 121.6, 67.2, 59.6, 54.7. HRMS (ESI, m/z): calcd. for $C_{18}H_{18}O_4S + Na^+$ $[M + Na]^+$: 353.0818; found: 353.0819.

(*E*)-3-(*p*-tolyl)allyl 2-(phenylsulfonyl)acetate (1ba)



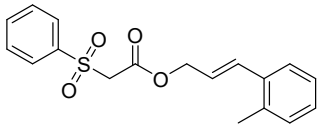
The title compound was prepared according to GP3 and isolated as a colorless oil. 75% yield, 1.239 g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.65 – 7.61 (m, 1H), 7.54 – 7.49 (m, 2H), 7.27 – 7.25 (m, 2H), 7.14 (d, *J* = 8 Hz, 2H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.08 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.71 (dd, *J* = 6.7, 1.3 Hz, 2H), 4.16 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 138.6, 138.5, 135.7, 134.4, 133.1, 129.5, 129.3, 128.7, 126.7, 120.5, 67.1, 61.1, 21.4. HRMS (ESI, m/z): calcd. for $C_{18}H_{18}O_4S + Na^+$ $[M + Na]^+$: 353.0818; found: 353.0821.

(*E*)-3-(*m*-tolyl)allyl 2-(phenylsulfonyl)acetate (1bb)



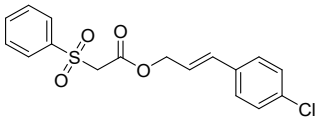
The title compound was prepared according to GP3 and isolated as a colorless oil. 70% yield, 1.156 g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.66 – 7.65 (m, 1H), 7.54 – 7.50 (m, 2H), 7.25 – 7.21 (m, 1H), 7.18 – 7.15 (m, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.12 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.72 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.16 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 138.6, 138.4, 135.8, 135.8, 134.4, 129.3, 129.3, 128.7, 128.7, 127.5, 124.0, 121.4, 67.0, 61.1, 21.5. HRMS (ESI, m/z): calcd. for $C_{18}H_{18}O_4S + Na^+$ $[M + Na]^+$: 353.0818; found: 353.0822.

(*E*)-3-(*o*-Tolyl)allyl 2-(phenylsulfonyl)acetate (1bc)



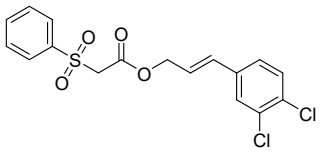
The title compound was prepared according to GP3 and isolated as a colorless oil. 66% yield, 1.090 g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.64 – 7.60 (m, 1H), 7.53 – 7.49 (m, 2H), 7.41 – 7.38 (m, 1H), 7.20 – 7.14 (m, 3H), 6.86 (d, *J* = 15.7 Hz, 1H), 6.01 (dt, *J* = 15.7, 6.6 Hz, 1H), 4.75 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.17 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 138.7, 135.9, 135.1, 134.5, 133.5, 130.5, 129.4, 128.7, 128.4, 126.3, 125.9, 123.0, 67.1, 61.1, 19.9. HRMS (ESI, m/z): calcd. for $C_{18}H_{18}O_4S + Na^+$ $[M + Na]^+$: 353.0818; found: 353.0819.

(*E*)-3-(4-chlorophenyl)allyl 2-(phenylsulfonyl)acetate (1be)



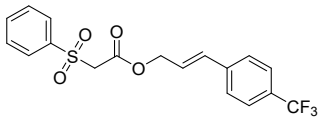
The title compound was prepared according to GP3 and isolated as a colorless oil. 69% yield, 1.210 g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 7.65 – 7.61 (m, 1H), 7.54 – 7.50 (m, 2H), 7.31 – 7.26 (m, 4H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.10 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.72 (dd, *J* = 6.5, 1.4 Hz, 2H), 4.16 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 138.6, 134.5, 134.4, 134.1, 134.1, 129.4, 129.0, 128.7, 128.0, 122.4, 66.6, 61.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}{}^{35}ClO_4S + Na^+$ $[M + Na]^+$: 373.0272; found: 373.0277.

(*E*)-3-(3,4-dichlorophenyl)allyl 2-(phenylsulfonyl)acetate (1bf)



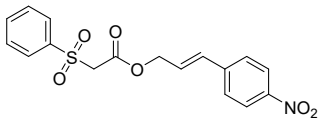
The title compound was prepared according to GP3 and isolated as a white solid. 80% yield, 1.541 g. mp 46 - 51 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 2H), 7.68 – 7.64 (m, 1H), 7.56 – 7.52 (m, 2H), 7.41 (d, *J* = 2.1 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.17 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.11 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.72 (d, *J* = 6.3 Hz, 2H), 4.17 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 138.7, 136.1, 134.5, 132.9, 132.5, 132.1, 130.7, 129.4, 128.6, 128.4, 126.0, 123.8, 66.2, 61.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{14}{}^{35}Cl_2O_4S + Na^+$ $[M + Na]^+$: 406.9882; found: 406.9884.

(*E*)-3-(4-(trifluoromethyl)phenyl)allyl 2-(phenylsulfonyl)acetate (1bg)



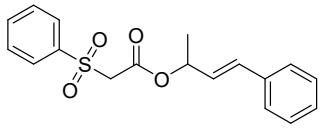
The title compound was prepared according to GP3 and isolated as a white solid. 67% yield, 1.288 g, mp 73 - 76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.67 – 7.63 (m, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.24 (dt, *J* = 16.0, 6.2 Hz, 1H), 4.77 (dd, *J* = 6.2, 1.4 Hz, 2H), 4.18 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 139.4, 138.7, 134.5, 133.5, 130.1 (q, J_{C-F} = 32.4 Hz), 129.4, 128.7, 127.0, 125.7 (q, J_{C-F} = 3.9 Hz), 124.4, 124.2 (q, J_{C-F} = 270.6 Hz), 66.3, 61.0. HRMS (ESI, m/z): calcd. for $C_{18}H_{15}F_3O_4S + Na^+$ [M + Na] $^+$: 407.0535; found: 407.0540.

(*E*)-3-(4-nitrophenyl)allyl 2-(phenylsulfonyl)acetate (1bh)



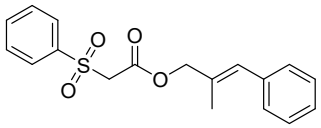
The title compound was prepared according to GP3 and isolated as a yellow solid. 77% yield, 1.391 g, mp 93 - 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.18 (m, 2H), 7.97 – 7.94 (m, 2H), 7.69 – 7.65 (m, 1H), 7.58 – 7.50 (m, 4H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.81 (dd, *J* = 6.0, 1.6 Hz, 2H), 4.19 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 147.5, 142.3, 138.7, 134.5, 132.3, 129.4, 128.6, 127.4, 126.6, 124.2, 66.0, 61.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}NO_6S + Na^+$ [M + Na] $^+$: 384.0512; found: 384.0535.

(*E*)-4-phenylbut-3-en-2-yl 2-(phenylsulfonyl)acetate (1bk)



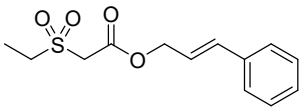
The title compound was prepared according to GP4 and isolated as a colorless oil. 69% yield, 1.140 g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.64 – 7.59 (m, 1H), 7.51 – 7.49 (m, 2H), 7.37 – 7.27 (m, 5H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.03 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.50 – 5.46 (m, 1H), 4.13 (s, 2H), 1.36 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 138.6, 136.0, 134.4, 132.9, 129.3, 128.8, 128.7, 128.4, 127.3, 126.8, 73.8, 61.3, 20.2. HRMS (ESI, m/z): calcd. for $C_{18}H_{18}O_4S + Na^+$ [M + Na] $^+$: 353.0818; found: 353.0823.

(*E*)-2-methyl-3-phenylallyl 2-(phenylsulfonyl)acetate (1bl)



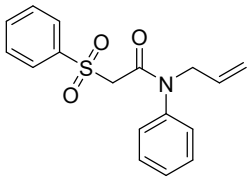
The title compound was prepared according to GP3 and isolated as a colorless oil. 75% yield, 1.239 g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 2H), 7.68 – 7.63 (m, 1H), 7.57 – 7.53 (m, 2H), 7.37 – 7.33 (m, 2H), 7.27 – 7.23 (m, 3H), 6.49 (s, 1H), 4.65 (s, 2H), 4.19 (s, 2H), 1.82 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 138.7, 136.7, 134.4, 131.5, 129.8, 129.4, 129.0, 128.7, 128.3, 127.2, 72.3, 61.1, 15.6. HRMS (ESI, m/z): calcd. for $C_{18}H_{18}O_4S + Na^+$ [M + Na] $^+$: 353.0818; found: 353.0825.

Cinnamyl 2-(ethylsulfonyl)acetate (1bn)



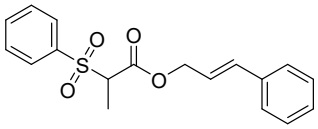
The title compound was prepared according to GP2 and isolated as a yellow oil. 61% yield, 817 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.35 – 7.28 (m, 3H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.27 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.86 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.00 (s, 2H), 3.29 (q, *J* = 7.5 Hz, 2H), 3.29 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 135.9, 135.8, 128.8, 128.5, 126.9, 121.6, 67.2, 56.6, 48.2, 6.7. HRMS (ESI, m/z): calcd. for $C_{13}H_{16}O_4S + Na^+$ [M + Na] $^+$: 291.0662; found: 291.0667.

N-allyl-N-phenyl-2-(phenylsulfonyl)acetamide (1bt)



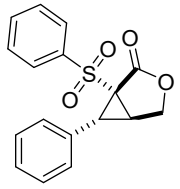
The title compound was prepared according to GP5 and isolated as a yellow oil. 60% yield, 946.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 2H), 7.68 – 7.64 (m, 1H), 7.58 – 7.54 (m, 2H), 7.42 – 7.36 (m, 3H), 7.16 – 7.14 (m, 2H), 5.82 – 5.75 (m, 1H), 5.14 – 5.08 (m, 2H), 4.26 (d, *J* = 6.2 Hz, 2H), 3.98 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 141.2, 139.5, 134.1, 132.0, 130.1, 129.1, 129.0, 128.9, 128.5, 118.7, 59.4, 52.7. HRMS (ESI, m/z): calcd. for $C_{17}H_{17}NO_3S + Na^+$ [M + Na] $^+$: 338.0821; found: 338.0820.

Cinnamyl 2-(phenylsulfonyl)propanoate (1b)



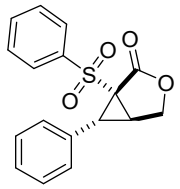
The title compound was isolated as a yellow oil. 80% yield, 1.322 g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.64 – 7.59 (m, 1H), 7.51 – 7.47 (m, 2H), 7.38 – 7.27 (m, 5H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.11 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.71 (d, *J* = 6.6 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 136.9, 135.9, 135.5, 134.4, 129.5, 129.2, 128.8, 128.5, 126.8, 121.8, 66.8, 65.5, 11.8. HRMS (ESI, m/z): calcd. for $C_{18}H_{18}O_4S + Na^+$ $[M + Na]^+$: 353.0818; found: 353.0824.

6-Phenyl-1-(phenylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2aa)



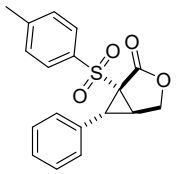
Purified by flash chromatography with EA/PE (1/4) as eluent, 87% yield, 54.7 mg; white solid. mp 174 - 178 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 1H), 7.46 – 7.43 (m, 2H), 7.36 – 7.29 (m, 3H), 7.26 – 7.23 (m, 2H), 7.04 – 7.02 (m, 2H), 4.61 (dd, *J* = 9.5, 4.8 Hz, 1H), 4.38 (d, *J* = 9.6 Hz, 1H), 3.84 (dd, *J* = 6.1, 4.5 Hz, 1H), 2.87 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 138.6, 134.0, 130.0, 128.6, 128.6, 128.6, 128.3, 127.9, 67.6, 52.7, 37.3, 28.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{14}O_4S + Na^+$ $[M + Na]^+$: 337.0505; found: 337.0508.

6-Phenyl-1-(phenylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one [2aa (1aa')]



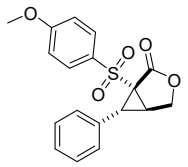
Purified by flash chromatography with EA/PE (1/3.5) as eluent, 78% yield, 49.4 mg; white solid. mp 176 - 179 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 1H), 7.45 – 7.43 (m, 2H), 7.36 – 7.30 (m, 3H), 7.27 – 7.23 (m, 2H), 7.04 – 7.02 (m, 2H), 4.63 (dd, *J* = 9.5, 4.8 Hz, 1H), 4.39 (d, *J* = 9.5 Hz, 1H), 3.84 (dd, *J* = 6.2, 4.6 Hz, 1H), 2.87 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 138.5, 134.0, 130.0, 128.6, 128.6, 128.6, 128.3, 127.9, 67.6, 52.7, 37.3, 28.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{14}O_4S + Na^+$ $[M + Na]^+$: 337.0505; found: 337.0507.

6-Phenyl-1-tosyl-3-oxabicyclo[3.1.0]hexan-2-one (2ab)



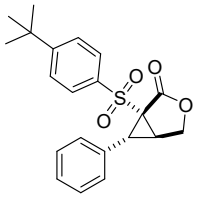
Purified by flash chromatography with EA/PE (1/4) as eluent, 89% yield, 58.5 mg; white solid. mp 184 - 188 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.13 – 7.11 (m, 2H), 7.09 – 7.06 (m, 2H), 4.62 (dd, *J* = 9.5, 4.7 Hz, 1H), 4.38 (d, *J* = 9.5 Hz, 1H), 3.81 (dd, *J* = 6.1, 4.8 Hz, 1H), 2.86 (d, *J* = 6.2 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 145.1, 135.6, 130.0, 129.2, 128.8, 128.6, 128.2, 128.1, 67.6, 52.7, 37.2, 27.9, 21.8. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}O_4S + Na^+$ [M + Na] $^+$: 351.0662; found: 351.0663.

1-((4-Methoxyphenyl)sulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2ac)



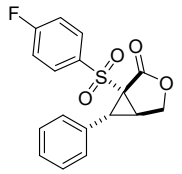
Purified by flash chromatography with EA/PE (1/5) as eluent, 82% yield, 56.5 mg; white solid. mp 155 - 160 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 3H), 7.30 – 7.26 (m, 2H), 7.09 – 7.07 (m, 2H), 6.79 – 6.76 (m, 2H), 4.59 (dd, *J* = 9.5, 4.6 Hz, 1H), 4.35 (d, *J* = 9.4 Hz, 1H), 3.83 (s, 3H), 3.79 (dd, *J* = 6.2, 4.7 Hz, 1H), 2.85 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 164.0, 131.1, 130.1, 128.6, 128.6, 128.2, 128.2, 113.7, 67.6, 55.8, 52.8, 37.1, 27.9. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}O_5S + Na^+$ [M + Na] $^+$: 367.0611; found: 367.0610.

1-((4-(t*ert*-Butyl)phenyl)sulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2ad)



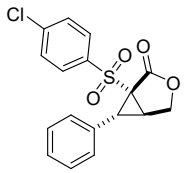
Purified by flash chromatography with EA/PE (1/6) as eluent, 71% yield, 52.9 mg; white solid. mp 224 - 228 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 5H), 7.26 – 7.22 (m, 2H), 7.06 – 7.03 (m, 2H), 4.62 (dd, *J* = 9.5, 4.7 Hz, 1H), 4.37 (d, *J* = 9.6 Hz, 1H), 3.81 (dd, *J* = 6.1, 4.6 Hz, 1H), 2.86 (d, *J* = 6.2 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 157.9, 135.6, 130.0, 128.6, 128.5, 128.2, 128.1, 125.6, 67.6, 52.8, 37.2, 35.3, 31.1, 28.0. HRMS (ESI, m/z): calcd. for $C_{21}H_{22}O_4S + Na^+$ [M + Na] $^+$: 393.1131; found: 393.1132.

1-((4-Fluorophenyl)sulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2ae)



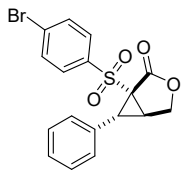
Purified by flash chromatography with EA/PE (1/5) as eluent, 85% yield, 56.6 mg; white solid. mp 210 - 215 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.38 – 7.34 (m, 1H), 7.30 – 7.26 (m, 2H), 7.06 – 7.03 (m, 2H), 7.02 – 6.95 (m, 2H), 4.65 (dd, *J* = 9.6, 4.7 Hz, 1H), 4.40 (d, *J* = 9.6 Hz, 1H), 3.84 (dd, *J* = 6.2, 4.7 Hz, 1H), 2.87 (d, *J* = 6.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.6 – -103.7 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 166.0 (d, J_{C-F} = 255.1 Hz), 134.5 (d, J_{C-F} = 3.0 Hz), 131.7 (d, J_{C-F} = 9.6 Hz), 130.0, 128.8, 128.3, 127.8, 115.8 (d, J_{C-F} = 22.7 Hz), 67.6, 52.7, 37.3, 27.9. HRMS (ESI, m/z): calcd. for $C_{17}H_{13}FO_4S + Na^+$ [M + Na] $^+$: 355.0411; found: 355.0418.

1-((4-Chlorophenyl)sulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2af)



Purified by flash chromatography with EA/PE (1/4) as eluent, 81% yield, 56.4 mg; white solid. mp 182 - 188 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 3H), 7.30 – 7.27 (m, 4H), 7.06 – 7.03 (m, 2H), 4.64 (dd, *J* = 9.6, 4.7 Hz, 1H), 4.40 (d, *J* = 9.6 Hz, 1H), 3.85 (dd, *J* = 6.3, 4.6 Hz, 1H), 2.88 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 140.8, 136.9, 130.2, 130.0, 128.9, 128.8, 128.3, 127.7, 67.7, 52.7, 37.3, 28.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{13}{}^{35}ClO_4S + Na^+$ [M + Na] $^+$: 371.0115; found: 371.0122.

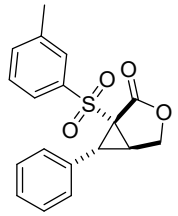
1-((4-Bromophenyl)sulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2ag)



Purified by flash chromatography with EA/PE (1/4) as eluent, 78% yield, 61.4 mg; white solid. mp 166 - 170 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.38 – 7.34 (m, 1H), 7.30 – 7.27 (m, 3H), 7.25 – 7.24 (m, 1H), 7.06 – 7.03 (m, 2H), 4.64 (dd, *J* = 9.6, 4.7 Hz, 1H), 4.40 (d, *J* = 9.6 Hz, 1H), 3.85 (dd, *J* = 6.3, 4.6 Hz, 1H), 2.88 (d, *J* = 6.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4,

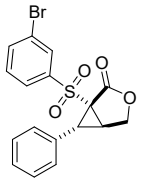
137.4, 131.9, 130.2, 130.0, 129.5, 128.8, 128.3, 127.7, 67.7, 52.7, 37.3, 28.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{13}{}^{79}BrO_4S + Na^+$ $[M + Na]^+$: 414.9610; found: 414.9618.

6-Phenyl-1-(*m*-tolylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2ah)



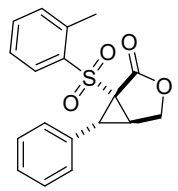
Purified by flash chromatography with EA/PE (1/4) as eluent, 87% yield, 57.1 mg; white solid. mp 180 - 183 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 1H), 7.36 – 7.32 (m, 2H), 7.28 – 7.22 (m, 3H), 7.05 – 7.03 (m, 2H), 6.98 – 6.97 (m, 1H), 4.61 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.37 (d, *J* = 9.6 Hz, 1H), 3.83 (dd, *J* = 6.2, 4.6 Hz, 1H), 2.85 (d, *J* = 6.2 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 138.6, 138.3, 134.7, 130.1, 128.8, 128.6, 128.6, 128.1, 128.0, 126.0, 67.6, 52.8, 37.2, 27.9, 21.3. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}O_4S + Na^+$ $[M + Na]^+$: 351.0662; found: 351.0662.

1-((3-Bromophenyl)sulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2ai)



Purified by flash chromatography with EA/PE (1/4) as eluent, 64% yield, 50.1 mg; white solid. mp 168 - 172 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 1H), 7.69 – 7.66 (m, 1H), 7.41 – 7.37 (m, 1H), 7.33 – 7.28 (m, 3H), 7.14 – 7.13 (m, 1H), 7.04 – 7.01 (m, 2H), 4.66 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.41 (d, *J* = 9.6 Hz, 1H), 3.87 (dd, *J* = 6.3, 4.7 Hz, 1H), 2.90 (d, *J* = 6.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 140.2, 137.0, 131.2, 130.3, 129.9, 129.1, 128.4, 127.6, 127.3, 122.4, 67.6, 52.6, 37.4, 28.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{13}{}^{79}BrO_4S + Na^+$ $[M + Na]^+$: 414.9610; found: 414.9619.

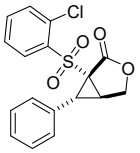
6-Phenyl-1-(*o*-tolylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2aj)



Purified by flash chromatography with EA/PE (1/4) as eluent, 79% yield, 51.9 mg; white solid. mp 133 - 136 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 1H), 7.43 – 7.39 (m, 1H), 7.32 –

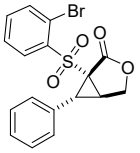
7.26 (m, 2H), 7.25 – 7.14 (m, 5H), 4.58 (dd, *J* = 9.5, 4.7 Hz, 1H), 4.39 (d, *J* = 9.6 Hz, 1H), 3.81 (dd, *J* = 6.2, 4.6 Hz, 1H), 3.01 (d, *J* = 6.1 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 139.2, 137.4, 133.8, 132.6, 130.6, 129.9, 128.7, 128.5, 128.4, 126.5, 67.4, 53.7, 37.5, 29.2, 20.6. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}O_4S + Na^+$ $[M + Na]^+$: 351.0662; found: 351.0662.

1-((2-Chlorophenyl)sulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2ak)



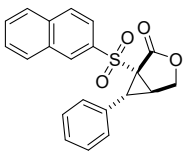
Purified by flash chromatography with EA/PE (1/4) as eluent, 62% yield, 43.3 mg; white solid. mp 192 - 198 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.14 (m, 1H), 7.56 – 7.33 (m, 8H), 4.60 (dd, *J* = 9.6, 4.7 Hz, 1H), 4.40 (d, *J* = 9.5 Hz, 1H), 3.89 (dd, *J* = 6.2, 4.7 Hz, 1H), 3.18 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 136.9, 135.2, 133.2, 131.7, 131.6, 129.9, 129.1, 128.9, 128.6, 127.6, 67.7, 52.2, 37.9, 31.6. HRMS (ESI, m/z): calcd. for $C_{17}H_{13}{}^{35}ClO_4S + Na^+$ $[M + Na]^+$: 371.0115; found: 371.0119.

1-((2-Bromophenyl)sulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2al)



Purified by flash chromatography with EA/PE (1/3) as eluent, 58% yield, 45.7 mg; white solid. mp 155 - 161 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.70 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 – 7.33 (m, 7H), 4.66 (dd, *J* = 9.5, 4.6 Hz, 1H), 4.41 (d, *J* = 9.6 Hz, 1H), 3.95 (dd, *J* = 6.2, 4.6 Hz, 1H), 3.17 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 138.5, 135.3, 135.2, 133.8, 130.0, 129.0, 128.9, 128.6, 128.1, 119.7, 67.7, 52.1, 37.8, 32.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{13}{}^{79}BrO_4S + Na^+$ $[M + Na]^+$: 414.9610; found: 414.9615.

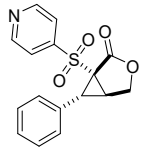
1-(Naphthalen-2-ylsulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2am)



Purified by flash chromatography with EA/PE (1/3) as eluent, 88% yield, 64.0 mg; white solid. mp 194 - 204 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 3H), 7.67 – 7.62 (m, 2H), 7.58 – 7.50 (m, 2H), 7.37 – 7.33 (m, 1H), 7.20 – 7.16 (m, 2H), 6.99 – 6.97 (m, 2H), 4.66 (dd, *J* = 9.5, 4.7 Hz,

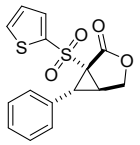
1H), 4.40 (d, *J* = 9.5 Hz, 1H), 3.89 (dd, *J* = 6.2, 4.6 Hz, 1H), 2.86 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 135.5, 135.3, 131.6, 130.7, 130.0, 129.8, 129.4, 128.9, 128.7, 128.2, 127.9, 127.8, 127.3, 123.4, 67.6, 52.5, 37.3, 27.9. HRMS (ESI, m/z): calcd. for $C_{21}H_{16}O_4S + Na^+$ [M + Na]$^+$: 387.0662; found: 387.0667.

6-Phenyl-1-(pyridin-4-ylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one(2an)



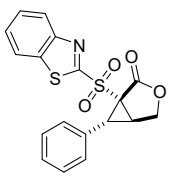
Purified by flash chromatography with EA/PE (1/2) as eluent, 57% yield, 36.0 mg; white solid. mp 203 - 206 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.76 (s, 2H), 7.35 – 7.23 (m, 5H), 7.16 – 7.14 (m, 2H), 4.69 (dd, *J* = 9.5, 4.9 Hz, 1H), 4.49 (d, *J* = 9.5 Hz, 1H), 4.28 (dd, *J* = 6.4, 4.6 Hz, 1H), 3.47 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 168.7, 151.3, 146.9, 130.6, 129.1, 128.8, 128.3, 121.0, 68.6, 52.5, 37.3, 29.3. HRMS (ESI, m/z): calcd. for $C_{16}H_{13}NO_4S + Na^+$ [M + Na]$^+$: 338.0458; found: 338.0460.

6-Phenyl-1-(thiophen-2-ylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2ao)



Purified by flash chromatography with EA/PE (1/3) as eluent, 62% yield, 39.5 mg; white solid. mp 196 - 203 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.21 (dd, *J* = 3.9, 1.4 Hz, 1H), 7.17 – 7.15 (m, 2H), 6.98 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.61 (dd, *J* = 9.5, 4.7 Hz, 1H), 4.39 (d, *J* = 9.6 Hz, 1H), 3.81 (dd, *J* = 6.0, 4.5 Hz, 1H), 2.95 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 138.8, 135.6, 134.9, 130.0, 128.8, 128.3, 128.0, 127.3, 67.5, 52.9, 37.6, 28.3. HRMS (ESI, m/z): calcd. for $C_{15}H_{12}O_4S_2 + Na^+$ [M + Na]$^+$: 343.0069; found: 343.0077.

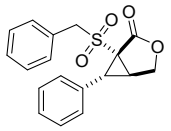
1-(Benzo[*d*]thiazol-2-ylsulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2ap)



Purified by flash chromatography with EA/PE (1/1) as eluent, 14% yield, 10.2 mg; white solid. mp 182 - 190 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.15 (m, 1H), 7.96 – 7.94 (m, 1H), 7.63 –

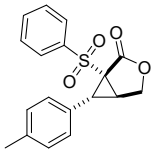
7.57 (m, 2H), 7.36 – 7.27 (m, 5H), 4.72 (dd, *J* = 9.5, 4.7 Hz, 1H), 4.48 (d, *J* = 9.5 Hz, 1H), 3.95 (dd, *J* = 6.3, 4.6 Hz, 1H), 3.26 (d, *J* = 6.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 165.1, 152.1, 137.2, 129.8, 129.0, 128.5, 128.5, 128.2, 127.6, 125.7, 122.3, 67.6, 51.8, 38.1, 29.8. HRMS (ESI, m/z): calcd. for $C_{18}H_{13}NO_4S_2 + Na^+$ $[M + Na]^+$: 394.0178; found: 394.0183.

1-(Benzylsulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2aq)



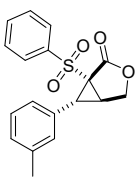
Purified by flash chromatography with EA/PE (1/3) as eluent, 64% yield, 42.1 mg; white solid. mp 177 - 183 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 6H), 7.24 – 7.19 (m, 4H), 4.65 (d, *J* = 13.6 Hz, 1H), 4.32 (d, *J* = 9.5 Hz, 1H), 4.24 (dd, *J* = 9.5, 4.4 Hz, 1H), 4.18 (d, *J* = 13.5 Hz, 1H), 3.39 (t, *J* = 5.2 Hz, 1H), 2.99 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 131.3, 129.6, 129.2, 129.0, 128.8, 128.7, 128.5, 126.2, 67.9, 59.8, 49.9, 36.9, 27.8. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}O_4S + Na^+$ $[M + Na]^+$: 351.0662; found: 351.0663.

1-(Phenylsulfonyl)-6-(p-tolyl)-3-oxabicyclo[3.1.0]hexan-2-one (2ba)



Purified by flash chromatography with EA/PE (1/4) as eluent, 85% yield, 55.9 mg; white solid. mp 207 - 213 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 1H), 7.50 – 7.45 (m, 2H), 7.34 – 7.31 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 4.61 (dd, *J* = 9.5, 4.8 Hz, 1H), 4.37 (d, *J* = 9.5 Hz, 1H), 3.81 (dd, *J* = 6.3, 4.7 Hz, 1H), 2.84 (d, *J* = 6.3 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 138.6, 133.9, 129.8, 128.9, 128.8, 128.7, 128.5, 124.9, 67.6, 52.7, 37.2, 28.0, 21.3. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}O_4S + Na^+$ $[M + Na]^+$: 351.0662; found: 351.0659.

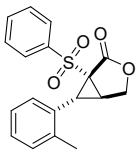
1-(Phenylsulfonyl)-6-(*m*-tolyl)-3-oxabicyclo[3.1.0]hexan-2-one (2bb)



Purified by flash chromatography with EA/PE (1/5) as eluent, 74% yield, 48.9 mg; white solid. mp 155 - 160 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 1H), 7.48 – 7.45 (m, 2H), 7.36 –

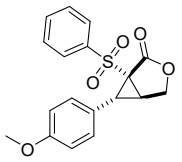
7.30 (m, 2H), 7.19 – 7.12 (m, 2H), 6.88 – 6.86 (m, 1H), 6.73 – 6.72 (m, 1H), 4.62 (dd, *J* = 9.5, 4.7 Hz, 1H), 4.37 (d, *J* = 9.5 Hz, 1H), 3.82 (dd, *J* = 6.3, 4.7 Hz, 1H), 2.84 (d, *J* = 6.2 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 138.6, 137.8, 133.8, 131.1, 129.4, 128.7, 128.5, 128.2, 127.7, 126.7, 67.6, 52.6, 37.3, 28.0, 21.3. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}O_4S + Na^+$ $[M + Na]^+$: 351.0662; found: 351.0667.

1-(Phenylsulfonyl)-6-(*o*-tolyl)-3-oxabicyclo[3.1.0]hexan-2-one (2bc)



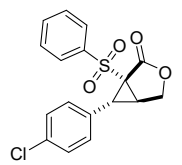
Purified by flash chromatography with EA/PE (1/4) as eluent, 75% yield, 49.1 mg; white solid. mp 128 - 133 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 1H), 7.41 – 7.38 (m, 2H), 7.34 – 7.27 (m, 4H), 7.25 – 7.22 (m, 1H), 6.97 – 6.95 (m, 1H), 4.66 (dd, *J* = 9.5, 4.8 Hz, 1H), 4.37 (d, *J* = 9.5 Hz, 1H), 3.89 (dd, *J* = 6.4, 4.8 Hz, 1H), 2.77 (d, *J* = 6.4 Hz, 1H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 139.7, 138.1, 134.2, 130.0, 128.9, 128.9, 128.6, 128.5, 126.2, 125.9, 67.8, 52.1, 35.8, 27.4, 18.8. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}O_4S + Na^+$ $[M + Na]^+$: 351.0662; found: 351.0665.

6-(4-Methoxyphenyl)-1-(phenylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2bd)



Purified by flash chromatography with EA/PE (1/3) as eluent, 58% yield, 40.0 mg; white solid. mp 170 - 175 °C. d.r. = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 1H), 7.50 – 7.47 (m, 2H), 7.36 – 7.32 (m, 2H), 6.96 – 6.94 (m, 2H), 6.79 – 6.77 (m, 2H), 4.61 (dd, *J* = 9.5, 4.8 Hz, 1H), 4.37 (d, *J* = 9.4 Hz, 1H), 3.83 (s, 3H), 3.78 (dd, *J* = 6.1, 4.6 Hz, 1H), 2.83 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 159.9, 138.7, 133.9, 131.1, 128.7, 128.6, 119.8, 113.6, 67.6, 55.5, 52.6, 37.1, 28.2. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}O_5S + Na^+$ $[M + Na]^+$: 367.0611; found: 367.0594.

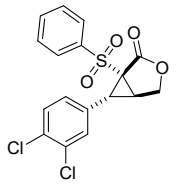
6-(4-Chlorophenyl)-1-(phenylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2be)



Purified by flash chromatography with EA/PE (1/3) as eluent, 76% yield, 52.8 mg; white solid. mp 180 - 185 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 1H), 7.53 – 7.51 (m, 2H), 7.41 –

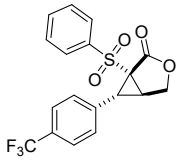
7.35 (m, 2H), 7.24 – 7.21 (m, 2H), 6.98 – 6.96 (m, 2H), 4.62 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.39 (d, *J* = 9.6 Hz, 1H), 3.79 (dd, *J* = 6.2, 4.7 Hz, 1H), 2.83 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 138.5, 134.7, 134.2, 131.2, 128.7, 128.5, 128.4, 126.7, 67.5, 52.7, 36.5, 28.2. HRMS (ESI, m/z): calcd. for $C_{17}H_{13}{}^{35}ClO_4S + Na^+$ $[M + Na]^+$: 371.0115; found: 371.0119.

6-(3,4-Dichlorophenyl)-1-(phenylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2bf)



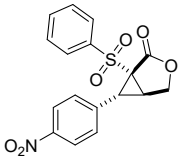
Purified by flash chromatography with EA/PE (1/6) as eluent, 90% yield, 68.6 mg; white solid. mp 191 - 200 °C. d.r. = 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 1H), 7.59 – 7.57 (m, 2H), 7.44 – 7.40 (m, 2H), 7.38 – 7.36 (m, 1H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.2 Hz, 1H), 4.63 (dd, *J* = 9.6, 4.7 Hz, 1H), 4.39 (d, *J* = 9.6 Hz, 1H), 3.77 (dd, *J* = 6.1, 4.7 Hz, 1H), 2.81 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 138.3, 134.4, 133.0, 132.5, 132.3, 130.2, 128.8, 128.8, 128.5, 128.4, 67.4, 52.6, 35.7, 28.2. HRMS (ESI, m/z): calcd. for $C_{17}H_{12}{}^{35}Cl_2O_4S + Na^+$ $[M + Na]^+$: 404.9726; found: 404.9730.

1-(Phenylsulfonyl)-6-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.1.0]hexan-2-one (2bg)



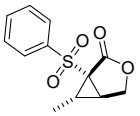
Purified by flash chromatography with EA/PE (1/6) as eluent, 83% yield, 63.7 mg; white solid. mp 191 - 197 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 1H), 7.51 – 7.46 (m, 4H), 7.35 – 7.31 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 4.65 (dd, *J* = 9.6, 4.7 Hz, 1H), 4.42 (d, *J* = 9.8 Hz, 1H), 3.87 (dd, *J* = 6.2, 4.6 Hz, 1H), 2.91 (d, *J* = 6.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 138.5, 134.2, 132.2, 130.8 (q, J_{C-F} = 32.7 Hz), 130.3, 128.8, 128.4, 125.1 (q, J_{C-F} = 3.6 Hz), 123.9 (q, J_{C-F} = 270.8 Hz), 67.5, 52.8, 36.4, 28.2. HRMS (ESI, m/z): calcd. for $C_{18}H_{13}F_3O_4S + Na^+$ $[M + Na]^+$: 405.0379; found: 405.0380.

6-(4-Nitrophenyl)-1-(phenylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2bh)



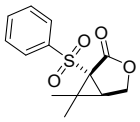
Purified by flash chromatography with EA/PE (1/3) as eluent, 43% yield, 31.0 mg; white solid. mp 149 - 152 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.13 (d, *J* = 8.2 Hz, 2H), 7.76 – 7.68 (m, 1H), 7.53 – 7.46 (m, 6H), 4.64 (dd, *J* = 9.6, 4.7 Hz, 1H), 4.47 (d, *J* = 9.5 Hz, 1H), 4.31 (t, *J* = 5.6 Hz, 1H), 3.60 (d, *J* = 6.3 Hz, 1H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 168.6, 147.6, 139.0, 137.9, 135.0, 131.9, 129.6, 128.3, 123.2, 68.3, 53.1, 35.8, 29.5. HRMS (ESI, m/z): calcd. for $C_{17}H_{13}NO_6S + Na^+$ $[M + Na]^+$: 382.0356; found: 382.0369.

6-Methyl-1-(phenylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2bi) [15]



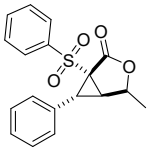
Purified by flash chromatography with EA/PE (1/5) as eluent, 46% yield, 23.3 mg; white solid. mp 169 - 178 °C. d.r. = 10 : 1; ^{1}H NMR (400 MHz, $CDCl_3$, two diastereoisomers) δ the major isomer 8.16 – 8.13 (m, 2H), 7.71 – 7.67 (overlapped, 1.1H), 7.61 – 7.57 (overlapped, 2.2H), 4.40 (dd, *J* = 9.5, 4.6 Hz, 1H), 4.23 (d, *J* = 9.5 Hz, 1H), 3.00 (t, *J* = 5.0 Hz, 1H), 1.75 – 1.70 (m, 1H), 1.51 (d, *J* = 6.4 Hz, 3H); the minor isomer 8.05 – 8.02 (m, 2H), 7.71 – 7.67 (overlapped, 1H), 7.61 – 7.57 (overlapped, 2H), 4.25 (dd, *J* = 10.2, 5.3 Hz, 1H), 4.13 (d, *J* = 10.2 Hz, 1H), 3.17 – 3.13 (m, 1H), 2.53 – 2.50 (m, 1H), 1.13 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, two diastereoisomers) δ the major isomer 169.0 (overlapped), 139.5 (overlapped), 134.3, 129.2, 128.9, 67.5, 50.9 (overlapped), 31.6, 29.1, 10.8; the minor isomer 169.0 (overlapped), 139.5 (overlapped), 134.4, 129.3, 129.0, 63.8, 50.9 (overlapped), 31.4, 25.1, 7.5.

6,6-Dimethyl-1-(phenylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2bj)



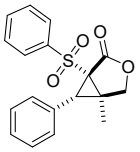
Purified by flash chromatography with EA/PE (1/4) as eluent, 61% yield, 32.5 mg; colorless oil. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.10 (m, 2H), 7.69 – 7.65 (m, 1H), 7.60 – 7.55 (m, 2H), 4.48 (dd, *J* = 10.2, 5.4 Hz, 1H), 4.15 (dd, *J* = 10.0, 0.9 Hz, 1H), 3.01 (dd, *J* = 5.2, 1.0 Hz, 1H), 1.52 (s, 3H), 1.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 140.0, 134.2, 129.2, 128.5, 64.9, 56.8, 36.6, 33.0, 19.9, 16.9. HRMS (ESI, m/z): calcd. for $C_{13}H_{14}O_4S + Na^+$ $[M + Na]^+$: 289.0505; found: 289.0508.

4-Methyl-6-phenyl-1-(phenylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2bk)



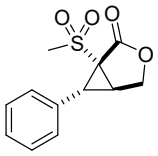
Purified by flash chromatography with EA/PE (1/3) as eluent, 65% yield, 42.7 mg; white solid. mp 210 - 216 °C. d.r. > 20 : 1 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 1H), 7.48 – 7.44 (m, 2H), 7.36 – 7.31 (m, 3H), 7.28 – 7.24 (m, 2H), 7.07 – 7.05 (m, 2H), 4.65 (q, *J* = 6.3 Hz, 1H), 3.57 (d, *J* = 6.2 Hz, 1H), 2.89 (d, *J* = 6.2 Hz, 1H), 1.60 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 138.4, 134.0, 130.0, 128.8, 128.6, 128.6, 128.3, 128.2, 76.0, 53.2, 37.7, 33.6, 22.0. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}O_4S + Na^+$ $[M + Na]^+$: 351.0662; found: 351.0663.

5-Methyl-6-phenyl-1-(phenylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-one (2bl)



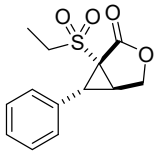
Purified by flash chromatography with EA/PE (1/4) as eluent, 54% yield, 35.4 mg; white solid. mp 135 - 140 °C. d.r. > 20 : 1 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.67 – 7.62 (m, 1H), 7.54 – 7.47 (m, 4H), 7.40 – 7.33 (m, 3H), 4.33 (d, *J* = 9.3 Hz, 1H), 4.03 (d, *J* = 9.2 Hz, 1H), 3.07 (s, 1H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 139.9, 134.4, 130.4, 129.9, 129.1, 129.1, 128.5, 128.4, 73.3, 52.4, 40.0, 37.4, 12.0. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}O_4S + Na^+$ $[M + Na]^+$: 351.0662; found: 351.0664.

1-(Methylsulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2bm)



Purified by flash chromatography with EA/PE (1/4) as eluent, 64% yield, 32.5 mg; white solid. mp 152 - 156 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 3H), 7.35 – 7.32 (m, 2H), 4.62 (dd, *J* = 9.4, 4.7 Hz, 1H), 4.43 (d, *J* = 9.6 Hz, 1H), 3.73 (dd, *J* = 6.1, 4.7 Hz, 1H), 3.06 (d, *J* = 6.1 Hz, 1H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 129.5, 129.1, 128.8, 128.5, 68.1, 51.1, 41.2, 37.0, 26.5. HRMS (ESI, m/z): calcd. for $C_{12}H_{12}O_4S + Na^+$ $[M + Na]^+$: 275.0349; found: 275.0354.

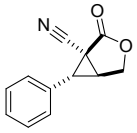
1-(Ethylsulfonyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2bn)



Purified by flash chromatography with EA/PE (1/4) as eluent, 72% yield, 38.6 mg; white solid. mp 138 - 141°C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 5H), 4.62 (dd, *J* = 9.6, 4.7 Hz, 1H),

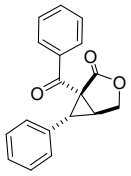
4.43 (d, J = 9.6 Hz, 1H), 3.72 (dd, J = 6.2, 4.7 Hz, 1H), 3.33 – 3.24 (m, 1H), 3.05 (d, J = 6.2 Hz, 1H), 2.81 – 2.72 (m, 1H), 1.22 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 129.6, 129.0, 128.8, 128.7, 68.1, 50.8, 48.0, 37.0, 26.8, 5.2. HRMS (ESI, m/z): calcd. for $C_{13}H_{14}O_4S + Na^+$ [M + Na] $^+$: 289.0505; found: 289.0509.

2-Oxo-6-phenyl-3-oxabicyclo[3.1.0]hexane-1-carbonitrile (2bo) [16]



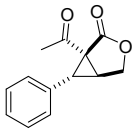
Purified by flash chromatography with EA/PE (1/4) as eluent, 63% yield, 25.2 mg; yellow oil. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 3H), 7.27 – 7.24 (m, 2H), 4.59 (dd, J = 9.7, 4.7 Hz, 1H), 4.43 (d, J = 9.7 Hz, 1H), 3.37 (t, J = 5.2 Hz, 1H), 2.93 (d, J = 5.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 130.8, 129.3, 129.2, 127.9, 113.1, 68.5, 36.5, 30.6, 26.2.

1-Benzoyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2bp) [17]



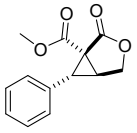
Purified by flash chromatography with EA/PE (1/4) as eluent, 52% yield, 29.2 mg; white solid. mp 152 - 156 ^{o}C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2H), 7.50 – 7.46 (m, 1H), 7.38 – 7.33 (m, 2H), 7.19 – 7.07 (m, 5H), 4.59 (dd, J = 9.4, 4.9 Hz, 1H), 4.47 (d, J = 9.4 Hz, 1H), 3.46 (t, J = 5.0 Hz, 1H), 3.05 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 171.2, 135.5, 133.9, 131.9, 130.2, 128.7, 128.2, 128.1, 127.7, 68.1, 44.7, 38.3, 26.2.

1-Acetyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2bq) [16]



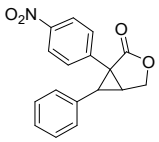
Purified by flash chromatography with EA/PE (1/10) as eluent, 58% yield, 25.2 mg; yellow oil. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 3H), 7.19 – 7.16 (m, 2H), 4.45 (dd, J = 9.4, 4.7 Hz, 1H), 4.37 (d, J = 9.3 Hz, 1H), 3.38 (t, J = 5.2 Hz, 1H), 3.00 (d, J = 5.6 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 172.1, 131.1, 128.8, 128.6, 128.4, 67.6, 45.5, 40.7, 29.7, 27.1.

Methyl 2-oxo-6-phenyl-3-oxabicyclo[3.1.0]hexane-1-carboxylate (2br) [18]



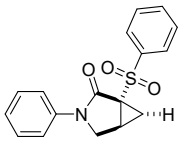
Purified by flash chromatography with EA/PE (1/5) as eluent, 64% yield, 29.8 mg; white solid. mp 115 - 121 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 3H), 7.26 – 7.23 (m, 2H), 4.51 (dd, *J* = 9.4, 4.8 Hz, 1H), 4.37 (d, *J* = 9.4 Hz, 1H), 3.52 (s, 3H), 3.31 (t, *J* = 5.2 Hz, 1H), 2.93 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 164.1, 131.8, 128.8, 128.6, 128.4, 67.4, 52.8, 37.9, 37.7, 27.8.

1-(4-Nitrophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2bs)



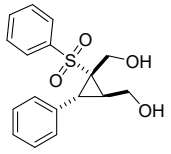
Purified by flash chromatography with EA/PE (1/3.5) as eluent, 34% yield, 20.0 mg; green oil. d.r. = 4 : 1; ^{1}H NMR (400 MHz, $CDCl_3$, two diastereoisomers) δ the major isomer 8.05 – 8.02 (m, 2H), 7.45 – 7.42 (m, 2H), 7.14 – 7.10 (m, 3H), 6.89 – 6.87 (m, 2H), 4.67 (dd, *J* = 9.4, 4.5 Hz, 1H), 4.56 (d, *J* = 9.4 Hz, 1H), 3.27 (t, *J* = 4.6 Hz, 1H), 2.87 (d, *J* = 4.6 Hz, 1H); the minor isomer 8.29 – 8.24 (m, 2H), 7.80 – 7.77 (m, 2H), 7.40 – 7.35 (m, 5H), 4.56 – 4.52 (overlapped, 1H), 4.23 (d, *J* = 10.0 Hz, 1H), 3.14 (d, 8.3 Hz, 1H), 3.08 (dd, *J* = 8.4, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, two diastereoisomers) δ the major isomer 174.3, 147.3, 137.7, 132.4, 131.2, 128.6, 128.1, 127.8, 123.4, 68.4, 39.3, 36.4, 27.1; the minor isomer 173.4, 147.4, 142.4, 131.4, 129.3, 129.2, 129.1, 128.5, 124.1, 64.6, 38.1, 35.6, 31.0. HRMS (ESI, m/z): calcd. for $C_{17}H_{13}NO_4$ + H^+ $[M + H]^+$: 296.0917; found: 296.0905.

3-Phenyl-1-(phenylsulfonyl)-3-azabicyclo[3.1.0]hexan-2-one (2bt)



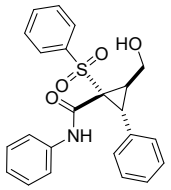
Purified by flash chromatography with EA/PE (1/4) as eluent, 30% yield, 18.9 mg; white solid. mp 160 - 165 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.11 (m, 2H), 7.70 – 7.66 (m, 1H), 7.61 – 7.57 (m, 2H), 7.46 – 7.43 (m, 2H), 7.35 – 7.30 (m, 2H), 7.16 – 7.12 (m, 1H), 4.12 (dd, *J* = 10.6, 5.9 Hz, 1H), 3.72 (d, *J* = 10.6 Hz, 1H), 3.04 – 2.99 (m, 1H), 2.11 (dd, *J* = 8.6, 5.1 Hz, 1H), 1.40 (t, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.0, 138.3, 134.2, 129.3, 129.1, 129.1, 125.5, 120.3, 49.1, 48.0, 20..4, 20.1. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}NO_3S$ + Na^+ $[M + Na]^+$: 336.0665; found: 336.0667.

(3-Phenyl-1-(phenylsulfonyl)cyclopropane-1,2-diyl)dimethanol (3)



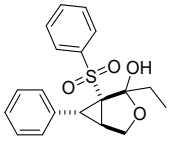
Purified by flash chromatography with EA/PE (1/6) as eluent, 72% yield, 46.0 mg; white solid. mp 132 - 136 °C. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 1H), 7.32 – 7.26 (m, 2H), 7.25 – 7.22 (m, 3H), 7.07 – 7.05 (m, 4H), 4.64 (d, *J* = 14.2 Hz, 1H), 4.28 (dd, *J* = 12.6, 4.9 Hz, 1H), 3.62 – 3.55 (m, 4H), 3.34 – 3.28 (m, 1H), 2.43 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 133.7, 130.9, 130.2, 128.8, 128.6, 128.2, 127.8, 63.3, 61.8, 54.5, 35.8, 27.7. HRMS (ESI, m/z): calcd. for $C_{17}H_{18}O_4S + Na^+$ $[M + Na]^+$: 341.0818; found: 341.0824.

2-(Hydroxymethyl)-N,3-diphenyl-1-(phenylsulfonyl)cyclopropane-1-carboxamide (4)



Purified by flash chromatography with EA/PE (1/6) as eluent, 89% yield, 72.5 mg; colorless oil. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.57 – 7.53 (m, 3H), 7.41 – 7.27 (m, 11H), 7.22 – 7.18 (m, 1H), 4.26 (dd, *J* = 12.0, 4.7 Hz, 1H), 3.62 (dd, *J* = 12.0, 9.0 Hz, 1H), 3.45 – 3.35 (m, 2H), 2.17 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 138.5, 137.3, 134.1, 131.0, 130.0, 129.3, 129.0, 128.1, 128.0, 125.4, 120.4, 61.6, 57.5, 35.2, 31.6. HRMS (ESI, m/z): calcd. for $C_{23}H_{21}NO_4S + Na^+$ $[M + Na]^+$: 430.1084; found: 430.1095.

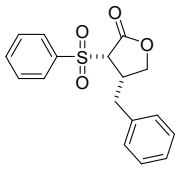
2-Ethyl-6-phenyl-1-(phenylsulfonyl)-3-oxabicyclo[3.1.0]hexan-2-ol (5)



Purified by flash chromatography with EA/PE (1/7) as eluent, 53% yield, 36.3 mg; colorless oil. d.r. = 7 : 1; ^{1}H NMR (400 MHz, $CDCl_3$, two diastereoisomers) δ the major isomer 7.57 – 7.52 (overlapped, 1H), 7.35 – 7.23 (overlapped, 7H), 7.14 – 7.11 (m, 2H), 5.49 (overlapped, 1H), 4.30 (dd, *J* = 8.8, 2.7 Hz, 1H), 3.94 (d, *J* = 8.8 Hz, 1H), 3.27 (dd, *J* = 6.1, 2.6 Hz, 1H), 2.77 (d, *J* = 6.2 Hz, 1H), 1.72 (q, overlapped, *J* = 7.5 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); the minor isomer 7.57 – 7.52 (overlapped, 1H), 7.46 – 7.40 (m, 4H), 7.35 – 7.23 (overlapped, 5H), 5.49 (overlapped, 1H), 4.15 – 7.09 (m, 1H), 3.41 – 3.36 (m, 1H), 3.18

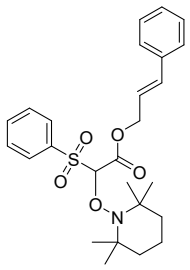
– 3.15 (m, 1H), 3.01 (d, J = 8.3 Hz, 1H), 1.75 – 1.64 (overlapped, 2H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, two diastereoisomers) δ the major isomer 139.0 (overlapped), 133.8, 131.3 (overlapped), 130.1, 128.7, 128.4, 128.1, 127.8, 105.5 (overlapped), 65.7, 58.9, 33.1, 30.7, 28.6, 7.9; the minor isomer 139.0 (overlapped), 133.9, 131.3 (overlapped), 129.7, 129.0, 128.3, 128.2, 127.9, 105.5 (overlapped), 61.6, 61.3, 37.0, 34.2, 32.6, 8.2. HRMS (ESI, m/z): calcd. for $C_{19}H_{20}O_4S + Na^+$ [M + Na] $^+$: 367.0975; found: 367.0981.

4-Benzyl-3-(phenylsulfonyl)dihydrofuran-2(3H)-one (6)



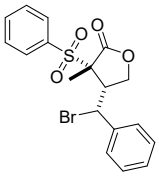
Purified by flash chromatography with EA/PE (1/5) as eluent, 59% yield, 37.3 mg; colorless oil. d.r. > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.73 – 7.69 (m, 1H), 7.60 – 7.55 (m, 2H), 7.35 – 7.27 (m, 3H), 7.17 – 7.14 (m, 2H), 4.52 (dd, J = 9.3, 7.1 Hz, 1H), 4.11 (dd, J = 9.2, 3.8 Hz, 1H), 3.80 (d, J = 4.2 Hz, 1H), 3.57 – 3.51 (m, 1H), 3.00 – 2.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 136.8, 136.3, 134.8, 129.4, 129.4, 129.2, 129.1, 127.5, 71.5, 68.2, 38.7, 38.3. HRMS (ESI, m/z): calcd. for $C_{17}H_{16}O_4S + Na^+$ [M + Na] $^+$: 339.0662; found: 339.0659.

Cinnamyl 2-(phenylsulfonyl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetate] (7)



Purified by flash chromatography with EA/PE (1/40) as eluent, 22% yield, 21.1 mg; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H), 7.68 – 7.64 (m, 1H), 7.54 – 7.50 (m, 2H), 7.40 – 7.27 (m, 5H), 6.65 (d, J = 15.8 Hz, 1H), 6.22 (dt, J = 15.9, 6.6 Hz, 1H), 5.55 (s, 1H), 4.80 – 4.76 (m, 2H), 1.47 – 1.40 (m, 8H), 1.29 – 1.23 (m, 4H), 0.95 – 0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 136.3, 136.1, 135.4, 134.5, 130.5, 128.8, 128.6, 128.4, 126.8, 121.7, 98.7, 66.7, 60.8, 40.8, 32.9, 20.6, 16.8. HRMS (ESI, m/z): calcd. for $C_{26}H_{33}NO_5S + Na^+$ [M + Na] $^+$: 494.1972; found: 494.1978.

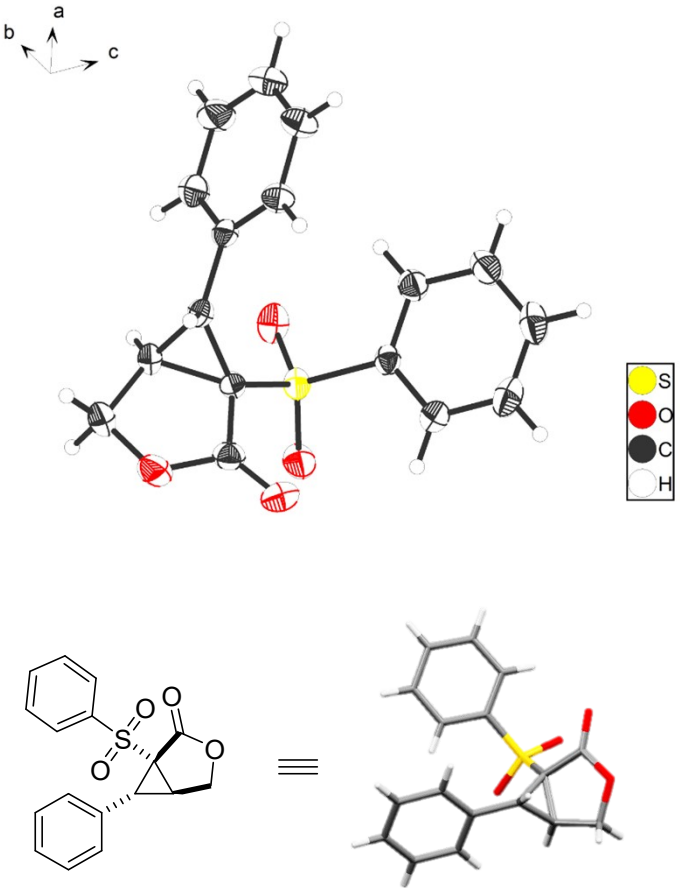
4-(Bromo(phenyl)methyl)-3-methyl-3-(phenylsulfonyl)dihydrofuran-2(3H)-one (9)



Purified by flash chromatography with EA/PE (1/10) as eluent, 23% yield, 19.1 mg; colorless oil. d.r. = 16 : 5 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.61 (m, 5H), 7.53 – 7.49 (m, 2H), 7.44 – 7.35 (m, 3H), 6.08(d, *J* = 12.0 Hz, 1H), 4.88 (dd, *J* = 11.4, 8.8 Hz, 1H), 4.77 (dd, *J* = 9.0, 8.8 Hz, 1H), 3.75 – 3.68 (m, 1H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 139.5, 135.3, 135.1, 130.6, 129.4, 128.8, 128.7, 128.6, 72.0, 71.1, 54.0, 50.1, 19.9. HRMS (ESI, m/z): calcd. for $C_{18}H_{17}{}^{79}BrO_4S + Na^+$ $[M + Na]^+$: 430.9923; found: 430.9904.

9. Single-crystal X-ray diffraction data for 2aa

Preparation of the single crystals of 2aa: 15.0 mg of pure **2aa** was dissolved in the combined solvents of petroleum ether and CH_2Cl_2 (5 mL, v/v = 9:1) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing the slow solvent evaporation at 0 °C. After about two days, several small crystals were observed at the bottom of the bottle. The crystals were collected and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **2aa**



(50% probability ellipsoids)

Table S7. Crystallographic data and structure refinement for compound (2aa).

Compound	2aa
Formula	$C_{17}H_{14}O_4S$
M, g mol^{-1}	314.34
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	13.8755(13)
b, Å	7.1896(5)
c, Å	14.6846(13)

α, deg	90
β, deg	93.679(3)
γ, deg	90
V, Å^3	1461.9(2)
Z	4
d_{cal}, g cm^{-3}	1.428
F(000)	656.0
Radiation	MoKα(λ = 0.71073)
Temperature, K	300
2θ range, deg	3.916 to 52.762
Completeness	0.997
Residual map, e Å^{-3}	0.20/-0.33
Goodness-of-fit on F^2	1.015
Final indices [I>2σ(I)]	R_1 = 0.0403, wR_2 = 0.0931
R indices (all data)	R_1 =0.0606, wR_2 = 0.1050

10. Computational Details

For this study, all DFT calculations were conducted using Gaussian 16 Rev. A.03.[19] To ensure the accuracy of results, molecular geometry optimizations and frequency calculations were performed with the B3LYP[20] functional with D3(BJ) dispersion correction[21], and a mixed basis set was employed using SDD[22] for Cu and Br, while 6-31G(d)[23] for all other atoms. Frequency calculations were crucial in determining stationary points (no imaginary frequencies) and transition state structures (only one imaginary frequency) in the system. Single point energies based upon the optimized structures were calculated at B3LYP-D3/Def2-TZVP[24] level with SMD[25] solvation model (DMF as solvent). The visualization of molecular structure was generated through the utilization of CYLview 1.0.[26]

The Cartesian Coordinates of calculated structures

1aa

C	-0.18648600	1.13417000	-0.13002200
H	0.49272200	0.33829600	-0.43801500
H	-0.83447500	1.44932800	-0.94850200
C	0.56953600	2.31524200	0.44531300
O	1.78264800	1.92694700	0.86738200
O	0.12194300	3.43494100	0.53594200
C	2.55212900	2.94772000	1.56498300
H	2.58211200	3.83837600	0.92772800
H	2.02331300	3.20735700	2.48648700
C	3.90924500	2.39417000	1.83247300
H	4.49175800	2.11722400	0.95613900
C	4.40434800	2.25015100	3.06937000
H	3.76120500	2.51669400	3.90837900
C	5.73437500	1.75620400	3.44395700
C	6.01153200	1.52258800	4.80090900
C	6.75115300	1.50328800	2.50592500
C	7.25343600	1.04129500	5.20990000
H	5.23742600	1.71739700	5.53899100
C	7.99116000	1.02280800	2.91271200
H	6.57302700	1.69335700	1.45197400
C	8.24870300	0.78788400	4.26643300
H	7.44336500	0.86572200	6.26497200
H	8.76389700	0.83519500	2.17237700
H	9.21928400	0.41525900	4.58093300
S	-1.27761300	0.43373100	1.17643400
O	-2.52589700	1.20552700	1.19393700
O	-0.45550600	0.27178300	2.38352500
C	-1.63625600	-1.19605400	0.51909000
C	-2.76965600	-1.37217000	-0.27399800

H	-3.43504800	-0.53498700	-0.45536300
C	-3.03112200	-2.63810900	-0.79745500
H	-3.91158100	-2.79608000	-1.41289700
C	-2.16710800	-3.70042700	-0.52338100
H	-2.37588800	-4.68466100	-0.93243100
C	-1.04048700	-3.50830900	0.28037800
H	-0.37936800	-4.34105500	0.50041100
C	-0.76746200	-2.24834300	0.81025700
H	0.08943600	-2.07729300	1.45327100

TS1

C	-0.66445200	0.24579400	0.43707300
H	-0.04943700	-0.64159200	0.58840900
H	-0.55370700	0.44032000	-0.87162800
C	-0.17081900	1.45900200	1.15500500
O	1.15478600	1.34913100	1.37471800
O	-0.84217600	2.42084100	1.45967900
C	1.78251700	2.51123400	1.99004500
H	1.40122300	3.40266600	1.47959100
H	1.47055700	2.56378100	3.03738200
C	3.25710700	2.35983100	1.84621800
H	3.62573500	2.27815200	0.82583000
C	4.09425100	2.34394300	2.89270500
H	3.66110400	2.40865900	3.89133300
C	5.55778000	2.24547700	2.86216300
C	6.25354100	2.14157300	4.07781000
C	6.30257200	2.24825100	1.66916300
C	7.64242400	2.03477200	4.10604200
H	5.69258300	2.14153300	5.00915600
C	7.68868400	2.14117400	1.69586000
H	5.79419700	2.34082300	0.71441300
C	8.36605800	2.03305100	2.91397600
H	8.15833900	1.95384000	5.05854500
H	8.24585900	2.14565900	0.76323000
H	9.44900800	1.95171400	2.93100300
S	-2.41096800	-0.13293700	0.70215300
O	-3.24147800	0.82549000	-0.03331600
O	-2.57084700	-0.32892500	2.15394900
C	-2.55201900	-1.73661300	-0.08778500
C	-2.55746800	-1.81157200	-1.48203000
H	-2.44695800	-0.91212900	-2.07628400
C	-2.67565100	-3.06460700	-2.08042500
H	-2.67597900	-3.14515400	-3.16322800
C	-2.79889100	-4.21134300	-1.29186900

H	-2.89587400	-5.18390300	-1.76581200
C	-2.79885100	-4.11583400	0.10110400
H	-2.89930900	-5.00946500	0.70968700
C	-2.67119900	-2.87025700	0.71521500
H	-2.67295900	-2.76317900	1.79426900
C	-0.28872900	1.84254600	-2.51290200
C	-0.35201800	1.68521100	-4.04948400
H	-1.32417300	1.28542800	-4.35092900
H	-0.21242400	2.66640400	-4.51579900
H	0.43391700	1.01018300	-4.40020700
C	-1.43926800	2.73145400	-2.02576000
H	-2.40170500	2.29102100	-2.29831300
H	-1.42407700	2.84240400	-0.93854000
H	-1.36325900	3.72835500	-2.47400100
C	1.08251500	2.39374000	-2.09712600
H	1.16440600	2.44677700	-1.00759200
H	1.88062200	1.74124800	-2.46538900
H	1.23727400	3.40130000	-2.49776700
O	-0.43818000	0.50399700	-2.06268300

INT1

C	-0.16928700	0.44778300	1.07481500
H	0.40186300	-0.44295800	0.84114100
C	0.46106100	1.63840900	1.63287600
O	1.79012500	1.43499500	1.78536200
O	-0.12001300	2.66762400	1.92391600
C	2.52162500	2.56768600	2.32961800
H	2.28363300	3.44424800	1.71579000
H	2.16478400	2.76641700	3.34503800
C	3.97302800	2.23161500	2.29961500
H	4.38473500	1.99646200	1.32039500
C	4.74382000	2.23485100	3.39593500
H	4.26773400	2.45656500	4.35159600
C	6.18441600	1.96675600	3.47404200
C	6.79086400	1.89435100	4.73882200
C	6.99249300	1.77661300	2.33885300
C	8.15267000	1.63112800	4.87090000
H	6.18085800	2.04356000	5.62637500
C	8.35169800	1.51333700	2.46918300
H	6.55577000	1.84317100	1.34718500
C	8.93901500	1.43806500	3.73551200
H	8.59877900	1.57821900	5.85995100
H	8.95886200	1.37056800	1.57964700
H	10.00148200	1.23484200	3.83335600

S	-1.91004800	0.42589900	0.76973200
O	-2.19957000	1.38940700	-0.30206900
O	-2.60322100	0.49339800	2.06428100
C	-2.13407400	-1.22447400	0.10654900
C	-2.03155700	-1.41988200	-1.27086300
H	-1.84462600	-0.57295400	-1.92215000
C	-2.19596000	-2.70778800	-1.77885800
H	-2.12489400	-2.87913700	-2.84865500
C	-2.46029600	-3.77236300	-0.91400600
H	-2.58916300	-4.77343900	-1.31508700
C	-2.56899800	-3.55757200	0.46195600
H	-2.78680200	-4.38711200	1.12775400
C	-2.40700100	-2.27471200	0.98323800
H	-2.50552900	-2.07774000	2.04527500

INT2

S	9.58954900	1.58242100	5.31938300
O	10.97769100	1.60437700	4.82222000
O	8.52919700	0.89754800	4.56067100
O	6.89819900	3.81705200	4.76605900
O	7.11839800	3.25277000	6.93579300
C	9.60403400	0.97091800	6.99626600
C	10.78964800	1.05232800	7.72801000
H	11.68548700	1.44799600	7.26225400
C	10.79384800	0.59661000	9.04480500
H	11.70729800	0.64537200	9.62957700
C	9.62691900	0.07277800	9.60621300
H	9.63501800	-0.28024900	10.63330500
C	8.45082300	-0.00344000	8.85708000
H	7.54782800	-0.41297900	9.29871100
C	8.42993200	0.44867900	7.53935900
H	7.52916100	0.39914500	6.93993300
C	7.60997200	3.45171000	5.85557300
C	7.73790500	3.88041400	3.59152600
H	7.39414900	4.72405600	2.99077600
H	7.61483800	2.94791400	3.03678200
C	9.17910200	4.05151400	4.10555100
H	9.88708700	3.53270400	3.44995100
C	10.89039900	5.89984200	4.60140100
C	11.16830300	7.28145800	4.80813700
H	10.35583400	7.99705200	4.71084500
C	12.44360200	7.71624100	5.12710300
H	12.62982300	8.77579100	5.27880300
C	13.49296500	6.79567700	5.25627400

H	14.49225800	7.13860900	5.50714700
C	13.24406100	5.43183500	5.05962300
H	14.05420200	4.71454500	5.15801000
C	11.97206600	4.98091100	4.73774900
H	11.80590900	3.91823900	4.59173300
C	9.08765200	3.34342400	5.47838600
H	9.72897800	3.77276800	6.24843600
C	9.57763500	5.48529100	4.28079600
H	8.79414300	6.23753900	4.22943800

INT3

S	10.98732600	3.08140700	4.86151600
O	10.91815300	2.69718400	3.43674000
O	10.38319800	2.21308300	5.88201200
O	8.74500200	5.06859500	6.81749500
O	10.94337900	5.40311500	7.18509000
C	12.67088300	3.46459700	5.28199400
C	13.43341900	4.20210100	4.37301500
H	13.02239000	4.50985200	3.41708600
C	14.73416000	4.54899100	4.72949900
H	15.33944700	5.13250800	4.04335900
C	15.24978700	4.15188600	5.96645300
H	16.26417100	4.42760000	6.23901700
C	14.47046800	3.41234700	6.85875200
H	14.87596200	3.11404800	7.82033900
C	13.16142700	3.06908600	6.52509200
H	12.52537500	2.51481000	7.20525300
C	10.04136900	5.12306300	6.44553100
C	7.87793300	4.70341100	5.74054400
H	7.08052600	5.44781200	5.69418800
H	7.45562900	3.72177500	5.96807200
C	8.72031200	4.65818600	4.43678100
H	8.55842600	3.69898300	3.92962400
C	8.67836500	5.69326900	2.04211900
C	8.12392200	6.69712600	1.18814400
H	7.41504200	7.40762100	1.60448800
C	8.50555600	6.77596500	-0.13874600
H	8.09530100	7.55021800	-0.77823000
C	9.43530500	5.85849500	-0.64843300
H	9.74542300	5.93193600	-1.68639100
C	9.96812600	4.85112400	0.16418100
H	10.68514500	4.14655000	-0.24340800
C	9.60731300	4.76338700	1.49817100
H	10.04343300	3.99542800	2.12776100

C	8.34653600	5.74283000	3.44401800
H	7.45213500	6.30629200	3.68933800
Cu	9.86982800	7.12684700	3.27872500
Br	8.95137000	8.21144200	5.11861500
Br	11.97690800	7.46246200	2.33636400
C	10.16473400	4.72335700	4.97310100
H	10.82995600	5.41499600	4.44969200

INT4

S	11.17848400	3.25306200	4.67767900
O	11.26309800	2.99125100	3.22522800
O	10.62459200	2.18994000	5.55105700
O	8.48052100	4.85089600	6.63340200
O	10.60891000	5.24490900	7.24346200
C	12.82647900	3.61121500	5.26442700
C	13.82950600	3.83913400	4.32549200
H	13.58020200	3.86681800	3.27324000
C	15.13497700	4.03289400	4.77424600
H	15.92678600	4.21926200	4.05483600
C	15.41452000	4.01569600	6.14084100
H	16.43181200	4.18122200	6.48648600
C	14.39449200	3.78963300	7.06901000
H	14.61498600	3.77892600	8.13255000
C	13.08843100	3.57662200	6.63432100
H	12.28608600	3.39706900	7.33718800
C	9.82235900	4.95537600	6.37556000
C	7.80486400	4.19948200	5.54361100
H	6.82512800	4.67050900	5.42814200
H	7.68268500	3.14165200	5.79911200
C	8.70381800	4.37328200	4.31743200
H	8.65910700	3.50997700	3.65108800
C	8.68335000	5.79393300	2.14944100
C	8.09866800	6.89346100	1.48427900
H	7.61332800	7.66290600	2.07491200
C	8.17072500	7.00551400	0.10194300
H	7.71045800	7.85652500	-0.39281000
C	8.84985400	6.03918000	-0.64751400
H	8.91702900	6.13488900	-1.72823100
C	9.45700700	4.96194200	0.00103600
H	10.00614100	4.21956900	-0.57177900
C	9.37981100	4.83350000	1.38525500
H	9.89564400	4.01721900	1.87858800
C	8.54496000	5.69043000	3.60353200
H	7.86267100	6.40147200	4.06107700

Cu	10.35774000	6.47778000	4.10482900
Br	9.43092200	8.74303300	4.28395800
Br	12.68802500	6.90682000	3.69987500
C	10.08645700	4.66026900	4.92016700

TS2

S	11.04401900	3.10187900	4.70152100
O	10.99479300	2.91221800	3.23685300
O	10.67119200	1.97482900	5.57879500
O	8.36926600	4.62603300	6.81744200
O	10.52509100	4.70995200	7.44986300
C	12.69390100	3.62727300	5.13535300
C	13.49208000	4.21138700	4.15265300
H	13.10679000	4.34801200	3.15015200
C	14.77702500	4.62902400	4.49635500
H	15.40129400	5.10600300	3.74772000
C	15.24151500	4.45816800	5.80067200
H	16.24022000	4.79473700	6.06590000
C	14.42799600	3.86726900	6.77192000
H	14.79224200	3.74273700	7.78749800
C	13.14135100	3.44620500	6.44523300
H	12.48619000	3.00052600	7.18213100
C	9.69824600	4.63877600	6.57302300
C	7.58534300	4.53397100	5.61661000
H	7.02547500	5.46665700	5.52017000
H	6.90735300	3.68471400	5.73433900
C	8.56936000	4.32941400	4.43715200
H	8.40358700	3.39885500	3.89229400
C	9.00420200	5.57459900	2.16286600
C	8.98990600	6.85141000	1.55431200
H	8.87864000	7.72824400	2.18616400
C	9.12732900	6.97295000	0.17852800
H	9.11764600	7.95726300	-0.27977400
C	9.29252000	5.82909000	-0.60949400
H	9.40996200	5.92489500	-1.68588200
C	9.31601700	4.56263500	-0.01679300
H	9.45571700	3.67741400	-0.63095500
C	9.17520300	4.42913900	1.35996100
H	9.24205400	3.45331200	1.82253400
C	8.78619400	5.53753100	3.59451200
H	8.44448900	6.47503300	4.06071600
Cu	10.66019100	6.15865000	4.33487000
Br	8.17492000	8.25094400	5.49561400
Br	12.32251200	7.52104000	3.43576900

C	9.94280400	4.47447900	5.09037000

INT5

S	11.07689100	2.81016400	4.98590800
O	10.95496000	2.54942300	3.53874300
O	10.82710300	1.74011500	5.95768100
O	8.09856800	4.60636700	6.69281800
O	10.04271400	4.24857200	7.78336000
C	12.67907300	3.54493200	5.28666200
C	13.47652300	3.89546200	4.19337900
H	13.13727600	3.67631000	3.18749000
C	14.69135500	4.53375800	4.43497300
H	15.32097100	4.82568400	3.60065600
C	15.08828500	4.81072400	5.74463900
H	16.02780200	5.32395000	5.92446400
C	14.28344100	4.44145300	6.82557400
H	14.59703800	4.66440300	7.84023300
C	13.06835500	3.79628200	6.60773100
H	12.41736700	3.52102600	7.42964000
C	9.43289000	4.32324600	6.74749000
C	7.56783600	4.39477000	5.36942100
H	6.85806900	5.19860900	5.16179800
H	7.04325900	3.43437800	5.35947400
C	8.76877400	4.38220900	4.41462500
H	8.67610000	3.65753600	3.60769100
C	9.80871300	6.02683200	2.66705100
C	9.97852900	7.38274100	2.30872200
H	9.77068200	8.15515700	3.04255200
C	10.43272600	7.72471400	1.04360500
H	10.55476300	8.76993900	0.77822700
C	10.75134200	6.72092500	0.12224800
H	11.11902200	6.98826700	-0.86401500
C	10.60832000	5.37505000	0.47246300
H	10.86595700	4.59709500	-0.23962500
C	10.14058600	5.02197000	1.73336400
H	10.07233400	3.97726800	2.01033600
C	9.95634500	4.18129000	5.34154200
C	9.27475100	5.72668500	3.98747400
H	8.87037100	6.57373900	4.54455700
Cu	11.04755000	5.80961200	5.10076100
Br	12.34259100	7.70116000	5.20848900

TS3

S	8.89088200	2.02344800	4.36735900

O	9.28925000	2.02902800	2.95203700
O	7.90281200	1.06446800	4.86682300
O	6.19158600	4.59499800	5.46754800
O	7.30476400	3.31045600	6.95562400
C	10.36094800	1.96662500	5.37780100
C	11.58949800	2.32608500	4.80571000
H	11.64037200	2.60580100	3.75957400
C	12.72267800	2.31844900	5.61589200
H	13.68155100	2.60958500	5.19993900
C	12.62078800	1.95351200	6.96034700
H	13.50545000	1.96838400	7.58882400
C	11.39142000	1.57871600	7.50757200
H	11.32174000	1.30308700	8.55446600
C	10.24373700	1.57688400	6.71828500
H	9.27467800	1.30853400	7.12236000
C	7.22483300	3.80142700	5.86194700
C	6.20653100	4.83666700	4.04663100
H	5.98879500	5.89504000	3.88581200
H	5.42492500	4.22633700	3.58518900
C	7.59106300	4.42514400	3.55919500
H	7.66800500	3.97386500	2.57529100
C	9.99845400	5.43651500	3.27657500
C	10.88091900	6.42991700	3.73989000
H	10.65161500	6.97196900	4.65203800
C	12.06307400	6.69887000	3.05716800
H	12.73503600	7.46348100	3.43380100
C	12.38366900	5.97965800	1.90411800
H	13.30953100	6.18340200	1.37433500
C	11.50785600	4.99988700	1.43205300
H	11.74711900	4.44169700	0.53188900
C	10.31908300	4.72944100	2.10724000
H	9.66641500	3.94941200	1.73976100
C	8.21372600	3.68240100	4.71336000
C	8.74293000	5.21728500	4.04294700
H	8.47695900	6.03204300	4.71705700
Cu	9.86246500	4.47043200	5.84547600
Br	11.16058700	5.52472100	7.41189000

2aa

S	9.56642300	1.41316300	5.07323800
O	10.82935500	1.63055000	4.34768900
O	8.69335700	0.28654600	4.72918800
O	6.56644500	3.71226100	4.02883700
O	6.40650400	2.19451400	5.68891100

C	9.92042100	1.39879400	6.82440700
C	11.24372900	1.51078200	7.24300600
H	12.03287300	1.60946400	6.50751600
C	11.51124000	1.52416000	8.61098300
H	12.53600600	1.61756800	8.95685800
C	10.46397500	1.43552900	9.52909400
H	10.67681600	1.45363900	10.59422200
C	9.14170200	1.32723300	9.08830800
H	8.33101100	1.25861000	9.80744000
C	8.85711000	1.30165200	7.72448200
H	7.83775200	1.22730600	7.35891000
C	8.59069900	2.91150200	4.85428900
C	7.09145600	2.83787600	4.93924800
C	7.57527600	4.24466300	3.14218400
H	7.40079900	5.32047100	3.05606600
H	7.45297400	3.77523100	2.16120100
C	8.91731200	3.89526800	3.76254000
H	9.76988400	3.70776700	3.12055400
C	9.12563300	4.32293900	5.17930000
H	8.34614600	4.96054500	5.59468000
C	10.44902100	4.53262700	5.83645200
C	10.45005100	4.83326900	7.20530500
H	9.50398800	4.89825000	7.73623700
C	11.64551000	5.01878000	7.89325700
H	11.62704000	5.24076400	8.95610600
C	12.86187300	4.90966500	7.21737200
H	13.79769100	5.05228400	7.75014400
C	12.86966800	4.61833200	5.85301800
H	13.81140000	4.53371000	5.31863200
C	11.67112100	4.43250800	5.16468200
H	11.69463900	4.18897700	4.10944400

t-BuO·

C	-0.65614700	0.02845600	0.02288700
C	-0.15703800	-1.42775100	-0.00530000
H	0.93772100	-1.44929000	-0.02306200
H	-0.49553800	-1.97749000	0.88002800
H	-0.52537500	-1.93614000	-0.90129000
C	-0.15687700	0.78106600	1.26981200
H	0.93789200	0.80675200	1.27978800
H	-0.52479500	1.81135800	1.26176800
H	-0.49578100	0.28959300	2.18862100
C	-2.21446800	0.05611100	-0.02469700
H	-2.57863200	1.08653200	-0.02750700

H	-2.57883700	-0.45649700	-0.91849300
H	-2.59396200	-0.45751500	0.86490900
O	-0.29730600	0.69499800	-1.13178400

t-BuOH

C	-0.67939300	0.02425800	0.03019200
C	-0.15619400	-1.41761000	0.00129100
H	0.94167500	-1.43234000	-0.00036400
H	-0.49397900	-1.98392700	0.87663000
H	-0.50602100	-1.92841900	-0.90146600
C	-0.15601500	0.77032000	1.26431000
H	0.94185900	0.77876100	1.27637000
H	-0.50550700	1.80765000	1.25503300
H	-0.49407800	0.29575000	2.19249900
C	-2.20699600	0.04945100	-0.01316700
H	-2.56746900	1.08290800	-0.02938100
H	-2.56761800	-0.45289300	-0.91641000
H	-2.62986600	-0.45567900	0.86149100
O	-0.26477600	0.71230400	-1.16177300
H	0.70578300	0.71587200	-1.16749100

t-BuO-

C	-0.64984100	0.07869500	-0.06414200
C	-0.16141800	-1.41977400	0.00310300
H	0.93747300	-1.42875700	-0.01601500
H	-0.49946800	-1.99326100	0.88620000
H	-0.50796000	-1.93966800	-0.90112400
C	-0.16121400	0.76985300	1.26704900
H	0.93768200	0.79070000	1.26527900
H	-0.50757700	1.81294300	1.26501800
H	-0.49937900	0.29201700	2.20531500
C	-2.22546900	0.04027500	0.00273700
H	-2.59992300	1.07343800	-0.01633900
H	-2.60006900	-0.45953200	-0.90162800
H	-2.65381500	-0.46957200	0.88569200
O	-0.20816400	0.70282400	-1.14546400

Br-

Br	1.60054800	0.71656300	-1.16820300

CuBr

Cu	-0.88627600	0.10026700	0.00000000
Br	-3.12400200	0.10026700	0.00000000

$CuBr_2$

Cu	-0.85013900	0.10026700	0.00000000
Br	1.39084700	0.10026700	0.00000000
Br	-3.09112500	0.10026700	0.00000000

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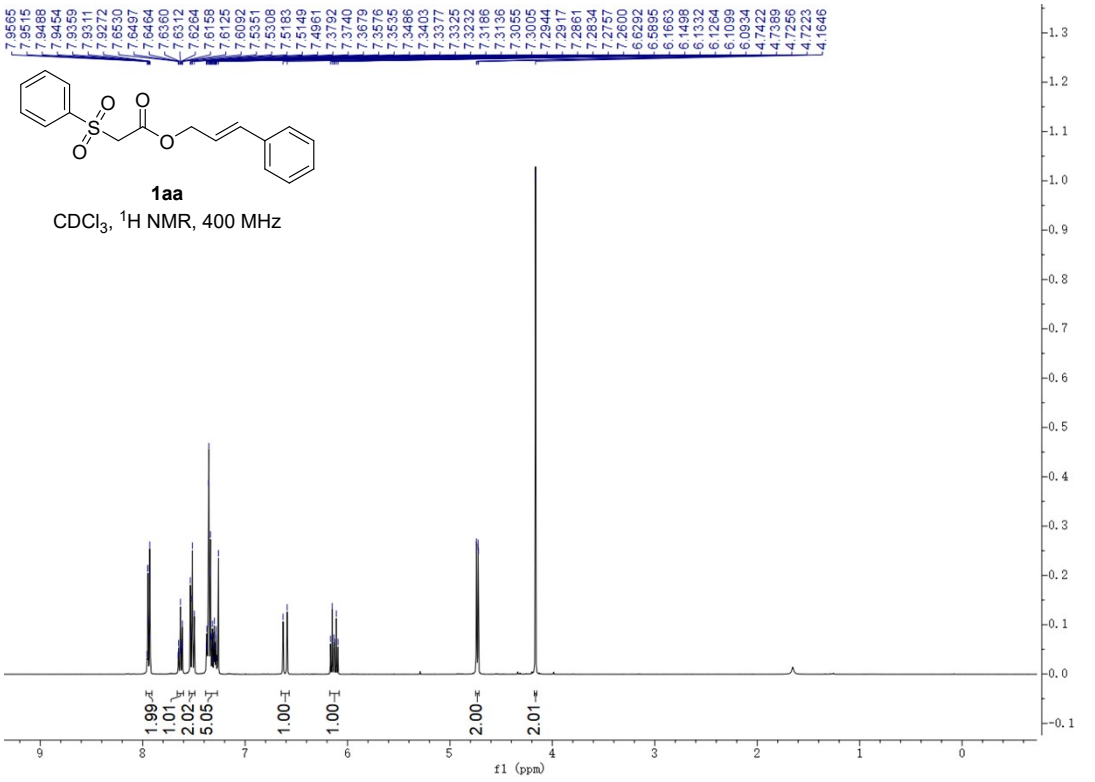
12. NMR Spectra



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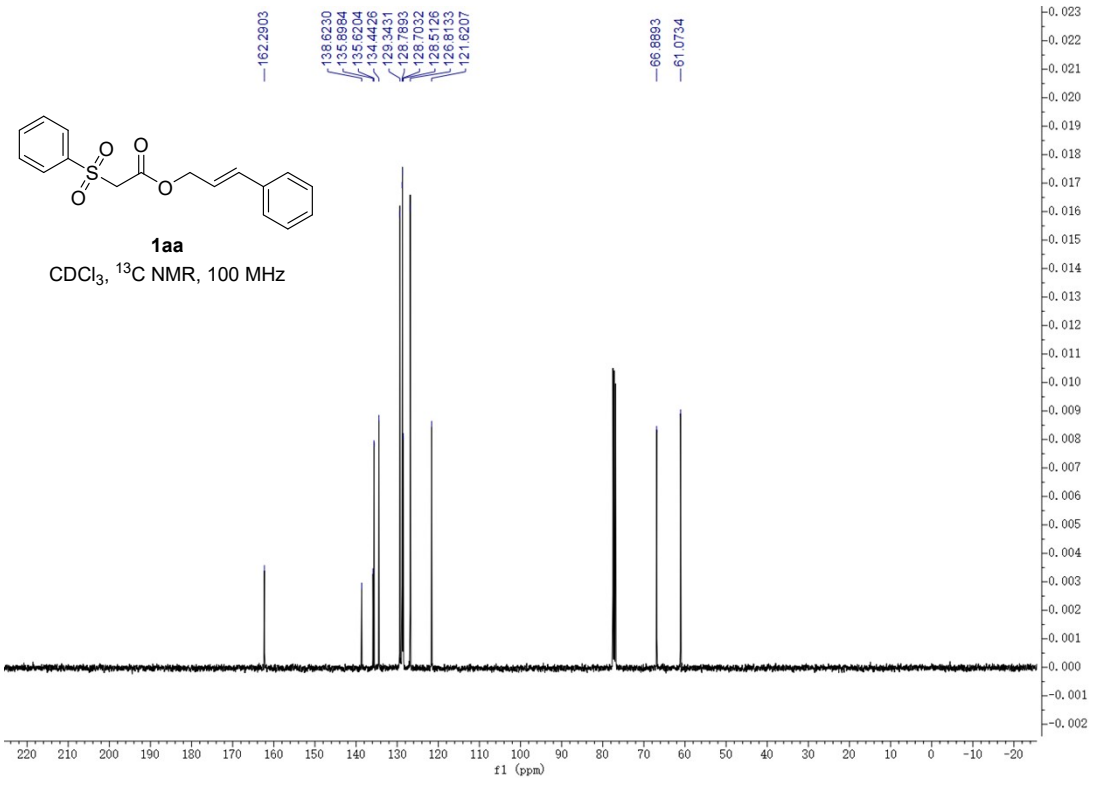
$CDCl_3$, ^1H NMR, 400 MHz



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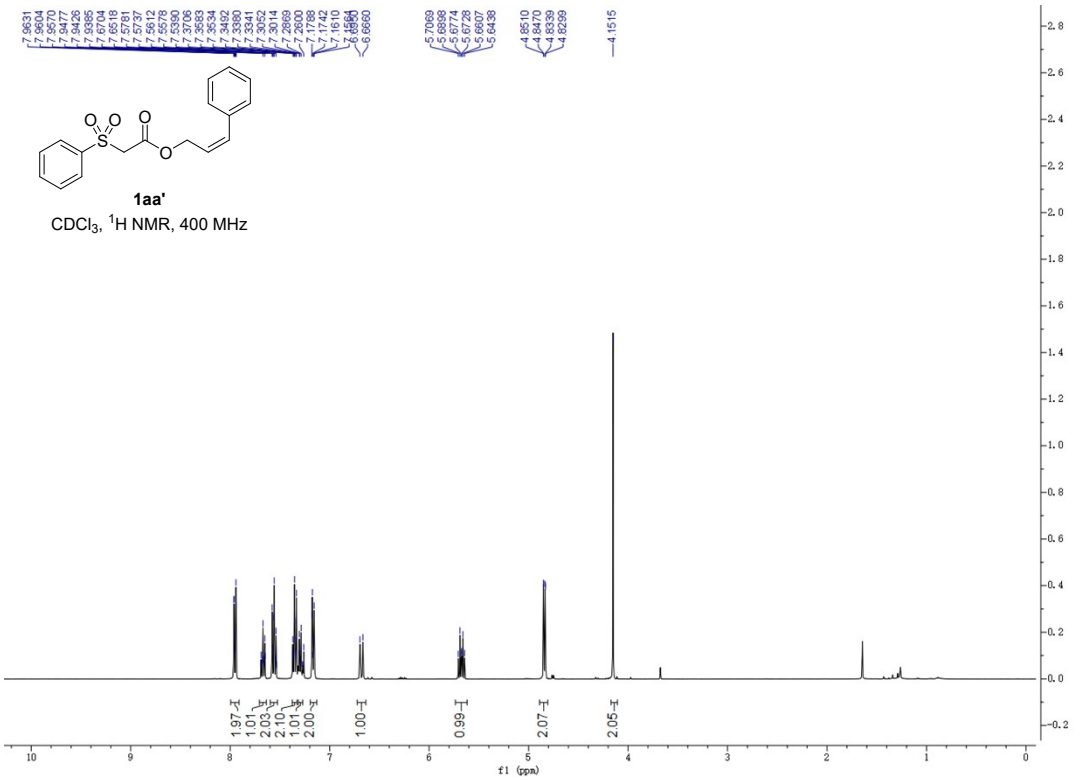

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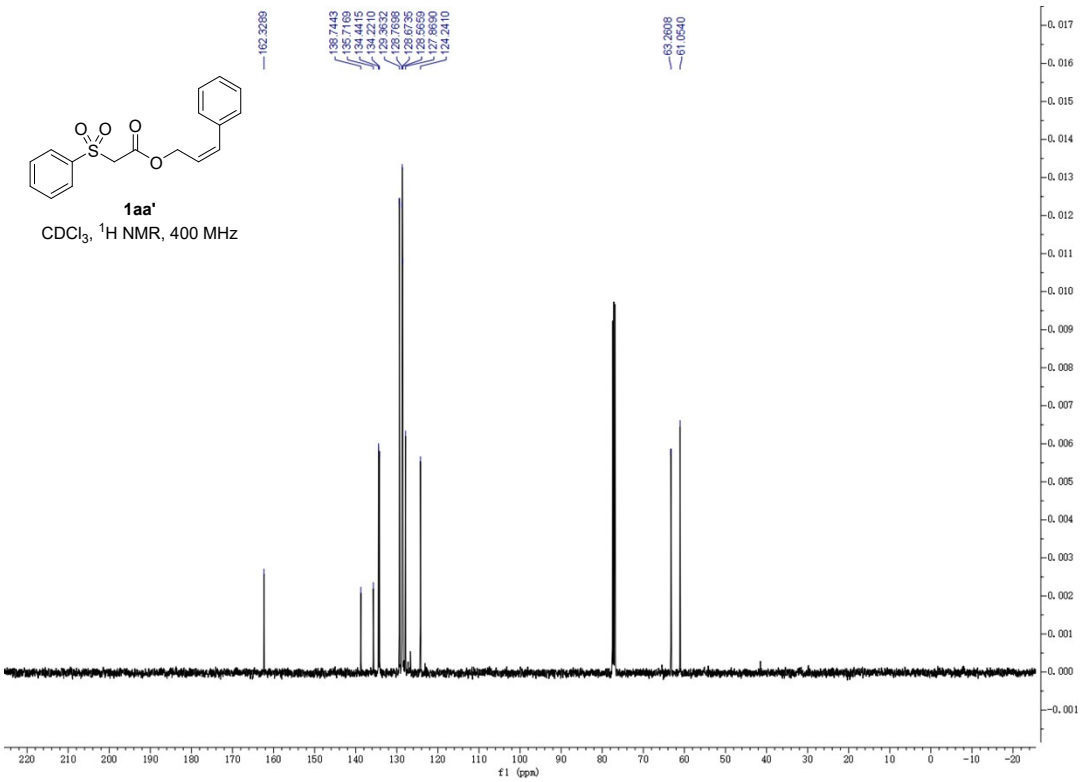

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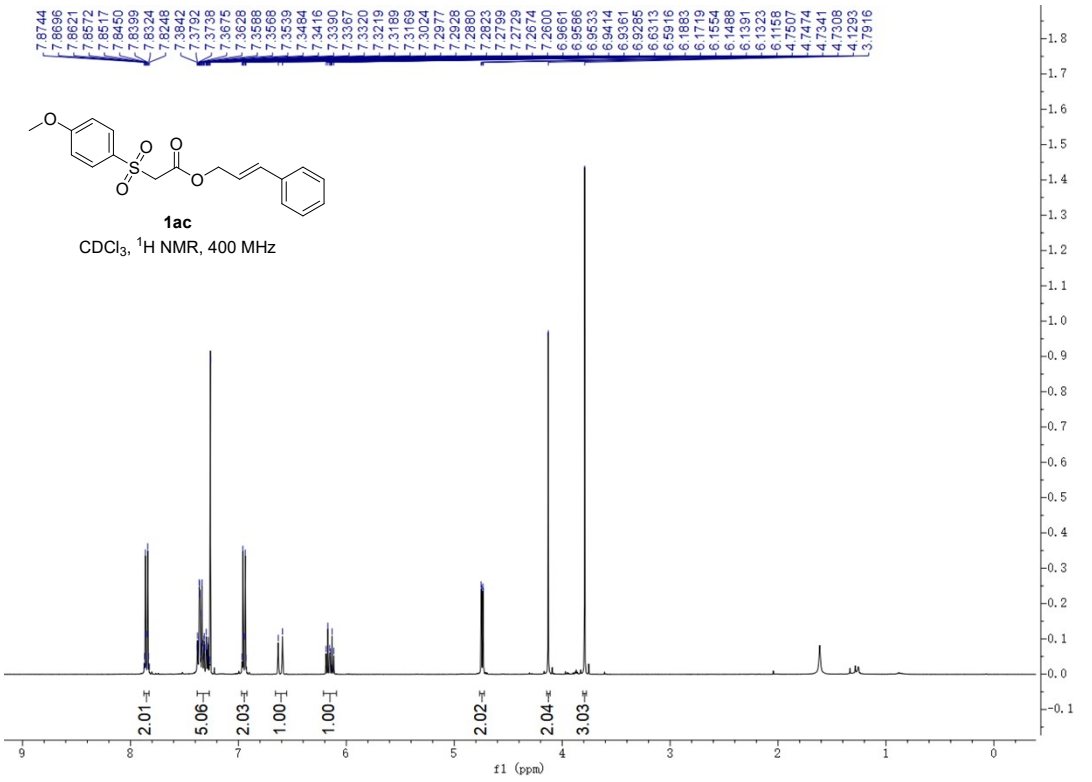

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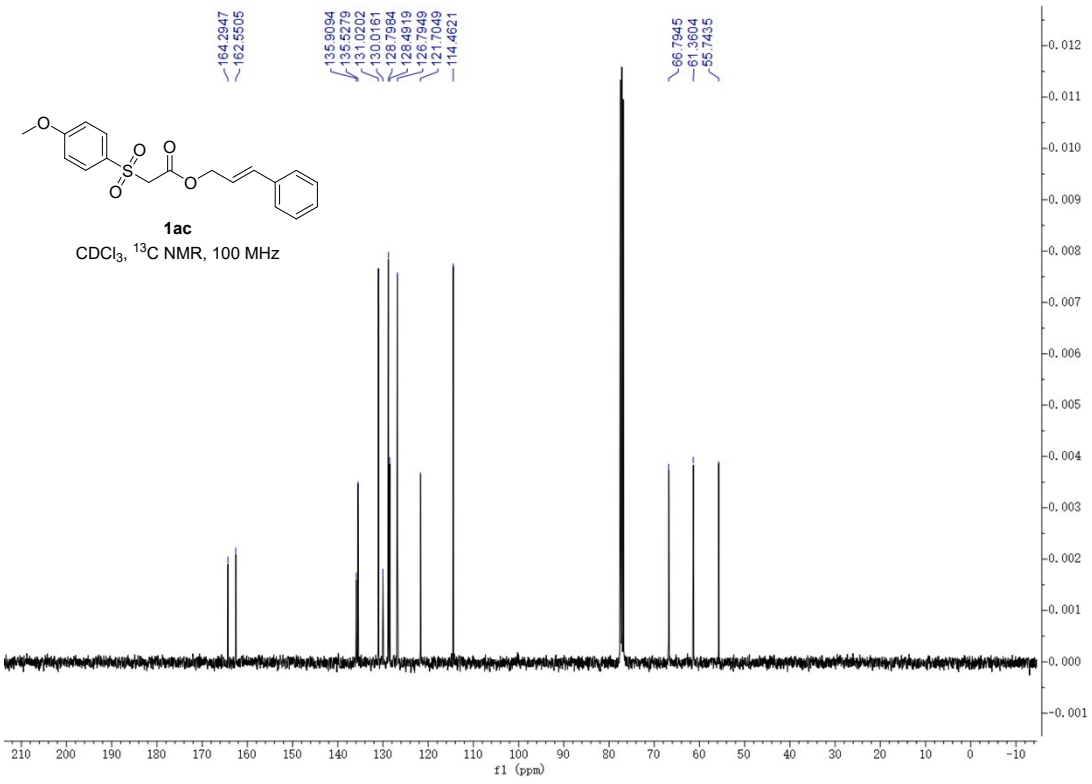

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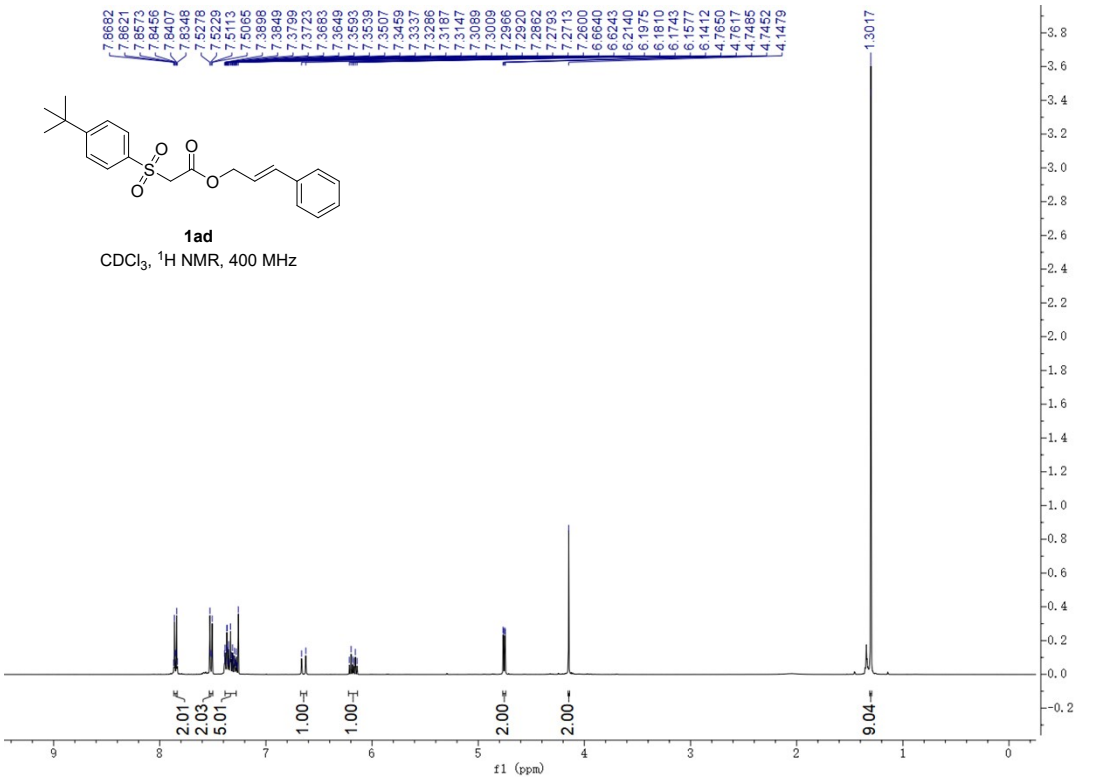

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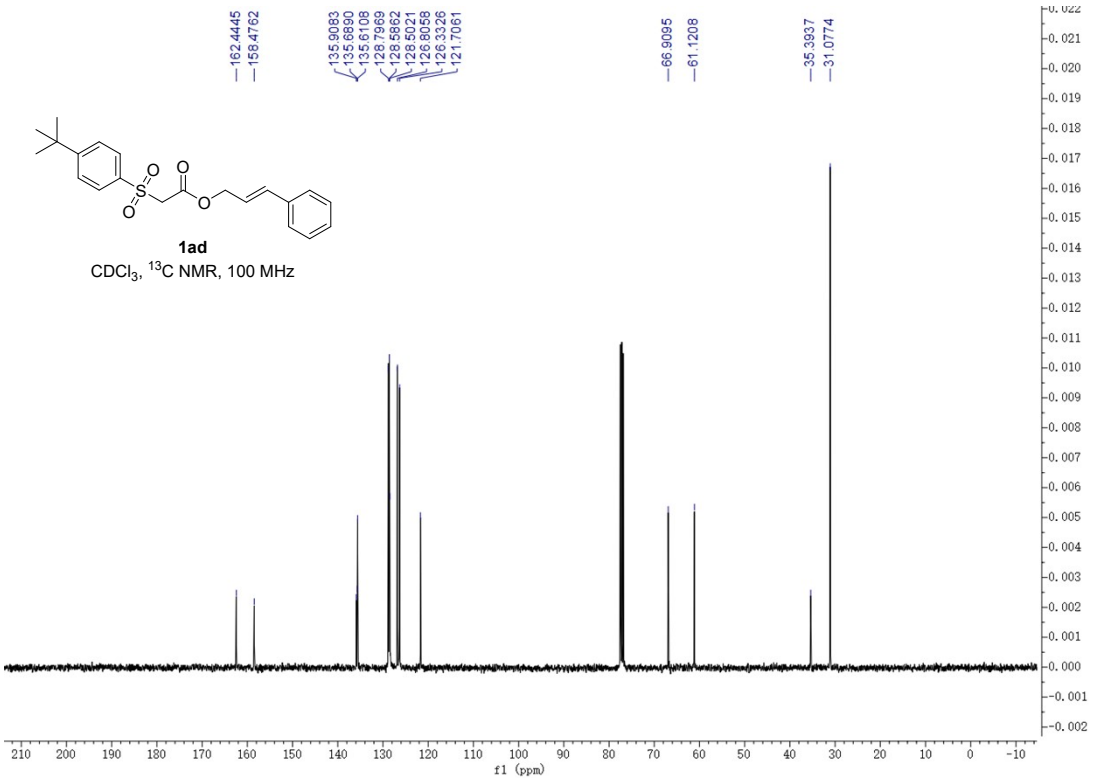

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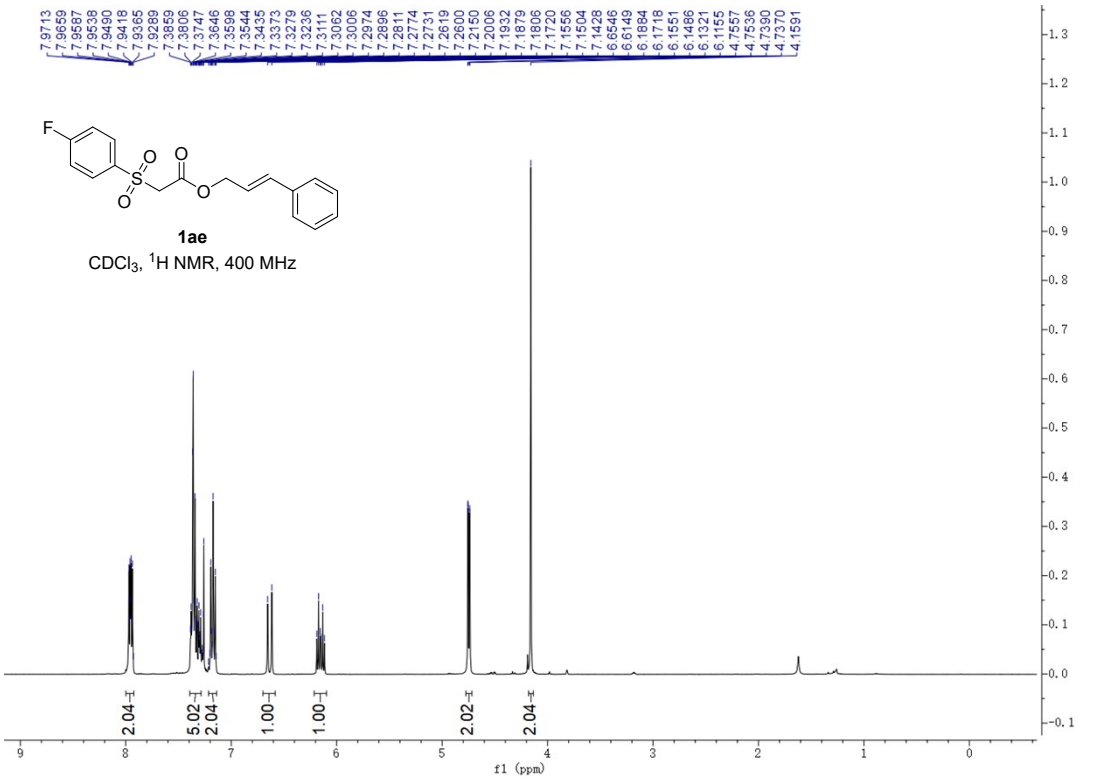
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7.3859
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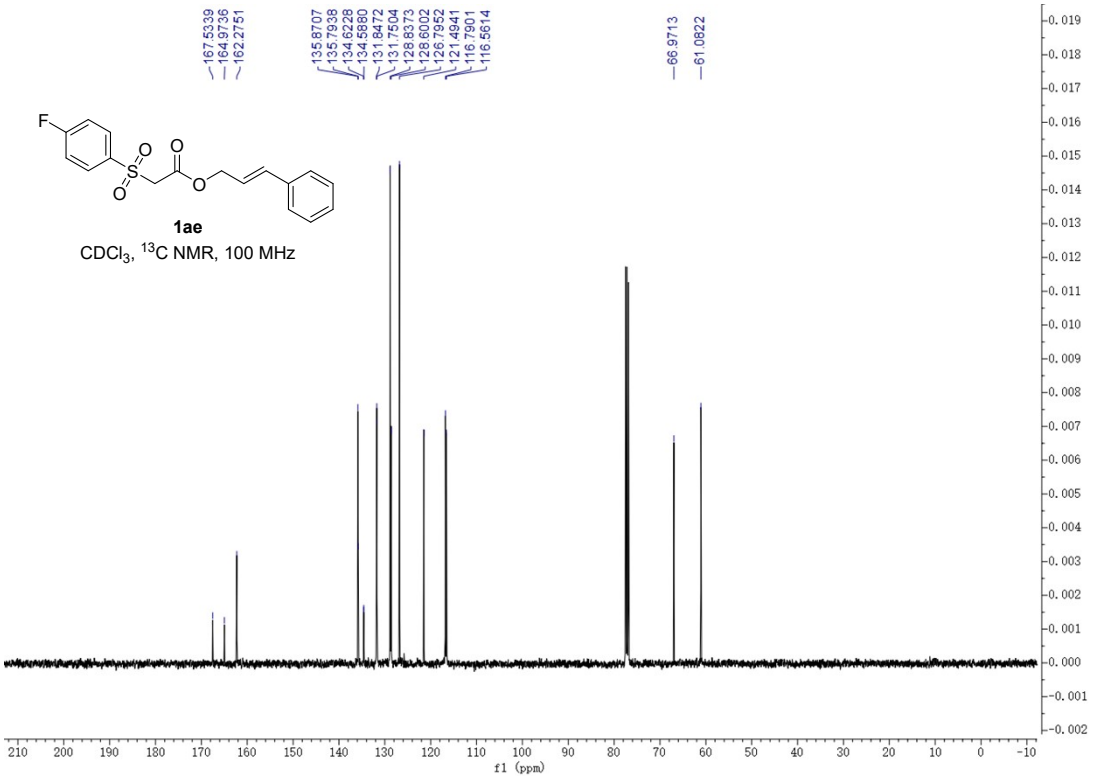
7.3747
7.3646
7.3598
7.3544
7.3435
7.3373
7.3279
7.3236
7.3111
7.3062
7.3006
7.2974
7.2896
7.2811
7.2774
7.2731
7.2619
7.2600
7.2150
7.2006
7.1932
7.1879
7.1806
7.1720
7.1556
7.1504
7.1428
6.6546
6.6149
6.1884
6.1718
6.1551
6.1486
6.1321
6.1155
4.7557
4.7536
4.7390
4.7370
4.1591
F
O
O
S
O
O
O
1ae
CDCl3, 1H NMR, 400 MHz
2.04
5.02
2.04
1.00
1.00
2.02
2.04
f1 (ppm)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135.7938
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131.7504
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128.6002
126.7952
121.4941
116.7901
116.5614
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F
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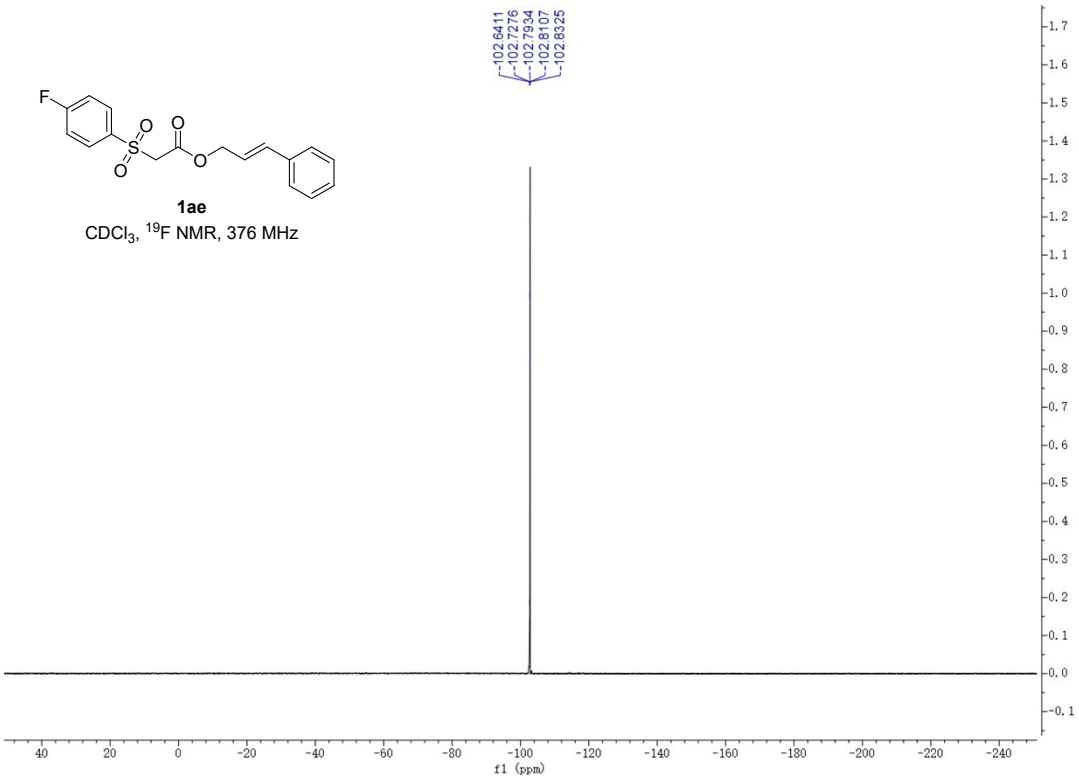
O
O
1ae
CDCl3, 13C NMR, 100 MHz
f1 (ppm)



1ae

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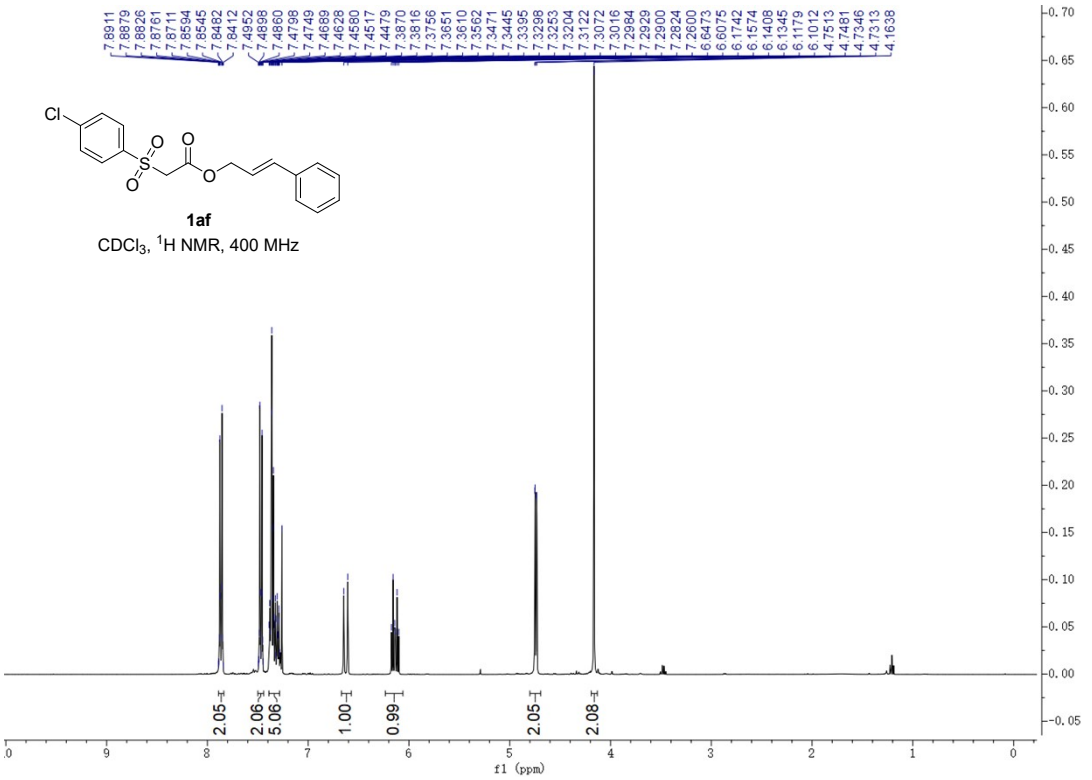

1af

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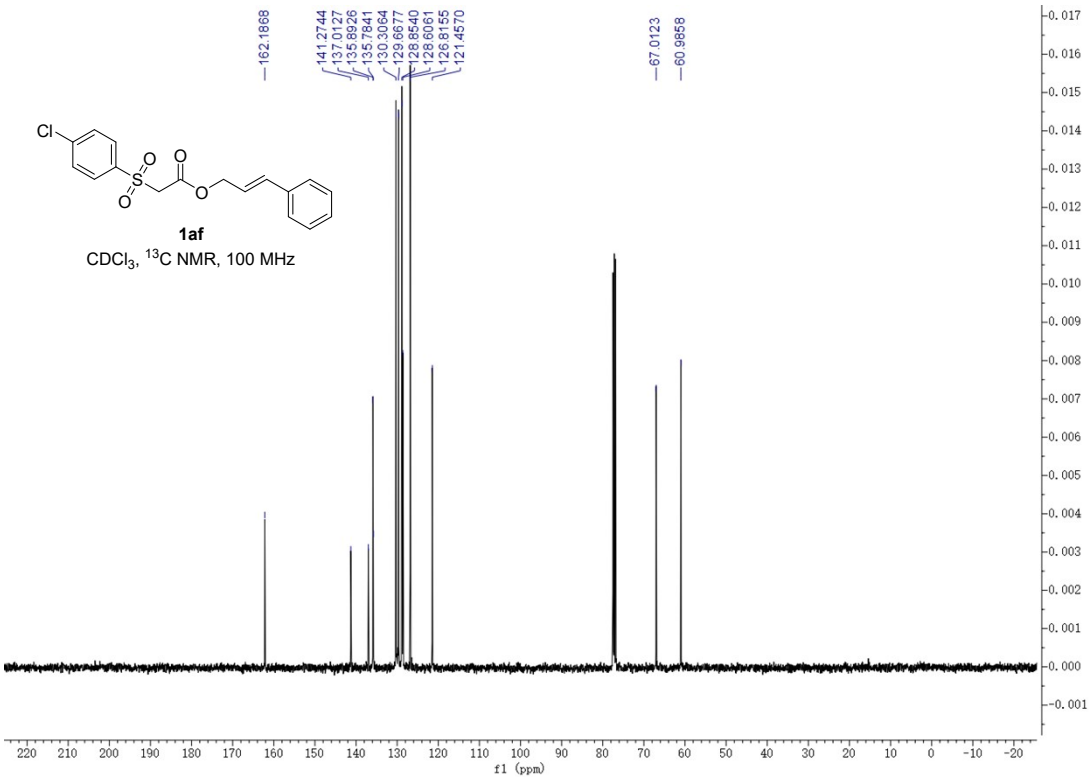
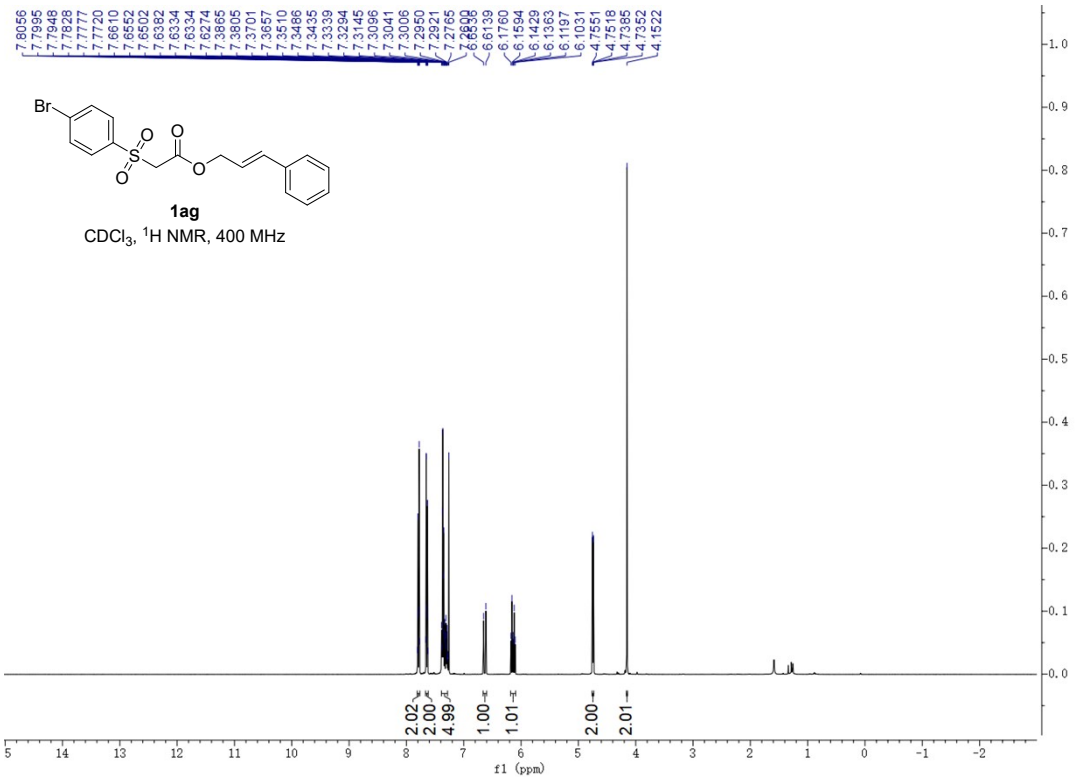


1af

$CDCl_3$, ^{13}C NMR, 100 MHz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7.7828
7.7777
7.7720
7.6610
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7.6502
7.6382
7.6334
7.6274
7.3865
7.3805
7.3701
7.3657
7.3510
7.3486
7.3435
7.3339
7.3294
7.3145
7.3096
7.3041
7.3006
7.2950
7.2921
7.2765
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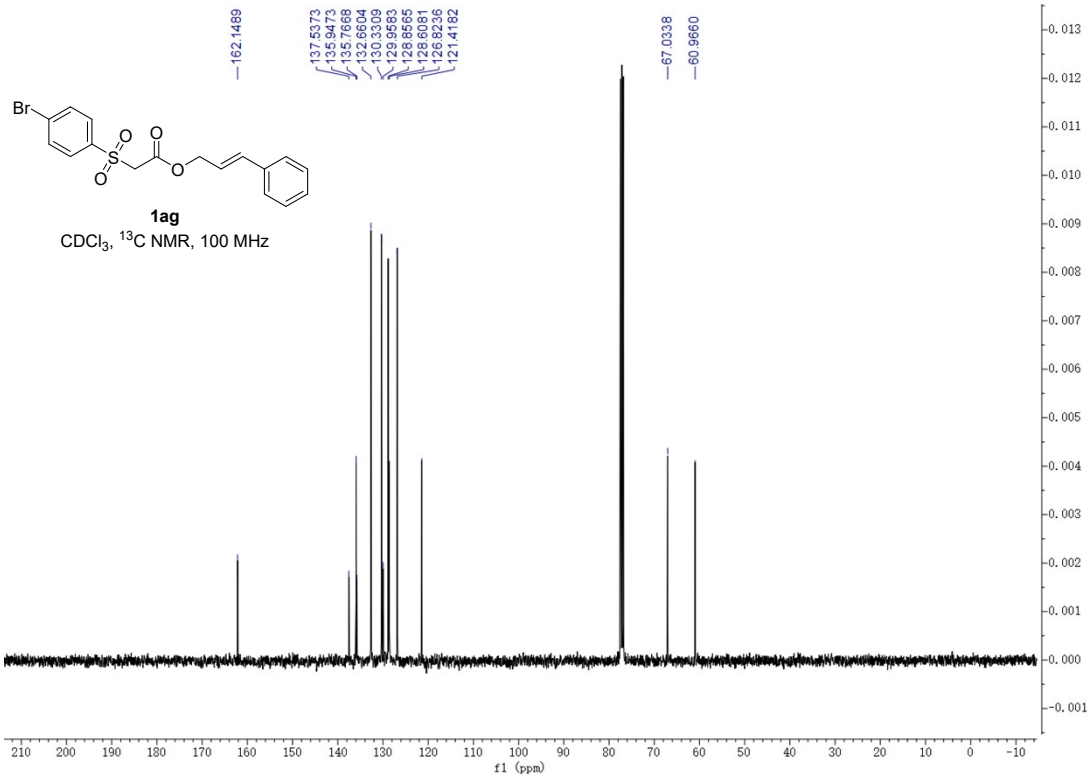
6.1760
6.1594
6.1429
6.1363
6.1197
6.1031
4.7551
4.7518
4.7385
4.7352
4.1522
Br
O
O
S
O
O
O
1ag
CDCl3, 1H NMR, 400 MHz
2.02
2.00
4.99
1.00
1.01
2.00
2.01
f1 (ppm)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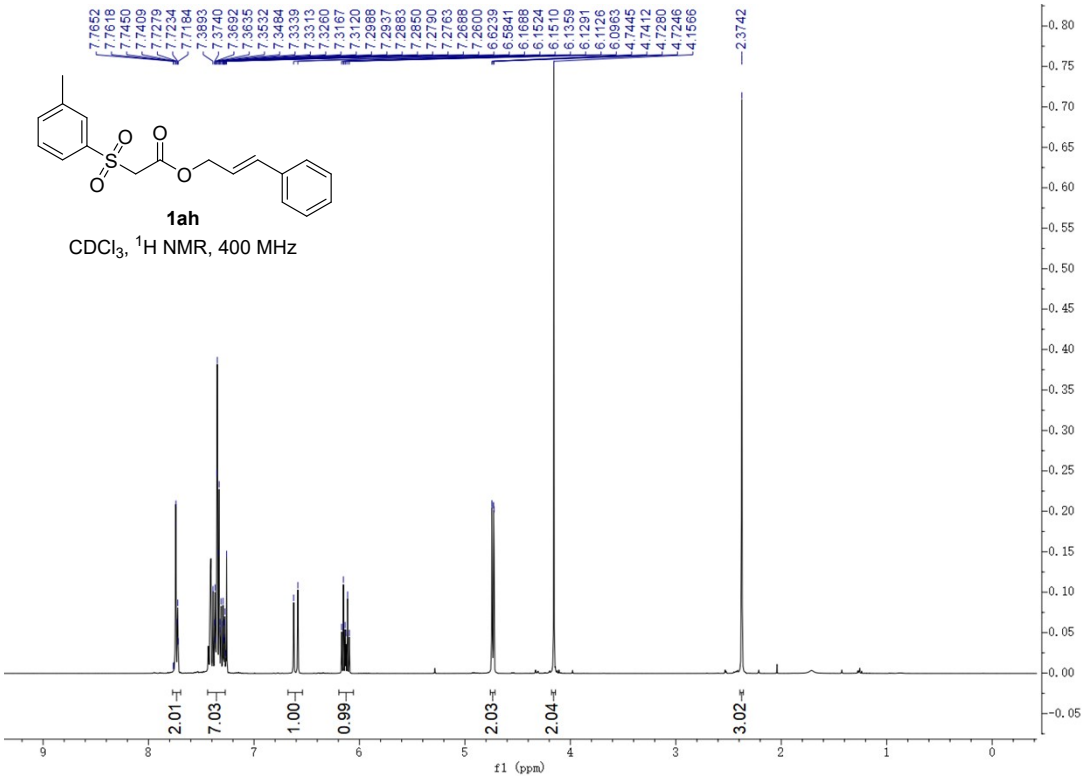
121.4182
67.0338
60.9660
Br
O
O
S
O
O
O
1ag
CDCl3, 13C NMR, 100 MHz
f1 (ppm)



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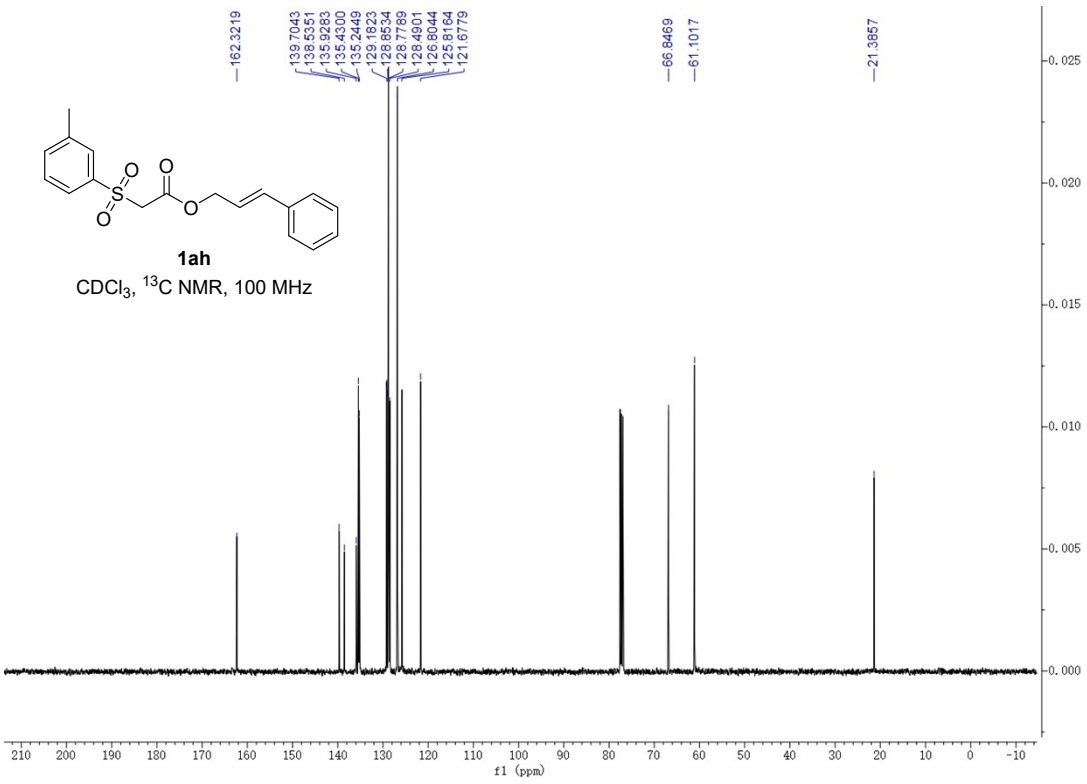
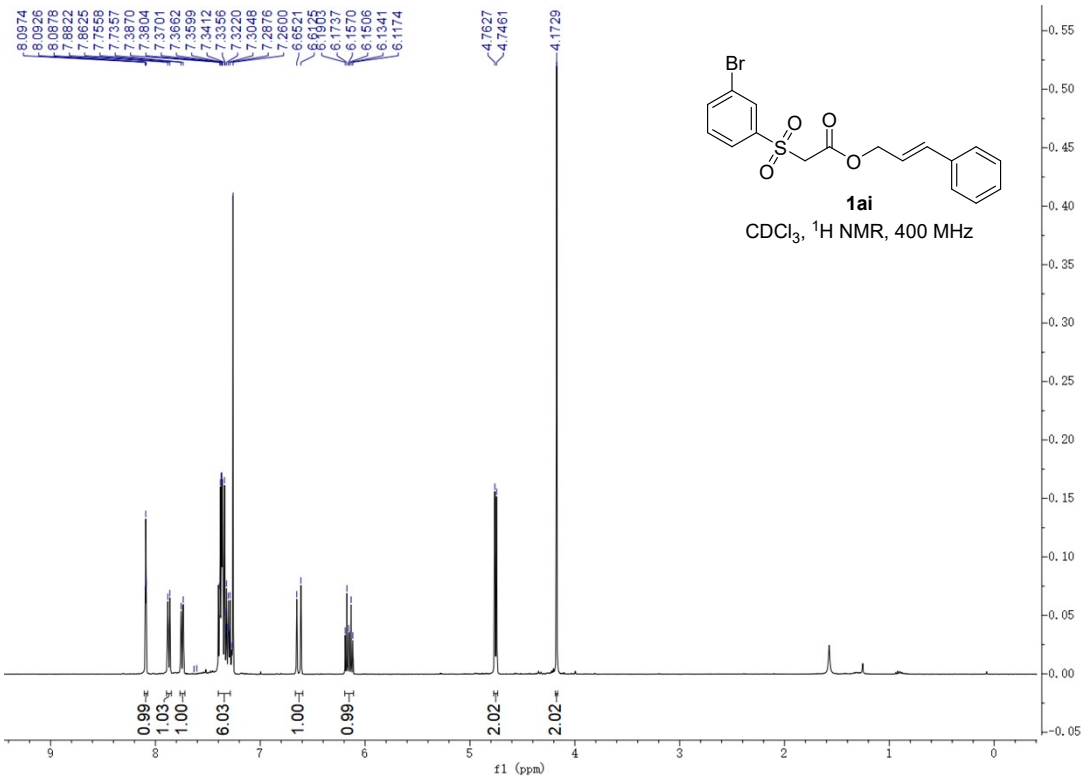


1ah

$CDCl_3$, ^{13}C NMR, 100 MHz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7.8625
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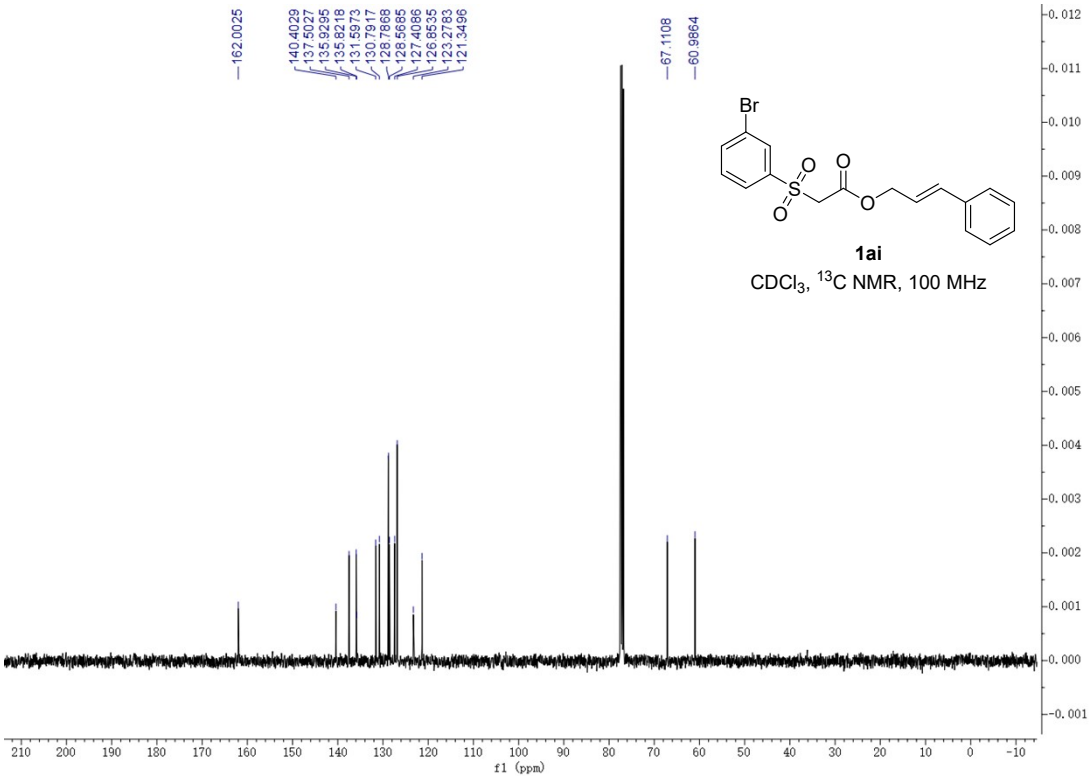
7.3701
7.3662
7.3599
7.3412
7.3356
7.3220
7.3048
7.2876
7.2600
6.6521
6.6465
6.1737
6.1570
6.1506
6.1341
6.1174
4.7627
4.7461
4.1729
0.99
1.03
1.00
6.03
1.00
0.99
2.02
2.02
f1 (ppm)
Br
O
O
S
O
O
O
1ai
CDCl3, 1H NMR, 400 MHz

0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127.4086
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123.2783
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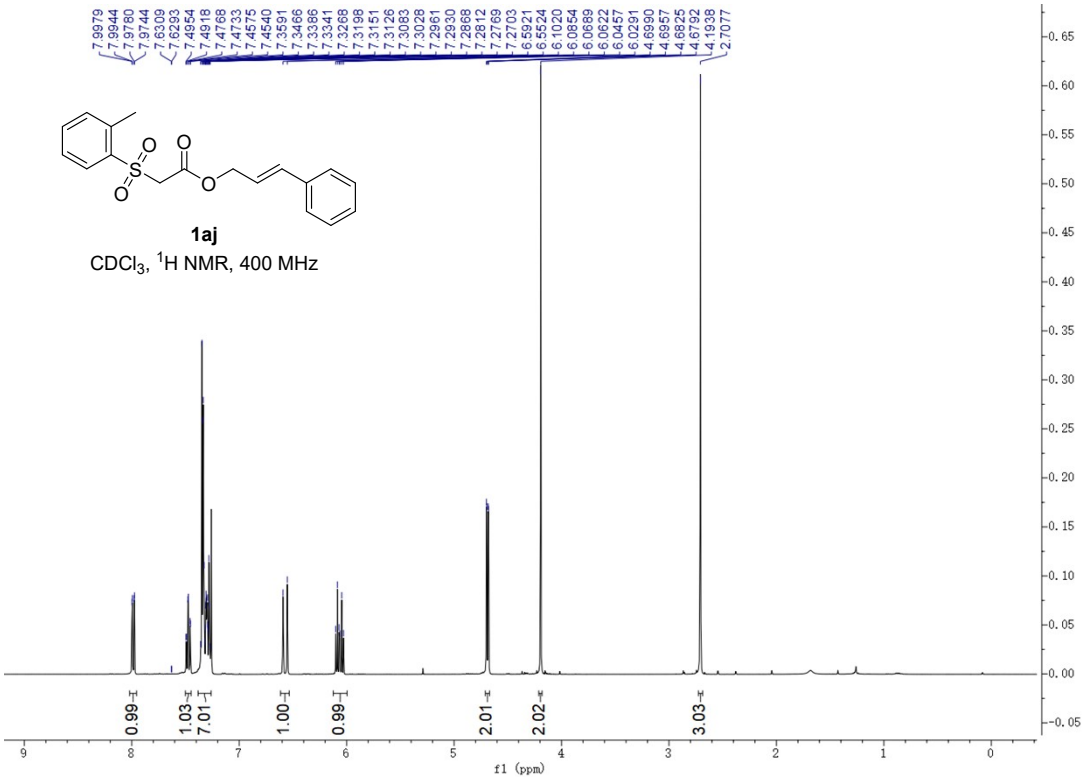
O
O
1ai
CDCl3, 13C NMR, 100 MHz



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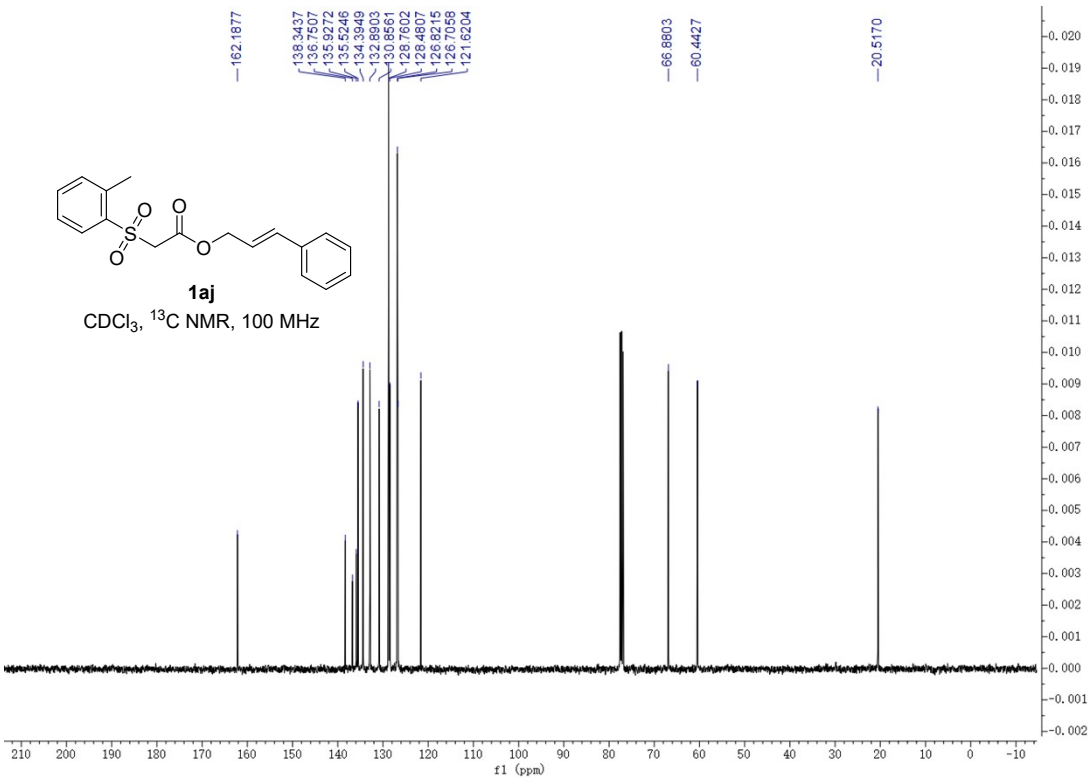

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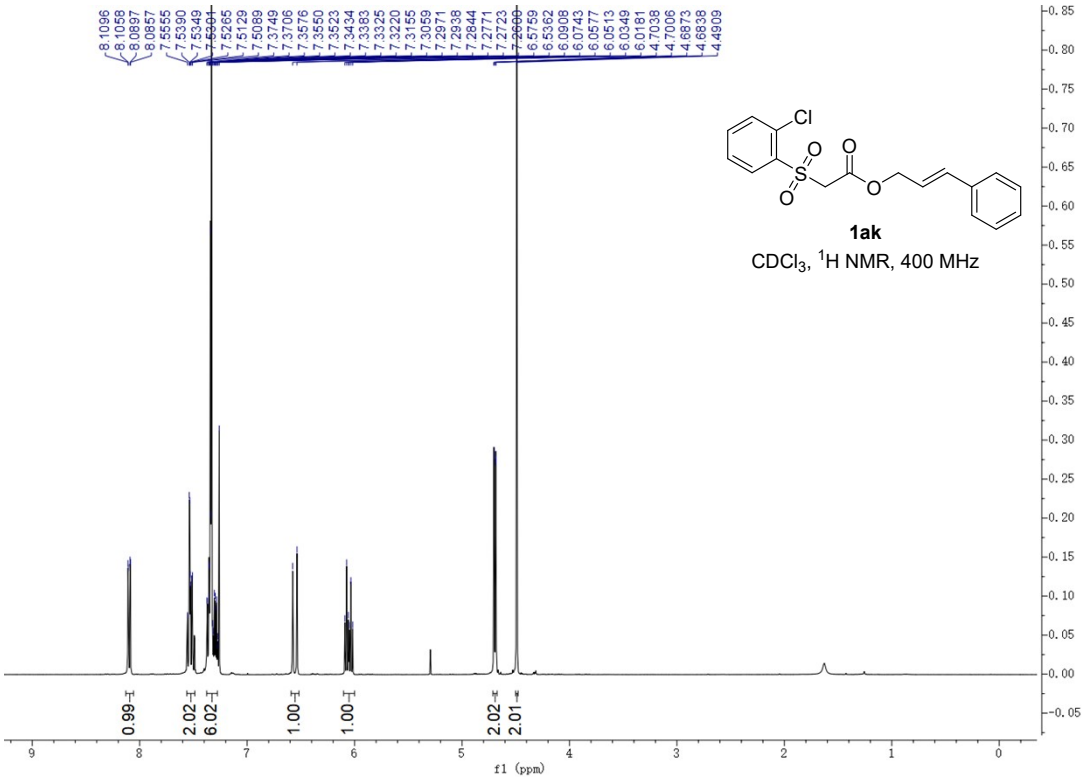

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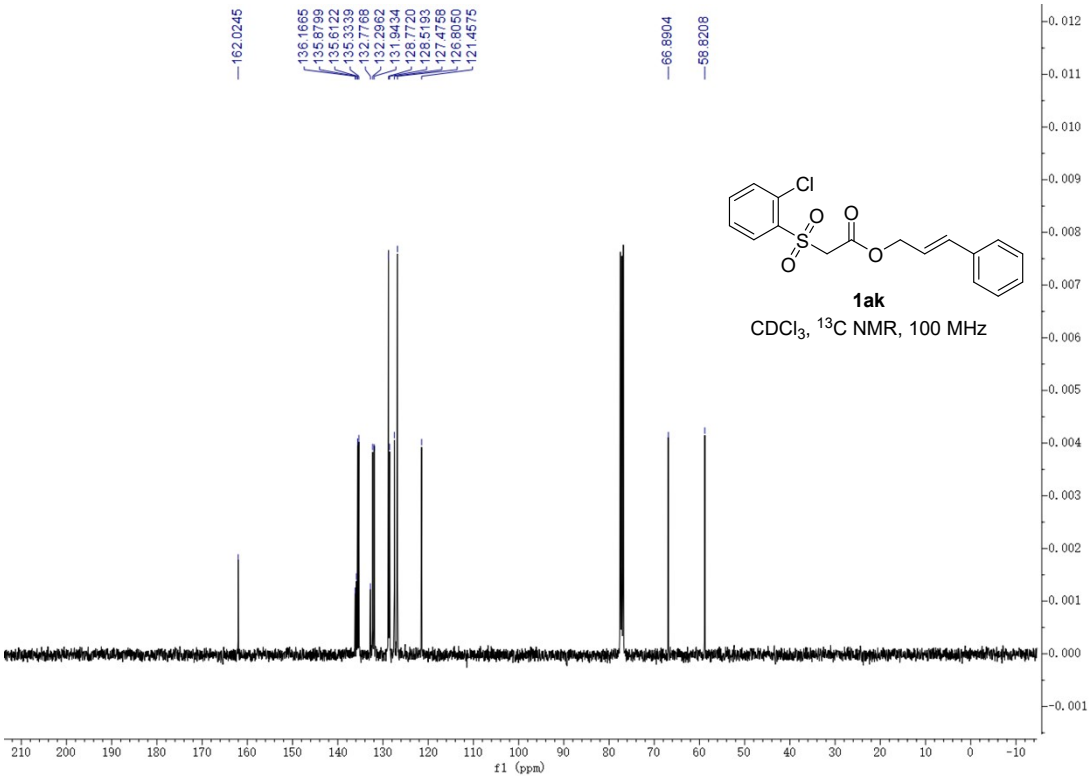

1ak

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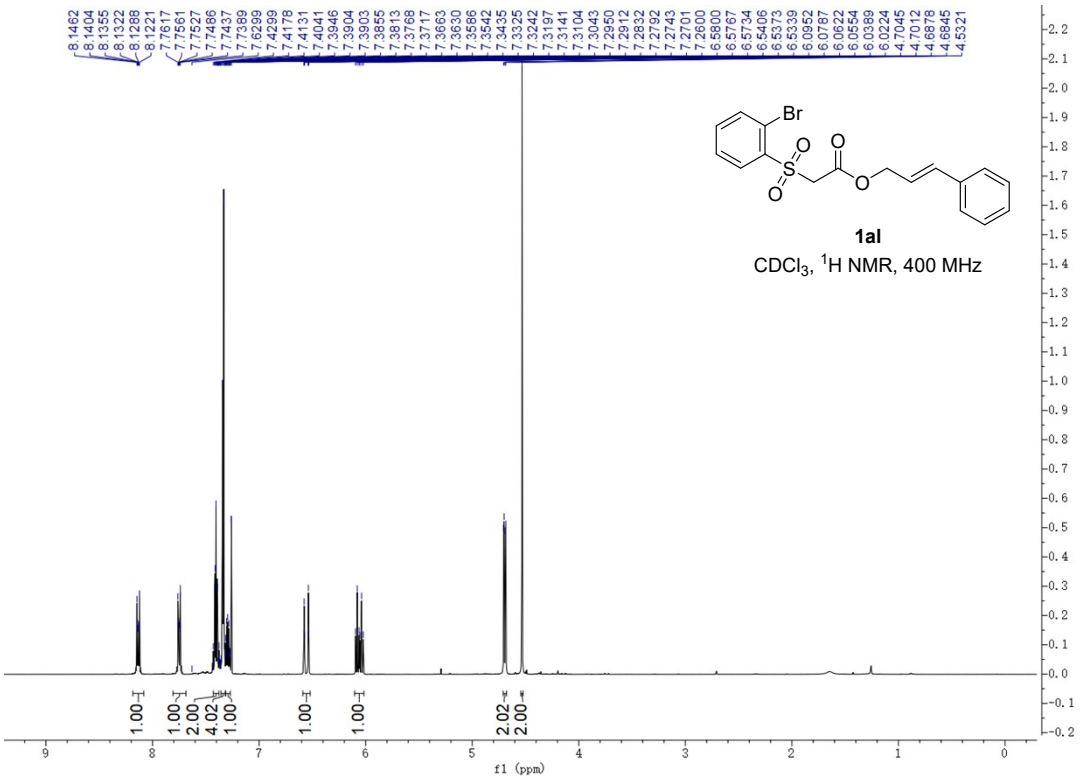
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8.1355
8.1322
8.1288
8.1221
7.7617
7.7561
7.7527
7.7486
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7.7389
7.6299
7.4299
7.4178
7.4131
7.4041
7.3946
7.3904
7.3903
7.3855
7.3813
7.3768
7.3717
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7.3542
7.3435
7.3325
7.3242
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7.3141
7.3104
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7.2950
7.2912
7.2832
7.2792
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7.2600
6.5800
6.5767
6.5734
6.5406
6.5373
6.5339
6.0952
6.0787
6.0622
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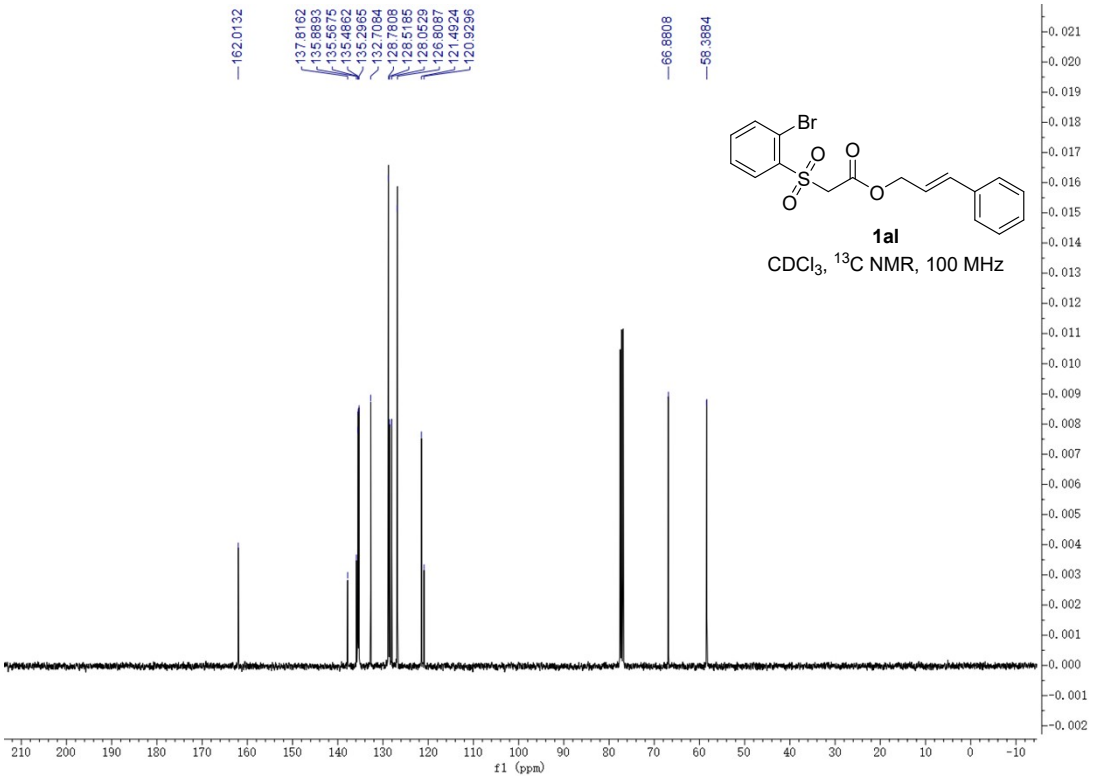
6.0389
6.0224
4.7045
4.7012
4.6878
4.6845
4.5321
1.00
1.00
2.00
4.02
1.00
1.00
1.00
2.02
2.00
f1 (ppm)
Br
O
O
S
O
O
O
1al
CDCl3, 1H NMR, 400 MHz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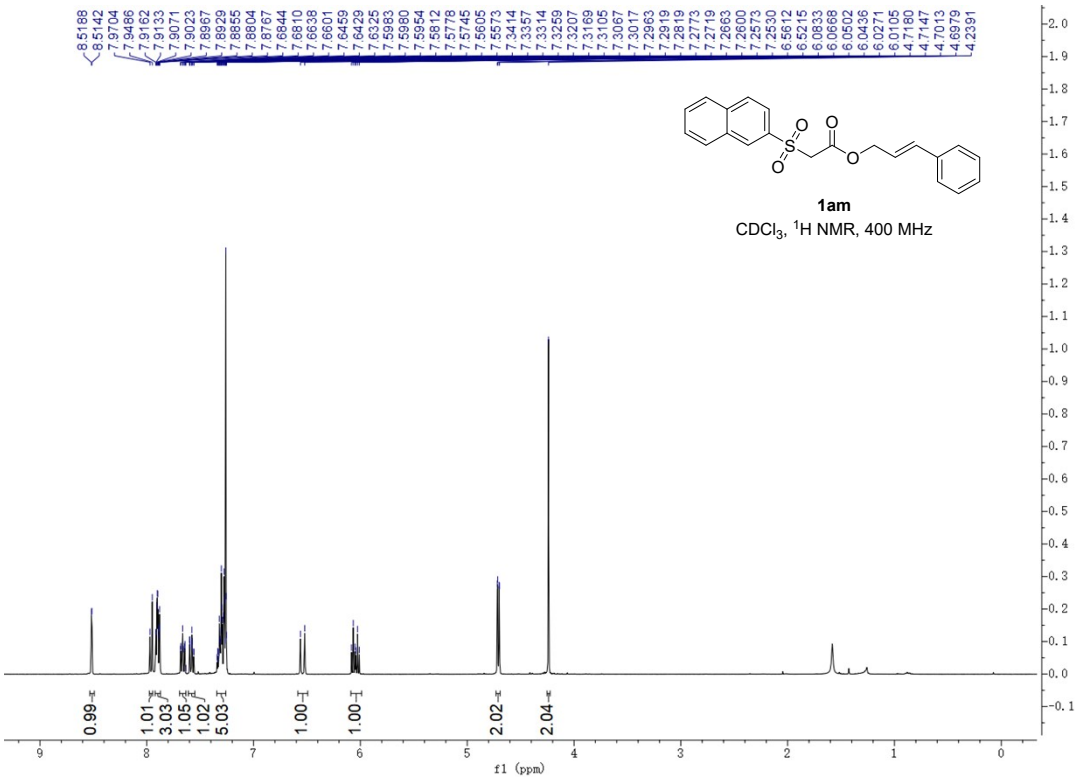
128.0529
126.8087
121.4924
120.9296
66.8808
58.3884
f1 (ppm)
Br
O
O
S
O
O
O
1al
CDCl3, 13C NMR, 100 MHz



1am

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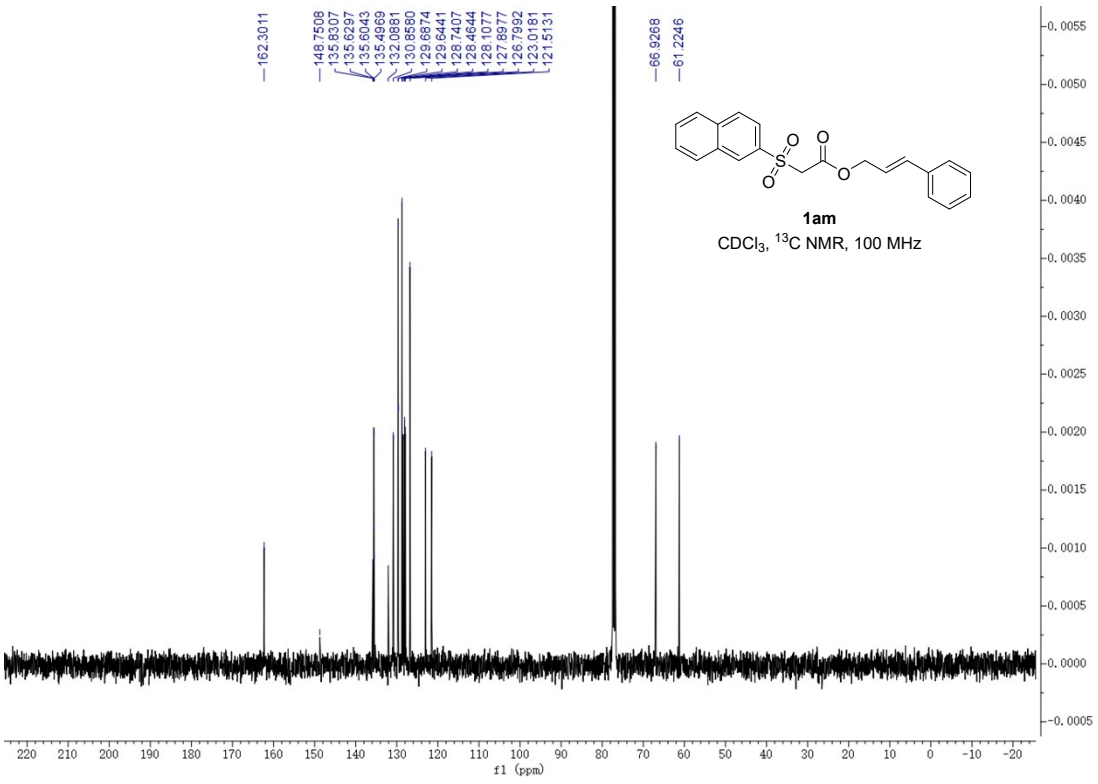

1am

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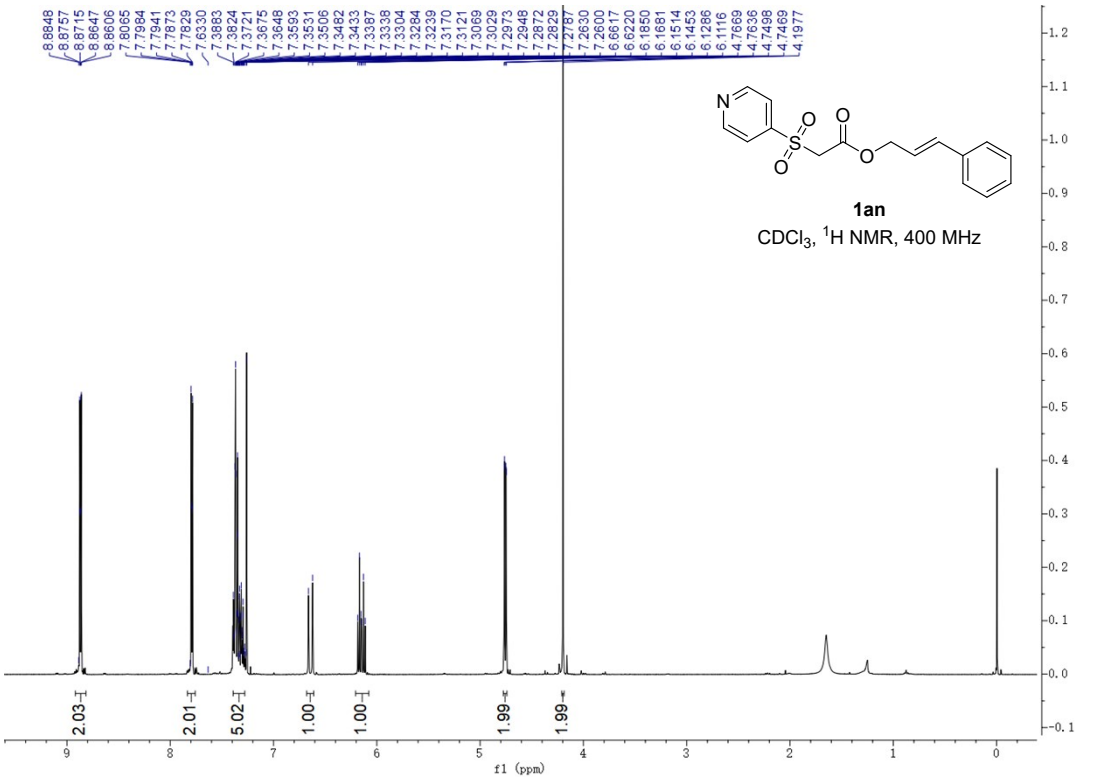
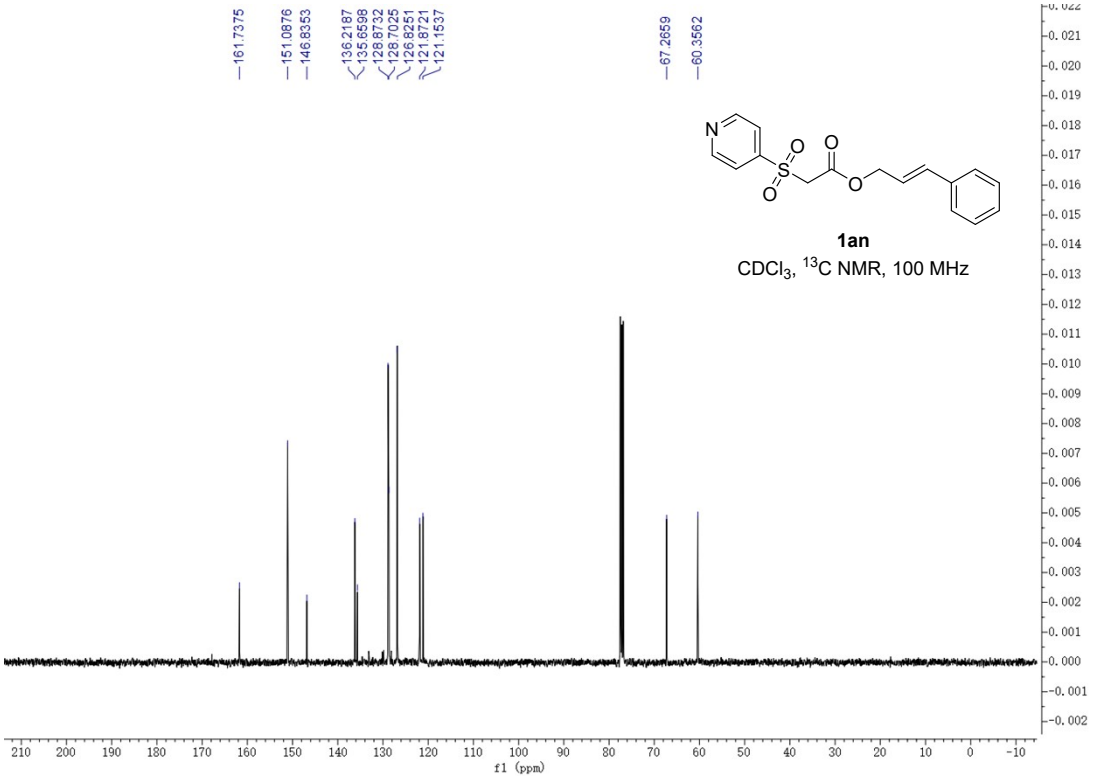


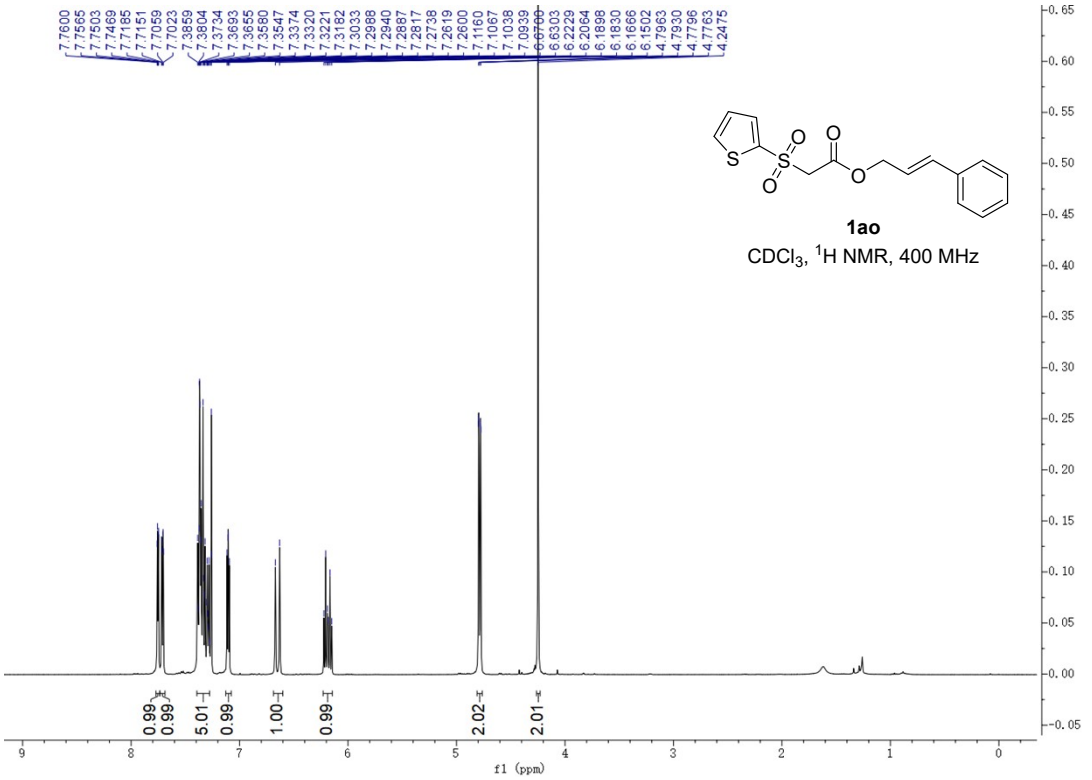
1an

$CDCl_3$, ^1H NMR, 400 MHz



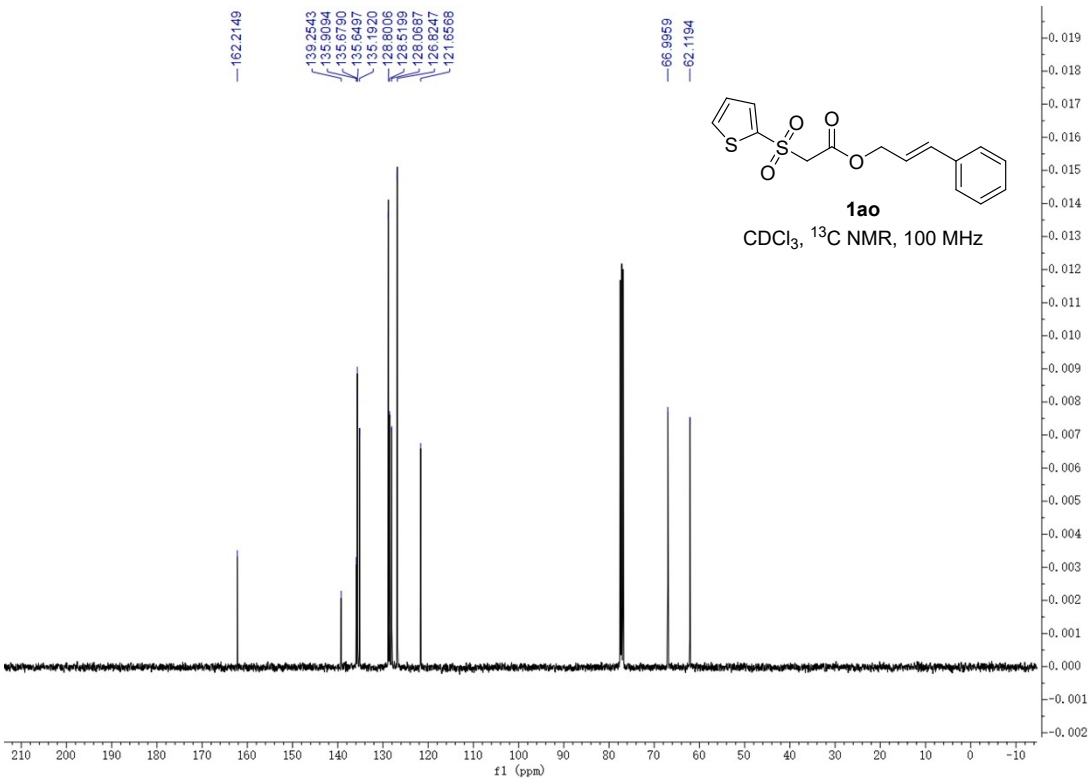
1an

$CDCl_3$, ^{13}C NMR, 100 MHz



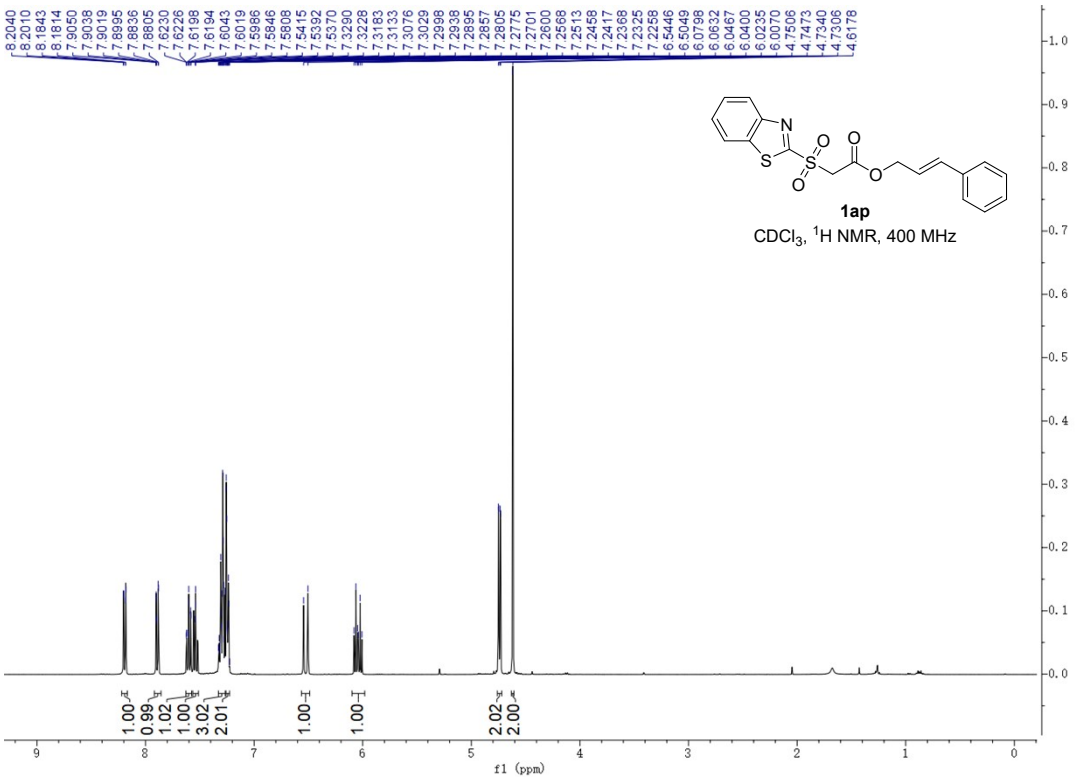
1ao

$CDCl_3$, ^1H NMR, 400 MHz



1ao

$CDCl_3$, ^{13}C NMR, 100 MHz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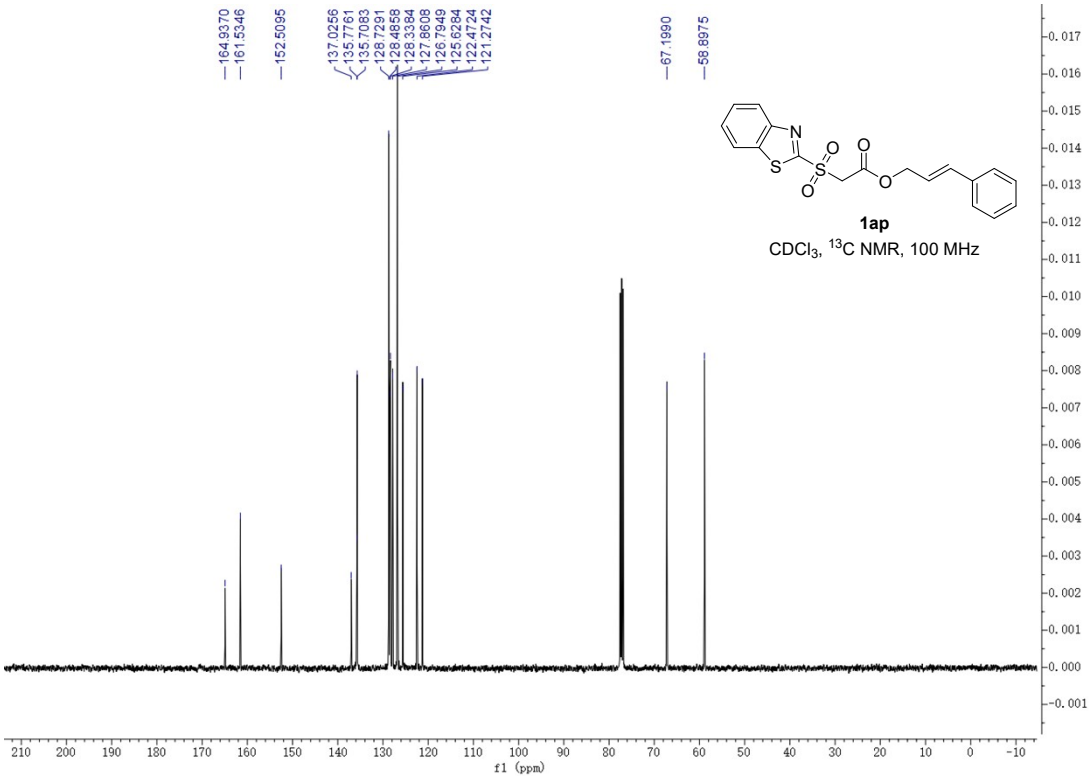
8.2010
8.1843
8.1814
7.9050
7.9038
7.9019
7.8995
7.8836
7.8805
7.6230
7.6226
7.6198
7.6194
7.6043
7.6019
7.5986
7.5846
7.5808
7.5415
7.5392
7.5370
7.3290
7.3228
7.3183
7.3133
7.3076
7.3029
7.2998
7.2938
7.2895
7.2857
7.2805
7.2775
7.2701
7.2600
7.2568
7.2513
7.2458
7.2417
7.2368
7.2325
7.2258
6.5446
6.5049
6.0798
6.0632
6.0467
6.0400
6.0235
6.0070
4.7506
4.7473
4.7340
4.7306
4.6178
1.00
0.99
1.02
1.00
3.02
2.01
1.00
1.00
2.02
2.00
f1 (ppm)
1ap
CDCl3, 1H NMR, 400 MHz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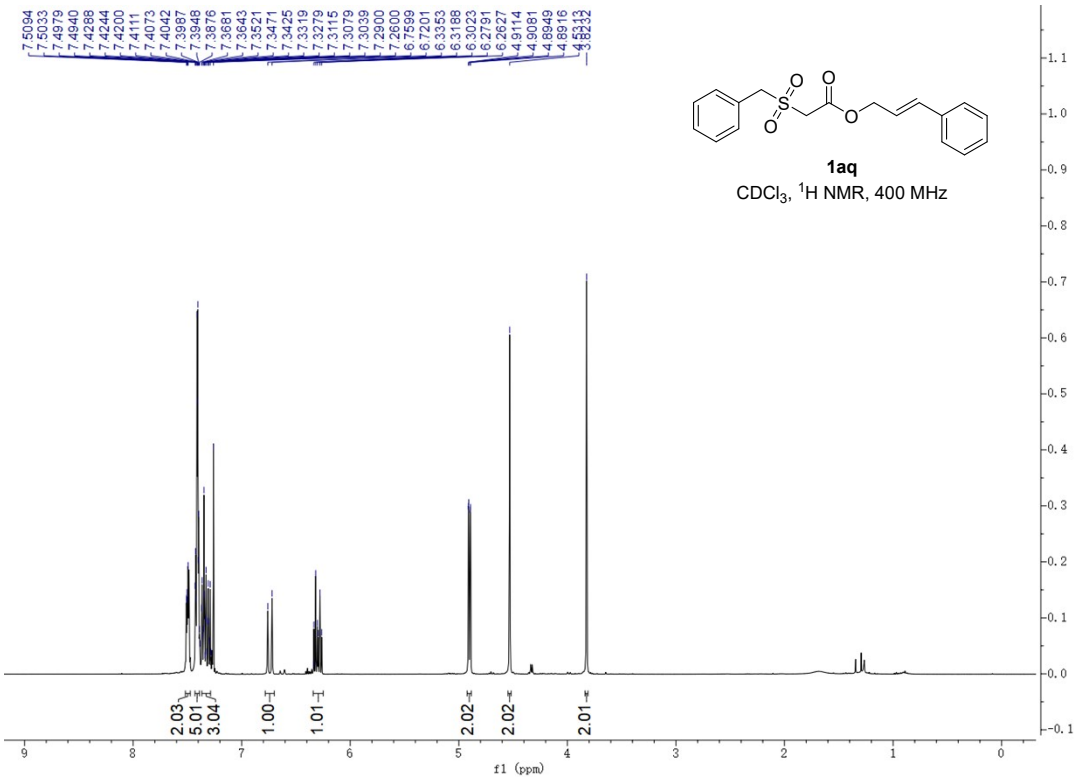
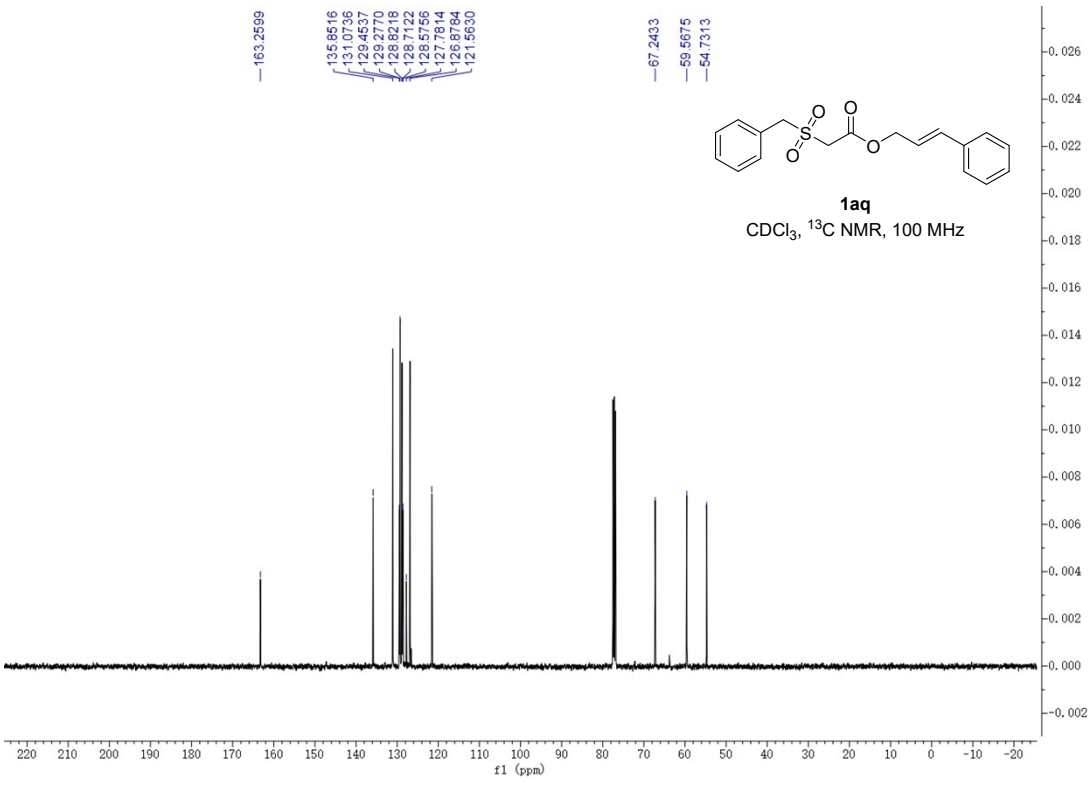
161.5346
152.5095
137.0256
135.7761
135.7083
128.7291
128.4858
128.3384
127.8608
126.7949
125.6284
122.4724
121.2742
67.1990
58.8975
f1 (ppm)
1ap
CDCl3, 13C NMR, 100 MHz



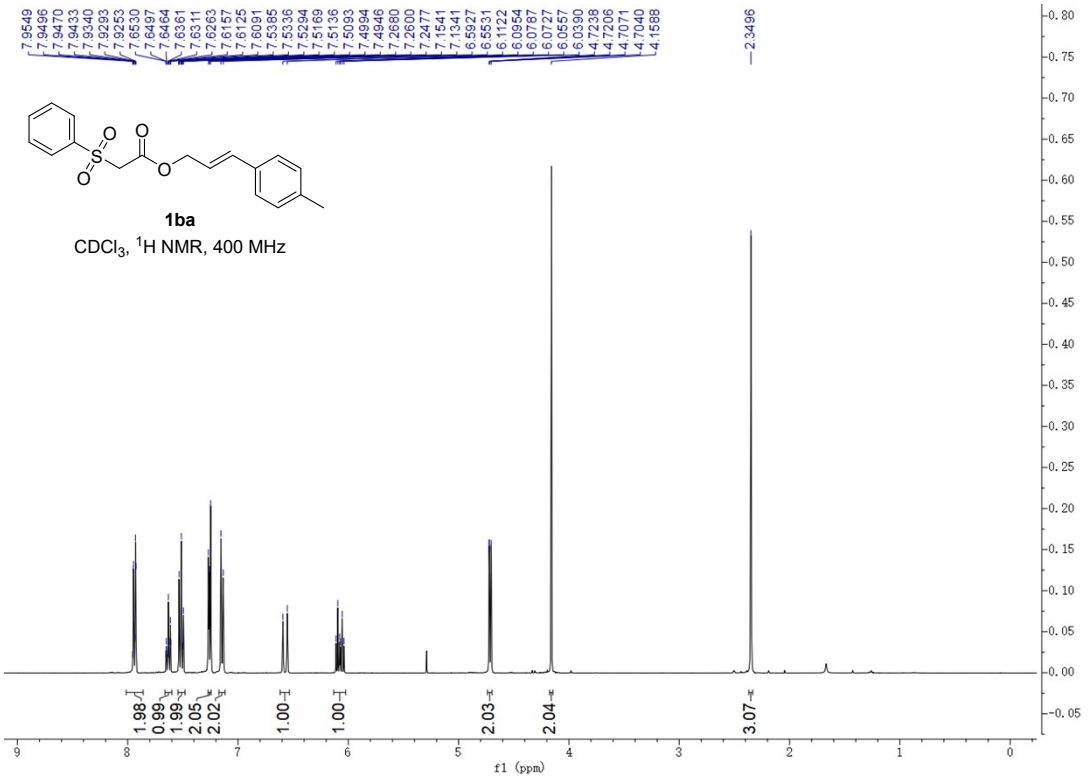
1aq

$CDCl_3$, ^1H NMR, 400 MHz



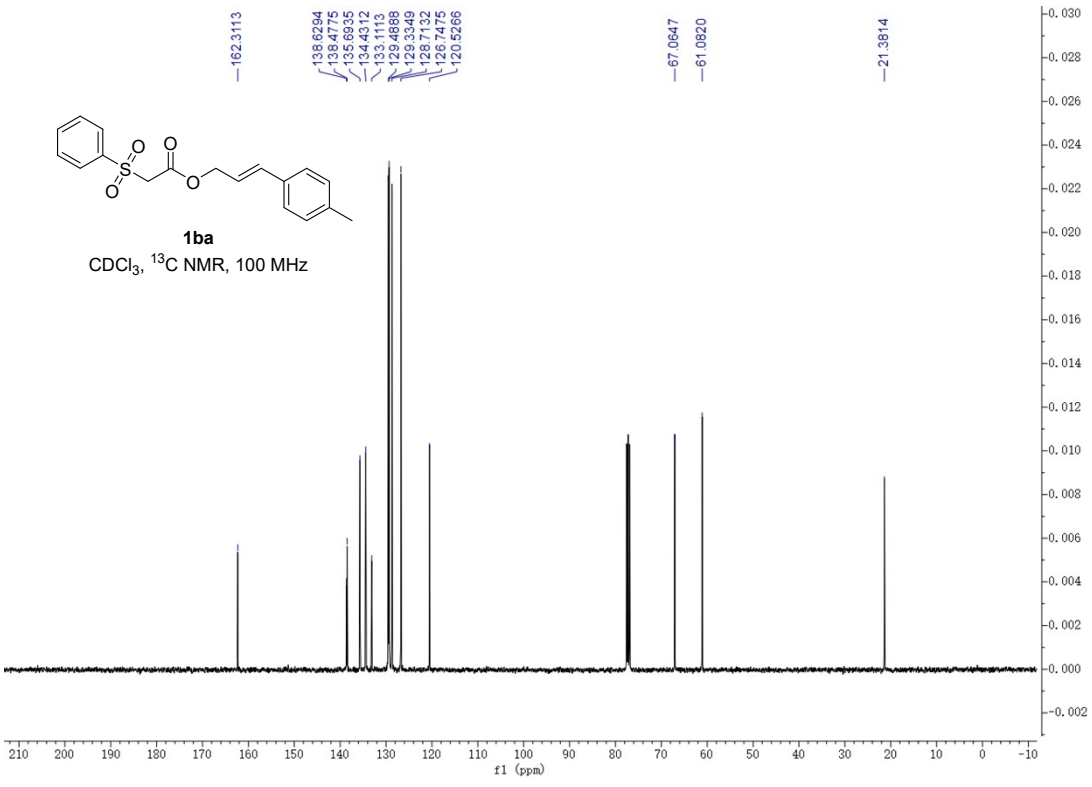
1aq

$CDCl_3$, ^{13}C NMR, 100 MHz



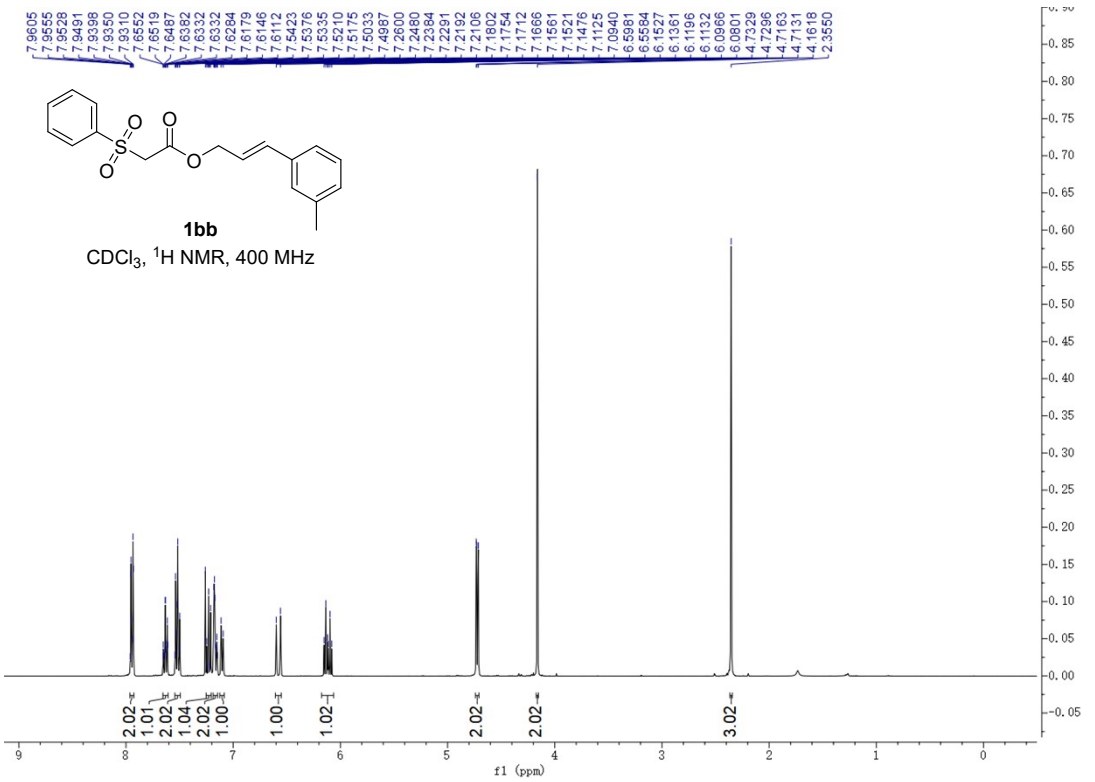
1ba

$CDCl_3$, ^1H NMR, 400 MHz



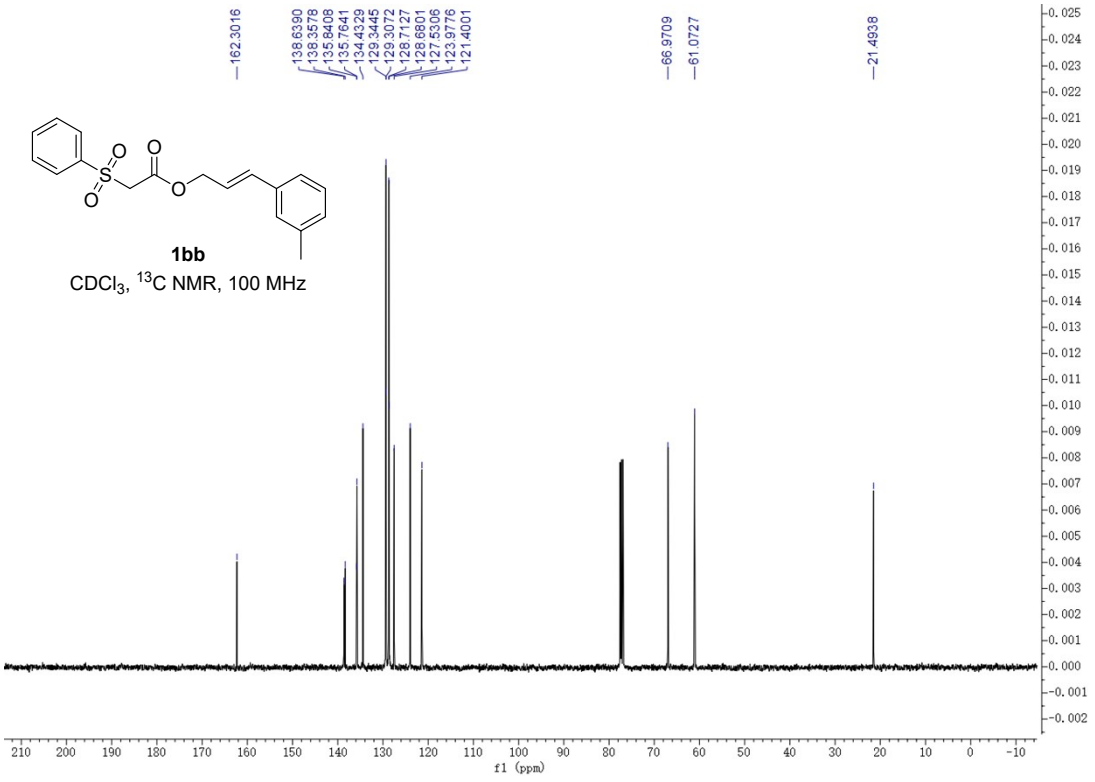
1ba

$CDCl_3$, ^{13}C NMR, 100 MHz



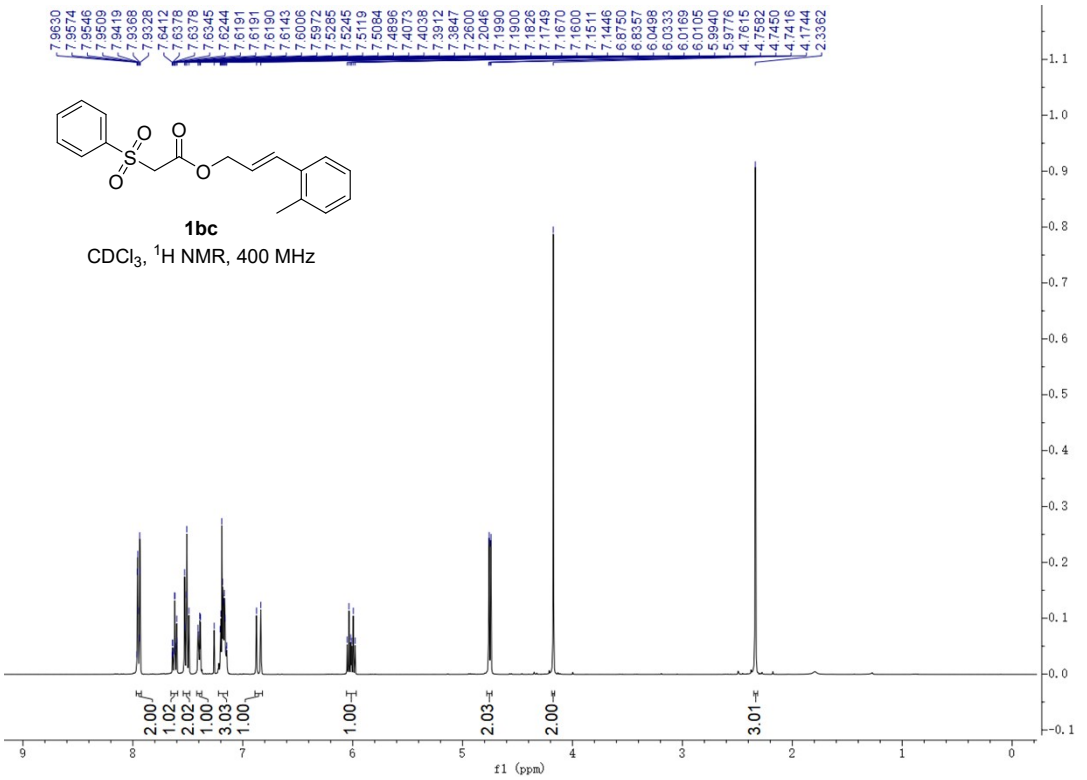
1bb

$CDCl_3$, ^1H NMR, 400 MHz



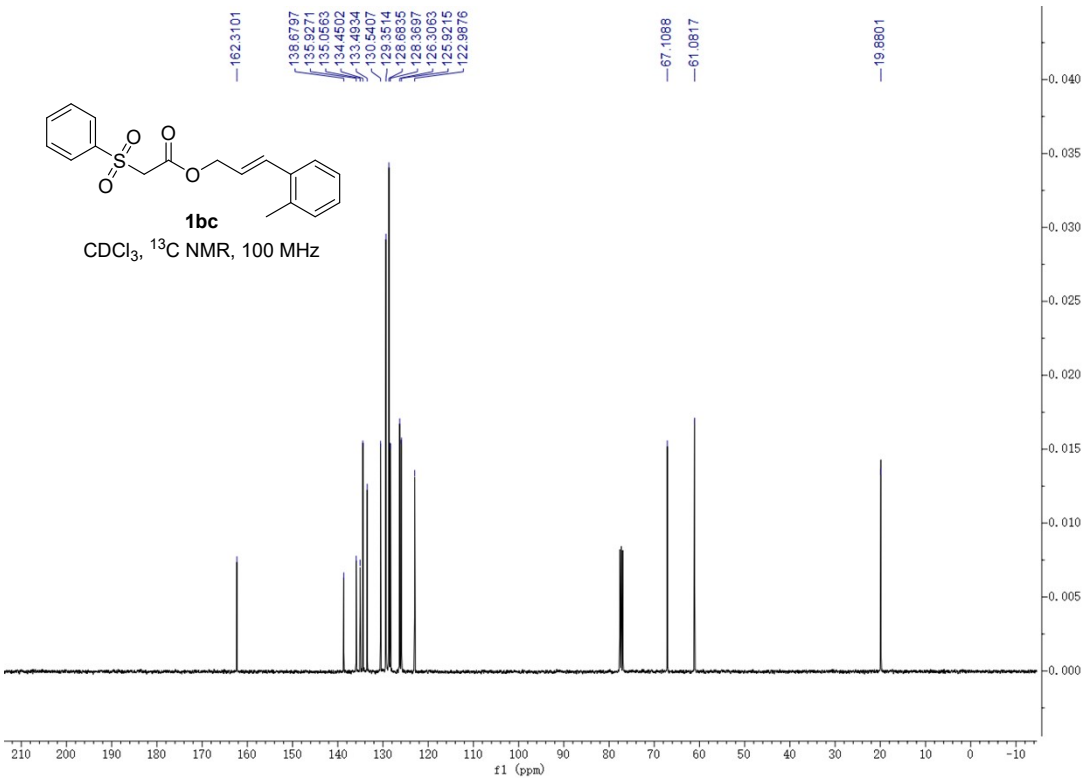
1bb

$CDCl_3$, ^{13}C NMR, 100 MHz



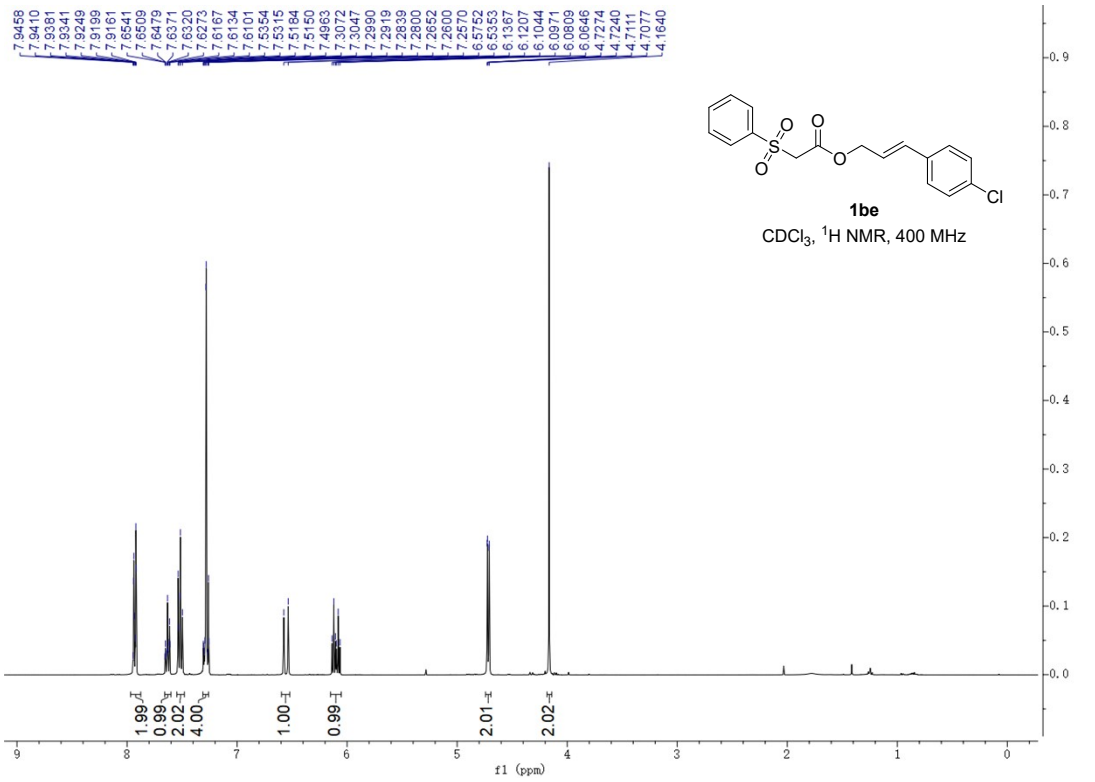
1bc

$CDCl_3$, ^1H NMR, 400 MHz



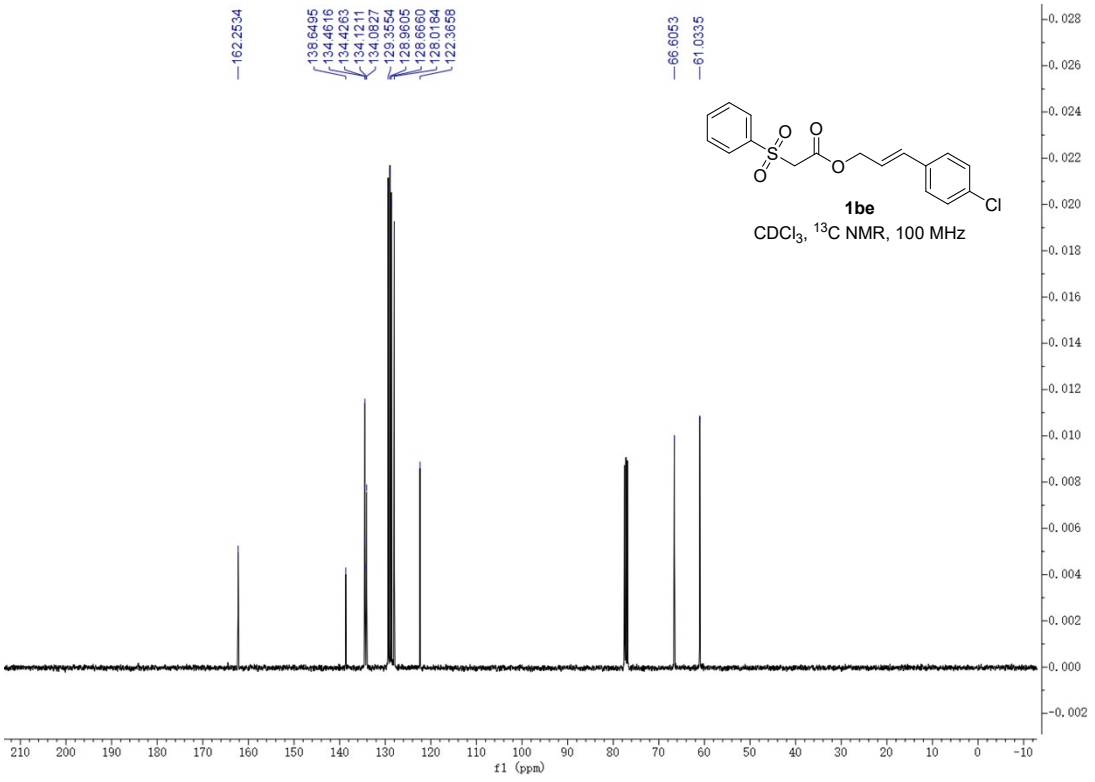
1bc

$CDCl_3$, ^{13}C NMR, 100 MHz



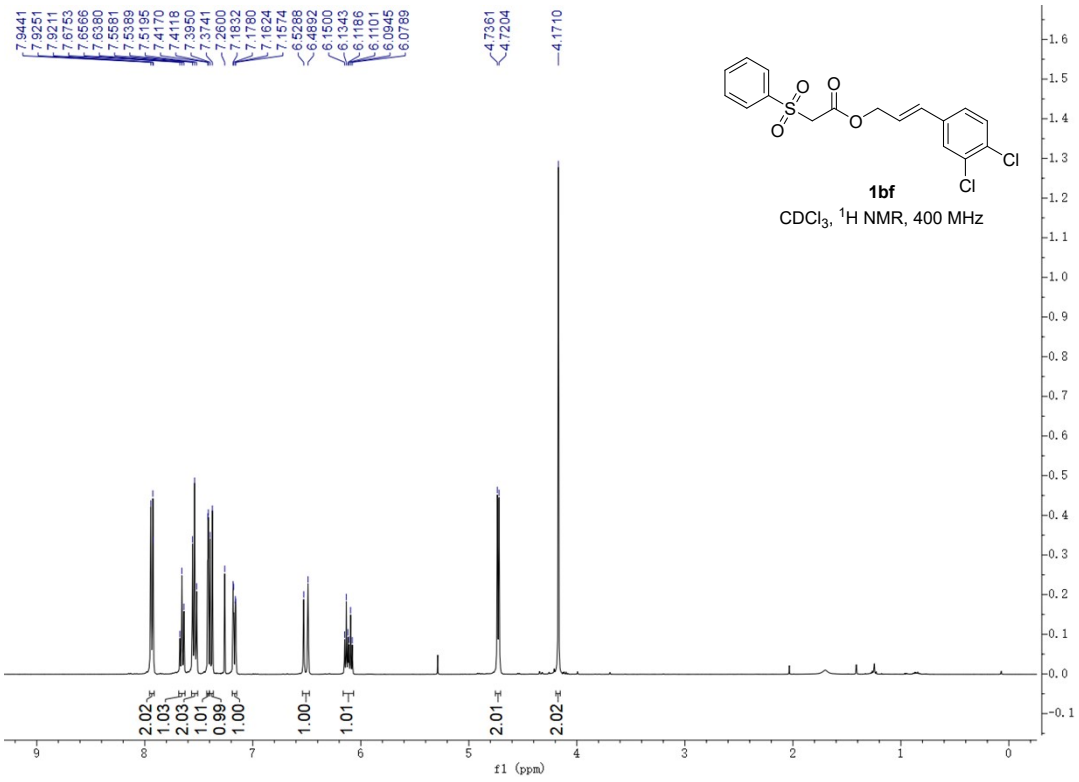
1be

$CDCl_3$, ^1H NMR, 400 MHz



1be

$CDCl_3$, ^{13}C NMR, 100 MHz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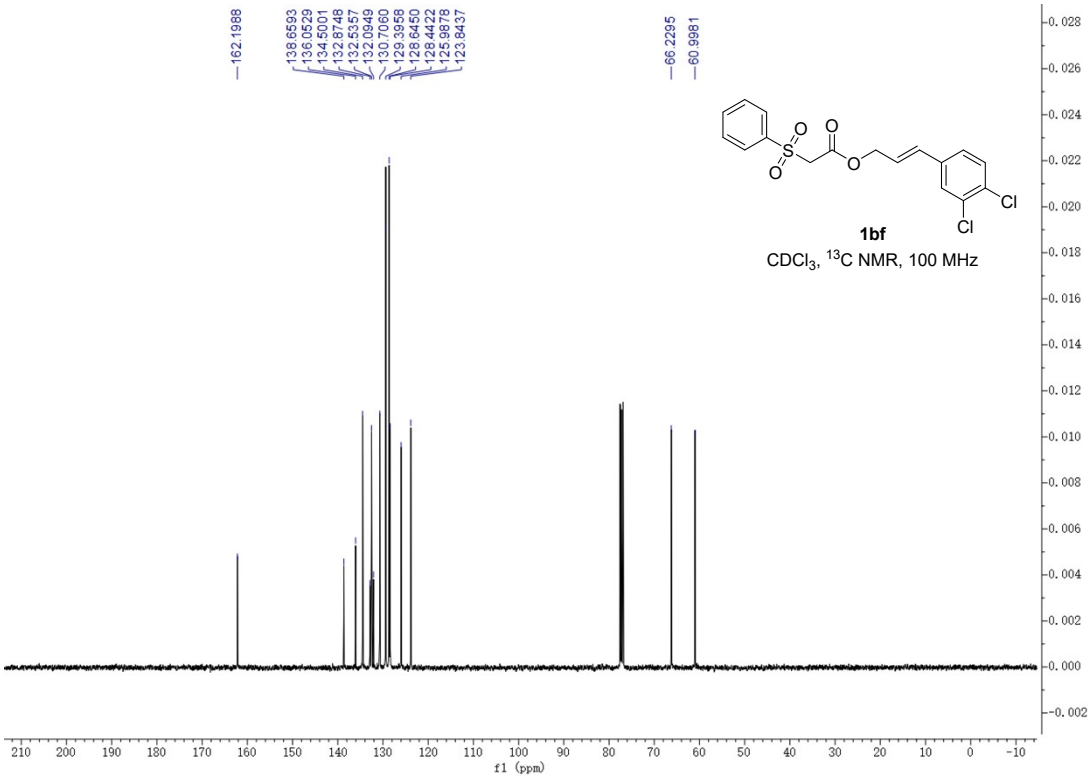
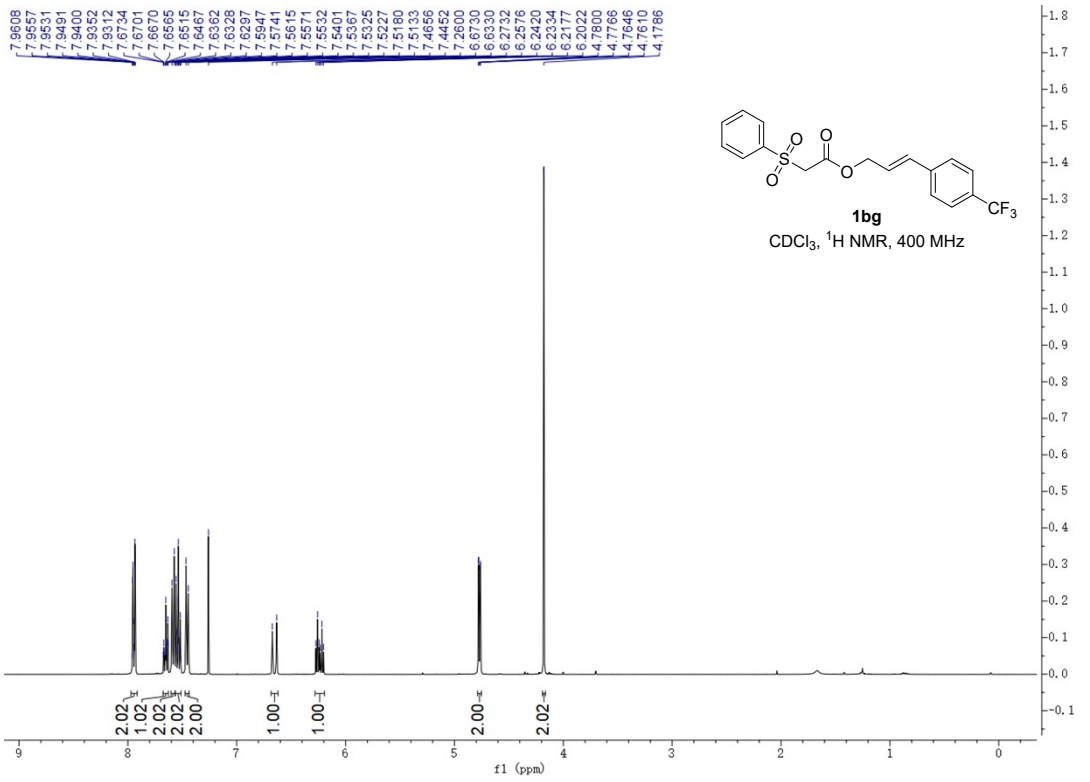
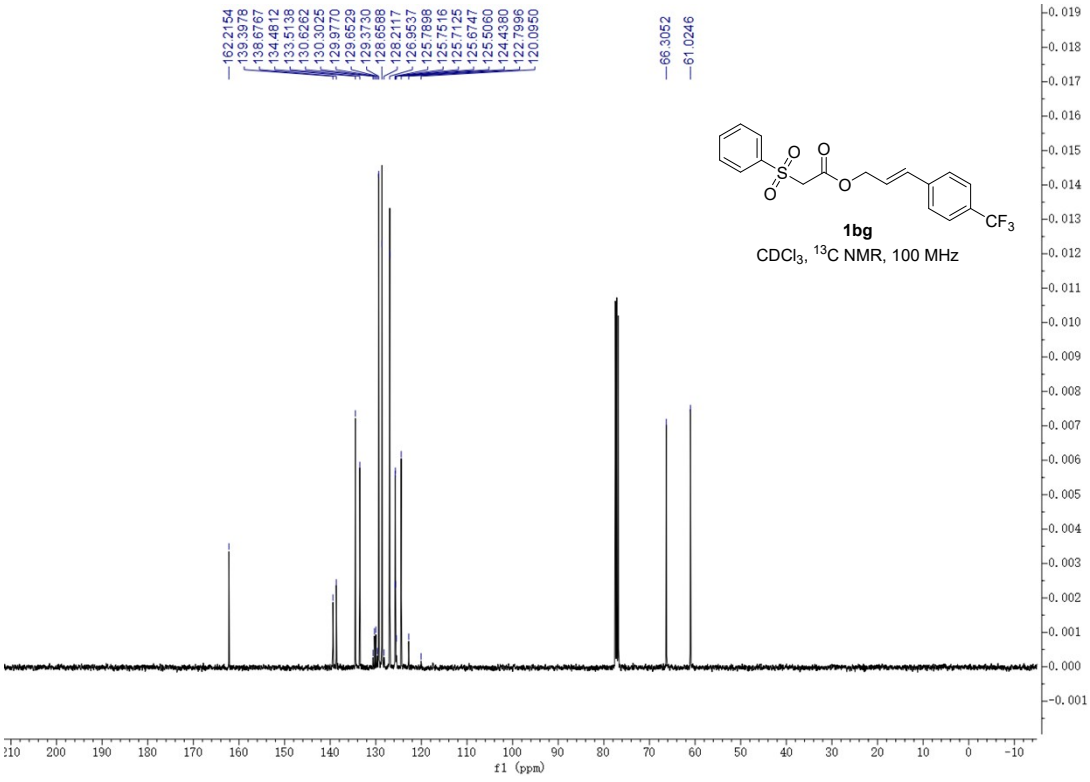
7.9251
7.9211
7.6753
7.6566
7.6380
7.5581
7.5389
7.5195
7.4170
7.4118
7.3950
7.3741
7.2600
7.1832
7.1780
7.1624
7.1574
6.5288
6.4892
6.1500
6.1343
6.1186
6.1101
6.0945
6.0789
4.7361
4.7204
4.1710
2.02
1.03
2.03
1.01
0.99
1.00
1.00
1.01
2.01
2.02
f1 (ppm)
1bf
CDCl3, 1H NMR, 400 MHz


162.1988
138.6593
136.0529
134.5001
132.8748
132.5357
132.0949
130.7060
129.3958
128.6450
128.4422
125.9878
123.8437
66.2295
60.9981
f1 (ppm)
1bf
CDCl3, 13C NMR, 100 MHz



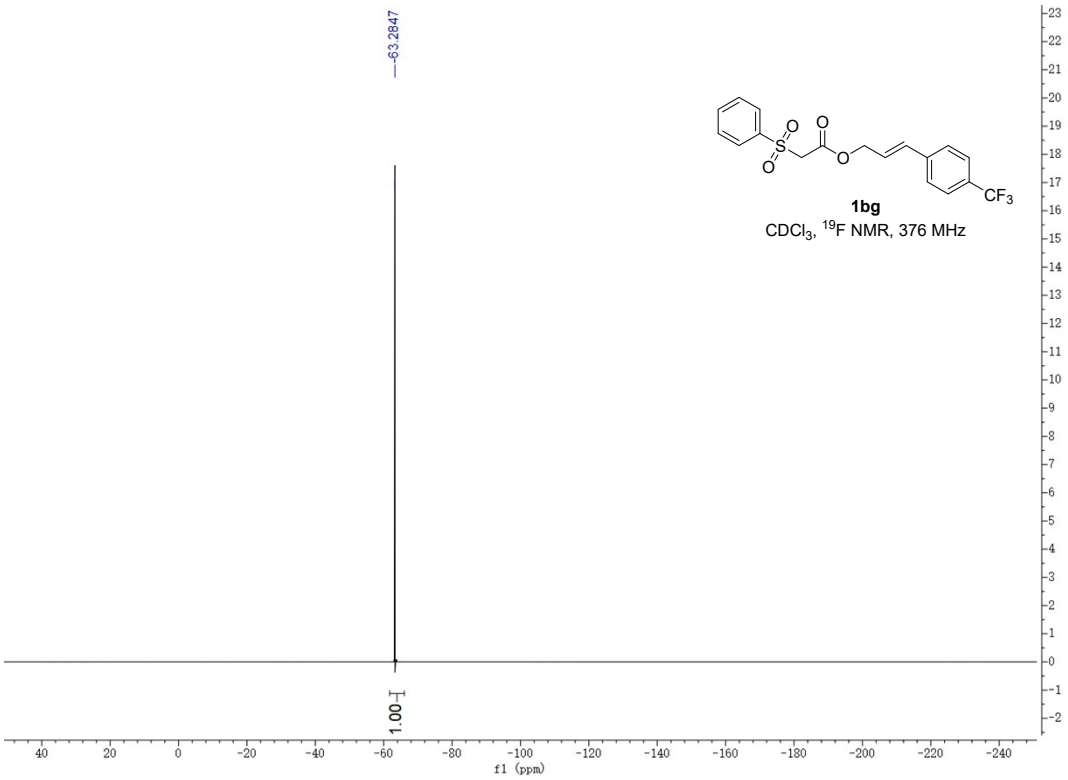
1bg

$CDCl_3$, ^1H NMR, 400 MHz



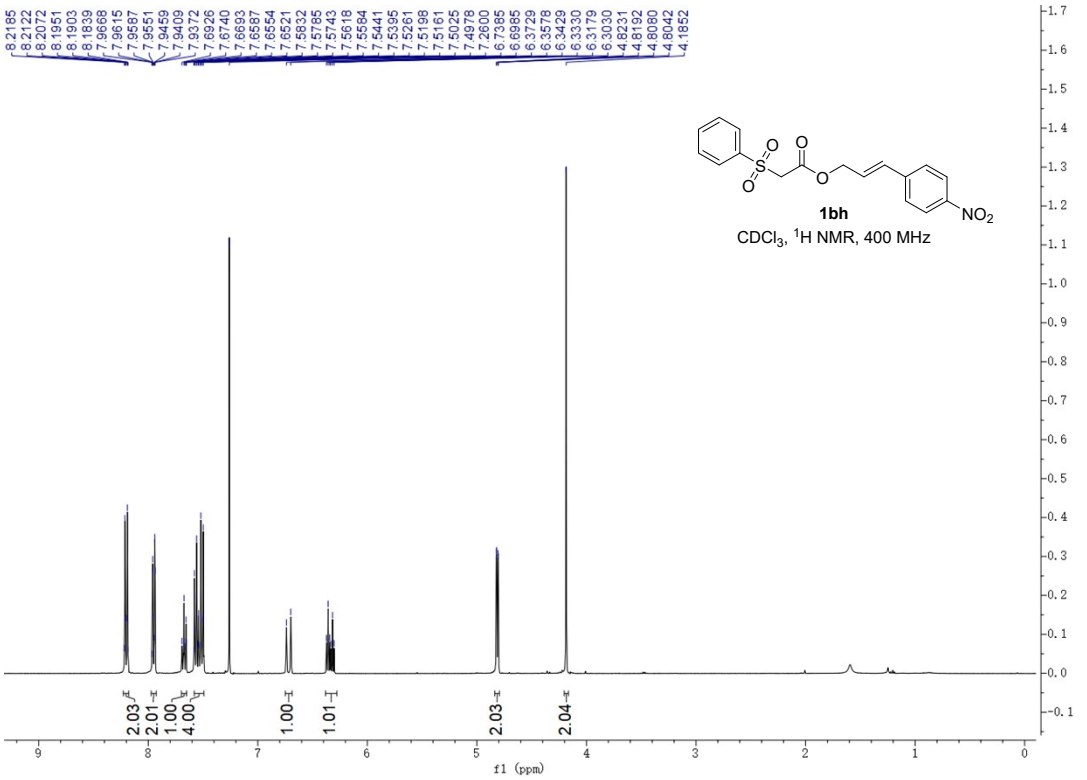
1bg

$CDCl_3$, ^{13}C NMR, 100 MHz



1bg

$CDCl_3$, ^{19}F NMR, 376 MHz


8.2185
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8.2072
8.1951
8.1903
8.1839
7.9668
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7.9587
7.9551
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7.9409
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7.6740
7.6693
7.6587
7.6554
7.6521
7.5832
7.5785
7.5743
7.5618
7.5584
7.5441
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7.5198
7.5161
7.5025
7.4978
7.2600
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6.6985
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6.3429
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6.3179
6.3030
4.8231
4.8192
4.8080
4.8042
4.1852
2.03
2.01
1.00
4.00
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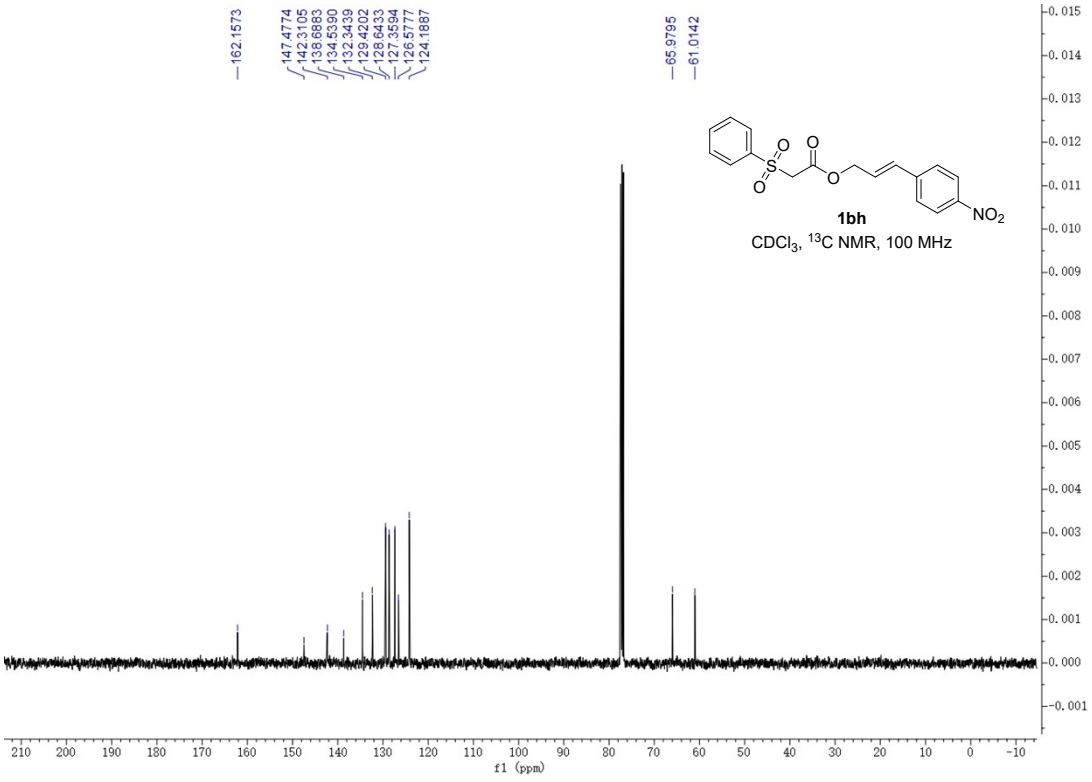
1.01
2.03
2.04
f1 (ppm)
1bh
CDCl3, 1H NMR, 400 MHz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142.3105
138.6883
134.5390
132.3439
129.4202
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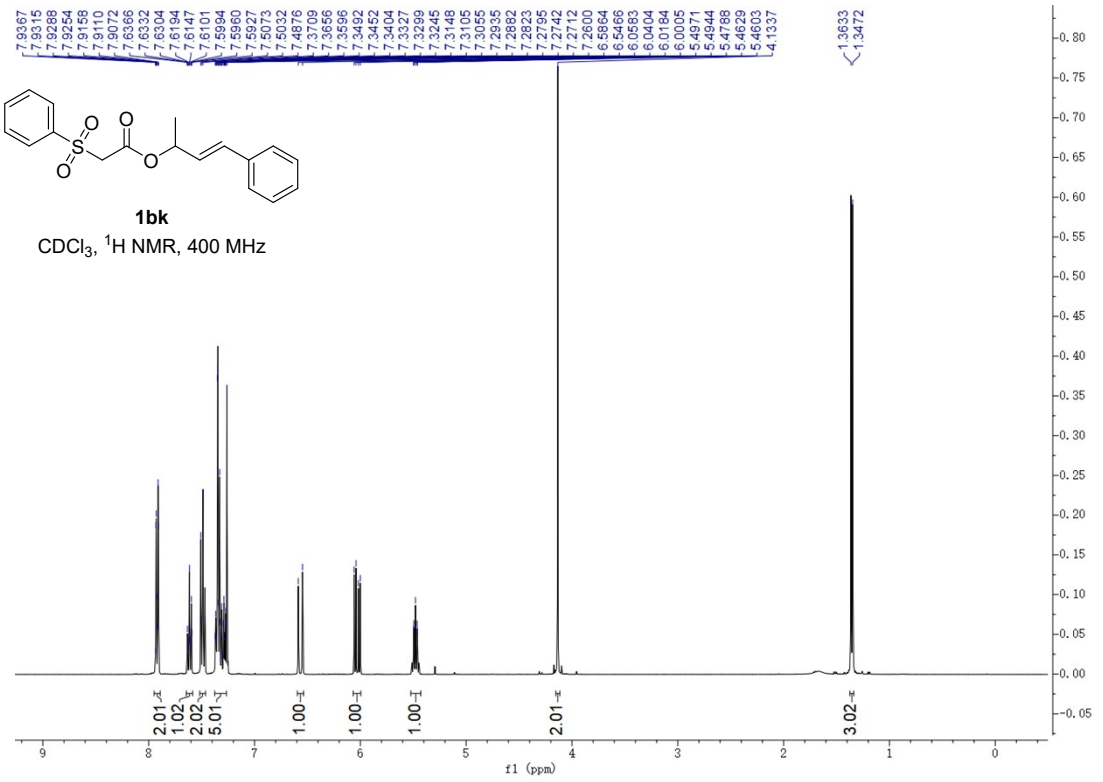
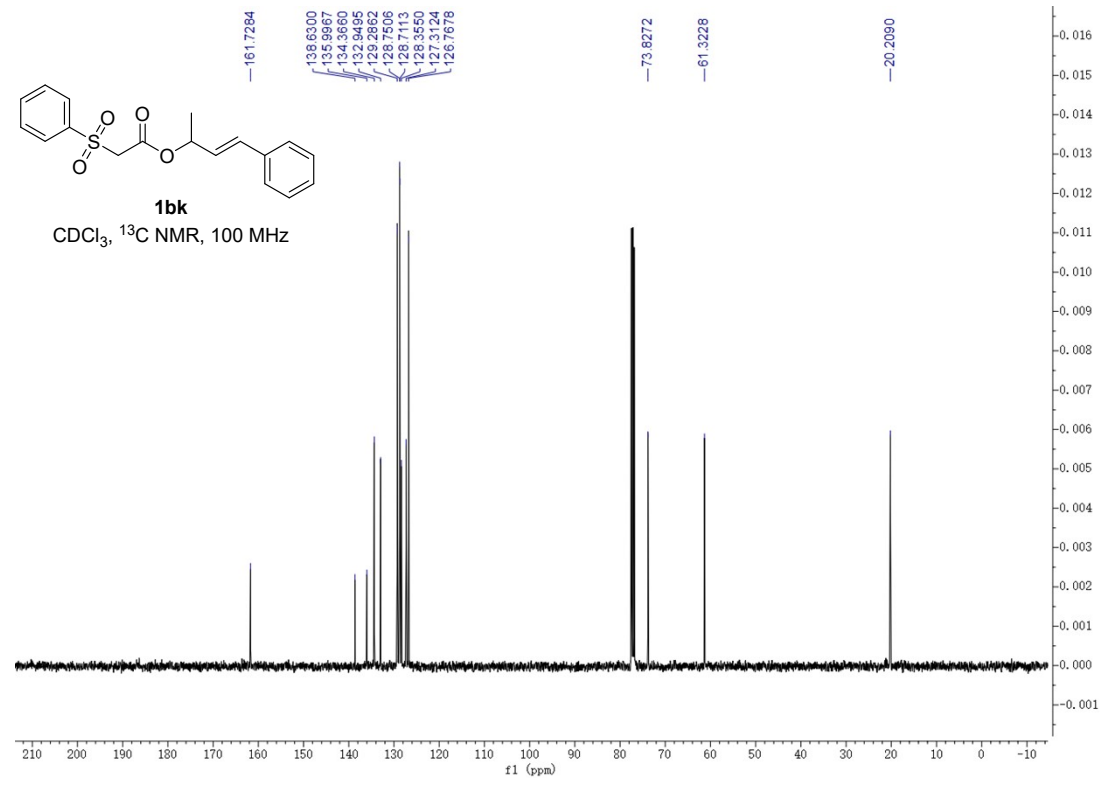
126.5777
124.1887
65.9795
61.0142
f1 (ppm)
1bh
CDCl3, 13C NMR, 100 MHz



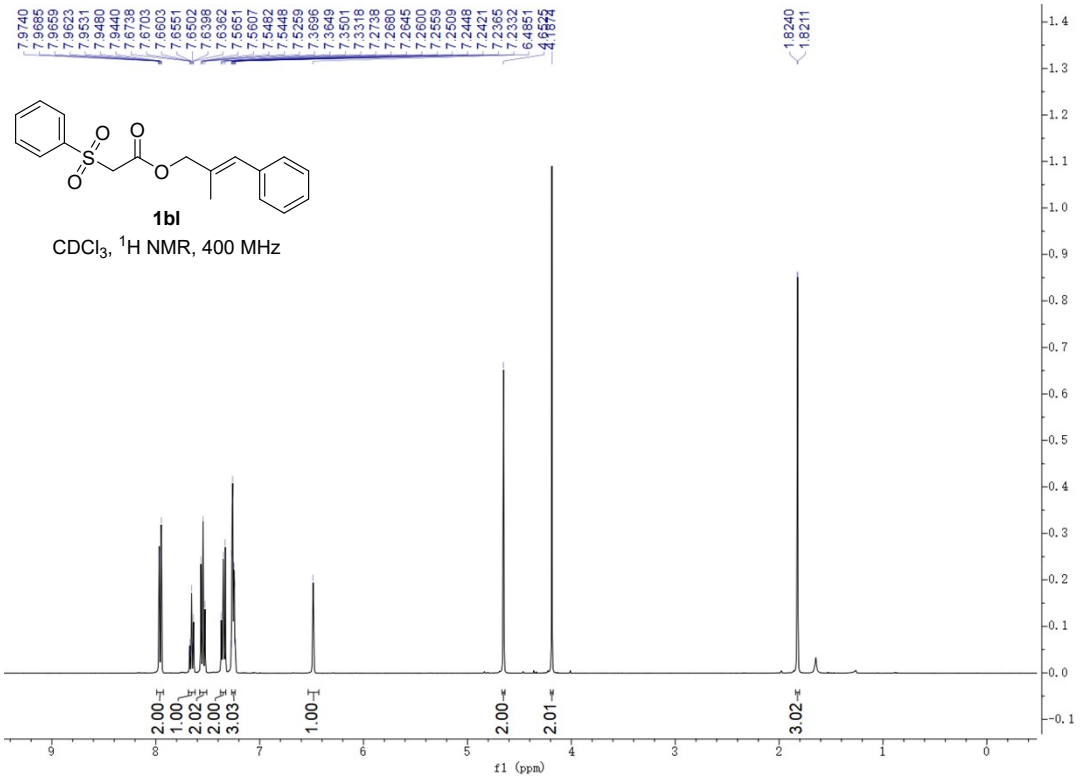
1bk

$CDCl_3$, ^1H NMR, 400 MHz



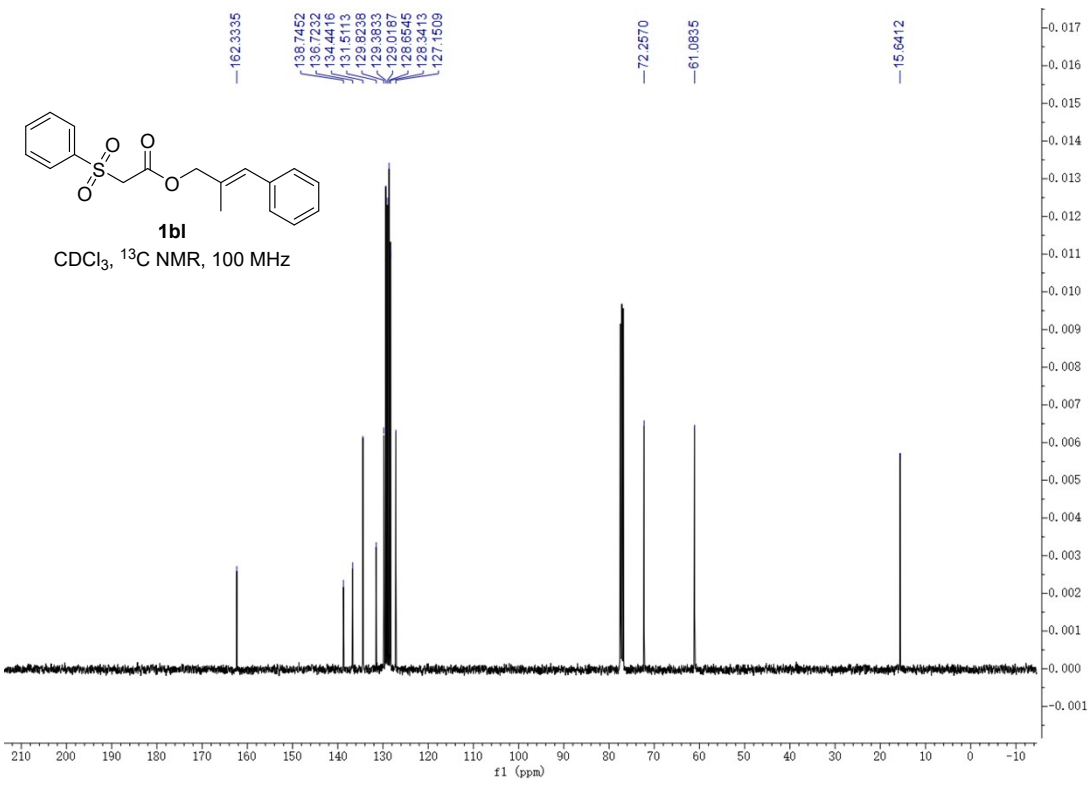
1bk

$CDCl_3$, ^{13}C NMR, 100 MHz



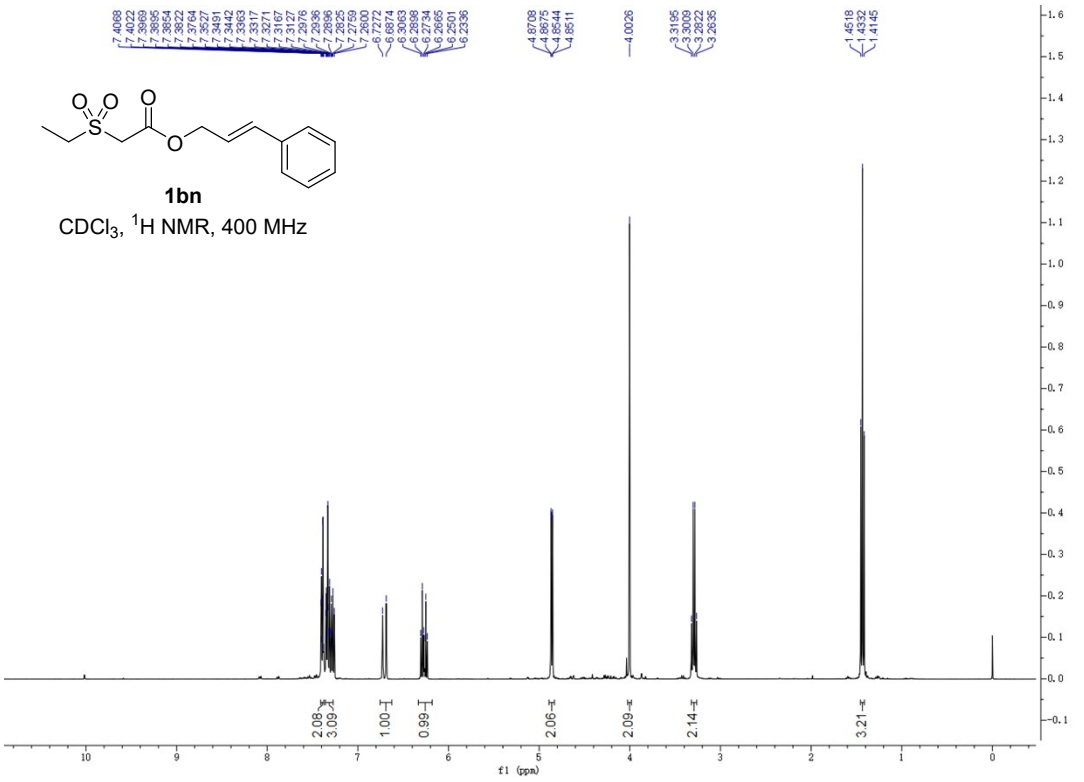
1bl

$CDCl_3$, ^1H NMR, 400 MHz



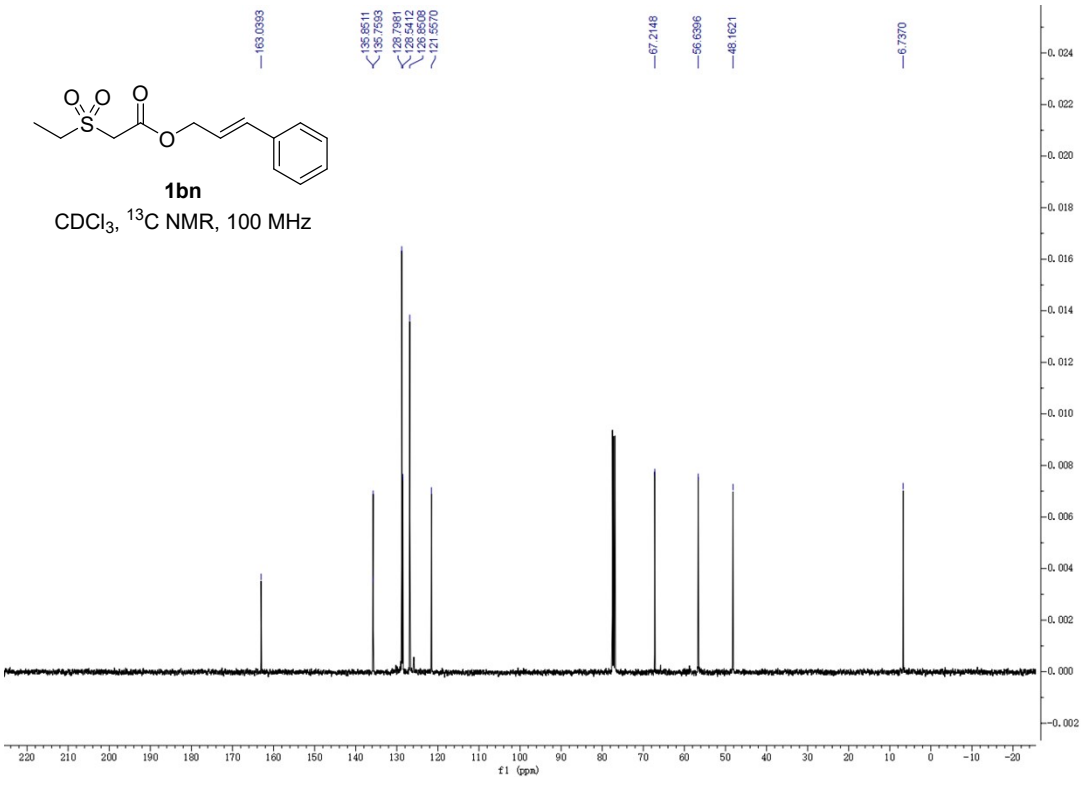
1bl

$CDCl_3$, ^{13}C NMR, 100 MHz



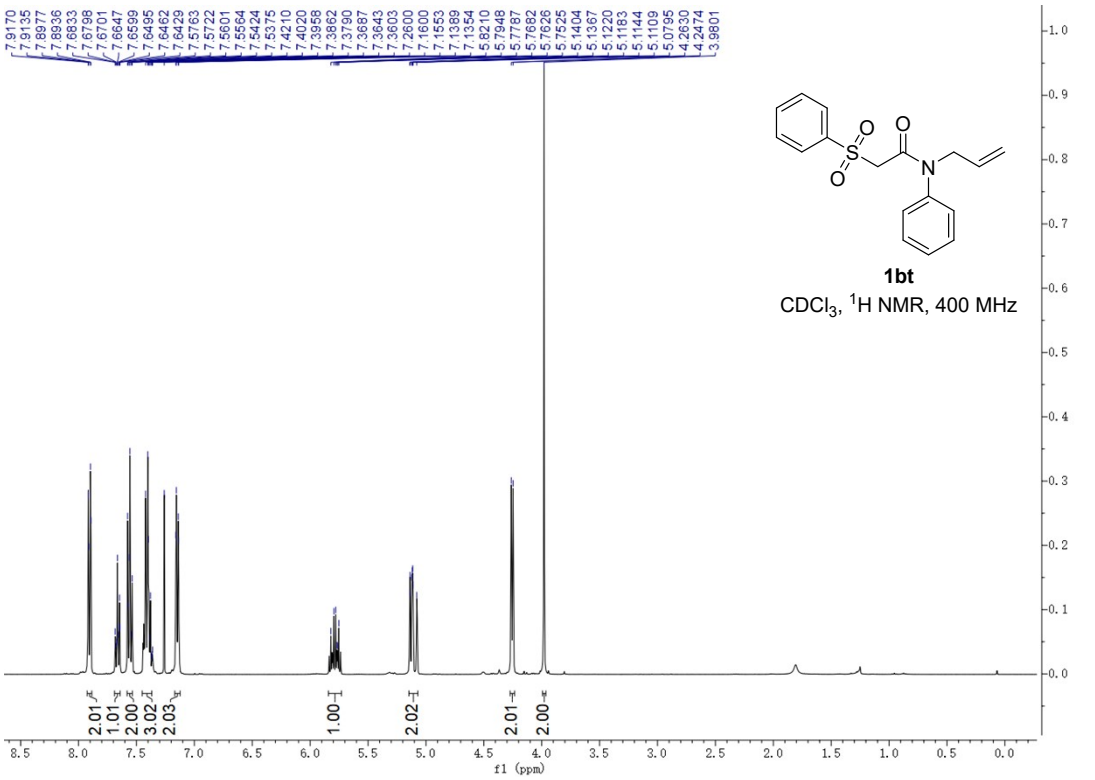
1bn

$CDCl_3$, ^1H NMR, 400 MHz



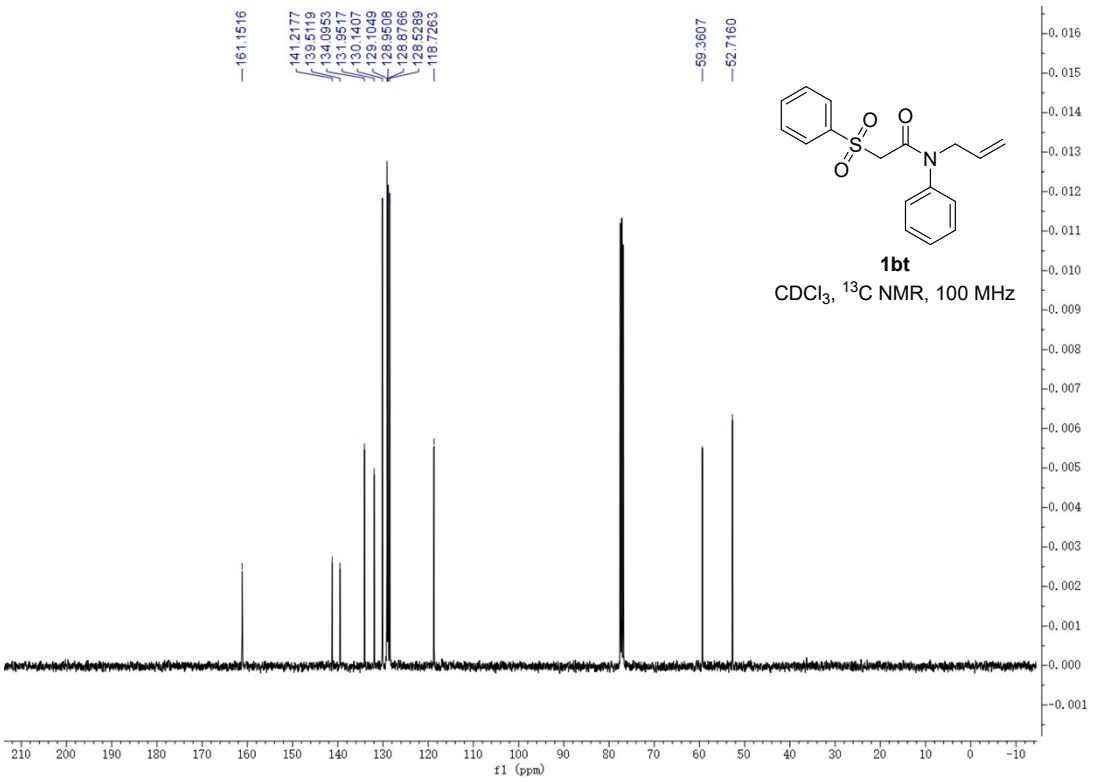
1bn

$CDCl_3$, ^{13}C NMR, 100 MHz



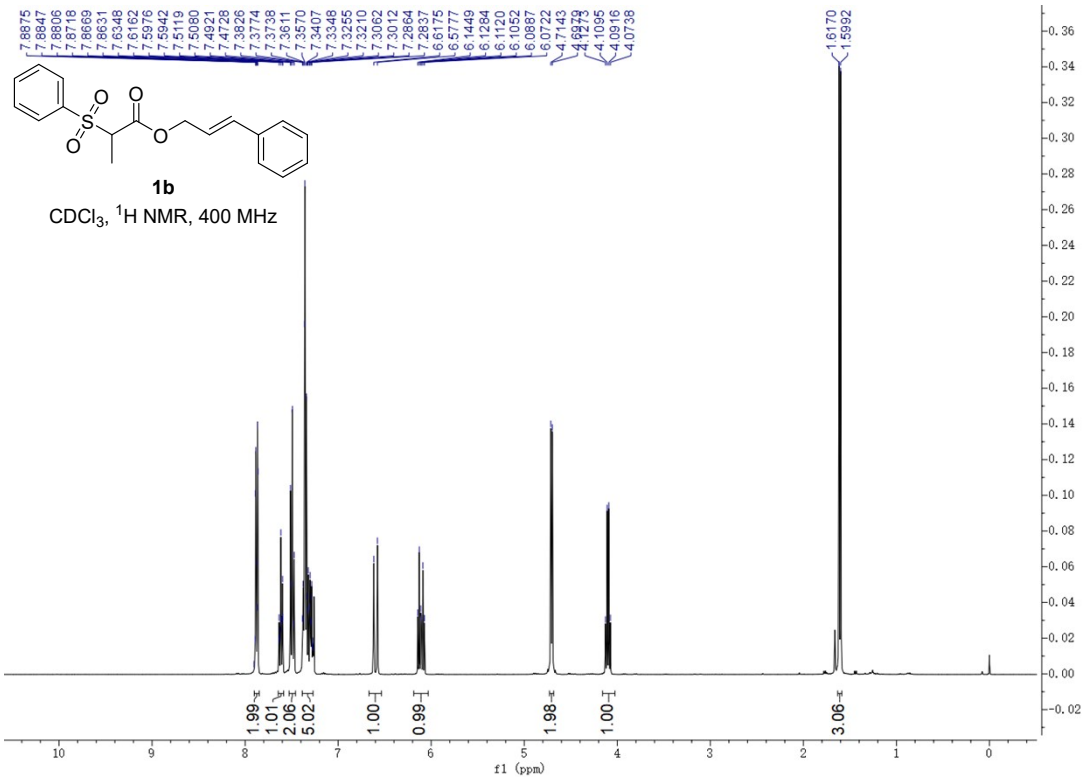
1bt

$CDCl_3$, ^1H NMR, 400 MHz



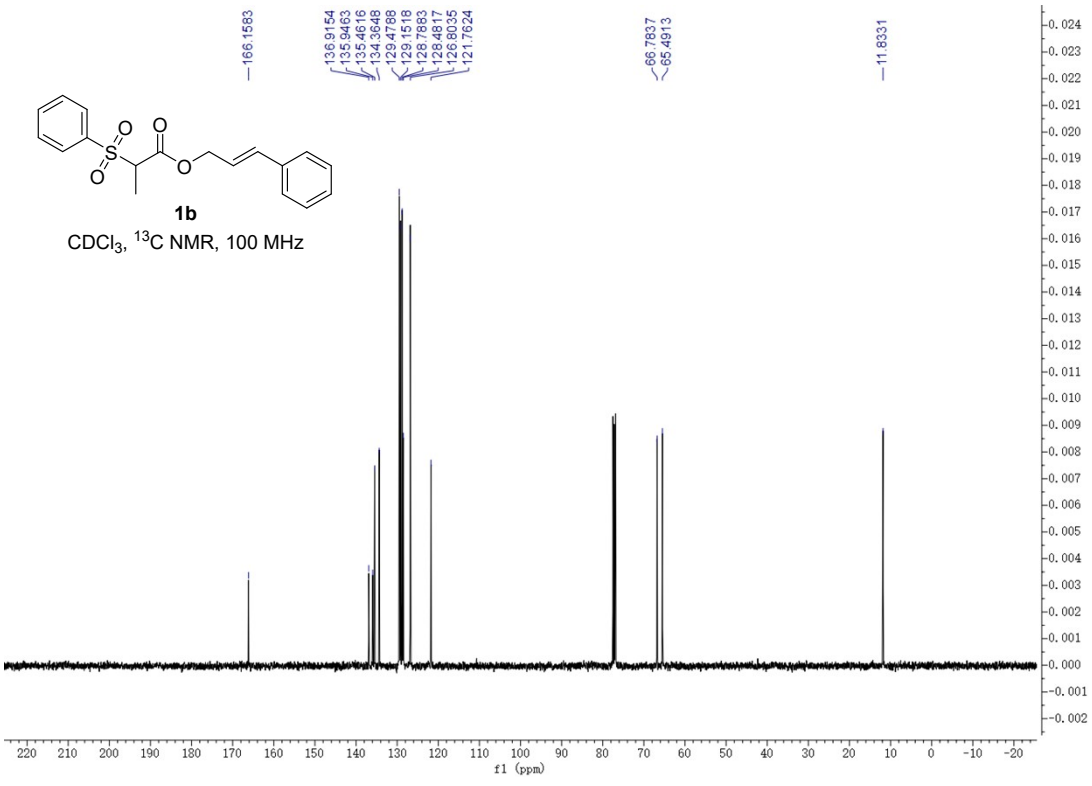
1bt

$CDCl_3$, ^{13}C NMR, 100 MHz



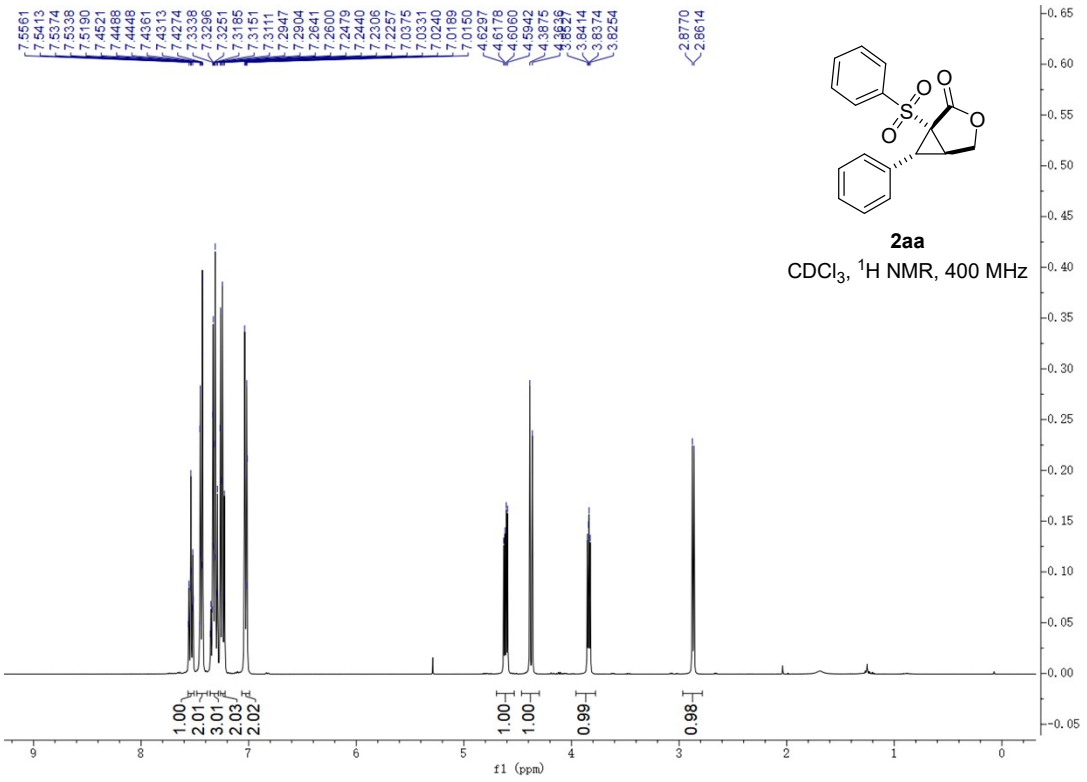
1b

$CDCl_3$, ^1H NMR, 400 MHz



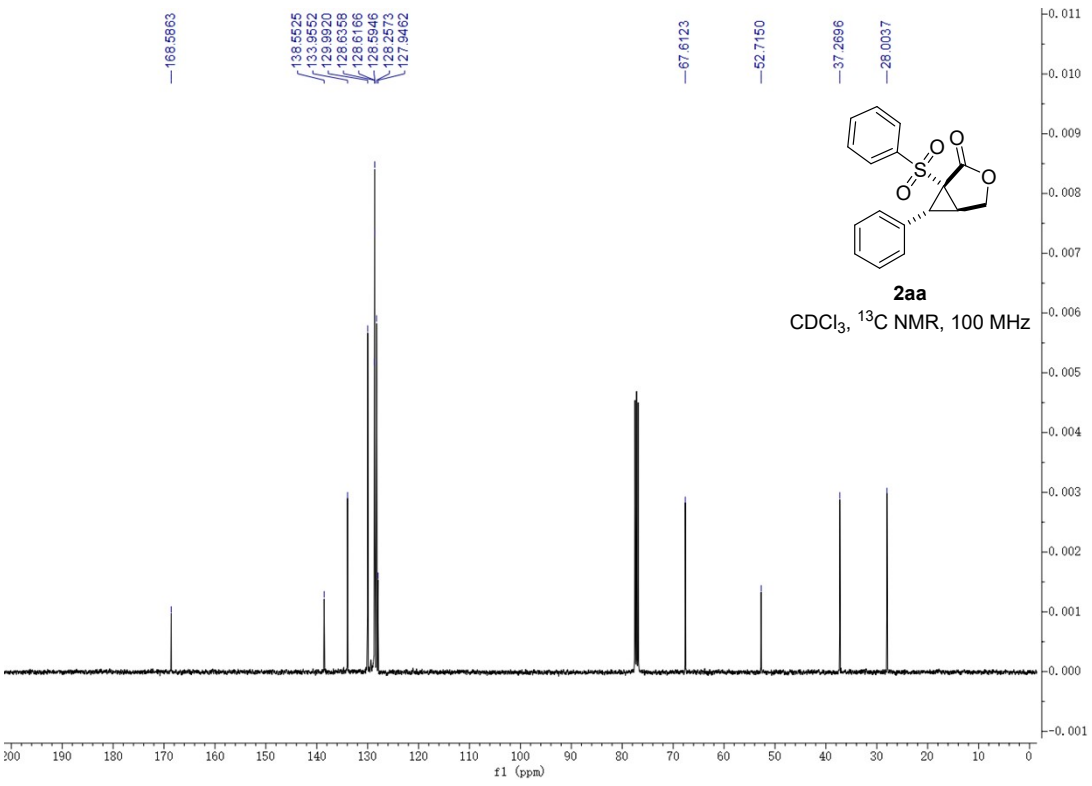
1b

$CDCl_3$, ^{13}C NMR, 100 MHz



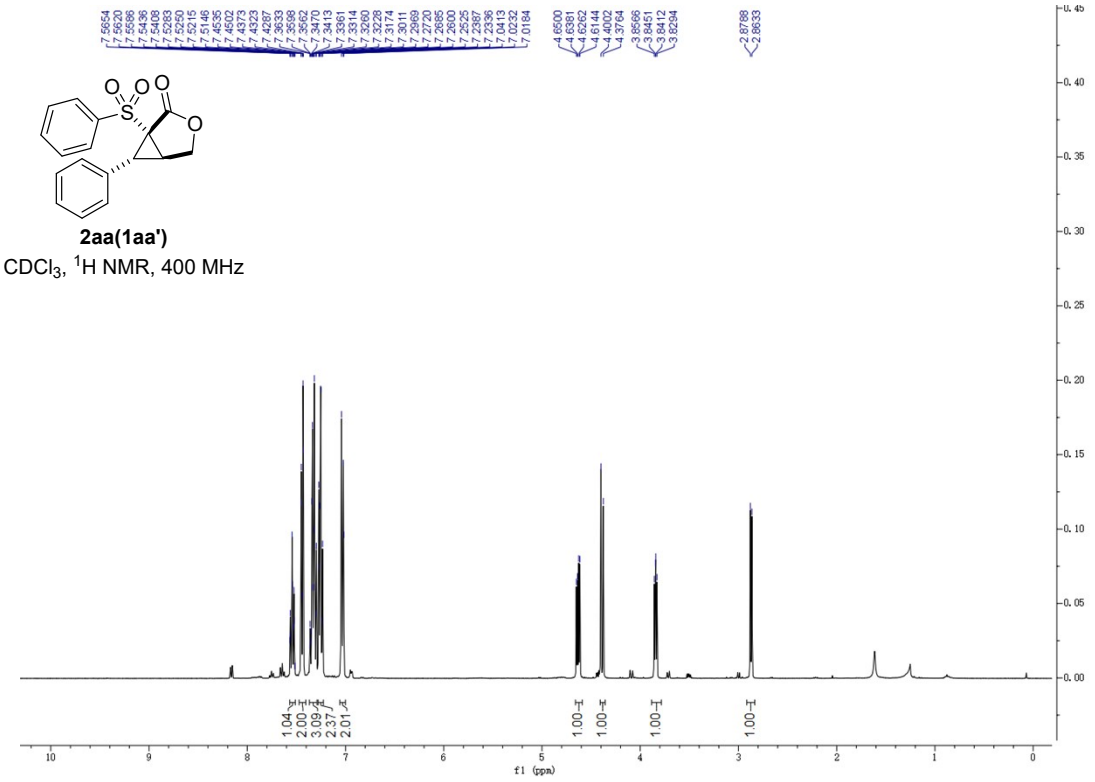
2aa

$CDCl_3$, ^1H NMR, 400 MHz



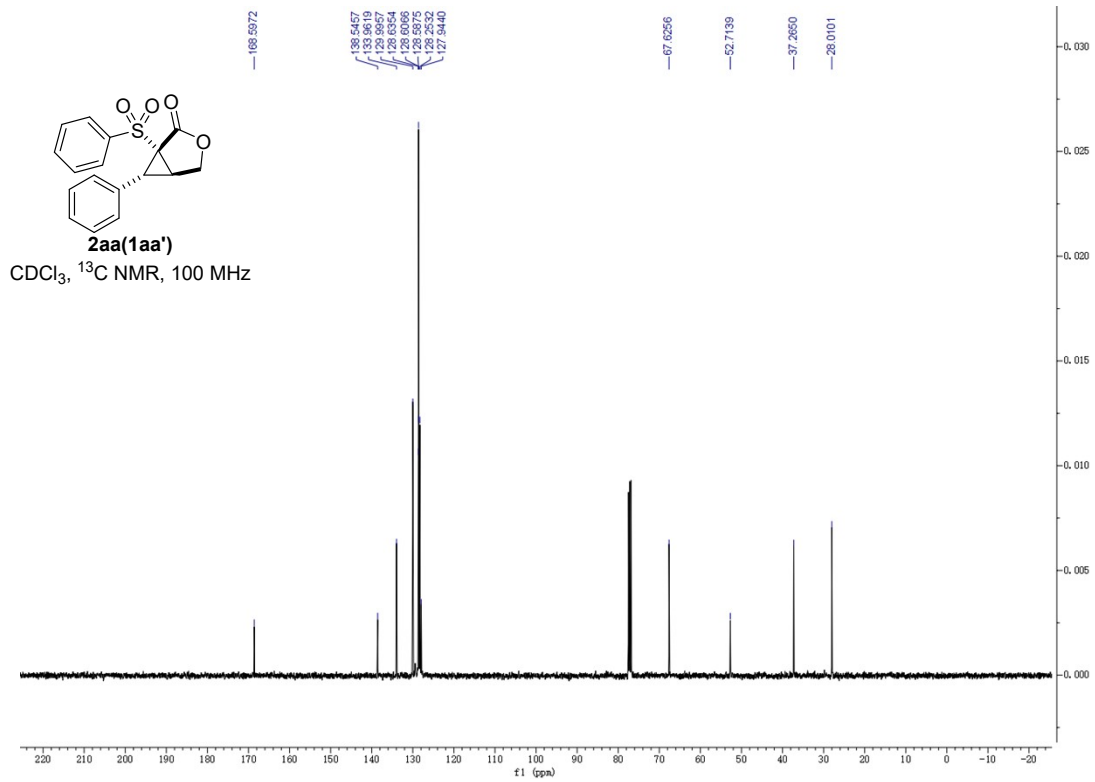
2aa

$CDCl_3$, ^{13}C NMR, 100 MHz



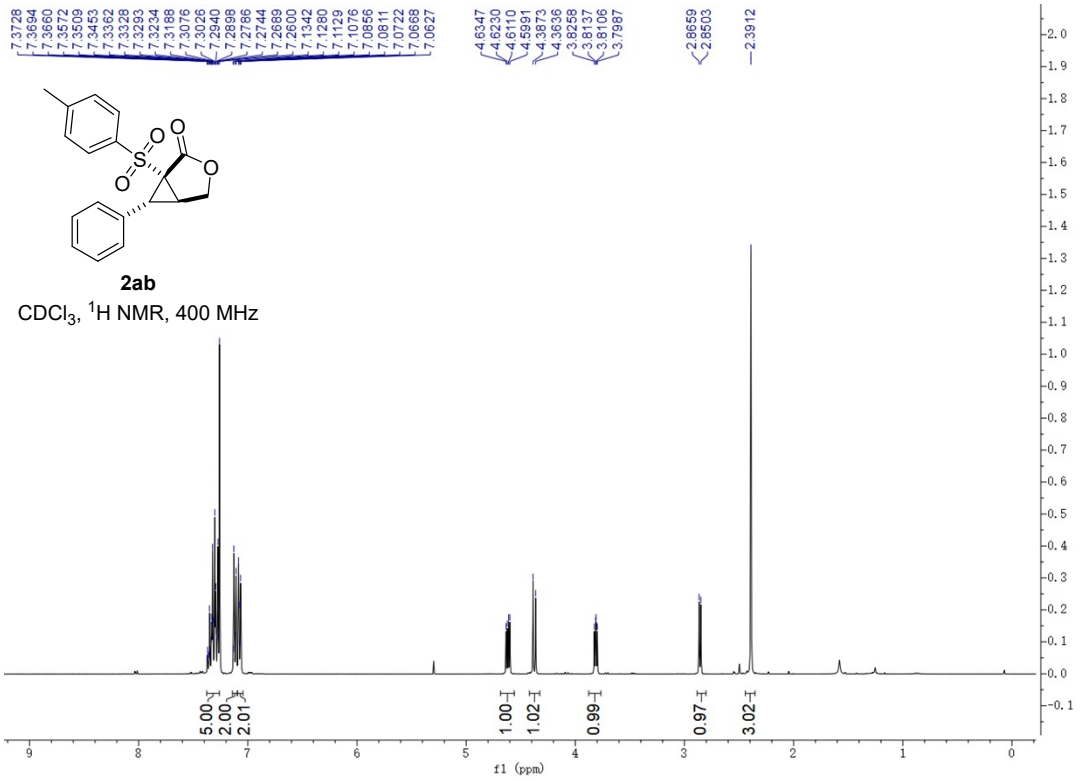
2aa(1aa')

$CDCl_3$, ^1H NMR, 400 MHz



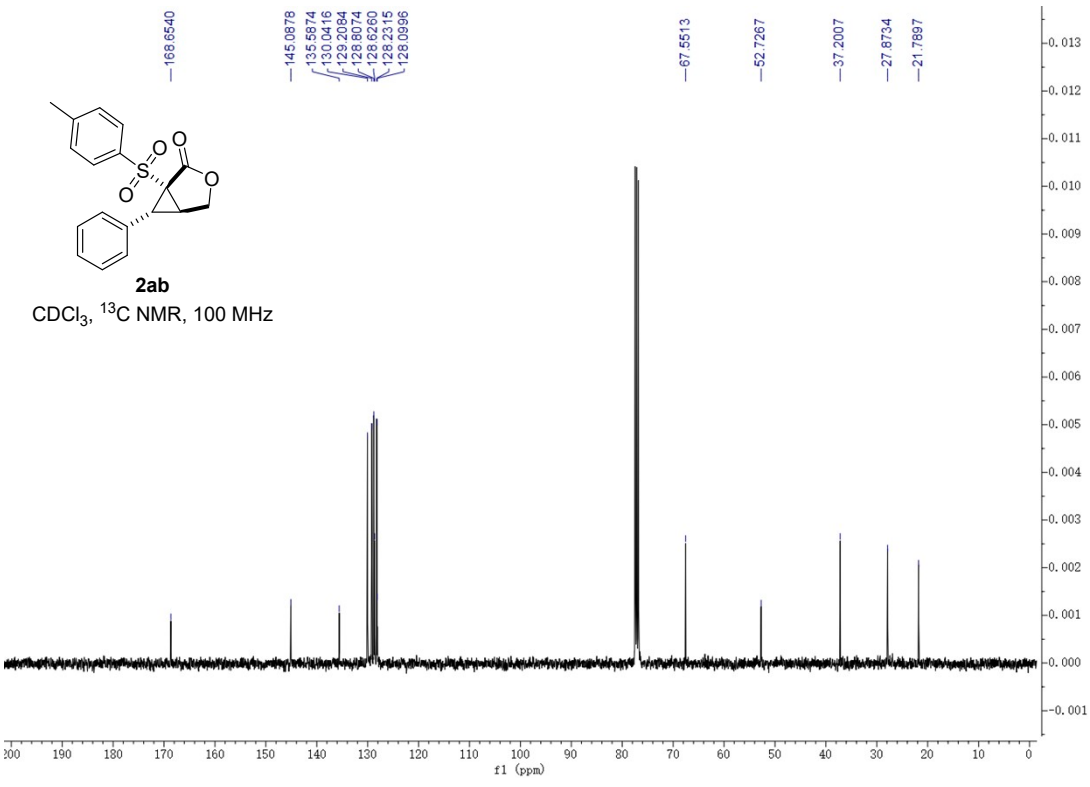
2aa(1aa')

$CDCl_3$, ^{13}C NMR, 100 MHz



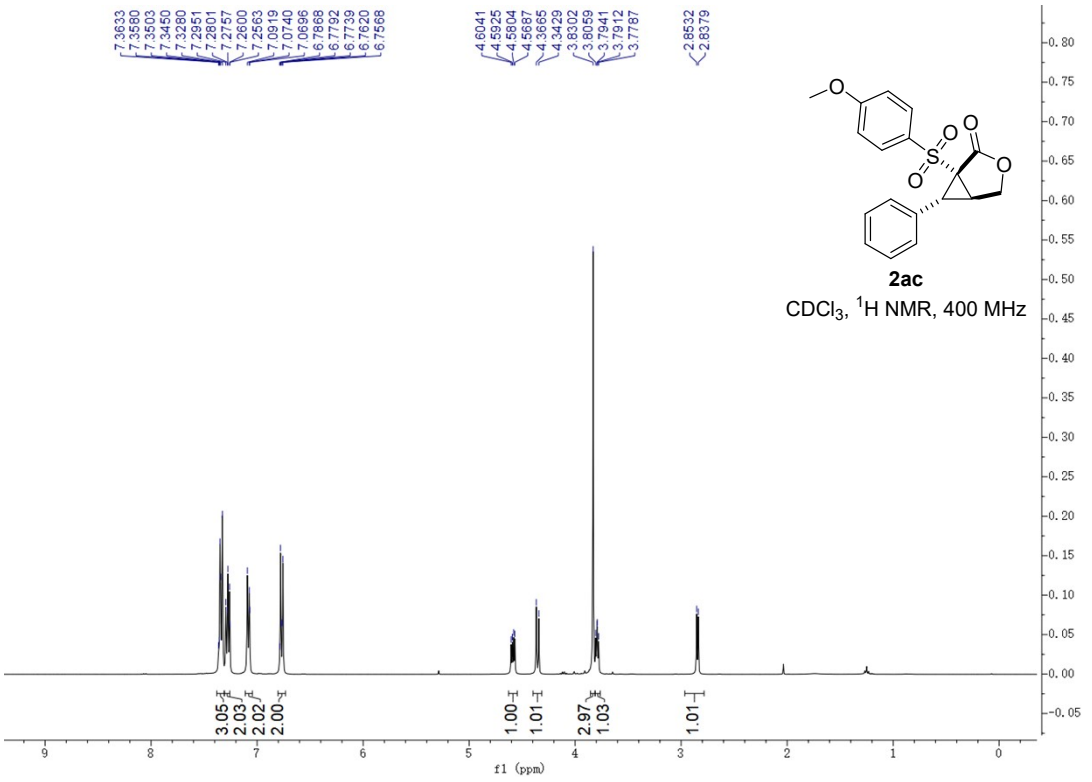
2ab

$CDCl_3$, ^1H NMR, 400 MHz



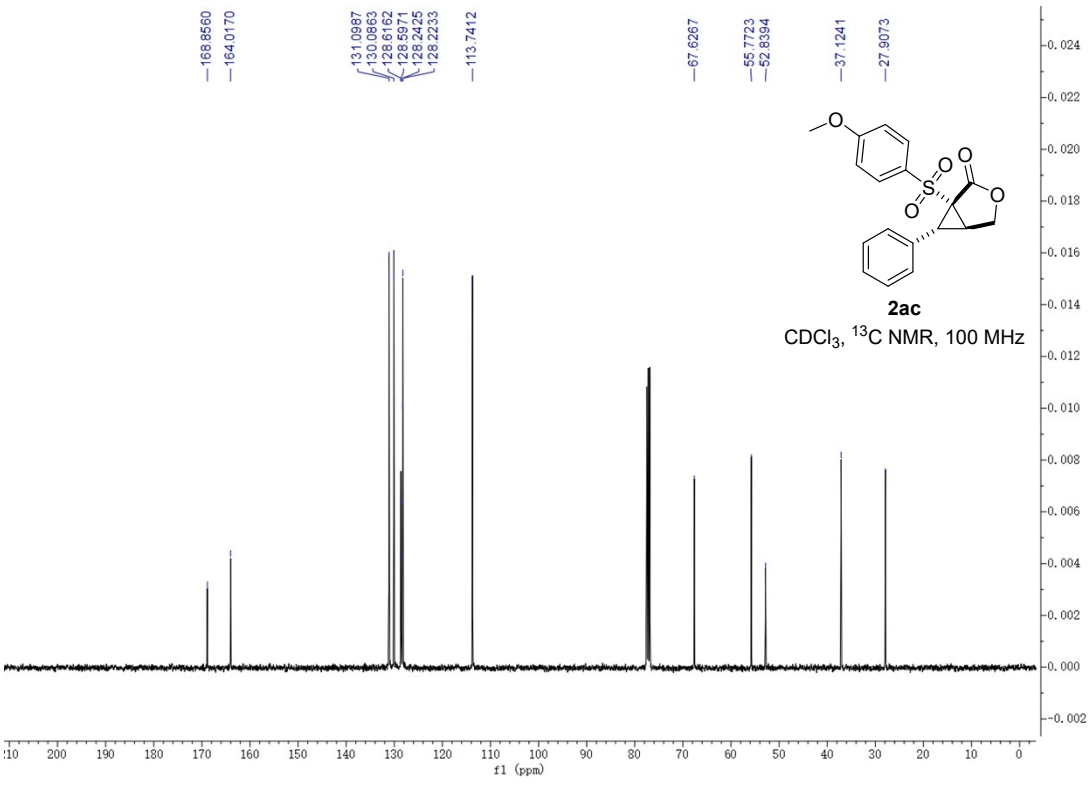
2ab

$CDCl_3$, ^{13}C NMR, 100 MHz



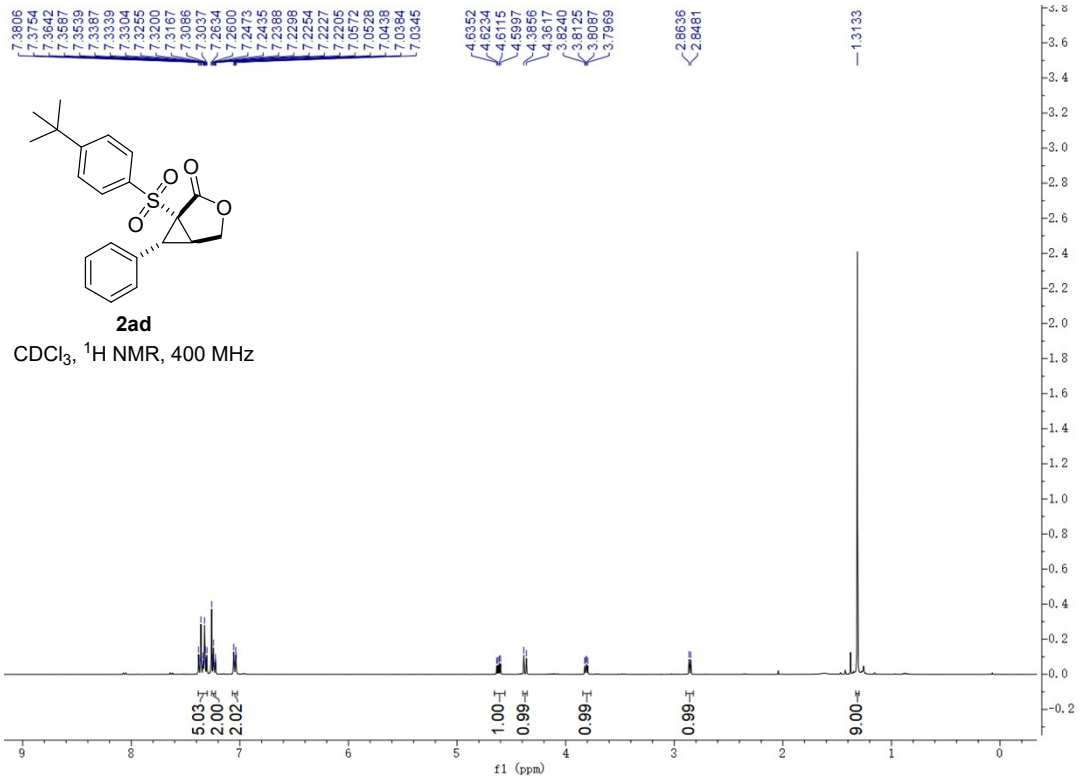
2ac

$CDCl_3$, ^1H NMR, 400 MHz



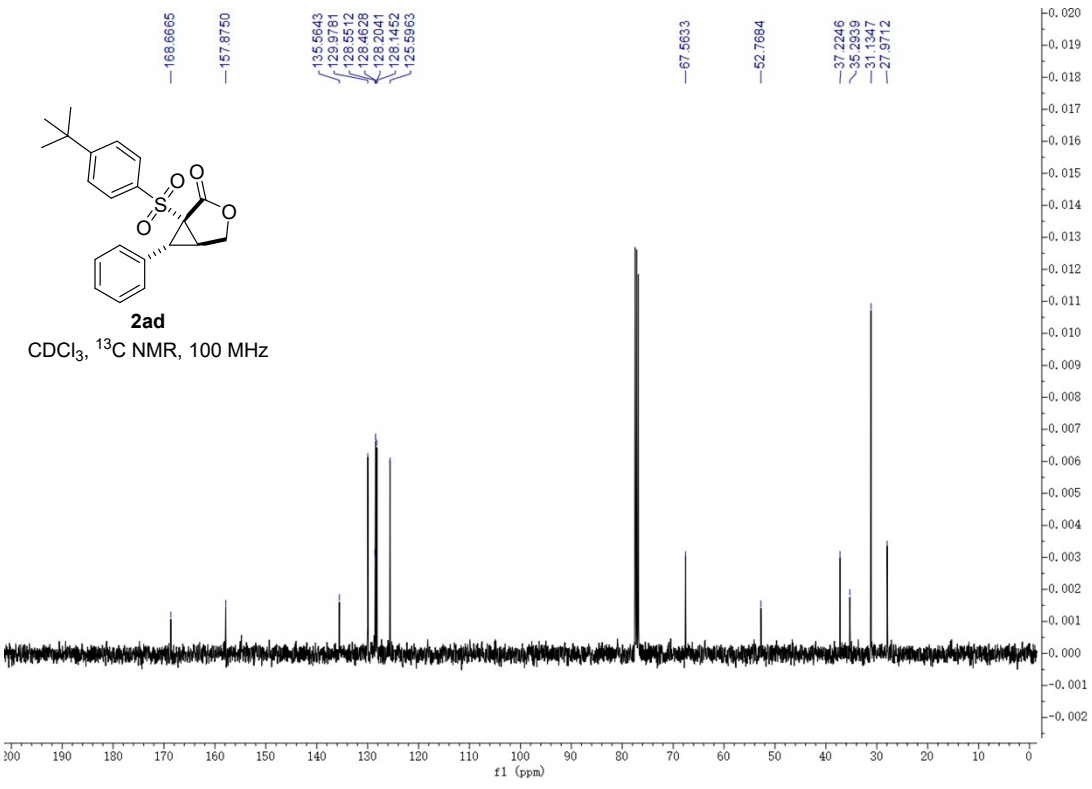
2ac

$CDCl_3$, ^{13}C NMR, 100 MHz



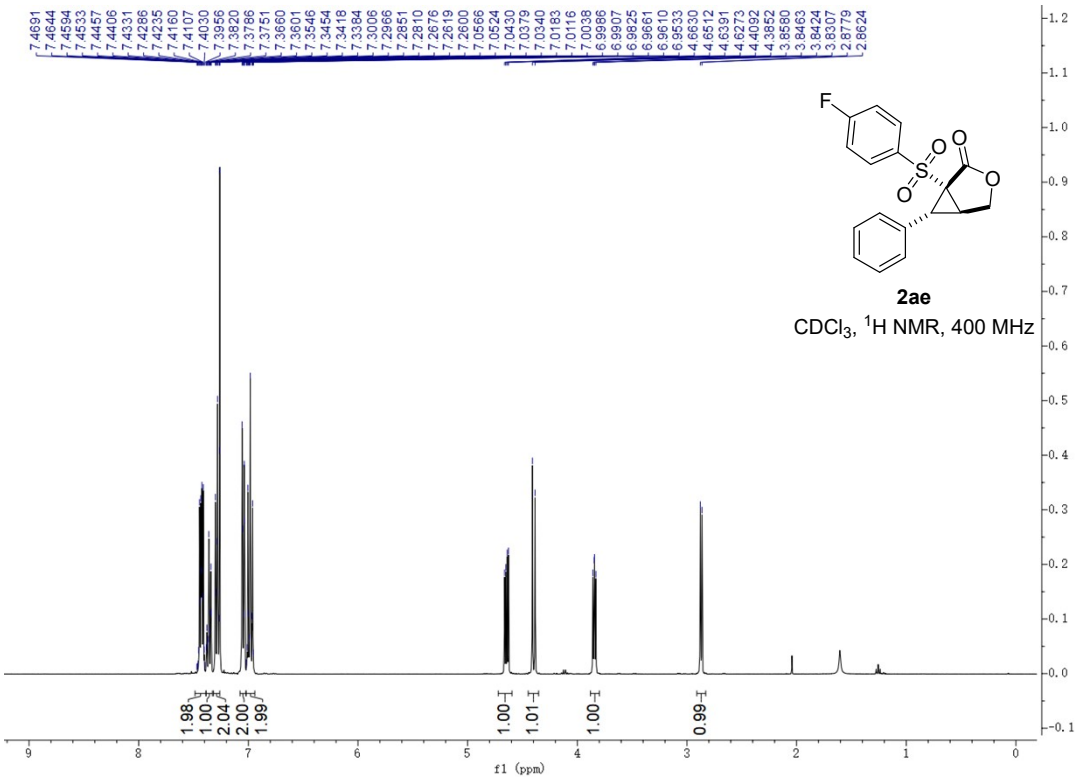
2ad

$CDCl_3$, ^1H NMR, 400 MHz



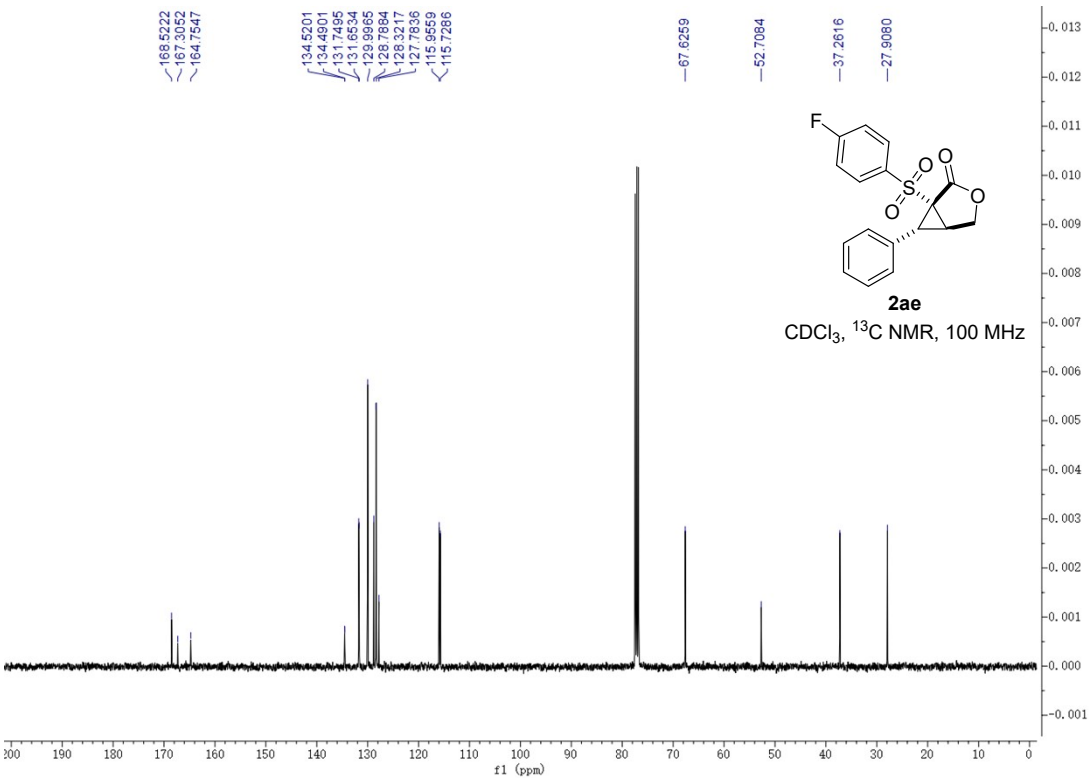
2ad

$CDCl_3$, ^{13}C NMR, 100 MHz



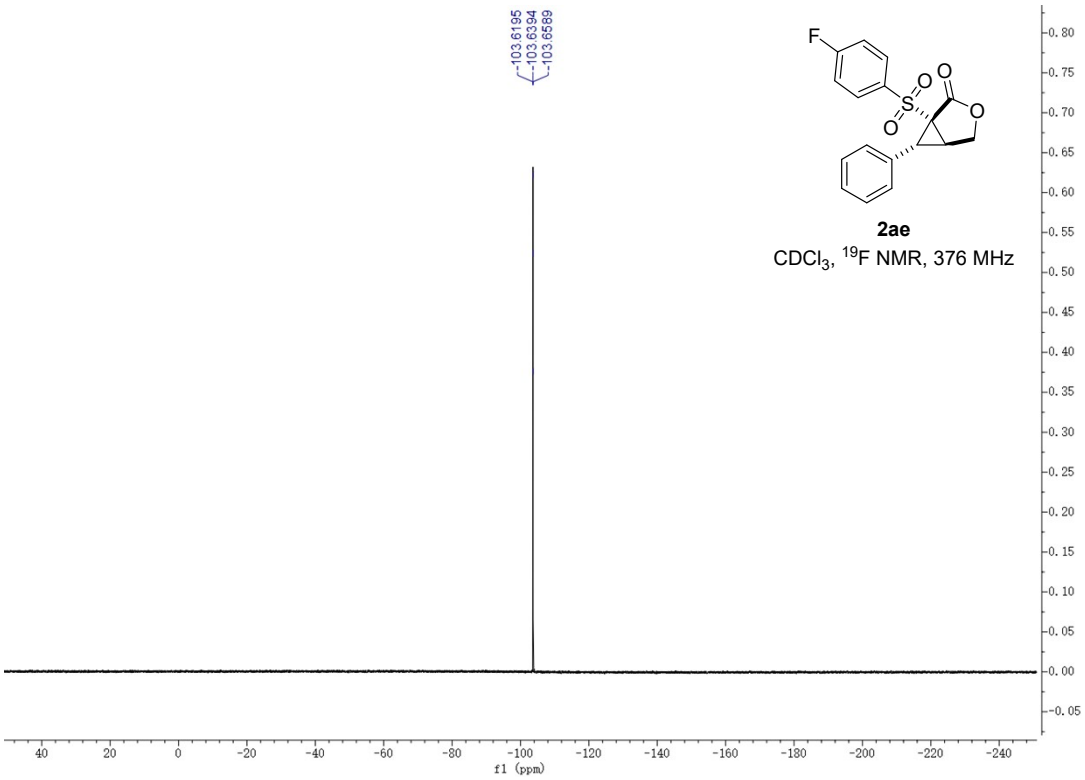
2ae

$CDCl_3$, ^1H NMR, 400 MHz



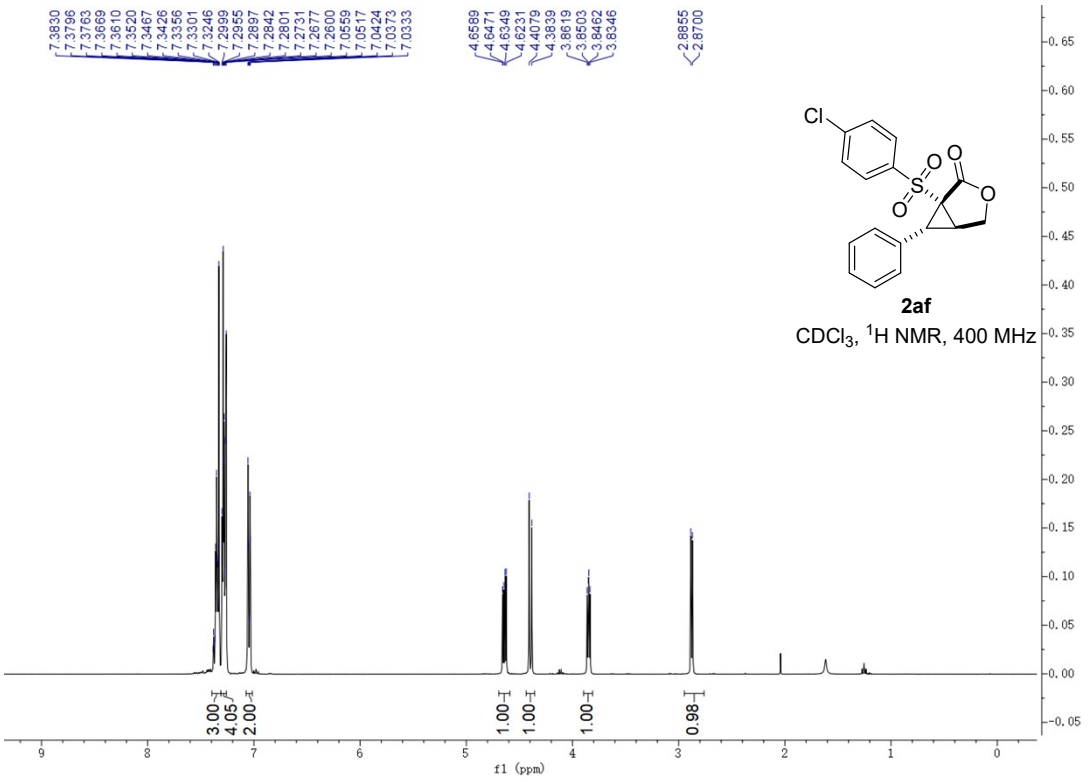
2ae

$CDCl_3$, ^{13}C NMR, 100 MHz



2ae

$CDCl_3$, ^{19}F NMR, 376 MHz


7.3830
7.3796
7.3763
7.3669
7.3610
7.3520
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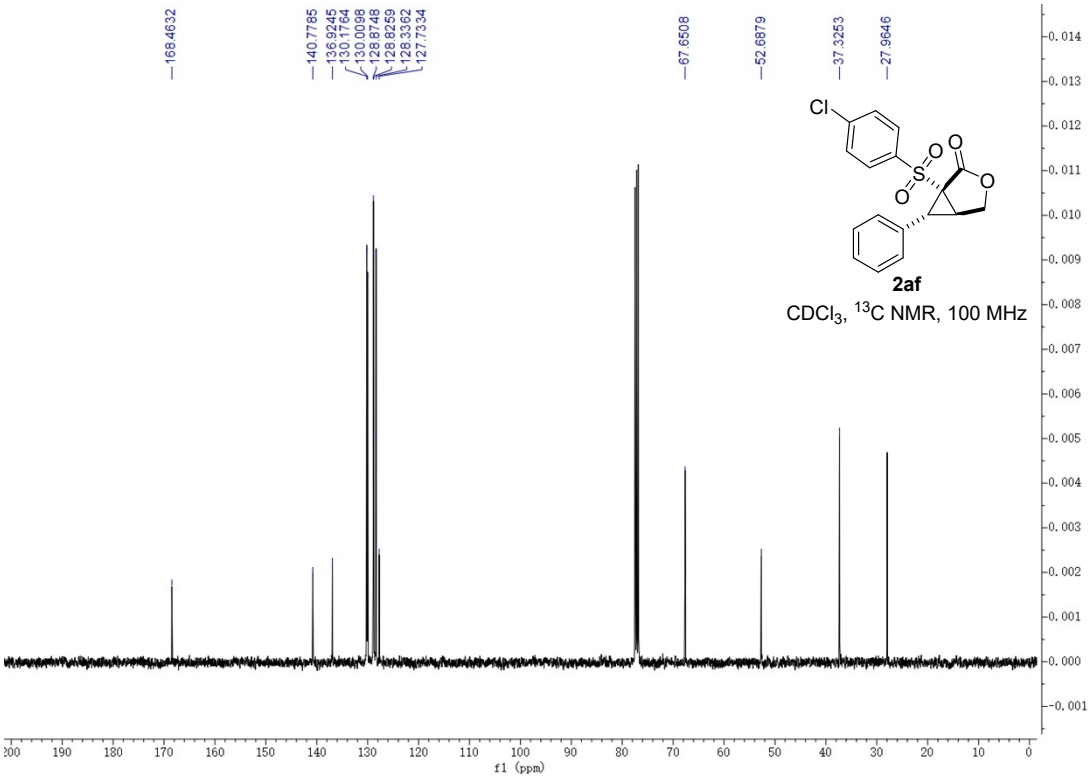
7.3356
7.3301
7.3246
7.2999
7.2955
7.2897
7.2842
7.2801
7.2731
7.2677
7.2600
7.0559
7.0517
7.0424
7.0373
7.0333
4.6589
4.6471
4.6349
4.6231
4.4079
4.3839
3.8619
3.8503
3.8462
3.8346
2.8855
2.8700
Cl
O
S
O
O
O
2af
CDCl3, 1H NMR, 400 MHz
3.00
4.05
2.00
1.00
1.00
1.00
0.98
f1 (ppm)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127.7334
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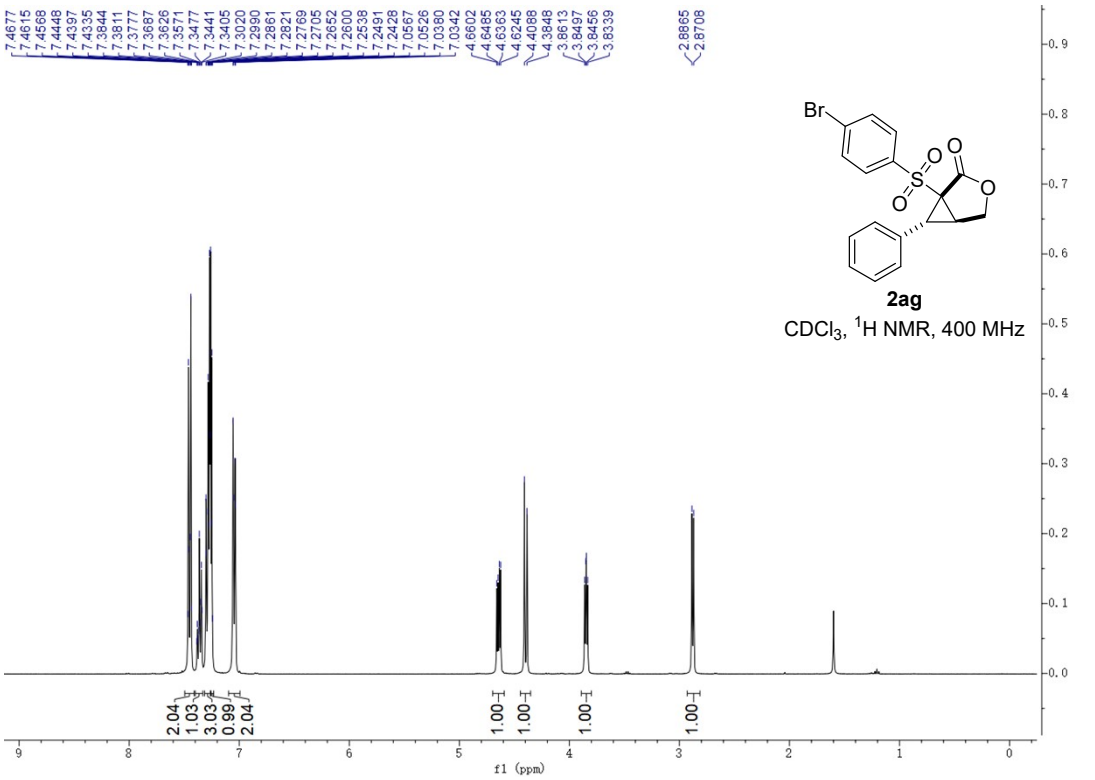
27.9646
Cl
O
S
O
O
O
2af
CDCl3, 13C NMR, 100 MHz
f1 (ppm)



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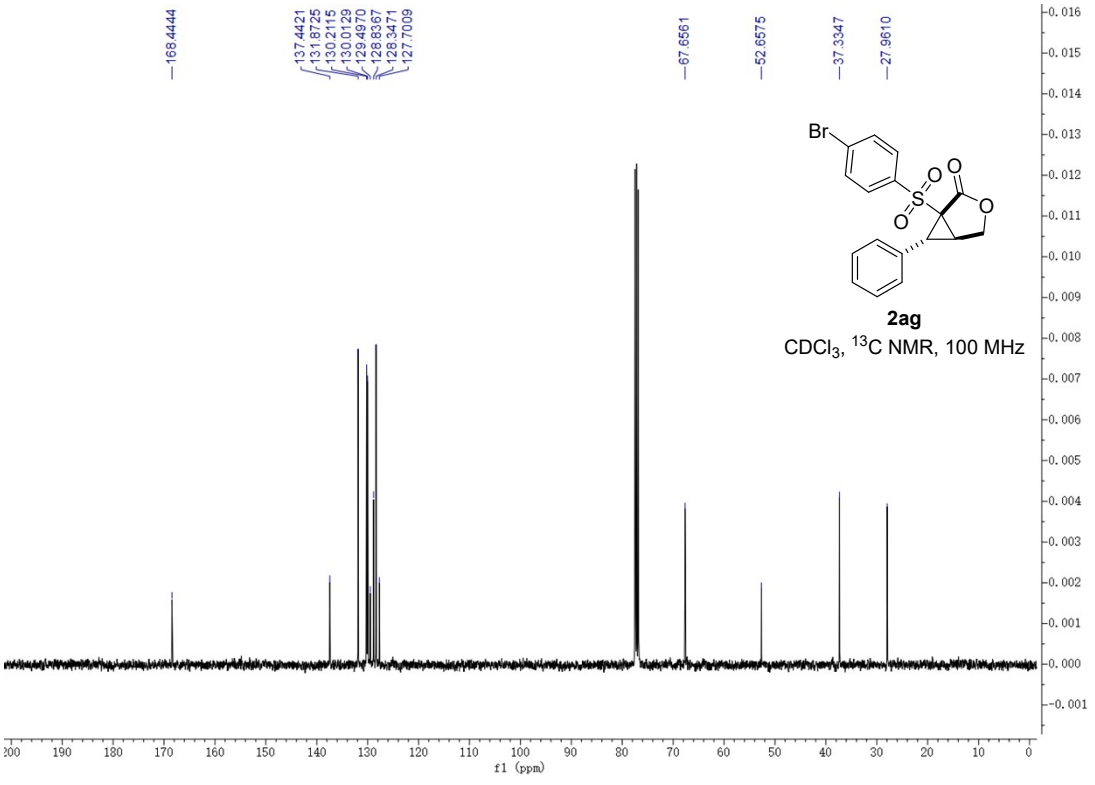
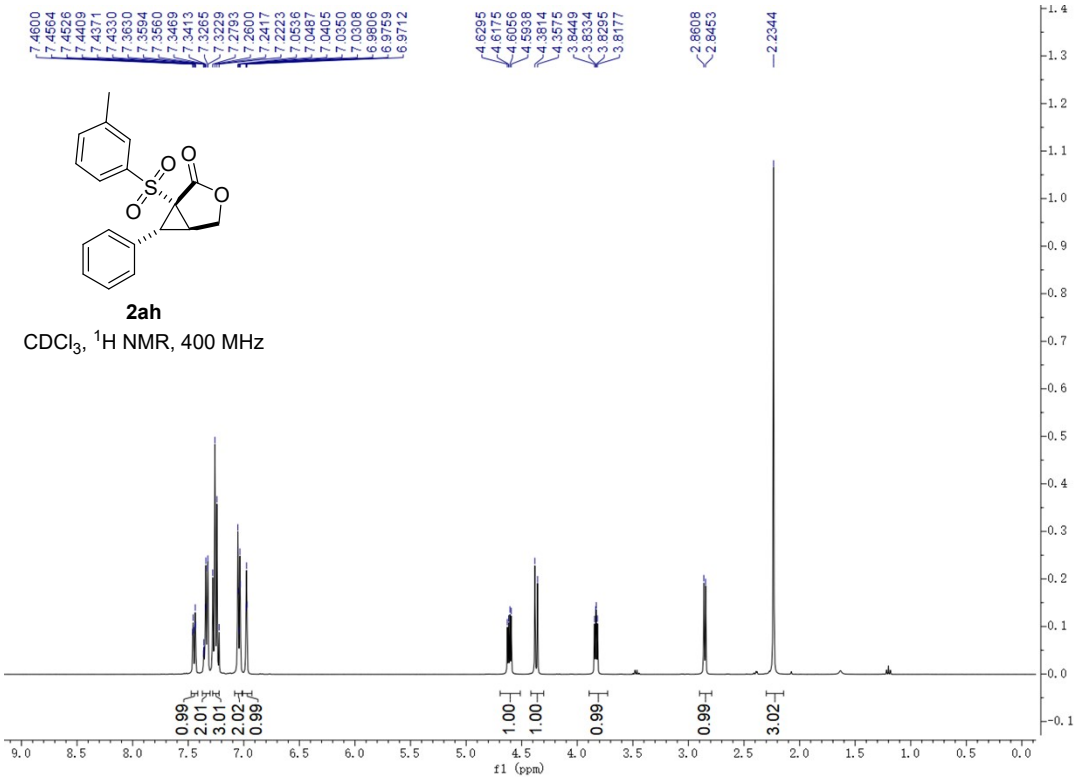
$CDCl_3$, ^1H NMR, 400 MHz



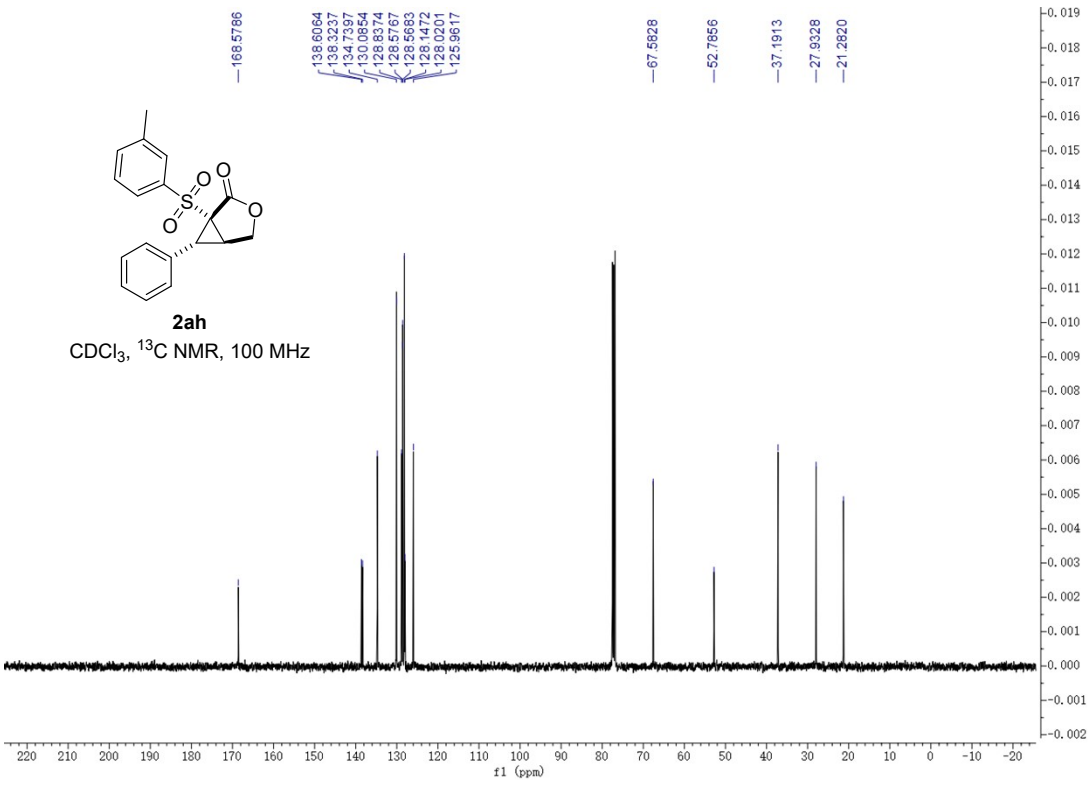
2ag

$CDCl_3$, ^{13}C NMR, 100 MHz



2ah

$CDCl_3$, ^1H NMR, 400 MHz



2ah

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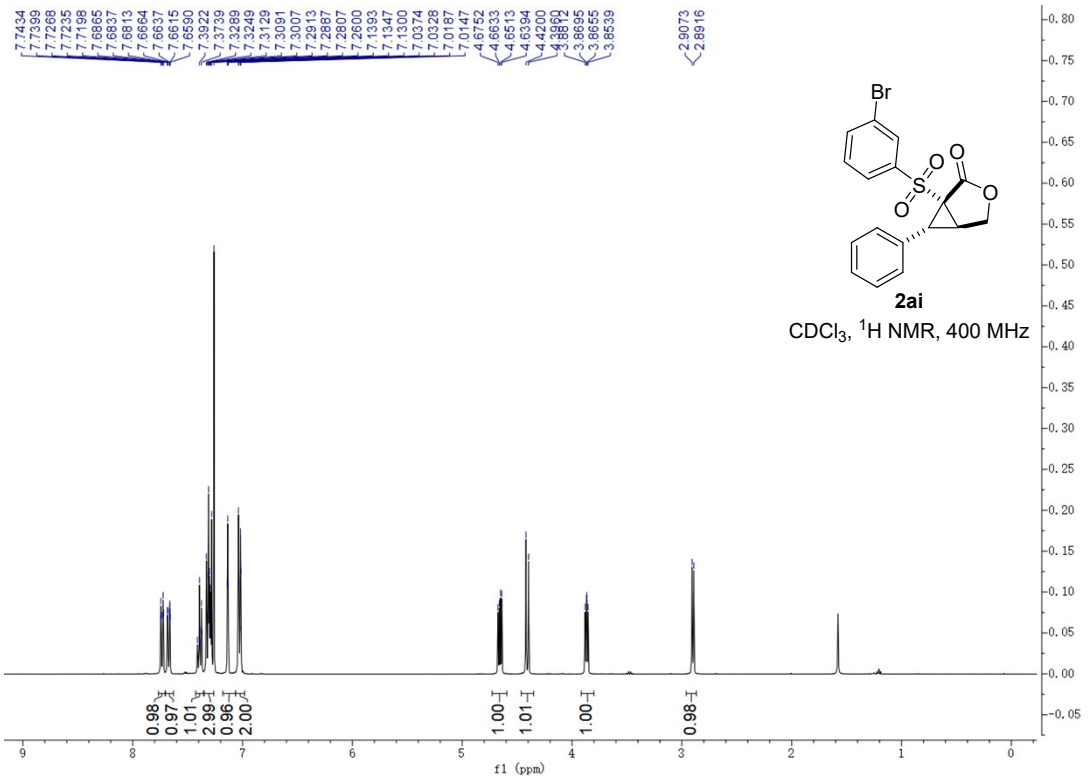
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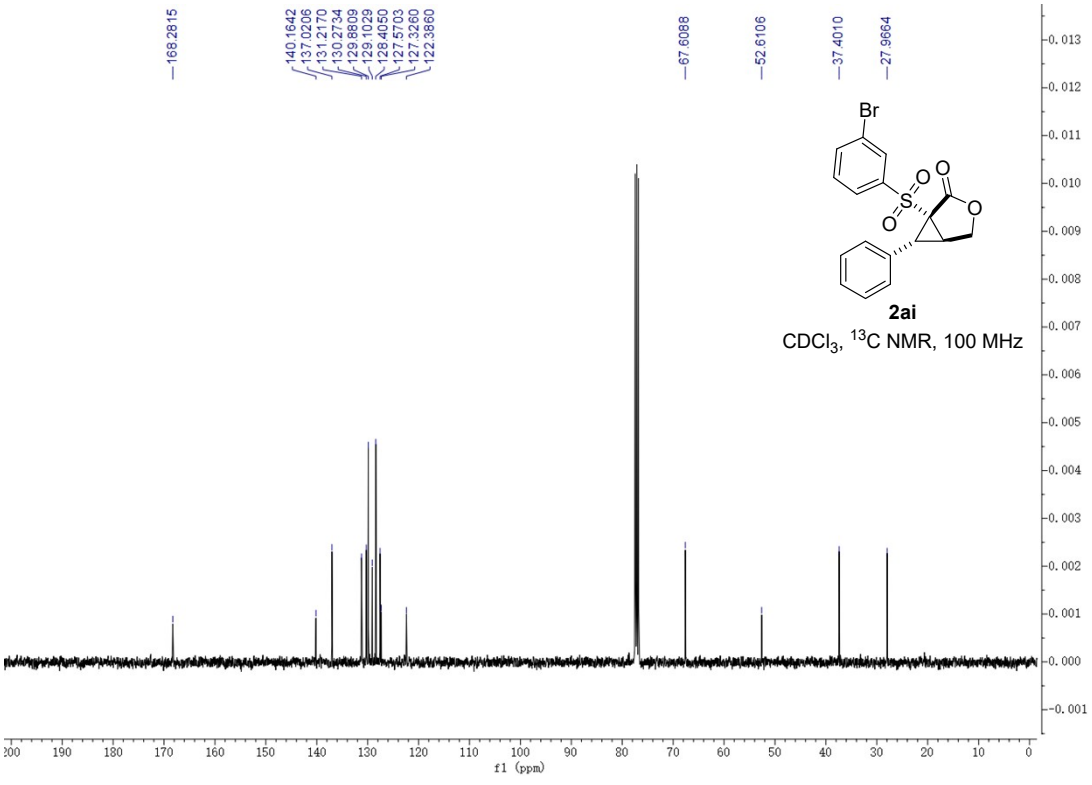
7.6664
7.6637
7.6615
7.6590
7.3922
7.3739
7.3289
7.3249
7.3129
7.3091
7.3007
7.2913
7.2887
7.2807
7.2600
7.1393
7.1347
7.1300
7.0374
7.0328
7.0187
7.0147
4.6752
4.6633
4.6513
4.6394
4.4200
3.8812
3.8695
3.8655
3.8539
2.9073
2.8916
0.98
0.97
1.01
2.99
0.96
2.00
1.00
1.01
1.00
0.98
f1 (ppm)
Br
O
S
O
O
O
2ai
CDCl3, 1H NMR, 400 MHz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67.6088
52.6106
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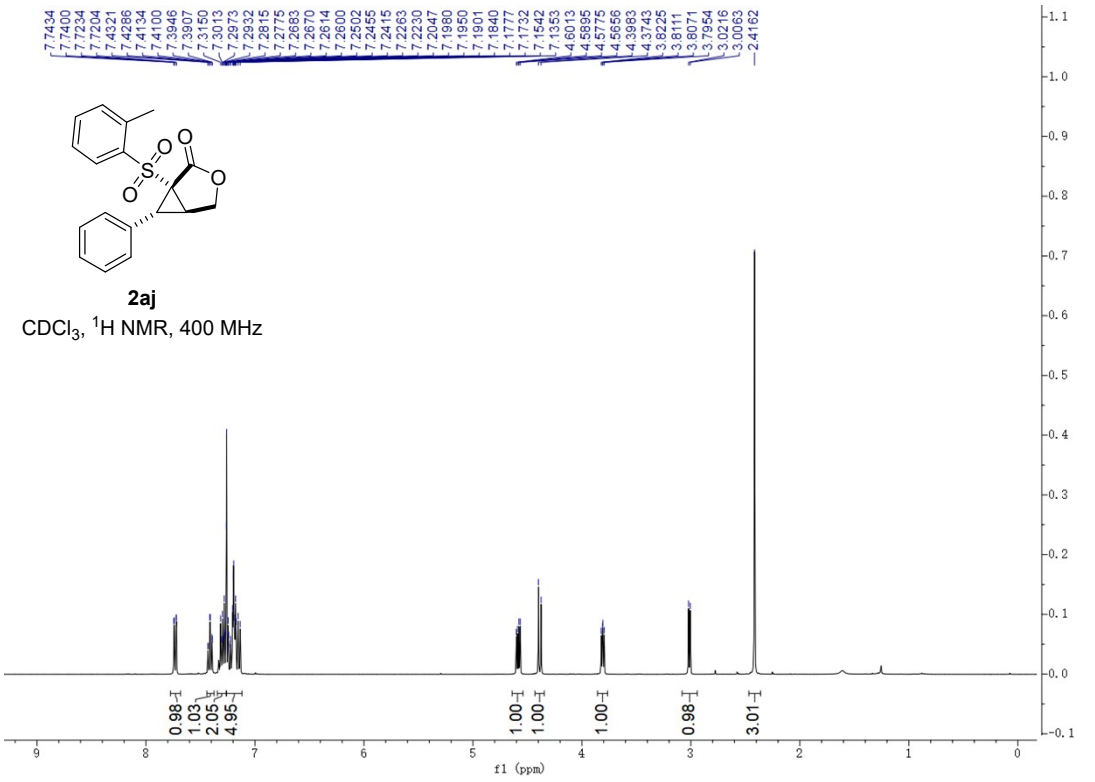
27.9664
f1 (ppm)
Br
O
S
O
O
O
2ai
CDCl3, 13C NMR, 100 MHz



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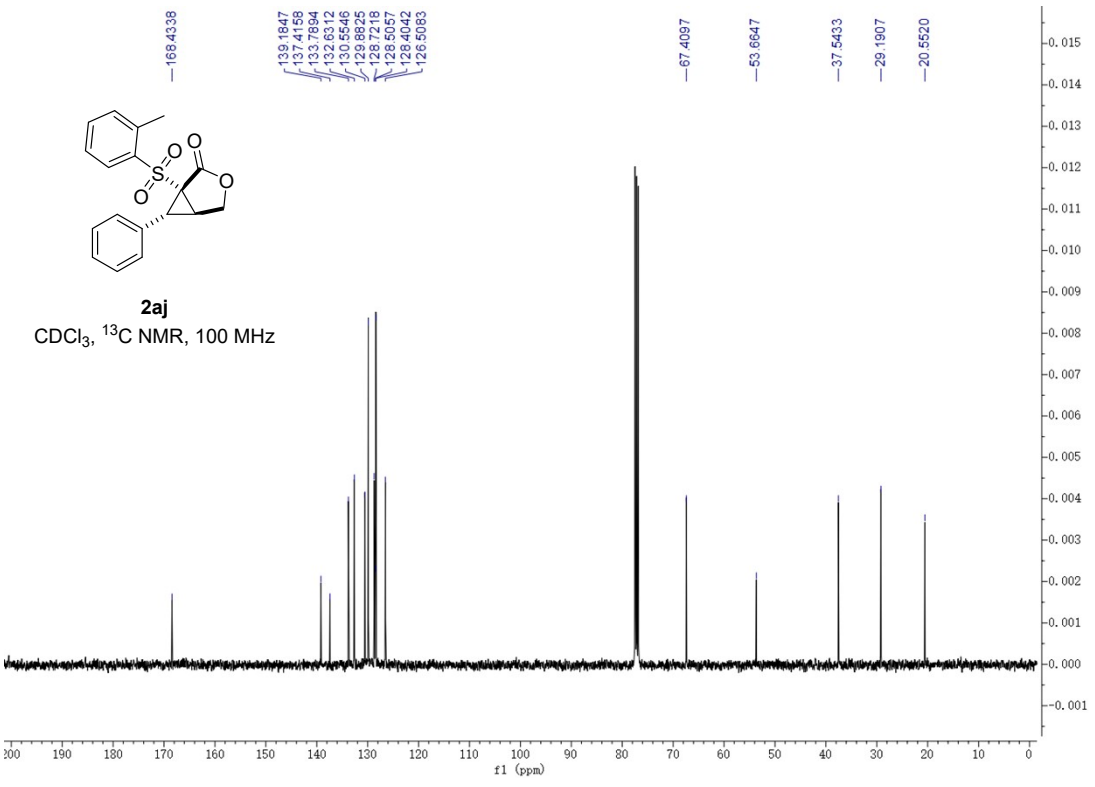
$CDCl_3$, ^1H NMR, 400 MHz



2aj

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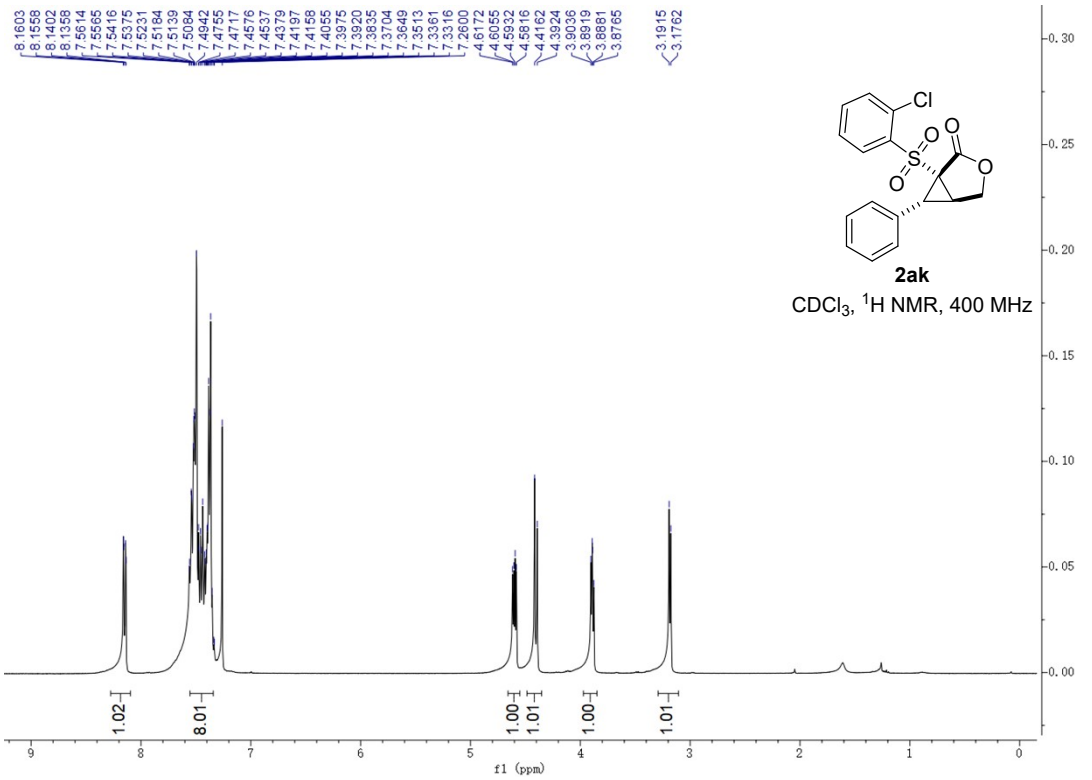
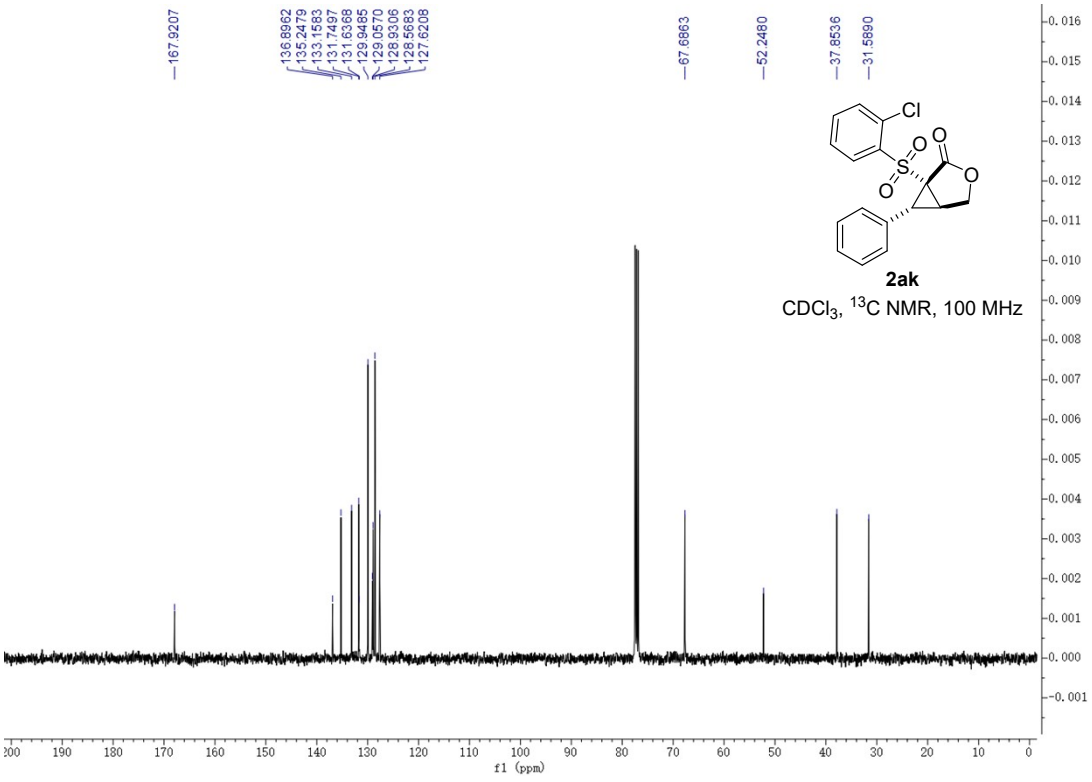


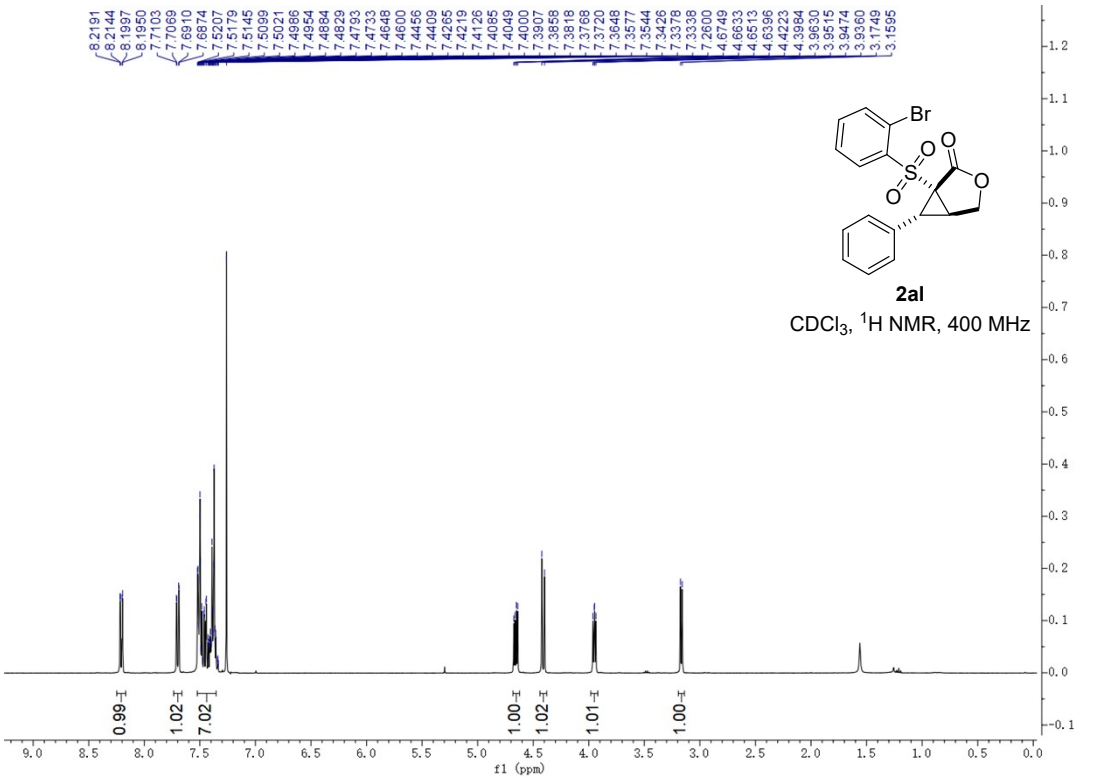
2ak

$CDCl_3$, ^1H NMR, 400 MHz



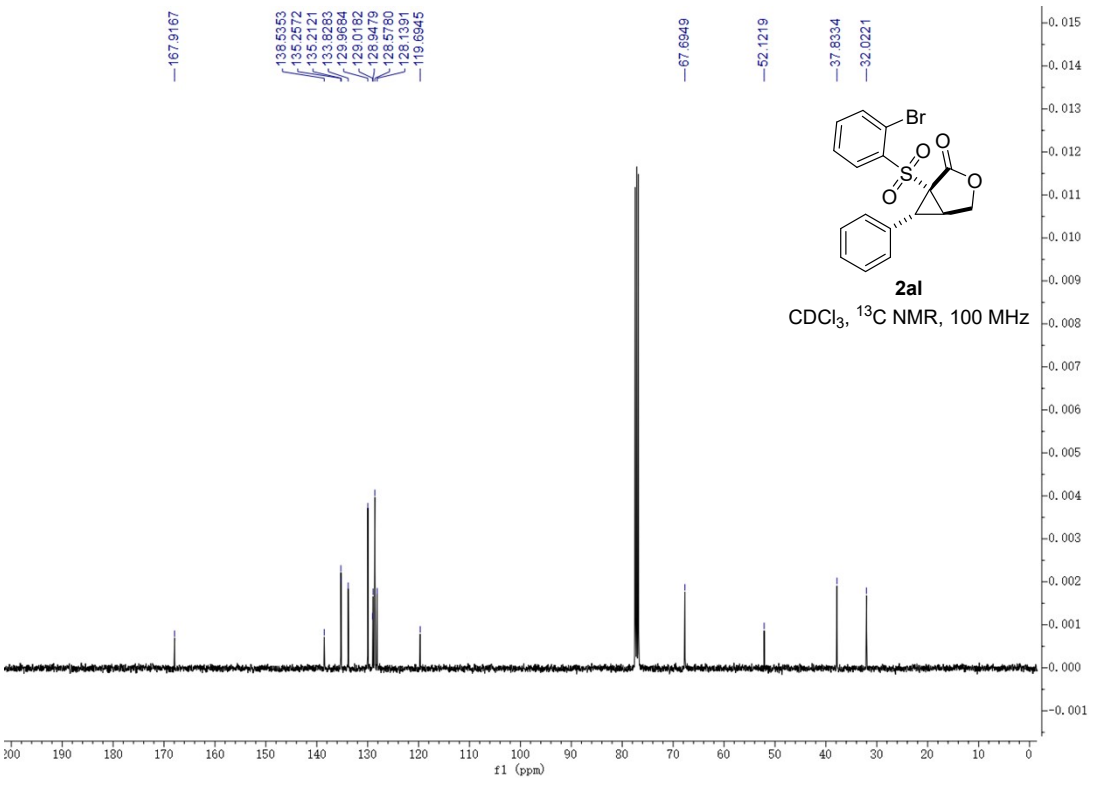
2ak

$CDCl_3$, ^{13}C NMR, 100 MHz



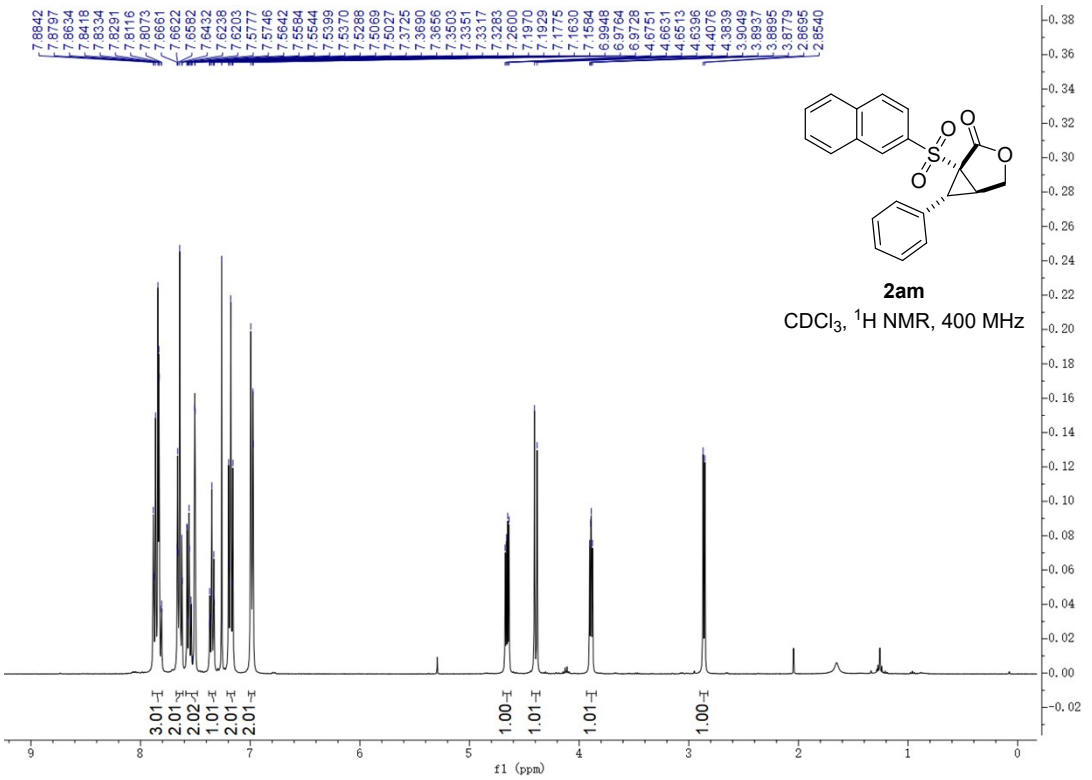
2al

$CDCl_3$, ^1H NMR, 400 MHz



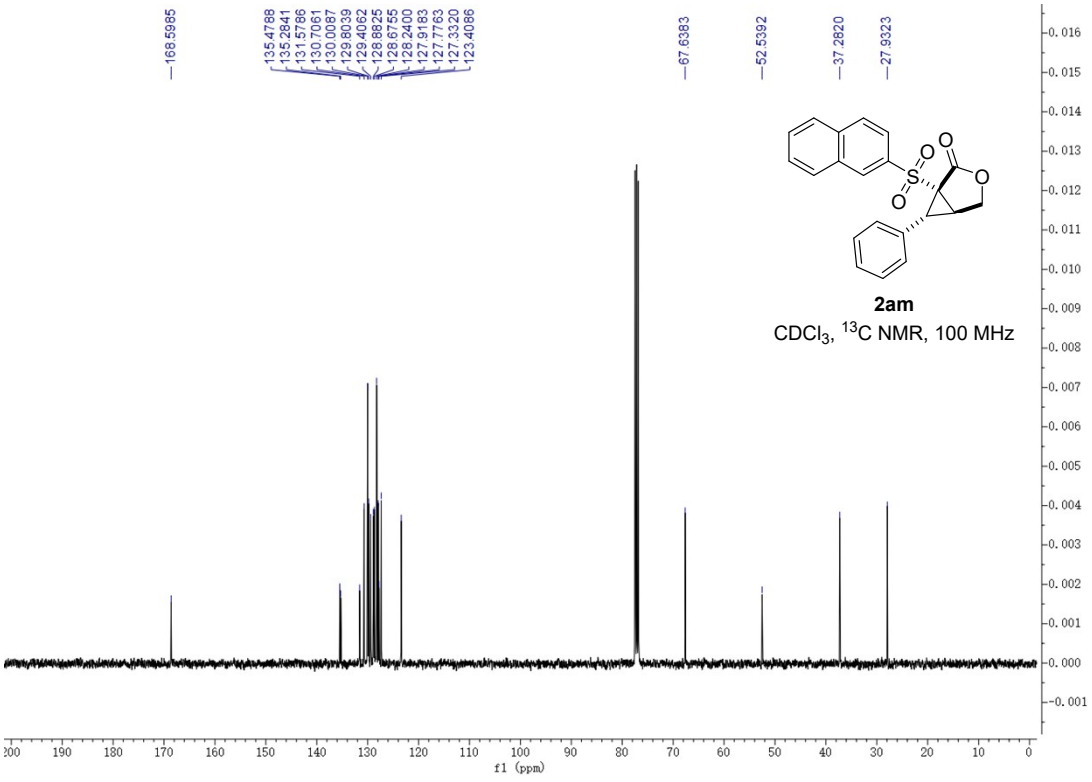
2al

$CDCl_3$, ^{13}C NMR, 100 MHz



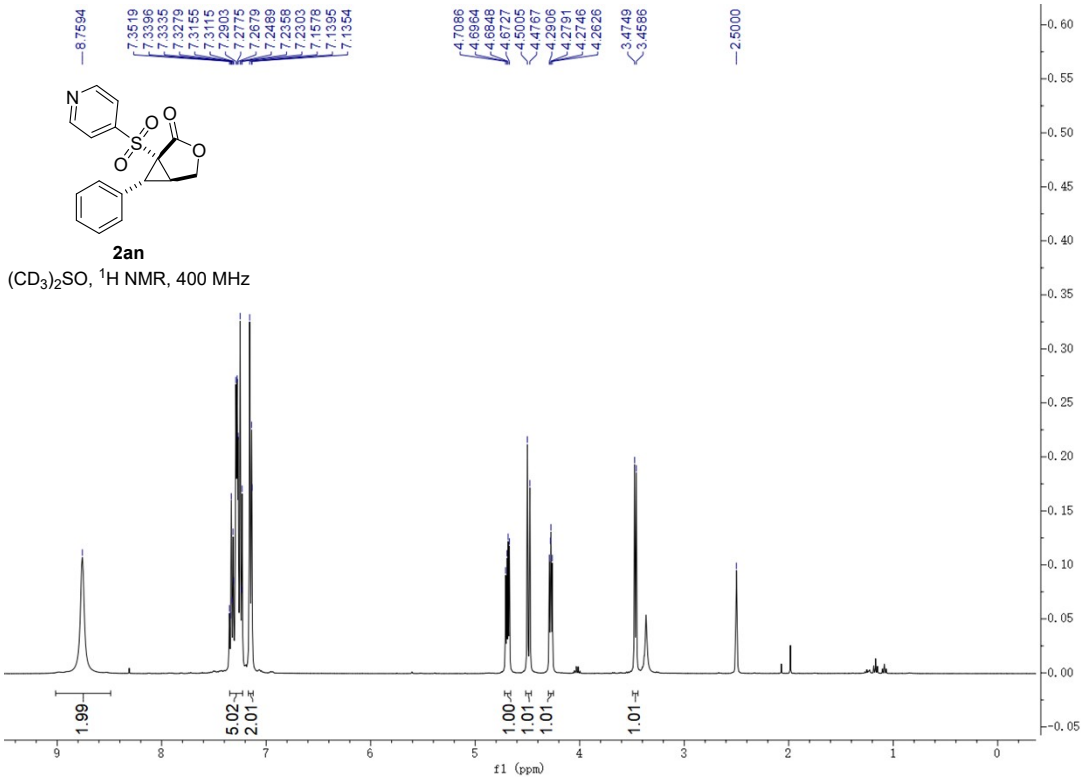
2am

$CDCl_3$, ^1H NMR, 400 MHz



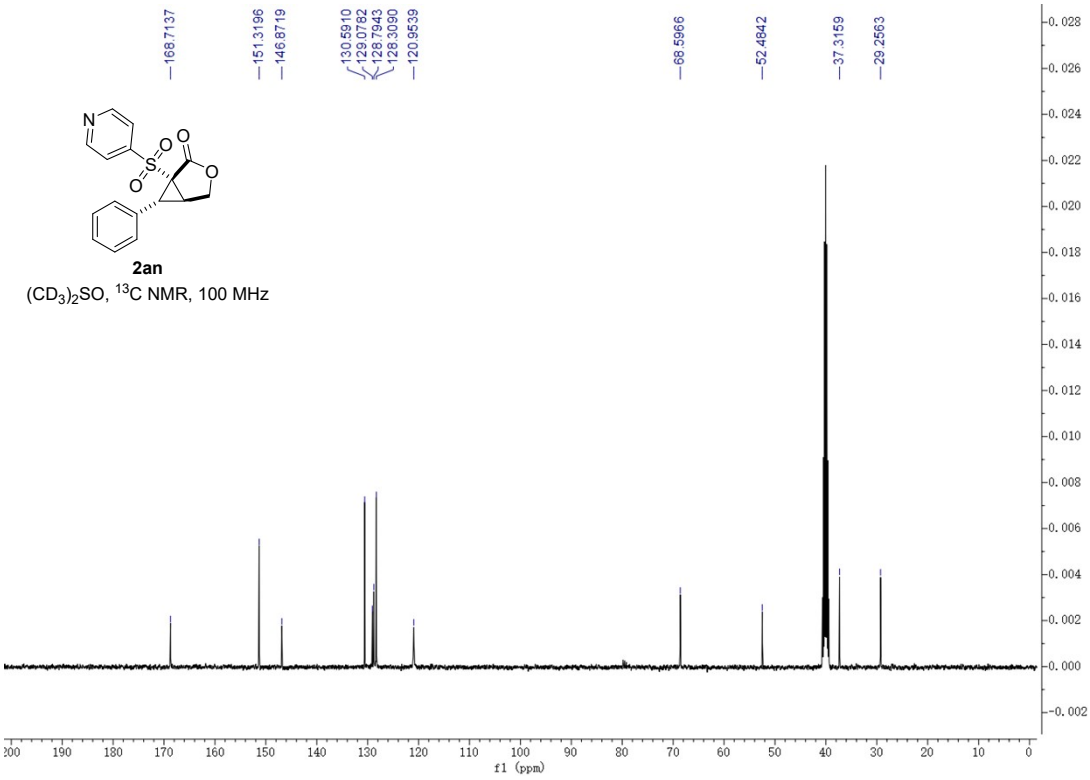
2am

$CDCl_3$, ^{13}C NMR, 100 MHz



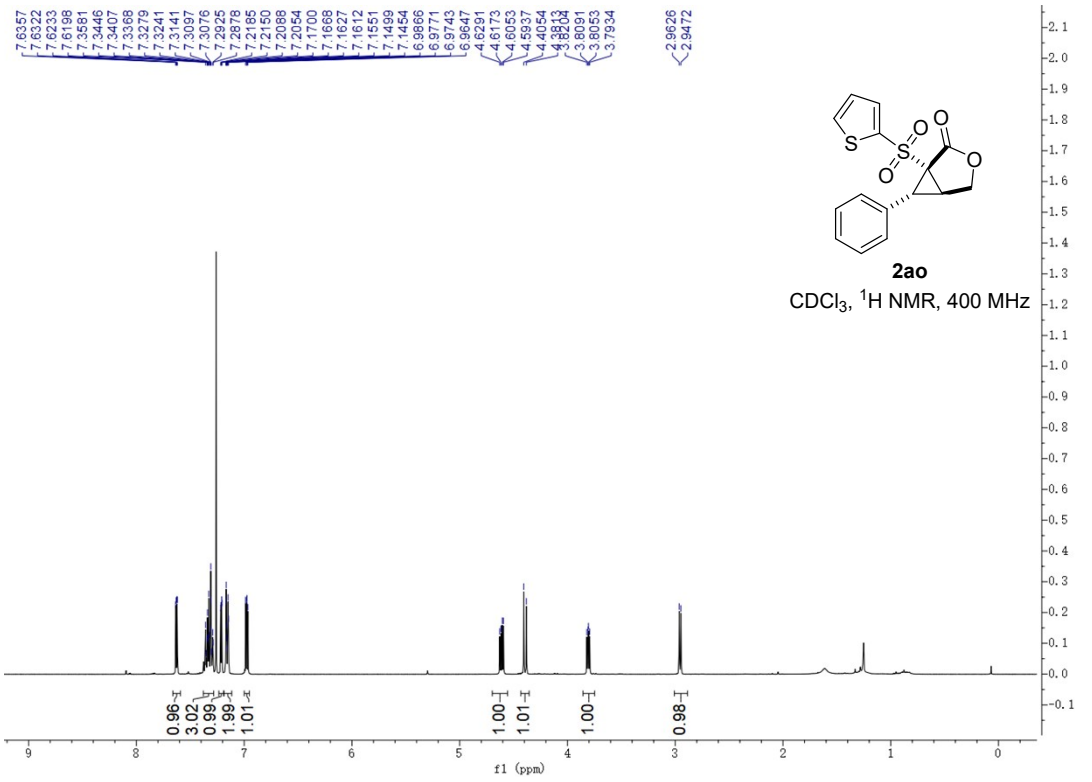
2an

$(CD_3)_2SO$, ^1H NMR, 400 MHz



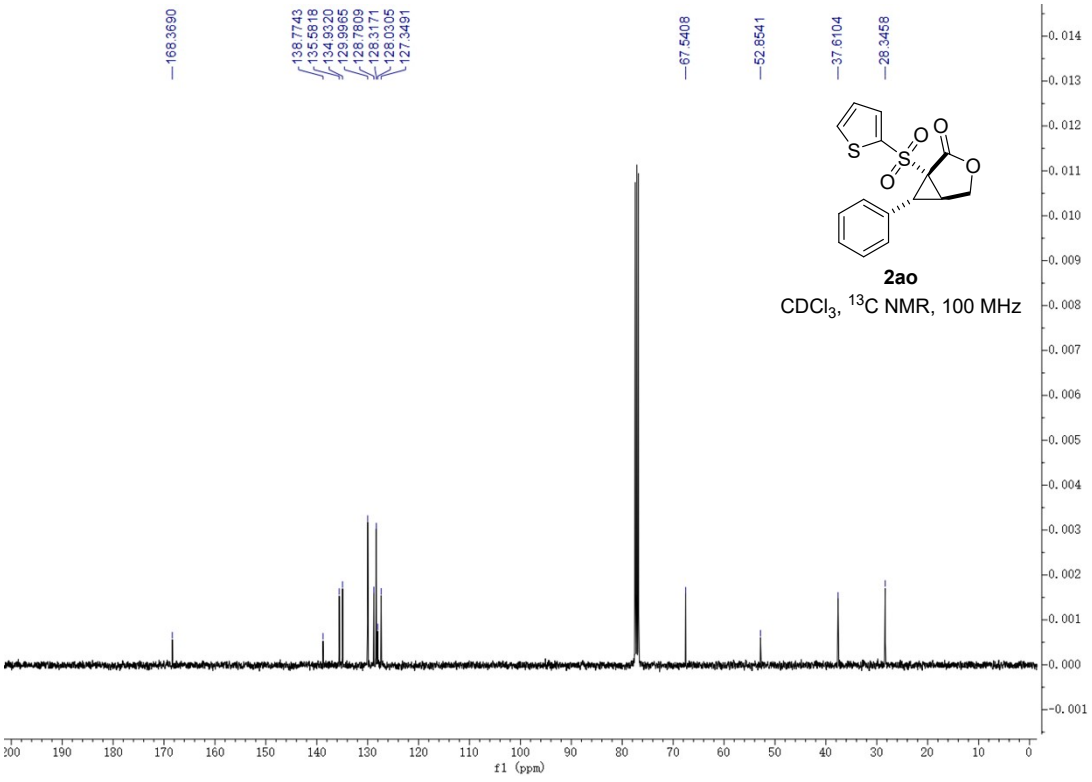
2an

$(CD_3)_2SO$, ^{13}C NMR, 100 MHz



2ao

$CDCl_3$, ^1H NMR, 400 MHz



2ao

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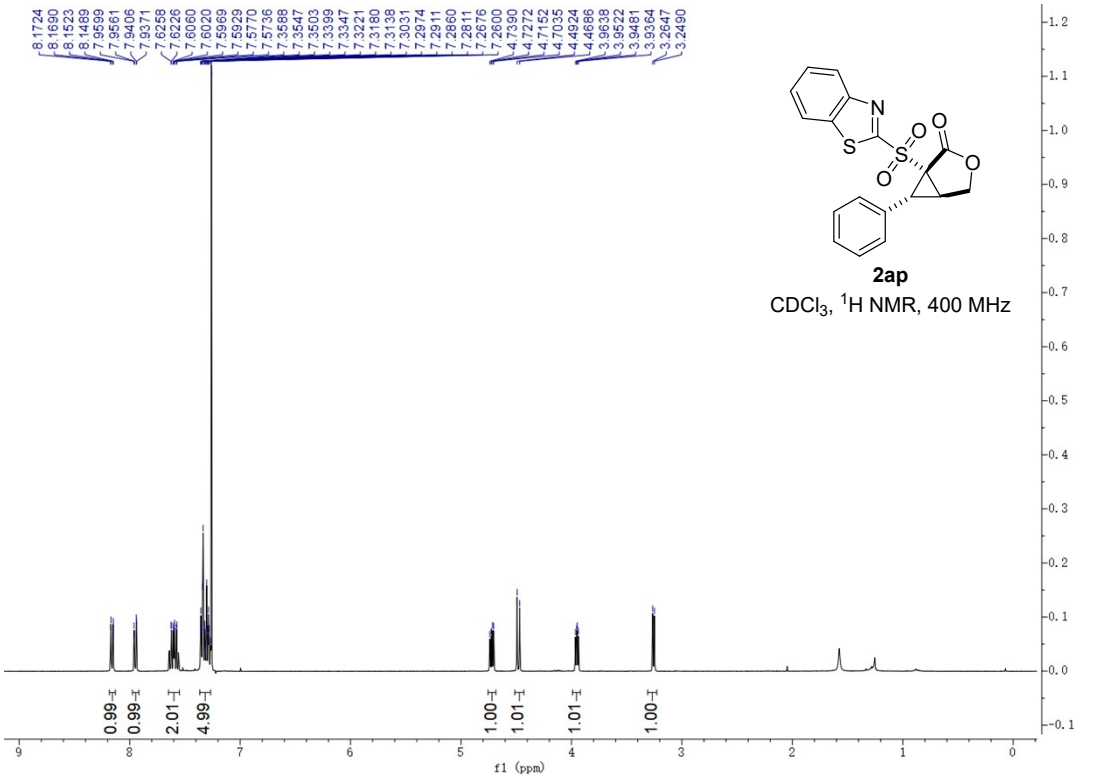

2ap

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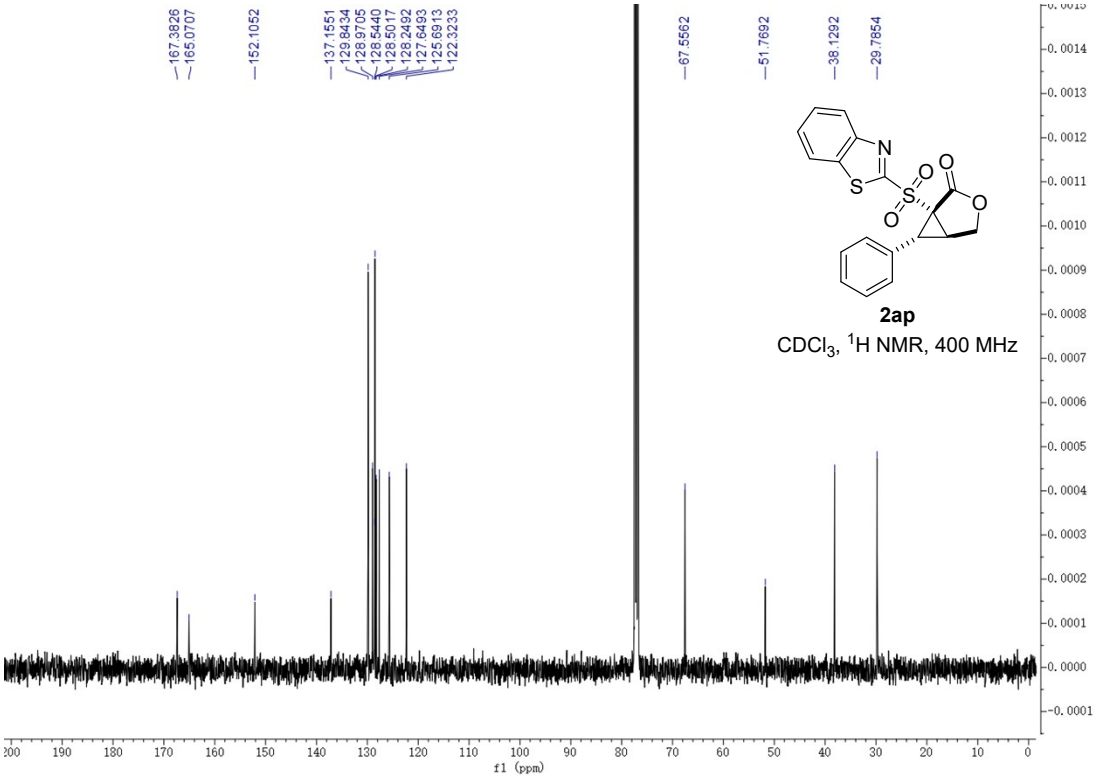

2ap

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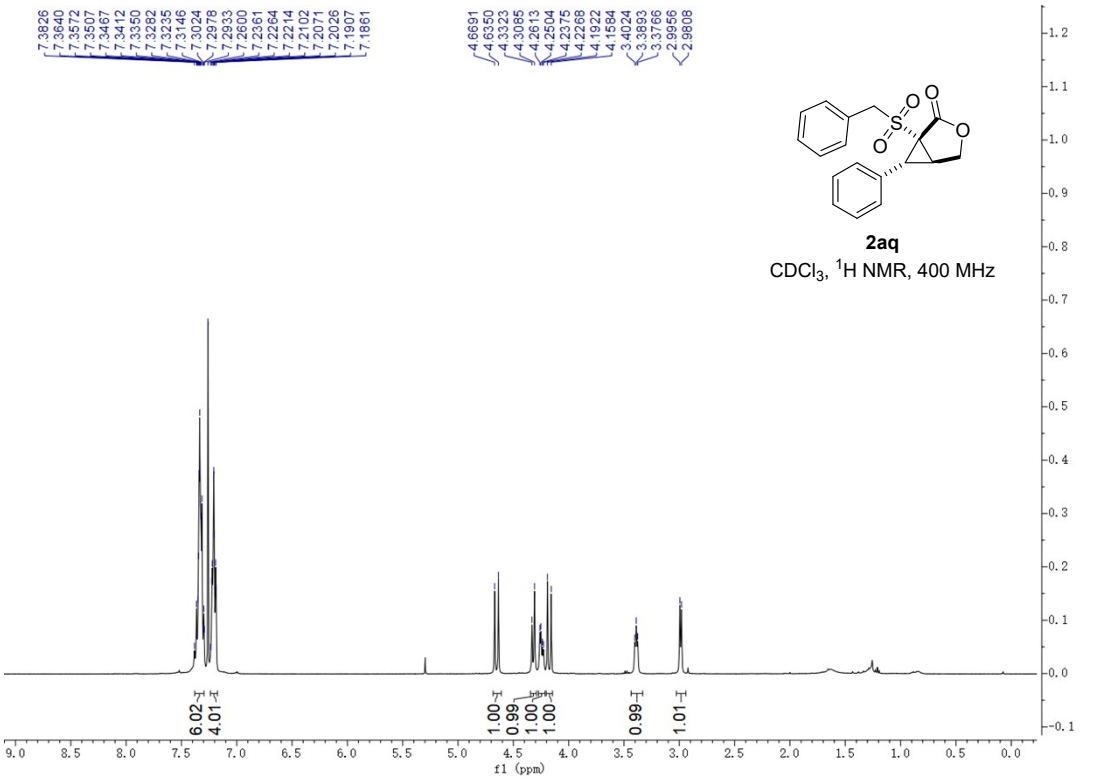
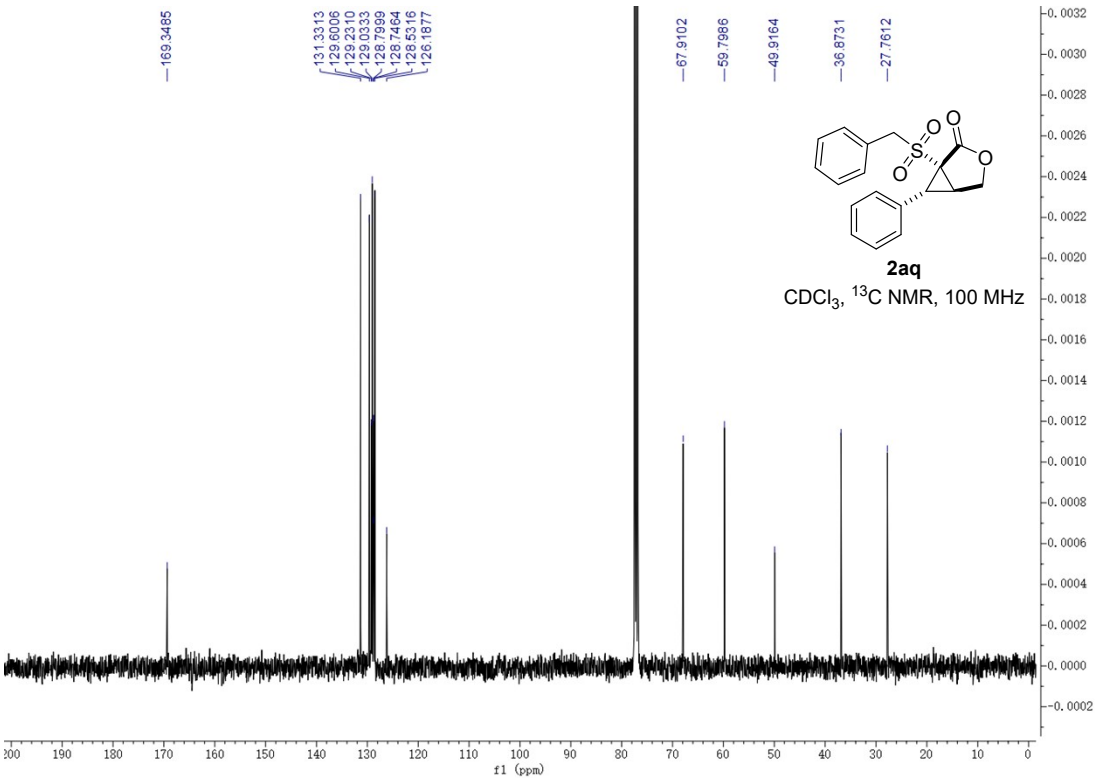


2aq

$CDCl_3$, ^1H NMR, 400 MHz



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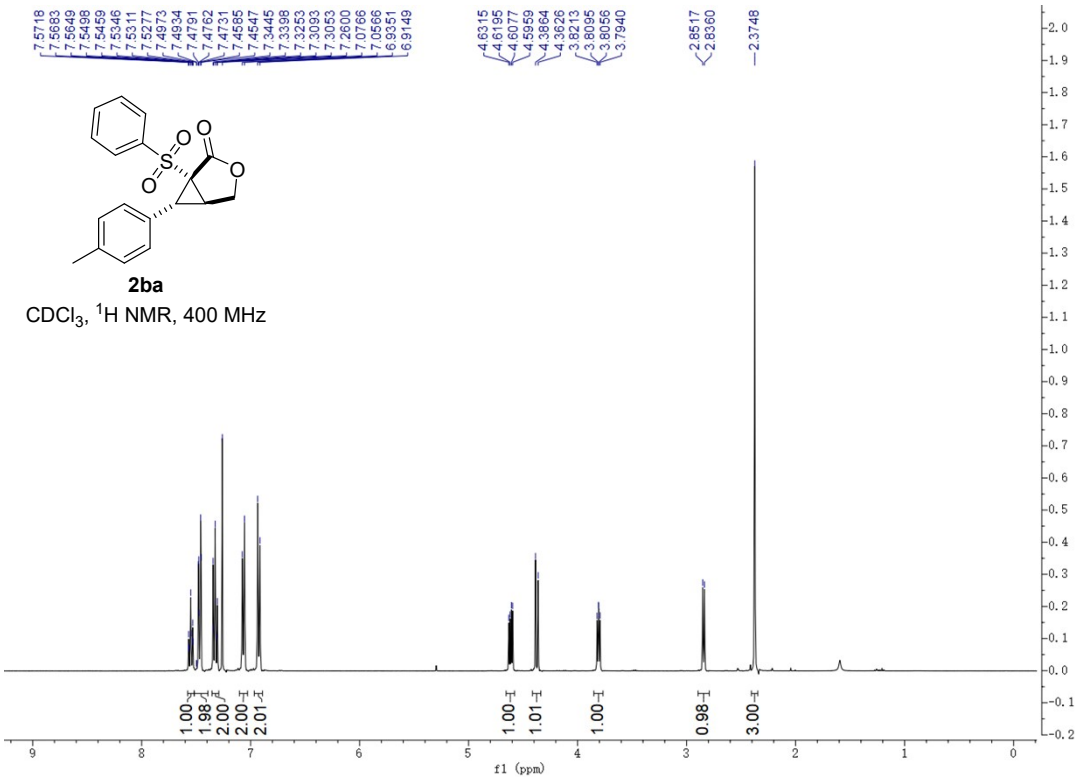

2ba

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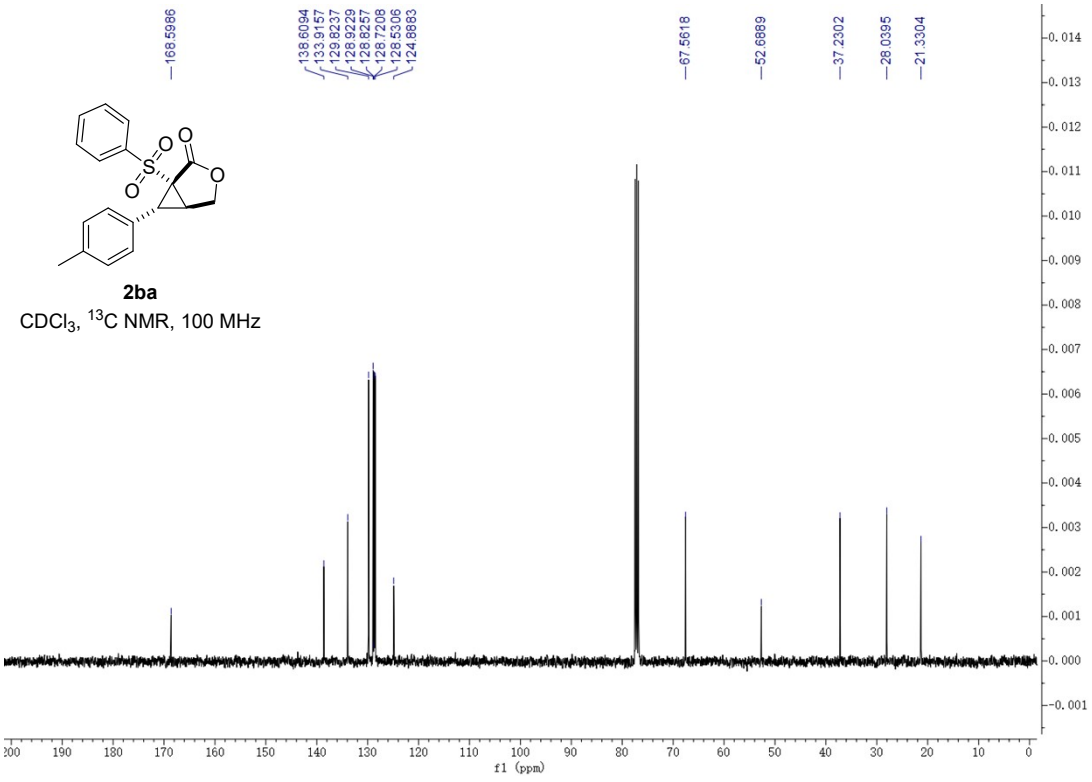

2ba

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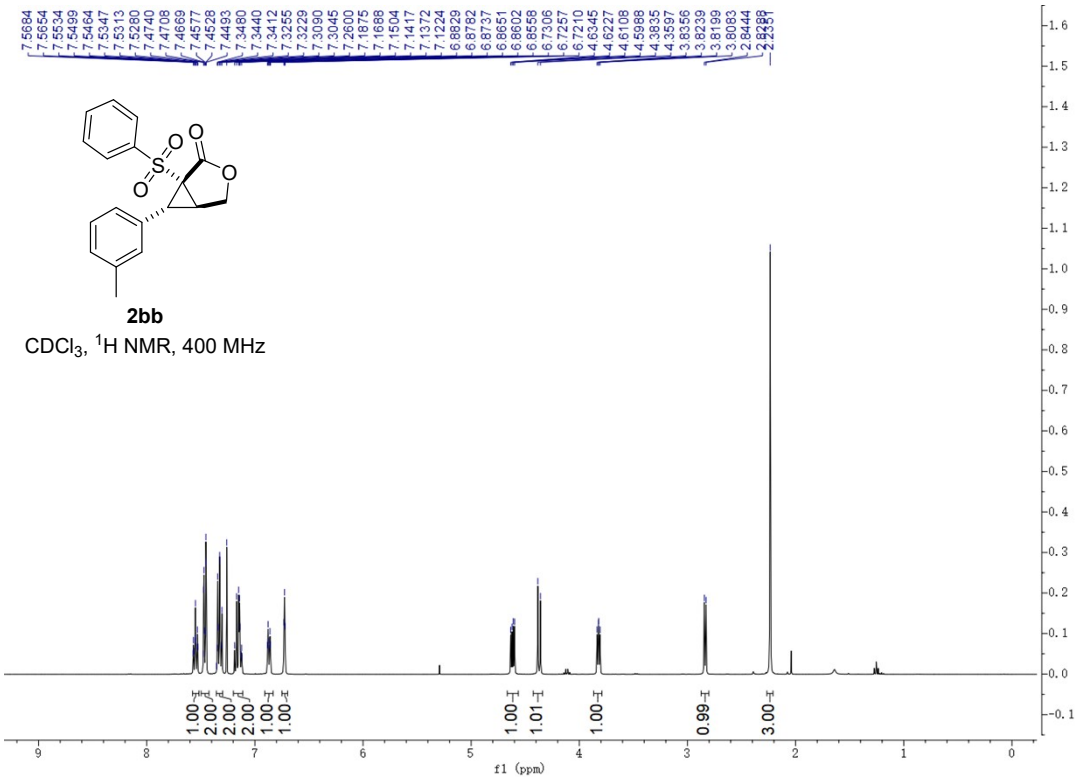
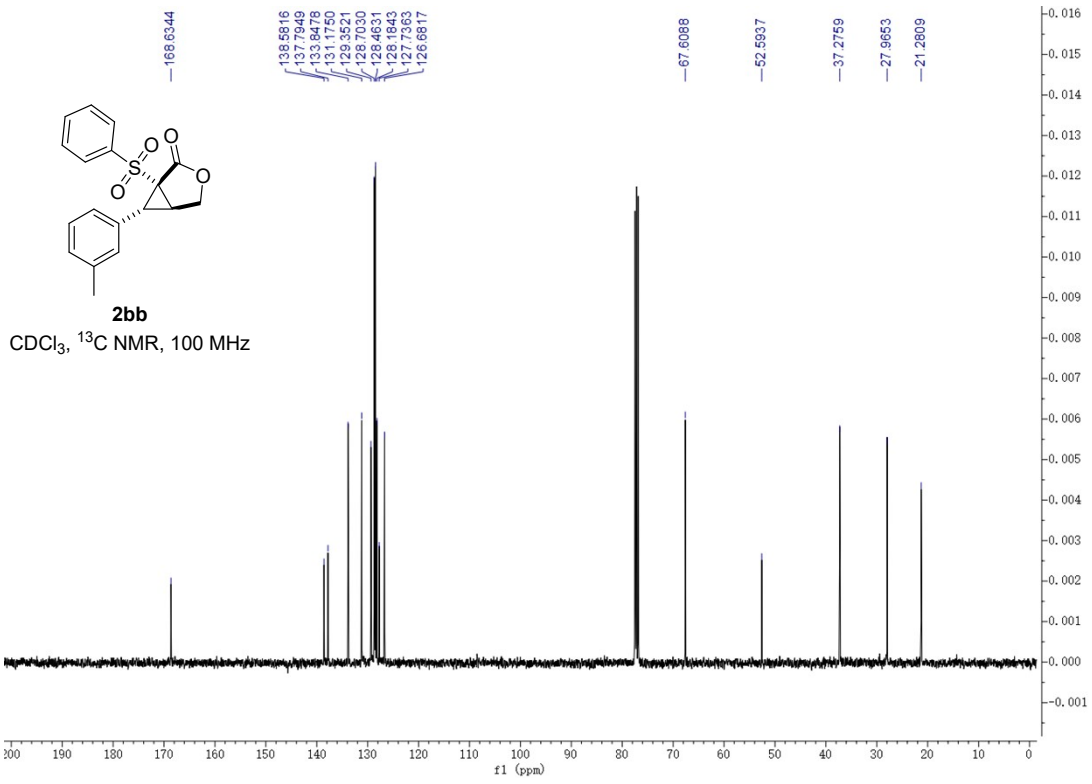


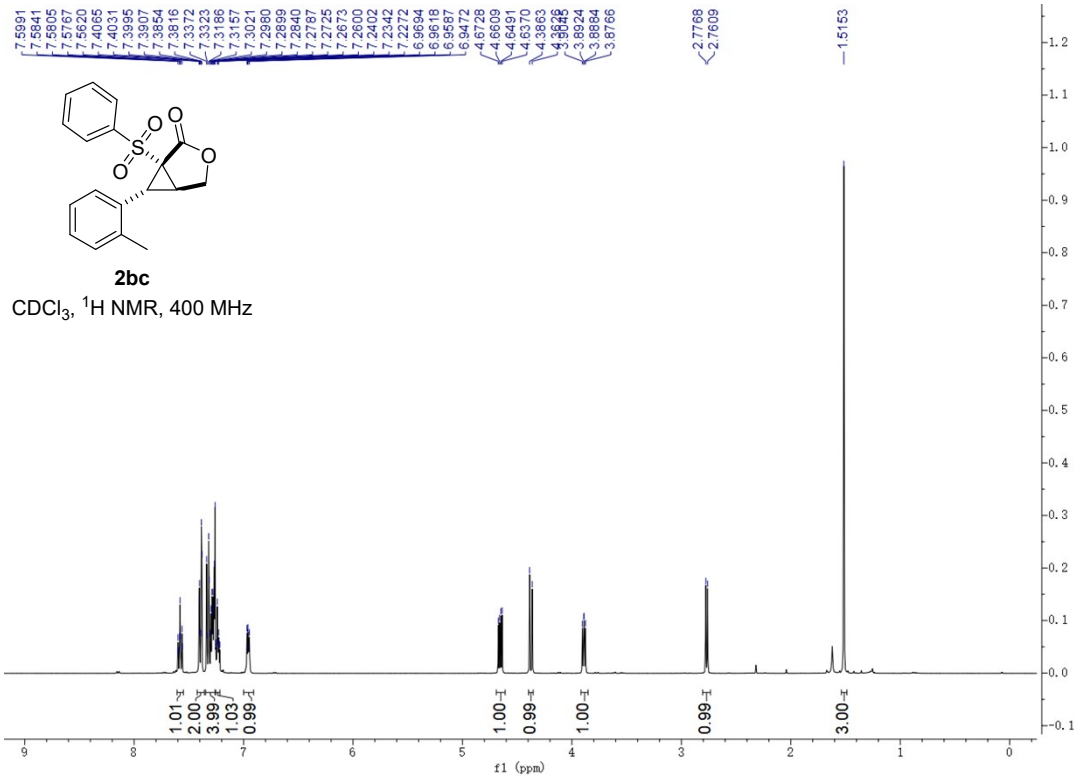
2bb

$CDCl_3$, ^1H NMR, 400 MHz



2bb

$CDCl_3$, ^{13}C NMR, 100 MHz



2bc

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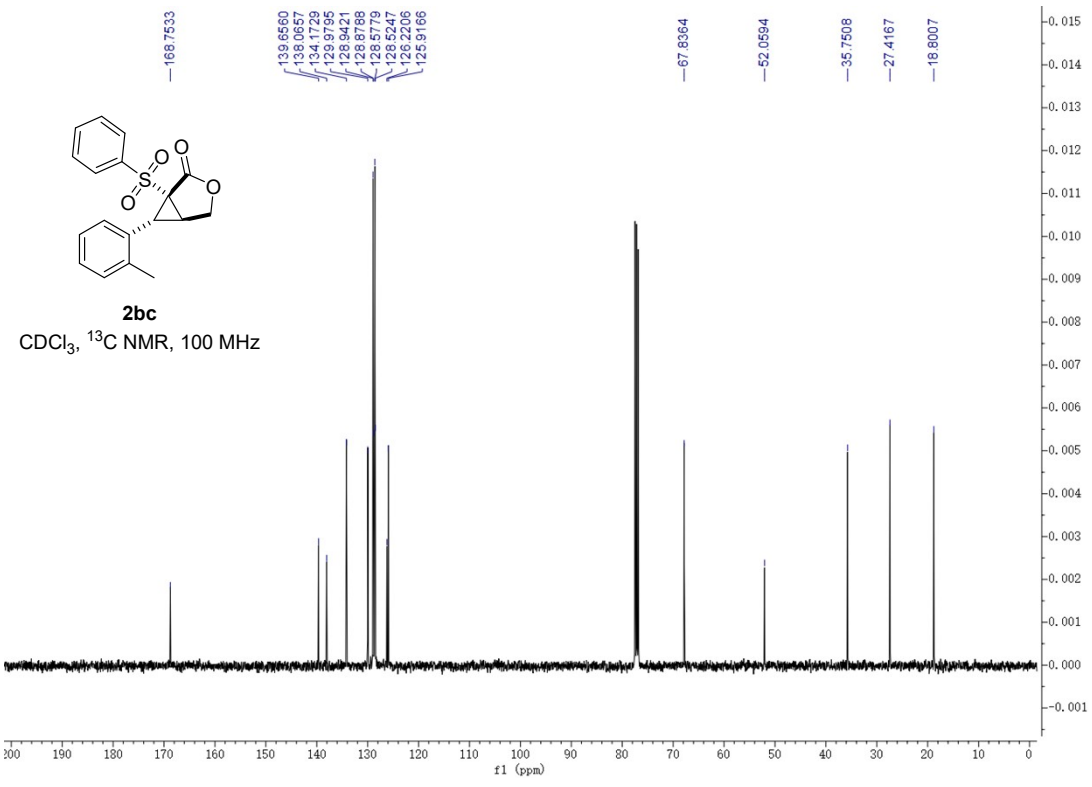
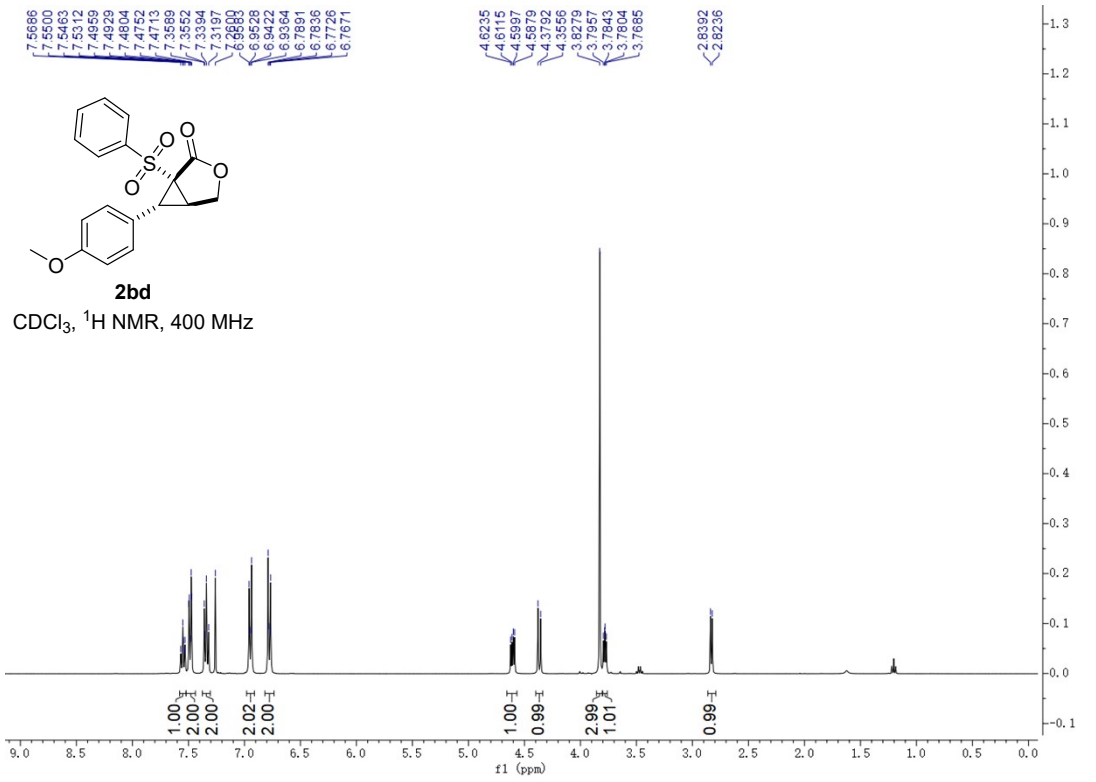


2bc

$CDCl_3$, ^{13}C NMR, 100 MHz



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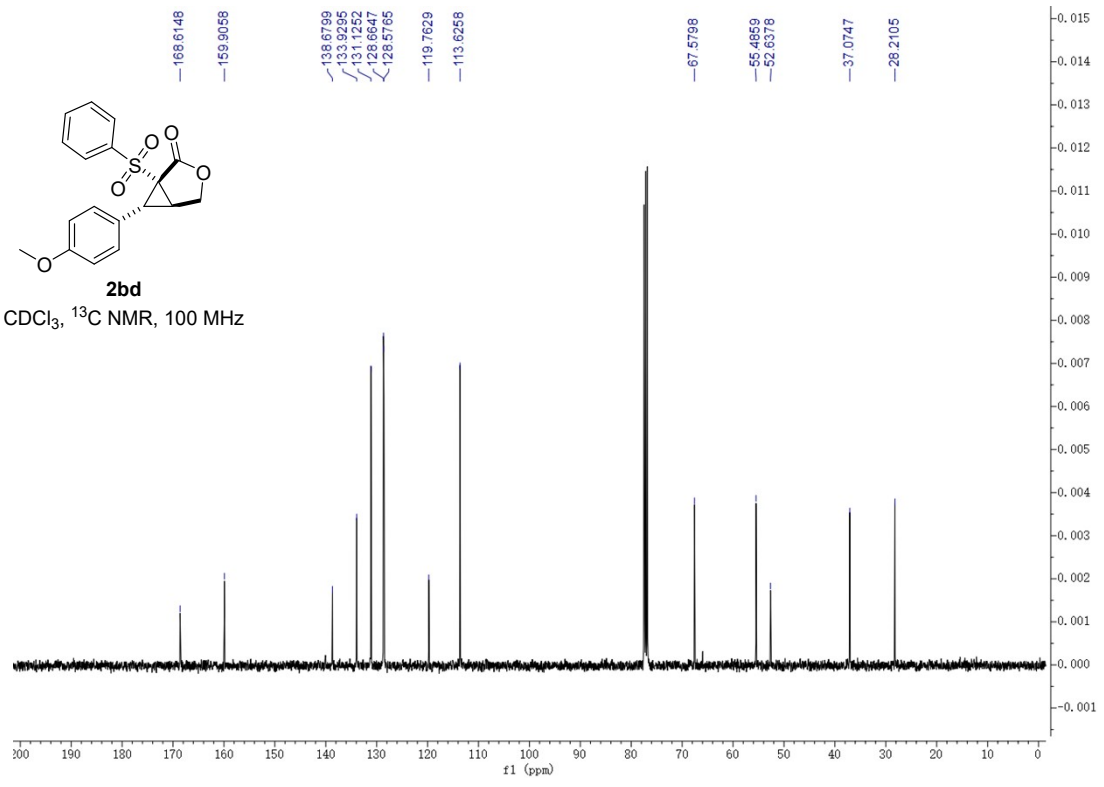

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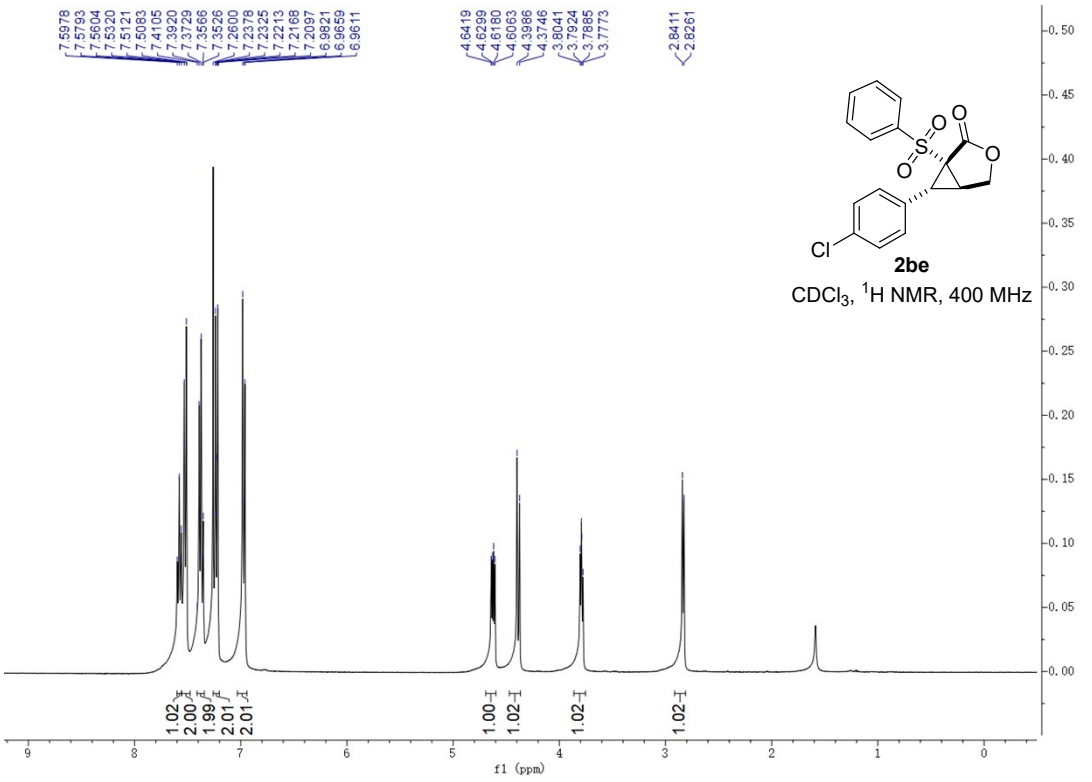
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3.7885
3.7773
2.8411
2.8261
1.02
2.00
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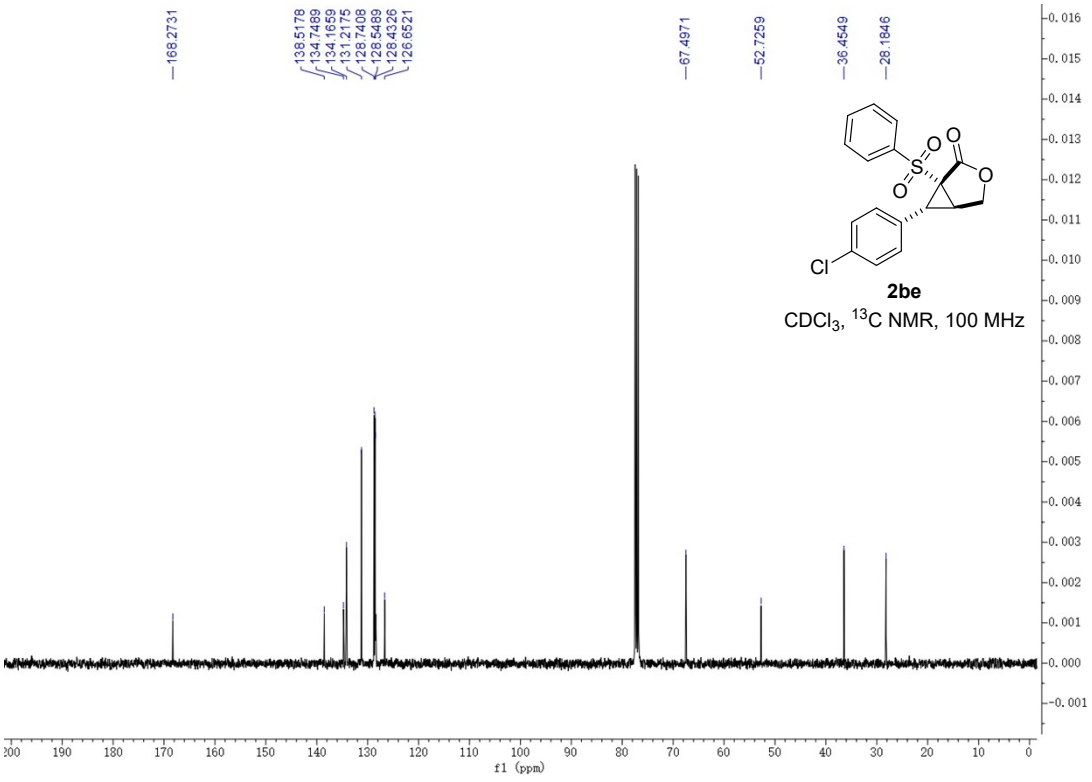
1.00
1.02
1.02
1.02
f1 (ppm)
2be
CDCl3, 1H NMR, 400 MHz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134.1659
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128.5489
128.4326
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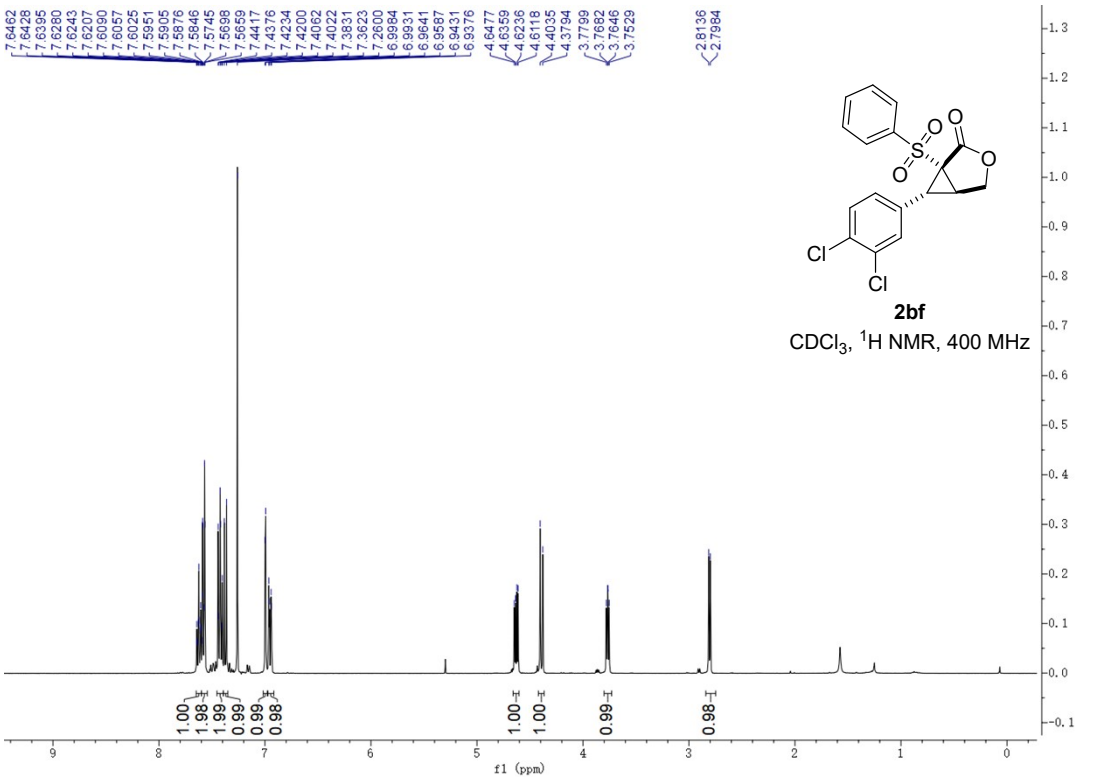
67.4971
52.7259
36.4549
28.1846
f1 (ppm)
2be
CDCl3, 13C NMR, 100 MHz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2.7984
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1.98
1.99
0.99
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1.00
1.00
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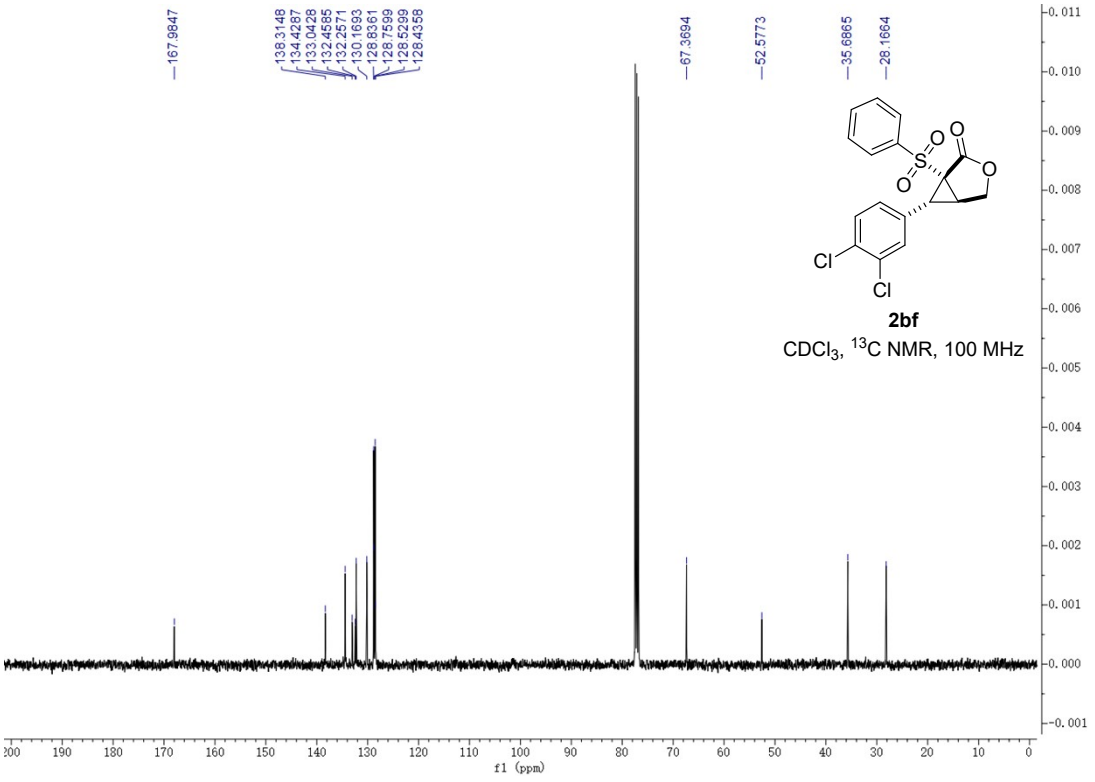
f1 (ppm)
Cl
Cl
2bf
CDCl3, 1H NMR, 400 MHz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52.5773
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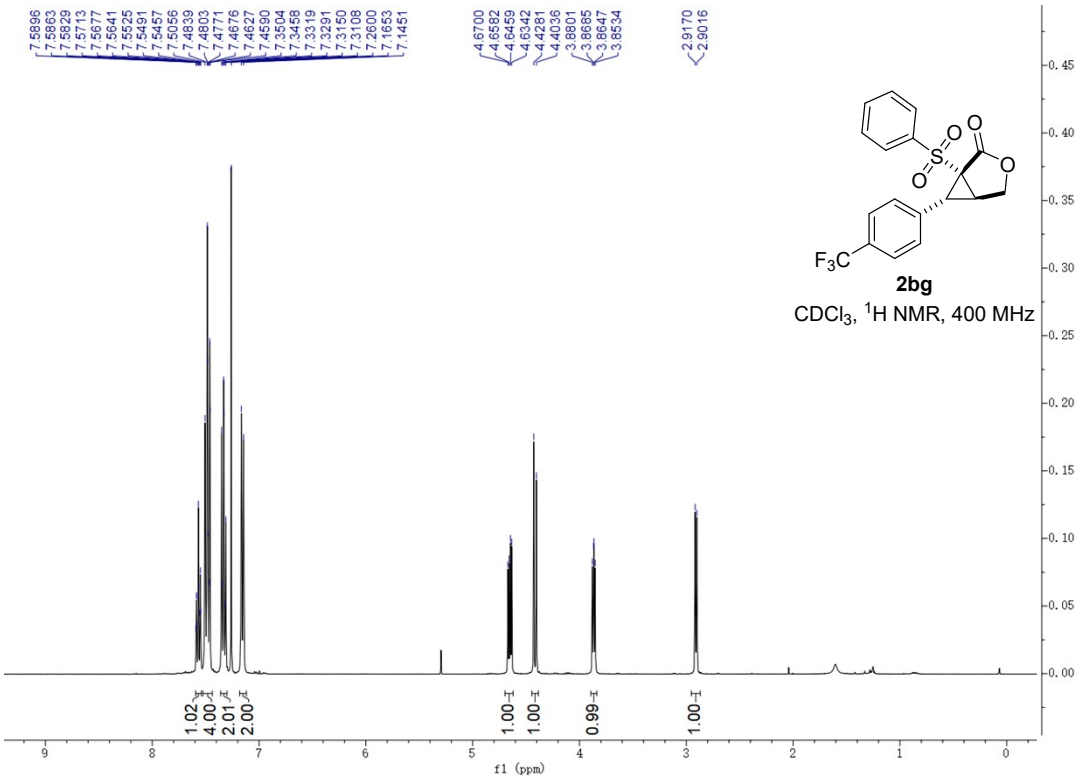
28.1664
f1 (ppm)
Cl
Cl
2bf
CDCl3, 13C NMR, 100 MHz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3.8647
3.8534
2.9170
2.9016
1.02
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2.01
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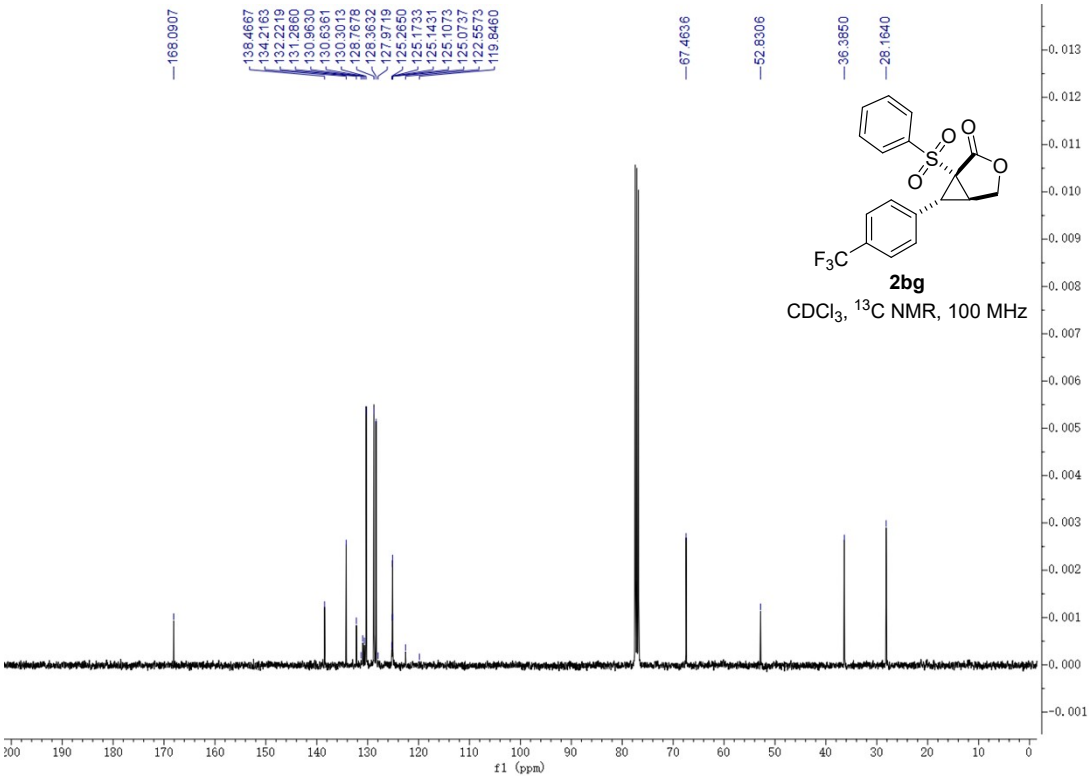
1.00
1.00
0.99
1.00
f1 (ppm)
F3C
2bg
CDCl3, 1H NMR, 400 MHz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125.2650
125.1733
125.1431
125.1073
125.0737
122.5573
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52.8306
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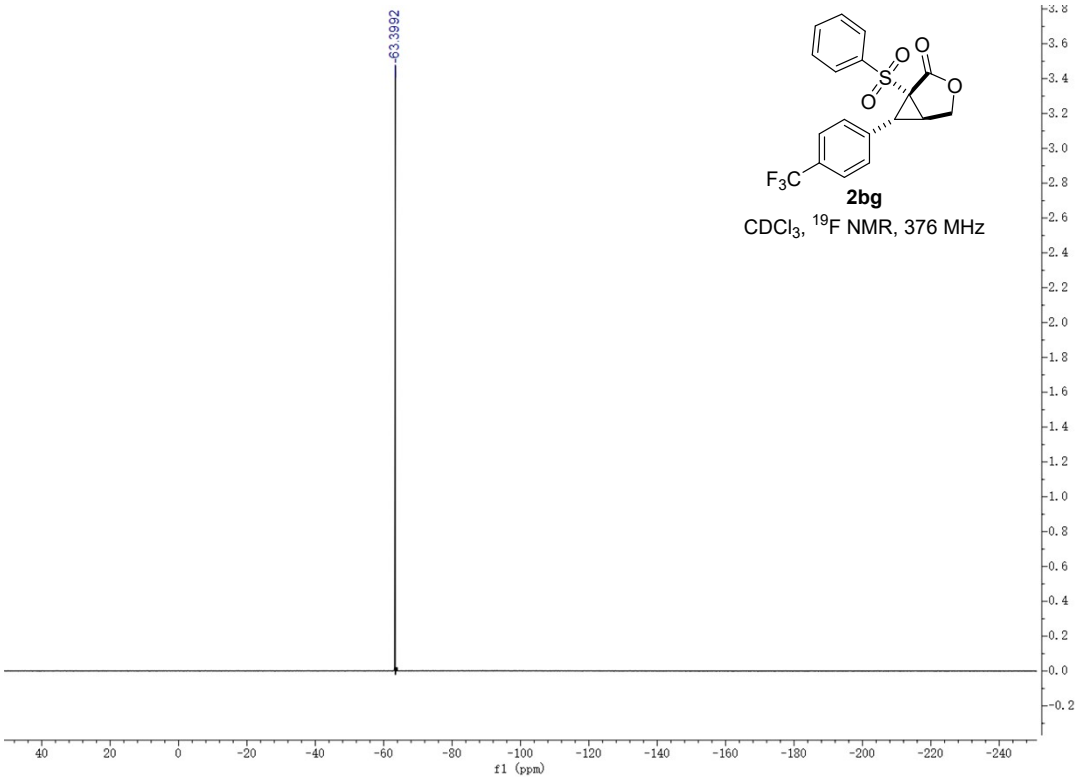
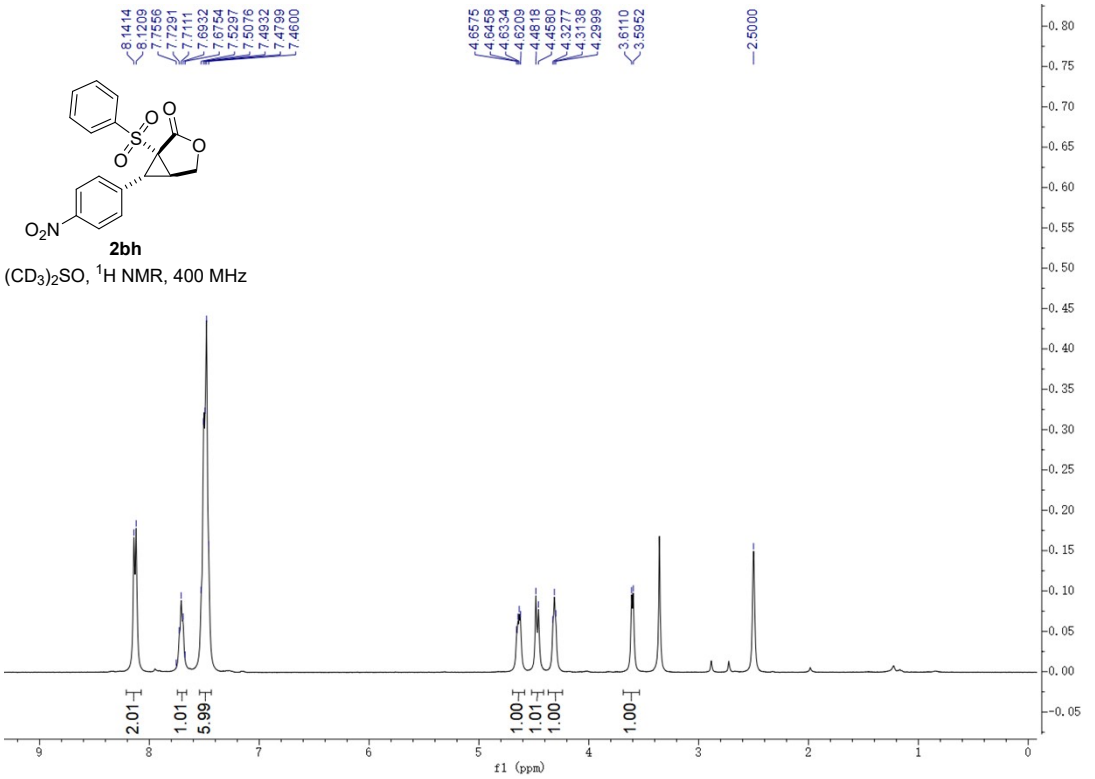
f1 (ppm)
F3C
2bg
CDCl3, 13C NMR, 100 MHz



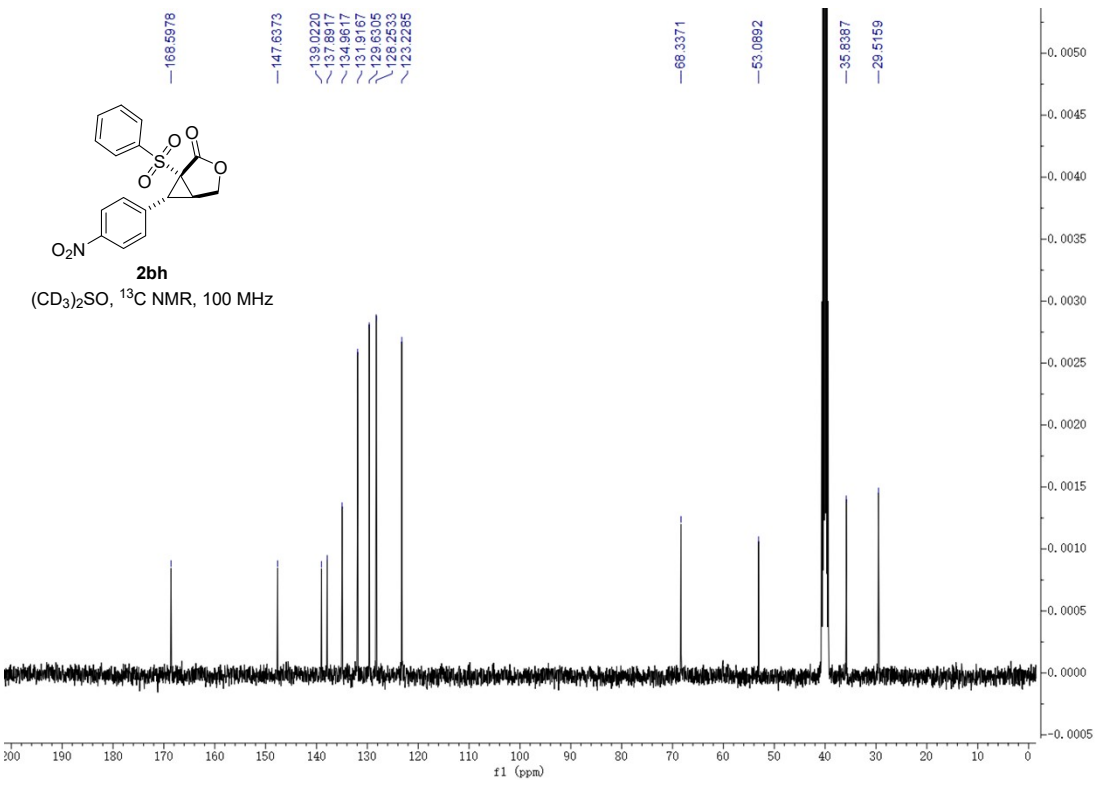
2bg

$CDCl_3$, ^{19}F NMR, 376 MHz



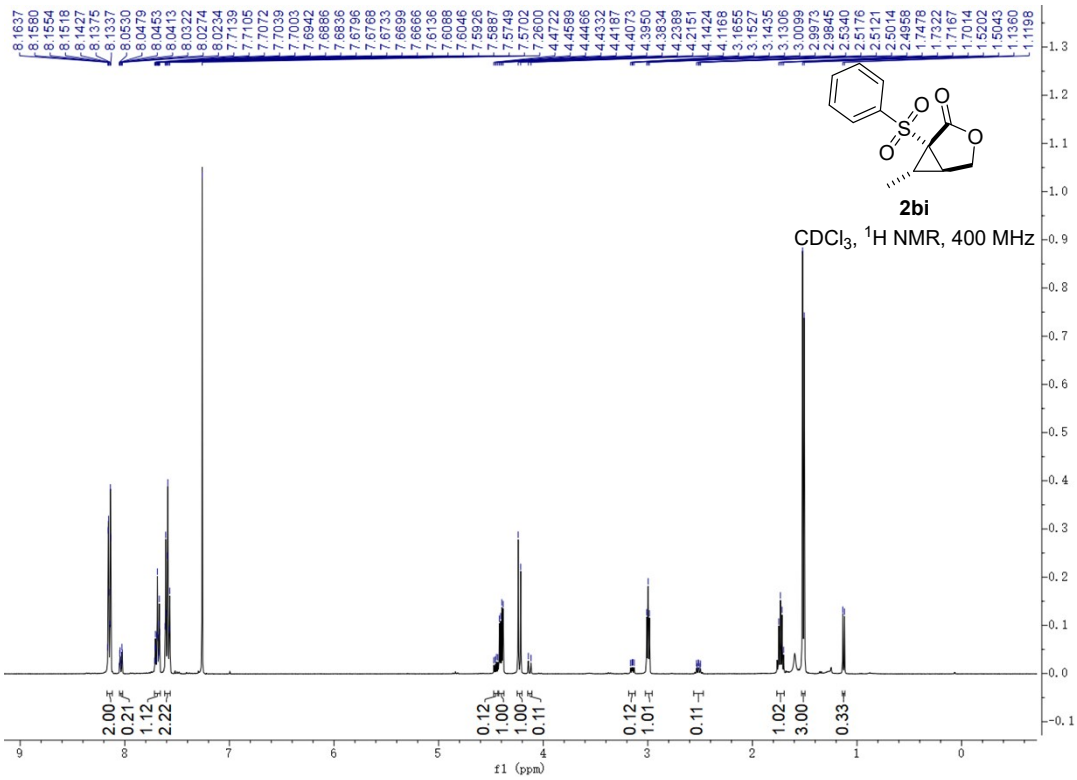
2bh

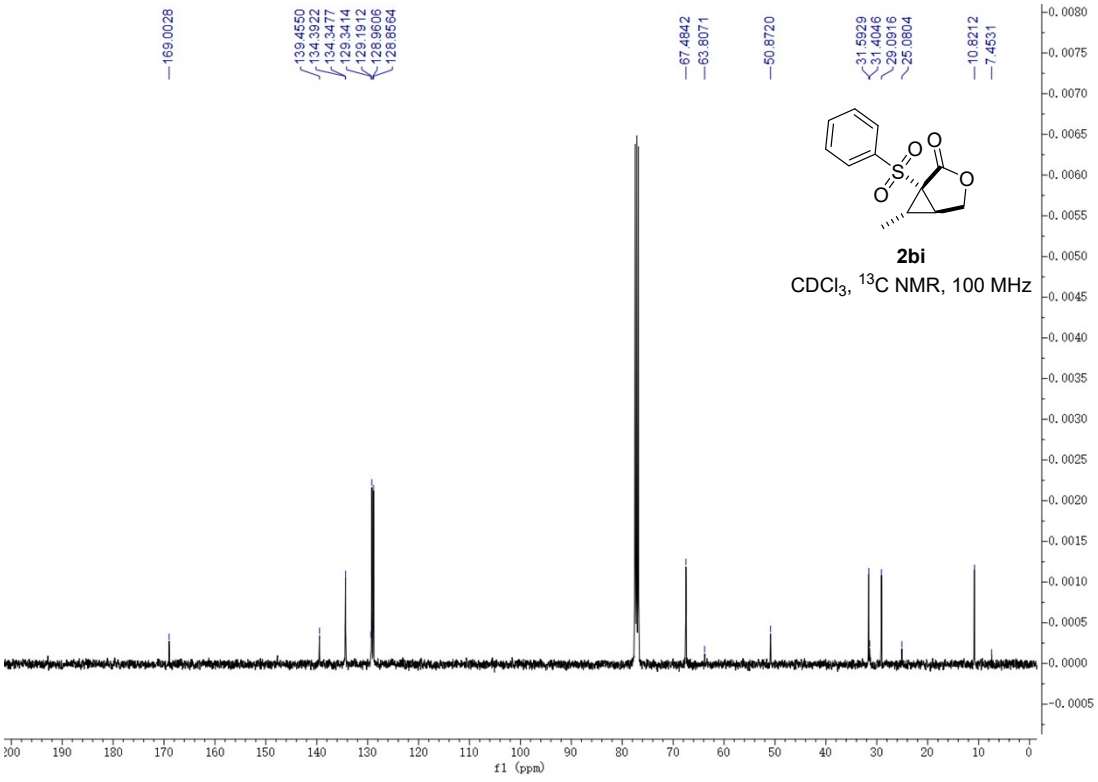
$(CD_3)_2SO$, ^1H NMR, 400 MHz

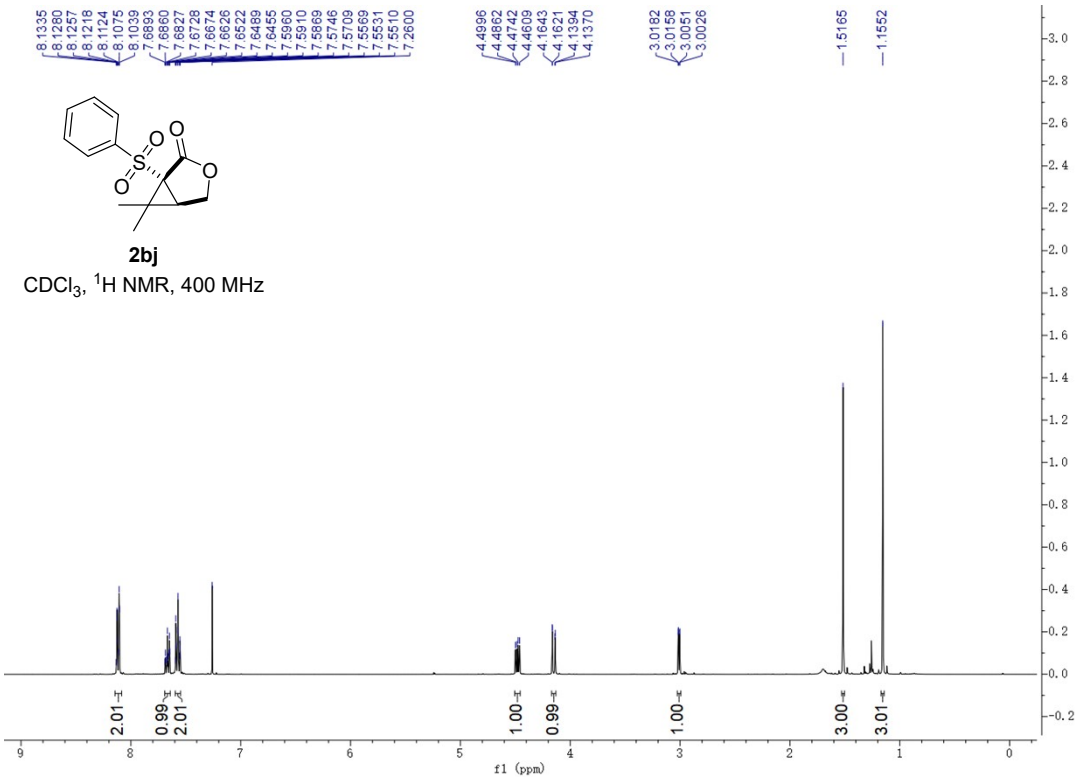


2bh

$(CD_3)_2SO$, ^{13}C NMR, 100 MHz

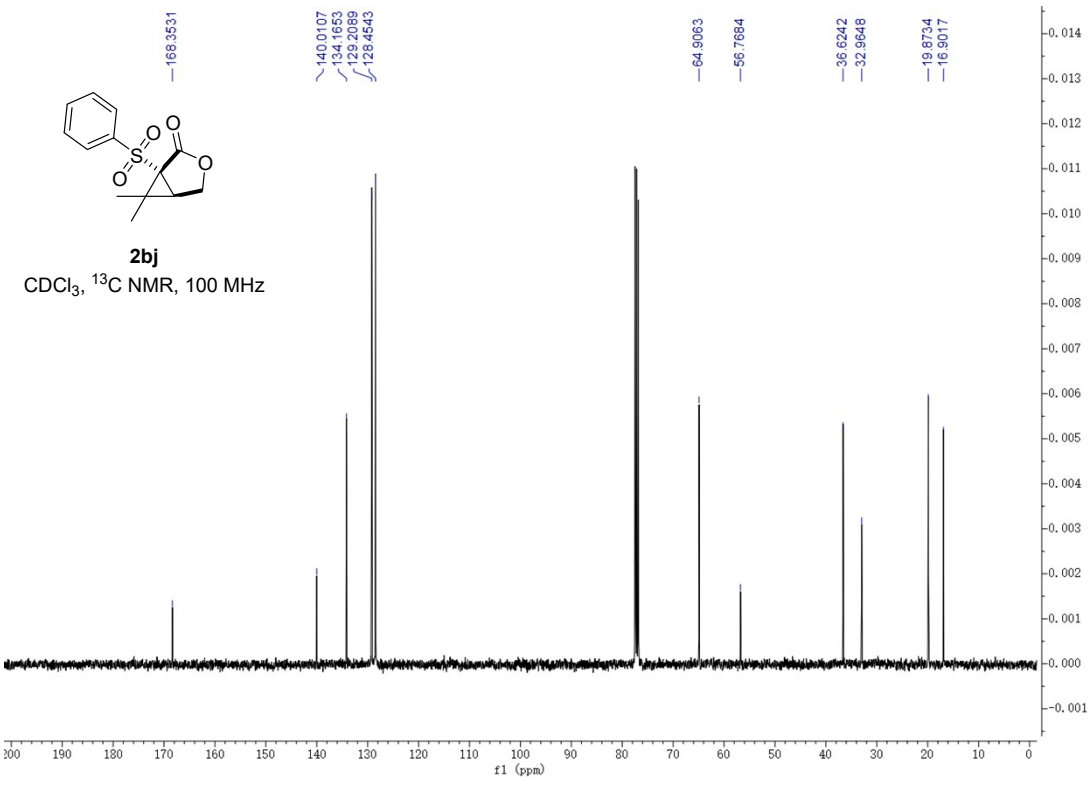

2bi
CDCl3, 1H NMR, 400 MHz
f1 (ppm)


2bi
CDCl3, 13C NMR, 100 MHz
f1 (ppm)



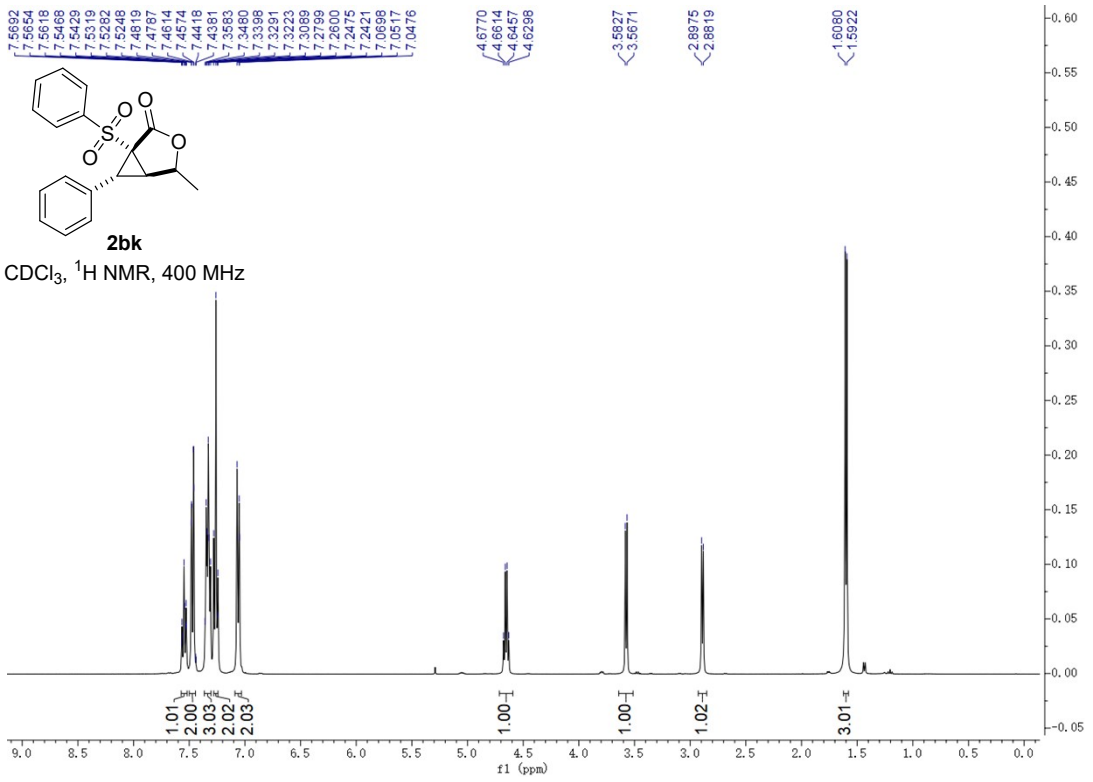
2bj

$CDCl_3$, ^1H NMR, 400 MHz



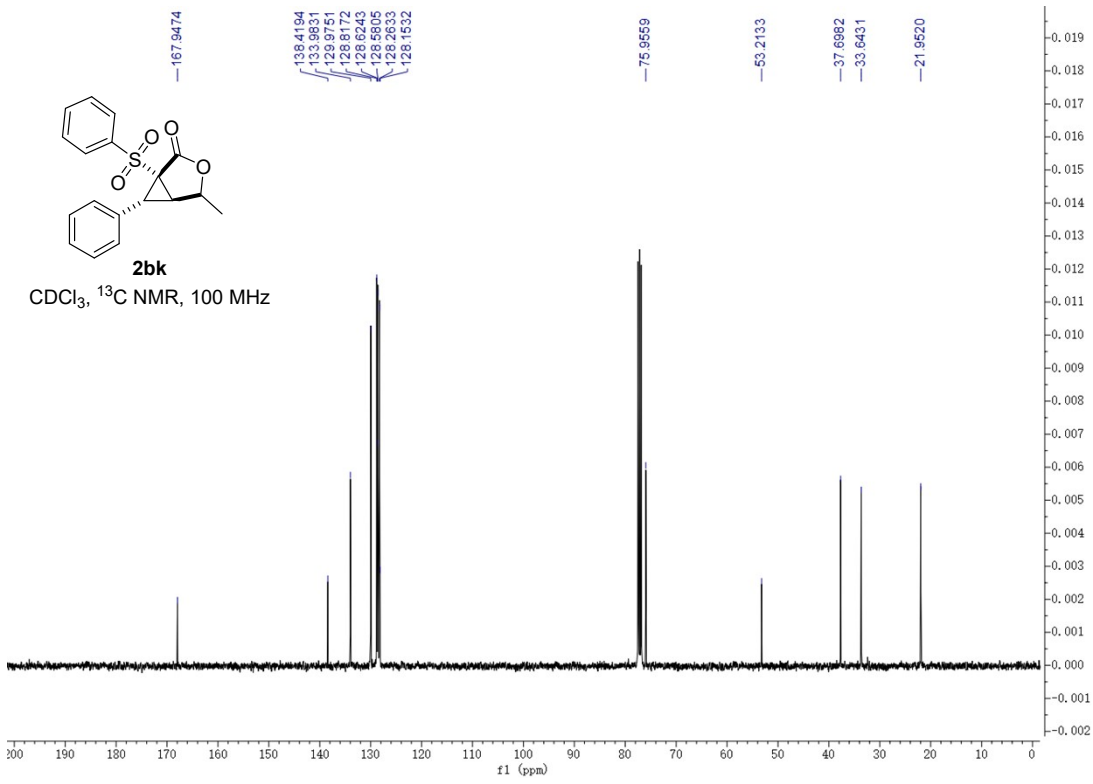
2bj

$CDCl_3$, ^{13}C NMR, 100 MHz



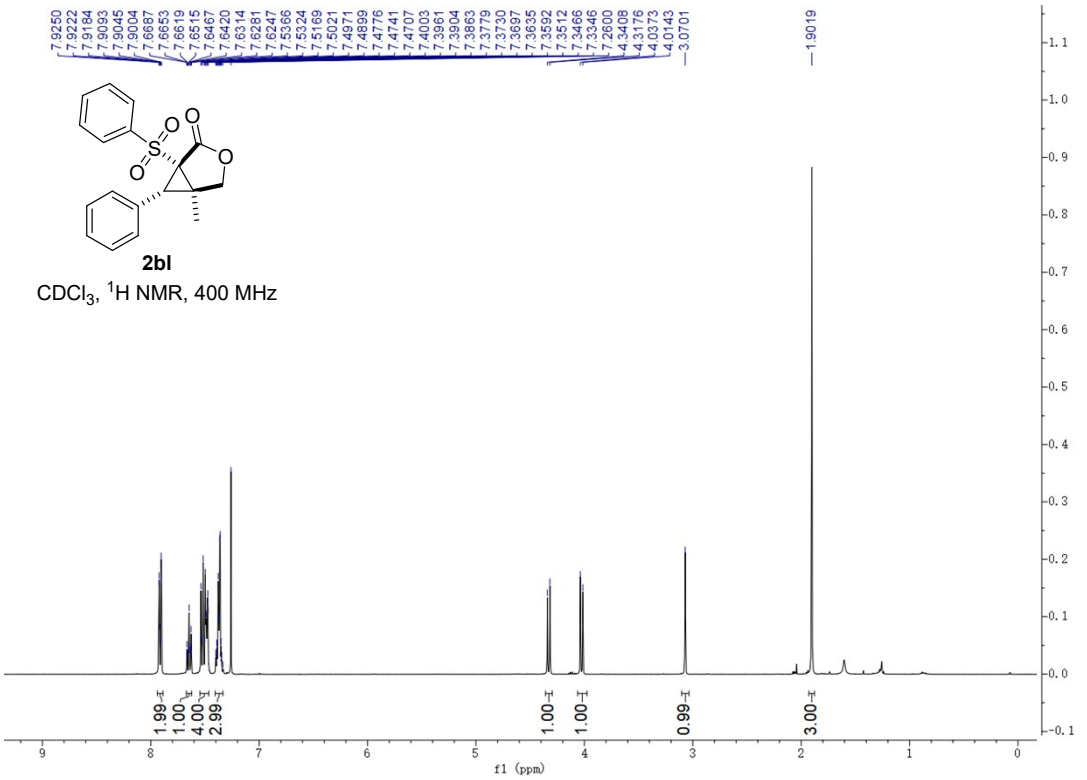
2bk

$CDCl_3$, ^1H NMR, 400 MHz



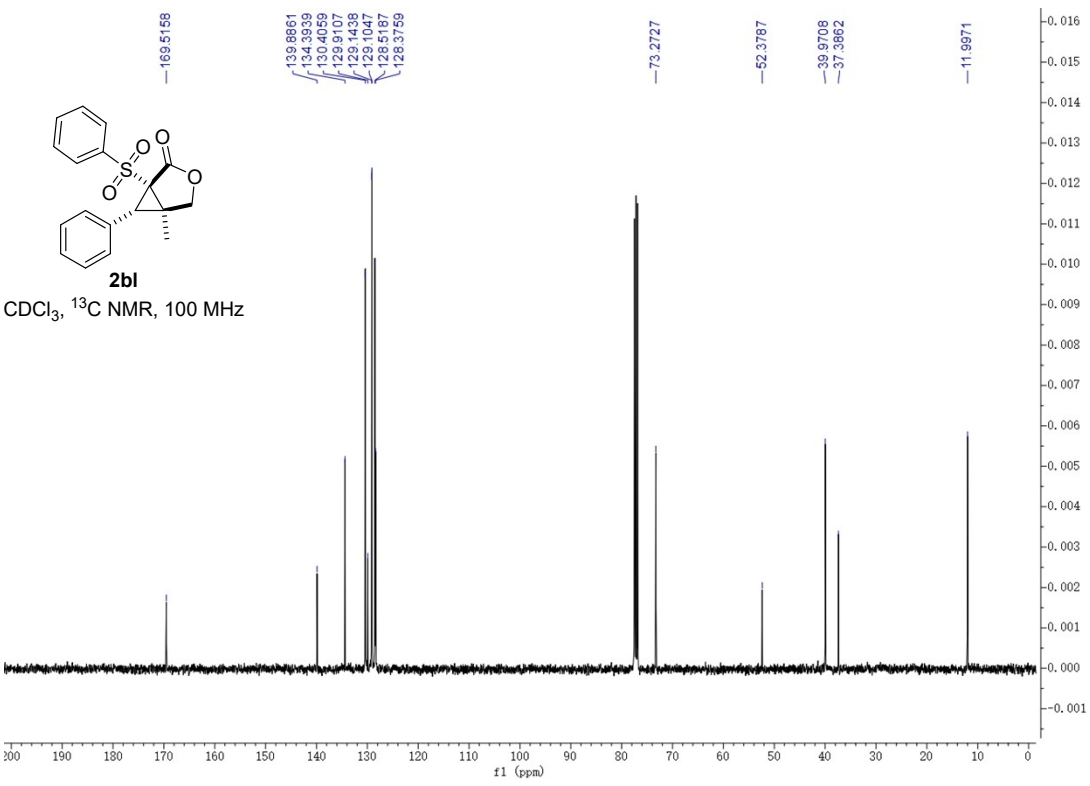
2bk

$CDCl_3$, ^{13}C NMR, 100 MHz



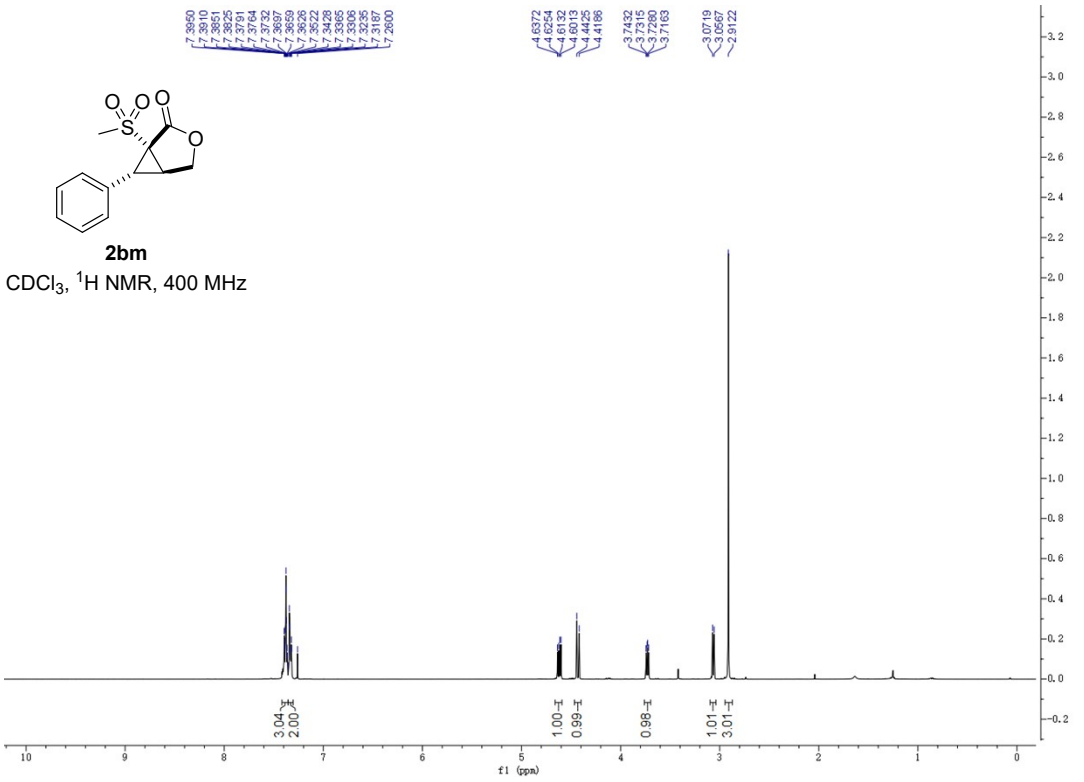
2bl

$CDCl_3$, ^1H NMR, 400 MHz



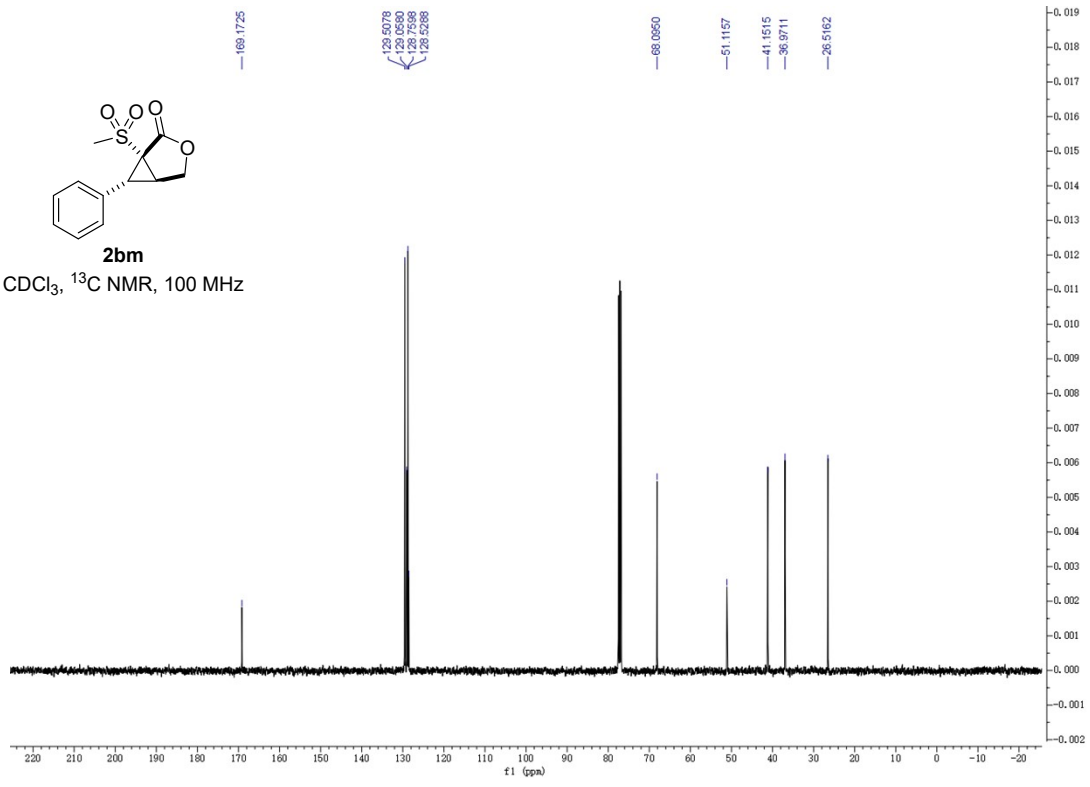
2bl

$CDCl_3$, ^{13}C NMR, 100 MHz



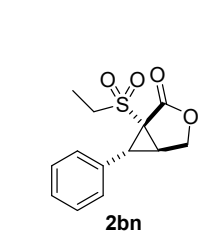
2bm

$CDCl_3$, ^1H NMR, 400 MHz



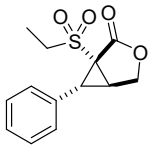
2bm

$CDCl_3$, ^{13}C NMR, 100 MHz



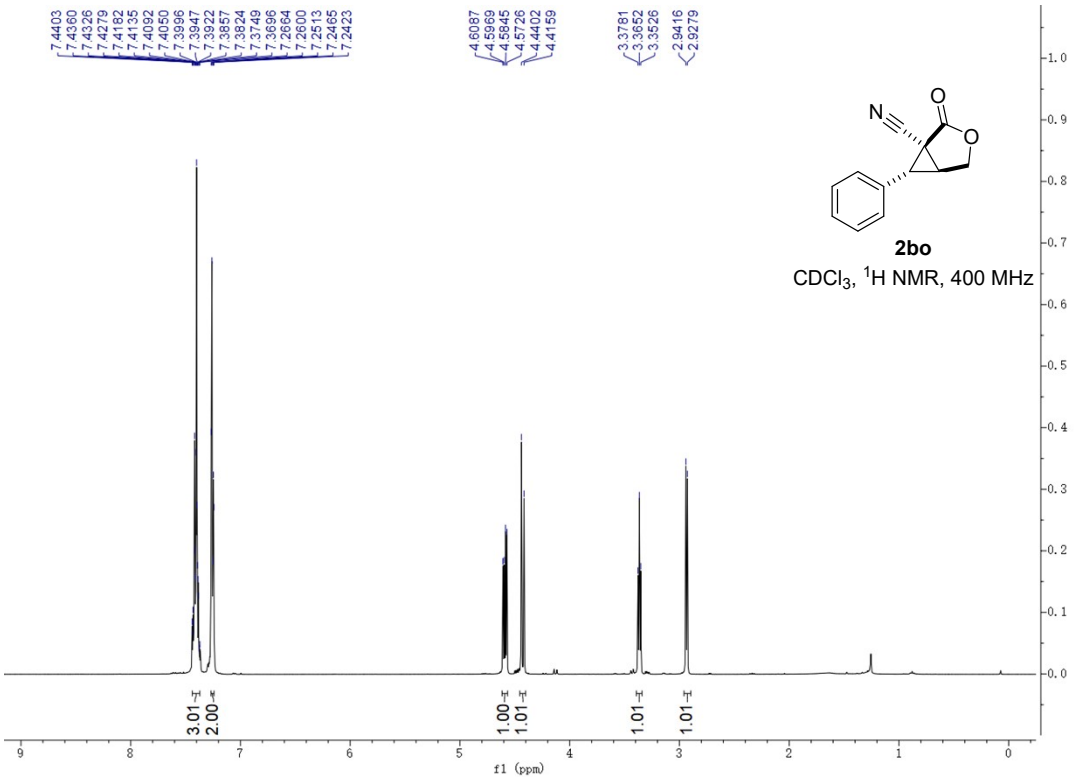
2bn

$CDCl_3$, ^1H NMR, 400 MHz



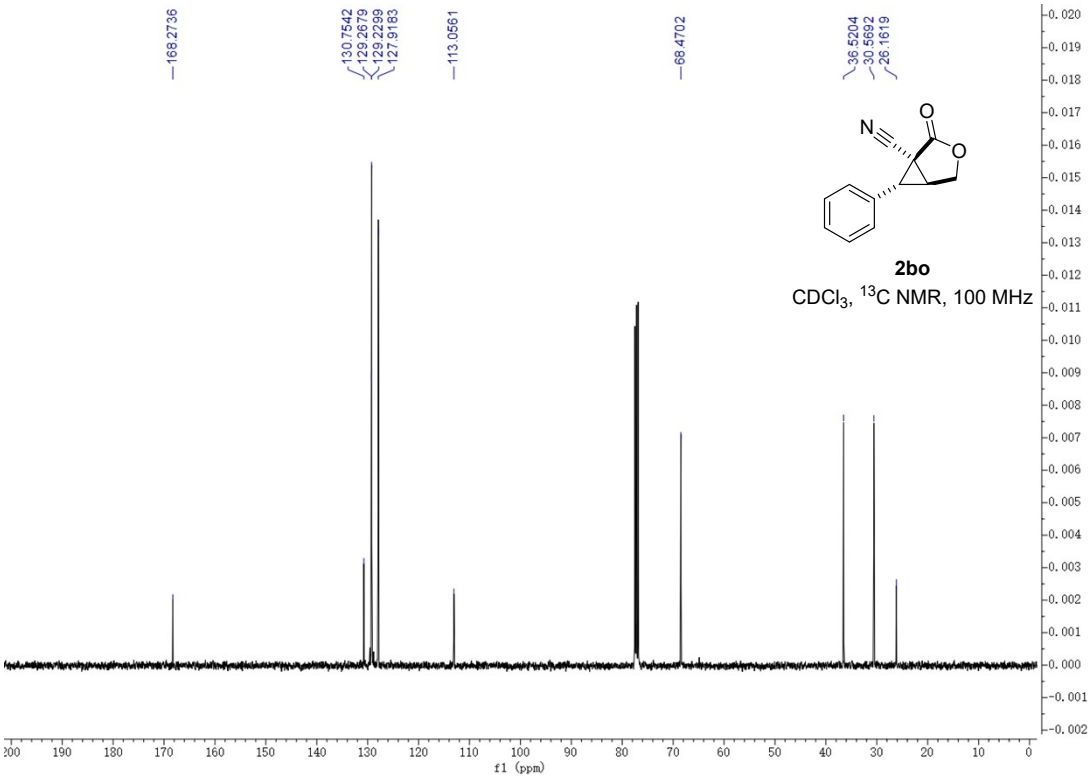
2bn

$CDCl_3$, ^{13}C NMR, 100 MHz



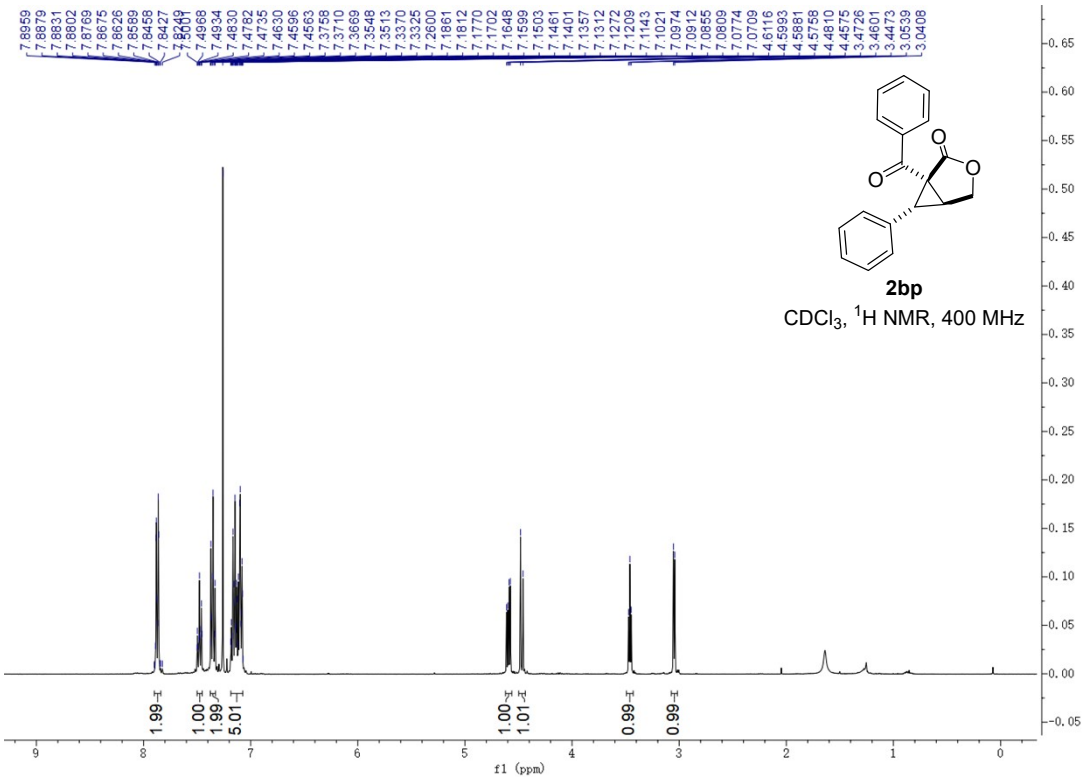
2bo

$CDCl_3$, ^1H NMR, 400 MHz



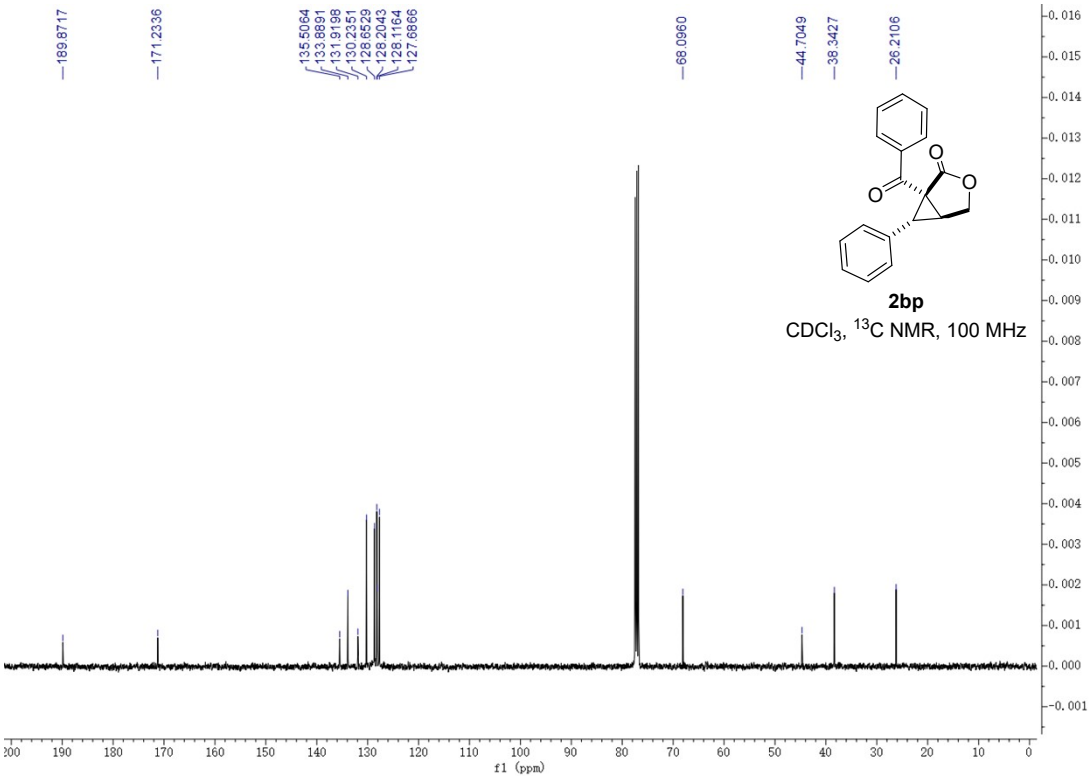
2bo

$CDCl_3$, ^{13}C NMR, 100 MHz



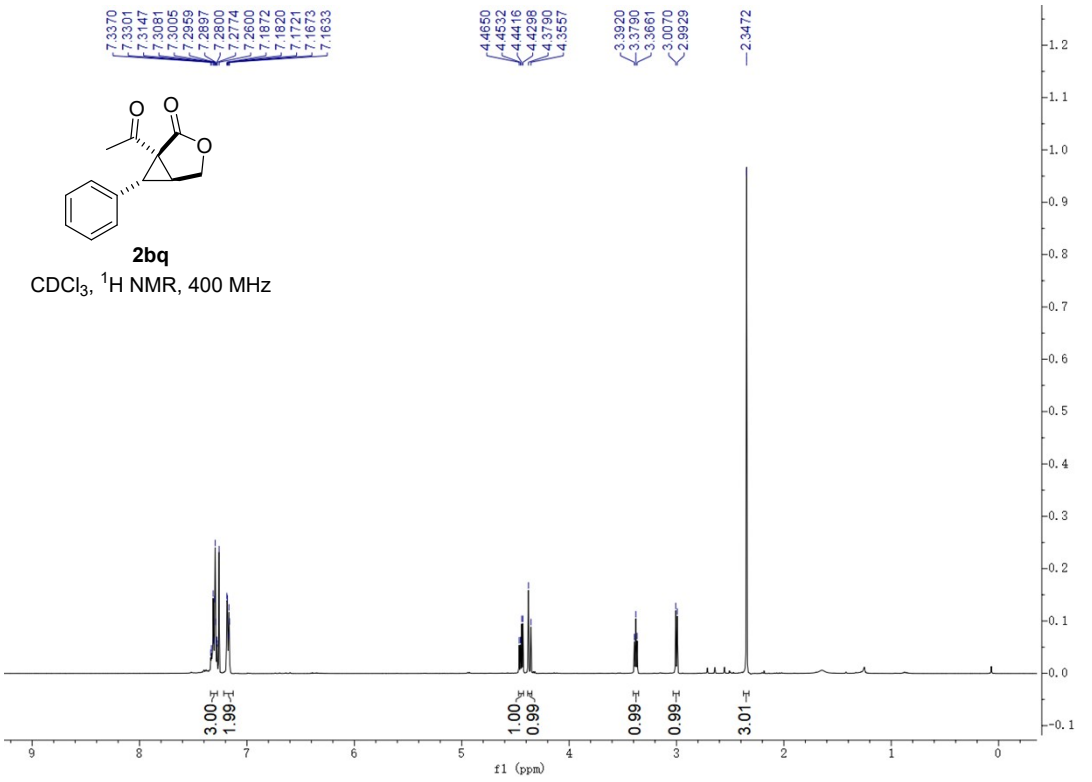
2bp

$CDCl_3$, ^1H NMR, 400 MHz



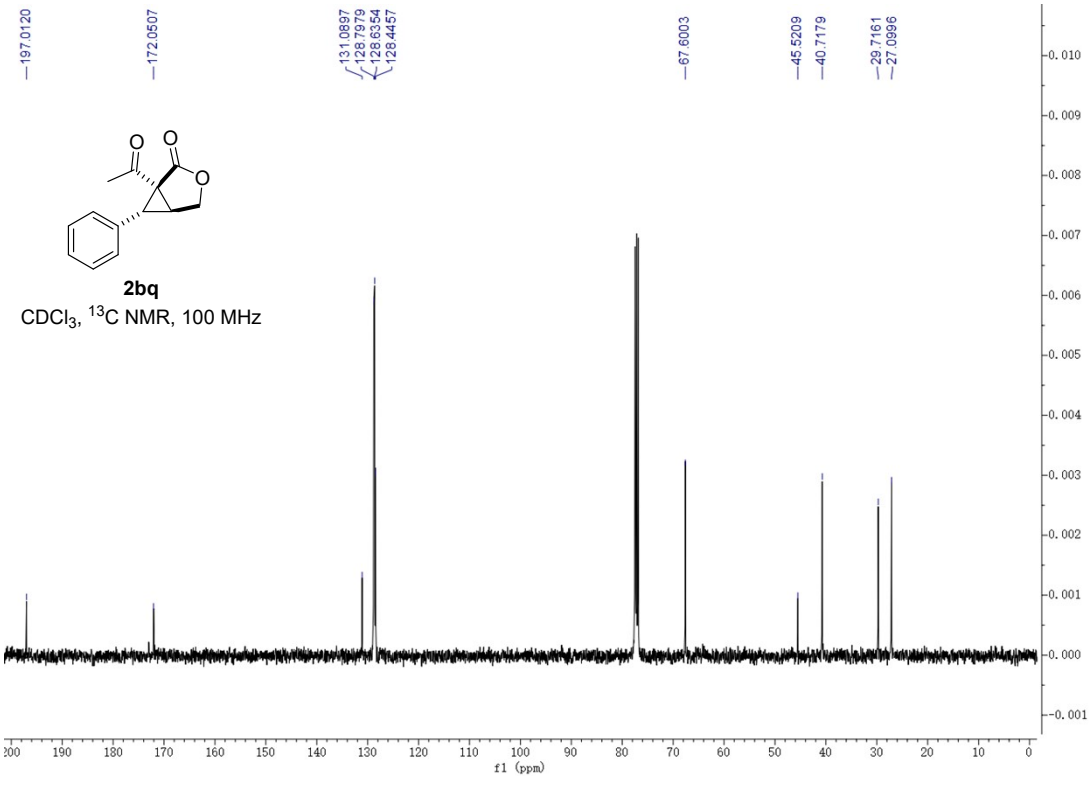
2bp

$CDCl_3$, ^{13}C NMR, 100 MHz



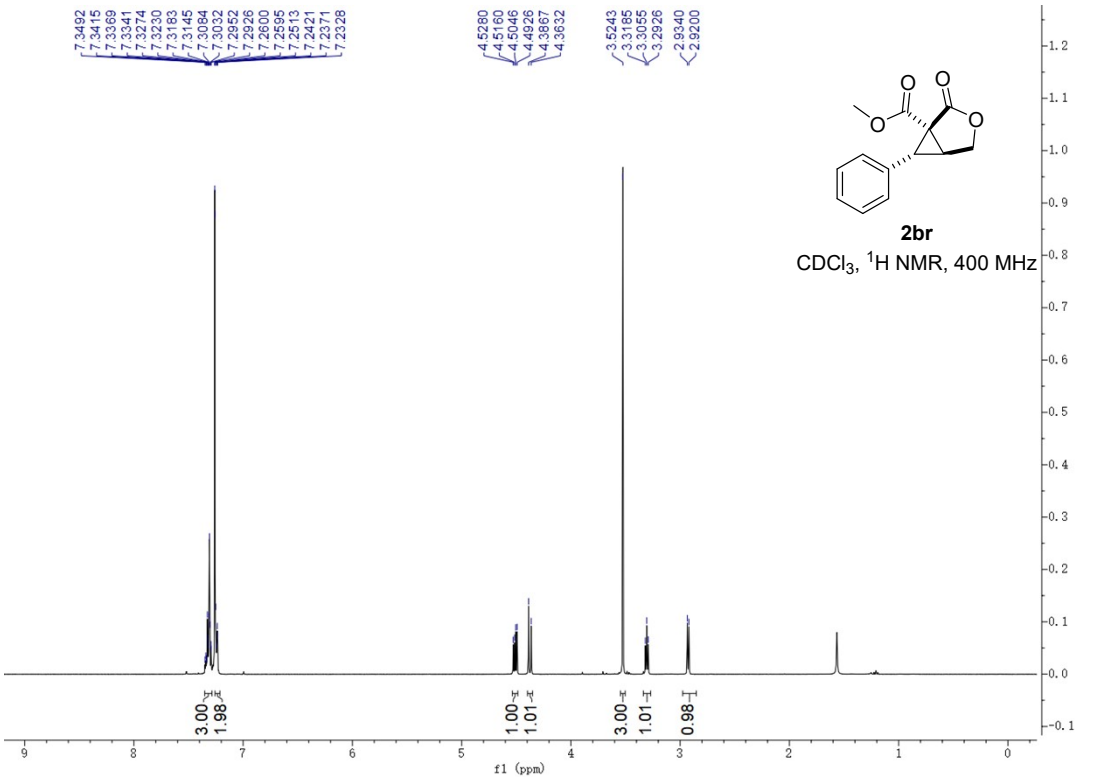
2bq

$CDCl_3$, ^1H NMR, 400 MHz



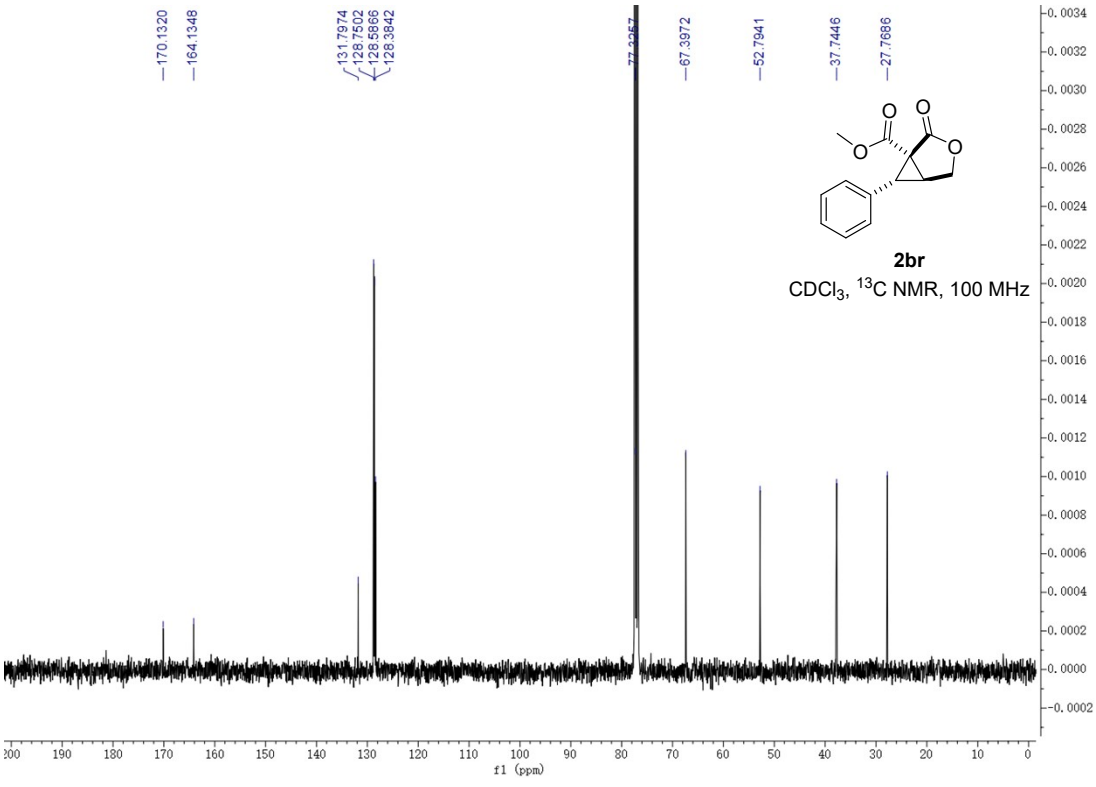
2bq

$CDCl_3$, ^{13}C NMR, 100 MHz



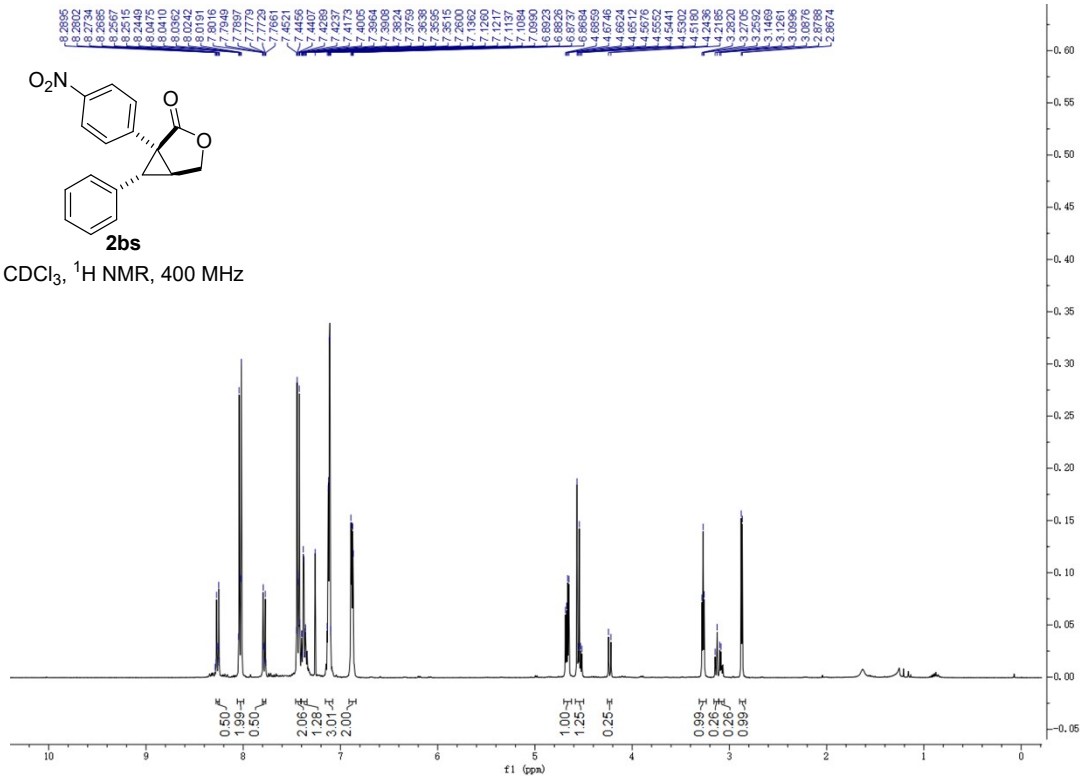
2br

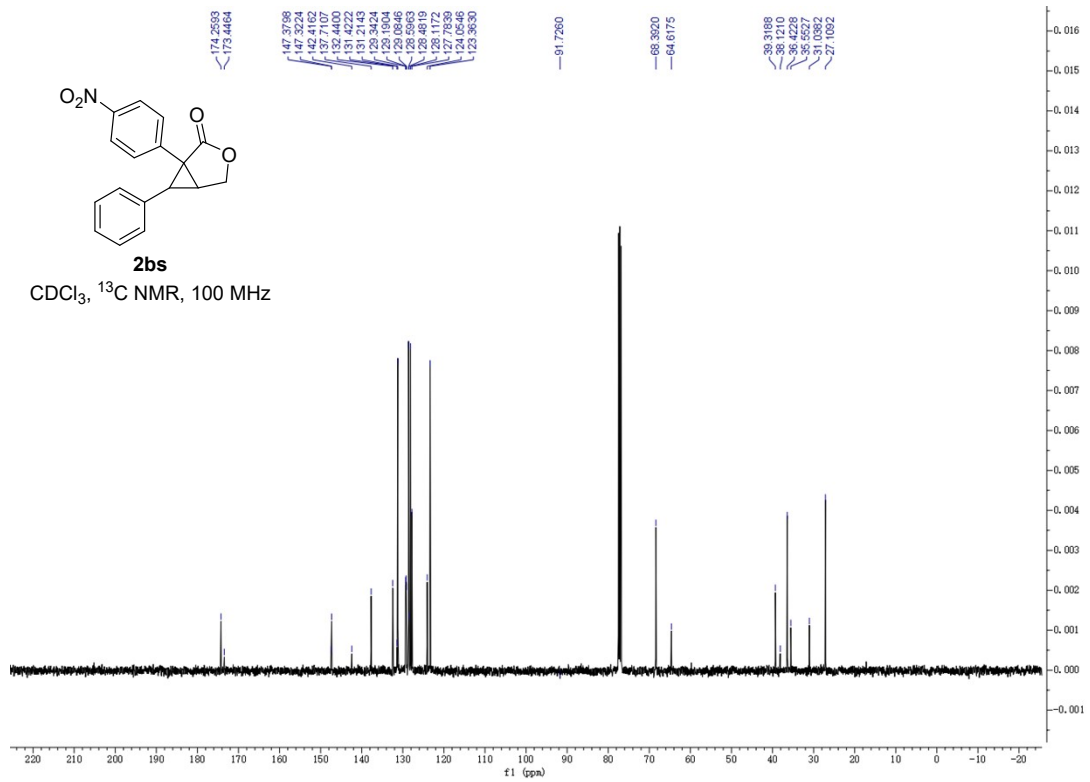
$CDCl_3$, ^1H NMR, 400 MHz

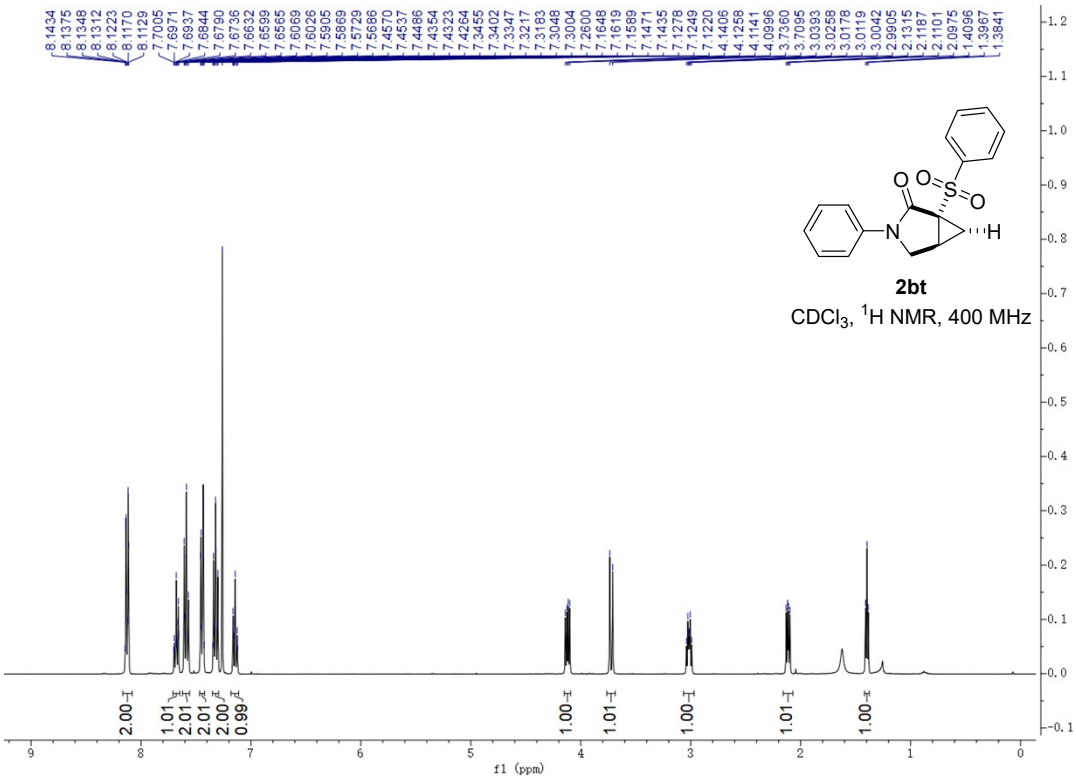


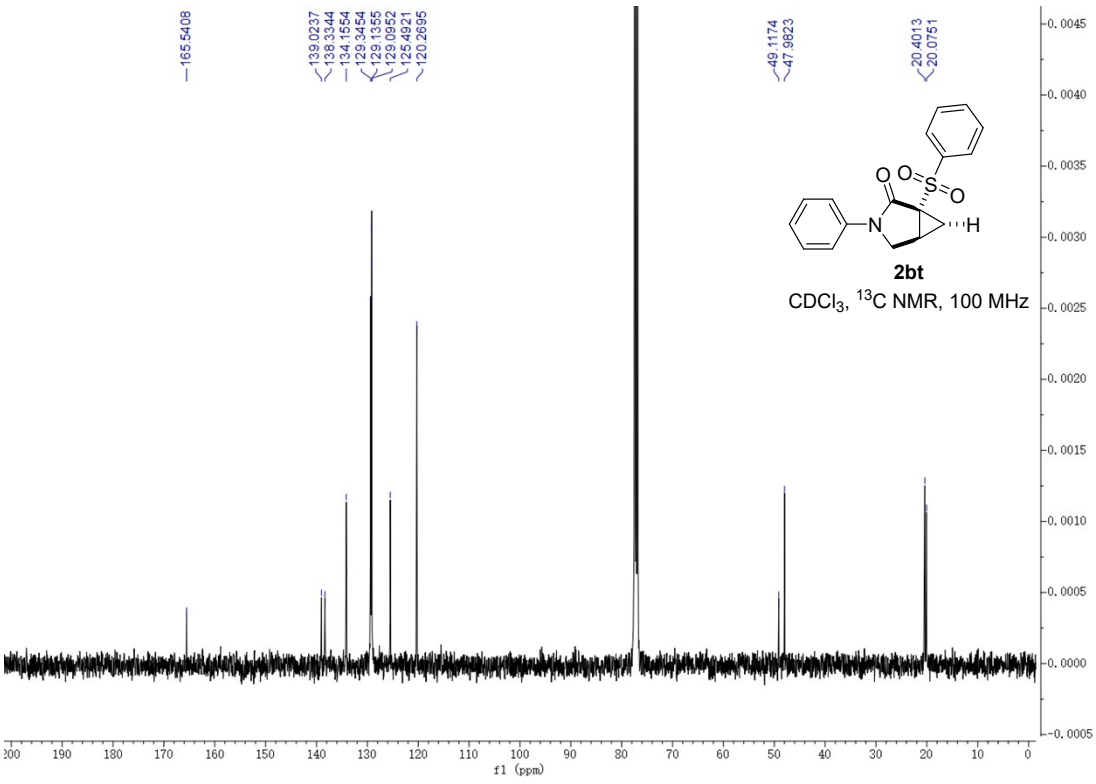
2br

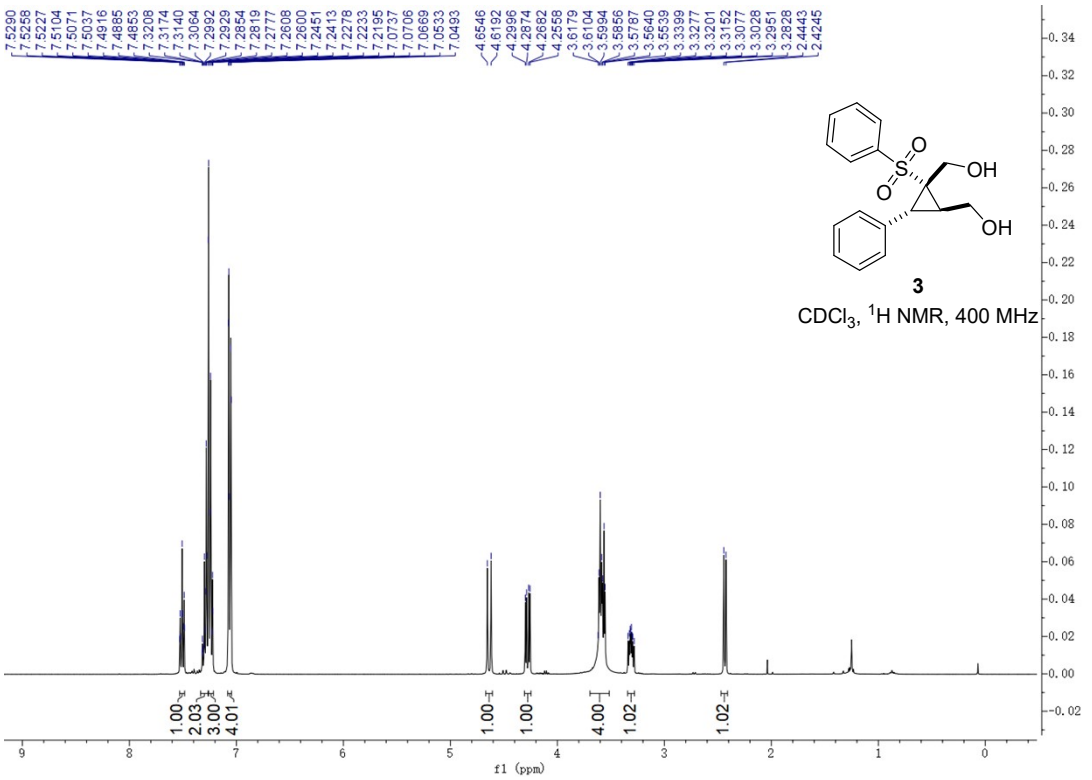
$CDCl_3$, ^{13}C NMR, 100 MHz

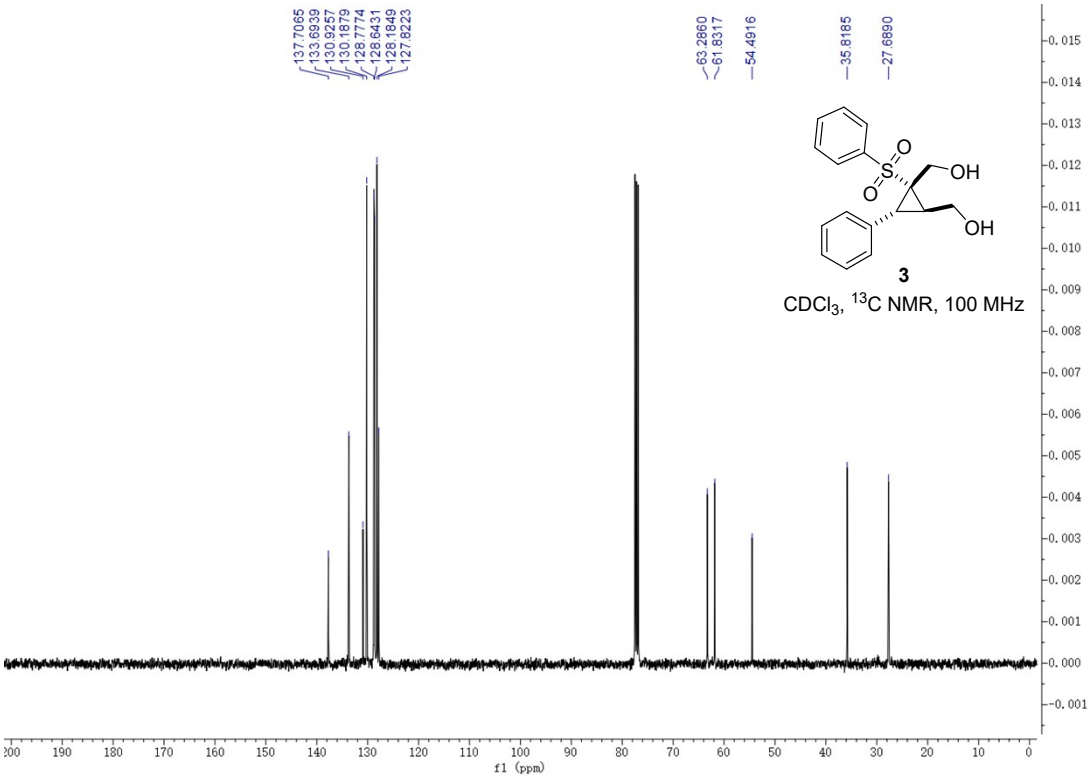

O2N
O
O
2bs
CDCl3, 1H NMR, 400 MHz
f1 (ppm)

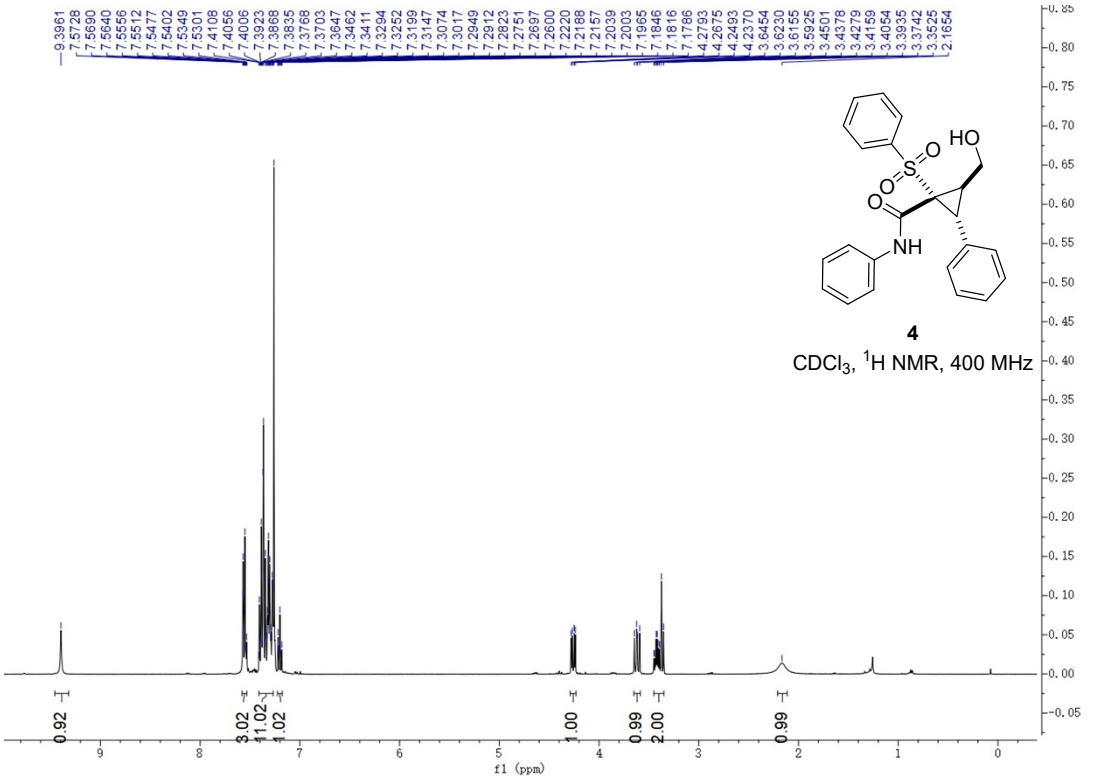

O2N
O
O
2bs
CDCl3, 13C NMR, 100 MHz
f1 (ppm)

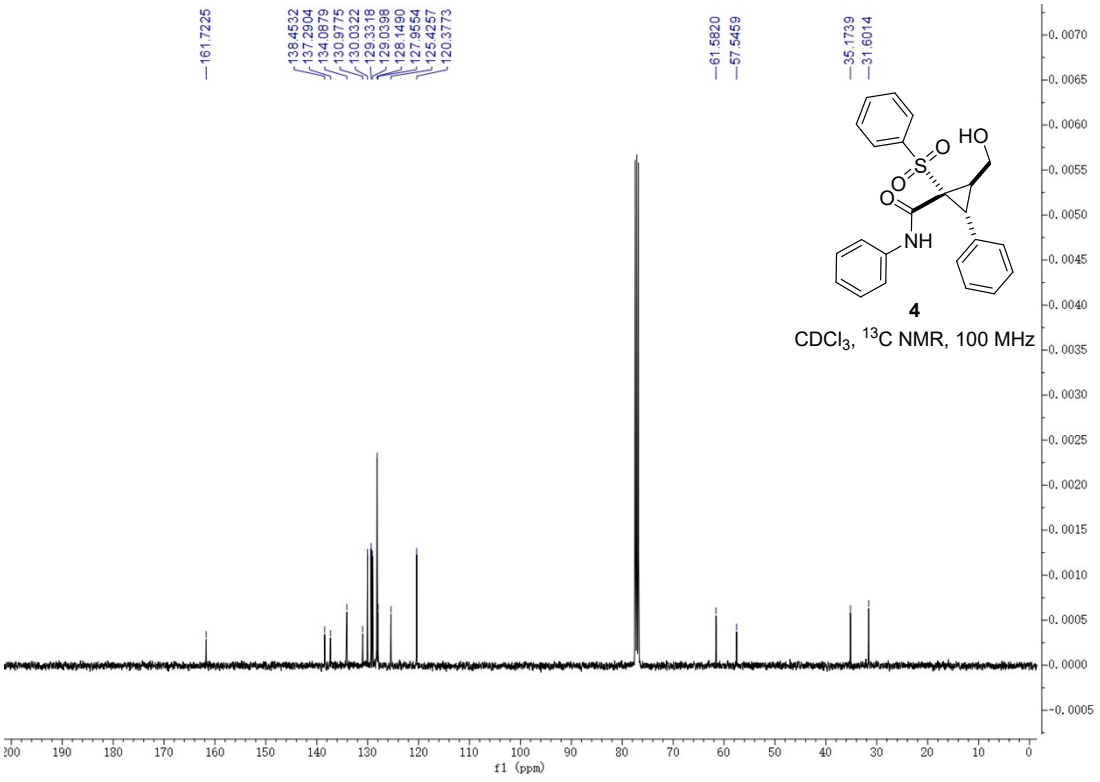

2bt
CDCl3, 1H NMR, 400 MHz
f1 (ppm)

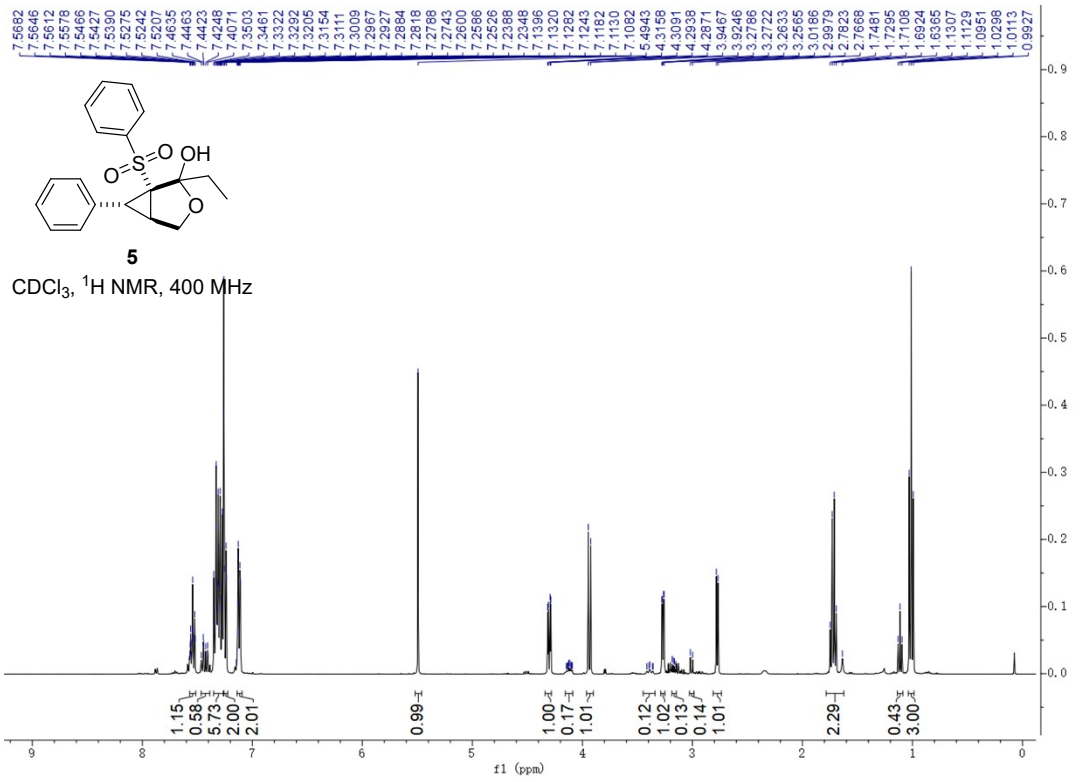

2bt
CDCl3, 13C NMR, 100 MHz
f1 (ppm)


7.5290
7.5258
7.5227
7.5104
7.5071
7.5037
7.4916
7.4885
7.4853
7.3208
7.3174
7.3140
7.3064
7.2992
7.2929
7.2854
7.2819
7.2777
7.2608
7.2600
7.2451
7.2413
7.2278
7.2233
7.2195
7.0737
7.0706
7.0669
7.0533
7.0493
4.6546
4.6192
4.2996
4.2874
4.2682
4.2558
3.6179
3.6104
3.5994
3.5856
3.5787
3.5640
3.5539
3.3399
3.3277
3.3201
3.3152
3.3077
3.3028
3.2951
3.2828
2.4443
2.4245
1.00
2.03
3.00
4.01
1.00
1.00
4.00
1.02
1.02
f1 (ppm)
OH
OH
3
CDCl3, 1H NMR, 400 MHz


137.7065
133.6939
130.9257
130.1879
128.7774
128.6431
128.1849
127.8223
63.2860
61.8317
54.4916
35.8185
27.6890
f1 (ppm)
OH
OH
3
CDCl3, 13C NMR, 100 MHz

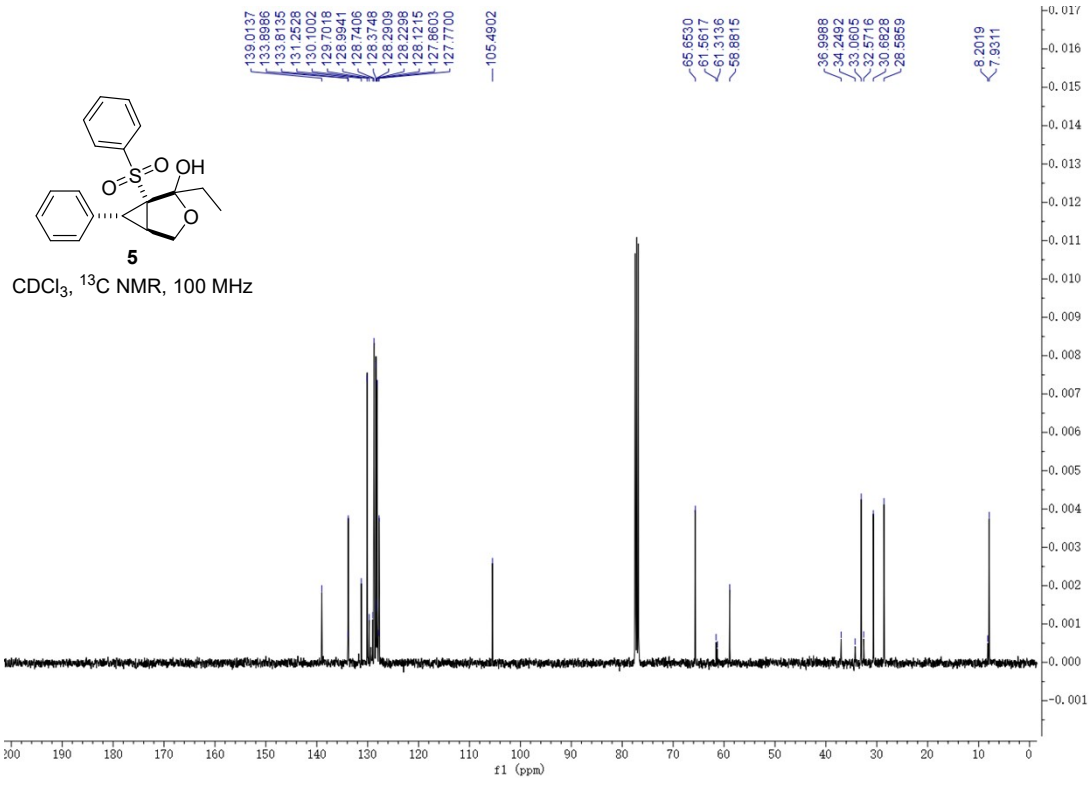

HO
O
S
O
O
NH
4
CDCl3, 1H NMR, 400 MHz
f1 (ppm)


HO
O
S
O
O
NH
4
CDCl3, 13C NMR, 100 MHz
f1 (ppm)



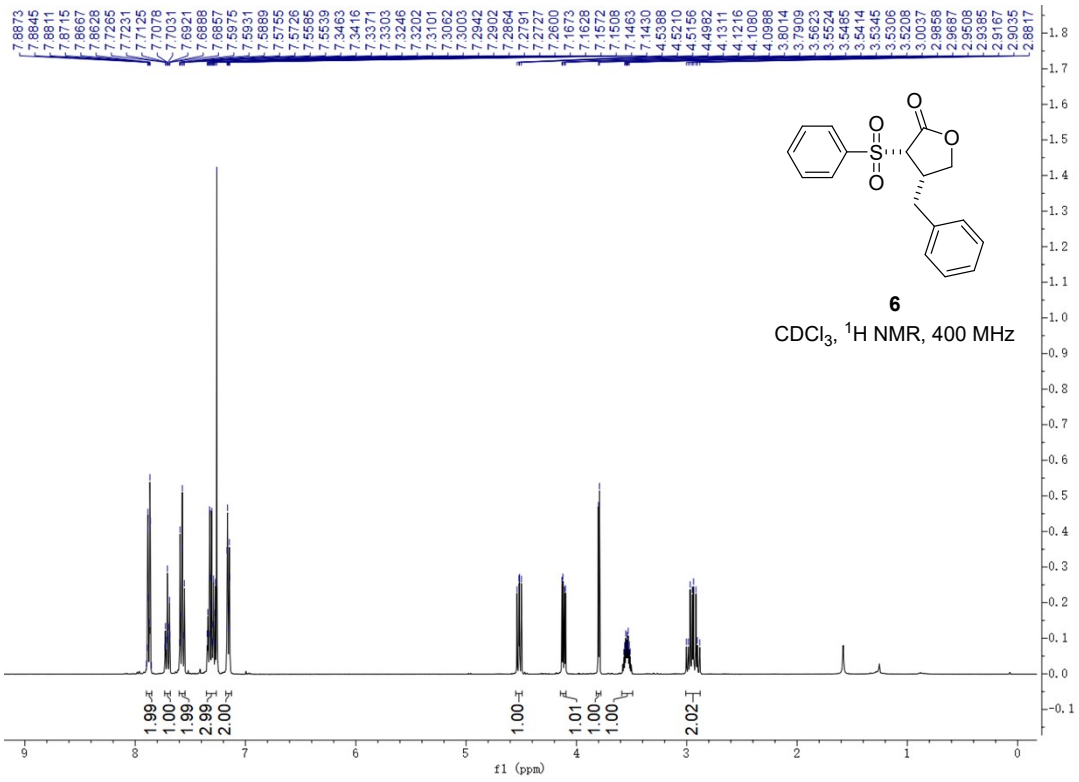
5

$CDCl_3$, ^1H NMR, 400 MHz



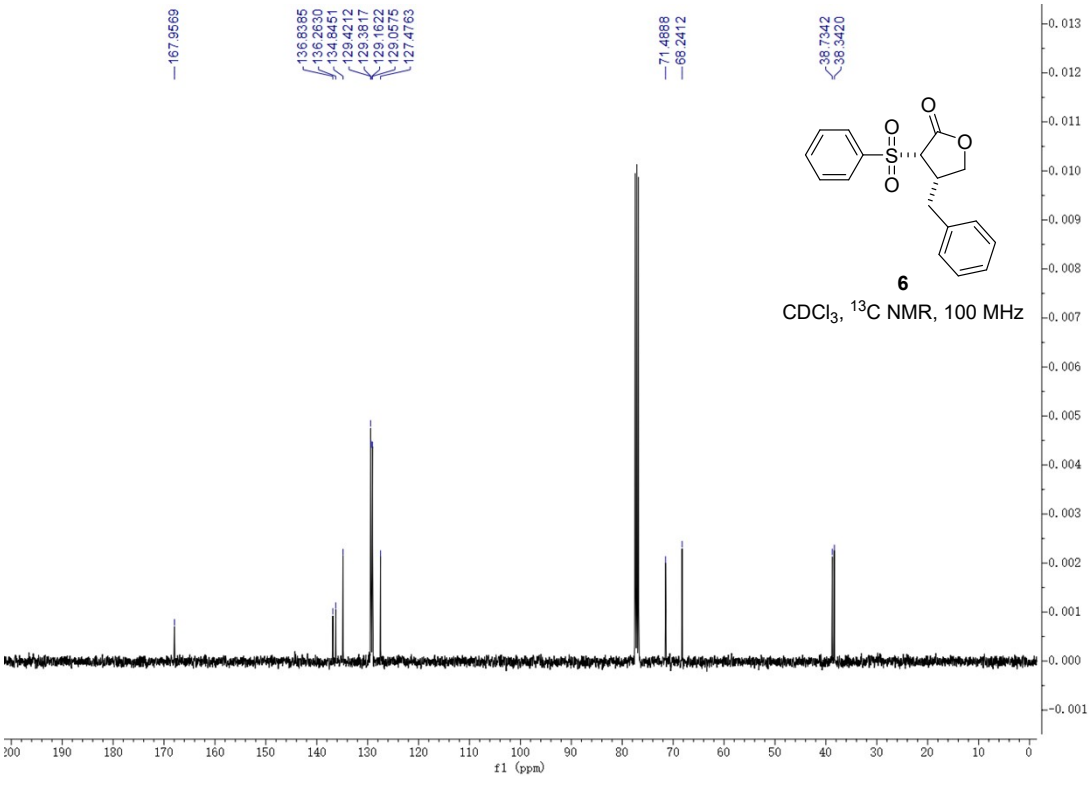
5

$CDCl_3$, ^{13}C NMR, 100 MHz



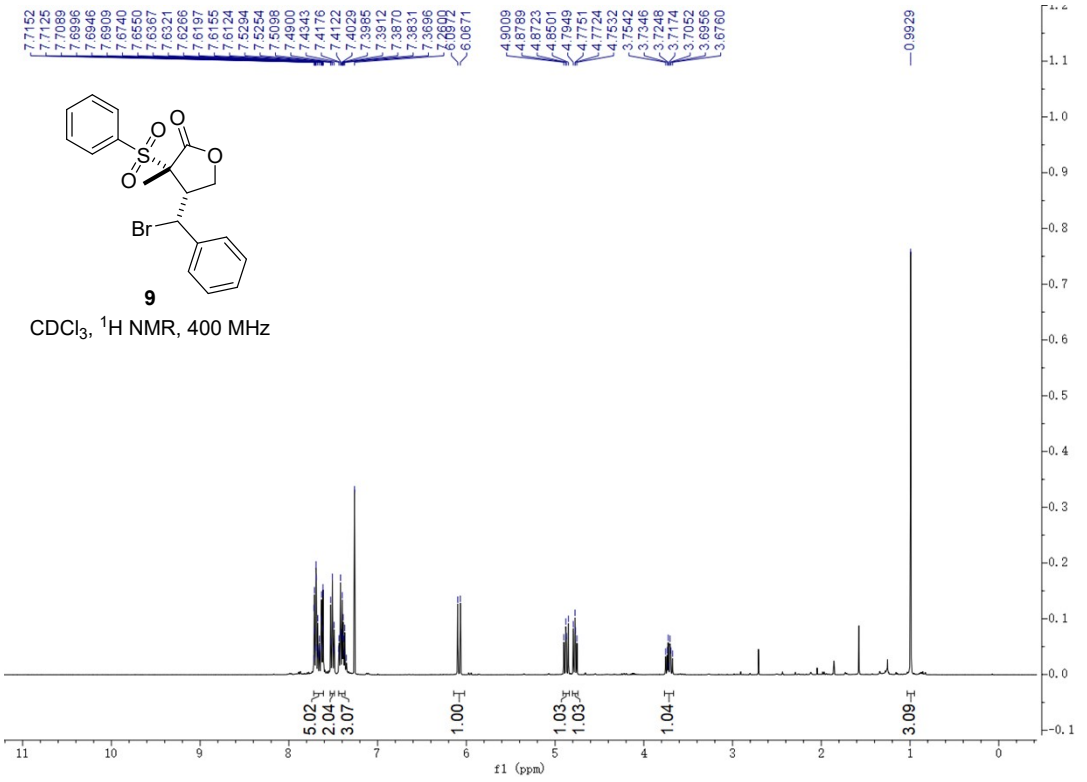
6

$CDCl_3$, ^1H NMR, 400 MHz



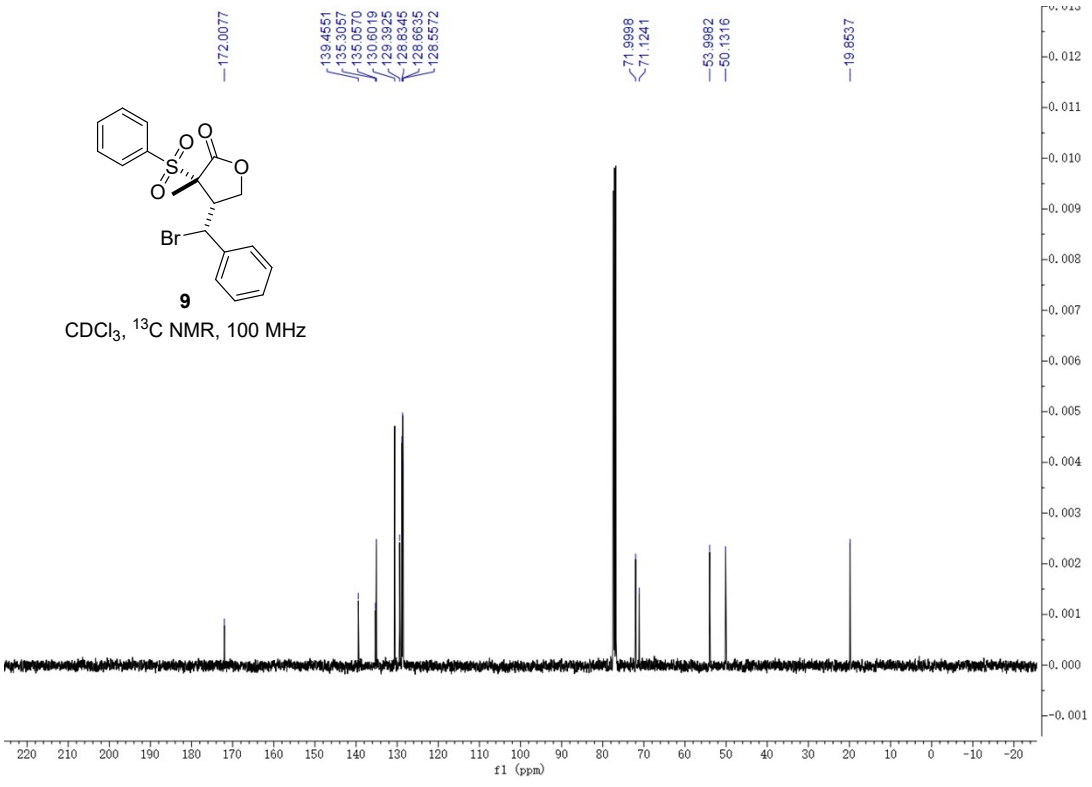
6

$CDCl_3$, ^{13}C NMR, 100 MHz



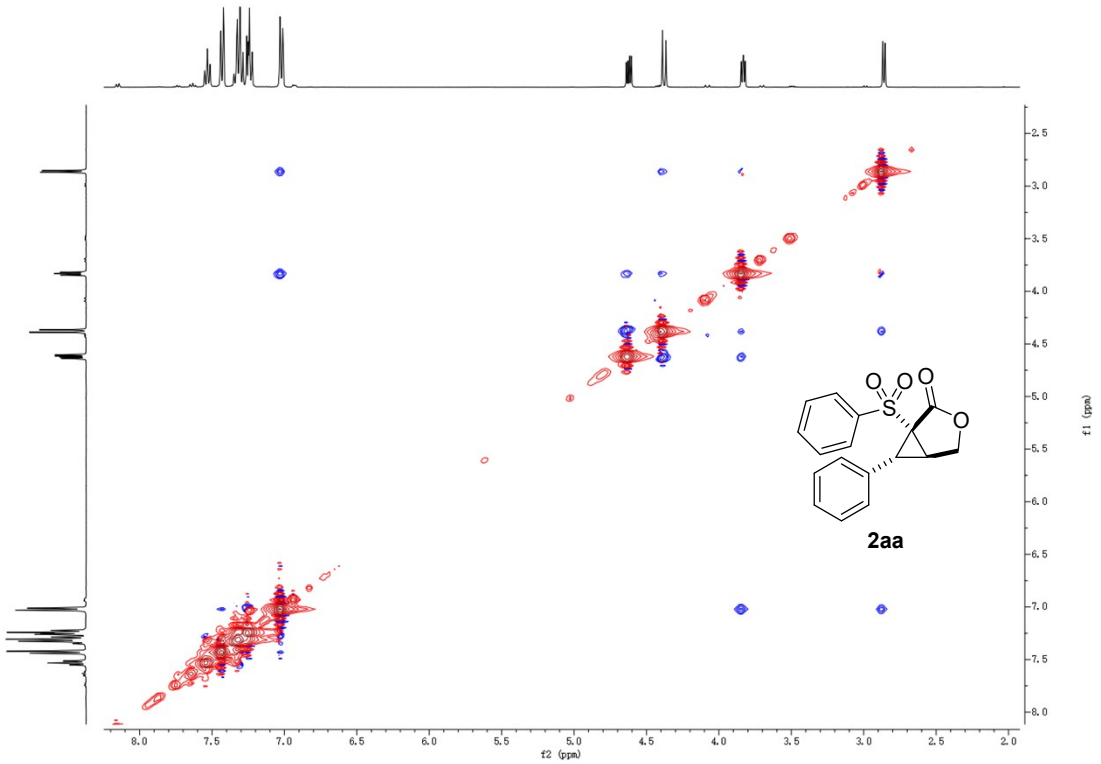
9

$CDCl_3$, ^1H NMR, 400 MHz

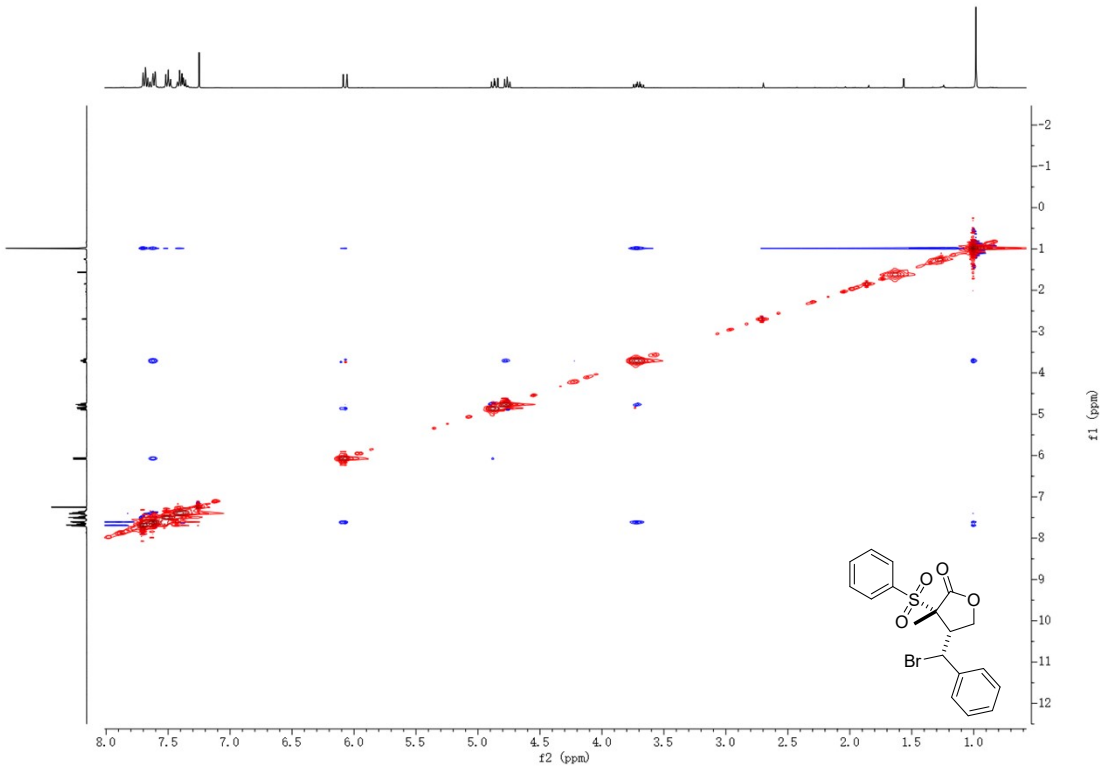


9

$CDCl_3$, ^{13}C NMR, 100 MHz



NOESY for compound **2aa**



NOESY for compound **9**