Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Atom- and Step-Economic 1,3-Difunctionalized Thiosulfonylation of Activated Allenes with Thiosulfonates to Access Vinyl Sulfones/Sulfides

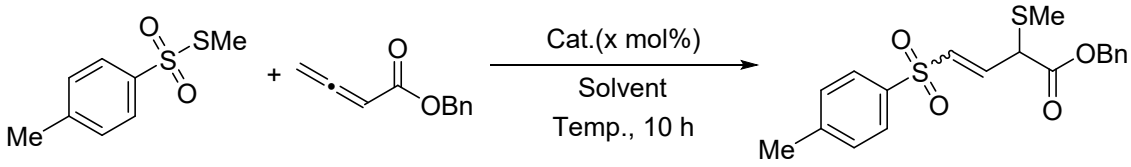
I. General information and materials

All reactions were performed with dry glassware under atmosphere of nitrogen unless otherwise noted. Anhydrous CH_3OH, EtOH, THF, *N*,*N*-dimethylformamide (DMF), Dichloromethane (CH_2Cl_2) were purchased from Energy-Chemical and directly used without further purification. All glassware was oven dried before use. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were purchased from Adamas-beta, Macklin Reagent, Energy Chemicals, Aladdin, JiuDing Chemicals or Bide Pharmatech Ltd.All the reactions were monitored by thin layer chromatography (TLC, Silica gel). The spots were visualized by UV light. Purification of products was conducted by flash chromatography on silica gel.

All experiments were conducted under inert atmosphere unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded on a Bruker Ascend™ 400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: ^1H (chloroform δ 7.26; DMSO δ 2.50), ^{13}C (chloroform δ 77.0; DMSO δ 39.5). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. Melting point (MP) was obtained on Hanon MP-430. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254nm. All GC-MS analyses were performed on an Agilent Technologies 8860 GC system equipped with a 5977B MS detector. High resolution mass spectra (HRMS) were obtained on Agilent 1290II-6545 spectrometer. Column chromatography was performed with silica gel (200-300 mesh ASTM).

The 2,3-dienoate adducts[1], allenyl phenyl ketone[2], disulfides[3], compound 5[4], selenium sulfonate[5] compound 1a and compound 1b were synthesized in one step from commercially available materials by literature methods.

II. Optimization of reaction conditions[a,b]

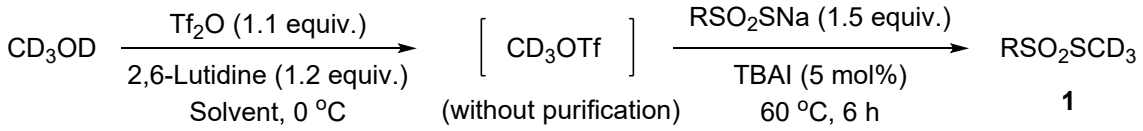


1a **2a** (1.5 equiv.) **3a**

Entry	Cat. (mol%)	Temp. (^{o}C)	Concentration (mL)	Solvent	Yield (%)
1	DABCO(10)	0	2	DCM	55
2	DABCO(10)	-10	2	DCM	66
3	DABCO(10)	-20	2	DCM	78
4	***DABCO(10)***	***-30***	***2***	***DCM***	***92***
5[d]	DABCO(10)	-35	2	DCM	73
6[e]	DABCO(10)	-40	2	DCM	66
7	DMAP(10)	-30	2	DCM	67
8	Quinine(10)	-30	2	DCM	trace
9	PPh_3(10)	-30	2	DCM	35
10[c]	DABCO(5)	-30	2	DCM	55
11	DABCO(15)	-30	2	DCM	78
12	DABCO(10)	-30	2	EA	69
13	DABCO(10)	-30	2	MeOH	50
14[c]	DABCO(10)	-30	2	DMSO	trace
15	DABCO(10)	-30	2	DMF	trace
16	DABCO(10)	-30	2	MeCN	trace
17	DABCO(10)	-30	1.5	DCM	83
18	DABCO(10)	-30	2.5	DCM	86

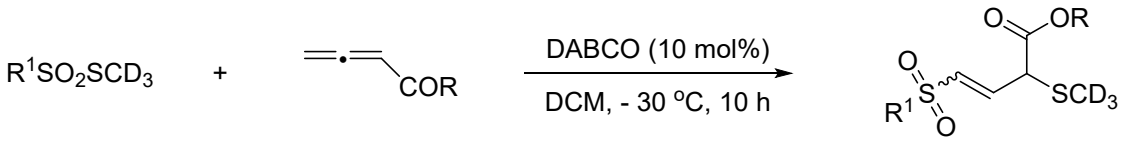
[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2a** (0.24 mmol, 1.2 equiv.), and catalyst (0.02 mmol, 10 mol%) were added to solvent for 10 h. [b]Yield was detected by ^{1}H-NMR. [c]Isolated yield. [d]The reaction was conducted at -30 ^{o}C for 16 h. [e]The reaction was conducted at -30 ^{o}C for 14 h.

III. General procedures for the synthesis of deuterated methylthiolating reagent [6]



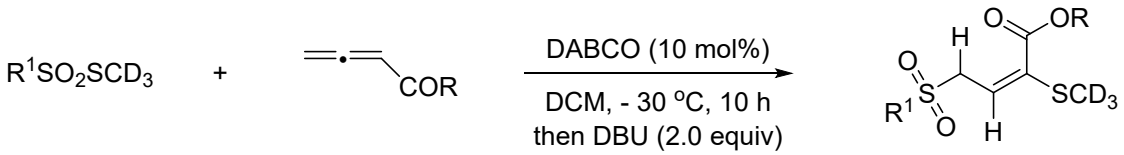
To a flame dried Schlenk tube equipped with a stirring bar were added CD_3OD (40.6 μL, 1 mmol, 1.0 equiv.), 2,6-lutidine (161.2 μL, 1.4 mmol, 1.4 equiv.), dry DMF (2 mL) and Tf_2O (201.8 μL, 1.2 mmol, 1.2 equiv.) added sequentially under N_2. The reaction mixture was stirred at 0 °C for 90 min. After that, sodium sulfonothioate (1.5 mmol, 1.5 equiv.) and TBAI (18.5 mg, 0.05 mmol, 5 mol%) was added to the mixture. The reaction was stirred for a further 6 h at 60 °C. The reaction mixture was quenched with water (10 mL) and then extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (15 mL), dried over sodium sulfate, filtrated and concentrated. The crude product was purified by column chromatography (Ethyl Acetate/ Petroleum Ether: 1/30 to 1/15) to afford deuterated methylthiolating reagent **1b-1i**.

IV. 1,3-Difunctionlizations of activated allenes to access sulfones/sulfides



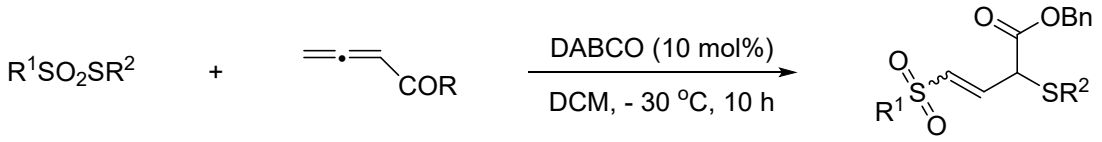
1 **2** **3**

To a Schlenk tube equipped with a stirring bar were added S-methylthiolating reagent **1** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C . The reaction mixture was stirred at -30 °C for 10 h. The reaction mixture was quenched with water (10 mL) and then extracted with DCM (3 × 10 mL). The combined organic layer was dried over sodium sulfate, filtrated and concentrated. The crude product was purified by column chromatography (Ethyl Acetate/ Petroleum Ether: 1/30 to 1/7) to afford compound **3a-3o.**



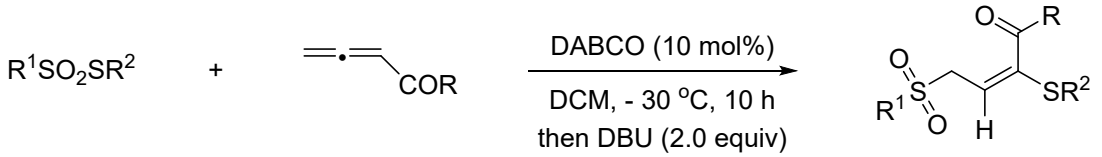
1 **2** **4**

To a Schlenk tube equipped with a stirring bar were added S-methylthiolating reagent **1** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C. The reaction mixture was stirred at -30 °C for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h. The reaction mixture was quenched with water (10 mL) and then extracted with DCM (3 × 10 mL). The combined organic layer was dried over sodium sulfate, filtrated and concentrated. The crude product was purified by column chromatography (Ethyl Acetate/ Petroleum Ether: 1/15 to 1/4) to afford compound **4a-4f**.



5 **2** **6**

To a Schlenk tube equipped with a stirring bar were added S-methylthiolating reagent **5** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C . The reaction mixture was stirred at -30 °C for 10 h. The reaction mixture was quenched with water (10 mL) and then extracted with DCM (3 × 10 mL). The combined organic layer was dried over sodium sulfate, filtrated and concentrated. The crude product was purified by column chromatography (Ethyl Acetate/ Petroleum Ether: 1/30 to 1/7) to afford compound **6a-6z.**

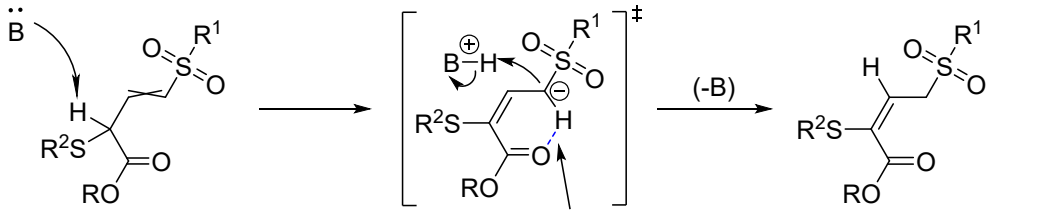


5 **2** **7**

To a Schlenk tube equipped with a stirring bar were added S-methylthiolating reagent **5** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C . The reaction mixture was stirred at -30 °C for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h. The reaction mixture was quenched with water (10 mL) and then extracted with DCM (3 × 10 mL). The combined organic layer was dried over sodium sulfate, filtrated and concentrated. The crude product was purified by column chromatography (Ethyl Acetate/ Petroleum Ether: 1/15 to 1/4) to afford compound **7a-7d**.

V. Mechanism of isomerization and its control experiments

The probable mechanism for synthesis of compound 4 or 7

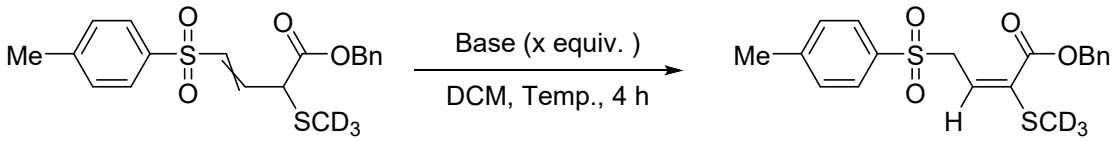


Compound **3** or **6**

The formation of intramolecular H-bond interaction can enhance the reactivity of anionic intermediate

4 or **7**
(*E*-configuration product)

Control experiments[a,b]

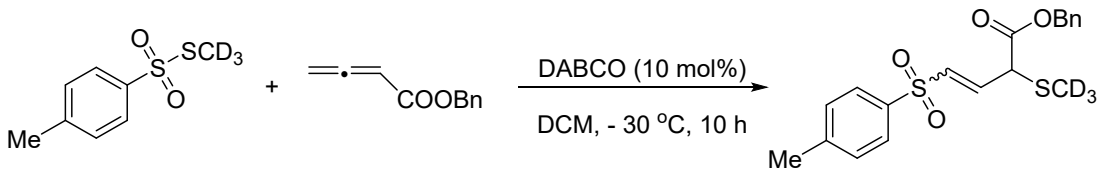


3a **4a**

Entry	Base	x	Temp. (°C)	Yield (%)
1	DABCO	0.1	reflux	N.R.
2	DABCO	2.0	r.t.	N.D.
3	DBU	2.0	r.t.	87

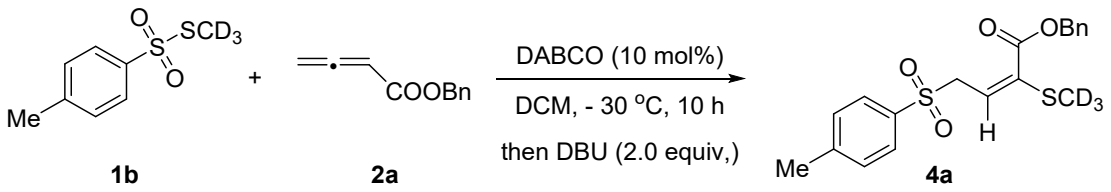
[a]N.R.= No reaction. [b]N.D.= Not detected.

VI. Gram-scale operations and further transformations



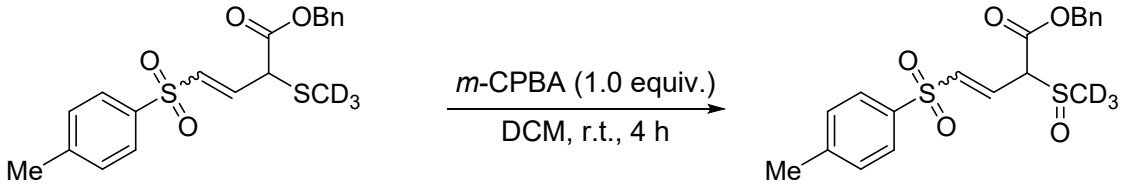
1b **2a** **3b**

To a Schlenk tube equipped with a stirring bar were added S-methylthiolating reagent **1b** (6.0 mmol, 1 equiv.), allenes **2a** (7.2 mmol, 1.2 equiv.), and DABCO (0.6 mmol, 10 mol%) were added to DCM at -30 °C . The reaction mixture was stirred at -30 °C for 10 h. The reaction mixture was quenched with water (50 mL) and then extracted with DCM (3 × 50 mL). The combined organic layer was dried over sodium sulfate, filtrated and concentrated. The crude product was purified by column chromatography (Ethyl Acetate/ Petroleum Ether: 1/20 to 1/7) to afford compound **3b** (1.93 g, 85 yield%, D.-inc > 99%) as yellow oil**.**



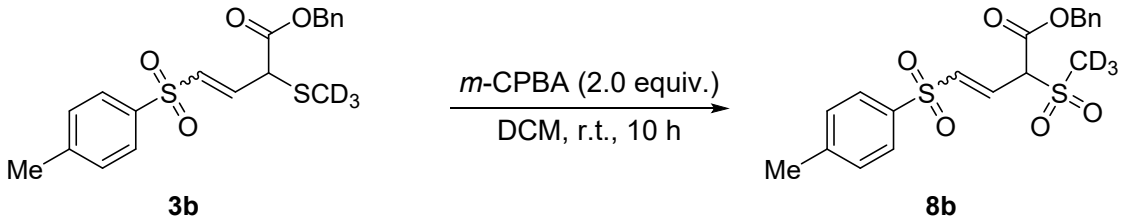
1b **2a** **4a**

To a Schlenk tube equipped with a stirring bar were added S-methylthiolating reagent **1b** (5.0 mmol, 1 equiv.), allenes **2a** (6.0 mmol, 1.2 equiv.), and DABCO (0.5 mmol, 10 mol%) were added to DCM at -30 °C . The reaction mixture was stirred at -30 °C for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h.The reaction mixture was quenched with water (50 mL) and then extracted with DCM (3 × 50 mL). The combined organic layer was dried over sodium sulfate, filtrated and concentrated. The crude product was purified by column chromatography (Ethyl Acetate/ Petroleum Ether: 1/15 to 1/4) to afford compound **4a** (1.18 g, 63 yield%, D.-inc > 99%) as yellow oil.



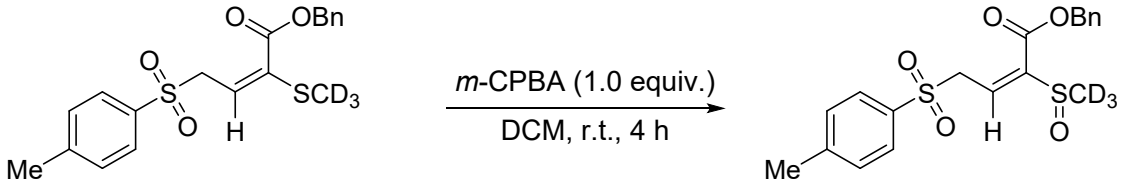
3b **8a**

To a Schlenk tube under air atmosphere were added **3b** (0.2 mmol, 1 equiv.), *m*-CPBA (85%, 0.2 mmol, 1.0 equiv.), and DCM (2.0 mL). The system was stirred at room temperature for 4 h to afford **8a** (68.7 mg, 87 % yield, D-inc. >99.9% and 1:1 *dr*) as a colourless oil.



3b **8b**

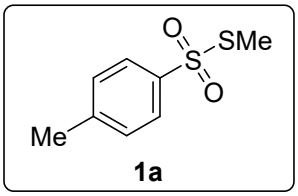
To a Schlenk tube under air atmosphere were added **3b** (0.2 mmol, 1 equiv.), *m*-CPBA (85%, 0.4 mmol, 2.0 equiv.), and DCM (2.0 mL). The system was stirred at room temperature for 10 h to afford **8a** (65.8 mg, 80 % yield, D-inc. >99.9%) as a colourless oil.



4a **9a**

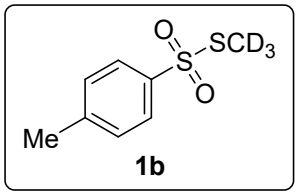
To a Schlenk tube under air atmosphere were added **4a** (0.2 mmol, 1 equiv.), *m*-CPBA (85%, 0.2 mmol, 1.0 equiv.), and DCM (2.0 mL). The system was stirred at room temperature for 4 h to afford **9a** (68.7 mg, 87% yield, D-inc. >99.9% and Z/E = 1/1) as a colourless oil.

VII. Spectroscopic data of compounds



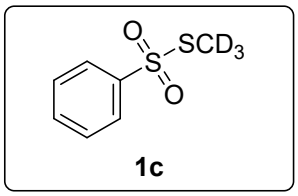
1a

To a flame dried Schlenk tube equipped with a stirring bar were added CH_3OH (40.4 μL, 1 mmol, 1.0 equiv.), 2,6-lutidine (138.2 μL, 1.2 mmol, 1.2 equiv.), dry DMF (2 mL) and Tf_2O (185.0 μL, 1.1 mmol, 1.1 equiv.) added sequentially under N_2. The reaction mixture was stirred at 0 °C for 90 min. After that, TsSNa (315.0 mg, 1.5 mmol, 1.5 equiv.) and TBAI (18.5 mg, 0.05 mmol, 5 mol%) was added to the mixture. The reaction was stirred for a further 6 h at 60 °C. The reaction mixture was quenched with water (10 mL) and then extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (15 mL), dried over sodium sulfate, filtrated and concentrated. The title compound **1a** was isolated as a white solid (163.6 mg, 81%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (70/1 to 50/1). (R_f 0.7, petroleum ether/ethyl acetate = 10/1). D-inc. >99% (determined by **^{1}H NMR**). **MP**: 56.0 – 57.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 2.49 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.9, 140.9, 129.9, 127.3, 21.8, 18.1. **MS** (EI) m/z 202.01 $[M]^+$.[7]



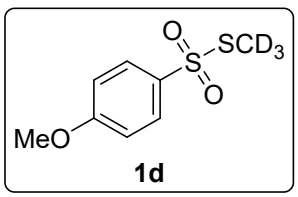
1b

The reaction of the CD_3OD (36.07 mg, 1.0 mmol, 1.0 equiv.), 2,6-Lutidine (150.1 mg, 1.4 mmol, 1.4 equiv.), Tf_2O (338.6 mg, 1.4 mmol, 1.4 equiv.), $C_7H_7NaO_2S$ (1.5 mmol, 1.5 equiv.), TBAI (0.05 mmol, 5 mol%) in DMF (dry., 2.5 ml) at 60 °C for 6 h afforded compound **1b** in 84 % total yield of two-step (151.1 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **1b** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 15/1). (Rf 0.5, petroleum ether/ethyl acetate = 15/1). **MP:** 56.5 – 57.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.9, 141.1, 129.9, 127.3, 21.8. **MS** (EI) m/z 205.03 $[M]^+$.[8]



1c

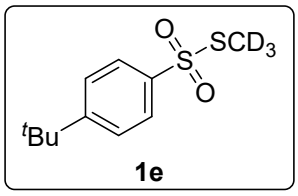
The reaction of the CD_3OD (36.07 mg, 1.0 mmol, 1.0 equiv.), 2,6-Lutidine (150.1 mg, 1.4 mmol, 1.4 equiv.), Tf_2O (338.6 mg, 1.4 mmol, 1.4 equiv.), $C_6H_5NaO_2S$ (1.5 mmol, 1.5 equiv.), TBAI (0.05 mmol, 5 mol%) in DMF (dry., 2.5 ml) at 60 °C for 6 h afforded compound **1c** in 80 % total yield of two-step (151.1 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **1c** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 15/1). (Rf 0.5, petroleum ether/ethyl acetate = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 2H), 7.67 – 7.61 (m, 1H), 7.59 – 7.53 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.7, 133.7, 129.2, 127.0, **HRMS (**ESI-TOF**)** for $C_7H_5D_3O_2S_2$ $[M+Na]^+$ calcd for 214.0046, found 214.0046.



1d

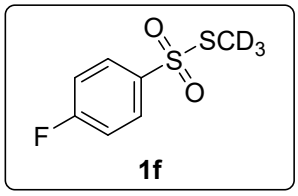
The reaction of the CD_3OD (36.07 mg, 1.0 mmol, 1.0 equiv.), 2,6-Lutidine (150.1 mg, 1.4 mmol, 1.4 equiv.), Tf_2O (338.6 mg, 1.4 mmol, 1.4 equiv.), $C_7H_7NaO_3S$ (1.5 mmol, 1.5 equiv.), TBAI (0.05 mmol, 5 mol%) in DMF (dry., 2.5 ml) at 60 °C for 6 h afforded compound **1d** in 84 % total yield of two-step (163.8 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a white oil. The title compound **1d** was isolated through flash

chromatography on silica gel eluting with petroleum ether/ethyl acetate (25/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.72 (m, 2H), 7.11 – 6.84 (m, 2H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.6, 135.2, 1293, 114.2, 55.7; **HRMS** (ESI-TOF) for $C_8H_7D_3O_3S_2$ $[M+Na]^+$ calcd for 244.0152, Found 244.0155.



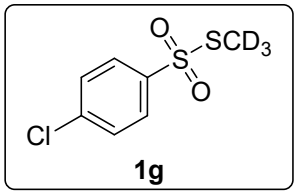
1e

The reaction of the CD_3OD (36.07 mg, 1.0 mmol, 1.0 equiv.), 2,6-Lutidine (150.1 mg, 1.4 mmol, 1.4 equiv.), Tf_2O (338.6 mg, 1.4 mmol, 1.4 equiv.), $C_{10}H_{13}NaO_2S$ (1.5 mmol, 1.5 equiv.), TBAI (0.05 mmol, 5 mol%) in DMF (dry., 2.5 ml) at 60 °C for 6 h afforded compound **1e** in 74 % total yield of two-step (183.1 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **1e** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (25/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 1.42 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 140.6, 126.8, 126.1, 35.1, 30.9; **HRMS (**ESI-TOF**)** for $C_{11}H_{13}D_3O_2S_2$ $[M+Na]^+$ calcd 270.0672, found 270.0672.



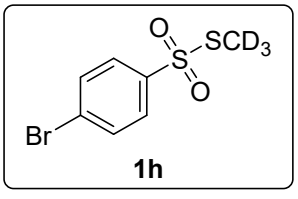
1f

The reaction of the CD_3OD (36.07 mg, 1.0 mmol, 1.0 equiv.), 2,6-Lutidine (150.1 mg, 1.4 mmol, 1.4 equiv.), Tf_2O (338.6 mg, 1.4 mmol, 1.4 equiv.), $C_6H_4FNaO_2S$ (1.5 mmol, 1.5 equiv.), TBAI (0.05 mmol, 5 mol%) in DMF (dry., 2.5 ml) at 60 °C for 6 h afforded compound **1f** in 79% total yield of two-step (165.3 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **1f** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 15/1). (Rf 0.5, petroleum ether/ethyl acetate = 15/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 1H), 7.24 – 7.17 (m, 1H); **^{13}C NMR** (100 MHz, CDCl3) δ 165.5 (d, $^1J_{C\text{-}F}$ = 1020 Hz), 139.7 (d, $^4J_{C\text{-}F}$ = 16 Hz), 123.0 (d, $^3J_{C\text{-}F}$ = 40 Hz), 116.5 (d, $^2J_{C\text{-}F}$ = 92 Hz); **^{19}F NMR** (376 MHz, CDCl3) δ -103.0; **HRMS (**ESI-TOF**)** for $C_7H_4D_3FO_2S_2$ $[M+Na]^+$ calcd 231.9952, found 231.9953.



1g

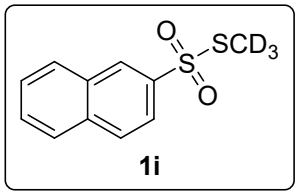
The reaction of the CD_3OD (36.07 mg, 1.0 mmol, 1.0 equiv.), 2,6-Lutidine (150.1 mg, 1.4 mmol, 1.4 equiv.), Tf_2O (338.6 mg, 1.4 mmol, 1.4 equiv.), $C_6H_4ClNaO_2S$ (1.5 mmol, 1.5 equiv.), TBAI (0.05 mmol, 5 mol%) in DMF (dry., 2.5 ml) at 60 °C for 6 h afforded compound **1g** in 80% total yield of two-step (180.6 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **1g** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 15/1). (Rf 0.5, petroleum ether/ethyl acetate = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.58 – 7.49 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.7, 132.5, 128.9, 128.5; **HRMS (**ESI-TOF**)** for $C_7H_4D_3ClrO_2S_2$ $[M+Na]^+$ calcd 247.9656, found 247.9655.



1h

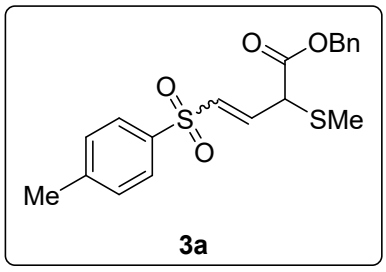
The reaction of the CD_3OD (36.07 mg, 1.0 mmol, 1.0 equiv.), 2,6-Lutidine (150.1 mg, 1.4 mmol, 1.4 equiv.), Tf_2O (338.6 mg, 1.4 mmol, 1.4 equiv.), $C_6H_4BrNaO_2S$ (1.5 mmol, 1.5 equiv.), TBAI (0.05 mmol, 5 mol%) in DMF (dry., 2.5 ml) at 60 °C for 6 h afforded compound **1h** in 78% total yield of two-step (210.8 mg) and D-inc.＞99%

(determined by **^{1}H NMR**) as a yellow oil. The title compound **1h** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 15/1). (Rf 0.5, petroleum ether/ethyl acetate = 15/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 2H); **^{13}C NMR** (100 MHz, CDCl3) δ 142.6, 132.5, 128.8, 128.5. **HRMS (**ESI-TOF**)** for $C_7H_4D_3BrO_2S_2$ $[M+Na]^+$ calcd 291.9151, found 291.9155.



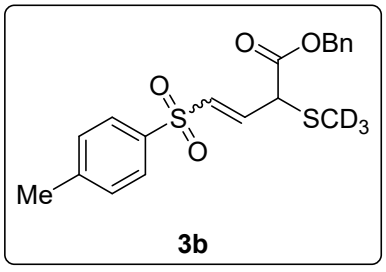
1i

The reaction of the CD_3OD (36.07 mg, 1.0 mmol, 1.0 equiv.), 2,6-Lutidine (150.1 mg, 1.4 mmol, 1.4 equiv.), Tf_2O (338.6 mg, 1.4 mmol, 1.4 equiv.), $C_{10}H_7NaO_2S_2$ (1.5 mmol, 1.5 equiv.), TBAI (0.05 mmol, 5 mol%) in DMF (dry., 2.5 ml) at 60 °C for 6 h afforded compound **1i** in 77 % total yield of two-step (185.8 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a yellow oil**.** The title compound **1i** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 15/1). (Rf 0.5, petroleum ether/ethyl acetate = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.02 – 7.97 (m, 2H), 7.95 – 7.87 (m, 2H), 7.71 – 7.61 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.2, 135.1, 131.7, 129.9, 129.5, 129.4, 128.6, 128.0, 127.9, 122.0. **HRMS (**ESI-TOF**)** for $C_{11}H_7D_3O_2S_2$ $[M+Na]^+$ calcd 262.0203, found 262.0200.



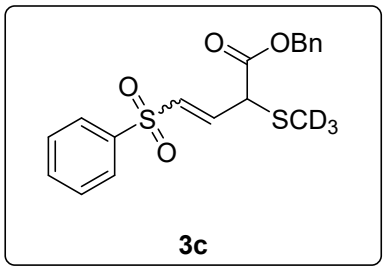
3a

The reaction of the S-methylthiolating reagent **1a** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3a** in 91% yield (68.5 mg) as a yellow oil. The title compound **3a** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.25 – 7.19 (m, 4H), 6.63 (s, 1H), 6.36 (s, 1H), 4.99 (d, *J* = 12.3 Hz, 1H), 4.93 (d, *J* = 12.3 Hz, 1H), 4.26 (s, 1H), 2.36 (s, 3H), 1.94 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 145.7, 144.8, 135.6, 134.9, 129.8, 128.7, 128.5, 128.4, 128.3, 128.0, 67.5, 45.8, 21.6, 15.0; **HRMS (**ESI-TOF**)** for $C_{19}H_{24}O_4S_2$ $[M+Na]^+$ calcd 399.0695, Found 399.0696.



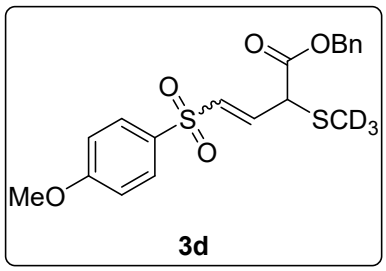
3b

The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3b** in 92% yield (70.5 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a colourless oil. The title compound **3b** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.24 (m, 3H), 7.21 – 7.16 (m, 4H), 6.60 (s, 1H), 6.33 (s, 1H), 4.95 (d, *J* = 12.3 Hz, 1H), 4.90 (d, *J* = 12.3 Hz, 1H), 4.22 (s, 1H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 145.7, 144.9, 135.6, 135.0, 129.8, 128.7, 128.5, 128.4, 128.4, 128.0, 67.5, 45.7, 21.6; **HRMS (**ESI-TOF**)** for $C_{19}H_{17}D_3O_4S_2$ $[M+Na]^+$ calcd 405.1118, Fund 405.1118.



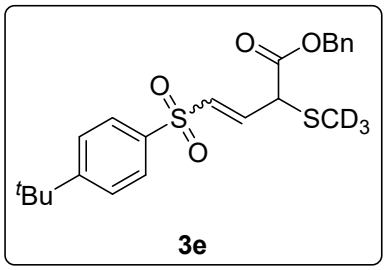
3c

The reaction of the S-methylthiolating reagent **1c** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3c** in 88% yield (64.4 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a colourless oil. The title compound **3c** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.44 – 7.38 (m, 2H), 7.27 (d, *J* = 5.9 Hz, 3H), 7.20 – 7.16 (m, 2H), 6.63 (s, 1H), 6.37 (s, 1H), 4.94 (d, *J* = 12.3 Hz, 1H), 4.89 (d, *J* = 12.3 Hz, 1H), 4.23 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 145.6, 138.6, 134.9, 133.8, 129.2, 128.5, 128.4, 128.1, 67.6, 45.7; **HRMS (**ESI-TOF**)** for $C_{18}H_{15}D_3O_4S_2$ $[M+Na]^+$ calcd 388.0727, found 388.0730.



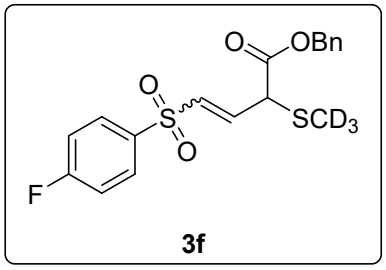
3d

The reaction of the S-methylthiolating reagent **1d** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3d** in 85% yield (67.3 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a colourless oil according. The title compound **3d** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.24 – 7.20 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.61 (s, 1H), 6.34 (s, 1H), 5.00 (d, *J* = 12.3 Hz, 1H), 4.94 (d, *J* = 12.3 Hz, 1H), 4.26 (s, 1H), 3.80 (s, 3H);**^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 163.9, 146.0, 135.0, 130.7, 129.9, 128.5, 128.4, 128.2, 128.0, 114.4, 67.6, 55.6, 45.8; **HRMS (**ESI-TOF**)** for $C_{19}H_{17}D_3O_5S_2$ $[M+Na]^+$ calcd 418.0833, Found 418.0835.



3e

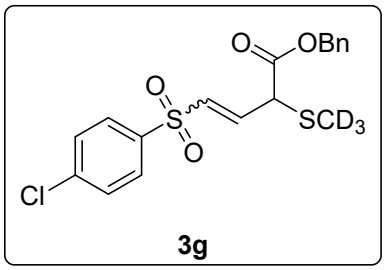
The reaction of the S-methylthiolating reagent **1e** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3e** in 85% yield (71.8 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a colourless oil . The title compound **3e** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15/1 to 5/1). (Rf 0.5, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.26 (m, 3H), 7.24 – 7.20 (m, 2H), 6.63 (d, *J* = 0.6 Hz, 1H), 6.37 (s, 1H), 4.97 (d, *J* = 12.4 Hz, 1H), 4.90 (d, *J* = 12.4 Hz, 1H), 4.27 (s, 1H), 1.27 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 157.8, 145.8, 135.4, 135.0, 128.7, 128.5, 128.3, 128.3, 127.9, 126.2, 67.4, 45.9, 35.2, 30.9; **HRMS** (ESI-TOF) for $C_{22}H_{23}D_3O_4S_2$ $[M+Na]^+$ calcd 444.1353, Found 444.1354.



3f

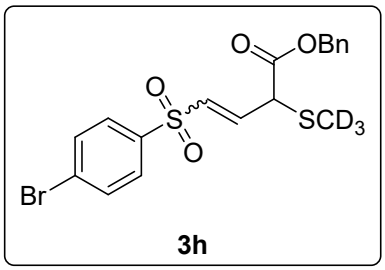
The reaction of the S-methylthiolating reagent **1f** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO

(0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3f** in 87% yield (71.8 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a colourless oil. The title compound **3f** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.30 – 7.26 (m, 3H), 7.20 – 7.18 (m, 2H), 7.08 – 7.03 (m, 2H), 6.63 (s, 1H), 6.38 (s, 1H), 4.97 (d, *J* = 12.2 Hz, 1H), 4.93 (d, *J* = 12.2 Hz, 1H), 4.23 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 165.8 (d, $^1J_{C\text{-}F}$ = 255 Hz), 145.4, 134.8 (d, $^4J_{C\text{-}F}$ = 3 Hz), 134.7, 131.3, 131.2, 128.9 (d, $^2J_{C\text{-}F}$ = 83 Hz), 128.5, 128.1, 116.4 (d, $^3J_{C\text{-}F}$ = 22 Hz), 67.6, 45.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.7; **HRMS (**ESI-TOF**)** for $C_{18}H_{14}D_3FO_4S_2$ $[M+Na]^+$ calcd 406.0633, Found 406.0637.



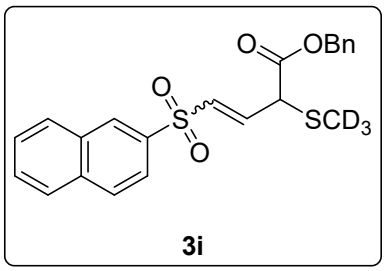
3g

The reaction of the S-methylthiolating reagent **1g** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3g** in 87% yield (72.9 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a colourless oil. The title compound **3g** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 5.8 Hz, 3H), 7.20 – 7.15 (m, 2H), 6.62 (s, 1H), 6.38 (s, 1H), 4.95 (d, *J* = 12.3 Hz, 1H), 4.90 (d, *J* = 12.3 Hz, 1H), 4.22 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 145.3, 140.5, 137.3, 134.8, 129.8, 129.7, 129.5, 128.6, 128.5, 128.1, 67.7, 45.6. ; **HRMS (**ESI-TOF**)** for $C_{18}H_{14}D_3ClO_4S_2$ $[M+Na]^+$ calcd 422.0337, Found 422.0337.



3h

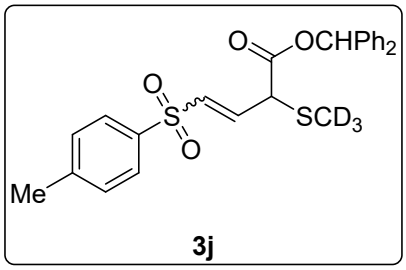
The reaction of the S-methylthiolating reagent **1h** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3h** in 84% yield (74.4 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **3h** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.22 – 7.18 (m, 2H), 6.65 (s, 1H), 6.40 (s, 1H), 4.97 (d, *J* = 12.3 Hz, 1H), 4.92 (d, *J* = 12.2 Hz, 1H), 4.24 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.9, 145.1, 137.7, 134.7, 132.4, 129.8, 129.7, 129.2, 128.5, 128.5, 128.1, 67.6, 45.5; **HRMS (**ESI-TOF**)** for $C_{18}H_{14}DBrO_4S_2$ $[M+Na]^+$ calcd 444.0013, Found 444.0017.



3i

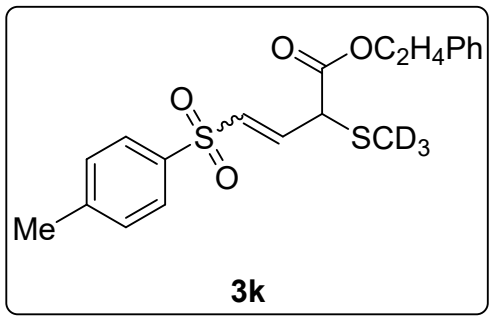
The reaction of the S-methylthiolating reagent **1i** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3i** in 84% yield (73.8 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **3i** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to

7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.88 – 7.76 (m, 3H), 7.70 – 7.63 (m, 1H), 7.60 – 7.48 (m, 2H), 7.18 – 7.15 (m, 3H), 7.08 – 6.96 (m, 2H), 6.68 (s, 1H), 6.38 (s, 1H), 4.81 (d, *J* = 12.3 Hz, 1H), 4.69 (d, *J* = 12.3 Hz, 1H), 4.27 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 145.5, 135.3, 135.2, 134.8, 131.9, 130.4, 129.5, 129.4, 129.4, 129.3, 128.4, 128.3, 128,0 127.9, 127.7, 122.8, 67.48, 45.76; **HRMS (**ESI-TOF**)** for $C_{22}H_{17}D_3O_4S_2$ $[M+Na]^+$ calcd 438.0884, Found 438.0884.



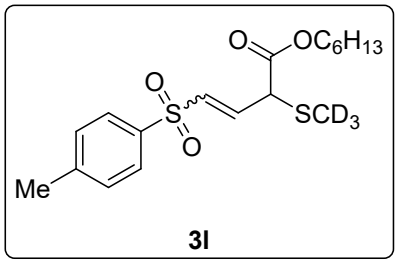
3j

The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3j** in 87% yield (79.2 mg) and D-inc. > 99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **3j** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.27 (m, 5H), 7.26 – 7.19 (m, 5H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.65 (s, 1H), 6.64 (s, 1H), 6.34 (s, 1H), 4.40 (s, 1H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.1, 145.7, 144.8, 139.2, 139.2, 135.6, 129.8, 128.7, 128.4, 128.4, 128.1, 128.0, 127.0, 126.9, 78.4, 77.3, 45.7, 21.6; **HRMS (**ESI-TOF**)** for $C_{25}H_{21}D_3O_4S_2$ $[M+Na]^+$ calcd 478.1197, Found 478.1198.



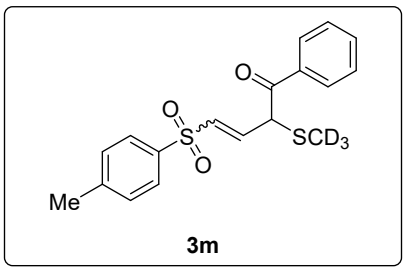
3k

The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3k** in 76% yield (59.9 mg) and D-inc. > 99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **3k** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 6.67 (s, 1H), 6.37 (s, 1H), 4.26 (s, 1H), 4.23 – 4.16 (m, 2H), 2.87 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 145.7, 144.8, 137.2, 135.6, 129.7, 128.8, 128.5, 128.4, 126.6, 66.2, 45.8, 34.6, 21.5; **HRMS (**ESI-TOF**)** for $C_{20}H_{19}D_3O_4S_2$ $[M+Na]^+$ calcd 416.1040, Found 416.1040.



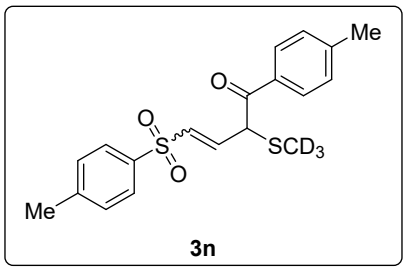
3l

The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **3l** in 86% yield (64.3 mg) and D-inc. > 99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **3l** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.62 (s, 1H), 6.35 (s, 1H), 4.18 (s, 1H), 3.94 – 3.82 (m, 2H), 2.37 (s, 3H), 1.49 – 1.40 (m, 2H), 1.22 (d, *J* = 14.9 Hz, 6H), 0.82 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 145.8, 144.8, 135.6, 129.8, 128.6, 128.5, 66.1, 45.8, 31.2, 28.2, 25.3, 22.4, 21.6, 13.9; **HRMS (**ESI-TOF**)** for $C_{18}H_{23}D_3O_4S_2$ $[M+Na]^+$ calcd 396.1353, Found 396.1355.



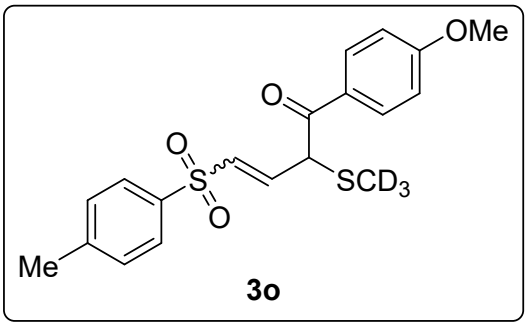
3m

The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -50 °C for 10 h afforded compound **3m** in 73% yield (60.0 mg) and D-inc. > 99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **3m** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.6, petroleum ether/ethyl acetate = 7/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.46 – 7.40 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 1H), 6.53 (s, 1H), 5.35 (s, 1H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.3, 146.2, 144.8, 135.7, 135.1, 133.6, 129.8, 129.3, 128.6, 128.6, 128.5, 46.5, 21.6; **HRMS (**ESI-TOF**)** for $C_{18}H_{15}D_3O_3S_2$ $[M+Na]^+$ calcd 372.0778, Found 372.0777.



3n

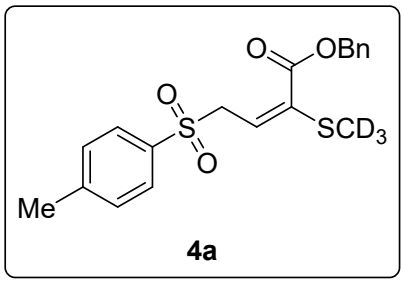
The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -50 °C for 16 h afforded compound **3n** in 55% yield (60.0 mg) and D-inc. > 99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **3n** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.6, petroleum ether/ethyl acetate = 7/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.16 (m, 4H), 6.72 (s, 1H), 6.51 (s, 1H), 5.33 (s, 1H), 2.41 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.9, 146.3, 144.8, 144.6, 135.7, 132.5, 129.7, 129.3, 129.2, 128.7, 128.4, 46.3, 21.7, 21.6; **HRMS (**ESI-TOF**)** for $C_{19}H_{17}D_3O_3S_2$ $[M+Na]^+$ calcd 386.0934, Found 386.0933.



3o

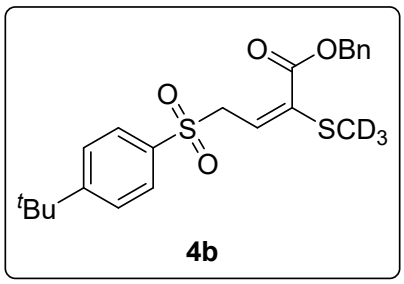
The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -50 °C for 16 h afforded compound **3o** in 52% yield (60.0 mg) and D-inc. > 99% (determined by **^{1}H NMR**) as a yellow

oil. The title compound **3o** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.71 (s, 1H), 6.49 (s, 1H), 5.32 (s, 1H), 3.86 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9, 163.9, 146.3, 144.7, 135.7, 131.0, 129.7, 129.1, 128.4, 127.7, 113.8, 55.5, 46.2, 21.5; **HRMS (**ESI-TOF**)** for $C_{19}H_{17}D_3O_4S_2$ $[M+Na]^+$ calcd 402.0884, Found 402.0884.



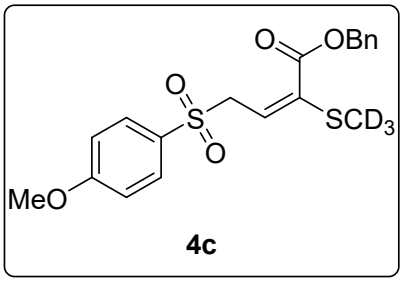
4a

The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C under N_2 atmosphere for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h afforded compound **4a** in 81% total yield of two-step (61.4 mg) and D-inc.＞99% (determined by ^{1}H NMR) as a yellow oil. The title compound **4a** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.21 (d, *J* = 7.9 Hz, 4H), 4.88 (s, 2H), 3.39 (s, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 147.4, 144.1, 136.3, 135.3, 129.7, 128.4, 128.2, 128.1, 127.9, 127.9, 66.8, 33.2, 21.6; **HRMS (**ESI-TOF**)** for $C_{19}H_{17}D_3O_4S_2$ $[M+Na]^+$ calcd 402.0884, Found 402.0884.



4b

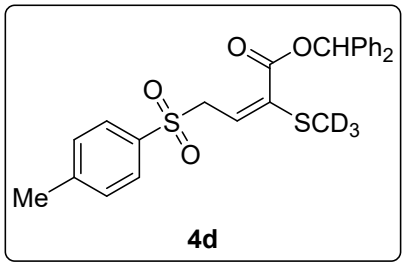
The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C under N_2 atmosphere for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h afforded compound **4b** in 67 % total yield of two-step (56.4 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **4b** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.20 (m, 3H), 7.15 (d, *J* = 7.0 Hz, 2H), 4.78 (s, 2H), 3.31 (s, 2H), 1.22 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 157.0, 147.4, 136.1, 135.2, 128.4, 128.1, 127.9, 127.8, 127.8, 126.0, 66.7, 35.1, 33.2, 30.9; **HRMS (**ESI-TOF**)** for $C_{22}H_{23}D_3O_4S_2$ $[M+Na]^+$ calcd 444.1353, Found 444.1355.



4c

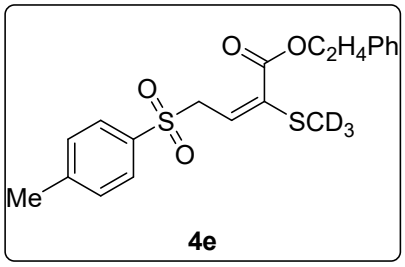
The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C under N_2 atmosphere for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h afforded compound **4c** in 71 % total yield of two-step (56.1

mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a colourless oil. The title compound **4c** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.73 (d, *J* = 8.9 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.25 – 7.16 (m, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 4.89 (s, 2H), 3.82 (s, 3H), 3.39 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 163.3, 146.8, 135.3, 130.5, 130.3, 128.4, 128.2, 128.1, 128.0, 114.2, 66.8, 55.6, 33.2; **HRMS (**ESI-TOF**)** for $C_{19}H_{17}D_3O_5S_2$ $[M+Na]^+$ calcd 418.0833, Found 418.0838.



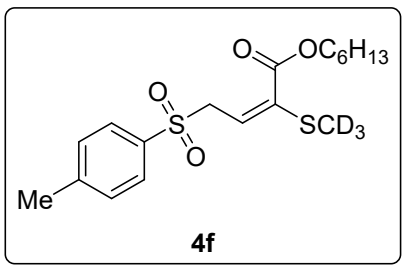
4d

The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C under N_2 atmosphere for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h afforded compound **4d** in 80 % total yield of two-step (72.8 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a colourless oil. The title compound **4d** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15/1 to 5/1). (Rf 0.5, petroleum ether/ethyl acetate = 5/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.33 – 7.13 (m, 10H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.53 (s, 1H), 3.43 (s, 2H), 2.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 147.4, 144.0, 139.7, 136.0, 129.6, 128.3, 127.9, 127.8, 126.9, 77.6, 33.5, 21.6; **HRMS (**ESI-TOF**)** for $C_{25}H_{21}D_3O_4S_2$ $[M+Na]^+$ calcd 478.1197, Found 478.1195.



4e

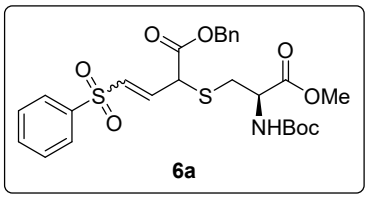
The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C under N_2 atmosphere for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h afforded compound **4e** in 67 % total yield of two-step (52.7 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a yellow oil. The title compound **4e** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15/1 to 5/1). (Rf 0.5, petroleum ether/ethyl acetate = 5/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.18 – 7.12 (m, 3H), 7.07 (d, *J* = 7.0 Hz, 2H), 3.94 (t, *J* = 7.1 Hz, 2H), 3.23 (s, 2H), 2.66 (t, *J* = 7.1 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 147.3, 144.1, 137.5, 136.2, 129.7, 128.9, 128.4, 128.1, 127.7, 126.5, 65.6, 34.7, 33.2, 21.5; **HRMS (**ESI-TOF**)** for $C_{25}H_{21}D_3O_4S_2$ $[M+Na]^+$ calcd 416.1040, Found 416.1040.



4f

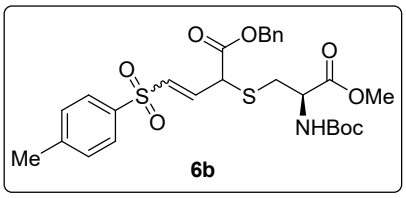
The reaction of the S-methylthiolating reagent **1b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C under N_2 atmosphere for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h afforded compound **4f** in 70 % total yield of two-step (52.2 mg) and D-inc.＞99% (determined by **^{1}H NMR**) as a yellow

oil. The title compound **4f** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15/1 to 4/1). (Rf 0.5, petroleum ether/ethyl acetate = 4/1).**^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 3.81 (t, *J* = 6.7 Hz, 2H), 3.31 (s, 2H), 2.40 (s, 3H), 1.46 – 1.39 (m, 2H), 1.30 – 1.20 (m, 6H), 0.87 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.7, 147.1, 144.0, 136.4, 129.6, 128.2, 128.1, 65.3, 33.3, 31.3, 28.2, 25.3, 22.4, 21.5, 13.9; **HRMS (**ESI-TOF**)** for $C_{18}H_{23}D_3O_4S_2$ $[M+Na]^+$ calcd 396.1353, Found 396.1355.



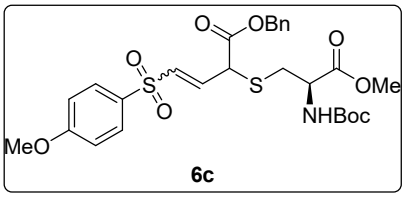
6a

The reaction of the Thiosulfinat **5a** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6a** in 88% yield (96.6 mg) and 1:1 *dr* (determined by **^{1}H NMR**) as a yellow oil. The title compound **6a** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.0 Hz, 2H), 7.58 – 7.55 (m, 1H), 7.45 (s, 2H), 7.32 (s, 3H), 7.21 (d, *J* = 2.2 Hz, 2H), 6.66 (s, 1H), 6.37 (s, 1H), 5.23 (d, *J* = 8.4 Hz, 1H), 4.98 (d, *J* = 12.5 Hz, 2H), 4.45 (s, 2H), 3.68 (s, 3H), 2.89 (s, 1H), 2.83 – 2.77 (m, 1H), 1.42 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 167.9, 154.9, 145.9, 138.3, 134.6, 133.8, 129.4, 129.1, 128.4, 128.4, 128.4, 128.1, 80.2, 67.7, 52.8, 52.5, 45.0, 34.2, 28.1; **HRMS (**ESI-TOF**)** for $C_{26}H_{31}NO_8S_2$ $[M+Na]^+$ calcd 572.1383, Fund 572.1388.



6b

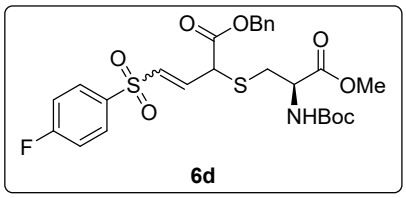
The reaction of the Thiosulfinat **5b** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6b** in 89% yield (100.2 mg) and 1:1 *dr* (determined by **^{1}H NMR**) as a yellow oil. The title compound **6b** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 3.6 Hz, 2H), 7.26 (s, 3H), 7.20 (d, *J* = 7.1 Hz, 4H), 6.57 (s, 1H), 6.28 (s, 1H), 5.20 (d, *J* = 7.7 Hz, 1H), 4.90 (d, *J* = 12.4 Hz, 2H), 4.38 (s, 2H), 3.62 (s, 3H), 2.84 (s, 1H), 2.78 – 2.72 (m, 1H), 2.33 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 168.0, 154.9, 146.0, 144.9, 135.2, 134.7, 129.8, 129.0, 128.9, 128.4, 128.3, 128.0, 80.1, 67.6, 52.8, 52.5, 45.0, 34.2, 28.1, 21.5; **HRMS (**ESI-TOF**)** for $C_{27}H_{33}NO_8S_2$ $[M+Na]^+$ calcd 586.1540, Fund 586.1540.



6c

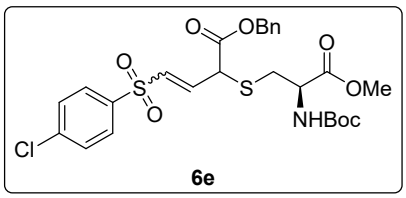
The reaction of the Thiosulfinat **5c** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6c** in 79% yield (91.6 mg) and 1:1 *dr* (determined by **^{1}H NMR**) as a yellow oil. The title compound **6c** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 3.2 Hz, 2H), 7.32 (s, 3H), 7.22 (d, *J* = 2.0 Hz, 2H), 6.92 (d, *J* = 0.9 Hz, 2H), 6.61 (s, 1H), 6.31 (s, 1H), 5.25 (d, *J* = 7.6 Hz, 1H), 4.97 (d, *J* = 12.4 Hz, 2H), 4.44 (s, 2H), 3.83 (s, 3H), 3.69 (s, 3H), 2.90 (s, 1H), 2.85 – 2.79 (m, 1H), 1.42 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 168.1, 163.9, 146.5,

134.8, 130.8, 129.6, 129.5, 128.6, 128.5, 128.4, 128.1, 114.4, 80.2, 67.8, 55.6, 53.3, 52.6, 45.1, 34.3, 28.2; **HRMS (**ESI-TOF**)** for $C_{27}H_{33}NO_9S_2$ $[M+Na]^+$ calcd 602.1489, Fund 602.1489.



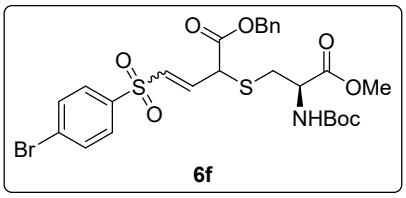
6d

The reaction of the Thiosulfinat **5d** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6d** in 80% yield (93.6 mg) and 1:1 *dr* (determined by **^{1}H NMR**) as a yellow oil. The title compound **6d** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, J = 5.3 Hz, 2H), 7.33 (s, 3H), 7.22 (s, 2H), 7.13 (d, 2H), 6.66 (s, 1H), 6.40 (s, 1H), 5.30 (d, J = 7.3 Hz, 1H), 4.99 (s, 2H), 4.46 (s, 2H), 3.69 (s, 3H), 2.91 (s, 1H), 2.85 – 2.80 (m, 1H), 1.42 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 168.0, 165.9 (d, $^1J_{C\text{-}F}$ = 256 Hz), 155.0, 145.9, 134.7, 134.5 (d, $^4J_{C\text{-}F}$ = 8 Hz), 131.4 (d, $^3J_{C\text{-}F}$ = 14 Hz), 129.8, 129.7, 128.4 (d, $^2J_{C\text{-}F}$ = 31 Hz), 116.7, 116.4, 80.3, 67.9, 53.2, 52.7, 45.1, 34.4, 28.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.4; **HRMS (**ESI-TOF**)** for $C_{26}H_{30}FNO_8S_2$ $[M+Na]^+$ calcd 590.1289, Fund 590.1288.



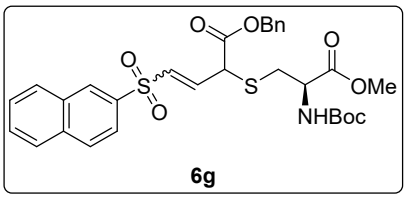
6e

The reaction of the Thiosulfinat **5e** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6e** in 85% yield (99.3 mg) and 1:1 *dr* (determined by **^{1}H NMR**) as a yellow oil. The title compound **6e** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 2.1 Hz, 2H), 7.41 (d, J = 1.7 Hz, 2H), 7.34 (d, J = 1.6 Hz, 3H), 7.22 (s, 2H), 6.67 (s, 1H), 6.40 (s, 1H), 5.28 – 5.23 (m, 1H), 4.99 (s, 2H), 4.46 (s, 2H), 3.70 (s, 3H), 2.92 (s, 1H), 2.86 – 2.80 (m, 1H), 1.43 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 167.9, 155.0, 145.9, 140.6, 137.0, 134.6, 130.2, 130.0, 129.9, 129.5, 128.5, 128.2, 80.2, 67.9, 53.2, 52.6, 45.0, 34.4, 28.1; **HRMS (**ESI-TOF**)** for $C_{26}H_{30}ClNO_8S_2$ $[M+Na]^+$ calcd 606.0994, Fund 606.0995.



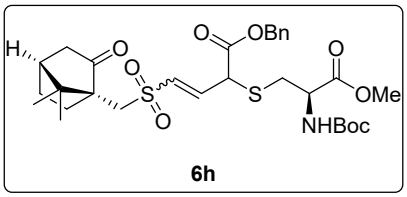
6f

The reaction of the Thiosulfinat **5f** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6f** in 87% yield (109.1 mg) and 1:1 *dr* (determined by **^{1}H NMR**) as a yellow oil. The title compound **6f** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 2.0 Hz, 2H), 7.57 (d, J = 1.7 Hz, 2H), 7.33 (s, 3H), 7.22 (s, 2H), 6.66 (s, 1H), 6.39 (s, 1H), 5.26 (d, J = 5.9 Hz, 1H), 4.98 (s, 2H), 4.46 (s, 2H), 3.69 (s, 3H), 2.92 (s, 1H), 2.85 – 2.80 (m, 1H), 1.42 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 167.9, 155.0, 145.9, 137.6, 134.6, 132.5, 130.1, 130.0, 129.9, 129.3, 128.5, 128.2, 80.3, 67.9, 53.2, 52.7, 45.1, 34.4, 28.2; **HRMS (**ESI-TOF**)** for $C_{26}H_{30}BrNO_8S_2$ $[M+Na]^+$ calcd 650.0488, Fund 650.0488.



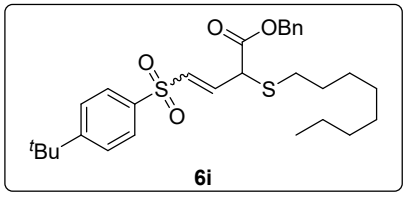
6g

The reaction of the Thiosulfinat **5g** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6g** in 87% yield (104.3 mg) and 1:1 *dr* (determined by **^{1}H NMR**) as a yellow oil. The title compound **6g** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.87 (s, 1H), 7.80 (d, *J* = 4.2 Hz, 2H), 7.67 – 7.65 (m, 1H), 7.55 – 7.51 (m, 2H), 7.17 – 7.13 (m, 3H), 6.97 (d, *J* = 1.8 Hz, 2H), 6.66 (s, 1H), 6.34 (s, 1H), 5.22 – 5.17 (m, 1H), 4.69 (t, *J* = 12.1 Hz, 2H), 4.36 (s, 2H), 3.52 (s, 3H), 2.81 (d, *J* = 7.9 Hz, 1H), 2.76 – 2.71 (m, 1H), 1.33 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 168.0, 155.0, 146.0, 135.2, 135.1, 134.5, 132.0, 130.7, 130.5, 129.8, 129.6, 129.5, 128.4, 128.4, 128.0, 127.9, 127.73, 122.8, 80.2, 67.8, 53.1, 52.6, 45.1, 34.4, 28.2; **HRMS (**ESI-TOF**)** for $C_{30}H_{33}NO_8S_2$ $[M+Na]^+$ calcd 622.1540, Fund 622.1540.



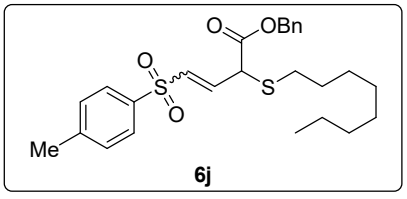
6h

The reaction of the Thiosulfinat **5h** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6h** in 72% yield (89.1mg) and 1:1 *dr* (determined by **^{1}H NMR**) as a yellow oil. The title compound **6h** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (3/1 to 1/1). (Rf 0.6, petroleum ether/ethyl acetate = 1/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 5H), 6.54 (d, 1H), 6.47 (s, 1H), 5.46 (d, *J* = 7.7 Hz, 1H), 5.19 (d, *J* = 12.2 Hz, 2H), 4.54 (s, 2H), 3.72 (s, 3H), 3.55 (d, *J* = 14.7 Hz, 1H), 3.04 – 2.94 (m, 2H), 2.91 (d, *J* = 14.7 Hz, 1H), 2.39 – 2.32 (m, 2H), 2.10 – 2.08 (m, 2H), 1.94 (s, 1H), 1.80 – 1.73 (m, 2H), 1.42 (s, 9H), 1.07 (s, 3H), 0.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.3, 171.1, 168.7, 155.1, 146.5, , 134.9, 130.6, 128.6, 128.5, 128.4, 80.2, 68.0, 58.9, 53.3, 52.7, 51.6, 48.2, 45.3, 42.5, 42.5, 34.7, 28.2, 27.0, 24.7, 19.8, 19.7; **HRMS (**ESI-TOF**)** for $C_{30}H_{41}NO_9S_2$ $[M+Na]^+$ calcd 646.2115, Fund 646.2115.



6i

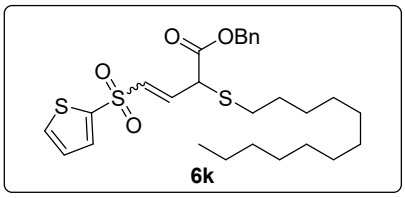
The reaction of the Thiosulfinat **5i** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6i** in 87% yield (89.8mg) as a yellow oil. The title compound **6i** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 10/1). (Rf 0.4, petroleum ether/ethyl acetate = 10/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.23 (d, *J* = 7.7 Hz, 2H), 6.66 (s, 1H), 6.41 (s, 1H), 4.97 (d, *J* = 12.4 Hz, 1H), 4.88 (d, *J* = 12.4 Hz, 1H), 4.28 (s, 1H), 2.43 – 2.26 (m, 2H), 1.31 (d, *J* = 3.3 Hz, 2H), 1.27 (s, 9H), 1.23 – 1.11 (m, 10H), 0.83 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 157.8, 146.3, 135.4, 135.0, 128.9, 128.5, 128.3, 128.3, 127.9, 126.2, 67.4, 44.9, 35.2, 32.4, 31.6, 30.9, 29.0, 28.9, 28.5, 28.5, 22.5, 14.0; **HRMS (**ESI-TOF**)** for $C_{29}H_{40}O_4S_2$ $[M+Na]^+$ calcd 539.2260, Fund 539.2260.



6j

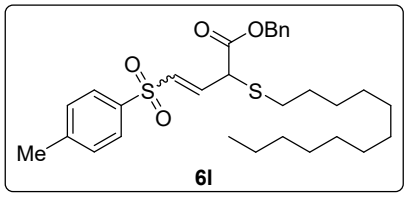
The reaction of the Thiosulfinat **5j** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded

compound **6j** in 87% yield (82.5mg) as a yellow oil. The title compound **6j** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 10/1). (Rf 0.4, petroleum ether/ethyl acetate = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 5.8 Hz, 3H), 7.19 (d, *J* = 5.5 Hz, 4H), 6.62 (s, 1H), 6.37 (s, 1H), 4.95 (d, *J* = 12.3 Hz, 1H), 4.88 (d, *J* = 12.3 Hz, 1H), 4.23 (s, 1H), 2.41 – 2.27 (m, 5H), 1.33 – 1.07 (m, 14H), 0.80 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 146.3, 144.8, 135.4, 135.0, 129.8, 128.9, 128.4, 128.3, 128.0, 67.5, 44.8, 32.4, 31.7, 29.0, 28.9, 28.5, 28.5, 22.5, 21.6, 14.0; **HRMS (**ESI-TOF**)** for $C_{26}H_{34}O_4S_2$ $[M+Na]^+$ calcd 497.1791, Fund 497.1790.



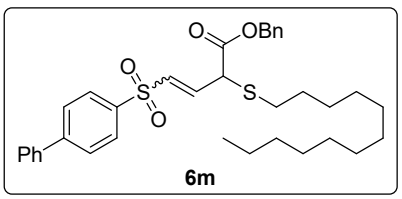
6k

The reaction of the Thiosulfinat **5k** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6k** in 89% yield (92.9mg) as a yellow oil. The title compound **6k** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 7.37 – 7.32 (m, 3H), 7.31 – 7.27 (m, 2H), 7.08 – 7.04 (m, 1H), 6.73 (s, 1H), 6.47 (s, 1H), 5.07 (d, *J* = 12.3 Hz, 1H), 5.02 (d, *J* = 12.3 Hz, 1H), 4.42 (s, 1H), 2.54 – 2.38 (m, 2H), 1.47 – 1.38 (m, 2H), 1.23 (d, *J* = 17.0 Hz, 18H), 0.88 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 146.7, 139.6, 135.1, 135.0, 134.9, 129.2, 128.5, 128.4, 128.2, 127.9, 67.7, 44.8, 32.6, 31.9, 29.6, 29.5, 29.5, 29.3, 29.0, 28.6, 28.6, 22.6, 14.1; **HRMS (**ESI-TOF) for $C_{27}H_{38}O_4S_3$ $[M+Na]^+$ calcd 545.1824, Found 545.1824.



6l

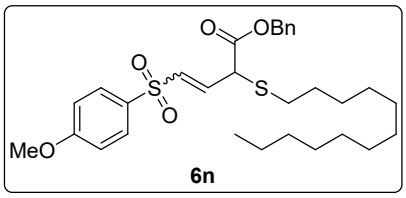
The reaction of the Thiosulfinat **5l** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6l** in 89% yield (96.6 mg) as a yellow oil. The title compound **6l** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.28 – 7.19 (m, 4H), 6.67 (s, 1H), 6.43 (s, 1H), 5.00 (d, *J* = 12.3 Hz, 1H), 4.93 (d, *J* = 12.3 Hz, 1H), 4.28 (s, 1H), 2.47 – 2.30 (m, 5H), 1.39 – 1.13 (m, 20H), 0.86 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 146.3, 144.8, 135.5, 135.0, 129.8, 129.0, 128.5, 128.3, 128.0, 67.5, 44.9, 32.5, 31.8, 29.6, 29.6, 29.5, 29.4, 29.3, 29.0, 28.6, 28.5, 22.6, 21.6, 14.1; **HRMS (**ESI-TOF**)** for $C_{30}H_{42}O_4S_2$ $[M+Na]^+$ calcd 553.2417, Found 553.2417.



6m

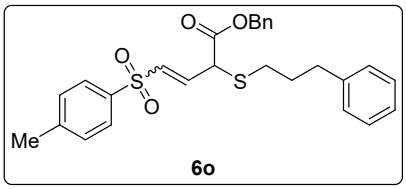
The reaction of the Thiosulfinat **5m** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6m** in 90% yield (106.5 mg) as a yellow oil. The title compound **6m** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.23 – 7.16 (m, 3H), 7.16 – 7.10 (m, 2H), 6.64 (s, 1H), 6.39 (s, 1H), 4.91 (d, *J* = 12.3 Hz, 1H), 4.83 (d, *J* = 12.3 Hz, 1H), 4.24 (s,

1H), 2.39 – 2.22 (m, 2H), 1.29 – 1.22 (m, 2H), 1.19 – 1.02 (m, 18H), 0.77 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 146.6, 146.2, 138.8, 137.0, 134.9, 129.4, 129.1, 129.0, 128.7, 128.5, 128.4, 128.0, 127.7, 127.3, 67.6, 44.9, 32.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.0, 28.6, 28.6, 22.6, 14.1; **HRMS (ESI)** for $C_{35}H_{44}O_4S_2$ $[M+Na]^+$ calcd 615.2573, Found 615.2574.



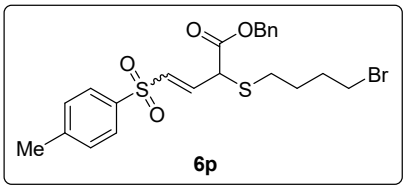
6n

The reaction of the Thiosulfinat **5n** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6n** in 89% yield (97.2 mg) as a yellow oil. The title compound **6n** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 2H), 7.38 – 7.27 (m, 3H), 7.25 – 7.17 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.62 (s, 1H), 6.38 (s, 1H), 4.99 (d, *J* = 12.4 Hz, 1H), 4.91 (d, *J* = 12.4 Hz, 1H), 4.26 (s, 1H), 3.80 (s, 3H), 2.47 – 2.29 (m, 2H), 1.39 – 1.13 (m, 20H), 0.84 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 163.8, 146.5, 135.0, 130.7, 129.7, 128.5, 128.3, 128.0, 114.4, 67.5, 55.6, 44.9, 32.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.0, 28.6, 28.6, 22.6, 14.1; **HRMS (ESI)** for $C_{30}H_{42}O_5S_2$ $[M+Na]^+$ calcd 569.2366, Found 569.2371.



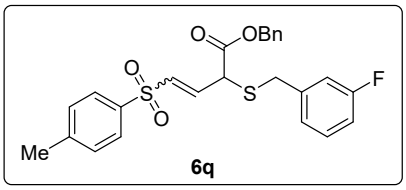
6o

The reaction of the Thiosulfinat **5o** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6o** in 83% yield (77.7 mg) as a yellow oil. The title compound **6o** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.23 (m, 3H), 7.20 – 7.06 (m, 7H), 6.99 (d, *J* = 7.3 Hz, 2H), 6.60 (s, 1H), 6.36 (s, 1H), 4.93 (d, *J* = 12.3 Hz, 1H), 4.86 (d, *J* = 12.3 Hz, 1H), 4.23 (s, 1H), 2.54 – 2.30 (m, 4H), 2.28 (s, 3H), 1.67 – 1.56 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 146.2, 144.8, 140.8, 135.3, 134.9, 129.8, 129.0, 128.4, 128.4, 128.3, 128.3, 128.3, 128.0, 125.9, 67.5, 44.7, 34.3, 31.7, 30.0, 21.5; **HRMS (**ESI-TOF**)** for $C_{27}H_{28}O_4S_2$ $[M+Na]^+$ calcd 491.1321, Found 491.1322.



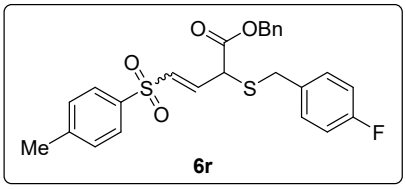
6p

The reaction of the Thiosulfinat **5p** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6p** in 85% yield (84.3 mg) aas a yellow oil. The title compound **6p** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 7/1). (Rf 0.5, petroleum ether/ethyl acetate = 7/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.23 – 7.15 (m, 4H), 6.61 (s, 1H), 6.35 (s, 1H), 4.95 (d, *J* = 12.3 Hz, 1H), 4.87 (d, *J* = 12.3 Hz, 1H), 4.22 (s, 1H), 3.20 (t, *J* = 6.6 Hz, 2H), 2.43 – 2.29 (m, 5H), 1.72 – 1.63 (m, 2H), 1.53 – 1.39 (m, 2H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 146.1, 145.0, 135.4, 134.9, 129.8, 129.0, 128.5, 128.4, 128.4, 128.1, 67.6, 44.6, 32.7, 31.4, 31.2, 26.9, 21.6; **HRMS (**ESI-TOF**)** for $C_{22}H_{25}BrO_4S_2$ $[M+Na]^+$ calcd 519.0270, Found 519.0271.



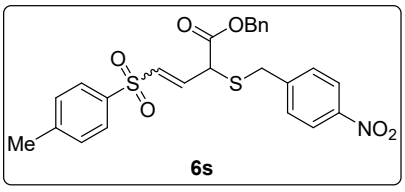
6q

The reaction of the Thiosulfinat **5q** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6q** in 91% yield (85.6 mg) as a yellow oil. The title compound **61** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.24 – 7.19 (m, 2H), 7.18 – 7.14 (m, 2H), 7.14 – 7.08 (m, 1H), 6.89 – 6.83 (m, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 9.6 Hz, 1H), 6.62 (s, 1H), 6.33 (s, 1H), 5.01 (d, *J* = 12.3 Hz, 1H), 4.93 (d, *J* = 12.3 Hz, 1H), 4.08 (s, 1H), 3.60 (d, *J* = 13.5 Hz, 1H), 3.47 (d, *J* = 13.5 Hz, 1H), 2.35 (s, 3H). ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 162.5 (d, $^1J_{C-F}$ = 245 Hz), 145.6, 144.8, 138.4 (d, $^6J_{C-F}$ = 7 Hz), 135.0 (d, $^2J_{C-F}$ = 28 Hz), 129.8 (d, $^5J_{C-F}$ = 9 Hz), 129.7, 128.9, 128.4, 128.4, 128.2, 128.0, 124.6, 124.6, 115.7 (d, $^3J_{C-F}$ = 21 Hz), 114.3 (d, $^4J_{C-F}$ = 21 Hz), 67.6, 43.9, 35.9, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.45; **HRMS (**ESI-TOF**)** for $C_{25}H_{23}FO_4S_2$ $[M+Na]^+$ calcd 493.0914, Found 493.0914.



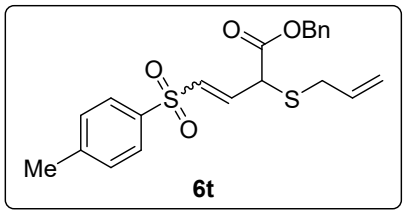
6r

The reaction of the Thiosulfinat **5r** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6r** in 91% yield (85.5 mg) as a yellow oil. The title compound **6r** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.20 – 7.11 (m, 4H), 6.98 – 6.91 (m, 2H), 6.85 – 6.74 (m, 2H), 6.58 (s, 1H), 6.28 (s, 1H), 4.97 (d, *J* = 12.3 Hz, 1H), 4.88 (d, *J* = 12.3 Hz, 1H), 4.00 (s, 1H), 3.57 (d, *J* = 13.4 Hz, 1H), 3.46 (d, *J* = 13.4 Hz, 1H), 2.32 (s, 3H). ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 161.9 (d, $^1J_{C-F}$ = 245 Hz), 145.7, 144.8, 135.1, 134.9, 131.6 (d, $^4J_{C-F}$ = 3 Hz), 130.5 (d, $^3J_{C-F}$ = 8 Hz), 129.7, 128.8, 128.5, 128.4, 128.2, 128.0, 115.2 (d, $^2J_{C-F}$ = 21 Hz), 67.5, 43.9, 35.7, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.45; **HRMS (**ESI-TOF**)** for $C_{25}H_{23}FO_4S_2$ $[M+Na]^+$ calcd 493.0914, Found 493.0914.



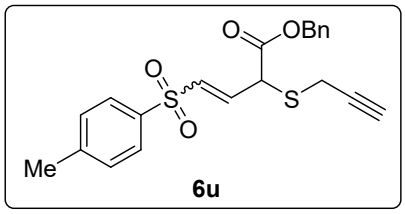
6s

The reaction of the Thiosulfinat **5s** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6s** in 97% yield (96.6 mg) as a yellow oil. The title compound **6s** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.27 – 7.18 (m, 6H), 6.67 (s, 1H), 6.38 (s, 1H), 5.04 (d, *J* = 12.2 Hz, 1H), 4.94 (d, *J* = 12.2 Hz, 1H), 4.06 (s, 1H), 3.76 (d, *J* = 13.8 Hz, 1H), 3.65 (d, *J* = 13.8 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 146.9, 145.4, 145.0, 143.7, 135.0, 134.7, 129.7, 129.1, 128.5, 128.2, 128.1, 123.5, 67.7, 43.9, 35.7, 21.5; **HRMS (**ESI-TOF**)** for $C_{25}H_{23}NO_6S_2$ $[M+Na]^+$ calcd 520.0859, Found 520.0860.



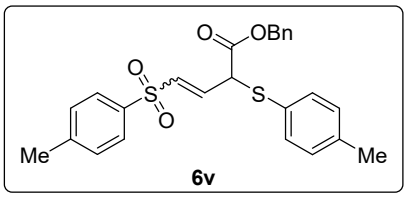
6t

The reaction of the Thiosulfinat **5t** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6t** in 85% yield (68.3 mg) as a yellow oil. The title compound **6t** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.26 (m, 3H), 7.26 – 7.18 (m, 4H), 6.63 (s, 1H), 6.37 (s, 1H), 5.55 – 5.43 (m, 1H), 5.02 – 4.85 (m, 4H), 4.19 (s, 1H), 3.11 – 2.93 (m, 2H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 146.2, 144.8, 135.4, 134.9, 132.0, 129.7, 128.9, 128.5, 128.4, 128.3, 127.9, 118.8, 67.5, 43.6, 35.3, 21.5. ; **HRMS (**ESI-TOF**)** for $C_{21}H_{22}O_4S_2$ $[M+Na]^+$ calcd 425.0852, Found 425.0853.



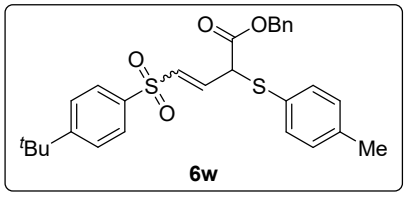
6u

The reaction of the Thiosulfinat **5u** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6u** in 97% yield (77.6 mg) as a yellow oil. The title compound **6u** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.19 (d, *J* = 8.3 Hz, 4H), 6.58 (s, 1H), 6.28 (s, 1H), 4.98 (d, *J* = 12.3 Hz, 1H), 4.93 (d, *J* = 12.3 Hz, 1H), 4.50 (s, 1H), 3.16 (d, *J* = 16.8, 2.6 Hz, 1H), 3.03 (dd, *J* = 16.8, 2.6 Hz, 1H), 2.31 (s, 3H), 2.07 (t, *J* = 2.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167. 9, 145.8, 144.9, 135.4, 134.8, 129.8, 129.1, 128.5, 128.4, 128.3, 128.0, 77. 9, 72.4, 67.7, 44.8, 21.5, 20.2; **HRMS (**ESI-TOF**)** for $C_{21}H_{20}O_4S_2$ $[M+Na]^+$ calcd 423.0695, Found 425.0695.



6v

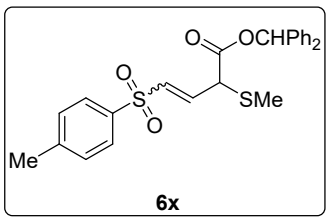
The reaction of the Thiosulfinat **5v** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6v** in 45% yield (40.6 mg) as a yellow oil. The title compound **6v** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.27 (s, 1H), 7.25 (s, 1H), 7.19 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 1H), 6.33 (s, 1H), 4.99 (d, *J* = 12.3 Hz, 1H), 4.91 (d, *J* = 12.3 Hz, 1H), 4.58 (s, 1H), 2.42 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 145.2, 144.8, 139.2, 135.4, 134.9, 133.9, 129.8, 129.3, 128.5, 128.4, 128.3, 128.1, 128.1, 67.6, 49.0, 21.6, 21.1; **HRMS (**ESI-TOF**)** for $C_{25}H_{24}O_4S_2$ $[M+Na]^+$ calcd 475.1008, Found 475.1010.



6w

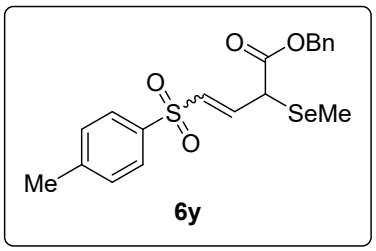
The reaction of the Thiosulfinat **5w** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded

compound **6w** in 47% yield (46.4 mg) as a yellow oil. The title compound **6w** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 2H), 7.54 – 7.48 (m, 2H), 7.38 – 7.29 (m, 3H), 7.24 – 7.15 (m, 2H), 7.04 – 6.94 (m, 4H), 6.65 (s, 1H), 6.34 (s, 1H), 4.99 (d, *J* = 12.3 Hz, 1H), 4.90 (d, *J* = 12.3 Hz, 1H), 4.58 (s, 1H), 2.29 (s, 3H), 1.33 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 157.8, 145.2, 139.2, 135.4, 134.9, 133.8, 129.8, 129.3, 128.5, 128.4, 128.3, 128.2, 128.1, 126.2, 77.3, 67.5, 49.1, 35.2, 31.0, 21.1; **HRMS (**ESI-TOF**)** for $C_{28}H_{30}O_4S_2$ $[M+Na]^+$ calcd 517.1478, Found 517.1478.



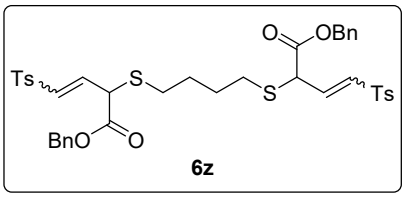
6x

The reaction of the S-methylthiolating reagent **1a** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6x** in 92% yield (83.2 mg) as a yellow oil. The title compound **6x** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.29 – 7.15 (m, 10H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.60 (s, 2H), 6.30 (s, 1H), 4.35 (s, 1H), 2.30 (s, 3H), 1.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 145.5, 144.8, 139.2, 139.1, 135.4, 129.8, 128.7, 128.4, 128.3, 128.1, 128.0, 126.9, 126.8, 78.4, 45.7, 21.6, 14.8; **HRMS (**ESI-TOF**)** for $C_{25}H_{24}O_4S_2$ $[M+Na]^+$ calcd 475.1008, Found 475.1008.



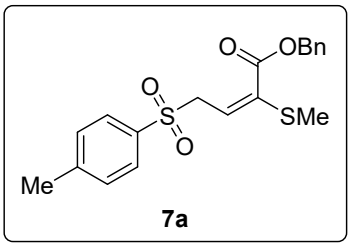
6y

The reaction of the Thiosulfinat **5y** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6y** in 90% yield (75.3 mg) as a yellow oil. The title compound **6y** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 6.5 Hz, 3H), 7.25 – 7.18 (m, 4H), 6.65 (s, 1H), 6.42 (s, 1H), 4.99 (d, *J* = 12.3 Hz, 1H), 4.93 (d, *J* = 12.3 Hz, 1H), 4.34 (s, 1H), 2.36 (s, 3H), 1.95 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 146.0, 144.8, 135.7, 135.1, 129.8, 128.8, 128.5, 128.4, 128.3, 128.0, 67.4, 34.2, 21.6, 6.4; **HRMS (**ESI-TOF**)** for $C_{19}H_{20}O_4SSe$ $[M+Na]^+$ calcd 441.0199, Found 441.0197.



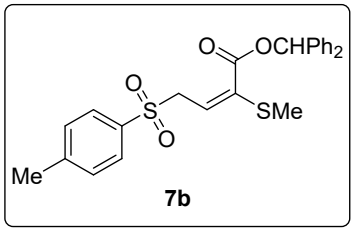
6z

The reaction of the Thiosulfinat **5z** (0.2 mmol, 1 equiv.), allenes **2** (0.34 mmol, 1.7 equiv.), and DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C for 10 h afforded compound **6z** in 74% yield (115.3 mg) as a yellow oil. The title compound **6z** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15/1 to 4/1). (Rf 0.5, petroleum ether/ethyl acetate = 4/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 5.8 Hz, 3H), 7.18 (d, *J* = 5.5 Hz, 4H), 6.60 (s, 1H), 6.36 (s, 1H), 4.93 (d, *J* = 12.3 Hz, 1H), 4.86 (d, *J* = 12.3 Hz, 1H), 4.21 (s, 1H), 2.40 – 2.24 (m, 5H), 1.40 – 1.01 (m, 14H), 0.79 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 146.2, 145.0, 135.4, 134.9, 129.8, 129.0, 128.5, 128.5, 128.4, 128.1, 67.6, 44.6, 32.8, 31.4, 31.2, 26.9, 21.7; **HRMS (**ESI-TOF**)** for $C_{40}H_{42}O_8S_2$ $[M+Na]^+$ calcd 801.1655, Found 801.1657.



7a

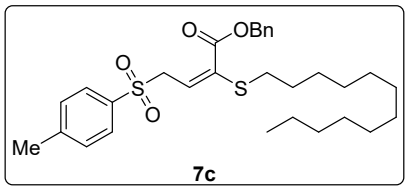
The reaction of the S-methylthiolating reagent **1a** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C under N_2 atmosphere for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h afforded compound **7a** in 81 % total yield of two-step (60.9 mg) as a yellow oil. The title compound **7a** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1).（5ab）**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.23 (m, 3H), 7.18 – 7.06 (m, 4H), 4.81 (s, 2H), 3.32 (s, 2H), 2.42 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 147.5, 144.1, 136.2, 135.3, 129.7, 128.4, 128.2, 128.1, 128.0, 127.8, 66.8, 33.2, 21.6, 17.6; **HRMS (**ESI-TOF**)** for $C_{19}H_{20}O_4S_2$ $[M+Na]^+$ calcd 399.0695, Found 399.0695.



7b

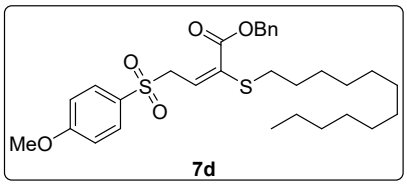
The reaction of the S-methylthiolating reagent **1a** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C under N_2 atmosphere for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.)

was added for reacting with another 4 h afforded compound **7b** in 80% total yield of two-step (72.3 mg) as a yellow oil according to the **general procedure C**. The title compound **7b** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.21 (m, 10H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.59 (s, 1H), 3.48 (s, 2H), 2.47 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 147.5, 144.0, 139.7, 136.0, 129.6, 128.3, 127.9, 127.8, 126.9, 77.6, 33.5, 21.5, 17.6; **HRMS (**ESI-TOF**)** for $C_{25}H_{24}O_4S_2$ $[M+Na]^+$ calcd 475.1008, Found 475.1008.



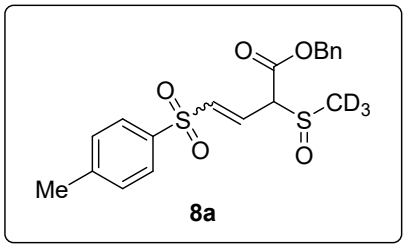
7c

The reaction of the Thiosulfinat **5l** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C under N_2 atmosphere for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h afforded compound **7c** in 74% total yield of two-step (78.4 mg) as a yellow oil. The title compound **7c** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1). (5ac)**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.32 (s, 3H), 7.20 (d, *J* = 7.6 Hz, 4H), 4.87 (s, 2H), 3.39 (s, 2H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.72 – 1.63 (m, 2H), 1.38 (s, 2H), 1.27 (s, 16H), 0.88 (t, *J* = 6.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 146.5, 144.0, 136.3, 135.3, 129.6, 128.4, 128.1, 128.0, 127.9, 127.6, 66.7, 34.9, 33.3, 31.8, 30.4, 29.6, 29.5, 29.4, 29.3, 29.0, 28.3, 22.6, 21.6, 14.1; **HRMS (**ESI-TOF**)** for $C_{30}H_{42}O_4S_2$ $[M+Na]^+$ calcd 553.2417, Found 553.2417.



7d

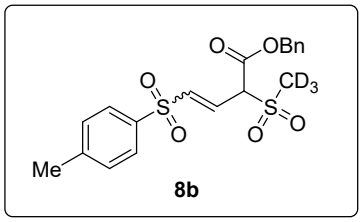
The reaction of the Thiosulfinat **5n** (0.2 mmol, 1 equiv.), allenes **2** (0.24 mmol, 1.2 equiv.), DABCO (0.02 mmol, 10 mol%) were added to DCM at -30 °C under N_2 atmosphere for 10 h. After the reaction was completed, DBU (0.4 mmol, 2 equiv.) was added for reacting with another 4 h afforded compound **7d** in 75% total yield of two-step (82.1 mg) as a yellow oil. The title compound **7d** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (Rf 0.5, petroleum ether/ethyl acetate = 3/1).（5ad）**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.72 (d, *J* = 8.9 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.25 – 7.15 (m, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.88 (s, 2H), 3.82 (s, 3H), 3.40 (s, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.41 – 1.24 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 163.3, 145.9, 135.3, 130.7, 130.2, 128.4, 128.1, 127.9, 114.2, 66.8, 55.6, 34.9, 33.3, 31.9, 30.5, 29.6, 29.5, 29.4, 29.3, 29.0, 28.4, 22.7, 14.1; **HRMS (**ESI-TOF**)** for $C_{30}H_{42}O_5S_2$ $[M+Na]^+$ calcd 569.2366, Found 569.2370.



8a

To a Schlenk tube under air atmosphere were added **3b** (0.2 mmol, 1 equiv.), *m*-CPBA (85%, 0.2 mmol, 1.0 equiv.), and DCM (2.0 mL). The system was stirred at room temperature for 4 h to afford **8a** (68.7 mg, 87 %, D-inc. >99.9% and 1:1 *dr*) as a colourless oil. The title compound **8a** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15/1 to 5/1). (Rf 0.5,

petroleum ether/ethyl acetate = 5/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 4.4 Hz, 2H), 7.60 (d, *J* = 4.4 Hz, 2H), 7.28 – 7.25 (m, 3H), 7.19 (d, *J* = 5.1 Hz, 2H), 7.11 – 7.08 (m, 2H), 6.68 (s, 1H), 6.46 (s, 1H), 4.98 – 4.88 (m, 2H), 4.46 (d, 1H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 145.1, 140.6, 135.0, 134.4, 131.6, 130.1, 128.6, 128.5, 128.4, 128.2, 68.3, 62.1, 21.6; **HRMS (**ESI-TOF**)** for $C_{19}H_{17}D_3O_5S_2$ $[M+Na]^+$ calcd 418.0833, Found 418.0833.

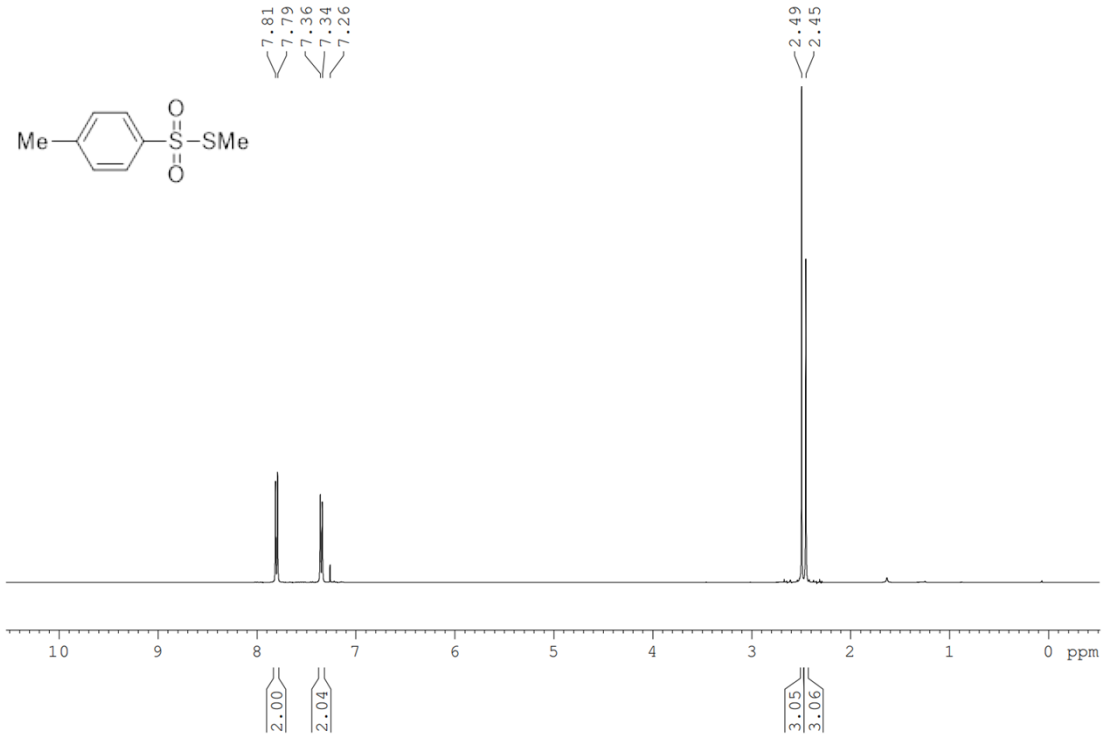


8b

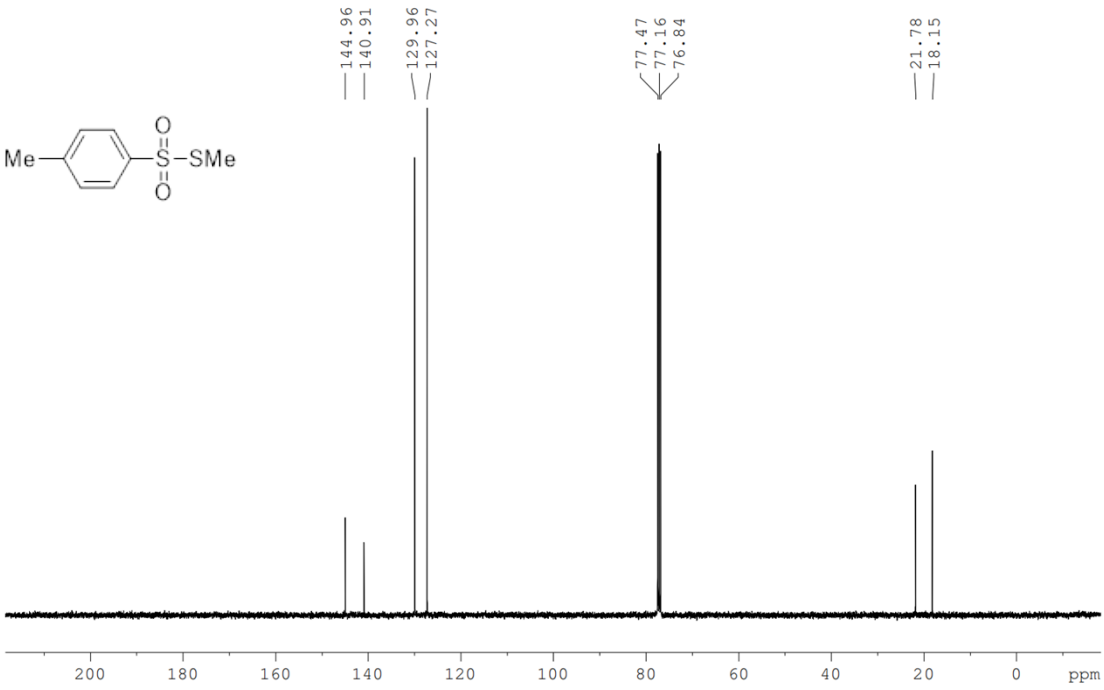
To a Schlenk tube under air atmosphere were added **3b** (0.2 mmol, 1 equiv.), *m*-CPBA (85%, 0.4 mmol, 2.0 equiv.), and DCM (2.0 mL). The system was stirred at room temperature for 10 h to afford **8b** (65.8 mg, 80 %, D-inc. >99.9%) as a colourless oil.The title compound **8b** was isolated through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 4/1). (Rf 0.4, petroleum ether/ethyl acetate = 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.31 (s, 7H), 7.15 (s, 1H), 5.22 (s, 2H), 5.17 (s, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 148.9, 146.0, 134.5, 134.4, 131.7, 130.3, 129.0, 128.9, 128.8, 128.7, 68.0, 60.6, 21.7; **HRMS (**ESI-TOF**)** for $C_{19}H_{17}D_3O_6S_2$ $[M+Na]^+$ calcd 434.0782, Found 434.0781.

VIII. Copies of ^{1}H ,^{13}C, ^{19}F and 2D spectrum of compounds

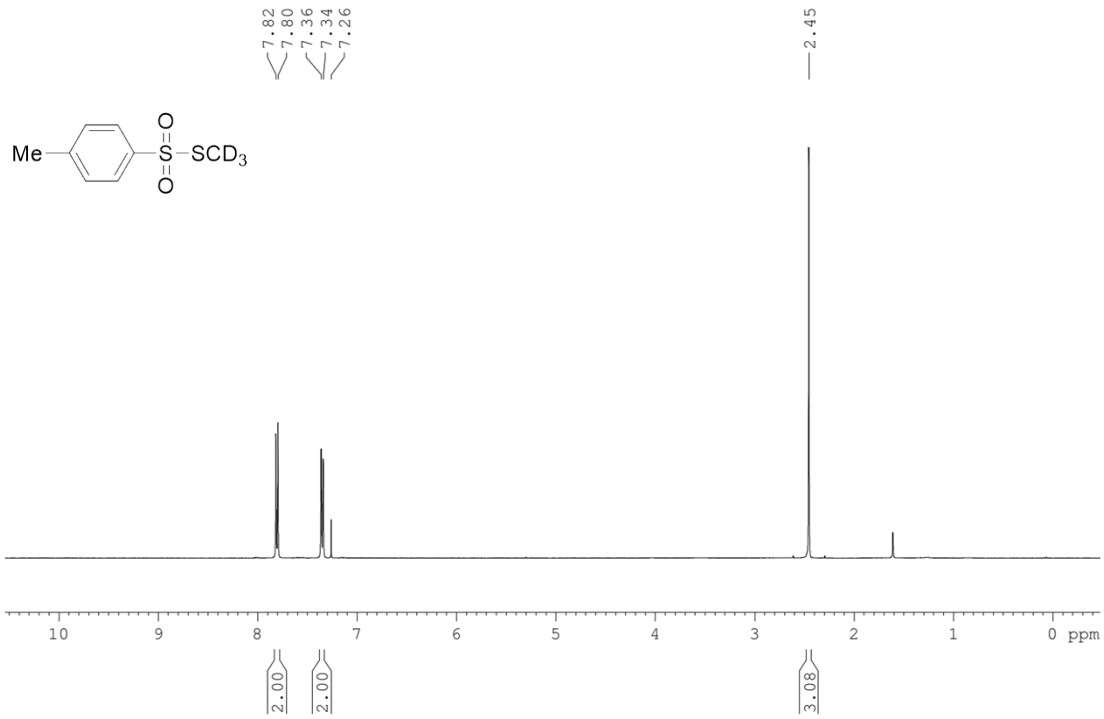
^{1}H NMR Spectrum of S-methylthiolating reagent **1a (400** MHz, $CDCl_3$)



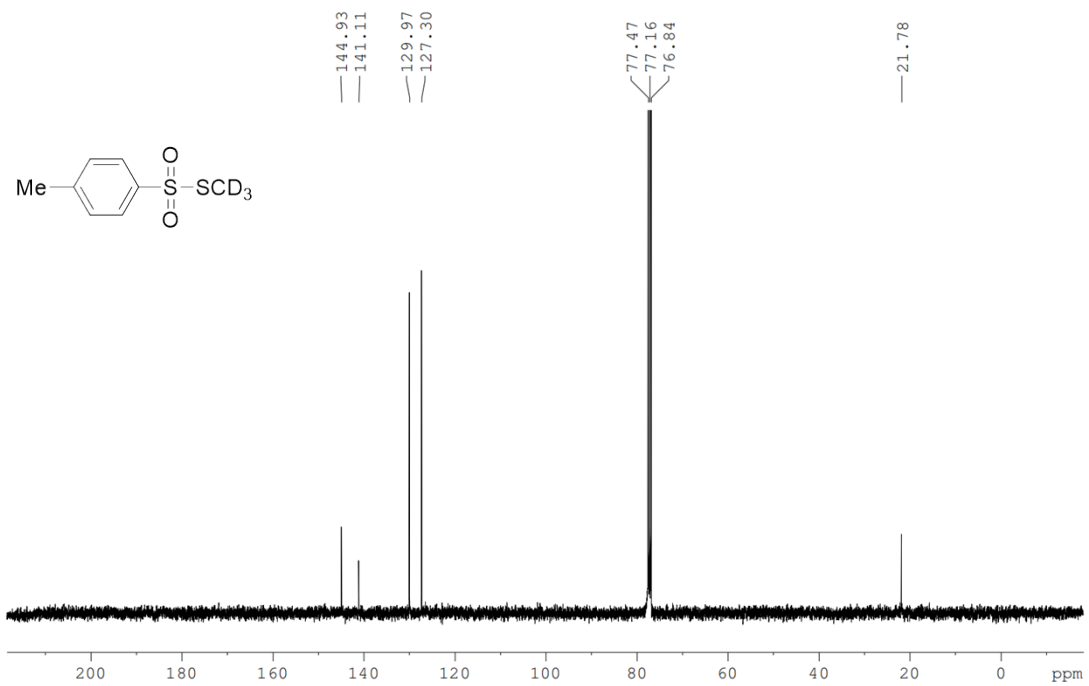
^{13}C NMR Spectrum of S-methylthiolating reagent **1a (100** MHz, $CDCl_3$)



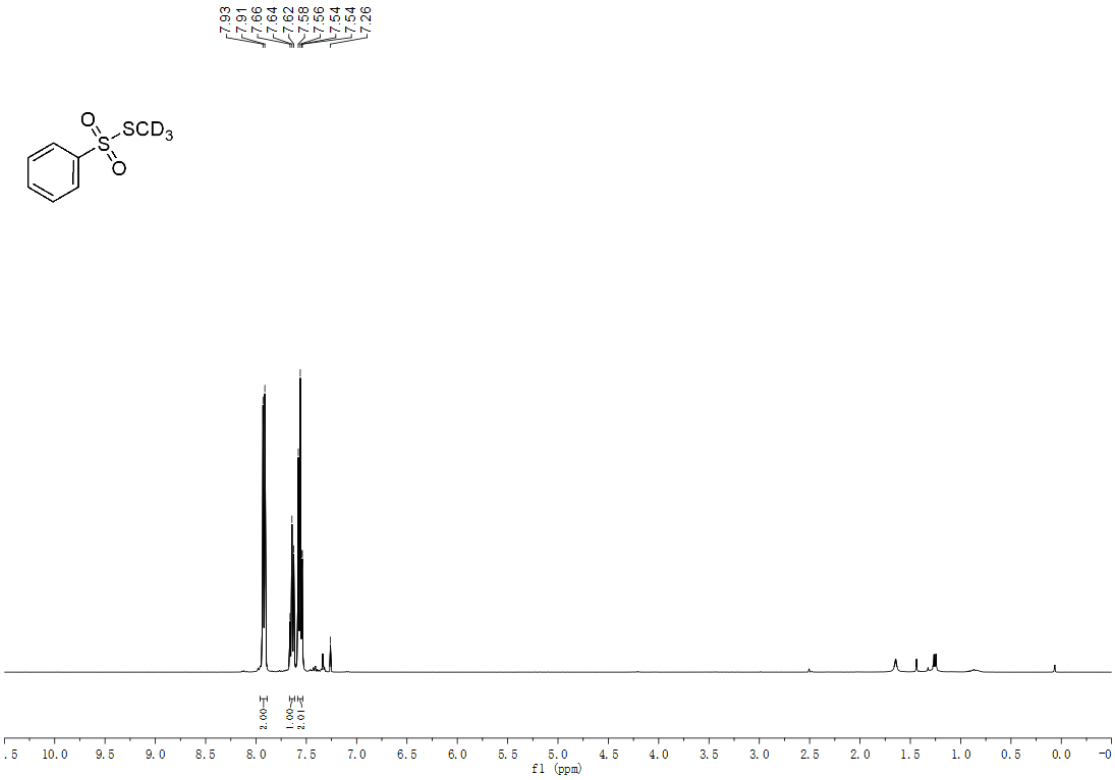
^{1}H NMR Spectrum of S-methylthiolating reagent **1b (400** MHz, $CDCl_3$)



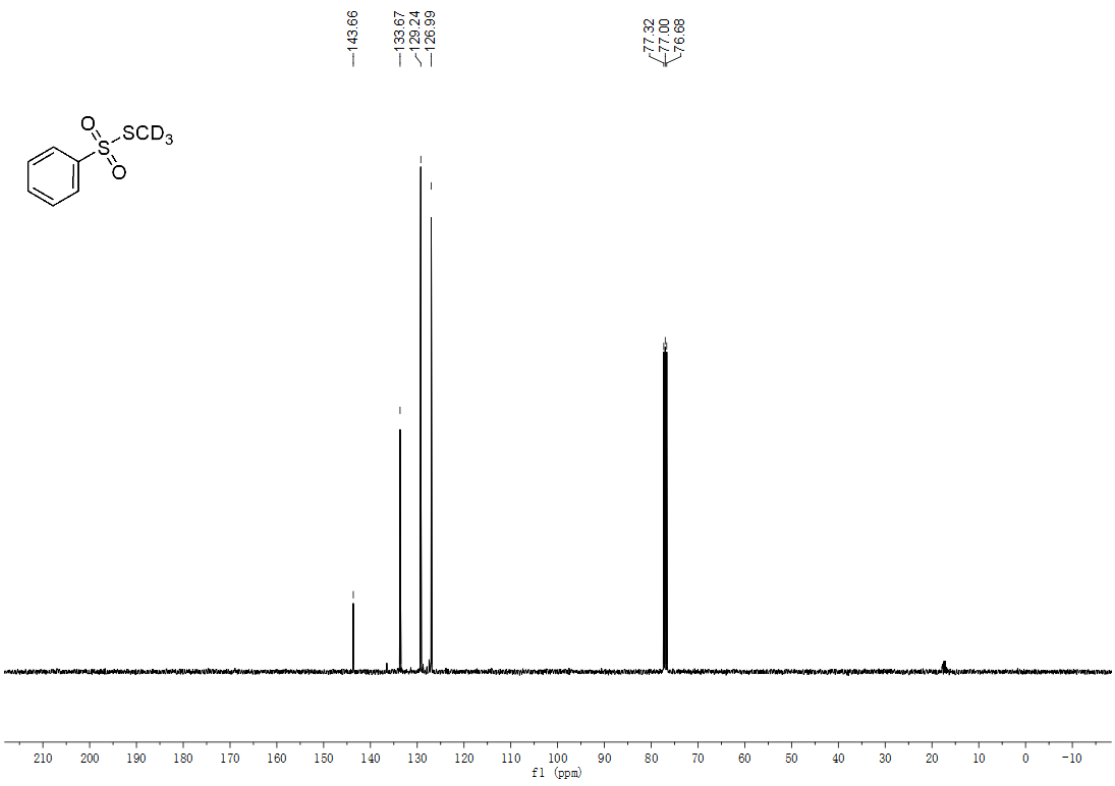
^{13}C NMR Spectrum of S-methylthiolating reagent **1b (100** MHz, $CDCl_3$)



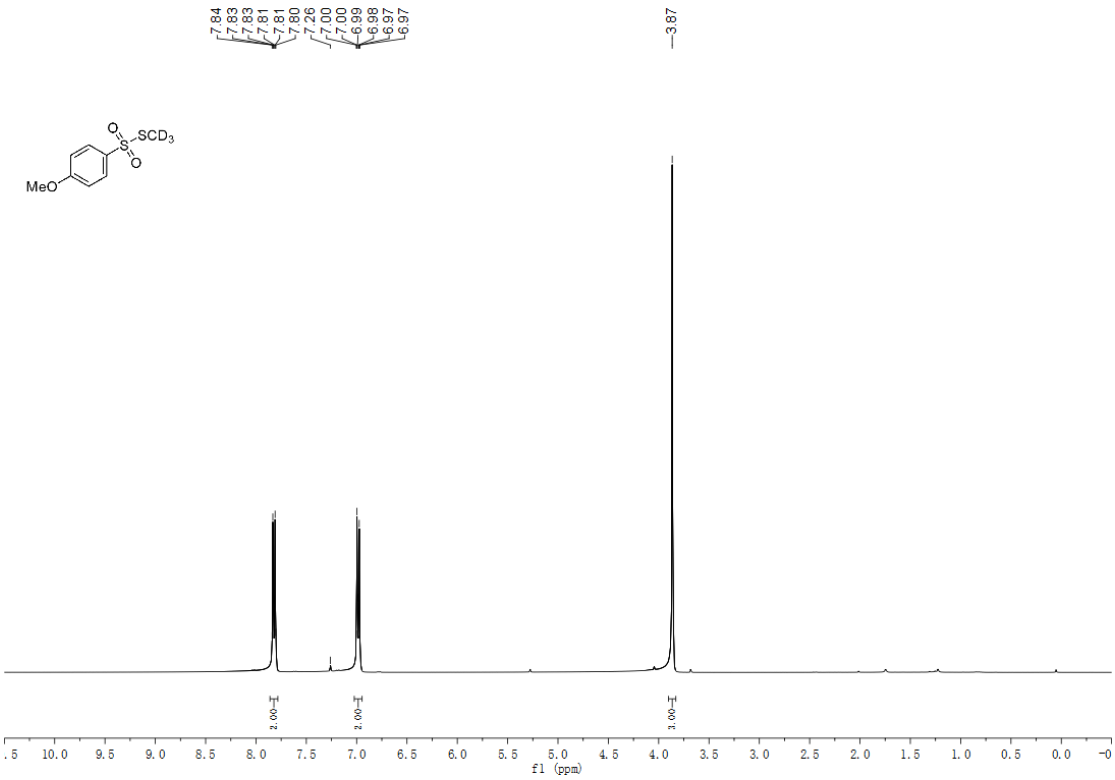
^{1}H NMR Spectrum of S-methylthiolating reagent **1c (400** MHz, $CDCl_3$)



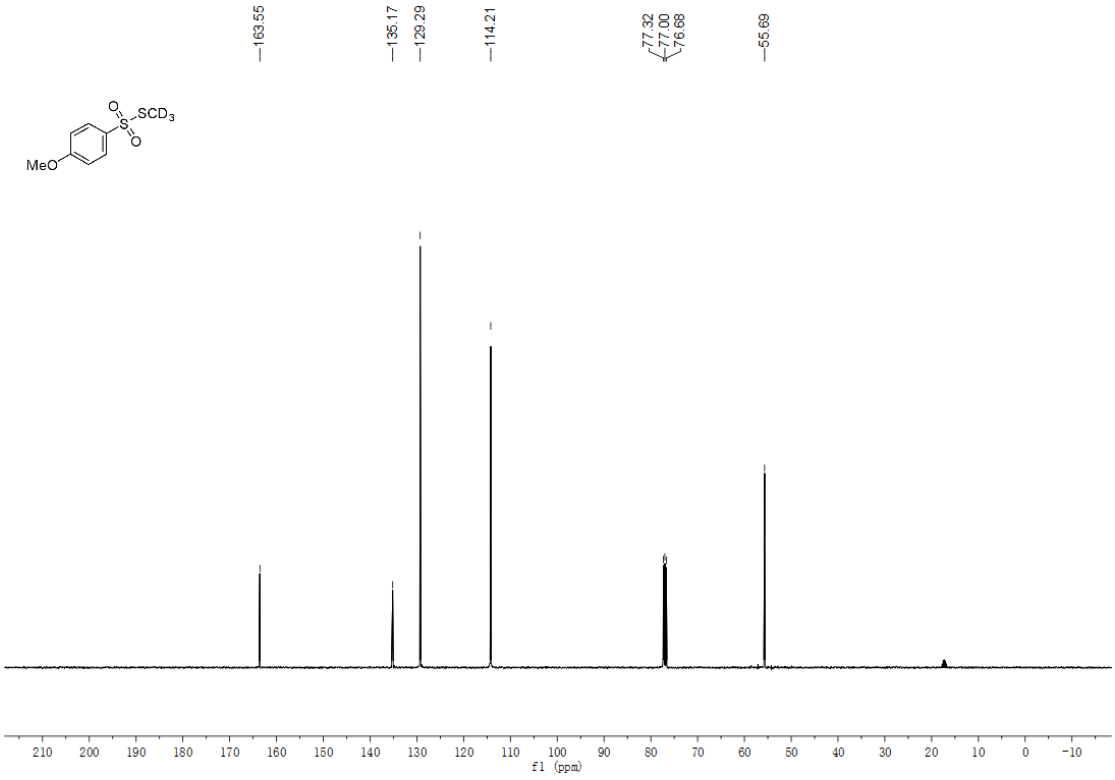
^{13}C NMR Spectrum of S-methylthiolating reagent **1c (100** MHz, $CDCl_3$)



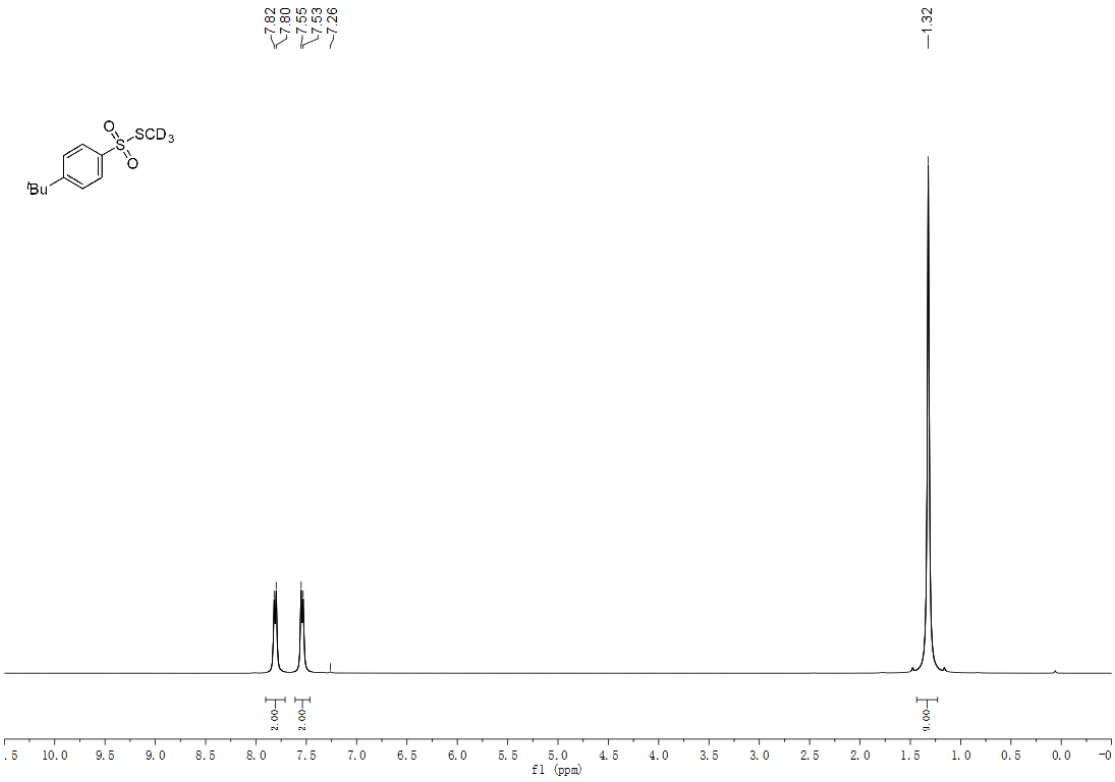
^{1}H NMR Spectrum of S-methylthiolating reagent **1d** (**400** MHz, $CDCl_3$)



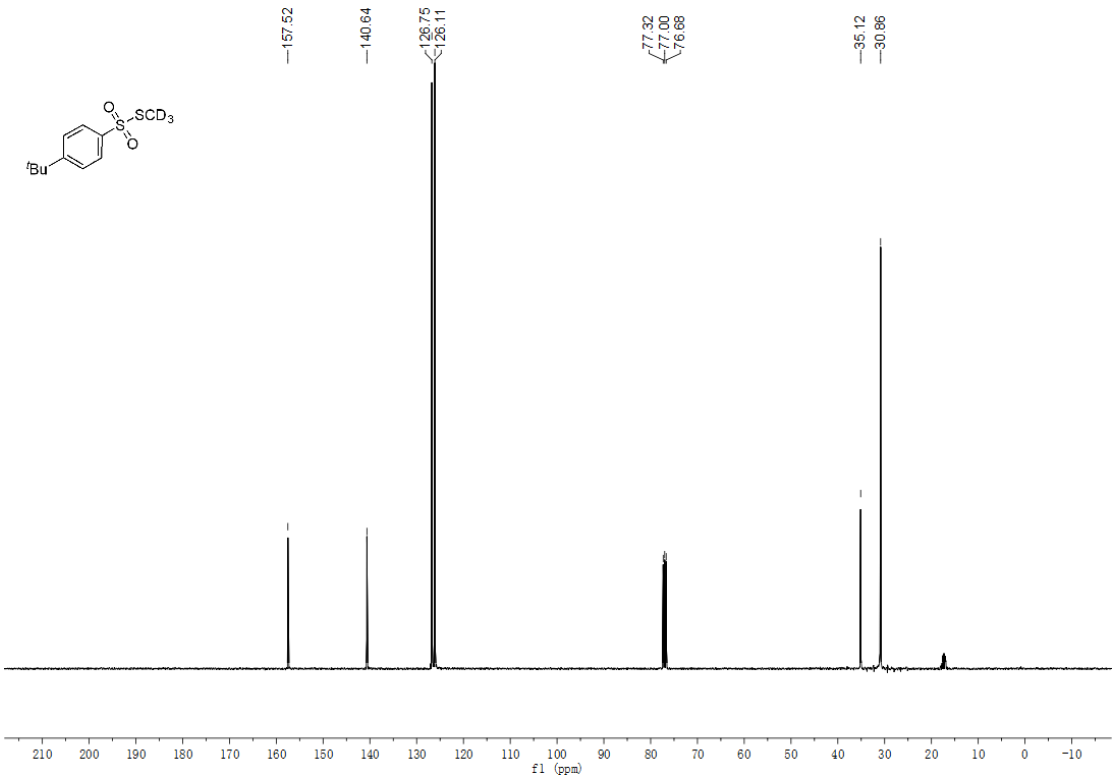
^{13}C NMR Spectrum of S-methylthiolating reagent **1d** (**100** MHz, $CDCl_3$)



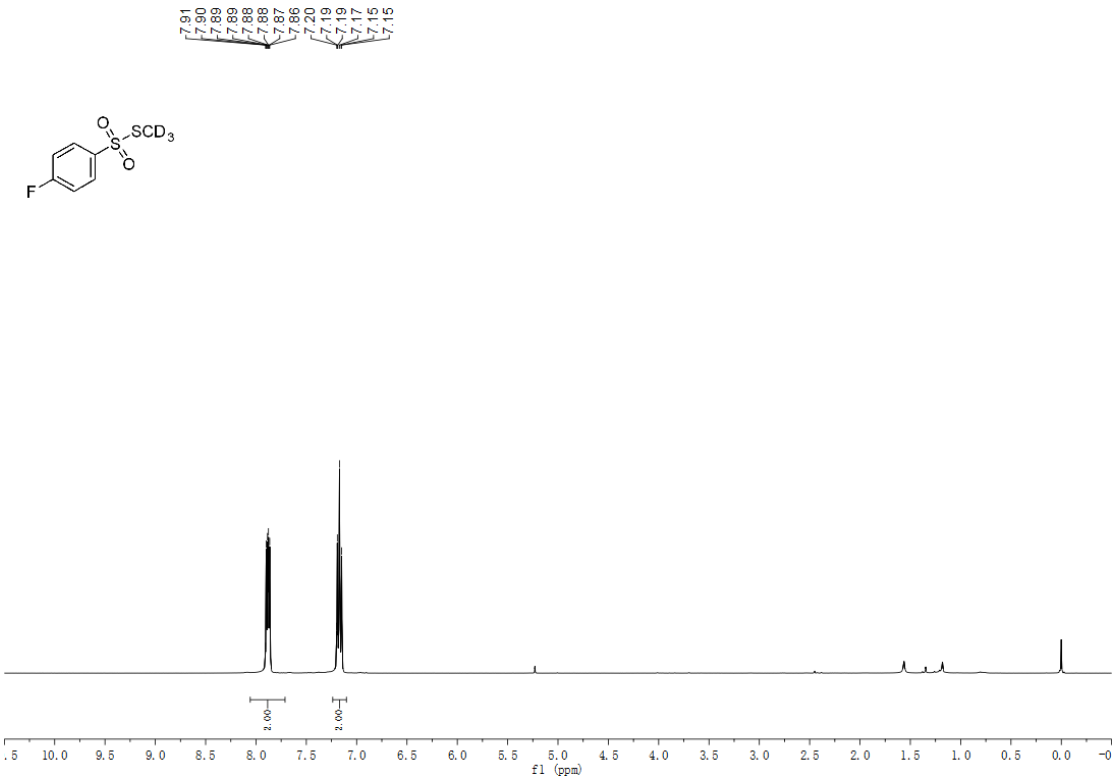
^{1}H NMR Spectrum of S-methylthiolating reagent **1e** (**400** MHz, $CDCl_3$)



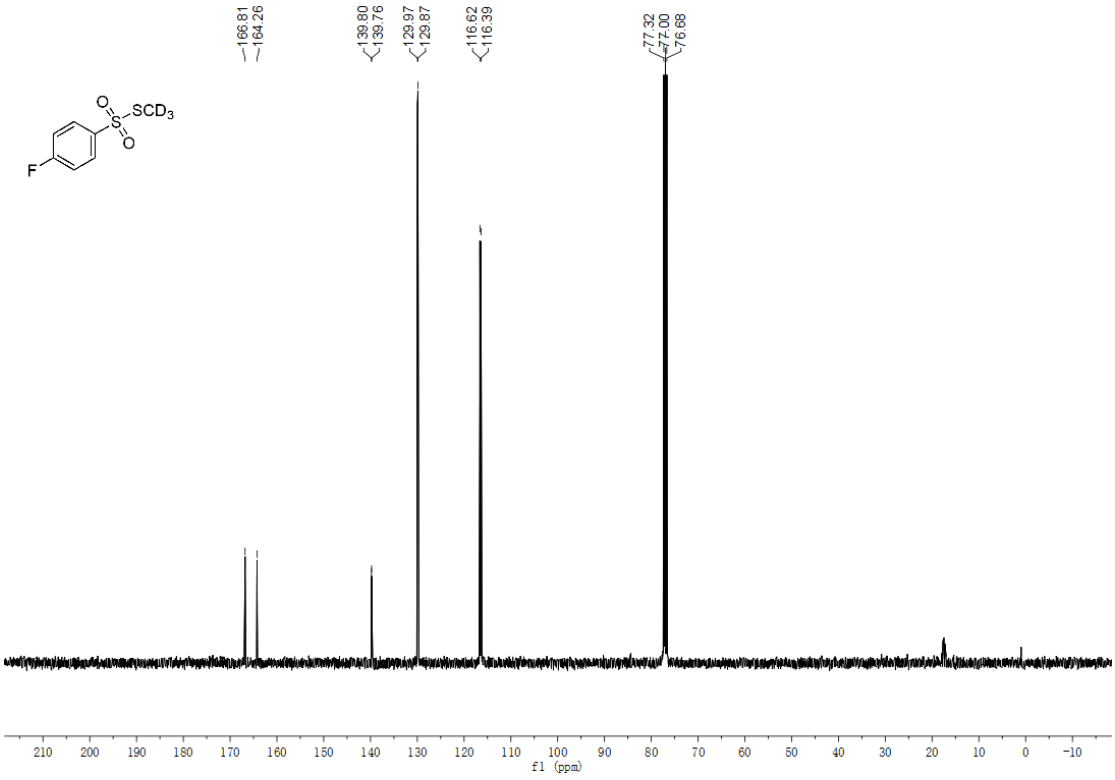
^{13}C NMR Spectrum of S-methylthiolating reagent **1e** (**100** MHz, $CDCl_3$)



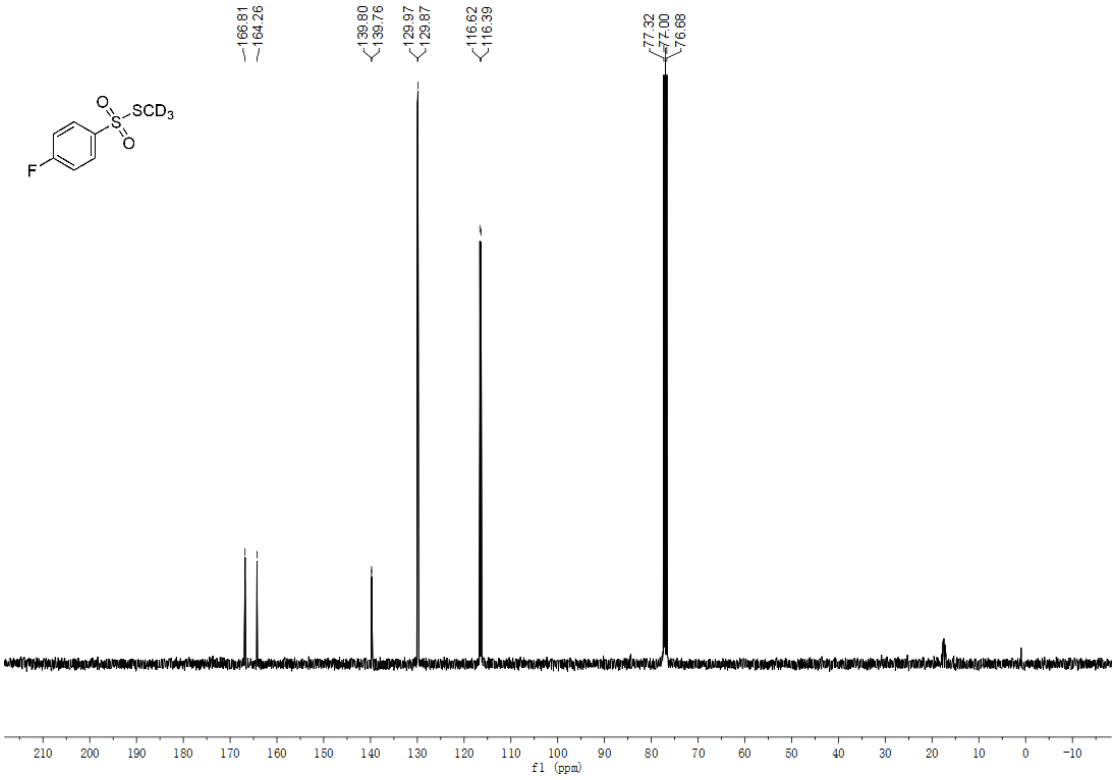
^{1}H NMR Spectrum of S-methylthiolating reagent **1f (400** MHz, $CDCl_3$)



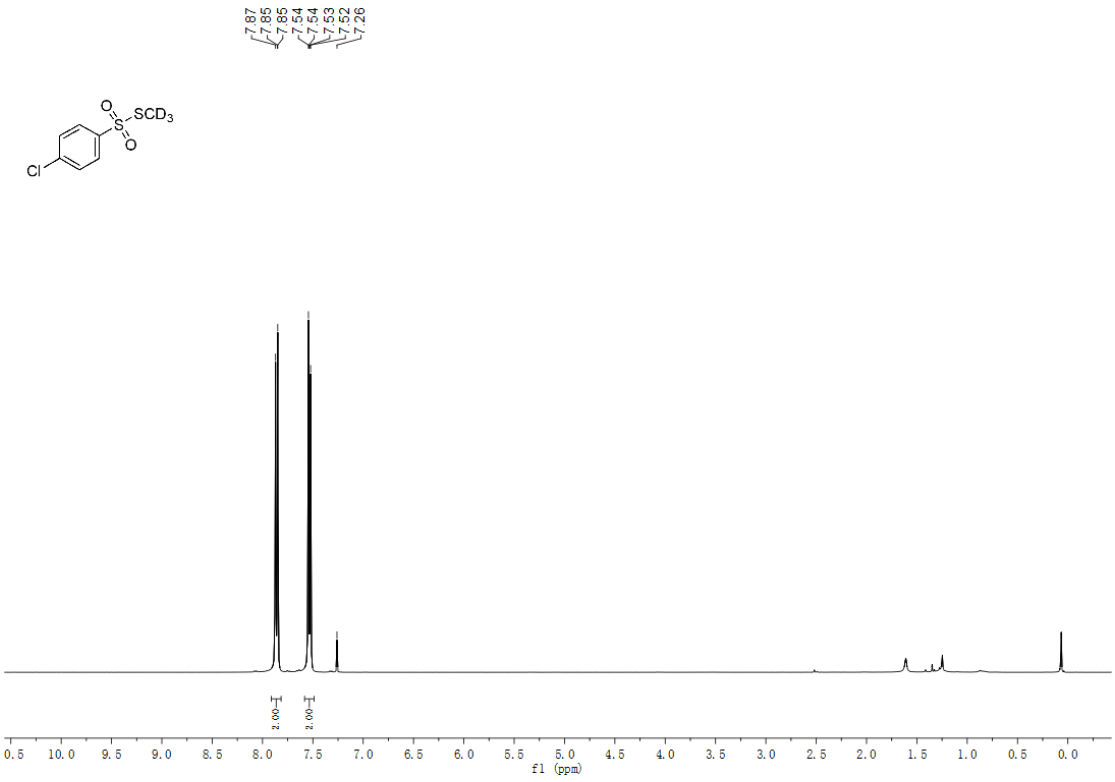
^{13}C NMR Spectrum of S-methylthiolating reagent **1f (400** MHz, $CDCl_3$)



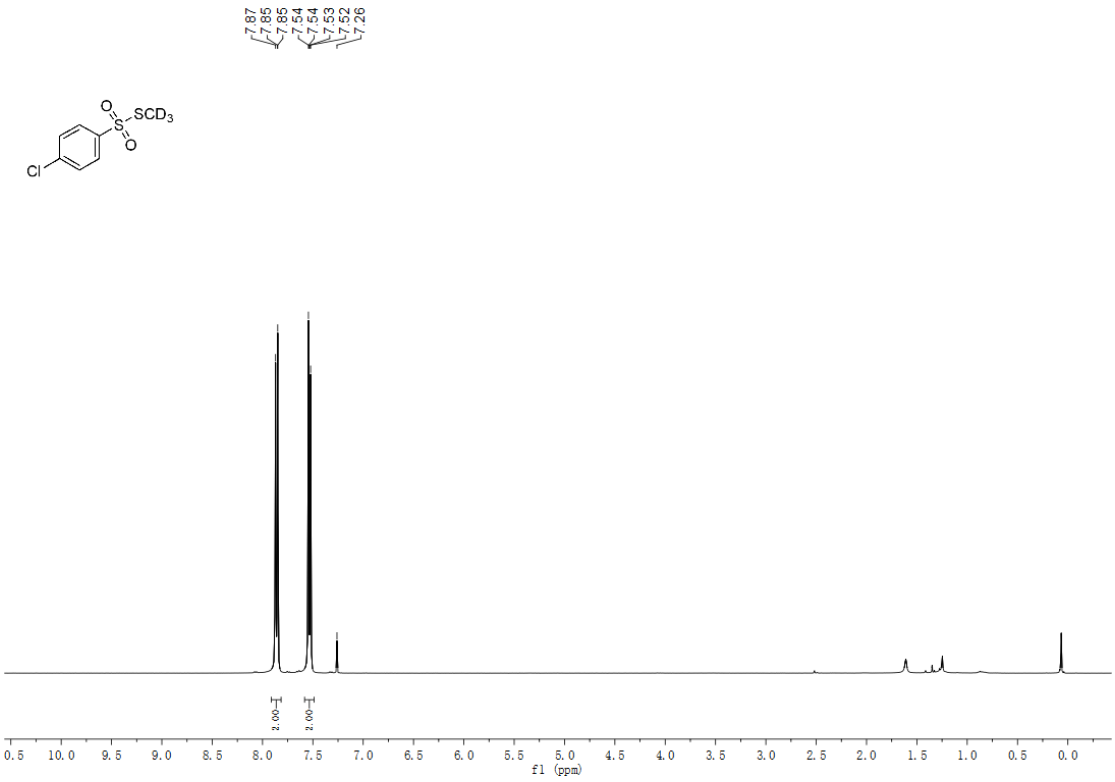
^{19}F NMR Spectrum of S-methylthiolating reagent **1f (376** MHz, $CDCl_3$)



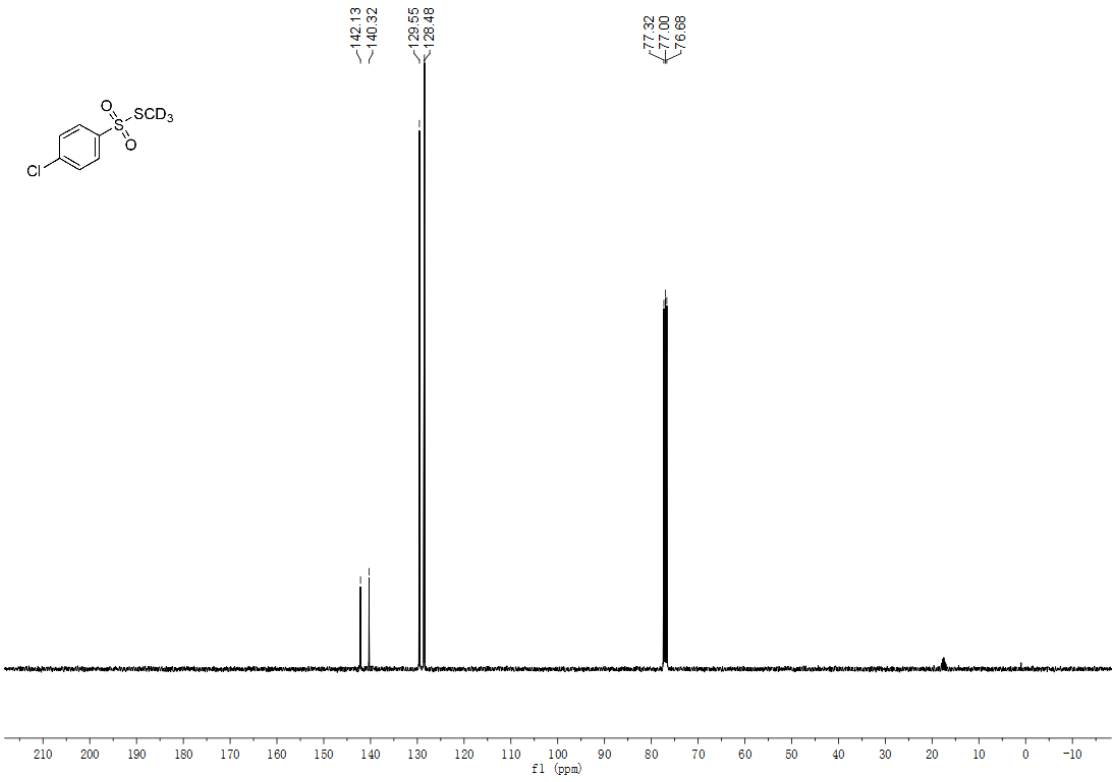
^{1}H NMR Spectrum of S-methylthiolating reagent **1g (400** MHz, $CDCl_3$)



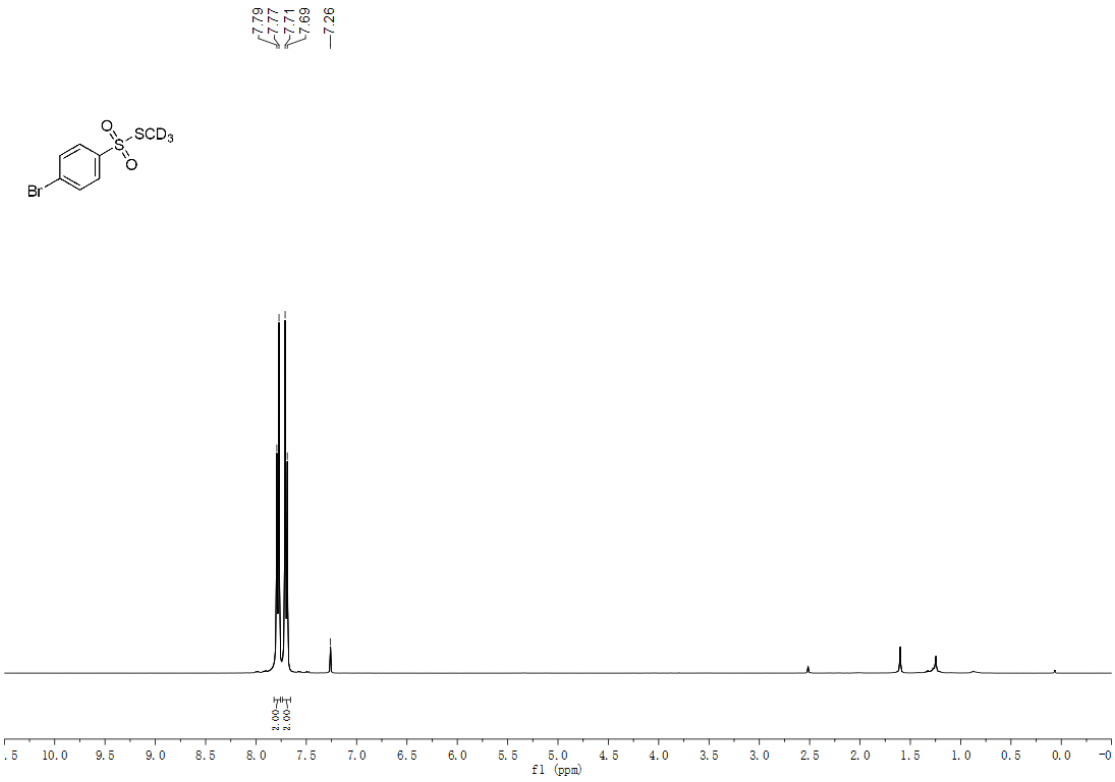
^{1}H NMR Spectrum of S-methylthiolating reagent **1g (400** MHz, $CDCl_3$)



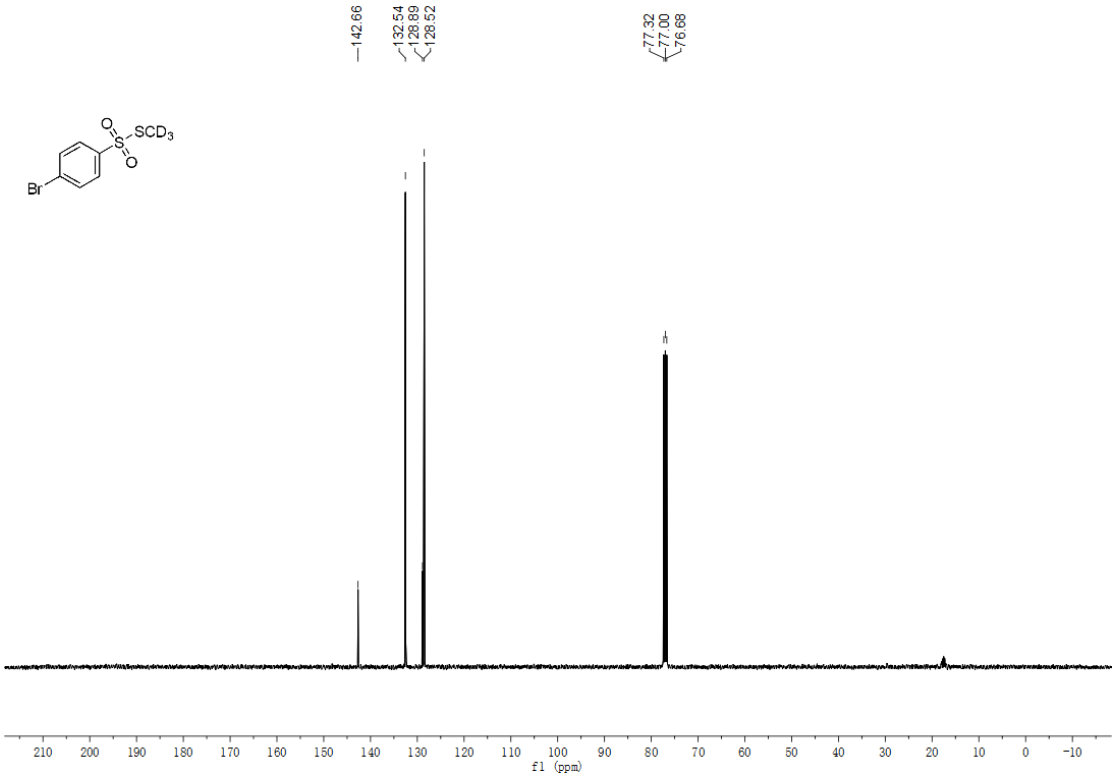
^{13}C NMR Spectrum of S-methylthiolating reagent **1g (100** MHz, $CDCl_3$)



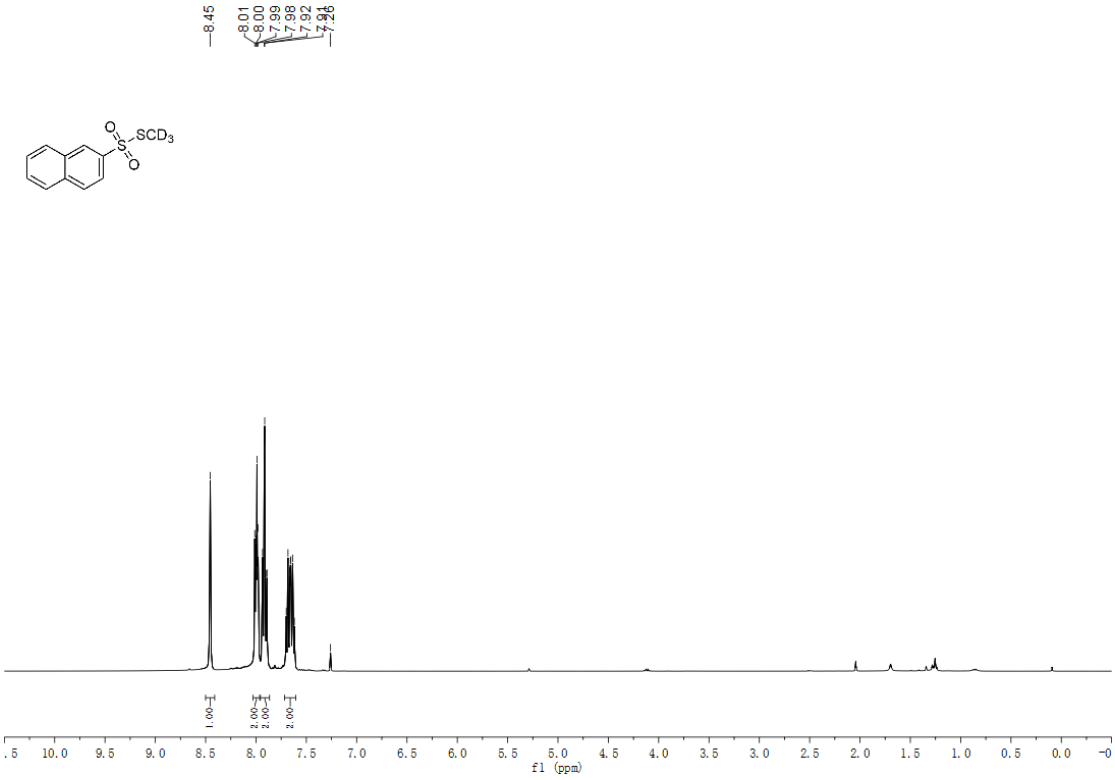
^{1}H NMR Spectrum of S-methylthiolating reagent **1h (400** MHz, $CDCl_3$)



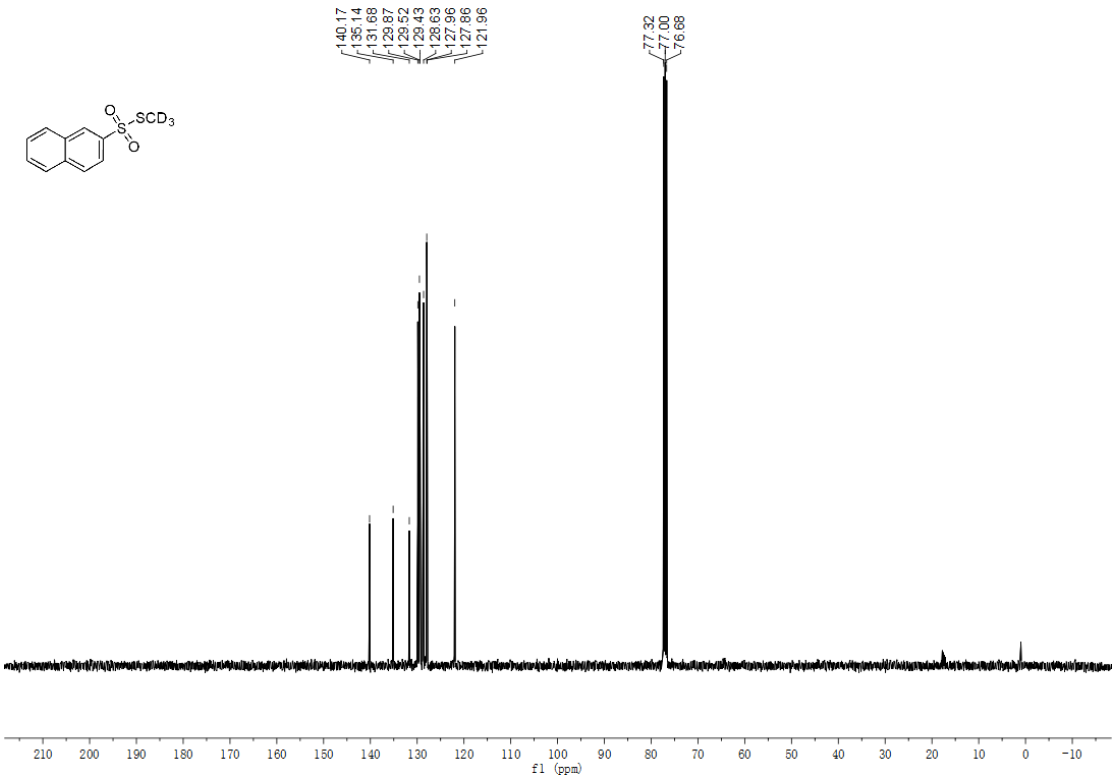
^{13}C NMR Spectrum of S-methylthiolating reagent **1h (100** MHz, $CDCl_3$)



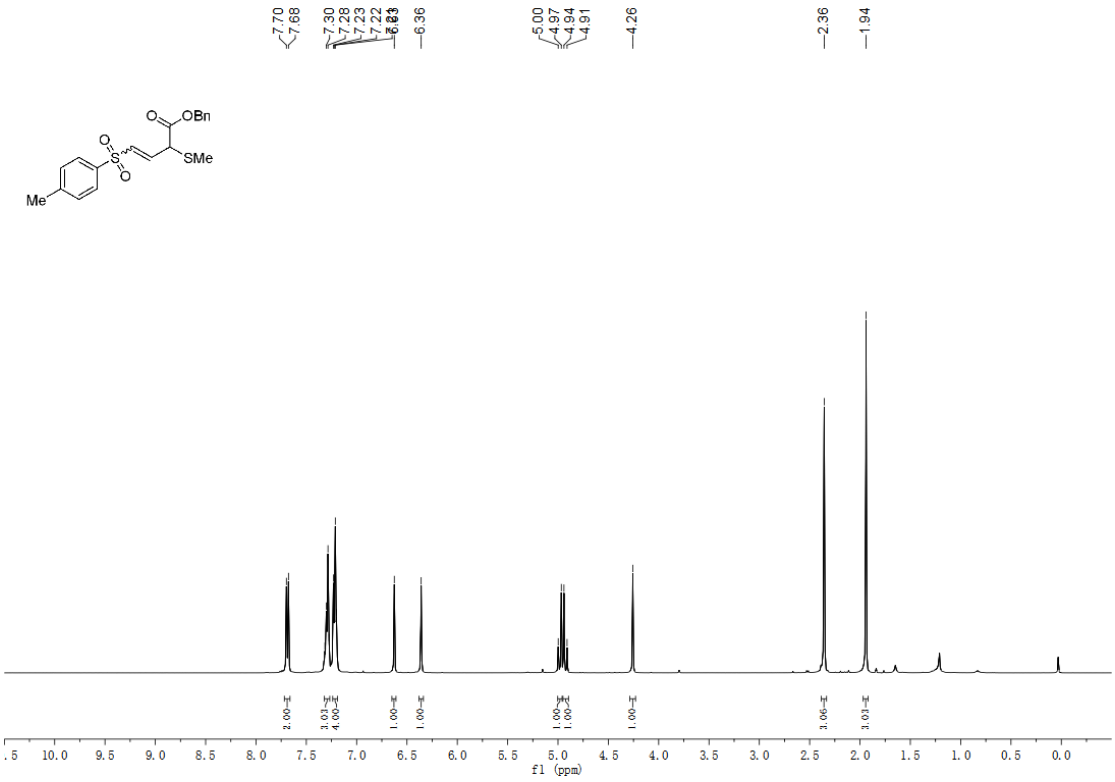
^{1}H NMR Spectrum of S-methylthiolating reagent **1i (400** MHz, $CDCl_3$)



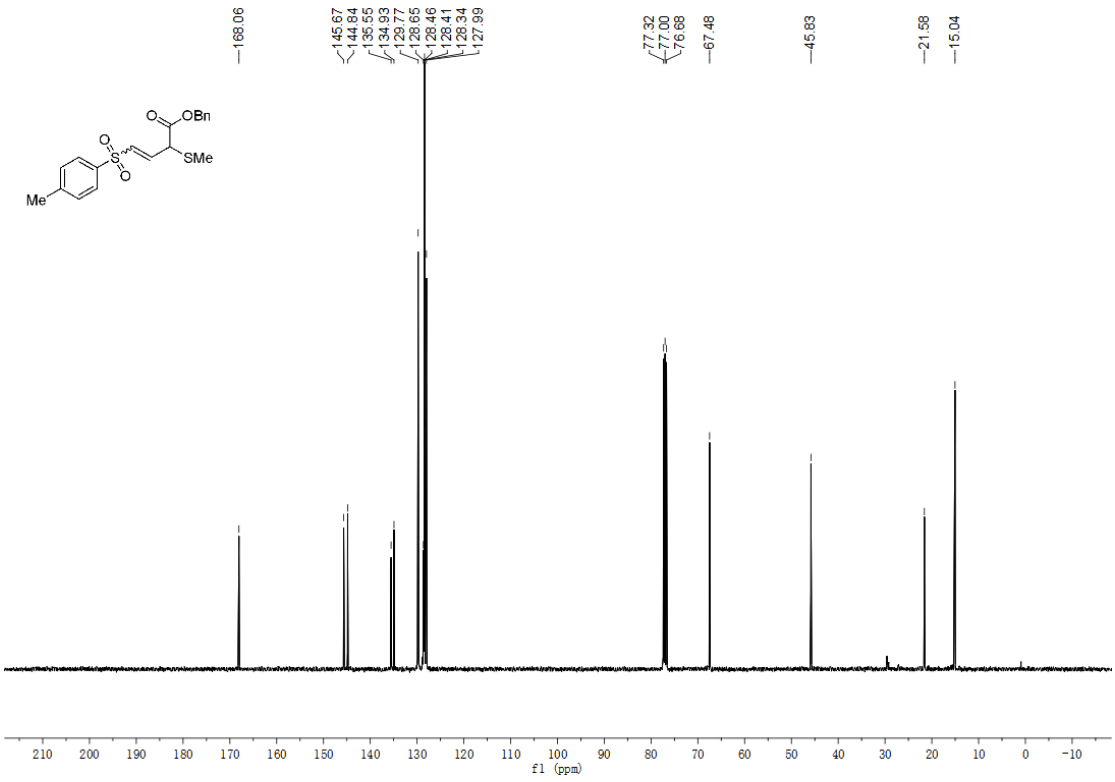
^{13}C NMR Spectrum of S-methylthiolating reagent **1i (100** MHz, $CDCl_3$)



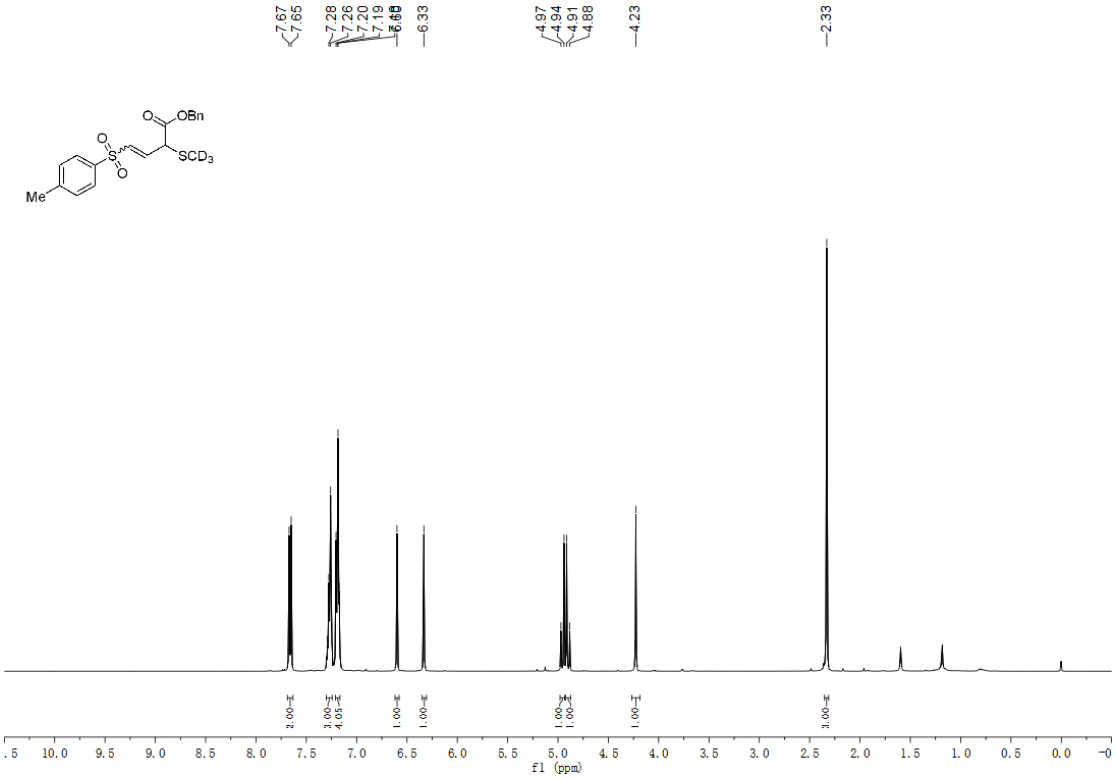
^{1}H NMR Spectrum of compound **3a (400** MHz, $CDCl_3$)



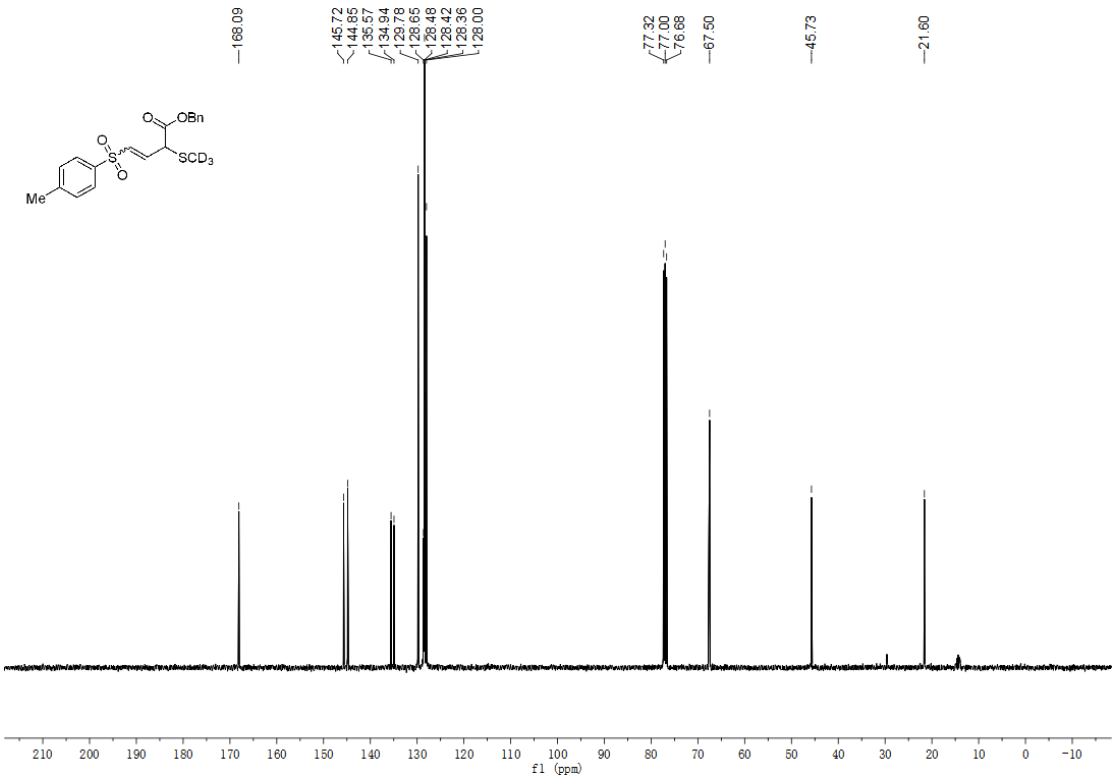
^{13}C NMR Spectrum of compound **3a (100** MHz, $CDCl_3$)



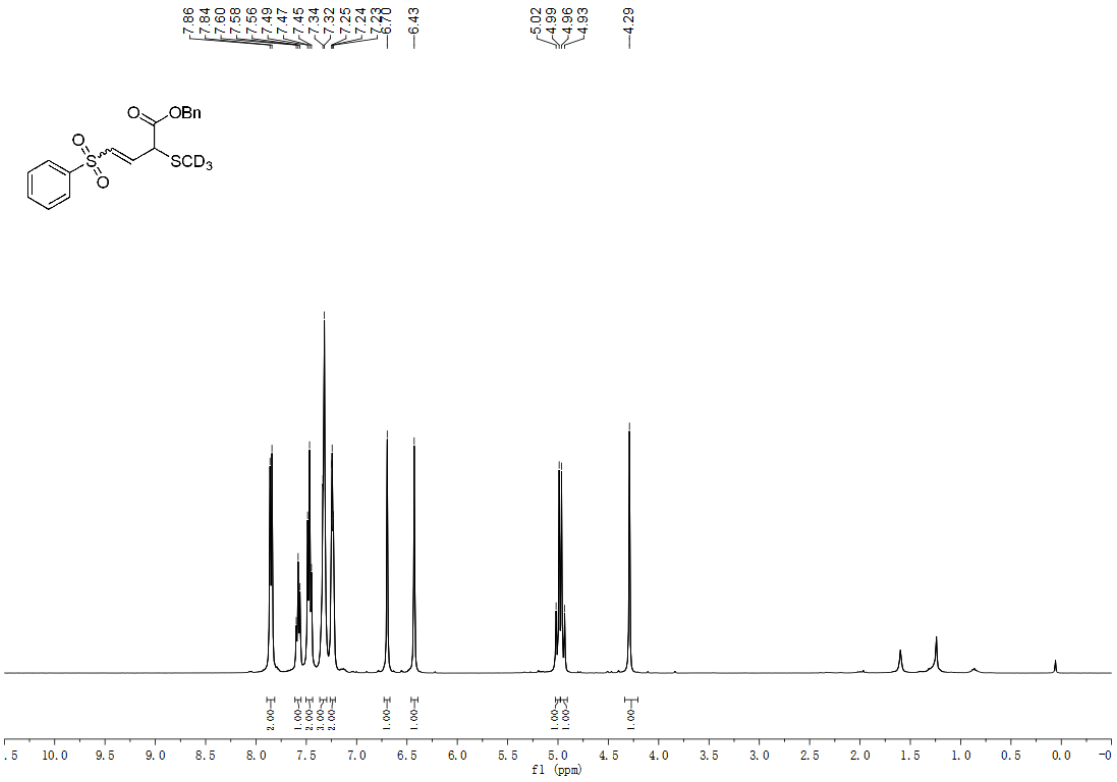
^{1}H NMR Spectrum of compound **3b (400** MHz, $CDCl_3$)



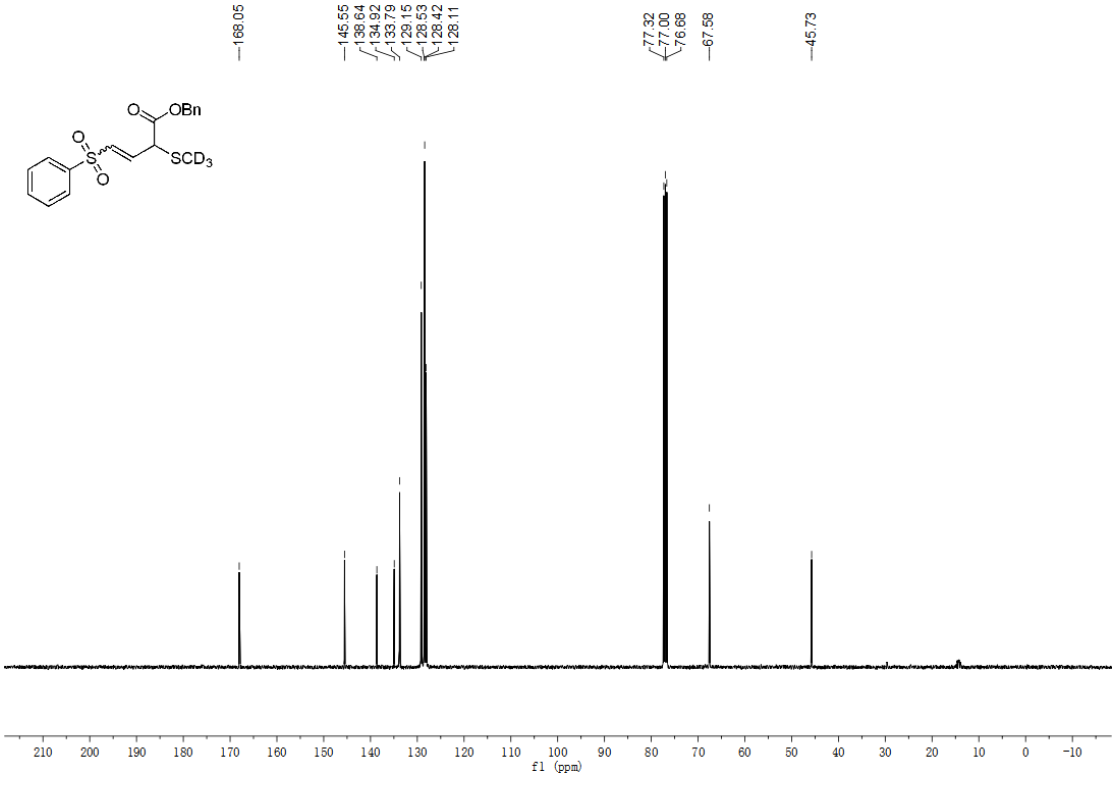
^{13}C NMR Spectrum of compound **3b (100** MHz, $CDCl_3$)



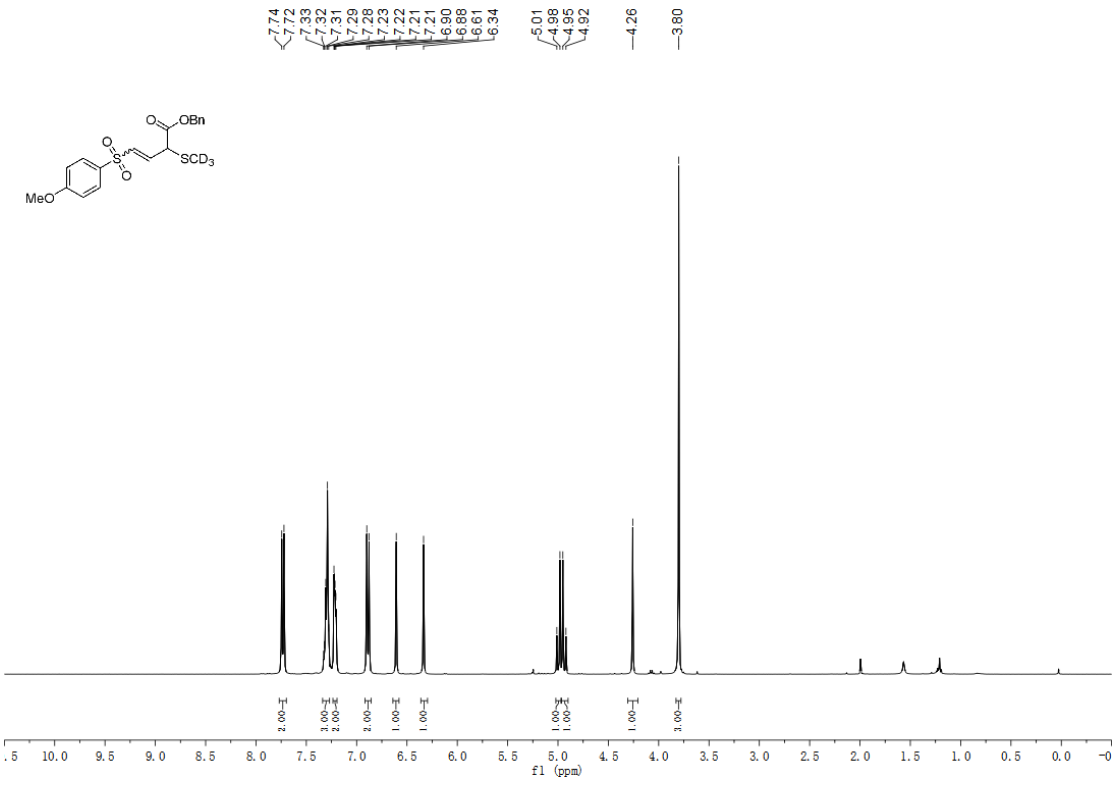
^{1}H NMR Spectrum of compound **3c** (**400** MHz, $CDCl_3$)



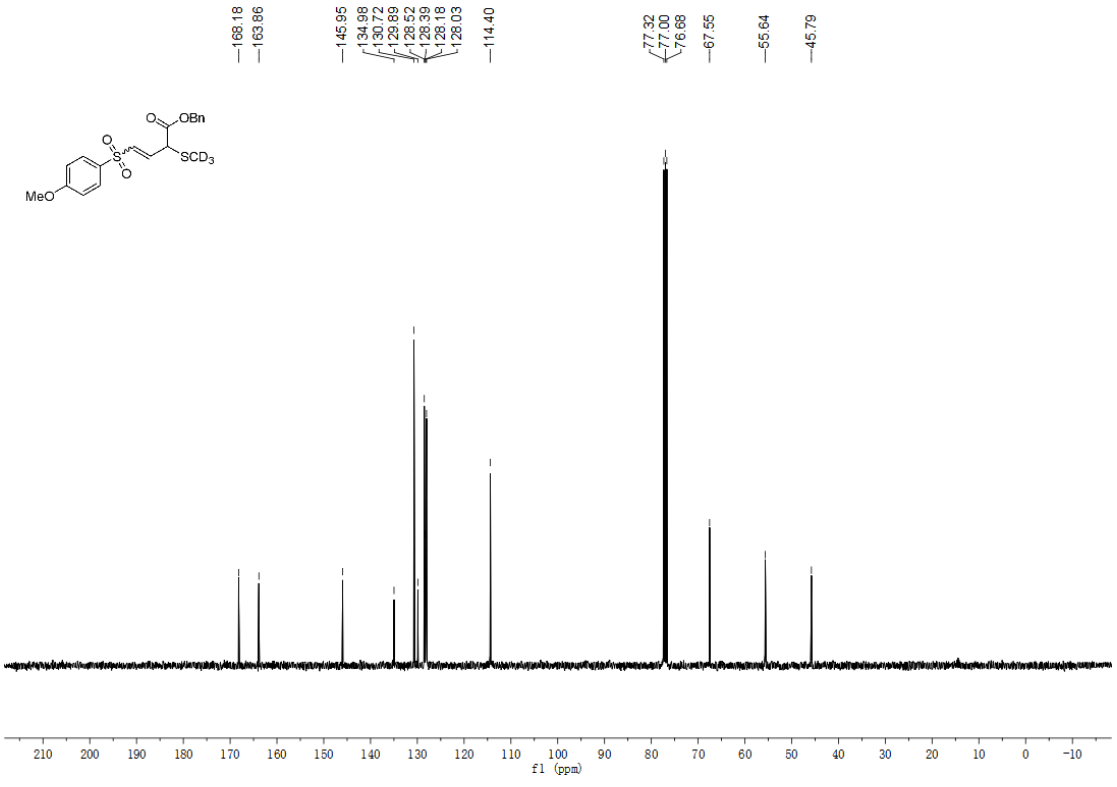
^{13}C NMR Spectrum of compound **3c** (**100** MHz, $CDCl_3$)



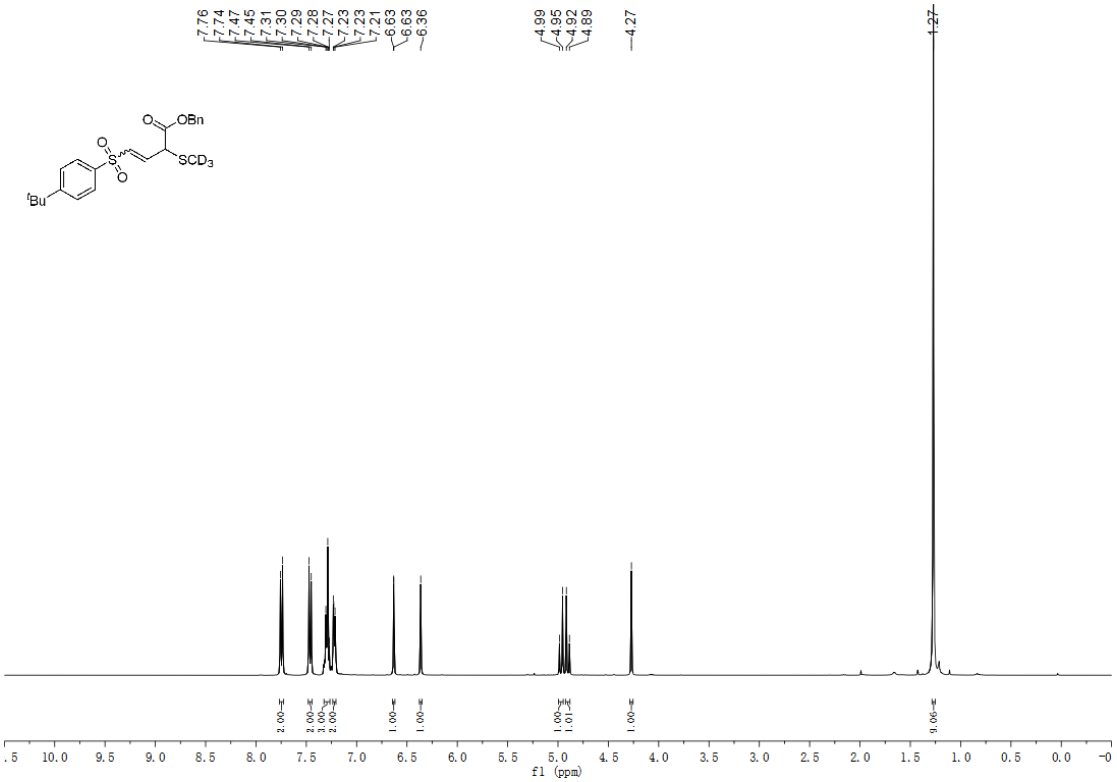
^{1}H NMR Spectrum of compound **3d (400** MHz, $CDCl_3$)



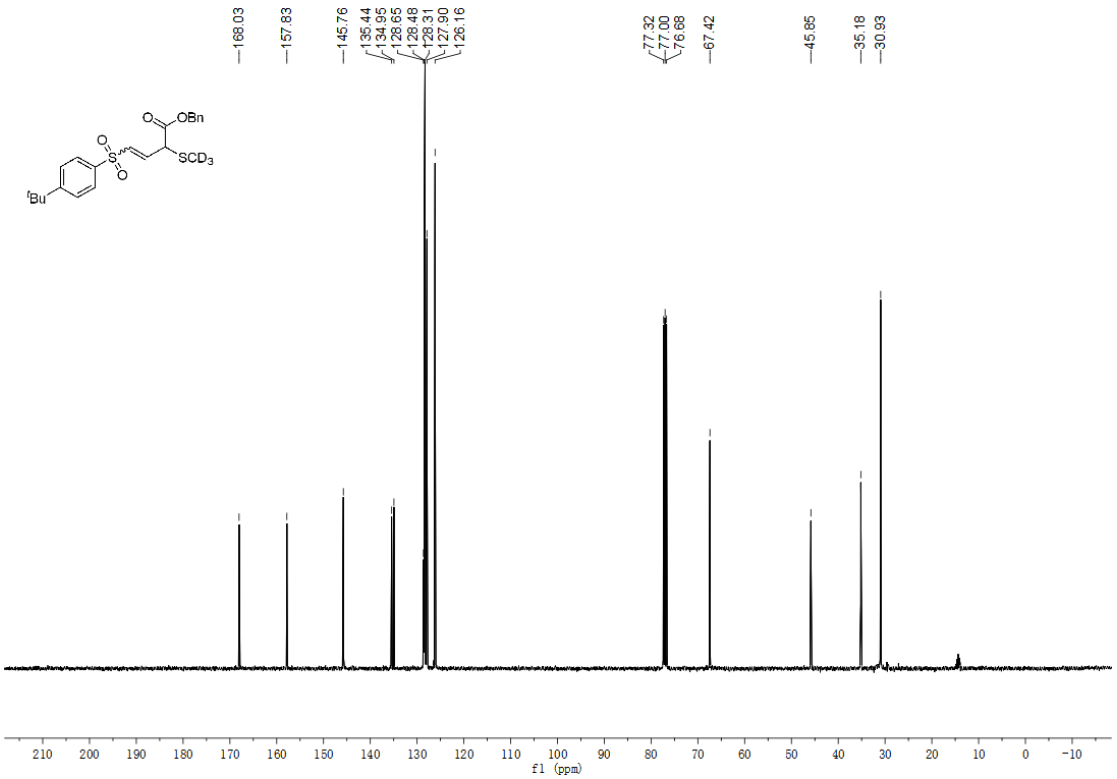
^{13}C NMR Spectrum of compound **3d (100** MHz, $CDCl_3$)



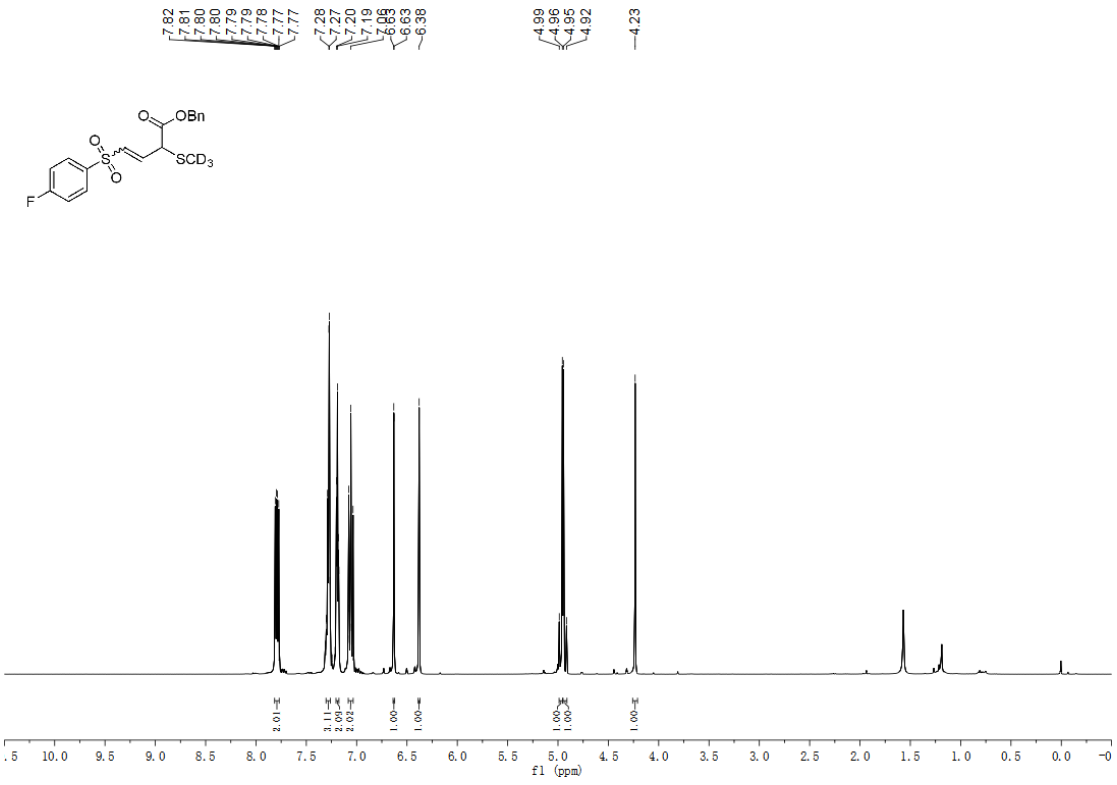
^{1}H NMR Spectrum of compound **3e** (**100** MHz, $CDCl_3$)



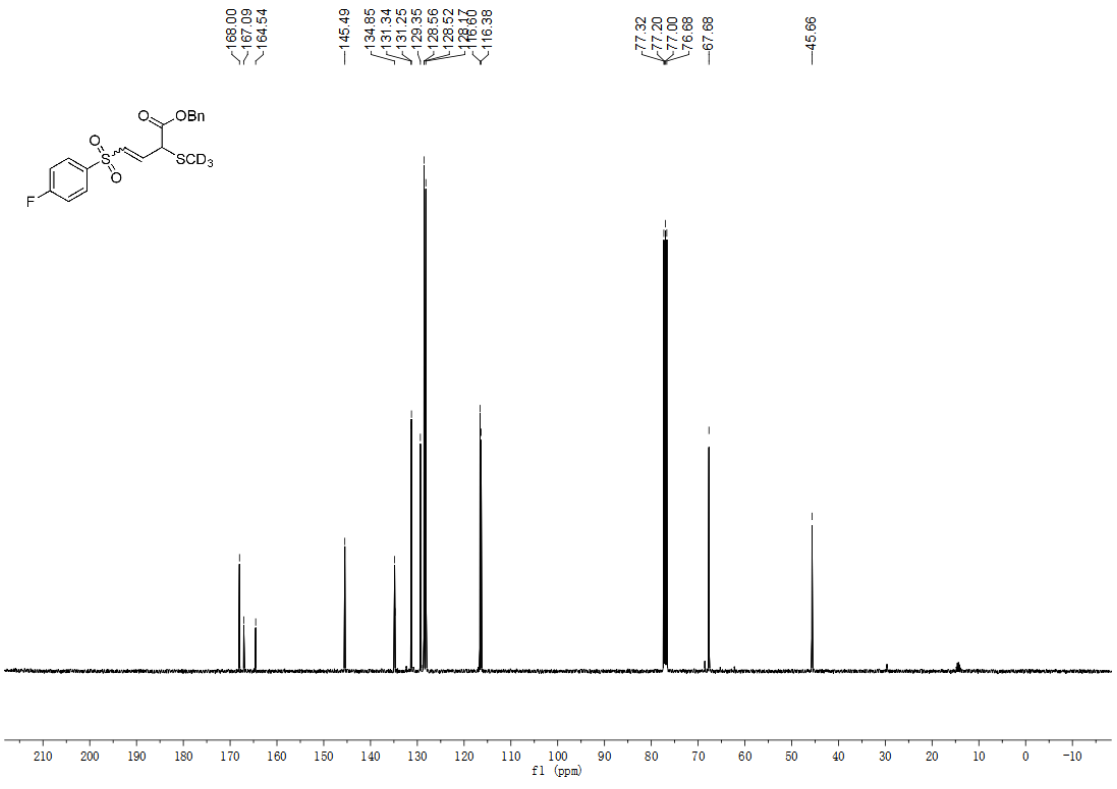
^{13}C NMR Spectrum of compound **3e** (**100** MHz, $CDCl_3$)



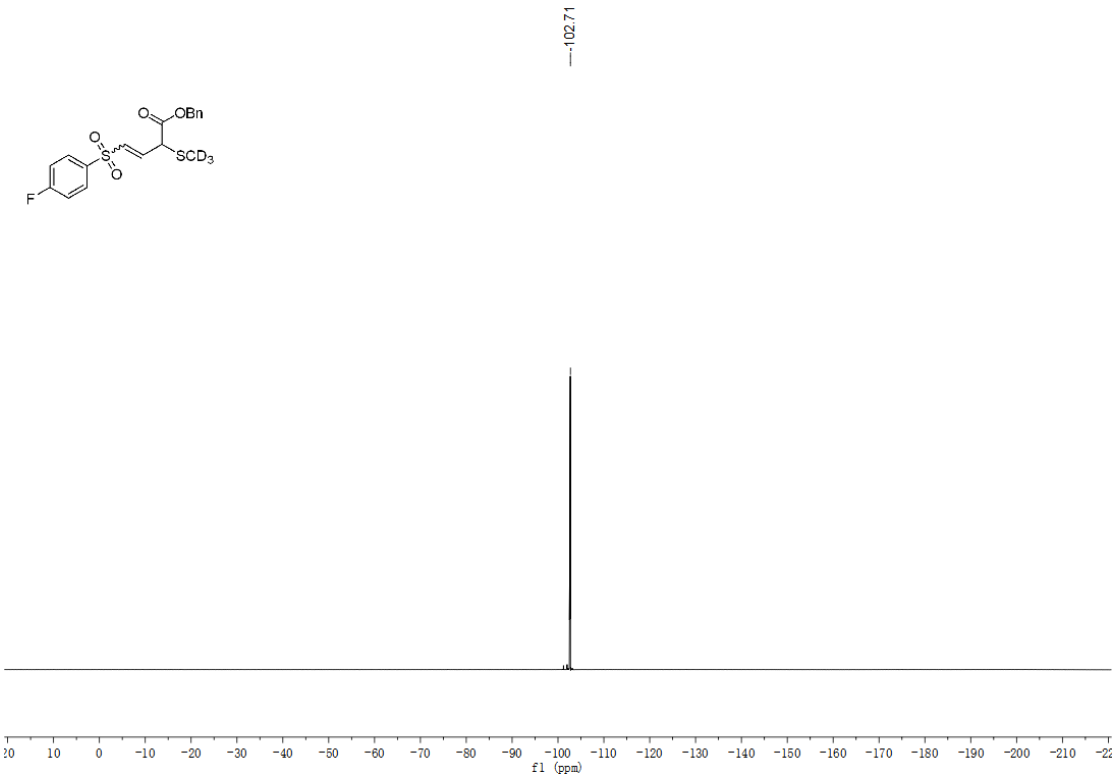
^{1}H NMR Spectrum of compound **3f (400** MHz, $CDCl_3$)



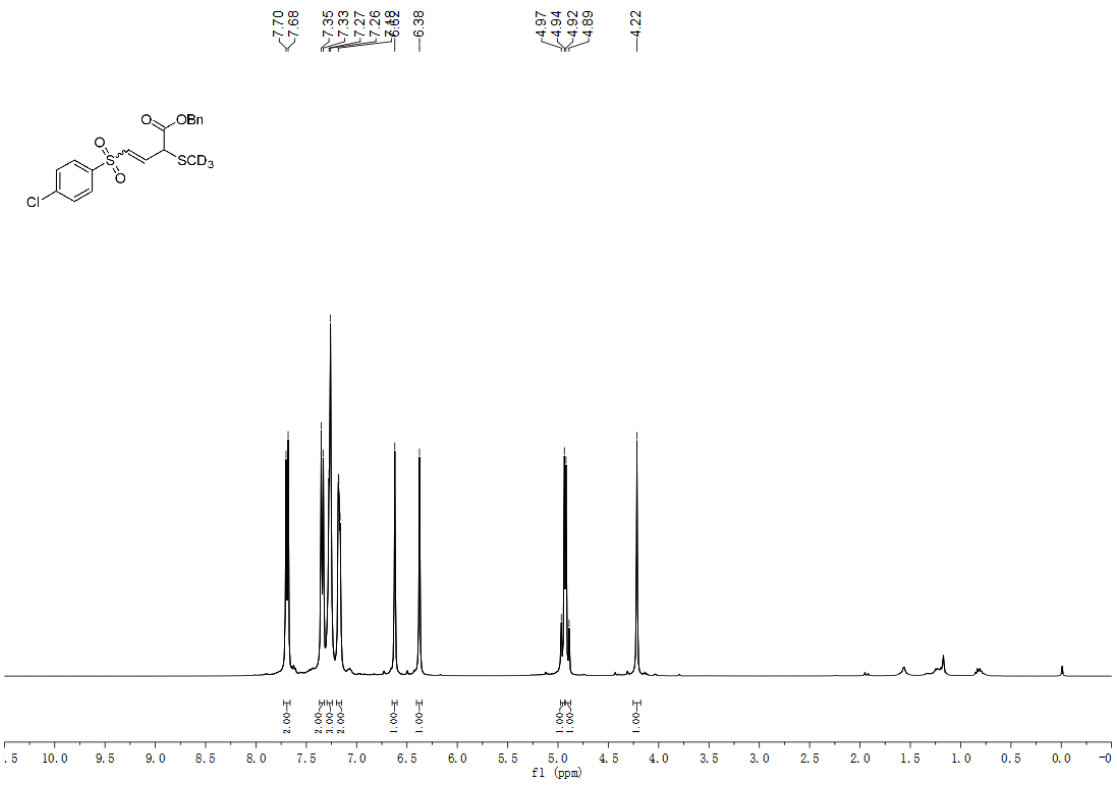
^{13}C NMR Spectrum of compound **3f (100** MHz, $CDCl_3$)



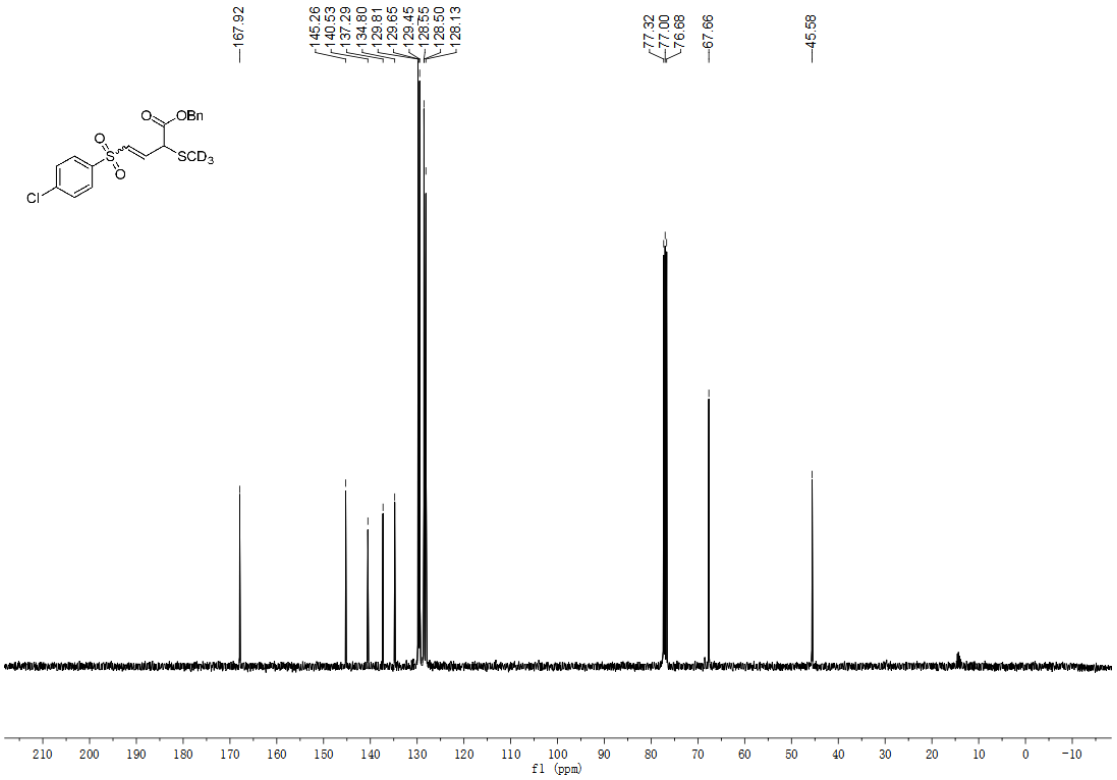
^{19}F NMR Spectrum of compound **3f (376** MHz, $CDCl_3$)



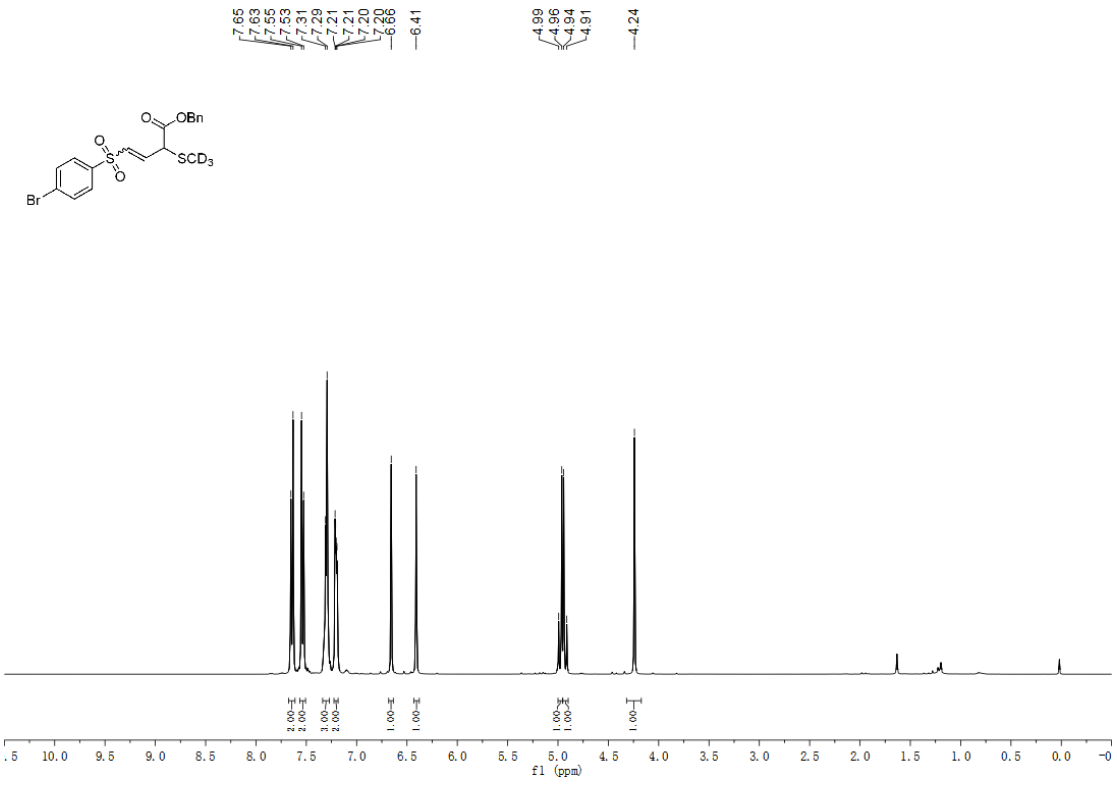
^{1}H NMR Spectrum of compound **3g (400** MHz, $CDCl_3$)



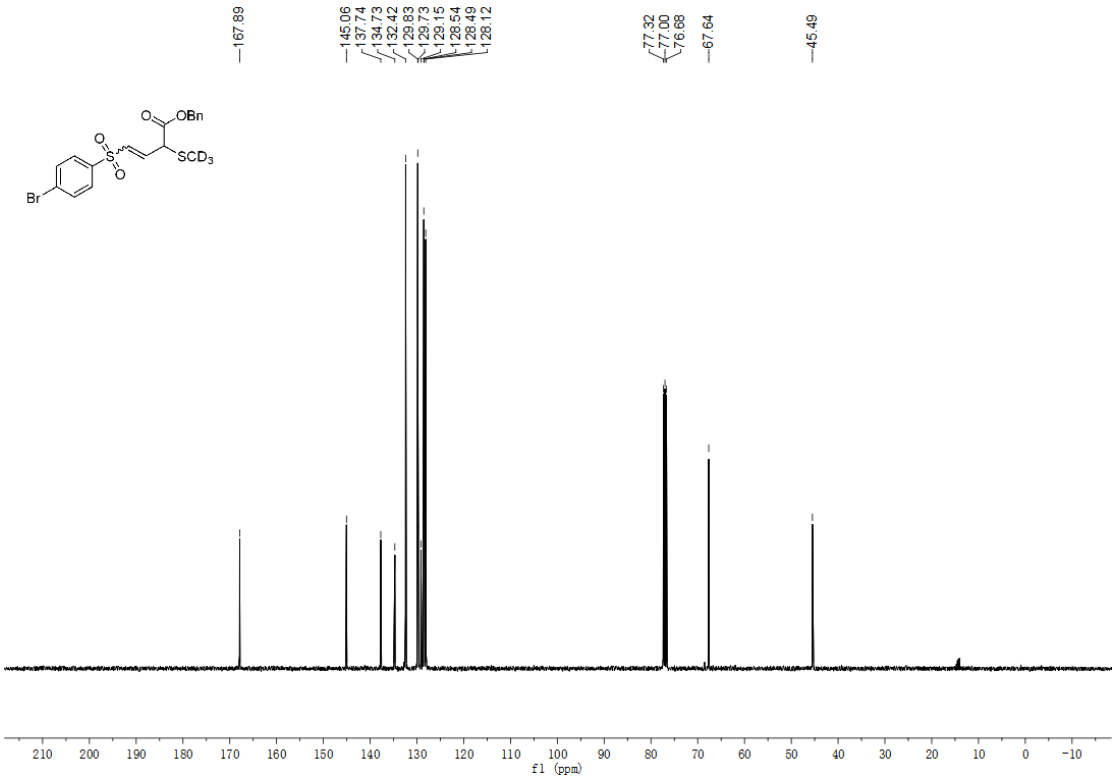
^{13}C NMR Spectrum of compound **3g (100** MHz, $CDCl_3$)



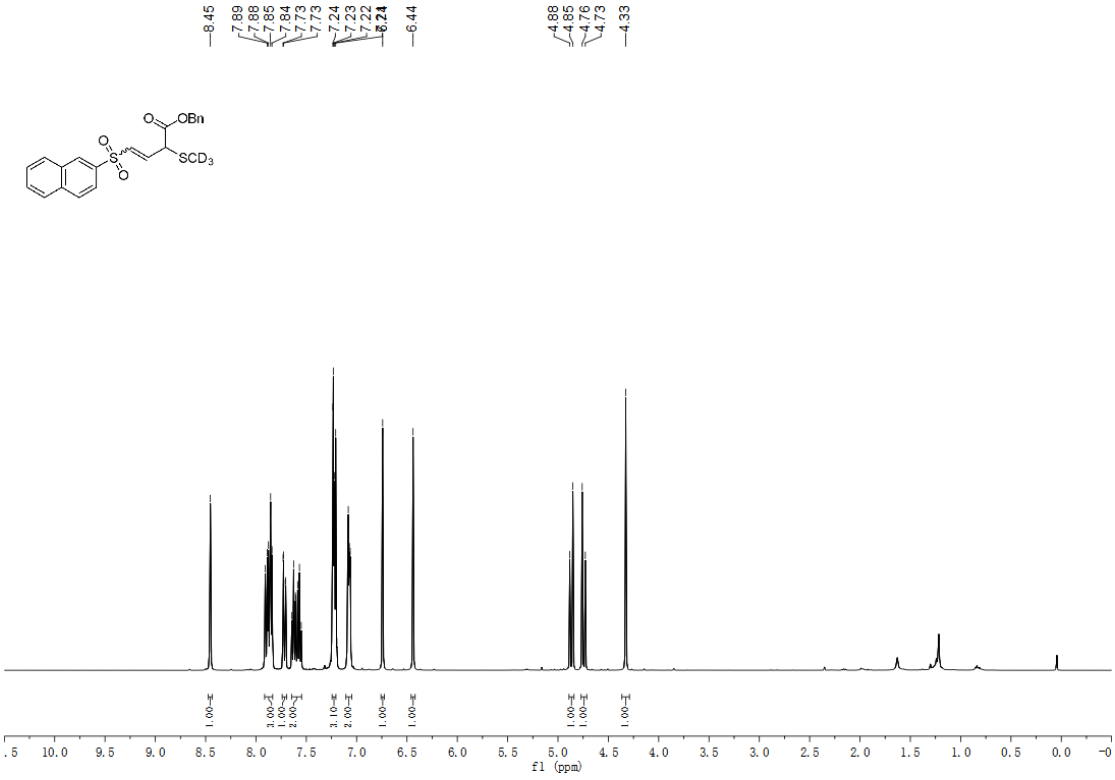
^{1}H NMR Spectrum of compound **3h (400** MHz, $CDCl_3$)



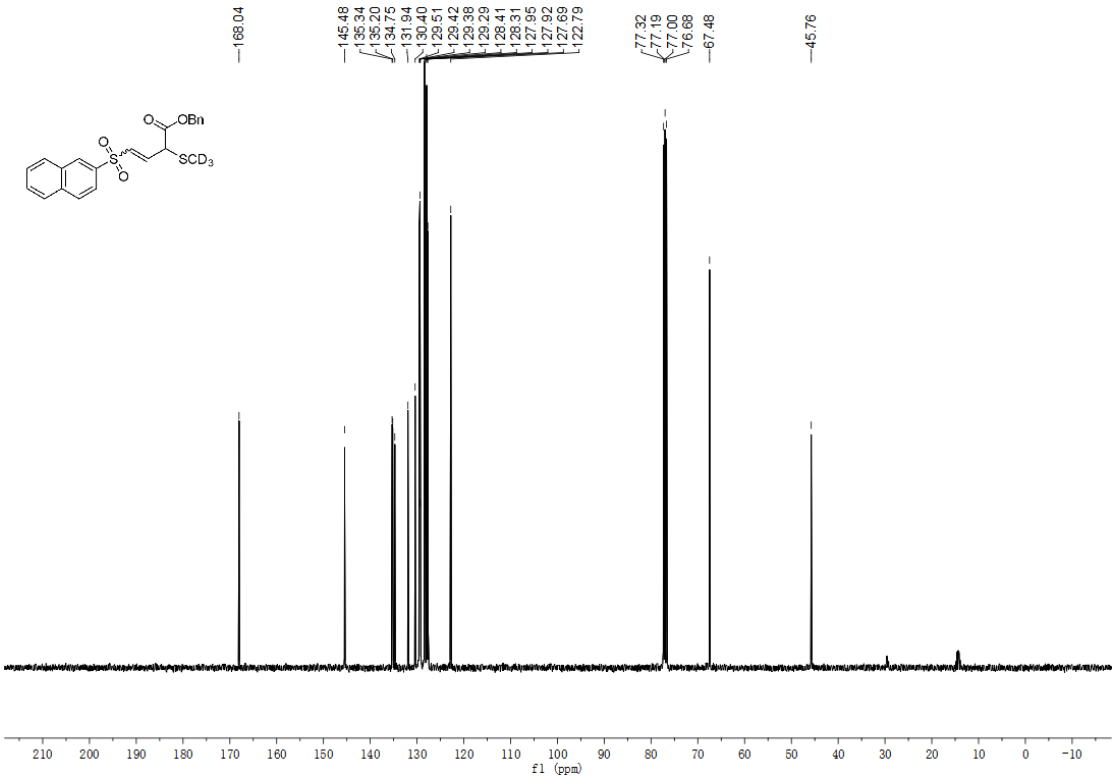
^{13}C NMR Spectrum of compound **3h (100** MHz, $CDCl_3$)



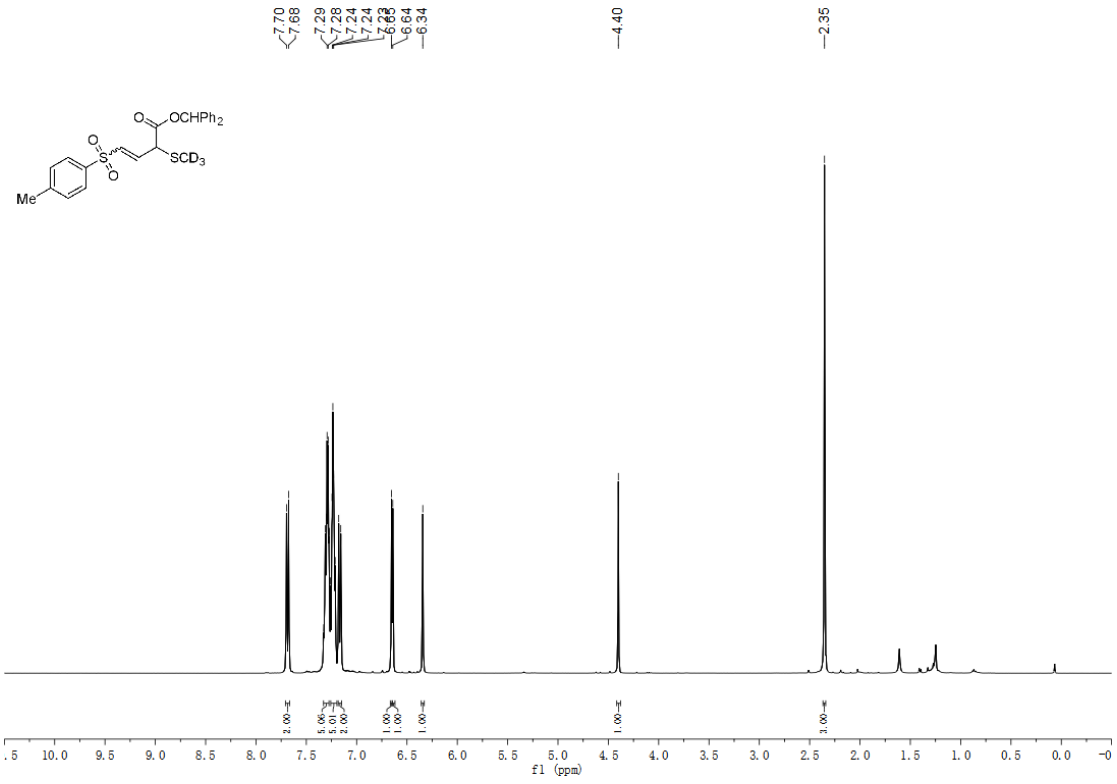
^{1}H NMR Spectrum of compound **3i (400** MHz, $CDCl_3$)



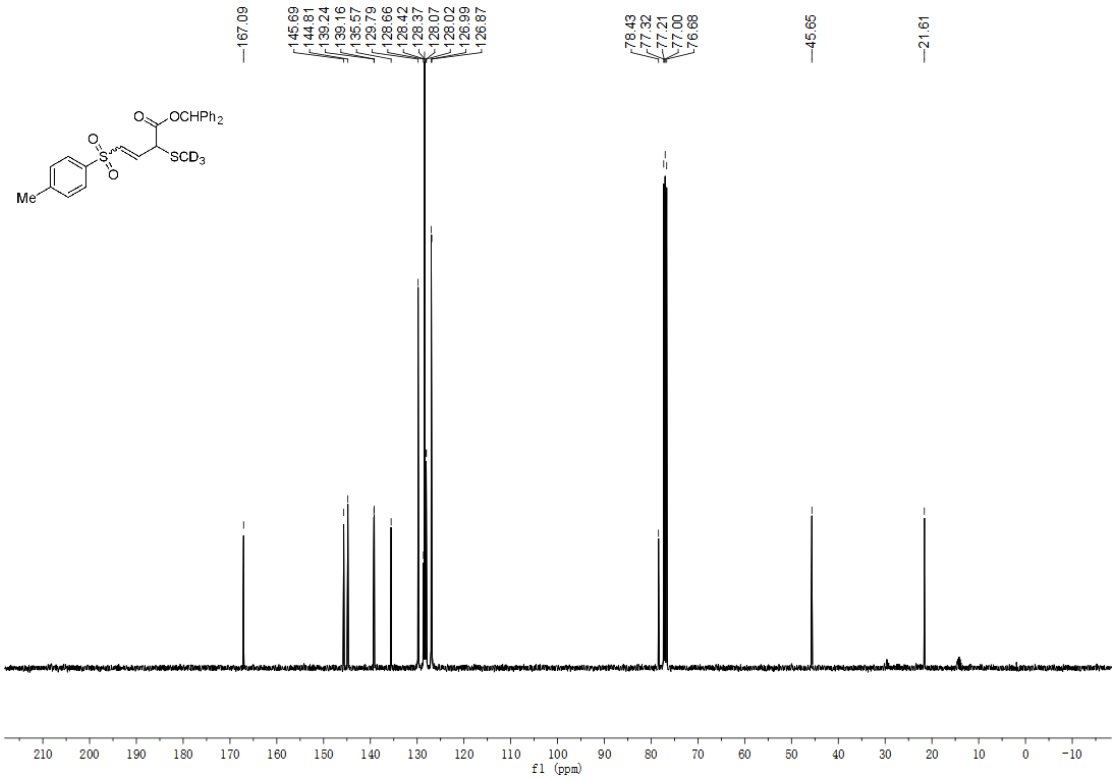
^{13}C NMR Spectrum of compound **3h (100** MHz, $CDCl_3$)



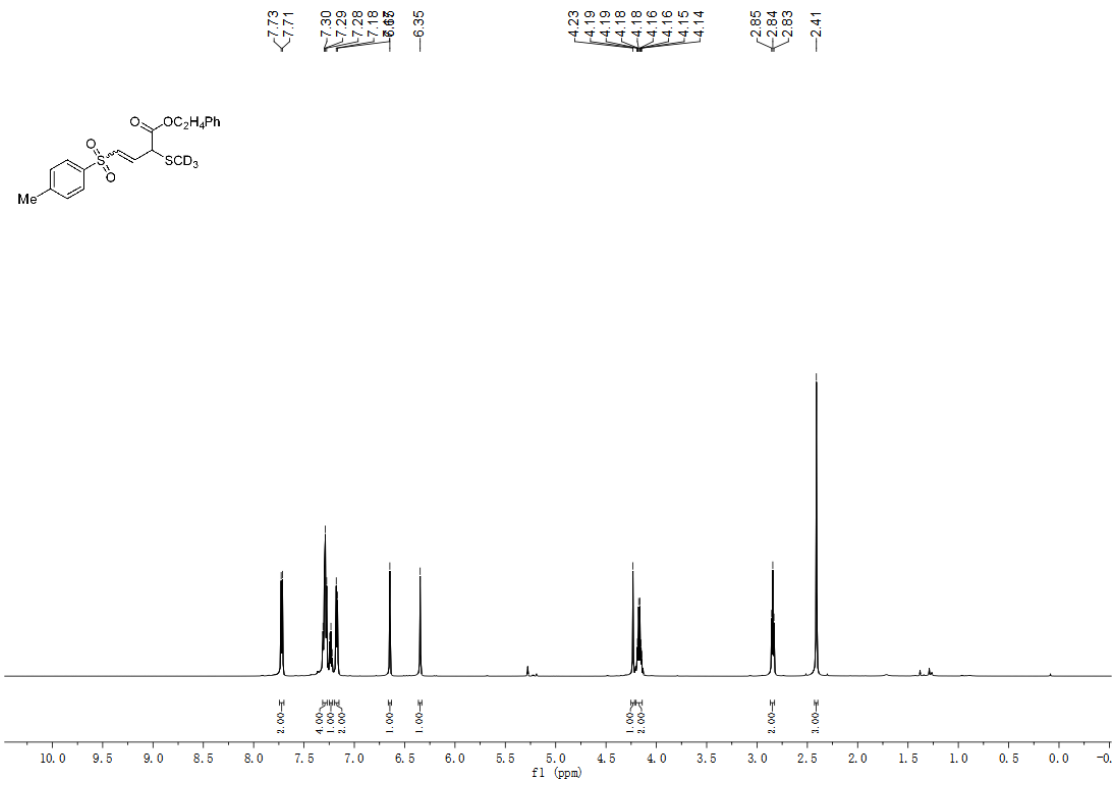
^{1}H NMR Spectrum of compound **3j (400** MHz, $CDCl_3$)



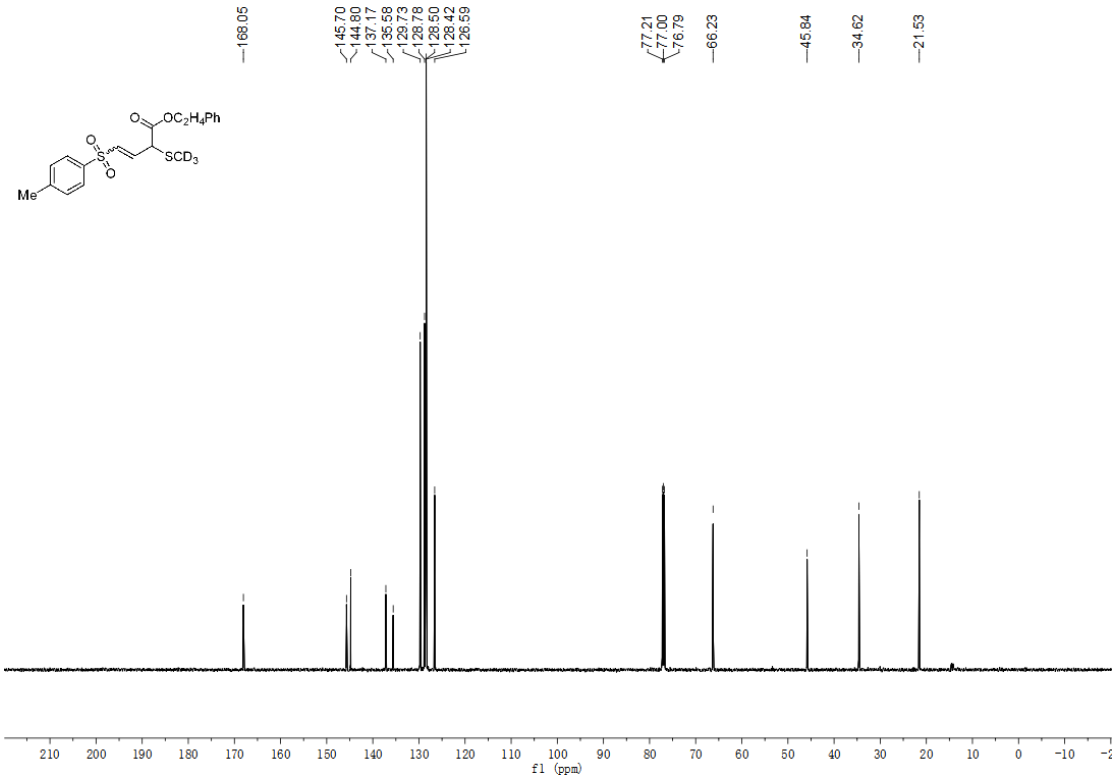
^{13}C NMR Spectrum of compound **3j (100** MHz, $CDCl_3$)



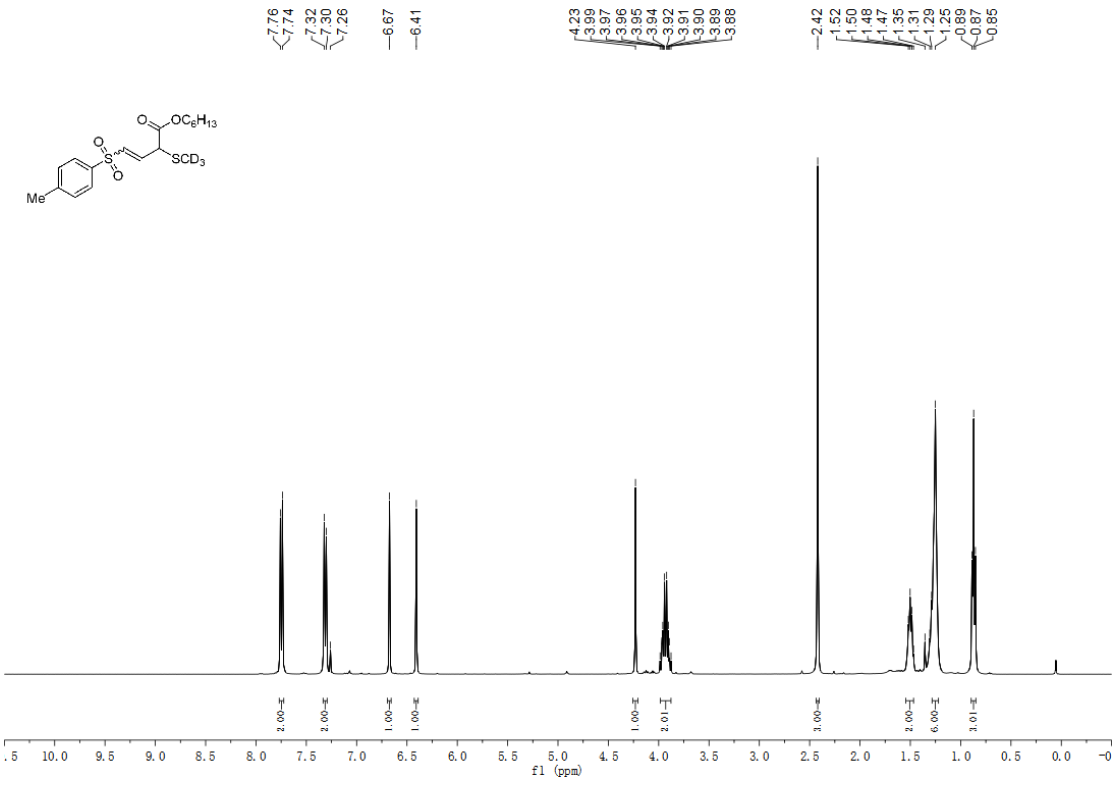
^{1}H NMR Spectrum of compound **3k (600** MHz, $CDCl_3$)



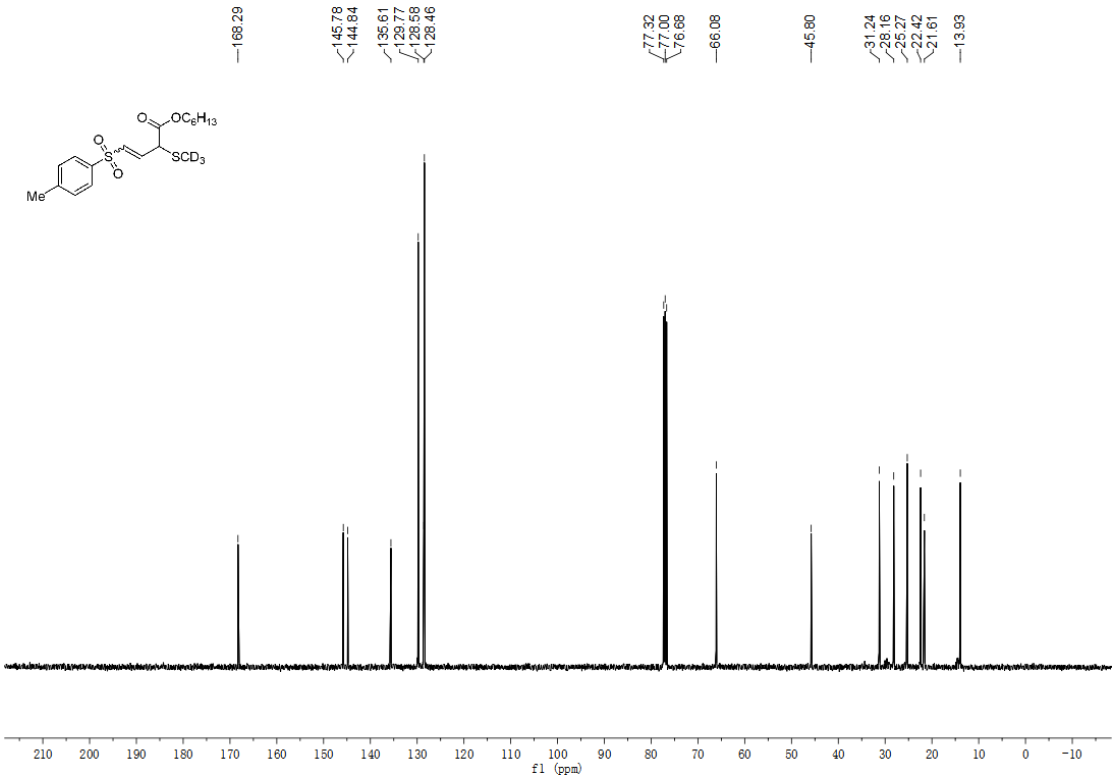
^{13}C NMR Spectrum of compound **3k (150** MHz, $CDCl_3$)



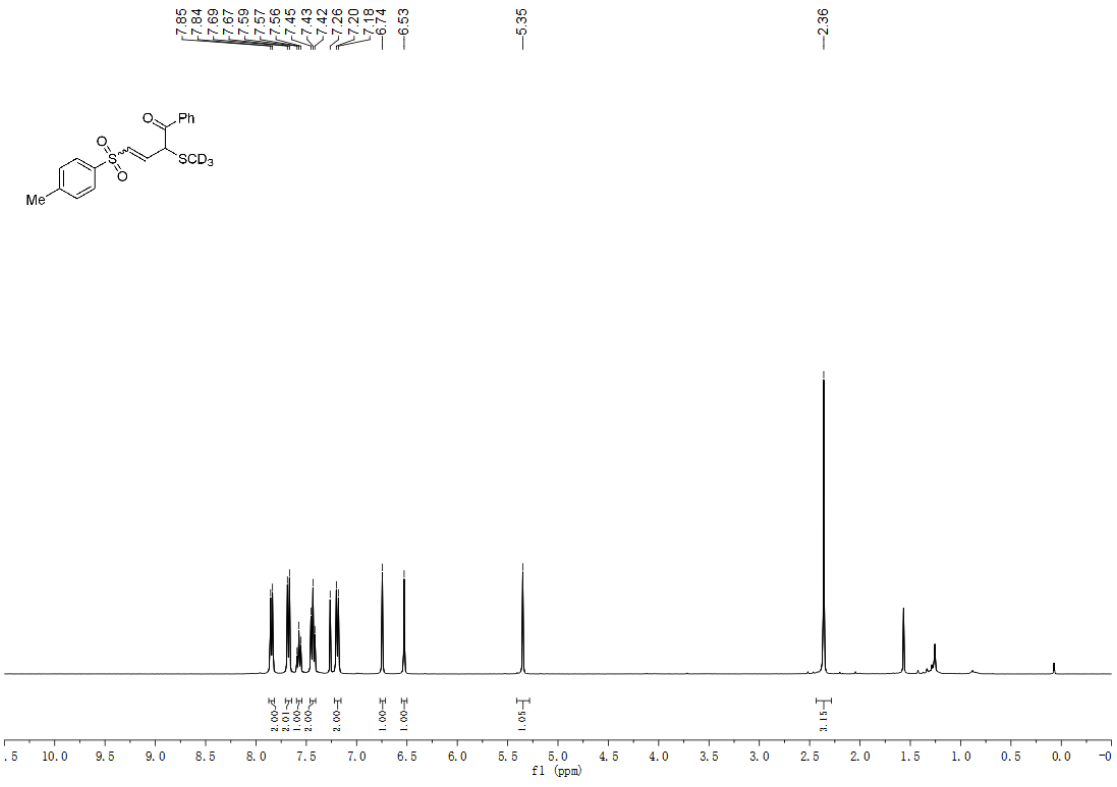
^{1}H NMR Spectrum of compound **3l (600** MHz, $CDCl_3$)



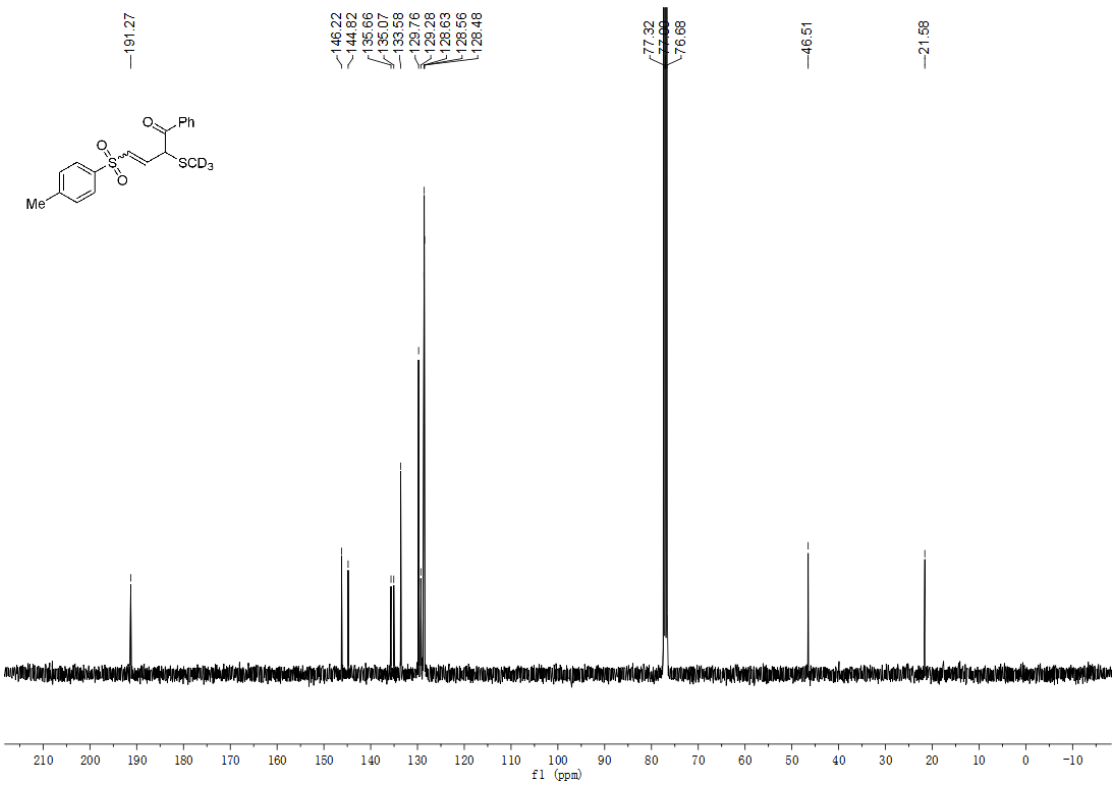
^{13}C NMR Spectrum of compound **3l (150** MHz, $CDCl_3$)



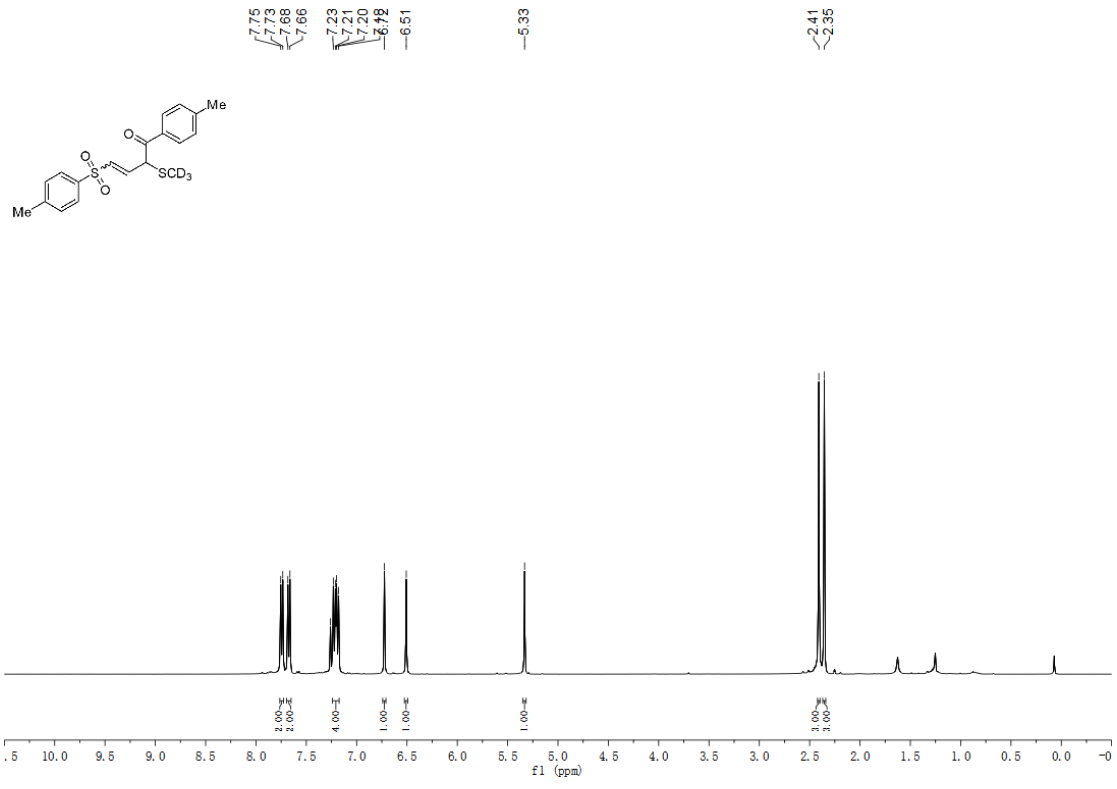
^{1}H NMR Spectrum of compound **3m (400** MHz, $CDCl_3$)



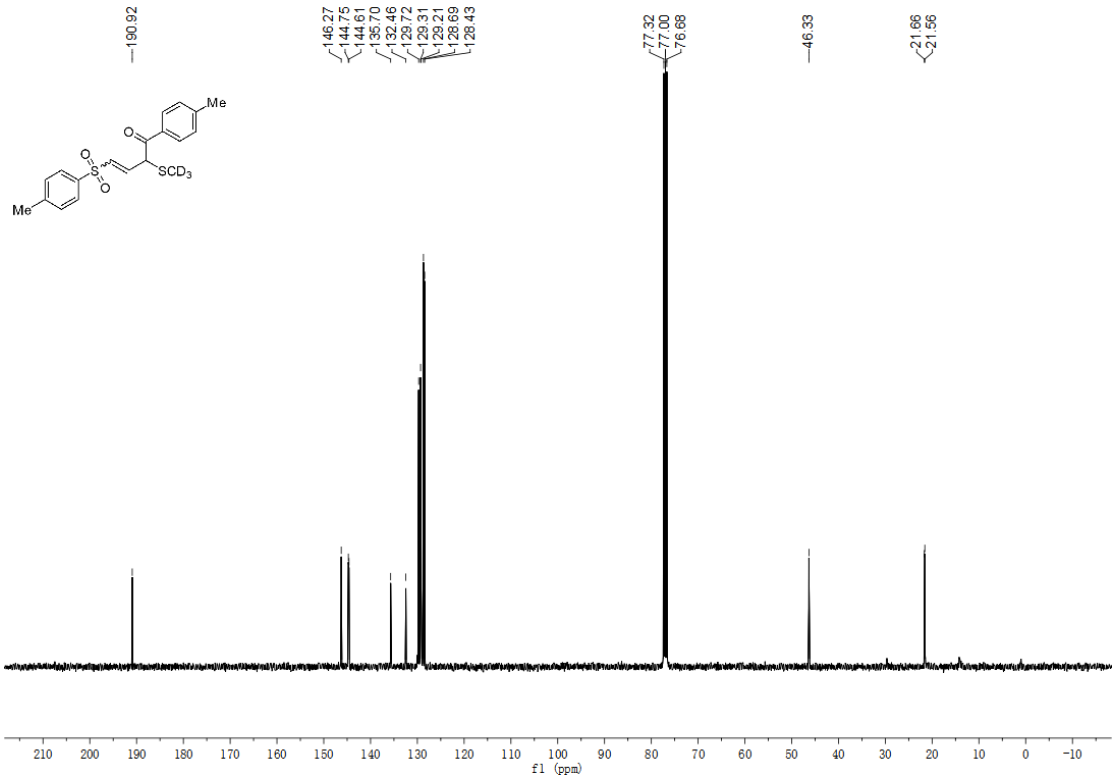
^{13}C NMR Spectrum of compound **3m (150** MHz, $CDCl_3$)



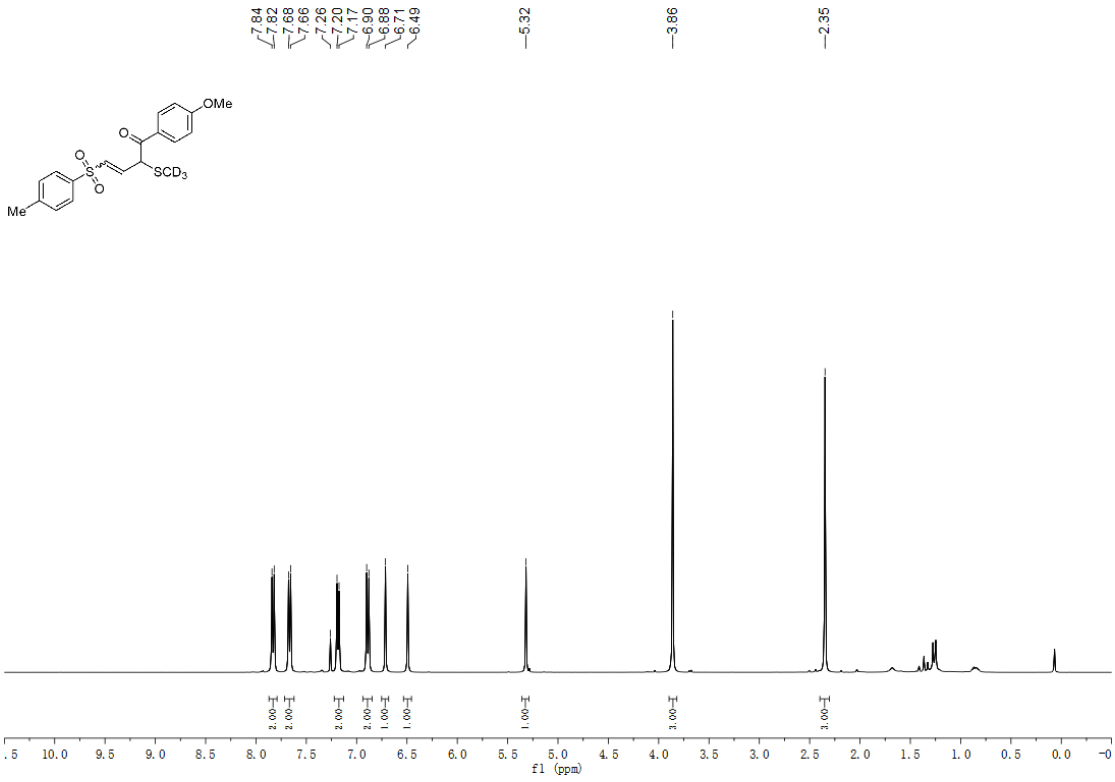
^{1}H NMR Spectrum of compound **3n (400** MHz, $CDCl_3$)



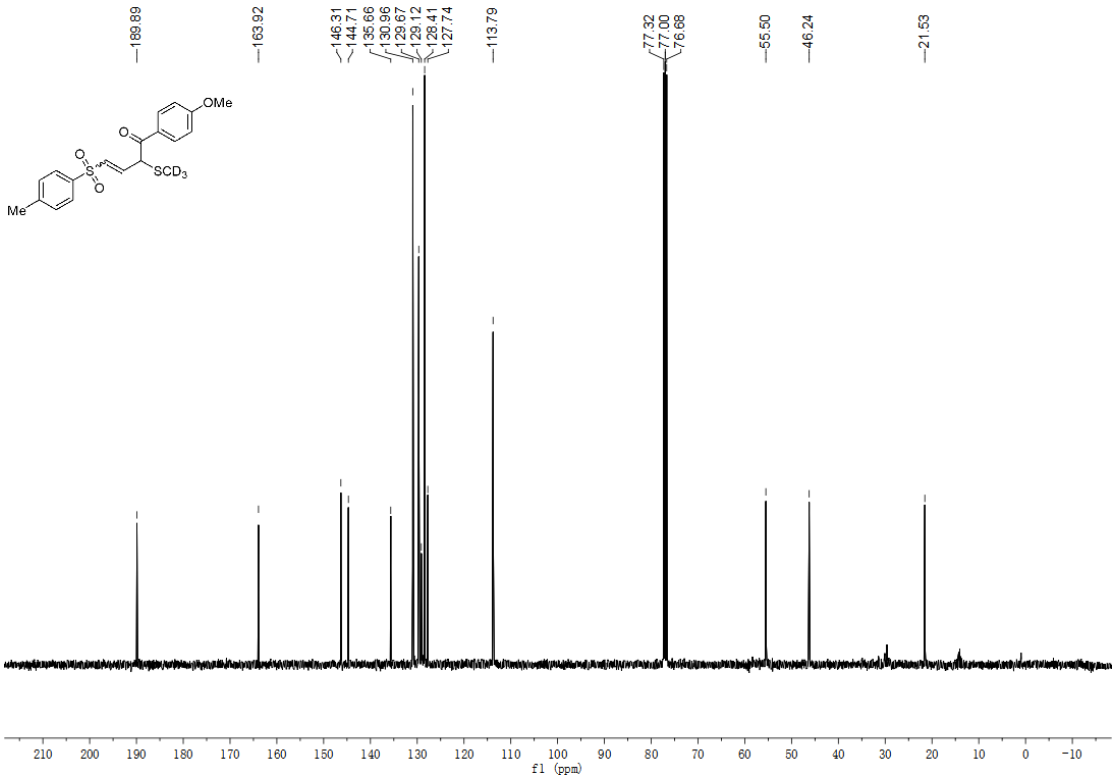
^{13}C NMR Spectrum of compound **3n (100** MHz, $CDCl_3$)



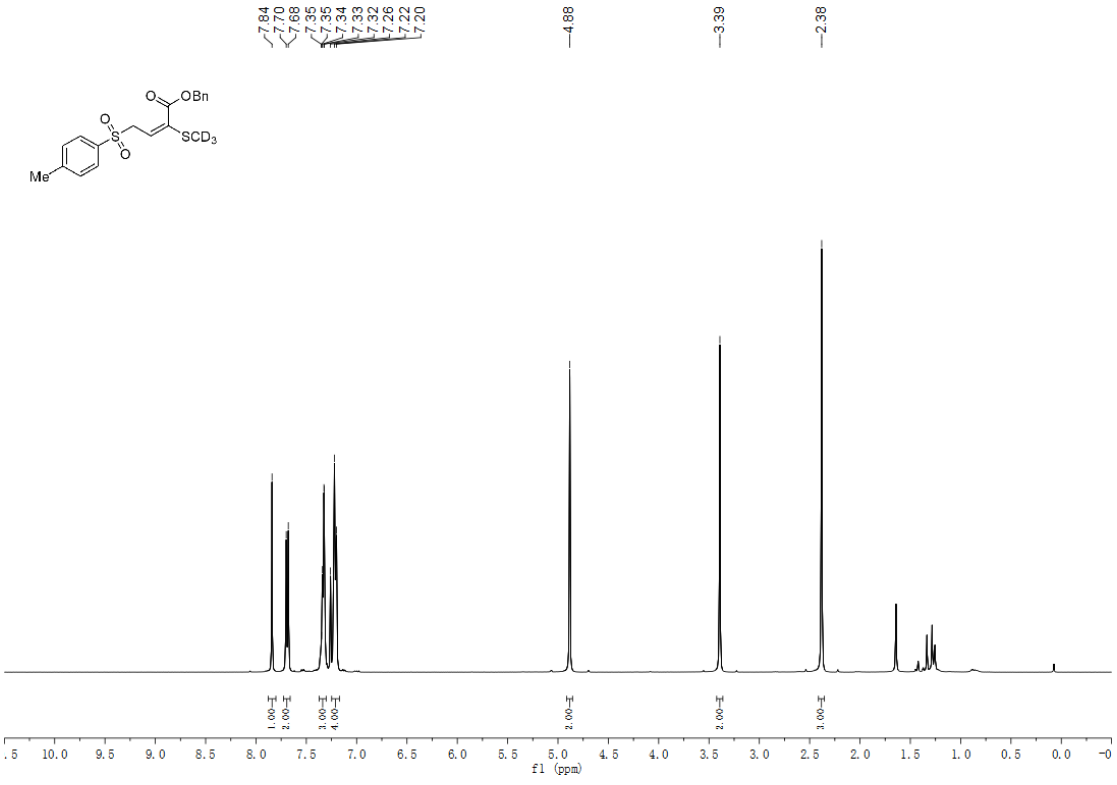
^{1}H NMR Spectrum of compound **3o (400** MHz, $CDCl_3$)



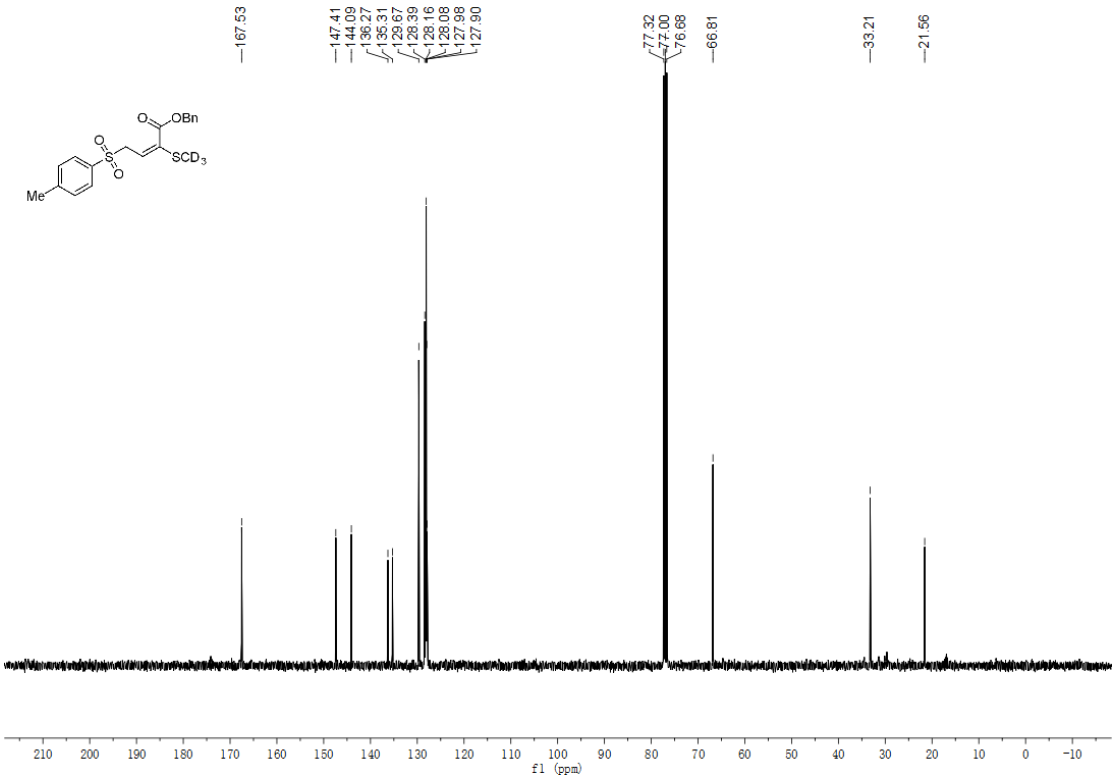
^{13}C NMR Spectrum of compound **3o (100** MHz, $CDCl_3$)



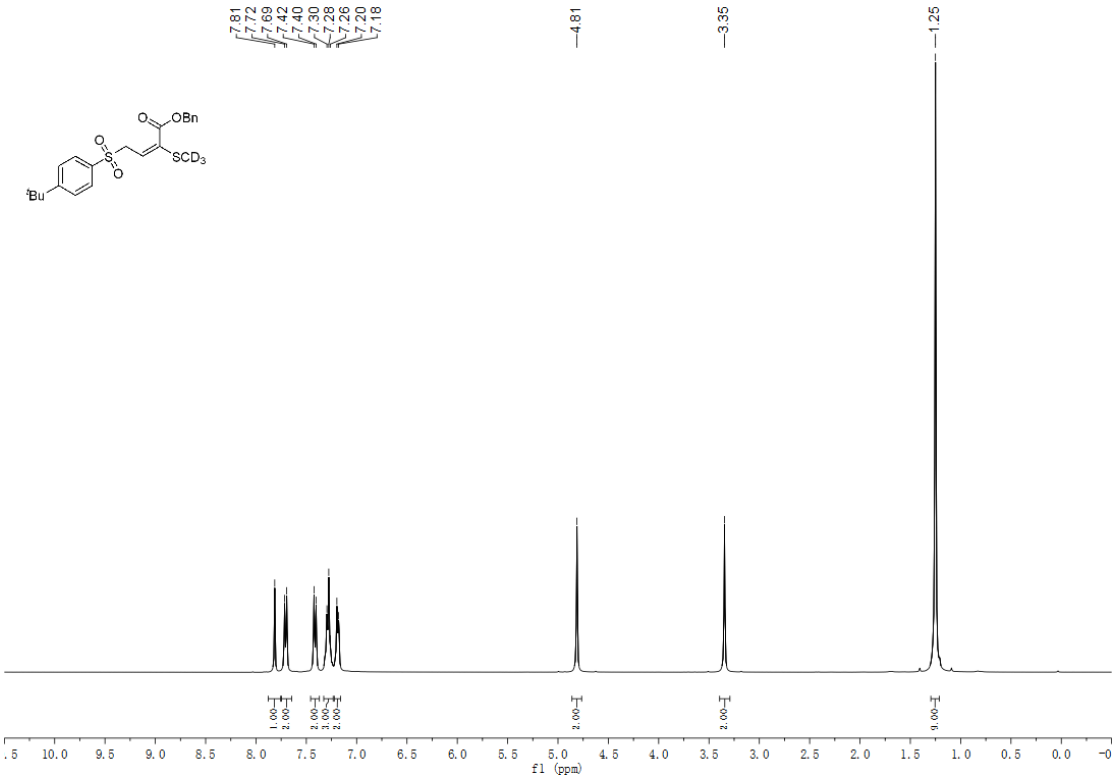
^{1}H NMR Spectrum of compound **4a (400** MHz, $CDCl_3$)



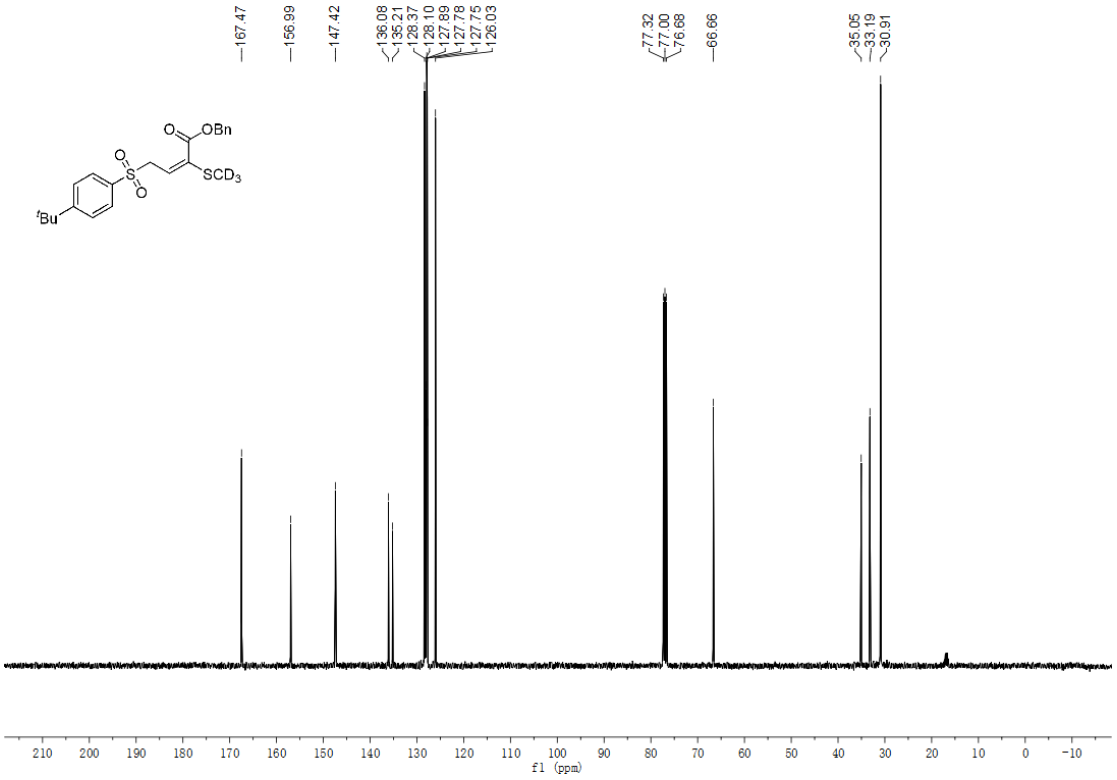
^{13}C NMR Spectrum of compound **4a (100** MHz, $CDCl_3$)



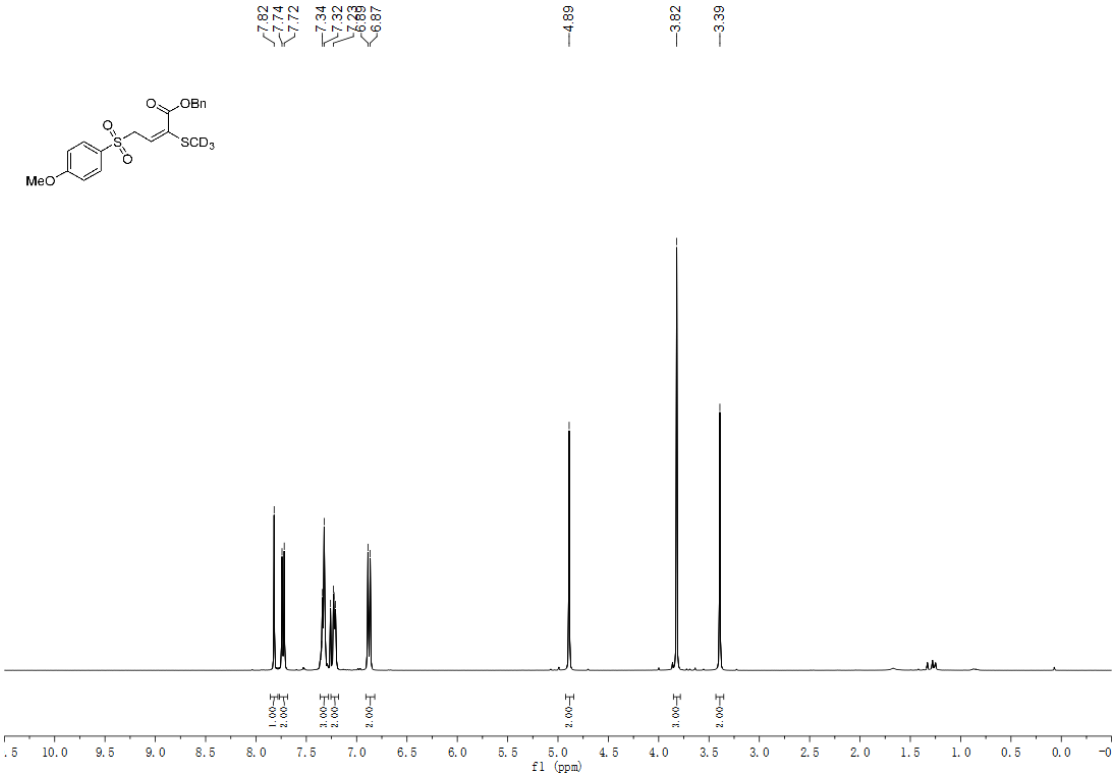
^{1}H NMR Spectrum of compound **4b (400** MHz, $CDCl_3$)



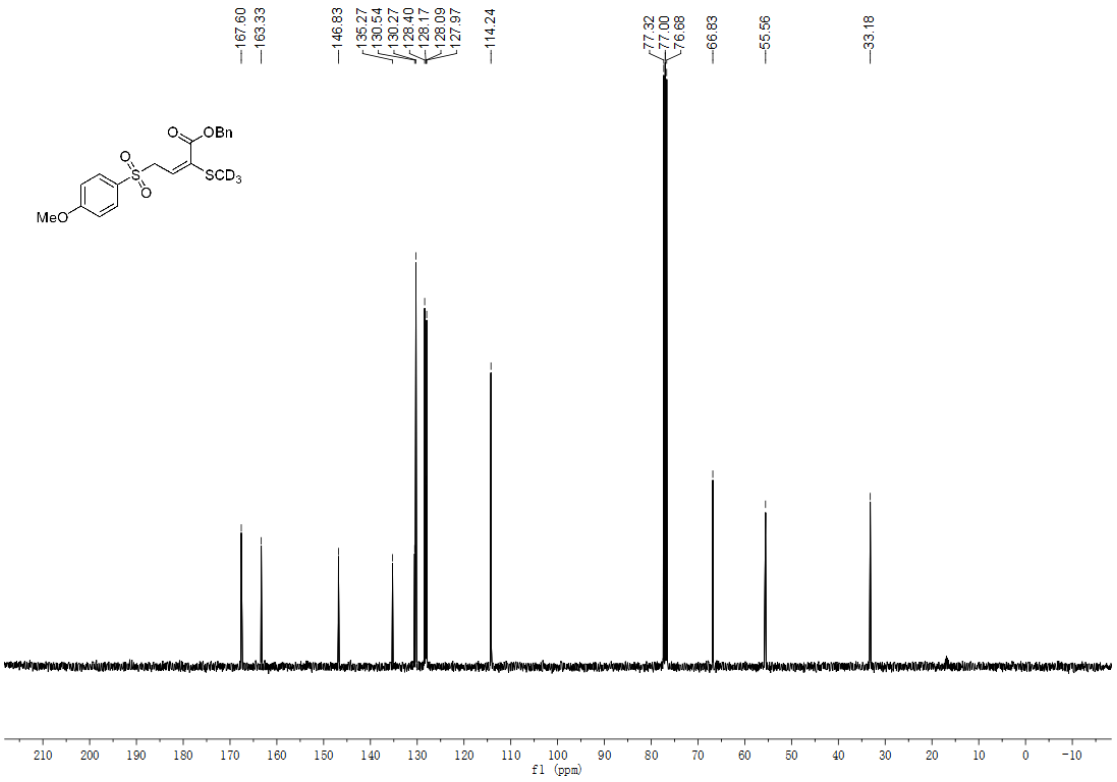
^{13}C NMR Spectrum of compound **4b (100** MHz, $CDCl_3$)



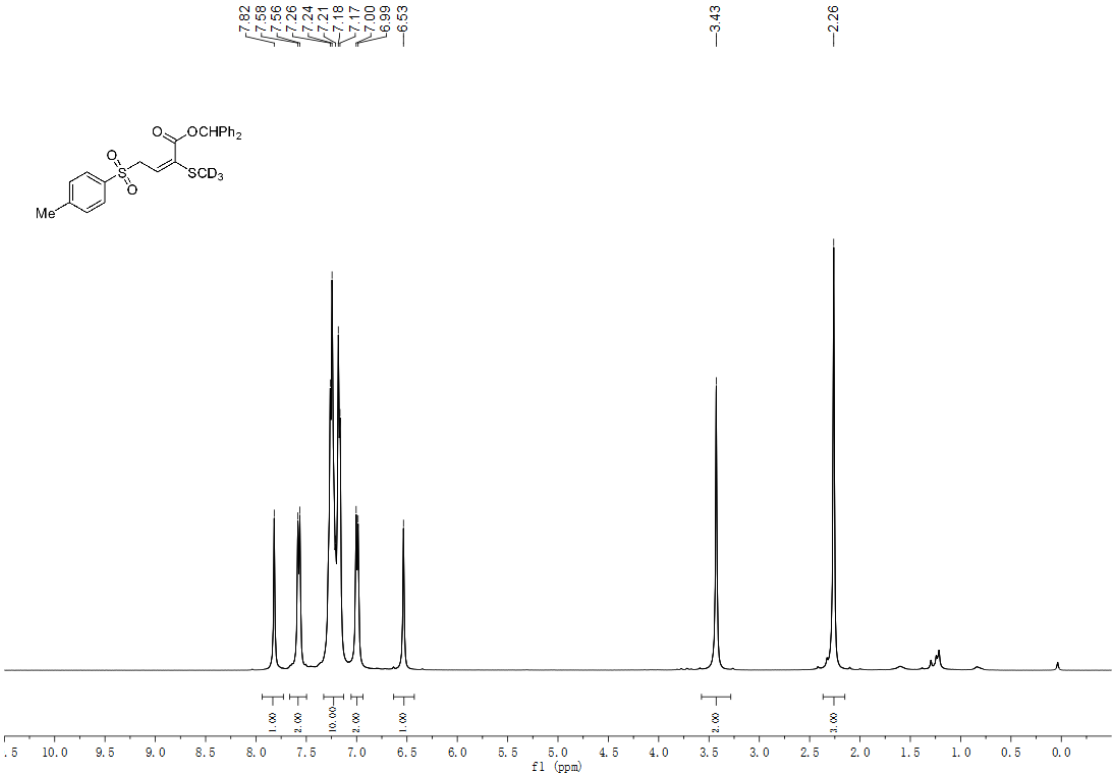
^{1}H NMR Spectrum of compound **4c (400** MHz, $CDCl_3$)



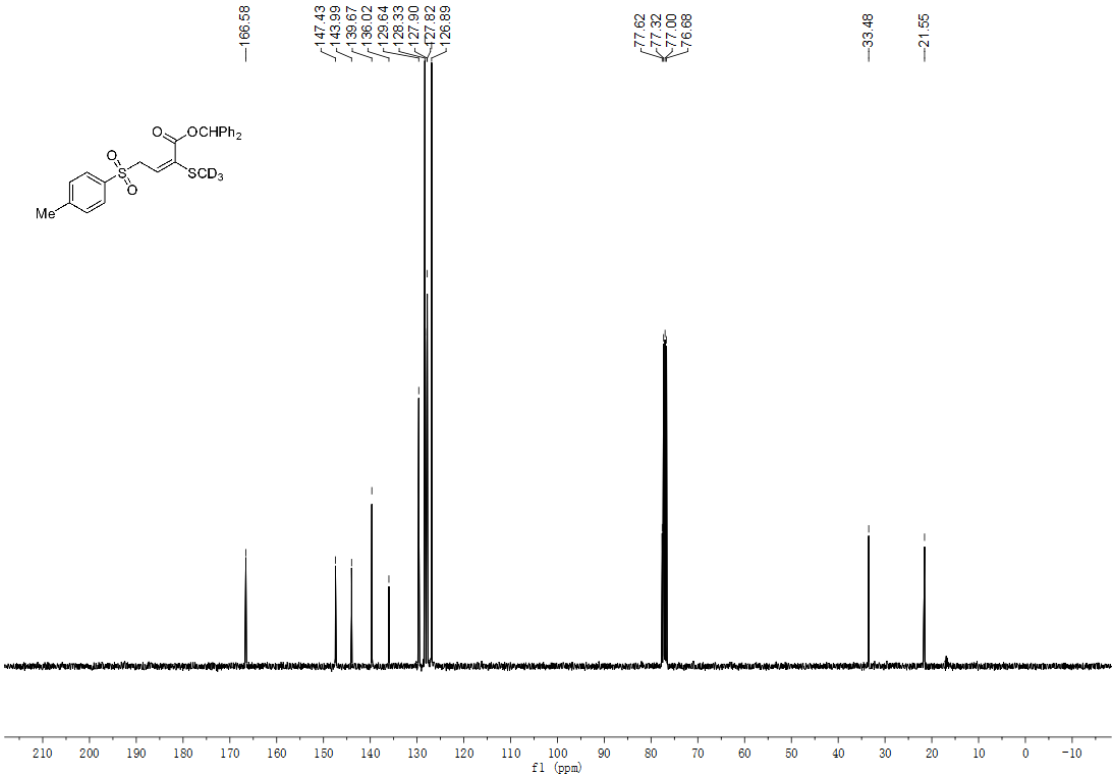
^{13}C NMR Spectrum of compound **4c** (**100** MHz, $CDCl_3$)



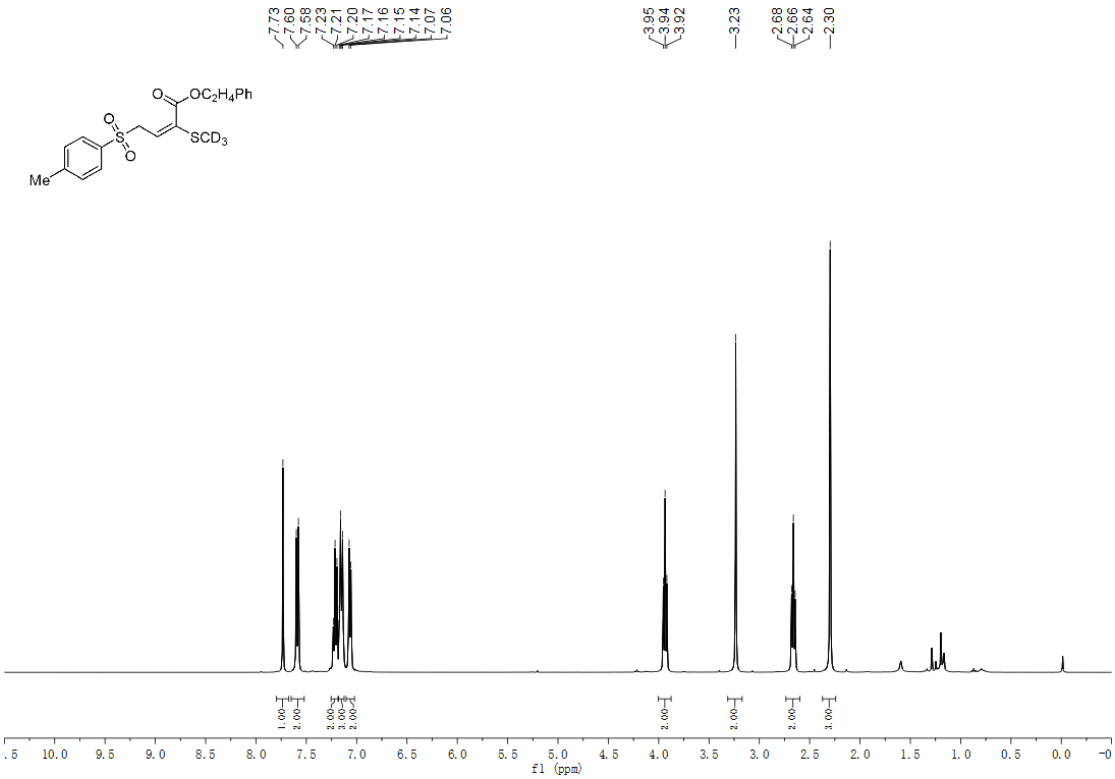
^{1}H NMR Spectrum of compound **4d** (**400** MHz, $CDCl_3$)



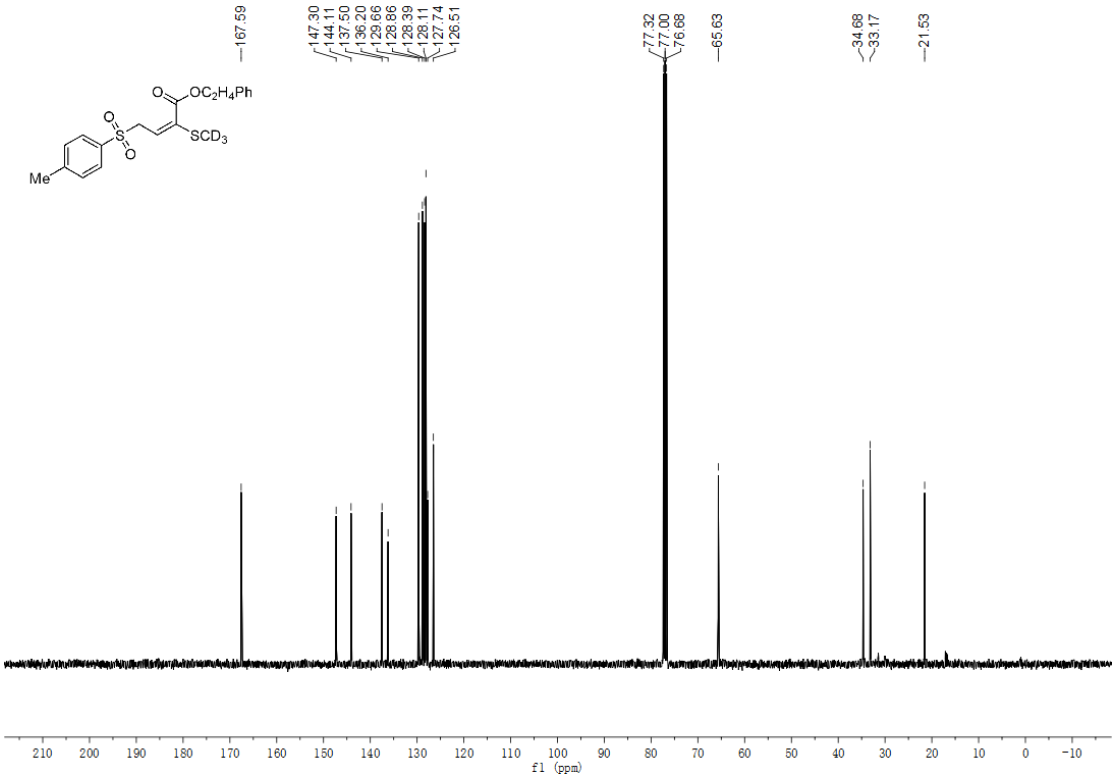
^{13}C NMR Spectrum of compound **4d (100** MHz, $CDCl_3$)



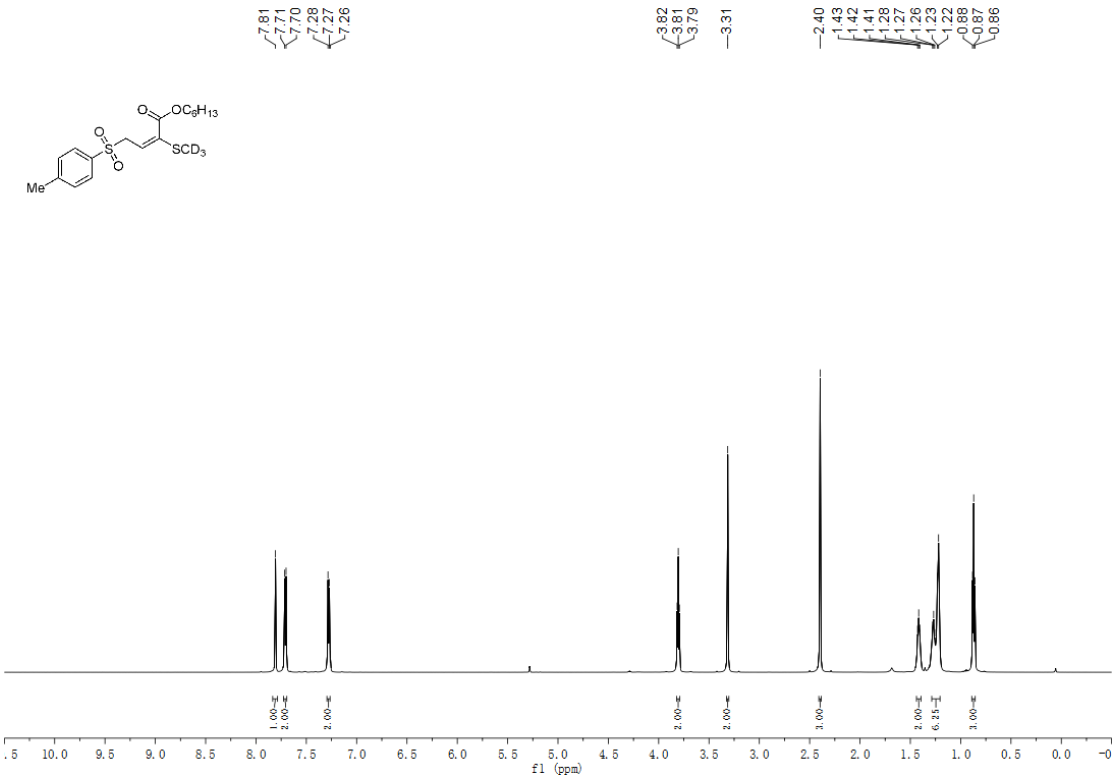
^{1}H NMR Spectrum of compound **4e (600** MHz, $CDCl_3$)



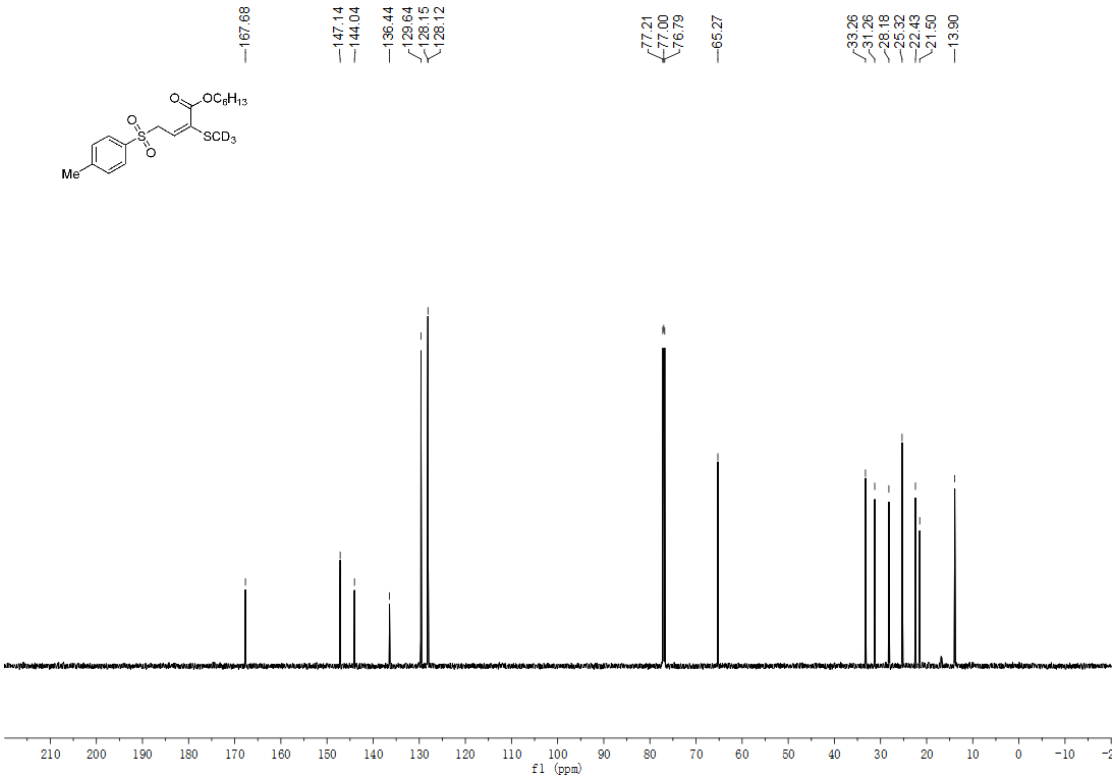
^{13}C NMR Spectrum of compound **4e (150** MHz, $CDCl_3$)



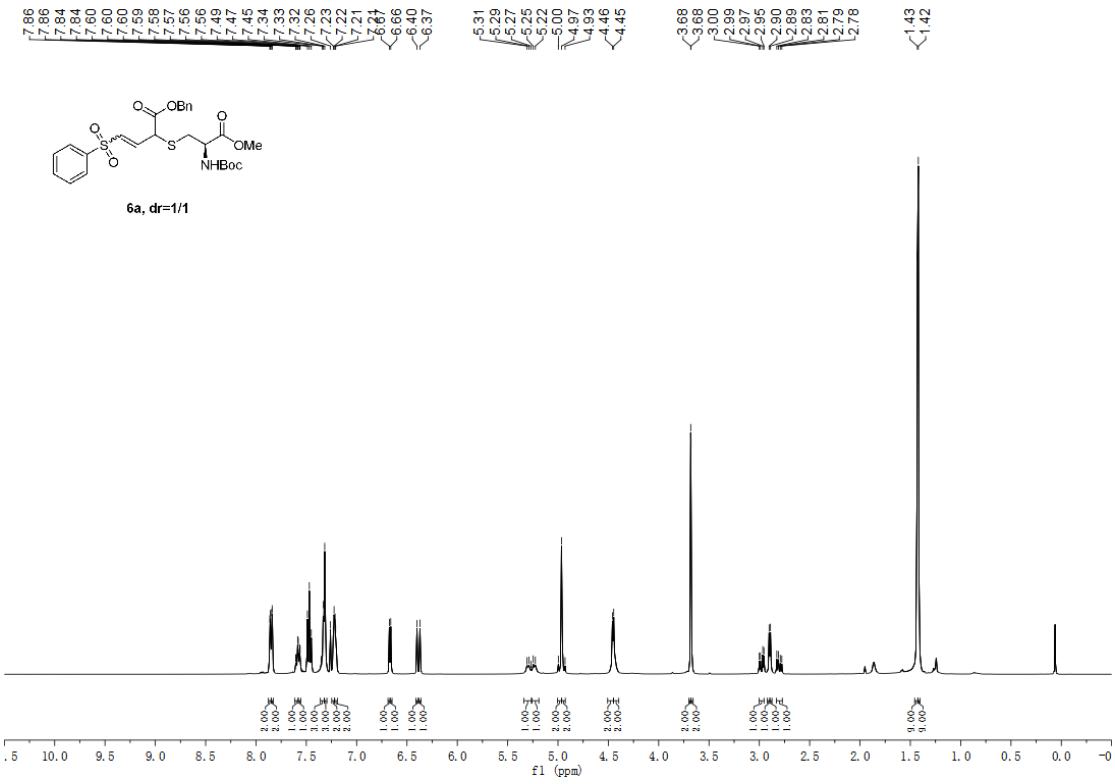
^{1}H NMR Spectrum of compound **4f (600** MHz, $CDCl_3$)



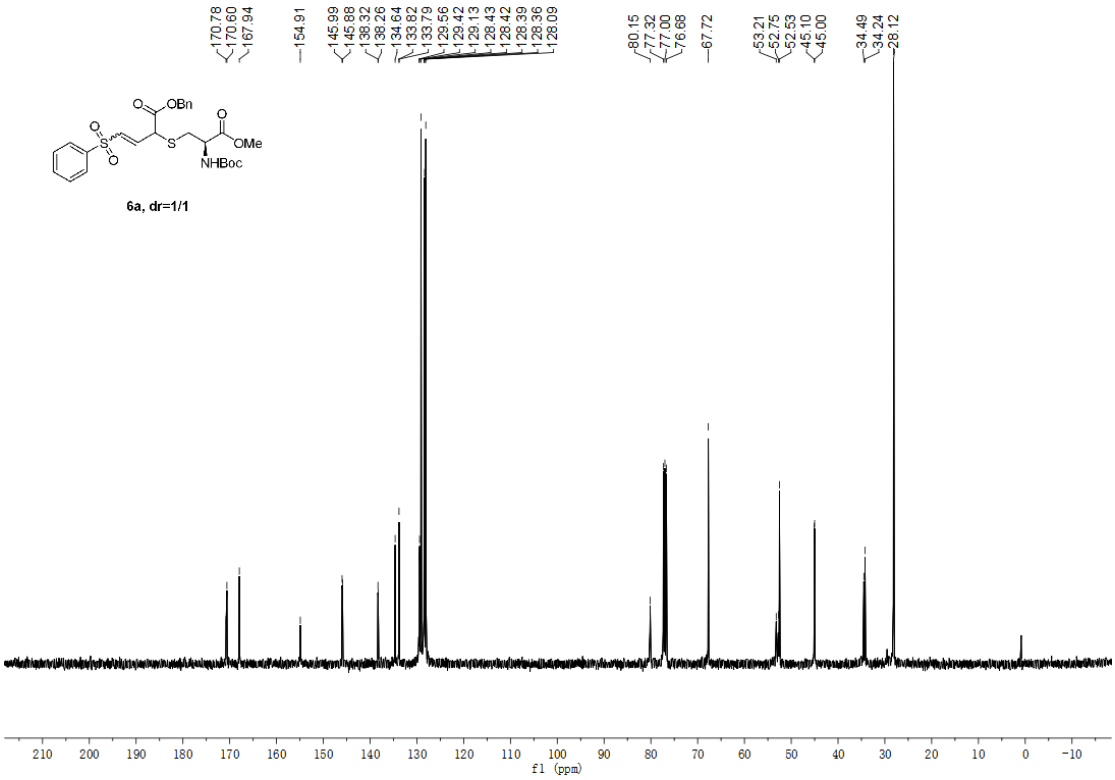
^{13}C NMR Spectrum of compound **4f (150** MHz, $CDCl_3$)



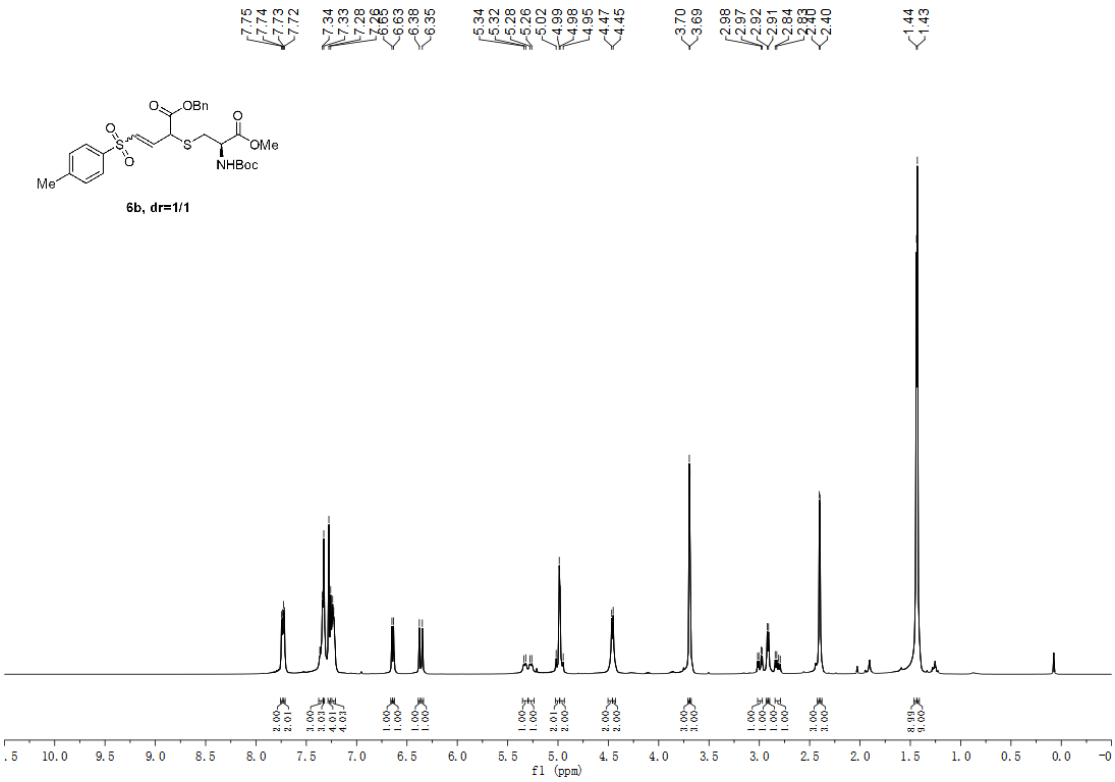
^{1}H NMR Spectrum of compound **6a (400** MHz, $CDCl_3$)



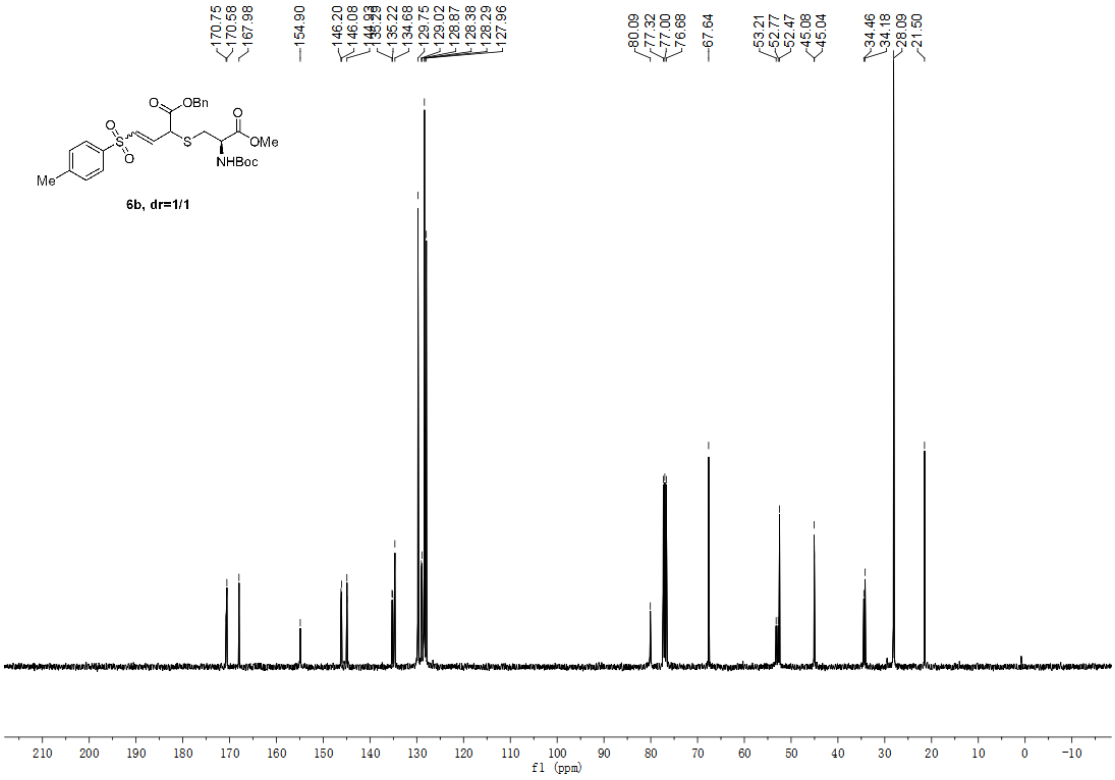
^{13}C NMR Spectrum of compound **6a (100** MHz, $CDCl_3$)



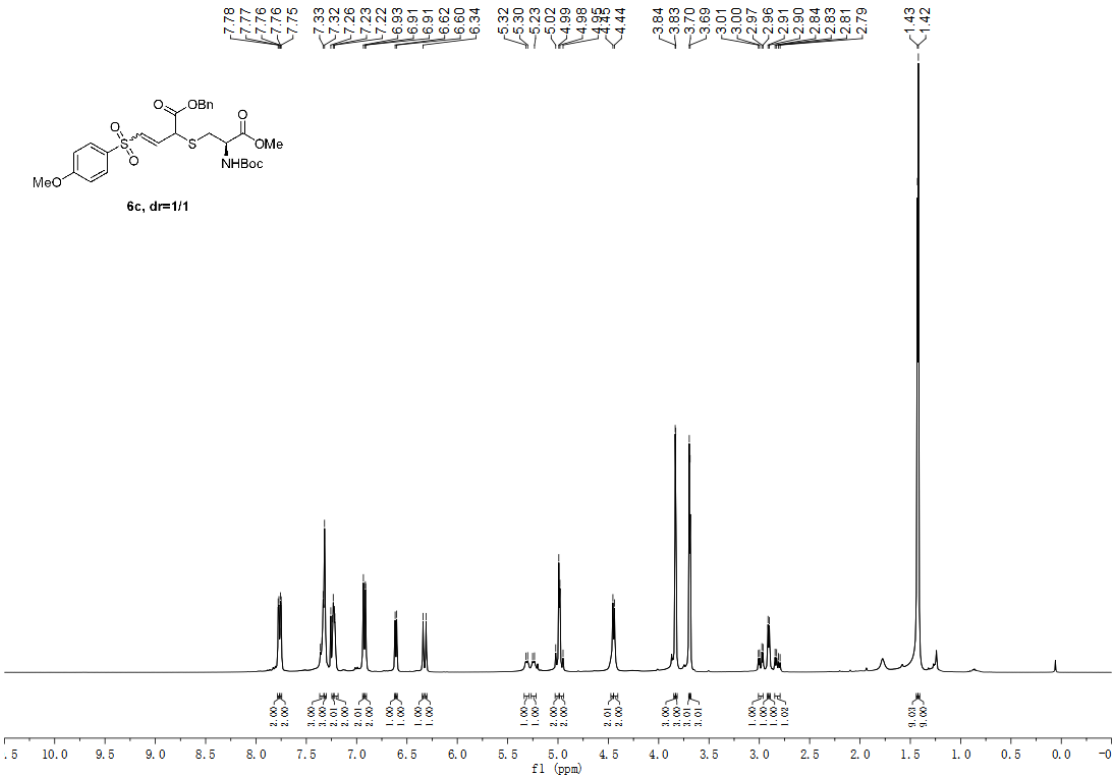
^{1}H NMR Spectrum of compound **6b (400** MHz, $CDCl_3$)



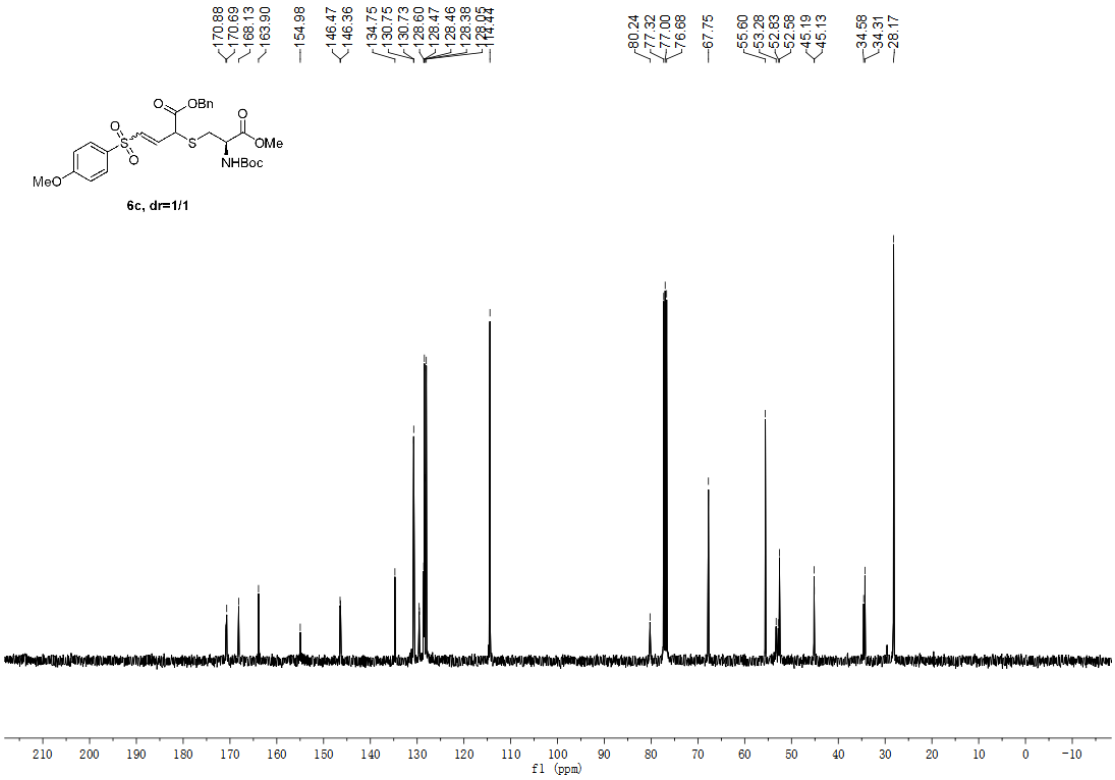
^{13}C NMR Spectrum of compound **6b (100** MHz, $CDCl_3$)



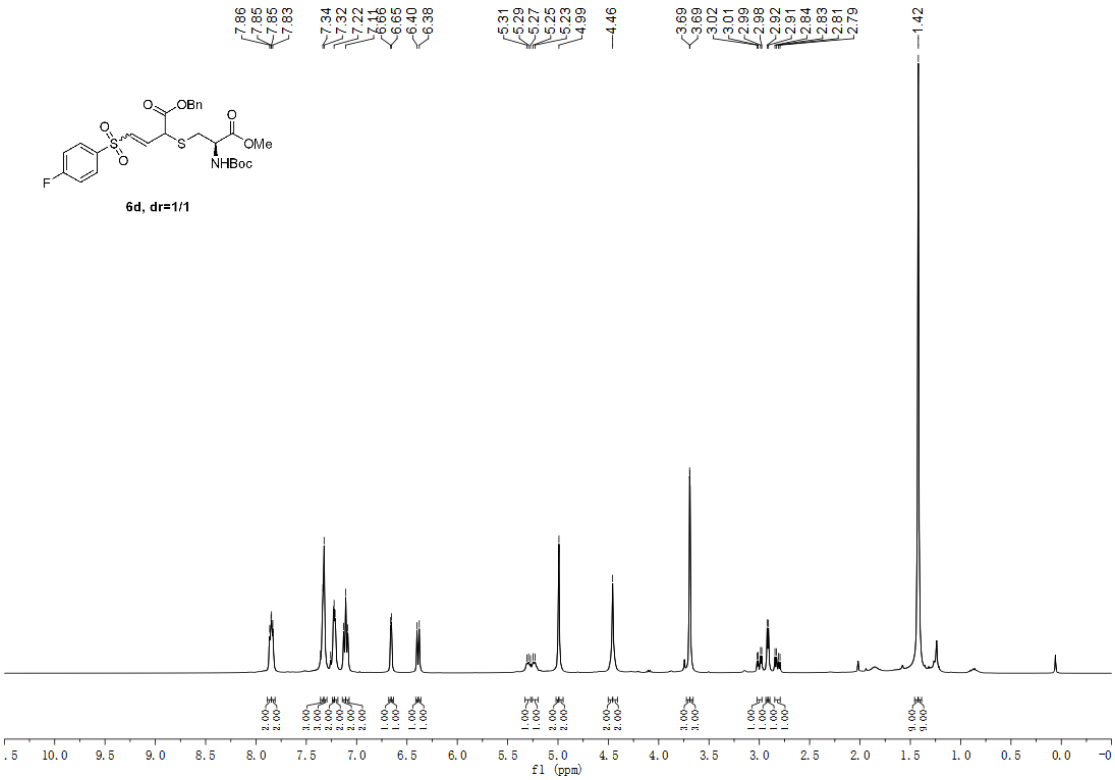
^{1}H NMR Spectrum of compound **6c (400** MHz, $CDCl_3$)



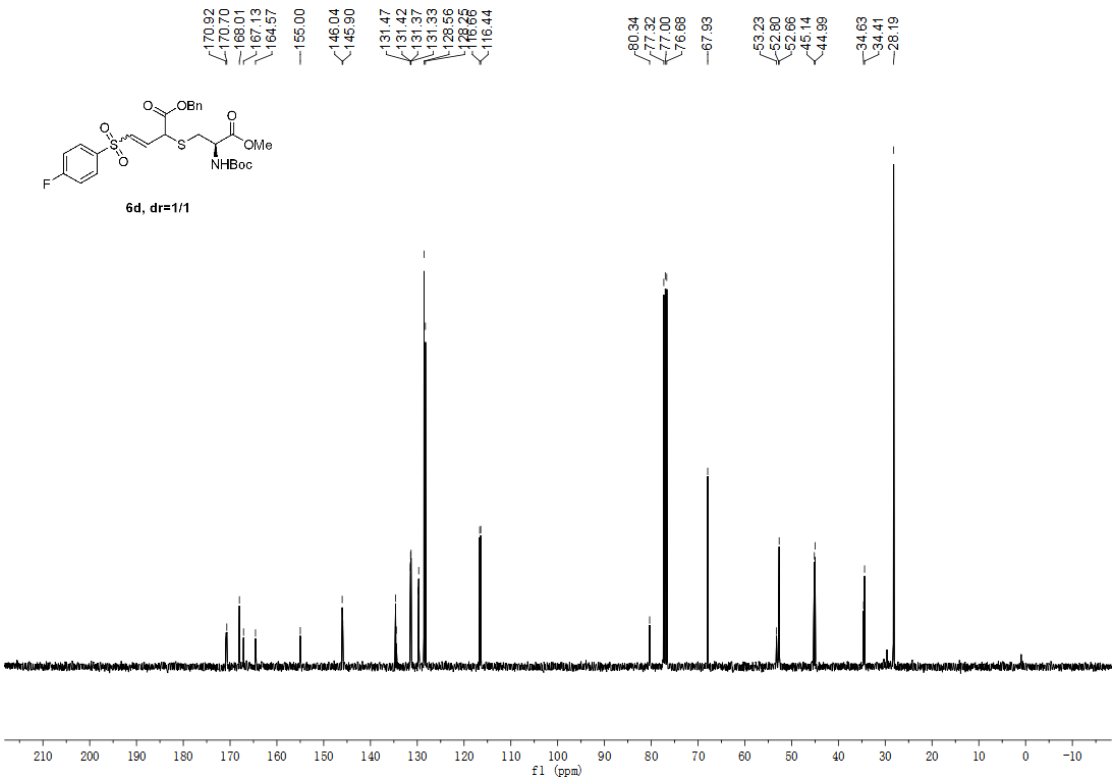
^{13}C NMR Spectrum of compound **6c (100** MHz, $CDCl_3$)



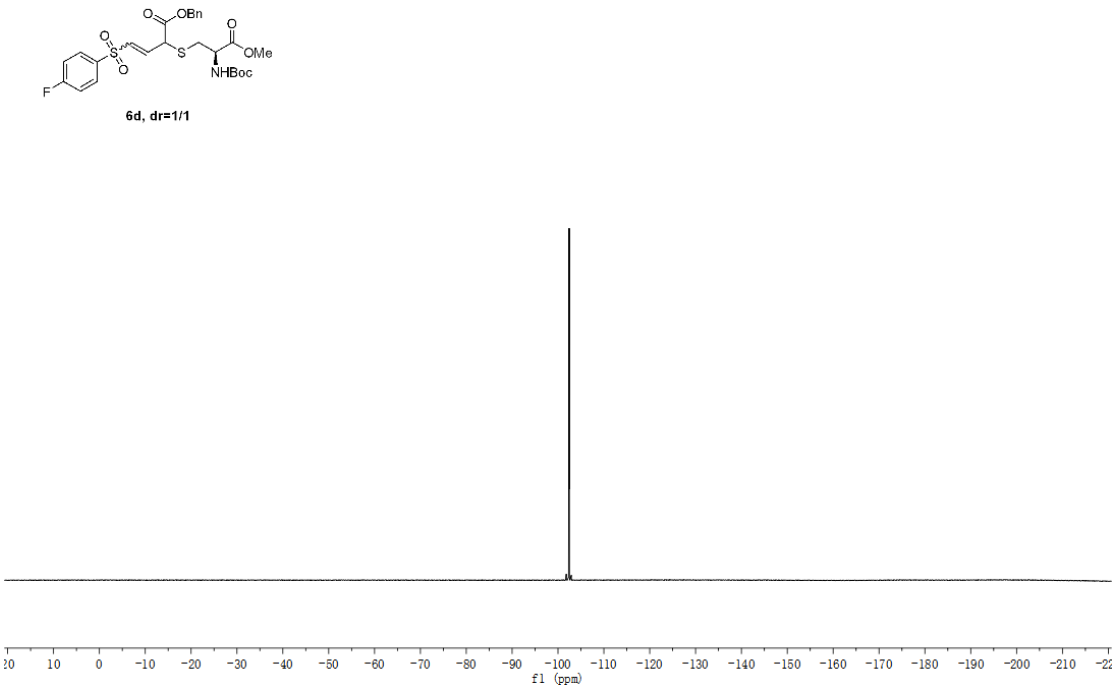
^{1}H NMR Spectrum of compound **6d (400** MHz, $CDCl_3$)



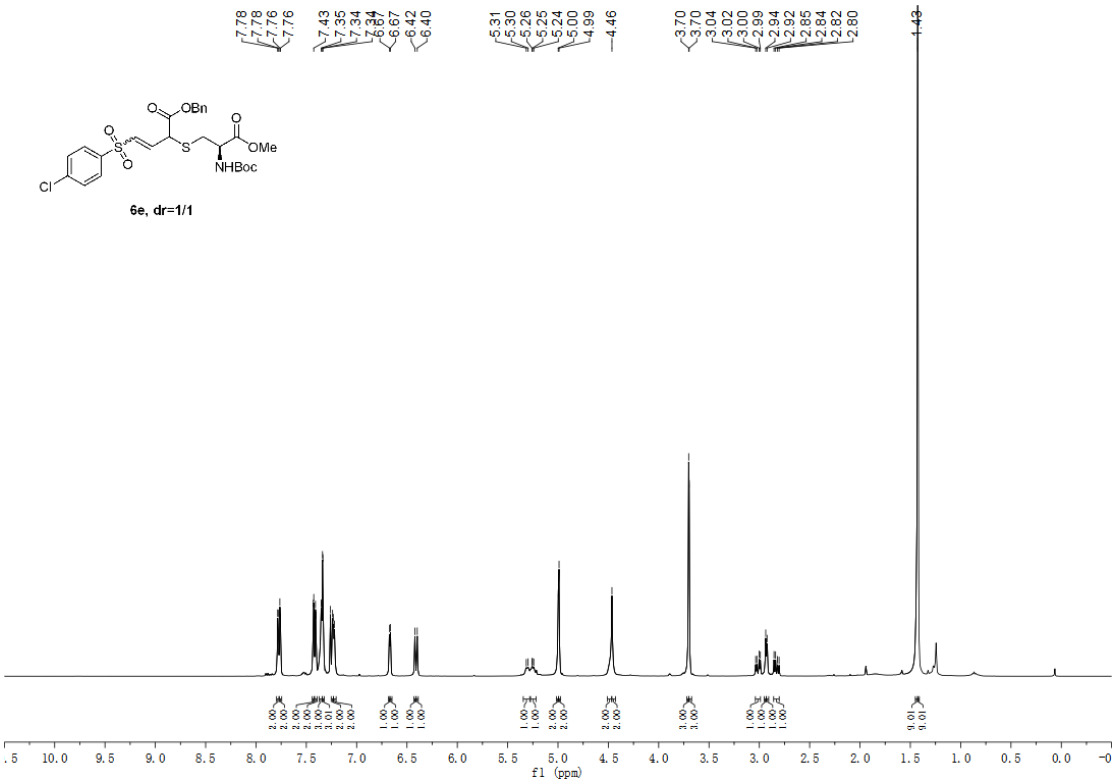
^{13}C NMR Spectrum of compound **6d (100** MHz, $CDCl_3$)



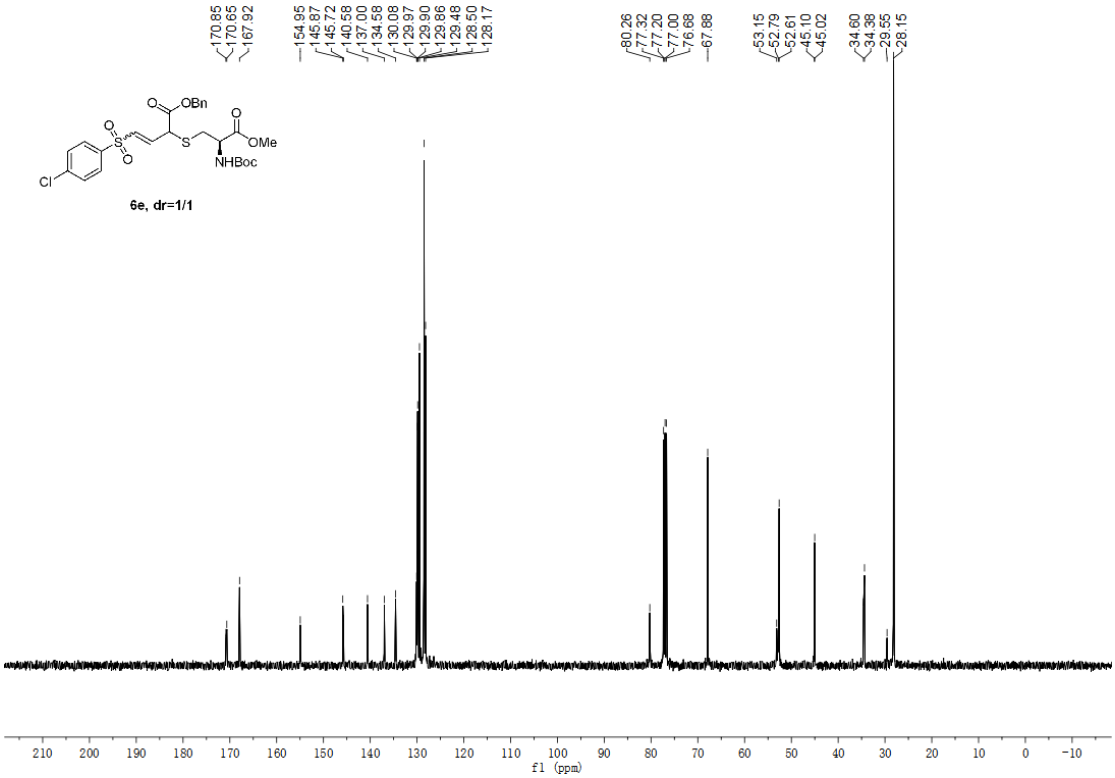
^{19}F NMR Spectrum of compound **6d (376** MHz, $CDCl_3$)



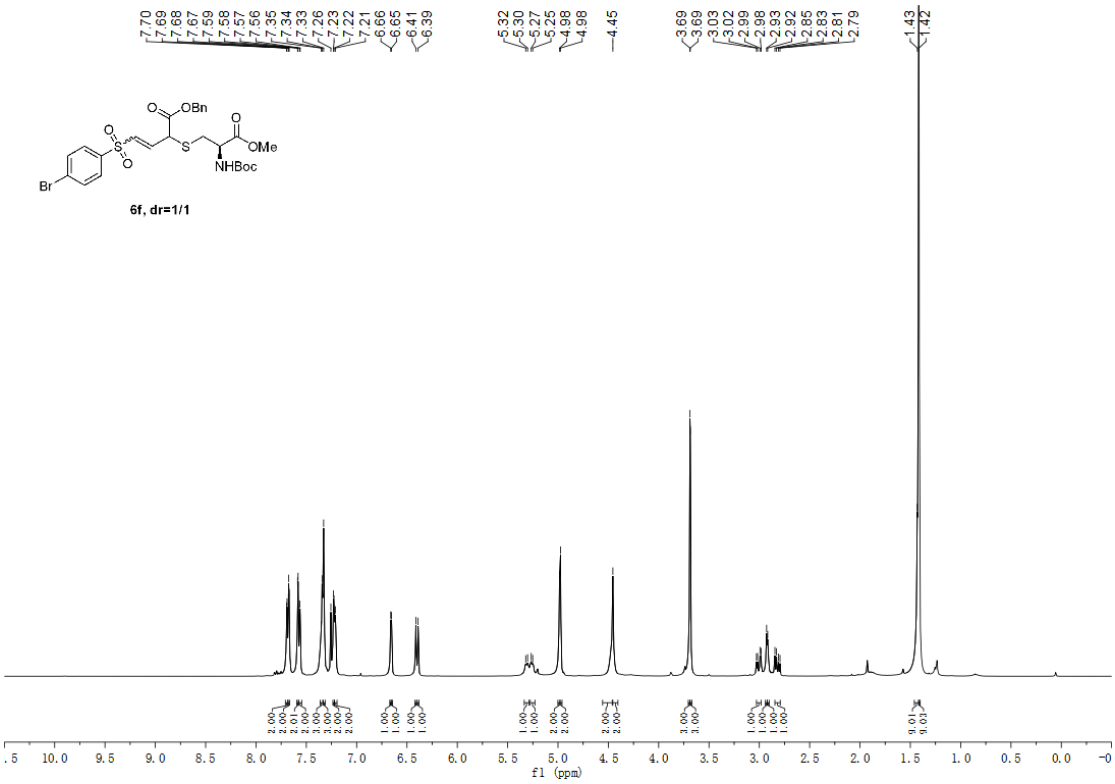
^{1}H NMR Spectrum of compound **6e (400** MHz, $CDCl_3$)



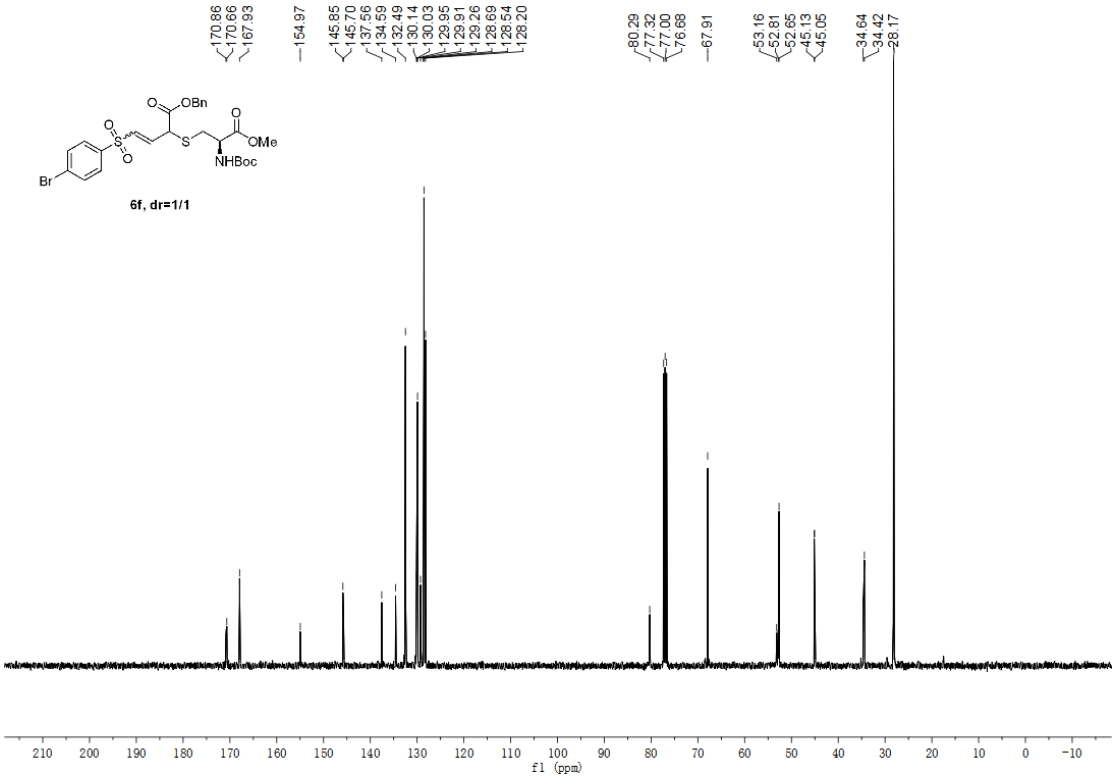
^{13}C NMR Spectrum of compound **6e (100** MHz, $CDCl_3$)



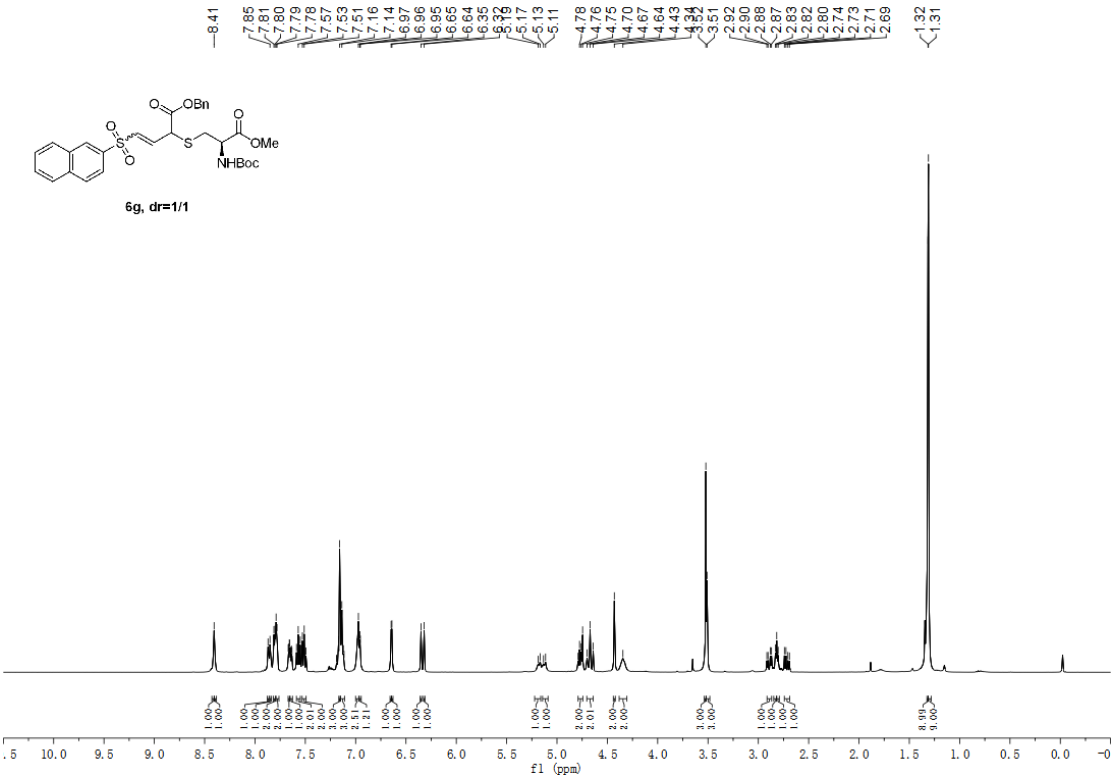
^{1}H NMR Spectrum of compound **6f (400** MHz, $CDCl_3$)



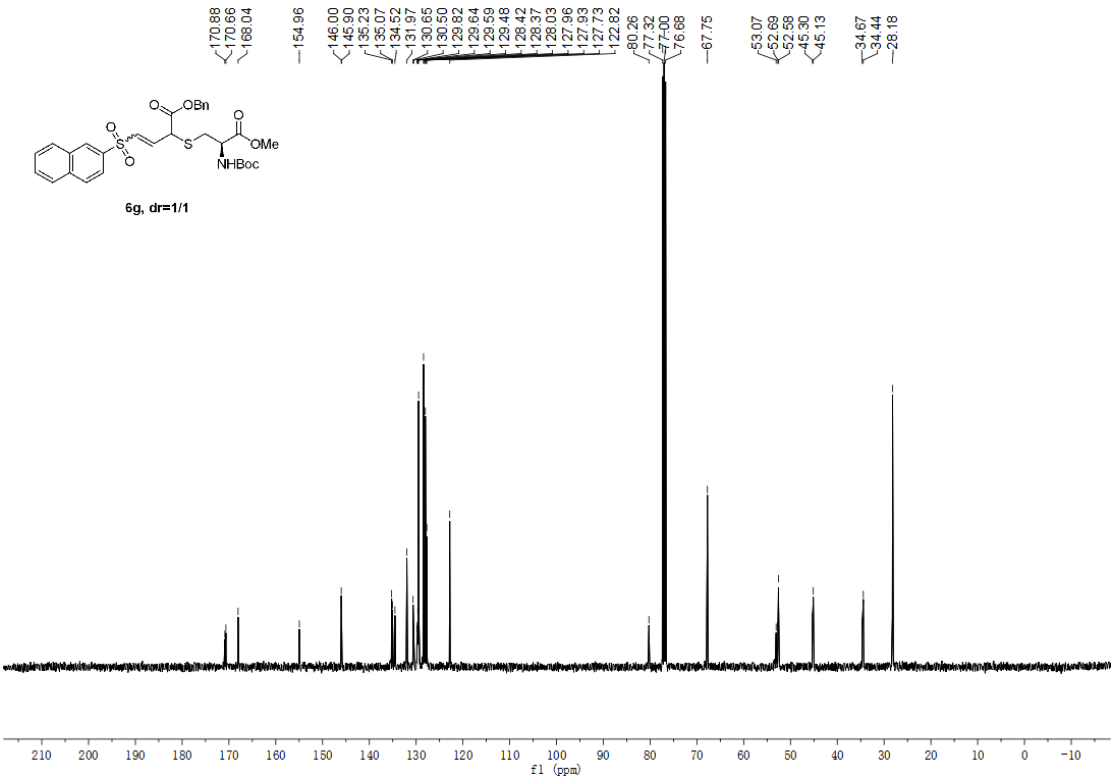
^{13}C NMR Spectrum of compound **6f (100** MHz, $CDCl_3$)



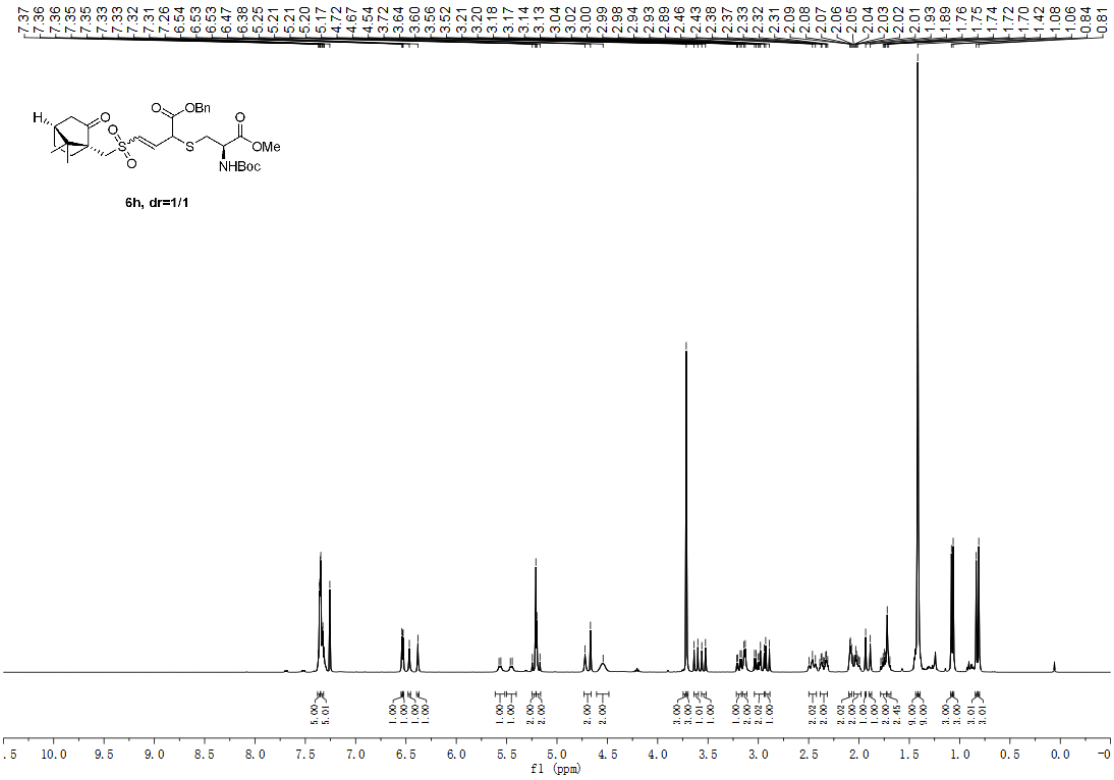
^{1}H NMR Spectrum of compound **6g (400** MHz, $CDCl_3$)



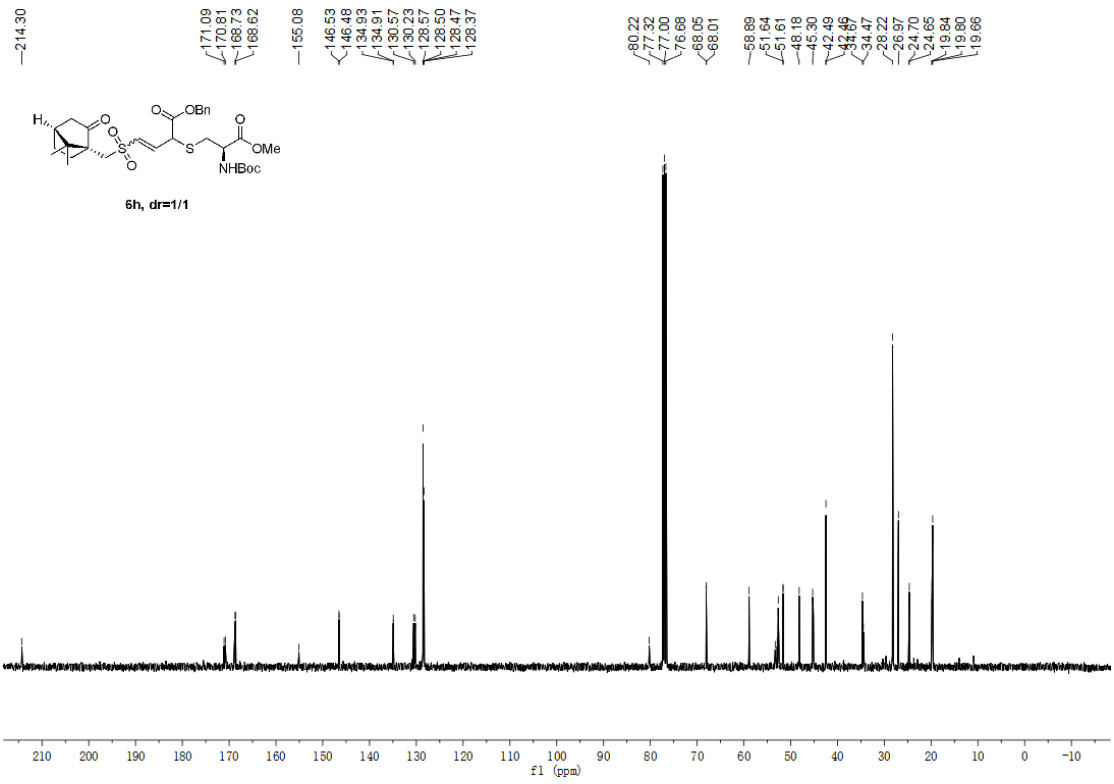
^{13}C NMR Spectrum of compound **6g (100** MHz, $CDCl_3$)



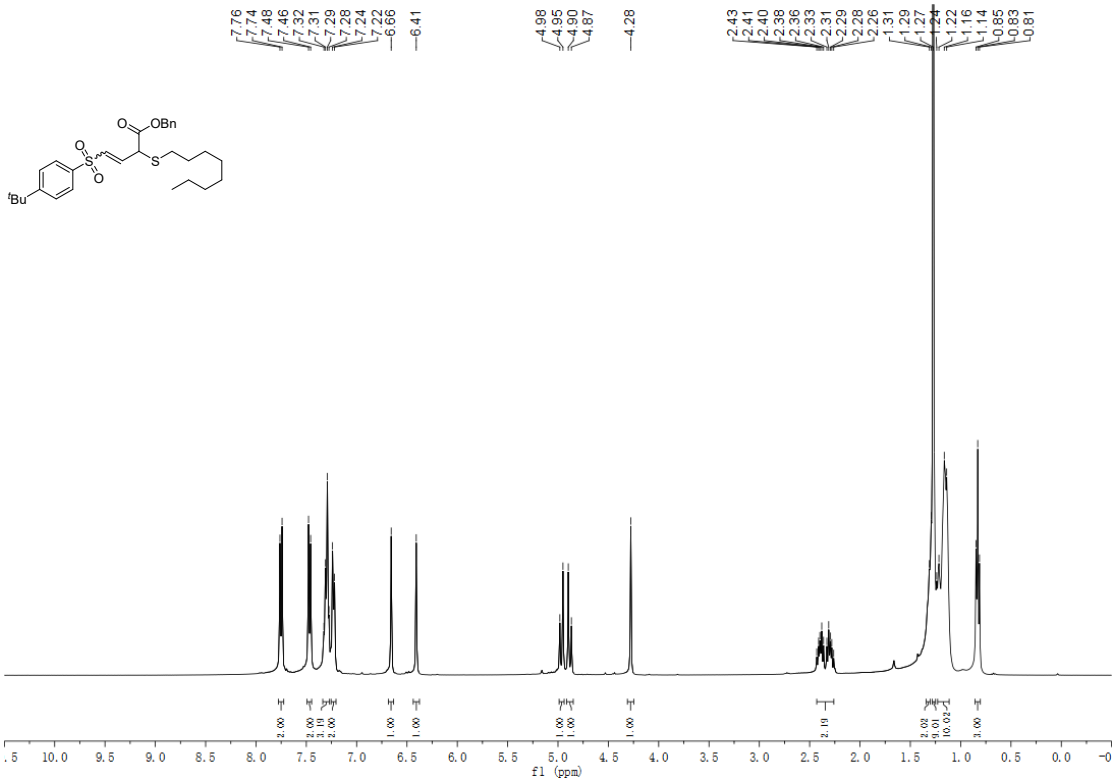
^{1}H NMR Spectrum of compound **6h (400** MHz, $CDCl_3$)



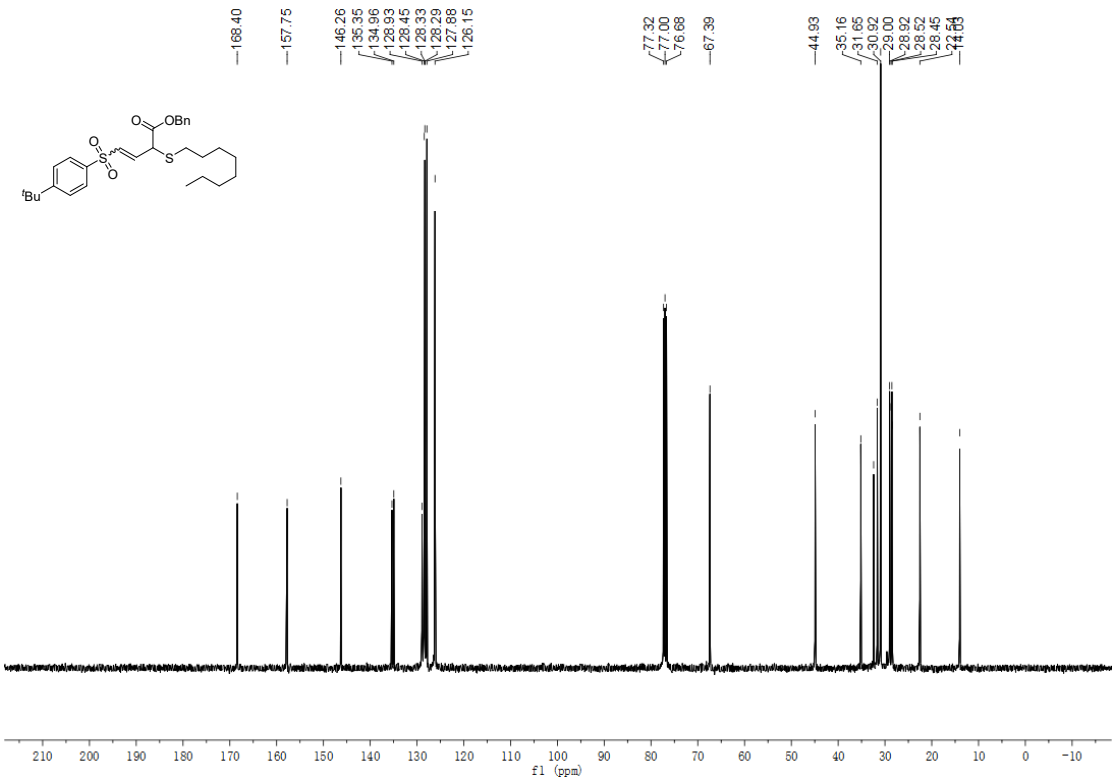
^{13}C NMR Spectrum of compound **6h (100** MHz, $CDCl_3$)



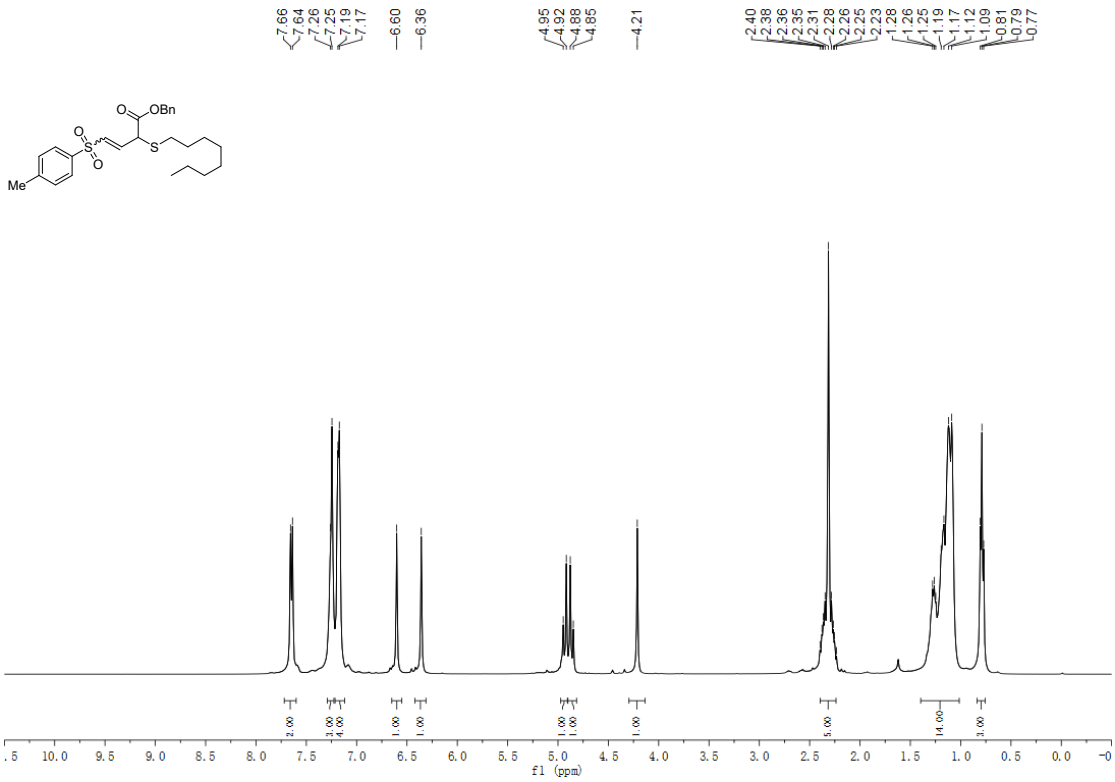
^{1}H NMR Spectrum of compound **6i (400** MHz, $CDCl_3$)



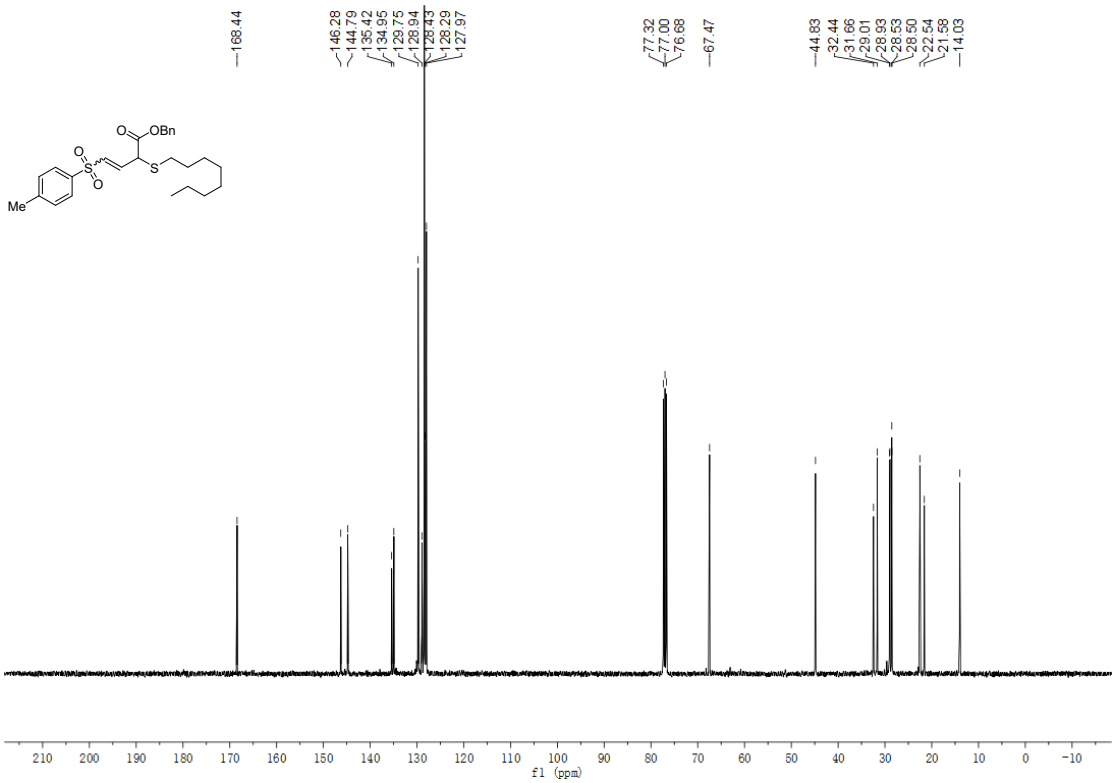
^{13}C NMR Spectrum of compound **6i (100** MHz, $CDCl_3$)



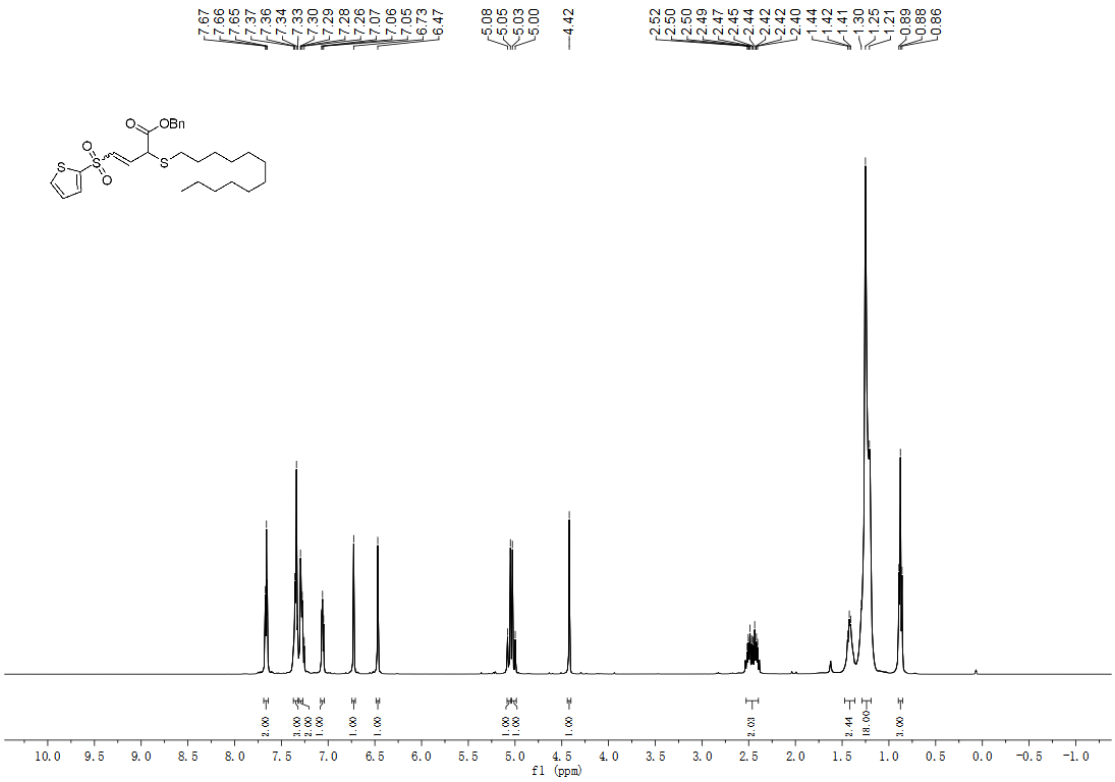
^{1}H NMR Spectrum of compound **6j (400** MHz, $CDCl_3$)



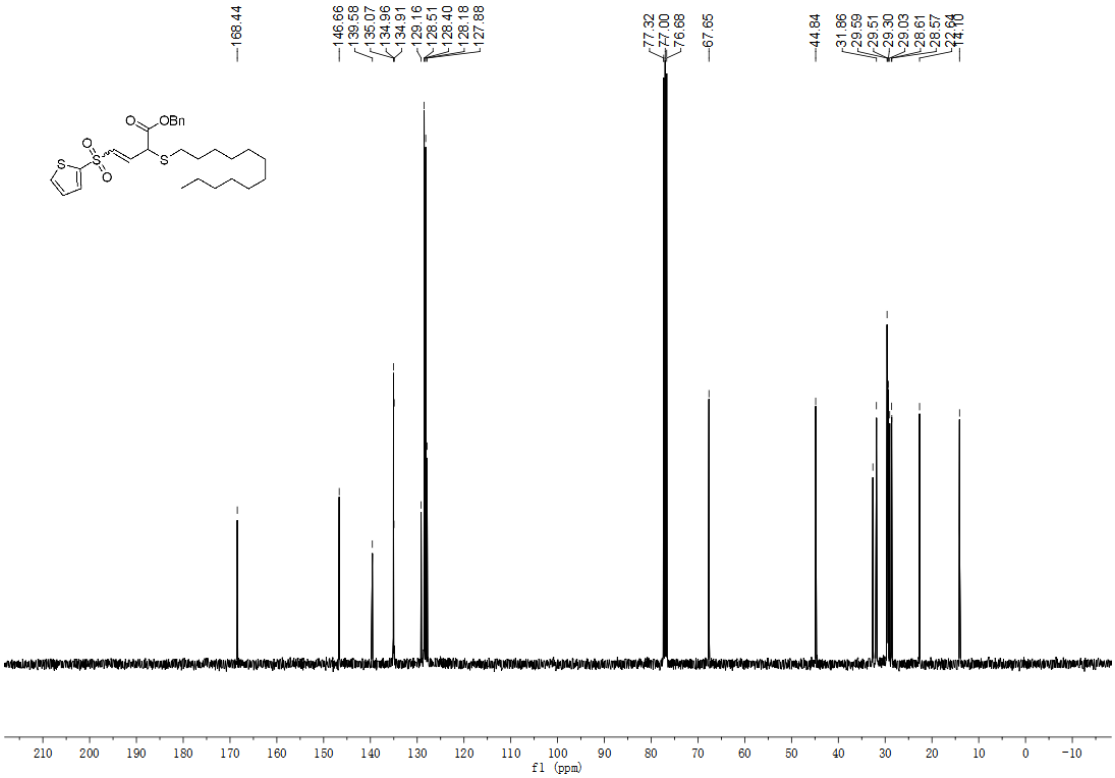
^{13}C NMR Spectrum of compound **6j (100** MHz, $CDCl_3$)



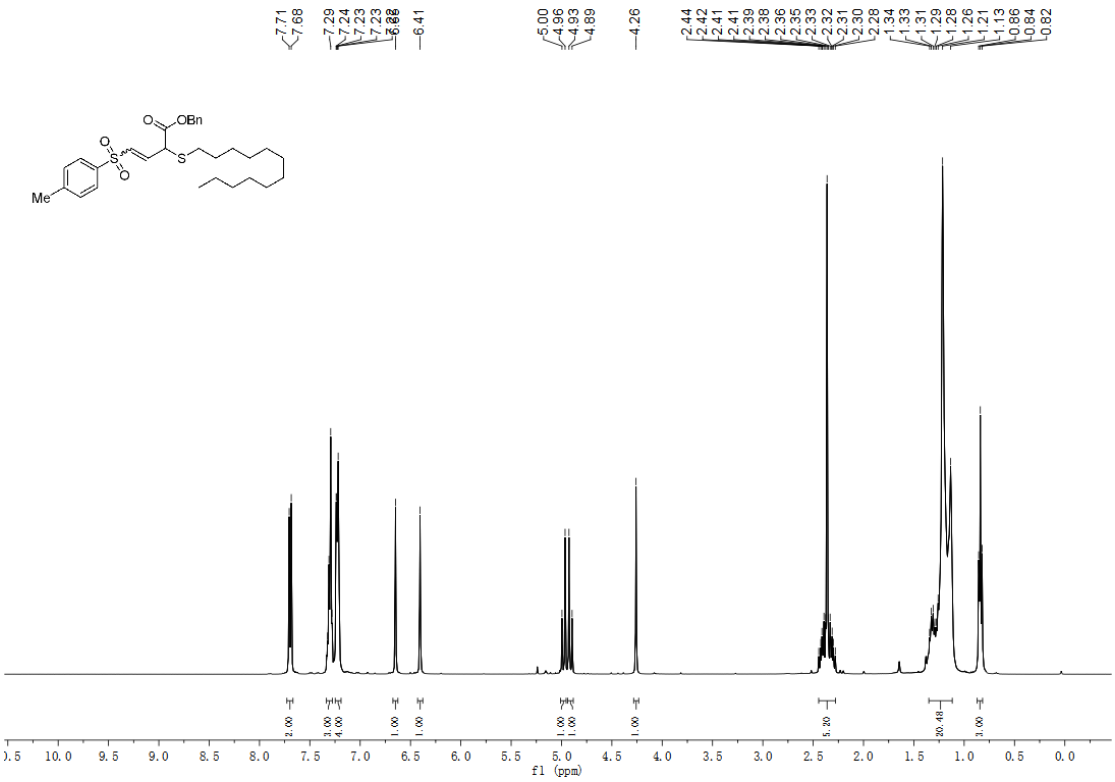
^{1}H NMR Spectrum of compound **6k (400** MHz, $CDCl_3$)



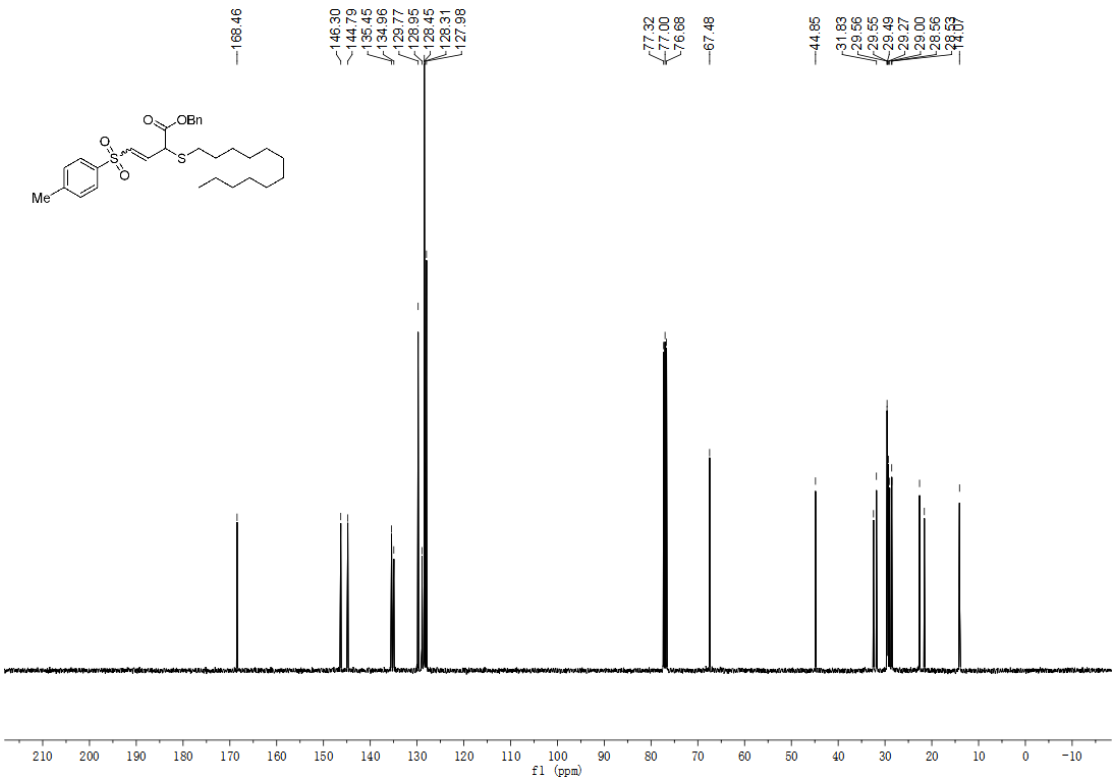
^{13}C NMR Spectrum of compound **6k (100** MHz, $CDCl_3$)



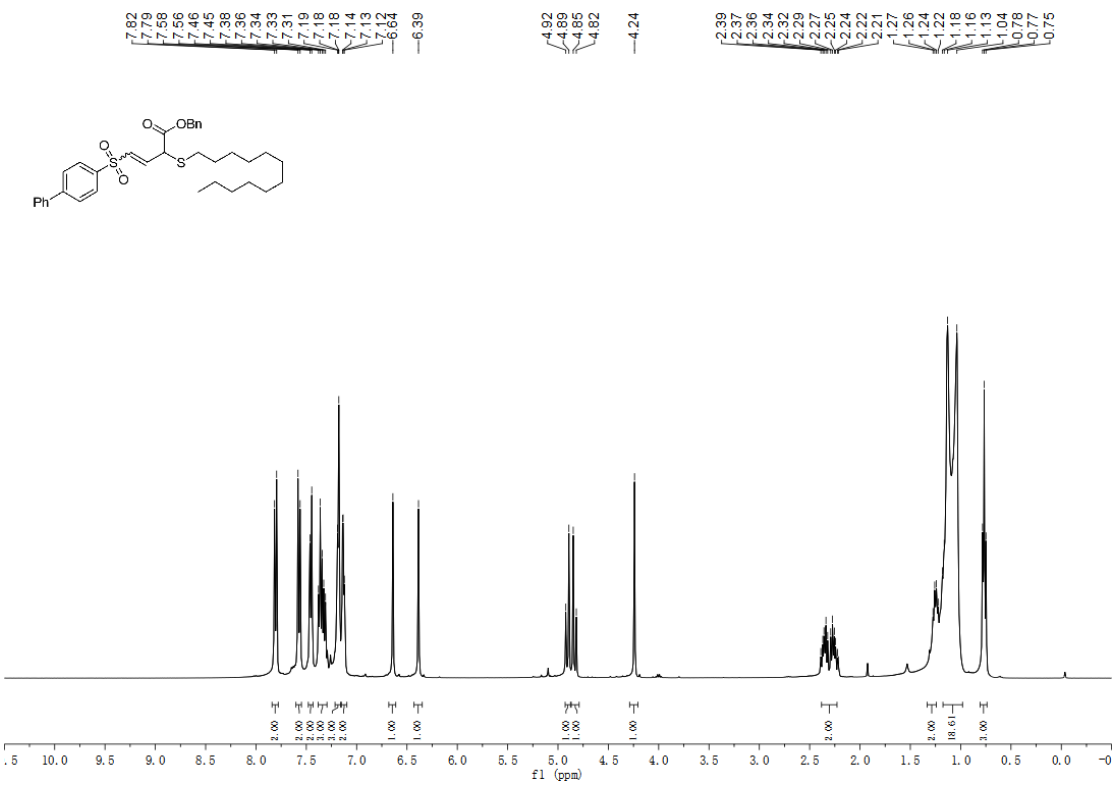
^{1}H NMR Spectrum of compound **6l (400** MHz, $CDCl_3$)



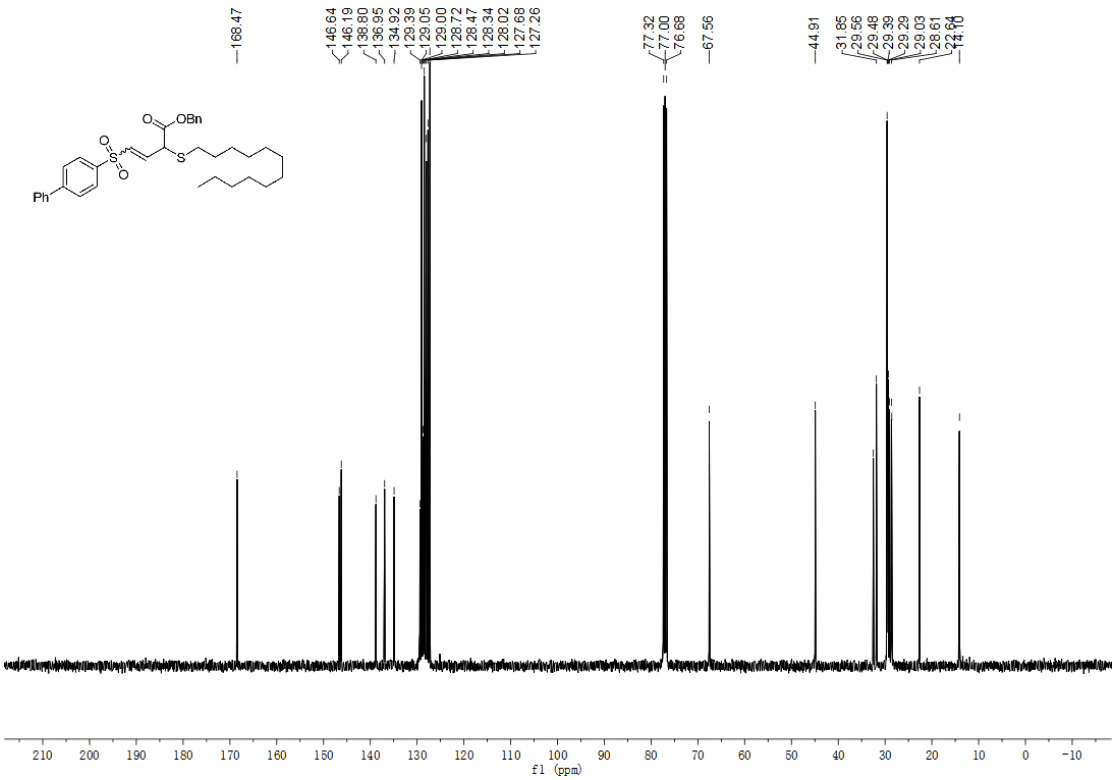
^{13}C NMR Spectrum of compound **6l (100** MHz, $CDCl_3$)



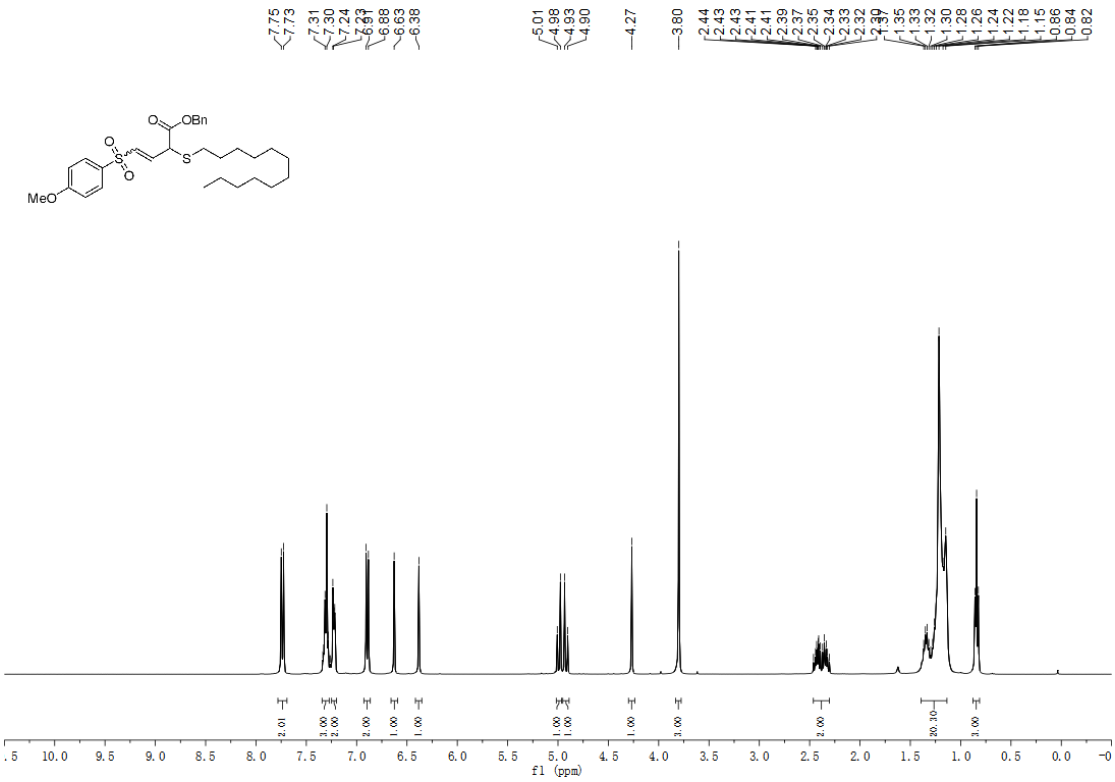
^{1}H NMR Spectrum of compound **6m (400** MHz, $CDCl_3$)



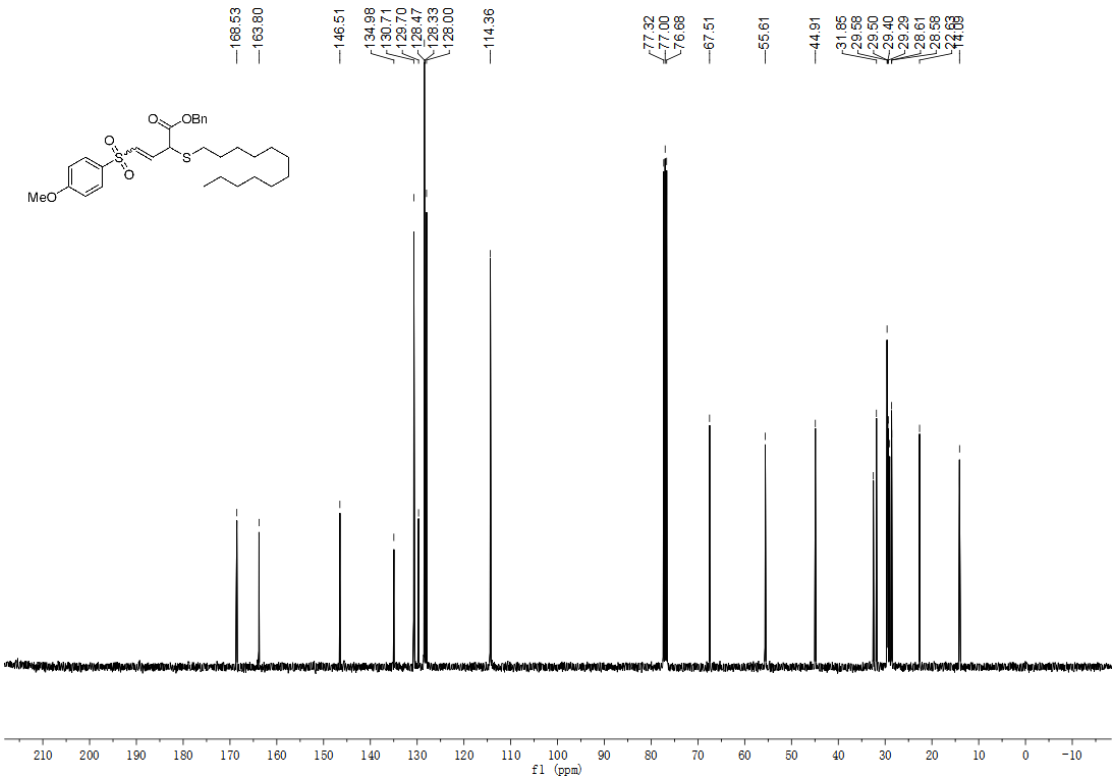
^{13}C NMR Spectrum of compound **6m (100** MHz, $CDCl_3$)



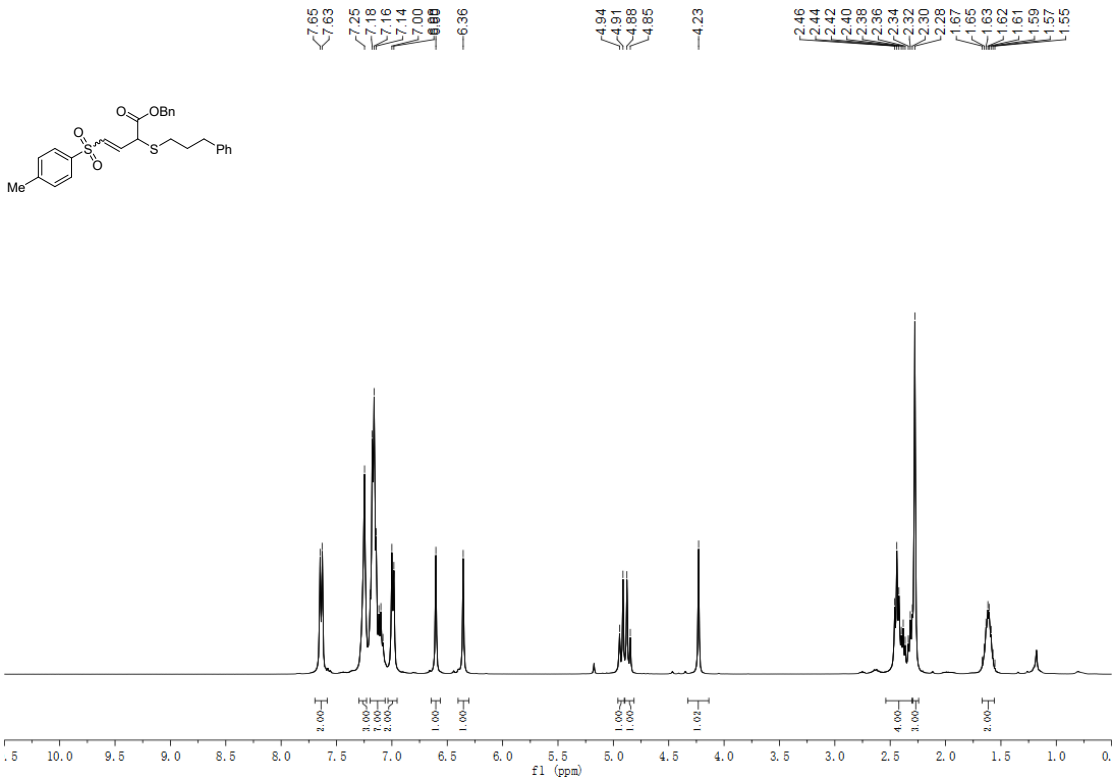
^{1}H NMR Spectrum of compound **6n (400** MHz, $CDCl_3$)



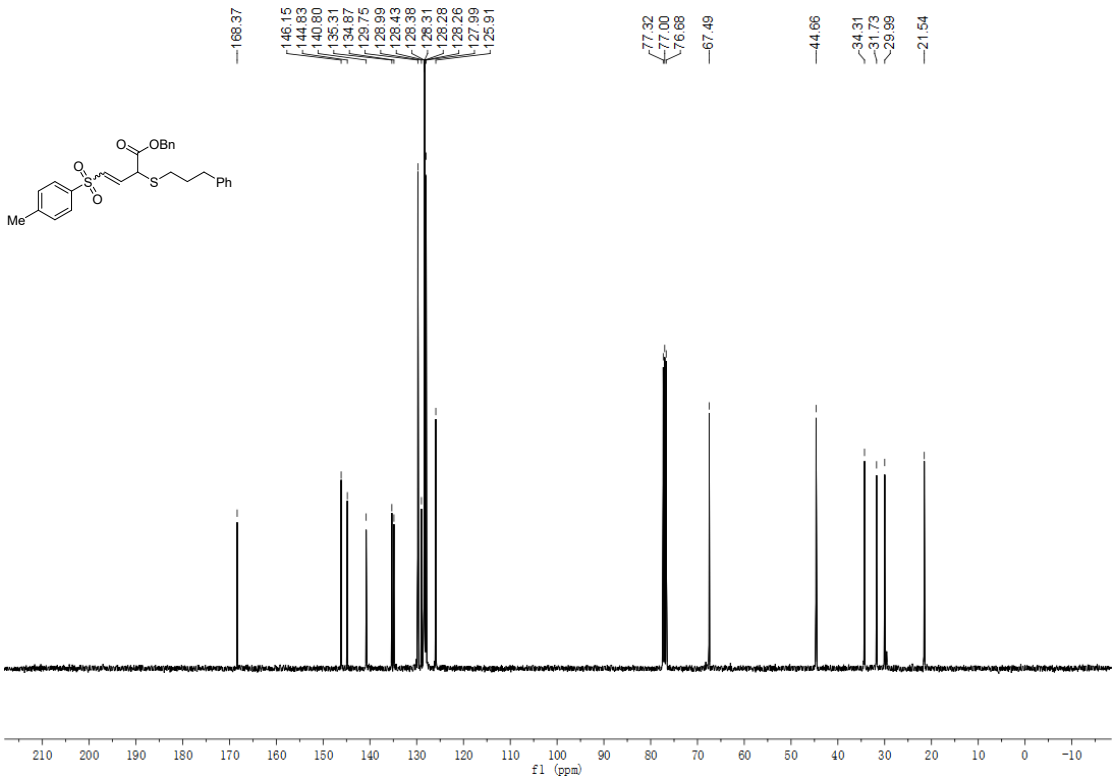
^{13}C NMR Spectrum of compound **6n (100** MHz, $CDCl_3$)



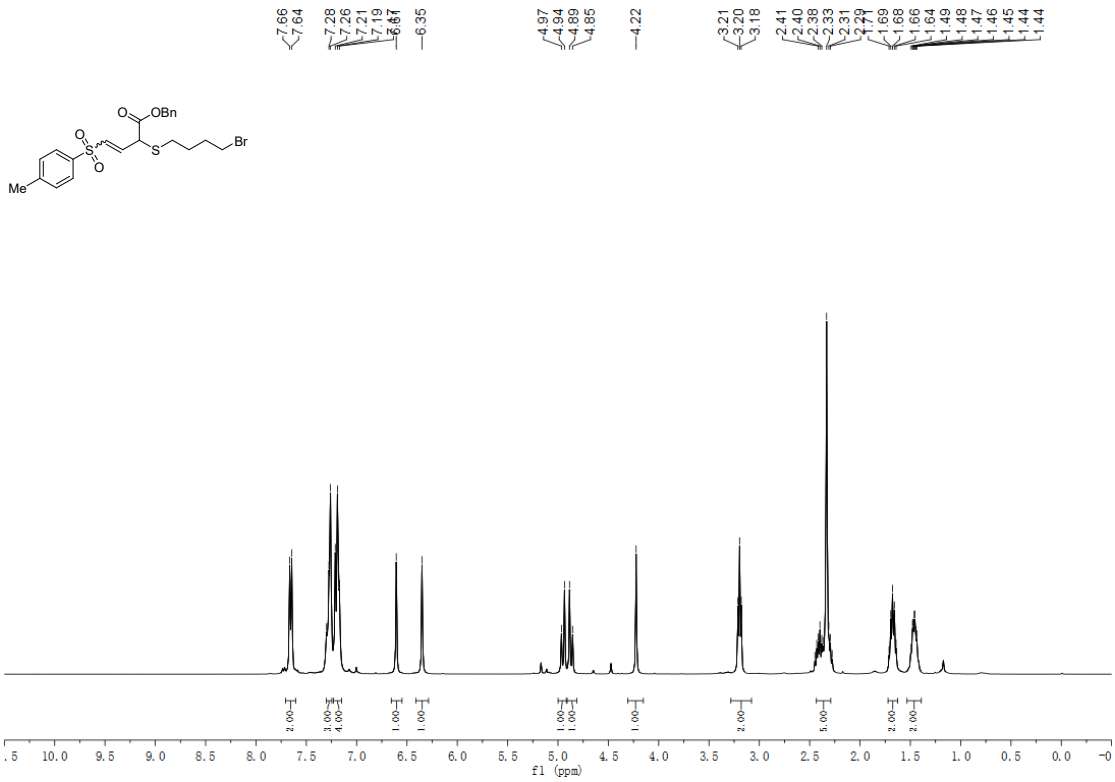
^{1}H NMR Spectrum of compound **6o (400** MHz, $CDCl_3$)



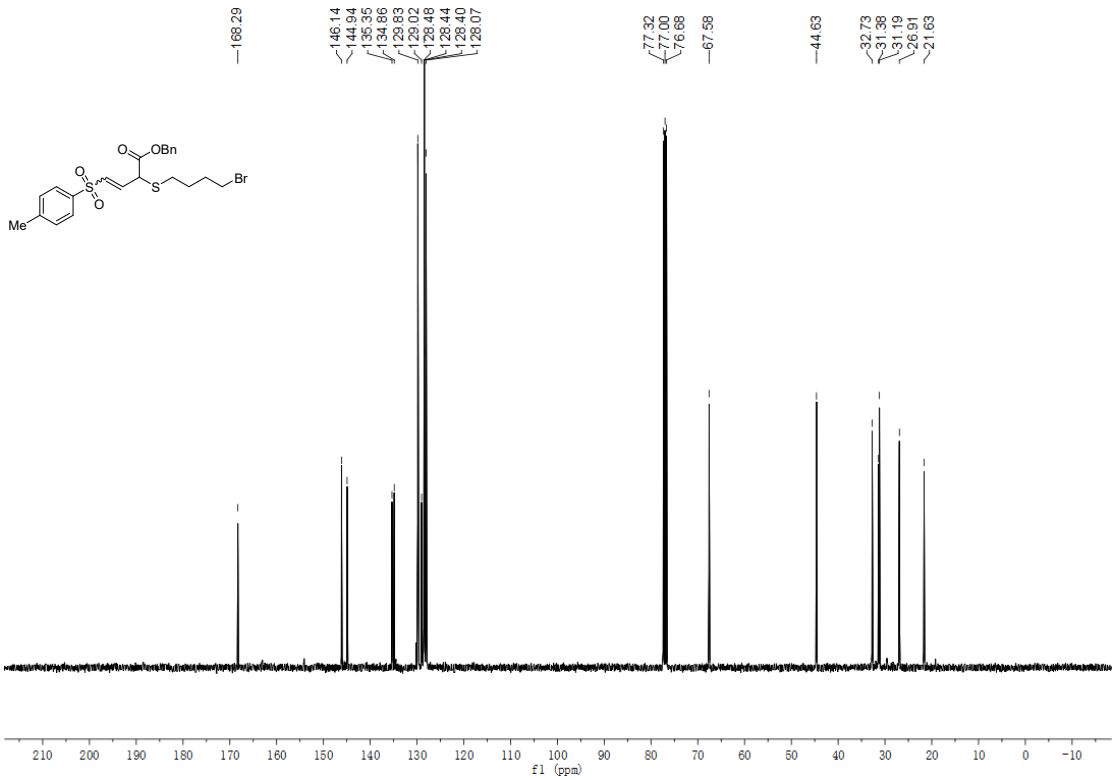
^{13}C NMR Spectrum of compound **6o (100** MHz, $CDCl_3$)



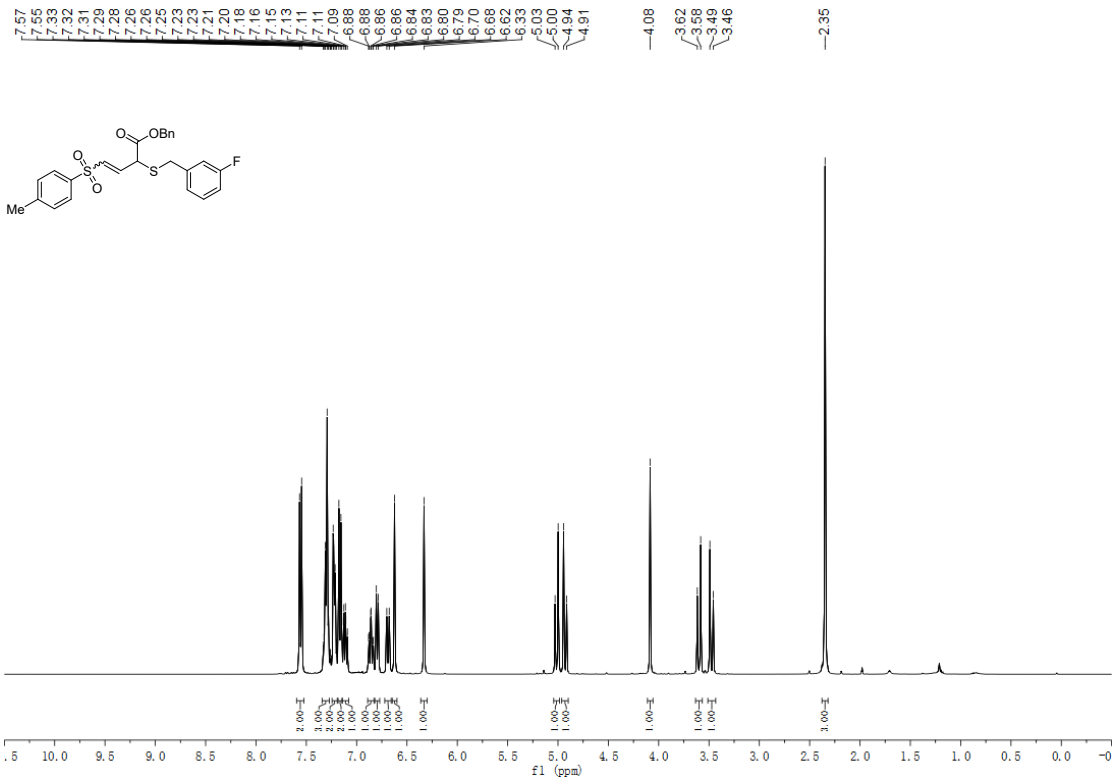
^{1}H NMR Spectrum of compound **6p (400** MHz, $CDCl_3$)



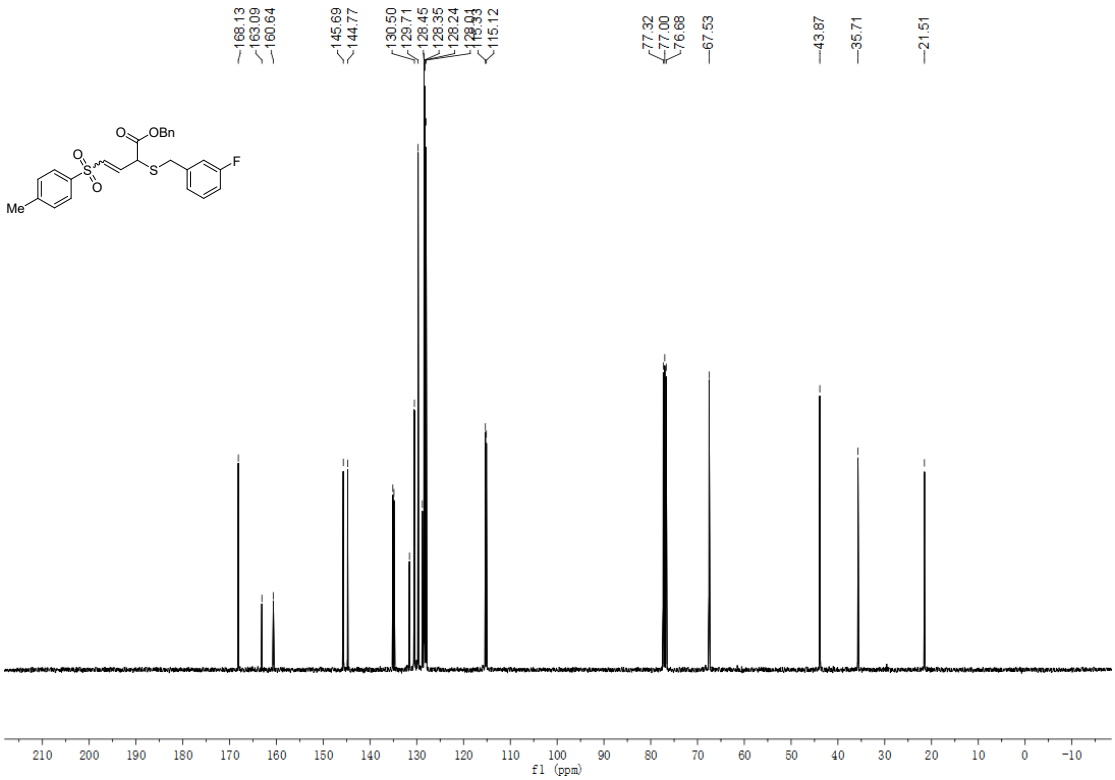
^{13}C NMR Spectrum of compound **6p (100** MHz, $CDCl_3$)



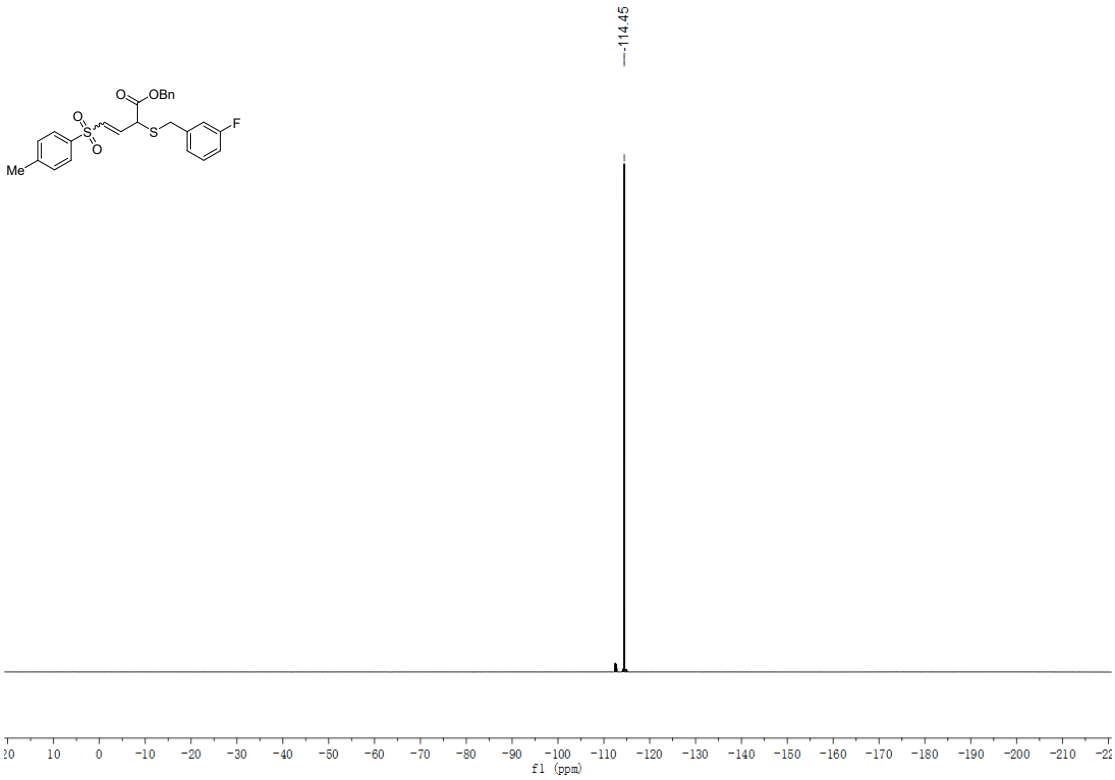
^{1}H NMR Spectrum of compound **6q (400** MHz, $CDCl_3$)



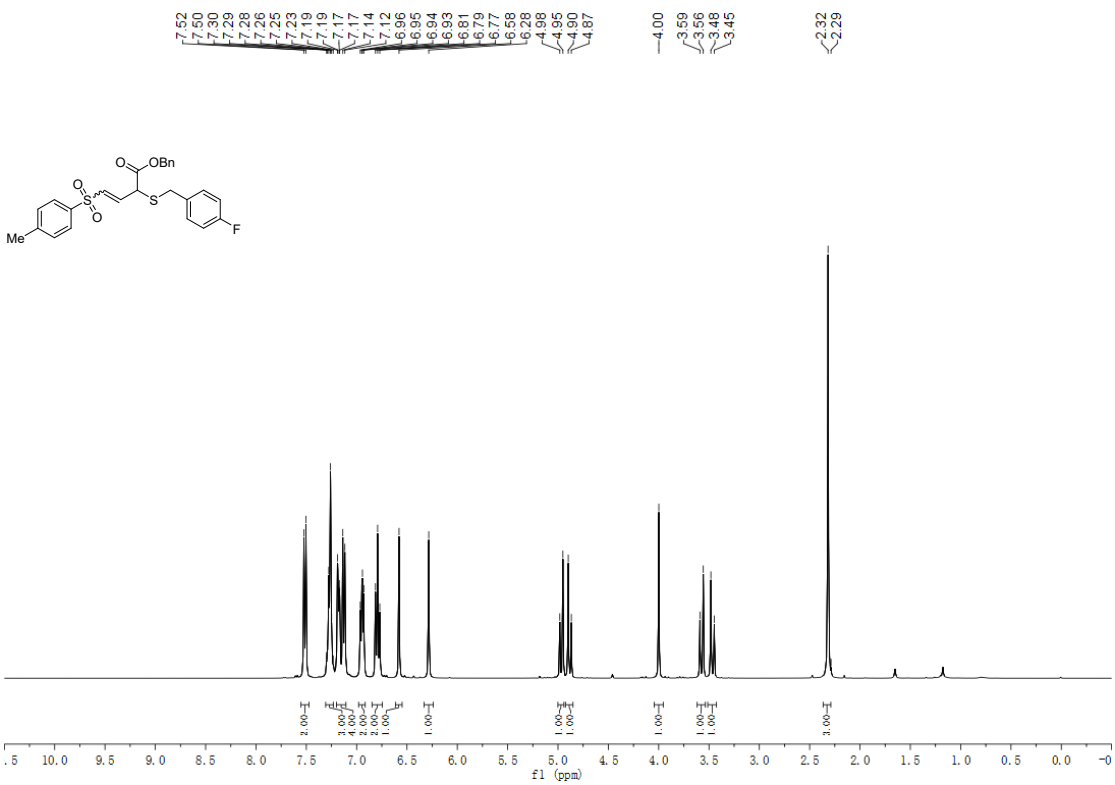
^{13}C NMR Spectrum of compound **6q (100** MHz, $CDCl_3$)



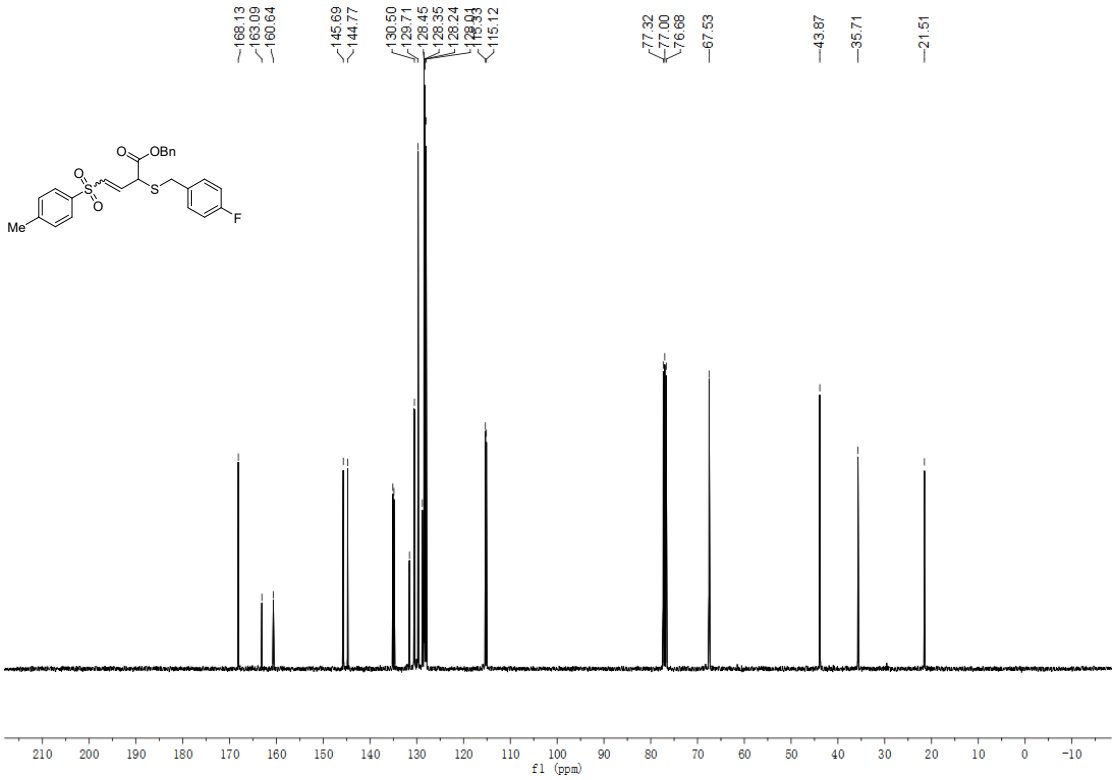
^{19}F NMR Spectrum of compound **6q (376** MHz, $CDCl_3$)



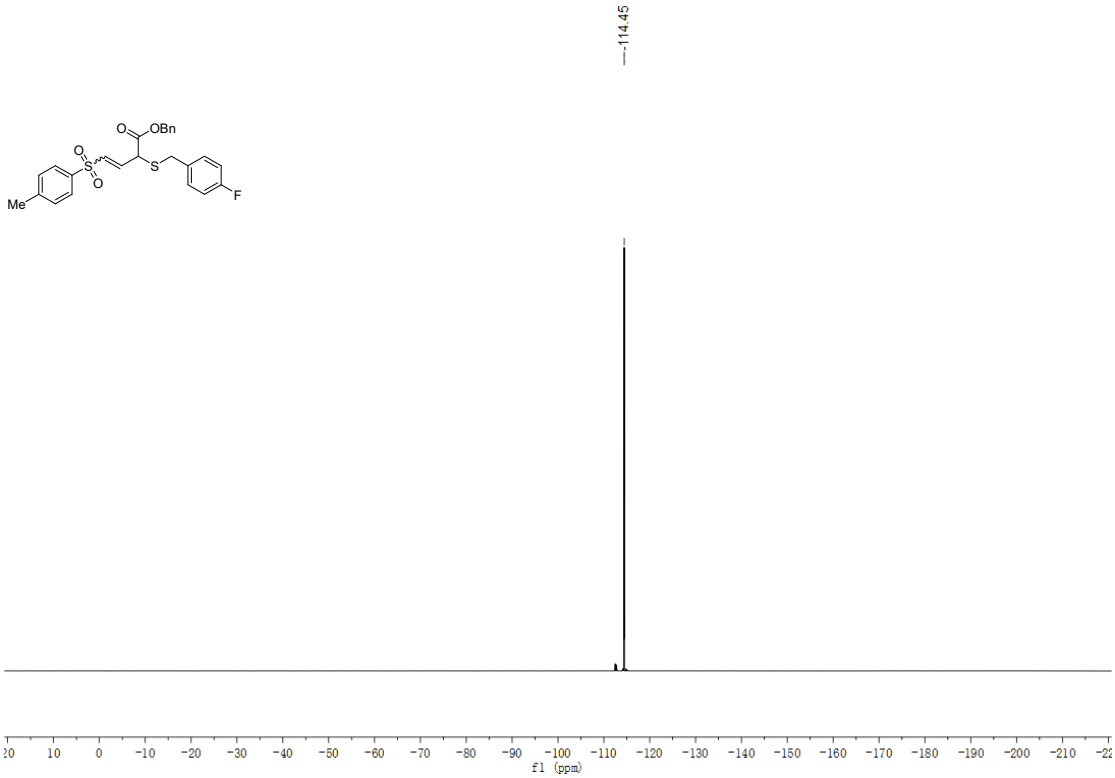
^{1}H NMR Spectrum of compound **6r (400** MHz, $CDCl_3$)



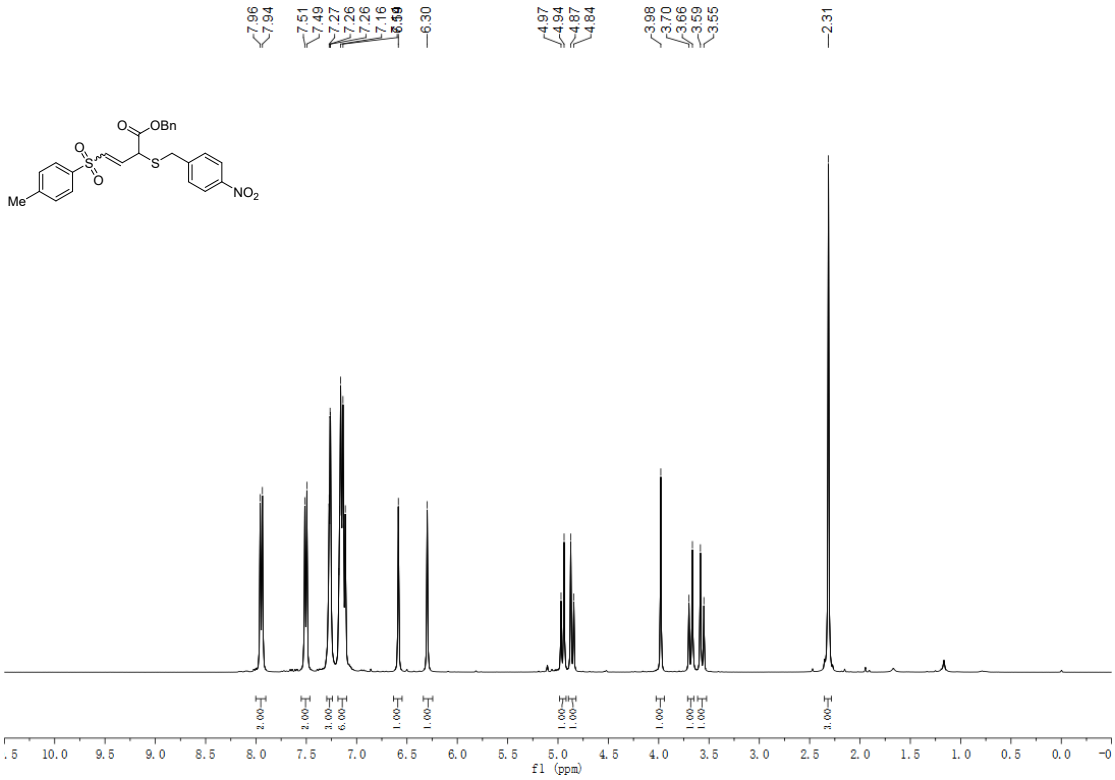
^{13}C NMR Spectrum of compound **6r (100** MHz, $CDCl_3$)



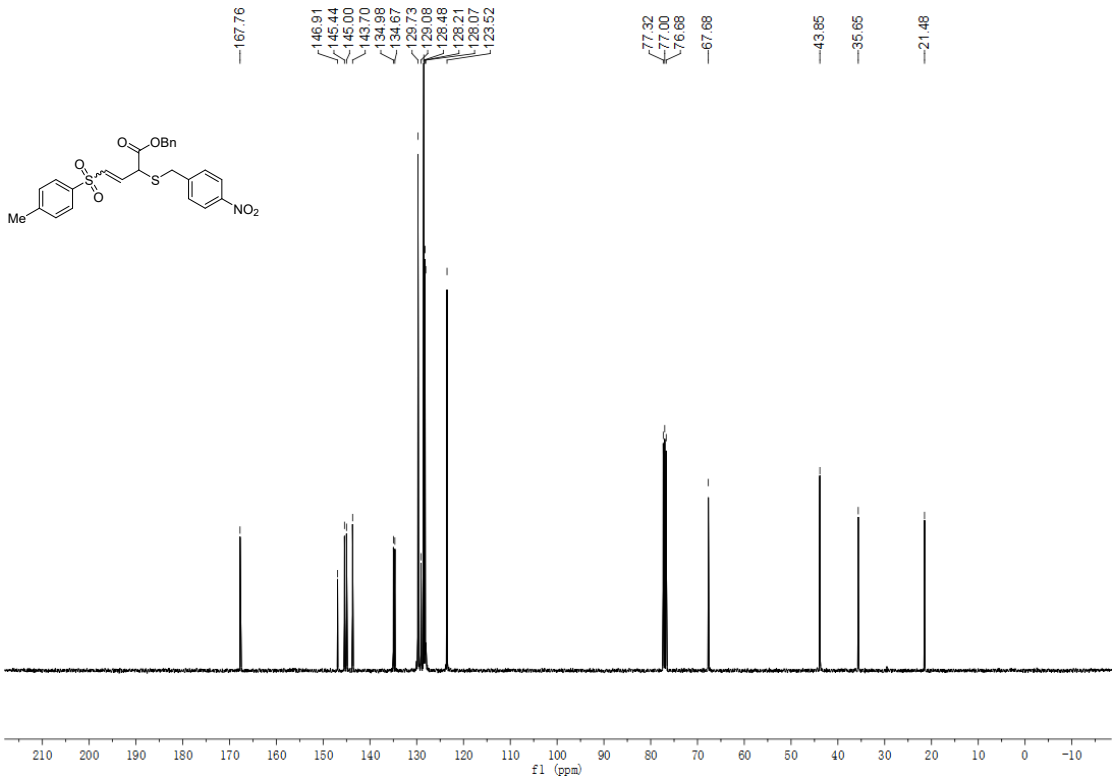
^{19}F NMR Spectrum of compound **6r (376** MHz, $CDCl_3$)



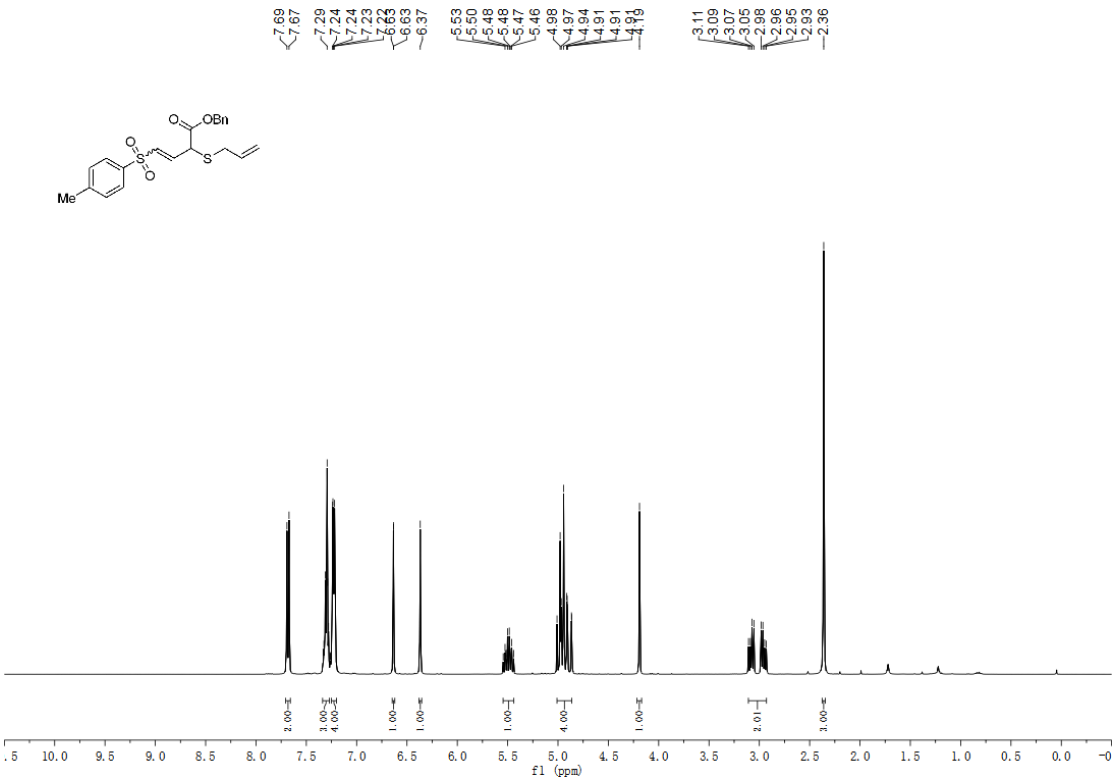
^{1}H NMR Spectrum of compound **6s (400** MHz, $CDCl_3$)



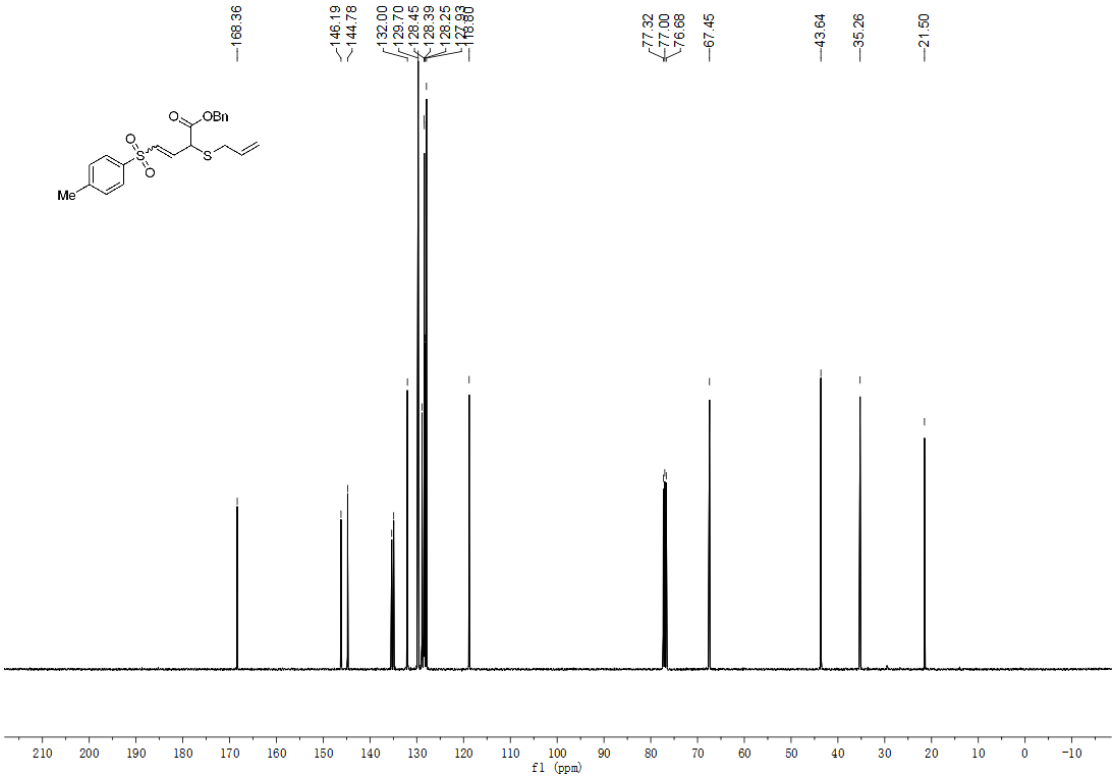
^{13}C NMR Spectrum of compound **6s (100** MHz, $CDCl_3$)



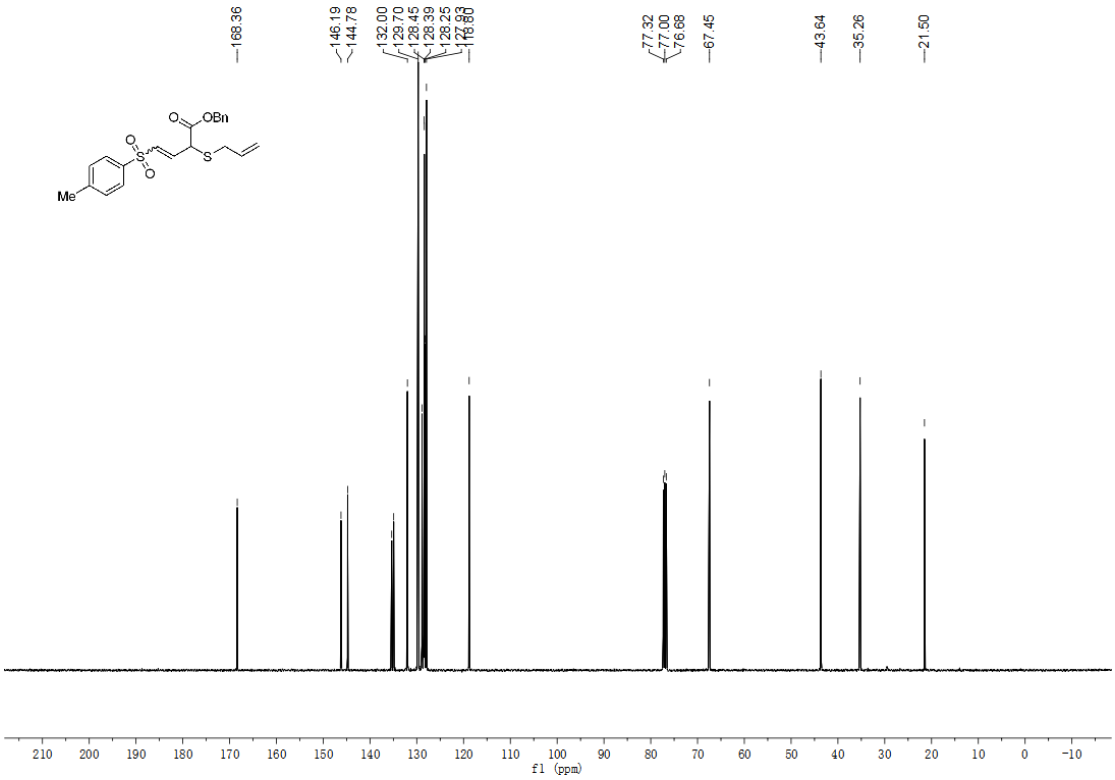
^{1}H NMR Spectrum of compound **6t (400** MHz, $CDCl_3$)



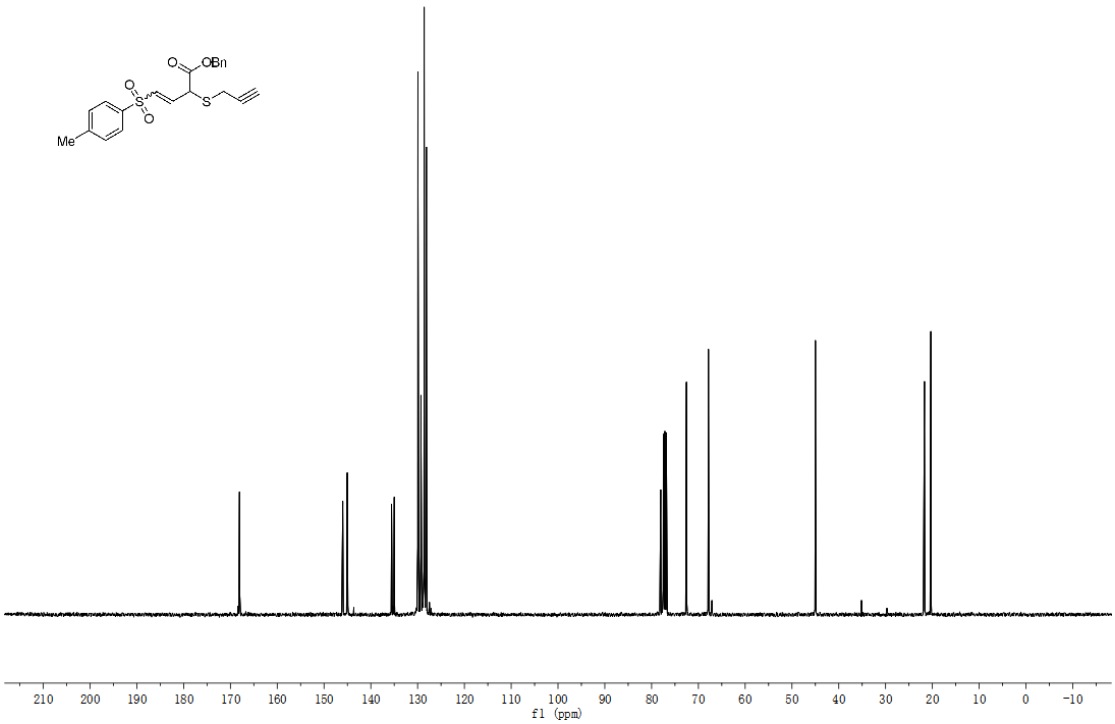
^{13}C NMR Spectrum of compound **6t (100** MHz, $CDCl_3$)



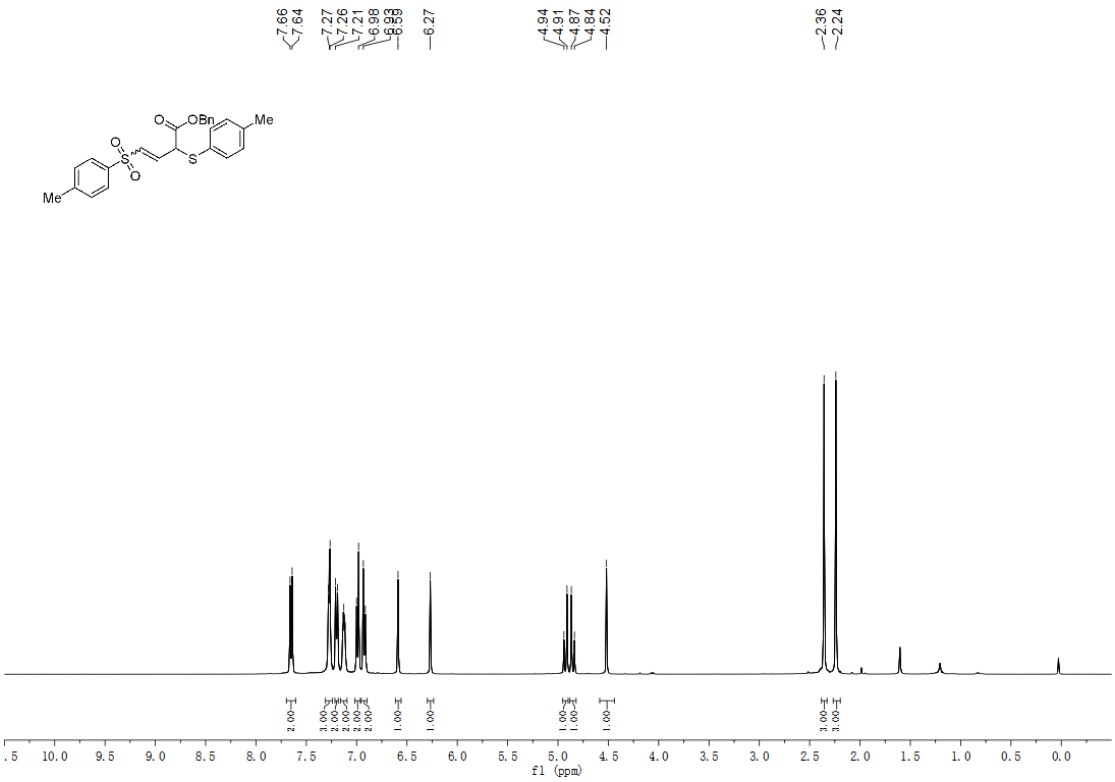
^{1}H NMR Spectrum of compound **6u (400** MHz, $CDCl_3$)



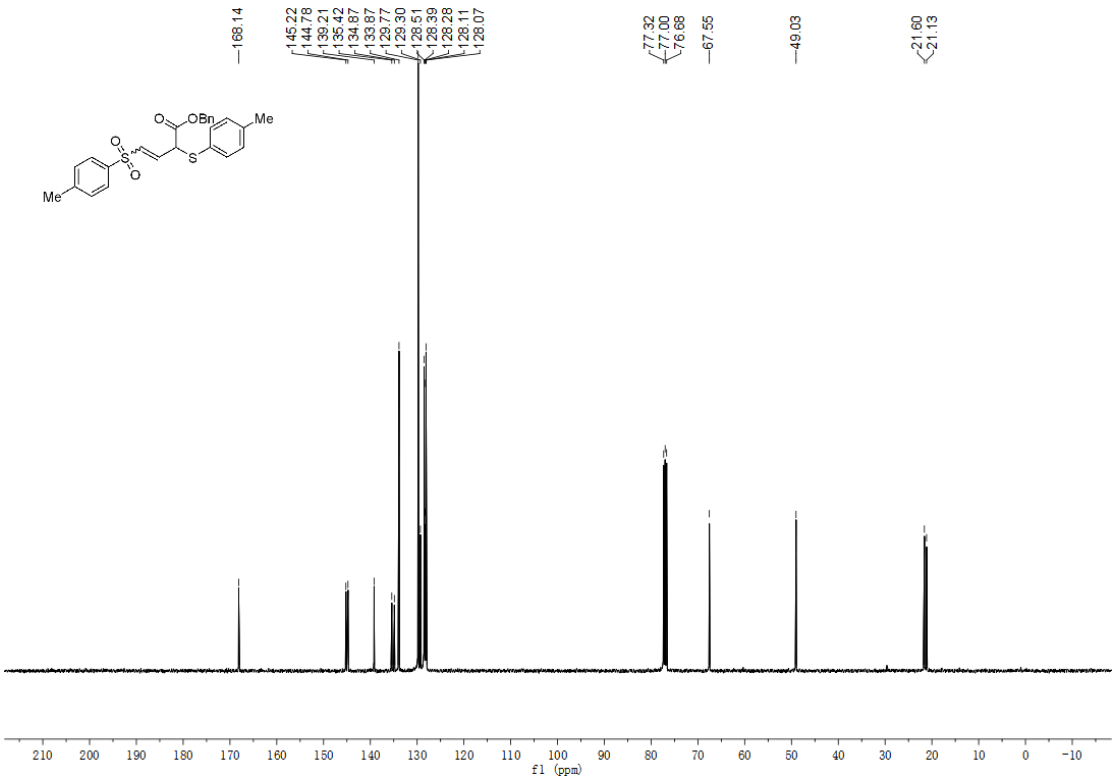
^{13}C NMR Spectrum of compound **6u (100** MHz, $CDCl_3$)



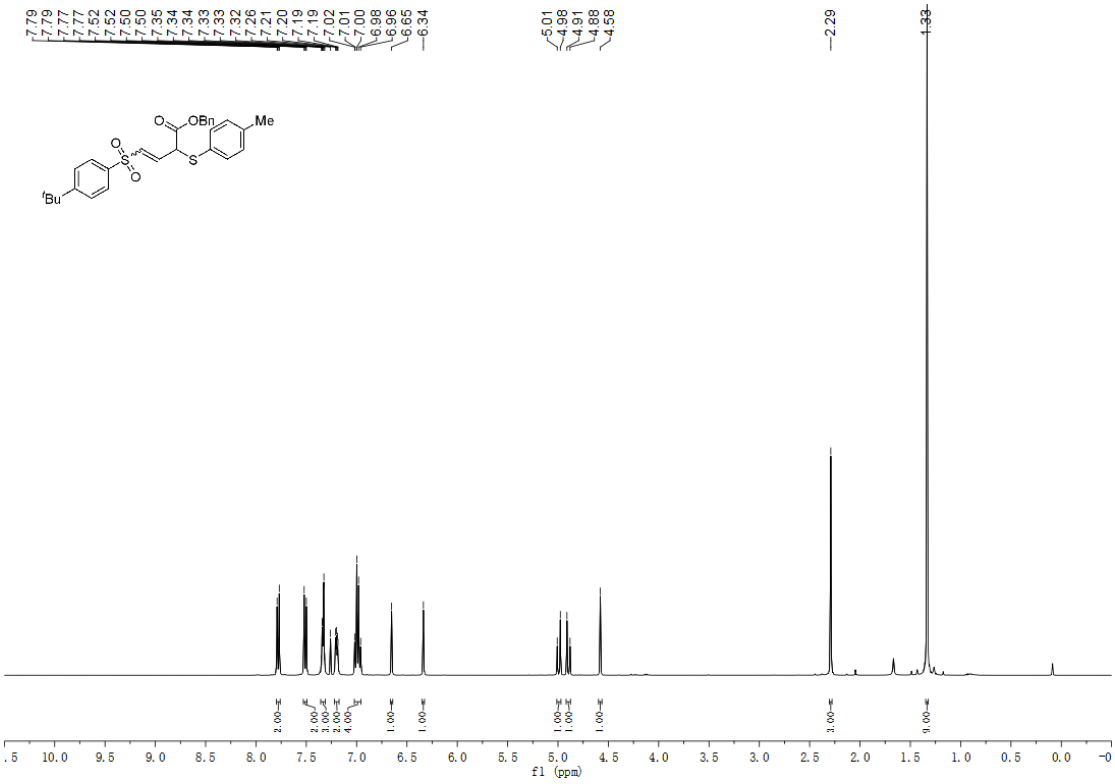
^{1}H NMR Spectrum of compound **6v (400** MHz, $CDCl_3$)



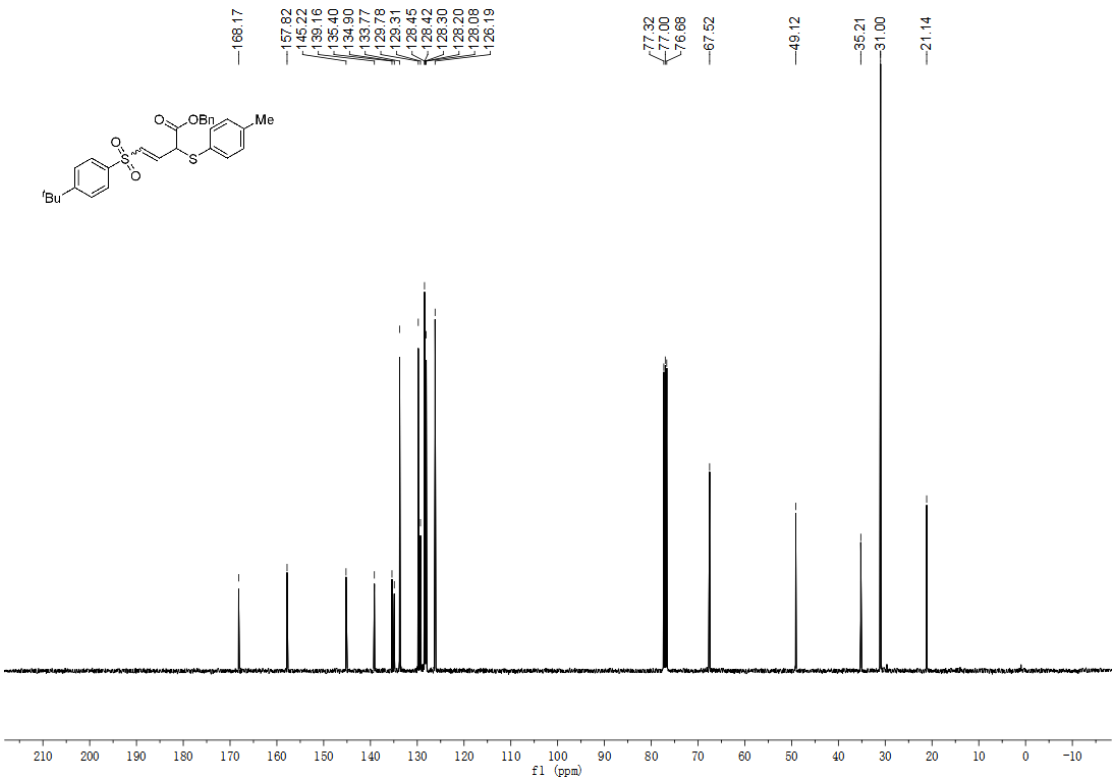
^{13}C NMR Spectrum of compound **6v (100** MHz, $CDCl_3$)



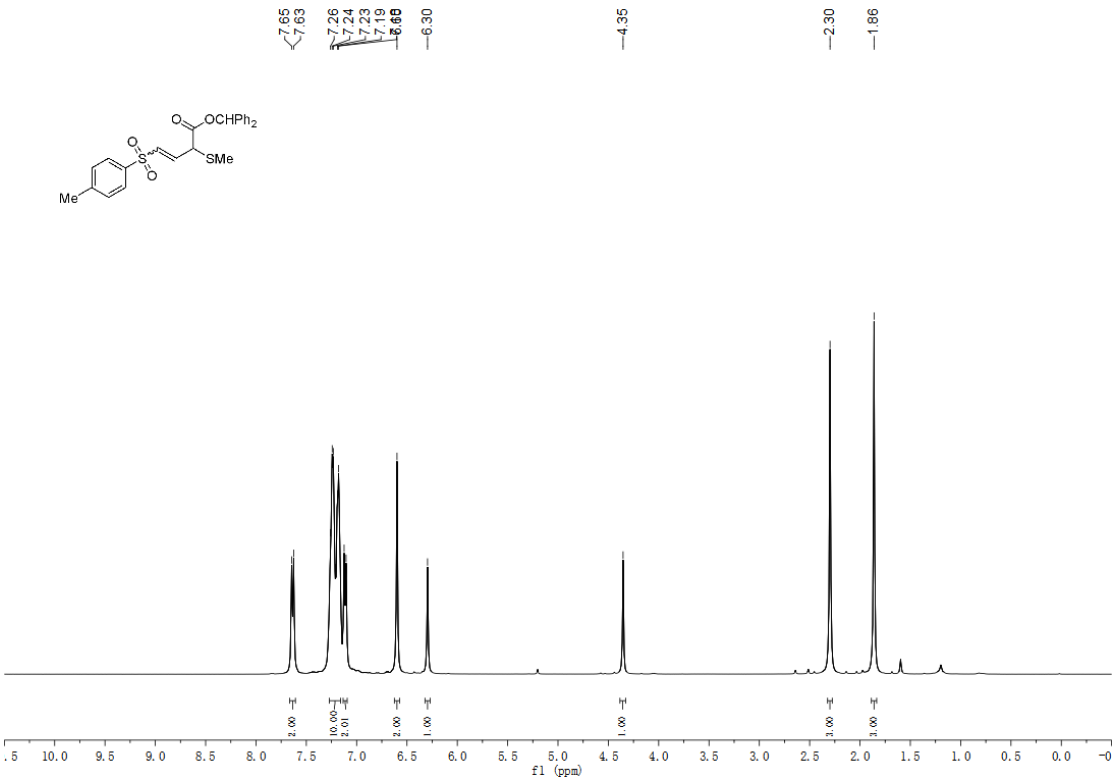
^{1}H NMR Spectrum of compound **6w (400** MHz, $CDCl_3$)



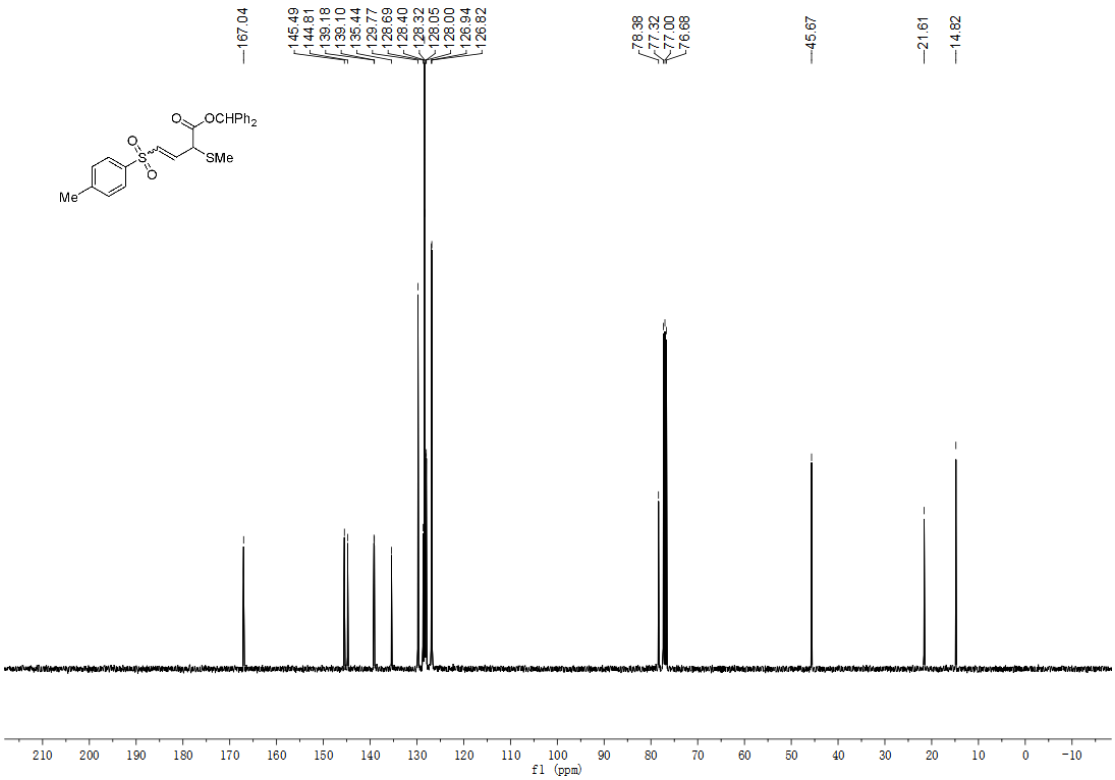
^{13}C NMR Spectrum of compound **6w (100** MHz, $CDCl_3$)



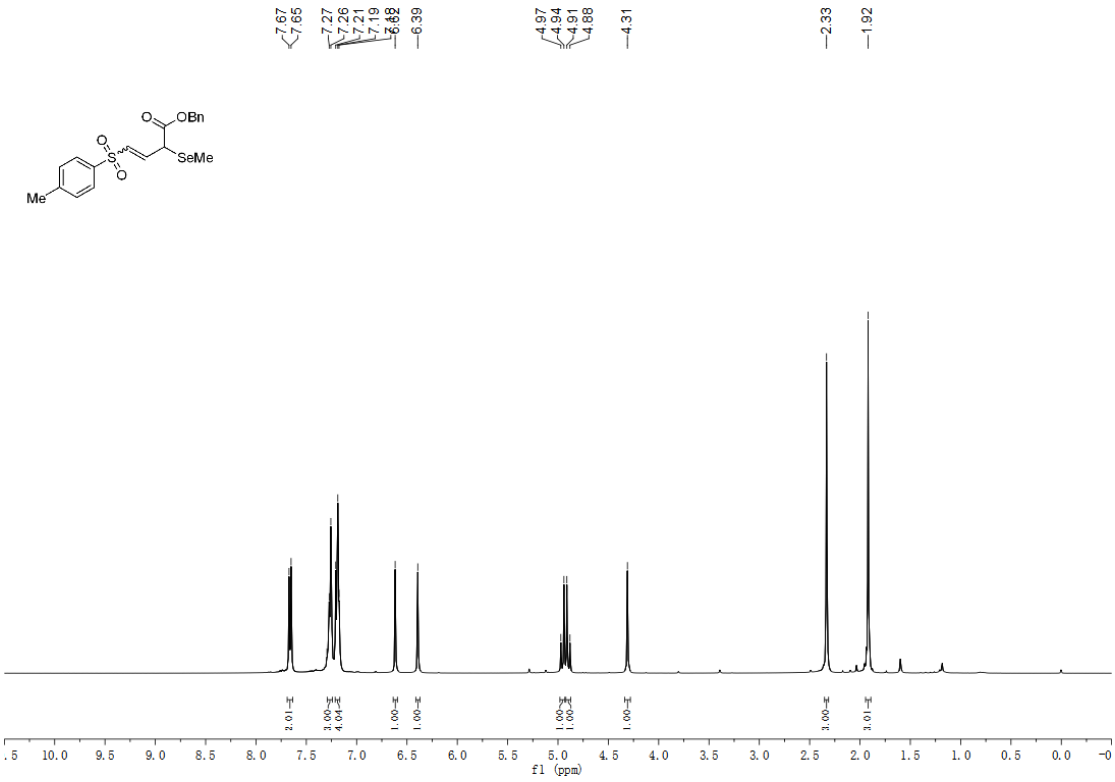
^{1}H NMR Spectrum of compound **6x (400** MHz, $CDCl_3$)



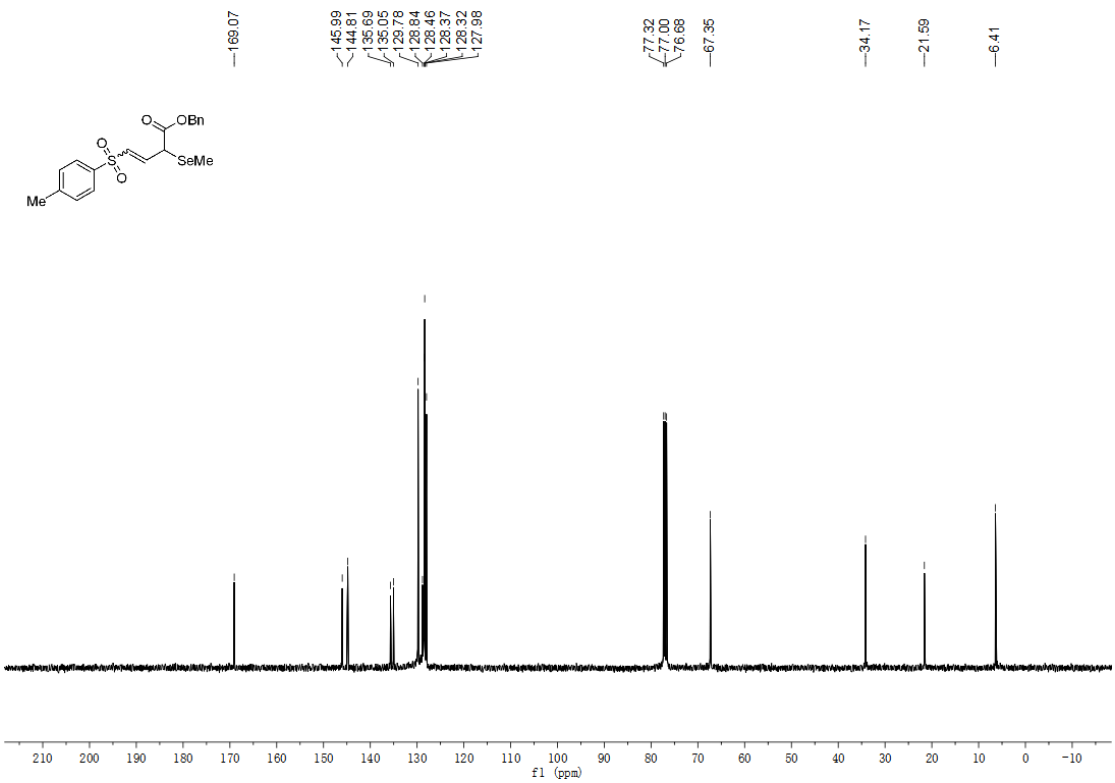
^{13}C NMR Spectrum of compound **6x (100** MHz, $CDCl_3$)



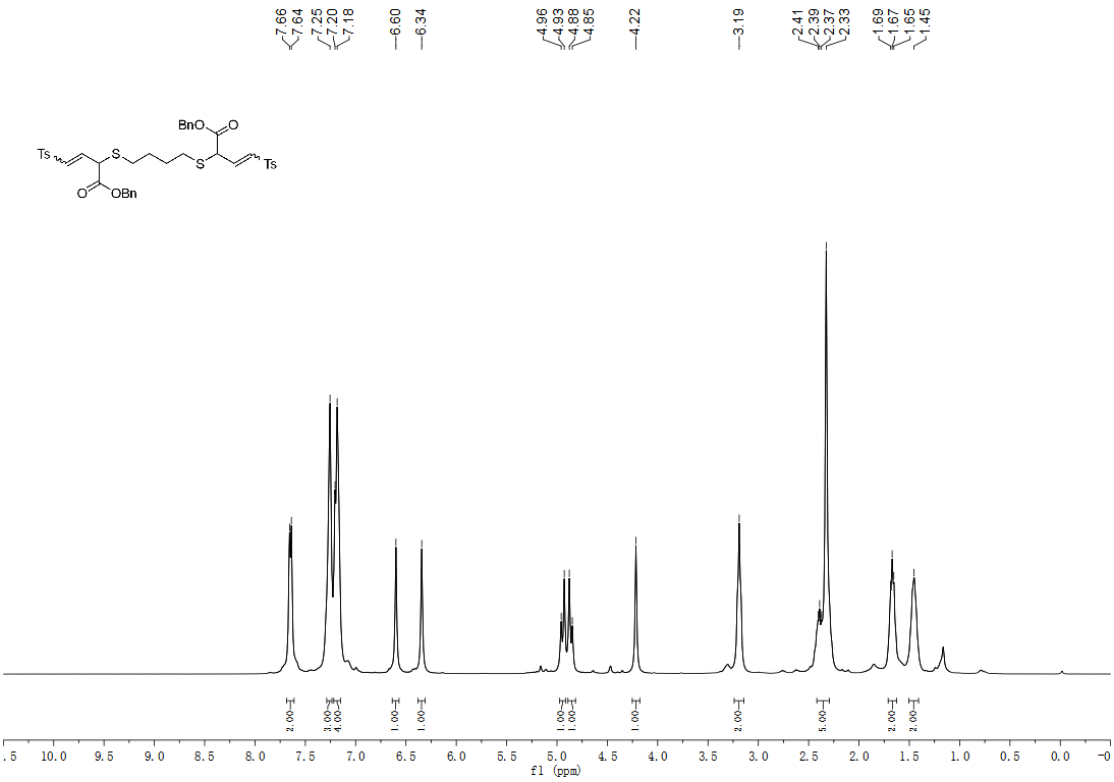
^{1}H NMR Spectrum of compound **6y** (**400** MHz, $CDCl_3$)



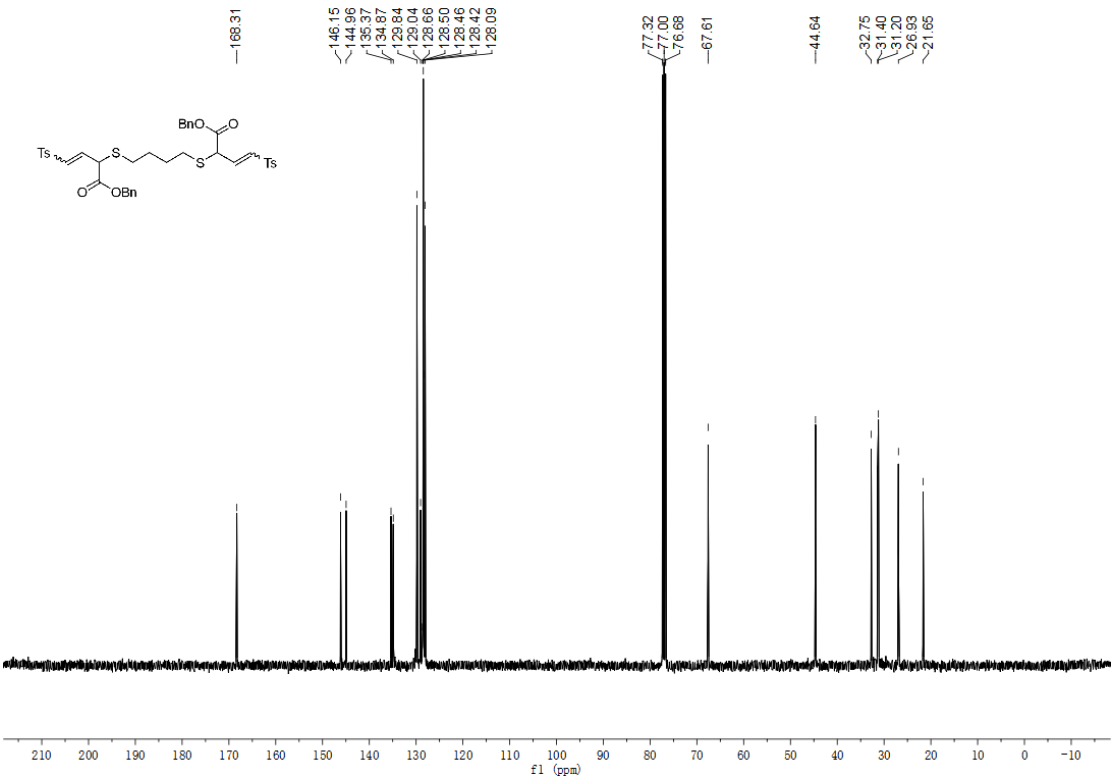
^{13}C NMR Spectrum of compound **6y** (**100** MHz, $CDCl_3$)



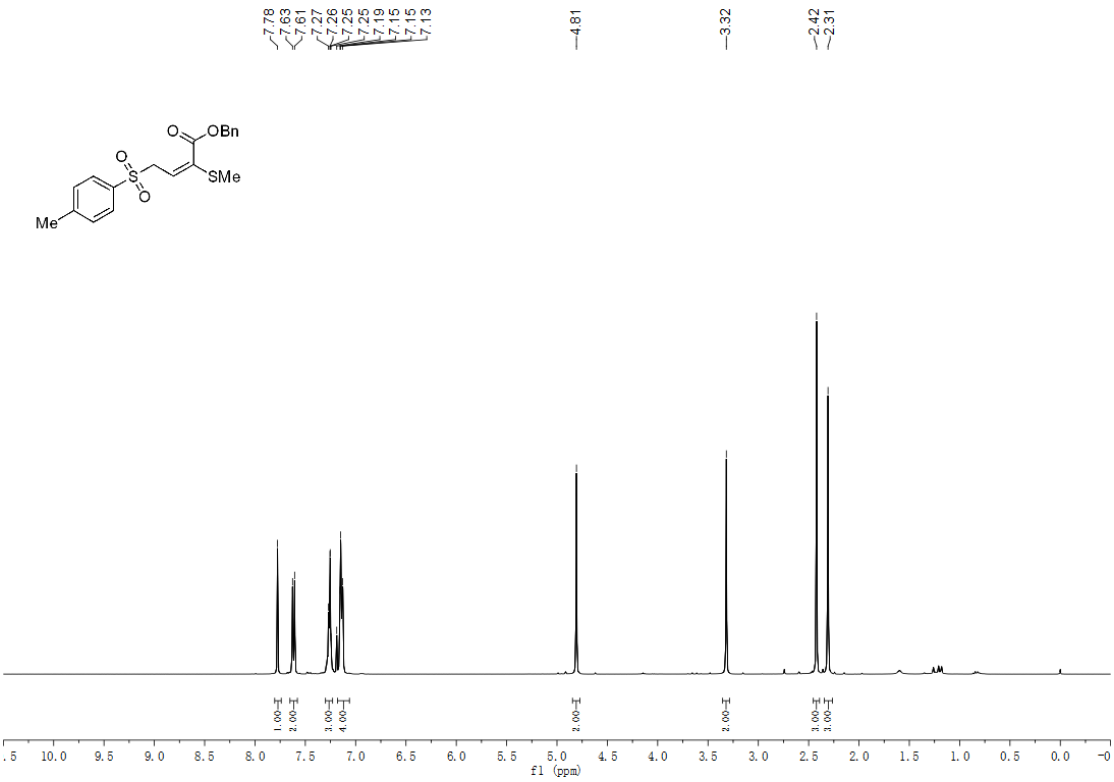
^{1}H NMR Spectrum of compound **6z (400** MHz, $CDCl_3$)



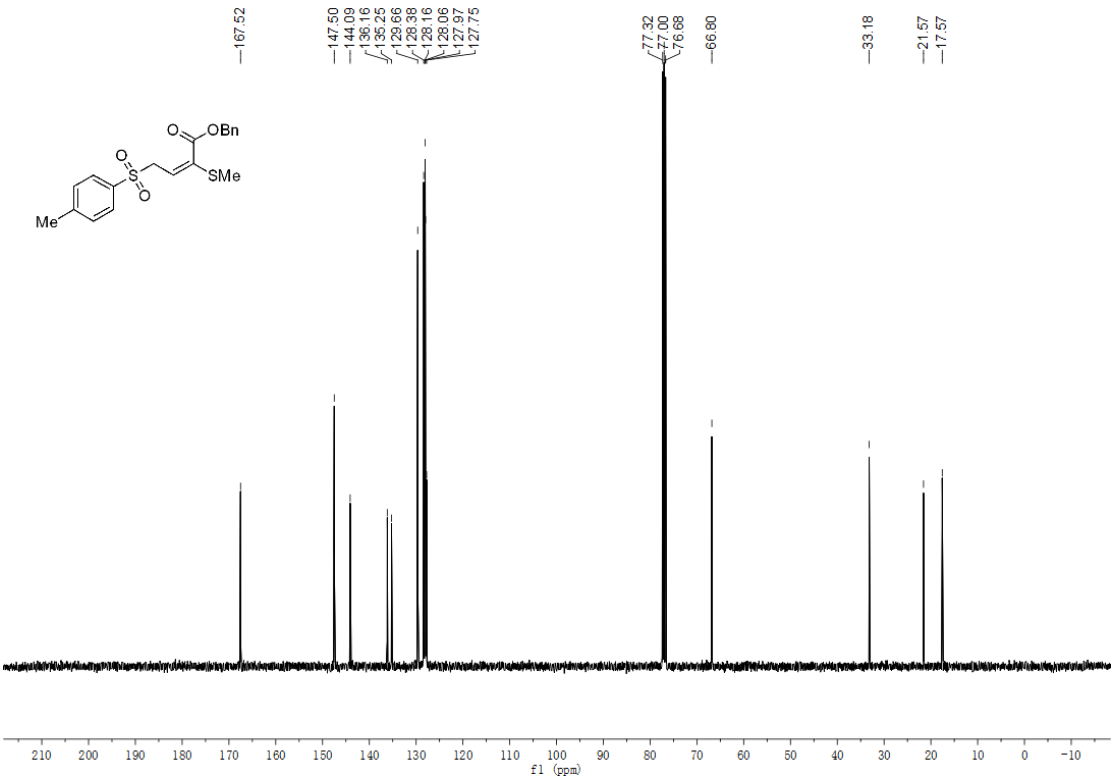
^{13}C NMR Spectrum of compound **6z (100** MHz, $CDCl_3$)



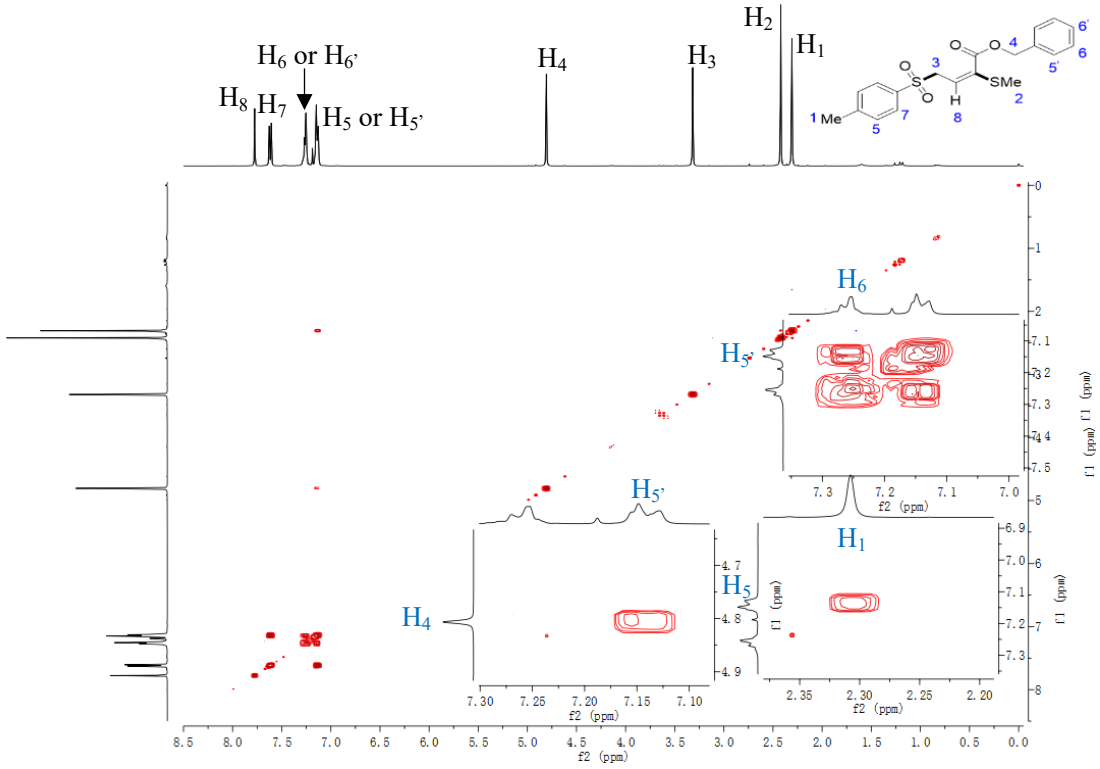
^{1}H NMR Spectrum of compound **7a (400** MHz, $CDCl_3$)



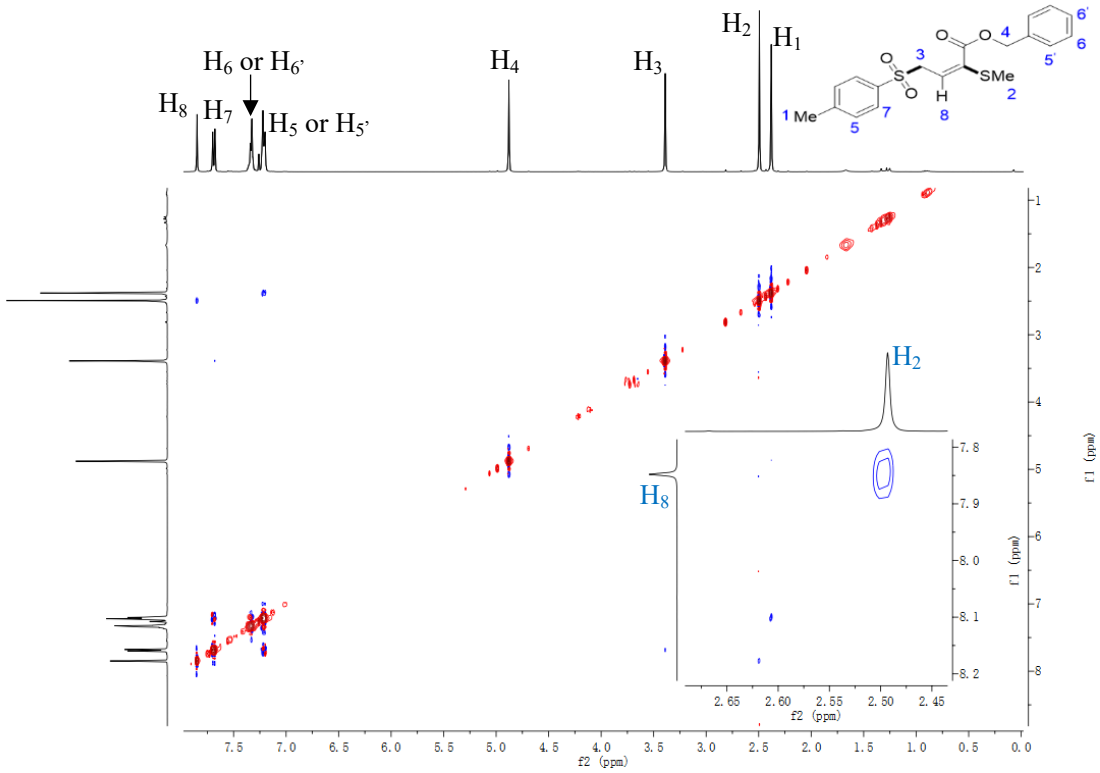
^{13}C NMR Spectrum of compound **7a (100** MHz, $CDCl_3$)



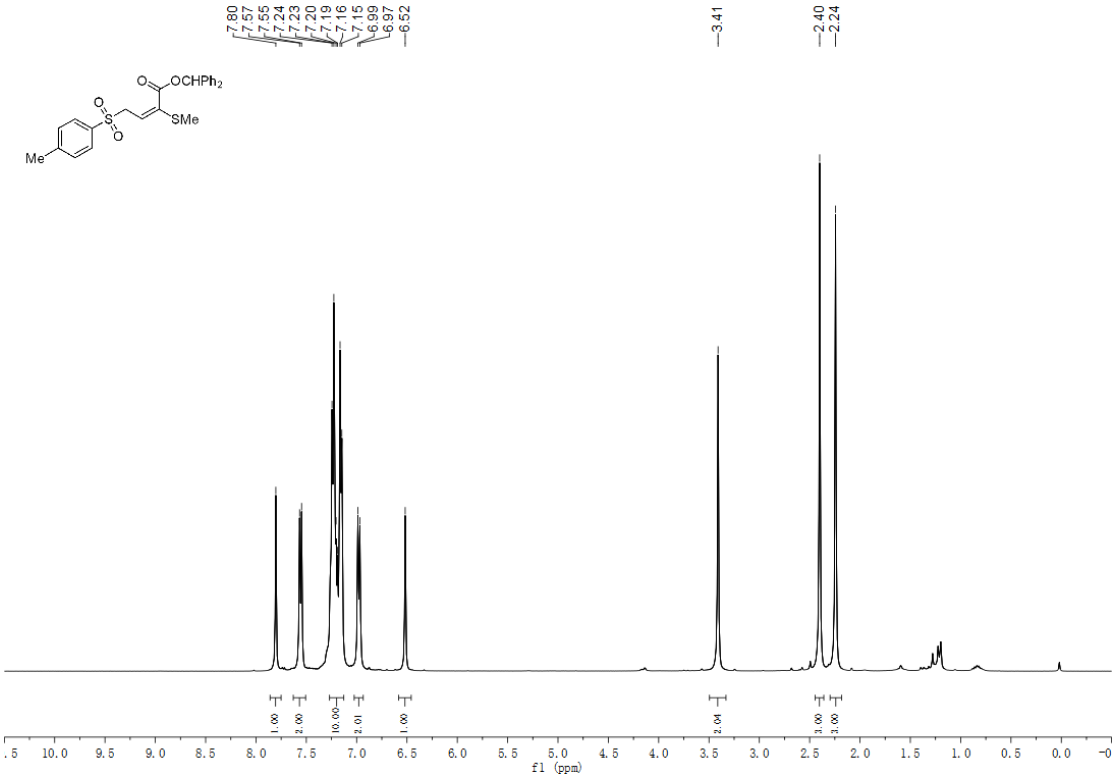
^{1}H-^{1}H Cosy Spectrum of compound **7a (100** MHz, $CDCl_3$)



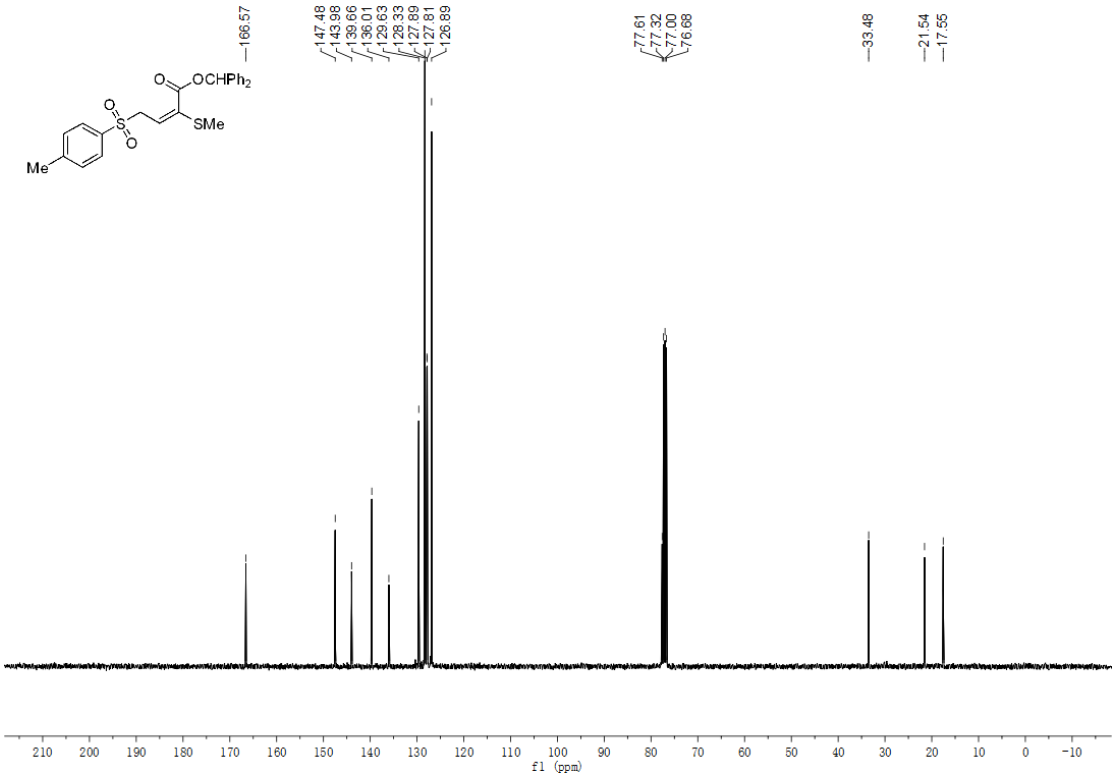
^{1}H-^{1}H NOE Spectrum of compound **7a (100** MHz, $CDCl_3$) (*E*-configuration of product **7a** was determined by the NOE spectroscopy)



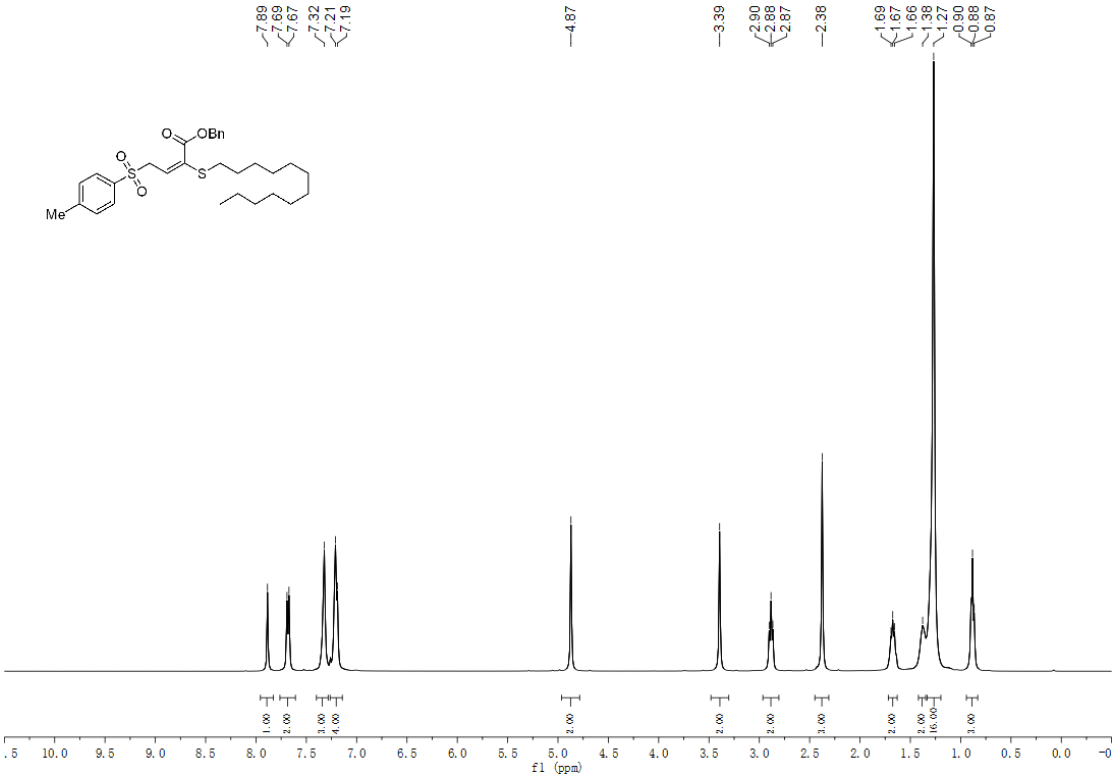
^{1}H NMR Spectrum of compound **7b (400** MHz, $CDCl_3$)



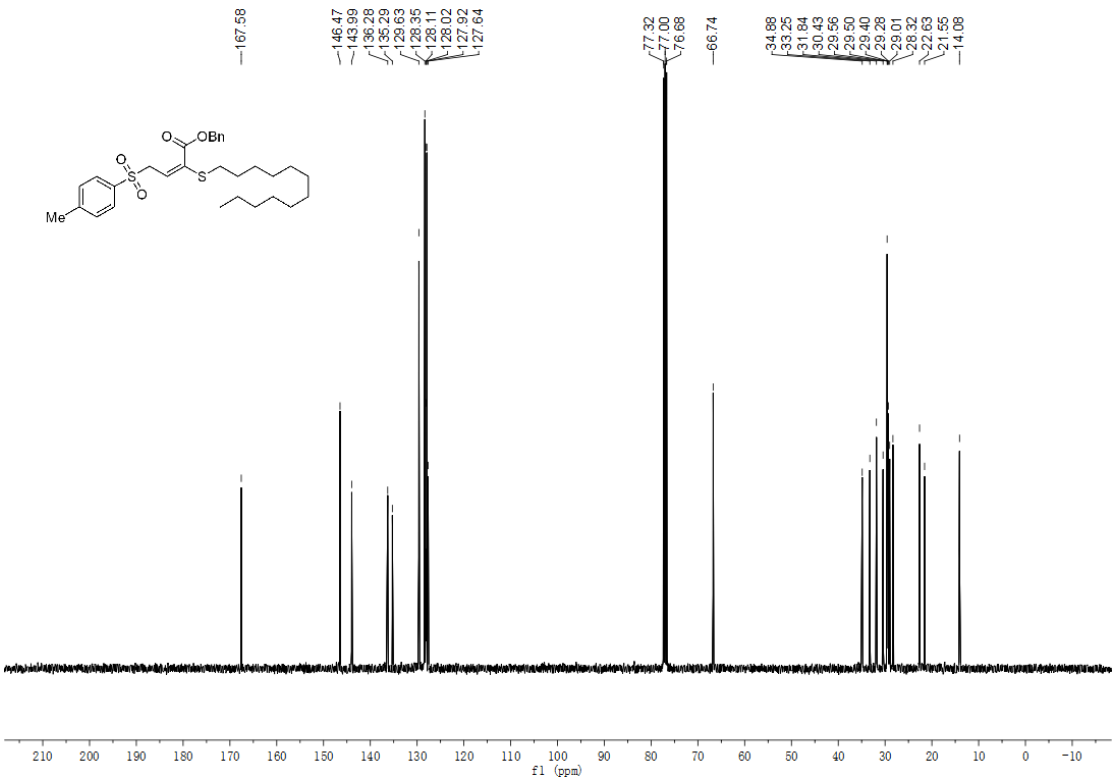
^{13}C NMR Spectrum of compound **7b (100** MHz, $CDCl_3$)



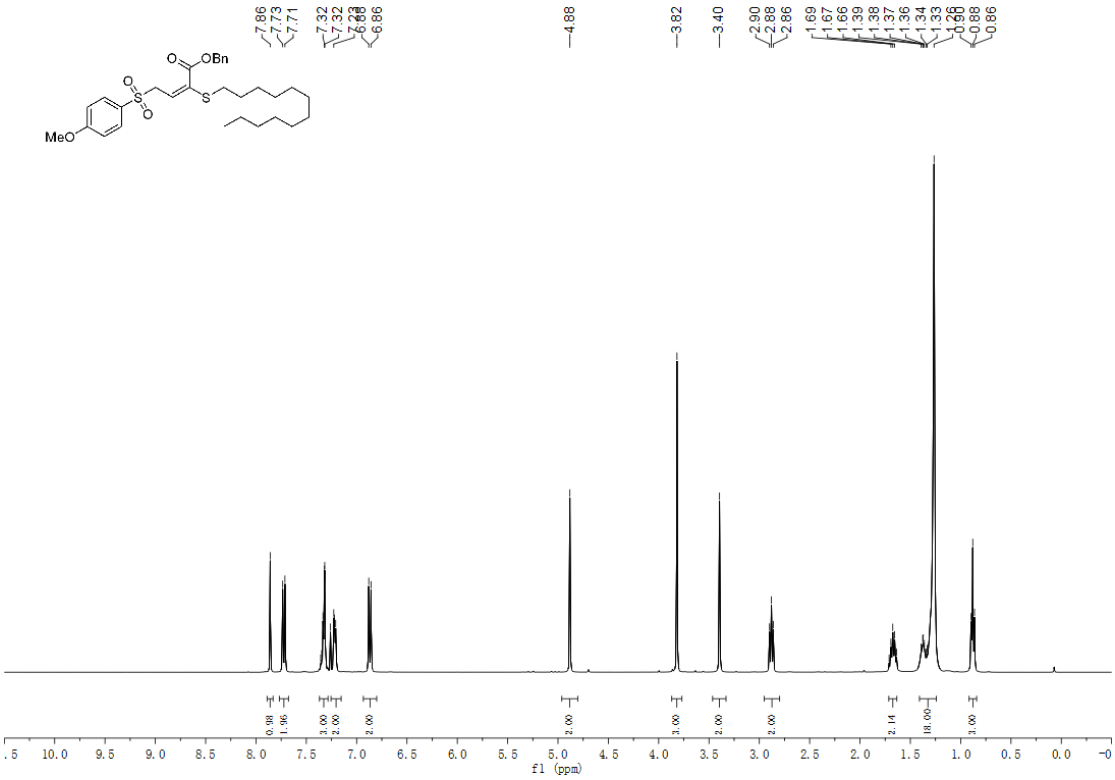
^{1}H NMR Spectrum of compound **7c (400** MHz, $CDCl_3$)



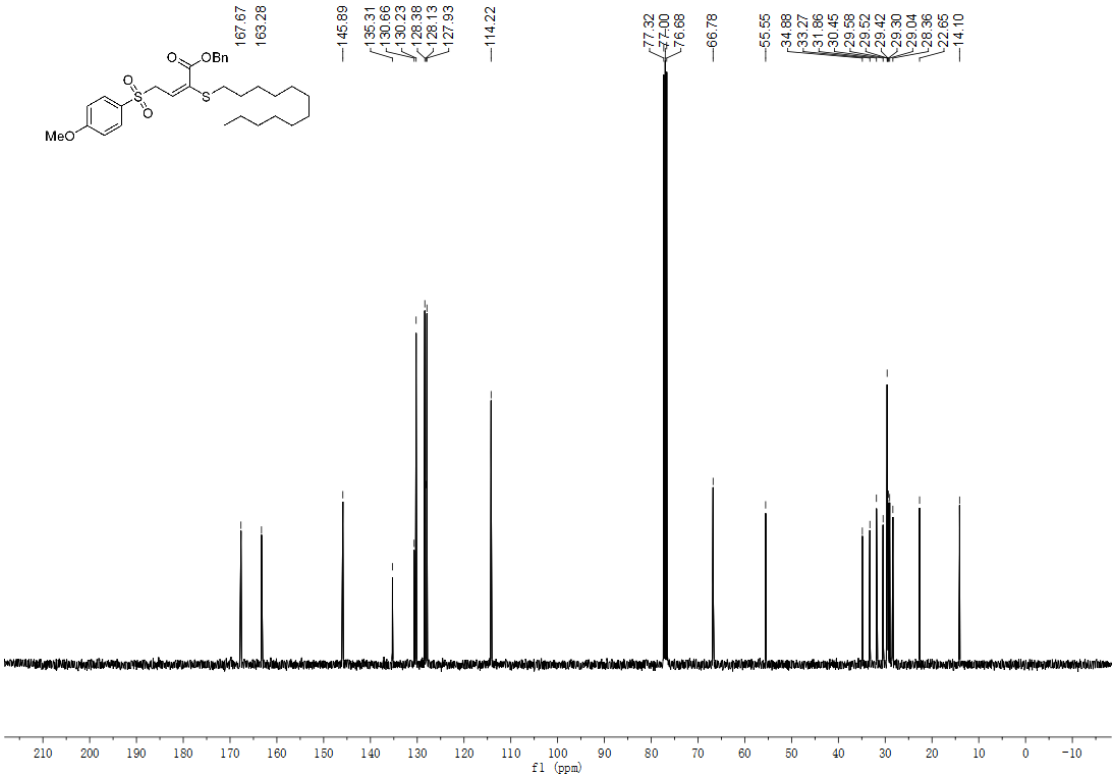
^{13}C NMR Spectrum of compound **7c (100** MHz, $CDCl_3$)



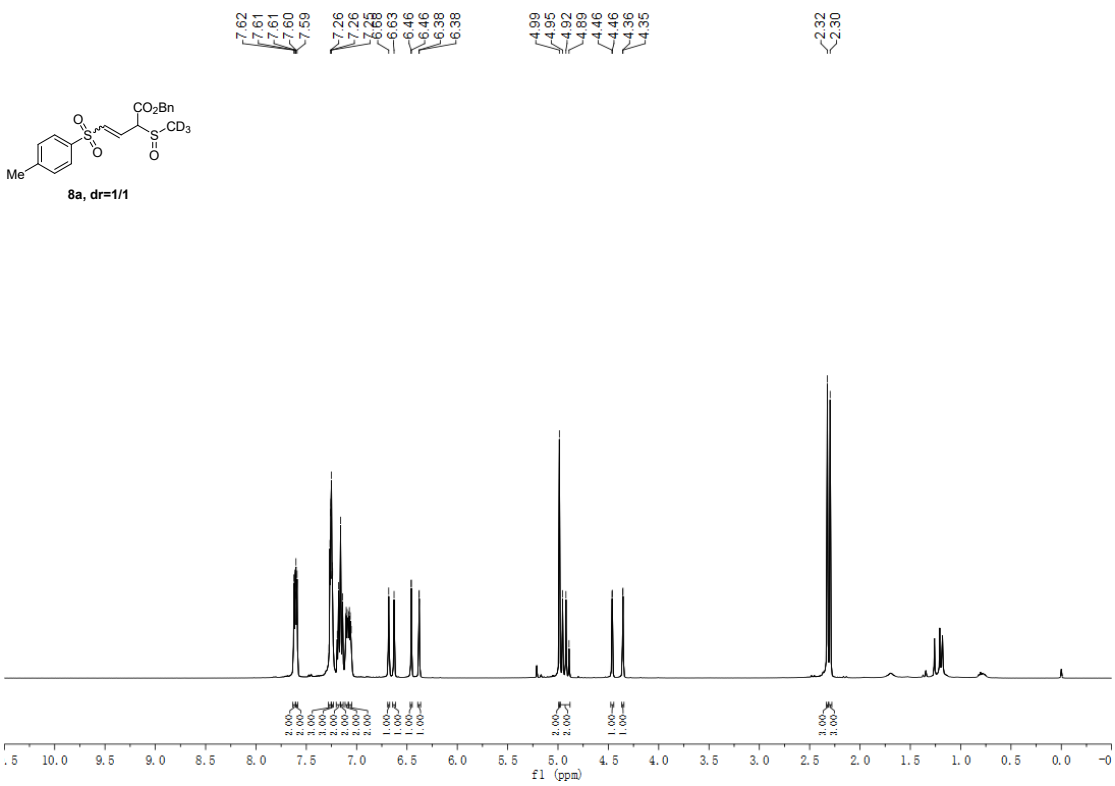
^{1}H NMR Spectrum of compound **7d (400** MHz, $CDCl_3$)



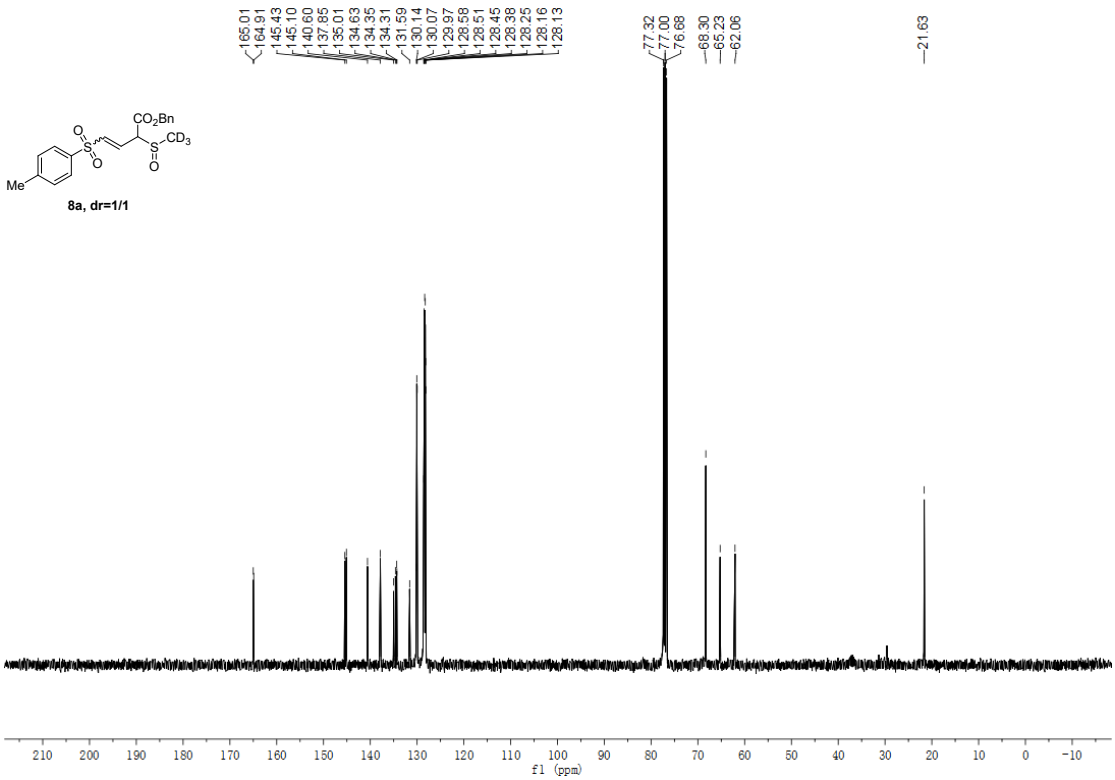
^{13}C NMR Spectrum of compound **7d (100** MHz, $CDCl_3$)



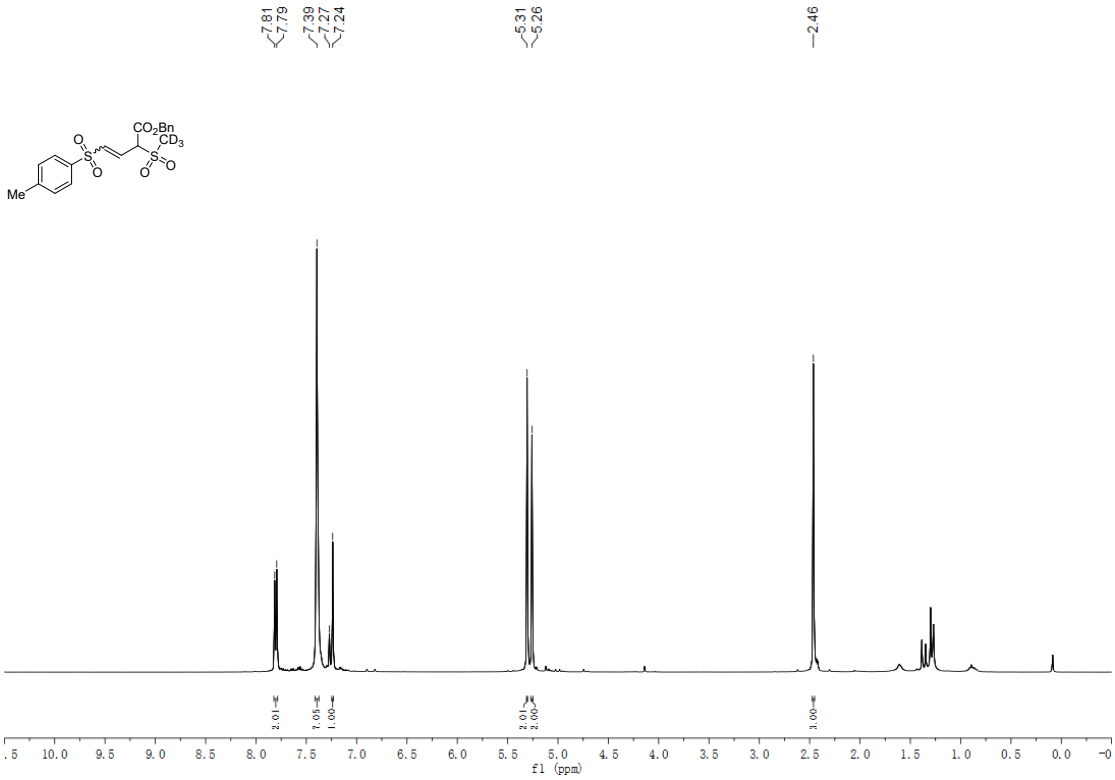
^{1}H NMR Spectrum of compound **8a (400** MHz, $CDCl_3$)



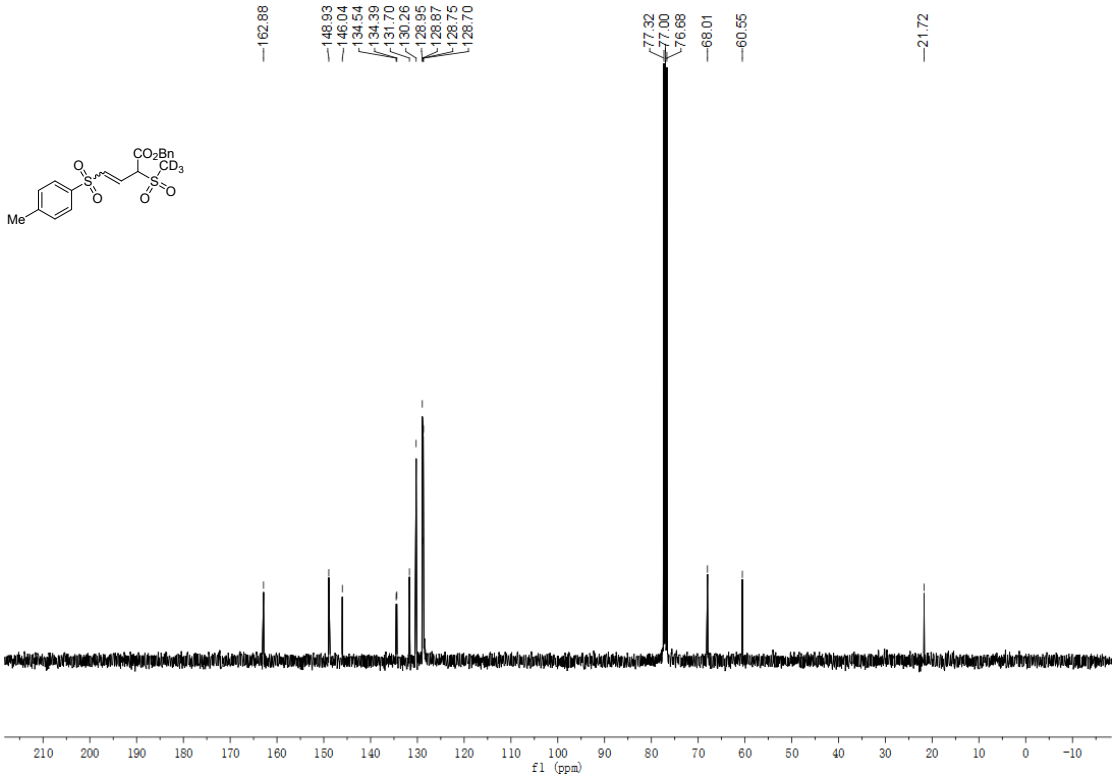
^{13}C NMR Spectrum of compound **8a (100** MHz, $CDCl_3$)



^{1}H NMR Spectrum of compound **8b (400** MHz, $CDCl_3$)



^{13}C NMR Spectrum of compound **8b (100** MHz, $CDCl_3$)



IX. References

(1) A. Raju, A. Rajitha, D. Ahuja, A. K. Sharma, B. Ramudu, R. Kapavarapu, K. V. L. Parsa and M. A. Pal, *Org. Biomol. Chem.,* 2014, **12**, 2514.

(2) S. Li, X.-X. Wu and S. Chen, *Org. Biomol. Chem.,* 2019, **17**, 789.

(3) X. Xiao, M. Feng and X. Jiang, *Chem. Commun.,* 2015, **51**, 4208.

(4) X. Xiao, M. Feng and X. Jiang, *Angew. Chem. Int. Ed.,* 2016, **55**, 14121.

(5) C.-M. Huang, J. Li, J.-J. Ai, X.-Y. Liu, W. Rao and S.-Y. Wang, *Org. Lett.,* 2020, **22**, 9128.

(6) X. Xiao, Y.-Q. Huang, H.-Y. Tian, J. Bai, F. Cheng, X. Wang, M.-L. Ke and F.-E. Chen, *Chem. Commun.,* 2022, **58**, 3015.

(7) V. Girijavallabhan, C. Alvarez and F. G. Njoroge, *J. Org. Chem.,* 2011, **76**, 6442.

(8) S. Yoshida, Y. Sugimura, Y. Hazama, Y. Nishiyama, T. Yano, S. Shimizu and T. Hosoya, *Chem. Commun.,* 2015, **51**, 16613.