Alkoxysulfonyl Radical Species: Acquisition and Transformation towards Sulfonate Esters through Electrochemistry

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Supporting Information

1. General method S2

2. Optimization of the reaction conditions S2

3. General Procedures S3

4. Hydrogen-deuterium exchange S4

5. Mechanistic Studies S5

6. Cyclic Voltammetry Studies S7

7. Characterization data.....S8

8. ^{1}H and ^{13}C NMR spectra **.....S30**

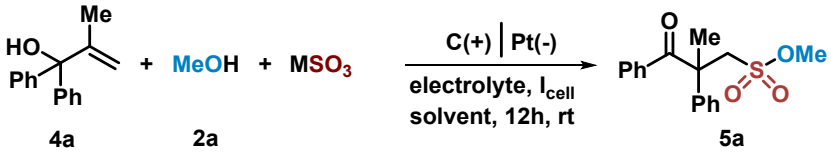
9. Crystallographic details of **3as** and **5m.....S95**

1. General method

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25-35 °C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H, and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values were quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument. The electrochemical reactions were performed on IKa ElectraSyn 2.0. Cyclic voltammograms were recorded on a CHI 760E potentiostat.

2. Optimization of the reaction conditions

Table S1. Initial studies for the electrochemical reaction of 2-methyl-1,1-diphenylprop-2-en-1-ol **4a**, inorganic sulfite, and Methanol **2a** [a]



4a **2a** **5a**

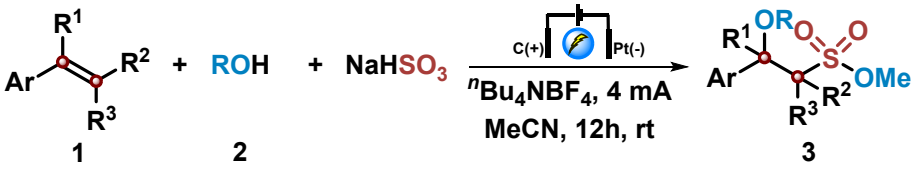
Entry	"SO_2" (equiv)	Solvent	electrolyte	I_{cell} (mA)	Yield (%)[b]
1	$NaHSO_3$ (4.0)	MeCN	$^{n}Bu_4NBF_4$	4	51
2	Na_2SO_3 (4.0)	MeCN	$^{n}Bu_4NBF_4$	4	10
3	$Na_2S_2O_5$ (4.0)	MeCN	$^{n}Bu_4NBF_4$	4	60
4	$Na_2S_2O_5$ (3.0)	MeCN	$^{n}Bu_4NBF_4$	4	63
5	$Na_2S_2O_5$ (3.0)	MeCN	$LiBF_4$	4	49
6	$Na_2S_2O_5$ (3.0)	MeCN	$^{n}Bu_4NClO_4$	4	66
7	$Na_2S_2O_5$ (3.0)	MeCN	$^{n}Bu_4NClO_4$	3	68
8	$Na_2S_2O_5$ (3.0)	EtOAc	$^{n}Bu_4NClO_4$	3	56
9	$Na_2S_2O_5$ (3.0)	THF	$^{n}Bu_4NClO_4$	3	81

10	$Na_2S_2O_5$ (3.0)	DMF	$^nBu_4NClO_4$	3	trace
11	$Na_2S_2O_5$ (3.0)	DCE	$^nBu_4NClO_4$	3	84
12	$Na_2S_2O_5$ (3.0)	DCM	$^nBu_4NClO_4$	3	90
13	$Na_2S_2O_5$ (2.0)	DCM	$^nBu_4NClO_4$	3	90
15[c]	$Na_2S_2O_5$ (2.0)	DCM	$^nBu_4NClO_4$	3	16

[a] Reaction conditions: **4a** (0.5 mmol), MeOH (2 mL), "SO2", solvent (8 mL), graphite anode, Pt cathode, undivided cell, constant current, room temperature.
[b] Isolated yield based on **4a**.
[c] MeOH (1 mL), MeCN (9 mL).

3. General Procedures

General Procedure I: Experimental procedures for the reaction of alkenes **1**, alcohols **2**, and $NaHSO_3$



To an ElectraSyn vial (10 mL) equipped with a magnetic stir bar, alkene **1** (0.5 mmol), $NaHSO_3$ (2.0 mmol, 208.0 mg), $^nBu_4NBF_4$ (0.5 mmol, 164.6 mg), alcohol **2** (2.0 mL) and MeCN (8.0 mL) were added under N_2 atmosphere. [Liquid compounds were added after the addition of alcohol and MeCN]. The ElectraSyn vial cap equipped with anode (graphite) and cathode (platinum plate) were inserted into the mixture. The reaction mixture was electrolyzed under a constant current of 4 mA for 12 hours. After electrolysis, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/EtOAc (v/v): 4/1) to give the corresponding product **3**.

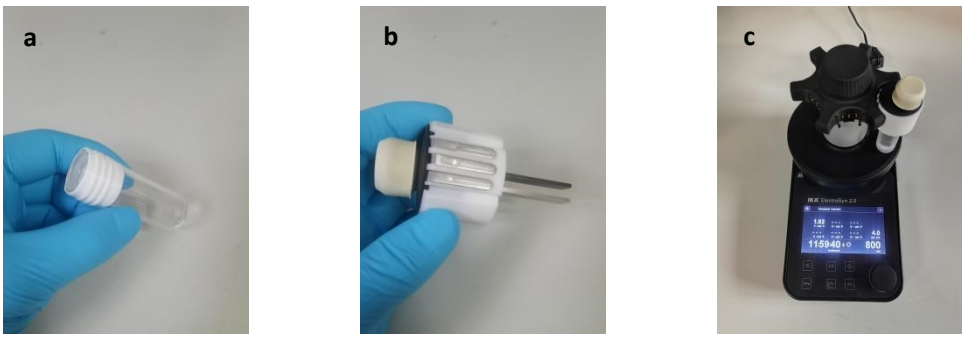
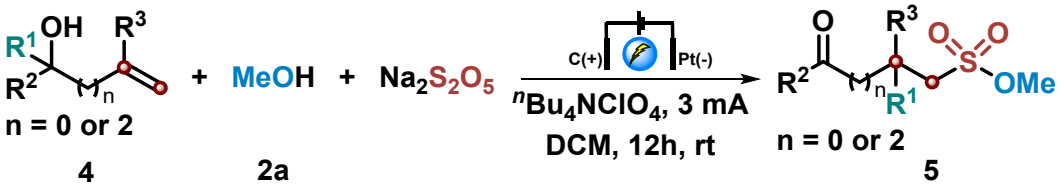


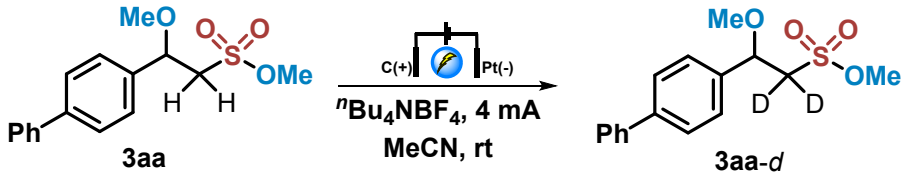
Figure S1. Reaction setup. (**a**) ElectraSyn 2.0 vial (10 mL). (**b**) ElectraSyn 2.0 cap equipped with Pt (down) and graphite (up). (**c**) ElectraSyn 2.0.

General Procedure II: Experimental procedures for the reaction of 2-methyl-1,1-diphenylprop-2-en-1-ol **4a**, Methanol **2a** and $Na_2S_2O_5$.



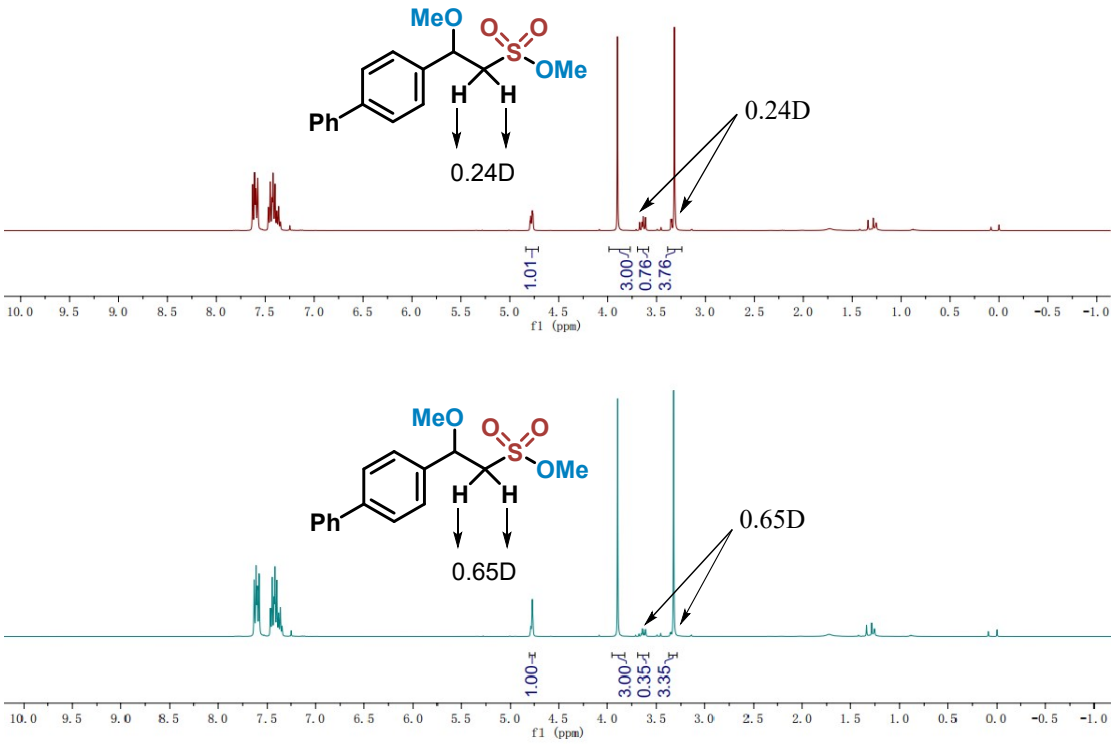
To an ElectraSyn vial (10 mL) equipped with a magnetic stir bar, tertiary alcohol **4** (0.5 mmol), $Na_2S_2O_5$ (1.0 mmol, 190.0 mg), $^nBu_4NClO_4$ (0.5 mmol, 171.0 mg), methanol **2a** (2.0 mL) and DCM (8.0 mL) were added under N_2 atmosphere. The ElectraSyn vial cap equipped with anode (graphite) and cathode (platinum plate) were inserted into the mixture. The reaction mixture was electrolyzed under a constant current of 3 mA for 12 hours. After electrolysis, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/EtOAc (v/v): 4/1) to give the corresponding product **5**.

4. Hydrogen-deuterium exchange of compound 3aa

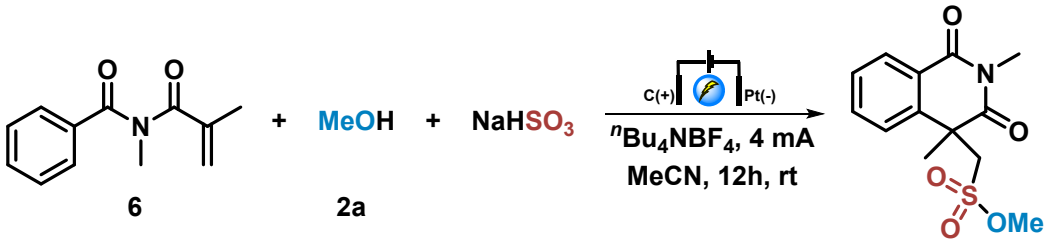


2 h, 89% yield, 24%D
4 h, 85% yield, 65%D

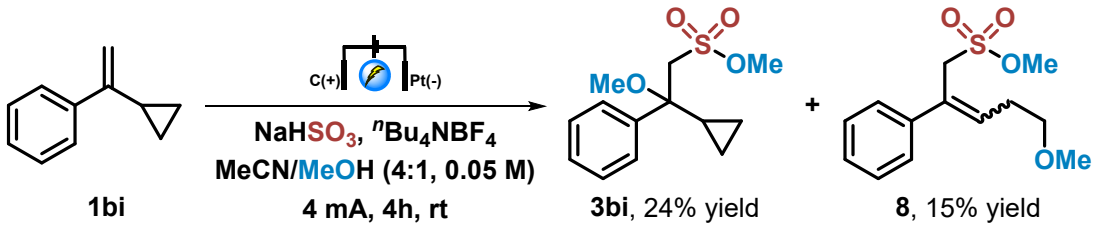
To an ElectraSyn vial (10 mL) equipped with a magnetic stir bar, **3aa** (61.3 mg, 0.2 mmol), $^nBu_4NBF_4$ (0.25 mmol, 82.3 mg), MeOD (1.0 mL) and MeCN (4.0 mL) were added under N_2 atmosphere. The ElectraSyn vial cap equipped with anode (graphite) and cathode (platinum plate) were inserted into the mixture. The reaction mixture was electrolyzed under a constant current of 4 mA. After electrolysis, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/EtOAc (v/v): 4/1) to give the corresponding product **3aa**-*d*.



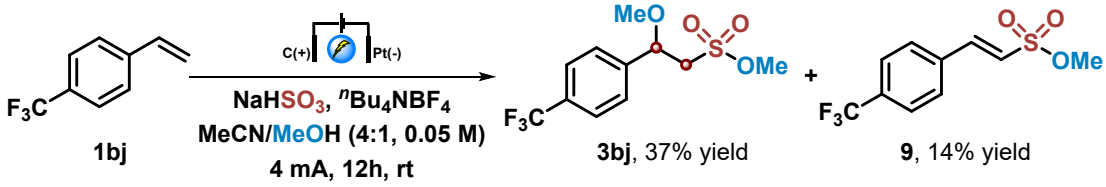
5. Mechanistic Studies



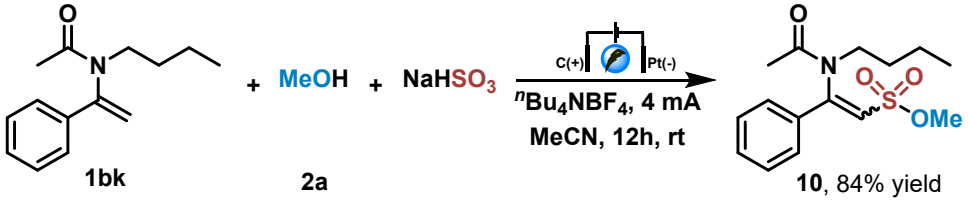
To an ElectraSyn vial (10 mL) equipped with a magnetic stir bar, *N*-methacryloyl-*N*-methylbenzamide **6** (0.5 mmol, 101.6 mg), $NaHSO_3$ (2.0 mmol, 208.0 mg), $^nBu_4NBF_4$ (0.5 mmol, 164.6 mg), MeOH (2.0 mL) and MeCN (8.0 mL) were added under N_2 atmosphere. The ElectraSyn vial cap equipped with anode (graphite) and cathode (platinum plate) were inserted into the mixture. The reaction mixture was electrolyzed under a constant current of 4 mA for 12 hours. After electrolysis, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/EtOAc (v/v): 3/1) to give the corresponding product **7** (25.6 mg, 18% yield).



To an ElectraSyn vial (10 mL) equipped with a magnetic stir bar, *N*-methacryloyl-*N*-methylbenzamide **8** (0.5 mmol, 72.1 mg), $NaHSO_3$ (2.0 mmol, 208.0 mg), $^nBu_4NBF_4$ (0.5 mmol, 164.6 mg), MeOH (2.0 mL) and MeCN (8.0 mL) were added under N_2 atmosphere. The ElectraSyn vial cap equipped with anode (graphite) and cathode (platinum plate) were inserted into the mixture. The reaction mixture was electrolyzed under a constant current of 4 mA for 12 hours. After electrolysis, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/EtOAc (v/v): 3/1) to give the corresponding products **3bj** (32.1 mg, 24% yield) and **9** (20.5 mg, 15% yield).



To an ElectraSyn vial (10 mL) equipped with a magnetic stir bar, 4-(Trifluoromethyl)styrene **1bj** (0.5 mmol, 101.6 mg), $NaHSO_3$ (2.0 mmol, 208.0 mg), $^nBu_4NBF_4$ (0.5 mmol, 164.6 mg), MeOH (2.0 mL) and MeCN (8.0 mL) were added under N_2 atmosphere. The ElectraSyn vial cap equipped with anode (graphite) and cathode (platinum plate) were inserted into the mixture. The reaction mixture was electrolyzed under a constant current of 4 mA for 12 hours. After electrolysis, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/EtOAc (v/v): 4/1) to give the corresponding product **3bj** (55.1 mg, 37% yield) and **9** (18.6 mg, 14% yield).



To an ElectraSyn vial (10 mL) equipped with a magnetic stir bar, N-butyl-N-(1-

phenylvinyl)acetamide **1bk** (0.5 mmol, 101.6 mg), $NaHSO_3$ (2.0 mmol, 208.0 mg), $^nBu_4NBF_4$ (0.5 mmol, 164.6 mg), MeOH (2.0 mL) and MeCN (8.0 mL) were added under N_2 atmosphere. The ElectraSyn vial cap equipped with anode (graphite) and cathode (platinum plate) were inserted into the mixture. The reaction mixture was electrolyzed under a constant current of 4 mA for 12 hours. After electrolysis, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/EtOAc (v/v): 4/1) to give the corresponding product **10** (130.7 mg, 84% yield).

6. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded at rt using a glassy carbon disk working electrode (diameter, 1.0 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate is 100 mV/s.

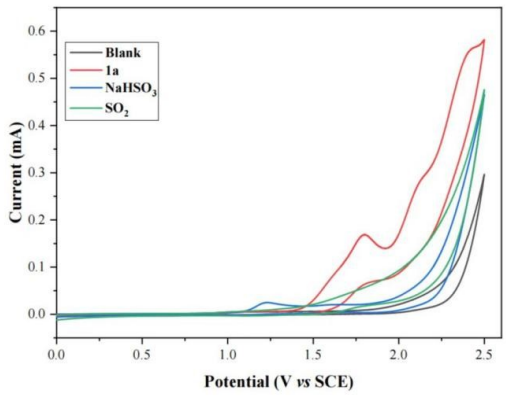


Figure S2. Cyclic voltammograms of compound **1a**, $NaHSO_3$ and SO_2 in MeCN/MeOH (v/v: 4/1) with 0.05 M $^nBu_4NBF_4$. Black, blank; Red, compound **1a** (10.0 mM), $E_{p/2}$ = 1.80 V; Blue, $NaHSO_3$ (2.5 mM), $E_{p/2}$ = 1.23 V; Green, SO_2.

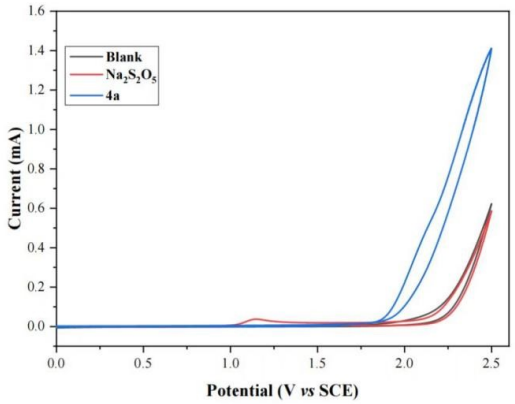


Figure S3. Cyclic voltammograms of compound **4a**, $Na_2S_2O_5$ in CH_2Cl_2/MeOH (v/v: 4/1) with 0.05 M $^nBu_4NClO_4$; Black, blank; Red, $Na_2S_2O_5$ (1.0 mM), $E_{p/2}$ = 1.15 V; Blue, compound **4a** (10.0 mM).

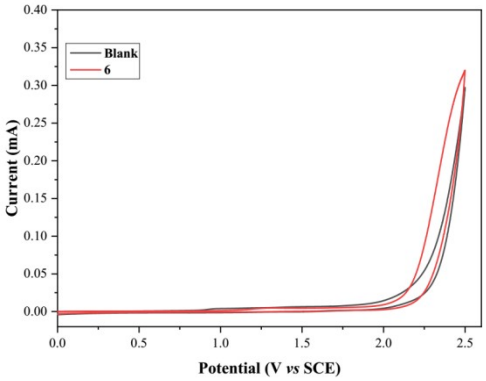
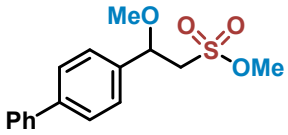


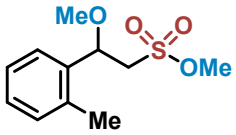
Figure S4. Cyclic voltammograms of compound **6** in MeCN/MeOH (v/v: 4/1) with 0.05 M $^nBu_4NBF_4$. Black, blank; Red, compound **6**.

7. Characterization data



3aa: Methyl 2-([1,1'-biphenyl]-4-yl)-2-methoxyethane-1-sulfonate

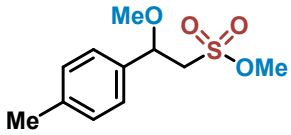
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.55 (m, 14H), 7.51-7.33 (m, 5H), 4.78 (dd, *J* = 9.3, 3.0 Hz, 1H), 3.91 (s, 3H), 3.65 (dd, *J* = 14.9, 9.3 Hz, 1H), 3.36 (dd, *J* = 14.9, 3.1 Hz, 1H), 3.32(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.4, 137.5, 128.9, 127.8, 127.7, 127.1, 127.0, 78.1, 57.2, 57.1, 56.2; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{18}O_4NaS^+$ 329.0818, found 329.0827.



3ab: Methyl 2-methoxy-2-(*o*-tolyl)ethane-1-sulfonate

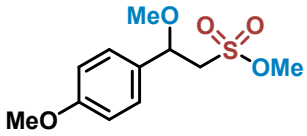
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 1H), 7.28-7.22 (m, 2H), 7.21-7.15 (m, 1H), 4.99 (dd, *J* = 9.2, 2.6 Hz, 1H), 3.91 (s, 3H), 3.54 (dd, *J* = 15.0, 9.2 Hz, 1H), 3.28 (s, 3H), 3.23 (dd, *J* = 15.0, 2.6 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

136.6, 135.5, 131.0, 128.4, 126.7, 125.7, 75.1, 56.9, 56.2, 18.9; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{11}H_{16}O_4NaS^+$ 267.0662, found 267.0673.



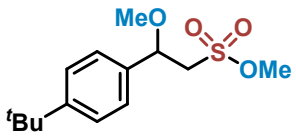
3ac: Methyl 2-methoxy-2-(*p*-tolyl)ethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.16 (m, 4H), 4.69 (dd, *J* = 9.2, 3.2 Hz, 1H), 3.88 (s, 3H), 3.60 (dd, *J* = 14.8, 9.2 Hz, 1H), 3.28(dd, *J* = 14.8, 3.2 Hz, 1H), 3.26(s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 135.6, 129.7, 126.6, 78.2, 57.3, 56.9, 56.1, 21.2; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{11}H_{16}O_4NaS^+$ 267.0662, found 267.0673.



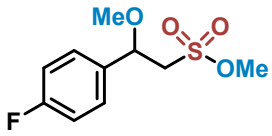
3ad: Methyl 2-methoxy-2-(4-methoxyphenyl)ethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.7 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 4.67 (dd, *J* = 9.1, 3.3 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.61 (dd, *J* = 14.8, 9.1 Hz, 1H), 3.28 (dd, *J* = 14.8, 3.4 Hz, 1H), 3.25(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 130.5, 127.9, 114.3, 77.9, 57.2, 56.7, 56.1, 55.4; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{11}H_{16}O_5NaS^+$ 283.0611, found 283.0619.



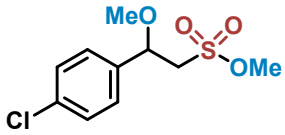
3ae: Methyl 2-(4-(*tert*-butyl)phenyl)-2-methoxyethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.37 (m, 2H), 7.29-7.23 (m, 2H), 4.71 (dd, *J* = 9.4, 2.9 Hz, 1H), 3.88 (s, 3H), 3.60 (dd, *J* = 14.9, 9.4 Hz, 1H), 3.29 (dd, *J* = 14.9, 2.9 Hz, 1H), 3.28 (s, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 135.5, 126.3, 125.9, 78.1, 57.2, 57.0, 56.1, 34.7, 31.3; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{14}H_{22}O_4NaS^+$ 309.1131, found 309.1140.



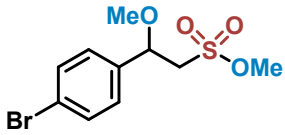
3af: Methyl 2-(4-fluorophenyl)-2-methoxyethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 2H), 7.13-7.04 (m, 2H), 4.71 (dd, *J* = 9.0, 3.4 Hz, 1H), 3.88 (s, 3H), 3.59 (dd, *J* = 14.8, 9.0 Hz, 1H), 3.27(dd, *J* = 14.8, 3.4 Hz, 1H), 3.27(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 247.6 Hz), 134.4 (d, *J* = 3.2 Hz), 128.3 (d, *J* = 8.3 Hz), 116.0 (d, *J* = 21.7 Hz), 77.8, 57.1, 57.0, 56.1; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{10}H_{13}O_4FNaS^+$ 271.0411, found 271.0422.



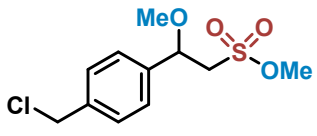
3ag: Methyl 2-(4-chlorophenyl)-2-methoxyethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.34 (m, 2H), 7.31-7.27 (m, 2H), 4.70 (dd, *J* = 8.9, 3.4 Hz, 1H), 3.89 (s, 3H), 3.58 (dd, *J* = 14.8, 9.0 Hz, 1H), 3.28(s, 3H), 3.26(dd, *J* = 14.8, 3.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 134.7, 129.3, 128.0, 77.8, 57.1, 57.0, 56.1; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{10}H_{13}O_4ClNaS^+$ 287.0115, found 287.0127.



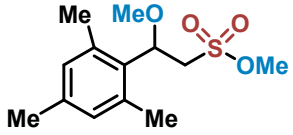
3ah: Methyl 2-(4-bromophenyl)-2-methoxyethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.50 (m, 2H), 7.26-7.20 (m, 2H), 4.69 (dd, *J* = 9.0, 3.4 Hz, 1H), 3.89 (s, 3H), 3.58 (dd, *J* = 14.8, 9.0 Hz, 1H); 3.28(s, 3H), 3.26(dd, *J* = 14.8, 3.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 132.2, 128.3, 122.8, 77.9, 57.1, 57.0, 56.1; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{10}H_{13}O_4BrNaS^+$ 330.9610, found 330.9615.



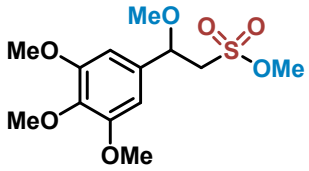
3ai: Methyl 2-(4-(chloromethyl)phenyl)-2-methoxyethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 4.74 (dd, J = 9.1, 3.2 Hz, 1H), 4.59 (s, 2H), 3.89 (s, 3H), 3.59 (dd, J = 14.8, 9.1 Hz, 1H), 3.29(s, 1H), 3.28(dd, J = 14.8, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.2, 129.3, 127.0, 78.1, 57.1, 56.1, 45.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{11}H_{15}O_4NaSCl^+$ 301.0272, found 3301.0277.



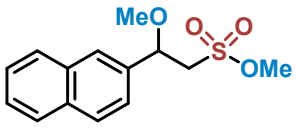
3aj: Methyl 2-mesityl-2-methoxyethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 2H), 5.23 (dd, J = 8.9, 3.0 Hz, 1H), 3.89 (s, 3H), 3.84 (dd, J = 15.0, 8.9 Hz, 1H), 3.28 (dd, J = 15.0, 3.0 Hz, 1H), 3.23 (s, 3H), 2.39 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 136.8, 130.8, 130.4 (m), 74.6, 56.3, 56.1, 54.6, 20.8, 20.3 (m); HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{13}H_{20}O_4NaS^+$ 295.0975, found 295.0985.



3ak: Methyl 2-methoxy-2-(3,4,5-trimethoxyphenyl)ethane-1-sulfonate

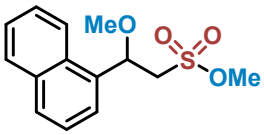
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 2H), 4.67 (dd, J = 9.5, 2.7 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 6H), 3.85 (s, 3H), 3.60 (dd, J = 14.9, 9.5 Hz, 1H), 3.32 (s, 2H), 3.31 (dd, J = 14.9, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 137.9, 134.2, 103.0, 78.4, 60.7, 57.1, 57.0, 56.1; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{13}H_{20}O_7NaS^+$ 343.0822, found 343.0832.



3al: Methyl 2-methoxy-2-(naphthalen-2-yl)ethane-1-sulfonate

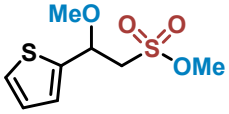
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.73 (m, 4H), 7.60-7.47 (m, 2H), 7.44 (dd, J = 8.5, 1.7 Hz, 1H), 4.89 (dd, J = 9.1, 3.1 Hz, 1H), 3.88 (s, 3H), 3.70 (dd, J = 14.9, 9.2 Hz, 1H), 3.37 (dd, J = 14.9, 3.2 Hz, 1H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

135.8, 133.5, 133.2, 129.1, 128.0, 127.8, 126.6, 126.6, 126.2, 123.5, 78.5, 57.0, 56.1; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{14}H_{16}O_4NaS^+$ 303.0662, found 303.0673.



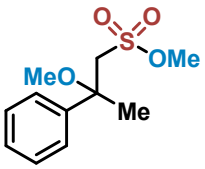
3am: Methyl 2-methoxy-2-(naphthalen-1-yl)ethane-1-sulfonate

^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.67-7.43 (m, 4H), 5.49 (dd, J = 9.3, 2.0 Hz, 1H), 3.93 (s, 3H), 3.69 (dd, J = 15.1, 9.3 Hz, 1H), 3.45 (dd, J = 15.1, 2.3 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 133.8, 130.3, 129.2, 126.9, 126.1, 125.5, 124.2, 122.4, 76.3, 57.4, 56.4, 56.3; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{14}H_{16}O_4NaS^+$ 303.0662, found 303.0673.



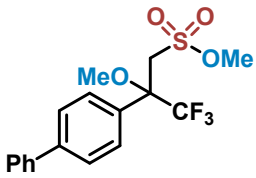
3an: Methyl 2-methoxy-2-(thiophen-2-yl)ethane-1-sulfonate

^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 5.0, 0.8 Hz, 1H), 7.07 (dd, J = 3.5, 0.7 Hz, 1H), 7.01 (dd, J = 5.0, 3.5 Hz, 1H), 5.00 (dd, J = 9.0, 3.5 Hz, 1H), 3.89 (s, 3H), 3.71 (dd, J = 14.8, 9.0 Hz, 1H), 3.42 (dd, J = 14.8, 3.5 Hz, 1H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 126.9, 126.5, 126.3, 74.1, 57.2, 56.9, 56.3; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_8H_{12}O_4NaS_2^+$ 259.0069, found 259.0079.



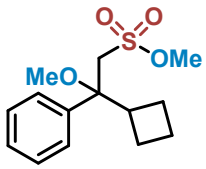
3ao: Methyl 2-methoxy-2-phenylpropane-1-sulfonate

^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 4H), 7.35-7.29 (m, 1H), 3.73 (s, 3H), 3.59 (d, J = 14.7 Hz, 1H), 3.43 (d, J = 14.7 Hz, 1H), 3.11 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 128.6, 128.1, 126.2, 76.9, 61.5, 55.8, 50.4, 21.0; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{11}H_{16}O_4NaS^+$ 267.0662, found 267.0672.



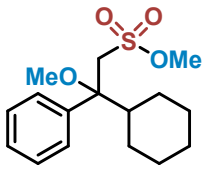
3ap: Methyl 2-((1,1'-biphenyl)-4-yl)-3,3,3-trifluoro-2-methoxypropane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.56 (m, 6H), 7.49-7.40 (m, 2H), 7.39-7.32 (m, 1H), 4.06 (d, J = 15.4 Hz, 1H), 3.90 (d, J = 15.4 Hz, 1H), 3.70 (s, 3H), 3.65-3.59 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 140.0, 131.9, 128.9, 127.8, 127.68, 127.67, 127.2, 127.1, 124.3 (q, J = 291.4 Hz), 80.0 (q, J = 27.4 Hz), 56.1, 54.1 (d, J = 1.8 Hz), 52.4; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{17}H_{17}O_4F_3NaS^+$ 397.0692, found 397.0696.



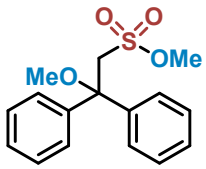
3aq: Methyl 2-cyclobutyl-2-methoxy-2-phenylethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.37 (m, 2H), 7.36-7.29 (m, 3H), 3.78(s, 3H), 3.73 (dd, J = 29.1, 14.9 Hz, 2H), 3.37-3.20 (m, 4H), 2.02-1.88 (m, 2H), 1.88-1.68 (m, 3H), 1.56-1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 128.1, 127.7, 127.2, 80.9, 55.4, 53.9, 51.9, 42.5, 24.2, 23.7, 17.3; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{14}H_{20}O_4NaS^+$ 307.0975, found 307.0983.



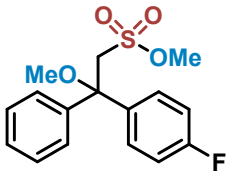
3ar: Methyl 2-cyclohexyl-2-methoxy-2-phenylethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.21 (m, 5H), 4.05 (d, J = 15.1 Hz, 1H), 3.83(d, J = 15.1 Hz, 1H), 3.82(s, 3H), 3.34 (s, 3H), 2.28-2.18 (m, 1H), 2.08-1.94 (m, 1H), 1.79-1.61 (m, 3H), 1.60-1.49 (m, 1H), 1.38-1.08 (m, 2H), 0.92-0.77 (m, 1H), 0.76-0.62 (m, 1H), 0.54-0.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 127.6, 127.4, 127.1, 82.5, 55.4, 51.9, 51.0, 44.7, 28.6, 26.5, 26.4, 26.09, 26.08; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{16}H_{24}O_4NaS^+$ 335.1288, found 335.1293.



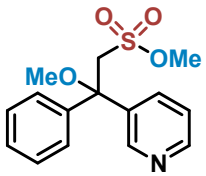
3as: Methyl 2-methoxy-2,2-diphenylethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 8H), 7.28-7.22 (m, 2H), 4.26 (s, 2H), 3.51 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 128.3, 127.6, 126.7, 80.4, 55.5, 55.4, 51.5; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{18}O_4NaS^+$ 329.0818, found 329.0824.



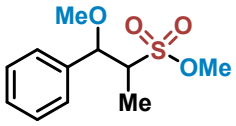
3at: Methyl 2-(4-fluorophenyl)-2-methoxy-2-phenylethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 7H), 7.03-6.95 (m, 2H), 4.26 (d, J = 14.8 Hz, 1H), 4.20 (d, J = 14.8 Hz, 1H), 3.57 (s, 3H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, J = 247.0 Hz), 142.5, 138.8 (d, J = 3.3 Hz), 128.5 (d, J = 8.3 Hz), 128.4, 127.9, 126.6, 115.1 (d, J = 21.5 Hz), 80.1, 55.4, 55.2, 51.4; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{17}O_4FNaS^+$ 347.0724, found 347.0732.



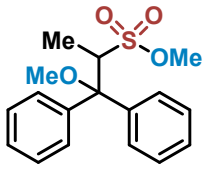
3au: Methyl 2-methoxy-2-phenyl-2-(pyridin-3-yl)ethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54-8.30 (m, 1H), 7.71-7.54 (m, 2H), 7.40-7.35 (m, 2H), 7.34-7.27 (m, 2H), 7.25-7.19 (m, 1H), 7.15-7.10 (m, 1H), 4.83 (d, J = 14.9 Hz, 1H), 4.38 (d, J = 14.9 Hz, 1H), 3.62 (s, 3H), 3.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 148.1, 141.8, 136.9, 128.3, 127.6, 126.1, 122.3, 121.0, 81.8, 55.6, 53.5, 51.8; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{17}NO_4NaS^+$ 330.0770, found 330.0776.



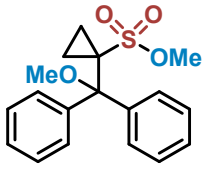
3av: Methyl 1-methoxy-1-phenylpropane-2-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.37 (m, 2H), 7.36-7.28 (m, 3H), 4.94 (d, J = 2.5 Hz, 1H), 3.91 (s, 3H), 3.42-3.22 (m, 4H), 1.35 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 128.8, 128.3, 126.6, 80.1, 63.3, 57.6, 55.9, 8.2; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{11}H_{16}O_4NaS^+$ 267.0662, found 267.0672.



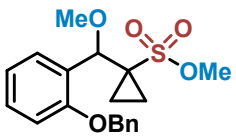
3aw: Methyl 1-methoxy-1,1-diphenylpropane-2-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.45 (m, 2H), 7.45-7.31 (m, 8H), 4.53 (q, J = 7.0 Hz, 1H), 3.71 (s, 3H), 2.91 (s, 3H), 1.50 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 137.7, 129.5, 129.3, 128.2, 128.0, 127.8, 127.4, 84.7, 63.5, 54.8, 52.0, 13.2; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{20}O_4NaS^+$ 343.0975, found 343.0981.



3ax: Methyl 1-(methoxydiphenylmethyl)cyclopropane-1-sulfonate

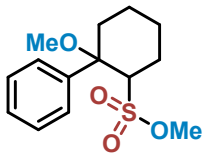
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 4H), 7.41-7.31 (m, 6H), 3.19 (s, 3H), 2.82 (s, 3H), 1.89-1.78 (m, 2H), 1.68-1.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 130.3, 128.0, 127.3, 81.6, 54.4, 51.1, 47.0, 12.3; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{20}O_4NaS^+$ 355.0975, found 355.0979.



3ay: Methyl 1-((2-(benzyloxy)phenyl)(methoxy)methyl)cyclopropane-1-sulfonate

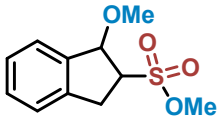
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.44 (m, 2H), 7.43-7.36 (m, 2H), 7.35-7.26 (m, 3H), 7.07-6.84 (m, 2H), 5.59 (s, 1H), 5.17-5.03 (m, 2H), 3.76 (s, 3H), 3.31 (s, 3H),

1.40-1.24 (m, 2H), 1.09-1.00 (m, 1H), 0.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 136.6, 129.5, 128.6, 128.1, 127.5, 126.8, 124.5, 120.9, 111.8, 75.1, 70.2, 57.6, 56.5, 41.2, 11.5, 7.1; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{19}H_{22}O_5NaS^+$ 385.1080, found 385.1088.



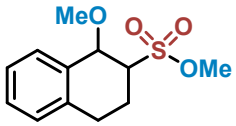
3az: Methyl-2-methoxy-2-phenylcyclohexane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.43 (m, 2H), 7.41-7.34 (m, 2H), 7.33-7.27 (m, 1H), 3.59-3.55 (m, 1H), 3.18 (s, 3H), 2.90 (s, 3H), 2.84-2.73 (m, 1H), 2.47-2.30 (m, 2H), 2.11-1.98 (m, 1H), 1.85-1.70 (m, 2H), 1.69-1.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 128.1, 127.9, 127.6, 77.2, 66.9, 54.5, 48.7, 24.6, 24.1, 20.6, 20.4; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{14}H_{20}O_4NaS^+$ 307.0975, found 307.0985.



3ba: Methyl-1-methoxy-2,3-dihydro-1*H*-indene-2-sulfonate

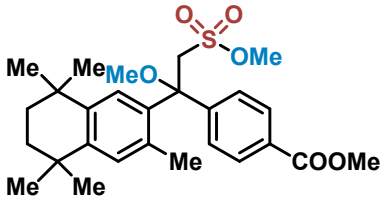
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 1H), 7.35-7.28 (m, 2H), 7.28-7.23 (m, 1H), 5.32 (d, J = 4.0 Hz, 1H), 4.04-3.95 (m, 1H), 3.92 (s, 3H), 3.59 (s, 3H), 3.56-3.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 139.3, 129.5, 127.7, 125.3, 124.8, 85.6, 64.4, 57.8, 55.5, 32.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{11}H_{14}O_4NaS^+$ 265.0505, found 265.0511.



3bb: Methyl 1-methoxy-1,2,3,4-tetrahydronaphthalene-2-sulfonate

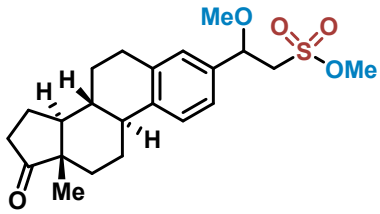
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.10 (m, 4H), 4.84 (d, J = 5.3 Hz, 0.67H), 4.66 (d, J = 2.2 Hz, 0.33H), 3.94 (s, 1H), 3.89 (s, 2H), 3.76-3.69 (m, 0.67H), 3.52-3.45 (m, 0.33H), 3.42 (s, 2H), 3.40 (s, 1H), 3.17-3.07 (m, 0.33H), 2.96-2.81 (m, 1.67H), 2.63-2.51 (m, 0.33H), 2.49-2.38 (m, 0.67H), 2.34-2.23 (m, 0.33H), 2.22-2.09 (m, 0.67H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 135.7, 133.7, 132.9, 130.0, 129.5, 129.2, 128.7,

128.4, 128.4, 126.5, 125.7, 76.2, 75.4, 62.3, 60.2, 56.6, 56.5, 56.0, 55.7, 27.7, 26.7, 22.5, 18.7; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{12}H_{16}O_4NaS^+$ 279.0662, found 279.0667.



3bc: Methyl 4-(1-methoxy-2-(methoxysulfonyl)-1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)benzoate

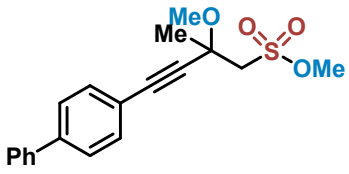
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.23 (s, 1H), 6.94 (s, 1H), 4.36 (d, *J* = 14.5 Hz, 1H), 4.09 (d, *J* = 14.5 Hz, 1H), 3.88 (s, 3H), 3.52 (s, 3H), 3.20 (s, 3H), 1.84 (s, 3H), 1.74-1.64 (m, 4H), 1.36-1.31(m, 6H), 1.24 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 147.7, 145.1, 142.0, 135.6, 134.2, 131.2, 128.9, 128.8, 127.3, 124.3, 81.2, 56.5, 55.1, 52.1, 51.1, 35.2, 35.0, 34.1, 33.9, 32.1, 32.0, 31.7, 31.6, 20.4; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{27}H_{36}O_6NaS^+$ 511.2125, found 511.2129.



3bd: Methyl 1-methoxy-1-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl)propane-2-sulfonate

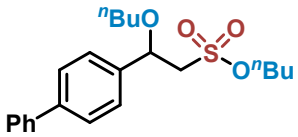
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.06 (s, 1H), 4.67 (dd, *J* = 9.4, 2.1 Hz, 1H), 3.91 (s, 3H), 3.59 (dd, *J* = 14.9, 9.5 Hz, 1H), 3.34-3.19 (m, 4H), 2.93 (dd, *J* = 8.7, 3.9 Hz, 2H), 2.57-2.47 (m, 1H), 2.46-2.39 (m, 1H), 2.35-2.26 (m, 1H), 2.21-2.12 (m, 1H), 2.12-2.02 (m, 2H), 2.00-1.94 (m, 1H), 1.69-1.42 (m, 6H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.9, 140.4, 137.3, 137.3, 135.9, 127.1, 127.0, 126.0, 123.9, 123.8, 57.2, 57.2, 57.0, 56.2, 50.5, 48.0, 44.4,

38.0, 35.9, 31.6, 29.4, 29.4, 26.4, 25.7, 21.6, 13.9; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{22}H_{30}O_5NaS^+$ 429.1706, found 429.1711.



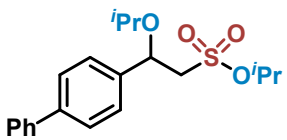
3be: Methyl 4-([1,1'-biphenyl]-4-yl)-2-methoxy-2-methylbut-3-yne-1-sulfonate

^1H NMR (400 MHz, $CDCl_3$) δ 7.62-7.50 (m, 6H), 7.49-7.42 (m, 2H), 7.40-7.33 (m, 1H), 3.95 (s, 3H), 3.71-3.55 (m, 2H), 3.50 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 140.2, 132.3, 128.9, 127.8, 127.10, 127.08, 120.7, 87.4, 87.2, 71.1, 58.6, 56.2, 52.0, 25.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{19}H_{20}O_4NaS^+$ 367.0975, found 367.0987.



3bf: Butyl 2-((1,1'-biphenyl)-4-yl)-2-butoxyethane-1-sulfonate

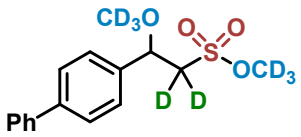
^1H NMR (400 MHz, $CDCl_3$) δ 7.63-7.55 (m, 4H), 7.48-7.39 (m, 4H), 7.38-7.32 (m, 1H), 4.87 (dd, J = 8.7, 3.5 Hz, 1H), 4.27-4.12 (m, 2H), 3.62 (dd, J = 14.8, 8.8 Hz, 1H), 3.40 (t, J = 6.6 Hz, 2H), 3.32 (dd, J = 14.8, 3.6 Hz, 1H), 1.72-1.62 (m, 2H), 1.61-1.52 (m, 2H), 1.44-1.33 (m, 4H), 0.96-0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 140.5, 138.6, 128.9, 127.63, 127.59, 127.1, 127.0, 76.6, 70.3, 69.3, 57.6, 31.8, 31.2, 19.3, 18.7, 13.9, 13.5; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{22}H_{30}O_4NaS^+$ 413.1757, found 413.1766.



3bg: Isopropyl 2-((1,1'-biphenyl)-4-yl)-2-isopropoxyethane-1-sulfonate

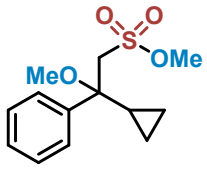
^1H NMR (400 MHz, $CDCl_3$) δ 7.63-7.53 (m, 4H), 7.49-7.40 (m, 4H), 7.39-7.31 (m, 1H), 5.02 (dd, J = 8.8, 3.5 Hz, 1H), 4.98-4.90 (m, 1H), 3.67-3.50 (m, 2H), 3.28 (dd, J = 14.6, 3.5 Hz, 1H), 1.40 (d, J = 6.3 Hz, 3H), 1.37 (d, J = 6.2 Hz, 3H), 1.24 (d, J = 6.0 Hz, 3H), 1.11 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 140.5, 139.5,

128.8, 127.5, 127.1, 127.0, 76.9, 73.9, 70.1, 59.0, 23.3, 23.2, 23.1, 21.0; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{20}H_{26}O_4NaS^+$ 385.1444, found 385.1448.



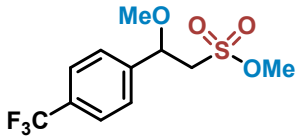
3bh: Bethyl-d_3 2-((1,1'-biphenyl)-4-yl)-2-(methoxy-d_3)ethane-1-sulfonate-1,1-d_2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.52 (m, 4H), 7.51-7.33 (m, 5H), 4.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.4, 137.5, 128.9, 127.7, 127.6, 127.1, 127.0, 77.9, 56.9 (m), 56.3 (m), 55.5 (m); HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{10}D_8O_4NaS^+$ 337.1320, found 337.1326.



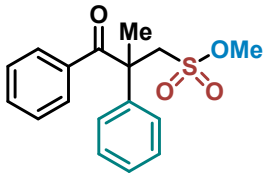
3bi: Methyl 2-cyclopropyl-2-methoxy-2-phenylethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.27 (m, 5H), 3.86 (d, J = 14.7 Hz, 1H), 3.79 (s, 3H), 3.72 (d, J = 14.7 Hz, 1H), 3.31 (s, 3H), 1.61-1.48 (m, 1H), 0.67-0.50 (m, 2H), 0.49-0.39 (m, 1H), 0.37-0.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 128.1, 127.9, 127.0, 79.2, 55.9, 55.5, 51.6, 19.4, 2.7, 2.0; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{13}H_{18}O_4NaS^+$ 293.0818, found 293.0828.



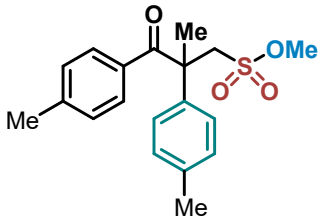
3bj: Methyl 2-methoxy-2-(4-(trifluoromethyl)phenyl)ethane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 4.80 (q, J = 9.0, 3.3 Hz, 1H), 3.90 (s, 3H), 3.60 (q, J = 14.8, 9.0 Hz, 1H), 3.30(s, 3H), 3.25(q, J = 14.8, 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 131.1 (q, J = 32.7 Hz), 127.0, 126.1 (q, J = 3.7 Hz), 123.9 (q, J = 272.1 Hz), 78.0, 57.4, 56.9, 56.1; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{11}H_{13}O_4F_3NaS^+$ 321.0379, found 321.0385.



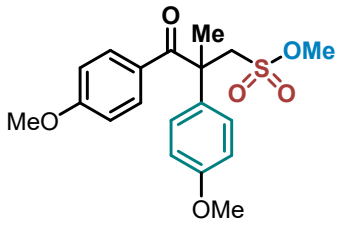
5a: Methyl 2-methyl-3-oxo-2,3-diphenylpropane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.42 (m, 8H), 7.21-7.25f (m, 2H), 4.03 (d, *J* = 14.8 Hz, 1H), 3.77 (d, *J* = 14.8 Hz, 1H), 3.64 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 139.4, 135.7, 132.2, 129.4, 129.4, 128.3, 128.2, 126.6, 59.2, 55.5, 52.9, 21.5; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{18}NaO_4S^+$ 341.0818, found 341.0832.



5b: Methyl 2-methyl-3-oxo-2,3-di-p-tolylpropane-1-sulfonate

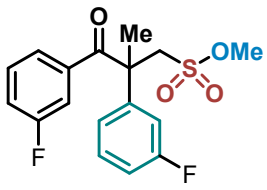
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 7.5 Hz, 2H), 3.99 (d, *J* = 14.4 Hz, 1H), 3.74 (d, *J* = 14.7 Hz, 1H), 3.64 (s, 3H), 2.35(s, 3H), 2.29 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 142.9, 137.9, 136.6, 132.8, 130.0, 129.8, 128.9, 126.5, 59.3, 55.5, 52.6, 21.6, 21.5, 21.1; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{19}H_{22}NaO_4S^+$ 369.1131, found 369.1141.



5c: Methyl 2,3-bis(4-methoxyphenyl)-2-methyl-3-oxopropane-1-sulfonate

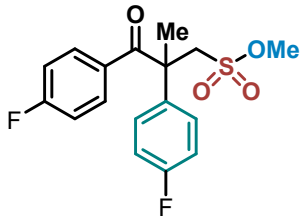
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.9 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.9 Hz, 2H), 3.93 (d, *J* = 14.9 Hz, 1H), 3.81 (s, 3H), 3.75-3.78 (m, 4H), 3.65 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1,

162.6, 159.3, 132.2, 131.6, 127.9, 127.6, 114.6, 113.4, 59.4, 55.5, 55.4, 55.3, 52.2, 21.9; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{19}H_{22}NaO_6S^+$ 401.1029, found 401.1035.



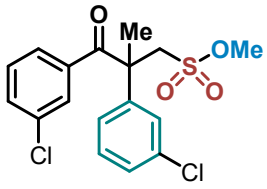
5d: Methyl 2,3-bis(3-fluorophenyl)-2-methyl-3-oxopropane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.45 (m, 1H), 7.21-7.27 (m, 1H), 7.07-7.18 (m, 6H), 3.99 (d, J = 14.8 Hz, 1H), 3.72–3.75 (m, 4H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 163.3 (d, $^1J_{C\text{-}F}$ = 247.0 Hz), 162.2 (d, $^1J_{C\text{-}F}$ = 247.0 Hz), 141.6 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 137.3 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 131.1 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 130.0 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 125.0 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 122.4 (d, $^4J_{C\text{-}F}$ = 2.0 Hz), 119.4 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 116.3 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 115.6 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 113.9 (d, $^2J_{C\text{-}F}$ = 22.0f Hz), 58.8, 55.6, 52.8 (d, $^4J_{C\text{-}F}$ = 1.0 Hz), 21.3; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}F_2NaO_4S^+$ 377.0630, found 377.0637.



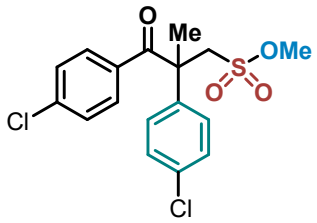
5e: Methyl 2,3-bis(4-fluorophenyl)-2-methyl-3-oxopropane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.47 (m, 2H), 7.36-7.39 (m, 2H), 7.12 (t, J = 8.5 Hz, 2H), 6.94 (t, J = 8.5 Hz, 2H), 3.94 (d, J = 14.8 Hz, 1H), 3.77 (d, J = 14.8 Hz, 1H), 3.69 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 164.9 (d, $^1J_{C\text{-}F}$ = 254.0 Hz), 162.5 (d, $^1J_{C\text{-}F}$ = 247.0 Hz), 135.0 (d, $^4J_{C\text{-}F}$ = 4.0 Hz), 132.3 (d, $^3J_{C\text{-}F}$ = 9.0 Hz), 131.3 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 128.5 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 116.4 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 115.4 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 59.1, 55.5, 52.4, 21.8; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}F_2NaO_4S^+$ 377.0630, found 377.0635.



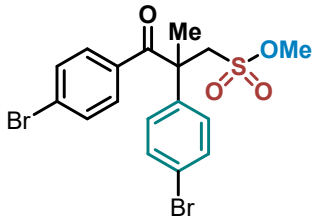
5f: Methyl 2,3-bis(3-chlorophenyl)-2-methyl-3-oxopropane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 1.7 Hz, 1H), 7.36-7.41 (m, 4H), 7.27-7.30 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.13-7.15 (m, 1H), 4.00 (d, *J* = 14.8 Hz, 1H), 3.70-3.73 (m, 4H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 141.0, 136.9, 135.6, 134.7, 132.4, 130.8, 129.6, 129.4, 128.8, 127.2, 126.8, 124.9, 58.8, 55.6, 52.8, 21.3; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}Cl_2NaO_4S^+$ 409.0039, found 409.0045.



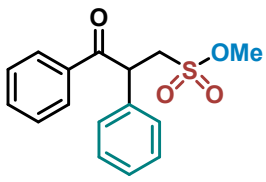
5g: Methyl 2,3-bis(4-chlorophenyl)-2-methyl-3-oxopropane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 3.94 (d, *J* = 14.8 Hz, 1H), 3.74 (d, *J* = 14.8 Hz, 1H), 3.70 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 138.9, 137.6, 134.5, 133.3, 131.0, 129.7, 128.7, 128.1, 58.9, 55.5, 52.6, 21.5; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}Cl_2NaO_4S^+$ 409.0039, found 409.0049



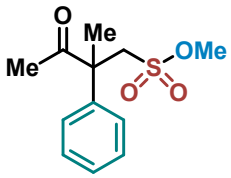
5h: Methyl 2,3-bis(4-bromophenyl)-2-methyl-3-oxopropane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.24-7.28 (m, 4H), 3.93 (d, *J* = 14.8 Hz, 1H), 3.70-3.74 (m, 4H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 138.1, 133.7, 132.7, 131.7, 131.0, 128.4, 127.6, 122.8, 58.9, 55.5, 52.6, 21.4; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}Br_2NaO_4S^+$ 496.9028, found 496.9032.



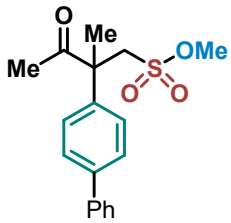
5i: Methyl 3-oxo-2,3-diphenylpropane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.98 (m, 2H), 7.49-7.53 (m, 1H), 7.39-7.42 (m, 2H), 7.30-7.32 (m, 4H), 7.24-7.28 (m, 1H), 5.23 (dd, *J* = 4.2, 8.4 Hz, 1H), 4.36 (dd, *J* = 8.4, 14.7 Hz, 1H), 3.74 (s, 3H), 3.41 (dd, *J* = 4.2, 14.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 136.2, 135.4, 133.7, 129.5, 128.9, 128.8, 128.3, 128.1, 56.1, 52.0, 48.5; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{16}NaO_4S^+$ 327.0662, found 327.0668.



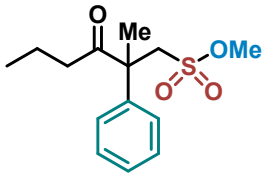
5j: Methyl 2-methyl-3-oxo-2-phenylbutane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.42 (m, 2H), 7.32-7.35 (m, 1H), 7.28-7.30 (m, 2H), 3.91 (d, *J* = 14.9 Hz, 1H), 3.61-3.66 (m, 4H), 1.98 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 138.5, 129.2, 128.2, 126.5, 57.3, 55.5, 53.6, 25.1, 19.4; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{12}H_{16}NaO_4S^+$ 279.0662, found 279.0667.



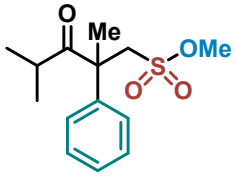
5k: Methyl 2-([1,1'-biphenyl]-4-yl)-2-methyl-3-oxobutane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.34-7.38 (m, 3H), 3.96 (d, *J* = 14.8 Hz, 1H), 3.63-3.67 (m, 4H), 2.03 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 141.0, 140.0, 137.5, 128.9, 127.7, 127.0, 126.9, 57.3, 55.5, 53.4, 25.2, 19.5; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{20}NaO_4S^+$ 355.0975, found 355.0981.



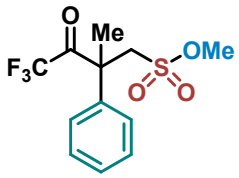
5l: Methyl 2-methyl-3-oxo-2-phenylhexane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.42 (m, 2H), 7.31-7.35(m, 1H), 7.26-7.28 (m, 2H), 3.95 (d, J = 14.9 Hz, 1H), 3.60-3.64 (m, 4H), 2.28-2.36 (m, 1H), 2.10-2.18 (m, 1H), 1.93 (s, 3H), 1.42-1.61z (m, 2H), 0.76 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 138.6, 129.1, 128.1, 126.5, 57.5, 55.5, 53.3, 38.9, 19.2, 17.5, 13.5; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{14}H_{20}NaO_4S^+$ 307.0975, found 307.0980.



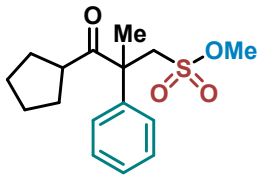
5m: Methyl 2,4-dimethyl-3-oxo-2-phenylpentane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.42 (m, 2H), 7.32-7.35 (m, 1H), 7.27-7.30 (m, 2H), 3.88 (d, J = 15.0 Hz, 1H), 3.68 (d, J = 15.0 Hz, 1H), 3.59 (s, 3H), 2.62-2.72 (m, 1H), 1.98 (s, 3H), 1.06 (d, J = 6.8 Hz, 3H), 0.78 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.6, 137.6, 128.9, 128.2, 127.0, 57.4, 55.4, 53.9, 35.4, 21.2, 20.9, 18.6; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{14}H_{20}NaO_4S^+$ 307.0975, found 307.0980.



5n: Methyl 4,4,4-trifluoro-2-methyl-3-oxo-2-phenylbutane-1-sulfonate

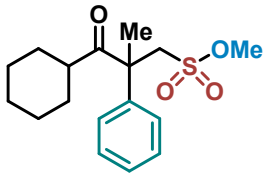
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.46 (m, 3H), 7.24-7.26 (m, 2H), 4.08 (d, J = 14.8 Hz, 1H), 3.75 (s, 3H), 3.56 (d, J = 14.8 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8 (q, $^2J_{C\text{-}F}$ = 33.0zz Hz), 135.3, 129.6, 129.0, 126.1, 115.9 (q, $^1J_{C\text{-}F}$ = 292.0 Hz), 57.5, 55.7, 51.5, 17.9 (q, $^4J_{C\text{-}F}$ = 2.0 Hz); HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{12}H_{13}F_3O_4S^+$ 333.0379, found 333.0384.



5o: Methyl 3-cyclopentyl-2-methyl-3-oxo-2-phenylpropane-1-sulfonate

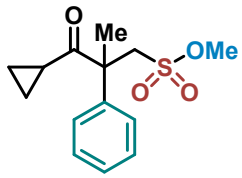
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.42 (m, 2H), 7.25-7.34 (m, 3H), 3.87 (d, J = 15.0 Hz, 1H), 3.66 (d, J = 15.0 Hz, 1H), 3.57 (s, 3H), 2.66-2.74 (m, 1H), 1.94 (s, 3H),

1.77-1.83 (m, 1H), 1.58-1.72 (m, 4H), 1.46-1.54 (m, 1H), 1.34-1.41 (m, 1H), 1.24-1.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 138.2, 129.0, 128.0, 127.0, 57.4, 55.4, 53.8, 46.4, 33.1, 33.0, 26.6, 26.3, 18.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{22}NaO_4S^+$ 333.1131, found 333.1137.



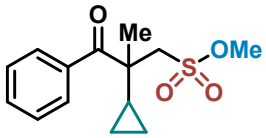
5p: Methyl 3-cyclohexyl-2-methyl-3-oxo-2-phenylpropane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.41 (m, 2H), 7.27-7.34 (m, 3H), 3.86 (d, *J* = 15.0 Hz, 1H), 3.66 (d, *J* = 15.0 Hz, 1H), 3.59 (s, 3H), 2.34-2.41 (m, 1H), 1.97 (s, 3H), 1.71-1.72 (m, 2H), 1.53-1.58 (m, 2H), 1.34-1.43 (m, 2H), 1.12-1.17 (m, 2H), 1.04-1.07 (m, 1H), 0.89-0.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.1, 137.5, 128.9, 128.1, 127.0, 57.4, 55.4, 53.8, 46.0, 30.9, 30.8, 25.6, 25.5, 25.4, 18.6; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{24}NaO_4S^+$ 347.1288, found 347.1285.



5qa: Methyl 3-cyclopropyl-2-methyl-3-oxo-2-phenylpropane-1-sulfonate

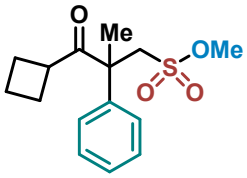
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.43 (m, 2H), 7.30-7.36 (m, 3H), 3.85 (d, *J* = 15.0 Hz, 1H), 3.67 (d, *J* = 15.0 Hz, 1H), 3.55 (s, 3H), 2.00 (s, 3H), 1.63-1.68 (m, 1H), 0.97-1.08 (m, 2H), 0.84-0.91 (m, 1H), 0.67-0.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 138.9, 129.0, 128.0, 127.1, 57.4, 55.4, 53.7, 19.7, 17.6, 12.9, 11.6; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{19}O_4S^+$ 283.0999, found 283.1000.



5qb: Methyl 2-cyclopropyl-2-methyl-3-oxo-3-phenylpropane-1-sulfonate

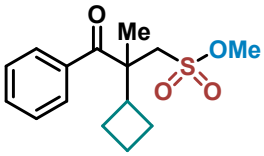
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.66 (m, 2H), 7.46-7.49 (m, 1H), 7.39-7.43 (m, 2H), 3.94 (d, *J* = 14.1 Hz, 1H), 3.88 (s, 3H), 3.53 (d, *J* = 14.1 Hz, 1H), 1.21-1.25 (m,

4H), 0.58-0.67 (m, 3H), 0.43-0.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 138.8, 130.8, 128.0, 127.4, 58.4, 55.6, 48.7, 18.8, 18.2, 3.2, 2.4; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{14}H_{19}O_4S^+$ 283.0999, found 283.0998.



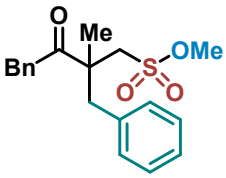
5ra: Methyl 3-cyclobutyl-2-methyl-3-oxo-2-phenylpropane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.40 (m, 2H), 7.28-7.33 (m, 1H), 7.21-7.23 (m, 2H), 3.93 (d, *J* = 14.9 Hz, 1H), 3.58-3.61 (m, 4H), 3.18-3.26 (m, 1H), 2.14-2.27 (m, 2H), 1.99-2.07 (m, 1H), 1.86 (s, 3H), 1.72-1.82 (m, 2H), 1.55-1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 138.4, 129.0, 128.0, 126.7, 57.4, 55.5, 53.0, 41.3, 27.0, 25.5, 18.5, 18.1; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{15}H_{20}NaO_4S^+$ 319.0975, found 319.0982.



5rb: Methyl 2-cyclobutyl-2-methyl-3-oxo-3-phenylpropane-1-sulfonate

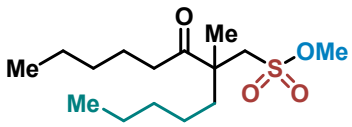
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.52 (m, 2H), 7.45-7.47 (m, 1H), 7.38-7.41 (m, 2H), 4.12 (d, *J* = 14.1 Hz, 1H), 3.86 (s, 3H), 3.14 (d, *J* = 14.1 Hz, 1H), 2.68-2.74 (m, 1H), 1.81-1.92 (m, 5H), 1.70-1.74 (m, 1H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 139.5, 130.6, 128.0, 127.0, 55.6, 55.4, 51.1, 44.0, 23.6, 23.5, 18.6, 17.0; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{15}H_{20}NaO_4S^+$ 319.0975, found 319.0982.



5s: Methyl 2-benzyl-2-methyl-3-oxo-4-phenylbutane-1-sulfonate

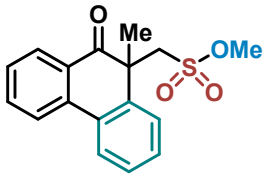
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.35 (m, 6H), 7.06-7.09 (m, 2H), 7.00-7.01 (m, 2H), 3.97 (d, *J* = 14.2 Hz, 1H), 3.84 (d, *J* = 18.0 Hz, 1H), 3.78 (s, 3H), 3.22 (d, *J* = 18.0 Hz, 1H), 3.11 (d, *J* = 14.2 Hz, 1H), 2.95 (d, *J* = 13.0 Hz, 1H), 2.67 (d, *J* = 13.0

Hz, 1H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 134.6, 133.5, 130.5 129.8, 128.5, 128.2, 127.4, 126.7, 57.7, 55.7, 49.8, 46.6, 46.3, 19.5; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{19}H_{22}NaO_4S^+$ 369.1131, found 369.1136.



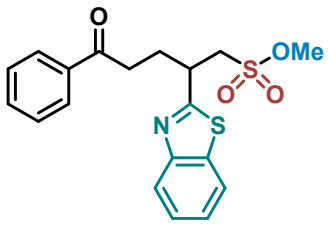
5t: Methyl 2-methyl-3-oxo-2-pentyloctane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.73 (d, *J* = 14.4 Hz, 1H), 3.20 (d, *J* = 14.4 Hz, 1H), 2.45-2.58 (m, 2H), 1.48-1.72 (m, 8H), 1.22-1.35 (m, 9H), 0.85-0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.0, 55.5, 55.4, 49.0, 38.8, 37.4, 31.8, 31.1, 23.4, 22.9, 22.3, 22.1, 20.6, 13.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{30}NaO_4S^+$ 329.1757, found 329.1766.



5u: Methyl (9-methyl-10-oxo-9,10-dihydrophenanthren-9-yl)methanesulfonate

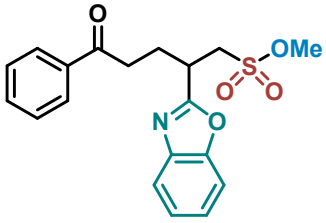
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.8 Hz, 1H), 8.08-8.11 (m, 2H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.50-7.52 (m, 1H), 7.41-7.47 (m, 3H), 4.49 (d, *J* = 14.6 Hz, 1H), 3.91 (d, *J* = 14.6 Hz, 1H), 3.59 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 138.5, 136.9, 135.1, 129.2, 129.1, 128.5, 128.3, 128.1, 127.9, 127.5, 124.2, 123.3, 57.9, 55.6, 48.8, 30.0; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}O_4S^+$ 339.0662, found 339.0664.



5v: Methyl 2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-phenylpentane-1-sulfonate

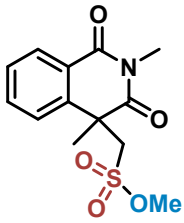
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.86-7.88 (m, 3H), 7.47-7.56 (m, 2H), 7.38-7.43 (m, 3H), 4.05 (dd, *J* = 7.7, 14.4 Hz, 1H), 3.92-3.99 (m, 1H), 3.77 (s, 3H), 3.58 (dd, *J* = 4.9, 14.4, Hz, 1H), 3.03 (t, *J* = 7.3 Hz, 2H), 2.37-2.54 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 170.7, 153.0, 136.5, 134.8, 133.3, 128.6, 128.0, 126.4, 125.4, 123.0, 121.8, 55.9, 53.6, 39.1, 35.1, 29.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{19}H_{19}NNaO_4S_2^+$ 412.0648, found 412.0654.



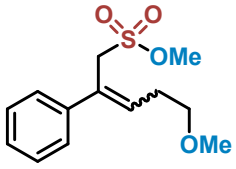
5w: Methyl 2-(benzo[*d*]oxazol-2-yl)-5-oxo-5-phenylpentane-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.66-7.70 (m, 1H), 7.47-7.55 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.31-7.35 (m, 2H), 3.97 (dd, *J* = 8.2, 14.5 Hz, 1H), 3.81-3.88 (m, 1H), 3.79 (s, 3H), 3.57 (dd, *J* = 4.8, 14.6 Hz, 1H), 3.00-3.10 (m, 2H), 2.34-2.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 165.3, 150.6, 140.7, 136.3, 133.2, 128.5, 127.8, 125.1, 124.5, 119.8, 110.6, 55.9, 51.9, 35.0, 27.5; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{19}H_{19}NNaO_5S^+$ 396.0876, found 396.0885.



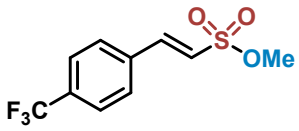
7: Methyl (2,4-dimethyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)methanesulfonte

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.73-7.65 (m, 1H), 7.54-7.49 (m, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 4.35 (d, *J* = 14.6 Hz, 1H), 3.80 (d, *J* = 14.6 Hz, 1H), 3.58 (s, 3H), 3.43 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 163.7, 139.2, 133.8, 129.4, 128.4, 125.7, 124.7, 58.6, 55.7, 45.3, 31.0, 27.5; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{13}H_{15}NO_5NaS^+$ 320.0563, found 320.0574.



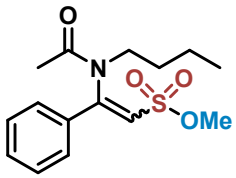
8: Methyl 5-methoxy-2-phenylpent-2-ene-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.37-7.32 (m, 2H), 7.31-7.25 (m, 1H), 6.18 (t, *J* = 7.3 Hz, 1H), 4.37 (s, 2H), 3.65 (s, 3H), 3.54 (t, *J* = 6.3 Hz, 2H), 3.36 (s, 3H), 2.63 (dd, *J* = 13.3, 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 135.2, 128.9, 128.6, 127.7, 126.5, 71.4, 58.8, 56.2, 51.5, 30.1; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{13}H_{18}O_4NaS$ 293.0818, found 293.0828.



9: Methyl (*E*)-2-(4-(trifluoromethyl)phenyl)ethene-1-sulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.68-7.61 (m, 3H), 6.84 (d, *J* = 15.6 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.44, 135.2, 133.0 (q, *J* = 32.8 Hz), 128.8, 126.2 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 273.6 Hz), 123.0, 56.4; HRMS (EI) m/z $[M]^+$calcd for $C_{10}H_9F_3O_3S^+$ 266.0219, found 266.0219.

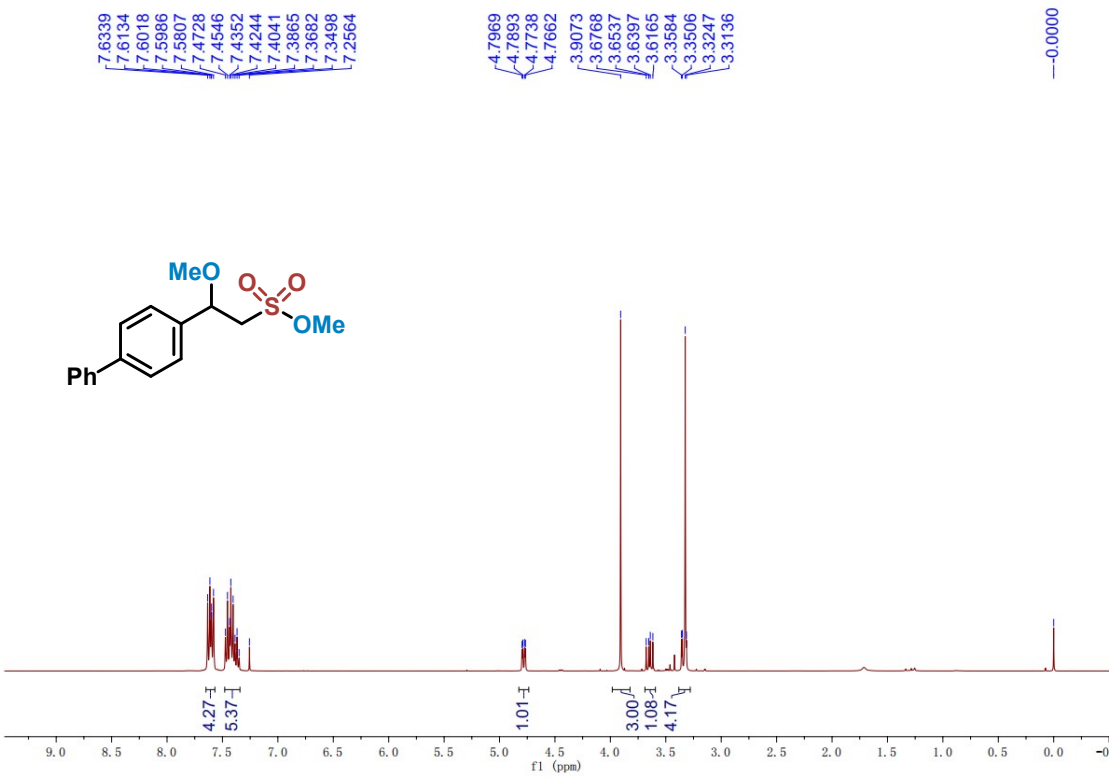


10: Methyl 2-(N-butylacetamido)-2-phenylethene-1-sulfonate

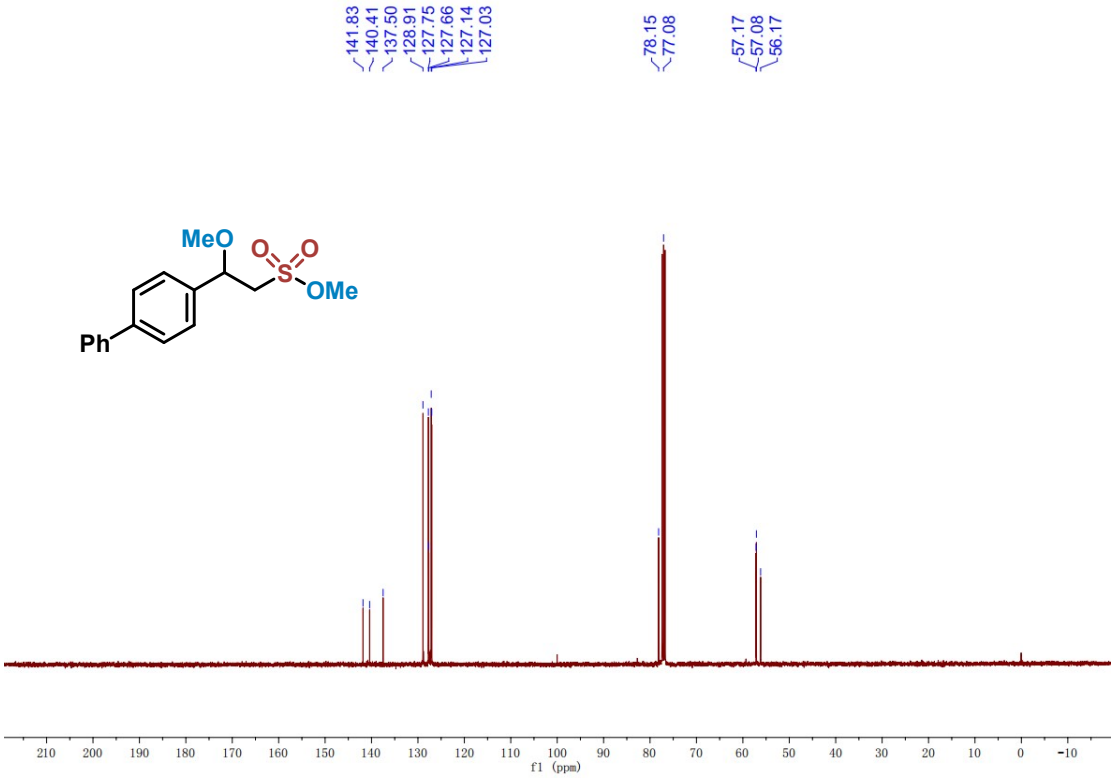
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.39 (m, 5H), 6.29 (s, 1H), 3.79 (s, 3H), 3.33 (t, *J* = 7.6 Hz, 2H), 2.25 (s, 3H), 1.53-1.41 (m, 2H), 1.26-1.17 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 154.0, 132.0, 131.6, 129.5, 128.7, 120.5, 55.9, 47.0, 30.3, 23.1, 19.97, 13.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{21}NNaO_4S^+$ 334.1083, found 334.1090.

8. ^{1}H and ^{13}C NMR spectra

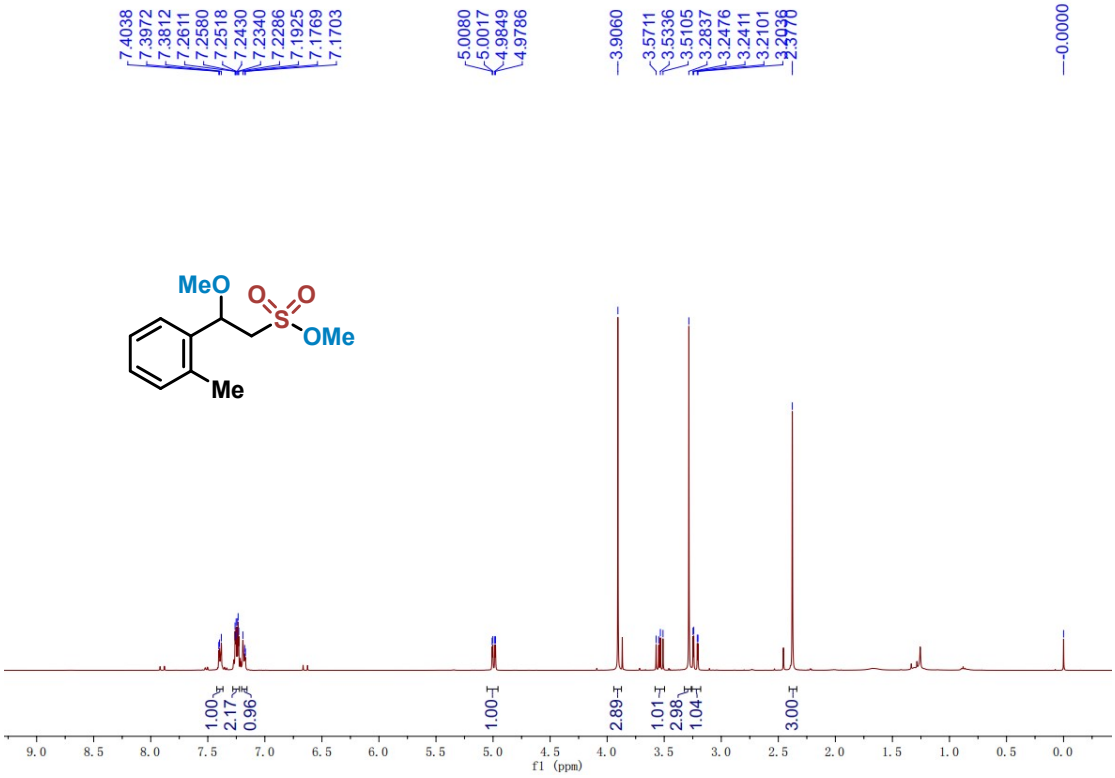
^{1}H NMR spectra of compound **3aa** (400MHz, $CDCl_3$)



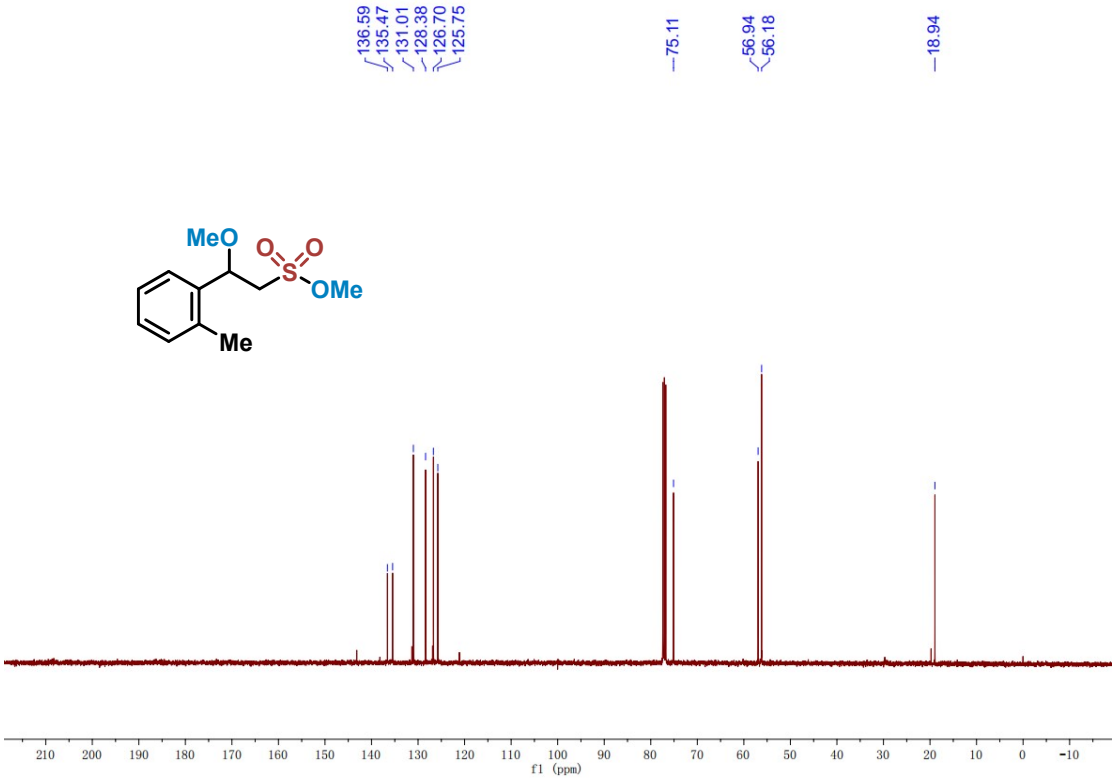
^{13}C NMR spectra of compound **3aa** (100MHz, $CDCl_3$)



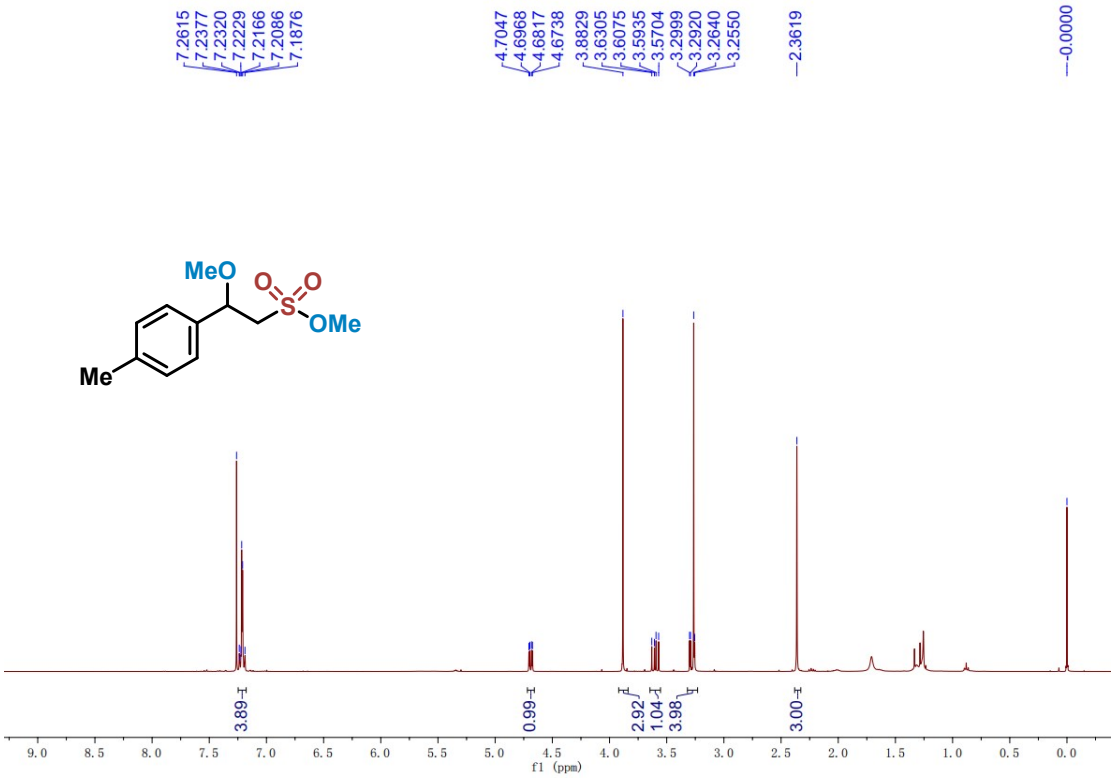
^{1}H NMR spectra of compound **3ab** (400MHz, $CDCl_3$)



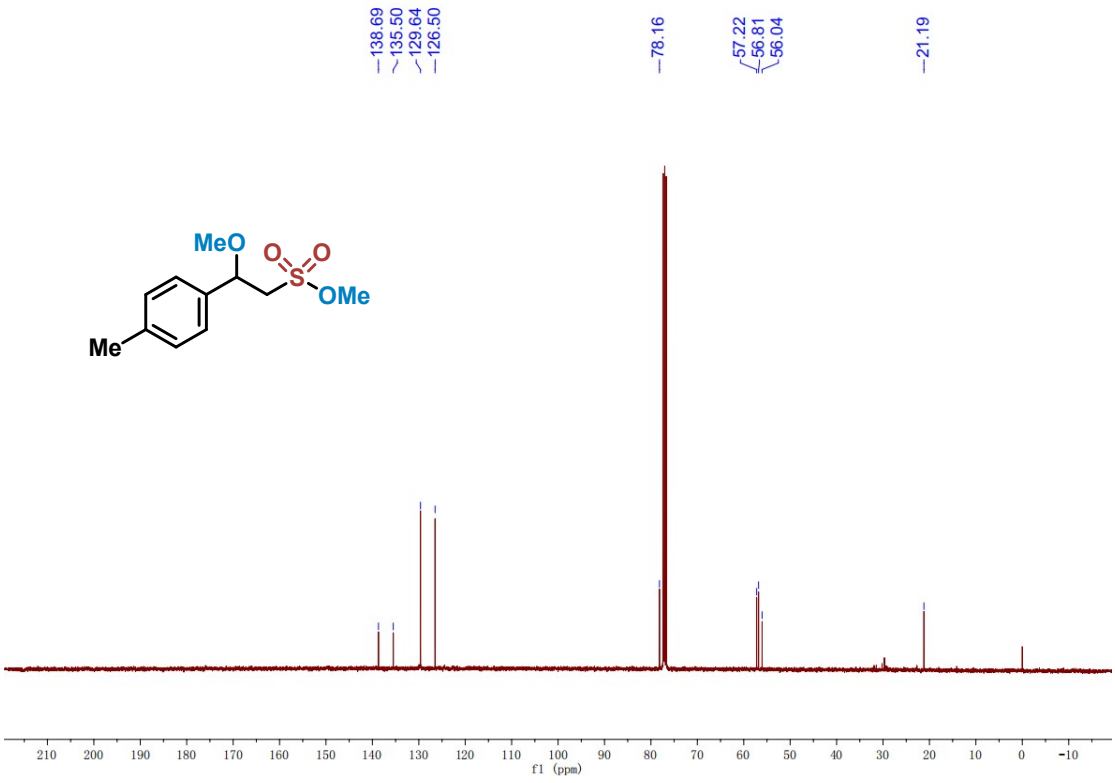
^{13}C NMR spectra of compound **3ab** (100MHz, $CDCl_3$)



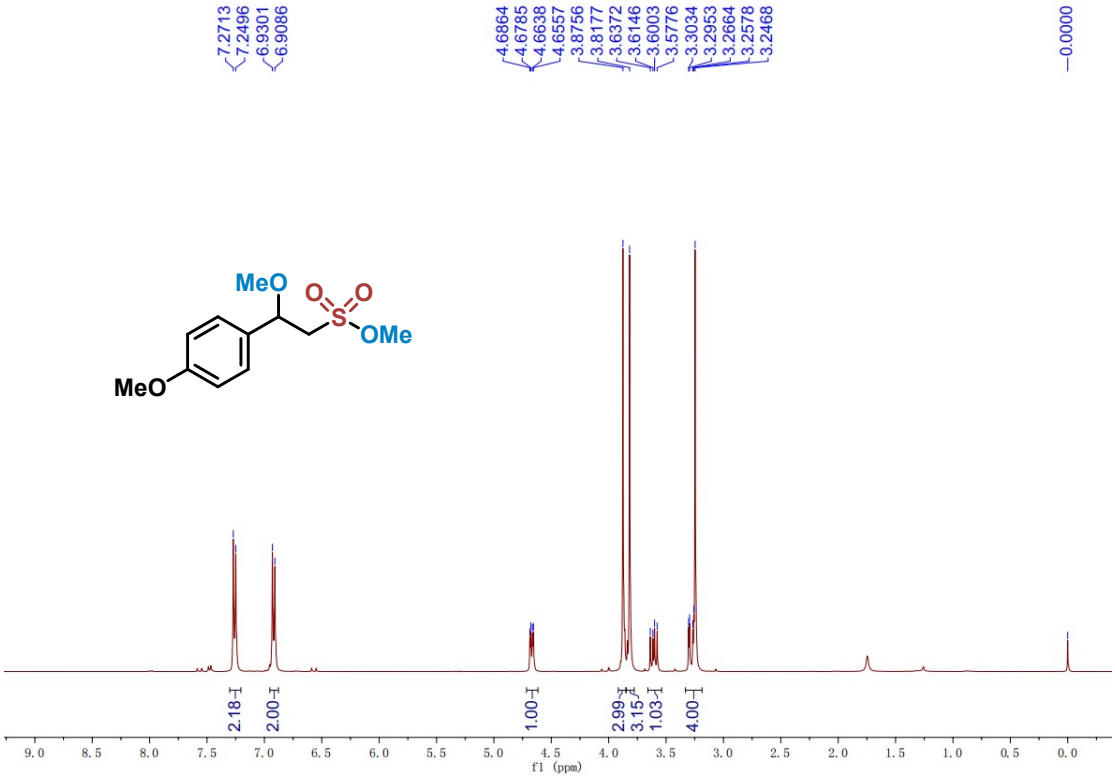
^{1}H NMR spectra of compound **3ac** (400MHz, $CDCl_3$)



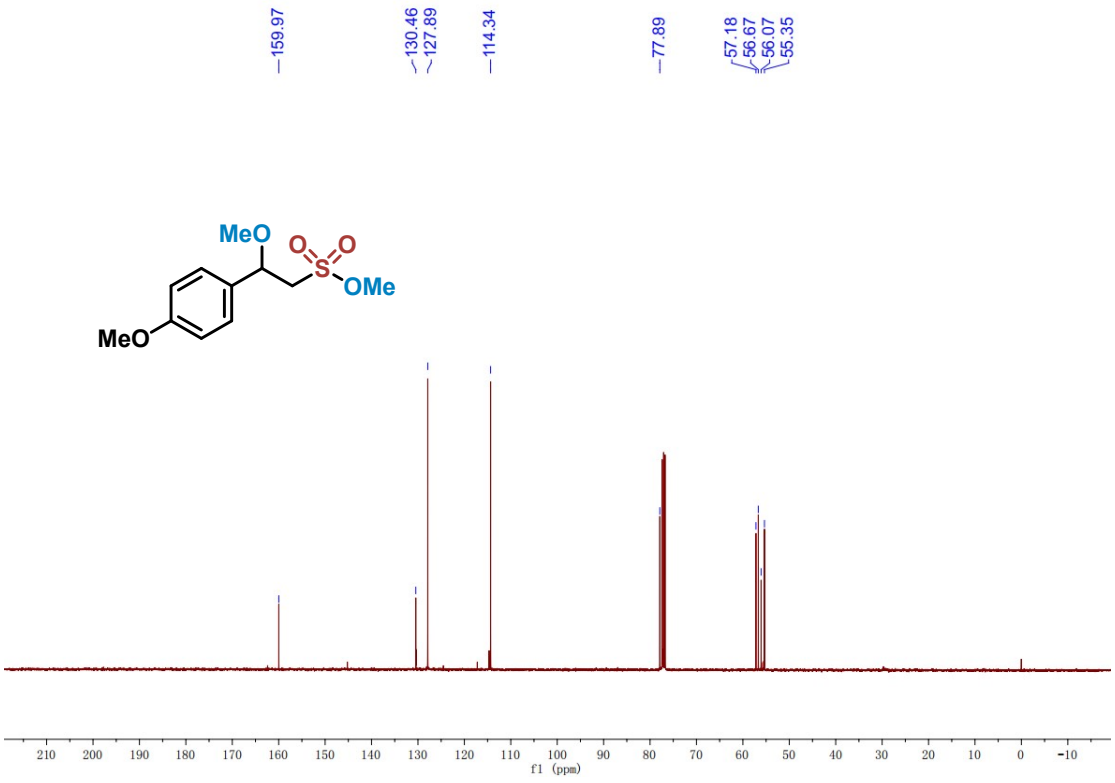
^{13}C NMR spectra of compound **3ac** (100MHz, $CDCl_3$)



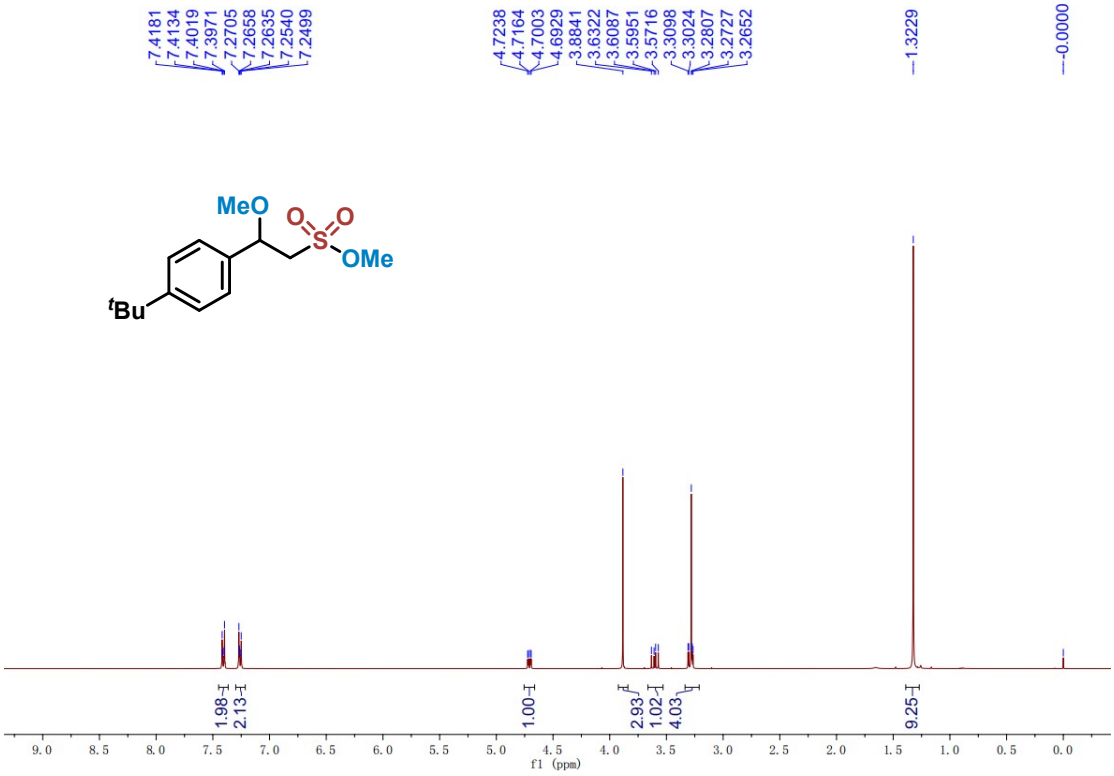
^{1}H NMR spectra of compound **3ad** (400MHz, $CDCl_3$)



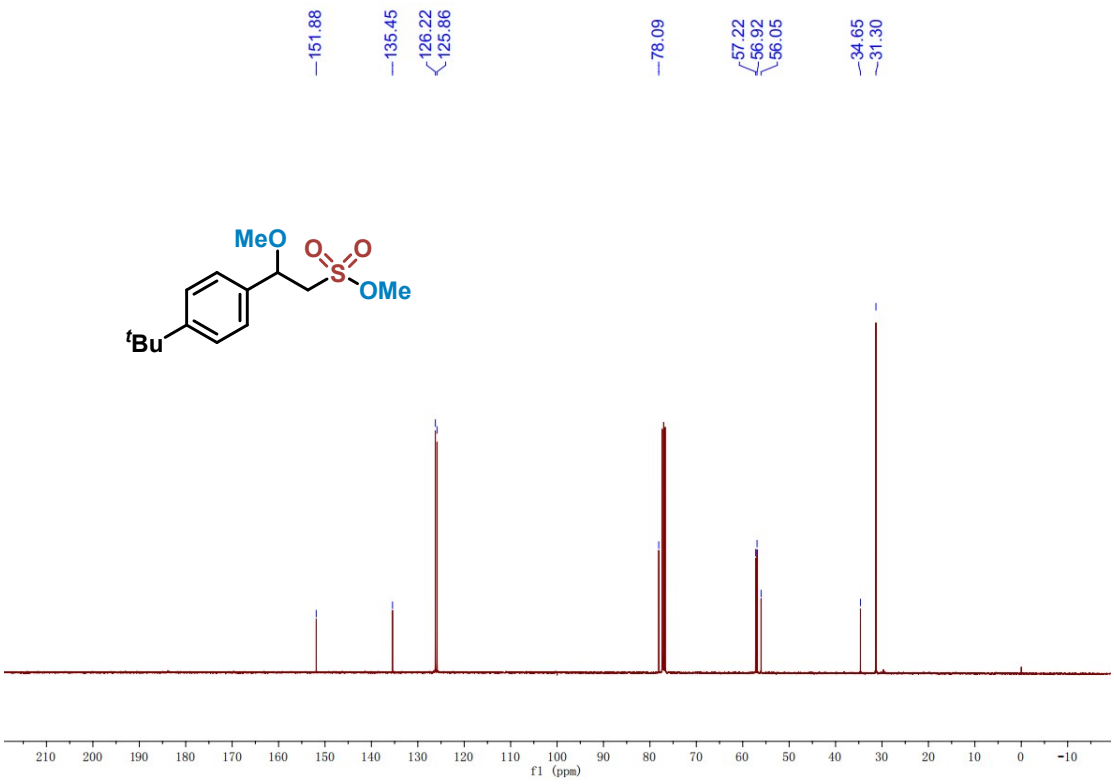
^{13}C NMR spectra of compound **3ad** (100MHz, $CDCl_3$)



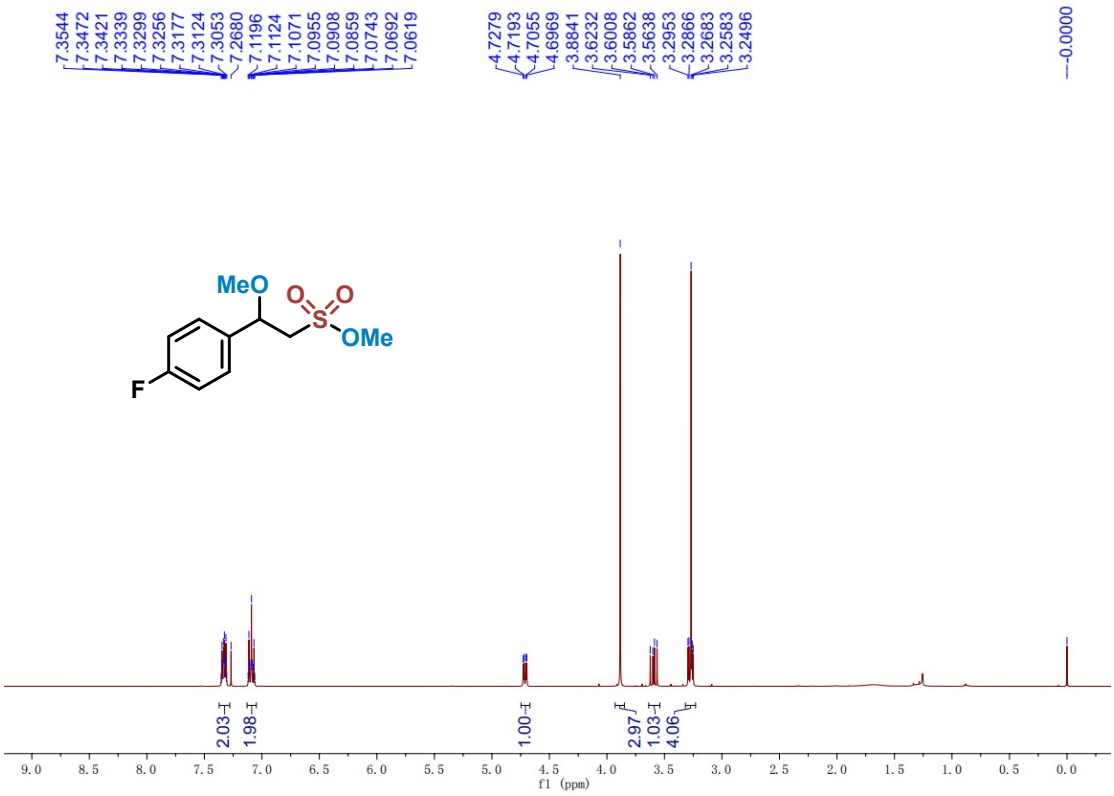
^{1}H NMR spectra of compound **3ae** (400MHz, $CDCl_3$)



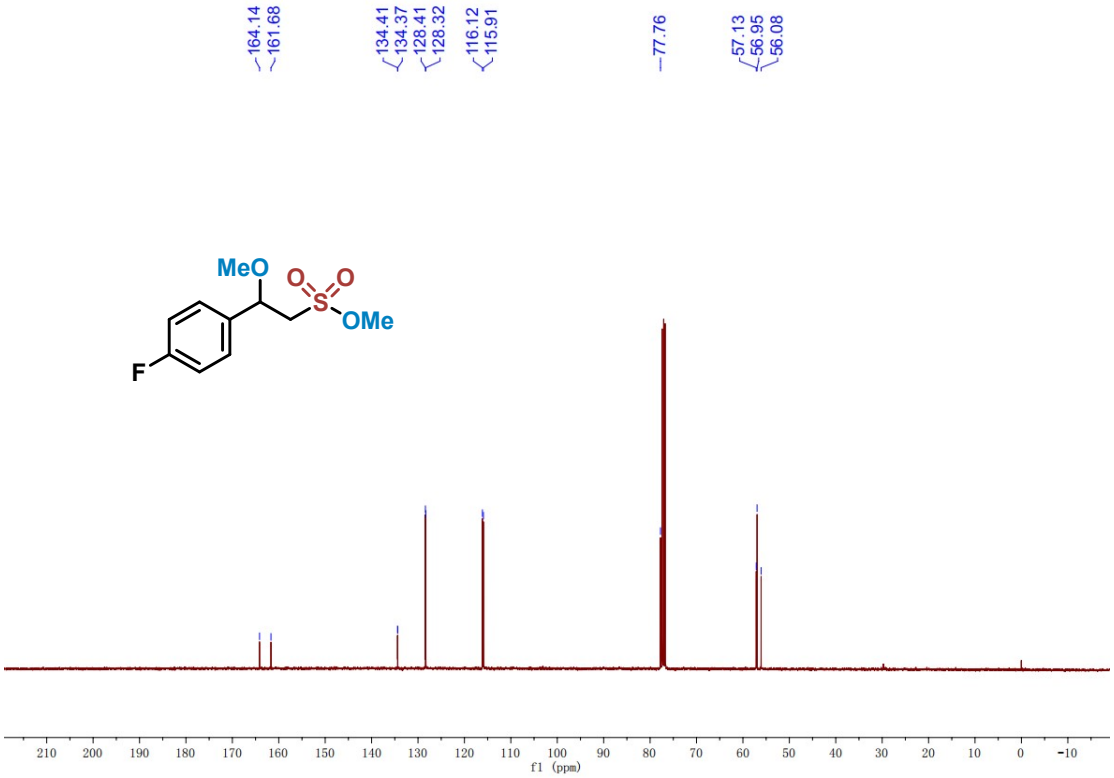
^{13}C NMR spectra of compound **3ae** (100MHz, $CDCl_3$)



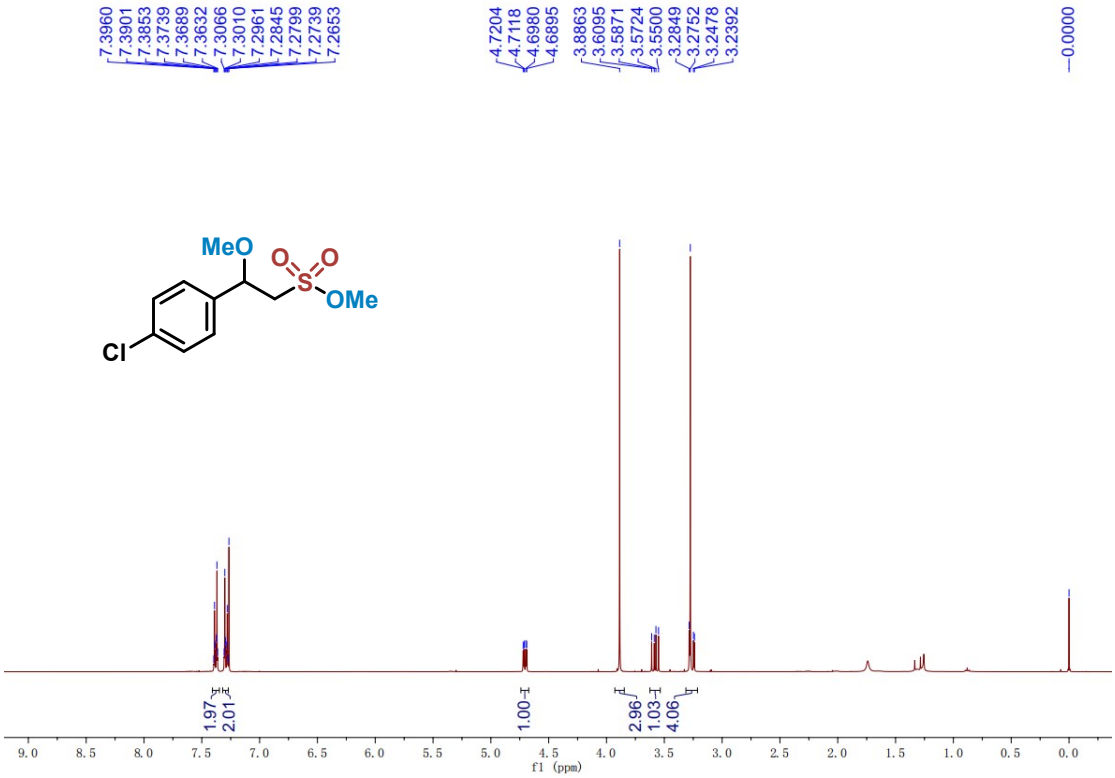
^{1}H NMR spectra of compound **3af** (400MHz, $CDCl_3$)



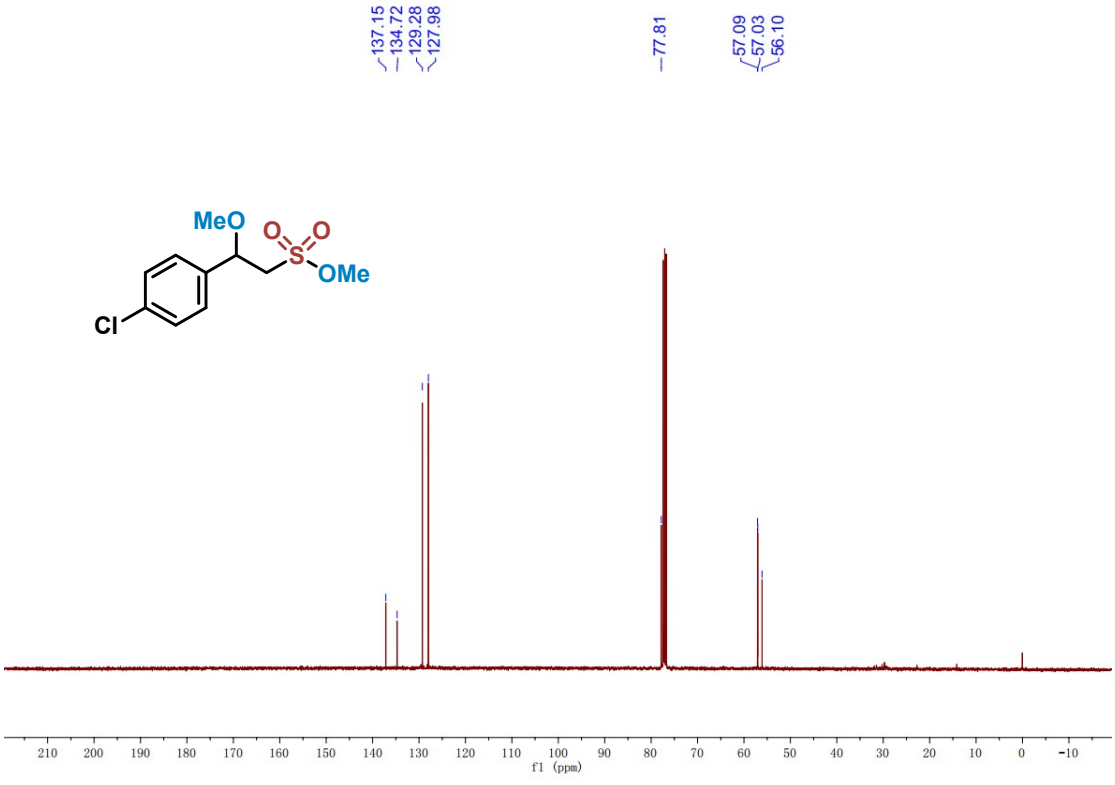
^{13}C NMR spectra of compound **3af** (100MHz, $CDCl_3$)



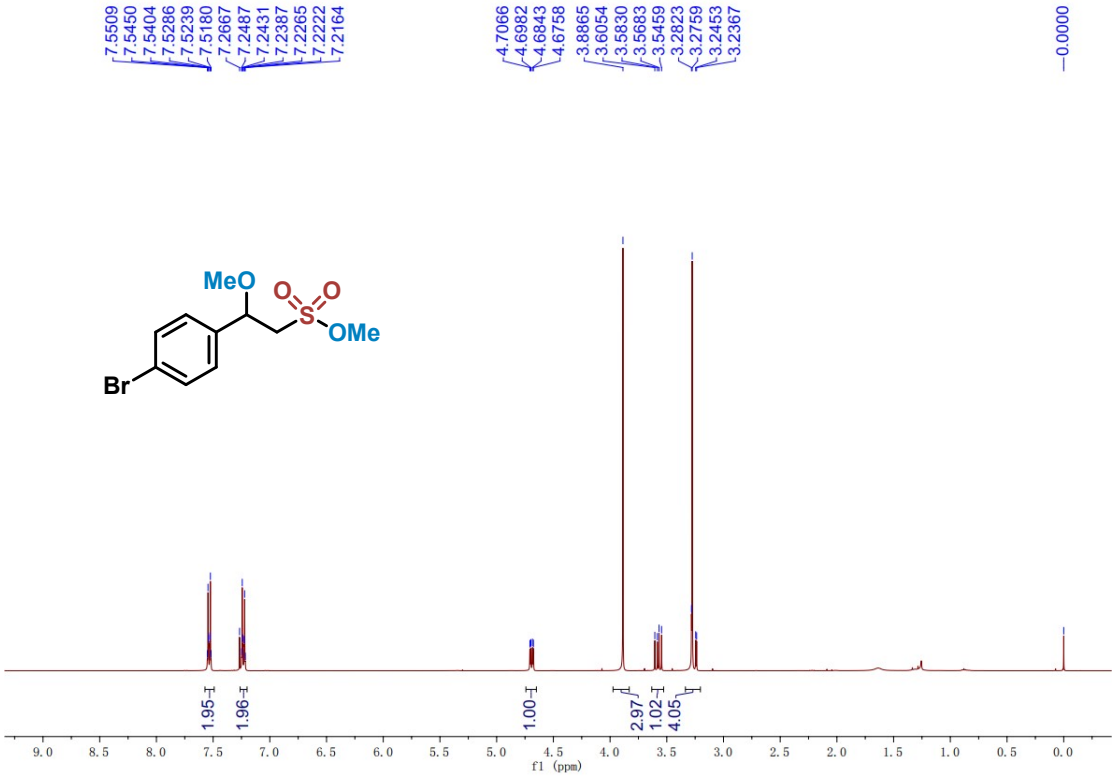
^{1}H NMR spectra of compound **3ag** (400MHz, $CDCl_3$)



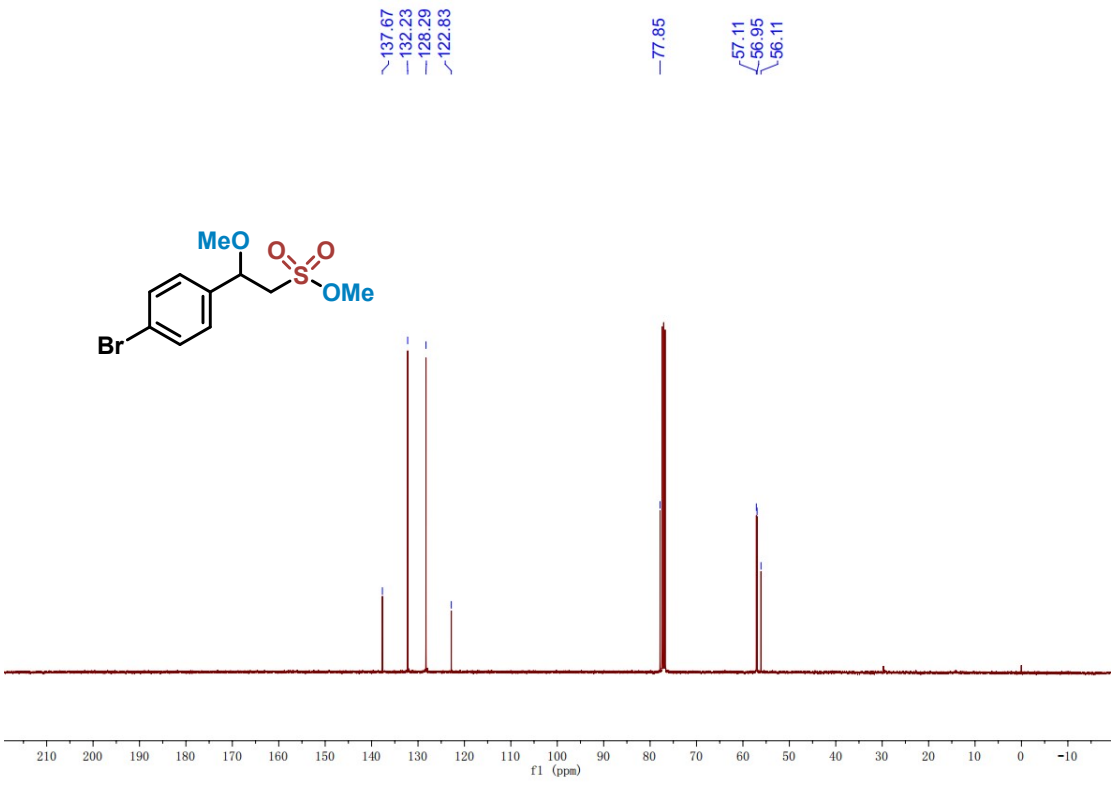
^{13}C NMR spectra of compound **3ag** (100MHz, $CDCl_3$)



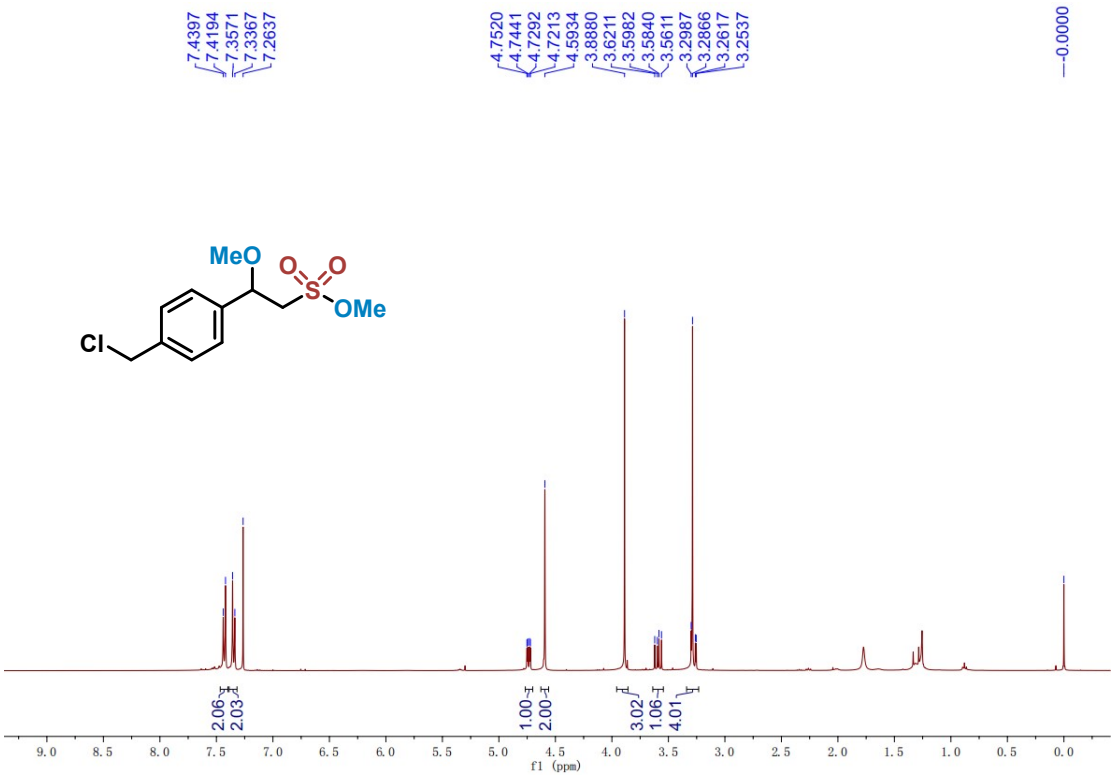
^{1}H NMR spectra of compound **3ah** (400MHz, $CDCl_3$)



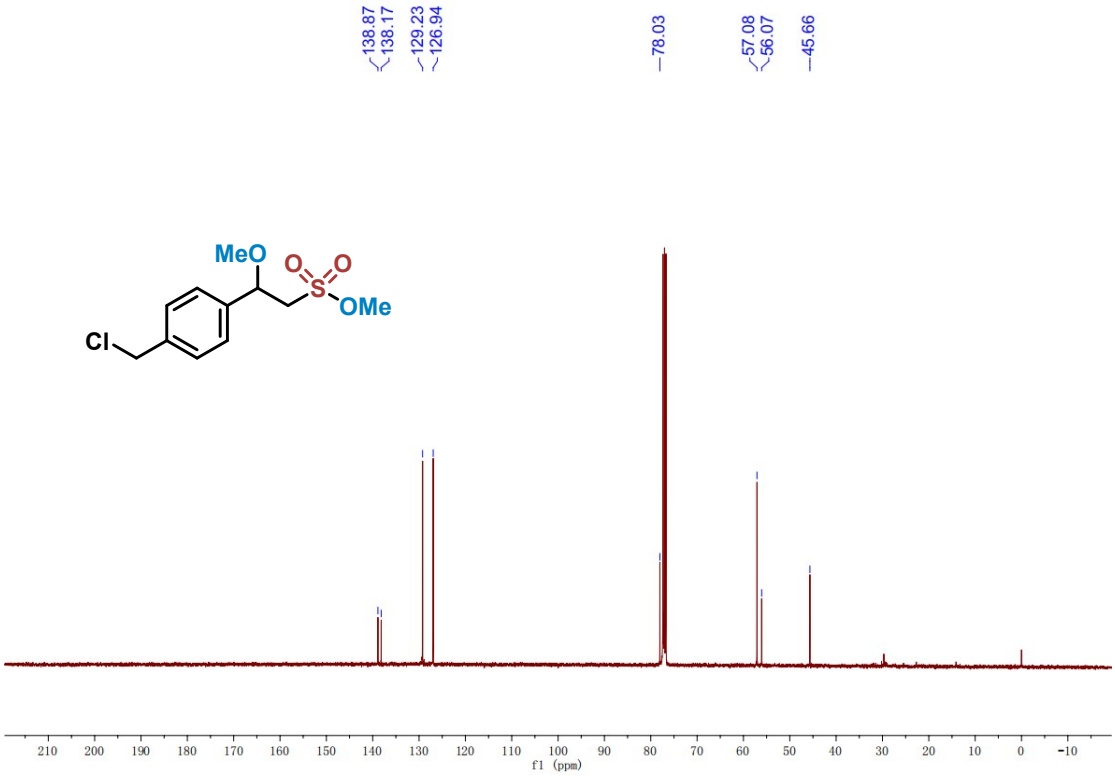
^{13}C NMR spectra of compound **3ah** (100MHz, $CDCl_3$)



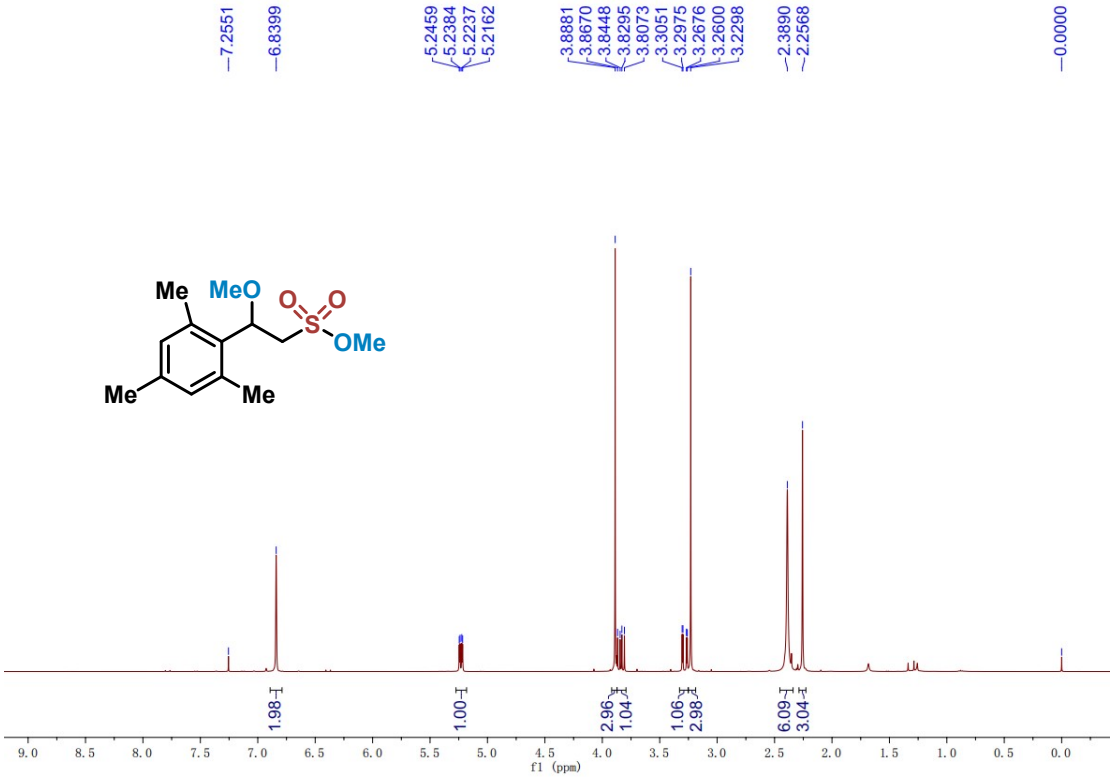
^{1}H NMR spectra of compound **3ai** (400MHz, $CDCl_3$)



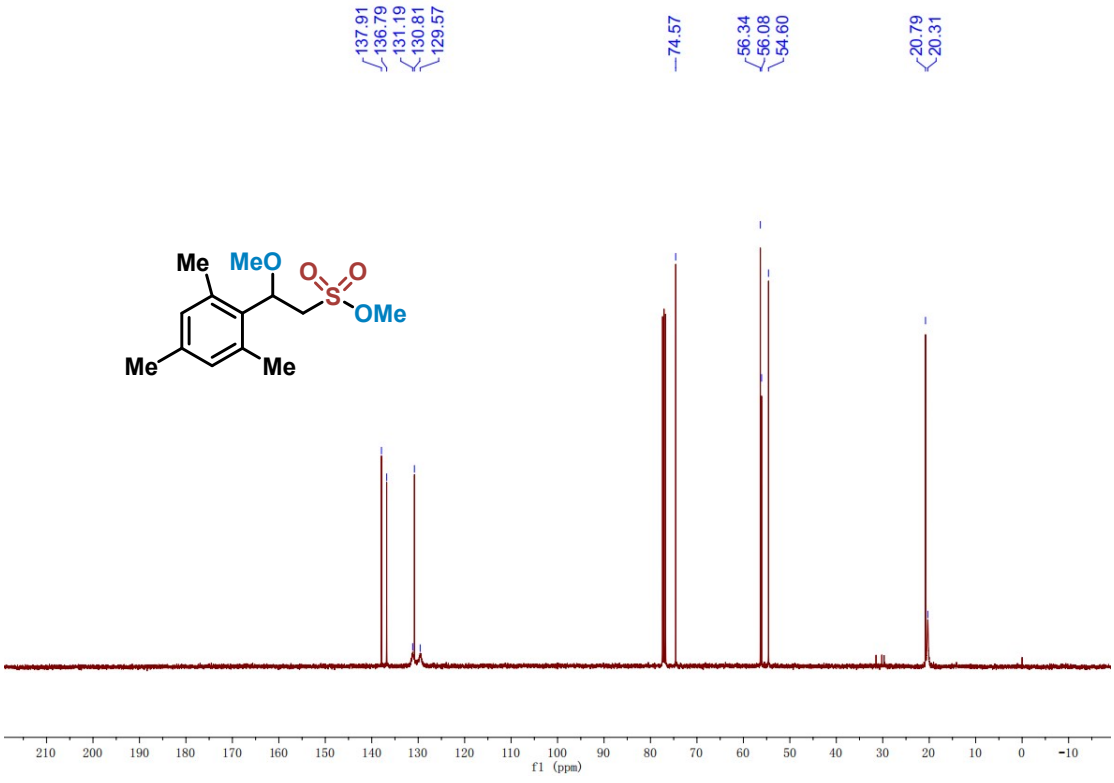
^{13}C NMR spectra of compound **3ai** (100MHz, $CDCl_3$)



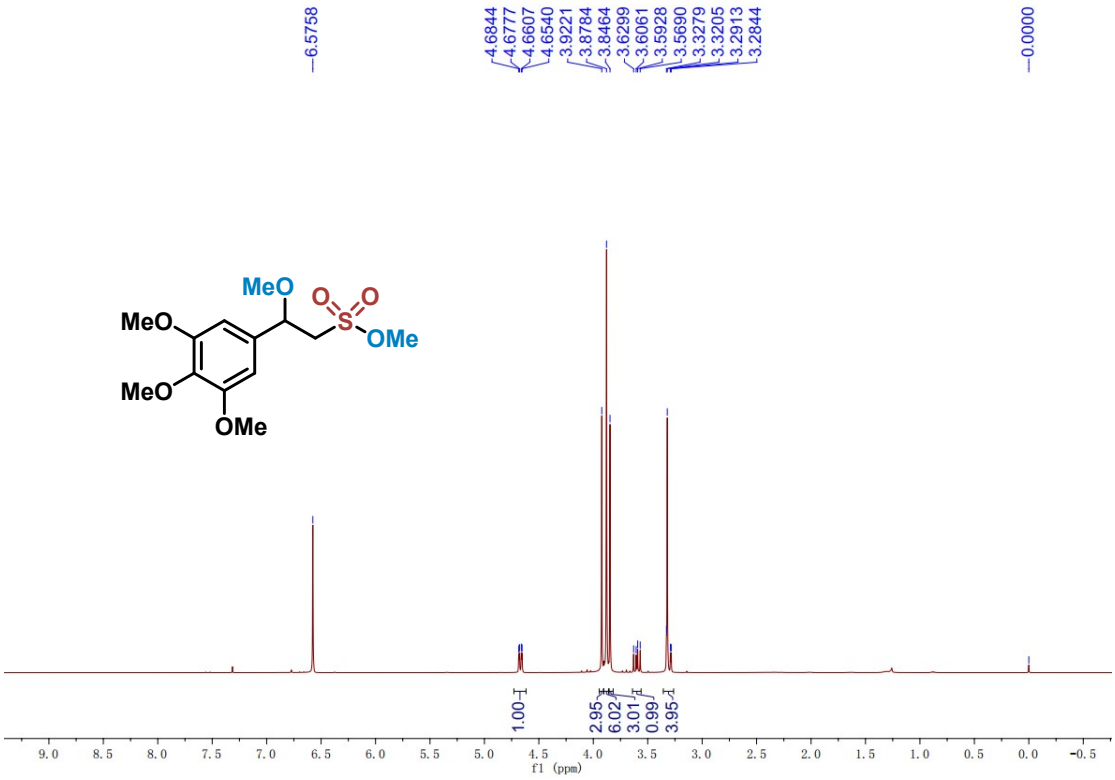
^{1}H NMR spectra of compound **3aj** (400MHz, $CDCl_3$)



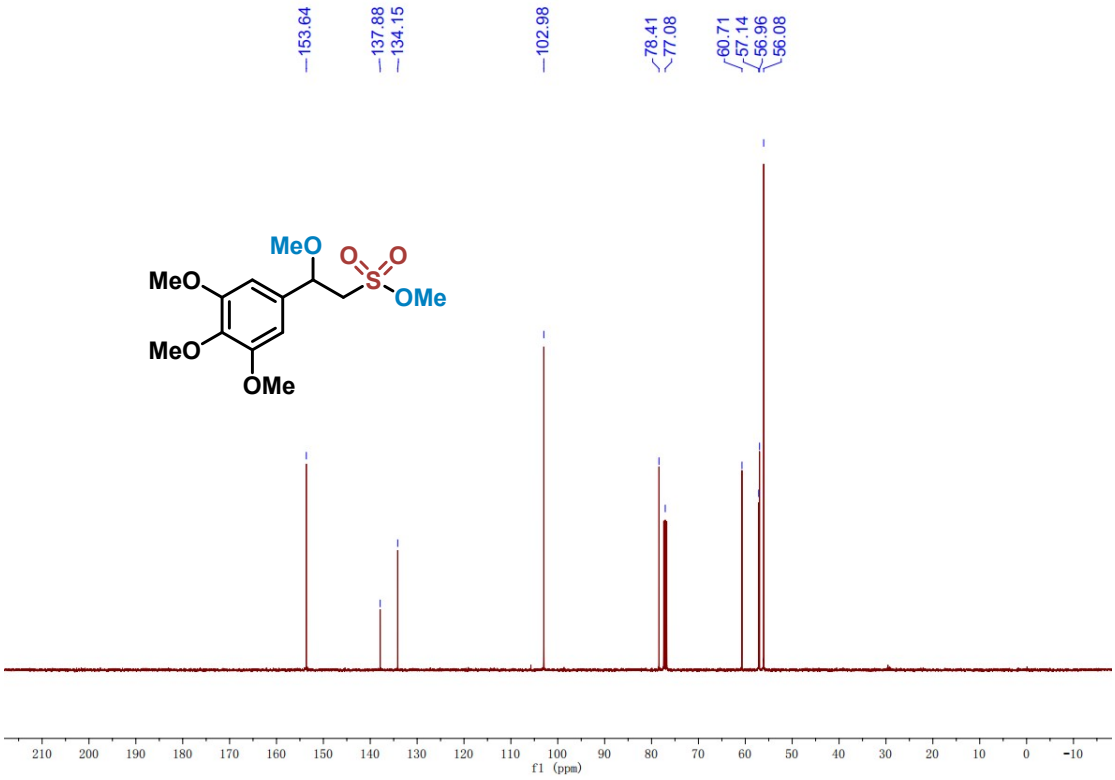
^{13}C NMR spectra of compound **3aj** (100MHz, $CDCl_3$)



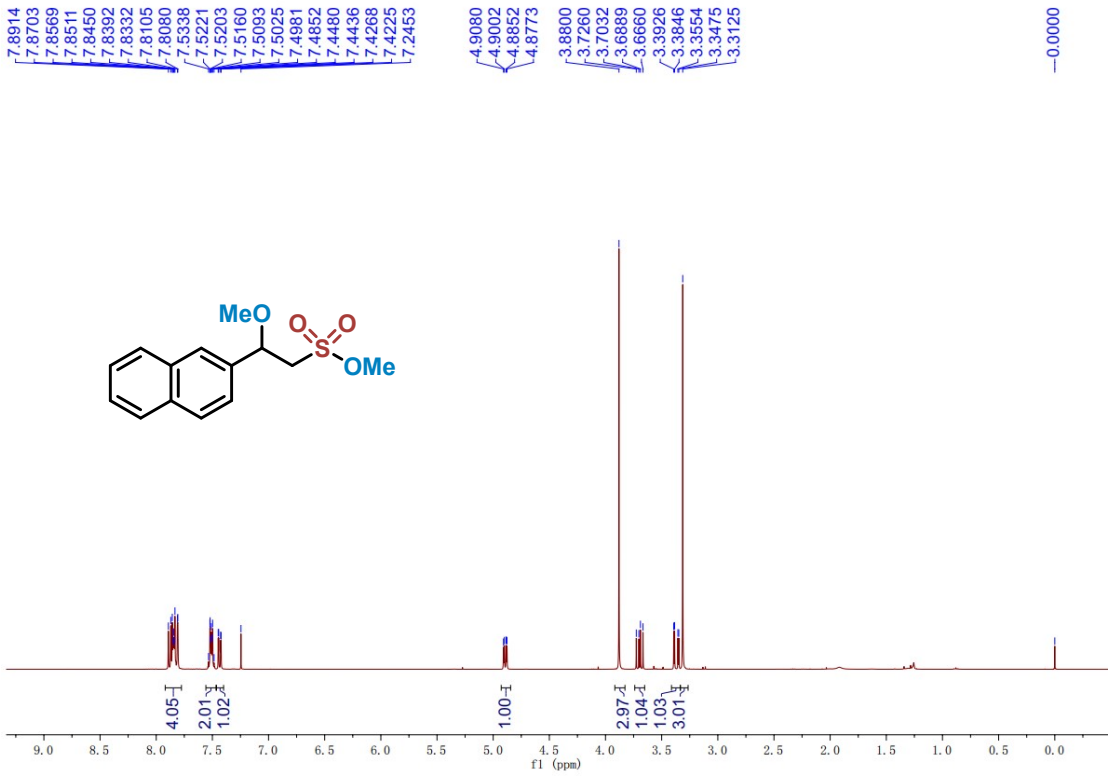
^{1}H NMR spectra of compound **3ak** (400MHz, $CDCl_3$)



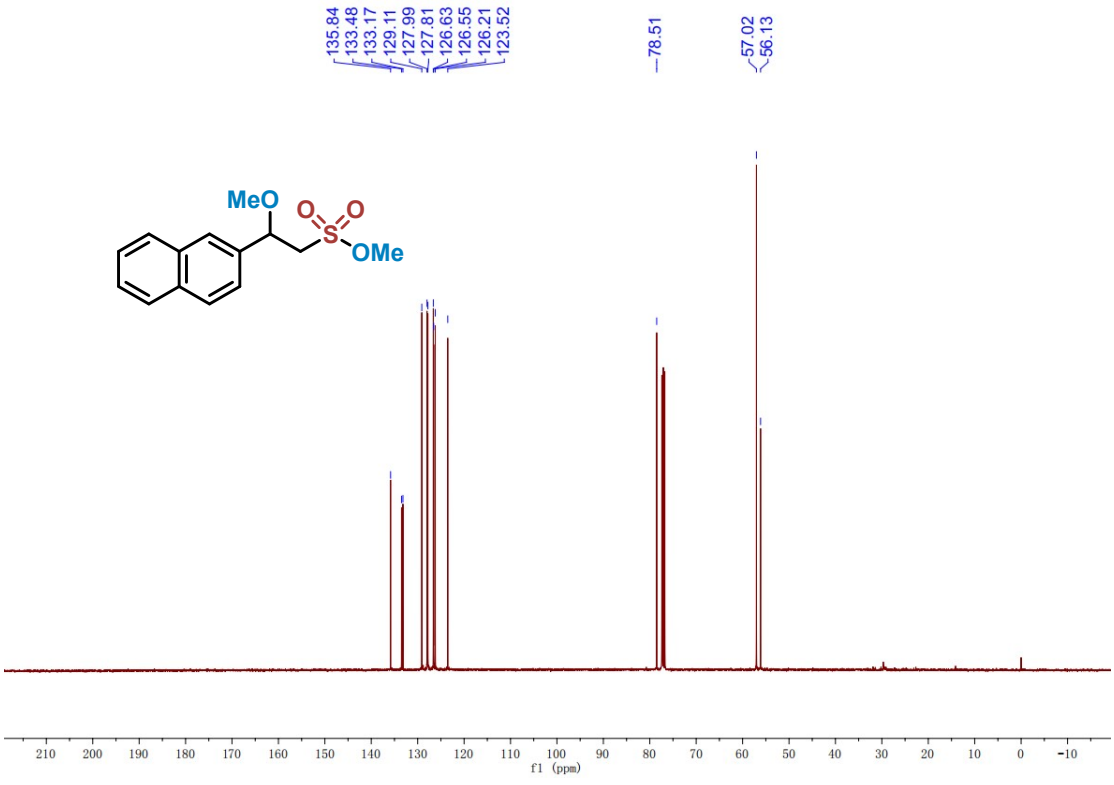
^{13}C NMR spectra of compound **3ak** (100MHz, $CDCl_3$)



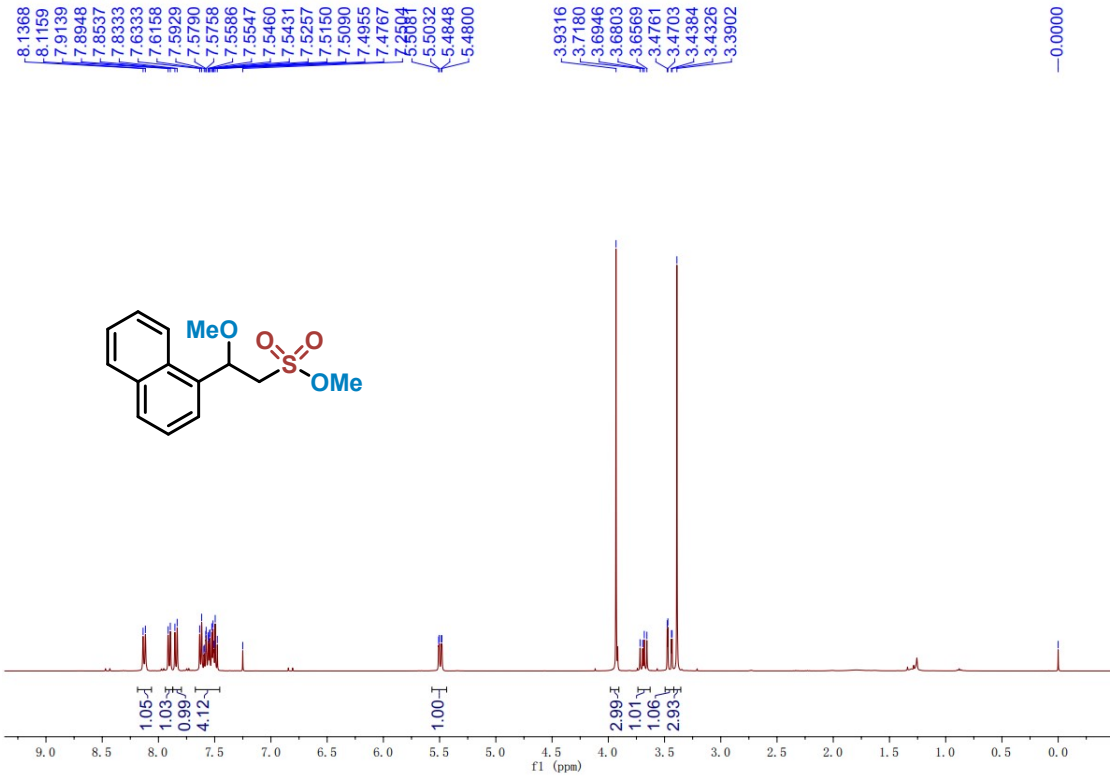
^{1}H NMR spectra of compound **3al** (400MHz, $CDCl_3$)



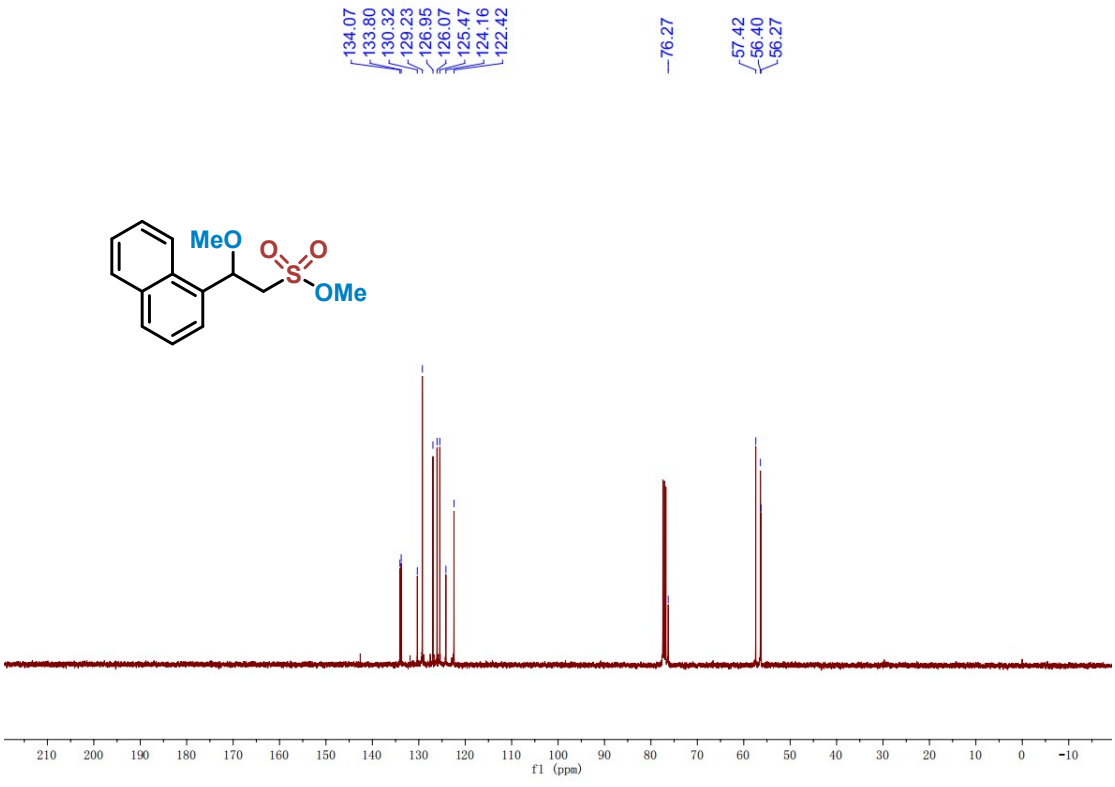
^{13}C NMR spectra of compound **3al** (100MHz, $CDCl_3$)



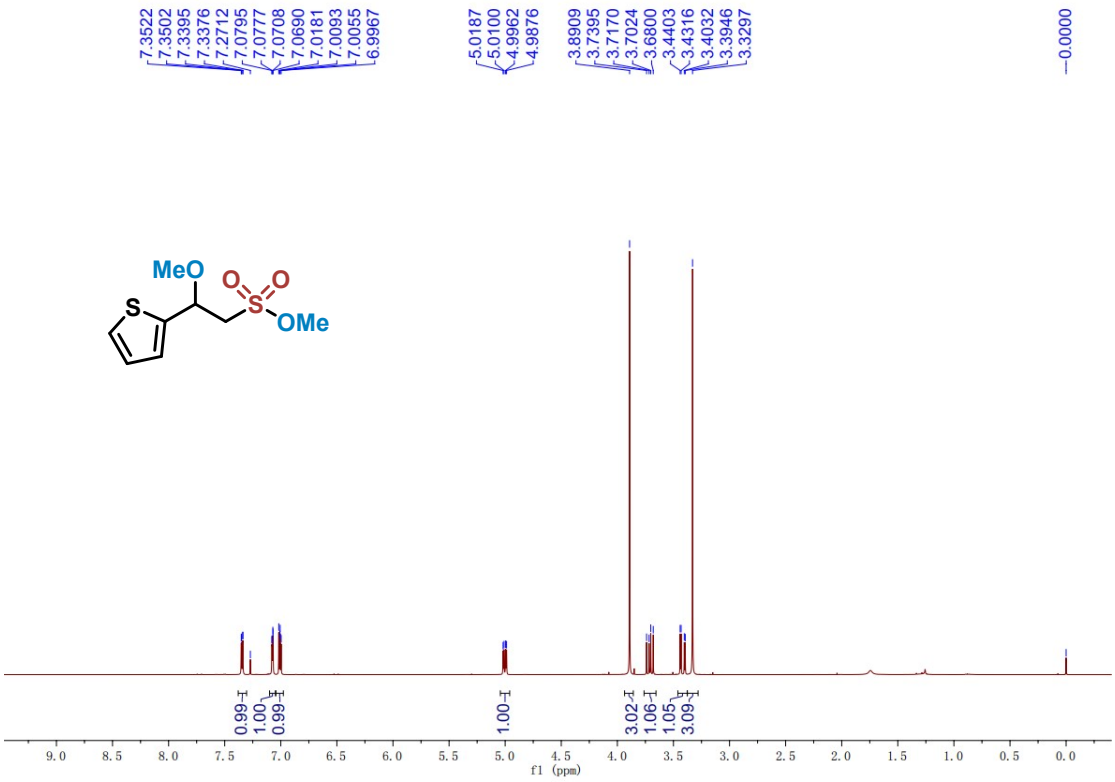
^{1}H NMR spectra of compound **3am** (400MHz, $CDCl_3$)



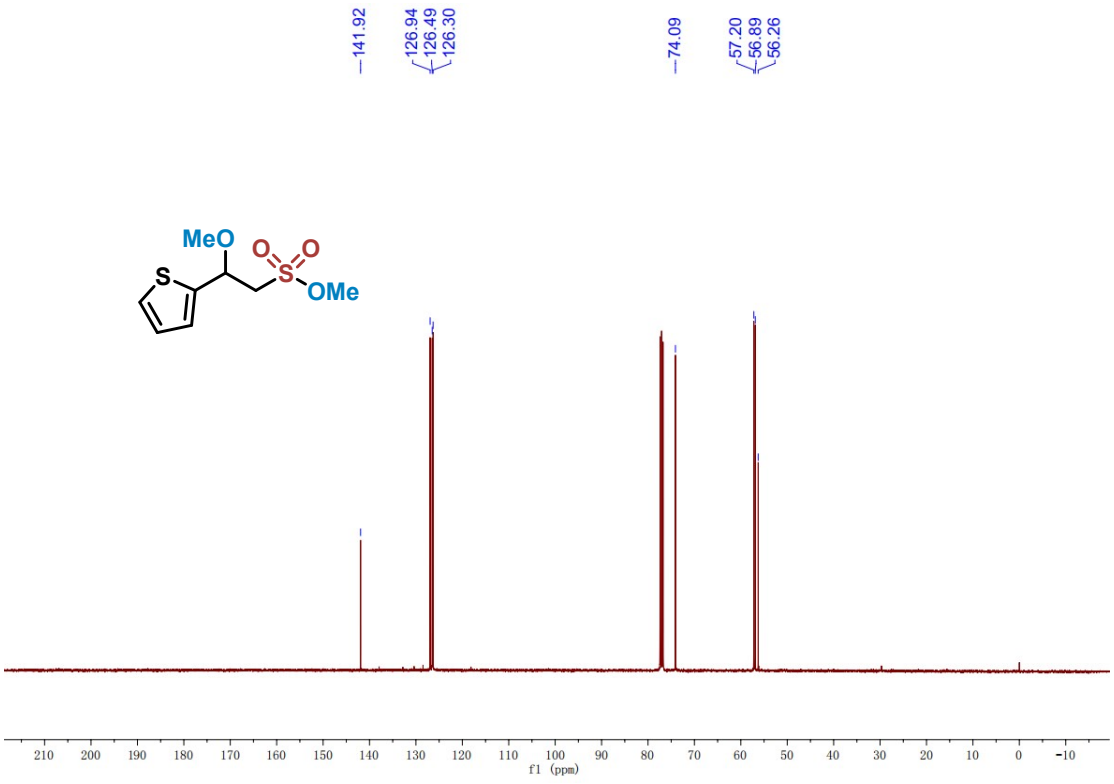
^{13}C NMR spectra of compound **3am** (100MHz, $CDCl_3$)



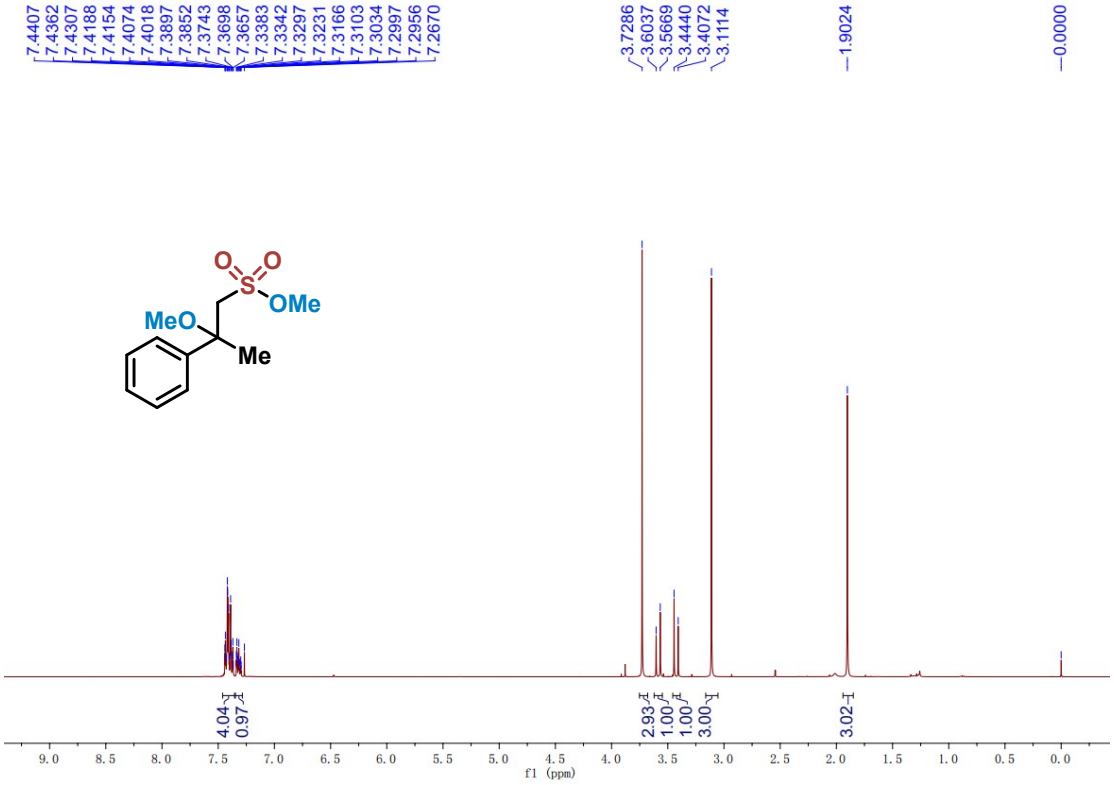
^{1}H NMR spectra of compound **3an** (400MHz, $CDCl_3$)



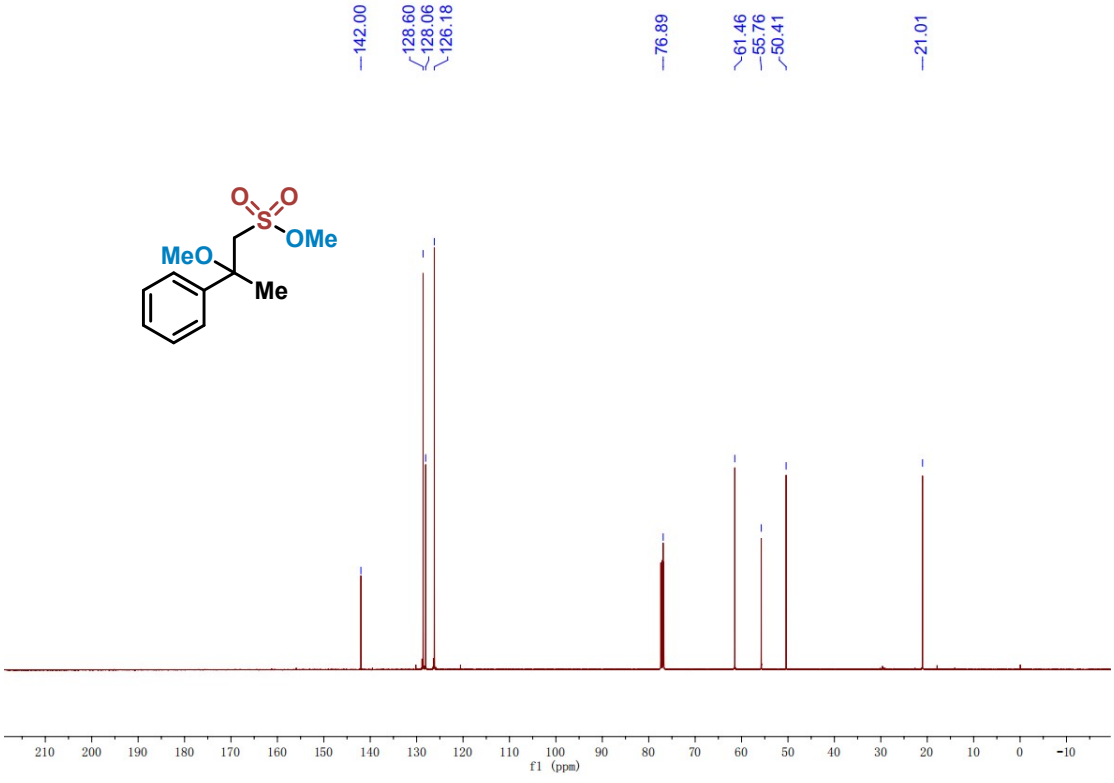
^{13}C NMR spectra of compound **3an** (100MHz, $CDCl_3$)



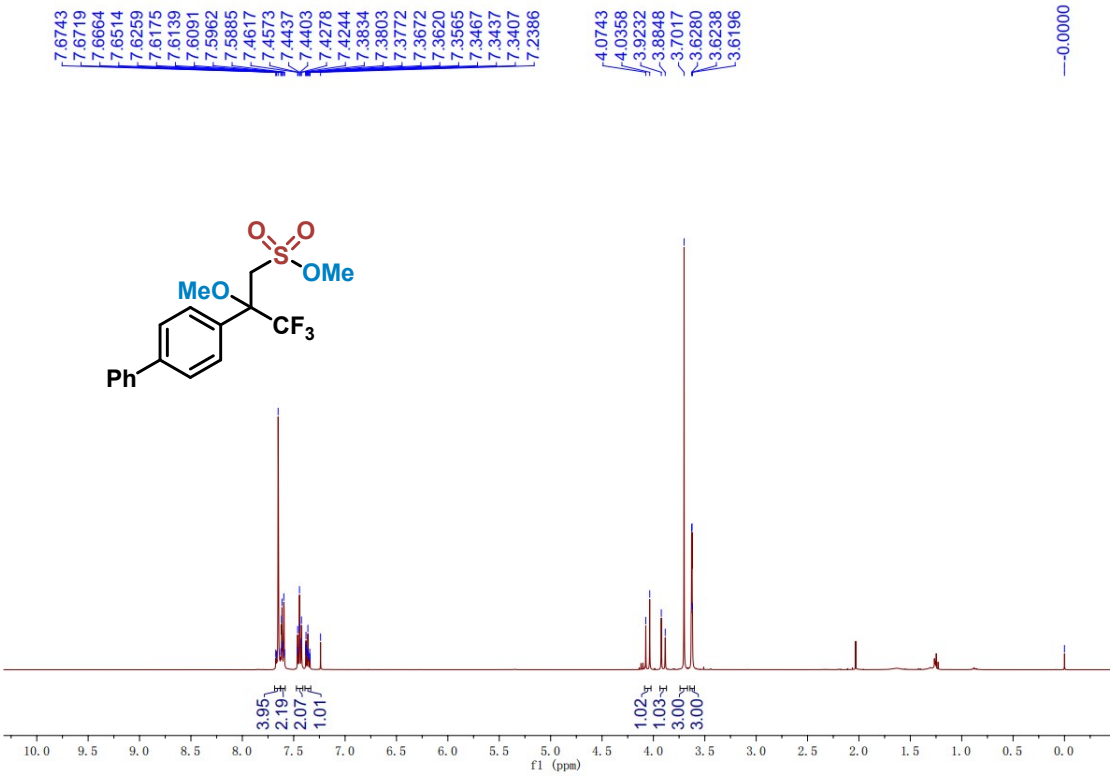
^{1}H NMR spectra of compound **3ao** (400MHz, $CDCl_3$)



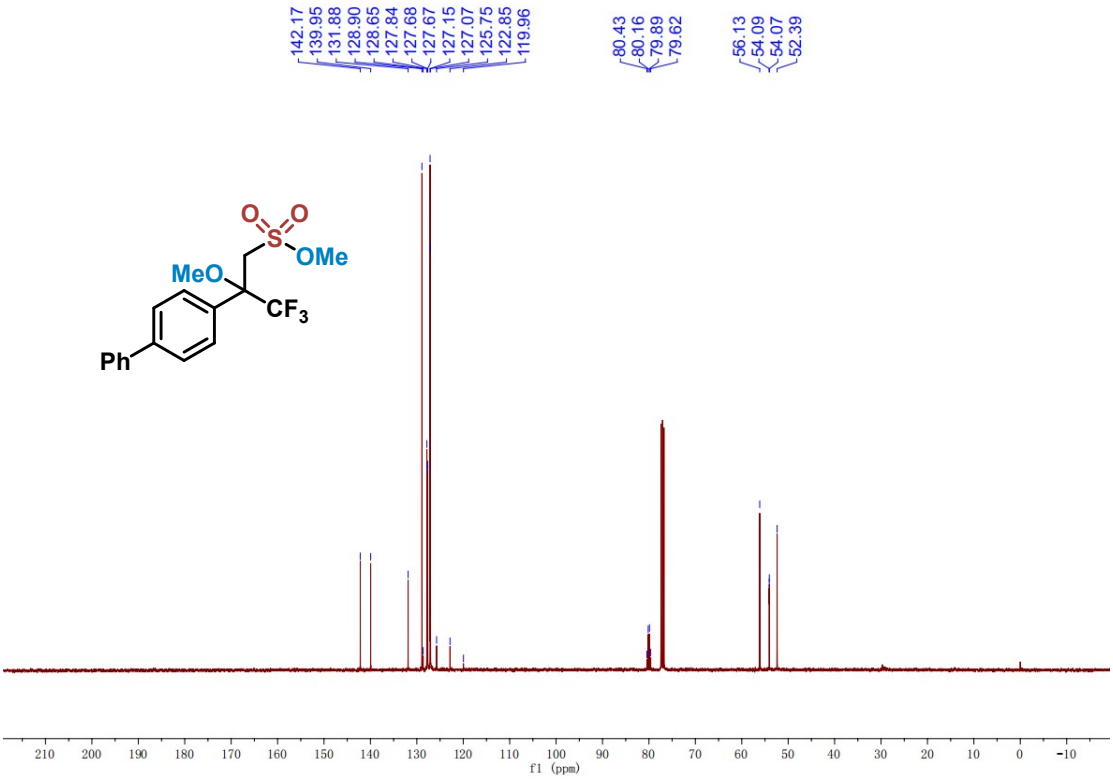
^{13}C NMR spectra of compound **3ao** (100MHz, $CDCl_3$)



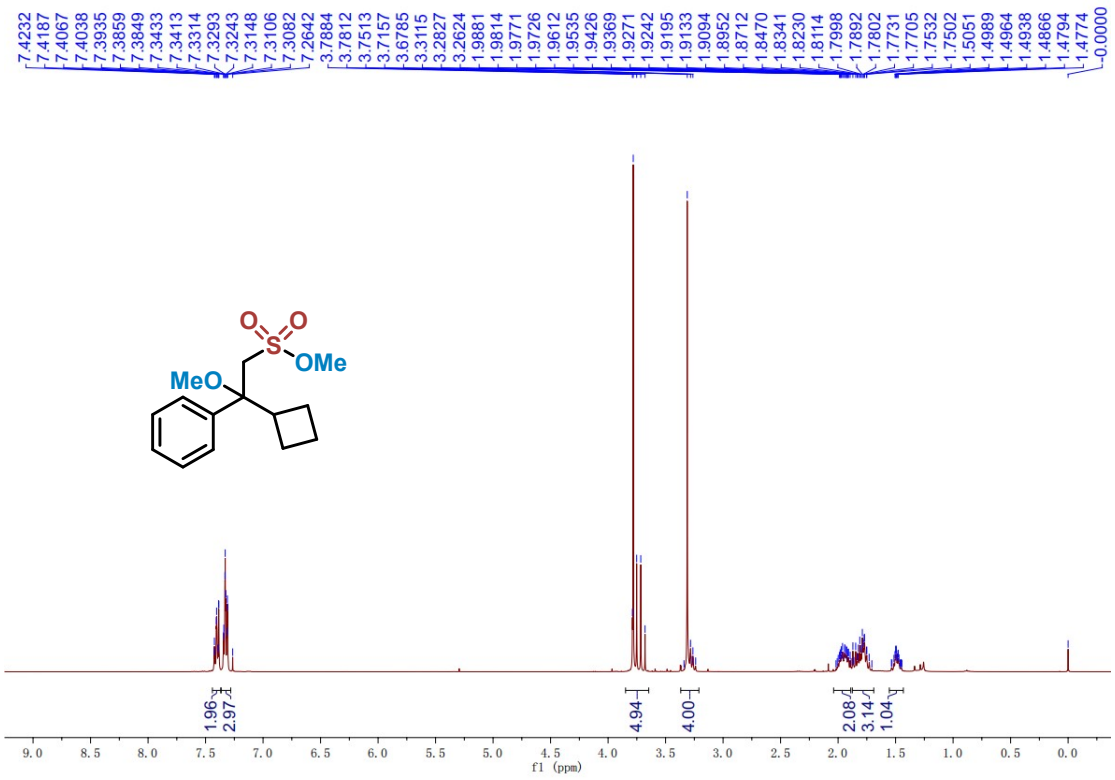
^{1}H NMR spectra of compound **3ap** (400MHz, $CDCl_3$)



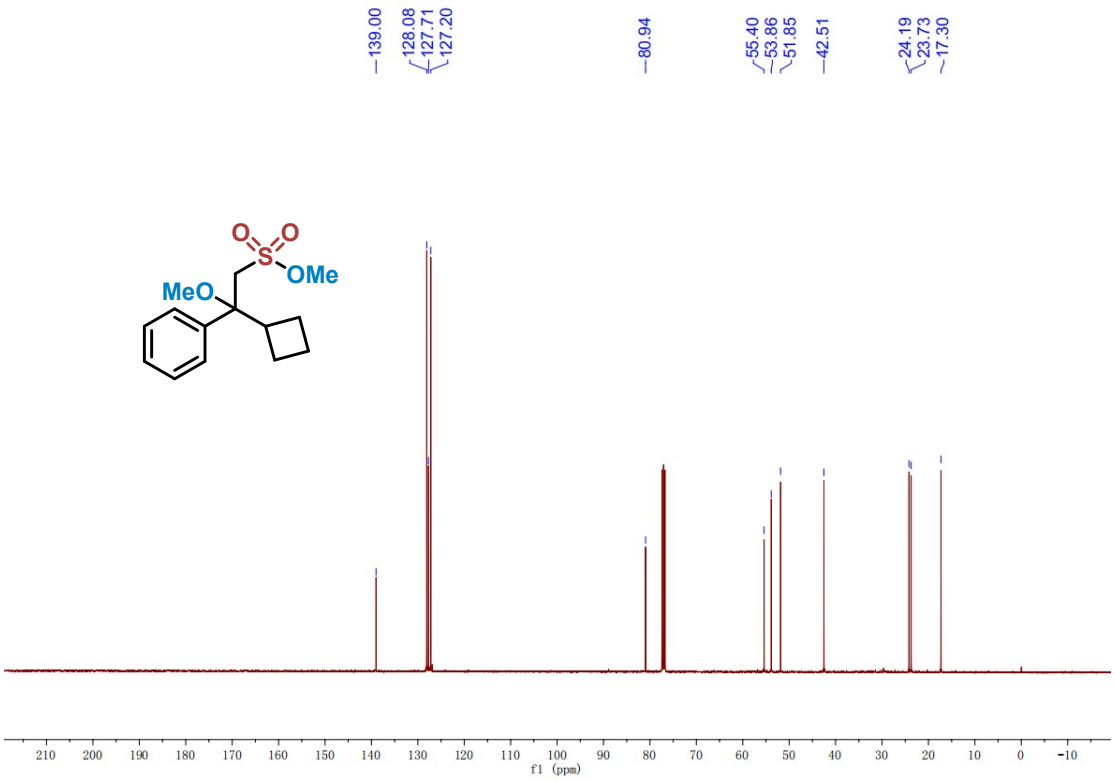
^{13}C NMR spectra of compound **3ap** (100MHz, $CDCl_3$)



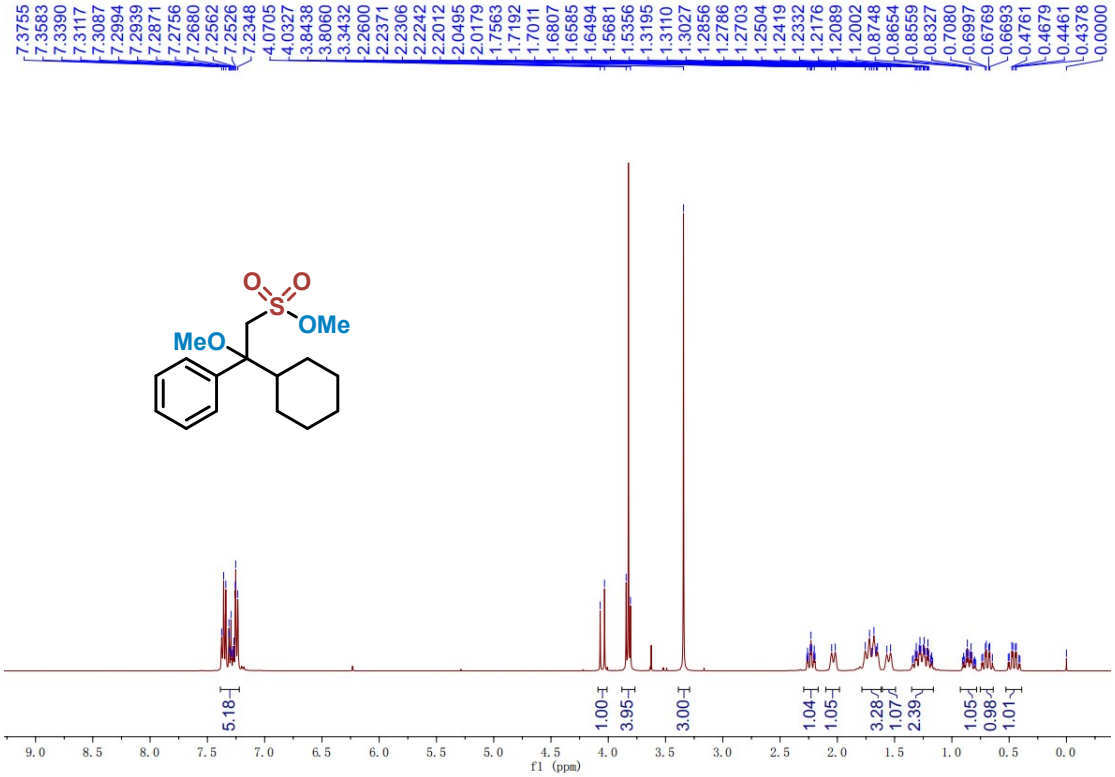
^{1}H NMR spectra of compound **3aq** (400MHz, $CDCl_3$)



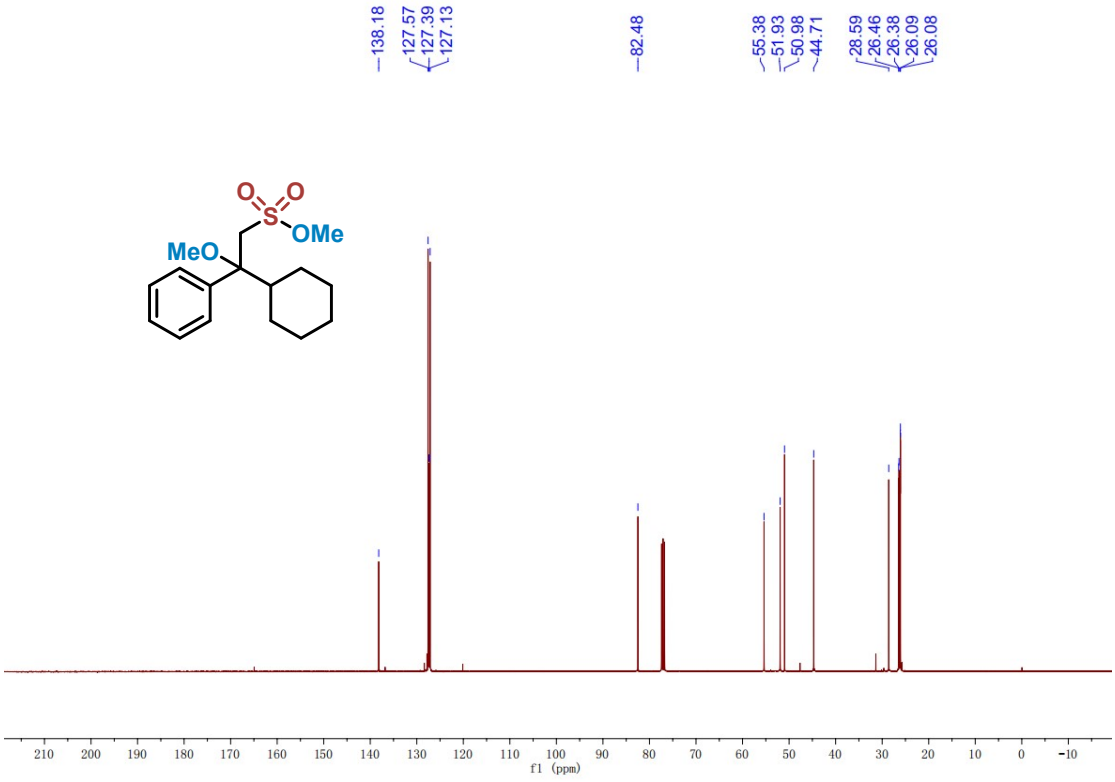
^{13}C NMR spectra of compound **3aq** (100MHz, $CDCl_3$)



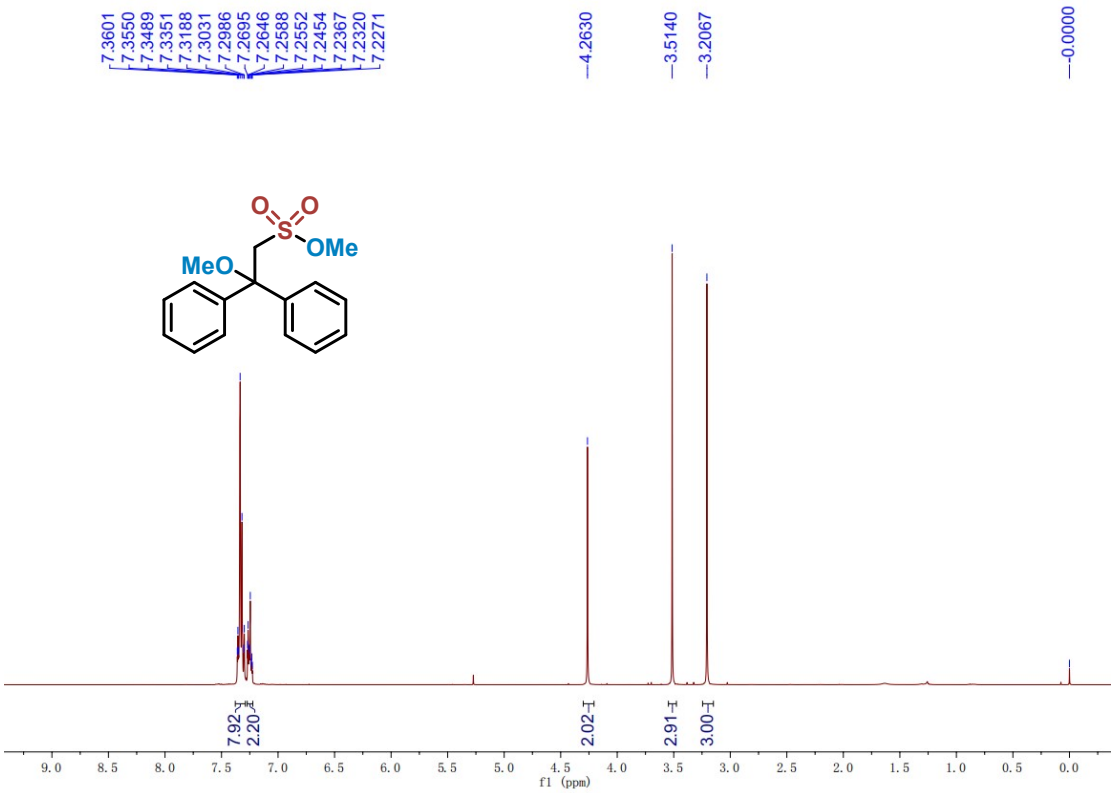
^{1}H NMR spectra of compound **3ar** (400MHz, $CDCl_3$)



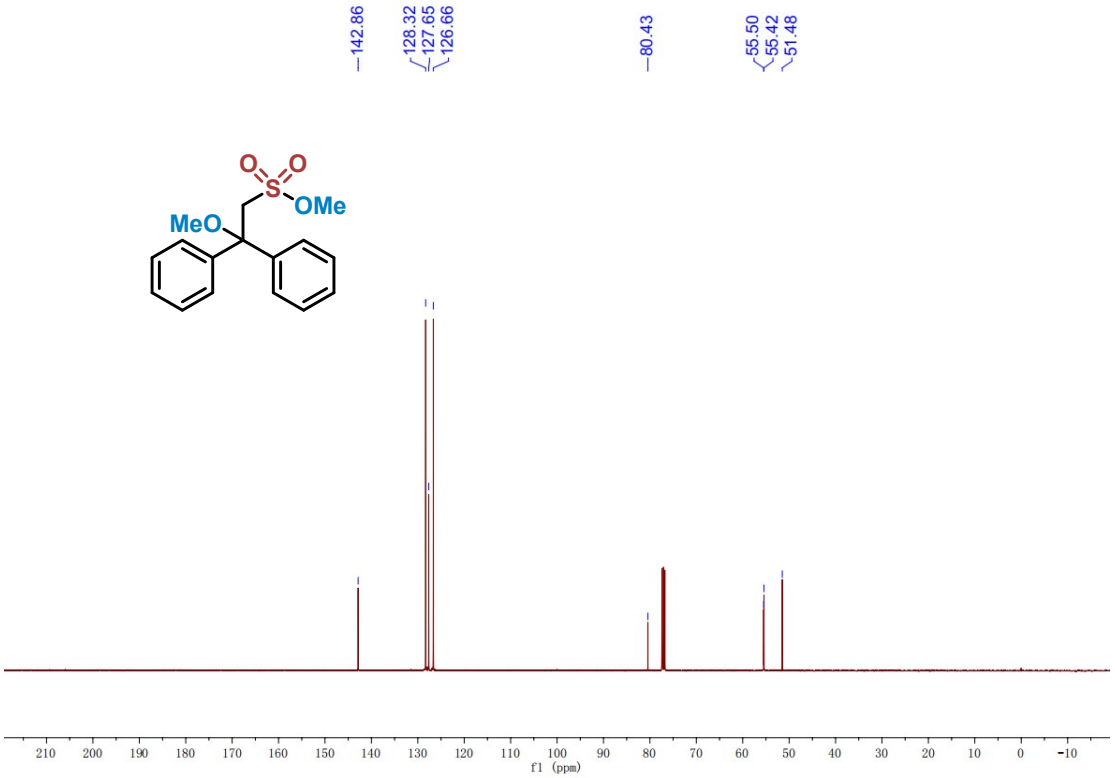
^{13}C NMR spectra of compound **3ar** (100MHz, $CDCl_3$)



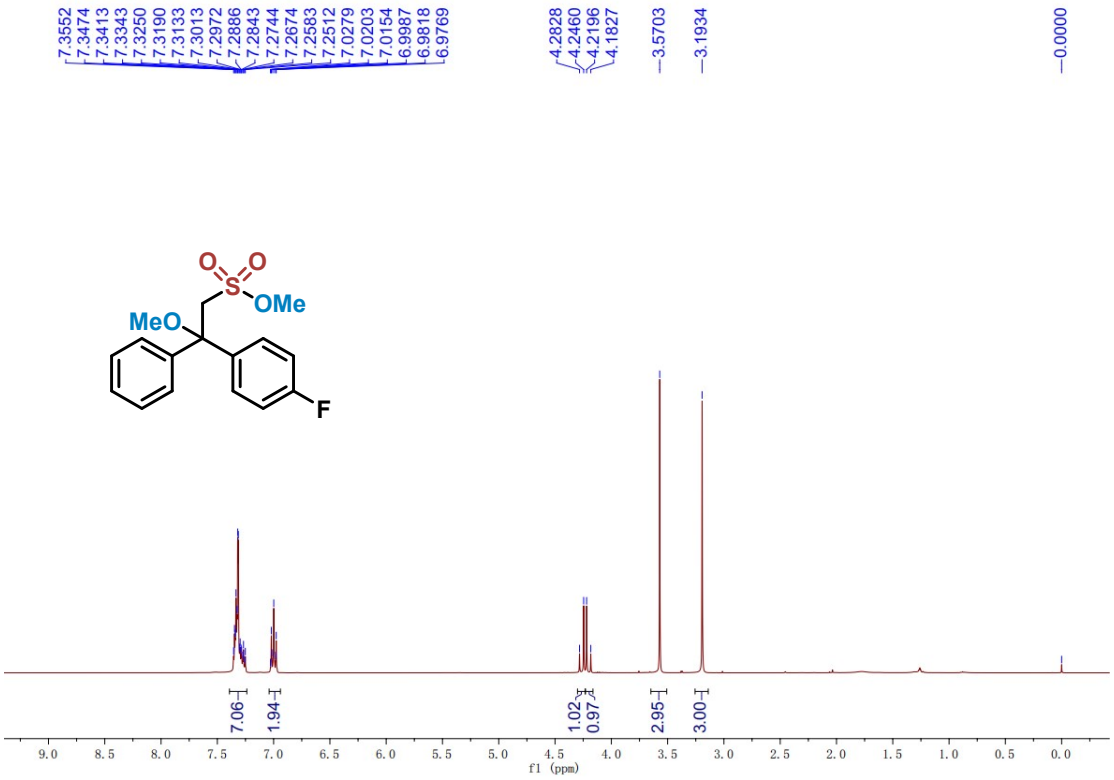
^{1}H NMR spectra of compound **3as** (400MHz, $CDCl_3$)



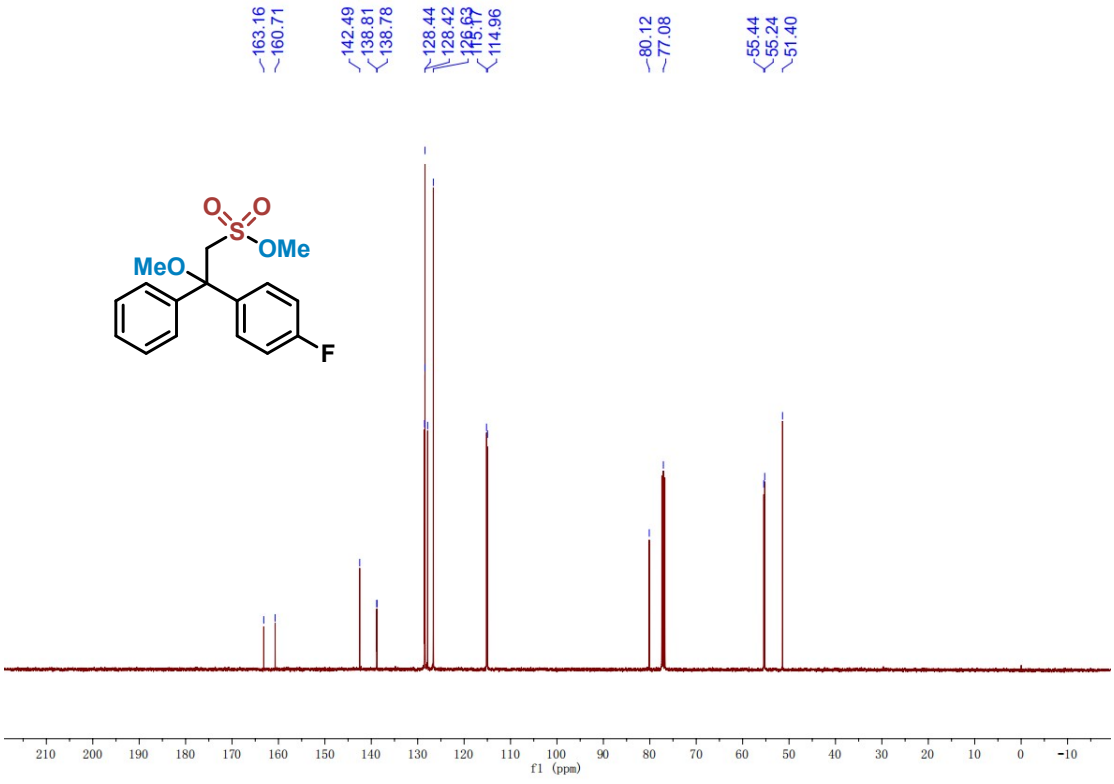
^{13}C NMR spectra of compound **3as** (100MHz, $CDCl_3$)



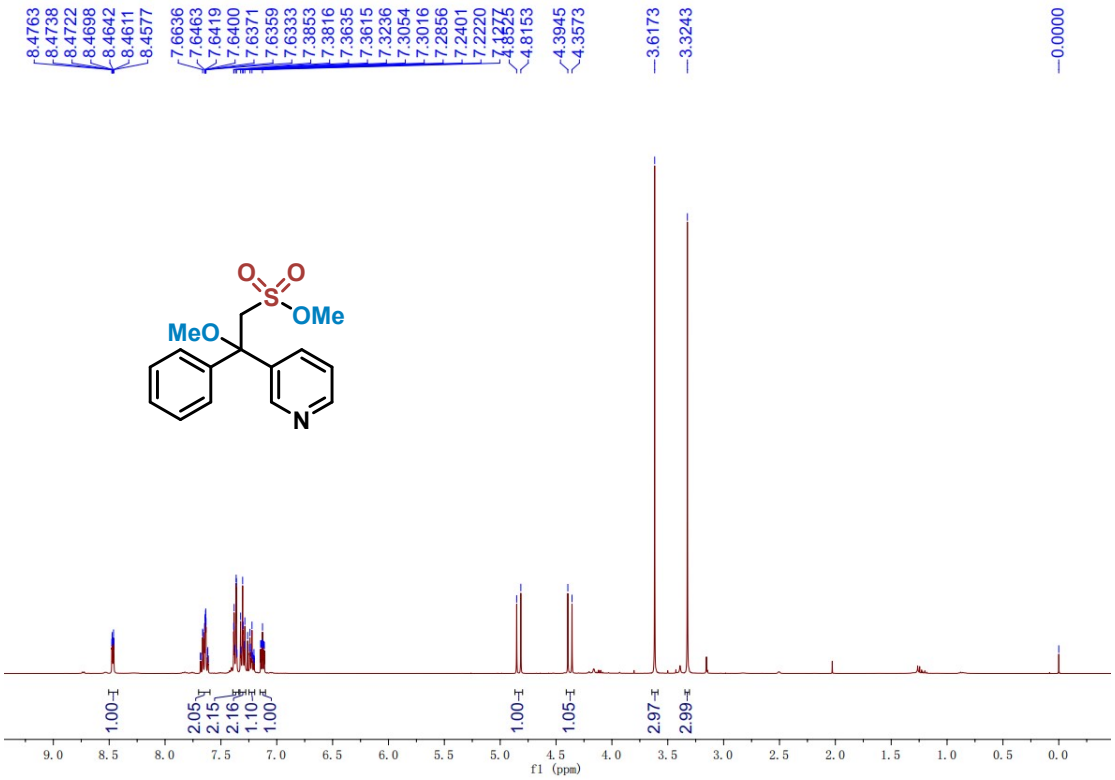
^{1}H NMR spectra of compound **3at** (400MHz, $CDCl_3$)



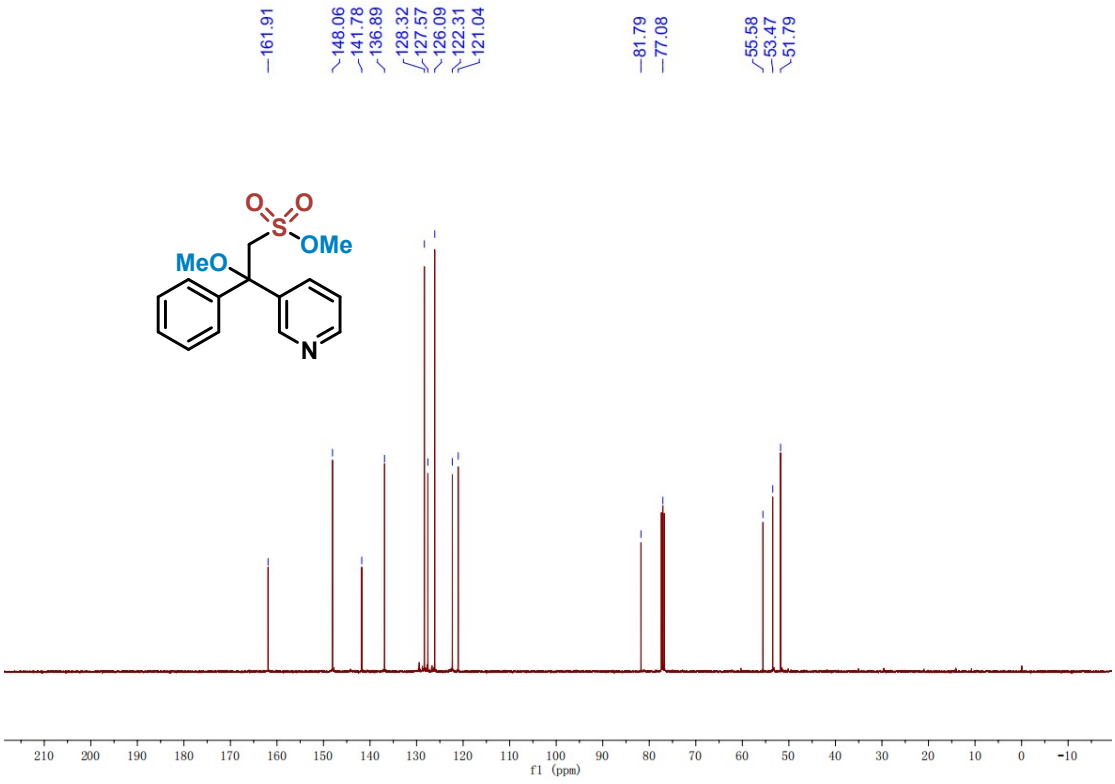
^{13}C NMR spectra of compound **3at** (100MHz, $CDCl_3$)



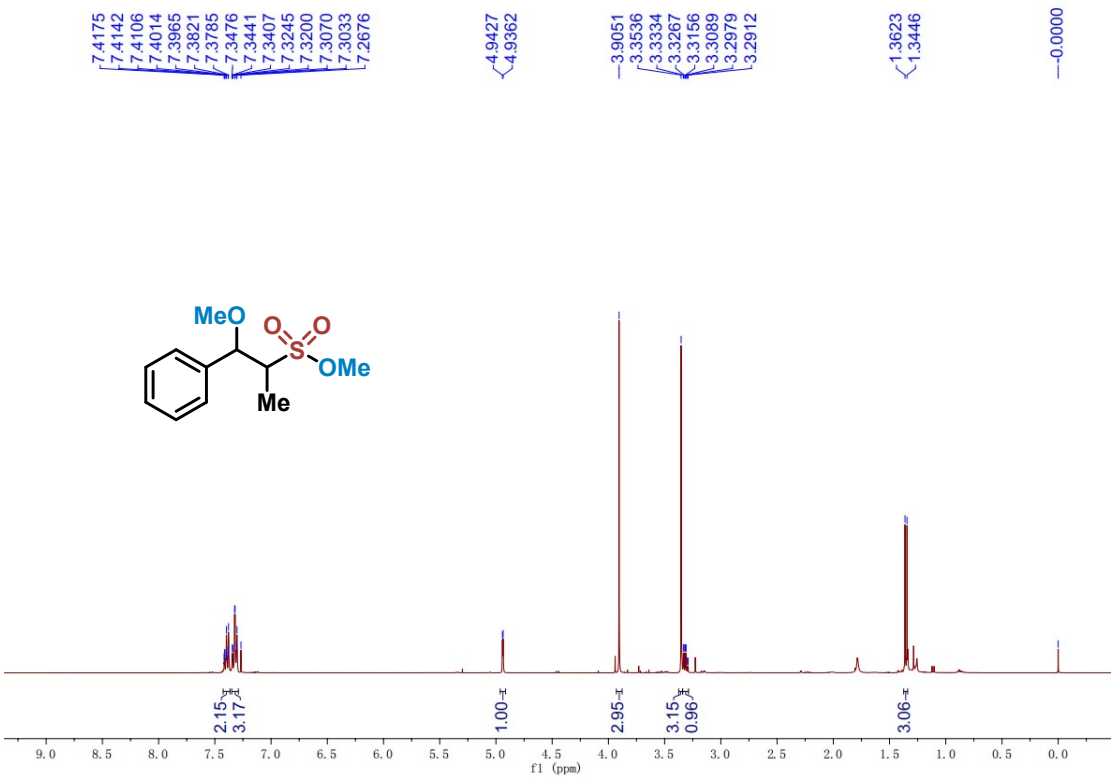
^{1}H NMR spectra of compound **3au** (400MHz, $CDCl_3$)



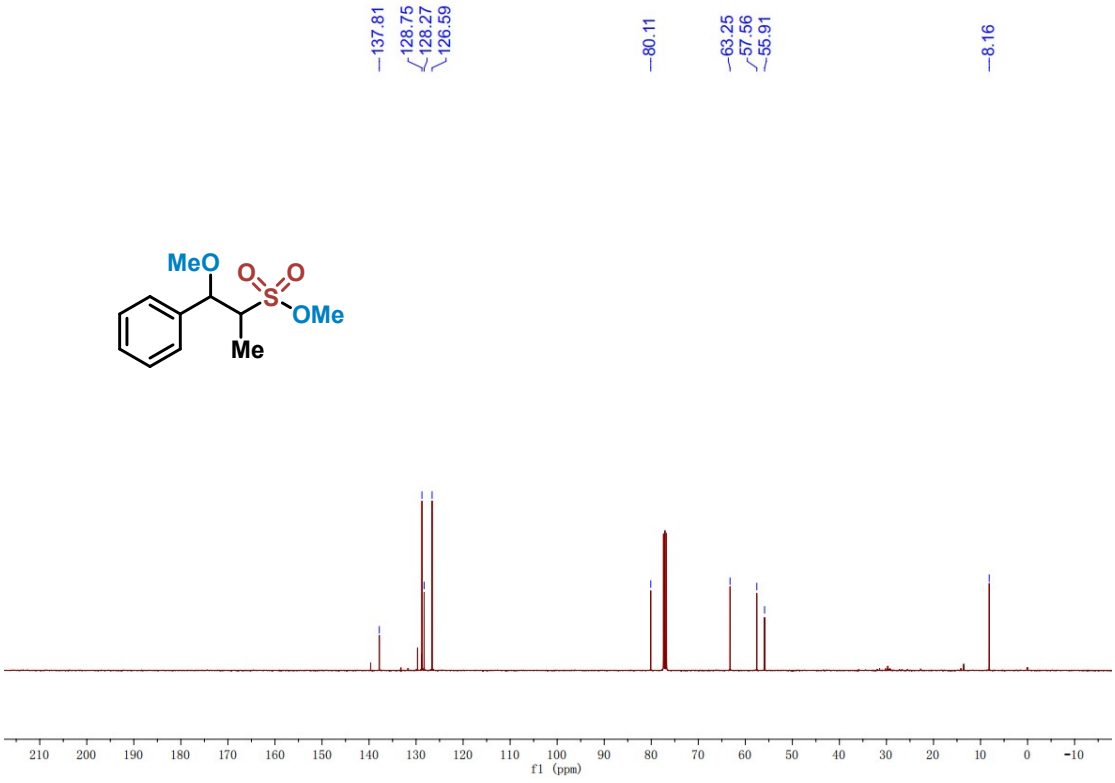
^{13}C NMR spectra of compound **3au** (100MHz, $CDCl_3$)



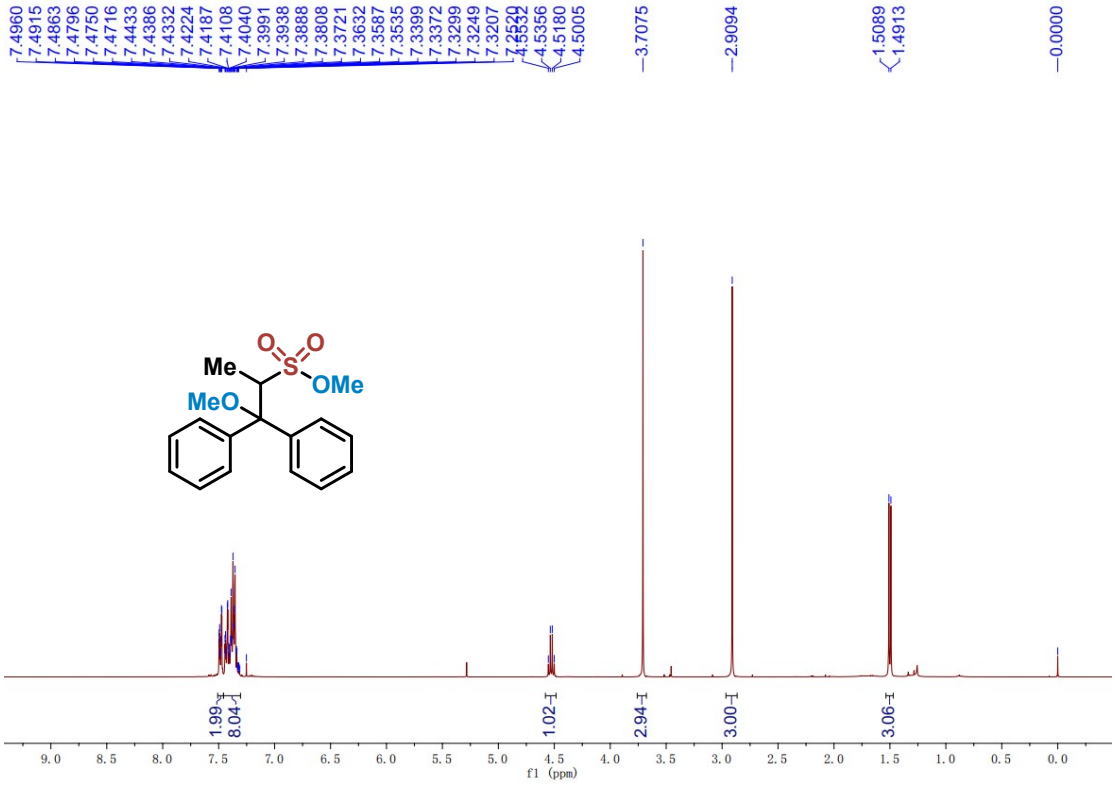
^{1}H NMR spectra of compound **3av** (400MHz, $CDCl_3$)



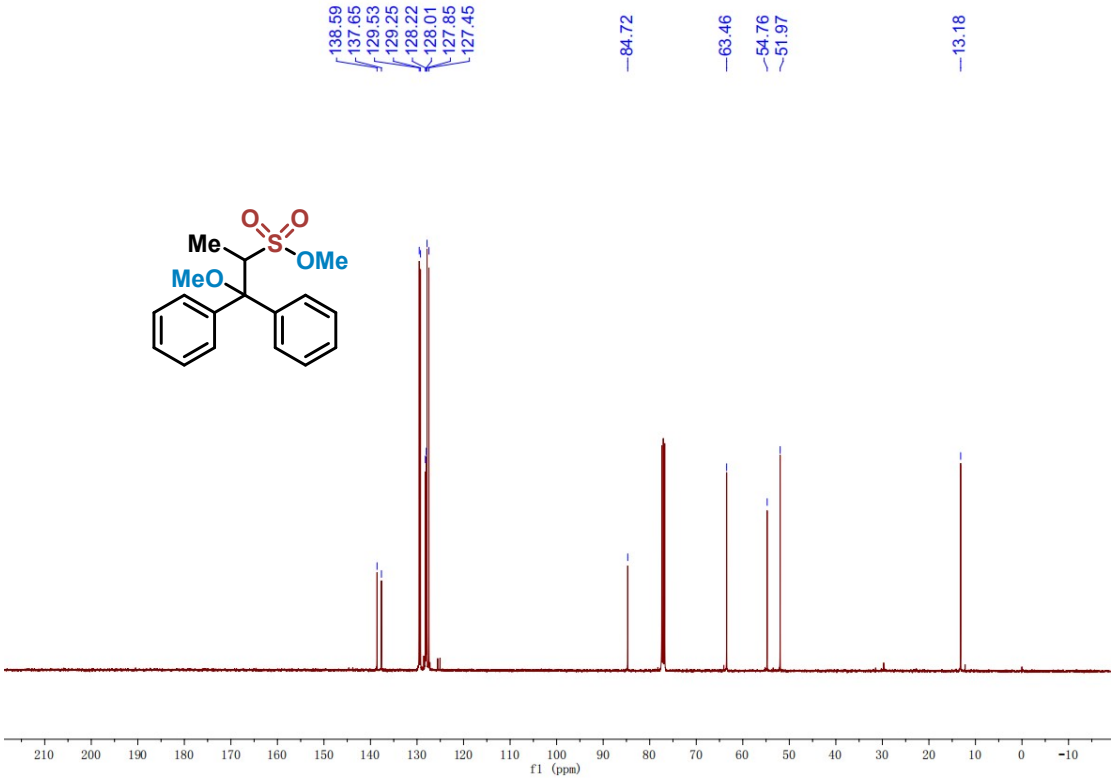
^{13}C NMR spectra of compound **3av** (100MHz, $CDCl_3$)



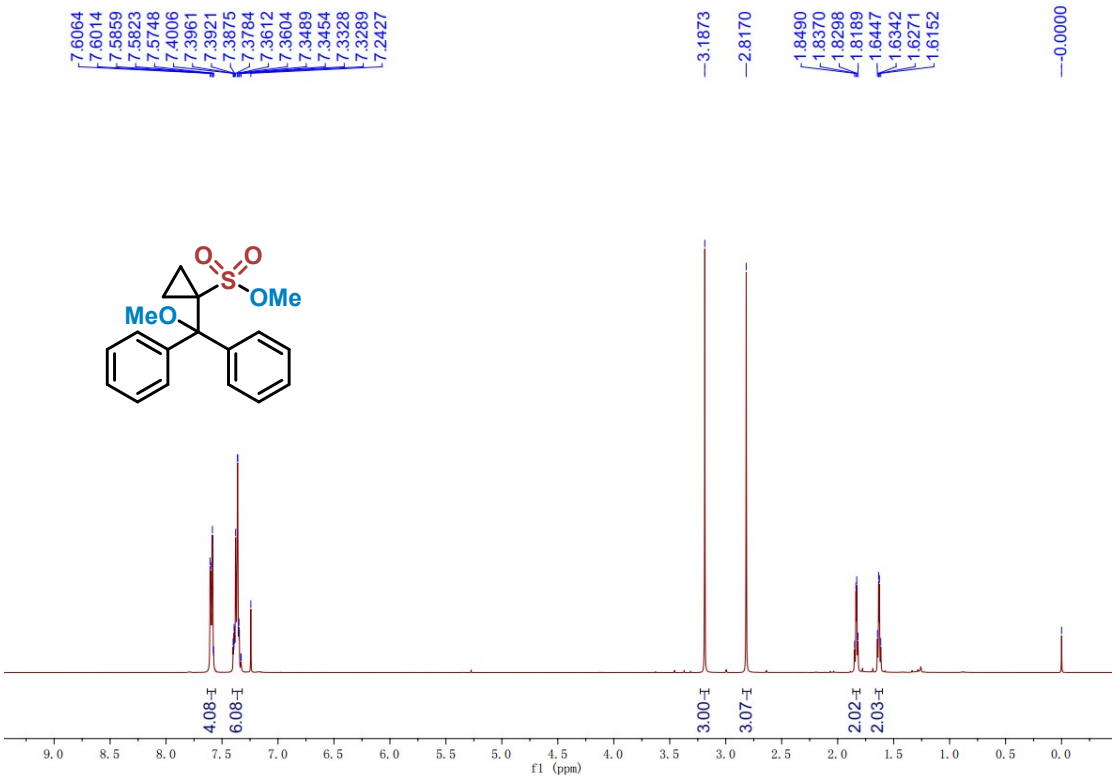
^{1}H NMR spectra of compound **3aw** (400MHz, $CDCl_3$)



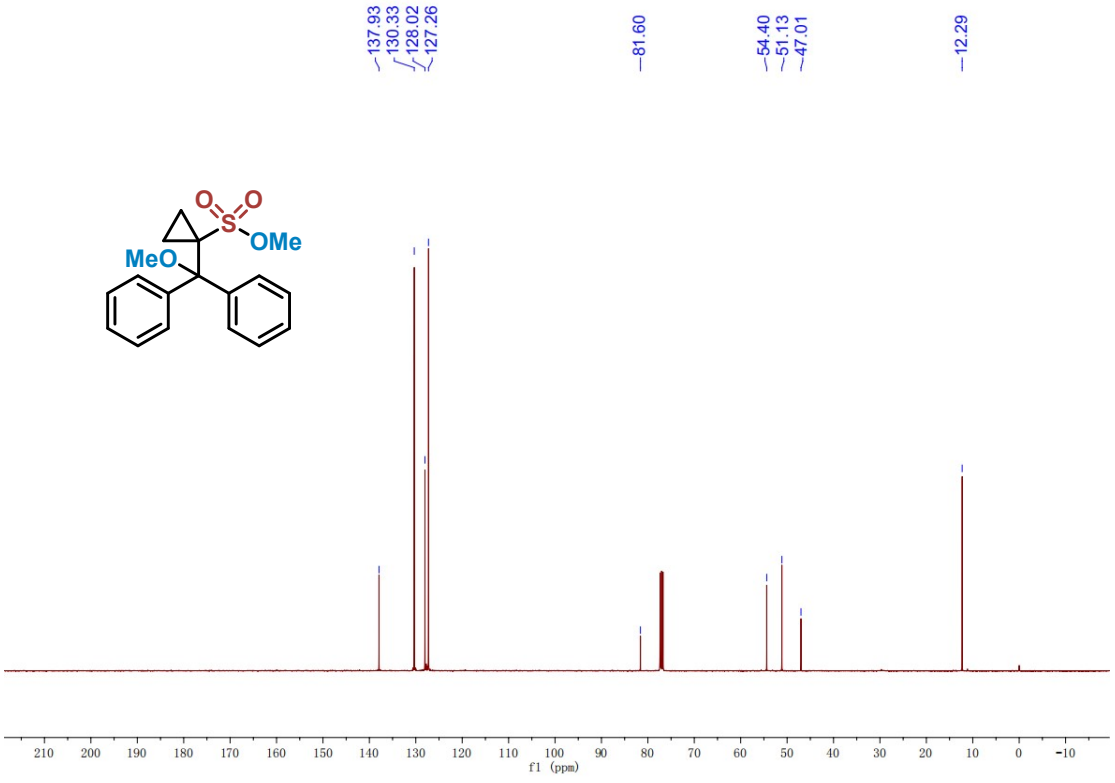
^{13}C NMR spectra of compound **3aw** (100MHz, $CDCl_3$)



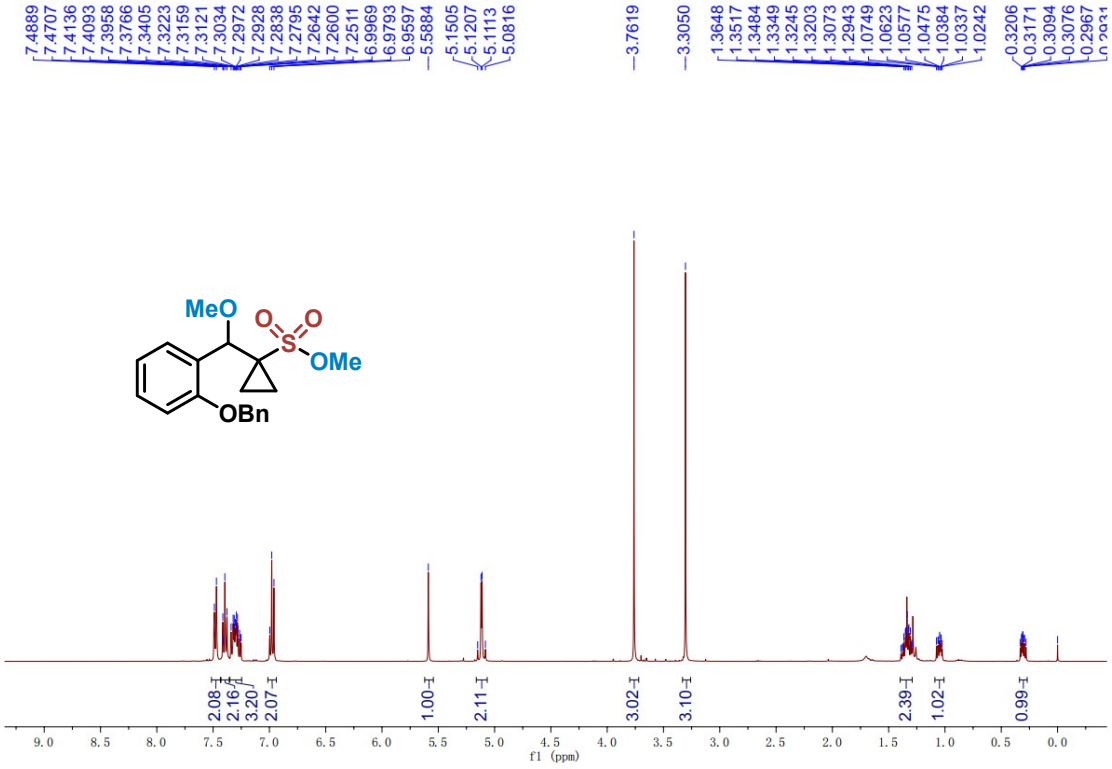
^{1}H NMR spectra of compound **3ax** (400MHz, $CDCl_3$)



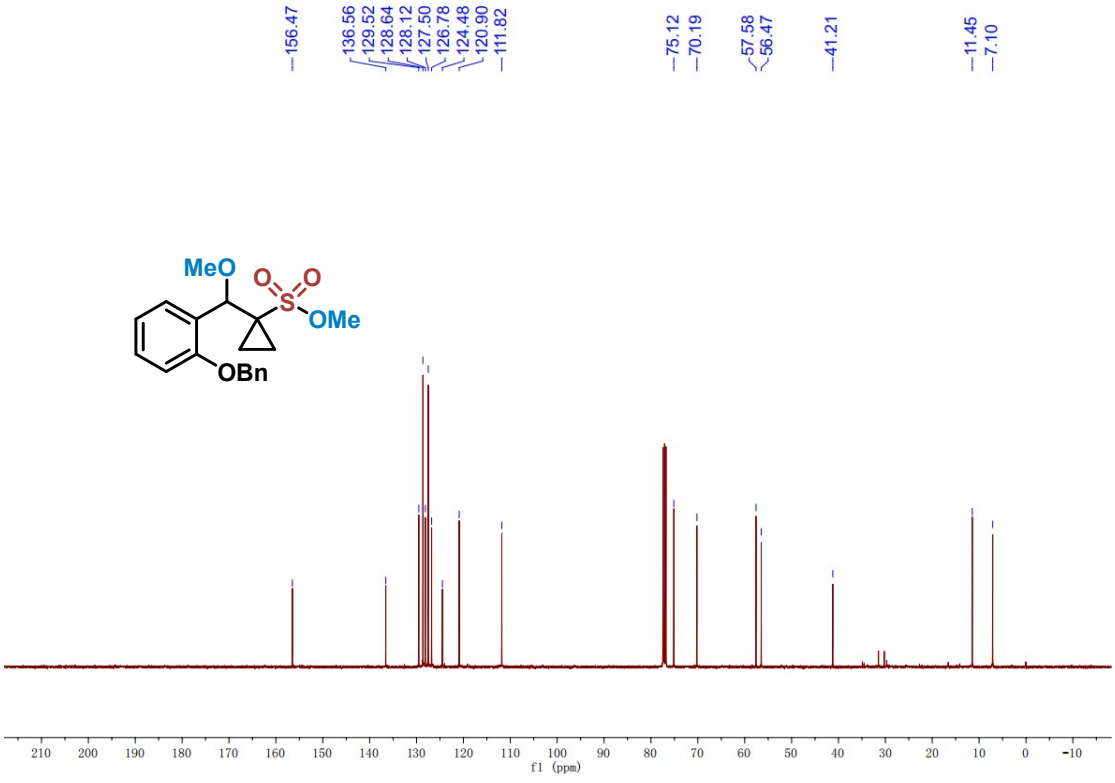
^{13}C NMR spectra of compound **3ax** (100MHz, $CDCl_3$)



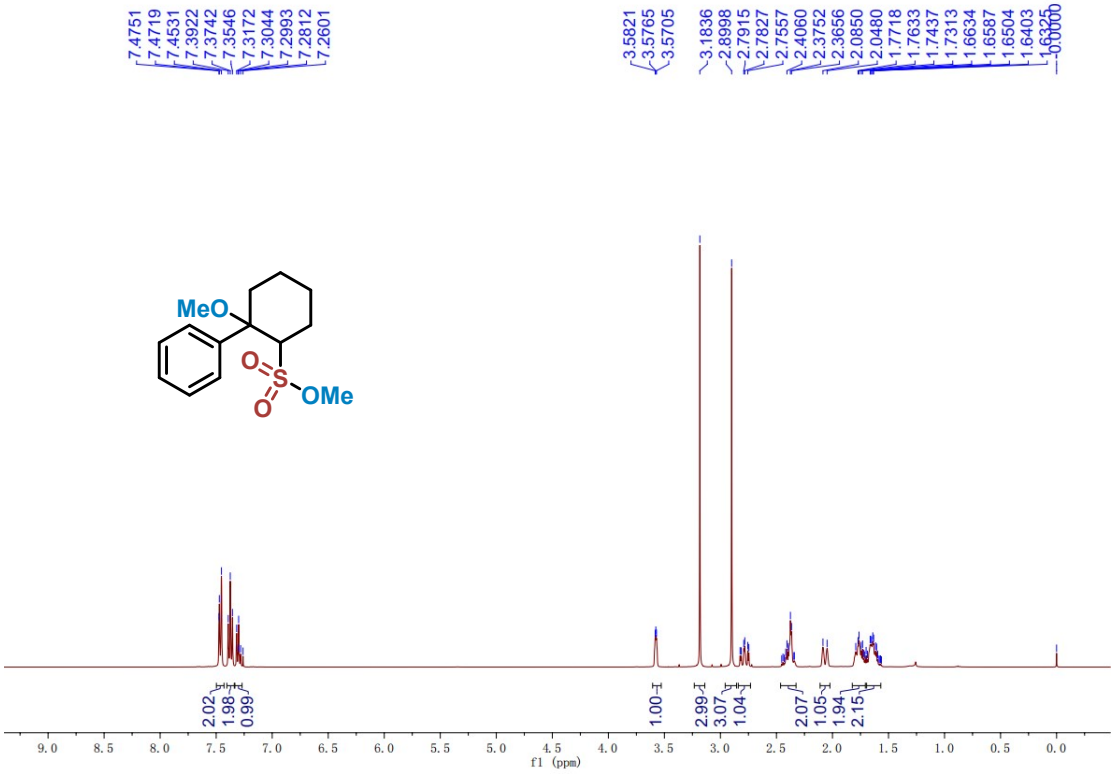
^{1}H NMR spectra of compound **3ay** (400MHz, $CDCl_3$)



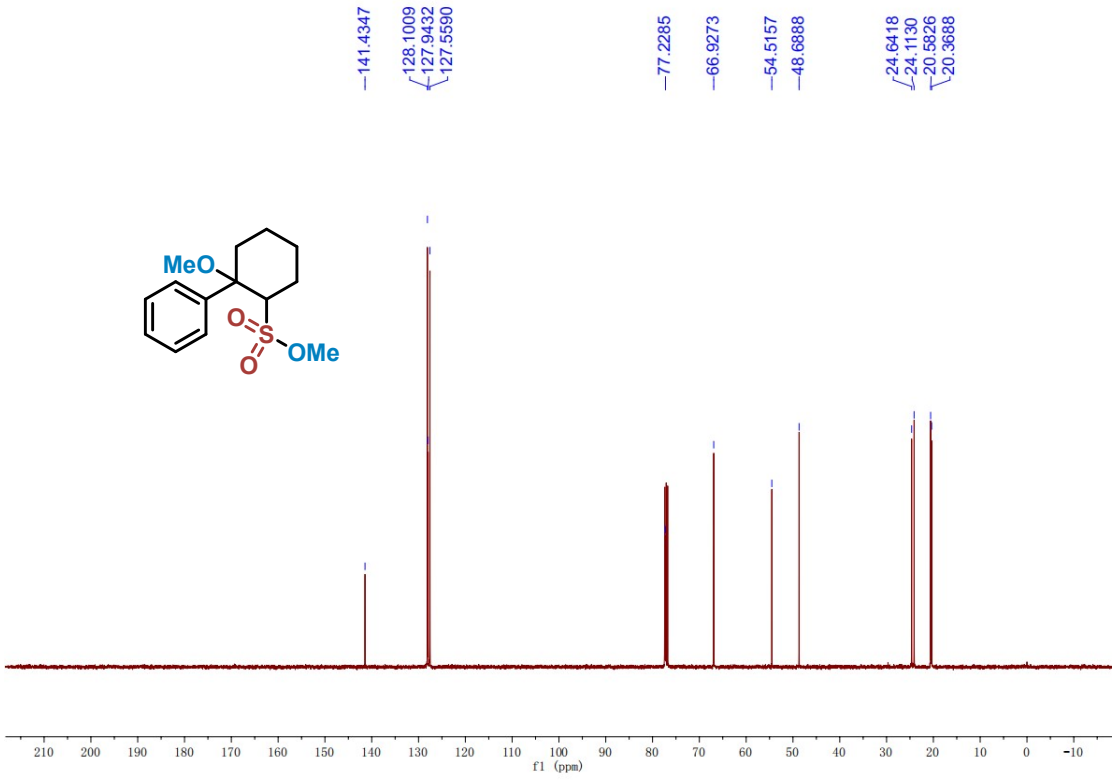
^{13}C NMR spectra of compound **3ay** (100MHz, $CDCl_3$)



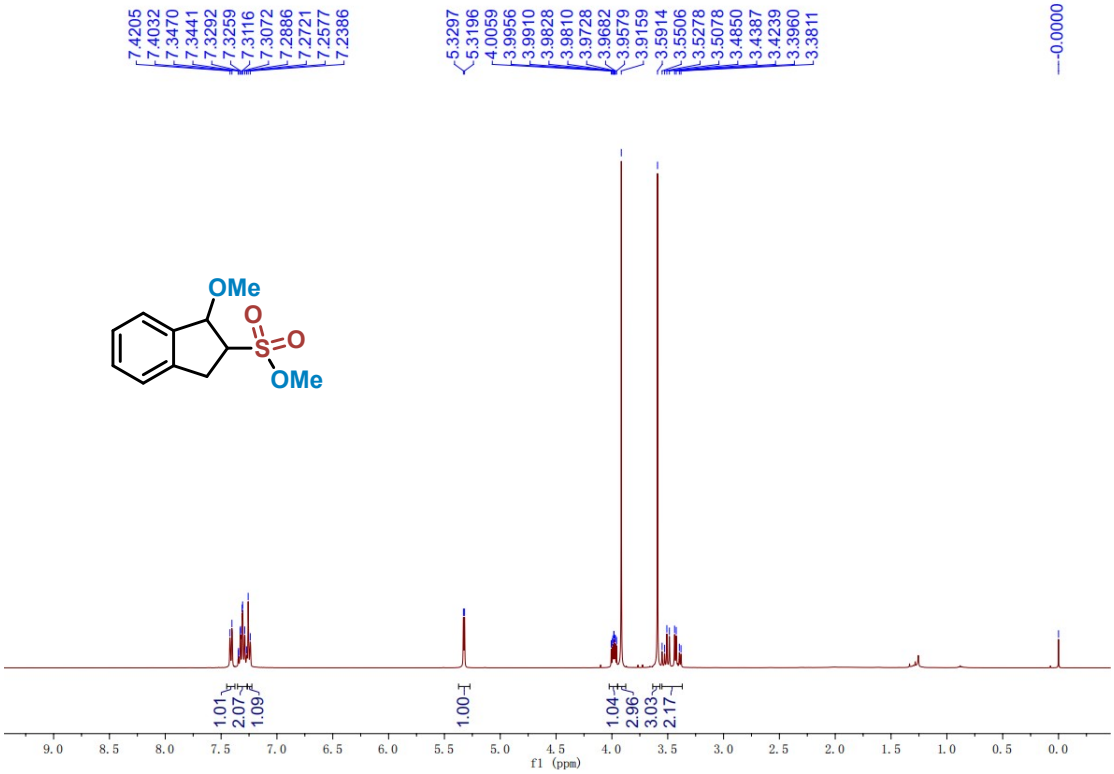
^{1}H NMR spectra of compound **3az** (400MHz, $CDCl_3$)



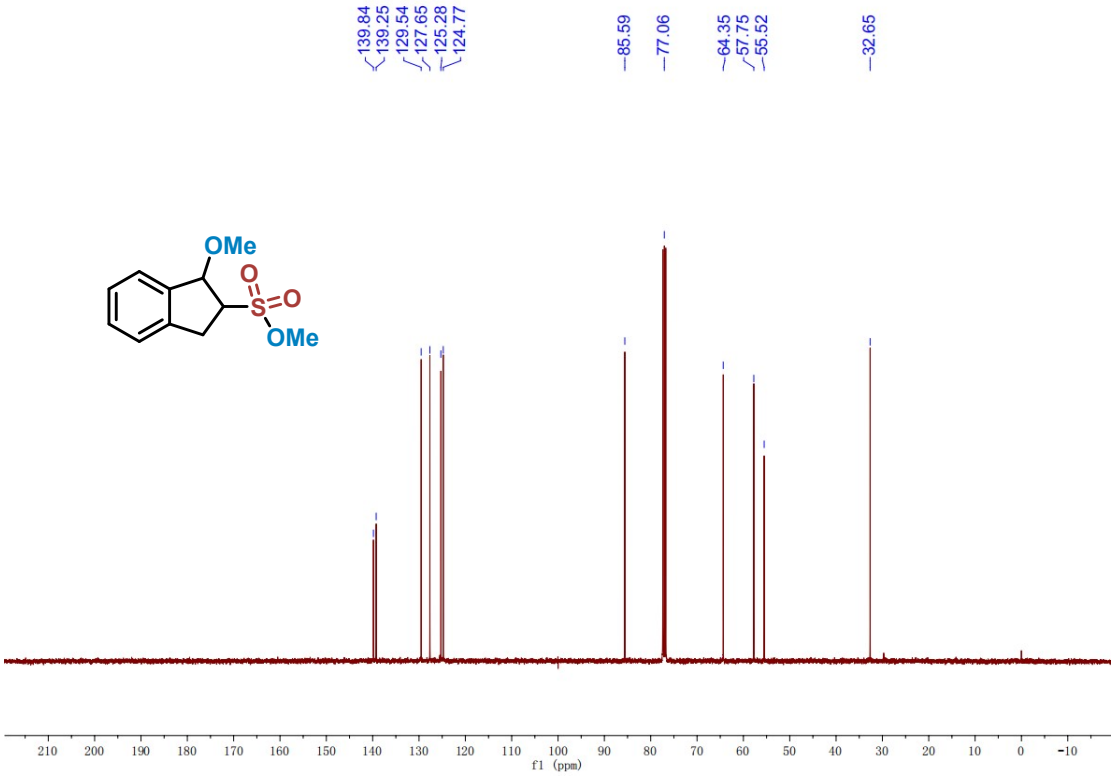
^{13}C NMR spectra of compound **3az** (100MHz, $CDCl_3$)



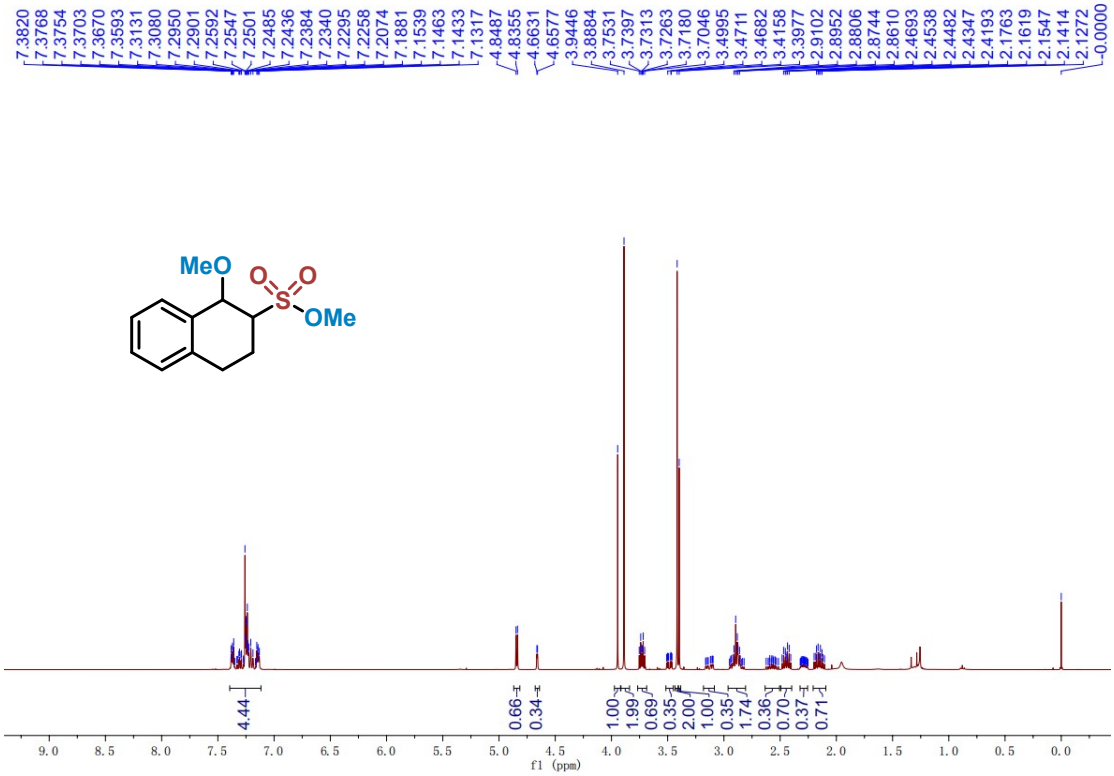
^{1}H NMR spectra of compound **3ba** (400MHz, $CDCl_3$)



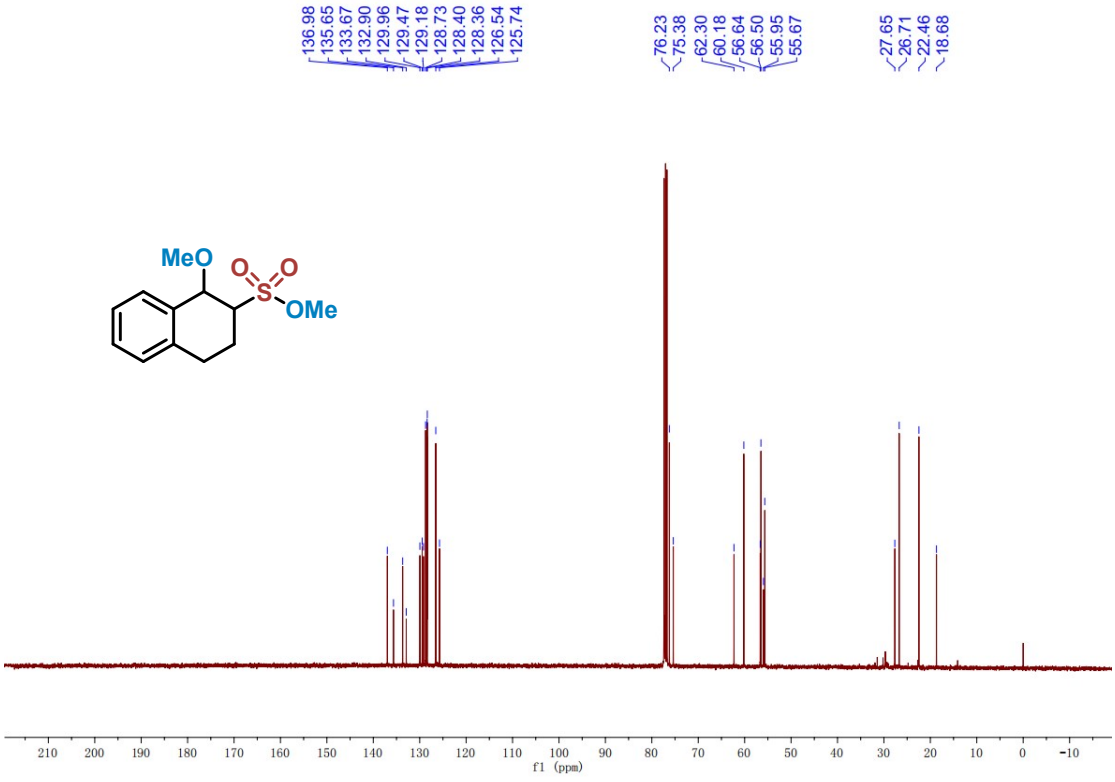
^{13}C NMR spectra of compound **3ba** (100MHz, $CDCl_3$)



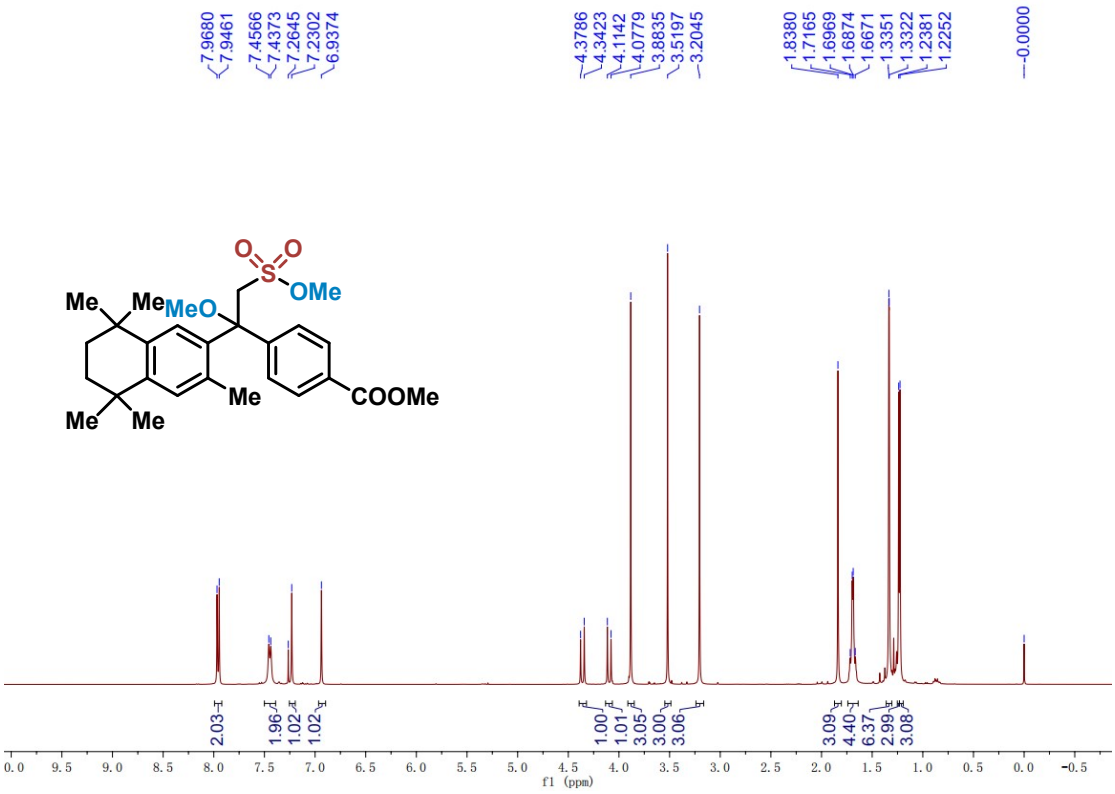
^{1}H NMR spectra of compound **3bb** (400MHz, $CDCl_3$)



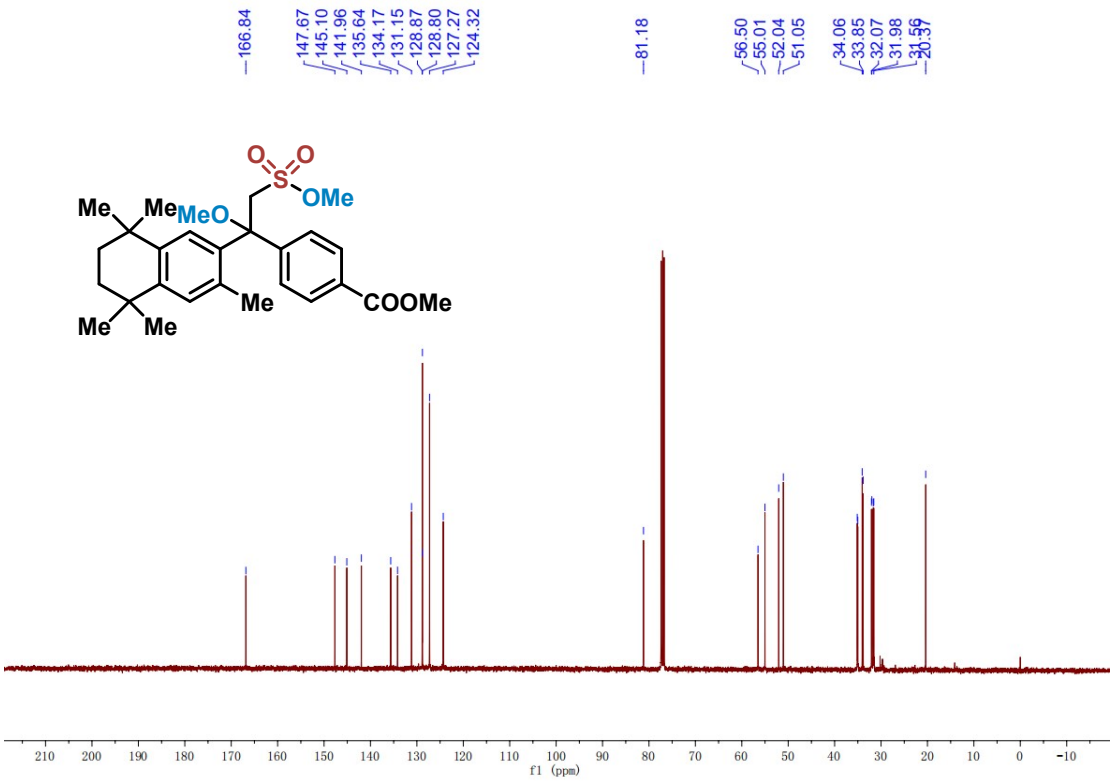
^{13}C NMR spectra of compound **3bb** (100MHz, $CDCl_3$)



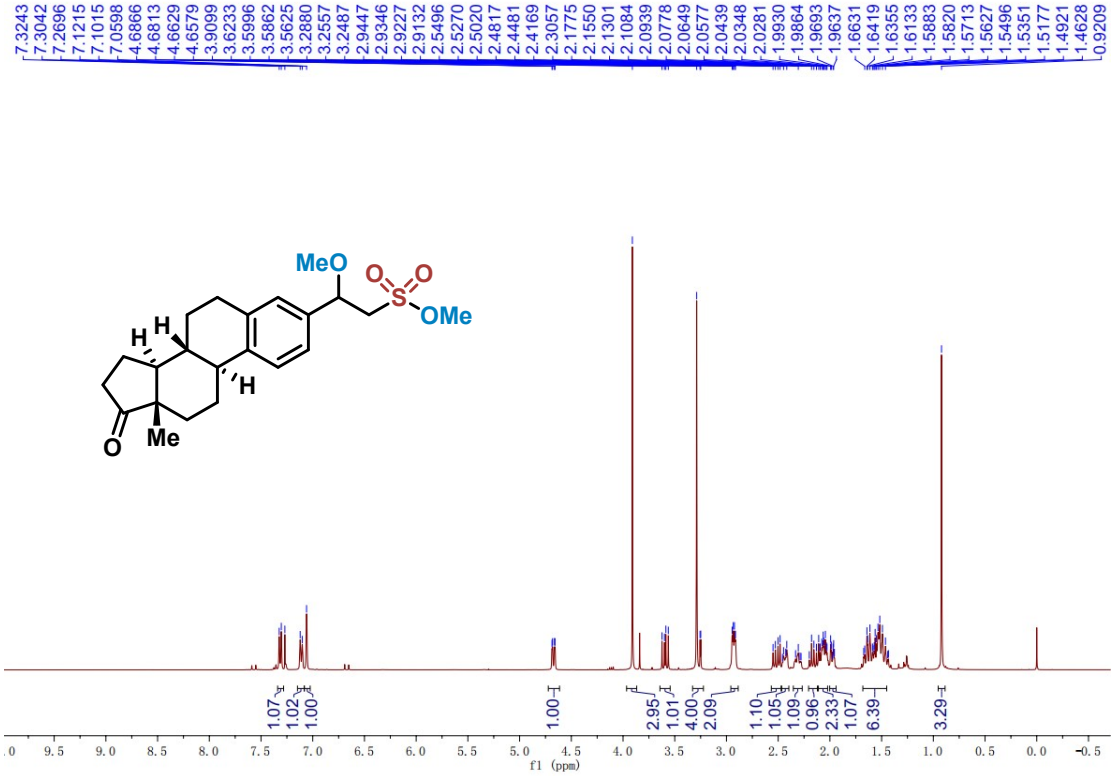
^{1}H NMR spectra of compound **3bc** (400MHz, $CDCl_3$)



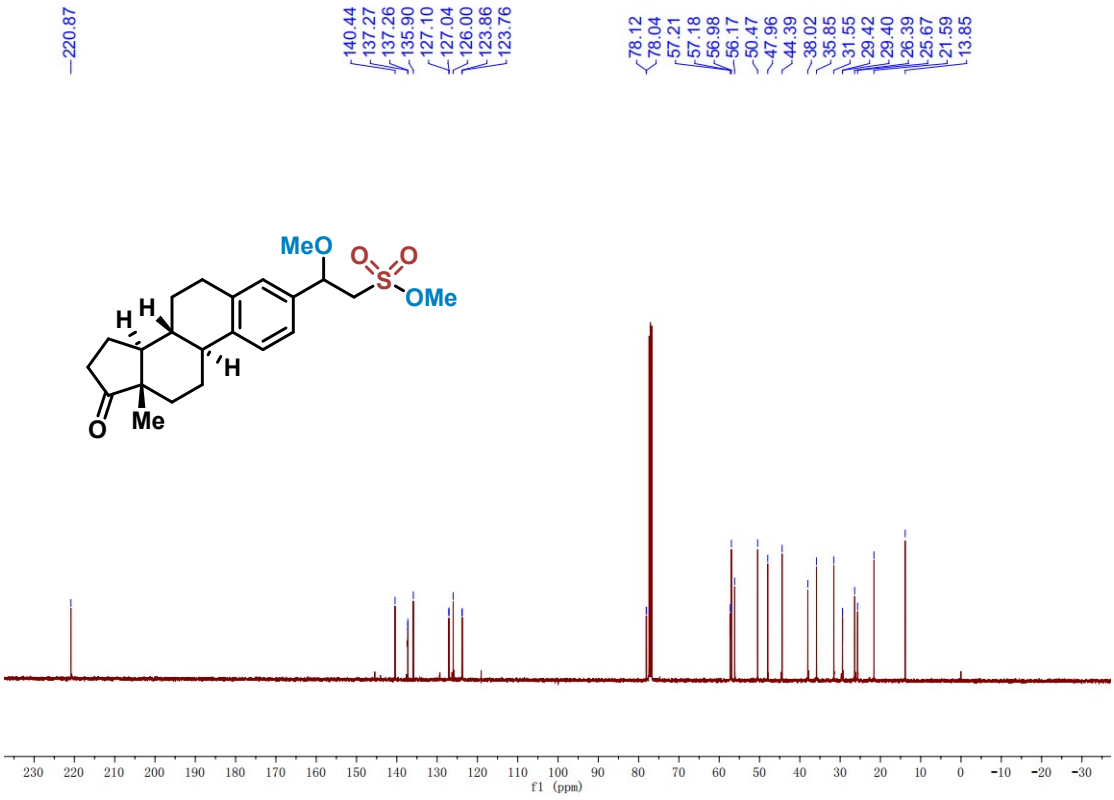
^{13}C NMR spectra of compound **3bc** (100MHz, $CDCl_3$)



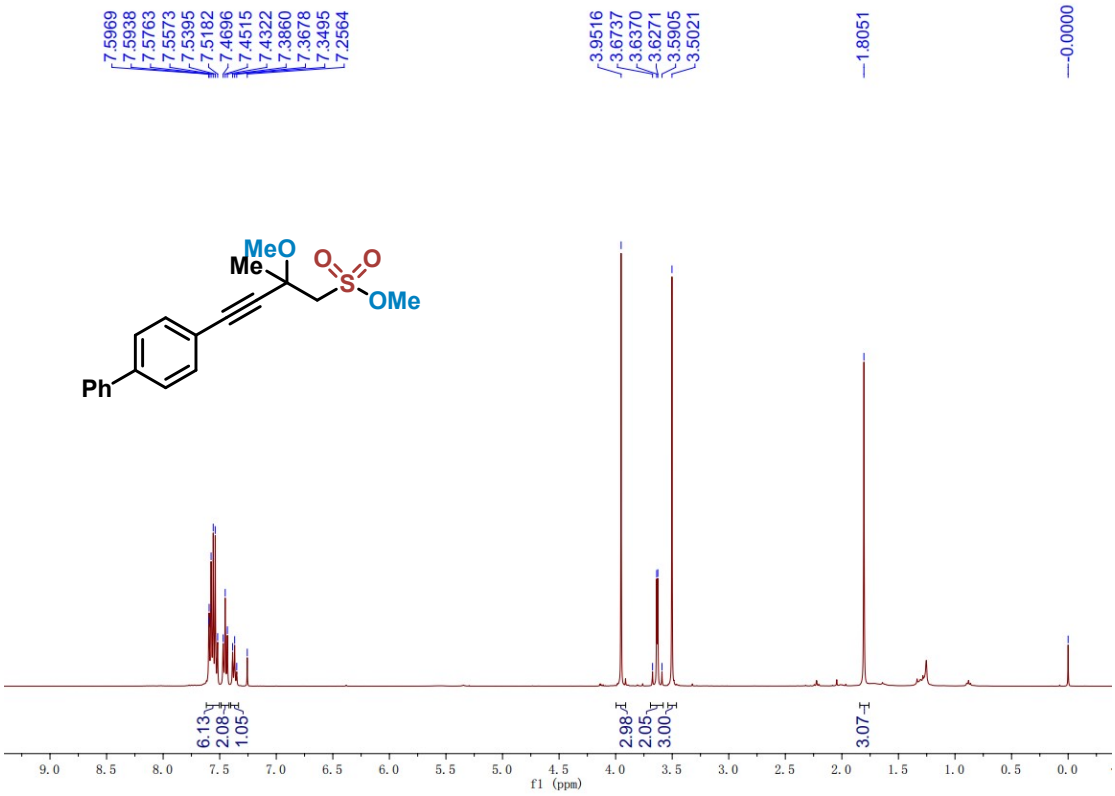
^{1}H NMR spectra of compound **3bd** (400MHz, $CDCl_3$)



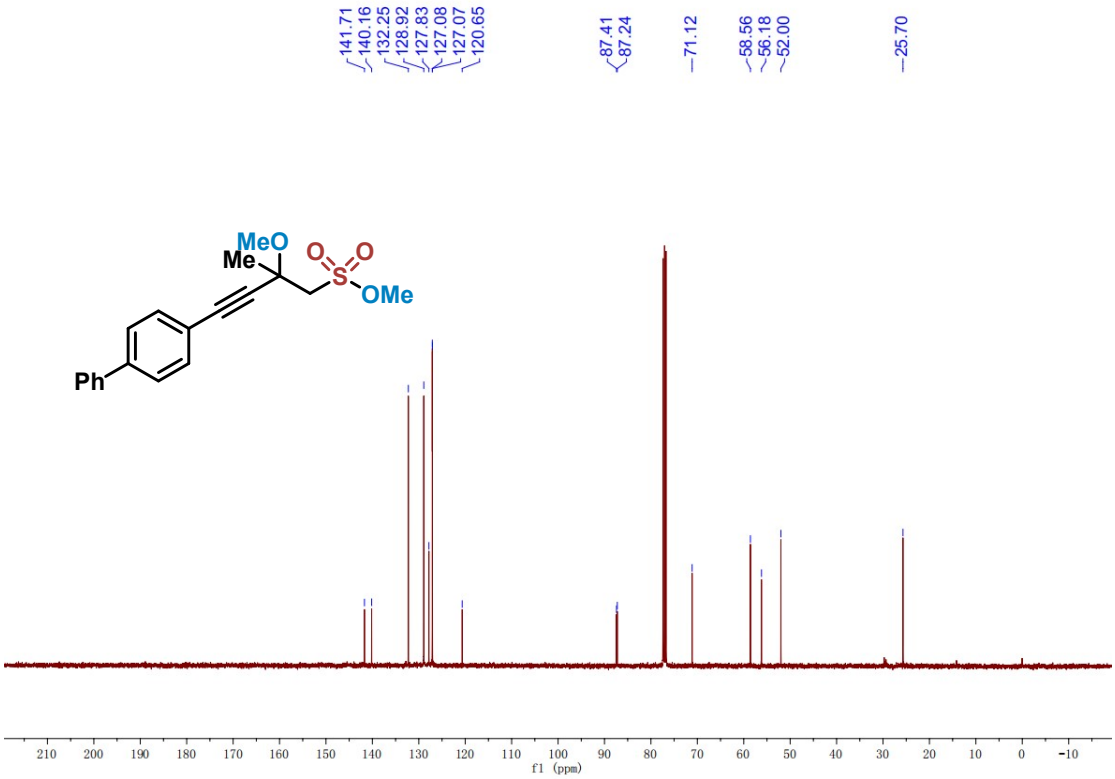
^{13}C NMR spectra of compound **3bd** (100MHz, $CDCl_3$)



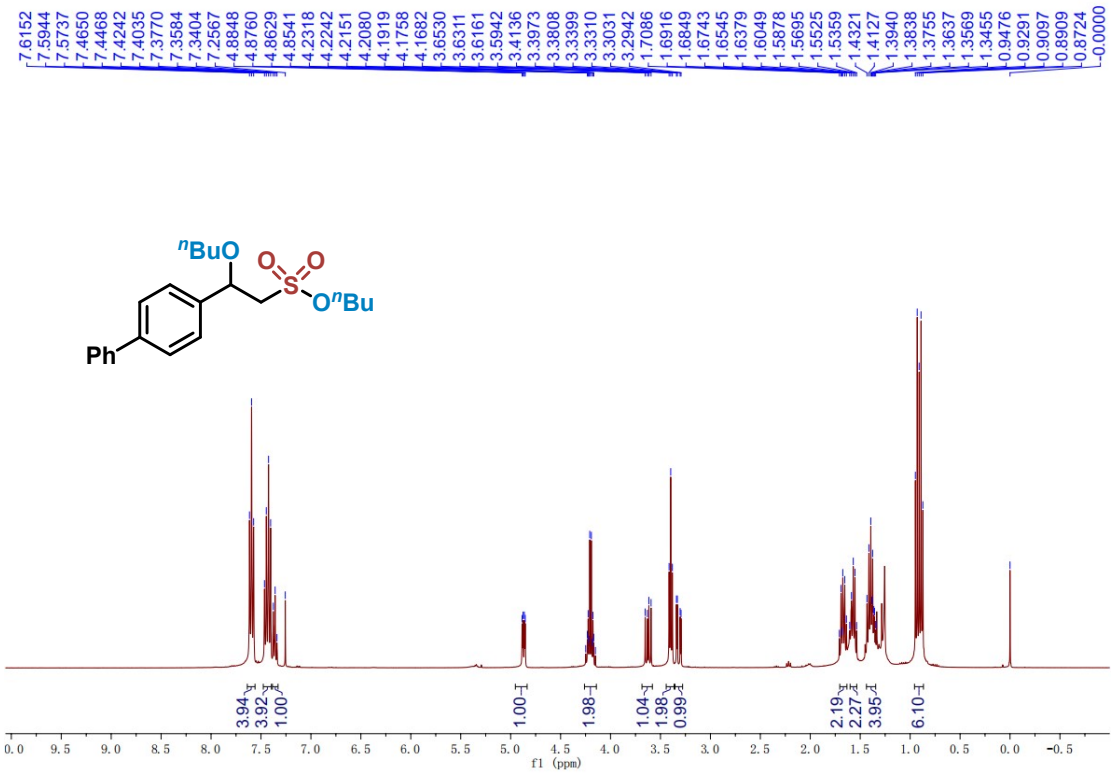
^{1}H NMR spectra of compound **3be** (400MHz, $CDCl_3$)



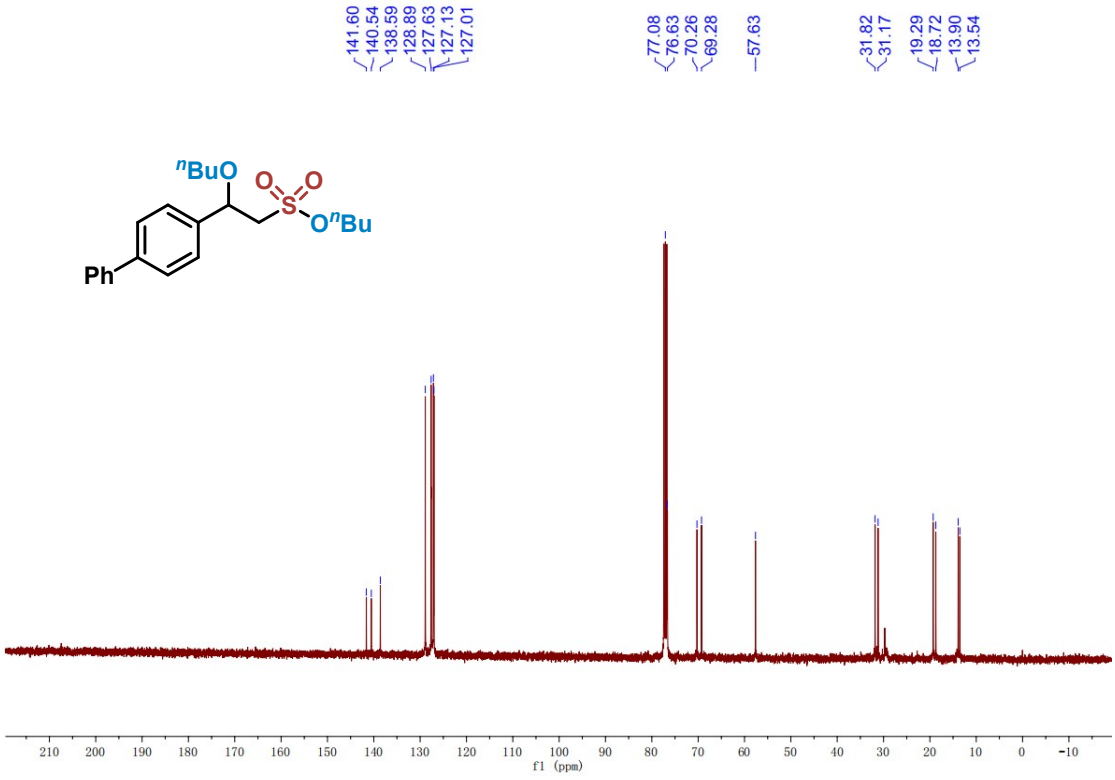
^{13}C NMR spectra of compound **3be** (100MHz, $CDCl_3$)



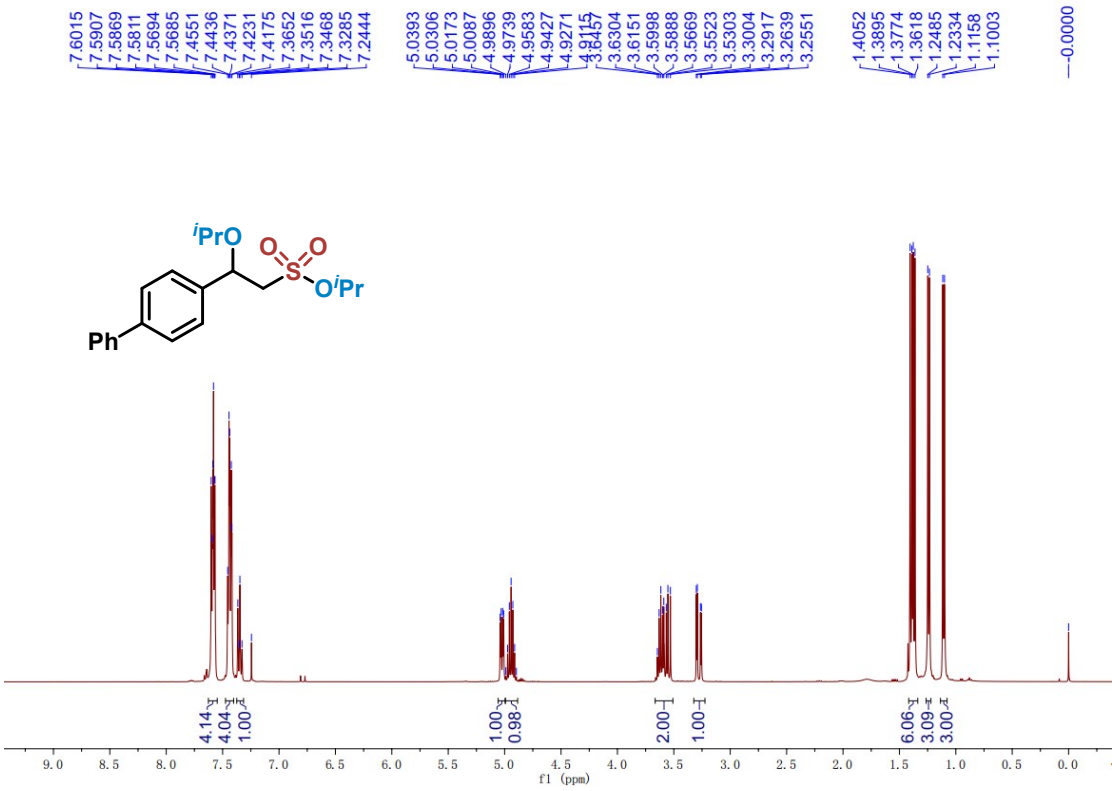
^{1}H NMR spectra of compound **3bf** (400MHz, $CDCl_3$)



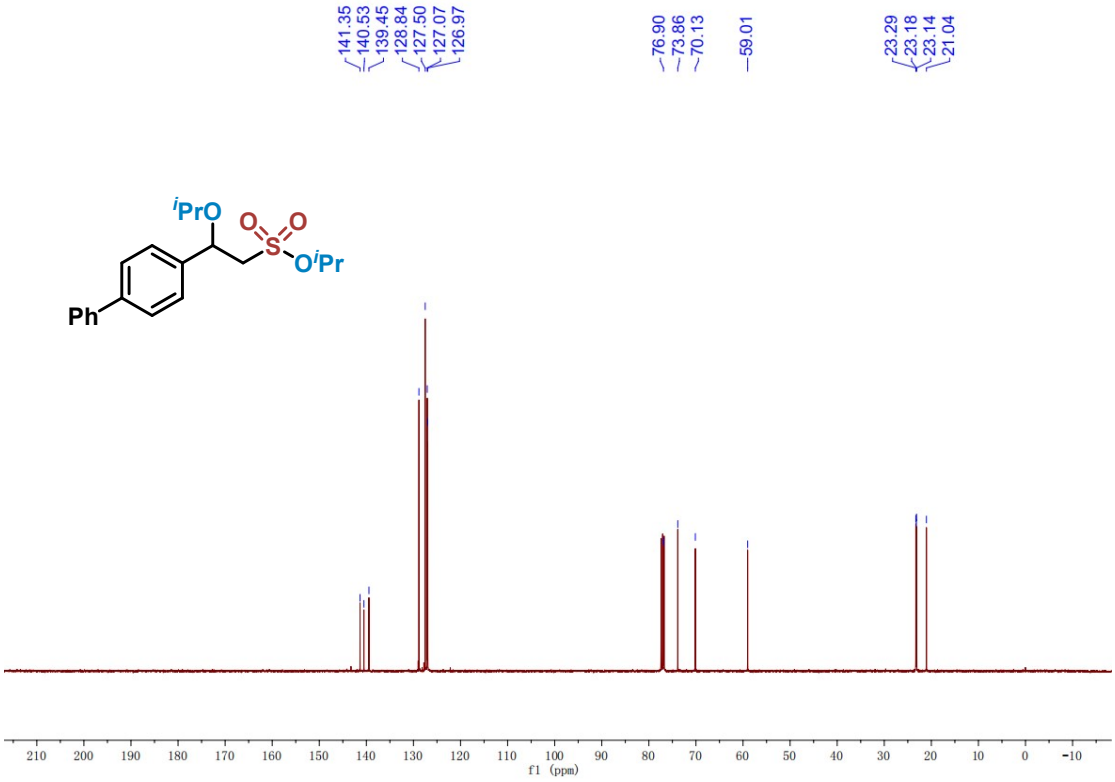
^{13}C NMR spectra of compound **3bf** (100MHz, $CDCl_3$)



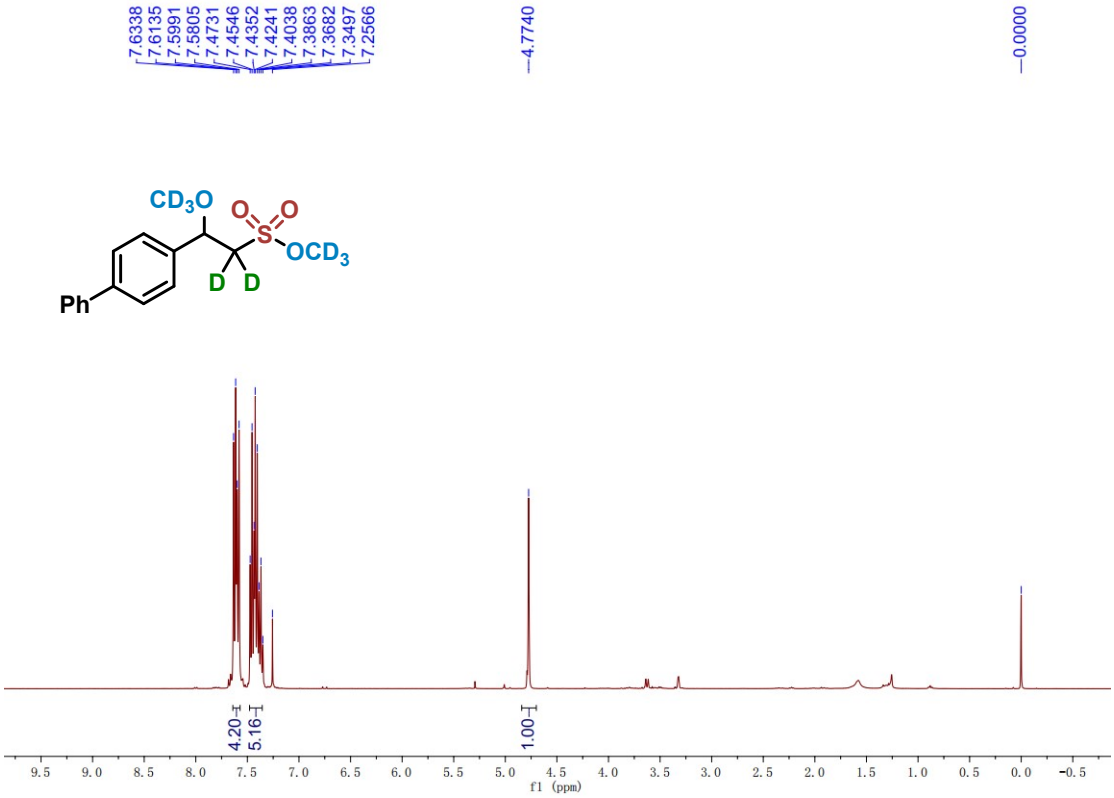
^{1}H NMR spectra of compound **3bg** (400MHz, $CDCl_3$)



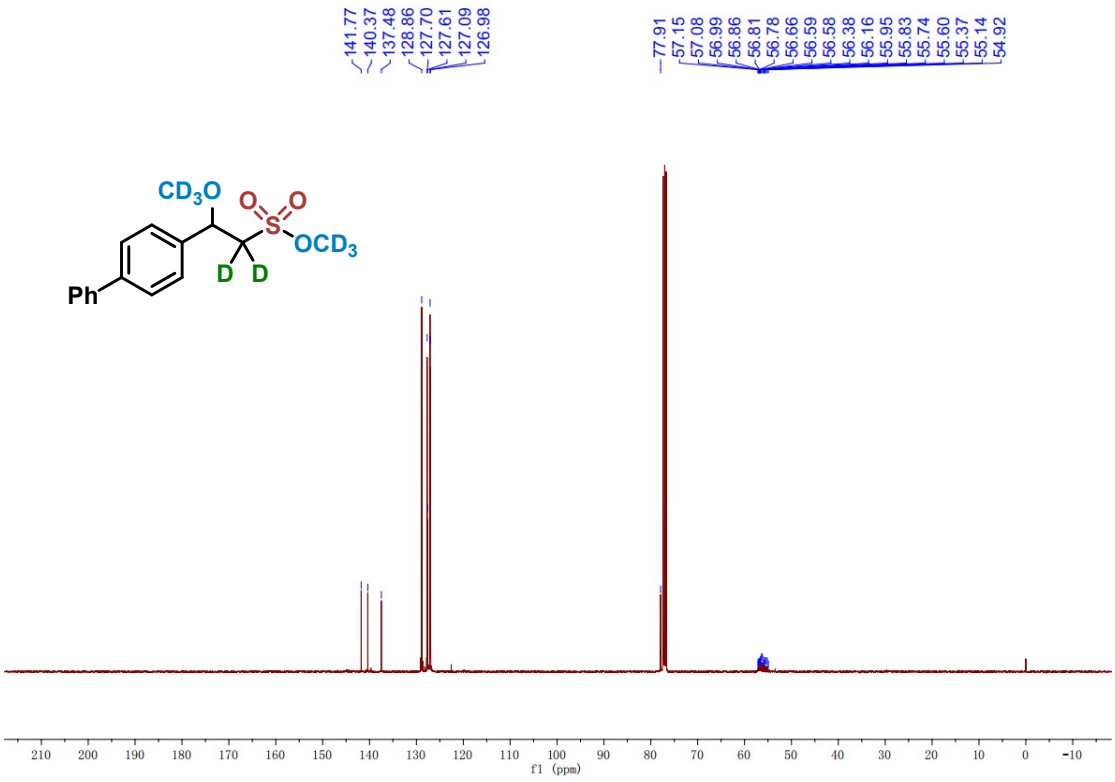
^{13}C NMR spectra of compound **3bg** (100MHz, $CDCl_3$)



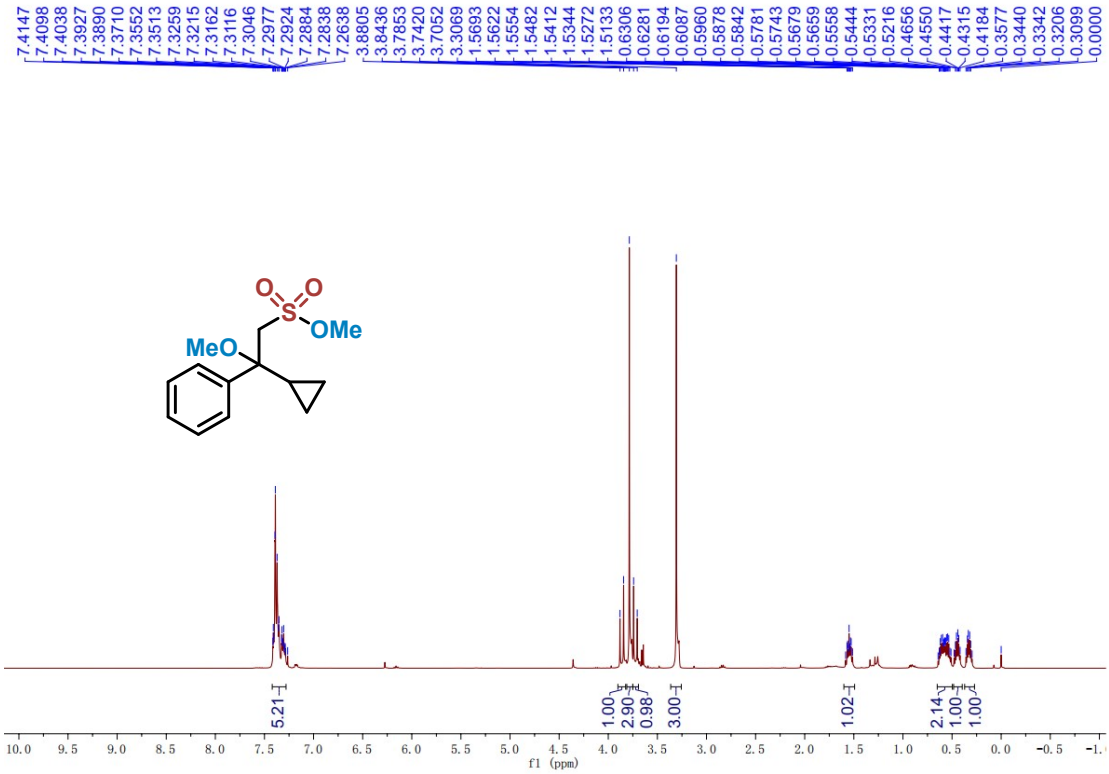
^{1}H NMR spectra of compound **3bh** (400MHz, $CDCl_3$)



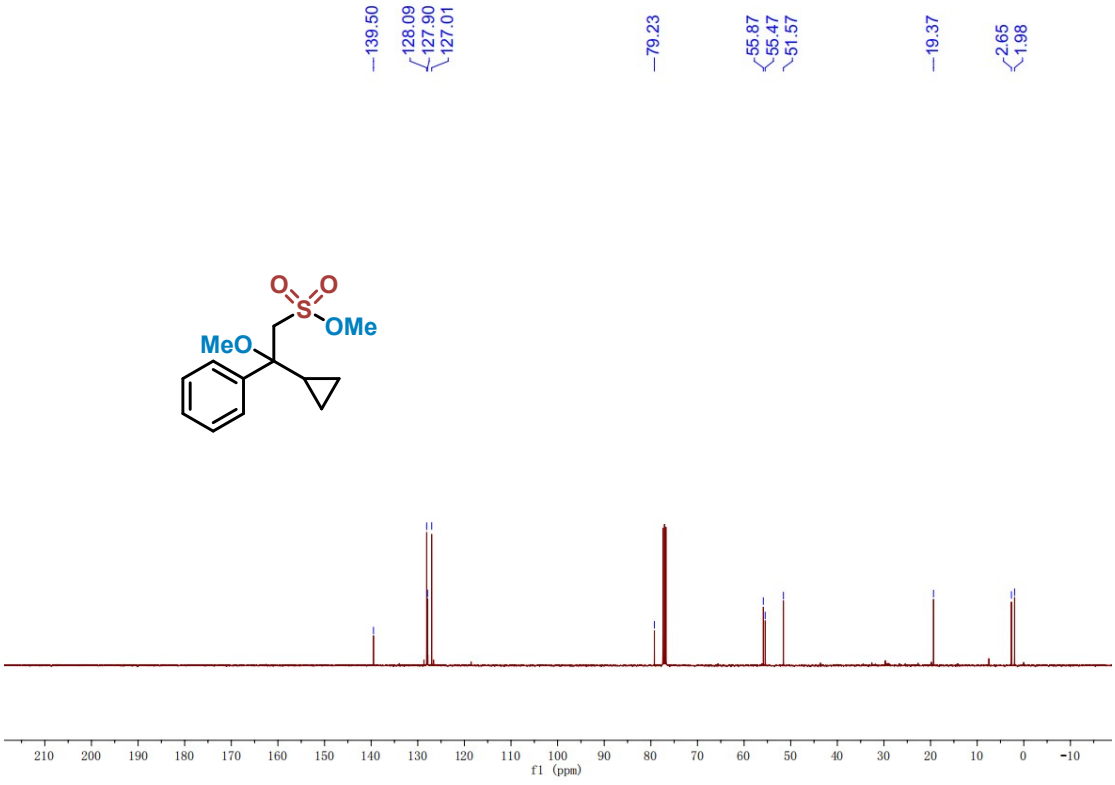
^{13}C NMR spectra of compound **3bh** (100MHz, $CDCl_3$)



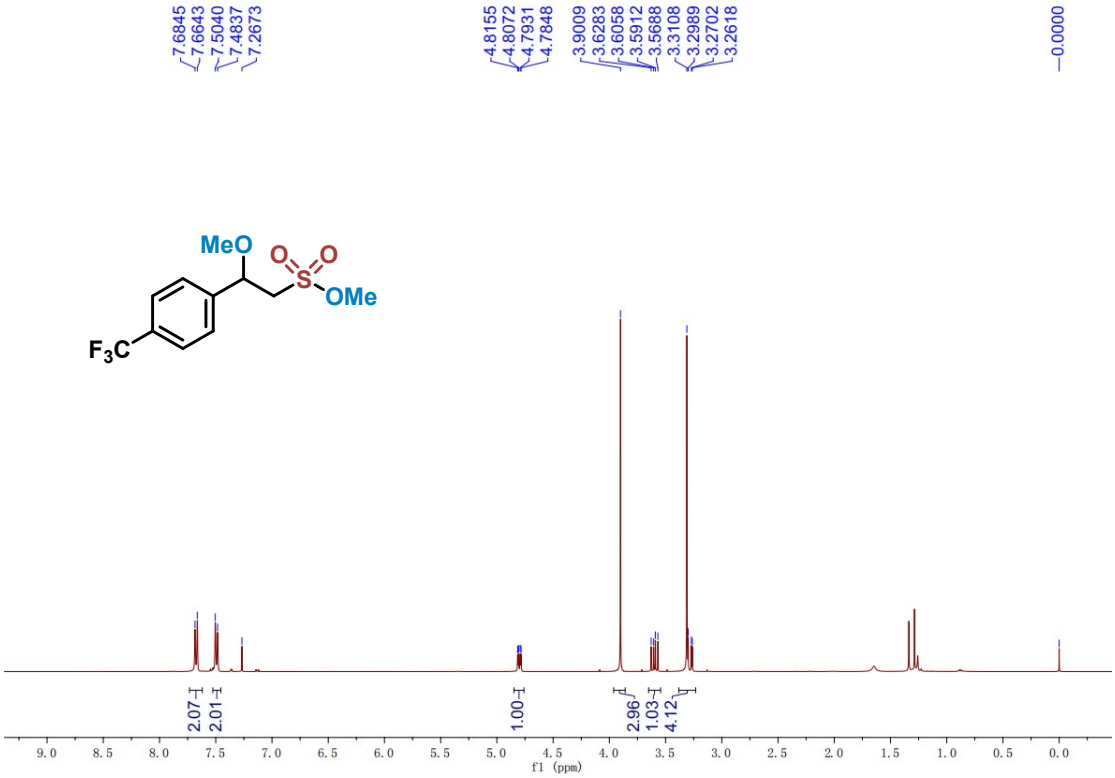
^{1}H NMR spectra of compound **3bi** (400MHz, $CDCl_3$)



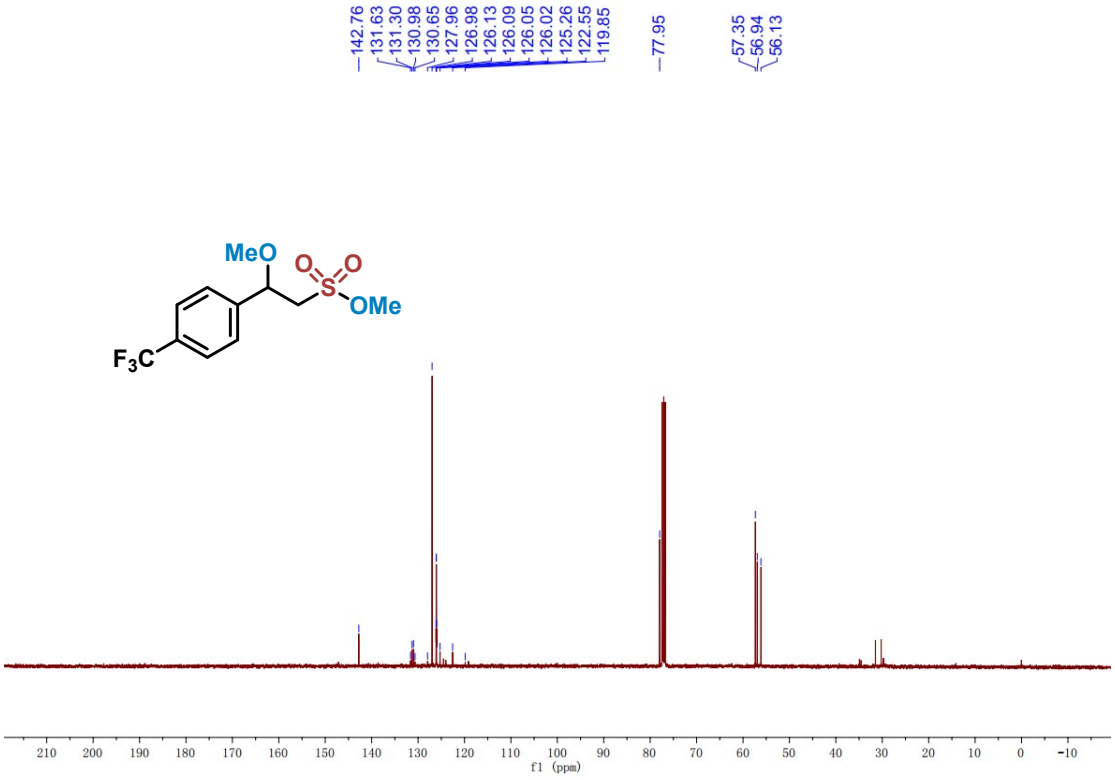
^{13}C NMR spectra of compound **3bi** (100MHz, $CDCl_3$)



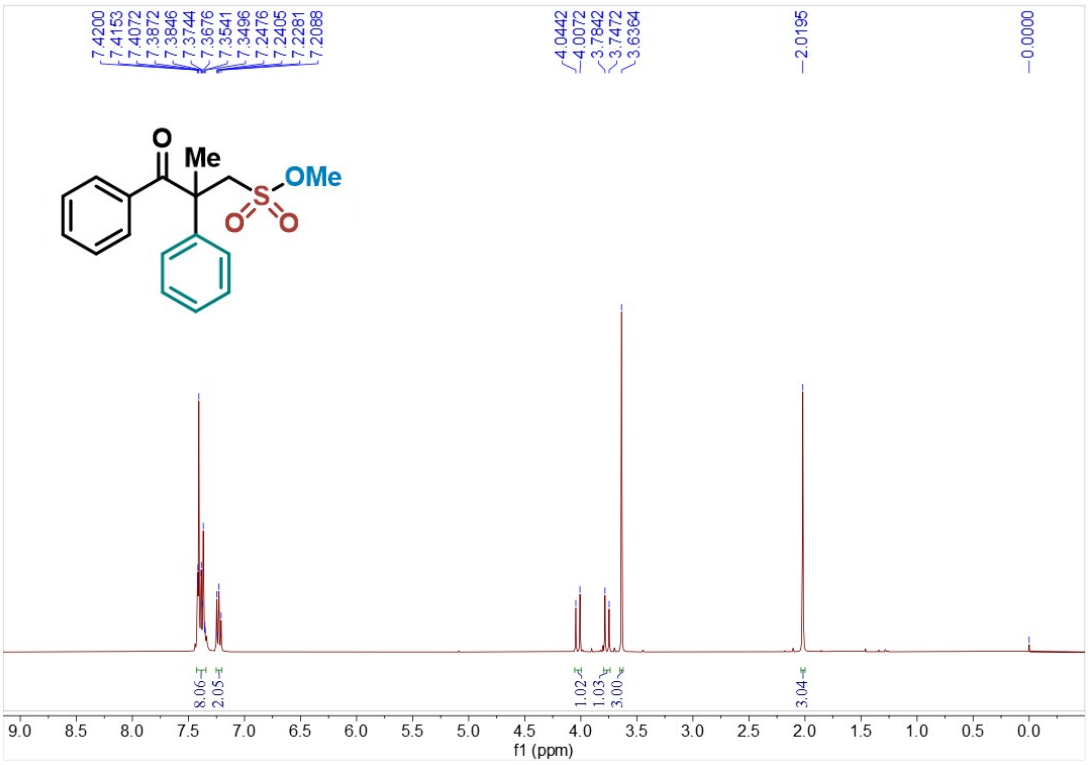
^{1}H NMR spectra of compound **3bj** (400MHz, $CDCl_3$)



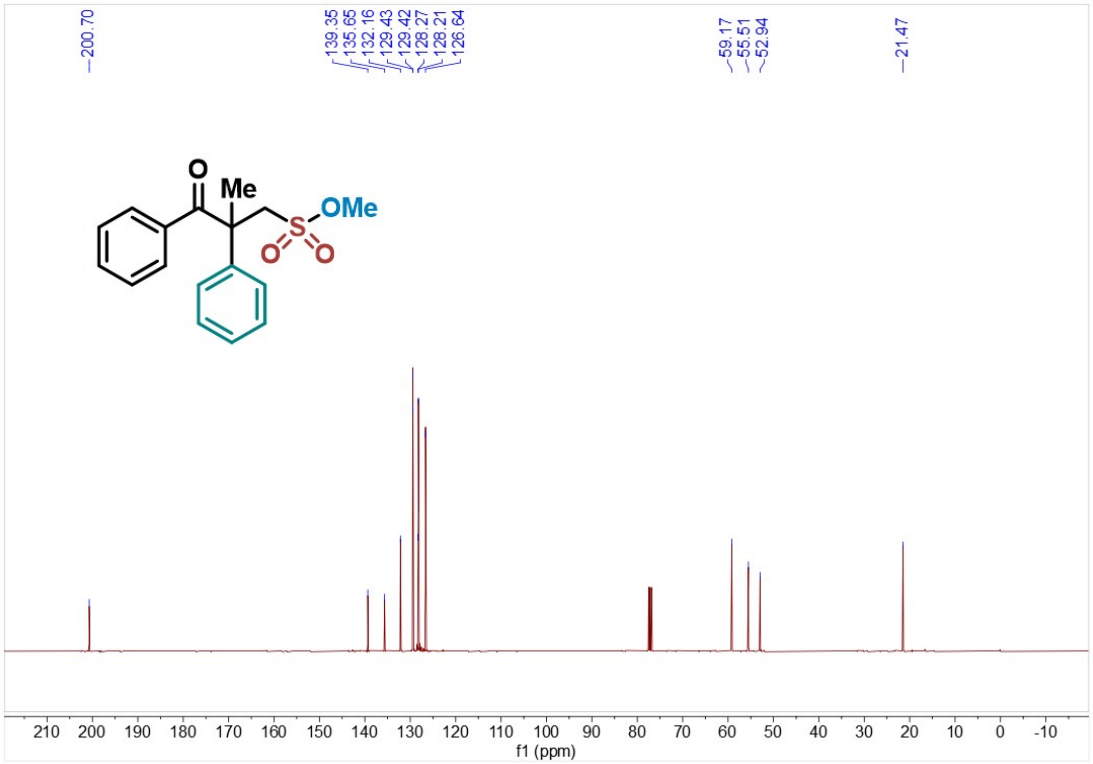
^{13}C NMR spectra of compound **3bj** (100MHz, $CDCl_3$)



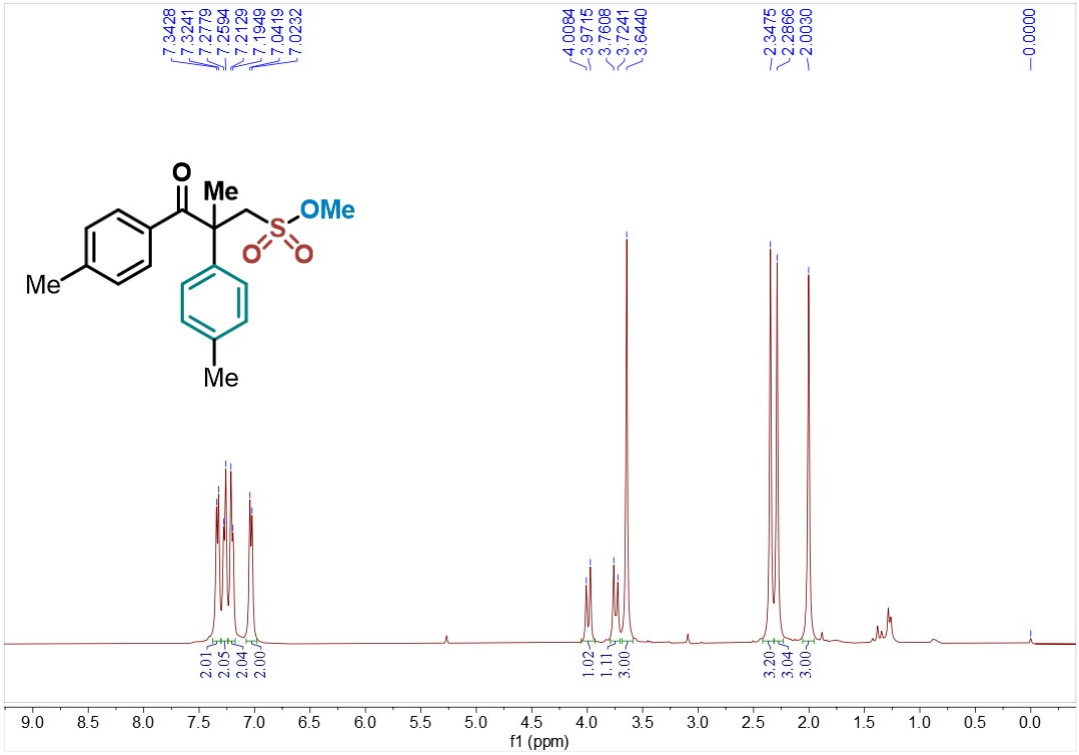
^{1}H NMR spectra of compound **5a** (400MHz, $CDCl_3$)



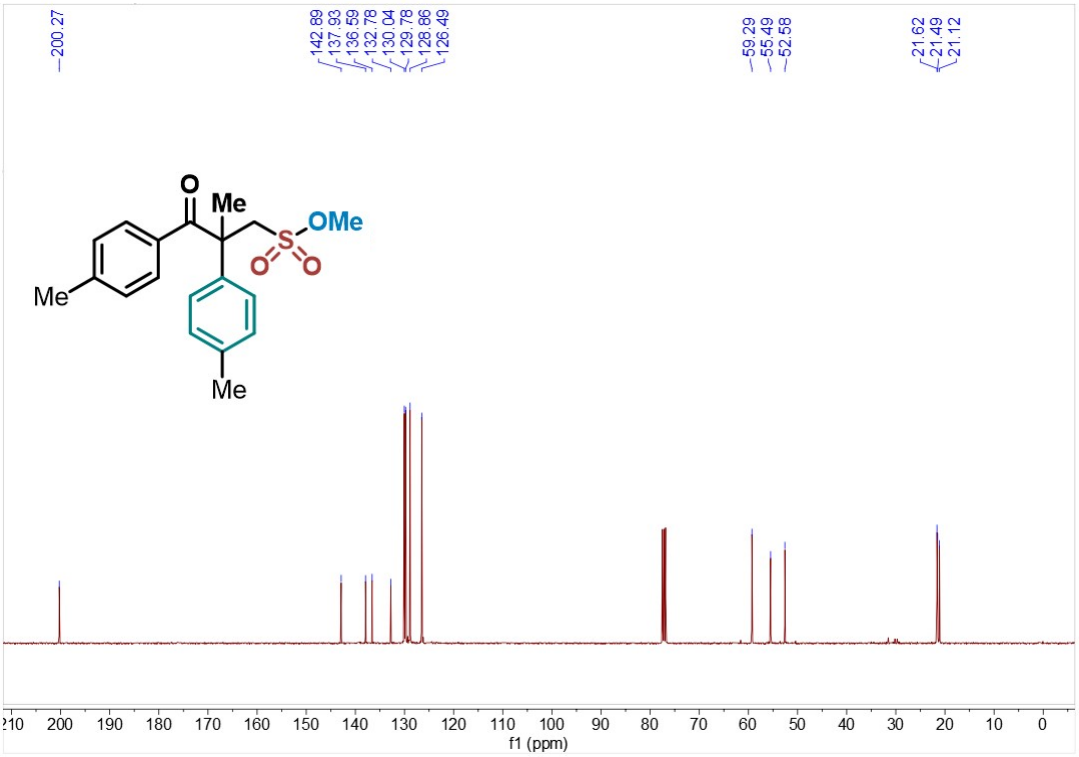
^{13}C NMR spectrum of compound **5a** (100 MHz, $CDCl_3$)



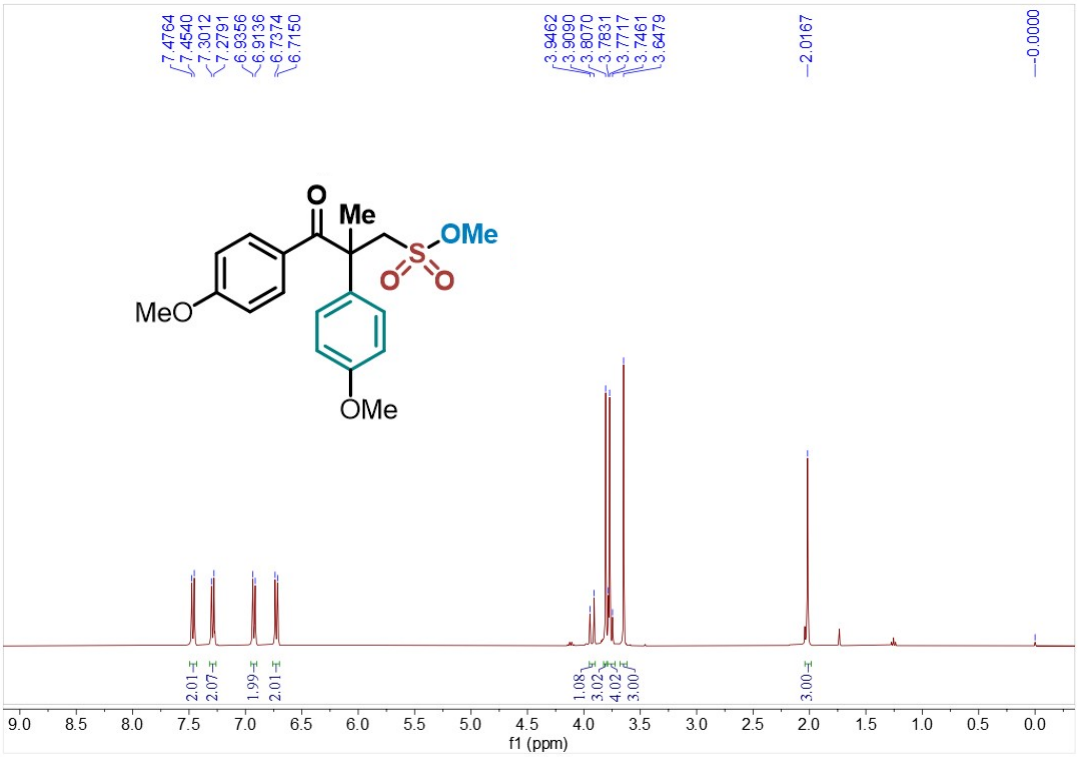
^{1}H NMR spectra of compound **5b** (400MHz, $CDCl_3$)



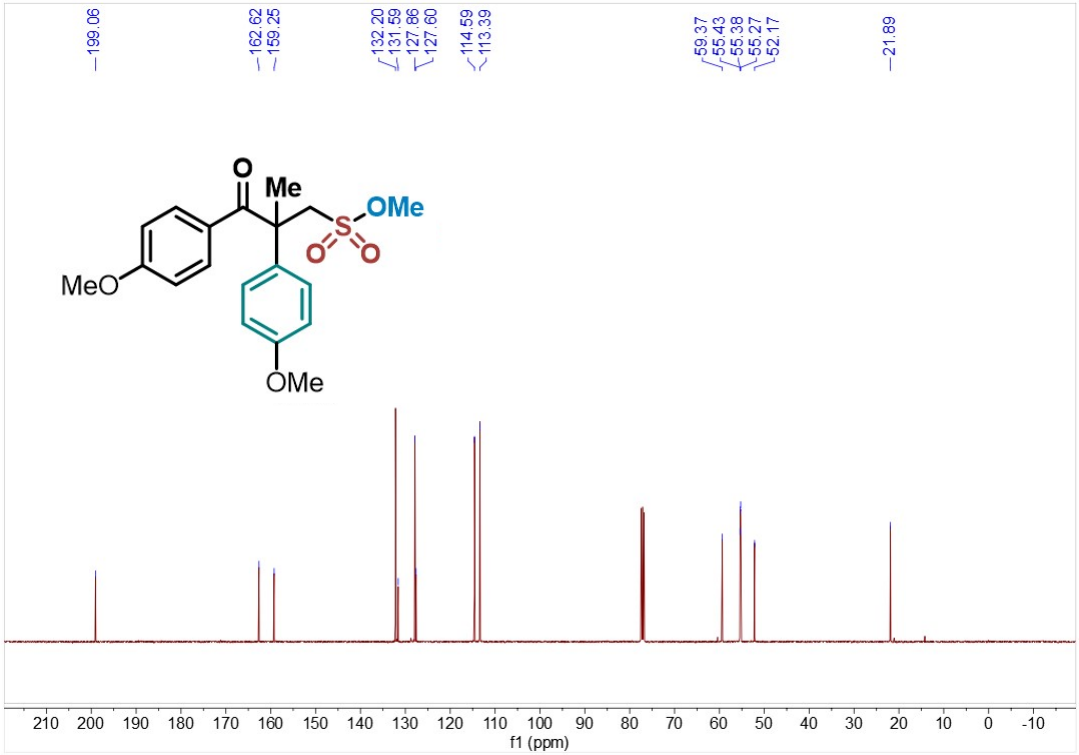
^{13}C NMR spectrum of compound **5b** (100 MHz, $CDCl_3$)



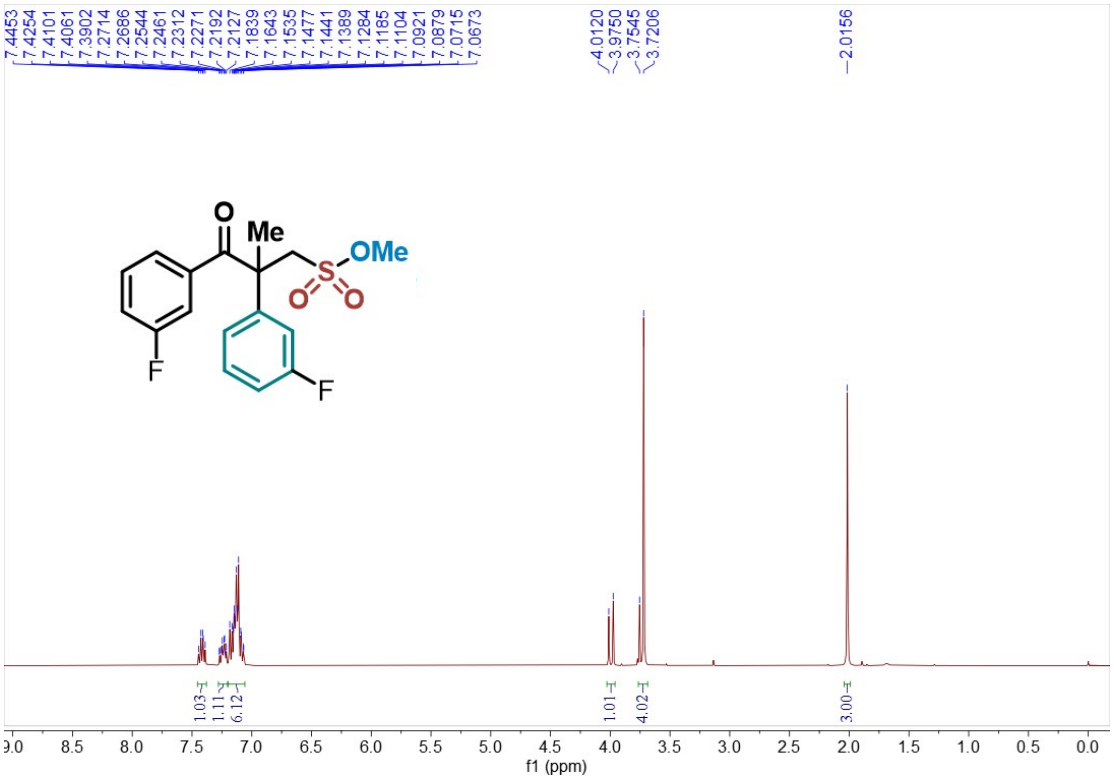
^{1}H NMR spectra of compound **5c** (400MHz, $CDCl_3$)



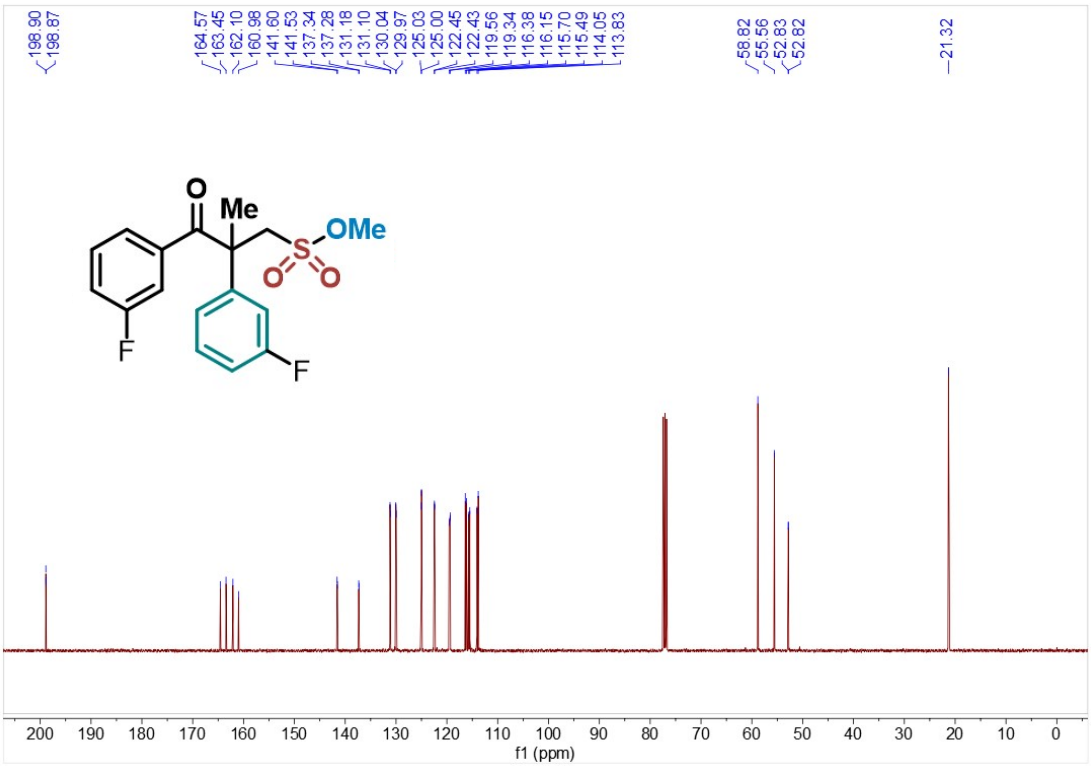
^{13}C NMR spectrum of compound **5c** (100 MHz, $CDCl_3$)



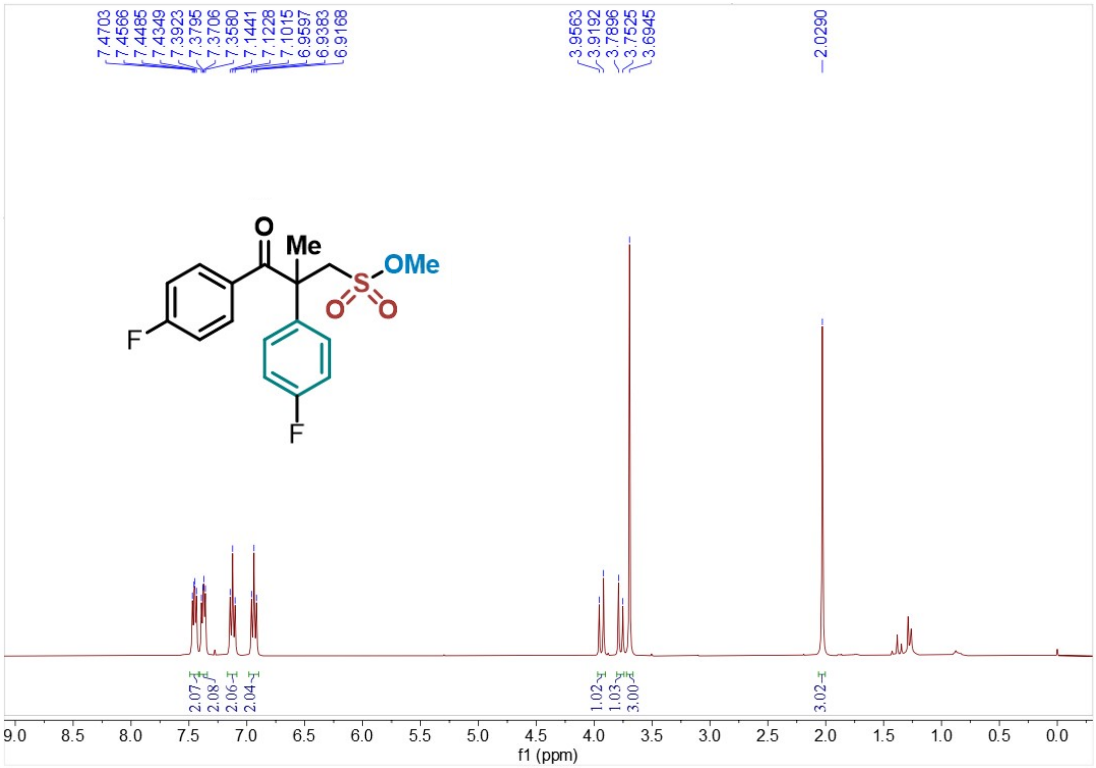
^{1}H NMR spectra of compound **5d** (400MHz, $CDCl_3$)



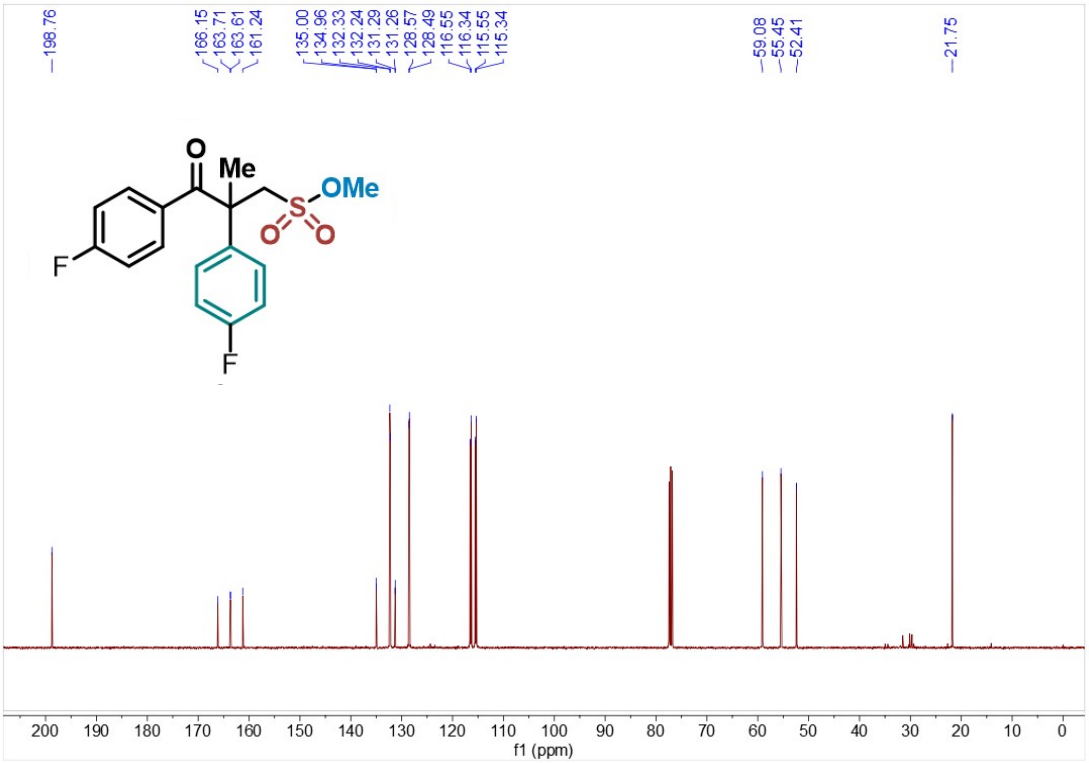
^{13}C NMR spectrum of compound **5d** (100 MHz, $CDCl_3$)



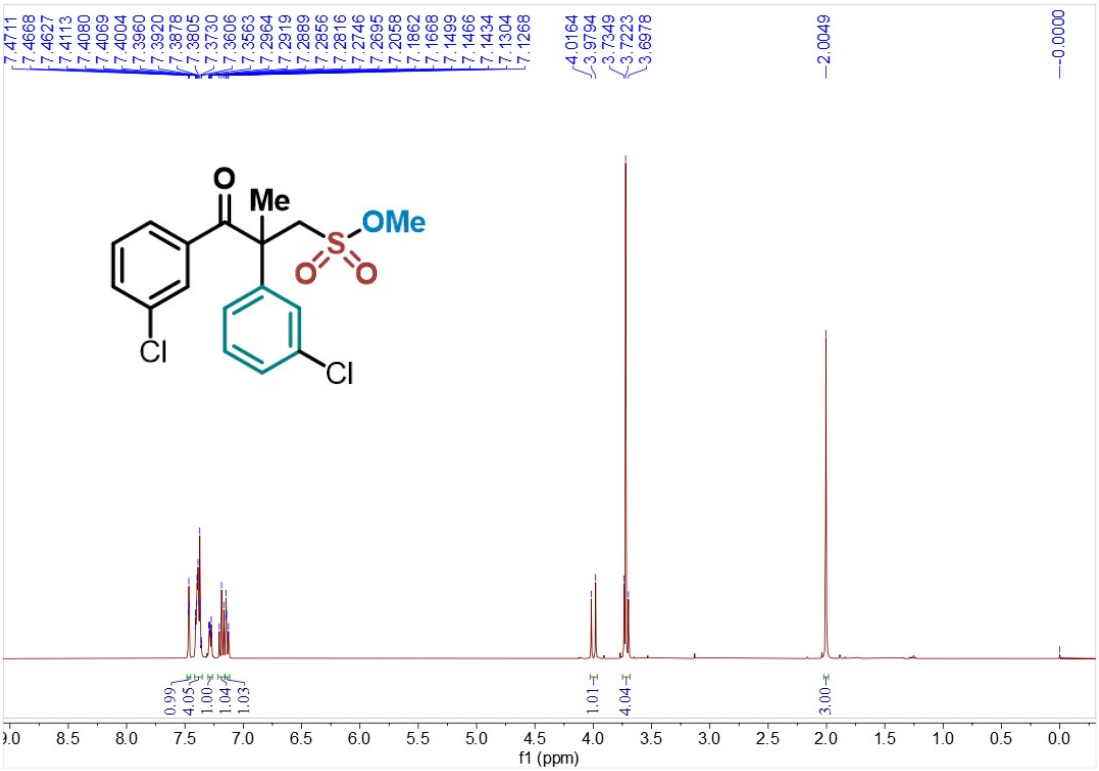
^{1}H NMR spectra of compound **5e** (400MHz, $CDCl_3$)



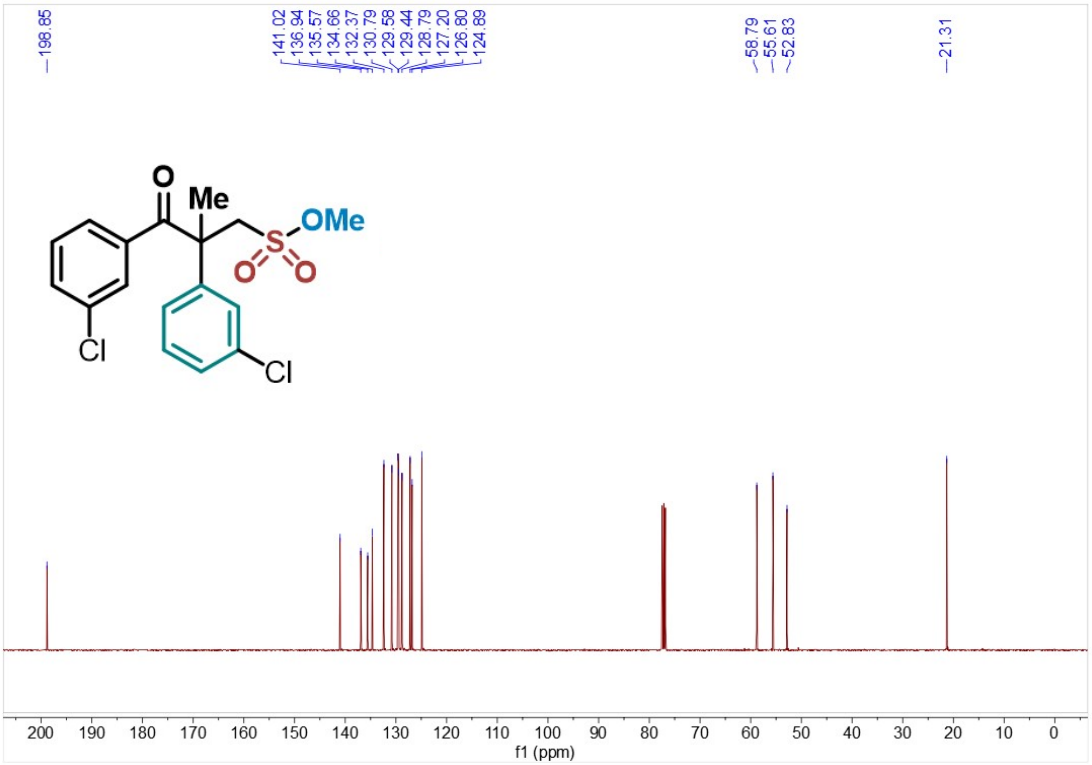
^{13}C NMR spectrum of compound **5e** (100 MHz, $CDCl_3$)



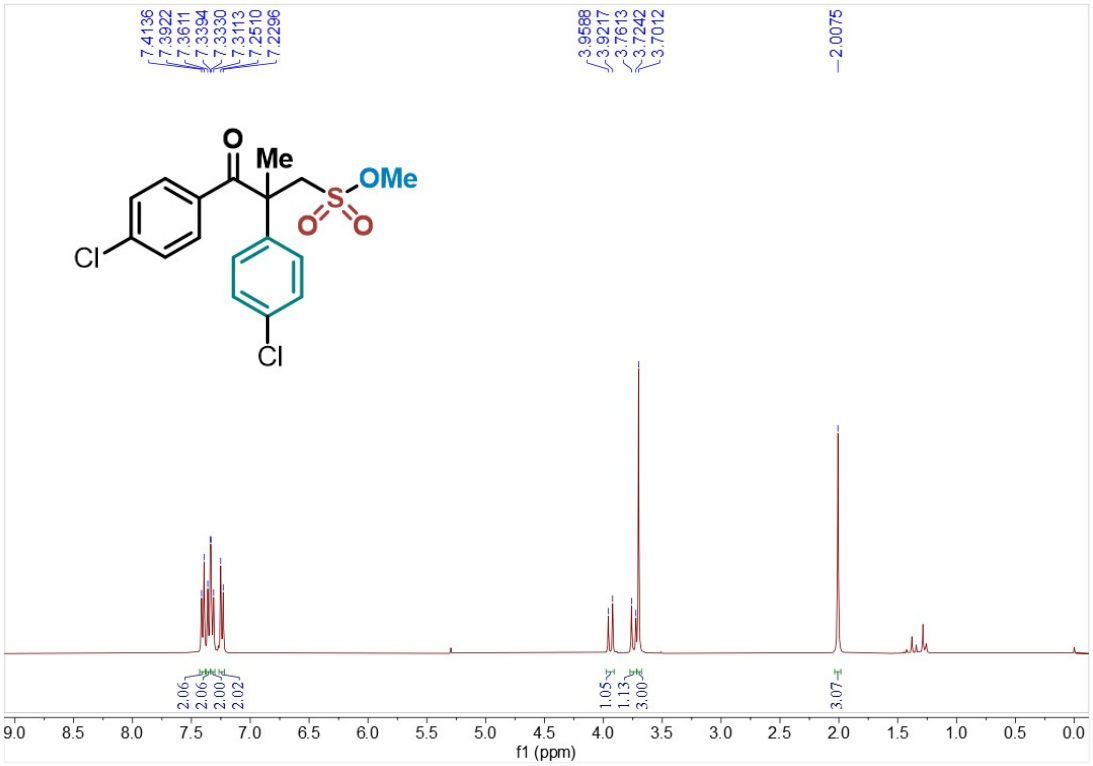
^{1}H NMR spectra of compound **5f** (400MHz, $CDCl_3$)



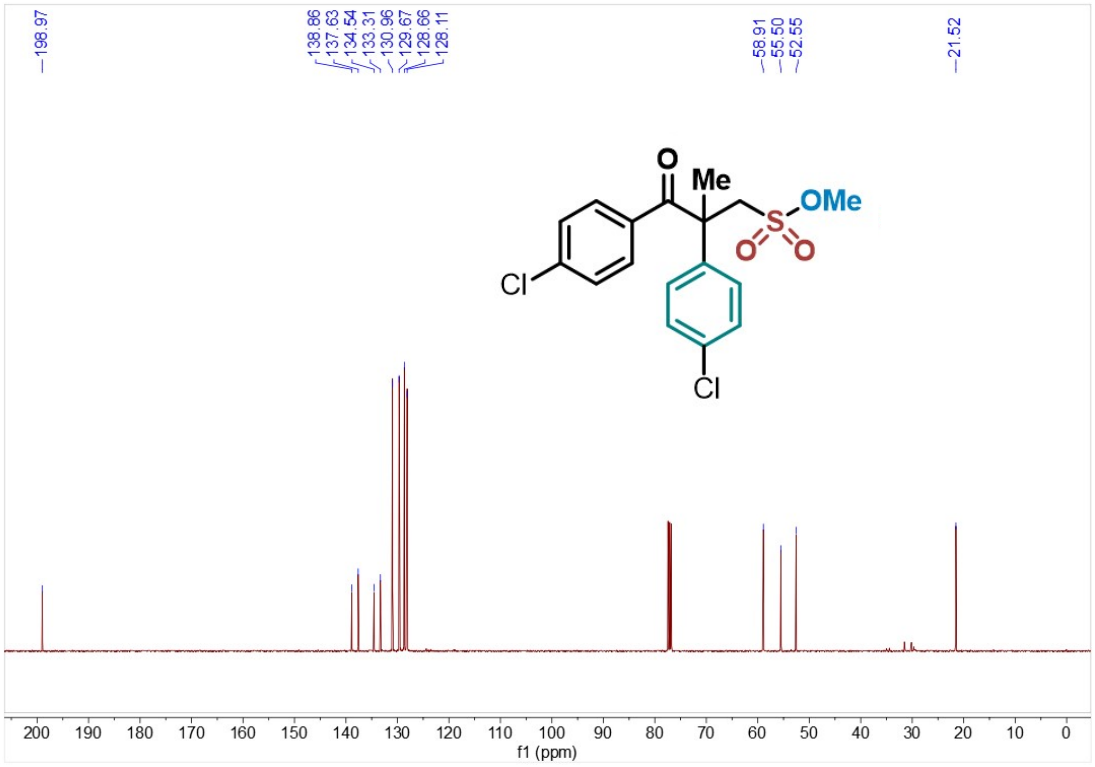
^{13}C NMR spectrum of compound **5f** (100 MHz, $CDCl_3$)



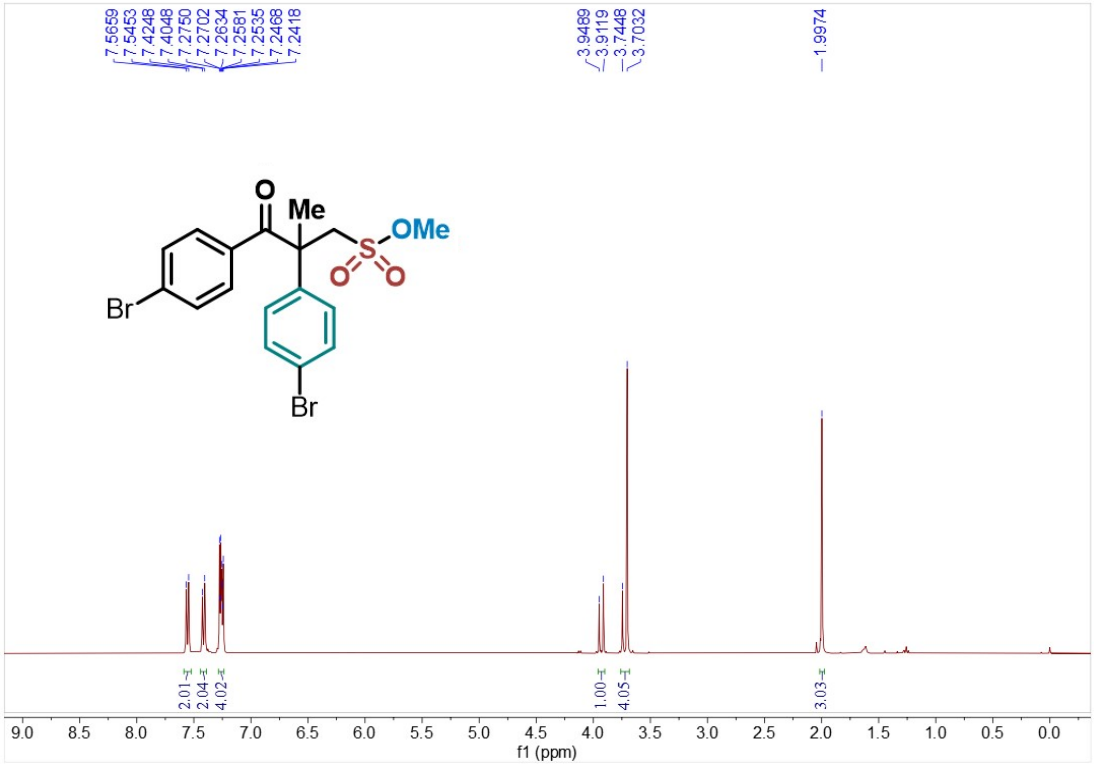
^{1}H NMR spectra of compound **5g** (400MHz, $CDCl_3$)



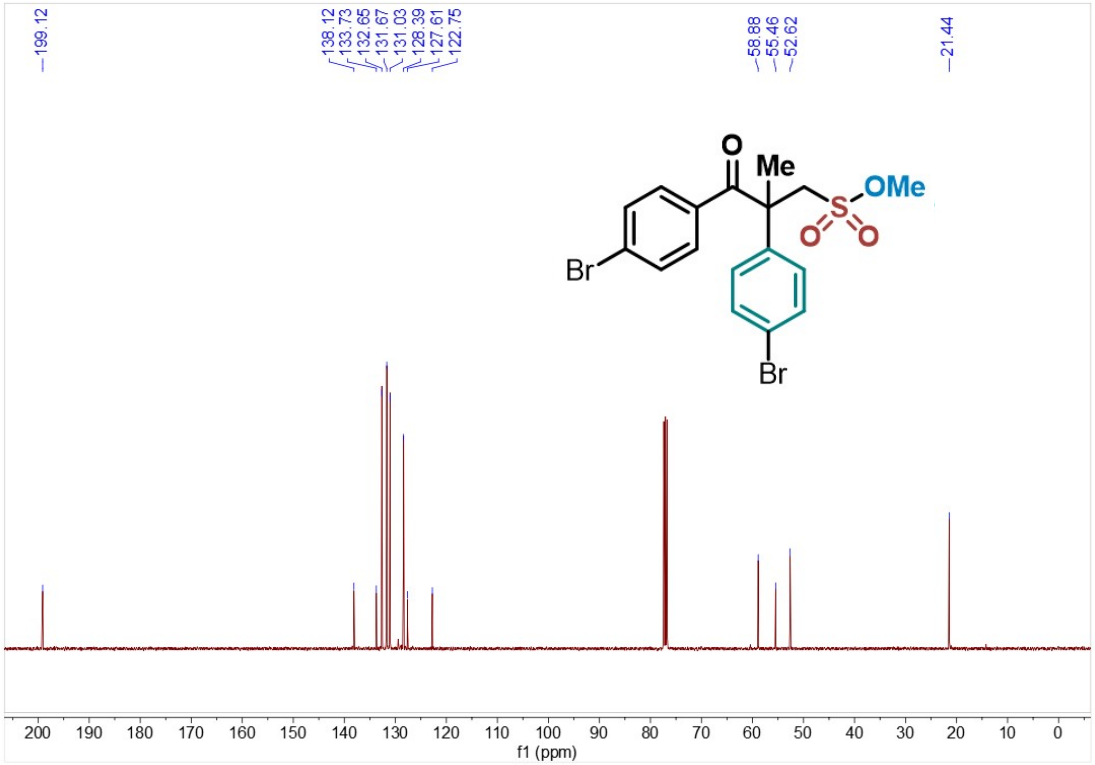
^{13}C NMR spectrum of compound **5g** (100 MHz, $CDCl_3$)



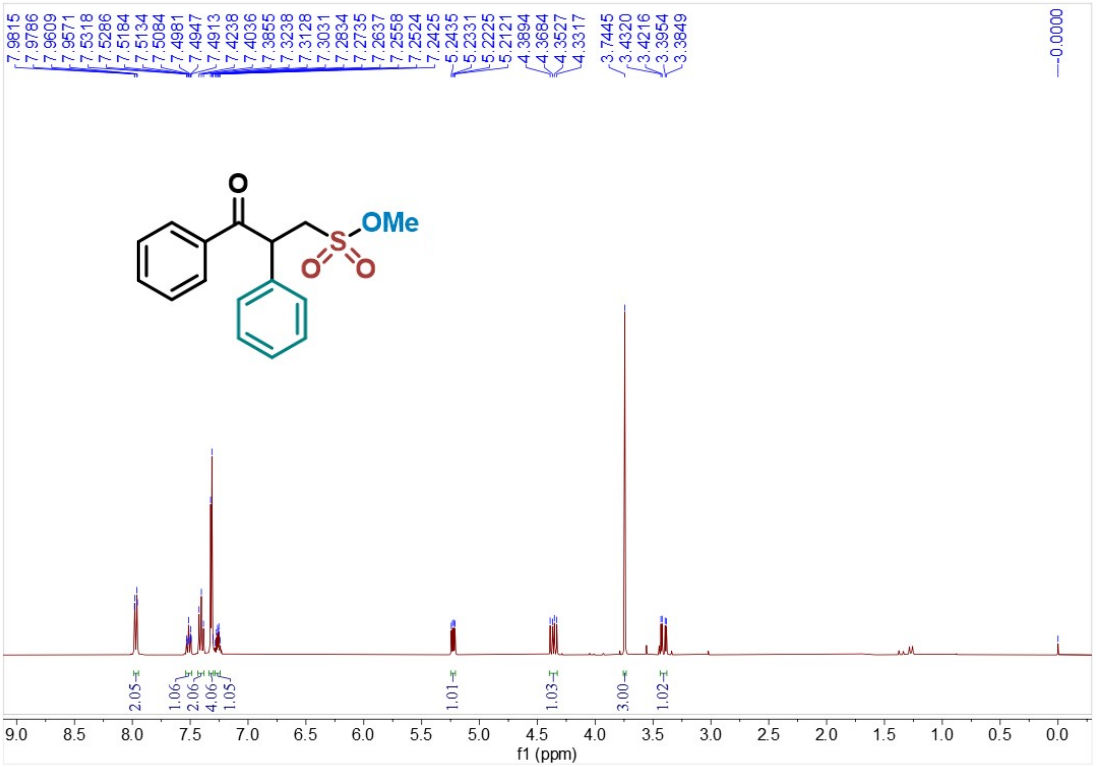
^{1}H NMR spectra of compound **5h** (400MHz, $CDCl_3$)



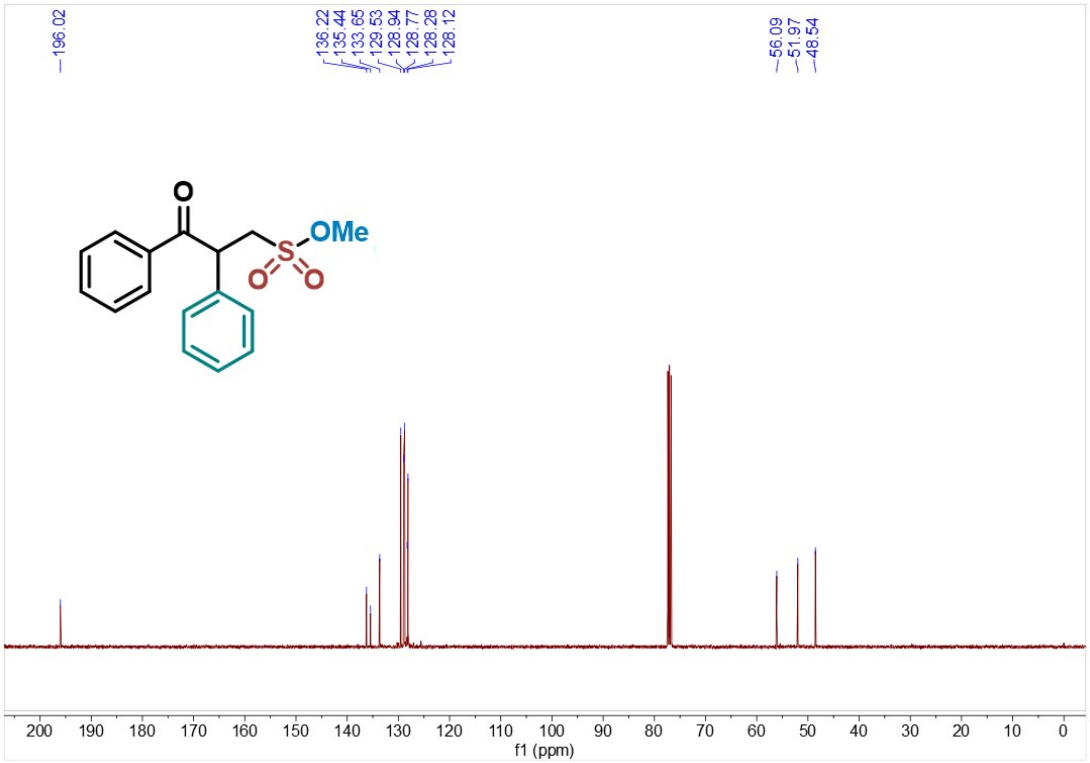
^{13}C NMR spectrum of compound **5h** (100 MHz, $CDCl_3$)



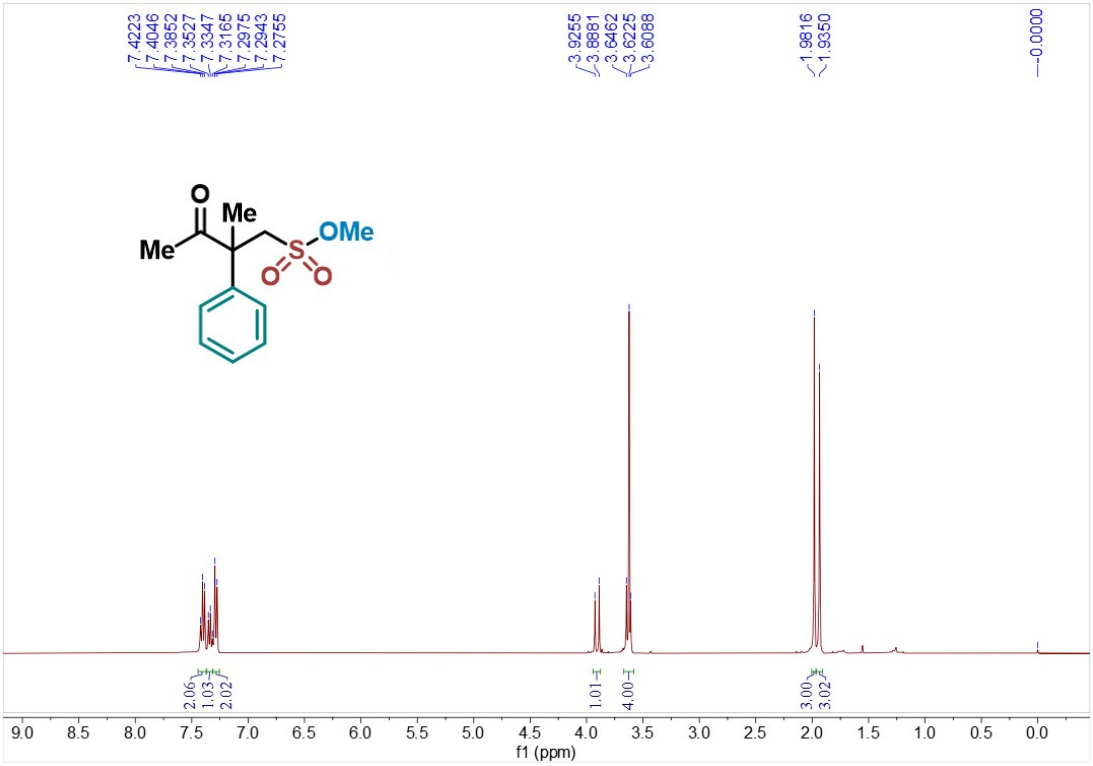
^{1}H NMR spectra of compound **5i** (400MHz, $CDCl_3$)



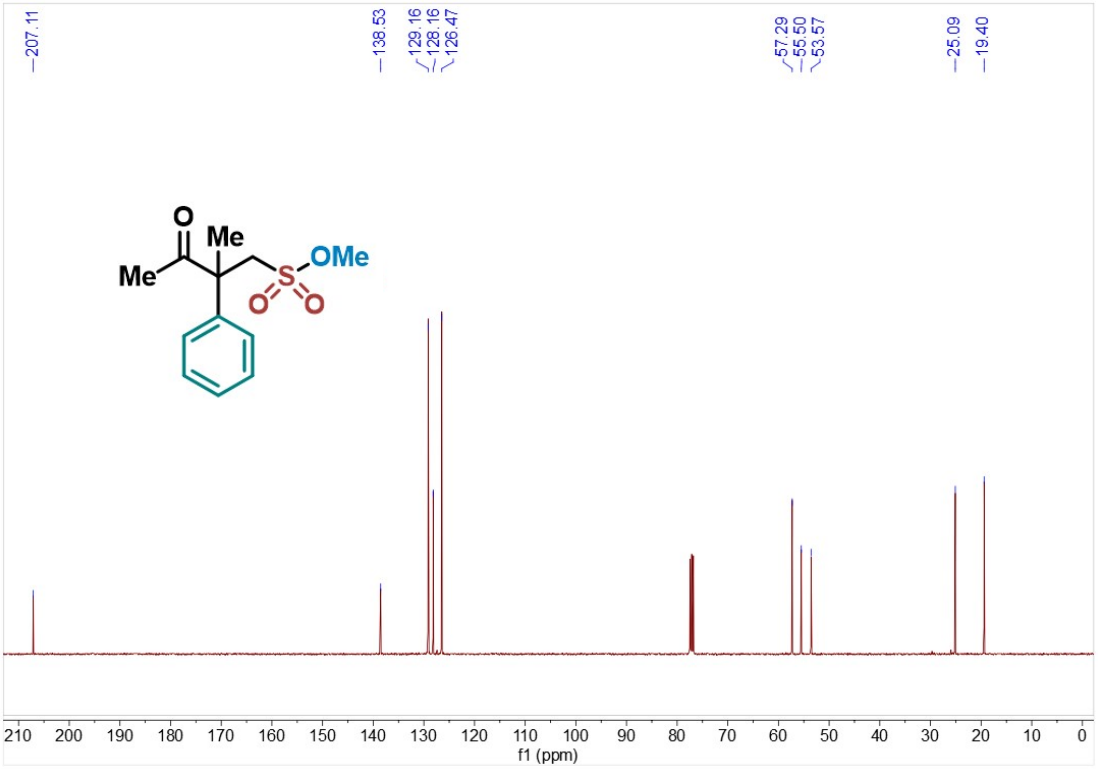
^{13}C NMR spectrum of compound **5i** (100 MHz, $CDCl_3$)



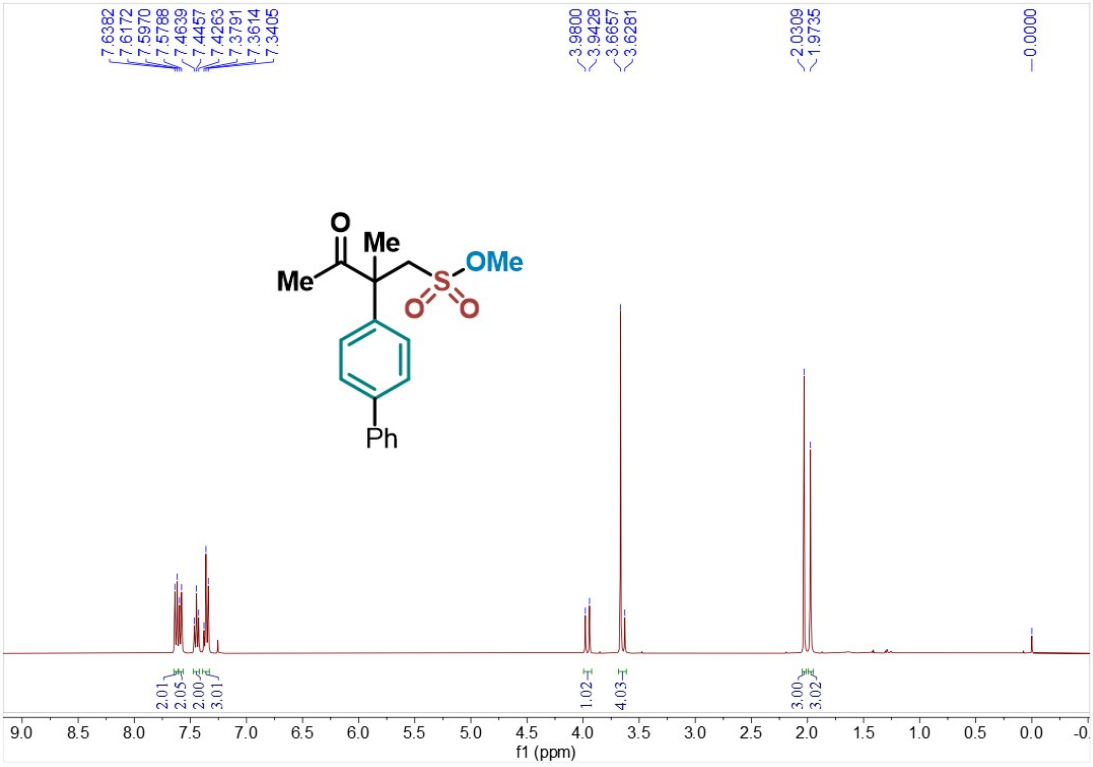
^{1}H NMR spectra of compound **5j** (400MHz, $CDCl_3$)



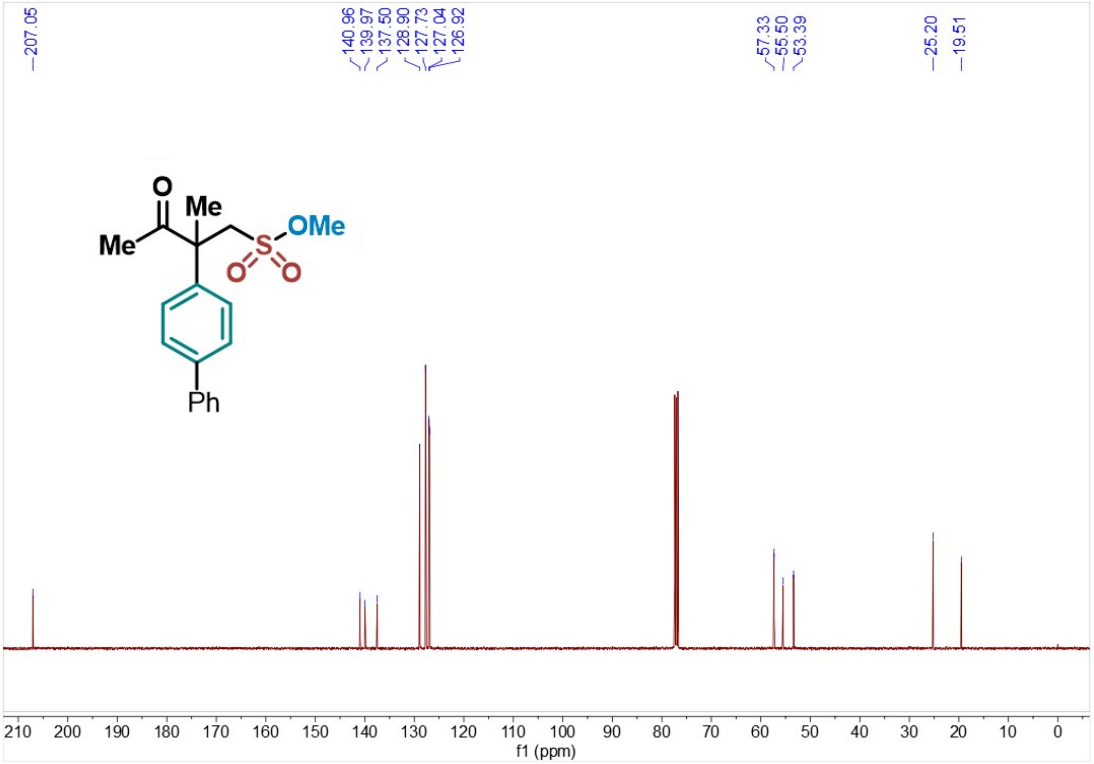
^{13}C NMR spectrum of compound **5j** (100 MHz, $CDCl_3$)



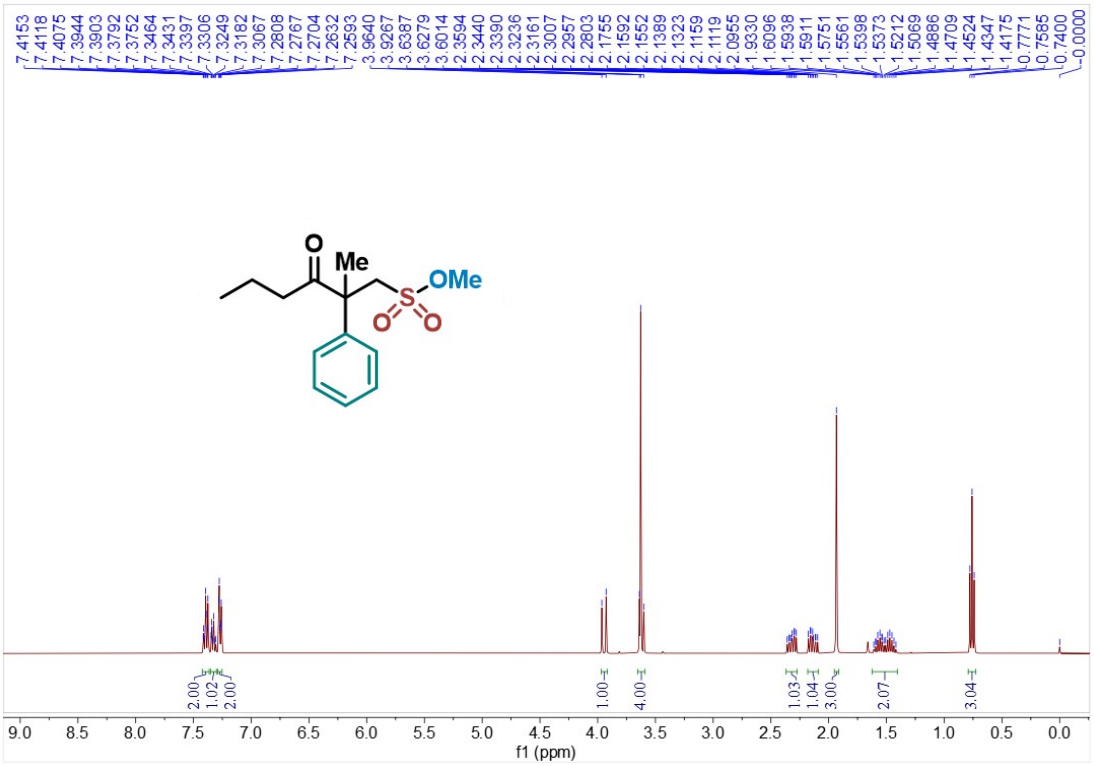
^{1}H NMR spectra of compound **5k** (400MHz, $CDCl_3$)



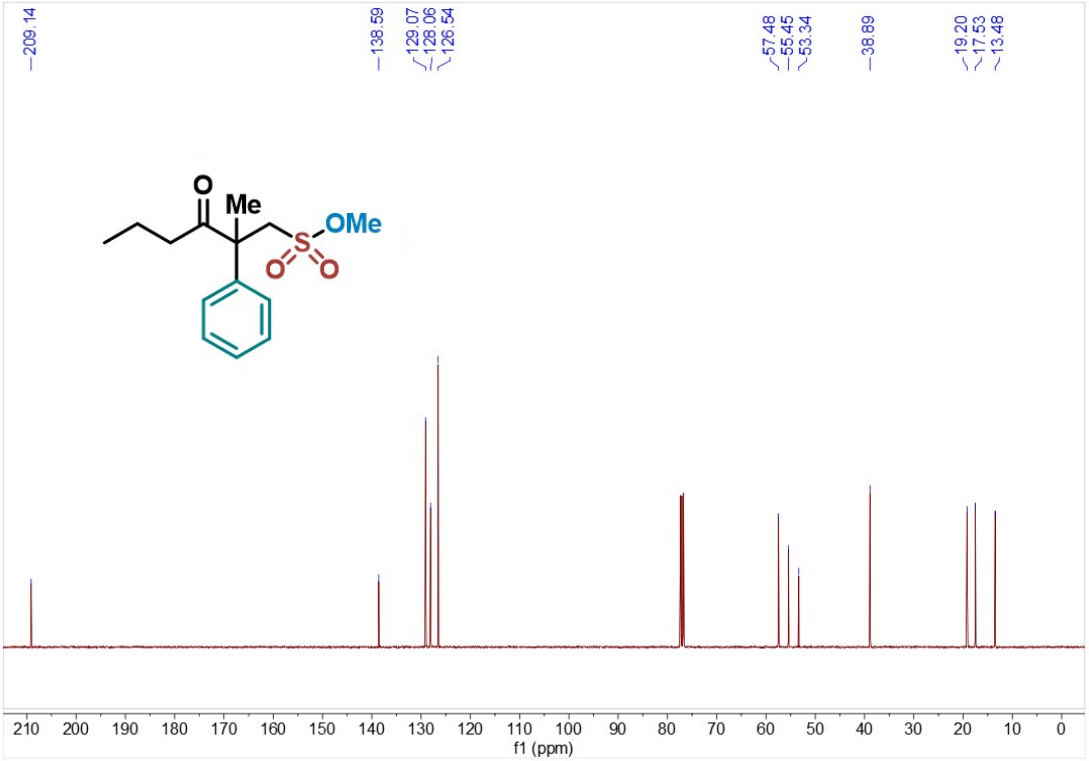
^{13}C NMR spectrum of compound **5k** (100 MHz, $CDCl_3$)



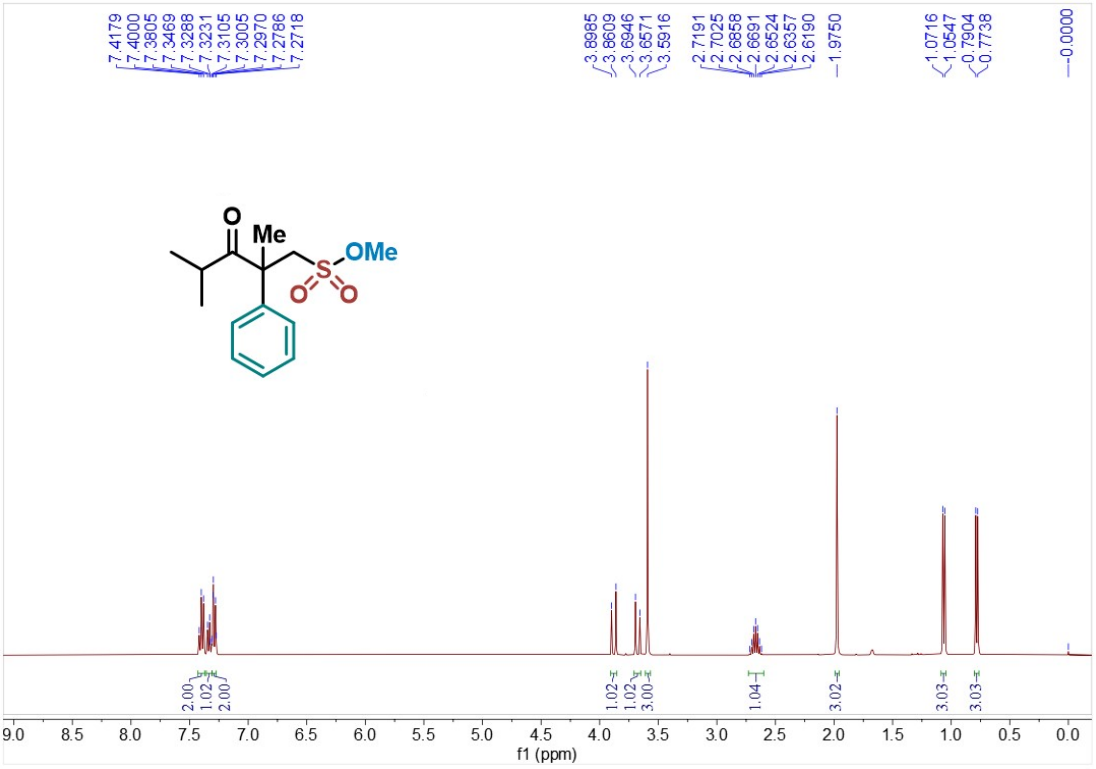
^{1}H NMR spectra of compound **5l** (400MHz, $CDCl_3$)



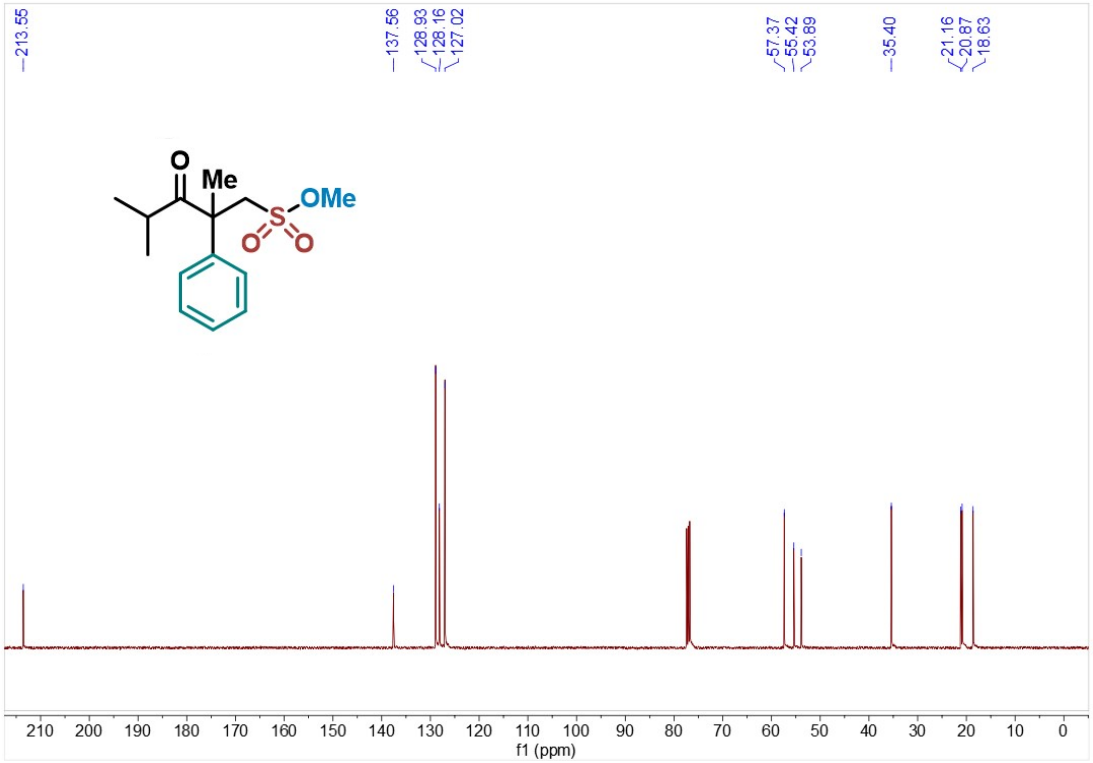
^{13}C NMR spectrum of compound **5l** (100 MHz, $CDCl_3$)



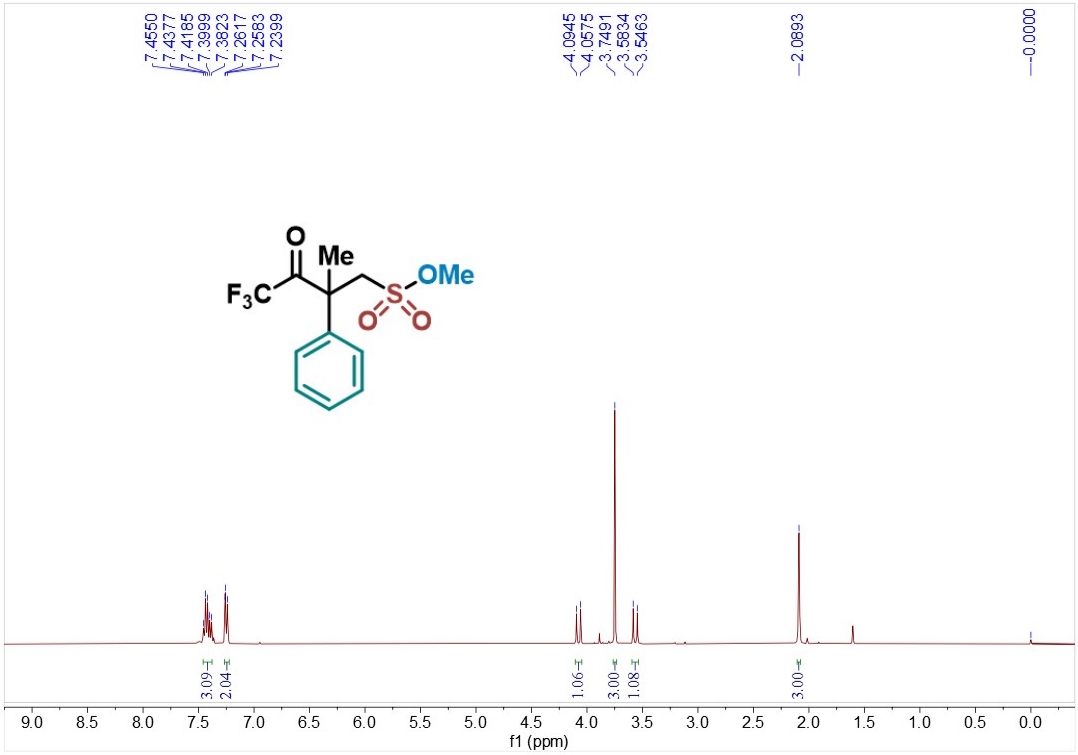
^{1}H NMR spectra of compound **5m** (400MHz, $CDCl_3$)



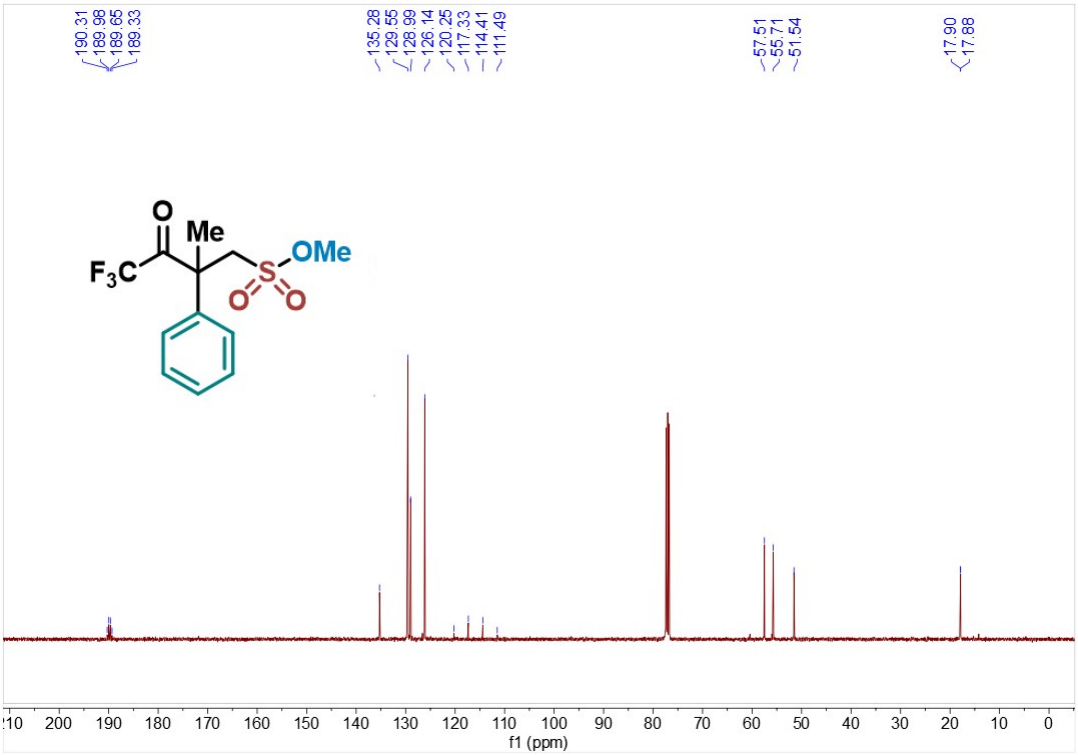
^{13}C NMR spectrum of compound **5m** (100 MHz, $CDCl_3$)



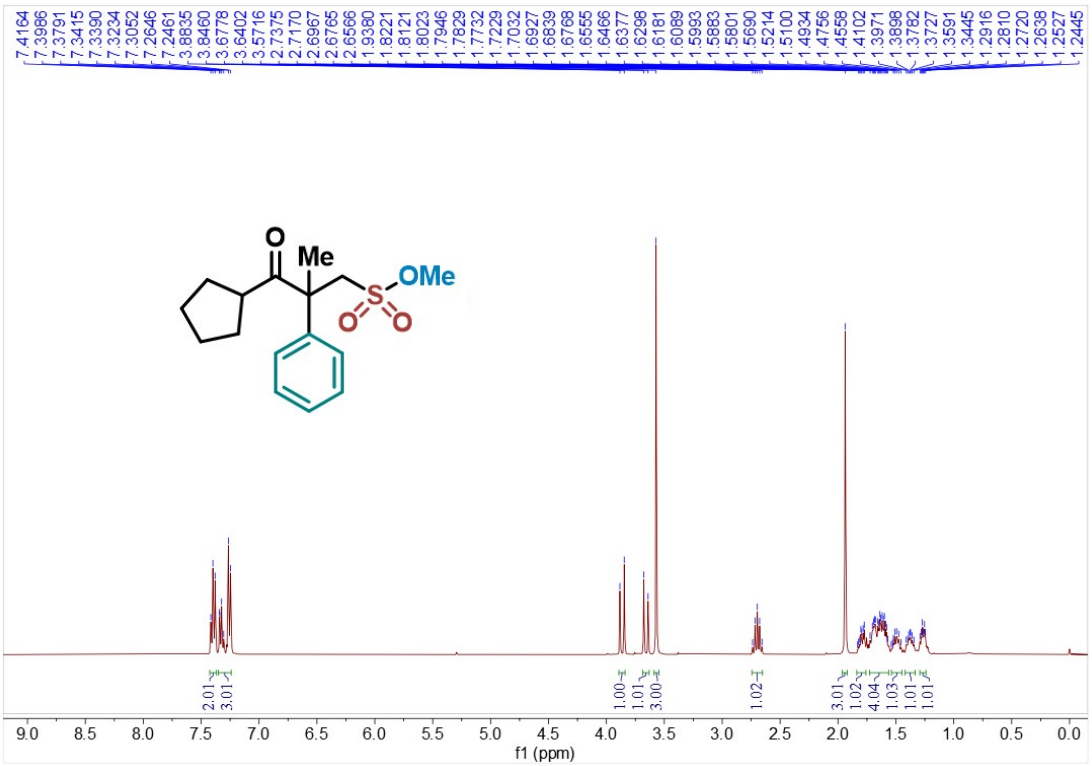
^{1}H NMR spectra of compound **5n** (400MHz, $CDCl_3$)



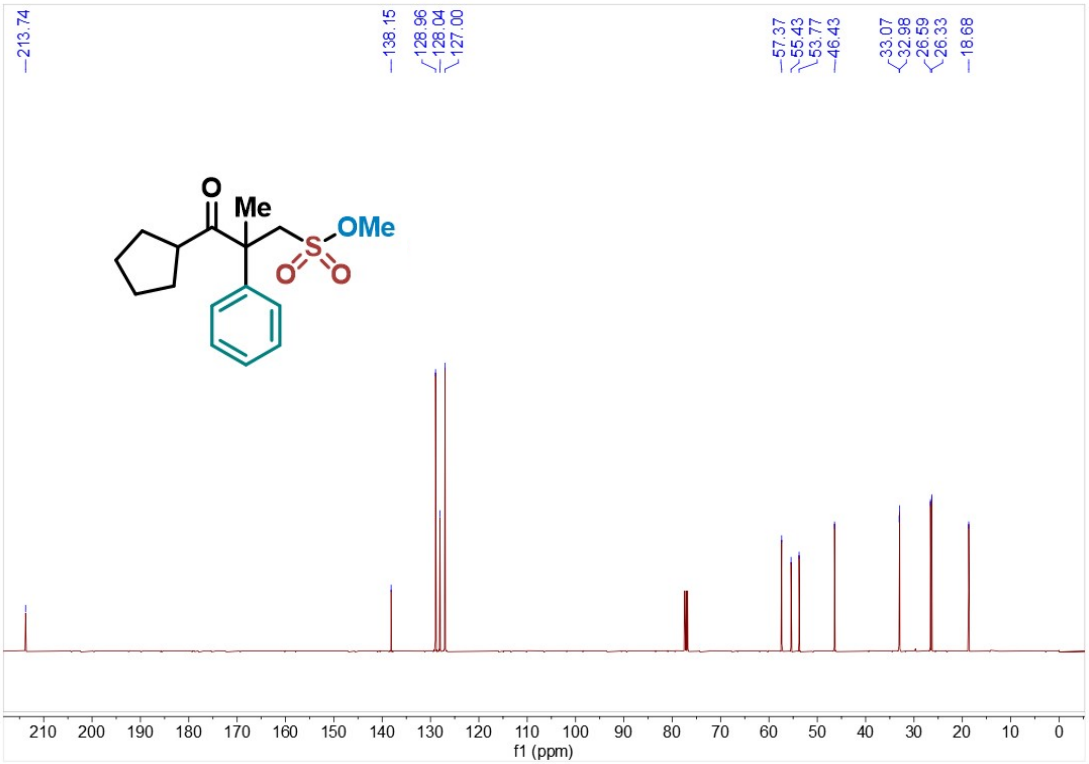
^{13}C NMR spectrum of compound **5n** (100 MHz, $CDCl_3$)



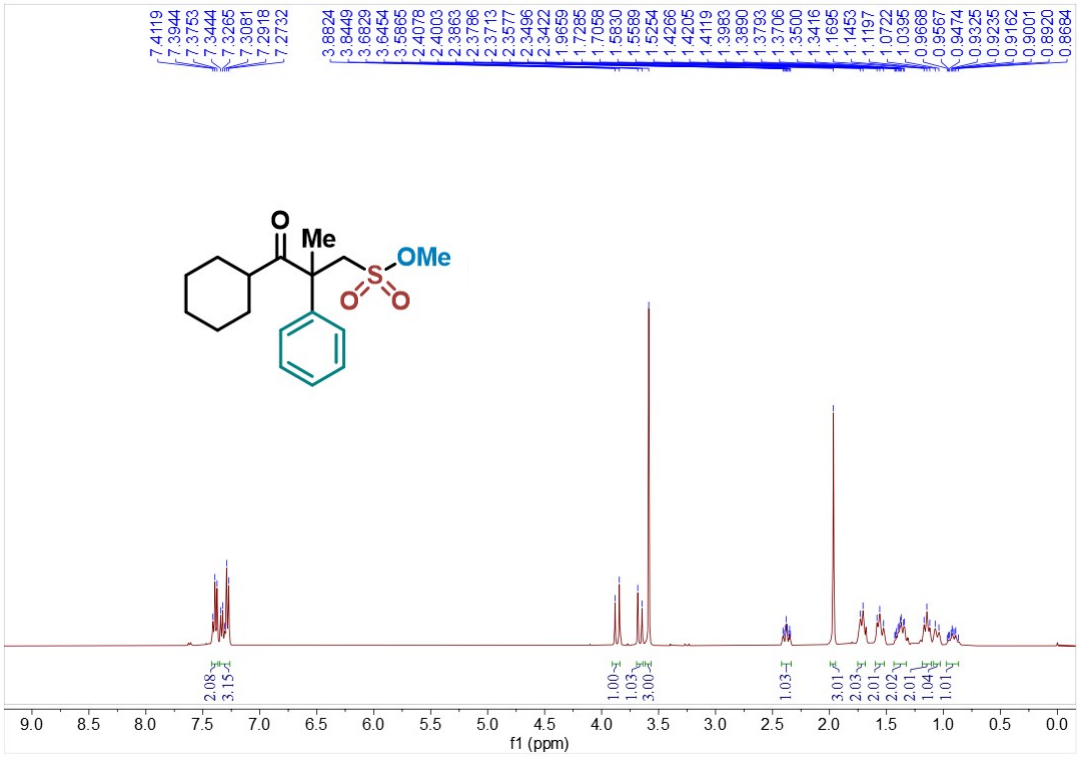
^{1}H NMR spectra of compound **5o** (400MHz, $CDCl_3$)



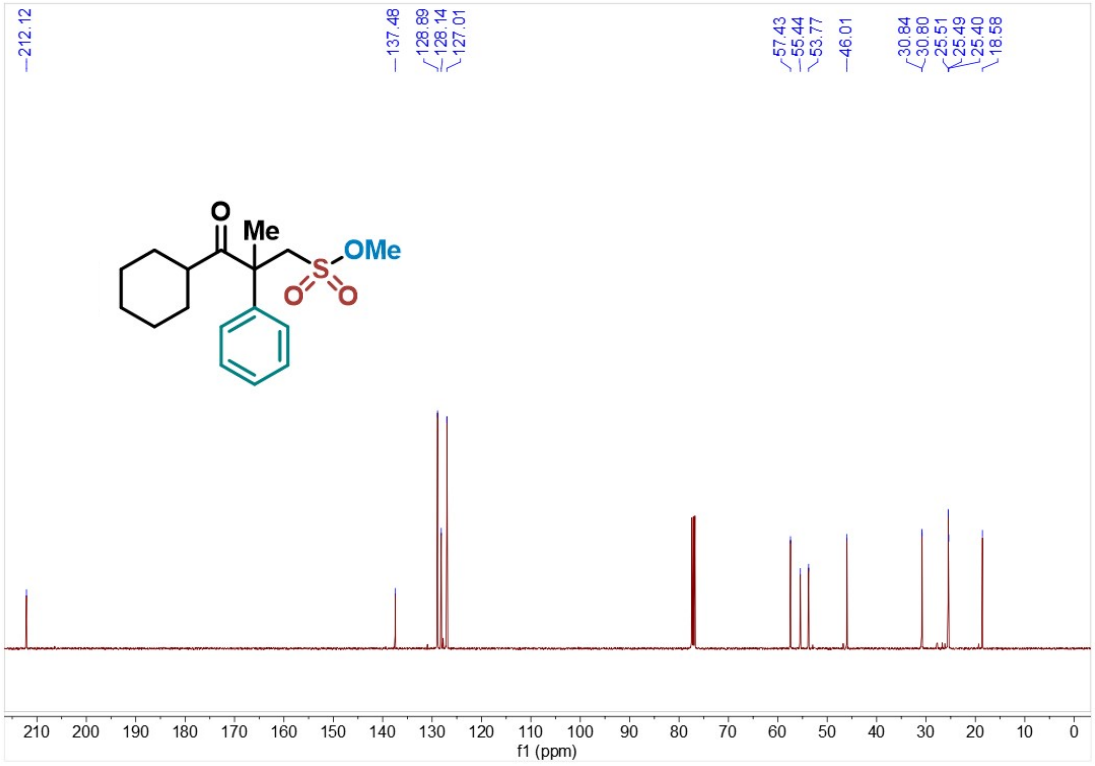
^{13}C NMR spectrum of compound **5o** (100 MHz, $CDCl_3$)



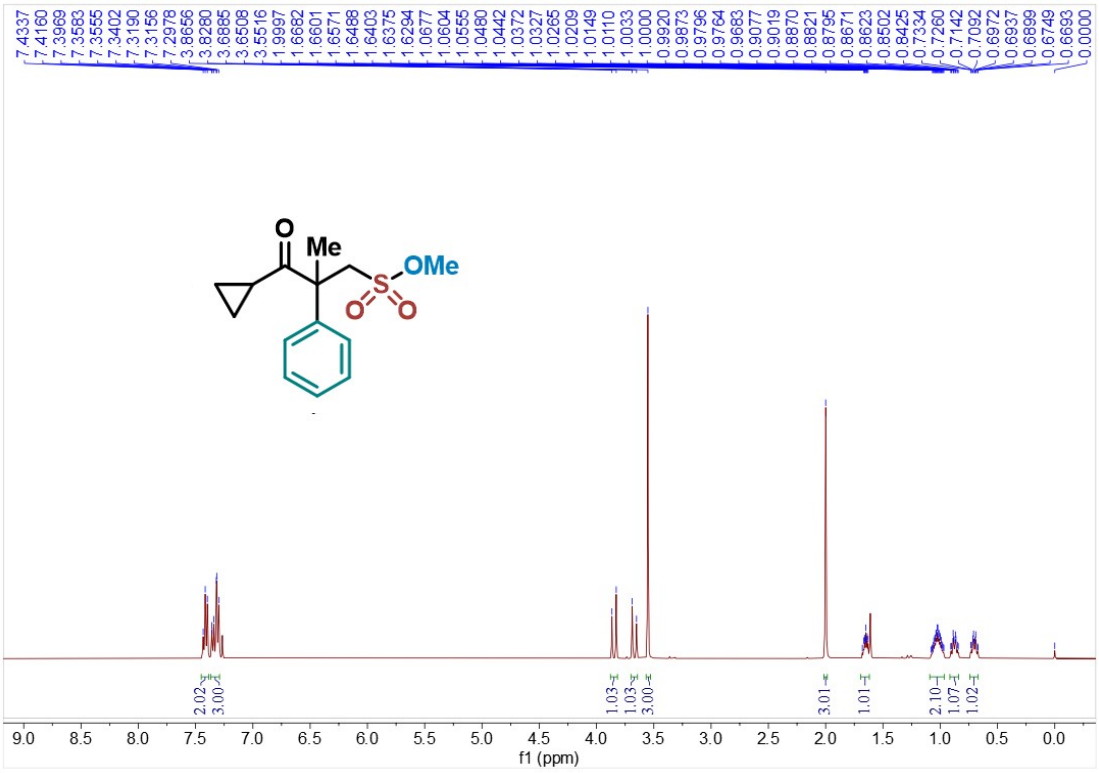
^{1}H NMR spectra of compound **5p** (400MHz, $CDCl_3$)



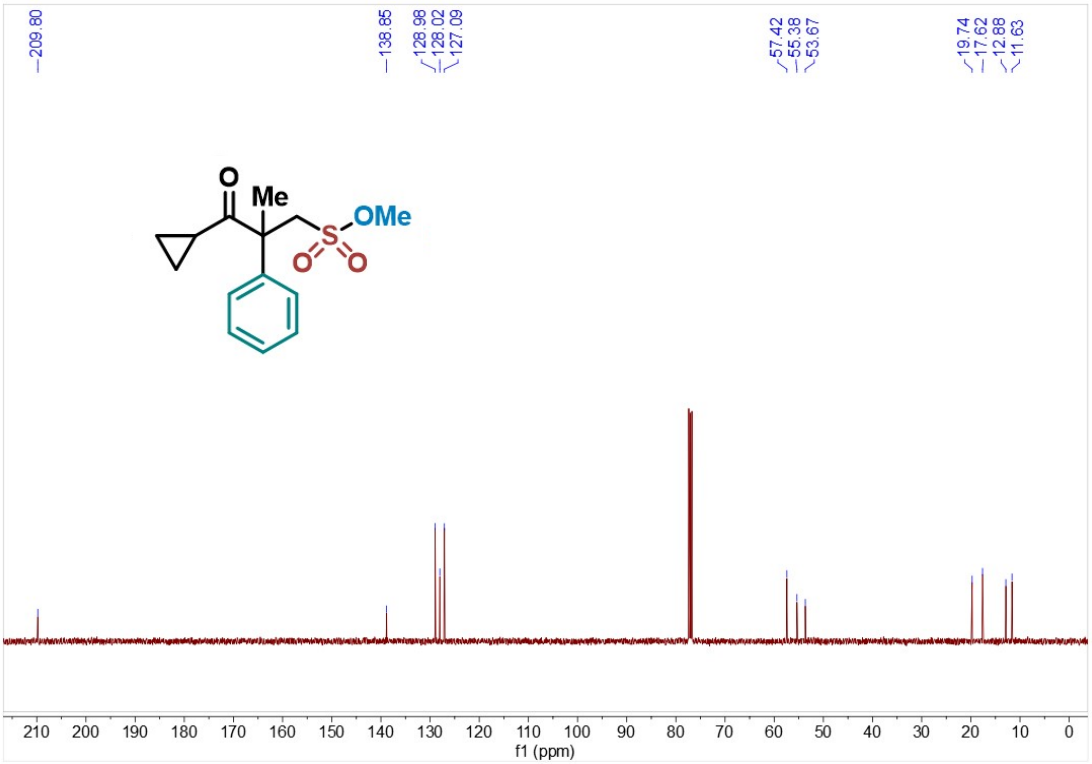
^{13}C NMR spectrum of compound **5p** (100 MHz, $CDCl_3$)



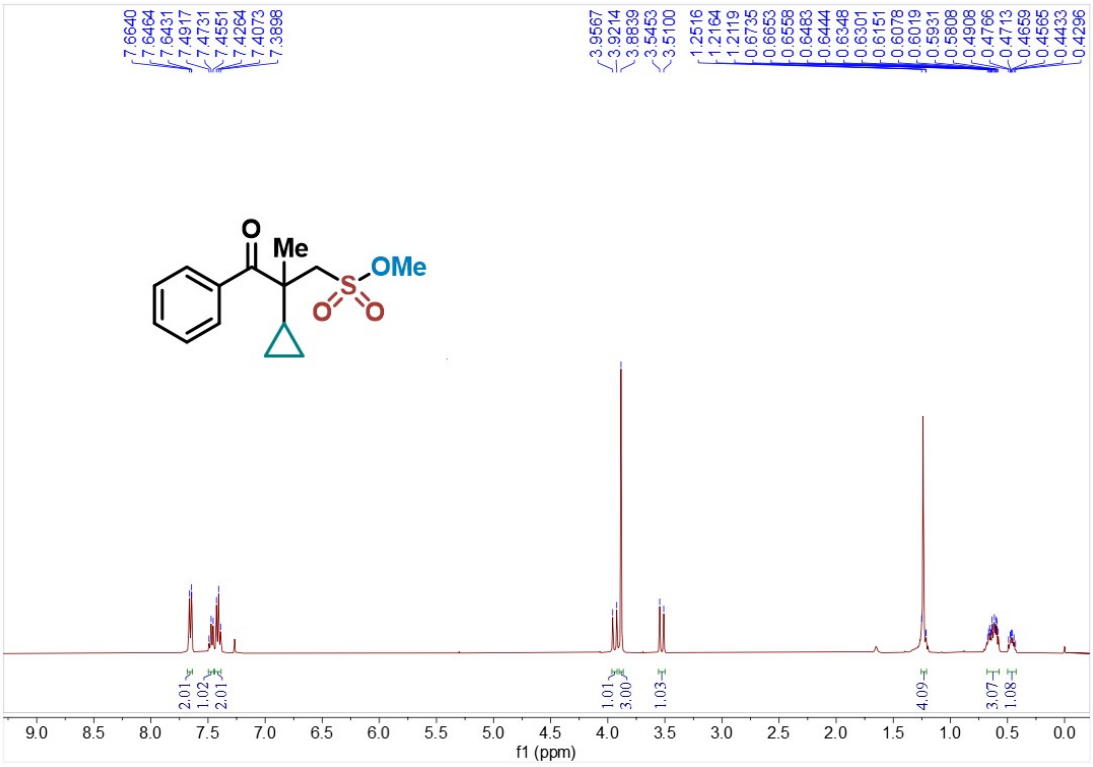
^{1}H NMR spectra of compound **5qa** (400MHz, $CDCl_3$)



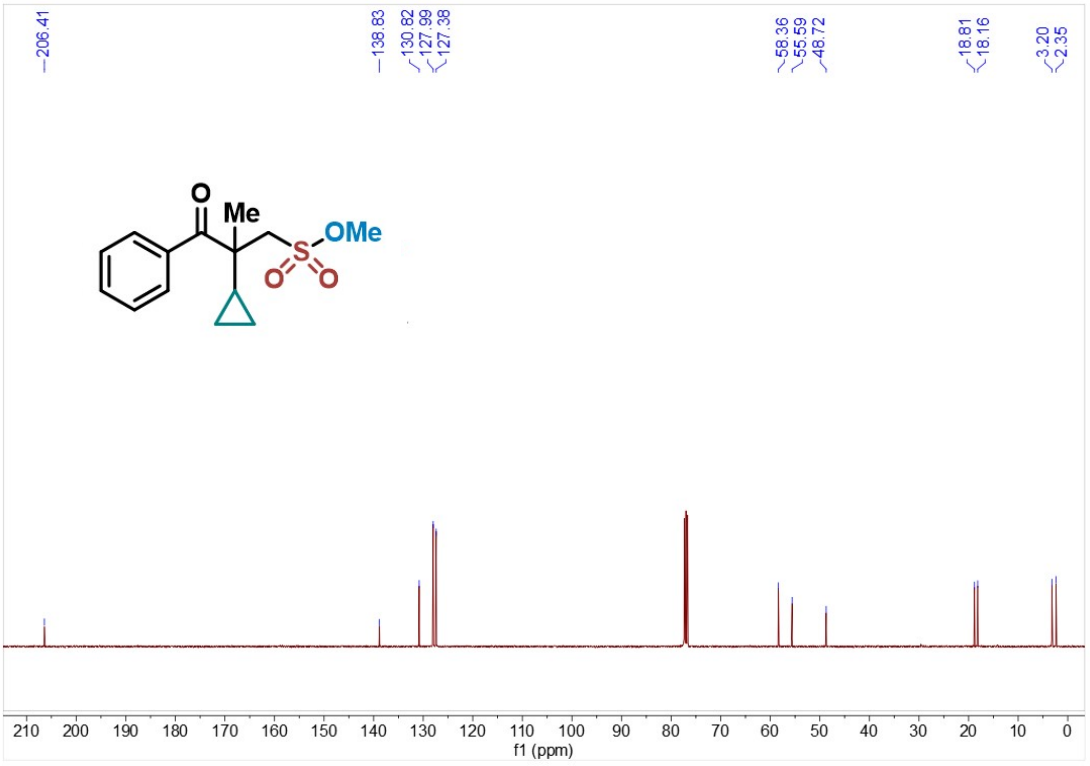
^{13}C NMR spectrum of compound **5qa** (100 MHz, $CDCl_3$)



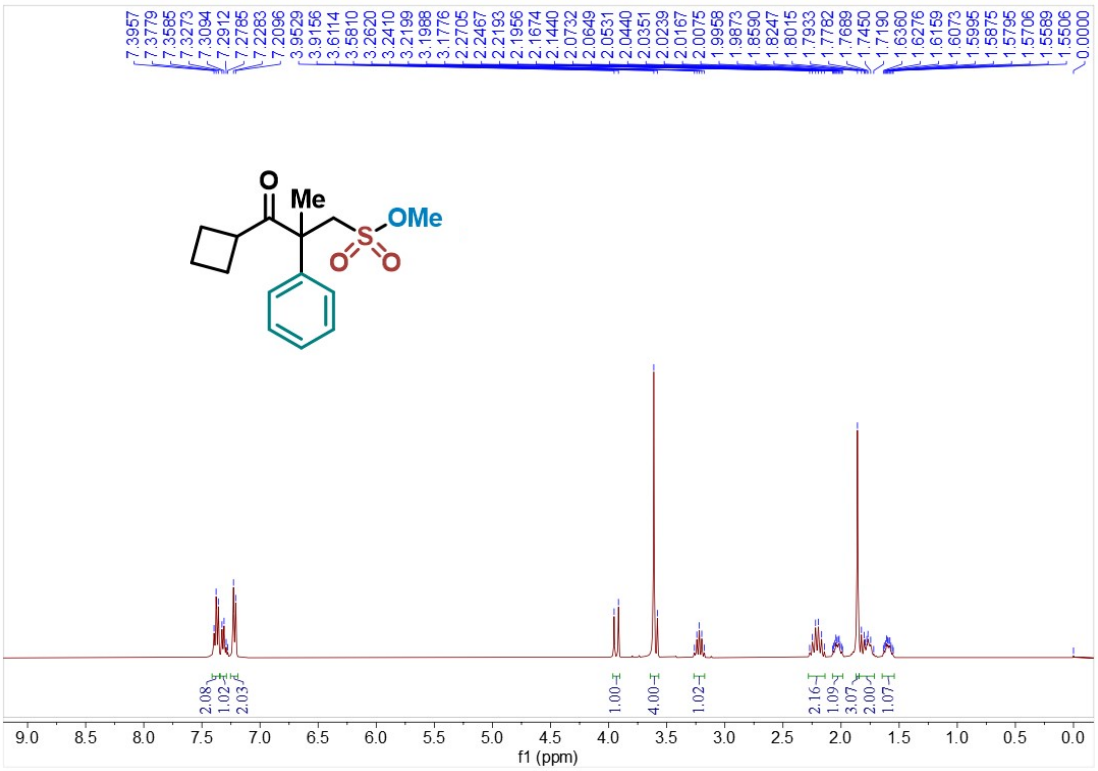
^{1}H NMR spectra of compound **5qb** (400MHz, $CDCl_3$)



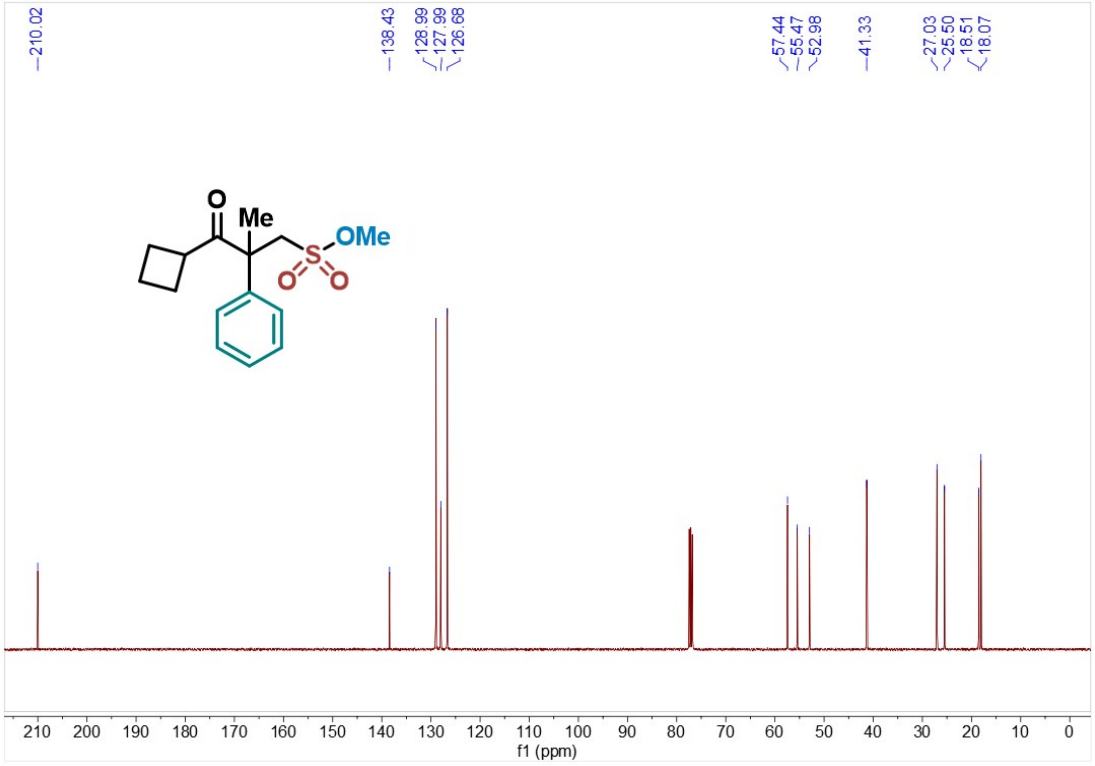
^{13}C NMR spectrum of compound **5qb** (100 MHz, $CDCl_3$)



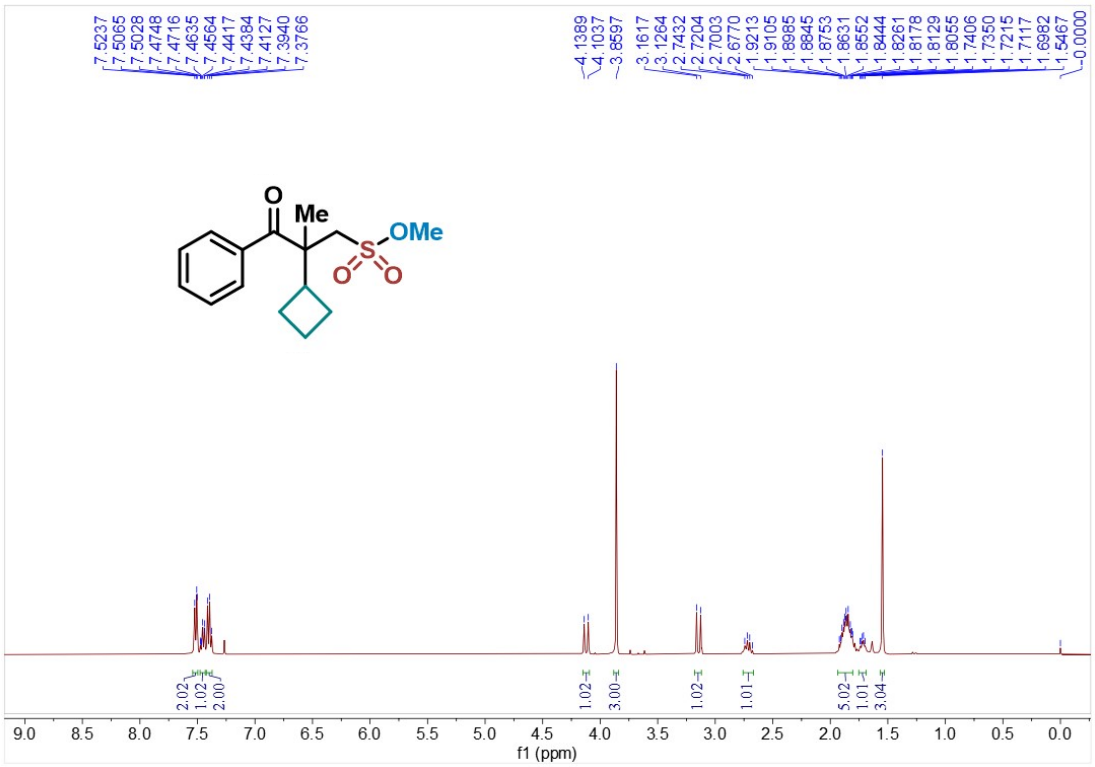
^{1}H NMR spectra of compound **5ra** (400MHz, $CDCl_3$)



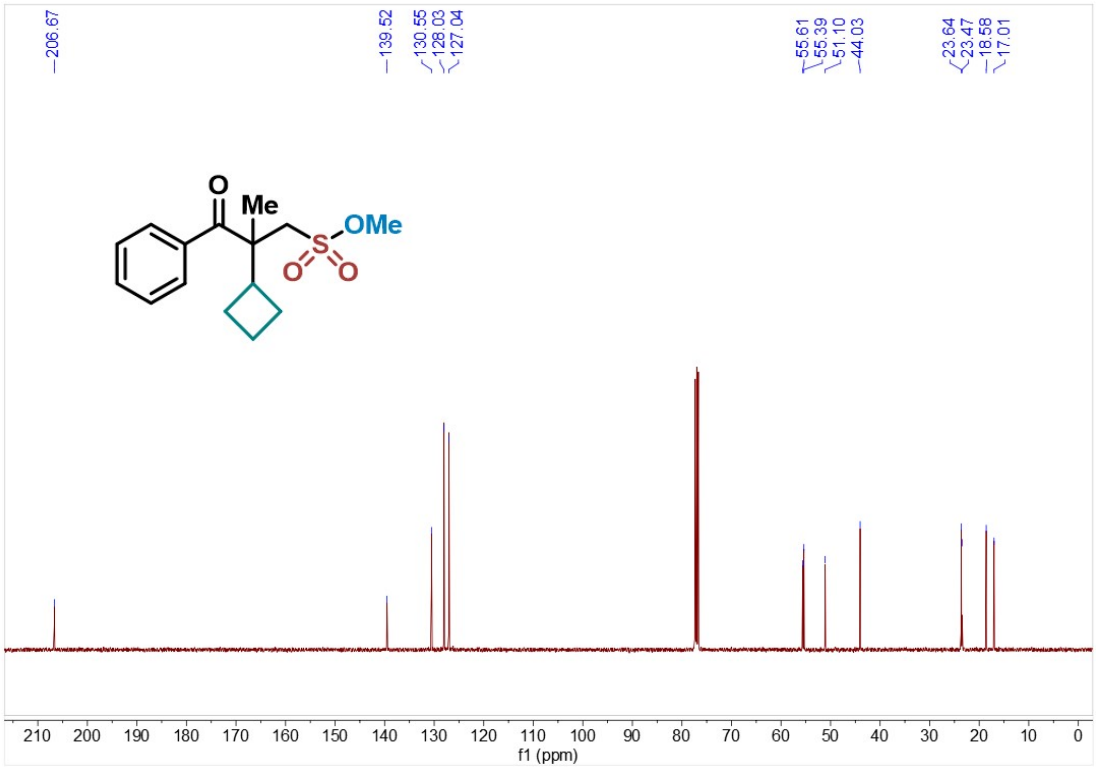
^{13}C NMR spectrum of compound **5ra** (100 MHz, $CDCl_3$)



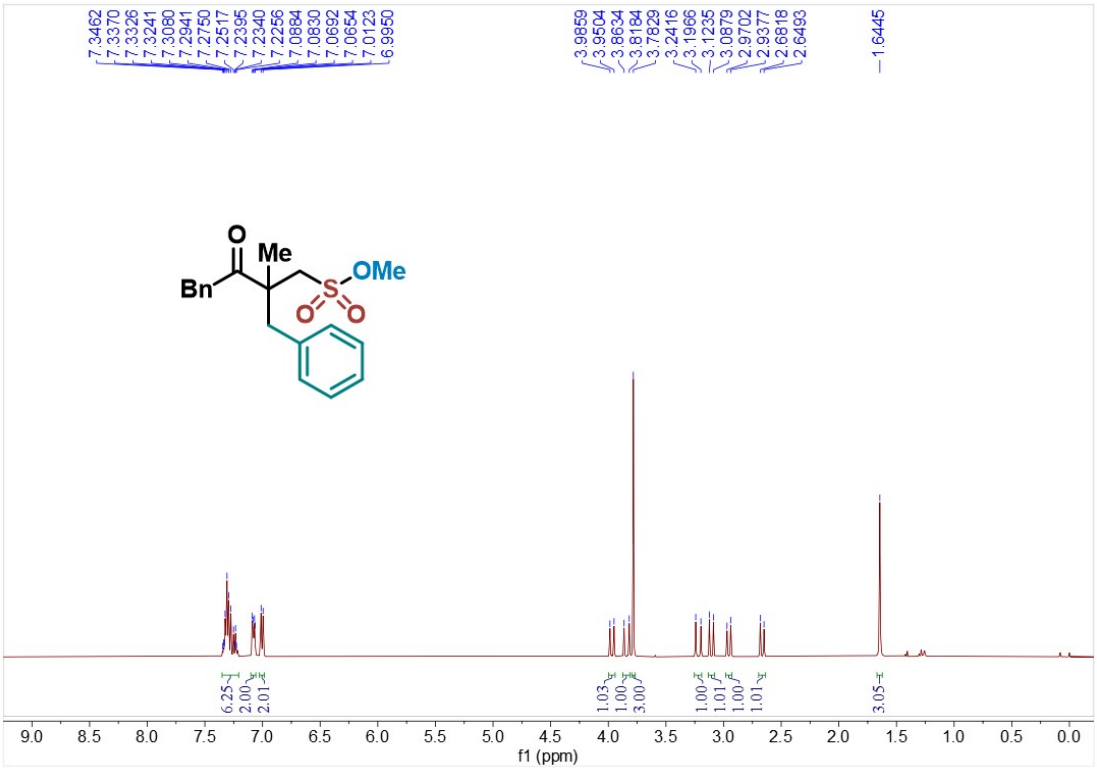
^{1}H NMR spectra of compound **5rb** (400MHz, $CDCl_3$)



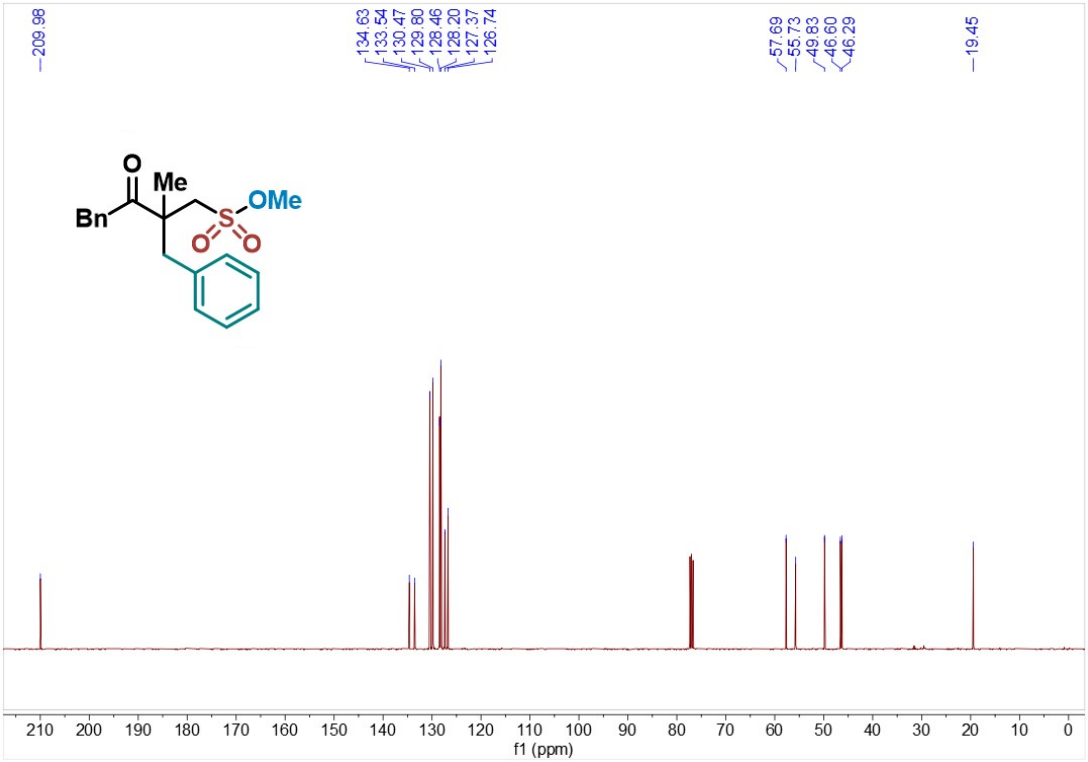
^{13}C NMR spectrum of compound **5rb** (100 MHz, $CDCl_3$)



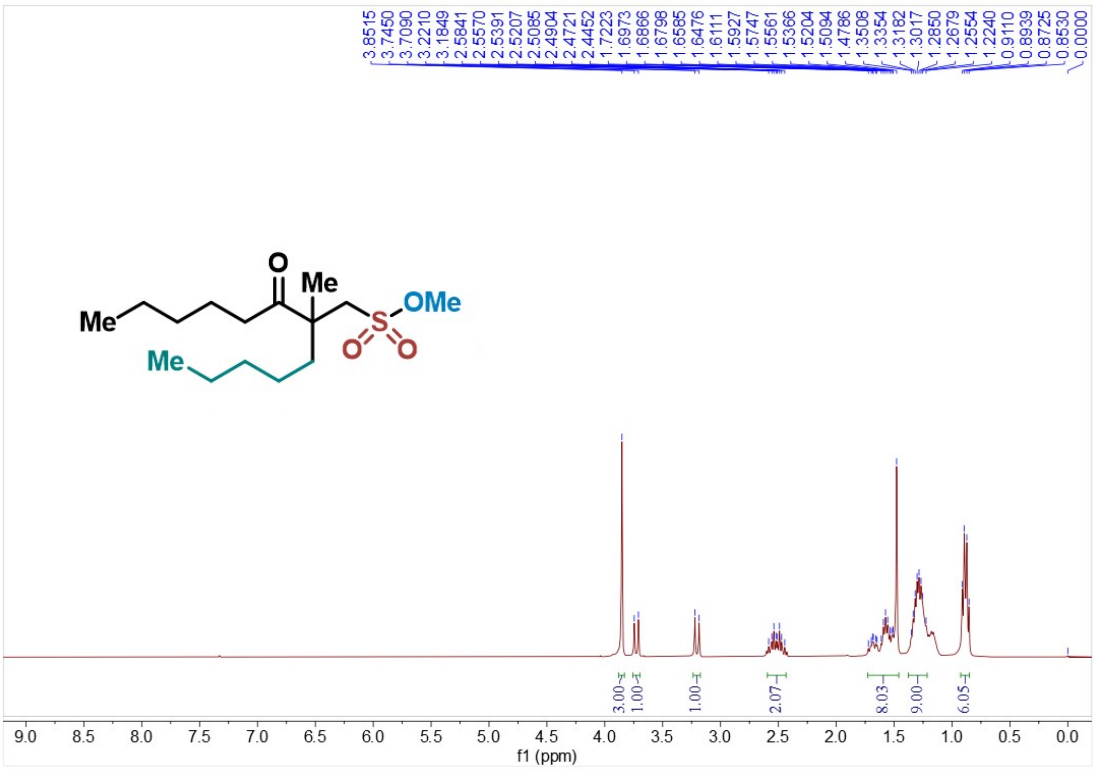
^{1}H NMR spectra of compound **5s** (400MHz, $CDCl_3$)



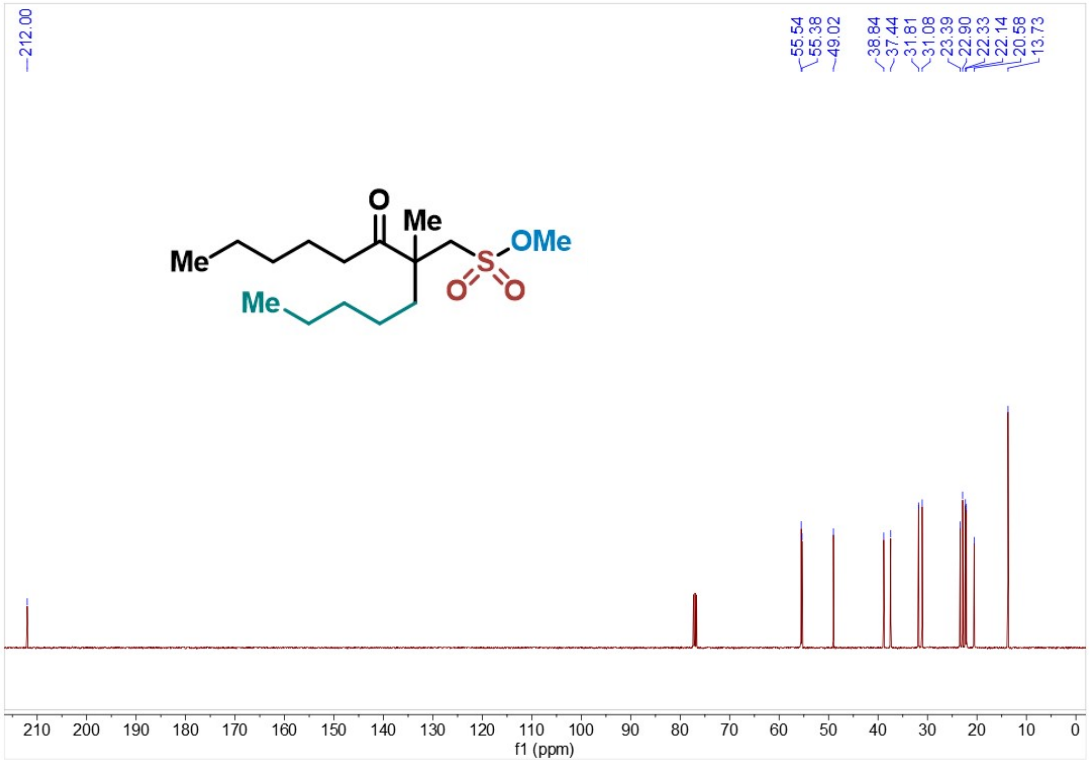
^{13}C NMR spectrum of compound **5s** (100 MHz, $CDCl_3$)



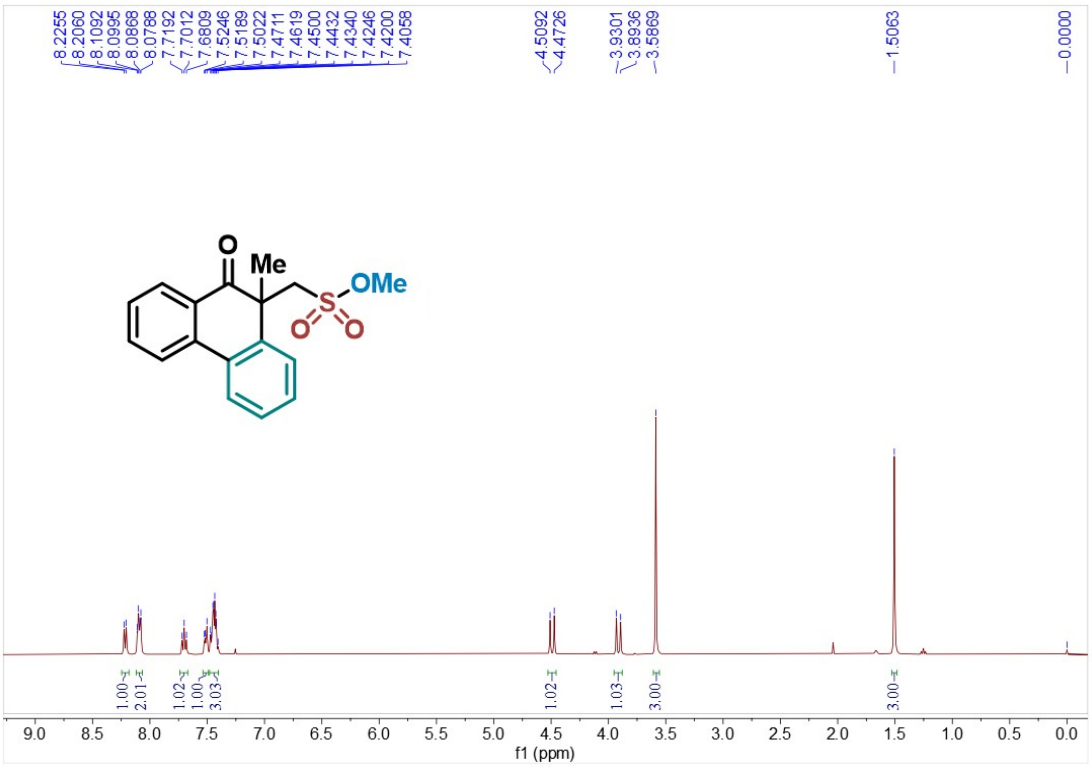
^{1}H NMR spectra of compound **5t** (400MHz, $CDCl_3$)



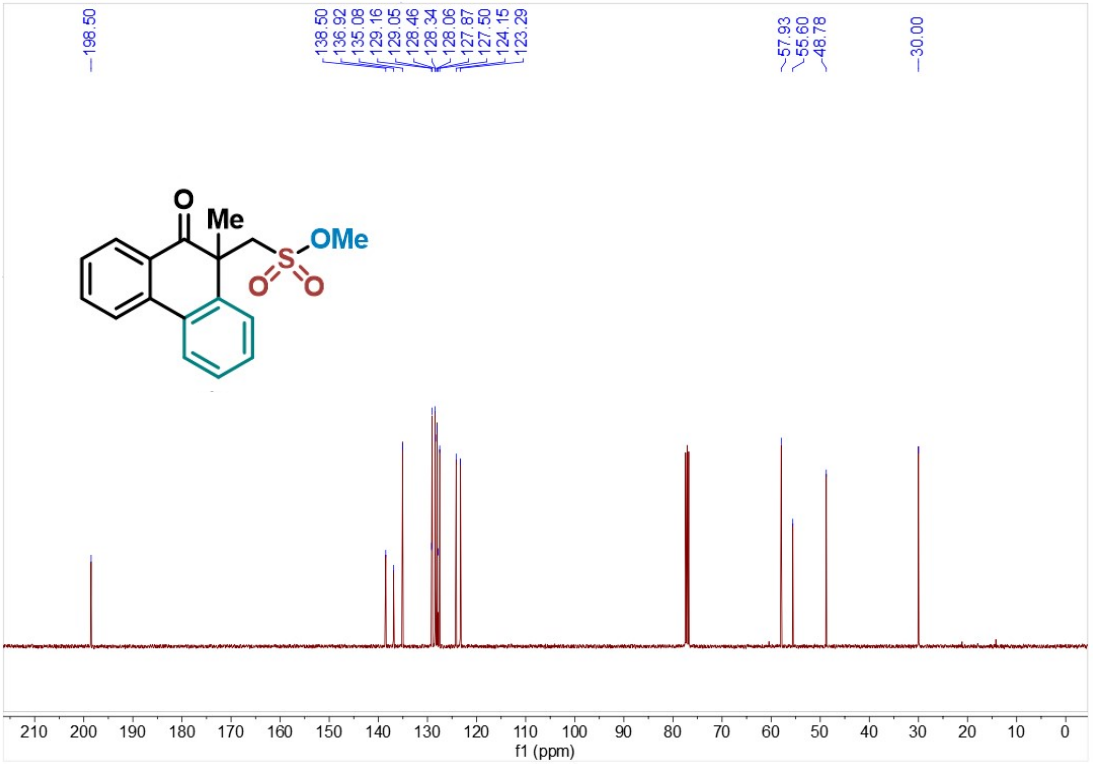
^{13}C NMR spectrum of compound **5t** (100 MHz, $CDCl_3$)



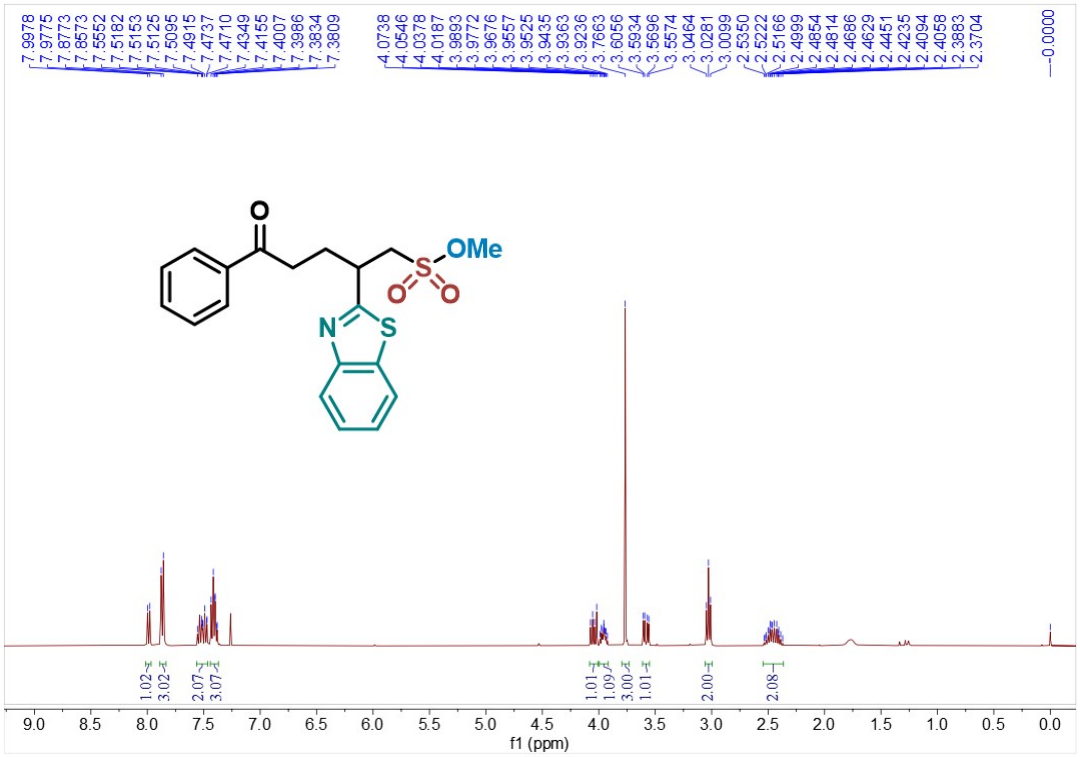
^{1}H NMR spectra of compound **5u** (400MHz, $CDCl_3$)



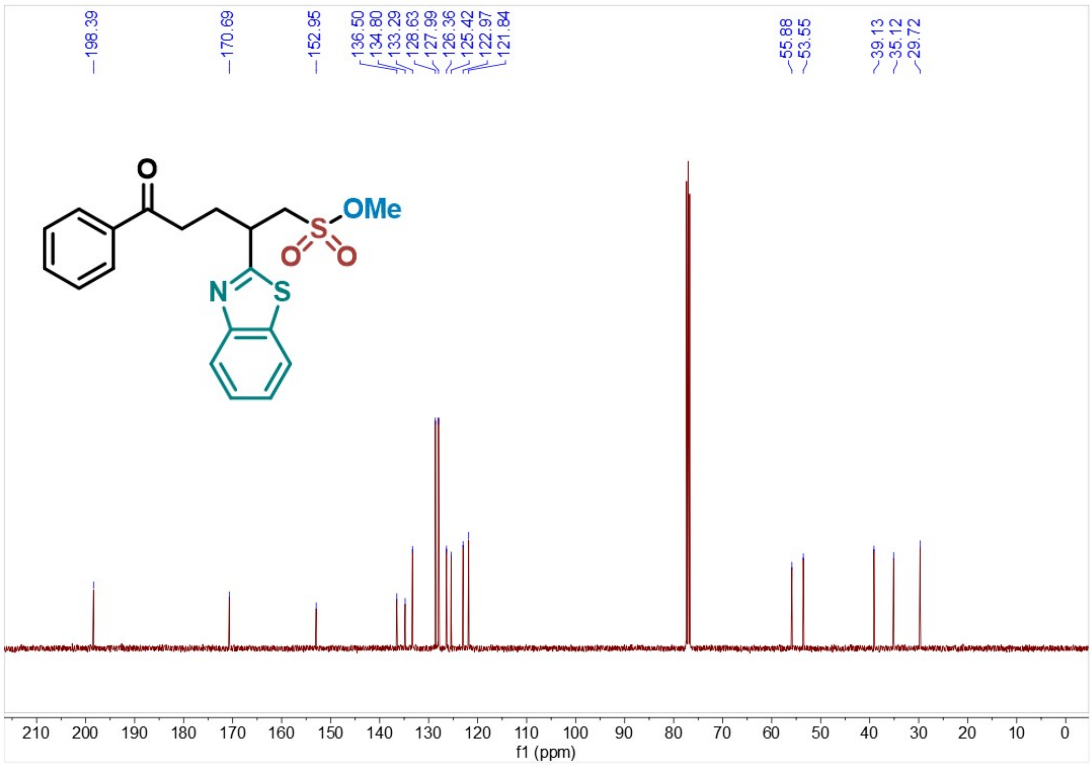
^{13}C NMR spectrum of compound **5u** (100 MHz, $CDCl_3$)



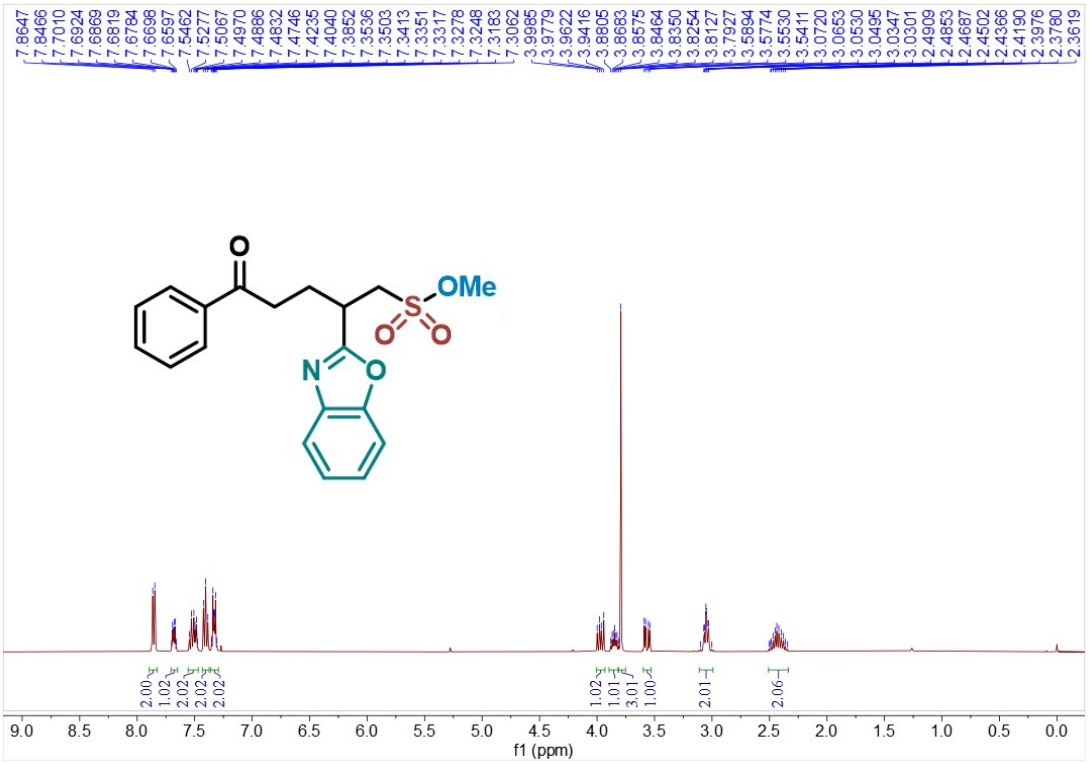
^{1}H NMR spectra of compound **5v** (400MHz, $CDCl_3$)



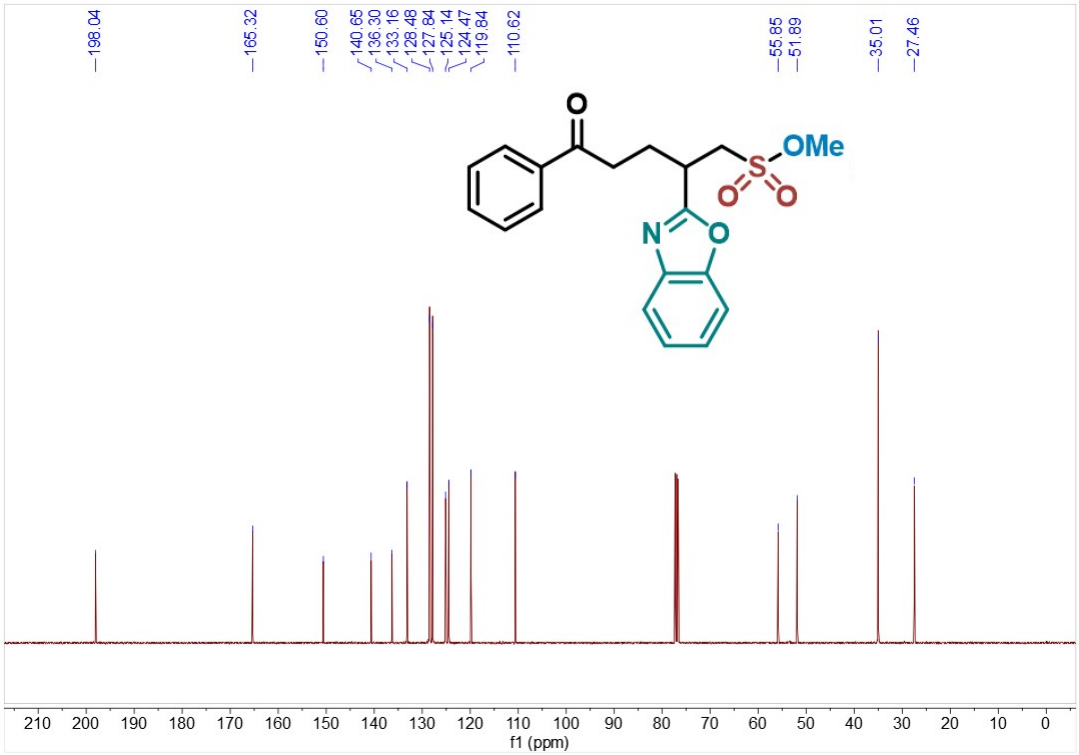
^{13}C NMR spectrum of compound **5v** (100 MHz, $CDCl_3$)



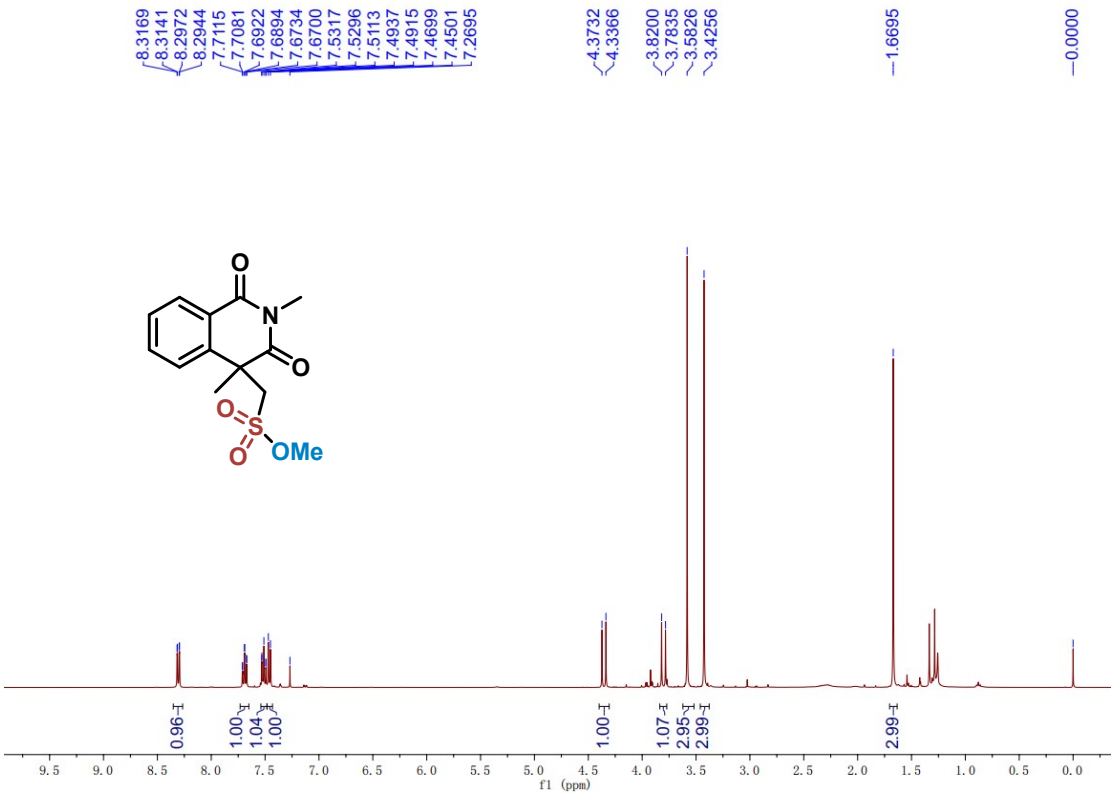
^{1}H NMR spectra of compound **5w** (400MHz, $CDCl_3$)



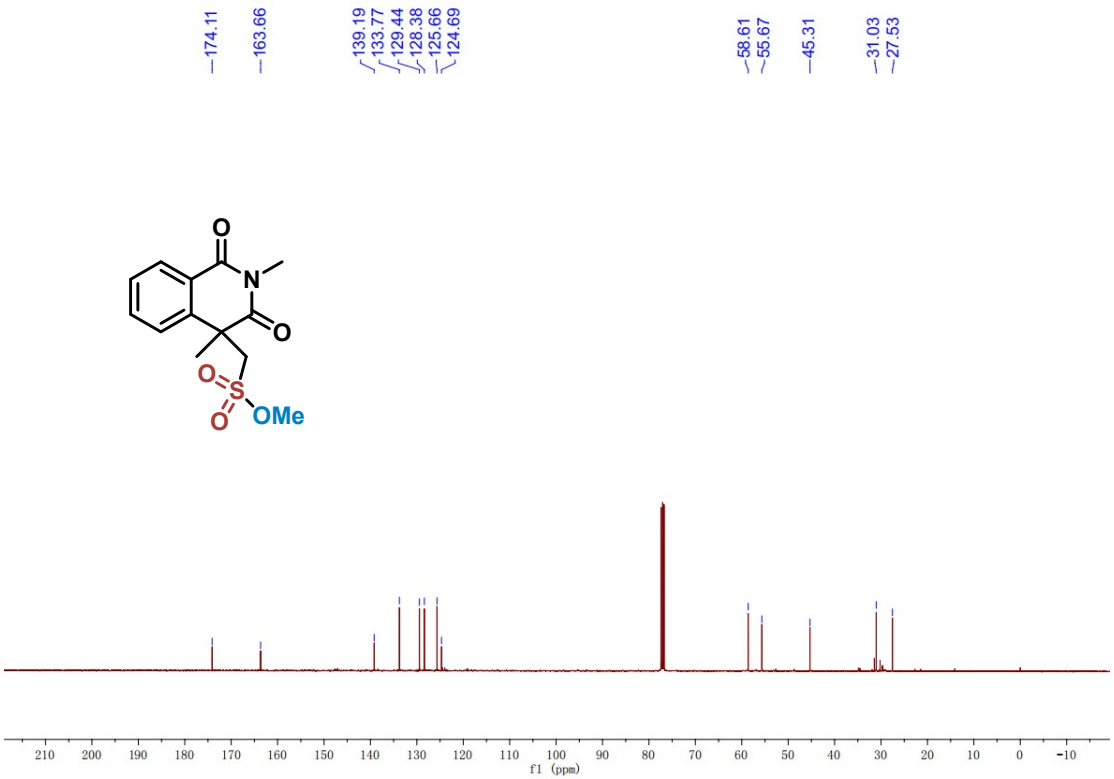
^{13}C NMR spectrum of compound **5w** (100 MHz, $CDCl_3$)



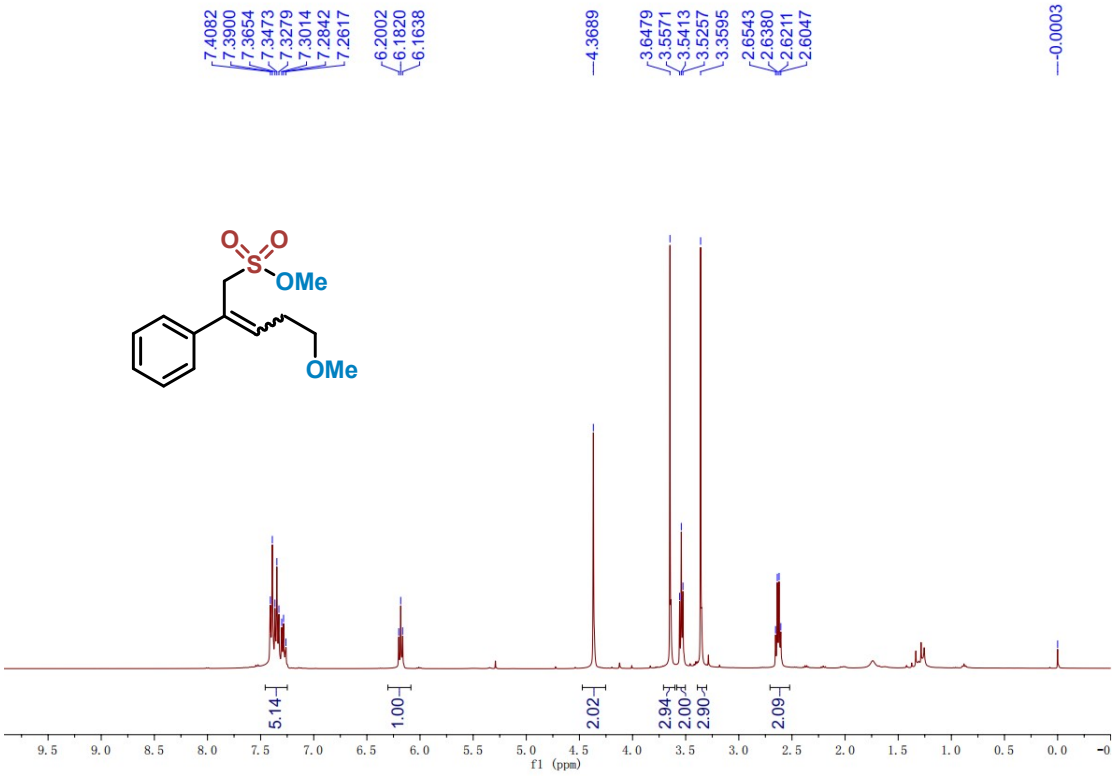
^{1}H NMR spectra of compound **7** (400MHz, $CDCl_3$)



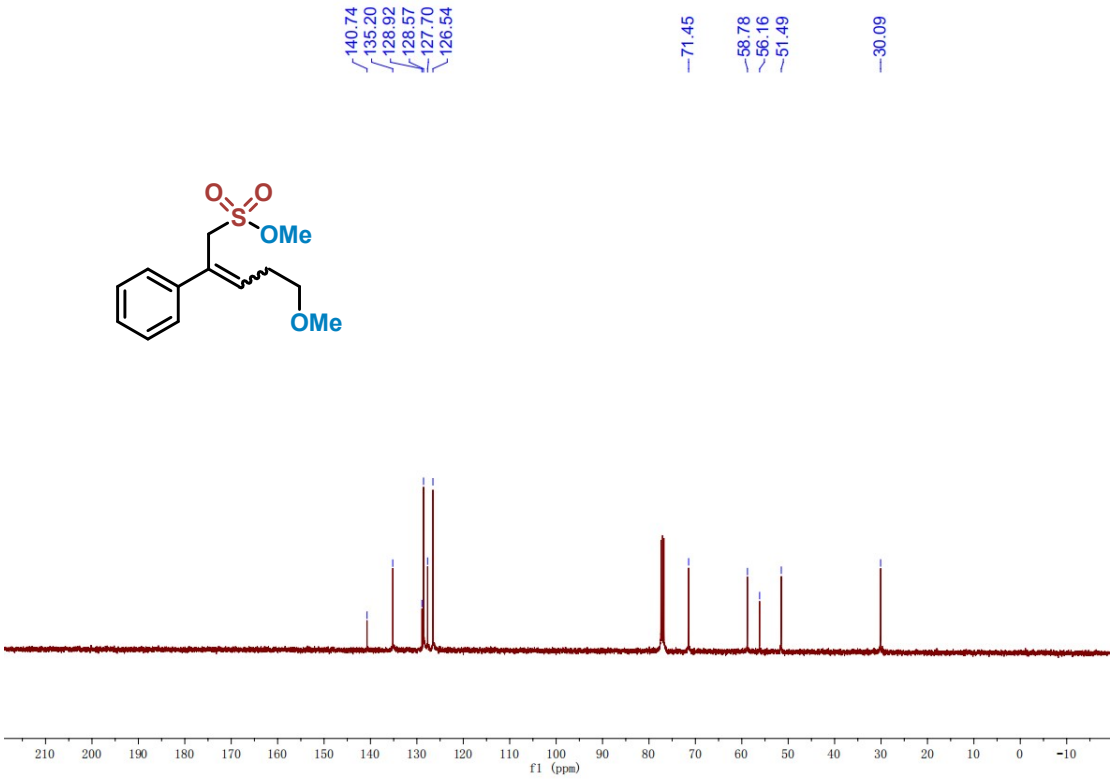
^{13}C NMR spectra of compound **7** (100MHz, $CDCl_3$)



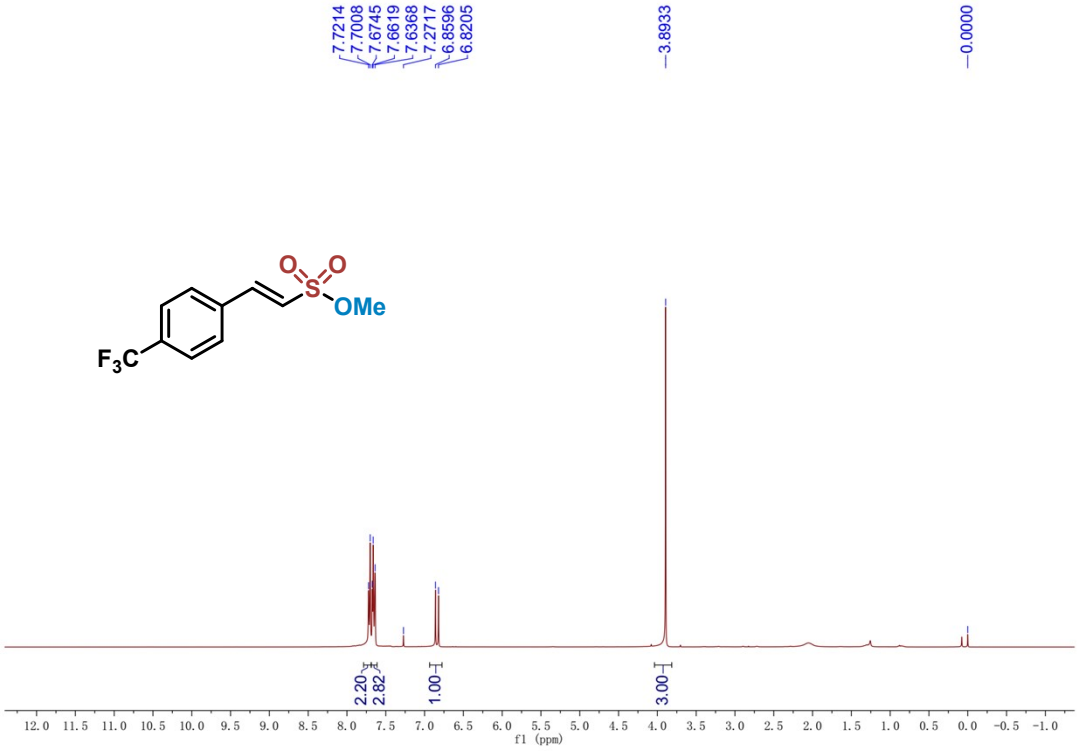
^{1}H NMR spectra of compound **8** (400MHz, $CDCl_3$)



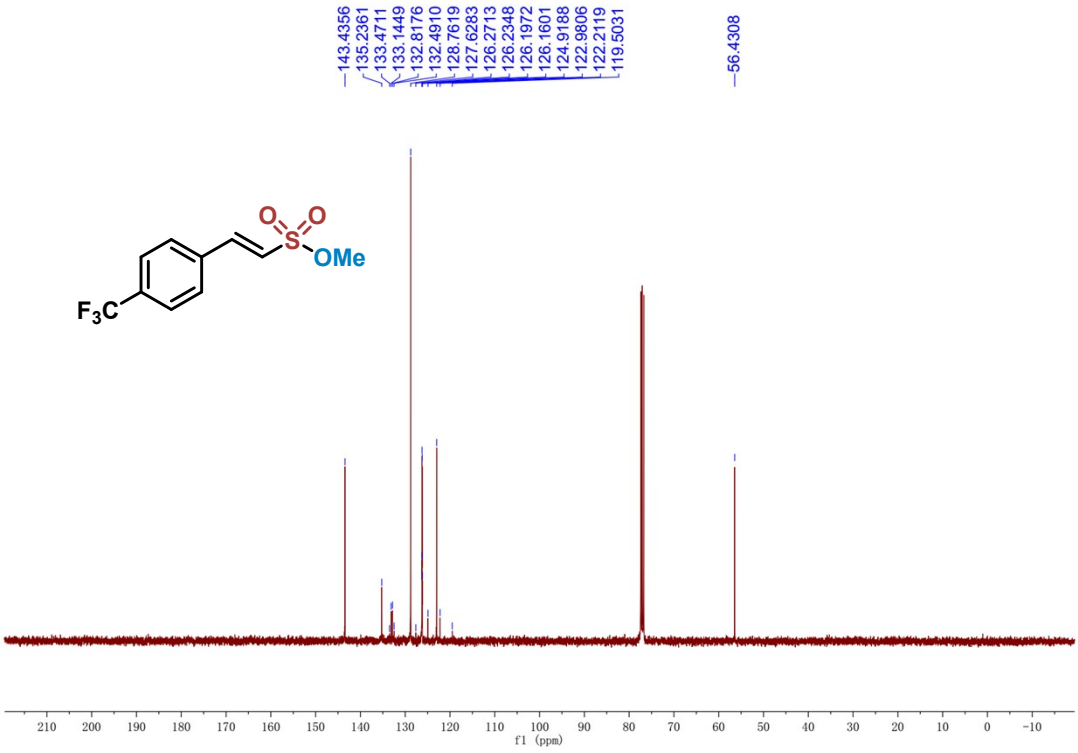
^{13}C NMR spectra of compound **8** (100MHz, $CDCl_3$)



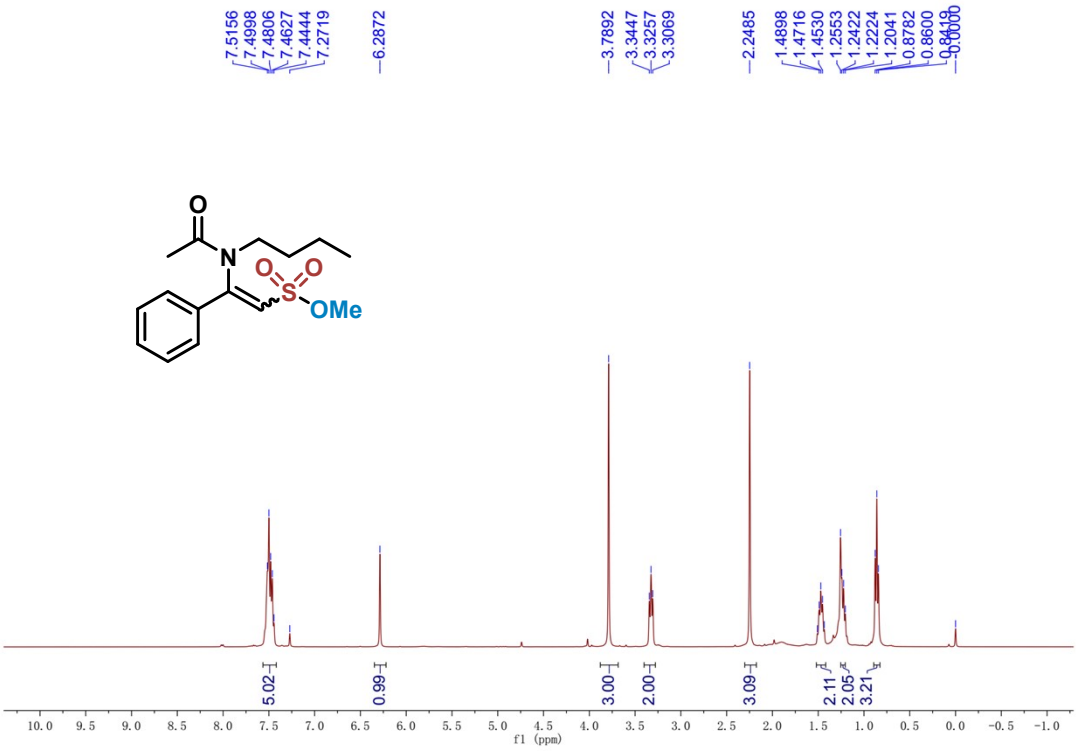
^{1}H NMR spectra of compound **9** (400MHz, $CDCl_3$)



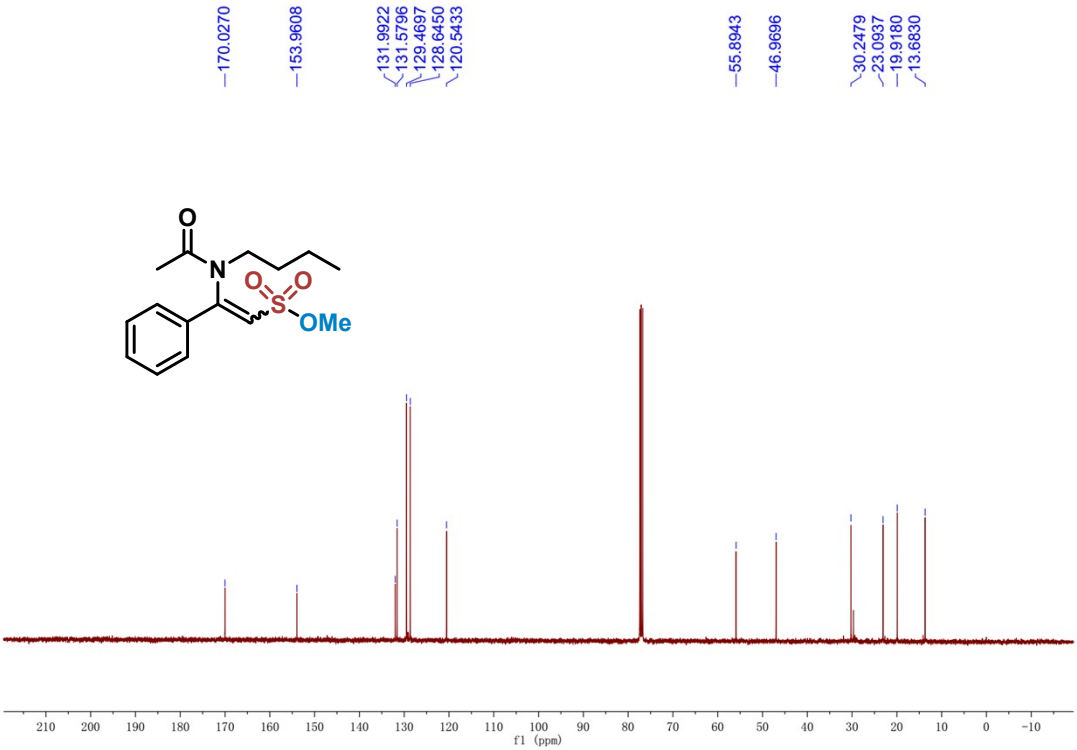
^{13}C NMR spectra of compound **9** (100MHz, $CDCl_3$)



^{1}H NMR spectra of compound **10** (400MHz, $CDCl_3$)



^{13}C NMR spectra of compound **10** (100MHz, $CDCl_3$)



9. Crystallographic details

9.1 Crystallographic details of 3as

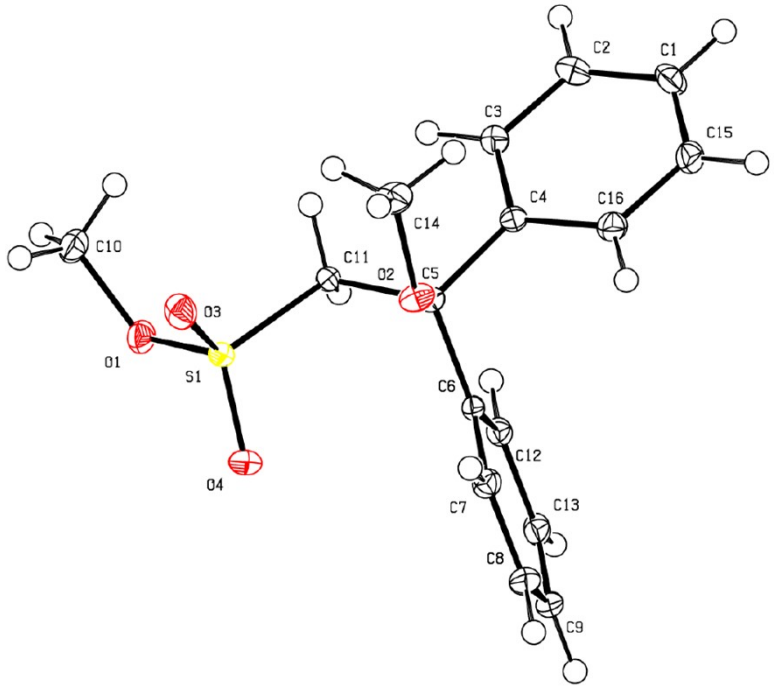


Table S2 Crystal data and structure refinement for 3as.

Identification code	cxy1479_0m
Empirical formula	$C_{16}H_{18}O_4S$
Formula weight	306.36
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.1786(3)
b/Å	18.5224(7)
c/Å	9.2041(3)
α/°	90
β/°	107.6160(10)
γ/°	90
Volume/Å^3	1491.41(9)
Z	4
ρ_{calc}g/cm^3	1.364
μ/mm^{-1}	0.230
F(000)	648.0
Crystal size/mm^3	0.33 × 0.29 × 0.28
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.398 to 56.632

Index ranges	$-12 \leq h \leq 10$, $-23 \leq k \leq 24$, $-12 \leq l \leq 12$
Reflections collected	21765
Independent reflections	3708 [R_{int} = 0.0378, R_{sigma} = 0.0274]
Data/restraints/parameters	3708/0/193
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0349, wR_2 = 0.0831
Final R indexes [all data]	R_1 = 0.0472, wR_2 = 0.0894
Largest diff. peak/hole / e $Å^{-3}$	0.41/-0.40

9.2 Crystallographic details of 5m

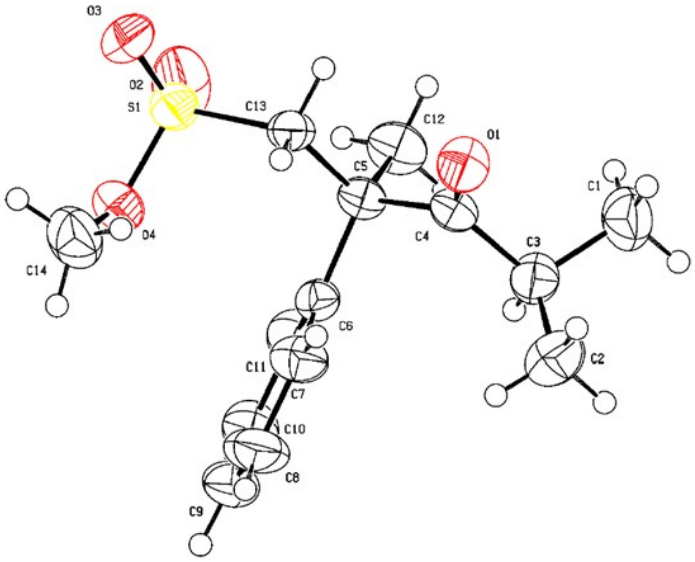


Table S2 Crystal data and structure refinement for 5m.

Identification code	1
Empirical formula	$C_{14}H_{20}O_4S$
Formula weight	284.36
Temperature/K	296(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.5469(15)
b/Å	8.3647(11)
c/Å	15.835(2)
α/°	90
β/°	105.211(2)
γ/°	90
Volume/$Å^3$	1475.9(3)
Z	4
ρ_{calc}g/cm^3	1.280
μ/mm^{-1}	0.226

F(000)	608.0
Crystal size/mm^3	0.260× 0.210 × 0.180
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.332 to 49.994
Index ranges	-13 ≤ h ≤ 9, -9 ≤ k ≤ 9, -18 ≤ l ≤ 18
Reflections collected	7236
Independent reflections	2589 [R_{int} = 0.0208, R_{sigma} = 0.0238]
Data/restraints/parameters	2589/0/176
Goodness-of-fit on F^2	0.984
Final R indexes [I>=2σ (I)]	R_1 = 0.079, wR_2 = 0.1025
Final R indexes [all data]	R_1 = 0.0523, wR_2 = 0.1099
Largest diff. peak/hole / e Å^{-3}	0.18/-0.28