Supporting Information

Electrochemical multi-component reaction of potassium metabisulfite with alkenes and alcohols enabling synthesis of sulfonate esters

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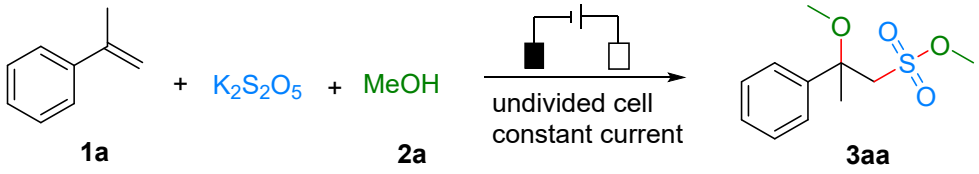
1. General information

All the commercial reagents including solvents (anhydrous) were used directly without further purification. All the experiments were monitored by thin layer chromatography (TLC) with UV light. The anode electrode and cathode electrode were graphite flakes (10×10×3 mm). The TLC employed 0.25 mm silica gel coated on glass plates. Purification of products was carried out by silica gel 60 F-254 TLC plates of 20 cm × 20 cm. Melting points were recorded without correction on RY-1G of Tianjin Xintianguang instrument company. NMR spectra were recorded on Bruker 400 MHz and 600 MHz spectrometers. High resolution mass spectra (HRMS) were measured on Agilent 6210 ESI/TOF MS instrument. Cyclic voltammetry (CV) was performed on a CHI660D electrochemical workstation (CHI Instruments Co., Shanghai, China). The X-ray data were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation.

2. Optimization of reaction conditions

Table S1 Optimization of reaction solvent.[a,b]



Entry	Electrolyte	Time (h)	Solvent	Electrode	Current density (mA/cm^2)	Yield (%)
1	*n*-Bu_4NBF_4	2.5	MeOH	C/C	6.0	67[c]
2	*n*-Bu_4NBF_4	2.5	MeCN	C/C	6.0	trace[d]

[a] Reaction conditions: α-methylstyrene (**1a**, 0.2 mmol), potassium metabisulfite (1.2 equiv),

solvent (8.0 mL), electrolyte (3.0 equiv), 4 Å MS (150 mg), in undivided cell at room temperature. [b] Isolated yield based on α-methylstyrene **1a**. [c] MeOH (8 mL) used. [d] Acetonitrile (8 mL) and MeOH (0.5 mmol) used.

3. General procedure for the electrochemical reaction

Into the cell were taken alkene **1** (0.2 mmol), $K_2S_2O_5$ (1.2 equiv, 0.24 mmol), *n*-Bu_4NBF_4 (3.0 equiv, 0.6 mmol), 4 Å MS (150 mg), alcohol **2** (4.0 mL) and MeCN (4.0 mL). The mixture was electrolyzed under constant current (6 mA/cm^2) with a graphite anode (1.0 cm^2) and a graphite cathode (1.0 cm^2) at room temperature for 2.5 h. Then, H_2O (10 mL) and CH_2Cl_2 (15 mL) was added and the organic layer was taken, followed by extraction with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated to provide a residue. The crude product **3** was purified by TLC plate of 20 cm × 20 cm using petroleum ether/ethyl acetate (4:1, v/v) as eluent.

4. Procedure for large-scale synthesis

α-Methylstyrene **1a** (10 mmol, 1.18 g), potassium metabisulfite (1.2 equiv, 12 mmol, 2.66 g), *n*Bu_4NBF_4 (3.0 equiv, 6 mmol, 1.97 g), methanol (25 mL), acetonitrile (25 mL), 4 Å MS (2.0 g) were placed in a dried 100 mL glass beaker. The bottle was equipped with graphite plate (10×10×3 mm). The mixture was stirred at a constant current of 50 mA at room temperature for 50 h. The solvent was removed under reduced pressure, then H_2O (25 mL) and CH_2Cl_2 (25 mL) was added and the organic layer was taken, followed by extraction with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated to provide

a residue. The crude product **3aa** was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (4:1, v/v) as eluent.

5. Control experiment

Into a cell were taken α-methylstyrene **1a** (0.2 mmol), $K_2S_2O_5$ (1.2 equiv, 0.24 mmol), *n*-Bu_4NBF_4 (3.0 equiv, 0.6 mmol), TEMPO (5.0 equiv), 4 Å MS (150 mg), methanol (4 mL) and MeCN (4 mL). The mixture was stirred under constant current (6 mA) with a graphite anode and a graphite cathode at room temperature for 2.5 h.

6. X-ray crystallography of 3va

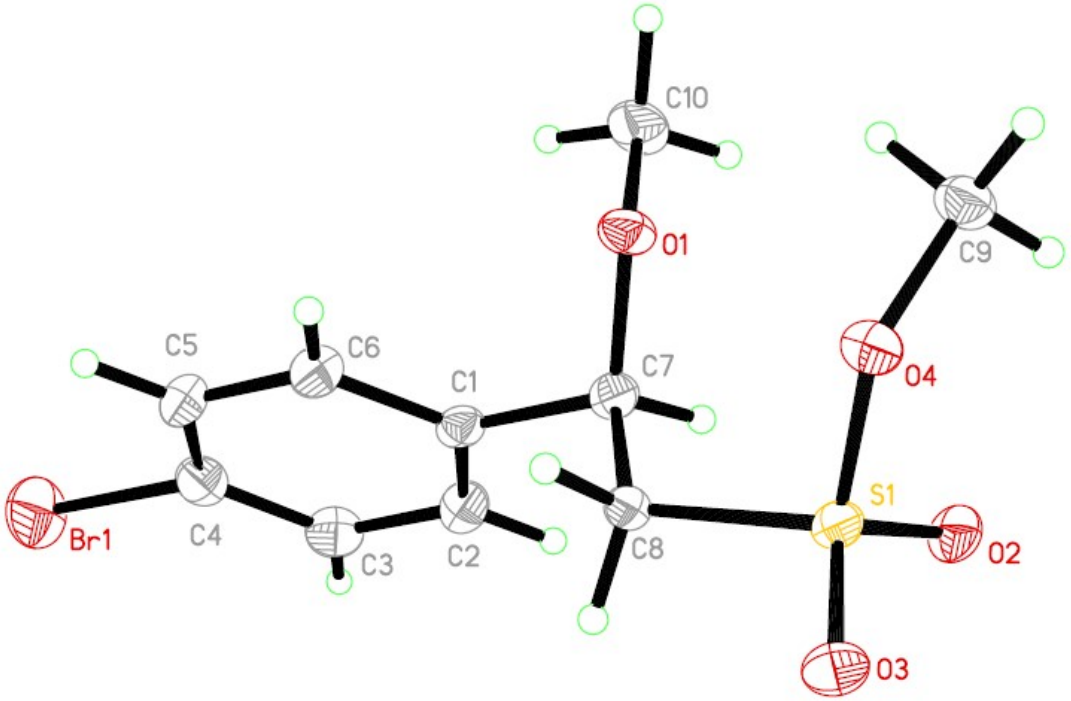


Figure S1. ORTEP diagram showing of **3va**.

(CCDC number is 2173393)

Suitable crystals of compound **3va** were obtained by slowly evaporating a mixture of petroleum ether and ethyl acetate solution at ambient temperature.

7. Cyclic voltammetry (CV) experiment

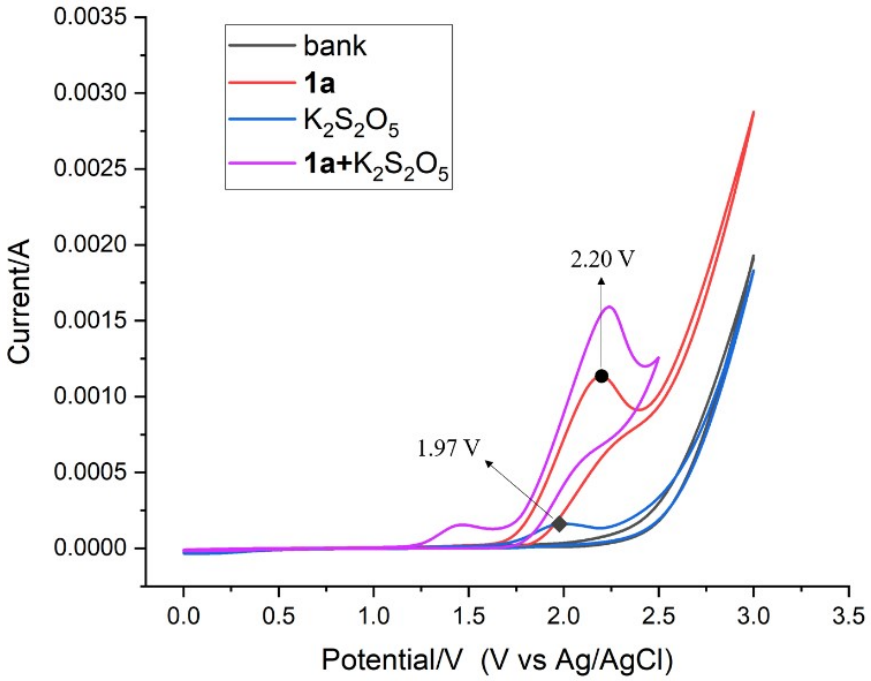


Figure S2. Cyclic voltammetry experiment

Cyclic voltammetry experiments were performed in a three-electrode cell connected to a schlenk line at room temperature. The working electrode was a glass carbon electrode, the counter electrode a glass carbon electrode. The reference was an Ag|AgCl electrode submerged in saturated KCl (3 M) solution, and separated from reaction by a salt bridge. MeCN (5.0 mL) and MeOH (5.0 mL) containing 2.0 mmol *n*-Bu_4NBF_4 was tested as blank background. The scan rate is 100 mV/s.

The concentration of compounds is: α-methylstyrene **1a** (0.05 mM); potassium metabisulfite (0.05 mM).

8. Electrosynthesis equipment

Micro electrosynthesis equipment

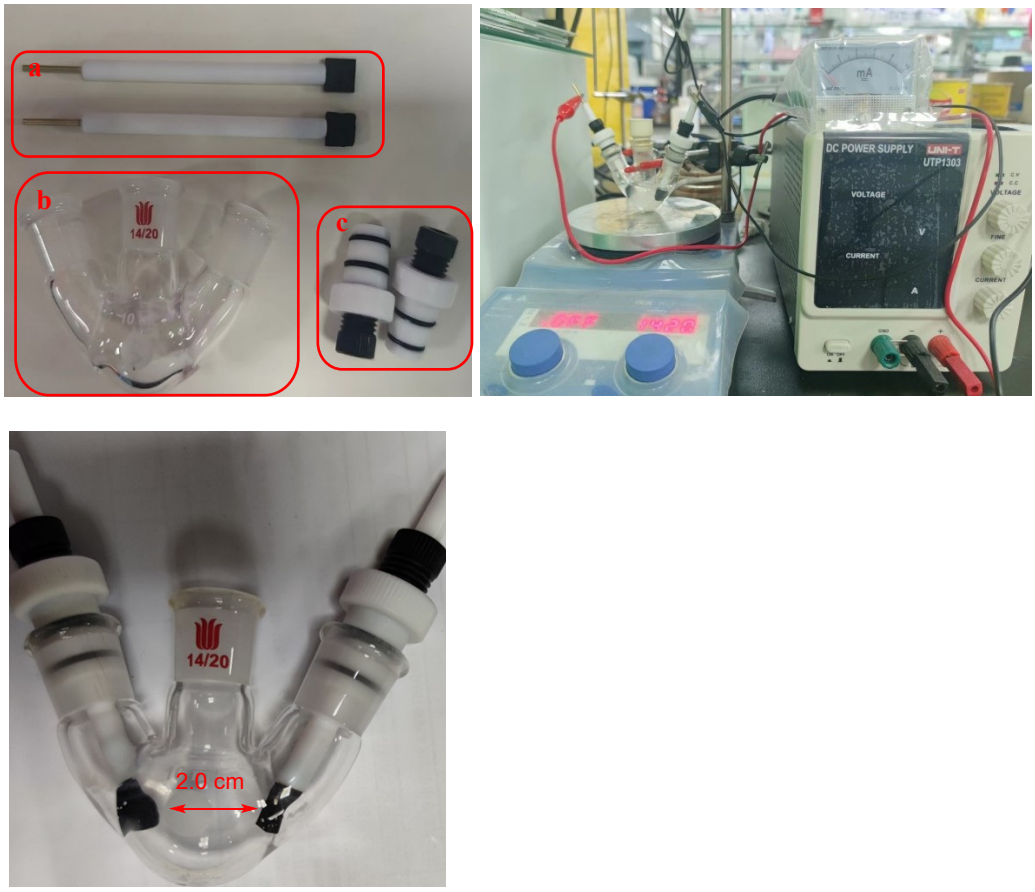


Figure S3. Micro electrosynthesis equipment.

a: graphite sheet electrode (1.0 cm × 1.0 cm); b: 10 mL three-necked flask; c: plug

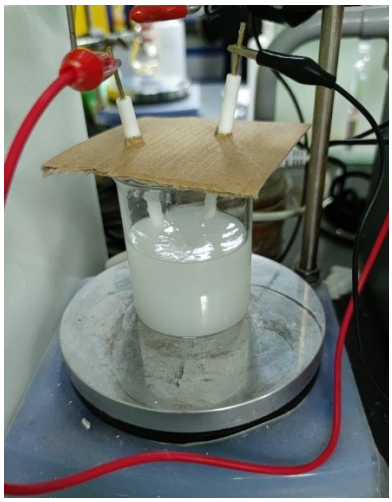
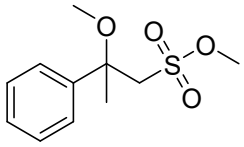
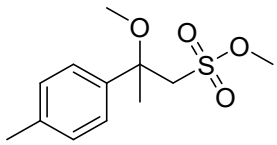


Figure S4. Macro electrosynthesis equipment.

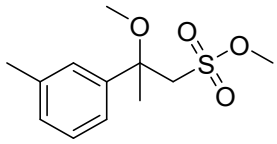
9. Characterization data of compounds 3



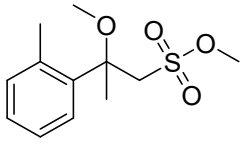
Compound **3aa**: 37.8 mg, 77% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.40 (m, 4H), 7.36-7.33 (m, 1H), 3.76 (s, 3H), 3.62 (d, *J* = 14.3 Hz, 1H), 3.46 (d, *J* = 14.7 Hz, 1H), 3.14 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0, 128.7, 128.1, 126.2, 77.0, 61.6, 55.8, 50.5, 21.0. HRMS (ESI) m/z: calculated for $C_{11}H_{16}NaO_4S^+$ $[M+Na]^+$ 267.0662, found 267.0673.



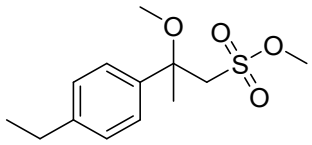
Compound **3ba**: 35.8 mg, 69% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.04 Hz, 2H), 3.77 (s, 3H), 3.61 (d, *J* = 14.76 Hz, 1H), 3.43 (d, *J* = 14.70 Hz, 1H), 3.12 (s, 3H), 2.38 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.0, 137.9, 129.3, 126.2, 76.8, 61.6, 55.8, 50.4, 21.0. HRMS (ESI) m/z: calculated for $C_{12}H_{18}NaO_4S^+$ $[M+Na]^+$ 281.0818, found 281.0827.



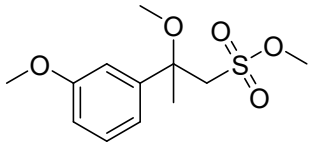
Compound **3ca**: 32.4 mg, 63% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31-7.28 (m, 1H), 7.25-7.23 (m, 2H), 7.16-7.15 (m, 1H), 3.78 (s, 3H), 3.62 (d, *J* = 14.76 Hz, 1H), 3.43 (d, *J* = 14.76 Hz, 1H), 3.14 (s, 3H), 2.40 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.1, 138.3, 128.8, 128.6, 126.8, 123.3, 76.9, 61.6, 55.8, 50.5, 21.6, 21.0. HRMS (ESI) m/z: calculated for $C_{12}H_{18}NaO_4S^+$ $[M+Na]^+$ 281.0818, found 281.0828.



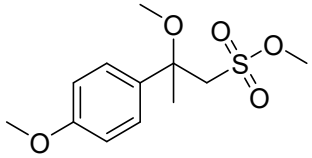
Compound **3da**: 27.1 mg, 52% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31-7.29 (m, 1H), 7.24-7.18 (m, 3H), 3.73 (d, *J* = 14.76 Hz, 1H), 3.70 (s, 3H), 3.60 (d, *J* = 14.76 Hz, 1H), 3.07 (s, 3H), 2.56 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.3, 137.0 132.9, 128.4, 128.3, 126.1, 78.4, 59.4, 55.6, 50.0, 23.0, 21.2. HRMS (ESI) m/z: calculated for $C_{12}H_{18}NaO_4S^+$ $[M+Na]^+$ 281.0818, found 281.0828.



Compound **3ea**: 36.6 mg, 67% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.22 Hz, 2H), 7.25 (d, *J* = 8.10 Hz, 2H), 3.77 (s, 3H), 3.62 (d, *J* = 14.70 Hz, 1H), 3.44 (d, *J* = 14.70 Hz, 1H), 3.13 (s, 3H), 2.70 (q, *J* = 7.62 Hz, 2H), 1.92 (s, 3H), 1.28 (t, *J* = 7.62 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.2, 139.3, 128.1, 126.2, 76.9, 61.7, 55.8, 50.4, 28.4, 21.0, 15.4. HRMS (ESI) m/z: calculated for $C_{13}H_{20}NaO_4S^+$ $[M+Na]^+$ 295.0975, found 295.0981.

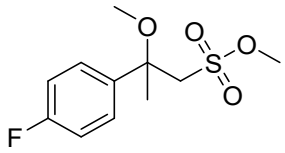


Compound **3fa**: 38.2 mg, 70% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.21 (m, 1H), 6.92-6.90 (m, 2H), 6.80-6.77 (m, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.52 (d, *J* = 14.76 Hz, 1H), 3.34 (d, *J* = 14.72 Hz, 1H), 3.05 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 144.0, 129.7, 118.5, 113.1, 112.3, 76.9, 61.5, 55.9, 55.3, 50.6, 21.0. HRMS (ESI) m/z: calculated for $C_{12}H_{18}NaO_5S^+$ $[M+Na]^+$ 297.0767, found 297.0768.

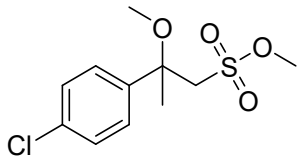


Compound **3ga**: 47.8 mg, 87% yield, white solid, mp 53-54 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ =

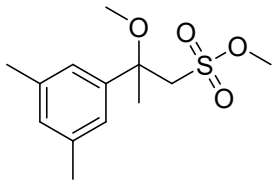
7.36-7.35 (m, 2H), 6.93-6.92 (m, 2H), 3.83 (s, 3H), 3.76 (s, 3H), 3.60 (d, J = 14.76 Hz, 1H), 3.44 (d, J = 14.76 Hz, 1H), 3.10 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.3, 133.8, 127.6, 113.9, 76.6, 61.7, 55.7, 55.3, 50.2, 21.0. HRMS (ESI) m/z: calculated for $C_{12}H_{18}NaO_5S^+$ $[M+Na]^+$ 297.0767, found 297.0778.



Compound **3ha**: 29.5 mg, 56% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43-7.41 (m, 2H), 7.11-7.08 (m, 2H) 3.76 (s, 3H), 3.59 (d, J = 14.70 Hz, 1H), 3.44 (d, J = 14.70 Hz, 1H), 3.12 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ =163.2 (d, J = 245.85 Hz), 137.7 (d, J = 3.23 Hz), 128.2 (d, J = 8.12 Hz), 115.6 (d, J = 21.24 Hz), 76.6, 61.6, 55.7, 50.3, 21.2. ^{19}F NMR (565 MHz, $CDCl_3$): δ = -114.1 HRMS (ESI) m/z: calculated for $C_{11}H_{15}FNaO_4S^+$ $[M+Na]^+$ 285.0567, found 285.0578.

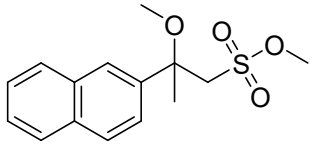


Compound **3ia**: 45.5 mg, 82% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40-7.37 (m, 4H), 3.77 (s, 3H), 3.58 (d, J = 14.7 Hz, 1H), 3.44 (d, J = 14.7 Hz, 1H), 3.13 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.5, 134.1, 128.8, 127.8, 76.6, 61.4, 55.7, 50.4, 21.1. (ESI) m/z: calculated for $C_{11}H_{15}ClNaO_4S^+$ $[M+Na]^+$ 301.0272, found 301.0274.

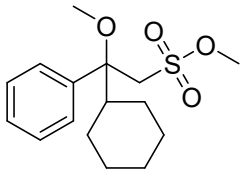


Compound **3ja**: 40.1 mg, 74% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94 (s, 2H),

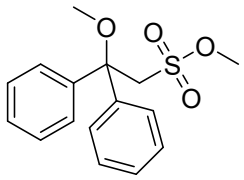
6.88 (s, 1H), 3.70 (s, 3H), 3.52 (d, *J* = 14.80 Hz, 1H), 3.32 (d, *J* = 14.72 Hz, 1H), 3.04 (s, 3H), 2.26 (s, 6H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.2, 138.2, 129.7, 123.9, 76.9, 61.7, 55.8, 50.6, 21.5, 21.0. HRMS (ESI) m/z: calculated for $C_{13}H_{20}NaO_4S^+$ $[M+Na]^+$ 295.0975, found 295.0975.



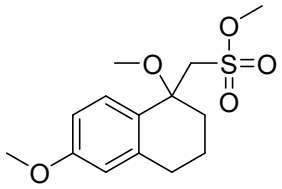
Compound **3ka**: 44.2 mg, 75% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.86 (m, 4H), 7.61-7.58 (m, 1H), 7.55-7.53 (m, 2H), 3.75-3.71 (m, 4H), 3.57 (d, *J* = 14.72 Hz, 1H), 3.17 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 133.1, 132.9, 128.6, 128.3, 127.6, 126.6, 126.5, 125.8, 123.8, 61.3, 55.8, 50.6, 21.2. HRMS (ESI) m/z: calculated for $C_{15}H_{18}NaO_4S^+$ $[M+Na]^+$ 317.0818, found 317.0832. 335.1288



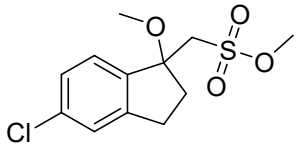
Compound **3la**: 55.5 mg, 89% yield, white solid, mp 100-100.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39-7.36 (m, 2H), 7.33-7.30 (m, 1H), 7.27-7.25 (m, 2H), 4.08 (d, *J* = 15.06 Hz, 1H), 3.86-3.83 (m, 4H), 3.36 (s, 3H), 2.27-2.22 (m, 1H), 2.06-2.04 (m, 1H), 1.77-1.67 (m, 3H), 1.58 (d, *J* = 13.20 Hz, 1H), 1.35-1.21 (m, 2H), 0.91-0.84 (m,1H), 0.74-0.67 (m, 1H), 0.51-0.44 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.2, 127.6, 127.4, 127.2, 82.5, 55.4, 52.0, 51.0, 44.8, 28.6, 26.5, 26.4, 26.2, 26.1. HRMS (ESI) m/z: calculated for $C_{16}H_{24}NaO_4S^+$ $[M+Na]^+$ 335.1288, found 335.1285.



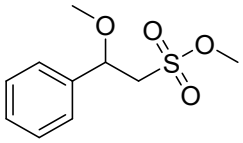
Compound **3ma**: 26.5 mg, 43% yield, white solid, mp 153-154 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37-7.33 (m, 8H), 7.30-7.29 (m, 2H), 4.29 (s, 2H), 3.55 (s, 3H), 3.24 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.8, 128.3, 127.6, 126.6, 80.4, 77.2, 55.5, 51.5. HRMS (ESI) m/z: calculated for $C_{16}H_{18}NaO_4S^+$ $[M+Na]^+$ 329.0818, found 329.0814.



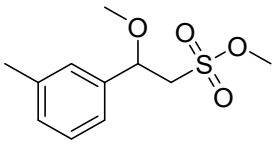
Compound **3na**: 36.2 mg, 60% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.72 Hz, 1H), 6.83-6.80 (m, 1H), 6.65-6.64 (m, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 3.60-3.52 (m, 2H), 3.10 (s, 3H), 2.86-2.72 (m, 2H), 2.61-2.55 (m, 1H), 2.21-2.54 (m, 1H), 2.06-1.97 (m, 1H), 1.94-1.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 140.5, 128.8, 127.9, 113.4, 113.0, 76.6, 60.1, 56.0, 55.2, 50.4, 29.7, 28.2, 20.8. HRMS (ESI) m/z: calculated for $C_{14}H_{20}NaO_5S^+$ $[M+Na]^+$ 323.0924, found 323.0927.



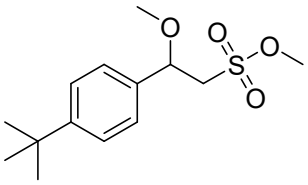
Compound **3oa**: 34.9 mg, 60% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28-7.21 (m, 3H), 3.90-3.86 (m, 4H), 3.43 (d, *J* = 14.68 Hz, 1H), 3.14-2.90 (m, 5H), 2.70-2.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.5, 139.2, 135.5, 127.1, 125.6, 125.1, 85.4, 57.5, 55.9, 50.7, 33.4, 30.0. HRMS (ESI) m/z: calculated for $C_{12}H_{15}ClNaO_4S^+$ $[M+Na]^+$ 313.0272, found 313.0284.



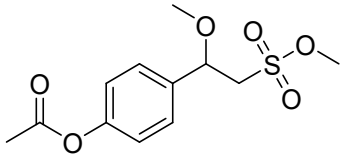
Compound **3pa**: 35.5 mg, 77% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41-7.39 (m, 2H), 7.36-7.34 (m, 3H), 4.74 (dd, *J* = 3.12, 9.18 Hz, 1H), 3.88 (s, 3H), 3.63 (dd, *J* = 3.12, 9.18 Hz, 1H), 3.31-3.28 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.6, 129.0, 128.8, 126.5, 78.4, 57.2, 57.0, 56.1. HRMS (ESI) m/z: calculated for $C_{10}H_{15}O_4S^+$ $[M+H]^+$ 231.0686, found 231.0670.



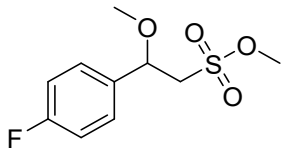
Compound **3qa**: 31.6 mg, 65% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.22-7.29 (m, 1H), 7.09-7.05 (m, 3H), 4.62 (dd, *J* = 2.94, 9.30 Hz, 1H), 3.82 (s, 3H), 3.54 (dd, *J* = 9.30, 14.88 Hz, 1H), 3.22-3.19 (m, 4H), 2.30 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.8, 138.5, 129.6, 128.9, 127.1, 123.6, 78.4, 57.2, 57.0, 56.1, 21.4. HRMS (ESI) m/z: calculated for $C_{11}H_{17}O_4S^+$ $[M+H]^+$ 245.0842, found 245.0842.



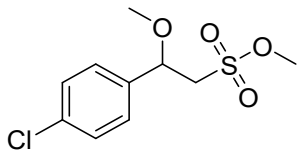
Compound **3ra**: 43.6 mg, 76% yield, white solid, mp 44-45 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34-7.32 (m, 2H), 7.19-7.18 (m, 2H), 4.64 (dd, *J* = 2.88, 9.42 Hz, 1H), 3.81 (s, 3H), 3.54 (dd, *J* = 9.42, 14.88 Hz, 1H), 3.23-3.20 (m, 4H), 1.25 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.9, 135.5, 126.2, 125.9, 78.1, 57.2, 56.9, 56.1, 34.7, 31.3. HRMS (ESI) m/z: calculated for $C_{14}H_{22}NaO_4S^+$ $[M+Na]^+$ 309.1131, found 309.1143.



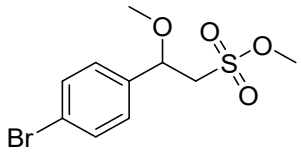
Compound **3sa**: 17.5 mg, 30% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.34 Hz, 2H), 7.15 (d, *J* = 8. 4 Hz, 2H), 4.76 (dd, *J* = 2.82, 9.18 Hz, 1H), 3.90 (s, 3H), 3.62 (dd, *J* = 9.18, 14.88 Hz, 1H), 3.31-3.28 (m, 4H), 2.33 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.4, 150.9, 136.1, 127.6, 122.2, 77.8, 57.1, 57.0, 56.1, 21.1. HRMS (ESI) m/z: calculated for $C_{12}H_{16}NaO_6S^+$ $[M+Na]^+$ 311.0560, found 311.0569. $C_{10}H_{13}FNaO_4S^+$271.0411



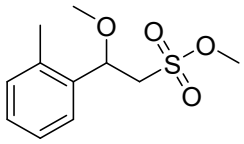
Compound **3ta**: 28.9 mg, 58% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.27-7.24 (m, 2H), 7.03-7.00 (m, 2H), 4.65 (dd, *J* = 3.42, 8.94 Hz, 1H), 3.81 (s, 3H), 3.54 (dd, *J* = 8.94, 14.82 Hz, 1H), 3.21-3.18 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.7 (d, *J* = 246.1 Hz), 134.4 (d, *J* = 3.2 Hz), 128.4 (d, *J* = 8.2 Hz), 116.0 (d, *J* = 21.5 Hz), 77.7, 57.1, 56.9, 56.1. ^{19}F NMR (565 MHz, $CDCl_3$): δ = -112.83. HRMS (ESI) m/z: calculated for $C_{10}H_{13}FNaO_4S^+$ $[M+Na]^+$ 271.0411, found 271.0419.



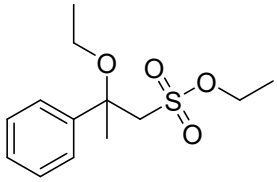
Compound **3ua**: 31.8 mg, 60% yield, white solid, mp 61-62 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41-7.39 (m, 2H), 7.32-7.30 (m, 2H), 4.74 (dd, *J* = 3.42, 8.94 Hz, 1H), 3.91 (s, 3H), 3.62 (dd, *J* = 8.94, 14.82 Hz, 1H), 3.30-3.27 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 137.1, 134.7, 129.2, 127.9, 77.8, 57.1, 57.0, 56.1. HRMS (ESI) m/z: calculated for $C_{10}H_{14}ClO_4S^+$ $[M+H]^+$ 3265.0296, found 265.0296.



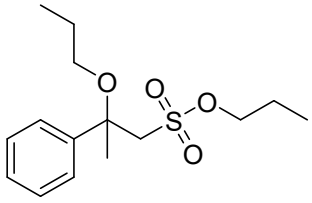
Compound **3va**: 35.1 mg, 57% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.34 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.72 (dd, *J* = 3.36, 8.94 Hz, 1H), 3.90 (s, 3H), 3.61 (dd, *J* = 9.00, 14.88 Hz, 1H), 3.30-3.26 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.6, 132.2, 128.3, 122.8, 77.8, 57.1, 57.0, 56.1. HRMS (ESI) m/z: calculated for $C_{10}H_{14}BrO_4S^+$ $[M+H]^+$ 308.9791, found 308.9796.



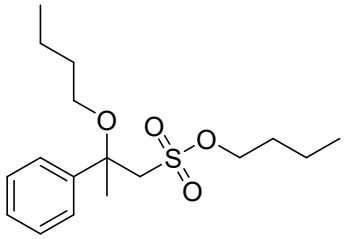
Compound **3wa**: 27.9 mg, 57% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33-7.31 (m, 1H), 7.19-7.14 (m, 2H), 7.11-7.10 (m, 1H), 4.93 (dd, *J* = 2.58, 9.21 Hz, 1H), 3.83 (s, 3H), 3.49 (dd, *J* = 9.24, 15.0 Hz, 1H), 3.21 (s, 3H), 3.17 (dd, *J* = 2.64, 15.00 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 136.6, 135.4, 131.0, 128.4, 126.7, 125.7, 75.1, 56.9, 56.2, 56.1, 18.9. HRMS (ESI) m/z: calculated for $C_{11}H_{16}NaO_4S^+$ $[M+Na]^+$ 267.0662, found 267.0670.



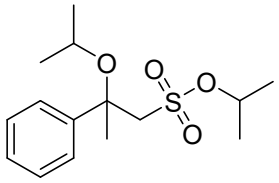
Compound **3ab**: 30.8 mg, 57% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.45 (m, 2H), 7.42-7.38 (m, 2H), 7.35-7.31 (m, 1H), 4.22-4.08 (m, 2H), 3.62 (d, *J* = 14.72 Hz, 1H), 3.46-3.38 (m, 2H), 3.17-3.10 (m, 1H), 1.94 (s, 3H), 1.30 (t, *J* = 14.24 Hz, 3H), 1.21 (t, *J* = 13.96 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.8, 128.6, 128.0, 126.1, 76.7, 66.5, 62.2, 58.0, 21.7, 15.5, 14.9. HRMS (ESI) m/z: calculated for $C_{13}H_{20}NaO_4S^+$ $[M+Na]^+$ 295.0975, found 295.0987.



Compound **3ac**: 38.5 mg, 64% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.45 (m, 2H), 7.42-7.38 (m, 2H), 7.35-7.31 (m, 1H), 4.08-3.97 (m, 2H), 3.63 (d, *J* = 14.68 Hz, 1H), 3.47 (d, *J* = 14.72 Hz, 1H), 3.32-3.26 (m, 1H), 3.07-3.01 (m, 1H), 1.94 (s, 3H), 1.69-1.55 (m, 4H), 0.95-0.91 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.8, 128.5, 128.0, 126.3, 76.4, 71.6, 64.1, 62.3, 23.3, 22.6, 21.6, 10.7, 10.0. HRMS (ESI) m/z: calculated for $C_{15}H_{24}NaO_4S^+$ $[M+Na]^+$ 323.1288, found 323.1288.

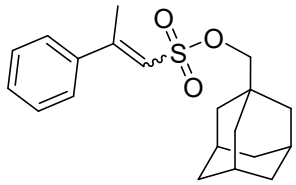


Compound **3ad**: 24.5 mg, 37% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.44 (m, 2H), 7.42-7.38 (m, 2H), 7.35-7.31 (m, 1H), 4.12-4.01 (m, 2H), 3.61 (d, *J* = 14.68 Hz, 1H), 3.46 (d, *J* = 14.68 Hz, 1H), 3.36-3.30 (m, 1H), 3.09-3.04 (m, 1H), 1.94 (s, 3H), 1.63-1.52 (m, 4H), 1.43-1.32 (m, 4H), 0.84-0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 128.5, 127.9, 126.3, 76.4, 69.9, 62.3, 62.2, 32.1, 31.1, 21.6, 19.3, 18.6, 14.0, 13.5. HRMS (ESI) m/z: calculated for $C_{17}H_{28}NaO_4S^+$ $[M+Na]^+$ 351.1601, found 351.1610.



Compound **3ae**: 29.1 mg, 48% yield, white solid, mp 42-43 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ =

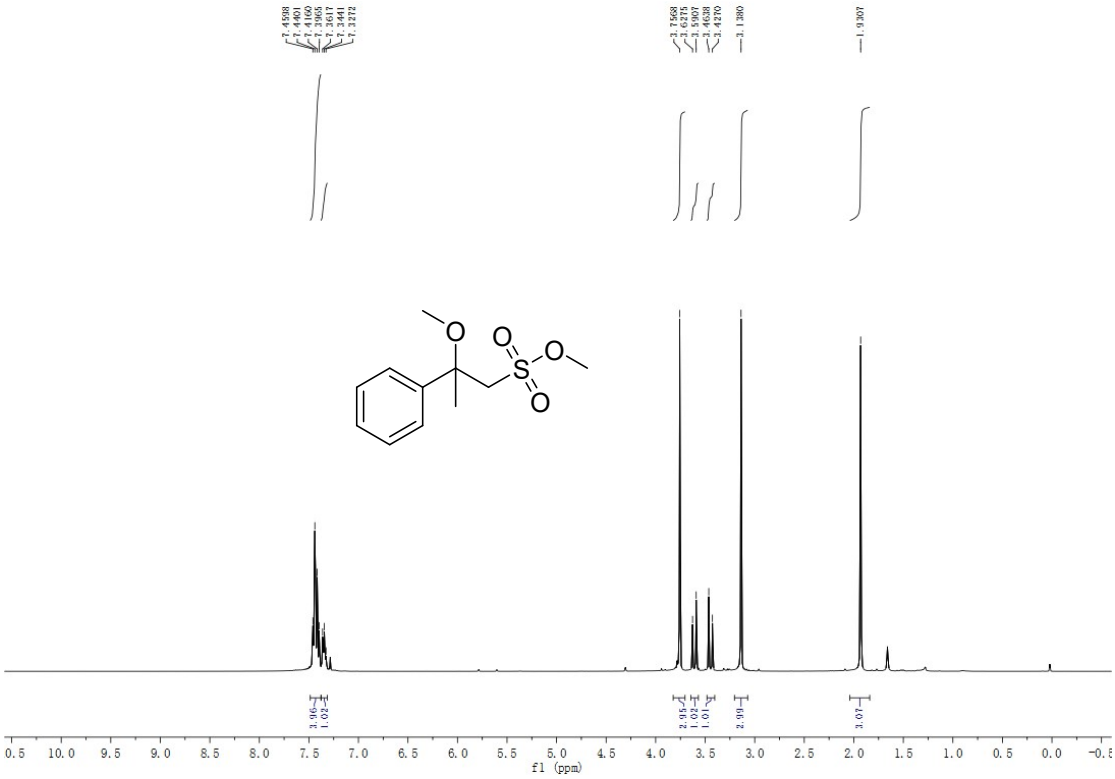
7.53-7.52 (m, 2H), 7.40-7.38 (m, 2H), 7.34-7.32 (m, 1H), 4.89-4.82 (m, 1H), 3.60-3.43 (m, 3H), 2.00 (s, 3H), 1.32-1.30 (m, 6H), 1.20 (d, J = 6.06 Hz, 3H), 0.99 (d, J = 6.12 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.2, 128.1, 128.0, 126.9, 76.9, 76.3, 65.9, 64.1, 24.9, 24.3, 23.1, 23.0, 22.2. HRMS (ESI) m/z: calculated for $C_{15}H_{24}NaO_4S^+$ $[M+Na]^+$ 323.1288, found 323.1288.



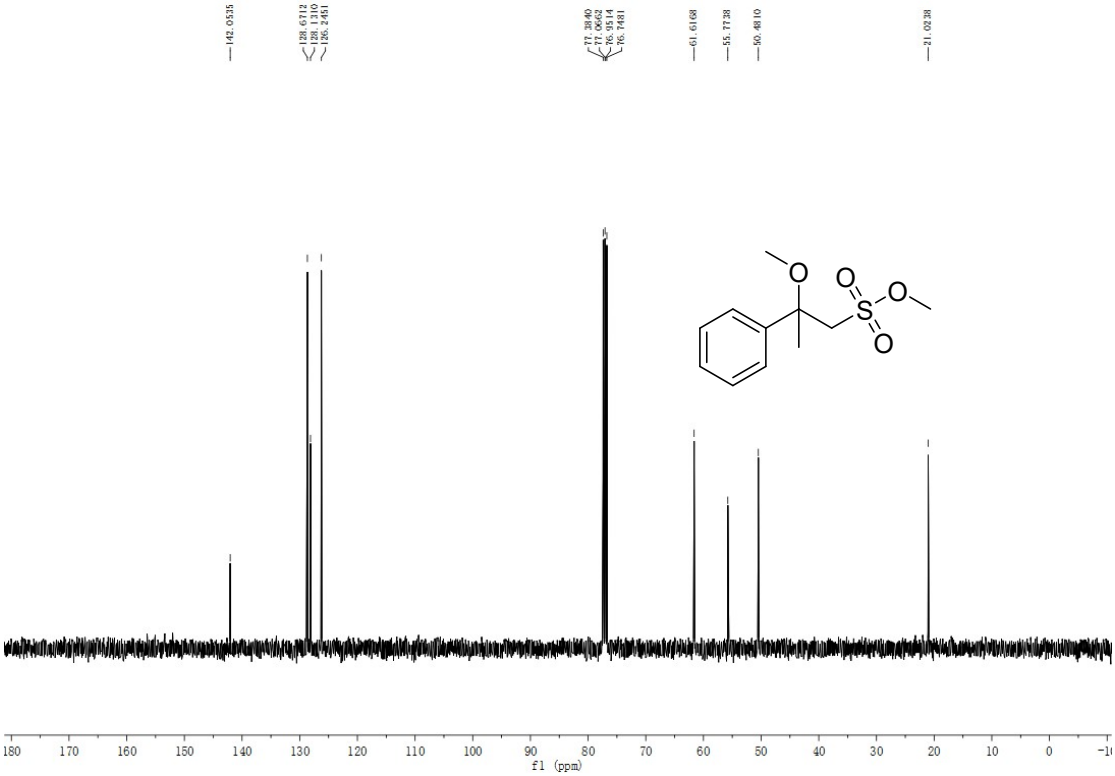
Compound **4**: 18.2 mg, 26% yield, white solid, mp 128-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.28 (m, 5H), 7.24-7.20 (m, 1H), 2.76-2.69 (m, 2H), 2.01-1.97 (m, 3H), 1.77-1.68 (m, 6H), 1.59-1.58 (m, 6H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =146.9, 127.8, 126.3, 126.2, 126.1, 126.0, 77.2, 71.9, 71.8, 40.1, 37.4, 35.2, 35.0, 34.9, 33.9, 28.5, 24.9, 24.7. HRMS (ESI) m/z: calculated for $C_{20}H_{26}NaO_3S^+$ $[M+Na]^+$ 369.1495, found 369.1495.

10. ^{1}H and ^{13}C NMR spectra of 3 and 4

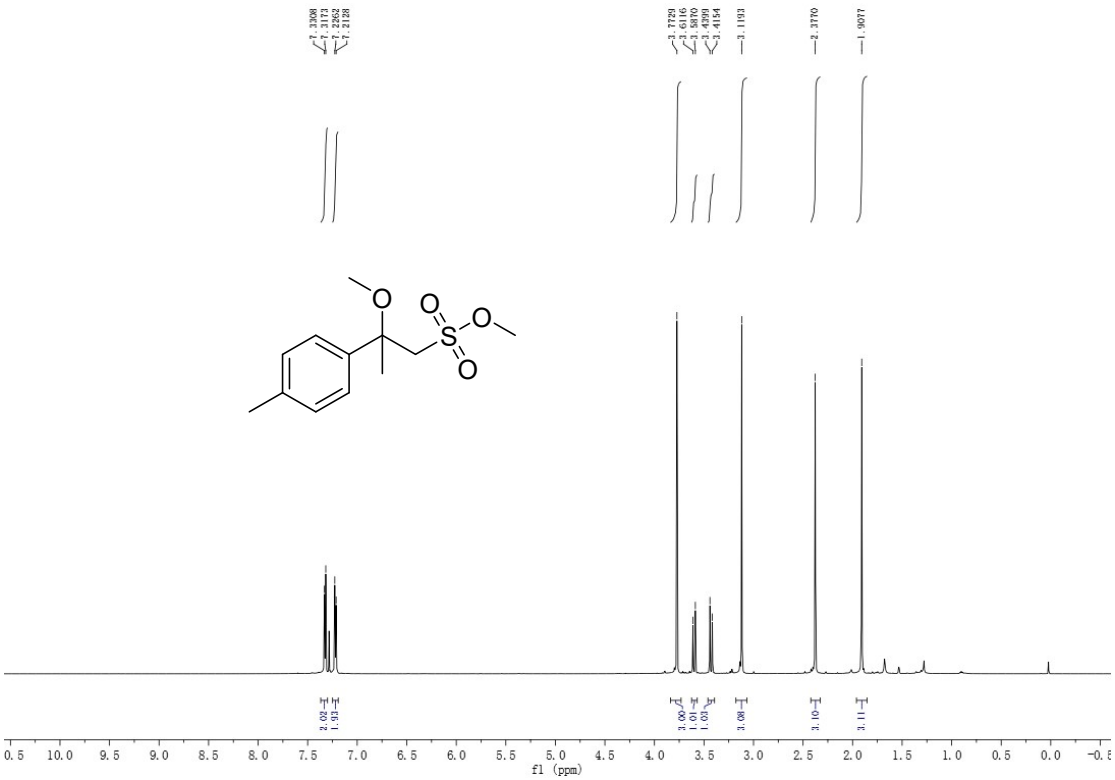
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**:



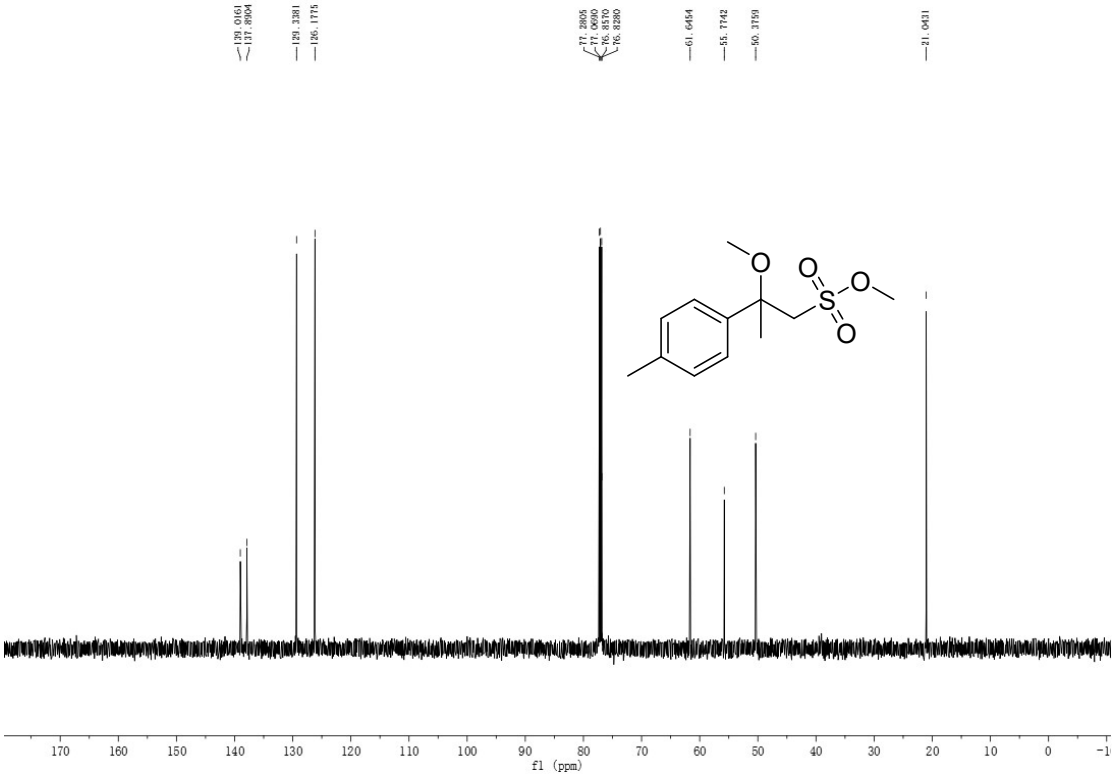
^{13}C NMR (100 MHz, $CDCl_3$) of **3aa**:



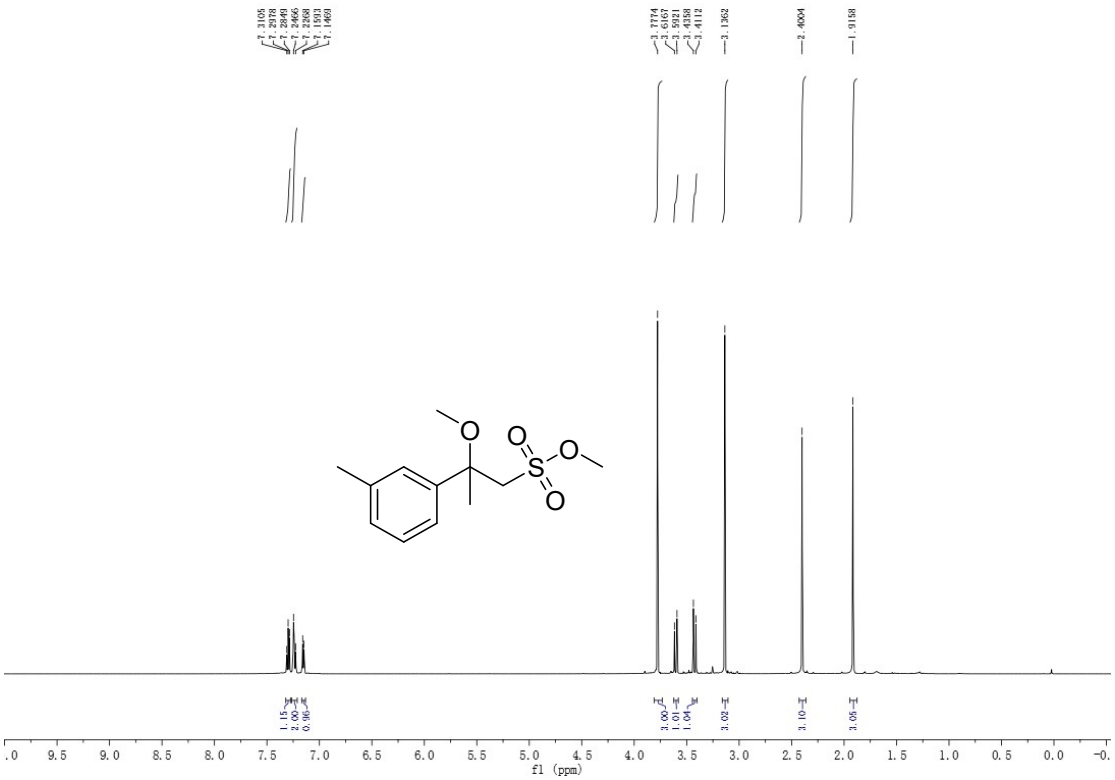
^{1}H NMR (600 MHz, $CDCl_3$) of **3ba**:



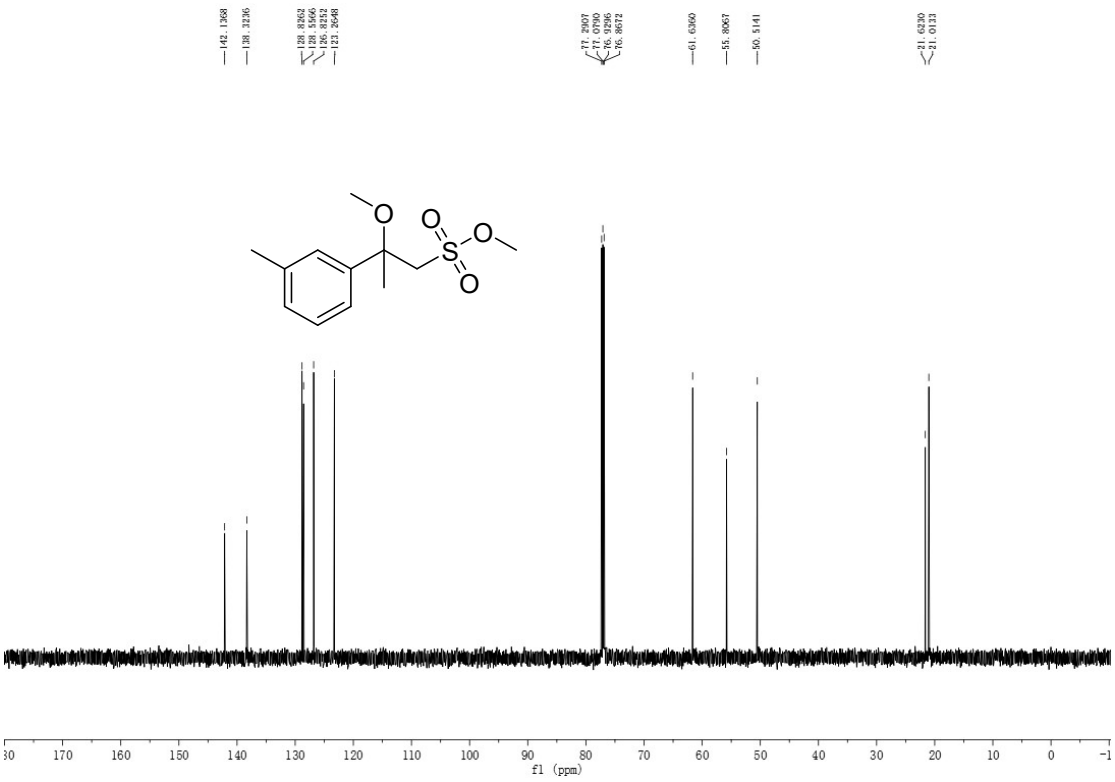
^{13}C NMR (150 MHz, $CDCl_3$) of **3ba**:



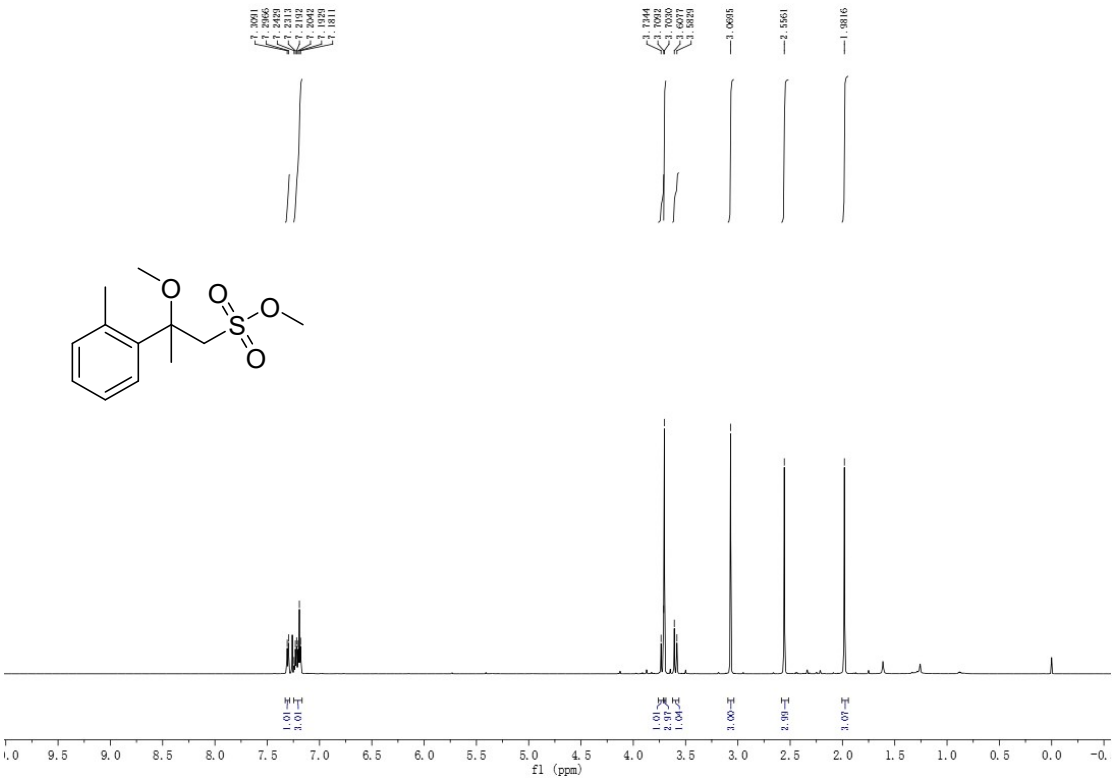
^{1}H NMR (600 MHz, $CDCl_3$) of **3ca**:



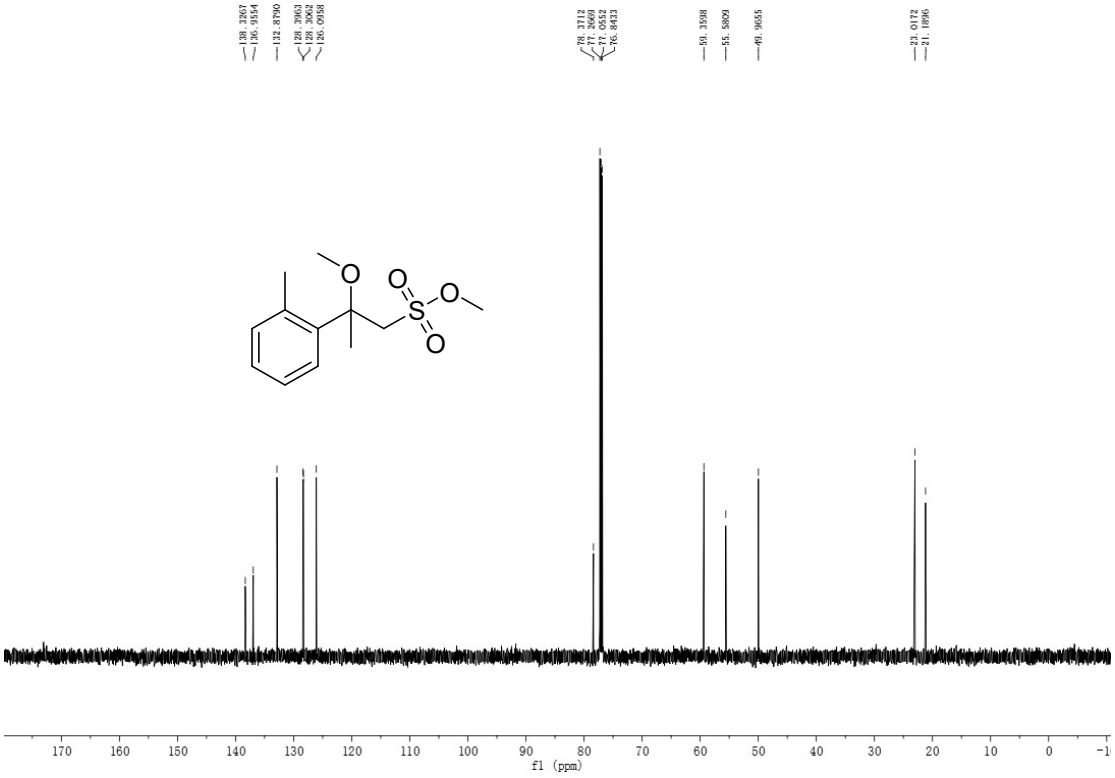
^{13}C NMR (150 MHz, $CDCl_3$) of **3ca**:



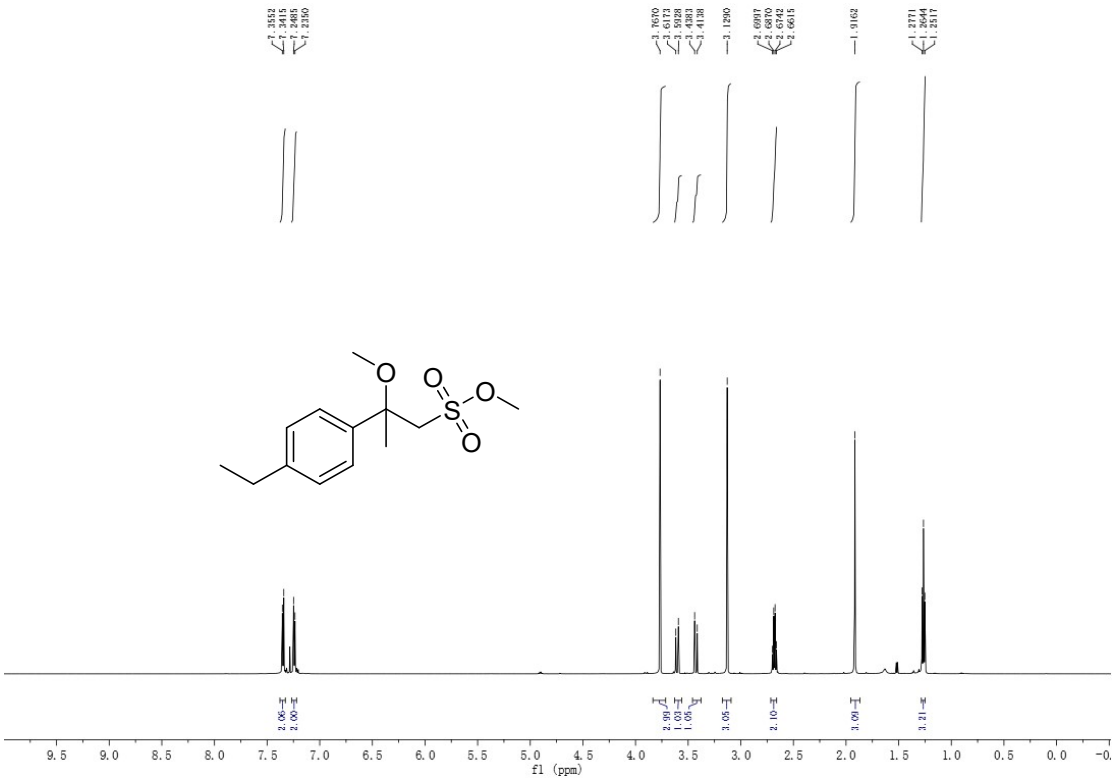
^{1}H NMR (600 MHz, $CDCl_3$) of **3da**:



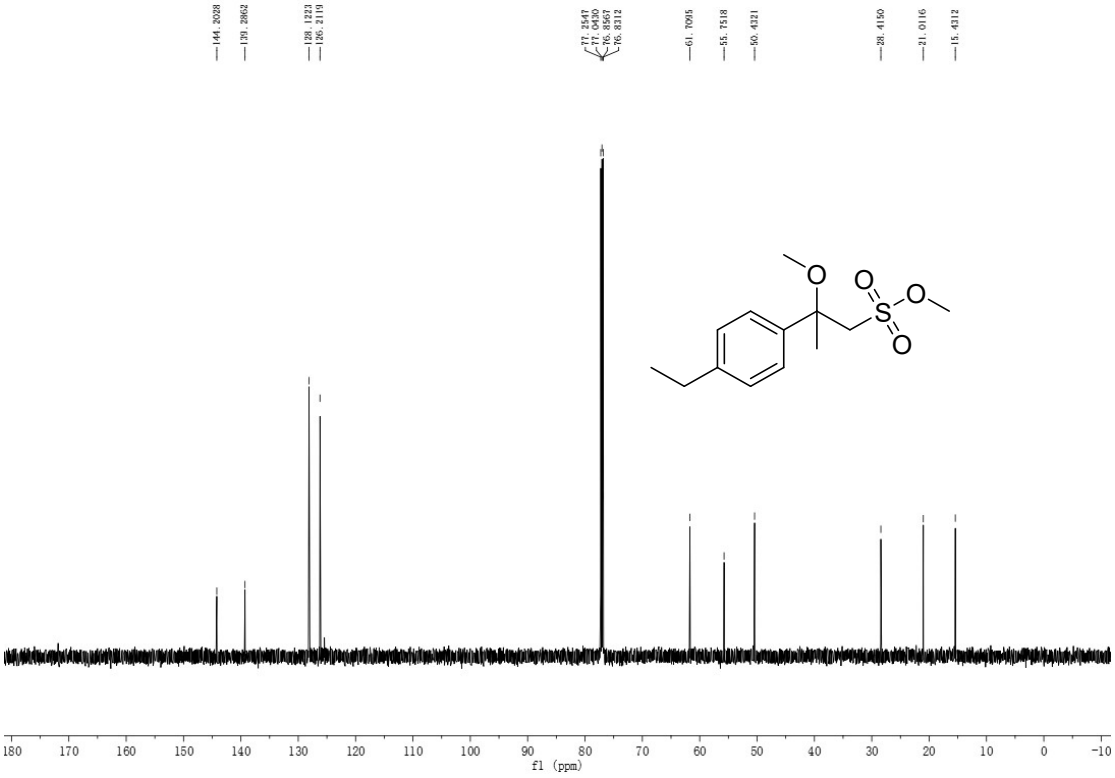
^{13}C NMR (150 MHz, $CDCl_3$) of **3da**:



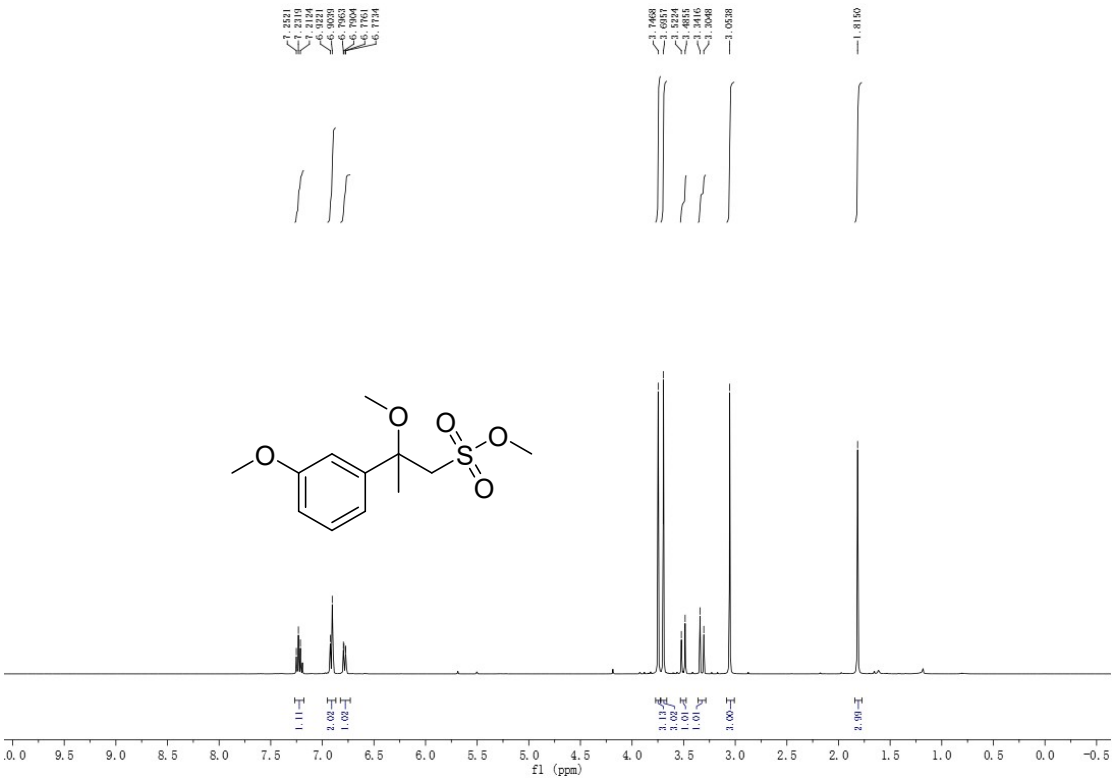
^{1}H NMR (600 MHz, $CDCl_3$) of **3ea**:



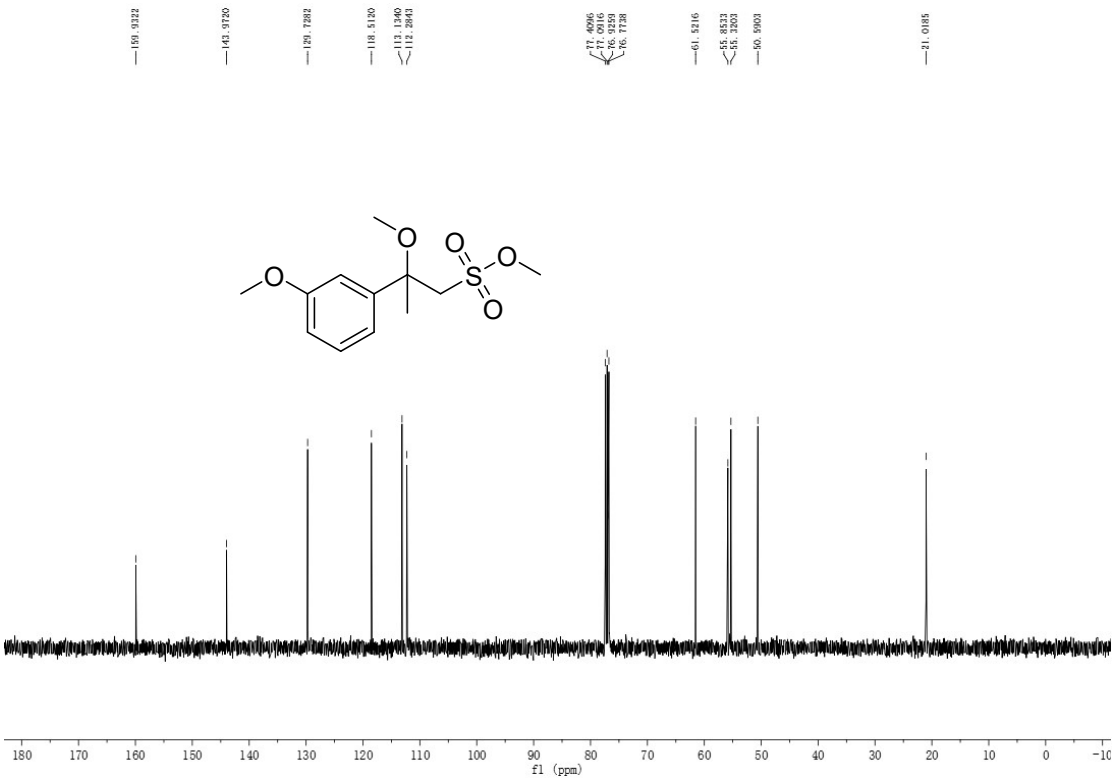
^{13}C NMR (150 MHz, $CDCl_3$) of **3ea**:



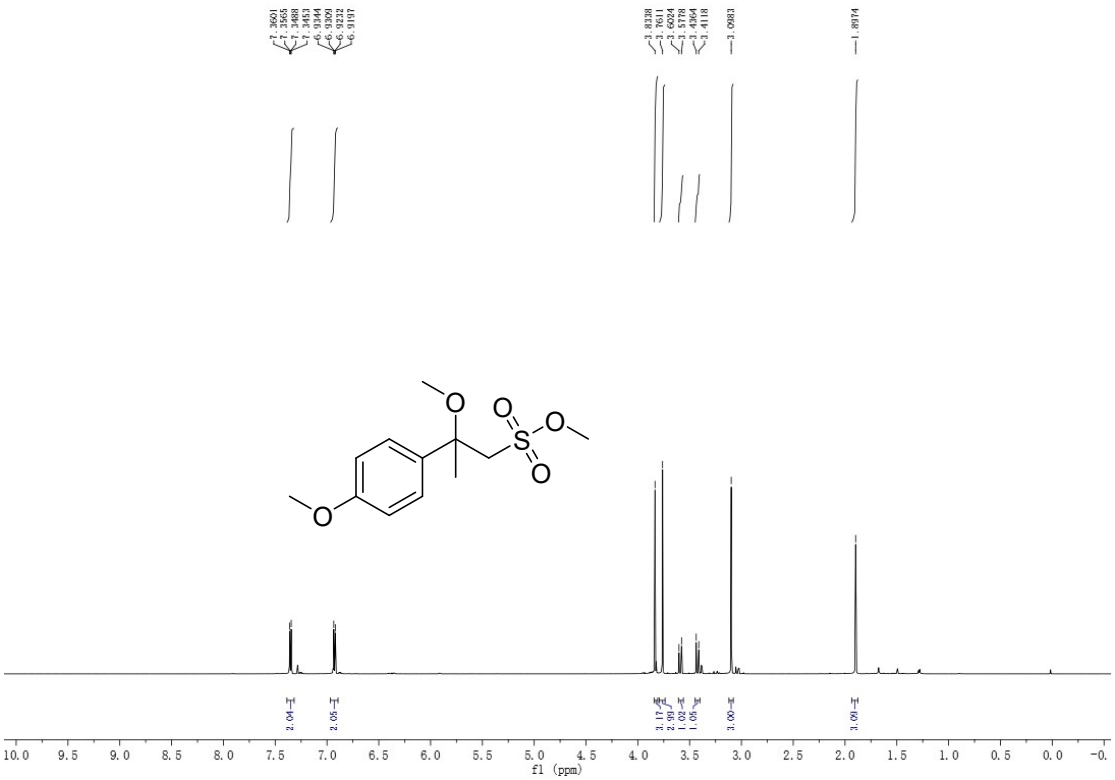
^{1}H NMR (600 MHz, $CDCl_3$) of **3fa**:



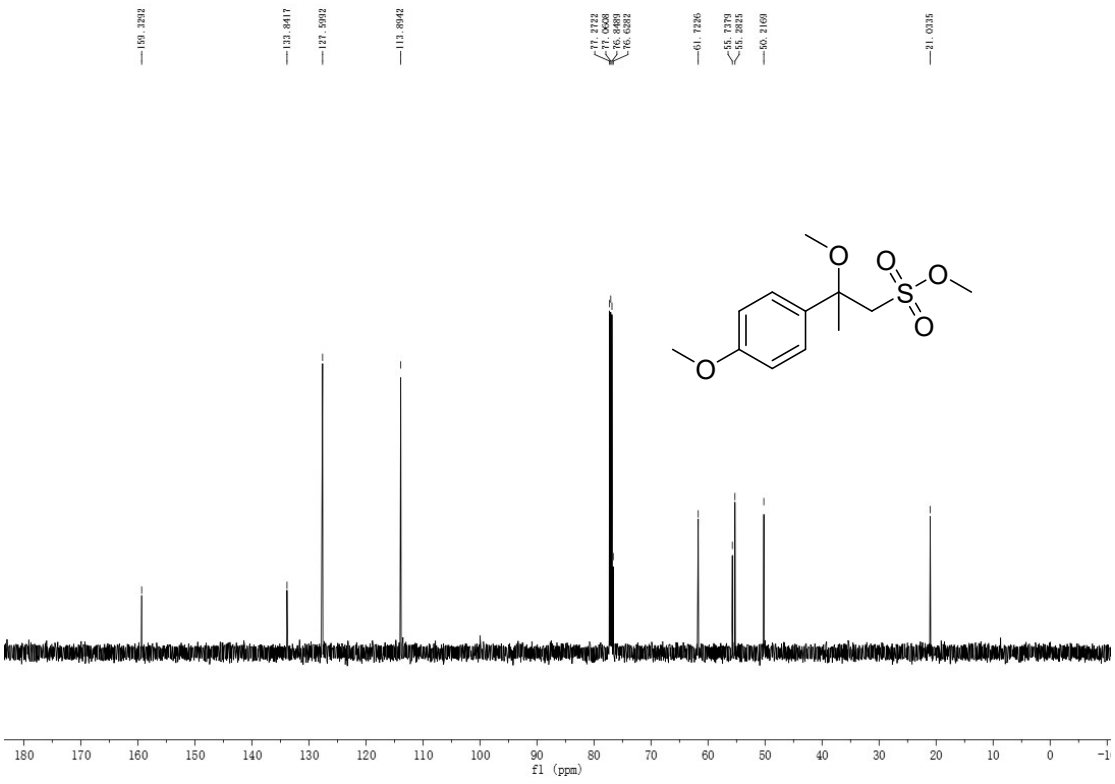
^{13}C NMR (150 MHz, $CDCl_3$) of **3fa**:



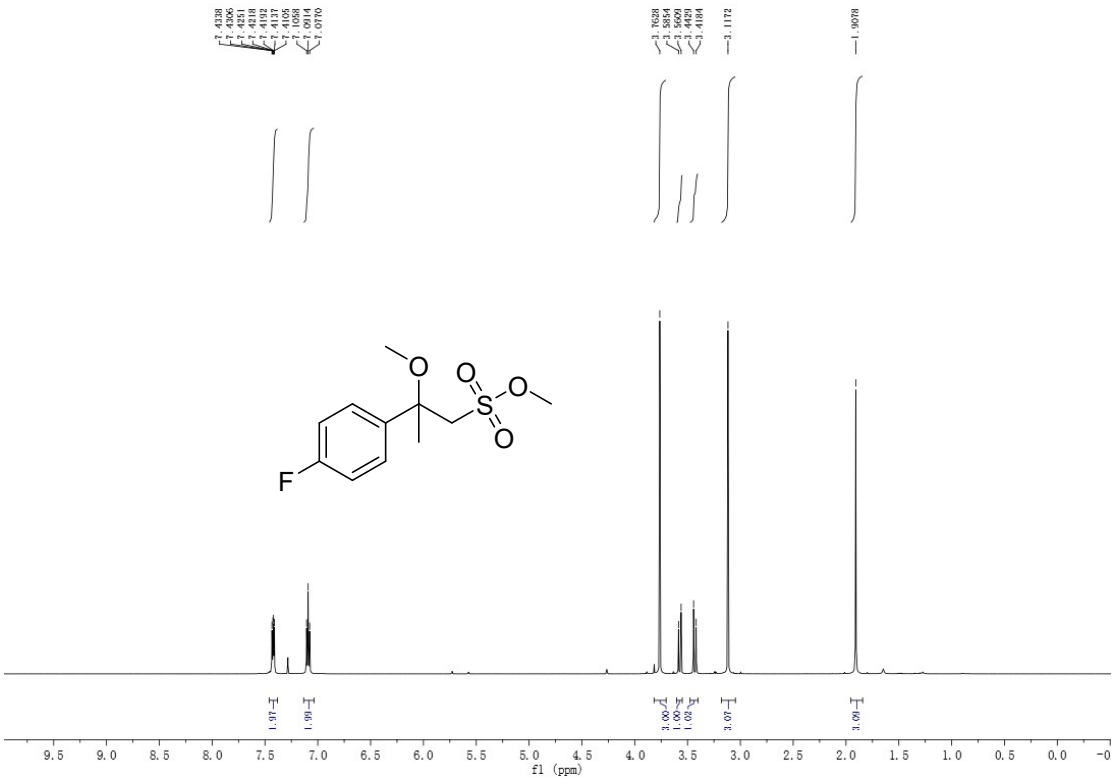
^{1}H NMR (600 MHz, $CDCl_3$) of **3ga**:



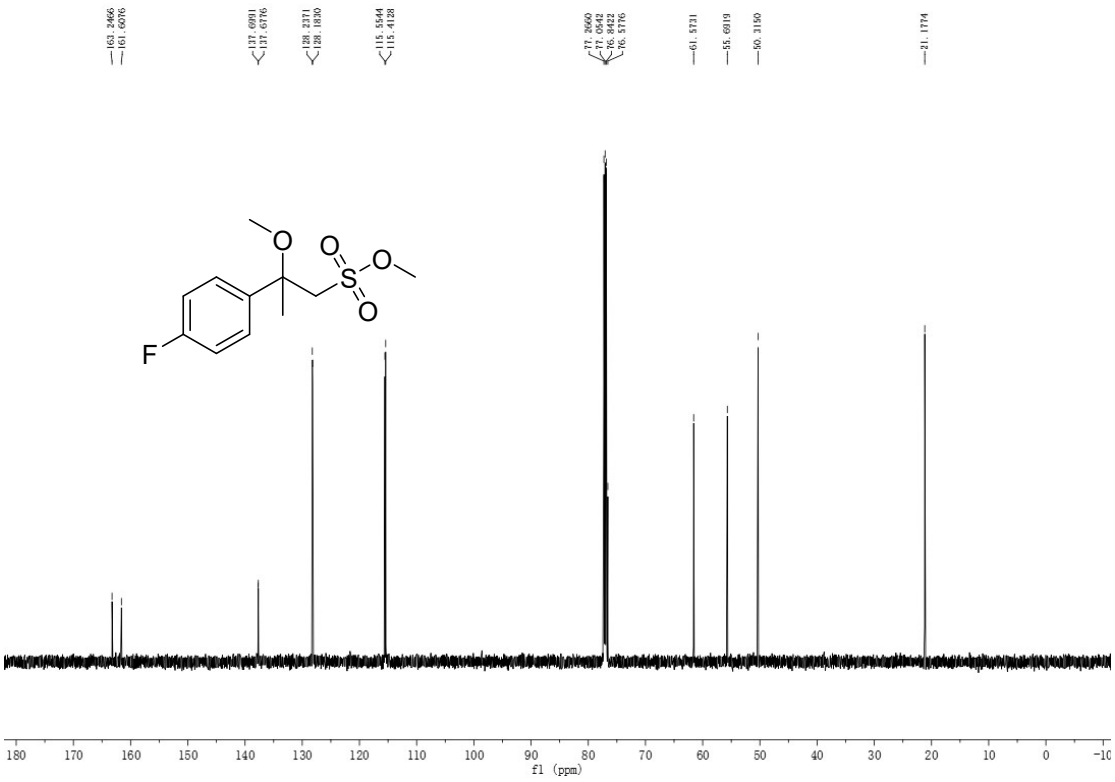
^{13}C NMR (150 MHz, $CDCl_3$) of **3ga**:



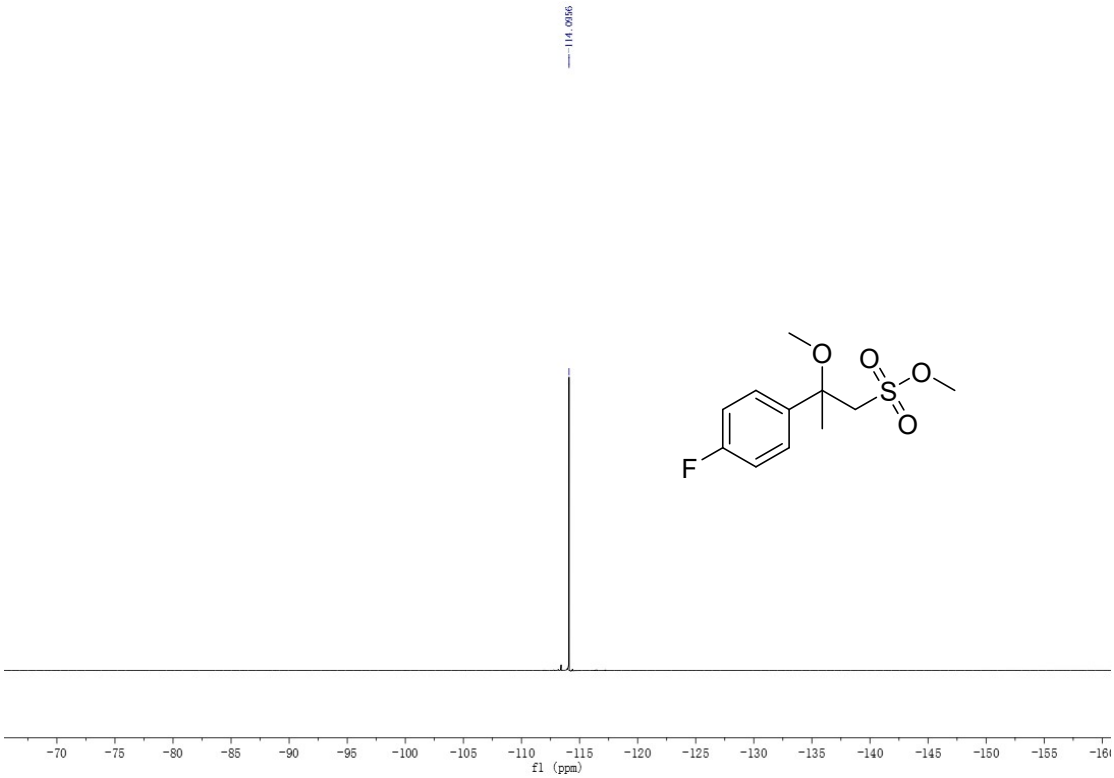
^{1}H NMR (600 MHz, $CDCl_3$) of **3ha**:



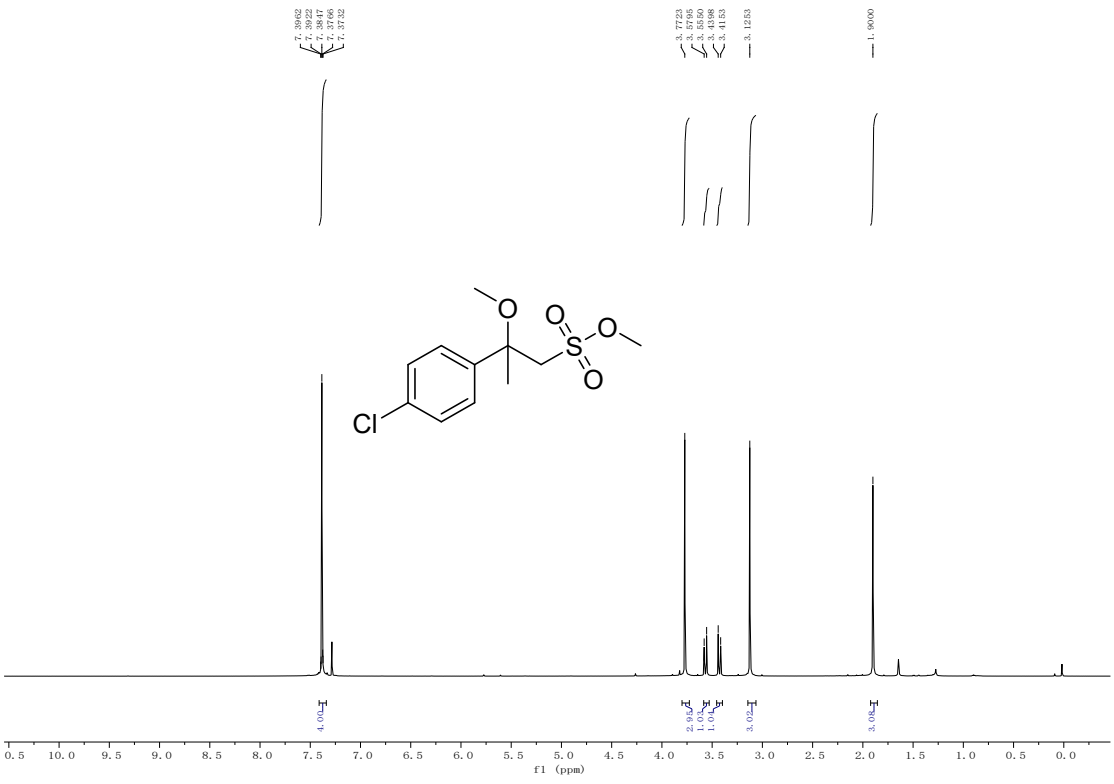
^{13}C NMR (150 MHz, $CDCl_3$) of **3ha**:



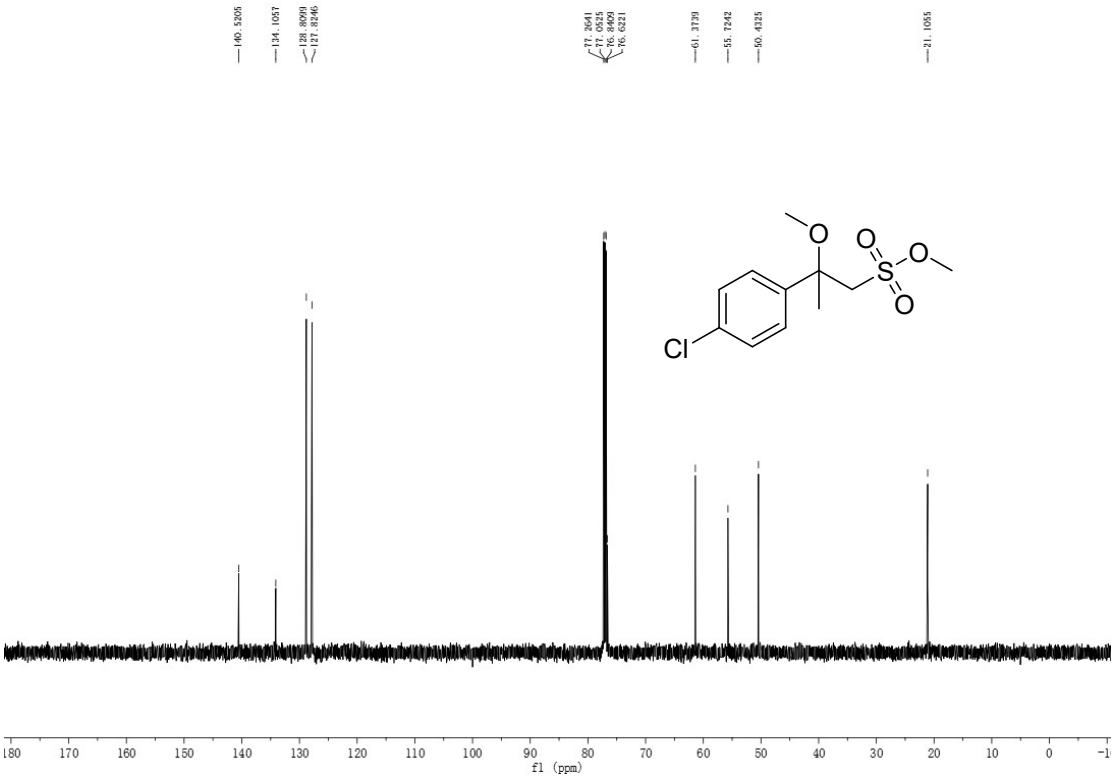
^{19}F NMR (565 MHz, $CDCl_3$) of **3ha**:



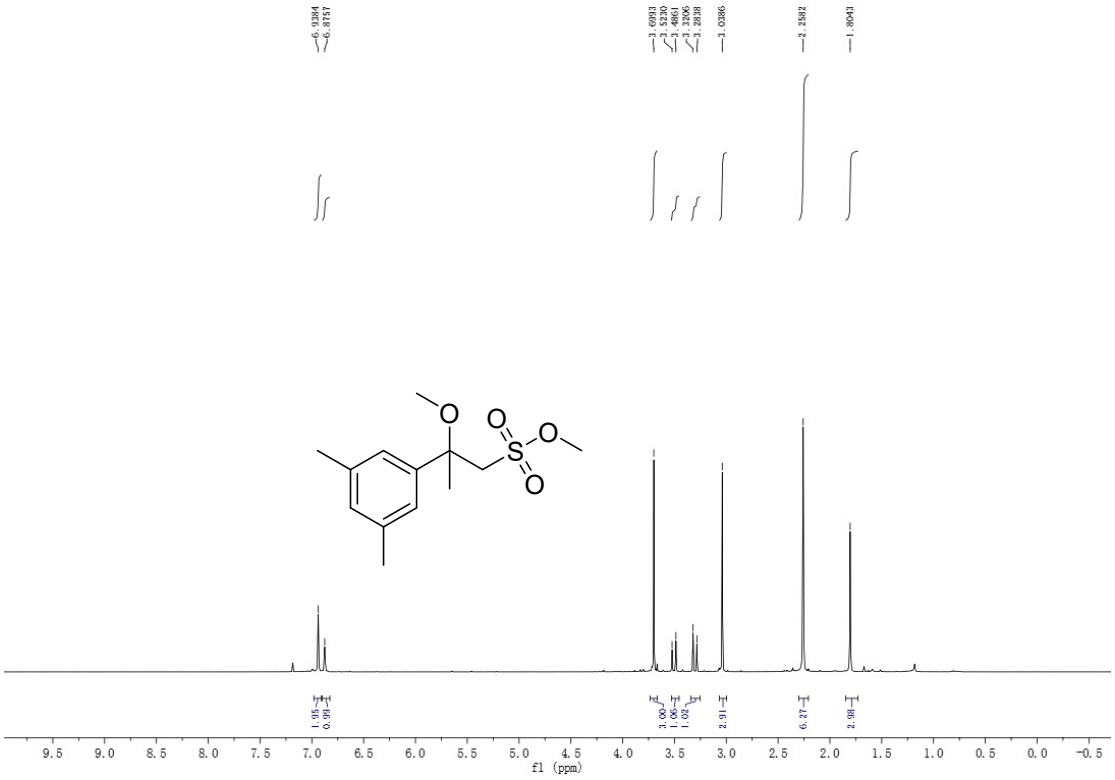
^{1}H NMR (600 MHz, $CDCl_3$) of **3ia**:



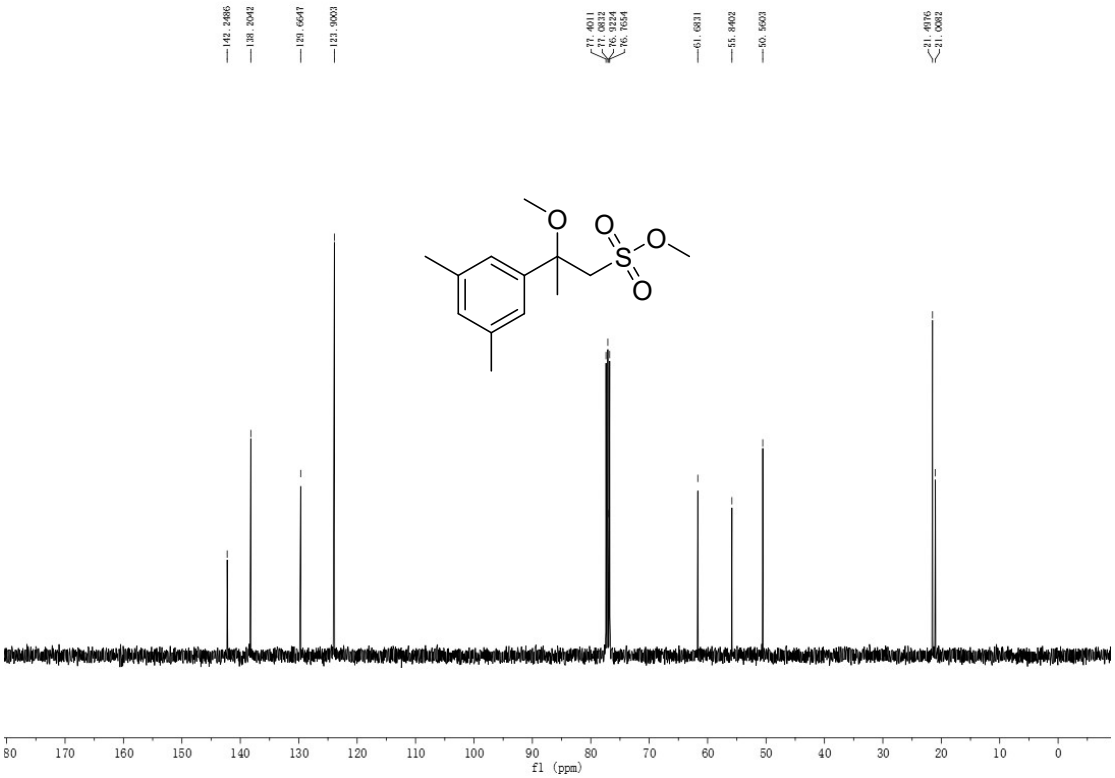
^{13}C NMR (150 MHz, $CDCl_3$) of **3ia**:



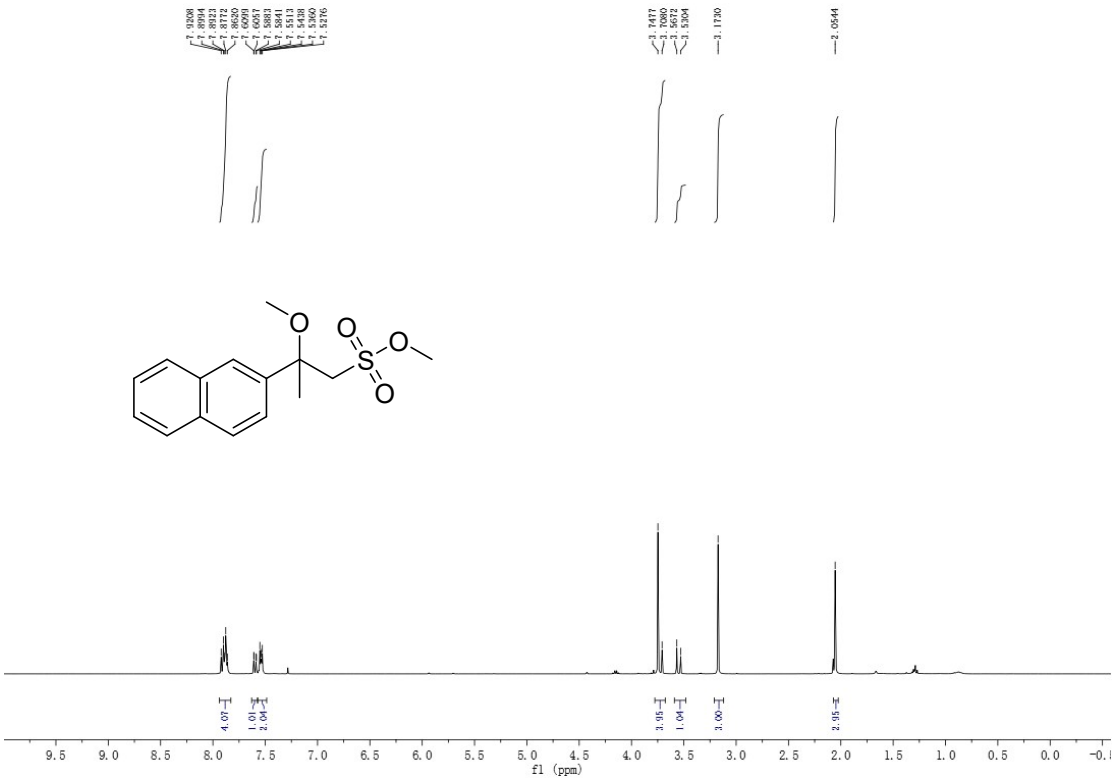
^{1}H NMR (400 MHz, $CDCl_3$) of **3ja**:



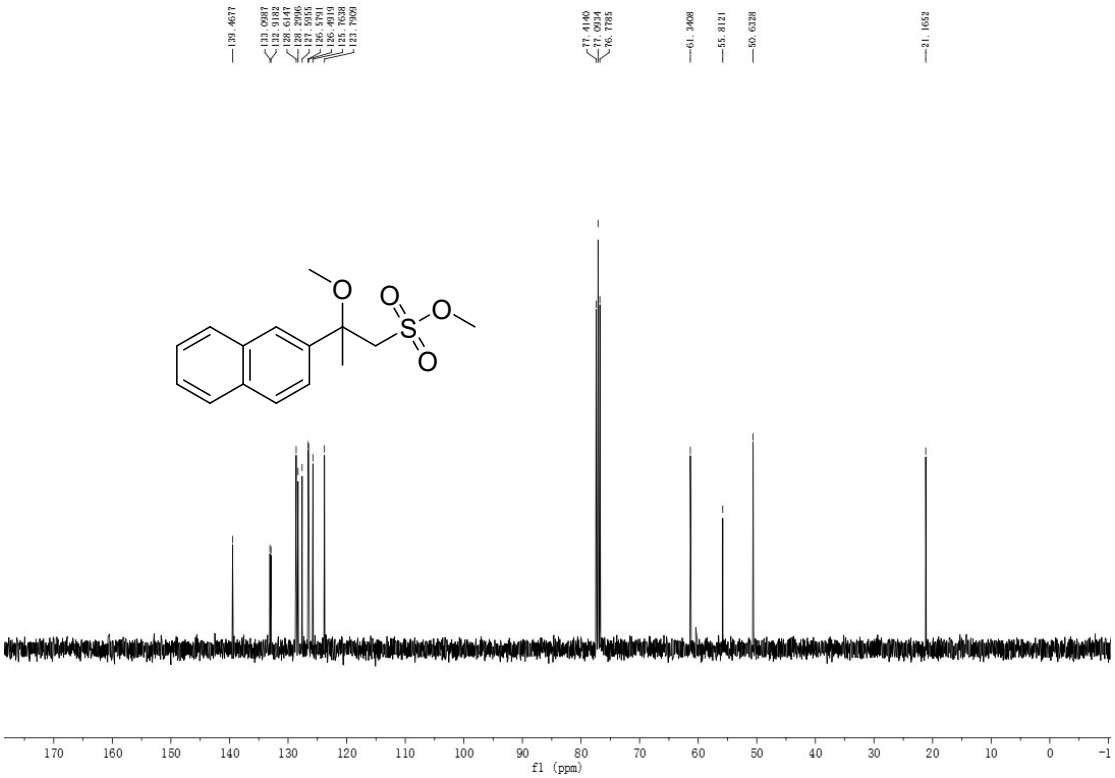
^{13}C NMR (150 MHz, $CDCl_3$) of **3ja**:



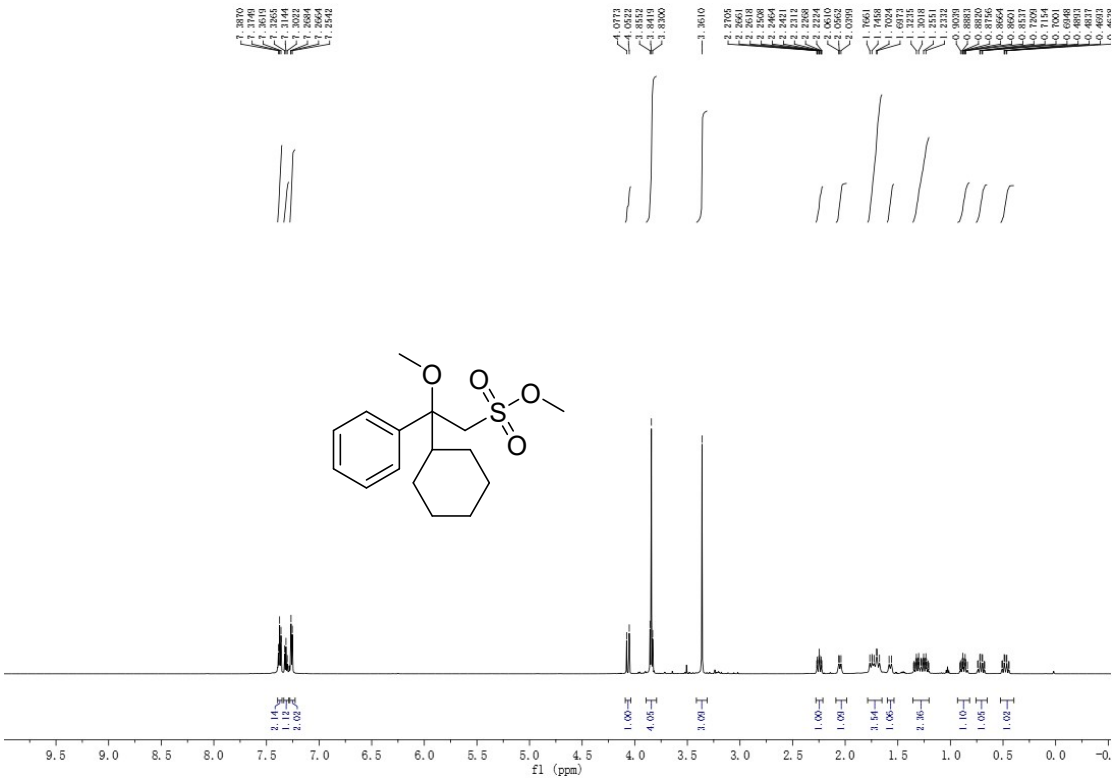
^{1}H NMR (400 MHz, $CDCl_3$) of **3ka**:



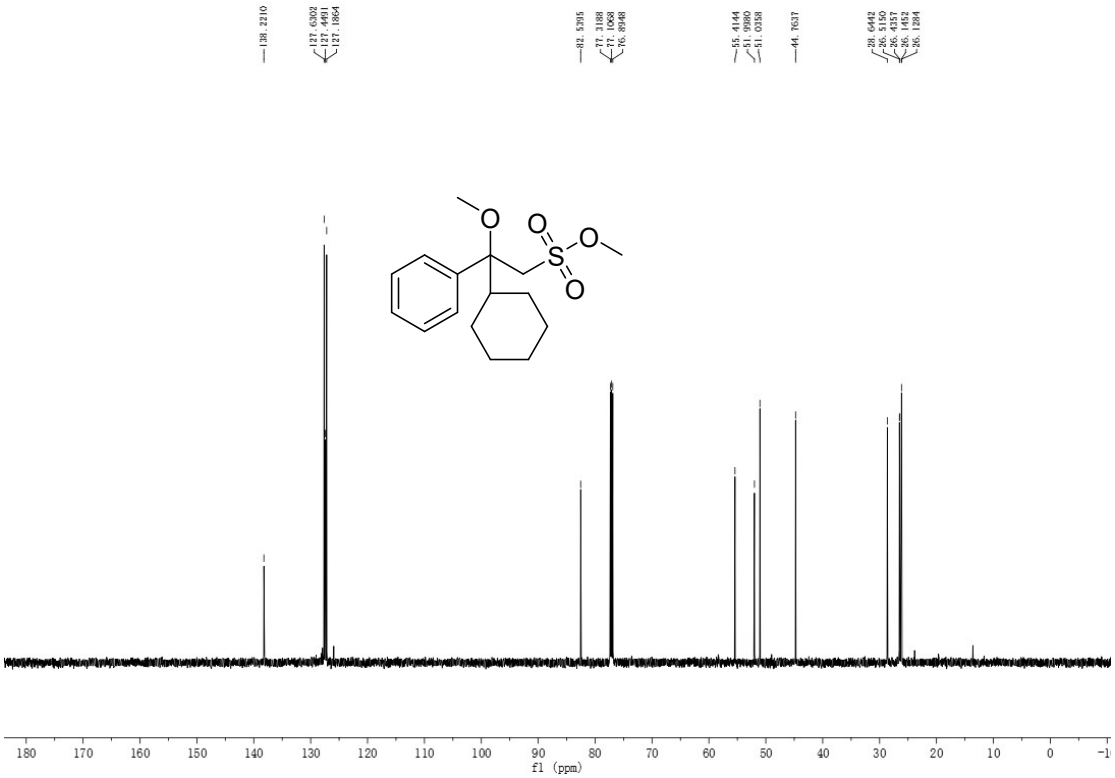
^{13}C NMR (150 MHz, $CDCl_3$) of **3ka**:



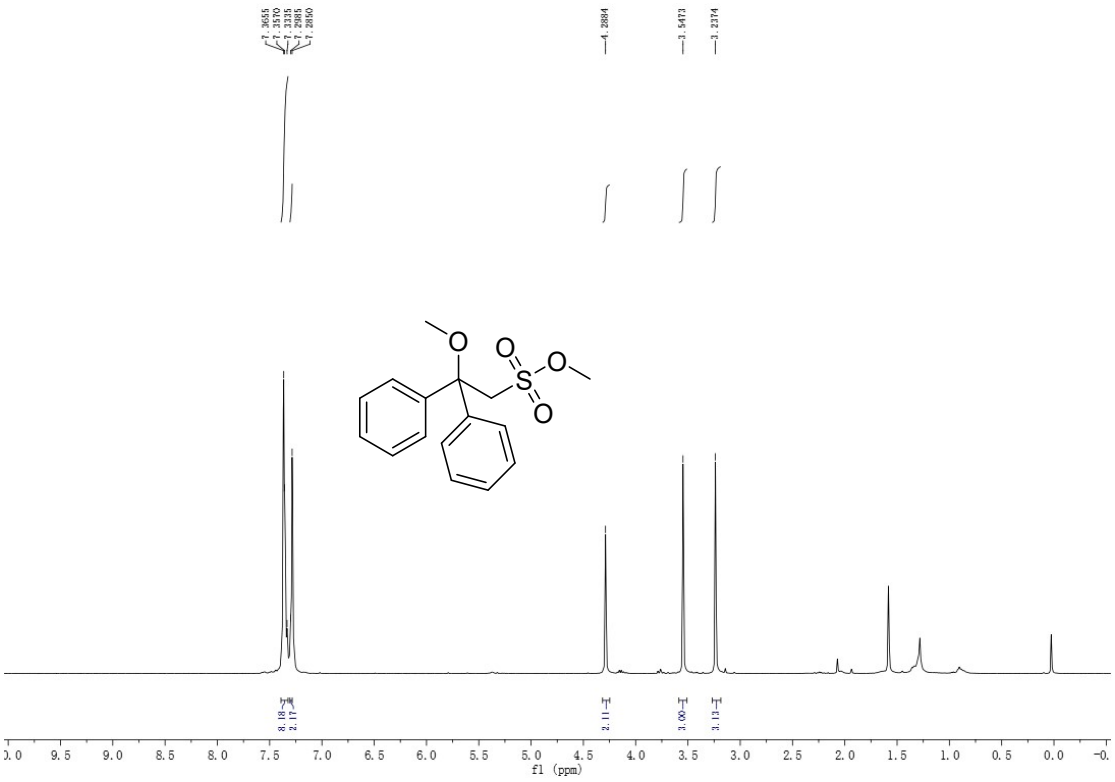
^{1}H NMR (600 MHz, $CDCl_3$) of **3la**:



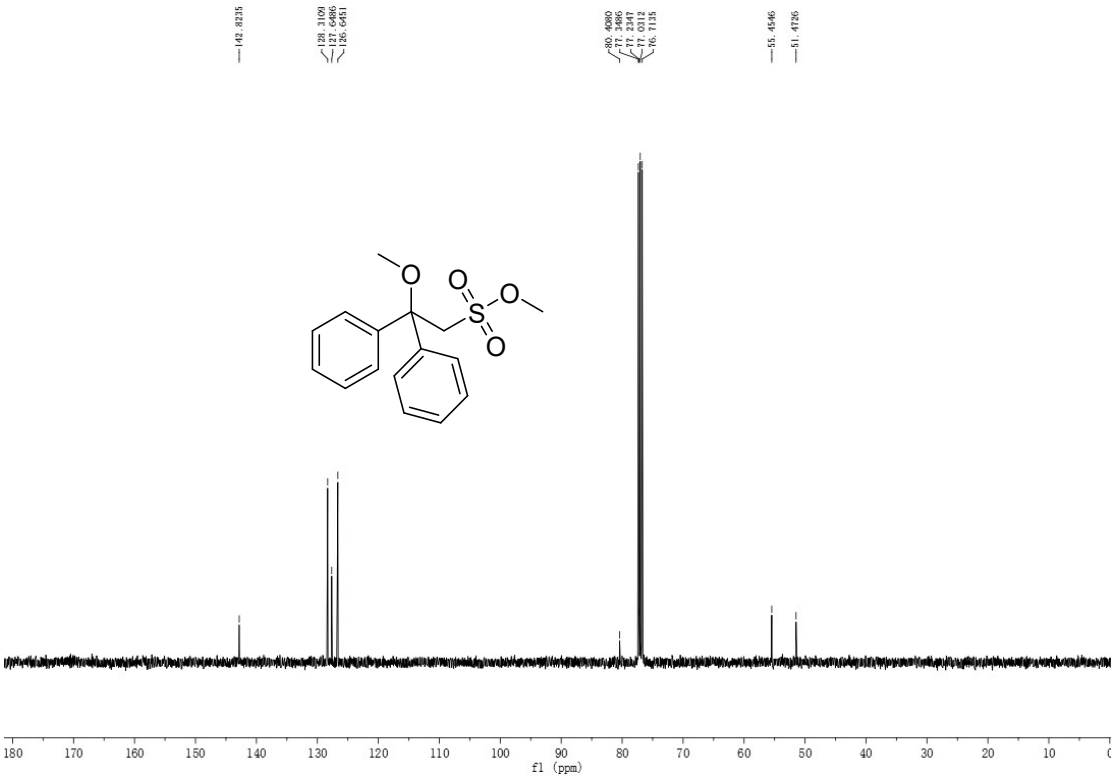
^{13}C NMR (150 MHz, $CDCl_3$) of **3la**:



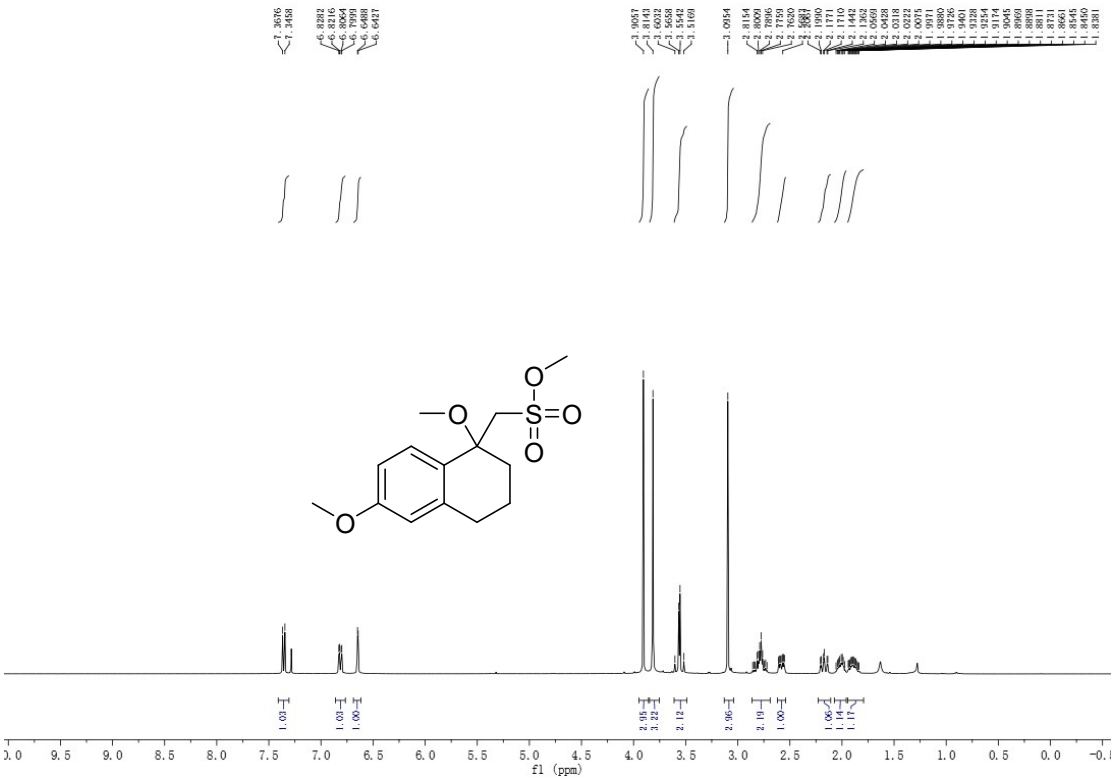
^{1}H NMR (600 MHz, $CDCl_3$) of **3ma**:



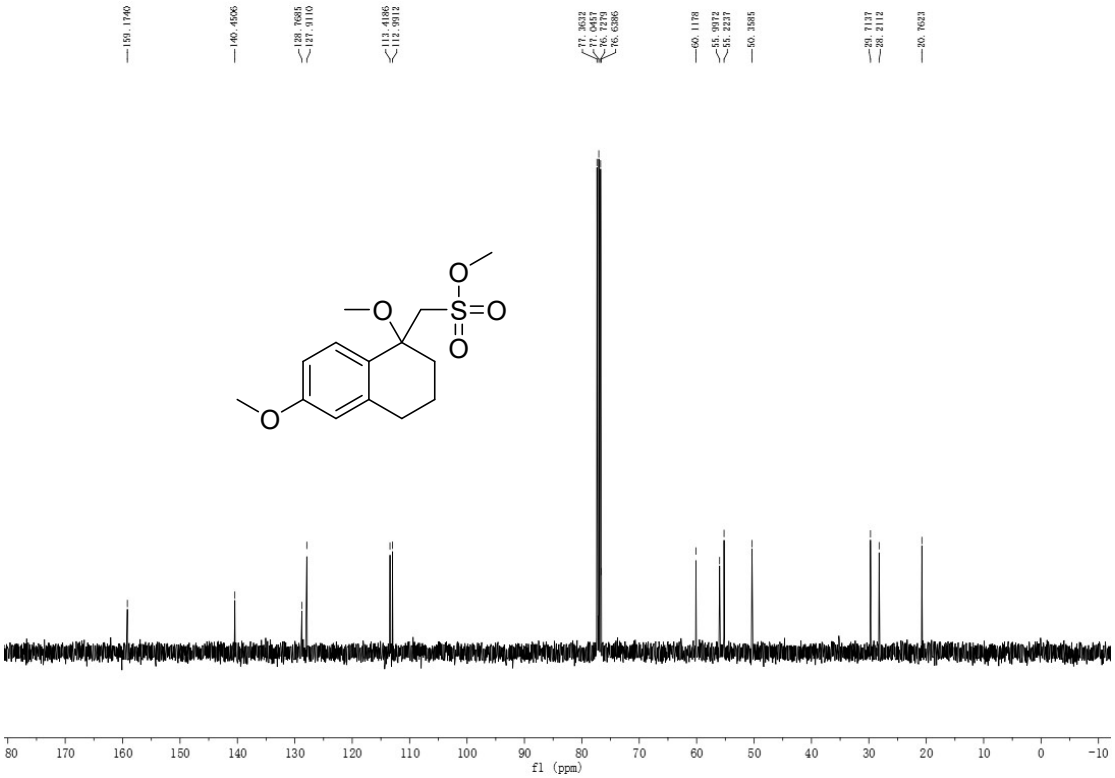
^{13}C NMR (150 MHz, $CDCl_3$) of **3ma**:



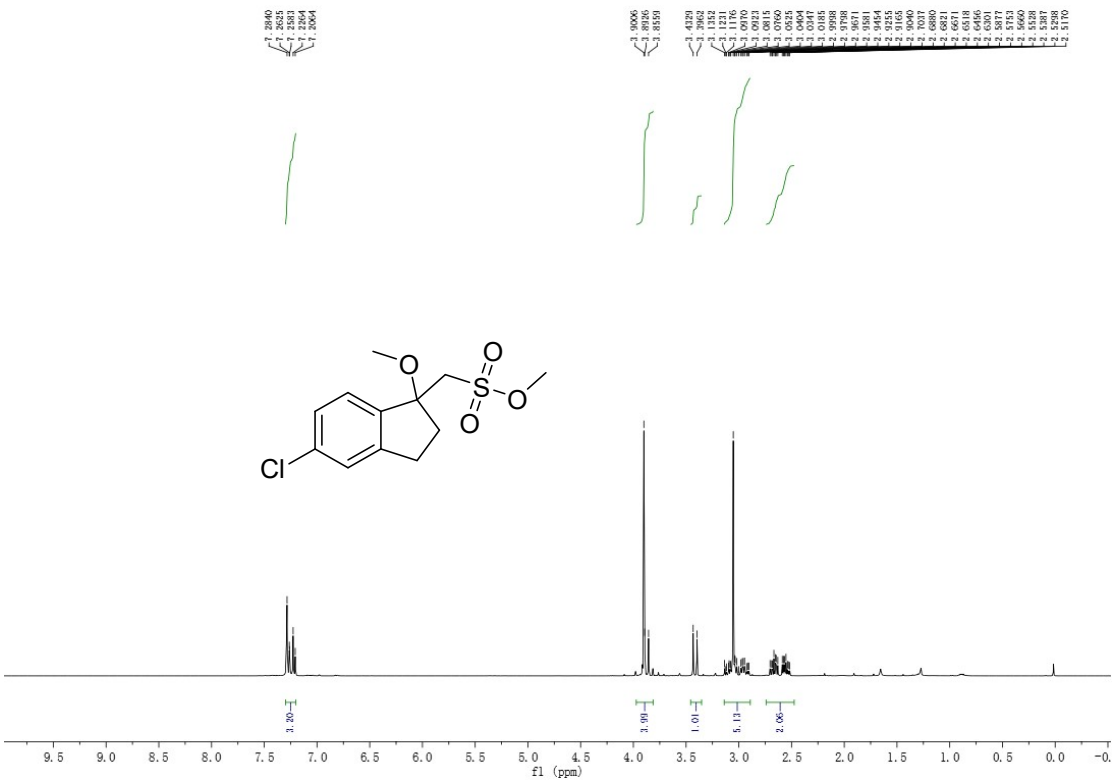
^{1}H NMR (400 MHz, $CDCl_3$) of **3na**:



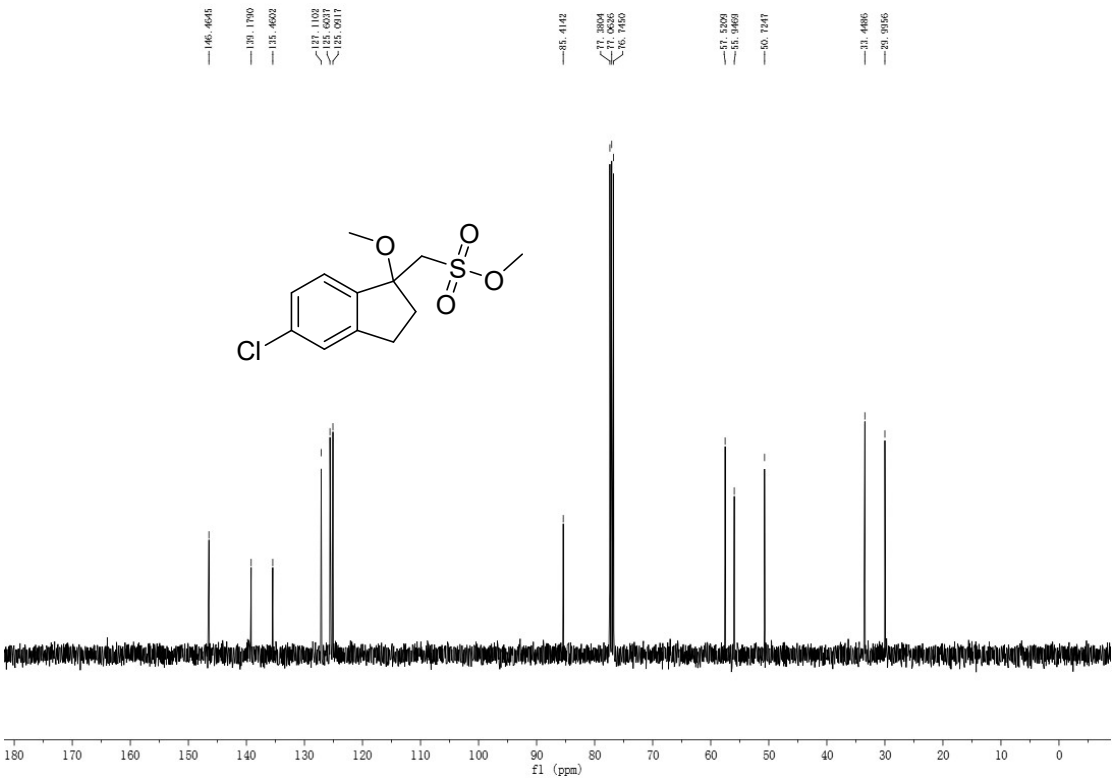
^{13}C NMR (100 MHz, $CDCl_3$) of **3na**:



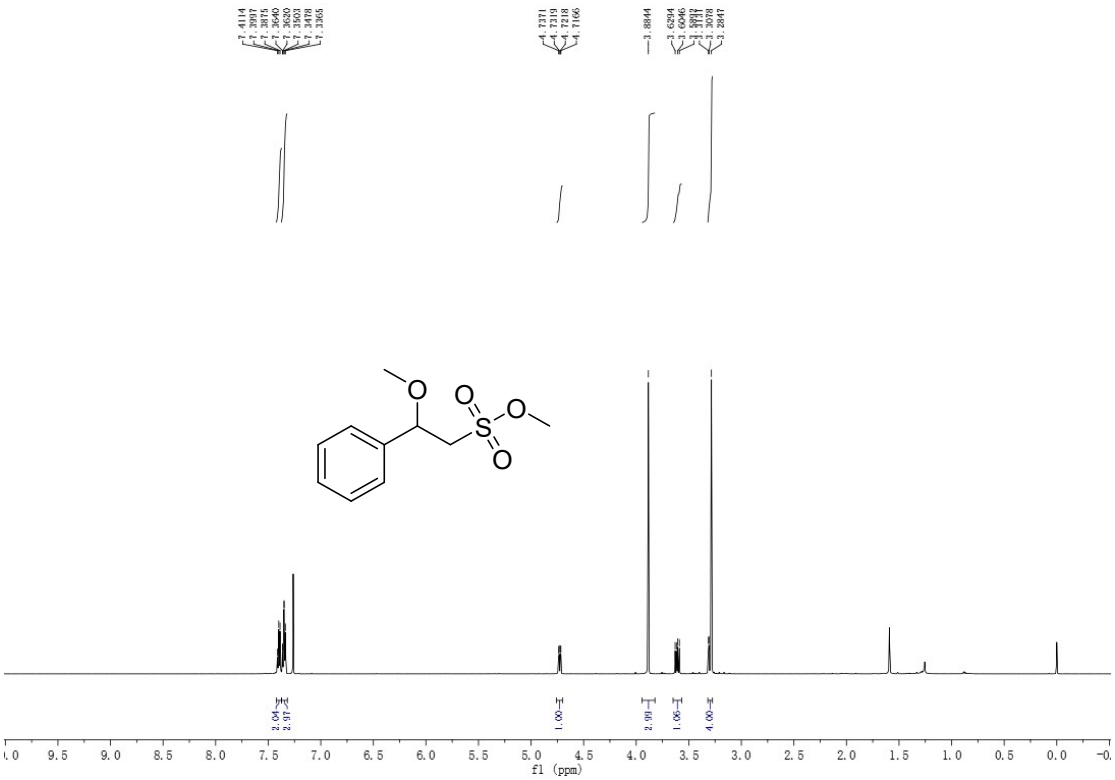
^{1}H NMR (400 MHz, $CDCl_3$) of **3oa**:



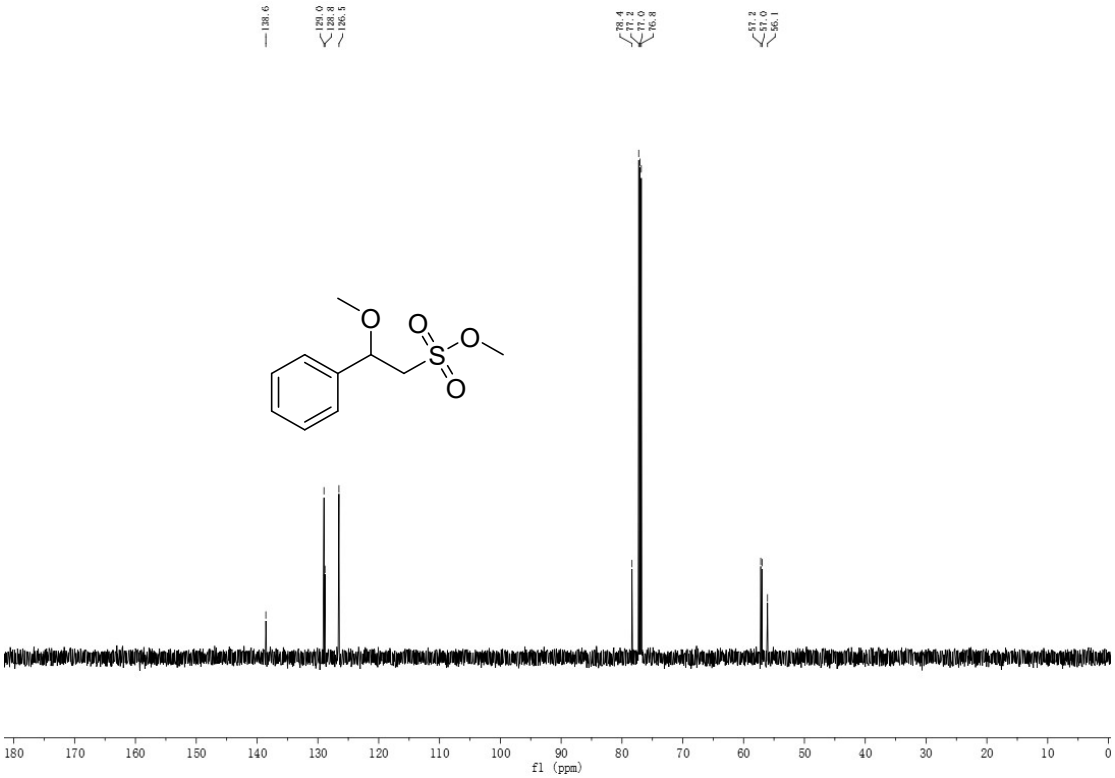
^{13}C NMR (100 MHz, $CDCl_3$) of **3oa**:



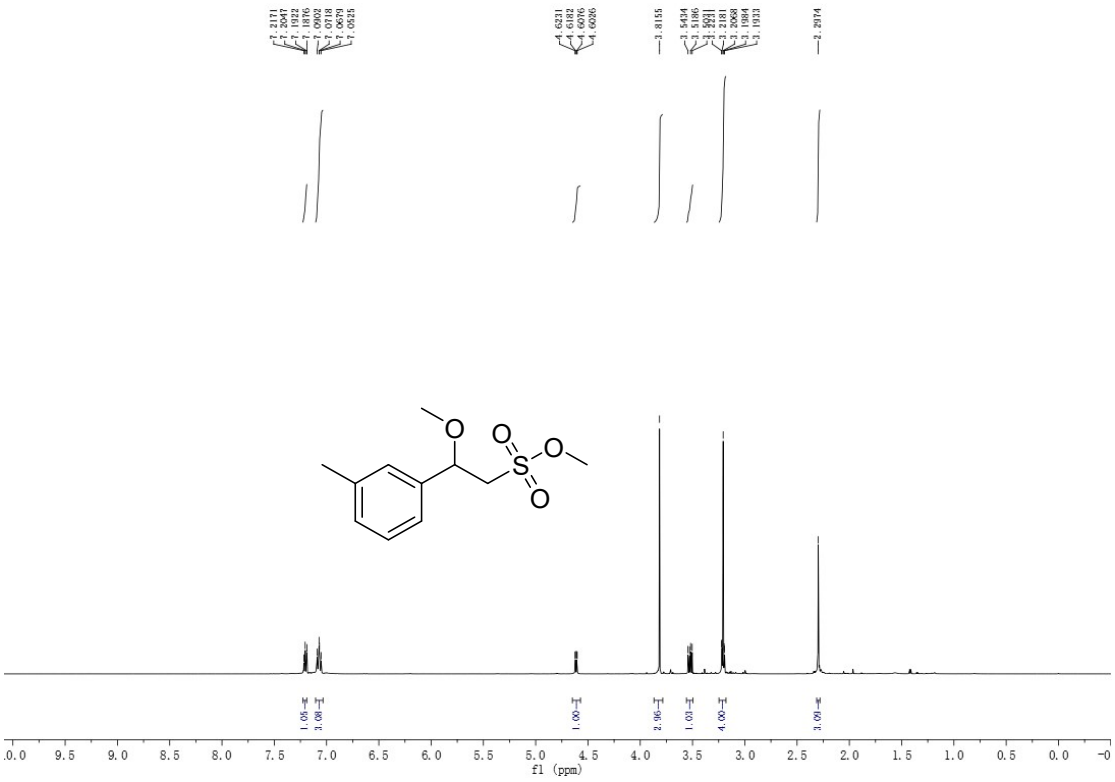
^{1}H NMR (600 MHz, $CDCl_3$) of **3pa**:



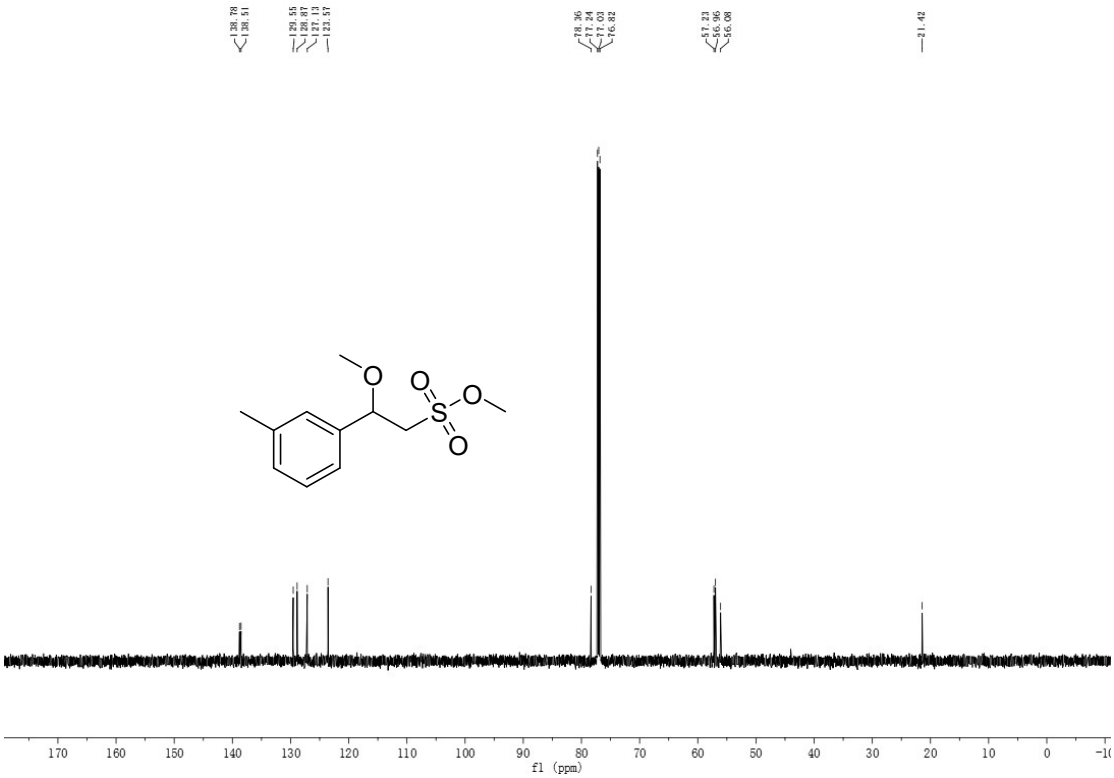
^{13}C NMR (150 MHz, $CDCl_3$) of **3pa**:



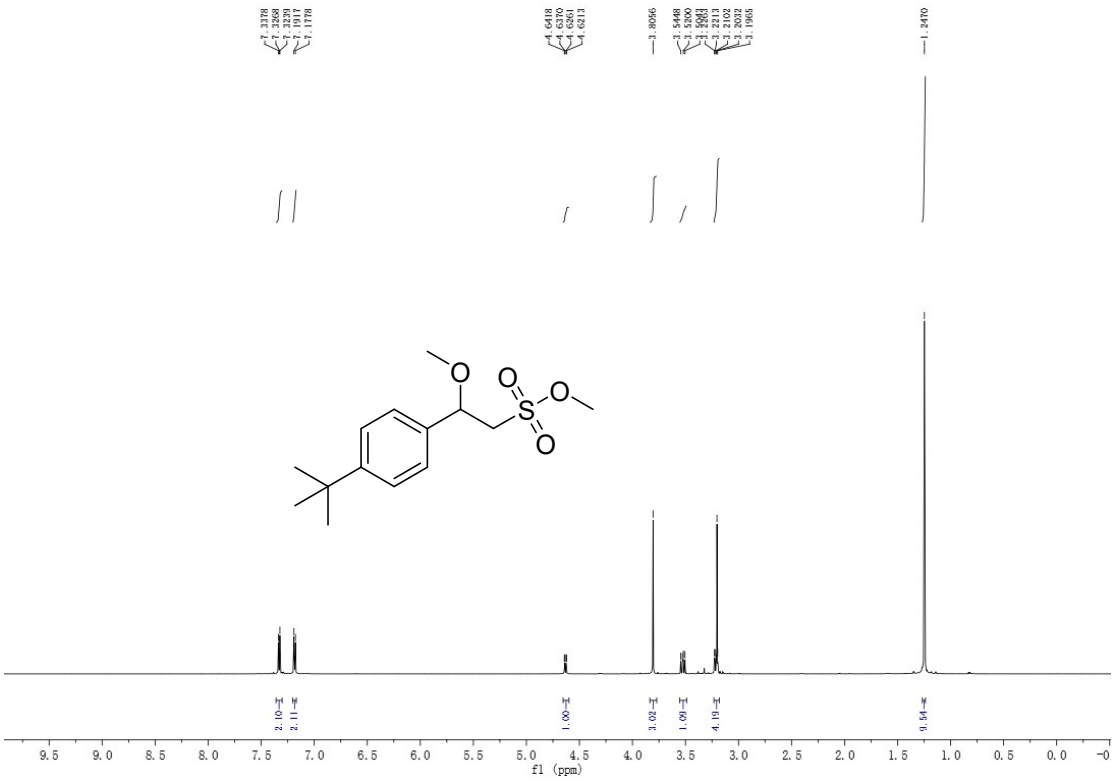
^{1}H NMR (600 MHz, $CDCl_3$) of **3qa**:



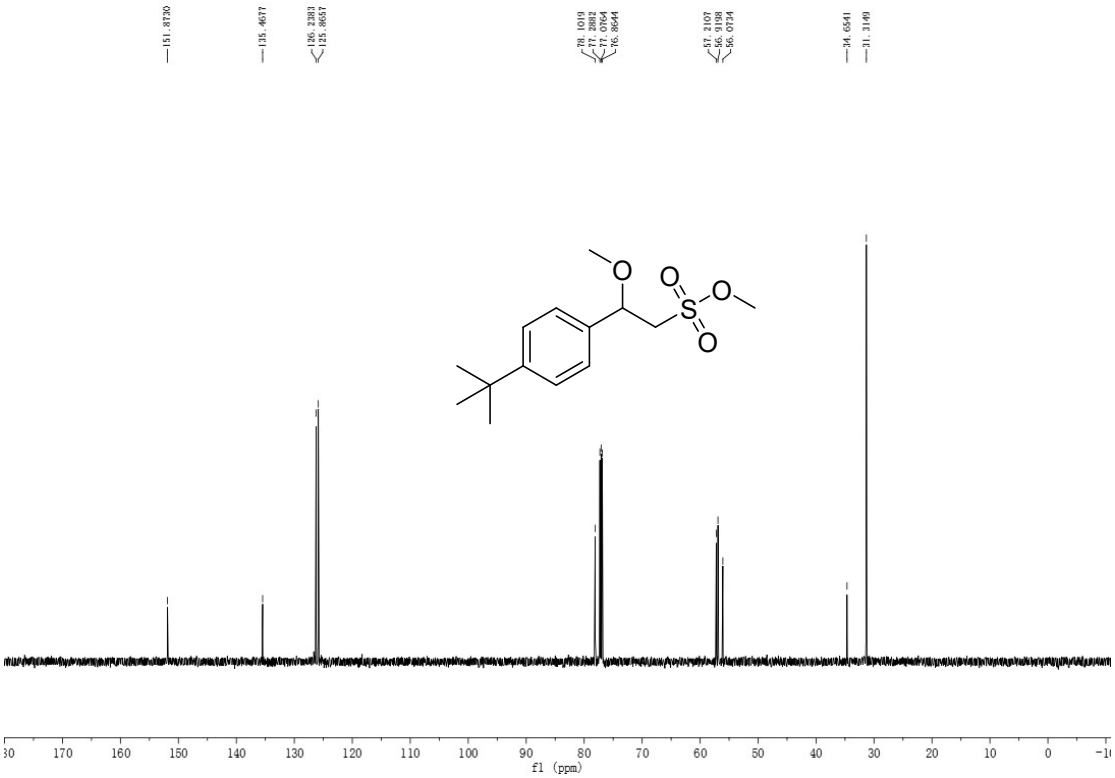
^{13}C NMR (150 MHz, $CDCl_3$) of **3qa**:



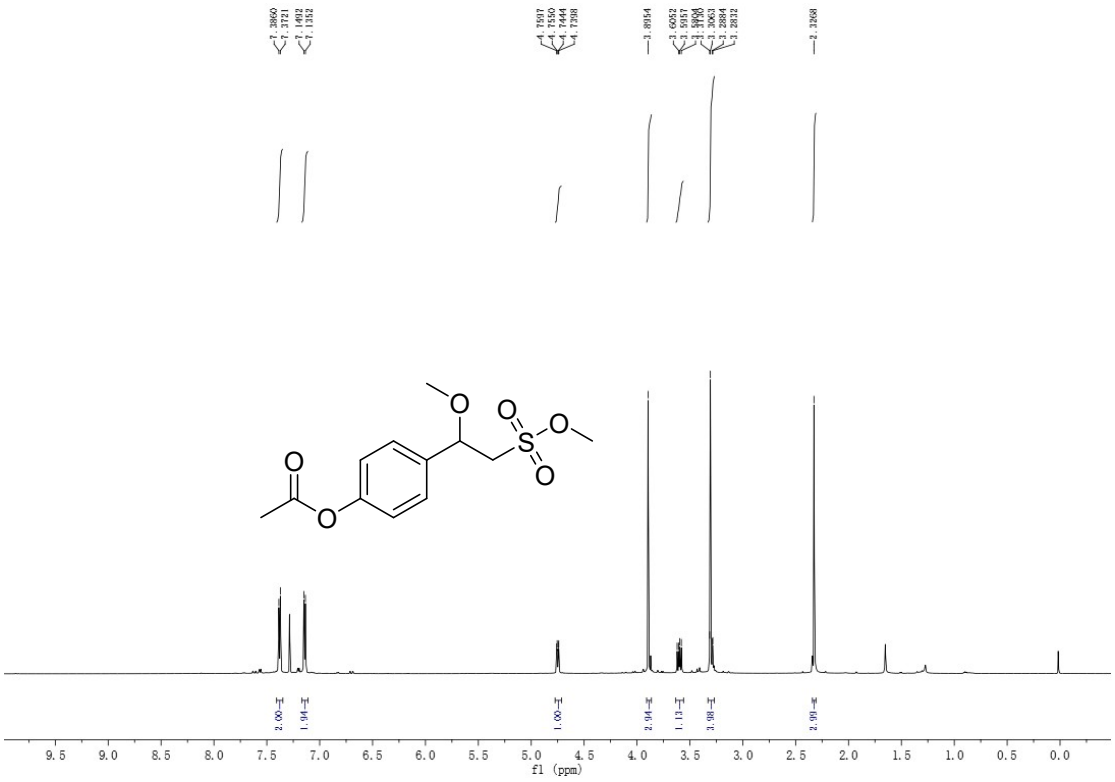
^{1}H NMR (600 MHz, $CDCl_3$) of **3ra**:



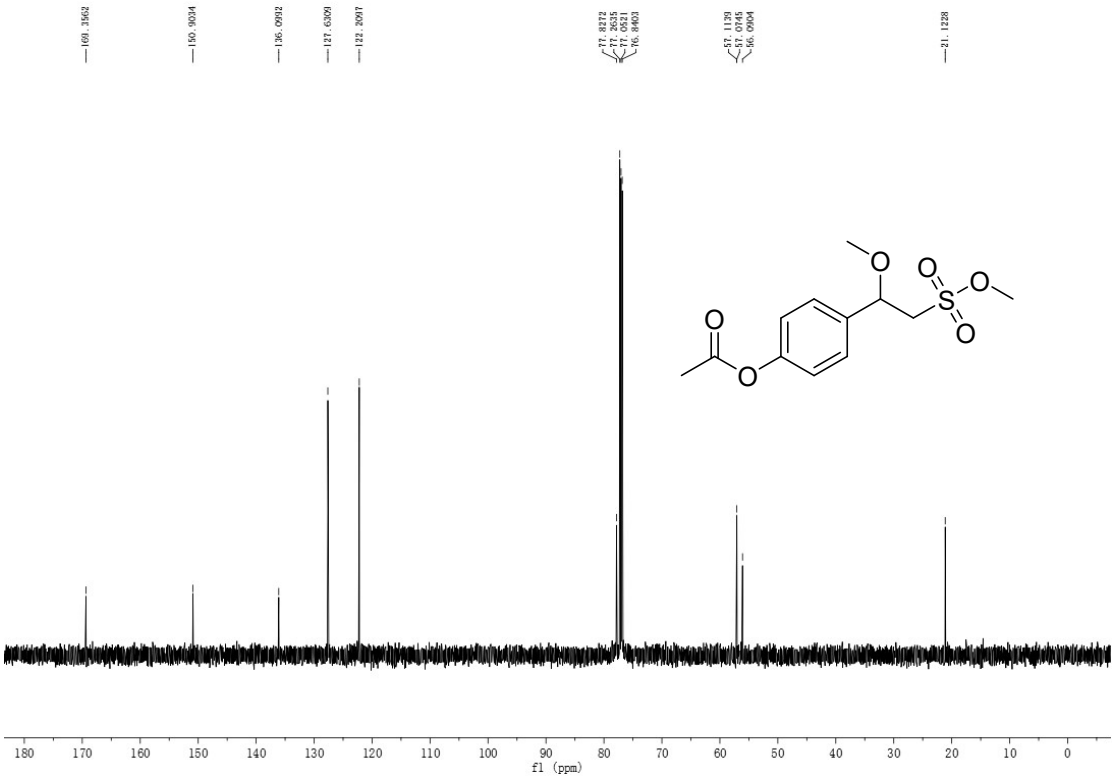
^{13}C NMR (150 MHz, $CDCl_3$) of **3ra**:



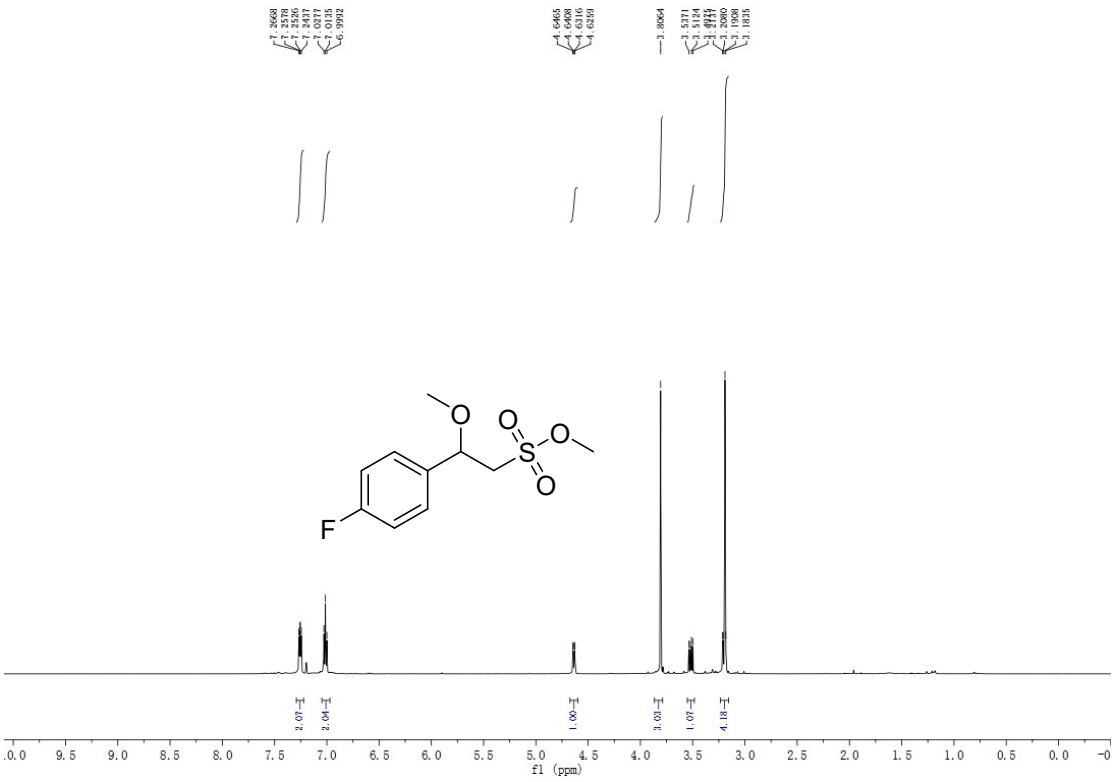
^{1}H NMR (600 MHz, $CDCl_3$) of **3sa**:



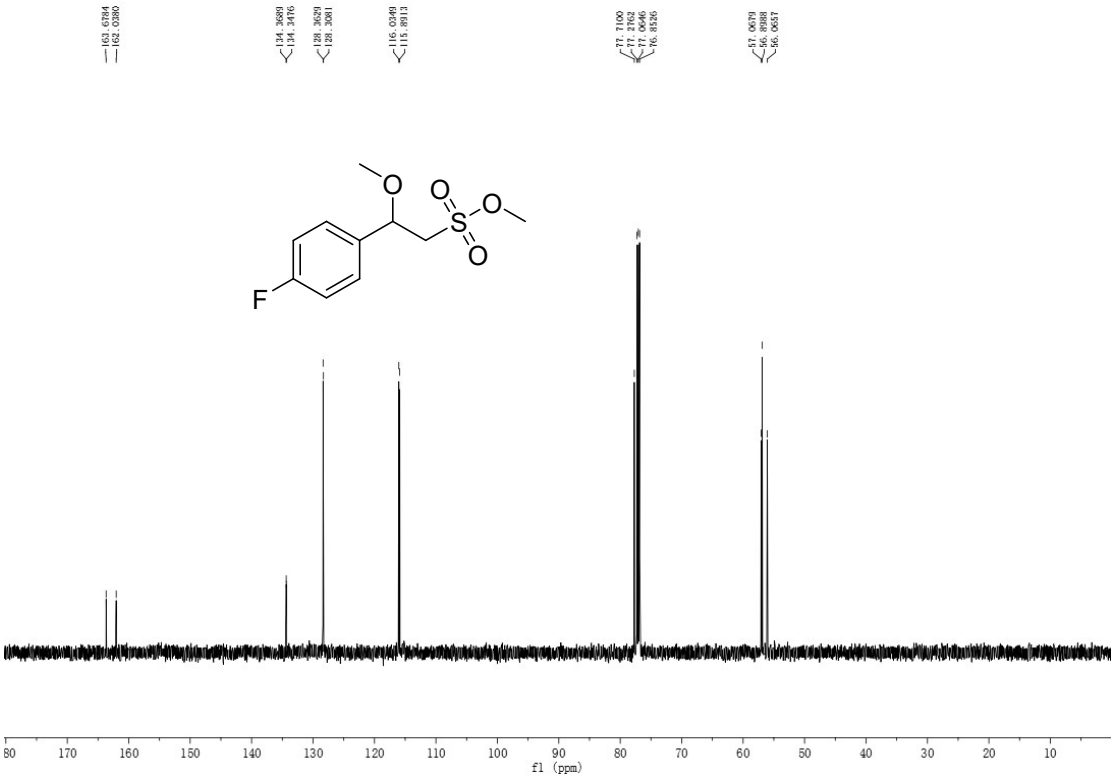
^{13}C NMR (150 MHz, $CDCl_3$) of **3sa**:



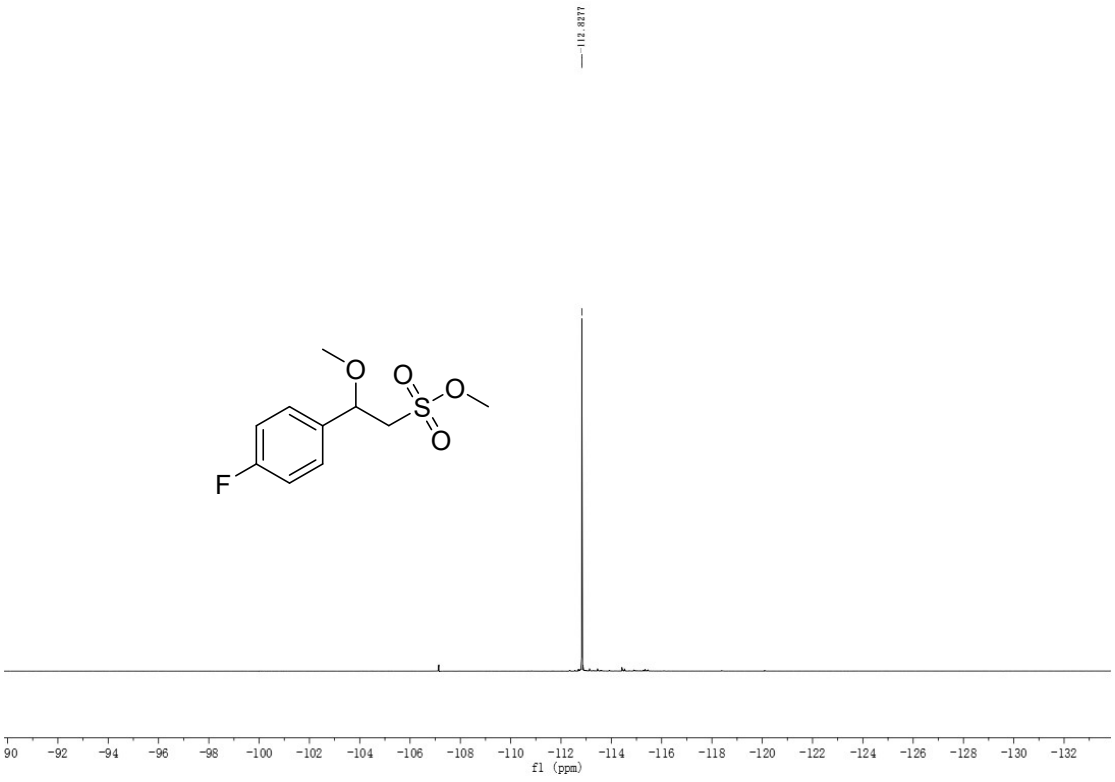
^{1}H NMR (600 MHz, $CDCl_3$) of **3ta**:



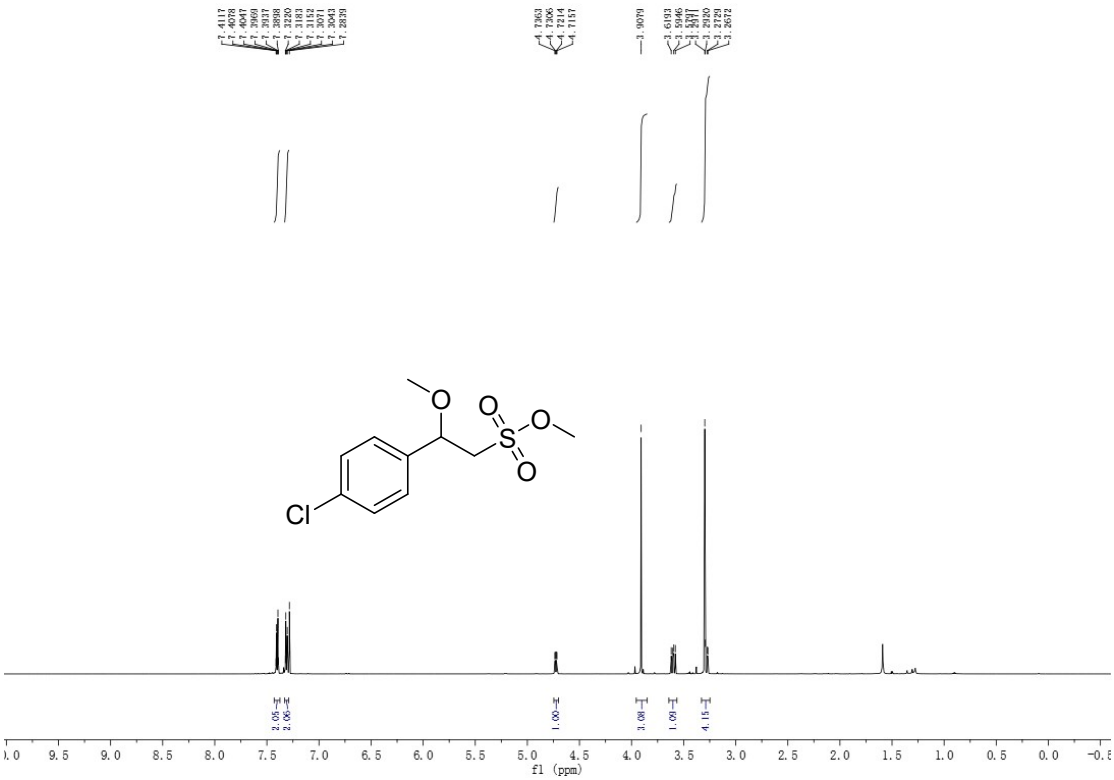
^{13}C NMR (150 MHz, $CDCl_3$) of **3ta**:



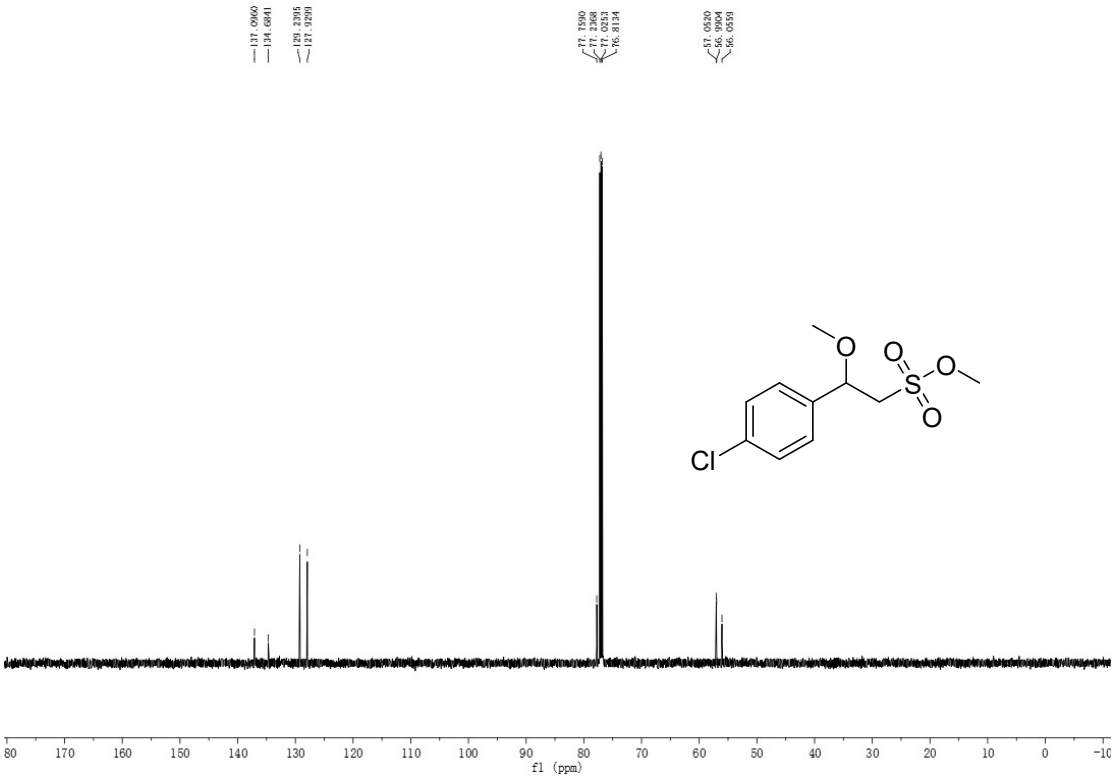
^{19}F NMR (565 MHz, $CDCl_3$) of **3ta**:



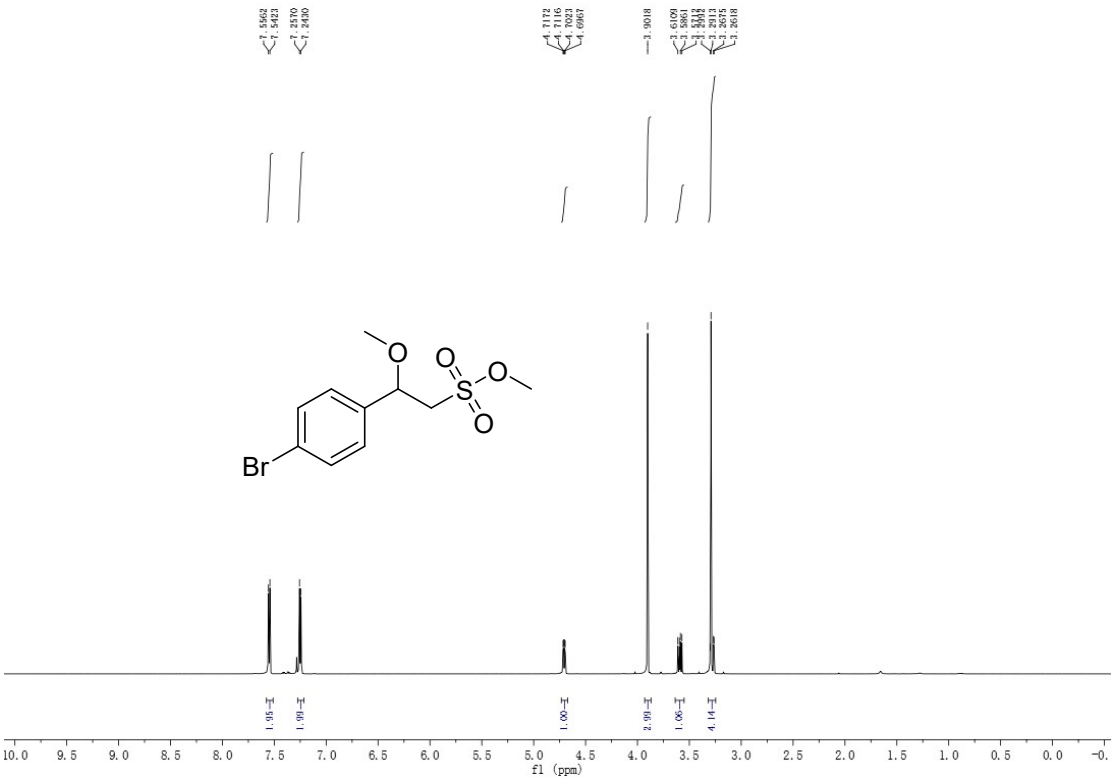
^{1}H NMR (600 MHz, $CDCl_3$) of **3ua**:



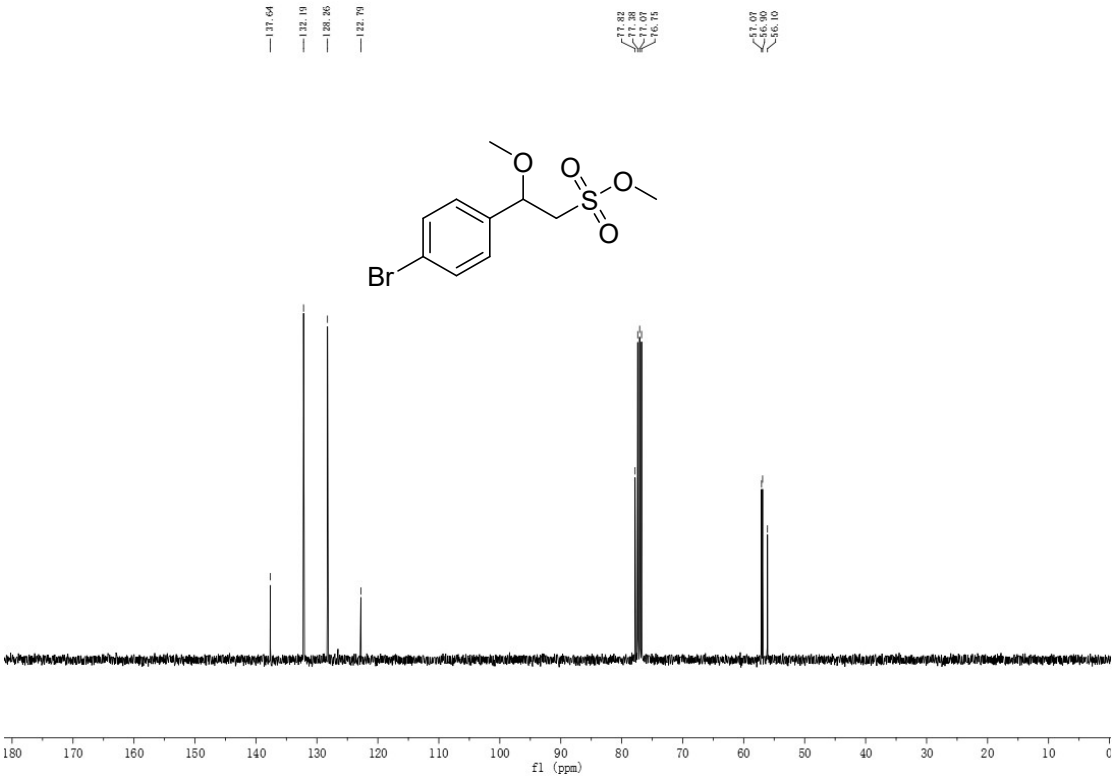
^{13}C NMR (150 MHz, $CDCl_3$) of **3ua**:



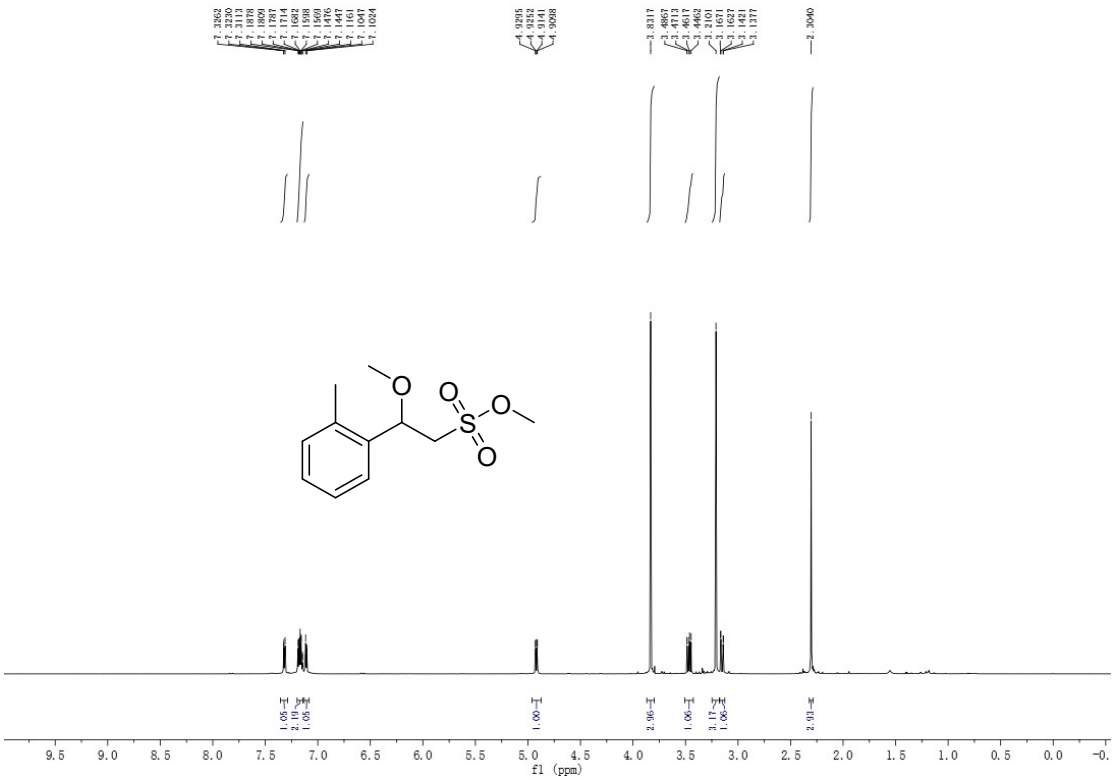
^{1}H NMR (600 MHz, $CDCl_3$) of **3va**:



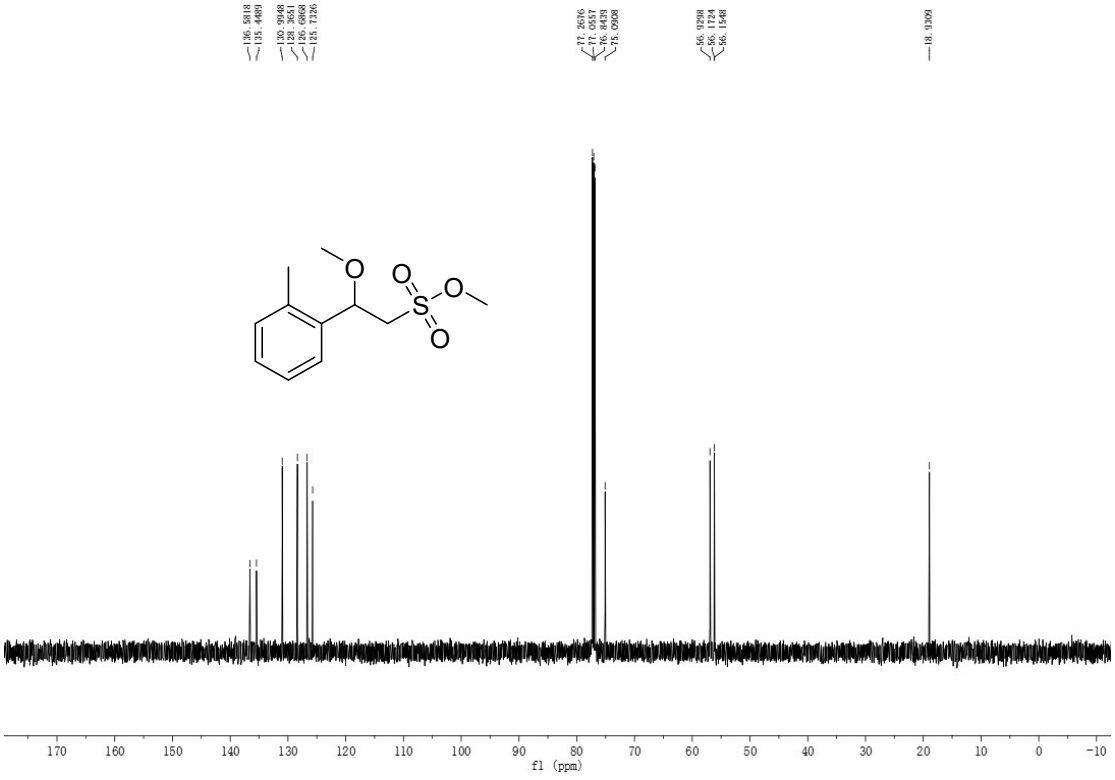
^{13}C NMR (100 MHz, $CDCl_3$) of **3va**:



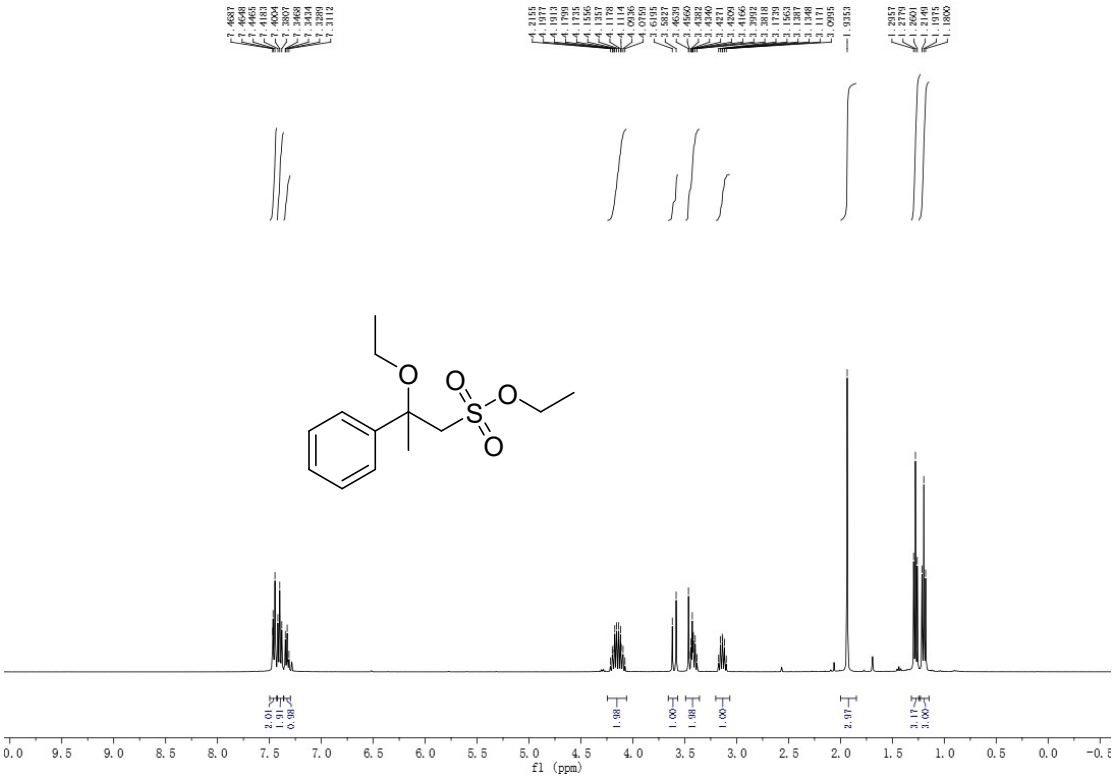
^{1}H NMR (600 MHz, $CDCl_3$) of **3wa**:



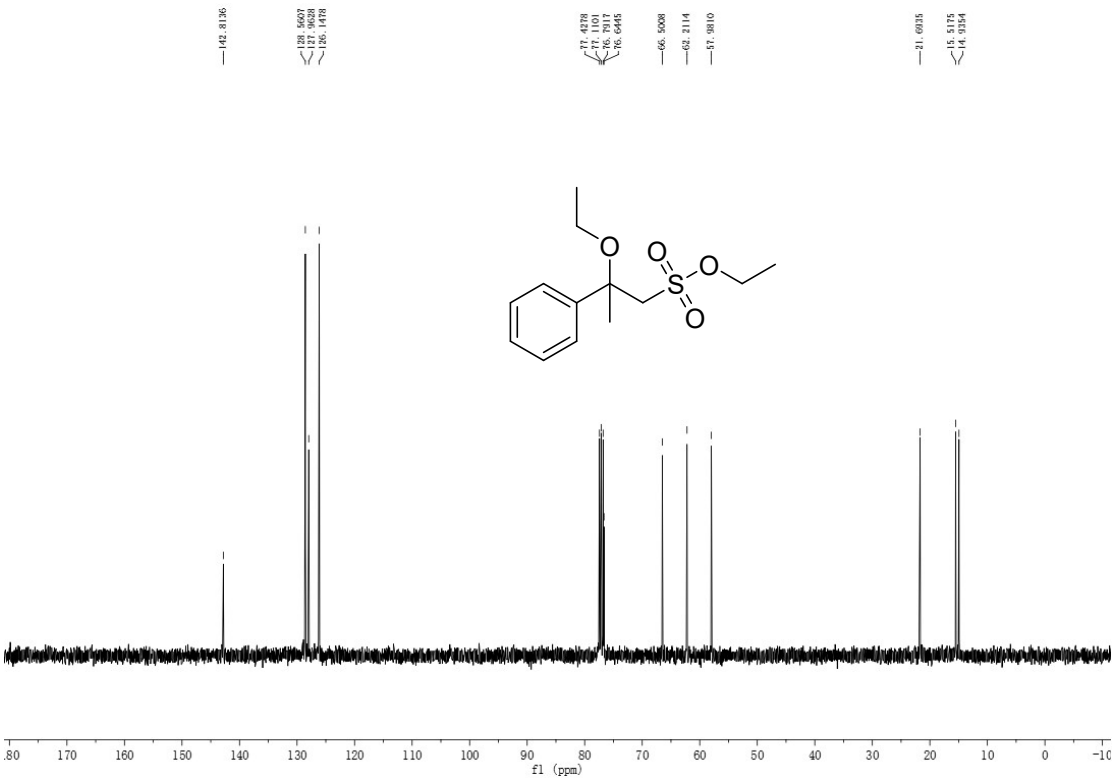
^{13}C NMR (150 MHz, $CDCl_3$) of **3wa**:



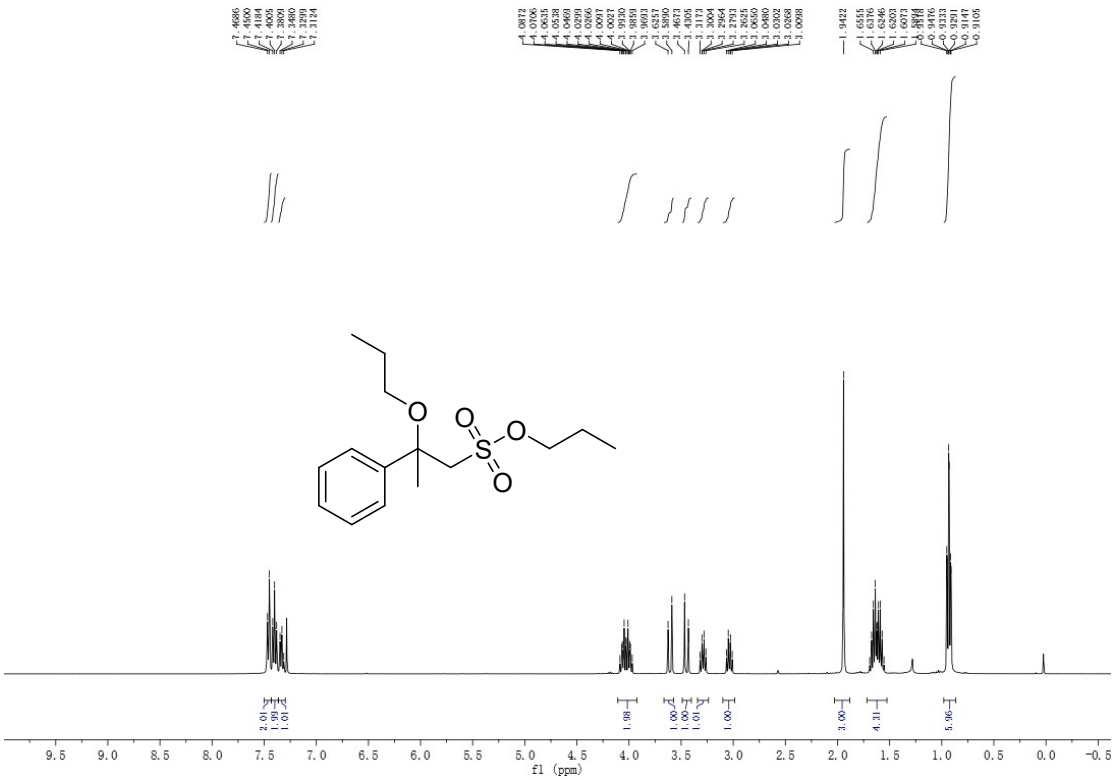
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**:



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

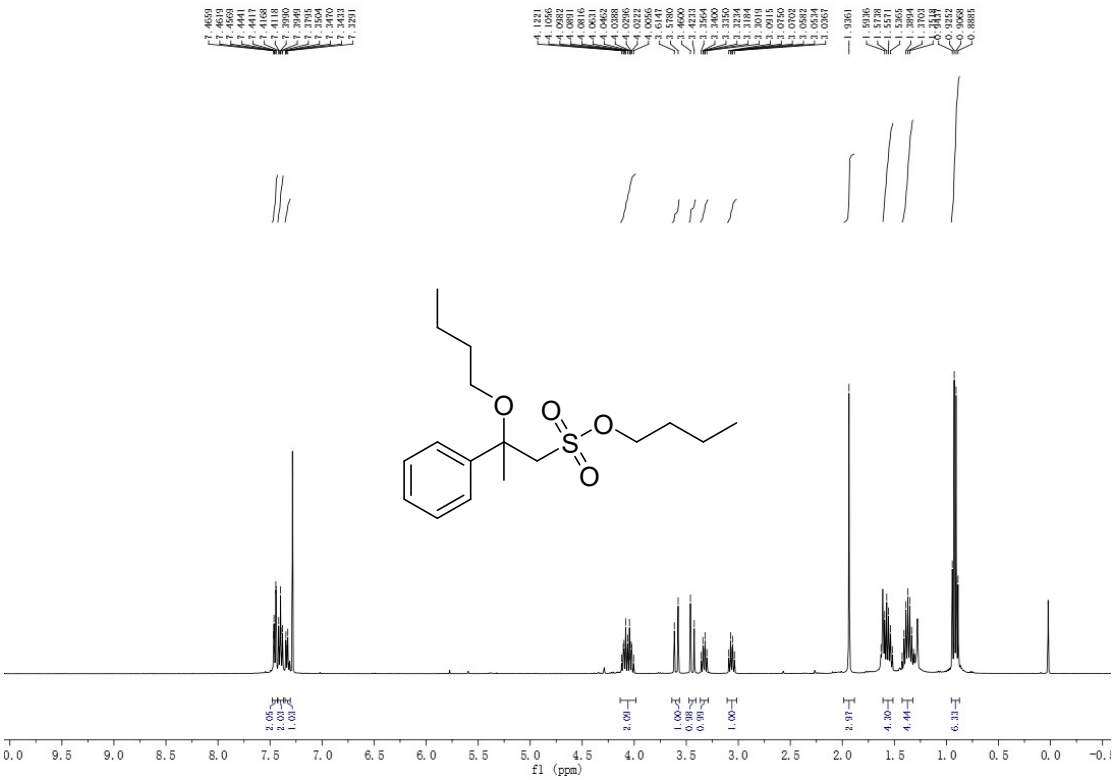


^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**:

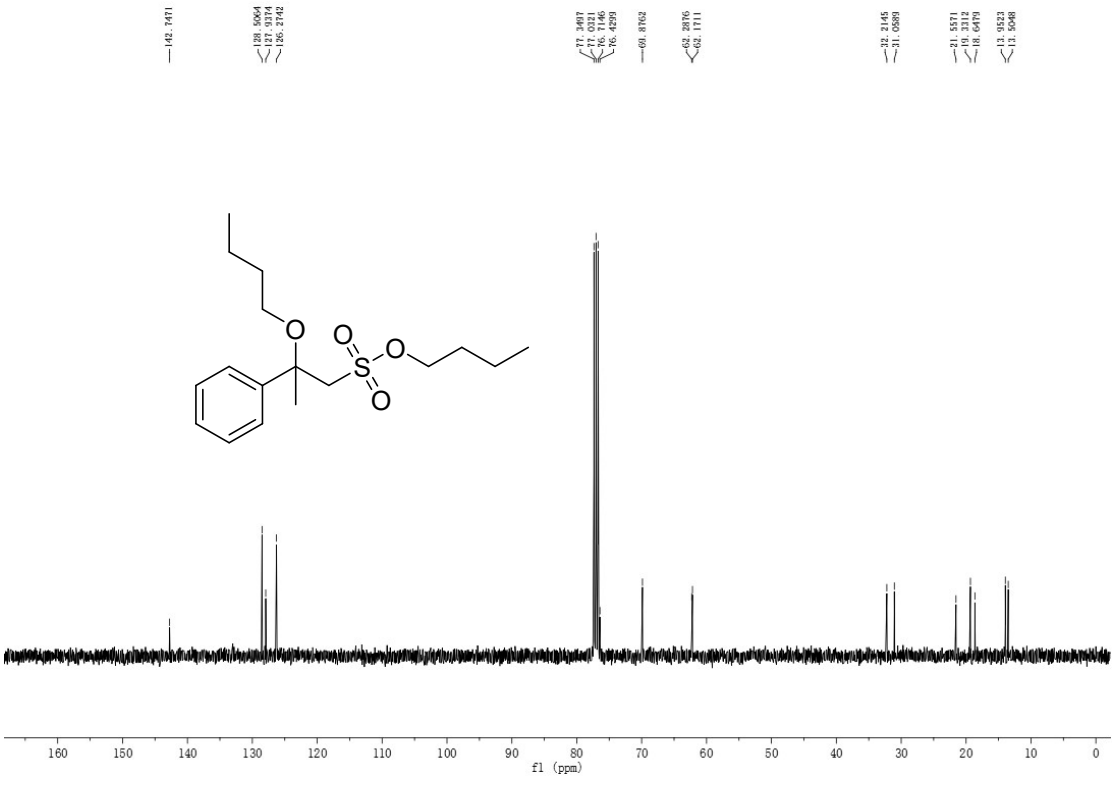


^{13}C NMR (100 MHz, $CDCl_3$) of **3ac**:

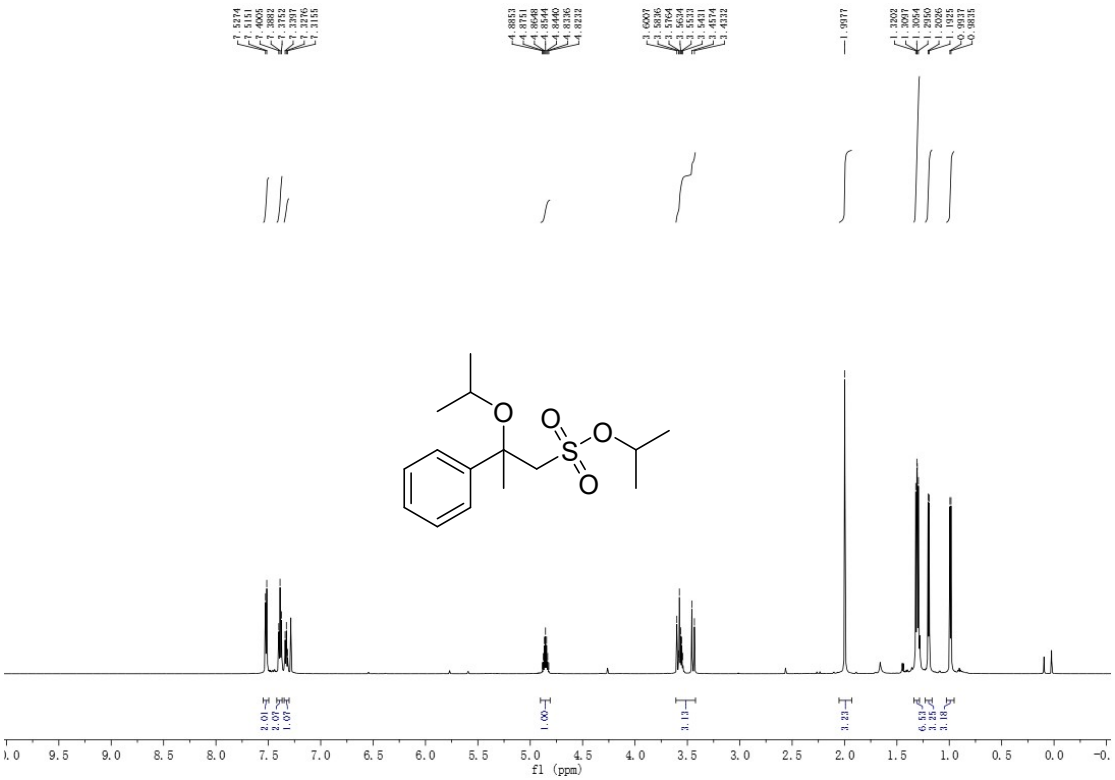
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**:



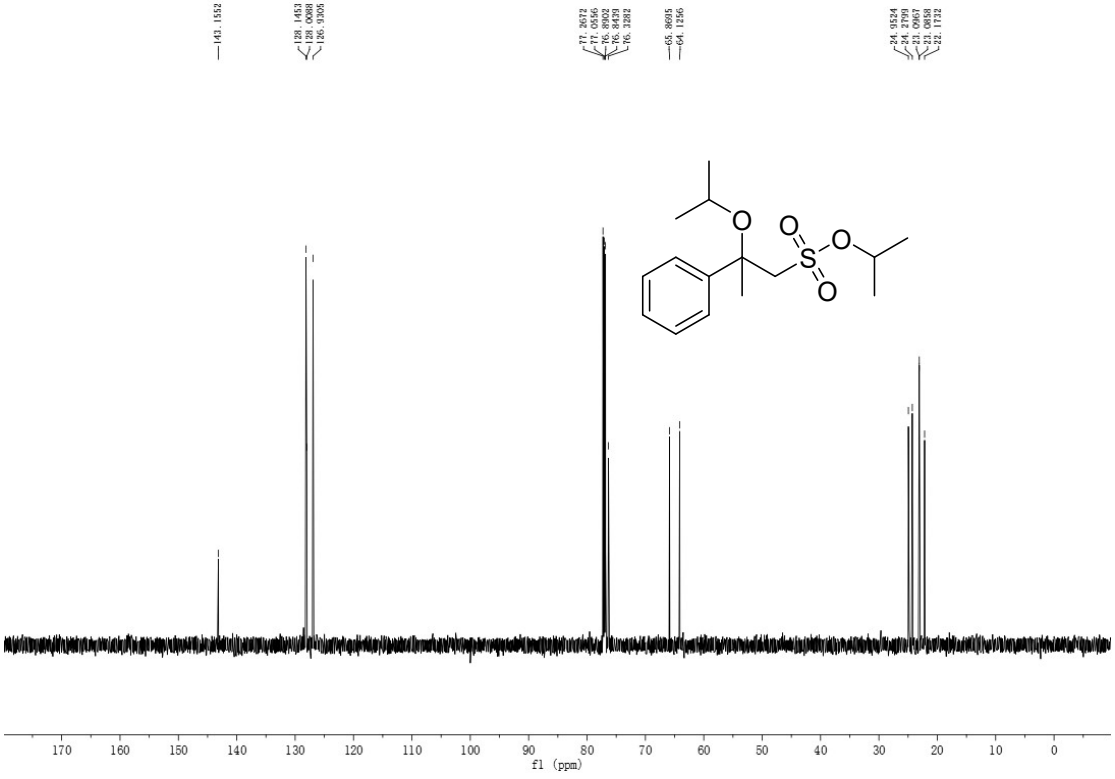
^{13}C NMR (100 MHz, $CDCl_3$) of **3ad**:



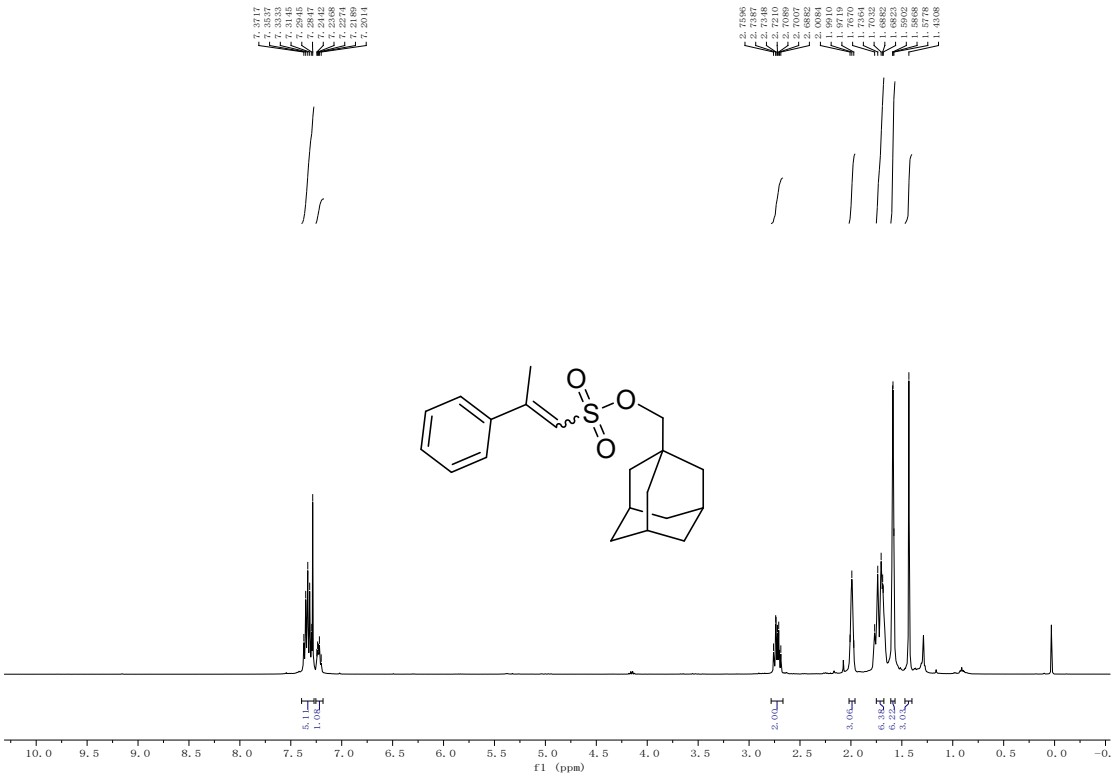
^{1}H NMR (600 MHz, $CDCl_3$) of **3ae**:



^{13}C NMR (150 MHz, $CDCl_3$) of **3ae**:



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



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