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Supporting Information

Copper(II) Acetate Catalysed Ring-Opening Cross-Coupling of Cyclopropanols with Sulfonyl Azides

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I General Information and Materials

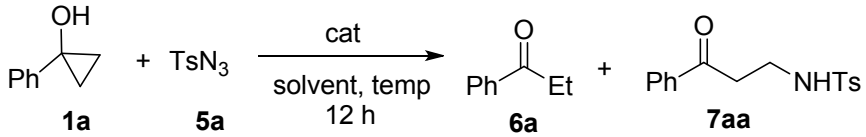
NMR spectra were recorded using Bruker AV-300 / AV-400 spectrometers. The data are reported as follows: chemical shift in ppm on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were acquired on an agilent 6230 spectrometer and were obtained by peak matching. Gas Chromatography-Mass Spectra were acquired on a Agilent7890A-5975C spectrometer. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator and/or by exposure to phosphormolybdic acid/cerium (IV) sulfate/ ninhydrine followed by brief heating with a heat gun. Liquid chromatography (flash chromatography) was performed on 60Å (40 – 60 μm) mesh silica gel (SiO_2). All reactions were carried out under nitrogen or argon with anhydrous solvents in oven-dried glassware, unless otherwise noted. All reagents were commercially obtained and, where appropriate, purified prior to use

II Supporting Table

Conditions optimization for the reaction of cyclopropanols and Sulfonyl Azides.

To a solution of cyclopropanol **1a** (0.5 mmol, 1eq.) in 2 mL solvent in a flame dried Schlenk tube was added dropwise Tosyl Azide (0.75 mmol, 1.5eq.) and catalyst. Then the solution was evacuated three times with N_2 and stirred for 12h at temperature indicated in the table below. After cooling to room temperature, solvent was removed in vacuum; the residue was purified by column chromatography to give the product.

Table 1. Catalyst screening and conditions optimazation[a]



1a **5a** **6a** **7aa**

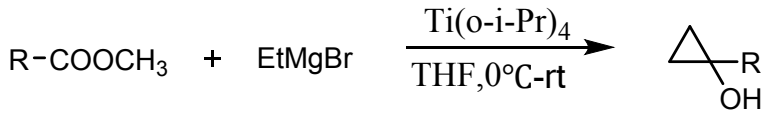
entry	cat	solvent	temp	products (yield)
1	$Cu(OAc)_2$ (0.2 eq)	DCM	30 °C (rt)	NR
2	$Cu(OAc)_2$ (0.2 eq)	DCM	60 °C (reflux)	**6a** (51%) and **7aa** (38%)
3	$Mn(OAc)_2$ (0.2 eq)	DCM	reflux	**6a** only
4	$Cu(OTf)_2$ (0.05 eq)	DCM	reflux	**6a** only
5	$Ga(OTf)_3$ (0.05 eq)	DCM	reflux	**6a** only
6	$La(OTf)_3$ (0.05 eq)	DCM	reflux	**6a** only
7	$AgNO_3$ (0.05 eq)	DCM	reflux	**6a** only
8	AgOAc (0.05 eq)	DCM	reflux	**6a** only
9	TsOH (0.2 eq)	DCM	reflux	**6a** only
10	$Mn(acac)_3$ (0.2 eq)	DCE	100 °C reflux	**6a** only

11	CAN (0.2 eq)	DCE	reflux	**6a** only
12	$Co(OAc)_2$ (0.2 eq)	DCE	reflux	**6a** only
13	$Ni(acac)_2$ (0.05 eq)	DCE	reflux	**6a** only
14	$Fe(acac)_3$ (0.2 eq)	DCE	reflux	**6a** only
15	$Cu(acac)_2$ (0.2 eq)	DCE	reflux	**6a** and **7aa** (37%)
16	$Cu(hfacac)_2$ (0.2 eq)	DCE	reflux	**6a** and **7aa** (15%)
17	CuCl (0.2 eq)	DCE	reflux	**6a** only
18	CuBr (0.2 eq)	DCE	reflux	**6a** only
19	CuI (0.2 eq)	DCE	reflux	**6a** only)
20	$CuBr_2$ (0.2 eq)	DCE	reflux	**6a** only
21	$Cu(OAc)_2$ (0.2 eq)	DCE	reflux	**6a** and **7aa** (40%)
22	$Cu(OAc)_2$ (0.2 eq)	THF	reflux	**6a** and **7aa** (29%)
23	$Cu(OAc)_2$ (0.2 eq)	CH_3CN	reflux	NR
24	$Cu(OAc)_2$ (0.2 eq)	DMF	120 ℃	NR
25	$Cu(OAc)_2$ (0.2 eq)	DMSO	120 ℃	NR
26	$Cu(OAc)_2$ (0.2 eq)	$CHCl_3$	reflux	**6a** and **7aa** (27%)
27	$Cu(OAc)_2$ (0.2 eq)	toluene	130 °C (reflux)	**6a** and **7aa** (69%)
28	$Pd(OA)_2$ (0.05 eq)	toluene	reflux	**6a** only
29	Pd_2dba_3 (0.05 eq)	toluene	reflux	**6a** only
30	$Cu(acac)_2$ (0.2 eq)	toluene	reflux	**6a** and **7aa** (51%)
31	$Cu(hfacac)_2$ (0.05 eq)	toluene	reflux	**6a** and **7aa** (15%)
32	TcCu (0.05 eq)	toluene	reflux	**6a** and **7aa** (11%)
33	$FeCl_3.6H_2O$ (0.2 eq)	toluene	reflux	NR
a，isolated yields；b, yields are reported for **7aa** only				

III Preparation of Cyclopropanols

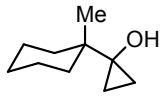
Starting cyclopropanols **1a**[1],**1b**[2],**1c**[2],**1d**[1],**1e**[3],**1f**[3],**1g**[1],**1i**[4],**1k**[3],**1l**[3] are prepared according to the previously reported procedures.

General method for the preparation of cyclopropanols



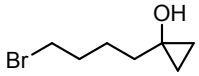
EtMgBr (2.8 eq., 3M in Et_2O) in THF was added dropwise over 30 minutes at 0 ℃ to a solution of ester (1equiv.) and $Ti(O\text{-}i\text{-}Pr)_4$ (1.4 eq.) in THF. The mixture was warmed to room temperature and stirred overnight. Then the mixture was quenched with water and the precipitated solid was removed by filtration. The filtrate was extracted with DCM, washed with water and dried over Na_2SO_4 followed by filtration

and concentration. The residue was subjected to column chromatography to afford the cyclopropanols **1h**, **1j**, **1m**, **1n**.



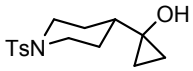
1h

1h: Colorless oil (yield 55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.94 (s, 1H), 1.66 – 1.62 (m, 1H), 1.56-1.0 (m, 2H), 1.46 – 1.32 (m, 4H), 1.20 – 1.00 (m, 3H), 0.97 (s, 3H), 0.65 – 0.62 (m, 2H), 0.55 – 0.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.7, 35.9, 33.0, 26.4, 21.9, 19.2, 10.1. GC-MS: *m/z* Calculated for $C_{10}H_{18}O$ 154.1, found 154.1.



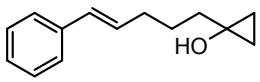
1j

1j: Yellow oil (yield 54%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.44 (t, *J* = 6.7 Hz, 2H), 1.98-1.90 (m, 2H), 1.88 (s, 1H), 1.71 – 1.66 (m, 2H), 1.65 – 1.55 (m, 2H), 0.78 – 0.74 (m, 2H), 0.48 – 0.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 37.4, 33.9, 32.7, 24.7, 13.7.GC-MS: *m/z* Calculated for $C_7H_{13}BrO$ 192.0, found 192.0.



1m

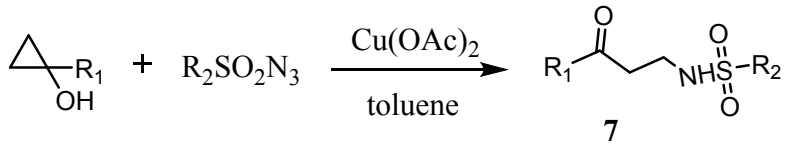
1m: White solid, mp: 127 ℃ (yield 74%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.84 (dd, *J* = 9.6, 2.0 Hz, 2H), 2.40 (s, 3H), 2.18 (s, 1H), 2.14 (dd, *J* = 11.6, 2.4 Hz, 2H), 1.77 – 1.58 (m, 4H), 0.90 – 0.82 (m, 1H), 0.70 – 0.67 (m, 2H), 0.37 – 0.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 133.1, 129.6, 127.7, 58.0, 46.5, 42.5, 27.4, 21.5, 12.6. HRMS (ESI) *m/z* Calculated for $C_{15}H_{22}NO_3S^+$ $[M + H]^+$ 296.1315, found 296.1313.



1n

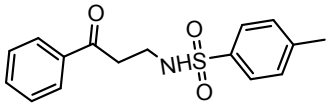
1n: yellow oil (yield 45%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 4H), 7.20 (t, *J* = 8.2 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.24 (dt, *J* = 15.6, 6.8Hz, 1H), 2.32 – 2.26 (m, 2H), 1.97 (br, 1H), 1.76 – 1.68 (m, 2H), 1.66 – 1.55 (m, 2H), 0.77 – 0.71 (m, 2H), 0.48-0.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 130.7, 130.1, 128.5, 126.9, 126.0, 55.7, 37.8, 32.9, 25.7, 13.6. HRMS (ESI) *m/z* Calculated for $C_{14}H_{18}NaO^+$ $[M + Na]^+$ 225.1250, found 225.1249.

IV Synthesis and Characterization of the β -Tosylamidl ketone.



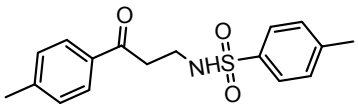
General Procedure for the synthesis of the β-Tosylamidl ketone:

To a solution of cyclopropanol (0.5 mmol, 1 eq.) in 2mL toluene in a flame dried Schlenk tube was added dropwise sulfonyl azide (0.75 mmol, 1.5 eq.) and Cupric acetate (0.1 mmol, 0.2 eq.). Then the solution was evacuated and refilled with N_2 three times and stirred for 8 h at 120 ℃. After cooling to room temperature, solvent was removed in vacuum; the residue was purified by column chromatography to give the product of **7**.



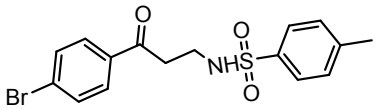
7aa

7aa: Brown solid, mp: 86 ℃ (yield 69 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 8 Hz, 2H), 5.38 (br, 1H), 3.34 – 3.29 (m, 2H), 3.19 (t, *J* = 5.8 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 143.5, 137.1, 136.1, 133.7, 129.8, 128.7, 128.0, 127.1, 38.4, 38.2, 21.6. HRMS (ESI) *m/z* Calculated for $C_{16}H_{18}NO_3S^+$ $[M + H]^+$ 304.1002, found 304.1001.



7ba

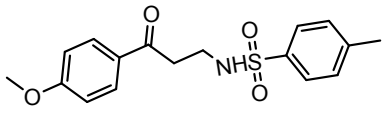
7ba: Brown solid, mp: 96 ℃ (yield 71%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.1 Hz, 2H), 7.65 (d, *J* = 2.1 Hz, 2H) 7.20 – 7.12 (m, 4H), 5.38 (t, *J* = 3.3 Hz, 1H), 3.26 – 3.18 (m, 2H), 3.08 (t, *J* = 5.7 Hz, 2H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 144.6, 143.4, 137.1, 133.7, 129.8, 129.4, 128.1, 127.1, 38.5, 38.1, 21.7, 21.5. HRMS (ESI) *m/z* Calculated for $C_{17}H_{20}NO_3S^+$ $[M + H]^+$ 318.1158, found 318.1158.



7ca

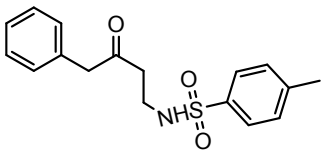
7ca: Brown solid, mp: 123 ℃ (yield 52%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 2.0 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.32

(t, *J* = 6.6 Hz, 1H), 3.33 – 3.28 (m, 2H), 3.15 (t, *J* = 5.6 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 143.5, 137.1, 134.9, 132.0, 129.8, 129.5, 128.9, 127.0, 38.3, 38.2, 21.5. HRMS (ESI) *m/z* Calculated for $C_{16}H_{17}BrNO_3S^+$ $[M + H]^+$ 382.0107, found 382.0103.



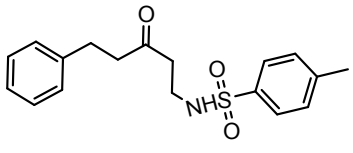
7da

7da: Brown solid, mp: 122 ℃ (yield 76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H),7.29 – 7.25 (m, 2H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 5.30 (t, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 3.33 – 3.28 (m, 2H), 3.16 (t, *J* = 5.6 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 163.9, 143.4, 137.1, 130.3, 129.8, 129.3, 127.0, 113.9, 55.5, 38.5, 37.7, 21.5. HRMS (ESI) *m/z* Calculated for $C_{17}H_{20}NO_4S^+$ $[M + H]^+$ 334.1108, found 334.1104.



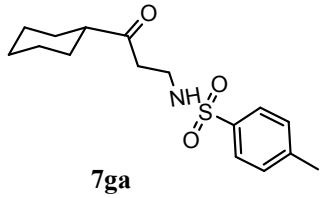
7ea

7ea: Light yellow solid, mp: 82 ℃ (yield 64%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.1 Hz, 1H), 7.68 (d, *J* = 1.8 Hz, 1H),7.34 – 7.22 (m, 5H), 7.13 (d, *J* = 1.8 Hz, 1H), 7.11 (d, *J* = 1.5 Hz, 1H), 5.25 (t, *J* = 6.6 Hz, 1H), 3.62 (s, 2H), 3.12 – 3.05(m, 2H), 2.65 (t, *J* = 5.8 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 143.5, 136.9, 133.5, 129.8, 129.4, 128.9, 127.3, 127.0, 50.1, 41.4, 38.1, 21.6. HRMS (ESI) *m/z* Calculated for $C_{17}H_{20}NO_3S^+$ $[M + H]^+$ 318.1158, found 318.1157.



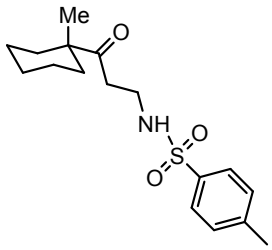
7fa

7fa: Light yellow solid, mp: 88 ℃ (yield 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.25(m, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 5.19 (t, *J* = 6.4 Hz, 1H), 3.15 – 3.10 (m, 2H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.61 (t, *J* = 5.8 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 143.5, 140.6, 137.0, 129.8, 128.6, 128.3, 127.1, 126.3, 44.3, 42.2, 38.0, 29.5, 21.6. HRMS (ESI) *m/z* Calculated for $C_{18}H_{22}NO_3S^+$ $[M + H]^+$ 332.1315, found 332.1312.



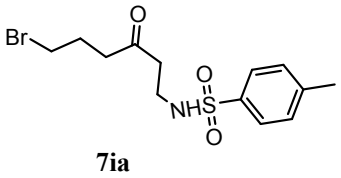
7ga

7ga: White solid, mp: 87 ℃ (yield 98%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.1 Hz, 1H), 7.72 (d, *J* = 2.1 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 5.21 (br, 1H), 3.16 – 3.09 (m, 2H), 2.70 – 2.65 (m, 2H), 2.42 (s, 3H), 2.29 – 2.20 (m, 1H), 1.77 – 1.62 (m, 5H), 1.32 – 1.12 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.5, 143.4, 137.1, 129.8, 127.0, 50.7, 39.8, 38.2, 28.3, 25.7, 25.5, 21.5. HRMS (ESI) *m/z* Calculated for $C_{16}H_{24}NO_3S^+$ $[M + H]^+$ 310.1471, found 310.1470.



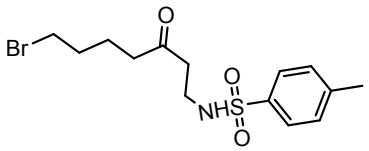
7ha

7ha: Colorless viscous oil (yield 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.6 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.22 (t, *J* = 6.6 Hz, 1H), 3.17 – 3.12 (m, 2H), 2.70 (t, *J* = 5.6 Hz, 2H), 2.42 (s, 3H), 1.87 – 1.80 (m, 2H), 1.56 – 1.46 (m, 2H), 1.45 – 1.19 (m, 6H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.7, 143.4, 137.1, 129.8, 127.0, 48.1, 38.5, 36.3, 34.4, 25.7, 24.8, 22.8, 21.5. HRMS (ESI) *m/z* Calculated for $C_{17}H_{26}NO_3S^+$ $[M + H]^+$ 324.1628, found 324.1629.



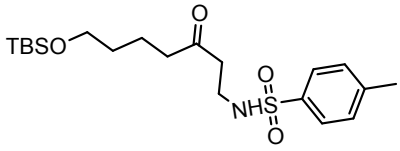
7ia

7ia: Light yellow solid, mp: 70 ℃ (yield 69%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.16 (t, *J* = 6.6 Hz, 1H), 3.39 (t, *J* = 6.4 Hz, 2H), 3.16 – 3.11 (m, 2H), 2.67 (t, *J* = 5.6 Hz, 2H), 2.55 (t, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 2.10 – 2.03 (m, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.7, 143.6, 136.9, 129.8, 127.0, 42.2, 40.8, 38.0, 33.1, 26.1, 21.6. HRMS (ESI) *m/z* Calculated for $C_{13}H_{19}BrNO_3S^+$ $[M + H]^+$ 348.0264, found 348.0263.



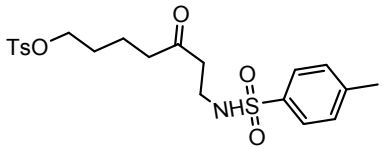
7ja

7ja: Light yellow solid, mp: 69 ℃ (yield 71%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.8 Hz, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.33 (d, *J* = 0.9 Hz, 1H), 7.30 (d, *J* = 0.9 Hz, 1H), 5.17 (t, *J* = 5.5 Hz, 1H),, 3.38 (t, *J* = 6.5 Hz, 2H), 3.17 – 3.11 (m, 2H), 2.66 (t, *J* = 5.8 Hz, 2H), 2.43 (s, 3H), 2.40 (t, *J* = 7.2 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.73 – 1.65 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.4, 143.5, 137.0, 129.8, 127.0, 42.0, 41.7, 38.0, 33.2, 31.9, 22.0, 21.6. HRMS (ESI) *m/z* Calculated for $C_{14}H_{21}BrNO_3S^+$ $[M + H]^+$ 362.0420, found 362.0416.



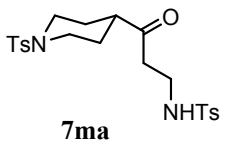
7ka

7ka: Yellow viscous oil (yield 81%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.8 Hz, 1H), 7.89 (d, *J* = 1.8 Hz, 1H), 7.48 (d, *J* = 0.9 Hz, 1H), 7.45 (d, *J* = 0.6 Hz, 1H), 5.31 (t, *J* = 6.8 Hz, 1H), 3.75 (t, *J* = 6.1 Hz, 2H), 3.32 –3.26 (m, 2H), 2.81 (t, *J* = 5.7 Hz, 2H), 2.59 (s, 3H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.78 – 1.67 (m, 2H), 1.66 – 1.57 (m, 2H), 1.05 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.2, 143.4, 137.0, 129.8, 127.0, 62.7, 42.6, 41.8, 38.1, 32.1, 26.0, 21.5, 20.1, 18.3. HRMS (ESI) *m/z* Calculated for $C_{20}H_{36}NO_4SSi^+$ $[M + H]^+$ 414.2129, found 414.2129.



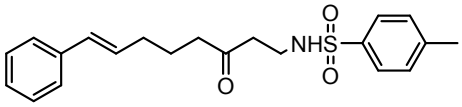
7la

7la: Light yellow solid, mp: 67 ℃ (yield 57%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 1.6 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.08 (br, 1H), 3.98 (t, *J* = 5.8 Hz, 2H), 3.10 (t, *J* = 5.8 Hz, 2H), 2.60 (t, *J* = 5.8 Hz, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 2.32 (t, *J* = 6.8 Hz, 2H), 1.64 – 1.50 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 144.9, 143.5, 136.9, 132.9, 129.9, 129.8, 127.9, 127.0, 70.0, 42.0, 41.7, 38.0, 28.1, 21.7, 21.5, 19.4. HRMS (ESI) *m/z* Calculated for $C_{21}H_{28}NO_6S_2^+$ $[M + H]^+$ 454.1353, found 454.1351.



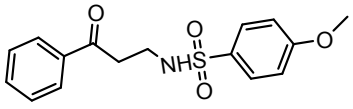
7ma

7ma: White solid, mp: 170 ℃ (yield 64%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.0 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.97 (t, *J* = 6.6 Hz, 1H), 3.75 – 3.70 (m, 2H), 3.14 – 3.09 (m, 2H), 2.66 (t, *J* = 5.8 Hz, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 2.34 (td, *J* = 11.6, 2.8 Hz, 2H), 2.18 (tt, *J* = 11.2, 4.0 Hz, 1H), 1.87 – 1.81 (m, 2H), 1.70 – 1.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 143.8, 143.6, 136.9, 133.0, 129.82, 129.75, 127.7, 127.0, 47.5, 45.5, 40.1, 37.9, 26.8, 21.6,21.5. HRMS (ESI) *m/z* Calculated for $C_{22}H_{29}N_2O_5S_2^+$ $[M + H]^+$ 465.1512, found 465.1512.



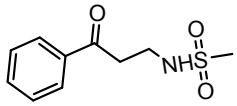
7na

7na: Light yellow viscous oil (yield:57%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.36 – 7.28 (m, 6H), 7.24 – 7.19 (m, 1H), 6.40 – 6.35 (m, 1H), 6.18 – 6.10 (m, 1H), 5.22 (t, *J* = 6.8 Hz, 1H), 3.16 – 3.08 (m, 2H), 2.65 (t, *J* = 5.8 Hz, 2H), 2.43 (s, 3H), 2.40 (t, *J* = 6.8 Hz, 2H), 2.24 – 2.17 (m, 2H), 1.78 – 1.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 143.5, 137.5, 137.0, 130.9, 129.8, 129.6, 128.6, 127.11, 127.05, 126.0, 42.1, 38.1, 32.3, 23.0, 21.5. HRMS (ESI) *m/z* Calculated for $C_{21}H_{25}NNaO_3S^+$ $[M + Na]^+$ 394.1447, found394.1452.



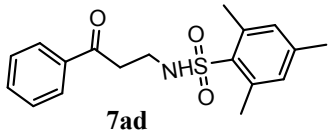
7ab

7ab: Yellow solid, mp: 77℃ (yield 56%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 1.2 Hz, 1H), 7.85 (d, *J* = 1.5 Hz, 1H), 7.82 (d, *J* = 0.3 Hz, 1H), 7.79 (d, *J* = 2.1 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.47 – 7.41 (m, 2H), 6.96 (d, *J* = 2.1 Hz, 1H), 6.93 (d, *J* = 2.1 Hz, 1H), 5.32 (t, *J* = 6.6 Hz, 1H), 3.83 (s, 3H), 3.36 – 3.30 (m, 2H), 3.23 – 3.18 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9, 162.9, 136.2, 133.7, 131.7, 129.1, 128.7, 128.0, 114.3, 55.6, 38.3, 38.2. HRMS (ESI) *m/z* Calculated for $C_{16}H_{18}NO_4S^+$ $[M + H]^+$ 320.0951, found 320.0948.



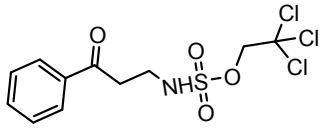
7ac

7ac: Yellow solid, mp: 106℃ (yield 61%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.17 (t, *J* = 6.8 Hz, 1H), 3.55 – 3.50(m, 2H), 3.31 (t, *J* = 5.4 Hz, 2H), 2.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 136.2, 133.8, 128.8, 128.1, 40.2, 38.9, 38.3. HRMS (ESI) *m/z* Calculated for $C_{10}H_{14}NO_3S^+$ [M + H]$^{+61}$28.0689, found 228.0687.



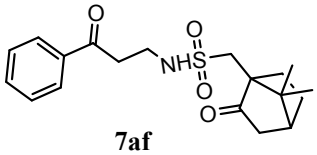
7ad

7ad: Brown viscous oil (yield 31%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 1.2 Hz, 1H), 7.84 (d, *J* = 1.5 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.48 – 7.42 (m, 2H), 6.92 (d, *J* =0.9 Hz, 2H), 5.44 (t, *J* = 6.6 Hz, 1H), 3.32 – 3.26 (m, 2H), 3.20 –3.15 (m, 2H), 2.67 (s, 6H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 142.1, 138.9, 136.1, 134.0, 133.7, 132.0, 128.7, 128.0, 37.9, 37.8, 22.8, 20.9. HRMS (ESI) *m/z* Calculated for $C_{18}H_{21}NNaO_3S^+$ [M + Na]$^+$ 354.1134, found 354.1136.



7ae

7ae: Brown viscous oil (yield 18%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.2 Hz, 1H), 7.94 (d, *J* = 1.5 Hz, 1H),7.65 – 7.60 (m, 1H), 7.52 – 7.47 (m, 2H), 5.70 (t, *J* = 6.3 Hz, 1H), 4.63 (s, 2H), 3.69 – 3.63 (m, 2H)不是 t, 3.38 (t, *J* = 5.4 Hz,2H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 136.0, 134.0, 128.9, 128.1, 93.5, 78.2, 39.3, 37.6. HRMS (ESI) *m/z* Calculated for $C_{11}H_{12}C_{l3}NNaO_4S^+$ [M + Na]$^+$ 381.9445, found 381.9447.



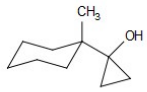
7af

7af: Brown viscous oil (yield 44%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 7.60 – 7.54 (m, 1H), 7.48 – 7.26 (m, 2H), 5.66 (t, *J* = 5.5 Hz, 1H), 3.60 – 3.51 (m, 2H), 3.47 (d, *J* = 15.0 Hz, 1H), 3.35 – 3.30(m, 2H), 2.94 (d, *J* = 15.0 Hz, 1H), 2.43 – 2.22 (m, 2H), 2.12 – 1.83 (m, 4H), 1.47 – 1.38 (m, 1H), 1.03 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.4, 198.7, 136.3, 133.6, 128.7, 128.1, 59.0, 49.4, 48.6, 42.9, 42.8, 39.1, 38.6, 27.0, 26.1, 19.9, 19.6. HRMS (ESI) *m/z* Calculated for $C_{19}H_{25}NNaO_4S^+$ [M + Na]$^+$ 386.1397, found 386.1399.

V References.

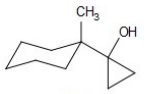
1: .Jingliang Jiao, Larry X. Nguyen, Dennis R. Patterson, and Robert A. Flowers, II.*Org. Lett*. **2007**, 9(7), 1323-1326.
2: Wang, Y.-F.; Chiba, S. J. Am. Chem. Soc. 2009, 131(35), 12570-12572.
3: Yong Li,Zhishi Ye,Tabitha M. Bellman, Teng Chi, Mingji Dai.Org. Lett., 2015, 17 (9), 2186 – 2189.
4: Yu Kuo-Long, Civiello. Rital. WO2001095910, 2001,14775.

VI NMR Spectra of Compounds



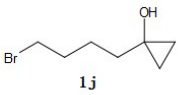
1h

^{1}H NMR (400 MHz,$CDCl_3$)



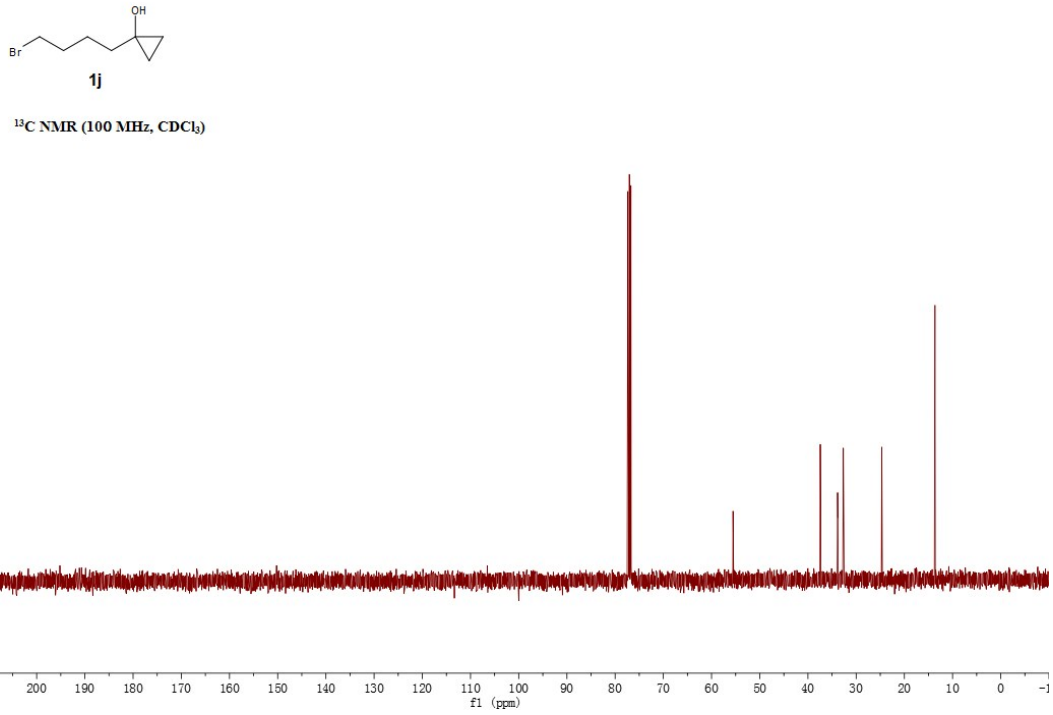
1h

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



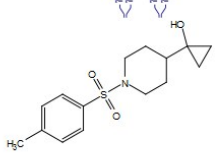
1j

^{1}H NMR (300 MHz, $CDCl_3$)



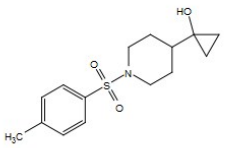
1j

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



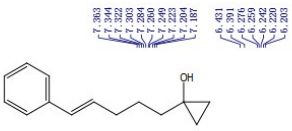
1m

^{1}H NMR (400 MHz, $CDCl_3$)



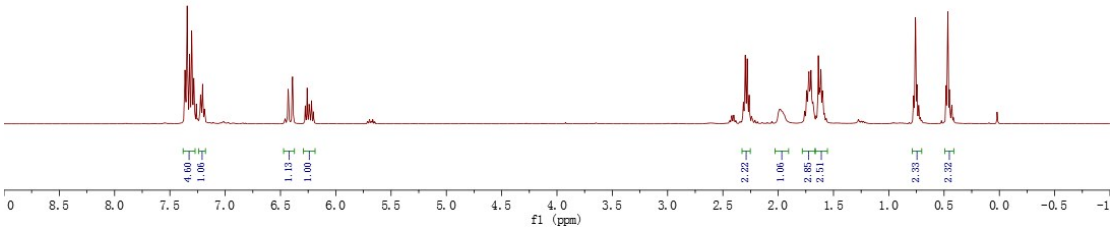
1m

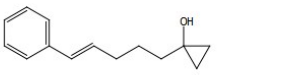
^{13}C NMR (100 MHz, $CDCl_3$)



1n

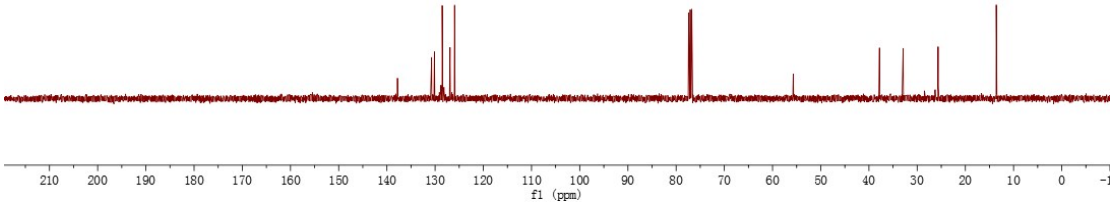
^{1}H NMR (400 MHz, $CDCl_3$)

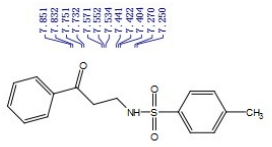




1n

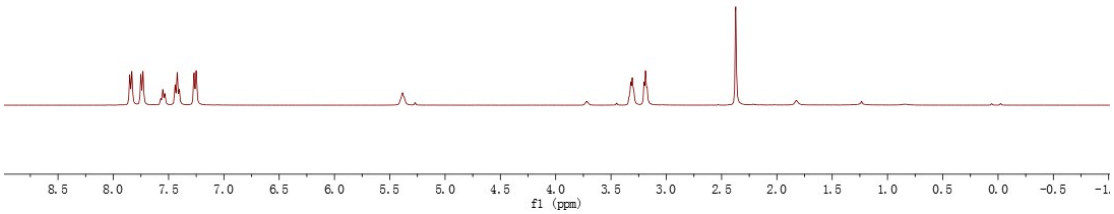
^{13}C NMR (100 MHz, $CDCl_3$)

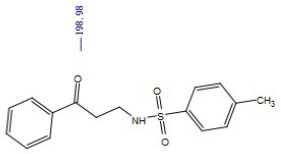




7aa

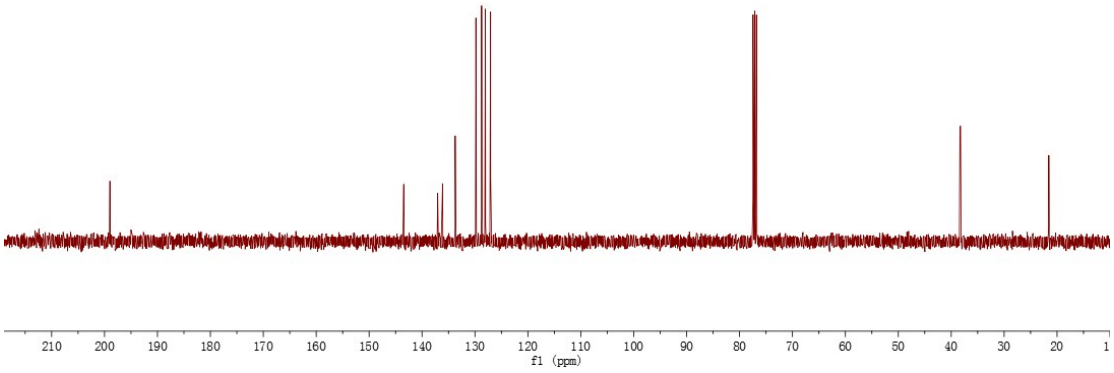
^{1}H NMR (400 MHz, $CDCl_3$)

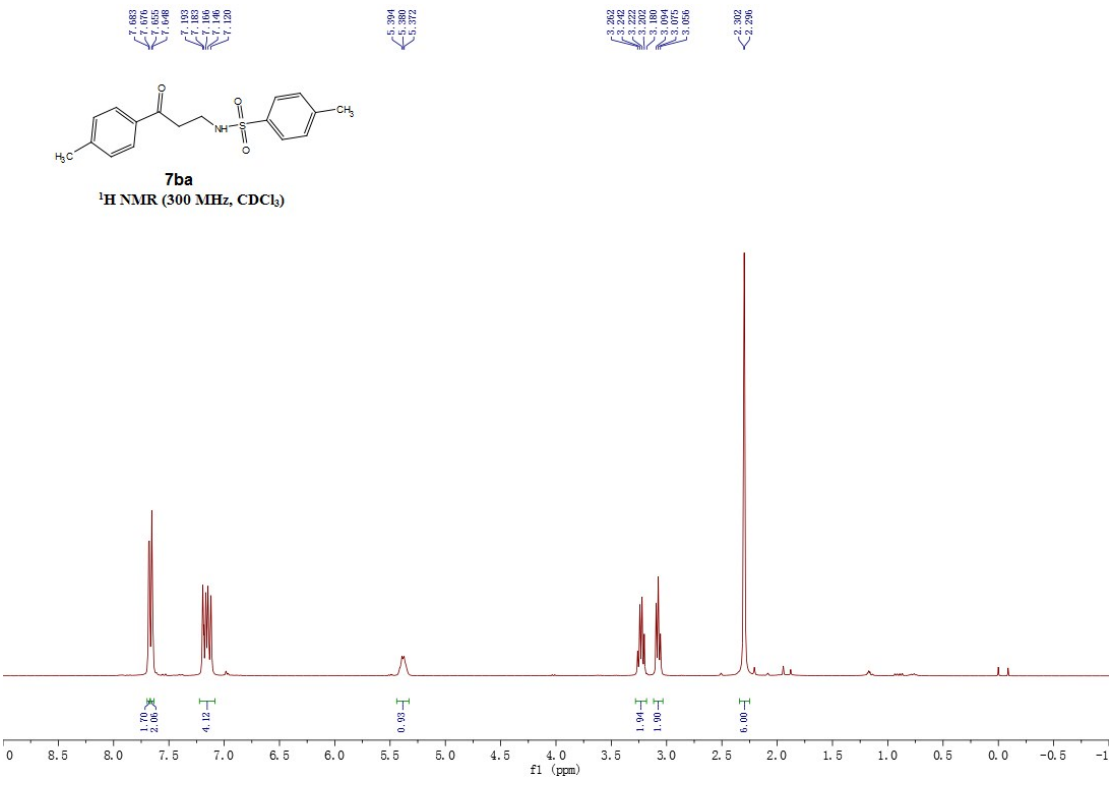




7aa

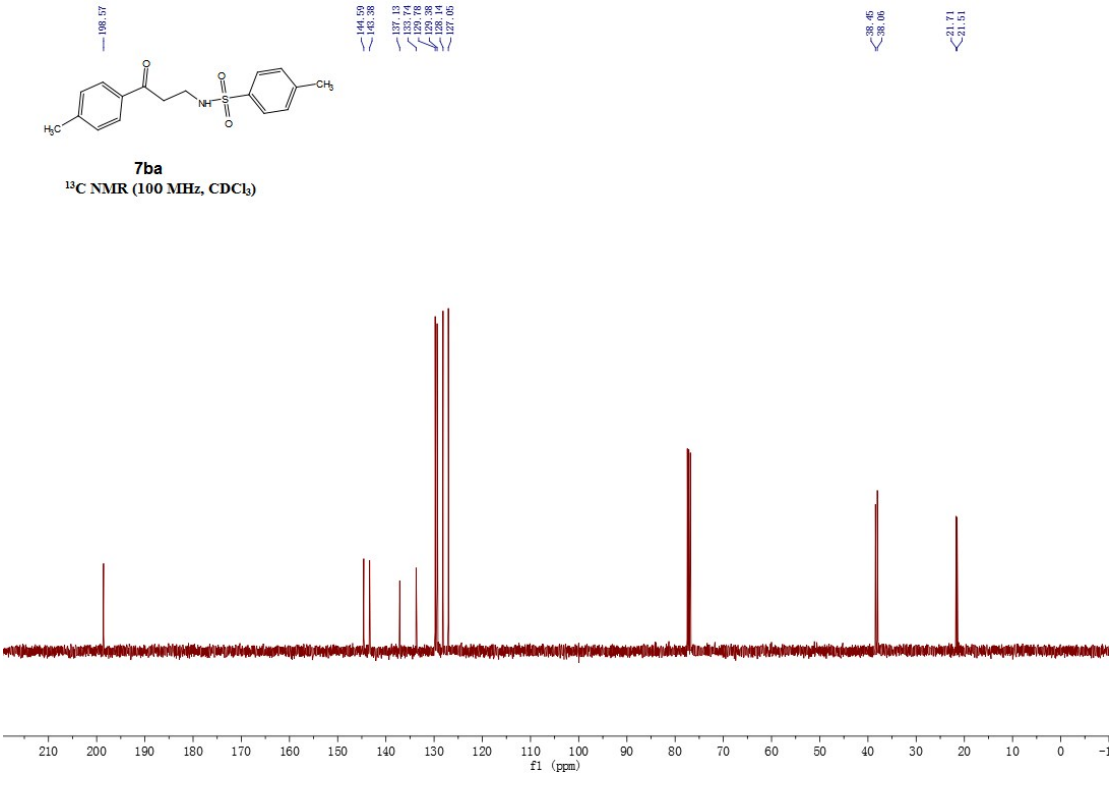
^{13}C NMR (100 MHz, $CDCl_3$)





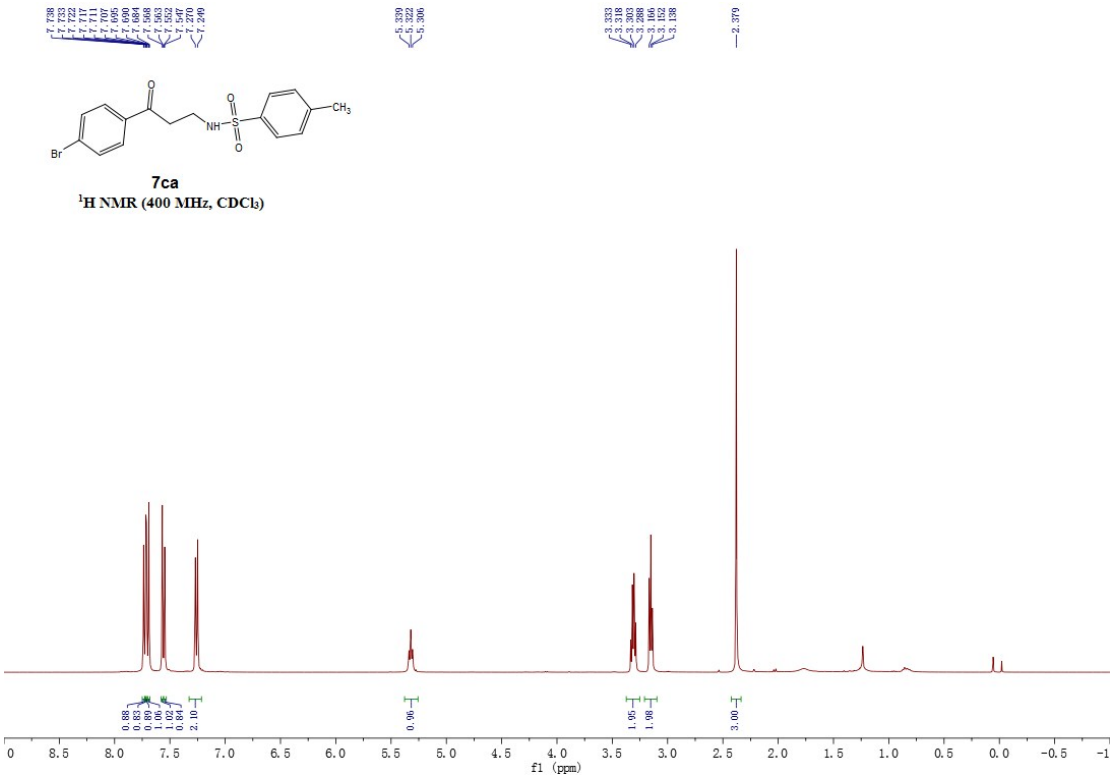
7ba

^{1}H NMR (300 MHz, $CDCl_3$)



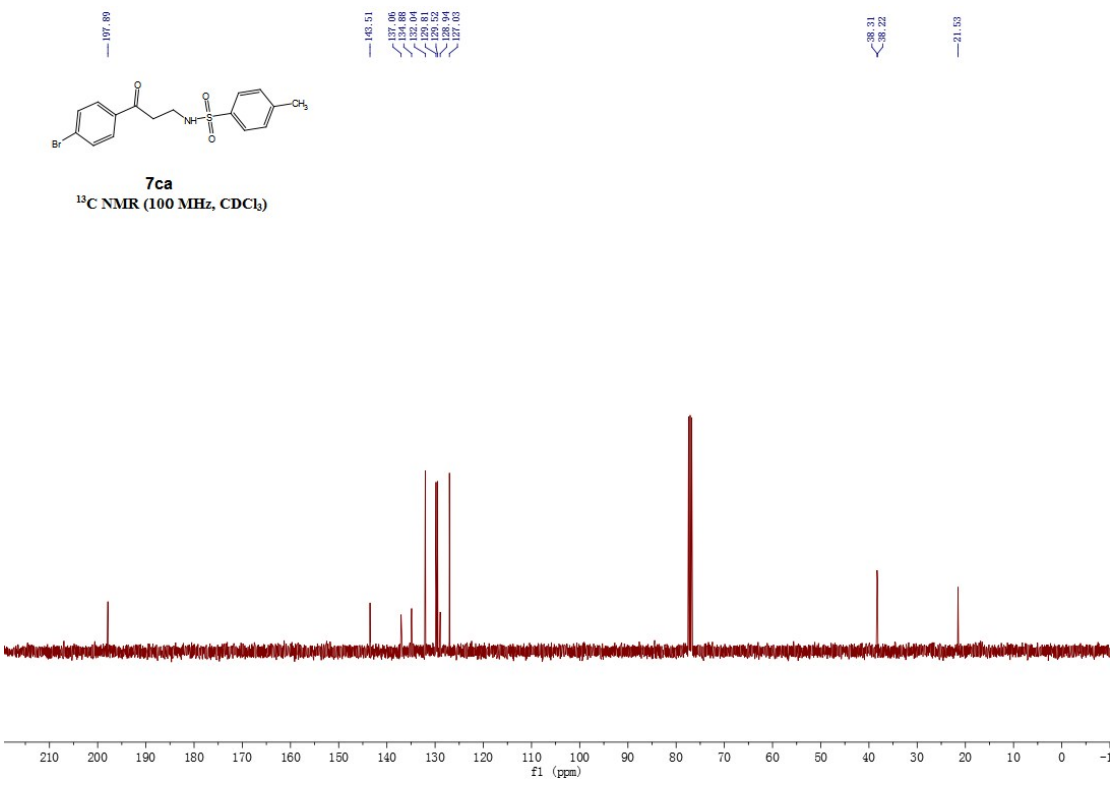
7ba

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



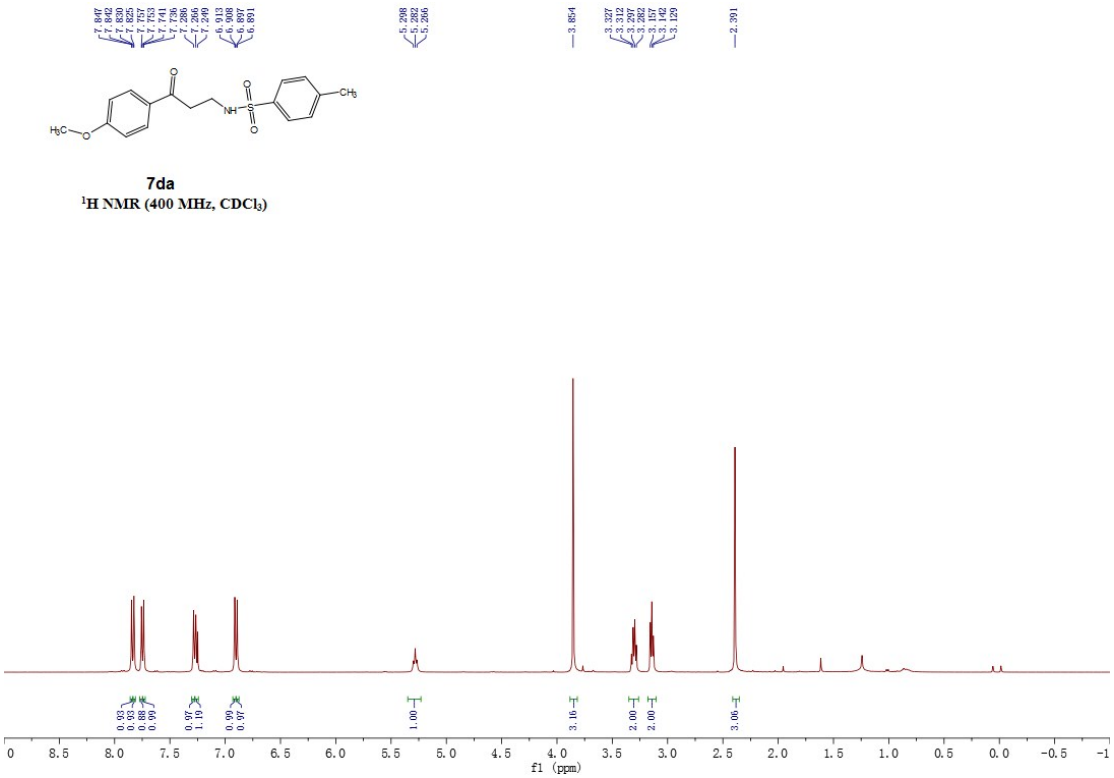
7ca

^{1}H NMR (400 MHz, $CDCl_3$)

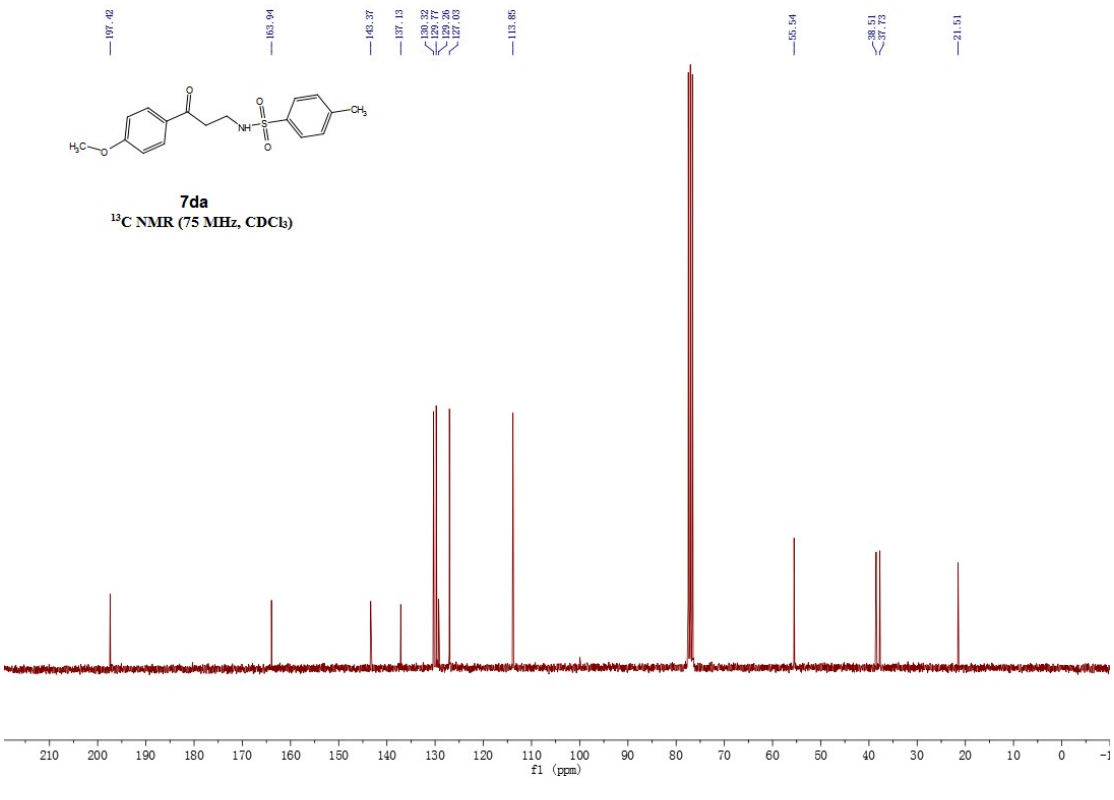


7ca

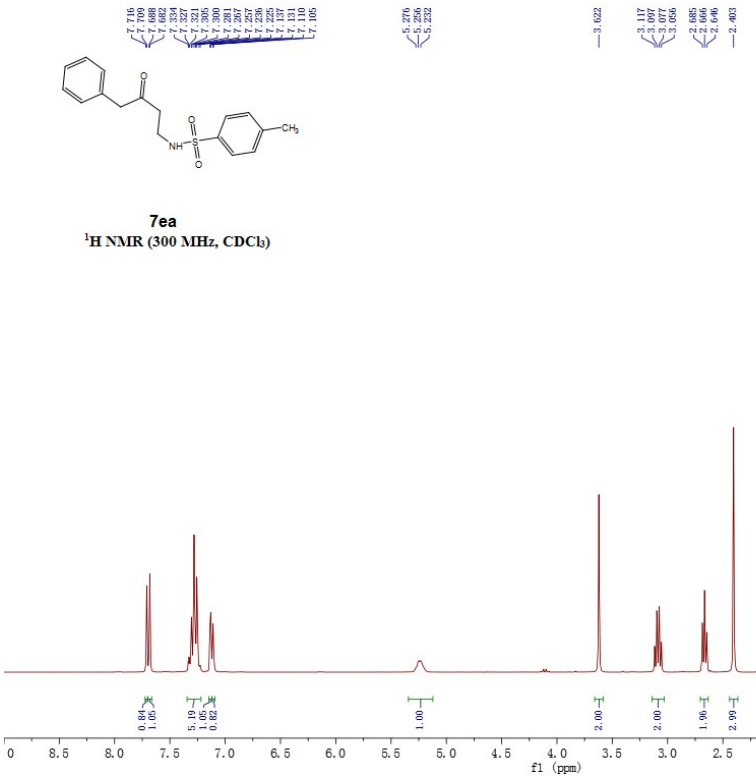
^{13}C NMR (100 MHz, $CDCl_3$)



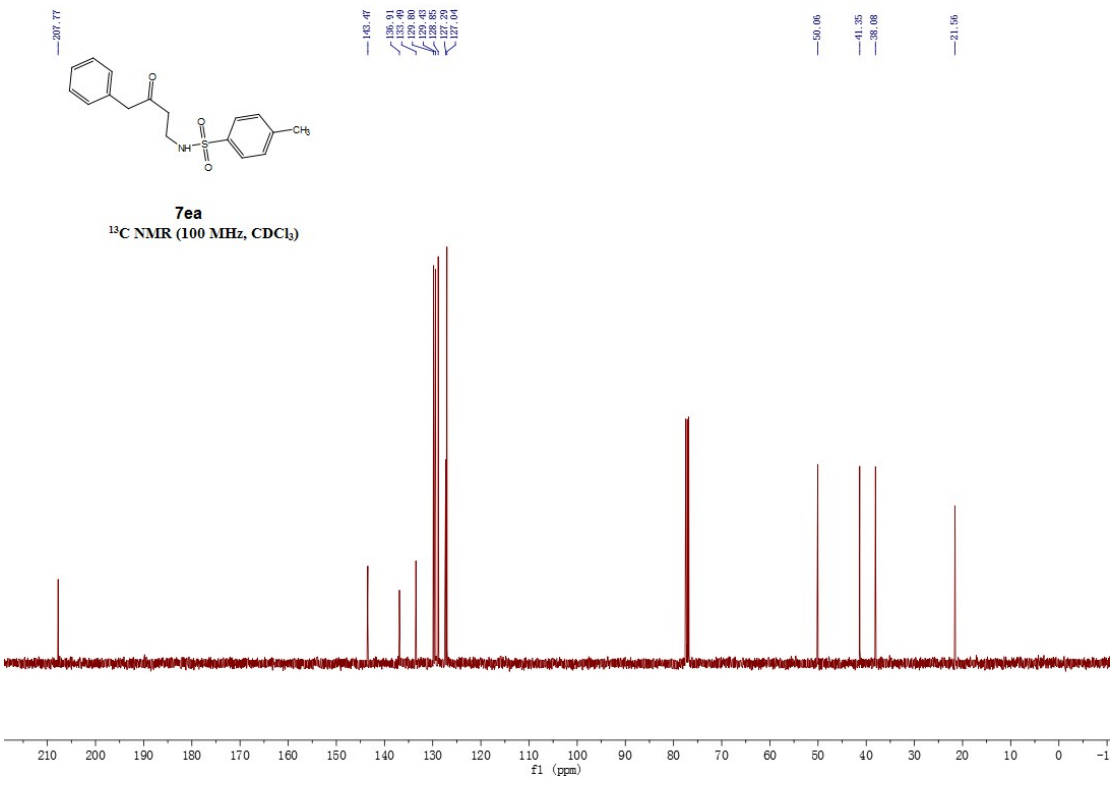
7da
^{1}H NMR (400 MHz, $CDCl_3$)



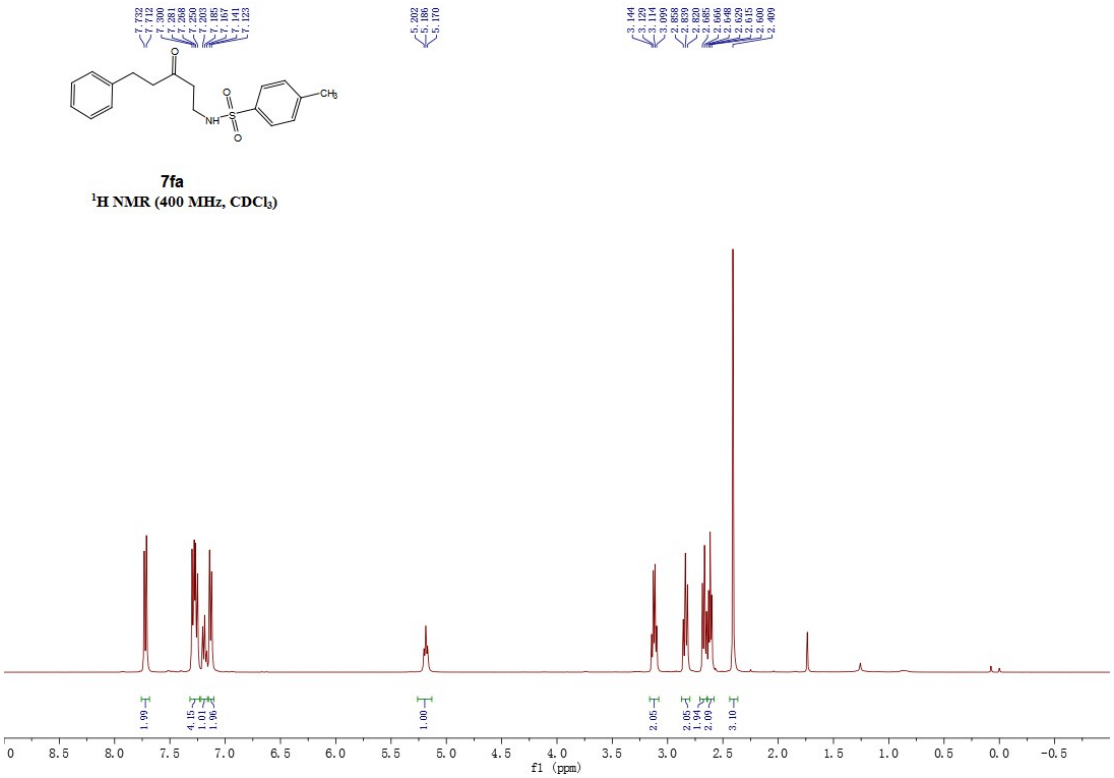
7da
^{13}C NMR (75 MHz, $CDCl_3$)



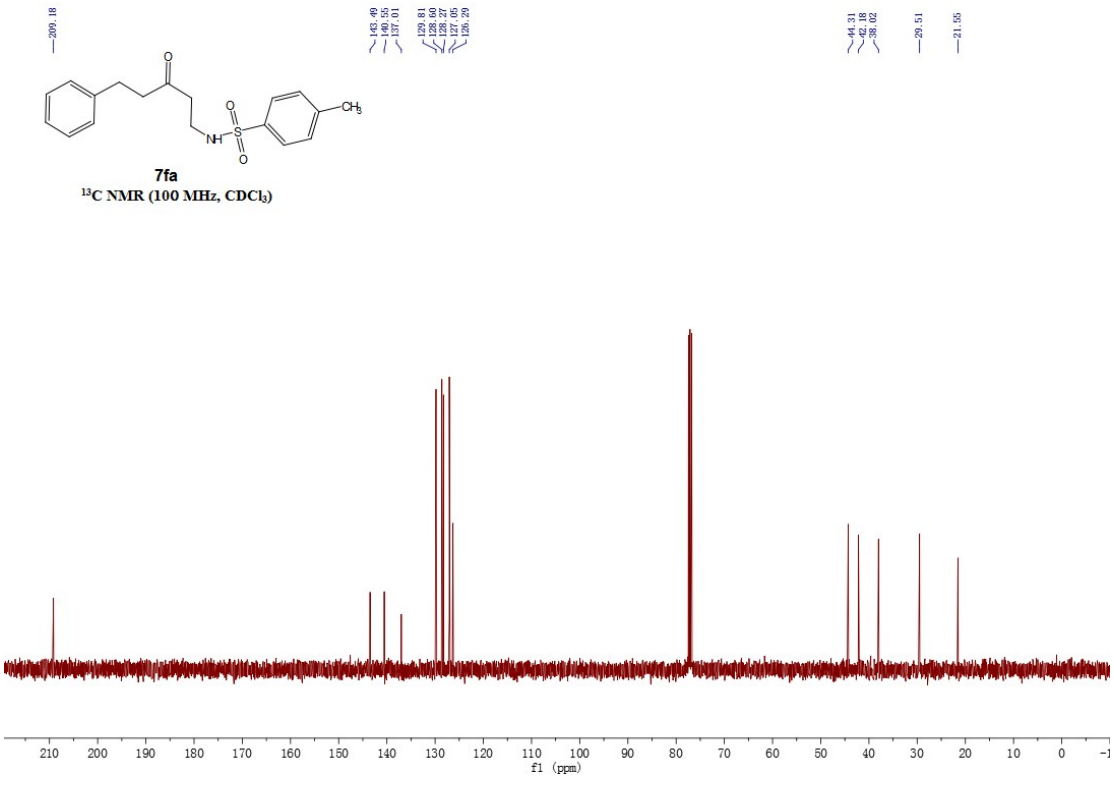
7ea
^{1}H NMR (300 MHz, $CDCl_3$)



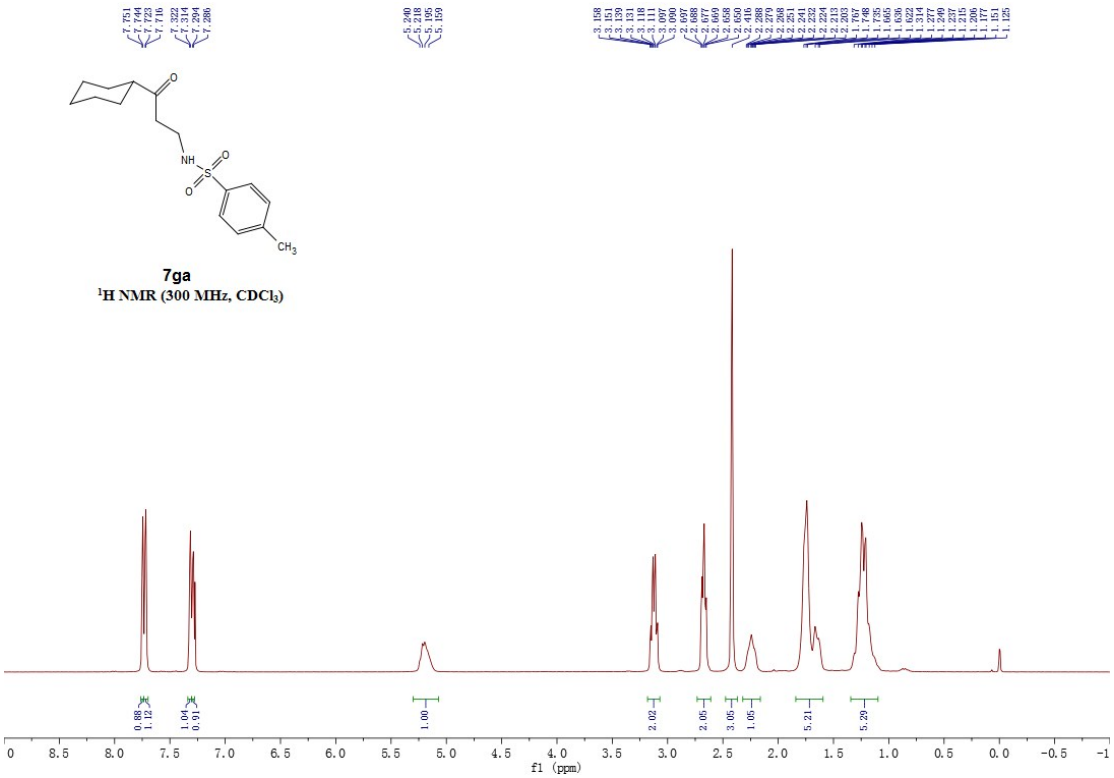
7ea
^{13}C NMR (100 MHz, $CDCl_3$)



7fa
^{1}H NMR (400 MHz, $CDCl_3$)

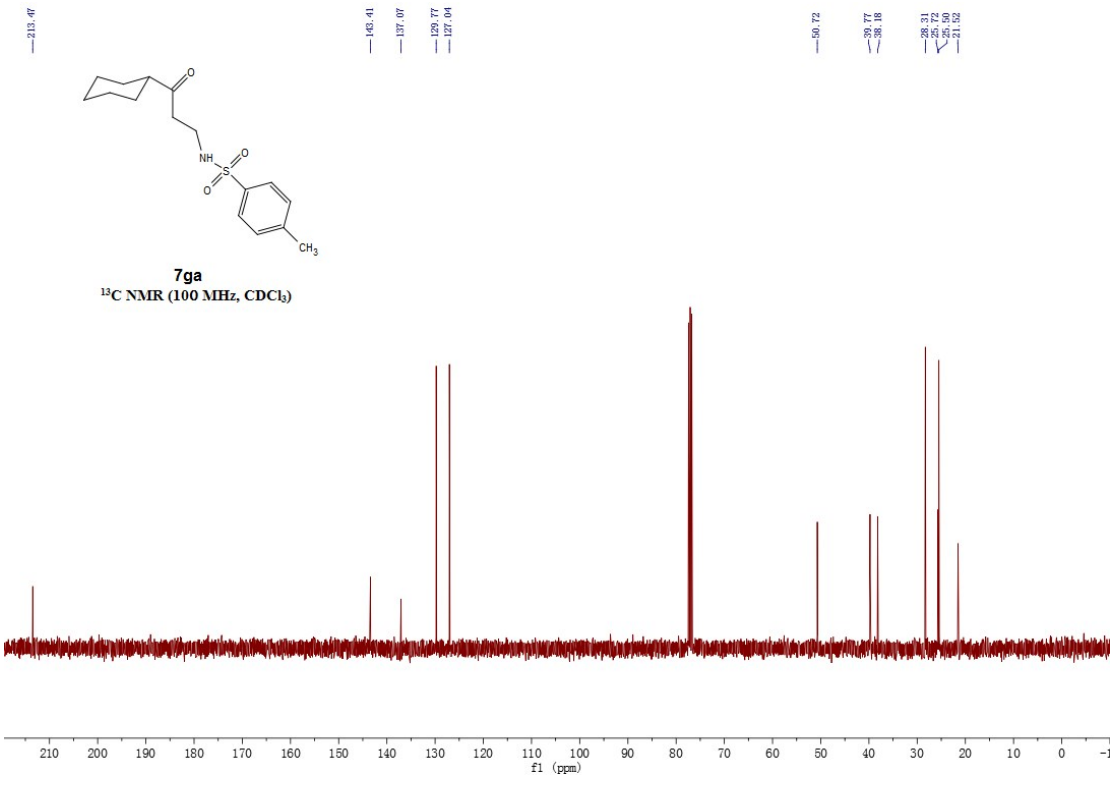


7fa
^{13}C NMR (100 MHz, $CDCl_3$)



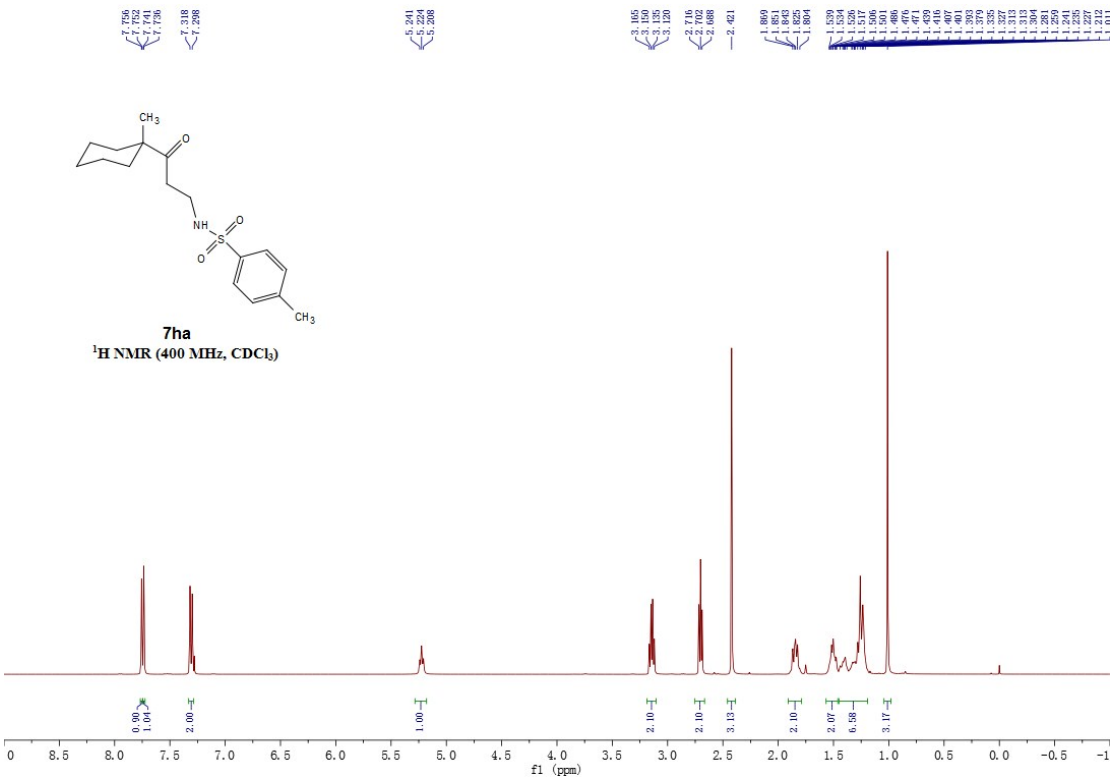
7ga

^{1}H NMR (300 MHz, $CDCl_3$)



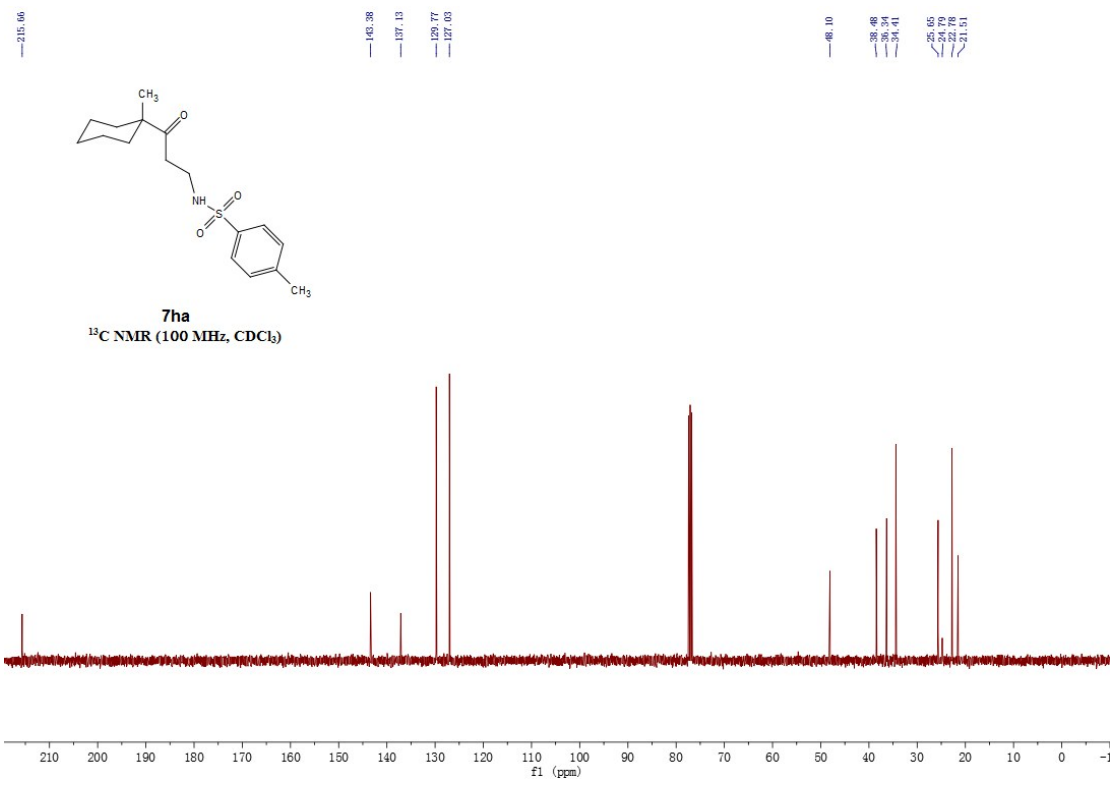
7ga

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



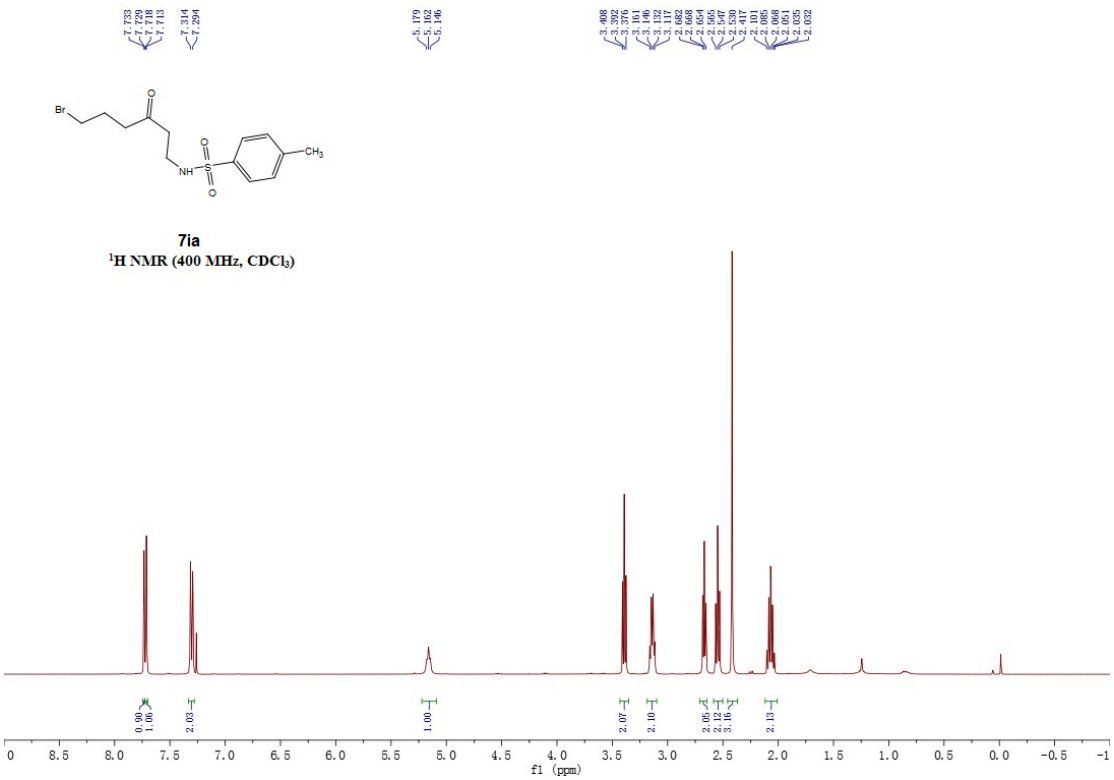
7ha

^{1}H NMR (400 MHz, $CDCl_3$)



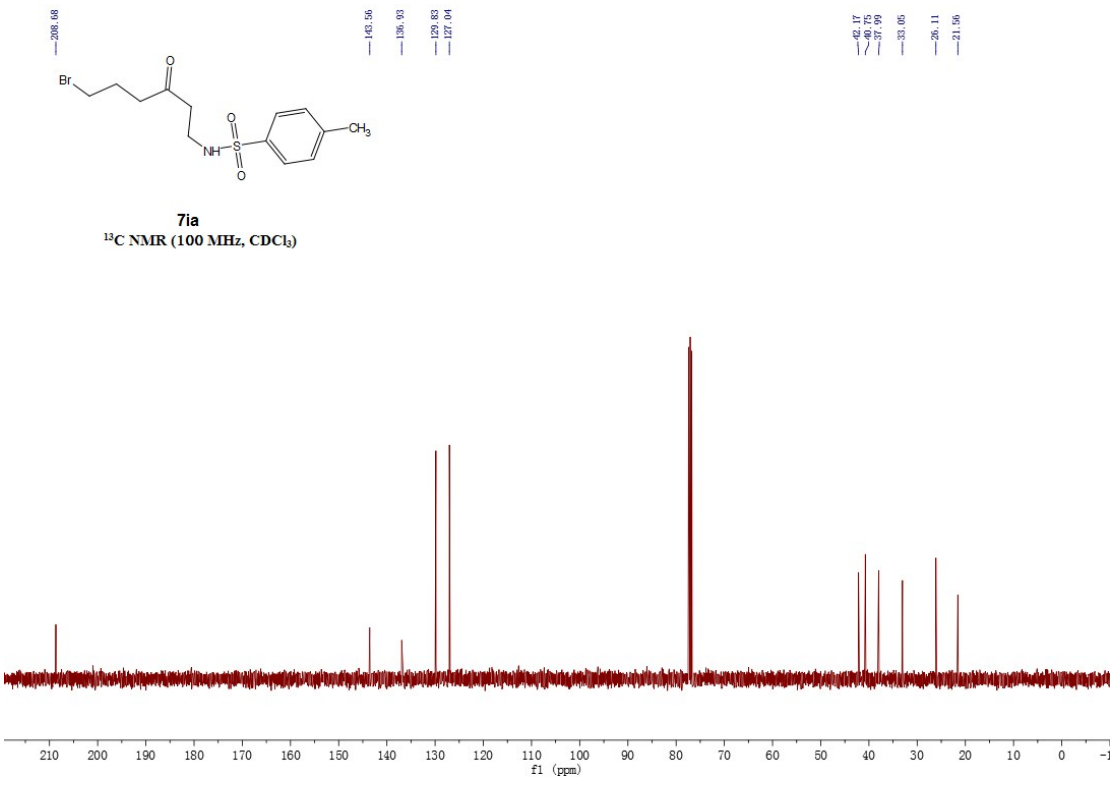
7ha

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



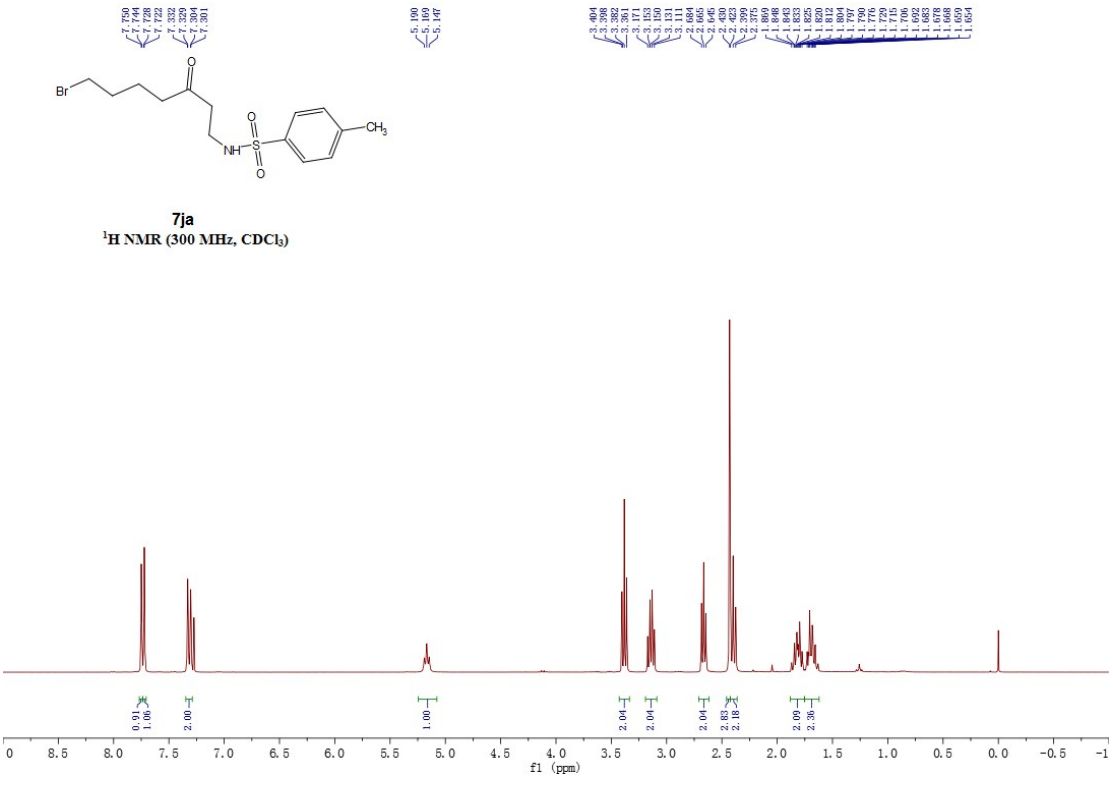
7ia

^{1}H NMR (400 MHz, $CDCl_3$)

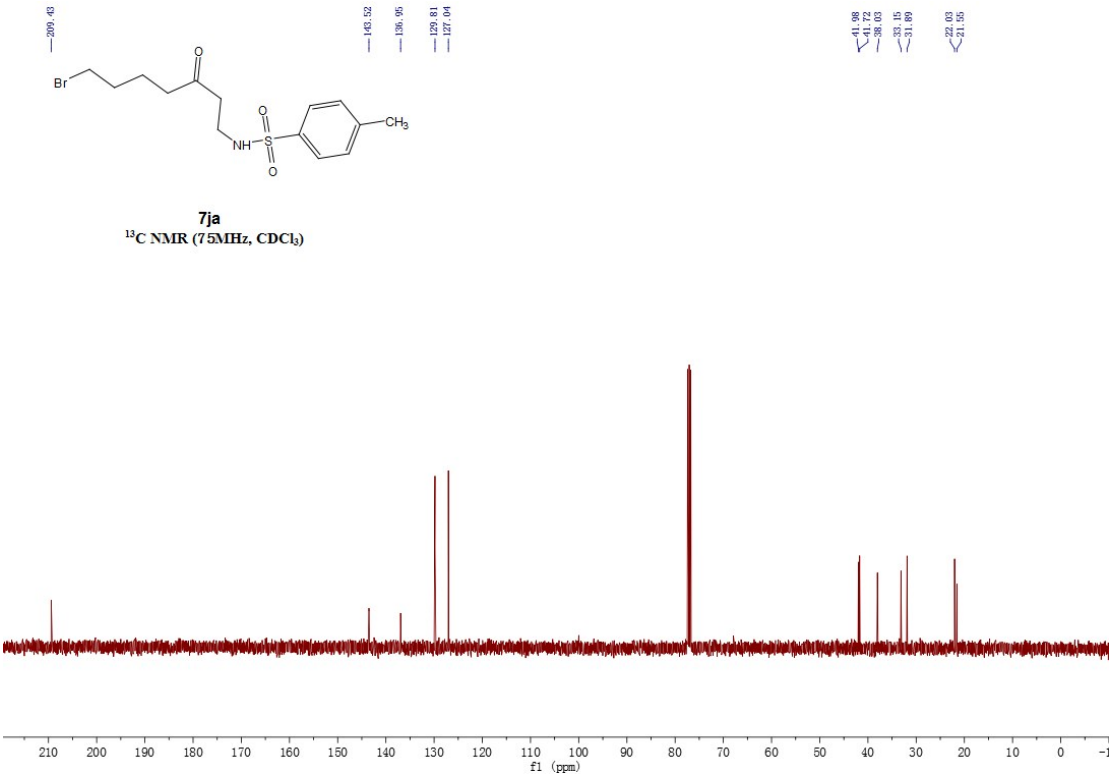


7ia

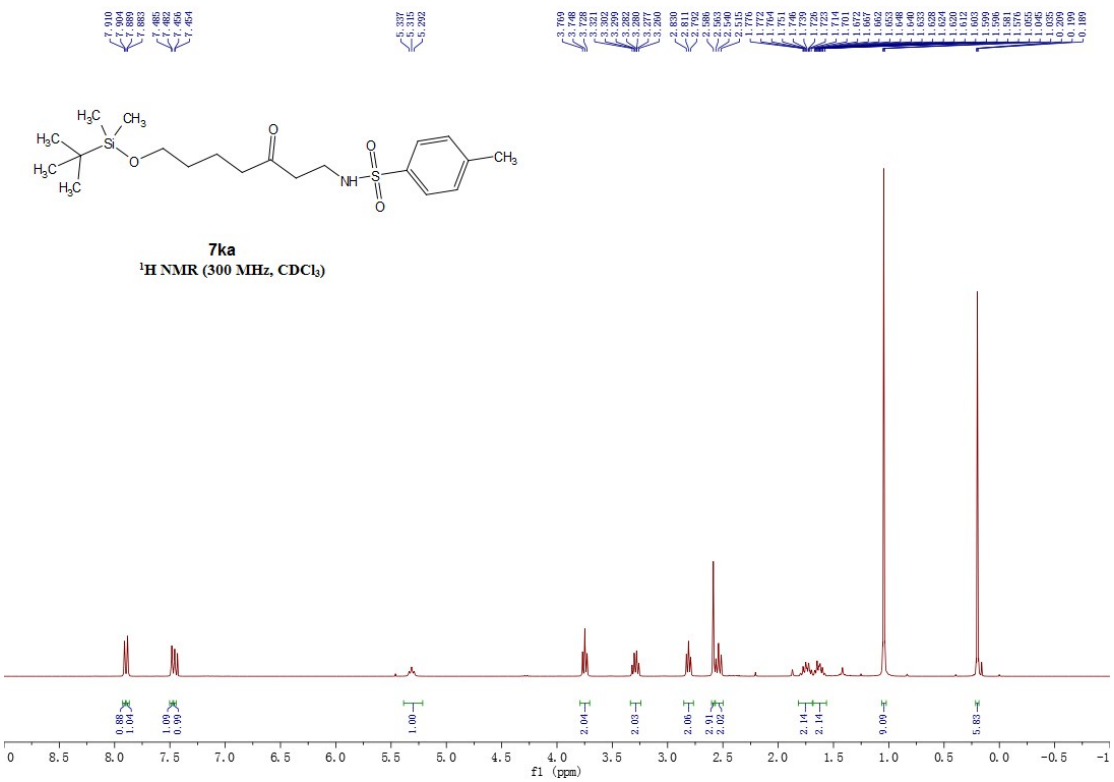
^{13}C NMR (100 MHz, $CDCl_3$)



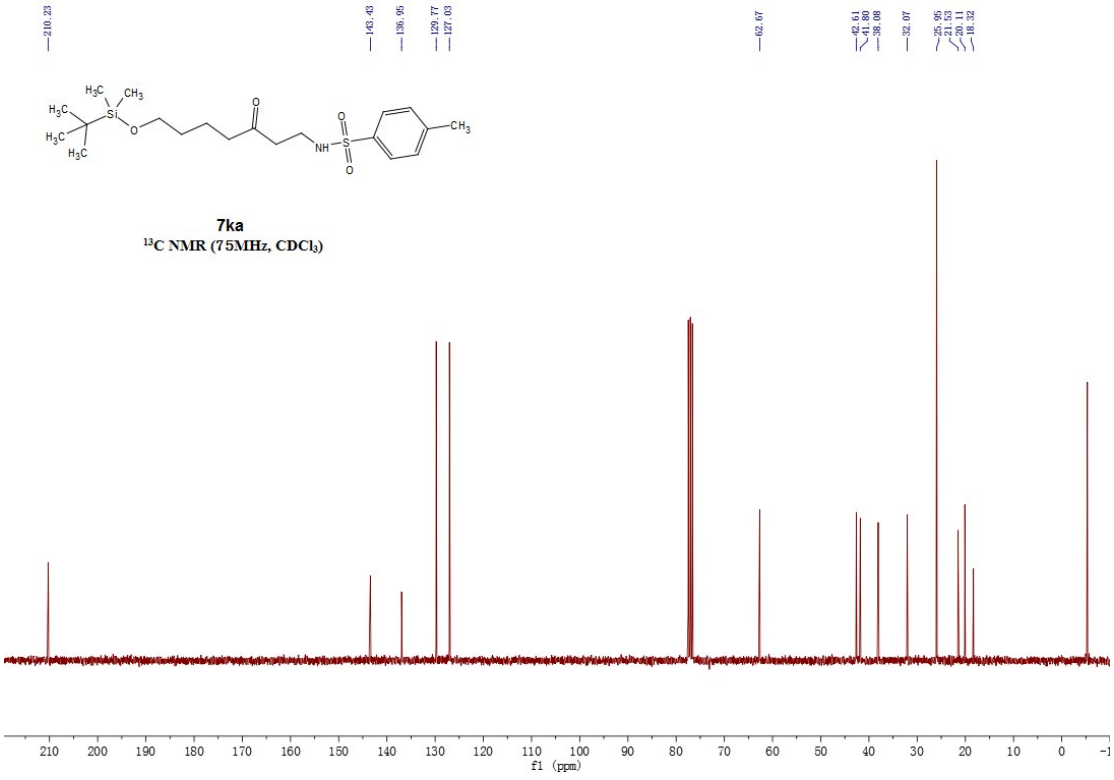
7ja
^{1}H NMR (300 MHz, $CDCl_3$)



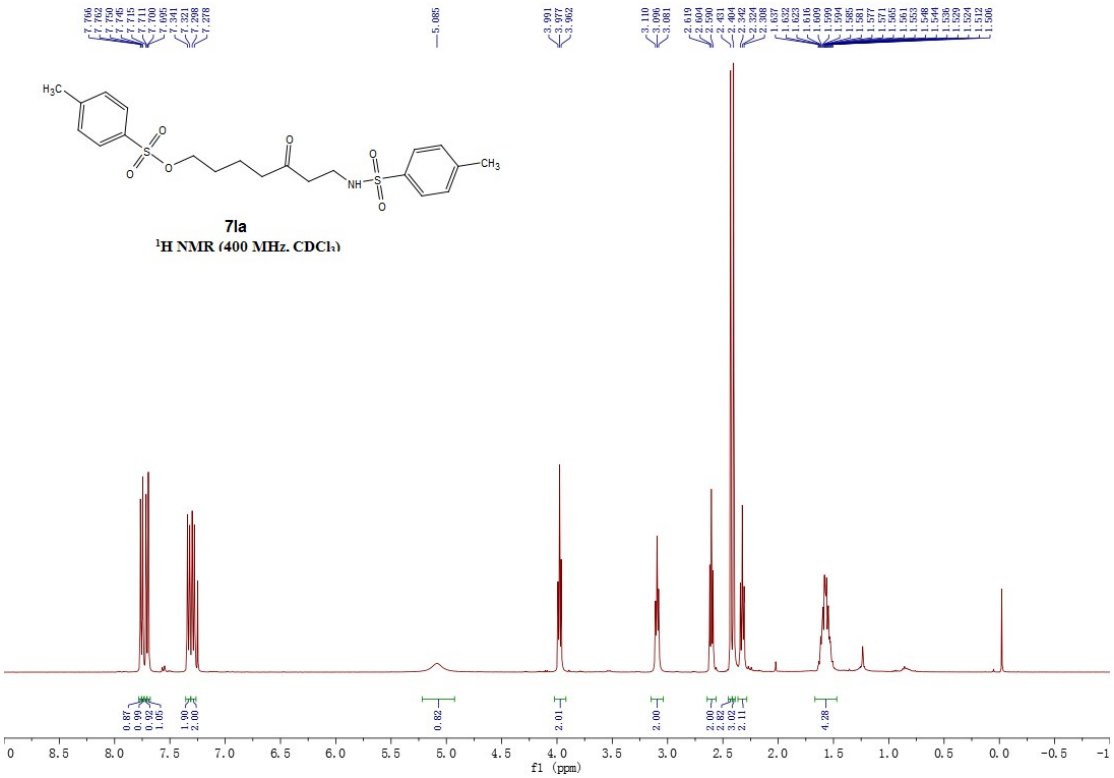
7ja
^{13}C NMR (75MHz, $CDCl_3$)



7ka
^{1}H NMR (300 MHz, $CDCl_3$)

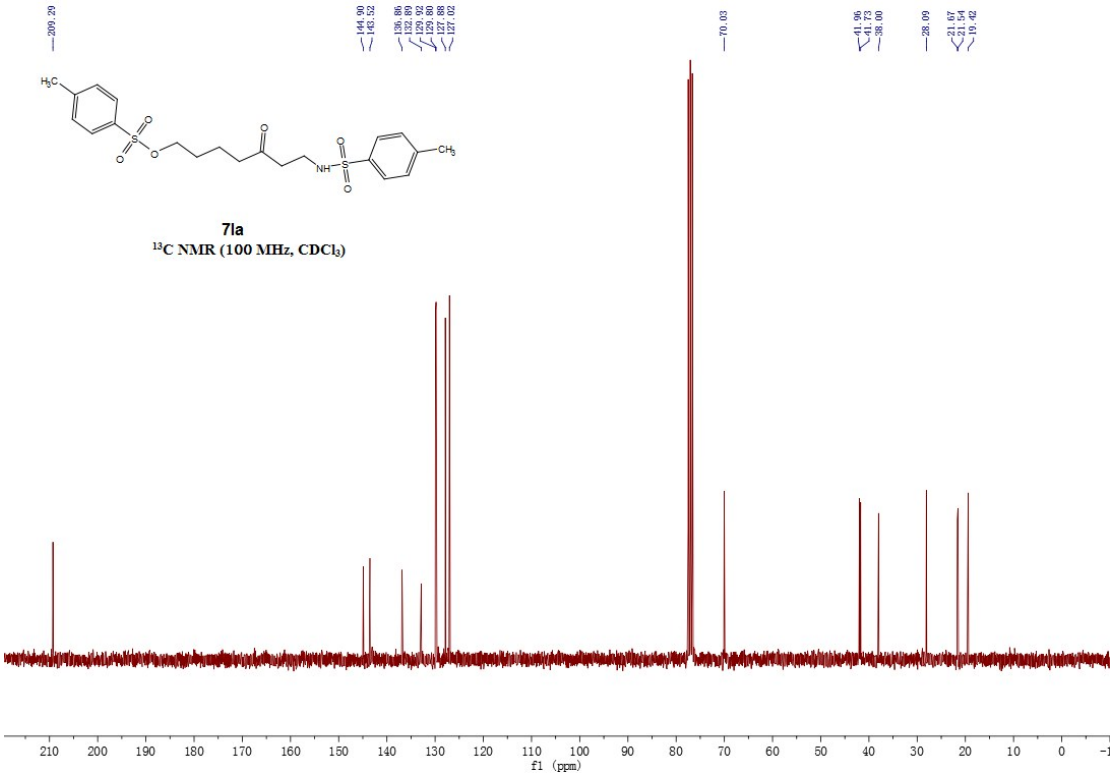


7ka
^{13}C NMR (75MHz, $CDCl_3$)



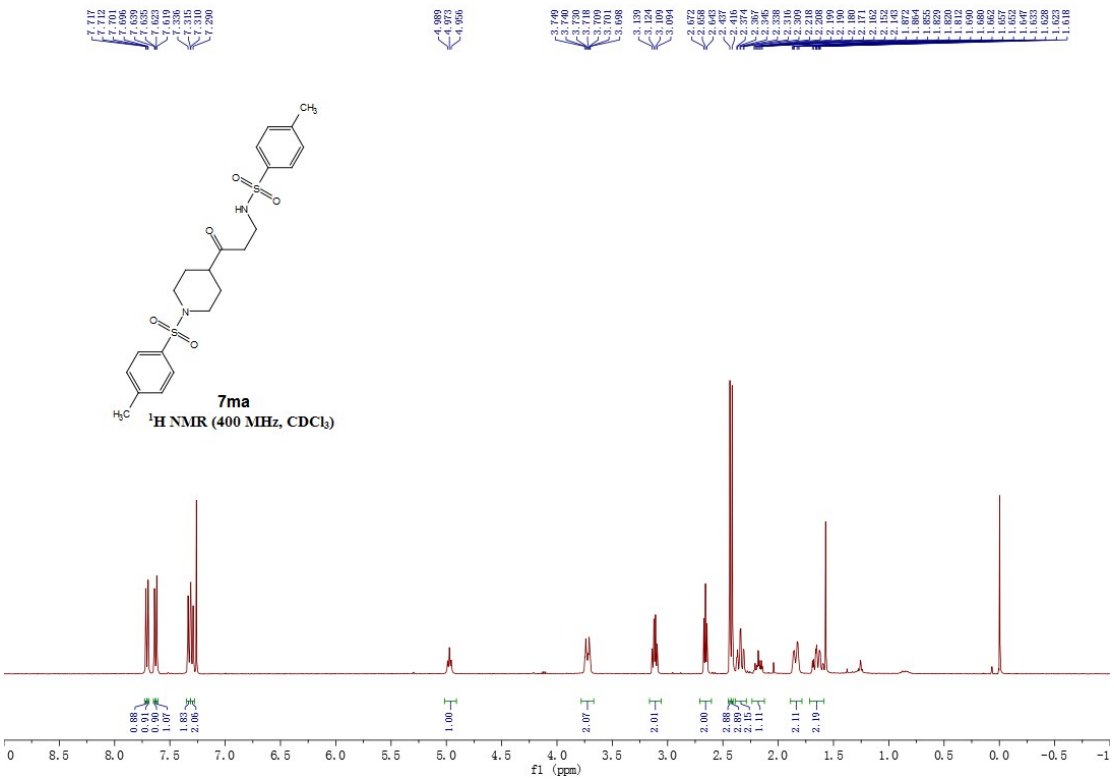
7la

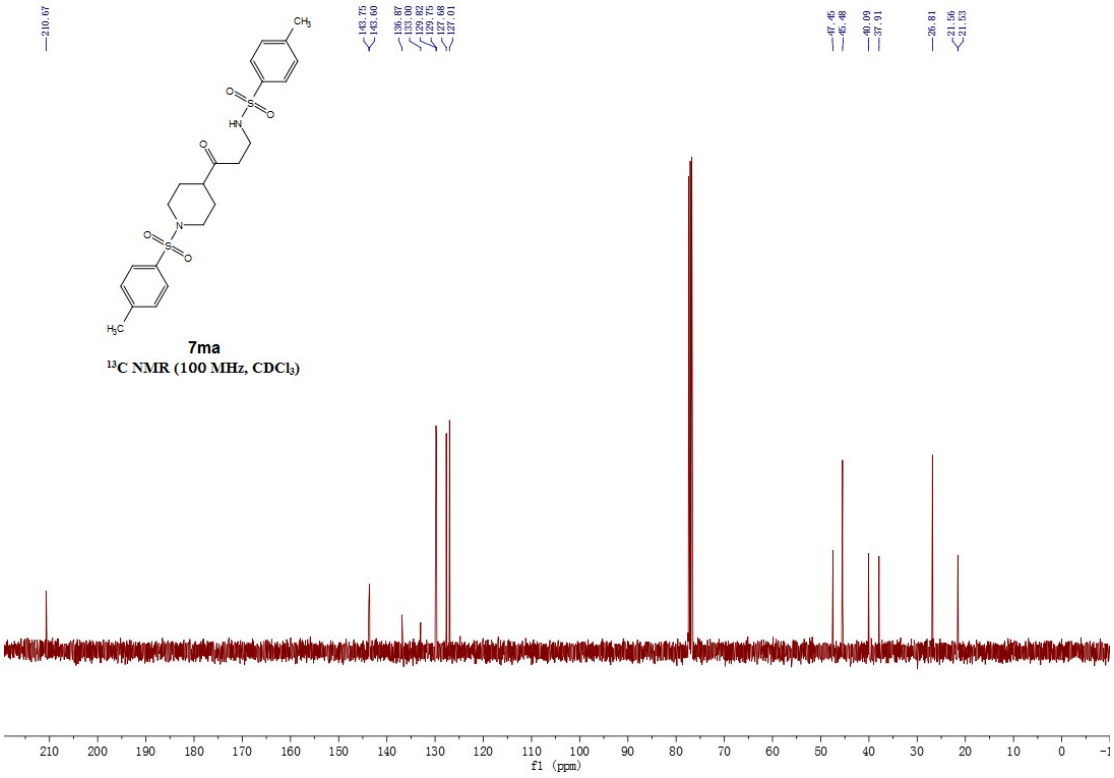
^{1}H NMR (400 MHz, $CDCl_3$)

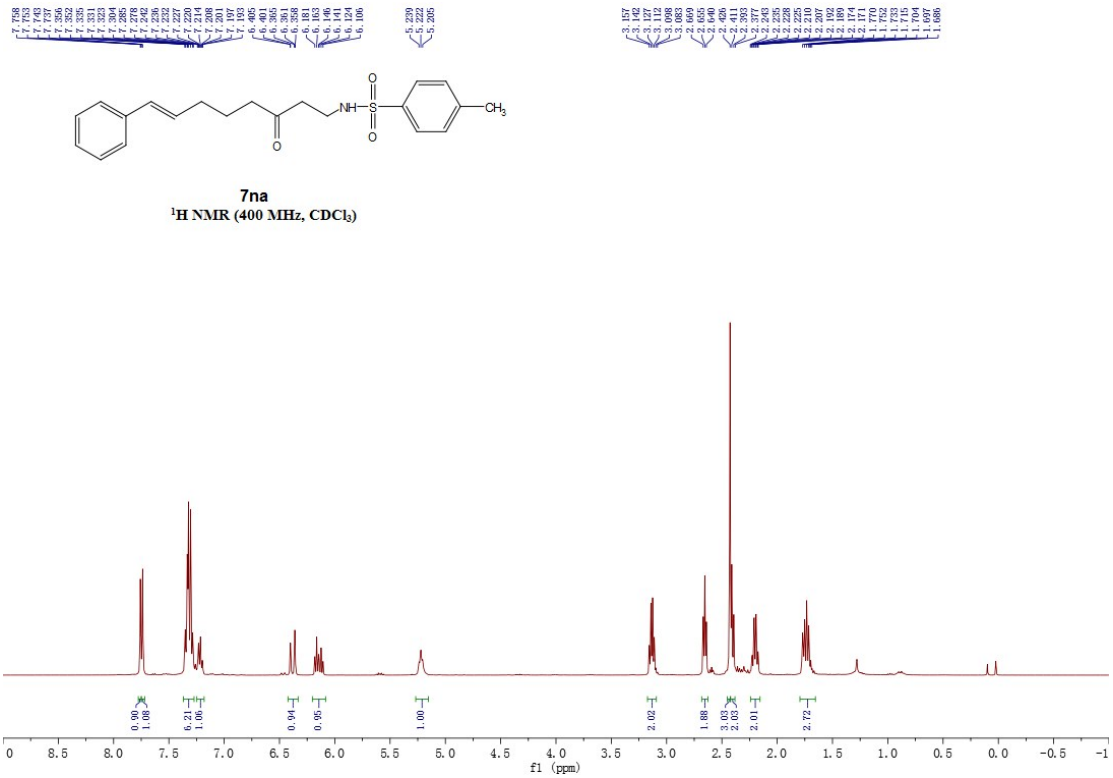


7la

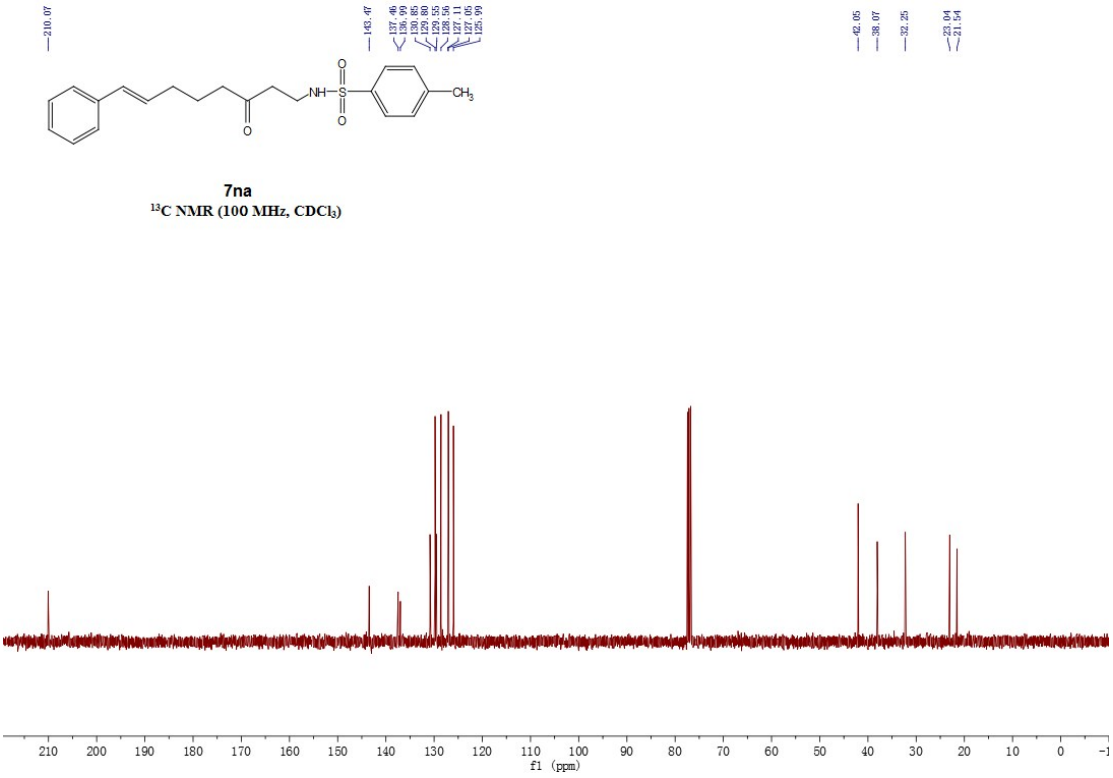
^{13}C NMR (100 MHz, $CDCl_3$)


7ma
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

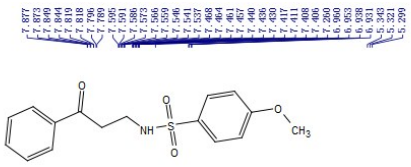

7ma
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



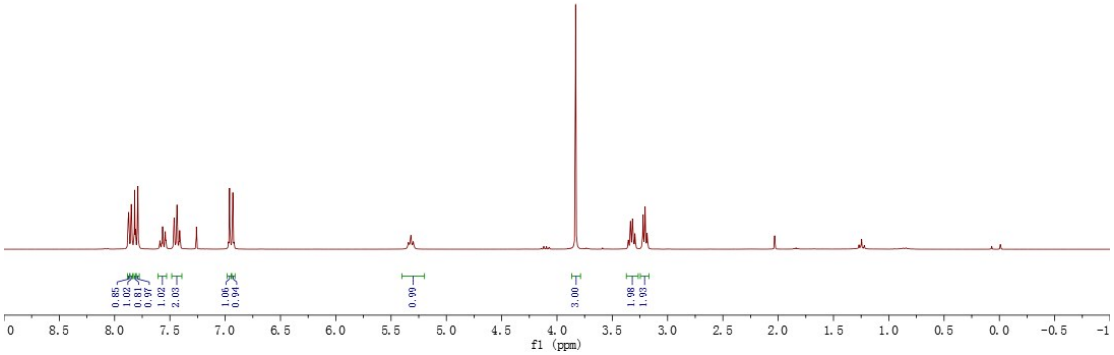
7na
^{1}H NMR (400 MHz, $CDCl_3$)

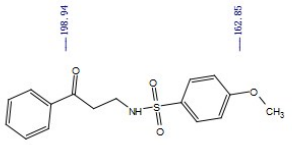


7na
^{13}C NMR (100 MHz, $CDCl_3$)

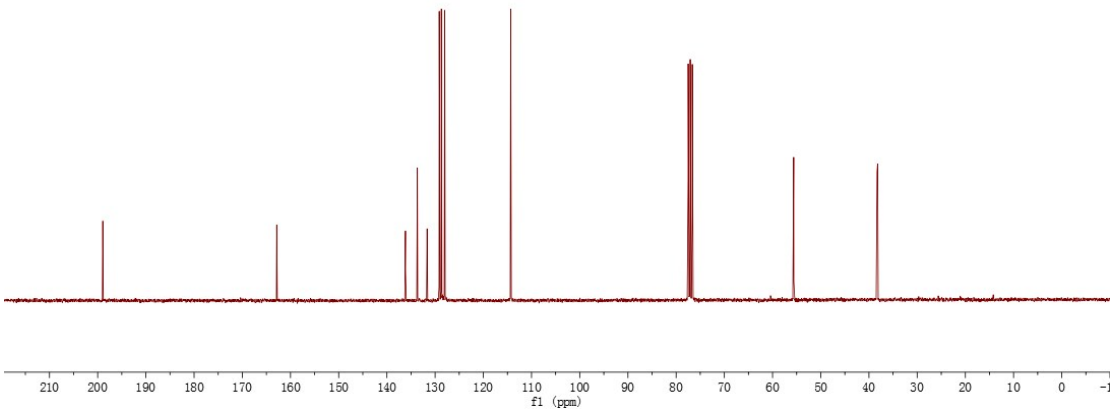


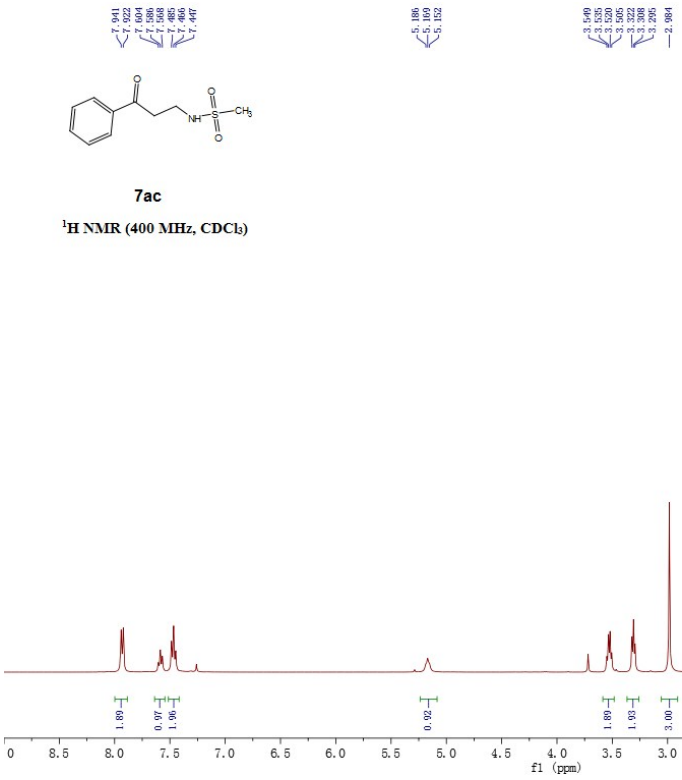
7ab
^{1}H NMR (300 MHz, $CDCl_3$)





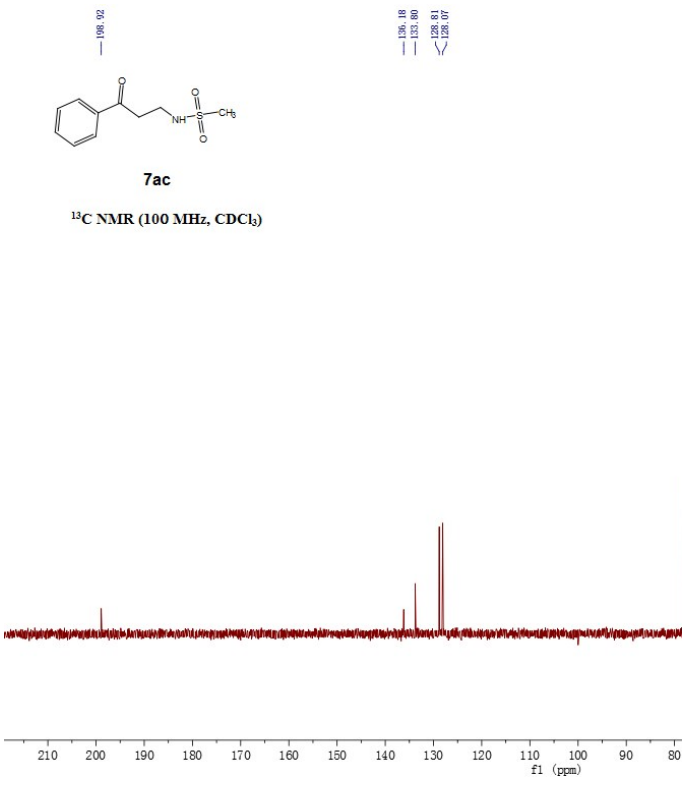
7ab
^{13}C NMR (75MHz, $CDCl_3$)





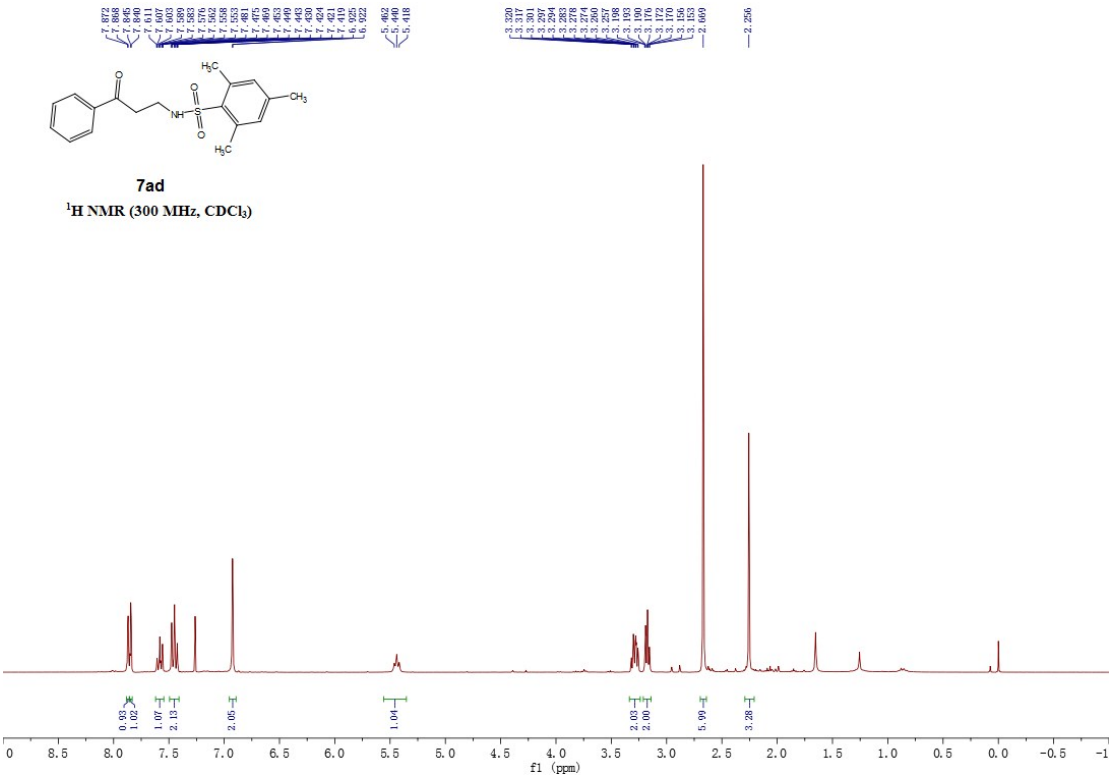
7ac

^{1}H NMR (400 MHz, $CDCl_3$)



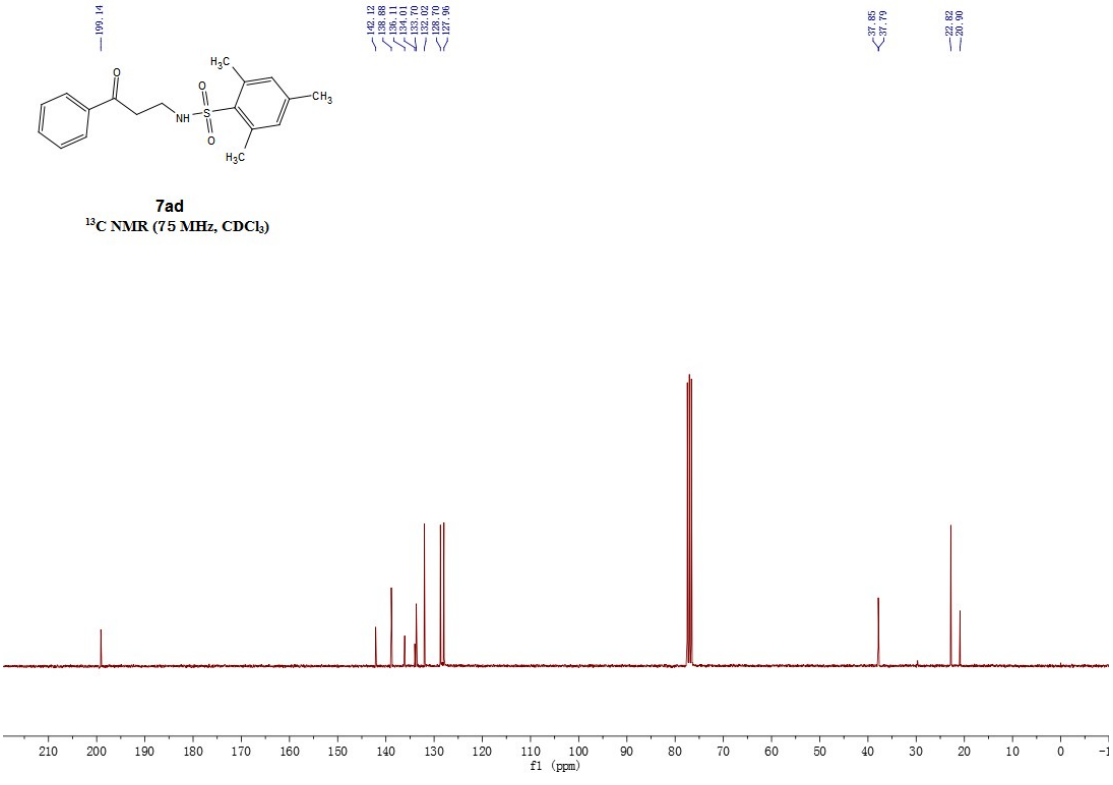
7ac

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



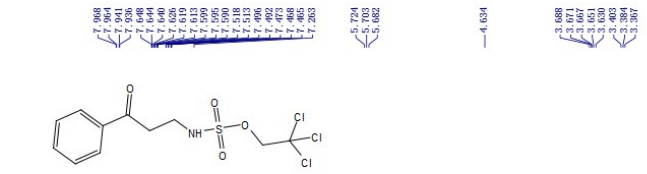
7ad

^{1}H NMR (300 MHz, $CDCl_3$)



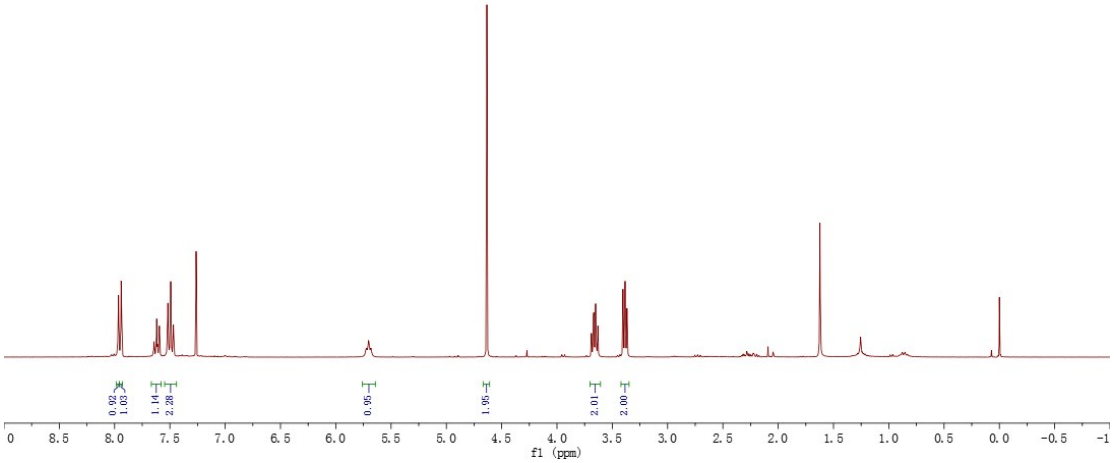
7ad

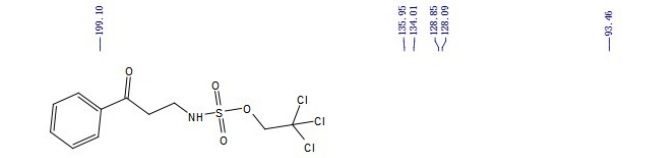
^{13}C NMR (75 MHz, $CDCl_3$)



7ae

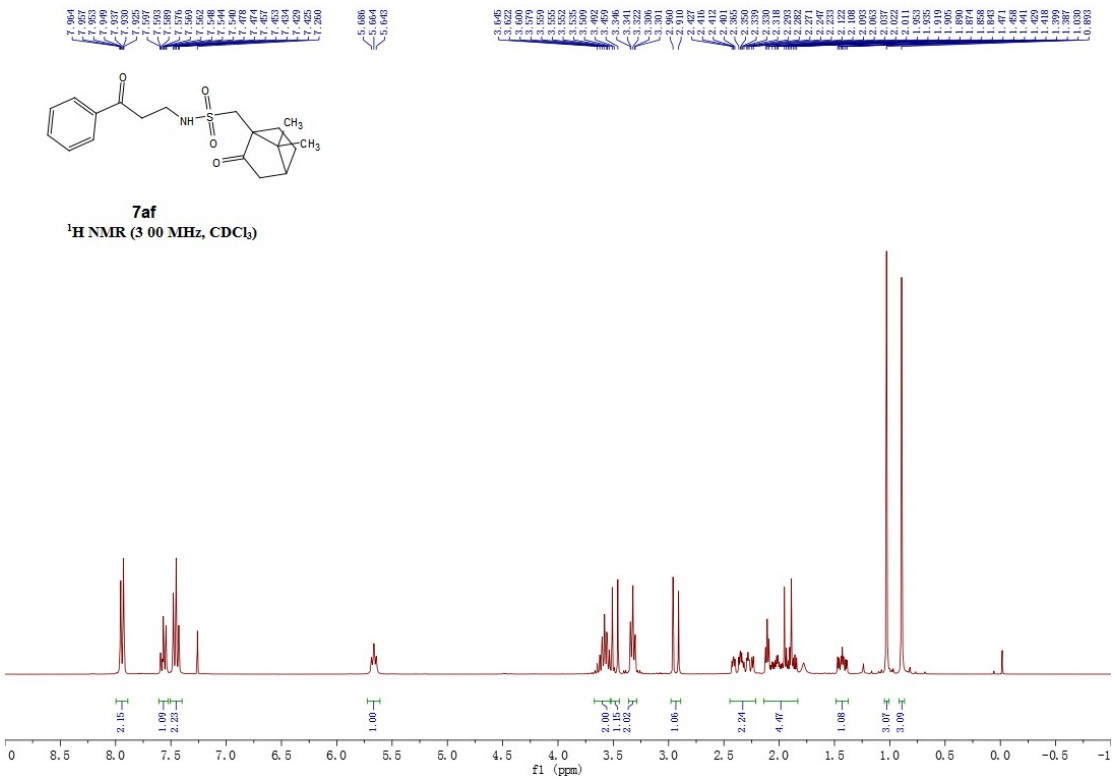
^{1}H NMR (300 MHz, $CDCl_3$)





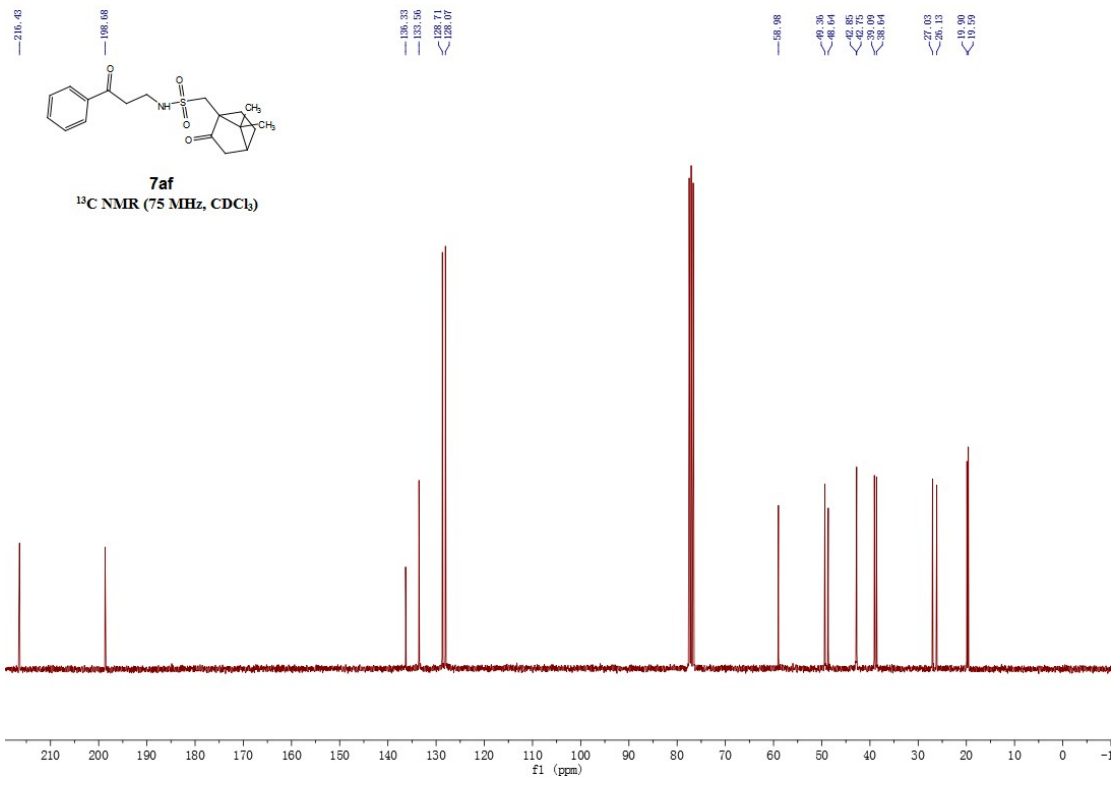
7ae

^{13}C NMR (75 MHz, $CDCl_3$)



7af

^{1}H NMR (3 00 MHz, $CDCl_3$)



7af

^{13}C NMR (75 MHz, $CDCl_3$)