Supporting Information

Copper-Catalyzed Sulfonamides Formation from Sodium Sulfinates and Amines

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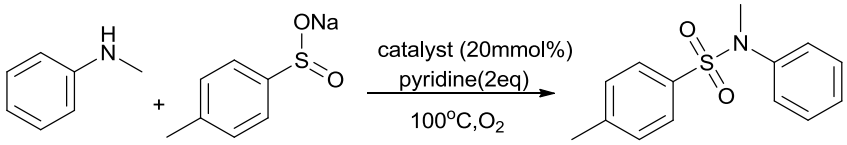
General Information

^{1}H and ^{13}C NMR spectra were recorded on **BRUKER DRX-400** spectrometer using **$CDCl_3$** as solvent and **TMS** as an internal standard. Gas chromatograph mass spectra were obtained with a **SHIMADZU** model **GCMS-QP5000** spectrometer.

Screening Reaction Conditions for Method B [a]



Entry	Catalyst	Solvent	Yield[b](%)
1	$CuBr_2$	DMF	16
2	**$CuBr_2$**	**DMSO**	**64**
3	$CuBr_2$	Toluene	42
4[c]	$CuBr_2$	DMSO	22
5[d]	$CuBr_2$	DMSO	20
6[e]	$CuBr_2$	DMSO	17
7[f]	$CuBr_2$	DMSO	0
8[g]	$CuBr_2$	DMSO	0
9	$PdCl_2$	DMSO	trace
10	$FeCl_3$	DMSO	trace

[a] Conditions: **1n** (0.6 mmol), **2a** (0.5 mmol), solvent (2 mL), 24 h. [b] Isolated yield based on **2a**. [c] Without pyridine. [d] Under N_2. [e] Without pyridine and under N_2. [f] 1 equiv of TEMPO was added. [g] 1 equiv of 2β-di-tert-butyl-4-methylphenol (BHT) was added.

General Procedure

Method A (3a-3n, 3r-3x):

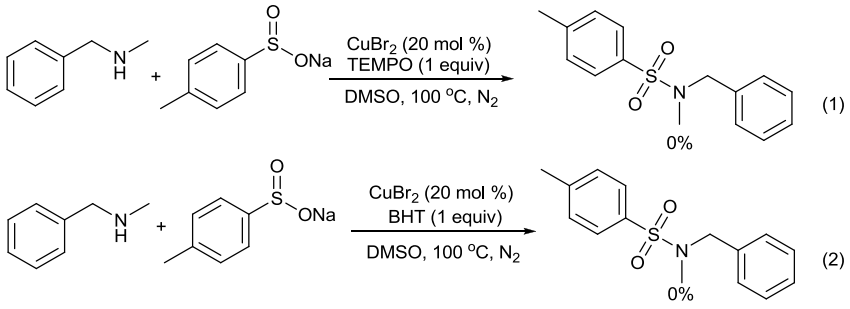
General Procedure for the Synthesis of *N*-benzyl-*N*,4-dimethylbenzenesulfonamide (3a) *N*-benzylmethylamine (0.6 mmol, **1a**), $CuBr_2$ (0.1 mmol) and sodium *p*-toluenesulfinate (0.5 mmol, **2a**) in DMSO (2 mL) were stirred at 100 °C for 24 h in a 25 mL Schlenk tube. The tube was evacuated and backfilled with nitrogen three times again. After cooling to room temperature, water (8 mL) was added after completion of the reaction, the aqueous solution was extracted with diethyl ether (3 × 5 mL), and the combined extract was dried with anhydrous $MgSO_4$. The solvent was removed and the crude product was separated by column chromatography to give a pure sample of **3a**.

Method B (3o-3q):

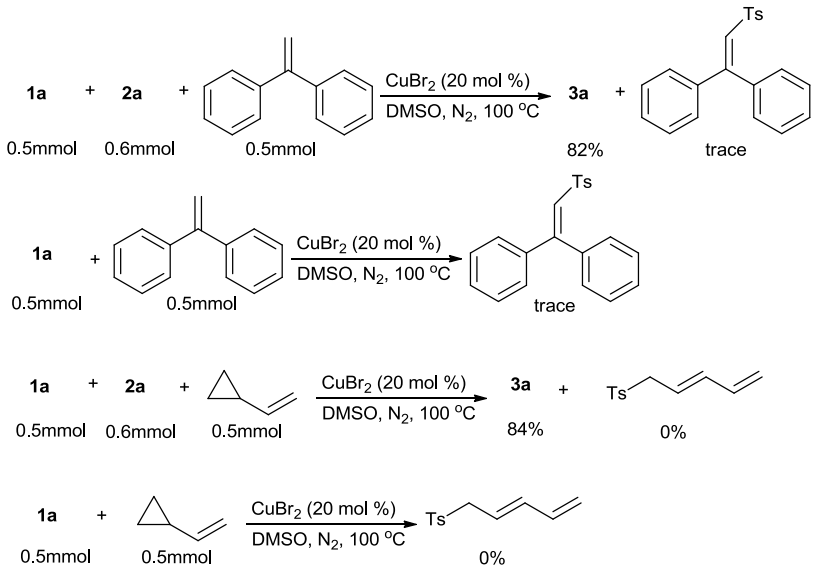
General Procedure for the Synthesis of *N*,4-dimethyl-*N*-phenylbenzenesulfonamide(3n) *N*-methylbenzenamine (0.6 mmol, **1o**), pyridine (1 mmol), $CuBr_2$ (0.1 mmol) and sodium p-toluenesulfinate (0.5mmol, **2a**) in DMSO (2 mL) were stirred at 100°C for 24h in a 10mL tube with a balloon O_2. After cooling to room temperature, water (8 mL) was added after completion of the reaction, the aqueous solution was extracted with diethyl ether (3 × 5 mL), and the combined extract was dried with anhydrous $MgSO_4$. The solvent was removed and the crude product was separated by column chromatography to give a pure sample of **3o**.

Mechanism

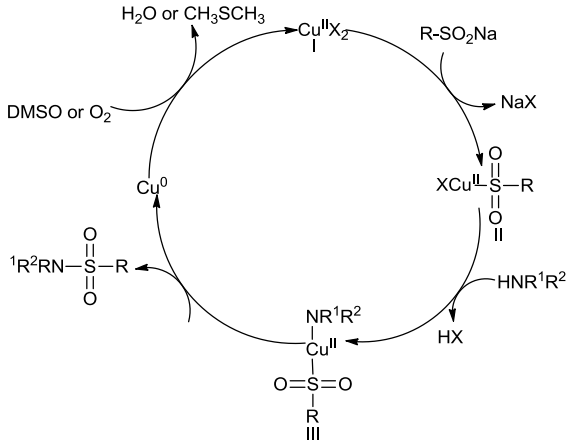
No sulfonamide product was detected in the presence of the radical scavenger TEMPO or BHT.



When we try to trap the radical intermolecularly by using 1,1-diphenylethylene or a tethered vinylcyclopropane in the presence or absence of amine, we did not observe the radical coupling products.



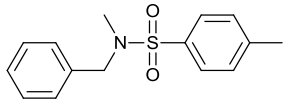
A proposed organometallic pathway:



As far as sodium sulfinates are concerned, a plausible mechanism is illustrated. The organometallic pathway involves the following several steps: (1) coordination of the sodium sulfinates to copper gives complex II;[1,2,3] (2) coordination of the amine to complex II forms complex III;[1] (3) reductive elimination of complex III affords the desired product along with a Cu^0 species,[1,4] which is oxidized to Cu^{II} by DMSO and/or oxygen for the next catalytic cycle.[4]

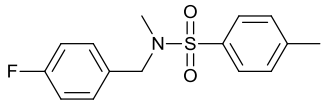
Analytical Data for 3a–x

N-benzyl-N,4-dimethylbenzenesulfonamide ($3a_1$)[5]



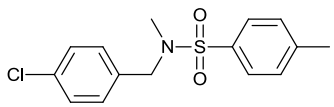
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.43-7.26 (m, 7H), 4.12 (s, 2H), 2.58 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 135.7, 134.4, 129.8, 128.6, 128.4, 127.9, 127.5, 54.2, 34.3, 21.5. MS (EI, 70 eV) *m/z* (%): 275 (M+), 256, 212, 155, 120, 91, 77.

N-(4-fluorobenzyl)-N,4-dimethylbenzenesulfonamide ($3a_2$)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30-7.27 (m, 2H), 7.06- 6.99 (m, 2H), 4.09 (s, 2H), 2.57 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.3, 143.6, 134.3, 131. 5, 130.1, 130.0, 129.8, 127.5, 115. 7, 115. 5, 53.5, 34.3, 21.6. MS (EI, 70 eV) *m/z* (%): 293 (M+), 228, 155, 138, 109, 91, 83. Anal. Calcd for $C_{15}H_{16}FNO_2S$ (293.09): C, 61.41; H, 5.50; N, 4.77. Found: C, 61.39; H, 5.52; N, 4.76.

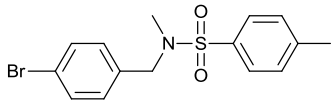
N-(4-chlorobenzyl)-N,4-dimethylbenzenesulfonamide ($3a_3$)[5]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 2.8 Hz, 2H), 4.09(s, 2H), 2.58 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

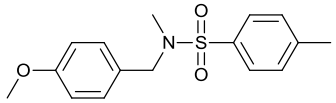
143.6, 134.3, 134.3, 133. 8, 129.8, 129.7, 128.9, 127.5, 53.5, 34.4, 21.5. MS (EI, 70 eV) *m/z* (%): 309 (M+), 244, 198, 154, 125, 91, 65.

N-(4-bromobenzyl)-N,4-dimethylbenzenesulfonamide ($3a_4$)



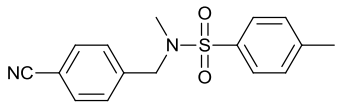
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.07 (s, 2H), 2.58 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 134.8, 134.2, 131.8, 130.0, 129.8, 127.5, 121.9, 53.6, 34.4, 21. 6. MS (EI, 70 eV) *m/z* (%): 353 (M+), 253, 198, 169, 118,91,65. Anal. Calcd for $C_{15}H_{16}BrNO_2S$ (353.01): C, 50.86; H, 4.55; N, 3.95. Found: C, 50.84; H, 4.57; N, 3.96.

N-(4-methoxybenzyl)-N,4-dimethylbenzenesulfonamide ($3a_5$)[15]



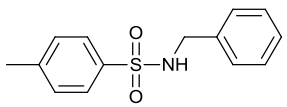
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.06 (s, 2H), 3.80 (s, 3H), 2.55 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 143.4, 134.4, 129.8, 129.7, 127.6, 127.5, 114.0, 55.3, 53.6, 34.1, 21.5. MS (EI, 70 eV) *m/z* (%): 305 (M+), 253, 149, 121, 91, 77.

N-(4-cyanobenzyl)-N,4-dimethylbenzenesulfonamide ($3a_6$)



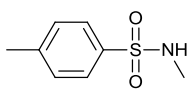
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.19 (s, 2H), 2.62 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 141.5, 134.2, 132.5, 129.9, 128.8, 127.5, 118.5, 111.9, 53.8, 34.8, 21. 6. MS (EI, 70 eV) *m/z* (%):300 (M+), 198, 145, 116, 91, 77, 65. Anal. Calcd for $C_{16}H_{16}N_2O_2S$ (300.09): C, 63.98; H, 5.37; N, 9.33. Found: C, 63.99; H, 5.39; N, 9.31.

N-benzyl-4-methylbenzenesulfonamide(3b)[6]



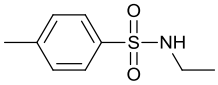
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.40-7.17 (m, 7H), 5.09 (br, 1H), 4.13 (d, *J* = 6.0, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.9, 136.4, 129.7, 128.6, 127.9, 127.8, 127.2, 47.2, 21.5. MS (EI, 70 eV) *m/z* (%): 261 (M+), 209, 176, 155, 106, 79.

N,4-dimethylbenzenesulfonamide ($3c_1$)[15]



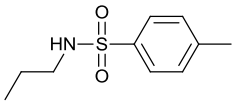
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.82 (br, 1H), 2.63 (d, *J* = 4.0Hz, 3H), 2.43 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 143.5, 135. 8, 129.7, 127.3, 29.3, 21.5. MS (EI, 70 eV) *m/z* (%): 185(M+),155, 121, 91, 77.

N-ethyl-4-methylbenzenesulfonamide($3c_2$)[10]



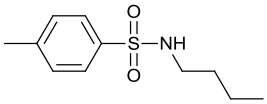
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 4.76 (br, 1H), 2.97-3.02 (m, 2H), 2.42 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.0, 129.7, 127.1, 38.2, 21.5, 15.0. MS (EI, 70 eV) *m/z*(%): 199(M+), 184, 155, 91, 77.

4-methyl-N-propylbenzenesulfonamide($3c_3$)[8]



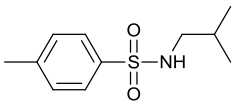
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.81 (br, 1H), 2.87-2.92 (m, 2H), 2.43 (s, 3H), 1.53-1.43 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.1, 129.7, 127.1, 45.0, 22. 9, 21.5, 11.09. MS (EI, 70 eV) *m/z* (%): 213(M+), 184, 155, 91, 77.

N-butyl-4-methylbenzenesulfonamide ($3c_4$)[7]



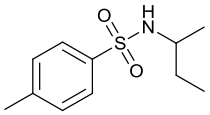
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.78 (br, 1H), 2.93-2.96 (m, 2H), 2.44 (s, 3H), 1.53-1.39 (m, 2H), 1.36-1.21 (m, 2H), 0.85 (t, *J* = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.0, 129.7, 127.1, 42.9, 31.6, 21.5, 19.7, 13.5. MS (EI, 70 eV) *m/z* (%): 227(M+), 184, 155, 91, 77.

N-isobutyl-4-methylbenzenesulfonamide ($3c_5$)[13]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.69 (br, 1H), 2.72-2.76 (m, 2H), 2.43 (s, 3H), 1.70 (m, 1H), 0.87 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.1, 129.7, 127.1, 50.6, 28.4, 21.5, 19.9. MS (EI, 70 eV) *m/z* (%): 227(M+), 184, 155, 91, 77.

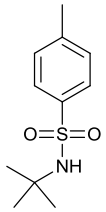
N-sec-butyl-4-methylbenzenesulfonamide ($3c_6$)[13]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.65 (br , 1H),

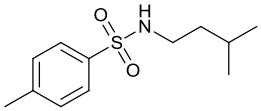
3.14-3.17 (m, 1H), 2.35 (s, 3H), 1.30-1.34 (m, 2H), 0.94 (d, *J* = 7.4Hz, 3H), 0.72 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 138.3, 129.6, 127.0, 51.4, 30.2, 21.5, 21.0, 9.9. MS (EI, 70 eV) *m/z* (%): 227 (M+), 198, 155, 91, 77.

N-tert-butyl-4-methylbenzenesulfonamide ($3c_7$)[18]



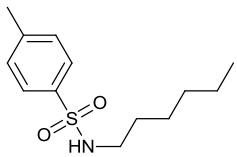
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz,2H), 4.84 (br, 1H), 2.41 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 142.8, 140.6, 129.5, 127.0, 54.5, 30.1, 21.5. MS (EI, 70 eV) *m/z* (%): 227 (M+), 212, 155, 91, 77.

N-isopentyl-4-methylbenzenesulfonamid ($3c_8$)[21]



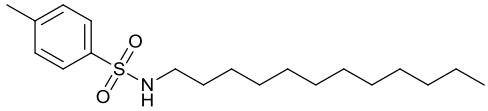
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.1 Hz, 2H), 4.52 (br, 1H), 2.94-2.95 (m, 2H), 2.43(s, 3H), 1.67-1.46 (m, 1H), 1.33-1.34 (m, 2H), 0.83 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 136.9, 129. 7, 127.1, 41.5, 38.4, 25.4, 22.2, 21.5. MS (EI, 70 eV) *m/z* (%): 241(M+), 184, 172, 155, 91, 77.

N-hexyl-4-methylbenzenesulfonamide ($3c_9$)[6]



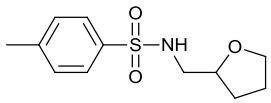
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.75 (br, 1H), 2.90-2.94 (m, 2H), 2.42 (s, 3H), 1.49-1.39 (m, 2H), 1.35-1.12 (m, 6H), 0.84 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.1, 129.7, 127.1, 43.2, 31.2, 29.5, 26.2, 22.4, 21.5, 13.9. MS (EI, 70 eV) *m/z* (%): 255(M+), 184, 155, 100, 91, 77.

N-dodecyl-4-methylbenzenesulfonamid ($3c_{10}$)[12]



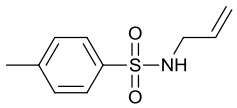
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.48 (s, 1H), 2.90-2.94 (m, 2H), 2.42 (s, 3H), 1.20-1.25 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.1, 129.7, 127.1, 43.2, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 26.5, 22.7, 21.5, 14.1. MS (EI, 70 eV) *m/z* (%): 339(M+), 184, 172, 155, 91, 77.

4-methyl-N-((tetrahydrofuran-2-yl)methyl)benzenesulfonamide(3d)[17]



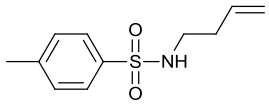
^{1}H NMR (400 MHz, acetone) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.30 (br, 1H), 3.96-3.81 (m, 1H), 3.76-3.53 (m, 2H), 3.05-2.89 (m, 2H), 2.42 (s, 3H), 1.93-1.57 (m, 4H). ^{13}C NMR (100 MHz, acetone) δ143.7, 139.3, 130.4, 127.8, 78.2, 68.5, 47.9, 29.3, 26.2, 21.4. MS (EI, 70 eV) *m/z* (%): 255(M+), 212, 155, 116, 91, 77.

N-allyl-4-methylbenzenesulfonamide (3e)[8]



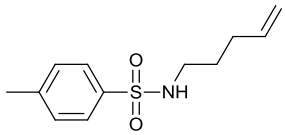
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 2H), 5.78-5.64 (m, 1H), 5.08-5.18 (m, 2H), 4.62 (br, 1H), 3.58 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 143.3, 137.0, 133.0, 129.7, 127.2, 117.7, 45.8, 21.5. MS (EI, 70 eV) *m/z* (%): 211(M+), 184, 155, 91, 77.

N-(but-3-enyl)-4-methylbenzenesulfonamide (3f)[16]



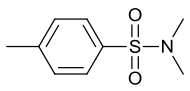
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.50-5.60 (m, 1H), 4.94-5.00 (m, 2H), 4.56 (br, 1H), 2.91-2.96 (m, 2H), 2.35 (s, 3H), 2.10-2.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 137.0, 134.2, 129.7, 127.1, 118.1, 42.1, 33.6, 21.5. MS (EI, 70 eV) *m/z* (%): 225(M+), 184, 155, 91, 77

4-methyl-N-(pent-4-en-1-yl)benzenesulfonamide (3g)[16]



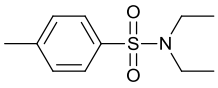
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.69 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.24 (br, 1H), 4.99-4.88 (m, 2H), 2.92 (dd, *J* = 12.2, 6.7 Hz, 2H), 2.42 (s, 3H), 2.02 (dd, *J* = 14.5, 7.0 Hz, 2H), 1.61-1.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.3, 137.0, 129.8, 127.1, 115.4, 42.6, 30.6, 28.6, 21.5. MS (EI, 70 eV) *m/z* (%): 239(M+), 210, 184, 155, 91, 84, 70.

N,N,4-trimethylbenzenesulfonamide(3h)[11]



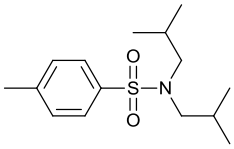
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.69 (s, 6H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 132.5, 129.6, 127.8, 37.9, 21.5. MS (EI, 70 eV) *m/z* (%): 199(M+), 184, 155, 91, 77

N,N-diethyl-4-methylbenzenesulfonamide (3i)[10]



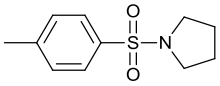
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.22 (q, *J* = 7.1 Hz, 4H), 2.41 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 137.3, 129.6, 127.0, 42.0, 21.5, 14.1. MS (EI, 70 eV) *m/z* (%): 227(M+), 184, 155, 91, 77.

N,N-diisobutyl-4-methylbenzenesulfonamide(3j)



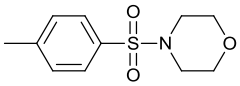
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.84 (d, *J* = 7.5 Hz, 4H), 2.42 (s, 3H), 1.89 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 136.7, 129.5, 127.4, 57.1, 27.1, 21.5, 20.2. MS (EI, 70 eV) *m/z* (%): 283(M+), 240, 184, 155, 91, 77. Anal. Calcd for $C_{15}H_{25}NO_2S$ (283.16): C, 63.56; H, 8.89; N, 4.94. Found: C, 63.47; H, 8.95; N, 4.98.

1-tosylpyrrolidine (3k)[9]



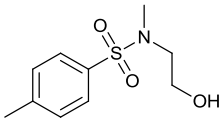
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 3.23 (t, 4H), 2.43 (s, 3H), 1.75 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 134.0, 129.6, 127.5, 47.9, 25.2, 21.5. MS (EI, 70 eV) *m/z* (%): 225(M+), 155, 91, 77.

4-tosylmorpholine (3l)[6]



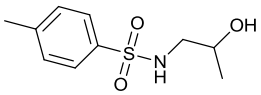
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.74 (t, *J* = 6.0 Hz, 4H), 3.01 (t, *J* = 6.0 Hz, 4H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 132.1, 129.8, 127.9, 66.1, 46.0, 21.5. MS (EI, 70 eV) *m/z* (%): 241(M+), 198, 155, 106, 91, 77.

N-(2-hydroxyethyl)-N,4-dimethylbenzenesulfonamide(3m)



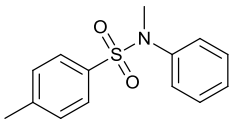
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.76 (t, *J* = 5.3 Hz, 2H), 3.15 (t, *J* = 5.3 Hz, 2H), 2.82 (s, 3H), 2.44 (s, 3H), 1.70 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 136.7, 129.8, 127.5, 60.3, 52.6, 36.1, 21.5. MS (EI, 70 eV) *m/z* (%): 229(M+), 198, 155, 91, 77. Anal. Calcd for $C_{10}H_{15}NO_3S$ (229.08): C, 52.38; H, 6.59; N, 6.11. Found: C, 52.27; H, 6.65; N, 6.18.

N-(2-hydroxypropyl)-4-methylbenzenesulfonamide(3n)[20]



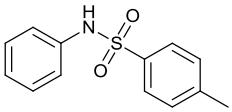
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.26 (br, 1H), 3.98 -3.84 (m, 1H), 2.99-3.06 (m, 1H), 2.74-2.80 (m, 1H), 2.43 (s, 3H), 2.20 (br, 1H), 1.14 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 136.7, 129. 8, 127.1, 66.6, 50.1, 21.5, 20.6. MS (EI, 70 eV) *m/z* (%): 229(M+), 198, 155, 91, 77.

N,4-dimethyl-N-phenylbenzenesulfonamide(3o)[18]



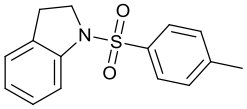
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.32–7.20 (m, 5H), 7.10 (m, 2H), 3.16 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.7, 133.6, 129.3, 128.8, 127.9, 127.2, 126.6, 38.1, 21.5 MS (EI, 70 eV) *m/z* (%): 261(M+), 197, 155, 106, 91, 77.

4-methyl-N-phenylbenzenesulfonamide(3p)[6]



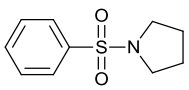
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 2H), 7.66 (br,1H),7.22 -7.01 (m, 7H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.90, 136.76, 136.01, 129.69, 129.29, 127.34, 125.12, 121.35, 77.47, 77.15, 76.83, 21.53. MS (EI, 70 eV) *m/z* (%): 247(M+), 182, 155, 91, 77.

1-tosylindoline (3q)[11]



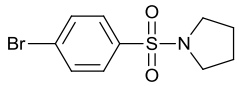
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.63(m, 3H), 7.23-7.17 (m, 3H), 7.08-7.06 (m, 1H), 6.98-6.95 (m, 1H), 3.91 (t, *J* = 8.4 Hz, 2H), 2.88 (t, *J* = 8.4 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 134.1, 131.8, 129.6, 127.7, 127.3, 125.1, 123.7, 115.0, 49.9, 27.9, 21.51. MS (EI, 70 eV) *m/z* (%): 273(M+), 226, 118, 91, 77.

1-(phenylsulfonyl)pyrrolidine (3r)[9]



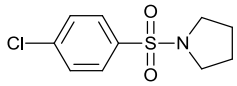
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.57 (m, 3H), 3.25 (t, *J* = 6.6 Hz, 4H), 1.75 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 132. 6, 129.0, 127.5, 47.9, 25.2. MS (EI, 70 eV) *m/z* (%): 211(M+), 141, 91, 77.

1-(4-bromophenylsulfonyl)pyrrolidine (3s)



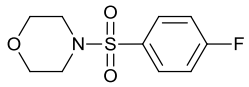
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89- 7.64 (m, 4H), 3.24 (t, *J* = 6.7 Hz, 4H), 1.86-1.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 132.3, 129.0, 127.5, 48.0, 25.3. MS (EI, 70 eV) *m/z* (%): 290(M+), 220, 155, 141, 77. Anal. Calcd for $C_{10}H_{12}BrNO_2S$ (288.98): C, 41.39; H, 4.17; N, 4.83. Found: C,41.27; H, 4.25; N, 4.88.

1-(4-chlorophenylsulfonyl)pyrrolidine (3t)[9]



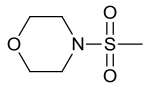
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 3.24 (t, *J* = 6.6 Hz, 4H), 1.92–1.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 135.6, 129.3, 128.8, 47.9, 25.3. MS (EI, 70 eV) *m/z* (%): 244(M+), 175, 159, 111, 77.

4-(4-fluorophenylsulfonyl)morpholine (3u)



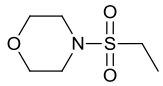
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 3.88 (t, 4H), 3.74 (t, 2H), 3.34-3.24 (m, 2H), 3.01-2.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 129.7, 123.8, 113.7, 66.5, 66.1, 47.5, 46.0. MS (EI, 70 eV) *m/z* (%): 246(M+), 186, 155, 91, 77. Anal. Calcd for $C_{10}H_{12}FNO_3S$ (245.05): C, 48.97; H, 4.93; N, 5.71. Found: C, 48.87; H, 4.95; N, 5.88.

4-(methylsulfonyl)morpholine (3v)[6]



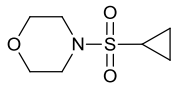
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (t,J=8.0Hz 4H), 3.22 (t, *J* = 8.0Hz, 4H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ66.3, 45.9, 34.0. MS (EI, 70 eV) *m/z* (%): 165(M+), 122, 107, 86.

4-(ethylsulfonyl)morpholine (3w)[19]



^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (t, *J* = 8.0 Hz 4H), 3.29 (t, *J* = 8.0 Hz 4H), 2.97 (q, *J* = 7.4 Hz 2H), 1.39 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ66.7, 45.9, 43.6, 7.7. MS (EI, 70 eV) *m/z* (%): 179(M+), 148, 136, 86.

4-(cyclopropylsulfonyl)morpholine (3x)[14]



^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (t, *J* = 8.0 Hz, 4H), 3.29 (t, *J* = 8.0Hz ,4H), 2.32-2.24 (m, 1H), 1.20-1.13 (m, 2H), 1.06-0.96 (m,2H). ^{13}C NMR (100MHz, $CDCl_3$) δ66.4, 46.2, 25.1, 4.2. MS (EI, 70 eV) *m/z* (%): 191(M+), 160, 148, 105, 86.

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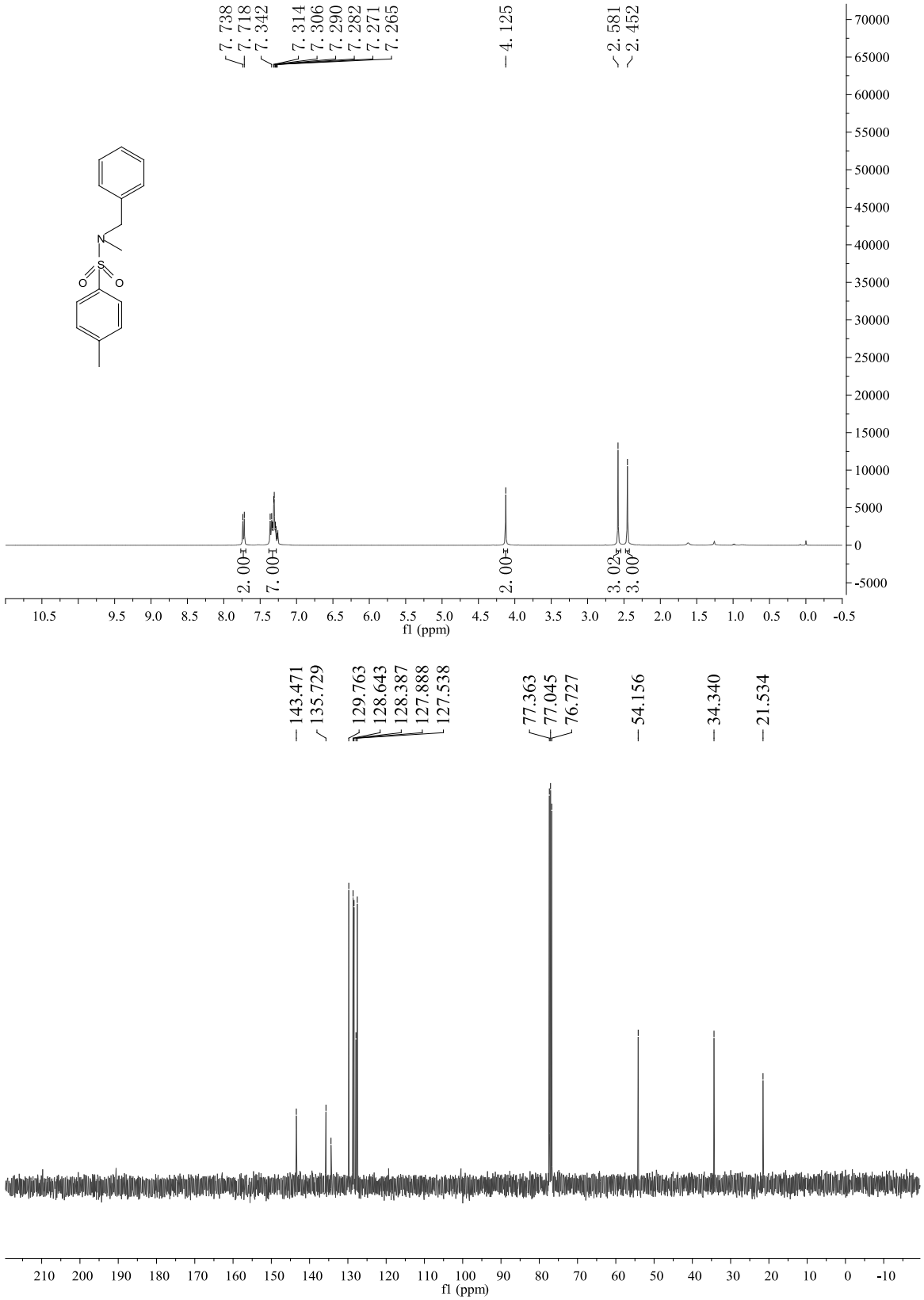
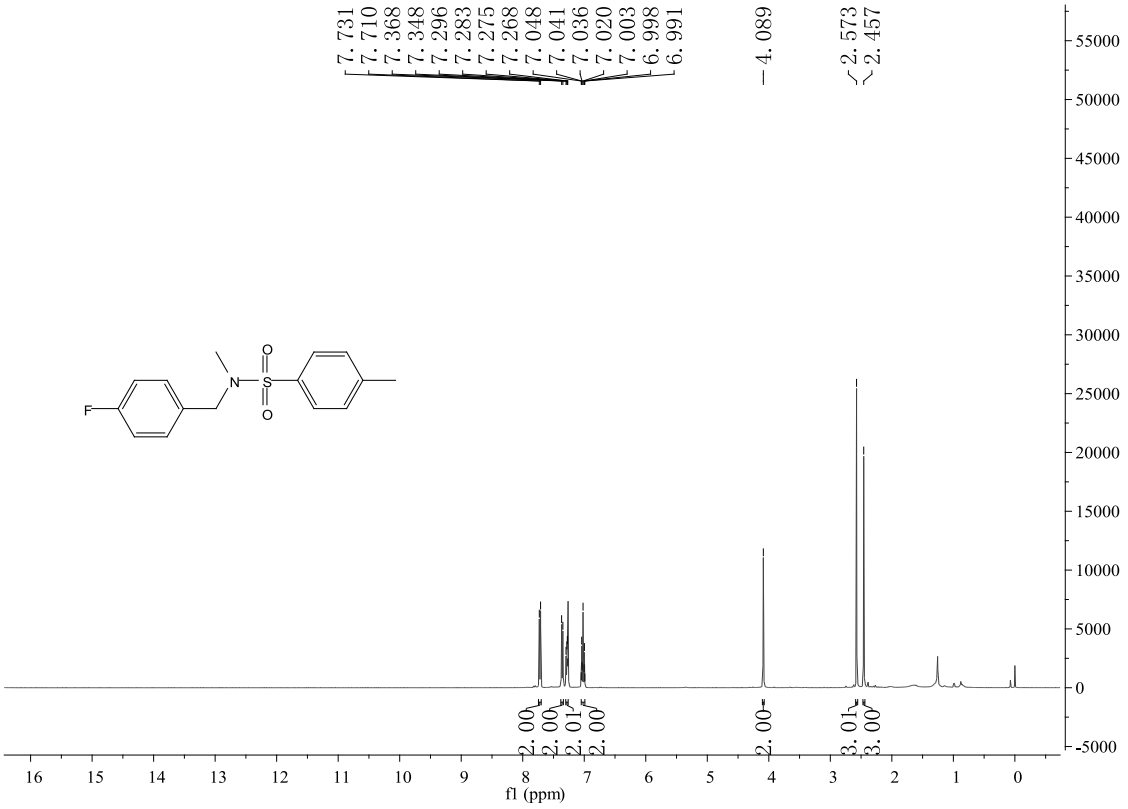
NMR Spectra for the Compounds 3a–x



3a1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7.275
7.268
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7.041
7.036
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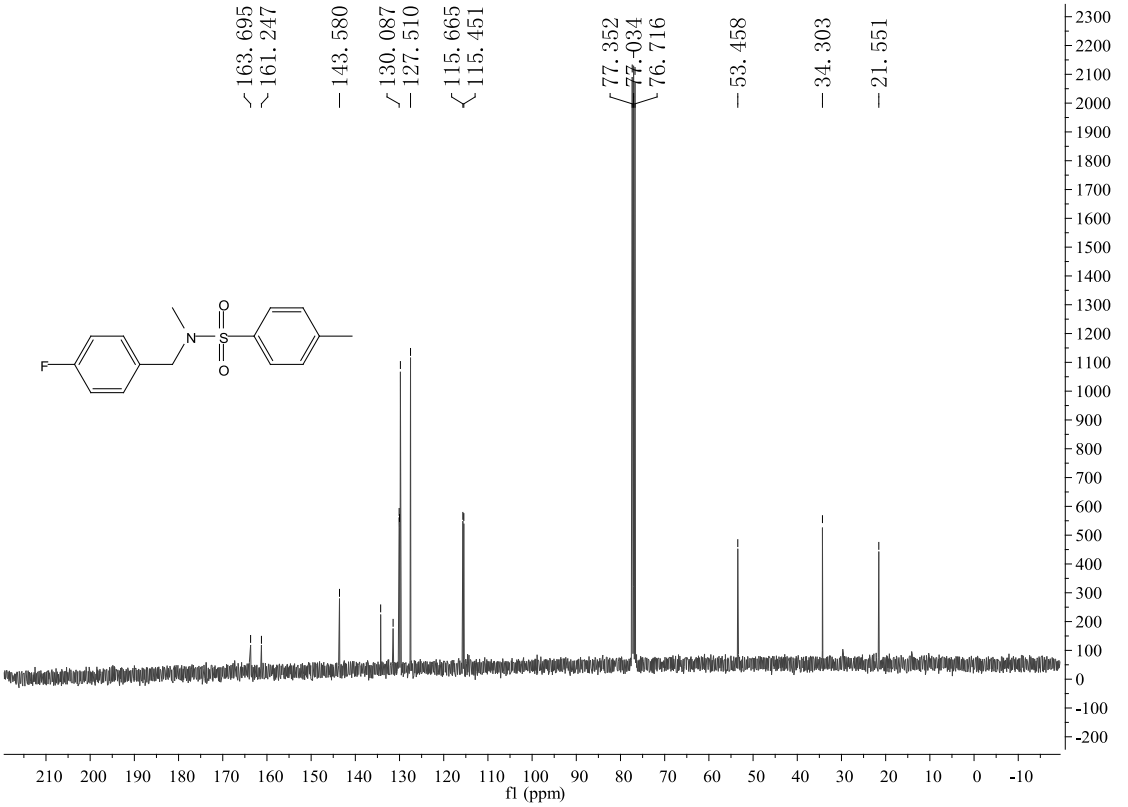
7.003
6.998
6.991
4.089
2.573
2.457
2.00
2.00
2.01
2.00
2.00
3.01
3.00
f1 (ppm)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161.247
143.580
130.087
127.510
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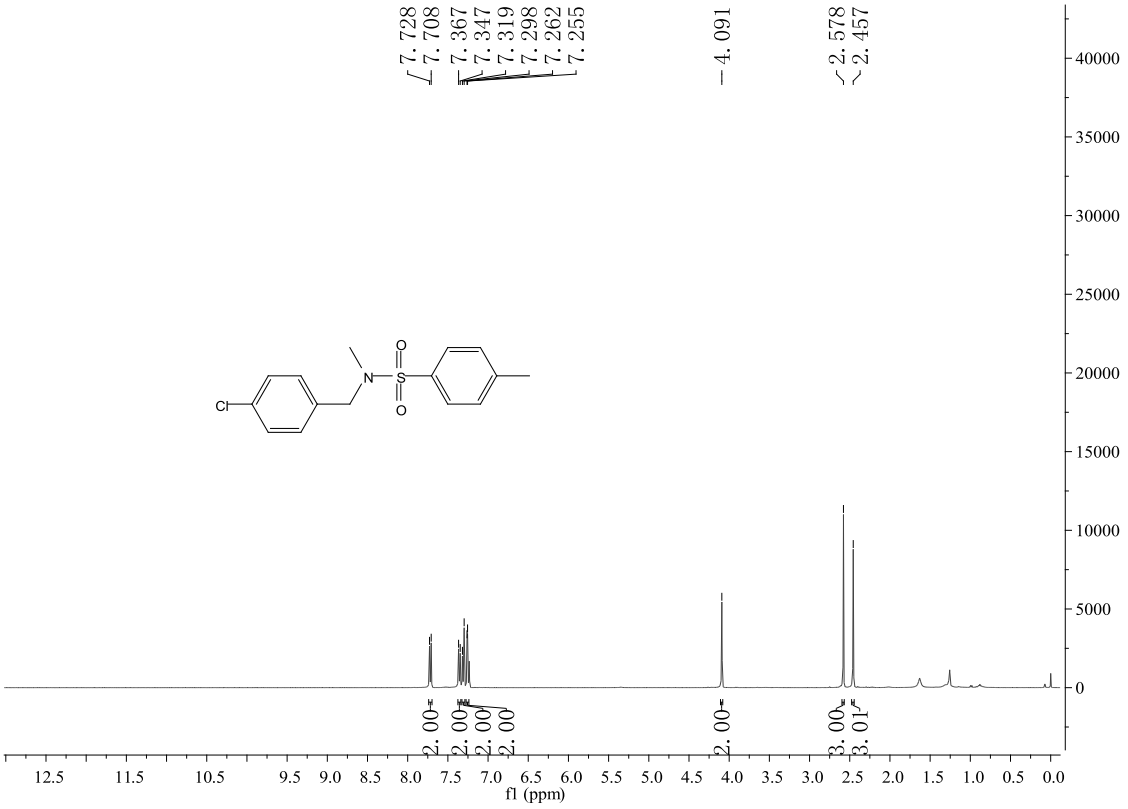
115.451
77.352
77.034
76.716
53.458
34.303
21.551
f1 (ppm)

3a2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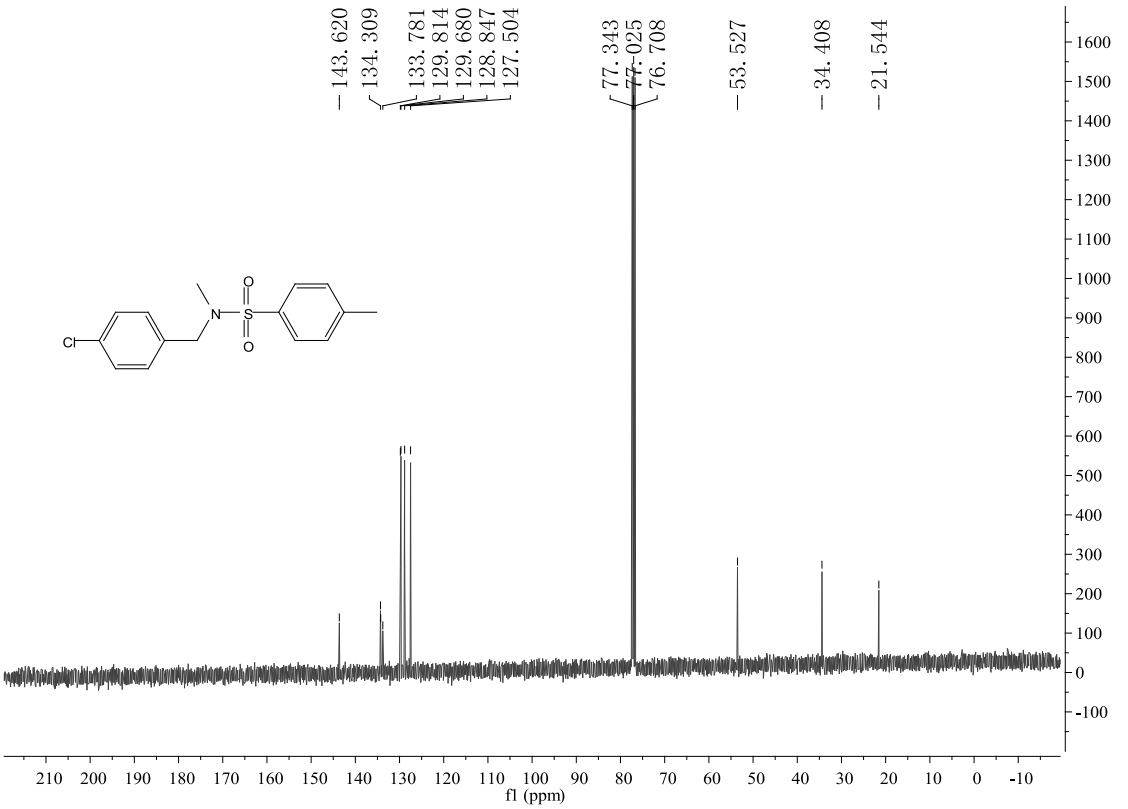
7.708
7.367
7.347
7.319
7.298
7.262
7.255
4.091
2.578
2.457
Cl
N
S
O
2.00
2.00
2.00
2.00
2.00
3.00
3.01
f1 (ppm)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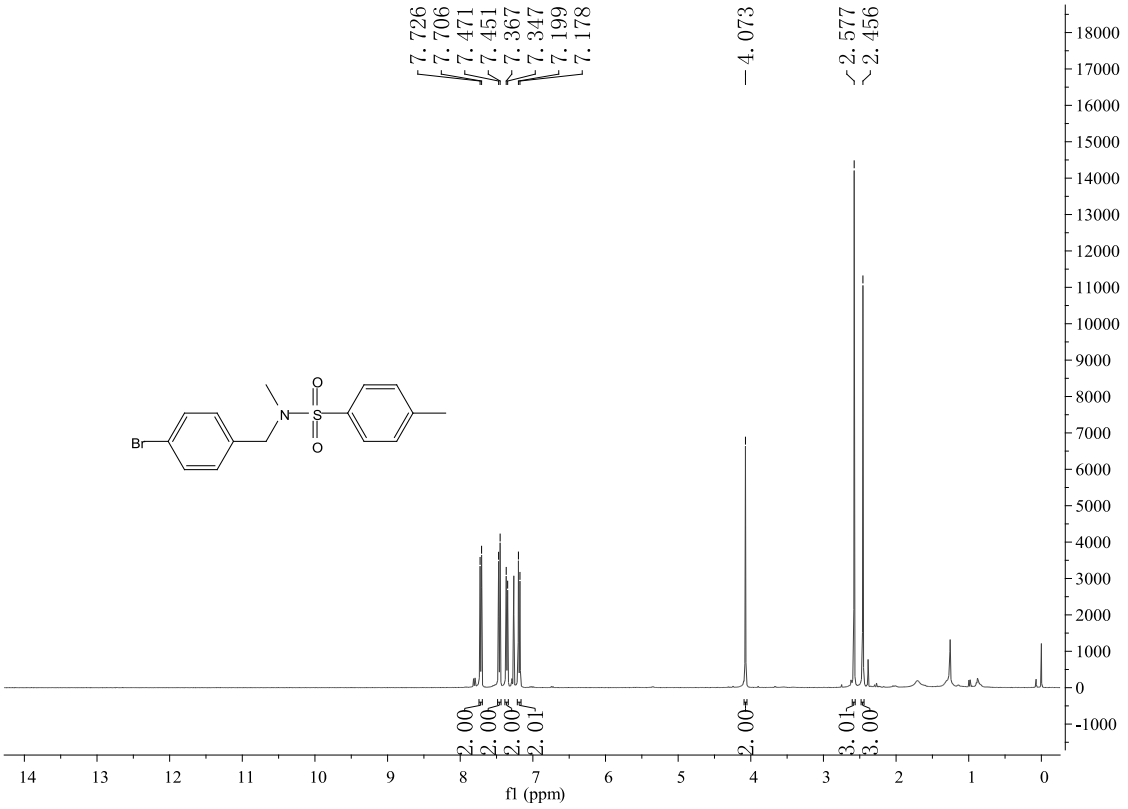
134.309
133.781
129.814
129.680
128.847
127.504
77.343
77.025
76.708
53.527
34.408
21.544
Cl
N
S
O
f1 (ppm)

3a3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7.451
7.367
7.347
7.199
7.178
4.073
2.577
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Br
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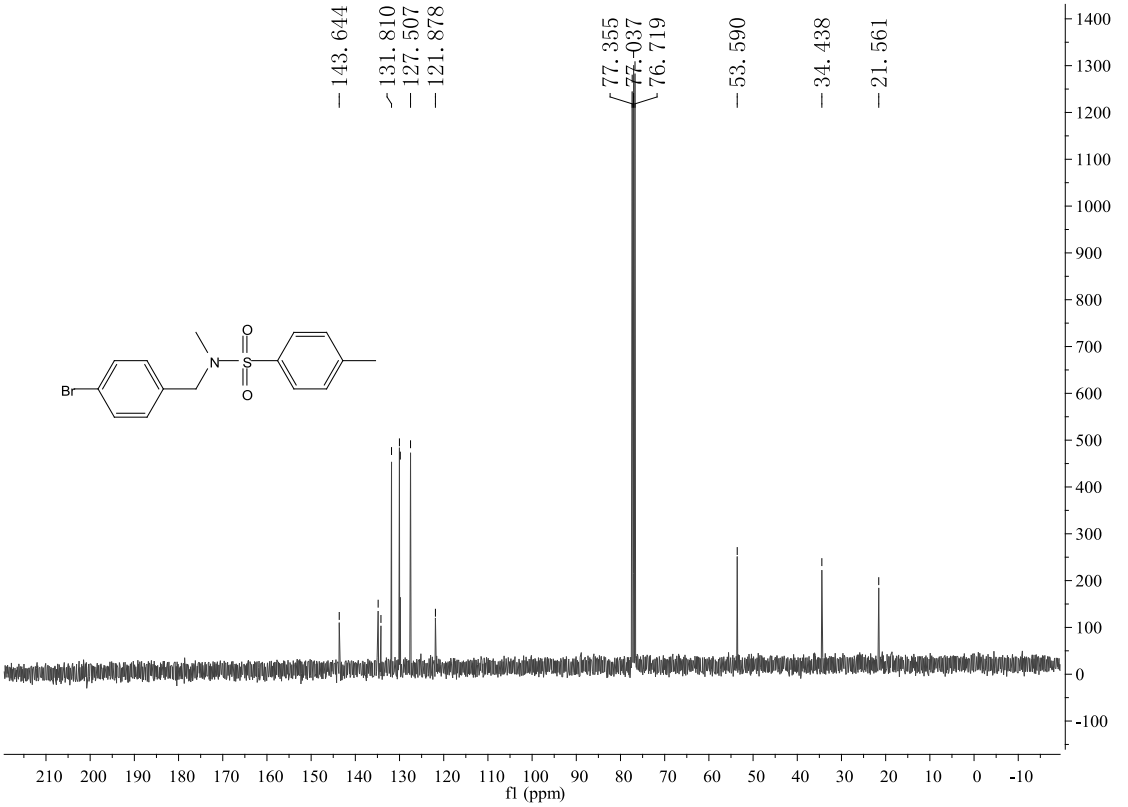
S
O
2.00
2.00
2.00
2.01
2.00
3.01
3.00
f1 (ppm)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131.810
127.507
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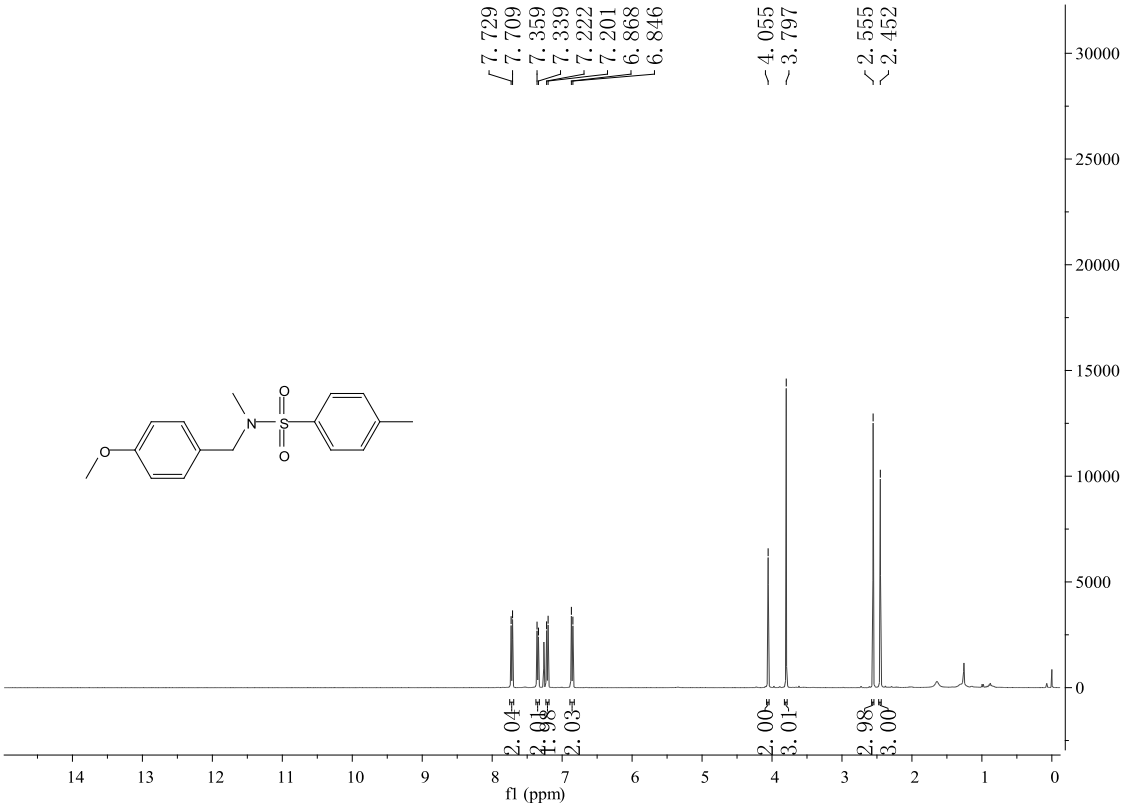
77.037
76.719
53.590
34.438
21.561
Br
N
S
O
f1 (ppm)

3a4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7.339
7.222
7.201
6.868
6.846
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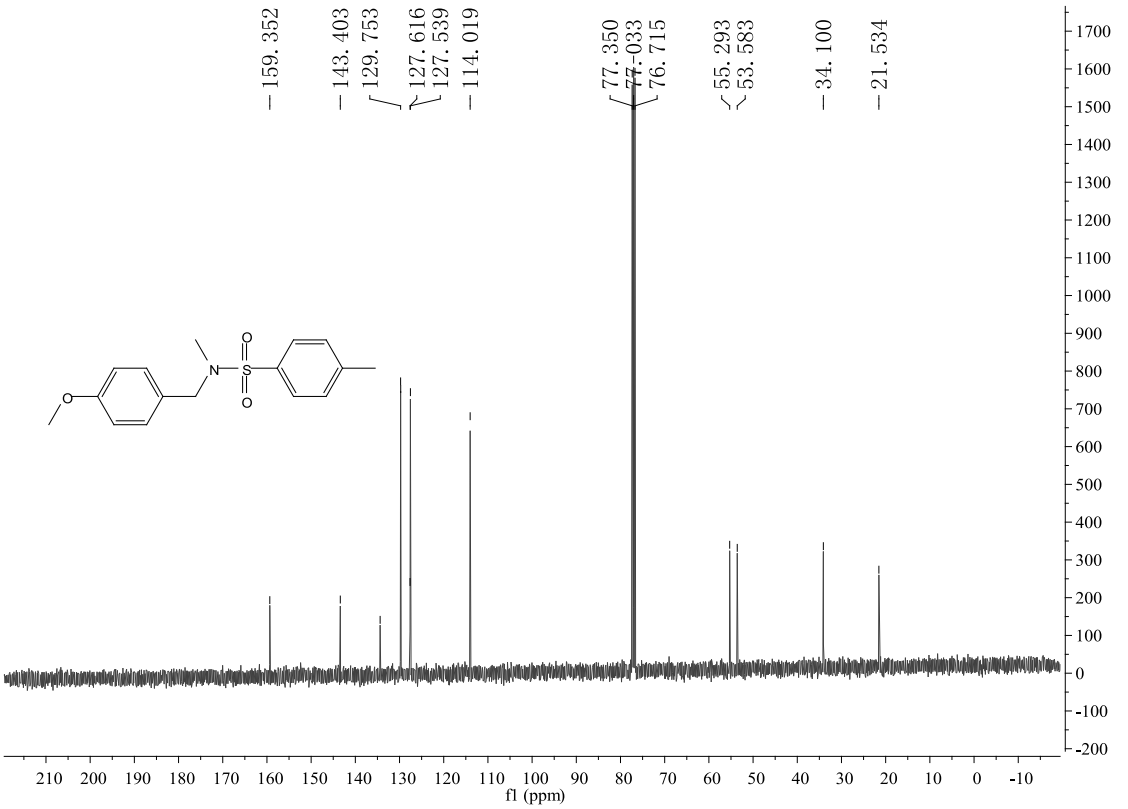
2.04
2.01
1.98
2.03
2.00
3.01
2.98
3.00
f1 (ppm)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77.033
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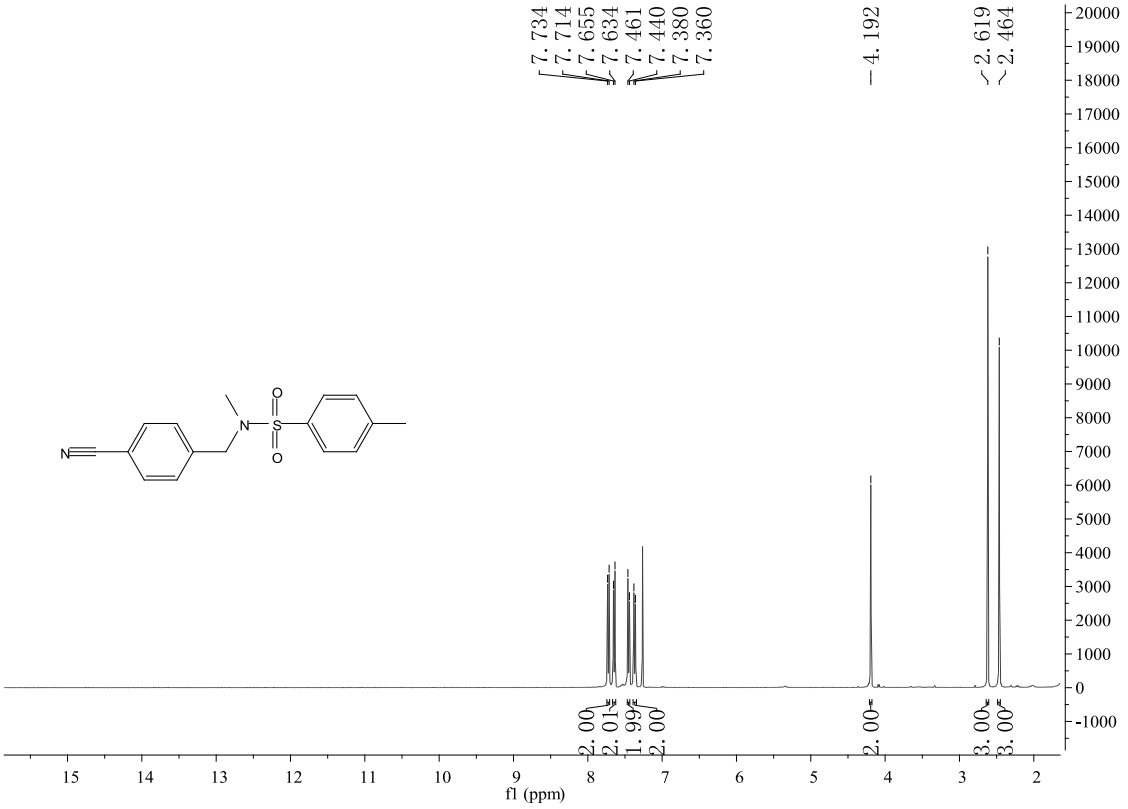
34.100
21.534
f1 (ppm)

3a5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7.714
7.655
7.634
7.461
7.440
7.380
7.360
4.192
2.619
2.464
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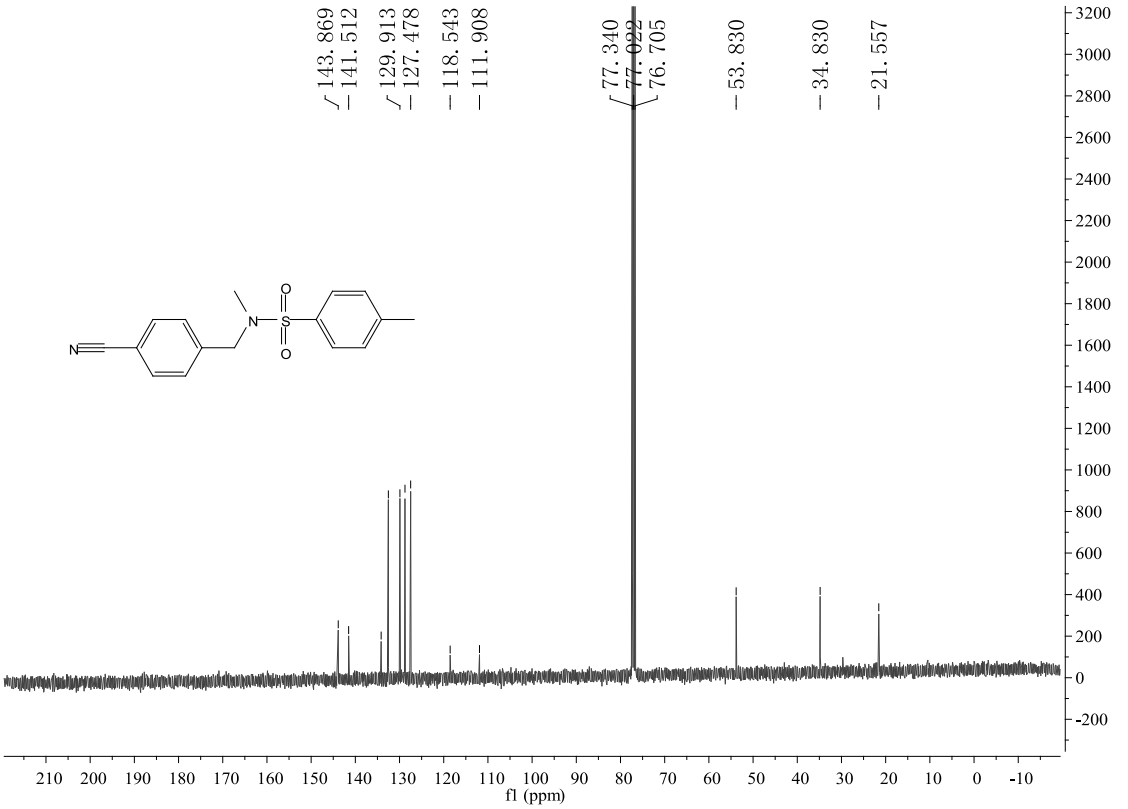
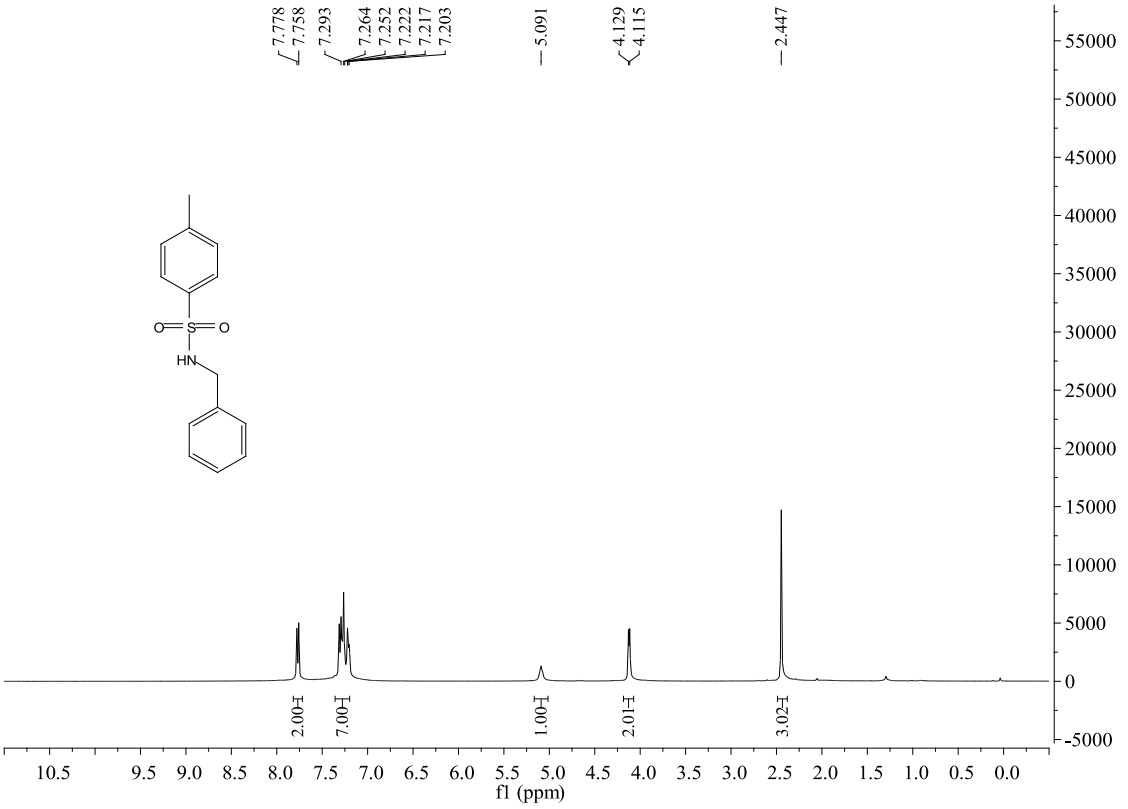
2.00
2.00
3.00
3.00
f1 (ppm)


143.869
141.512
129.913
127.478
118.543
111.908
77.340
77.022
76.705
53.830
34.830
21.557
f1 (ppm)

3a6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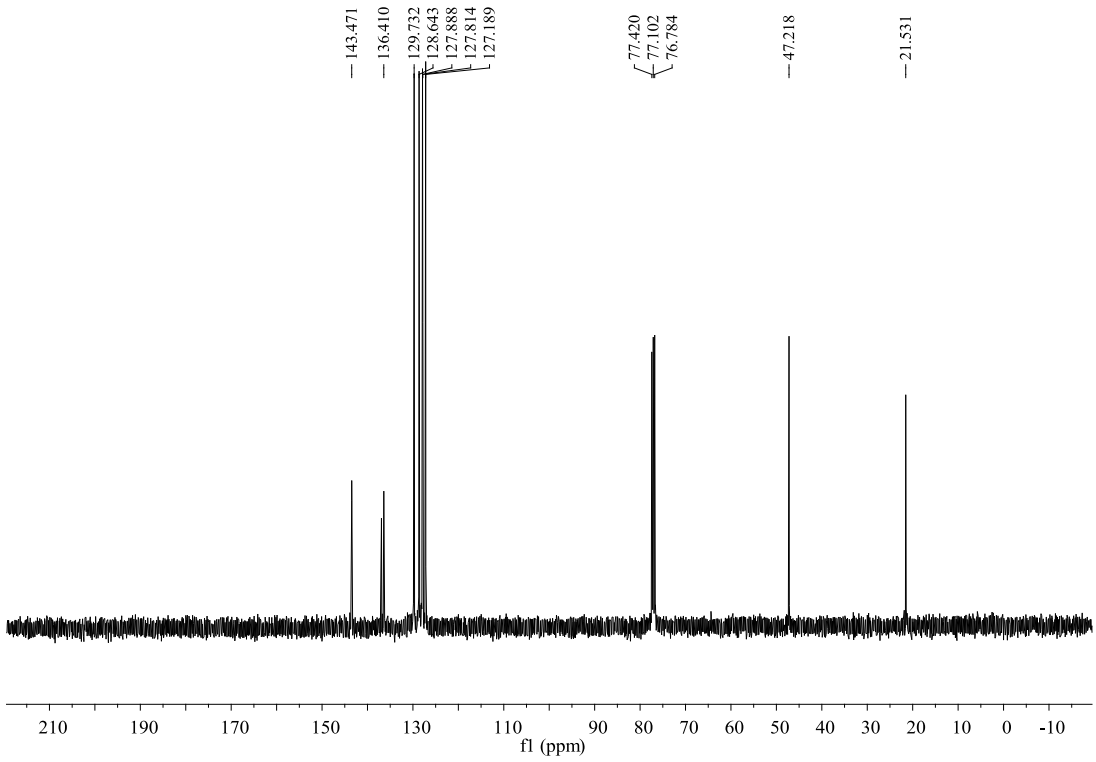
7.758
7.293
7.264
7.252
7.222
7.217
7.203
5.091
4.129
4.115
2.447
O
S
O
HN
2.00
7.00
1.00
2.01
3.02
f1 (ppm)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136.410
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127.814
127.189
77.420
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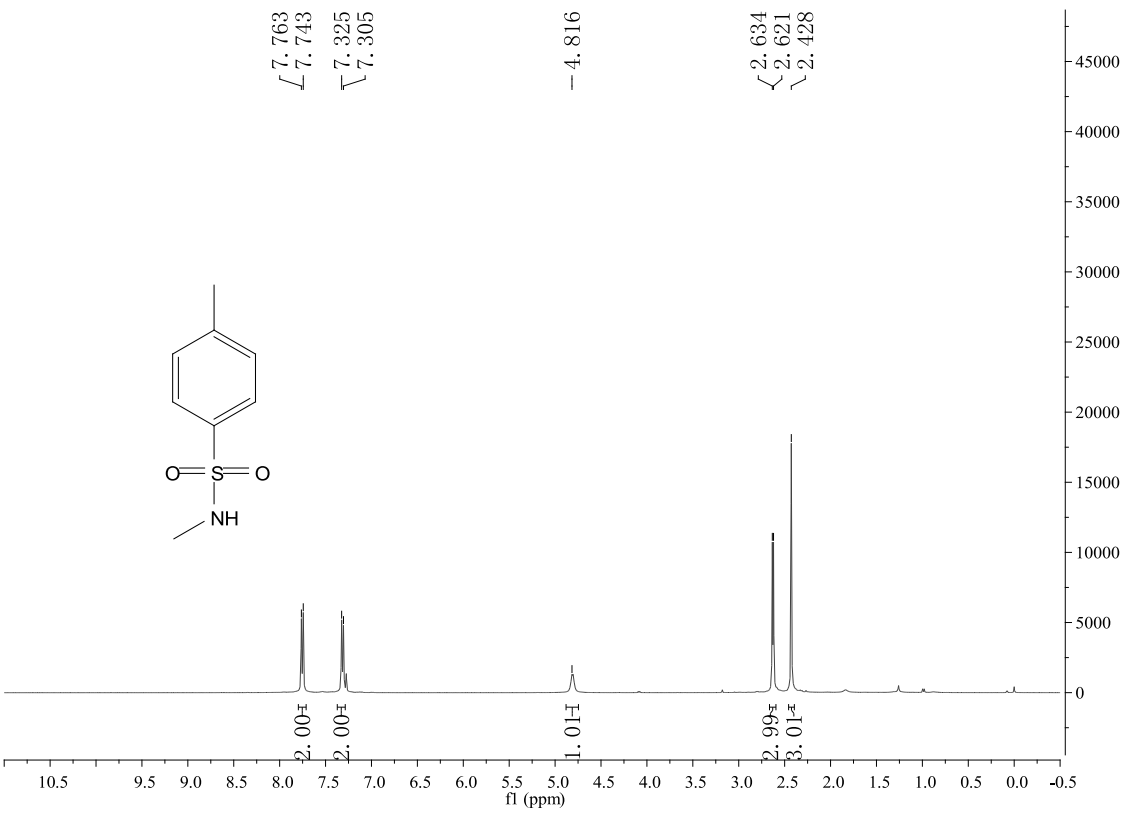
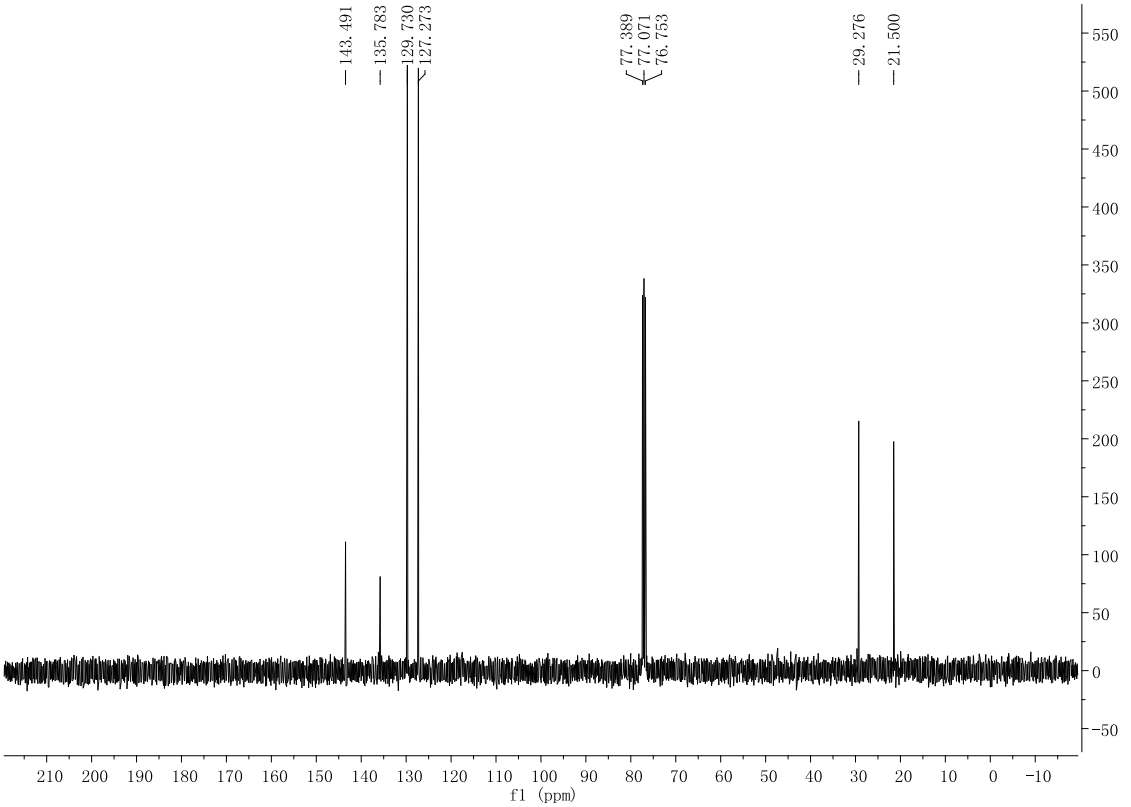
76.784
47.218
21.531
f1 (ppm)

3b


7.763
7.743
7.325
7.305
4.816
2.634
2.621
2.428
O
S
O
NH
2.00
2.00
1.01
2.99
3.01
f1 (ppm)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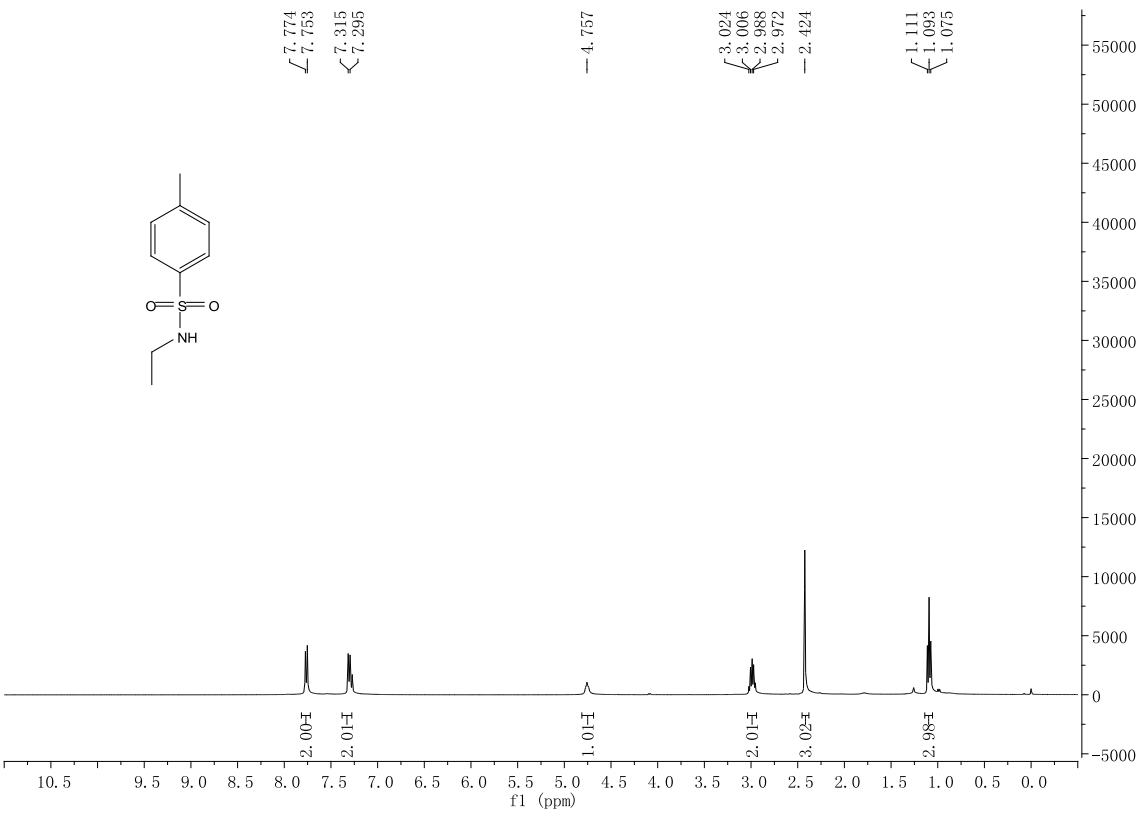
76.753
29.276
21.500
f1 (ppm)

3c1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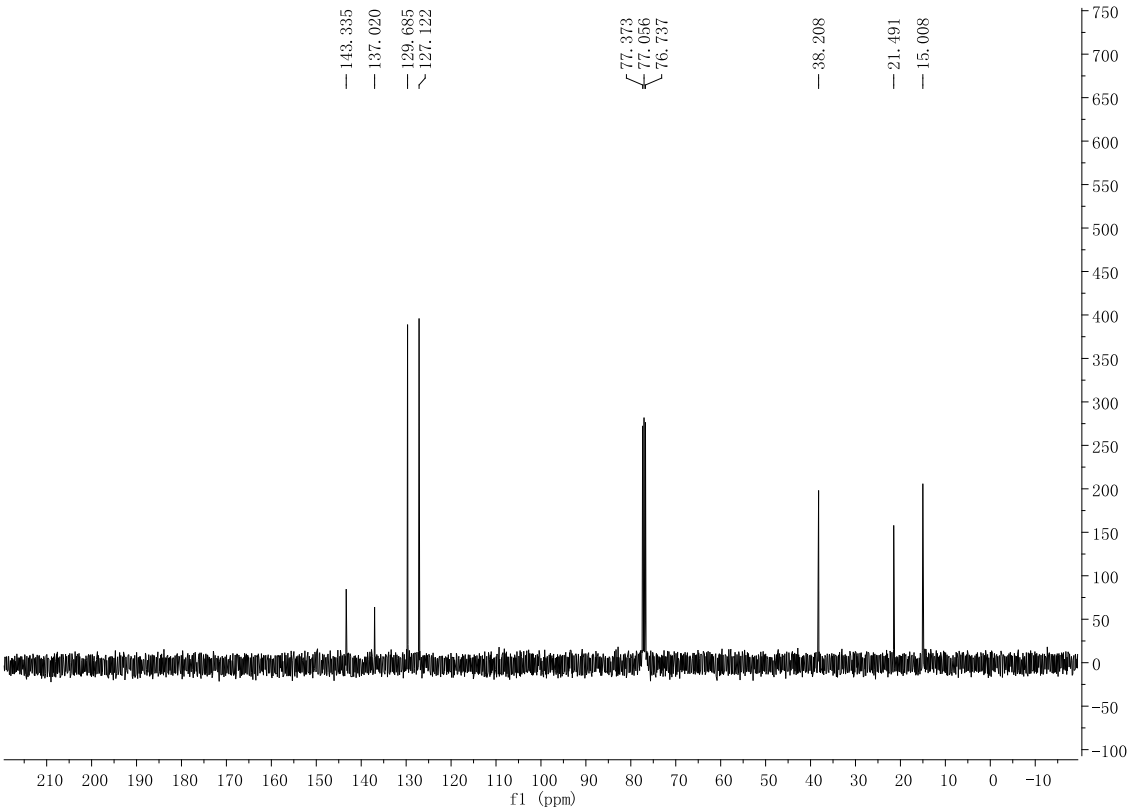
7.753
7.315
7.295
4.757
3.024
3.006
2.988
2.972
2.424
1.111
1.093
1.075
O
S
O
NH
2.00
2.01
1.01
2.01
3.02
2.98
f1 (ppm)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77.056
76.737
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15.008
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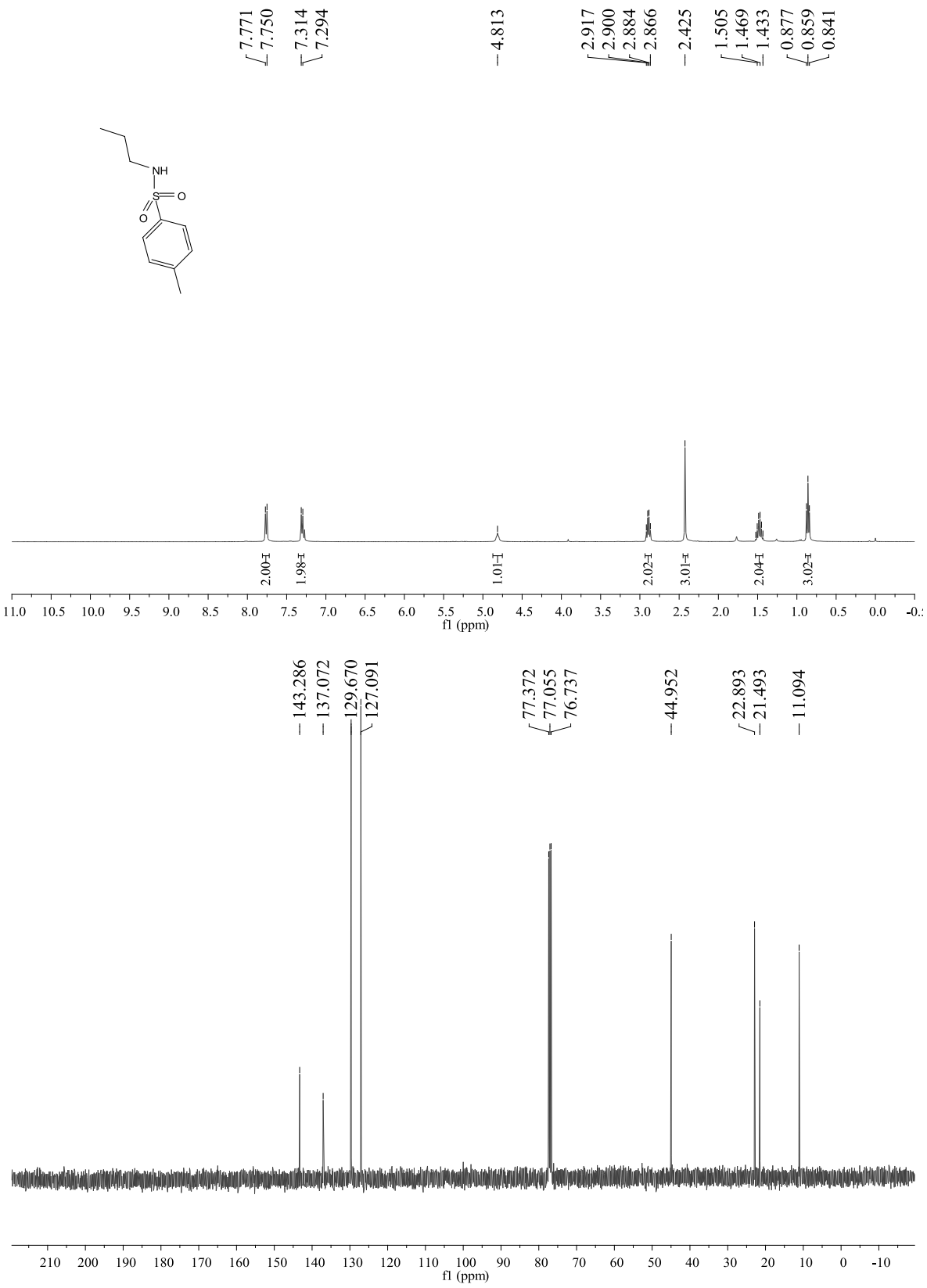
3c2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7.750
7.314
7.294
4.813
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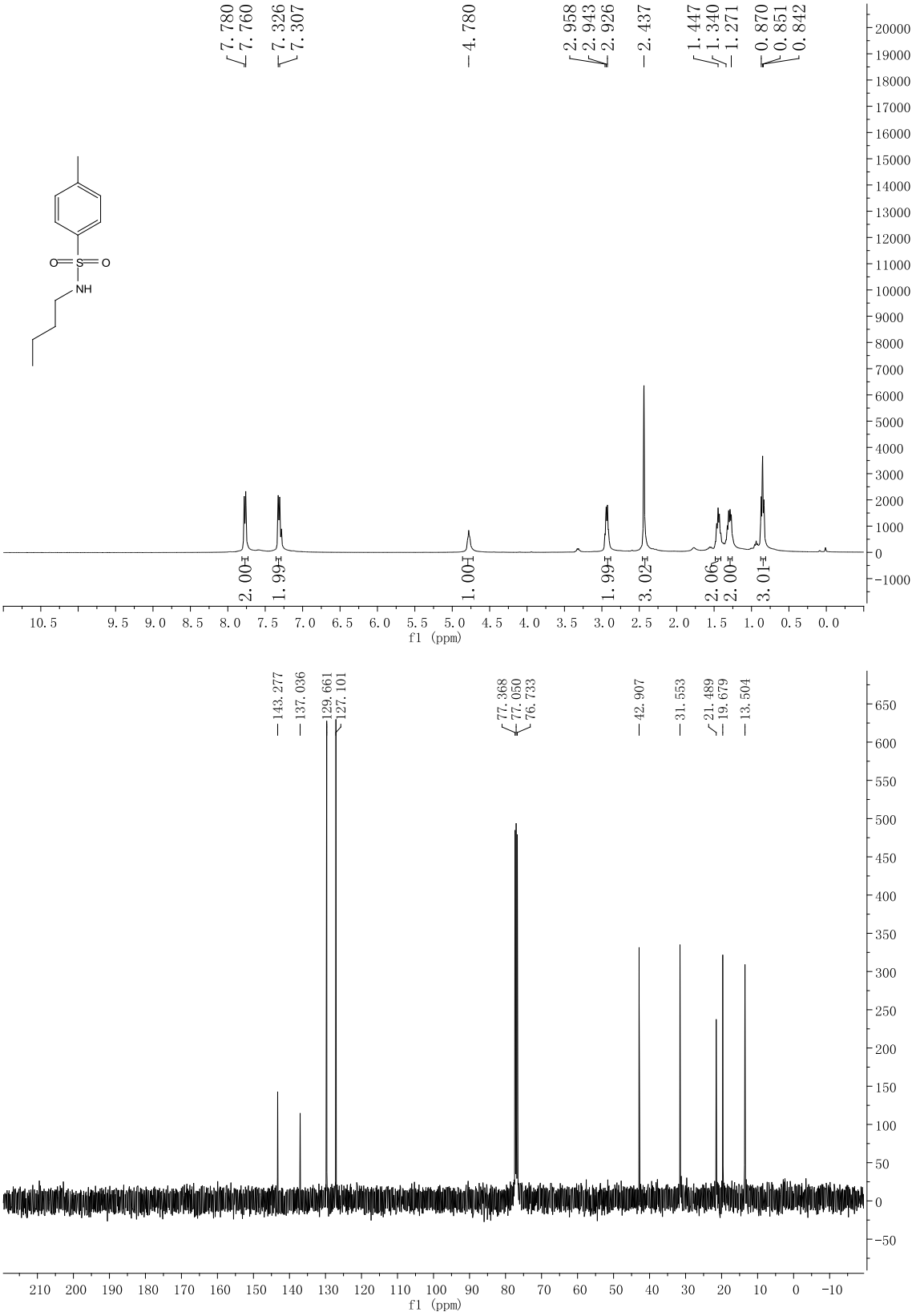
2.900
2.884
2.866
2.425
1.505
1.469
1.433
0.877
0.859
0.841
NH
S
O
O
2.00
1.98
1.01
2.02
3.01
2.04
3.02
fl (ppm)
143.286
137.072
129.670
127.091
77.372
77.055
76.737
44.952
22.893
21.493
11.094
fl (ppm)

3c3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7.307
4.780
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2.926
2.437
1.447
1.340
1.271
0.870
0.851
0.842
O
S
O
NH
2.00
1.99
1.00
1.99
3.02
2.06
2.00
3.01
f1 (ppm)
143.277
137.036
129.661
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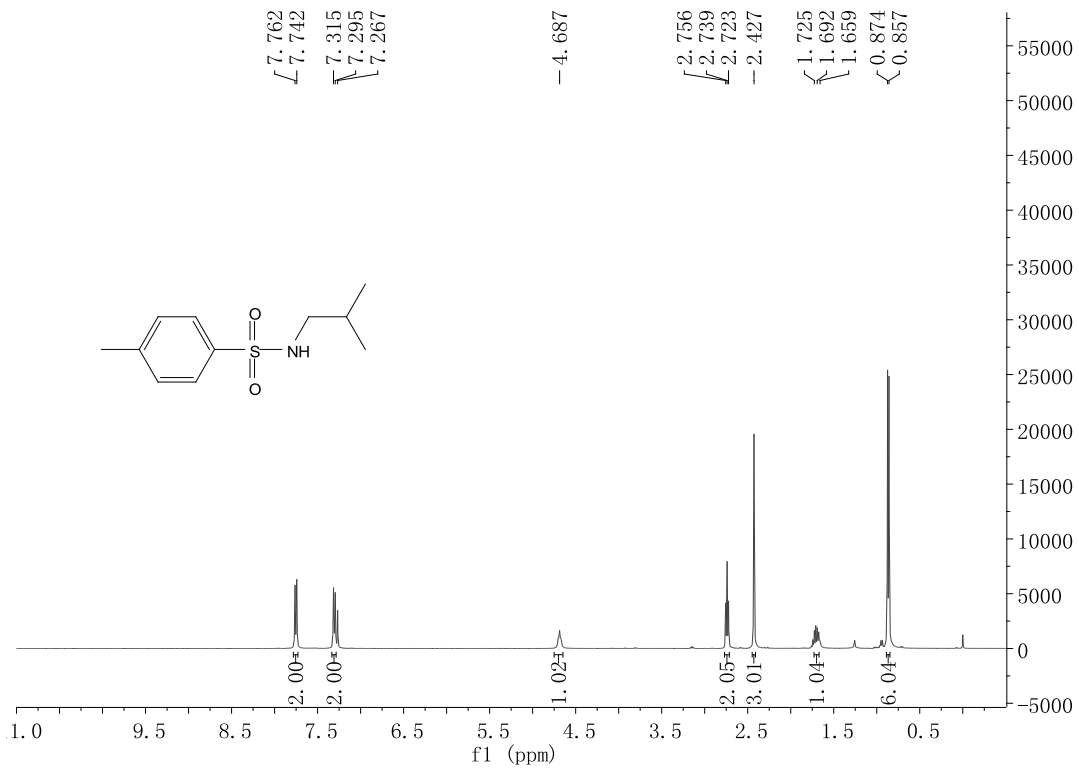
77.050
76.733
42.907
31.553
21.489
19.679
13.504
f1 (ppm)

3c4


7.762
7.742
7.315
7.295
7.267
4.687
2.756
2.739
2.723
2.427
1.725
1.692
1.659
0.874
0.857
O
S
NH
O
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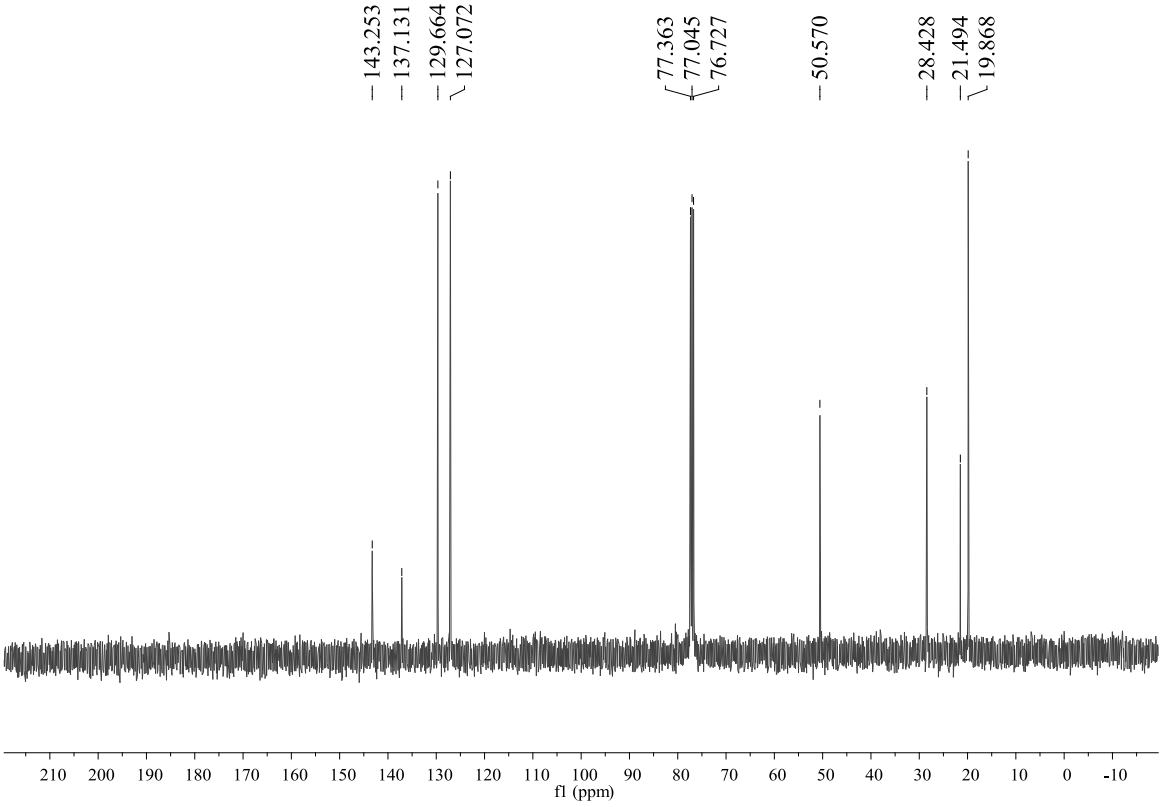
2.00
1.02
2.05
3.01
1.04
6.04
f1 (ppm)


143.253
137.131
129.664
127.072
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77.045
76.727
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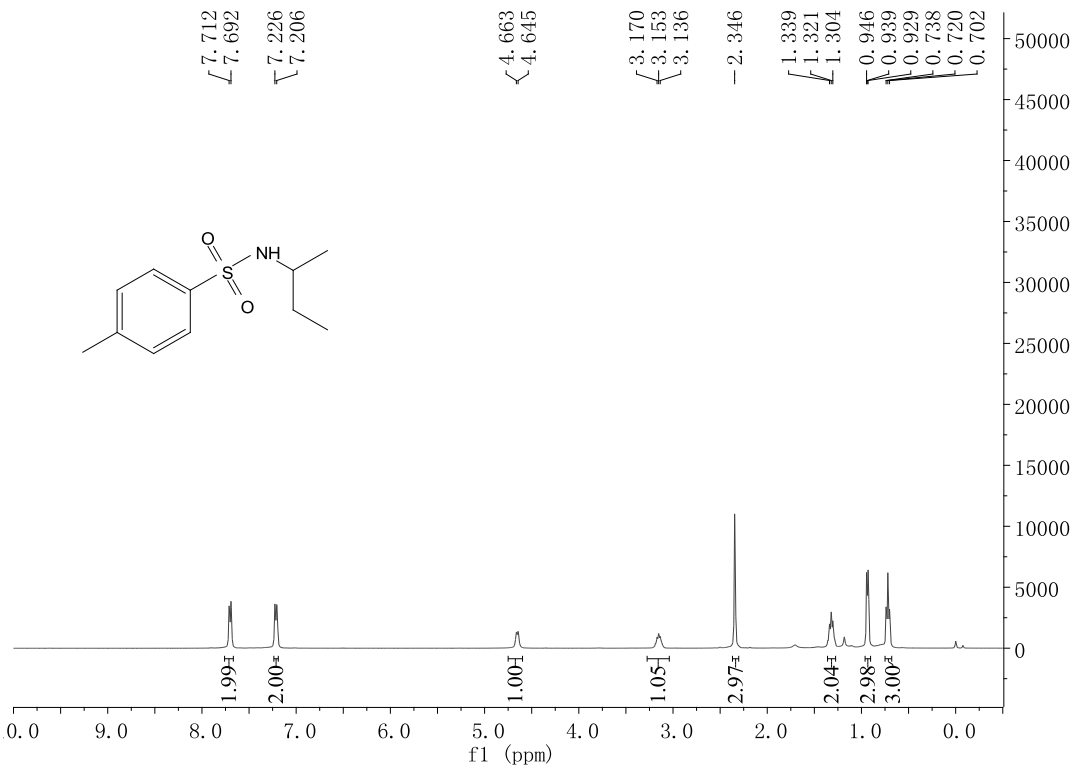
28.428
21.494
19.868
f1 (ppm)

3c5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7.206
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4.645
3.170
3.153
3.136
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1.339
1.321
1.304
0.946
0.939
0.929
0.738
0.720
0.702
O
NH
S
O
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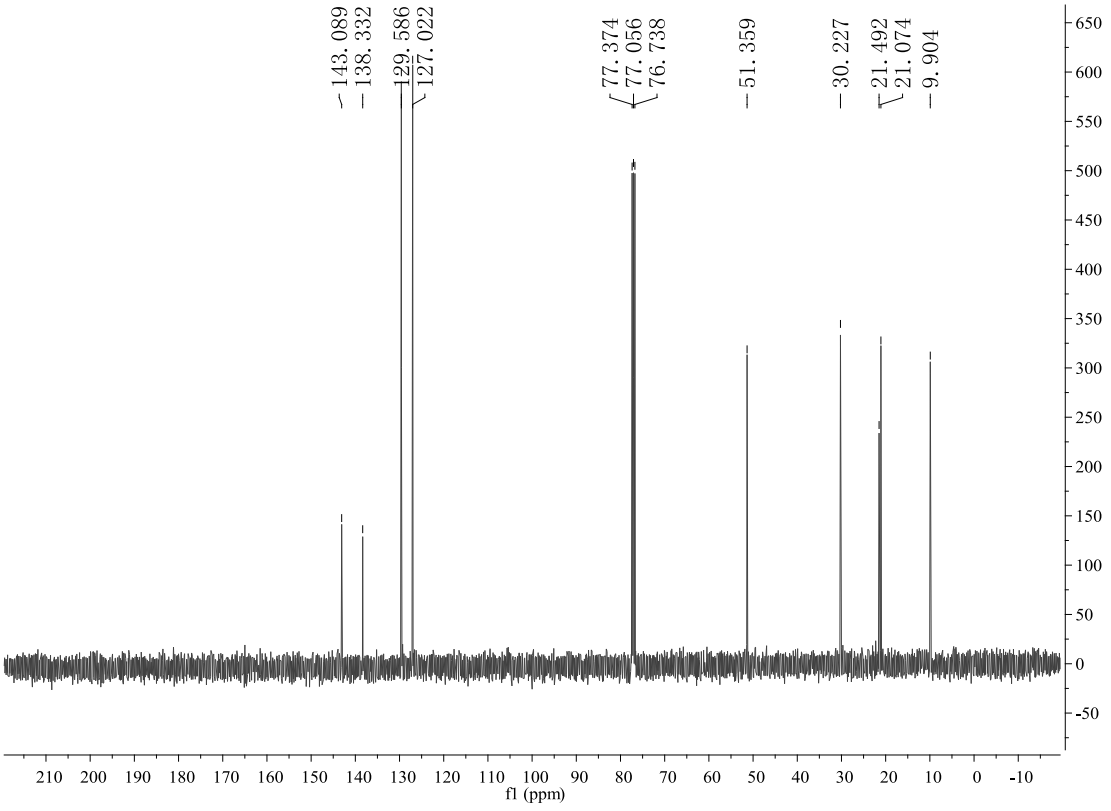
2.00
1.00
1.05
2.97
2.04
2.98
3.00
f1 (ppm)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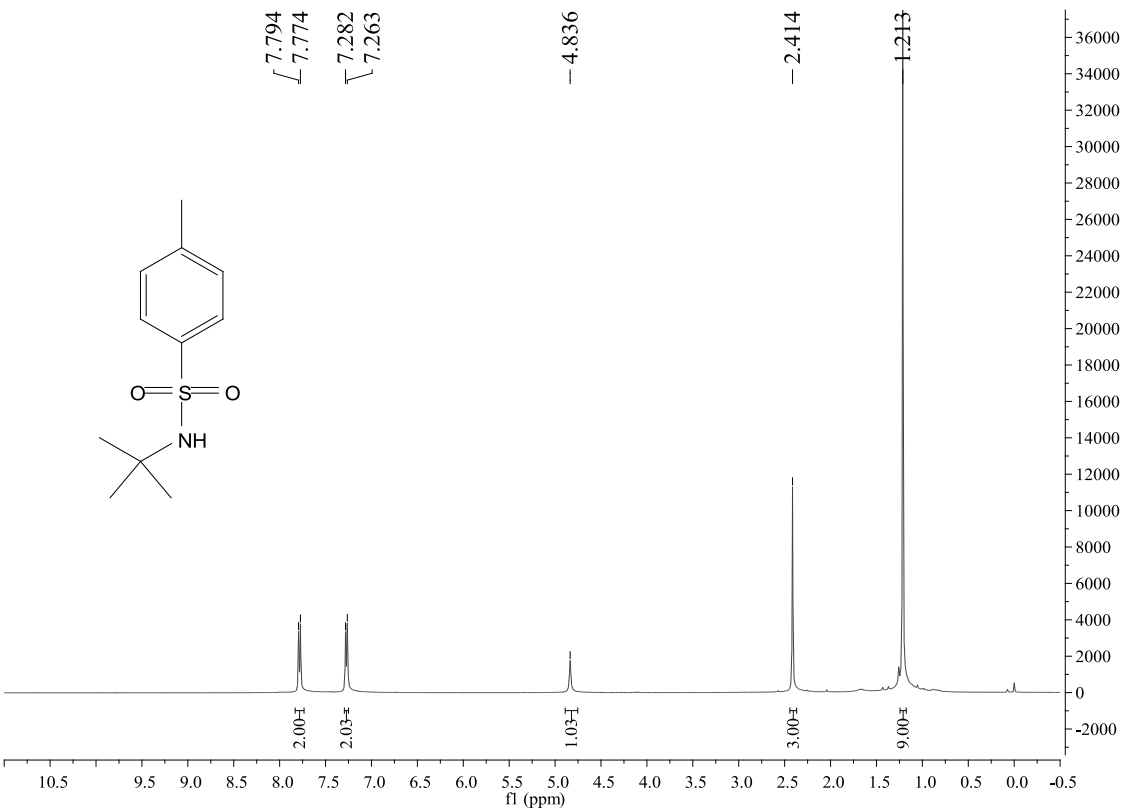
3c6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7.263
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O
S
O
NH
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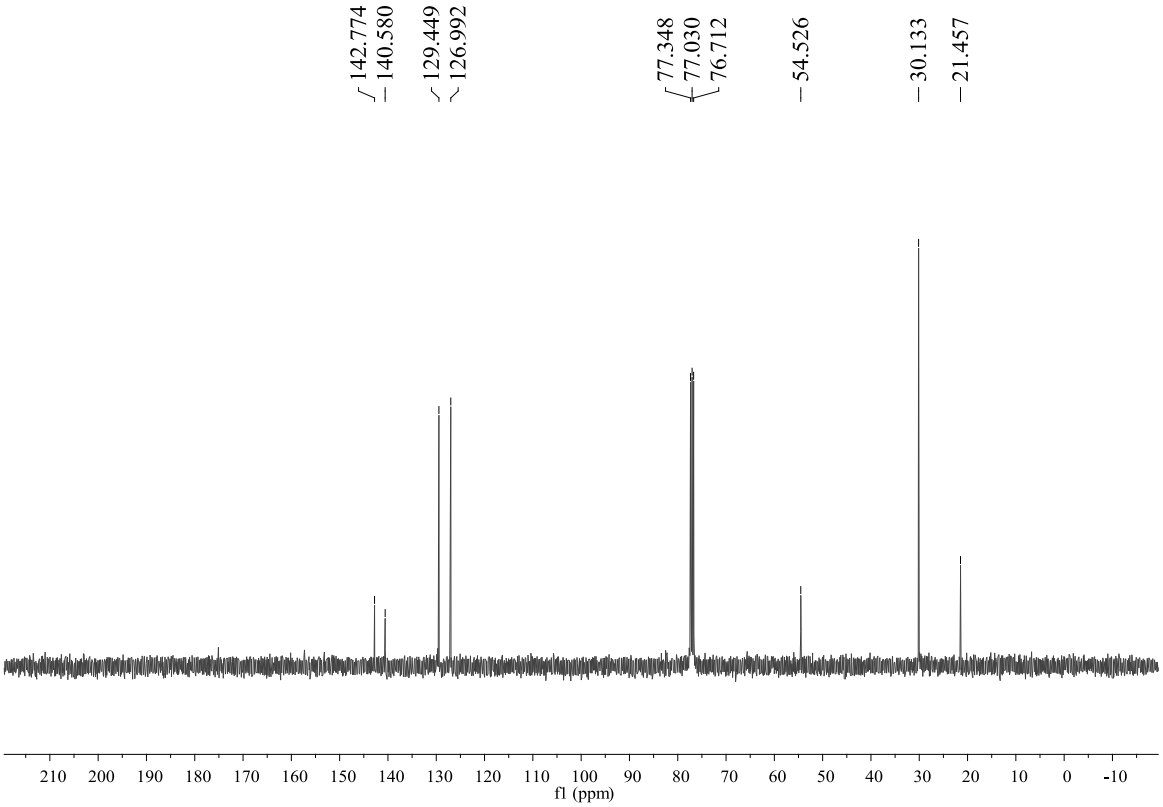
1.03
3.00
9.00
fl (ppm)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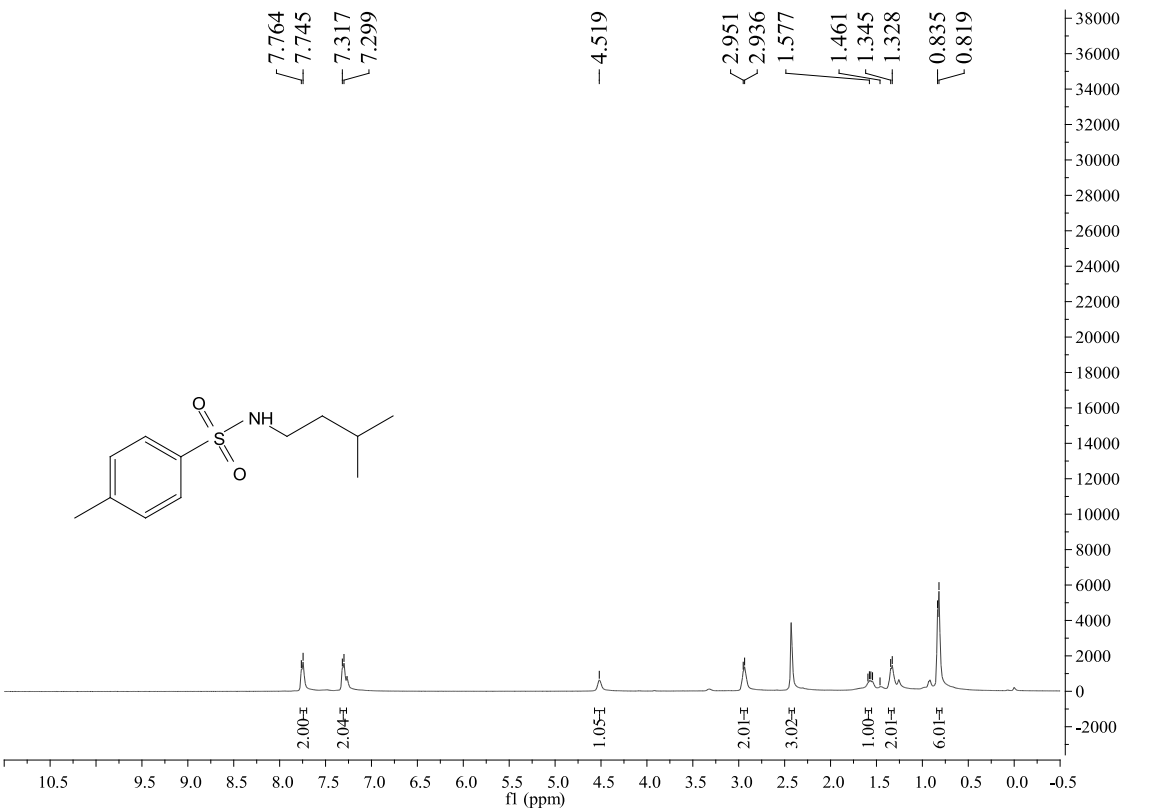
129.449
126.992
77.348
77.030
76.712
54.526
30.133
21.457
fl (ppm)

3c7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7.745
7.317
7.299
4.519
2.951
2.936
1.577
1.461
1.345
1.328
0.835
0.819
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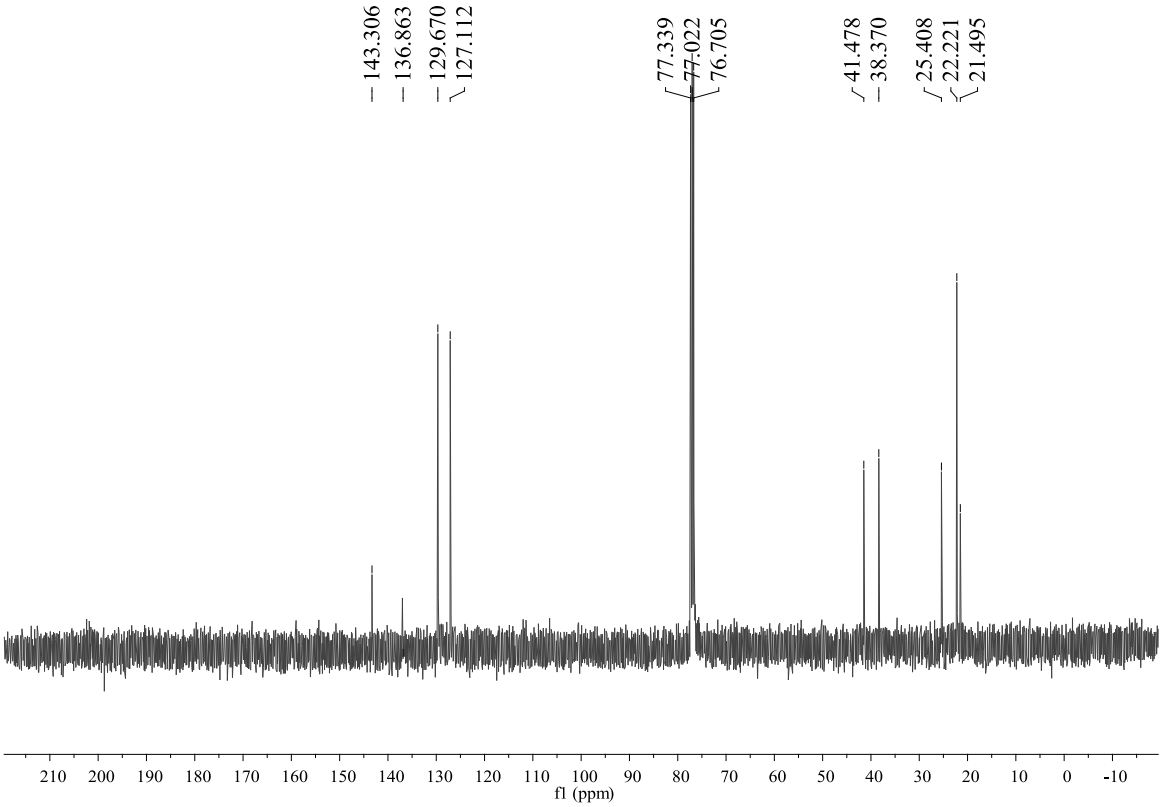
1.05
2.01
3.02
1.00
2.01
6.01
fl (ppm)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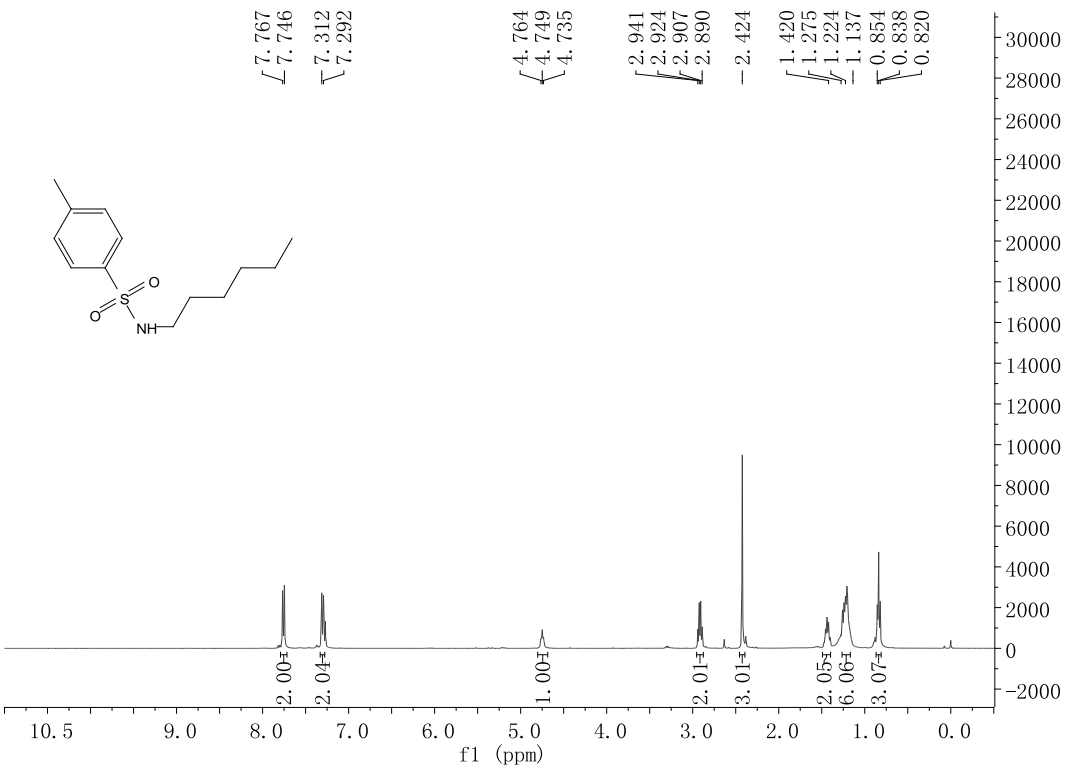
22.221
21.495
fl (ppm)

3c8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2.924
2.907
2.890
2.424
1.420
1.275
1.224
1.137
0.854
0.838
0.820
O
O
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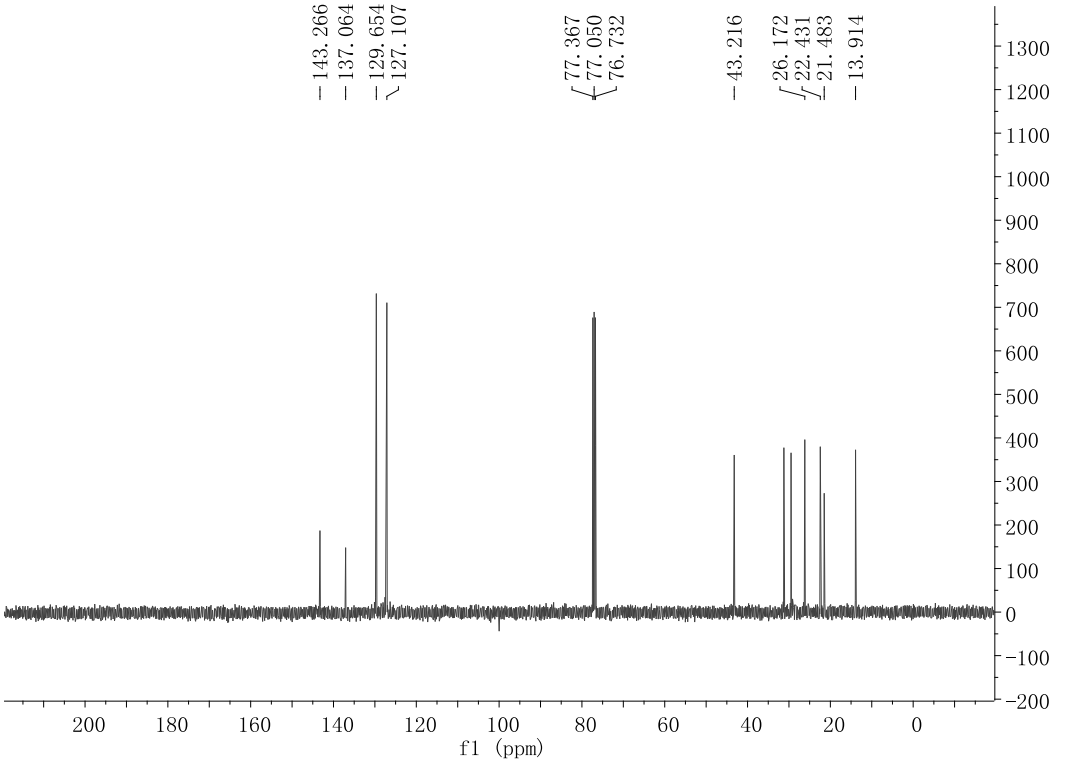
2.01
3.01
2.05
6.06
3.07
f1 (ppm)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77.050
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43.216
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22.431
21.483
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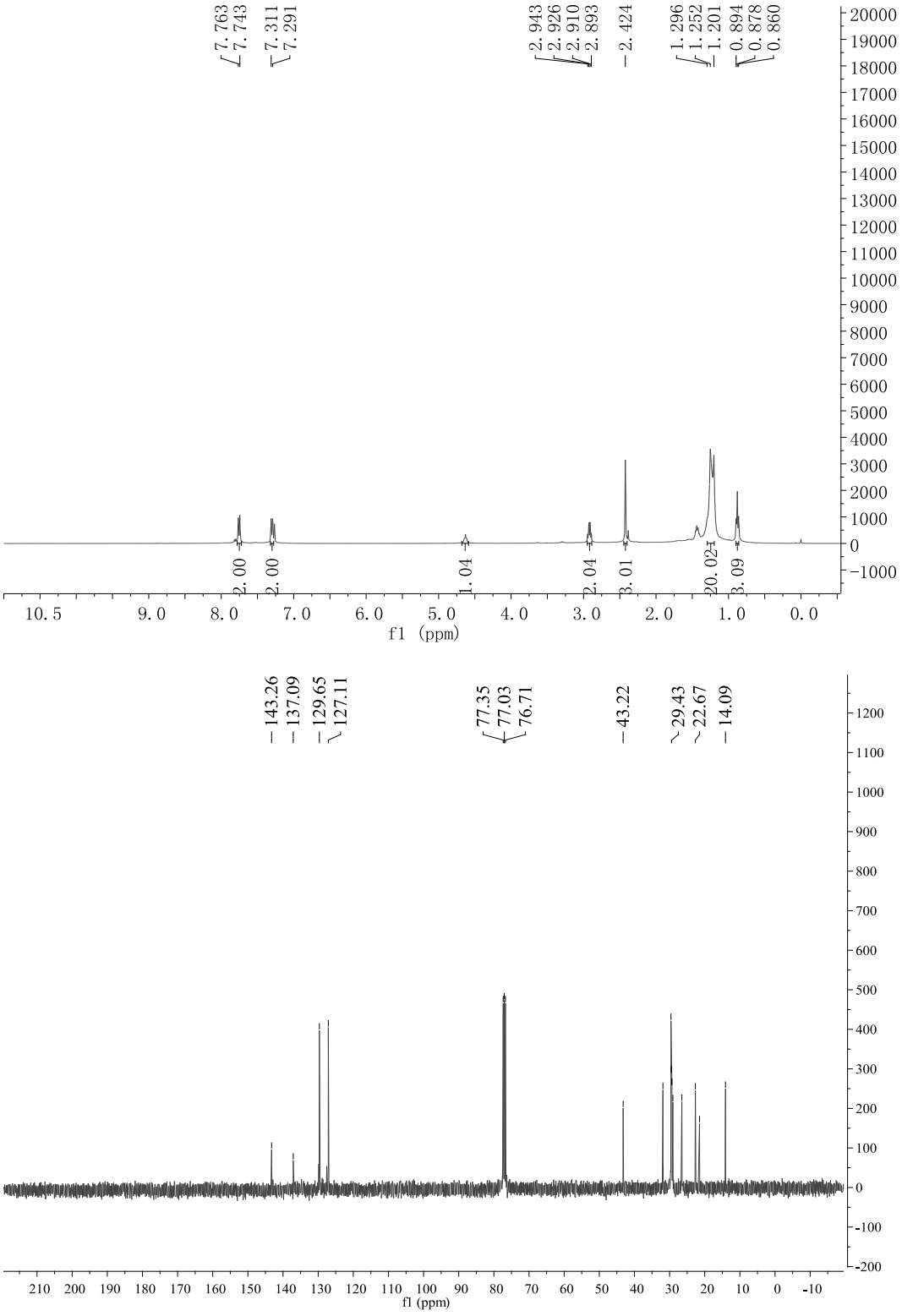
f1 (ppm)

3c9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7.743
7.311
7.291
2.943
2.926
2.910
2.893
2.424
1.296
1.252
1.201
0.894
0.878
0.860
2.00
2.00
1.04
2.04
3.01
20.02
3.09
f1 (ppm)
143.26
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127.11
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77.03
76.71
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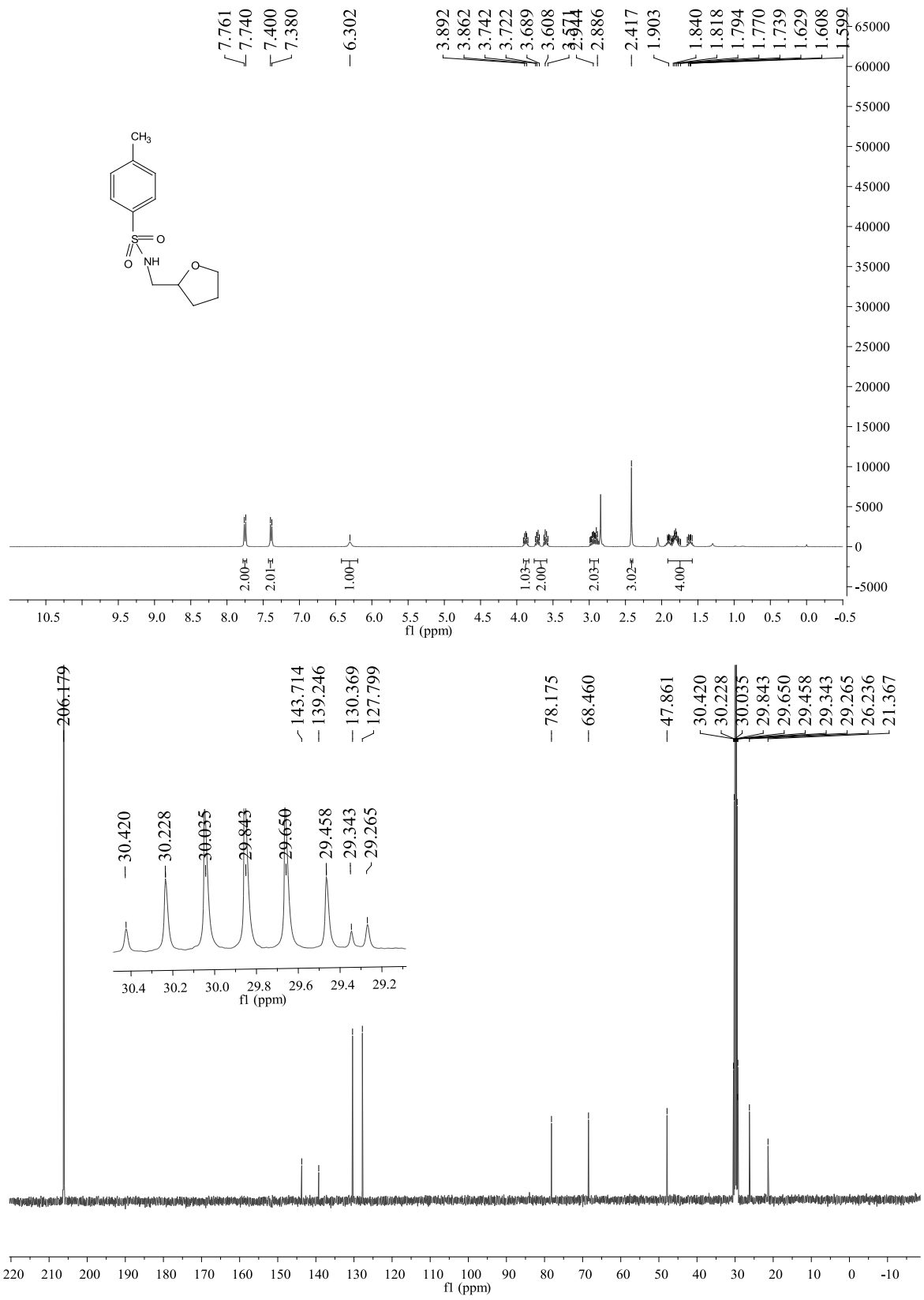
29.43
22.67
14.09
f1 (ppm)

3c10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7.400
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6.302
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3.608
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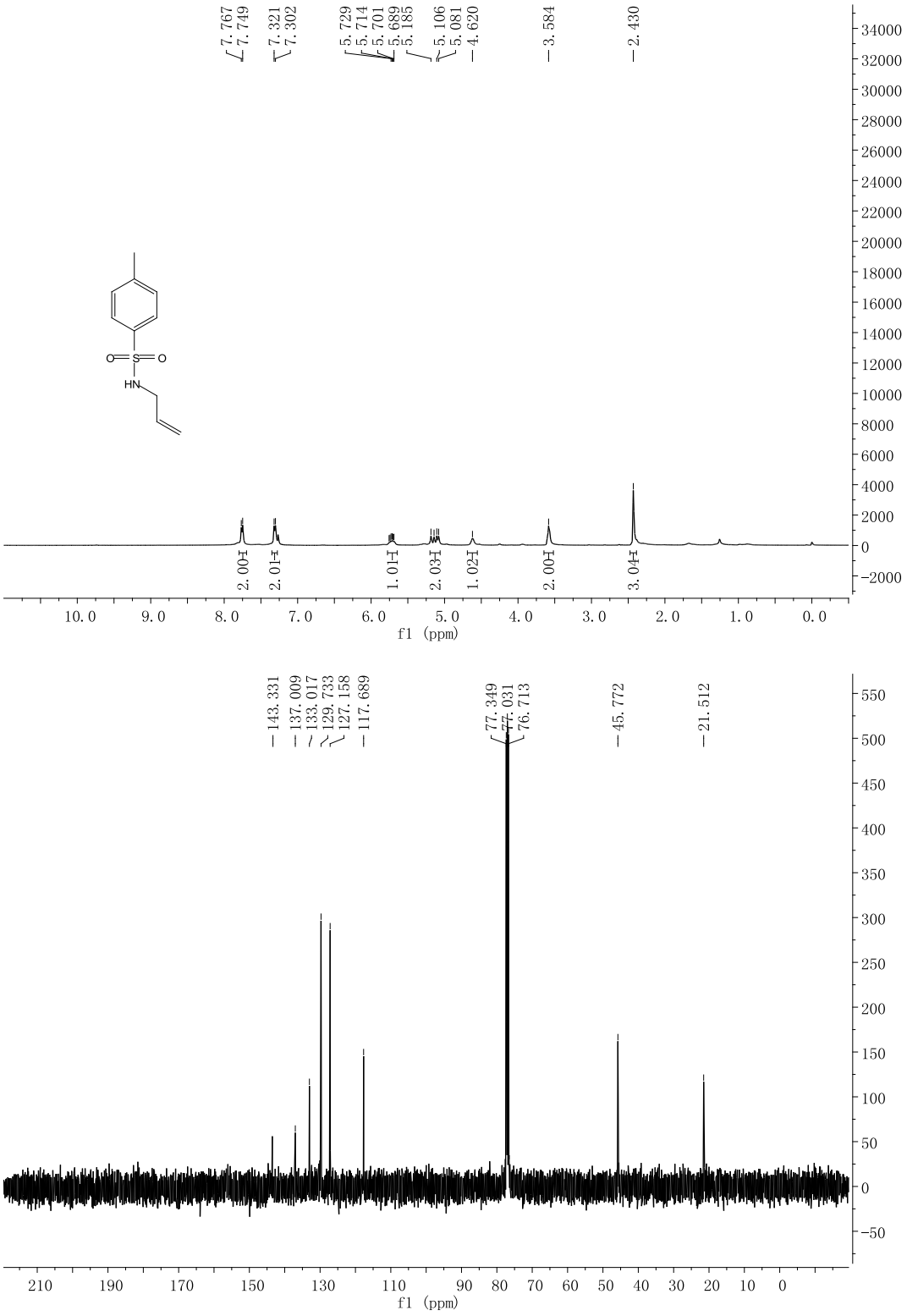
2.886
2.417
1.903
1.840
1.818
1.794
1.770
1.739
1.629
1.608
1.599
CH3
S
O
NH
O
2.00
2.01
1.00
1.03
2.00
2.03
3.02
4.00
fl (ppm)
206.179
143.714
139.246
130.369
127.799
78.175
68.460
47.861
30.420
30.228
30.035
29.843
29.650
29.458
29.343
29.265
26.236
21.367
fl (ppm)

3d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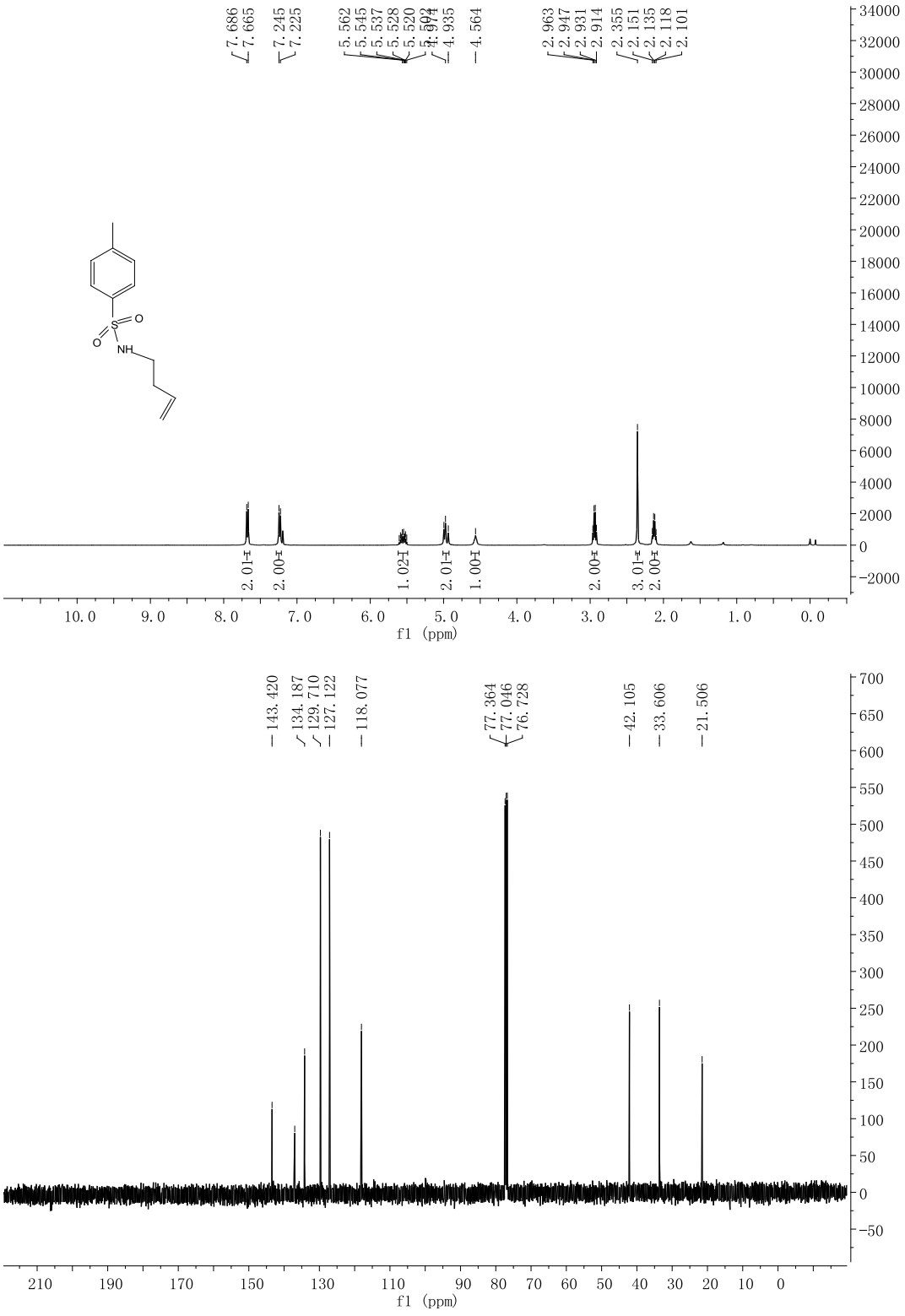
7.302
5.729
5.714
5.701
5.689
5.185
5.106
5.081
4.620
3.584
2.430
O
S
O
HN
2.00
2.01
1.01
2.03
1.02
2.00
3.04
f1 (ppm)
143.331
137.009
133.017
129.733
127.158
117.689
77.349
77.031
76.713
45.772
21.512
f1 (ppm)

3e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7.665
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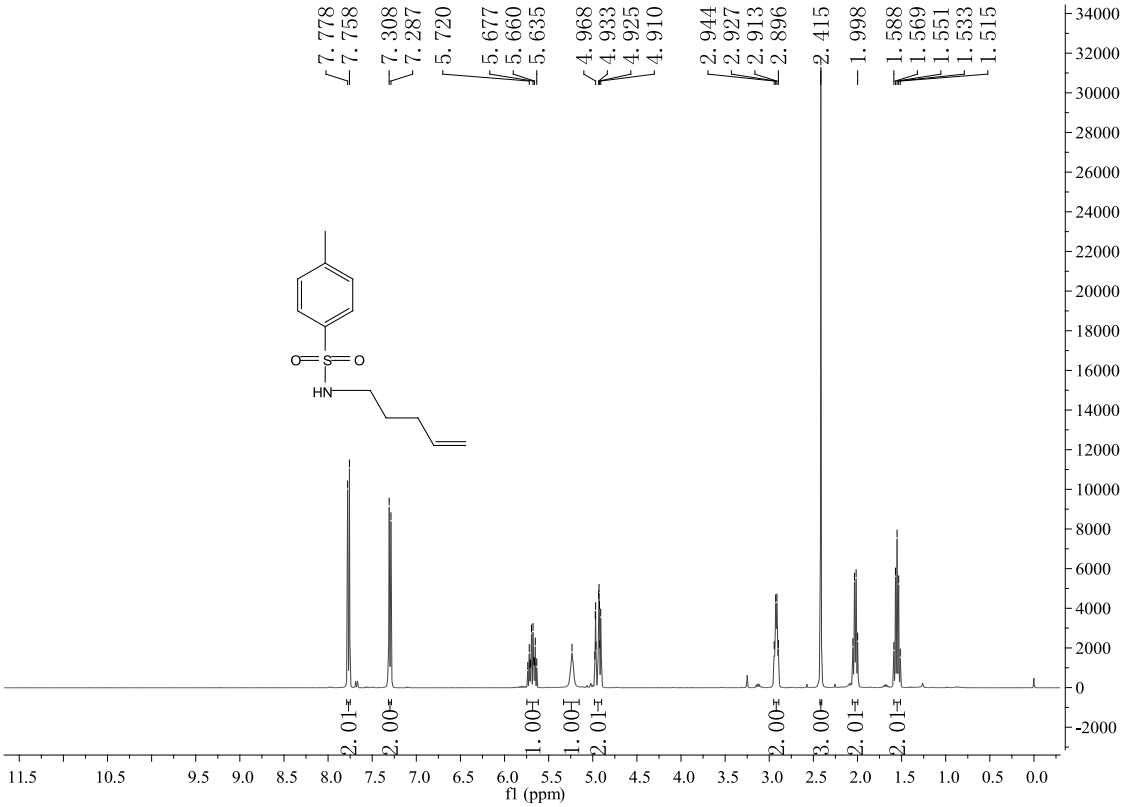
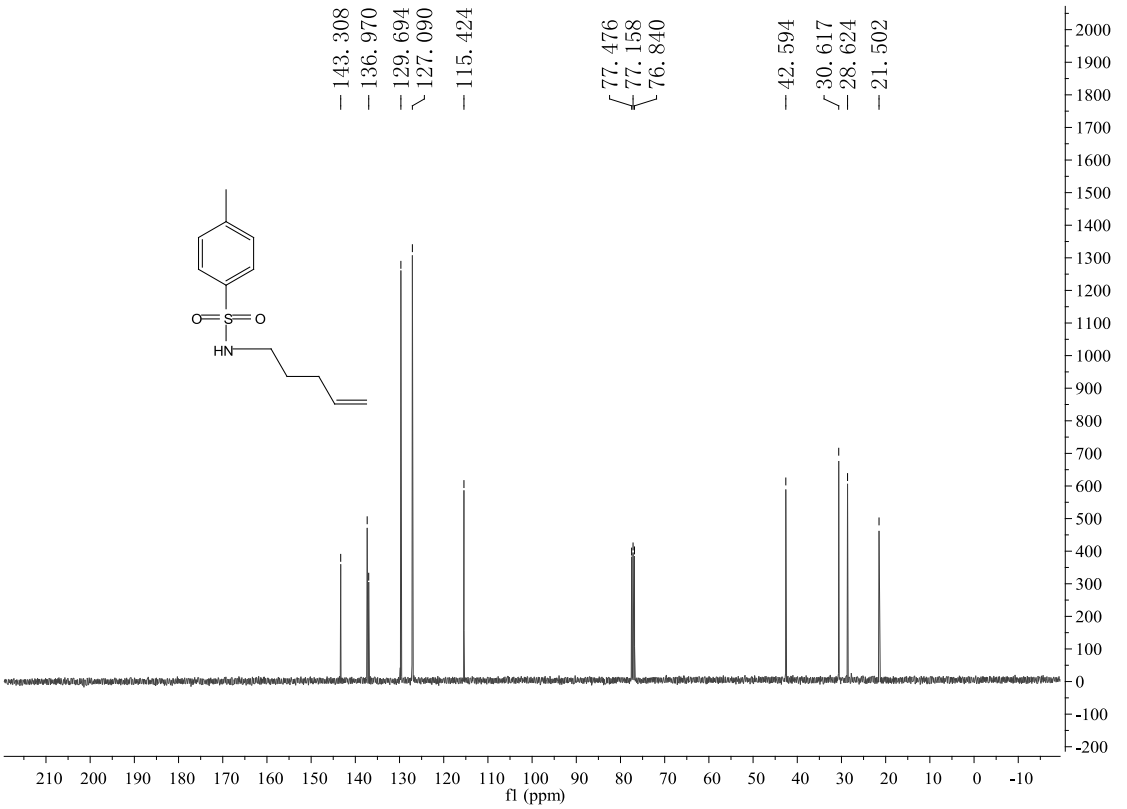
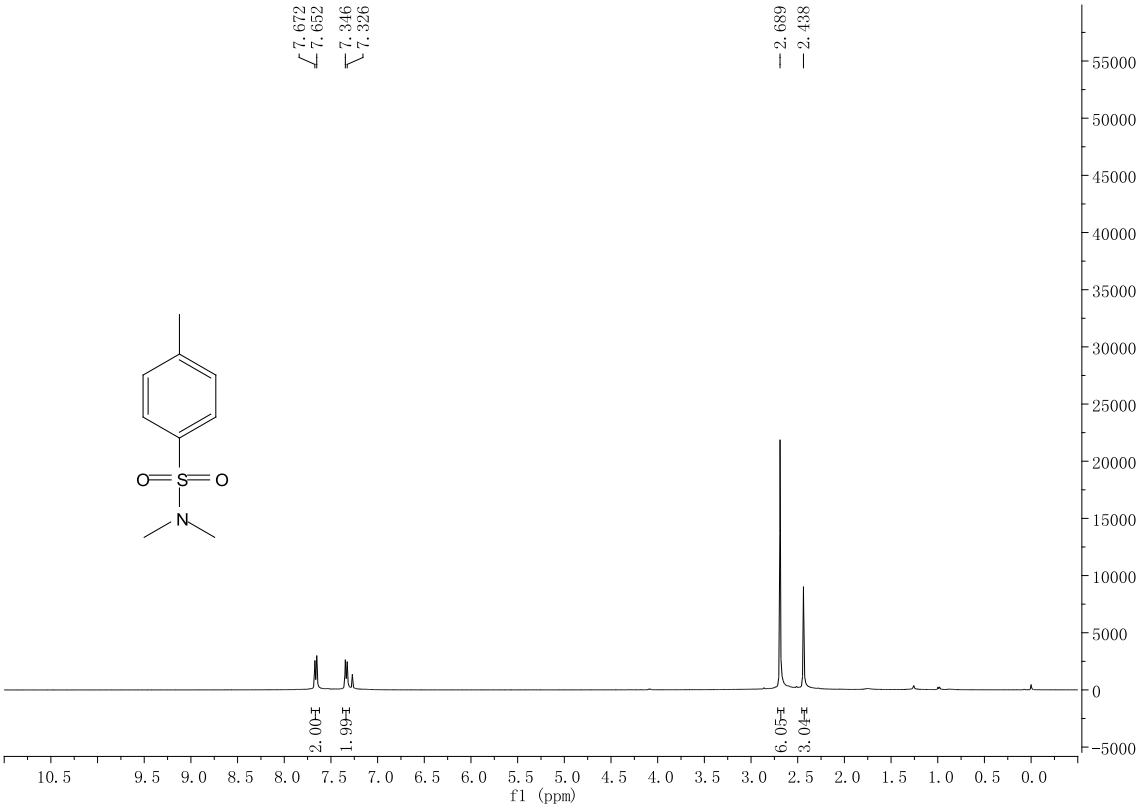
5.545
5.537
5.528
5.520
4.935
4.564
2.963
2.947
2.931
2.914
2.355
2.151
2.135
2.118
2.101
2.01
2.00
1.02
2.01
1.00
2.00
3.01
2.00
f1 (ppm)
143.420
134.187
129.710
127.122
118.077
77.364
77.046
76.728
42.105
33.606
21.506
f1 (ppm)

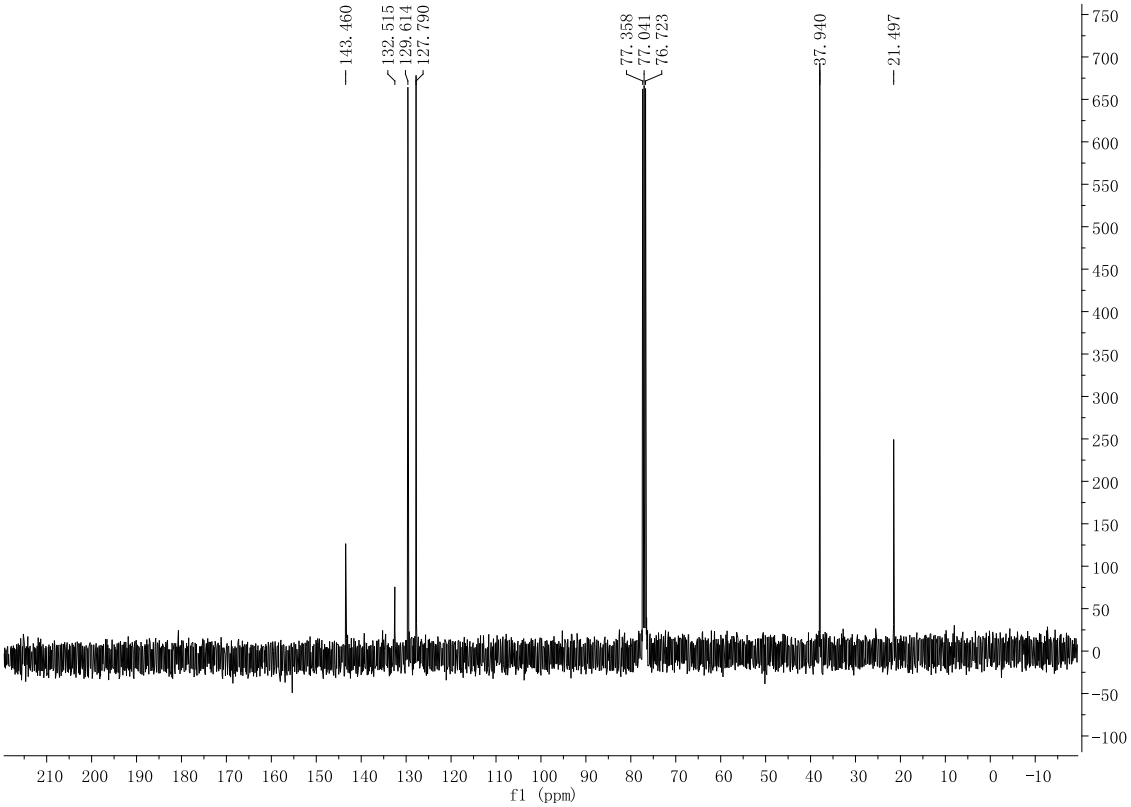
3f


7.778
7.758
7.308
7.287
5.720
5.677
5.660
5.635
4.968
4.933
4.925
4.910
2.944
2.927
2.913
2.896
2.415
1.998
1.588
1.569
1.551
1.533
1.515
HN
2.01
2.00
1.00
1.00
2.01
2.00
3.00
2.01
2.01
f1 (ppm)

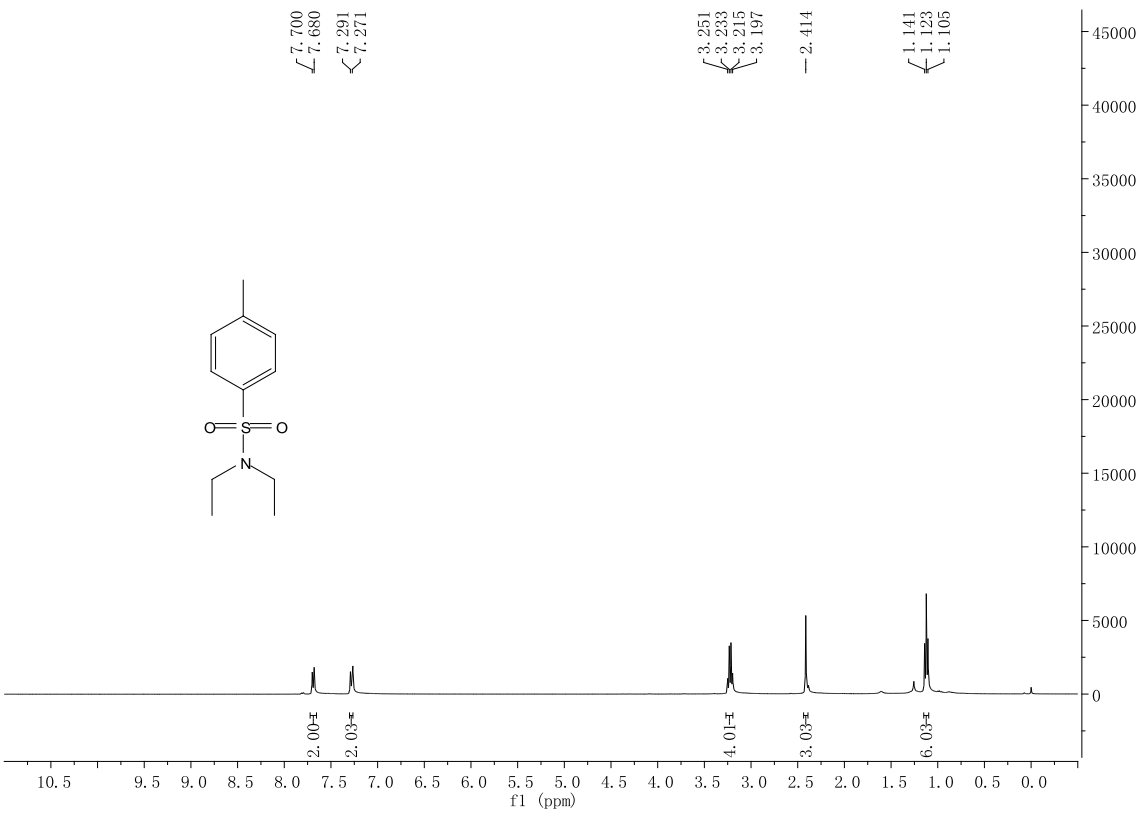

143.308
136.970
129.694
127.090
115.424
77.476
77.158
76.840
42.594
30.617
28.624
21.502
HN
f1 (ppm)

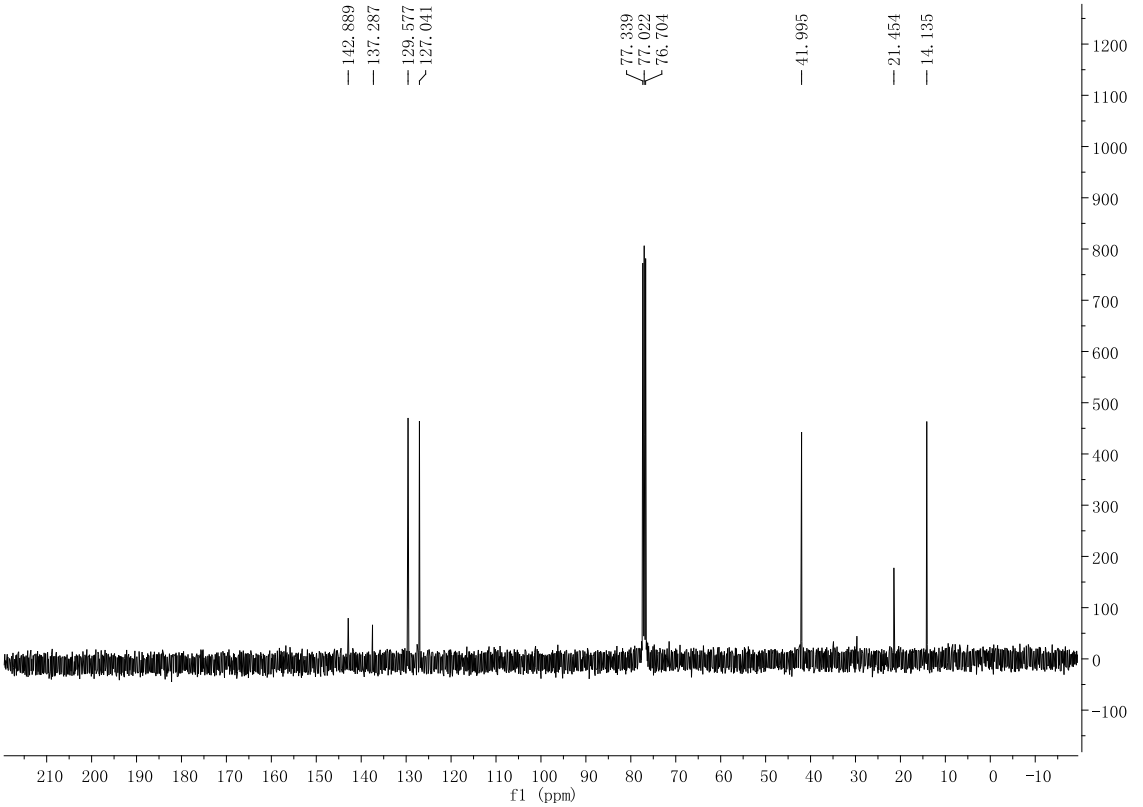
3g


7.672
7.652
7.346
7.326
2.689
2.438
2.00
1.99
6.05
3.04
f1 (ppm)

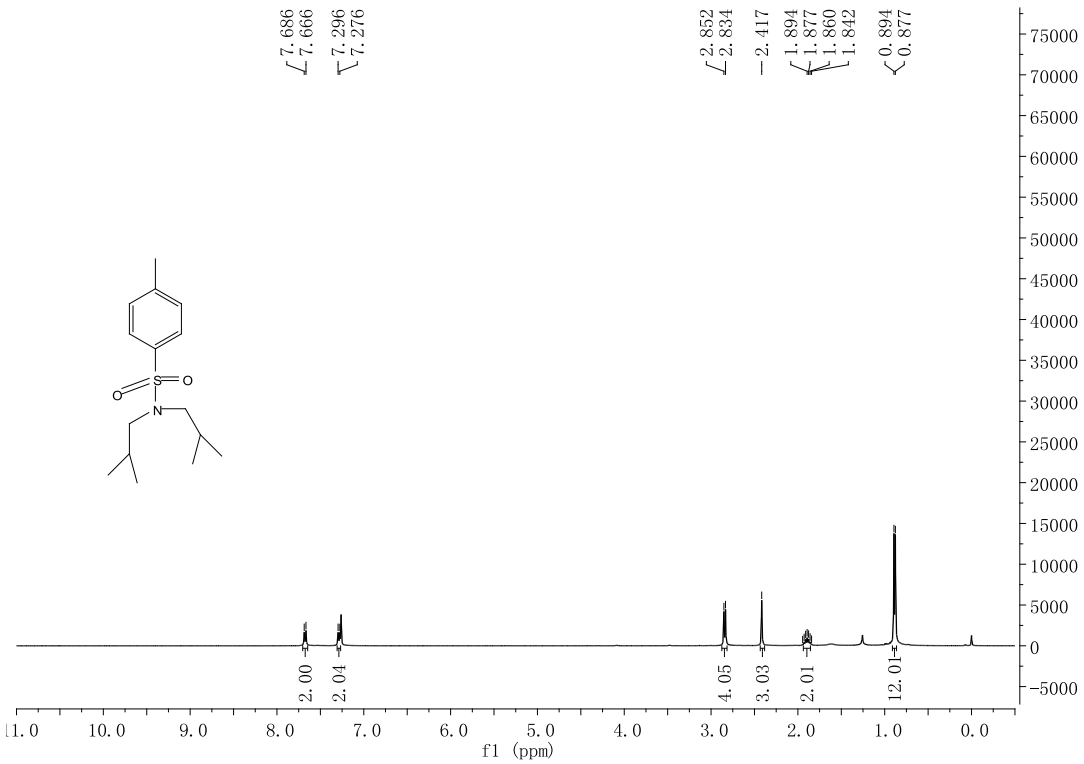

143.460
132.515
129.614
127.790
77.358
77.041
76.723
37.940
21.497
f1 (ppm)

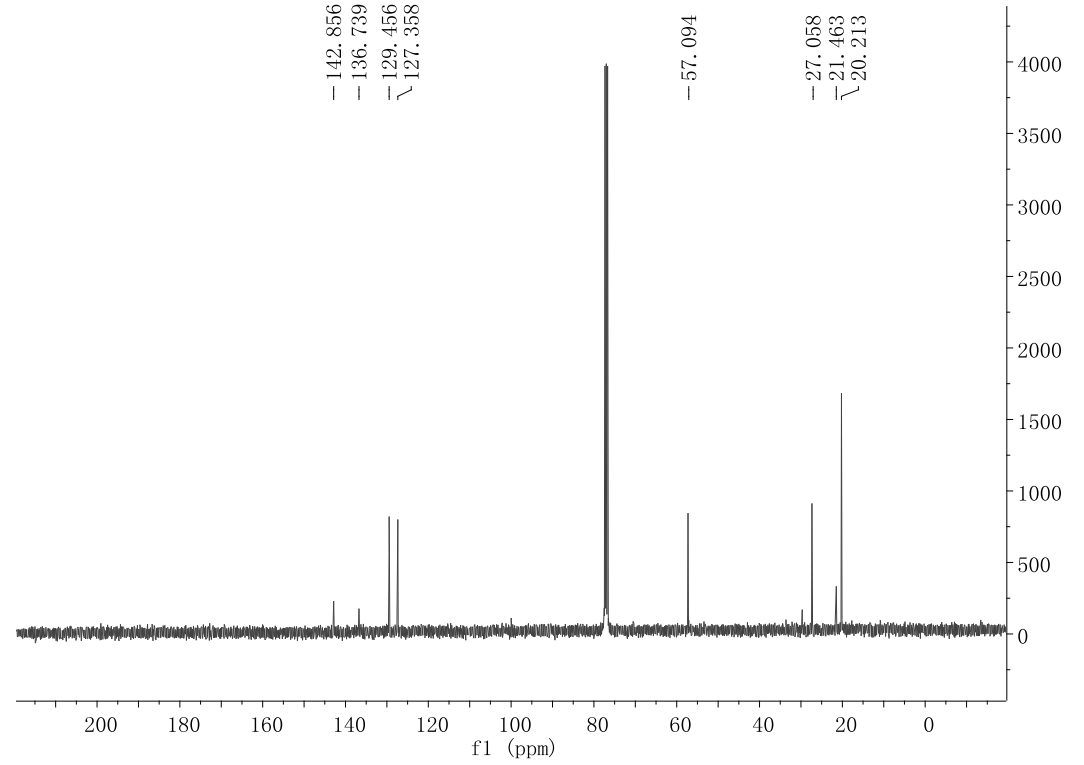
3h


7.700
7.680
7.291
7.271
3.251
3.233
3.215
3.197
2.414
1.141
1.123
1.105
2.00
2.03
4.01
3.03
6.03
f1 (ppm)

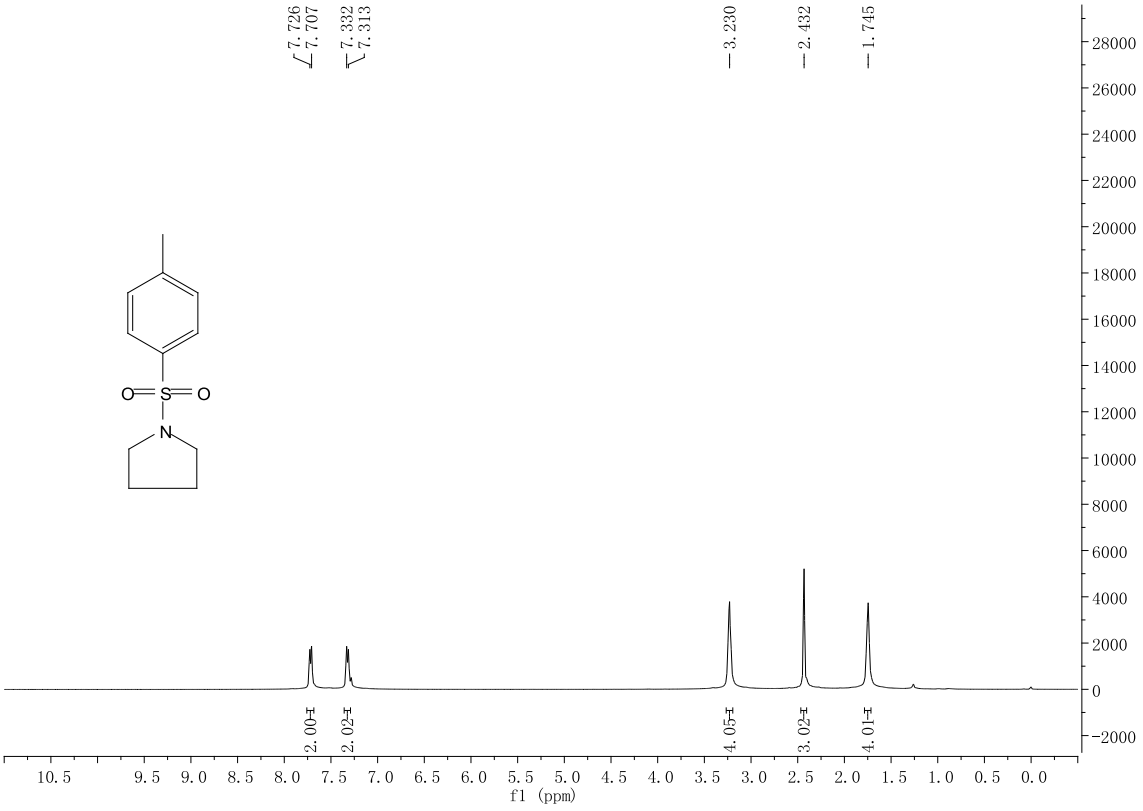

142.889
137.287
129.577
127.041
77.339
77.022
76.704
41.995
21.454
14.135
f1 (ppm)

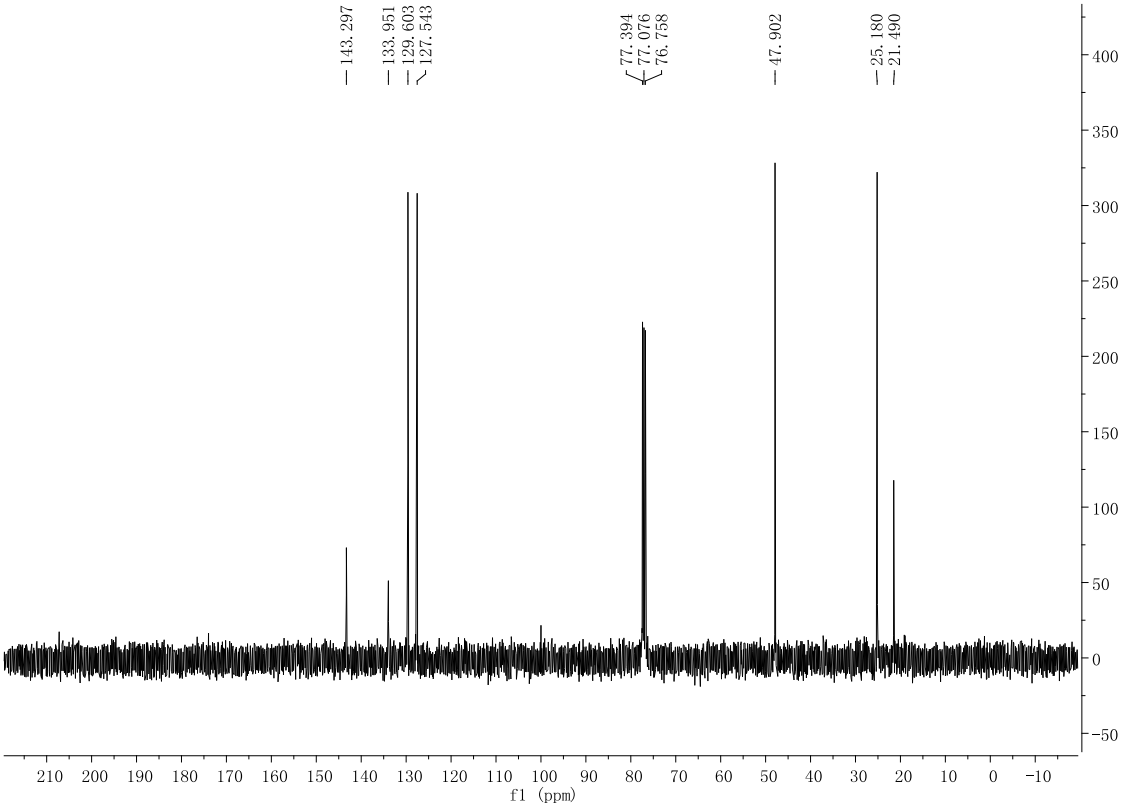
3i


7.686
7.666
7.296
7.276
2.852
2.834
2.417
1.894
1.877
1.860
1.842
0.894
0.877
2.00
2.04
4.05
3.03
2.01
12.01
f1 (ppm)

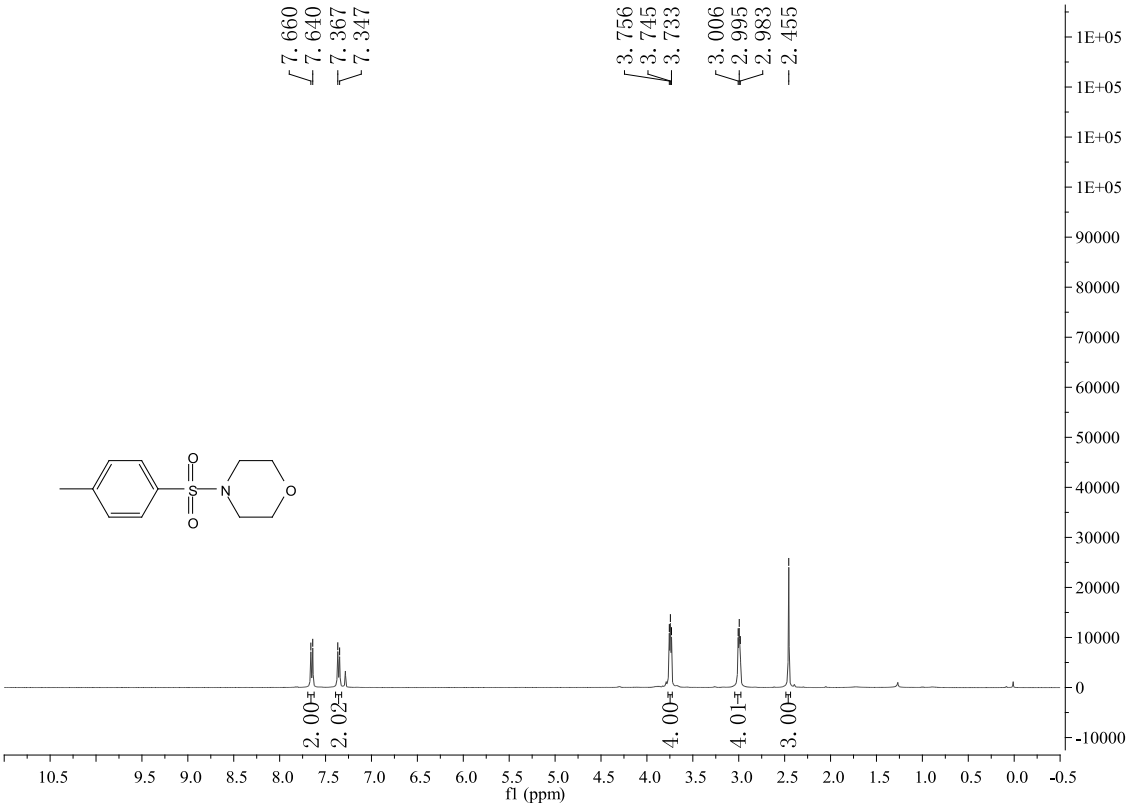

142.856
136.739
129.456
127.358
57.094
27.058
21.463
20.213
f1 (ppm)

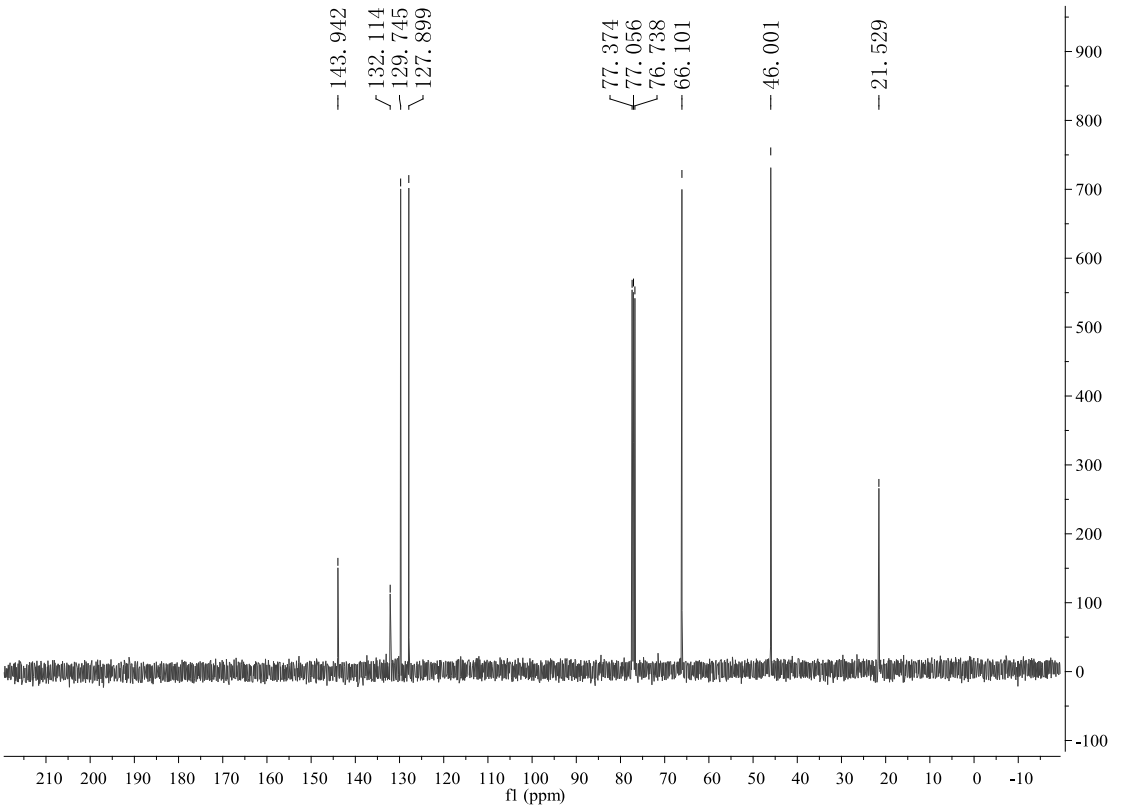
3j


7.726
7.707
7.332
7.313
3.230
2.432
1.745
2.00
2.02
4.05
3.02
4.01
f1 (ppm)

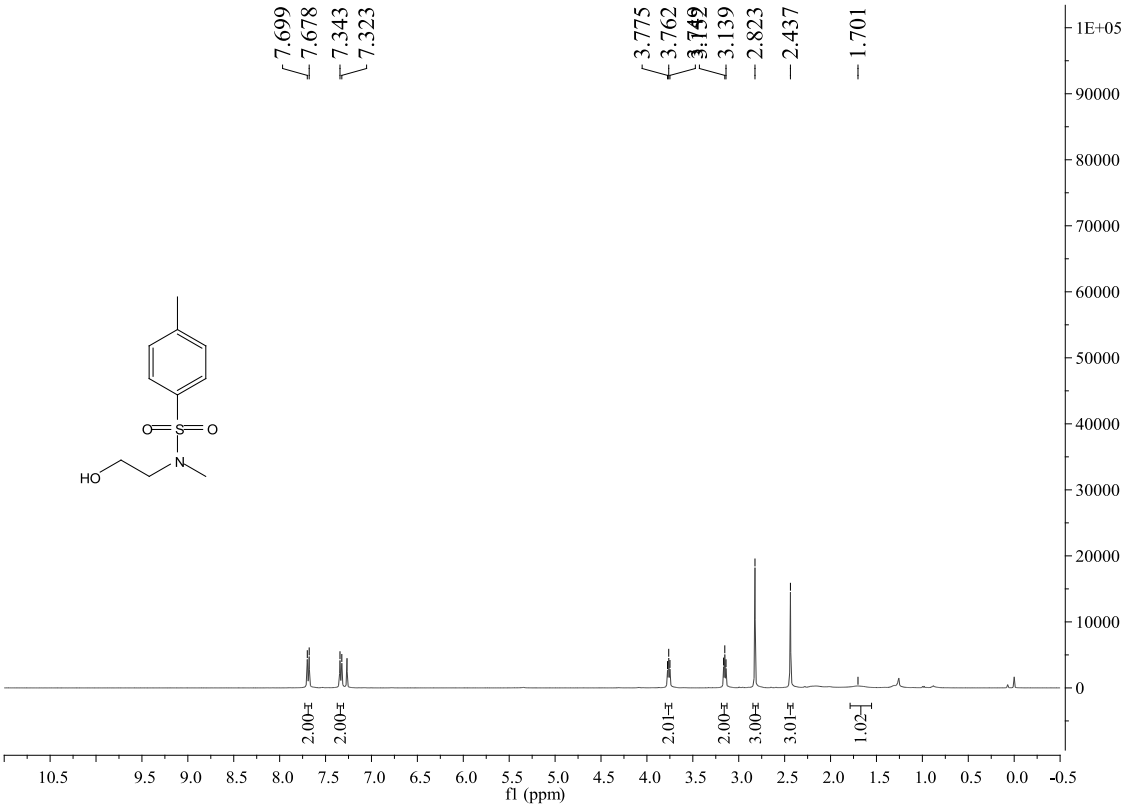

143.297
133.951
129.603
127.543
77.394
77.076
76.758
47.902
25.180
21.490
f1 (ppm)

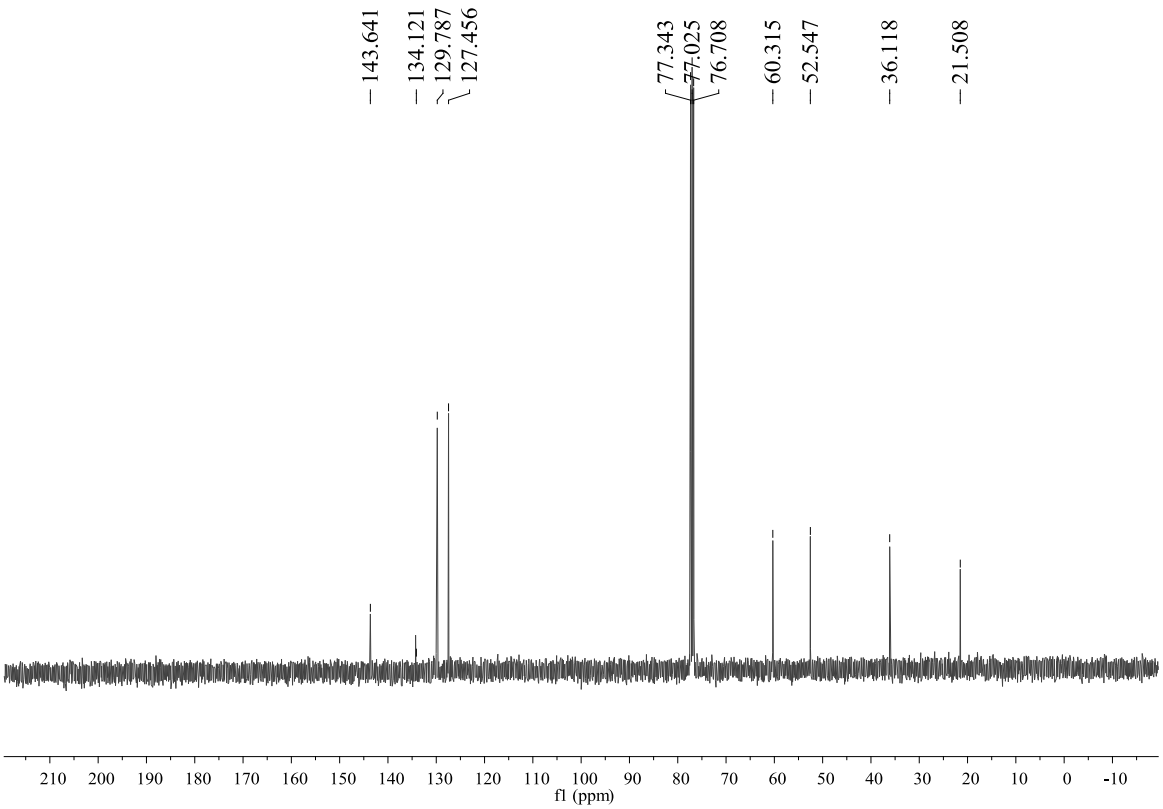
3k


7.660
7.640
7.367
7.347
3.756
3.745
3.733
3.006
2.995
2.983
2.455
2.00
2.02
4.00
4.01
3.00
f1 (ppm)

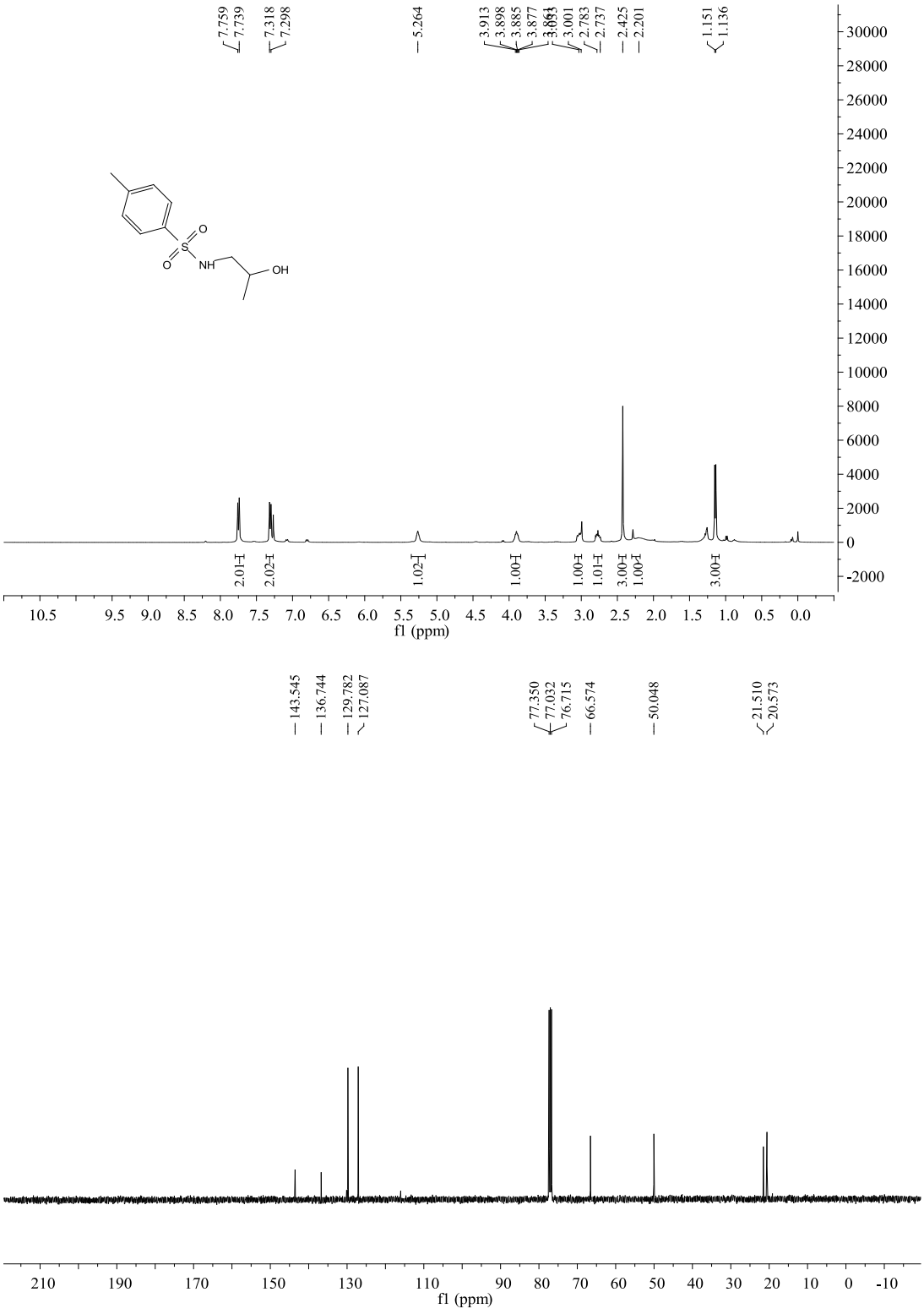

143.942
132.114
129.745
127.899
77.374
77.056
76.738
66.101
46.001
21.529
f1 (ppm)

3l

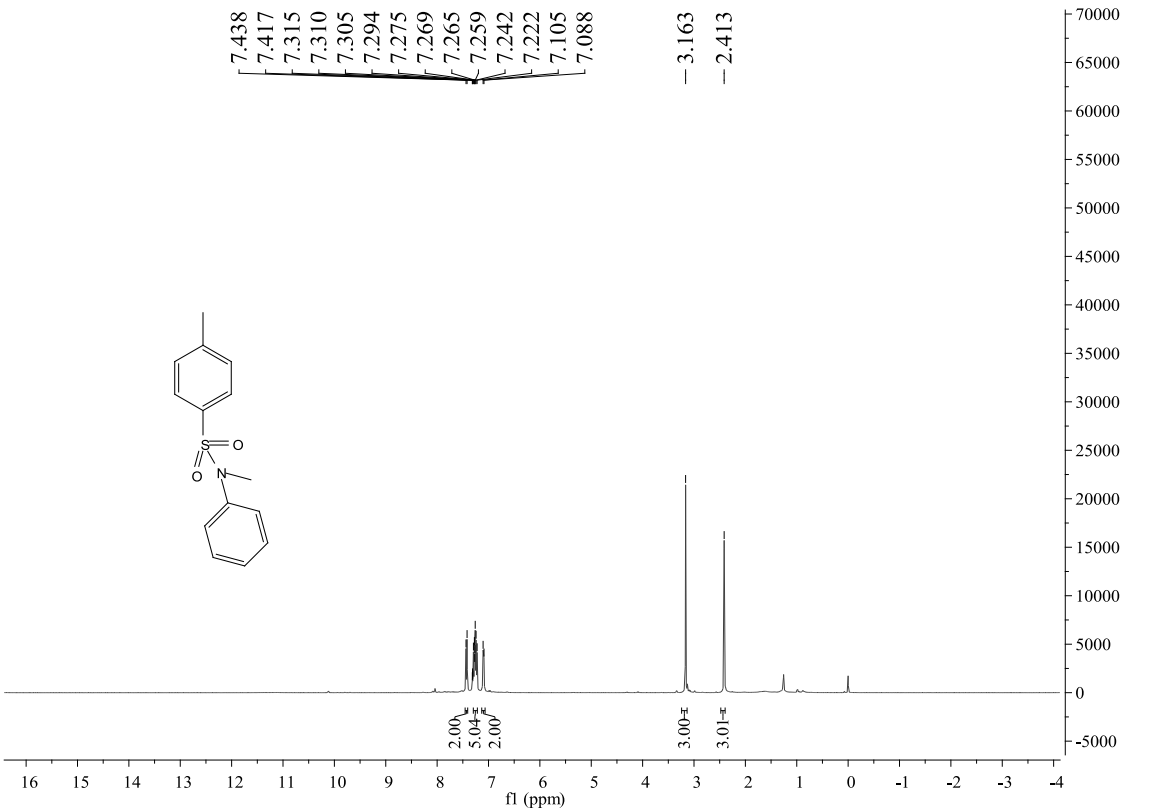

7.699
7.678
7.343
7.323
3.775
3.762
3.749
3.139
2.823
2.437
1.701
HO
2.00
2.00
2.01
2.00
3.00
3.01
1.02
fl (ppm)

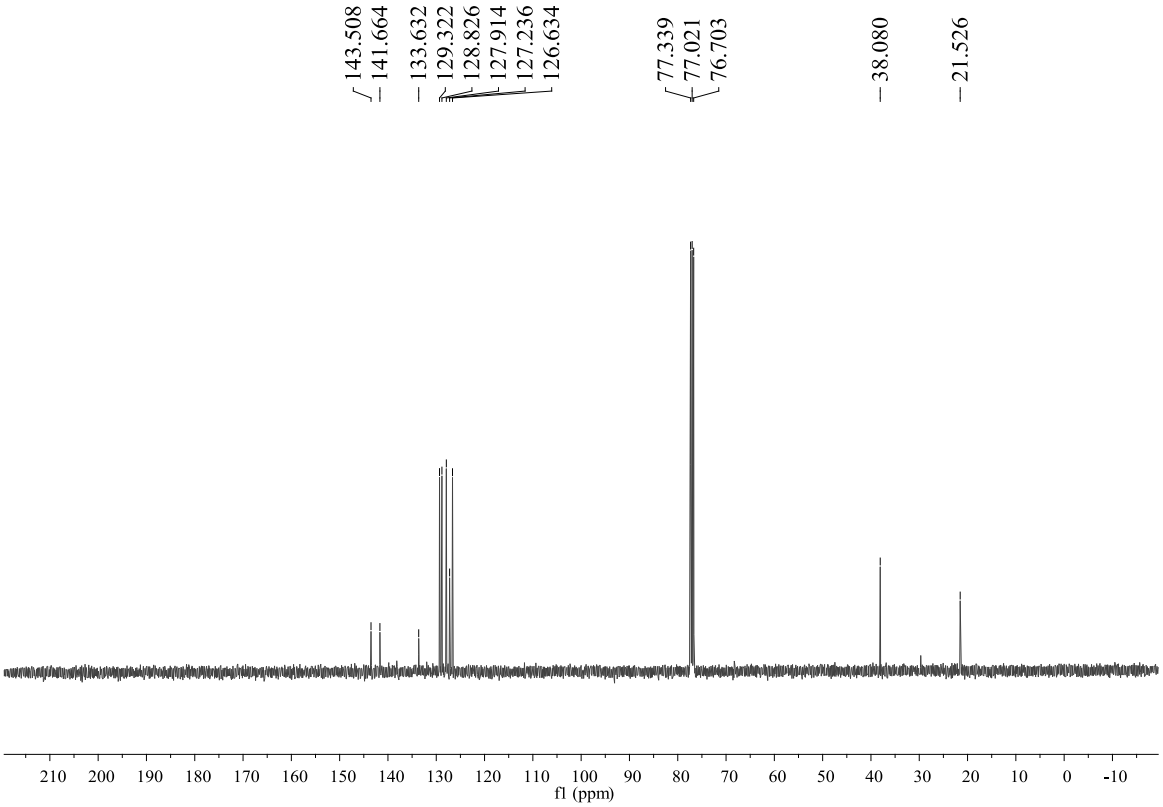

143.641
134.121
129.787
127.456
77.343
77.025
76.708
60.315
52.547
36.118
21.508
fl (ppm)

3m

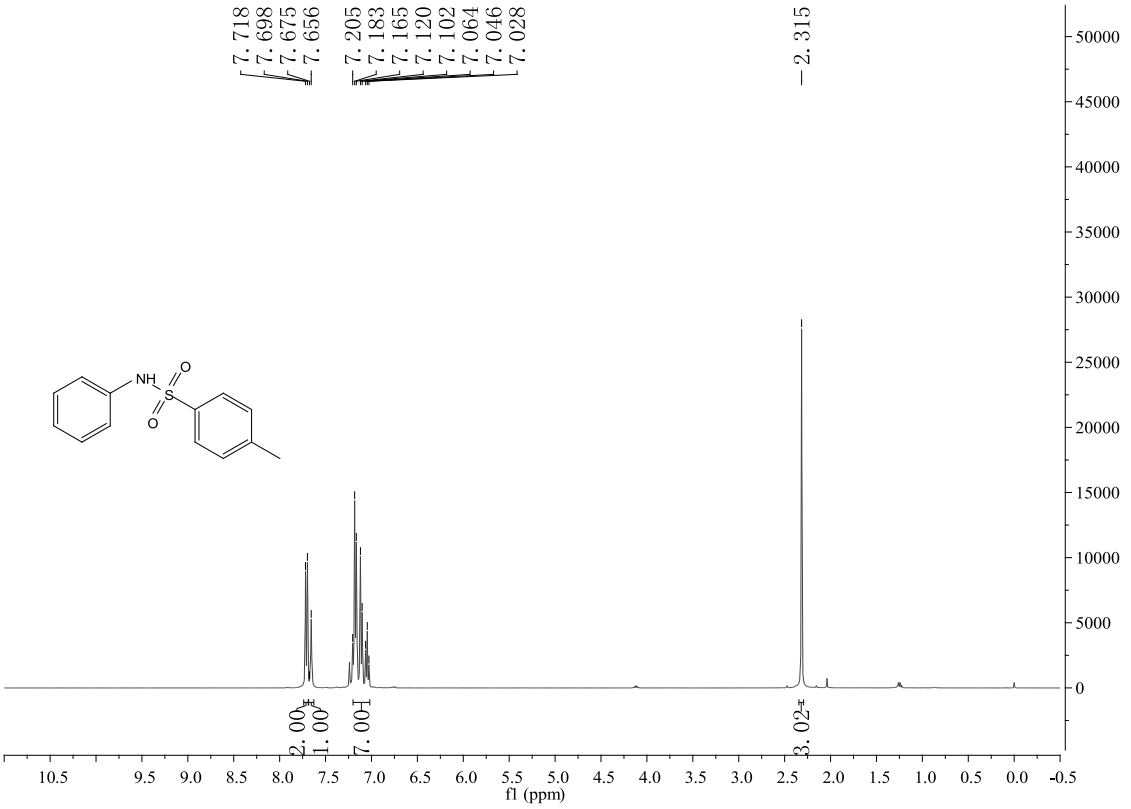

7.759
7.739
7.318
7.298
5.264
3.913
3.898
3.885
3.877
3.001
2.783
2.737
2.425
2.201
1.151
1.136
O
S
O
NH
OH
2.01
2.02
1.02
1.00
1.00
1.01
3.00
1.00
3.00
fl (ppm)
143.545
136.744
129.782
127.087
77.350
77.032
76.715
66.574
50.048
21.510
20.573
fl (ppm)

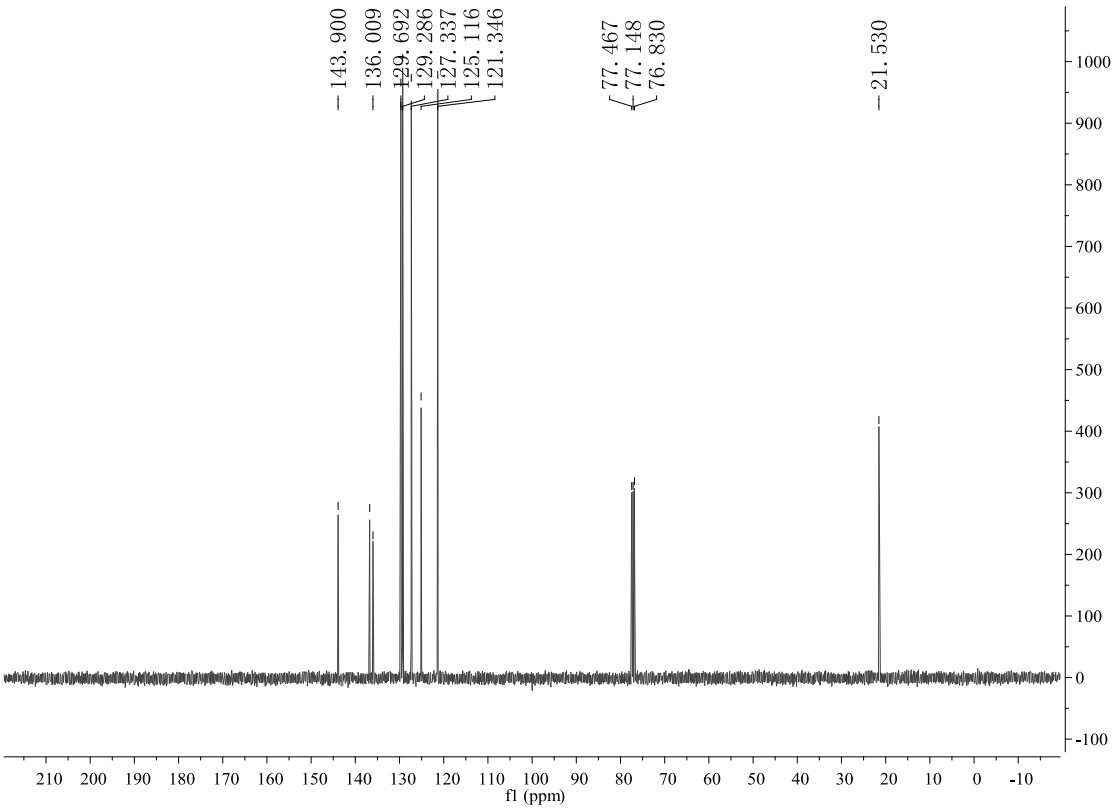
3n


7.438
7.417
7.315
7.310
7.305
7.294
7.275
7.269
7.265
7.259
7.242
7.222
7.105
7.088
3.163
2.413
2.00
5.04
2.00
3.00
3.01
fl (ppm)

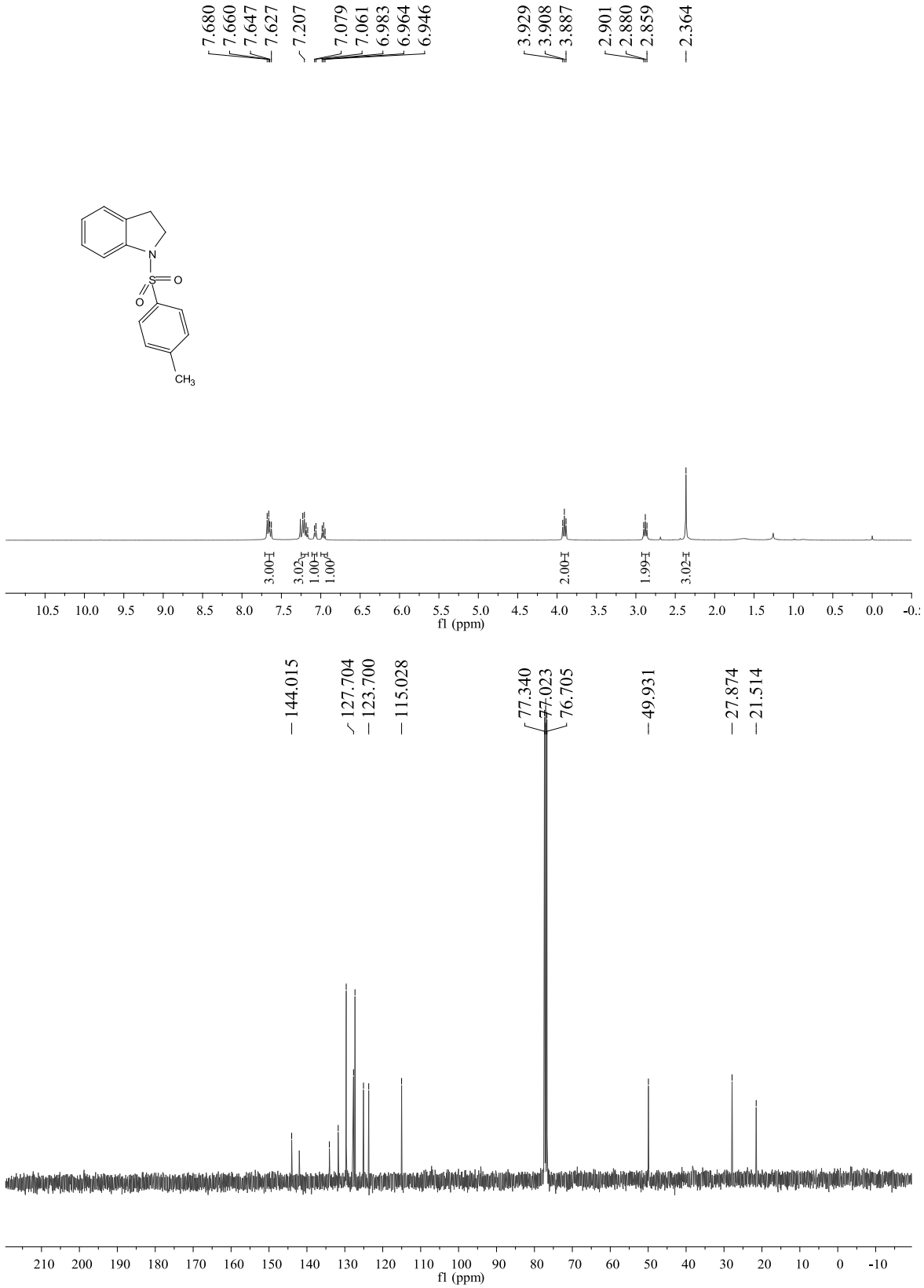

143.508
141.664
133.632
129.322
128.826
127.914
127.236
126.634
77.339
77.021
76.703
38.080
21.526
fl (ppm)

3o

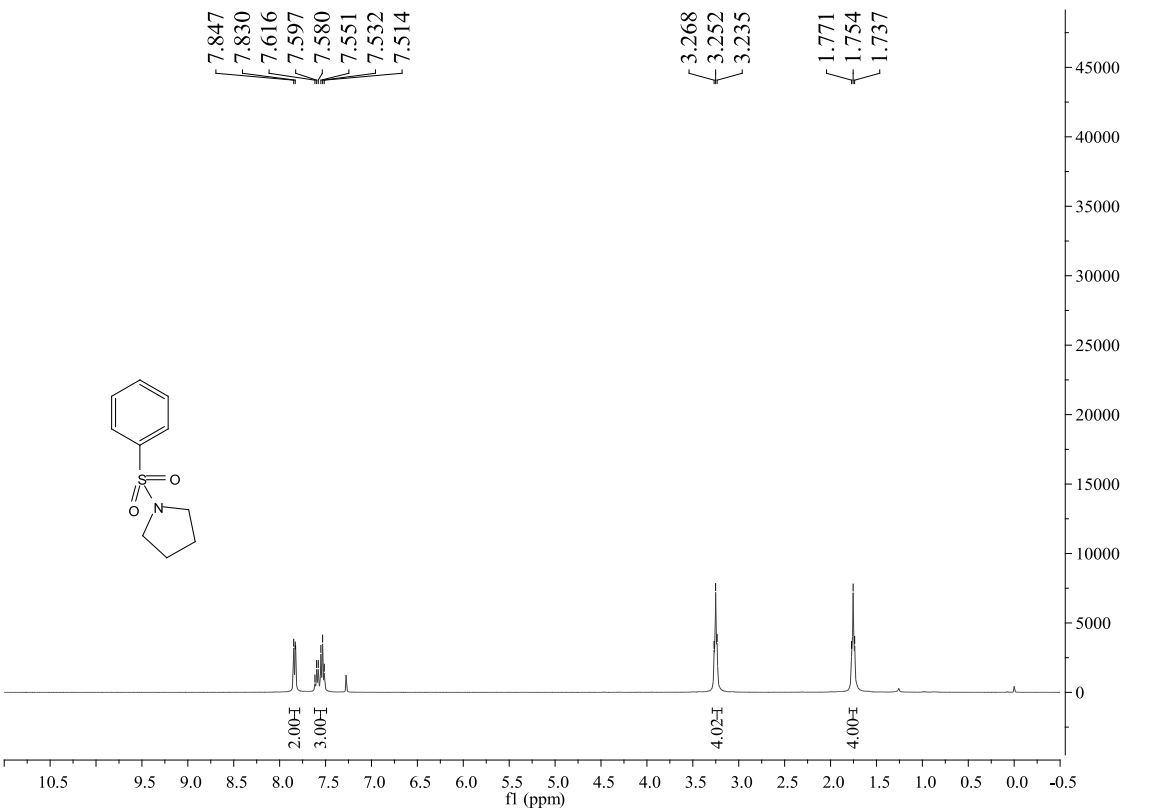

7.718
7.698
7.675
7.656
7.205
7.183
7.165
7.120
7.102
7.064
7.046
7.028
2.315
NH
O
S
O
2.00
1.00
7.00
3.02
fl (ppm)

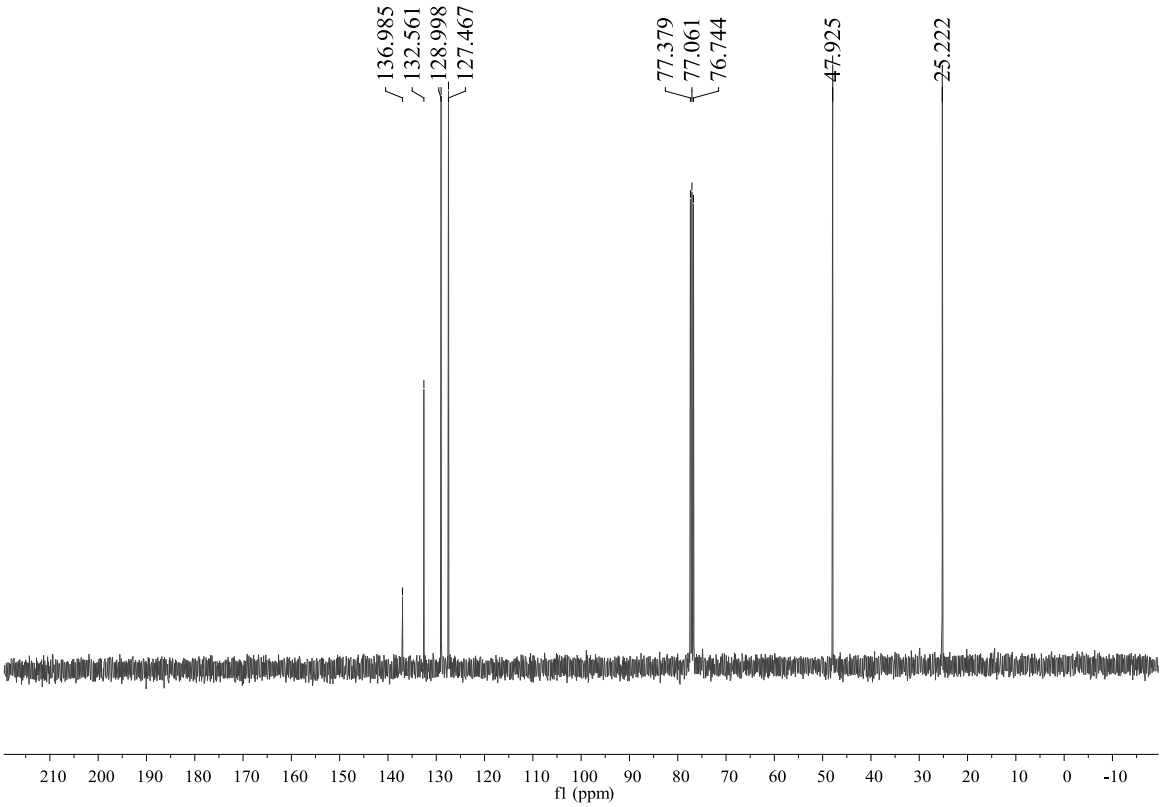

143.900
136.009
129.692
129.286
127.337
125.116
121.346
77.467
77.148
76.830
21.530
fl (ppm)

3p

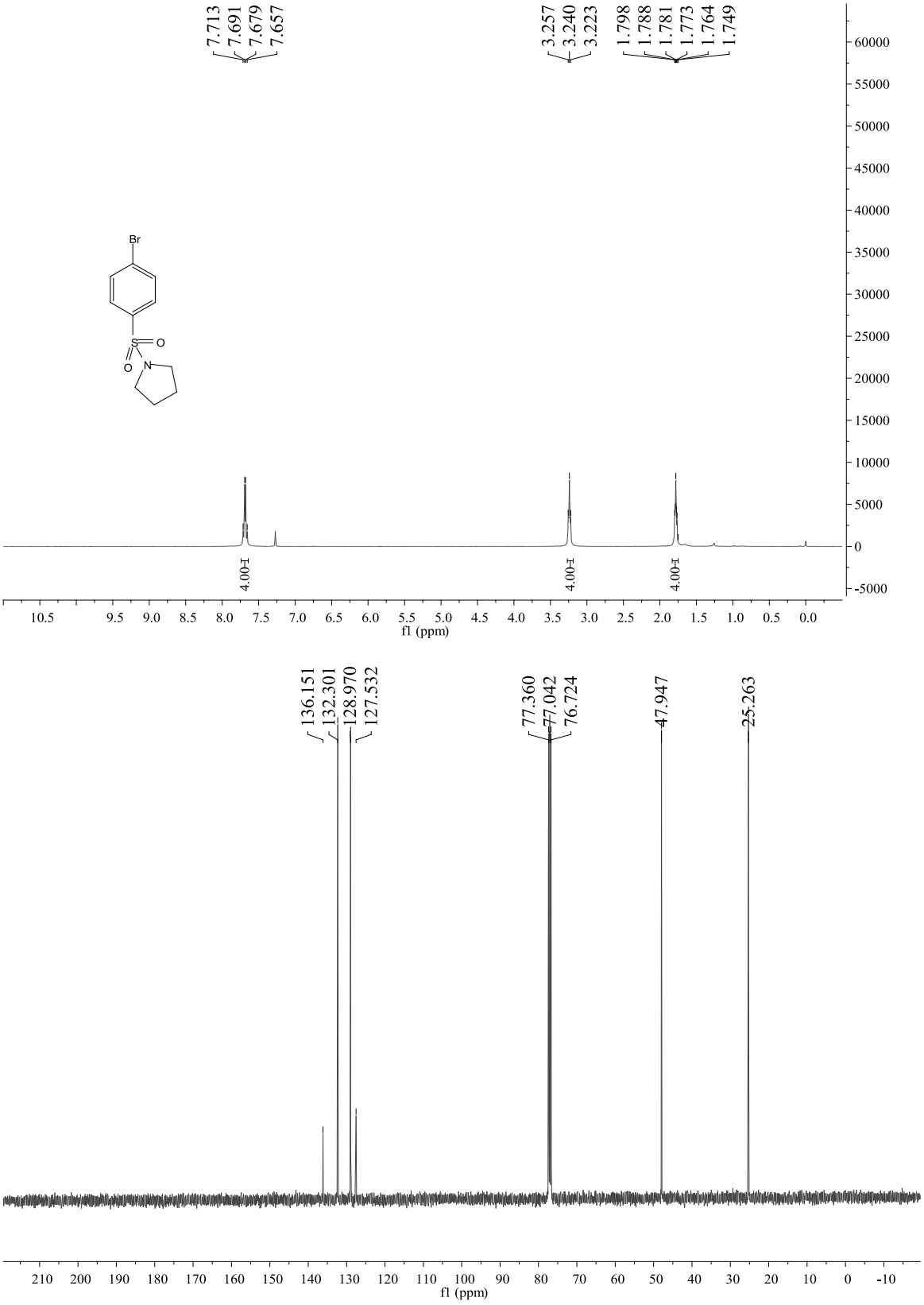

7.680
7.660
7.647
7.627
7.207
7.079
7.061
6.983
6.964
6.946
3.929
3.908
3.887
2.901
2.880
2.859
2.364
N
S
O
O
CH3
3.00
3.02
1.00
1.00
2.00
1.99
3.02
f1 (ppm)
144.015
127.704
123.700
115.028
77.340
77.023
76.705
49.931
27.874
21.514
f1 (ppm)

3q

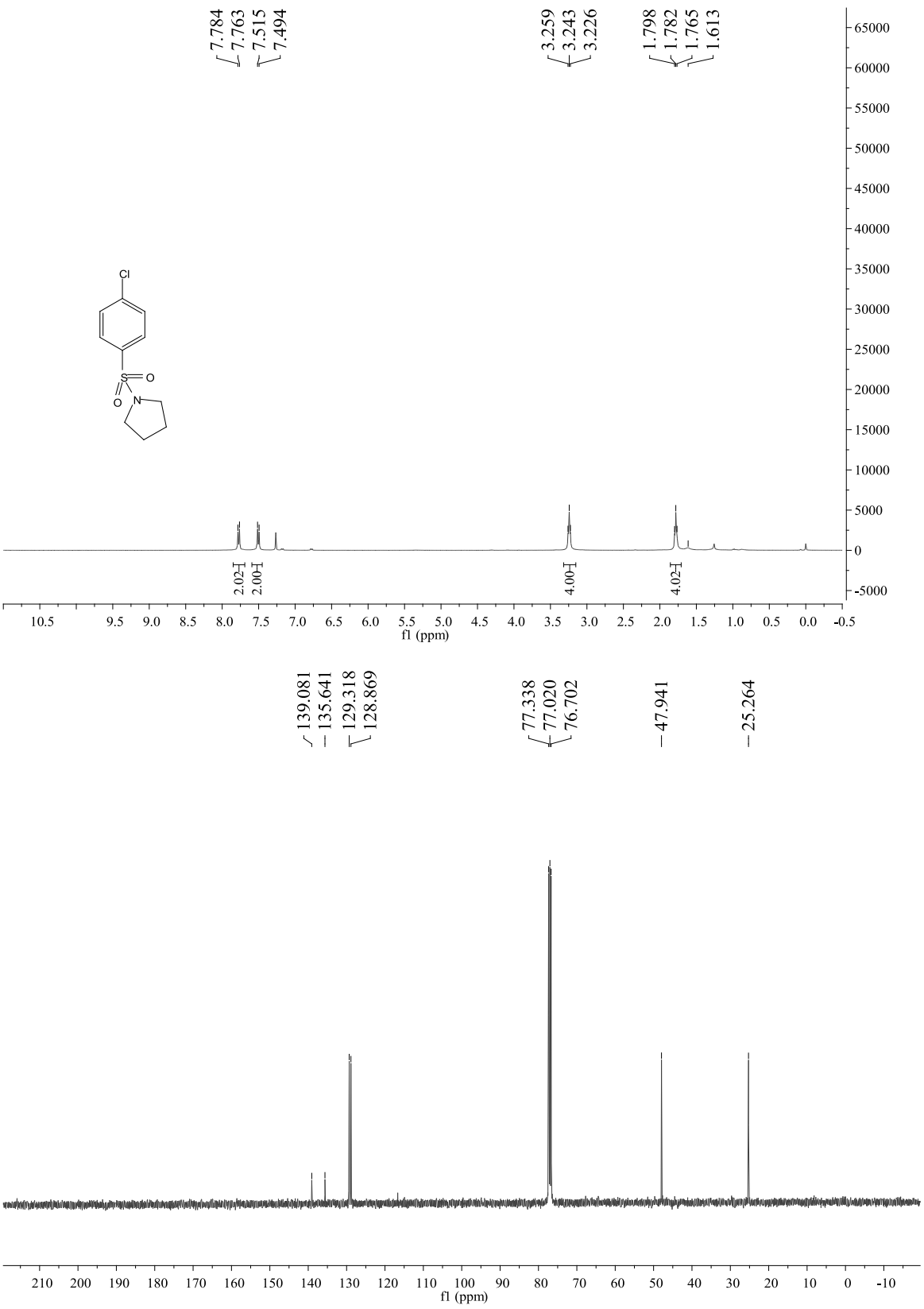

7.847
7.830
7.616
7.597
7.580
7.551
7.532
7.514
3.268
3.252
3.235
1.771
1.754
1.737
2.00
3.00
4.02
4.00
f1 (ppm)


136.985
132.561
128.998
127.467
77.379
77.061
76.744
47.925
25.222
f1 (ppm)

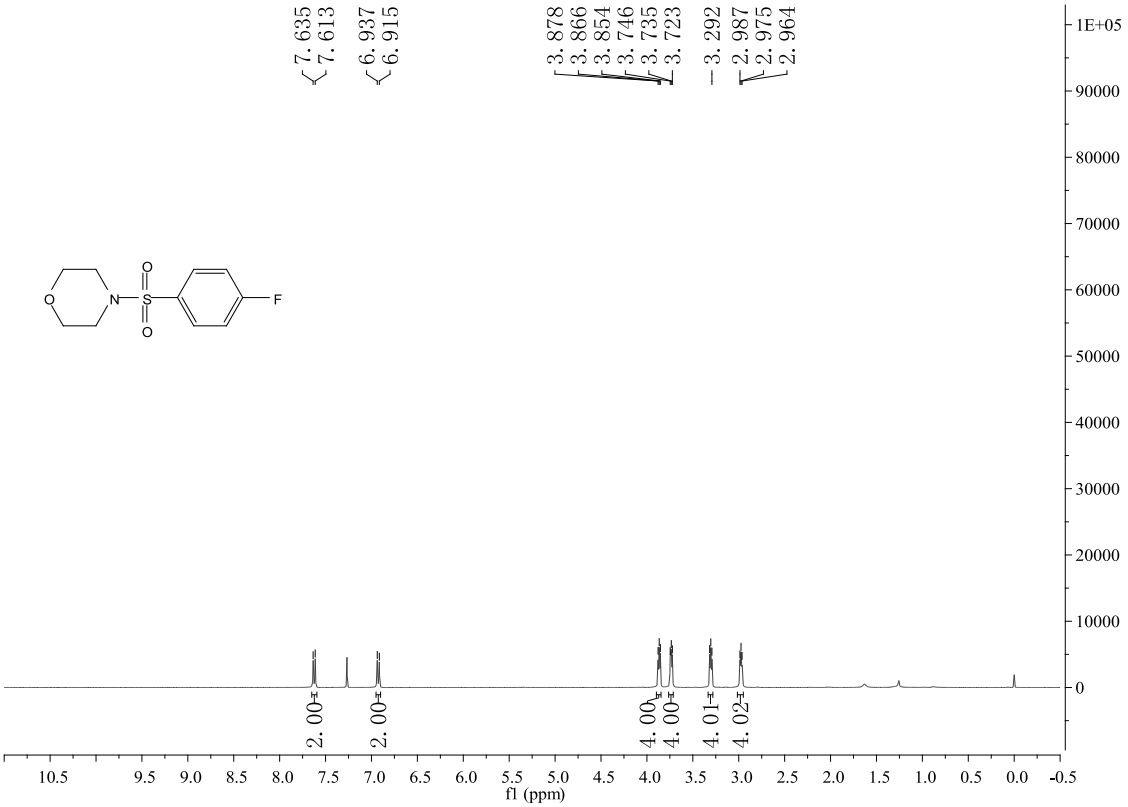
3r

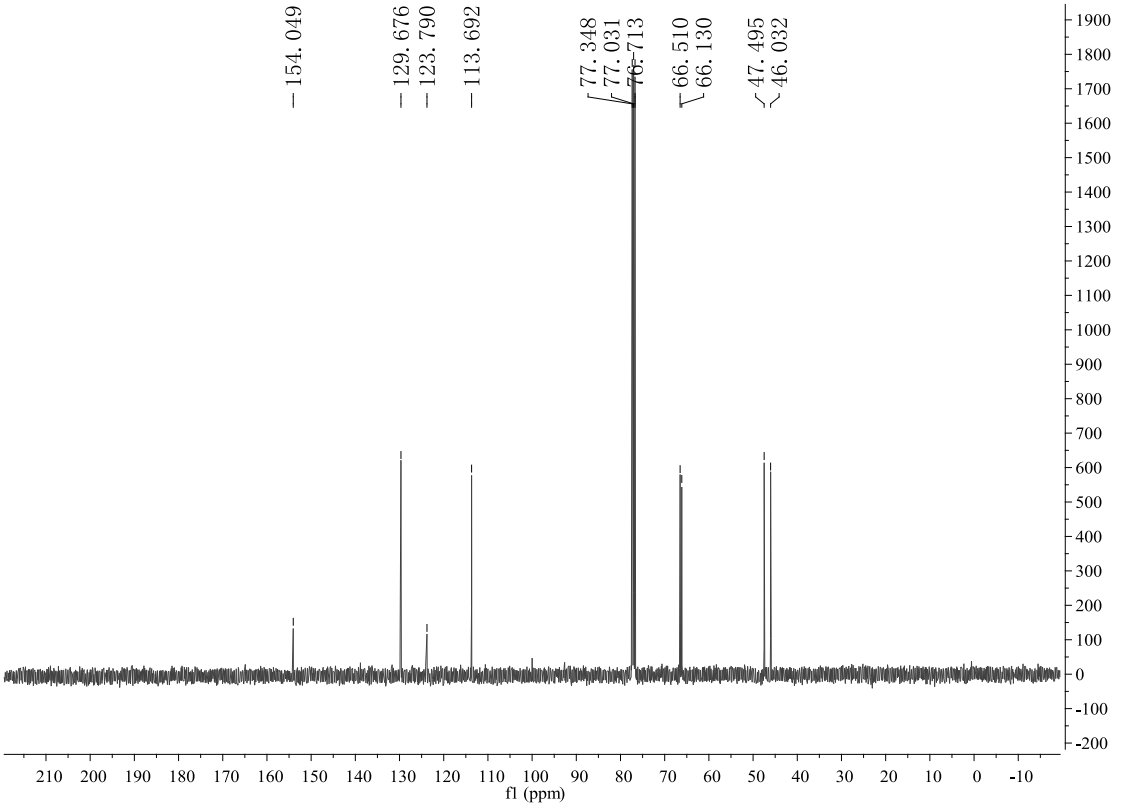

7.713
7.691
7.679
7.657
3.257
3.240
3.223
1.798
1.788
1.781
1.773
1.764
1.749
Br
S
O
O
N
4.00
4.00
4.00
fl (ppm)
136.151
132.301
128.970
127.532
77.360
77.042
76.724
47.947
25.263
fl (ppm)

3s

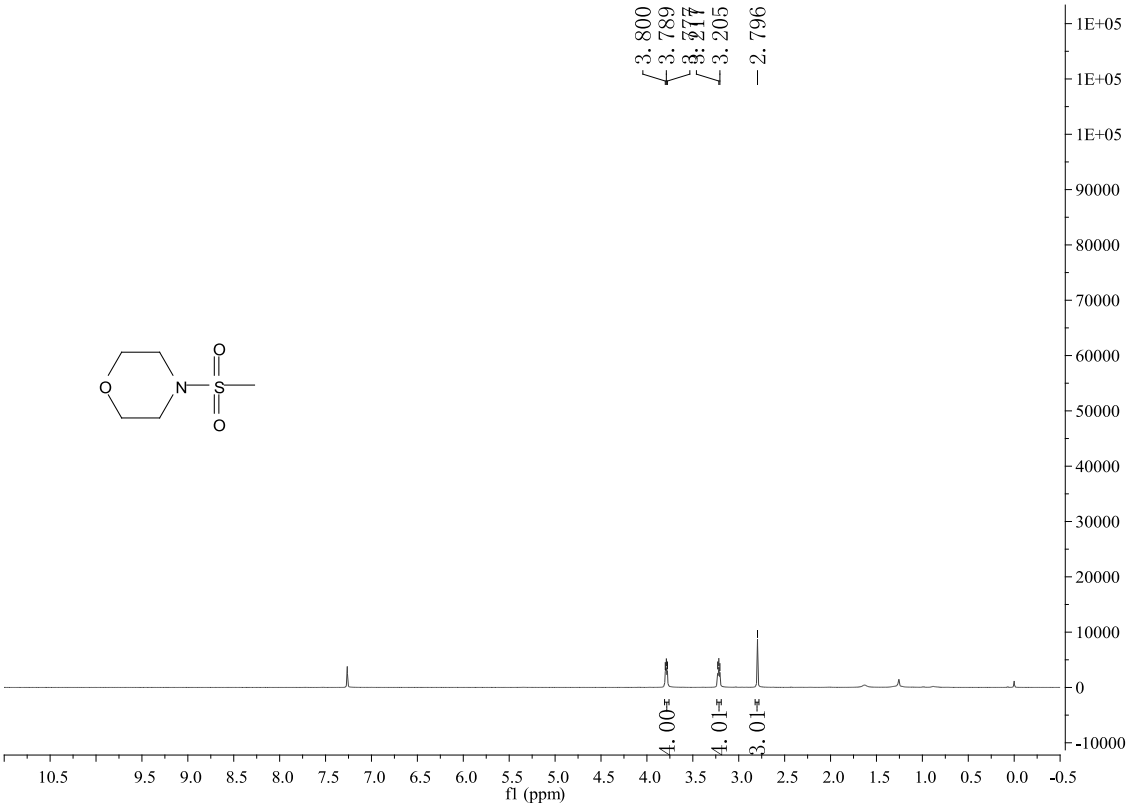

7.784
7.763
7.515
7.494
3.259
3.243
3.226
1.798
1.782
1.765
1.613
Cl
S
O
O
N
2.02
2.00
4.00
4.02
f1 (ppm)
139.081
135.641
129.318
128.869
77.338
77.020
76.702
47.941
25.264
f1 (ppm)

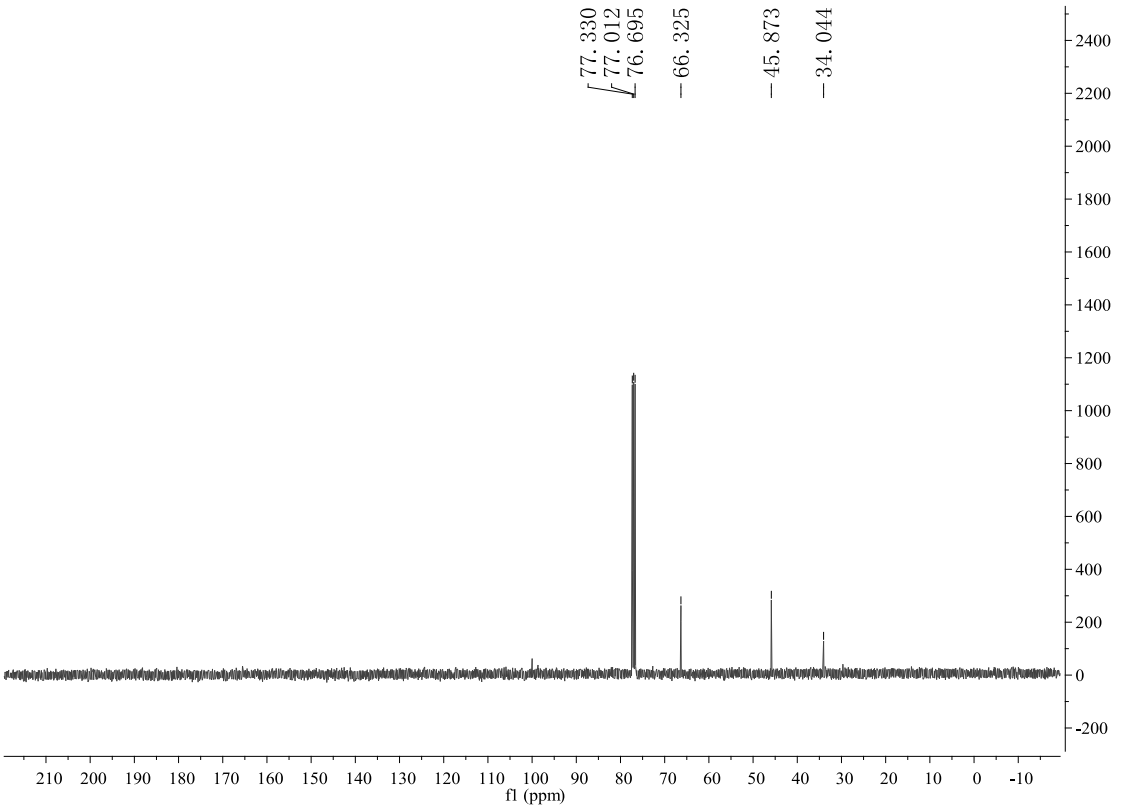
3t


7.635
7.613
6.937
6.915
3.878
3.866
3.854
3.746
3.735
3.723
3.292
2.987
2.975
2.964
O
N
S
O
O
F
2.00
2.00
4.00
4.00
4.01
4.02
fl (ppm)

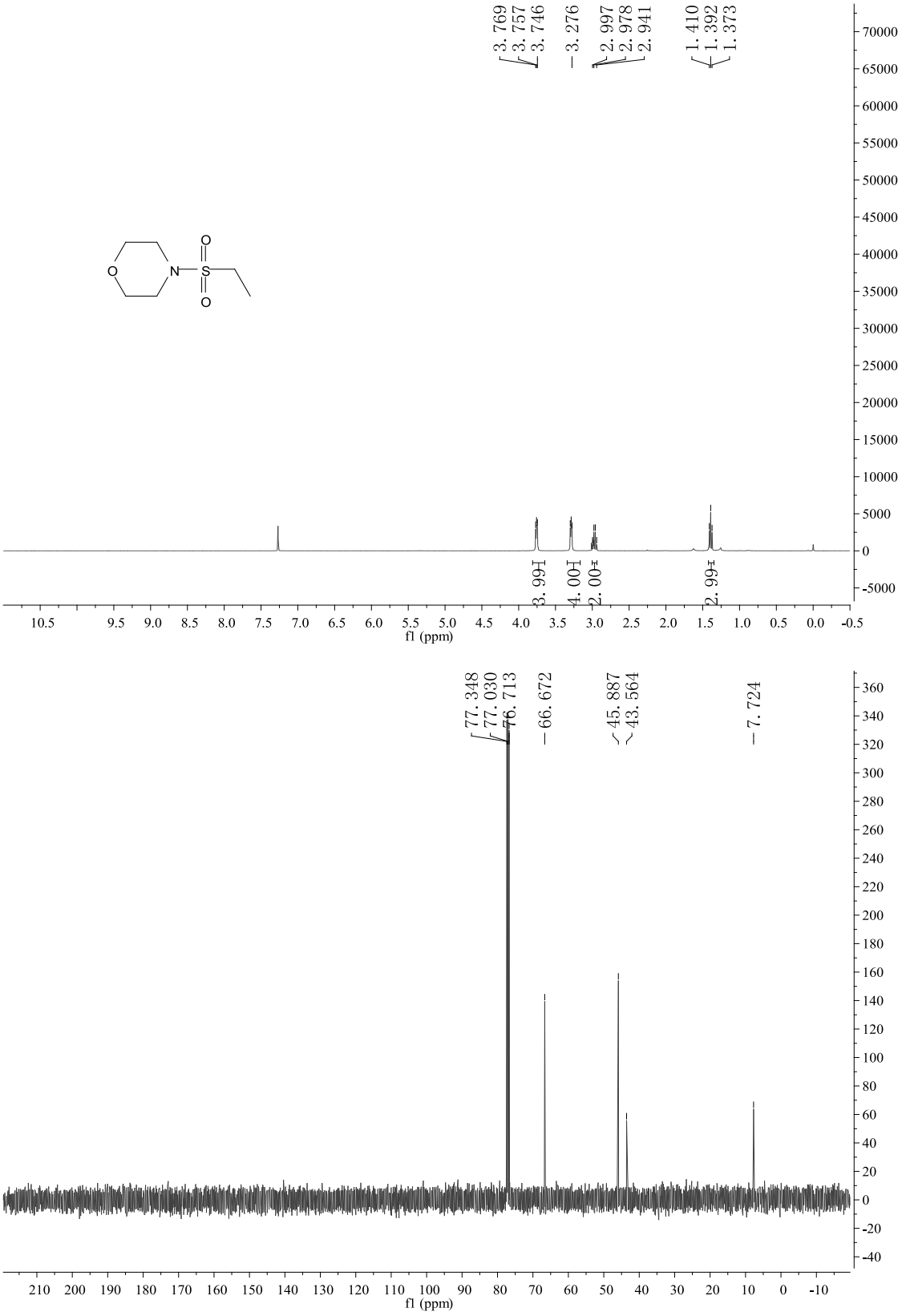

154.049
129.676
123.790
113.692
77.348
77.031
76.713
66.510
66.130
47.495
46.032
fl (ppm)

3u

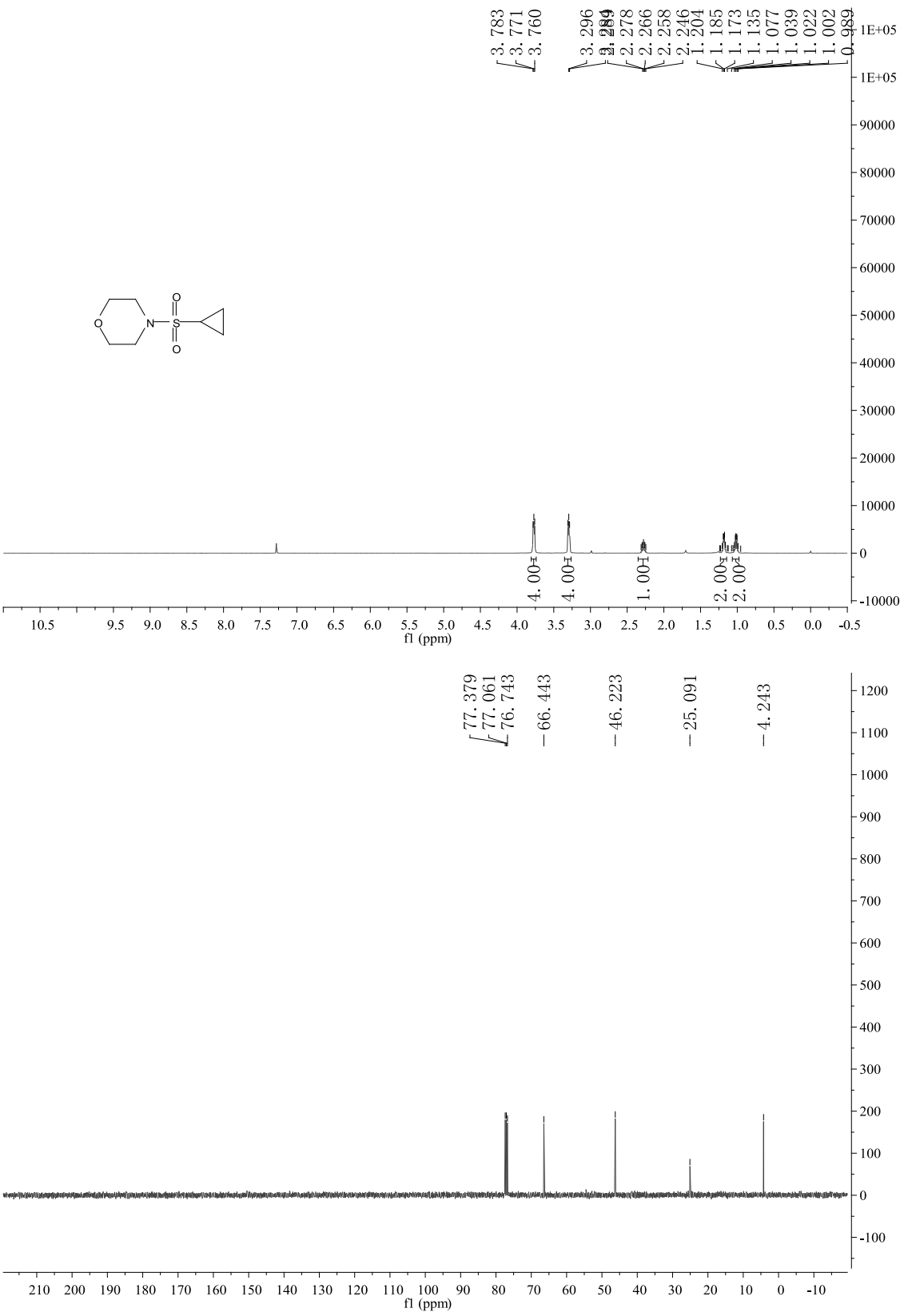

3.800
3.789
3.277
3.217
3.205
2.796
4.00
4.01
3.01
f1 (ppm)


77.330
77.012
76.695
66.325
45.873
34.044
f1 (ppm)

3v


3.769
3.757
3.746
3.276
2.997
2.978
2.941
1.410
1.392
1.373
3.99
4.00
2.00
2.99
f1 (ppm)
77.348
77.030
76.713
66.672
45.887
43.564
7.724
f1 (ppm)

3w


3.783
3.771
3.760
3.296
2.278
2.266
2.258
2.246
2.204
1.185
1.173
1.135
1.077
1.039
1.022
1.002
0.989
4.00
4.00
1.00
2.00
2.00
fl (ppm)
77.379
77.061
76.743
66.443
46.223
25.091
4.243
fl (ppm)

3x