Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper-mediated S-N formation via oxygen-activated radical process: A new synthesis method for sulfonamide

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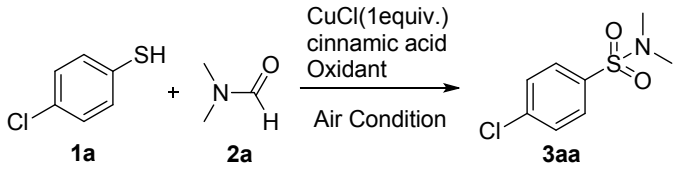
I General Information

All reagents used in the experiments were obtained from commercial sources and used without further purification. Unless otherwise noted, all reactions were carried out at air atmosphere. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. All NMR spectra were recorded on Bruker AVANCE DMX-500 spectrometry at 500 MHz and 125 MHz for 1H and 13C NMR in $CDCl_3$, respectively. The NMR chemical shift was reported in ppm relative to 7.26 and 77.160 ppm of $CDCl_3$ solvent as the standards of 1H and 13C NMR, respectively. The HRMS of new products were tested on Agilent 6210 TOF LC/MS equipped with an electrospray source.

II Optimization of time, temperature, solvent and oxidant

Table S1: Optimization of reaction conditions for time, temperature, solvent and oxidant [a]



1a **2a** **3aa**

Entry	Oxidant(equiv.)	Time(h)	Temperature(°C)	Solvent(ml)	Yield(%)[b]
1	$Cu(OAc)_2$ (1)	12	110	DMF(1.5)	73
2	$Cu(OAc)_2$(1)	24	110	DMF(1.5)	83
3	$Cu(OAc)_2$(1)	36	110	DMF(1.5)	84
4	$Cu(OAc)_2$(1)	24	90	DMF(1.5)	35
5	$Cu(OAc)_2$(1)	24	130	DMF(1.5)	81
6	$Cu(OAc)_2$(1)	24	110	H_2O(1.5)	Trace
7[c]	$Cu(OAc)_2$(1)	24	110	TCE(1.5)	10
8	$Cu(OAc)_2$(1)	24	110	DMSO(1.5)	trace
9[d]	$Cu(OAc)_2$(1)	24	110	DMA(1.5)	56
10	$Cu(OAc)_2$(1)	24	110	toluene(1.5)	36
11	$Cu(OAc)_2$(1)	24	110	1,4-dioxane(1.5)	27
12	$Cu(OAc)_2$(1)	24	110	AcOH(1.5)	8
13	/	24	110	DMF(1.5)	52
14[e]	TBHP(2)	24	110	DMF(1.5)	20
15	DTBP(2)	24	110	DMF(1.5)	24

[a] Reaction Condition: **1a** (0.5mmol), **2a** (1.5ml), CuCl (1equiv), cinnamic acid (1.0equiv), solvent (1.5 ml), air condition. [b] Isolated yields. [c] TCE (1,1,2- trichloroethane).

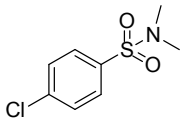
[d] DMA (N,N-dimethylacetamide). [e] TBHP (tert-butyl hydroperoxide,70% in water).

III General Procedure

General Procedure for the Synthesis of N,N-dimethyl-4-chloro-sulfonamide(3aa)

Under air atmosphere, 4-Cl-thiophenol (0.5mmol,**1a**), CuCl (1 equiv), $Cu(OAc)_2$ (1 equiv) and cinnamic acid (1 equiv) in DMF(1.5ml, **2a**) was stirred at 110°C for 24h in a 25ml flask. After cooling to room temperature, the mixture was washed with water and extracted with ethyl acetate then dried over Na_2SO_4. The organic layer was then evaporated under reduced pressure and the residue was separated by column chromatography on silica gel with Petroleum/Ethyl acetate mixtures (5/1) to get the desired product **3aa**.

IV Characterization data for the products

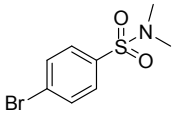


4-Chloro- N,N-dimethylbenzenesulfonamide (3aa)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J=8.0 Hz, 2H), 7.45(d, J=8.5 Hz, 2H), 2.64(s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 134.3, 129.5, 129.3, 38.0.

HRMS (ESI) calculated for $C_8H_{10}ClNO_2S$ $[M+H]^+$: 220.0194; found 220.0196.

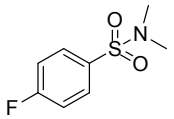


4-Bromo-N,N-dimethylbenzenesulfonamide(3ba)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J=8.5 Hz, 2H), 7.57(d, J=7.5 Hz, 2H), 2.65(s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 134.8, 132.5, 129.3, 127.9, 38.0.

HRMS (ESI) calculated for $C_8H_{10}BrNO_2S$ $[M+H]^+$: 263.9689; found 2663.9687.

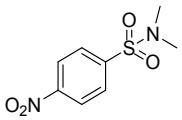


4-Fluoro-N,N-dimethylbenzenesulfonamide(3ca)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74-7.72 (m, 2H), 7.18-7.14(m, 2H), 2.64(s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 164.3, 131.8, 130.5, 130.4, 116.5, 116.3, 38.0.

HRMS (ESI) calculated for $C_8H_{10}FNO_2S$ $[M+H]^+$: 204.0489; found 204.0491.

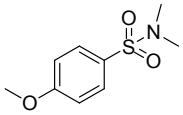


4-Nitro-N,N-dimethylbenzenesulfonamide(3da)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J=7.5 Hz, 2H), 7.90(d, J=7.5 Hz, 2H), 2.71(s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 140.7, 127.8, 123.3, 36.8.

HRMS (ESI) calculated for $C_8H_{10}N_2O_4S$ $[M+H]^+$: 231.0434; found 231.0435.

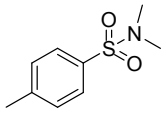


4-Methoxy-N,N-dimethylbenzenesulfonamide(3ea)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J=8.0 Hz, 2H), 6.94(d, J=7.5 Hz, 2H), 3.81(s, 3H), 2.61(s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 129.9, 127.1, 114.3, 55.7, 38.1.

HRMS (ESI) calculated for $C_9H_{13}NO_3S$ $[M+H]^+$: 216.0689; found 216.0689.

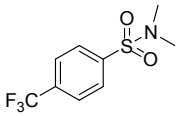


4-Methyl-N,N-dimethylbenzenesulfonamide(3fa)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J=8.0 Hz, 2H), 7.26(d, J=8.0 Hz, 2H), 2.61(s, 6H), 2.37(s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 132.5, 129.7, 127.9, 38.1, 21.6.

HRMS (ESI) calculated for $C_9H_{13}NO_2S$ $[M+H]^+$: 200.0740; found 200.0738.

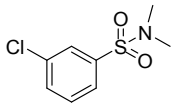


4-Trifluoromethyl-N,N-dimethylbenzenesulfonamide(3ga)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J=8.0 Hz, 2H), 7.75(d, J=8.0 Hz, 2H), 2.68(s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 134.7, 134.4, 128.3, 126.3, 124.5, 122.3, 38.0.

HRMS (ESI) calculated for $C_9H_{10}F_3NO_2S$ $[M+H]^+$: 254.0457; found 254.0459.

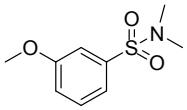


3-Chloro-N,N-dimethylbenzenesulfonamide(3ha)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69(s, 1H), 7.59 (d, J=7.5 Hz, 1H), 7.51(d, J=8.0 Hz, 1H), 7.44-7.41(m, 1H), 2.67(s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 135.4, 132.9, 130.5, 127.7, 125.9, 38.0.

HRMS (ESI) calculated for $C_8H_{10}ClNO_2S$ $[M+H]^+$: 220.0194; found 220.0195.

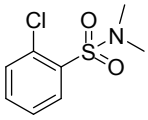


3-Methoxy-N,N-dimethylbenzenesulfonamide(3ia)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.36 (m, 1H), 7.27(d, J=7.5 Hz, 1H), 7.20(s, 1H), 7.05(d, J=8.5 Hz, 1H), 3.79(s, 3H), 2.64(s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 136.6, 130.2, 119.9, 118.8, 112.7, 55.7, 38.0.

HRMS (ESI) calculated for $C_9H_{13}NO_3S$ $[M+H]^+$: 216.0689; found 216.0689.

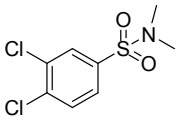


2-Chloro-N,N-dimethylbenzenesulfonamide(3ja)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J=7.5Hz, 1H), 7.46(d, J=8.0 Hz, 1H), 7.43-7.40(m, 1H), 7.35-7.32(m, 1H), 2.82(s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.2, 133.6, 132.4, 132.3, 132.2, 127.0, 37.5.

HRMS (ESI) calculated for $C_8H_{10}ClNO_2S$ $[M+H]^+$: 220.0194; found 220.0196.

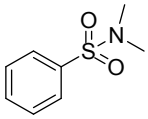


3,4-Dichloro-N,N-dimethylbenzenesulfonamide(3ka)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.57-7.52(m, 2H), 2.67(s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 135.7, 133.9, 131.3, 129.6, 126.8, 38.0.

HRMS (ESI) calculated for $C_8H_9Cl_2NO_2S$ $[M+H]^+$: 253.9804; found 253.9797.

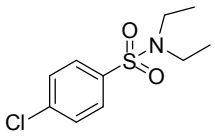


N,N-dimethylbenzenesulfonamide(3la)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J=8.5 Hz, 2H), 7.56-7.52(m, 1H), 7.49-7.46(m, 2H), 2.63(s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 135.5, 132.8, 129.1, 127.8, 38.0.

HRMS (ESI) calculated for $C_8H_{11}NO_2S$ $[M+H]^+$: 186.0583; found 186.0581.

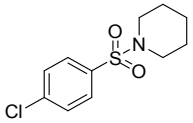


4-Chloro-N,N-diethylbenzenesulfonamide(3ab)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J=7.0 Hz, 2H), 7.46(d, J=7.5Hz, 2H), 3.25-3.21(m, 4H), 1.14-1.11(m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 138.7, 129.3, 128.5, 42.1, 14.2.

HRMS (ESI) calculated for $C_{10}H_{14}ClNO_2S$ $[M+H]^+$: 248.0507; found 248.0505.

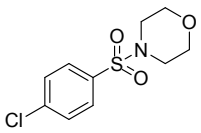


1-(4-chloro-benzenesulfonyl)-piperidine(3ad)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J=8.5 Hz, 2H), 7.43(d, J=8.5Hz, 2H), 2.92-2.90(m, 4H), 1.60-1.57(m, 4H), 1.39-1.34(m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 135.0, 129.4, 129.2, 47.0, 25.2, 23.6.

HRMS (ESI) calculated for $C_{11}H_{14}ClNO_2S$ $[M+H]^+$: 260.0507; found 260.0505.

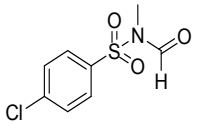


4-(4-Chlorophenylsulfonyl)morpholine(3ae)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J=7.5 Hz, 2H), 7.46(d, J=7.5Hz, 2H), 3.69-3.67(m, 4H), 2.94-2.92(m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 133.7, 129.6, 129.3, 66.1, 46.0.

HRMS (ESI) calculated for $C_{10}H_{12}ClNO_3S$ $[M+H]^+$: 262.0299; found 262.0298.

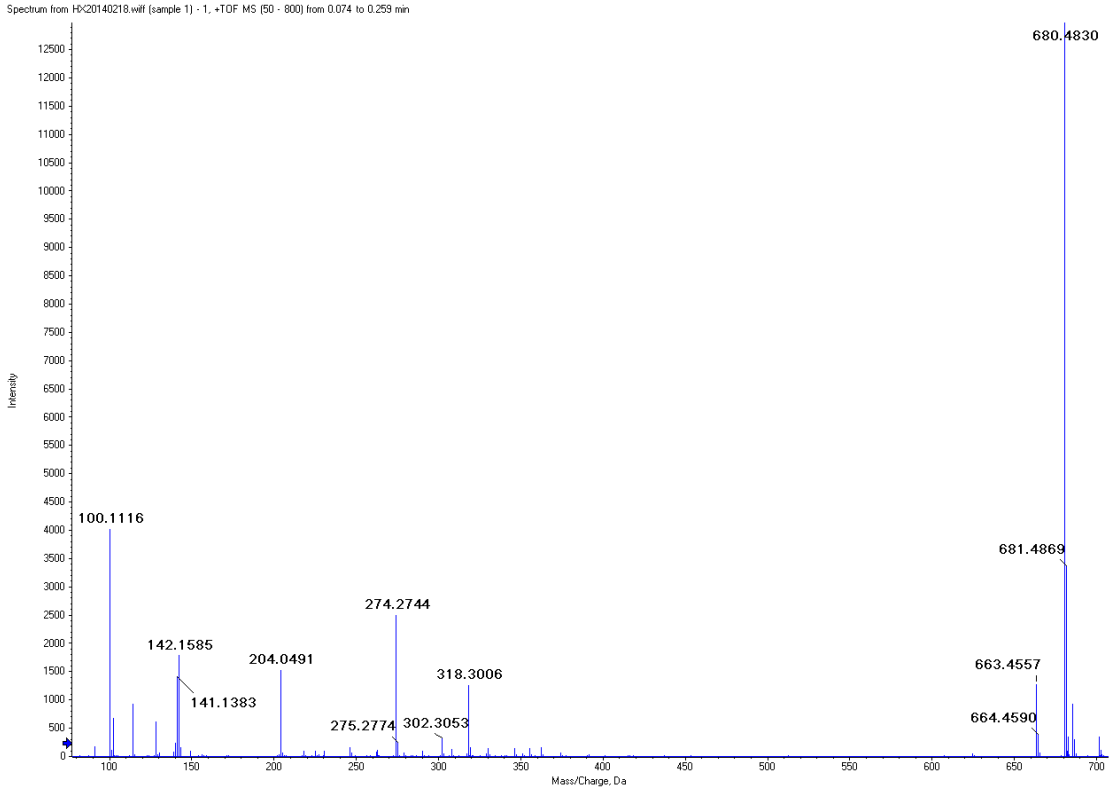


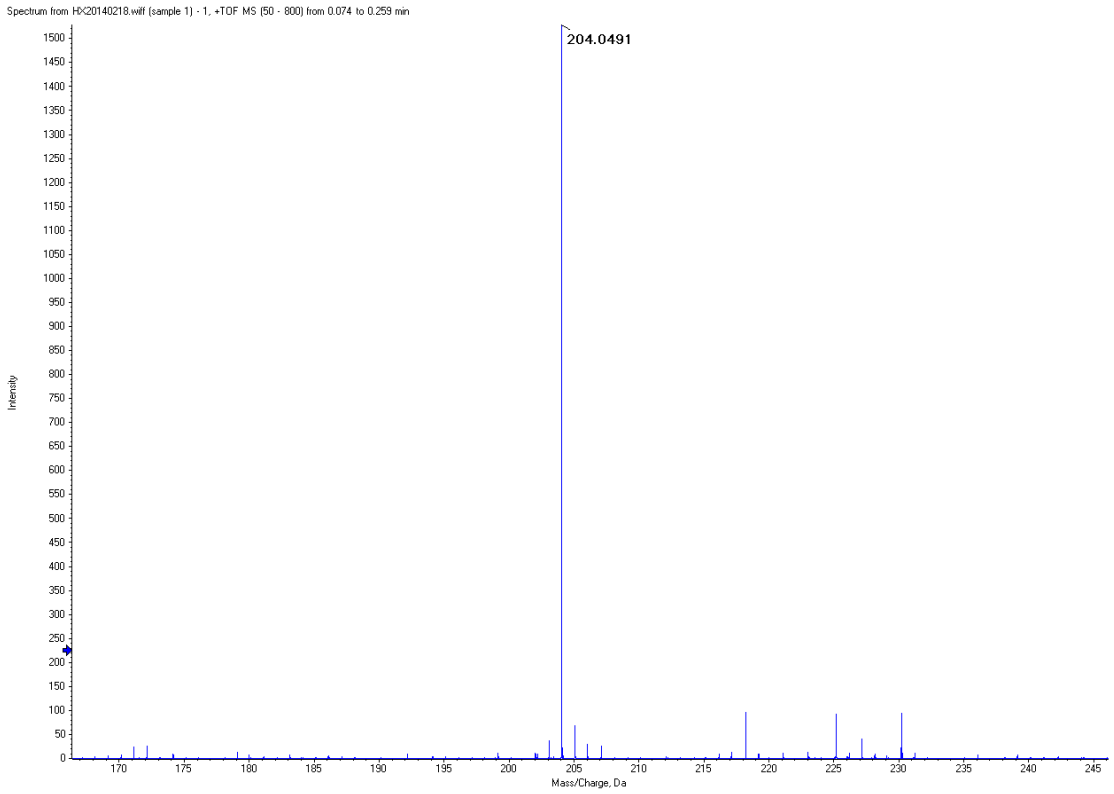
***N*-formyl-*N*-methyl-4-chloro-benzenesulfonamide(3af)**

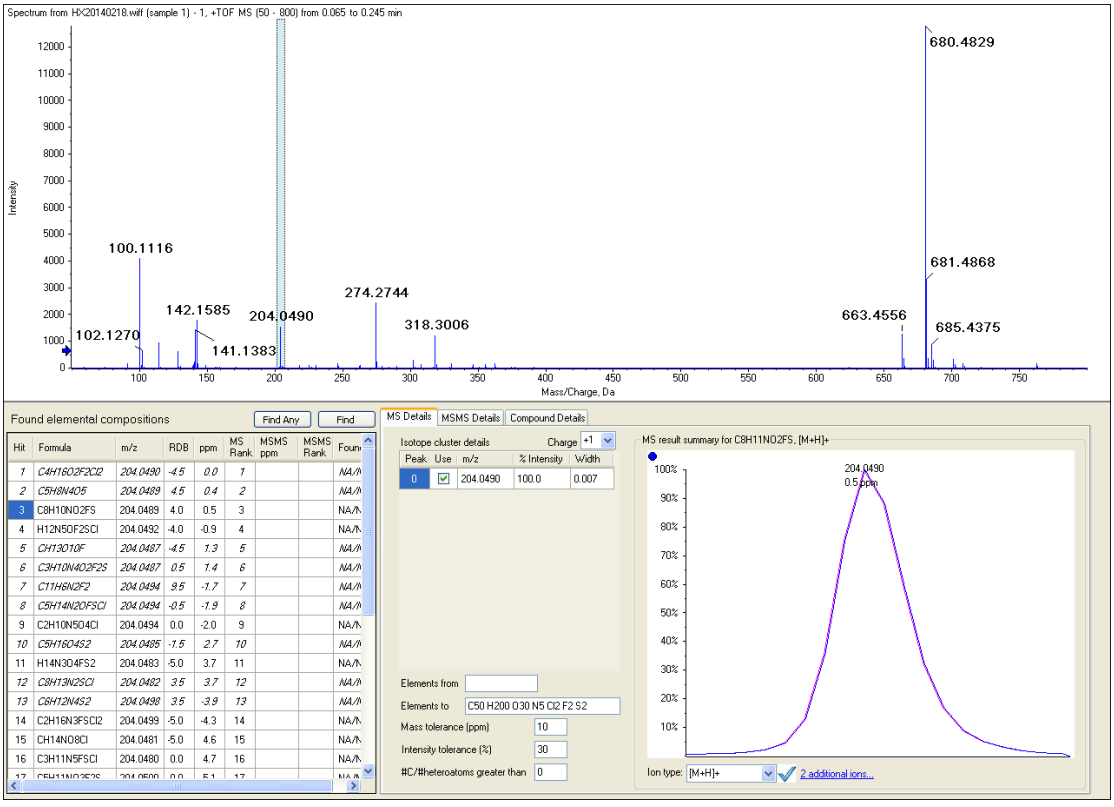
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38(s, 1H), 7.28 (d, J=7.5 Hz, 2H), 7.09(d, J=8.0Hz, 2H), 3.10(s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 135.1, 134.2, 129.8, 127.4, 35.6.

The ESI-MS spectral of **3ca** for example





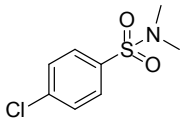


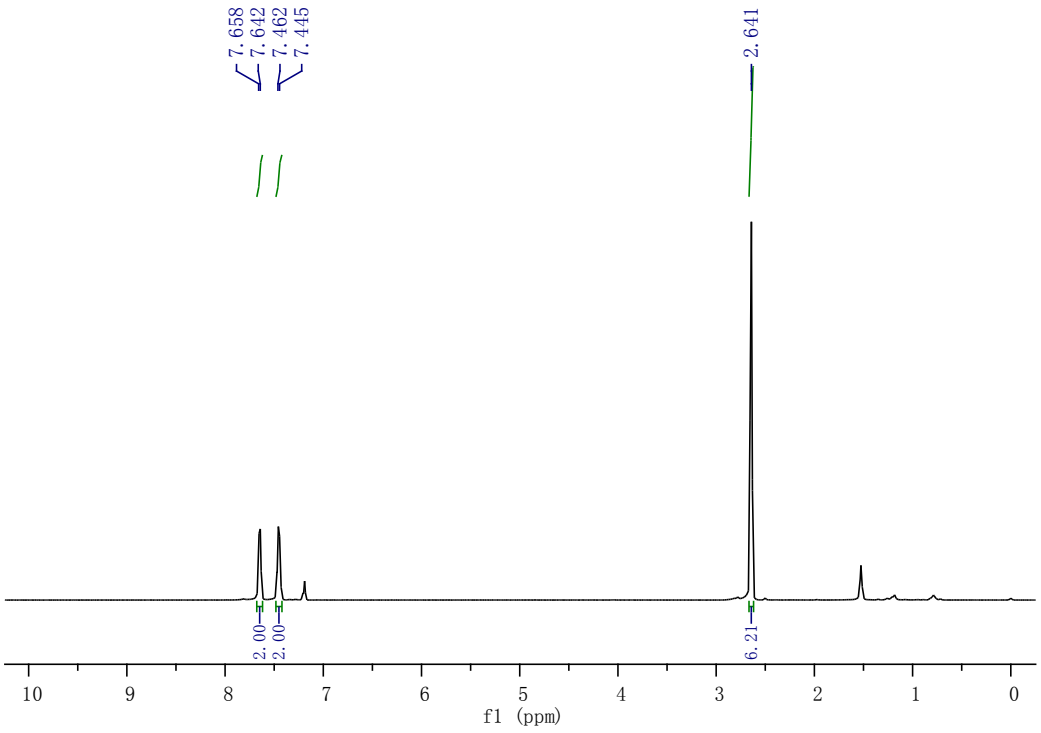
V References

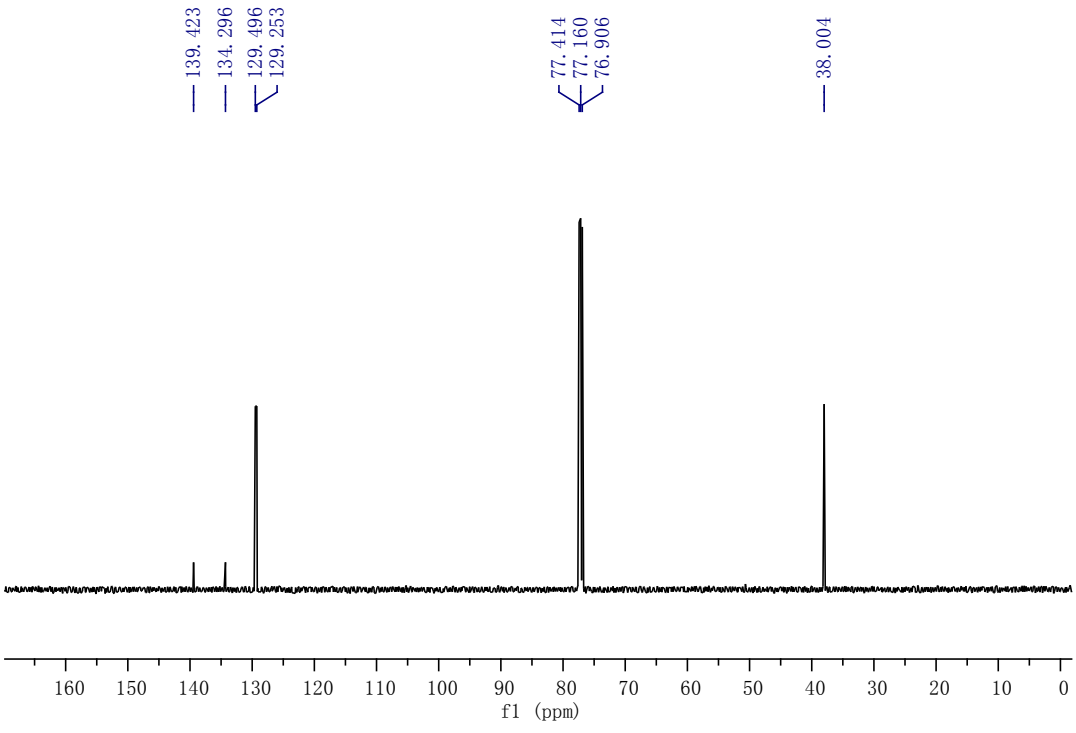
1 M. R. Banks, R. F. Hudson. J. Chem. Soc., Chem. Commun., 1985.

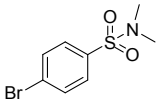
2 X. Tang, L. Huang, C. Qi, X. Wu, W. Wu and H. Jiang, Chem. Commun., 2013, **49**, 6102.

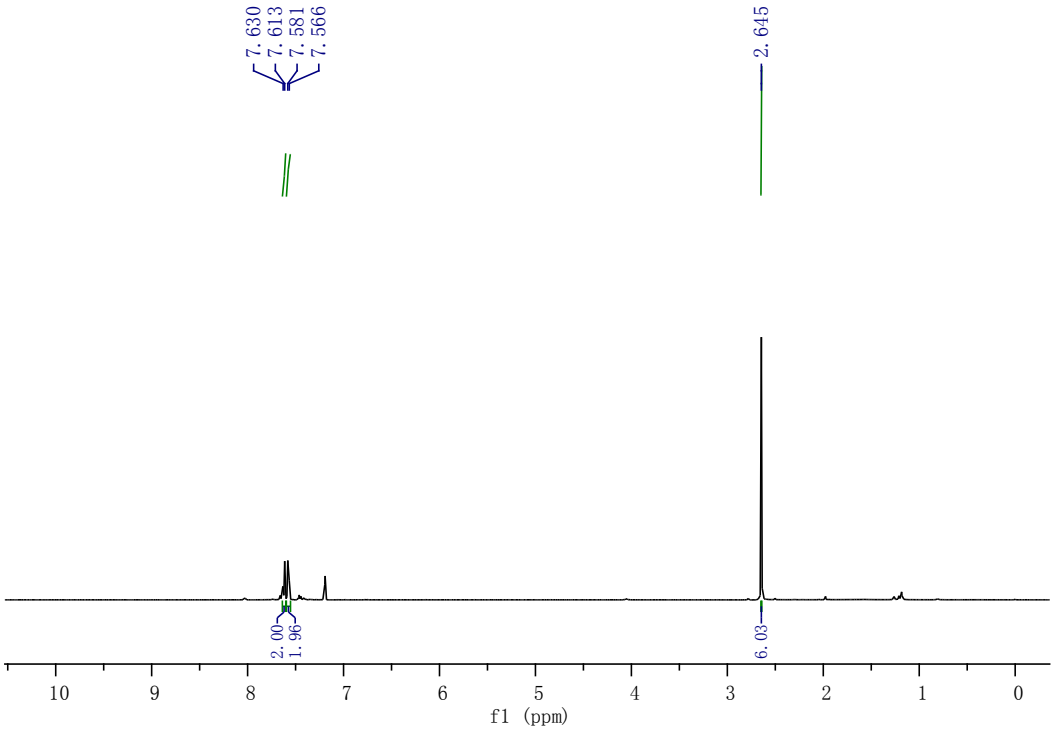
VI NMR Spectra for the Compounds








O
N
S
O
Br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7.613
7.581
7.566
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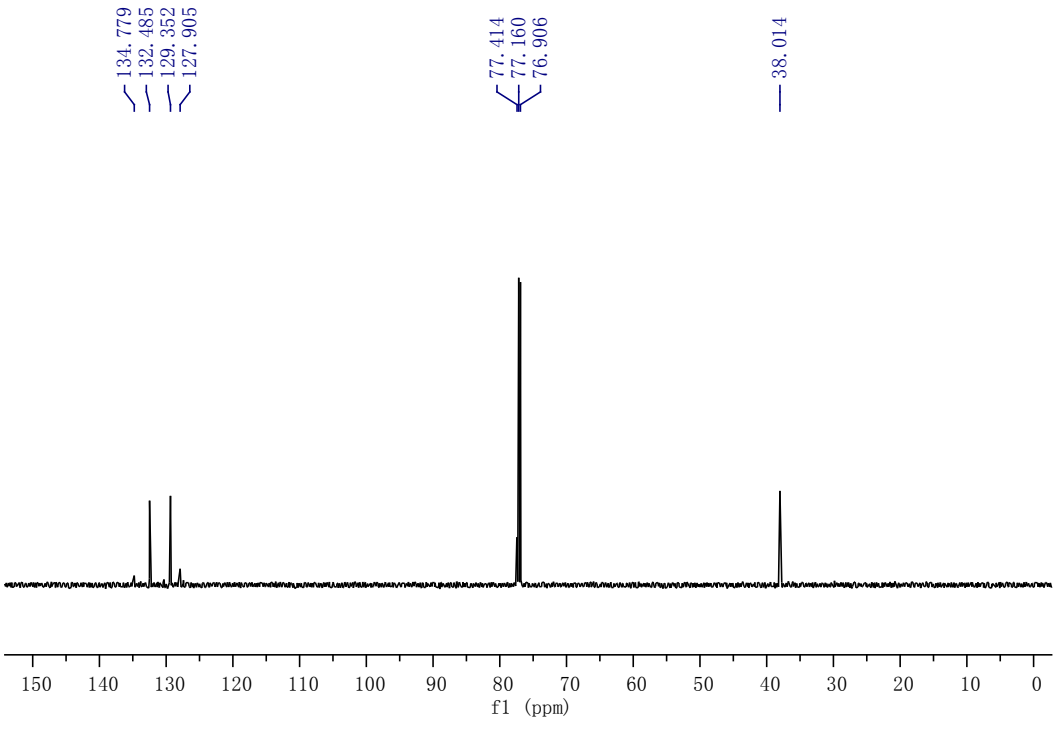
1.96
6.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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77.160
76.906
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140
130
120
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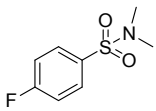
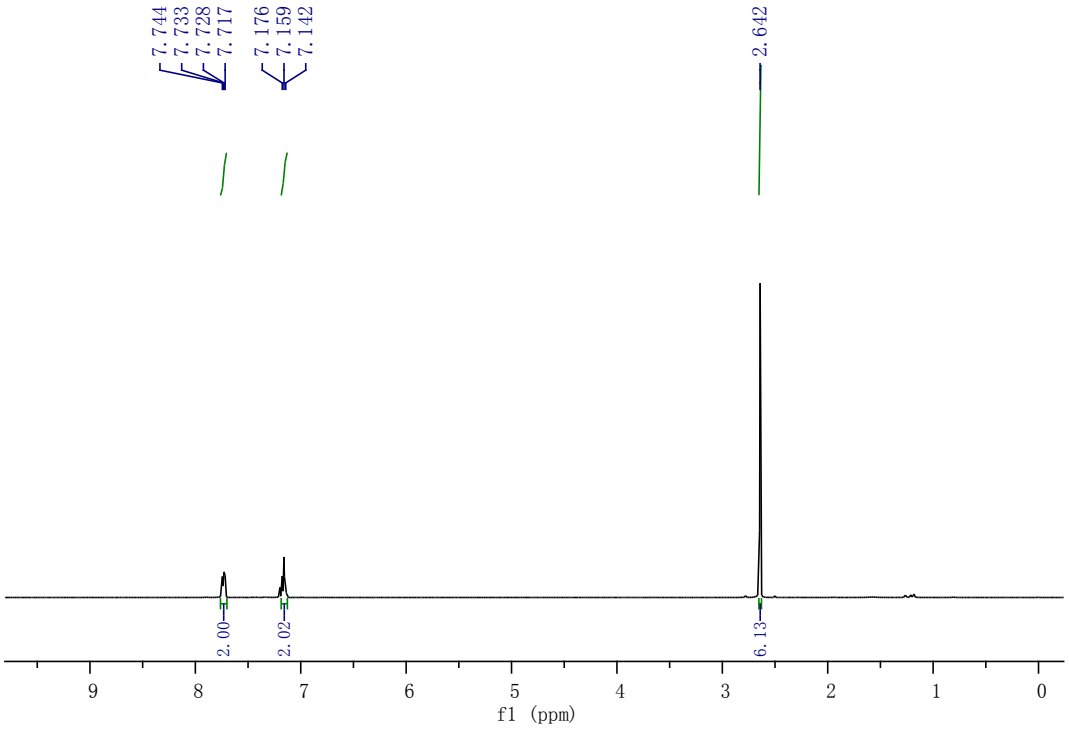
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
S
O
F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7.717
7.176
7.159
7.142
2.642
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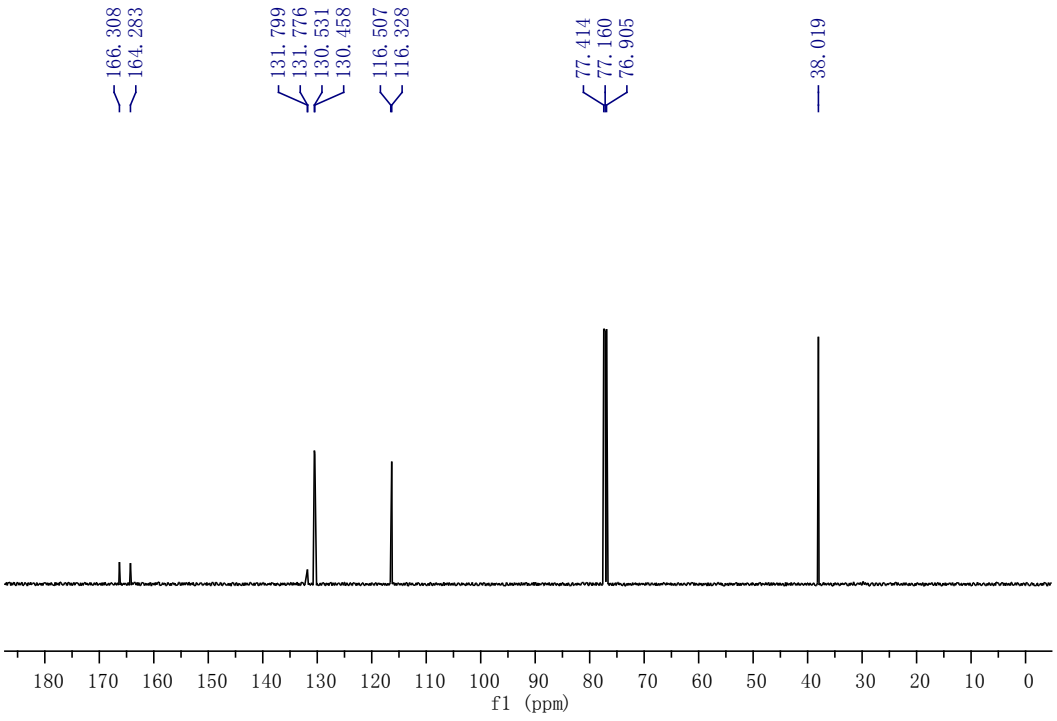
2.02
6.13
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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131.776
130.531
130.458
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116.328
77.414
77.160
76.905
38.019
180
170
160
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90
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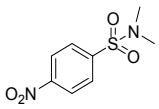
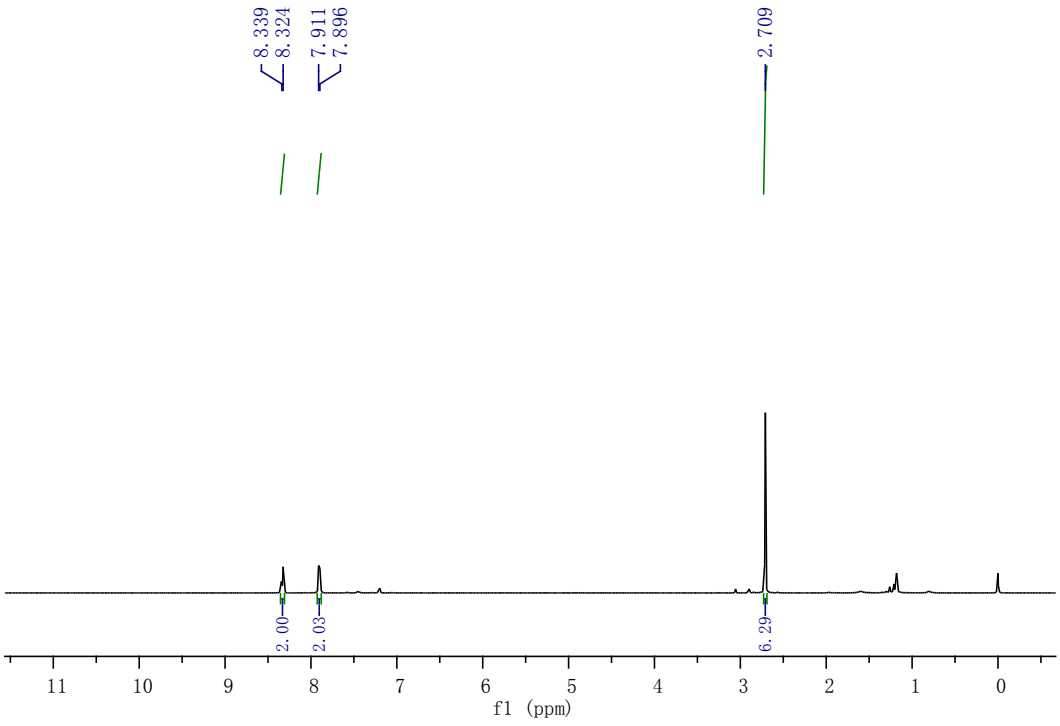
10
0
f1 (ppm)

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8.324
7.911
7.896
2.709
2.00
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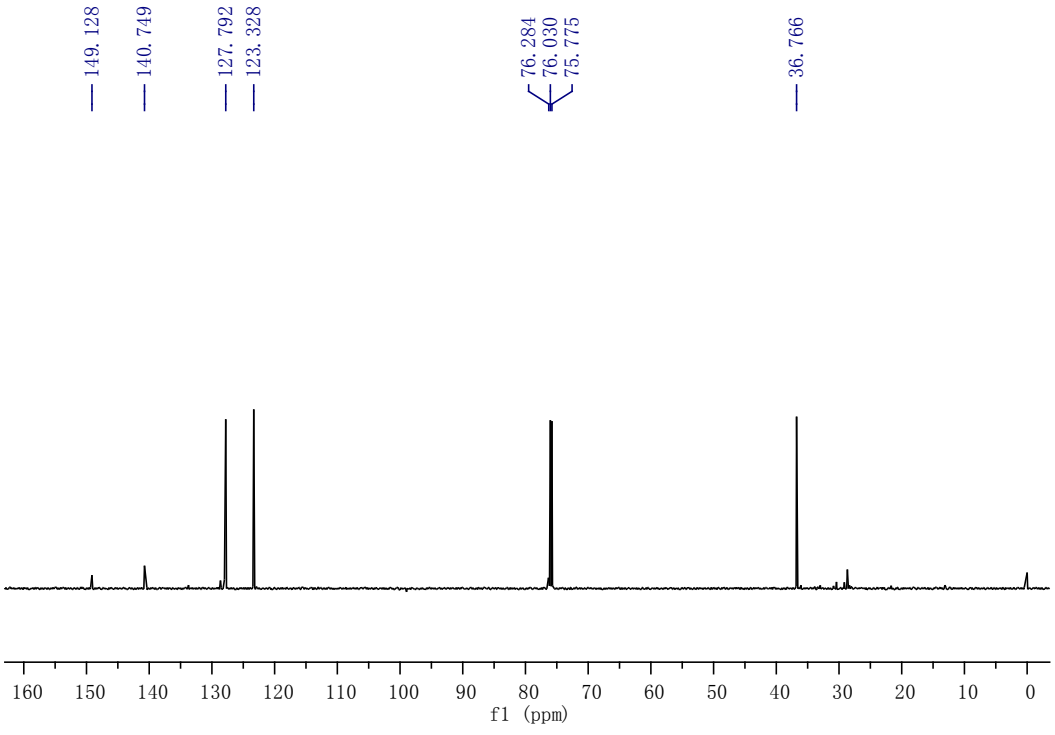
6.29
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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140.749
127.792
123.328
76.284
76.030
75.775
36.766
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150
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130
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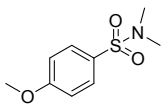
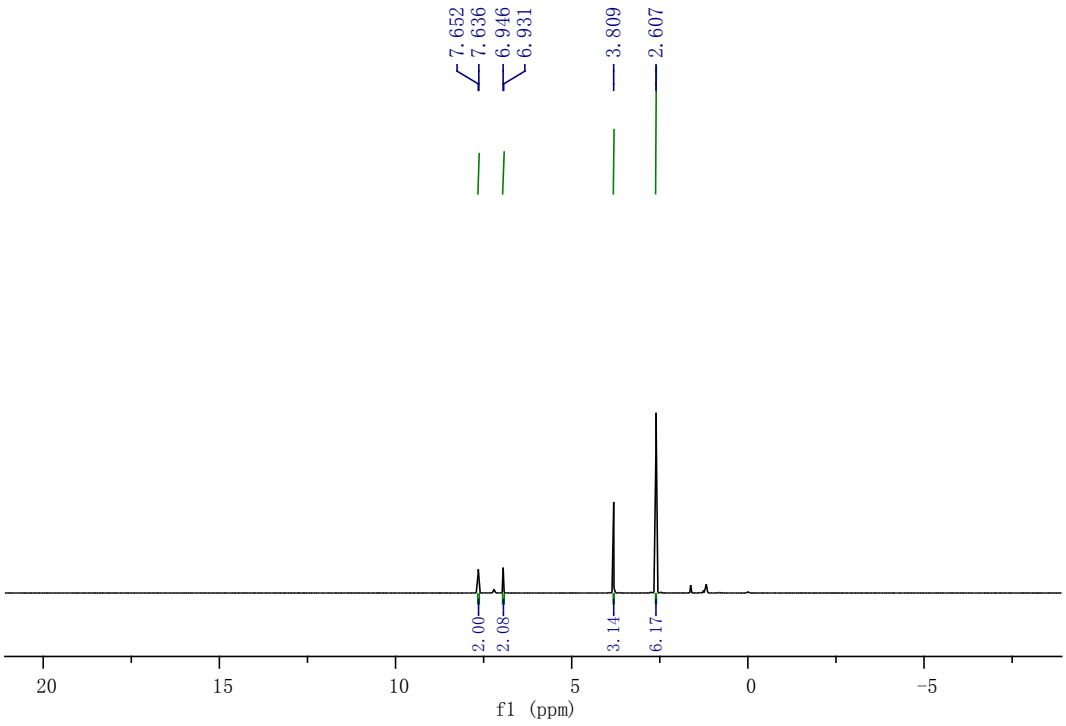
f1 (ppm)

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7.636
6.946
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2.08
3.14
6.17
20
15
10
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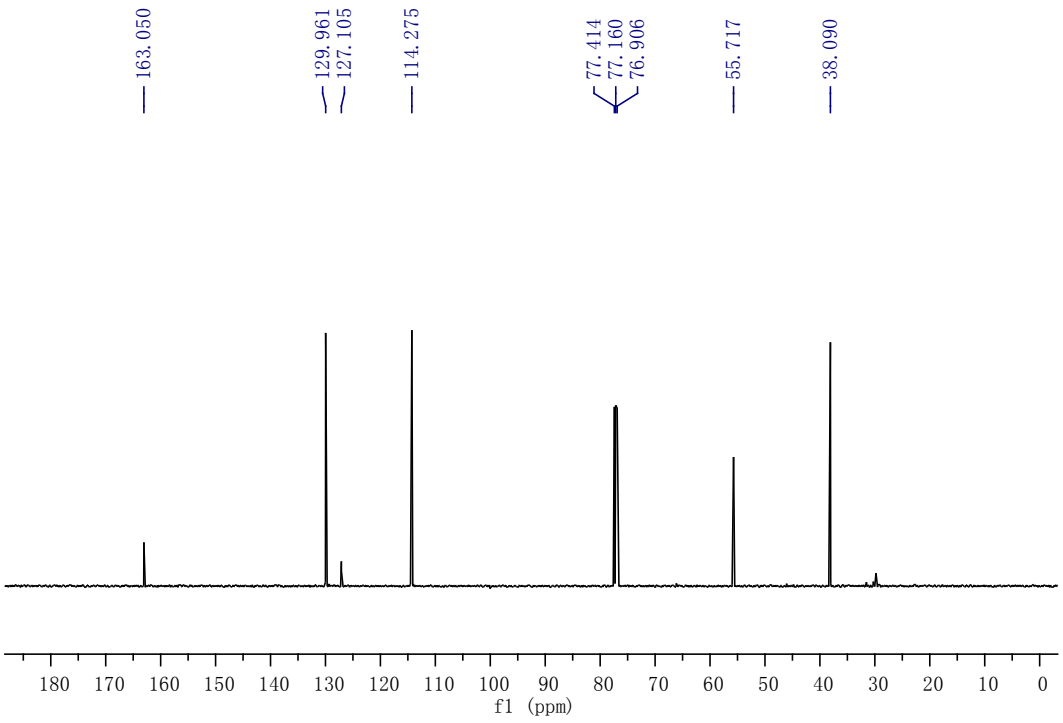
-5
f1 (ppm)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129.961
127.105
114.275
77.414
77.160
76.906
55.717
38.090
180
170
160
150
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130
120
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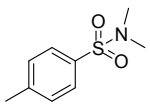
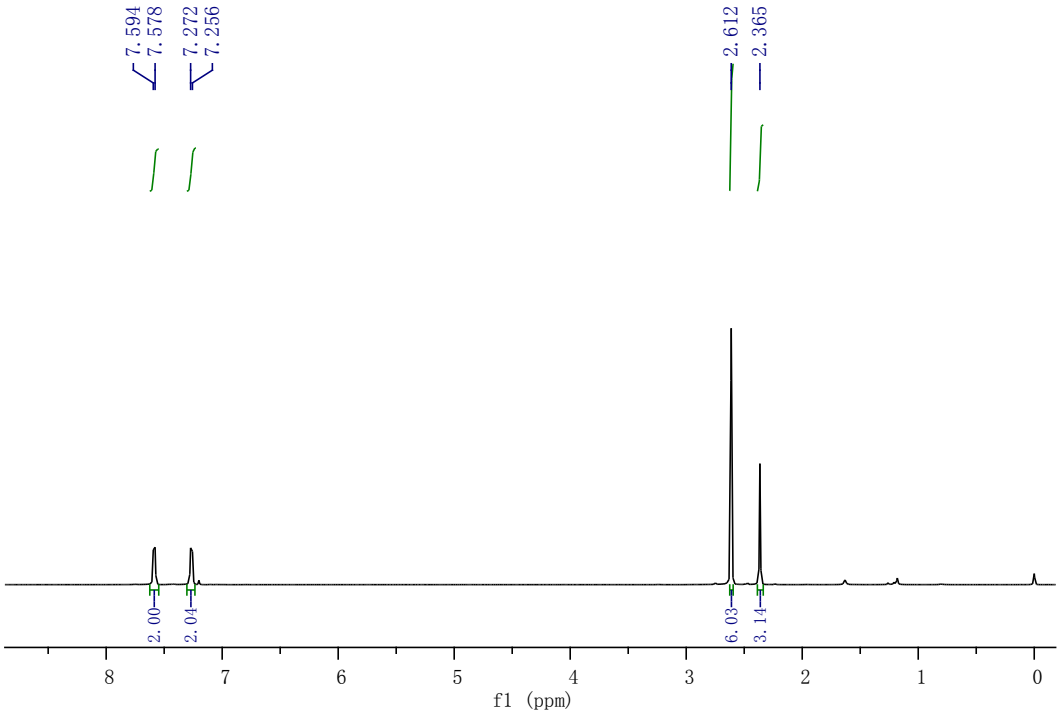
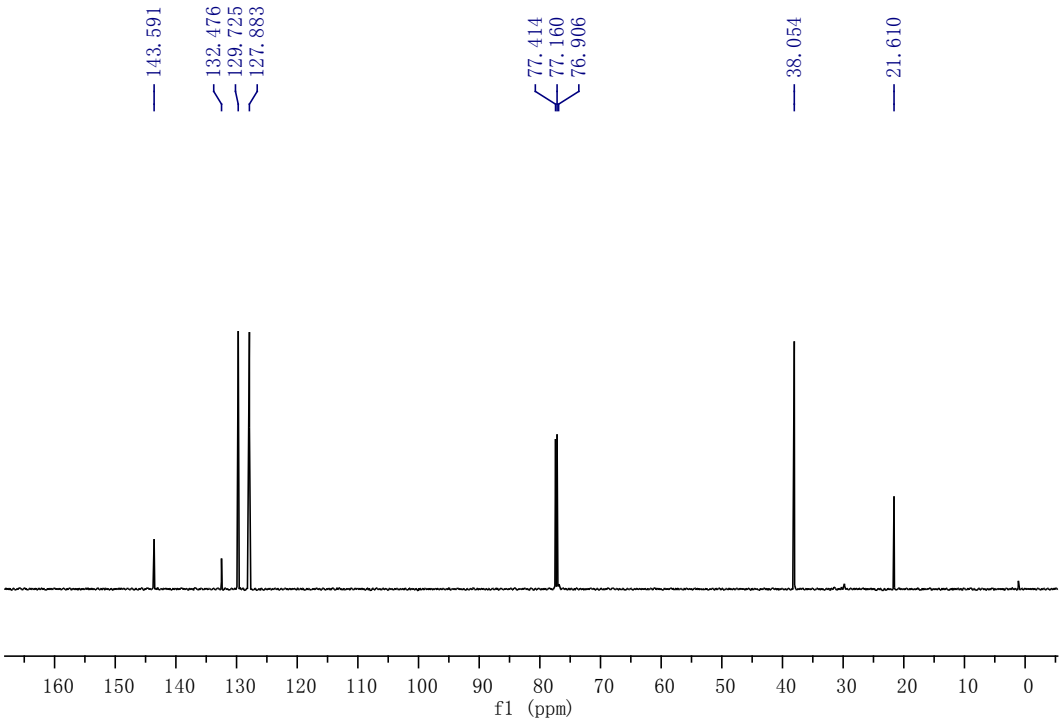
f1 (ppm)




7.594
7.578
7.272
7.256
2.612
2.365
2.00
2.04
6.03
3.14
8
7
6
5
4
3
2
1
0
f1 (ppm)


143.591
132.476
129.725
127.883
77.414
77.160
76.906
38.054
21.610
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150
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130
120
110
100
90
80
70
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50
40
30
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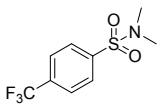
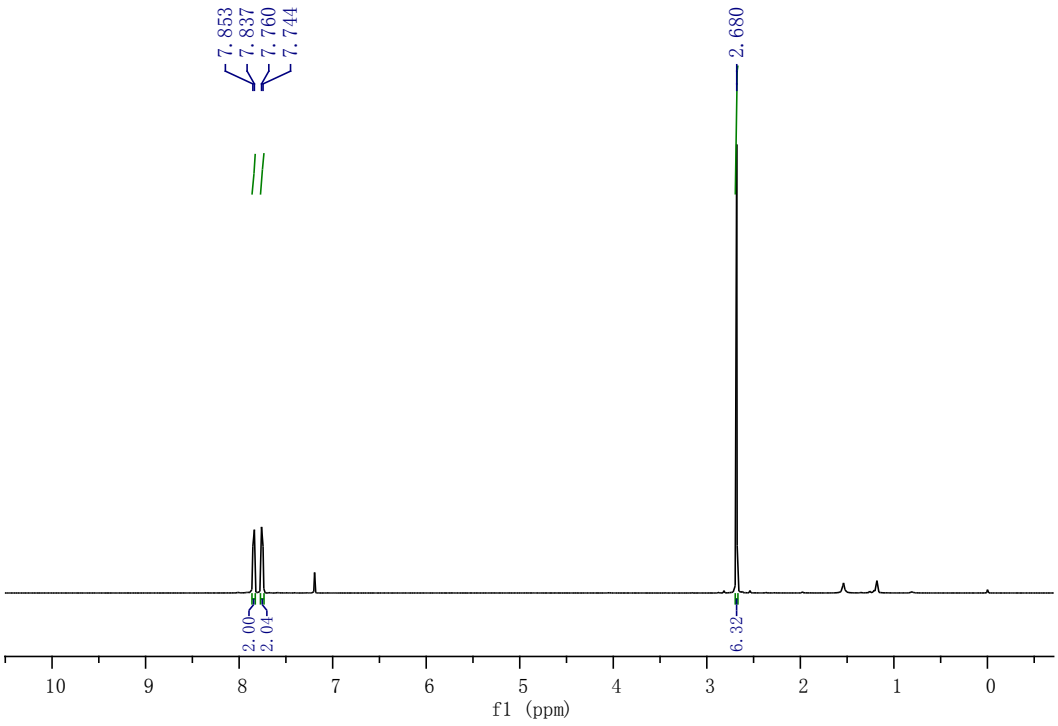
10
0
f1 (ppm)


O
N
S
O
F3C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7.837
7.760
7.744
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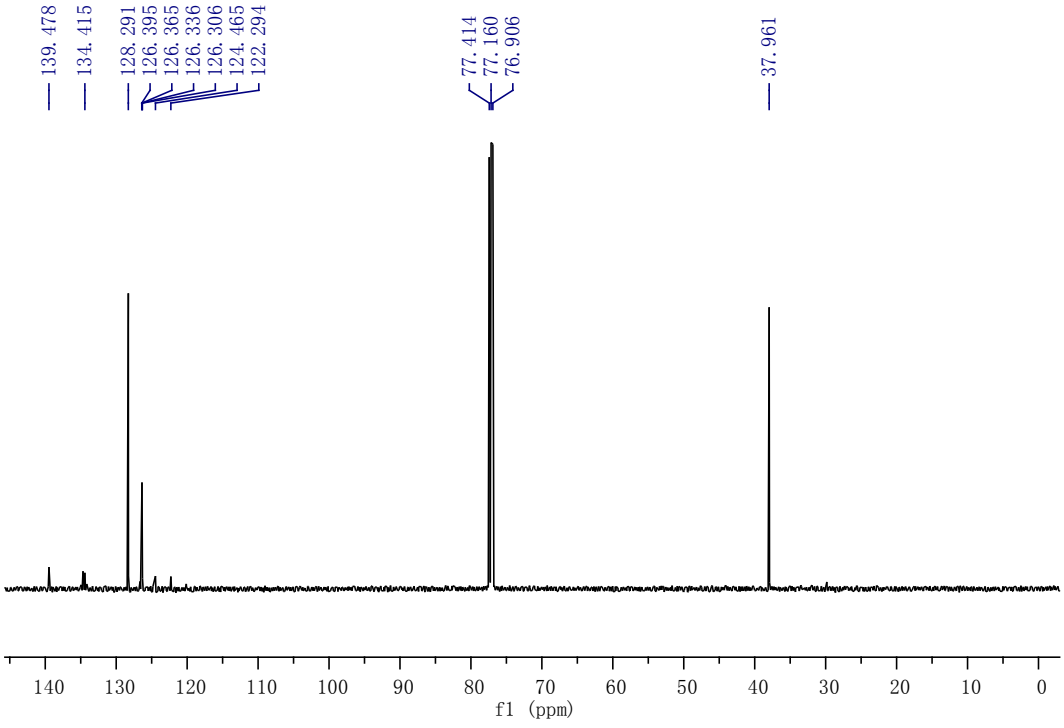
2.00
2.04
6.32
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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134.415
128.291
126.395
126.365
126.336
126.306
124.465
122.294
77.414
77.160
76.906
37.961
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130
120
110
100
90
80
70
60
50
40
30
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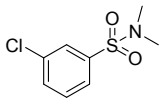
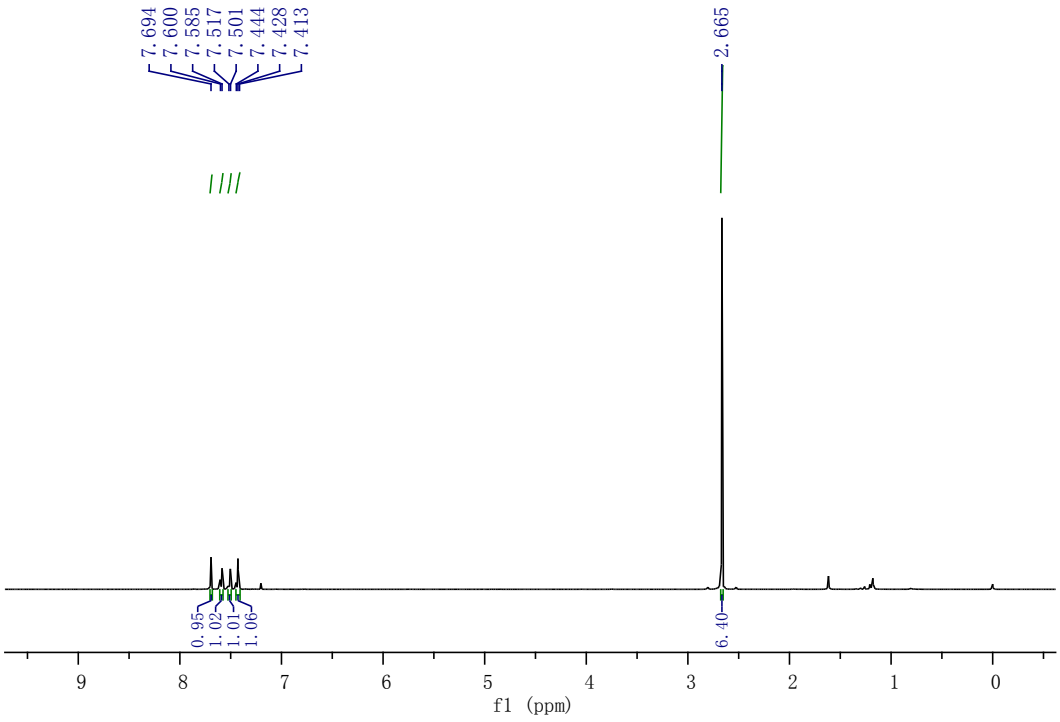
10
0
f1 (ppm)


Cl
S
O
O
N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7.600
7.585
7.517
7.501
7.444
7.428
7.413
2.665
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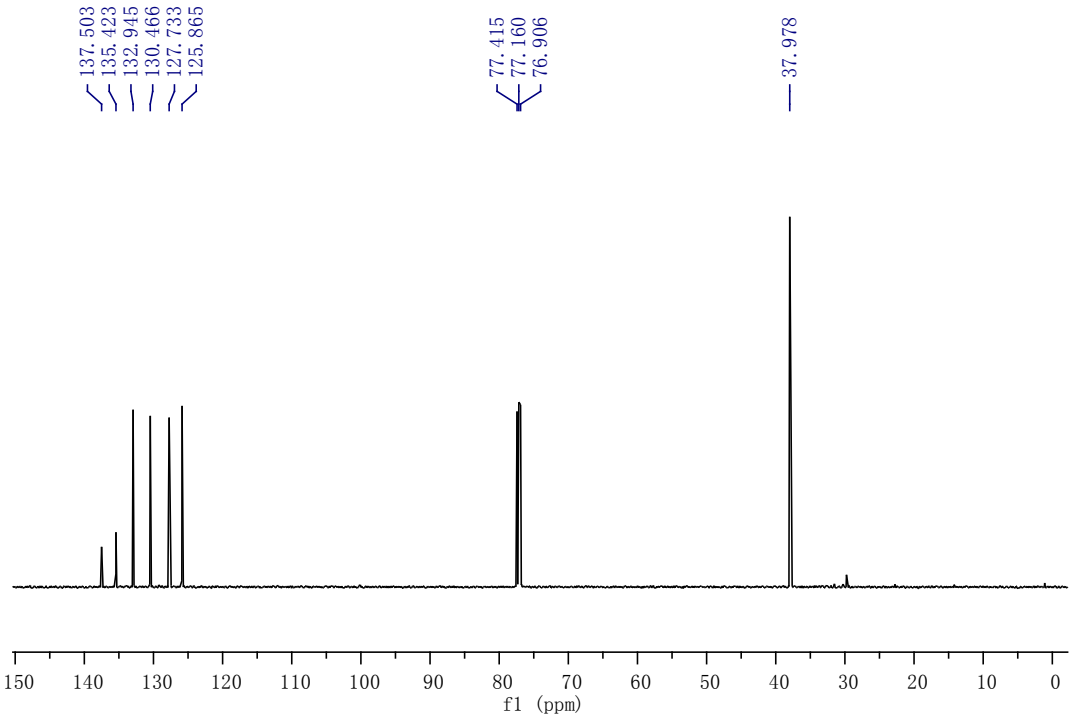
1.02
1.01
1.06
6.40
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


137.503
135.423
132.945
130.466
127.733
125.865
77.415
77.160
76.906
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130
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50
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30
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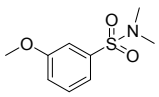
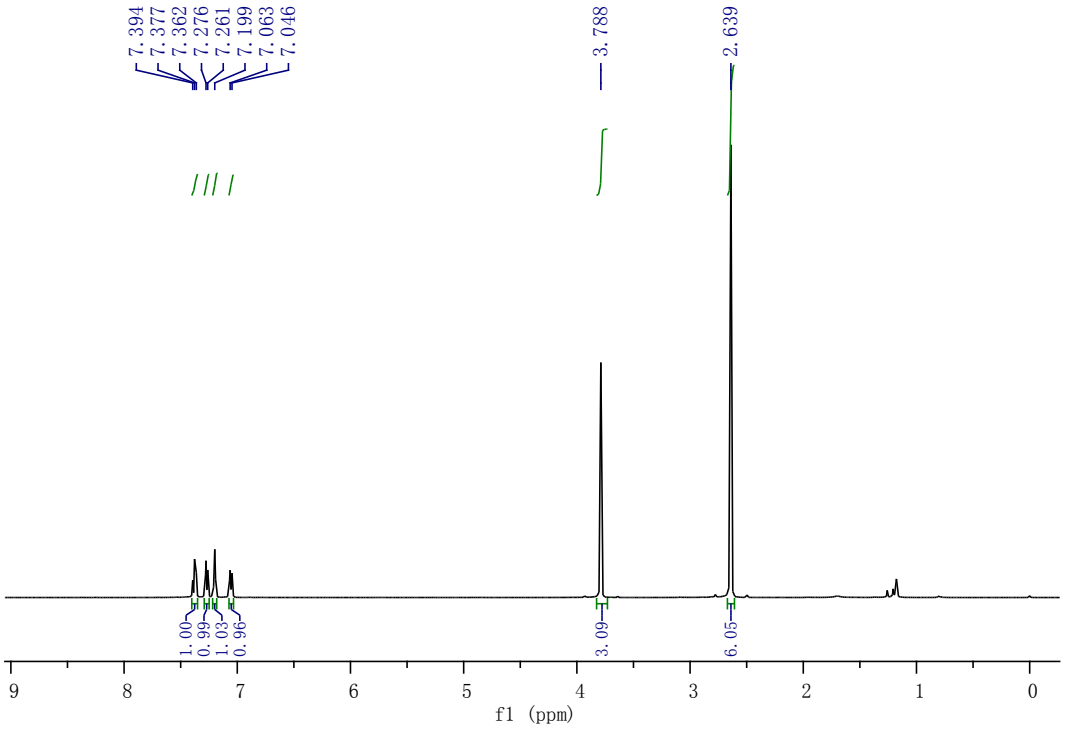
10
0
f1 (ppm)

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7.377
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7.276
7.261
7.199
7.063
7.046
3.788
2.639
1.00
0.99
1.03
0.96
3.09
6.05
9
8
7
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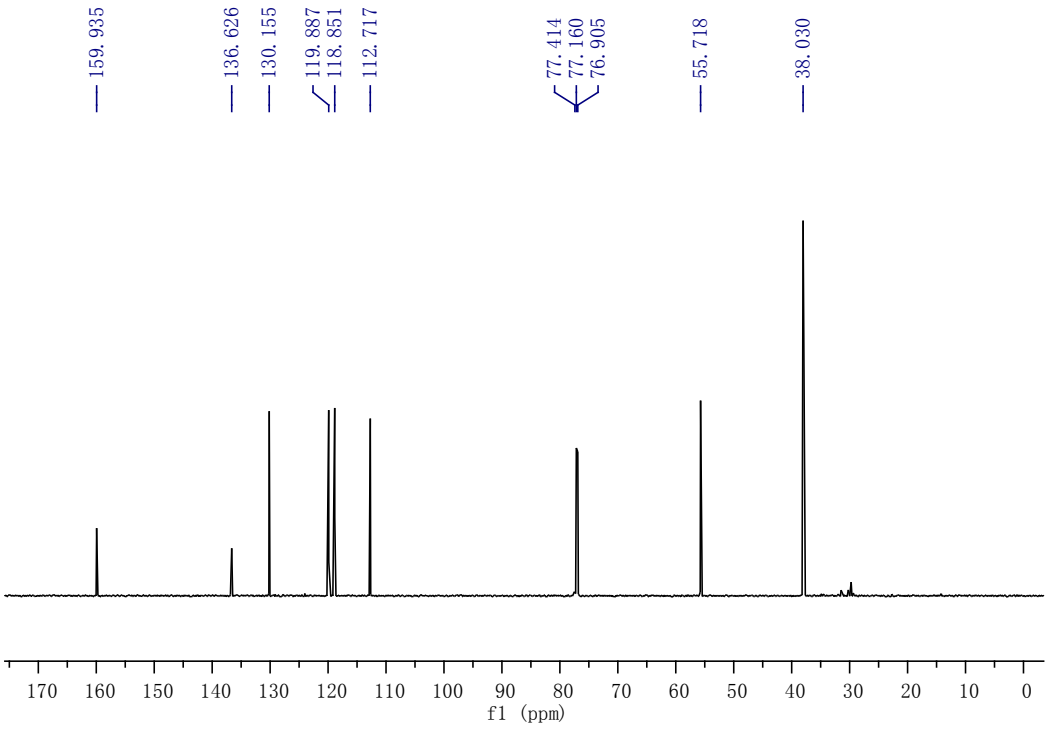
5
4
3
2
1
0
f1 (ppm)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119.887
118.851
112.717
77.414
77.160
76.905
55.718
38.030
170
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150
140
130
120
110
100
90
80
70
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50
40
30
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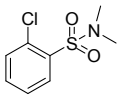
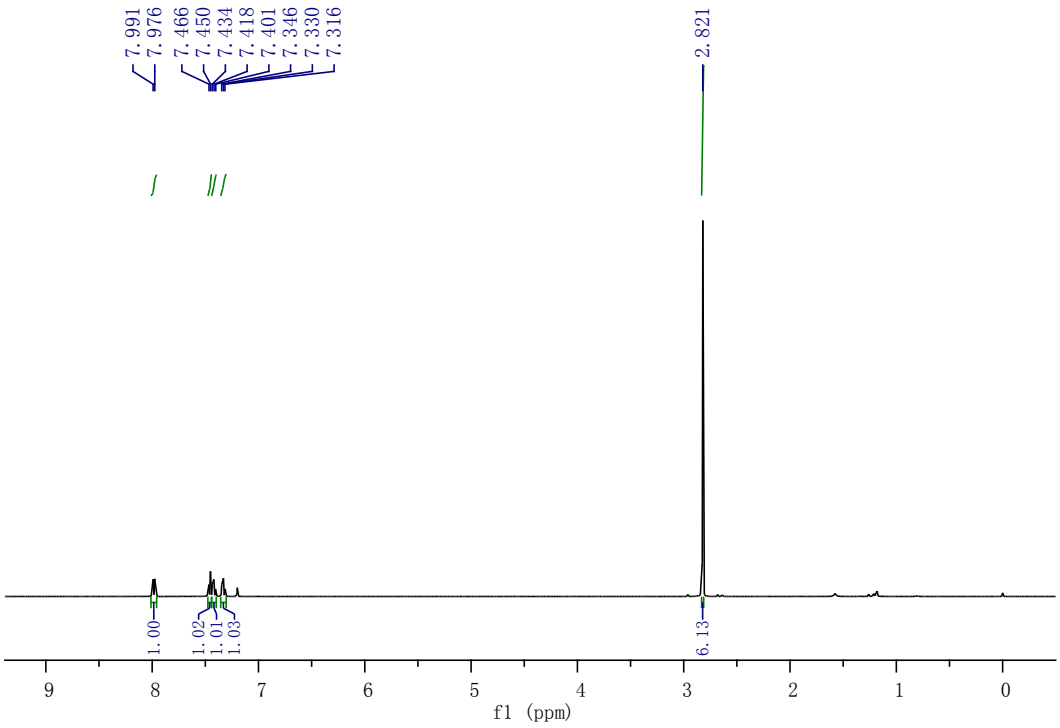
10
0
f1 (ppm)


Cl
O
N
S
O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7.976
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7.450
7.434
7.418
7.401
7.346
7.330
7.316
2.821
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1.02
1.01
1.03
6.13
9
8
7
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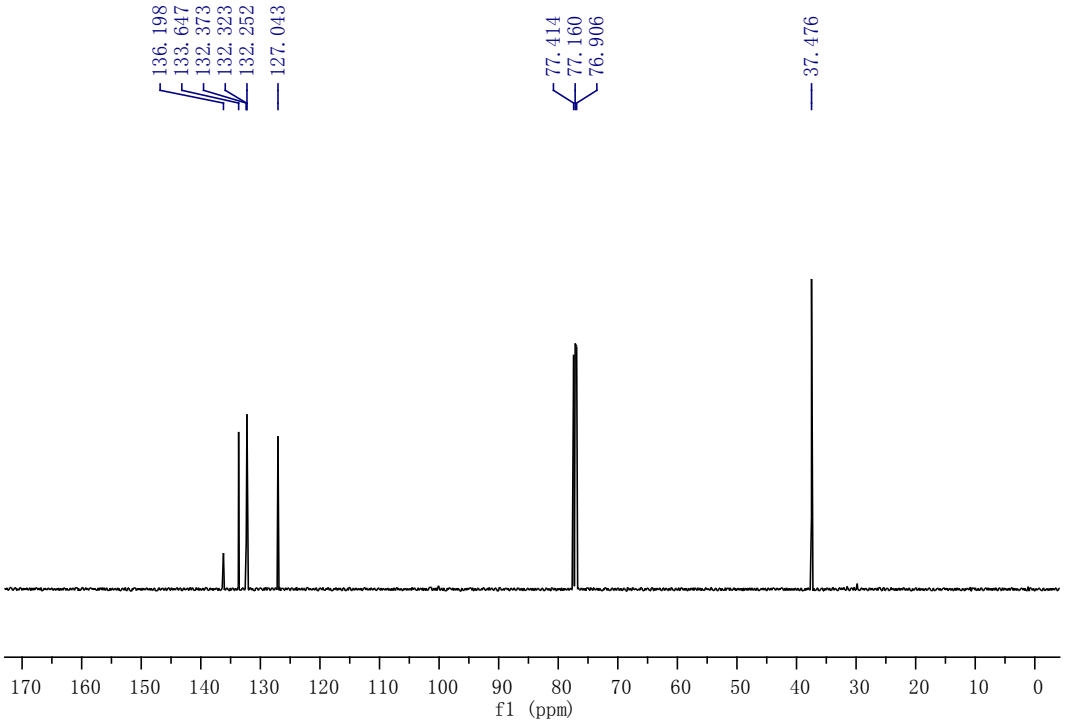
5
4
3
2
1
0
f1 (ppm)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132.373
132.323
132.252
127.043
77.414
77.160
76.906
37.476
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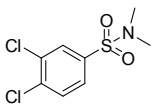
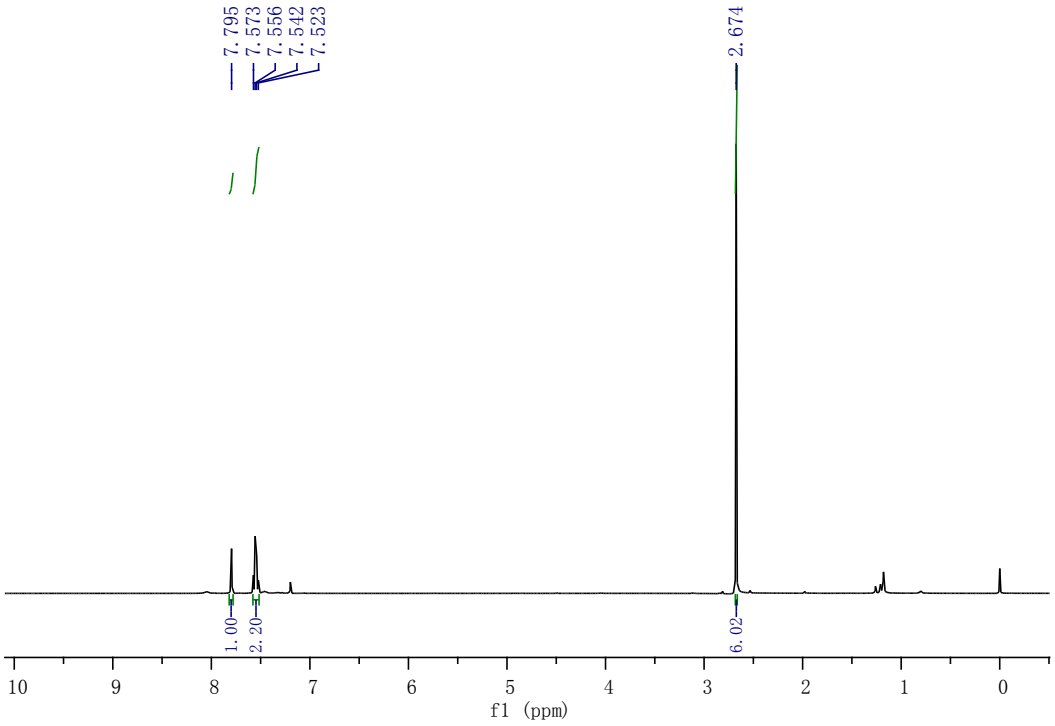
f1 (ppm)


Cl
Cl
O
N
S
O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7.523
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6.02
10
9
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5
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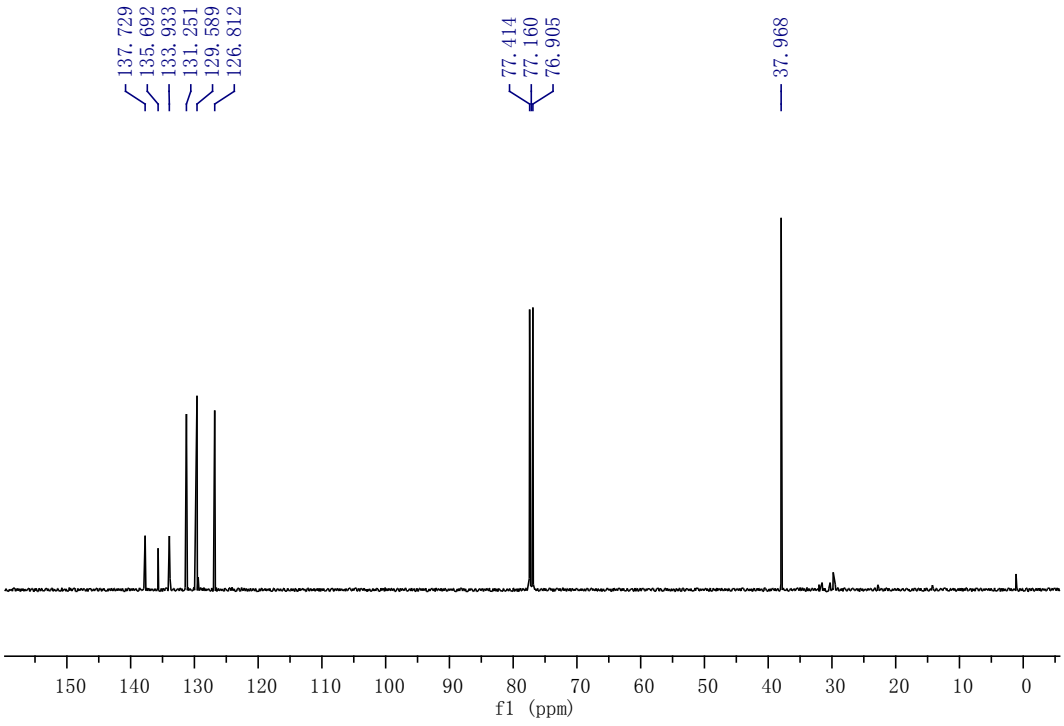
f1 (ppm)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131.251
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126.812
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77.160
76.905
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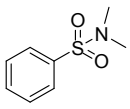
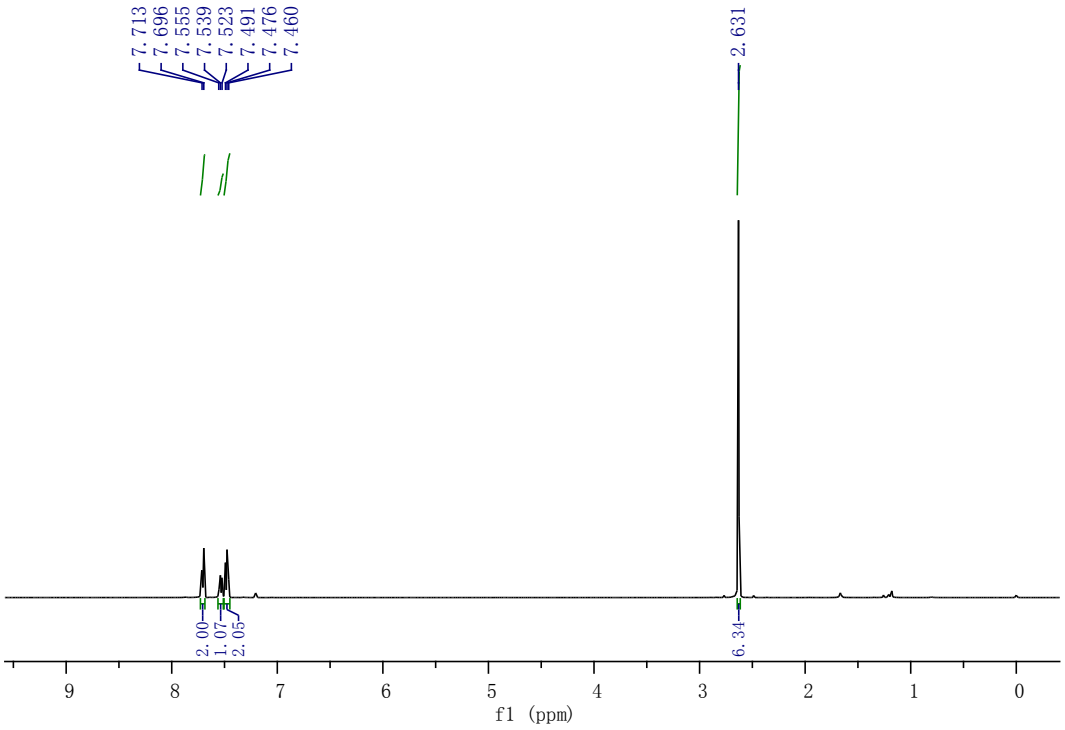
f1 (ppm)

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7.555
7.539
7.523
7.491
7.476
7.460
2.631
2.00
1.07
2.05
6.34
9
8
7
6
5
4
3
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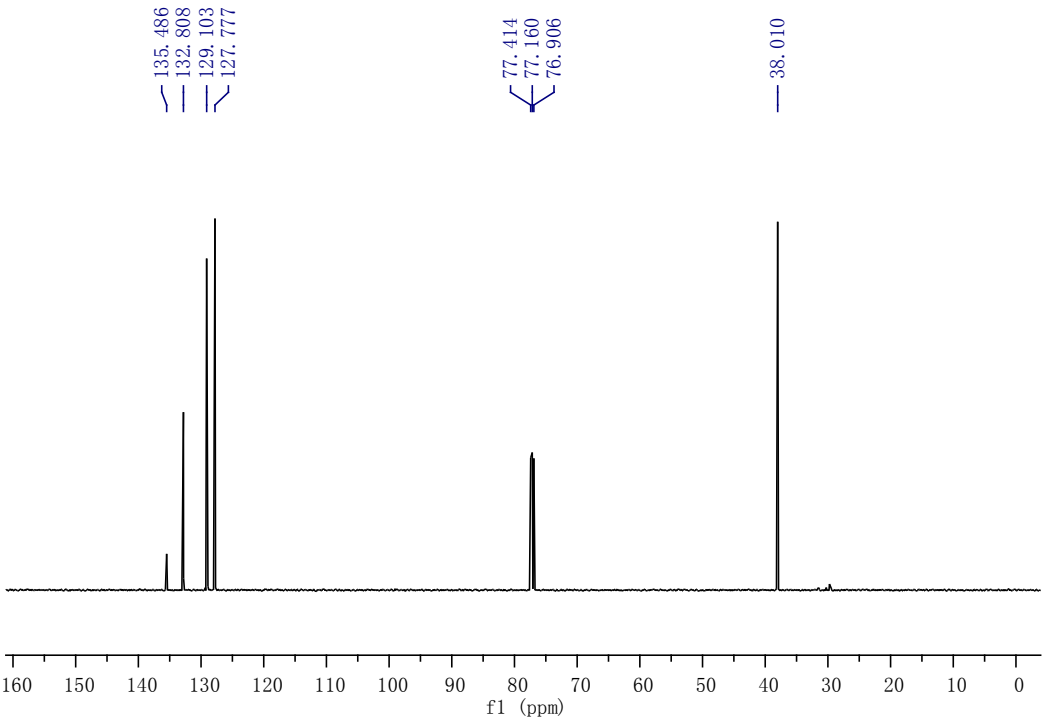
1
0
f1 (ppm)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77.160
76.906
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130
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40
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10
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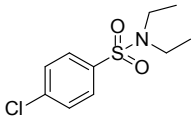
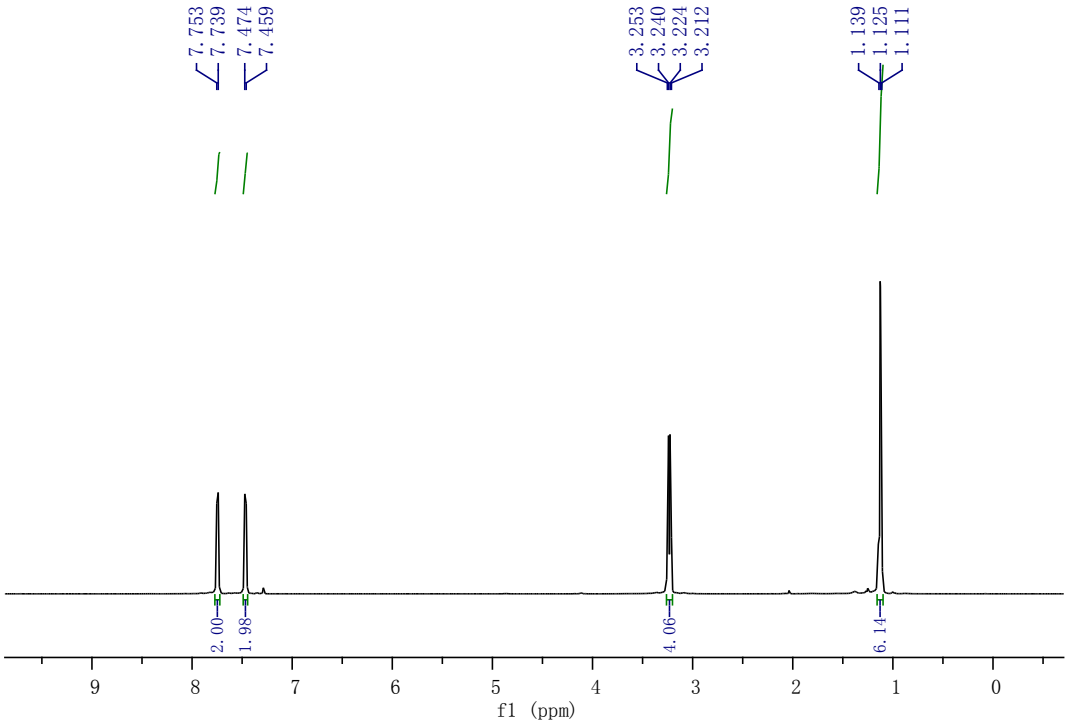
f1 (ppm)


O
N
S
O
Cl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3.212
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1.125
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4.06
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9
8
7
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5
4
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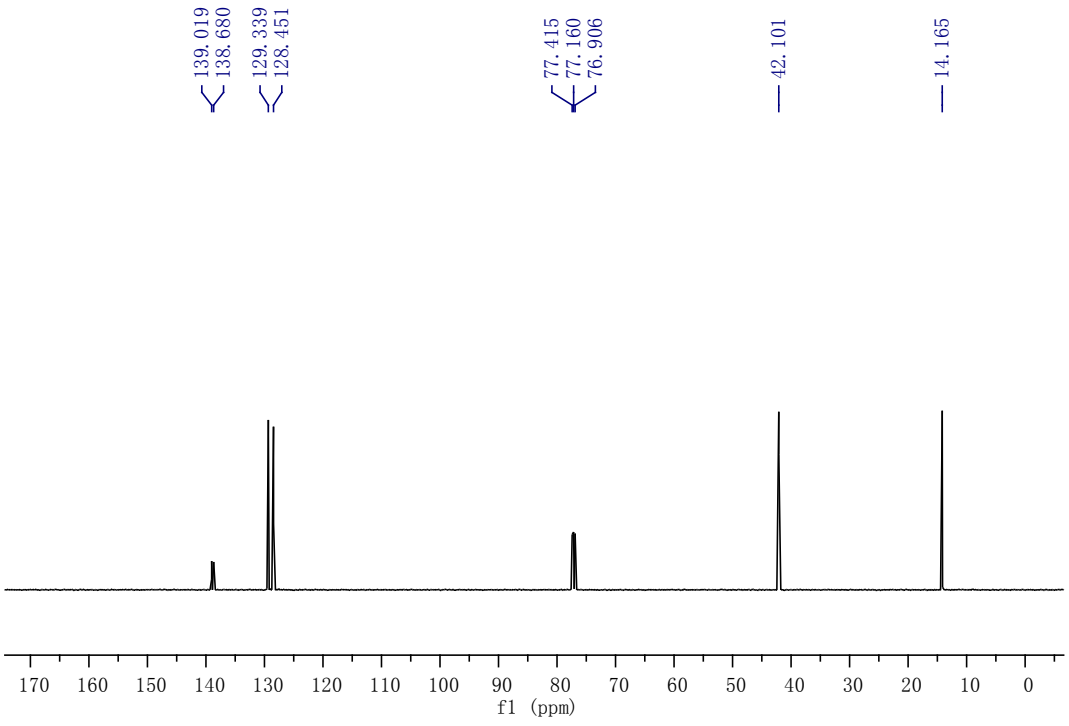
f1 (ppm)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128.451
77.415
77.160
76.906
42.101
14.165
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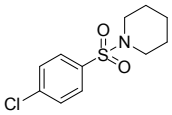
f1 (ppm)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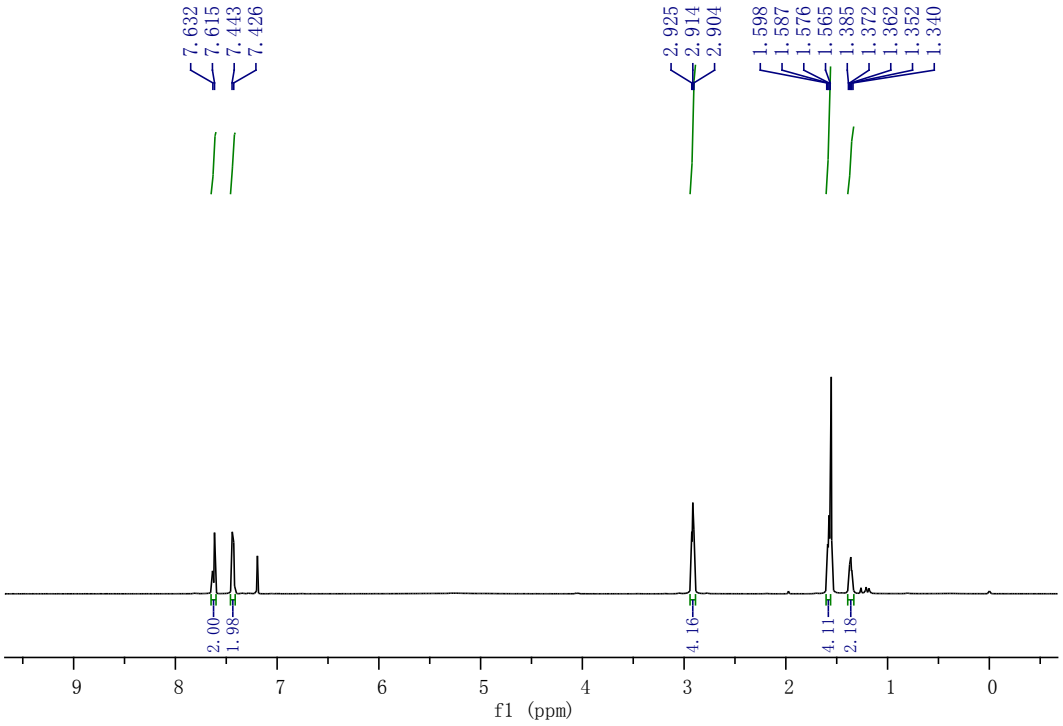
N
S
O
Cl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1.385
1.372
1.362
1.352
1.340
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4.11
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9
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4
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1
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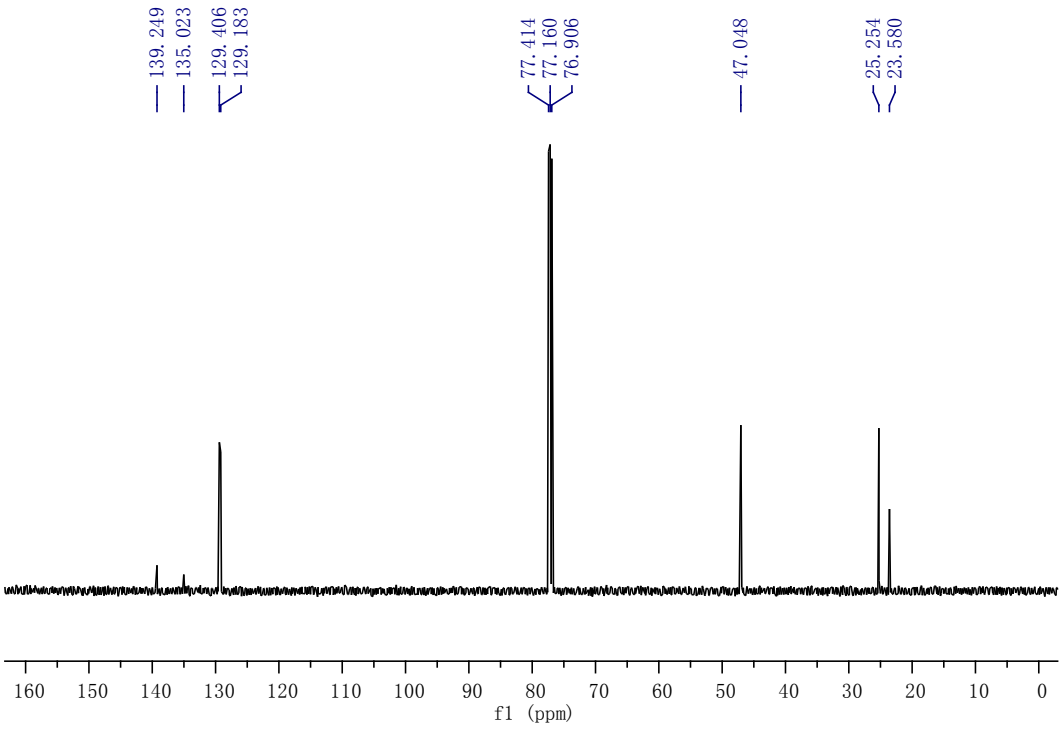
f1 (ppm)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77.414
77.160
76.906
47.048
25.254
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50
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10
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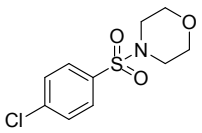
f1 (ppm)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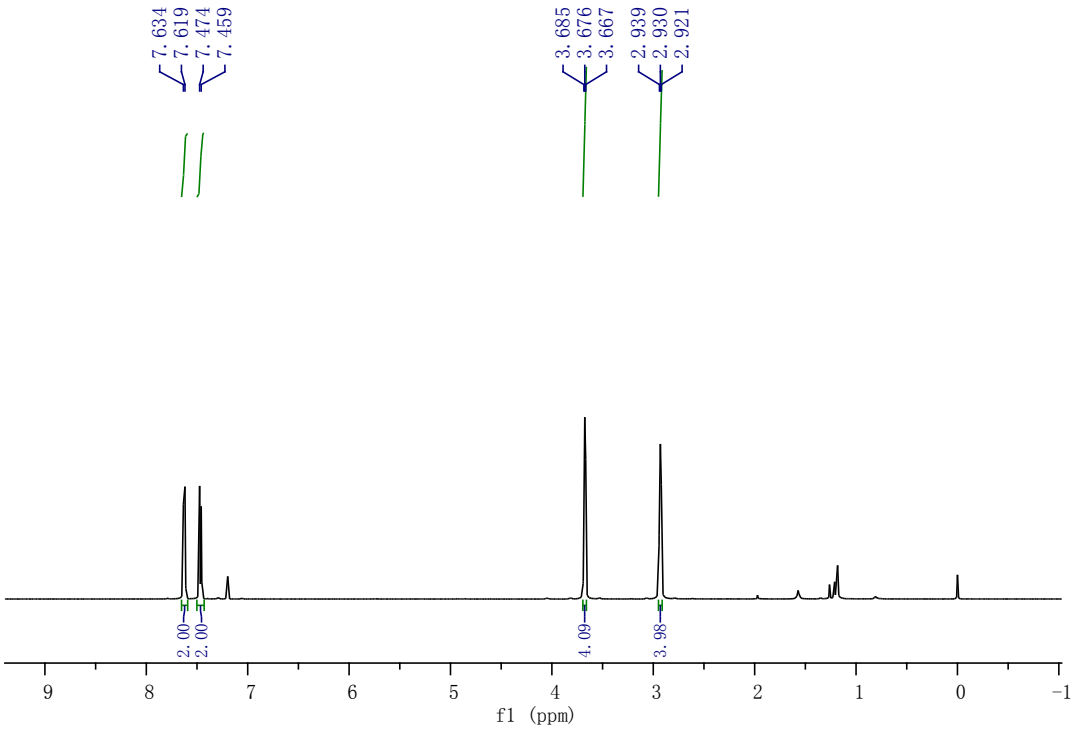
O
N
S
O
Cl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7.619
7.474
7.459
3.685
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3.667
2.939
2.930
2.921
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2.00
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3.98
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8
7
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4
3
2
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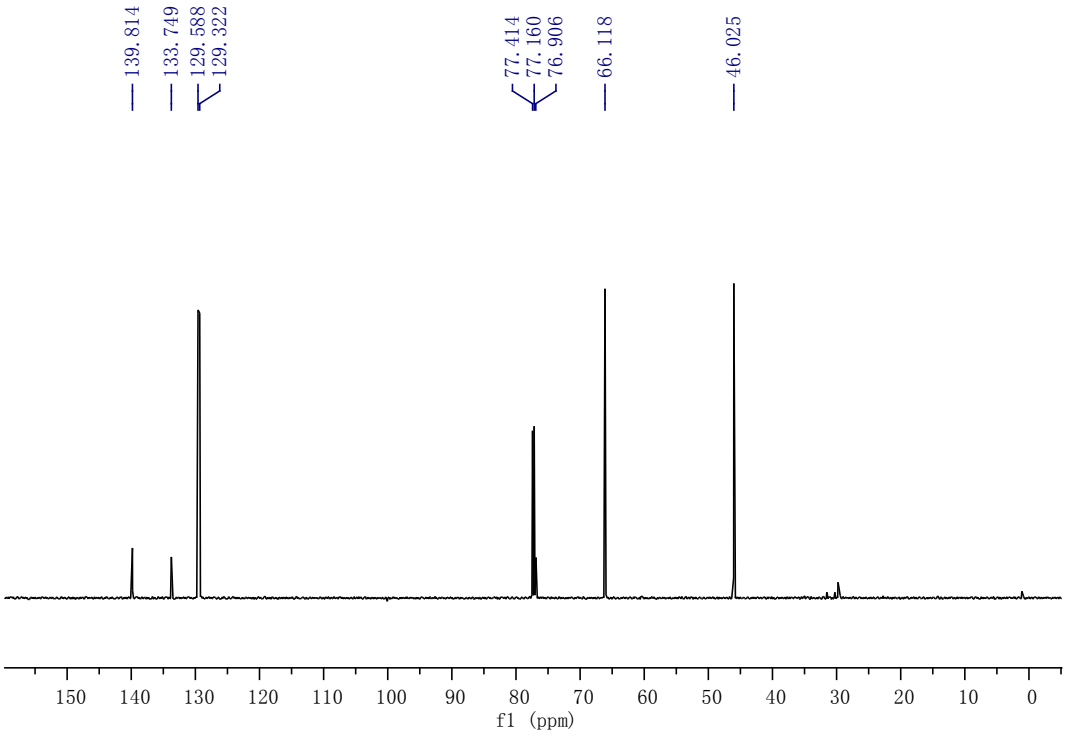
0
-1
f1 (ppm)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77.160
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66.118
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50
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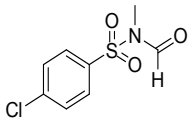
f1 (ppm)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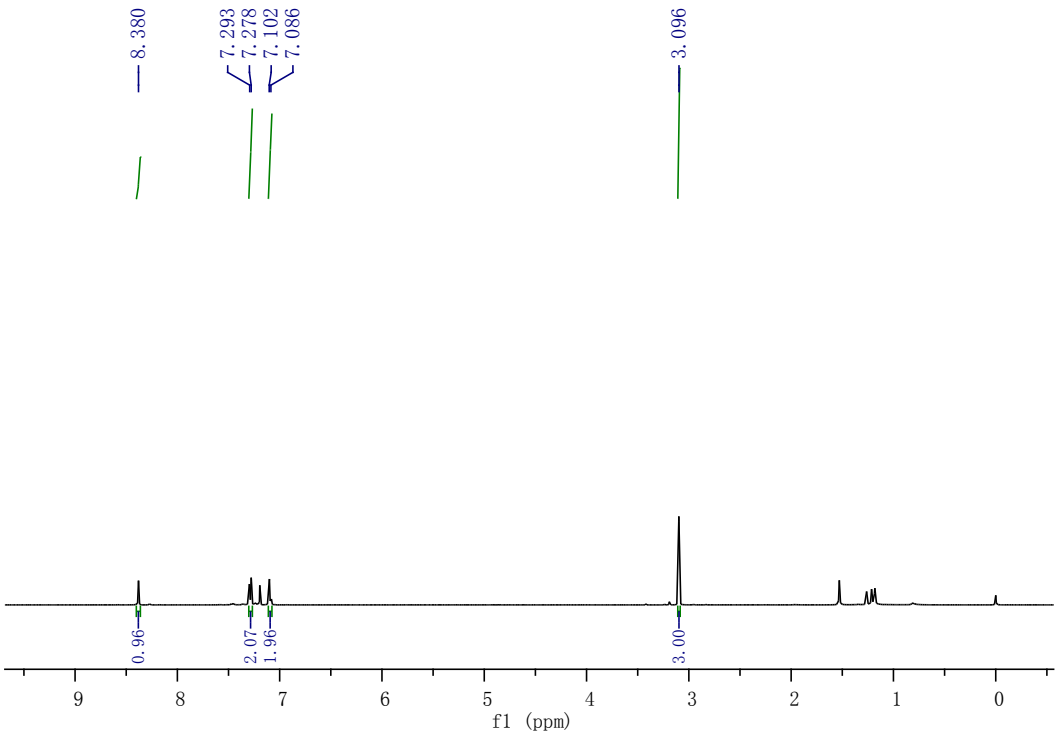
N
O
S
O
H
Cl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5
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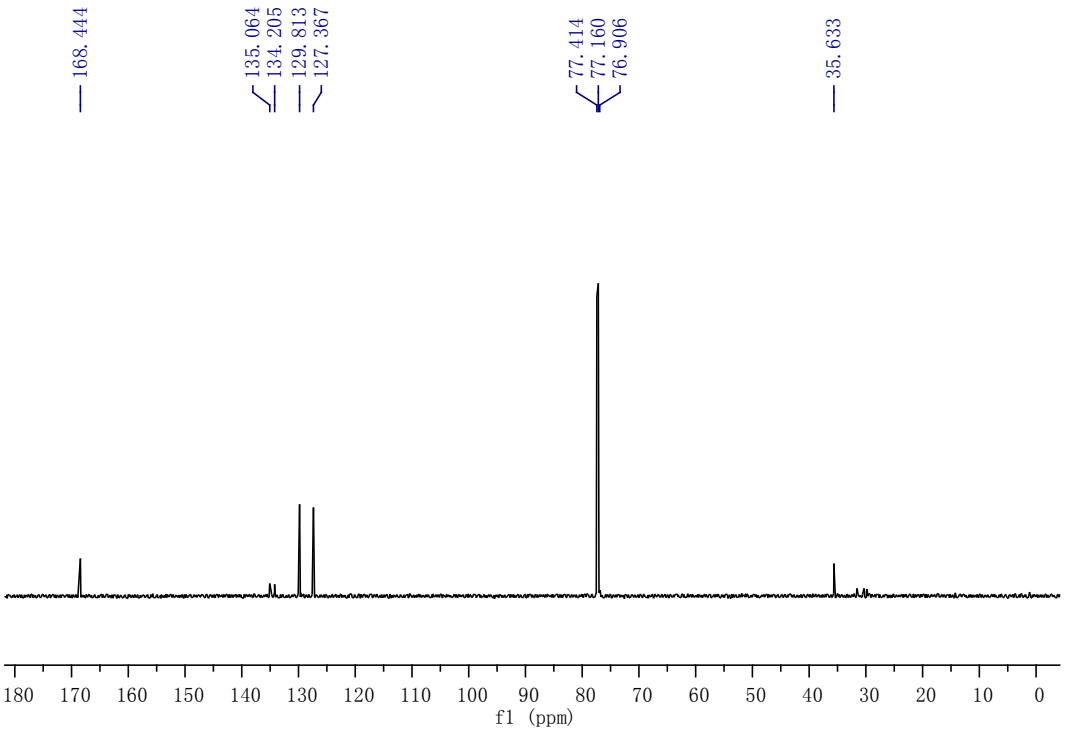
f1 (ppm)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76.906
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70
60
50
40
30
20
10
0
f1 (ppm)