A Copper-Catalyzed Three-Component Reaction of Triethoxysilanes, Sulfur Dioxide, and Hydrazines

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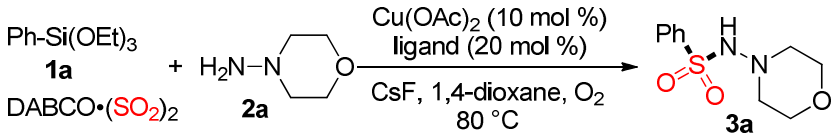
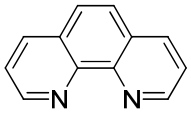
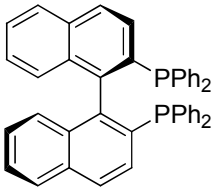
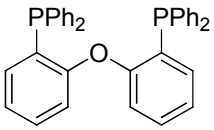
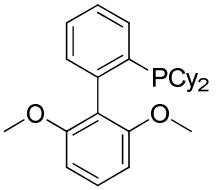
Supporting Information

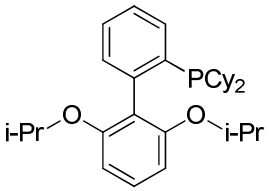
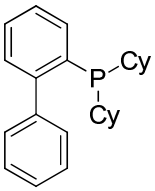
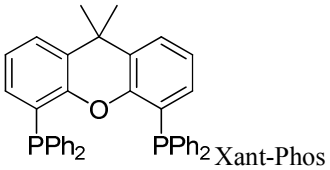
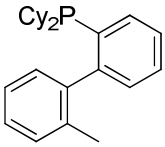
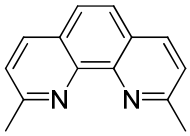
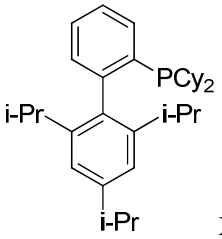
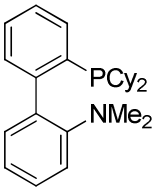
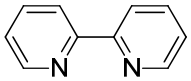
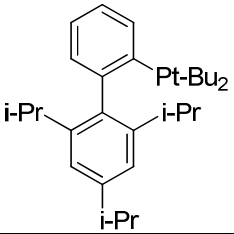
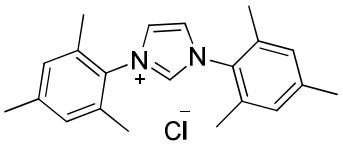
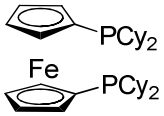
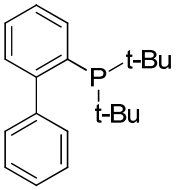
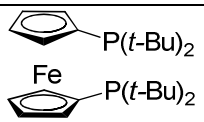
General experimental methods:

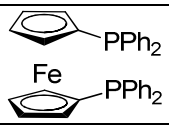
Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63μm, standard grade). Analytical thin–layer chromatography was performed using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

Results of screening ligands:

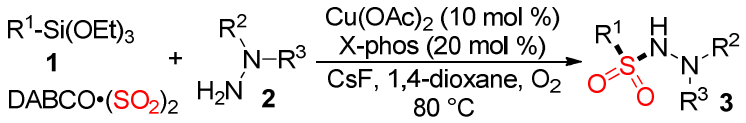


Entry	Ligand	Yield	Entry	Ligand	Yield
L1		55%	**L14**		51%
L2		50%	**L15**		60%

L3		54%	**L16**		62%
L4	 Xant-Phos	51%	**L17**		57%
L5		48%	**L18**	$PCy_3\,HBF_4$	43%
L6	 X-phos	71%	**L19**	DPPE	50%
L7	P^tBu_3	56%	**L20**		34%
L8		49%	**L21**	DPPB	44%
L9	PPh_3	53%	**L22**		62%
L10		18%	**L23**		43%%
L11		62%	**L24**		44%%

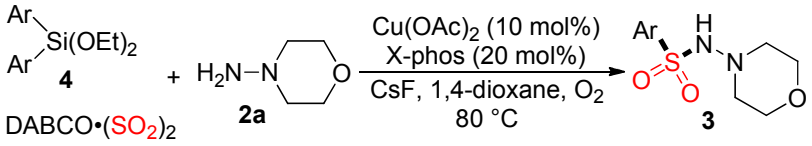
L12	Au_2P^tBu	19%			
L13		50%			

General experimental procedure for the copper-catalyzed three-component reaction of triethoxysilanes, sulfur dioxide and hydrazines:



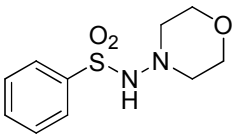
Triethoxysilanes **1** (0.3 mmol)[1] was added to a solution of DABCO•$(SO_2)_2$ (2.0 equiv),[2] copper acetate (10 mol %), X-Phos (20 mol %), CsF (2.0 equiv) in 1,4-dioxane (1.0 mL). Then hydrazine **2** (2.0 equiv) and 1,4-dioxane (1.0 mL) were added. The mixture was stirred at 80 °C under O_2 atmosphere. After completion of reaction as indicated by TLC, The solvent was evaporated and the residue was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:2) to provide the product **3**.

*General experimental procedure for the aminosulfonylation reaction of diethoxydiarylsilane **4** with DABCO•$(SO_2)_2$ and morpholin-4-amine **2a**:*



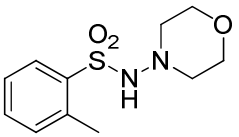
Diethoxydiarylsilane **4** (0.3 mmol)[1] was added to a solution of DABCO•$(SO_2)_2$ (2.0 equiv),[2] copper acetate (10 mol %), X-Phos (20 mol %), CsF (2.0 equiv) in 1,4-dioxane (1.0 mL). Then morpholin-4-amine **2a** (2.0 equiv) and 1,4-dioxane (1.0 mL) were added. The mixture was stirred at 80 °C under O_2 atmosphere. After completion of reaction as indicated by TLC, The solvent was evaporated and the residue was purified by column chromatography on silica gel

(EtOAc/petroleum ether, 1:2) to provide the product **3**.



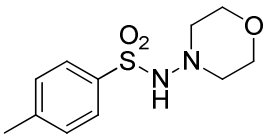
N-Morpholinobenzenesulfonamide (**3a**)[3]

Yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (t, *J* = 4.6 Hz, 4H), 3.60 (t, *J* = 4.6 Hz, 4H), 5.51 (s, 1H), 7.51-7.55 (m, 2H), 7.59-7.63 (m, 1H), 7.97-7.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.6, 66.5, 128.1, 128.8, 133.1, 138.6; HRMS (ESI) calcd for $C_{10}H_{14}N_2O_3S$: 243.0798 ($M + H^+$), found: 243.0800.



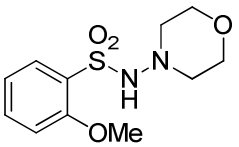
2-Methyl-*N*-morpholinobenzenesulfonamide (**3b**)[3]

Yield: 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (t, *J* = 4.6 Hz, 4H), 2.70 (s, 3H), 3.57 (t, *J* = 4.5 Hz, 4H), 5.77 (s, 1H), 7.29-7.36 (m, 2H), 7.46-7.50 (m, 1H), 8.06-8.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 56.6, 66.5, 126.1, 131.0, 132.3, 133.2, 136.4, 137.9.



4-Methyl-*N*-morpholinobenzenesulfonamide (**3c**)[3]

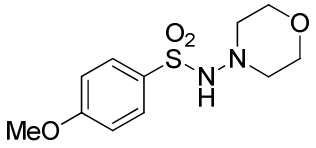
Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 2.62 (t, *J* = 4.6 Hz, 4H), 3.60 (t, *J* = 4.5 Hz, 4H), 5.95 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 56.5, 66.6, 128.1, 129.4, 135.6, 144.0.



2-Methoxy-*N*-morpholinobenzenesulfonamide (**3d**)[3]

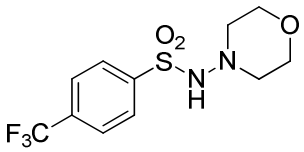
Yield: 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (t, *J* = 4.6 Hz, 4H), 3.57 (t, *J* = 4.5 Hz, 4H), 4.00 (s, 3H), 5.99 (s, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H),

7.55-7.60 (m, 1H), 8.00-8.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.3, 56.5, 64.4, 112.0, 120.8, 131.8, 135.1, 156.2.



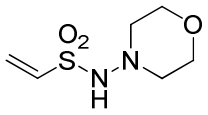
4-Methoxy-*N*-morpholinobenzenesulfonamide (**3e**)[3]

Yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (t, *J* = 4.6 Hz, 4H), 3.61 (t, *J* = 4.5 Hz, 4H), 3.88 (s, 3H), 5.69 (s, 1H), 6.97-6.99 (m, 2H), 7.89-7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 56.6, 66.6, 114.0, 130.0, 130.3, 163.2.



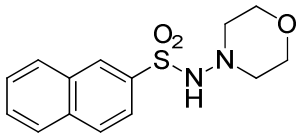
N-Morpholino-4-(trifluoromethyl)benzenesulfonamide (**3f**)[3]

Yield: 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (t, *J* = 4.5 Hz, 4H), 3.62 (t, *J* = 4.5 Hz, 4H), 5.98 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 8.12 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.7, 66.5, 123.2 (q, J_{CF} = 271.4 Hz), 126.0 (q, J_{CF} = 3.2 Hz), 128.6, 134.8 (q, J_{CF} = 32.9 Hz), 142.3; ^{19}F NMR (378 MHz, $CDCl_3$) -63.10.



N-Morpholinoethenesulfonamide (**3g**)

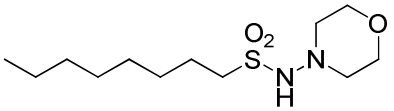
Yield: 51%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (t, *J* = 4.4 Hz, 4H), 3.73 (t, *J* = 4.6 Hz, 4H), 5.37 (s, 1H), 6.06 (d, *J* = 9.8 Hz, 1H), 6.40 (d, *J* = 16.6 Hz, 1H), 6.61 (dd, *J* = 16.7, 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.2, 66.6, 128.9, 134.6; HRMS (ESI) calcd for $C_6H_{12}N_2O_3S$: 193.0641 ($M + H^+$), found: 193.0641.



N-Morpholinonaphthalene-2-sulfonamide (**3h**)[3]

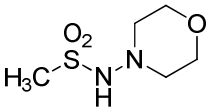
Yield: 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (t, *J* = 4.6 Hz, 4H), 3.57 (t, *J* = 4.5 Hz, 4H), 5.77-5.86 (m, 1H), 7.60-7.68 (m, 2H), 7.91-8.00 (m, 4H), 8.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.5, 66.5, 123.0, 127.4, 127.8, 128.9, 129.0, 129.2,

129.6, 131.9, 134.9, 135.5.



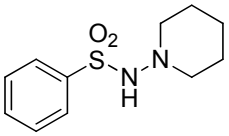
N-Morpholinooctane-1-sulfonamide (**3i**)

Yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.1 Hz, 3H), 1.27-1.42 (m, 10H), 1.78-1.85 (m, 2H), 2.87 (s, 4H), 3.12 (t, *J* = 7.9 Hz, 2H), 3.76 (t, *J* = 4.5 Hz, 4H), 5.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 23.2, 28.3, 29.0, 29.1, 31.7, 50.1, 57.5, 66.6; HRMS (ESI) calcd for $C_{12}H_{26}N_2O_3S$: 279.1737 ($M + H^+$), found: 279.1737.



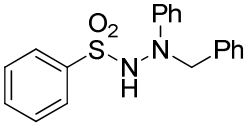
N-Morpholinomethanesulfonamide (**3j**)

Yield: 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (s, 4H), 3.04 (s, 3H), 3.78 (t, *J* = 4.3 Hz, 4H), 5.45-5.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.0, 57.2, 66.6; HRMS (ESI) calcd for $C_5H_{12}N_2O_3S$: 181.0641 ($M + H^+$), found: 181.0641.



N-(Piperidin-1-yl)benzenesulfonamide (**3k**)[4]

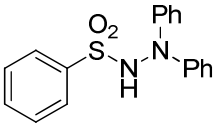
Yield: 56%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25-1.32 (m, 2H), 1.46-1.52 (m, 4H), 2.53 (t, *J* = 1.3 Hz, 4H), 5.57 (s, 1H), 7.49-7.53 (m, 2H), 7.57-7.62 (m, 1H), 7.96-7.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0, 25.6, 57.7, 128.1, 128.6, 132.8, 138.7.



N'-Benzyl-*N*'-phenylbenzenesulfonohydrazide (**3l**)[4]

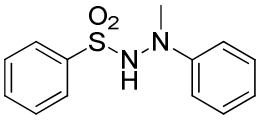
Yield: 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (s, 2H), 6.42 (s, 1H), 6.80-6.88 (m, 3H), 7.00-7.02 (m, 2H), 7.09-7.13 (m, 2H), 7.21-7.24 (m, 3H), 7.39-7.43 (m, 2H), 7.49-7.53 (m, 1H), 7.88-7.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 58.1, 115.3,

121.0, 127.9, 128.0, 128.2, 128.7, 128.9, 133.2, 134.5, 138.8, 148.6.



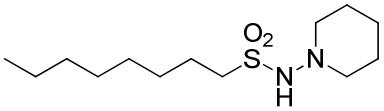
N',*N*'-diphenylbenzenesulfonohydrazide (**3m**)[4]

Yield: 53%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94-6.99 (m, 6H), 7.11-7.16 (m, 4H), 7.25-7.29 (m, 3H), 7.40-7.44 (m, 1H), 7.73-7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.7, 123.9, 128.1, 128.7, 129.0, 133.0, 138.5, 146.7.



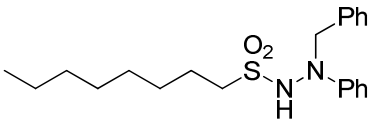
N'-Methyl-*N*'-phenylbenzenesulfonohydrazide (**3n**)[4]

Yield: 52%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (s, 3H), 6.41 (s, 1H), 6.81-6.86 (m, 3H), 7.12-7.16 (m, 2H), 7.46-7.50 (m, 2H), 7.56-7.60 (t, *J* = 7.4 Hz, 1H), 7.93-7.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.6, 114.3, 120.9, 128.1, 128.9, 129.0, 133.3, 138.5, 149.6.



N-(Piperidin-1-yl)octane-1-sulfonamide (**3o**)

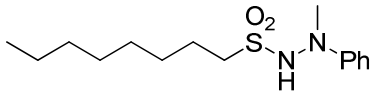
Yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86-0.88 (m, 3H), 1.25-1.42 (m, 12H), 1.63-1.69 (m, 4H), 1.77-1.85 (m, 2H), 2.79 (s, 4H), 3.12 (t, *J* = 7.9 Hz, 2H), 4.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 23.1, 23.3, 25.6, 28.3, 28.9, 29.0, 31.7, 50.0, 58.6; HRMS (ESI) calcd for $C_{13}H_{28}N_2O_2S$: 277.1944 (M + H^+), found: 277.1937.



N'-Benzyl-*N*'-phenyloctane-1-sulfonohydrazide (**3p**)

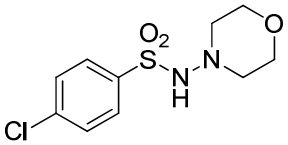
Yield: 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.7 Hz, 3H), 1.20-1.33 (m, 10H), 1.70-1.76 (m, 2H), 2.97 (t, *J* = 7.8 Hz, 2H), 4.83 (s, 2H), 5.81 (s, 1H), 6.98 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.15-7.16 (m, 2H), 7.28-7.30 (m, 5H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 14.0, 22.5, 23.0, 28.1, 28.8, 28.9, 31.6, 51.4, 59.7, 116.1, 121.6, 128.2, 128.9, 129.0, 129.3, 134.0, 149.1; HRMS (ESI) calcd for $C_{21}H_{30}N_2O_2S$: 375.2101 (M + H^+), found: 375.2101.



N'-Methyl-*N*'-phenyloctane-1-sulfonohydrazide (**3q**)

Yield: 46%; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.5 Hz, 3H), 1.24-1.36 (m, 10H), 1.80-1.88 (m, 2H), 3.09 (t, *J* = 7.8 Hz, 2H), 3.28 (s, 3H), 5.88 (s, 1H), 6.95 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.5, 23.0, 28.2, 28.8, 29.0, 31.6, 44.3, 51.2, 114.5, 121.12, 129.2, 149.9; HRMS (ESI) calcd for $C_{15}H_{26}N_2O_2S$: 299.1788 (M + H^+), found: 299.1778.

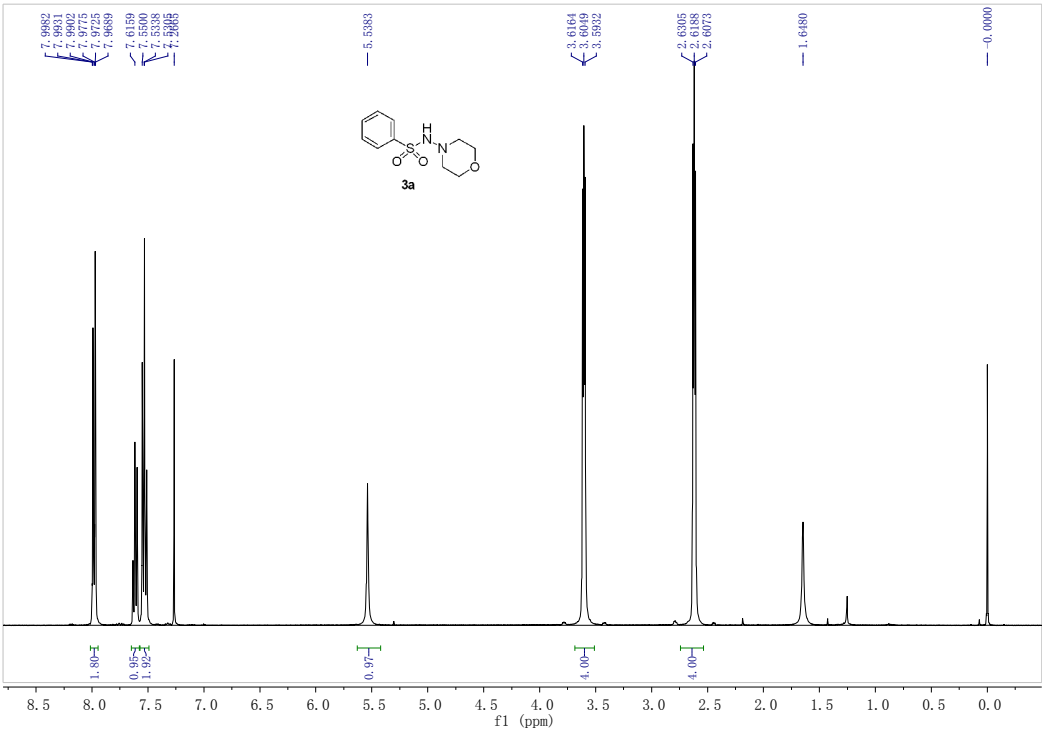


4-Chloro-*N*-morpholinobenzenesulfonamide (**3r**)[4]

Yield: 95%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.65 (t, *J* = 4.6 Hz, 4H), 3.62 (t, *J* = 4.6 Hz, 4H), 5.77 (s, 1H), 7.50-7.52 (m, 2H), 7.91-7.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.7, 66.6, 129.1, 129.6, 137.1, 139.7.

References:

1. Manoso, A. S.; Ahn, C.; Soheili, A.; Handy, C. J.; Correia, R.; Seganish W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 8305.
2. Santos, P. S.; Mello, M. T. S. *J. Mol. Struct.* **1988**, *178*, 121.
3. Nguyen, B.; Emmett, E. J.; Willis, M. C. *J. Am. Chem. Soc.* **2010**, *132*, 16372.
4. Zheng, D.; An, Y.; Li, Z.; Wu, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 2451.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3.6164
3.6049
3.5932
2.6305
2.6188
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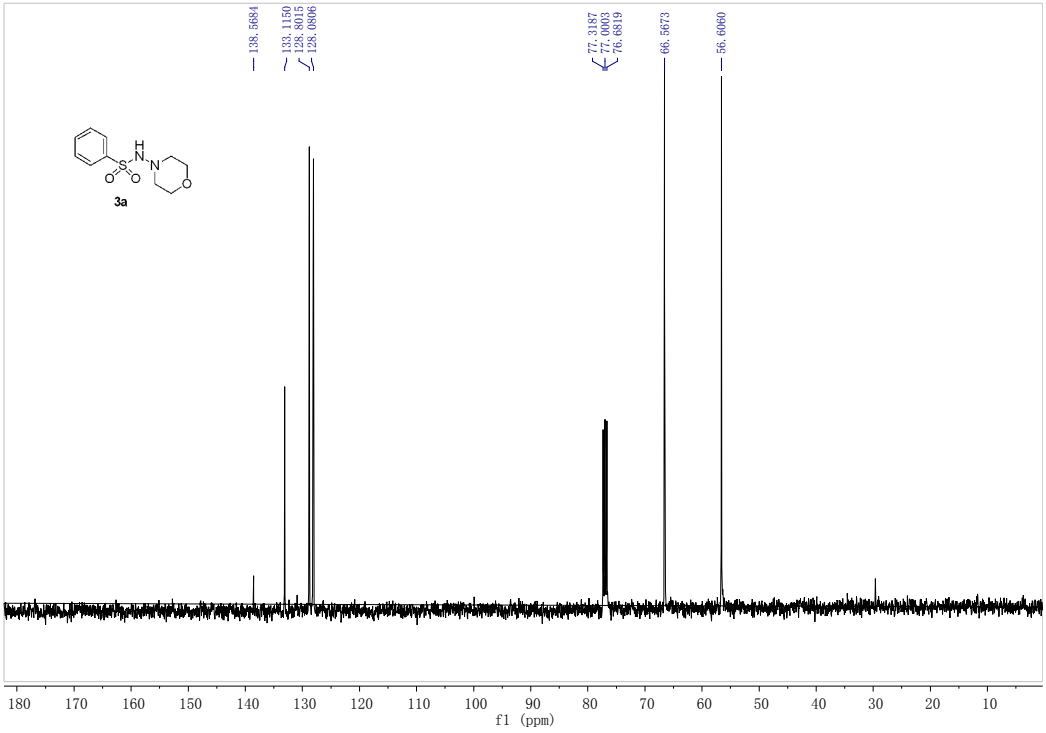
3a
1.80
0.95
1.92
0.97
4.00
4.00
f1 (ppm)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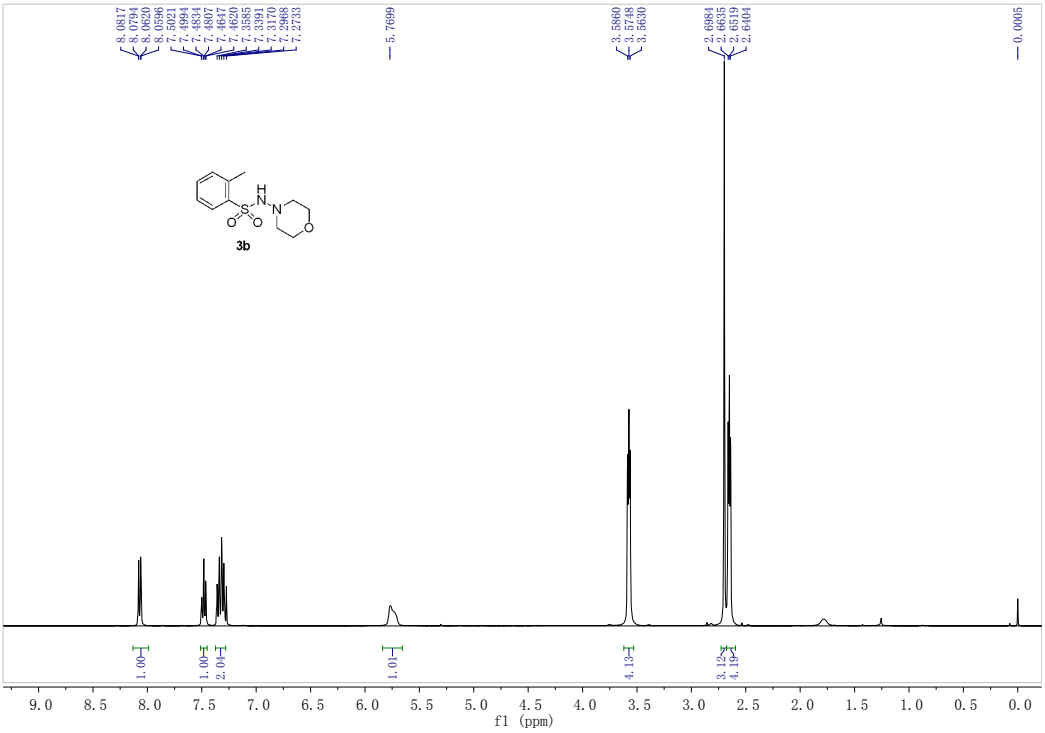
f1 (ppm)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3.5630
2.6984
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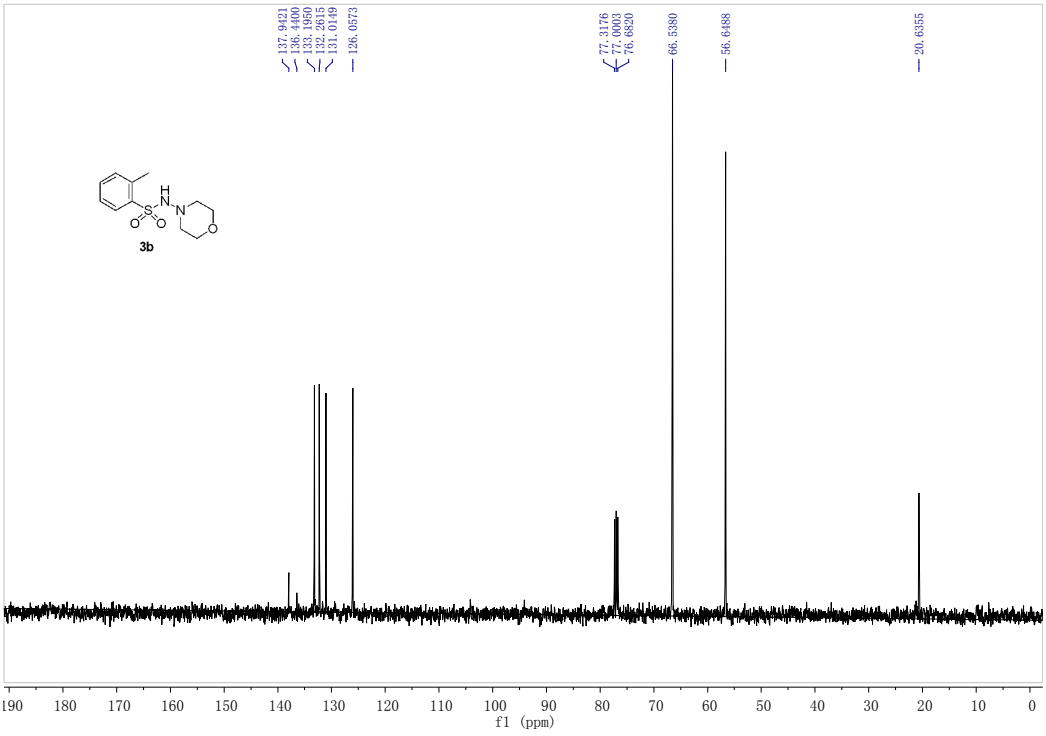
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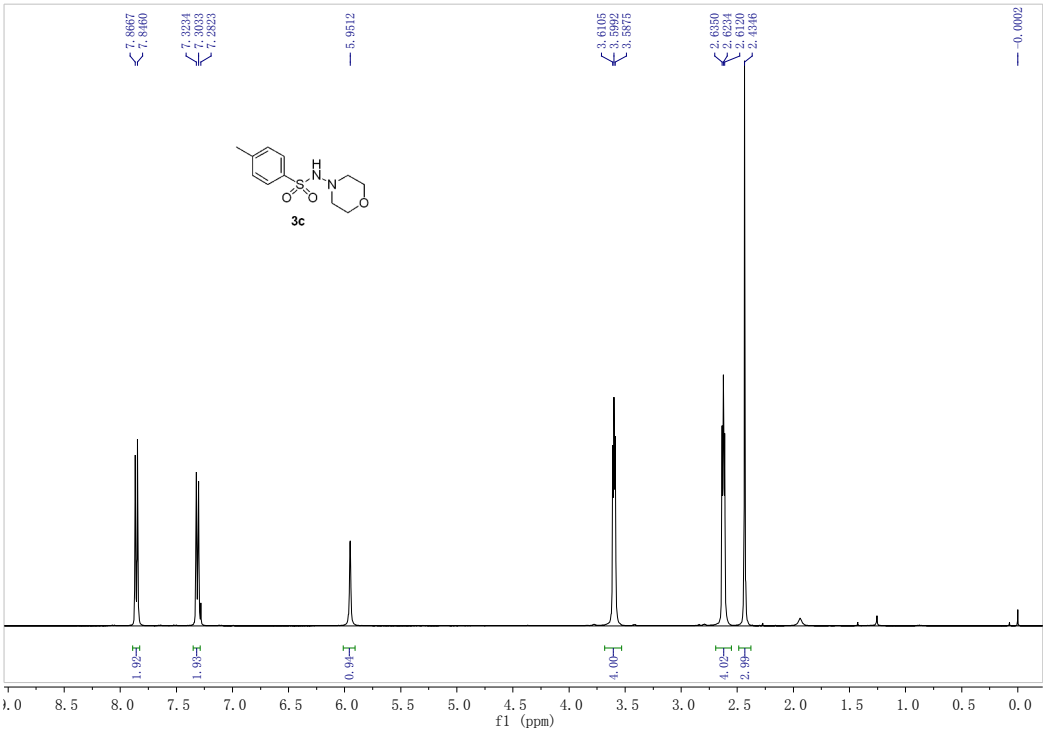
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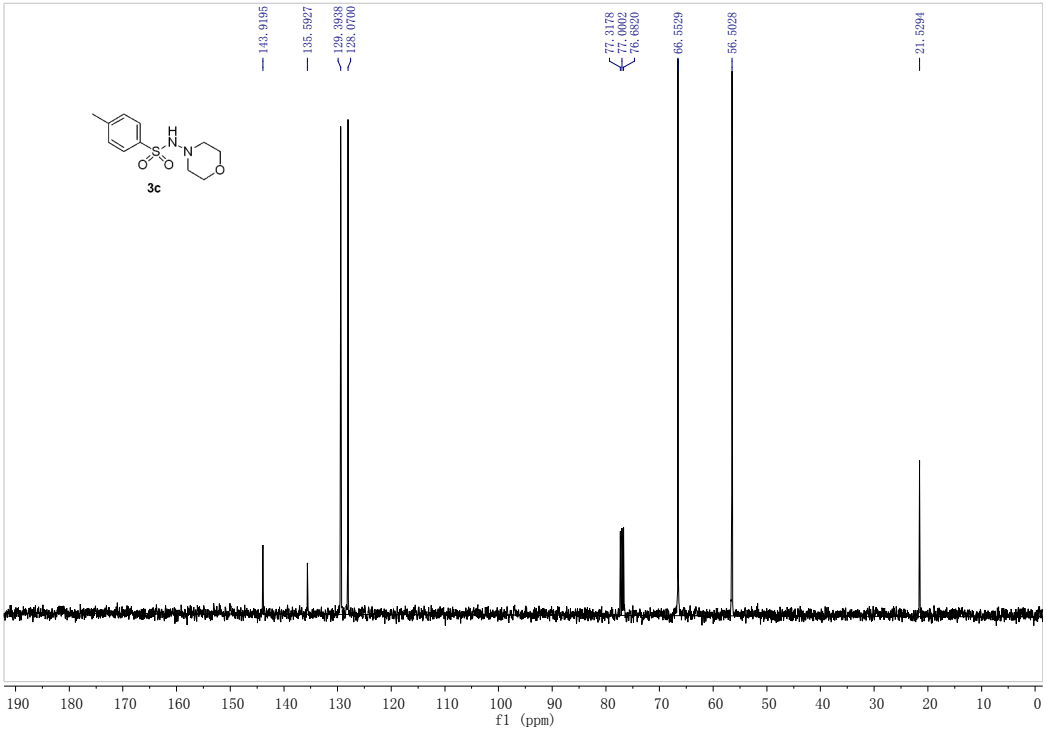
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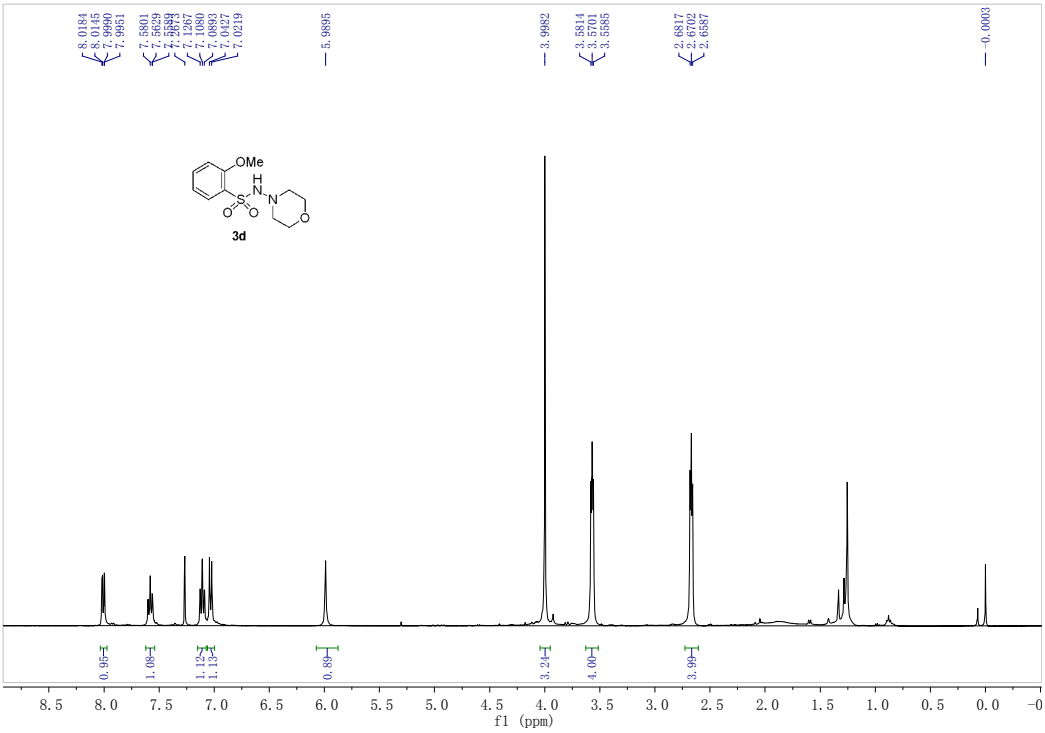
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O
N
O
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1.12
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4.00
3.99
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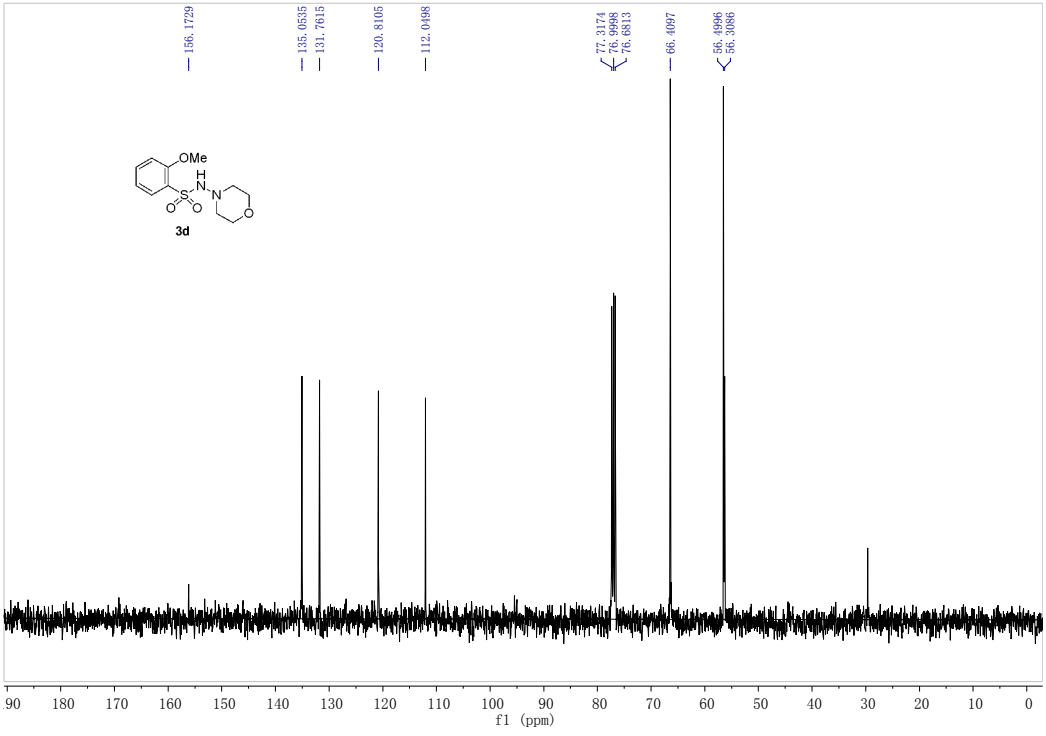
f1 (ppm)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N
O
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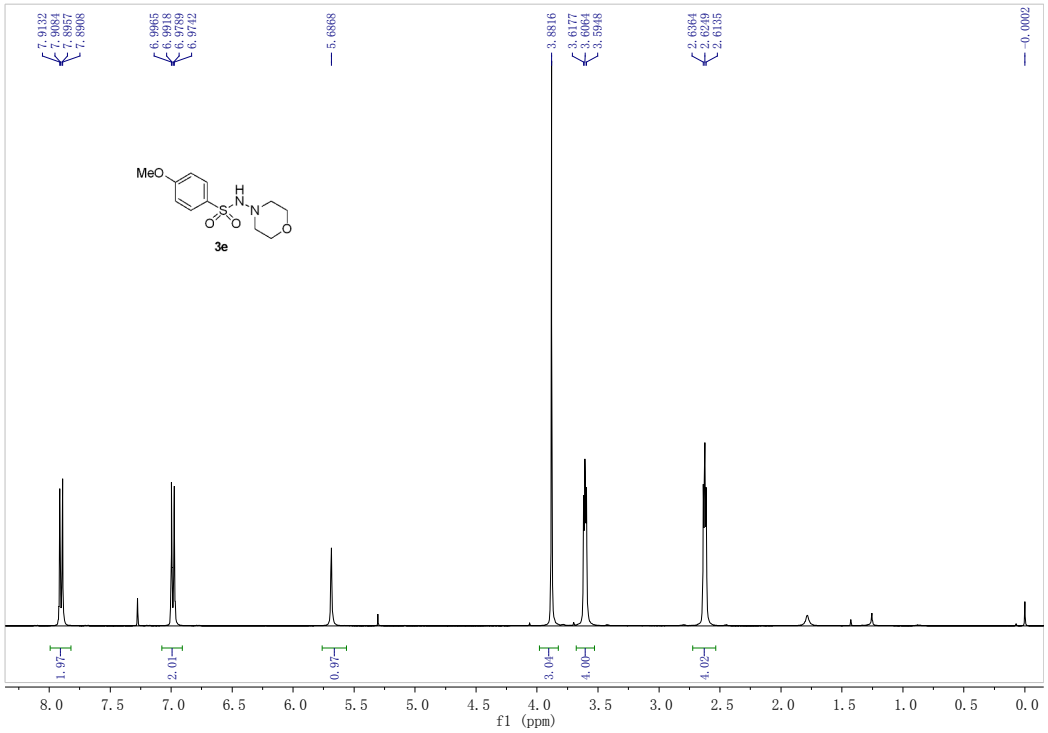
f1 (ppm)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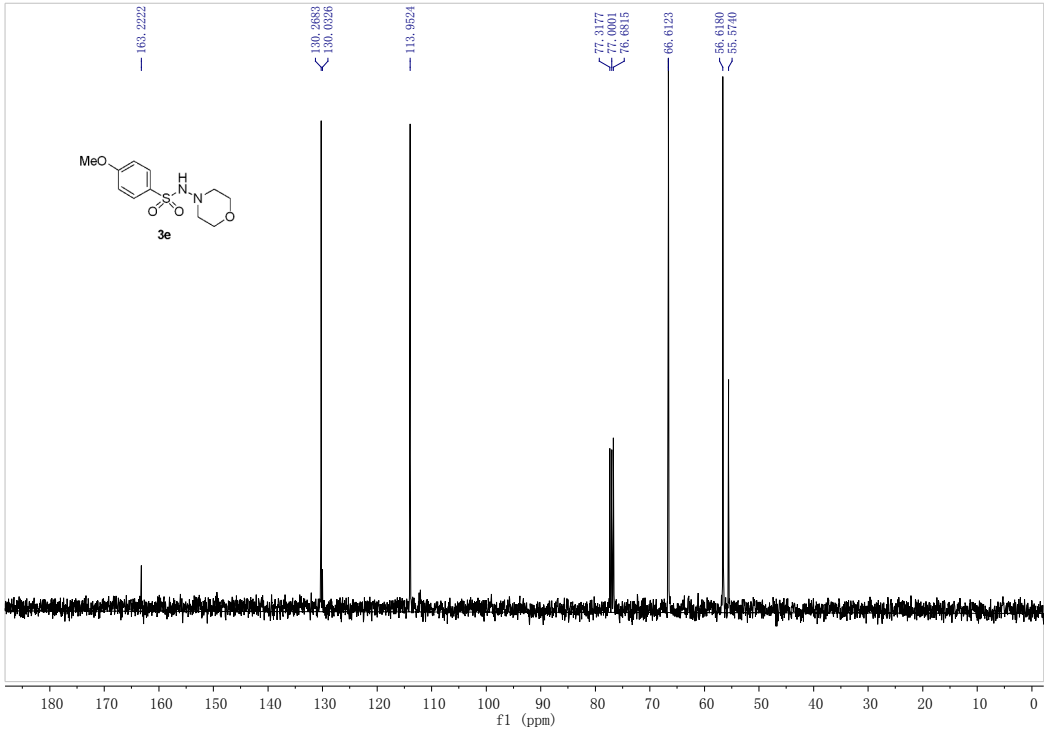
f1 (ppm)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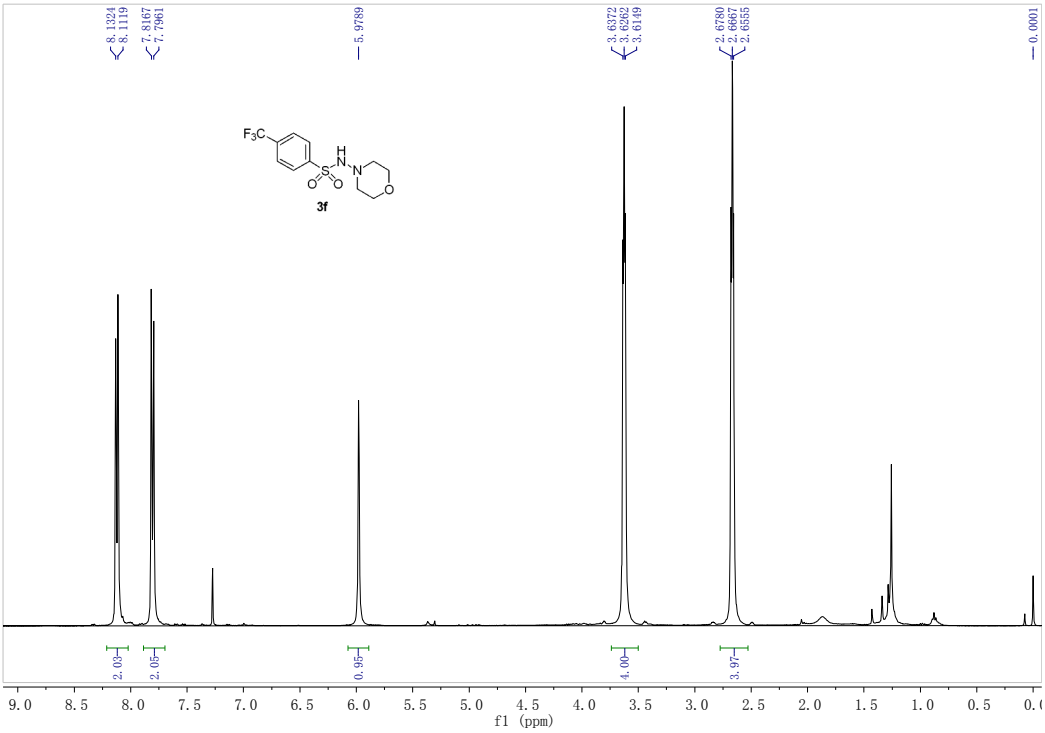
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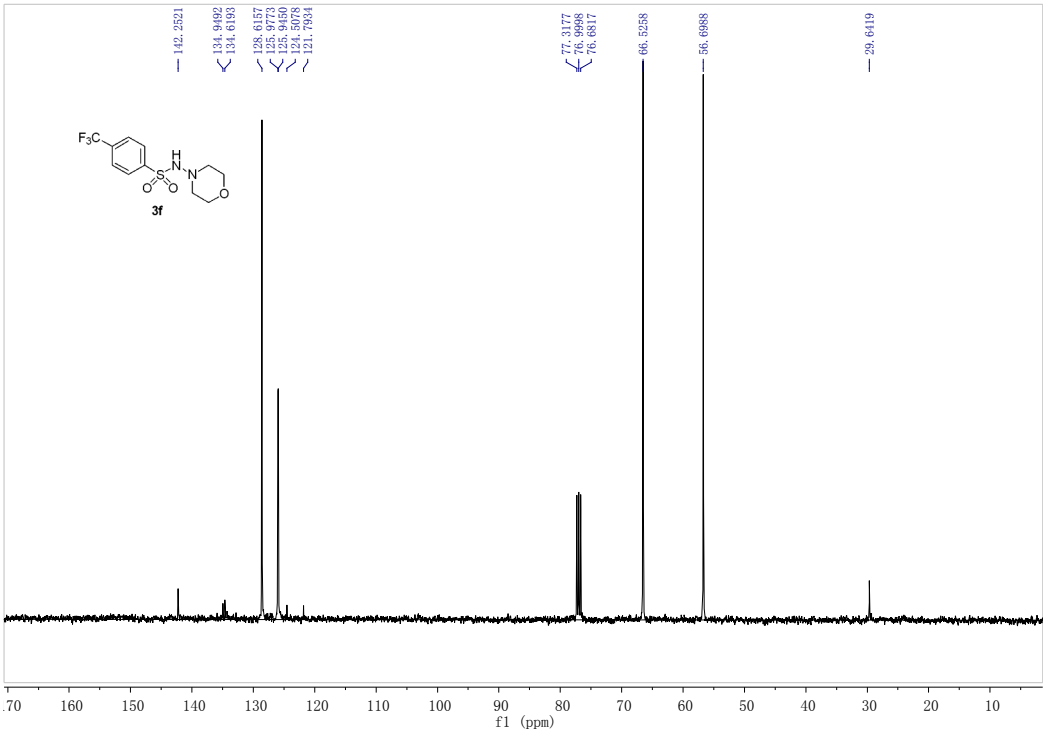
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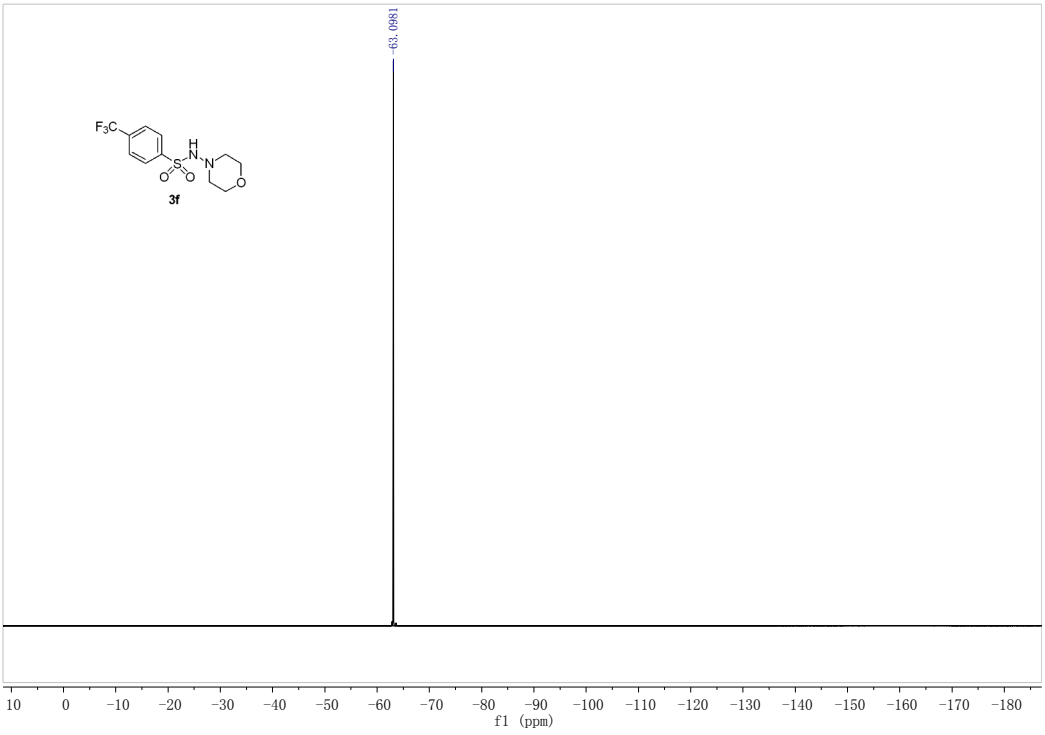
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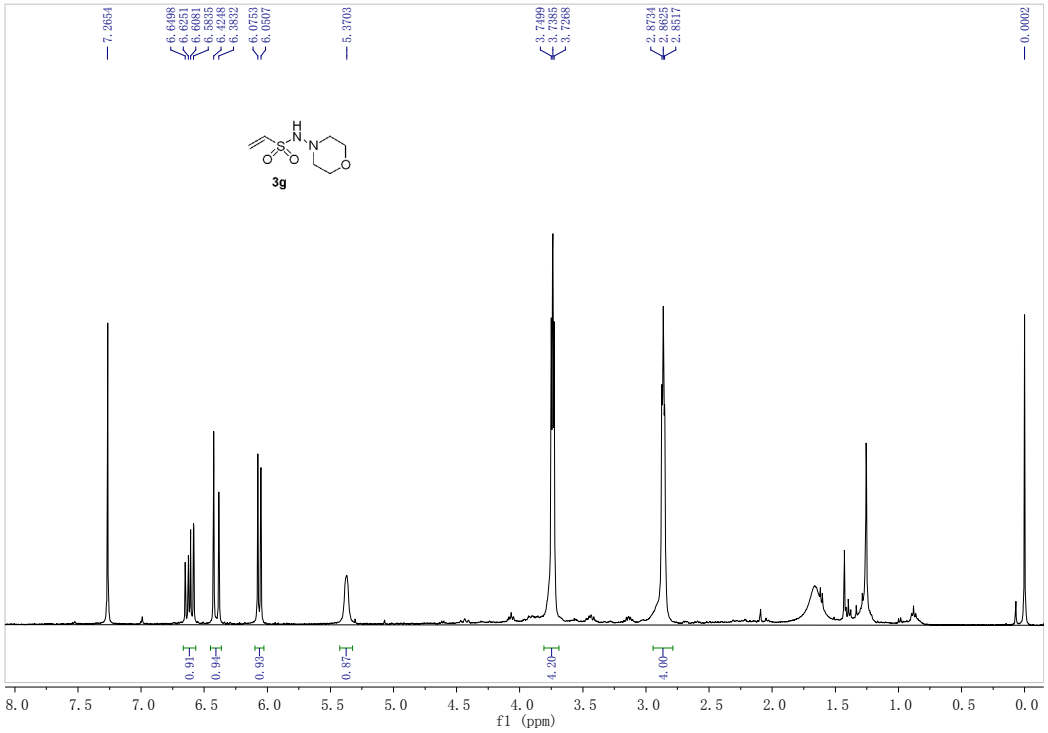
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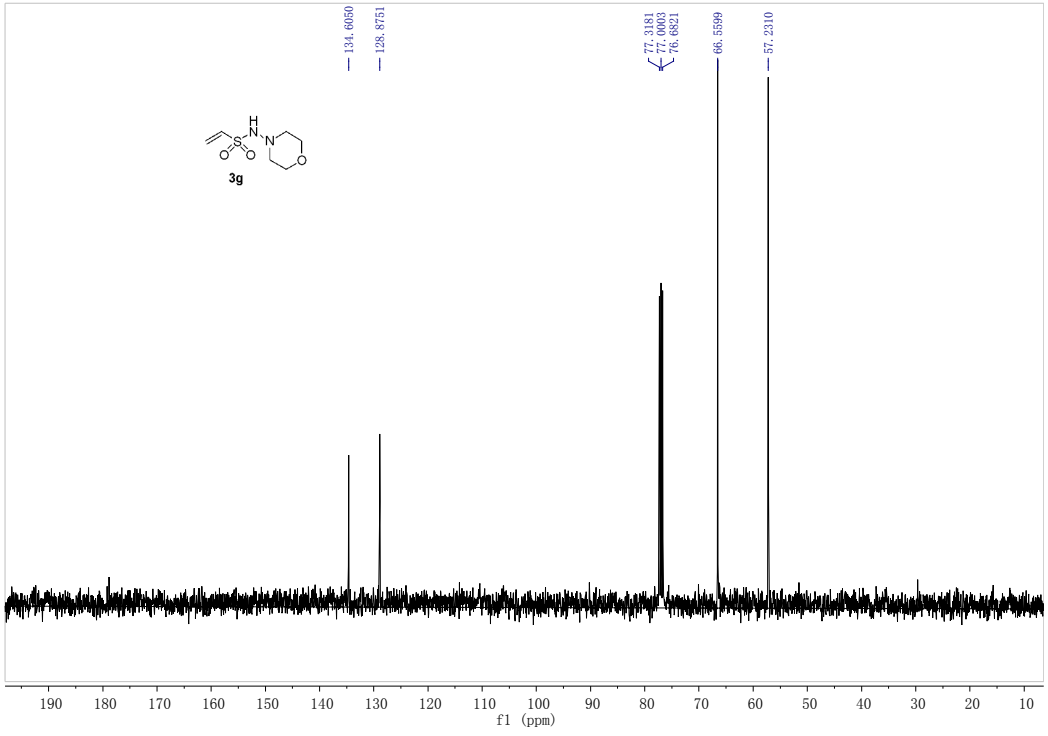
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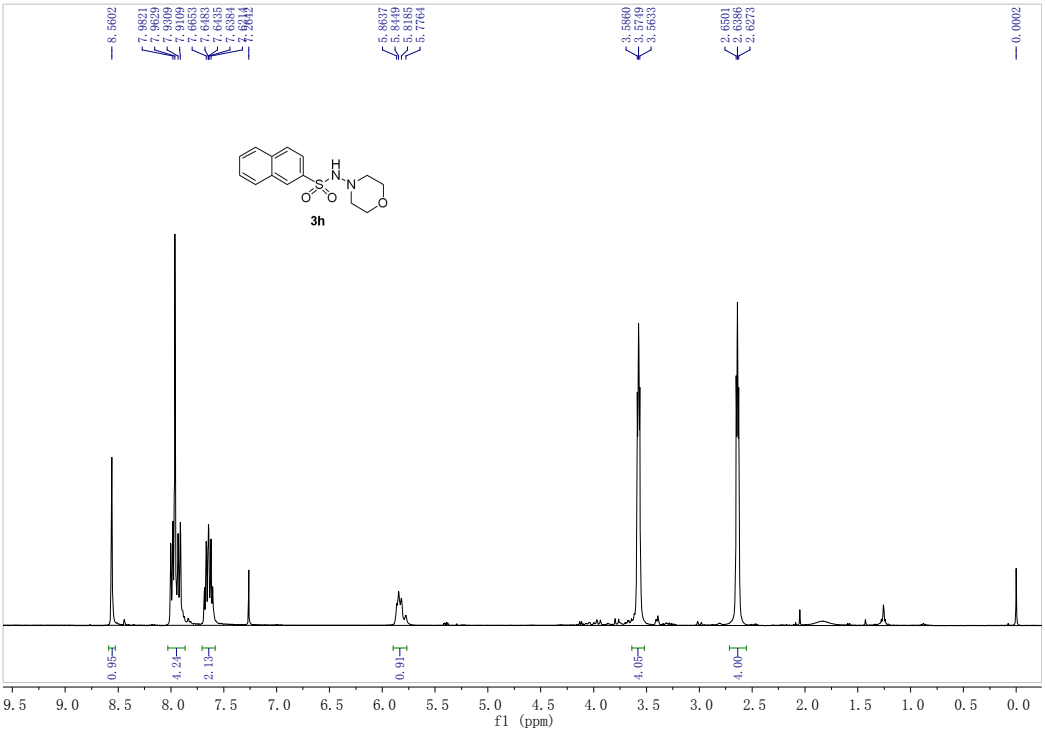
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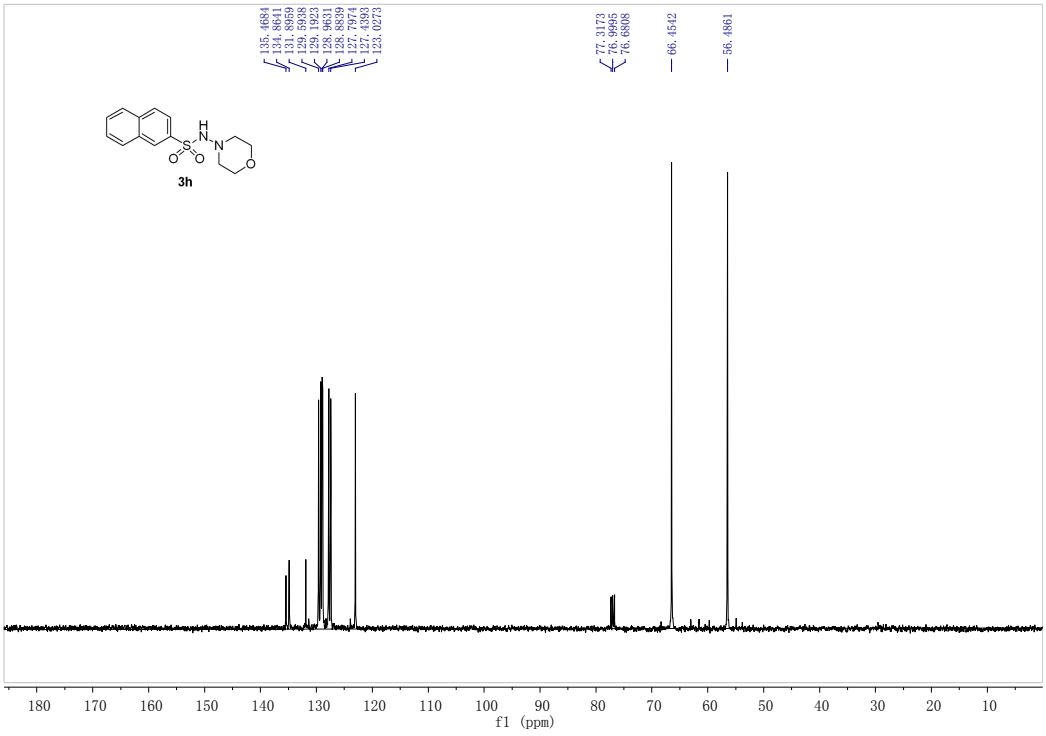
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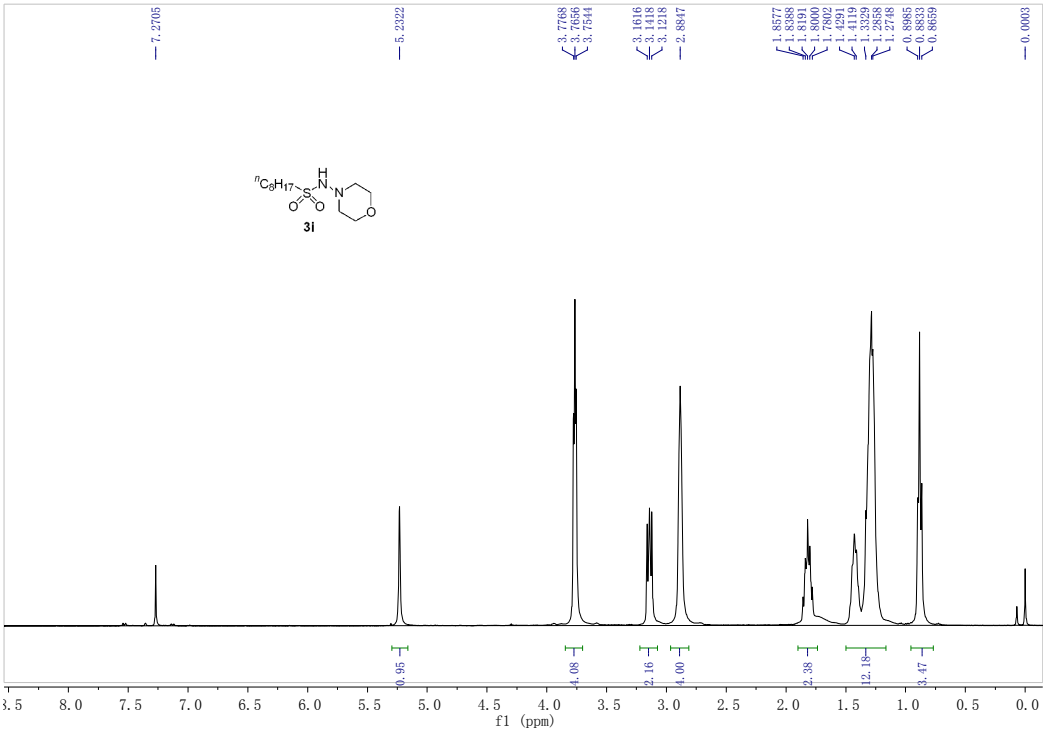
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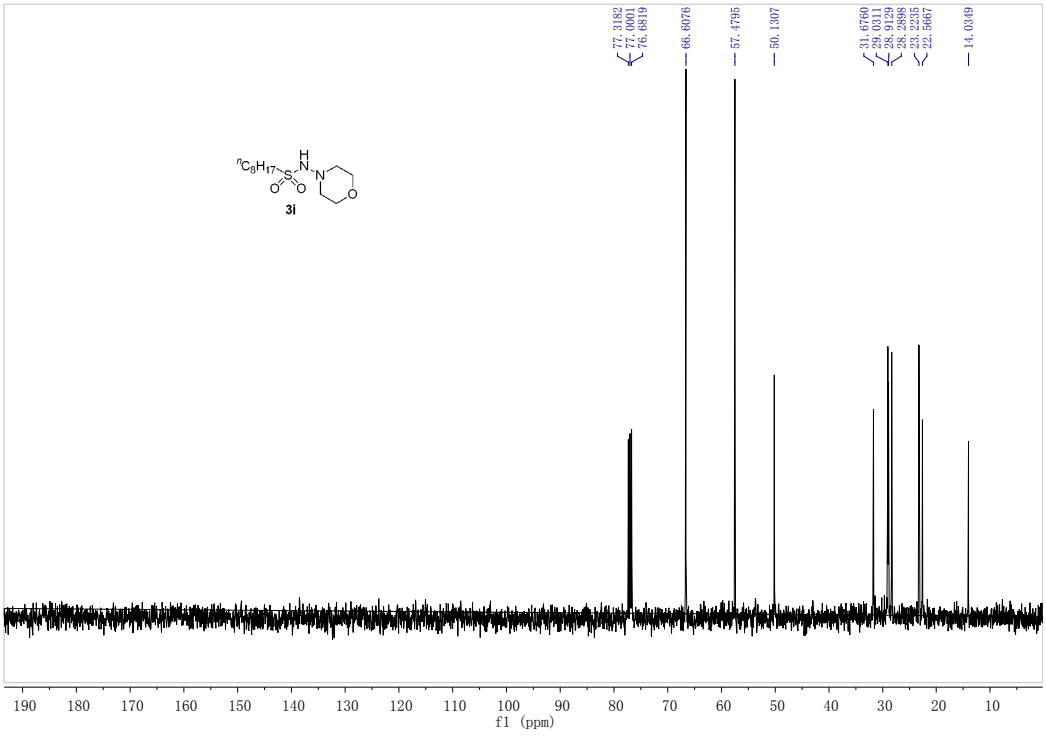
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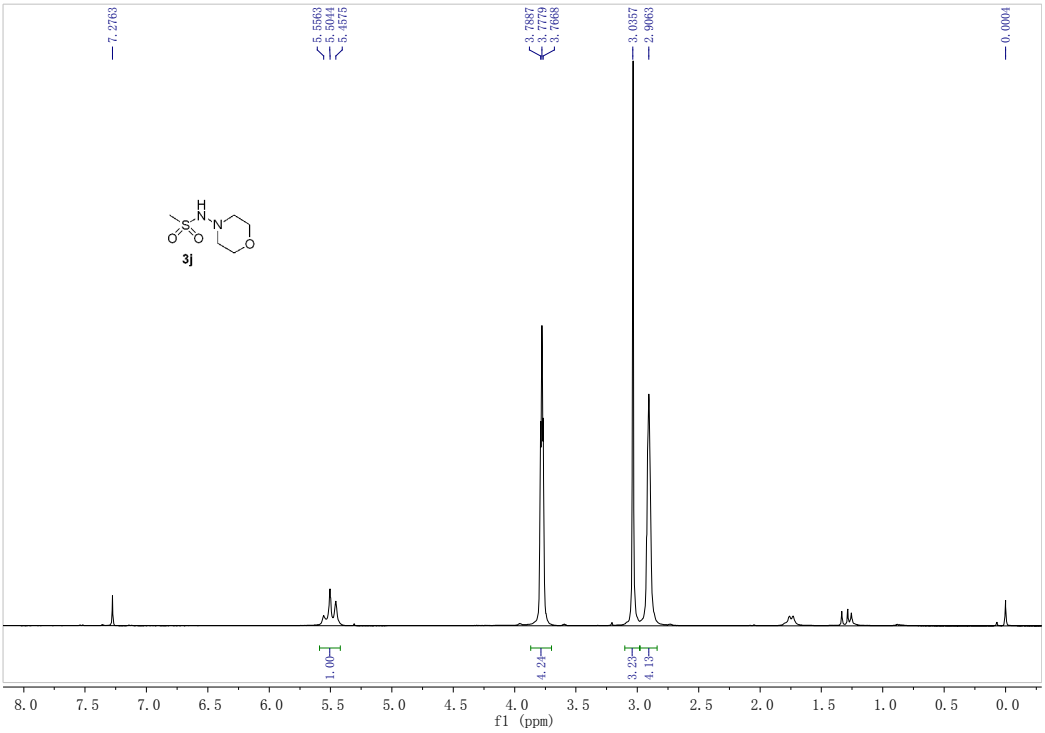
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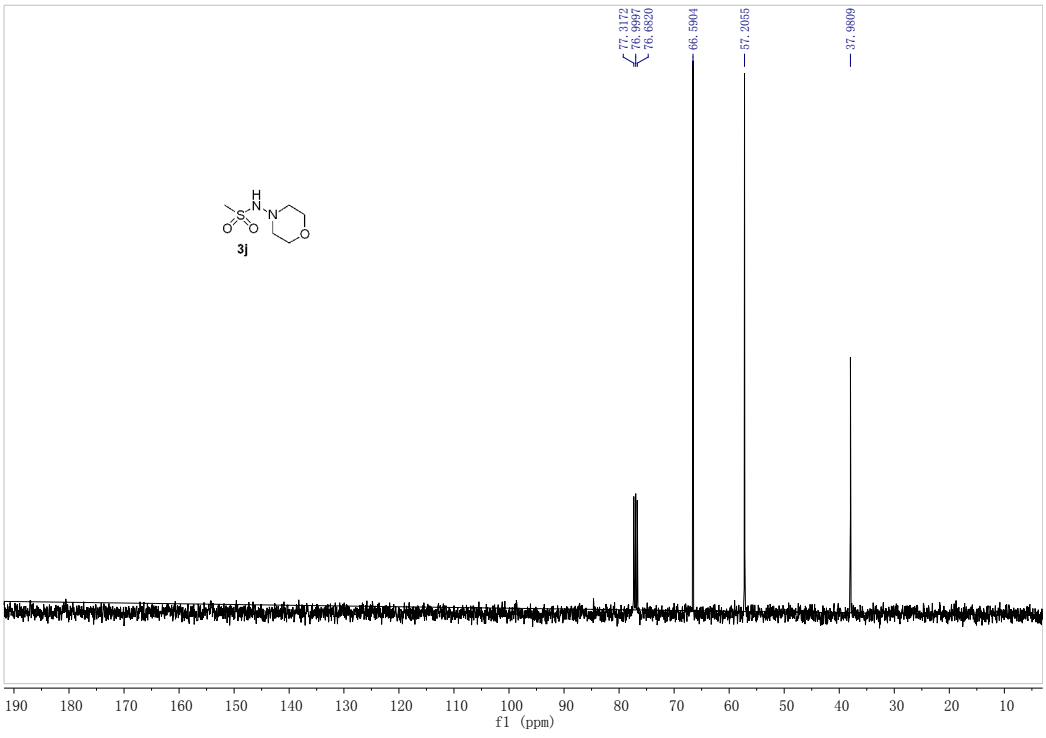
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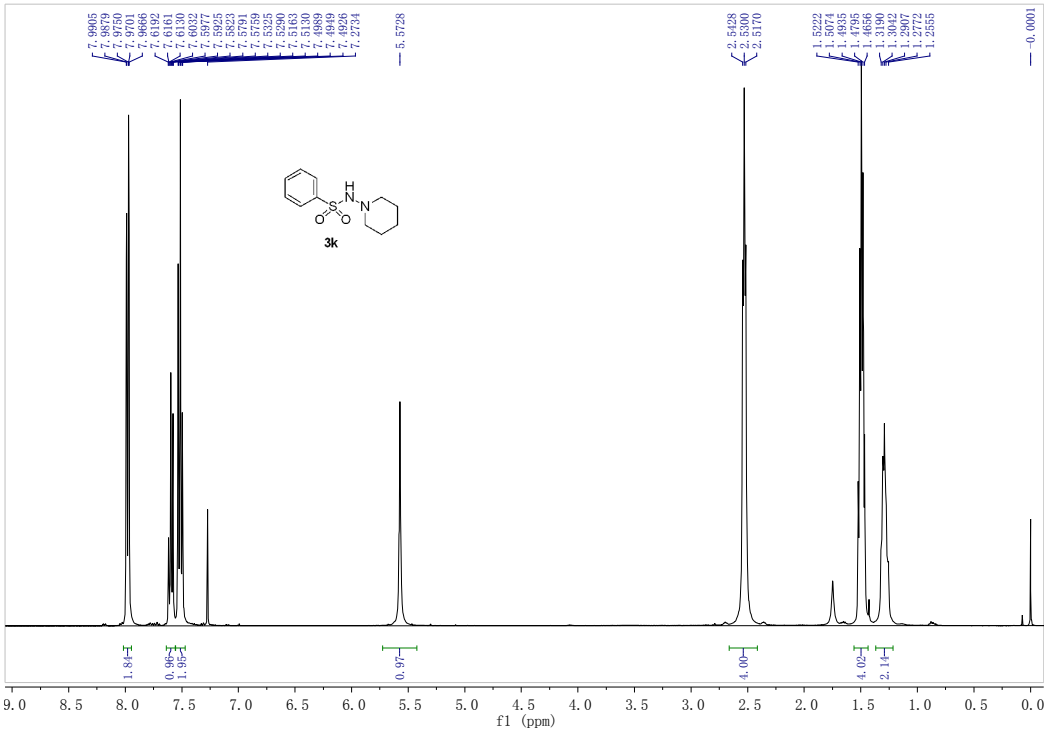
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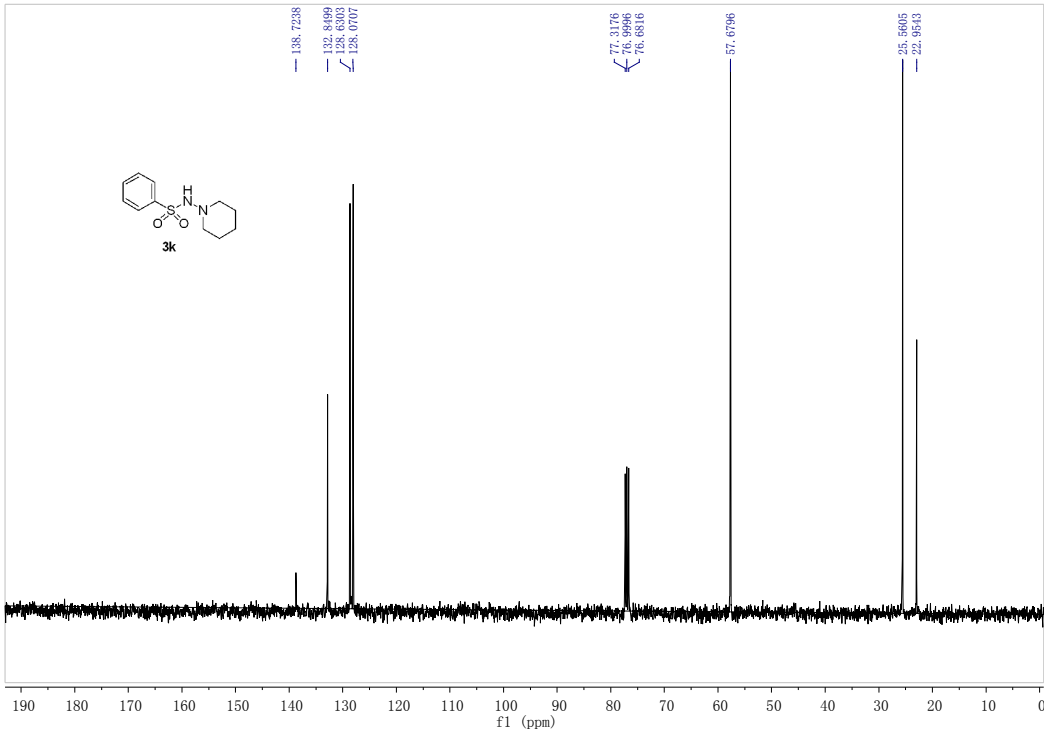
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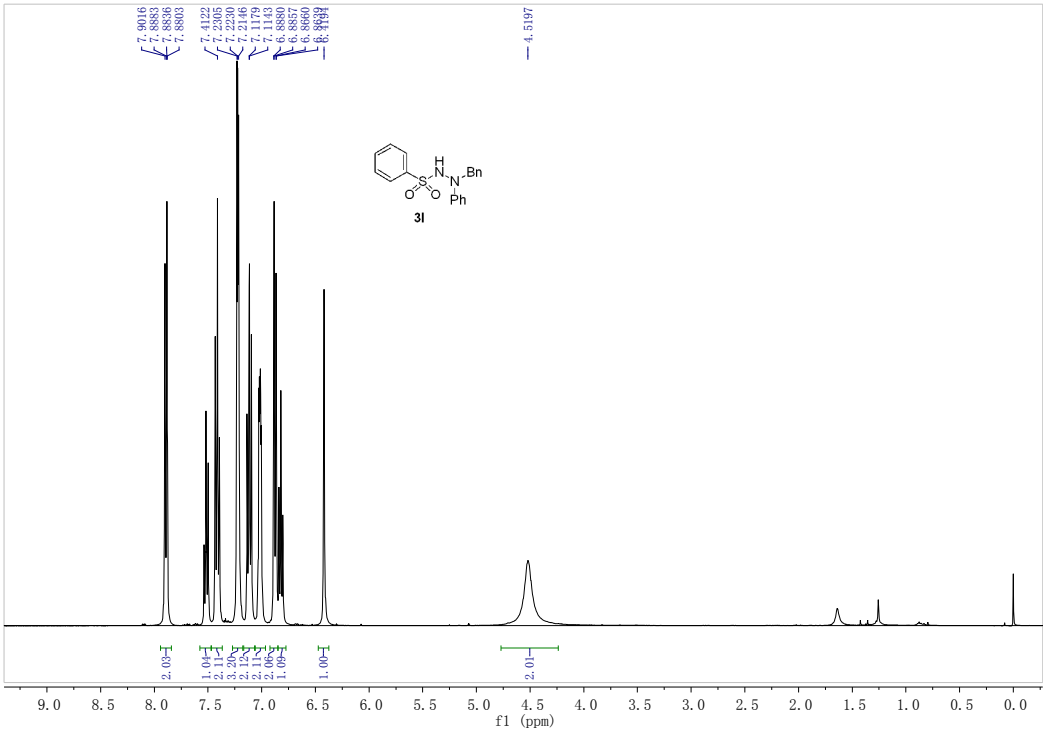
3k
f1 (ppm)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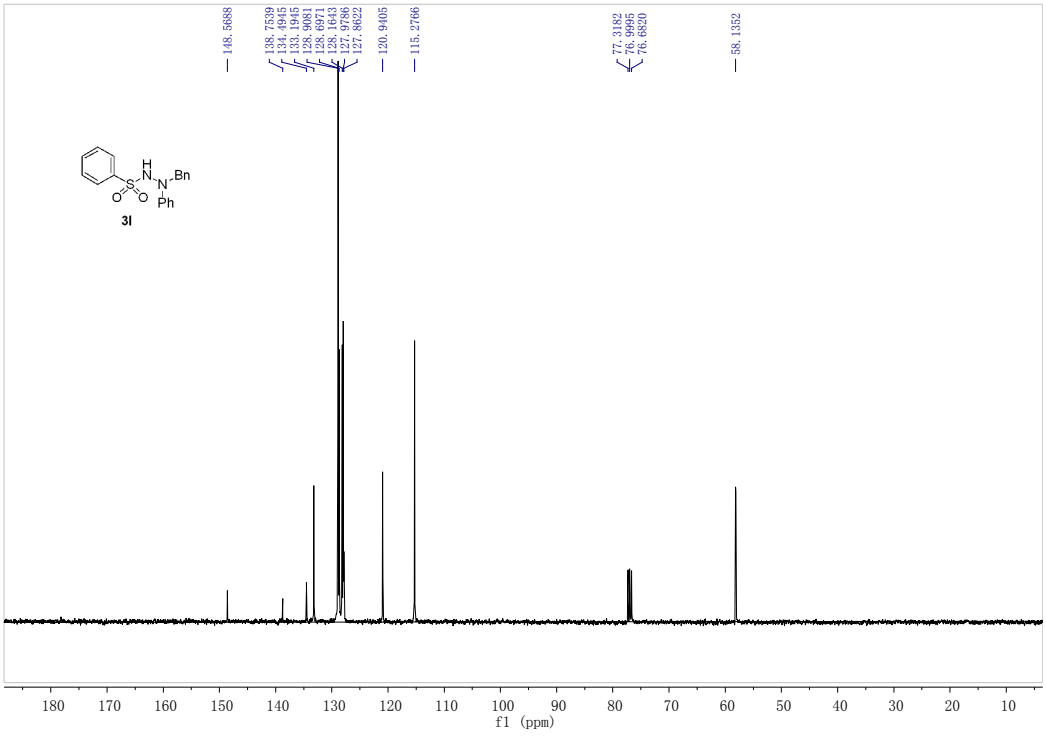
7.8836
7.8803
7.4122
7.2305
7.2230
7.2146
7.1179
7.1133
6.8880
6.8857
6.8660
6.8639
6.8194
4.5197
3l
2.03
1.04
2.11
3.26
2.12
2.11
2.06
1.05
1.00
2.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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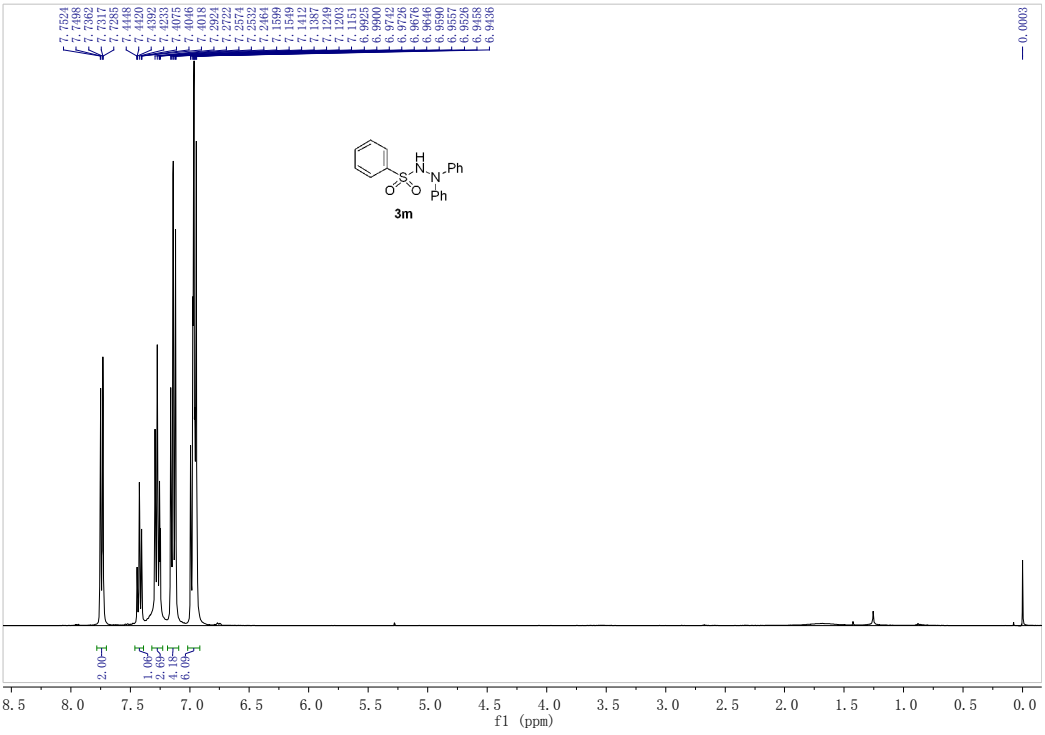
138.7539
134.4945
133.1945
128.9081
128.6971
128.1643
127.9786
127.8622
120.9405
115.2766
77.3182
76.9995
76.6820
58.1352
3l
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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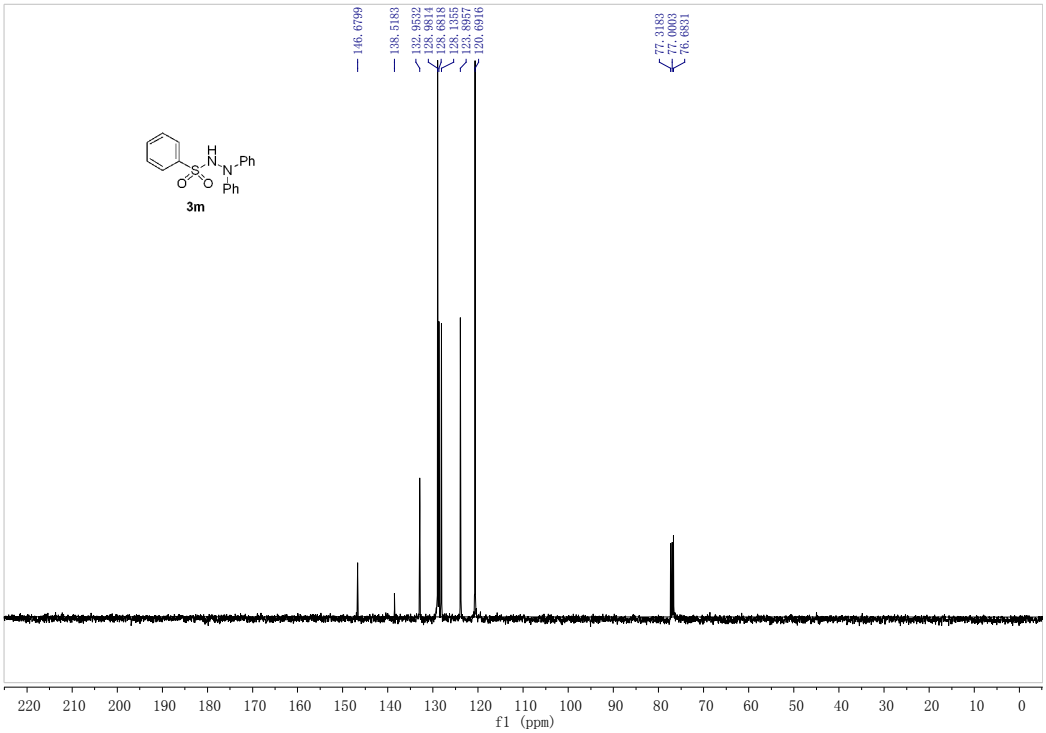
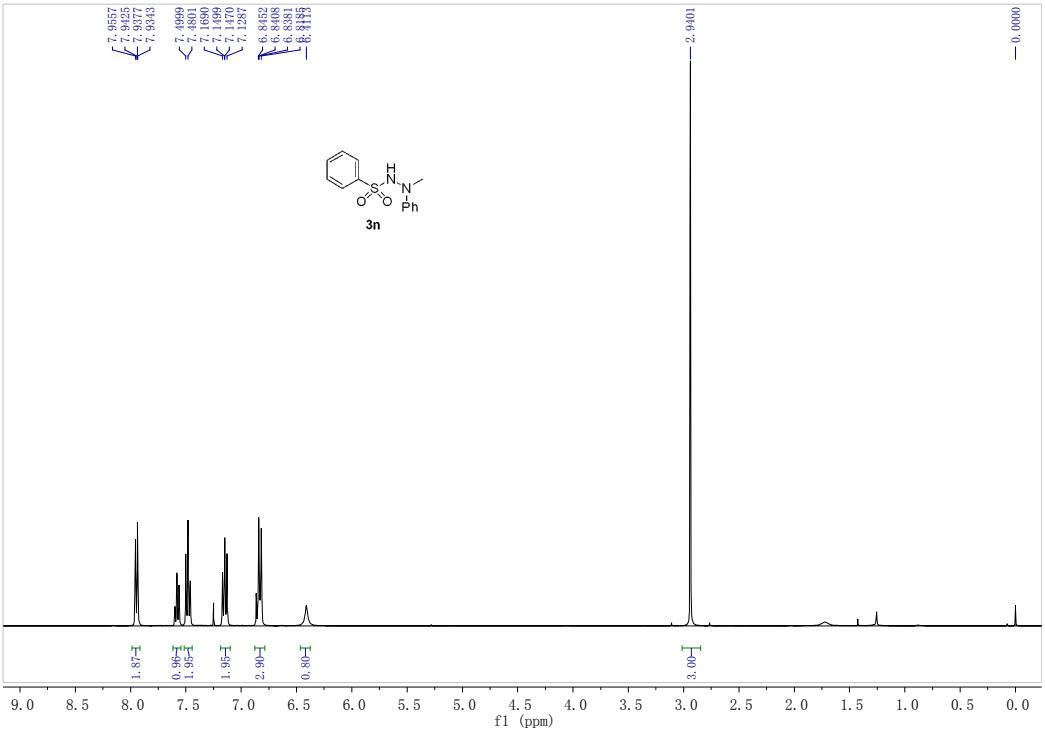
7.7498
7.7362
7.7317
7.7295
7.7285
7.4448
7.4420
7.4392
7.4233
7.4075
7.4046
7.4018
7.2924
7.2722
7.2574
7.2552
7.2464
7.1599
7.1549
7.1412
7.1387
7.1249
7.1203
7.1151
6.9935
6.9900
6.9742
6.9726
6.9676
6.9646
6.9590
6.9557
6.9526
6.9458
6.9436
0.0003
2.00
1.06
2.69
4.18
6.09
3m
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


146.6799
138.5183
132.9532
128.9814
128.6818
128.1355
123.8957
120.6916
77.3183
77.0003
76.6831
3m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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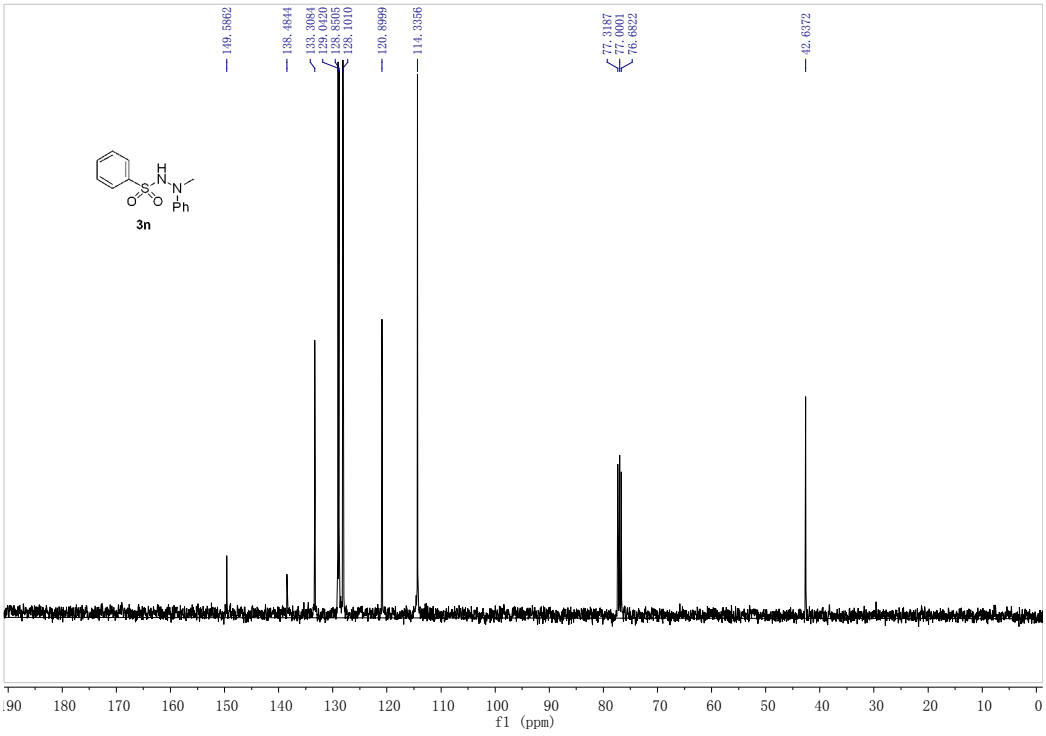
7.9425
7.9377
7.9343
7.4999
7.4801
7.1690
7.1499
7.1470
7.1287
6.8452
6.8408
6.8381
2.9401
0.0000
3n
1.87
0.96
1.95
1.95
2.90
0.80
3.00
f1 (ppm)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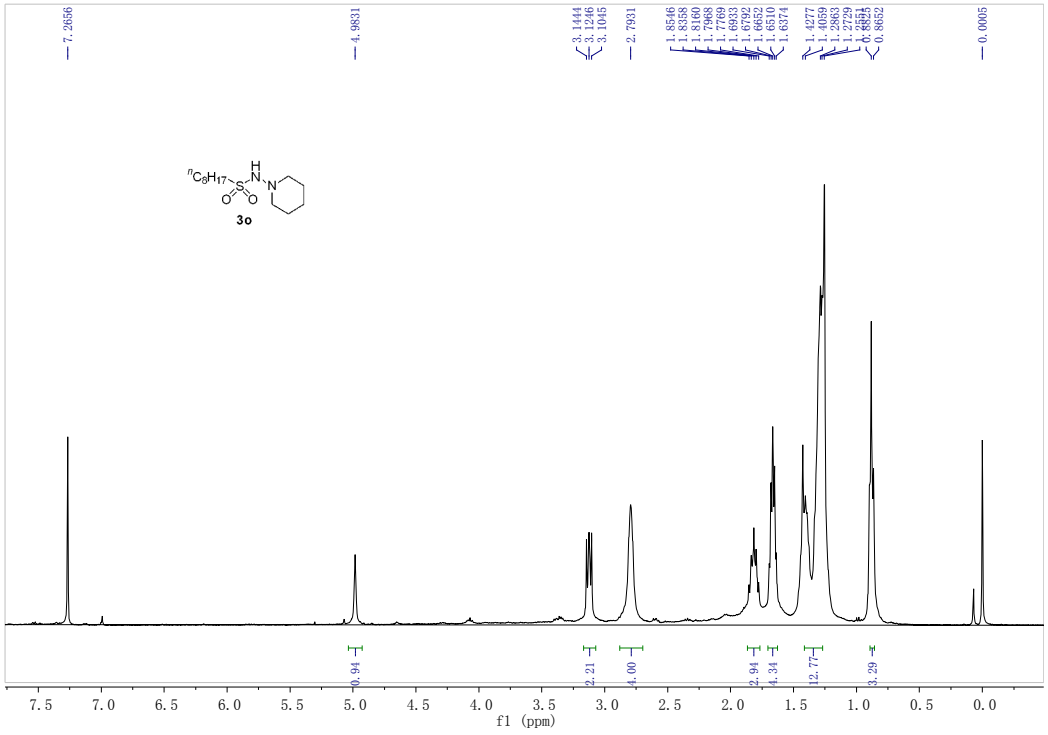
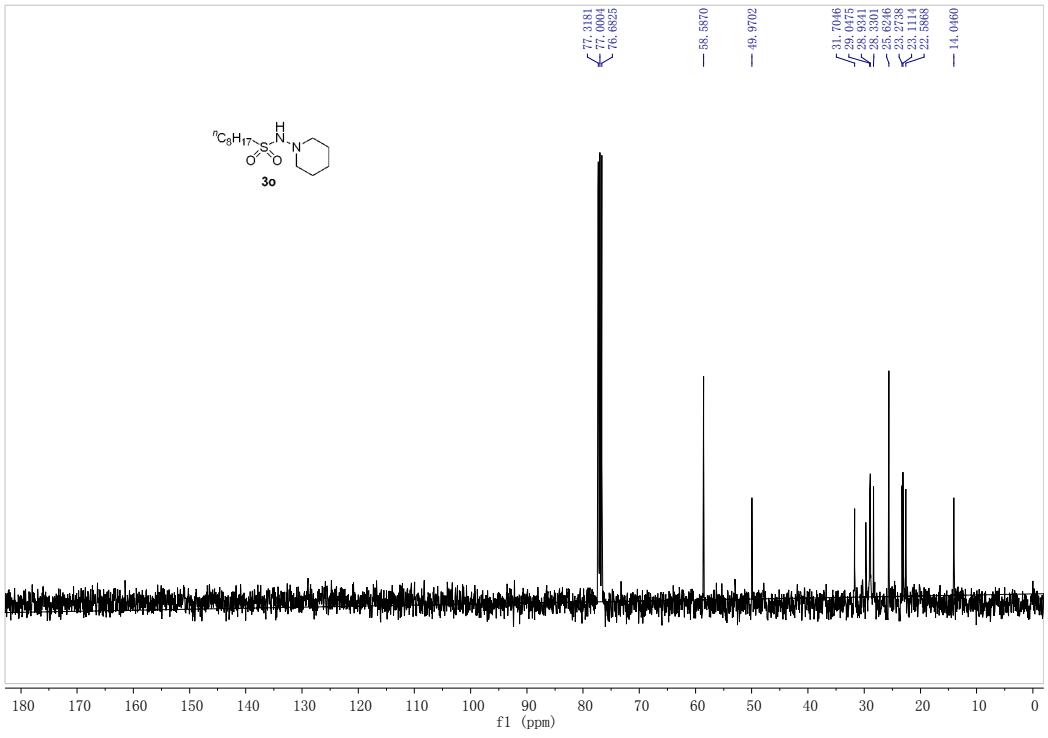
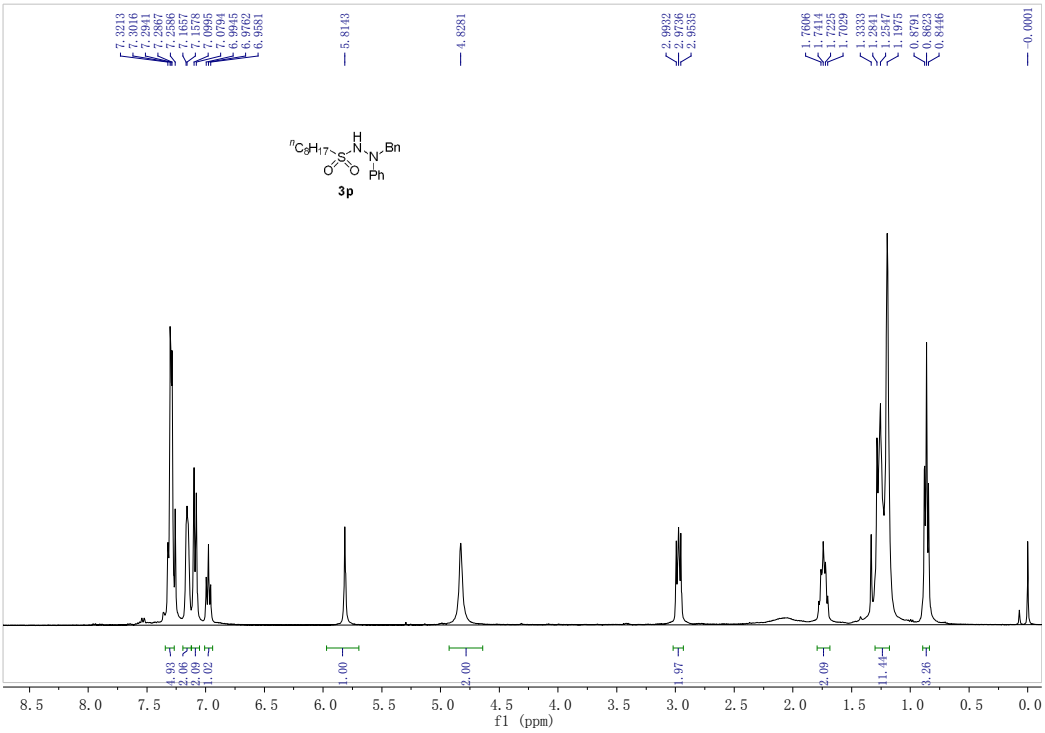
133.3084
129.0420
128.8505
128.1010
120.8999
114.3356
77.3187
77.0001
76.6822
42.6372
3n
f1 (ppm)


7.2656
4.9831
3.1444
3.1246
3.1045
2.7931
1.8546
1.8358
1.8160
1.7968
1.7769
1.6933
1.6752
1.6652
1.6510
1.6374
1.4277
1.4059
1.2863
1.2729
0.8652
0.0005
0.94
2.21
4.00
2.94
4.34
12.77
3.29
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
3o


77.3181
77.0004
76.6825
58.5870
49.9702
31.7046
29.0475
28.9341
28.5301
25.6246
23.2738
23.1114
22.5868
14.0460
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3o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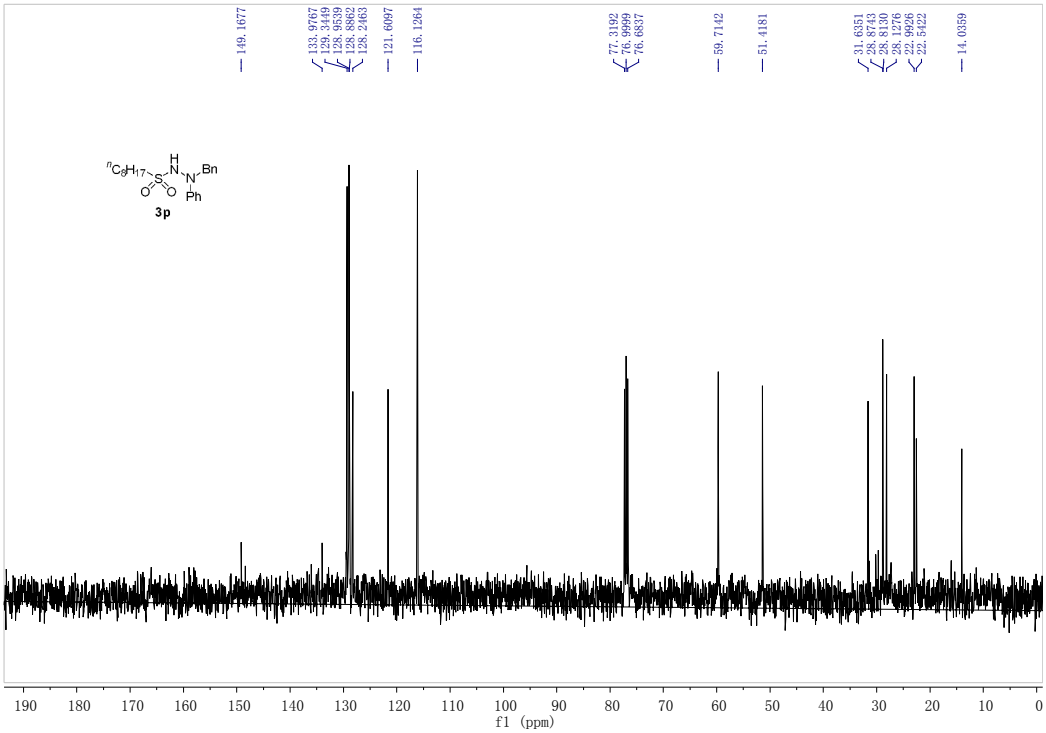
7.3016
7.2941
7.2867
7.2586
7.1557
7.1578
7.0995
7.0794
6.9945
6.9762
6.9581
5.8143
4.8281
2.9932
2.9736
2.9535
1.7606
1.7414
1.7225
1.7029
1.3333
1.2841
1.2547
1.1975
0.8791
0.8623
0.8446
0.0001
3p
4.93
2.86
2.09
1.02
1.00
2.00
1.97
2.09
11.44
3.26
f1 (ppm)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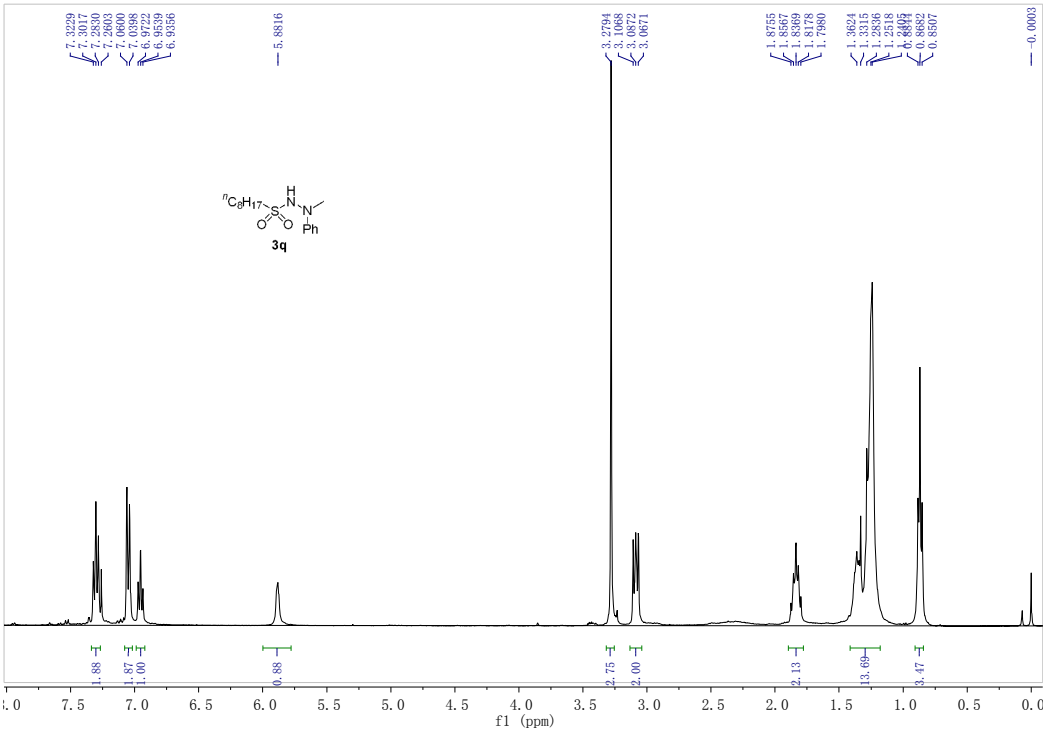
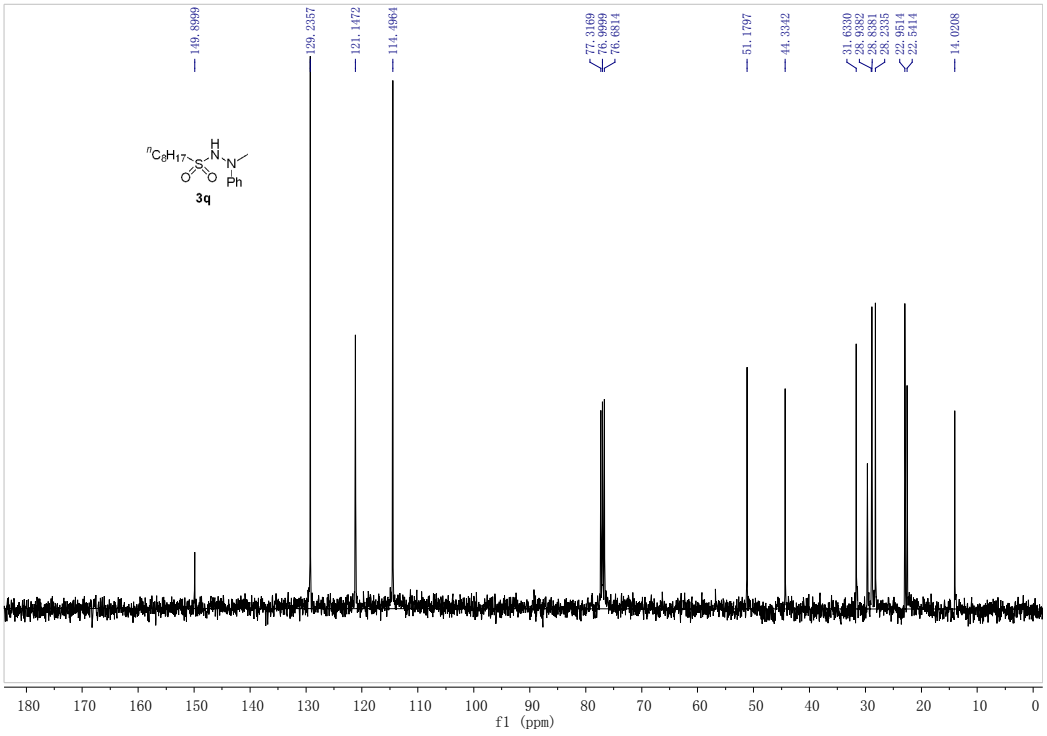
133.9767
129.2349
128.9539
128.8862
128.2463
121.6097
116.1264
77.3192
76.9999
76.6837
59.7142
51.4181
31.6351
28.8753
28.8130
28.1276
22.9936
22.5422
14.0359
3p
f1 (ppm)


7.3229
7.3017
7.2830
7.2603
7.0600
7.0398
6.9722
6.9539
6.9366
5.8816
3.2794
3.1098
3.0872
3.0671
1.8755
1.8567
1.8369
1.8178
1.7980
1.3624
1.3315
1.2836
1.2518
0.8682
0.8507
0.0003
1.88
1.87
1.00
0.88
2.75
2.00
2.13
13.69
3.47
3q
f1 (ppm)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121.1472
114.4964
77.3169
76.9999
76.6814
51.1797
44.3342
31.6330
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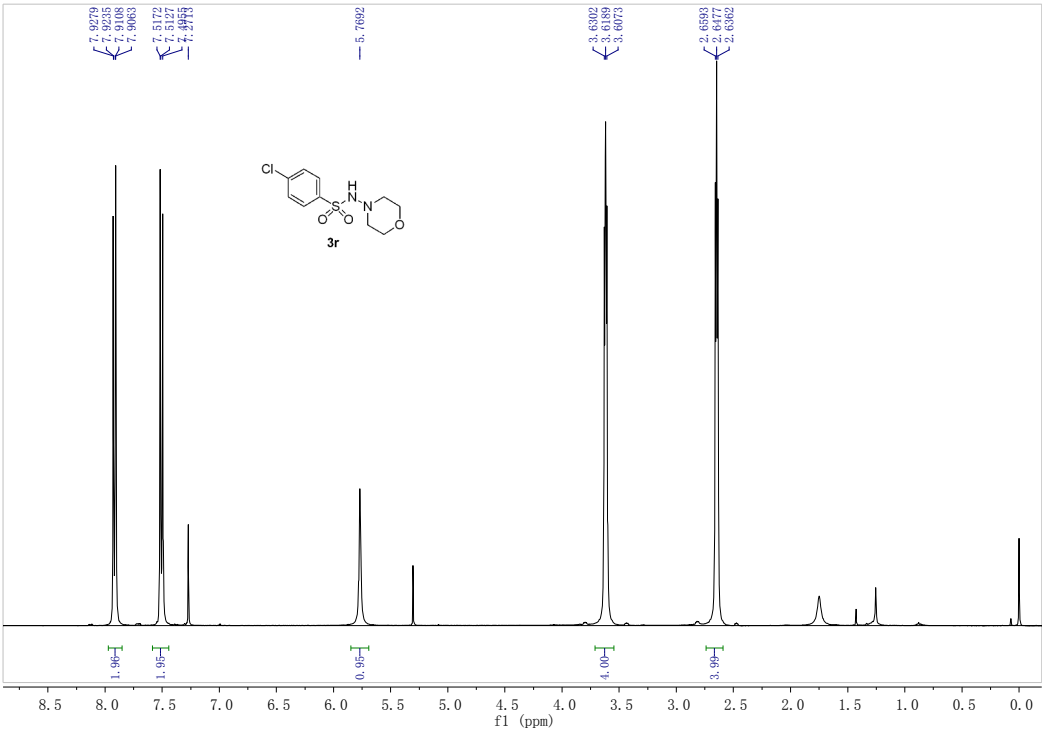
22.9514
22.5414
14.0208
3q
f1 (ppm)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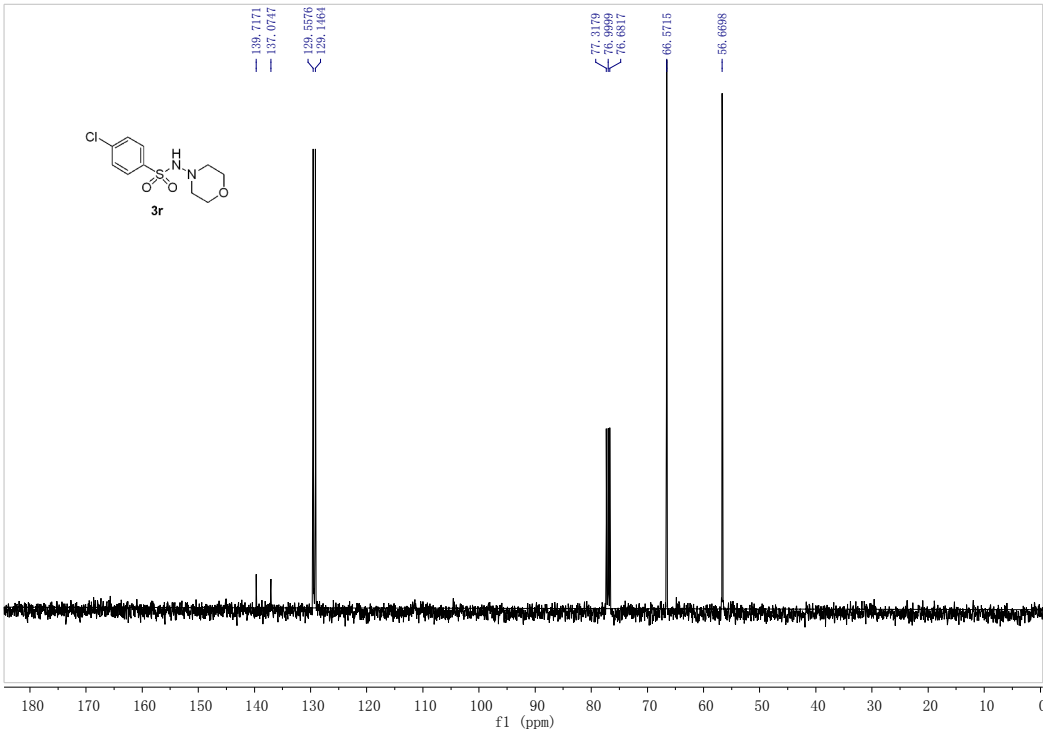
7.9235
7.9108
7.9063
7.5172
7.5157
7.4957
7.4913
5.7892
3.6302
3.6189
3.6073
2.6593
2.6477
2.6362
Cl
S
O
O
H
N
N
O
3r
1.96
1.95
0.95
4.00
3.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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137.0747
129.5576
129.1464
77.3179
76.9999
76.6817
66.5715
56.6698
Cl
S
O
O
H
N
N
O
3r
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)