Supporting information

N-2-Hydroxybenzaldehyde acylhydrazone-Fe(III) complex: Synthesis, crystal structure and its efficient and selective N-methylation

Zhiyou Li, [a] Lamei Wu [a,*] Tao Zhang, [a] Zhengxi Huang, [a] Guofu Qiu, [b] Zhongqiang Zhou, [a] Longfei Jin [a]

[a] Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, South-Central University for Nationalities, Wuhan, 430074, P. R. China.

[b] College of Pharmacy, Wuhan University, Wuhan, 430072, China.

* Fax: +86-27-67842752. E-mail: wlm52875@163.com.

Supporting information

1. General Procedure for the Synthesis of the N-2-Hydroxybenzaldehyde Acylhydrazones (4a–4g).

The N-2-hydroxybenzaldehyde acylhydrazones were prepared according to a previously reported method. [22] Briefly, to an ethanol solution (20 ml) of the appropriate acylhydrazine (4.0 mmol) and 2-hydroxybenzaldehyde (4.0 mmol), a few drops of AcOH were added. The mixture was heated at reflux for 1 h and then cooled to r.t. The crystalline solid was collected by filtration, washed with cold ethanol, and dried in air.

1.1. Synthesis of N'-(4-Diethylamino-2-hydroxybenzylidene)-2-[4-(2-methyl propyl) phenyl]propane hydrazide (**4a**).

The title compound was obtained in 94.9% yield, 1.50 g, as a thin yellow solid with mp 84–86 °C. ^{1}H NMR (400 MHz, DMSO) δ11.42, 10.96 (5:1, s, 1H), 11.241, 9.93 (5:1, s, 1H), 8.15, 7.98 (5:1, s, 1H), 7.25, 7.20 (5:1, d, 2H, J = 8.0 Hz), 7.11 (m, 3H), 6.23(d, 1H, J = 2.0 Hz), 6.07 (d, 1H, J = 2.0 Hz), 4.36, 3.60 (1:5, q, 1H, J= 7.2 Hz), 3.44, 3.34 (1:5, q, 4H, J= 7.2 Hz), 2.40, 2.37 (5:1, d, 2H, J = 6.8Hz), 1.79(m, 1H), 1.38,1.33 (5:1, d, 3H, J = 6.8Hz), 1.08, 1.05 (5:1, t, 6H, J = 6.8Hz), 0.84, 0.83 (d, 6H, J = 6.8Hz). ^{13}C NMR (100MHz, DMSO) δ 174.1, 169.4; 160.0, 158.7; 150.5, 150.3; 149.3, 144.3; 140.0, 139.6; 139.5, 139.3; 131.9, 130.0; 129.4, 129.3; 127.5, 127.4; 107.5, 106.8; 104.4, 104.0; 97.97, 97.90; 44.7; 44.2; 43.9, 40.9; 30.0; 22.6; 19.3, 18.9; 12.9. IR (KBr) 3415(s), 3192(m), 3017(m), 2971(s), 1657(vs), 1634(vs), 1597(s), 1518(s). Anal. Calcd for $C_{24}H_{33}N_3O_2$: C, 72.88; H, 8.41; N, 10.62. Found: C, 72.71; H, 8.30; N, 10.81.

1.2. Synthesis of *N'-(4-Diethylamino-2-hydroxybenzylidene)-2-(6-methoxy naphthyl)propane hydrazide (**4b**).*

The title compound was obtained in 94.3% yield, 1.58 g, as a thin yellow solid with mp 91–92 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.50, 9.91 (s, 1H), 11.25, 11.02 (s, 1H), 8.16, 7.99 (s, 1H),7.82-7.02 (m, 3H), 7.48, 7.43 (dd, 1H, Jax = 8.0 Hz, Jbx = 1.2 Hz), 7.28 (m, 1H), 7.14 (m, 2H), 6.22, 6.20 (dd, 1H, Jax = 8.8 Hz, Jbx = 2.0 Hz), 6.07 (s, 1H), 4.55, 3.78 (q, 1H, J = 6.8 Hz), 3.86, 3.84 (s, 3H), 3.32 (q, 4H, J = 6.8 Hz), 1.48, 1.43 (d, 3H, J = 6.8 Hz). 1.07 (t, 6H, J = 6.8 Hz). ^{13}C NMR (100MHz, DMSO) δ 174.0, 169.3; 159.9, 158.7; 157.5, 157.4; 150.4, 150.3; 149.3, 144.1; 137.5, 137.1; 133.7, 133.5; 131.8, 129.8; 129.6, 129.5; 128.9, 128.8; 127.2, 127.1; 126.7; 125.8, 125.7;

119.1; 107.5, 106.7; 106.1; 104.3, 103.9; 97.8, 97.7; 55.6; 44.2; 41.4; 19.4, 18.9; 12.9. IR (KBr) 3416(m), 3193(m), 3037(w), 2974(m), 1633(vs), 1600(s), 1519(s). Anal. Calcd for $C_{25}H_{29}N_3O_3$: C, 71.57; H, 6.97; N, 10.02. Found: C, 71.42; H, 6.86; N, 10.23.

1.3. Synthesis of *N'-(2-Hydroxybenzylidene)-2-(6-methoxynaphthyl)propane hydrazide* (***4c***).

The title compound was obtained in 93.1% yield, 1.30 g, as a colorless solid with mp 175–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.87, 9.99（s, 1H）. 9.01, 8.32(s, 1H). 8.16, 7.75(s, 1H). 7.71, 7.46(d, 1H, J = 2.0 Hz). 7.71 (m, 2H); 7.19–6.81 (m, 7H); 4.46, 3.82(q, 1H, J = 6.8 Hz). 3.92, 3.88(s, 3H). 1.68, 1.61(d, 3H, J = 6.8 Hz). ^{13}C NMR (100MHz, DMSO) δ 175.1, 170.1; 157.8, 157.5; 157.7, 157.6; 147.7, 141.2; 137.5, 136.9; 133.7, 133.5; 131.7, 131.3; 129.8, 129.4; 129.6; 128.9, 128.8; 127.3; 126.7; 125.9; 120.6, 119.7; 119.9, 119.1; 119.0; 116.7, 116.5; 106.2; 55.6; 44.3, 41.4; 19.1, 18.9. IR (KBr): 3447(w), 3202(s), 3062(m), 2996(w), 1657(vs), 1612(s), 1551(s). Anal. Calcd for $C_{21}H_{20}N_2O_3$: C 72.40, H 5.79, N 8.04; found: C 72.24, H 5.86, N 8.12.

1.4. Synthesis of *N'-(4-Diethylamino-2-hydroxybenzylidene)-benzohydrazide* (***4d***).

The title compound was obtained in 97.4% yield, 1.21 g, as a yellow solid with mp 215–217 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.79 (s, 1H), 11.47 (s, 1H), 8.42 (s, 1H), 7.91 (dd, 2H, Jax = 6.8Hz, Jbx = 1.6 Hz), 7.59 (m, 1H), 7.53 (m, 2H), 7.20 (d, 1H, J = 8.4Hz), 6.27 (dd, 1H, Jax = 8.8Hz, Jbx = 2.4 Hz), 6.13 (d, 1H, J = 2.4 Hz), 3.36 (q, 4H, J = 6.8 Hz), 1.11 (t, 6H, J = 6.8 Hz). ^{13}C NMR (100MHz, DMSO) δ 162.6, 160.2, 150.6, 150.4, 133.6, 132.1, 128.9, 127.9, 106.9, 104.0, 97.9, 44.2, 12.9. IR (KBr) 3448(m), 3200(m), 3034(w), 2973(m), 1630(vs), 1587(s), 1518(vs). Anal. Calcd for $C_{18}H_{21}N_3O_2$: C, 69.43; H, 6.80; N, 13.49. Found: C, 69.55; H, 6.95; N, 13.66.

1.5. Synthesis of *N'-(4-Diethylamino-2-hydroxybenzylidene)-4-methoxybenzo hydrazide* (***4e***).

The title compound was obtained in 96.5% yield, 1.30 g, as a colorless solid with mp 210–212 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.68 (s, 1H), 11.53 (s, 1H), 8.40 (s, 1H), 7.90 (d, 2H, J = 8.8 Hz),7.18 (d, 1H, J = 8.8 Hz), 7.06 (d, 2H, J = 8.4 Hz), 6.26 (dd, 1H, Jax = 8.8 Hz, Jbx = 2.0 Hz), 6.12 (d, 1H, J = 2.0 Hz), 3.84 (s, 3H), 3.36 (q, 4H,

J = 6.8 Hz), 1.11(t, 6H, J = 6.8 Hz). ^{13}C NMR (100MHz, DMSO) δ 162.4, 161.1, 160.1, 150.4, 149.9, 132.0, 129.8, 125.6, 114.1, 106.9, 104.0, 97.9, 55.8, 44.2, 12.9. IR (KBr) 3447(w), 3236(m), 3074(w), 2970(m), 1629(vs), 1586(m), 1506(s). Anal. Calcd for $C_{19}H_{23}N_3O_3$: C, 66.84; H, 6.79; N, 12.31. Found: C, 67.03; H, 6.92; N, 12.45.

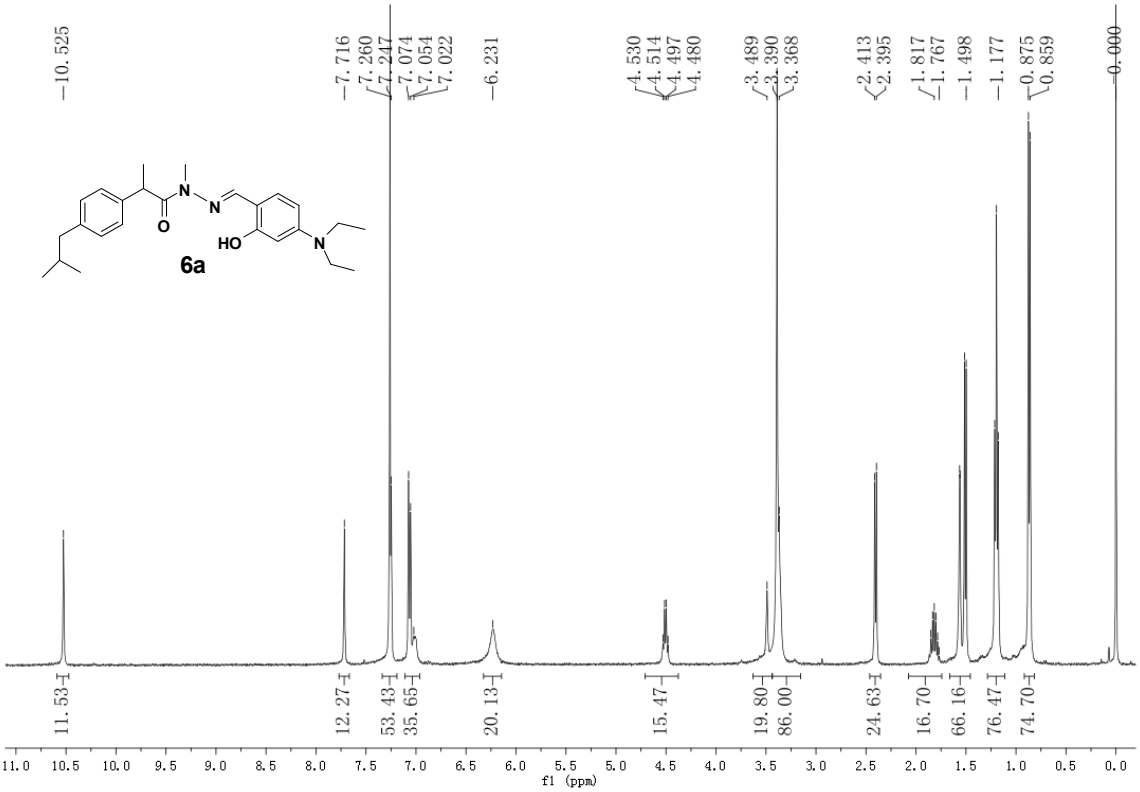
1.6. Synthesis of *N'-(4-Diethylamino-2-hydroxybenzylidene)-3,4,5-trimethoxy -benzohydrazide (**4f**).*

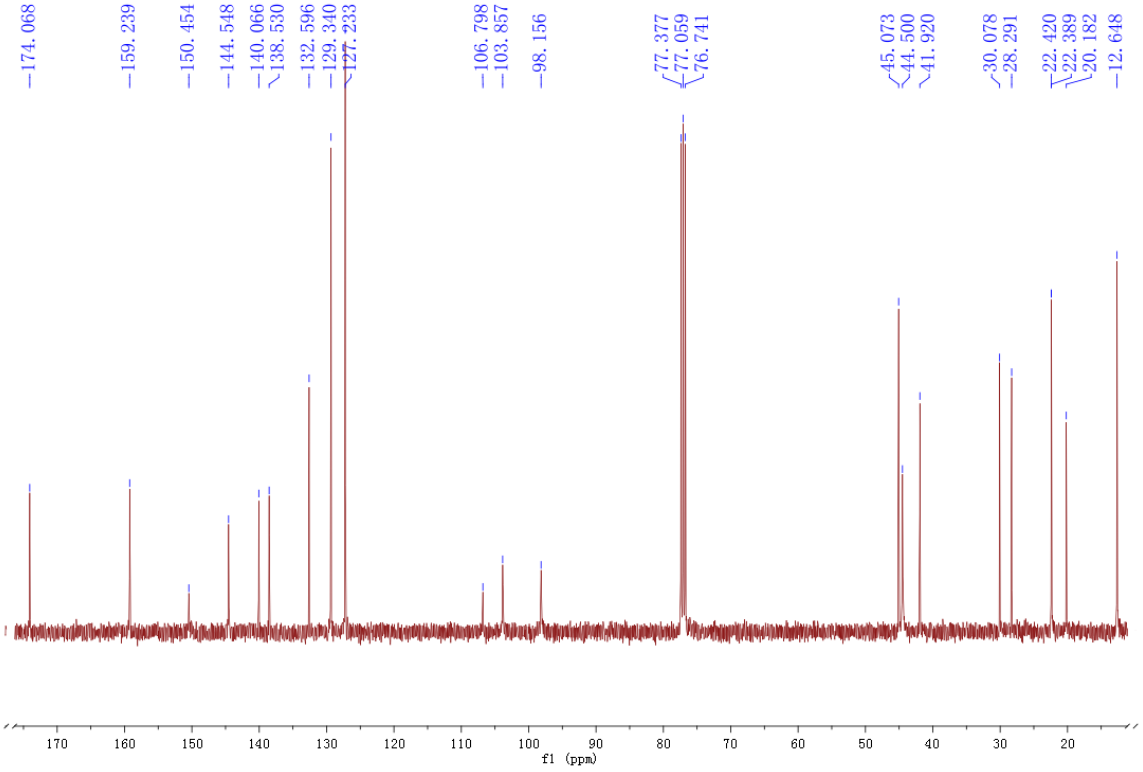
The title compound was obtained in 95.5% yield, 1.53 g, as a gray solid with mp 98–100 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.66 (s, 1H), 11.43 (s, 1H), 8.43 (s, 1H), 7.24 (s, 2H), 7.22 (d, 1H, J = 8.8 Hz), 6.27 (d, 1H, J = 8.4 Hz), 6.13 (s, 1H), 3.86 (s, 6H), 3.72 (s, 3H), 3.35 (q, 4H, J = 6.4 Hz), 1.10(t, 6H, J = 7.2 Hz). ^{13}C NMR (100MHz, DMSO) δ 162.1, 160.1, 153.1, 150.6, 150.2, 140.7, 131.9, 128.7, 106.9, 105.4, 104.1, 97.9, 60.5, 56.5, 49.0, 44.2, 12.9. IR (KBr) 3422(m), 3211(m), 2969(m), 1631(vs), 1588(vs), 1517(s). Anal. Calcd for $C_{21}H_{27}N_3O_5$: C, 62.83; H, 6.78; N,10.47. Found: C, 62.64; H, 6.86; N, 10.33.

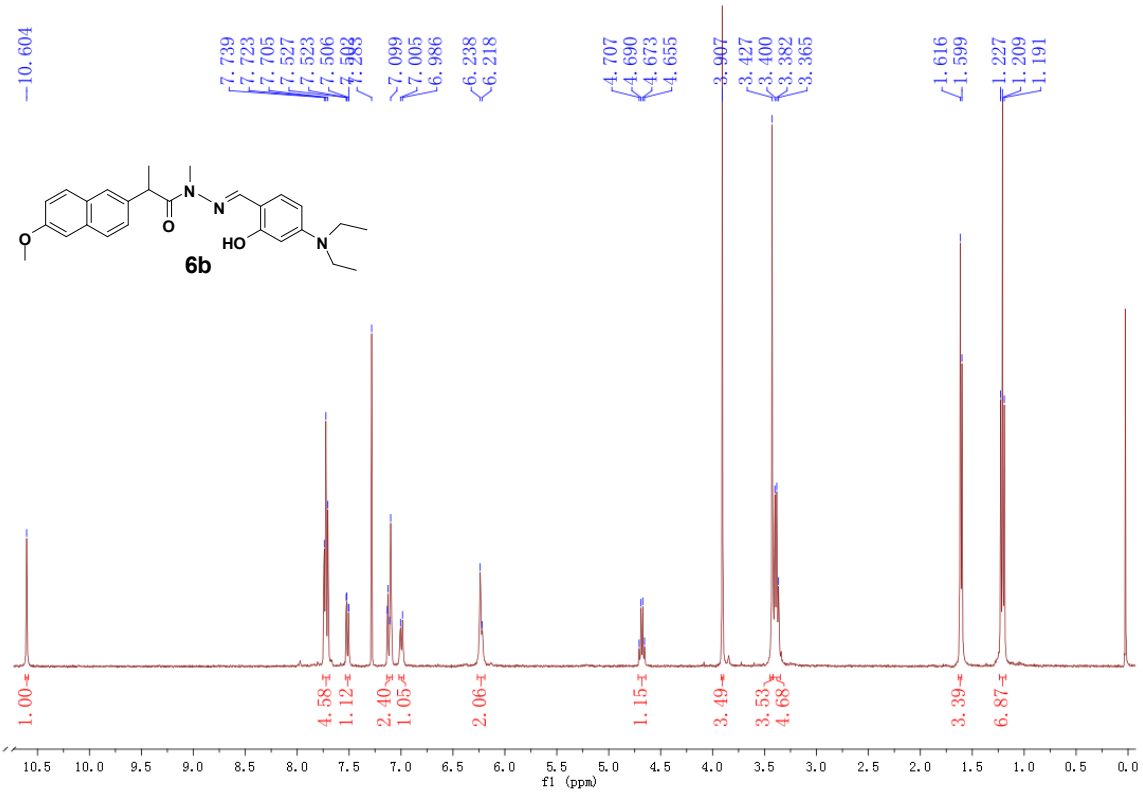
1.7. Synthesis of *N'-(4-Diethylamino-2-hydroxybenzylidene)-4-hydroxybenzo hydrazide (**4g**).*

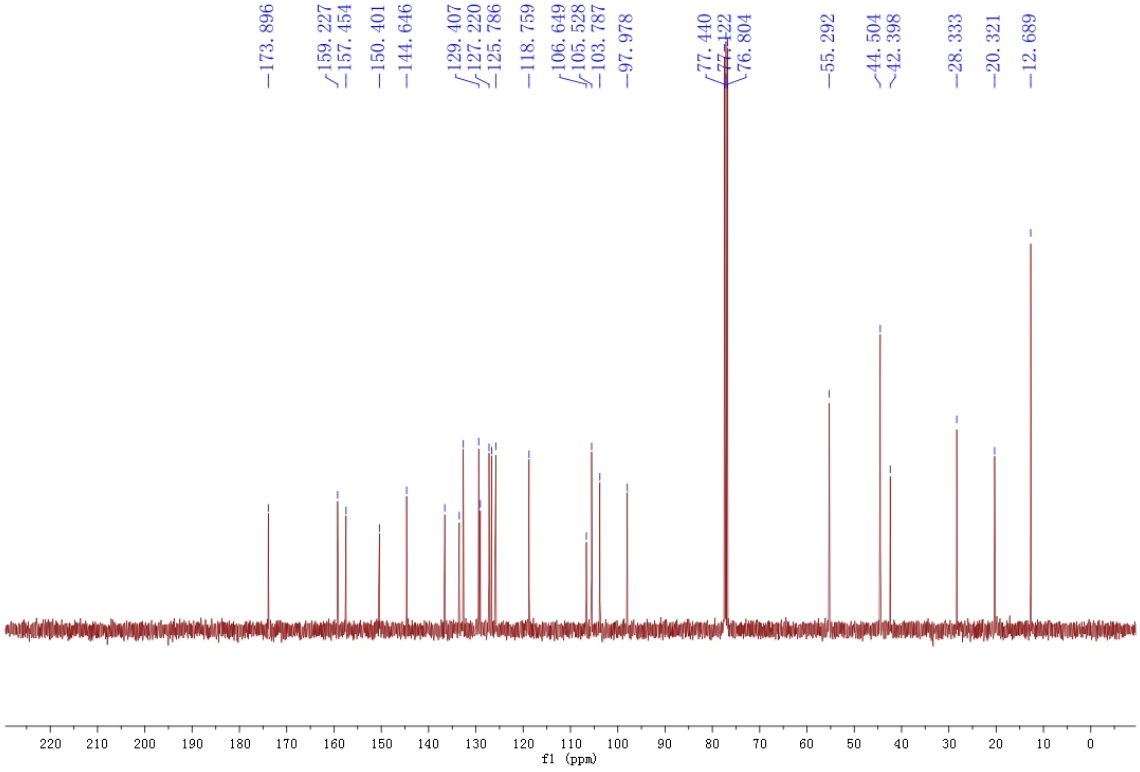
The title compound was obtained in 94.7% yield, 1.24 g, as a colorless solid with mp 218–220 °C. 1H NMR (400 MHz, DMSO) δ 11.58 (s, 1H), 11.56 (s, 1H), 10.10 (s, 1H), 8.39 (s, 1H), 7.79 (d, 2H, J = 8.4 Hz), 7.16 (d, 1H, J = 8.8 Hz), 6.86 (d, 1H, J = 8.4 Hz), 6.25 (d, 1H, J = 8.8 Hz), 6.12 (s, 1H), 3.35 (q, 4H, J = 6.8 Hz), 1.10(t, 6H, J = 6.8 Hz). 13C NMR (100MHz, DMSO) δ 162.4, 161.0, 160.1, 150.4, 149.7, 132.0, 129.9, 124.1, 115.5, 107.0, 104.0, 98.0, 44.2, 13.0. IR (KBr) 3390(s), 3222(m), 3083(m), 2974(m), 1634(vs), 1594(vs), 1512(s). Anal. Calcd for C18H21N3O3: C, 66.04; H, 6.47; N, 12.84. Found: C, 66.18; H, 6.66; N, 12.75.

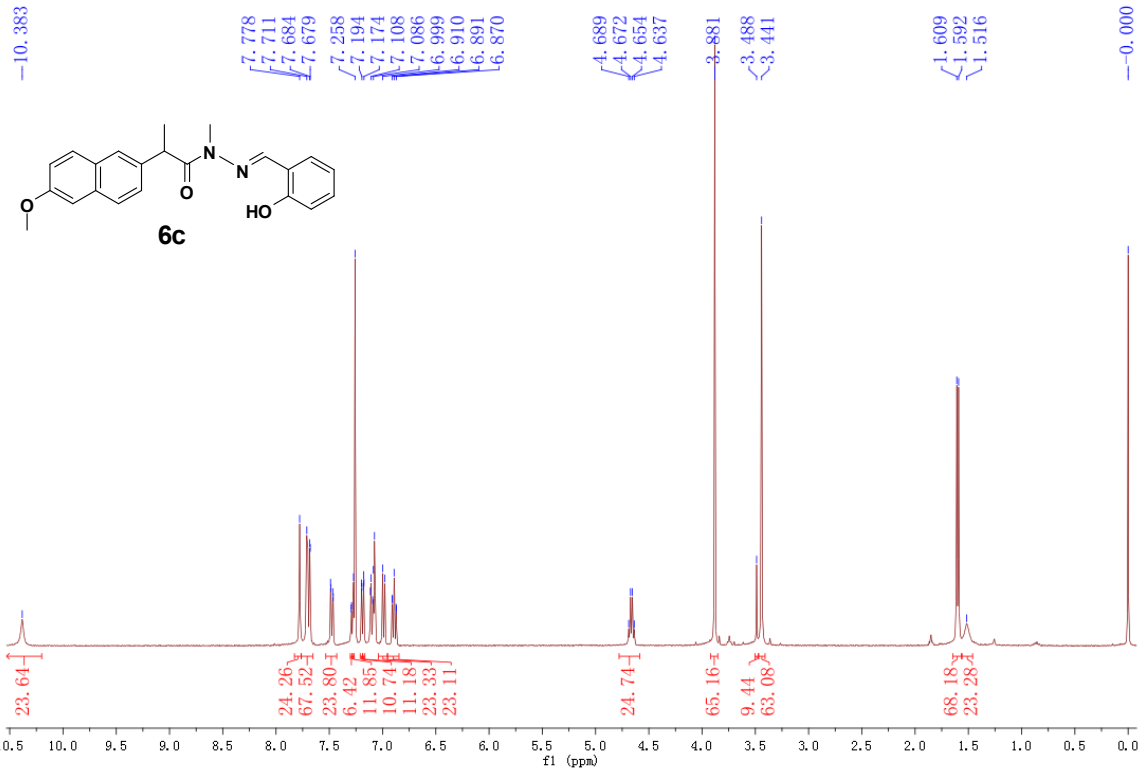
2. ^{1}H, ^{13}C NMR spectra **6a-6g**

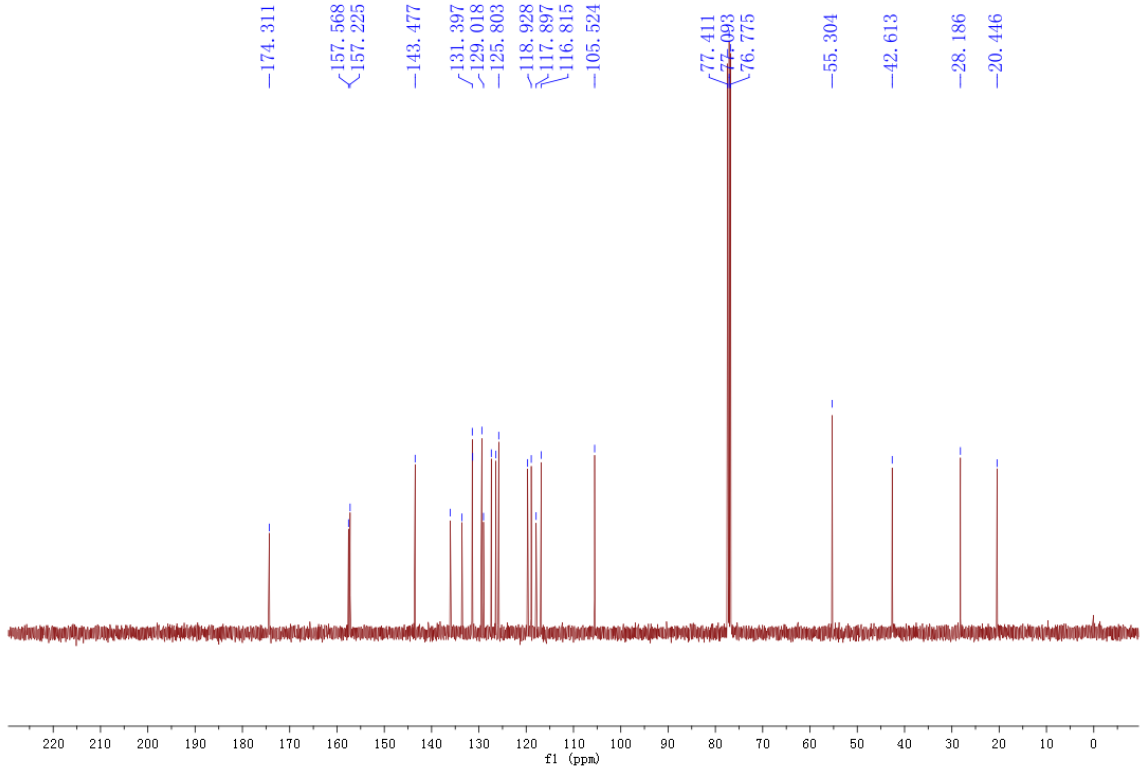


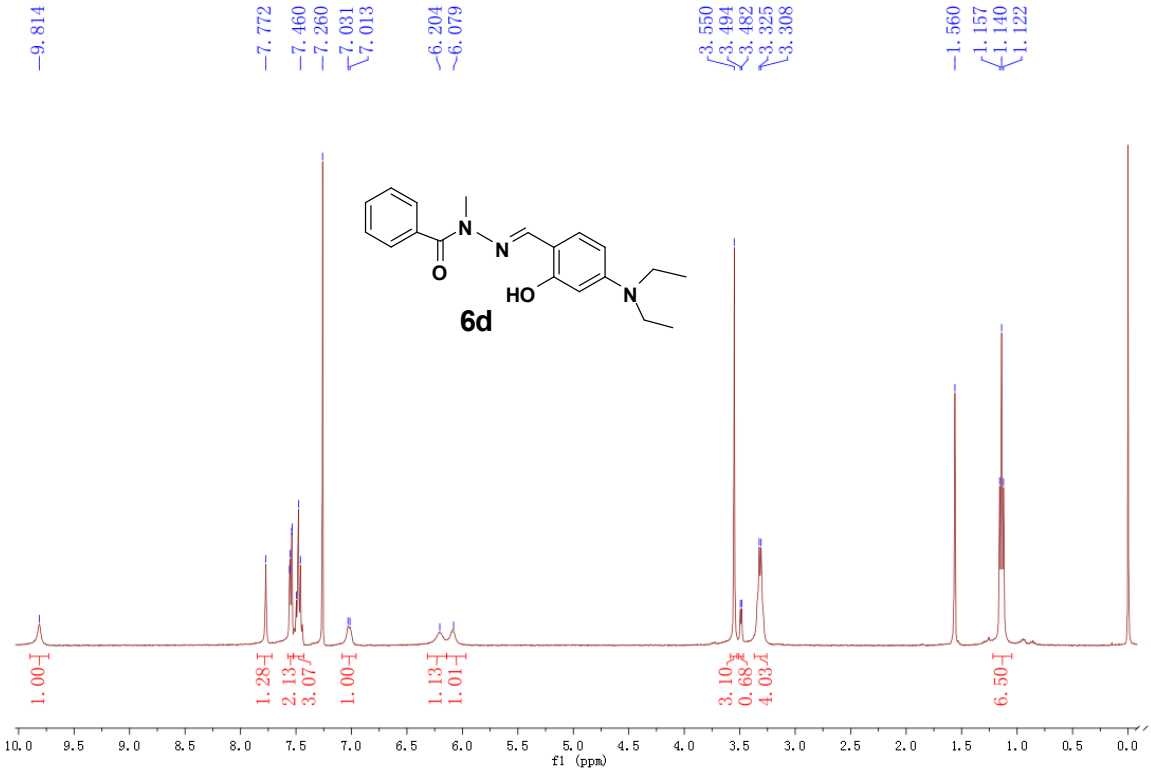

174.068
159.239
150.454
144.548
140.066
138.530
132.596
129.340
127.233
106.798
103.857
98.156
77.377
77.059
76.741
45.073
44.500
41.920
30.078
28.291
22.420
22.389
20.182
12.648
f1 (ppm)


10.604
7.739
7.723
7.705
7.527
7.523
7.506
7.283
7.099
7.005
6.986
6.238
6.218
4.707
4.690
4.673
4.655
3.907
3.427
3.400
3.382
3.365
1.616
1.599
1.227
1.209
1.191
6b
1.00
4.58
1.12
2.40
1.05
2.06
1.15
3.49
3.53
4.68
3.39
6.87
f1 (ppm)


173.896
159.227
157.454
150.401
144.646
129.407
127.220
125.786
118.759
106.649
105.528
103.787
97.978
77.440
77.122
76.804
55.292
44.504
42.398
28.333
20.321
12.689
f1 (ppm)

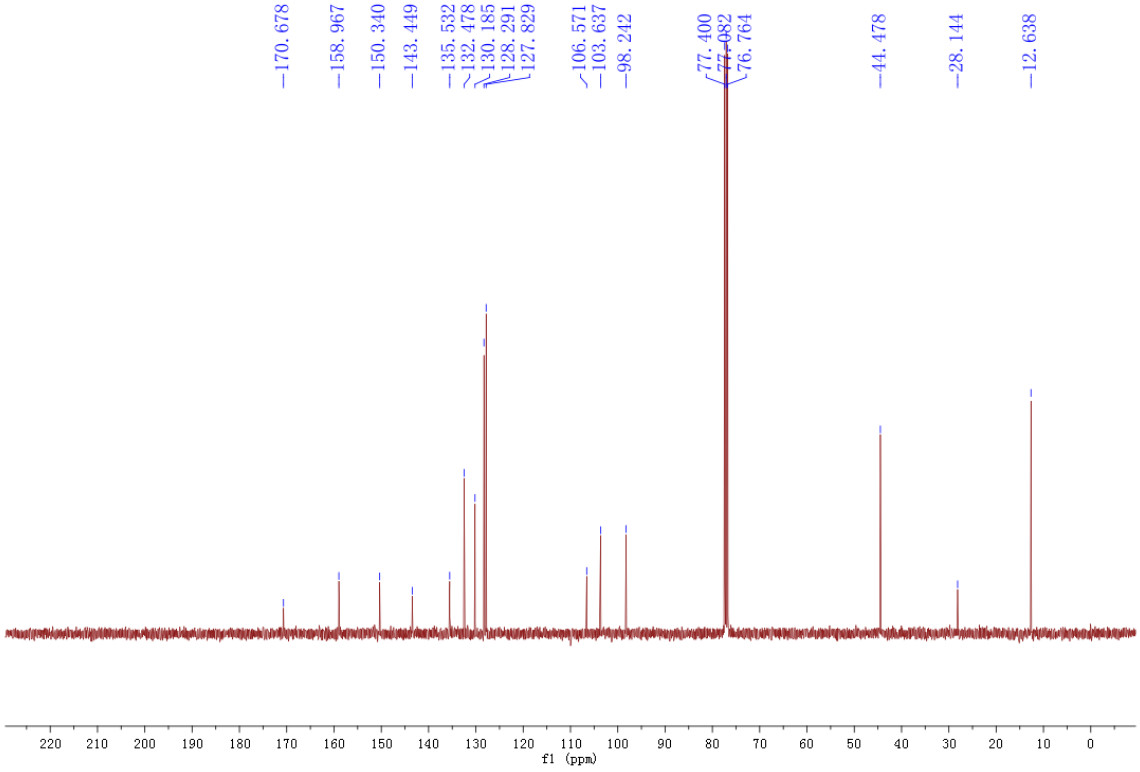

10.383
7.778
7.711
7.684
7.679
7.258
7.194
7.174
7.108
7.086
6.999
6.910
6.891
6.870
4.689
4.672
4.654
4.637
3.881
3.488
3.441
1.609
1.592
1.516
0.000
O
N
N
O
HO
6c
23.64
24.26
67.52
23.80
6.42
11.85
10.74
11.18
23.33
23.11
24.74
65.16
9.44
63.08
68.18
23.28
f1 (ppm)

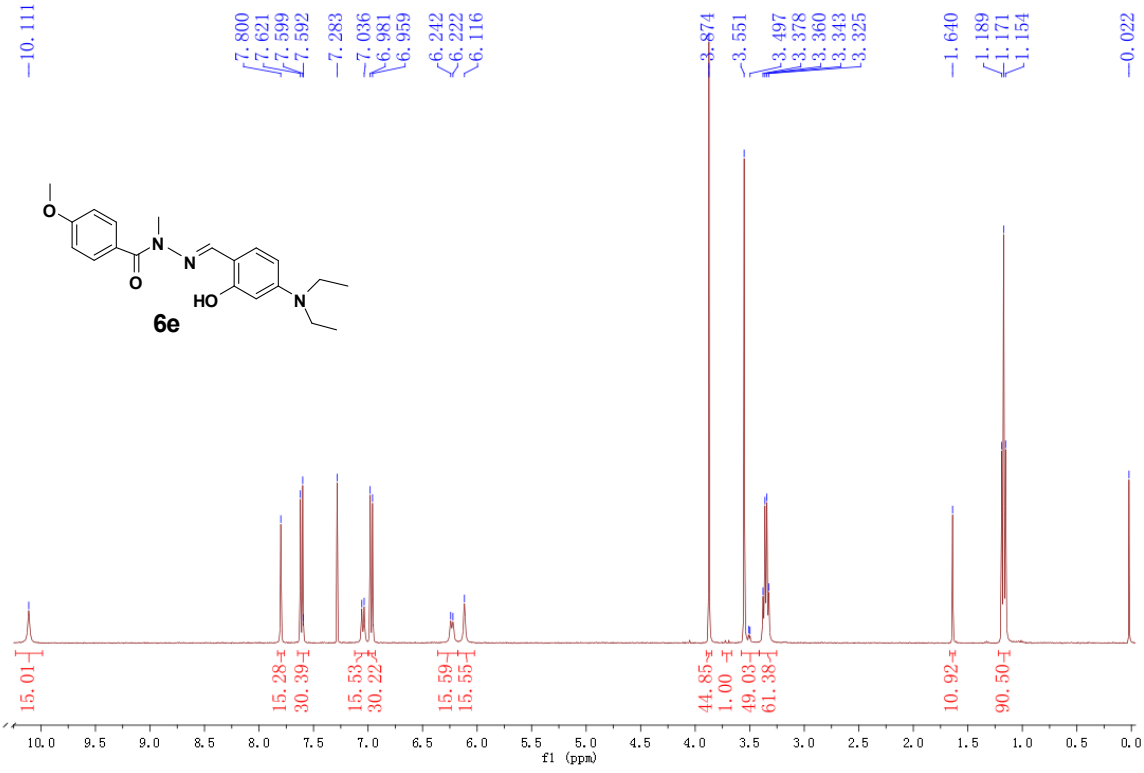

174.311
157.568
157.225
143.477
131.397
129.018
125.803
118.928
117.897
116.815
105.524
77.411
77.093
76.775
55.304
42.613
28.186
20.446
f1 (ppm)

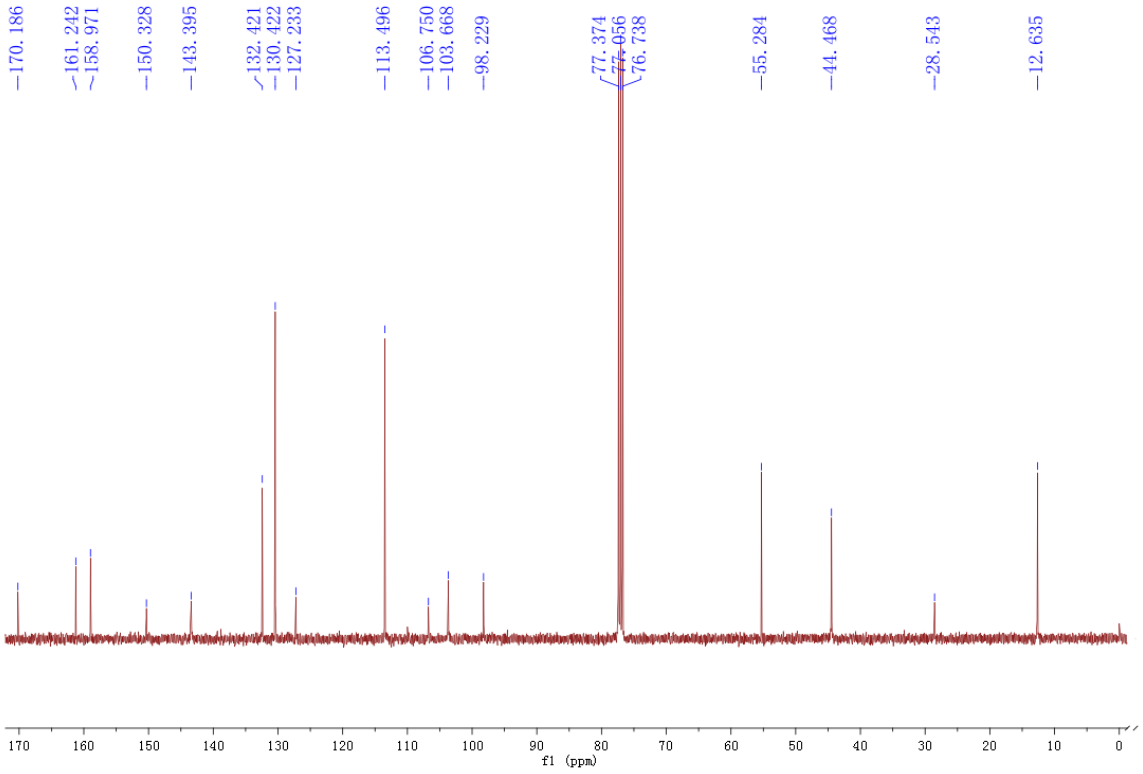

9.814
7.772
7.460
7.260
7.031
7.013
6.204
6.079
3.550
3.494
3.482
3.325
3.308
1.560
1.157
1.140
1.122
1.00
1.28
2.13
3.07
1.00
1.13
1.01
3.10
0.68
4.03
6.50
f1 (ppm)

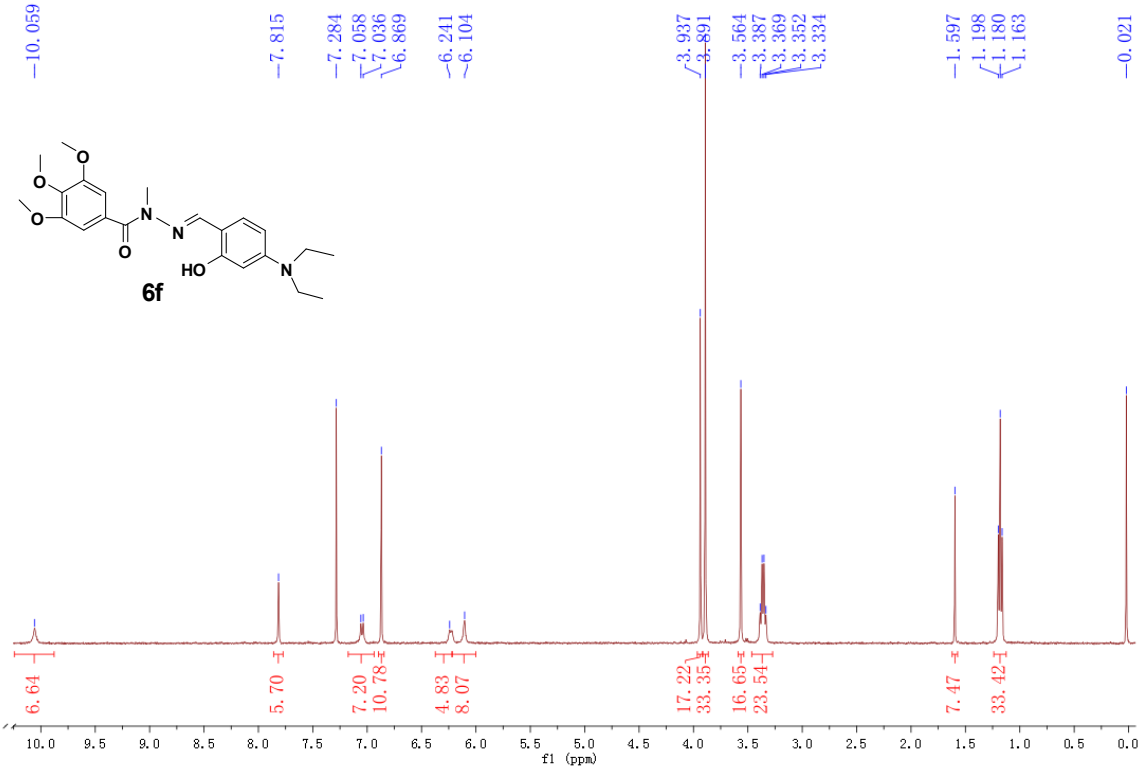
N
N
O
HO
N

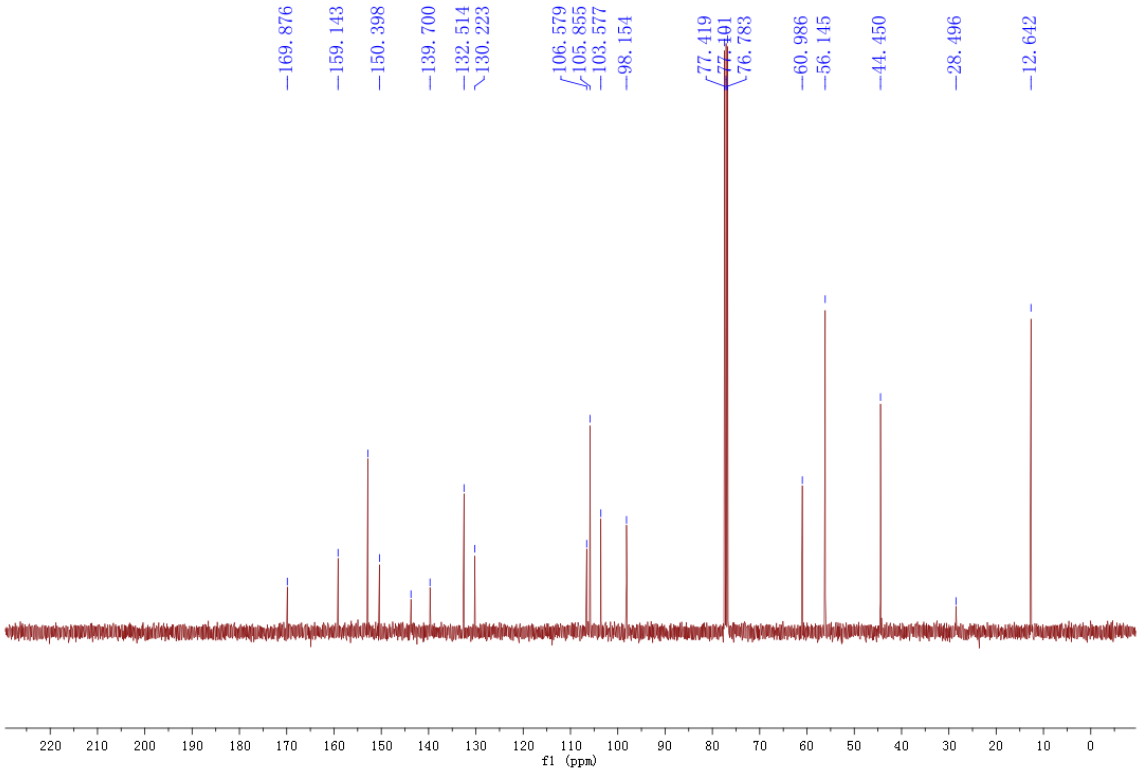
6d

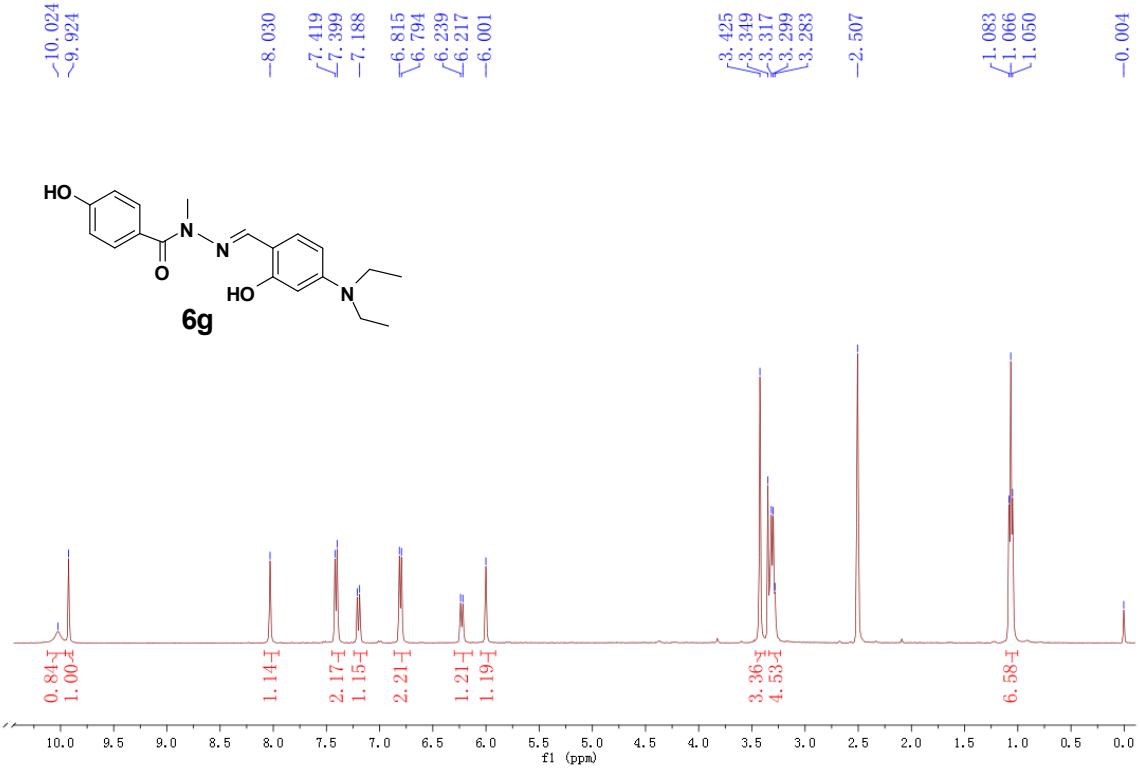

170.678
158.967
150.340
143.449
135.532
132.478
130.185
128.291
127.829
106.571
103.637
98.242
77.400
77.082
76.764
44.478
28.144
12.638
f1 (ppm)

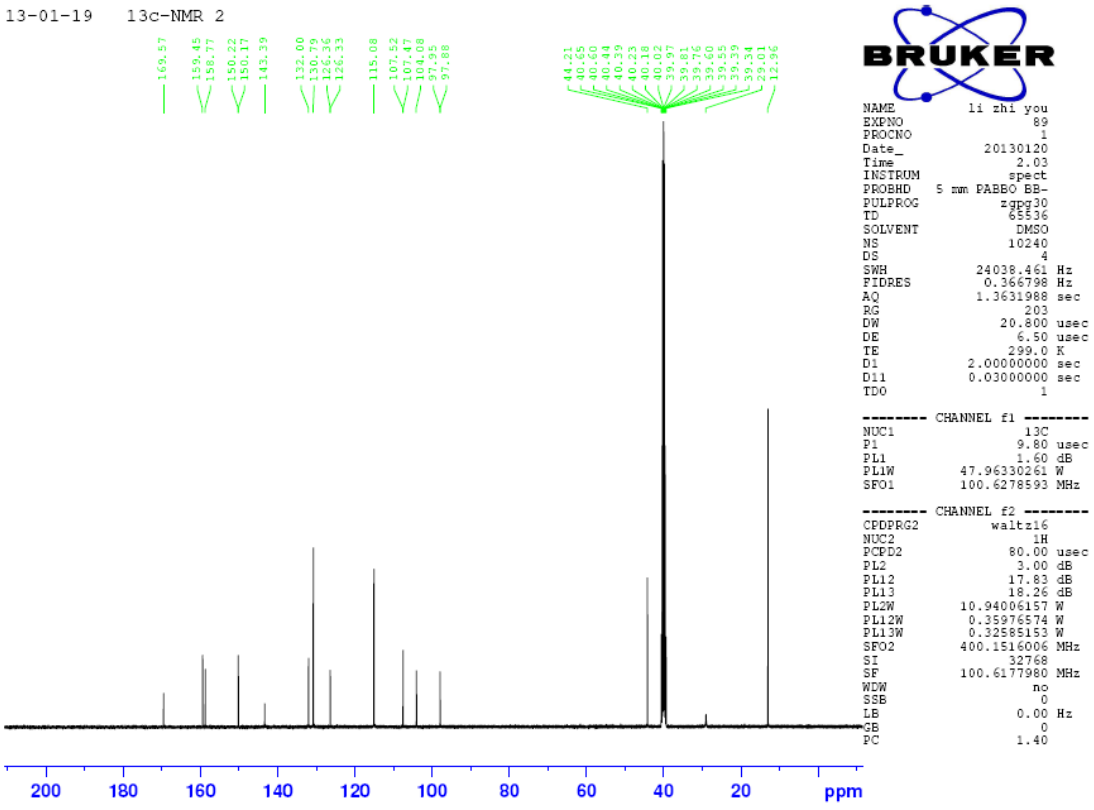

10.111
7.800
7.621
7.599
7.592
7.283
7.036
6.981
6.959
6.242
6.222
6.116
3.874
3.551
3.497
3.378
3.360
3.343
3.325
1.640
1.189
1.171
1.154
0.022
6e
15.01
15.28
30.39
15.53
30.22
15.59
15.55
44.85
1.00
49.03
61.38
10.92
90.50
f1 (ppm)


170.186
161.242
158.971
150.328
143.395
132.421
130.422
127.233
113.496
106.750
103.668
98.229
77.374
77.056
76.738
55.284
44.468
28.543
12.635
f1 (ppm)


10.059
7.815
7.284
7.058
7.036
6.869
6.241
6.104
3.937
3.891
3.564
3.387
3.369
3.352
3.334
1.597
1.198
1.180
1.163
0.021
6f
6.64
5.70
7.20
10.78
4.83
8.07
17.22
33.35
16.65
23.54
7.47
33.42
f1 (ppm)

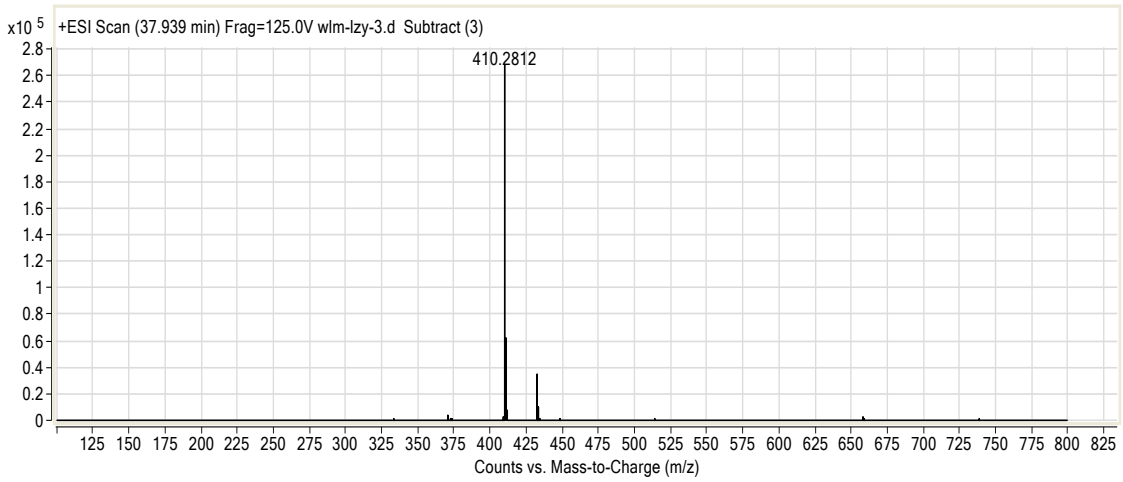

169.876
159.143
150.398
139.700
132.514
130.223
106.579
105.855
103.577
98.154
77.419
77.101
76.783
60.986
56.145
44.450
28.496
12.642
f1 (ppm)


10.024
9.924
8.030
7.419
7.399
7.188
6.815
6.794
6.239
6.217
6.001
3.425
3.349
3.317
3.299
3.283
2.507
1.083
1.066
1.050
0.004
HO
N
N
O
HO
N
6g
0.84
1.00
1.14
2.17
1.15
2.21
1.21
1.19
3.36
4.53
6.58
f1 (ppm)

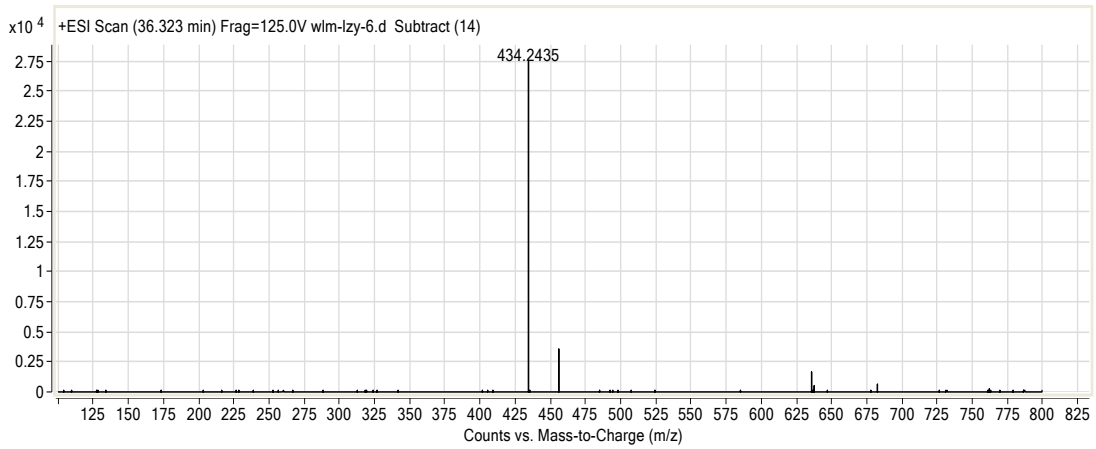


3. HRMS spectra of **6a-6g**

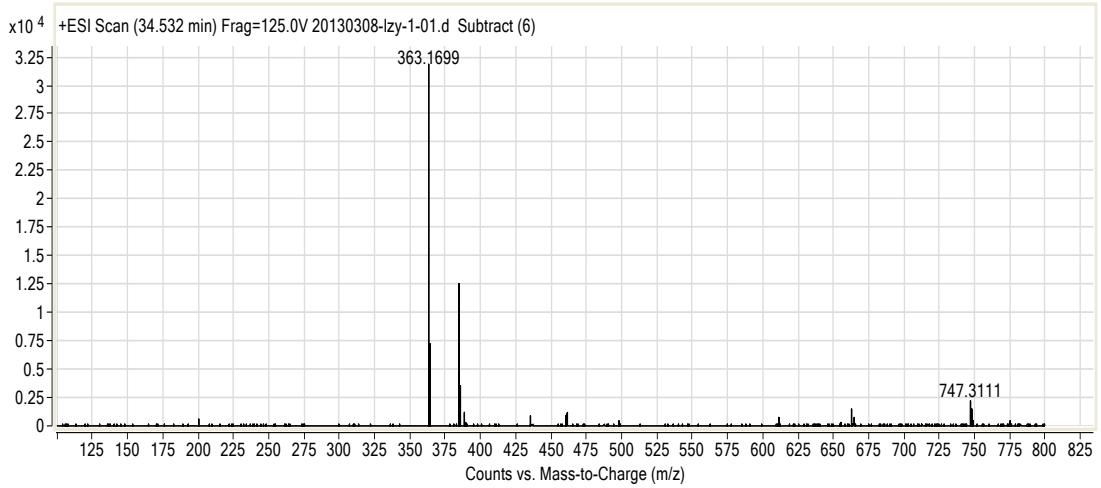
6a



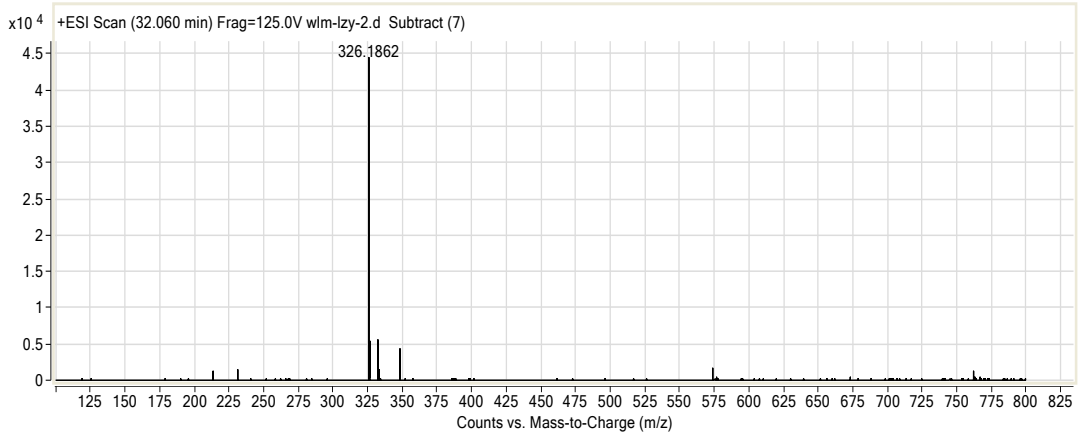
6b


x10 4
+ESI Scan (36.323 min) Frag=125.0V wlm-lzy-6.d Subtract (14)
434.2435
Counts vs. Mass-to-Charge (m/z)

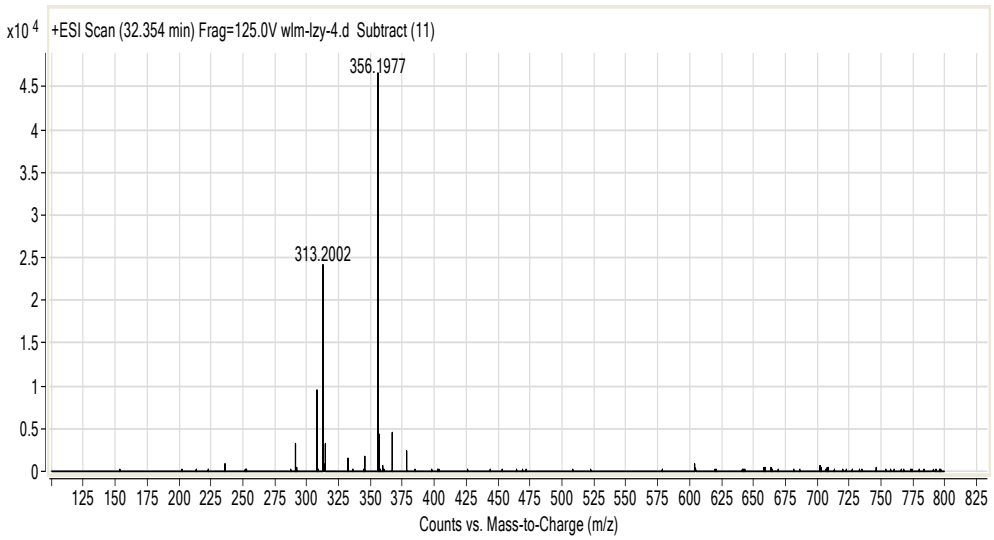
6c


x10 4
+ESI Scan (34.532 min) Frag=125.0V 20130308-lzy-1-01.d Subtract (6)
363.1699
747.3111
Counts vs. Mass-to-Charge (m/z)

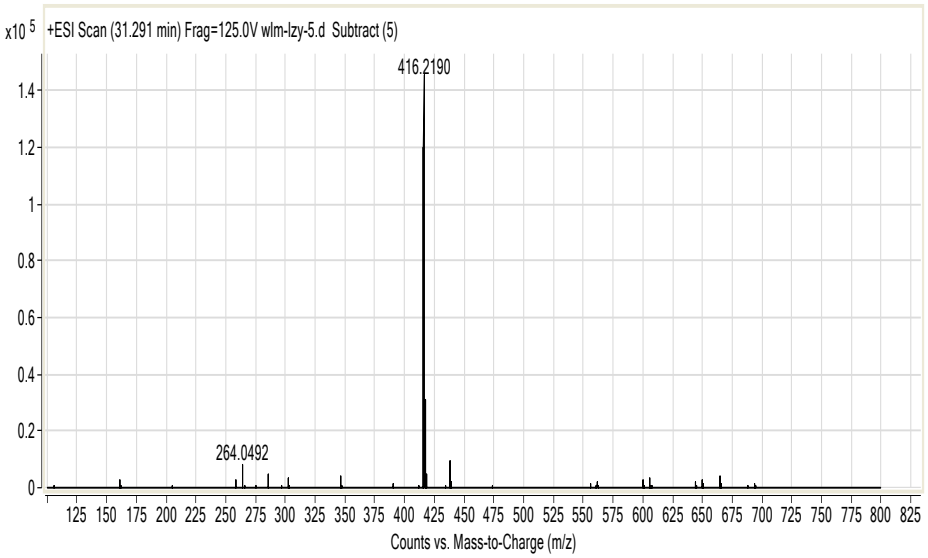
6d


x10 4
+ESI Scan (32.060 min) Frag=125.0V wlm-lzy-2.d Subtract (7)
326.1862
Counts vs. Mass-to-Charge (m/z)

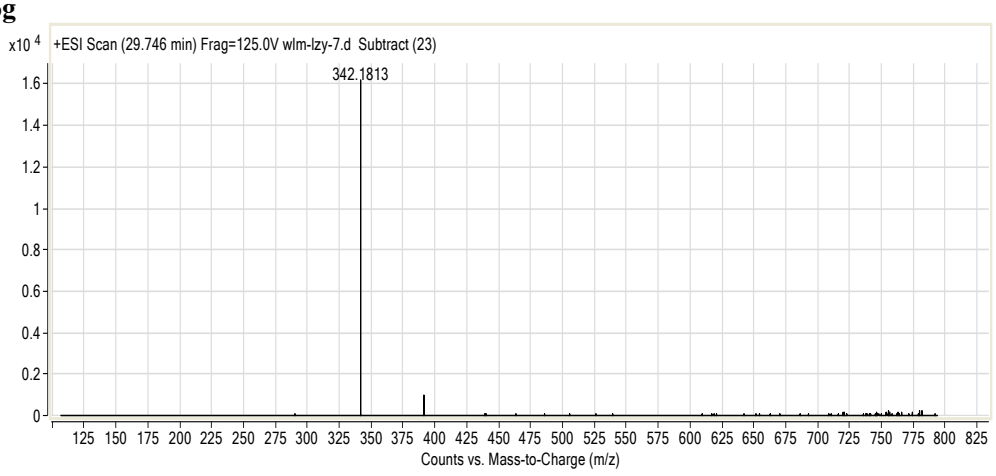
6e


x10 4
+ESI Scan (32.354 min) Frag=125.0V wlm-lzy-4.d Subtract (11)
356.1977
313.2002
Counts vs. Mass-to-Charge (m/z)

6f


x10 5
+ESI Scan (31.291 min) Frag=125.0V wlm-lzy-5.d Subtract (5)
416.2190
264.0492
Counts vs. Mass-to-Charge (m/z)

6g


x10 4
+ESI Scan (29.746 min) Frag=125.0V wlm-lzy-7.d Subtract (23)
342.1813
Counts vs. Mass-to-Charge (m/z)

4. The elemental analyses and IR spectra of metal complexes of **5a-5g**

Ferric (III) complex of N'-(4-diethylamino-2-Hydroxybenzylidene)-2-[4-(2-methylpropyl) phenyl] propane-hydrazide (**5a**), black solid, IR (KBr) 3452(m), 2952(m), 1614(vs), 1533(m), 1497(vs). Anal. Calcd for $C_{49}H_{68}ClFeN_6O_5$: C, 64.50; H, 7.51; N, 9.21. Found: C, 64.32; H, 7.43; N, 9.37.

Zinc (II) complex of N'-(4-diethylamino-2-Hydroxybenzylidene)-2-[4-(2-methylpropyl) phenyl] propane-hydrazide (**5a'**), yellow solid, IR (KBr) 3450(w), 2948(m), 1613(vs), 1530(m), 1498(vs). Anal. Calcd for $C_{48}H_{64}ZnN_6O_4$: C, 67.47; H, 7.55; N, 9.84. Found: C, 67.40; H, 7.58; N, 9.91.

Ferric (III) complex of N'-(4-diethylamino-2-Hydroxybenzylidene)-2-(6-methoxynaphthyl) propane- hydrazide (**5b**), black solid, IR (KBr) 3445(w),3187(w), 2973(m), 1600(vs), 1514(s). Anal. Calcd for $C_{51}H_{60}ClFeN_6O_7$: C, 63.78; H, 6.30; N, 8.75. Found: C, 63.87; H, 6.14; N, 8.87.

Ferric (III) complex of N'-(2-Hydroxybenzylidene)-2-(6-methoxynaphthyl) propane-hydrazide (**5c**), black solid, IR (KBr): 3444(w), 2973(w), 1606(vs); 1540(m). Anal. Calcd for $C_{43}H_{42}$ Cl Fe N_4 O_7: C, 63.13; H, 5.17; N, 6.85. Found: C, 62.97; H, 5.32; N, 6.78.

Ferric(III) complex of N'-(4-diethylamino-2-Hydroxybenzylidene)-benzohydrazide (**5d**), black solid, IR (KBr) 3423(w), 3216(w), 3090(w), 2975(w), 1595(vs), 1566(s), 1513(s). Anal. Calcd for C_{37} H_{46} Cl Fe N_6 O_6: C, 58.31; H, 6.08; N, 11.03. Found: C, 58.08; H, 6.21; N, 11.15.

Ferric(III) complex of N'-(4-diethylamino-2-Hydroxybenzylidene) -4-methoxybenzohydrazide (**5e**), black solid, IR (KBr) 3447(w), 2970(w), 1596(vs), 1508(s). Anal. Calcd for C_{38} H_{48} Cl Fe N_6 O_8: C, 56.48; H, 5.99; N, 10.40. Found: C, 56.36; H, 6.09; N, 10.56.

Ferric(III) complex of N'-(4-diethylamino-2-Hydroxybenzylidene) -3,4,5-trimethoxy benzohydrazide (**5f**), black solid, IR (KBr) 3447(w), 3248(w), 2972(w), 1594(vs), 1568(s), 1509(s). Anal. Calcd for C_{42} H_{56} Cl Fe N_6 O_{12}: C, 54.35; H, 6.08; N, 9.05. Found: C, 54.22; H, 6.21; N, 8.87.

Ferric(III) complex of N'-(4-diethylamino-2-Hydroxybenzylidene)-4-Hydroxybenzohydrazide (**5g**), black solid, IR (KBr) 3427(w), 3263(w), 2975(w), 1601(vs), 1511(s). Anal. Calcd for C_{37} H_{46} Cl Fe N_6 O_8: C, 55.96; H, 5.84; N, 10.58. Found: C, 55.85; H, 5.93; N, 10.64.