Electronic Supplementary Information (ESI)

Monomeric Vanadium Oxide: Very Efficient Species for Promoting Aerobic Oxidative Dehydrogenation of N-Heterocycles

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1. Supporting figures and tables

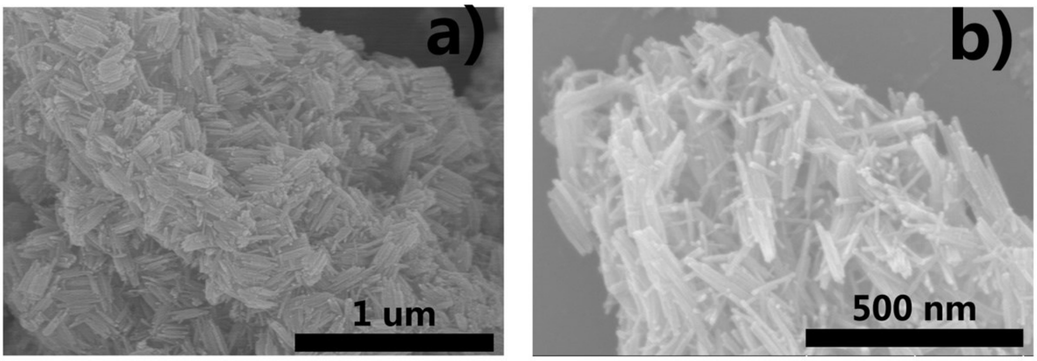

Fig. S1 SEM images of NbO_y@C before thermal-treatment.

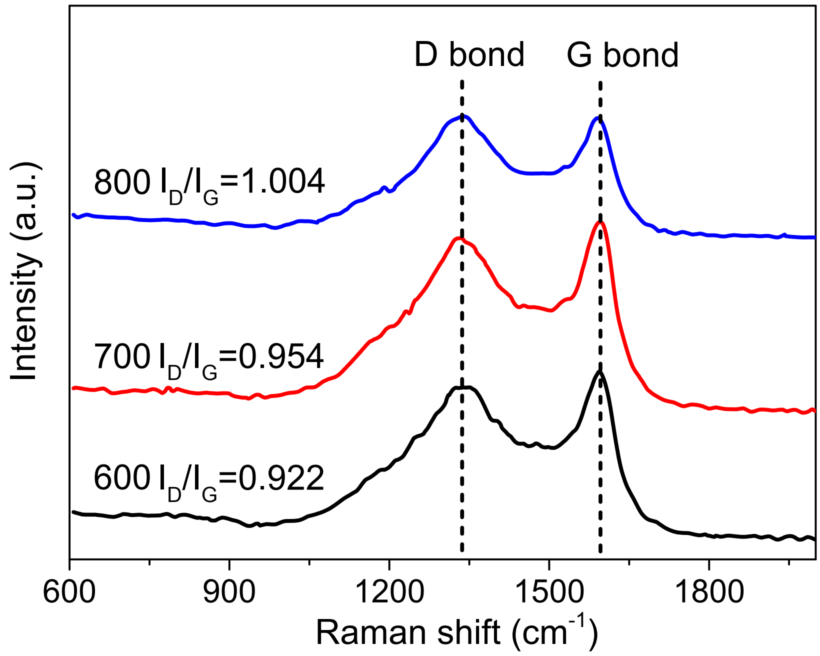

Fig. S2 Raman spectra of the VO_x-NbO_y@C materials after thermal-treatment at different temperatures.

The relative intensity of the D and G bonds (I_D/I_G) is an indicator of the disorder degree in a graphite structure. The I_D/I_G ratio decreased with elevating the thermal-treatment temperature, indicating that the introduction of vanadium and niobium resulted in various defects in the carbon framework.

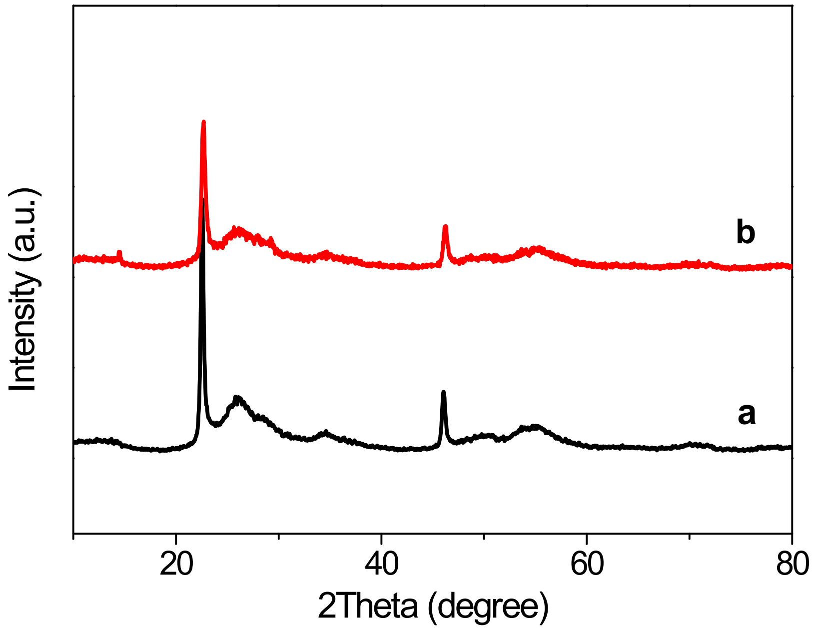

Fig. S3 XRD patterns of NbO_y@C (a) and VO_x-NbO_y@C (b) before thermal treatment.

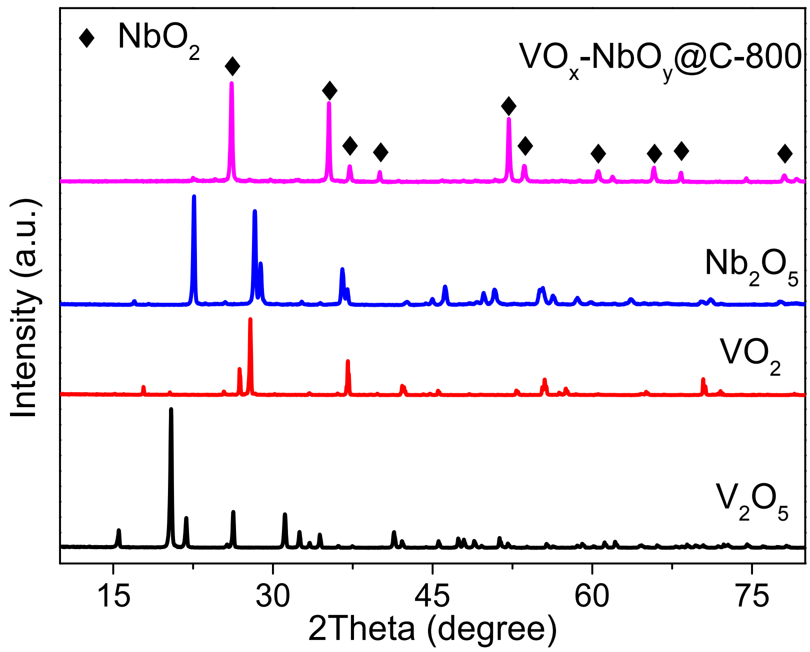

Fig. S4 XRD patterns of the as-prepared VO_x-NbO_y@C-800 and the commercial metal oxides.

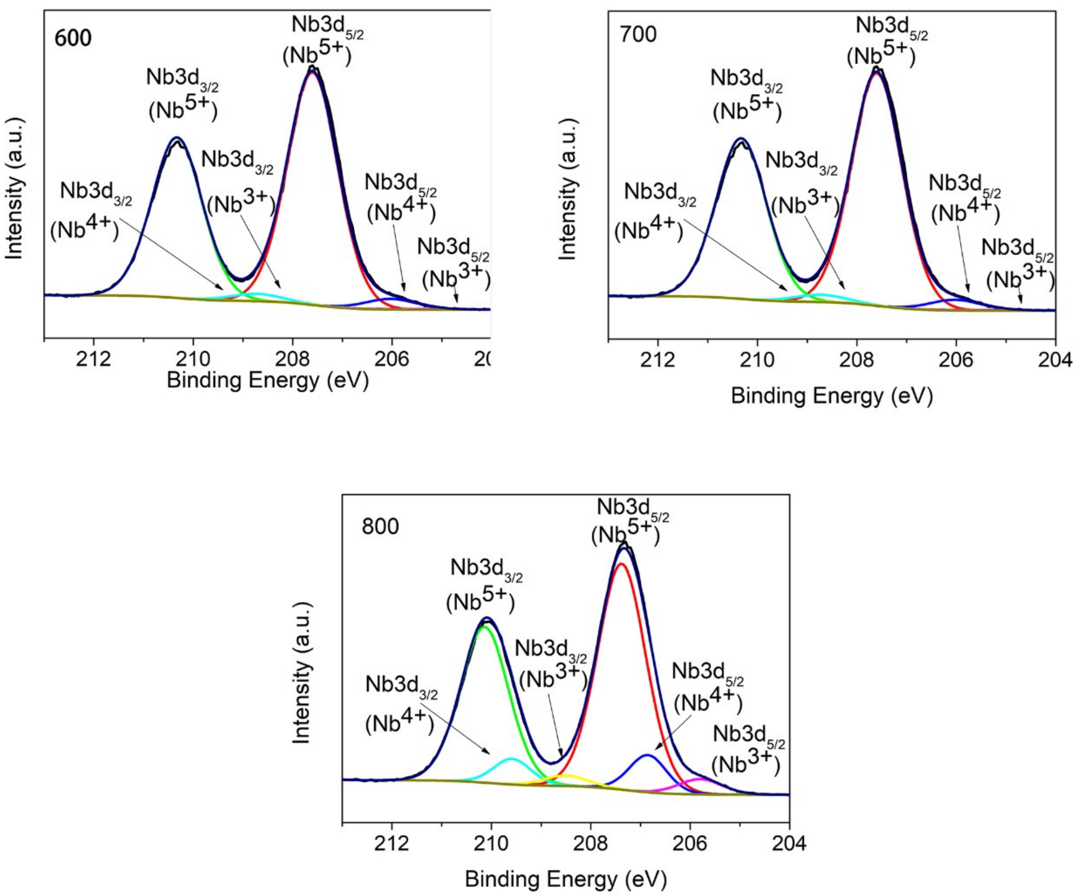

Fig. S5 XPS curve-fitting of Nb 3d photoelectronic peaks of VO_x-NbO_y@C catalysts after thermal-treatment at different temperatures.

Table S1 XPS peak parameters and area% of different components in Nb 3d region of VO_x-NbO_y@C

Sample	VO_x-NbO_y@C-600			VO_x-NbO_y@C-700			VO_x-NbO_y@C-800		
Atom% of Nd 3d	17.8			16.9			14.5		
Chemical state	Nb^{5+}	Nb^{4+}	Nb^{3+}	Nb^{5+}	Nb^{4+}	Nb^{3+}	Nb^{5+}	Nb^{4+}	Nb^{3+}
Peak position (eV)	207.30	206.80	-	207.45	206.90	205.72	207.35	206.85	205.80
FWHM	1.12	1.44	-	1.12	0.87	1.09	1.19	0.92	1.08
Area %	95.00	4.9	-	91.7	6.8	1.5	84.2	10.7	5.1

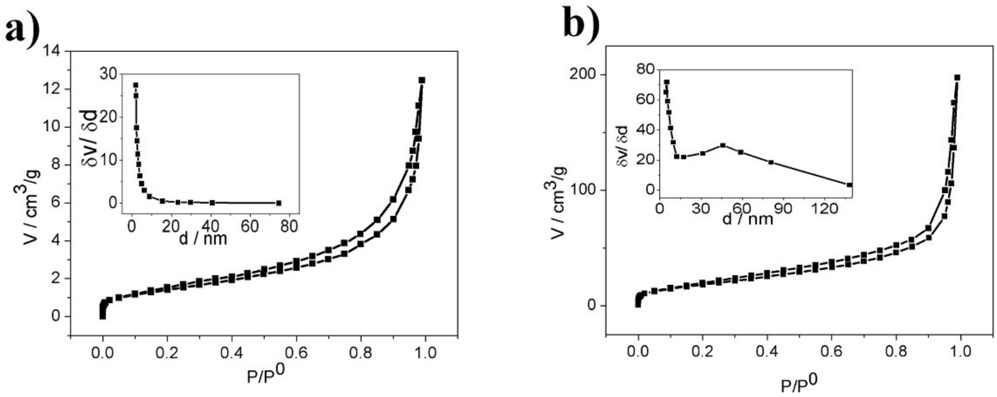

Fig. S6 N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves of VO_x-NbO_y@C-800 before (a) and after thermal-treatment (b).

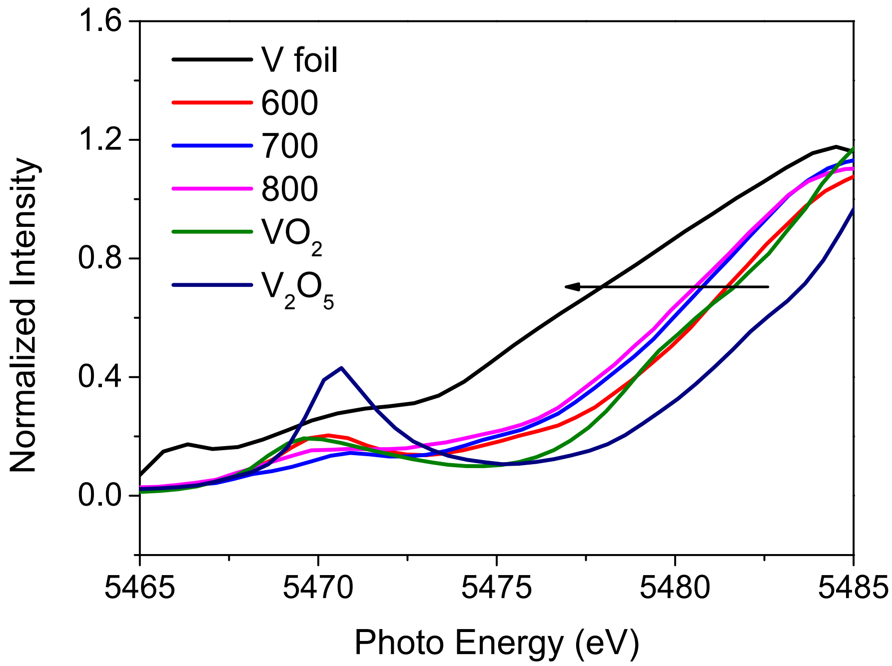

Fig. S7. V K-edge XANES spectra of VO_x-NbO_y@C catalysts and the standard V foil, VO_2 and V_2O_5 reference.

Table S2 Optimization of reaction conditions of oxidative dehydrogenation of tetrahydroquinoline with VO_x-NbO_y@C.[a]

Entry	Solvent	Temp. (°C)/ time (h)	Con. (%)	Yield. (%)[b]
1	DMSO	120 / 12	100	76.4
2	DMSO	120 / 16	100	91.8
3[c]	DMSO	120 / 12	100	71.8
4[d]	DMSO	120 / 12	100	74.6
5[e]	DMSO	120 / 12	100	73.1
6[f]	DMSO/H_2O	120 / 16	100	92.5
7[g]	DMSO/H_2O	120 / 16	100	61.7
8[h]	DMSO/H_2O	120 / 16	100	77.8
6	1,3,5-Trimethylbenzene	120 / 16	77.4	39.2
7	Benzotrifluoride	120 / 16	76.9	37.5
8	PhCN	120 / 16	100	58.3
9	CH_3CN	120 / 16	100	75.3
10	dioxane	120 / 16	100	50.3
11	DMF	120 / 16	100	52.0
12	t-BuOH	120 / 16	77.0	65.9

[a] Reaction condition: 1, 2, 3, 4-tetrahydroquinoline (0.5 mmol), VO_X-NbO_y@C-800 (50 mg), solvent (2.0 mL), O_2 (0.5 MPa); [b] The yields were obtained by GC using chlorobenzene as internal standard; [c] VO_X-NbO_y@C-800 (40 mg); [d] O_2 (1 MPa); [e] O_2 (0.25 MPa); [f] DMSO 1.5 mL, H_2O 0.5 mL; [g] DMSO 1.75 mL, H_2O 0.25 mL; [h] DMSO 1.0 mL, H_2O 1.0 mL.

Table S3. The effect of reaction time on the catalytic performance of the VOx-NbOy@C.

Entry	Solvent	time (h)	Con. (%)	Yield. (%)[b]
1	DMSO/H_2O	4	67.1	34.6
2	DMSO/H_2O	8	83.0	56.5
3	DMSO/H_2O	12	100	61.5
4	DMSO/H_2O	16	100	92.5

Reaction condition: 1,2,3,4-tetrahydroquinoline (0.5 mmol), catalyst (50 mg), DMSO (1.5 mL), H_2O (0.5 mL), O_2 (0.5 MPa), 120 °C

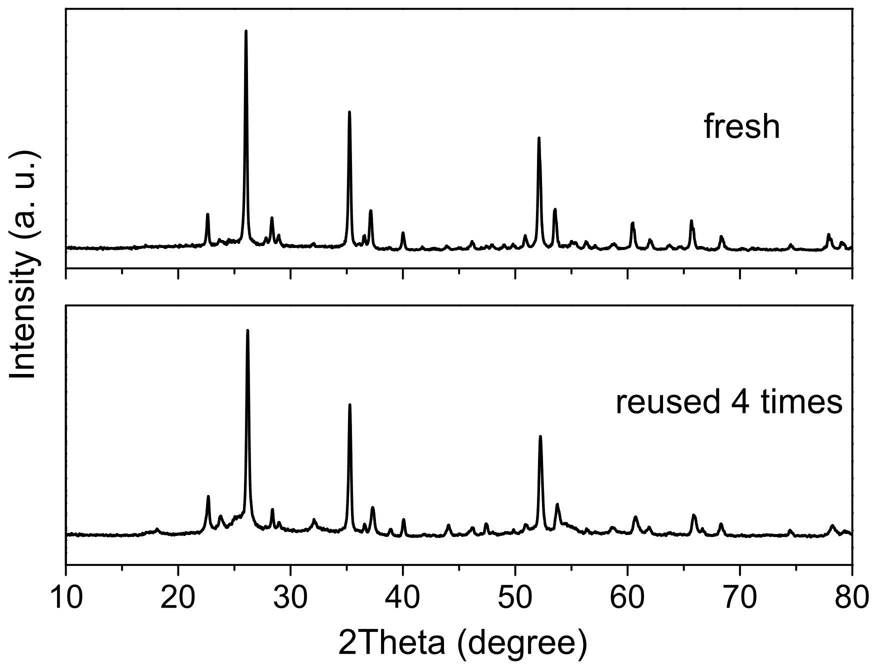

Fig. S8 XRD patterns of the fresh and reused VO_x-NbO_y@C catalysts.

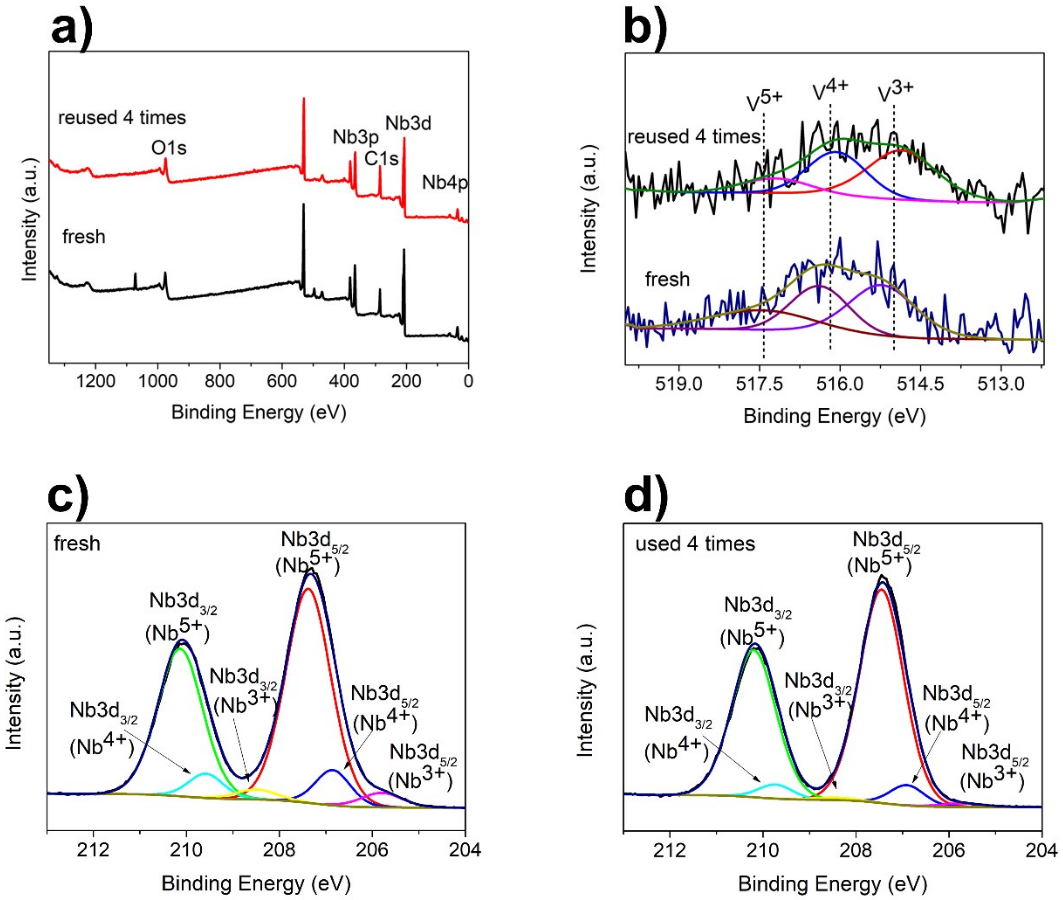

Fig. S9 a) XPS survey spectra of the fresh and recycled VO_x-NbO_y@C catalysts; b) high resolution V $2p_{3/2}$ XPS spectra of the fresh and recycled VO_x-NbO_y@C catalysts; c) high resolution Nb 3d XPS spectra of the fresh catalyst; d) high resolution Nb 3d XPS spectra of the recycled catalyst.

Table S4. Comparison of the aerobic oxidative dehydrogenation of N-heterocycles of reported catalysts.

Catalyst	T (ºC)	Time (h)	P_{O2} (MPa)	Solvent	Yield(%) [X Substrates]	Refs.
VO_X-NbO_y@C	120	16	0.5	H_2O+ DMSO	53.9～93.6% [12 Substrates]	This work
FeOx@NGr-C	100	12	1.5 MPa (Air)	heptane	51～89% [23 Substrates]	1
Ni_2Mn-LDH	120	2.5-9	0.1	mesitylene	31～93% [24 Substrates]	2
manganese oxide molecular sieve (OMS-2)	80	6	0.1	dimethyl carbonate	38～99% [29 Substrates]	3
Co@N-doped graphene shells	80	6	0.1	MeOH +K_2CO_3	76～98% [5 Substrates]	4
mesoporous manganese oxide	130	20	0.1	DMF	69～99% [8 Substrates]	5
Co NC/N-C catalyst	50	12	0.1 (Air)	MeOH	28.1～99.9% [12 Substrates]	6
palladium nanocatalyst stabilized by carbon metal covalent bonds	RT	18	TBHP (8eq)	H_2O	39～96% [17 Substrates]	7
polymaleimide	120	24	0.1	MeOH+H_2O	62～96% [23 Substrates]	8
boron carbon	RT	12	visible-	H_2O	41～95%	9

nitride (h-BCN)			light irradiation		[14 Substrates]	

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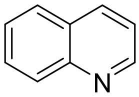
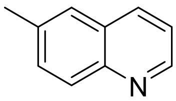
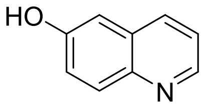
2. General Analysis Data for products.



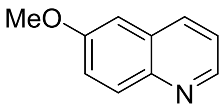
Quinoline, colorless oil. Yield (60.7 mg, 92.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, J = 4.2, 1.6 Hz, 1H), 8.17 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.76 – 7.67 (m, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.41 (dd, J = 8.3, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.55, 148.42, 136.25, 129.63, 129.59, 128.46, 127.94, 126.71, 121.24.



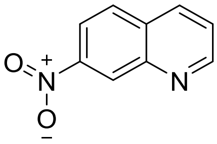
6-Methylquinoline, colorless oil. Yield (67 mg, 93.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 3.8 Hz, 1H), 8.03 (dd, J = 25.3, 8.4 Hz, 2H), 7.59 – 7.39 (m, 2H), 7.33 (dd, J = 21.9, 17.6 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.62, 146.98, 136.52, 135.52, 131.88, 129.18, 128.44, 126.70, 121.19, 21.69.



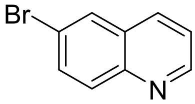
6-Hydroxyquinoline, white solid. Yield (49.4mg, 65.9%). ^{1}H NMR (400 MHz, DMSO) δ 9.99 (s, 1H), 8.65 (dd, J = 4.1, 1.5 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 9.1 Hz, 1H), 7.39 (dd, J = 8.3, 4.2 Hz, 1H), 7.31 (dd, J = 9.1, 2.7 Hz, 1H), 7.13 (d, J = 2.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 155.43, 147.10, 143.04, 134.09, 130.38, 129.28, 121.92, 121.37, 108.29.



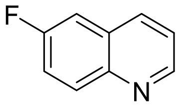
6-Methoxyquinoline, yellow oil. Yield (45.2 mg, 53.9%).^{1}H NMR (400 MHz, CDCl3) δ 8.77 (s, 1H), 8.02 (dd, J = 18.1, 8.7 Hz, 2H), 7.36 (t, J = 9.4 Hz, 2H), 7.07 (s, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 157.86, 148.08, 144.58, 134.90, 131.01, 129.44, 122.40, 121.50, 105.24, 77.48, 77.16, 76.84, 55.66.



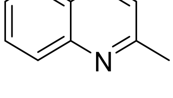
7-Nitroquinoline, yellow solid. Yield (76 mg, 87.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (dd, J = 4.1, 1.4 Hz, 1H), 9.02 (d, J = 2.0 Hz, 1H), 8.34 (dd, J = 9.0, 2.2 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 9.0 Hz, 1H), 7.60 (dd, J = 8.4, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.84, 148.28, 147.34, 136.06, 131.53, 129.62, 126.02, 124.07, 120.28.



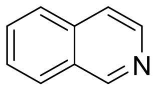
6-Bromoquinoline, colorless oil. Yield (82 mg, 78.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 3.5 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 8.02 – 7.90 (m, 2H), 7.78 (dd, J = 9.0, 2.0 Hz, 1H), 7.42 (dd, J = 8.3, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.85, 146.94, 135.19, 133.08, 131.33, 129.92, 129.48, 122.02, 120.59.



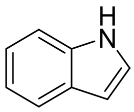
6-Fluoroquinoline, yellow oil. Yield (45.8mg, 61.9%). ^{1}H NMR (400 MHz, CDCl3) δ 8.89 (dd, J = 4.1, 1.3 Hz, 1H), 8.16 – 8.05 (m, 2H), 7.49 (ddd, J = 9.1, 8.4, 2.8 Hz, 1H), 7.43 (ddd, J = 6.5, 5.3, 3.5 Hz, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 161.78 (s), 159.32 (s), 149.85 (d, J = 2.8 Hz), 145.56 (s), 135.56 (d, J = 5.4 Hz), 132.15 (d, J = 9.2 Hz), 129.04 (d, J = 10.1 Hz), 121.93 (s), 119.91 (d, J = 25.8 Hz), 110.84 (d, J = 21.6 Hz).



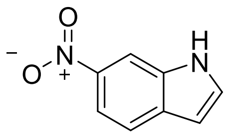
2-Methylquinoline, yellow oil. Yield (53.4mg, 74.2%). ^{1}H NMR (400 MHz, CDCl3) δ 8.04 (s, 1H), 7.79 (t, J = 9.5 Hz, 1H), 7.72 – 7.62 (m, 1H), 7.52 – 7.39 (m, 1H), 7.33 – 7.23 (m, 1H), 2.75 (s, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 159.15, 148.03, 136.31, 129.56, 128.79, 127.63, 126.64, 125.79 – 125.64, 122.15, 25.53.



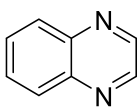
Isoquinoline, colorless oil. Yield (58 mg, 89.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.53 (d, J = 5.8 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.73 – 7.49 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.60, 143.06, 135.84, 130.41, 128.75, 127.69, 127.31, 126.53, 120.53.



Indole, colorless oil. Yield (36.4 mg, 62.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.19 (t, J = 6.5 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 6.56 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.93, 128.00, 124.23, 122.12, 120.87, 119.95, 111.14, 102.78.

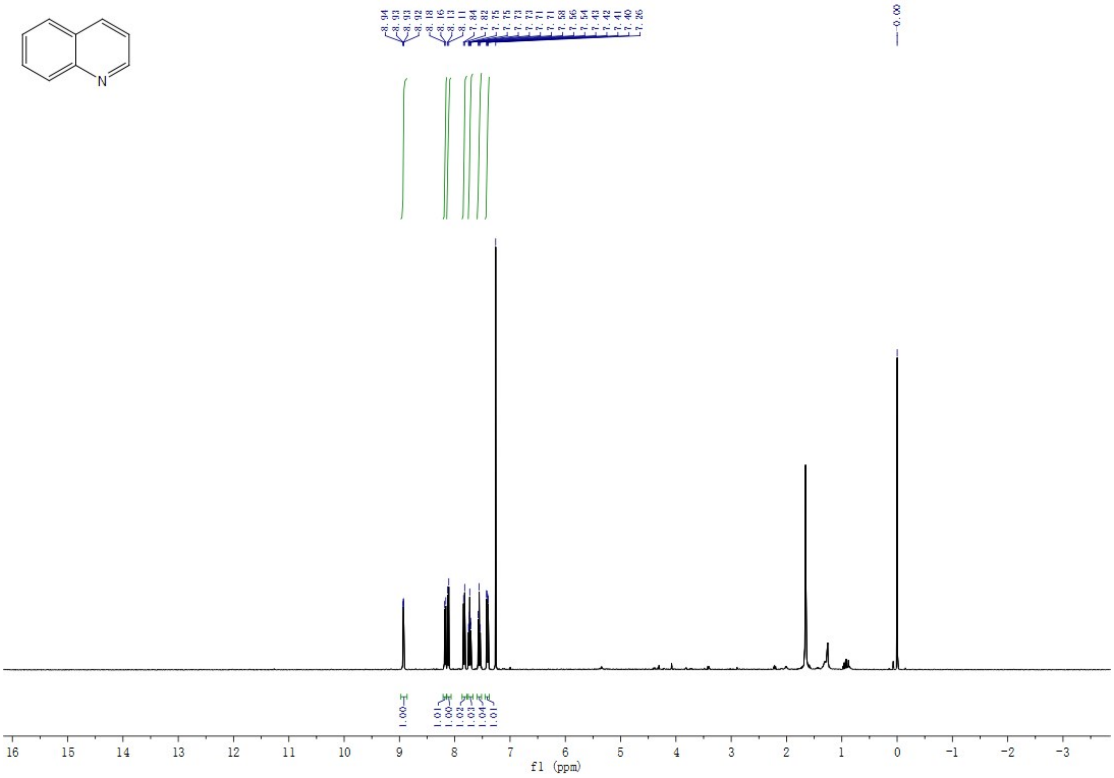


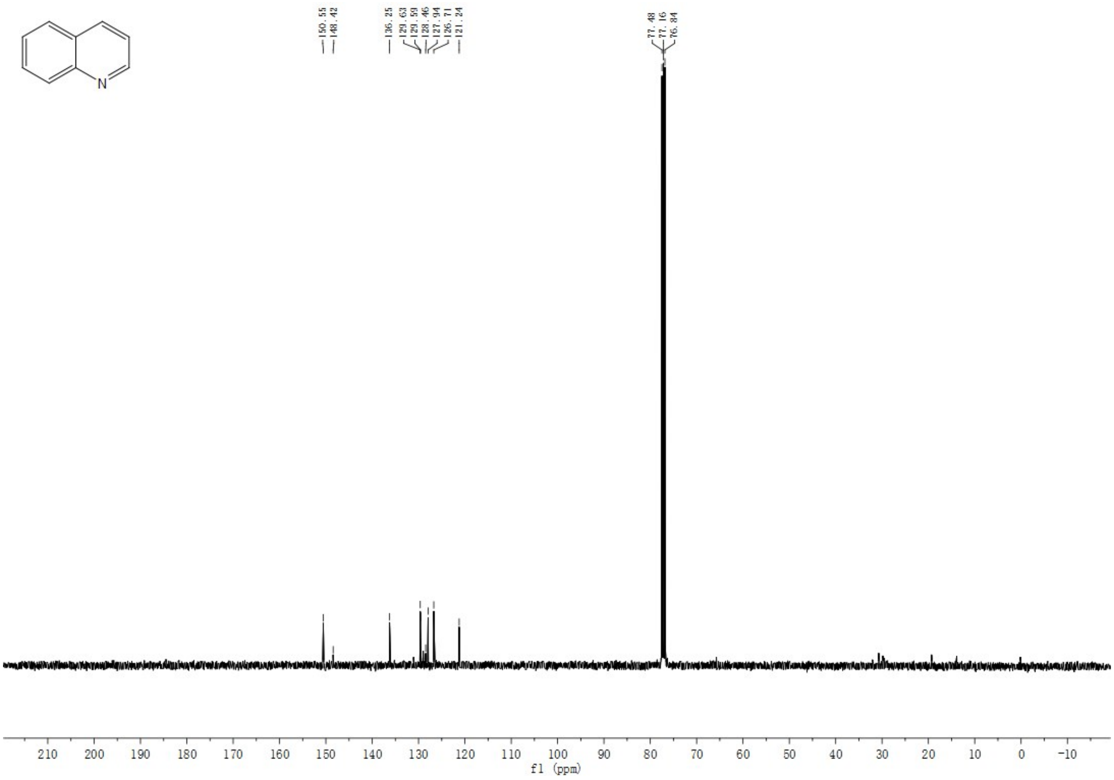
6-Nitroindole, yellow solid. Yield (70 mg, 86.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.39 (s, 1H), 8.04 (dd, J = 8.8, 1.9 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.51 (t, J = 2.7 Hz, 1H), 6.68 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.44, 134.41, 132.95, 130.20, 120.76, 115.53, 108.23, 103.75.

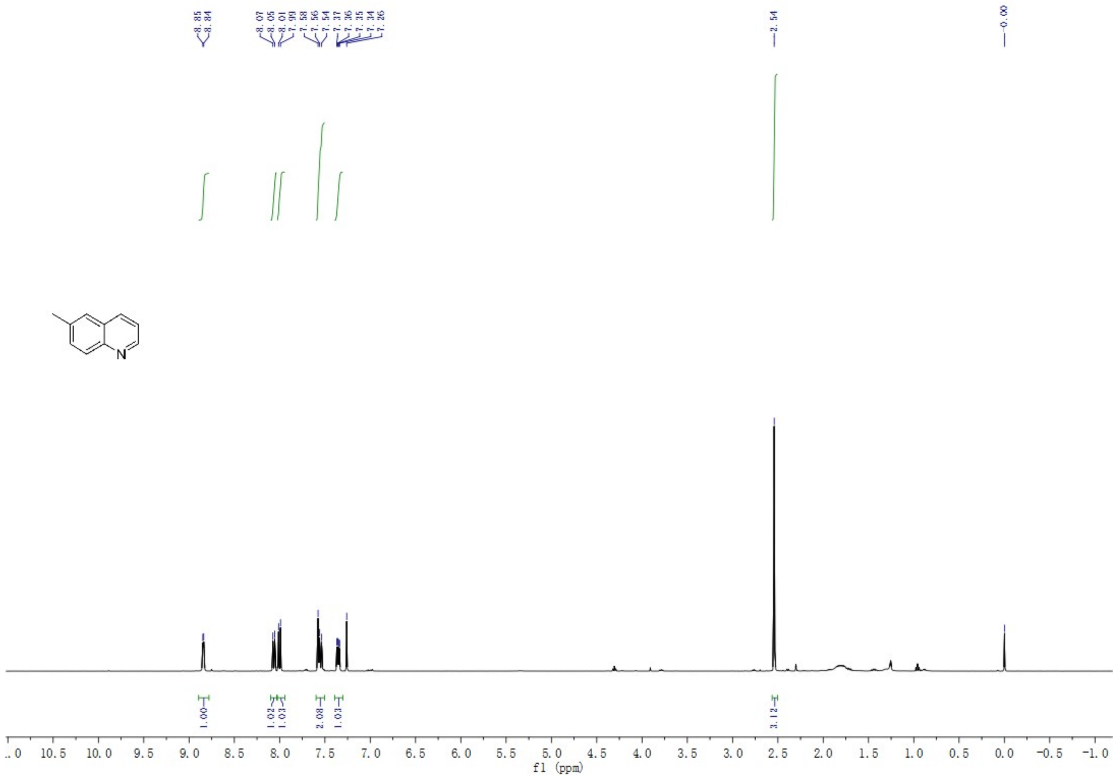


Quinoxaline, colorless oil. Yield (52 mg, 79.9%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 2H), 8.28 – 7.98 (m, 2H), 7.84 – 7.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.14, 143.22, 130.24, 129.68.

3. NMR Spectra



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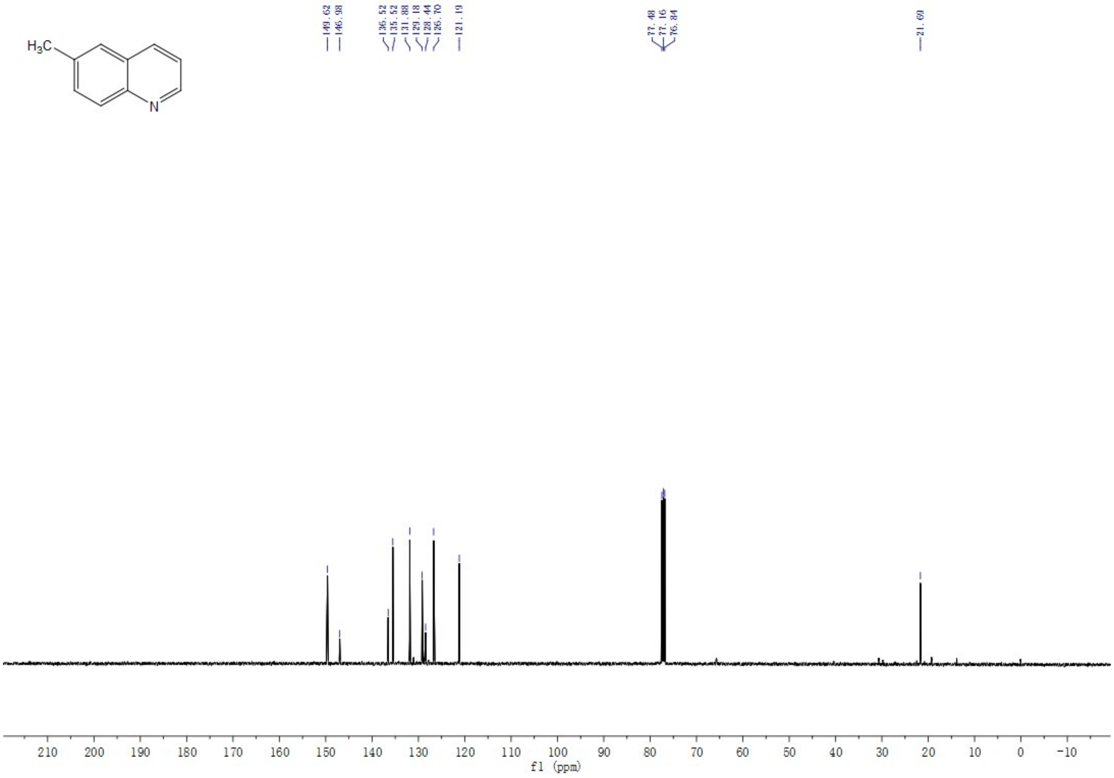
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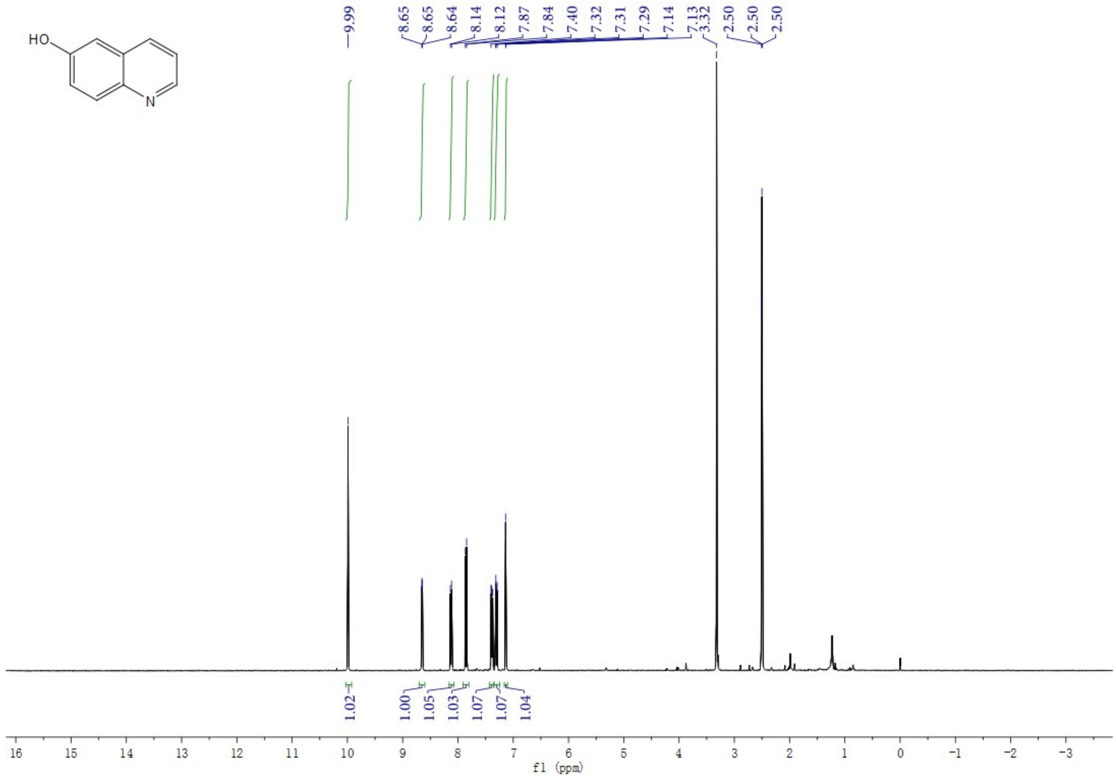
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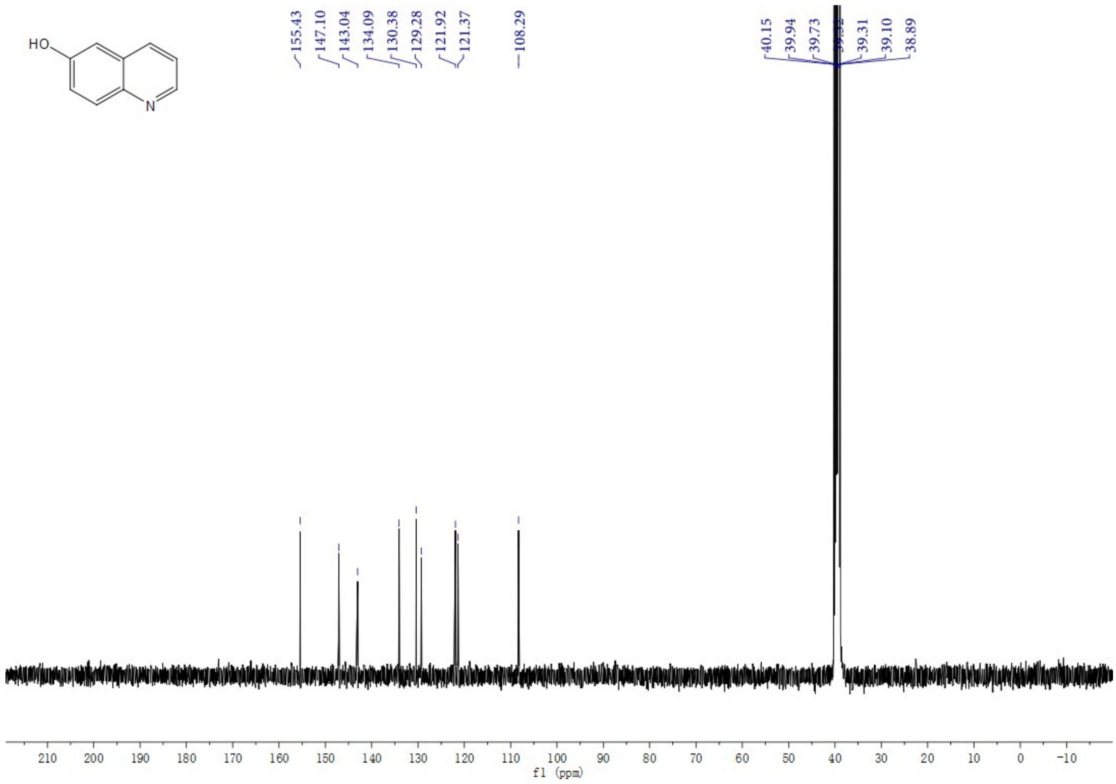
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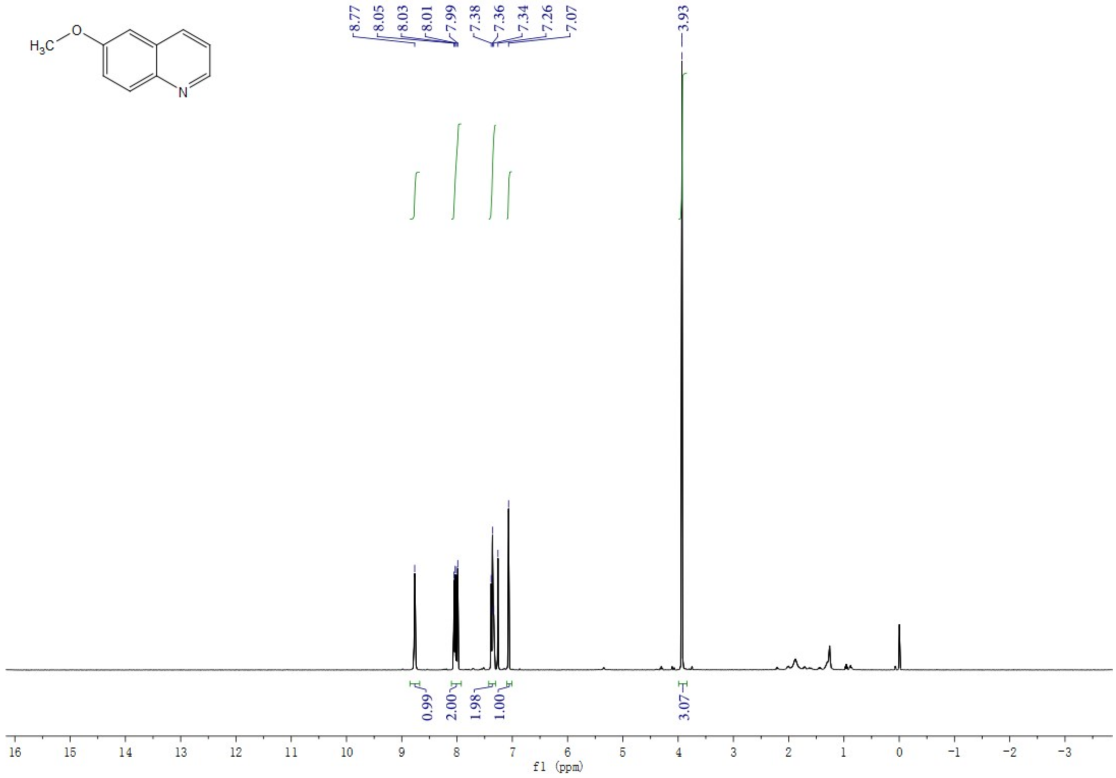
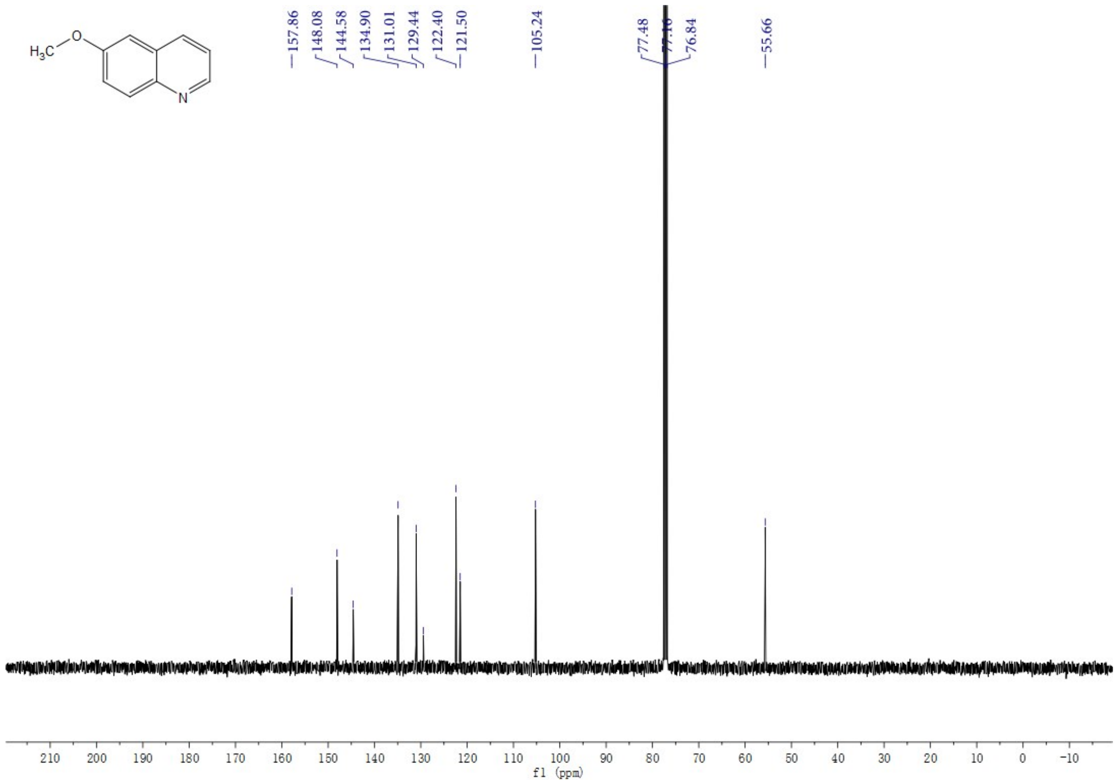
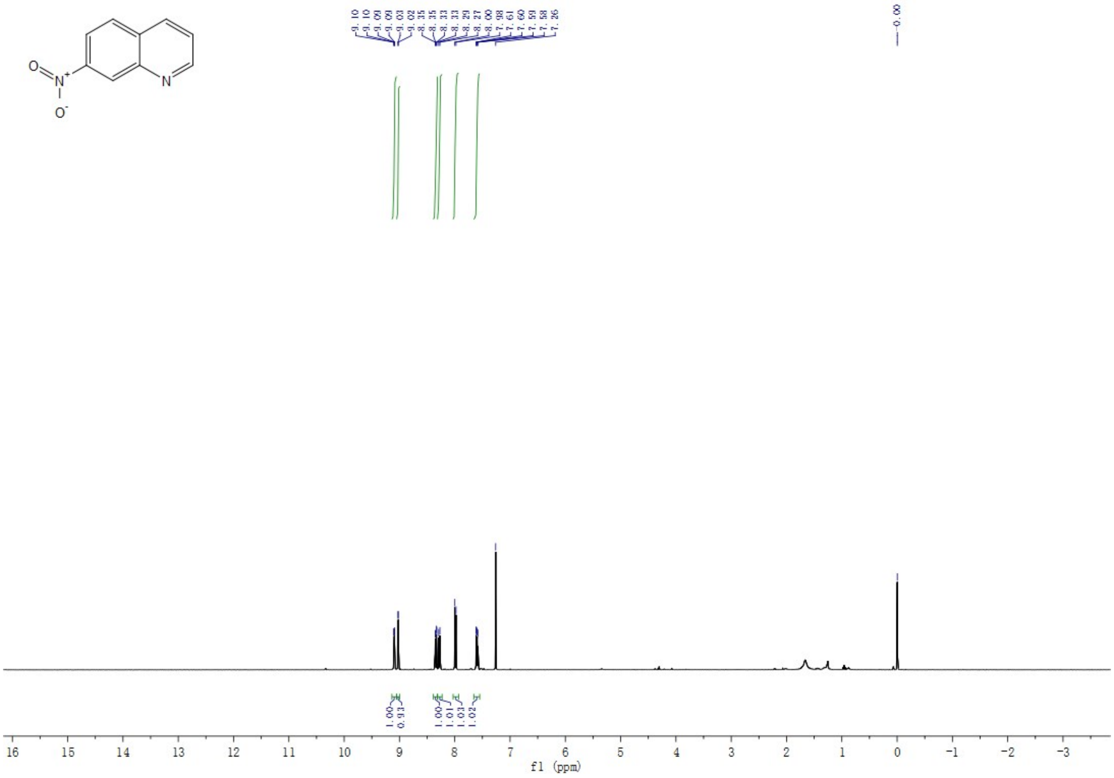
39.10
38.89
f1 (ppm)

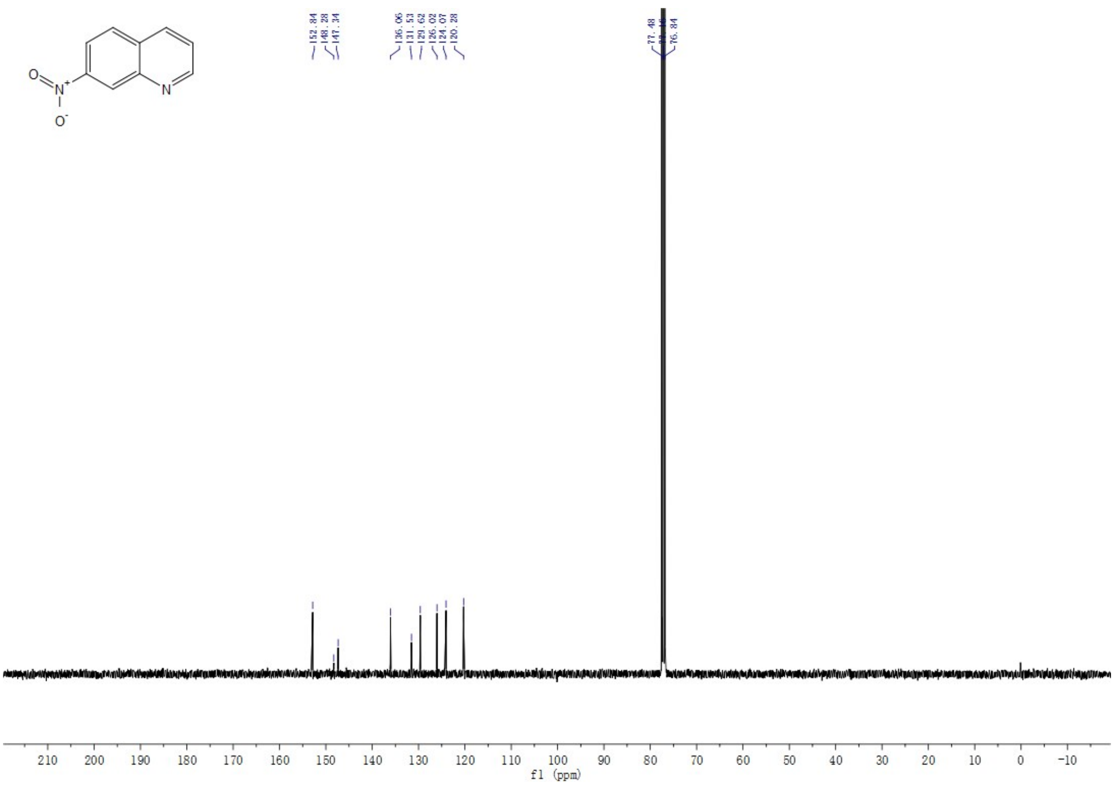


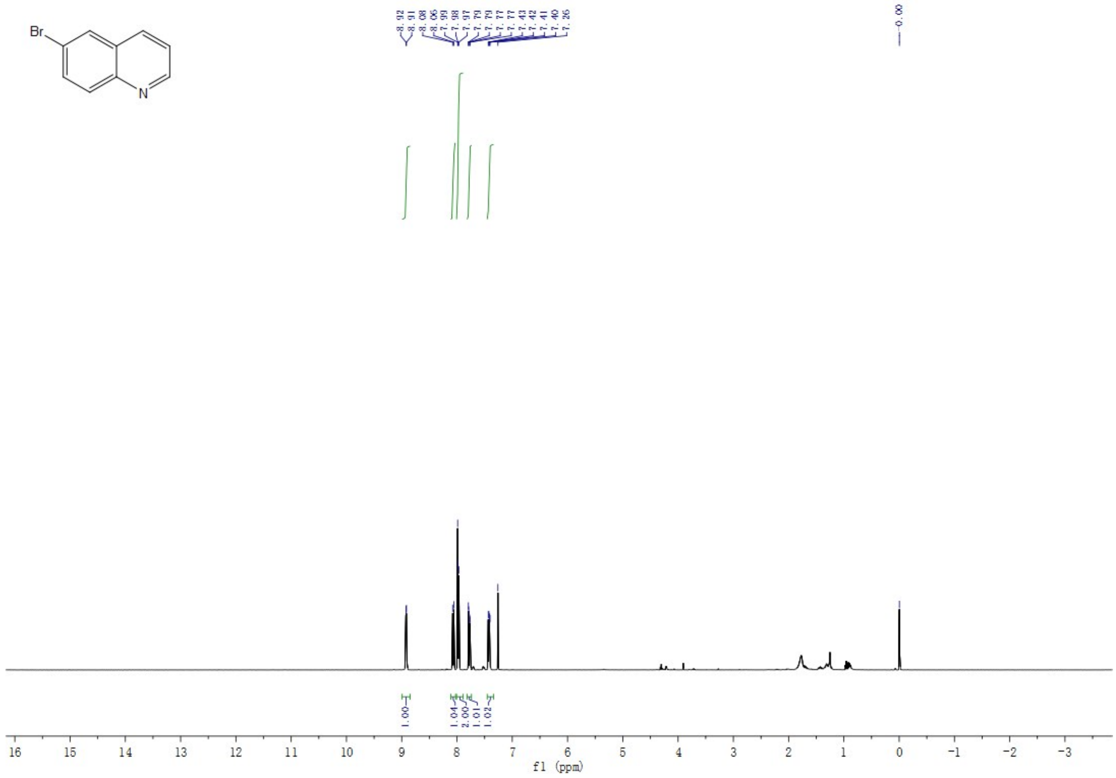
H3C
O
N
8.77
8.05
8.03
8.01
7.99
7.38
7.36
7.34
7.26
7.07
3.93
0.99
2.00
1.98
1.00
3.07
f1 (ppm)

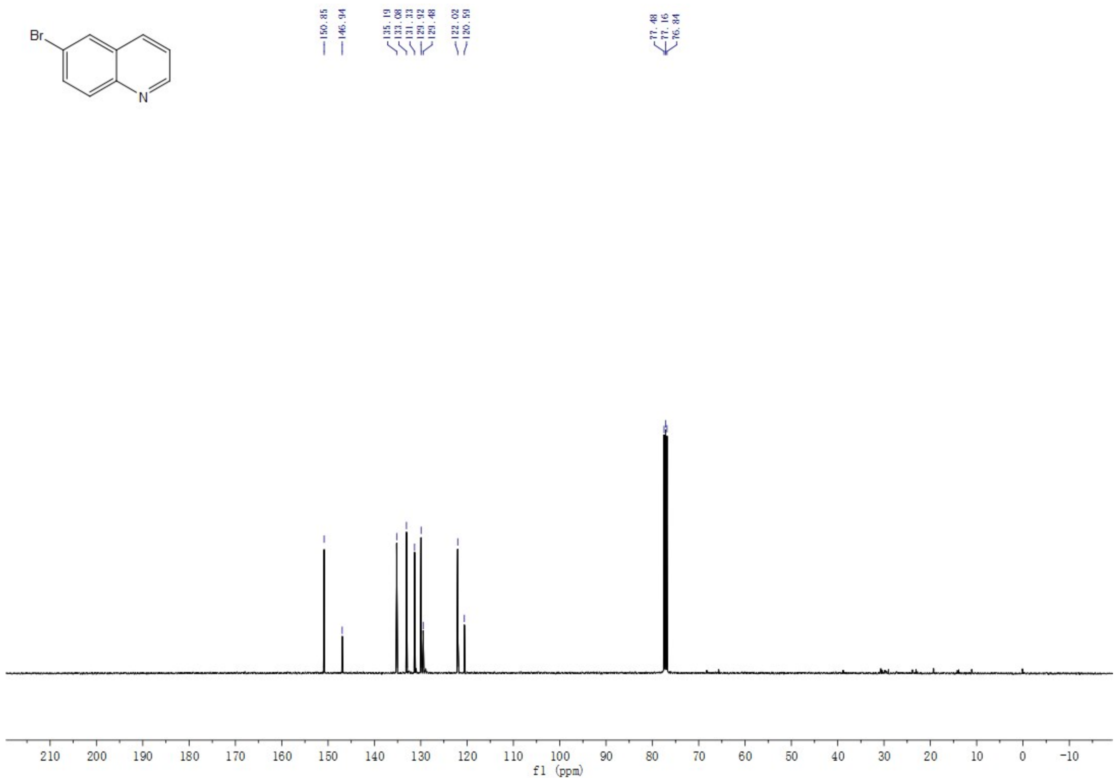


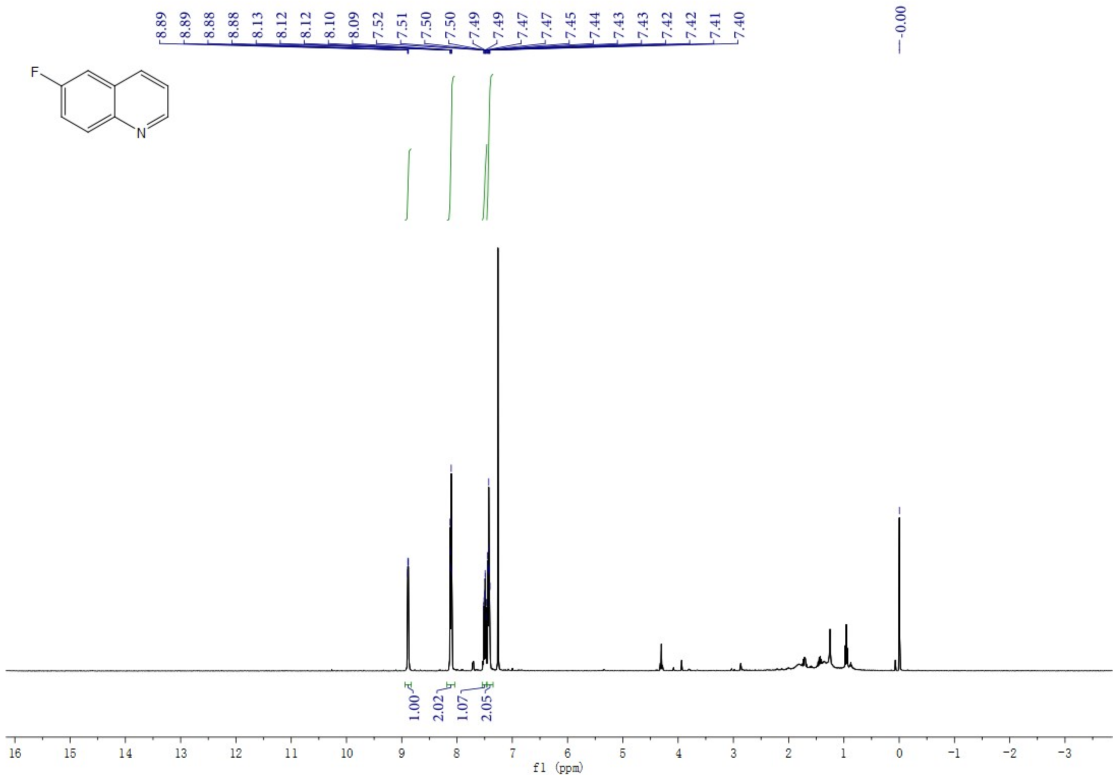
H3C
O
N
157.86
148.08
144.58
134.90
131.01
129.44
122.40
121.50
105.24
77.48
77.16
76.84
55.66
f1 (ppm)



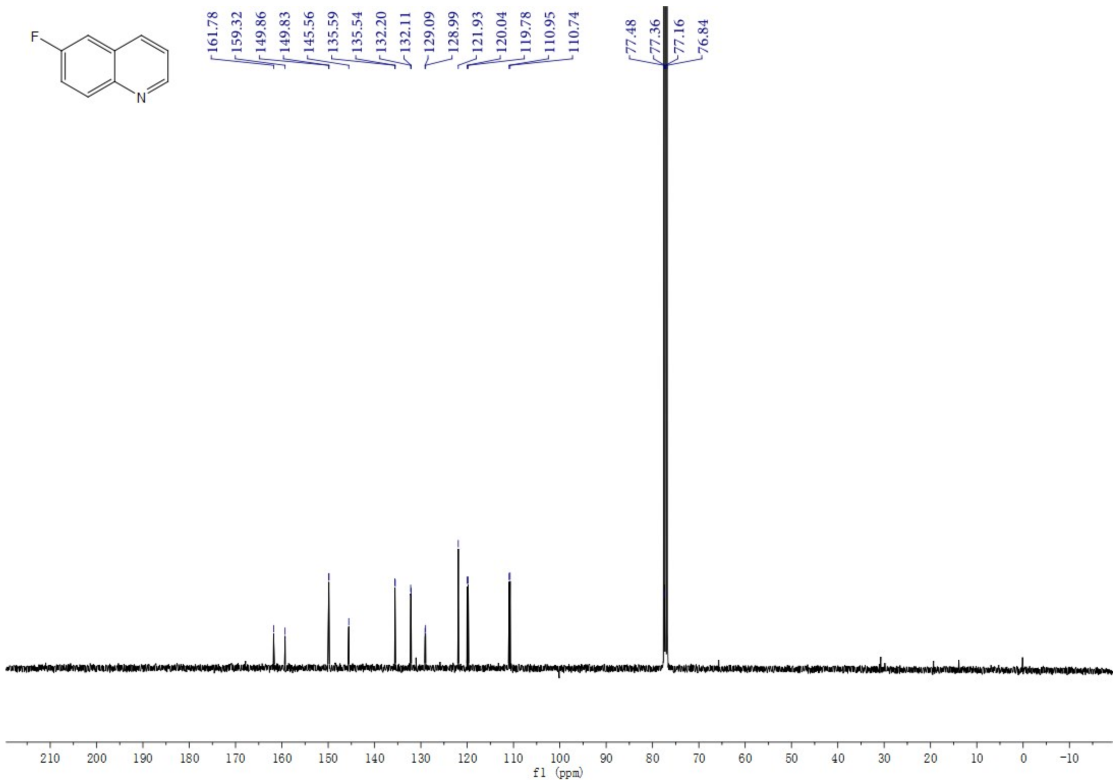



Br
N
8.92
8.91
8.08
8.06
7.99
7.98
7.97
7.79
7.79
7.77
7.43
7.42
7.41
7.40
7.26
0.00
1.00
1.04
2.00
1.01
1.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

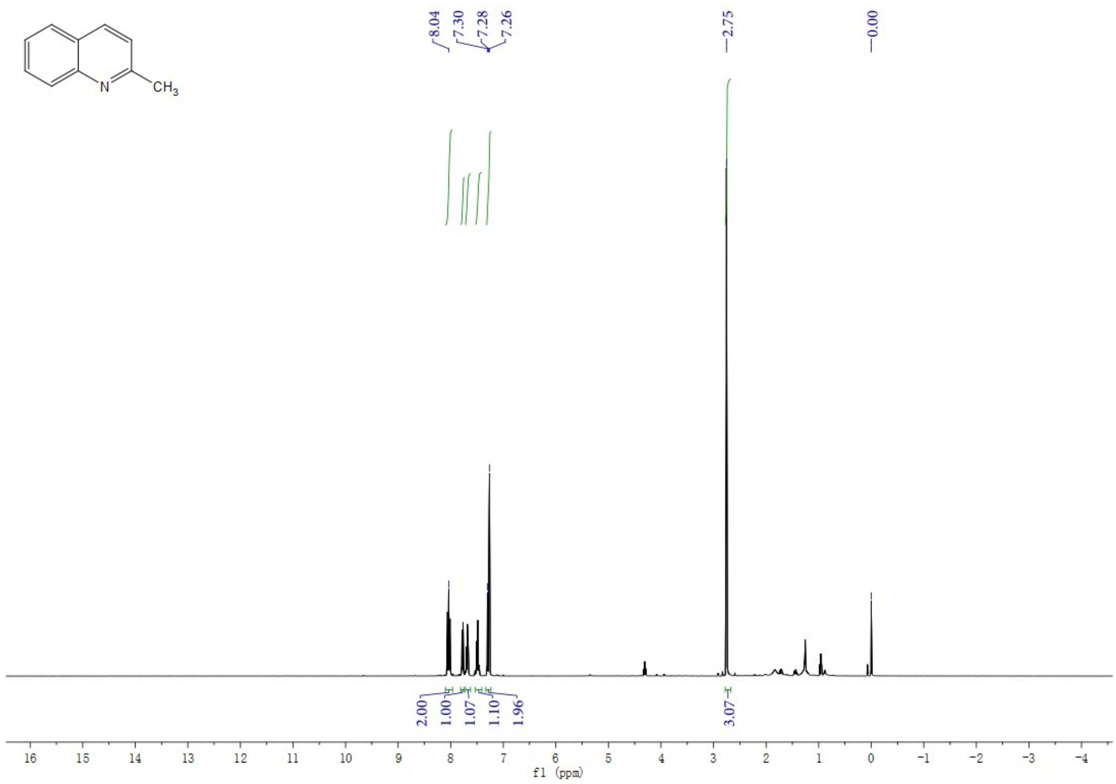

Br
N
150.85
146.94
135.19
133.08
131.33
129.92
129.48
122.02
120.59
77.48
77.16
76.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



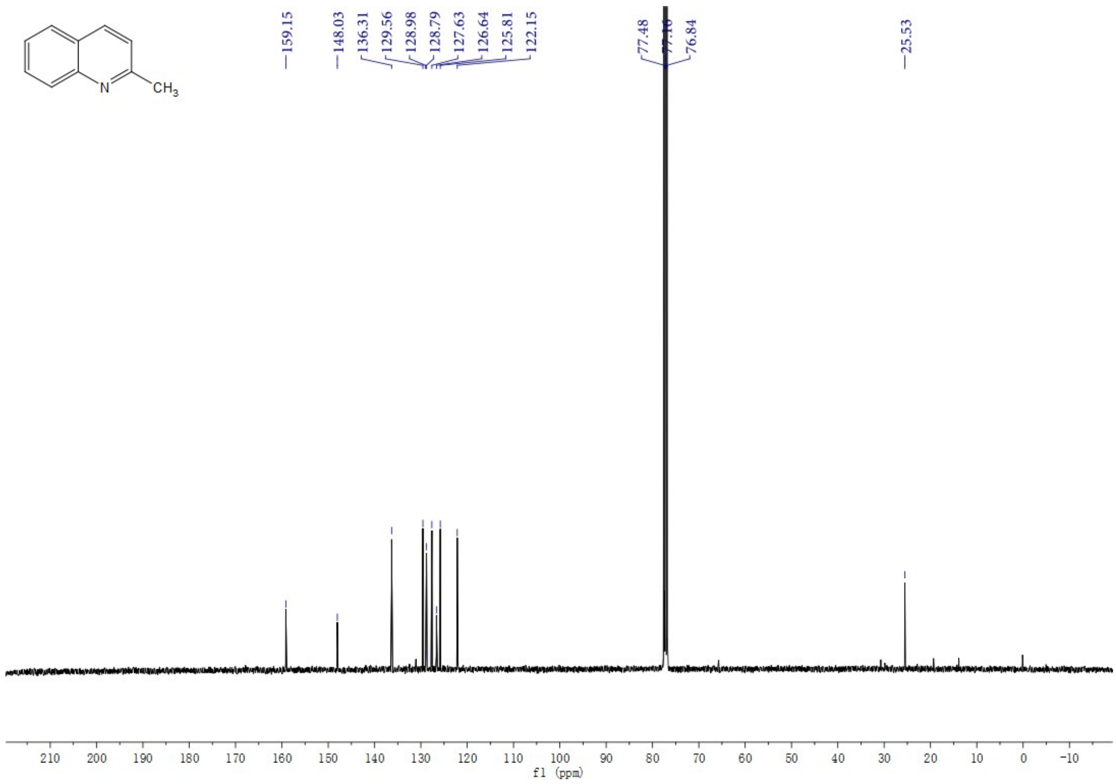
8.89
8.89
8.88
8.88
8.13
8.12
8.12
8.10
8.09
7.52
7.51
7.50
7.50
7.49
7.49
7.47
7.47
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.40
-0.00
F
N
1.00
2.02
1.07
2.05
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)



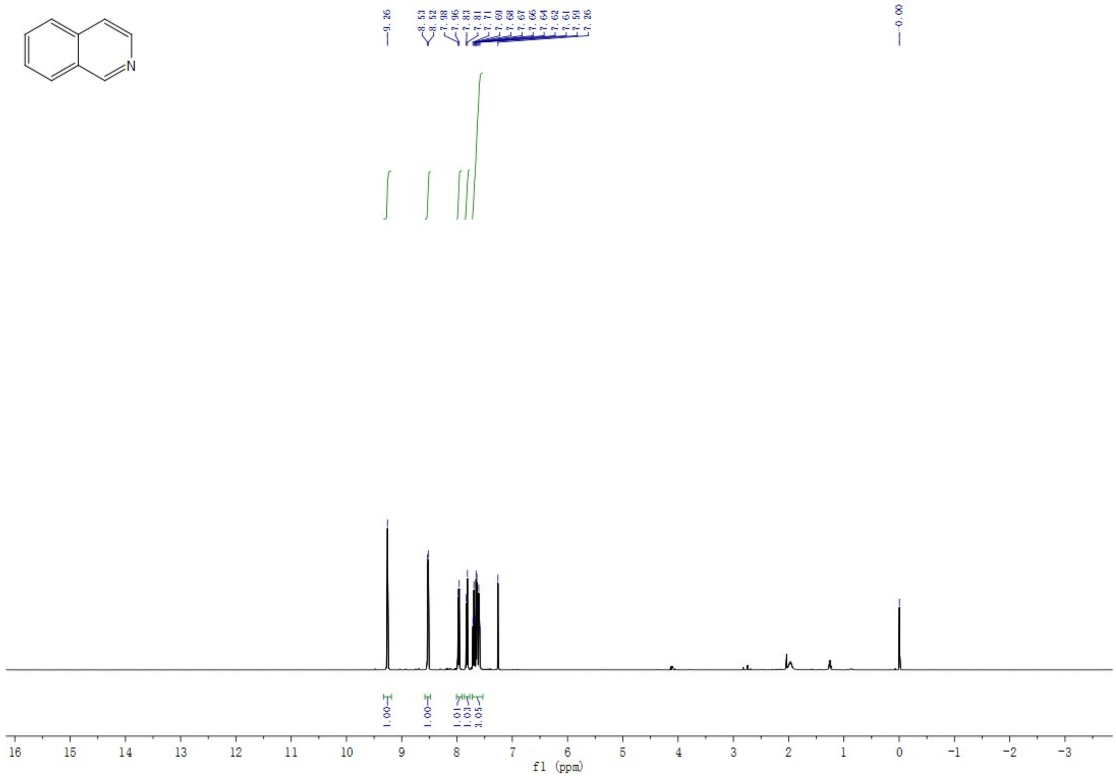
161.78
159.32
149.86
149.83
145.56
135.59
135.54
132.20
132.11
129.09
128.99
121.93
120.04
119.78
110.95
110.74
77.48
77.36
77.16
76.84
F
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

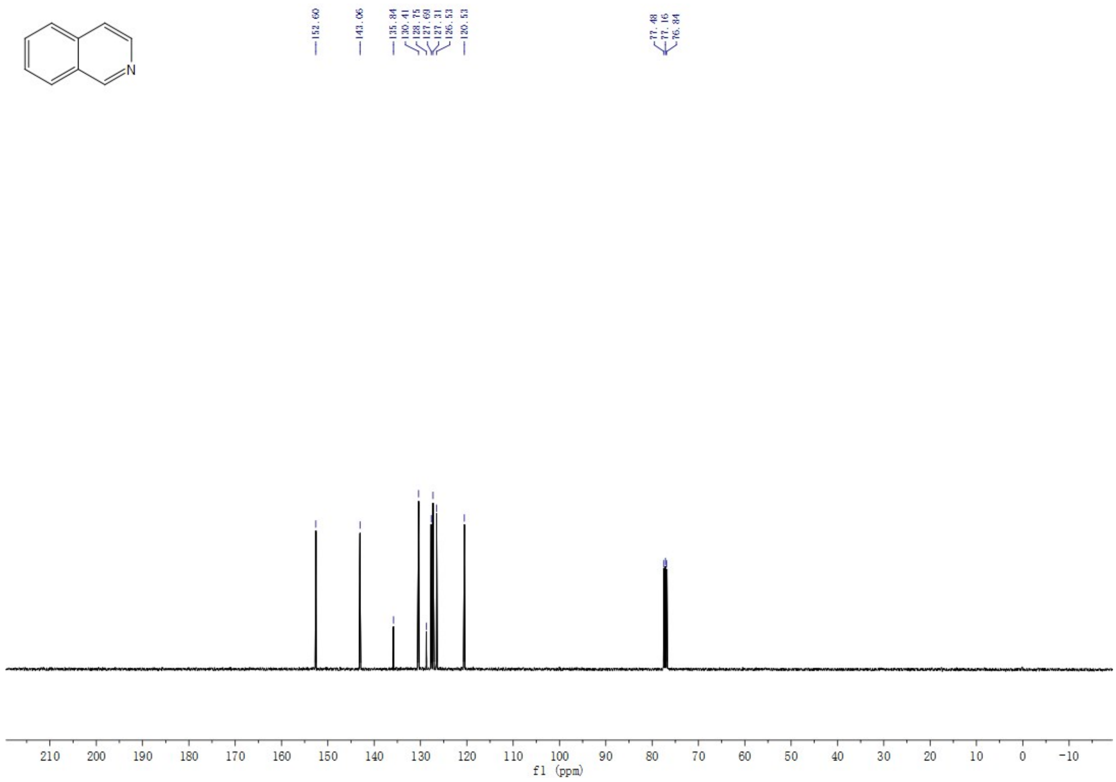


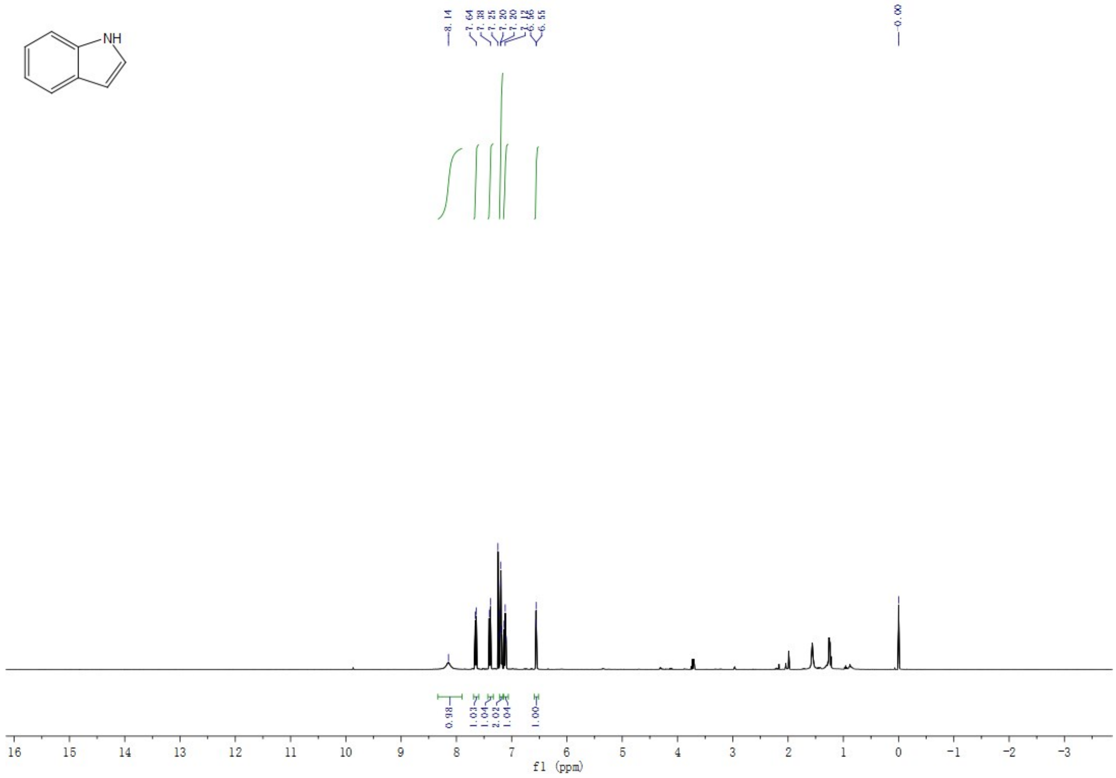
N
CH3
8.04
7.30
7.28
7.26
2.75
0.00
2.00
1.00
1.07
1.10
1.96
3.07
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

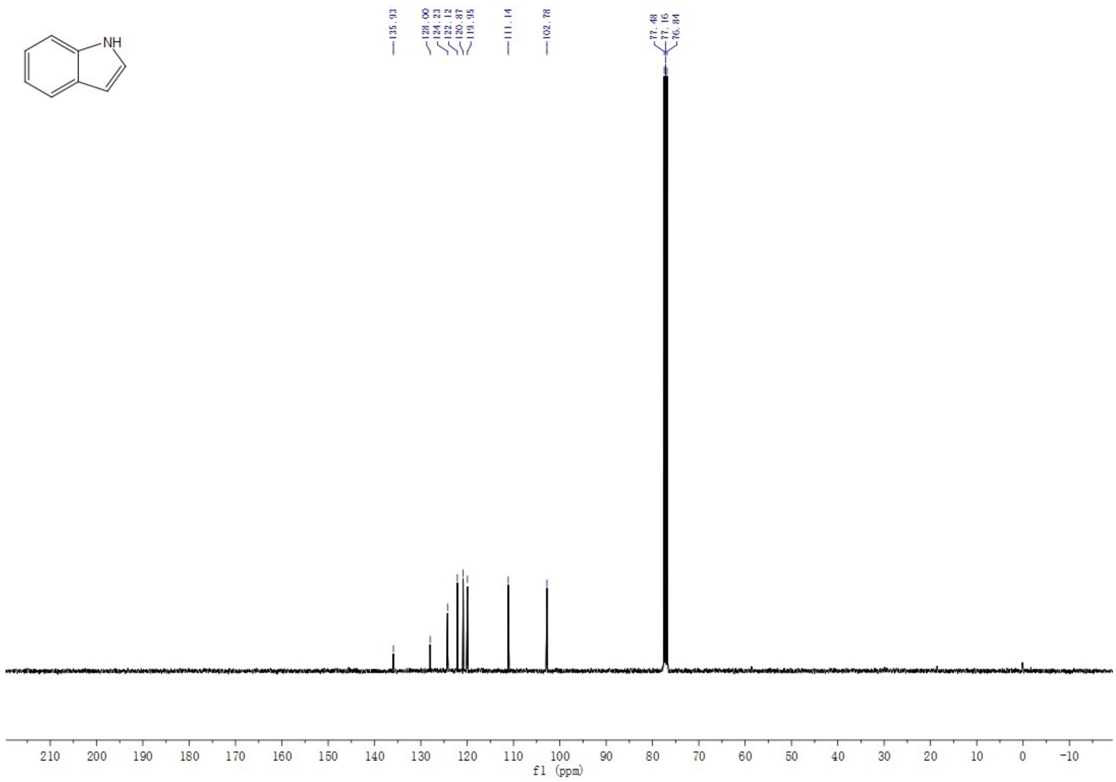


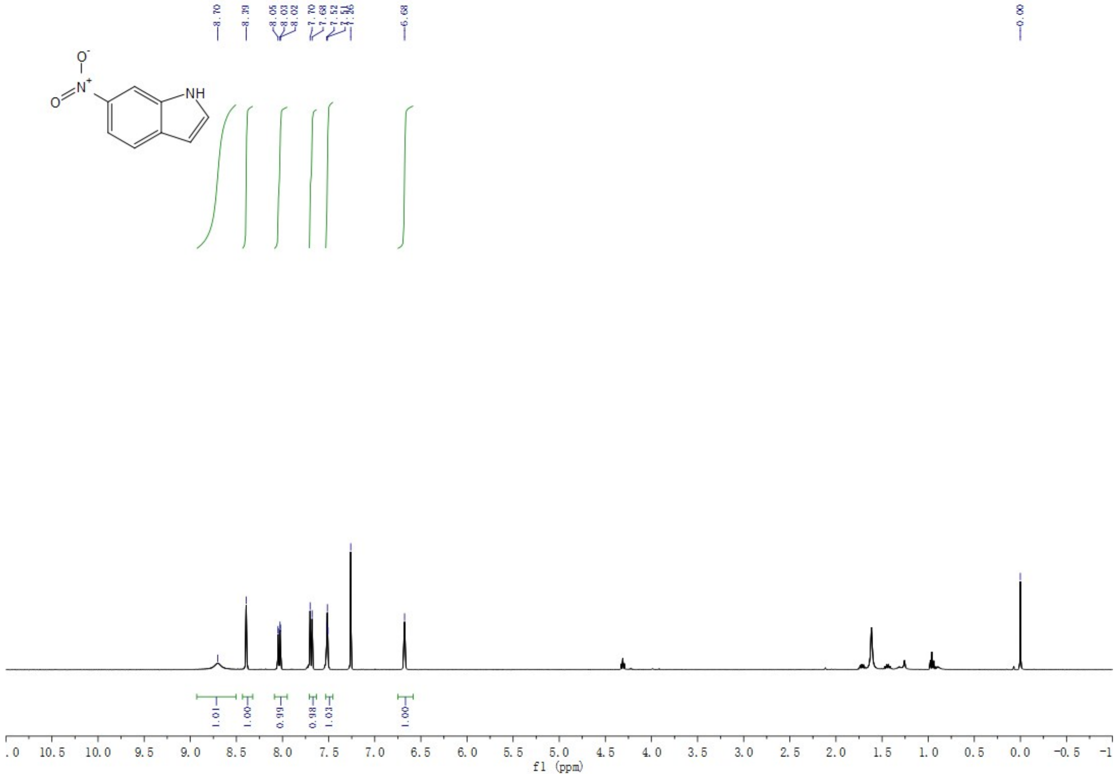
N
CH3
159.15
148.03
136.31
129.56
128.98
128.79
127.63
126.64
125.81
122.15
77.48
77.16
76.84
25.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
9.26
8.53
8.52
7.98
7.96
7.83
7.81
7.71
7.69
7.68
7.67
7.66
7.64
7.62
7.61
7.59
7.26
0.00
1.00
1.00
1.01
1.03
3.05
f1 (ppm)

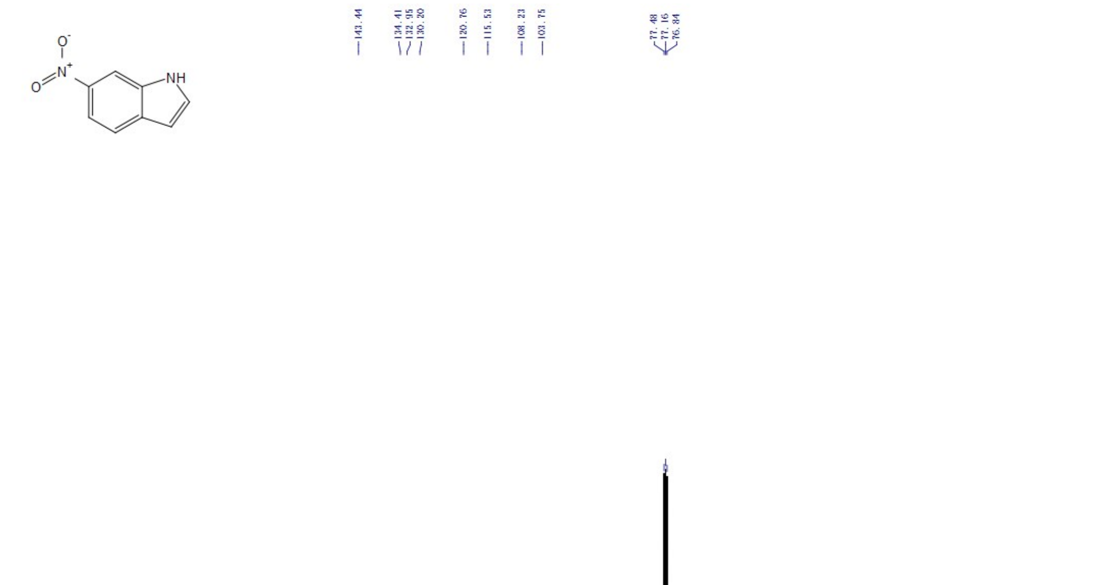

N
152.60
143.06
135.84
130.41
128.75
127.69
127.31
126.53
120.53
77.48
77.16
76.84
f1 (ppm)


NH
8.14
7.64
7.38
7.25
7.20
7.20
7.12
6.56
6.55
0.00
0.98
1.03
1.04
2.02
1.04
1.00
f1 (ppm)

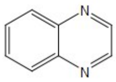

NH
135.93
128.00
124.23
122.12
120.87
119.95
111.14
102.78
77.48
77.16
76.84
f1 (ppm)

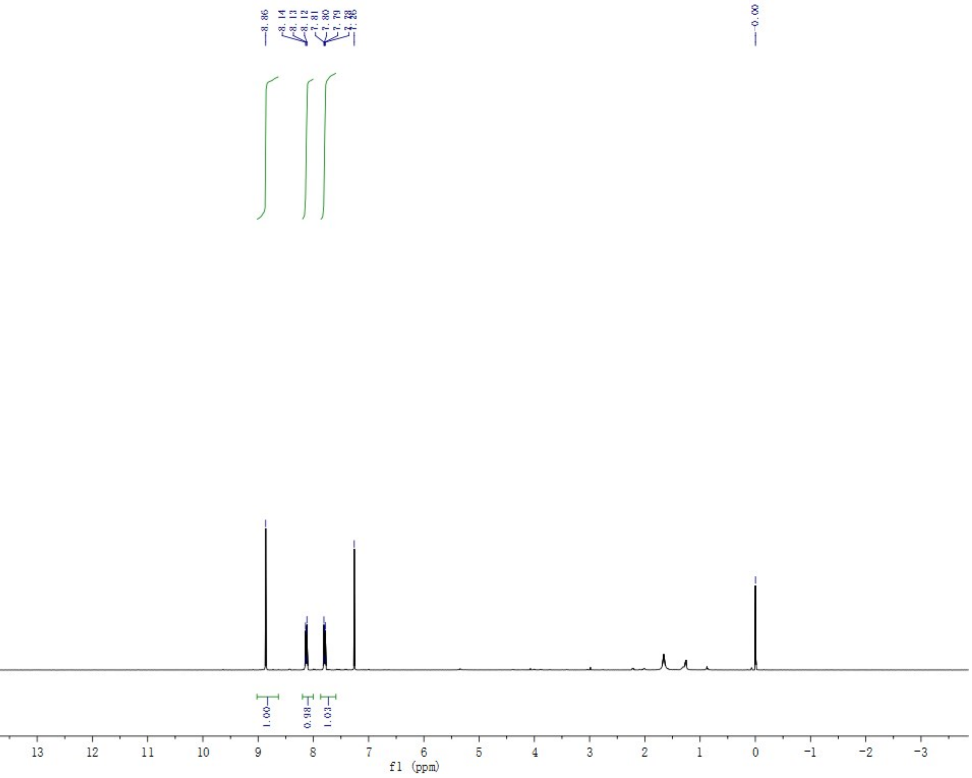


8.70
8.39
8.05
8.03
8.02
7.70
7.68
7.52
7.51
7.26
6.68
0.00
1.01
1.00
0.99
0.98
1.03
1.00
f1 (ppm)

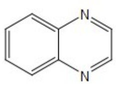


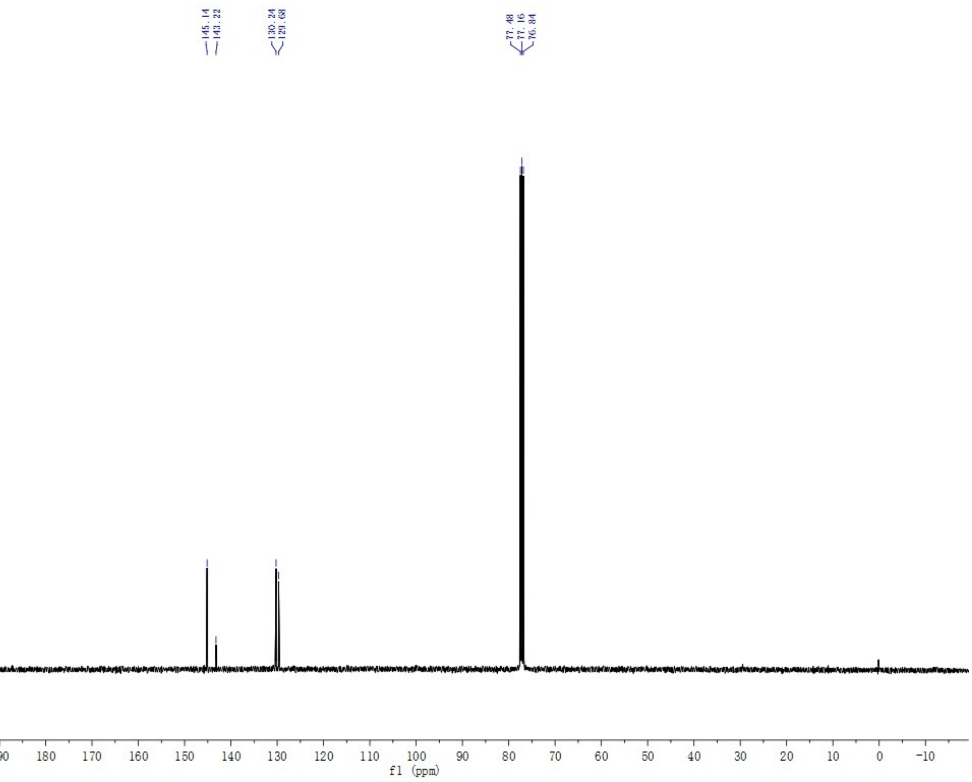
143.44
134.41
132.95
130.20
120.76
115.53
108.23
103.75
77.48
77.16
76.84
f1 (ppm)





8.86
8.14
8.13
8.12
7.81
7.80
7.79
7.28
7.26
0.00
1.00
0.98
1.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)





145.14
143.22
130.24
129.68
77.48
77.16
76.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)