Supporting information

Efficient hydrogenation of imines over Fe and ZnO powder in self-neutralization acidic CO_2/H_2O system

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Contents Table

1. Table S1.

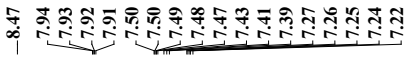
Table S1 Optimization the amount of Fe and ZnO [a]

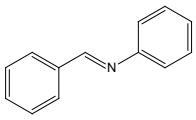
Entry	Fe (equiv.)	ZnO (equiv.)	Conv. (%)	Yield[b] (%)
1	1	1	33	2
1	4	0	34.1	22.2
2	4	2	71.9	44.3
3	4	4	74	51
4	2	4	32.9	21.9

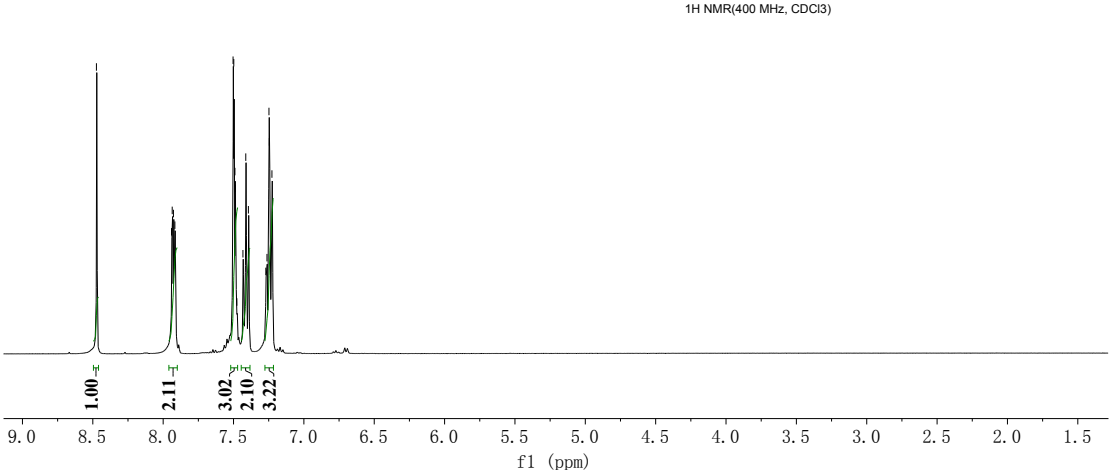
[a] Reaction conditions: N-benzylideneaniline (1 mmol, 181.2 mg), H_2O (3 mL), 80 °C, 10 h, 750 r/min. [b] Determined by GC with biphenyl as the internal standard.

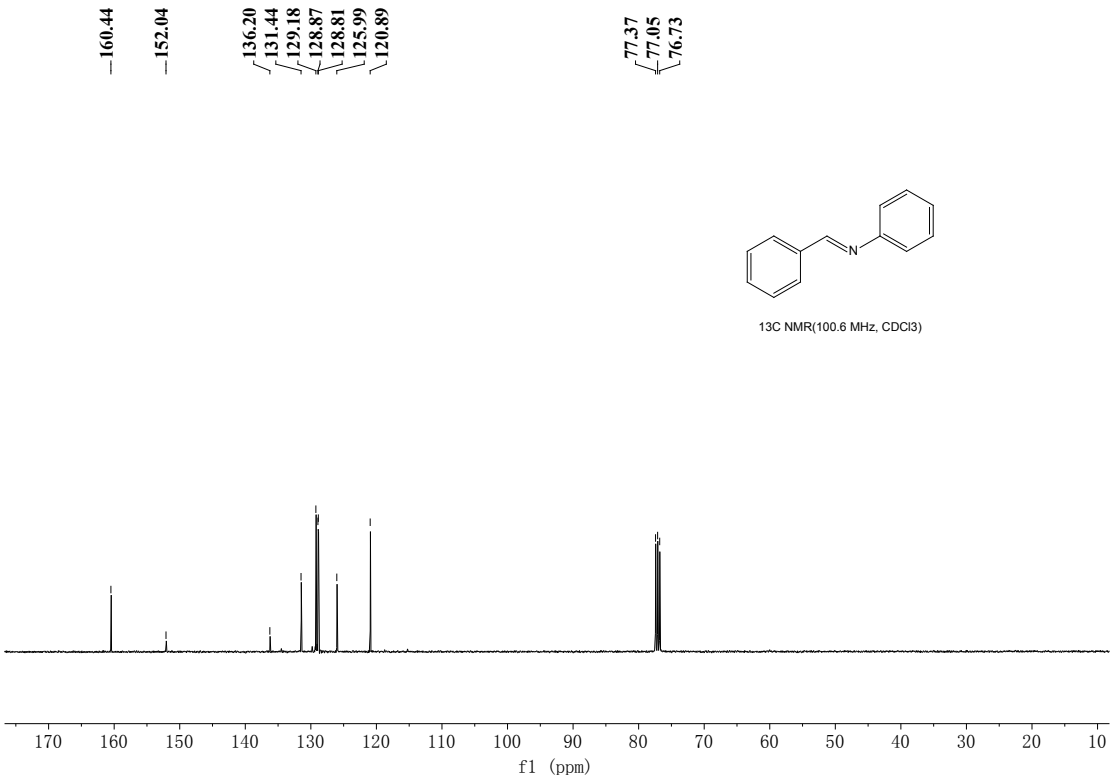
2. Analytic data and NMR spectra of the substrate

N-benzylideneaniline.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (s, 1H), 7.93 (dd, J = 6.5, 3.0 Hz, 2H), 7.52 – 7.47 (m, 3H), 7.41 (t, J = 7.8 Hz, 2H), 7.27 – 7.21 (m, 3H).^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 160.44, 152.04, 136.20, 131.44, 129.18, 128.87, 128.81, 125.99, 120.89.

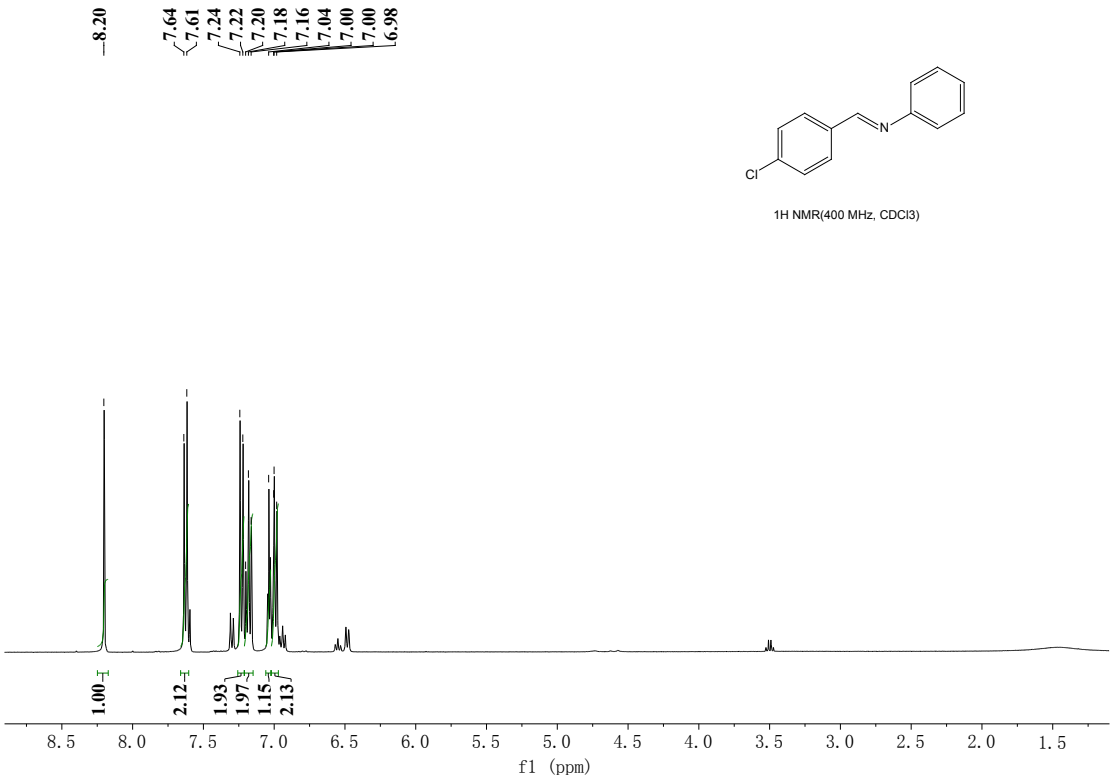


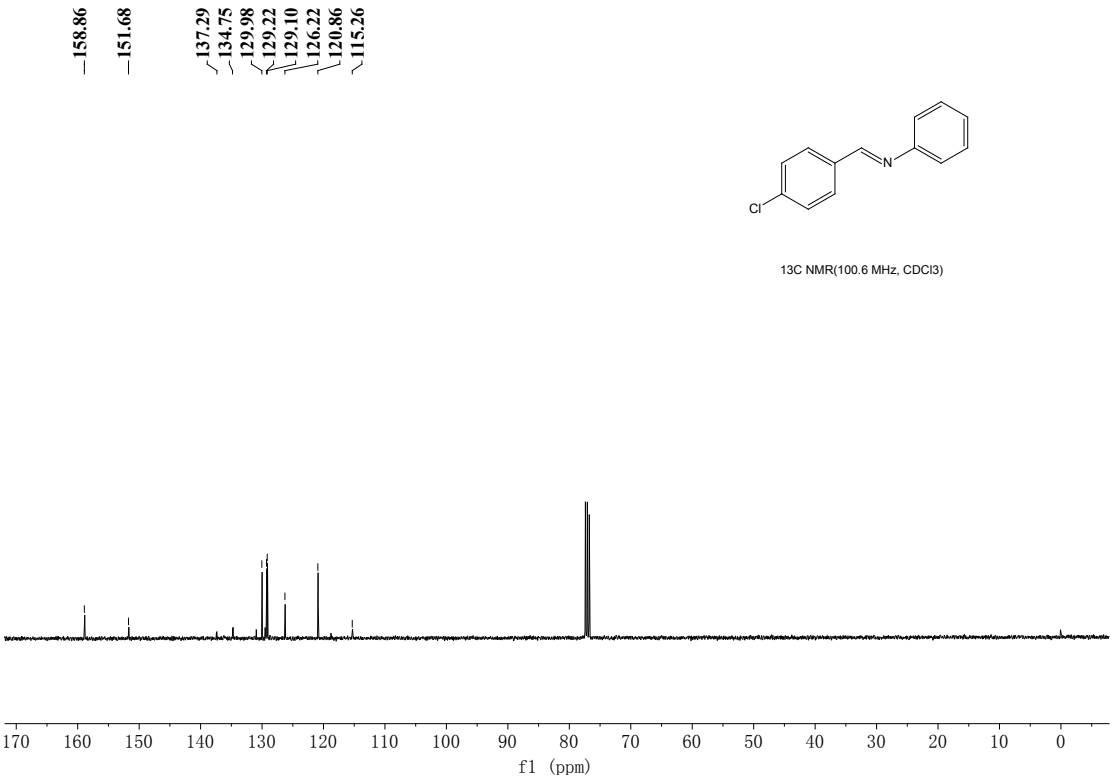




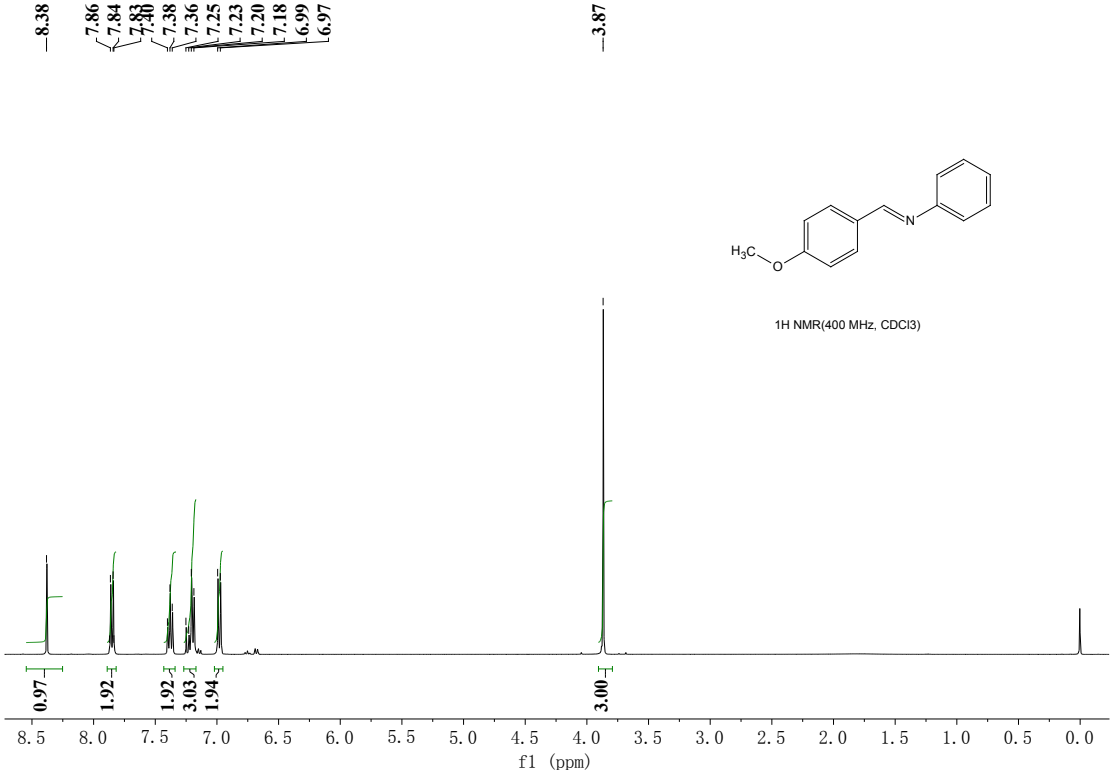


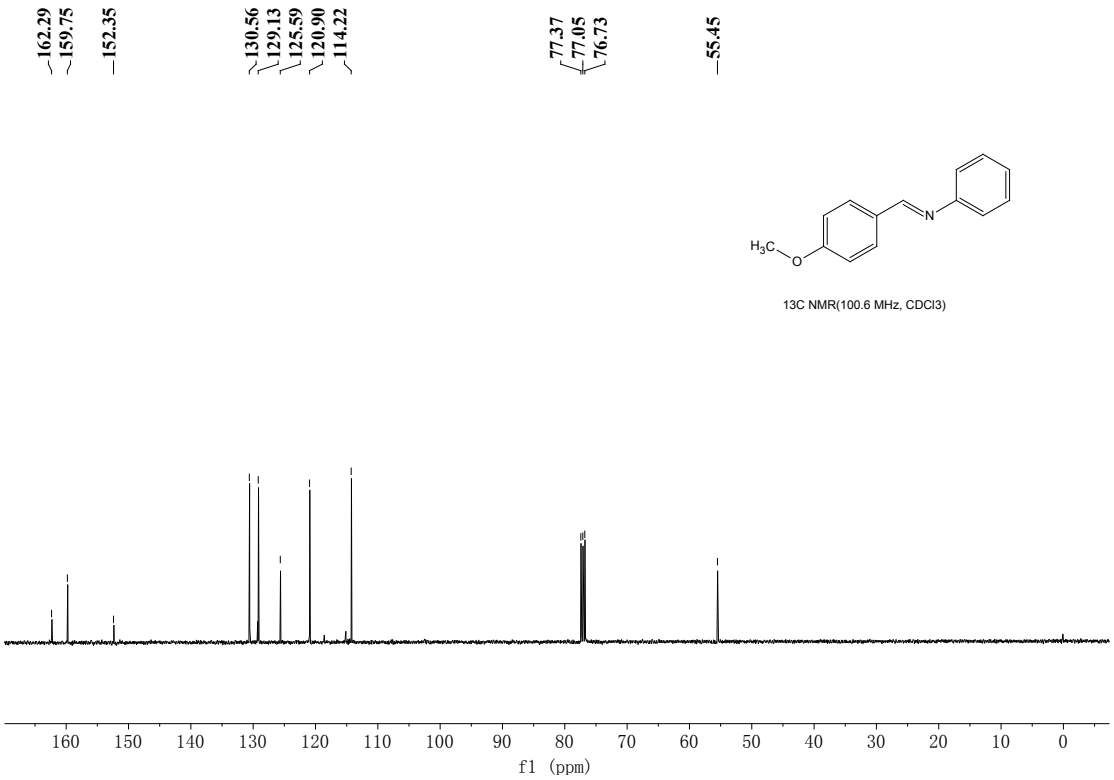
N-(4-chlorobenzylidene)aniline:[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (s, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 7.18 (t, J = 7.8 Hz, 2H), 7.04 (t, J = 3.7 Hz, 1H), 7.01 – 6.97 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 158.86, 151.68, 137.29, 134.75, 129.98, 129.22, 129.10, 126.22, 120.86, 115.26.



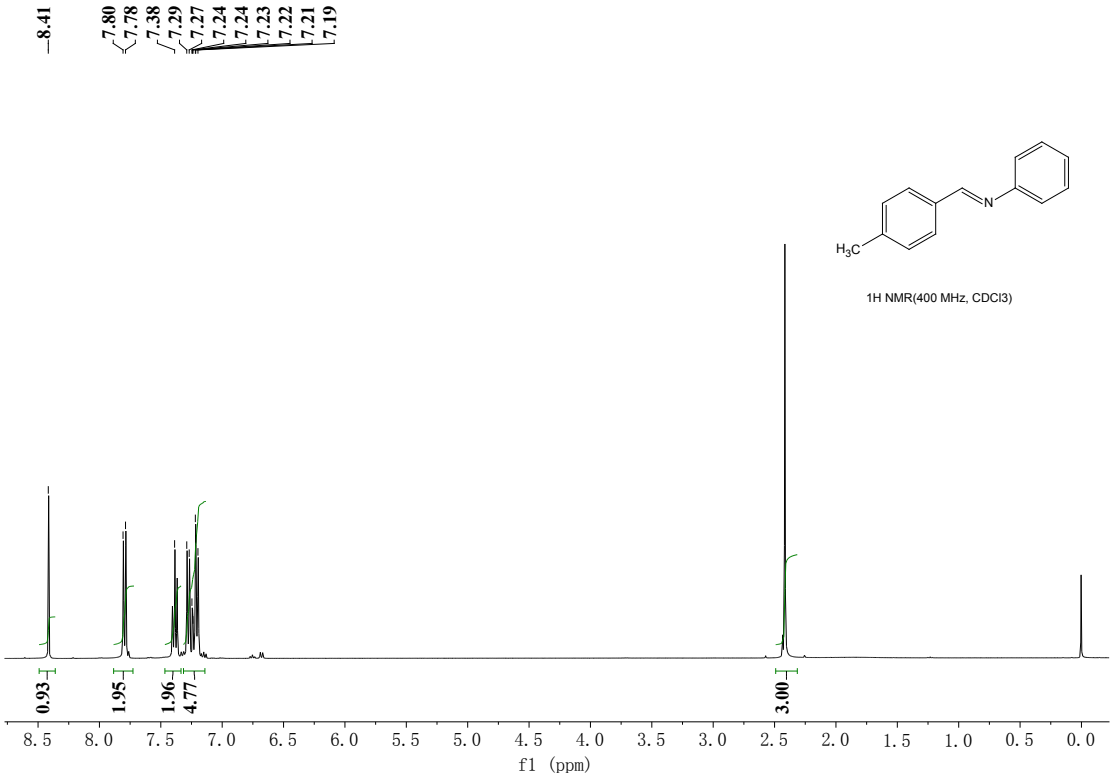


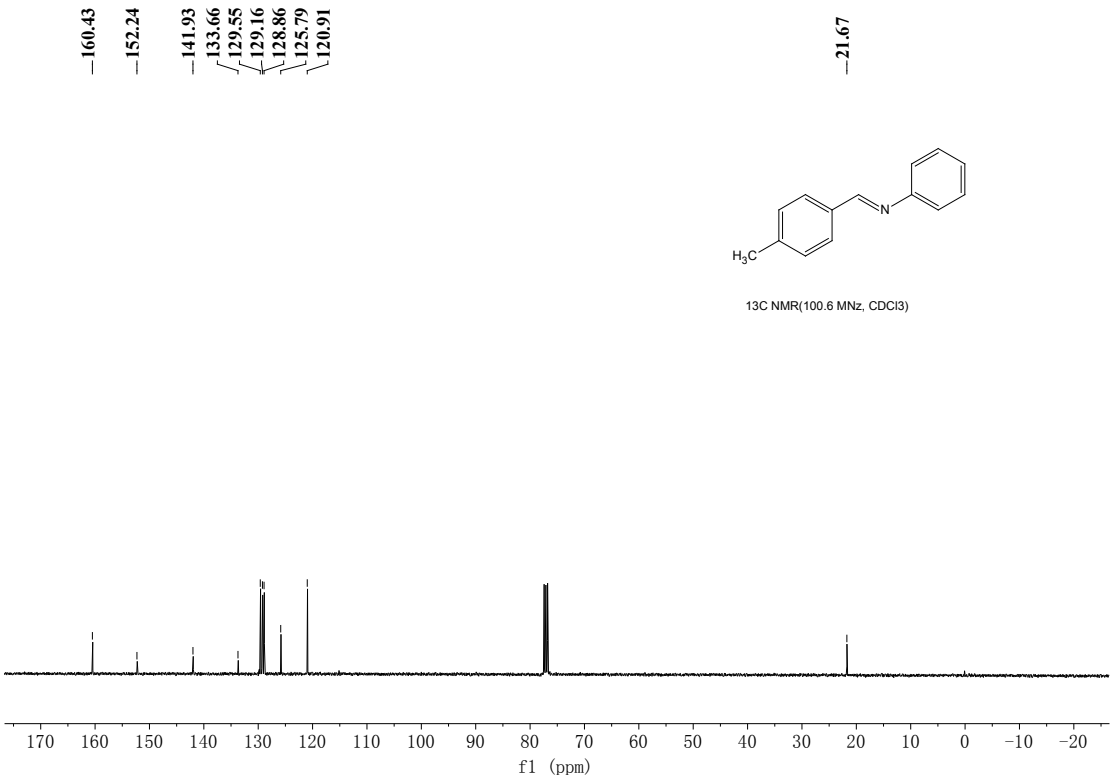
N-(4-methoxybenzylidene)aniline:[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38 (s, 1H), 7.93 – 7.78 (m, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.22 (dd, *J* = 17.1, 8.8 Hz, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H).^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 162.29, 159.75, 152.35, 130.56, 129.13, 125.59, 120.90, 114.22, 55.45.



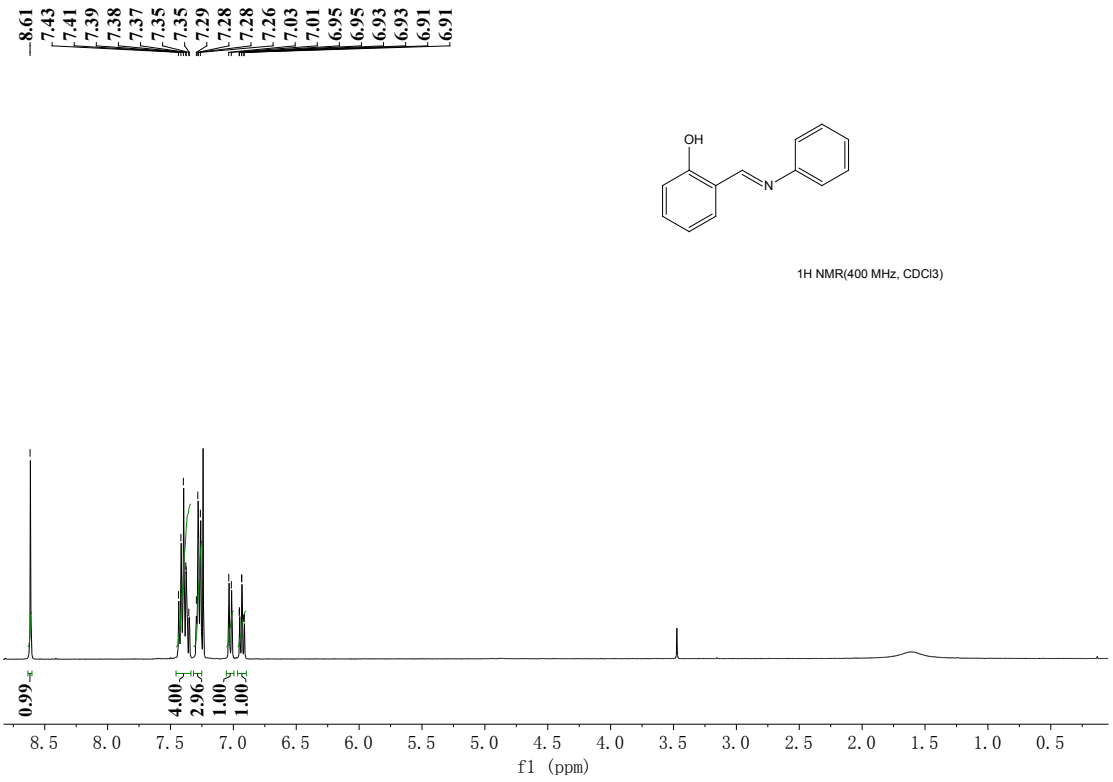


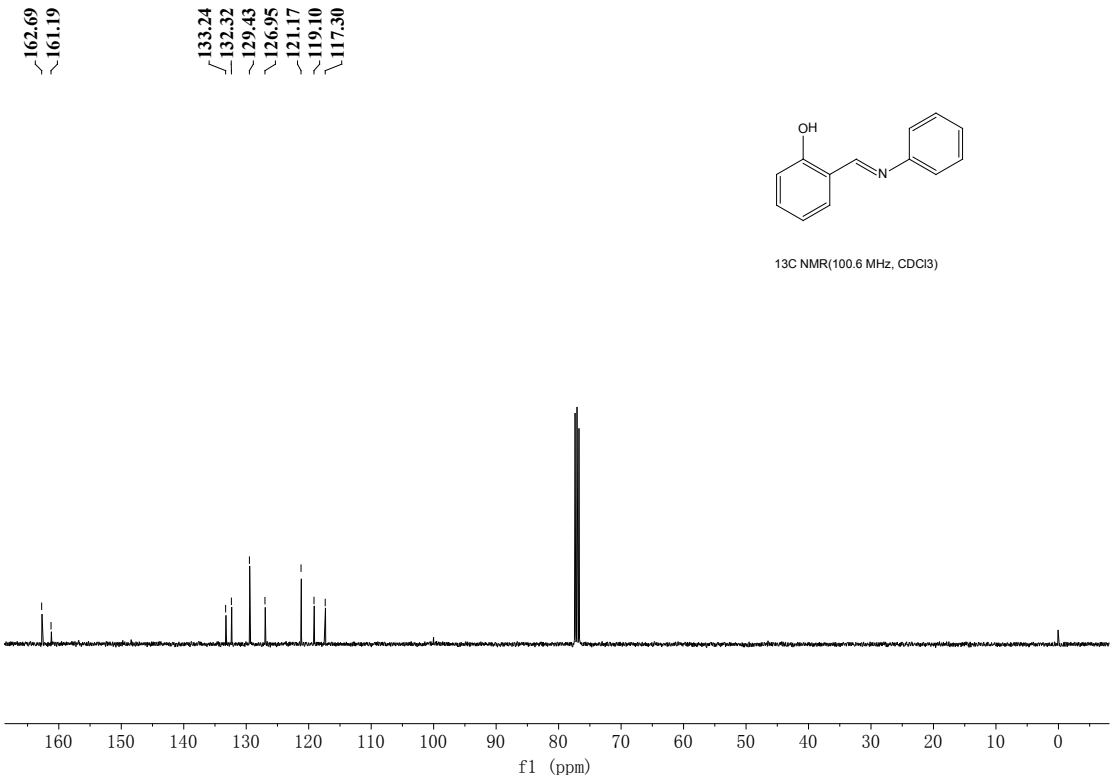
N-(4-methylbenzylidene)aniline:[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (s, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.38 (s, 2H), 7.32 – 7.14 (m, 5H), 2.42 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 160.43, 152.24, 141.93, 133.66, 129.55, 129.16, 128.86, 125.79, 120.91, 21.67.



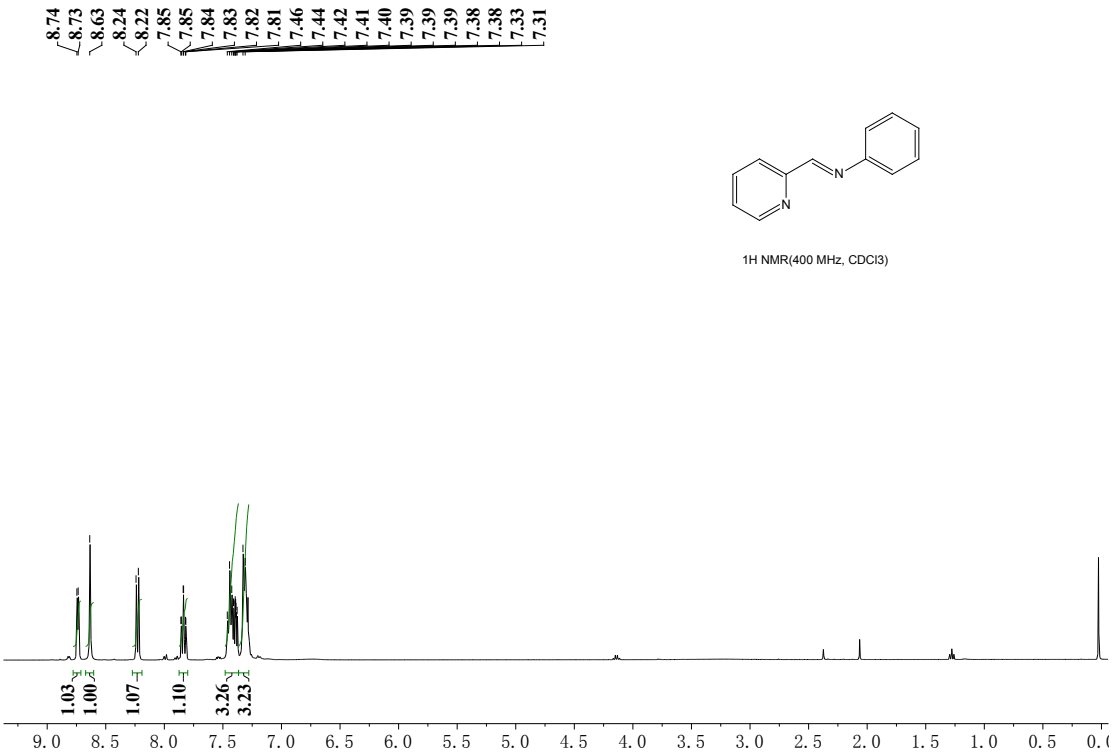


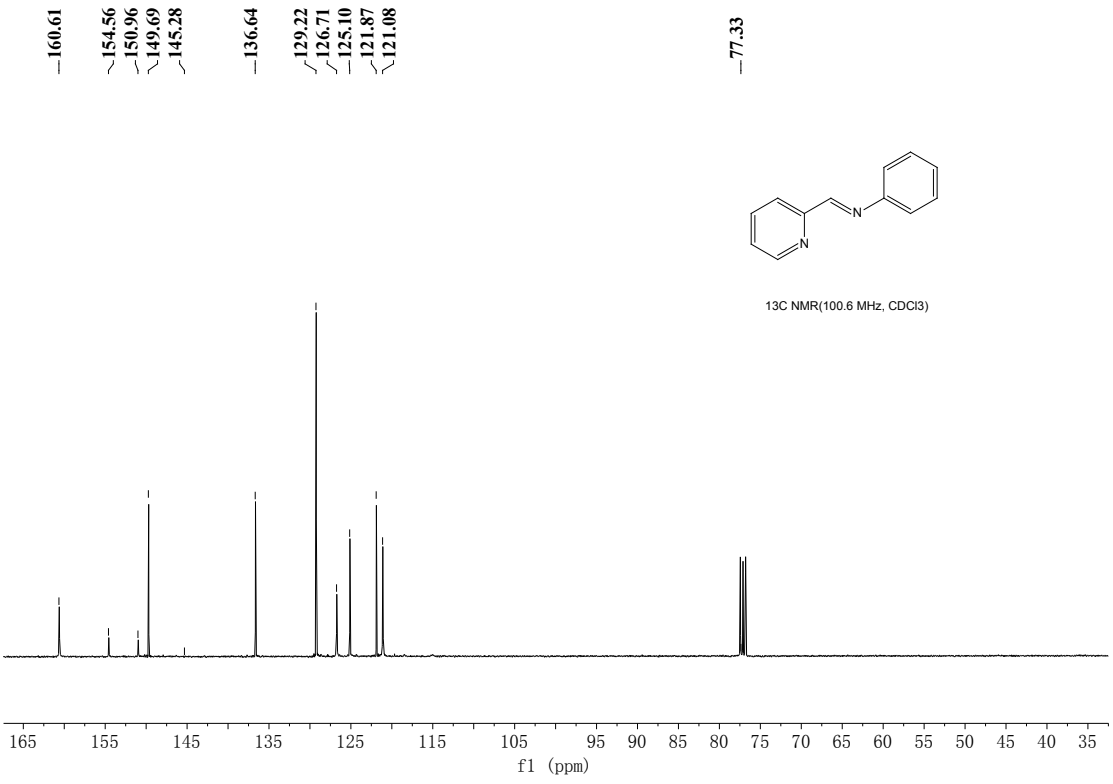
2-((phenylimino)methyl)phenol.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.47 – 7.33 (m, 4H), 7.28 (dd, J = 7.3, 5.4 Hz, 3H), 7.02 (d, J = 8.2 Hz, 1H), 6.93 (td, J = 7.5, 0.8 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 162.69, 161.19, 133.24, 132.32, 129.43, 126.95, 121.17, 119.10, 117.30.



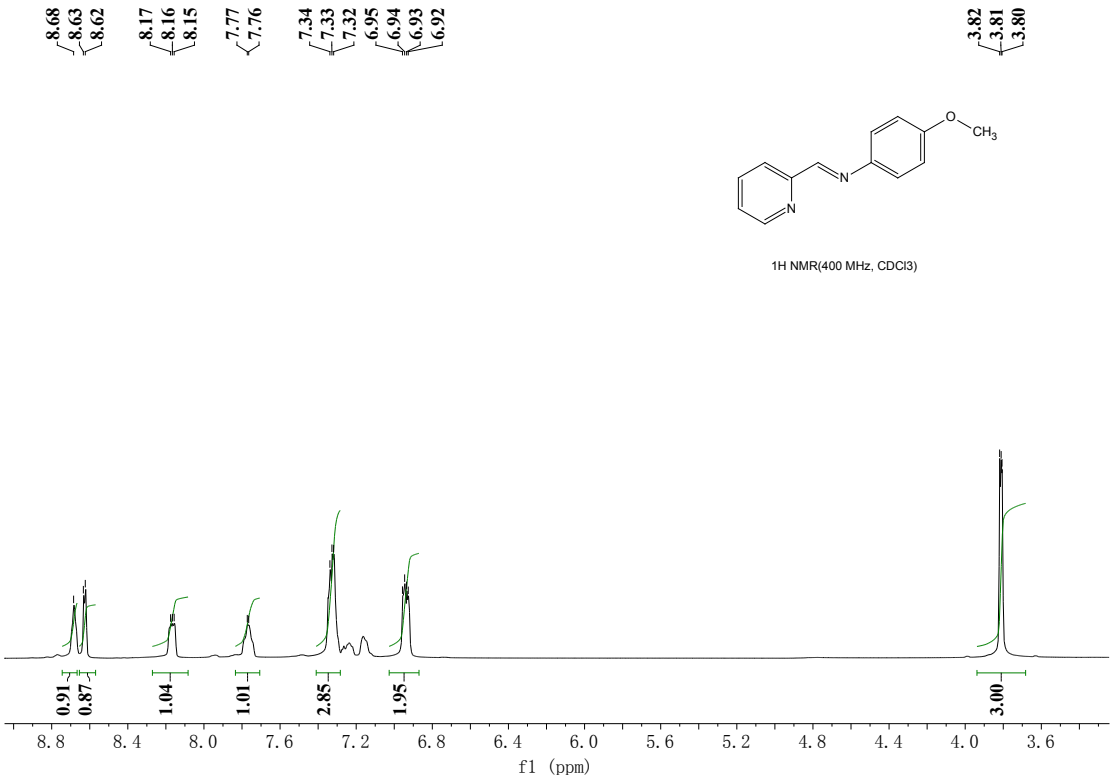


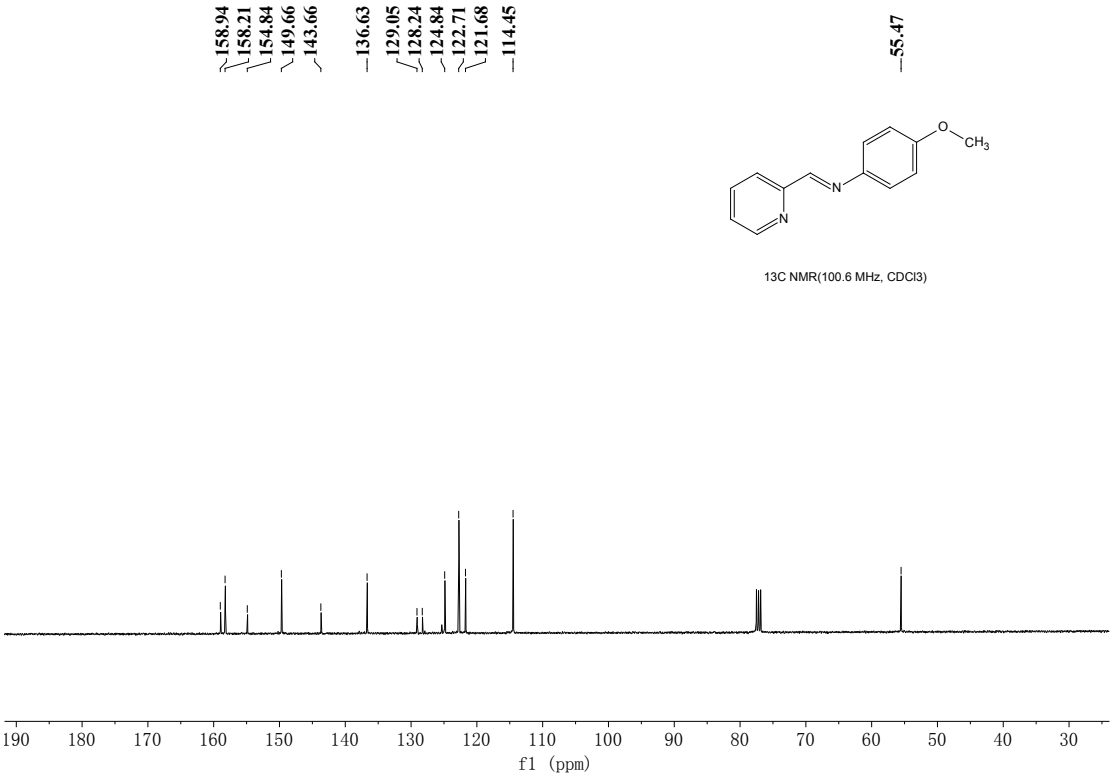
N-(pyridin-2-ylmethylene)aniline.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74 (d, J = 4.3 Hz, 1H), 8.63 (s, 1H), 8.23 (d, J = 7.9 Hz, 1H), 7.83 (td, J = 7.7, 1.3 Hz, 1H), 7.51 – 7.36 (m, 3H), 7.32 (d, J = 7.5 Hz, 3H).^{13}C NMR (400 MHz, $CDCl_3$) δ: 160.61, 154.56, 150.96, 149.69, 136.64, 129.22, 126.71, 125.10, 121.87, 121.08, 26.88.



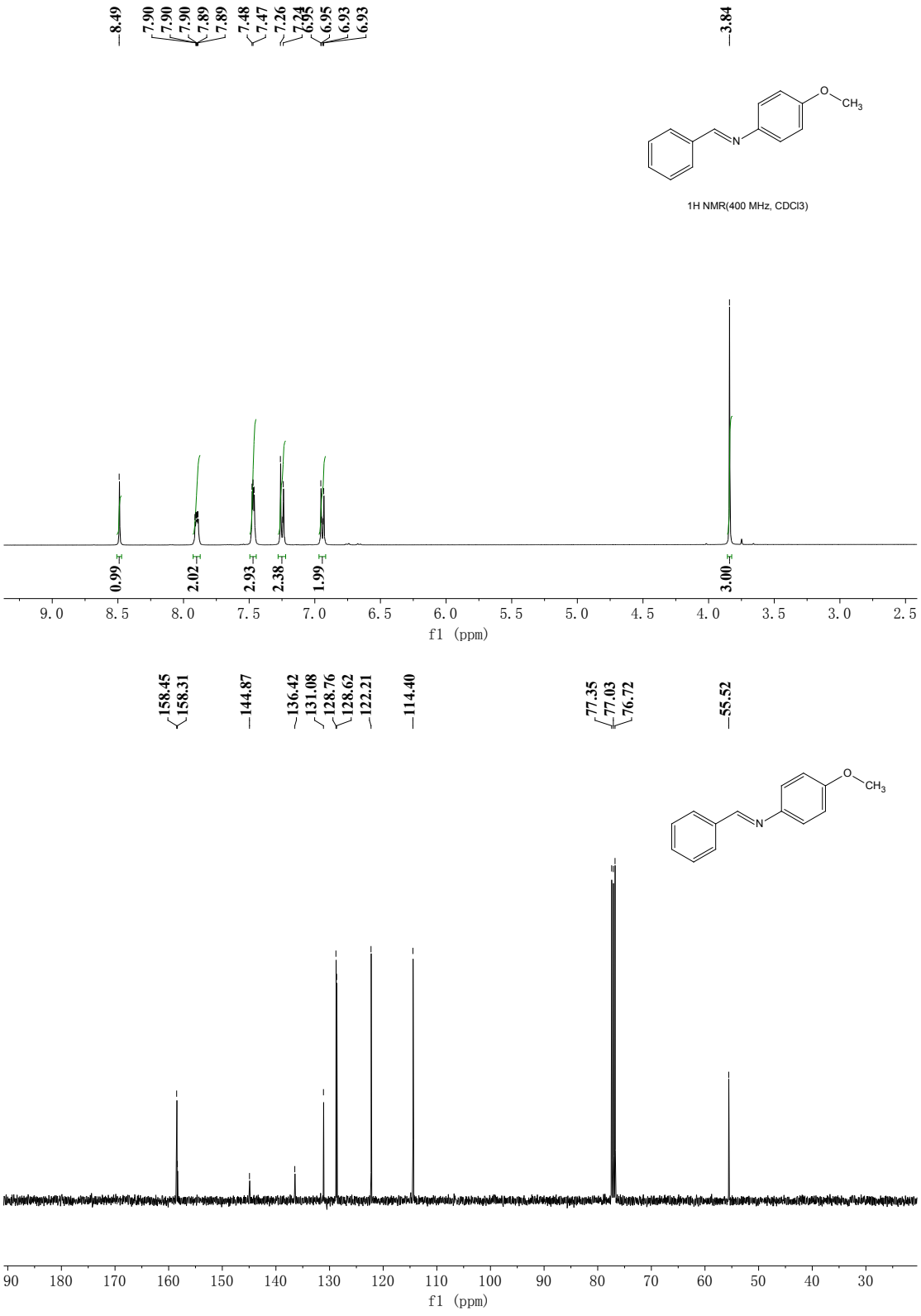


4-methoxy-N-(pyridin-2-ylmethylene)aniline:[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.63 (d, J = 4.0 Hz, 1H), 8.29 – 8.06 (m, 1H), 7.77 (d, J = 3.0 Hz, 1H), 7.43 – 7.27 (m, 3H), 6.94 (dd, J = 8.1, 4.0 Hz, 2H), 3.96 – 3.72 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 158.94, 158.21, 154.84, 149.66, 143.66, 136.63, 129.05, 128.24, 124.84, 122.71, 121.68, 114.45, 55.47.

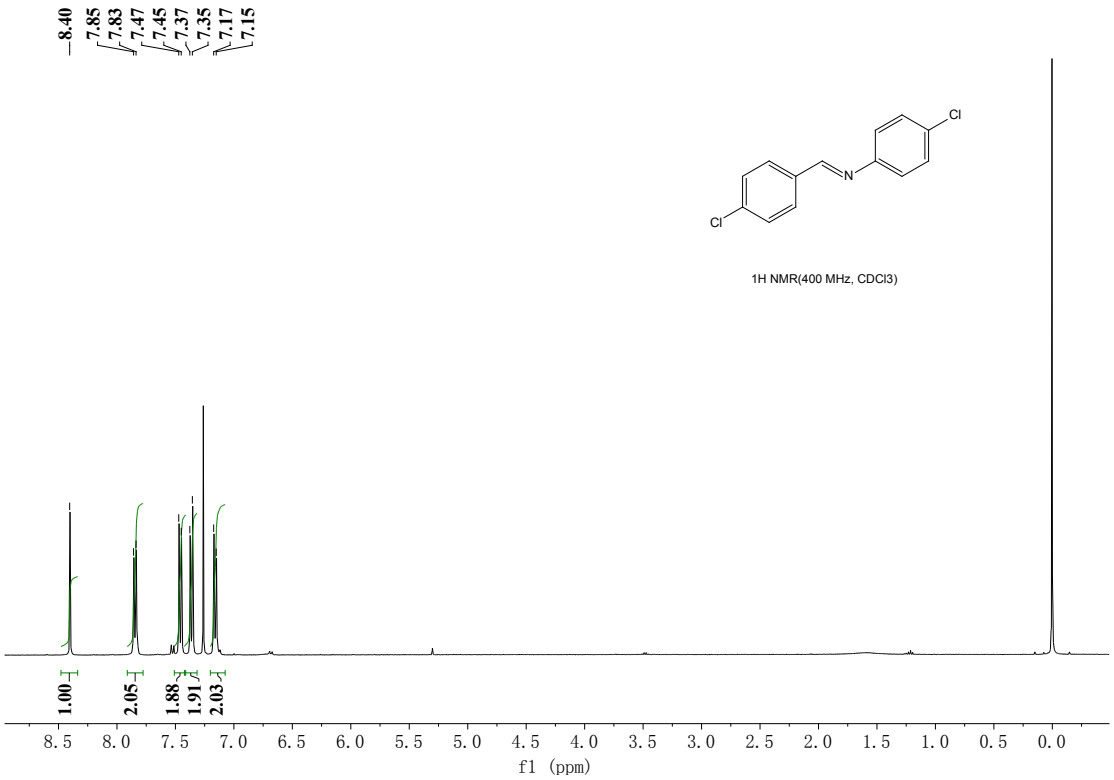


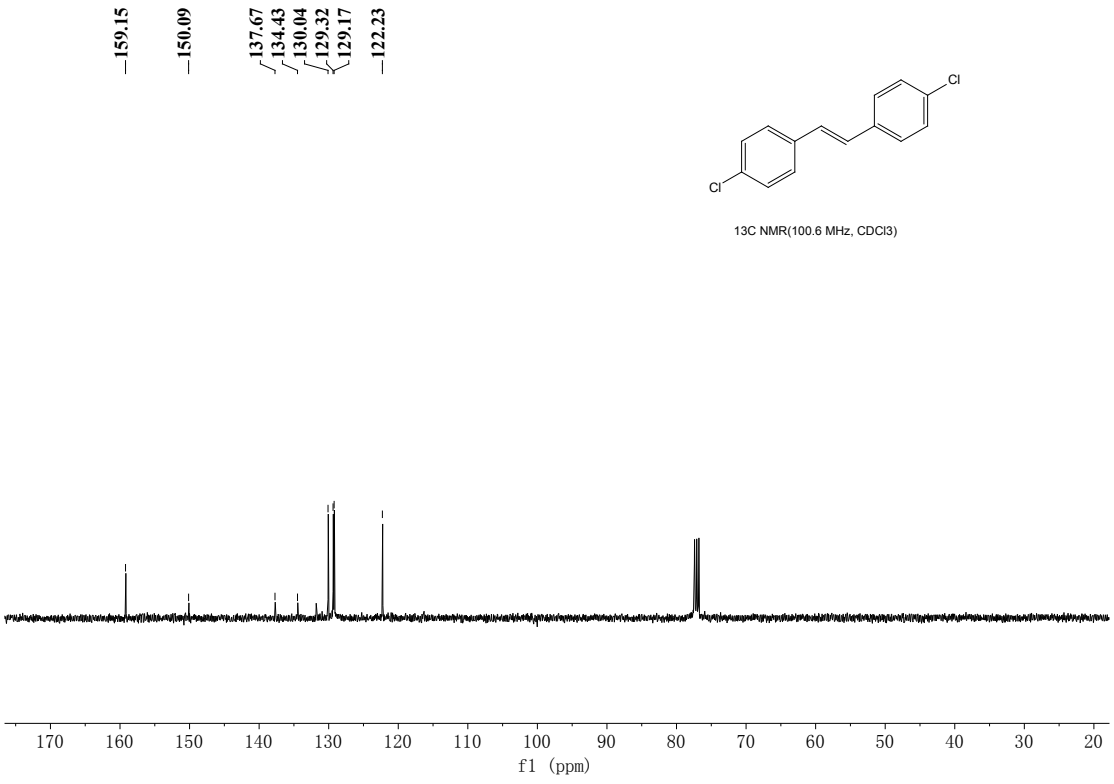


N-benzylidene-4-methoxyaniline:[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (s, 1H), 7.99 – 7.81 (m, 2H), 7.55 – 7.41 (m, 3H), 7.32 – 7.19 (m, 2H), 7.02 – 6.88 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 158.45, 158.31, 144.87, 136.42, 131.08, 128.76, 128.62, 122.21, 114.40, 55.52.

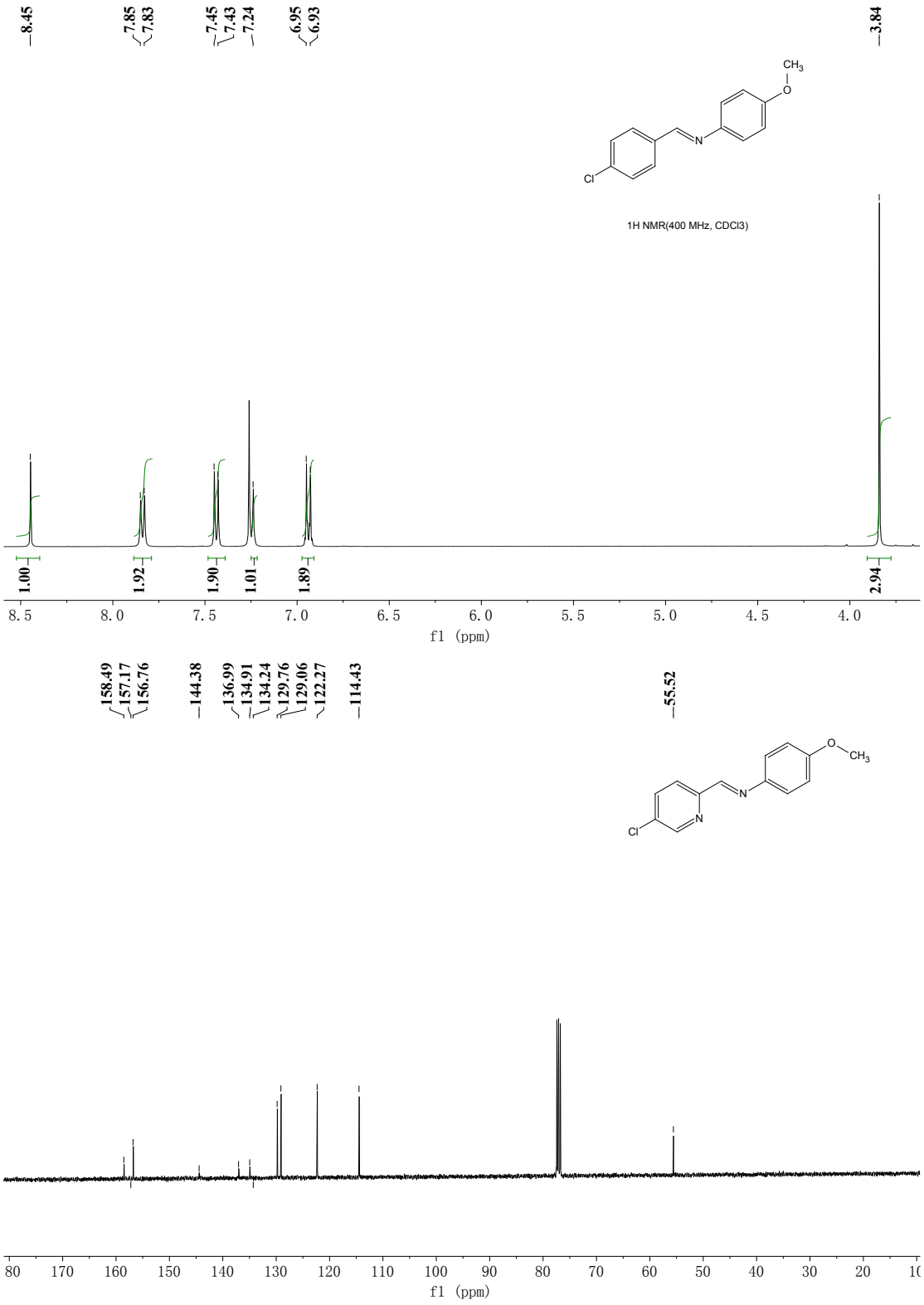


4-chloro-N-(4-chlorobenzylidene)aniline:[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.84 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 159.15, 150.09, 137.67, 134.43, 130.04, 129.32, 129.17, 122.23.



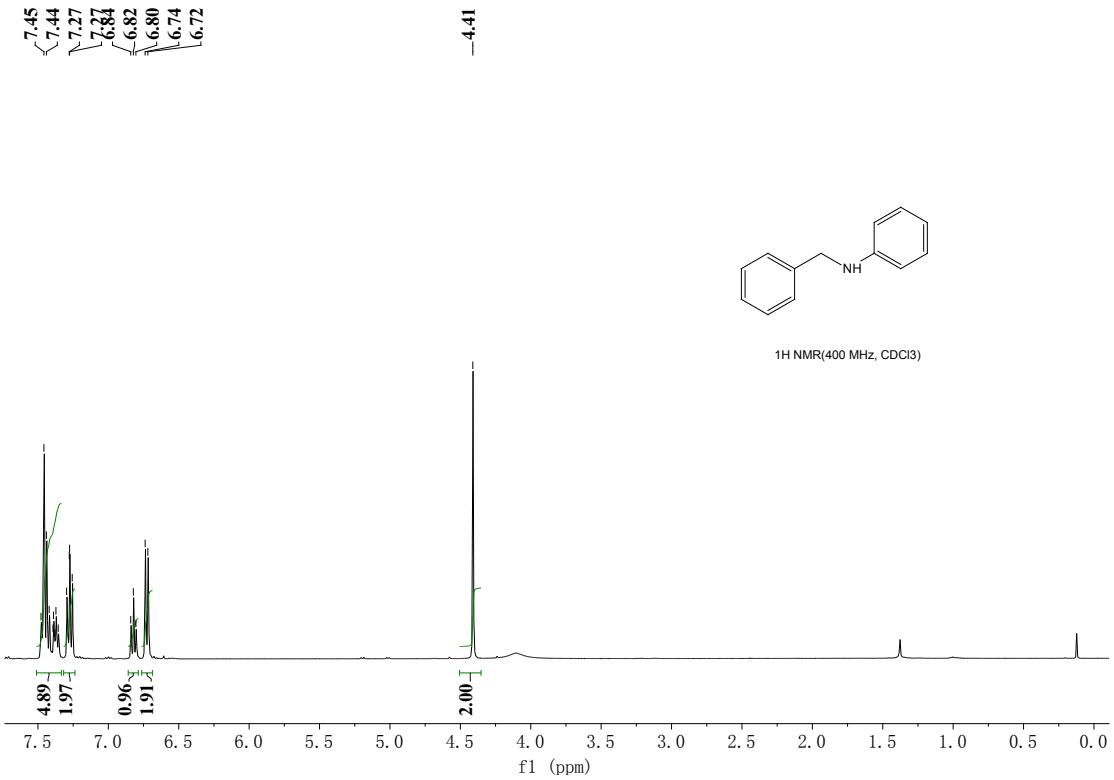


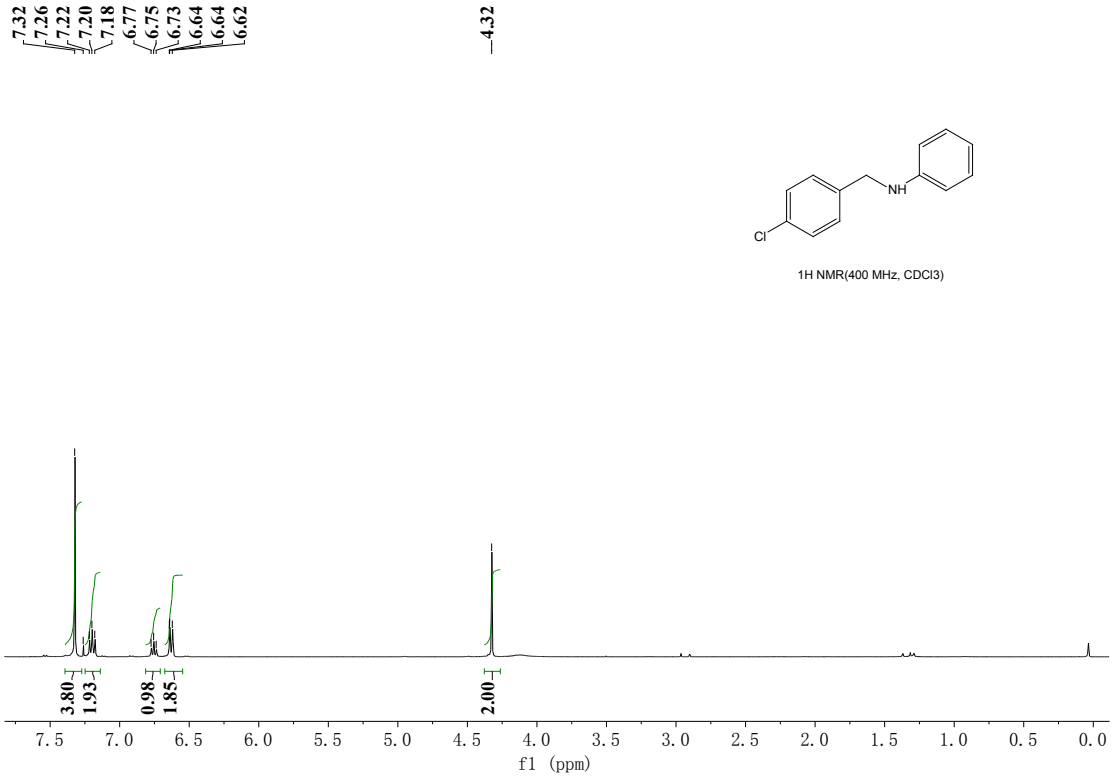
N-(4-chlorobenzylidene)-4-methoxyaniline.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.45 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.24 (s, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 158.49, 157.17, 156.76, 144.38, 136.99, 134.91, 134.24, 129.76, 129.06, 122.27, 114.43, 55.52.

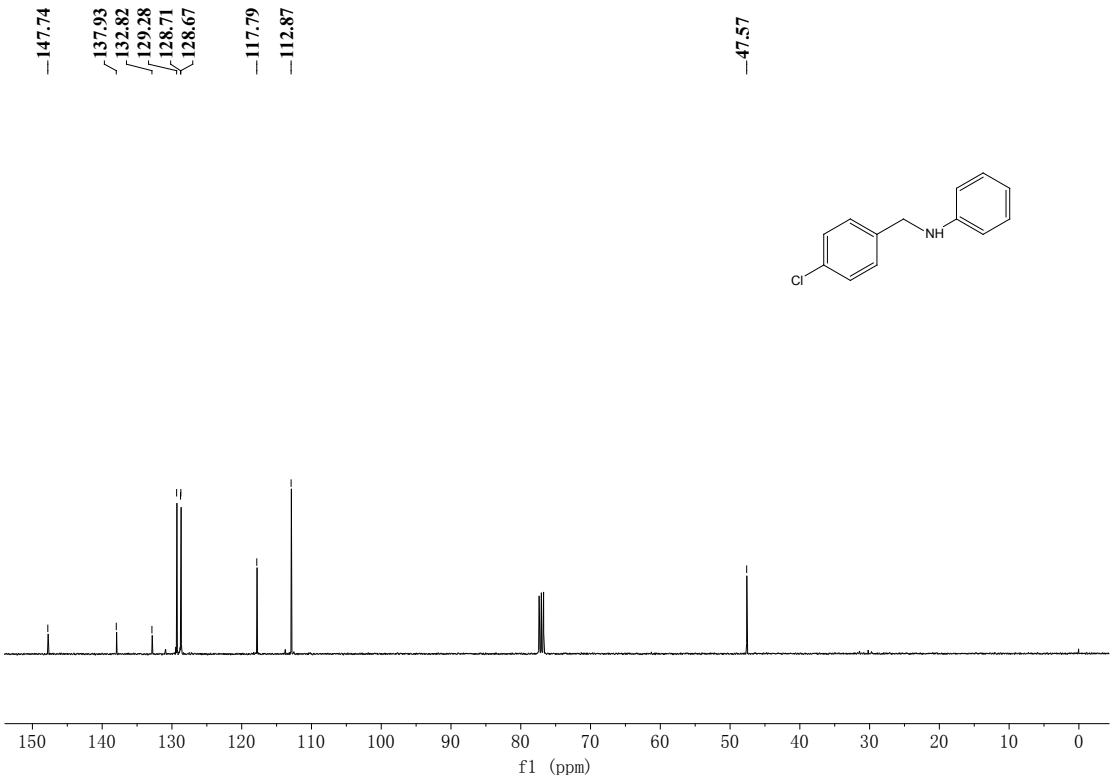


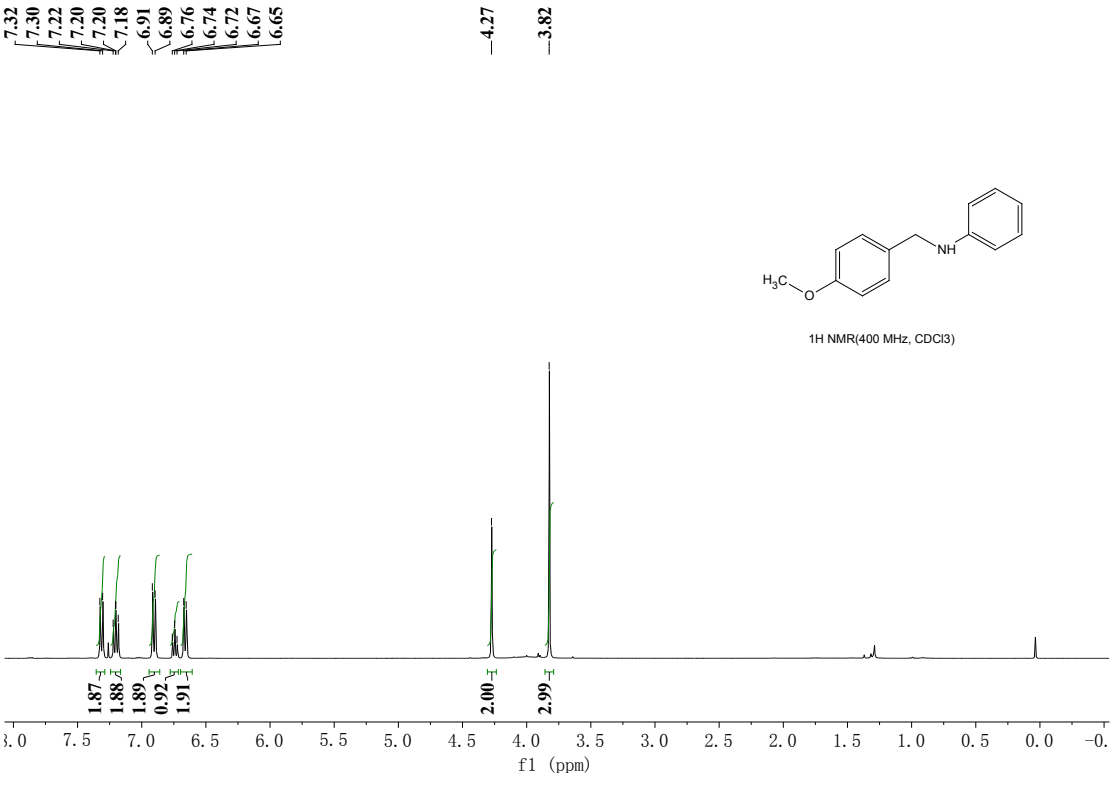
3. NMR spectra of the products

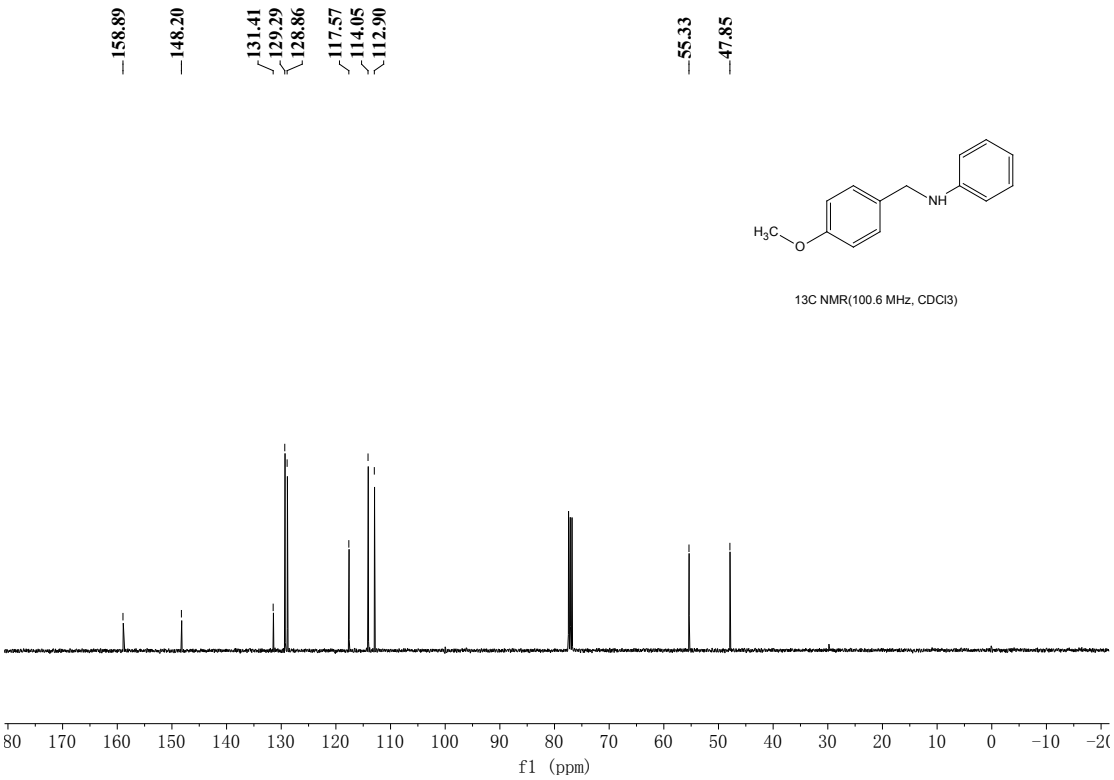
Table3 entry 1

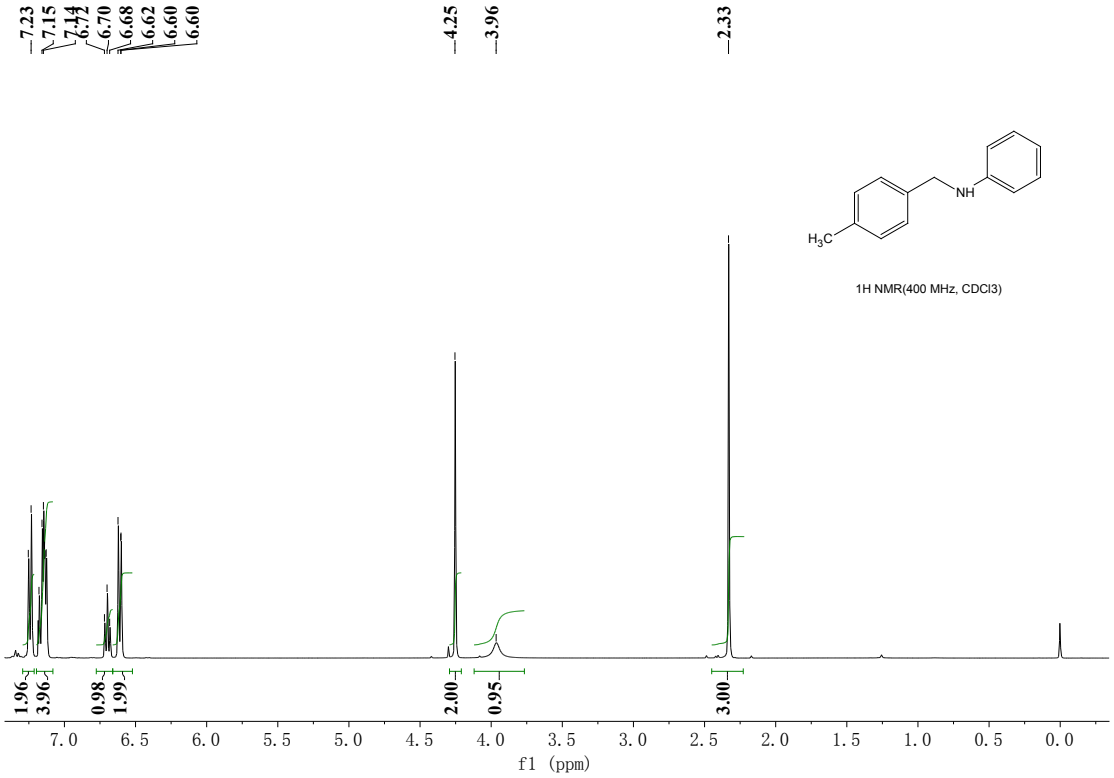


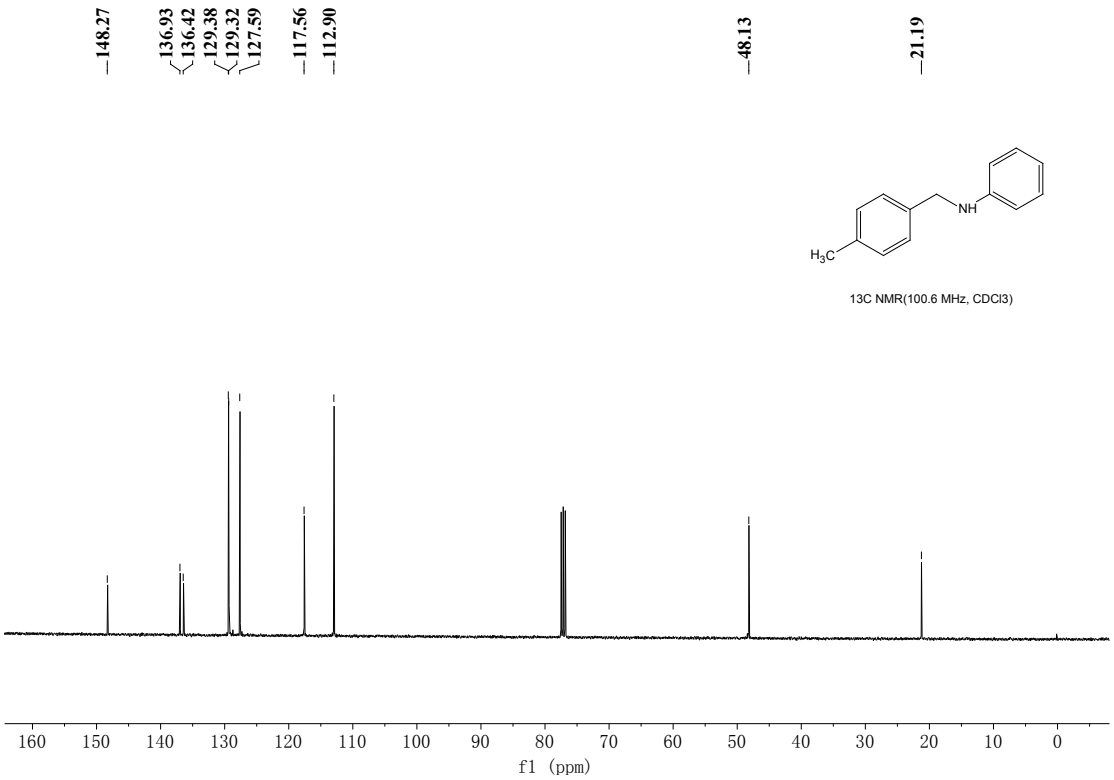


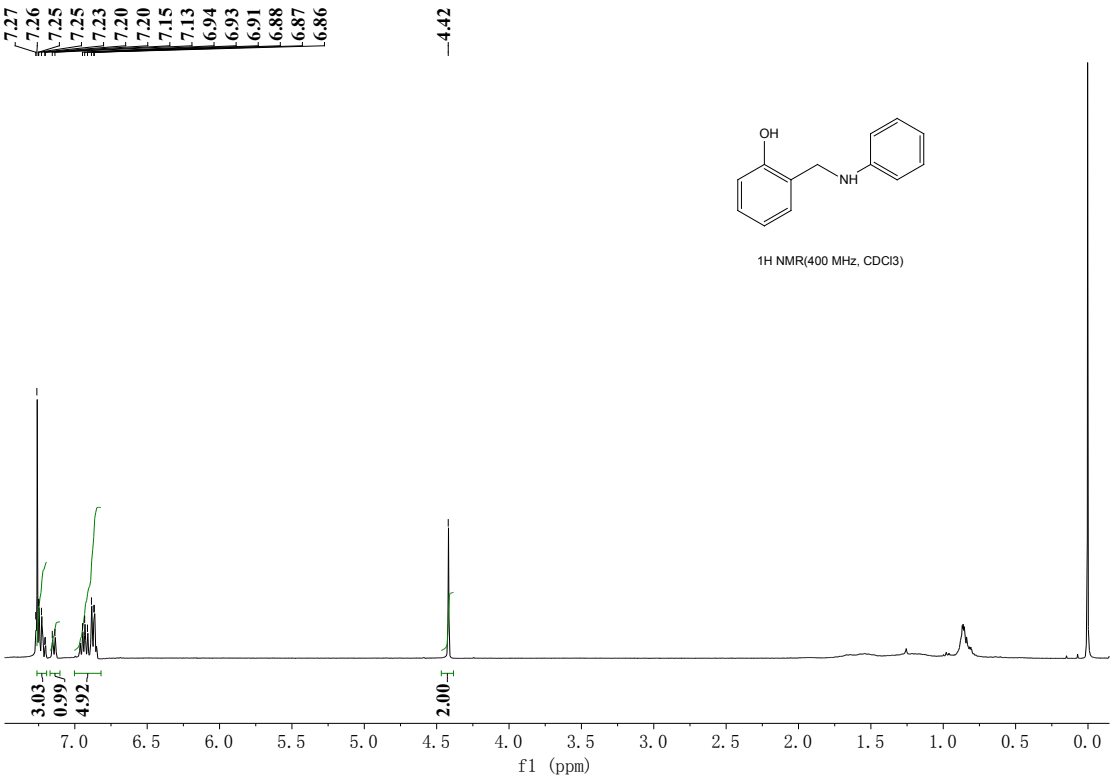


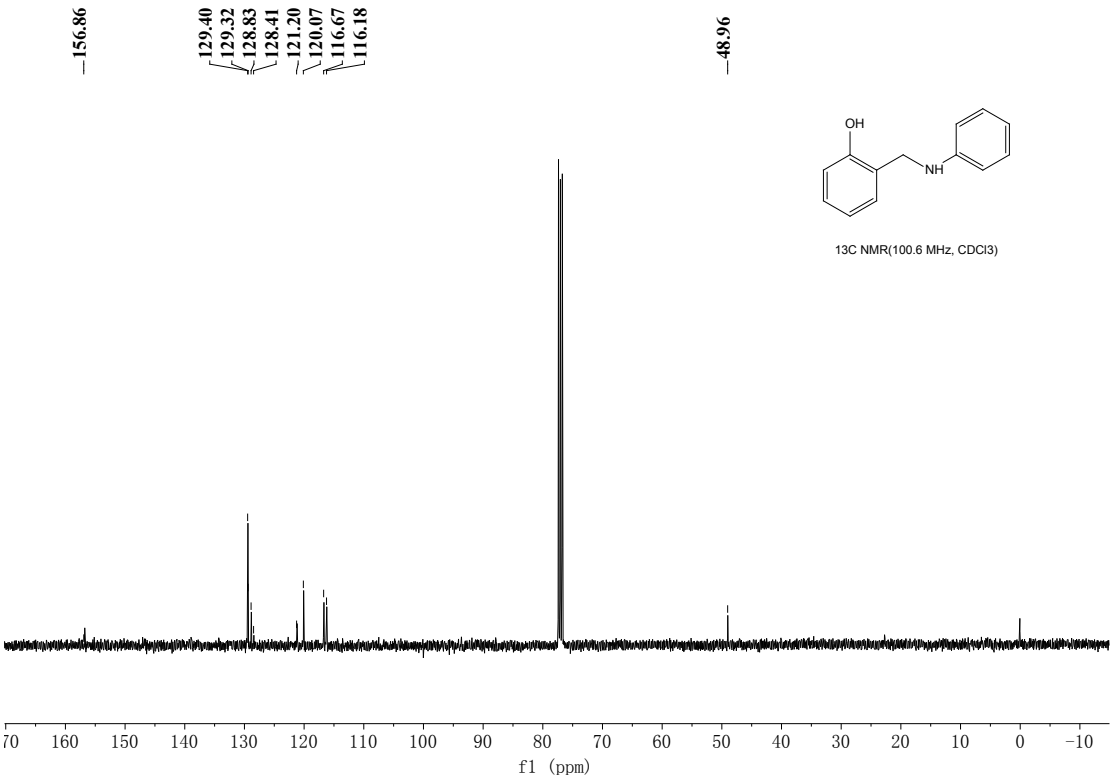


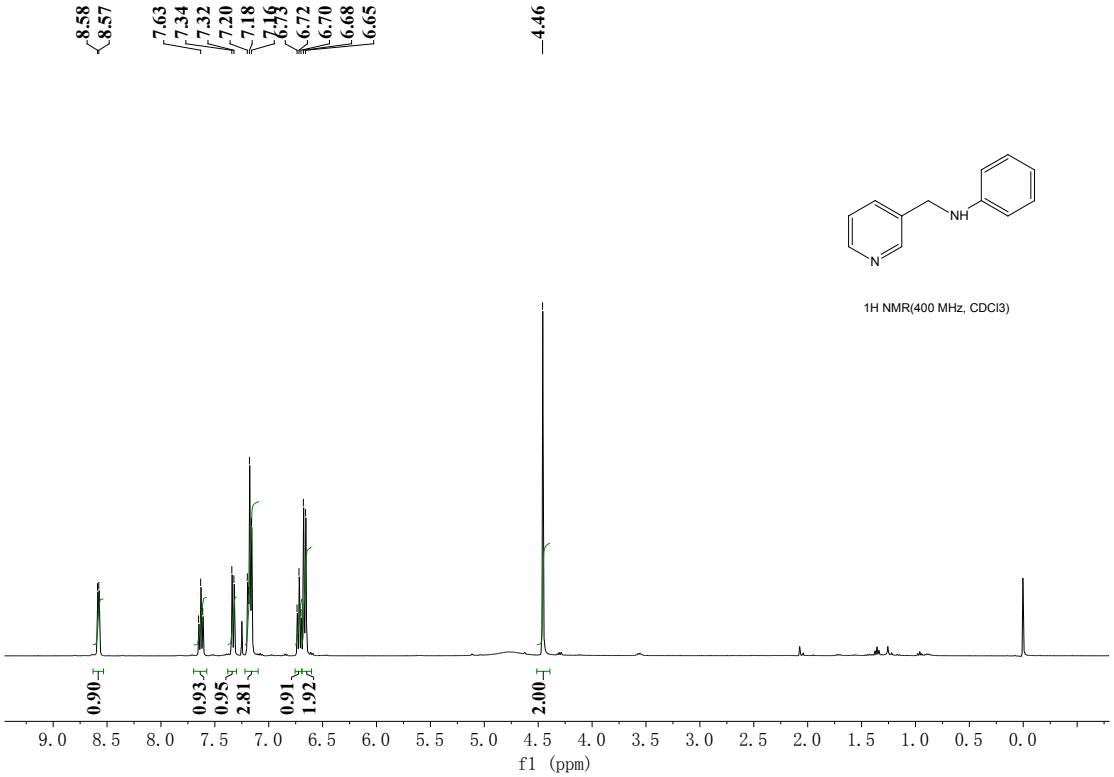


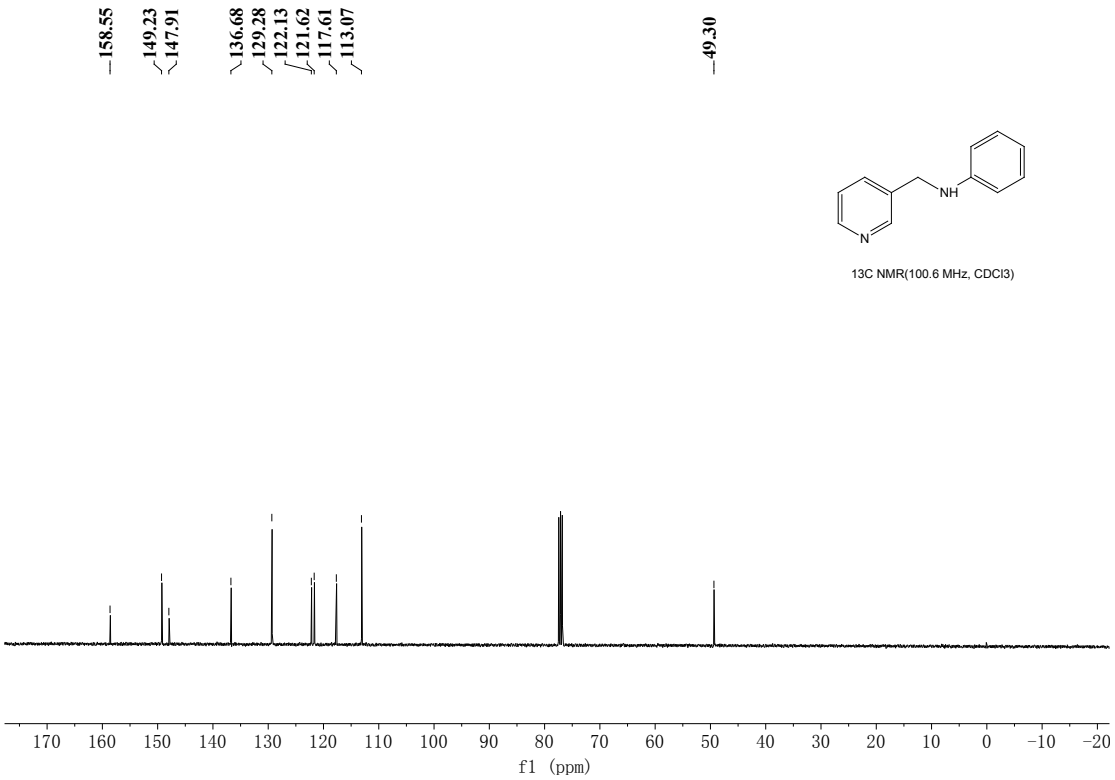


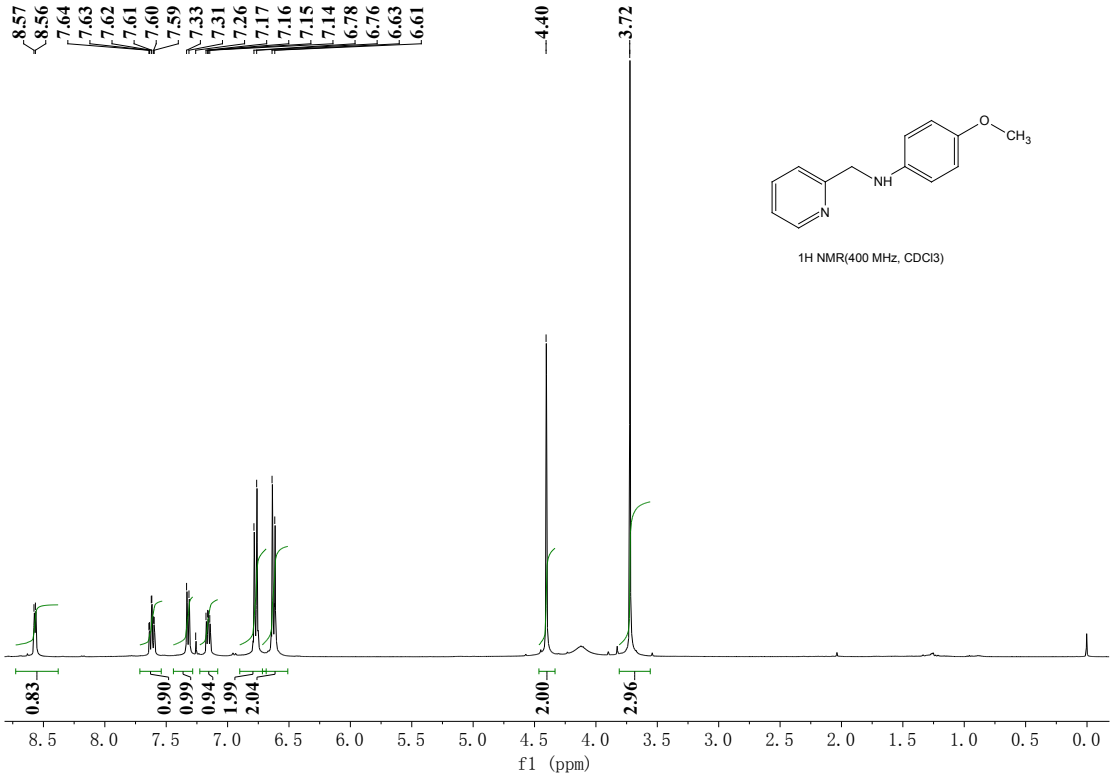


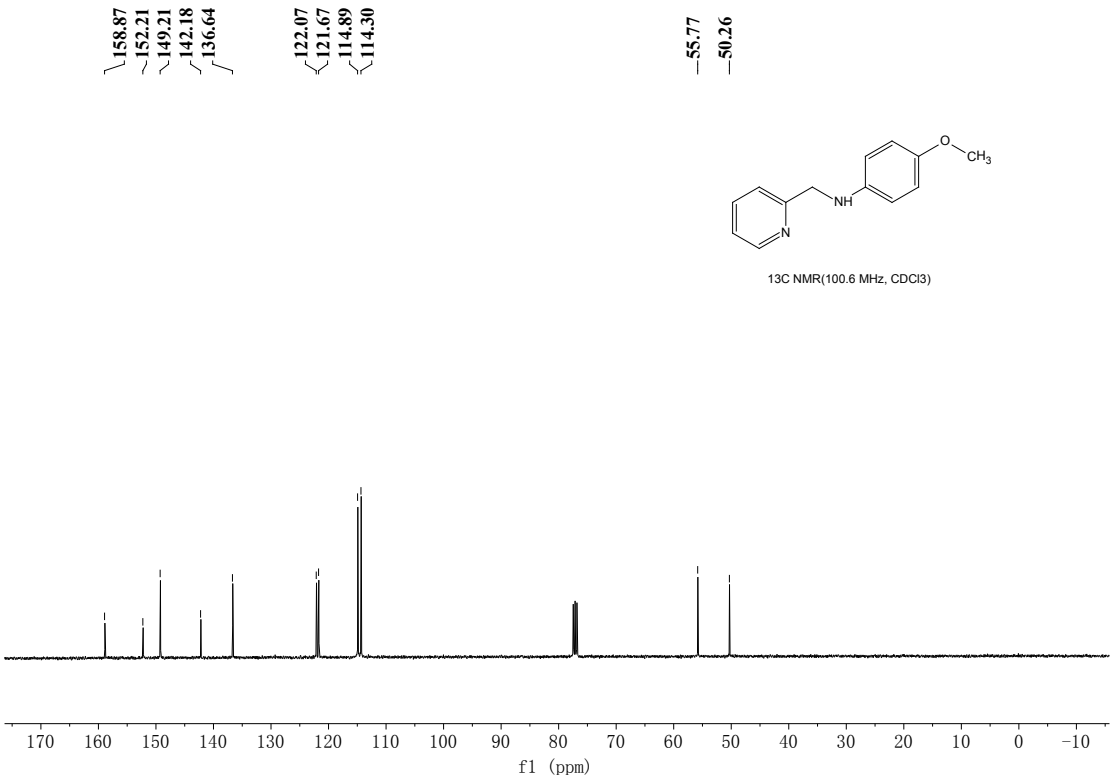




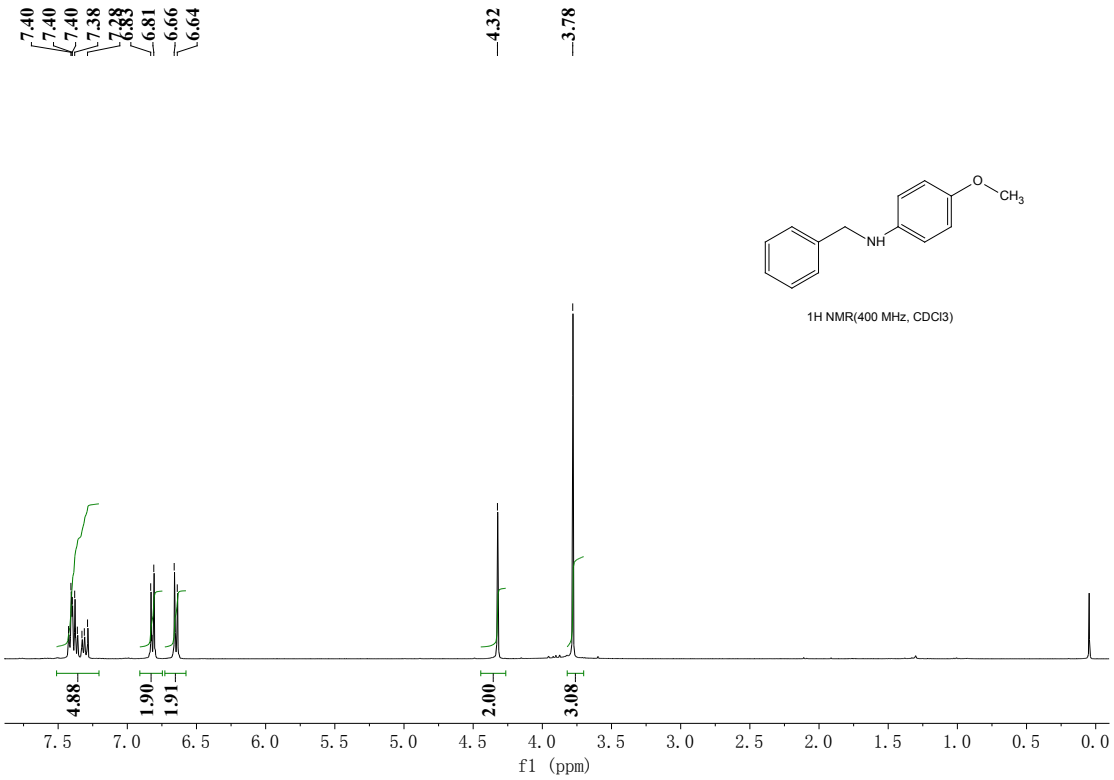




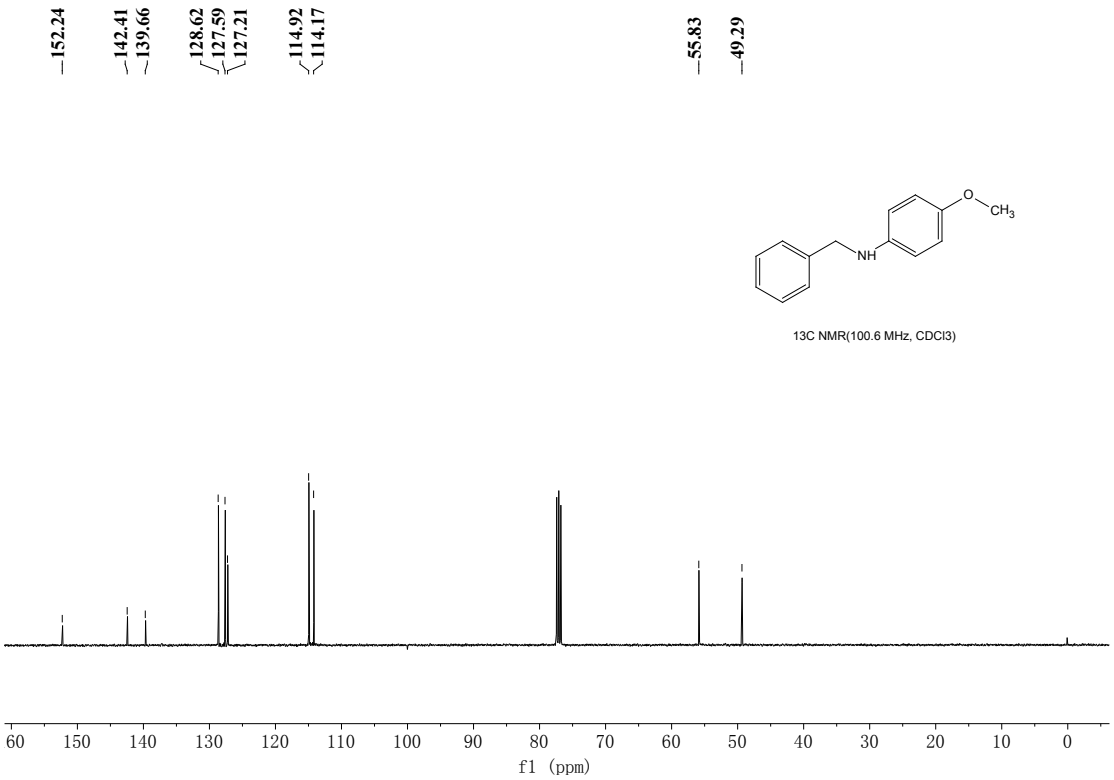


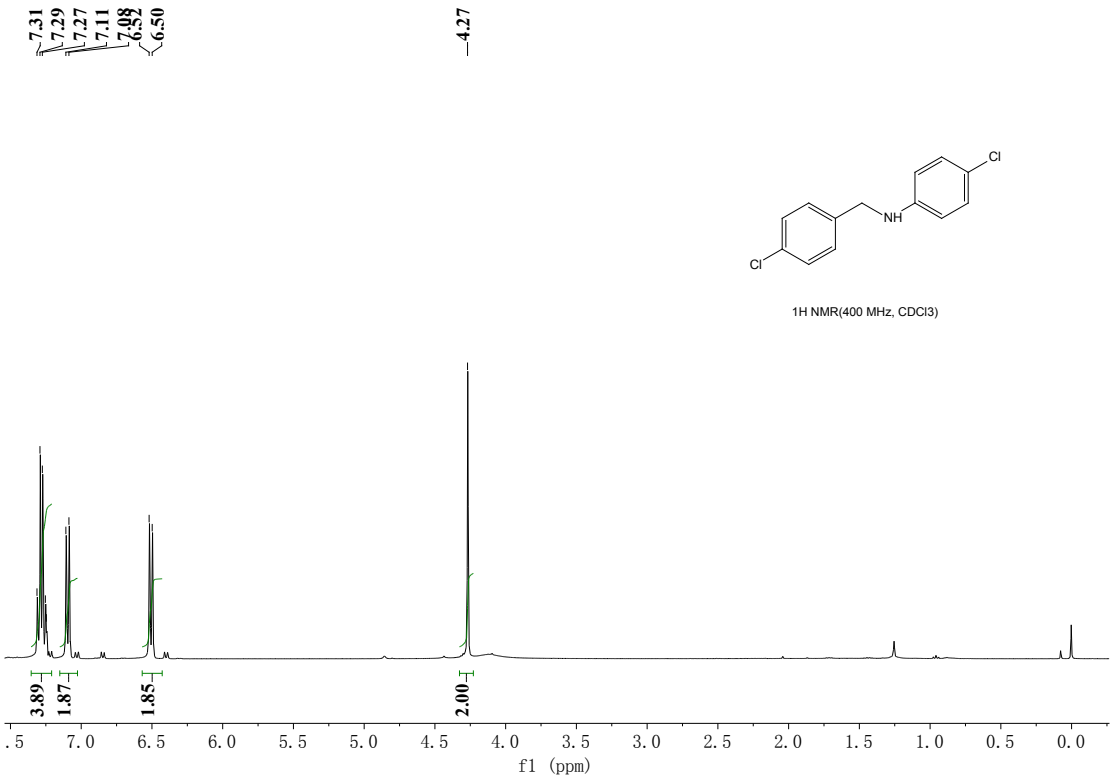


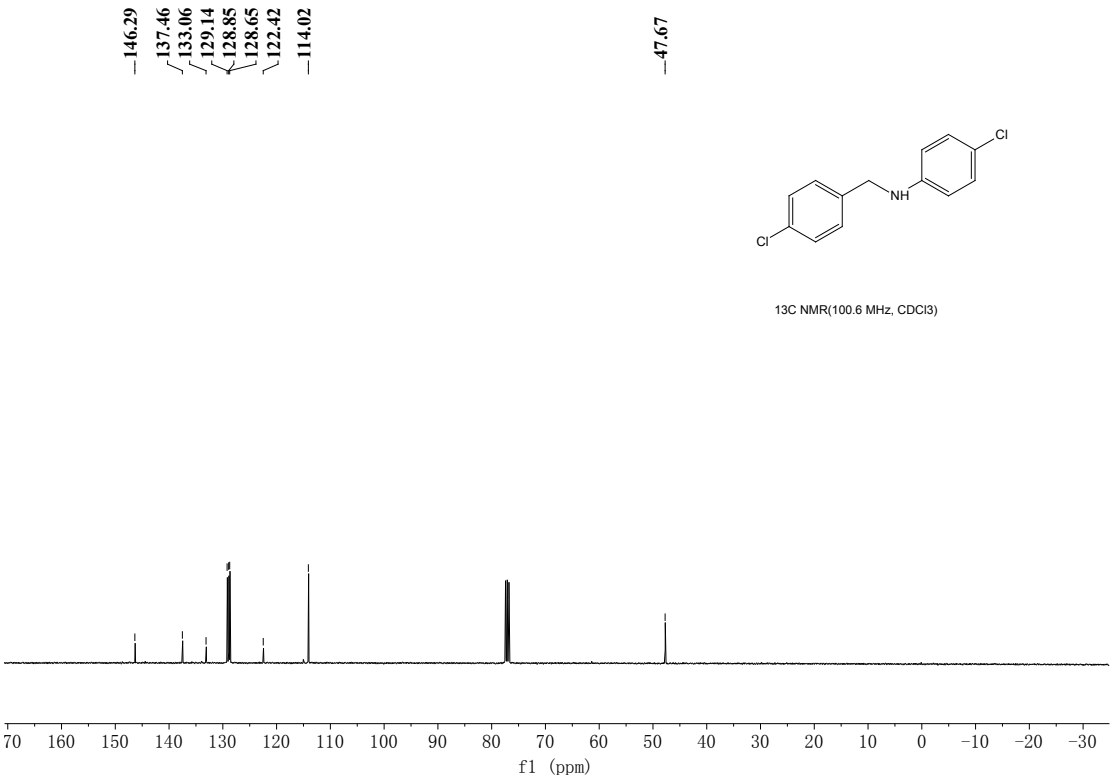
13C NMR(100.6 MHz, CDCl3)

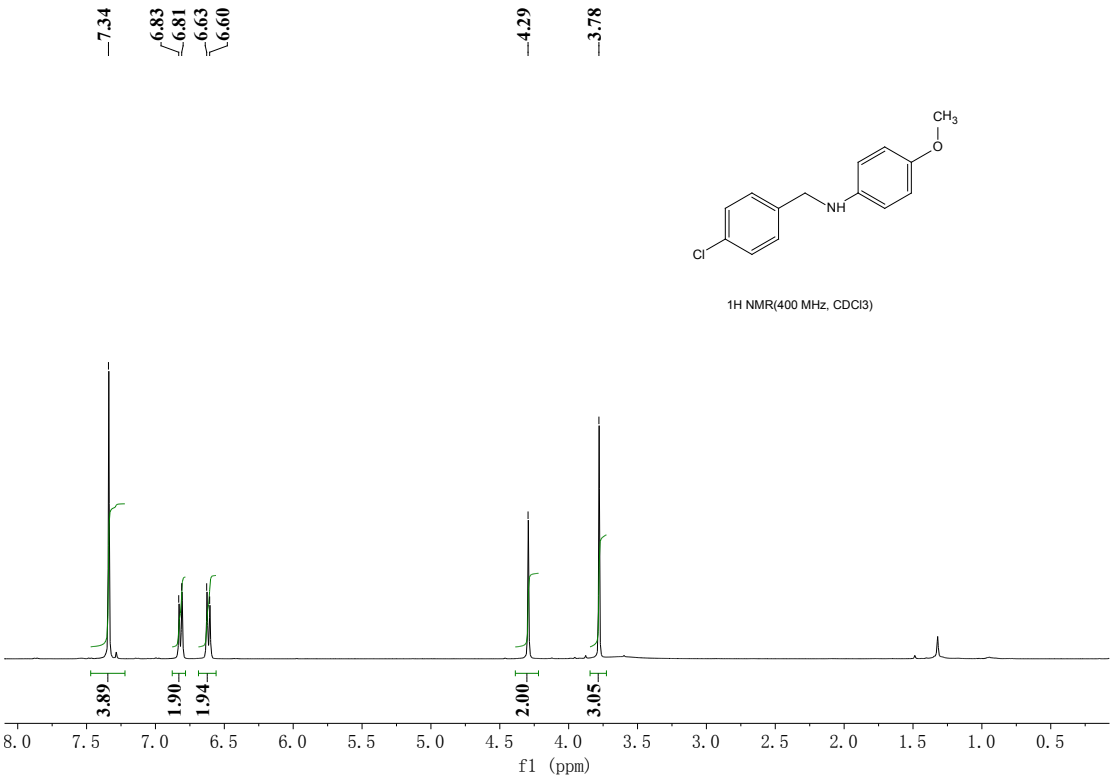


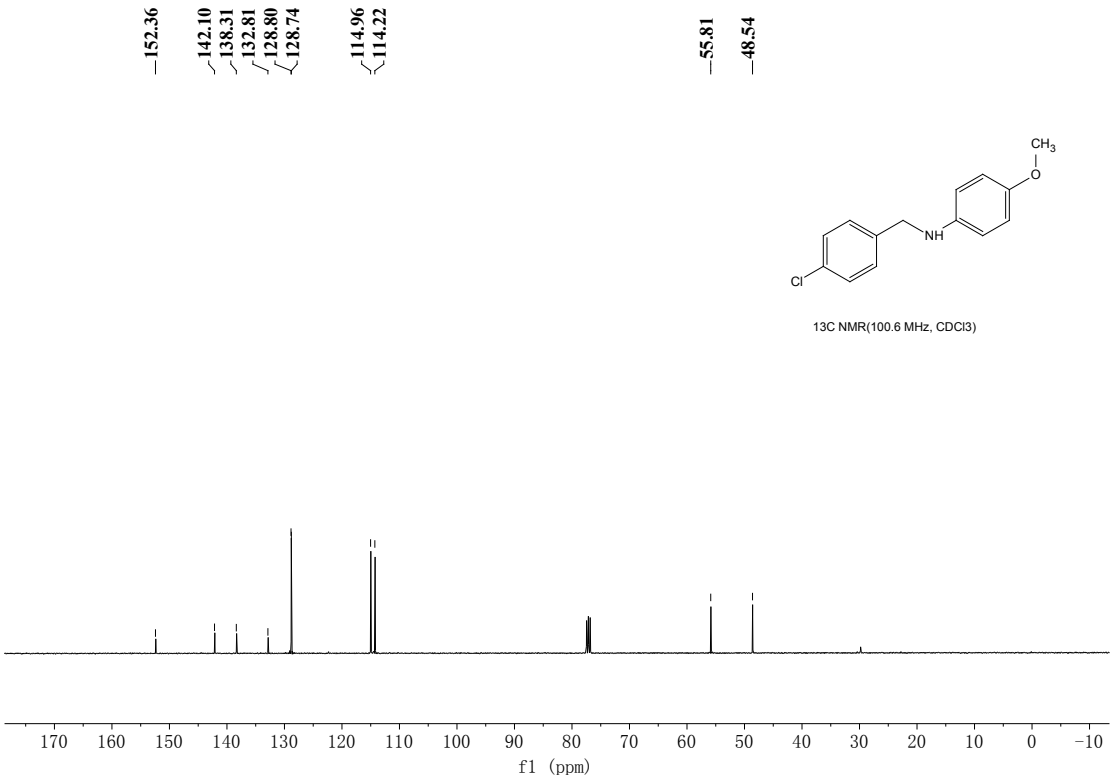
1H NMR(400 MHz, CDCl3)


152.24
142.41
139.66
128.62
127.59
127.21
114.92
114.17
55.83
49.29
O
CH3
NH
13C NMR(100.6 MHz, CDCl3)
f1 (ppm)

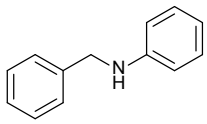

7.31
7.29
7.27
7.11
7.08
6.52
6.50
4.27
Cl
NH
Cl
1H NMR(400 MHz, CDCl3)
3.89
1.87
1.85
2.00
f1 (ppm)

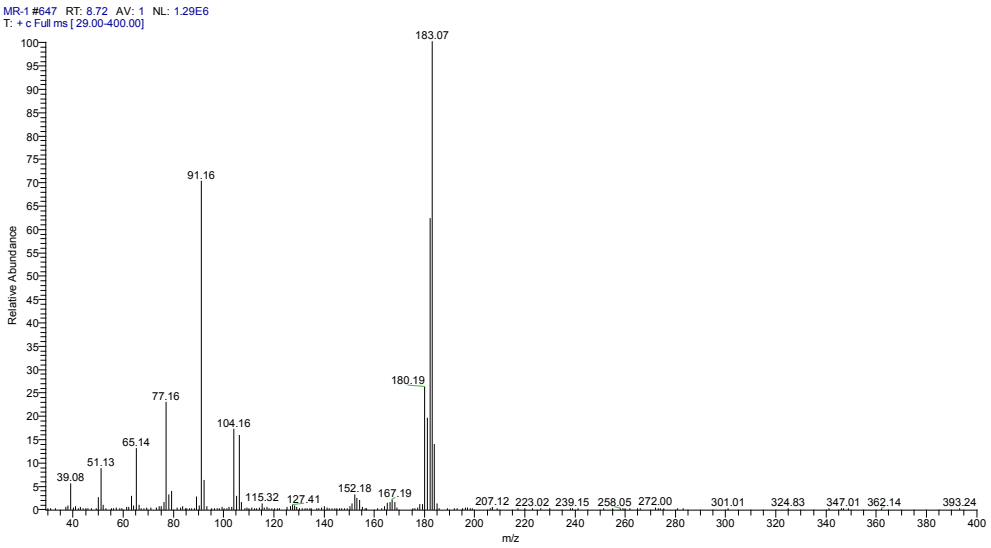


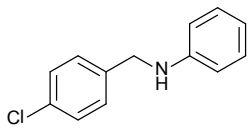


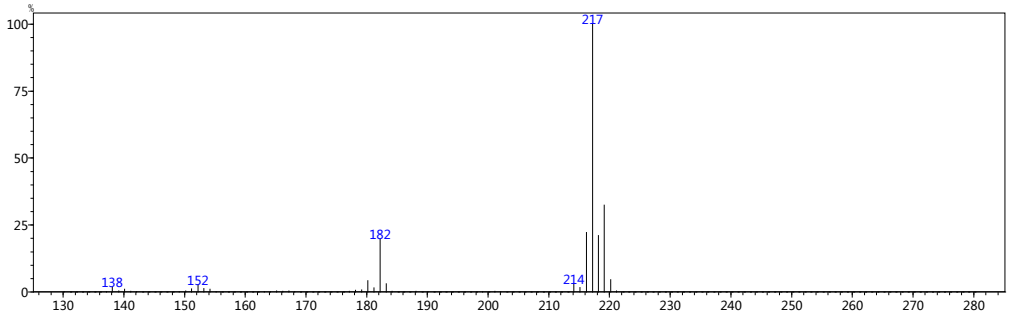


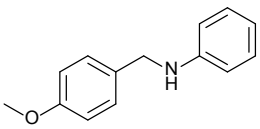
4. GC-MS spectra of the products

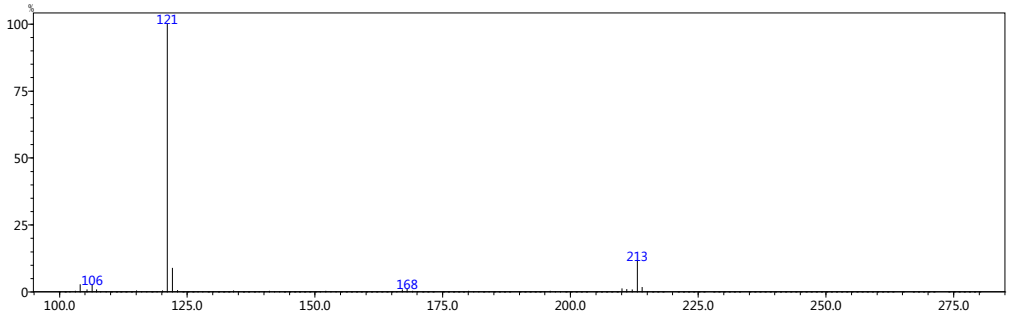


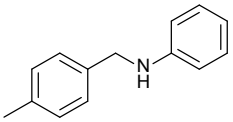


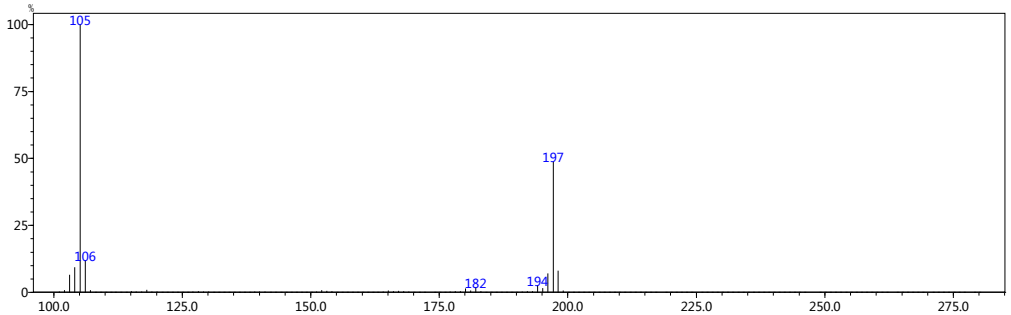


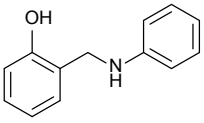


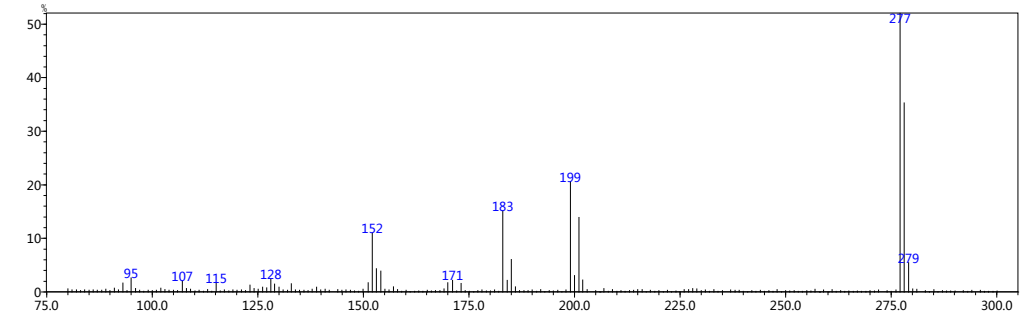


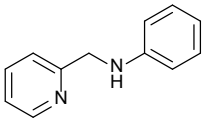


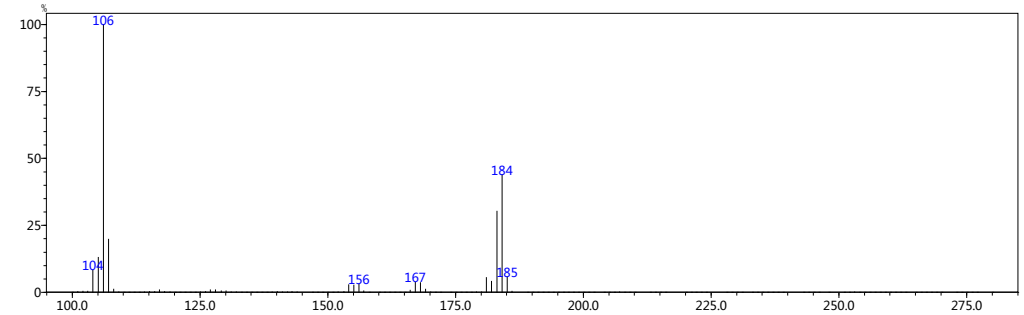


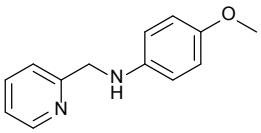


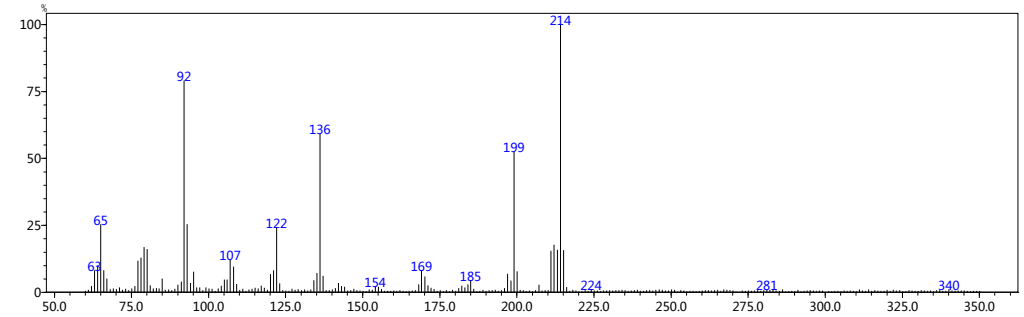


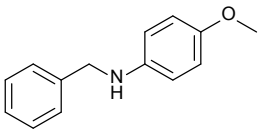


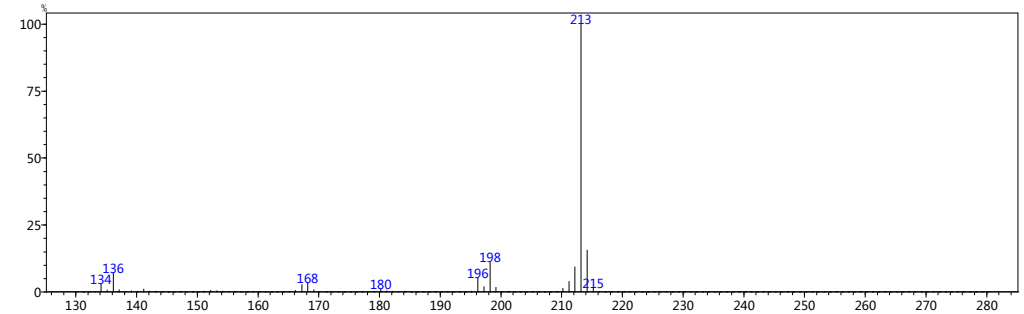


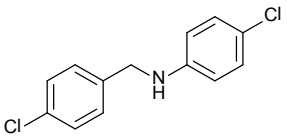


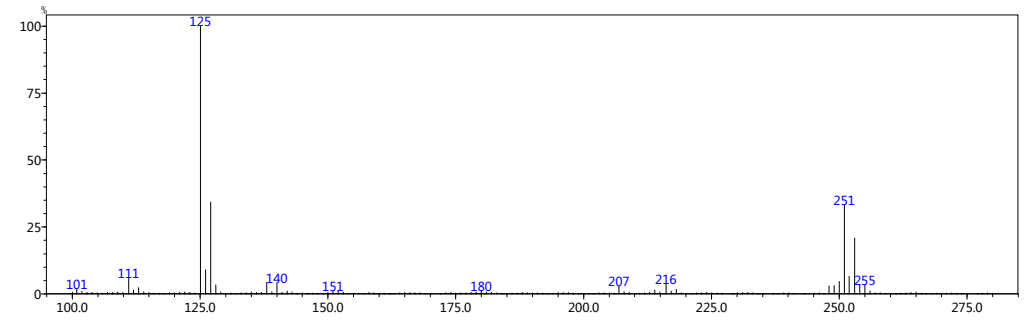


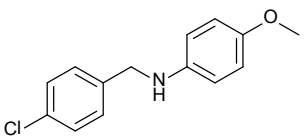


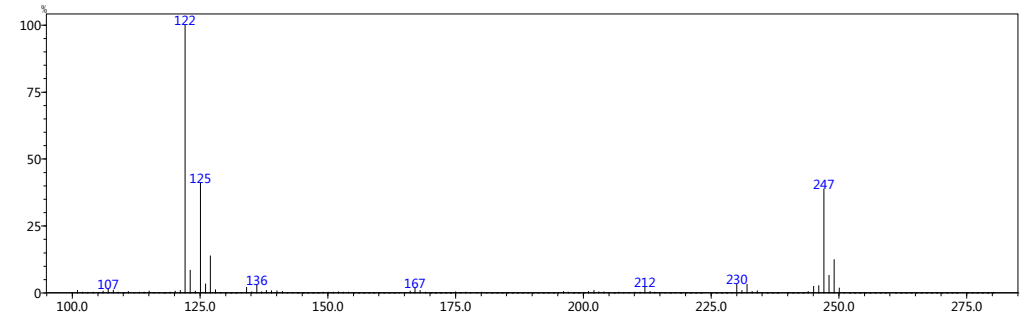












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