Electronic Supplementary Information

Gold supported on titania for efficient and selective mono-hydrogenation of dinitroaromatics in the liquid phase

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Experimental Details

I. Catalytic materials

Gold catalysts including 1.0 wt% Au/TiO_2, 1.0 wt% Au/ZnO and 1.0 wt% Au/Al_2O_3 were supplied by Mintek. 4.5 wt% Au/Fe_2O_3 (type C, lot no. Au/Fe_2O_3 no. 02-5) were supplied by the World Gold Council (WGC). TiO_2 (Evonik P25, specific surface area: 45 $m^2 \cdot g^{-1}$ nonporous, 70% anatase and 30% rutile, purity> 99.5%). $PdCl_2$, $RuCl_3 \cdot xH_2O$,$H_2PtCl_6 \cdot 6H_2O$ and $HAuCl_4 \cdot 4H_2O$, were supplied by Aldrich and used without further purification.

Au/CeO_2, Au/ZrO_2, Au/SiO_2, Au/C: Au/CeO_2, Au/ZrO_2were prepared based on the method described in ref. S1 and Au/SiO_2, Au/C were prepared according to the method described in ref. S2.

Pt/TiO_2, Pd/TiO_2, Ru/TiO_2:1 wt% Pt/TiO_2, 1 wt% Pd/TiO_2, 1 wt% Ru/TiO_2 catalysts were prepared by incipient-wetness impregnation of the support (P25) with aqueous solution of $H_2PtCl_6 \cdot 6H_2O$, $PdCl_2$, $RuCl_3 \cdot xH_2O$ precursors of appropriate amounts (typically 1.0 $mL \cdot g^{-1}$ support), respectively. After a perfect mixing of the corresponding slurries, samples were dried under vacuum at room temperature for 12 h and then reduced in 5vol% H_2/Ar at 450 ^oC for 3 h.

II. Catalytic activity measurements

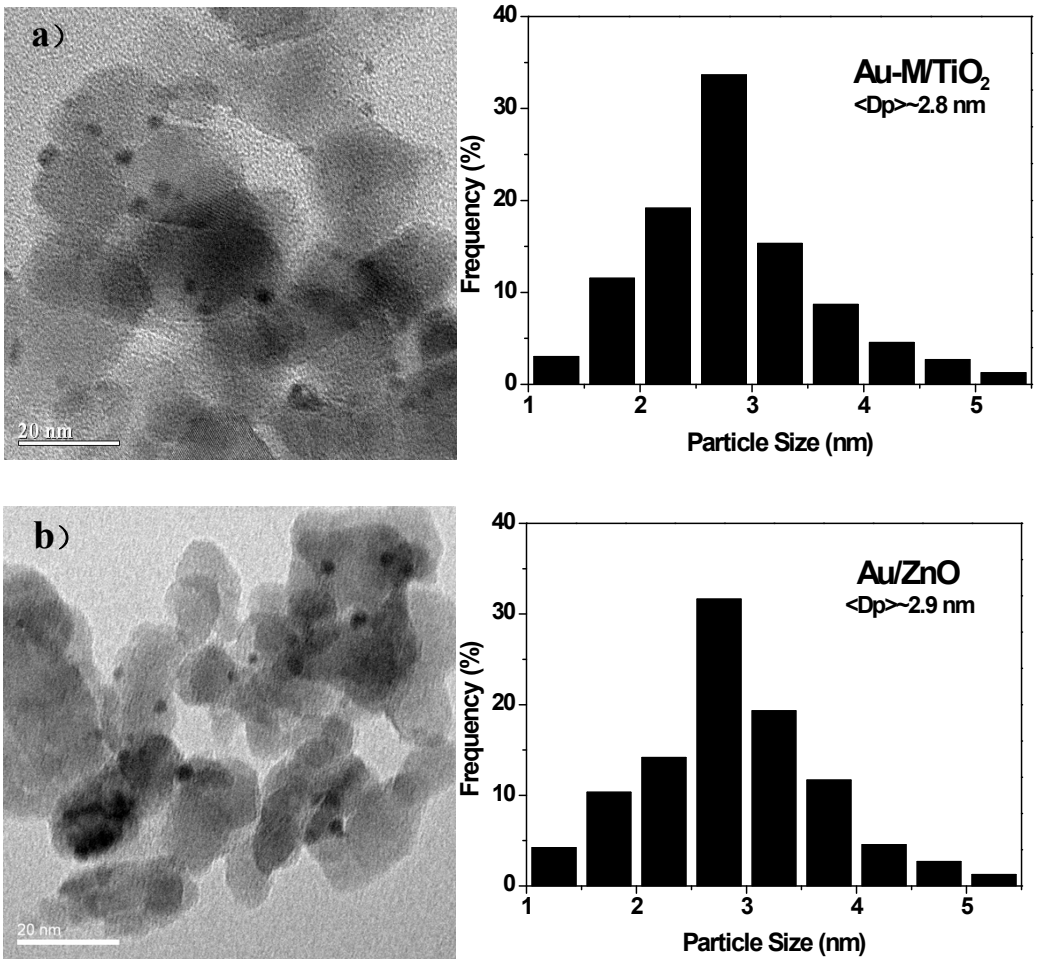
A. Table S1. The gold loading and mean size of Au NPs of the supported Au catalysts.

Entry	Catalyst	Au （wt.%）	Mean size of Au NPs(nm)[a]
1	Au-M/TiO_2	1.0	2.8
2	Au/ZnO	1.0	2.9
3	Au/Al_2O_3	1.0	2.8

4	Au/Fe_2O_3	4.5	3.3
5	Au/CeO_2	0.5	2.9[b]
6	Au/ZrO_2	0.8	2.0[b]
7	Au/SiO_2	1.0	1.9[c]
8	Au/C	1.0	3.2[c]

[a] Determined from TEM. [b] See ref. S1. [c] See ref. S2.

B. TEM images



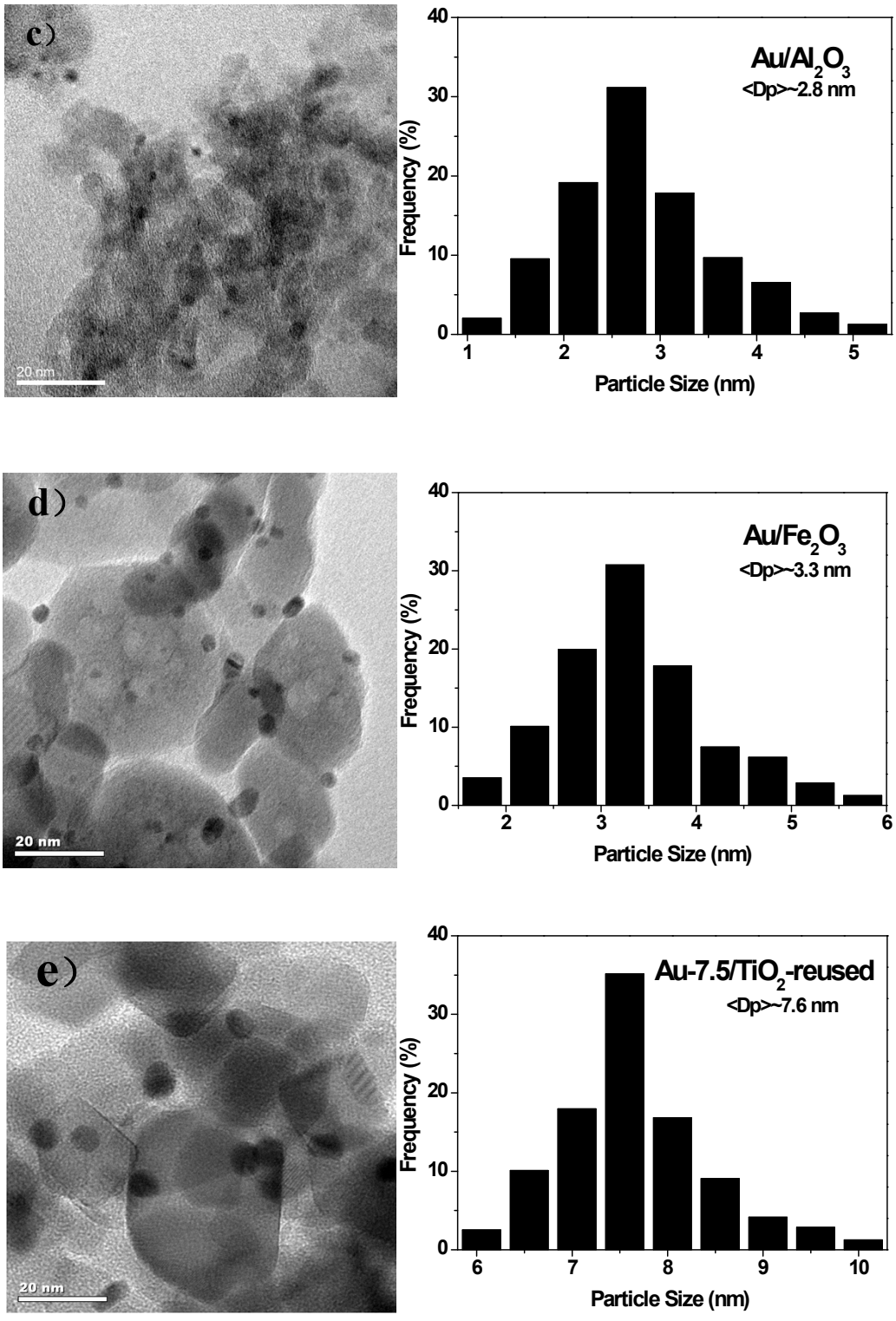


Figure S1 RepresentativeTEM image and size distribution of a) Au/TiO_2; b) Au/ZnO; c) Au/Al_2O_3; d) Au/Fe_2O_3; e) Au-7.5/TiO_2 (after five runs).

C. XPS

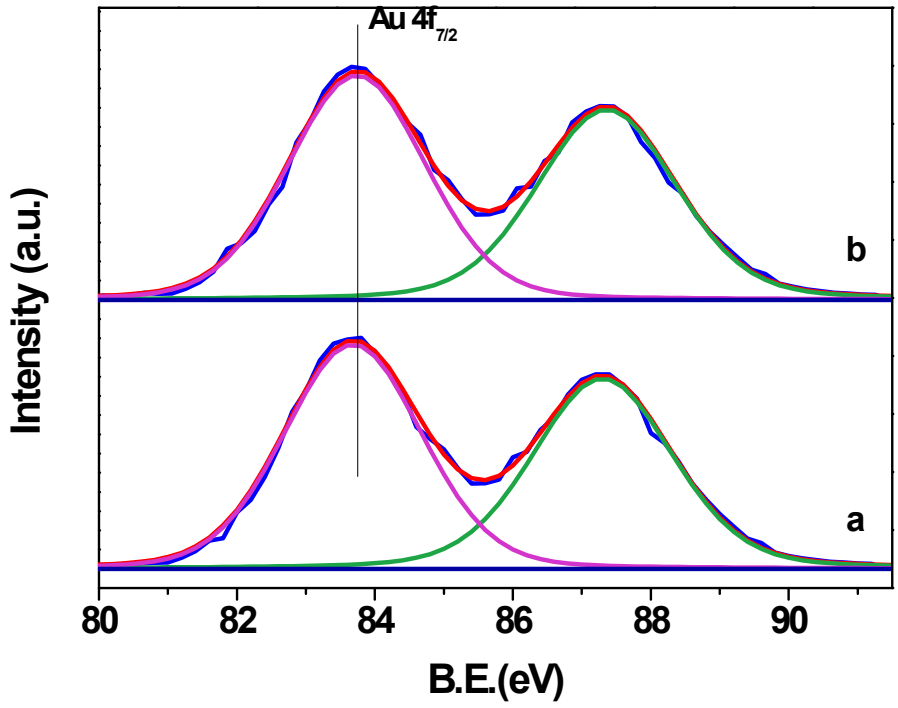


Figure S2. XP spectra of the Au (4f) signal for Au/ TiO_2: (a) Au-7.5/TiO_2; (b) Au-7.5/TiO_2 after five runs.

Table S2. Effect of solvents on the reduction of *m*-DNB over Au-M/TiO_2.[a]

Entry	Conv.[b](%)	Sel.[b](%)		
		m-NA	*m*-PDA	*m*-NNB
Ethanol	98	66	18	16
i-Propanol	99	55	23	22
THF	75	63	15	22
Toluene	40	65	16	19
CH_2Cl_2	29	66	19	15
Dioxane	31	65	25	10

[a] Reaction conditions: 0.5mmol *m*-DNB, Au-M/TiO_2(Au: 0.5mol%), 5 ml solvent, 60 ^oC, 3 MPa H_2,1 h. [b] Conversion and selectivity determined by GC.

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Table S3. Effect of solvents on the reduction of *m*-DNB over Au-M/TiO_2.[a]

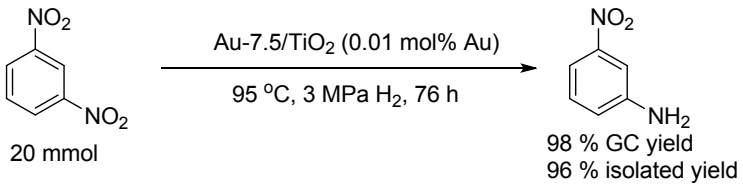
Entry	T [°C]	P [MPa]	t [h]	Conv.[b] [%]	Sel.[b] for *m*-NA [%]
1	60	4	0.7	98	59
2	60	3	1.0	98	66
3	60	2	1.5	95	64
4	60	1	3.5	98	67
5	100	3	0.5	97	60
6	80	3	0.6	98	61
7	40	3	4.5	97	68

[a] Reaction conditions: 0.5 mmol *m*-DNB, Au-M /TiO_2(Au: 0.5 mol%), 5 ml ethanol.

[b] Conversion and selectivity determined by GC

.

D. 20-mmol scale synthesis of *m*-NA



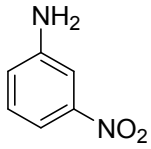
Scheme S1. 20mmol scale reduction of *m*-DNB.

References

[S1]X. Liu, S. Ye, H. Q. Li, Y. M. Liu, Y. Cao and K. N. Fan, *Catal. Sci. Technol.*, 2013, **3**, 3200.

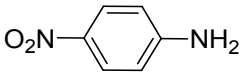
[S2]Y. M. Liu, L. He, M. M. Wang, Y. Cao, H. Y. He and K. N. Fan, *ChemSusChem*, 2012, **5**, 1392.

Characterization of Products



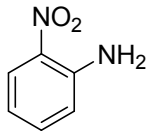
3-Nitroaniline

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 8.0, 2.2 Hz, 1 H), 7.49 (t, *J* = 2.2 Hz, 1 H), 7.27 (t ,*J* = 8.0 Hz, 1 H), 6.95 (dd, *J* = 8.0, 2.2 Hz, 1 H), 4.00 (s, 2 H).^{13}C NMR (100 MHz, $CDCl_3$): δ 149.27, 147.49, 129.94, 120.66, 113.15, 109.03.



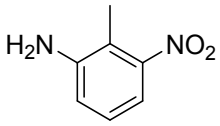
4-Nitroaniline

^{1}H NMR (400 MHz, DMSO): δ 7.93 (d, *J* = 9.2 Hz, 2 H), 6.71 (br, 2 H), 6.58 (d, *J* = 9.0 Hz, 2 H).^{13}C NMR (100 MHz, DMSO): δ 155.76, 135.65, 126.46, 112.42.



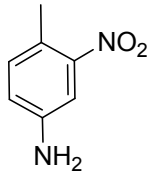
2-Nitroaniline

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.0 Hz, 1 H), 7.36 (t, *J* = 8.1 Hz, 1 H), 6.81 (d, *J* = 8.3 Hz, 1 H), 6.70 (t, *J* = 8.0 Hz, 1 H), 5.98 (s, 2 H).



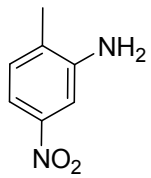
2-Methyl-3-nitroaniline

^{1}H NMR (400 MHz, DMSO): δ 7.07 (t, *J* = 8.0 Hz, 1 H), 6.93 (d, *J* = 7.9 Hz, 1 H), 6.88 (d, *J* = 8.0 Hz, 1 H), 5.54 (s, 2 H), 2.07 (s, 3 H).^{13}C NMR (100 MHz, DMSO): δ 151.98, 149.07, 127.13, 117.89, 113.97, 111.00, 12.88.



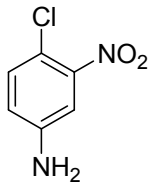
4-Methyl-3-nitroaniline

^{1}H NMR (400 MHz, DMSO): δ 7.15 (d, *J* = 2.4 Hz, 1 H), 7.09 (d, *J* = 8.3 Hz, 1 H), 6.80 (dd, *J* = 8.2, 2.4 Hz, 1 H), 5.55 (s, 2 H), 2.31 (s, 3 H).^{13}C NMR (100 MHz, DMSO): δ 149.26, 147.96, 133.07, 119.02, 118.58, 108.21, 18.78.



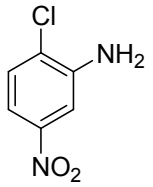
2-Methyl-5-nitroaniline

^{1}H NMR (400 MHz, DMSO): δ 7.79 (d, *J* = 2.5 Hz, 1H), 7.56 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 2.16 (s, 3 H).



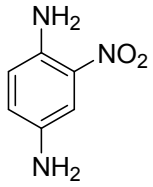
4-Chloro-3-nitroaniline

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.6 Hz, 1 H), 7.13 (d, *J* = 2.6 Hz, 1 H), 6.78 (dd, *J* = 8.6, 2.7 Hz, 1 H), 4.00 (s, 2 H).^{13}C NMR (125 MHz, $CDCl_3$): δ 148.34, 145.99, 132.28, 119.38, 114.96, 110.94.



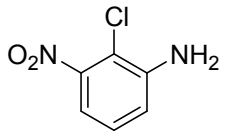
2-Chloro-5-nitroaniline

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 2.4 Hz, 1H), 7.53 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 4.40 (s, 2 H).^{13}C NMR (125 MHz, $CDCl_3$): δ 147.60, 143.78, 130.07, 125.40, 113.47, 109.87.



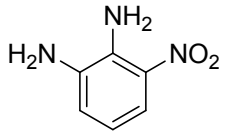
2-Nitrobenzene-1,4-diamine

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, *J* = 2.6 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 1H), 5.71 (br, 2H), 3.49 (br, 2H).^{13}C NMR (125 MHz, $CDCl_3$): δ 145.10, 127.51, 118.58, 114.39, 110.75, 105.78.

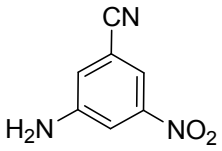


2-Chloro-3-nitroaniline

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21–7.11 (m, 2 H), 6.97–6.89 (m, 1 H), 4.40 (br, 2 H).^{13}C NMR (125 MHz, $CDCl_3$): δ 147.61, 143.77, 130.07, 125.40, 113.47, 109.87.

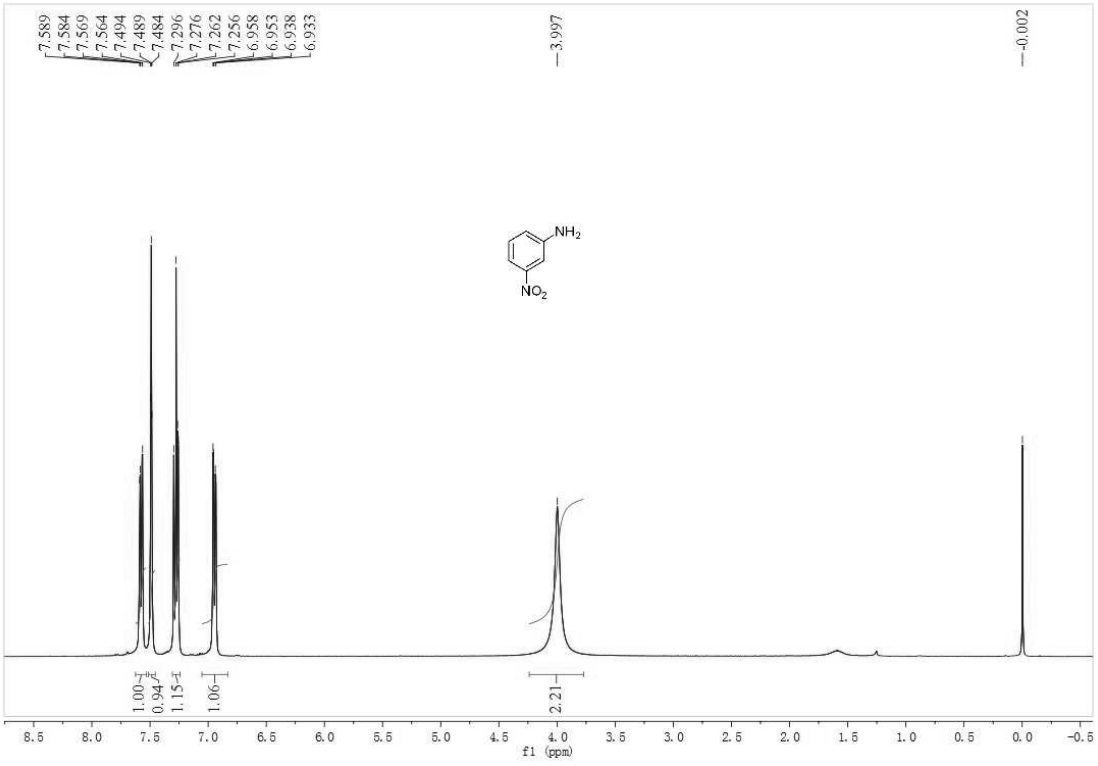


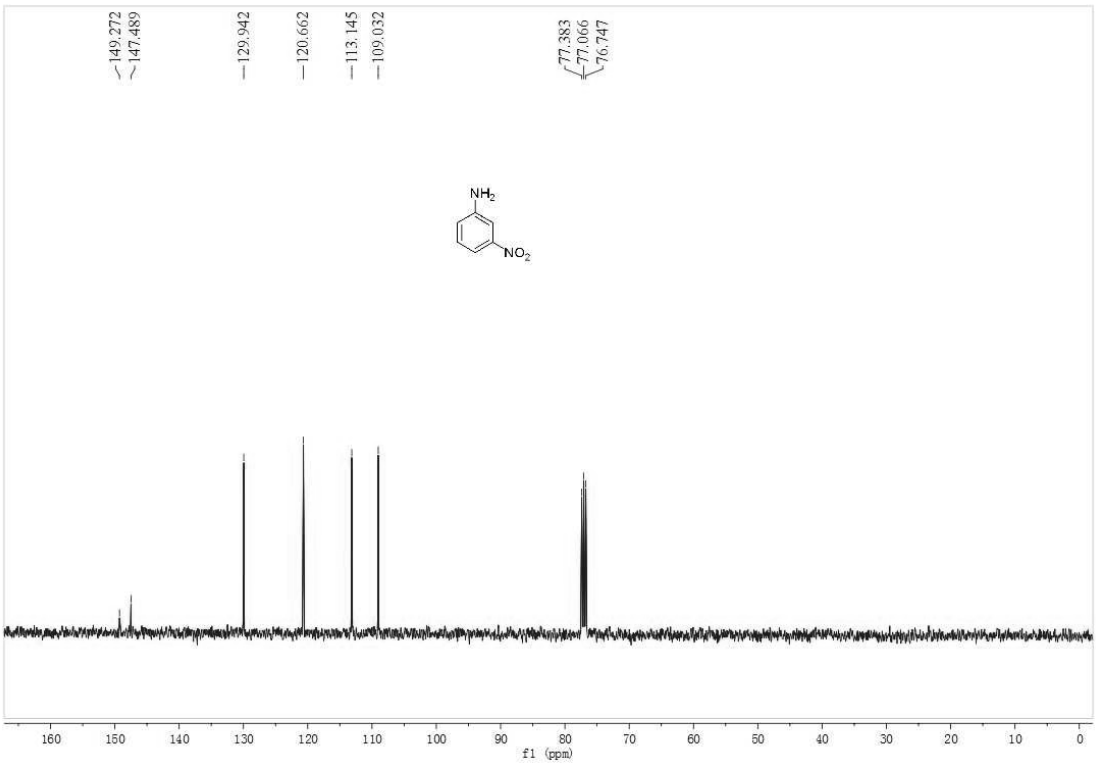
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.7 Hz, 1 H), 6.93 (d, *J* = 7.4 Hz, 1 H), 6.62 (t, J = 8.1 Hz, 1 H), 5.94 (br, 2 H), 3.43 (br, 2 H).^{13}C NMR (125 MHz, $CDCl_3$): δ 136.78, 135.50, 133.66, 122.25, 118.13, 116.73.



3-Amino-5-nitrobenzonitrile

^{1}H NMR (400 MHz, DMSO): δ 7.70–7.66 (m, 1 H), 7.63 (t, *J* = 2.2 Hz, 1 H), 7.25–7.22 (m, 1 H), 6.33 (br, 2 H).^{13}C NMR (100 MHz, DMSO): δ 151.28, 149.46, 121.84, 118.14, 113.23, 112.84, 111.88.

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110
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50
40
30
20
10
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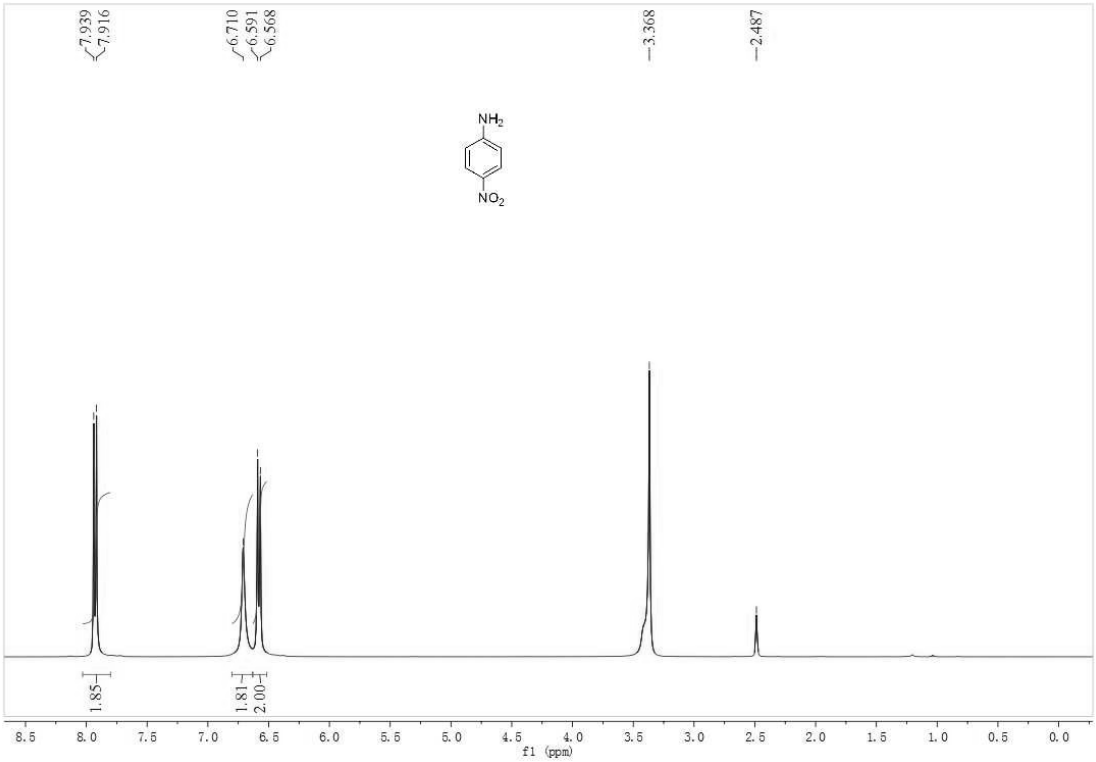
f1 (ppm)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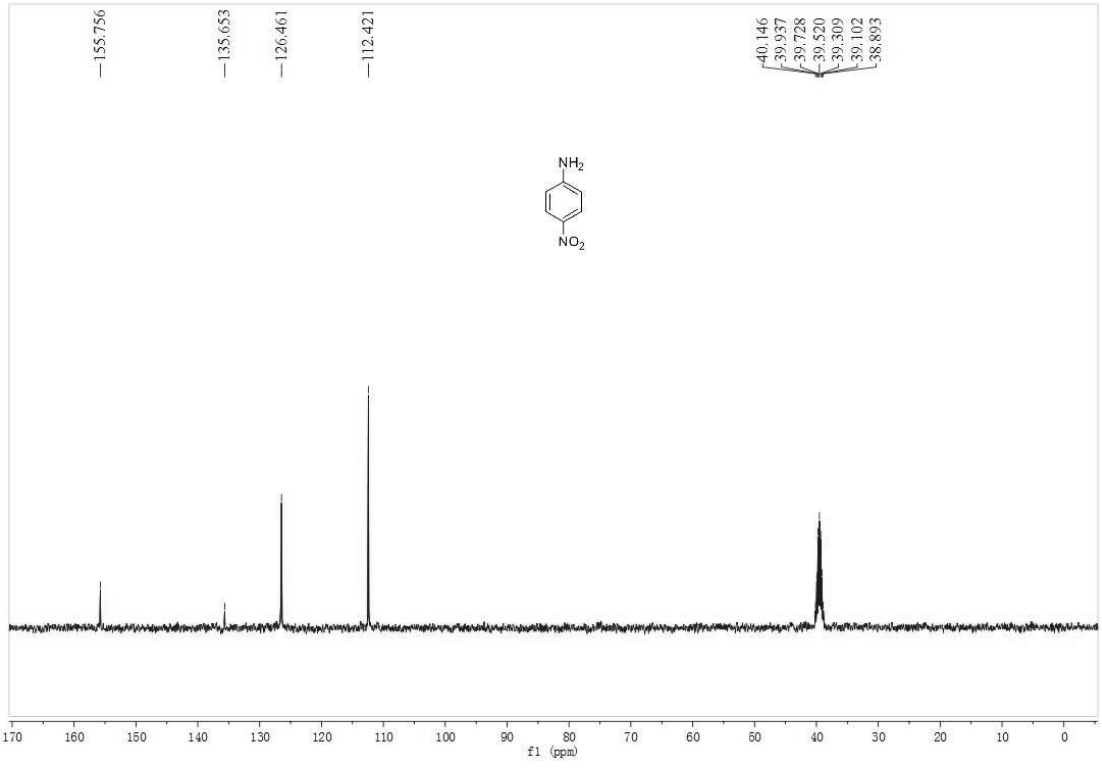
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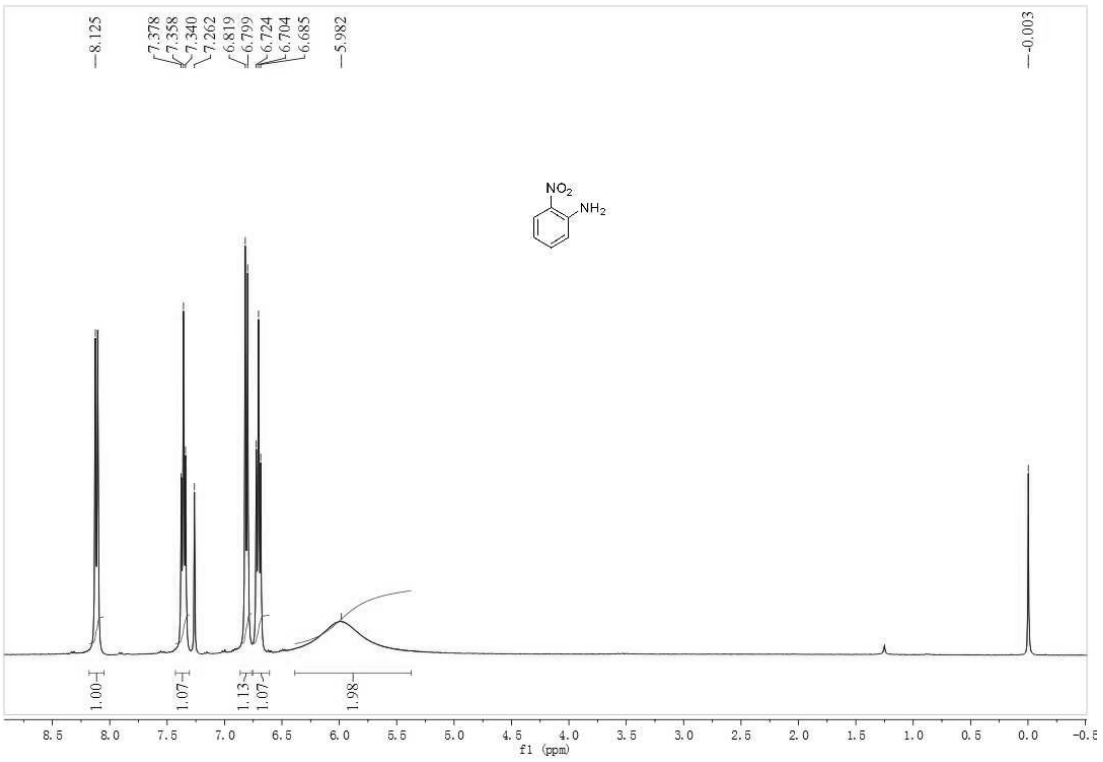
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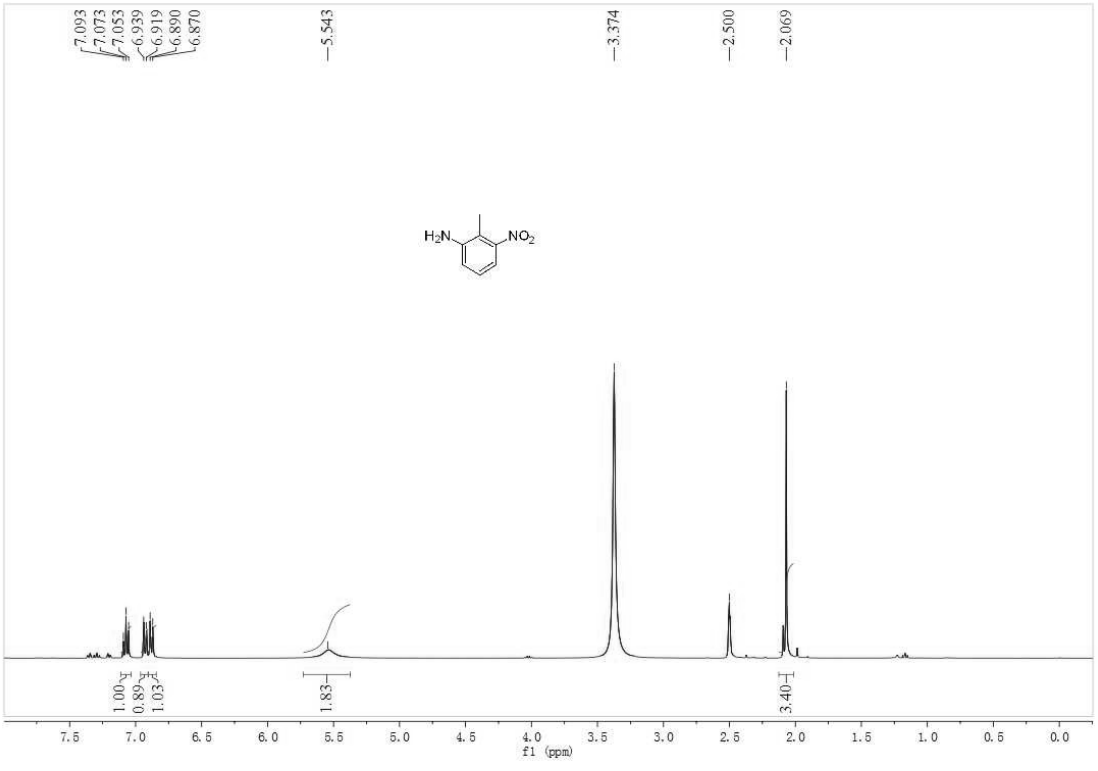
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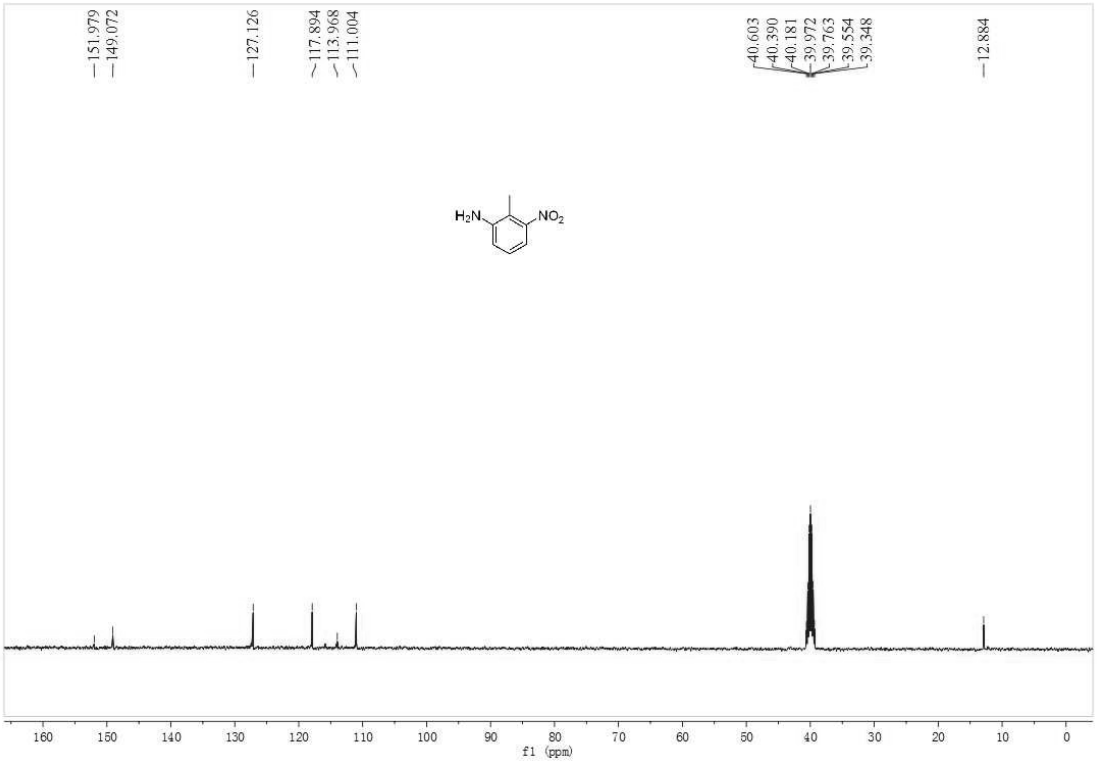
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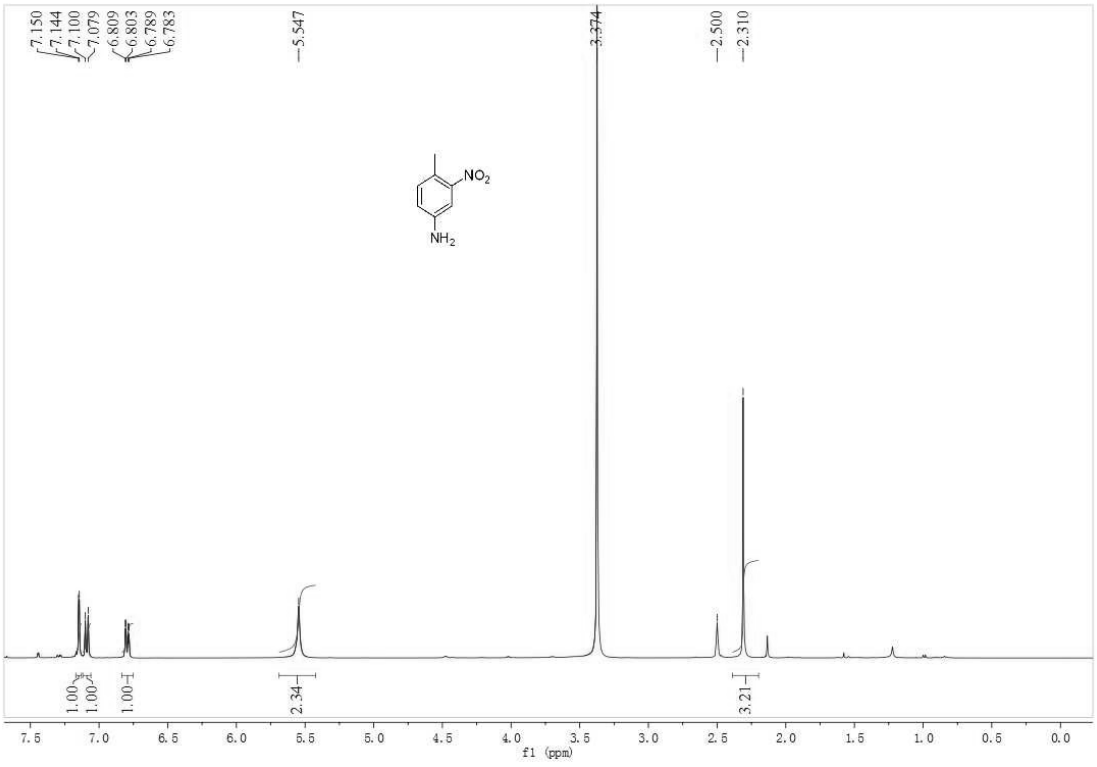
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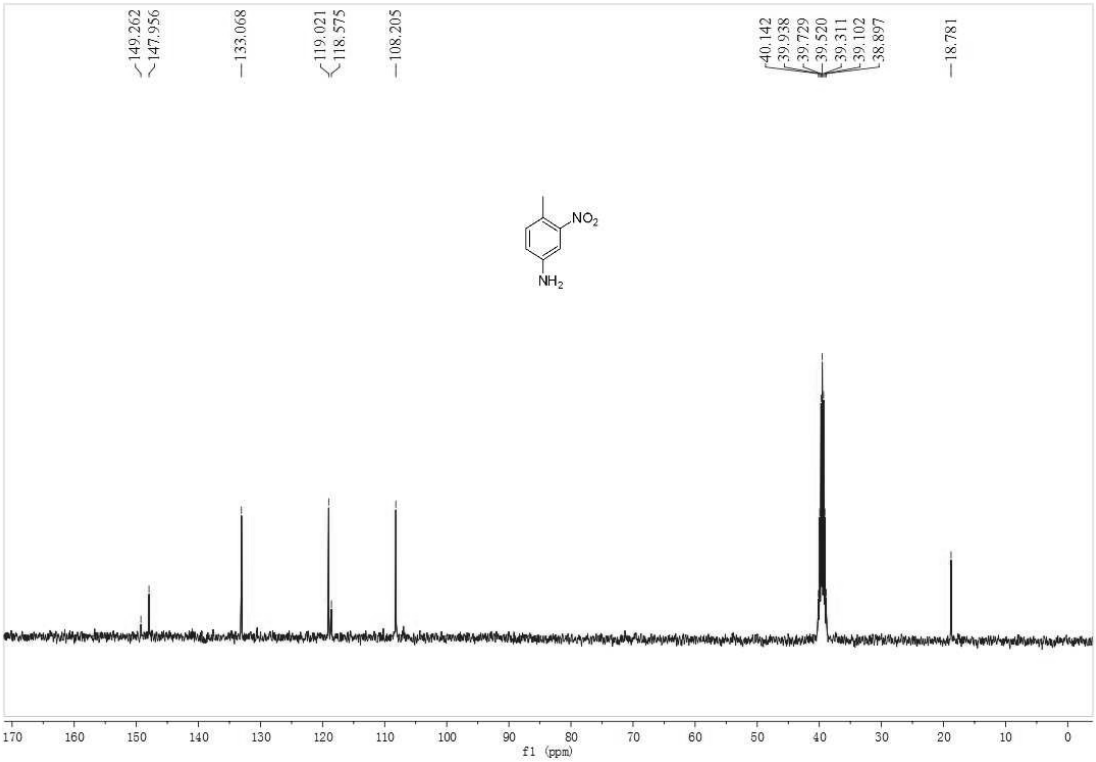
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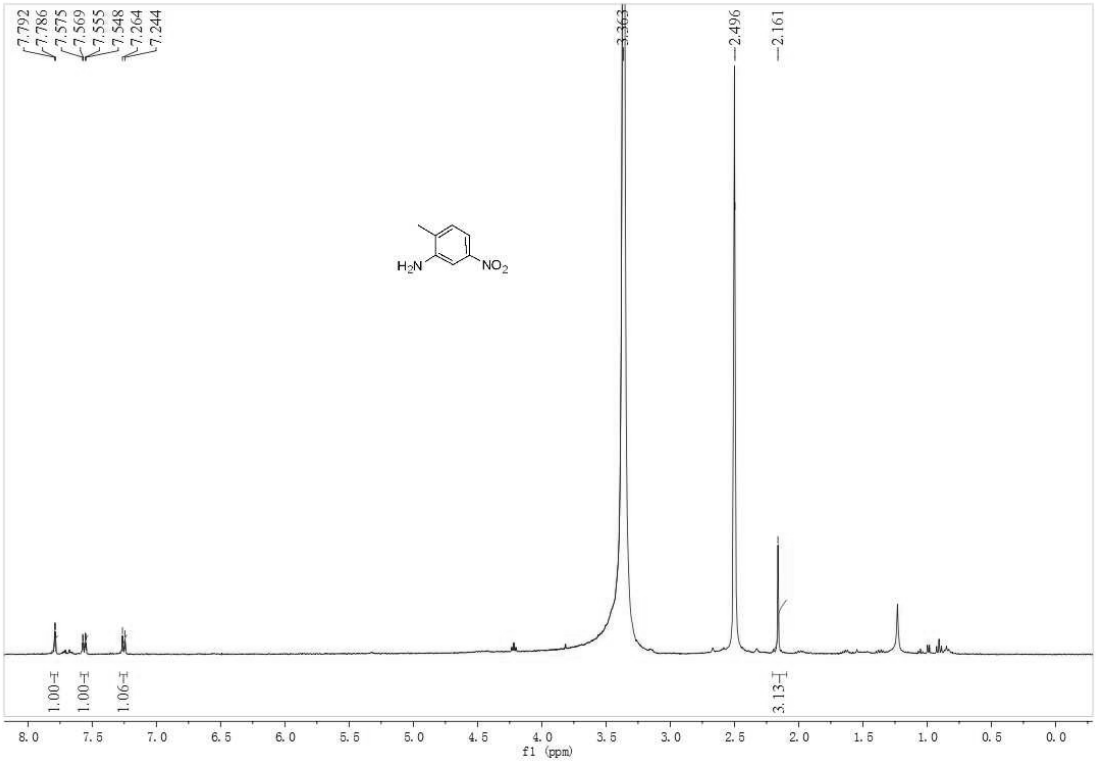
f1 (ppm)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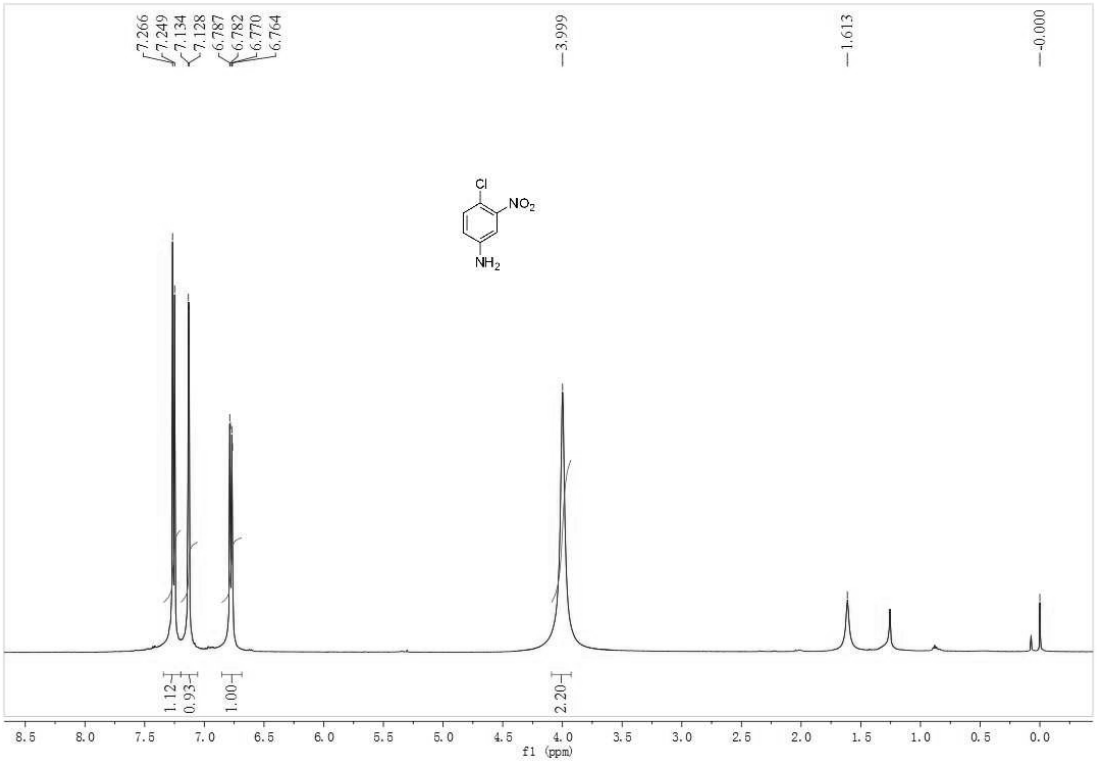
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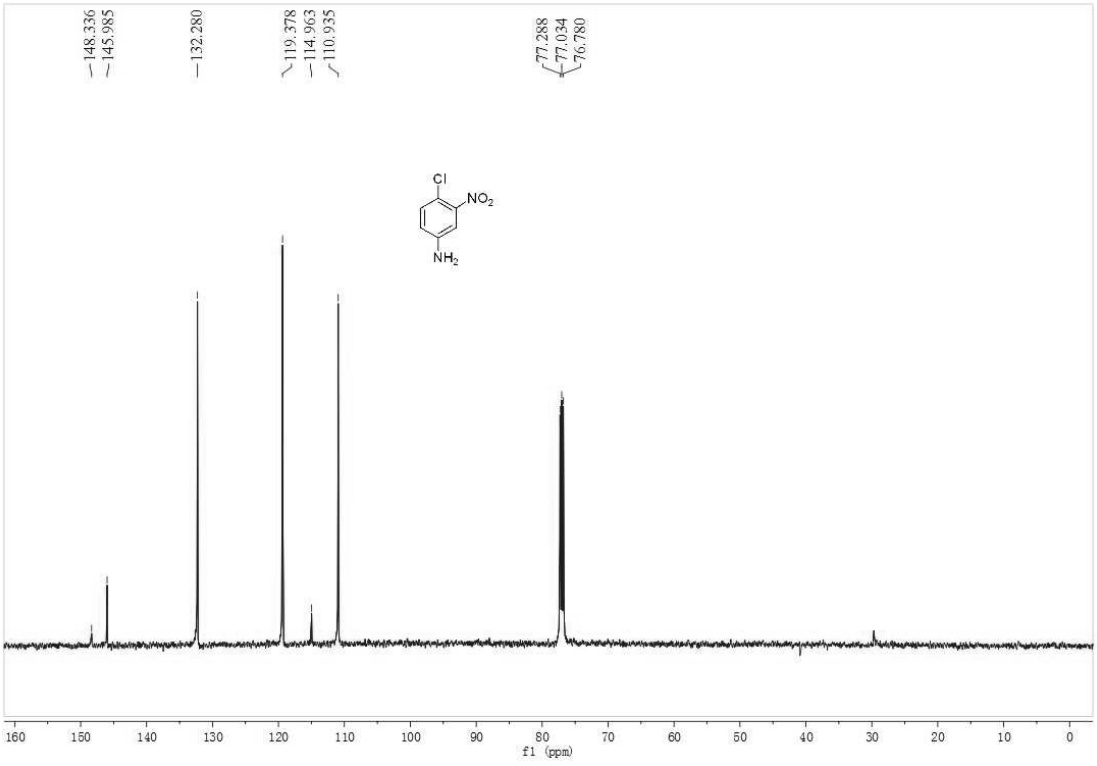
f1 (ppm)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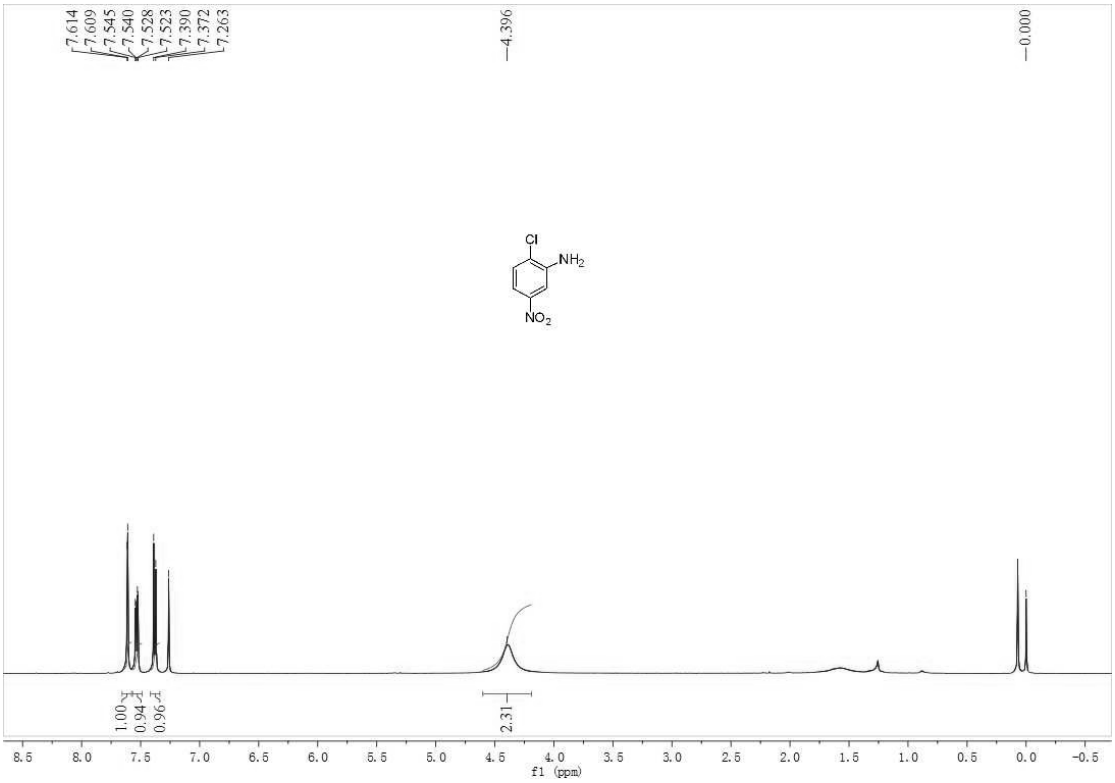
f1 (ppm)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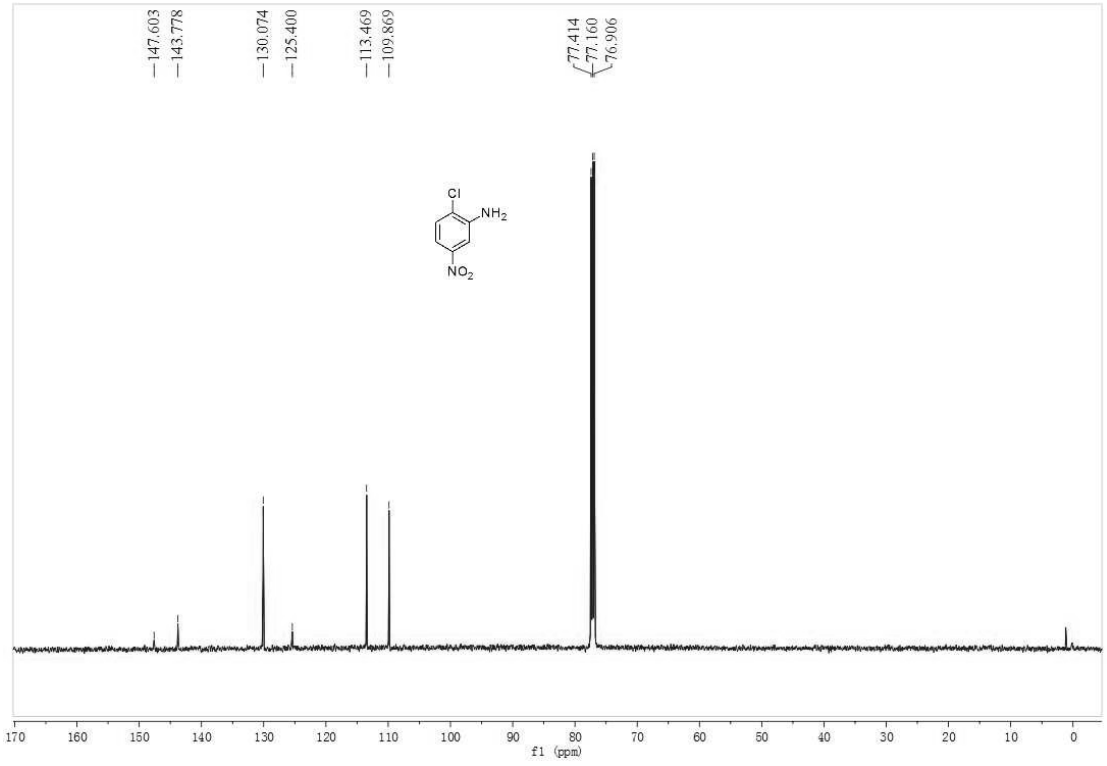
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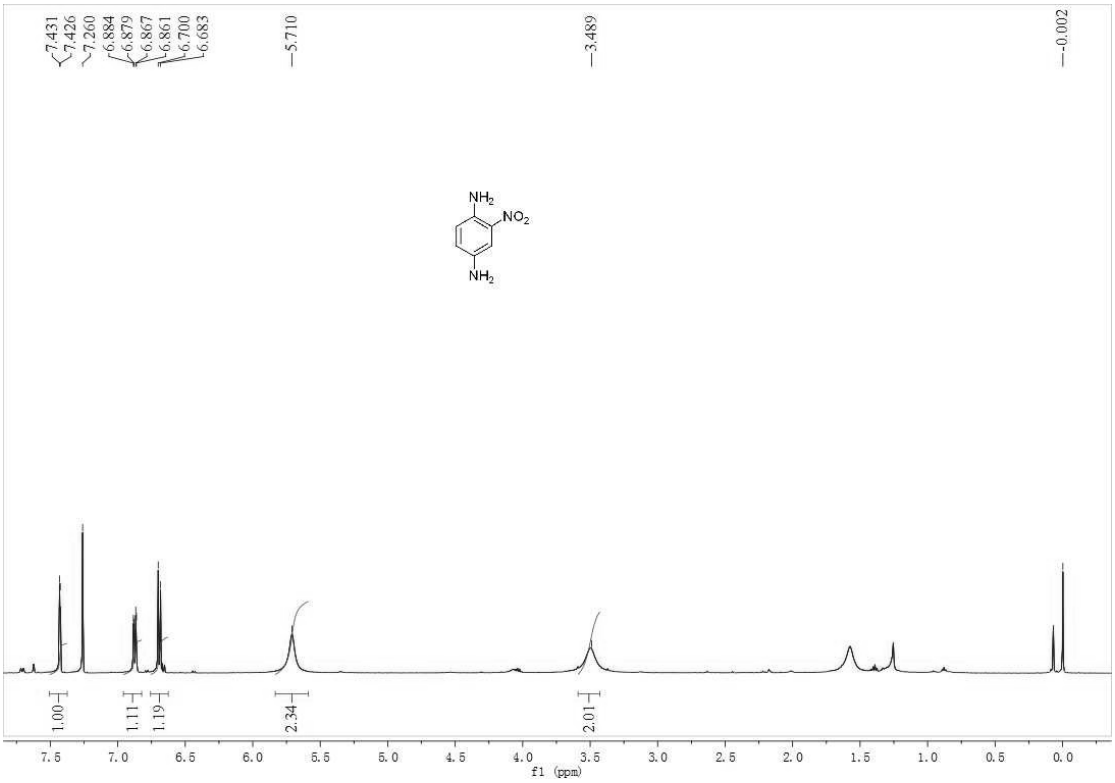
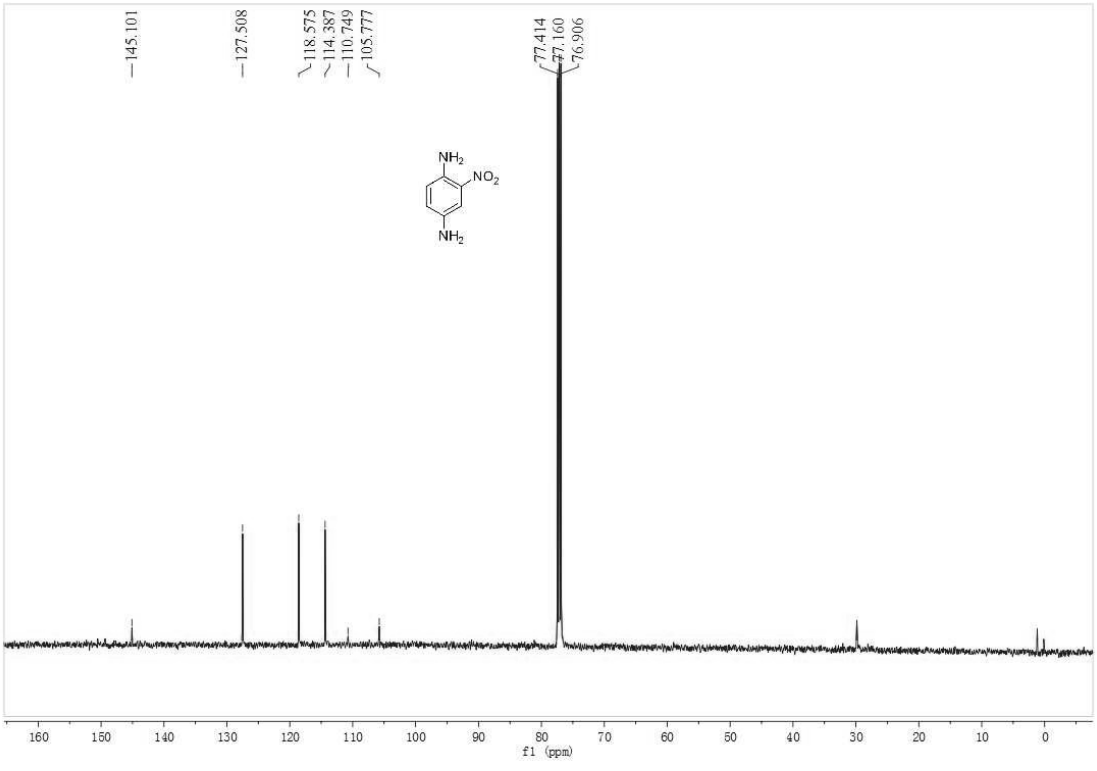
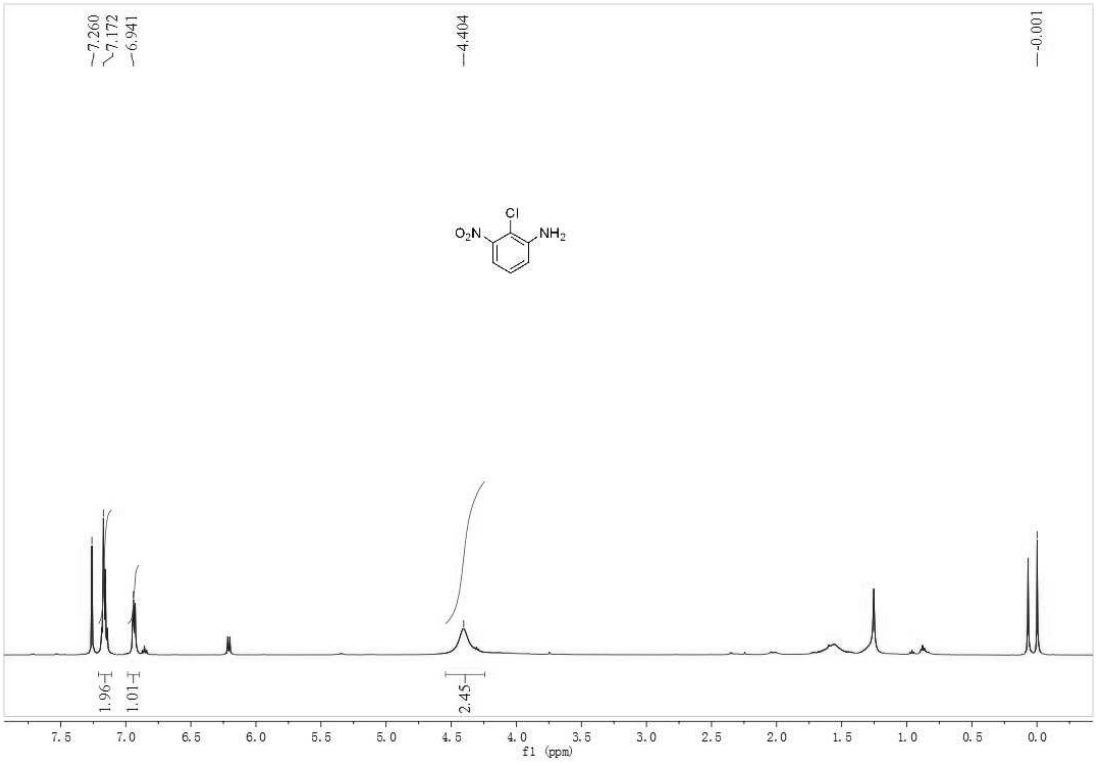
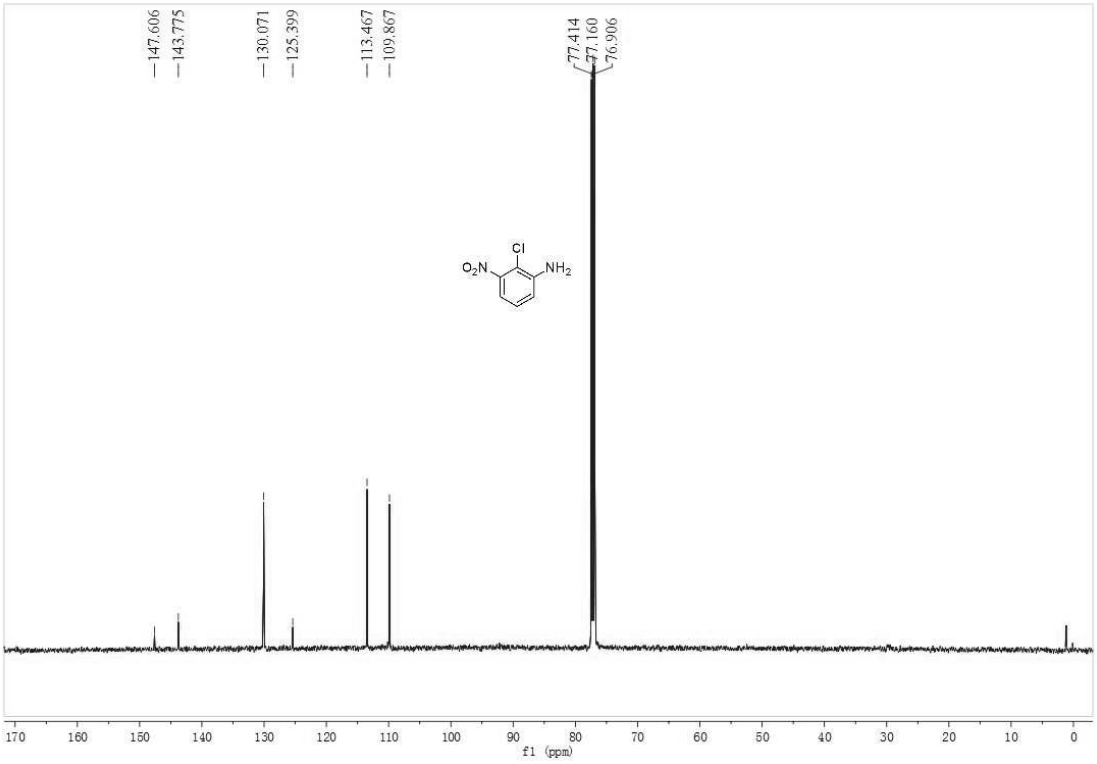
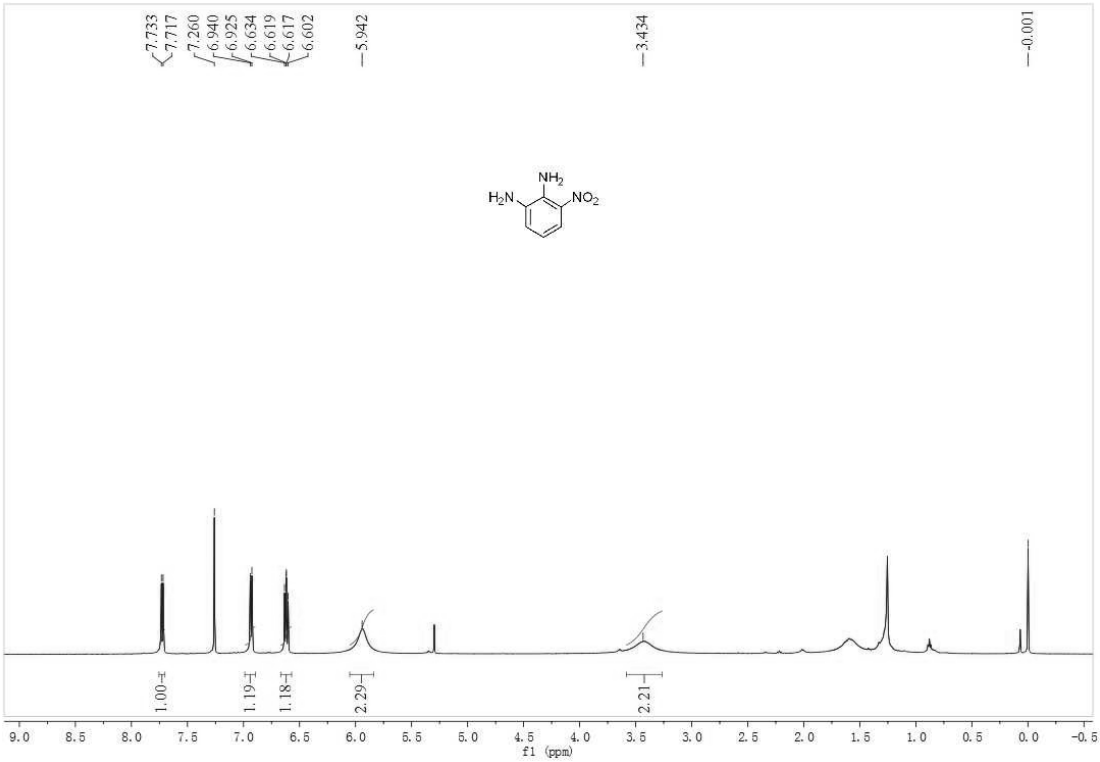
Cl
NH2
NO2
f1 (ppm)

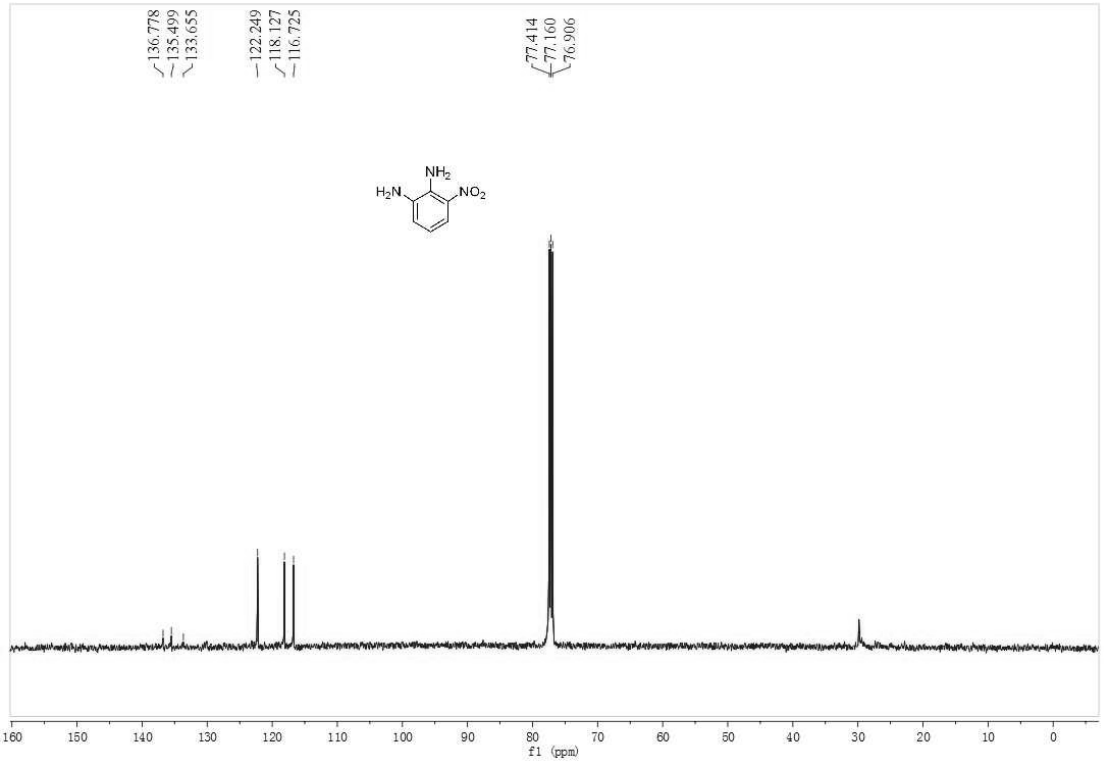

7.431
7.426
7.260
6.884
6.879
6.867
6.861
6.700
6.683
5.710
3.489
0.002
NH2
NO2
NH2
1.00
1.11
1.19
2.34
2.01
f1 (ppm)

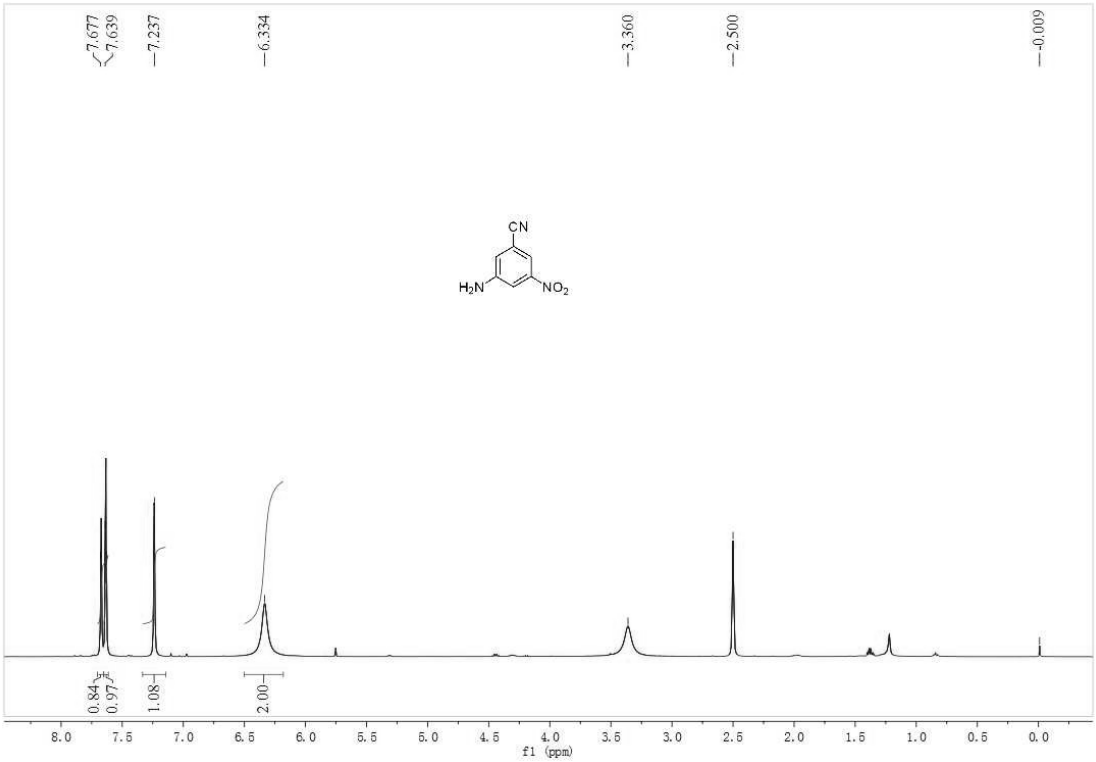

145.101
127.508
118.575
114.387
110.749
105.777
77.414
77.160
76.906
NH2
NO2
NH2
f1 (ppm)

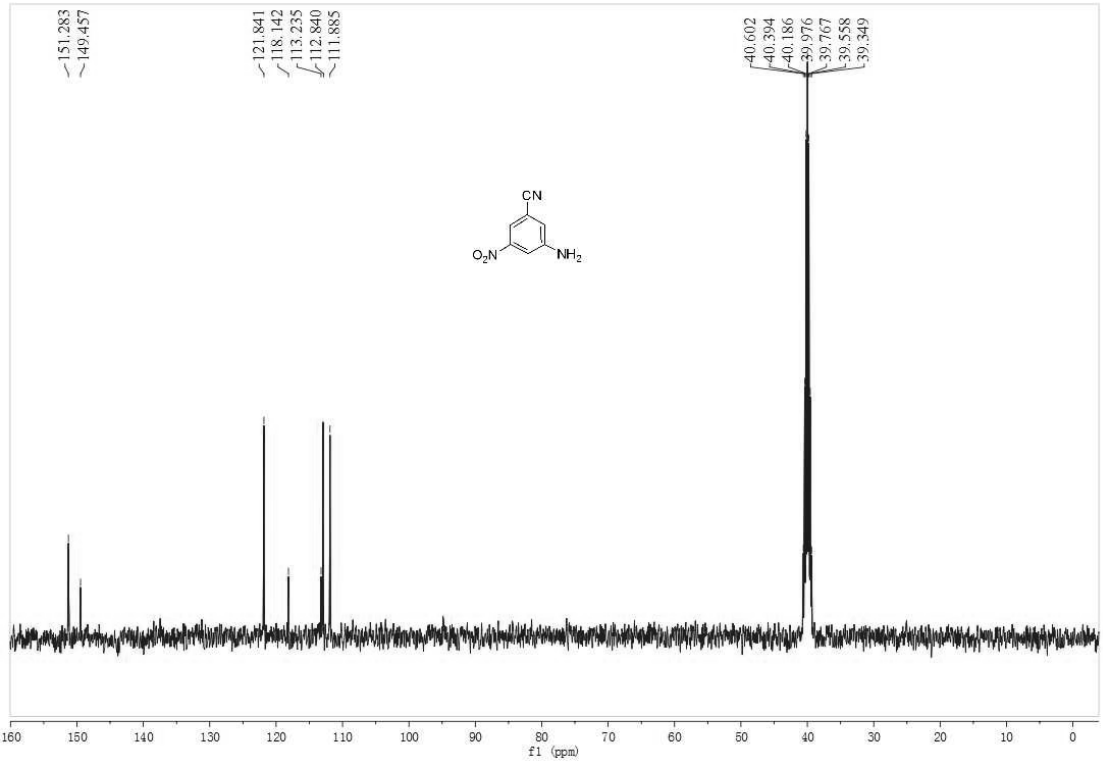

7.260
7.172
6.941
4.404
0.001
Cl
O2N
NH2
1.96
1.01
2.45
f1 (ppm)


147.606
143.775
130.071
125.399
113.467
109.867
77.414
77.160
76.906
Cl
O2N
NH2
f1 (ppm)


7.733
7.717
7.260
6.940
6.925
6.634
6.619
6.617
6.602
5.942
3.434
0.001
NH2
H2N
NO2
1.00
1.19
1.18
2.29
2.21
f1 (ppm)


136.778
135.499
133.655
122.249
118.127
116.725
77.414
77.160
76.906
NH2
H2N
NO2
f1 (ppm)


7.677
7.639
7.237
6.334
3.360
2.500
0.009
CN
H2N
NO2
0.84
0.97
1.08
2.00
f1 (ppm)


151.283
149.457
121.841
118.142
113.235
112.840
111.885
40.602
40.394
40.186
39.976
39.767
39.558
39.349
CN
O2N
NH2
f1 (ppm)