Electronic Supplementary Material (ESI) for Nanoscale

Design of an ultrasmall Au nanocluster-CeO_2 Mesoporous Nanocomposite Catalyst for Nitrobenzene Reduction

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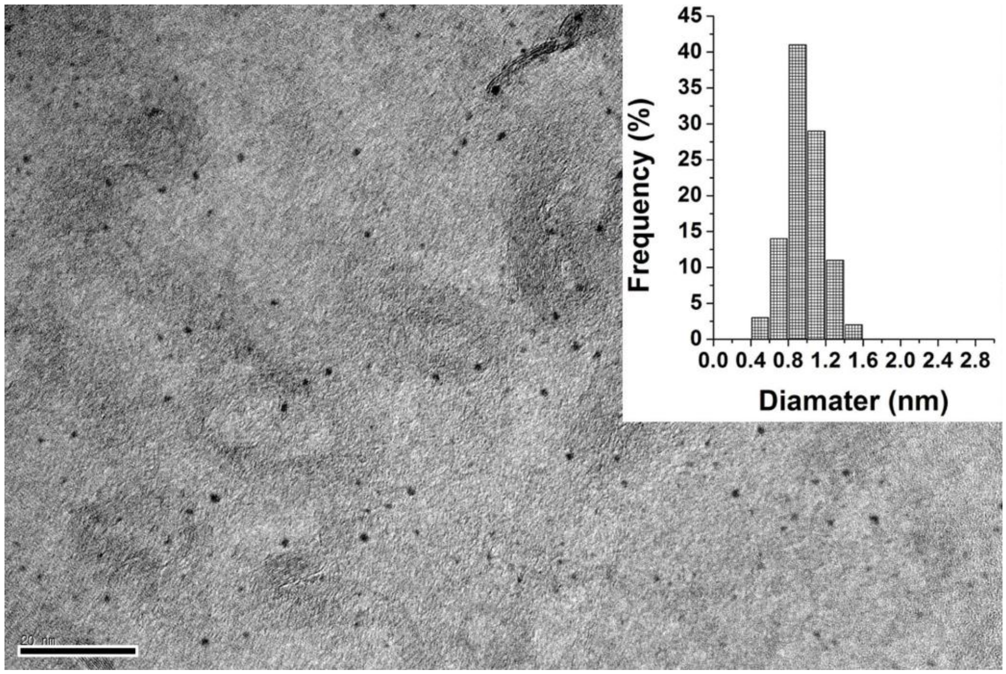


Figure S1. TEM image of Au NCs, the scale bar is 20 nm (The inset is size distribution of them)

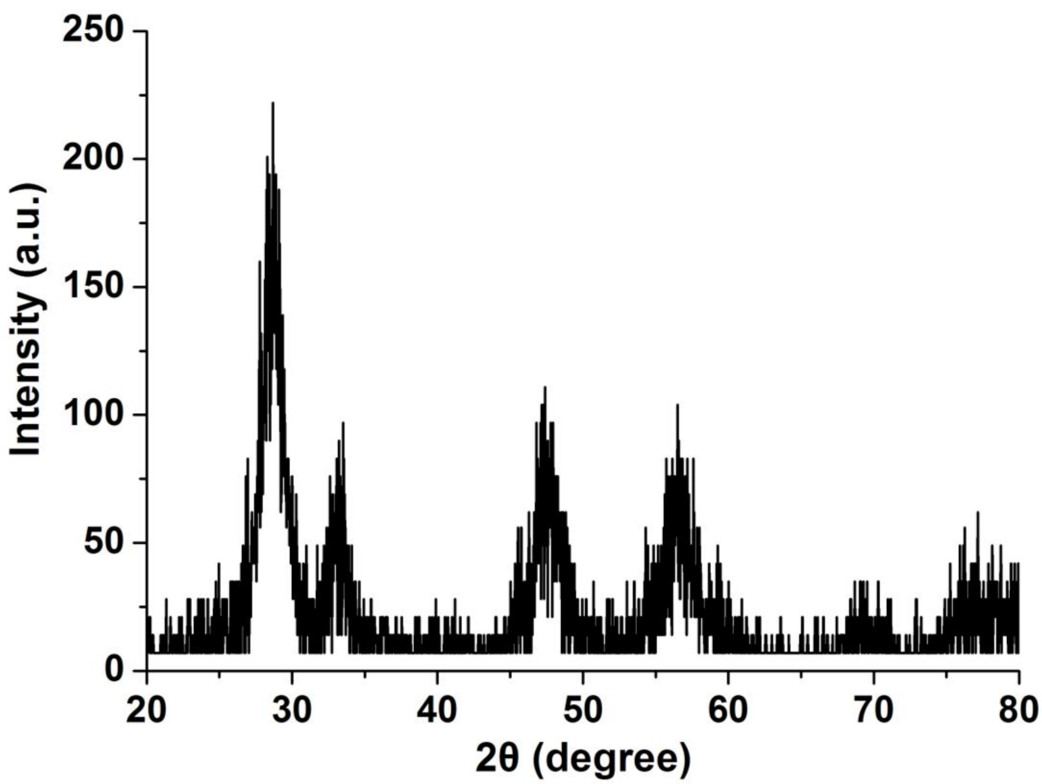


Figure S2. XRD pattern of CeO_2 mesoporous spheres.

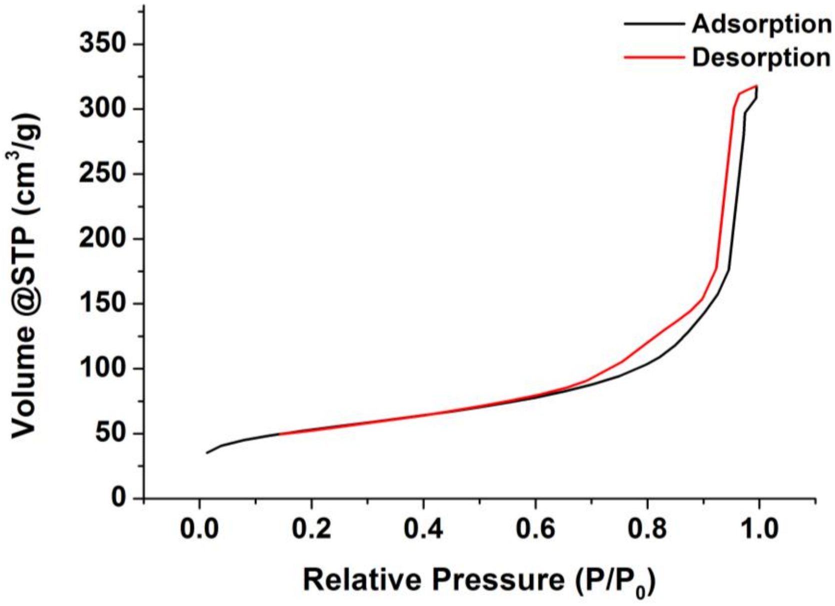


Figure S3. N_2 adsorption-desorption isotherm of Au@CeO_2[P]

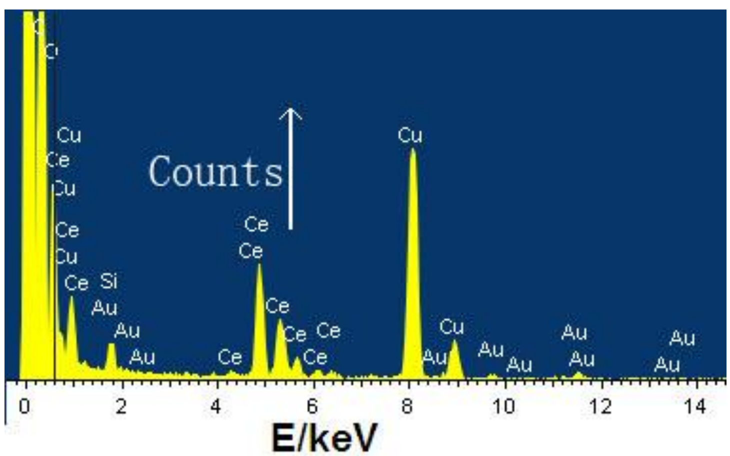


Figure S4. EDS analysis of Au@CeO_2[P].

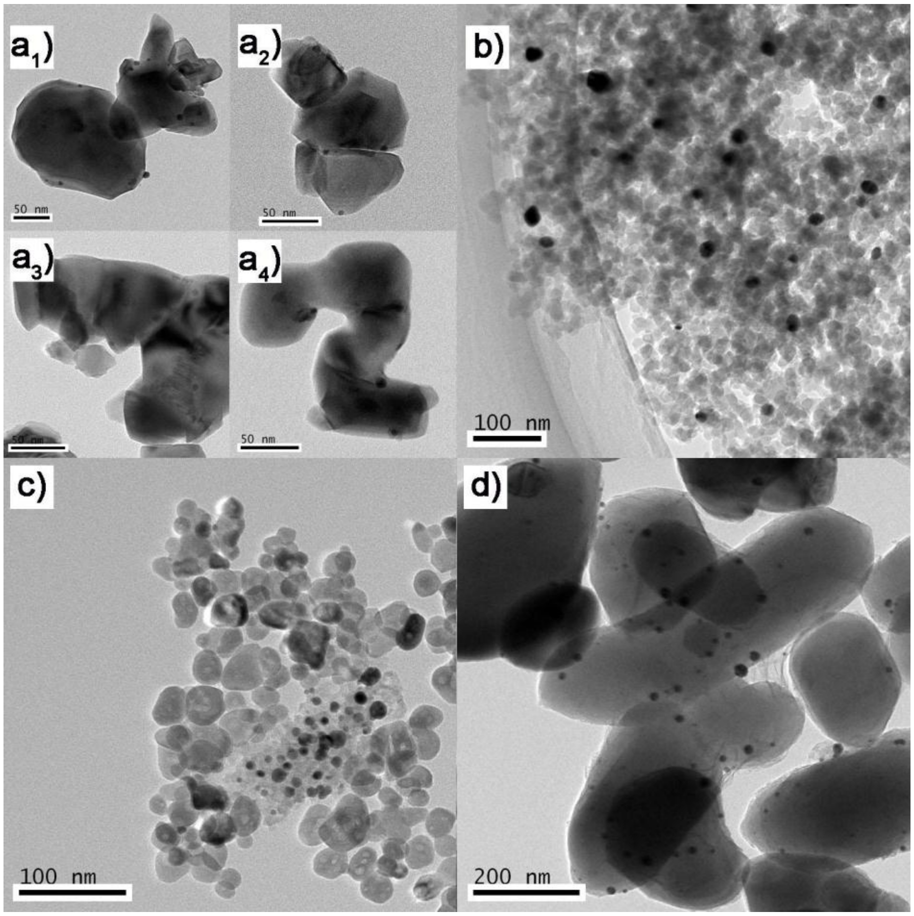


Figure S5. TEM images of Au NCs immobilized on different metal oxide supports (a: amorphous CeO_2; b: SiO_2; c: Fe_2O_3; d: TiO_2. Scales in a, b, c, d are 50 nm, 100 nm, 100 nm and 200 nm, respectively).

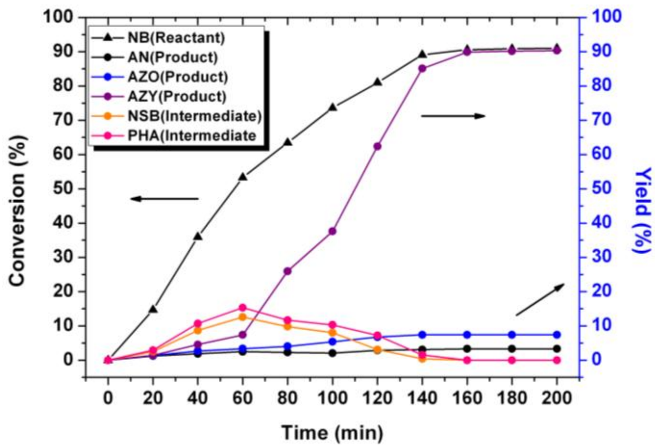
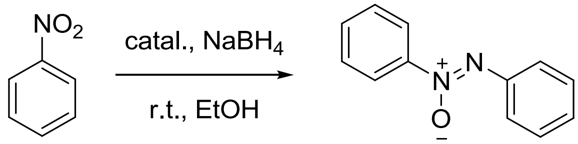


Figure S6. Time conversion plot (yield was determined by GC)

Table S1. Azoxybenzene formation from nitrobenzene at the presence of different reducing agents[a].



Entry	Reducing agent	Time(h)	Conversion(%)
1	$NaBH_4$	3	91
2[b]	H_2	24	NR[c]
3	$LiAlH_4$	3	93.3

[a] All reactions were carried out with 0.2 mL nitrobenzene (2 mmol) and 100/0.25 substrate/Au loading. Sodium borohydride or lithium aluminum hydride was loaded 2 equiv. (4 mmol) of nitrobenzene. All the loading of Au was 0.25% mol of substrate

[b] Hydrogen was provided by bubbling.

[c] NR represents no reaction

Spectroscopic characterization of products

(Z)-1,2-diphenyldiazene oxide

^{1}H NMR (400 MHz, [D$_1$]CDCl$_3$, TMS): δ =7.38 (t, ^3J=(H,H)=7.36Hz, 1H, CH), 7.52 (m, 5H, CH), 8.17 (m, 2H, CH), 8.30 ppm (m, 2H, CH); ^{13}C NMR (100 MHz, [D$_1$]CDCl$_3$, TMS): δ =144.04, 131.58, 129.60, 128.80, 128.70, 125.53, 122.36 ppm.

N-phenylhydroxylamine

^{1}H NMR (400 MHz, $[D_1]CDCl_3$, TMS): δ =6.74 (t, ^{3}J(H,H)=7.27, 1H, CH), 6.84 (d, ^{3}J(H,H)=8.33, 2H, CH), 7.16 (t, ^{3}J(H,H)=7.68, 2H, CH), 8.23(s, 1H, NH), 8.28 ppm (s, 1H, OH); ^{13}C NMR (100 MHz, $[D_1]CDCl_3$, TMS): δ = 149.29, 128.97, 122.63, 114.99 ppm.

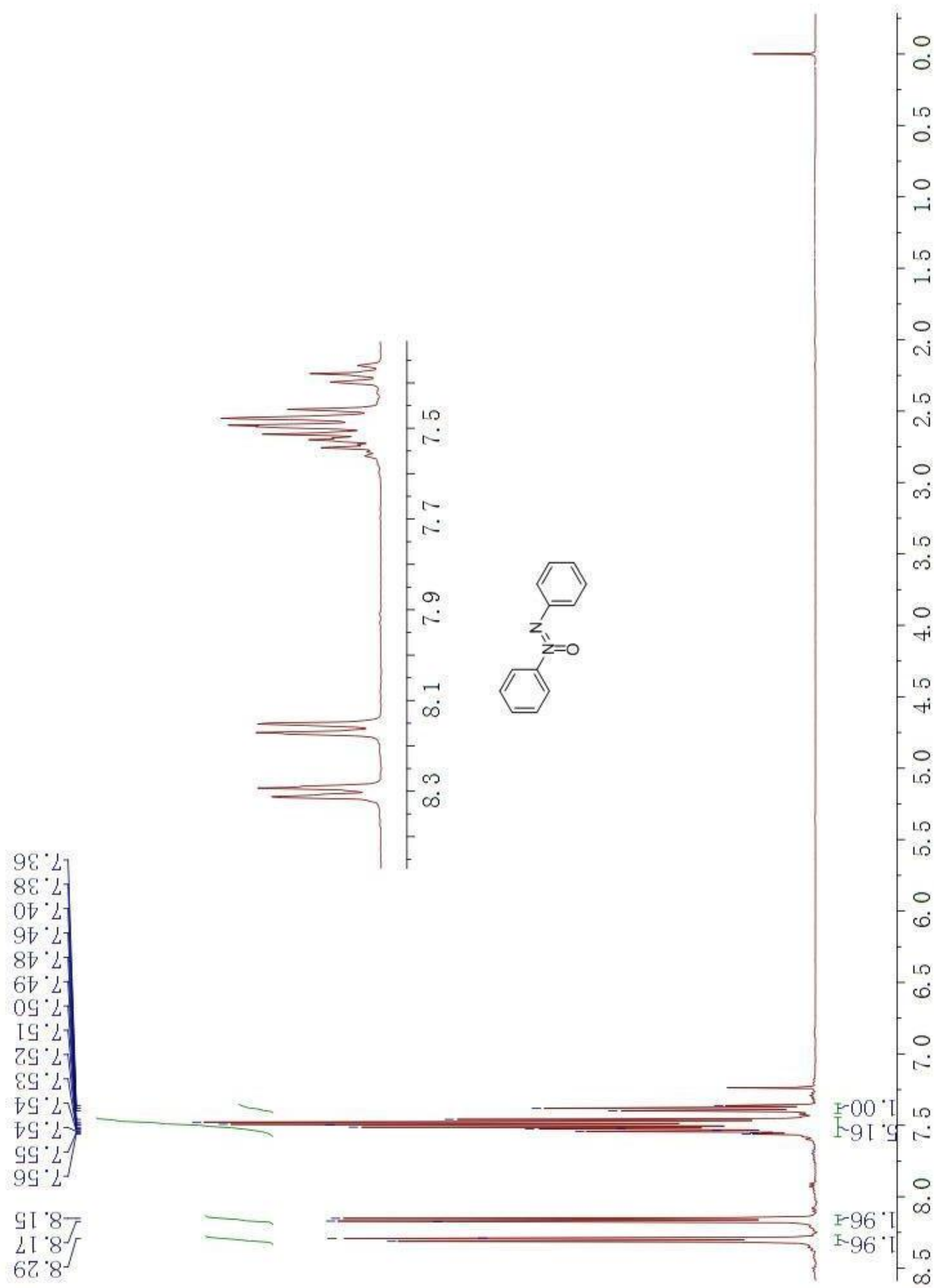
Aniline

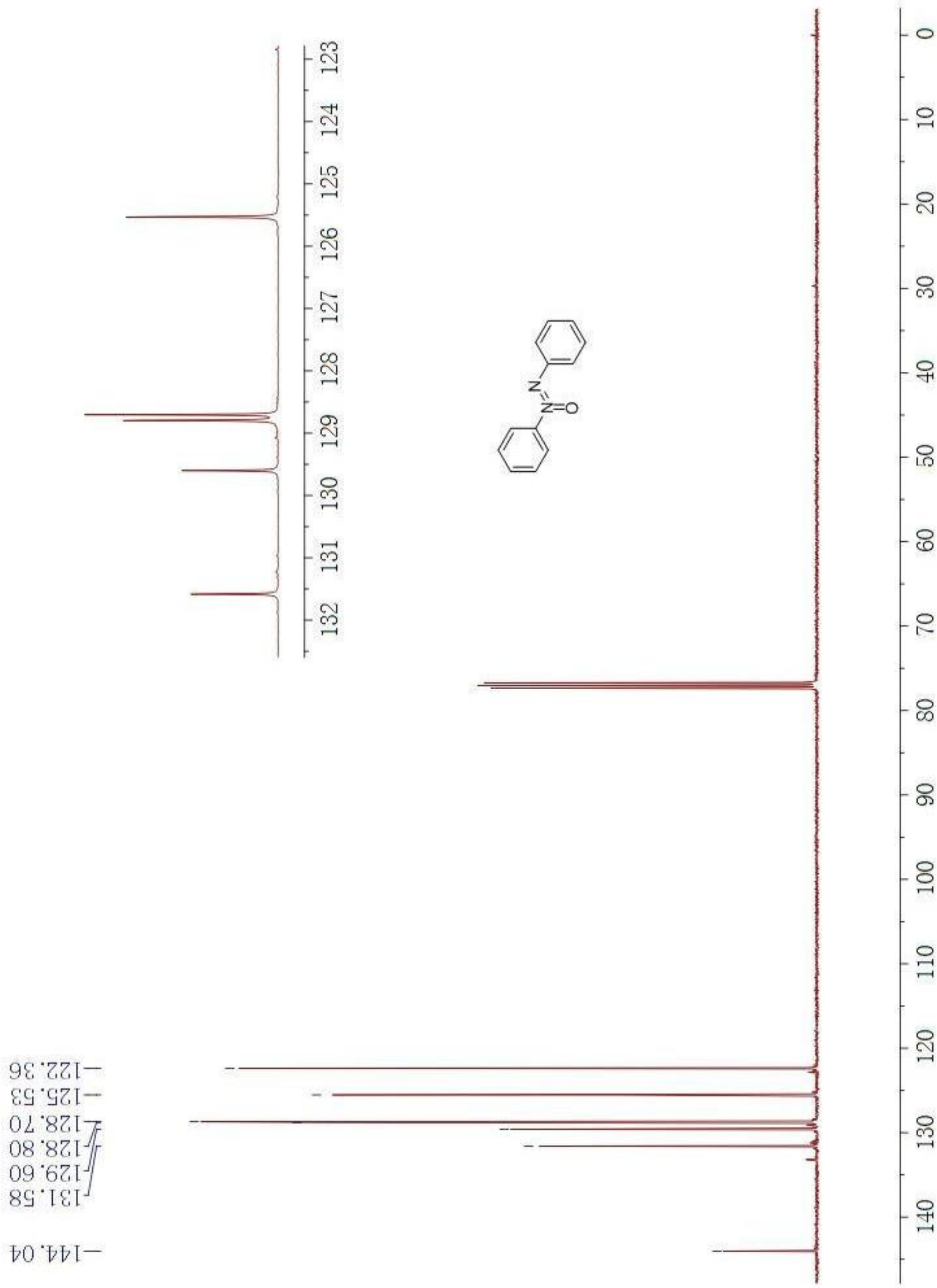
^{1}H NMR (400 MHz, $[D_1]CDCl_3$, TMS): δ =3.53 (s, 2H, NH), 6.60 (d, ^{3}J(H,H)=17.33, 2H, CH), 6.73 (t, ^{3}J(H,H)=6.71, 1H, CH), 8.23(s, 1H, CH), 7.13 ppm (t, ^{3}J(H,H)=7.04, 1H, CH); ^{13}C NMR (100 MHz, $[D_1]CDCl_3$, TMS): δ = 146.57, 129.41, 118.59, 115.22 ppm.

Azobenzene

^{1}H NMR (400 MHz, $[D_1]CDCl_3$, TMS): δ =7.92 (d, ^{3}J(H,H)=7.83, 2H, CH), 7.50 ppm (m, 3H, CH); ^{13}C NMR (100 MHz, $[D_1]CDCl_3$, TMS): δ = 152.69, 131.00, 129.10, 122.86 ppm.

NMR spectrum of products:

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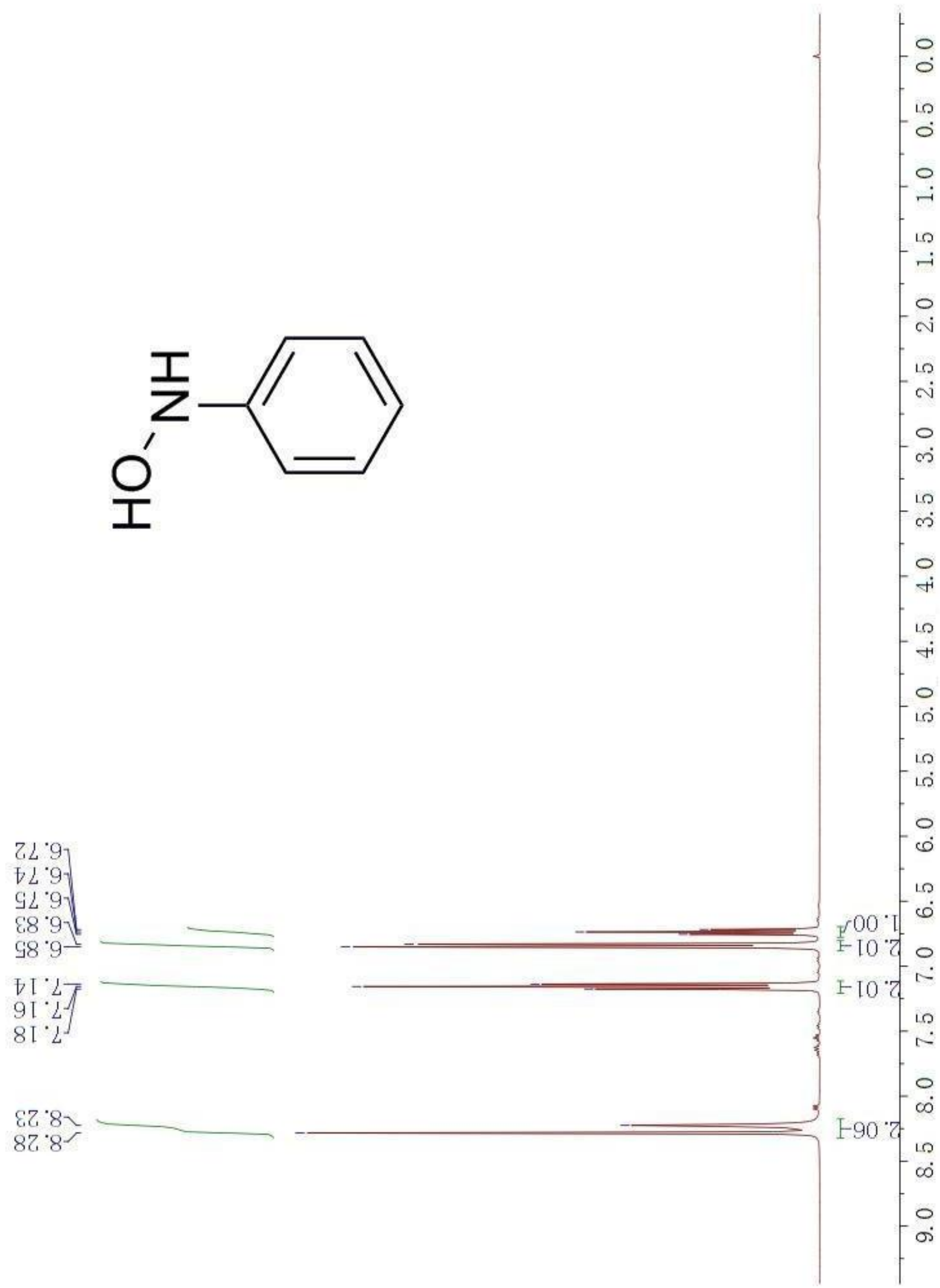
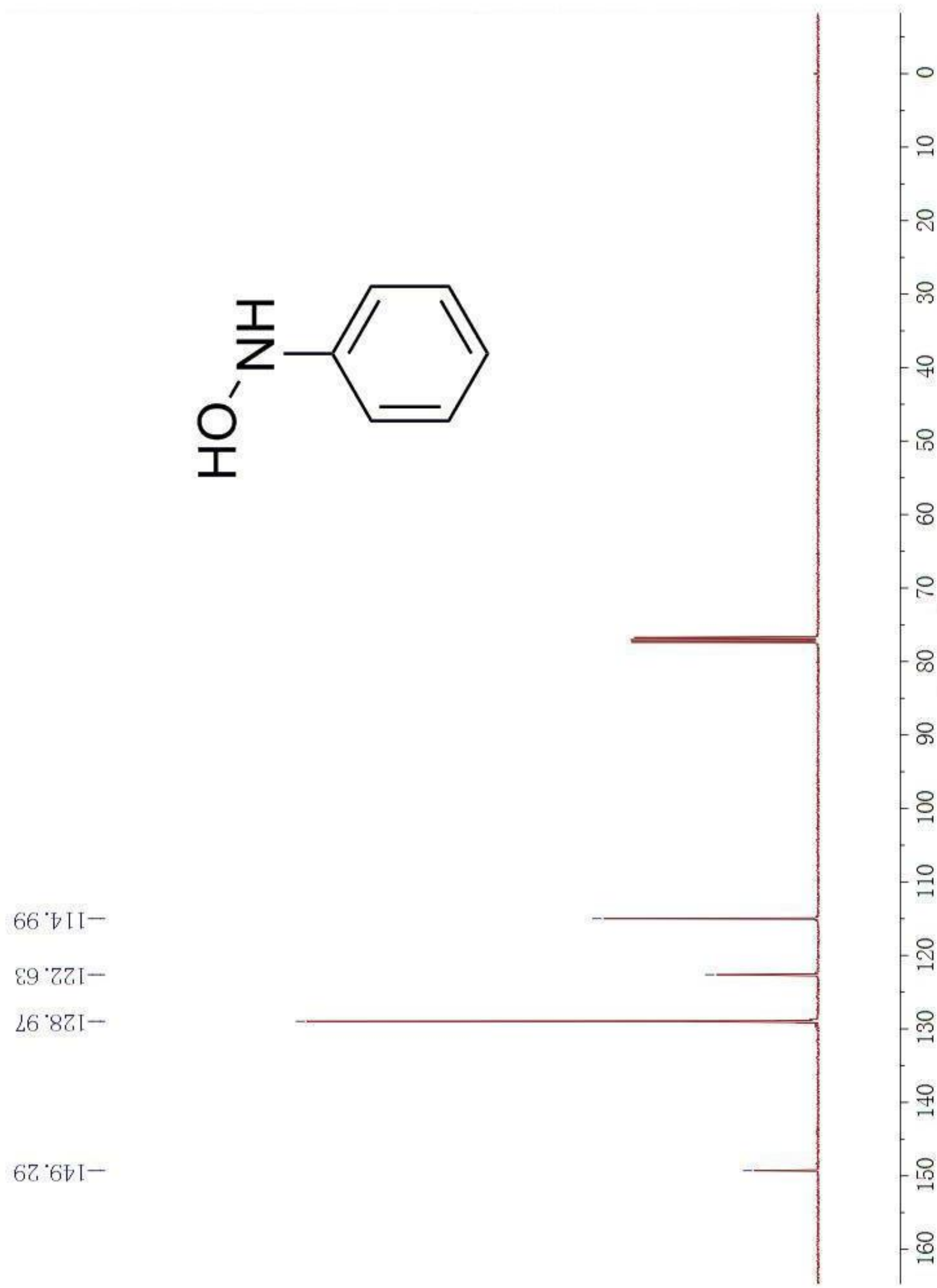
125.53
128.70
128.80
129.60
131.58
144.04


HO
NH
6.72
6.74
6.75
6.83
6.85
7.14
7.16
7.18
8.23
8.28
1.00
2.01
2.01
2.06
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0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128.97
149.29
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

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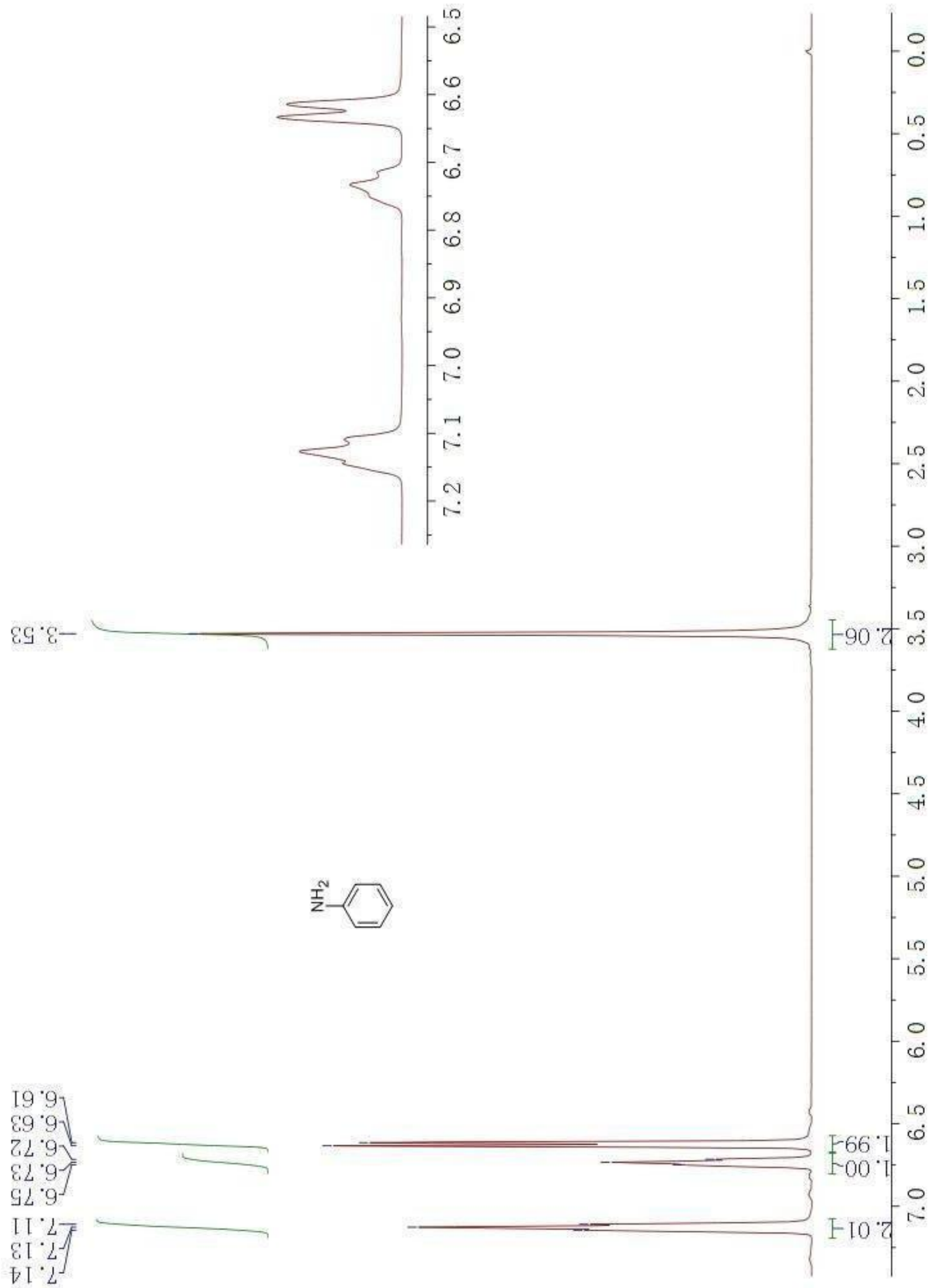

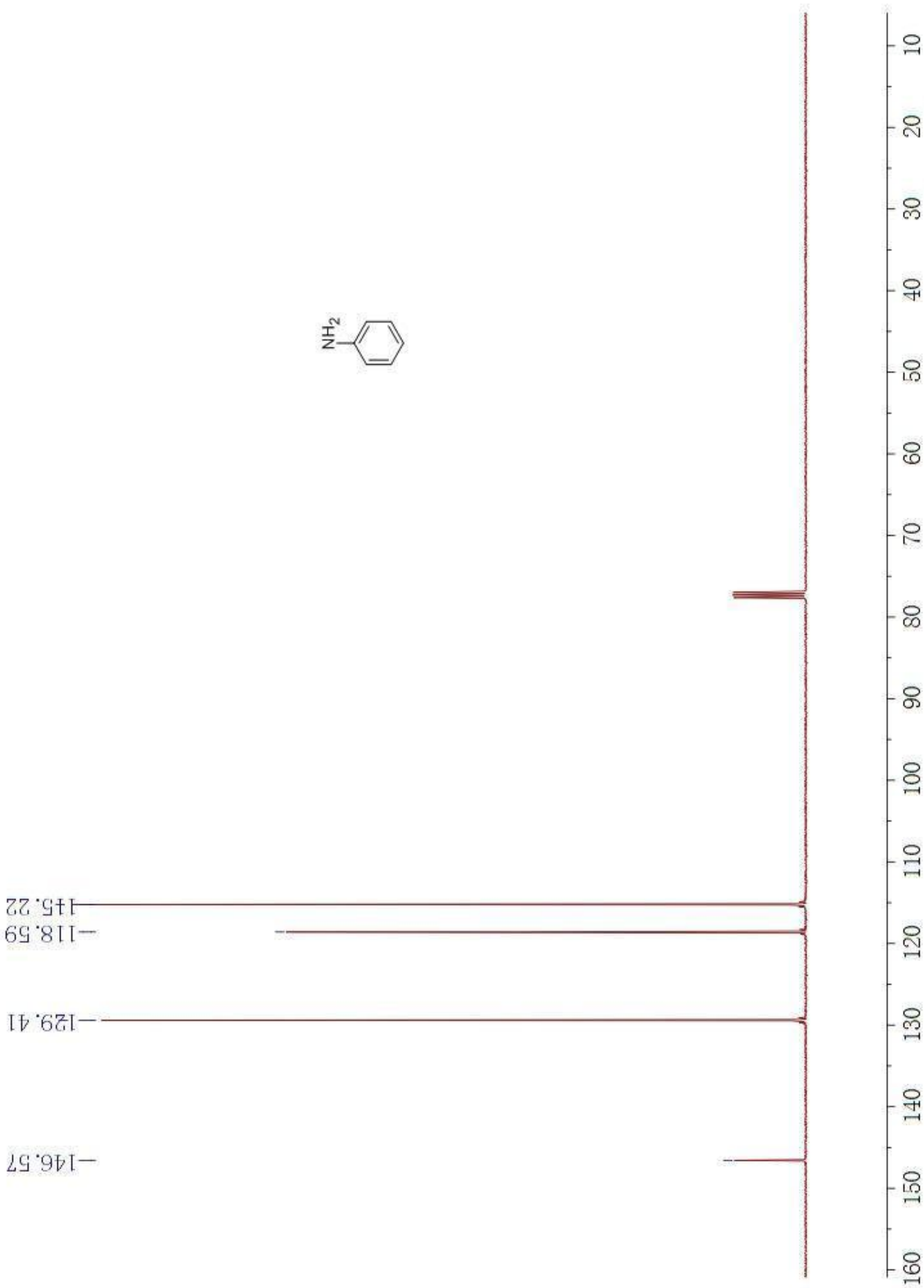
NH2
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115.22
10
20
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40
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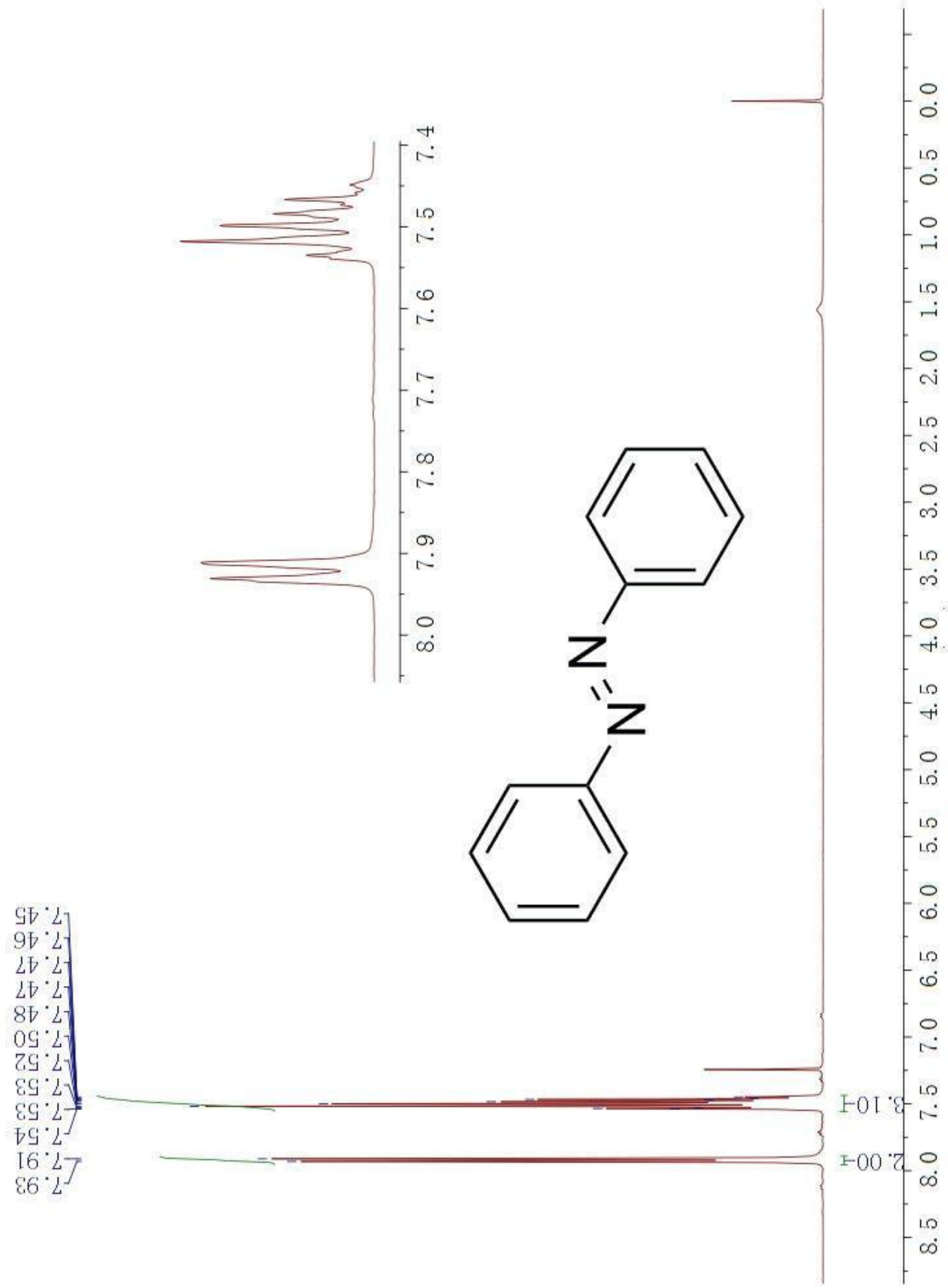
160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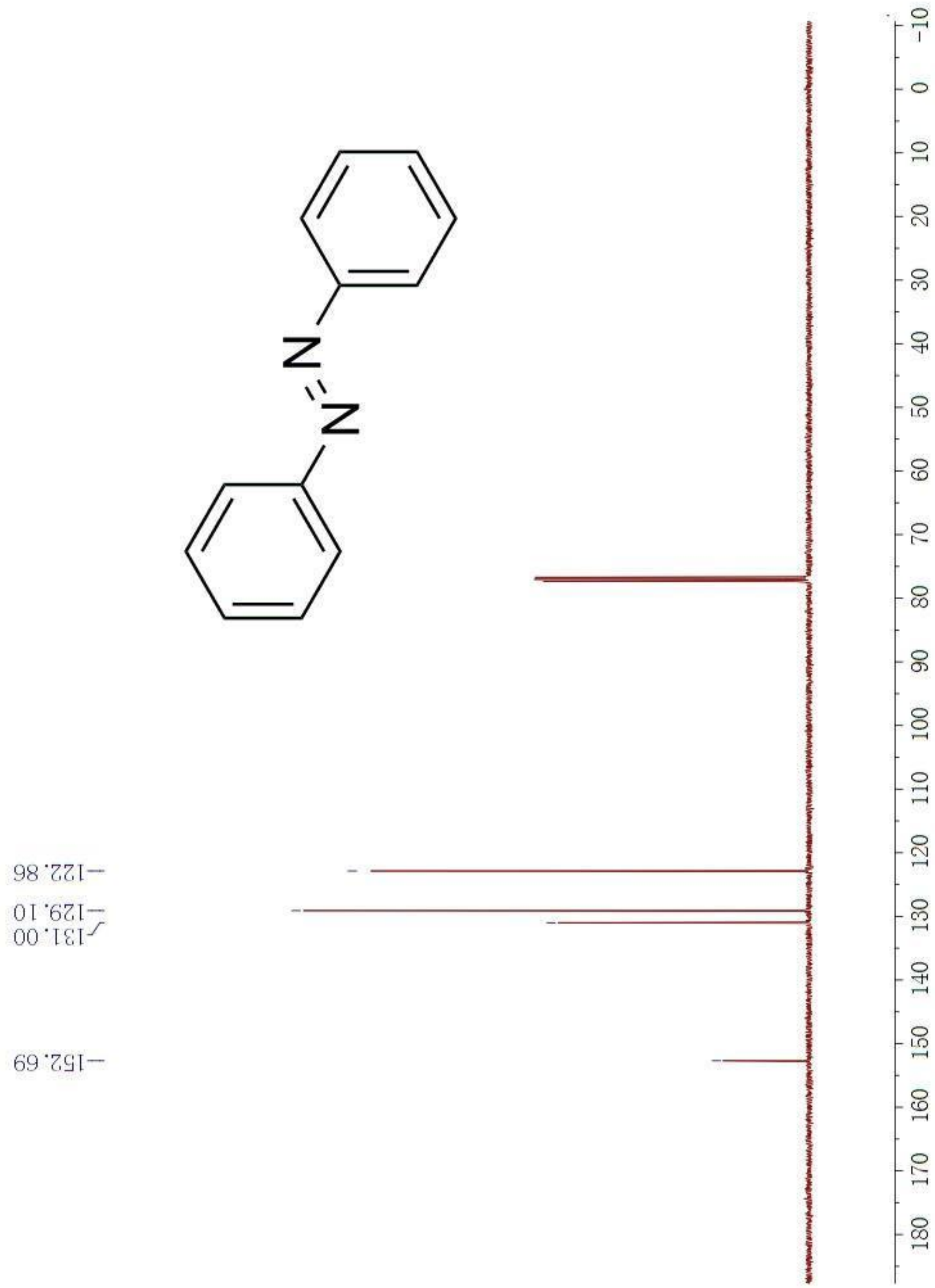
7.50
7.52
7.53
7.53
7.54
7.91
7.93
3.10
2.00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129.10
131.00
152.69
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180