Supporting Information

for

Palladium-modified functionalized cyclodextrin as an efficient and recyclable catalyst for reduction of nitroarenes

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Content

Experimental details.

General Information： β-cyclodextrin (AR, 98%, MW=1134.98), cyclohexanediamine (AR, 99%, MW=114.19), $Pd(OAc)_2$ (metals basis, 99.9%, MW=224.51), *p*-T-oluenesulfonyl chloride (AR,99%, MW=190.65) were purchased from from Aladdin Industrial Corporation in Shanghai, PR China. NaOH, DMF, CH_3CN were purchased from Tianjin Fengchuan Chemical Reagent Technologies, PR China. All experiments were carried out using ultrapure water and all the chemicals were used without further purification. The XRD patterns were obtained by using PHI 5000 VersaProbe II with Cu-Kα radiation (k = 1.5460 Å, 40 kV, 100 mA), at a scanning rate of 5°/min. Powder samples were mounted on a vitreous sample holder and scanned with a step size of 2θ = 0.02° between 2θ = 5° and 90°. TEM and EDS were determined on a Tecnai G^2 TF30 S-Twin. The NMR spectra was conducted on a Bruker Avance DRX spectrometer at 500 MHz, tetramethylsilane (TMS) as internal reference, 298 k in Yunnan University, Kunming 650091, P.R. China. ICP-OES was used with Agilent 5100 instrument. TG measurements were performed with a NETZSCH STA449F3 instrument, at the heating rate of 10 °C/min from room temperature to 450 °C in a dynamic nitrogen atmosphere (flow rate = 100 mL/min).

Synthesis of 6-O-monotosyl-β-CD: β-CD (210g, 185 mM) was dissolved in 1.3L H_2O, then, a solution of NaOH (50mL, 8.6 mol/L) was slowly dropped in 1.5h with vigorous stirring. After that, the temperature was lowed to around 5°C, the solution of *p*-T-oluenesulfonyl chloride (26g) in CH_3CN (80mL) was added slowly in 2h. The insoluble substance was removed by filtration and PH of the filtrate was adjusted to 7.5 by adding the solution of HCl (2mol/L) and the crude product was precipitated. After filtration, the crude production was washed with water, recrystallized by water for five times and dried in vacuum. Yield: (25.2%)

Synthesis of ligand DACH-β-CD: 6-O-monotosyl-β-CD (3.22 g, 2.5 mmol) and DACH (1.14 g, 10.0 mmol) were dissolved in anhydrous DMF. The mixture was stirred for 12 h at 80 °C. Afterward, the reaction solution was added dropwise in acetone (3×500mL) to remove the excess DACH. The final pure DACH-β-CD was dried overnight in vacuum at 50°C. Yield: (82%)

Synthesis of catalyst DACH-Pd-β-CD: $Pd(OAc)_2$ (0.0225g, 0.1mM) was dissolved in toluene (15mL) and DACH-β-CD (0.369g, 0.3 mM) was added . The suspension was stirred at room temperature for 24h. Then, the precipitation was washed with a large number of acetone (300mL) for three times to remove the unreacted $Pd(OAc)_2$. After which, the catalyst was dried in vacuum at 50°C for 24h, and a light yellow powder was get (containing 4.5%w Pd by ICP-OES).

General procedure for the reduction of nitroarenes

The general experimental procedure is that 1.0 mmol of nitroarenes, 3 mmol of $NaBH_4$ (0.1135 g) and 0.5 mol% DACH-Pd-β-CD (11.9mg, containing 4.5%$_w$ Pd) were added in a sealed tube with 2.0 mL H_2O. The mixture was stirred at rt for 3 h and monitored by TLC. After the reaction completion, the aqueous phase was extracted with ethyl acetate for 3 times (3×5 mL). Then the combined organic layers were dried by anhydrous $MgSO_4$ and the crude product was further purified by column chromatography.

General procedure for the separation and reusing of catalyst

After every cycle, 3×5 mL ethyl acetate was added to separate the organic phase. The combined organic layers were dried by anhydrous $MgSO_4$ and the crude product was further purified by column chromatography. In addition, the aqueous phase was used in the next run with adding 1 mmol nitrobenzene (0.123 g, 0.102 mL) and 3 mmol $NaBH_4$ (0.1135 g). The same progress was repeated for another new cycle.

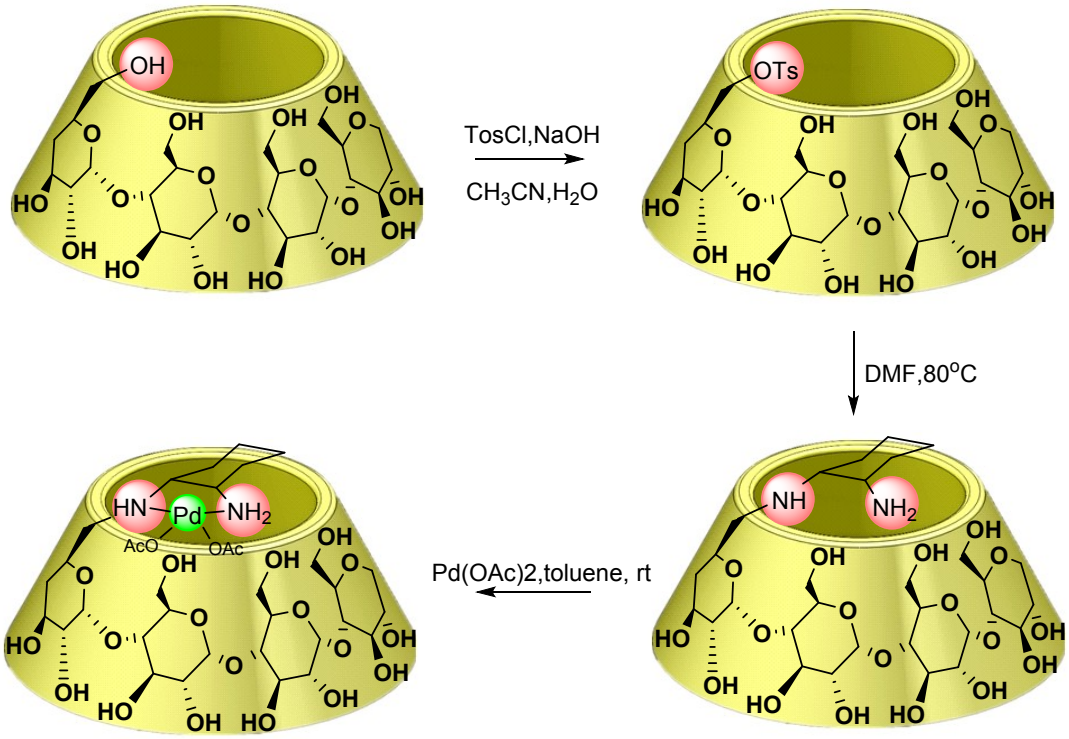


Fig. S1 The progress of synthesis of DACH-Pd-β-CD

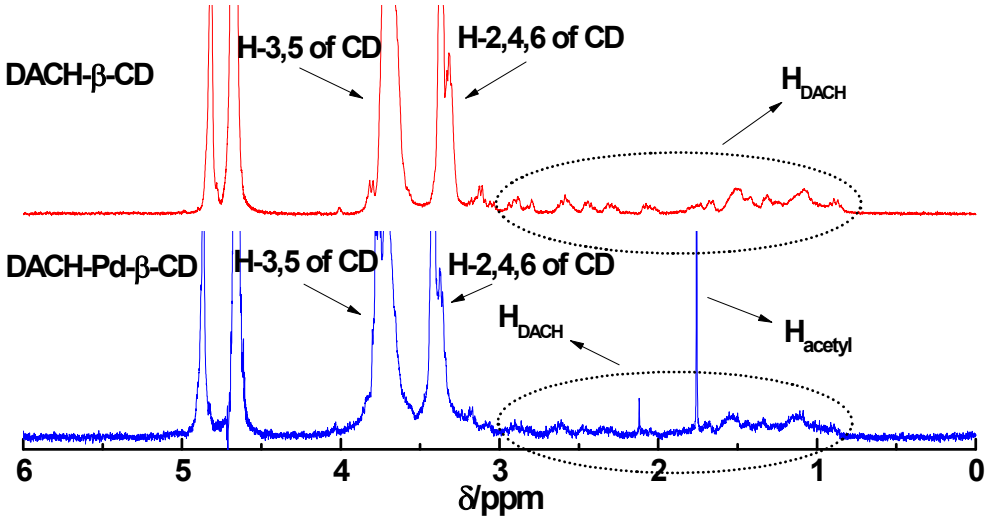


Fig. S2 ^{1}H NMR of DACH-β-CD and DACH-Pd-β-CD

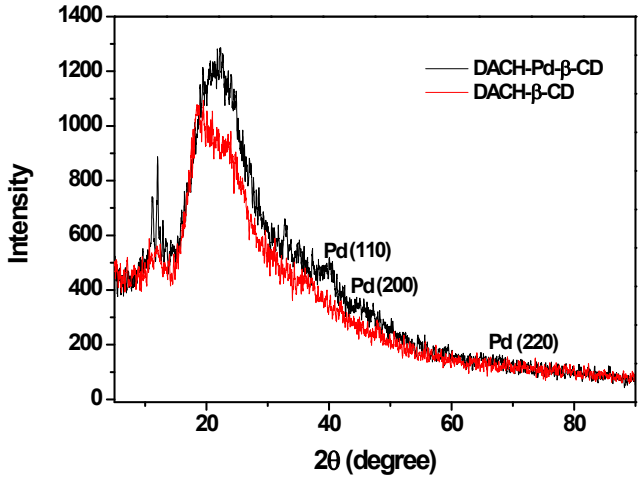


Fig. S3 XRD patterns of DACH-β-CD and DACH-Pd-β-CD

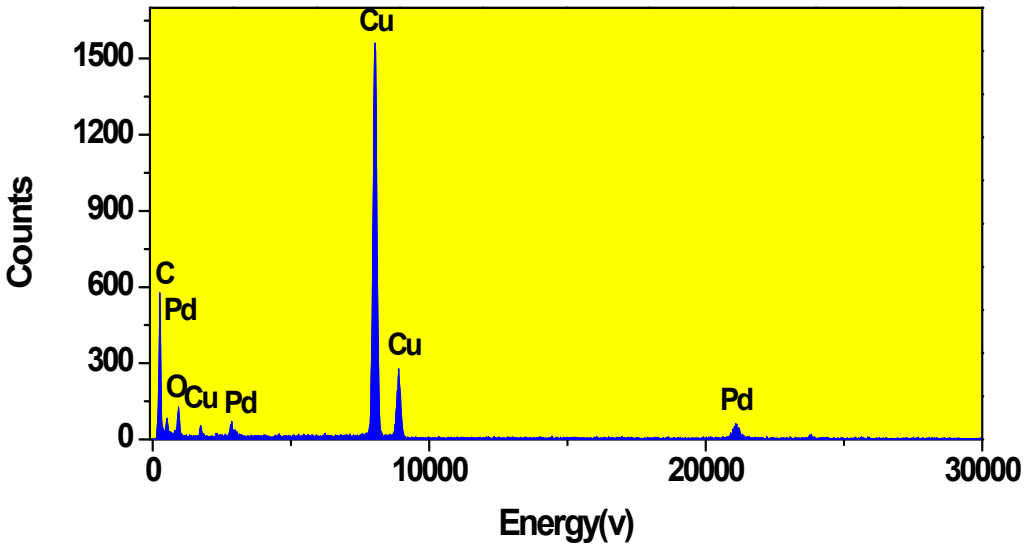


Fig. S4 EDS pattern of DACH-Pd-β-CD

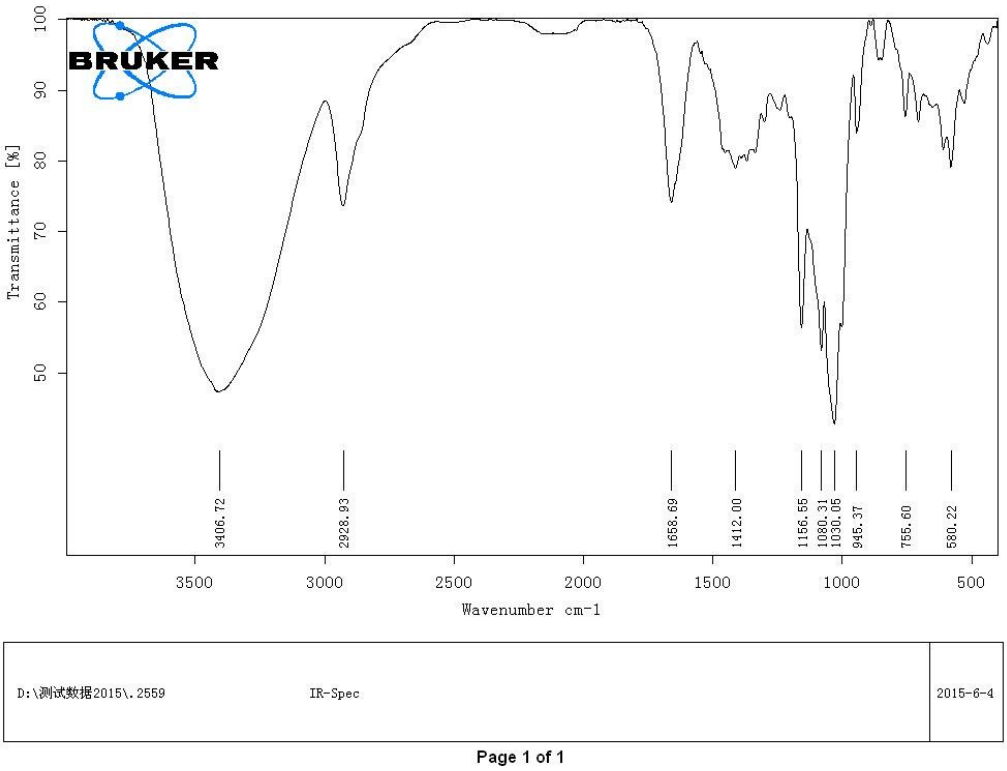


Fig. S5 FT-IR of DACH-β-CD

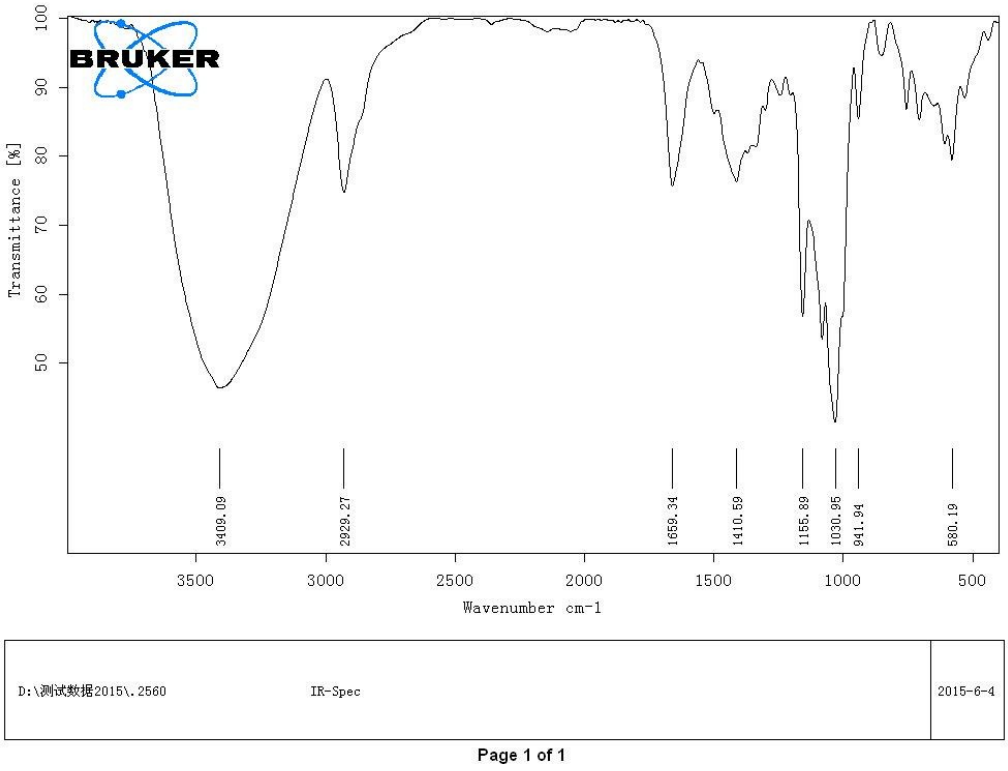


Fig. S6 FT-IR of DACH-Pd-β-CD

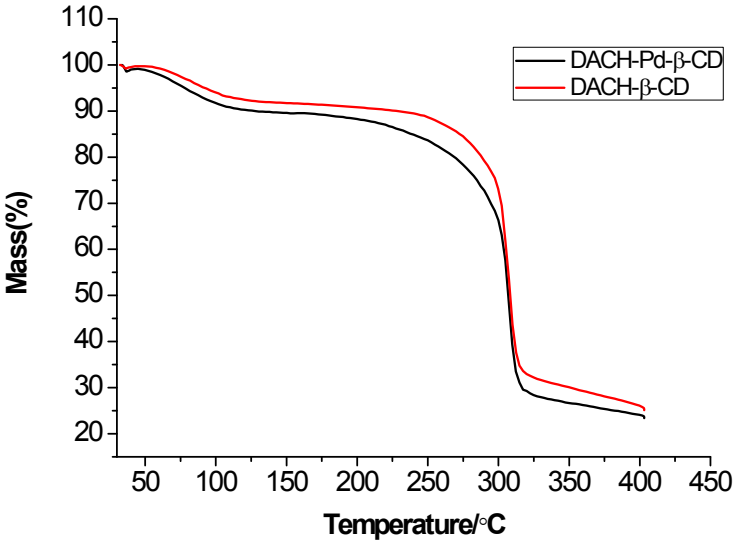


Fig. S7 TG of DACH-β-CD and DACH-Pd-β-CD

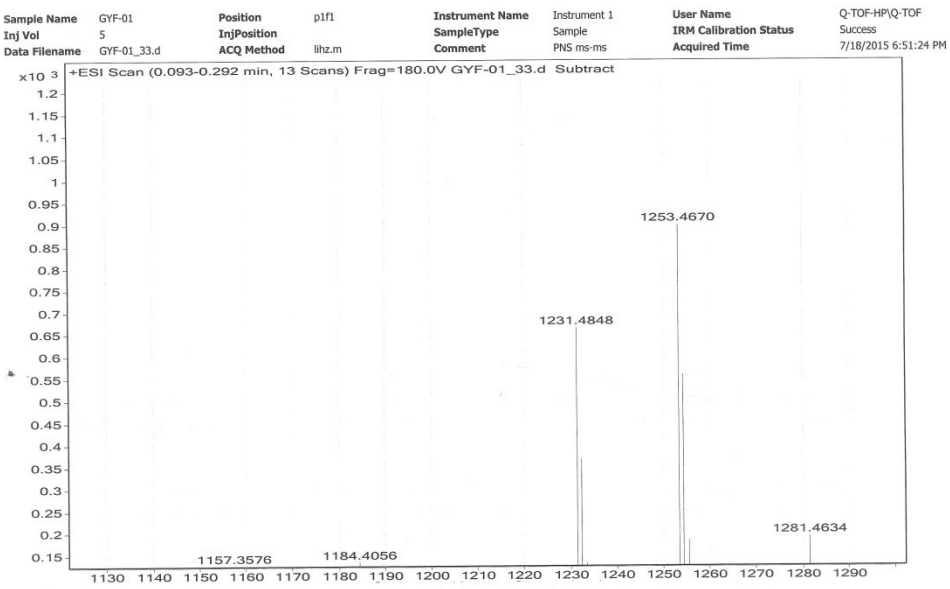


Fig. S8 HR-MS of DACH-β-CD

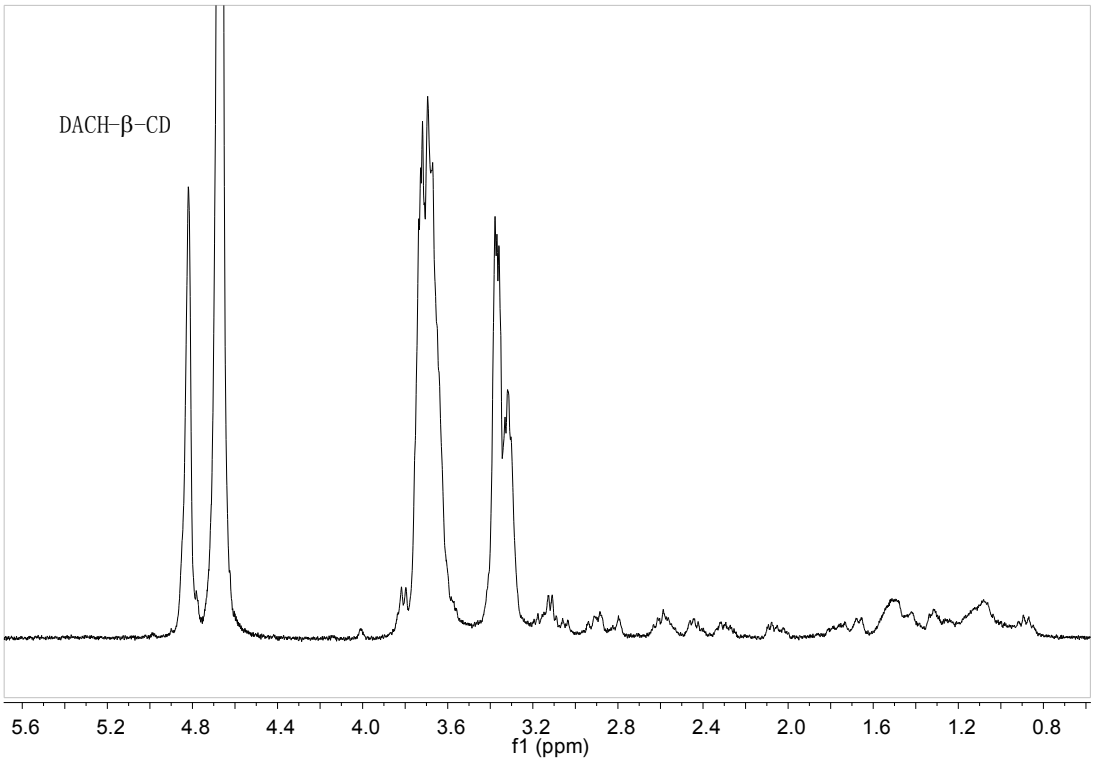


Fig. S9 ^{1}H NMR of DACH-β-CD

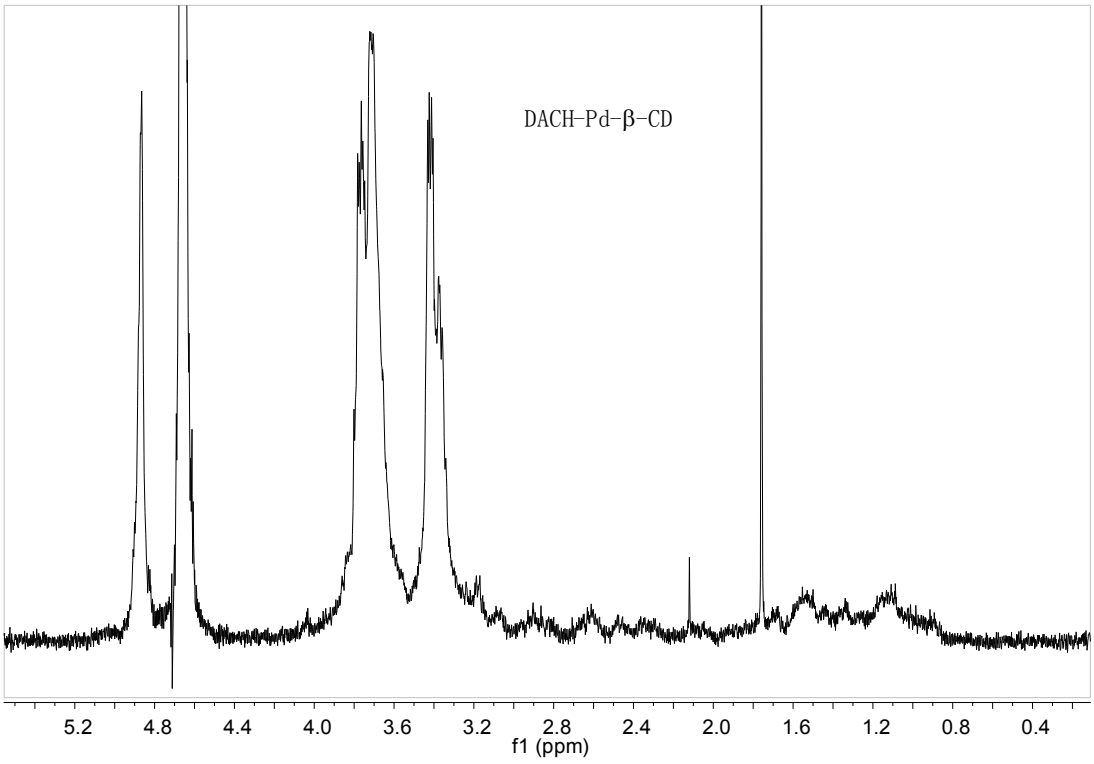


Fig. S10 ^{1}H NMR of DACH-Pd-β-CD

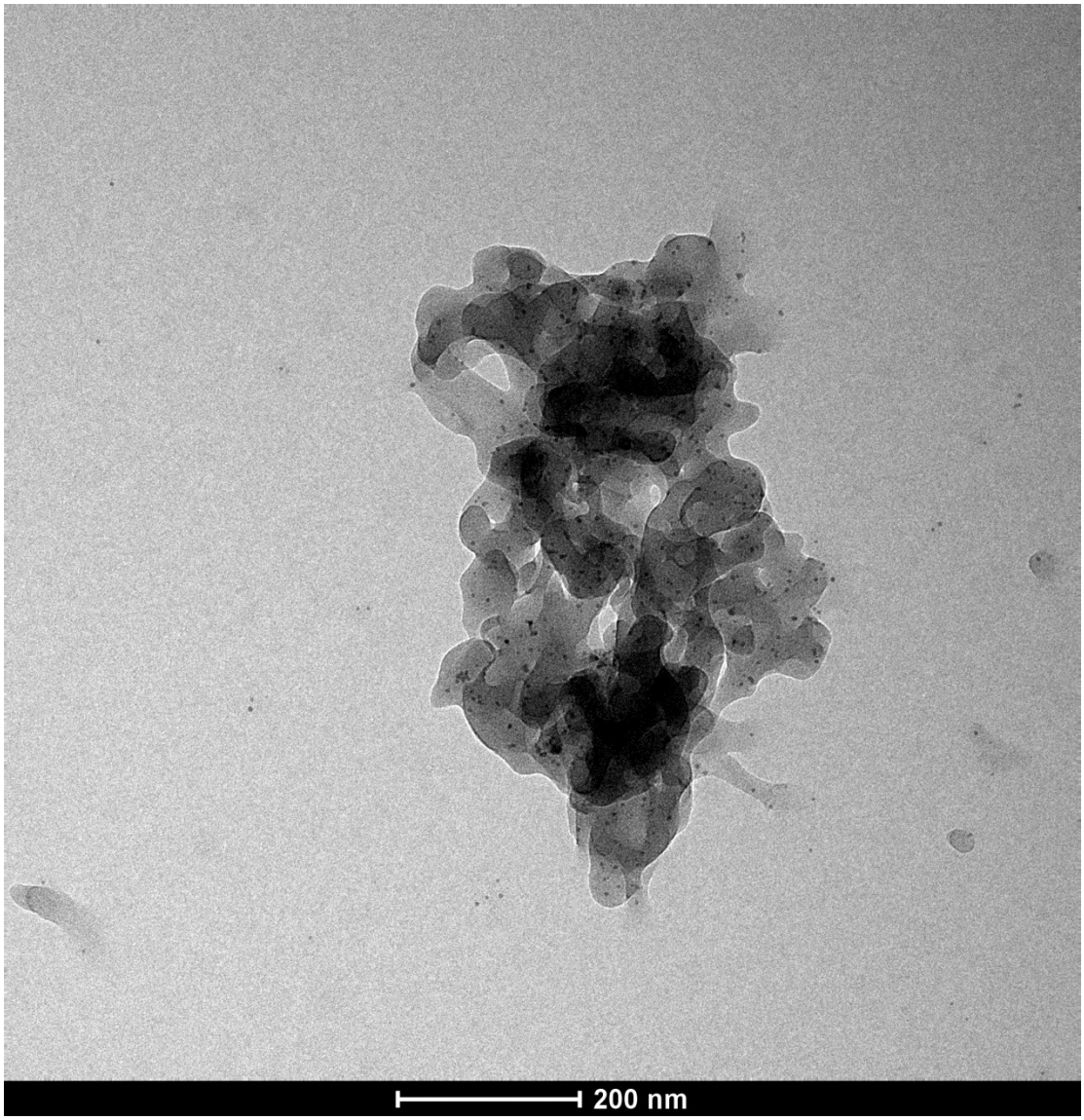


Fig. S11 TEM of DACH-Pd-β-CD

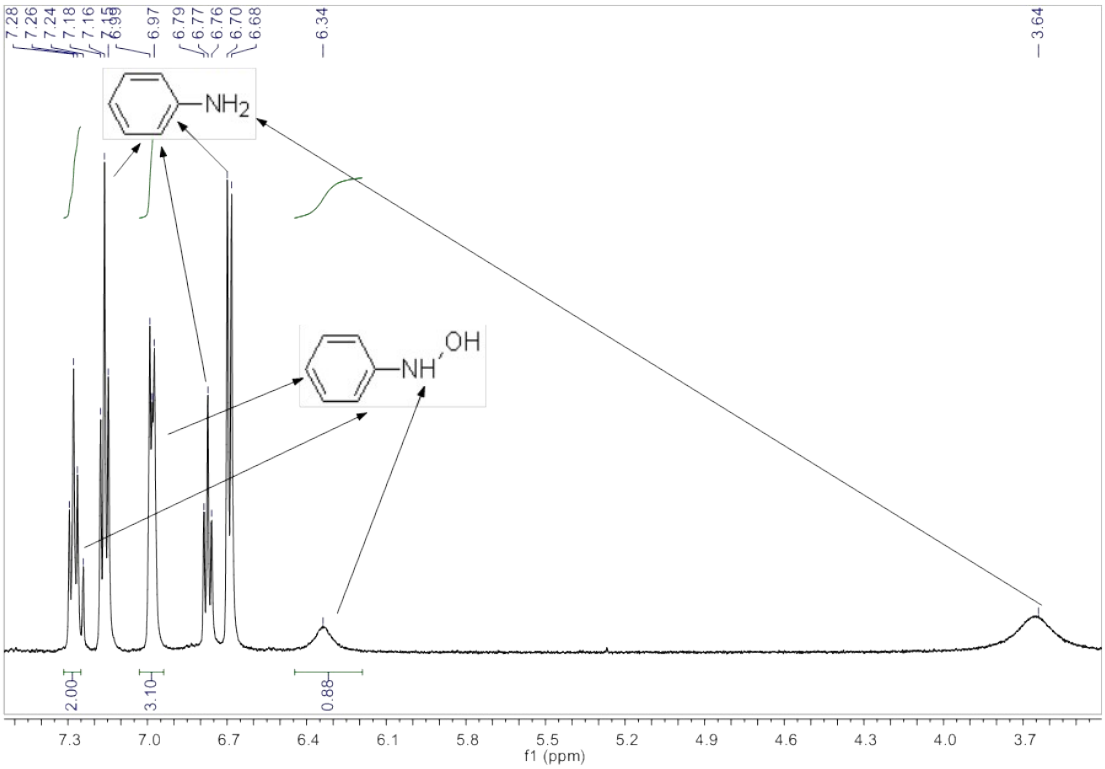
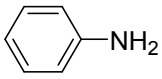
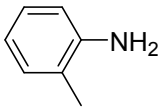


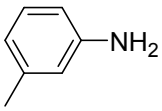
Fig. S12 ^{1}H NMR of arylhydroxylamine (III) and aniline



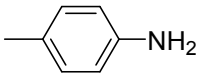
δ_H (500 MHz, $CDCl_3$) 7.17 (2 H, t, *J* 7.9), 6.77 (1 H, t, *J* 7.3), 6.69 (2 H, d, *J* 8.3), 3.63 (2 H, s). δ_C (126 MHz, $CDCl_3$) 146.83, 129.73, 118.97, 115.54.



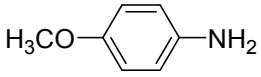
δ_H (500 MHz, $CDCl_3$) 7.06 (2 H, t, *J* 8.0), 6.82-6.57 (2 H, m), 3.59 (2 H, s), 2.18 (3 H, s).δ_C (126 MHz, $CDCl_3$) 145.00, 130.88, 127.40, 122.75, 119.06, 115.37, 17.77.



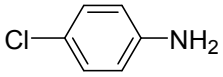
δ_H (500 MHz, CDCl3) 7.10 (1H, t, J 7.6), 6.64 (1 H, d, J 7.4), 6.53 (2 H, d, J 8.7), 3.61 (2 H, s), 2.32 (3 H, s). δ_C (126 MHz, $CDCl_3$) 146.90, 139.56, 129.64, 119.89, 116.41, 112.75, 21.91.



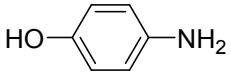
δ_H (500 MHz, $CDCl_3$) 6.97 (2 H, d, *J* 8.1), 6.61 (1 H, d, *J* 8.2), 3.49 (1 H, s), 2.25 (2 H, s). δ_C (126 MHz, $CDCl_3$) 144.27, 130.19, 128.20, 116.87, 115.70, 115.26, 20.88.



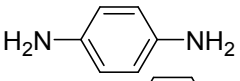
δ_H (500 MHz, $CDCl_3$) 6.73 (2 H, d, *J* 10.2), 6.63 (2 H, d, *J* 8.7), 3.73 (3 H, s), 3.36 (2 H, s). δ_C (126 MHz, $CDCl_3$) 153.23, 140.37, 116.84, 115.24, 56.15.



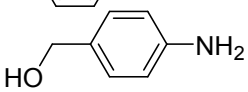
8.7), 3.63 (2 H, s). δ_C δ_H (500 MHz, $CDCl_3$) 7.08 (2 H, d, *J* 8.6), 6.58 (2 H, d, *J* (126 MHz, $CDCl_3$) 145.41, 129.53, 123.52, 116.66.



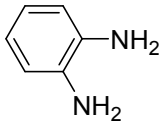
δ_H (500 MHz, 4.32 (2 H, s). DMSO) 8.31 (1 H, s), 6.44 (2 H, d, *J* 8.4), 6.38 (2 H, d, *J* 8.6), δ_C (126 MHz, $CDCl_3$) 149.08, 141.50, 116.40, 116.11.



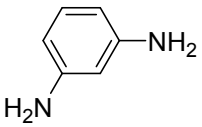
δ_H (500 MHz, DMSO) 6.32 (1 H, s), 4.14 (1 H, s). δ_C (126 MHz, $CDCl_3$) 139.78, 116.28.



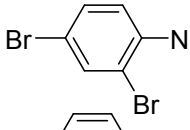
δ_H (500 MHz, $CDCl_3$) 7.10 (2 H, d, *J* 8.3), 6.62 (2 H, d, *J* 8.3), 4.48 (2 H, s). δ_C (126 MHz, $CDCl_3$) 146.36, 131.56, 129.16, 115.61, 65.52.



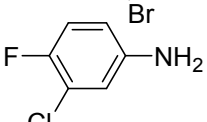
δ_H (500 MHz, $CDCl_3$) 6.90 – 6.54 (4 H, m), 3.38 (4 H, s). δ_C (126 MHz, $CDCl_3$) 135.19, 120.69, 117.18.



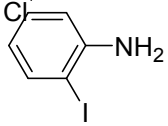
δ_H (500 MHz, $CDCl_3$) 6.93 (1 H, t, *J* 7.9), 6.09 (2 H, s), 5.98 (1 H, s), 3.51 (4 H, s). δ_C (126 MHz, $CDCl_3$) 148.01, 130.60, 106.39, 102.45.



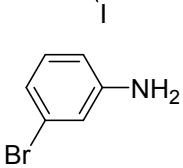
δ_H (500 MHz, $CDCl_3$) 7.51 (1 H, s), 7.17 (1 H, d, *J* 8.5), 6.62 (1 H, d, *J* 8.4), 3.99 (2 H, s). δ_C (126 MHz, $CDCl_3$) 143.68, 134.88, 131.58, 117.11, 110.00, 77.72, 77.46, 77.21, 77.13.



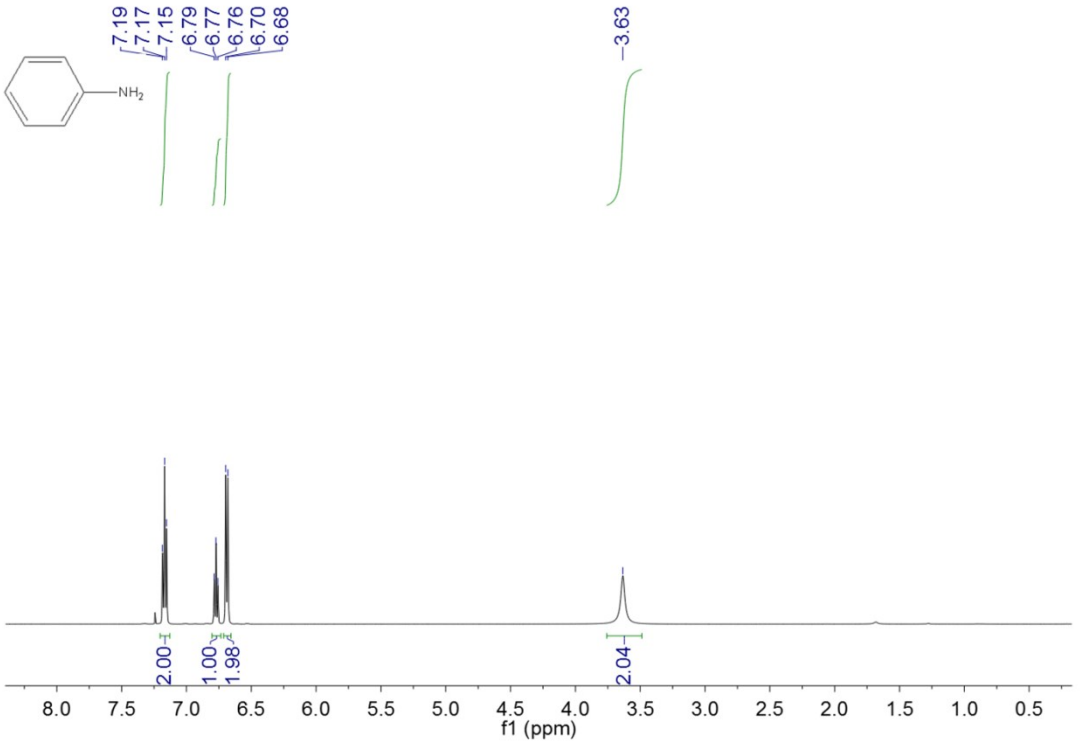
δ_H (500 MHz, $CDCl_3$) 6.89 (1 H, t, *J* 8.8), 6.65 (1 H, dd, *J* 6.1, 2.8), 6.47 (1 H, dt, *J* 8.7, 3.2), 3.58 (2 H, s). δ_C (126 MHz, $CDCl_3$) 152.91, 151.02, 143.66, 121.36, 121.21, 117.34, 117.16, 116.77, 114.73, 114.68.

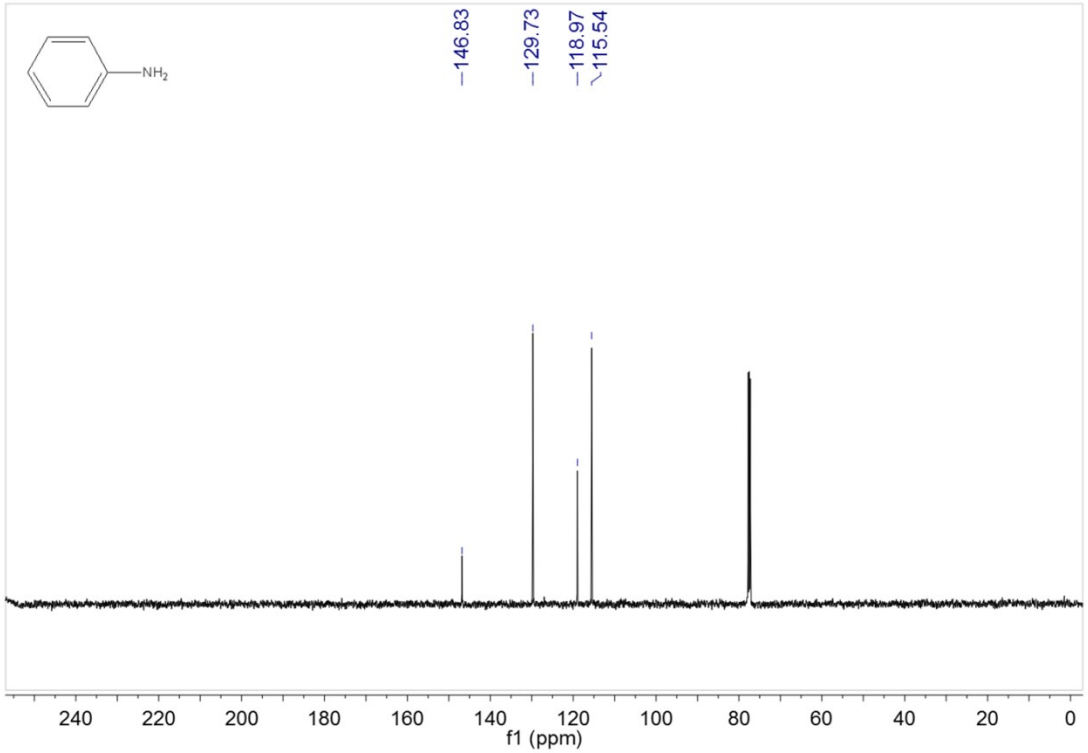


δ_H (500 MHz, $CDCl_3$) 7.62 (1 H, d, *J* 9.1), 7.12 (1 H, t, *J* 8.2), 6.73 (1 H, d, *J* 6.7), 6.46 (1 H, t, *J* 7.6), 4.06 (2 H, s). δ_C (126 MHz, $CDCl_3$) 147.17, 139.41, 129.76, 120.40, 115.15.



δ_H (500 MHz, $CDCl_3$) 6.97 (1 H, t, *J* 8.1), 6.84 (1 H, d, *J* 8.0), 6.79 (1 H, s), 6.54 (1 H, d, *J* 8.0), 3.73 (2 H, s). δ_C (126 MHz, $CDCl_3$) 171.72, 148.40, 131.05, 127.00, 123.42, 121.61, 118.18, 114.07.


7.19
7.17
7.15
6.79
6.77
6.76
6.70
6.68
3.63
NH2
2.00
1.00
1.98
2.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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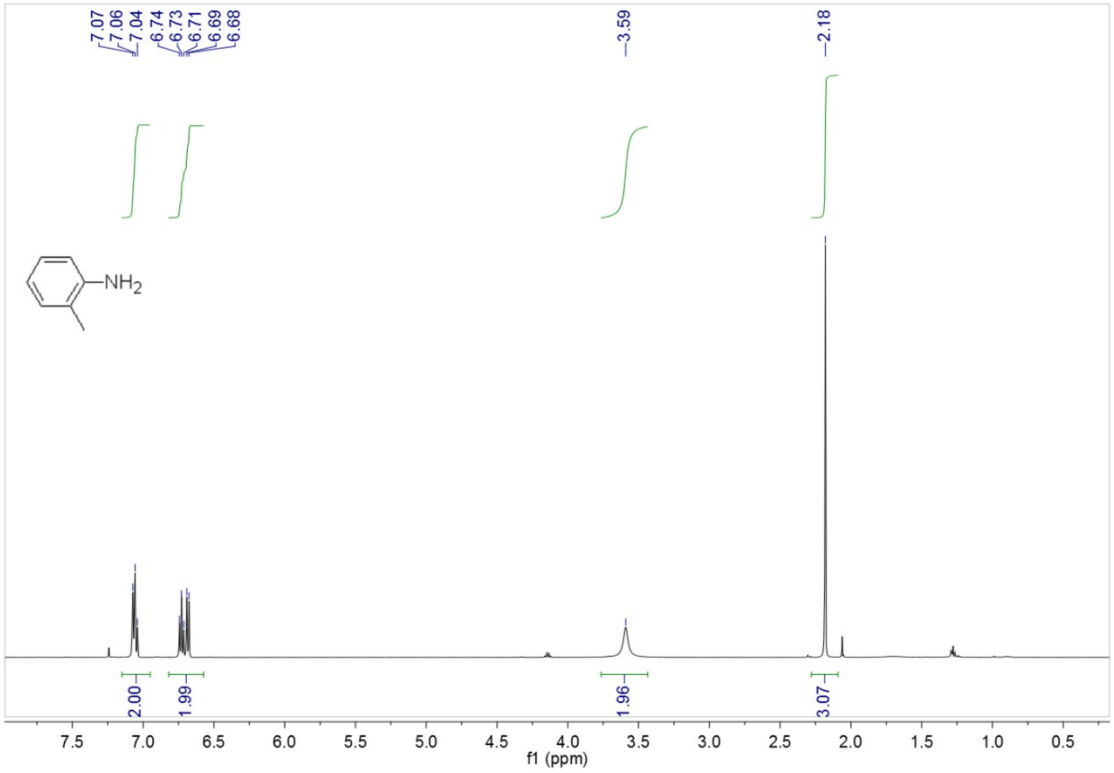
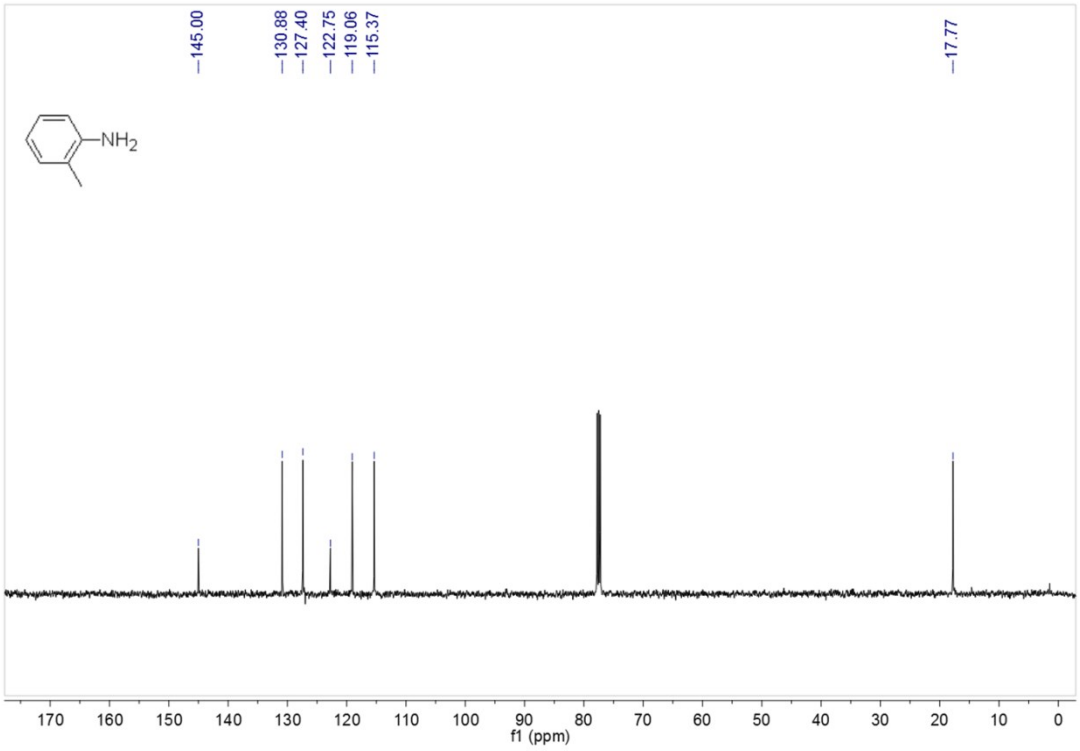
129.73
118.97
115.54
NH2
240
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.07
7.06
7.04
6.74
6.73
6.71
6.69
6.68
3.59
2.18
NH2
2.00
1.99
1.96
3.07
f1 (ppm)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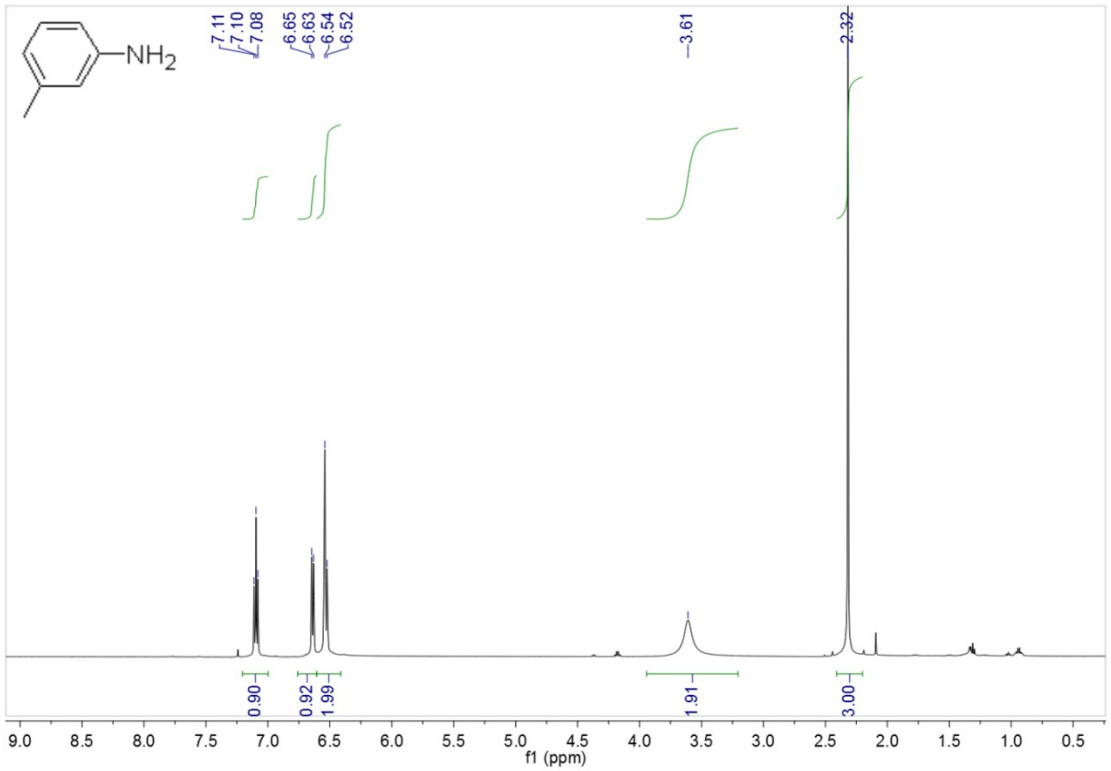
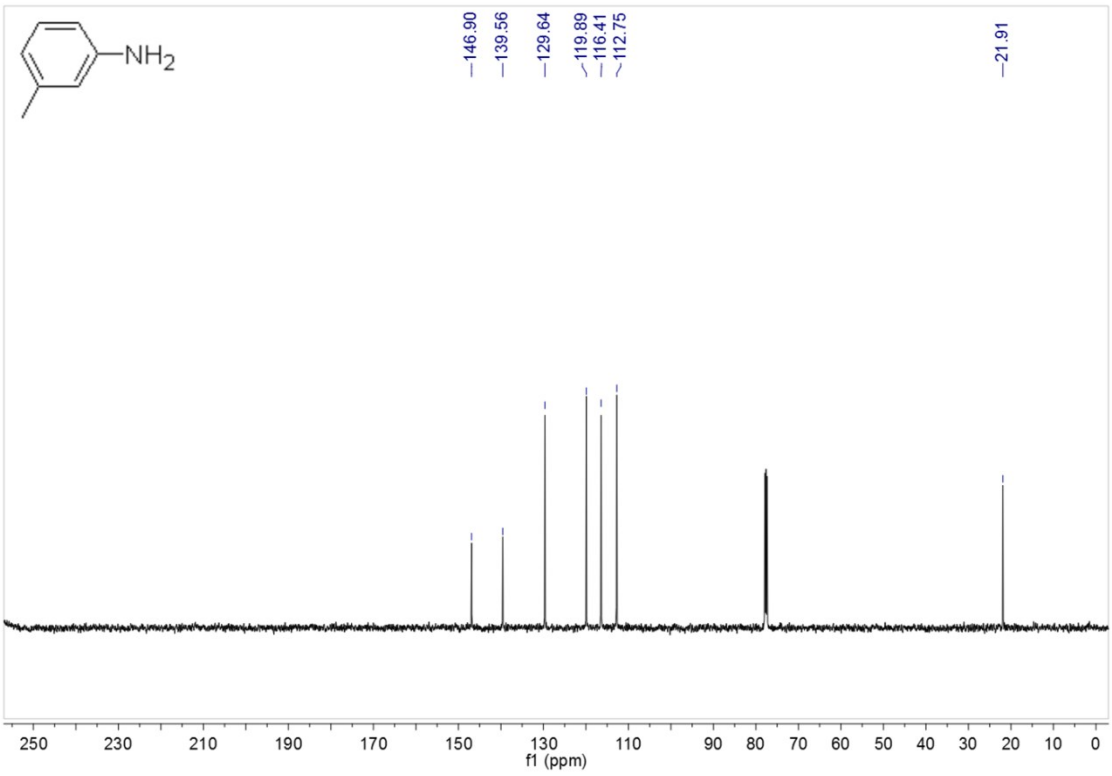
127.40
122.75
119.06
115.37
17.77
NH2
f1 (ppm)


NH2
7.11
7.10
7.08
6.65
6.63
6.54
6.52
3.61
2.32
0.90
0.92
1.99
1.91
3.00
f1 (ppm)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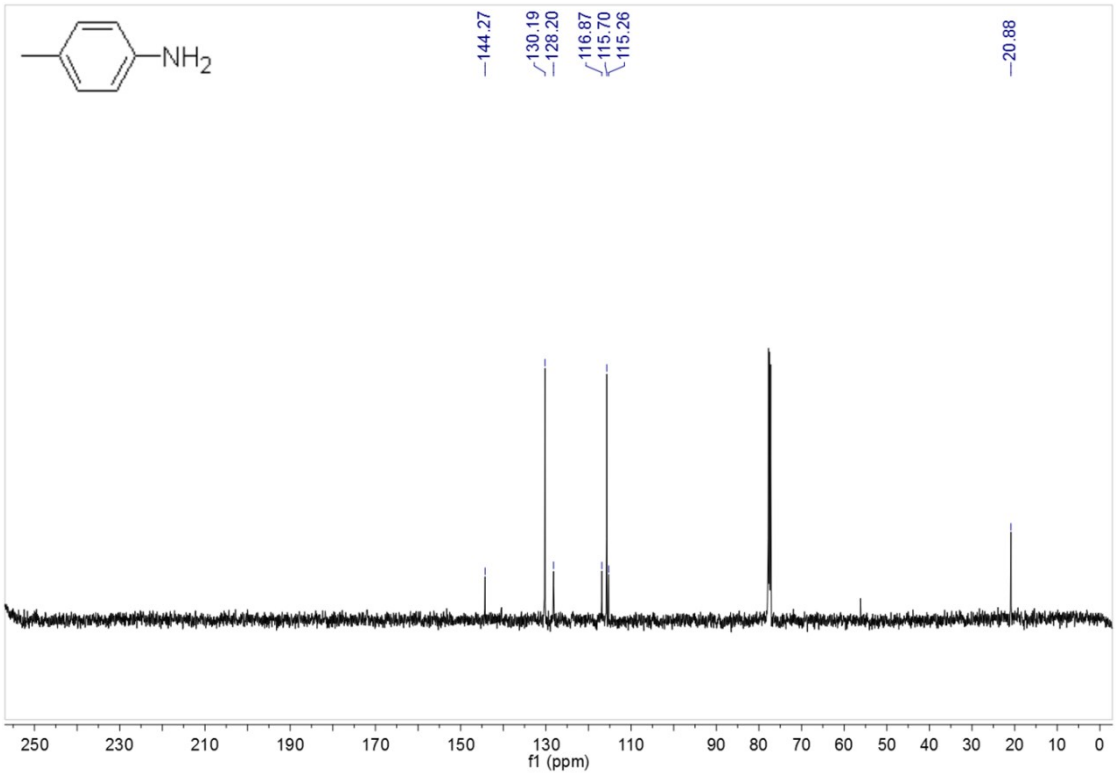
21.91
f1 (ppm)


NH2
144.27
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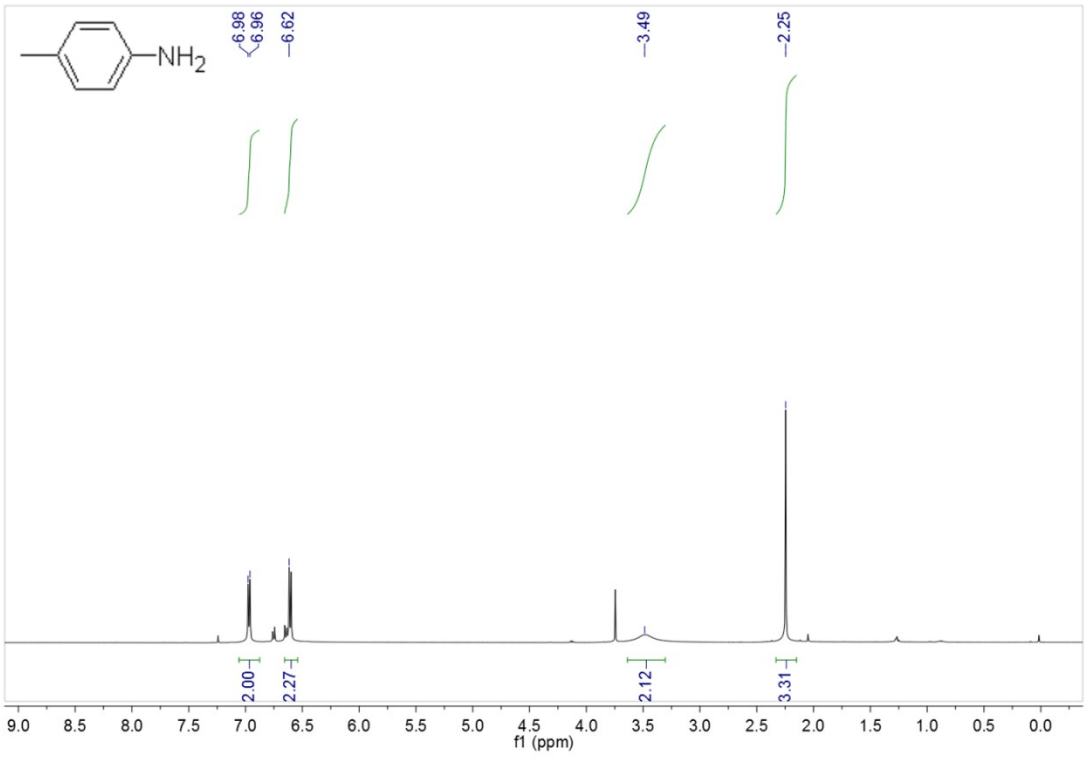
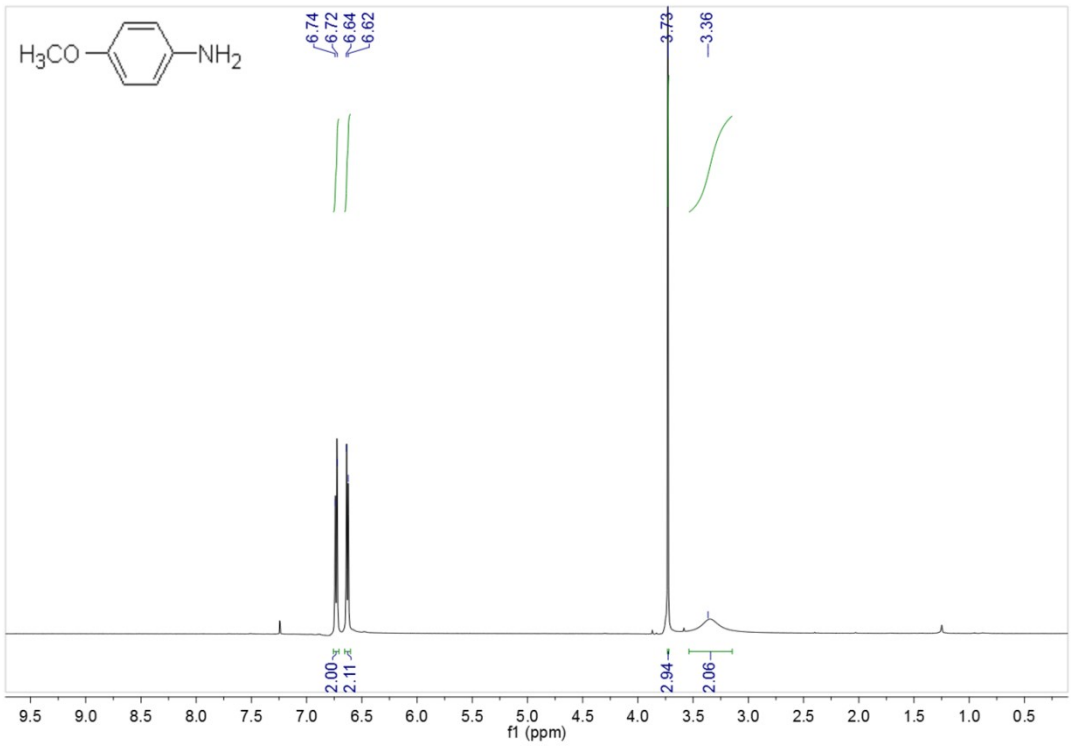
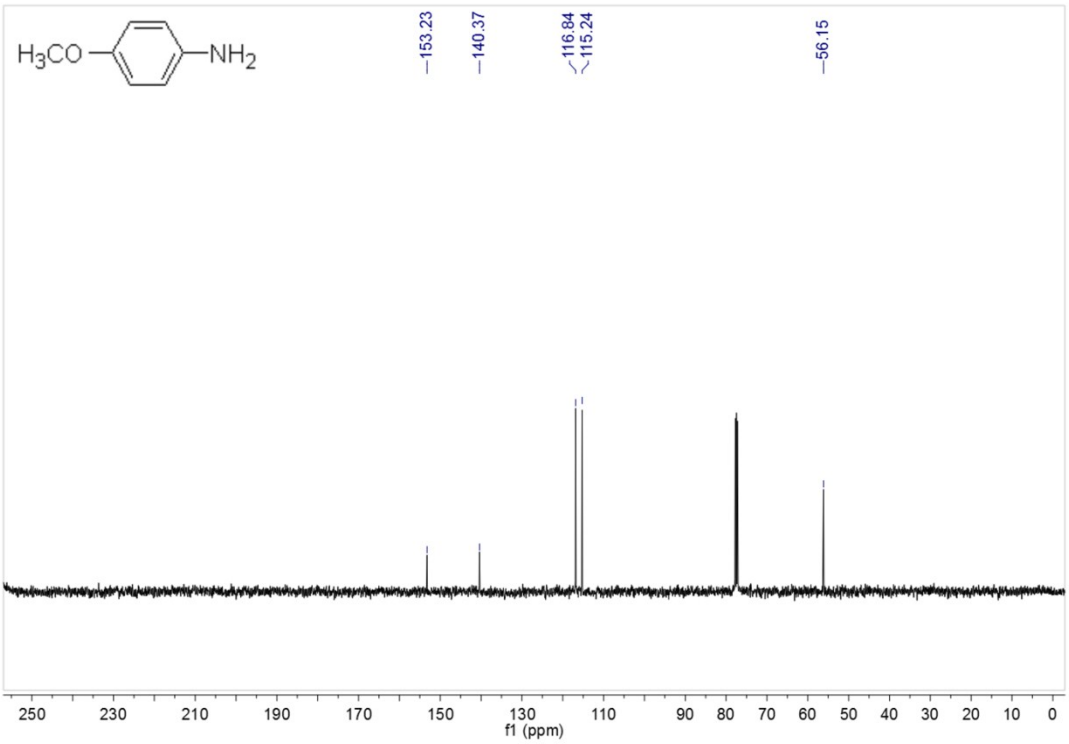
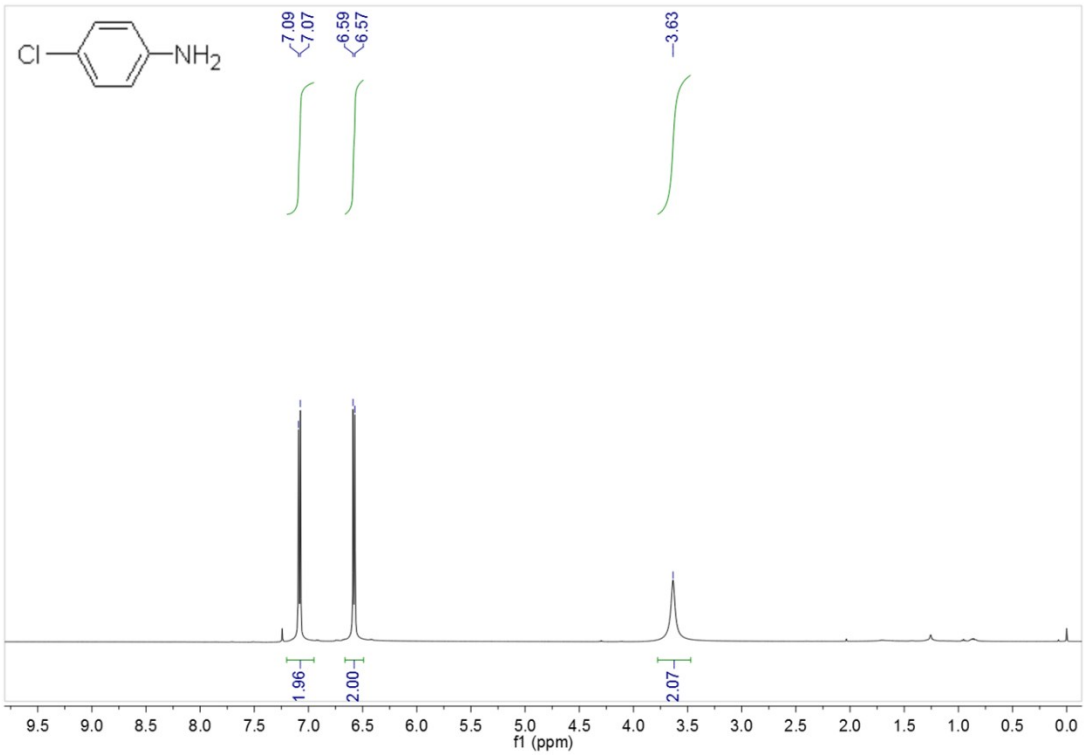
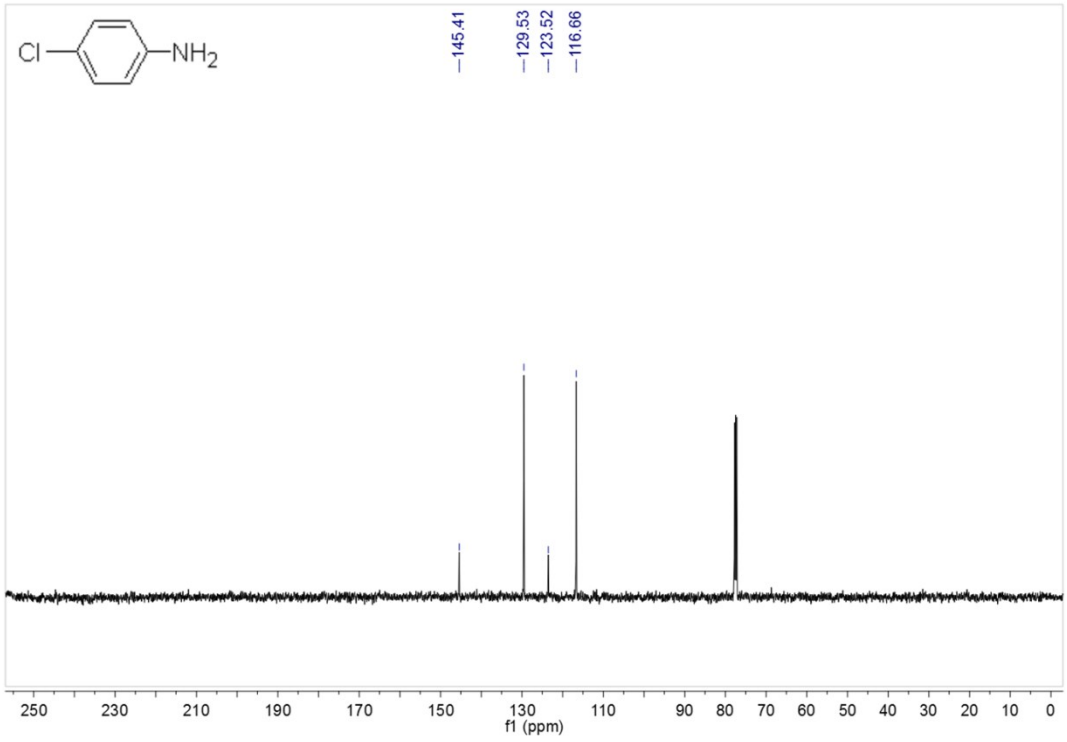
128.20
116.87
115.70
115.26
20.88
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

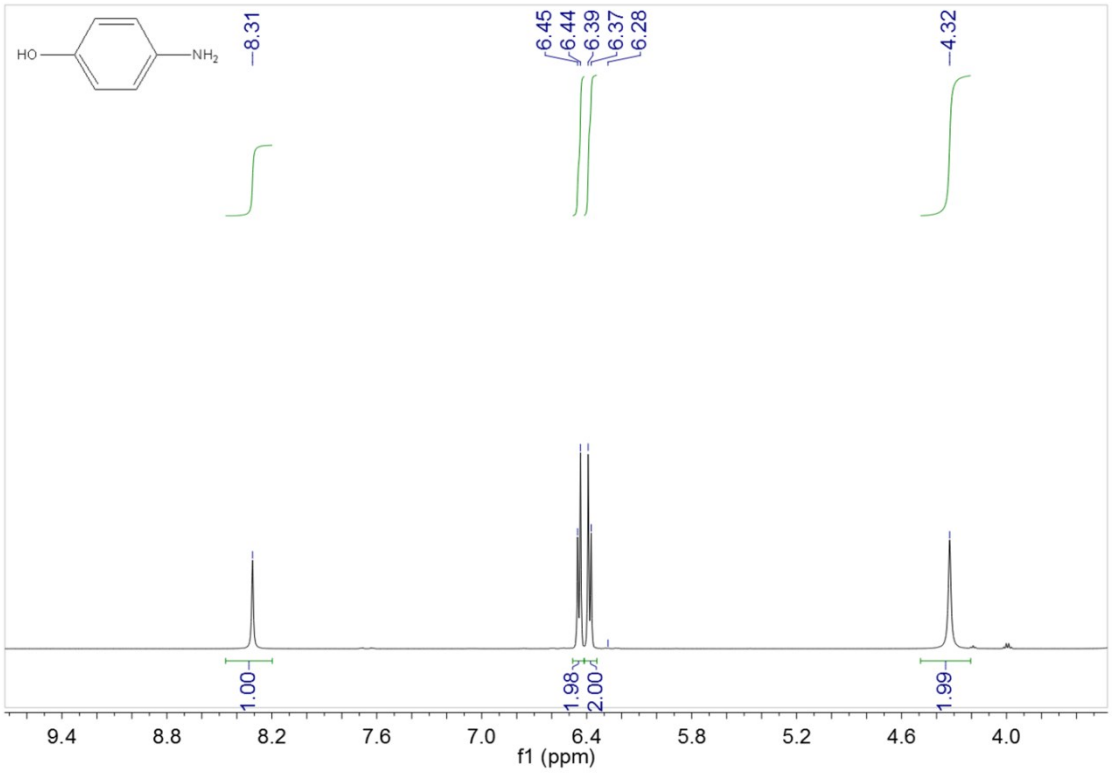

NH2
6.98
6.96
6.62
3.49
2.25
2.00
2.27
2.12
3.31
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

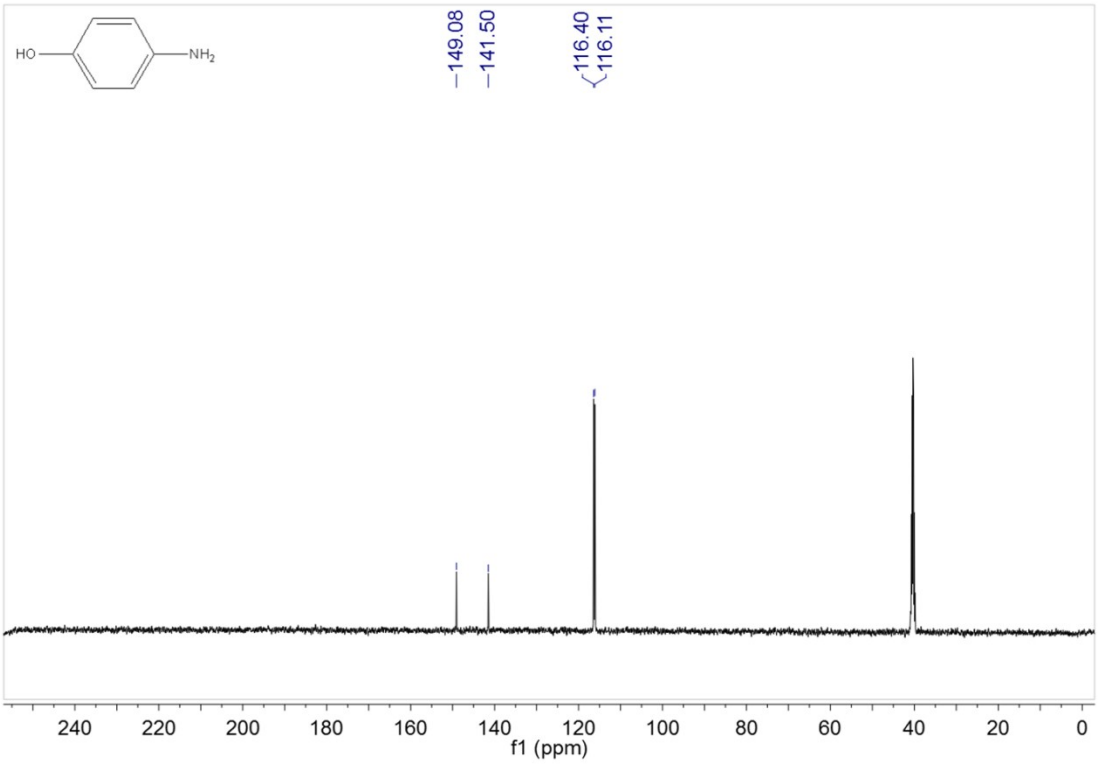

H3CO
NH2
6.74
6.72
6.64
6.62
3.73
3.36
2.00
2.11
2.94
2.06
f1 (ppm)

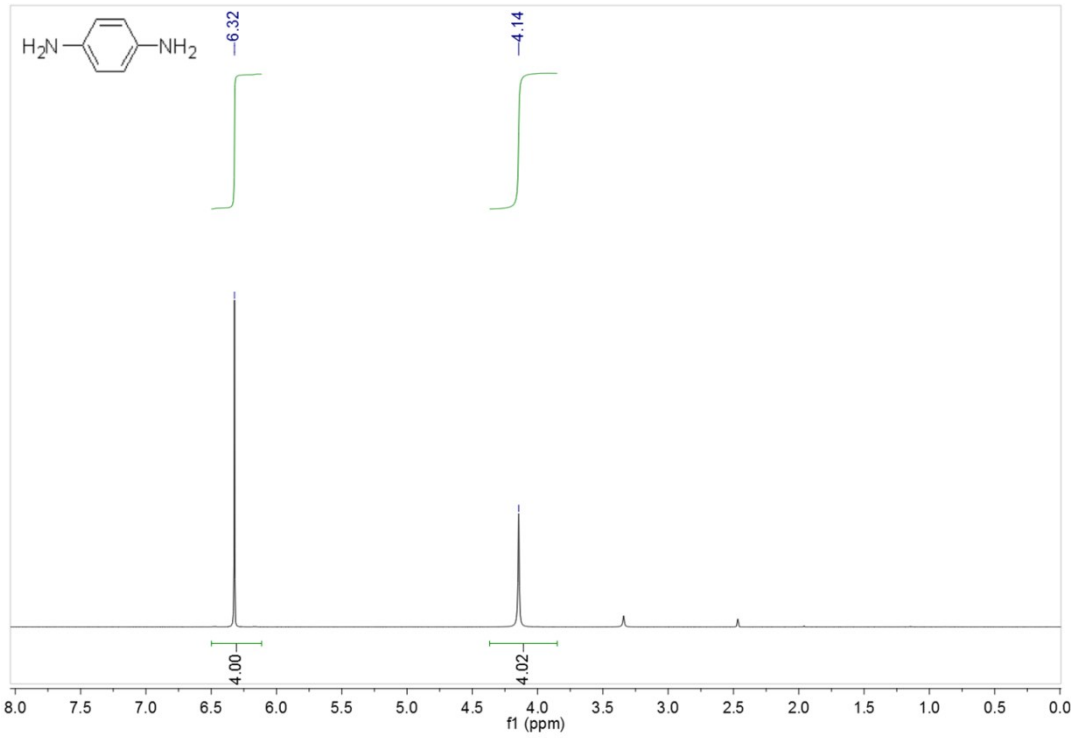

H3CO
NH2
153.23
140.37
116.84
115.24
56.15
f1 (ppm)

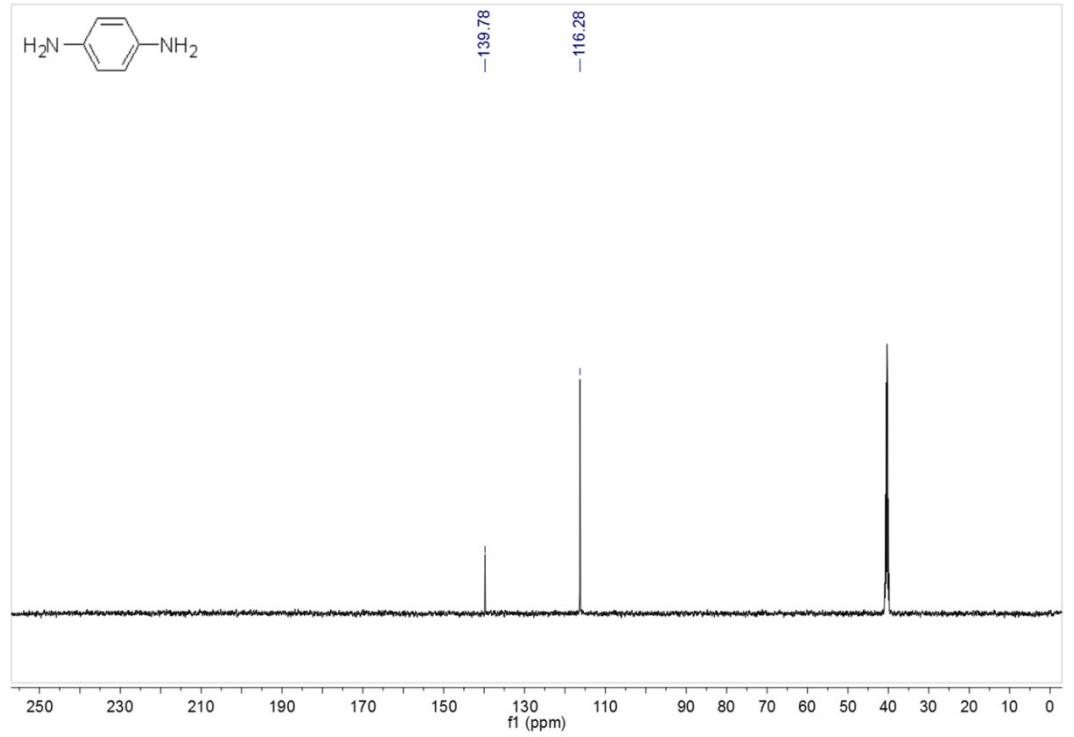

Cl
NH2
7.09
7.07
6.59
6.57
3.63
1.96
2.00
2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

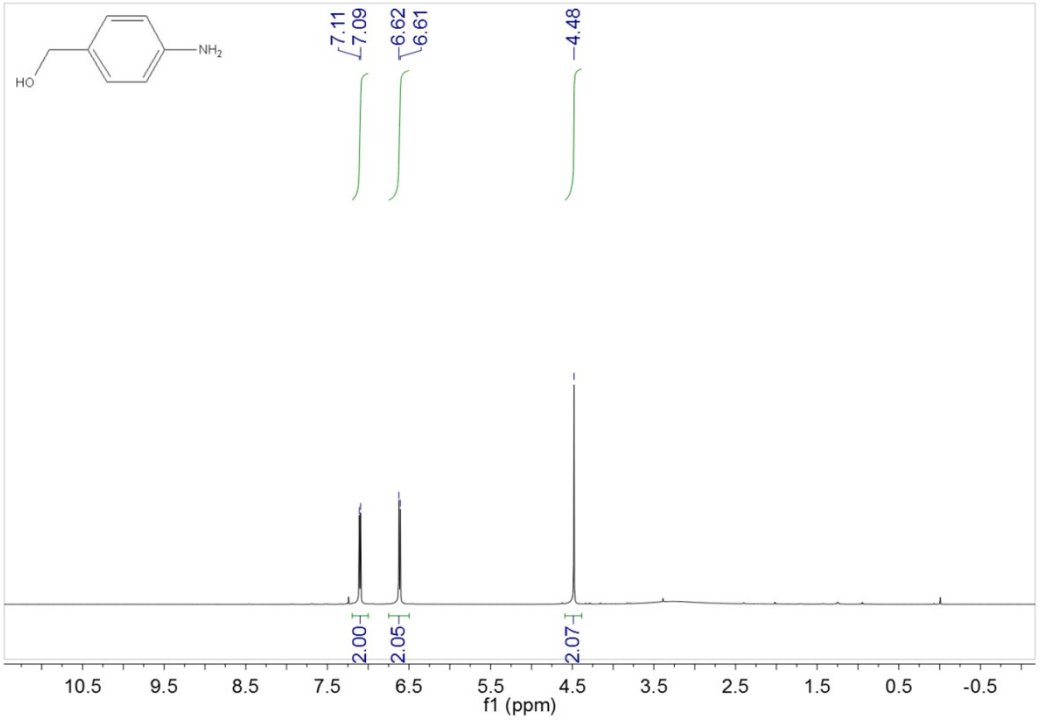

Cl
NH2
145.41
129.53
123.52
116.66
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

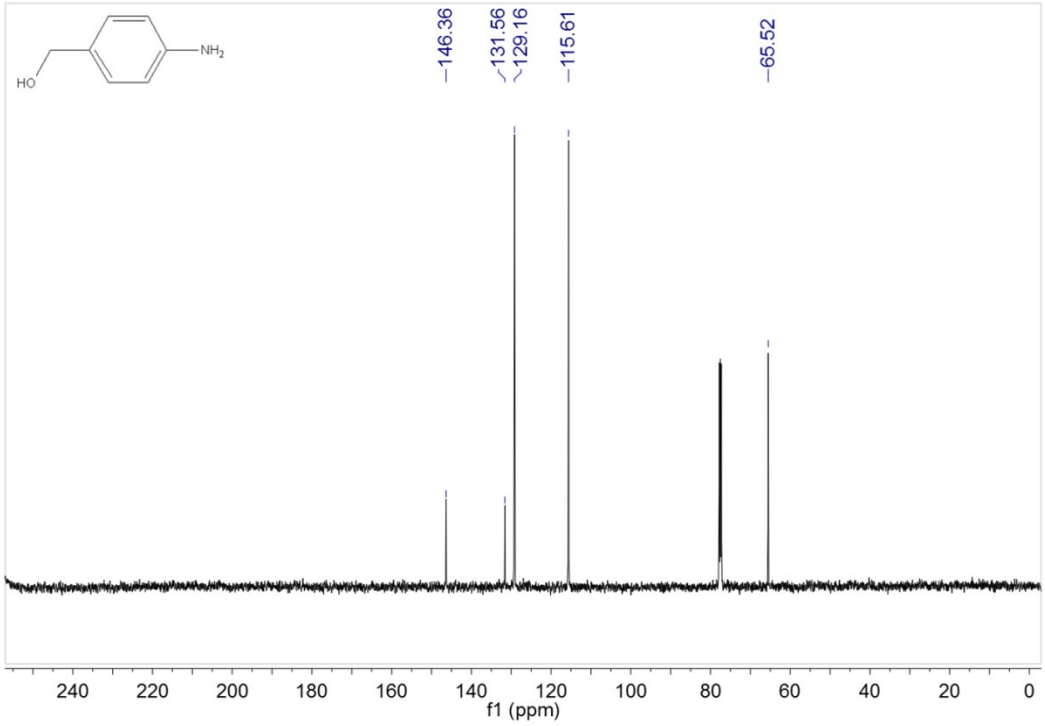

HO
NH2
8.31
6.45
6.44
6.39
6.37
6.28
4.32
1.00
1.98
2.00
1.99
9.4
8.8
8.2
7.6
7.0
6.4
5.8
5.2
4.6
4.0
f1 (ppm)

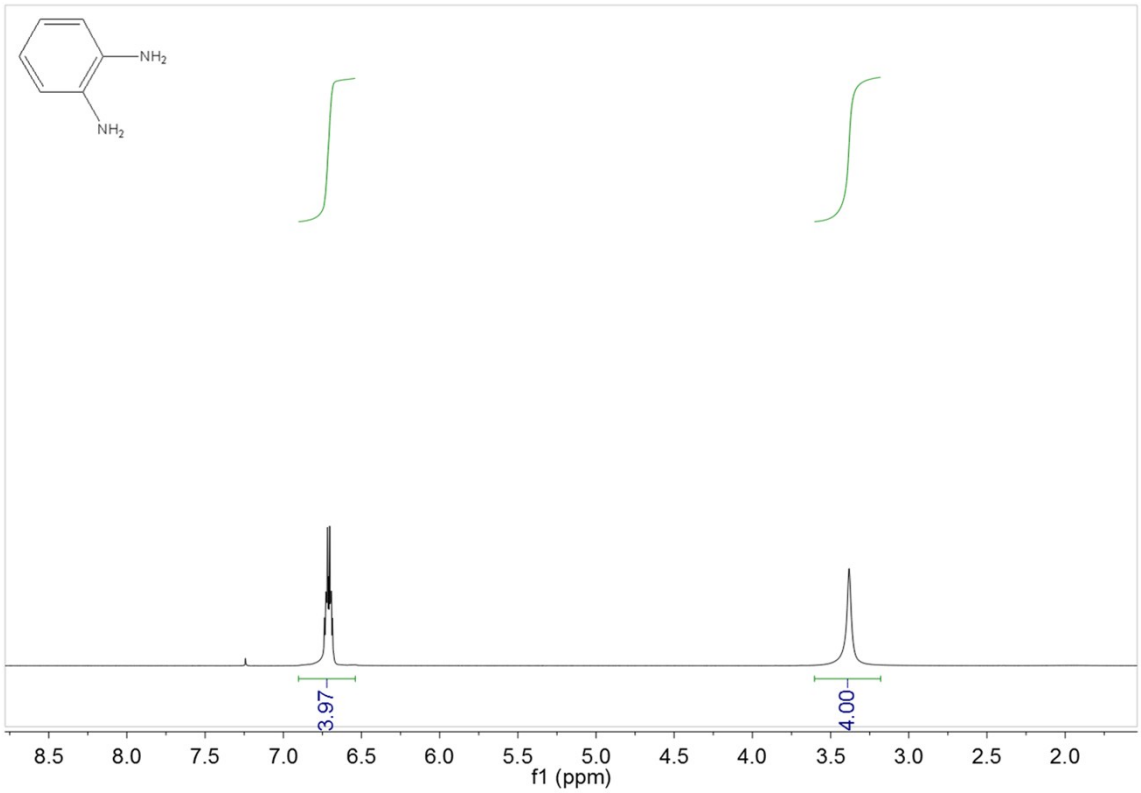

HO
NH2
149.08
141.50
116.40
116.11
240
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

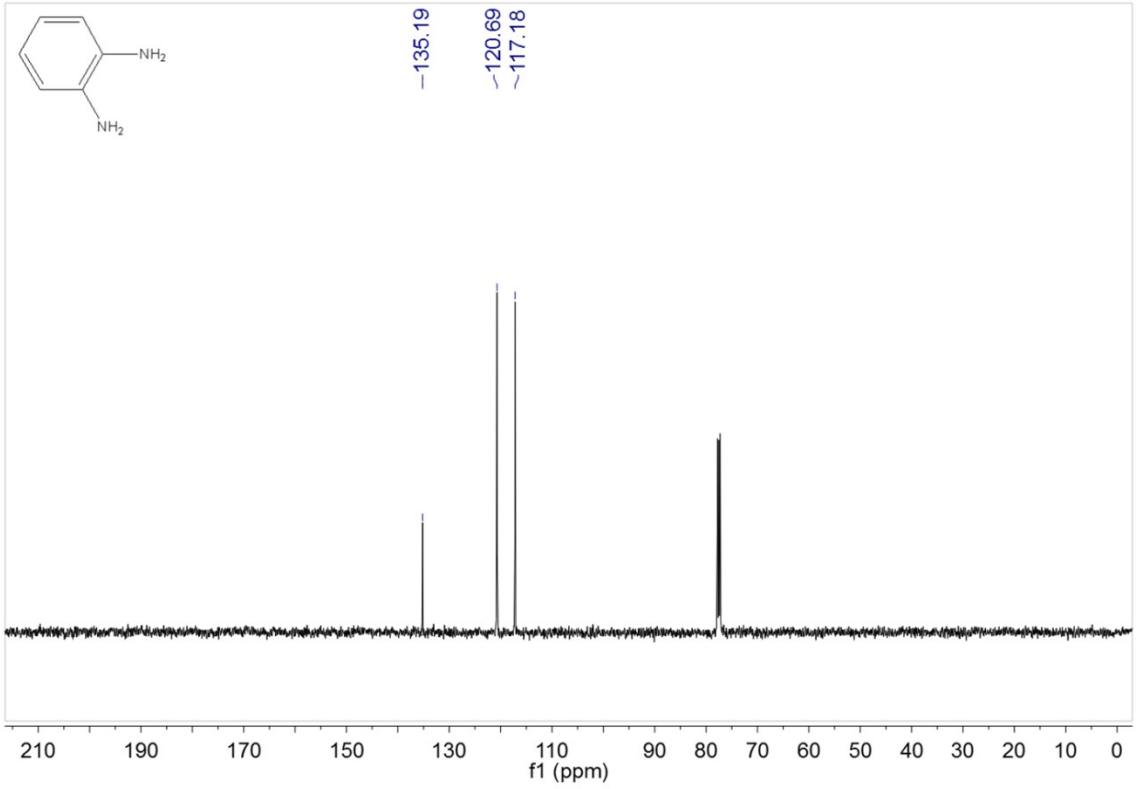

H2N
NH2
6.32
4.14
4.00
4.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

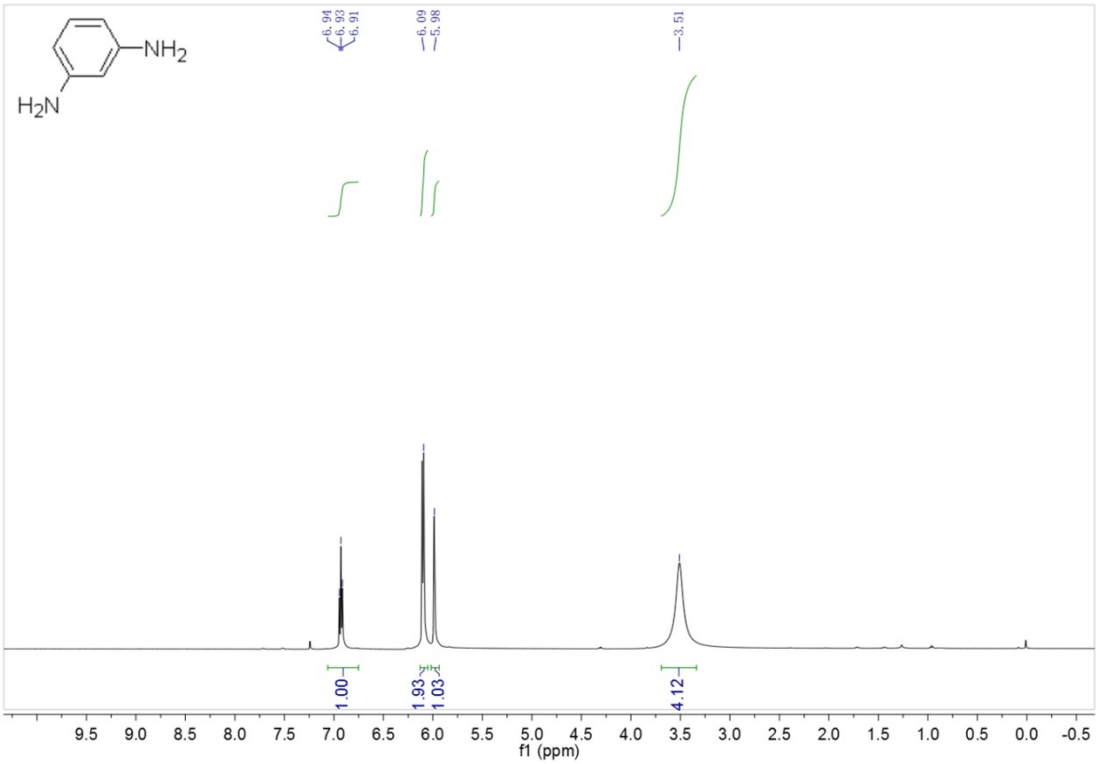

H2N
NH2
139.78
116.28
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

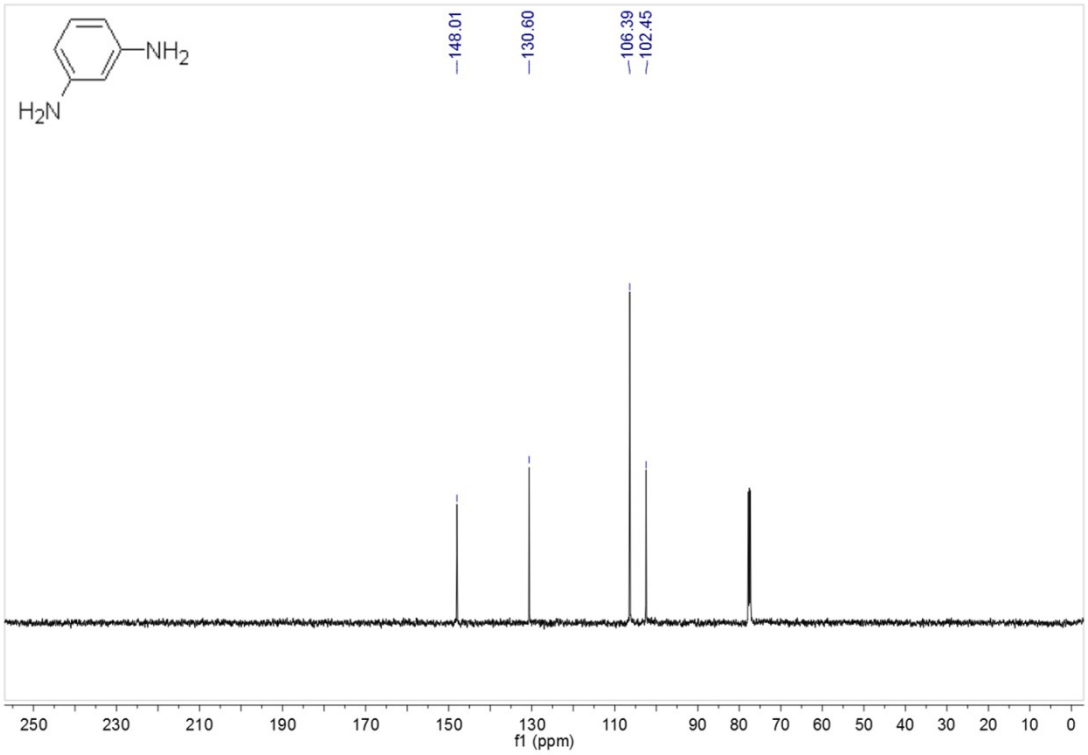

HO
NH2
7.11
7.09
6.62
6.61
4.48
2.00
2.05
2.07
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

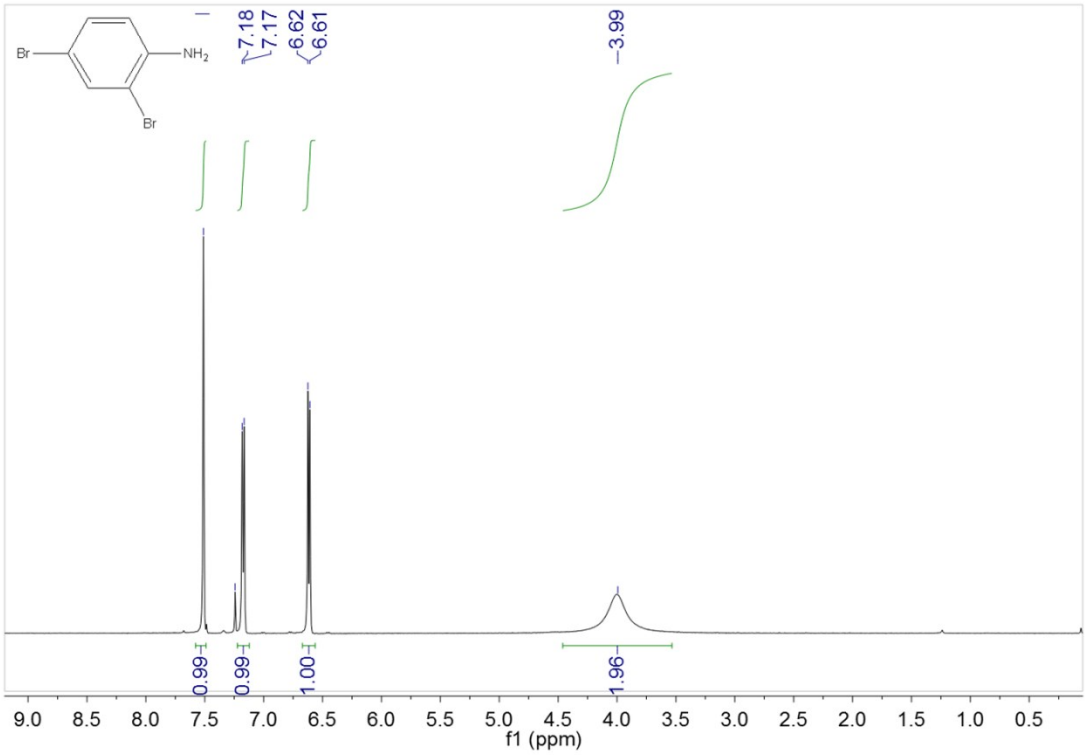

HO
NH2
146.36
131.56
129.16
115.61
65.52
240
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

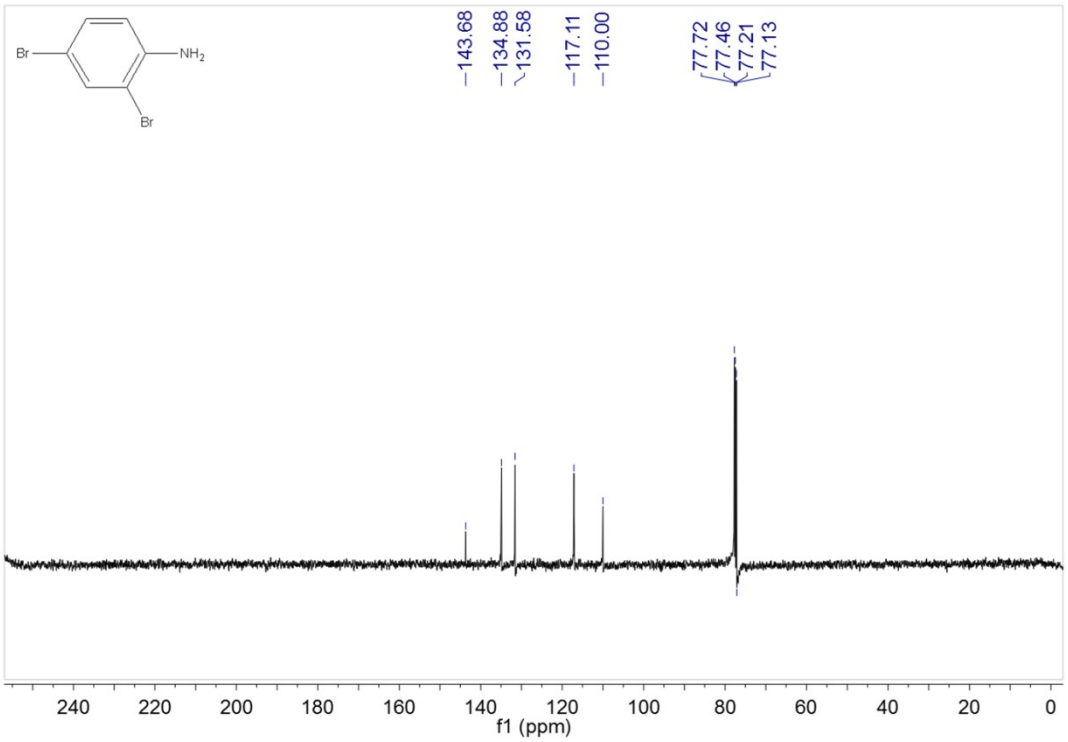

NH2
NH2
3.97
4.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

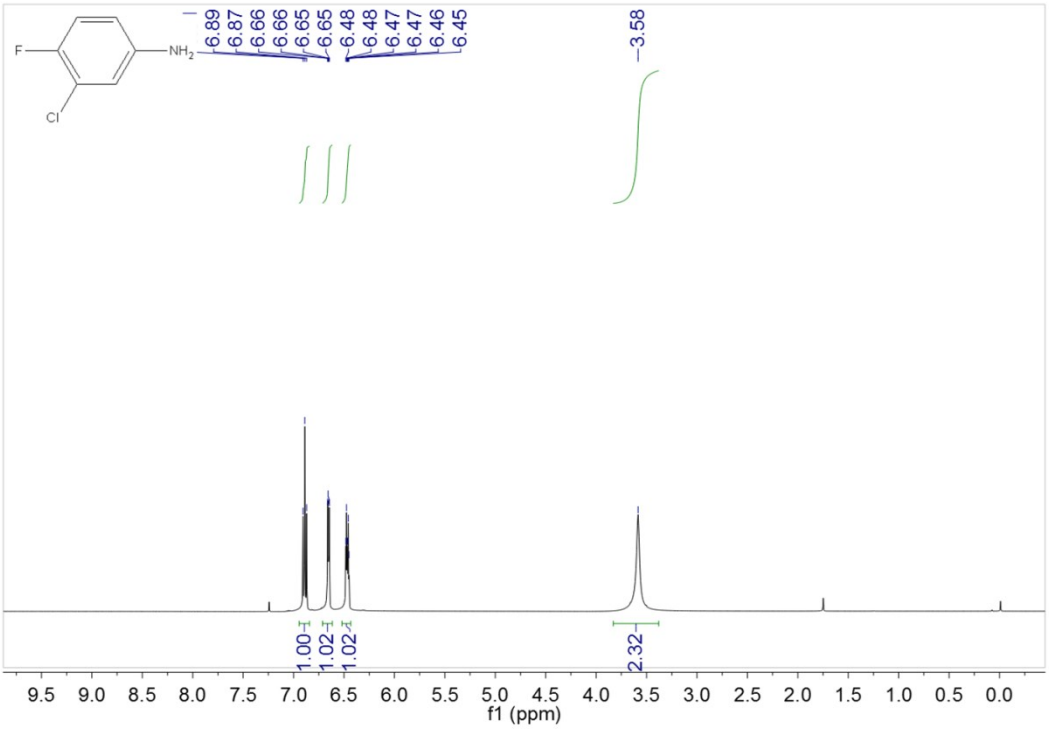

NH2
NH2
135.19
120.69
117.18
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

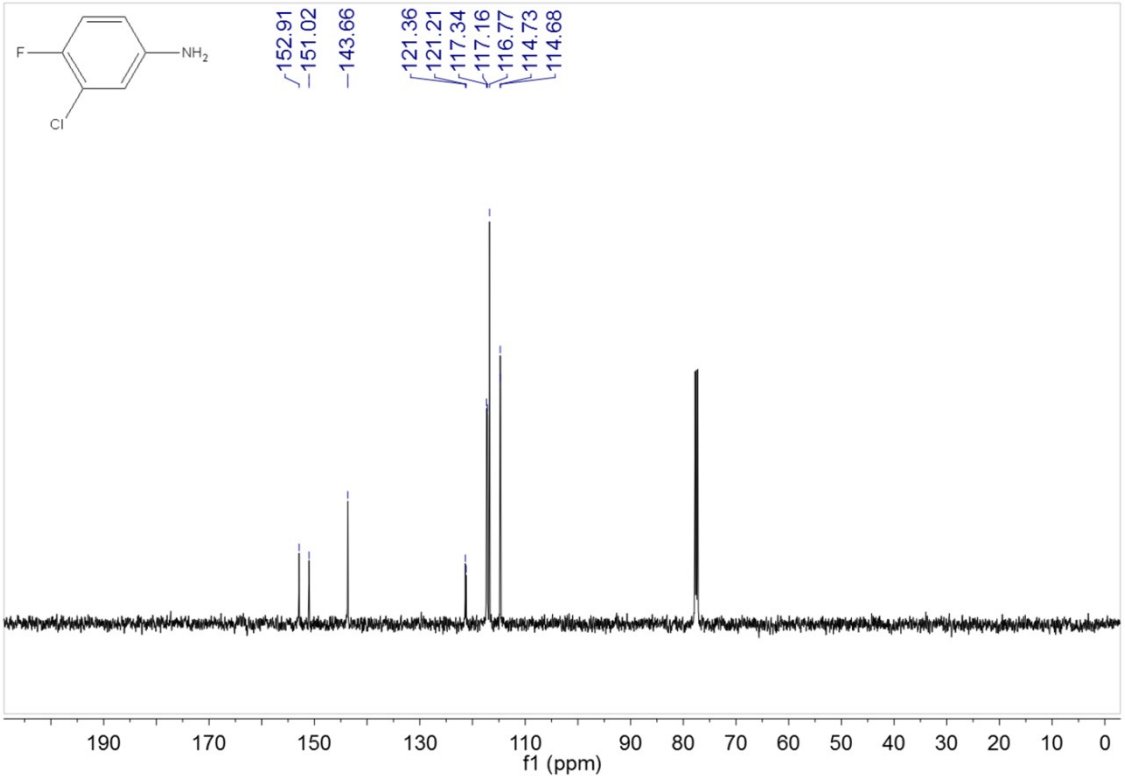

NH2
H2N
6.94
6.93
6.91
6.09
5.98
3.51
1.00
1.93
1.03
4.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

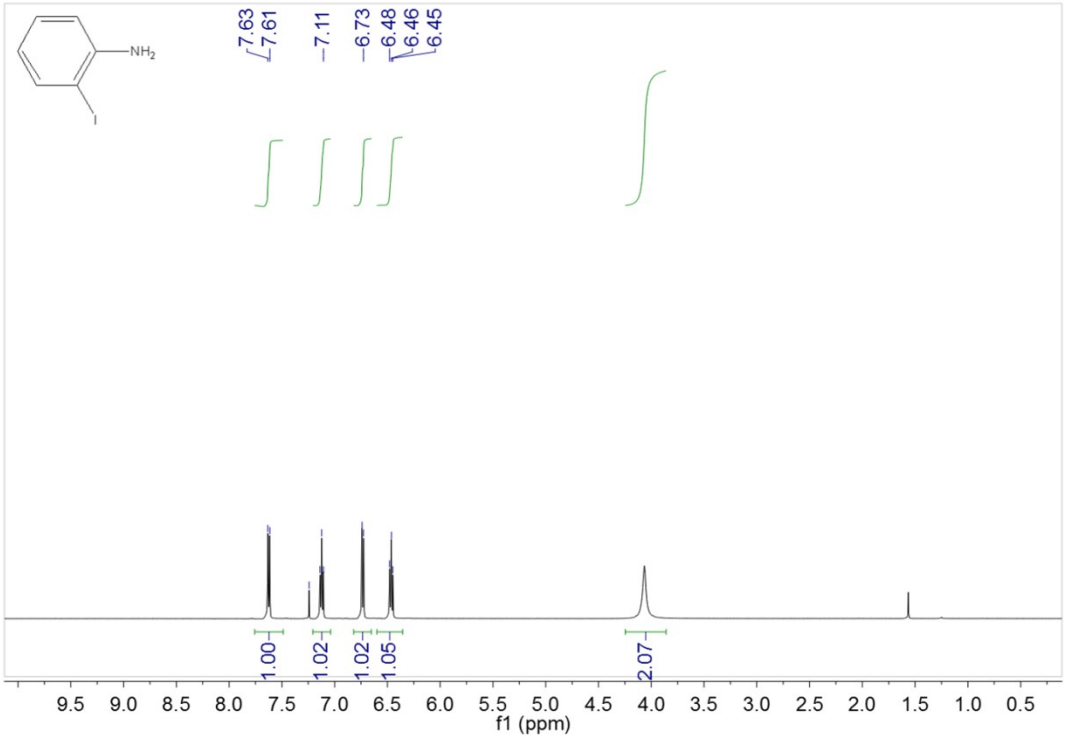

NH2
H2N
148.01
130.60
106.39
102.45
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

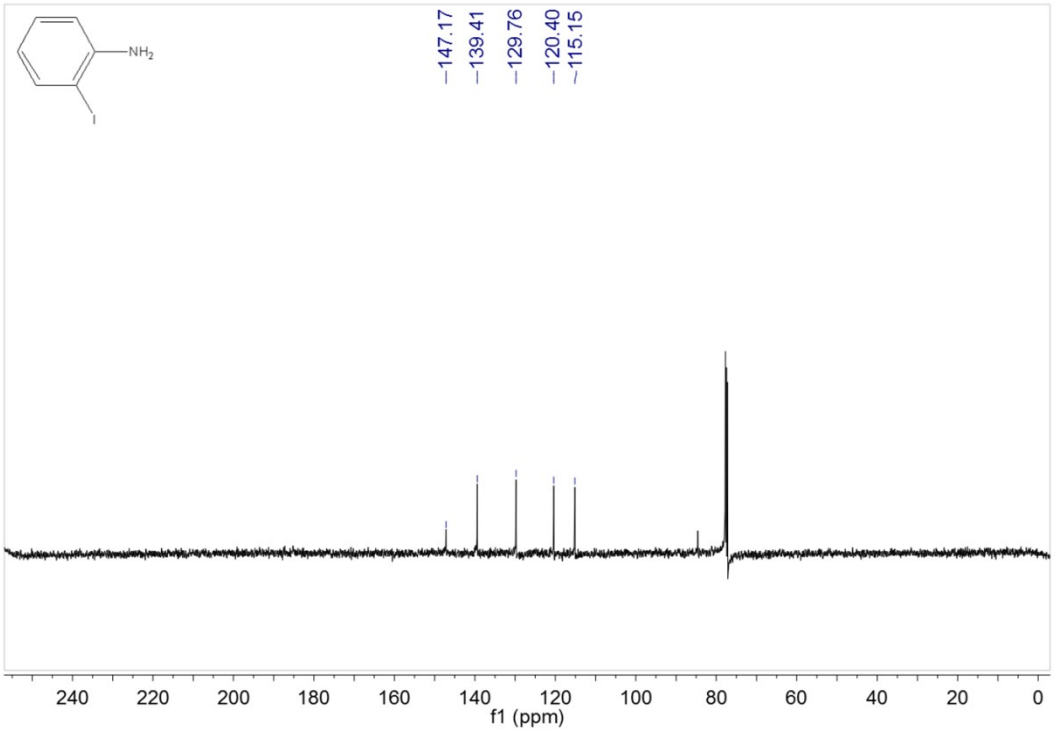

Br
NH2
Br
7.18
7.17
6.62
6.61
3.99
0.99
0.99
1.00
1.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

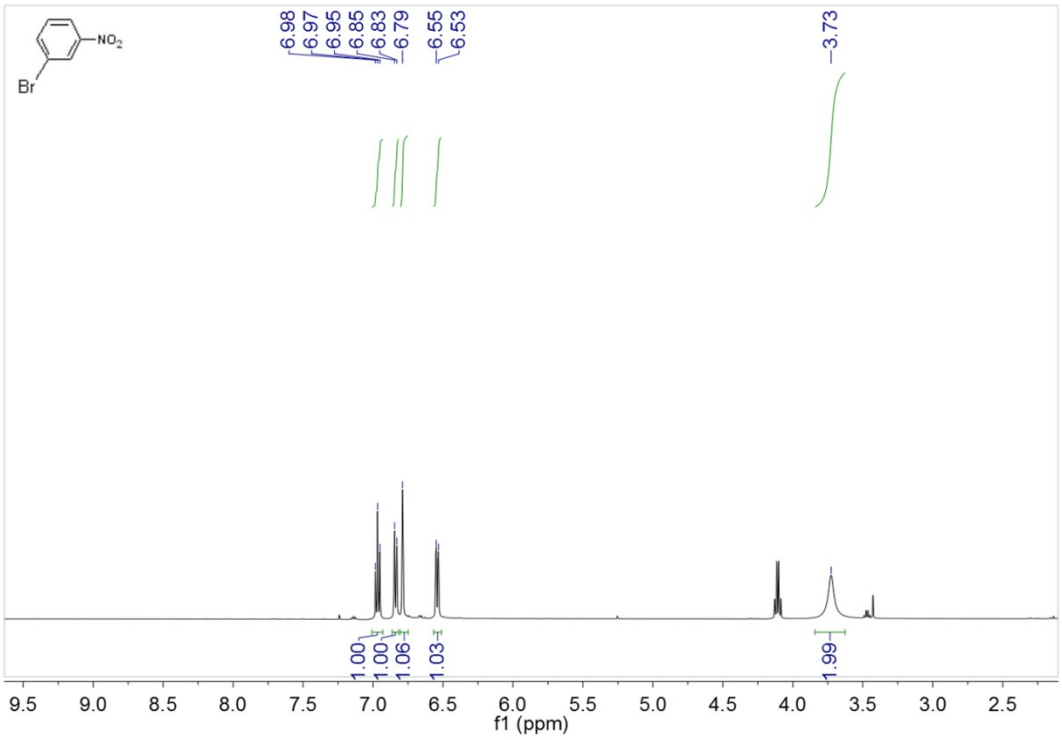

Br
NH2
Br
143.68
134.88
131.58
117.11
110.00
77.72
77.46
77.21
77.13
240 220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

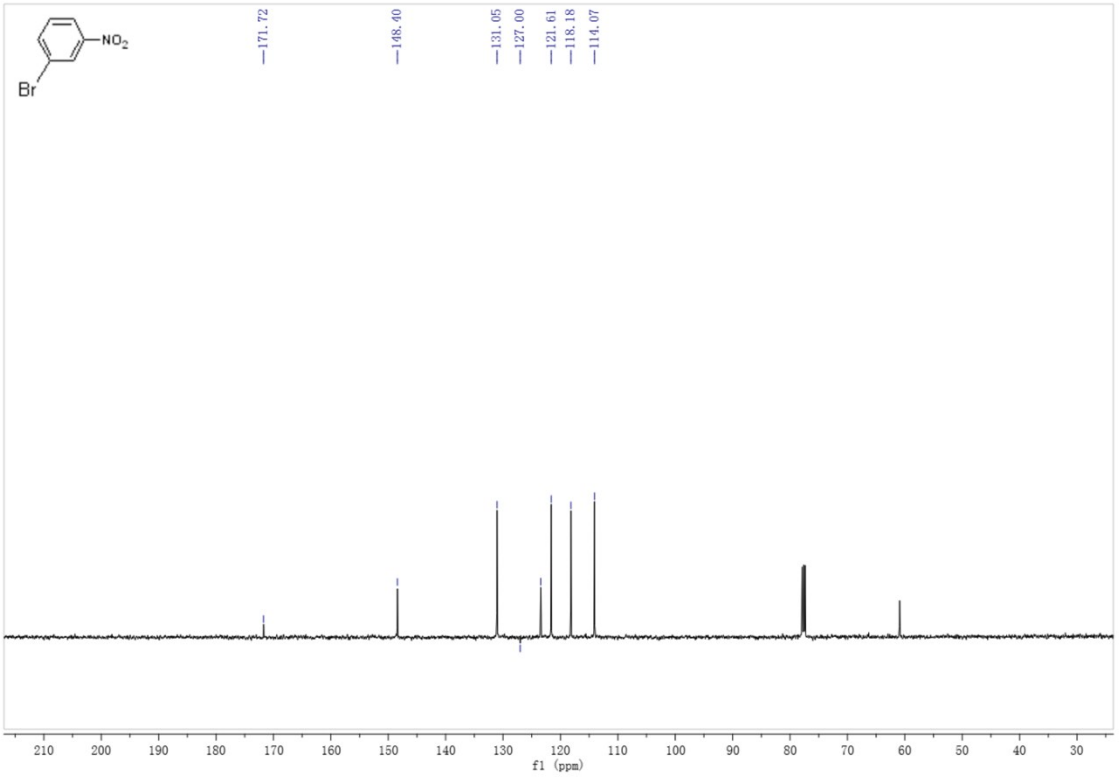

F
NH2
Cl
6.89
6.87
6.66
6.66
6.65
6.65
6.48
6.48
6.47
6.47
6.46
6.45
3.58
1.00
1.02
1.02
2.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


F
NH2
Cl
152.91
151.02
143.66
121.36
121.21
117.34
117.16
116.77
114.73
114.68
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NH2
I
7.63
7.61
7.11
6.73
6.48
6.46
6.45
1.00
1.02
1.02
1.05
2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


NH2
I
147.17
139.41
129.76
120.40
115.15
240 220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


NO2
Br
6.98
6.97
6.95
6.85
6.83
6.79
6.55
6.53
3.73
1.00
1.00
1.06
1.03
1.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5
f1 (ppm)


NO2
Br
171.72
148.40
131.05
127.00
121.61
118.18
114.07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)

References

1. H.X. Zhao, Y.X. Wang, R.H. Wang, *Chem. Commun*., 2014, **50**, 10871.
2. M. M. Dell'Anna, S. Intinia, G. Romanazzia, A. Rizzutia, C. Leonellib, F. Piccinnia, P. Mastrorillia, *J. Mol. Catal. A-Chem*., 2014, **395**, 307.