Supplementary Material (ESI) for Chemical Communications
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Electronic Supplementary Information

Cobalt-modified molybdenum carbide as an efficient catalyst for chemoselective reduction of aromatic nitro compounds†

Zhongkui Zhao,* Hongling Yang, and Yu Li

State Key Laboratory of Fine Chemicals, Department of Catalysis Chemistry and Engineering, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China; E-mail: zkzhao@dlut.edu.cn

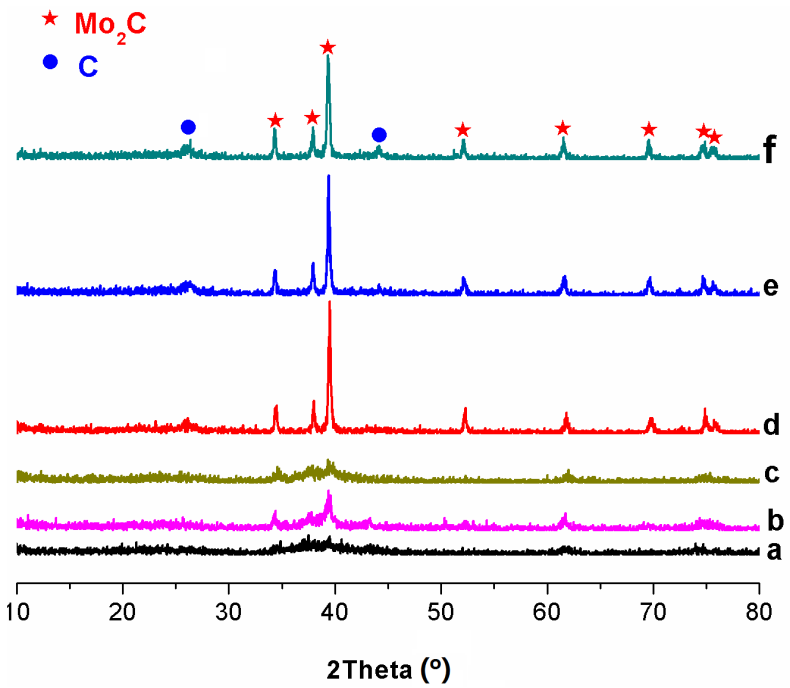


Fig. S1 XRD patterns of (a) 25%Mo_2C/AC (b) 2.5%Cu 25%Mo_2C/AC (c) 2.5%Cr 25%Mo_2C/AC (d) 2.5%Fe 25%Mo_2C/AC (e) 2.5%Co 25%Mo_2C/AC and (f) 2.5%Ni 25%Mo_2C/AC.

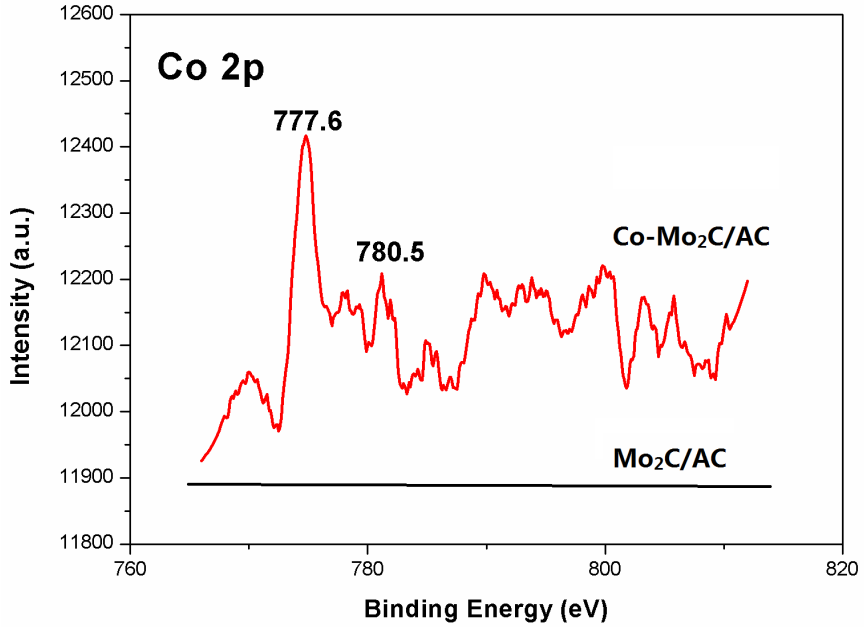


Fig. S2 The XPS spectrum of Co 2p in the Co-Mo_2C/AC and Mo_2C/AC catalysts**.**

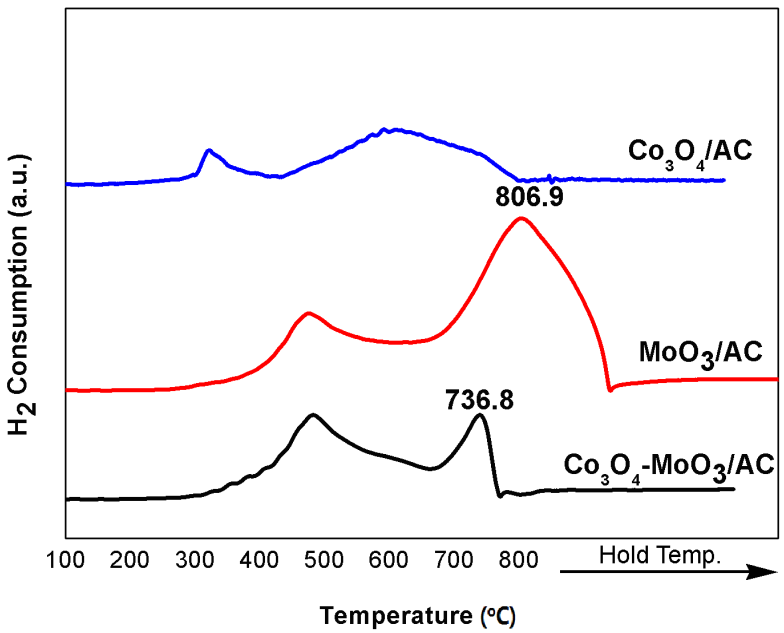


Fig. S3 H_2-TPR profiles of Co_3O_4/AC, MoO_3/AC and Co_3O_4-MoO_3/AC.

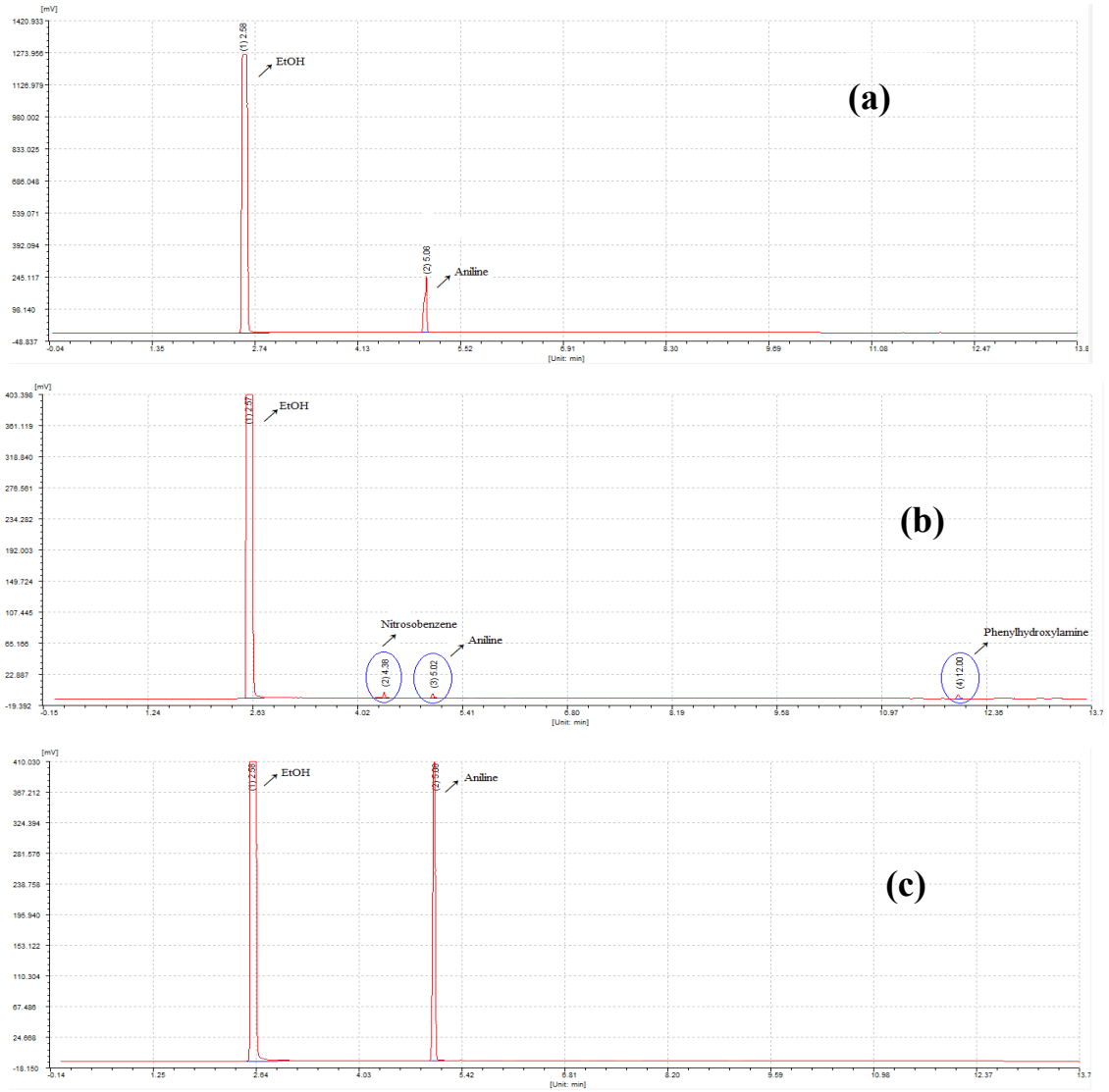


Fig. S4 Degree of sensitivity of GC for reaction mixture: (a) Typical GC of reaction mixture; (b) GC of the standard solution containing nitrosobenzene, aniline, and phenylhydroxylamine with the 4, 4 and 2 ppm of concentrations, respectively; (c) the amplified GC of (a).

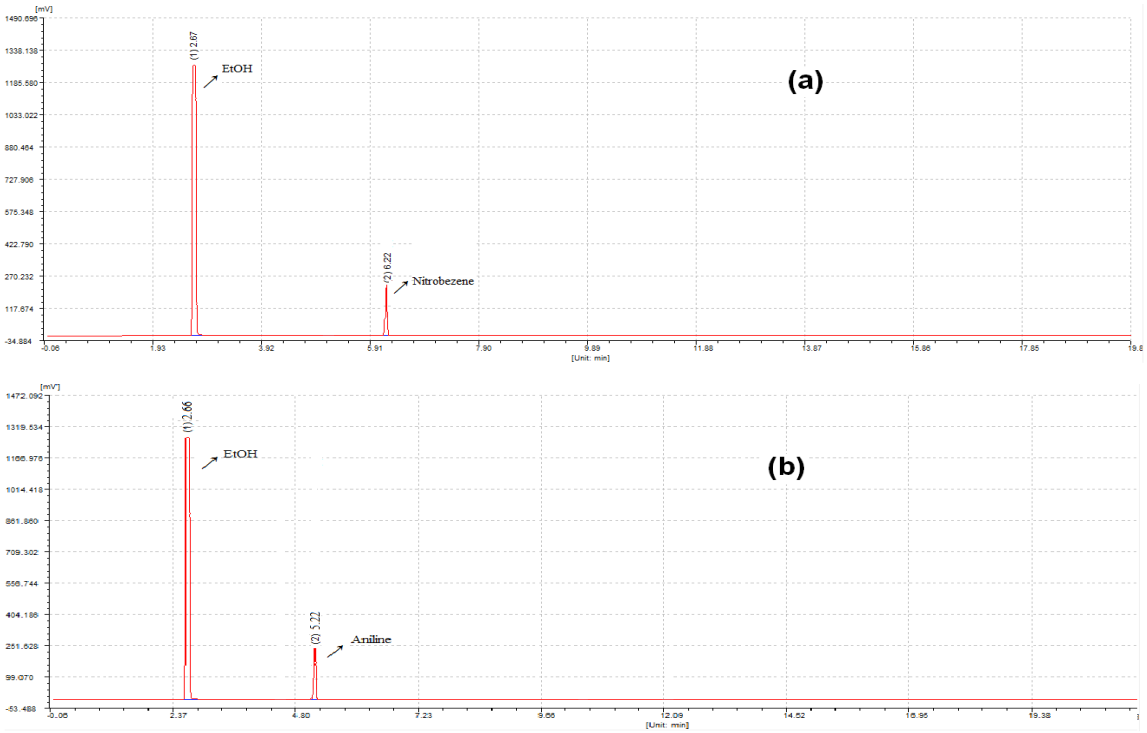


Fig. S5 GC of the reaction mixture while the nitrobenzene is used as substrate: (a) before reaction; (b) after reaction.

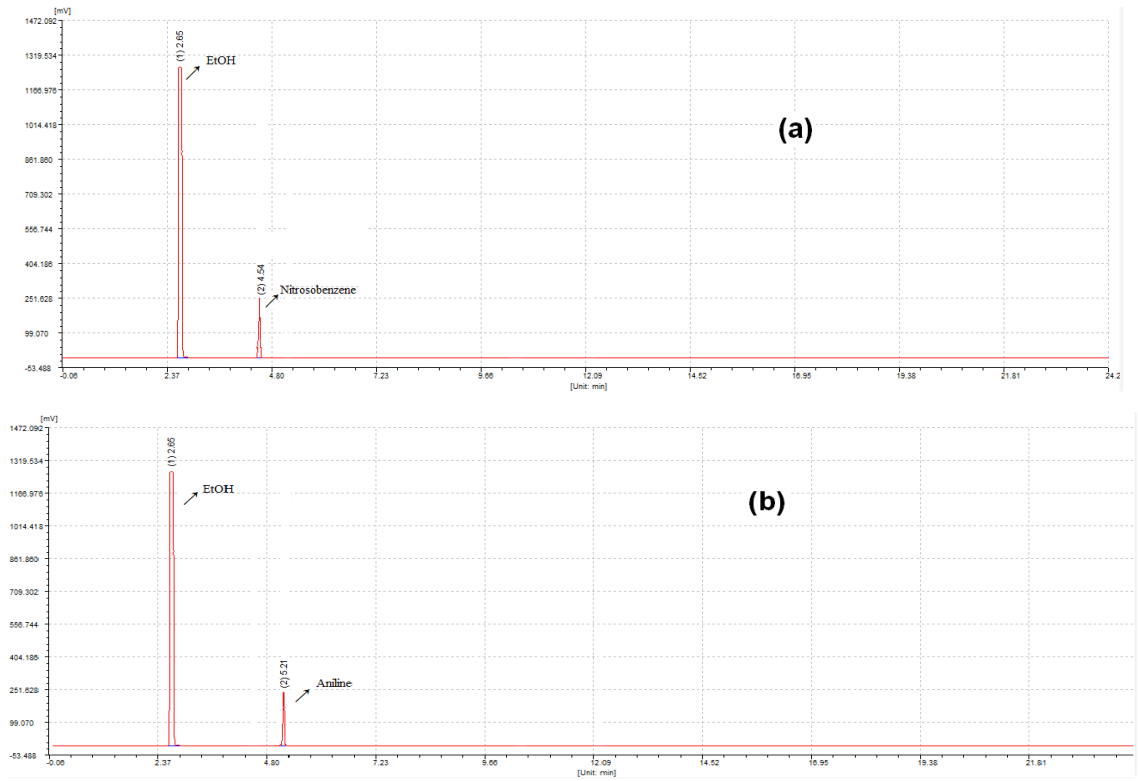


Fig. S6 GC of the reaction mixture while the nitrosobenzene is used as substrate: (a) before reaction; (b) after reaction.

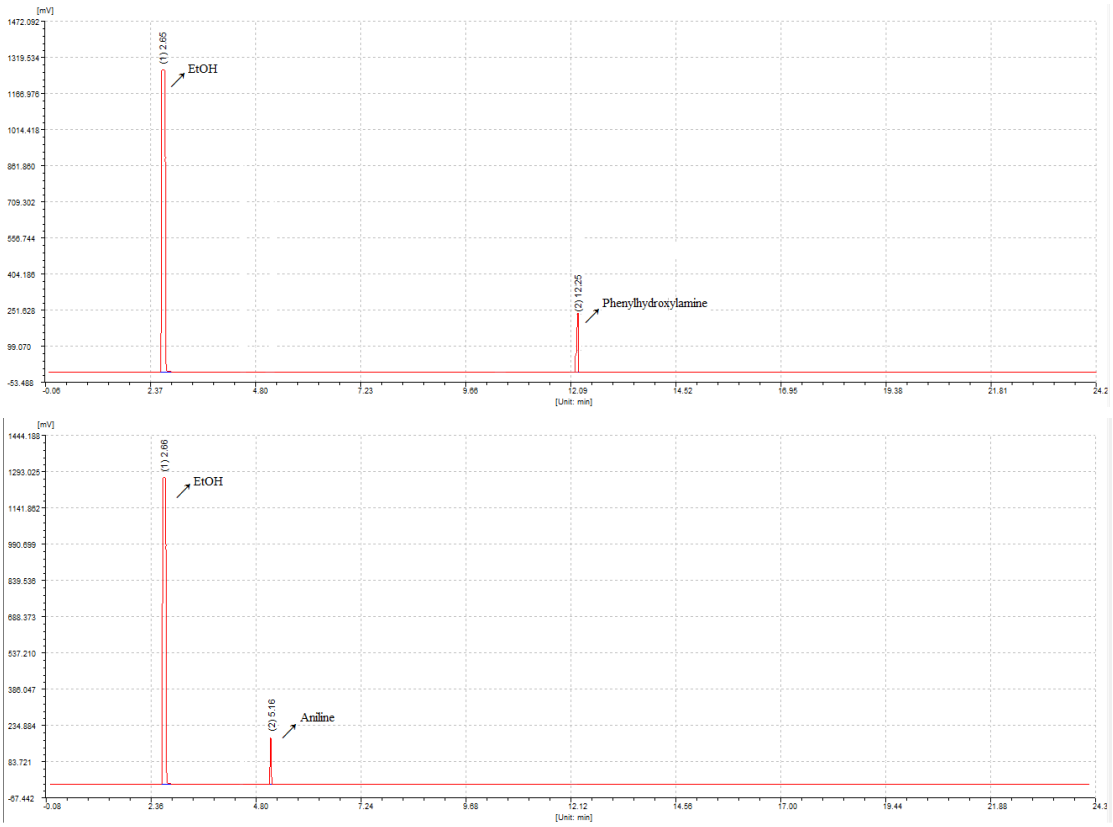


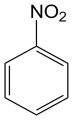
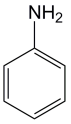
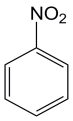
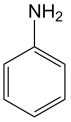
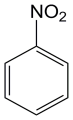
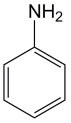
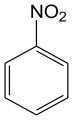
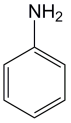
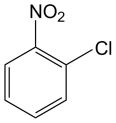
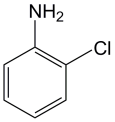
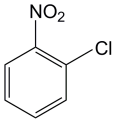
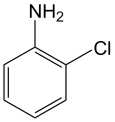
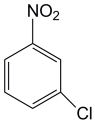
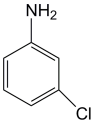
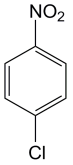
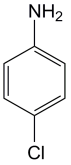
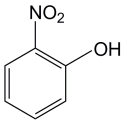
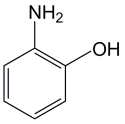
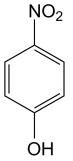
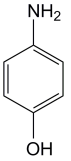
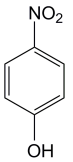
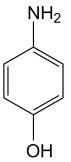
Fig. S7 GC of the reaction mixture while the phenylhydroxylamine is used as substrate: (a) before reaction; (b) after reaction.

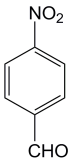
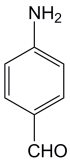
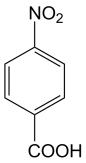
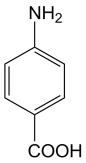
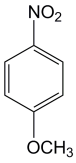
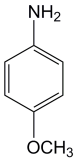
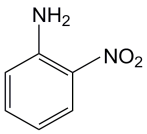
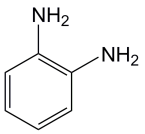
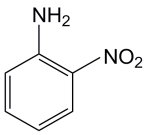
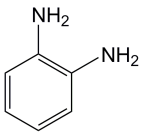
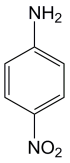
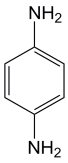
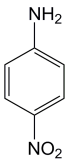
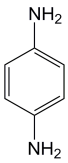
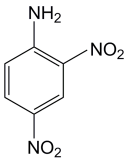
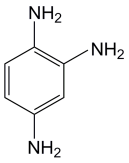
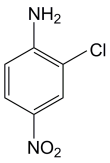
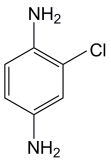
Table S1 Different loading of the catalysts for the performance of the reduction of nitrobenzene[a]

Entry	Catalyst	Reaction time (h)	Sel./Yield (%)[b]
1	1.5%Co25%Mo_2C/AC	1	100/75
2	2.5%Co25%Mo_2C/AC	1	100/84.4
3	3.0%Co25%Mo_2C/AC	1	100/82
3	3.5%Co25%Mo_2C/AC	1	100/78
4	5.0%Co25%Mo_2C/AC	1	100/72

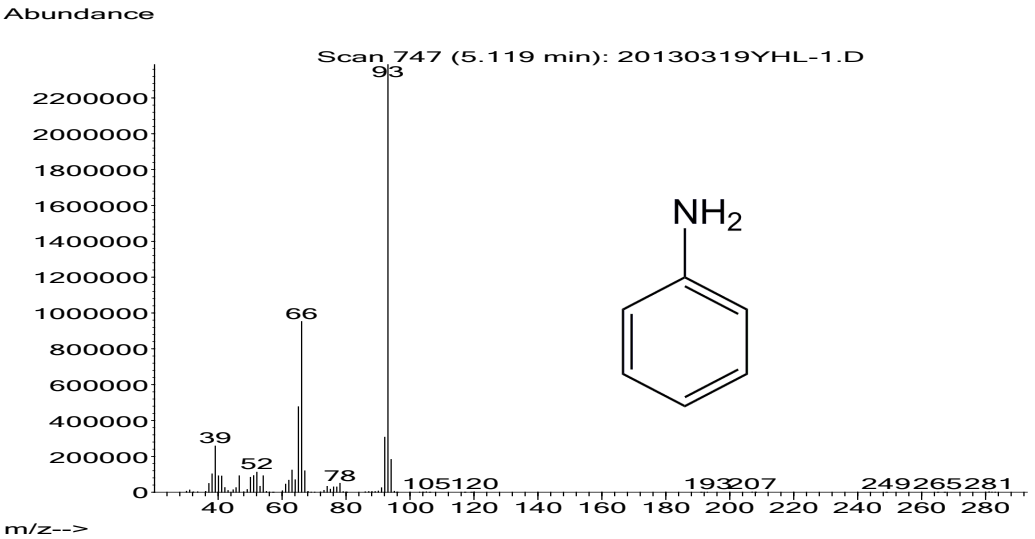
[a] Reaction conditions: 94 mg catalyst, 1 mmol nitrobenzene, 2 equivalent hydrazine hydrate; [b] the products were detected by GC-MS and ^{1}H-NMR.

Table S2 Summary on the reduction of various substituted nitrobenzenes[a]

Entry	Substrate	Product	Hydrazine equiv.	Reaction time(h)	Sel./Yield (%)[b]
1			2	1	100/84.4
2			2.5	1	100/97.4
3			3	1	100/100
4			2	2	100/100
5			6	1	100/100
6			6	1	100/100
7			6	1	100/100
8			6	1	100/100
9			6	1	100/100
10			8	1	95.2/63.8
11			7	3	100/100

12			1	1	100/100
13			6	1	100/100[c]
14			6	1	100/100
15			6	1	100/81.3
16			10	3	100/100
17			6	1	100/54.5
18			8	2	100/100
19			14	3	100/100[c]
20			6	1	100/100

[a] Reaction condition :94mg catalyst, 1mmol substrate, the products were detected by GC-MS,NMR, [b] detected by GC-MS and NMR; [c] LC-MS was used.


Abundance
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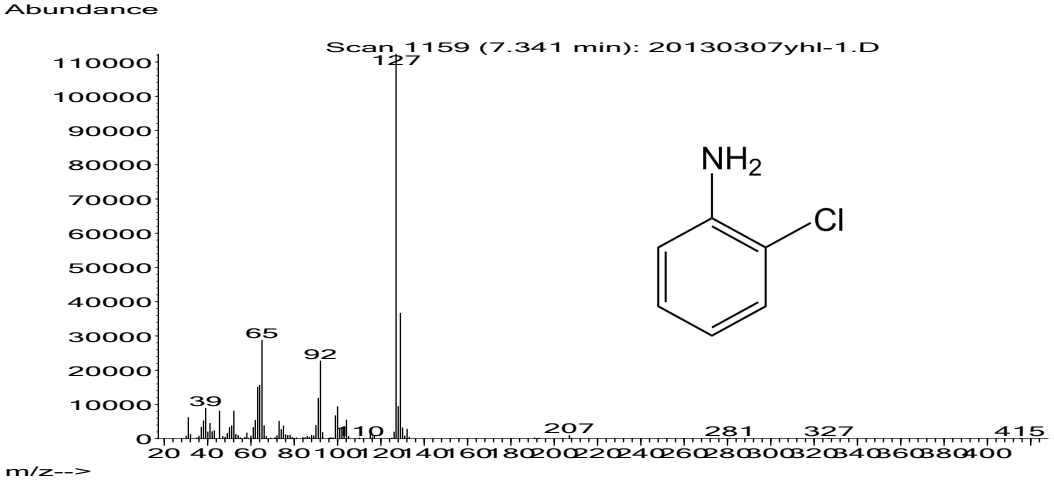
93
66
39
52
78
105120
193207
249265281
NH2
m/z-->


Abundance
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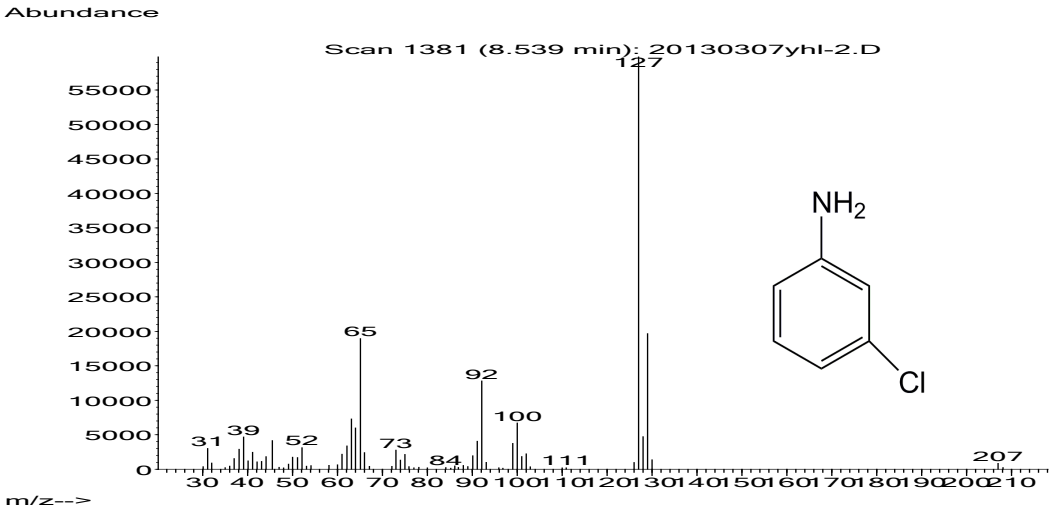
65
92
39
10
207
281
327
415
NH2
Cl
m/z-->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Scan 1381 (8.539 min): 20130307yhl-2.D
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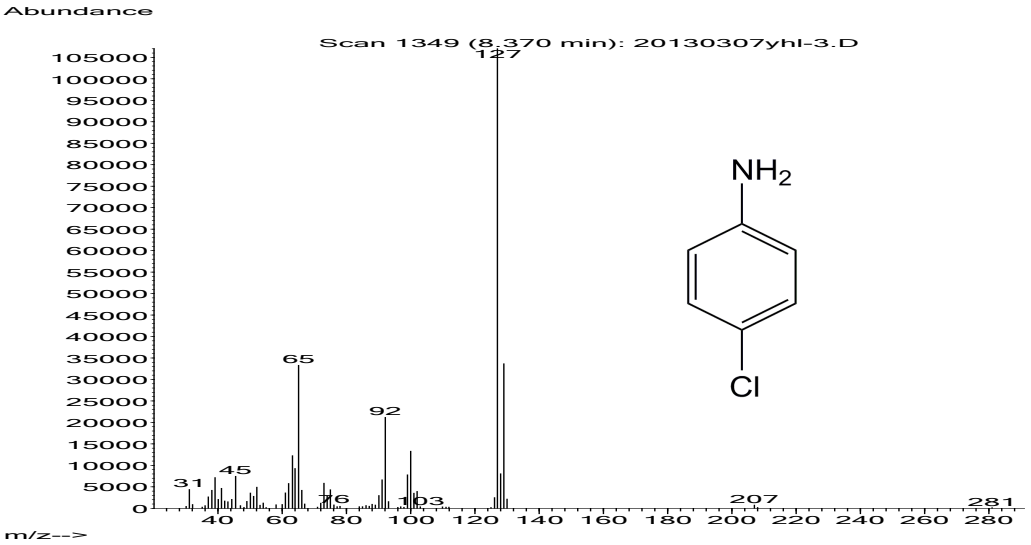
65
92
100
39
31
52
73
84
111
207
NH2
Cl
m/z-->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92
45
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76
103
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281
NH2
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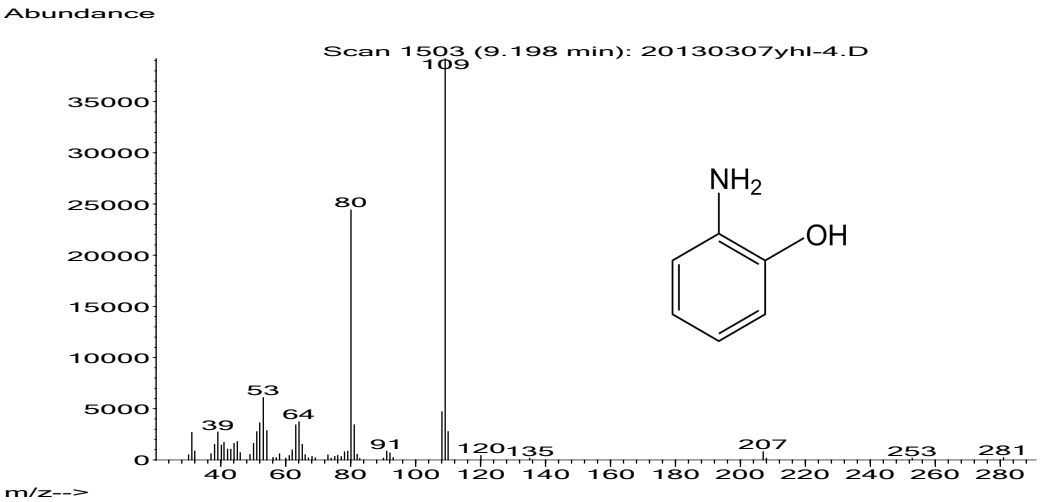
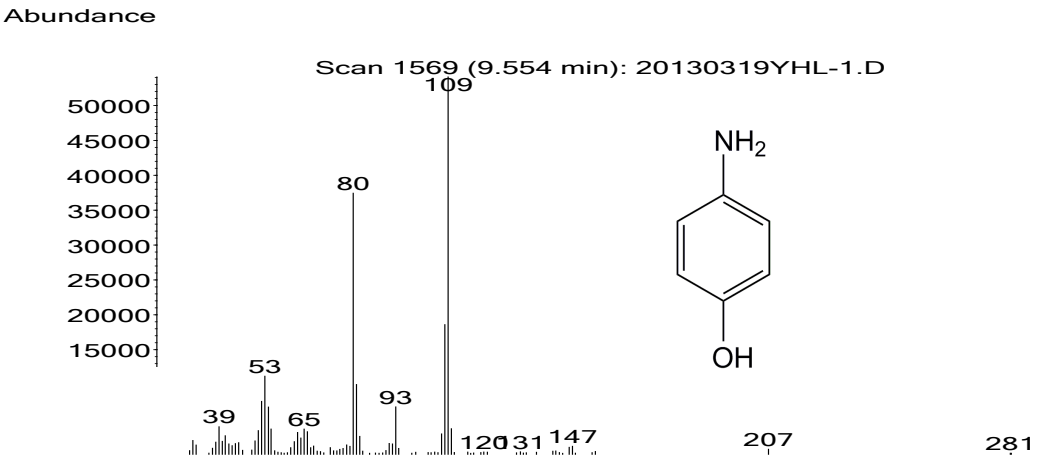
m/z-->


Abundance
Scan 1503 (9.198 min): 20130307yhl-4.D
109
80
53
64
39
91
120
135
207
253
281
NH2
OH
m/z-->


Abundance
Scan 1569 (9.554 min): 20130319YHL-1.D
109
80
53
93
39
65
120
131
147
207
281
NH2
OH

Supplementary Material (ESI) for Chemical Communications
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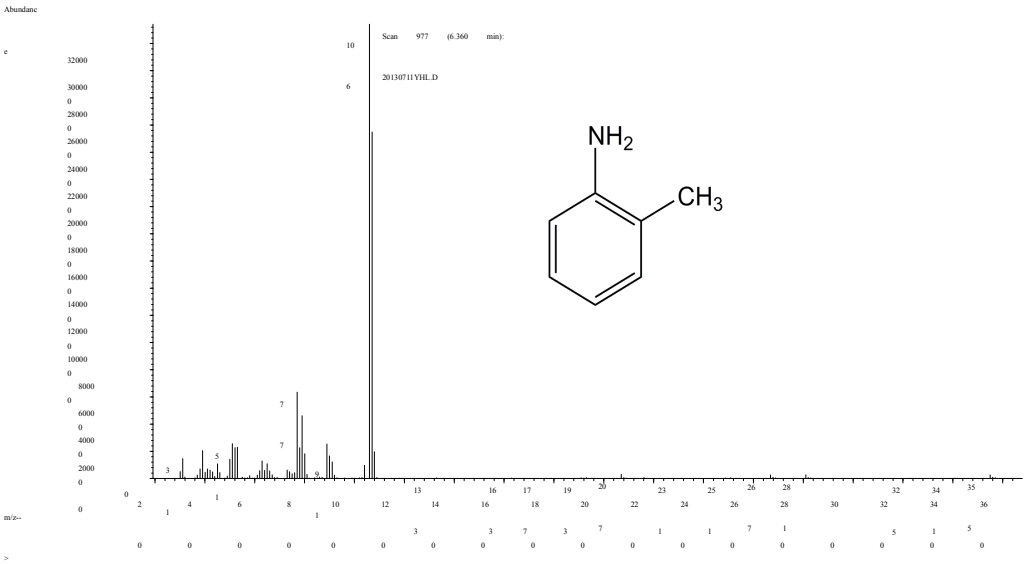

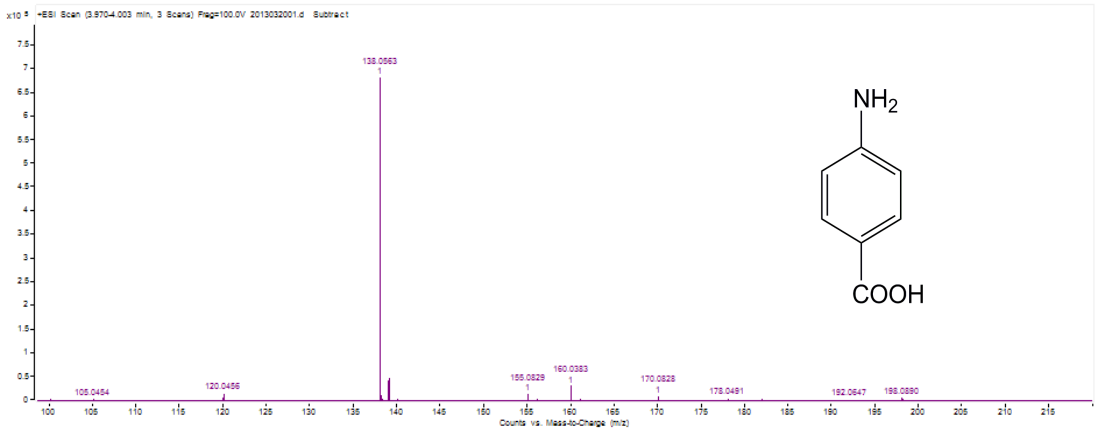

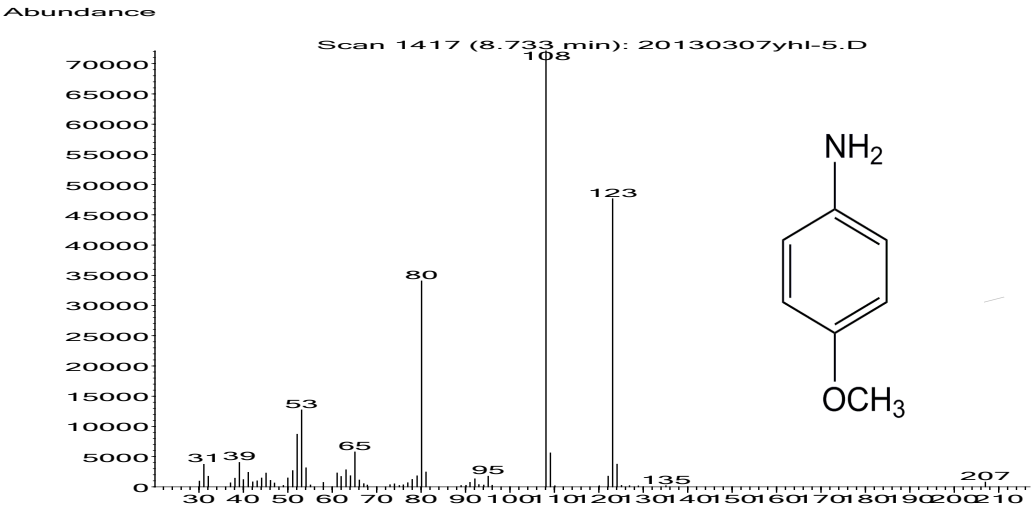

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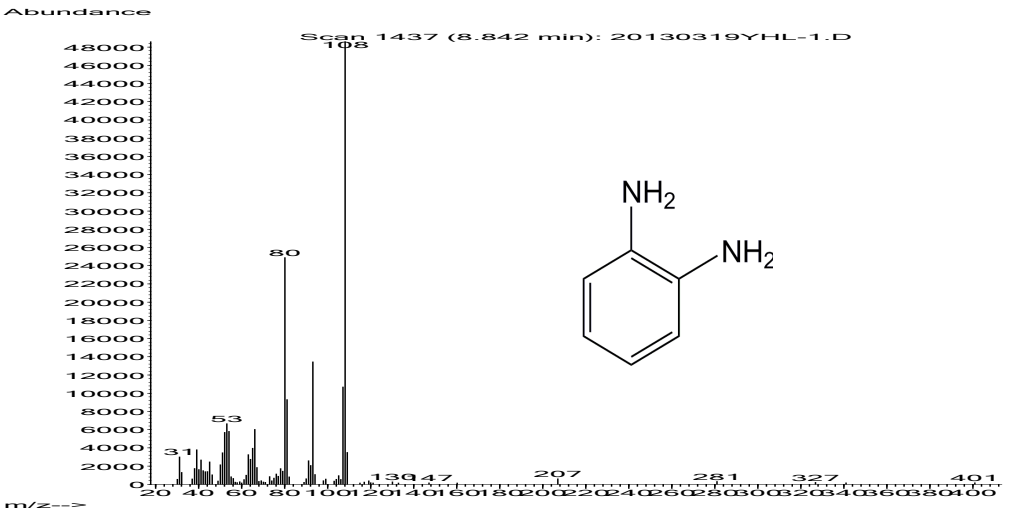
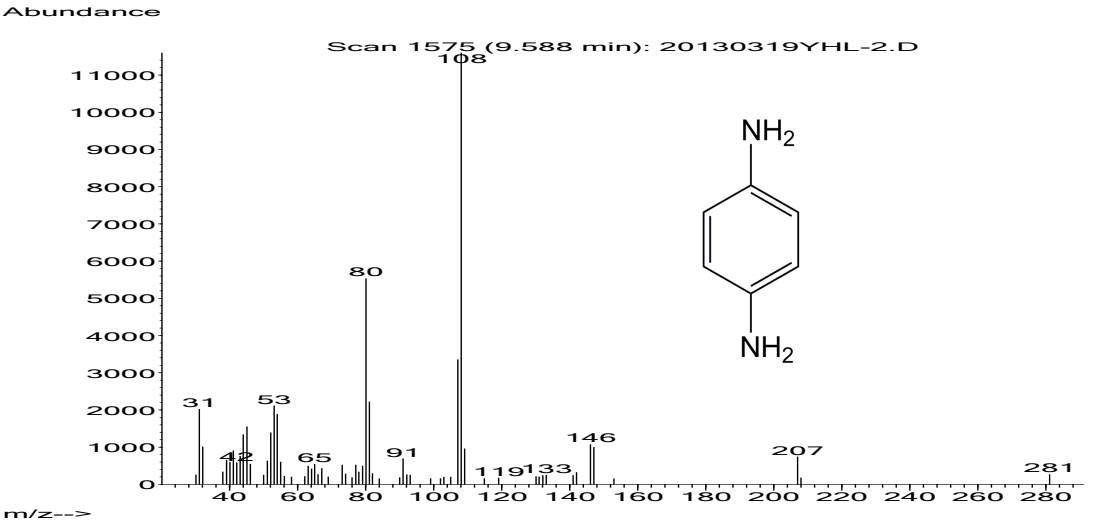
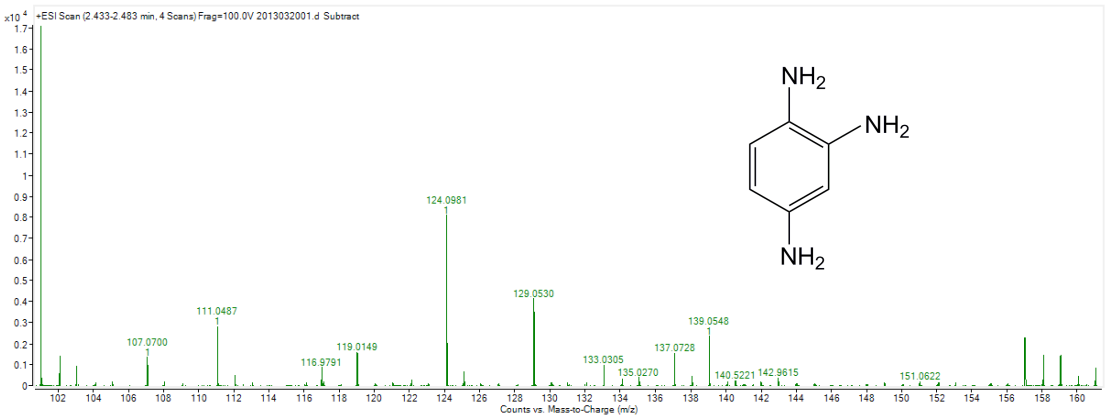
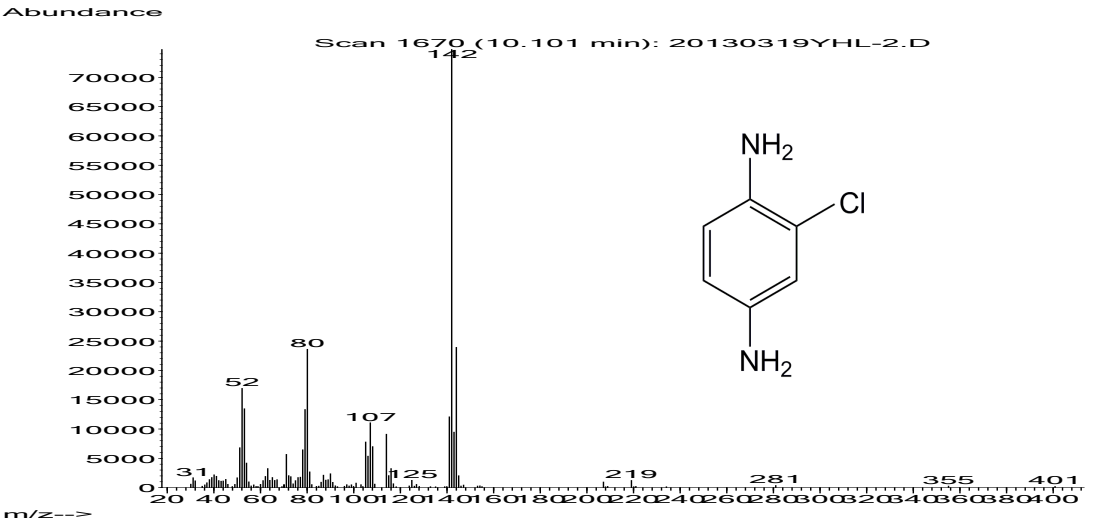








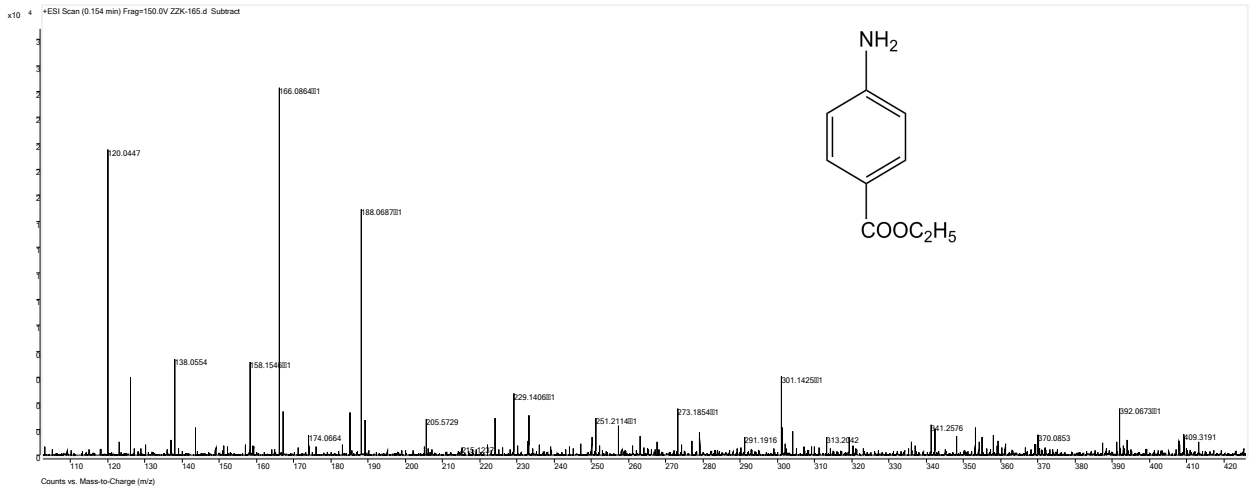
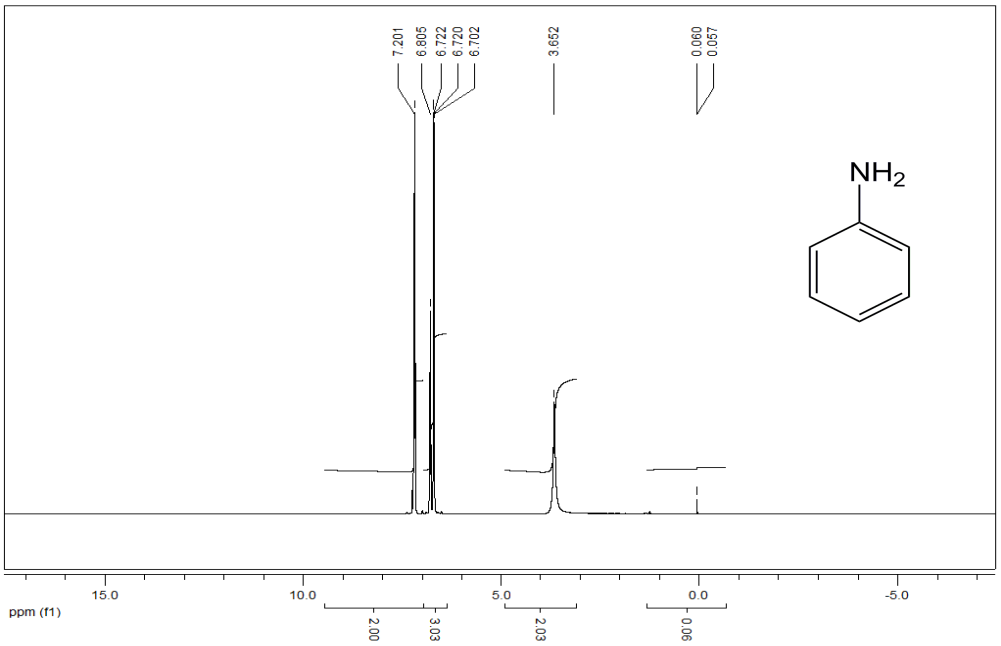
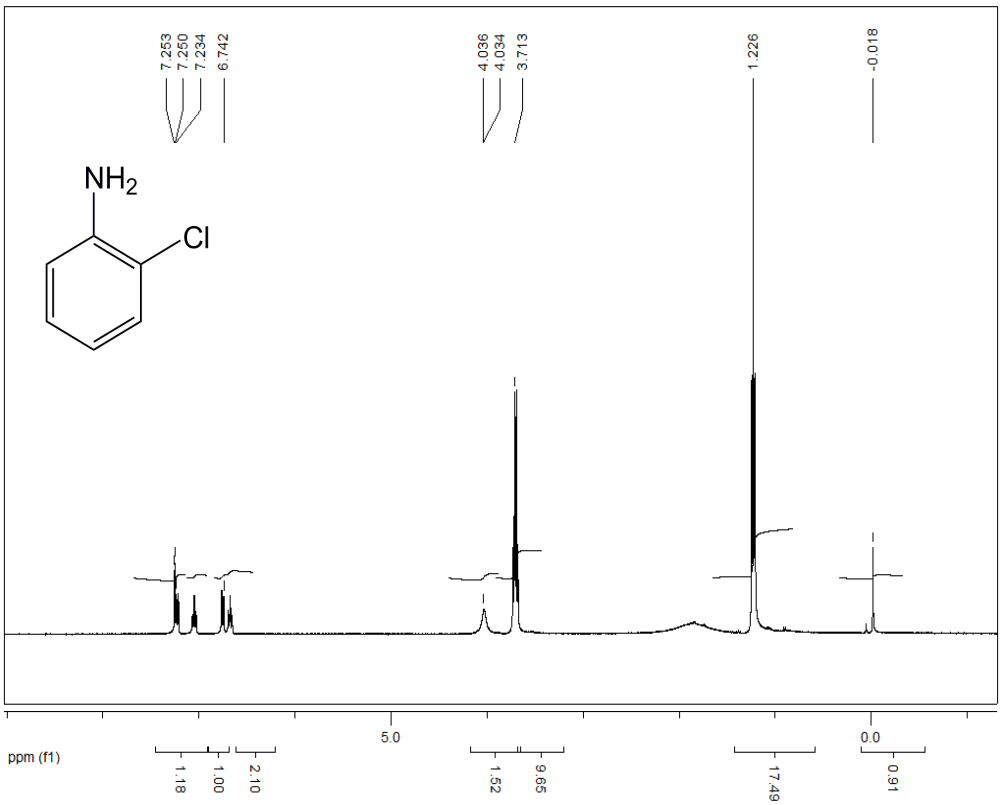


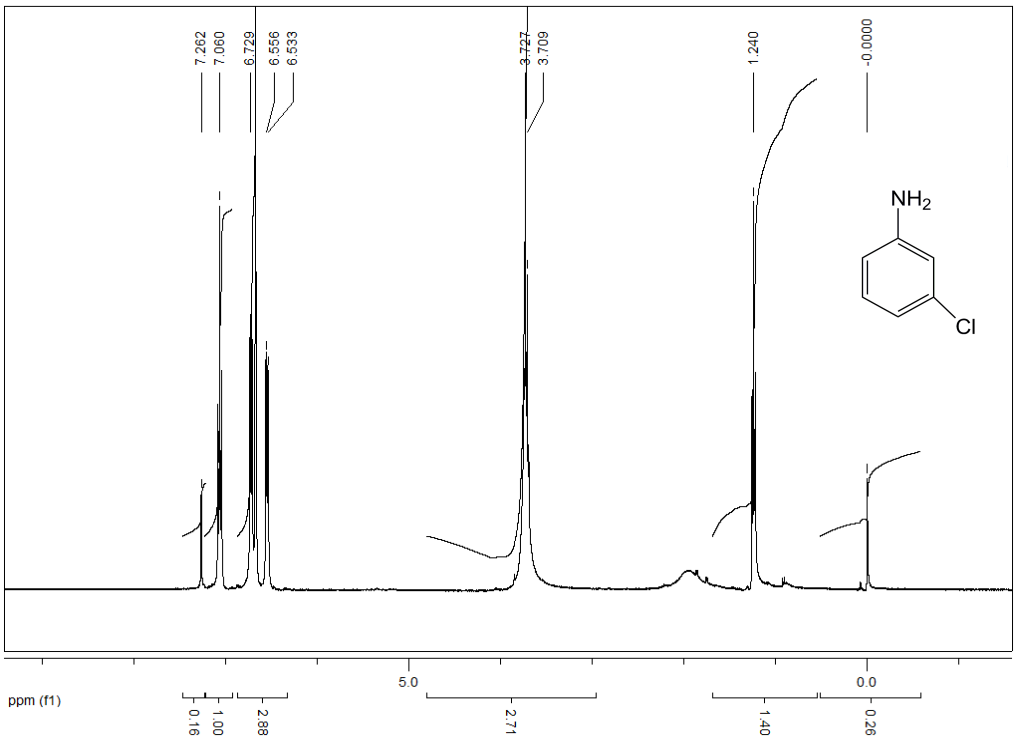
Fig. S8 Mass spectra of the various products.



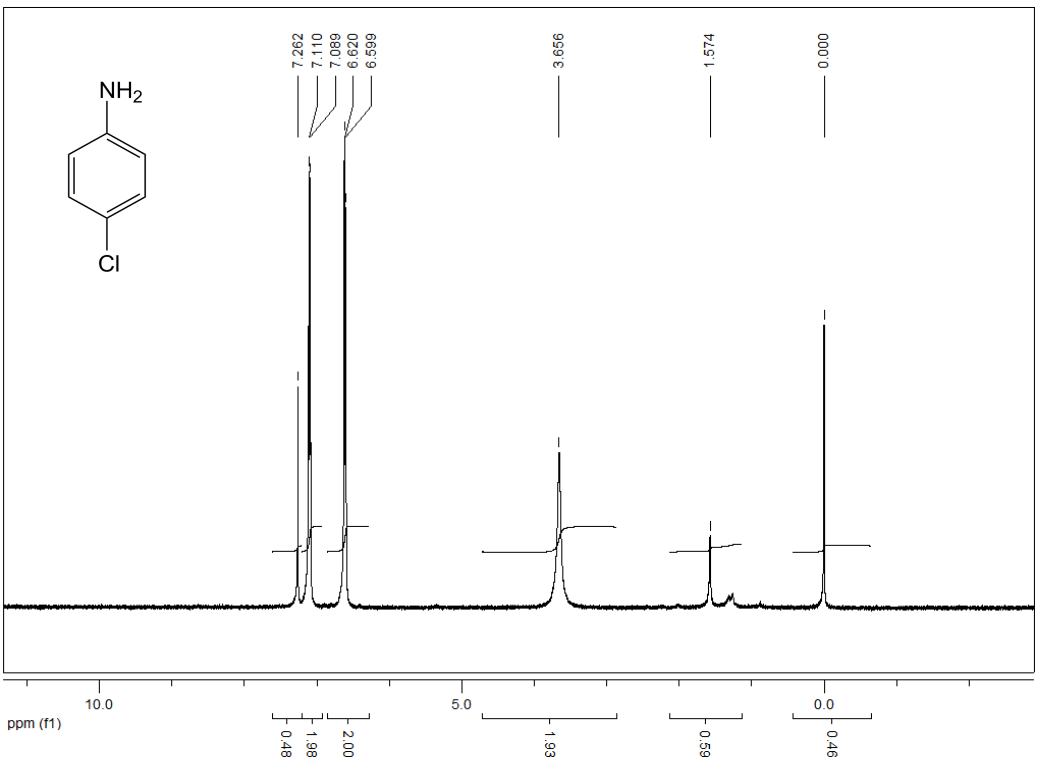
aniline: δ6.702-7.201 (m, AR-H); δ6.805 (m, AR-H); δ3.652 (s, NH_2)



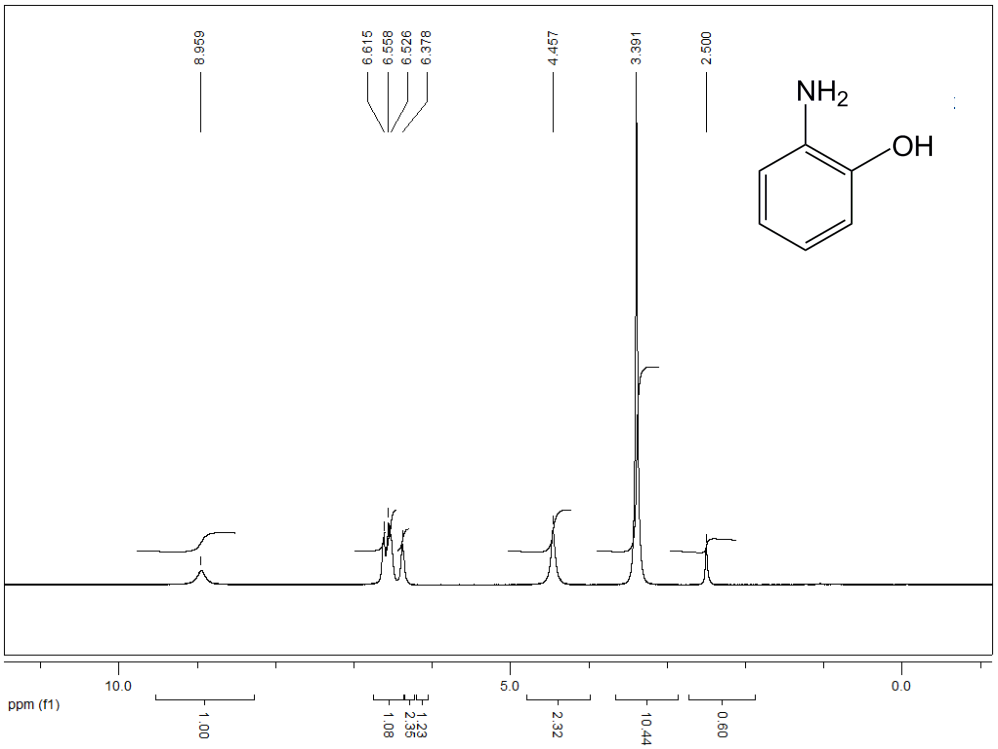
o-chloroaniline: δ6.742-7.251 (m, AR-H); δ4.034-4.036 (s, NH_2); δ1.226(m, solvent C_2H_5OH)



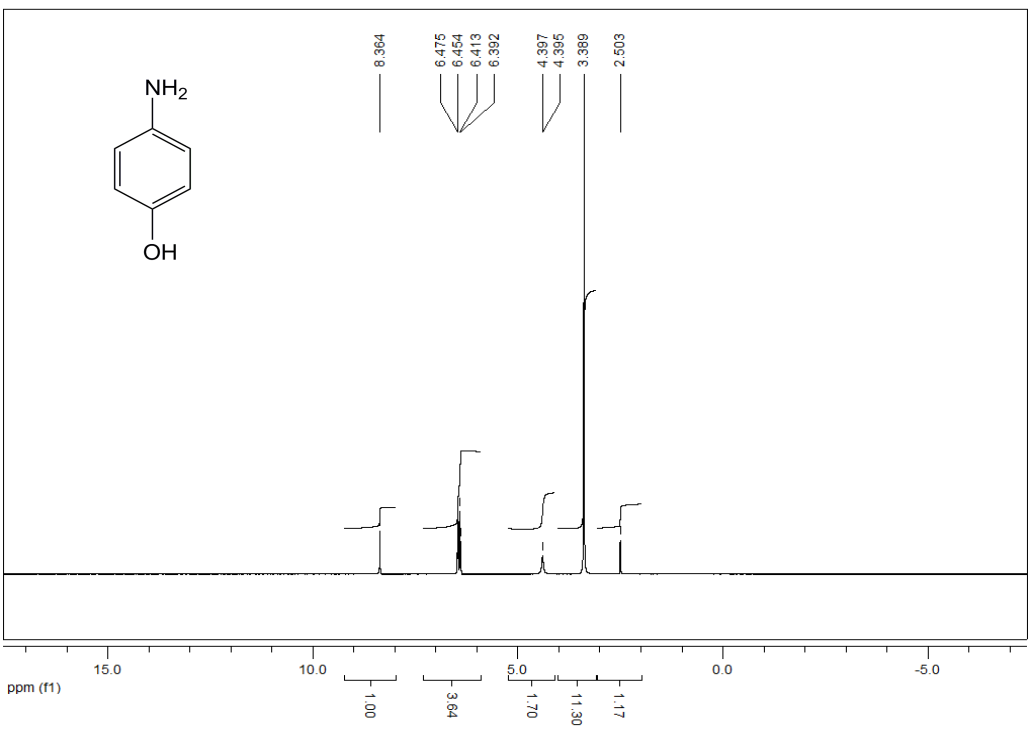
m-chloroaniline: δ7.262 (s, $CHCl_3$); δ6.533-7.060 (m, AR-H); δ3.709-3.727 (s, NH_2); δ1.240 (m, C_2H_5OH)



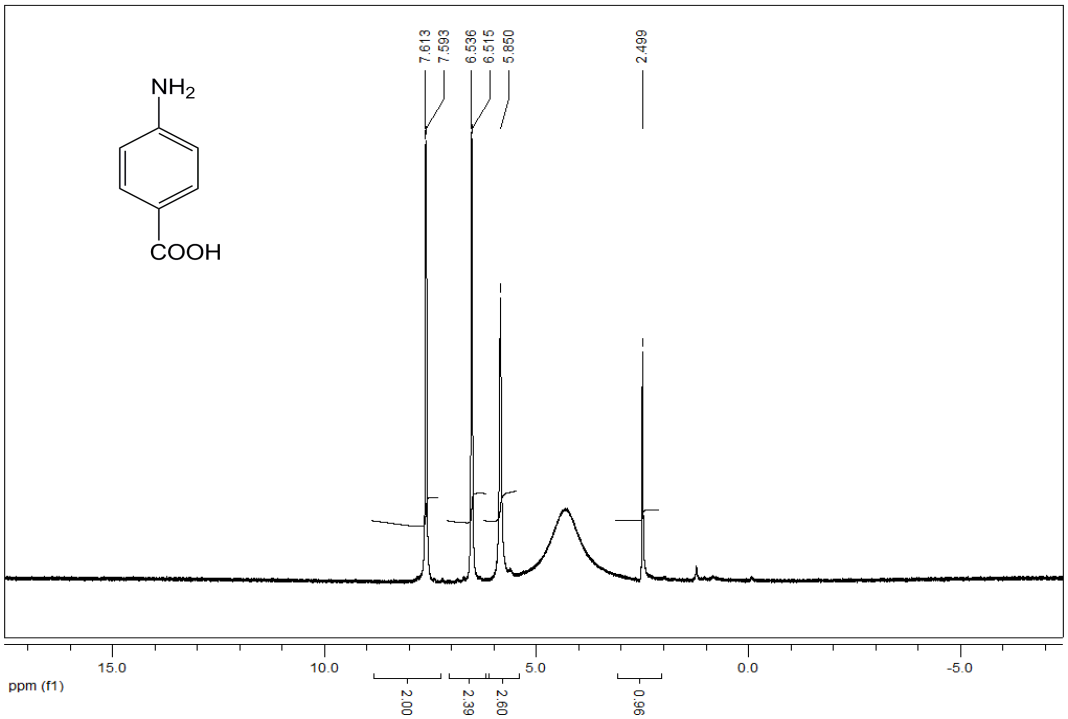
p-chloroaniline: δ7.262 (s, $CHCl_3$); δ6.599-7.110 (m, AR-H); δ3.656(S, NH_2); δ1.573 (m, C_2H_5OH)



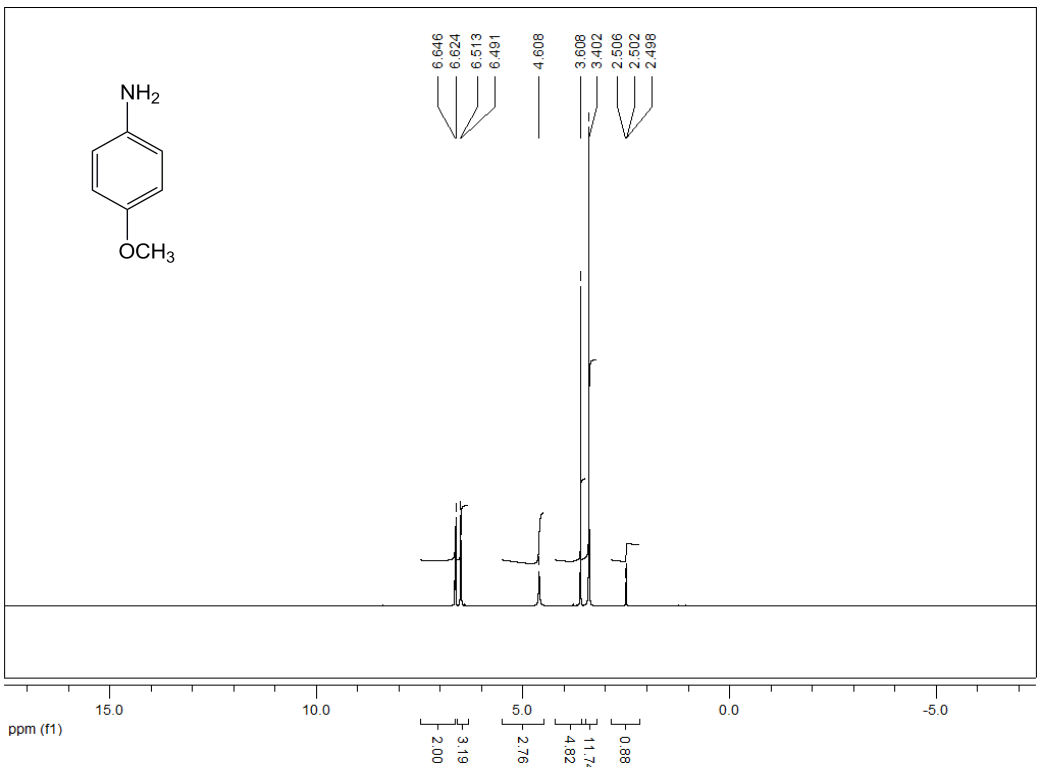
o-aminophenol: δ8.959 (s, AR-OH); δ6.378-6.615 (m, AR-H); δ4.457 (s, NH_2); δ3.391 (m, DMSO); δ2.50 (m, C_2H_5OH)



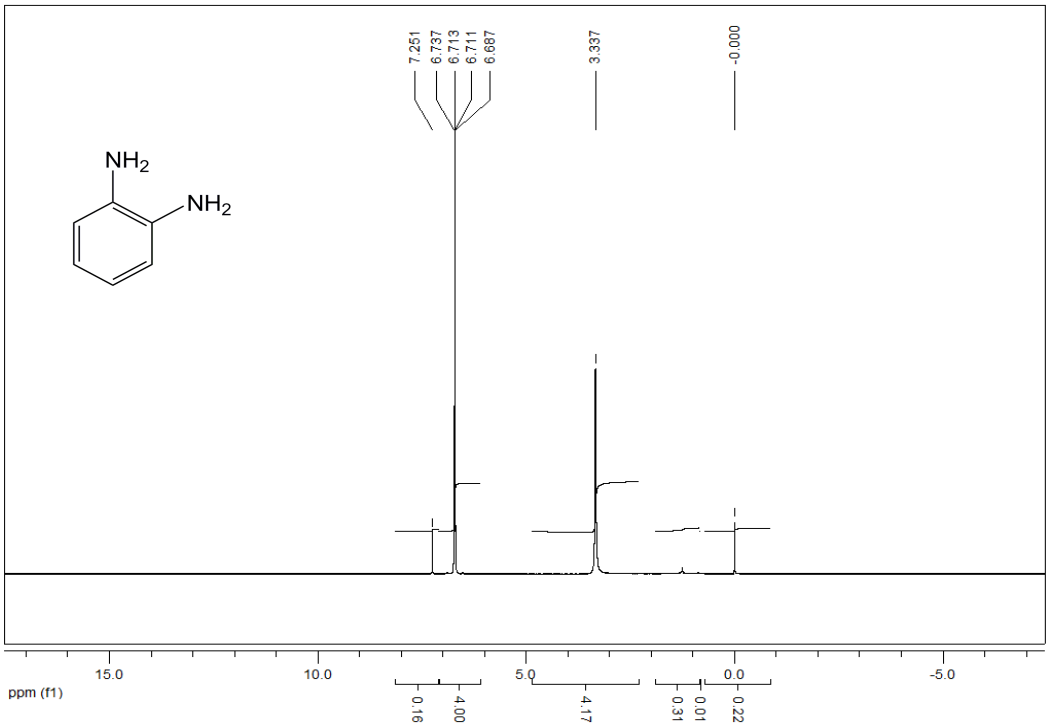
p-aminophenol: δ8.364 (s, OH); δ6.454 (m, AR-H); δ4.395 (s, NH_2); δ3.389 (m, DMSO); δ2.503 (s, C_2H_5OH)



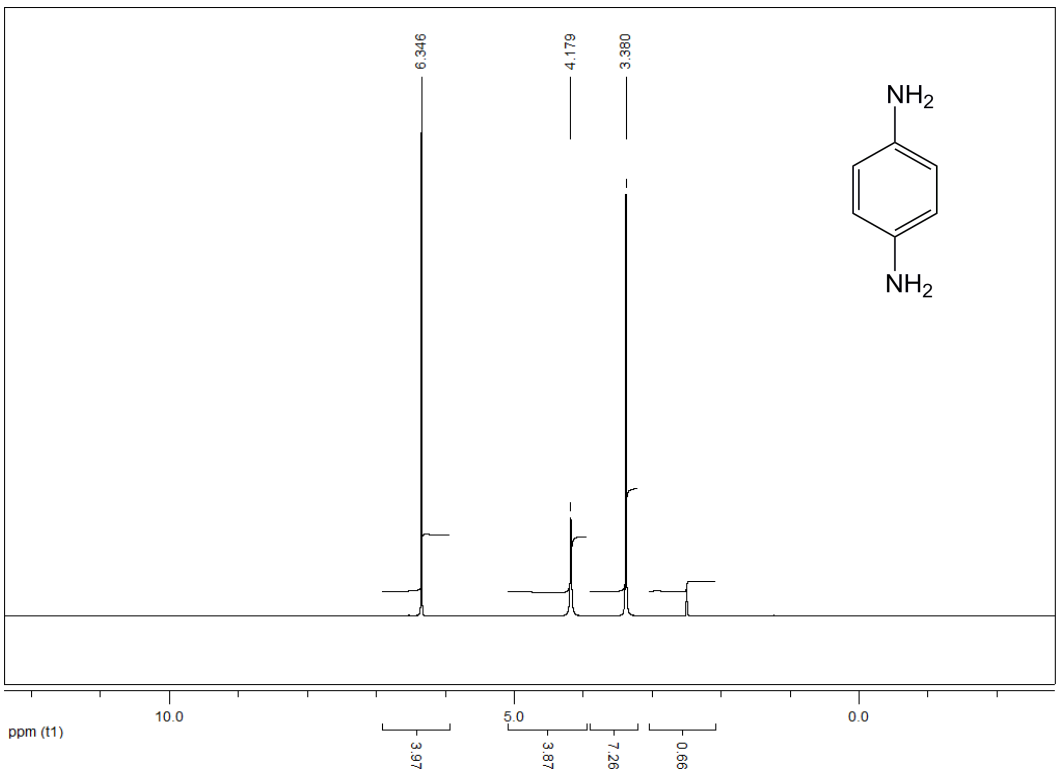
p-aminobenzoic acid: δ7.613 (m, AR-H); δ5.850 (s, NH_2); δ2.499 (m. C_2H_5OH)



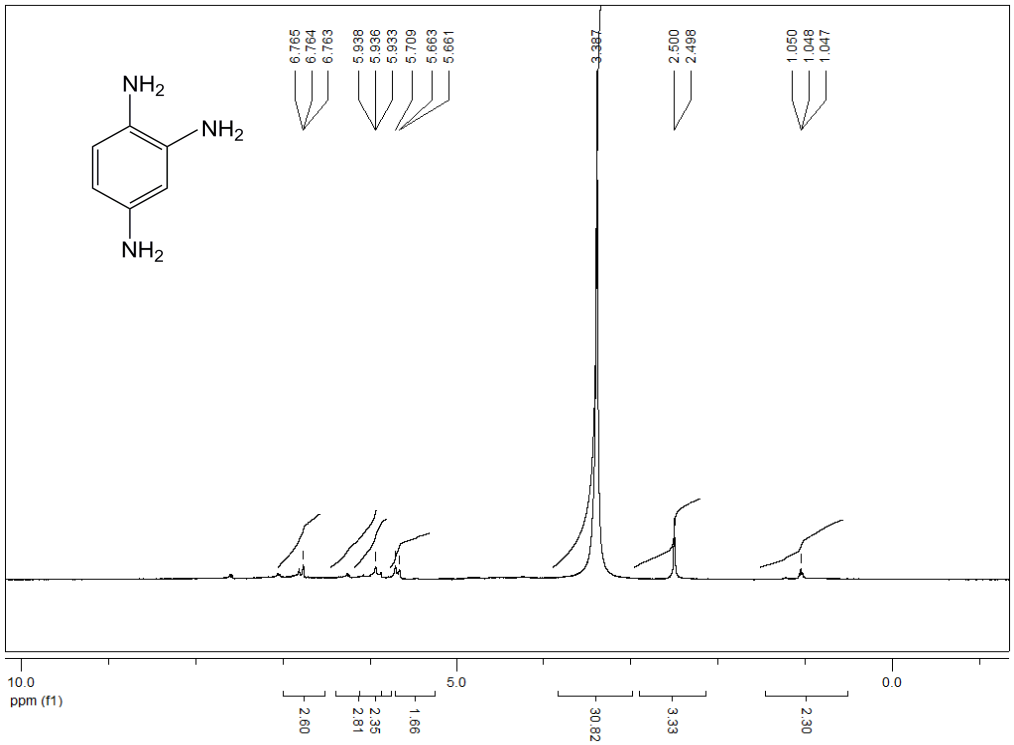
p-methoxyaniline: δ6.491-6.646 (m, AR-H); δ4.608 (s, NH_2); δ3.608 (s, OCH_3); δ3.402 (m, DMSO); δ2.506 (m. C_2H_5OH)



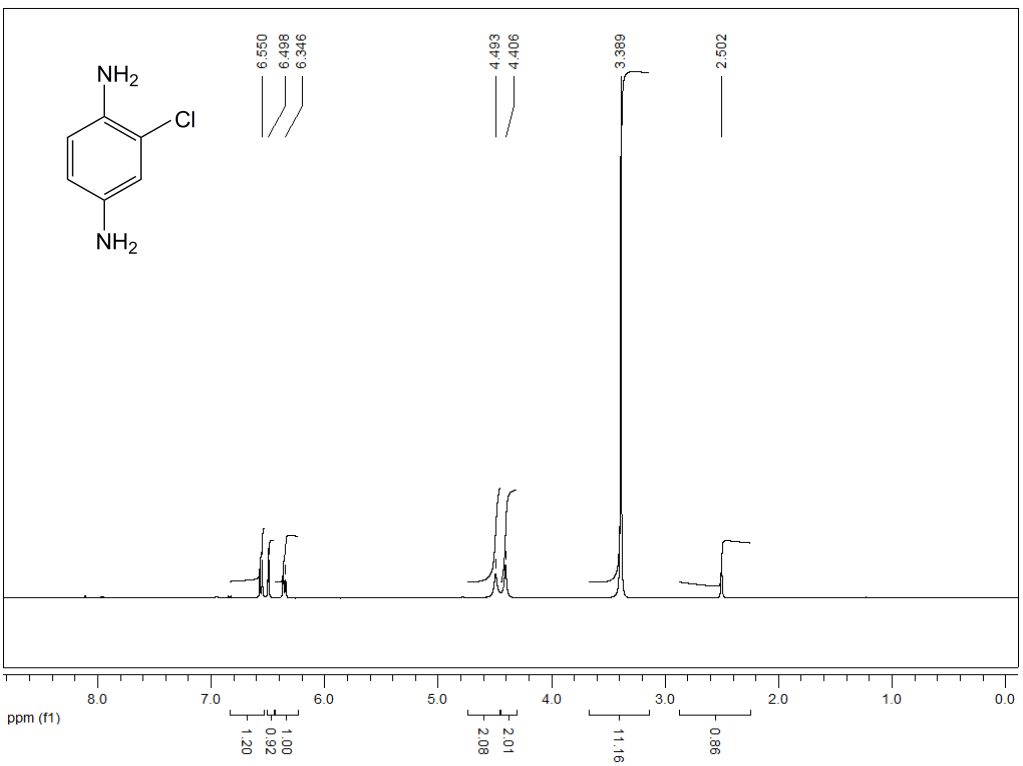
o-phenylenediamine: δ7.251 (S, $CHCl_3$); δ6.687-6.711 (m, AR-H); δ3.337 (s, NH_2)



p-phenylenediamine: δ6.346 (m, AR-H); δ4.179 (s, NH_2); δ3.380 (DMSO);

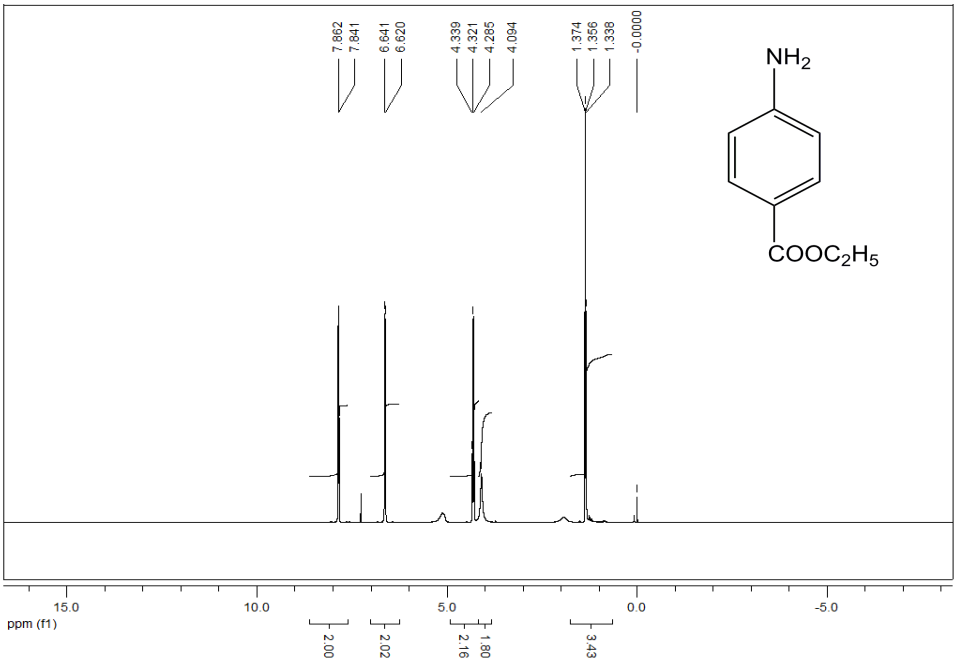


1,2,4- triphenylamine: δ6.765 (m, AR-H); δ5.933 (s, NH_2); δ3.387 (m, DMSO); δ2.50 (m, C_2H_5OH)

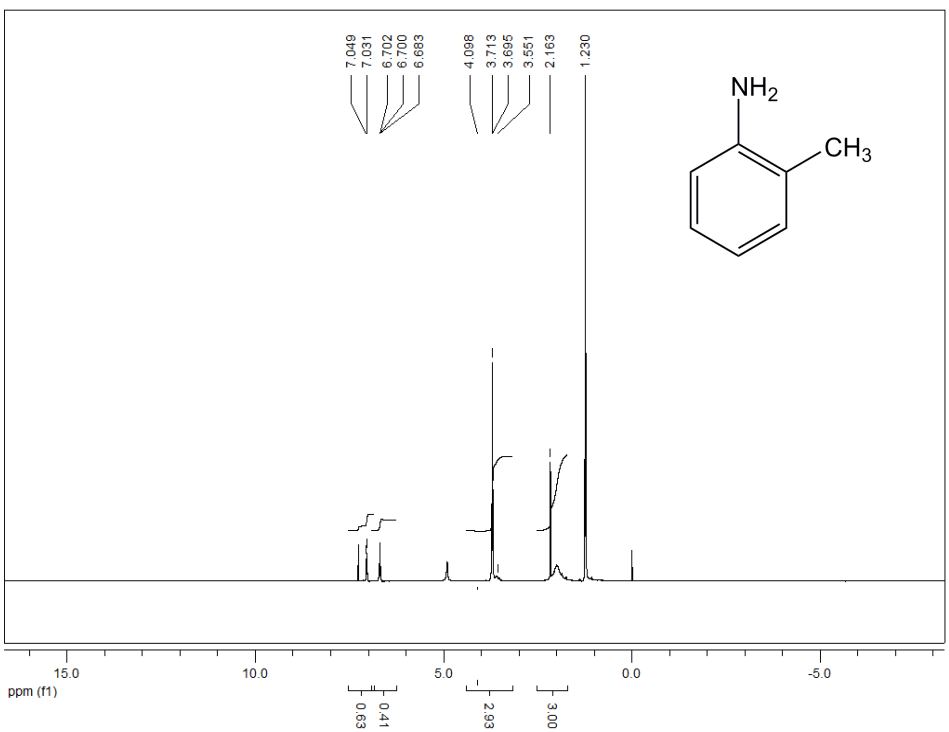


2-chloride-1,4-phenylenediamine: δ6.346-6.550 (m, AR-H); δ4.406-4.493 (s, NH_2); δ3.389 (m, DMSO); δ2.502 (m,

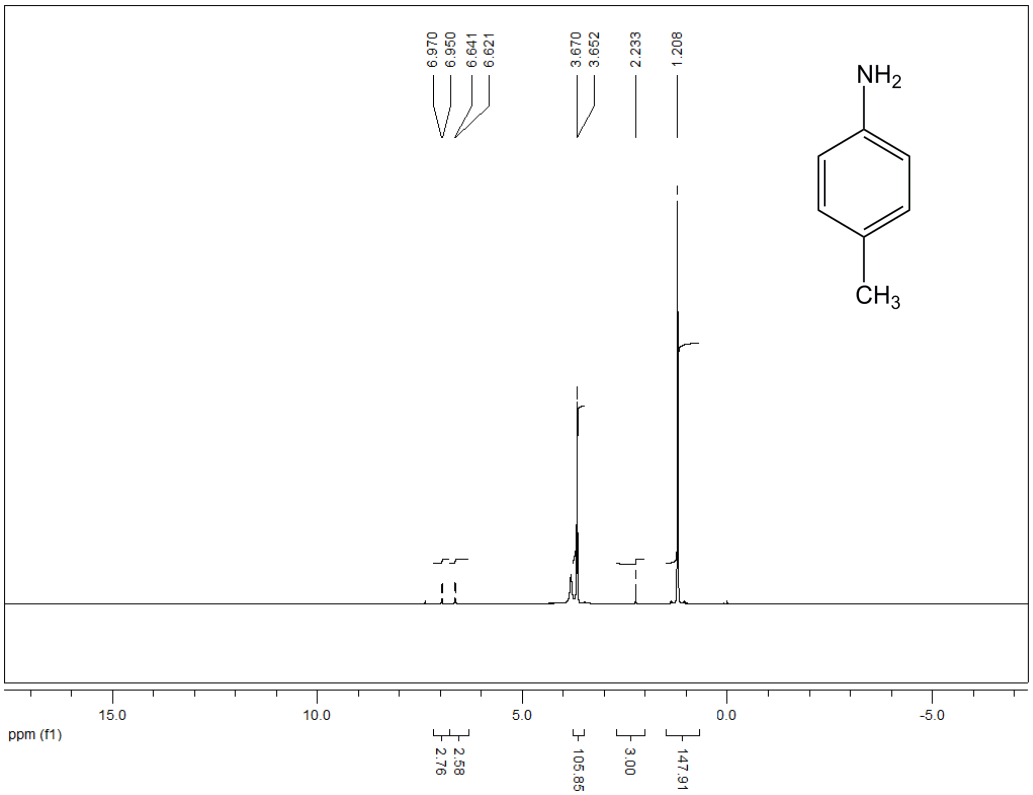
C_2H_5OH)



ethyl 4-aminobenzoate: δ7.862 (d, 2H, Ar-H); δ6.620 (D, 2H, Ar-H); δ4.339 (Q, 2H, CH_3CH-H); δ4.094 (br, 2H, NH_2); δ1.356 (t, 3H, CH_2-H-CH_2)



o-toluidine: δ7.049 (t, 2H, Ar-H)); δ6.702 (t, 1H, Ar-H); δ6.700 (d, 1H, Ar-H); δ3.695 (s, 2H, NH_2); δ2.163 (s, 3H, CH_3); δ1.230 (m, C_2H_5OH)



p-toluidine: δ6.950 (d, 2H, Ar-H); δ6.641 (d, 2H, Ar-H); δ3.652 (s, 2H, NH_2); δ2.233 (s, 3H, CH_3); δ1.208 (m, C_2H_5OH)

Fig. S9 ^{1}HNMR of the various products.