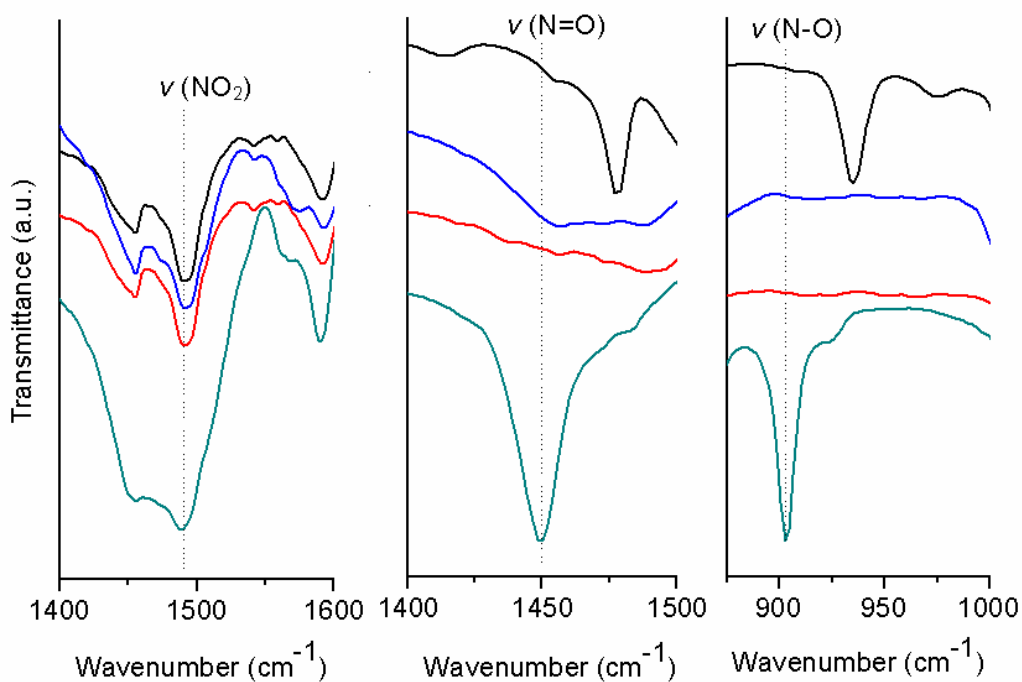


## Electronic Supplementary Information

### Synergistic effect from Lewis acid and the Ni-W<sub>2</sub>C/AC catalyst for highly active and selective hydrogenation of aryl nitro to aryl amine†

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**Fig. S1** FTIR spectra for (left) NO<sub>2</sub>, (middle) N=O and (right) N-O stretching vibrations for NB, NSB and PHA, respectively, in their sole liquids (cyan) and in the presence of Lewis acid (blue), Ni-W<sub>2</sub>C/AC catalyst (red), dual Lewis acid and Ni-W<sub>2</sub>C/AC catalyst (black).

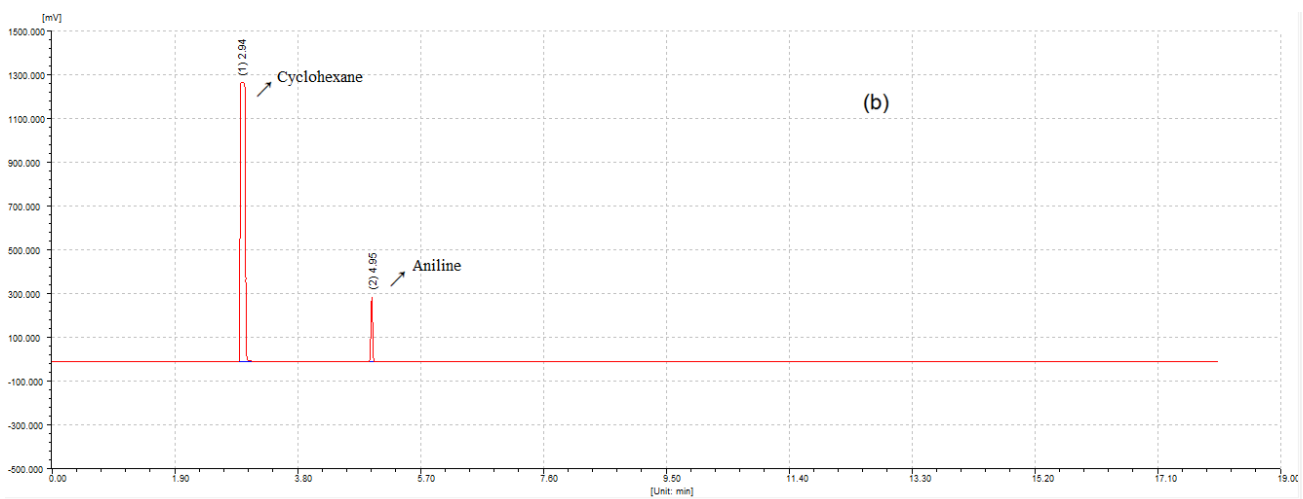
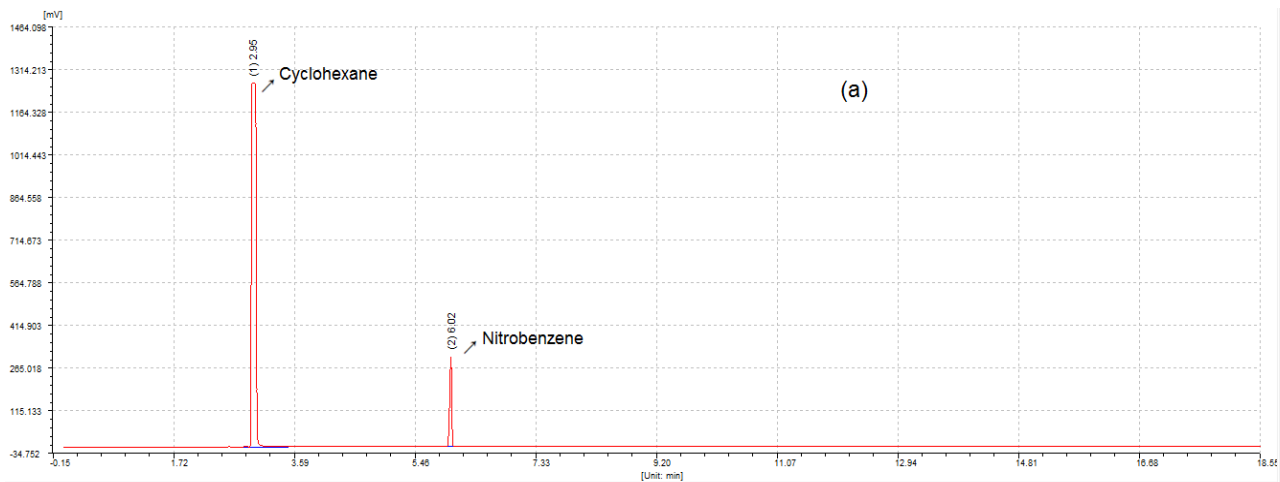
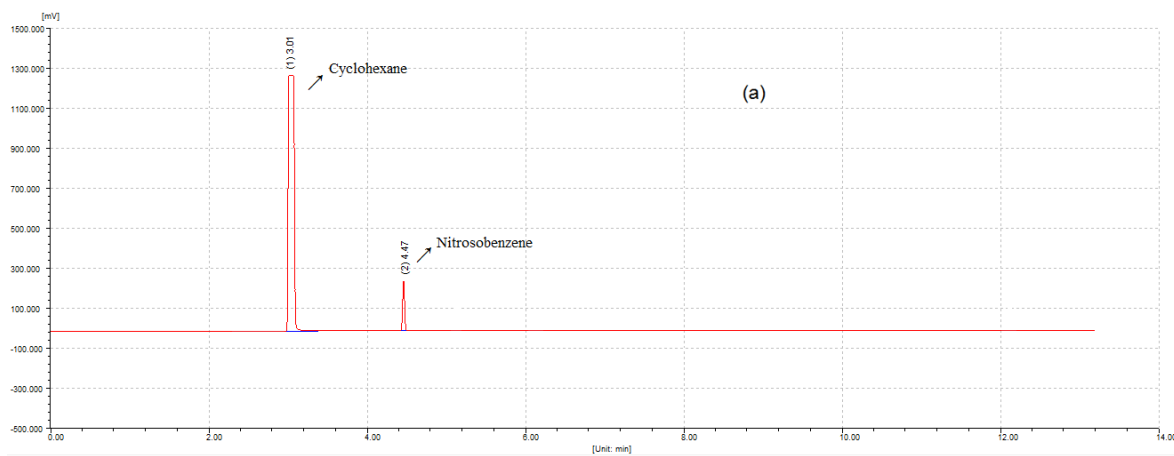


Fig. S2 GC of the reaction mixture while the nitrobenzene is used as substrate: (a) before reaction; (b) after reaction.



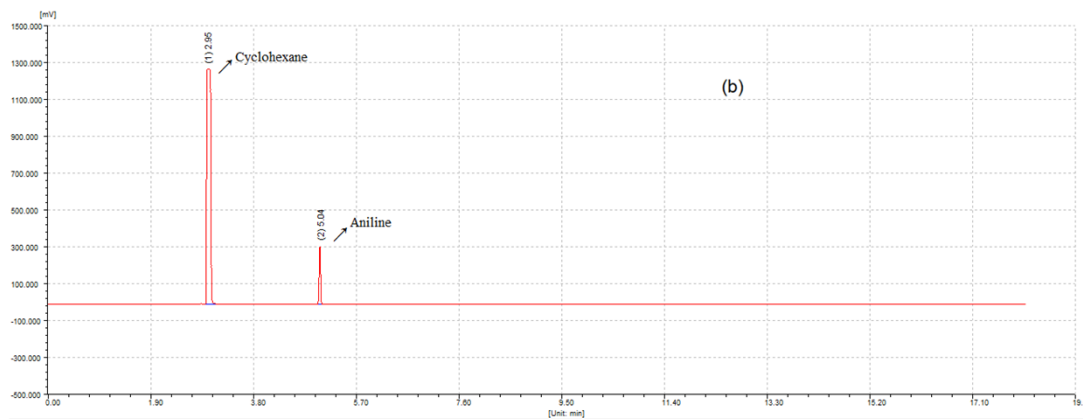


Fig. S3 GC of the reaction mixture while the nitrosobenzene is used as substrate: (a) before reaction; (b) after reaction.

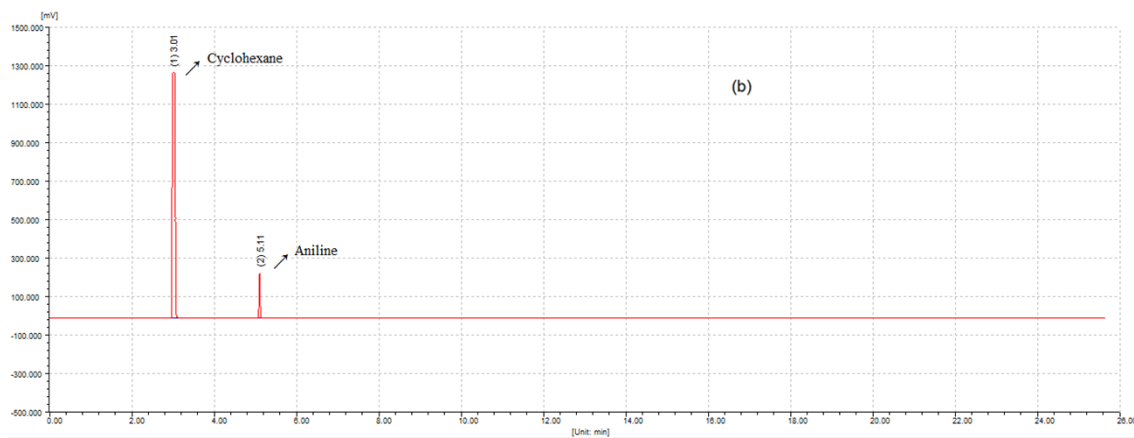
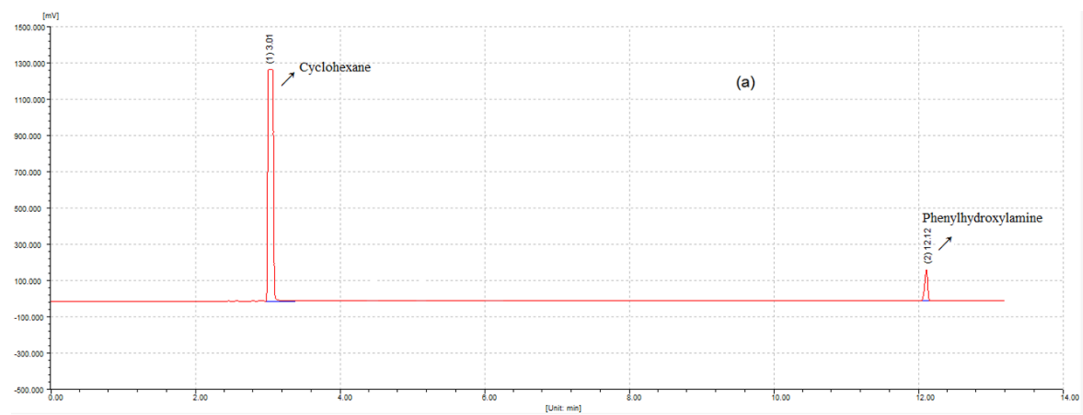
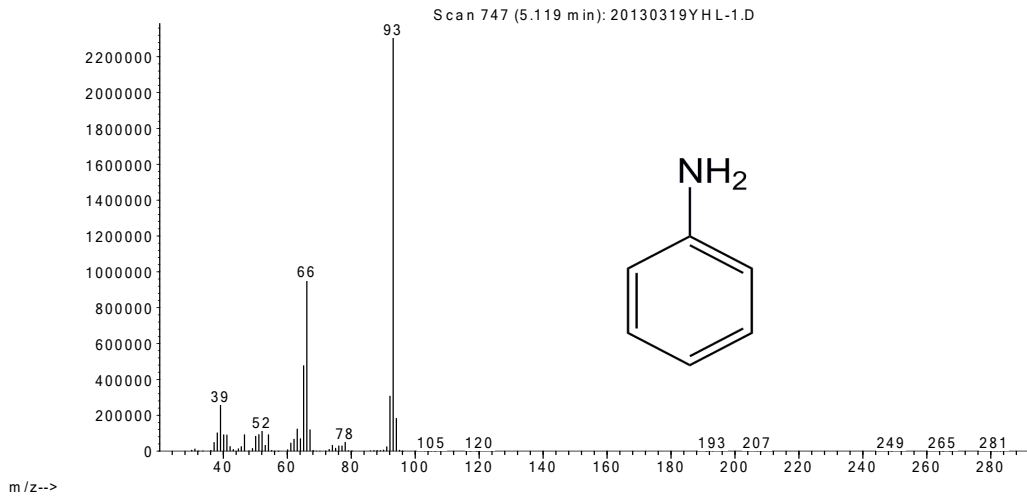
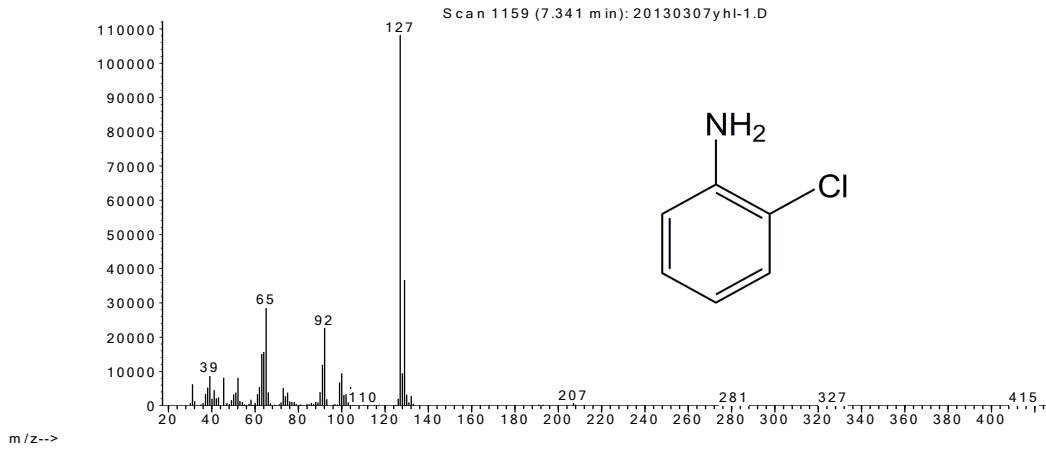


Fig. S4 GC of the reaction mixture while the phenylhydroxylamine is used as substrate: (a) before reaction; (b) after reaction.

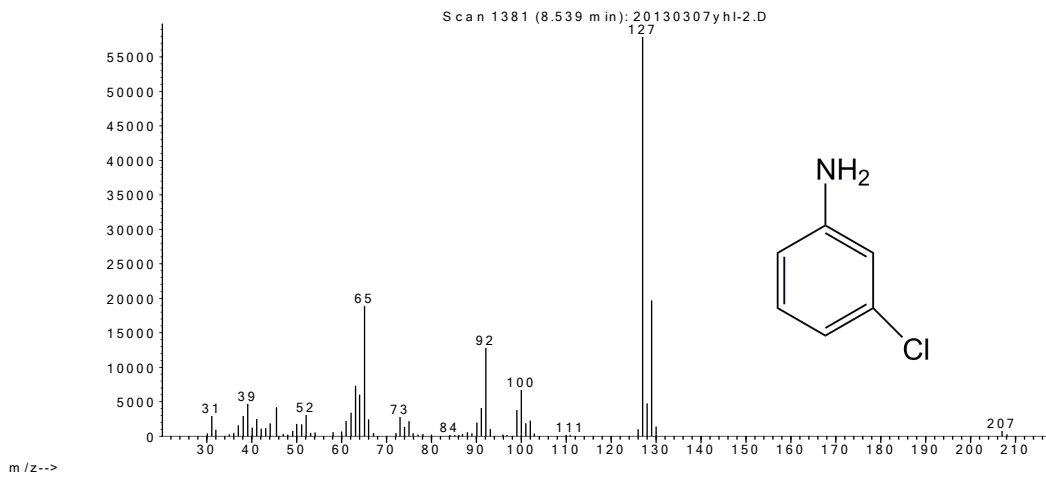
Abundance

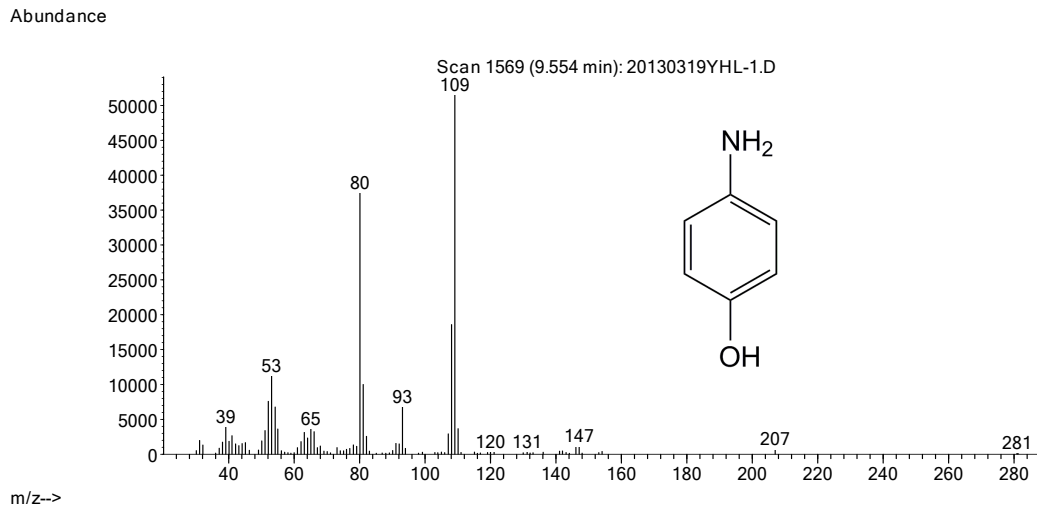
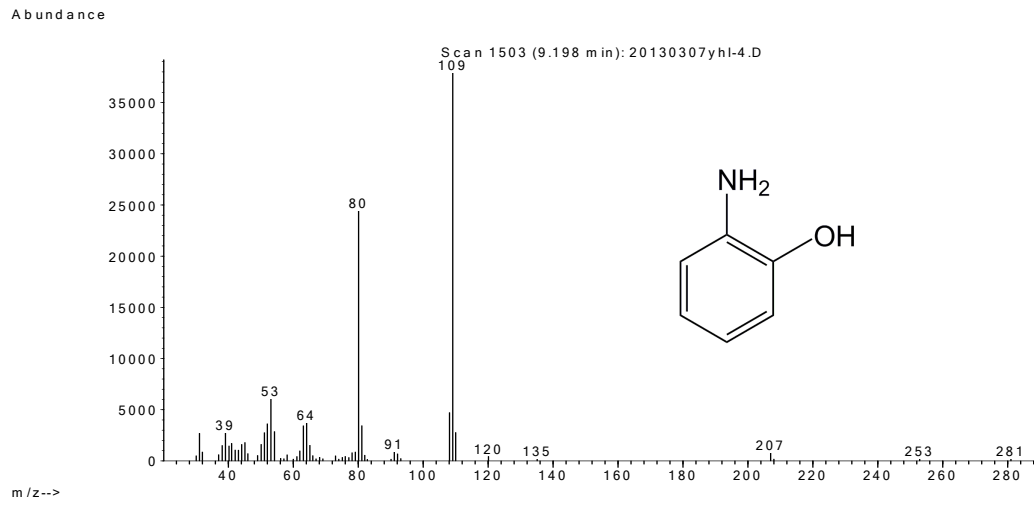
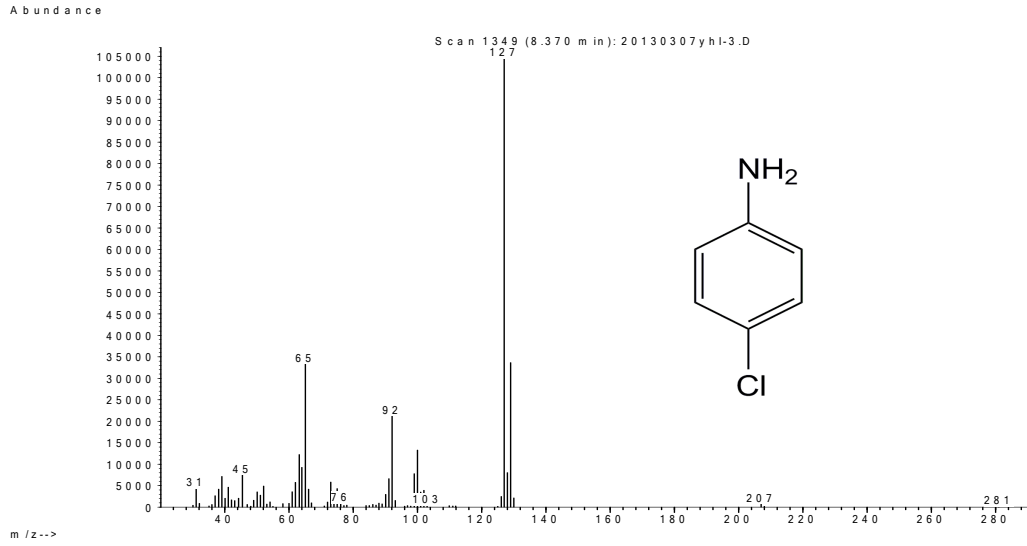


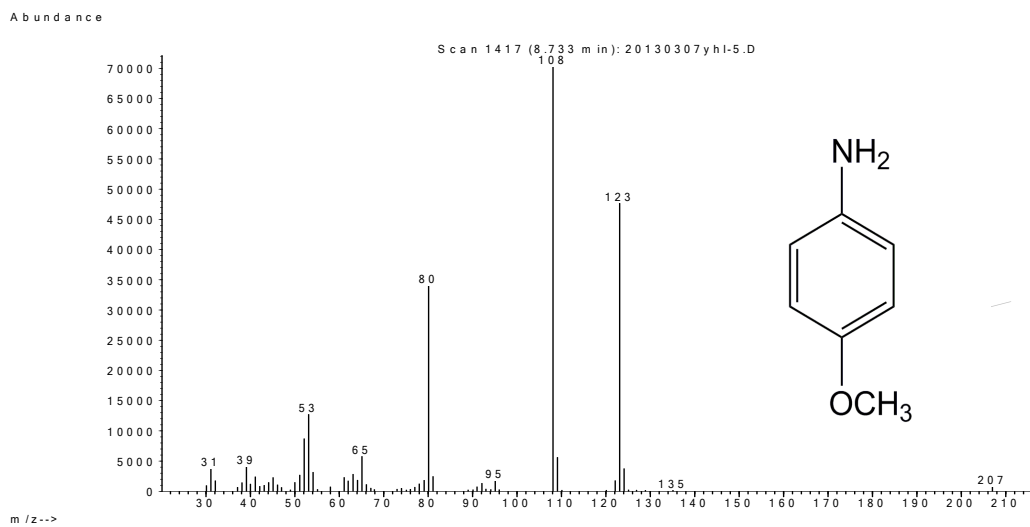
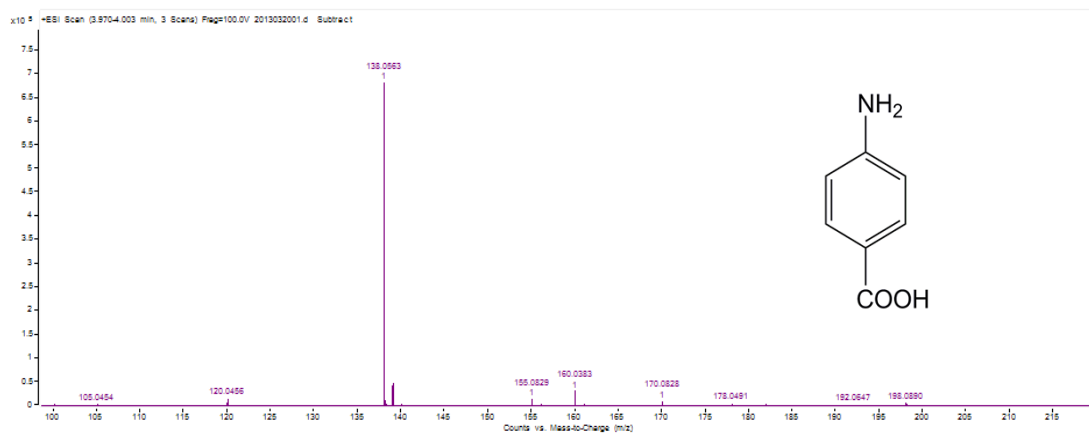
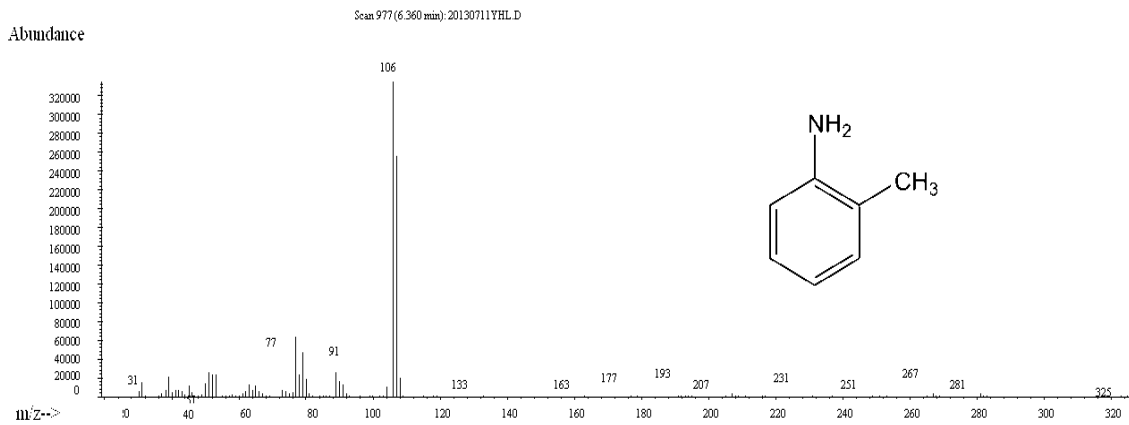
Abundance

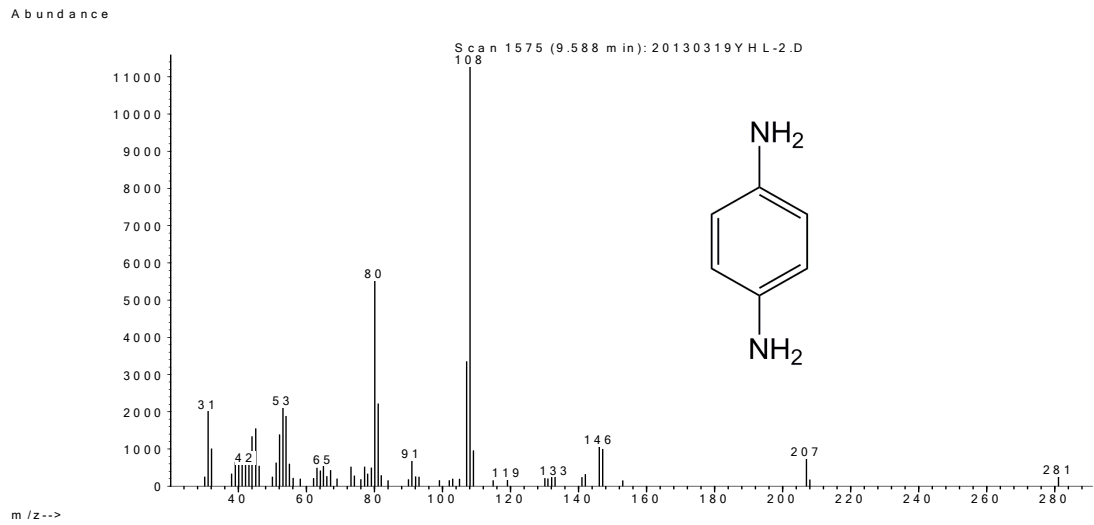
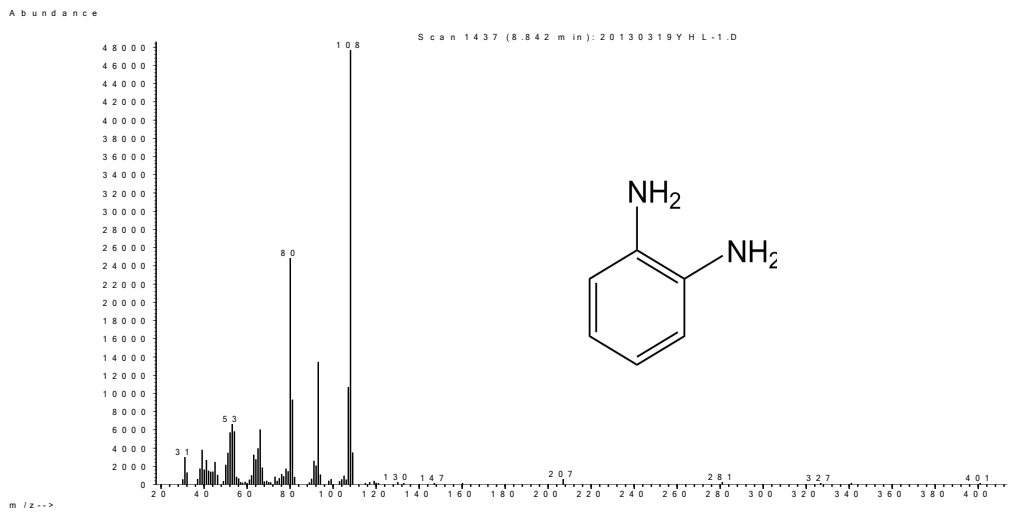


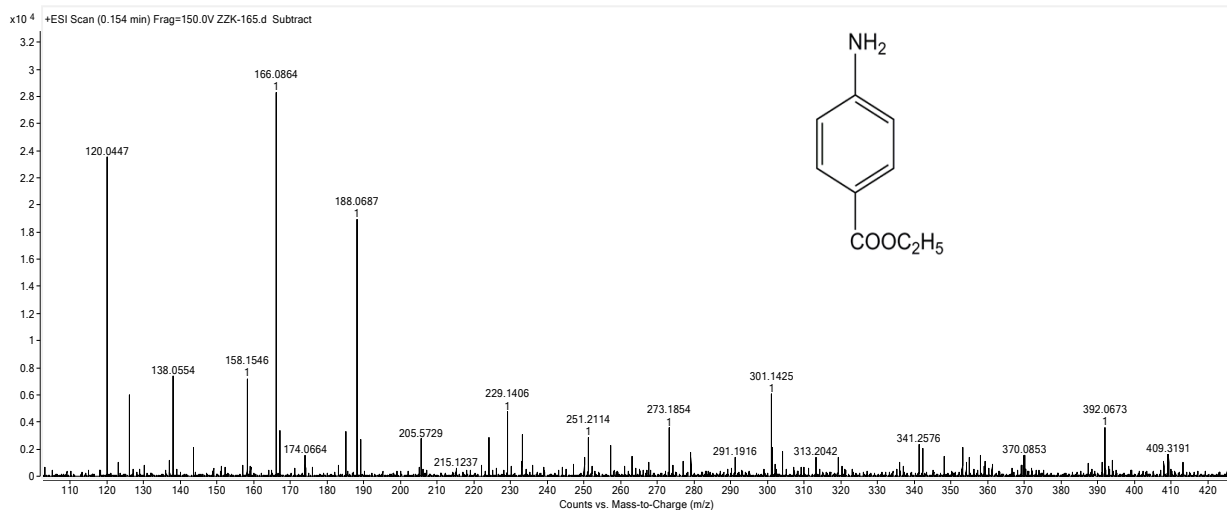
Abundance



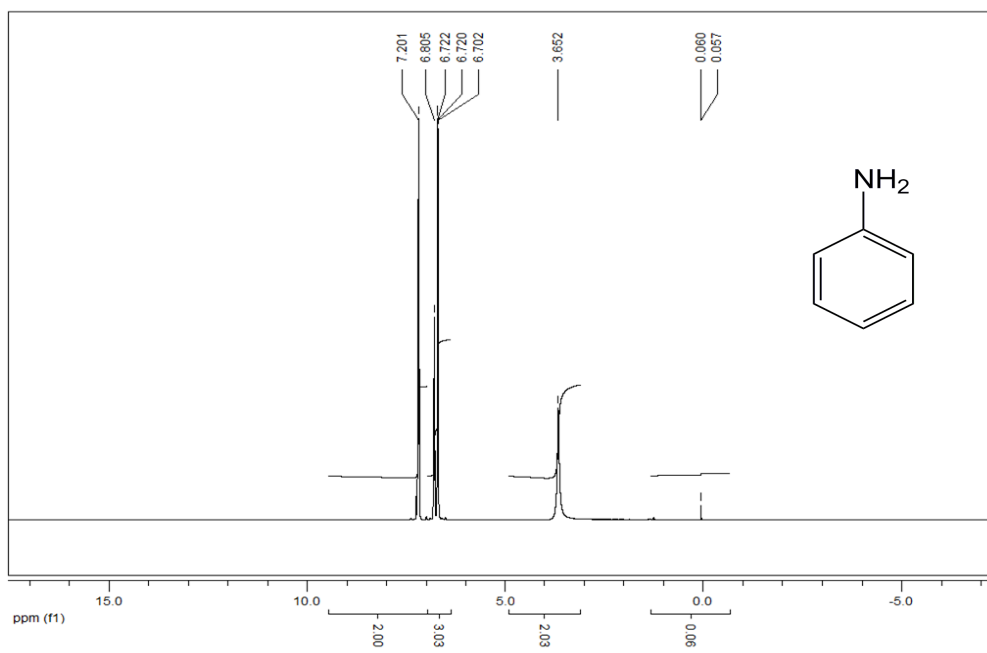






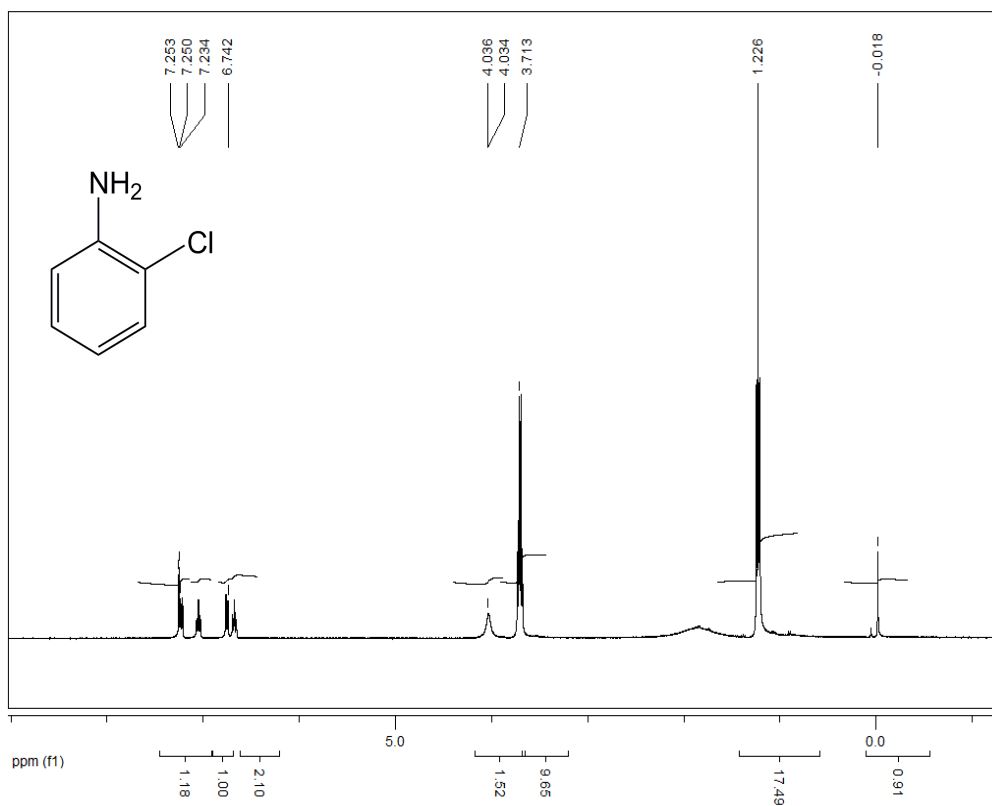


**Fig. S5** Mass spectra of the various products.

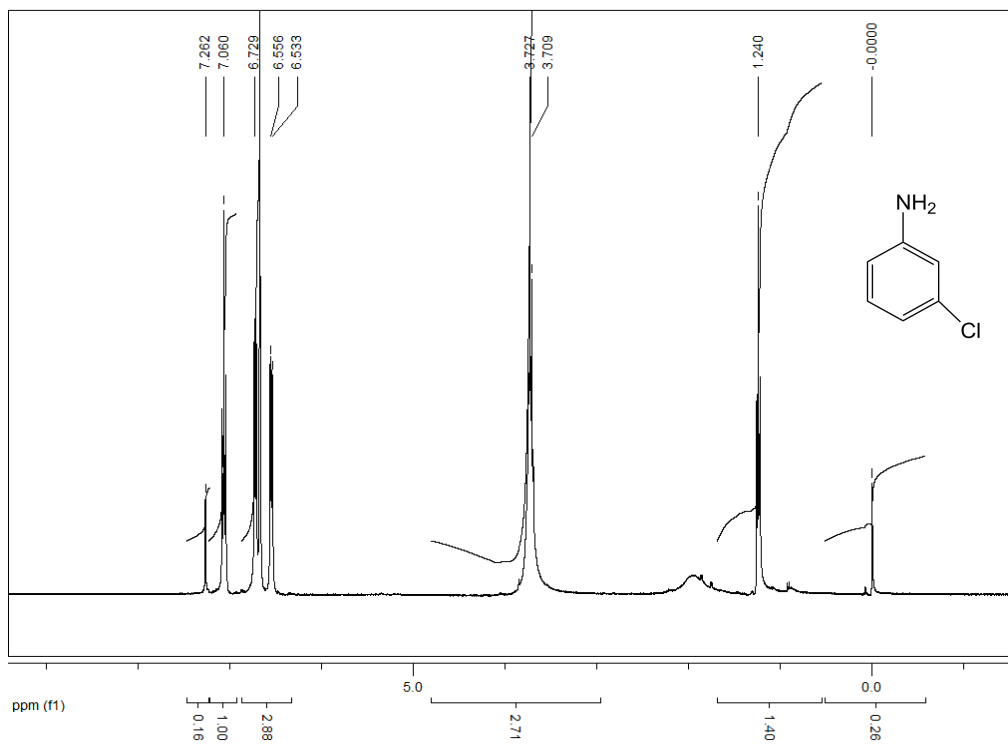


aniline:  $\delta$ 6.702-7.201 (m, AR-H);  $\delta$ 6.805 (m, AR-H);  $\delta$ 3.652 (s, NH<sub>2</sub>)

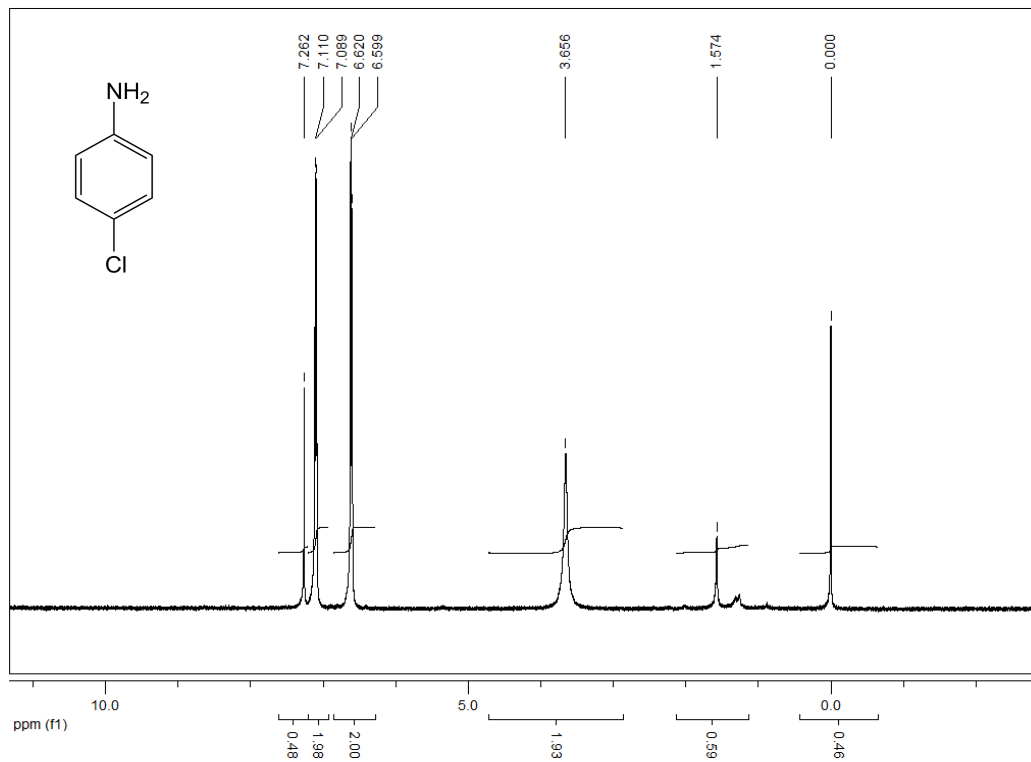




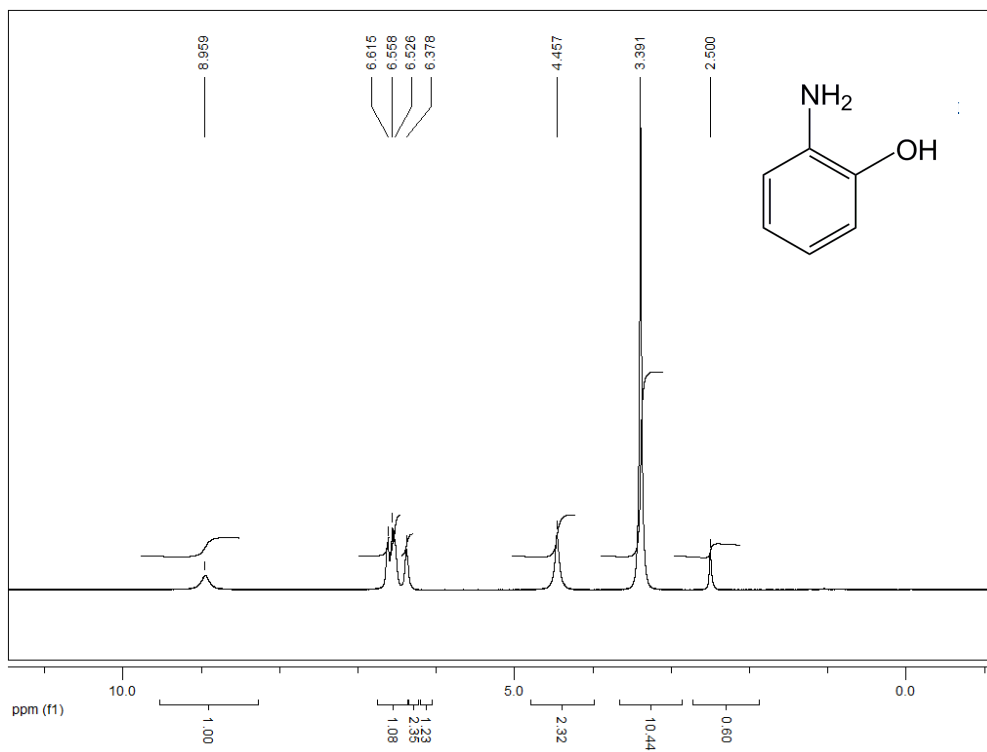
*o*-chloroaniline:  $\delta$ 6.742-7.251 (m, AR-H);  $\delta$ 4.034-4.036 (s, NH<sub>2</sub>);  $\delta$ 1.226 (m, solvent C<sub>2</sub>H<sub>5</sub>OH)



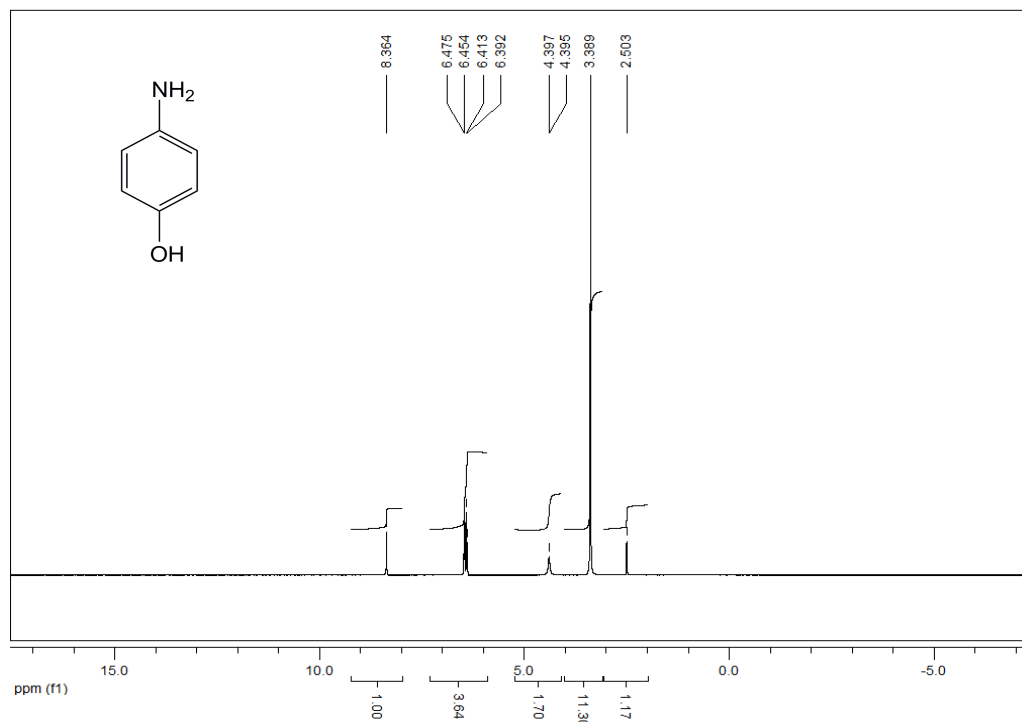
*m*-chloroaniline:  $\delta$ 7.262 (s, CHCl<sub>3</sub>);  $\delta$ 6.533-7.060 (m, AR-H);  $\delta$ 3.709-3.727 (s, NH<sub>2</sub>);  $\delta$ 1.240 (m, C<sub>2</sub>H<sub>5</sub>OH)



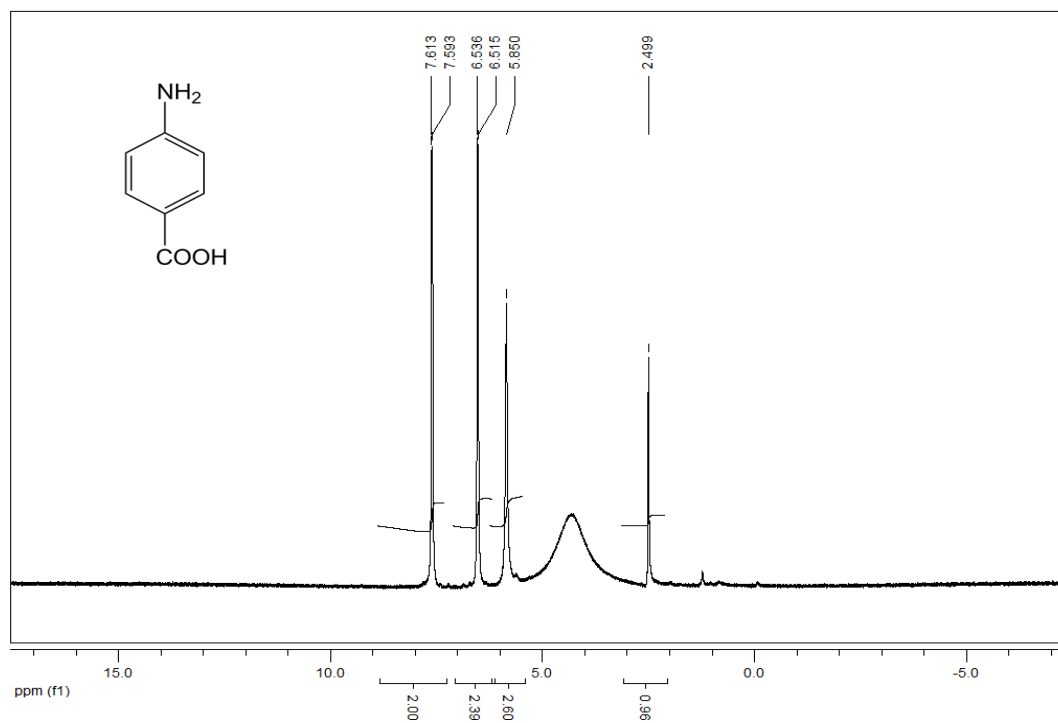
*p*-chloroaniline:  $\delta$ 7.262 (s, CHCl<sub>3</sub>);  $\delta$ 6.599-7.110 (m, AR-H);  $\delta$ 3.656 (s, NH<sub>2</sub>);  $\delta$ 1.573 (m, C<sub>2</sub>H<sub>5</sub>OH)



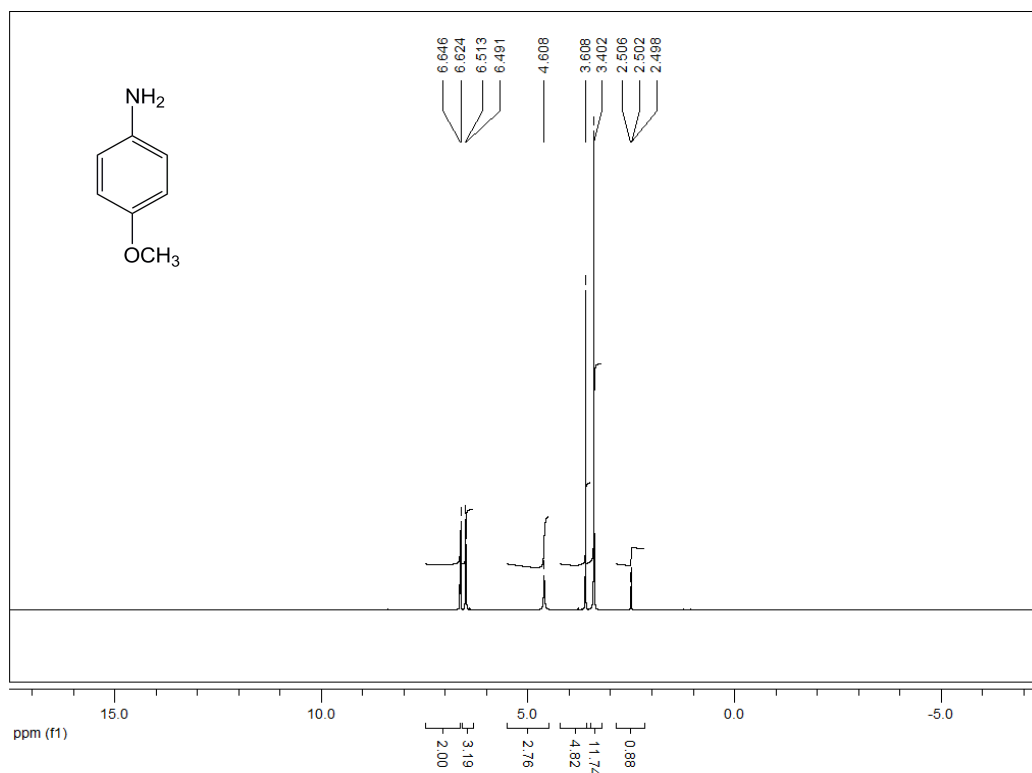
*o*-aminophenol:  $\delta$ 8.959 (s, AR-OH);  $\delta$ 6.378-6.615 (m, AR-H);  $\delta$ 4.457 (s, NH<sub>2</sub>);  $\delta$ 3.391 (m, DMSO);  $\delta$ 2.50 (m, C<sub>2</sub>H<sub>5</sub>OH)



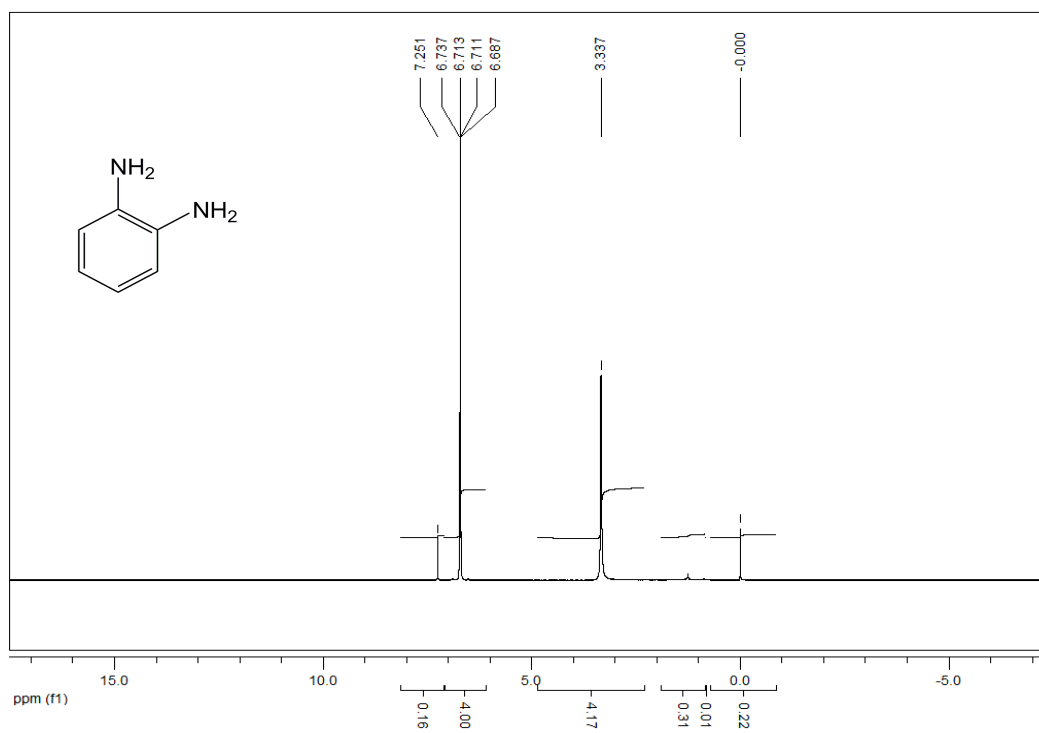
*p*-aminophenol:  $\delta$ 8.364 (s, OH);  $\delta$ 6.454 (m, AR-H);  $\delta$ 4.395 (s, NH<sub>2</sub>);  $\delta$ 3.389 (m, DMSO);  $\delta$ 2.503 (s, C<sub>2</sub>H<sub>5</sub>OH)



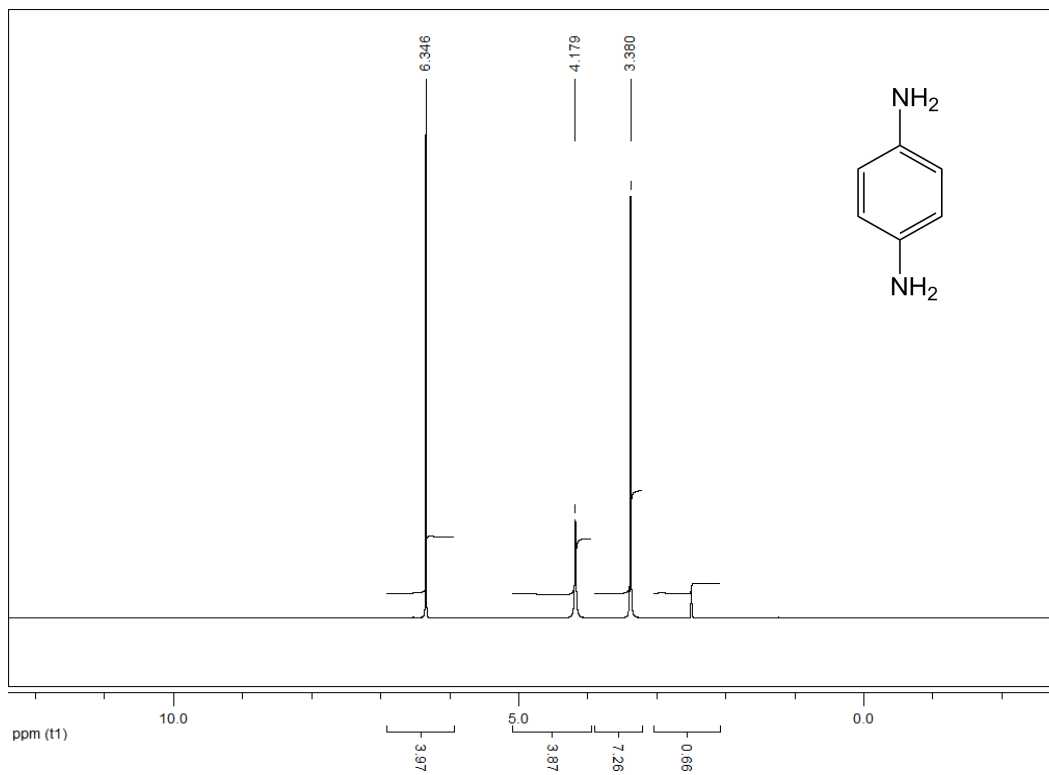
*p*-aminobenzoic acid:  $\delta$ 7.613 (m, AR-H);  $\delta$ 5.850 (s, NH<sub>2</sub>);  $\delta$ 2.499 (m, C<sub>2</sub>H<sub>5</sub>OH)



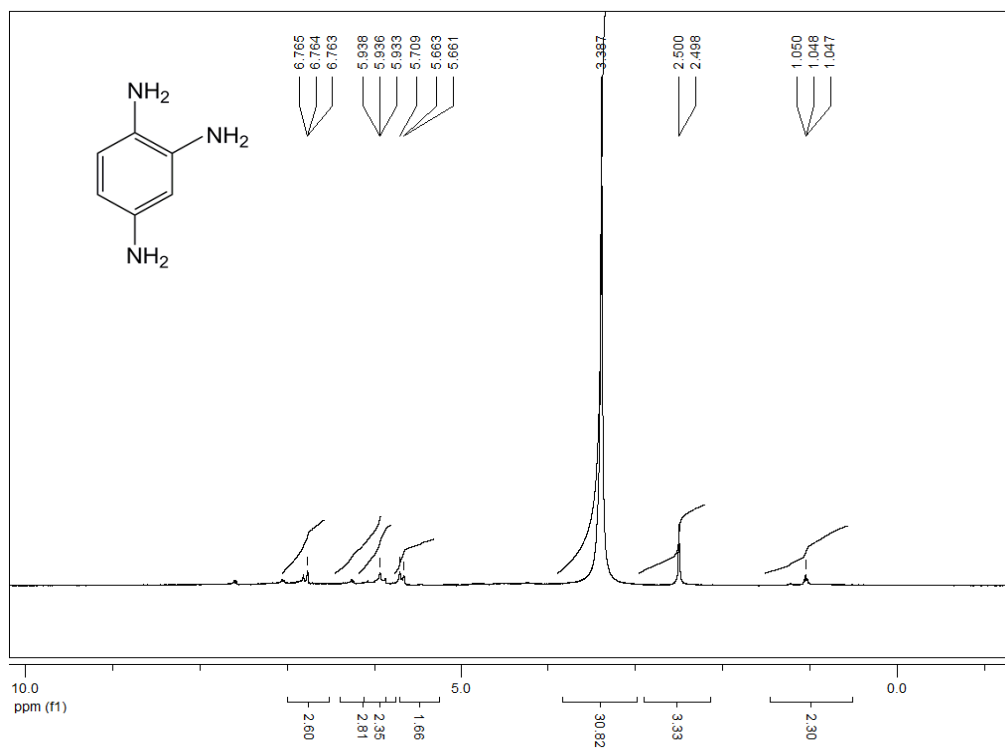
*p*-methoxyaniline:  $\delta$ 6.491-6.646 (m, AR-H);  $\delta$ 4.608 (s, NH<sub>2</sub>);  $\delta$ 3.608 (s, OCH<sub>3</sub>);  $\delta$ 3.402 (m, DMSO);  $\delta$ 2.506 (m, C<sub>2</sub>H<sub>5</sub>OH)



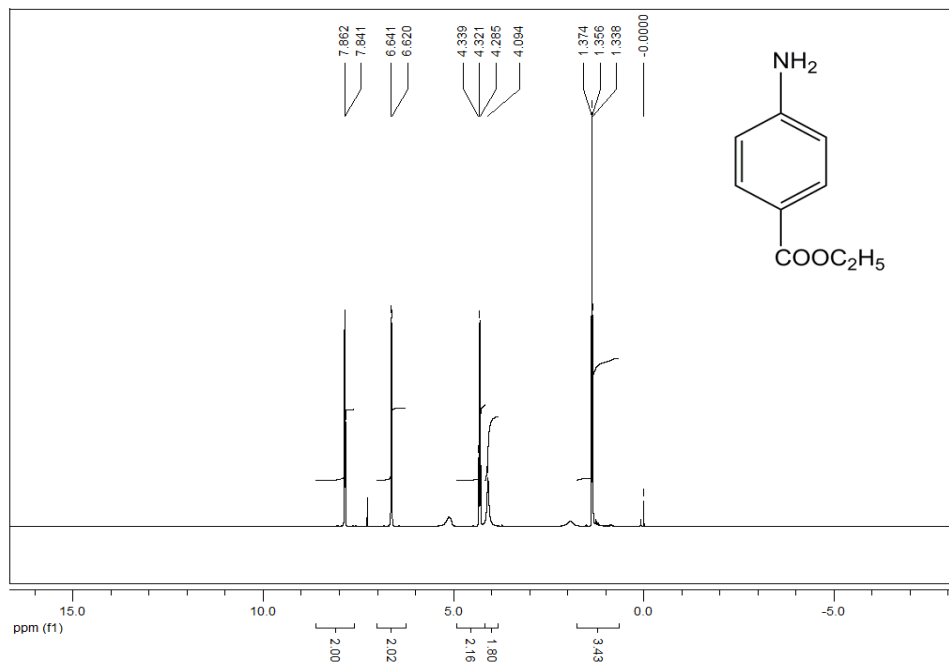
*o*-phenylenediamine:  $\delta$ 7.251 (s, CHCl<sub>3</sub>);  $\delta$ 6.687-6.711 (m, AR-H);  $\delta$ 3.337 (s, NH<sub>2</sub>)



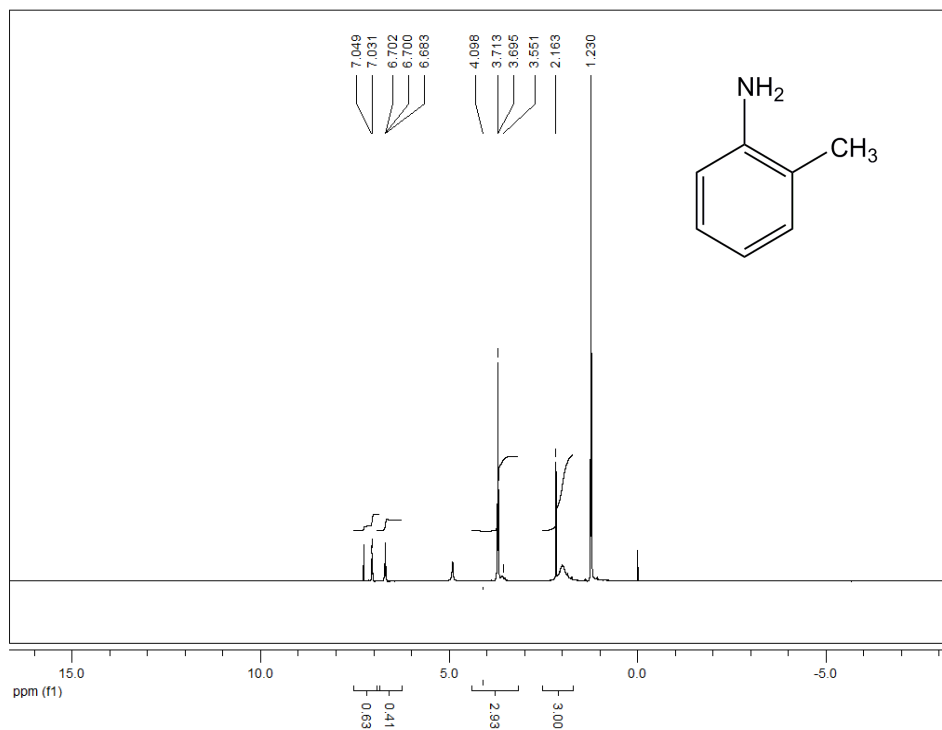
*p*-phenylenediamine:  $\delta$ 6.346 (m, Ar-H);  $\delta$ 4.179 (s, NH<sub>2</sub>);  $\delta$ 3.380 (DMSO);



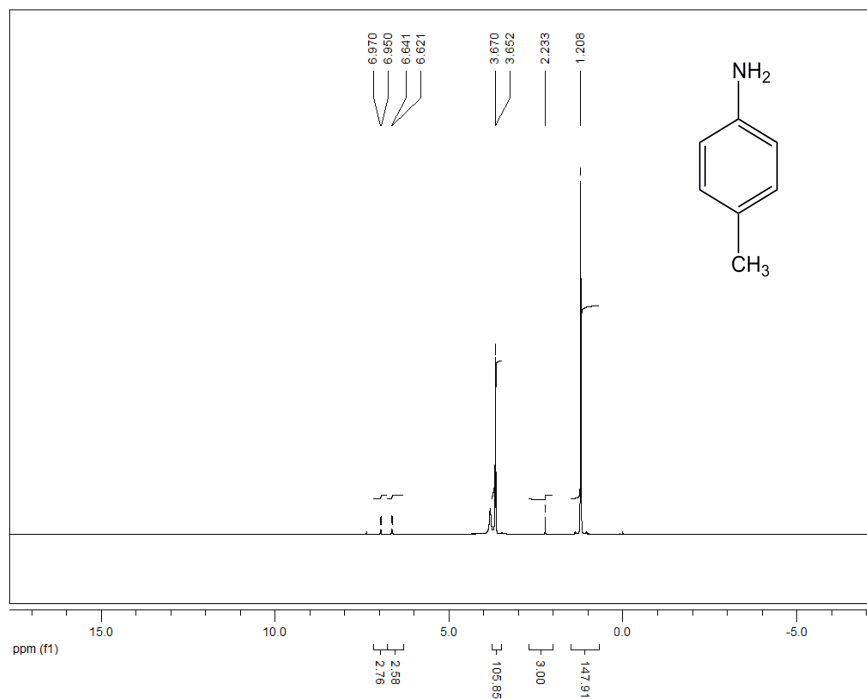
1,2,4- triphenylamine:  $\delta$ 6.765 (m, Ar-H);  $\delta$ 5.933 (s, NH<sub>2</sub>);  $\delta$ 3.387 (m, DMSO);  $\delta$ 2.50 (m, C<sub>2</sub>H<sub>5</sub>OH)



ethyl 4-aminobenzoate:  $\delta$ 7.862 (d, 2H, Ar-H);  $\delta$ 6.620 (D, 2H, Ar-H);  $\delta$ 4.339 (Q, 2H, CH<sub>3</sub>CH-H);  $\delta$ 4.094 (br, 2H, NH<sub>2</sub>);  $\delta$ 1.356 (t, 3H, CH<sub>2</sub>-H-CH<sub>2</sub>)



o-toluidine:  $\delta$ 7.049 (t, 2H, Ar-H);  $\delta$ 6.702 (t, 1H, Ar-H);  $\delta$ 6.700 (d, 1H, Ar-H);  $\delta$ 3.695 (s, 2H, NH<sub>2</sub>);  $\delta$ 2.163 (s, 3H, CH<sub>3</sub>);  $\delta$ 1.230 (m, C<sub>2</sub>H<sub>5</sub>OH)



p-toluidine:  $\delta$ 6.970 (d, 2H, Ar-H);  $\delta$ 6.641 (d, 2H, Ar-H);  $\delta$ 3.652 (s, 2H, NH<sub>2</sub>);  $\delta$ 2.233 (s, 3H, CH<sub>3</sub>);  $\delta$ 1.208 (m, C<sub>2</sub>H<sub>5</sub>OH)

**Fig. S6** <sup>1</sup>HNMR of the various products.