Electronic Supplementary Material (ESI) for New Journal of Chemistry.

PLA-TiO_2 particle brush as novel support for CuNPs: A catalyst for fast sequential reduction and N-arylation of nitroarenes

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Synthesis of Poly (lactic Acid) grafted TiO_2 nanoparticles (PLA-TiO_2)

Freshly prepared TiO_2 nanoparticles (100 mg) and lactic acid (2 g) were taken in a round bottom flask of 50 ml and 30 ml of 1,4 dioxane was added to it. The mixture was stirred for one hour at 60 ºC to disperse the nanoparticles and the dioxane was distilled out under vacuum. The temperature of reaction mixture was raised to 130 ºC and monomers allowed to polymerize under vacuum. After 24 hours, the residue was dispersed in 10 ml chloroform and re-precipitated by adding methanol. The re-precipitated PLA grafted TiO_2 nanocomposite was separated by centrifugation and dried in a desiccator overnight.

Additional data for catalyst

FTIR of CuNPs@PLA-TiO_2

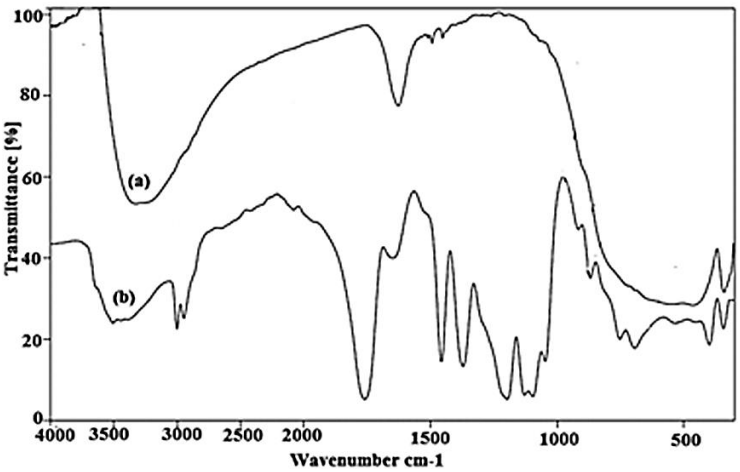


Fig. S1 FT-IR spectra of a) TiO_2 and b) PLA-TiO_2

FT-IR spectroscopy was used to characterize PLA-TiO_2 and CuNPs@PLA-TiO_2 and results are shown in Figure S1. It showed characteristic peaks of PLA. Infra red spectra of non-grafted titania is characterized by strong peaks in the range of 400-1000 cm^{-1} corresponding to Ti-O-Ti and Ti-O linkage (ESI Fig.S8). It does not show any peaks around 2900 and 1700 cm^{-1}. After polymerization many new bands appeared in this region and were used to confirm the formation of PLA around it. PLA has a strong characteristic stretching band at 1759 cm^{-1} due to the ester group present in the polymer backbone. This was clearly observed in both the spectra. Other characteristic band at 1187, 1133 and 1044 were assigned to C-O stretching, the band at 1362 cm^{-1} was assigned to bending vibration of the C-H group and those at 2998, 2947 cm^{-1} to the symmetric and asymmetric stretching vibrations of CH_3 group present in the PLA chain.

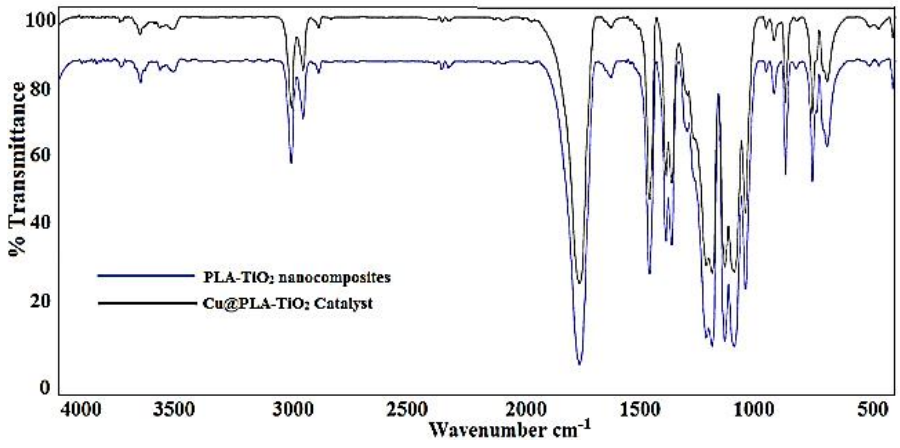


Fig. S2. FT-IR spectra of a) PLA-$TiO_2$and CuNPs@PLA-TiO_2

TGA of CuNPs@PLA-TiO_2

TGA studies for PLA-TiO_2 and CuNPs@PLA-TiO_2 were carried out and the graph of the percentage weight loss versus temperature is shown in figure S3. The shape of graph is typical of any grafted polymer. In case of PLA-TiO_2 slow initial weight loss was attributed to moisture or

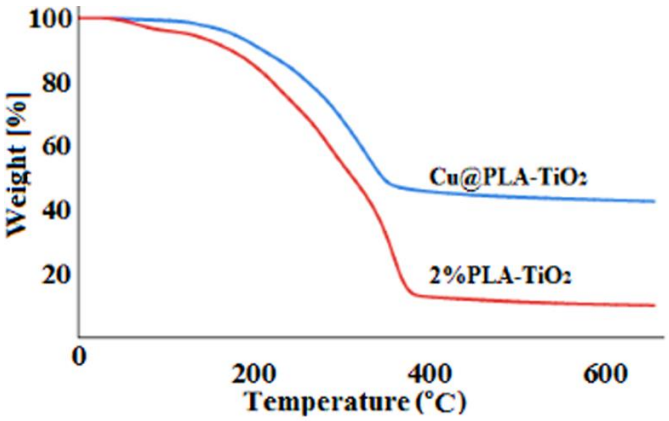


Fig. S3. TGA data of PLA-TiO_2 and CuNPs@PLA-TiO_2

monomers thereafter, the degradation was rapid between 200 and 380 °C which is attributed to degradation of polymer chain. A slow degradation was again observed between 380 to 650°C which is characteristic of polymer grafted to inorganic materials. Final residue at 650 °C was 10.18 %. TGA of Cu@PLA-TiO_2 showed similar pattern however, in comparison the residue left at 650°C was large (42.72%). This large increase in the amount of residue was mainly attributed to oxidation of copper nanoparticles to copper oxide

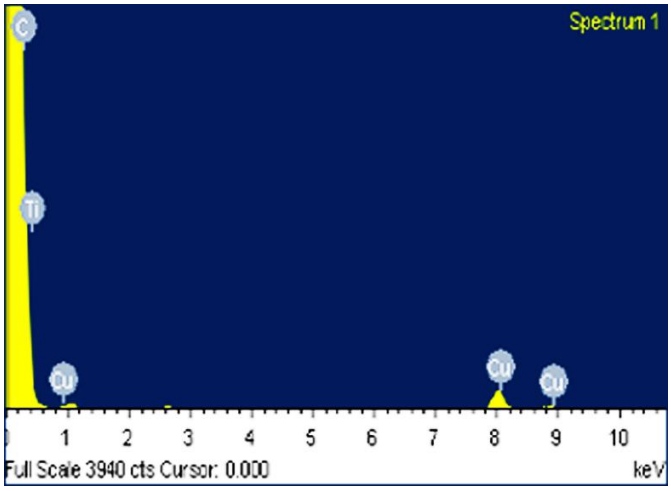


Fig. S4 EDAX of the Copper Catalyst

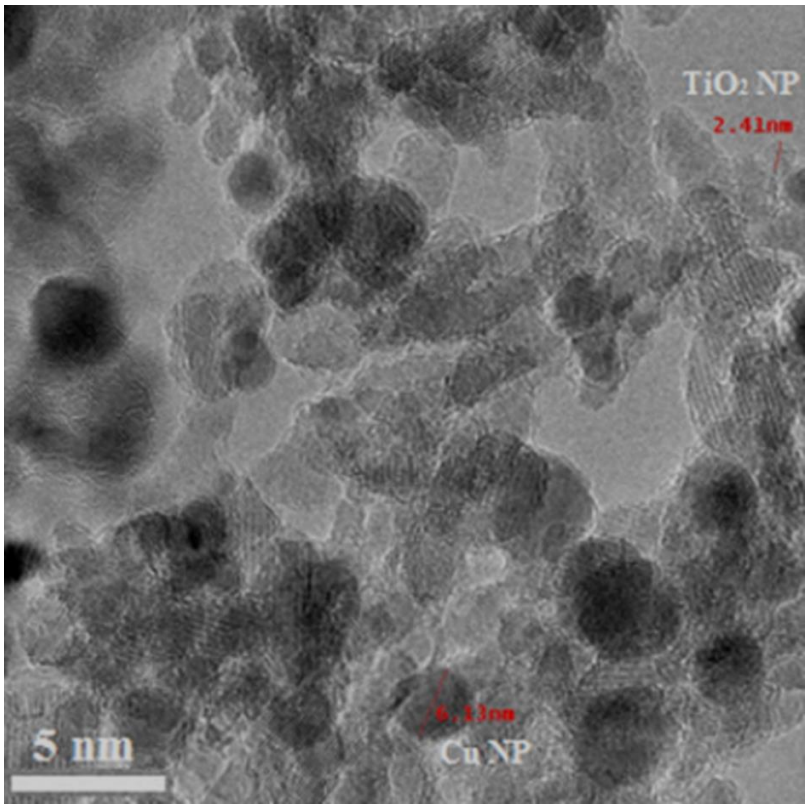


Fig. S5 HR-TEM of TiO_2NPs in CuNPs @PLA-TiO_2

Particle Size analysis of PLA-TiO_2 and CuNPs @PLA-TiO_2

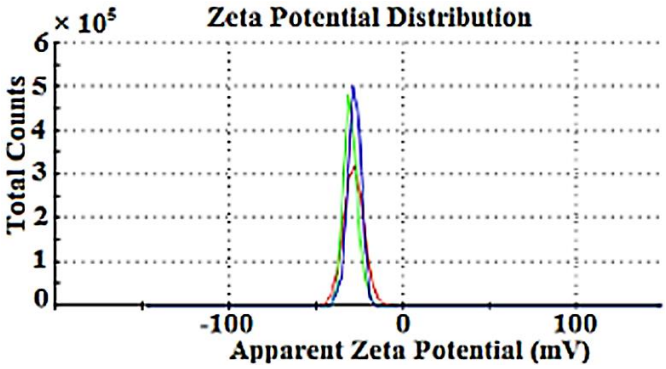


Fig. S6 Zeta potential distribution of PLA-TiO_2

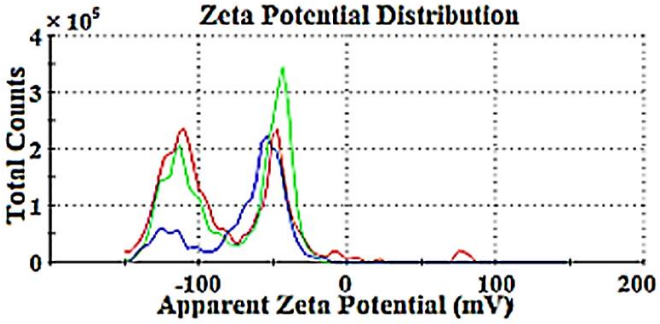


Fig. S7 Zeta potential distribution of CuNPs@PLA-TiO_2

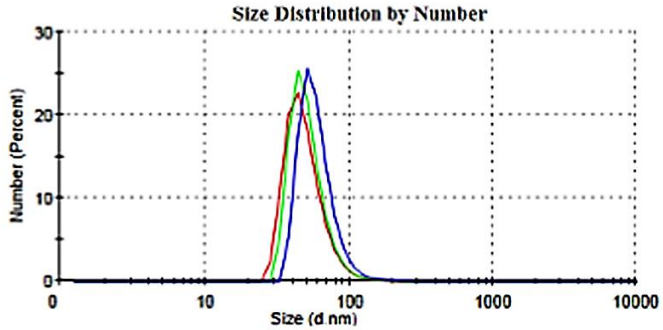


Fig. S8 Particle size distribution of 2% PLA-TiO_2

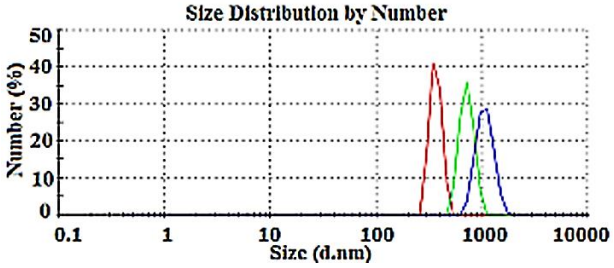


Fig. S9 Particle size distribution of CuNPs@PLA-TiO_2

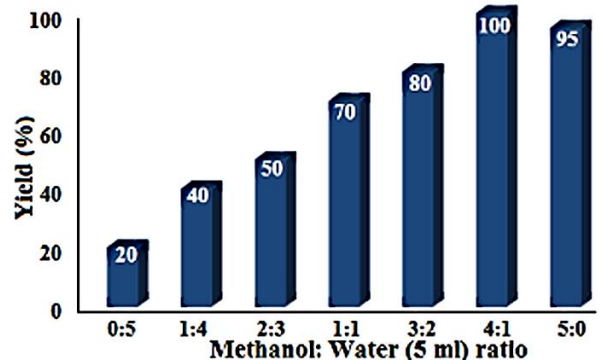


Fig. S10. Reduction of nitroarenes at different solvent ratio

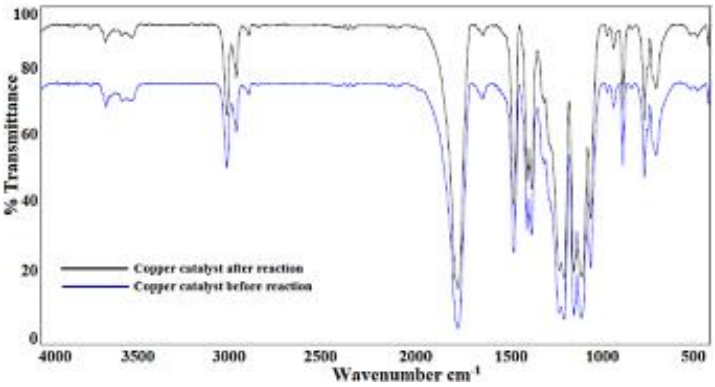
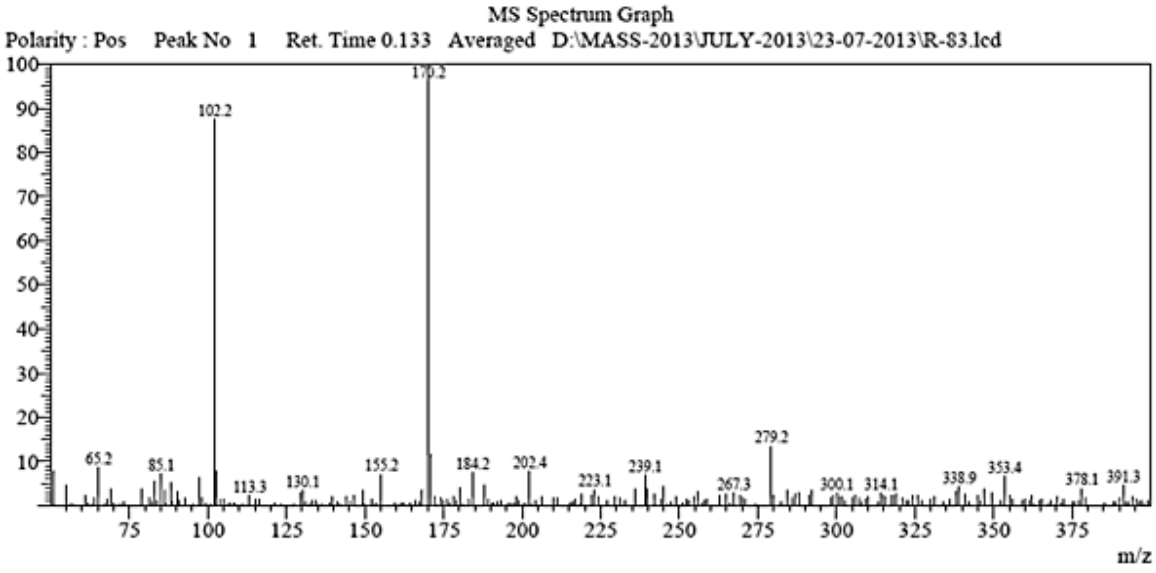


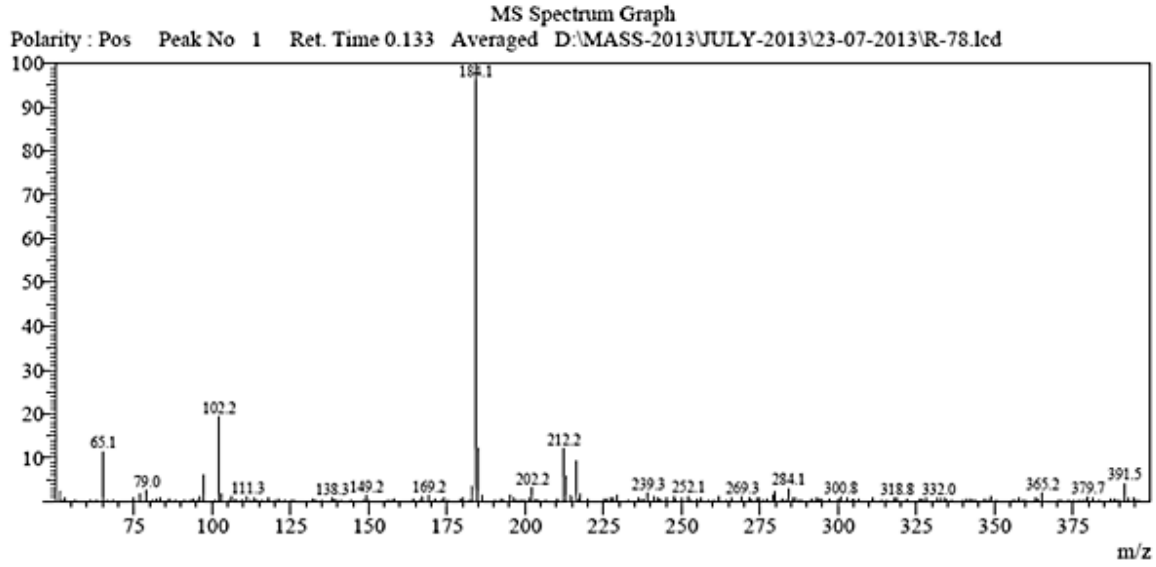
Fig. S11. FT-IR spectra of Copper Catalyst a) before and b) after the reaction.

Mass spectral data of some of the synthesized compounds mentioned in Table 3

Entry 1. *N*-phenylaniline



Entry 2. 4-methyl-*N*-phenylaniline



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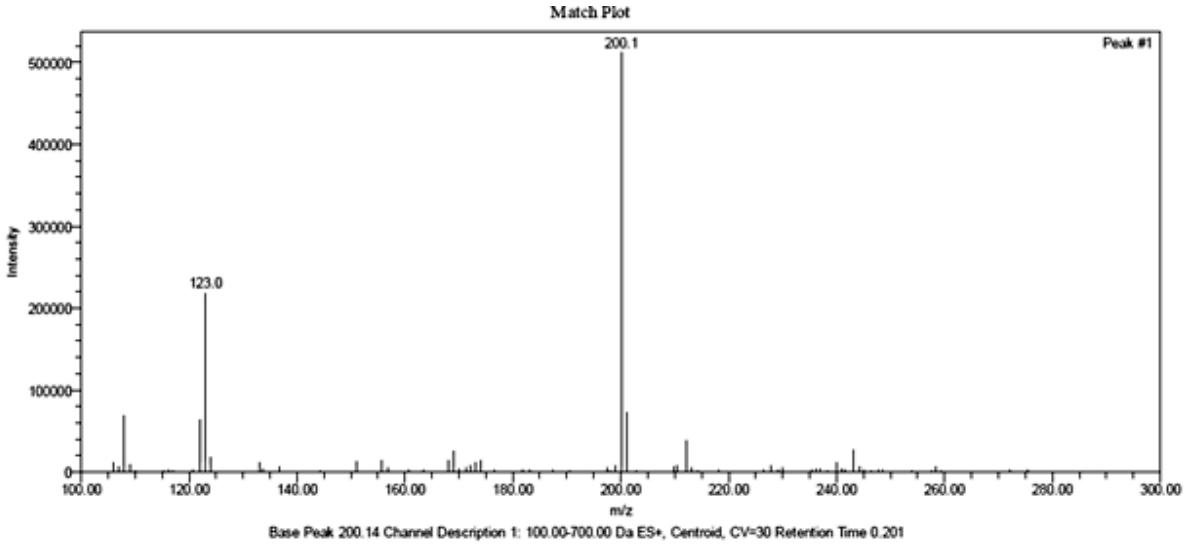
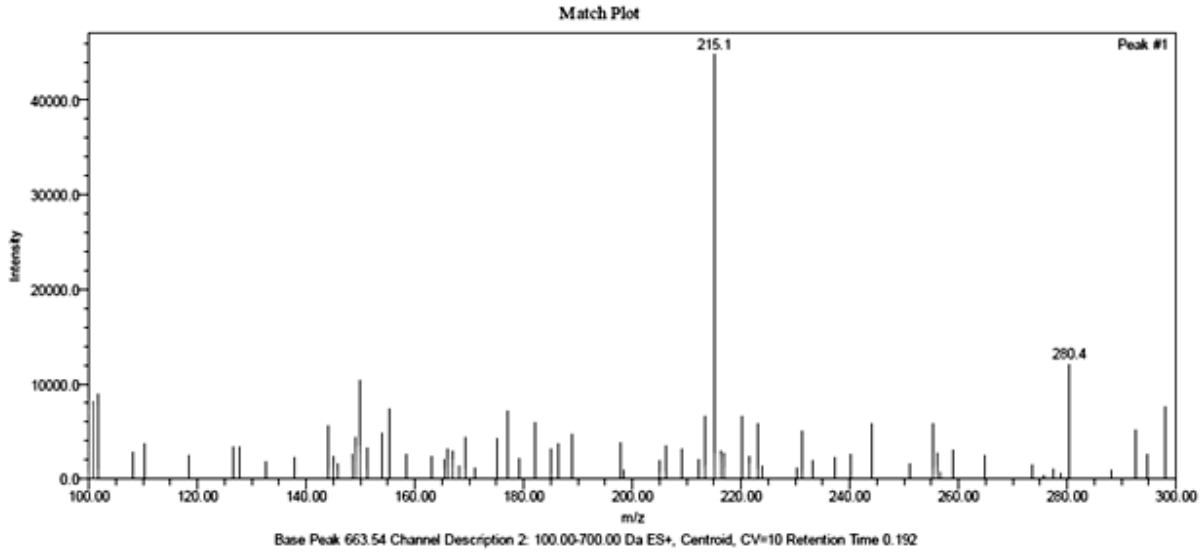
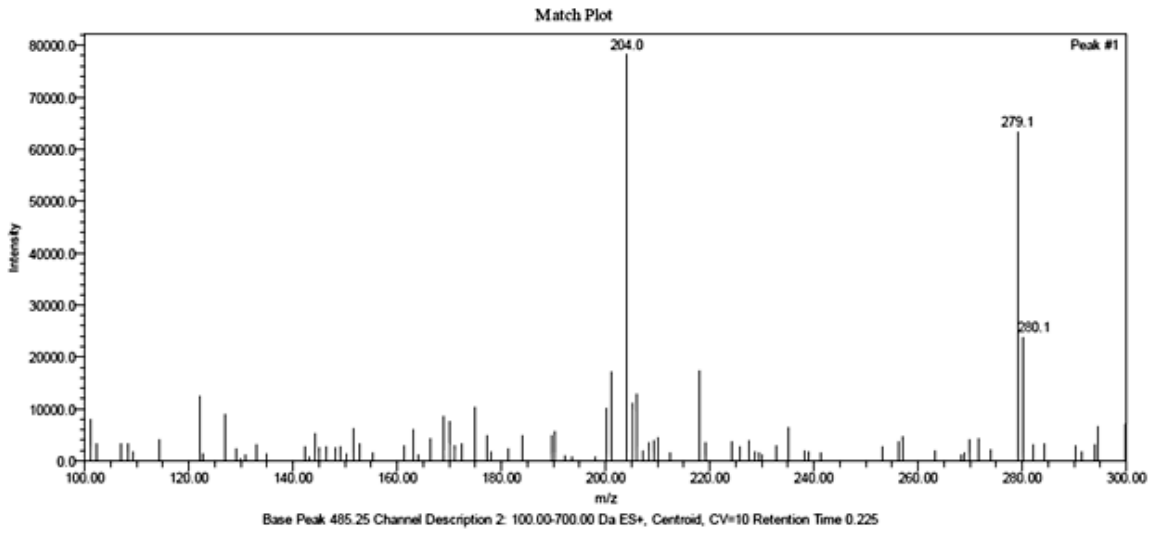


Entry 4. 4-nitro-*N*-phenylaniline

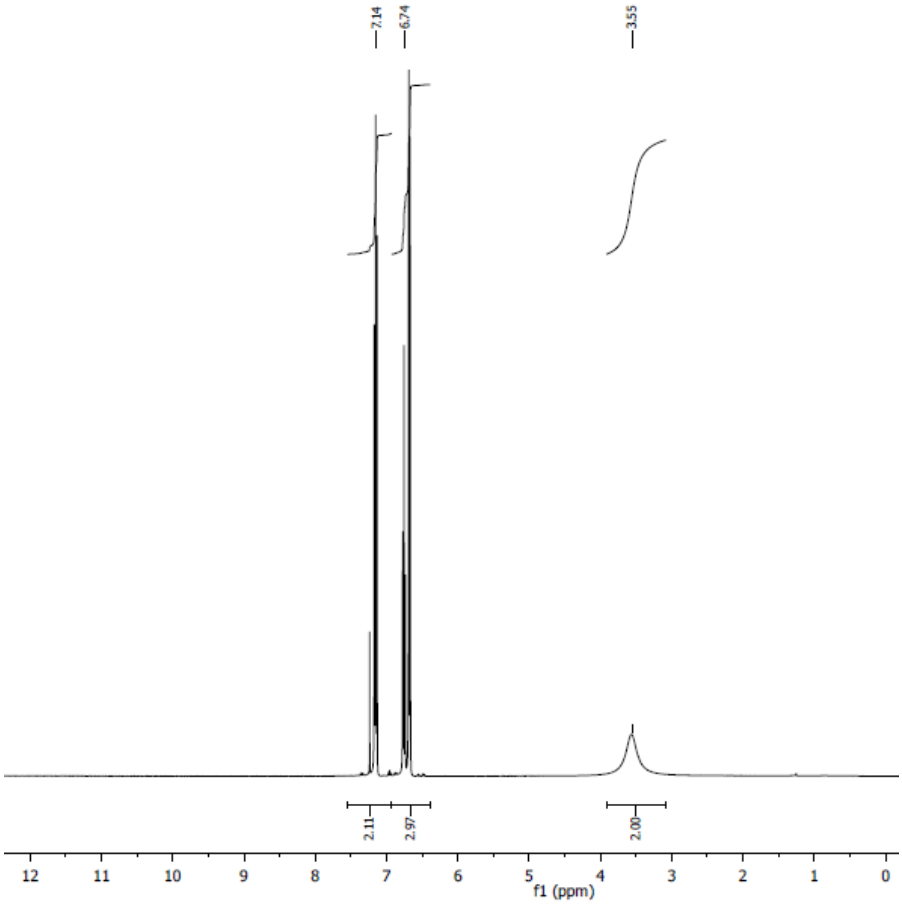


Entry 10. 4-chloro-*N*-phenylaniline



^{1}H NMR data of some of the synthesized compounds mentioned in Table 2

Entry 1. Aniline



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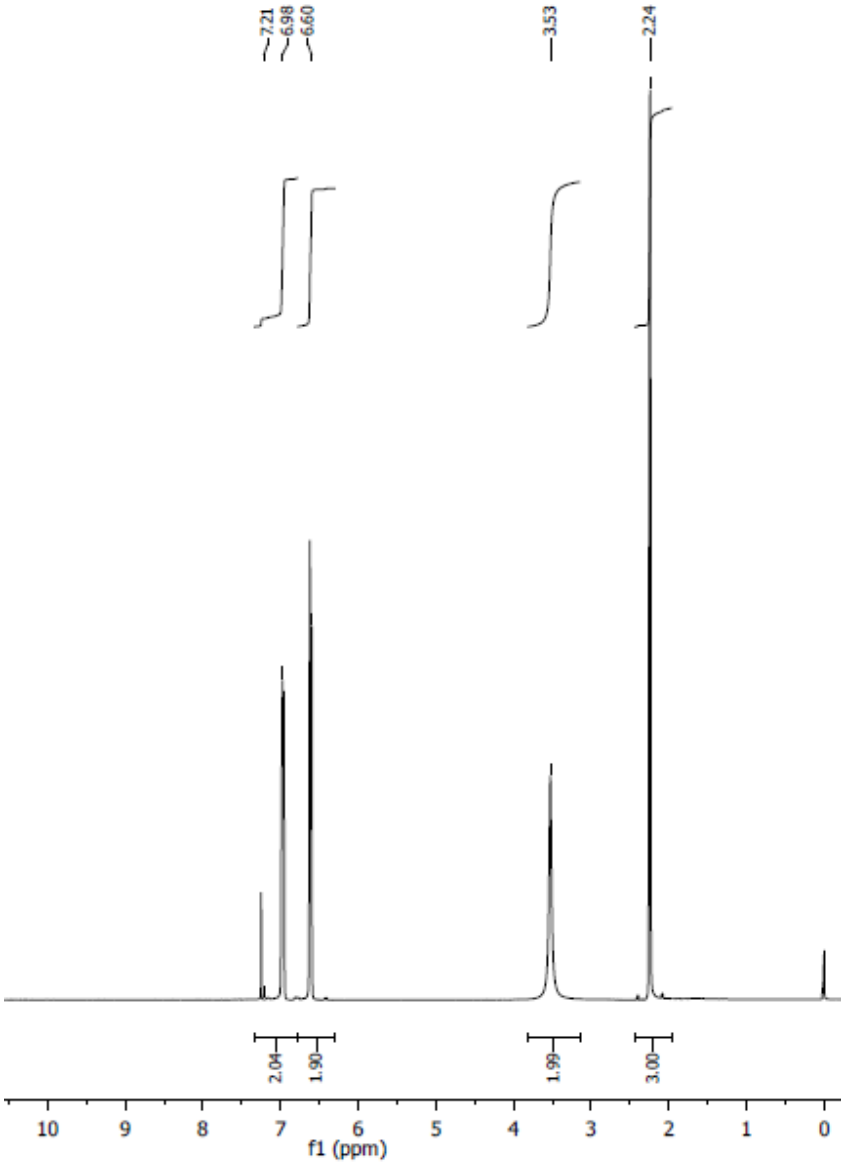

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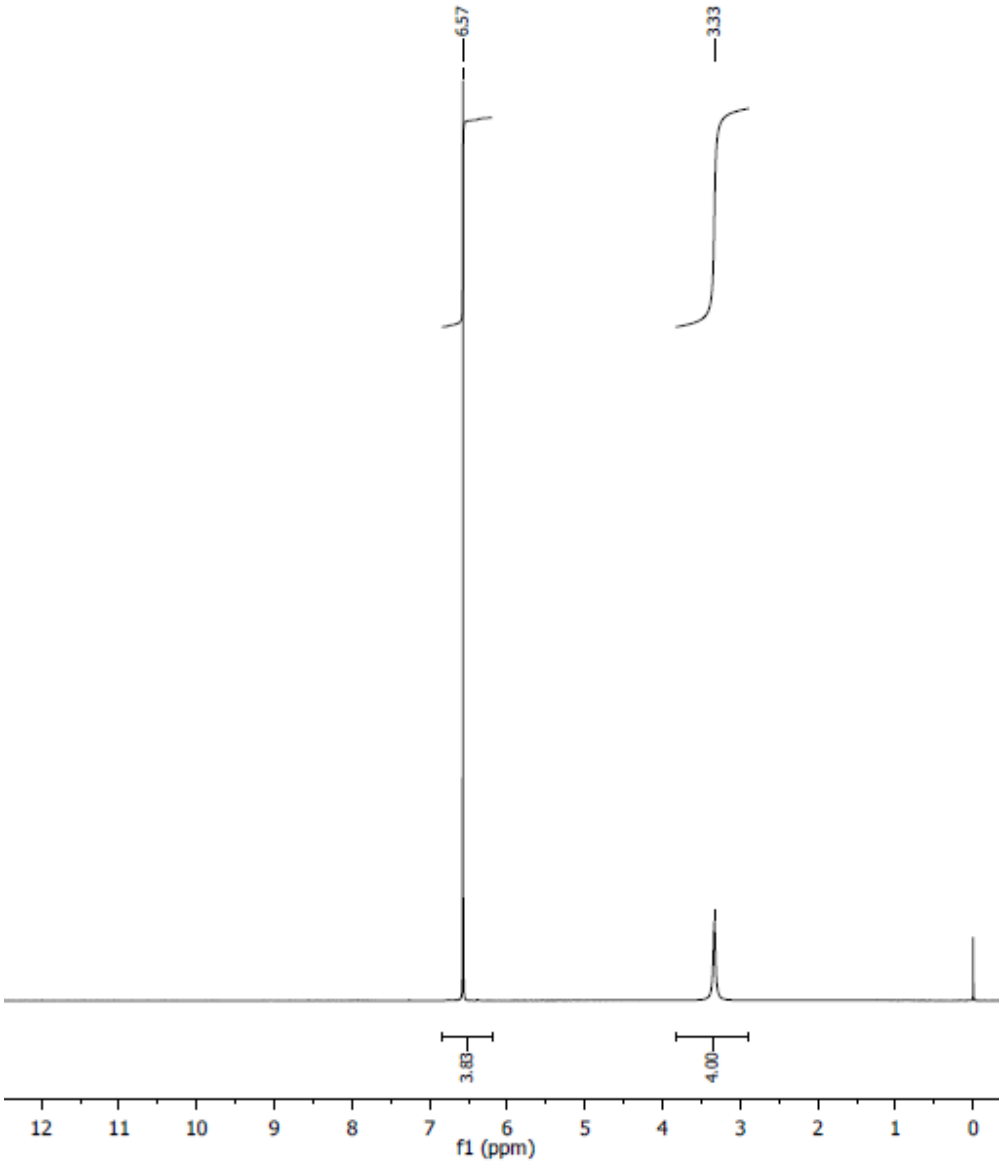

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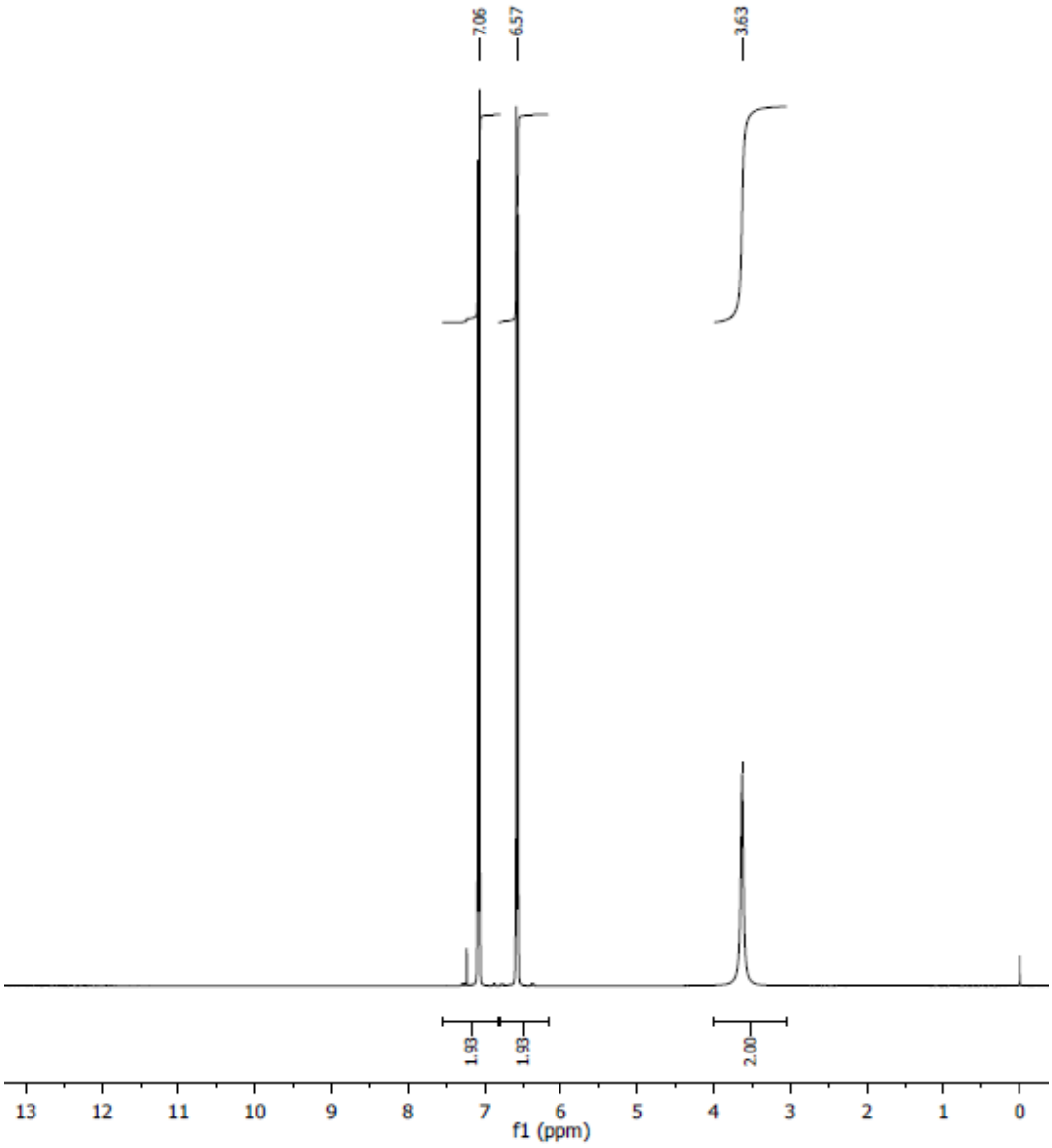
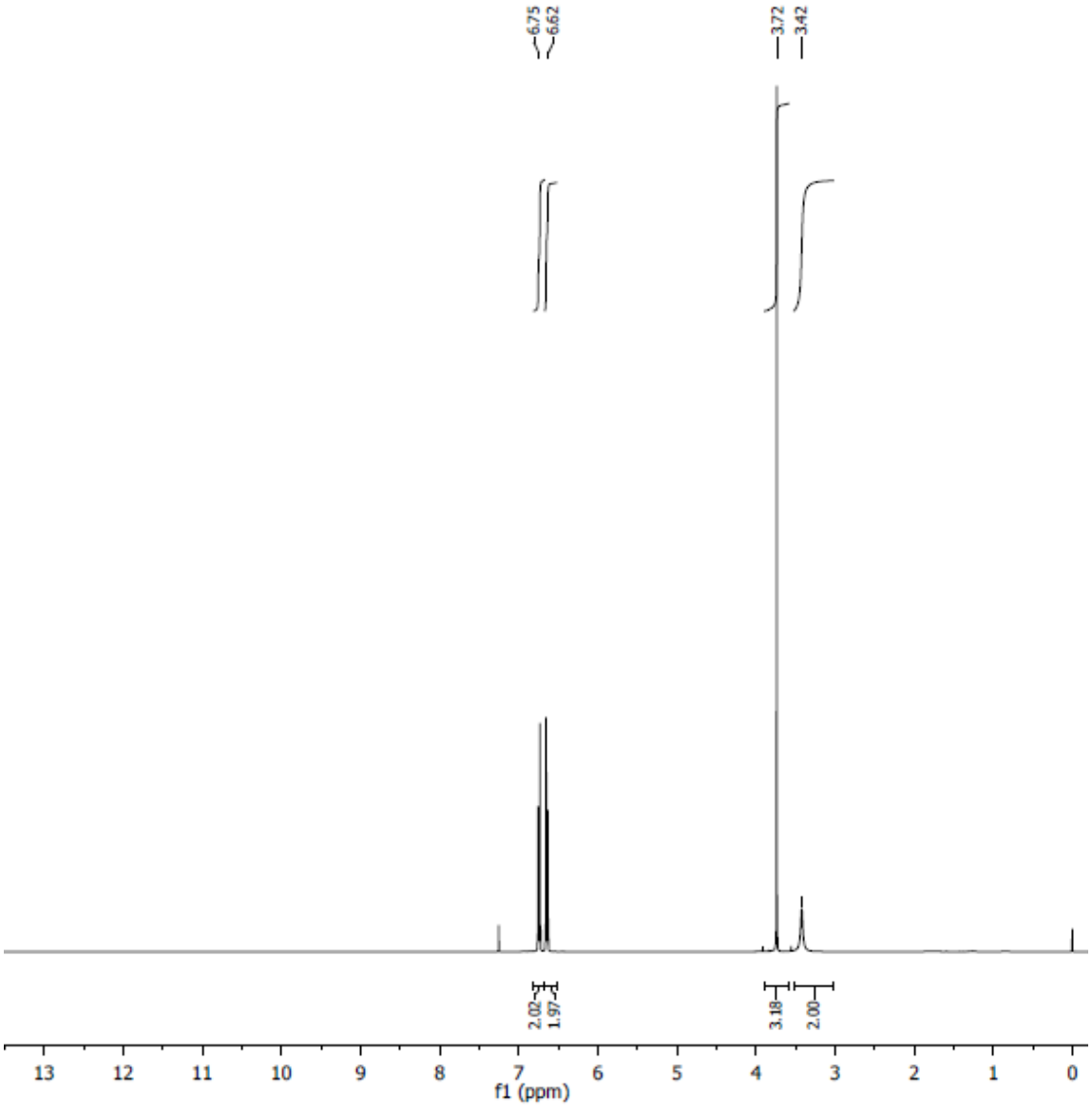
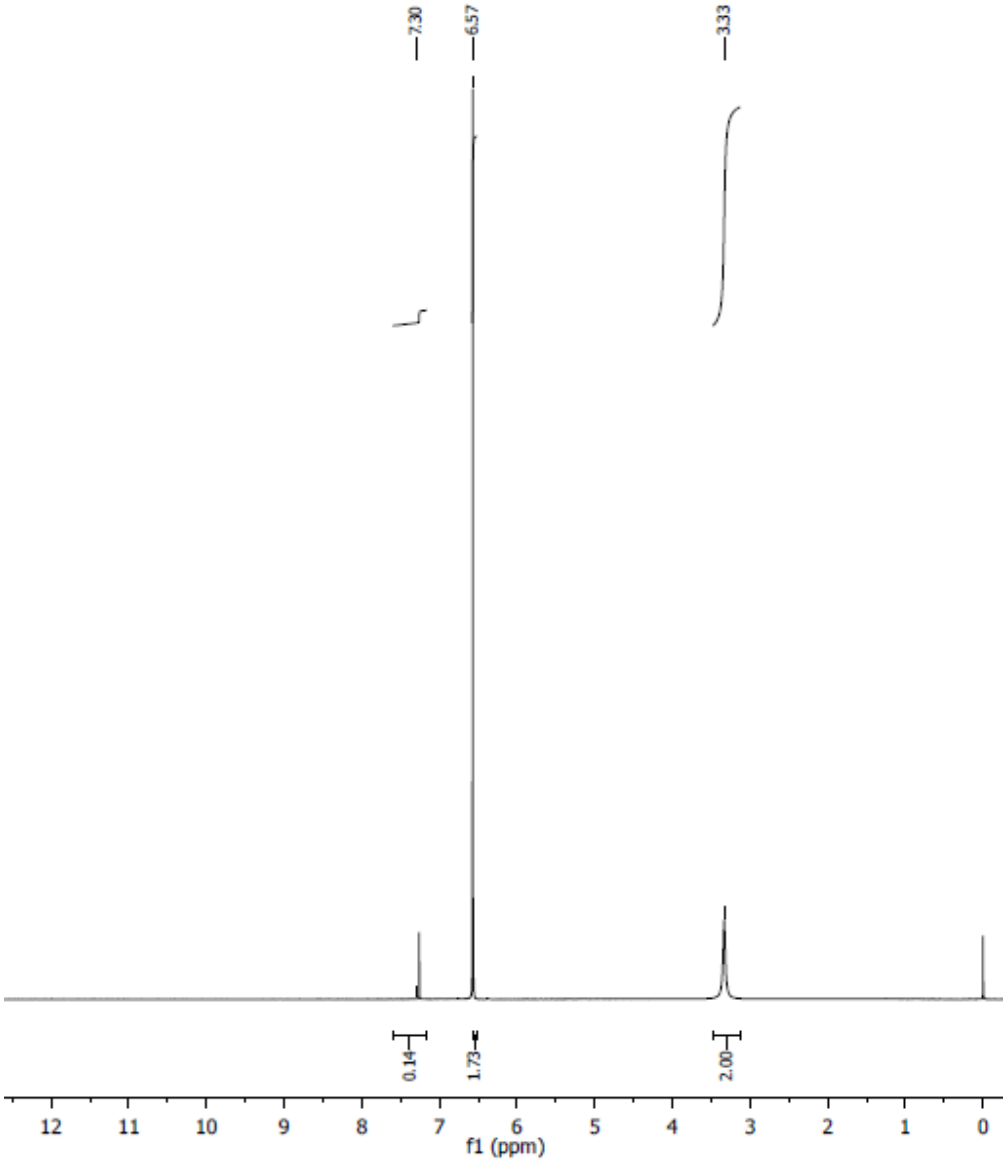


Entry 6. p-Anisidine

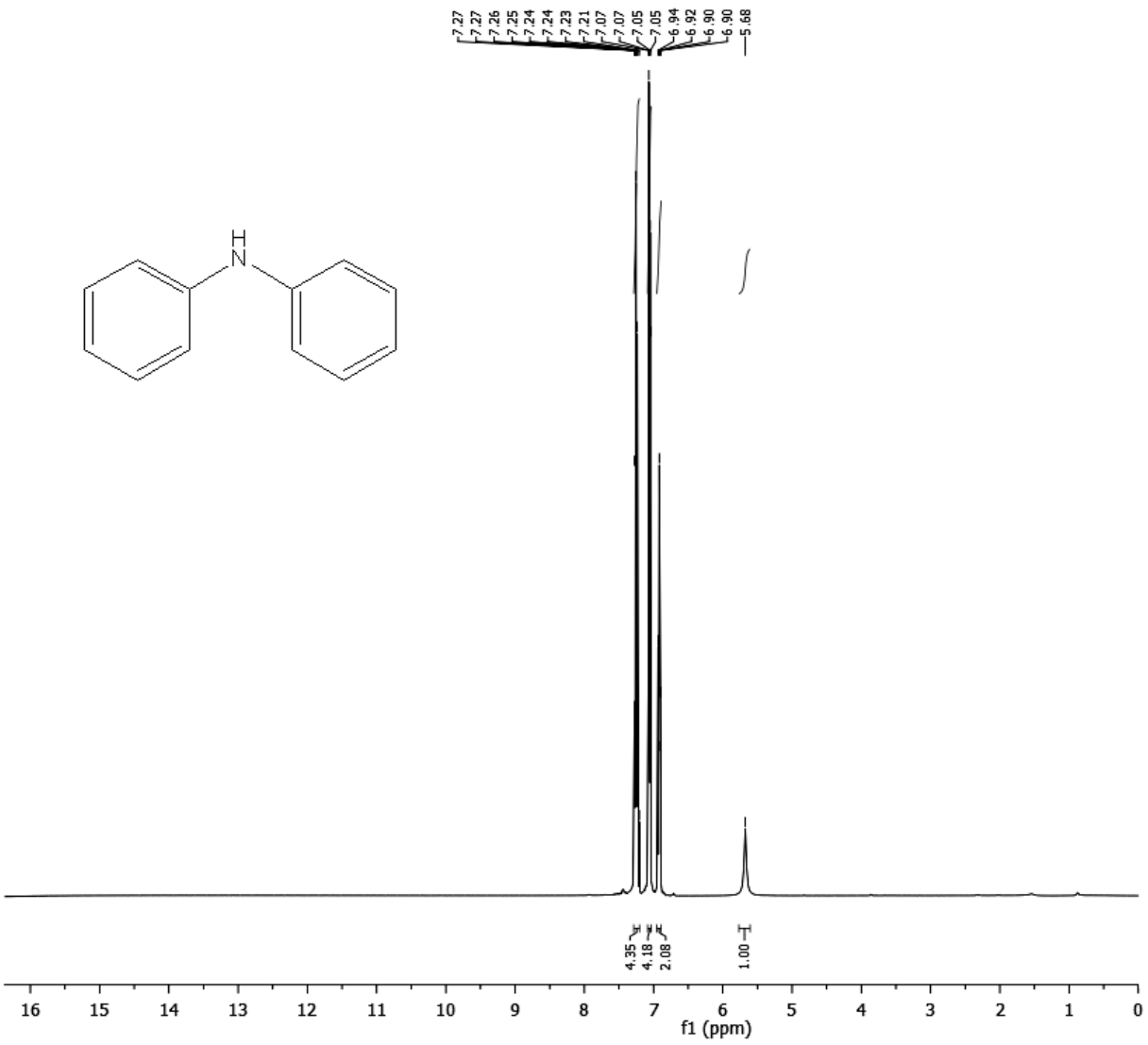


Entry 8. O-Aminophenol

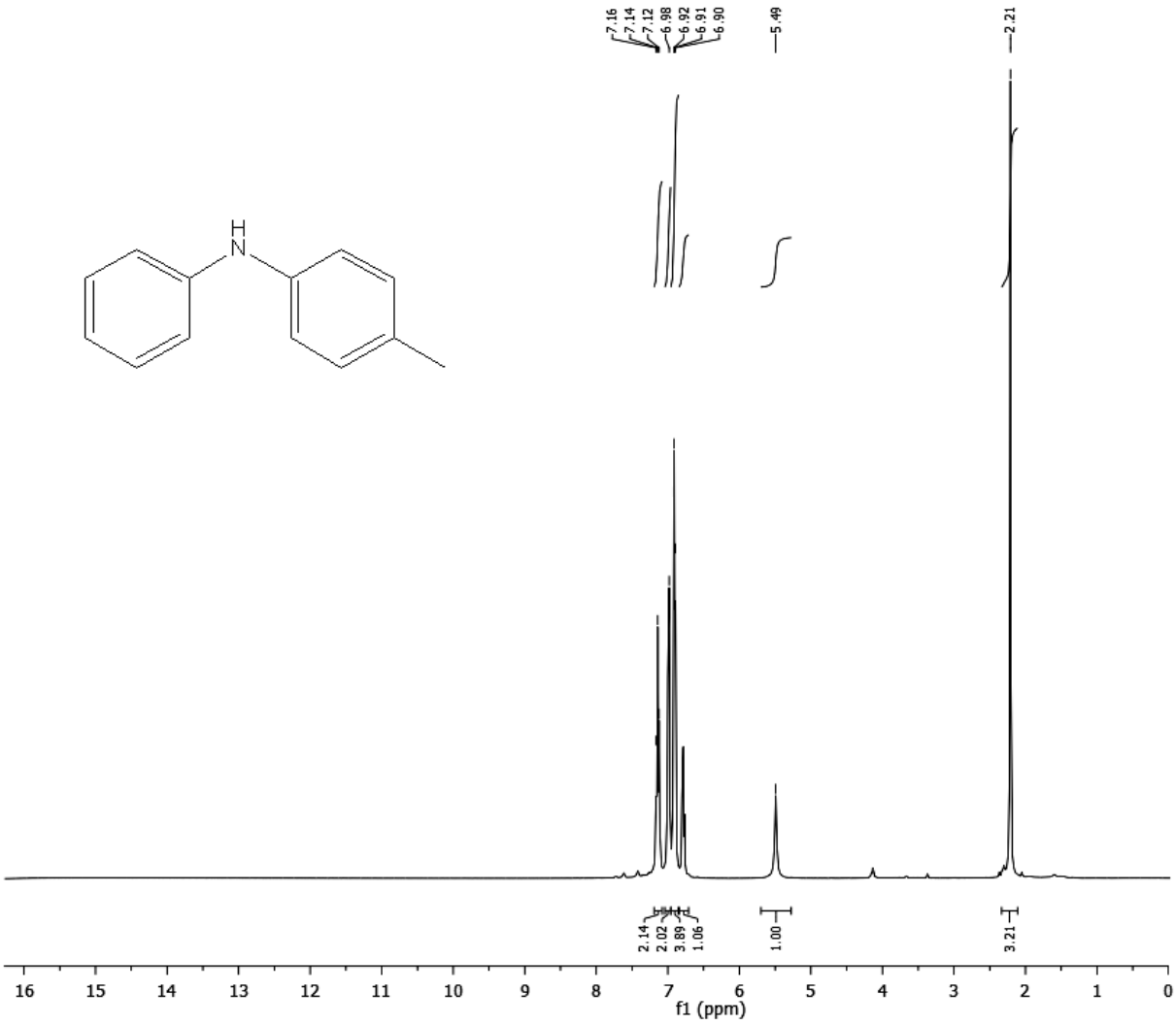


^{1}H NMR data of some of the synthesized compounds mentioned in Table 3

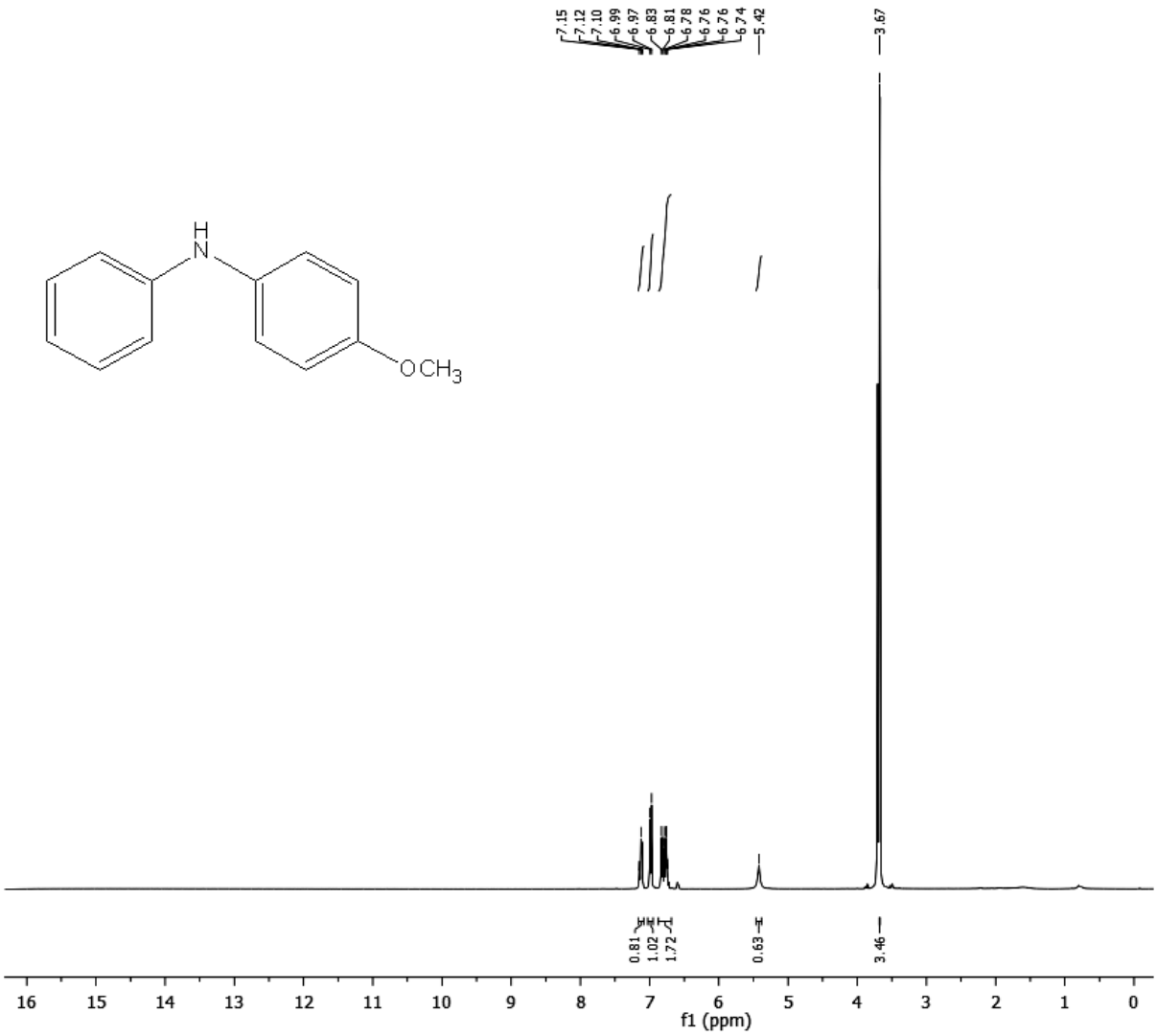
Entry 1. N-phenylaniline



Entry 2. 4-methyl-N-phenylaniline



Entry 3. 4-methoxy-N-phenylaniline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7.12
7.10
6.99
6.97
6.83
6.81
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6.76
6.76
6.74
5.42
3.67
H
N
OCH3
0.81
1.02
1.72
0.63
3.46
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
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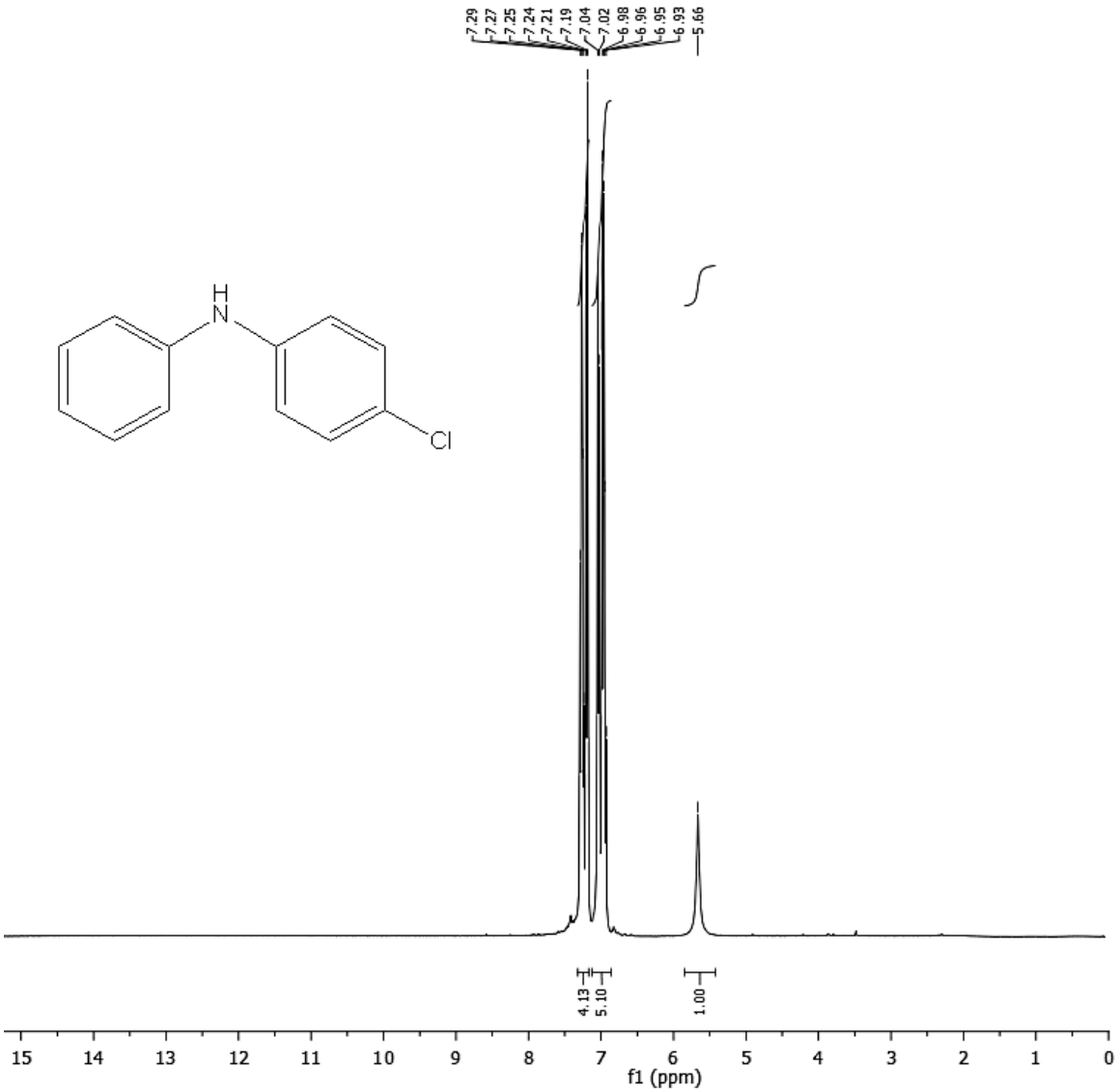
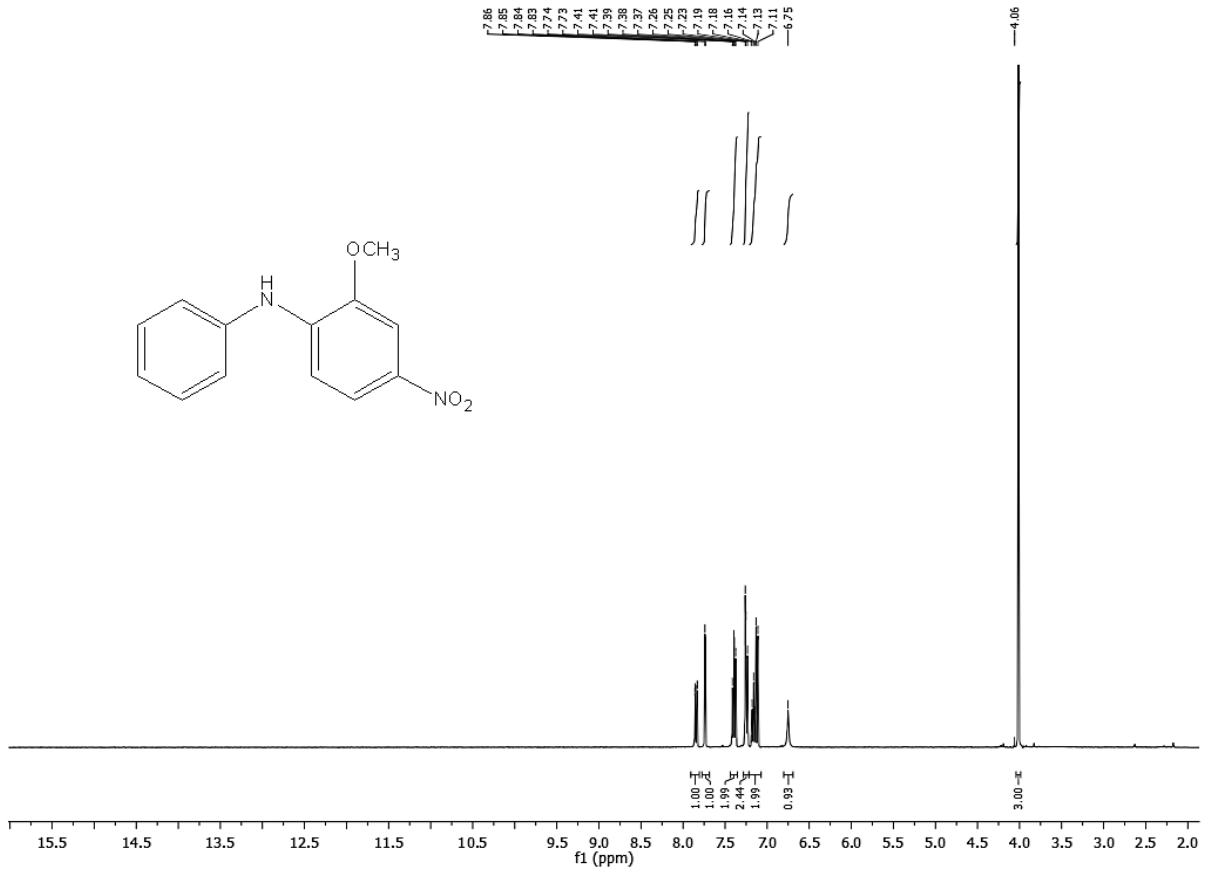
0
f1 (ppm)

Entry 10. 4-chloro-N-phenylaniline



Entry 11. 2-Methoxy-4-nitro-N-phenylaniline



Entry 12. N-phenylpyrimidin-2-amine