Supporting Information

Pd^{II} on guanidine functionalized Fe_3O_4 nanoparticles as efficient heterogeneous catalyst for Suzuki-Miyaura cross-coupling and reduction of nitroarenes in aqueous media

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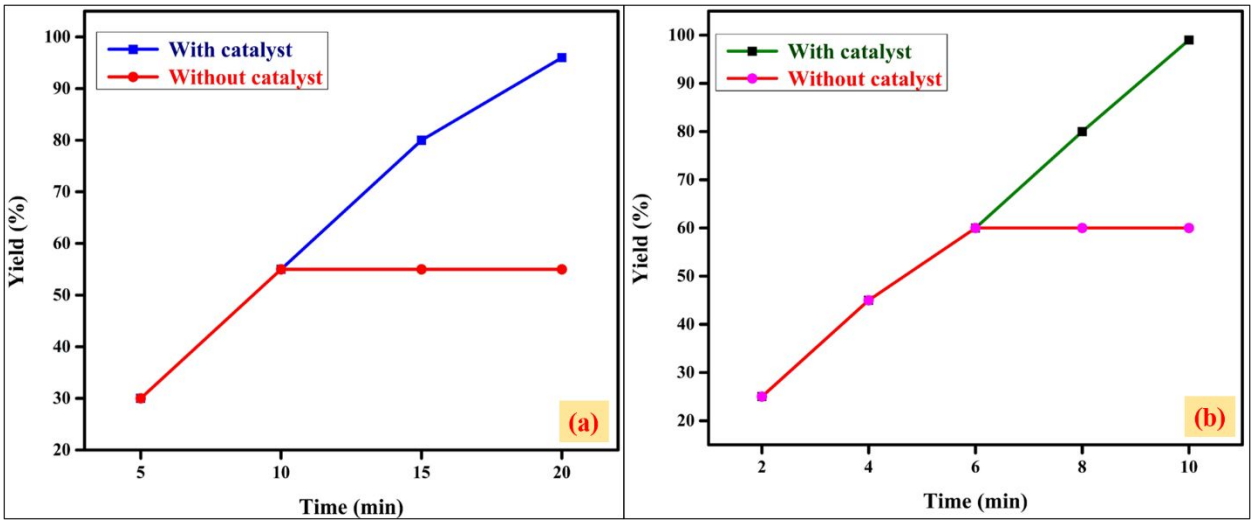


Figure S1. Hot filtration and leaching test of Fe_3O_4@Guanidine-Pd in the (a) Suzuki–Miyaura cross-coupling and (b) nitrobenzene reduction reactions.

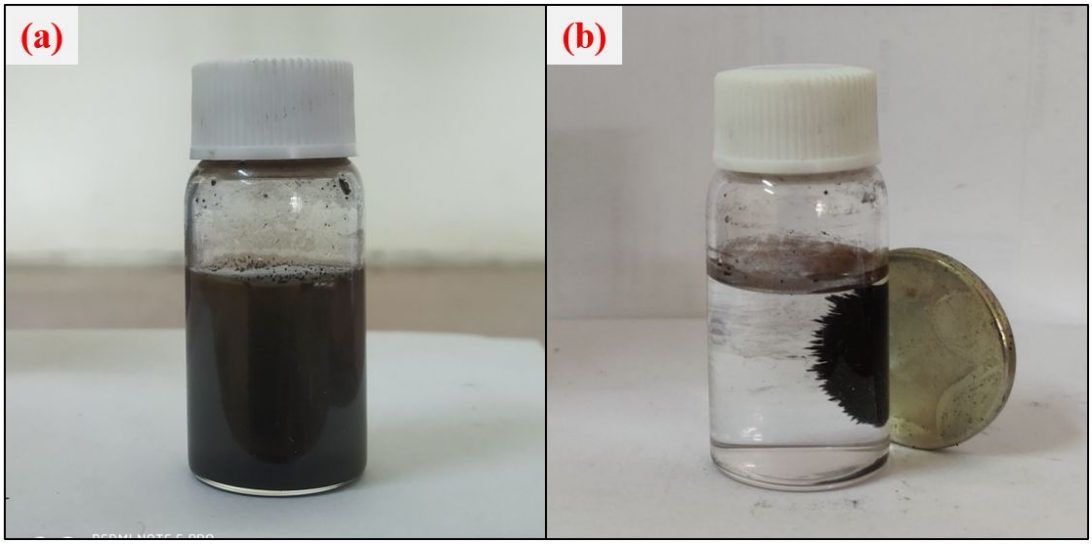


Figure S2. Magnetic removal of the catalyst after the catalytic run (a) after catalyzing reaction (b) separation of the catalyst using an external magnet.

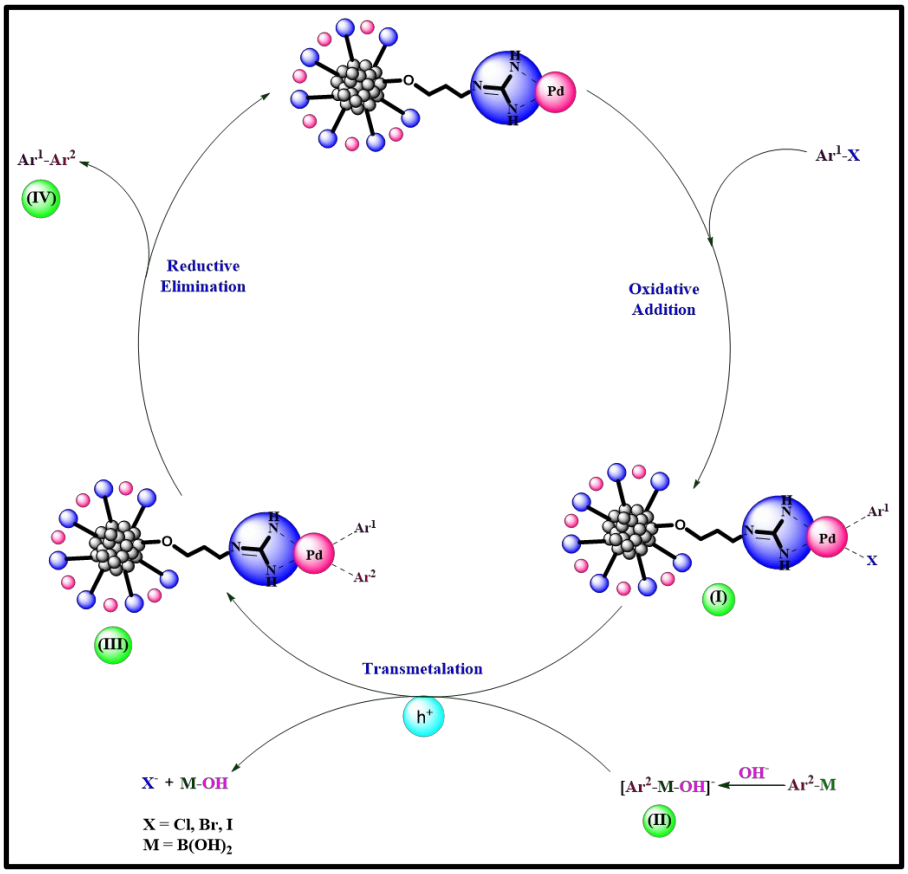


Figure S3. A plausible mechanism for the Suzuki–Miyaura cross-coupling reaction

A plausible mechanism for the Suzuki–Miyaura cross-coupling reaction catalyzed by Fe_3O_4@Guanidine-Pd in aqueous media.

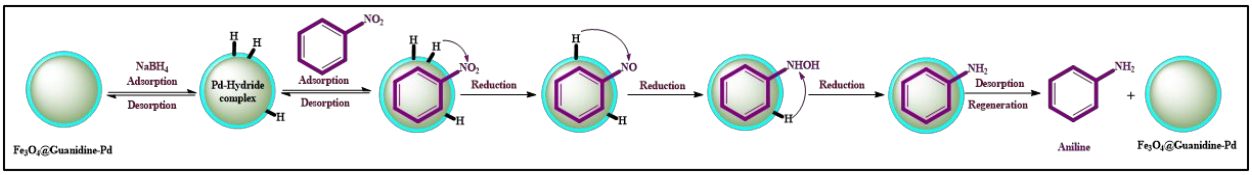


Figure S4. A plausible mechanism for the reduction of nitroarenes

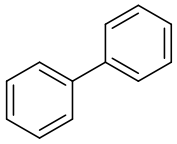
A plausible mechanism for the reduction of nitro compounds to corresponding amines with $NaBH_4$ catalyzed by Fe_3O_4@Guanidine-Pd in aqueous media at room temperature.

General Information

All chemicals were purchased from diverse commercial sources and were used without further purification. The reaction was monitored by thin layer chromatography using Silica gel 60 F_{254} Plates. Products were purified by column chromatography on 100–200 mesh silica gel. The ^{1}H NMR spectra were recorded on 400 MHz spectrometers in DMSO and $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane as an internal standard. The splitting patterns of protons are described as s (singlet), d (doublet), dd (doublet of doublets), t (triplet) and m (multiplet). The products were confirmed by ^{1}H NMR spectroscopic analysis.

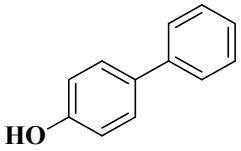
Characterization data of products (yields are corresponding to the Suzuki coupling and reduction of nitroarenes reactions given in Table 2 and Table 4)

Biphenyl



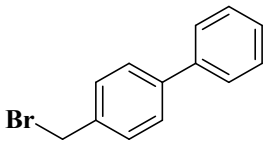
Yield: 96%, White solid; m.p. 69-72 °C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 7.67-7.64 (4H, d, Ar-H), 7.487-7.443 (4H, t, Ar-H),7.387-7.344 (2H, d, Ar-H).

***p*-hydroxy biphenyl**



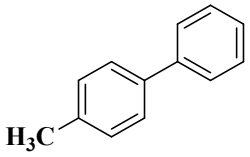
Yield: 94%, White solid; m.p. 163-165 °C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 9.5(1H, s, -OH), 7.575-7.554(2H, dd, Ar-H), 7.495-7.459(2H, dt, Ar-H), 7.418-7.380(2H, t, Ar-H), 7.285-7.249(1H, t, Ar-H), 6.867-6.830(2H, dt, Ar-H).

***p*-bromomethyl biphenyl**



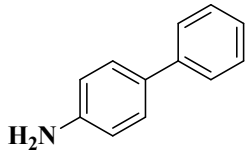
Yield: 88%, Yellow solid; m.p. 82-84 °C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 7.763-7.641(4H, m, Ar-H), 7.6-7.5(2H, d, Ar-H), 7.479-7.441(2H, t, Ar-H), 7.410-7.345(1H, m, Ar-H), 4.795-4.758 (2H, S, -CH_2-Br)

***p*-methyl biphenyl**



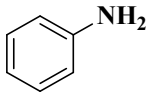
Yield: 90%, White solid; m.p. 41-44 °C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 7.634-7.605 (d, 2H, Ar-H), 7.555-7.534 (d, 2H, Ar-H), 7.452-7.414 (t, 2H, Ar-H), 7.345-7.34 (d, 1H, Ar-H), 7.329-7.251 (q, 2H, Ar-H), 2.347-2.332 (S, 3H, -CH_3).

***p*-amino biphenyl**



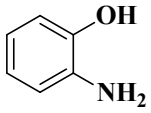
Yield: 88%, Light yellow color solid; m.p. 50-53°C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 7.524-7.5 (dd, 2H, Ar-H) 7.368-7.325 (m, 4H, Ar-H), 7.210-7.191 (m, 1H, Ar-H), 6.630-6.609 (d, 2H, Ar-H), 5.210 (S, 2H, -NH_2).

Aniline



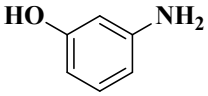
Yield: 99%; Colorless liquid; b.p. 184°C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 7.018-6.979(2H, t, Ar-H), 6.566-6.545(1H, t, Ar-H), 6.504-6.465(2H, d, Ar-H), 3.374(2H, s, -NH_2).

***o*-aminophenol**



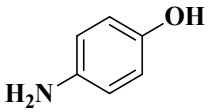
Yield: 94%; White crystals; m.p. 170-173°C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 8.895(1H, s, -OH), 6.643-6.621(1H, dd, Ar-H), 6.591-6.510(2H, dd, Ar-H),6.408-6.366(1H, t, Ar-H), 4.440(2H, s, -NH_2).

***m*-aminophenol**



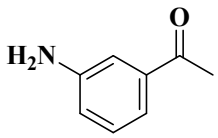
Yield: 96%; White crystals; m.p. 119-122°C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 8.813(1H, s, -OH), 6.796-6.757(1H, t, Ar-H), 6.017-5.999(2H, d, Ar-H),5.953-5.931(2H, dd, Ar-H), 4.846(2H, s, -NH_2).

***p*-aminophenol**



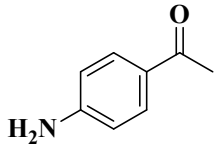
Yield: 99%; White crystalline powder; m.p. 186-189°C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 8.314(1H, s, -OH), 6.494-6.458(2H, dd, Ar-H), 6.432-6.403(2H, dd, Ar-H), 4.36(2H, s, -NH_2).

***m*-aminoacetophenone**



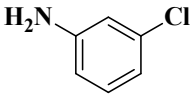
Yield: 97%; Slight yellow crystals; m.p. 96-98 °C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 7.163-7.084 (2H, dd, Ar-H), 6.810-6.6781(2H, dd, Ar-H), 3.322(2H, **s, -**NH_2), 2.509-2.475(3H, s**, -**CH_3).

***p*-aminoacetophenone**



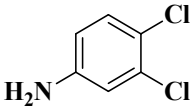
Yield: 99%; Brown crystals; m.p. 105-107 °C; ^{1}H NMR (400 MHz, $CdCl_3$): δH (ppm) = 7.807-7.787 (2H, dd, Ar-H), 6.646-6.626(2H, dd, Ar-H), 4.161(2H, **s, -**NH_2), 2.495(3H, s**, -**CH_3).

***m*-chloroaniline**



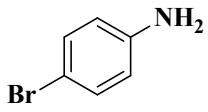
Yield: 96%; Light yellow liquid; b.p. 94-96 °C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 7.026-6.987 (1H, t, Ar-H), 6.616-6.607(1H, dd, Ar-H), 6.523-6.487(2H, dd, Ar-H), 3.422-3.376(2H, **s, -**NH_2),

3,4-dichloroaniline



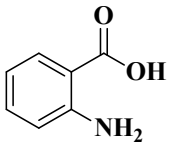
Yield: 92%; Dark brown crystals; m.p. 70-72 °C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 7.182-7.161 (1H, m, Ar-H), 6.741-6.735(1H, d, Ar-H), 6.531-6.503(1H, dd, Ar-H), 3.345-3.324(2H, **s, -**NH_2),

***p*-bromoaniline**



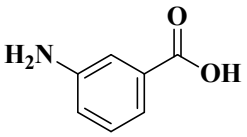
Yield: 90%; Brown solid; m.p. 66-66.5 °C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 7.137-7.099 (2H, d, Ar-H), 6.527-6.489 (2H, d, Ar-H), 3.324 (2H, s, -NH_2).

***o*-amino benzoic acid**



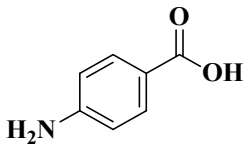
Yield: 88%; Yellow solid; m.p. 142-145°C; ^{1}H NMR (400 MHz, DMSO): δH (ppm = 8.4 (2H, s,-NH_2), 7.692-7668 (1H, dd, Ar-H), 7.232-7.190 (1H, dt, Ar-H), 6.738-6.714 (1H, dd, Ar-H), 6.514-6.473 (1H, dt, Ar-H), 3.3 (1H, s, -OH).

***m*-amino benzoic acid**



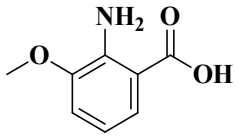
Yield: 92%; White solid; m.p. 178-180°C; ^{1}H NMR (400 MHz, DMSO): δH (ppm = 12.45 (1H, s, -OH), 7.188-7.181(1H, t, Ar-H), 7.131-7.073 (2H, m, Ar-H), 6.790-6.761 (1H, m, Ar-H), 5.4 (2H, s,-NH_2).

***p*-amino benzoic acid**



Yield: 96%; Light yellow powder; m.p. 186-188°C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 11.932(1H, s, -OH), 7.635-7.607(2H, dd, Ar-H), 6.567-6.539(2H, dd, Ar-H), 5.856(2H, s, -NH_2).

3-methoxy-*o*-aminobenzoic acid



Yield: 86%; White solid; m.p. 169-170°C; ^{1}H NMR (400 MHz, DMSO): δH (ppm) = 11(1H, s, -OH), 7.622-7.599(2H, d, Ar-H),7.163-7.145(1H, d, Ar-H), 6.484-6.446(2H, t, -NH_2), 3.325 (3H, s, -CH_3)

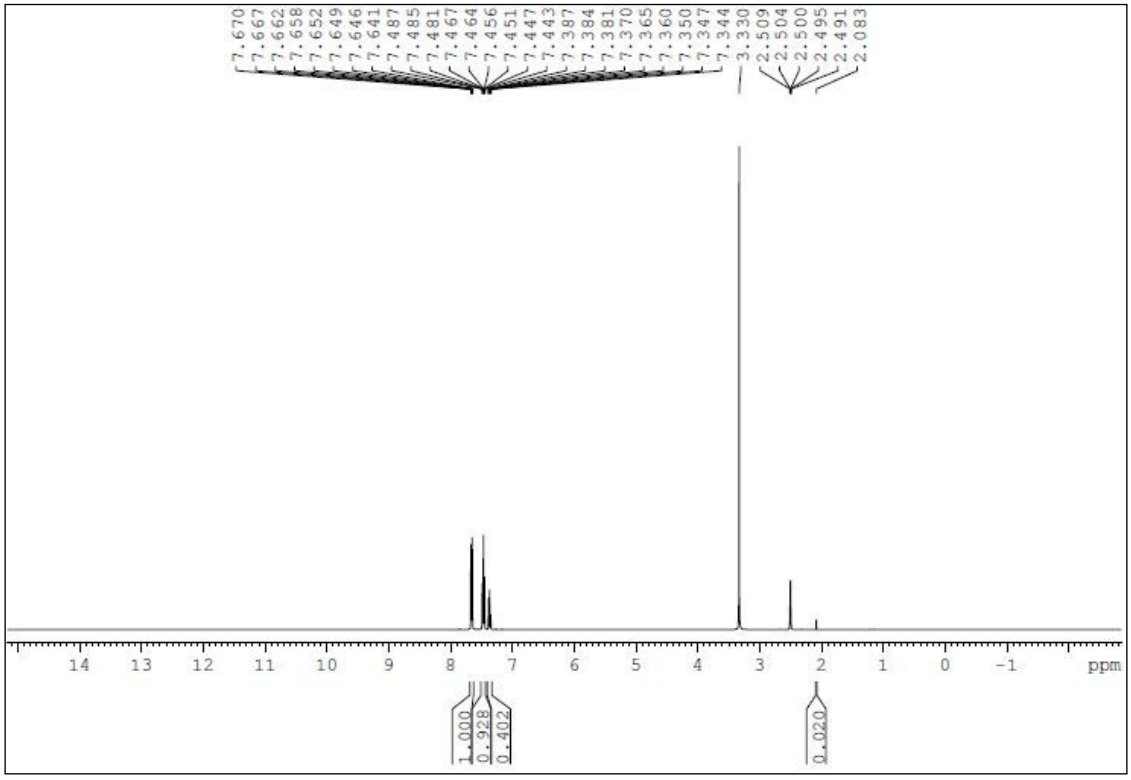


Figure S5. ^{1}H NMR spectrum of Biphenyl

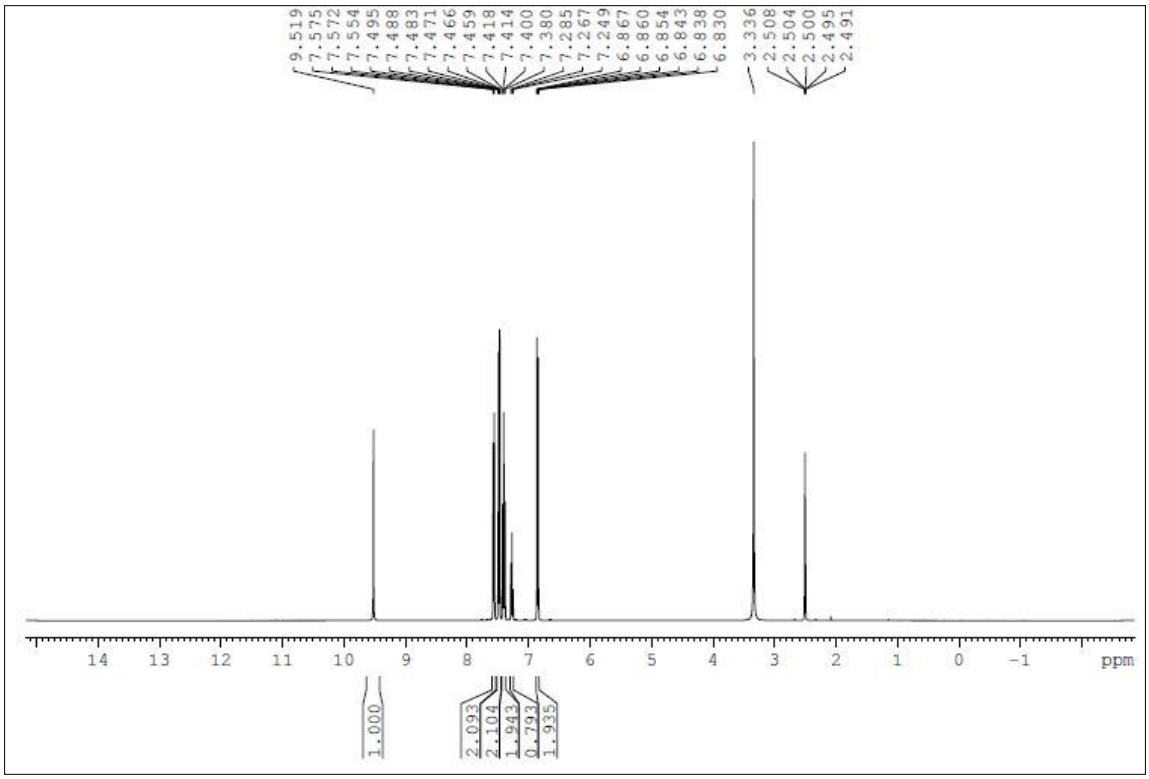


Figure S6. ^{1}H NMR spectrum of *p*-hydroxy biphenyl

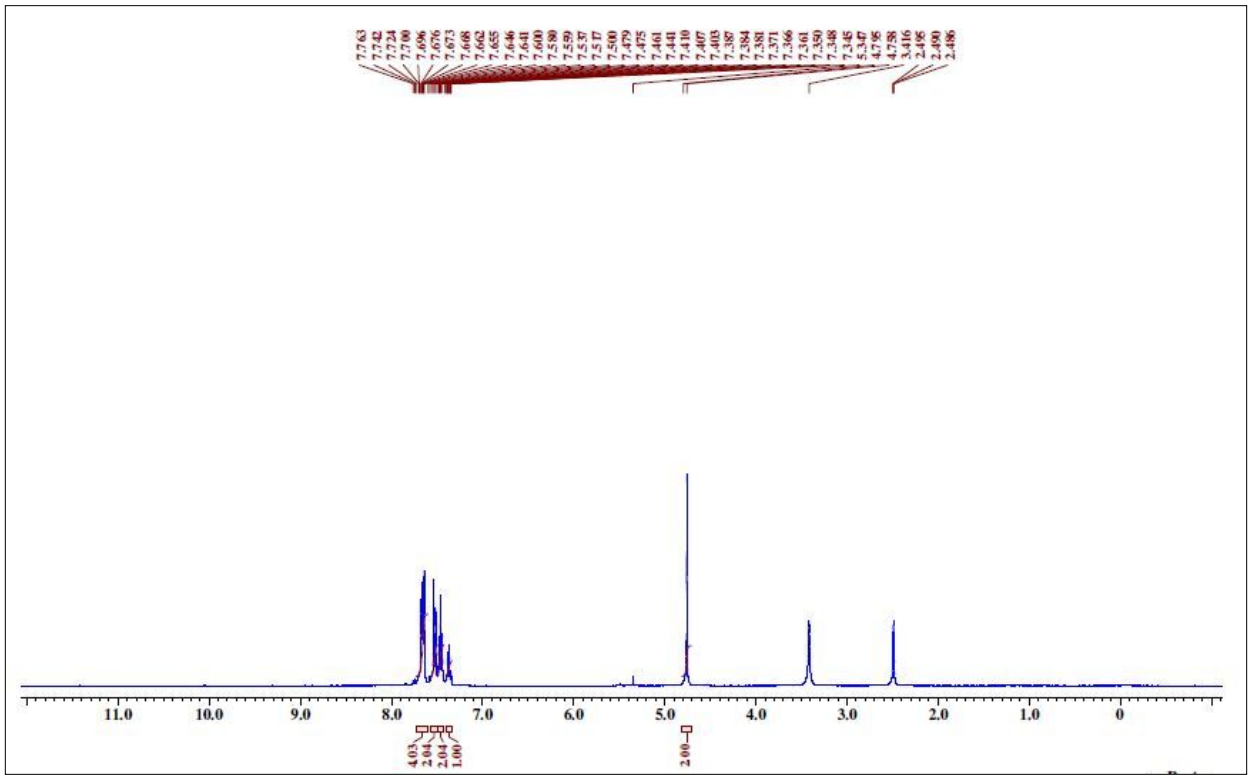


Figure S7. ^{1}H NMR spectrum of *p*-bromomethyl biphenyl

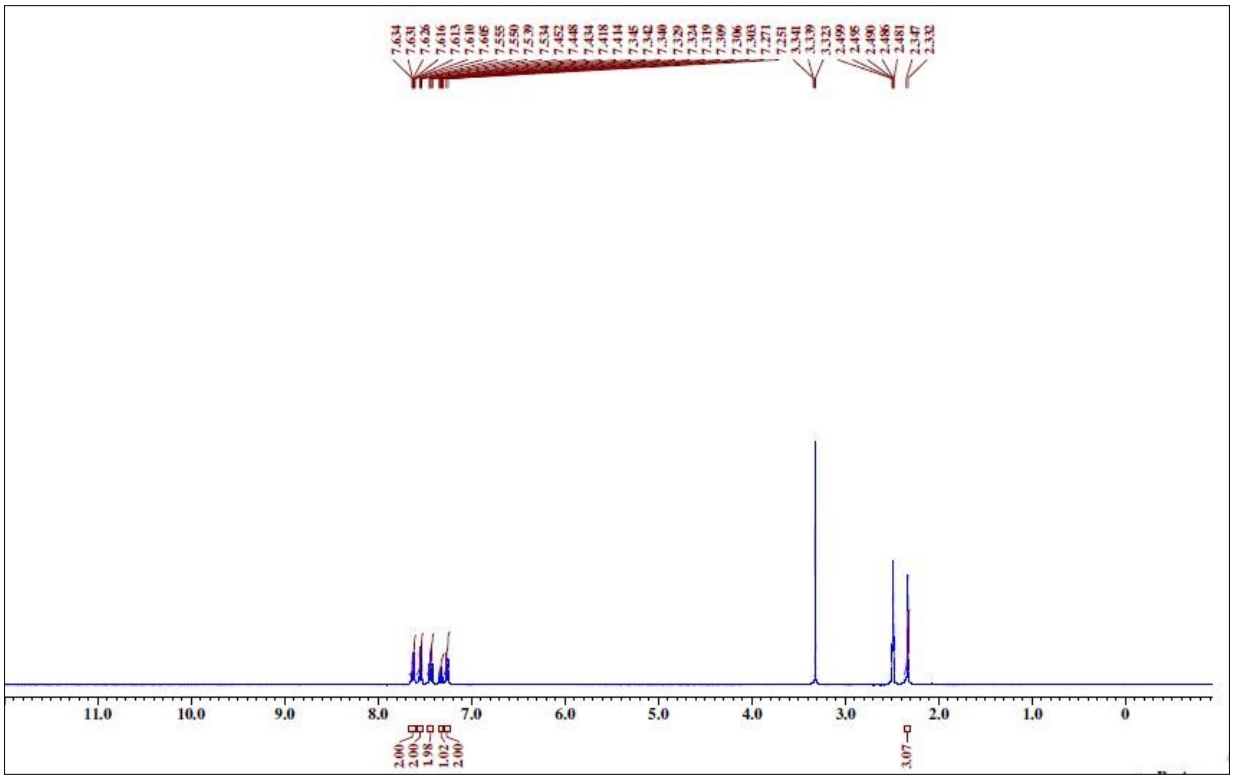


Figure S8. ^{1}H NMR spectrum of *p*-methyl biphenyl

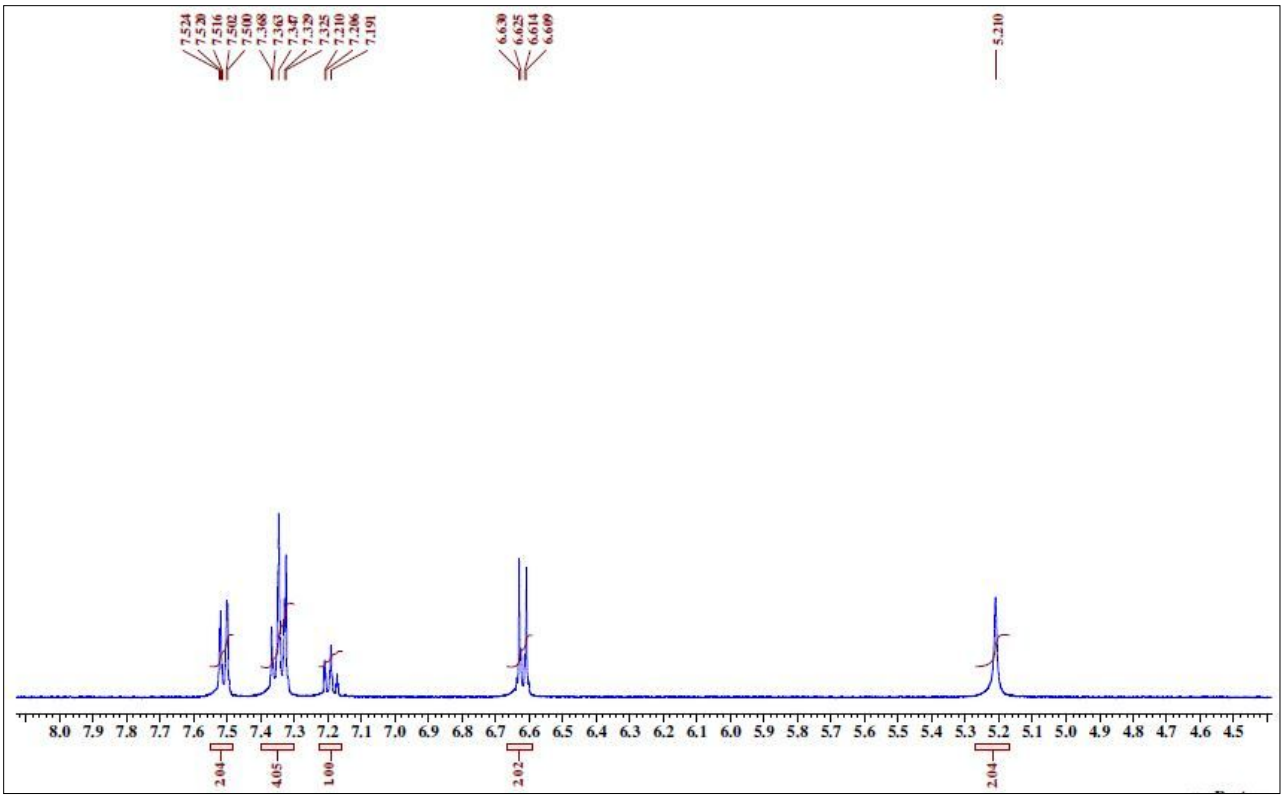


Figure S9. ^{1}H NMR spectrum of *p*-amino biphenyl

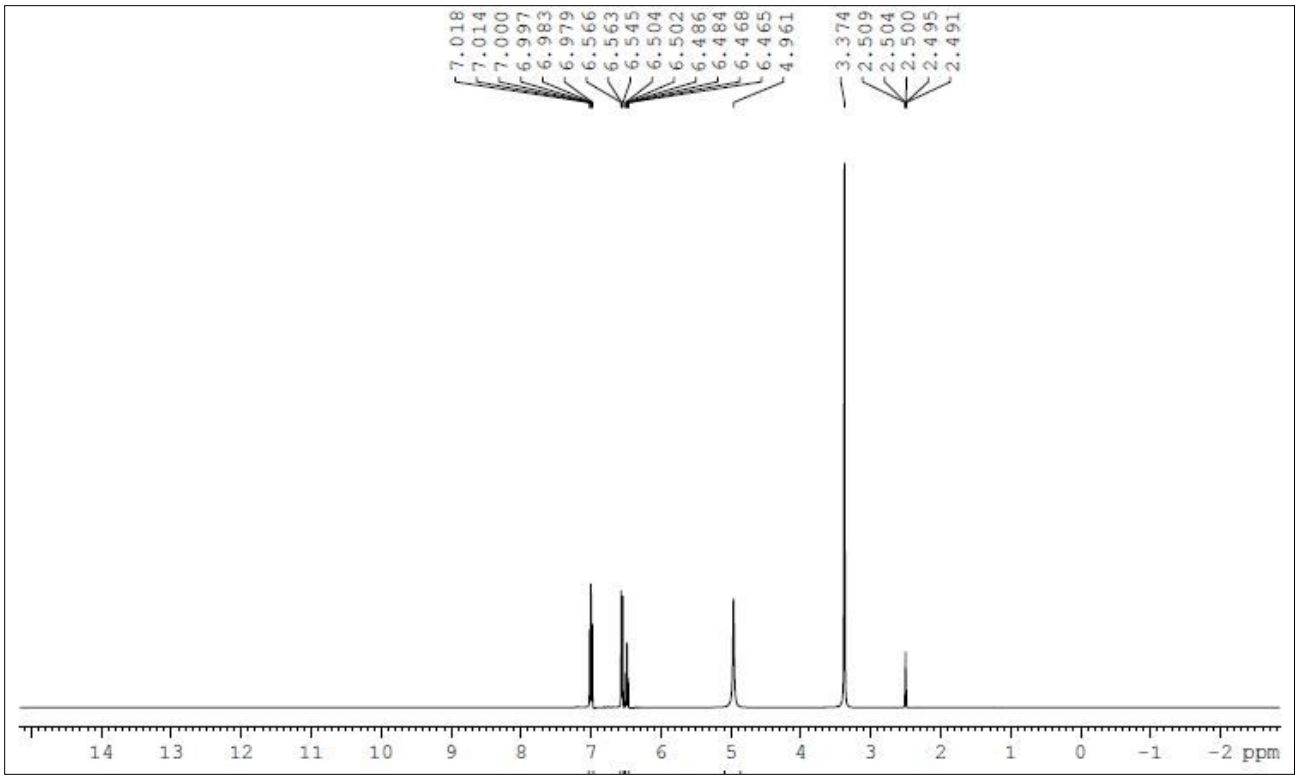


Figure S10. ^{1}H NMR spectrum of aniline

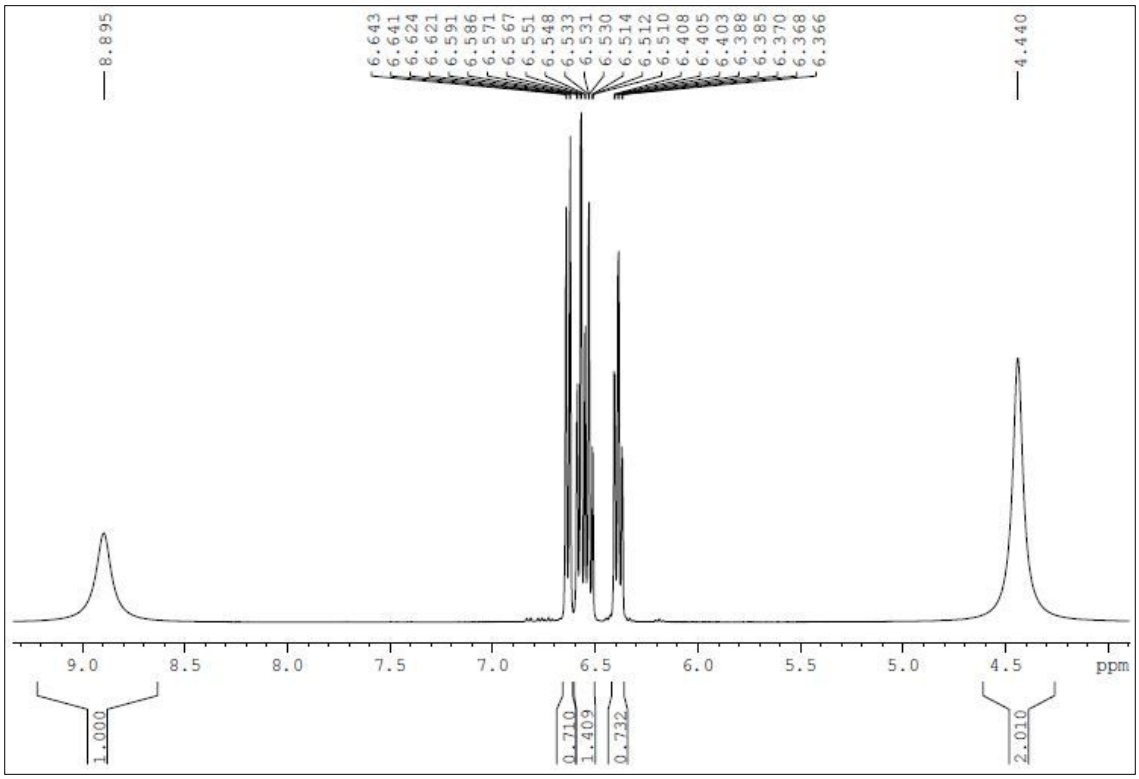


Figure S11. ^{1}H NMR spectrum of *o*-aminophenol

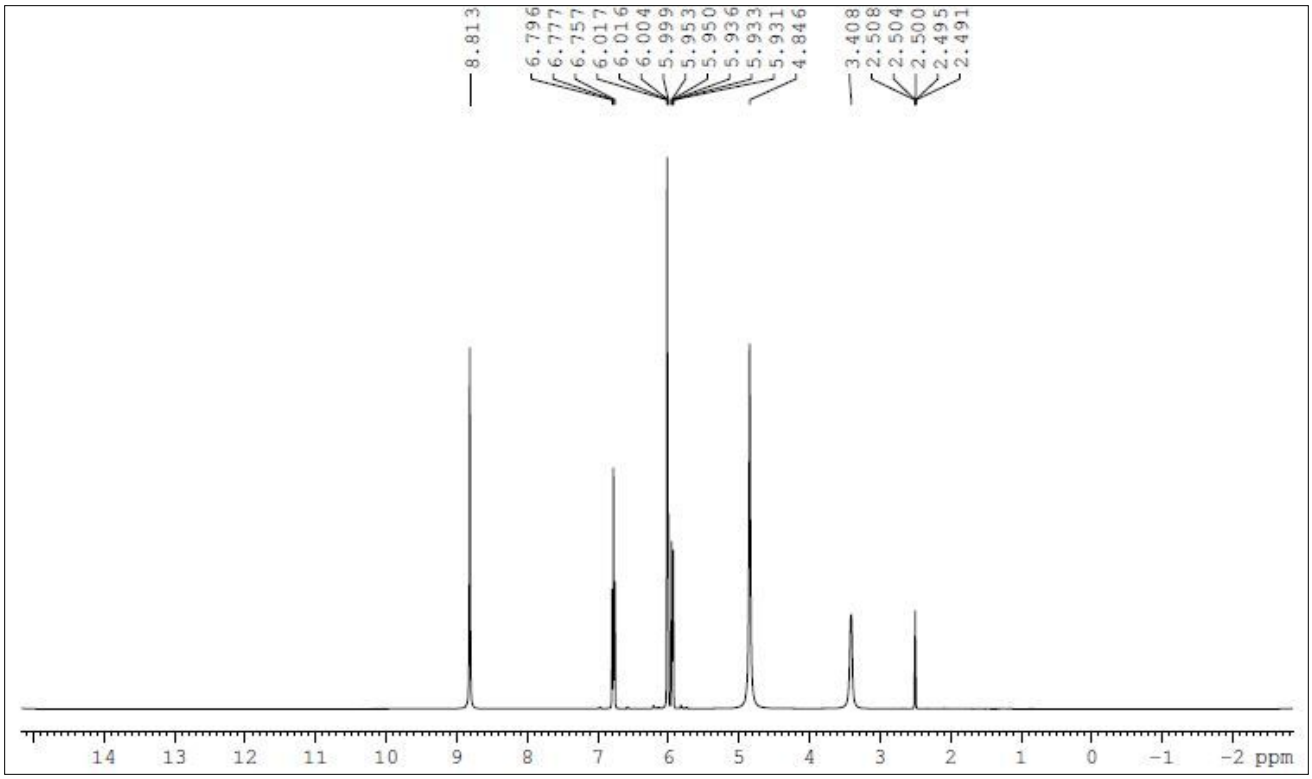


Figure S12. ^{1}H NMR spectrum of *m*-aminophenol

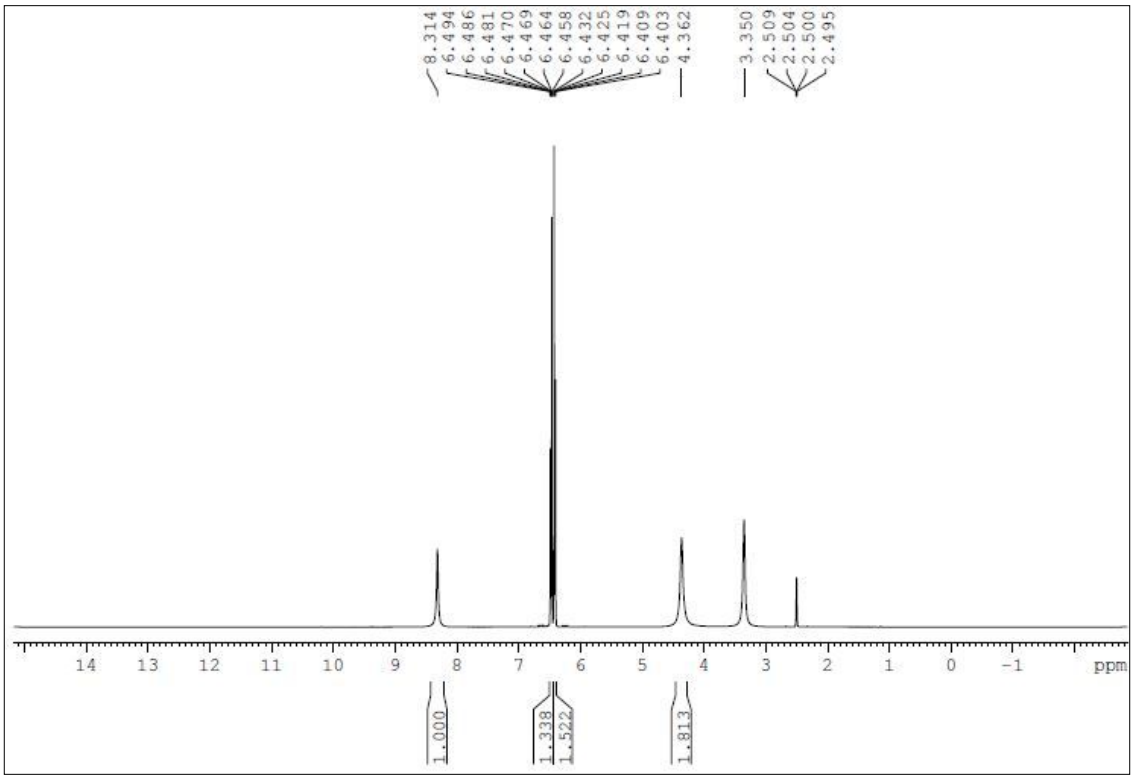


Figure S13. ^{1}H NMR spectrum of *p*-aminophenol

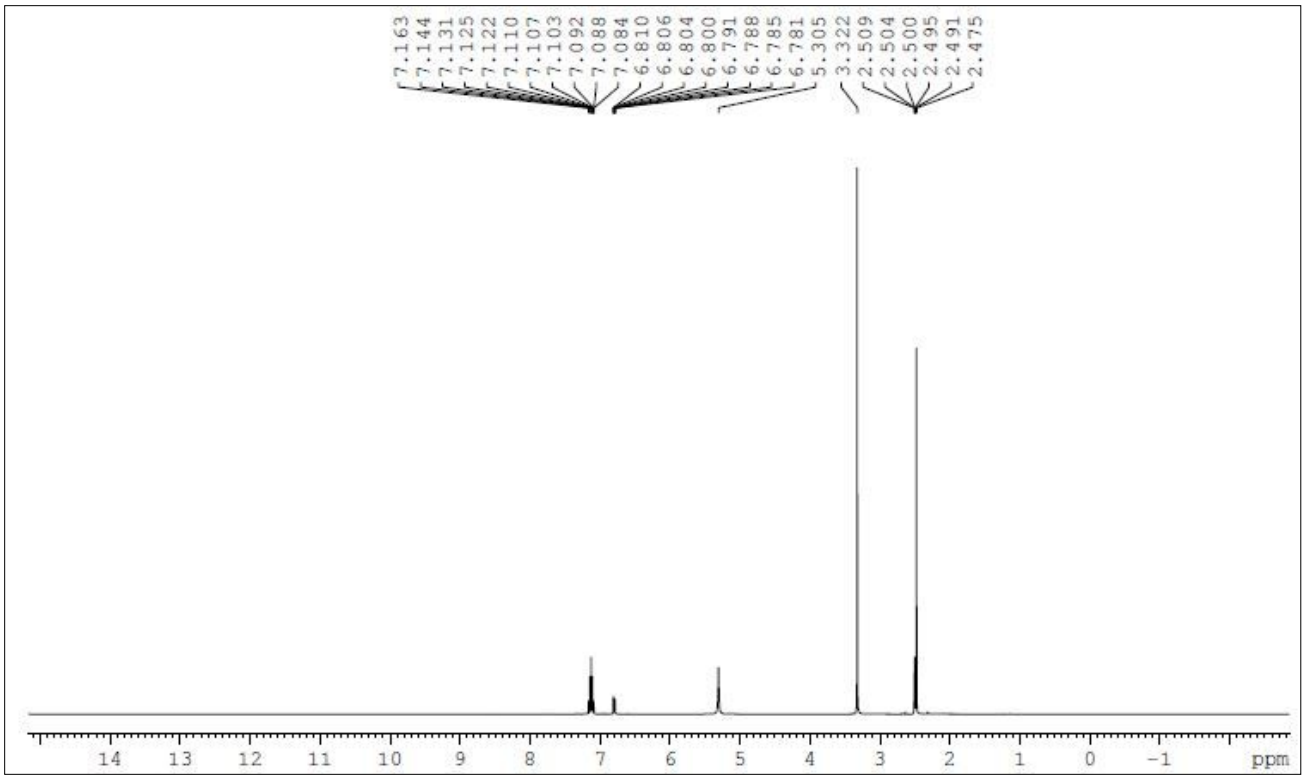


Figure S14. ^{1}H NMR spectrum of *m*-aminoacetophenone

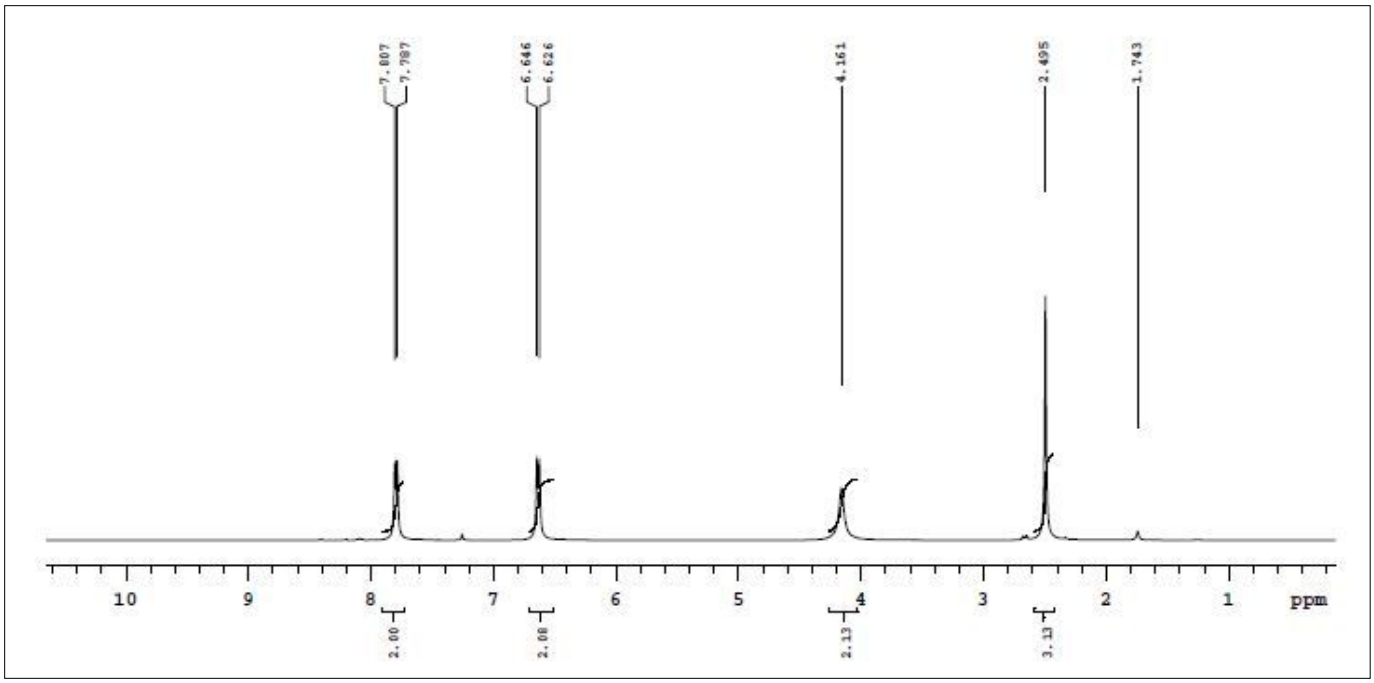


Figure S15. ^{1}H NMR spectrum of *p*-aminoacetophenone

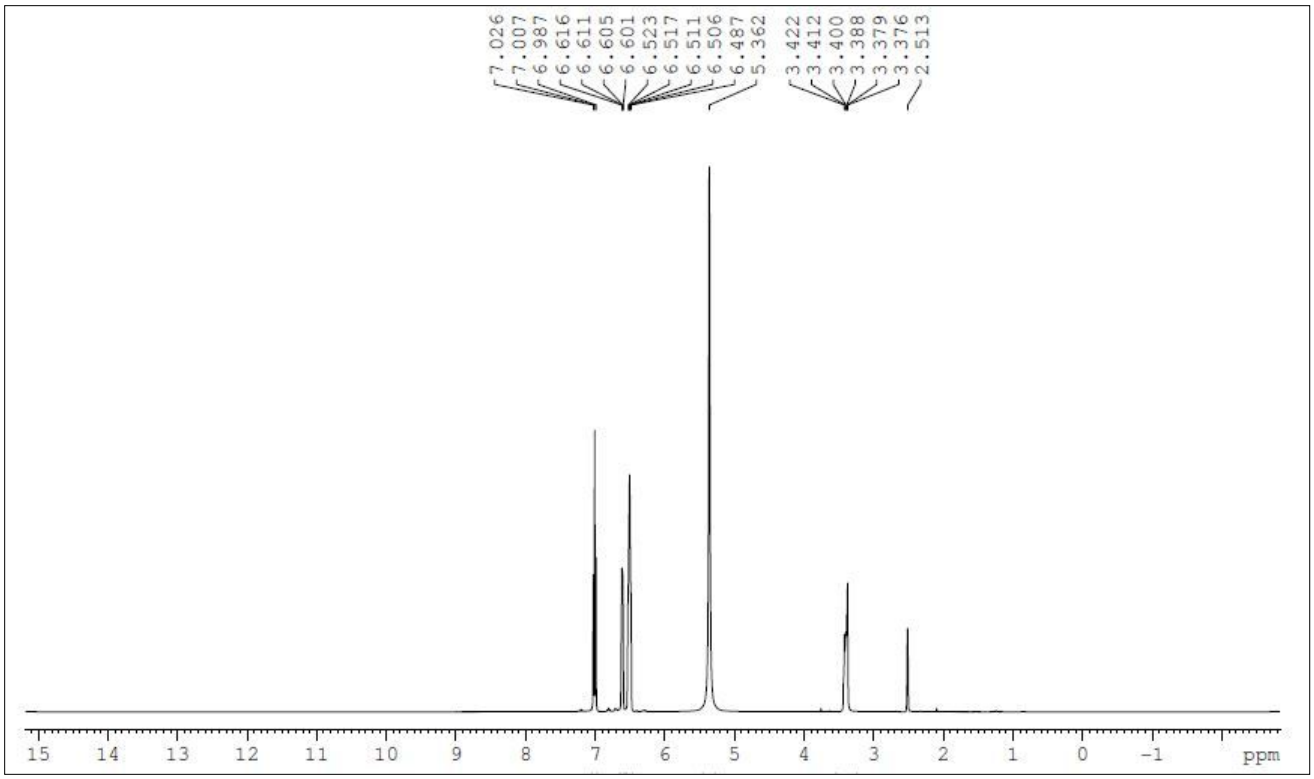


Figure S16. ^{1}H NMR spectrum of *m*-chloroaniline

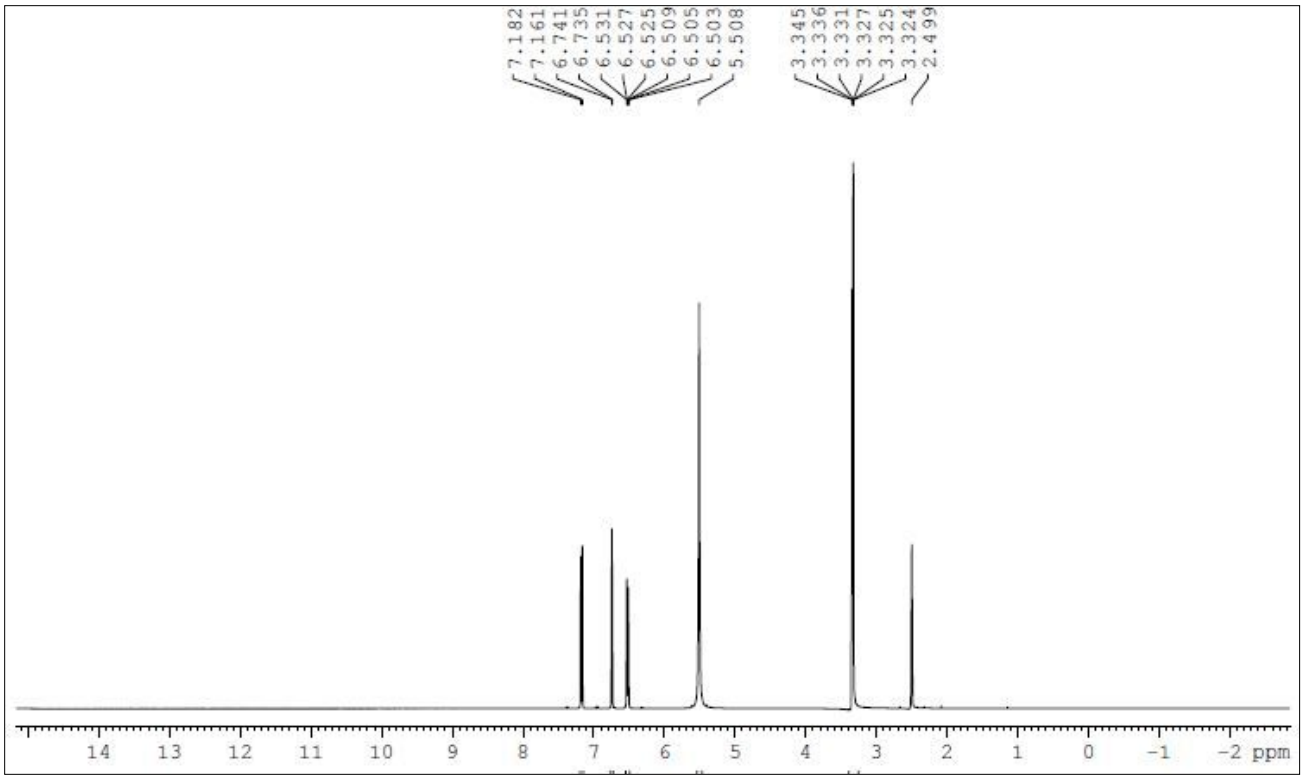


Figure S17. ^{1}H NMR spectrum of 3,4-dichloroaniline

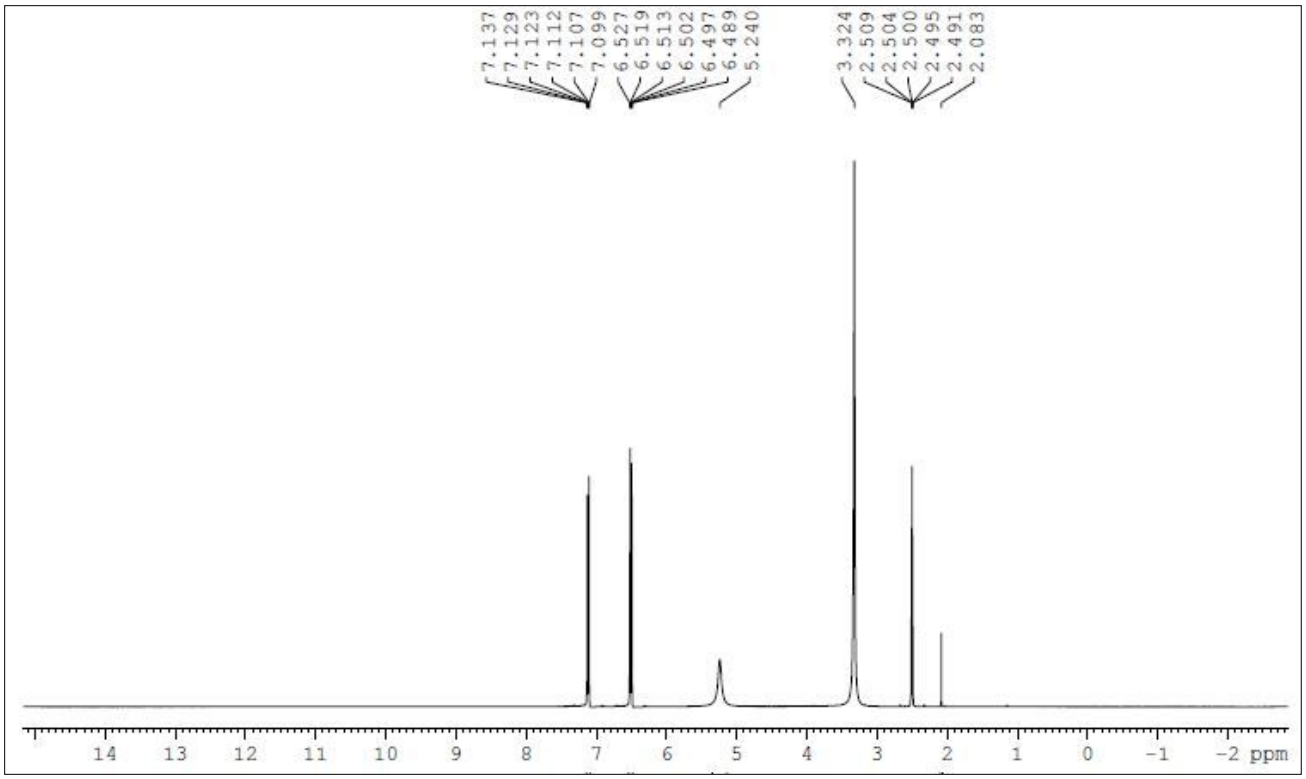


Figure S18. ^{1}H NMR spectrum of *p*-bromoaniline

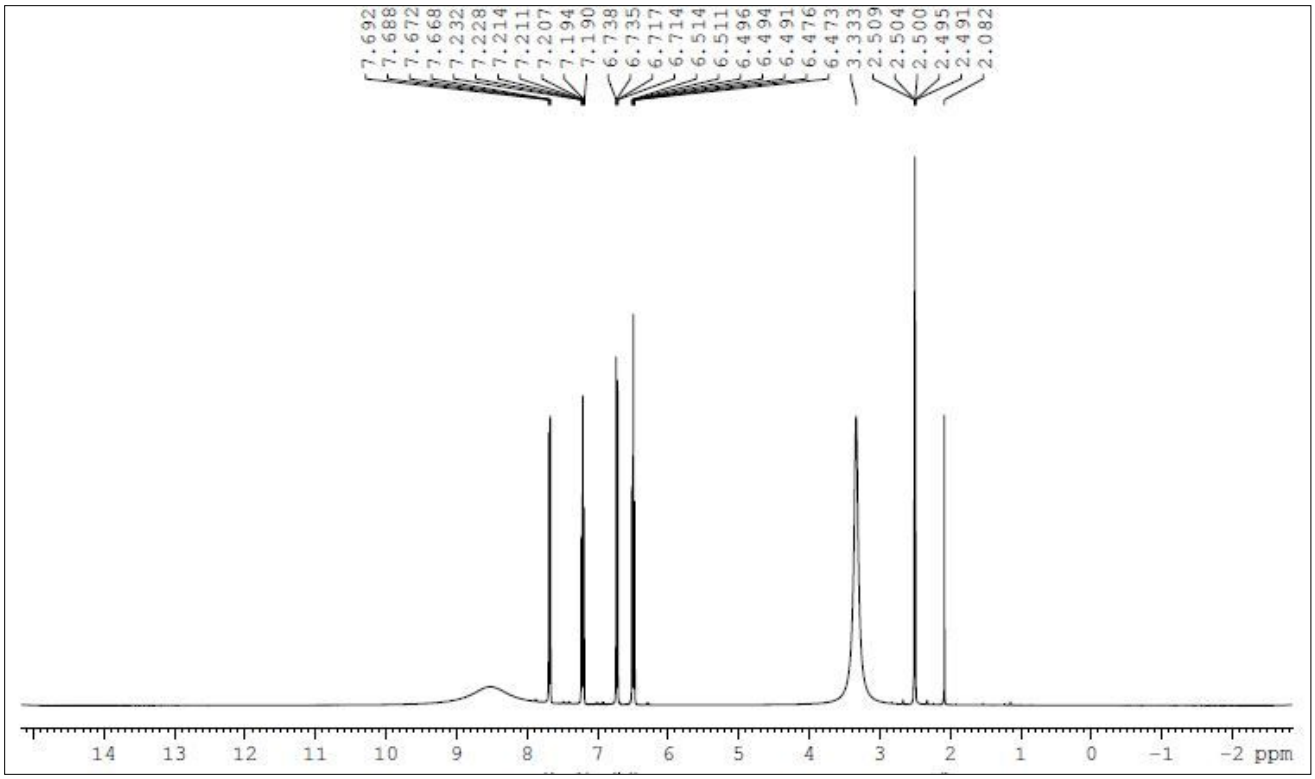


Figure S19. ^{1}H NMR spectrum of *o*-amino benzoic acid

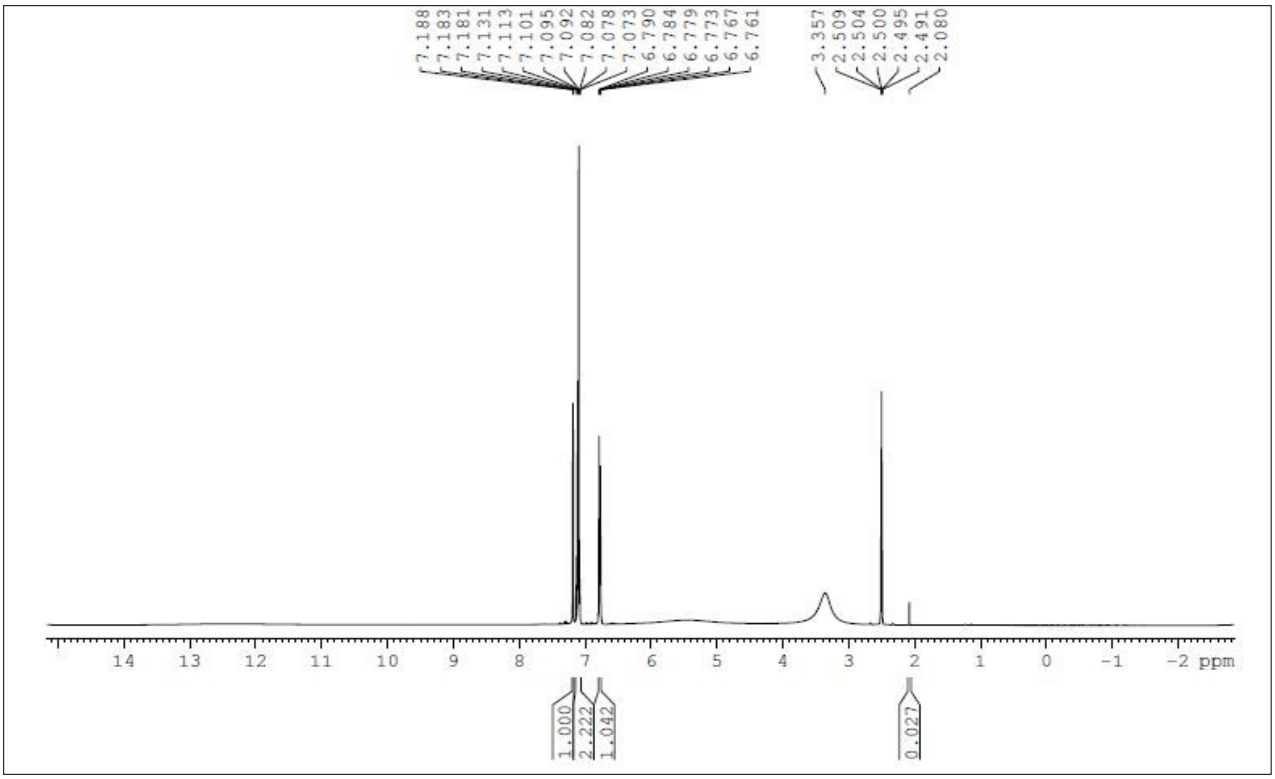


Figure S20. ^{1}H NMR spectrum of *m*-amino benzoic acid

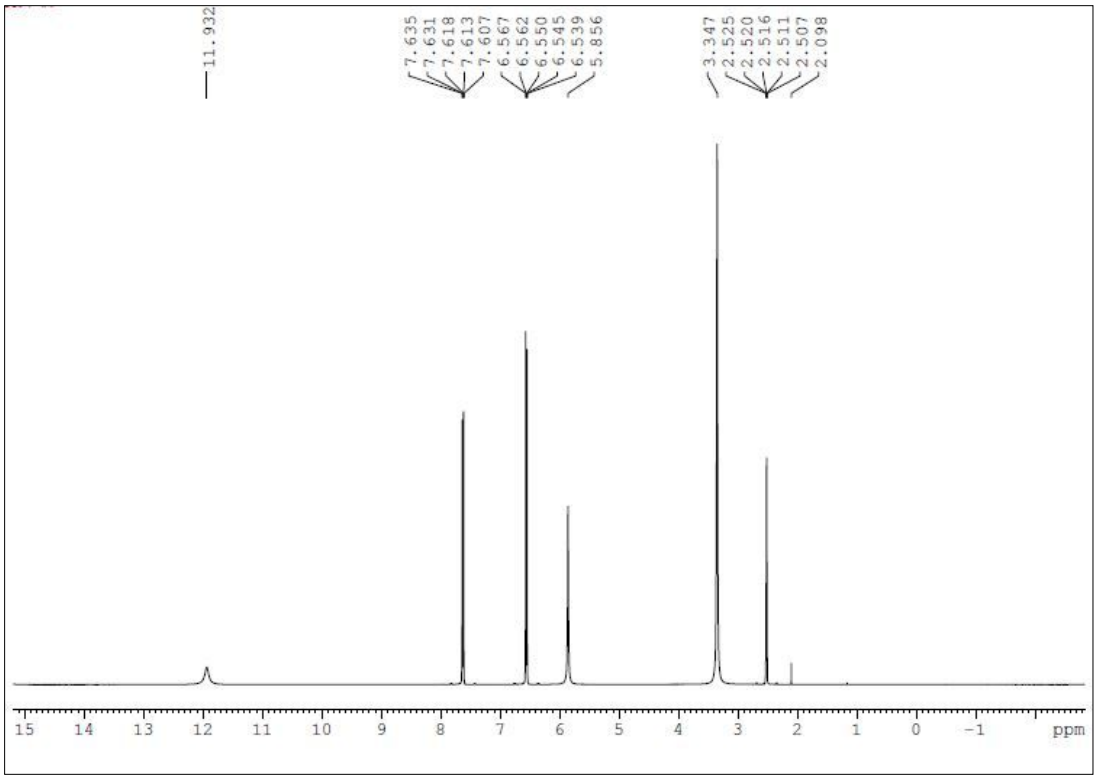


Figure S21. ^{1}H NMR spectrum of *p*-amino benzoic acid

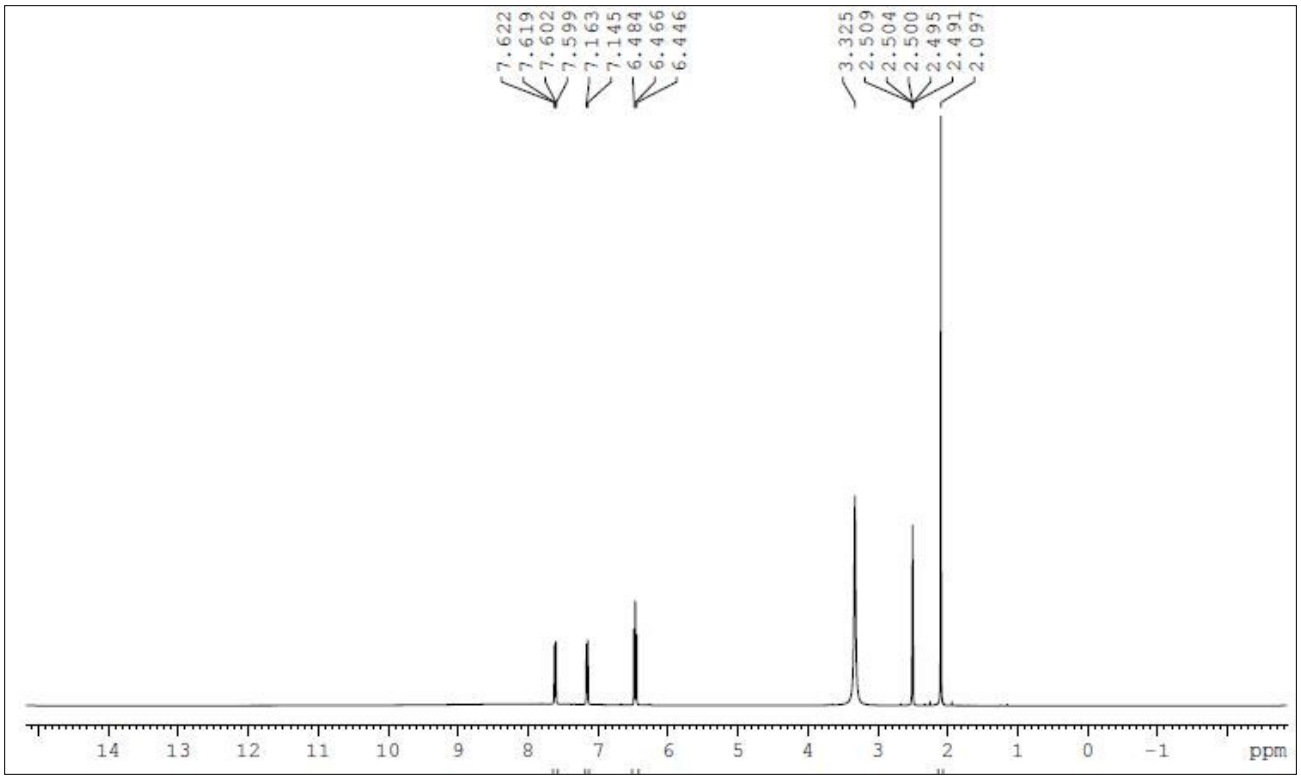


Figure S22. ^{1}H NMR spectrum of 3-methoxy-*o*-aminobenzoic acid