Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Practical photocatalytic and sonophotocatalytic reduction of nitroarenes in water under blue LED irradiation using β-CD modified TiO_2 as green nest photocatalyst

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Experimental

Materials

Nitro compounds, Sodium sulfide, Sodium sulfite, Thiourea, Oxalic acid, and Ammonium formate were purchased from Merck Co, Beta-cyclodextrin and acetic anhydride were purchased from Sigma and Degussa P25 from Degussa AG-Germany. All other reagents were analytical grade and used as received.

General procedure for photocatalytic reduction of nitro compounds

In a 25 ml round bottom Pyrex flask, 1.2 mmol Nitro compounds, 0.15 g of β-CD, 7.5 mg of TiO_2-P25, and 0.86 g (3.6 mmol) of $Na_2S.9H_2O$ as a sacrificial compound was dissolved in 10 ml of deionized water. The reaction mixture was deoxygenated by blowing argon gas (10 min) and sealed with a septum, and it was irradiated with sunlight and a blue LED separately. Reaction progress and product production efficiency were measured using Thin-layer chromatography (TLC) and Gas Chromatography. It should be noted that to check the reaction progress organic material was extracted with ethyl acetate then the organic phase was dried using anhydrous sodium sulfate (Table 2).

General procedure for sonophotocatalytic reduction of nitro compounds

In a 25 ml round bottom Pyrex flask, 1.2 mmol Nitro compounds, 0.15 g of β-CD, 7.5 mg of TiO_2-P25, and 0.86 g (3.6 mmol) of $Na_2S.9H_2O$ as a sacrificial compound was dissolved in 10 ml of water. The reaction mixture was deoxygenated by blowing argon gas (10 min), sealed with a septum, and then placed in an ultrasonic bath and then, the flask was irradiated with a blue LED for 2 hours. Reaction progress and product production efficiency were measured using Thin-layer chromatography (TLC) and Gas Chromatography. It should be noted that to check the reaction progress organic material was extracted with ethyl acetate then the organic phase was dried using anhydrous sodium sulfate (Table 2).

General procedure for one-pot *N*-acetylation of the nitro compounds

In a round, bottom Pyrex flask with a volume of 25 ml, 1.2 mmol Nitro compounds, and 3.6 mmol acetic android weight was added to the reaction flask. Then 0.15 g of β-CD, 7.5 mg of commercial TiO_2 (TiO_2-P25), and 0.86 g (3.6 mmol) of $Na_2S.9H_2O$ as a sacrificial compound were dissolved in 10 ml of water. The reaction mixture was deoxygenated by blowing argon gas (10 min) and sealed with a septum. Then the flask was irradiated under stirring with a blue LED for 12 hours. After completion of the reaction, organic material was extracted with ethyl acetate then the organic phase was dried using anhydrous sodium sulfate. Reaction progress and product production efficiency were measured using Thin-layer chromatography (TLC) and Gas Chromatography (Table 3).

Table S1. Photoreduction of nitrobenzene using β-CD-TiO_2 in present various sacrificial additives.

Entry	Additive	Yield (%)[a]
1	-	0
2	Thiourea	5
3	Oxalic acid	15
4	Ammonium formate	10
5	Sodium sulfite	8
6	sodium sulfide	98

[a]GC yield, Reaction condition: photocatalyst 7.5 mg; nitro compound (1.2 mmol); irradiation with blue LED (10 W) at 5hr.

Table S2. Optimization of acetylating agent amounts

Entry	Acetic anhydride	Yield (%)	Source of light
1	1.2	11	Blue LED
2	2.4	56	Blue LED
3	3.6	97	Blue LED
4	3.6	0	Sun light

Reaction condition: TiO_2 -P25 (7.5 mg); nitro compound (1.2 mmol); Na_2S (3.6 mmol); β-CD (15 mg).

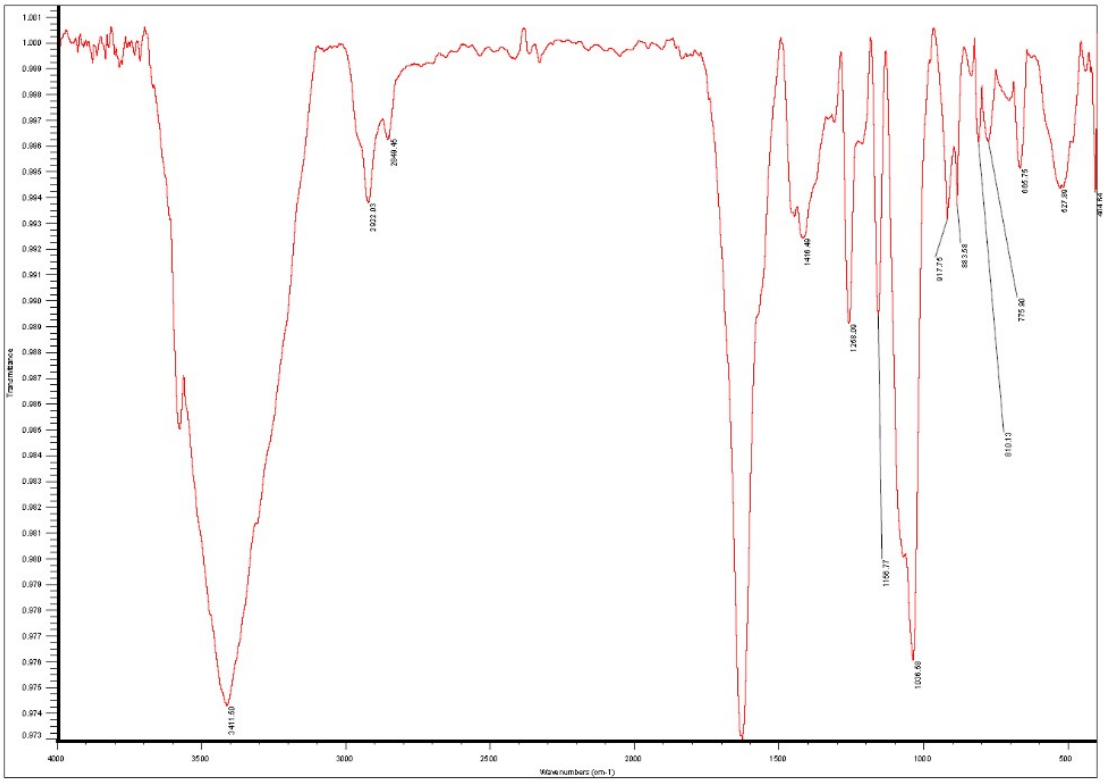

Fig S1: FTIR spectrum of TiO_2-P25

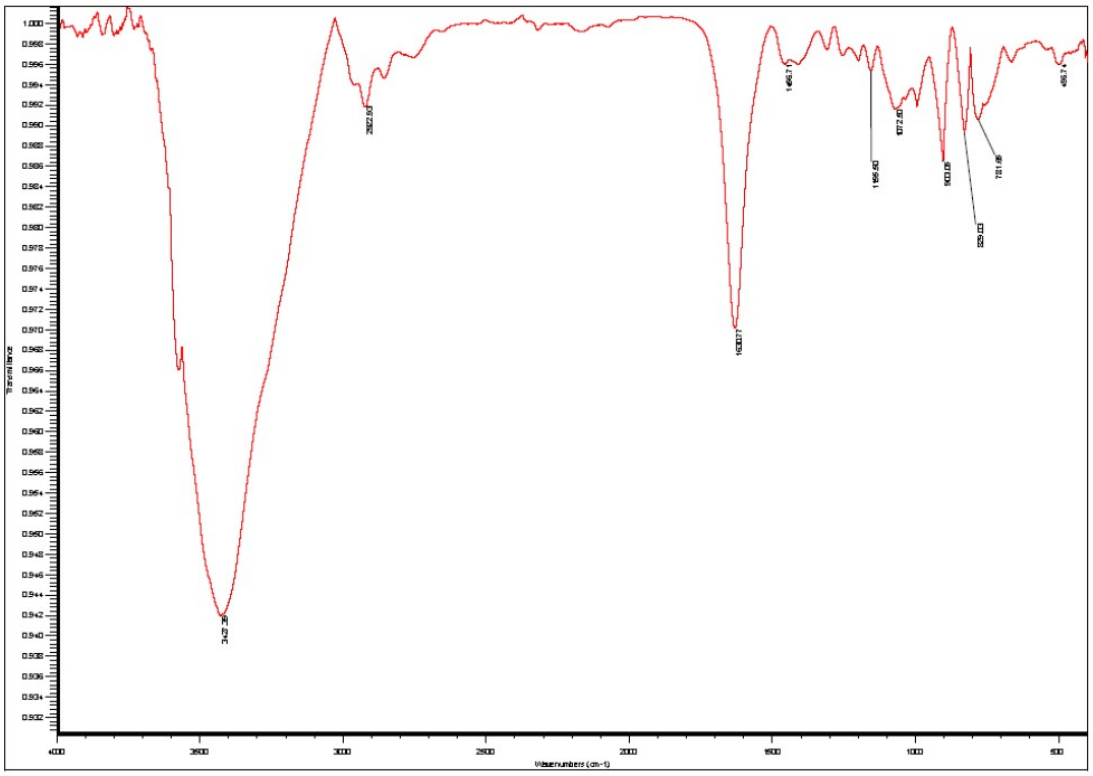

Fig S2: FTIR spectrum of β-CD-TiO_2

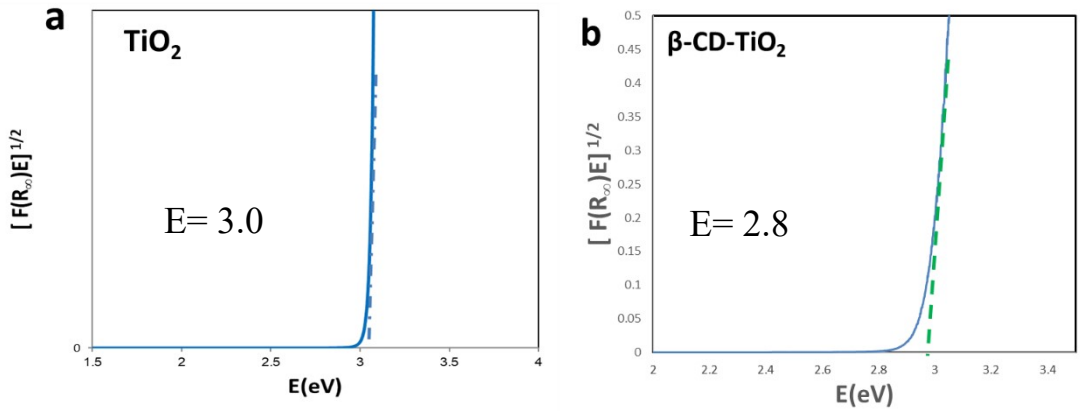

Fig S3: Plot of the transformed Kubelka–Munk function versus the energy of light absorbed by the TiO_2 (a) and (b) β-CD-TiO

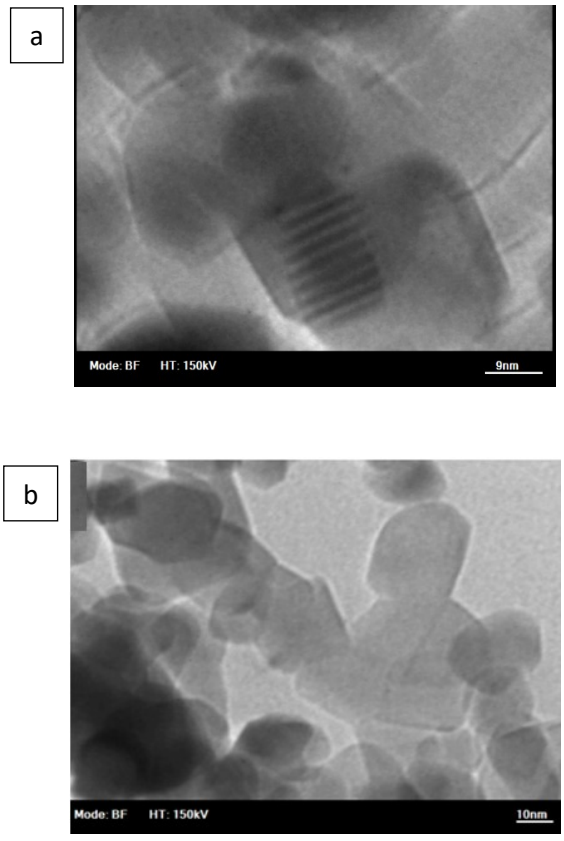

Fig S4: TEM images of *β*-CD-TiO_2 (a) and TiO_2 P25 (b)

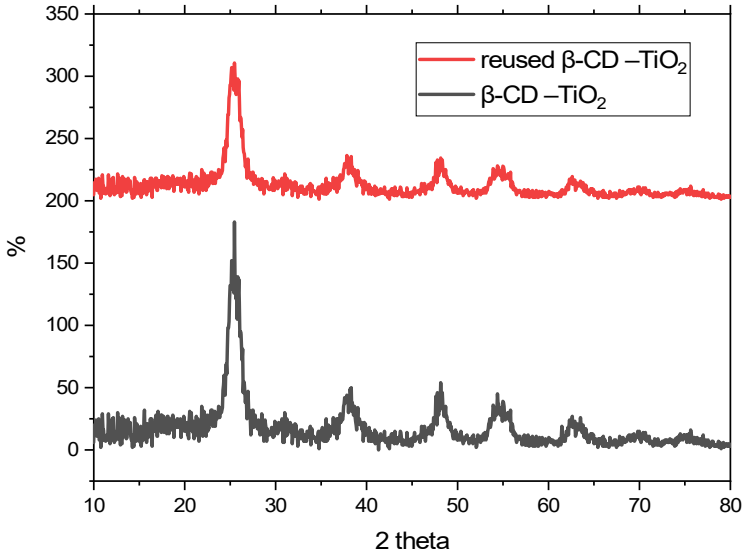

Fig S5: XRD β-CD-TiO_2 and reused β-CD-TiO_2

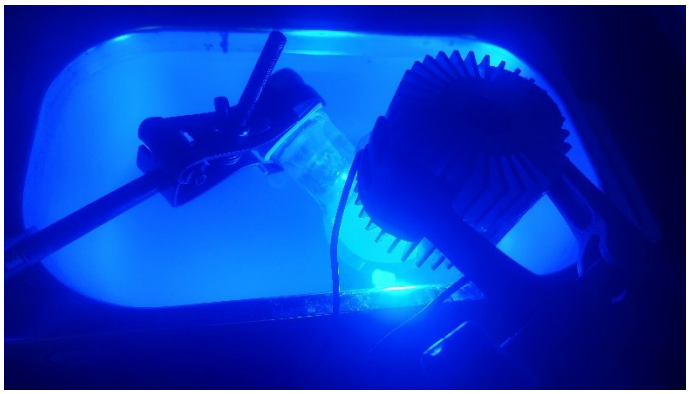

Figure S6: Schematic of Sonophoto reactor

Characterization of Products:

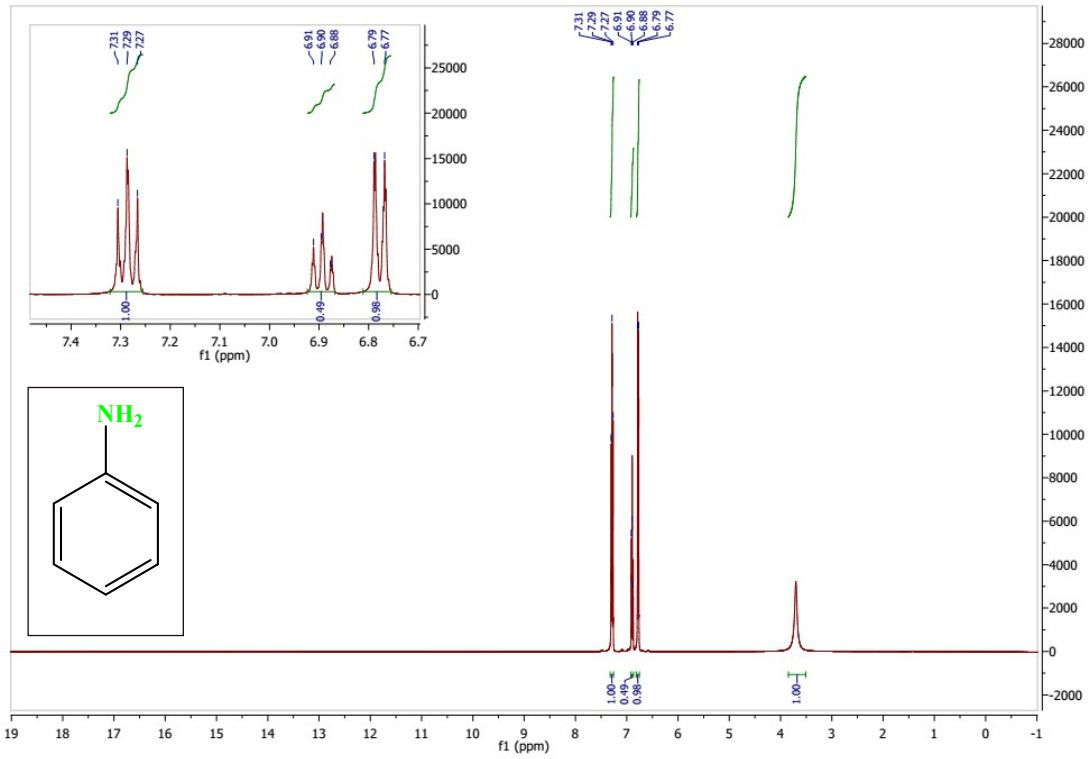

Fig S7: ^{1}H-NMR (400 MHz; $CDCl_3$) of Aniline

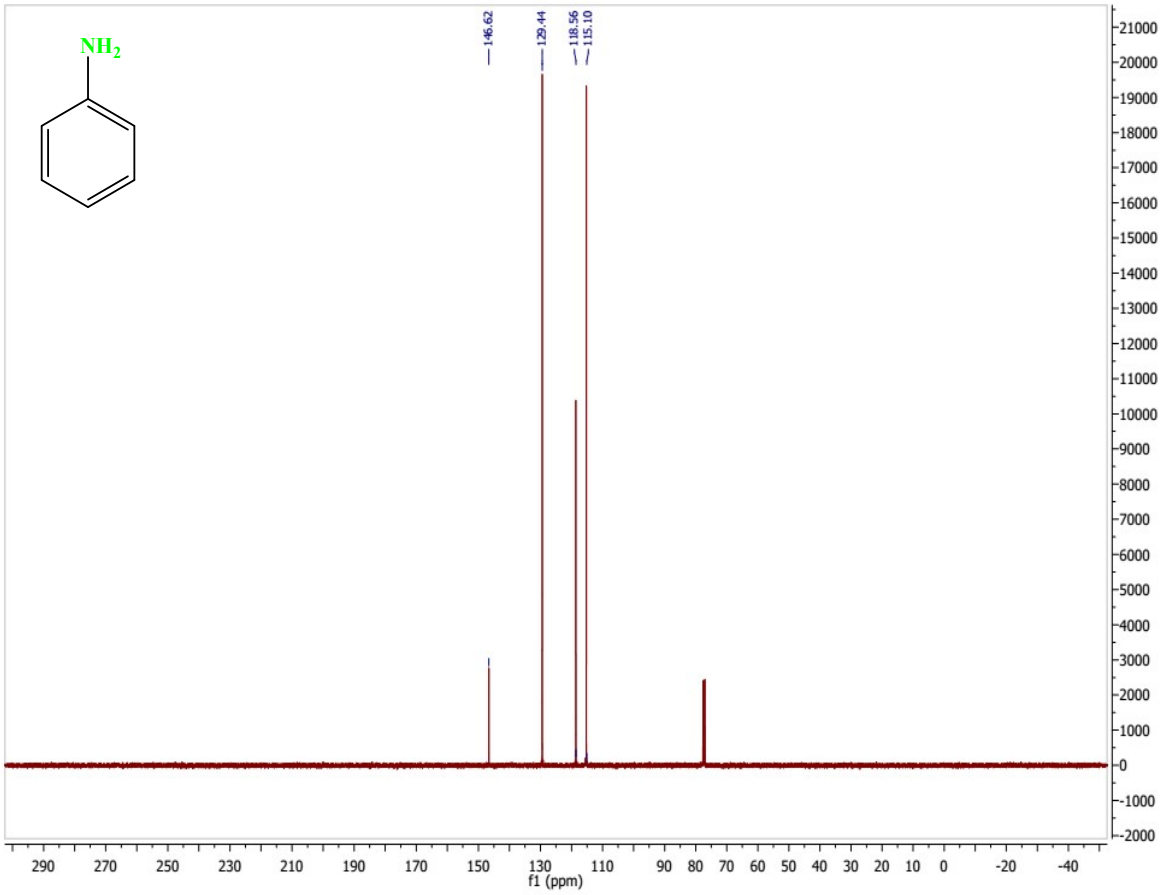

Fig S8: ^{13}C NMR (100 MHz; $CDCl_3$) of Aniline

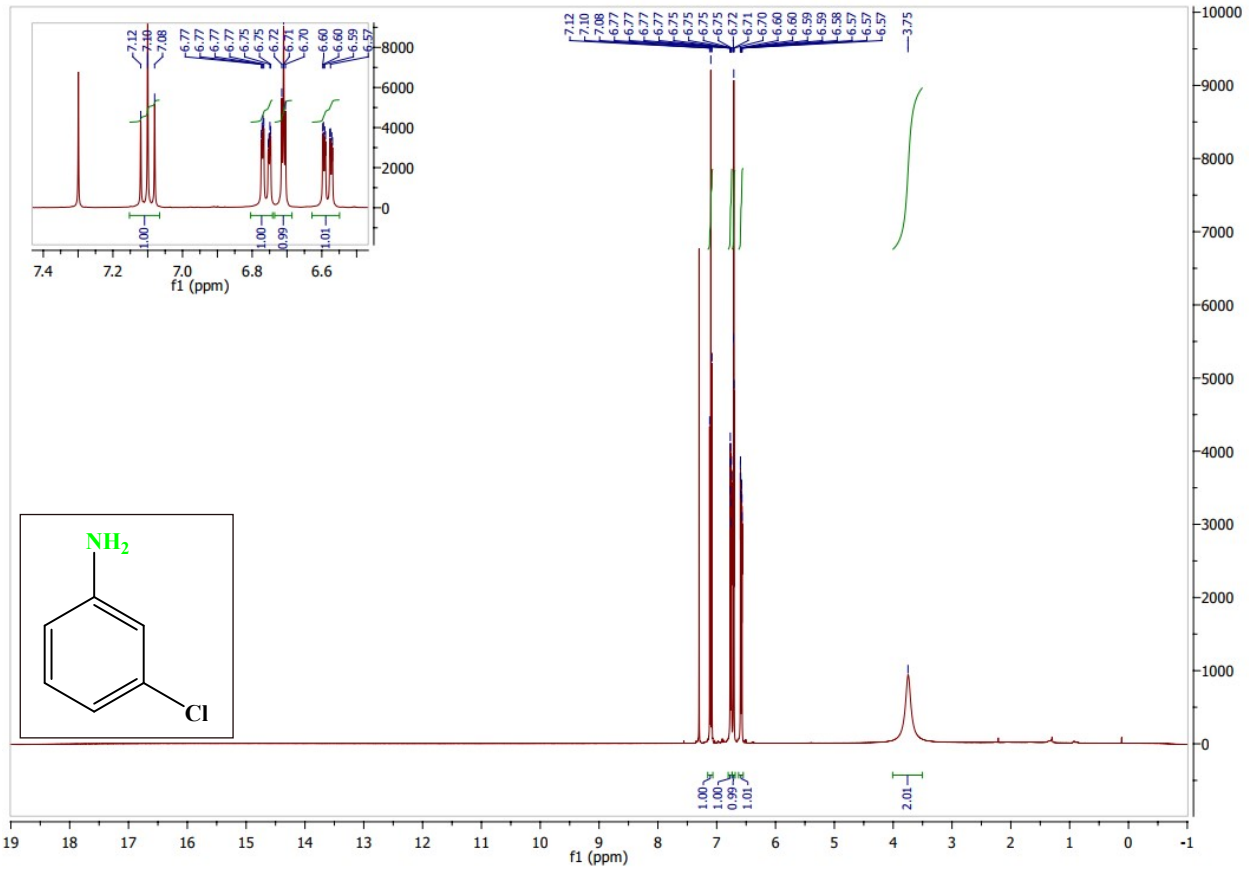

Fig S9:[1]H-NMR (400 MHz; $CDCl_3$) of 3-Chloroaniline

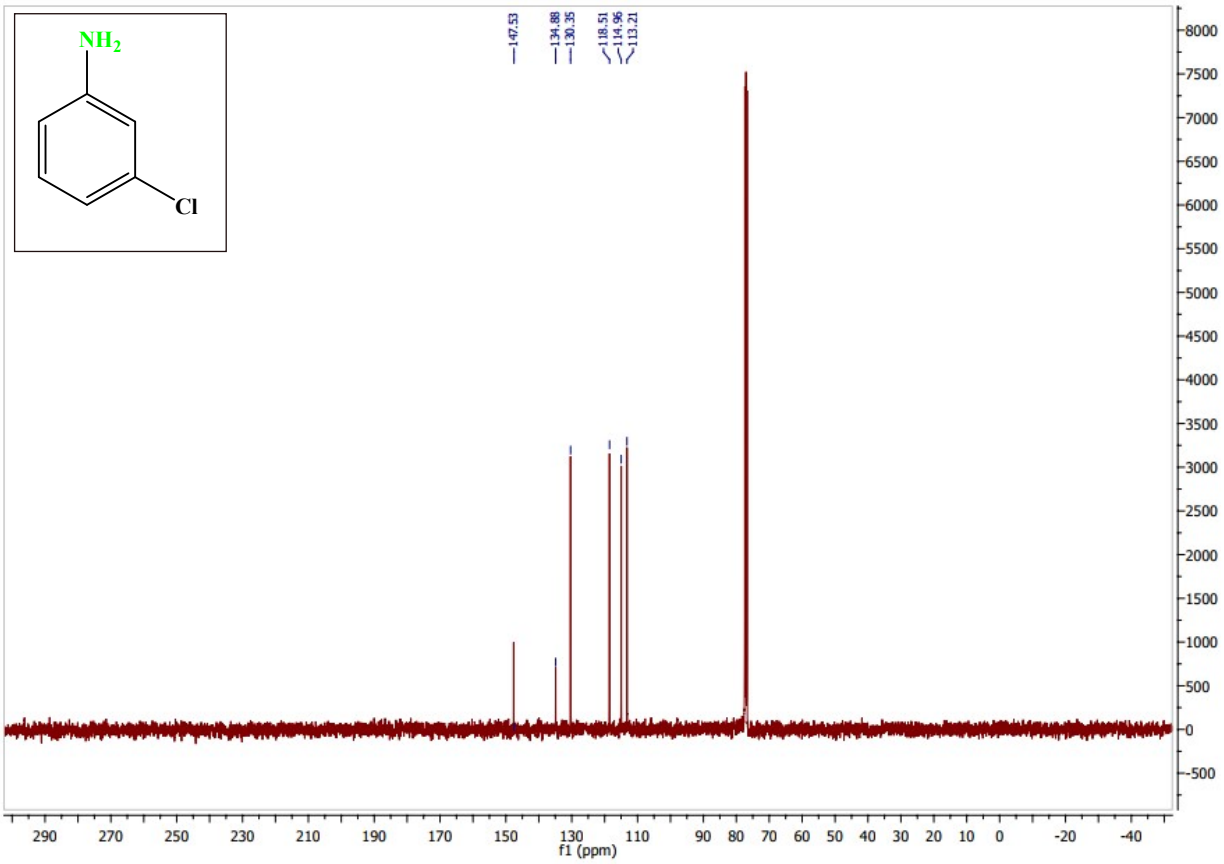

Fig S10: ^{13}C NMR (100 MHz; $CDCl_3$) of 3-Chloroaniline

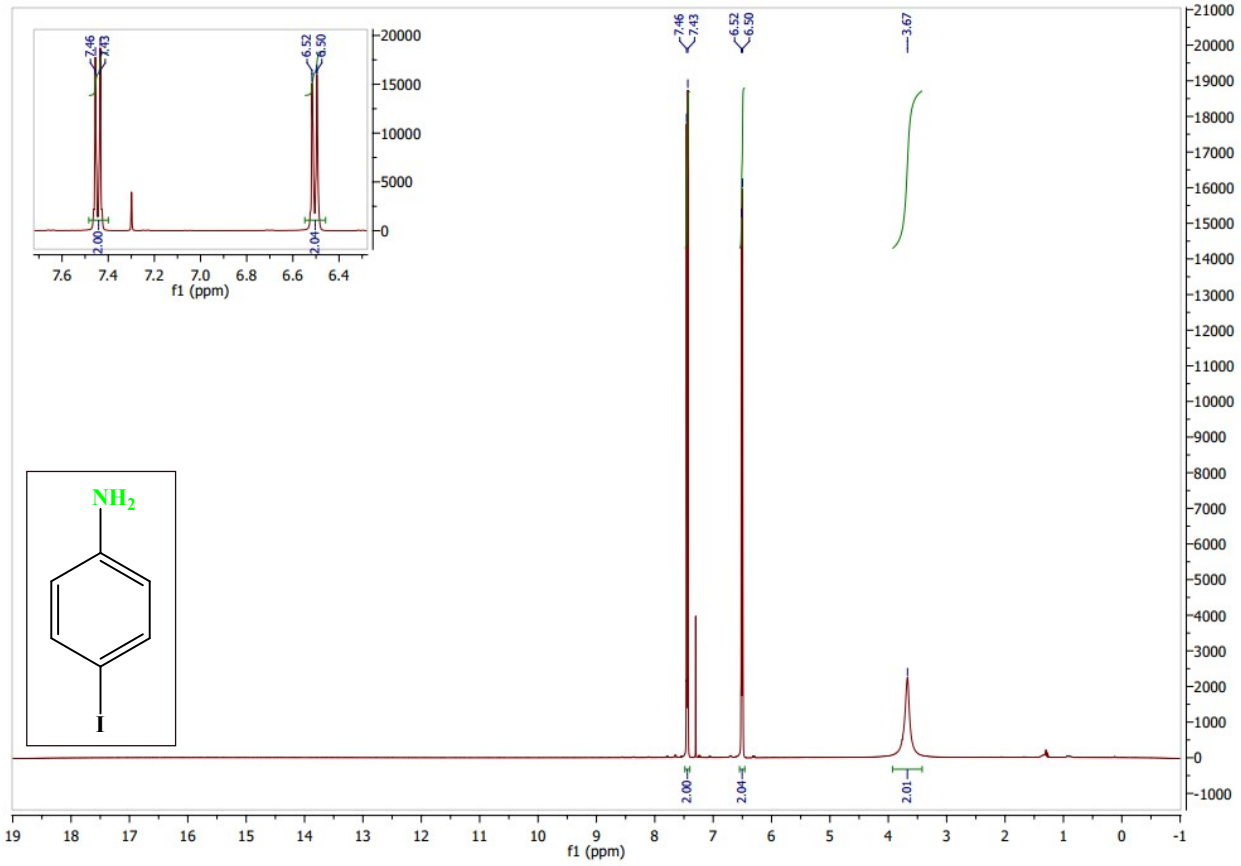

Fig S11:^{1}H-NMR (400 MHz; $CDCl_3$) of 4-Iodoaniline

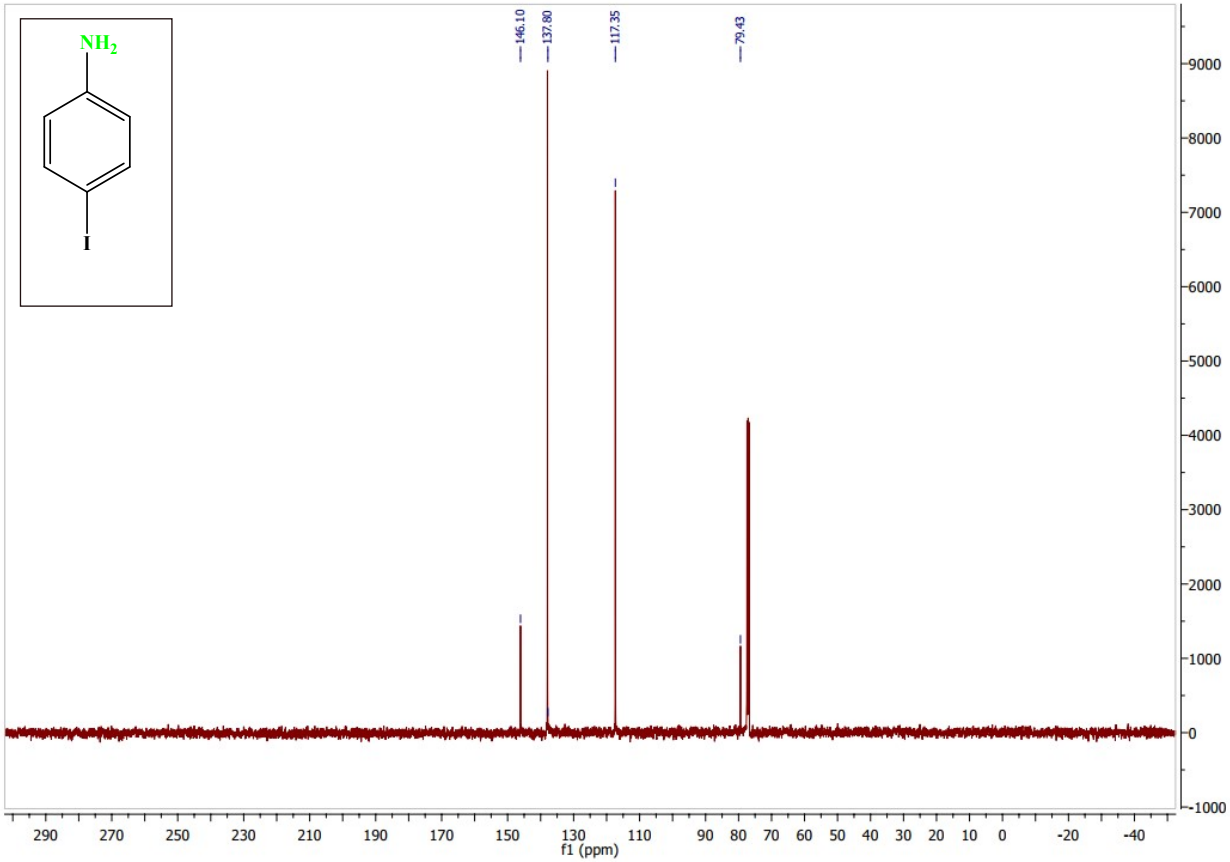

Fig S12: ^{13}C NMR (100 MHz; $CDCl_3$) of 4-Iodoaniline

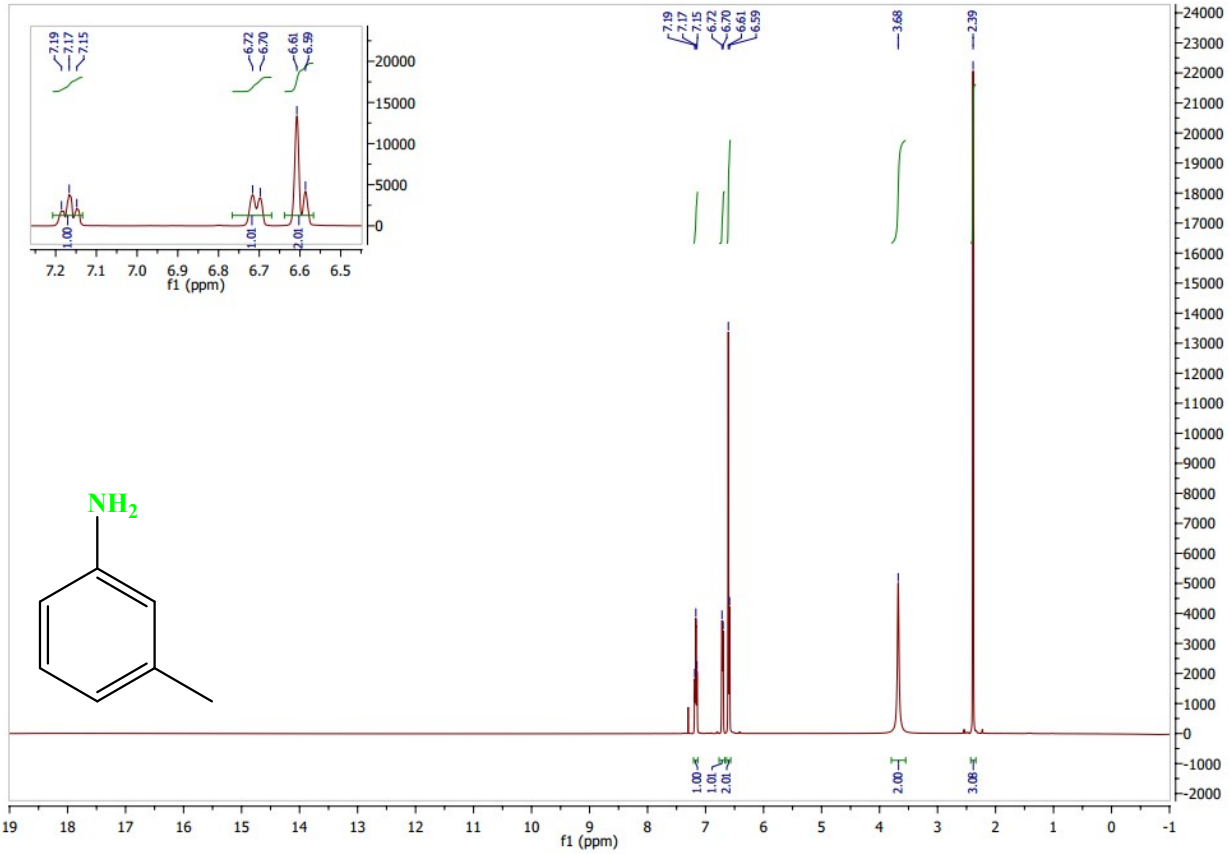

Fig S13:^{1}H-NMR (400 MHz; $CDCl_3$) of m-Toluidine

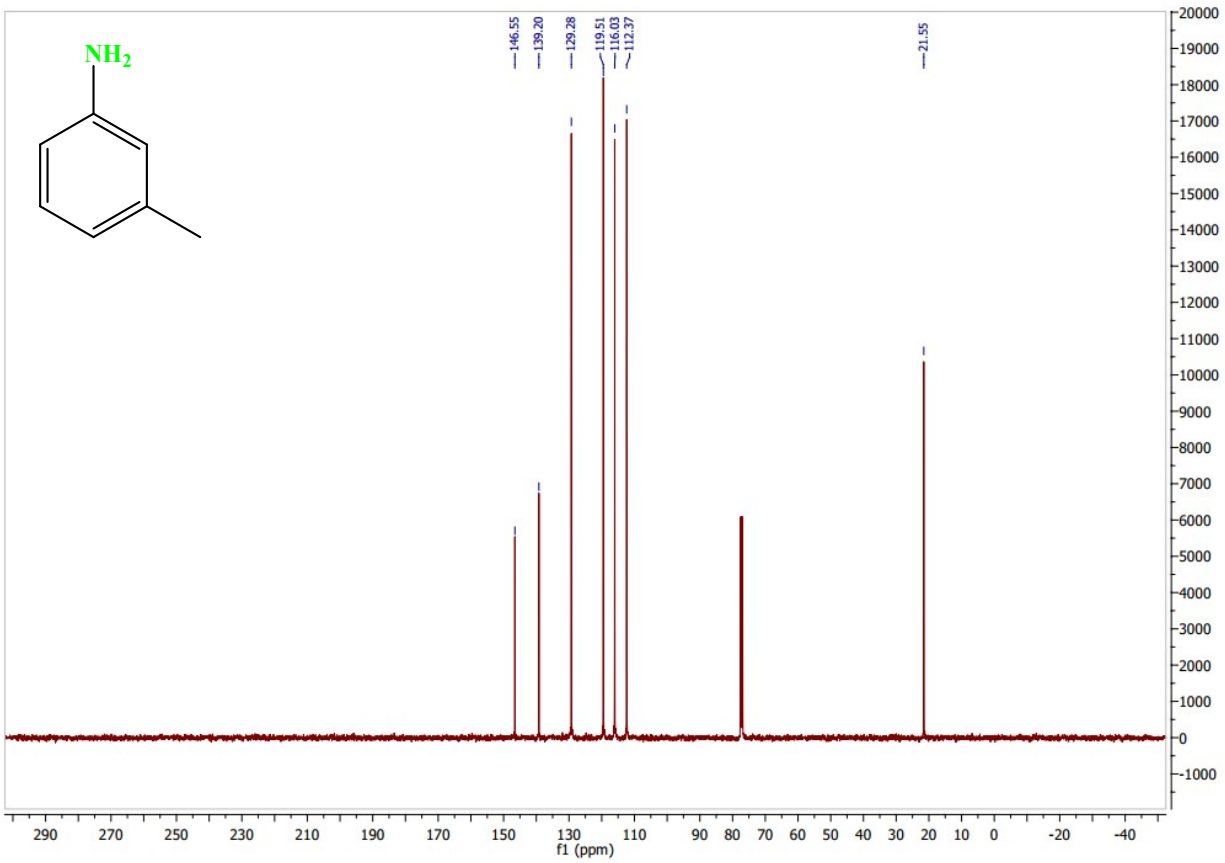

Fig S14: ^{13}C NMR (100 MHz; $CDCl_3$) of m-Toluidine

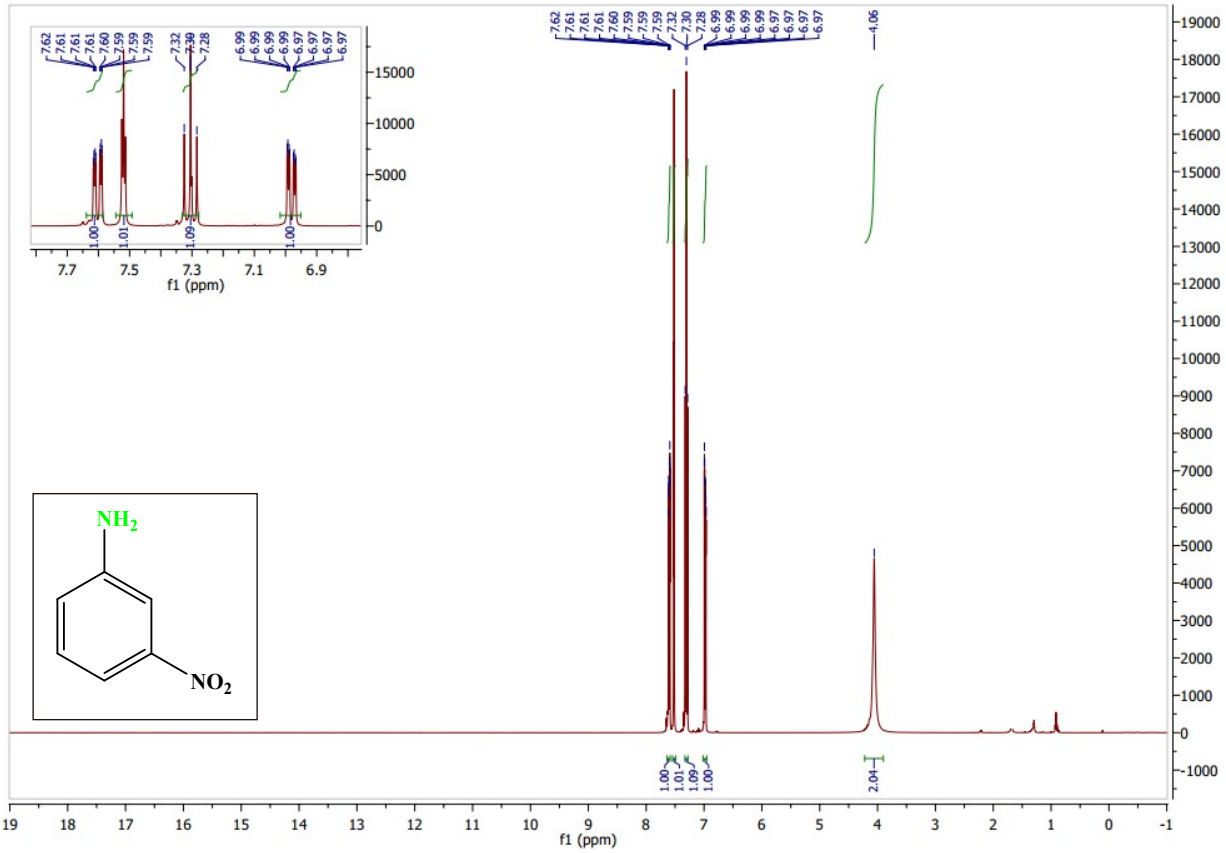

Fig S15:^{1}H-NMR (400 MHz; $CDCl_3$) of 3-Nitroaniline

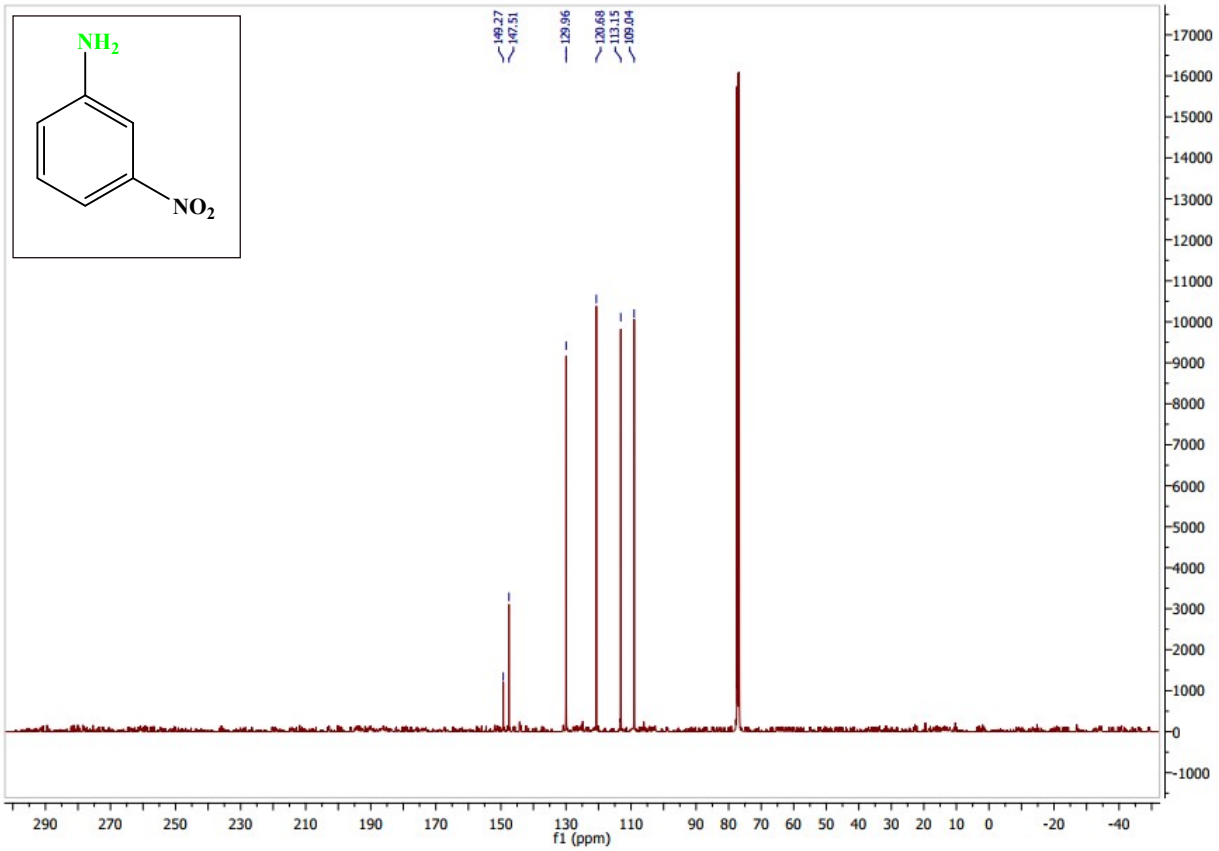

Fig S16:^{13}C-NMR (100 MHz; $CDCl_3$) of 3-Nitroaniline

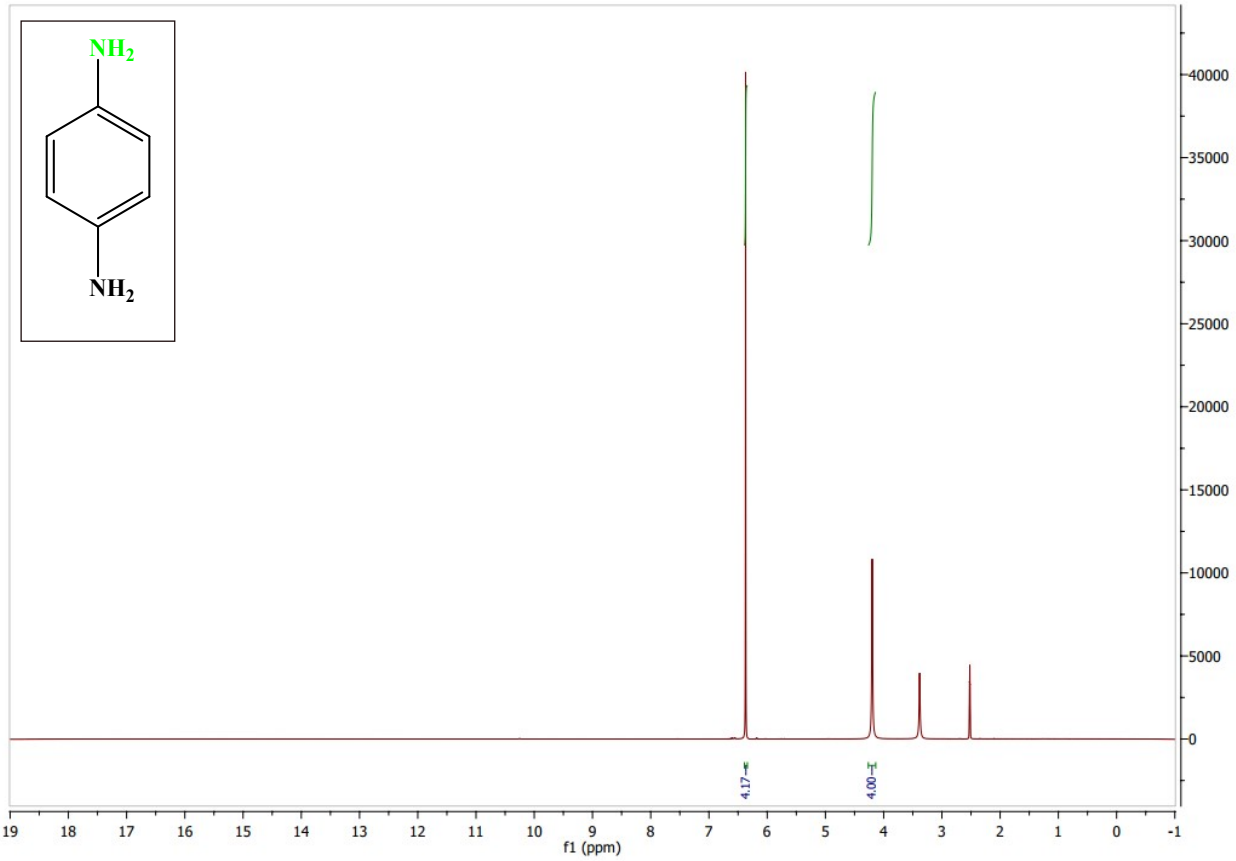

Fig S17:[1]H-NMR (400 MHz; DMSO) of 1,4-Diaminobenzene

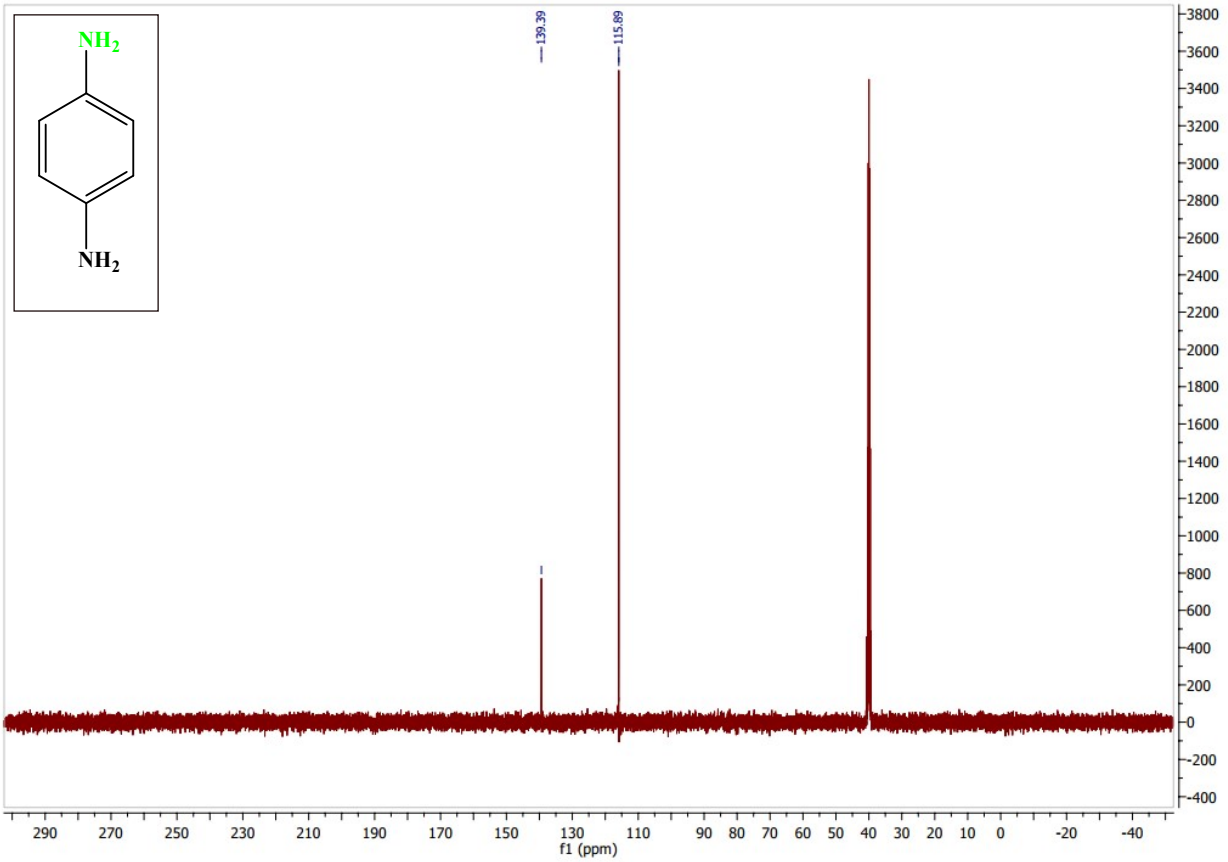

Fig S18:^{13}C-NMR (100 MHz; DMSO) of 1,4-Diaminobenzene

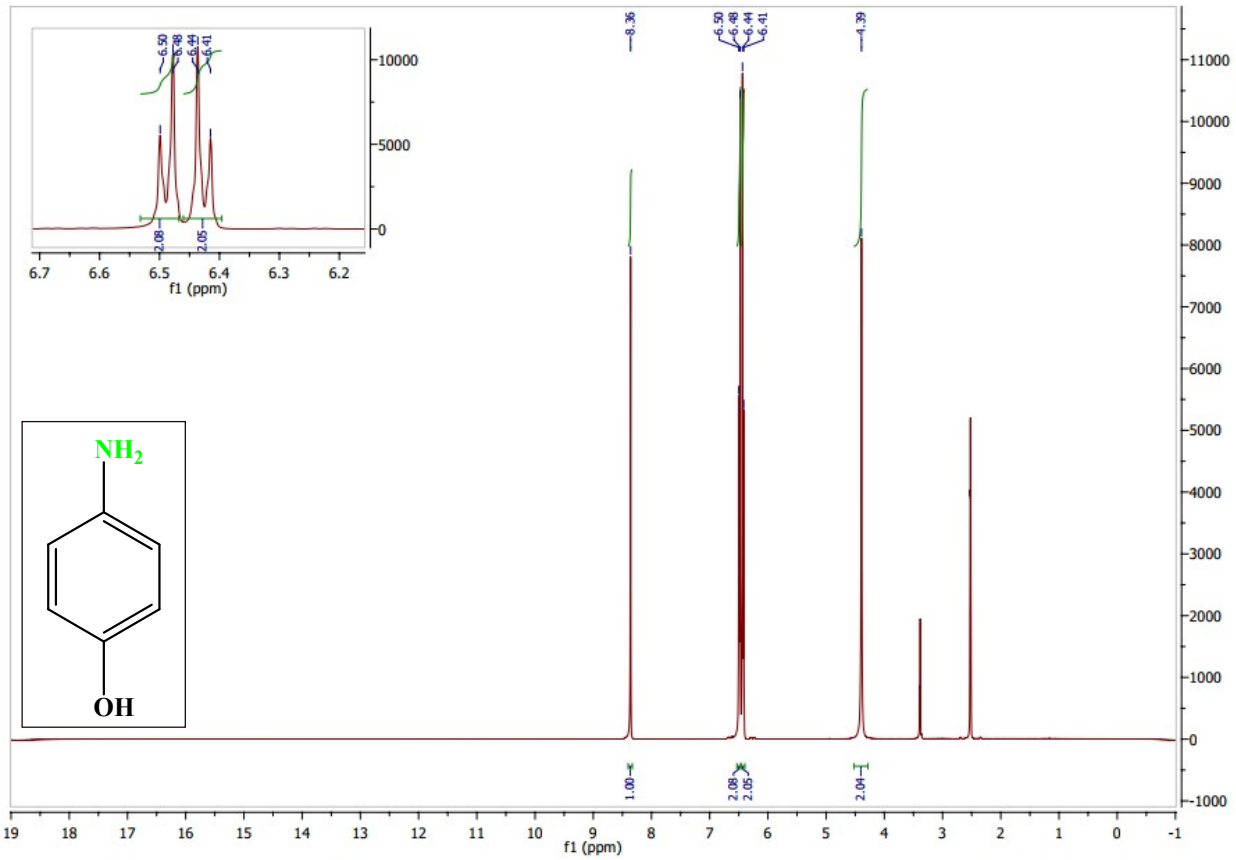

Fig S19:[1]H-NMR (400 MHz; DMSO) of 4-Aminophenol

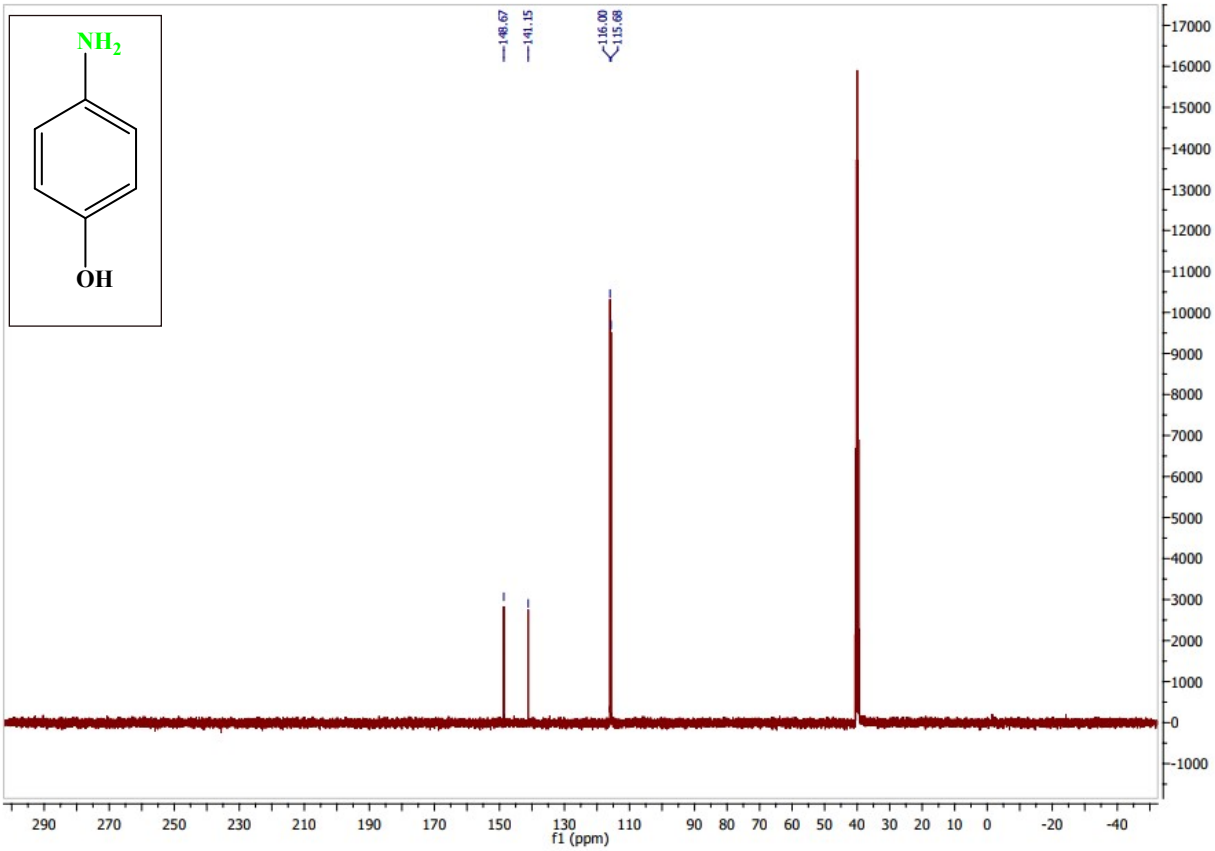

Fig S20:^{13}C-NMR (100 MHz; DMSO) of 4-Aminophenol

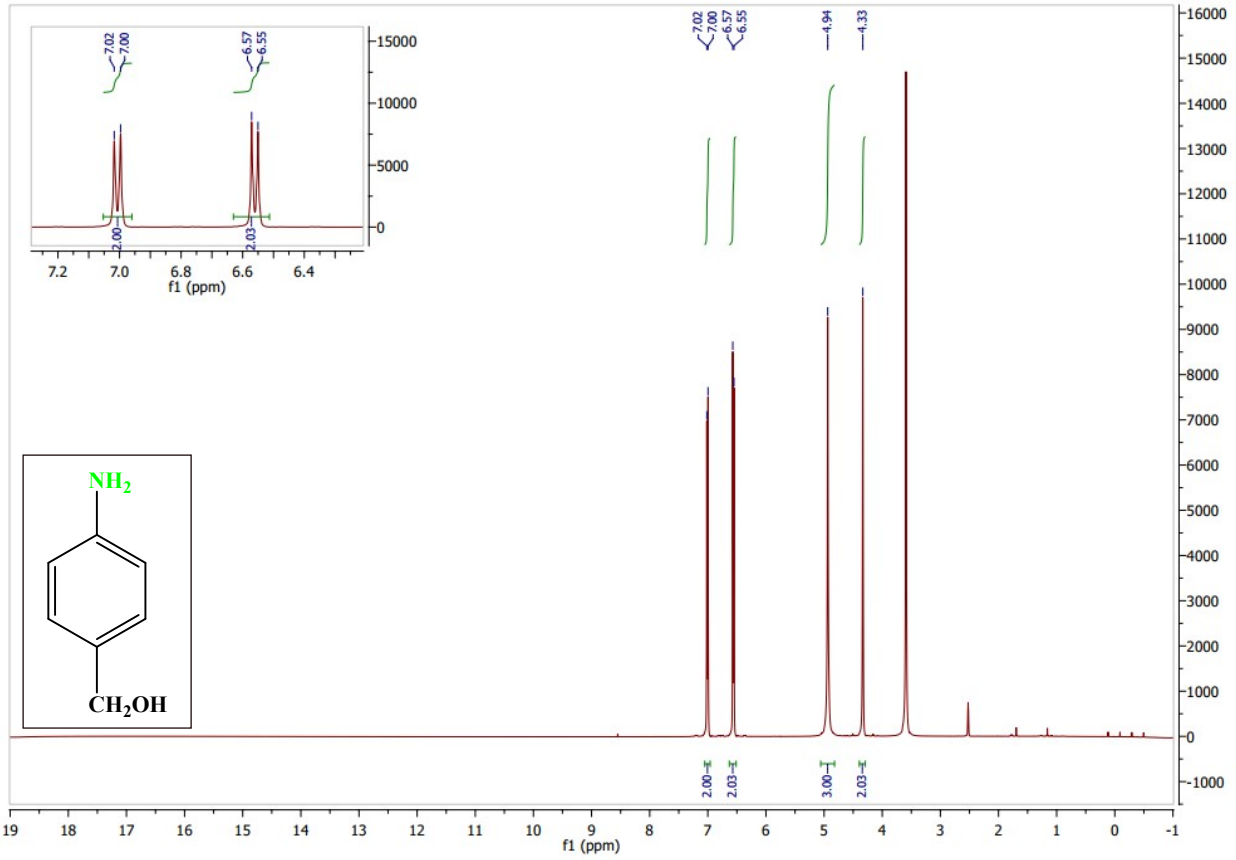

Fig S21:[1]H-NMR (400 MHz; DMSO) of 4-Aminobenzyl alcohol

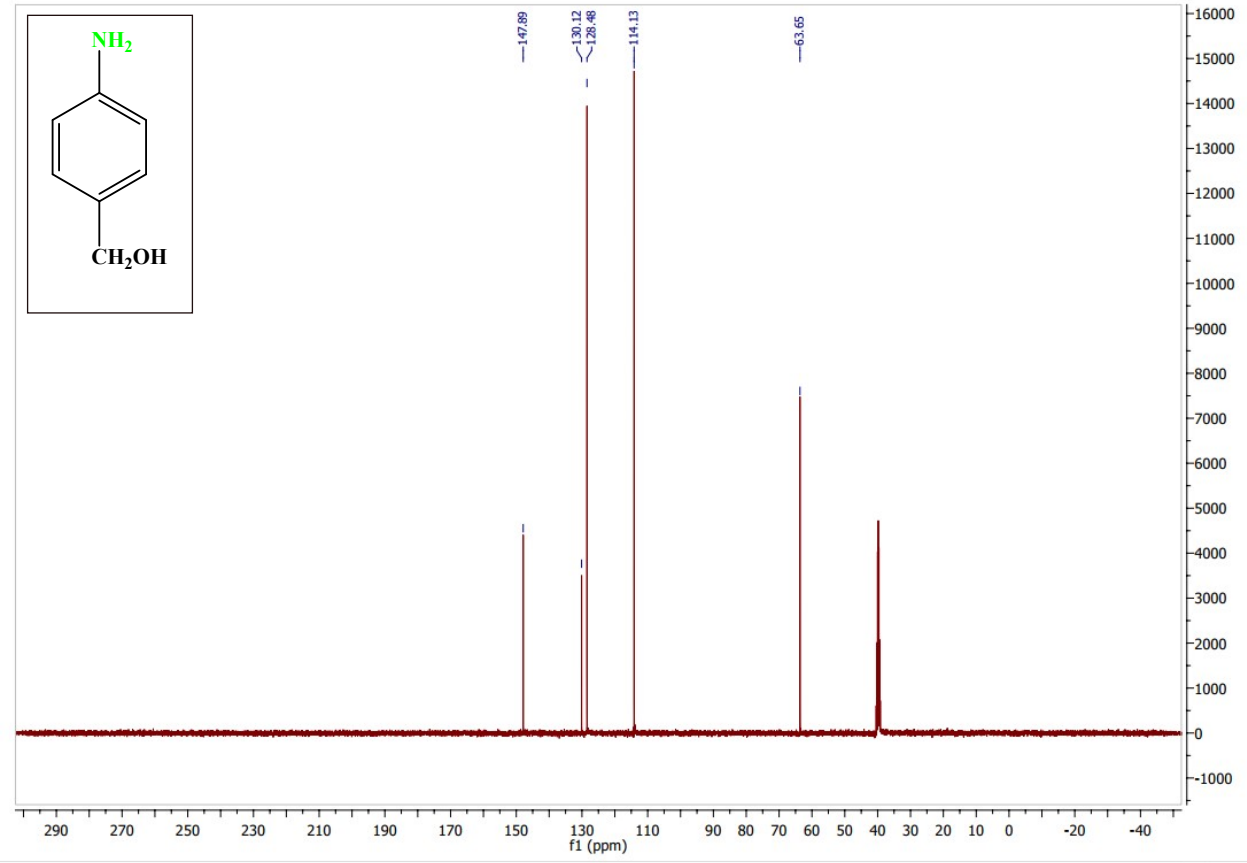

Fig S22:^{13}C-NMR (100 MHz; DMSO) of 4-Aminobenzyl alcohol

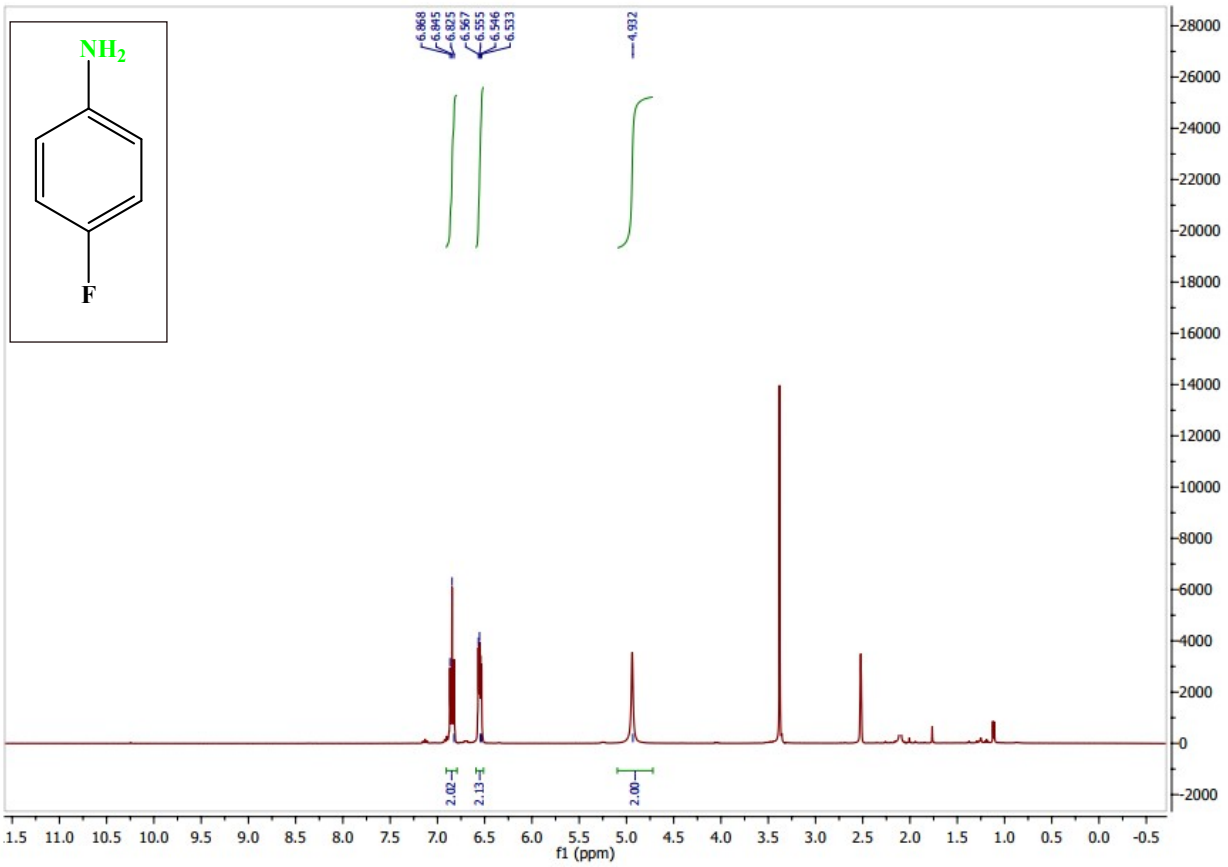

Fig S23:[1]H-NMR (400 MHz; DMSO) of 4-Fluoroaniline

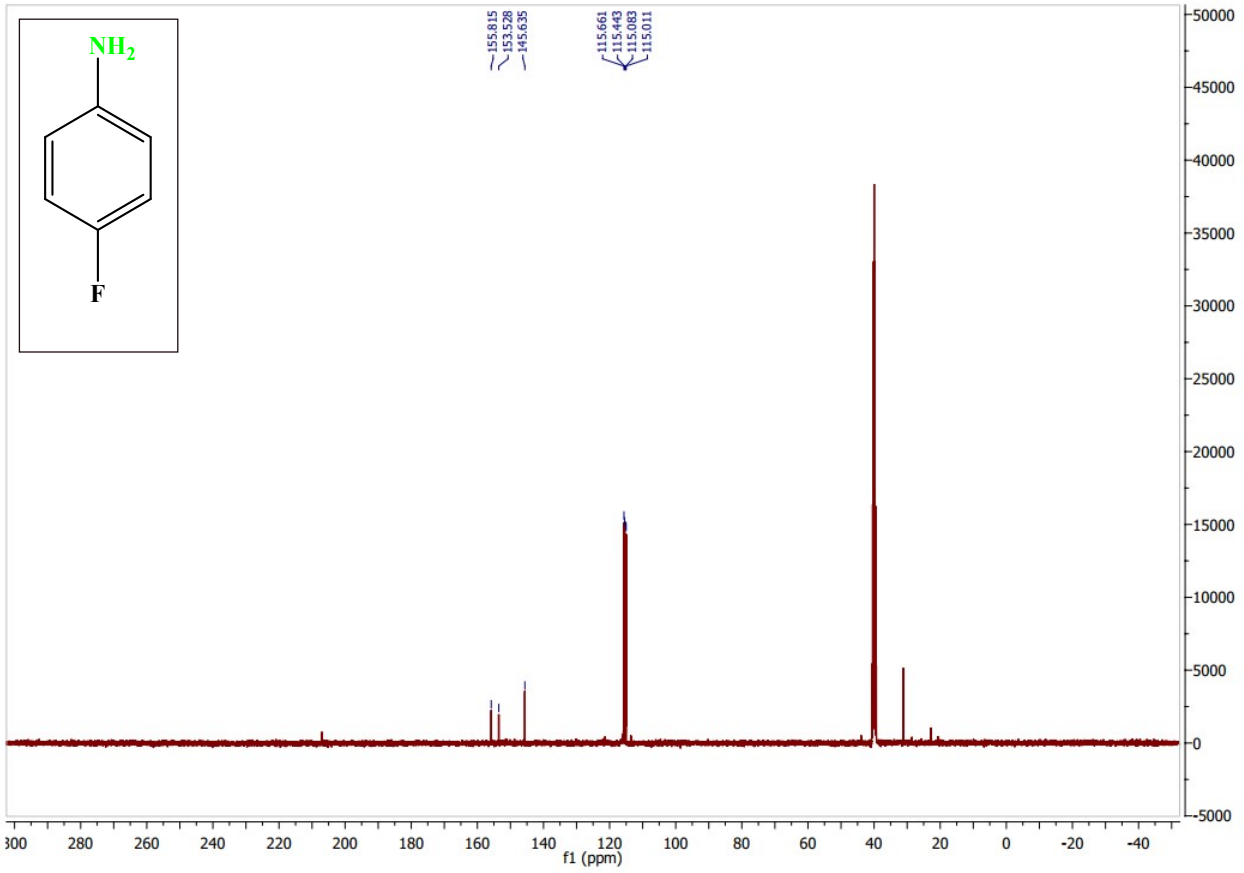

Fig S24:^{13}C-NMR (100 MHz; DMSO) of 4-Fluoroaniline

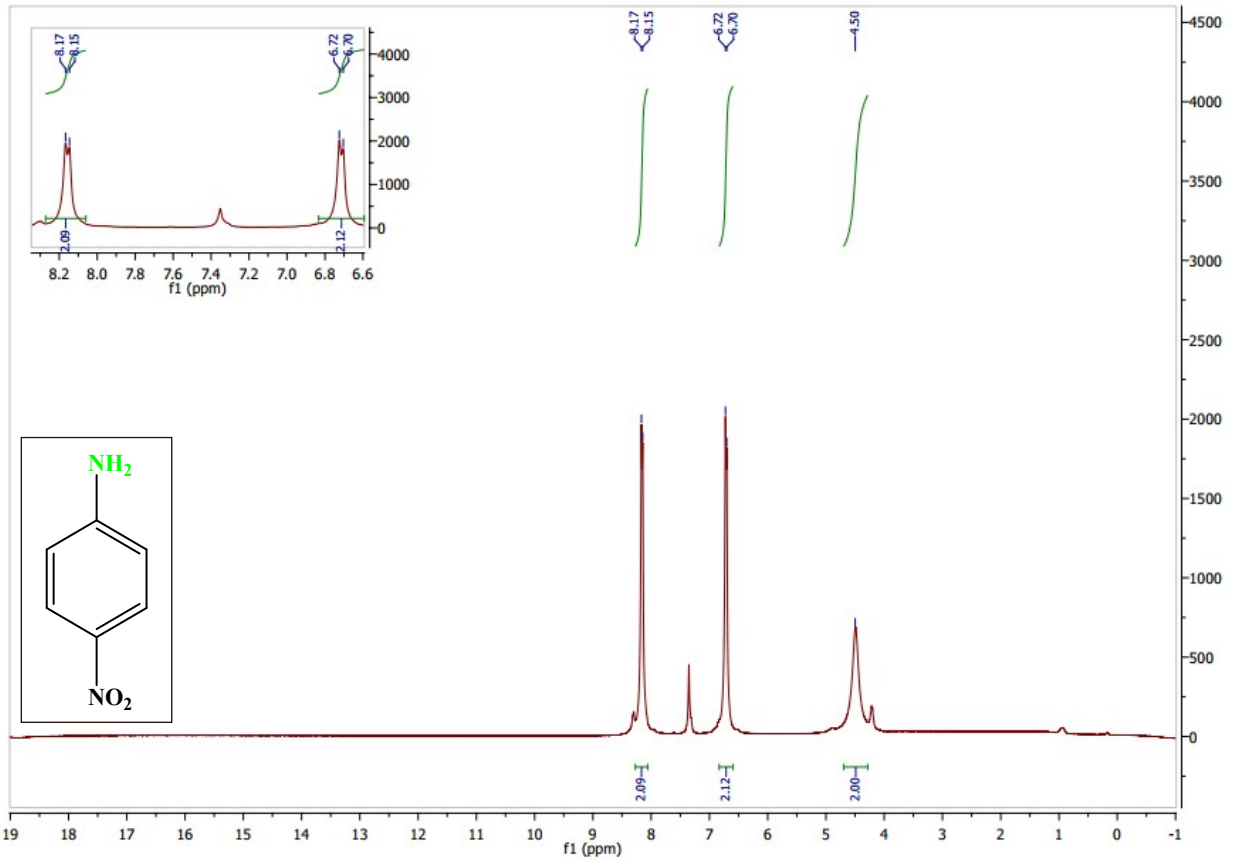

Fig S25:^{1}H-NMR (400 MHz; $CDCl_3$) of 4-Nitroaniline

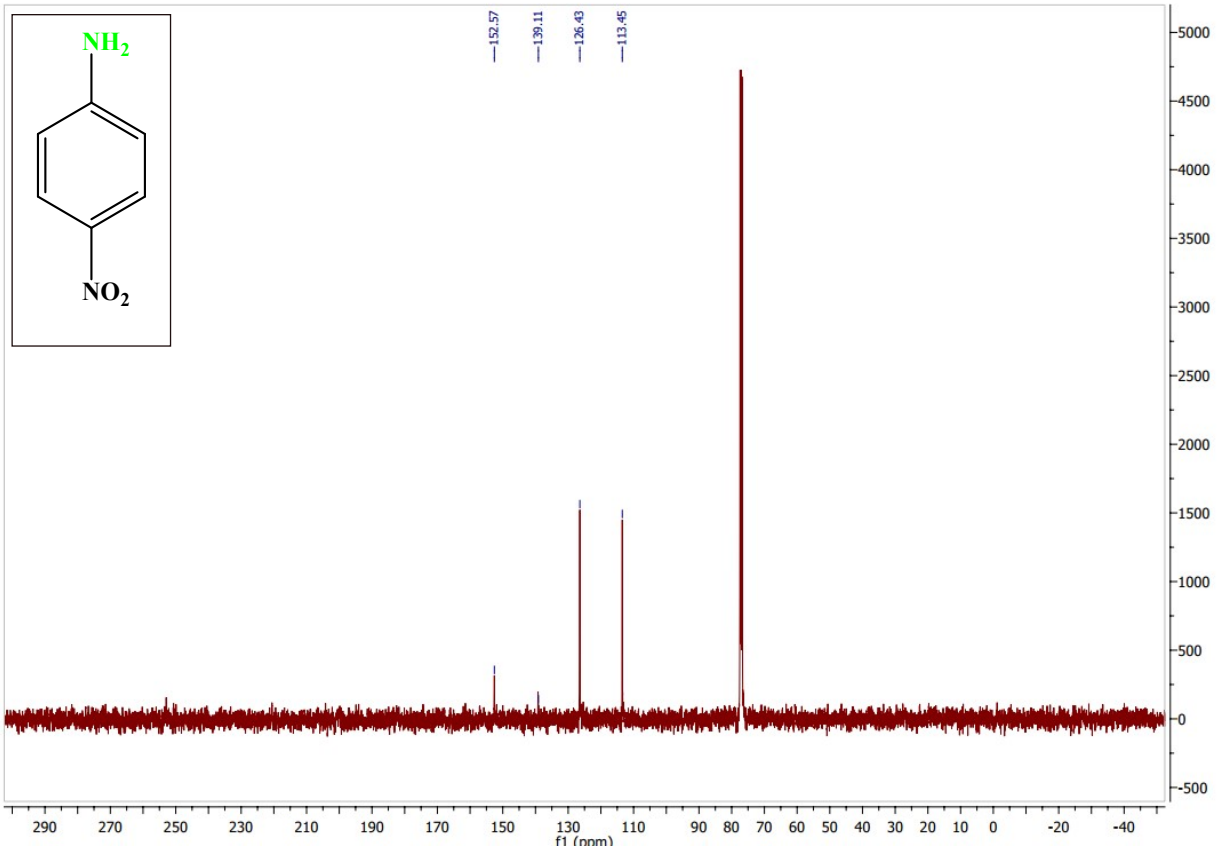

Fig S26:^{13}C-NMR (100 MHz; $CDCl_3$) of 4-Nitroaniline

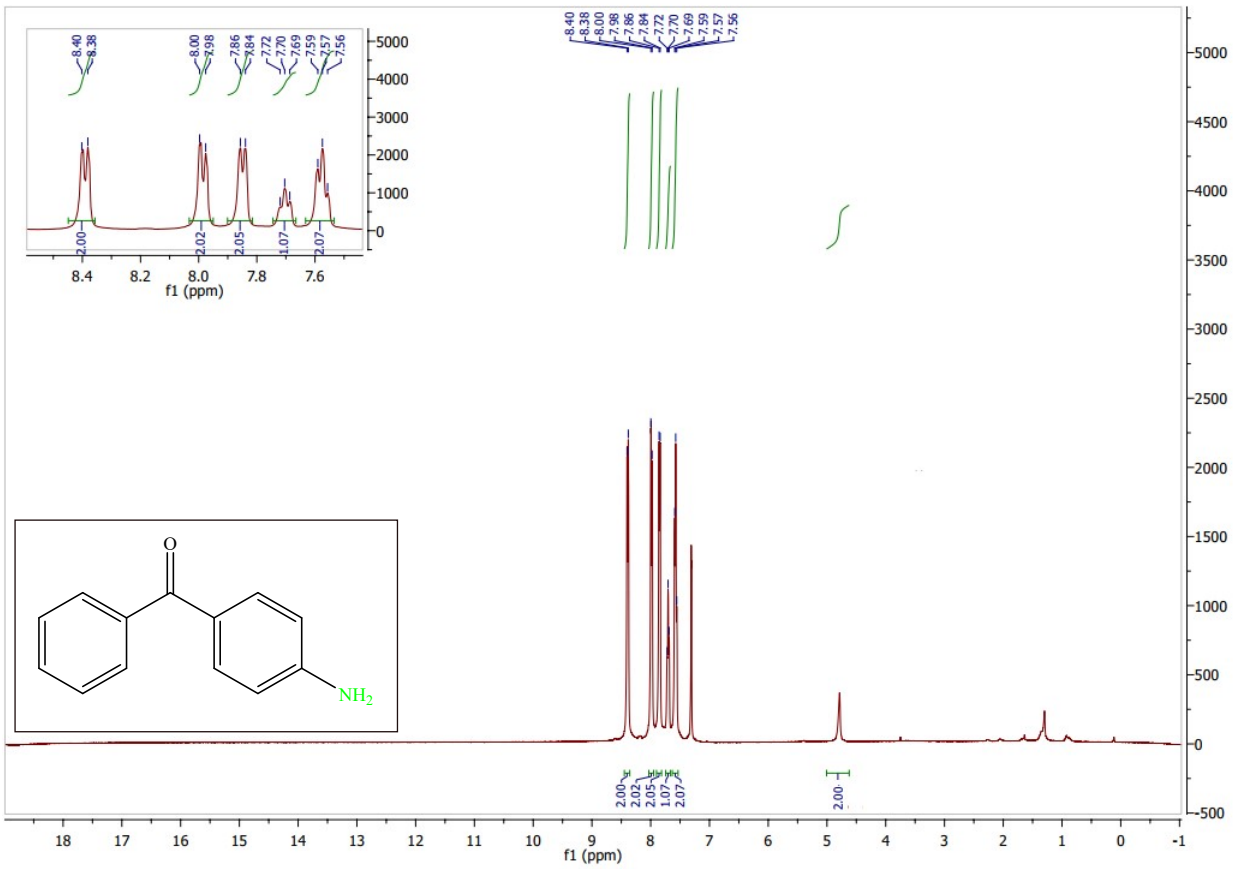

Fig S27:[1]H-NMR (400 MHz; $CDCl_3$) of 4-Aminobenzophenone

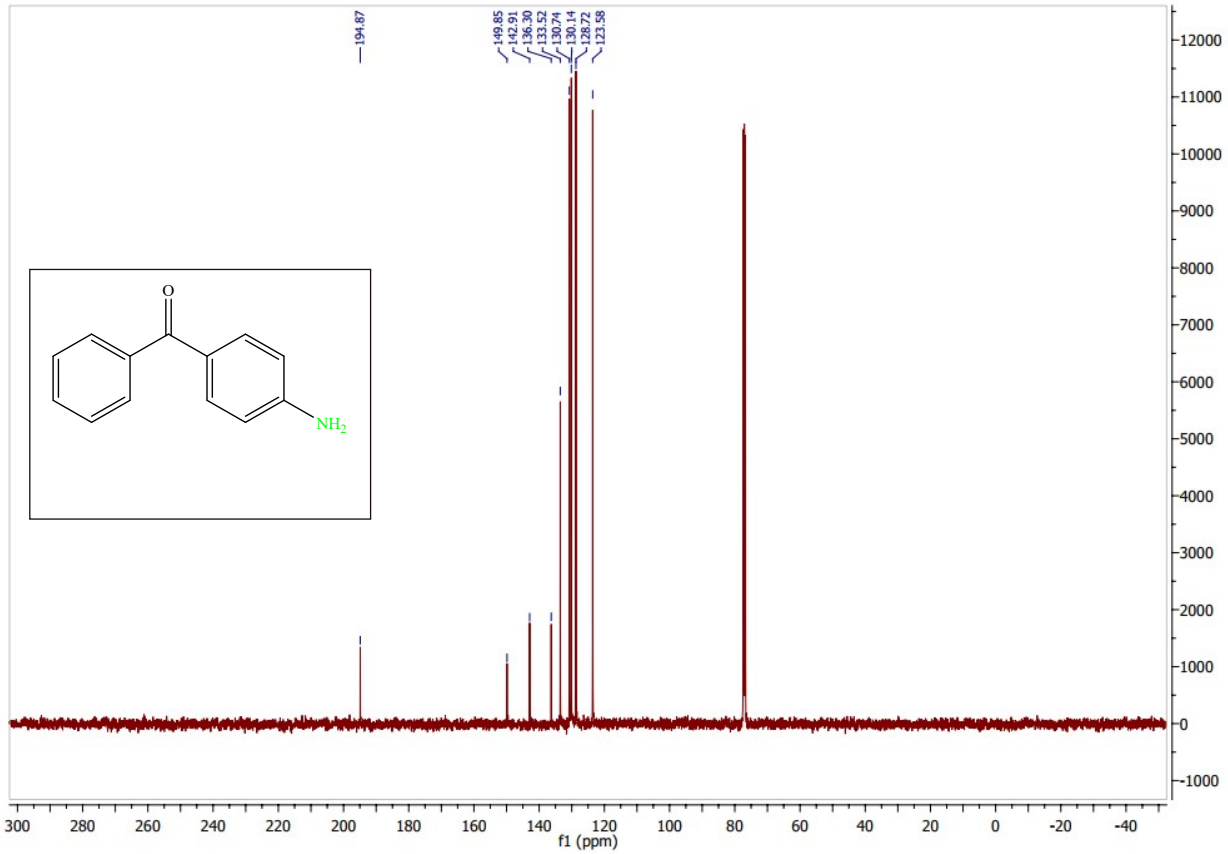

Fig S28:^{13}C-NMR (100 MHz; $CDCl_3$) of 4-Aminobenzophenone

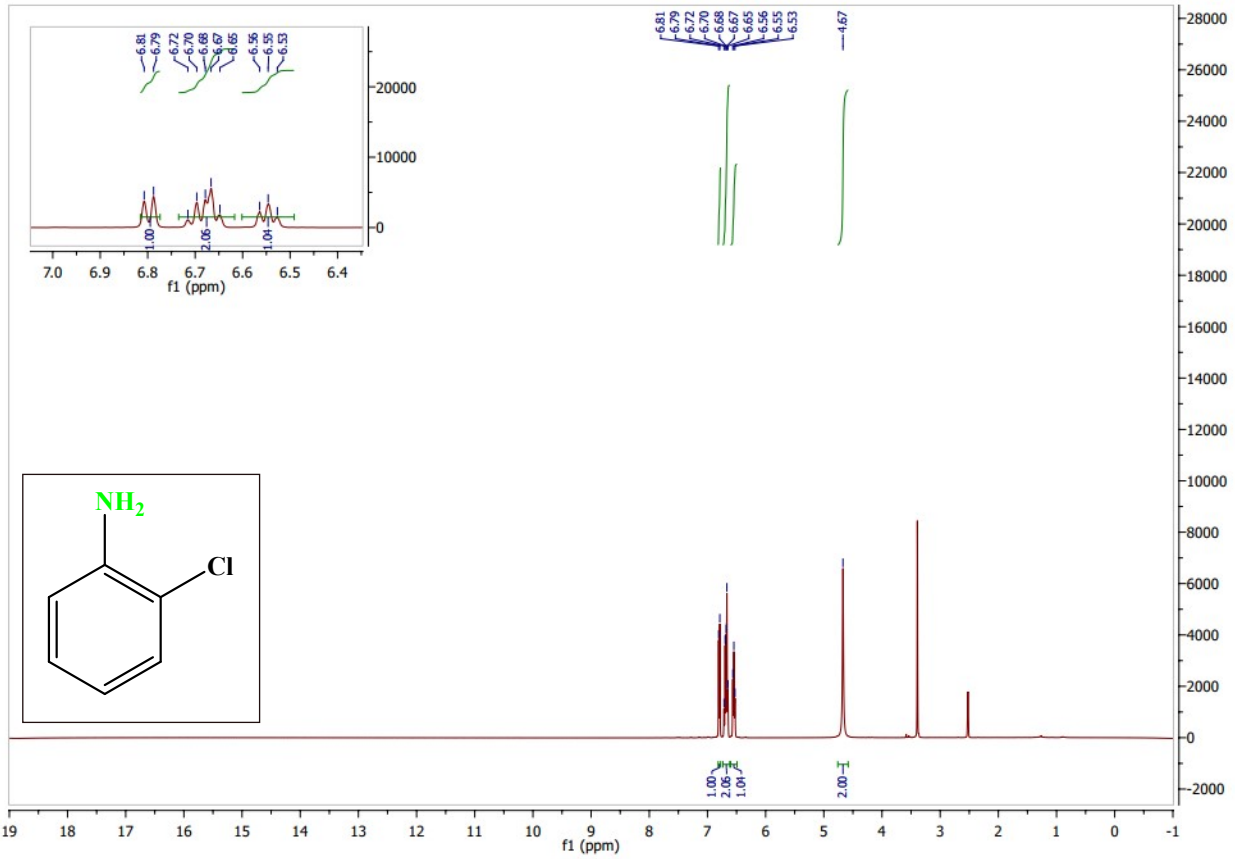

Fig S29:[1]H-NMR (400 MHz; DMSO) of 2-Chloroaniline

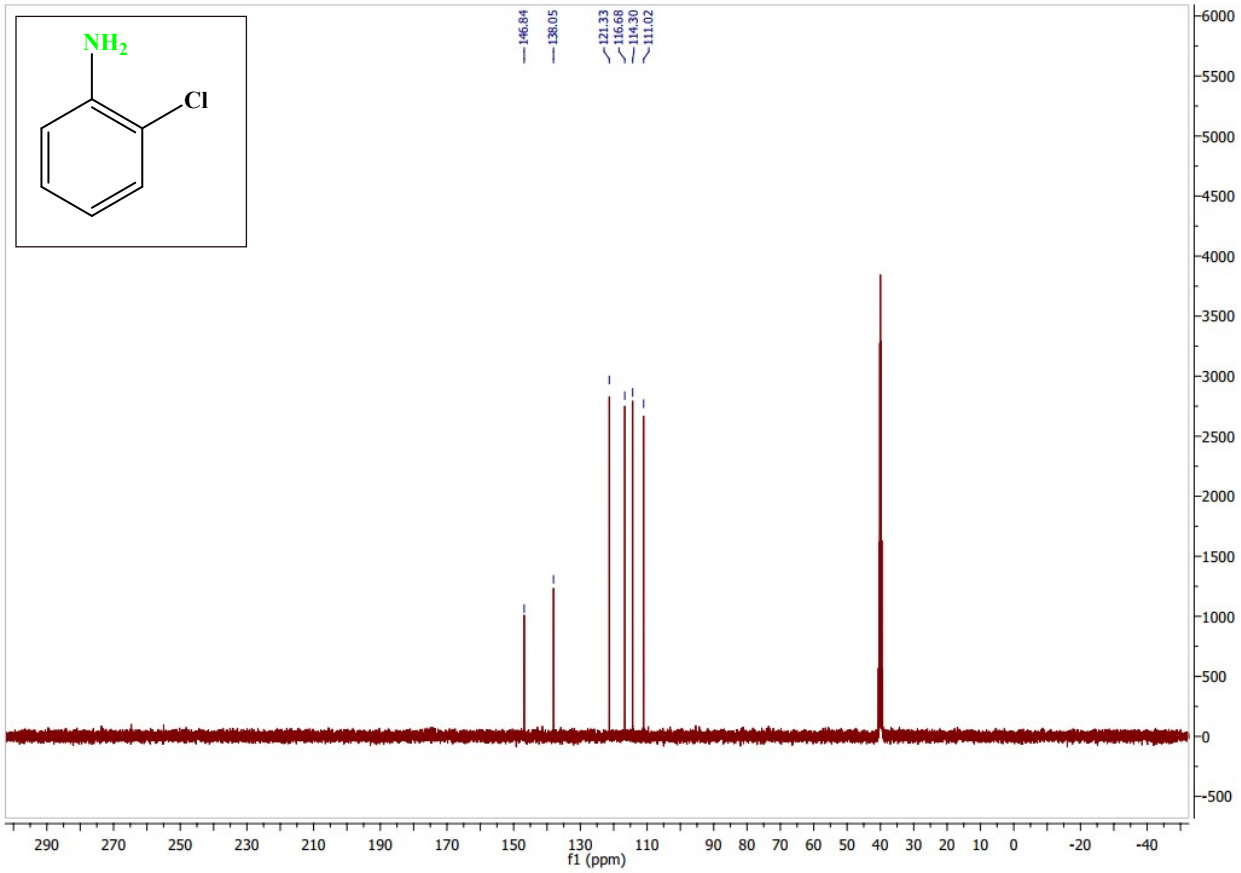

Fig S30:[1]H-NMR (100 MHz; DMSO) of 2-Chloroaniline

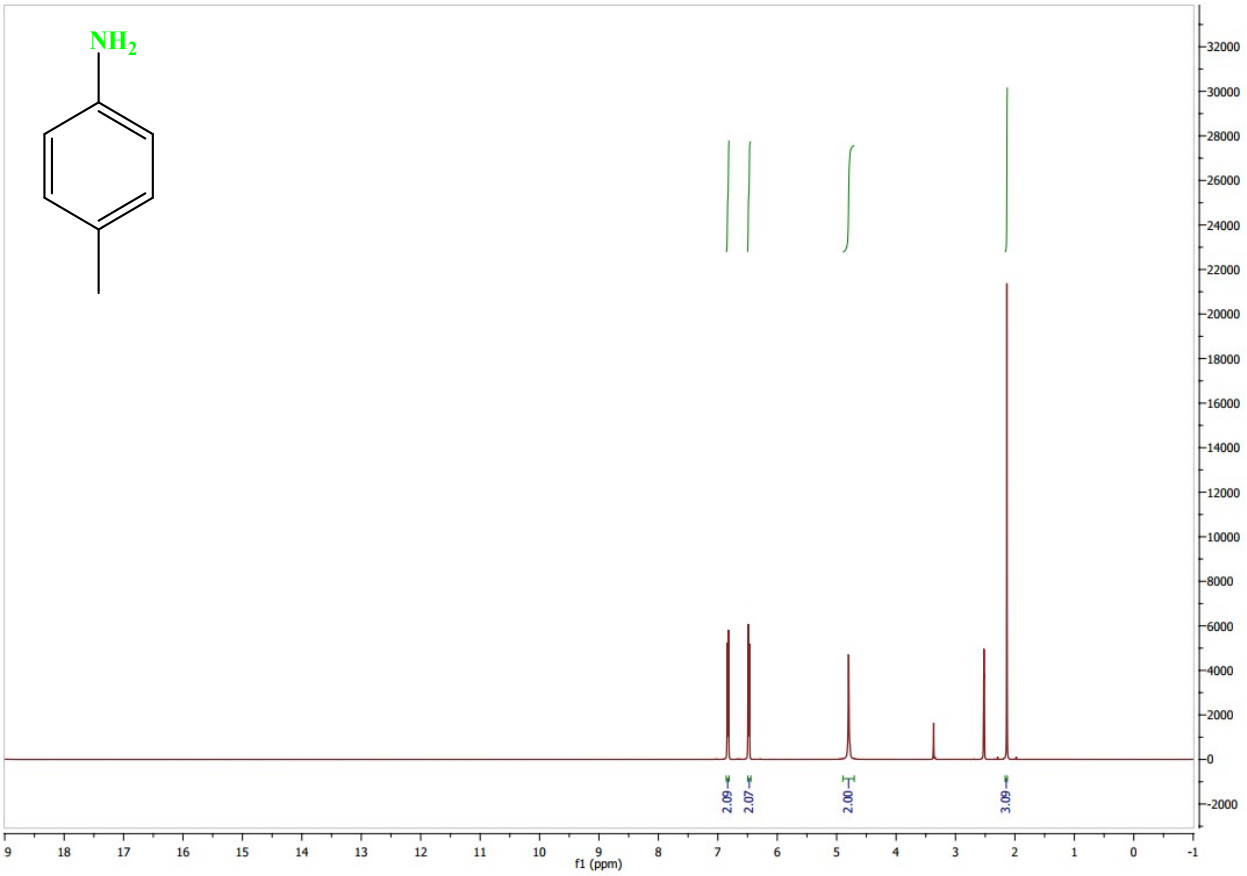

Fig S31:[1]H-NMR (400 MHz; DMSO) of p-Toluidine

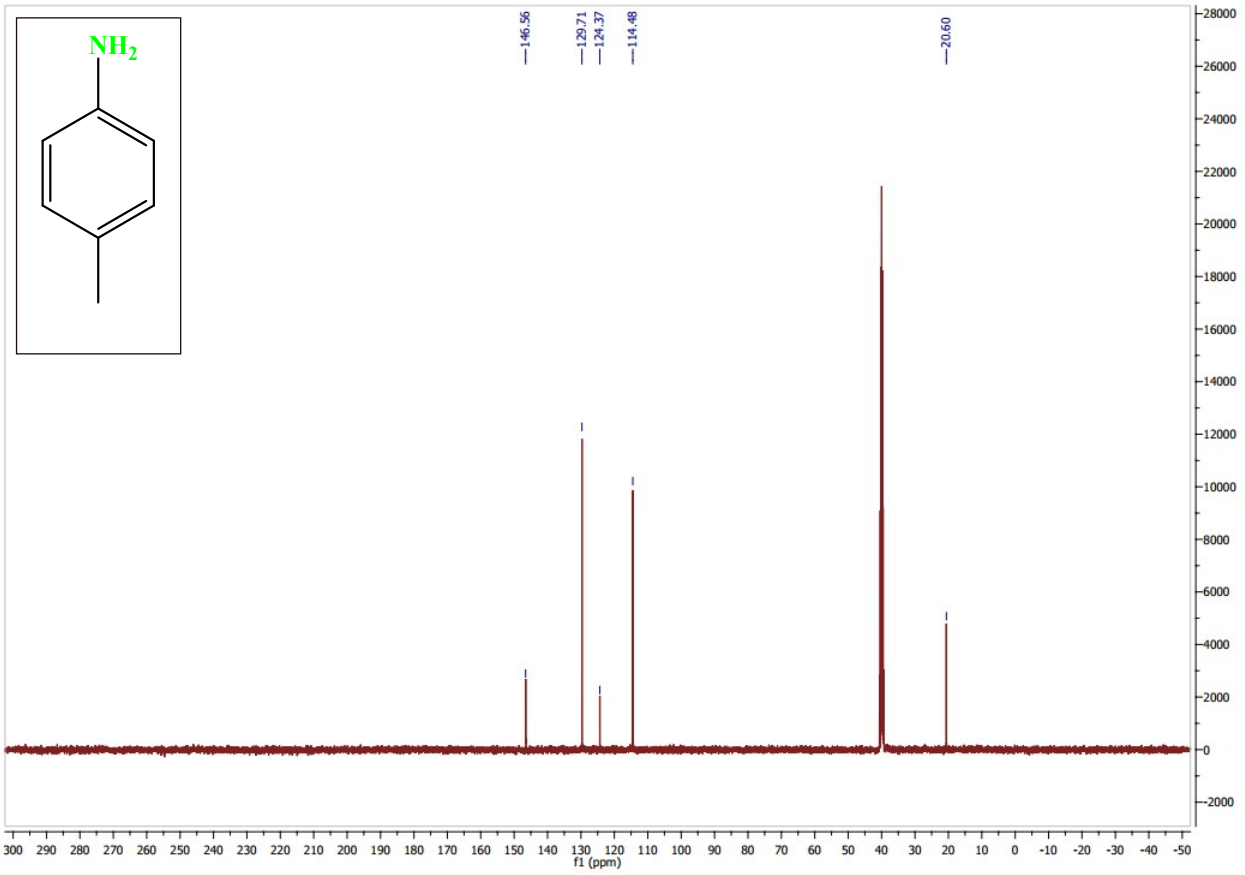

Fig S32: ^{13}C NMR (100 MHz; DMSO) of p-Toluidine

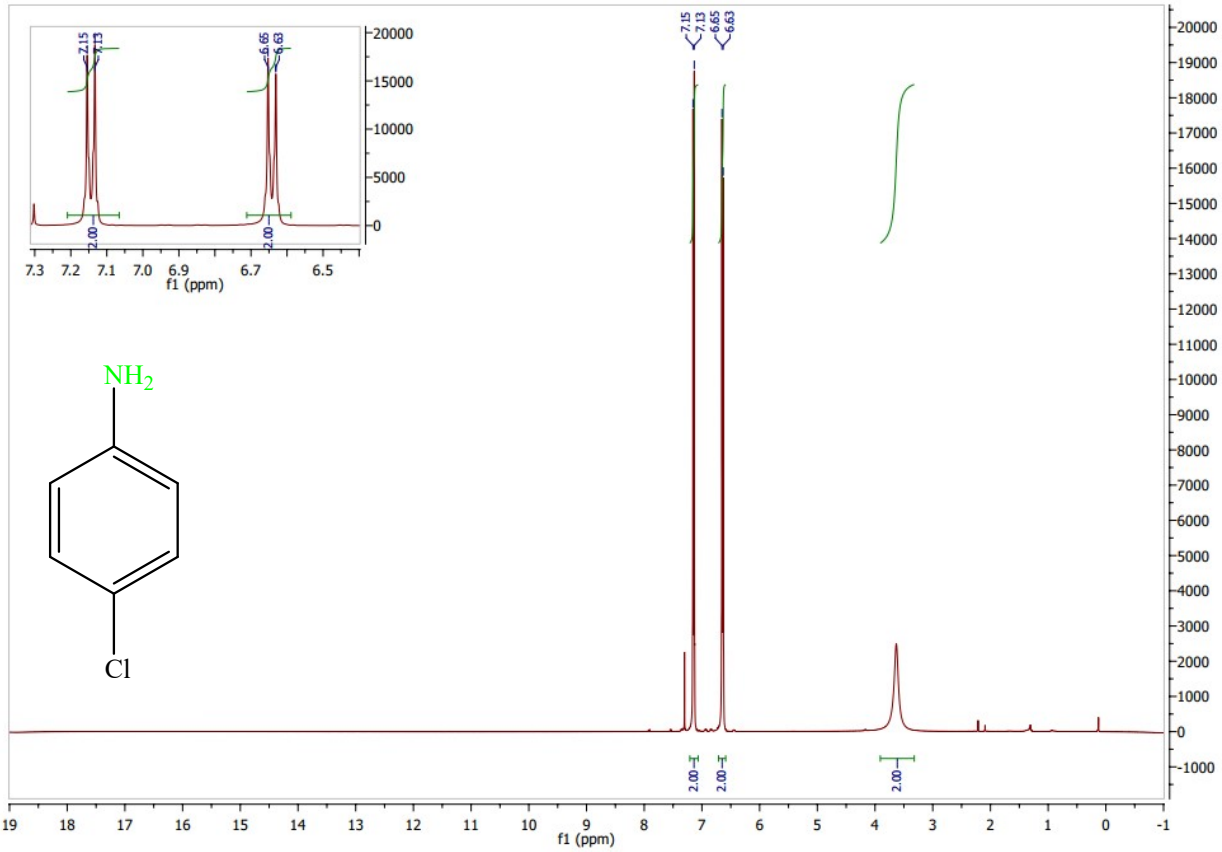

Fig S33:^{1}H-NMR (400 MHz; $CDCl_3$) of 4-Chloroaniline

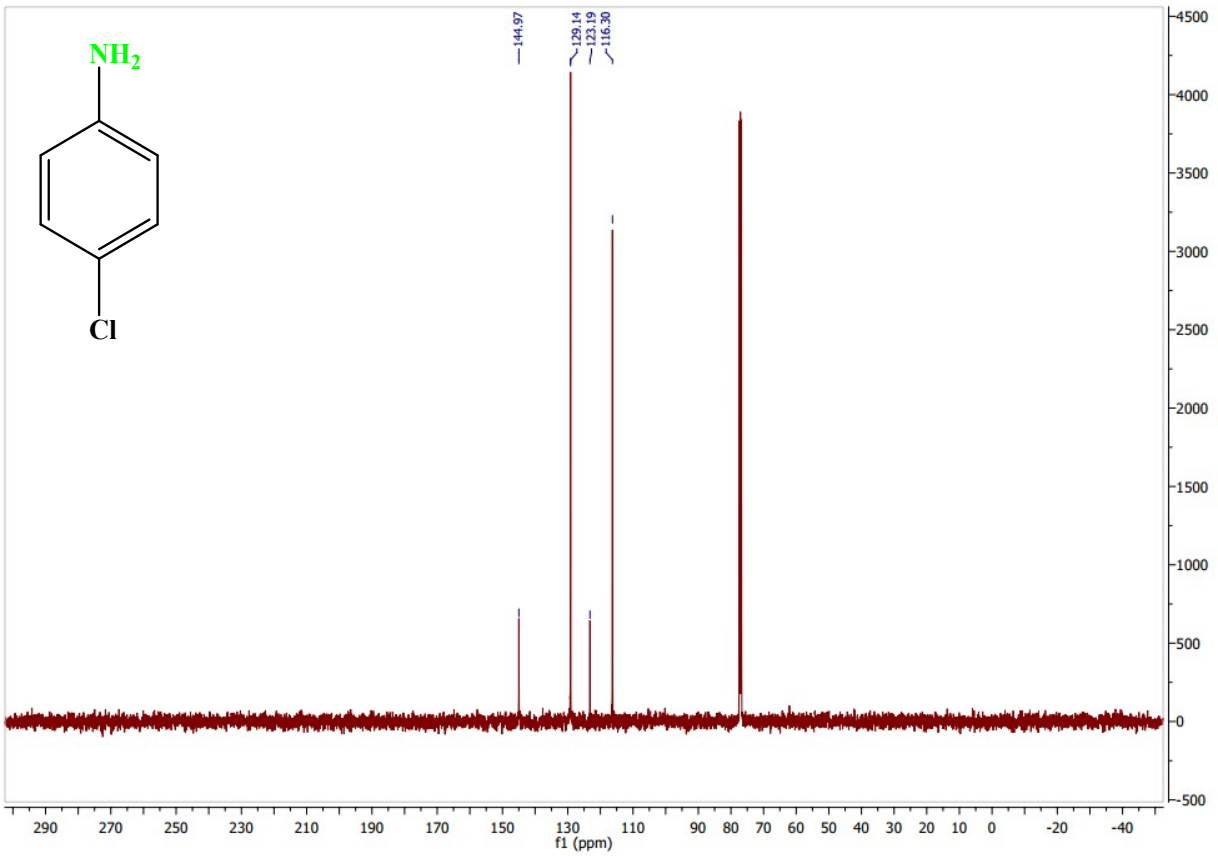

Fig S34:^{13}C-NMR (100 MHz; $CDCl_3$) of 4-Chloroaniline

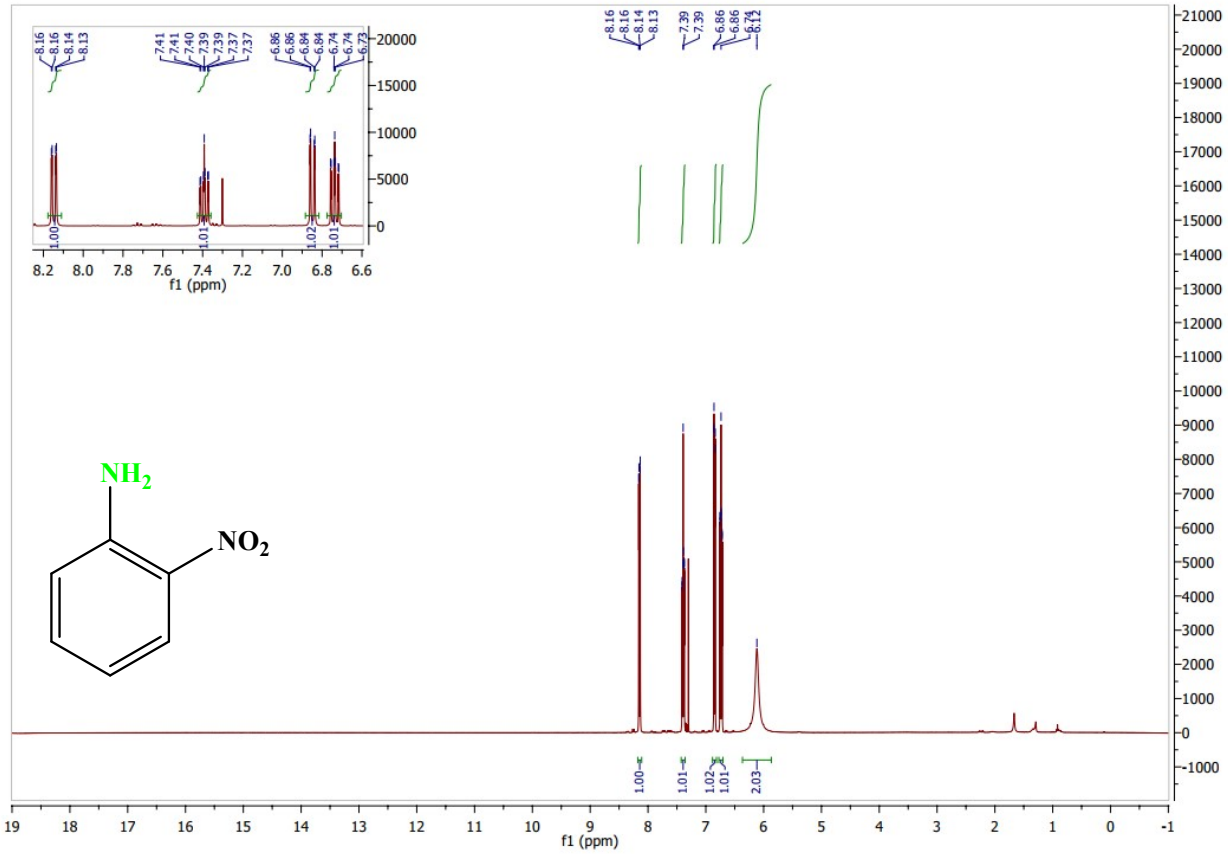

Fig S35:^{1}H-NMR (400 MHz; $CDCl_3$) of 2-Nitroaniline

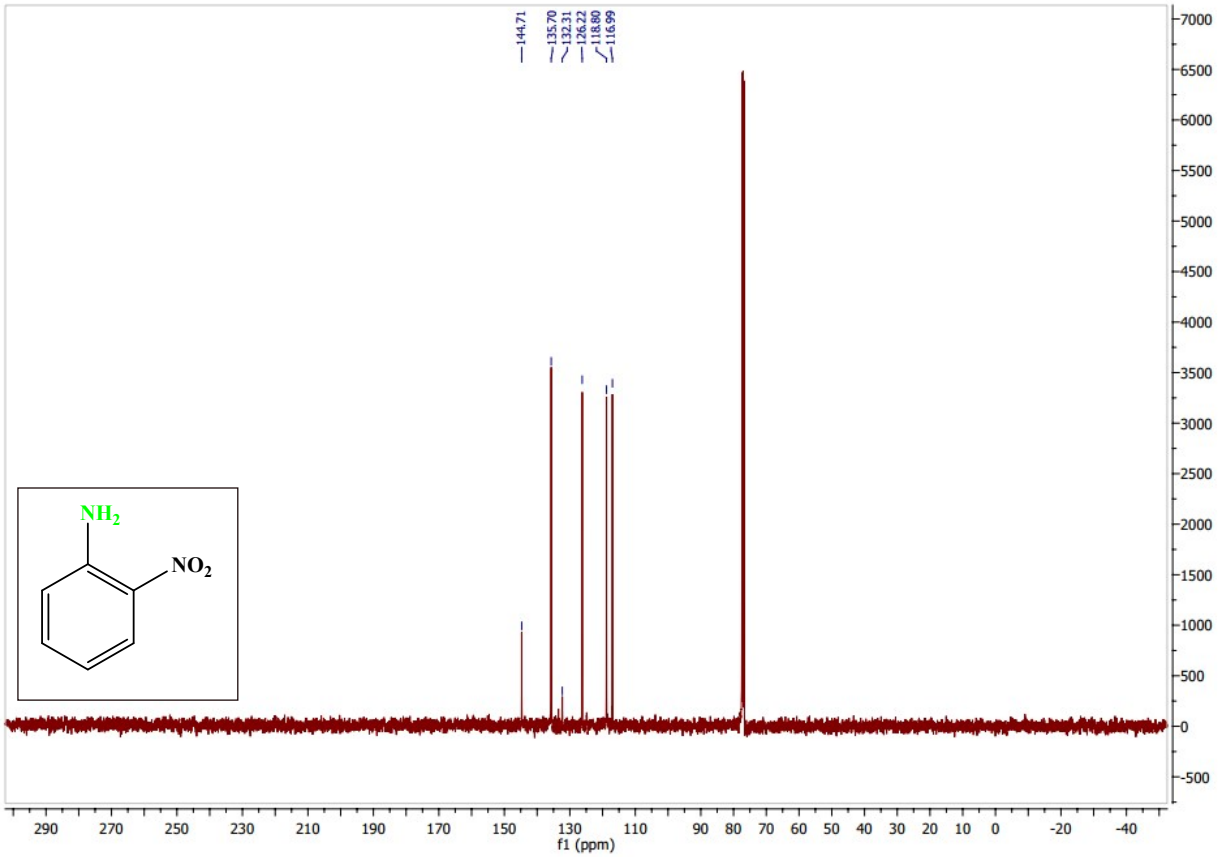

Fig S36:^{13}C-NMR (100 MHz; $CDCl_3$) of 2-Nitroaniline

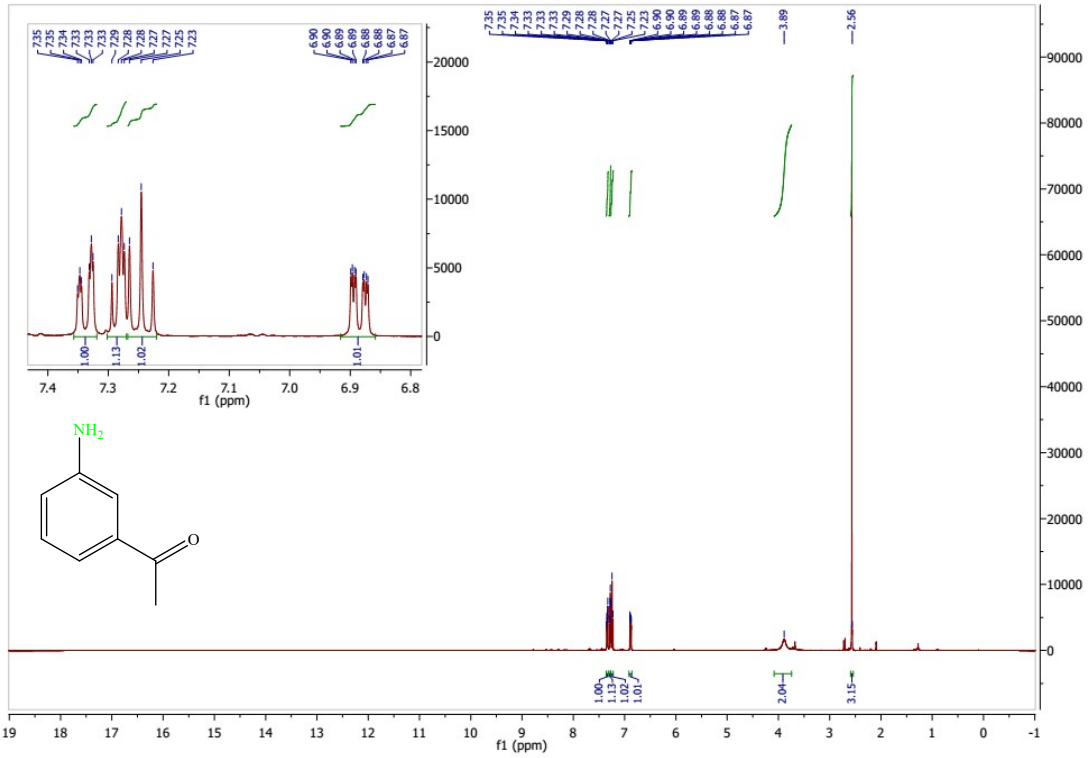

Fig S37:^{1}H-NMR (400 MHz; $CDCl_3$) of 3-Aminoacetophenone

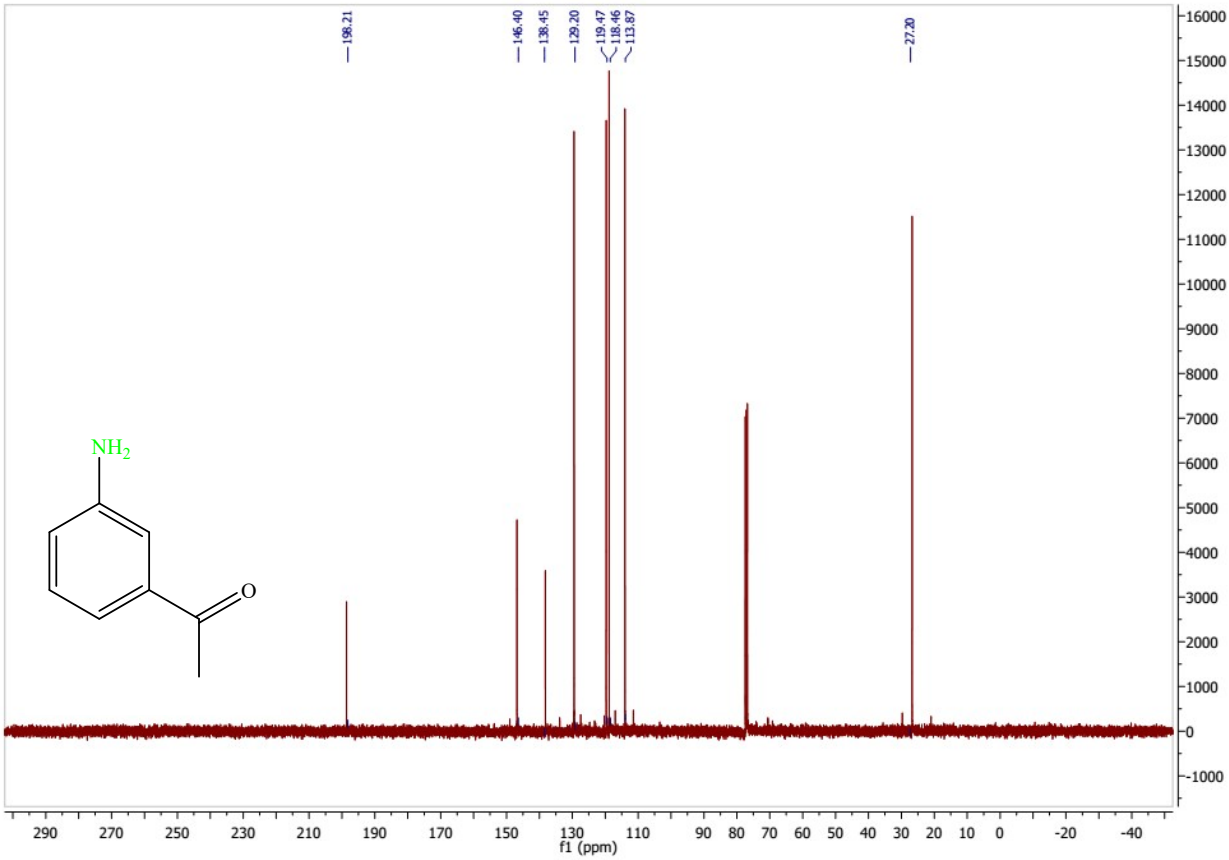

Fig S38:^{13}C-NMR (100 MHz; $CDCl_3$) of 3-Aminoacetophenone

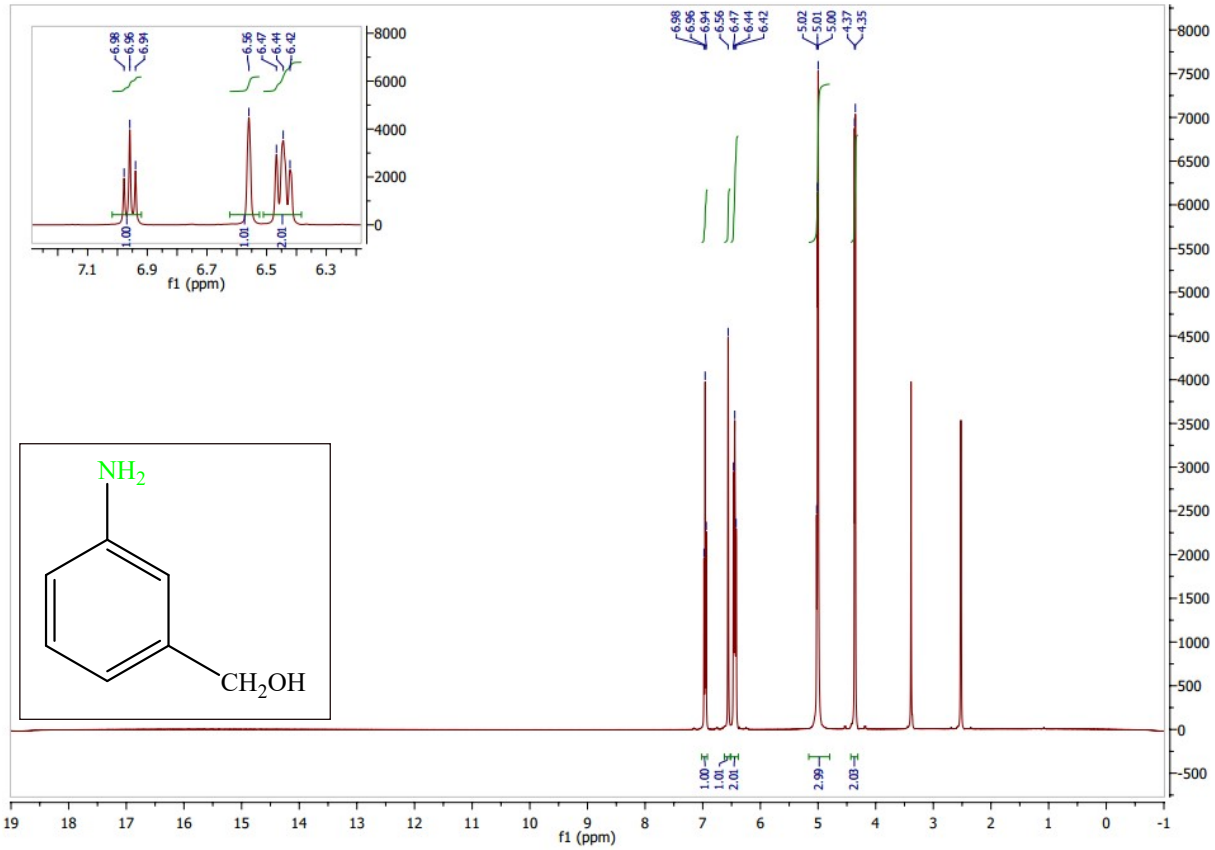

Fig S39:[1]H-NMR (400 MHz; DMSO) of 3-Aminobenzyl alcohol

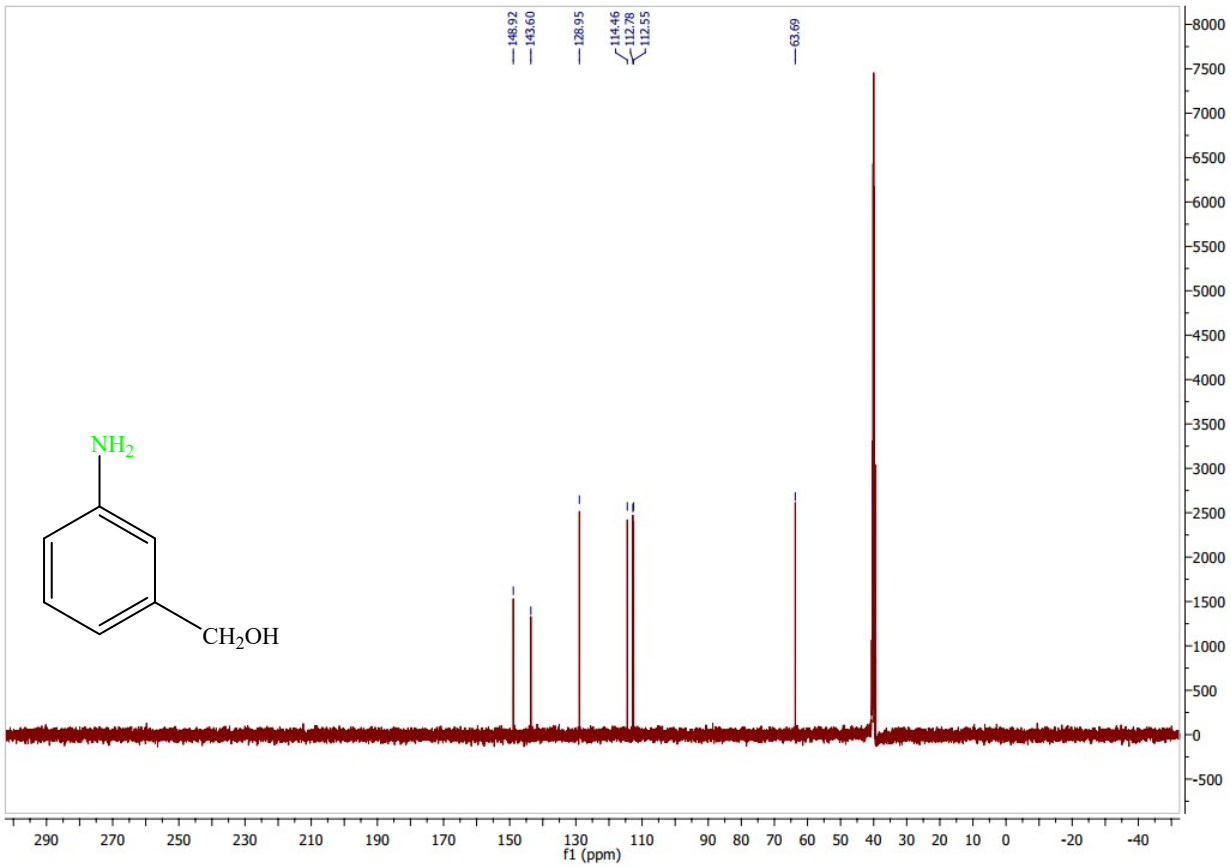

Fig S40:^{13}C-NMR (100 MHz; DMSO) of 3-Aminobenzyl alcohol

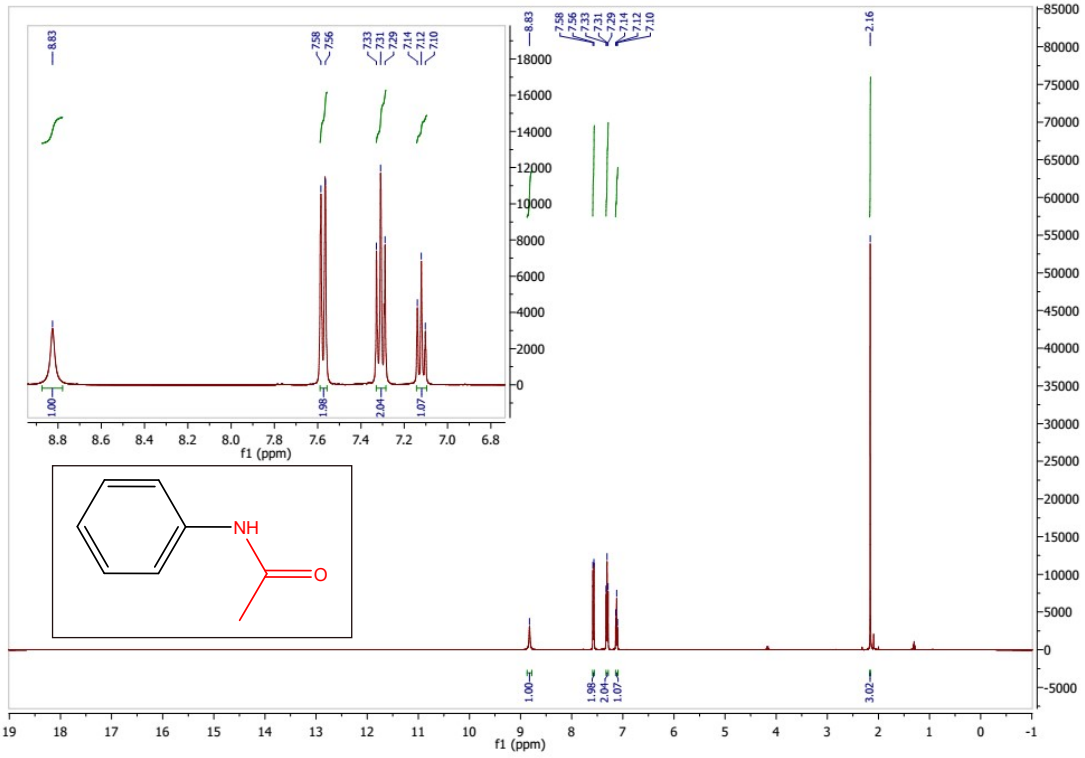

Fig S41:^{1}H-NMR (400 MHz; $CDCl_3$) of *N*-Phenylacetamide

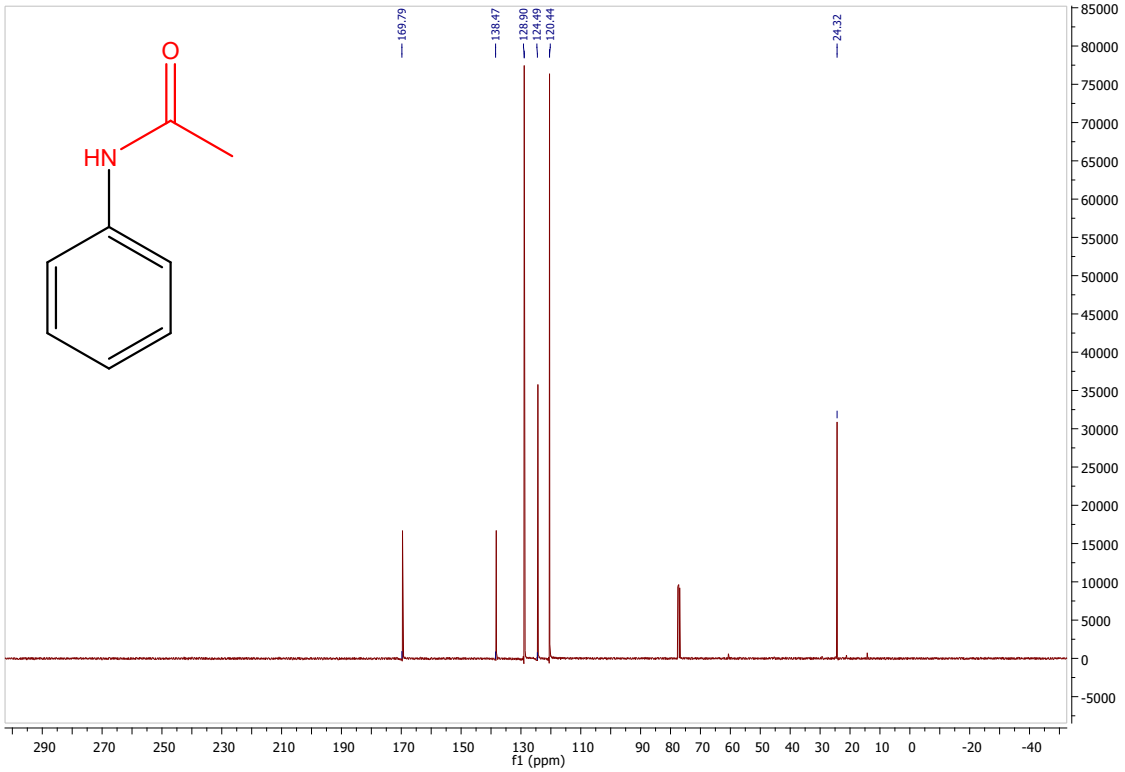

Fig S42:^{13}C-NMR (100 MHz; $CDCl_3$) of *N*-Phenylacetamide

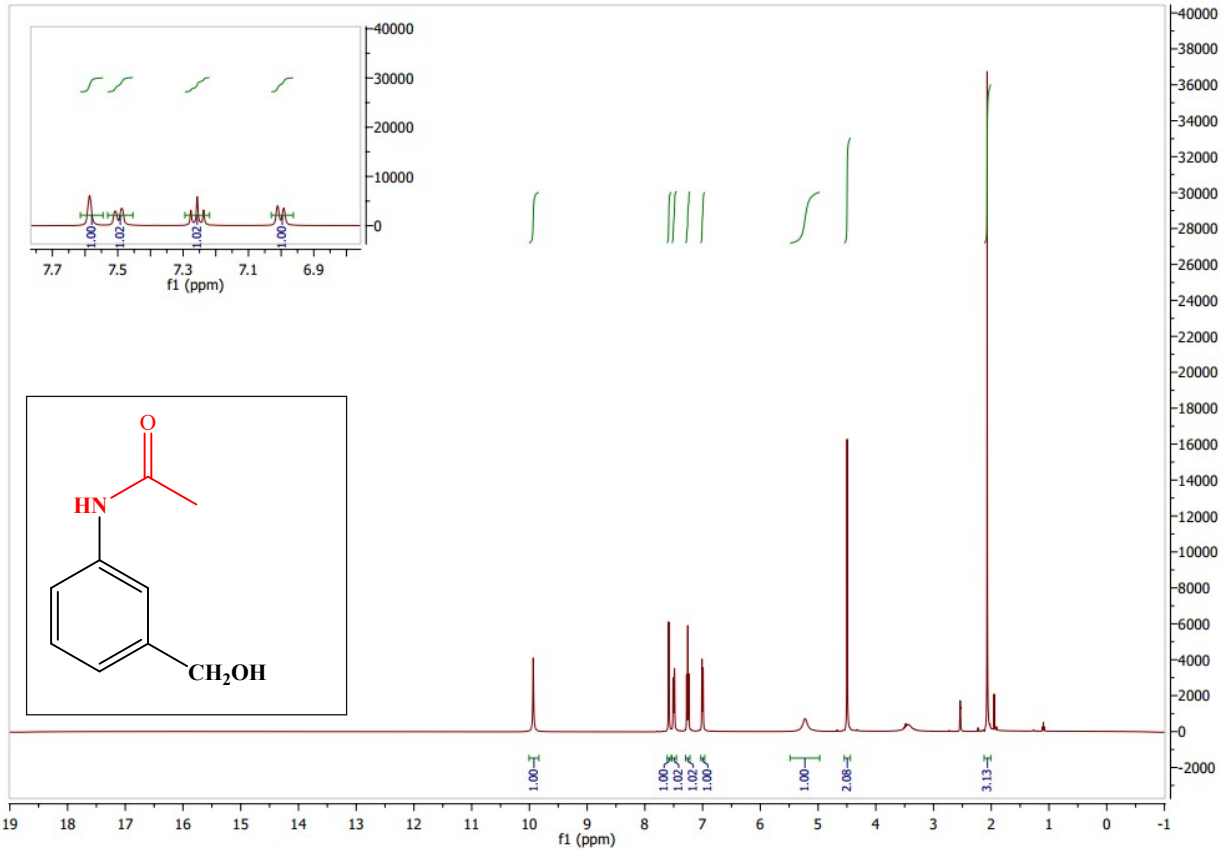

Fig S43:[1]H-NMR (400 MHz; DMSO) of *N*-(3-(Hydroxymethyl)phenyl)acetamide

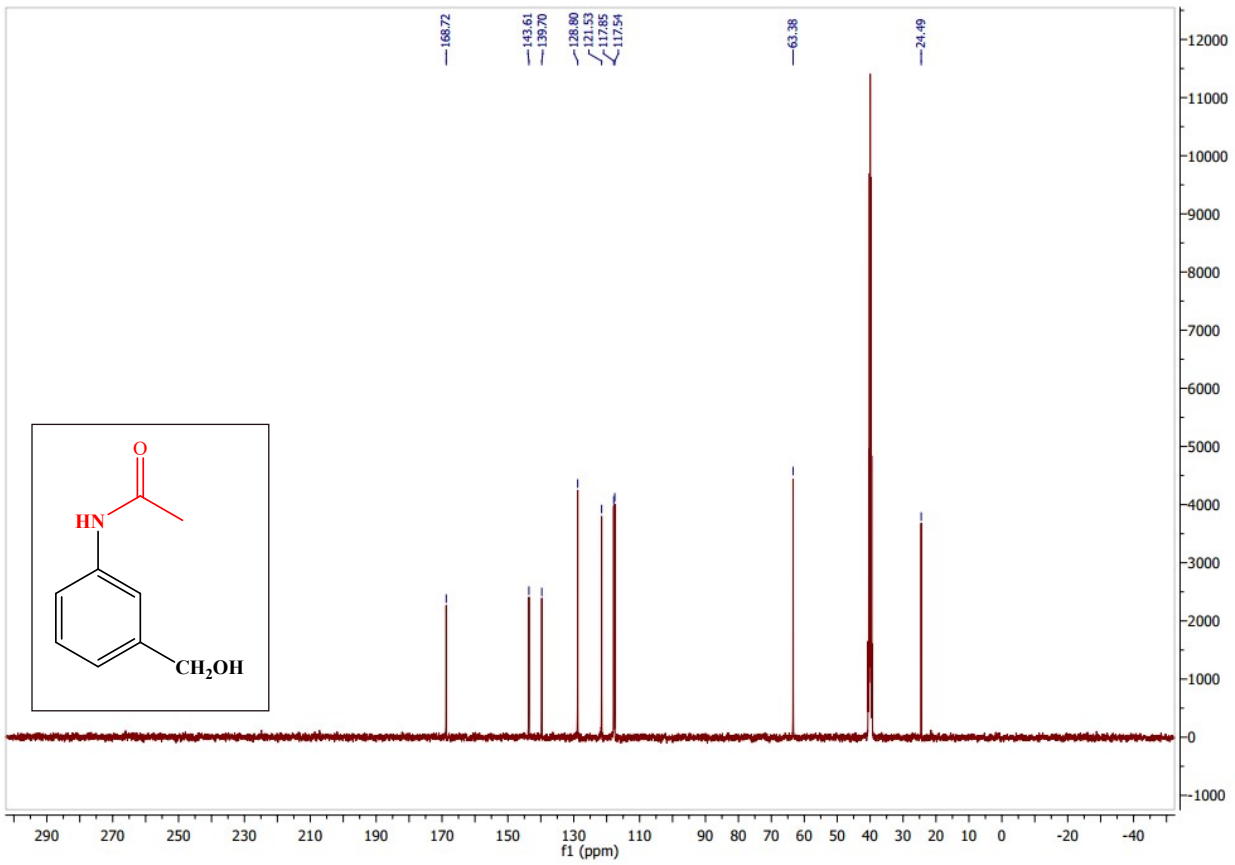

Fig S44:^{13}C-NMR (100 MHz; DMSO) of *N*-(3-(Hydroxymethyl)phenyl)acetamide

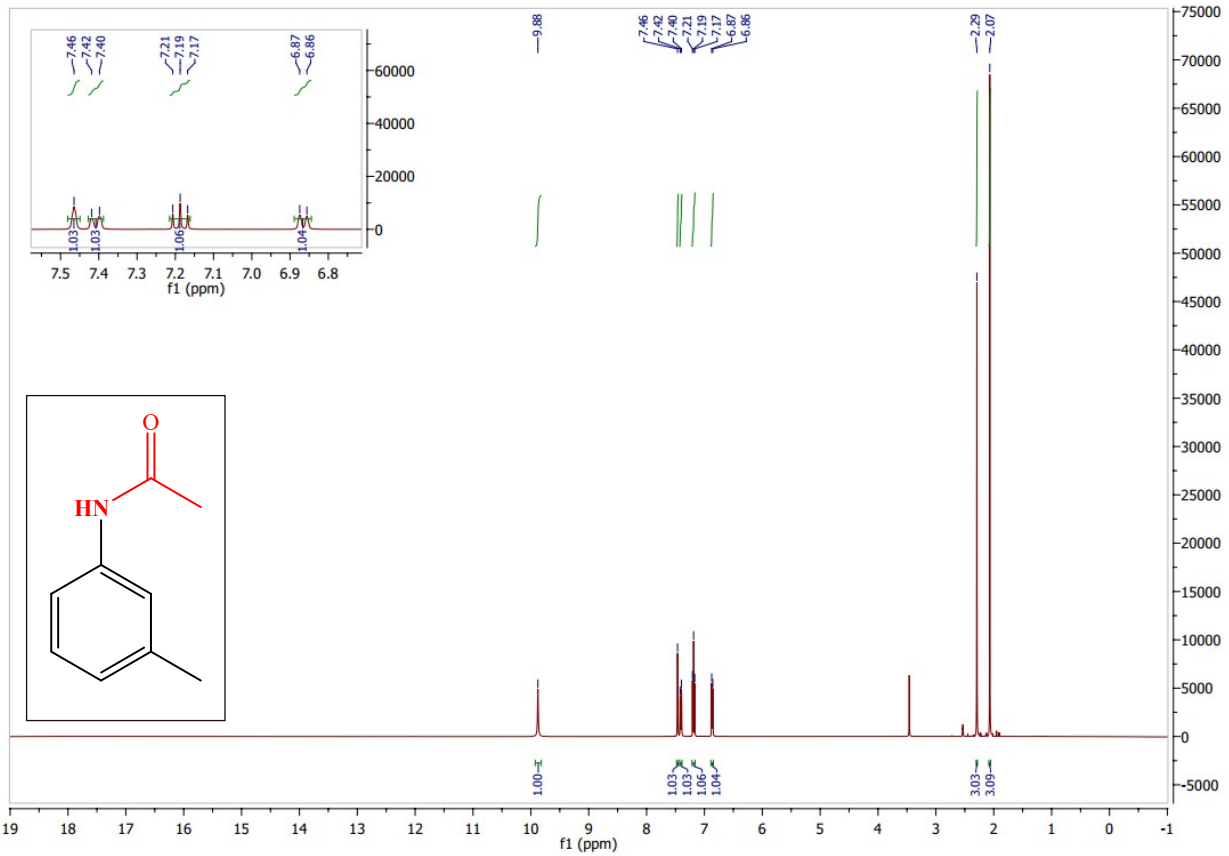

Fig S45:[1]H-NMR (400 MHz; DMSO) of *N*-(3-Methylphenyl)acetamide

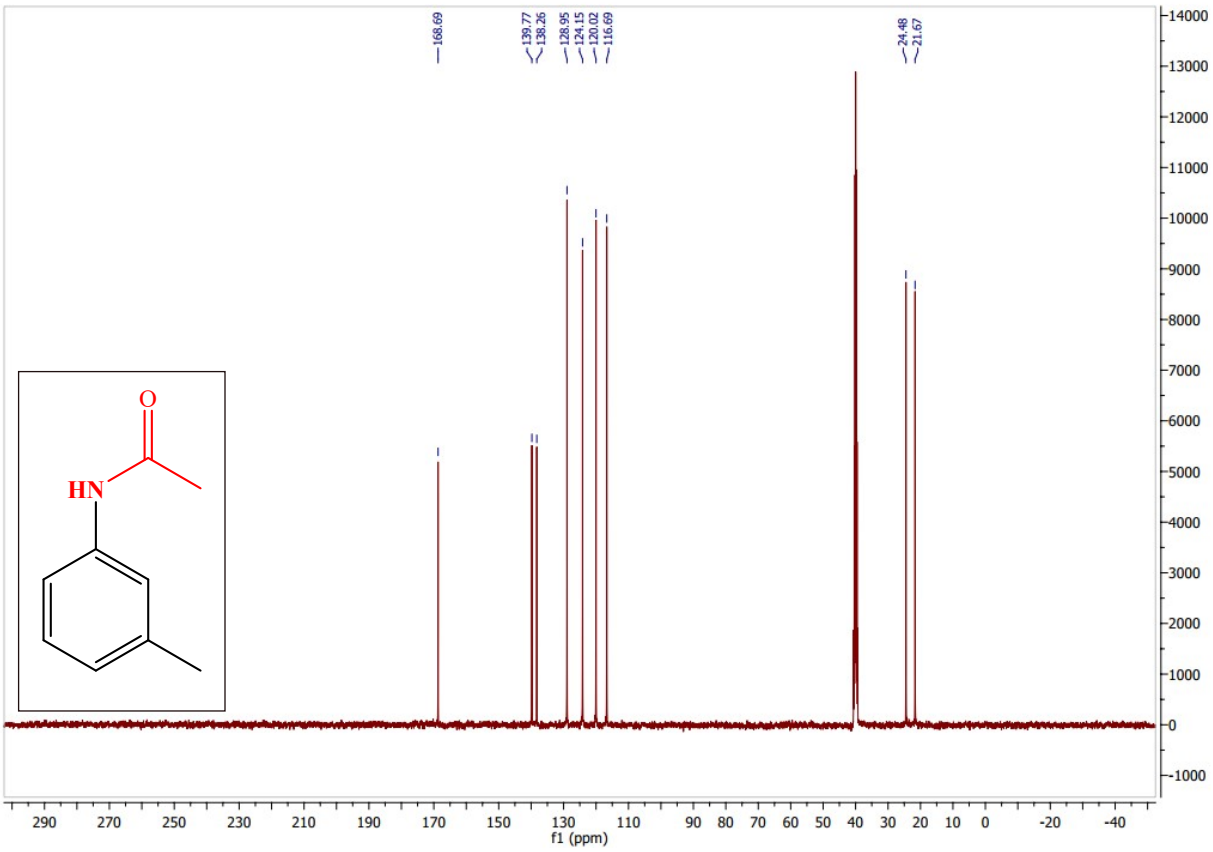

Fig S46:^{13}C-NMR (100 MHz; DMSO) of *N*-(3-Methylphenyl)acetamide

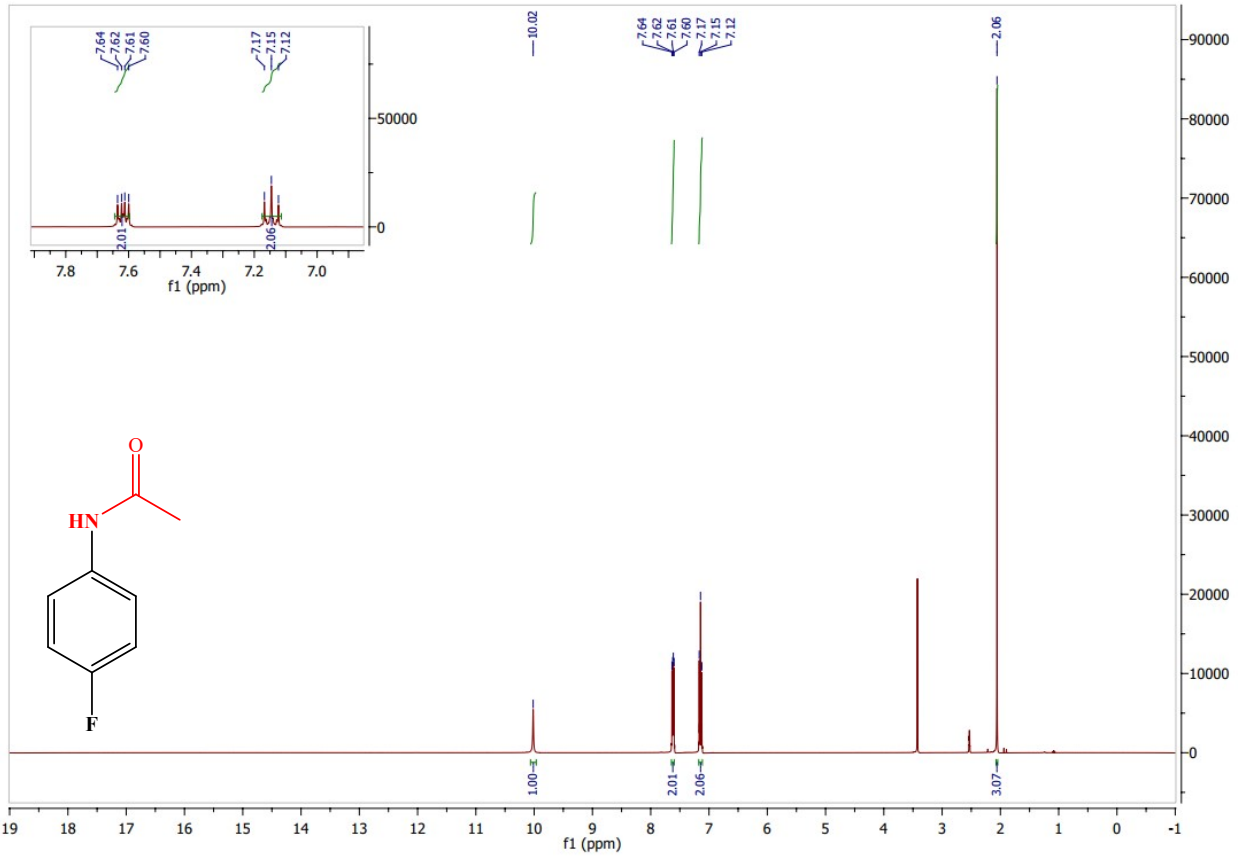

Fig S47:[1]H-NMR (400 MHz; DMSO) of *N*-(4-Fluorophenyl)acetamide

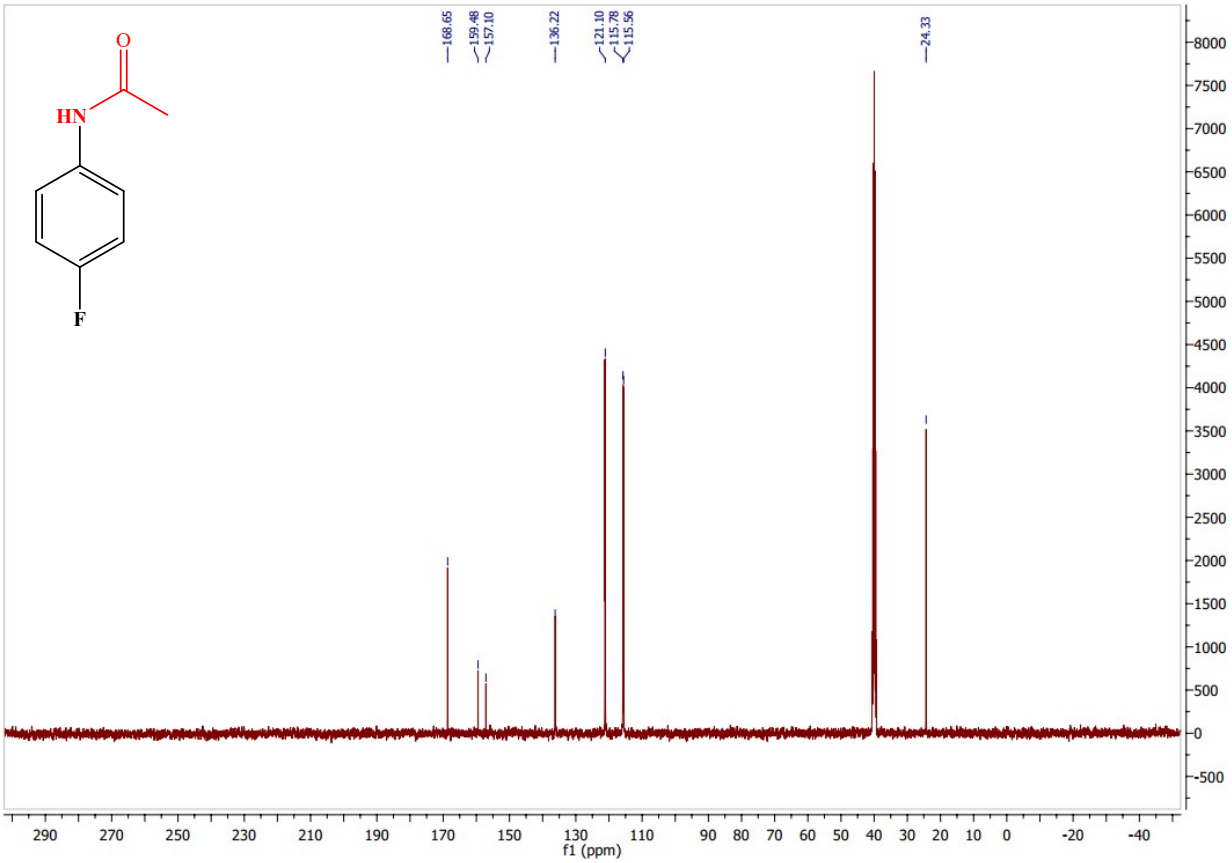

Fig S48:^{13}C-NMR (100 MHz; DMSO) of *N*-(4-Fluorophenyl)acetamide

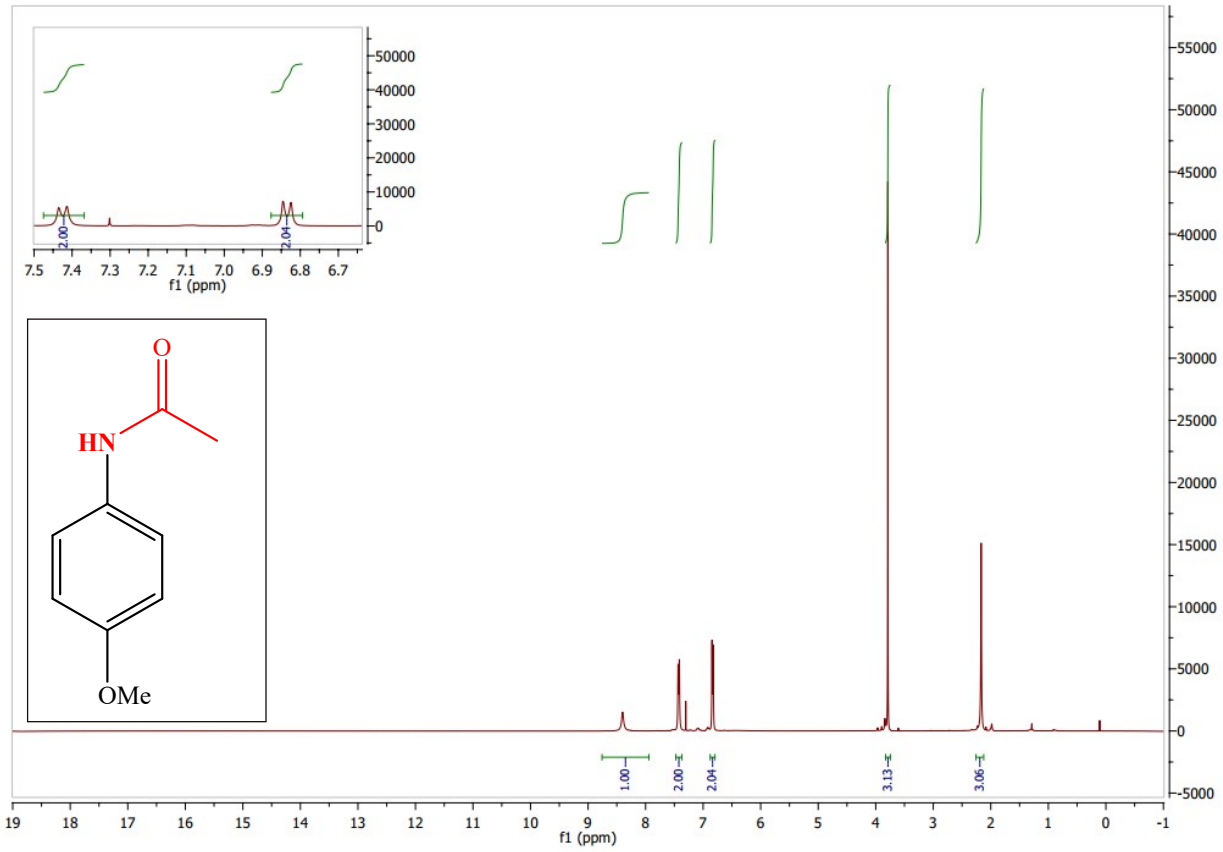

Fig S49:[1]H-NMR (400 MHz; $CDCl_3$) of *N*-(4-Methoyphenyl)acetamide

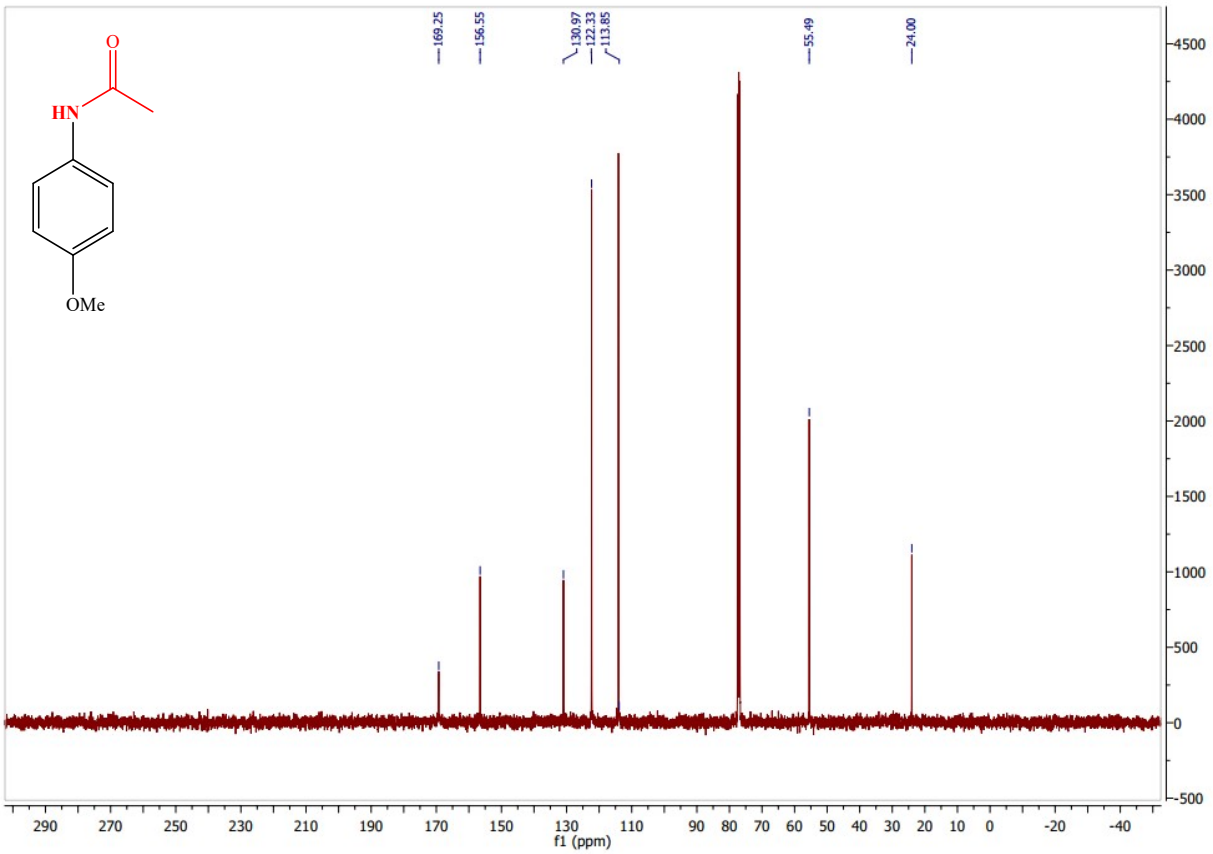

Fig S50:^{13}C-NMR (100 MHz; $CDCl_3$) of N-(4-Methoxyphenyl)acetamide

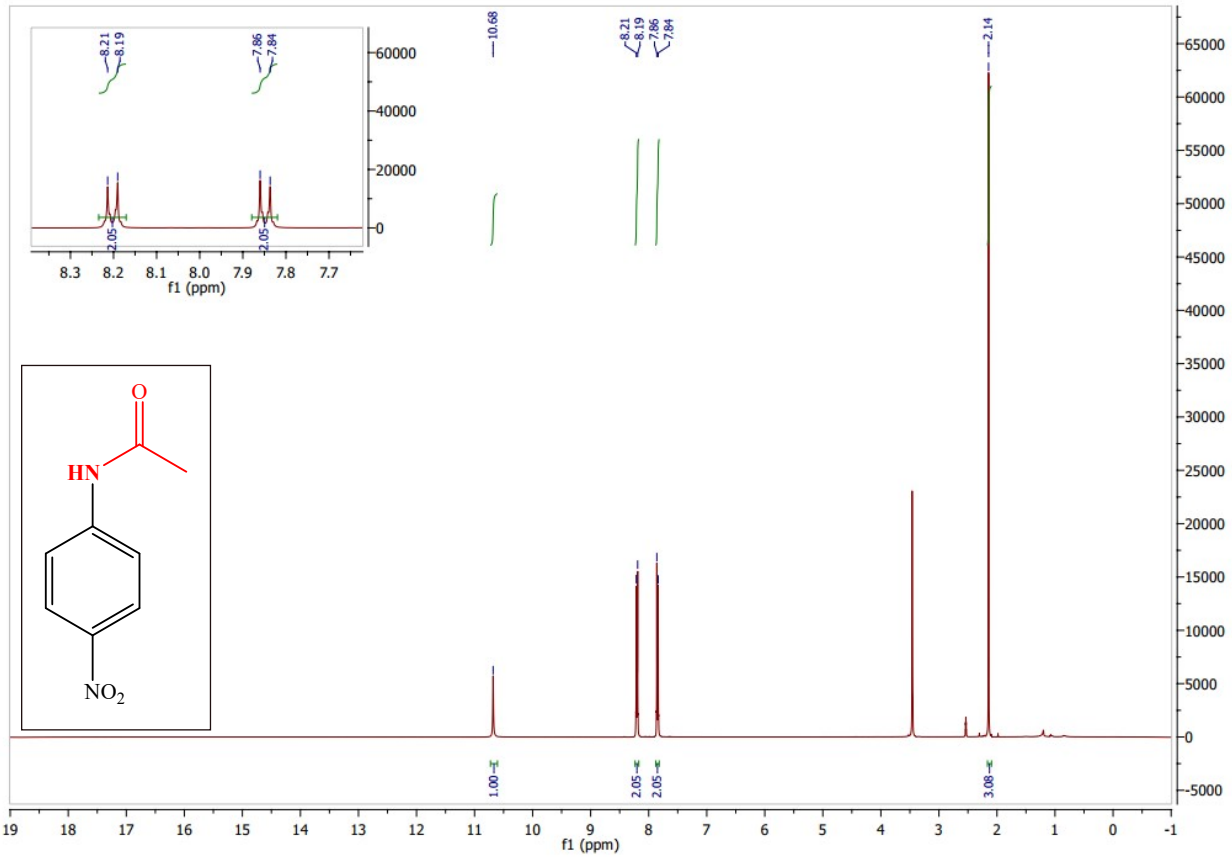

Fig S51:[1]H-NMR (400 MHz; DMSO) of *N*-(4-Nitrophenyl)acetamide

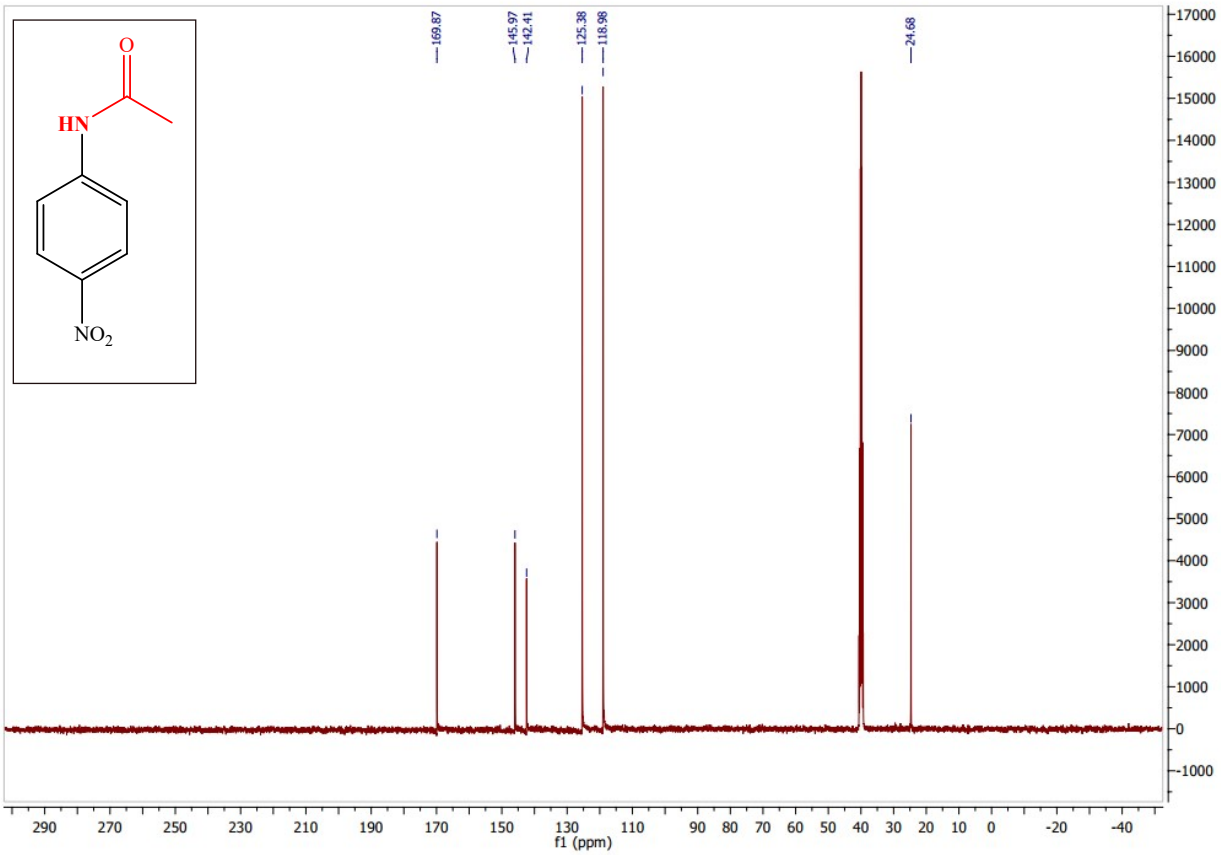

Fig S52:^{13}C-NMR (100 MHz; DMSO) of *N*-(4-Nitrophenyl)acetamide

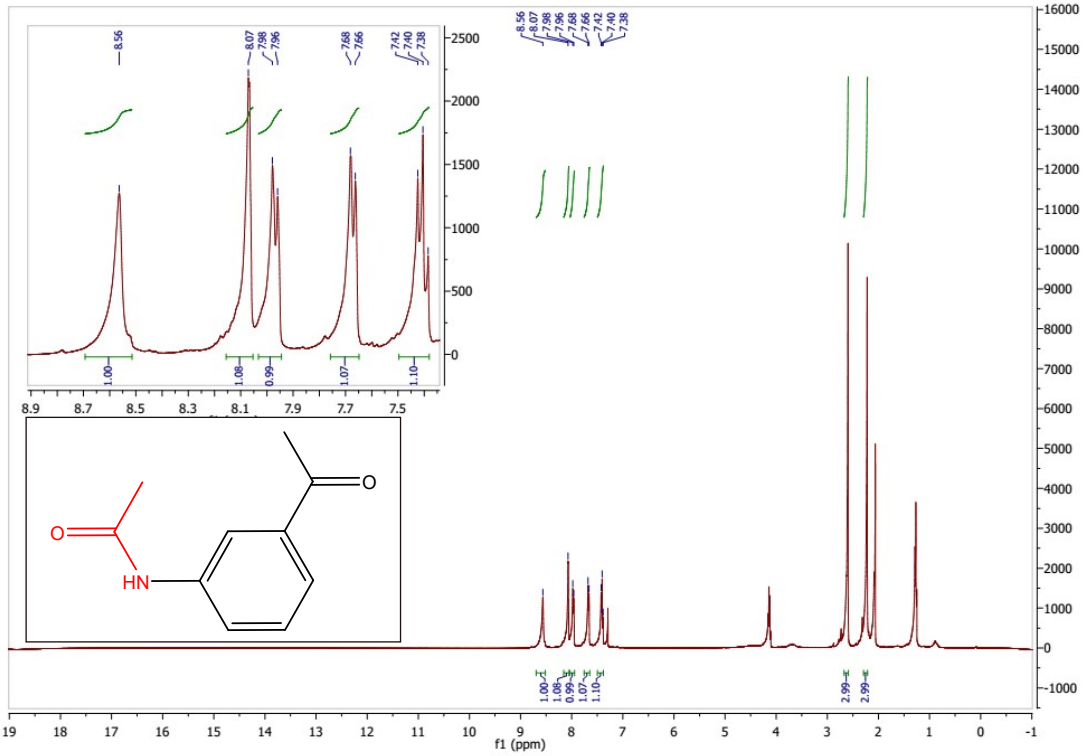

Fig S53:^{1}H-NMR (400 MHz; $CDCl_3$) of *N*-(3-Acetylphenyl)acetamide

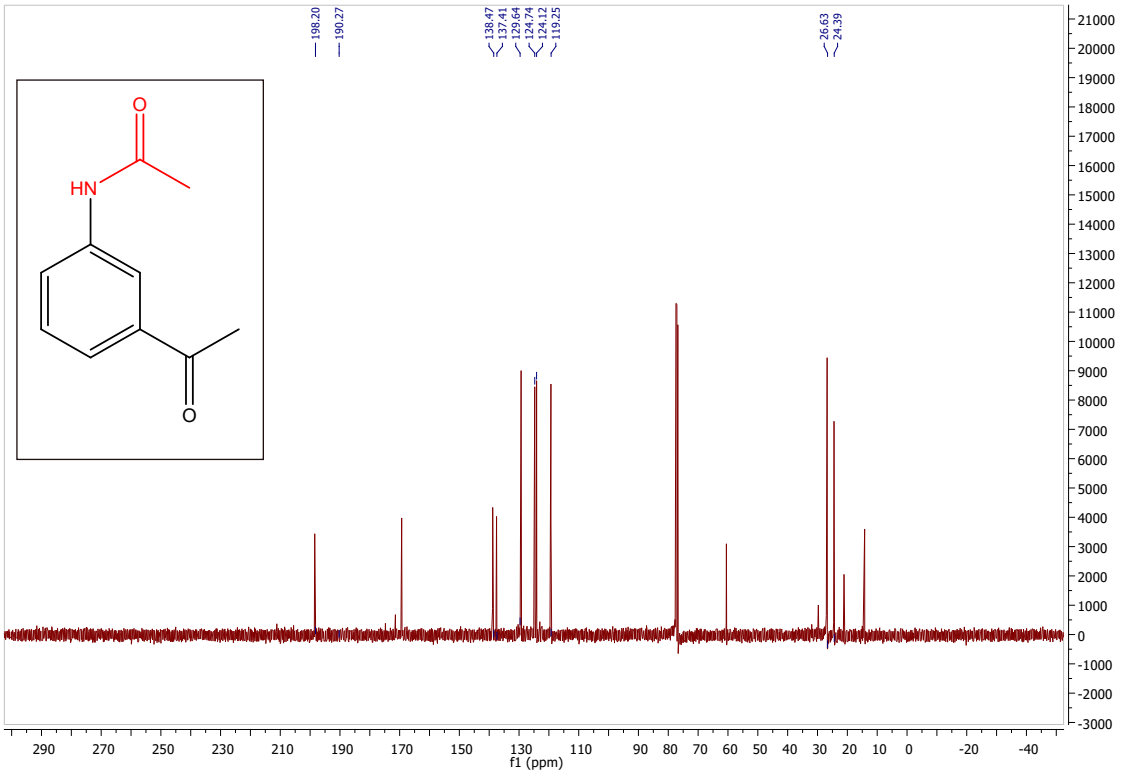

Fig S54:^{13}C-NMR (100 MHz; $CDCl_3$) of *N*-(3-Acetylphenyl)acetamide

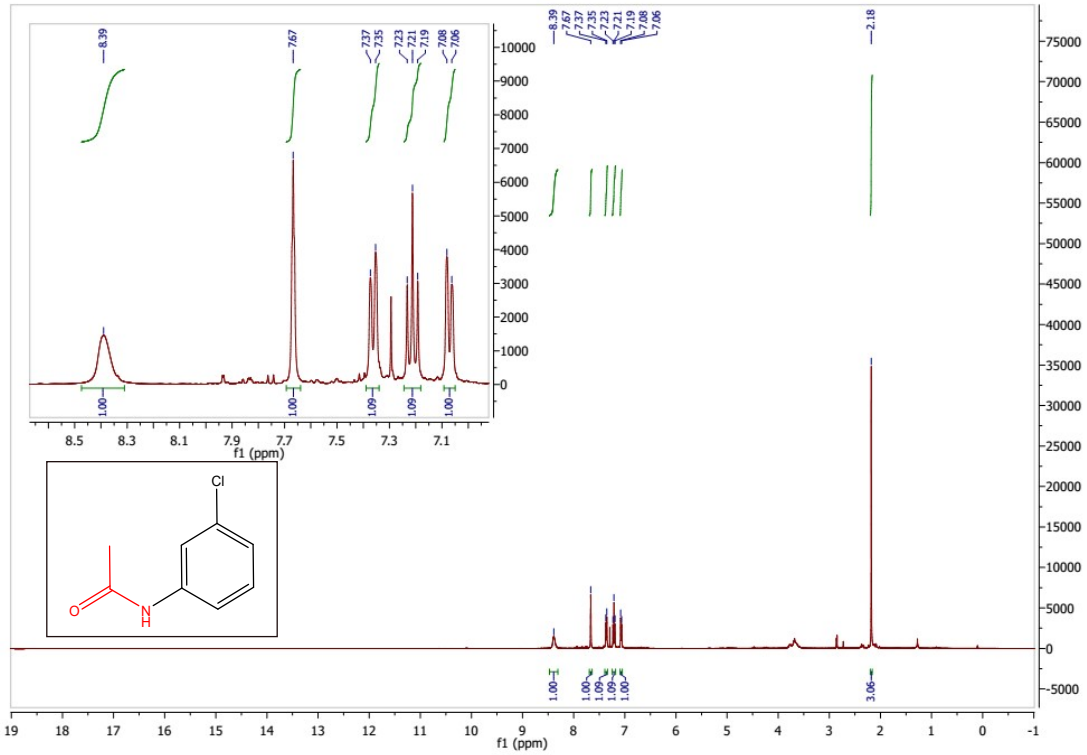

Fig S55:^{1}H-NMR (400 MHz; $CDCl_3$) of *N*-(3-Chlorophenyl)acetamide

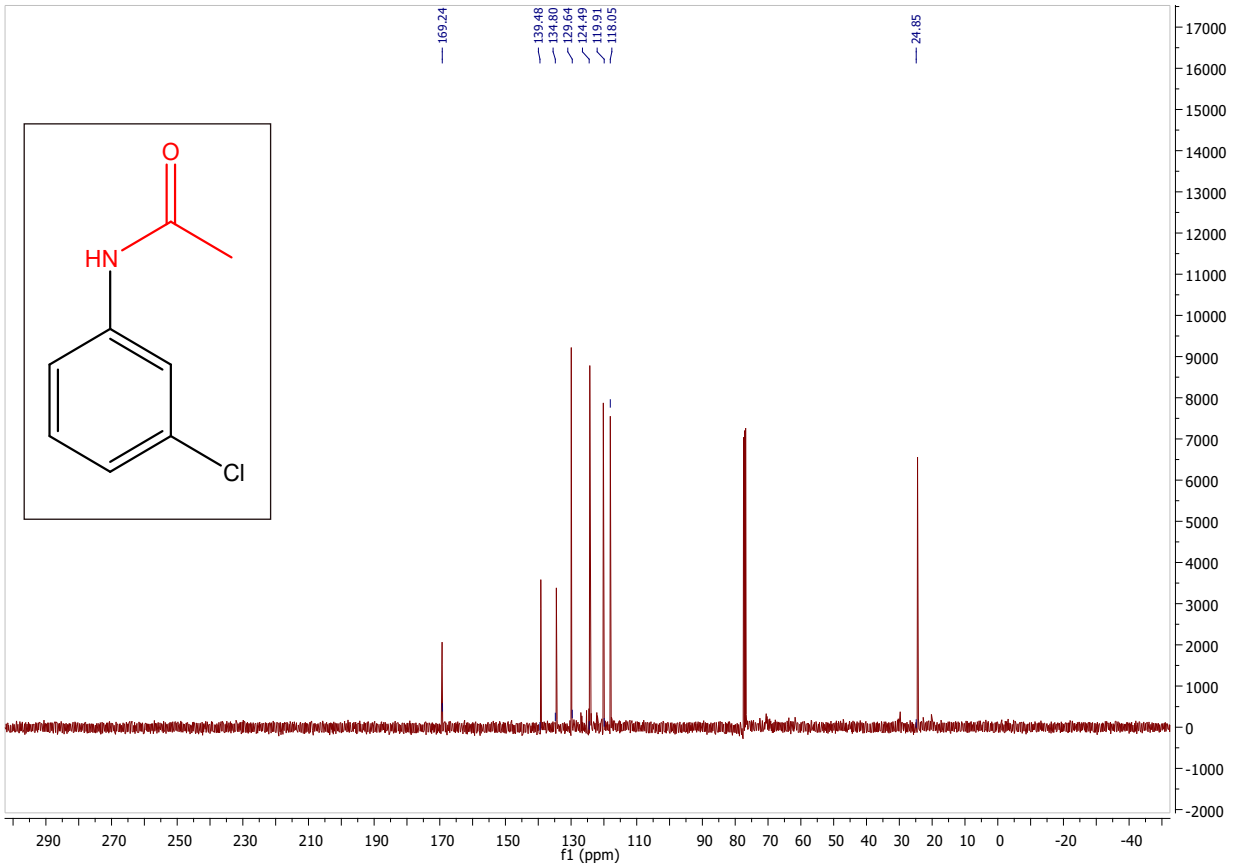

Fig S56:^{13}C-NMR (100 MHz; $CDCl_3$) of *N*-(3-Chlorophenyl)acetamide

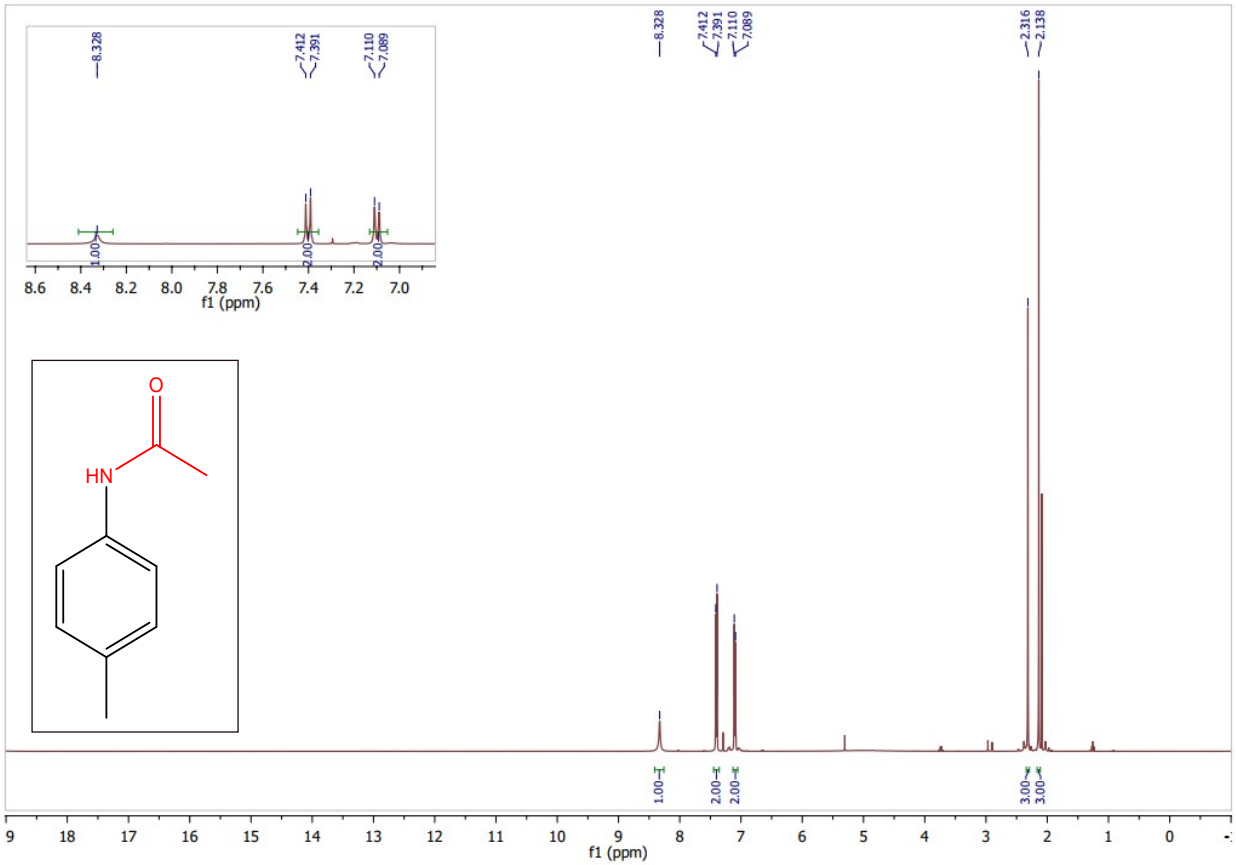

Fig S57:^{1}H-NMR (400 MHz; $CDCl_3$) of *N*-(p-Tolyl)acetamide

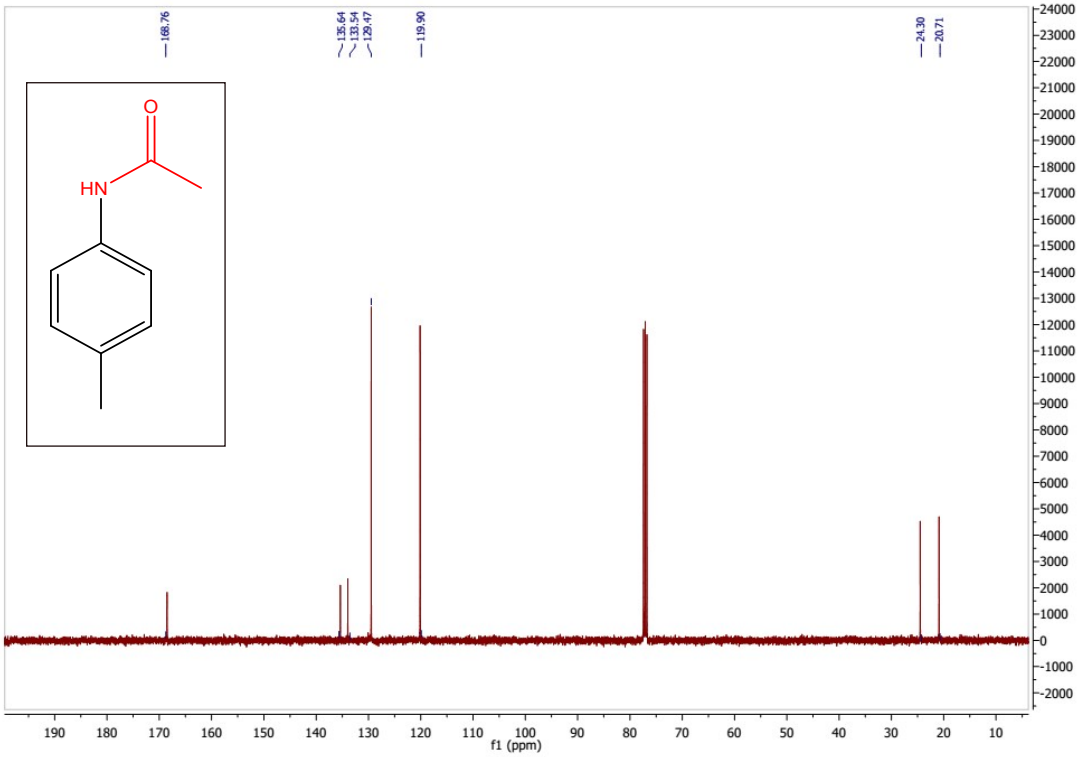

Fig S58:^{13}C-NMR (100 MHz; $CDCl_3$) of *N*-(p-Tolyl)acetamide