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# Supporting Information

## $Cu_2(BDC)_2(BPY)$-MOF: An Efficient and Reusable Heterogeneous Catalyst For The Aerobic Chan–Lam Coupling Prepared via Ball-milling Strategy

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## Materials and instruments

All reagents and starting materials including organic linker $H_2BDC$, metal salt $Cu(OAc)_2.H_2O$, 1,4-benzenedicarboxylate (BDC, 99%), 4,4'-bipyridine (BPY) were obtained from commercially available sources such as Sigma-Aldrich and Merck and used without any further purification. X-ray powder diffraction (XRD) patterns recorded using an X'pert MPD. The sample was characterized using a scanning electron microscope (SEM) with a ZEISS scanning electron microscope at 30 kV with gold coating. FT-IR spectra were recorded with a Shimadzu 8400s FT-IR spectrometer using potassium bromide pellets. Brunauer-Emmett-Teller (BET) surface area of the samples was determined from $N_2$ adsorption- desorption isotherms using a Quantachrome NovaWin2 analyzer. Transmission electron microscopy (TEM) was carried out using an EM10C-100 kV series microscope from the ZEISS Company, German and the actual loading of cupper was determined by Inductively Coupled Plasma (ICP) analysis on sequential plasma spectrometer, Shimadzu (ICPS-7000 ver. 2).

### Ball-milling Synthesis of the metal-organic framework $Cu_2(BDC)_2(BPY)$

A mixture of $Cu(OAc)_2.H_2O$ (0.6 mmol), $H_2BDC$ (0.6 mmol) and BPY (0.3 mmol) with molar ratio of 1:1:0.5 were ball-milled vigorously at 30Hz without any solvent at room temperature for 2 h. The obtained green powder was washed with DMF (2*10 mL). Solvent exchange was carried out with methanol (2*10 mL) at room temperature. To remove the guest molecules of MOFs, obtained powder was treated by heating under vacuum at 130 °C for 12 h. The resulting green powder was isolated with 96% yield and characterized by several techniques including PXRD, SEM, TEM, BET, CHN, ICP and FT-IR.

### General procedure for the N-Arylation of Aromatic amines

To a mixture of $Cu_2(BDC)_2BPY$ (20 mg) and aromatic amine (1 mmol) in $H_2O$/MeOH (4 mL, 1:1), phenylboronic acid (2 mmol) was added and the resultant mixture was stirred at room temperature for 1 h. After completion of the reaction (monitored by TLC) catalyst was filtered and washed by $H_2O$/methanol (2 ml, 1:1). Then, the filtrate was diluted with water (10 mL),

extracted with ethyl acetate (2×10 ml), and the combined extracts were dried with Na2SO4. The product was purified by column chromatography (silica gel, n-hexane/EtOAc) to afford diarylamines 3a–h. structure of all product was characterized by melting point and $^{1}$H-NMR spectra.

**Diphenylamine (3a):**

White solid, mp 51-52 °C; yield: 78 %; $^1$H NMR (500 MHz, $CDCl_3$) δ = 7.25-7.28 (m, 4H, CH of Ar), 7.05-7.07 (m, 4H, CH of Ar), 6.92-6.94 (m, 2H, CH of Ar), 5.65 (s, 1H, NH).

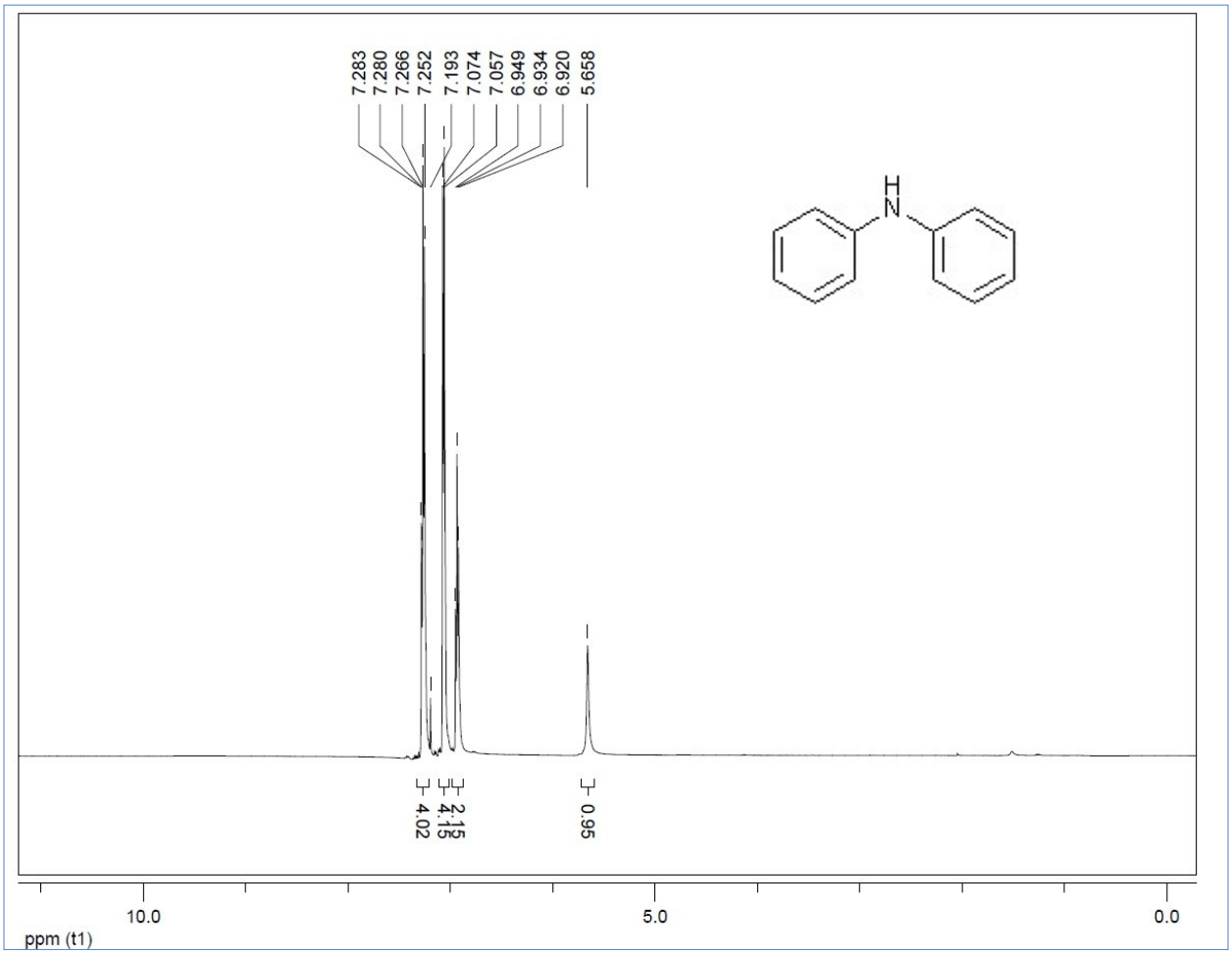


**Fig S1**. $^1$H-NMR of diphenylamine

**4-Methyl-*N*-Phenylaniline (3b)**:

White solid; mp 86-89 $^{o}$C; yield: 80 %; $^{1}$H NMR (500 MHz, $CDCl_3$) δ = 7.51 (t, J = 9.8 Hz, 2H, CH of Ar), 7.26-7.34 (m, 6H, CH of Ar), 7.12-7.17 (m, 1H, CH of Ar), 5.85 (s, 1H, NH), 2.57 (s, 3H, $CH_3$).

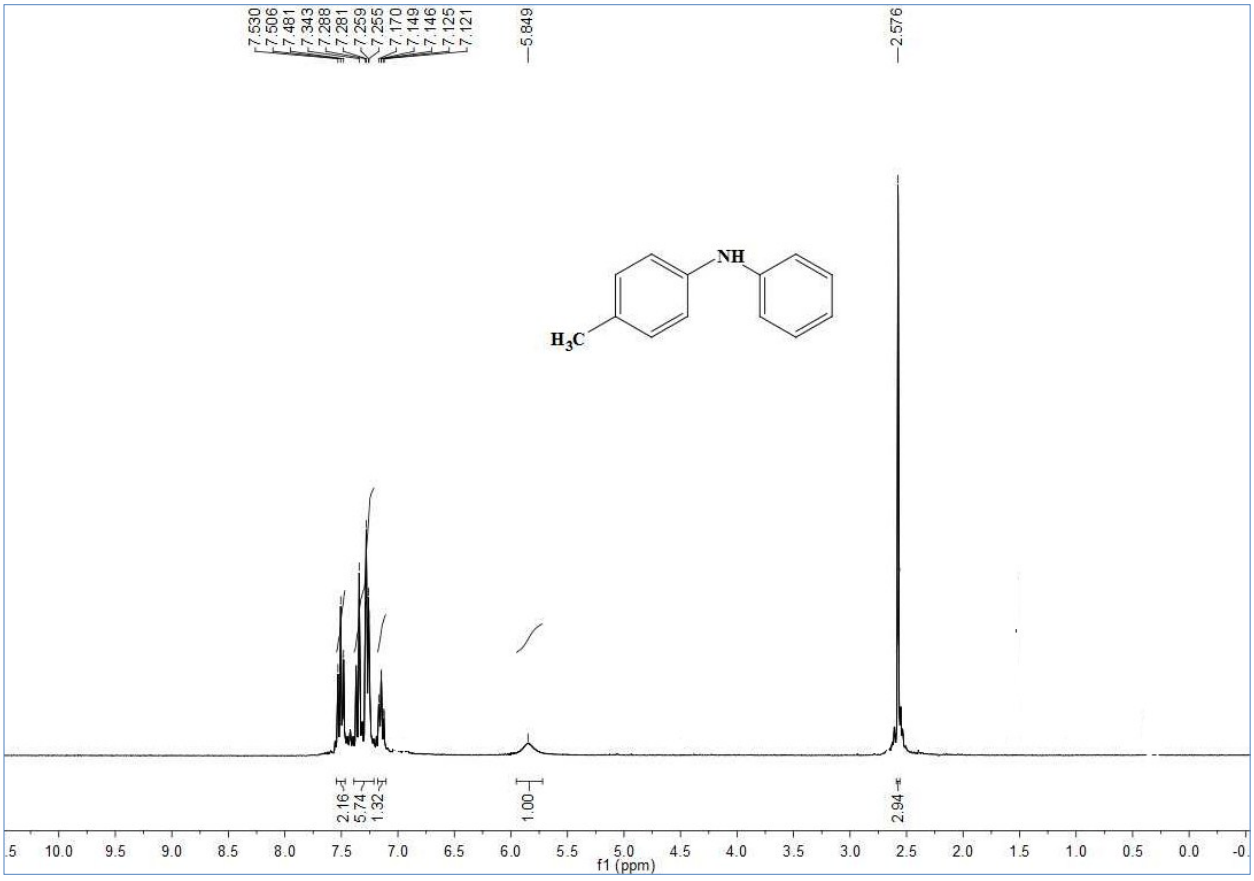


**Fig S2**. $^{1}$H-NMR of 4-Methyl-*N*-phenylaniline

**4-Nitro-*N*-Phenylaniline (3c)**:

Brown powder; mp 130-133 °C; yield: 81 %; $^1$H NMR (500 MHz, $CDCl_3$) δ = 7.63-7.69 (m, 2H, CH of Ar), 7.53-7.58 (m, 1H, CH of Ar), 7.45-7.48 (m, 2H, CH of Ar), 7.28-7.35 (m, 3H, CH of Ar), 7.16 (d, J = 10 Hz, 1H, CH of Ar), 6.04 (s, 1H, NH).

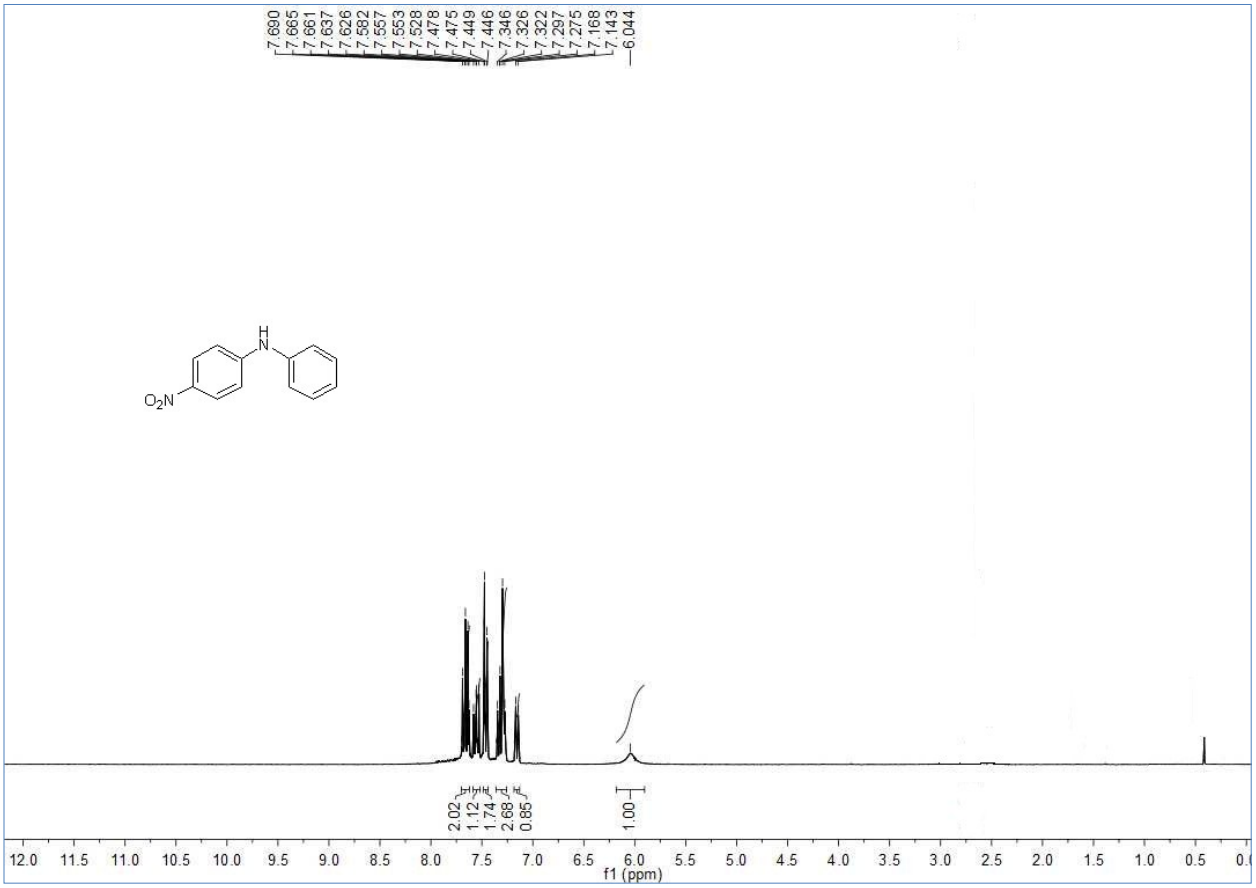


**Fig S3**. $^1$H-NMR of 4-nitro-*N*-phenylaniline

**4-Bromo-*N*-Phenylaniline (3d):**

Pale yellow; mp 85-89 °C, yield: 75 %; $^1$H NMR (500 MHz, $CDCl_3$) δ = 7.26-7.28 (m, 2H, CH of Ar), 7.21-7.22 (m, 2H, CH of Ar), 6.98-6.99 (m, 2H, CH of Ar), 6.89-6.91 (m, 1H, CH of Ar), 6.86-6.88 (m, 2H, CH of Ar), 5.61 (s, 1H, NH).

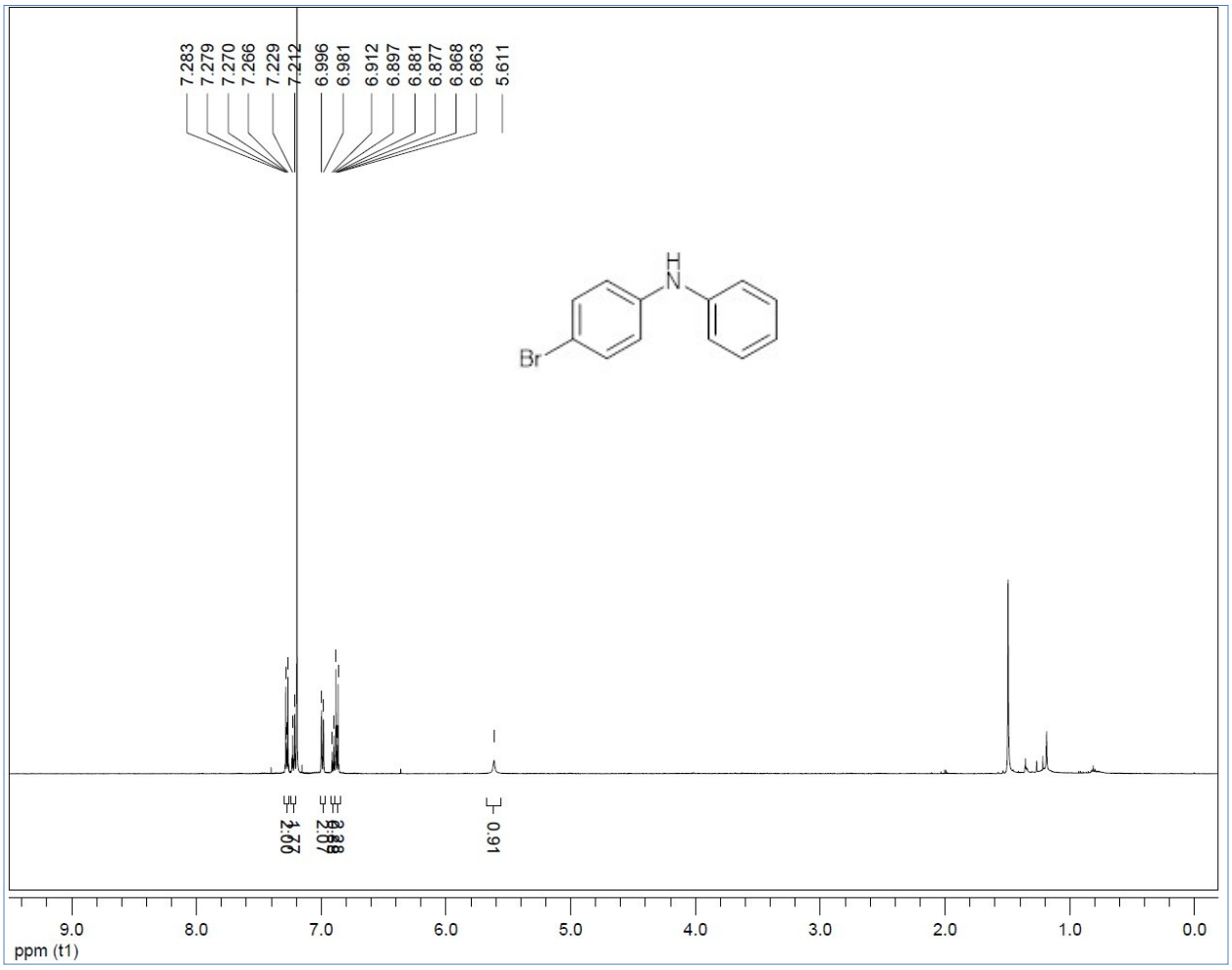


**Fig S4**. $^1$H-NMR of 4-bromo-*N*-phenylaniline

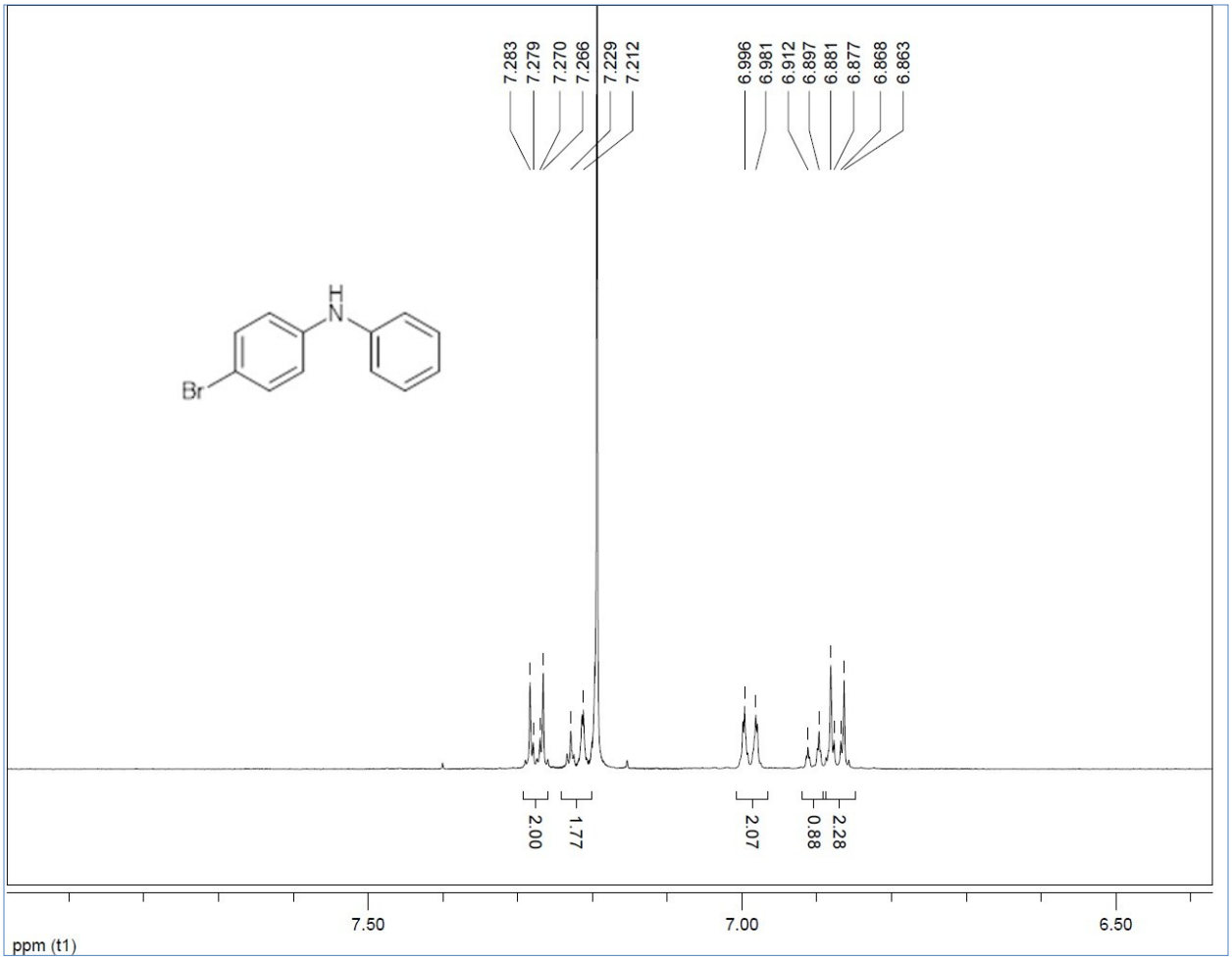


**Fig S5**. Expanded $^{1}$H-NMR spectrum of 4-bromo-*N*-phenylaniline

**4-Chloro-*N*-Phenylaniline (3e)**:

Yellow oil; yield: 79 %; $^1$H NMR (500 MHz, $CDCl_3$) δ = 7.24-7.22 (m, 2H, CH of Ar), 7.03-6.95 (m, 6H, CH of Ar), 6.91-6.87 (m, 1H, CH of Ar), 5.56 (s, 1H, NH)

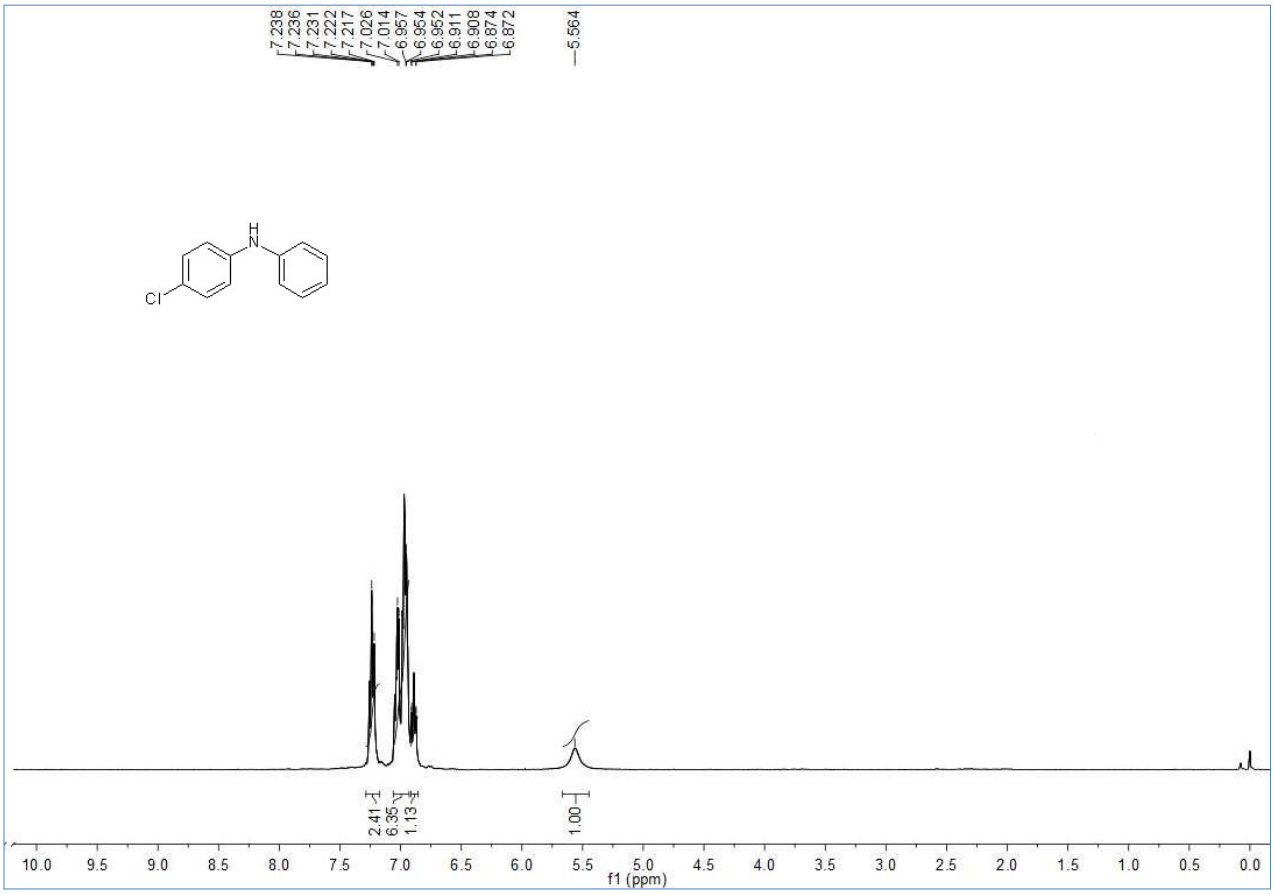


**Fig S6**. $^1$H-NMR of 4-chloro-*N*-phenylaniline

**N-phenylpyrimidin-2-amine (3f):**

White solid, mp 113-115 °C; yield: 82 %; $^1$H NMR (500 MHz, $CDCl_3$) δ = 8.35 (d, 2H, J= 5Hz, CH of Ar), 7.54 (d, J = 7.5 Hz, 2H, CH of Ar), 7.26-7.29 (m, 2H, CH of Ar), 7.03 (s, 1H, NH), 6.97-7.00 (m, 1H, CH of Ar), 6.64-6.66 (t, J = 9.5 Hz, 1H, CH of Ar).

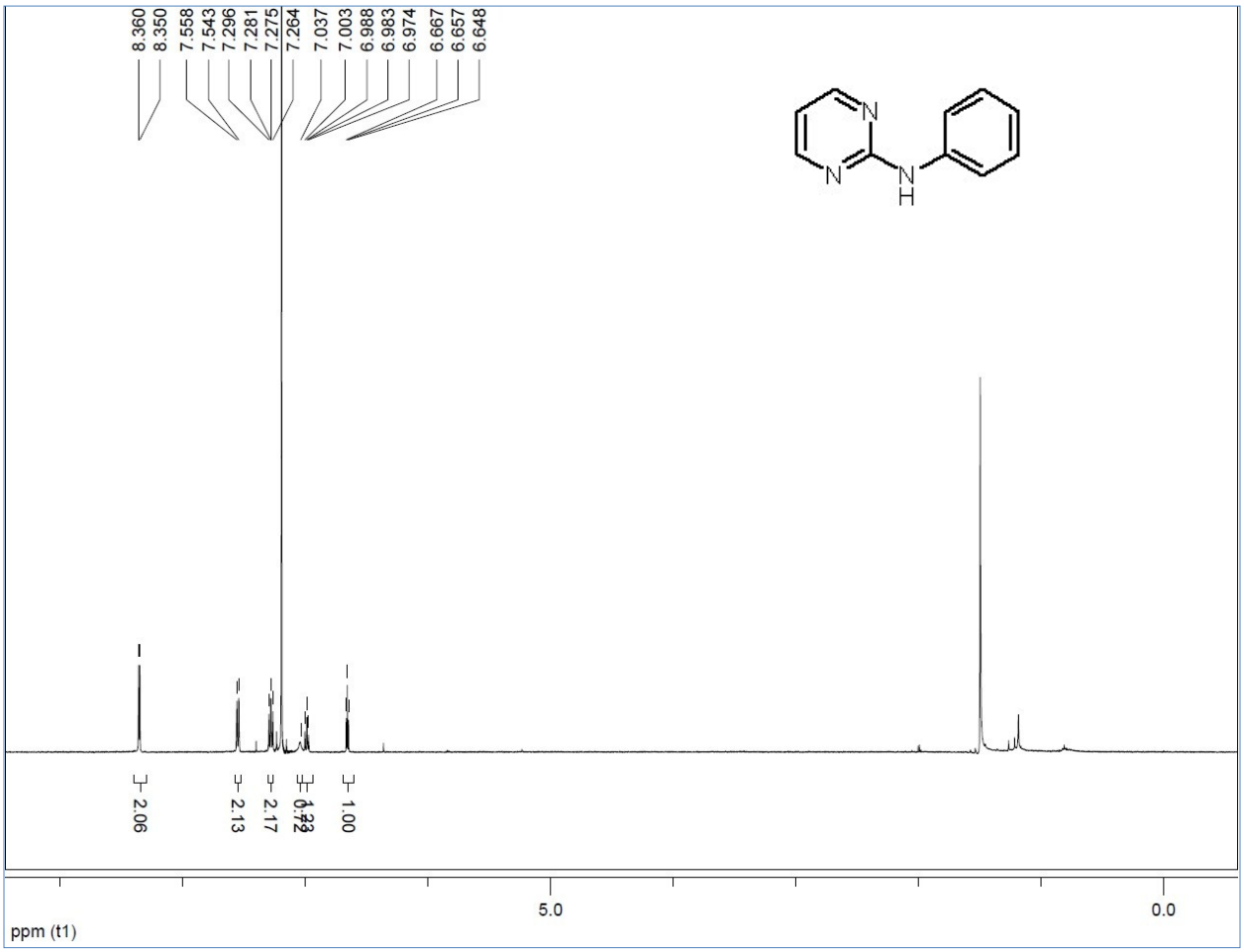


**Fig S7**. $^1$H-NMR of N-phenylpyrimidin-2-amine

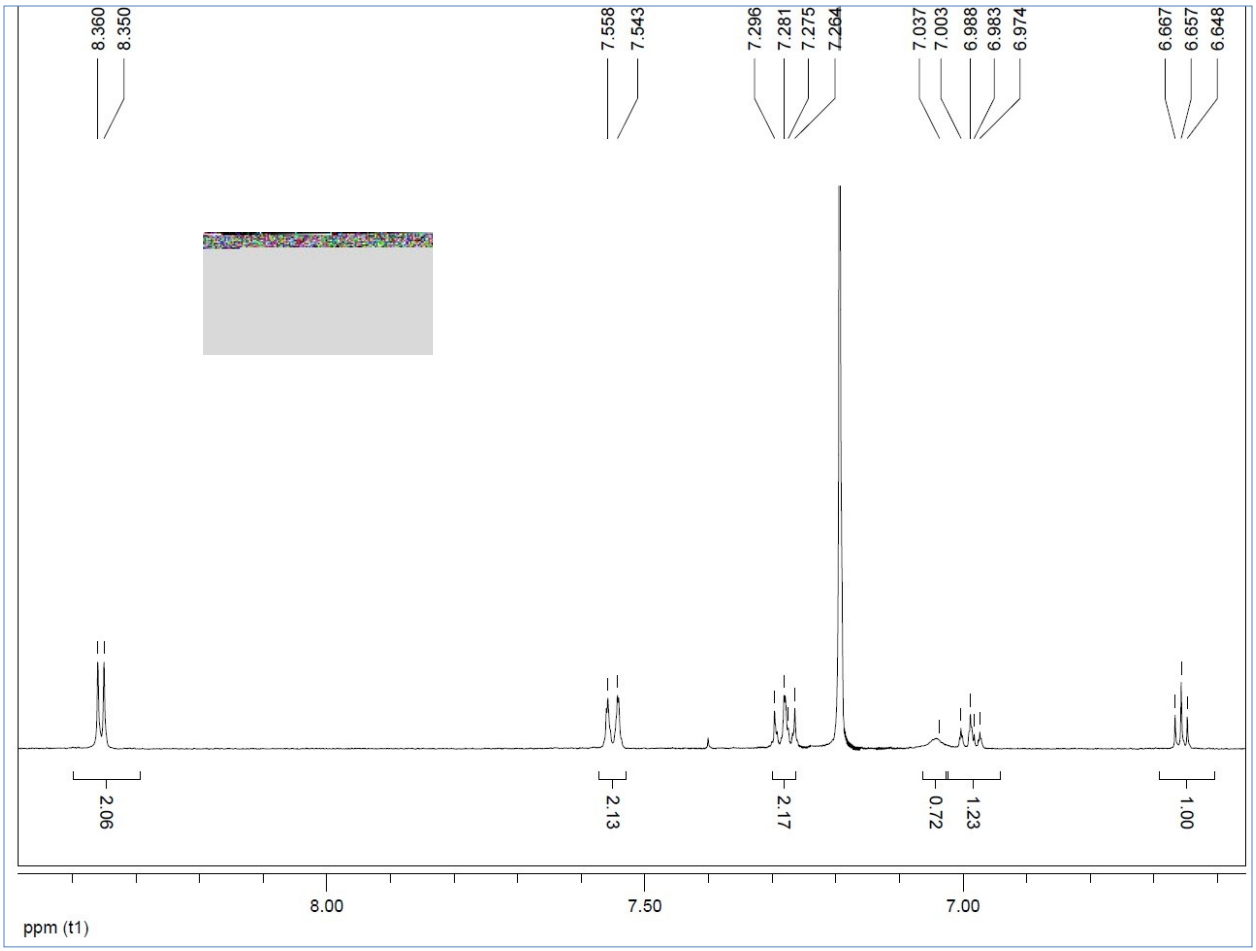


**Fig S8**. Expanded $^{1}$H-NMR spectrum of N-phenylpyrimidin-2-amine

***N*-Phenylnaphthalen-1-Amine (3g)**:

Reddish-violet solid, mp 58 - 60 °C; yield: 84 %; $^1$H NMR (500 MHz, $CDCl_3$) δ = 7.97 (d, J = 8 Hz, 1H, CH of Ar), 7.82 (d, J = 8 Hz, 1H, CH of Ar), 7.52 (d, J = 7.5 Hz, 1H, CH of Ar),7.40-7.47 (m, 2H, CH of Ar), 7.31-7.36 (m, 2H, CH of Ar), 7.19-7.23 (m, 2H, CH of Ar), 6.94 (d, J = 8 Hz, 2H, CH of Ar), 6.87 (t, J = 7 Hz, 1H, CH of Ar), 5.88 (s, 1H, NH).

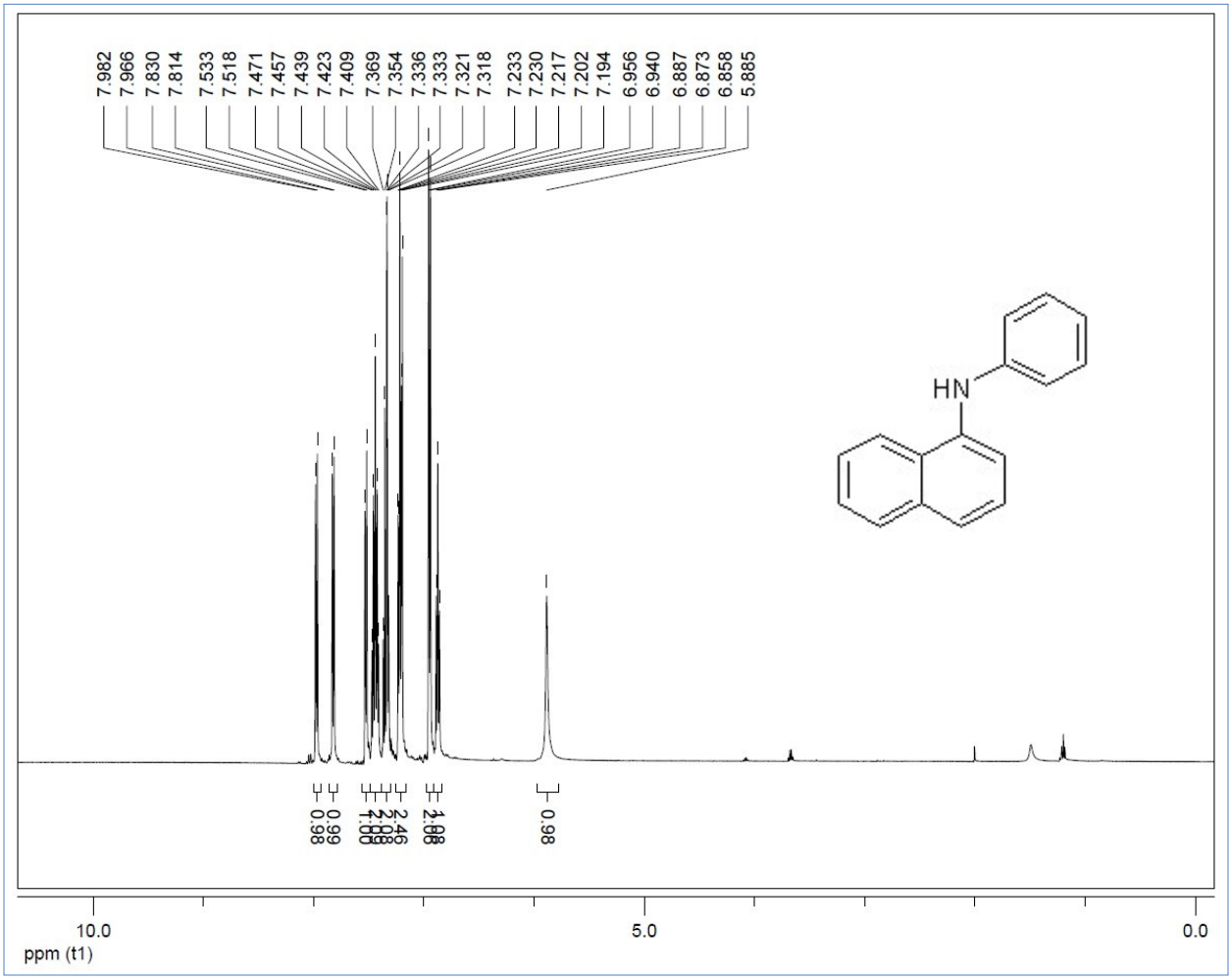


**Fig S9**. $^1$H-NMR of *N*-phenylnaphthalen-1-amine

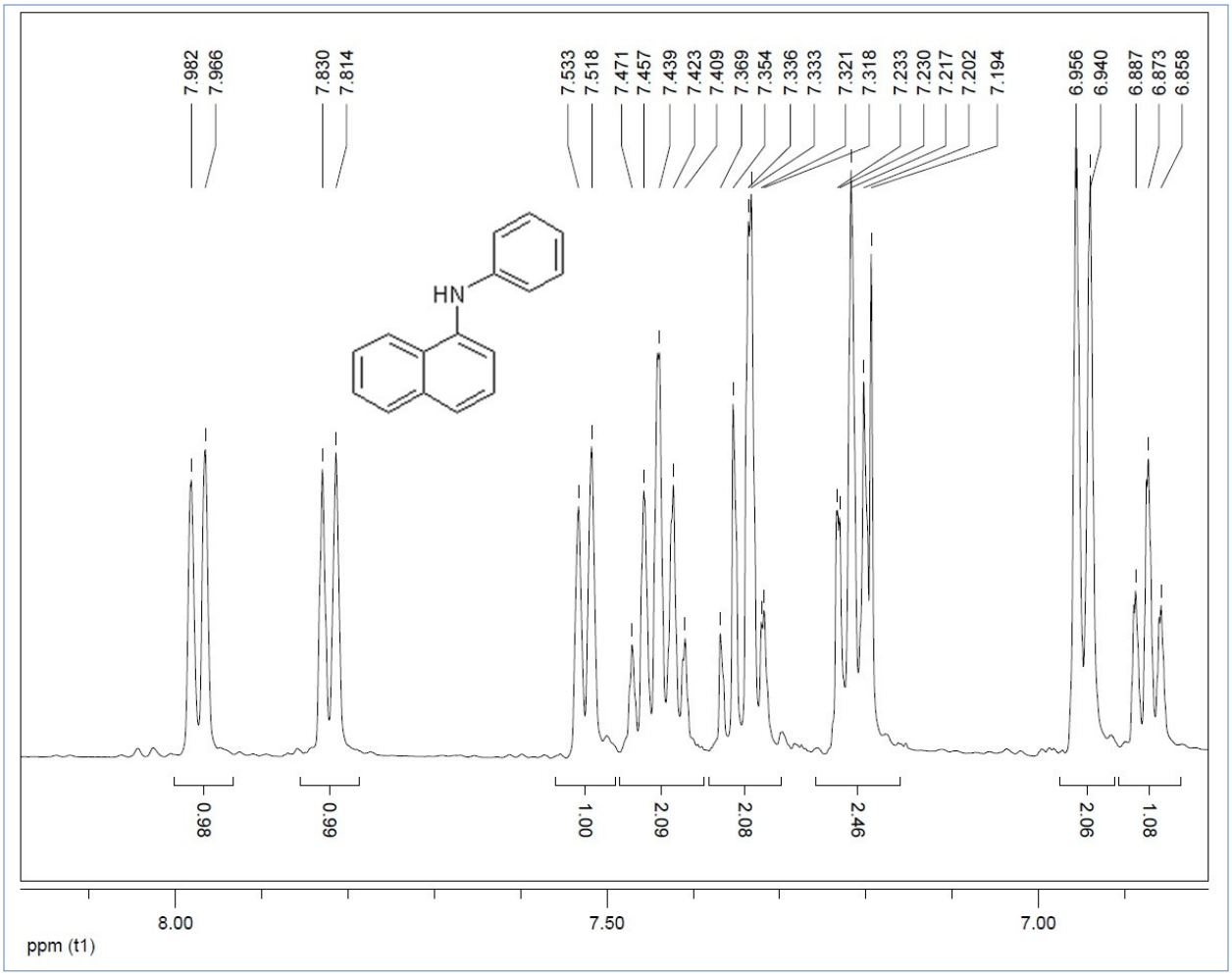


**Fig S10**. Expanded $^{1}$H-NMR spectrum of *N*-phenylnaphthalen-1-amine