

## **Supporting Information**

### **TiO<sub>2</sub> immobilized Ru(II) polyazine complex: a visible-light active photoredox catalyst for oxidative cyanation of tertiary amines.**

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<sup>1</sup>HNMR and <sup>13</sup>CNMR of the products

## 1.0 General:

### 1.1 Materials

2,2' bipyridine (99%), ruthenium chloride trihydrate, 1, 10 phenanthroline 5-amine(97%), 2, 2' bipyrimidine(95%), were purchased from Sigma Aldrich. Titanium (IV) ethoxide, 3-chloro-propyltrimethoxysilane (97%), ammonium hexafluorophosphate(99.9%) were procured from Alfa Aesar and used as received. All other chemicals were of analytical grade and used without further purification.

### 1.2 Techniques used

XRD Pattern was collected using a Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu K $\alpha$  radiation ( $\lambda= 0.15418$  nm). Sample was evenly spread on glass slide and analysed after drying well. Fourier Transform Infrared Spectroscopy (FT-IR) analysis of sample in KBr pellets was conducted by Perkin–Elmer Spectrum RX-1 IR spectrophotometer. Absorption spectra(UV-Vis) of ruthenium macromolecular unattached homogeneous complexes were collected in acetonitrile with a Perkin Elmer lambda-19 UV-VIS-NIR spectrophotometer using a 10 mm quartz cell. Solid spectra of nano-TiO $_2$  and ruthenium complex attached TiO $_2$  were recorded by using BaSO $_4$  as a reference. Morphology and EDX of catalyst was determined using Scanning electron microscopy (SEM) Jeol Model JSM-6340F. For SEM analysis aqueous dispersion of samples were deposited on glass slide. Transmission electron microscopy (HR-TEM) images with EDX data of TiO $_2$  immobilized ruthenium photocatalyst **2** on carbon coated copper grid was extracted using FEI-TecnaiG $^2$  Twin TEM operating at an acceleration voltage of 200 kV. Thermo gravimetric analyses (DT-TGA) curve for determining thermal stability of photocatalyst was plotted using a thermal analyzer TA-SDT Q-600 from 40 to 900 °C with heating rate of 10

°C/min under the nitrogen flow. Surface properties (surface area,  $S_{\text{BET}}$ ; pore volume, pore diameter) of samples were executed by  $\text{N}_2$  adsorption–desorption isotherms at 77 K, Micromeritics ASAP2010).  $^1\text{H-NMR}$  and  $^{13}\text{C NMR}$  of homogenous ruthenium complex in  $\text{DMSO } d_6$  was examined at 500 MHz by using Bruker Avance-II 500 MHz instrument. Ruthenium wt% in catalyst was calculated using Inductively coupled plasma Atomic emission spectrometer (ICP-AES, DRE, PS-3000UV, Leeman Labs Inc, USA). 0.1 g of sample was digested in minimum amount of conc.  $\text{HNO}_3$  with heating, and volume made up to 10 ml.

## 2.0 Synthesis of photocatalyst 2

### 2.1 Preparation of Nanocrystalline $\text{TiO}_2$

In a typical experiment, titanium (IV) ethoxide (5 g, 22 mmol) was added to 50 ml ethanol and stirred for 15 min. Then added distilled water (approx 25ml) drop wise for the period of one hour under vigorous stirring. After that concentrated nitric acid (3-5 ml) was added drop wise and the resulting solution was refluxed for 10 h. The solvent was removed under reduced pressure to give nanocrystalline  $\text{TiO}_2$ , which was further calcined at 500 °C for one h. The synthesized nanoparticles were crushed finely for the further reaction steps.

### 2.2. Functionalization of $\text{TiO}_2$ nanoparticles with 1,10-phenanthroline 5-amine.

Nanocrystalline  $\text{TiO}_2$  was functionalized with 3-chloropropyltrimethoxysilane (CPTS) by refluxing it in toluene at 110 °C for 24 h. After completion, the functionalized  $\text{TiO}_2$  was separated with centrifugation and washed three times with ethanol and dried at 50 °C for 6 h. For further modification, the resulting 3-chloropropyltrimethoxysilylated  $\text{TiO}_2$  was treated with 1, 10-phenanthroline-5-amine (0.8 g, mmol), triethylamine (2 ml) in ethanol (50 ml) and refluxed

for 18 h. Finally the product was separated with centrifugation and washed three times with ethanol.

### 2.3 Synthesis of $[\text{Ru}(\text{bpy})_2(\text{bpm})]\text{PF}_6$

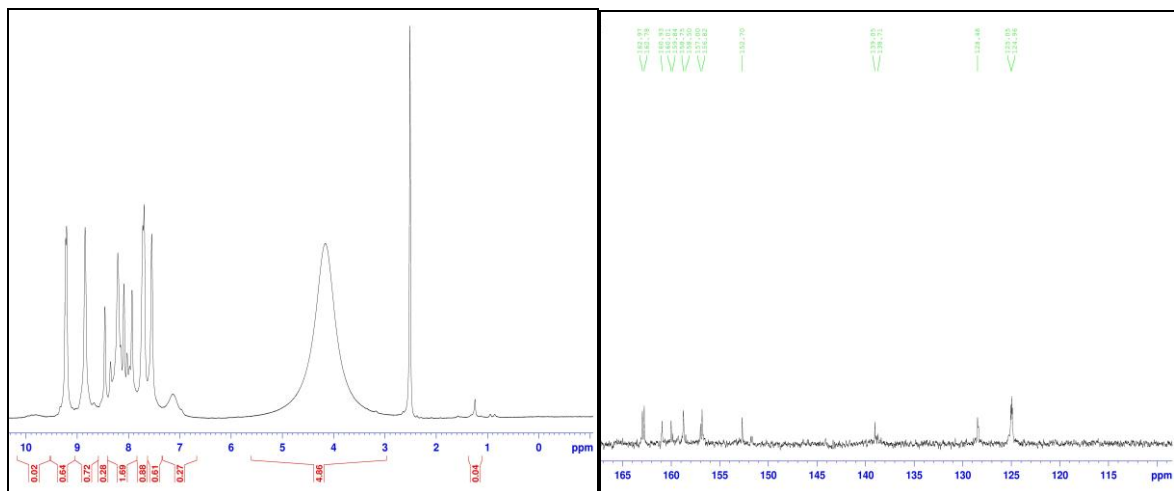
$\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (1.0 g, 2.0 mmol) and 2-2' bipyrimidine (0.98 g, 6.2 mmol) were added to deoxygenated 2:1 v/v ethanol-water mixture (50 ml). The resulting mixture was refluxed for 3h with continuous stirring. After cooling the reaction mixture to room temperature, saturated aqueous solution of  $\text{NH}_4\text{PF}_6$  was added slowly. The solution was kept at 0 °C for better precipitation. The resultant precipitate was isolated by membrane vacuum filtration and impurities were removed by dissolving precipitate in acetone and re-precipitation with diethyl ether. Further purification was carried out with column chromatography using 3/2 v/v toluene/acetonitrile as mobile phase and adsorption alumina as stationary phase. UV/Vis absorbance was found at  $\lambda_{\text{max}}$  value 245, 276 and 440nm.

### 2.4 Synthesis of $[(\text{bpy})_2\text{Ru}(\text{bpm})\text{RuCl}_2(\text{bpm})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$ complex

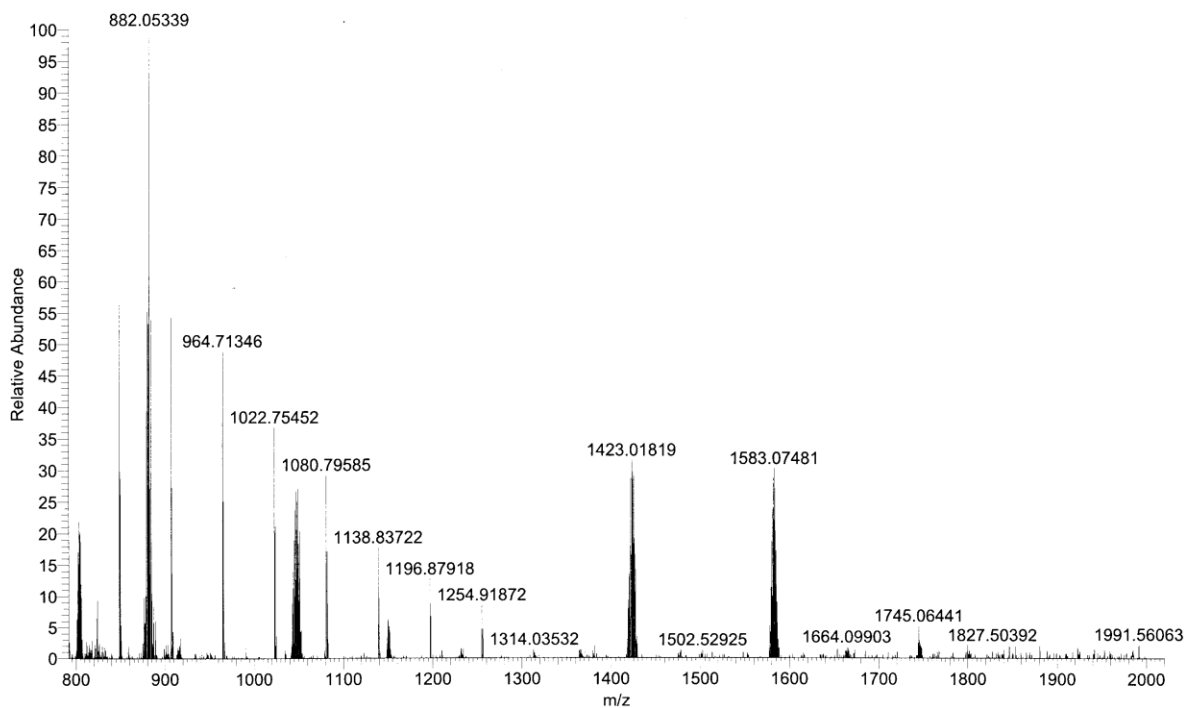
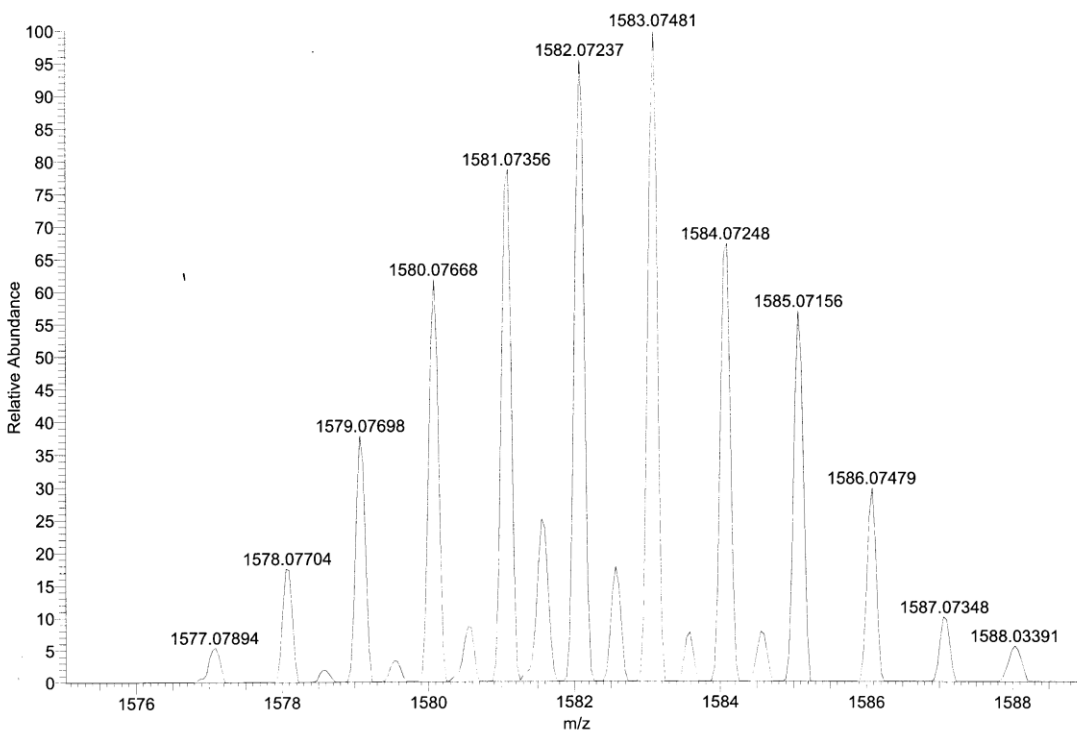
A mixture containing  $[\text{Ru}(\text{bpy})_2(\text{bpm})](\text{PF}_6)_2$  (0.865 mmol),  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (0.4605 mmol) and  $\text{LiCl}$  (4.715 mmol) in 95 % ethanol (50 ml of 95% was refluxed for 24 h with continuous stirring. After cooling the solution to room temperature, saturated aqueous solution of  $\text{NH}_4\text{PF}_6$  was added and the resulting solution was kept at 0 °C for 12 h for precipitation. The resultant precipitate of the crude product was isolated by vacuum filtration and dissolved in minimum amount of acetone, re-precipitated by adding diethyl ether. Subsequently, the product was purified by column chromatography using alumina as a stationary phase and 2:1 (v/v) toluene/acetonitrile as an eluent. The solvent was removed under reduced pressure and the resulting product was dissolved in acetone, re-precipitated with diethyl ether and isolated by

filtration, dried under vacuum. The successful synthesis of the complex was confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR (Supporting Fig. S1) and ESI-MS analysis (Supporting Fig. S2). The UV absorbance of the as-prepared complex was found at  $\lambda_{\text{max}}$  425nm and 260 nm.

**Supporting Fig S1:** a)  $^1\text{H}$  NMR and b)  $^{13}\text{C}$  NMR of  $[(\text{bpy})_2\text{Ru}(\text{bpm})\text{RuCl}_2(\text{bpm})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$  complex



### Supporting Fig S2: Mass Spectra of [(bpy)<sub>2</sub>Ru(bpm)RuCl<sub>2</sub>(bpm)Ru(bpy)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> complex

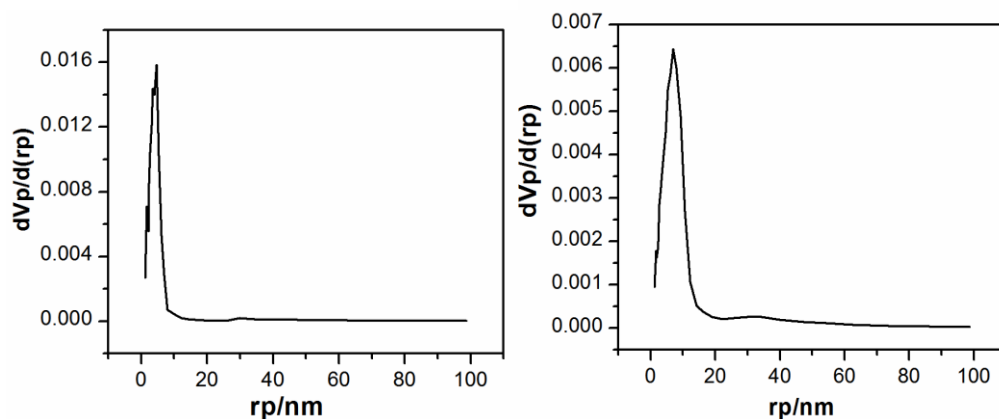


## 2.5 Immobilization of $[(bpy)_2Ru(bpm)RuCl_2(bpm)Ru(bpy)_2](PF_6)_4$ to $TiO_2$ support.

Chemically functionalized phenanthroline ligand containing  $TiO_2$  nanoparticles were added with  $[(bpy)_2Ru(bpm)RuCl_2(bpm)Ru(bpy)_2](PF_6)_4$  in 95% ethanol and the resulting suspension were refluxed for 24 h under nitrogen atmosphere. The resulting heterogeneous green ruthenium polyazine immobilized  $TiO_2$  was collected with centrifugation and washed several times with ethanol, dried under vacuum. Elemental analysis of  $TiO_2$  supported catalyst gave C% 7.38, N% 1.76, and H% 0.46. ICP-AES of catalyst showed ruthenium content of catalyst was 1.17 wt% that was in conformity for successful loading of complex to  $TiO_2$ . Further UV-Vis spectra show wide peaks at 480nm and 254 nm.

## 3.0 Characterization of the photocatalyst 1

### Supporting Fig. S3: Pore Diameter graph

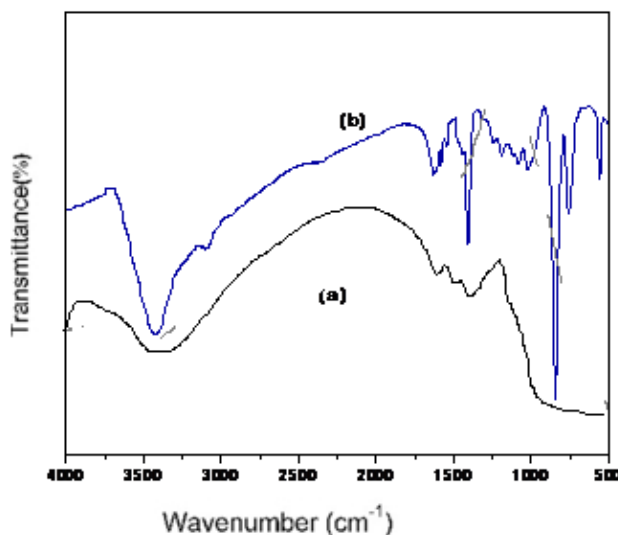


### FTIR

In the FTIR spectrum of  $TiO_2$  (supporting Fig. S4a) a broad peak at  $3448.80cm^{-1}$  revealed the presence of hydroxyl groups on the support, which were further functionalized for the immobilization of the ruthenium complex. Covalent coupling of CPTS with hydroxyl groups

of TiO<sub>2</sub> was confirmed by appearance of new vibrational signatures in the region of 2800-3000 cm<sup>-1</sup> attributed to methylene and methyl groups. Furthermore, presence of strong vibrational peaks corresponding to the C=N at 1637.38 cm<sup>-1</sup> confirmed the immobilization of ruthenium complex to the TiO<sub>2</sub> support (Supporting Fig. 4b).

**Supporting Fig. S4:** FTIR spectra of a) TiO<sub>2</sub> and b) TiO<sub>2</sub> grafted photocatalyst **2**

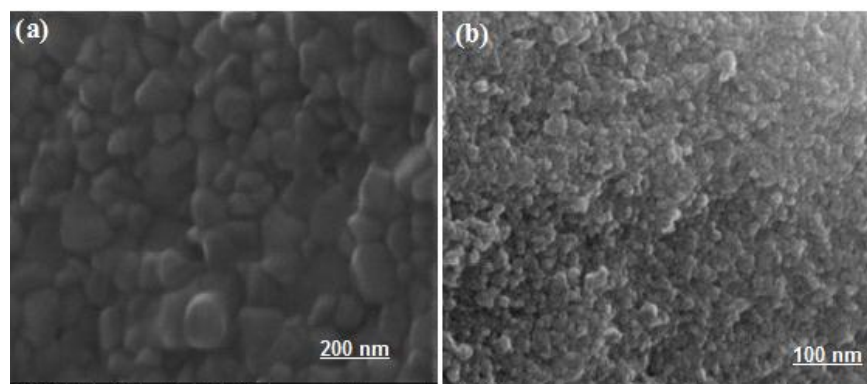


### **SEM**

SEM images of the as synthesized TiO<sub>2</sub> and TiO<sub>2</sub> immobilized photocatalyst **2** are shown in Fig. S5. Fig. S5a, clearly indicates that the particles are agglomerated and non-homogeneously distributed having truncated spherical shaped like morphology with particle size less than 100 nm. On the other hand, SEM image of TiO<sub>2</sub>-Ru(II) polyazine complex **2** (Fig S5b) reveals the homogenous distribution of ruthenium throughout the TiO<sub>2</sub> support with the particle size as similar to the TiO<sub>2</sub>. Furthermore, EDAX analysis supported the immobilization of the ruthenium complex onto the TiO<sub>2</sub> surface and gave 4.21% wt % of ruthenium.



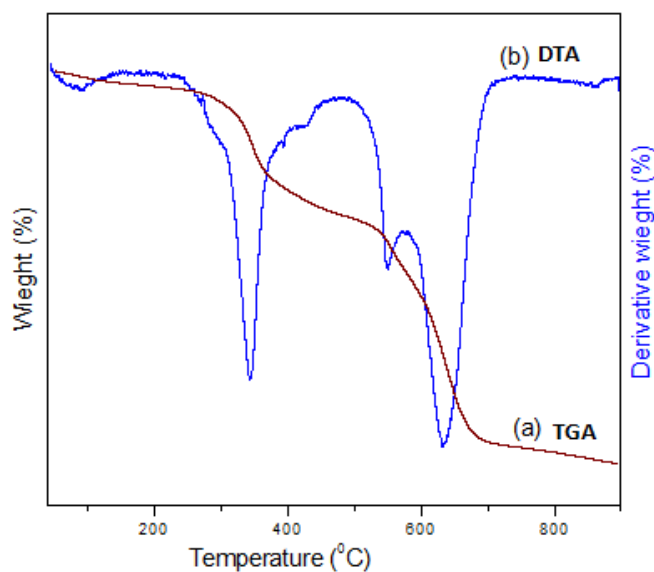
**Supporting Fig 5.** SEM image of a)  $\text{TiO}_2$ ; b)  $\text{TiO}_2$  immobilized photocatalyst 2



### ***TG-DTA***

Thermal stability of the as synthesized photocatalyst was determined by thermogravimetric (TGA) analysis (Fig. S6). It can be observed that the catalyst shows 0.51 % weight loss near at 100-150 °C, evidently owing to evaporation of water molecules which are held in the material. The second significant weight loss about 10 % is observed in the range of 266-448 °C, due to thermal decomposition of organic functionalized moieties. The third significant weight loss about 20 % is observed in the range of 499-732°C, due to thermal decomposition of metal bound organic functionalized moieties. At the end all metals about 60 % are found to be converted into their oxides.

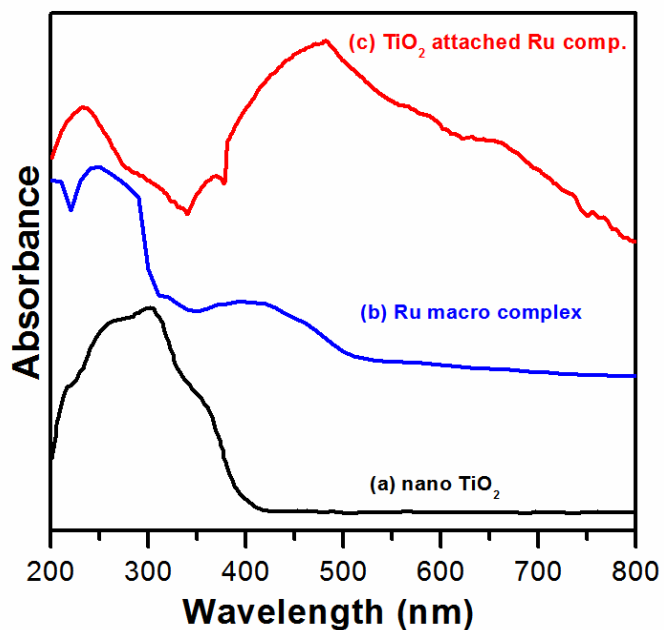
**Supporting Fig S3:** TG-DTA spectra of TiO<sub>2</sub> immobilized Ruthenium-polyazine photocatalyst **2**



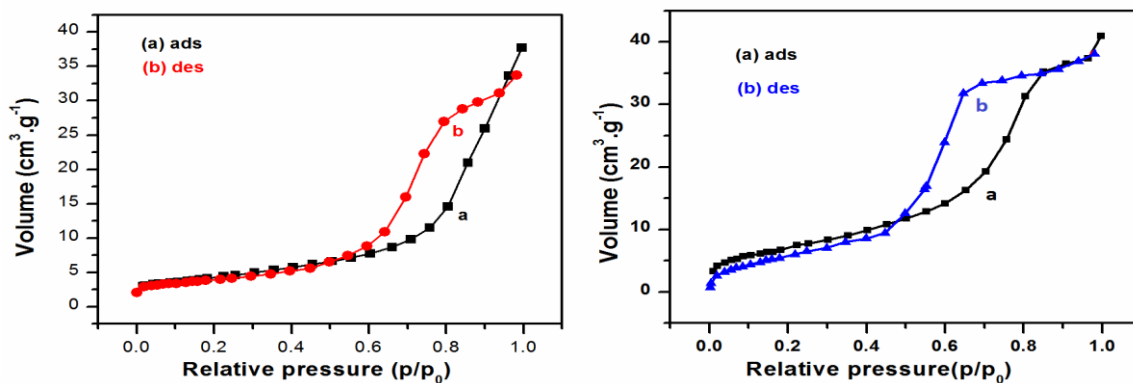
**UV-Vis**

UV-Vis diffuse reflectance spectra of TiO<sub>2</sub>, ruthenium polyazine complex and TiO<sub>2</sub>-immobilized Ru(II)polyazine photocatalyst **2** are shown in Fig. S7. The reflectance spectra of TiO<sub>2</sub> only exhibit the fundamental absorption band in the UV region ( $\lambda_{\text{max}} \sim 300$ ) Fig. S7a). Ru unattached macro complex show two peaks one at 260nm due to L→L charge transfer and another at 425nm due to M→L charge transfer (Fig. S7b). However, the ruthenium complex grafted TiO<sub>2</sub> Fig. S7c) shows an absorbance shoulder at 480 nm due to M→L charge transfer and another band at 254 nm due to the  $\pi \rightarrow \pi^*$  transition.

**Supporting Fig S7:** UV-Vis of a) TiO<sub>2</sub>; b) ruthenium polyazine complex; c) TiO<sub>2</sub> grafted ruthenium photocatalyst 2



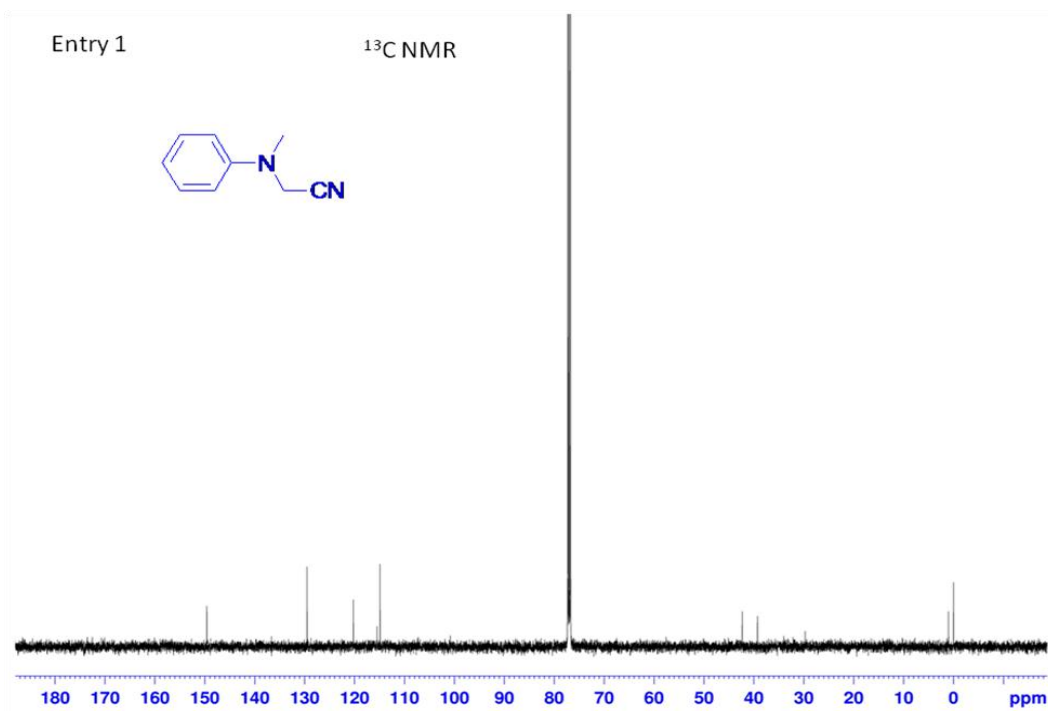
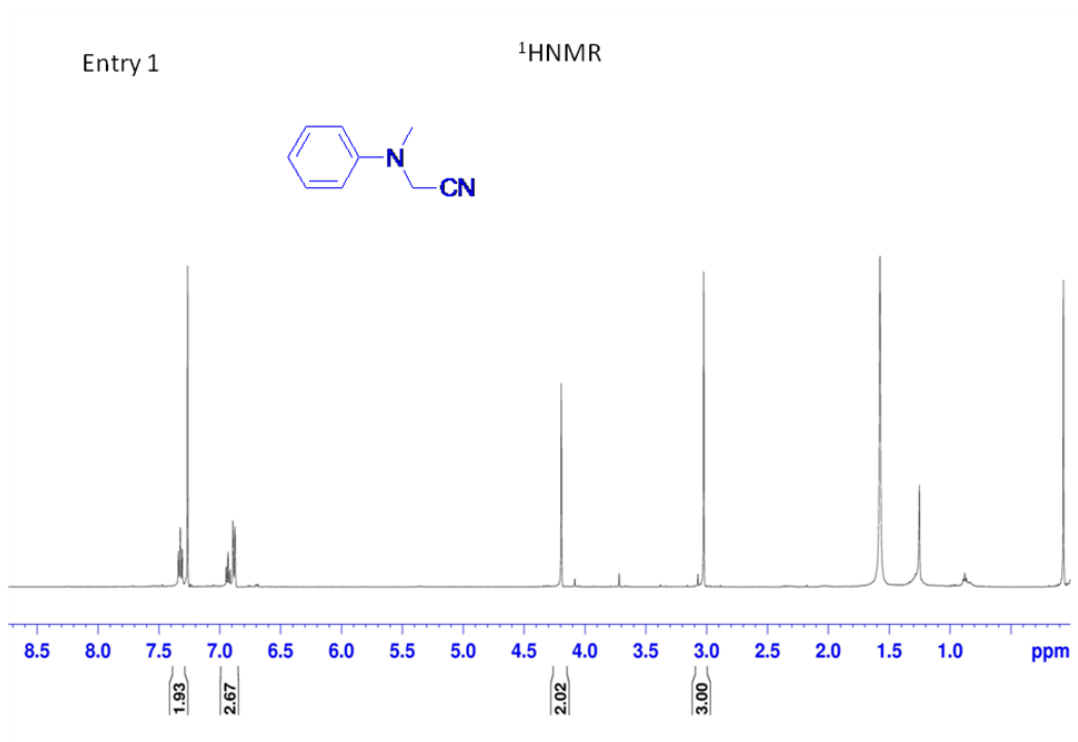
**Supporting Fig S8:** Adsorption Desorption isotherm of a) TiO<sub>2</sub> and b) TiO<sub>2</sub> immobilized photocatalyst 2

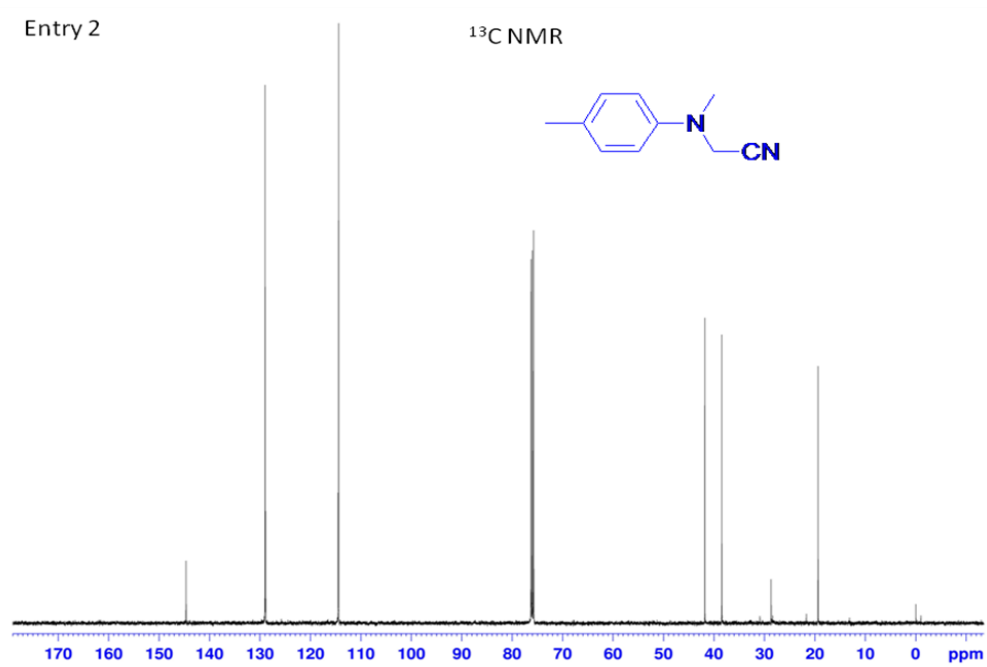
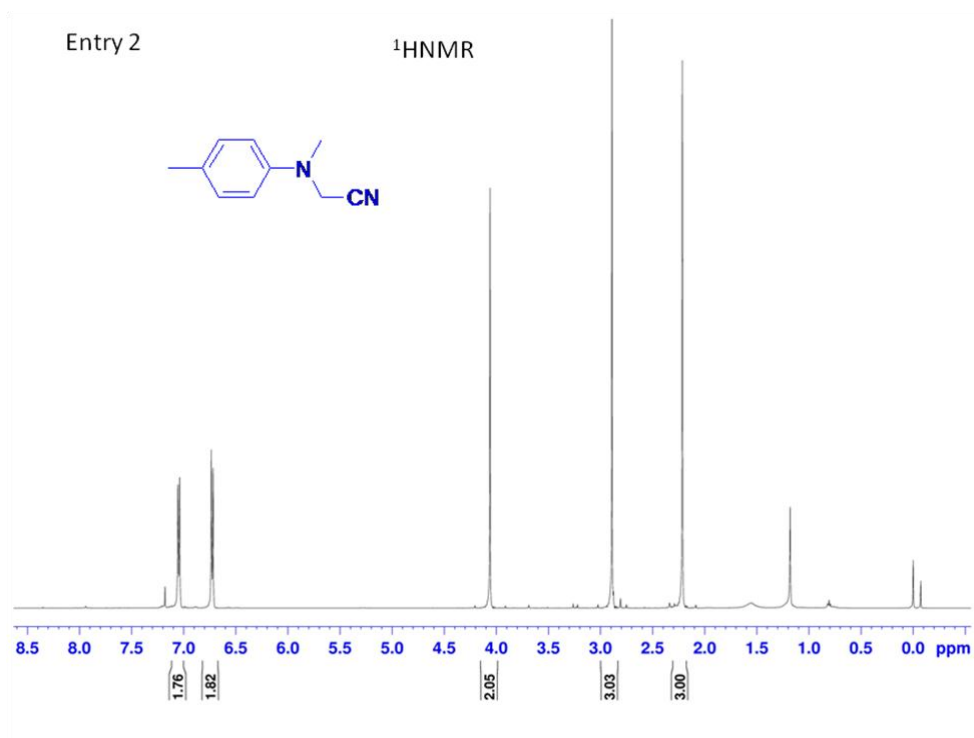


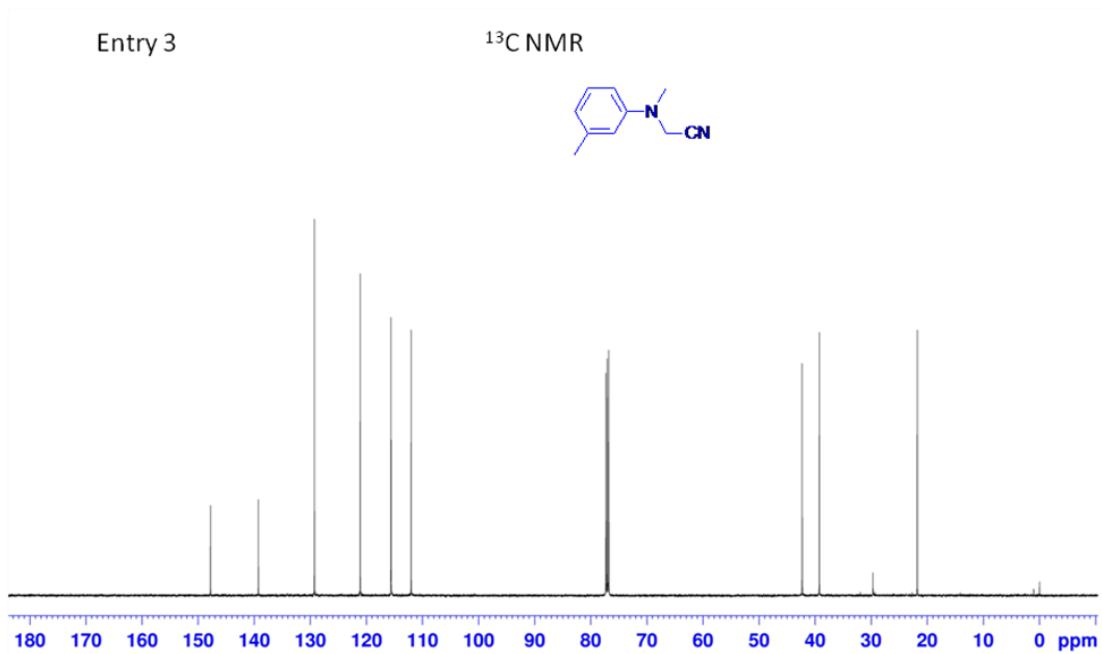
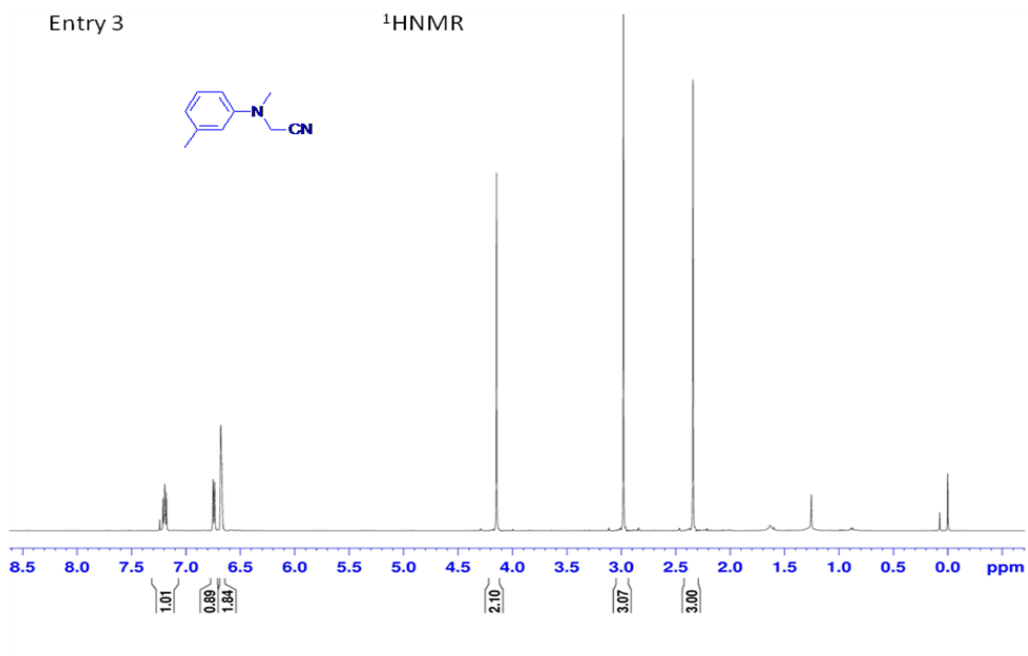
#### 4.0 General experimental procedure for photocatalytic oxidative cyanation

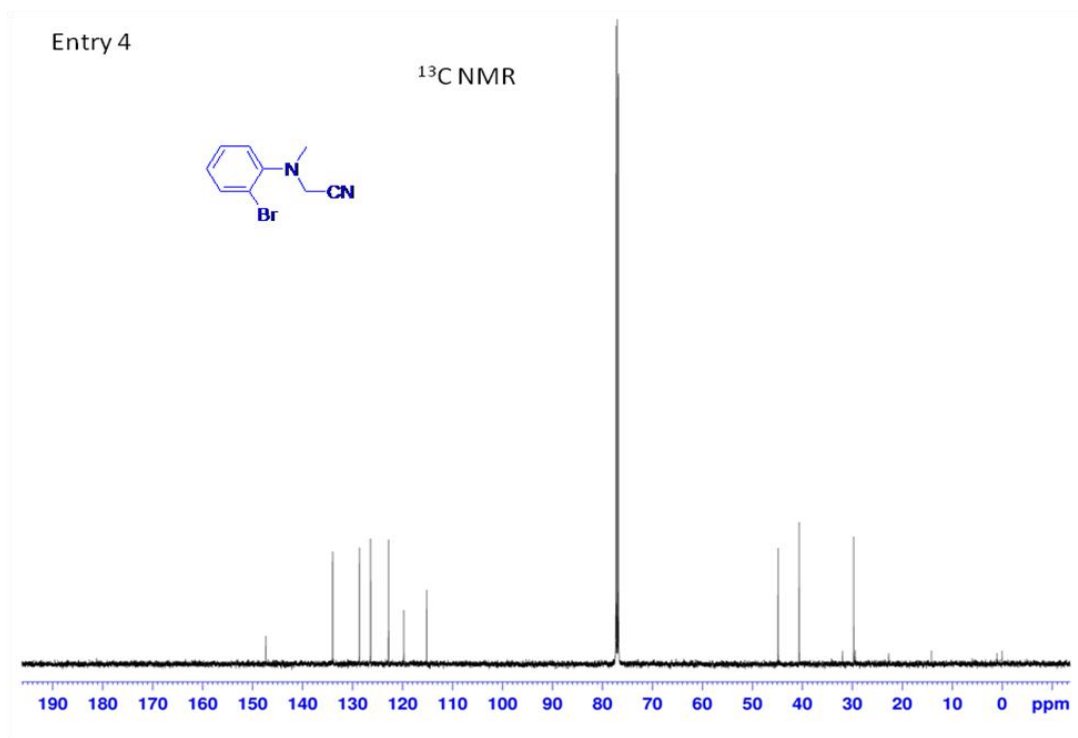
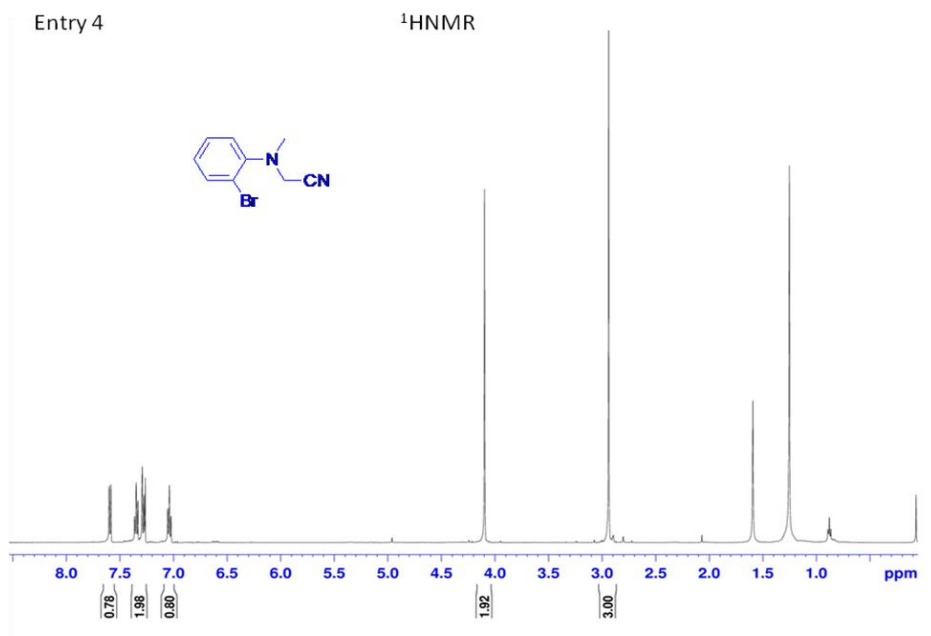
A 25 mL round bottomed flask equipped with a magnetic stirrer bar was charged with tertiary amine (1 mmol), NaCN (1.2 mmol), MeOH (2 mL), catalyst (1 mol %) and AcOH (1 mL). The stirring was continued at room temperature under an atmosphere under visible irradiation, using a household white LED (20 W). The progress of the reaction was monitored by TLC (SiO<sub>2</sub>). After completion of the reaction, the catalyst was recovered by adding diethyl ether followed by filtration. The obtained organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum to give crude product, which was purified by flash chromatography to afford pure  $\alpha$ -aminonitrile. The conversion of tertiary amines into corresponding  $\alpha$ -aminonitriles and their selectivity was determined by GC-MS (EI quadrupole mass analyzer, EM detector) and the identity of the selected products was established by comparing their spectral data with authentic samples.

#### <sup>1</sup>HNMR and <sup>13</sup>CNMR of the products

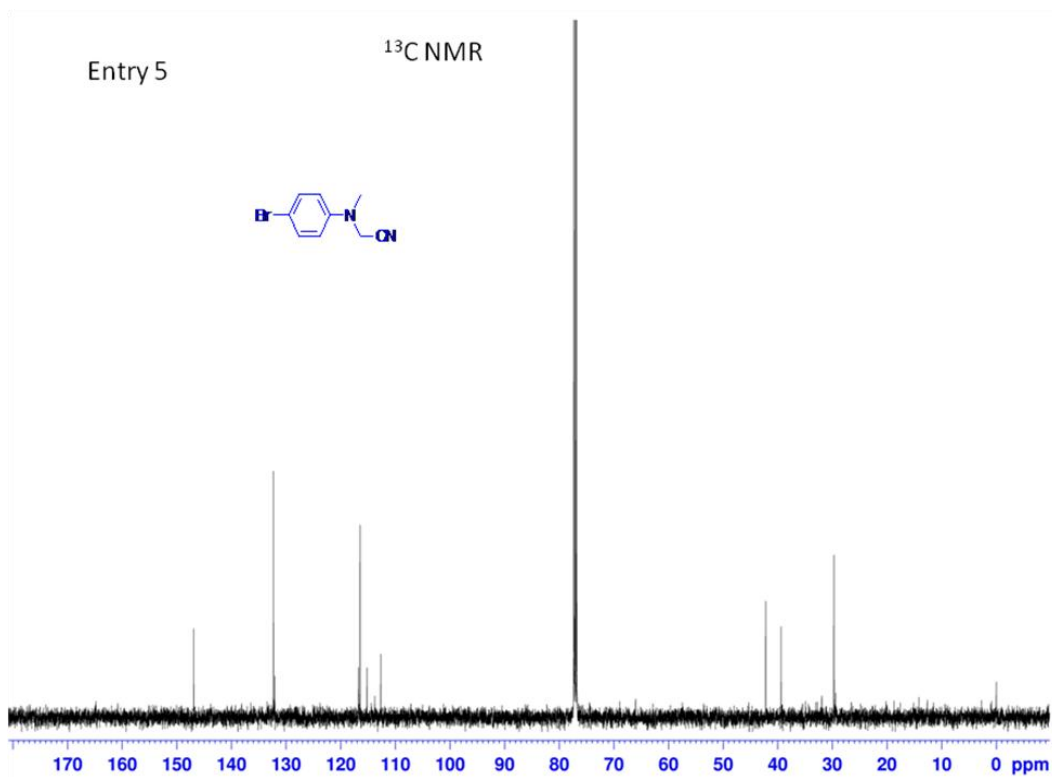
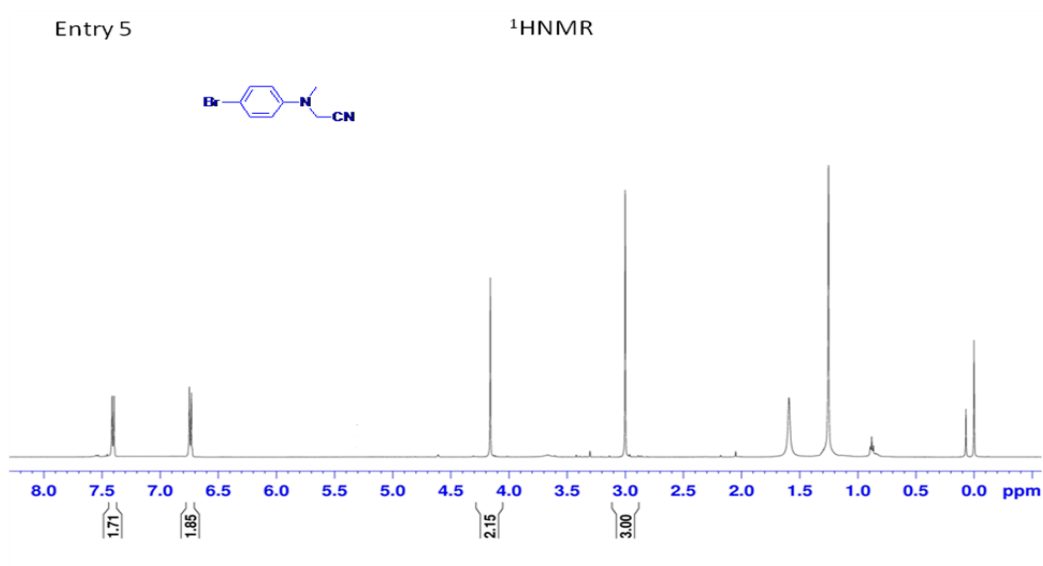






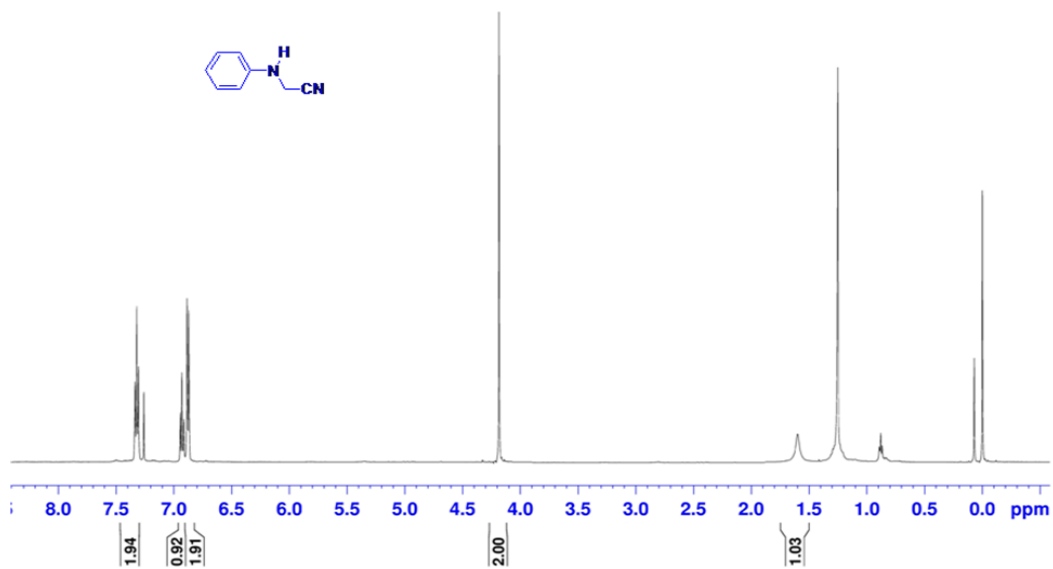






Entry 6

$^1\text{H}$ NMR



Entry 6

$^{13}\text{C}$ NMR

