Supplementary Materials

# Magnetically reusable $Fe_3O_4$@NC@Pt catalyst for selective reduction of nitroarenes

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# 1 General Information

## Materials

The reagent were commercially available Ferric chloride hexahydrate ($FeCl_3$•$6H_2O$), Glucose, Sodium acetateanhydrous, ethylene glycol, Vinylpyrrolidinone polymer (PVP) and ethylenediamine (EDA), they were purchased from Shanghai Aladdin Reagent Co. Ltd. Chloroplatinic acid hexahydrate ($H_2PtCl_6$•$6H_2O$, ≥37.50%) was purchased from J&K Scientific Ltd. All reagents are analytically pure and used as-received without further purification.

## Characterization

Fourier-transform infrared (FTIR) spectra were recorded with a Bruker Tensor 27 using KBr pellets. Transmission electron microscopy (TEM) images were performed on a FEI T20 microscope. The magnetic properties of the catalysts were tested on a vibrating sample magnetometer (VSM). $^1H$ and $^{13}C$ NMR spectra were carried out with a Bruker Advance 400 spectrometer by using TMS as the internal standard and DMSO-$d_6$ or $CDCl_3$ as solvents. The Pt content in the catalyst was carried out with a Perkin-Elmer Optima 2100 DV.

# 2 Experimental Section

**Preparation of $Fe_3O_4$ Microspheres**

$Fe_3O_4$ microspheres were obtained by according to a previous report[34]. In a typical experiment, 3 g $FeCl_3$•$6H_2O$, 4 g NaAc and 2 g PVP were dispersed in 60 mL ethylene glycol under magnetic stirring. Then the mixture was transferred to a Teflon-lined autoclave and maintained at 200 °C for 12 h. After that, the desired product was separated using an external magnet and washed with water and ethanol for several times, respectively. Finally, the black $Fe_3O_4$ microspheres were dried in a vacuum oven at 60 °C for 24 h.

**Preparation of $Fe_3O_4$@C Microspheres**

$Fe_3O_4$@C was fabricated by a simple carbonization of glucose on $Fe_3O_4$ surface under hydrothermal conditions. 200 mg $Fe_3O_4$ microspheres were dispersed in 10 mL water of glucose (3.2 g) aqueous solution and ultrasonicated for 0.5 h. After that they were added into a 100mL Teflon lined autoclave heated at 180 °C for 10 h. After cooling to room temperature, the final $Fe_3O_4$@C microspheres were obtained by an

external magnet and washed with ethanol followed by water. Finally, the product with black colored was dried in a vacuum oven for 24 h.

**Preparation of $Fe_3O_4$@NC Microspheres**

$Fe_3O_4$@NC was synthesized according to the previous report described in elsewhere [35]. 100 mg $Fe_3O_4$ microspheres were dispersed into 10 mL water of ethylenediamine (EDA) (0.2 mL) and 1.6 g glucose solution, then ultrasonicated for 0.5 h. Subsequently, the mixture was transferred into a Teflon-lined autoclave and treated at 180 ºC for 10 h. After cooling to room temperature, the obtained black product $Fe_3O_4$@NC microspheres were washed with ethanol and water, respectively. Lastly, they was dried in a vacuum oven for 24 h.

**Preparation of the $Fe_3O_4$@C@Pt and $Fe_3O_4$@NC@Pt Catalyst**

The $Fe_3O_4$@C@Pt and $Fe_3O_4$@NC@Pt catalyst were prepared according to the previous report with some modifications[36]. In a typical procedure, take the $Fe_3O_4$@NC preparation process for example, 400 mg $Fe_3O_4$@NC were dispersed in 40 mL ethanol by ultrasonic treatment for 0.5 h. And then 3 mL $H_2PtCl_6$•$6H_2$ O (35 mg) of ethanol solution were added into $Fe_3O_4$@NC suspension solution and continuously ultrasonicated for 1 h, the last a 8 mL sodium borohydride (1 g mg) of ethanol solution was dropped into the above mixture with vigorous stirring under 60 ºC. After 2 h of reduction, the products were separated and washed several times with water. The products were dried in a vacuum oven to obtain $Fe_3O_4$@NC@Pt. The same process for $Fe_3O_4$@C@Pt.

**General Procedure for the Selective Hydrogenation of Nitroarenes Reactions**

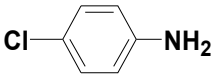
1 mmol nitro compounds was added to 2 mL distilled water and then 0.020 g ultrasonically dispersed $Fe_3O_4$@NC@Pt catalyst in water (2 mL) was introduced to this solution. Then 4 mmol $N_2H_4$•$H_2O$ was added and the mixture was stirred in 70 °C. The progress of reaction was detected by TLC (or GC). After completion of the reaction, the catalyst was magnetically removed and washed several times with ethanol and used after drying in subsequent reactions and then, the residual solvent was evaporated under vacuum to obtain the pure amines. The conversions were determined by the gas chromatography (GC) analysis. All of the synthesized amines were characterized by comparison of NMR spectral data with the reported values in literatures.

**General Procedure for Catalyst Recovery**

1.0 mmol 1-Chloro-4-nitrobenzene, 4.0 mmol $N_2H_4$•$H_2O$, and $Fe_3O_4$@NC@Pt were mixed in 3 mL $H_2O$. The mixture was stirred at 70 °C. After the reaction was complete, the catalyst was separated by an external magnet and washed with water for three times (2mL Water/time) and ethanol for three times (2mL ethanol/time), then dried in vacuum and directly used in the next run.

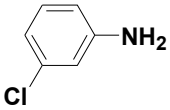
# 3. Characterization of the Prouducts

## 4-Chloroaniline 2a:



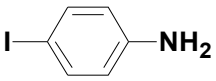

$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.13 – 7.04 (m, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 3.61 (s, 2H).

## 3-Chloroaniline 2b:



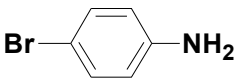

$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.02 (t, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 4.2 Hz, 1H), 6.49 (ddd, *J* = 8.1, 2.2, 0.8 Hz, 1H), 3.61 (s, 2H).

## 4-Iodoaniline 2c:



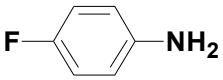

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.26 (d, *J* = 4.8 Hz, 2H), 6.41 (d, *J* = 4.8 Hz, 2H), 5.25 (s, 4H).

## 4-Bromoaniline 2d:



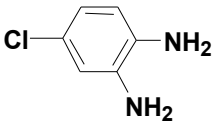

$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.23 – 7.19 (m, 2H), 6.53 (d, *J* = 8.7 Hz, 2H), 3.63 (s, 2H).

## 4-Fluoroaniline 2e:



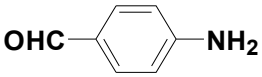
$^1$H NMR (600 MHz, Chloroform-*d*) δ 6.82 (t, *J* = 8.7 Hz, 2H), 6.55 (td, *J* = 4.5, 2.3 Hz, 2H), 3.45 (s, 2H).

## 4-Chloro-o-phenylenediamine 2f:



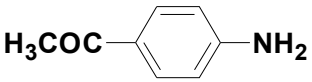
$^1$H NMR (400 MHz, DMSO-$d_6$) δ 6.51 – 6.50 (m, 1H), 6.46 (d, *J* = 8.2 Hz, 1H), 6.36 – 6.34 (m, 1H), 4.72 (s, 4H), 4.54 (s, 4H).

## 4-Aminobenzaldehyde 2g:



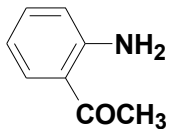
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 8.5 Hz, 2H), 5.23 (s, 2H).

## 4-Aminoacetophenone 2h:



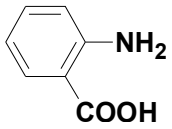
$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 2H), 6.66 – 6.63 (m, 2H), 4.14 (s, 2H), 2.51 (s, 3H).

## 2-Aminoacetophenone 2i:



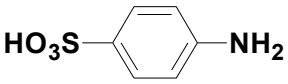
$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 1.5 Hz, 1H), 7.26 – 7.25 (m, 1H), 6.65 – 6.64 (m, 2H), 2.57 (s, 3H).

## Anthranilic acid 2j:



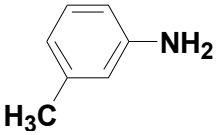

$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 1.6 Hz, 1H), 7.93 (t, *J* = 2.0 Hz, 1H), 7.33 – 7.30 (m, 2H), 6.69 – 6.67 (m, 3H).

## 4-aminobenzenesulfonic acid 2k:



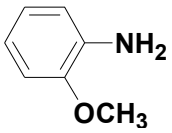

$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.53 – 7.27 (m, 2H), 6.47 – 6.39 (m, 2H), 3.65 (s, 2H).

## 3-Methylaniline 2l:



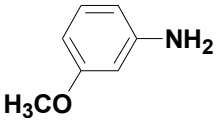

$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.03 – 6.96 (m, 1H), 6.54 (s, 1H), 6.43 – 6.37 (m, 2H), 3.40 (s, 2H), 2.22 (s, 3H).

## 2-Methoxyaniline 2m:



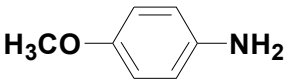

$^1$H NMR (600 MHz, Chloroform-*d*) δ 6.79 – 6.74 (m, 2H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 3.79 (s, 3H), 3.67 (s, 2H).

## 3-Methoxyaniline 2n:



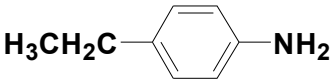

$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.03 (t, *J* = 8.0 Hz, 1H), 6.30 (d, *J* = 8.2 Hz, 1H), 6.24 (d, *J* = 8.7 Hz, 1H), 6.20 (s, 1H), 3.71 (s, 3H), 3.60 (s, 2H).

## 4-Methoxyaniline 2o:



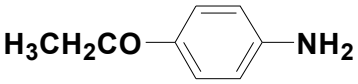
$^1$H NMR (600 MHz, Chloroform-*d*) δ 6.75 – 6.73 (m, 2H), 6.66 – 6.63 (m, 2H), 3.74 (s, 3H), 3.39 (s, 2H).

## 4-Ethylanilinee 2p:



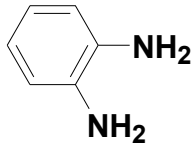
$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.16 (d, *J* = 7.7 Hz, 2H), 6.75 (d, *J* = 10.8 Hz, 2H), 3.57 (s, 2H), 2.71 (dd, *J* = 8.8, 4.7 Hz, 2H), 1.40 – 1.34 (m, 3H).

## 4-Ethoxyphenylamine 2q:



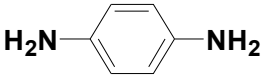
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 8.5 Hz, 2H), 5.23 (s, 2H).

## Benzene-1,2-diamine 2r:



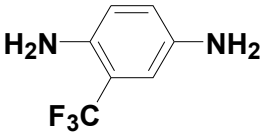
$^1$H NMR (500 MHz, DMSO-$d_6$) δ 6.60 – 6.44 (m, 2H), 6.38 (d, *J* = 5.2 Hz, 2H), 4.37 (s, 4H).

## Benzene-1,4-diamine 2s:



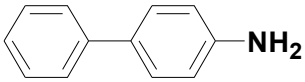
$^1$H NMR (600 MHz, Chloroform-*d*) δ 6.57 (d, *J* = 0.6 Hz, 4H), 3.33 (s, 4H).

## 2-(Trifluoromethyl)-1,4-phenylenediamine 2t:



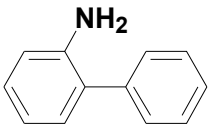

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 6.63 (d, $J$ = 2.2 Hz, 3H), 4.59 (s, 4H).

## 4-Aminebiphenyl 2u:



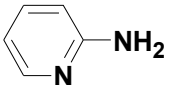

$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, $J$ = 7.1 Hz, 2H), 7.44 – 7.28 (m, 4H), 7.18 (t, $J$ = 6.9 Hz, 1H), 6.66 (d, $J$ = 7.6 Hz, 2H), 3.61 (s, 2H).

## 2-Aminebiphenyl 2v:



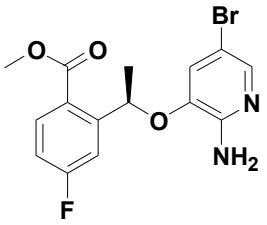

$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.43 (q, $J$ = 7.2 Hz, 4H), 7.33 (t, $J$ = 6.8 Hz, 1H), 7.14 (dd, $J$ = 18.0, 7.7 Hz, 2H), 6.82 (t, $J$ = 7.4 Hz, 1H), 6.75 (s, 1H), 3.64 (s, 2H).

## Pyridin-2-amine 2w:




$^1$H NMR (600 MHz, Chloroform-*d*) δ 8.06 (ddd, $J$ = 5.1, 1.8, 0.8 Hz, 1H), 7.41 (ddd, $J$ = 8.3, 7.2, 1.9 Hz, 1H), 6.64 – 6.61 (m, 1H), 6.48 (d, $J$ = 8.3 Hz, 1H), 4.55 (s, 2H).

key intermediate **4** of marketed drug *Lorlatini*:




$^1$H NMR (500 MHz, DMSO-$d_6$) δ 7.95 (d, $J$ = 2.8 Hz, 1H), 7.59 (d, $J$ = 7.9 Hz, 1H), 7.54 (d, $J$ = 1.7 Hz, 1H), 7.27 (d, $J$ = 2.4 Hz, 1H), 6.89 – 6.89 (m, 1H), 6.23 (d, $J$ = 6.2 Hz, 1H), 6.20 (s, 2H), 3.91 (s, 3H), 1.59 (d, $J$ = 6.2 Hz, 3H).

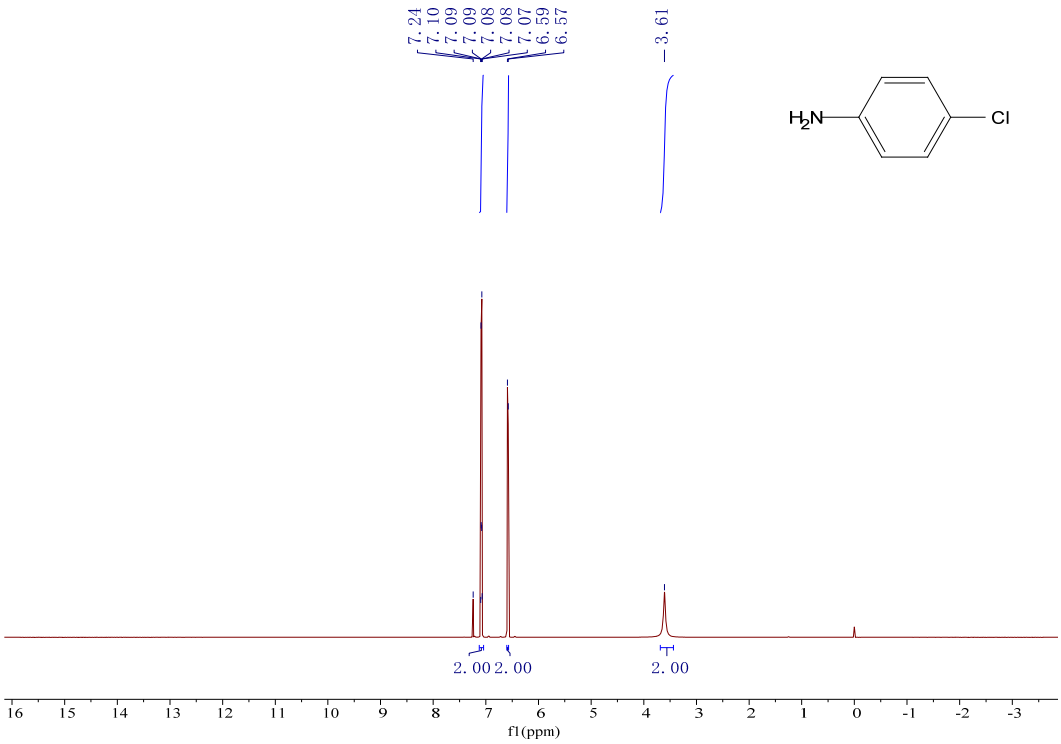



**Figure S1**: $^{1}$H NMR spectrum of **2a**, recorded in Chloroform-*d* at 25 ˚C.

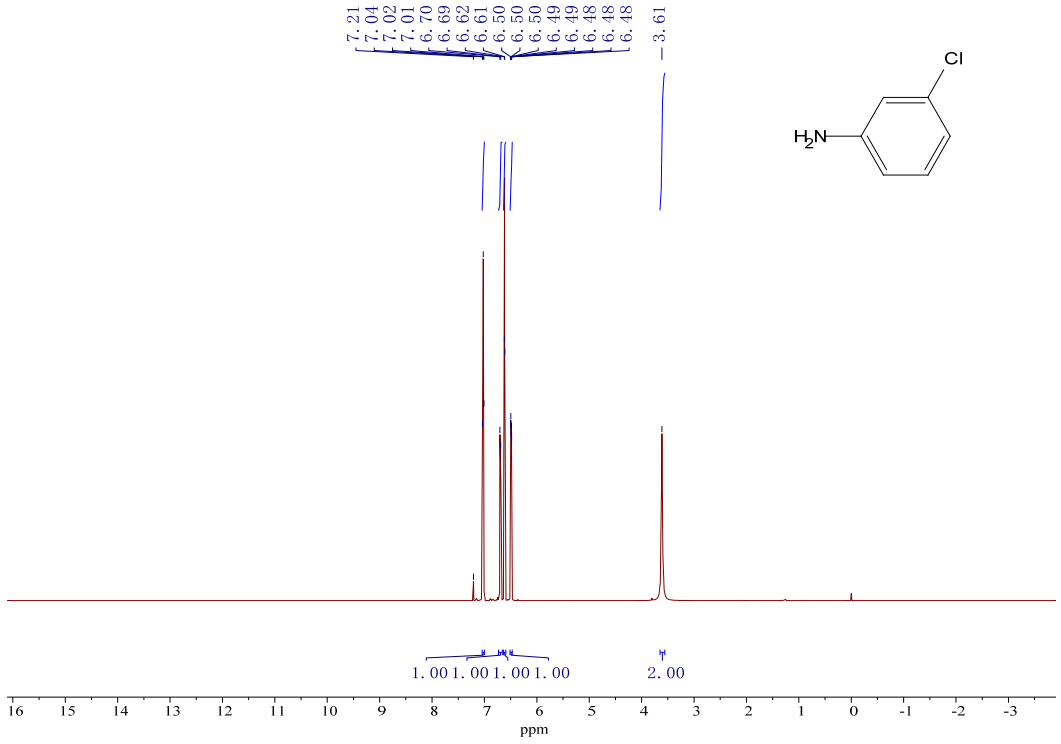



**Figure S2**: $^{1}$H NMR spectrum of **2b**, recorded in Chloroform-*d* at 25 ˚C.

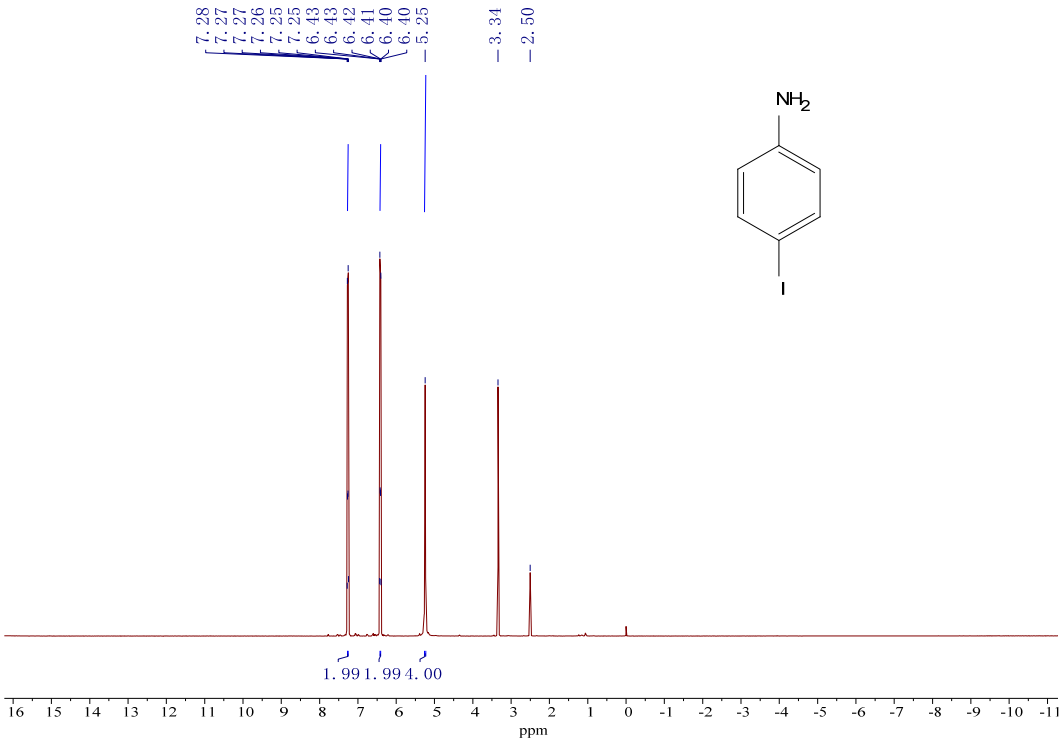



**Figure S3**: [1]H NMR spectrum of **2c**, recorded in DMSO-$d_6$ at 25 ˚C.

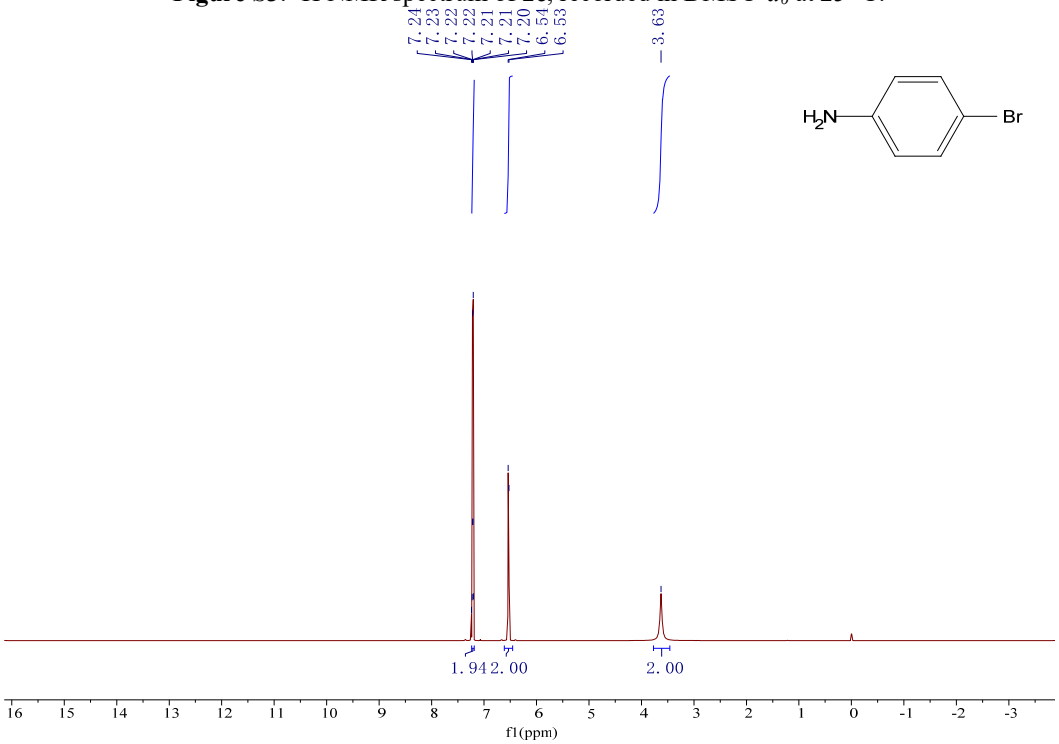



**Figure S4**: [1]H NMR spectrum of **2d**, recorded in Chloroform-*d* at 25 ˚C.

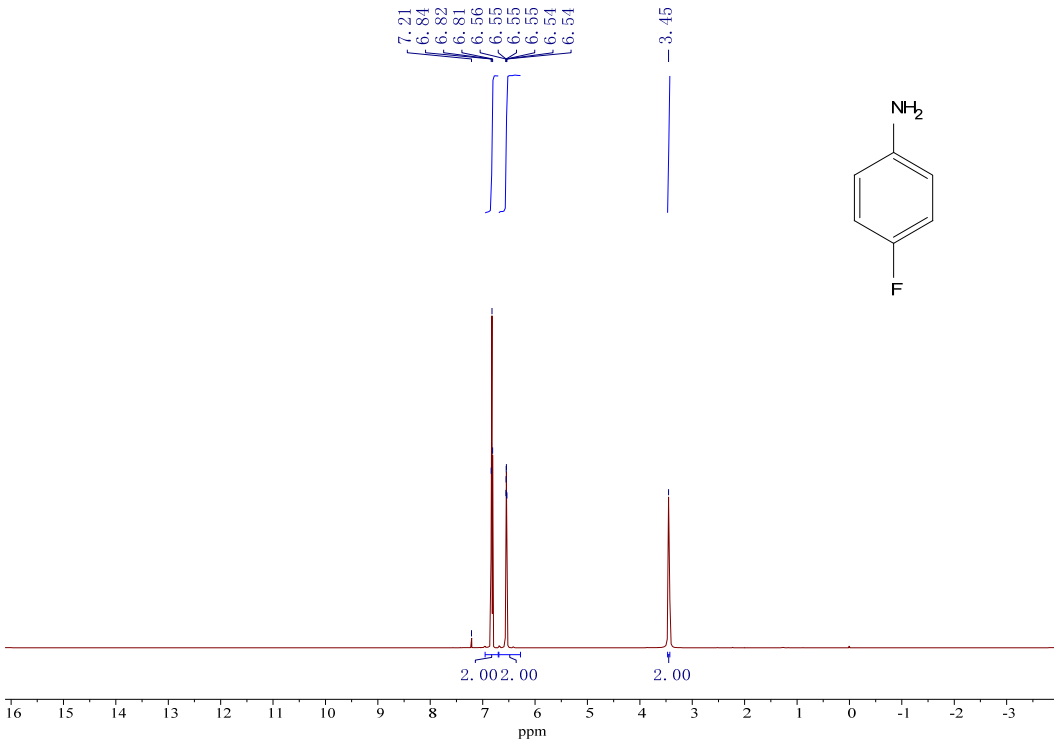



**Figure S5**: $^{1}$H NMR spectrum of **2e**, recorded in Chloroform-*d* at 25 ˚C.

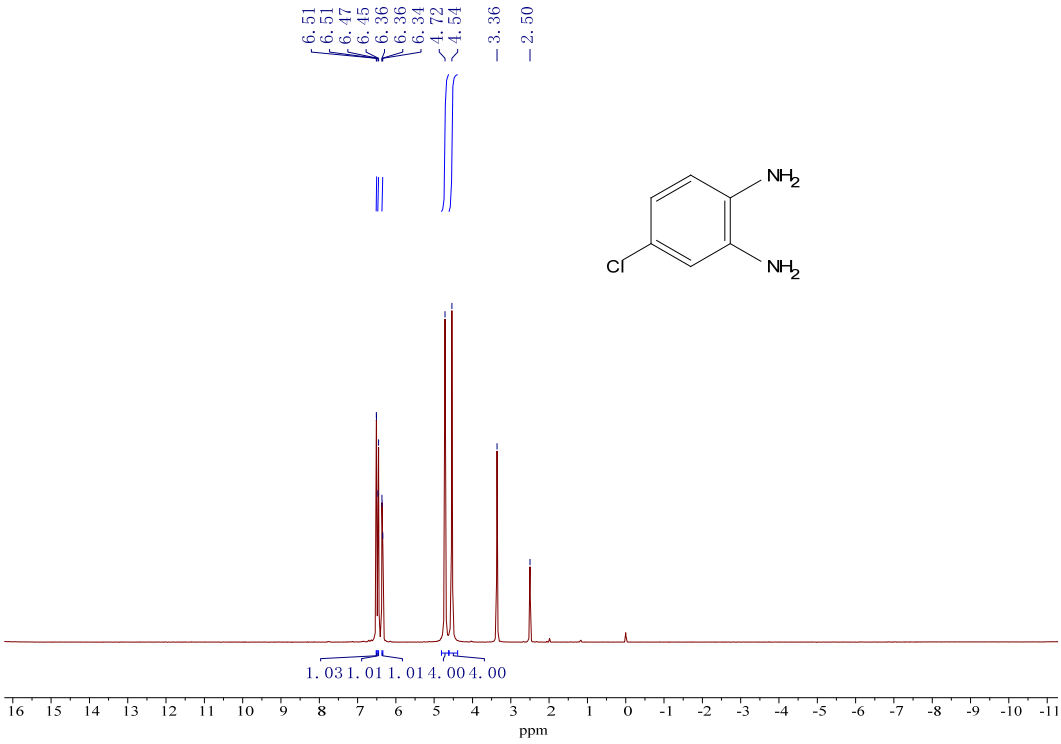



**Figure S6**: $^{1}$H NMR spectrum of **2f**, recorded in DMSO-$d_6$ at 25 ˚C.

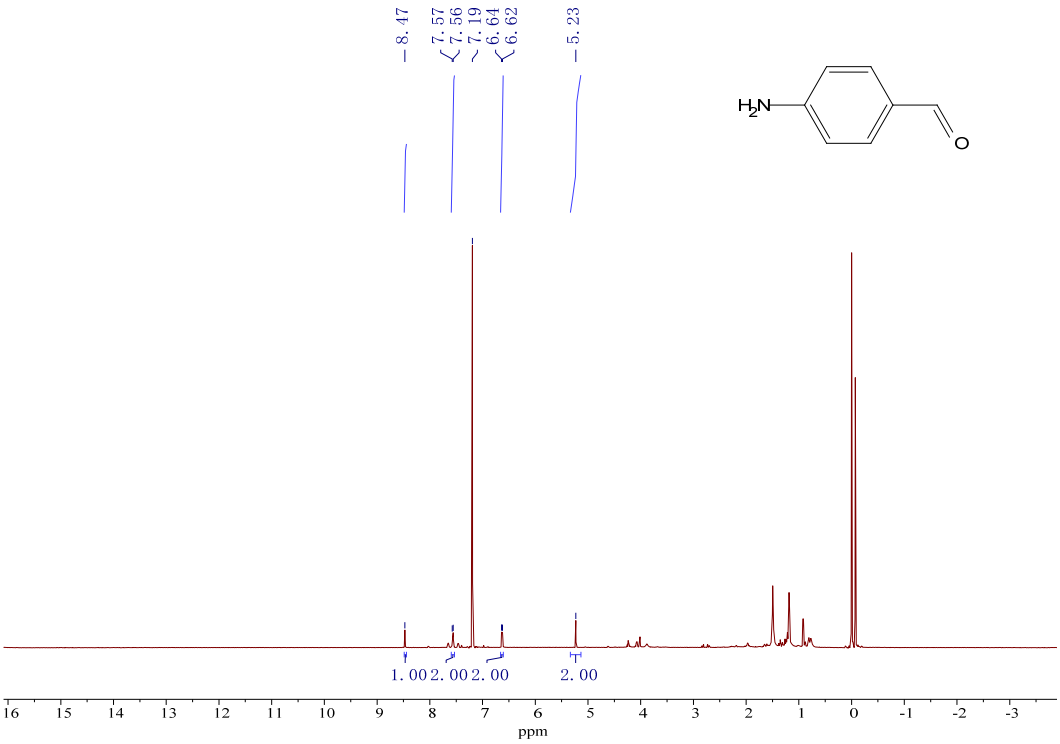



**Figure S7**: $^{1}$H NMR spectrum of **2g**, recorded in Chloroform-*d* at 25 ˚C.

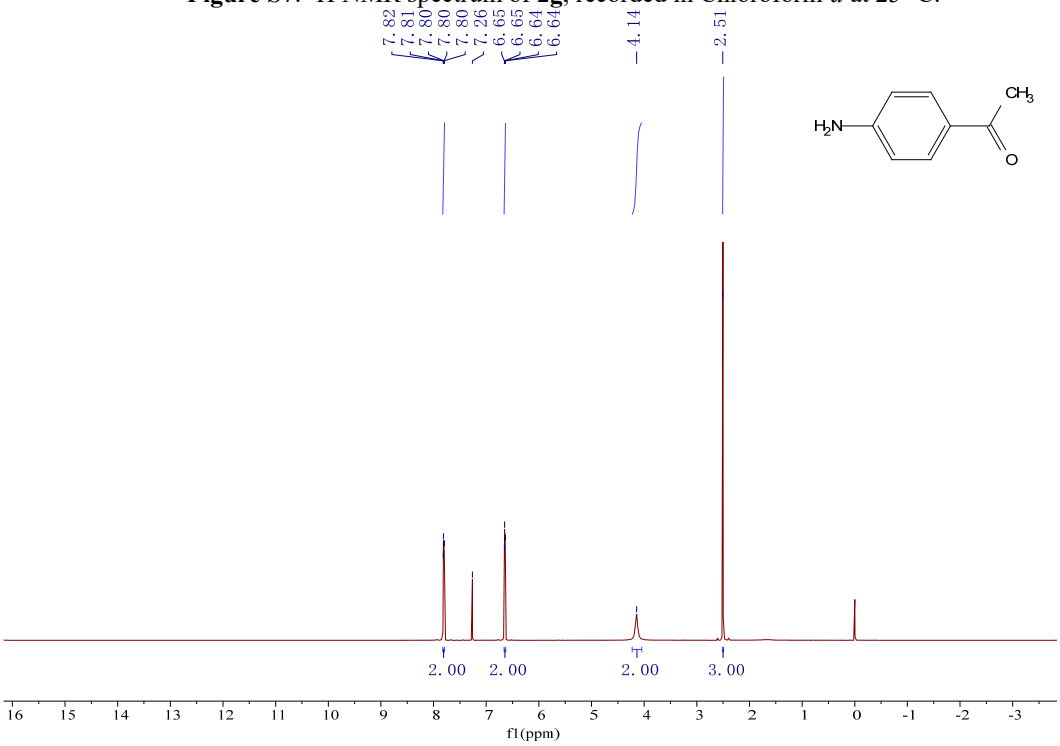



**Figure S8**: $^{1}$H NMR spectrum of **2h**, recorded in Chloroform-*d* at 25 ˚C.

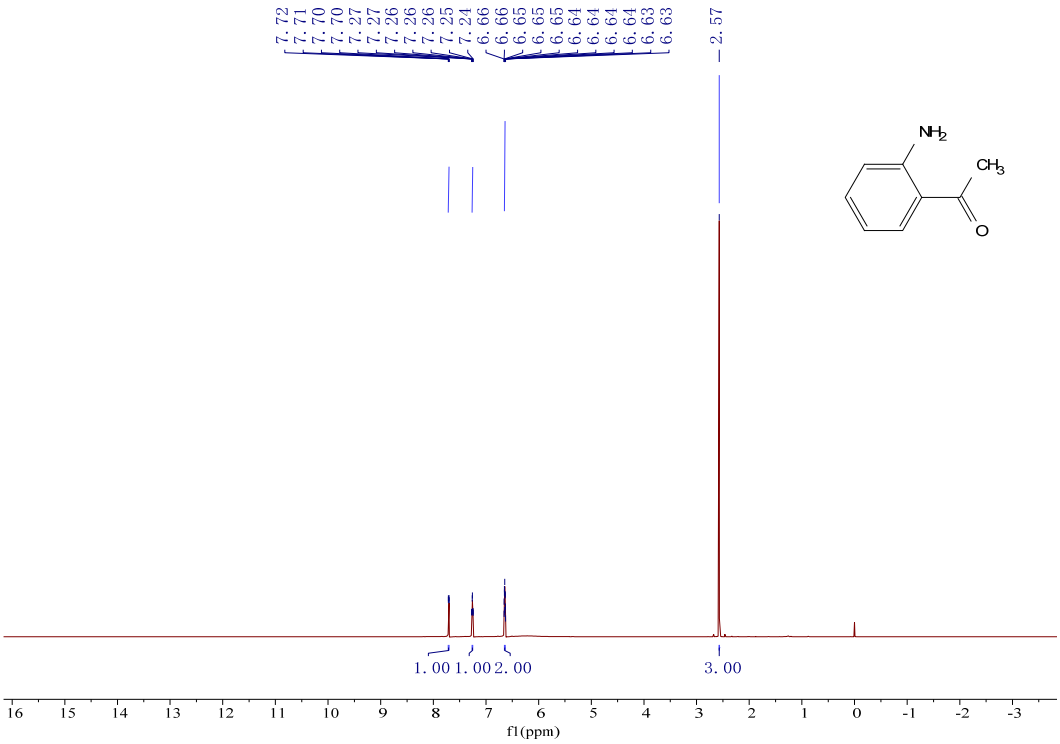



**Figure S9**: $^{1}$H NMR spectrum of **2i**, recorded in Chloroform-*d* at 25 ˚C.

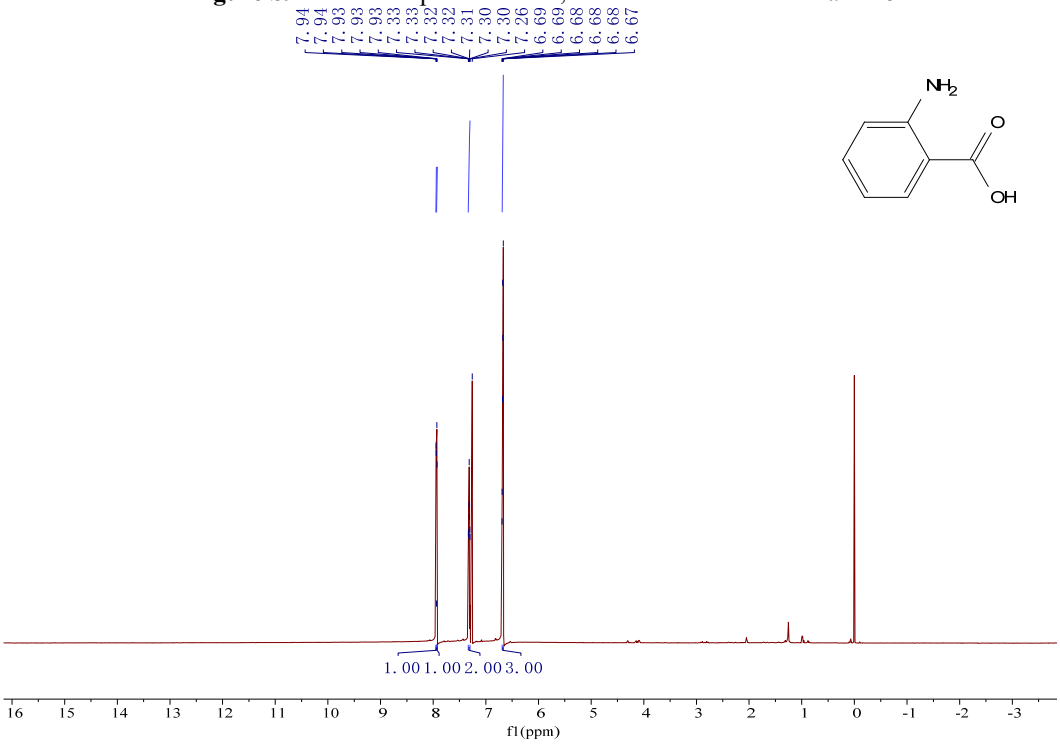



**Figure S10**: $^{1}$H NMR spectrum of **2j**, recorded in Chloroform-*d* at 25 ˚C.

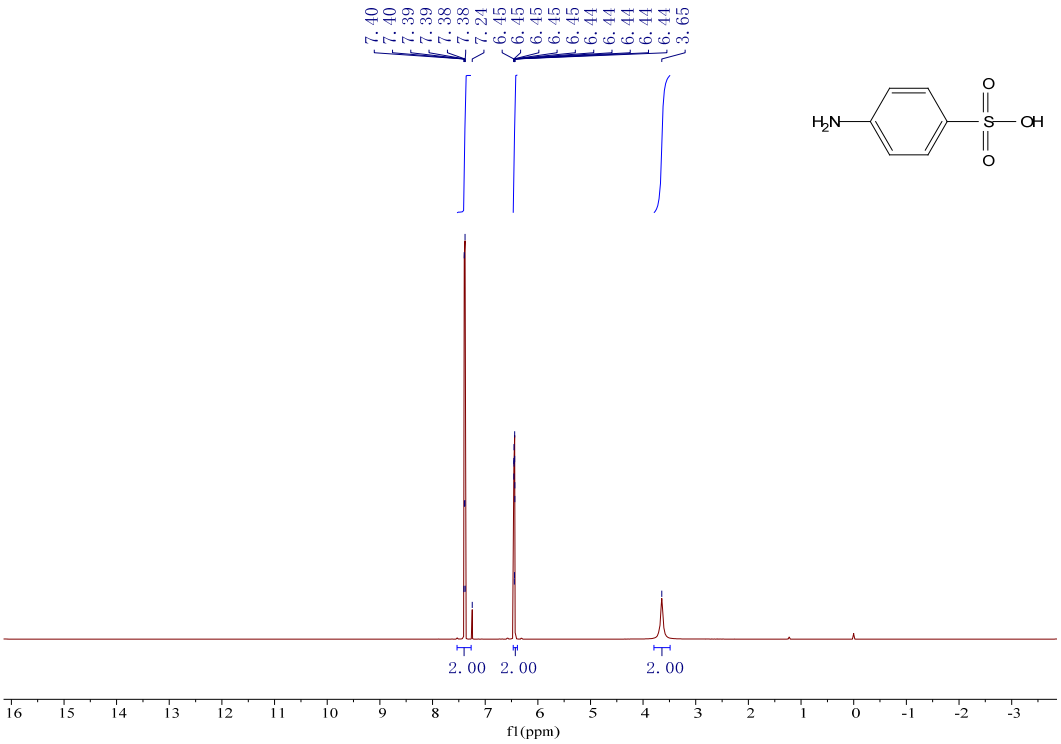



**Figure S11**: $^{1}$H NMR spectrum of **2k**, recorded in Chloroform-*d* at 25 ˚C.

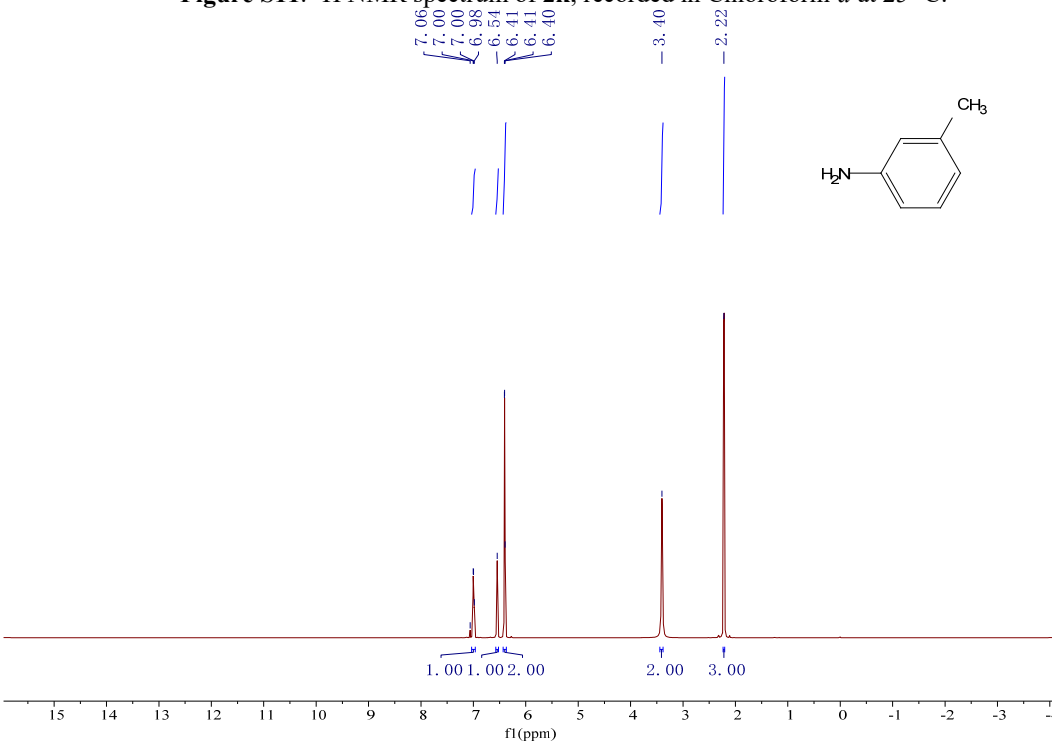



**Figure S12**: $^{1}$H NMR spectrum of **2l**, recorded in Chloroform-*d* at 25 ˚C.

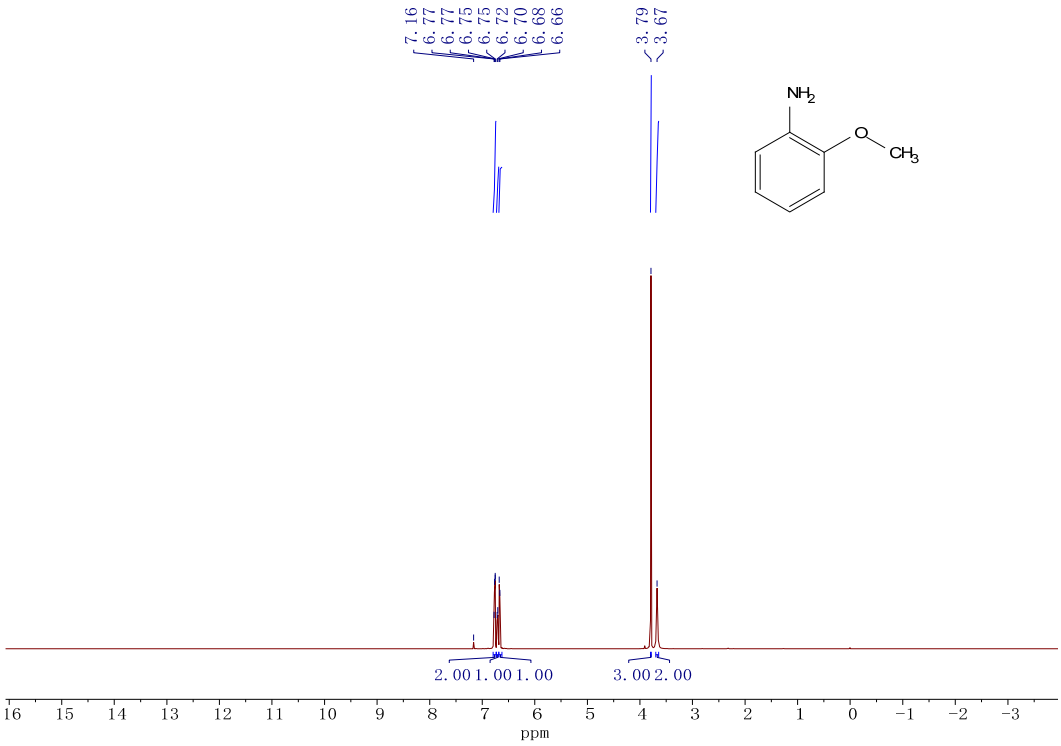



**Figure S13**: $^{1}$H NMR spectrum of **2m**, recorded in Chloroform-*d* at 25 ˚C.

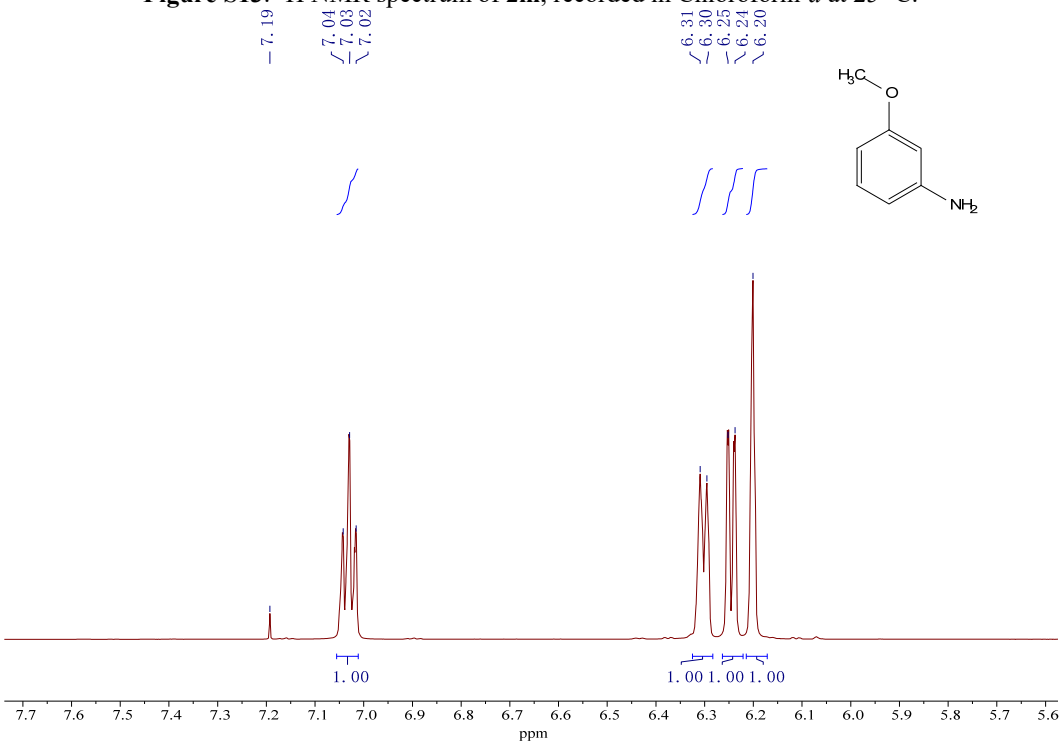



**Figure S14**: $^{1}$H NMR spectrum of **2n**, recorded in Chloroform-*d* at 25 ˚C.

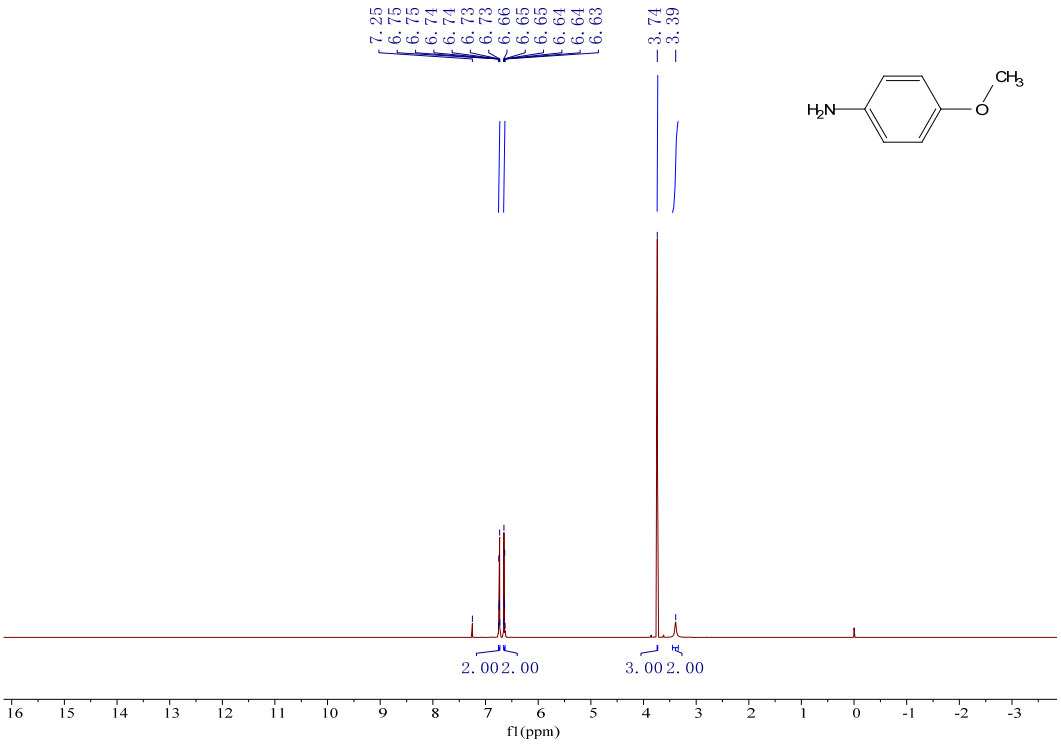



**Figure S15**: $^{1}$H NMR spectrum of **2o**, recorded in Chloroform-*d* at 25 ˚C.

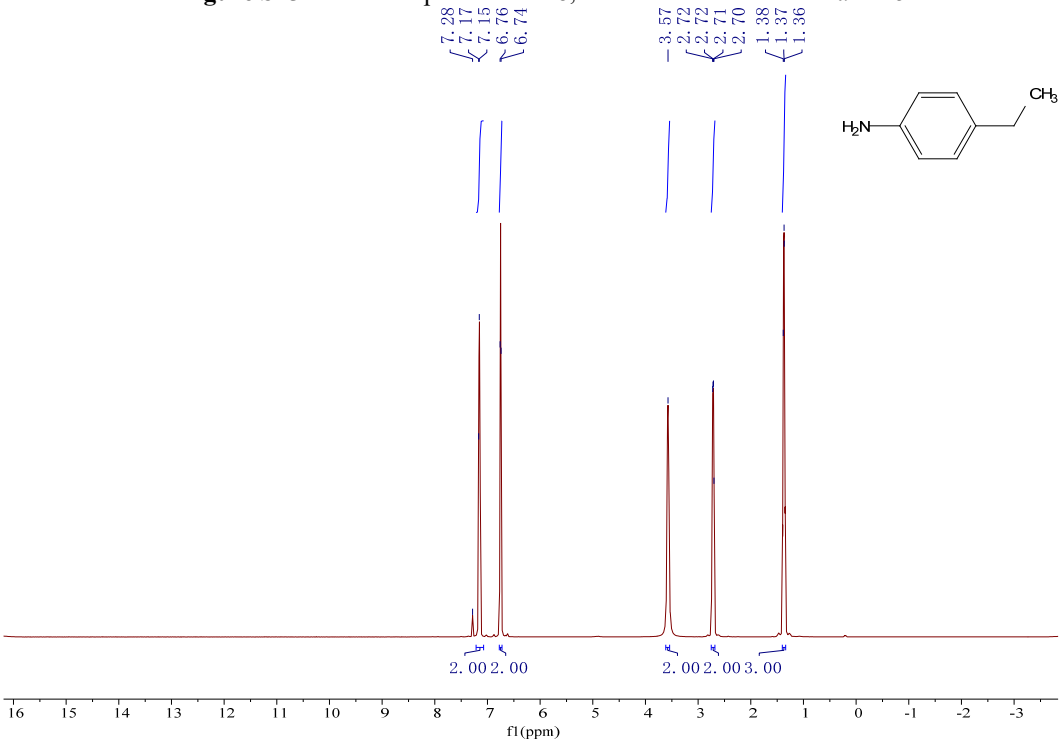



**Figure S16**: $^{1}$H NMR spectrum of **2p**, recorded in Chloroform-*d* at 25 ˚C.

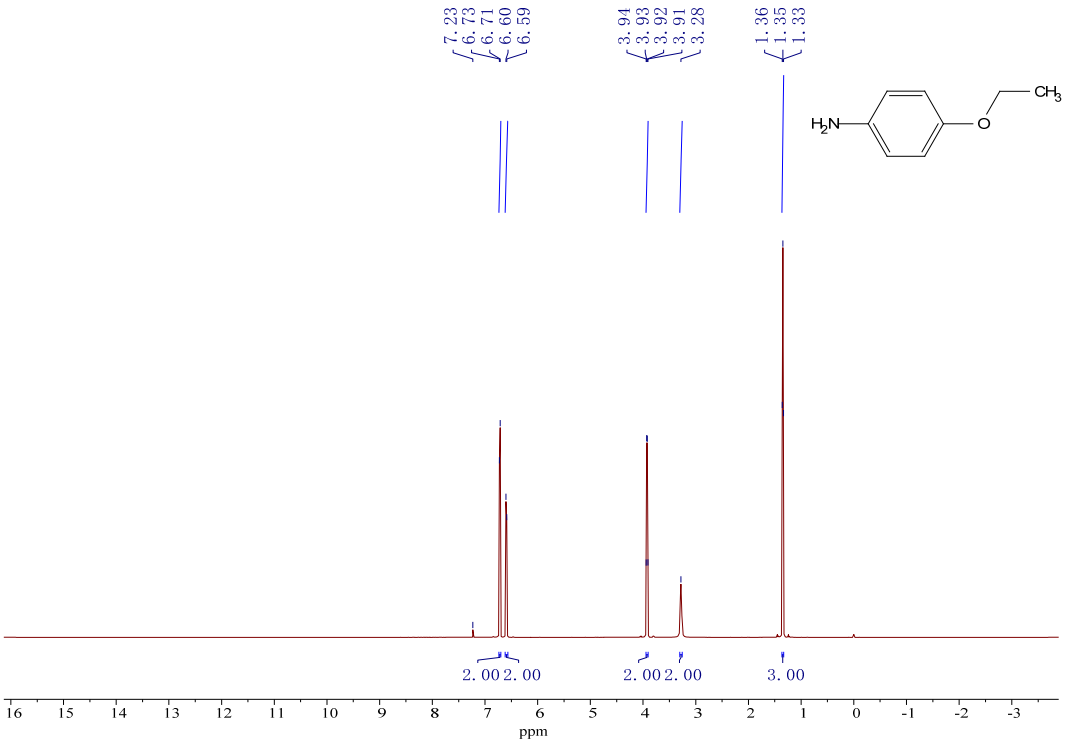



**Figure S17**: $^{1}$H NMR spectrum of **2q**, recorded in Chloroform-*d* at 25 ˚C.

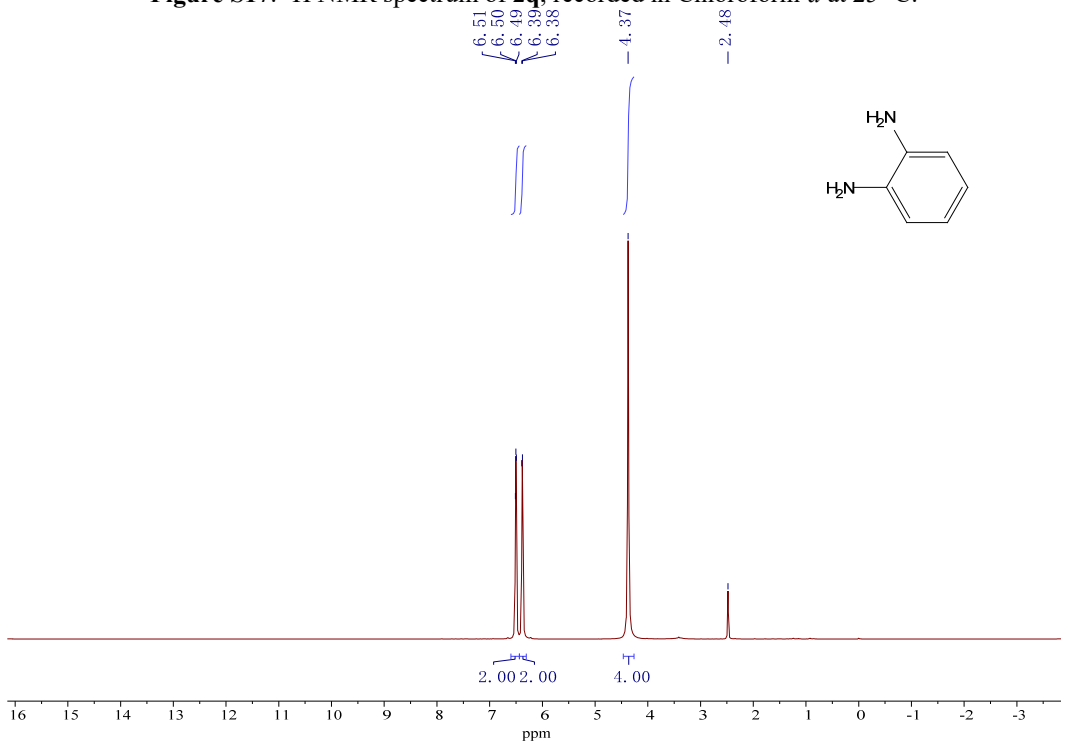



**Figure S18**: $^{1}$H NMR spectrum of **2r**, recorded in DMSO-$d_6$ at 25 ˚C.

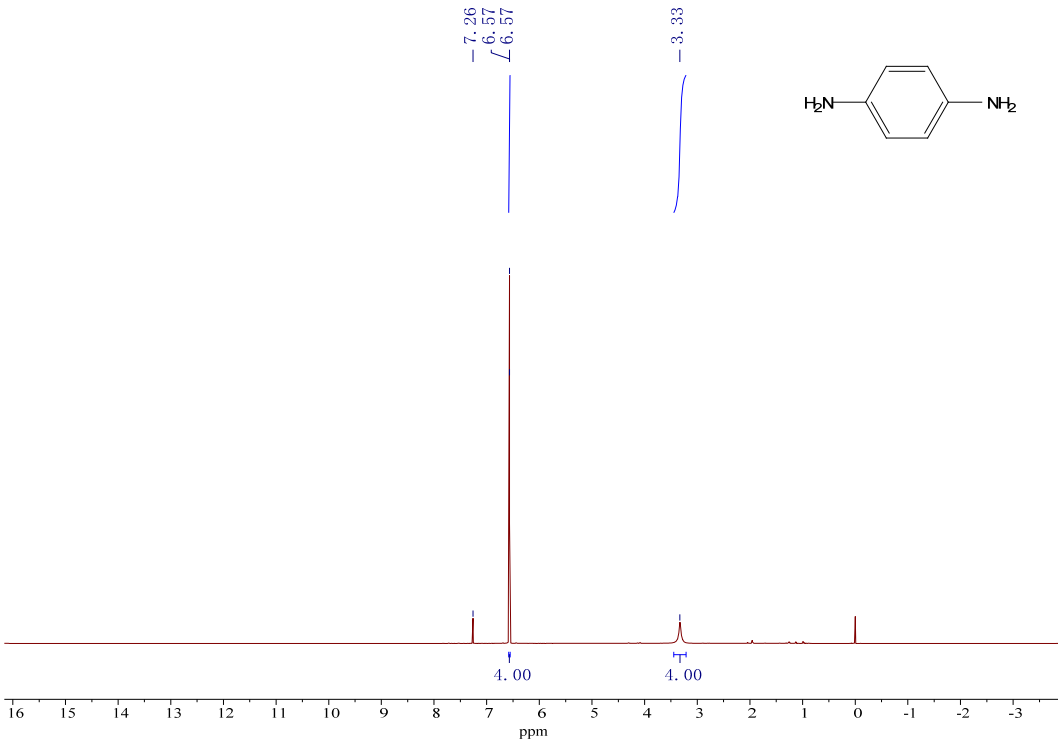



**Figure S19**: $^{1}$H NMR spectrum of **2s**, recorded in Chloroform-*d* at 25 ˚C.

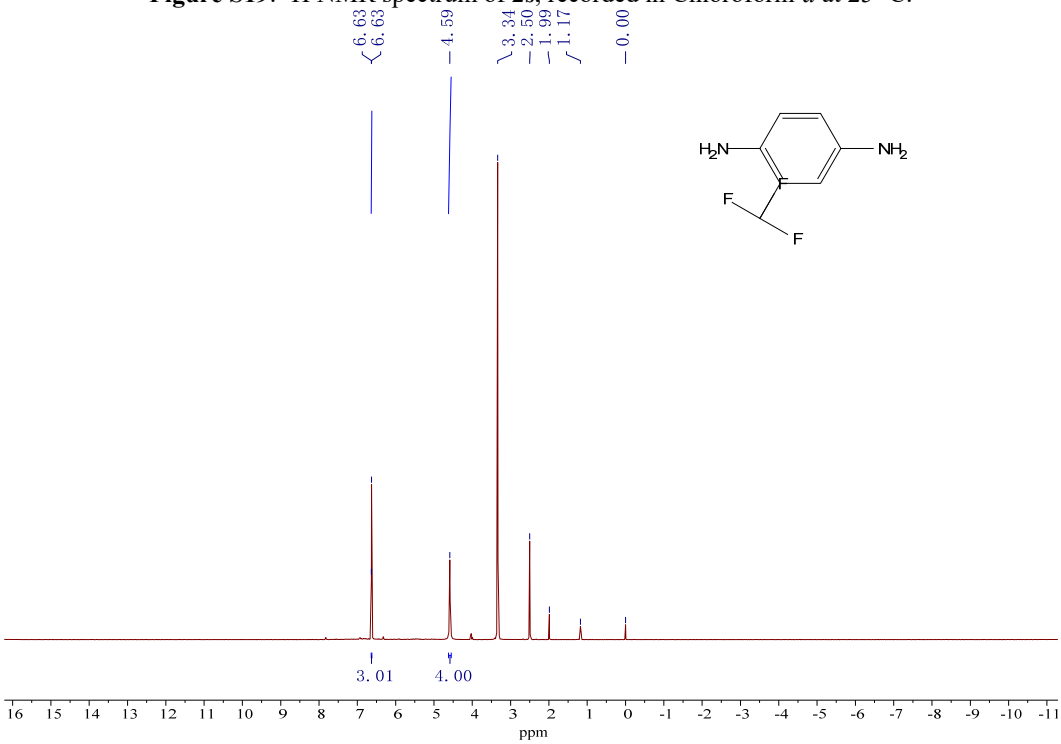



**Figure S20**: $^{1}$H NMR spectrum of **2t**, recorded in DMSO-$d_6$ at 25 ˚C.

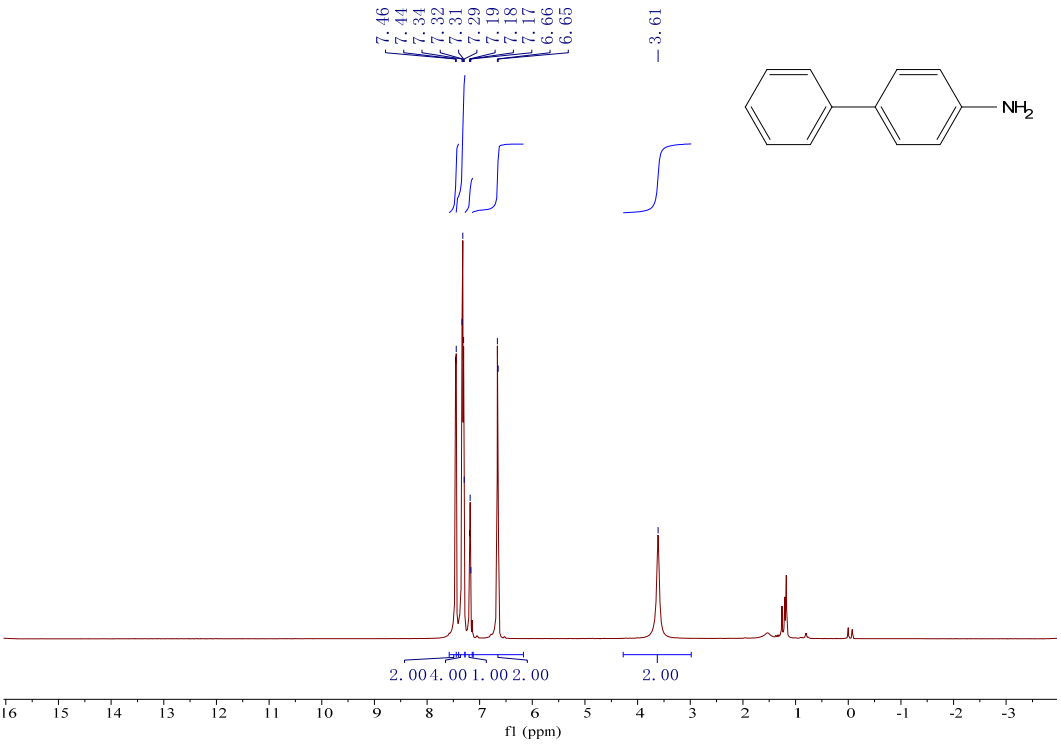



**Figure S21**: $^{1}$H NMR spectrum of **2u**, recorded in Chloroform-*d* at 25 ˚C.

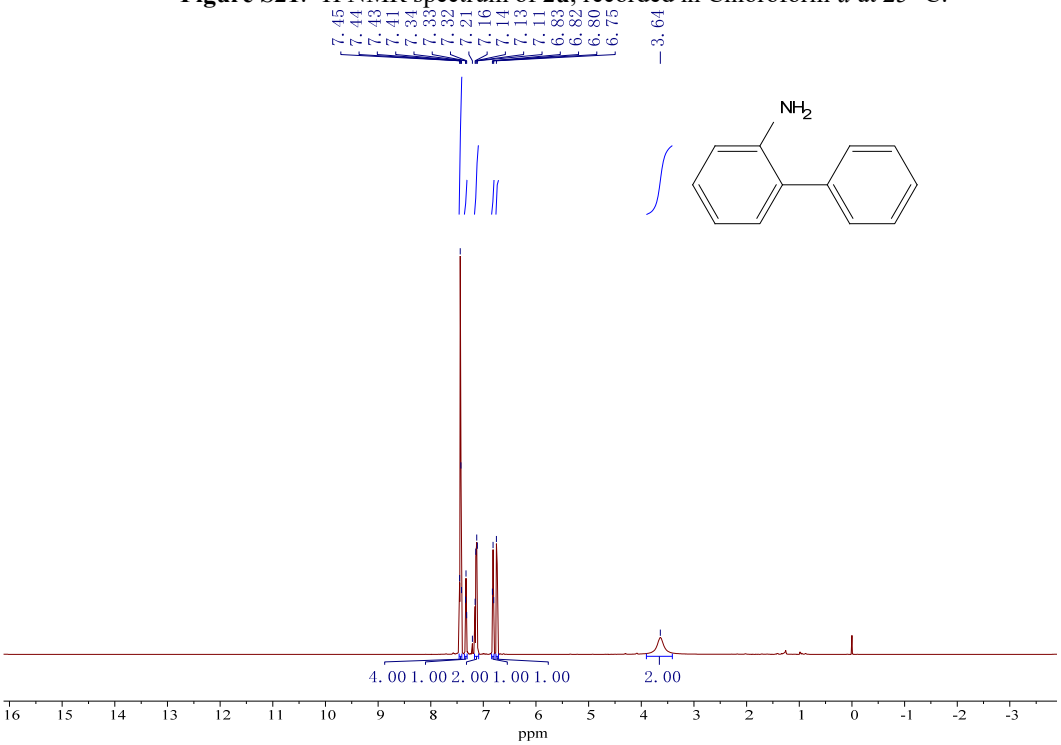



**Figure S22**: $^{1}$H NMR spectrum of **2v**, recorded in Chloroform-*d* at 25 ˚C.

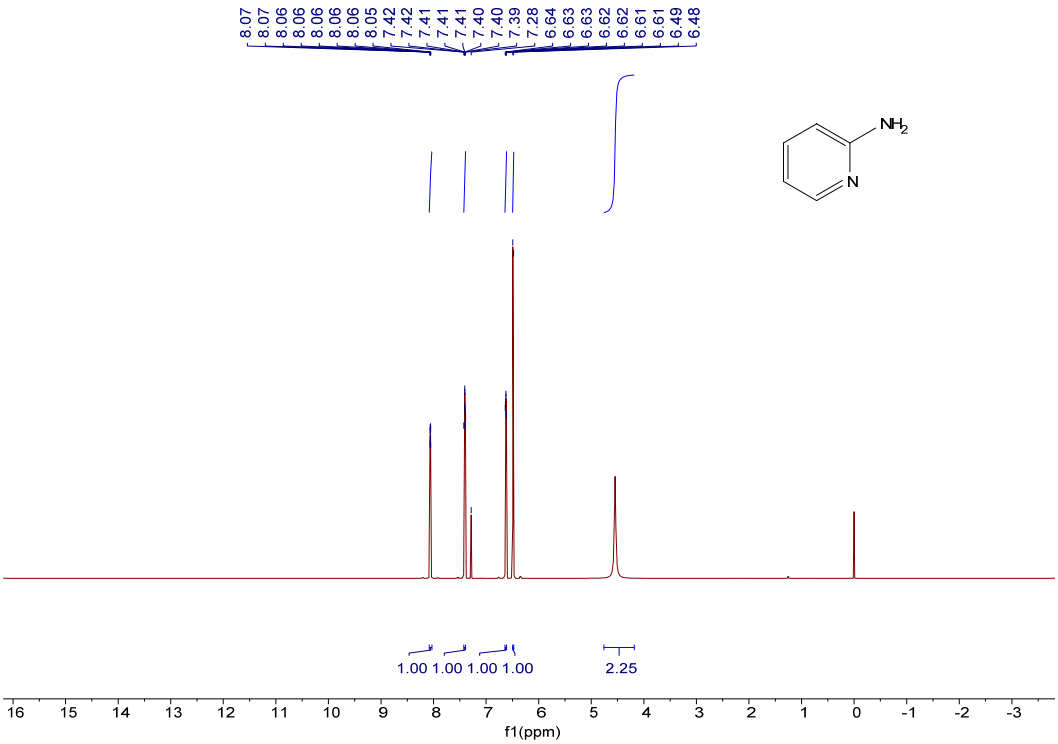



**Figure S23**: $^{1}$H NMR spectrum of **2w**, recorded in Chloroform-*d* at 25 ˚C.

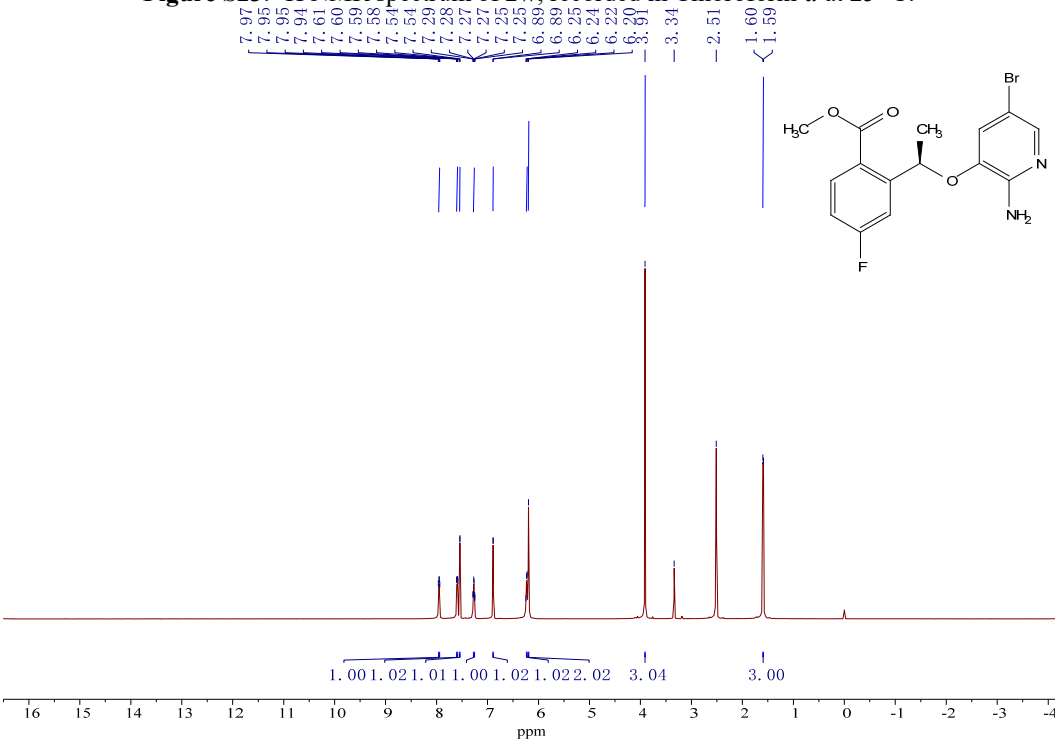



**Figure S24**: $^{1}$H NMR spectrum of **4**, recorded in DMSO-$d_6$ at 25 ˚C.