Supporting Information

Facile synthesis of gold nanoparticles using aggregates of pentacenequinone derivative and their catalytic activity for oxidative polymerization, homocoupling and reduction

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Contents

General experimental Procedures:

All reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium and benzophenone and kept over molecular sieves overnight before use. UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length, 1 cm). The cell holder was thermostatted at 25^0 C. The fluorescence spectra were recorded with a SHIMADZU 5301 PC spectrofluorimeter. Scanning electron microscope (SEM) images were obtained with a field-emission scanning electron microscope (SEM CARL ZEISS SUPRA 55). TEM images were recorded from Transmission Electron Microscope (TEM)-HITACHI. Atomic Force Microscopy (AFM) images were recorded with PARK XE70 instrument. ^{1}H NMR spectra were recorded on a JEOL-FT NMR–AL 300 MHz and Avance-II (Bruker) 400 MHz spectrophotometers using $CDCl_3$ as solvent and tetramethylsilane $SiMe_4$ as internal standards. UV-vis studies were performed in THF and H_2O/THF mixture. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet m = multiplet), coupling constants *J* (Hz), integration, and interpretation. Silica gel (60–120 mesh) was used for column chromatography.

Table S1: Comparison of present method for the homocoupling of phenylboronic acid by gold nanoparticles of derivative **3** over other reported systems in literature.

Physical state of AuNPs used	**Method of formation of AuNPs catalyst**	**Amount of AuNPs used for homocoupling**	**Nature of AuNPs catalyst**	**Materials used**	**Solvent**	**Temp. (in °C)**	**Rx. Time**	**%Yield Ph-Ph/Ph-OH**	**Papers**
Aqueous solution	**Wet Chemical Method (Room temp.)**	**2 mM, 1 mL**	**Un-supported**	**AuNPs, K_2CO_3**	**H_2O/Toluene**	**70 ^{0}C**	**7 h**	**80/20**	**Present manuscript**
Aqueous solution	Chemical reduction in organic synthesizer at 0 ^{0}C	0.5 mM, 10 mL	**PVP stabilized**	Au: PVP, acetate buffer, K_2CO_3	H_2O	30 ^{0}C	9 h	74/26	*Chem. Commun.*, 2013, **49**, 2542--2544
Solid	Chemical reduction below 25 ^{0}C	10 mg catalyst (Au loading 0.66 mol %)	**Supported**	Carbon-Supported AuNPs	H_2O/Toluene	70 ^{0}C	7 h	86/12	*Chem. Commun.*, 2013, **49**, 8235--8237
Solid	Anion-exchange followed by calcination at 400 ^{0}C	30 mg of Au catalyst	**Supported**	Au/MAO, dodecane	MeOH	100 ^{0}C	12h	90/10	*Chem. Commun.*, 2012, **48**, 5476–5478
Aqueous solution	Chitosan stabilized chemical reduction of $AuCl_4$ at 0 ^{0}C	0.5 mM, 10 mL	**Supported**	Au:chit, acetate buffer, K_2CO_3	H_2O	47 ^{0}C	24 h	93/6	*Chem. Asian J.*, 2012, **7**, 55
Aqueous solution	Redox rection and polymer stabilized	0.5 mM, 10 mL	**PVP stabilized**	PVP-Stabilized AuNPs, K_2CO_3	H_2O	80 ^{0}C	24 h	74/26	*Tetrahedron Letters,* 2012, **53**, 6104–6106.

Table S2: Comparison of present method over other reported procedure in literature for the reduction of *p*-nitrophenol to *p*-aminophenol by gold nanoparticles of derivative **3**.

Physical state of catalyst used	**Materials used**	**Amount of catalyst used for reduction of *p*-nitrophenol**	**Reaction time**	**Rate constant**	**Temp. (in °C)**	**Journals**
Aqueous solution	**AuNPs, $NaBH_4$**	**5 µL**	**8 min.**	**8.85×10^{-3} sec^{-1} (0.53 min^{-1})**	**Room temp.**	**Present manuscript**
Solid	Mesoporous gold leaves, $N_2H_4\cdot H_2O$	1 mg	10 min.	8.16×10^{-3} sec^{-1} (0.49 min^{-1})	Room temp.	*ACS Appl. Mater. Interfaces* 2014, **6**, 9134–9143
Solid	γ-Fe_2O_3@m-SiO2–SH–Au	13 µg	6 min.	5.33×10^{-3} sec^{-1} (0.32 min^{-1})	Room temp.	*J. Mater. Chem. A*, 2014, **2**, 10485–10491
Aqueous solution	Au@IB–YSN, $NaBH_4$	0.1 mL	6.66 min. (400 sec.)	7.7×10^{-3} sec^{-1} (0.46 min^{-1})	25 ^{0}C	*Chem. Commun.,* 2013, **49**, 9591-9593
Solid	Au-PNIPA yolk–shell, $NaBH_4$	-	40 min.	7.5×10^{-4} sec^{-1} (0.045 min^{-1})	15 ^{0}C	*Angew. Chem. Int. Ed.* 2012, **51**, 2229 –2233
Solid	USP Au/C, $NaBH_4$ (ultrasonic spray pyrolysis)	10 µg	9 min.	1.0×10^{-2} sec^{-1} (0.60 min^{-1})	25 ^{0}C	*Chem. Commun.,* 2012, **48**, 11094–11096
Solid	Au/graphene hydrogel, $NaBH_4$	0.1 mg	12 min.	3.17×10^{-3} sec^{-1} (0.19 min^{-1})	Room temp.	*J. Mater. Chem.*, 2012, **22**, 8426–8430
Solid	NAP-Mg-Au(0), $NaBH_4$	15 mg	7 min.	7.6×10^{-3} sec^{-1} (0.456 min^{-1})	Room temp.	*Green Chem.*, 2012, **14**, 3164–3174

Table S3: Comparison of present method over other reported procedure in literature for the reduction of *p*-nitroaniline to *p*-phenylenediamine by gold nanoparticles of derivative **3**.

Physical state of catalyst used	**Materials used**	**Amount of catalyst used for reduction of *p*-nitroaniline**	**Reaction time**	**Rate constant**	**Recyclability of catalyst**	**Temp. (in °C)**	**Journals**
Aqueous solution	**AuNPs, $NaBH_4$**	**5 µL**	**18 min.**	**4.53×10^{-3} sec^{-1} (0.272 min^{-1})**	**Yes**	**Room temp.**	**Present manuscript**
Solid	Fe_3O_4@Au/ MIL-100 (Fe), $NaBH_4$	1 mg	25 min.	2.53×10^{-3} sec^{-1} (0.152 min^{-1})	Yes	-	*Catal. Sci. Technol.*, 2014,**4**, 3013-3024
Aqueous solution	BPS-30-AuNPs, KBH_4	20 µL	25 min.	2.53×10^{-3} sec^{-1} (0.152 min^{-1})	No	Room temp.	*Cryst. Eng. Comm*, 2012, **14**, 7600–7606
Aqueous solution	AuNCs, $NaBH_4$	347 µL	15-40 min.	3.12×10^{-3} sec^{-1} (0.187 min^{-1})	No	36-40 ^{0}C	*J. Phys. Chem. C,* 2012, **116**, 23757−23763
Aqueous solution	Au–GO, $NaBH_4$	0.25 mL	40 min.	2.06×10^{-3} sec^{-1} (0.124 min^{-1})	No	Room temp.	*J. Mater. Chem.*, 2011, **21**, 15431–15436
Aqueous solution	AuNPs, ice cold KBH_4	-	56 min.	7.33×10^{-4} sec^{-1} (0.044 min^{-1})	No	Ice cold	*J. Phys. Chem. C* 2009**, 113***,* 17730–17736
Aqueous solution	AuNPs, ice cold $NaBH_4$	-	64 min.	4.67×10^{-4} sec^{-1} (0.028 min^{-1})	No	Ice cold	*J. Phys. Chem. C* 2009**, 113***,* 5150–5156

General Procedure for Homocoupling reaction

The aerobic homocoupling of phenyl boronic acid was carried out in a 10 ml Round Bottom Flask (RBF) at 70^{o} C. Phenylboronic acid (0.3 mmol, 36.6 mg), K_2CO_3 (0.425 mmol, 58.7 mg), 1 ml of 2 mM gold nanoparticles solution (2 μmol) were taken in a RBF and then 0.5 ml water and 1 ml toluene were added to the mixture. The mixture was heated at 70 ^{0}C with constant stirring for 7 h, under open flask condition. The progress of the reaction was monitored by TLC. After 7 h, the reaction mixture was extracted by ethyl acetate. The combined organic layer was concentrated and the crude product was purified by column chromatography, using hexane as eluent to obtain biphenyl (80%) and phenol (20%).

Spectroscopic characterization of the products through NMR analysis

Biphenyl. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 [d, 4H, J = 9.0 ArH], 7.44 [t, 4H, J = 7.5 ArH] 7.60 [d, 2H, J = 9.0 ArH], (see pS24 in ESI†).

Phenol. ^{1}H NMR (300 MHz, CD_3OD): δ = 4.89 [s, 1H, OH], 6.32 [d, 2H, J = 3.0 ArH], 6.57 [t, 1H, J = 7.5 ArH], 7.38 [d, 2H, J = 3.0 ArH] (see pS25 in ESI†).

Reduction of *p*-nitroaniline over gold nanoparticles of derivative 3. 300 μL of 1 mM *p*-nitroaniline, 300 μL of 10 mM $NaBH_4$ and 5 μL (10 nmol) of gold nanoparticles of derivative **3** were mixed. After that, different volumes of deionized water were added to the reaction mixture to nullify the dilution effect. The mixture was stirred vigorously with a magnetic stirrer. After stirring the reaction mixture, a colour change of the reaction mixture from yellow to colourless was observed which indicate the reduction of *p*-nitroaniline to *p*-phenylenediamine.[1] Complete reduction of *p*-nitroaniline to *p*-phenylenediamine over gold nanoparticles of derivative **3** took 18 minutes. The formation of the reduced product *p*-phenylenediamine was confirmed from UV-vis spectroscopy (See Fig. 7A in manuscript) and ^{1}H-NMR spectrum of the product (See pS26 in ESI†).

Reduction of *p*-nitrophenol over gold nanoparticles of derivative 3. To a 300 μL of an aqueous solution of *p*-nitrophenol (1 mM), 300 μL of 10 mM $NaBH_4$ and 5 μL (10 nmol) of AuNPs of derivative **3** were added. The mixture was diluted with water and stirred vigorously with a magnetic stirrer. The diluted solution was analyzed by UV-vis spectrometry and the conversion could be calculated according to the intensity decrease of *p*-nitrophenol. The reaction was stopped when the yellow color of the mixture disappeared, which indicate the reduction of *p*-nitrophenol to *p*-aminophenol.[2] Complete reduction of *p*-nitrophenol to *p*-aminophenol over gold nanoparticles of derivative **3** took 8 minutes. The formation of the reduced product *p*-aminophenol was confirmed from UV-vis spectroscopy (See Fig. 7B in manuscript) and ^{1}H-NMR spectrum of the product (See pS27 in ESI†).

Spectroscopic characterization of the products through NMR analysis

***p*-phenylenediamine.** ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.29$ [s, 4H, NH_2], 6.57 (s, 4H, ArH] (See pS26 in ESI†).

***p*-aminophenol.** ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.71$ [s, 2H, NH_2], 6.60 [d, 2H, J = 9 ArH], 6.67 [d, 2H, J = 6 ArH] (See pS27 in ESI†).

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[1] V. Reddy, R. S. Torati, S. Oh and C. Kim, *Ind. Eng. Chem. Res.*, 2013, **52**, 556.

[2] K. Layek, M. L. Kantam, M. Shirai, D. Nishio-Hamane, T. Sasaki and H. Maheswaran, *Green Chem.*, 2012, **14**, 3164.

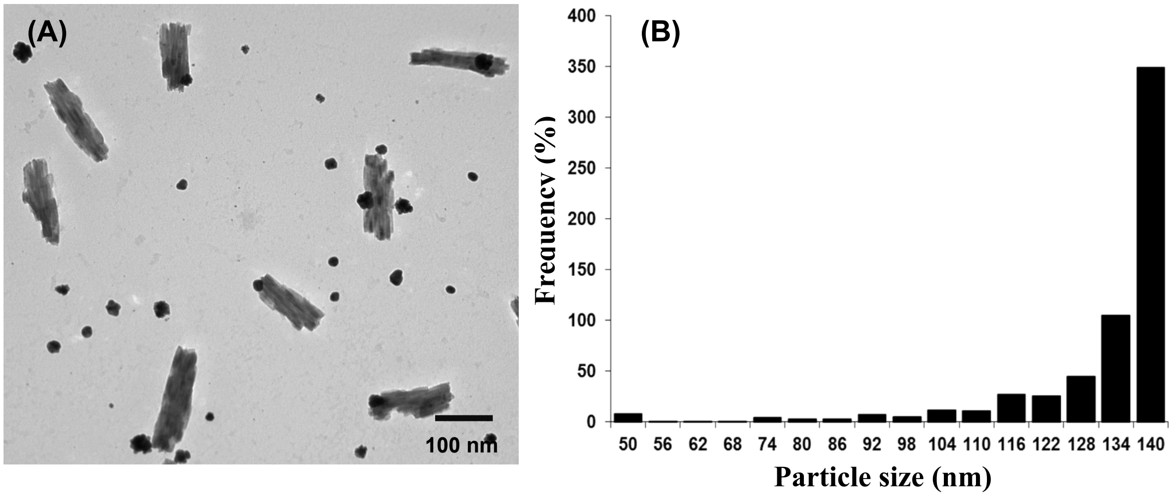

Fig. S1 (A) Transmission electron microscope (TEM) image and (B) Size distribution of colloidal suspension of derivative **3**. Scale bar 100 nm

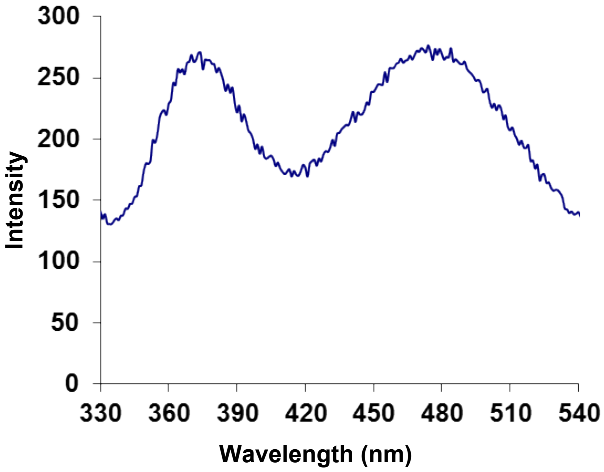

Fig. S2 Fluorescence spectrum of derivative **3** (10 μM) in 60% H_2O/THF mixture.

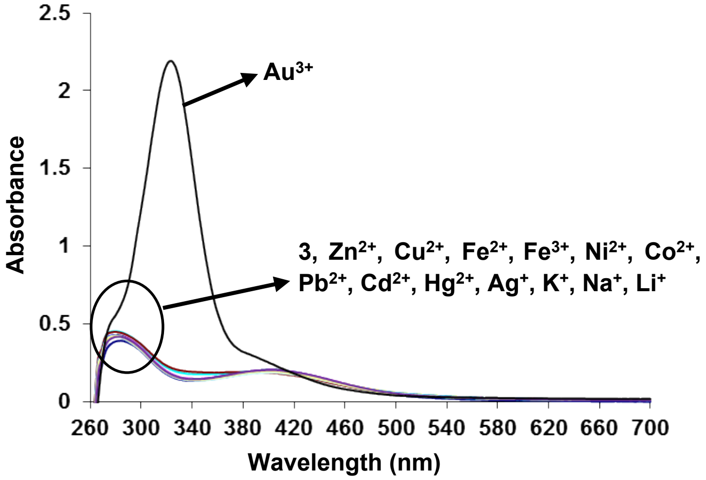

Fig. S3 UV-vis spectra of derivative **3** (10 µM) upon additions of 200 equivalents of various metal ions as their perchlorate salt in H_2O/THF (6/4), buffered with HEPES, pH = 7.0.

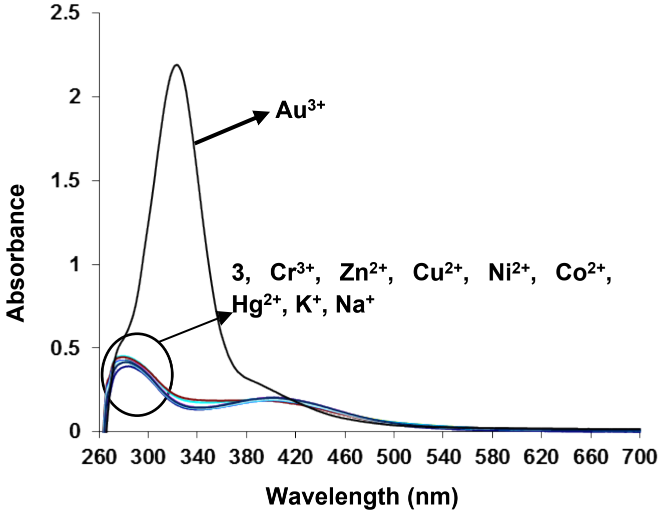

Fig. S4 UV-vis spectra of derivative **3** (10 µM) upon additions of 200 equivalents of various metal ions as their chloride salt in H_2O/THF (6/4), buffered with HEPES, pH = 7.0.

Regression Statistics	
Multiple R	0.997975
R Square	0.995954
Intercept	0.018383
Slope	0.00187

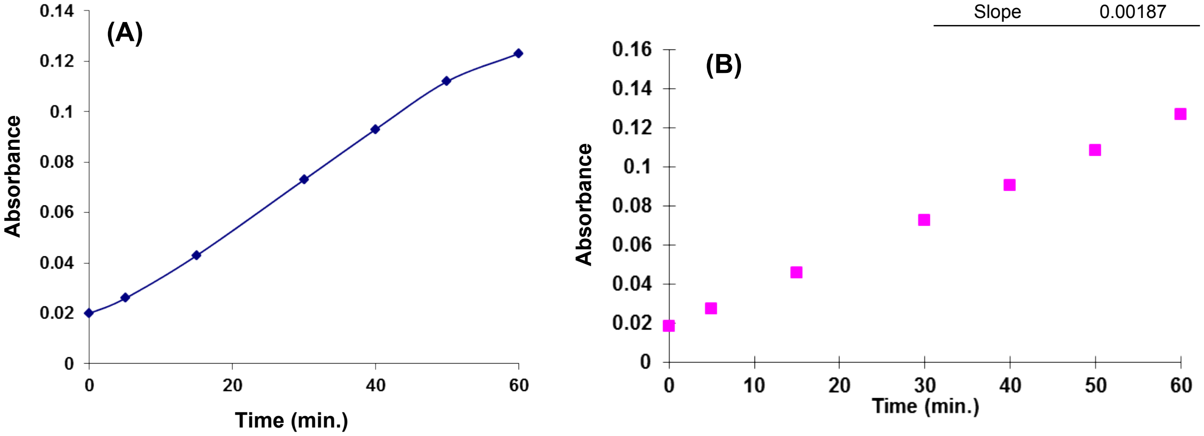

Fig. S5 Graphical representation of the rate of formation of gold nanoparticles of derivative **3**. (A) Time (min.) vs. absorbance plot at 560 nm (B) regression plot of A.

The first order[3] rate constant for the formation of gold nanoparticles was calculated from the changes of intensity of absorbance of aggregates of derivative **3** at 560 nm wavelength in the presence of Au^{3+} ions at different time interval[4].

From the time vs. absorbance plot at fixed wavelength 560 nm by using first order rate equation we get the rate constant = k = slope×2.303 = 7.18×10^{-5} Sec^{-1}.

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[3] Luty-Błocho, M.; Pacławski, K.; Wojnicki, M.; Fitzner, K. *Inorganica Chimica Acta* **2013**, 395 189–196.

[4] Goswami, S.; Das, S.; Aich, K.; Sarkar, D.; Mondal, T. K.; Quah, C. K.; Fun, H-K. *Dalton Trans*. **2013**, *42*, 15113–15119.

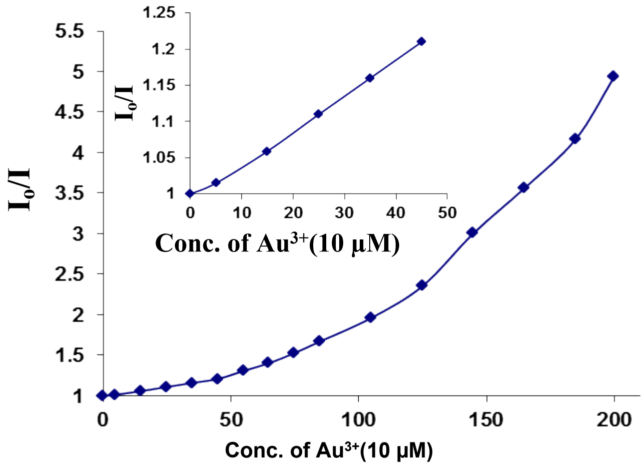

Fig. S6 Variation of fluorescence intensity of aggregates of derivative **3** (10 μM) at 477 nm in H_2O/THF (6:4, v/v) buffered with HEPES, pH =7.0, $\lambda_{ex.}$ = 287 nm in the presence of different concentrations of Au^{3+} ions (I_o/I; I_o = initial fluorescence intensity at 477 nm; I= fluorescence intensity after the addition of Au^{3+} ions at 477 nm). Inset shows the linear Stern-Volmer plot at lower concentration of Au^{3+} ions.

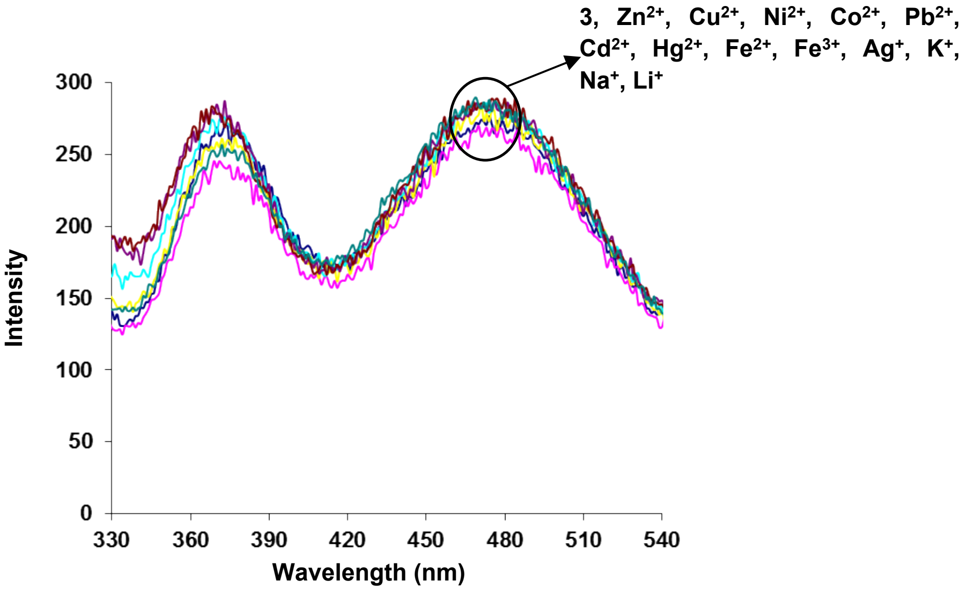

Fig. S7 Fluorescence spectra of derivative **3** (10 μM) upon additions of various metal ions (200 equivalents) as their perchlorate salt in H_2O/THF (6/4) buffered with HEPES, pH = 7.0.

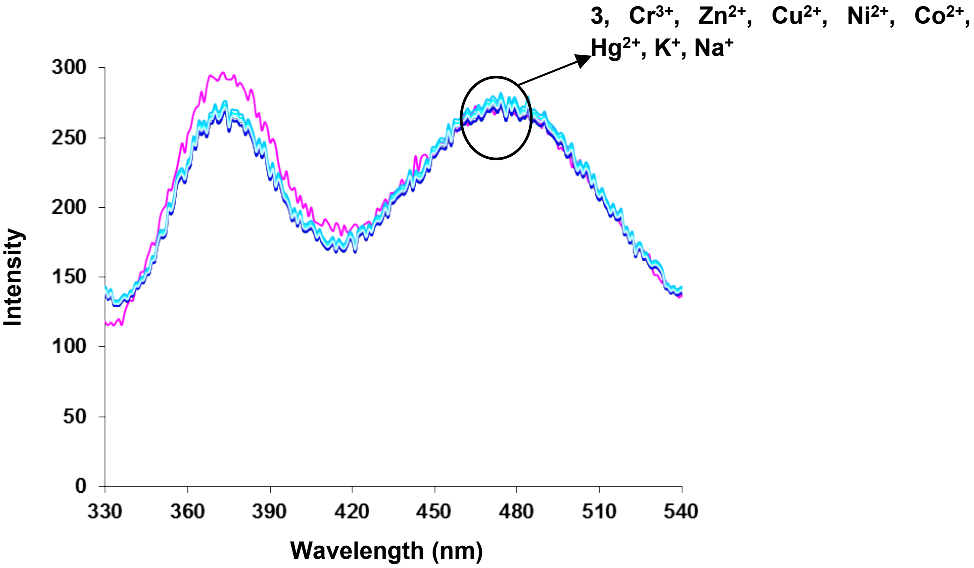

Fig. S8 Fluorescence spectra of derivative **3** (10 μM) upon additions of various metal ions (200 equivalents) as their chloride salt in H_2O/THF (6/4) buffered with HEPES, pH = 7.0.

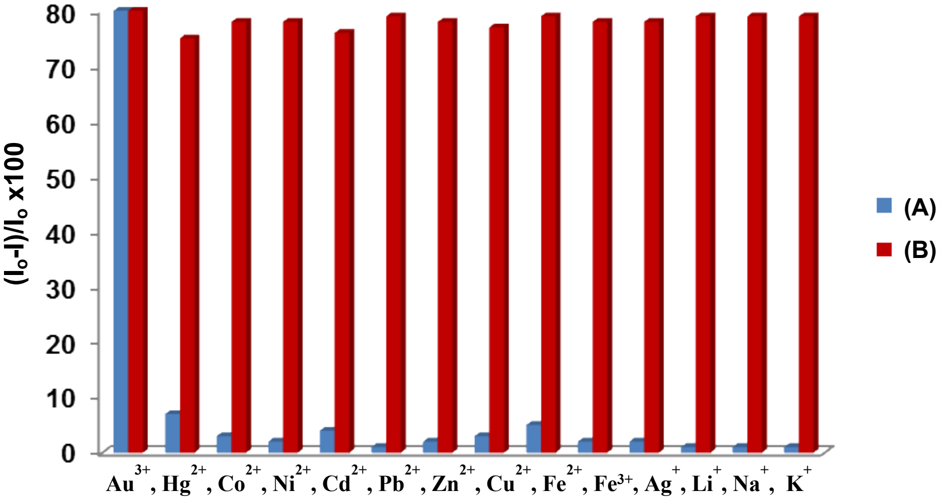

Fig. S9 Fluorescence response of derivative **3** (10 μM) to various metal ions (200 equivalents) in H_2O/THF (6/4); buffered with HEPES, pH = 7.0; λ_{ex} = 287 nm. Bars represent the emission intensity ratio $(I_o - I)/I_o \times 100$ (I_o = initial fluorescence intensity at 477 nm; I = final fluorescence intensity at 477 nm after the addition of Au^{3+} ions). (A) The sky blue bars represent the addition of individual metal ions, (B) the red bars represent the change in the emission that occurs upon the subsequent addition of Au^{3+} (200 equivalents) to the above solution.

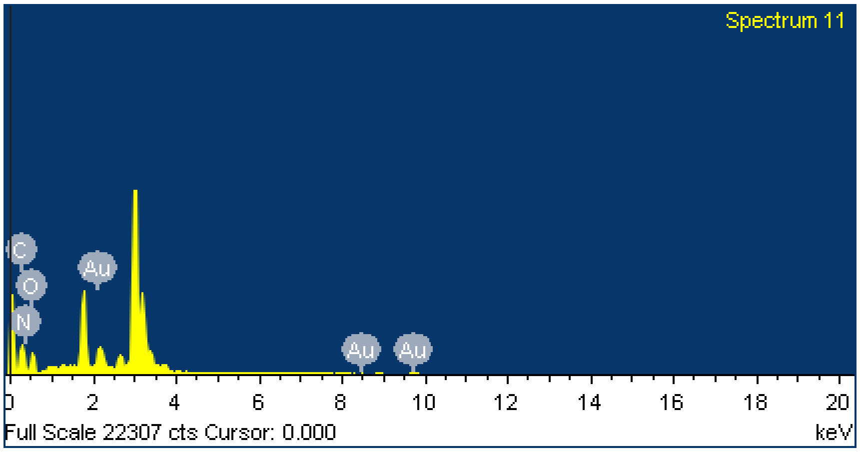

Fig. S10 Energy dispersive X-rays (EDX) analysis of the resulting precipitates using secondary electrons by SEM.

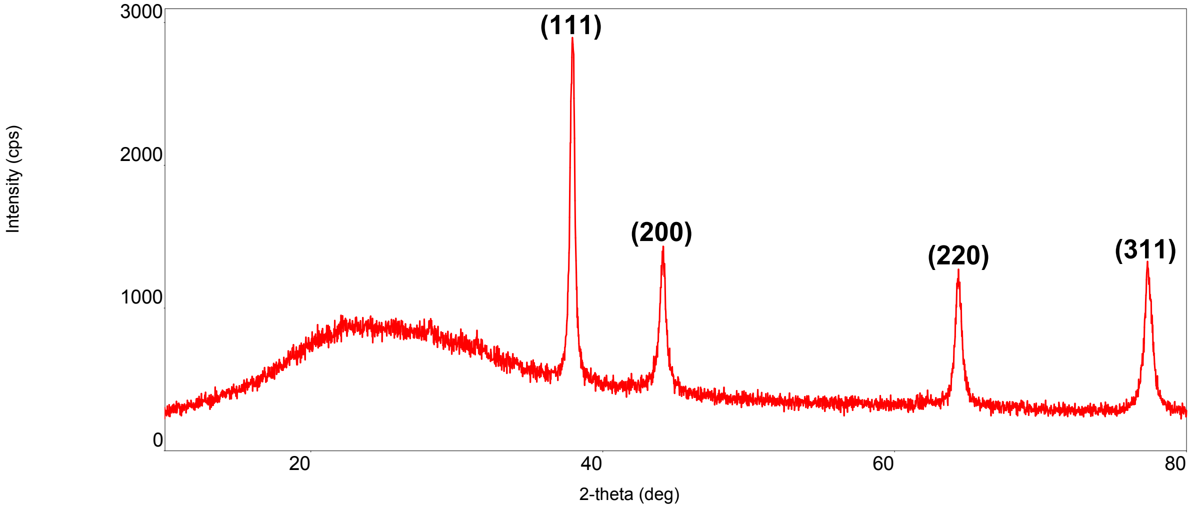

Fig. S11 XRD patterns of precipitates obtained after adding $AuCl_3$ to the aqueous solution of derivative **3**.

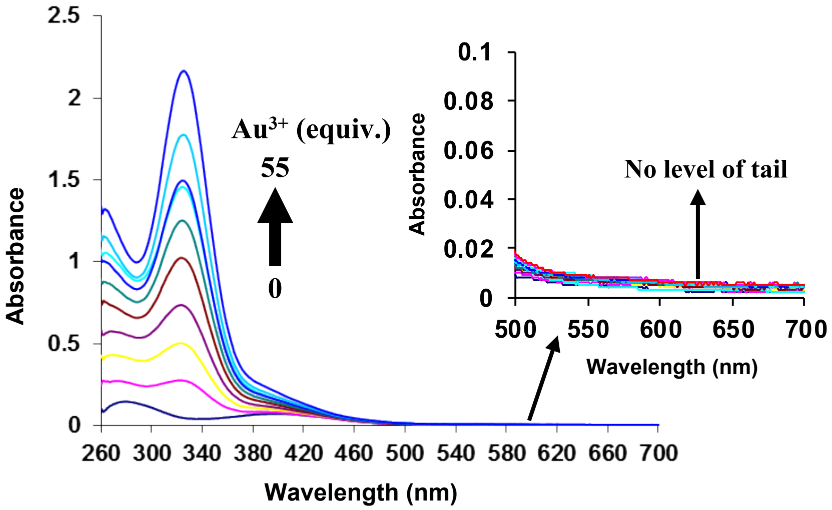

Fig. S12 UV-vis spectra of derivative **3** (10 μM) upon various additions of Au^{3+} ions in THF. Inset: enlarge UV-vis spectra of compound **3** (10 μM) in the range of 500-700 nm.

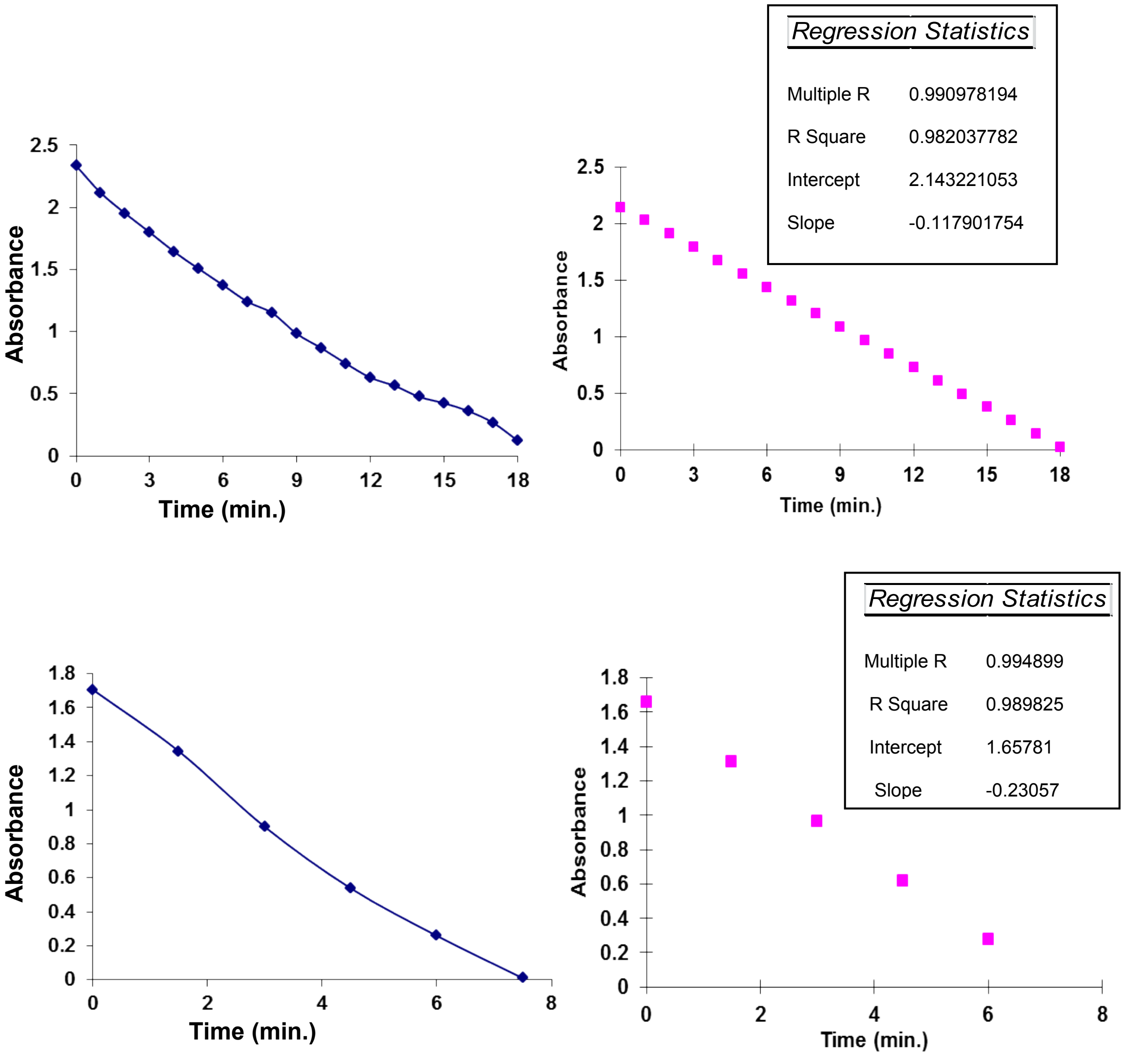

Fig. S13 Graphical representation of time vs. absorbance plot and regression plot for the reduction of *p*-nitroaniline (A) and (B) and *p*-nitrophenol (C) and (D) catalyzed by gold nanoparticles of derivative **3.**

Catalytic reduction of *p*-nitroaniline and *p*-nitrophenol follows Pseudo-first-order kinetics.[5] The apparent rate constants for the reduction of *p*-nitroaniline and *p*-nitrophenol by gold nanoparticles of derivatives **3** listed in following table:

Gold nanoparticles	Nitro derivatives	Rate constant
Derivative **3**	*p*-nitroaniline	4.53×10^{-3} sec^{-1}
	p-nitrophenol	8.85×10^{-3} sec^{-1}

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[5] (a) Zelentsov, S. V.; Simdyanov, I. V.; Kuznetsov, M. V. *High Energy Chemistry* 2005, **39**, 309; (b) M-Q. Yang, X. Pan, N. Zhang and Y-J. Xu, *CrystEngComm*, 2013, **15**, 6819.

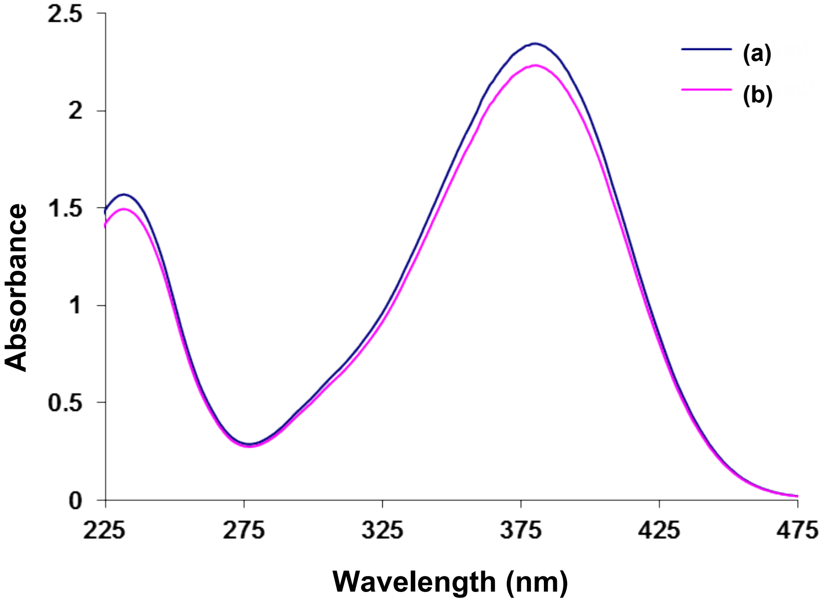


Fig. S14 UV–visible spectra for the chemical reduction of *p*-nitroaniline using $NaBH_4$ in the absence of gold nanoparticles catalyst: (a) 0 min and (b) after 24 hours.

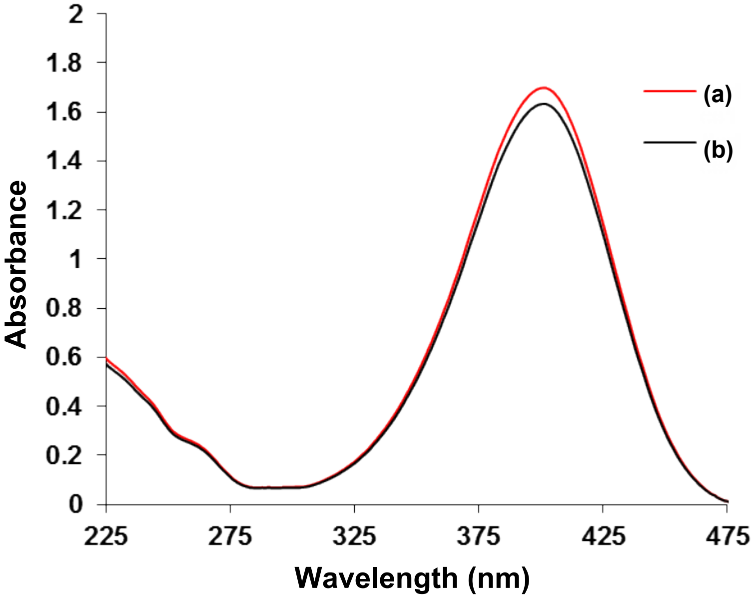
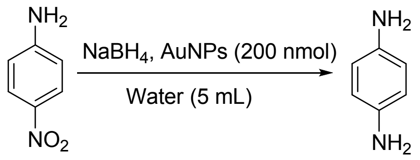


Fig. S15 UV–visible spectra for the chemical reduction of *p*-nitrophenol after adding the $NaBH_4$ in the absence of gold nanoparticles catalyst: (a) 0 min and (b) after 24 hours.

Procedure for the catalyst-reusing sequence in the AuNPs-catalyzed model reaction

The catalytic reduction of *p*-nitroaniline to *p*-phenylenediamine in the presence of $NaBH_4$ aqueous solution was chosen as a model reaction to investigate the reusability of AuNPs catalyst. After the catalytic reduction of *p*-nitroaniline, resulting reaction mixture containing AuNPs catalyst was subjected to reaction for the next catalytic sequence by adding *p*-nitroaniline (10 mg , 0.07 mmol) and $NaBH_4$ (2.6 mg, 0.07 mmol) to the reaction mixture. After seven cycles, colour of the reaction mixture changes from yellow to reddish brown.



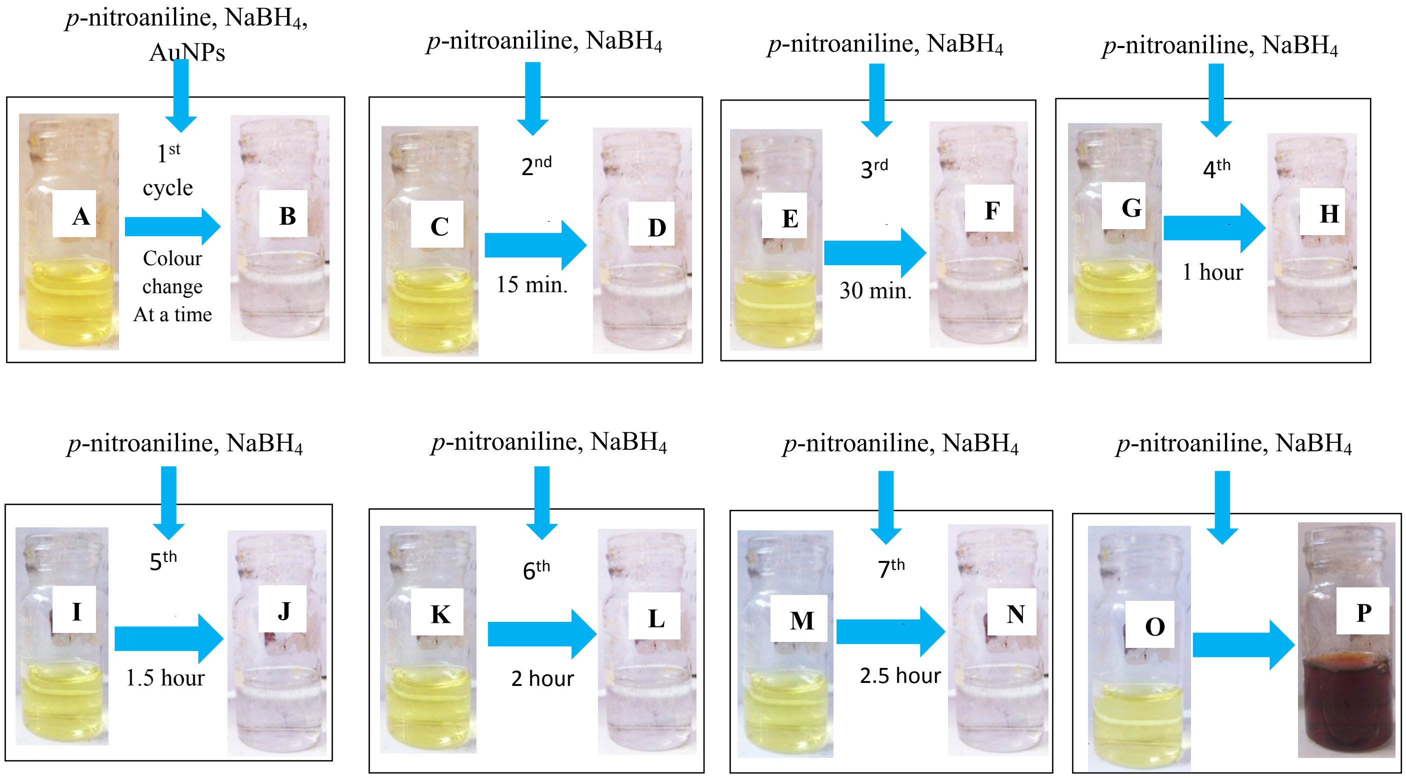


Fig. S16 Depiction of the catalyst-reusing

^{1}H NMR of polyaniline in $CDCl_3$

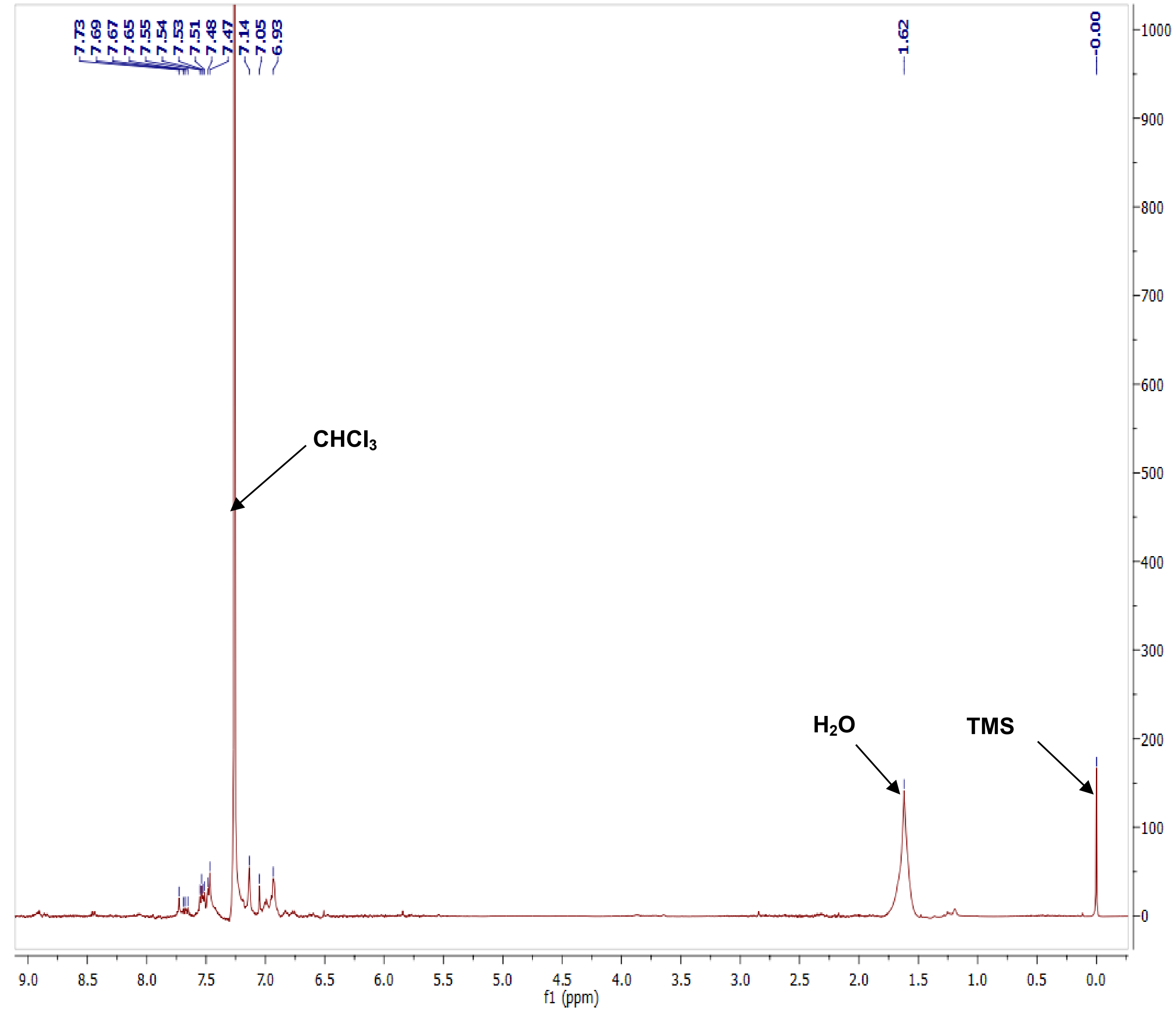


Fig. S17 ^{1}H NMR spectrum of polyaniline in $CDCl_3$.

^1H NMR spectrum of derivative **3**

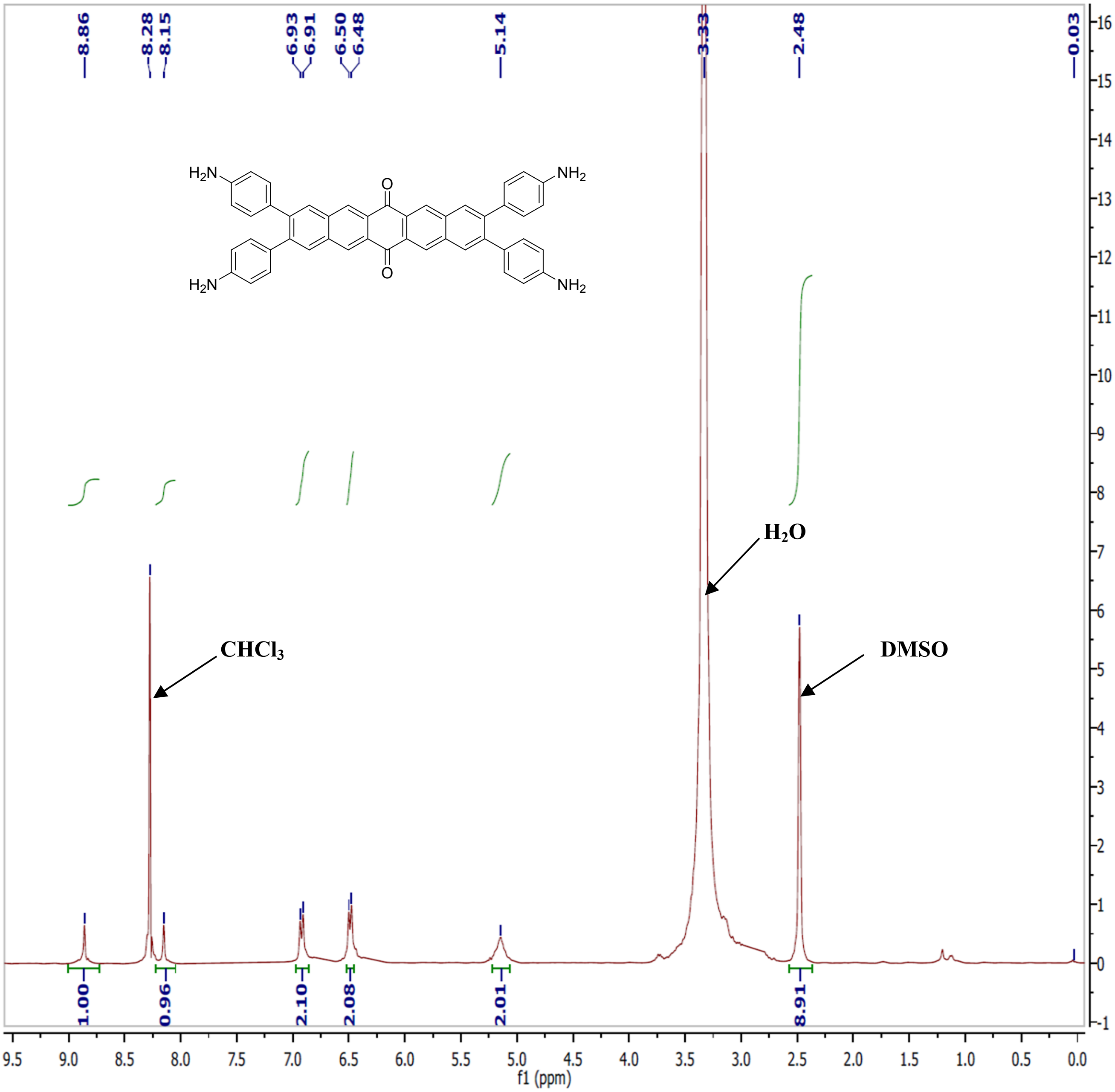


Fig. S18 ^1H NMR spectrum of compound **3** in DMSO**.**

Mass spectrum of derivative **3**

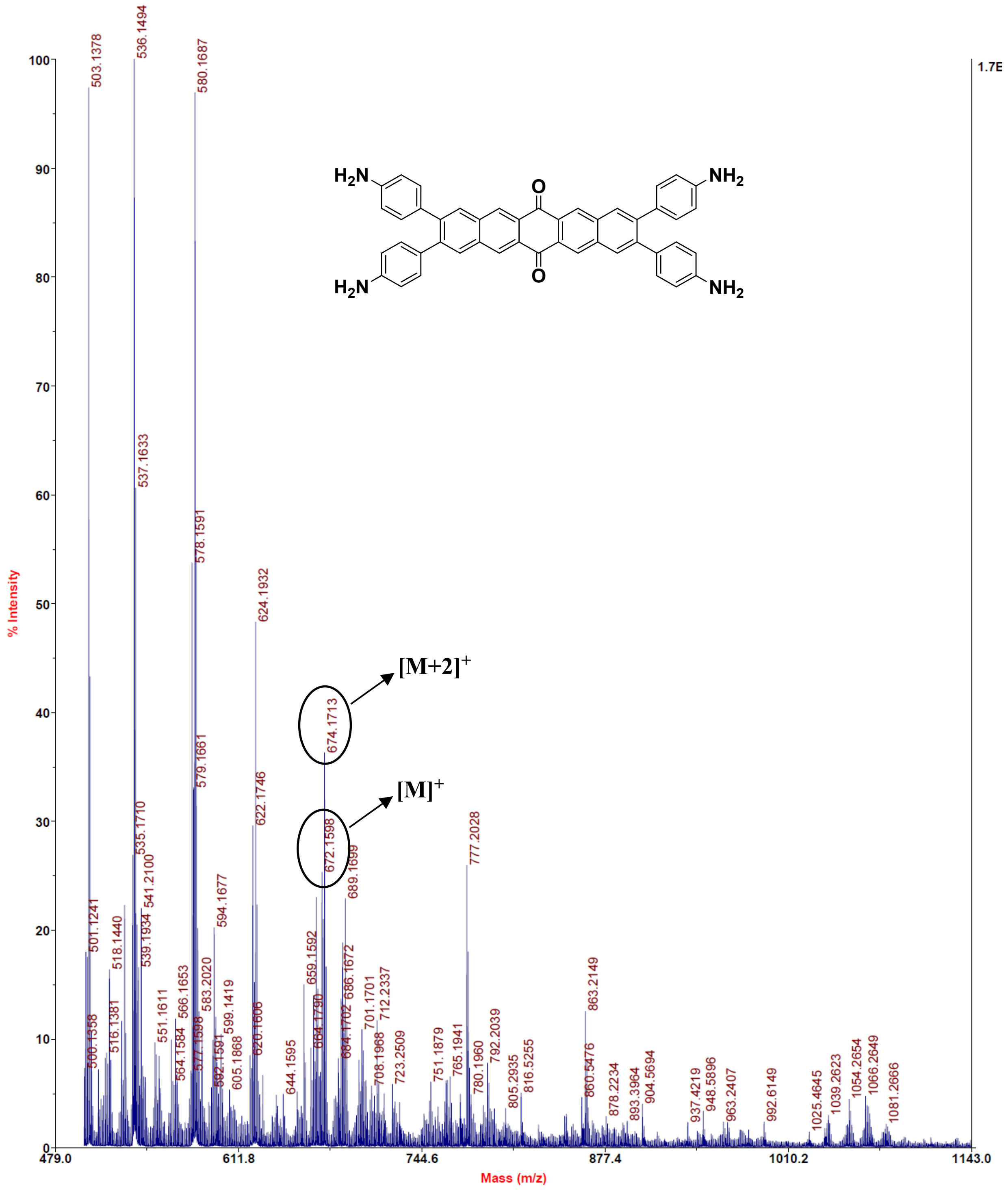


Figure S19 Mass spectrum of derivative **3.**

^{1}H NMR of biphenyl in CDCl$_3$

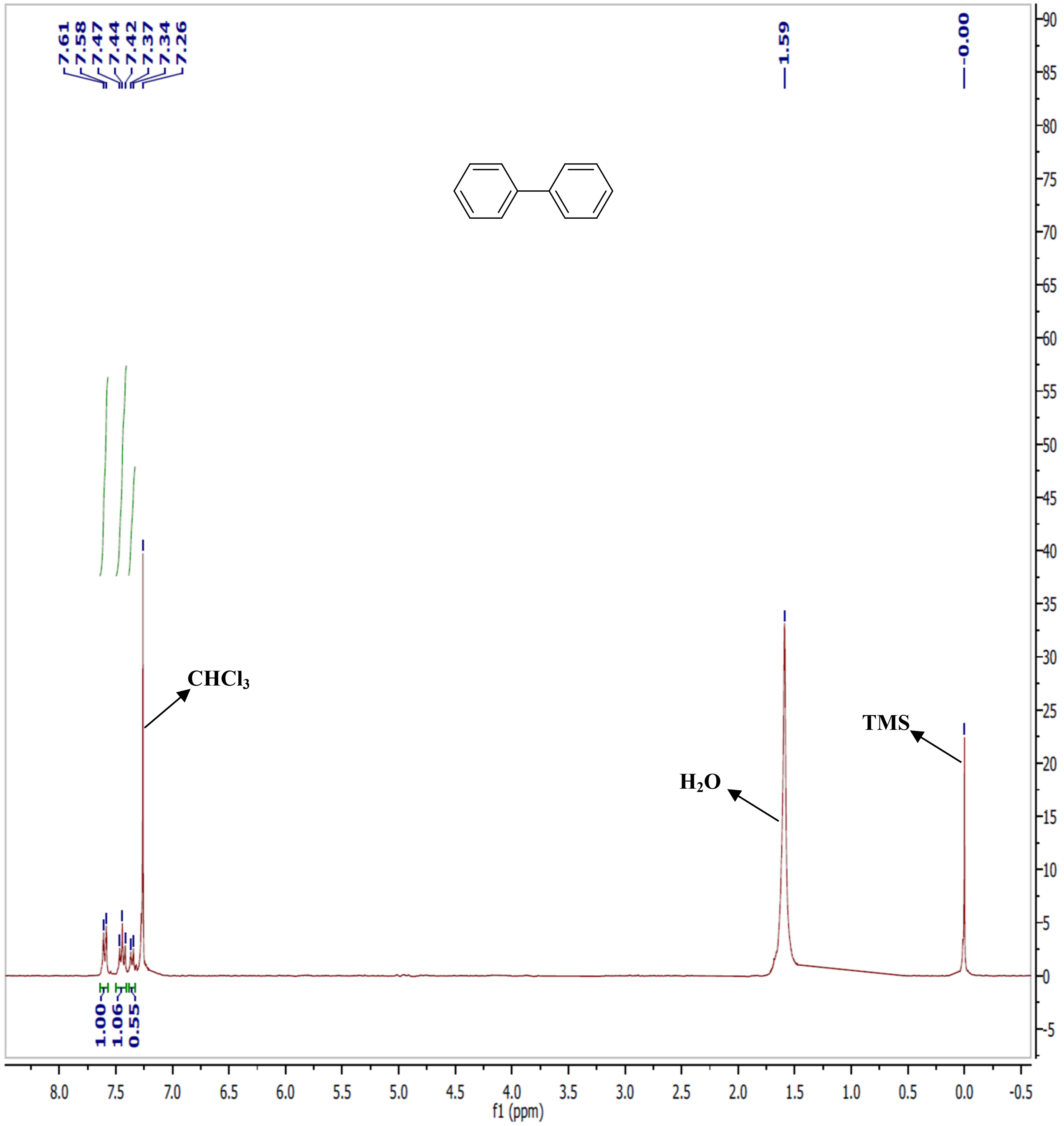


Fig. S20 The ^{1}H NMR spectra of biphenyl in CDCl$_3$.

^{1}H NMR of phenol in CD_3OD

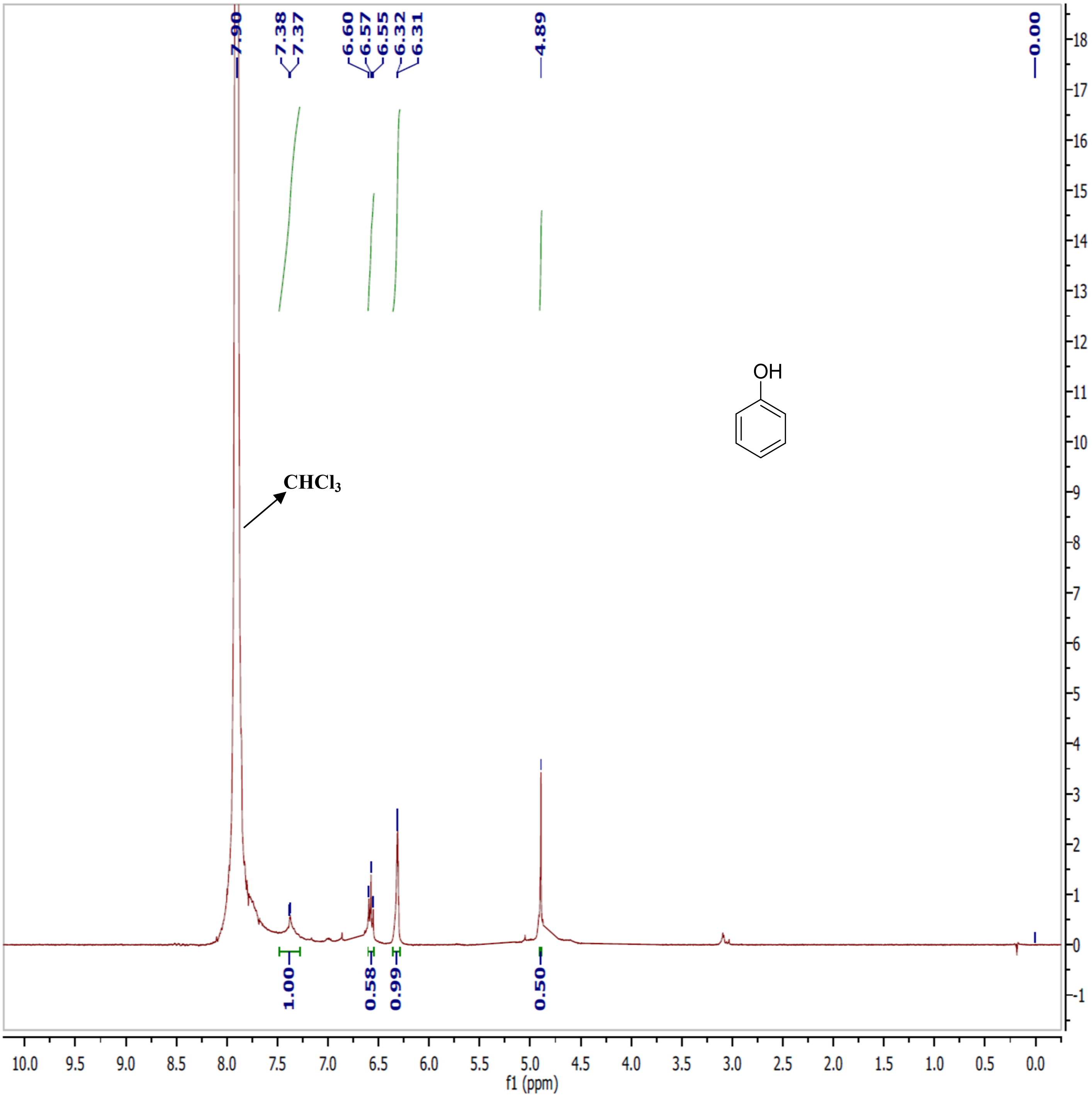


Fig. S21 The ^{1}H NMR spectra of isolated phenol in CD_3OD.

^{1}H NMR of *p*-phenylenediamine in $CDCl_3$

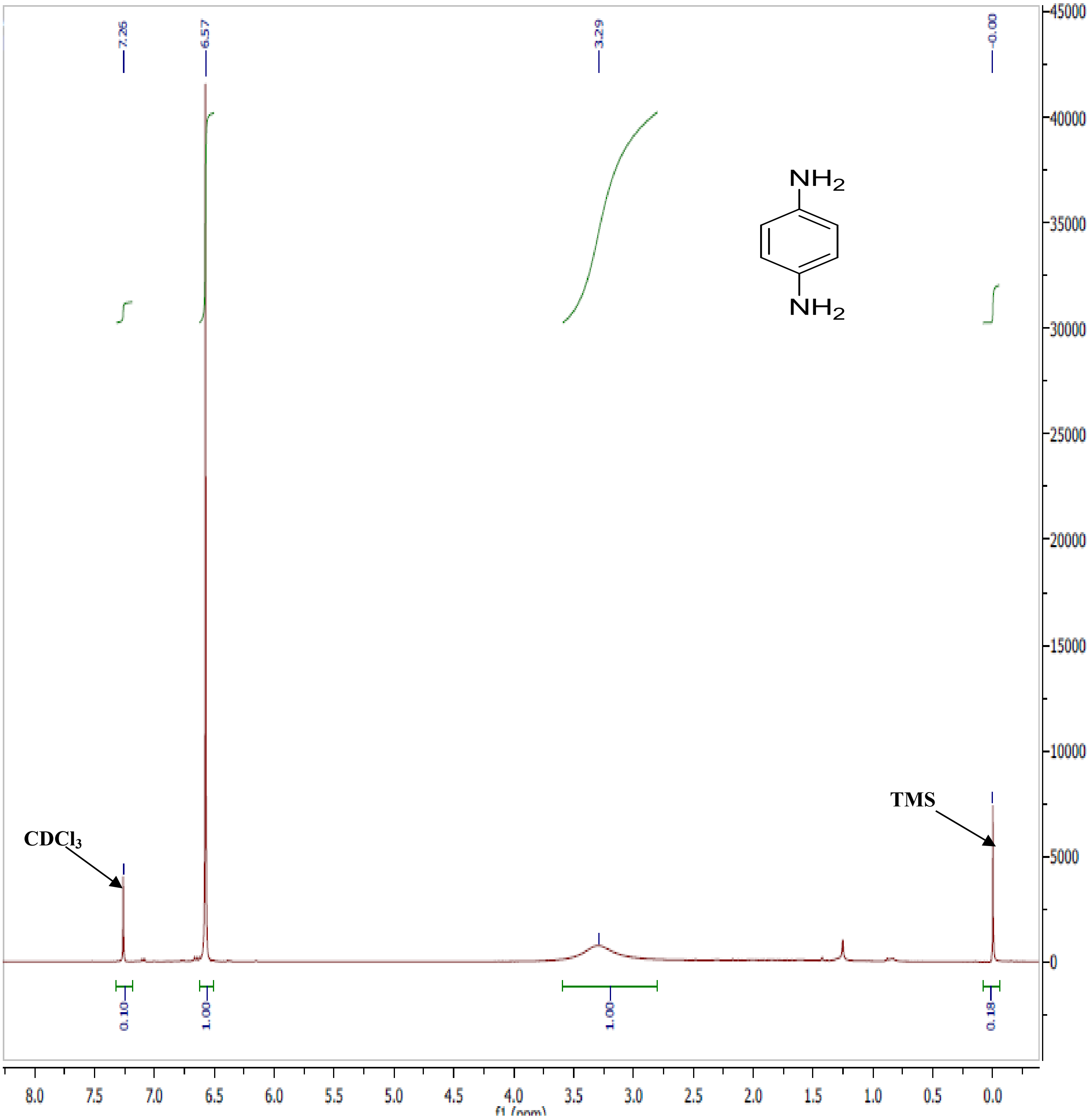


Fig. S22 The ^{1}H NMR spectra of the reduced product *p*-Phenylenediamine in $CDCl_3$.

^{1}H NMR of *p*-aminophenol in $CDCl_3$

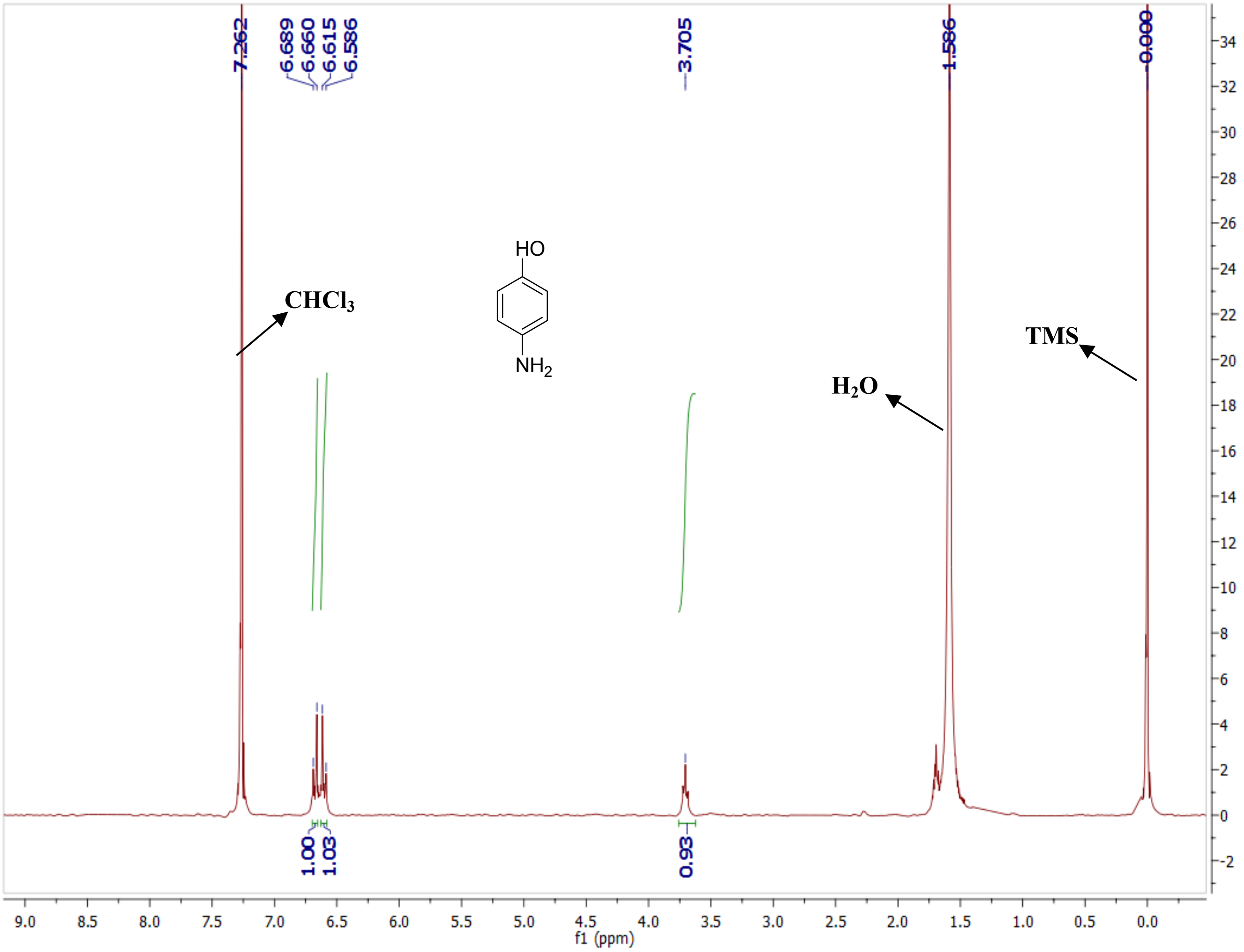


Figure S23 ^{1}H NMR spectrum of reduced product *p*-aminophenol.