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Electronic Supplementary information

Development of supramolecular ensemble of AIEE active hexaphenylbenzene derivative and Ag@Cu_2O core-shell NPs: An efficient photocatalytic system for C-H activation

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Page No. Contents

S14 UV-vis spectra of Ag@Cu_2O core-shell NPs by varying the ratio of AgNPs:Benedict's solution.

S15 Overlay NMR spectra of derivative **1** and residue obtained after filtration with THF/$CHCl_3$ mixture and fourier transforms infrared (FTIR) absorption spectrum of derivative **1** and Ag@Cu_2O NPs.

S16 Pictorial presentation illustrating the *in situ* generation of supramolecular ensemble **1a**:Ag@Cu_2O NPs.

S17 Table showing optimization of reaction conditions for C-H arylation of 1-methyl-1*H*-imidazole (**2**) with iodobenzene **(3a)** utilizing *in situ* generated supramolecular ensemble **1a**:Ag@Cu_2O NPs as catalyst and table showing effect of thickness of shell on photocatalytic efficiency of *in situ* generated supramolecular ensemble **1a**:Ag@Cu_2O NPs in C-H functionalization of 1-methyl-1*H*- imidazole (**2**) with **3a**.

S18 Thermogravimetric analysis (TGA) of derivative **1** and supramolecular ensemble **1a**:Ag@Cu_2O NPs.

S19 TEM image and X-Ray diffraction pattern of Cu_2O NPs stabilized by aggregates of derivative **1**.

S20 Table showing influence of the stabilizing agent on the photocatalytic efficiency of Cu_2O NPs and Ag@Cu_2O NPs in C-H activation reaction and table showing C-H activation of 1-methyl-1*H*-imidazole (**2**) with haloarenes (**3a/3b/3c**) catalyzed by *in situ* generated supramolecular ensemble **1a**:Ag@Cu_2O NPs in presence of visible light.

S21 Recyclability of *in situ* generated supramolecular ensemble **1a**:Ag@Cu_2O NPs as photocatalyst for synthesis of imidazole/benzimidazole derivatives and table showing

General experimental Procedures:

Materials :

All reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium using benzophenone and kept over molecular sieves overnight before use. For column chromatography, silica gel (60–120 mesh) was used.

Instruments :

UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer using a quartz cuvette (path length, 1 cm). The fluorescence spectra were obtained with a SHIMADZU 5301 PC spectrofluorimeter. TEM images were recorded from Transmission Electron Microscope (TEM)-JEOL 2100F. Infrared spectra were obtained on Varian 660-IR spectrometer using KBr pellets. Thermogravimetric analysis (TGA) was carried out on a EXSTAR TG/DTA 3600 at a heating rate of 10^0C/min under nitrogen atmosphere. The amount of Ag and Cu in catalyst was determined by atomic absorption spectrophotometer (GBC Avant Ver 1.31). Sample preparation was done by reflux assisted digestion of 2 mg of catalyst with concentrated HNO_3. The resulting solution was cooled, centrifuged and filtered. The filtrate was diluted to 10 times with deionized water. Photocatalytic experiments were carried out by using the 60 W tungsten filament bulb as irradiation source. Elemental analysis (C, H, N) was performed on a Flash EA 1112 CHNS-O analyzer (Thermo Electron Corp.). ^{1}H NMR was recorded on a JEOL-FT NMR-AL 300 MHz and Bruker (Avance II) FT-NMR 500 MHz spectrophotometer using $CDCl_3$, CD_3OD and DMSO-d_6 as solvents and tetramethylsilane ($Si(CH_3)_4$) for internal standards. Data was reported as follows: chemical shifts in ppm (δ) and coupling constants in Hz (*J*). Multiplicites of signals were expressed as follows: s = singlet, d = doublet and m = multiplet.

Synthesis of silver nanoparticles (AgNPs):

The quasi-spherical AgNPs were prepared by reducing the $AgNO_3$ with aggregates of derivative **1** according to the previously reported method.[1] Aggregates of derivative **1** were prepared by dissolving derivative **1** (10 μM) in H_2O:THF (7:3). To prepare AgNPs, 3 mL of aggregates of derivative **1** (10 μM) were added to 0.1 M $AgNO_3$ (60 μL). The reaction mixture so obtained was stirred at room temperature to yield greyish AgNPs. These AgNPs were washed with distilled water to remove unreacted $AgNO_3$ and were utilized as such in the formation of supramolecular ensemble **1a**:Ag@Cu_2O NPs. As determined by AAS, the concentration of AgNPs solution was found to be 1.9 mM.

Preparation of Benedict's stock solution (1M):

In a 100 mL volumetric flask, 10 g of Na_2CO_3 and 17.3 g of sodium citrate dihydrate was dissolved in 85 mL of distilled water. To this mixture, aqueous solution of copper sulfate pentahydrate (1.73g dissolved in 10 mL of water) was added slowly with stirring. Finally, distilled water was added to bring the final volume upto 100 mL. The resulting solution was diluted further to prepare 0.04 M Benedict's solution which was used in the generation of supramolecular ensemble **1a**:Ag@Cu_2O NPs.

Generation of supramolecular ensemble 1a:Ag@Cu_2O NPs:

(a) Ensemble consisting of 1a and Ag@Cu_2O NPs (1:1)

6 mL of AgNPs (1.9 mM) and 0.6 mL of Benedict's solution (0.04 M) were mixed and stirred at room temperature for 5 min. To this reaction mixture, 0.6 mL of aggregates of derivative **1** (0.002 M) in H_2O:THF (7:3) solution were added slowly with vigorous stirring. Immediately, color of solution was changed from dark blue to green indicating the generation of supramolecular ensemble **1a**:Ag@Cu_2O NPs. Black coloured precipitates were observed after stirring the reaction

mixture continuously for 15 min. at room temperature. The resulting reaction mixture was sonicated to obtain homogeneous catalytic solution consisting of Ag@Cu_2O NPs (1:1) and 3.5 mL of this catalytic solution was used as such for carrying out C-H activation reactions.

(b) Ensemble consisting of 1a and Ag@Cu_2O NPs (1:2)

For preparation of photocatalytic ensemble having Ag@Cu_2O NPs (1:2), 5 mL of AgNPs solution (1.9 mM), 0.8 mL of Benedict's solution (0.04 M) and 0.8 mL of aggregates of derivative **1** (0.002 M) in H_2O:THF (7:3) solution were mixed and 3.5 mL of this solution was used as such for carrying out C-H activation reactions.

(c) Ensemble consisting of 1a and Ag@Cu_2O NPs (2:1)

To generate photocatalytic ensemble consisting of Ag@Cu_2O NPs (2:1), 16 mL of AgNPs (1.9 mM), 0.6 mL of Benedict's solution (0.04 M) and 0.6 mL of aggregates of derivative **1** (0.002 M) in H_2O:THF (7:3) solution were mixed and 5.0 mL of this solution was used as such for carrying out photocatalytic C-H functionalization reactions.

General experimental procedure for photocatalytic C-H functionalization reactions utilizing *in situ* generated supramolecular ensemble 1a:Ag@Cu_2O NPs:

In a 25 ml round-bottom flask (RBF), 1-methyl-1*H*-imidazole, **2** (1.0 equiv, 0.1 g), iodobenzene, **3a** (1.5 equiv) and KO^{t}Bu (1.5 equiv) were mixed in 10 mL of H_2O:toluene (7:3) solvent mixture in presence of 3.5 mL of *in situ* generated supramolecular ensemble **1a**:Ag@Cu_2O NPs (0.02 mmol). After degassing the reaction mixture under vaccum for 2 min, the RBF was put in a water bath (to avoid heating effect) on magnetic stirrer and was irradiated with a 100 W tungsten filament bulb (0.4 W/cm^2) to provide visible light for 5.5 h. After completion of the reaction, solvent was evaporated under reduced pressure and the resulting residue was dissolved in DCM. The organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under

reduced pressure to yield the crude product which was recrystallized from DCM-hexane mixture to obtain pure product. The aqueous layer containing catalyst was reused as such for further photocatalytic reactions.

For preparation of imidazole and benzimidazole derivatives, reactants 1-methyl-1*H*-imidazole (**2**) and 1-phenyl-1*H*-benzimidazole (**5**) were synthesized according to previously reported methods.[2]

Table S1 Comparison of catalytic activity of supramolecular ensemble 1a:Ag@Cu_2O core shell NPs with other catalytic systems reported in literature for C-H functionalization of imidazole/benzimidazole.

Journal Name	Catalyst	Catalyst loading	Ligand/ base	Temperature	Solvent	Time (in h)	Yield
Present Manuscript	Ag@Cu_2O core shell NPs	0.02 mmol	KO^tBu	Visible light	Toluene-H_2O (3:7)	5-7	45-82%
ACS Catal., **2016**, *6*, 709	$[Cp^*RhCl_2]_2$	0.003 mmol	NaOAc, AgOTf	110^oC (under Ar atmosphere)	DCE	24	47-96%
Org. Biomol. Chem., **2016**, *14*, 1814	$[Cp^*RhCl_2]_2$	5 mol%	$Cu(OAc)_2 \cdot H_2O$	110^oC (under Ar atmosphere)	Toluene	12	5-97%
Chem. Sci., **2015**, *6*, 6792	$Ni(cod)_2$	10 mol%	Dcype, K_3PO_4	110^oC	t-AmylOH	12-36	53-95%
Org. Biomol. Chem., **2015**, *13*, 7695	$[Cp^*RhCl_2]_2$	5 mol%	$Cu(OAc)_2 \cdot H_2O$	80^oC (under Ar atmosphere)	t-AmylOH	4-12	53-99%
Adv. Synth. Catal,. **2015**, *357*, 3885	$[(p\text{-cymene})RuCl_2]_2$	10 mol%	$AgSbF_6$, $Cu(OAc)_2 \cdot H_2O$	140^oC	MeOH	24	68-99%
J. Org. Chem., **2014**, *79*, 5806	[NHC-Pd(II)-Im]	2-4 mol%	KO^tBu	120^oC	Toluene-H_2O	6-12	42-99%
Org. Biomol. Chem., **2013**, *11*, 2249	$[Cp^*RhCl_2]_2$	3 mol%	$Cu(OAc)_2$, PivOH	140^oC	Mesitylene	24	49-84%
Tetrahedron **2008**, *64*, 6060	$Pd(OAc)_2$	10 mol%	$P(2\text{-furyl})_3$, K_2CO_3	140^oC	DMF	27-87	43-73%

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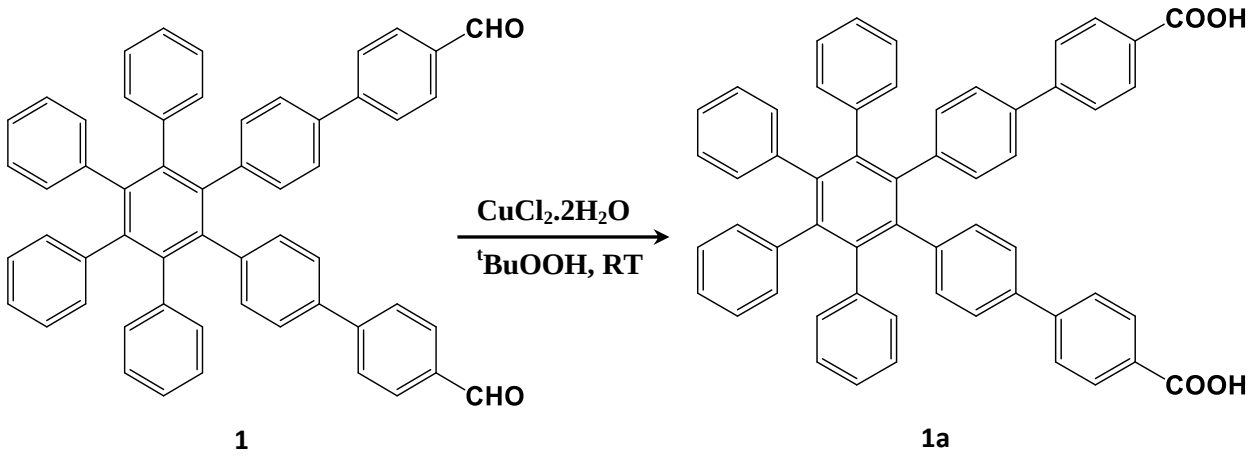
Synthetic scheme of derivative 1a:



1 **1a**

Procedure: A solution of derivative **1** (0.1 g, 0.05 mmol) and $CuCl_2.2H_2O$ (28 mg, 0.06 mmol) were mixed in THF. To this mixture, aqueous ^{t}BuOOH (12.15 µL, 0.05 mmol) was added. The resulting mixture was allowed to stir at room temperature for 24 h until the starting material disappeared (as indicated by TLC). After completion of the reaction, the residual solvent was evaporated. The crude product so obtained was treated with DCM and water. The organic layer was collected by adjusting the pH to 8.0-8.5. The organic layer was concentrated, dried over anhydrous Na_2SO_4 and purified by column chromatography to yield the derivative **1a** (0.06 g in 57.5% yield); m.p.>280^0C**.** ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.73 (d, 4H, J = 8.0 Hz), 7.32 (d, 4H, J = 8.0 Hz), 7.02 (d, 4H, J = 8.0 Hz), 6.80 (d, 4H, J = 8.0 Hz), 6.67-6.70 (m, 20H); *m/z* = 775.4733 $[M + H]^+$; Elemental Analysis: Calcd for $C_{56}H_{38}O_4$: C 86.80; H 4.94; O 8.26. Found: C 86.78; H 4.93; O 8.23.

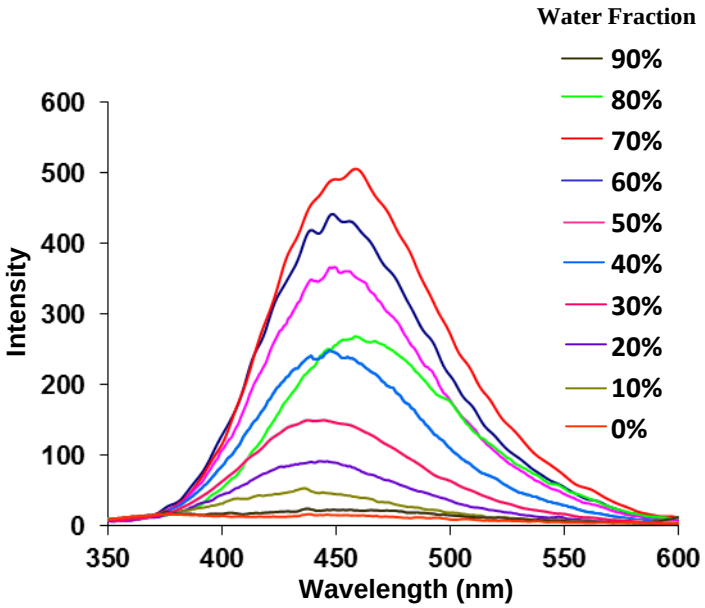


Fig. S1 Fluorescence spectra showing the variation of emission intensity of derivative **1** (5 μM) in H_2O/THF mixture with different fractions of H_2O; λ_{ex} = 305 nm.

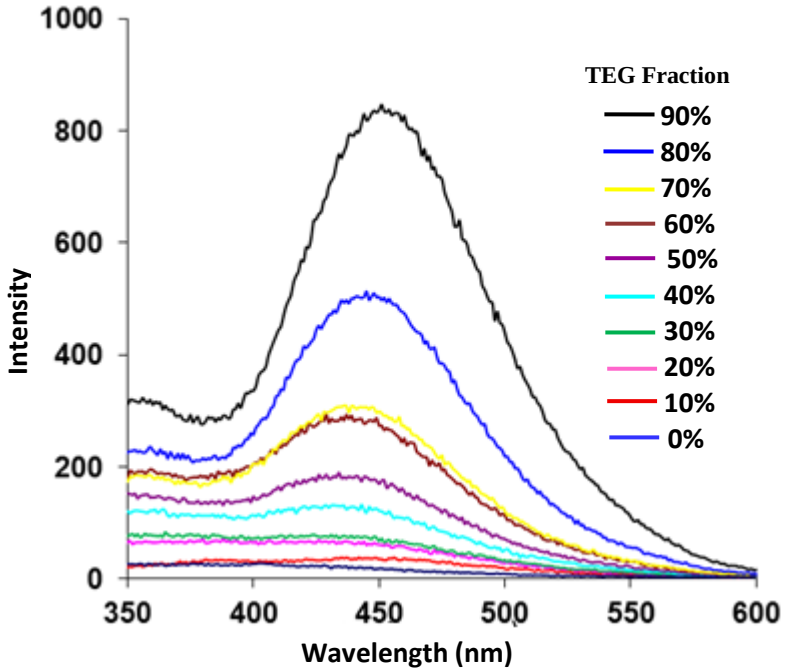


Fig. S2 Fluorescence spectra of derivative **1** (5 μM) showing the variation of emission intensity in TEG/THF mixture (0 to 90% volume fraction of TEG in THF); λ_{ex}= 305nm.

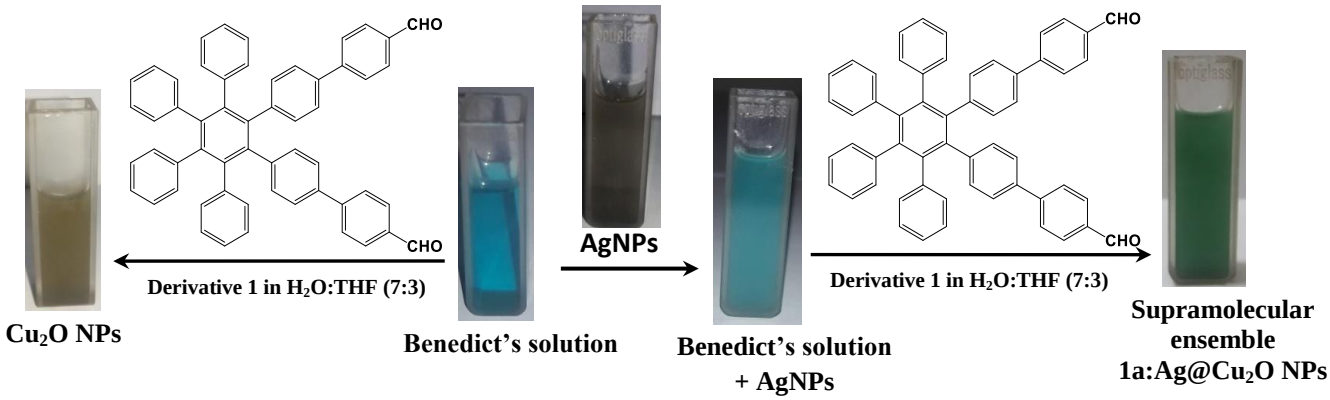


Fig. S3 Schematic diagram illustrating the generation of Cu_2O NPs and *in situ* generated supramolecular ensemble **1a**:Ag@Cu_2O NPs from Benedict's solution on addition of aggregates of derivative **1**.

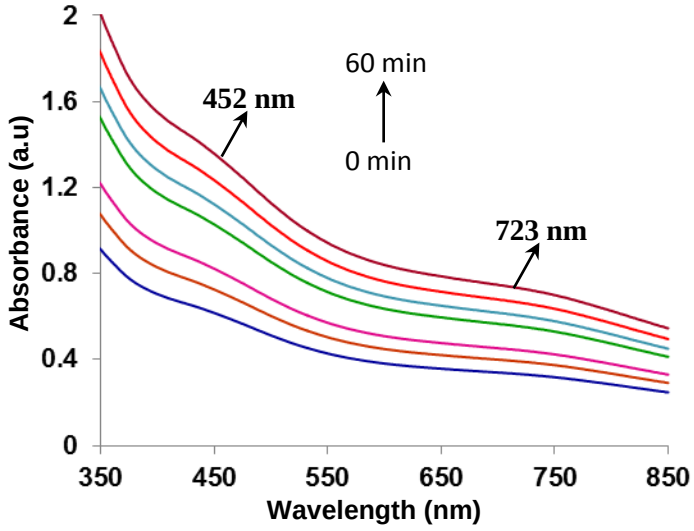


Fig. S4 UV-vis spectra with time for gradual addition of aggregates of derivative **1** (5 μM) to the aqueous solution of Benedict's reagent and AgNPs.

Regression Statistics	
Multiple R	0.996139
R Square	0.992294
Intercept	0.603839
Slope	0.012527

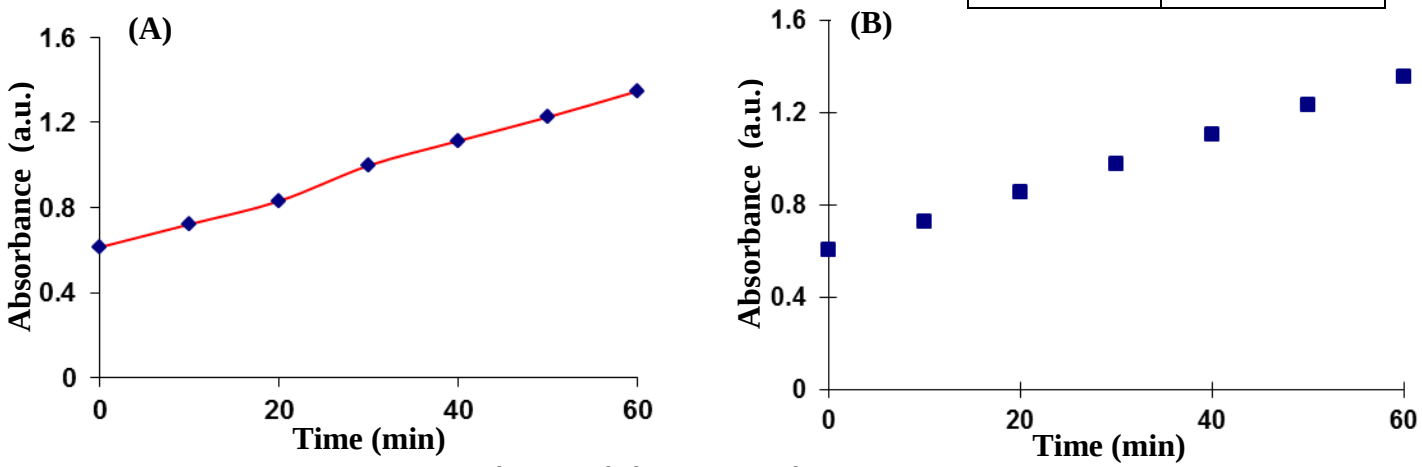


Fig. S5 Graphical representation of rate of formation of Ag@Cu_2O core-shell NPs (A) Time (min.) vs. absorbance plot at 452 nm (B) regression plot of A.

The first order[3] rate constant for the formation of Ag@Cu_2O NPs was calculated from the change of intensity of absorbance of Benedict's reagent and AgNPs in the presence of aggregates of derivative **1** at different time interval.[4]

From the time vs. absorbance plot at fixed wavelength 452 nm by using first order rate equation, we get the rate constant = k = slope×2.303 = 4.80×10^{-4} s^{-1}.

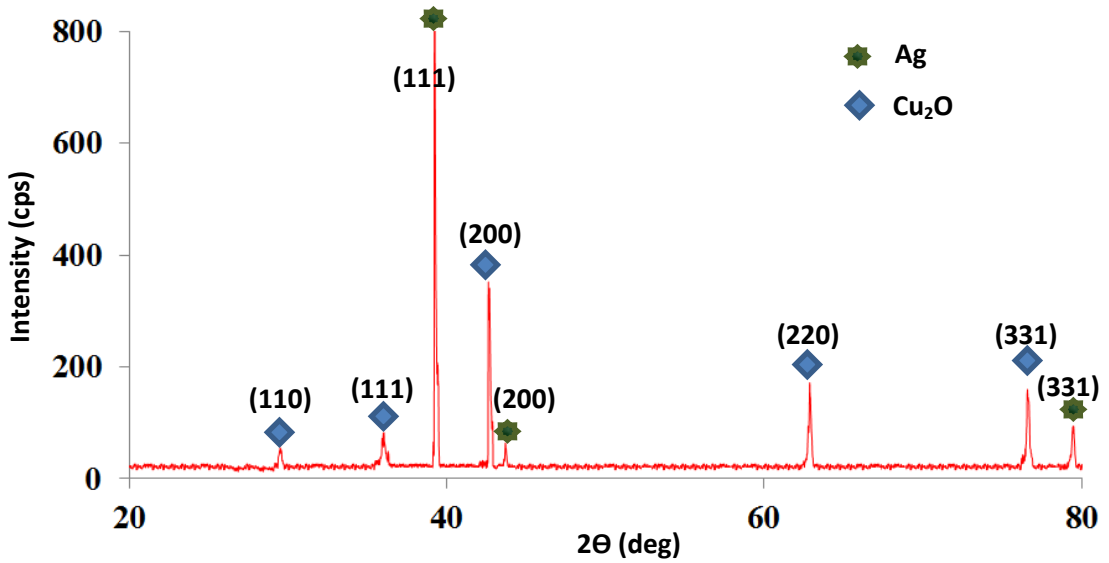


Fig. S6 X-Ray diffraction pattern of *in situ* generated Ag@Cu_2O core shell NPs.

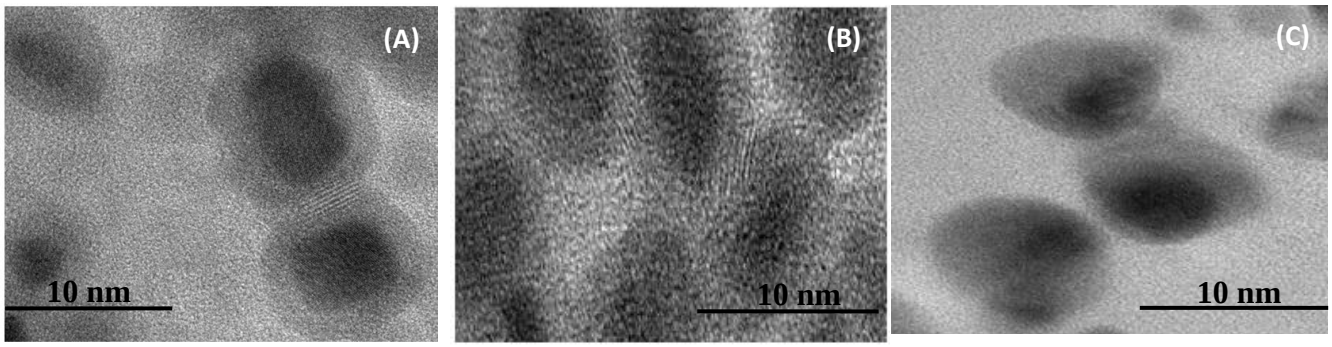


Fig. S7 TEM images of Ag@Cu_2O core shell NPs by varying the ratio of AgNPs:Benedict's solution.

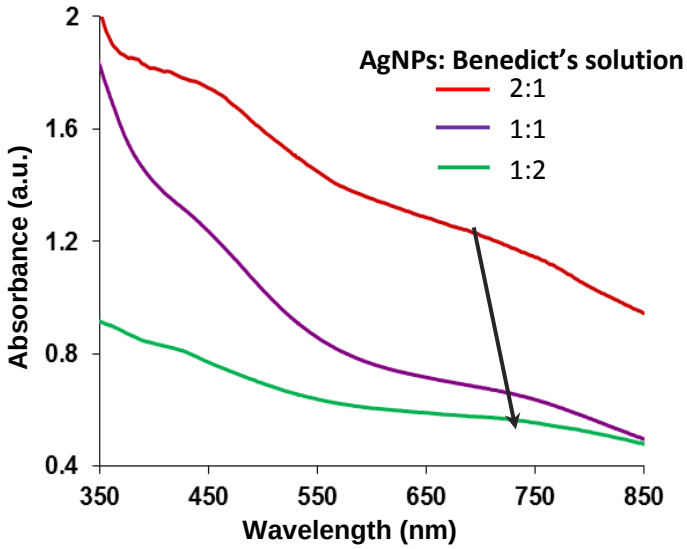


Fig. S8 UV-vis spectra of Ag@Cu_2O core-shell NPs by varying the ratio of AgNPs: Benedict's solution.

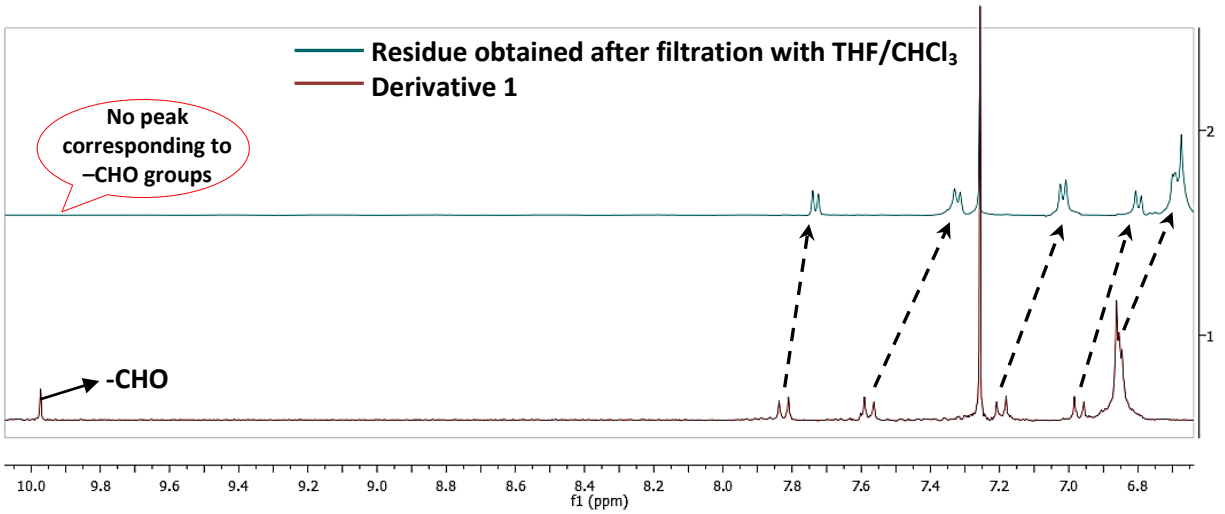


Fig. S9 Overlay NMR spectra of derivative **1** and residue obtained after filtration with THF/$CHCl_3$ mixture.

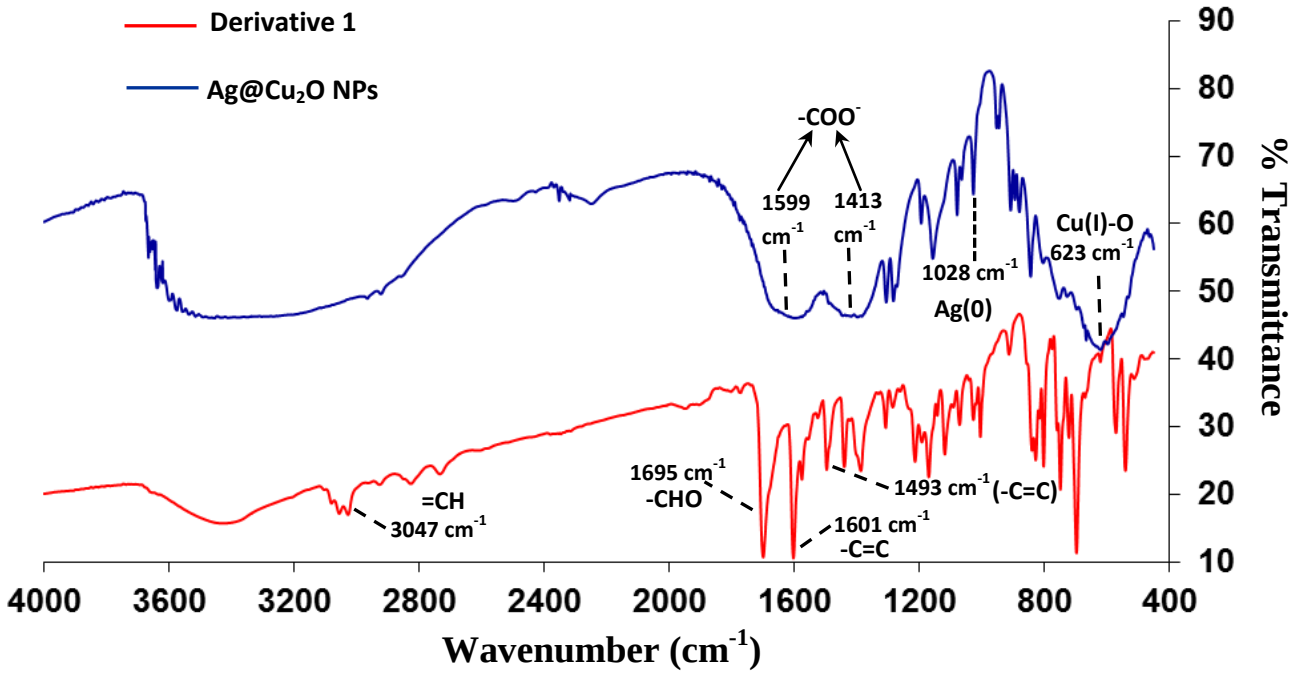


Fig. S10 Fourier transforms infrared (FTIR) absorption spectrum of derivative **1** and Ag@Cu_2O NPs.

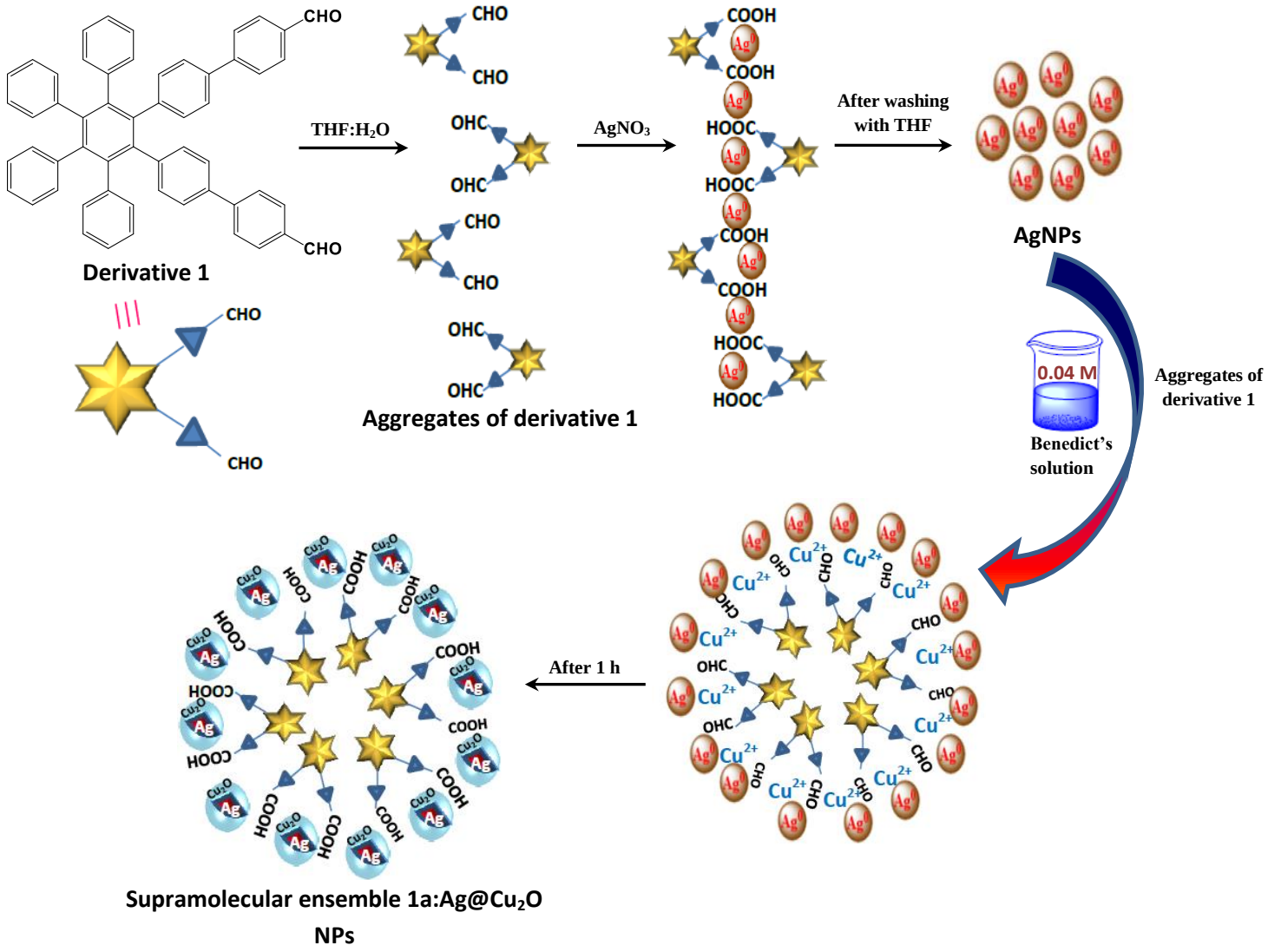
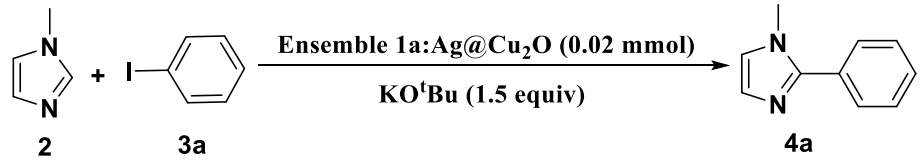


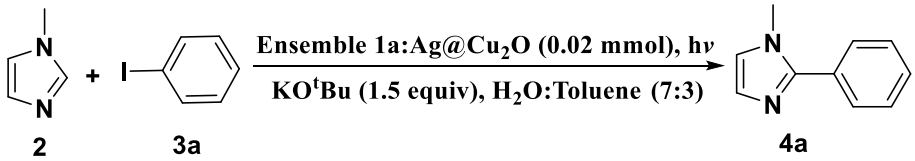
Fig. S11 Pictorial presentation illustrating the *in situ* generation of supramolecular ensemble **1a**:Ag@Cu_2O NPs.

Table S2 Optimization of reaction conditions for C-H arylation of 1-methyl-1*H*-imidazole (2) with iodobenzene (3a) utilizing *in situ* generated supramolecular ensemble 1a:Ag@Cu_2O NPs as catalyst.



S. No.	Solvent	Temperature	Time	Yield
1.	Toluene	150^0C	8 h	73%
2.	DMF	150^0C	15 h	48%
3.	H_2O:EtOH	90^0C	24 h	-
4.	H_2O:toluene (7:3)	150^0C	15 h	45%
5.	H_2O:toluene (7:3)	Visible light	5.5 h	80%

Table S3 Effect of thickness of shell on photocatalytic efficiency of *in situ* generated supramolecular ensemble 1a:Ag@Cu_2O NPs in C-H functionalization of 1-methyl-1*H*-imidazole (2) with 3a.



S. No.	Ensemble 1a:Ag@Cu_2O NPs (AgNPs: Benedict's solution)	Time	Yield	TOF (h^{-1})
1.	1:1	5.5 h	80%	8.88
2.	**1:2**	**5.5 h**	**84%**	**9.32**
3.	2:1	5.5 h	75%	8.33

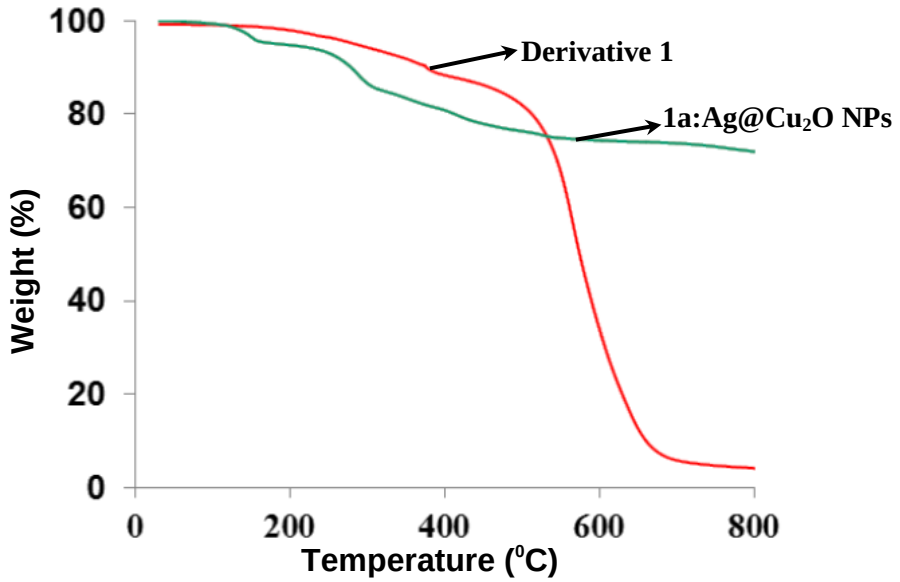


Fig. S12 Thermogravimetric analysis (TGA) of derivative **1** and supramolecular ensemble **1a**:Ag@Cu_2O NPs.

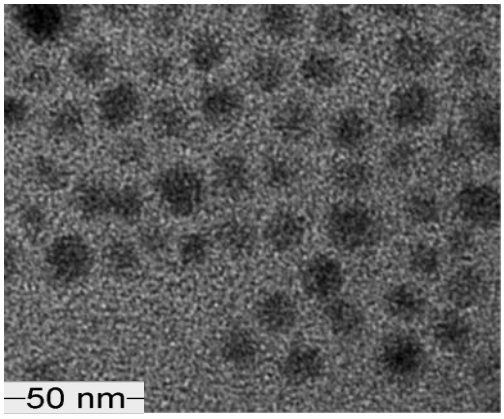


Fig. S13 TEM image showing spherical shape of Cu_2O NPs stabilized by aggregates of derivative **1**; scale bar 50 nm.

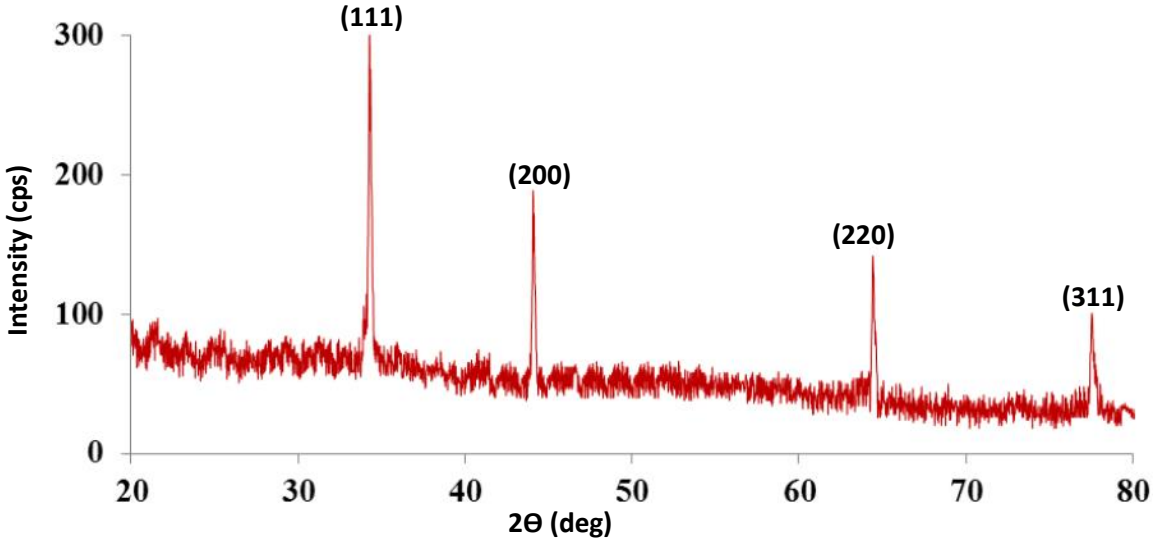
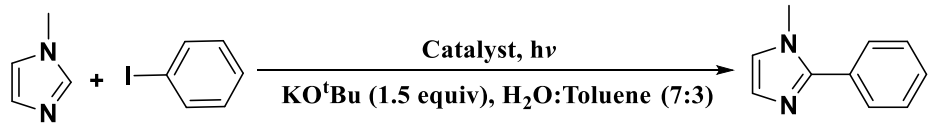


Fig. S14 X-Ray diffraction pattern of Cu_2O NPs stabilized by aggregates of derivative **1**.

Table S4 Influence of the stabilizing agent on the photocatalytic efficiency of Cu_2O NPs and Ag@Cu_2O NPs in C-H activation reaction.

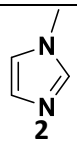
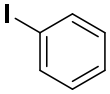
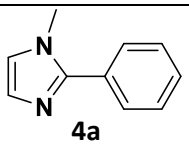
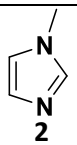
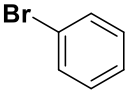
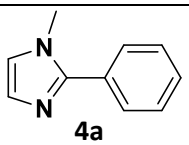
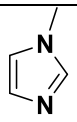
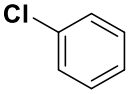
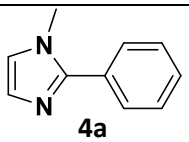


2 3a 4a

S. No.	Catalyst	Yield	Time
1.	Cu_2O NPs stabilized by aggregates of derivative **1**	23%	24 h
2.	**Supramolecular ensemble 1a:Ag@Cu_2O NPs**	**80%**	**5.5 h**
3.	Aggregates of derivative **1**	-	20 h
4.	Aggregates of oxidized derivative **1a**	-	20 h
5.	Bare Ag@Cu_2O NPs	32%	20 h
6.	Bare Ag@Cu_2O NPs + aggregates of derivative **1**	34 %	14 h
7.	Bare Ag@Cu_2O NPs + aggregates of oxidized derivative **1a**	78 %	8 h
8.	Ag@Cu_2O NPs stabilized by aggregates of pentacenequinone	42%	16 h

Bare Ag@Cu_2O[5]; Ag@Cu_2O NPs stabilized by aggregates of pentacenequinone[6]

Table S5 C-H activation of 1-methyl-1*H*-imidazole (2) with haloarenes (3a/3b/3c) catalyzed by *in situ* generated supramolecular ensemble 1a:Ag@Cu_2O NPs in presence of visible light.

S. No.	Reactant 1	Reactant 2	Product	Yield	Time
1.	 2	 3a	 4a	84%	5.5 h
2.	 2	 3b	 4a	68%	6 h
3.	 2	 3c	 4a	48%	7 h

Reaction conditions: **1** (1.0 equiv), **2** (1.5 equiv), **catalyst**; Supramolecular ensemble **1a**:Ag@Cu_2O NPs (0.02 mmol), **Base**; KO^{t}Bu (1.5 equiv), H_2O:toluene (7:3) under visible light.

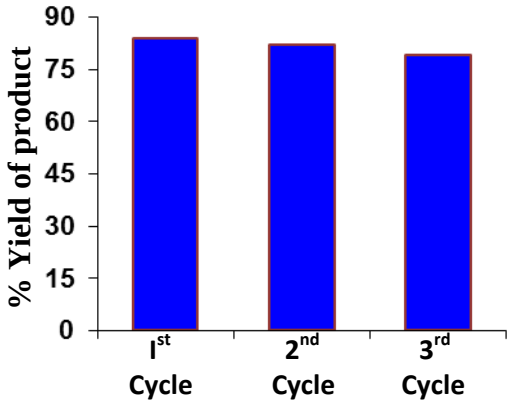
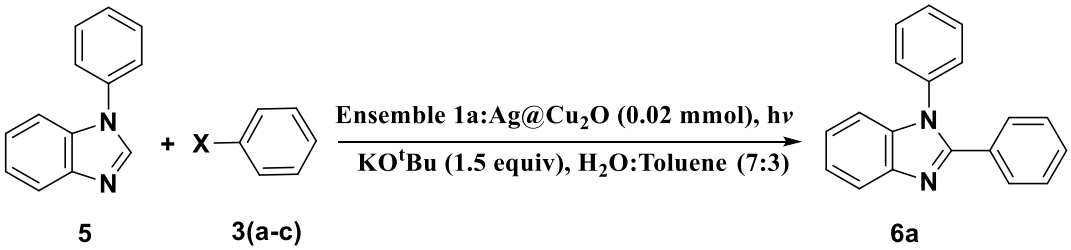


Fig. S15 Recyclability of *in situ* generated supramolecular ensemble **1a**:Ag@Cu_2O NPs as photocatalyst for synthesis of imidazole/benzimidazole derivatives.

Table S6 Photocatalytic C-H activation of 1-phenyl-1*H*-benzo[*d*]imidazole (5) with haloarenes (3a/3b/3c) utilizing *in situ* generated supramolecular ensemble 1a:Ag@Cu_2O NPs.



5 3(a-c) 6a

S. No.	X	Time (h)	Yield
1.	-I (**3a**)	4.5 h	82%
2.	-Br (**3b**)	6 h	74%
3.	-Cl (**3c**)	7 h	57%

Compound **4a**.[7] 1-methyl-2-phenyl-1*H* imidazole: (0.131 g in 68% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.61 (d, 2H, J = 8.1 Hz), 7.37−7.44 (m, 3H), 7.12 (s, 1H), 6.97 (s, 1H), 3.72 (s, 3H).

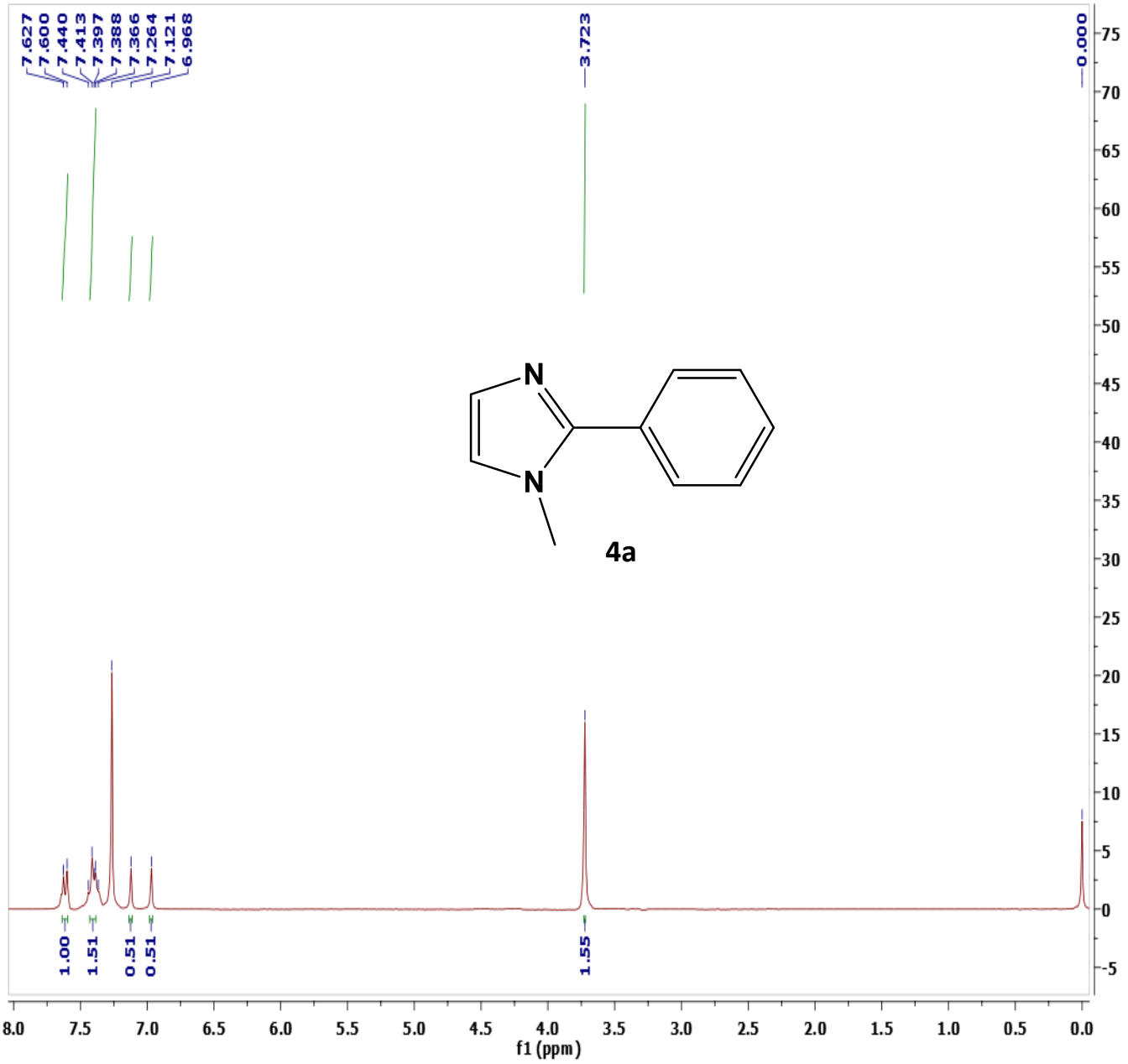


Fig. S16 ^{1}H NMR of compound **4a** in $CDCl_3$.

Compound **4b**.[8] 4-(1-methyl-1*H*-imidazol-2-yl)phenol: (0.172 g in 81% yield). ^{1}H NMR (500 MHz, CD_3OD, ppm): δ = 7.72 (d, 1H, J = 9.0 Hz), 7.44-7.47 (m, 4H), 7.00 (d, 1H, J = 9.0 Hz), 3.72 (s, 3H).

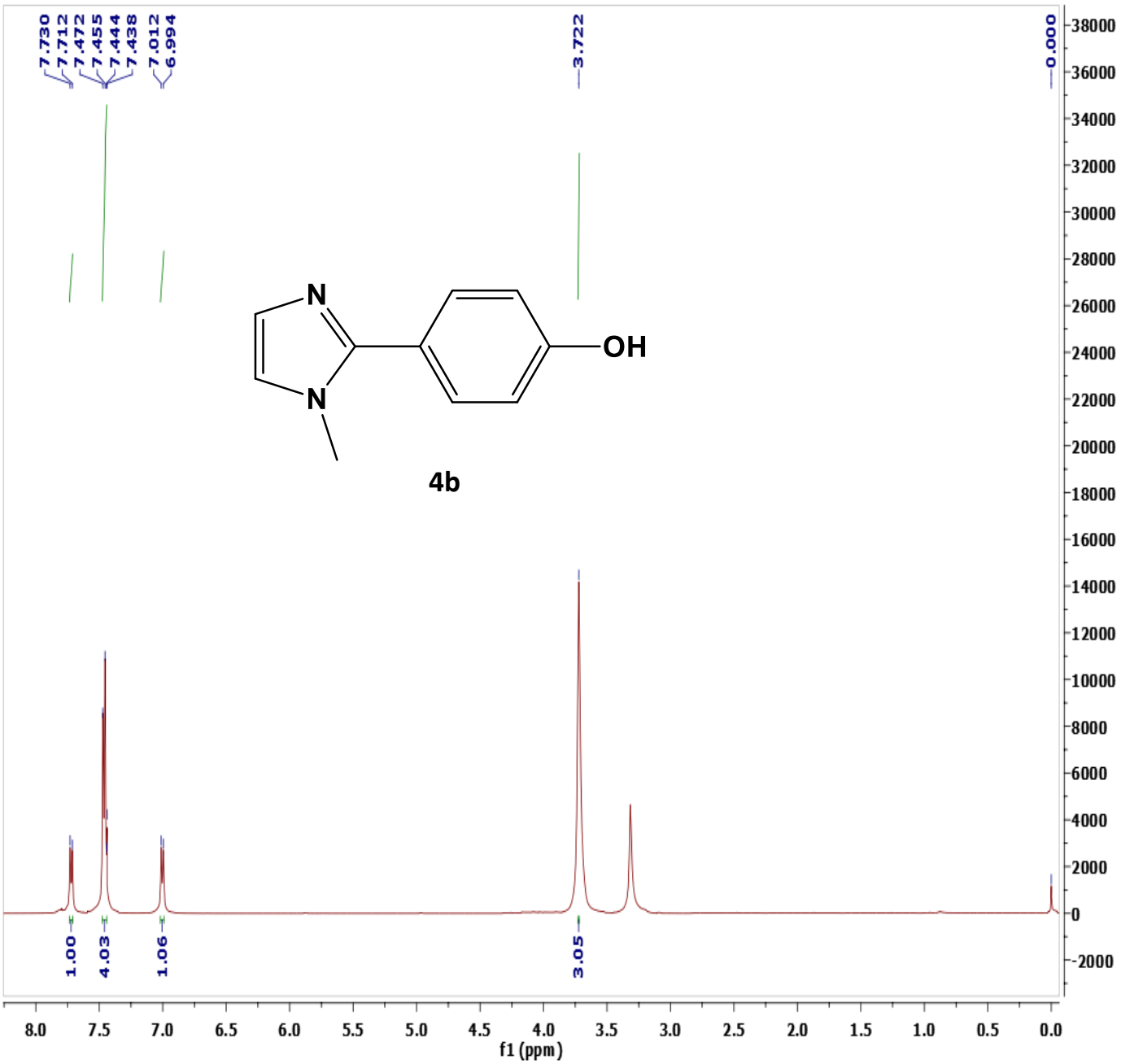


Fig. S17 ^{1}H NMR of compound **4b** in CD_3OD.

Compound **4c**.[9] 1-Methyl-2-(*p*-tolyl)imidazole: (0.168 g in 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.46 (d, 2H, J = 8.1 Hz), 7.18-7.22 (m, 2H), 7.03 (d, 1H, J = 0.9 Hz), 6.85 (d, 1H, J = 0.9 Hz), 3.65(s, 3H), 2.22 (s, 3H).

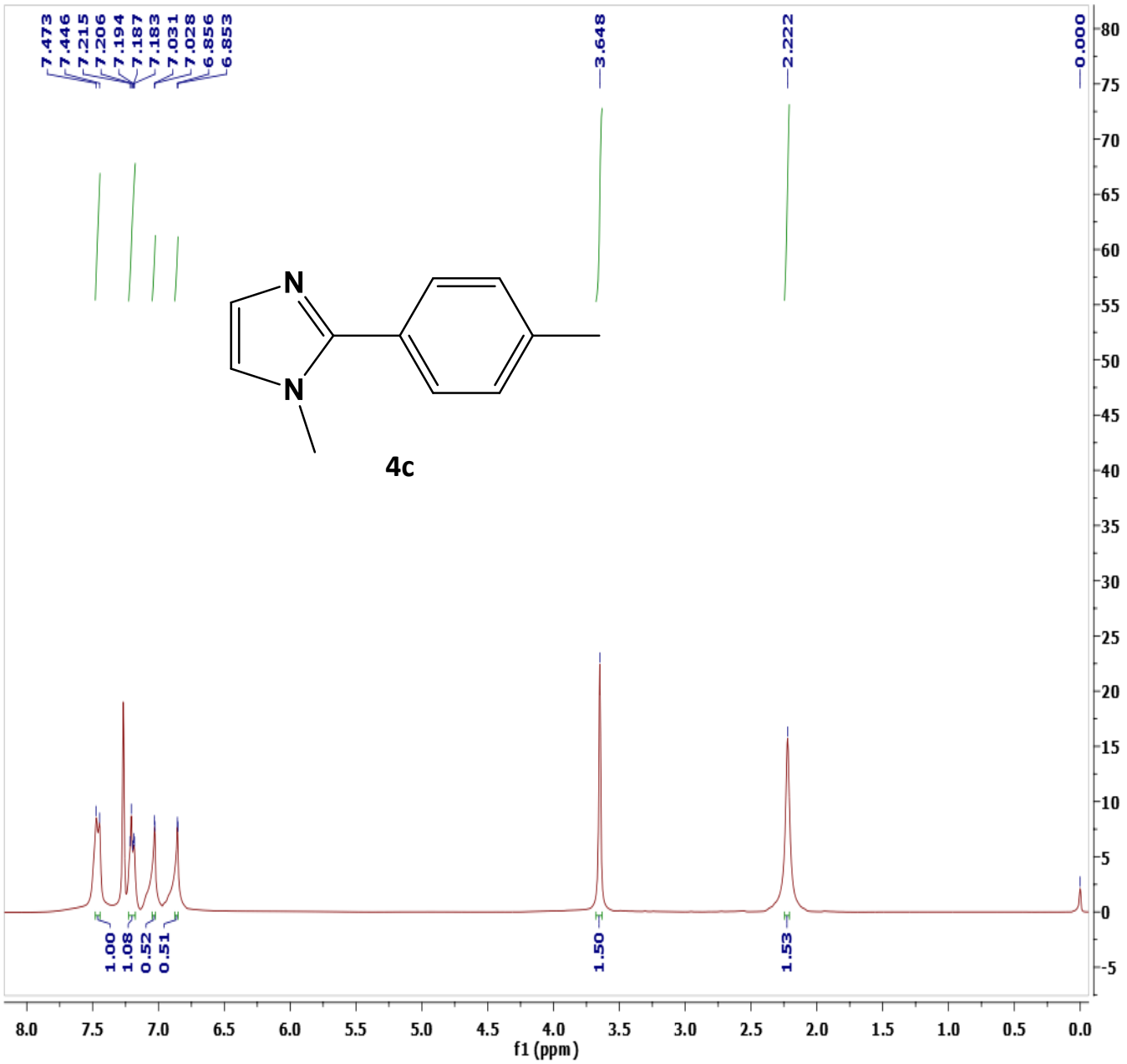


Fig. S18 ^{1}H NMR of compound **4c** in $CDCl_3$.

Compound **4d**.[8] 2-(4-methoxyphenyl)-1-methyl-1*H*-imidazole: (0.188 g in 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.58 (d, 2H, J = 9.0 Hz), 7.09 (s, 1H), 6.98 (d, 2H, J = 9.0 Hz), 6.93 (s, 1H), 3.84 (s, 3H), 3.73 (s, 3H).

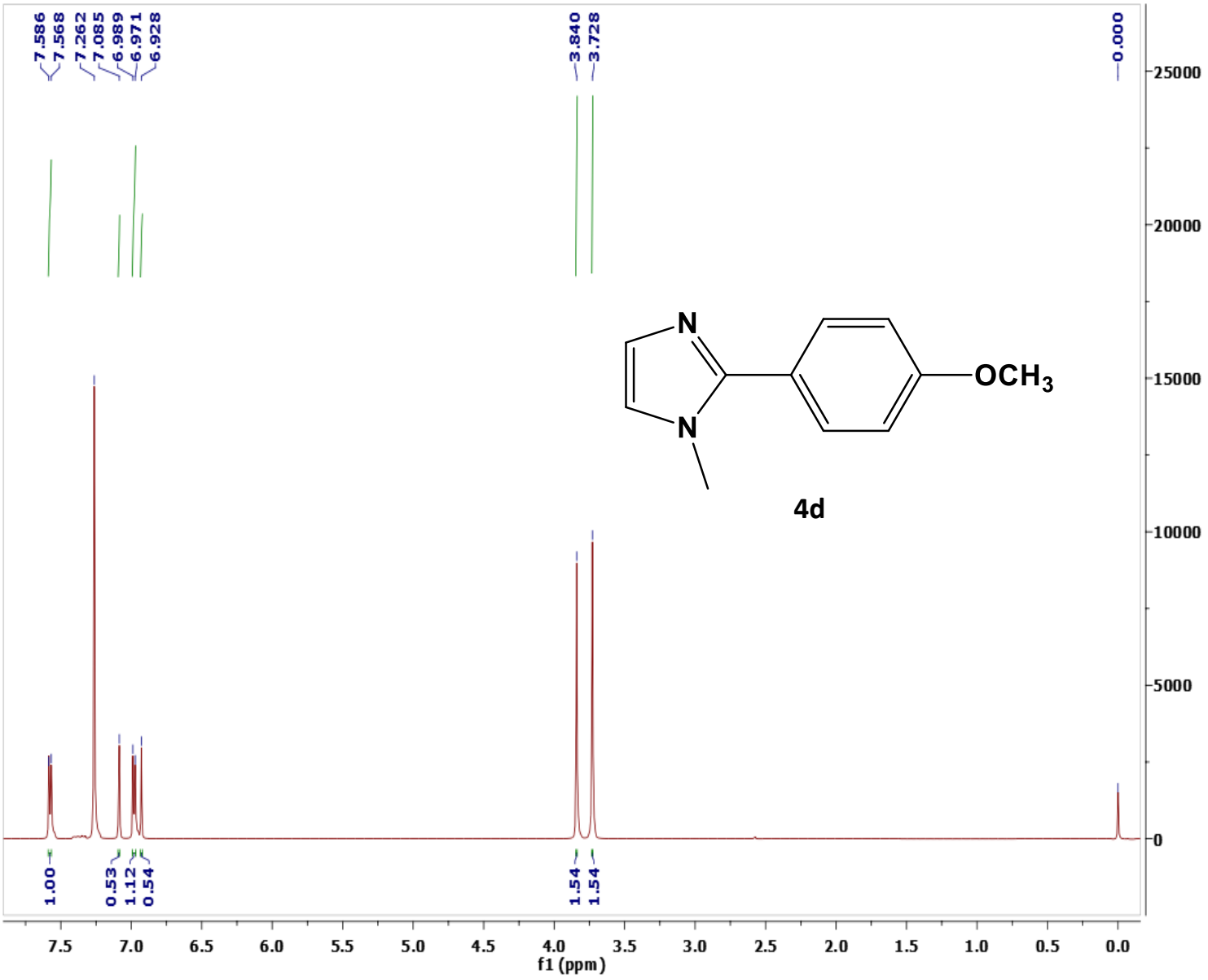


Fig. S19 ^{1}H NMR of compound **4d** in $CDCl_3$.

Compound **4e**.[10] 4-(1-Methylimidazol-2-yl)benzonitrile: (0.138 g in 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.63-7.94 (m, 4H), 7.14 (s, 1H), 7.00 (s, 1H), 3.79 (s, 3H).

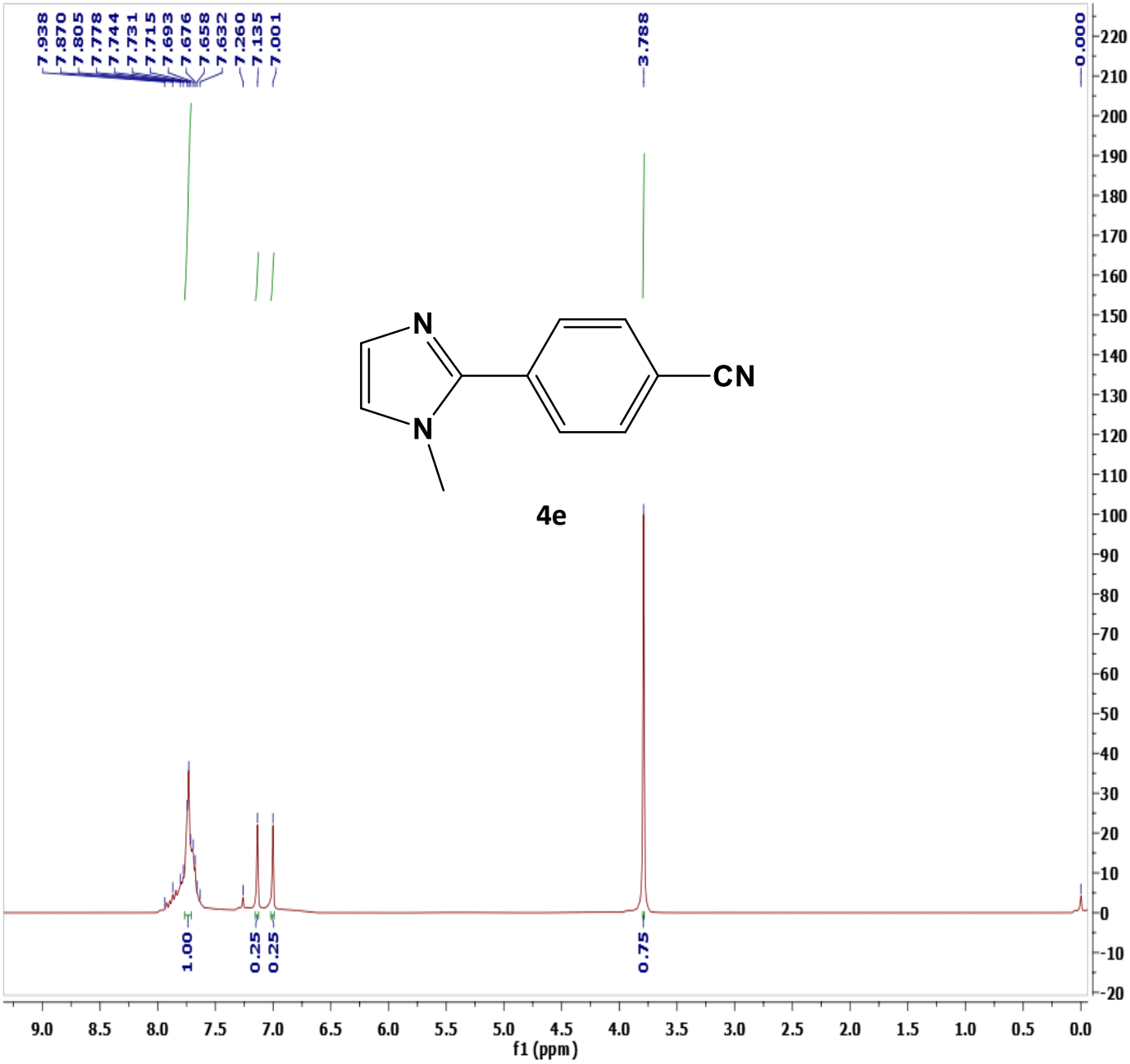


Fig. S20 ^{1}H NMR of compound **4e** in $CDCl_3$.

Compound **6a**.[11] 1,2-Diphenyl-1*H*-benzo[*d*]imidazole**:** (0.104 g in 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.90 (d, 1H, J = 7.2 Hz), 7.60 (d, 2H, J = 8.4 Hz), 7.45–7.54 (m, 3H), 7.23–7.40 (m, 8H).

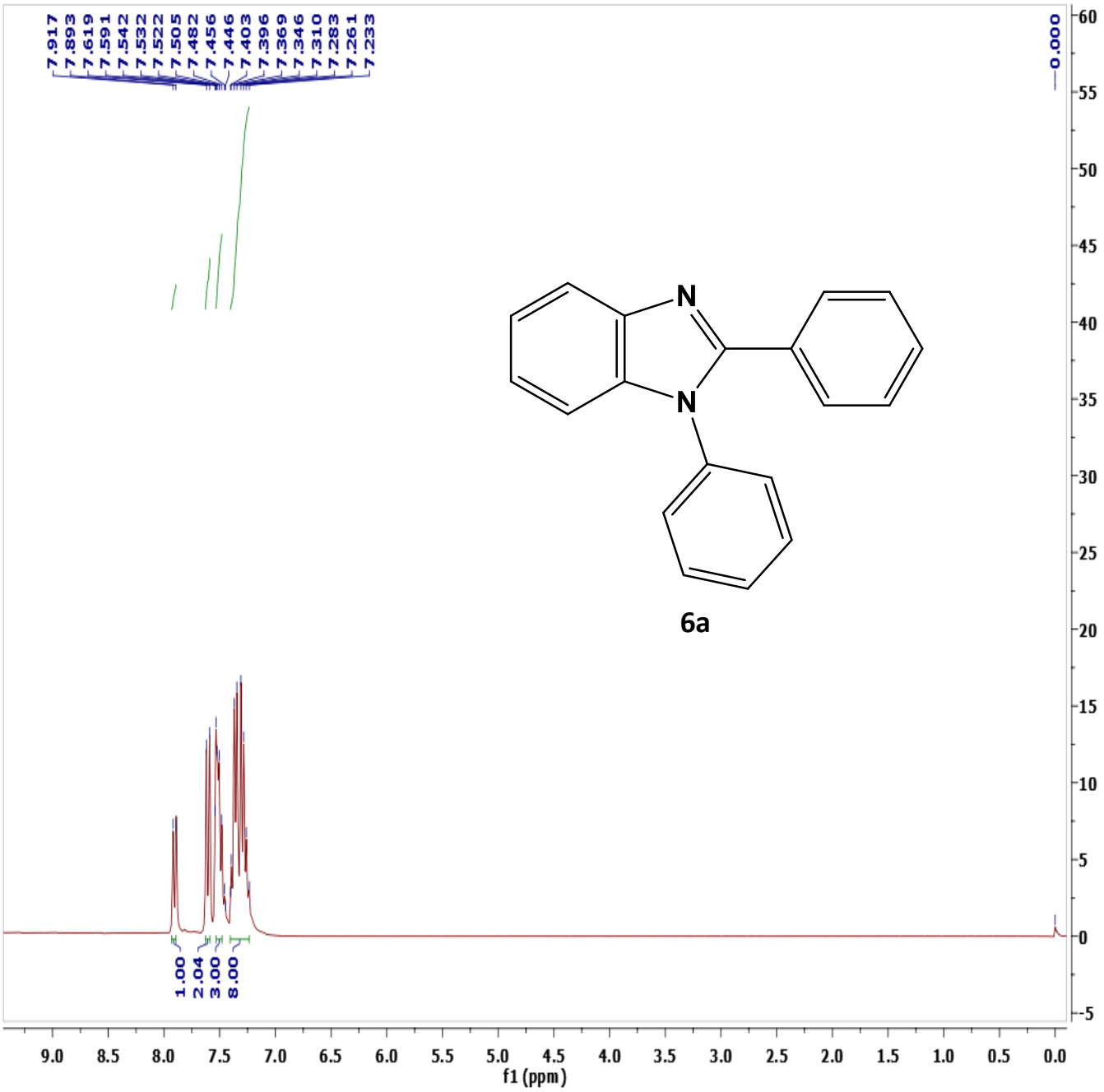


Fig. S21 ^{1}H NMR of compound **6a** in $CDCl_3$.

Compound **6b**.[12] 4-(1-Phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenol: (0.112 g in 76% yield). ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ = 7.73 (d, 1H, J = 7.5 Hz), 7.50–7.57 (m, 3H), 7.40 (d, 2H, J = 7.5 Hz), 7.35 (d, 2H, J = 8.4 Hz), 7.28 (t, 1H, J = 7.2 Hz), 7.19 (t, 1H, J = 7.2 Hz), 7.10 (d, 1H, J = 8.1 Hz), 6.68 (d, 2H, J = 8.4 Hz).

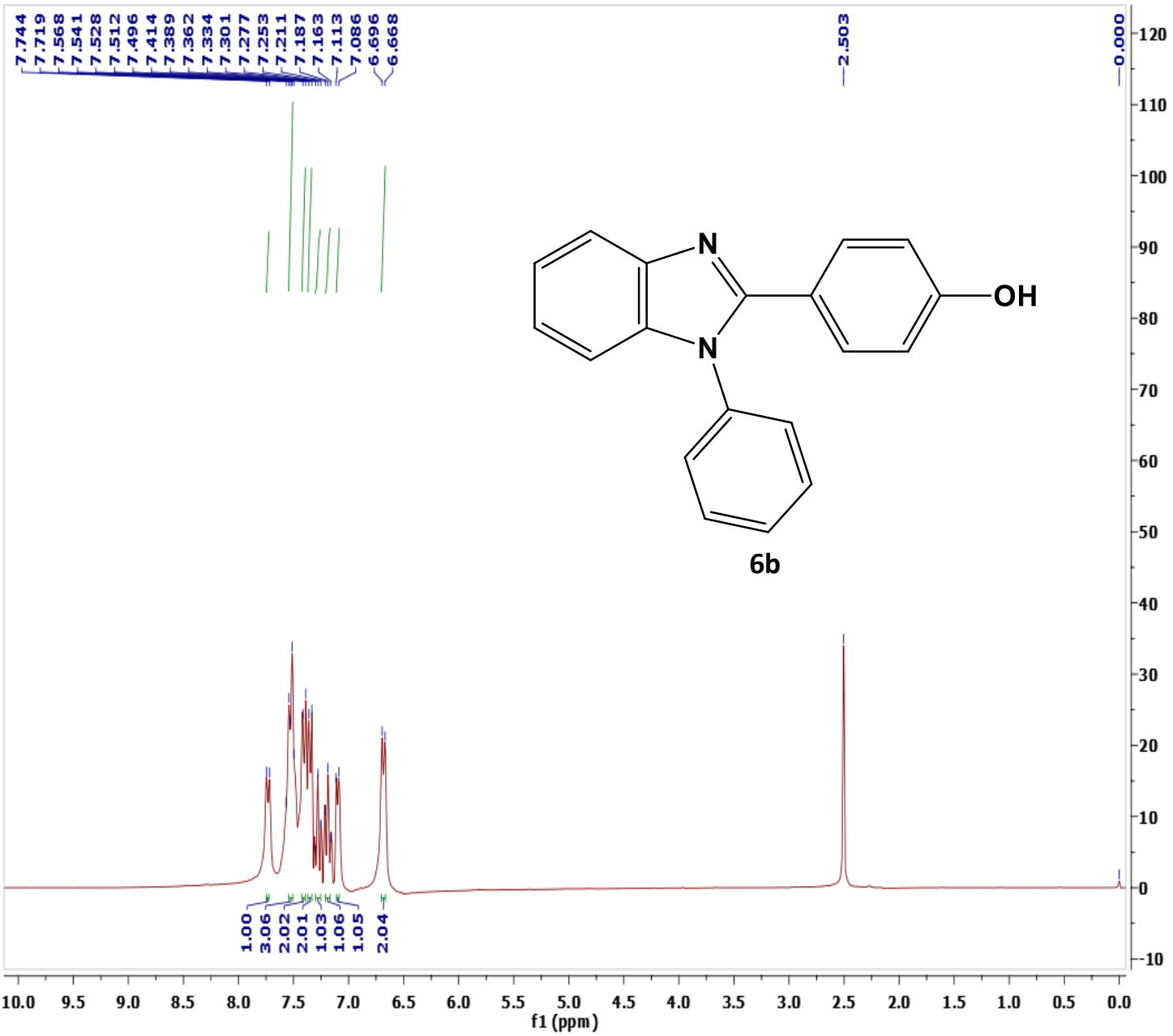


Fig. S22 ^{1}H NMR of compound **6b** in DMSO-d_6.

Compound **6c**.[13] 2-(3,4-dimethoxyphenyl)-1-phenyl-1*H*-benzo[*d*]imidazole: (0.143 g in 84% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.86 (d, 1H, J = 8.1 Hz), 7.46–7.56 (m, 3H), 7.27–7.36 (m, 3H), 7.14–7.19 (m, 3H), 7.10-7.11 (m, 1H), 6.73 (d, 1H, J = 8.4 Hz), 3.85 (s, 3H), 3.70 (s, 3H).

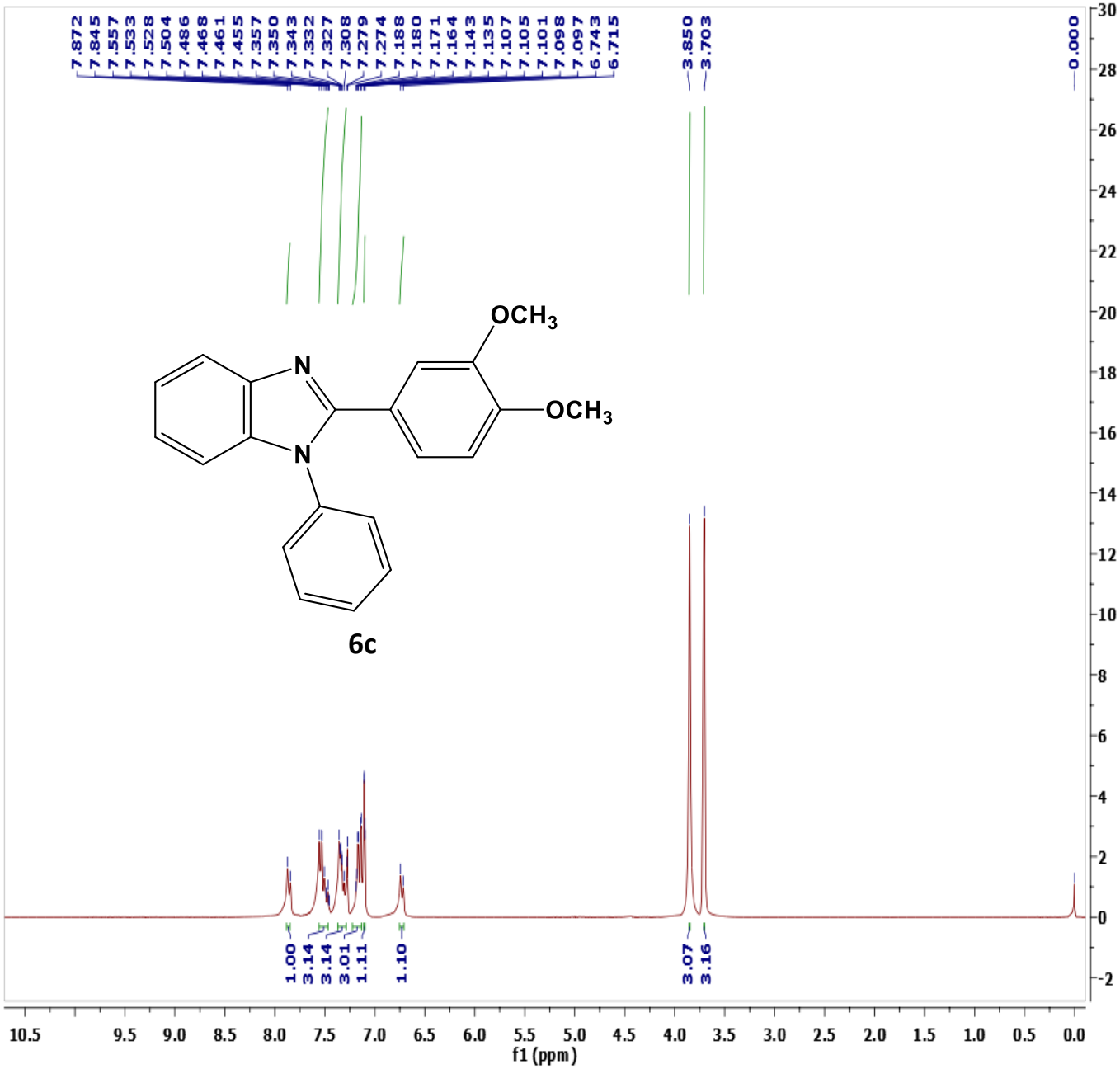


Fig. S23 ^{1}H NMR of compound **6c** in $CDCl_3$.

Compound **6d**.[14] 2-(4-Methylphenyl)-1-phenyl-1*H*-benzo[*d*]imidazole: (0.114 g in 78% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.89 (s, 1H), 7.45–7.51 (m, 5H), 7.33–7.35 (m, 3H), 7.25–7.27 (m, 2H), 7.12 (d, 2H, J = 8.7 Hz), 2.32 (s, 3H).

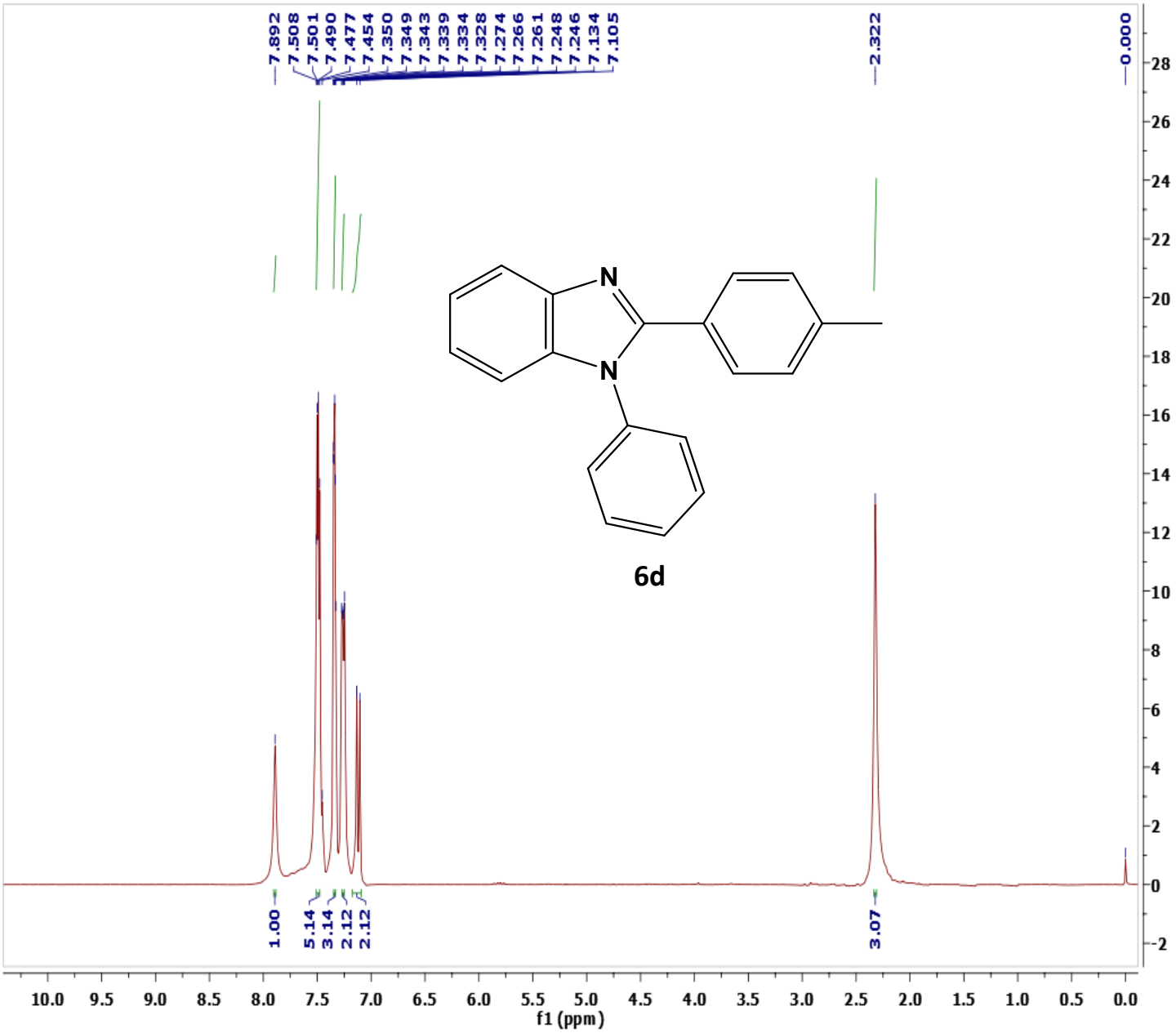


Fig. S24 ^{1}H NMR of compound **6d** in $CDCl_3$.

Compound **6e**.[15] 4-(1-Phenyl-1*H*-benzo[*d*]imidazol-2-yl)benzaldehyde: (0.108 g in 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 9.98 (s, 1 H), 7.91–7.94 (m, 1H), 7.83 (d, 2 H, J = 8.5 Hz), 7.75 (d, 2 H, J = 8.5 Hz), 7.53–7.58 (m, 3 H), 7.28–7.36 (m, 5 H).

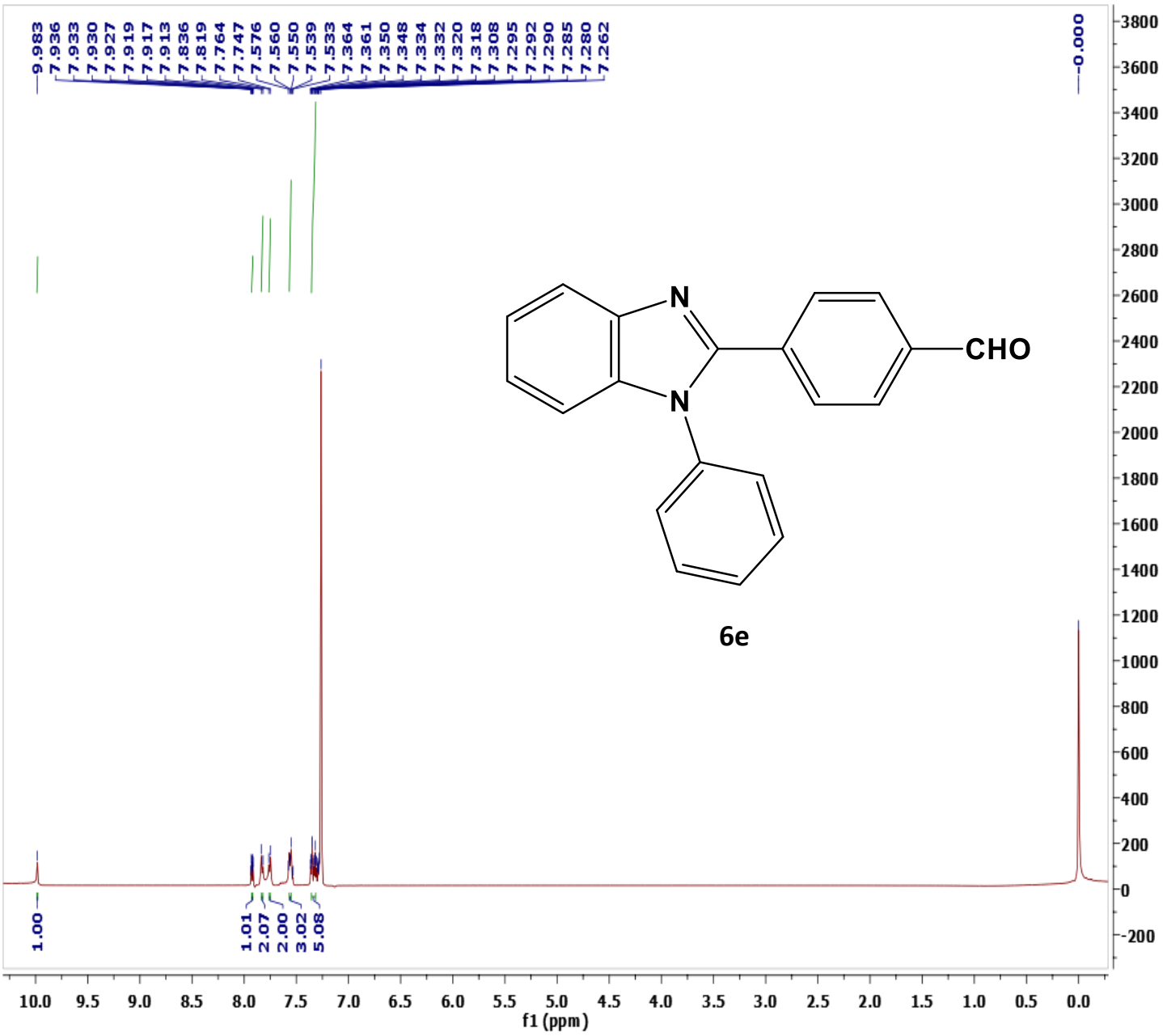


Fig. S25 ^{1}H NMR of compound **6e** in $CDCl_3$.

Compound **1a**: (0.06 g in 57.5% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.73 (d, 4H, J = 8.0 Hz), 7.32 (d, 4H, J = 8.0 Hz), 7.02 (d, 4H, J = 8.0 Hz), 6.80 (d, 4H, J = 8.0 Hz), 6.67-6.70 (m, 20H).

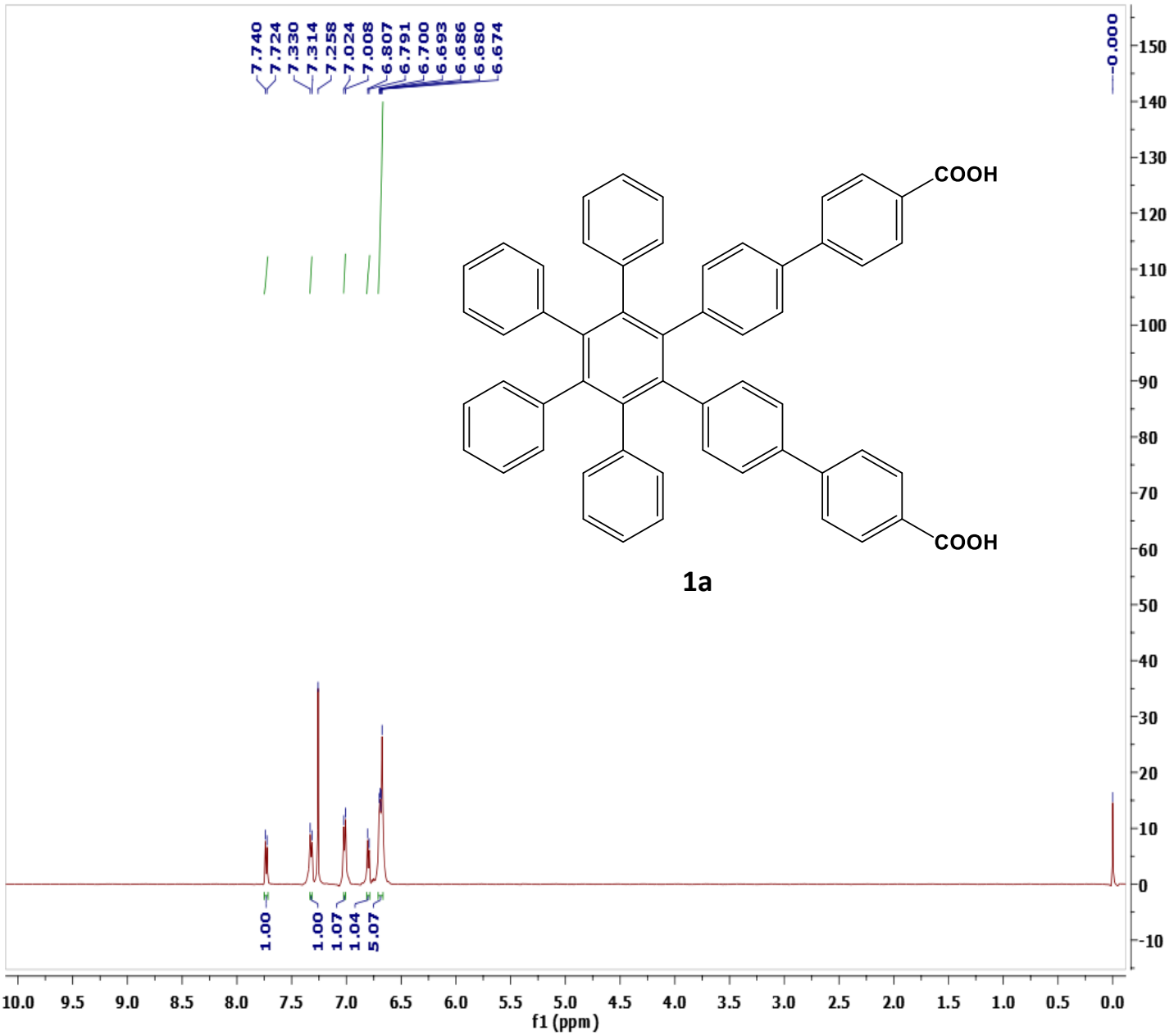


Fig. S26 ^{1}H NMR of derivative **1a** in $CDCl_3$.

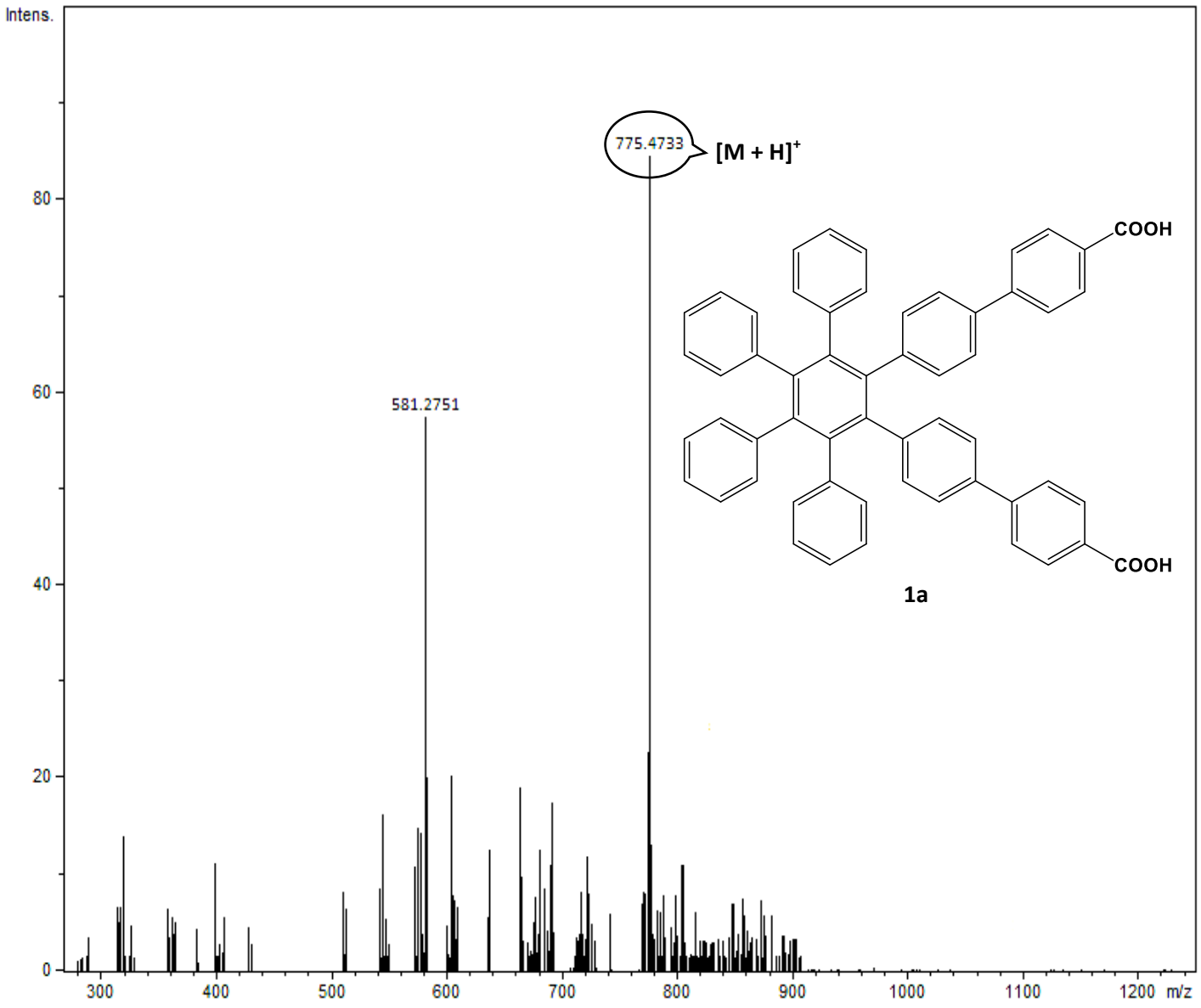


Fig. S27 Mass spectrum of derivative **1a**.

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