Supramolecular ensemble of PBI derivative and Cu_2O NPs: Potential photo catalysts for Suzuki and Suzuki type coupling reactions

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Contents

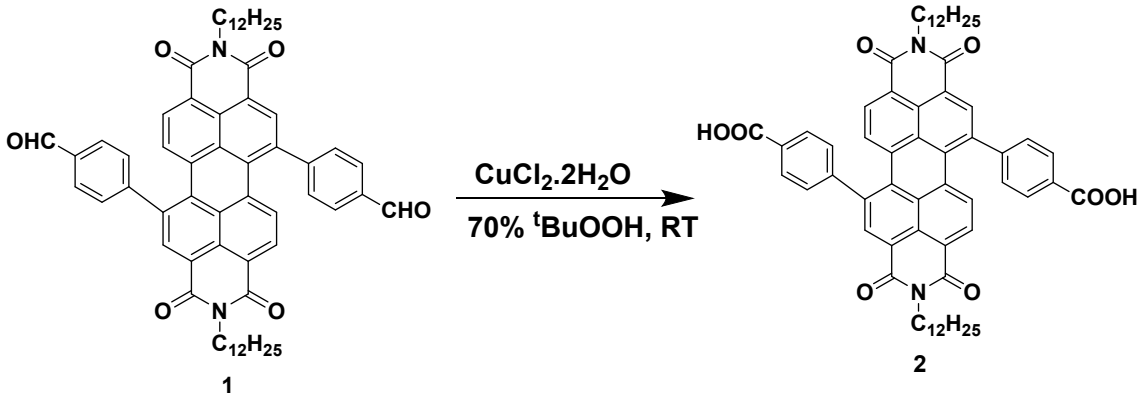
Table S1: Comparison of method for the preparation of supramolecular ensemble 2: Cu_2O in this manuscript with other reported methods in the literature for the preparation of Cu_2O NPs.

Entry	Method of preparation of NPs	NPs	Reducing agent	Special additive or surfactant	Temp. (° C)	Time	Shape of NPs	Recyclability /Reusability	Application of NPs	Journals
1	**Wet chemical method**	**Supramolecular ensemble 2:Cu_2O**	**NO**	**NO**	**Room temp.**	**8 h**	**Spherical**	**Yes**	**Photocatalytic Suzuki coupling**	**Present manuscript**
2	Chemical method	Cu_2O NPs	Yes	Yes	15	30 min	Rod	No	NH_3 gas sensing.	J. Mater. Chem. A, 2015, 3, 1174–1181
3	Chemical method	Cu_2O NPs	Yes	Yes	80-90	2-3 h	Spherical	No	antibacterial activity	RSC Adv., 2015, 5, 12293–12299 | 12293
4	Chemical method	Cu_2O NPs	Yes	Yes	80	12 h	Cube	No	-	CrystEngComm, 2011, 13, 6265–6270
5	Chemical method	Cu_2O NPs	Yes	Yes	30-50	30–90 min,	Cube	No	-	CrystEngComm, 2011, 13, 4060–4068
6	Chemical method	Cu_2O NPs	Yes	Yes	80	10 h	Cube,octahedron and sphere	No	-	Crystal Growth & Design, Vol. 10, No. 1, 2010
7	Chemical method	Cu_2O NPs	Yes	Yes	150	18 h	Octahedron Microcrystals	No	Photocatalytic	Crystal Growth & Design, Vol. 10, No. 5, 2010
8	Chemical method	Cu_2O NPs	Yes	Yes	140	1 h	Spherical and cube	No	-	J. Mater. Chem., 2008, 18, 4069-4073
9	Chemical method	Cu_2O NPs	Yes	Yes	Room temp	30 min	Cube	No	-	J. Mater. Chem., 2004, 14, 735–738
10	Chemical method	Cu_2O NPs	Yes	No	60-80	4 h	octahedral to microrod	No	-	CrystEngComm, 2012, 14, 8338–8341

Table S2: Comparison of catalytic efficiency of supramolecular ensemble 2: Cu_2O for the photocatalytic Suzuki-coupling reactions with other reported photocatalysts in literature.

Entry	Source of light	Photo catalyst	Amount of catalyst	Reaction conditions	Reaction temp	Time	TOF (h^{-1})	Recyclability /Reusability	Journals
1	**100 W tungsten filament bulb**	**Supramolecular ensemble 2:Cu_2O**	**0.02 mmol**	**H_2O/EtOH (1:1), K_2CO_3 (1.5 eq.)**	**Room temp.**	**8 h**	**1.45 (bromobenzene)**	**Yes**	**Present manuscript**
2	300 W Xe lamp	Pd/SiC	10 mg	DMF/H_2O (3:1), Cs_2CO_3 (3 eq.)	30 °C	1.33 h	1053 (Iodobenzene)	Yes	*J. Phys. Chem. C* 2015, **119**, 3238−3243
3	Xe lamp (150W)	Pd/Au/PN-CeO_2	15 mg	DMF/H_2O (3:1), 0.6 mmol K_2CO_3,	Room temp.	1 h	-	Yes	ACS Catal. 2015, 5, 6481−6488
4	100 W tungsten filament bulb	Ag@Cu_2O	0.02 mmol	H_2O/EtOH (3:1), K_2CO_3 (1.5 eq.)	Room temp.	5 h	-	Yes	*Chem. Commun.,* 2015, 51, 12529-12532
5	White LED lamp	Pd@B-BO_3	10 mg	DMF/H_2O (1:1), K_2CO_3 (1.5 eq.)	Room temp.	2 h	-	Yes	*Chem. mater.* 2015, **27**, 1921
6	500 W Xe lamp	Ru–Pd bimetallic complex	5×10^{-4} mmol	EtOH, PPh_3, K_2CO_3, Ar-atmosphere	Room temp.	6 h	-	No	*Chem. Commun*., 2014, **50**, 14501-14503
7	Halogen lamp	Au–Pd alloy NP	50 mg	DMF/H_2O (3:1), K_2CO_3 (3 eq.), Ar atmosphere	30 °C	6 hr	14.5 (bromobenzene)	Yes	*Green Chem*., 2014, **16**, 4272–4285
8	Sunlight	Au−Pd nanostructures	0.49 μmol	NaOH, CTAB, H_2O	Room temp.	2 h	162 (bromobenzene)	Yes	*J. Am. Chem. Soc*. 2013, **135**, 5588−5601

Scheme 1: Synthetic scheme of compound **2**.



Synthesis of compound 2. To a solution of derivative **1** (50 mg, 0.05 mmol) and $CuCl_2.2H_2O$ (0.45 mg, 0.06 mmol) in acetonitrile/THF (3:1) mixture was slowly added aqueous ^{t}BuOOH (11.76 μL, 0.05 mmol, 70% in water) over 24 h. The resulting reaction mixture was stirred at room temperature until the disappearance of starting material (TLC). After completion of the reaction, the solvent was evaporated and to the resulting crude reaction mixture water was added. The pH was adjusted to 8.0–8.5 with saturated sodium bicarbonate solution and then the reaction mixture was extracted with ethyl acetate. The aqueous layer was acidified to pH 2.0 using 2 N HCl and extracted with ethyl acetate. The organic layer was concentrated and purified by silica gel column chromatography to give the carboxylic acid.

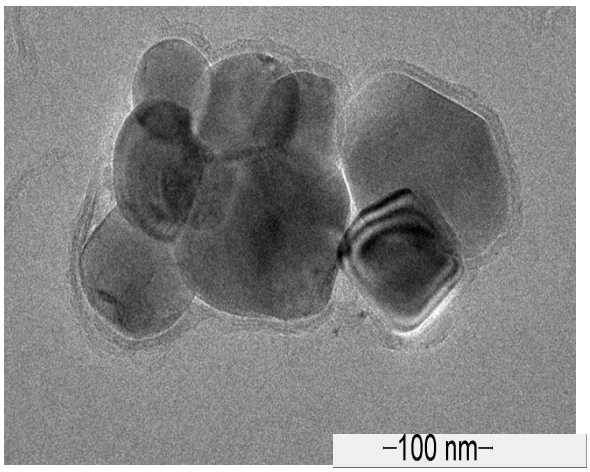


Fig.S1: TEM image of derivative **1** showing irregular shapes aggregates.

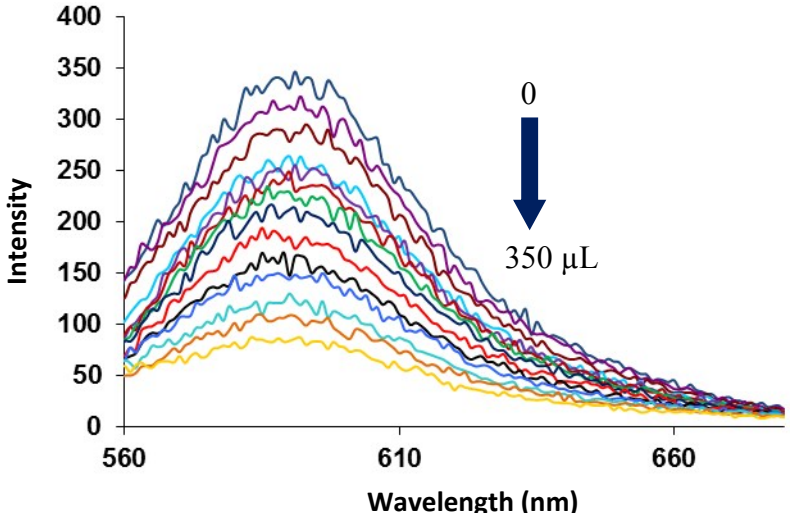


Fig.S2: Fluorescence spectra of derivative **1** (10 µM) upon addition of Benedict's solution (350 µL, 0.04 M).

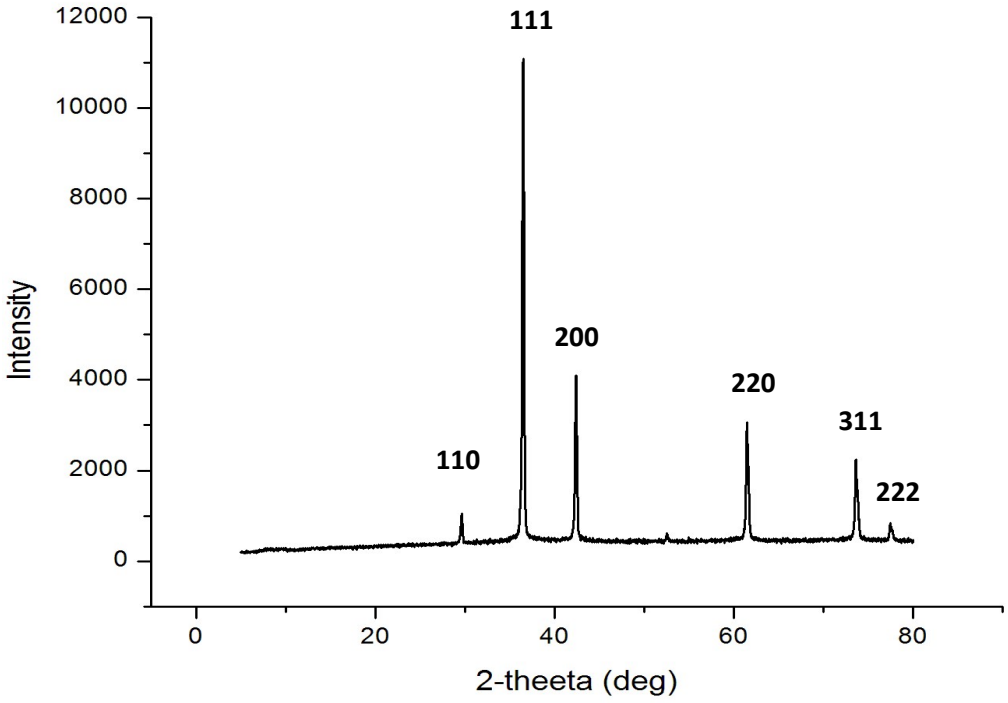


Fig. S3: X-Ray Diffraction (XRD) pattern of Cu_2O NPs.

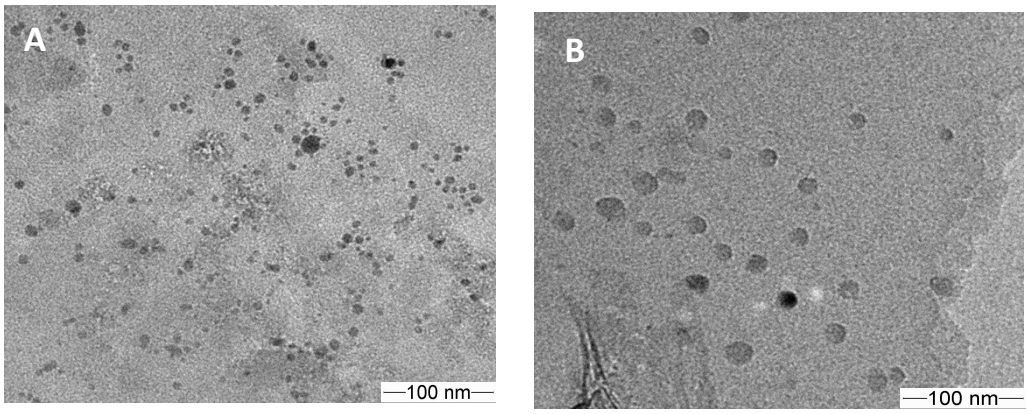


Fig. S4: (A) TEM images of spherical supramolecular ensemble 2:Cu_2O; (A) 2:1 (derivative **1**: Benedict's solution); (B) 1:2 (derivative **1** : Benedict's solution)

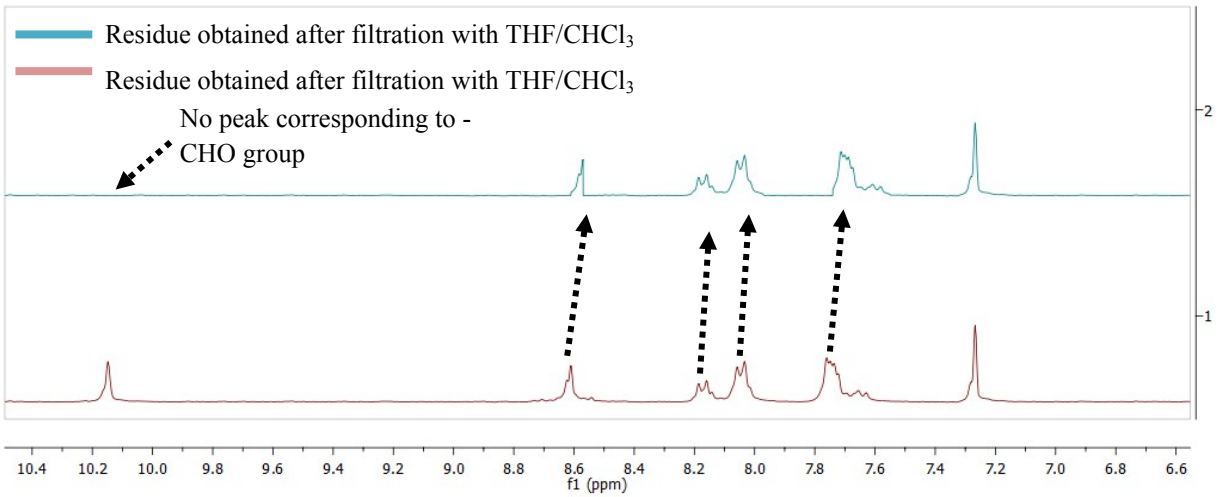


Fig. S5: Overlay NMR spectra of derivative **1** and residue obtained after filtration with THF/$CHCl_3$ mixture.

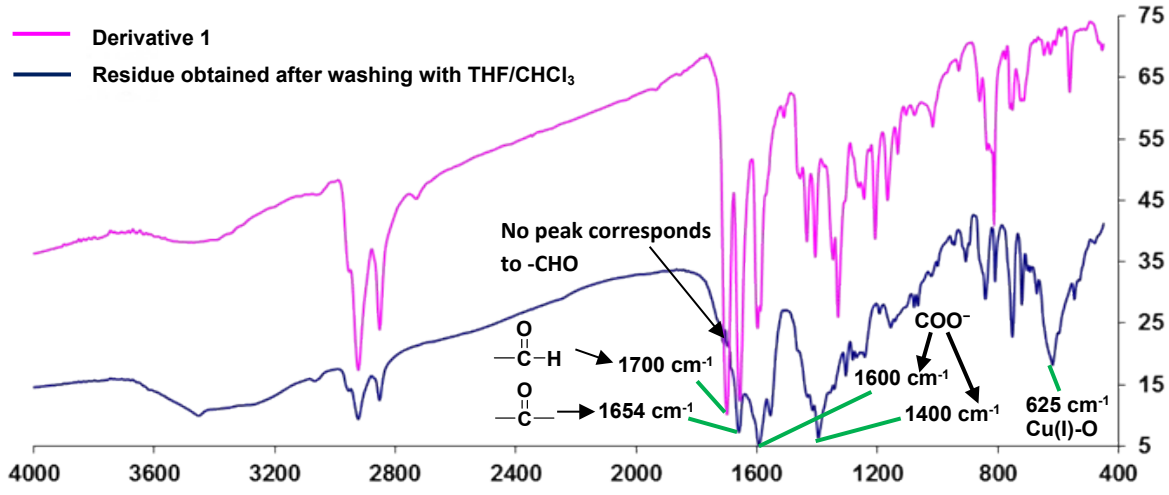


Fig. S6: FT infrared absorption spectra of derivative **1** and residue obtained after filteration with THF/$CHCl_3$.

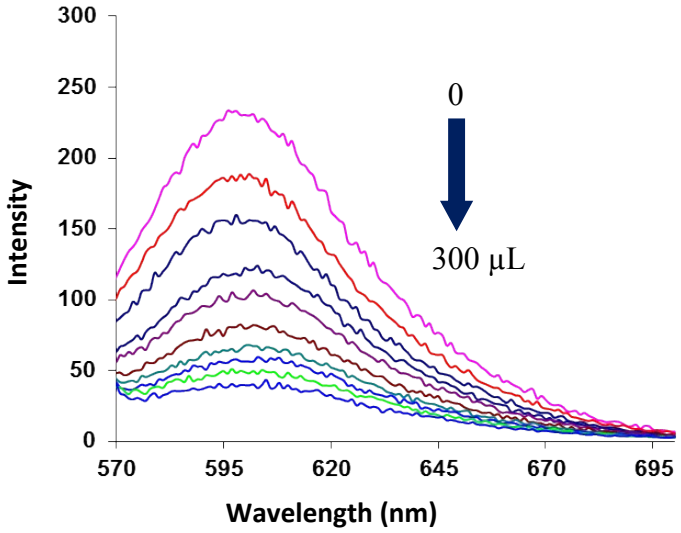


Fig. S7: Fluorescence spectra of oxidized species **2** (10 µM) upon addition Cu_2O NPs (300 µL).

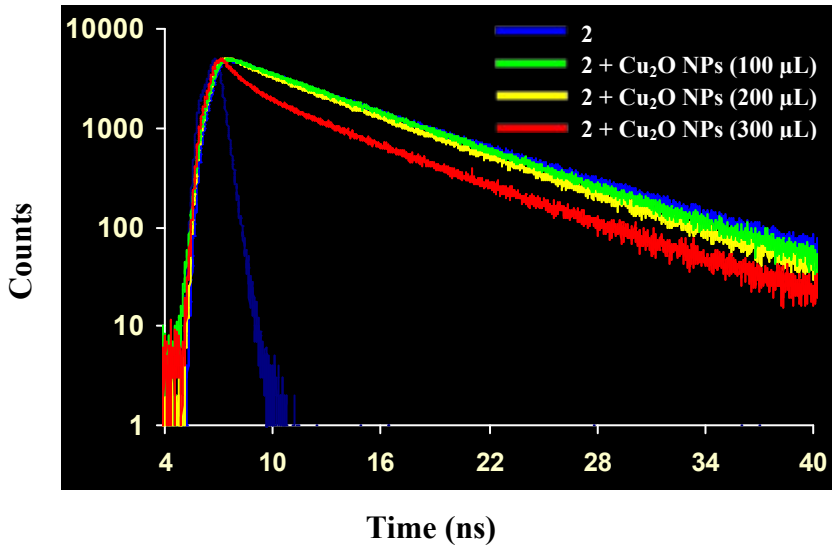


Fig. S8: Exponential fluorescence decays of oxidized species of **2** on addition of various amount of bare Cu_2O NPs measured at 600 nm. Spectra were acquired in Water-THF mixture (1:1), λ_{ex}= 540 nm.

Table S3: Fluorescence lifetime of oxidized species of **2** on addition of various amount of bare Cu_2O NPs measured at 600 nm in Water-THF mixture (1:1). $\mathbf{A_1}$, $\mathbf{A_2}$**:** fractional amount of molecules in each environment. $\boldsymbol{\tau_1}$**,** $\boldsymbol{\tau_2}$ and $\boldsymbol{\tau_{avg}}$**:** bi-exponential and average life time; λ_{ex}= 540 nm.

Sample	$\mathbf{A_1}$	$\mathbf{A_2}$	$\boldsymbol{\tau_1}$ **(ns)**	$\boldsymbol{\tau_2}$ **(ns)**	$\boldsymbol{\tau_{avg}}$ **(ns)**
Cpd 3 oxidized	100	-	7.12	-	7.12
Cpd 3 Oxidized + Cu_2O NPs (100 µL)	100	-	6.84	-	6.84
Cpd 3 Oxidized + Cu_2O (200 µL)	100	-	6.47	-	6.47
Cpd 3 Oxidized + Cu_2O (300 µL)	20.38	79.62	0.91	6.46	2.87

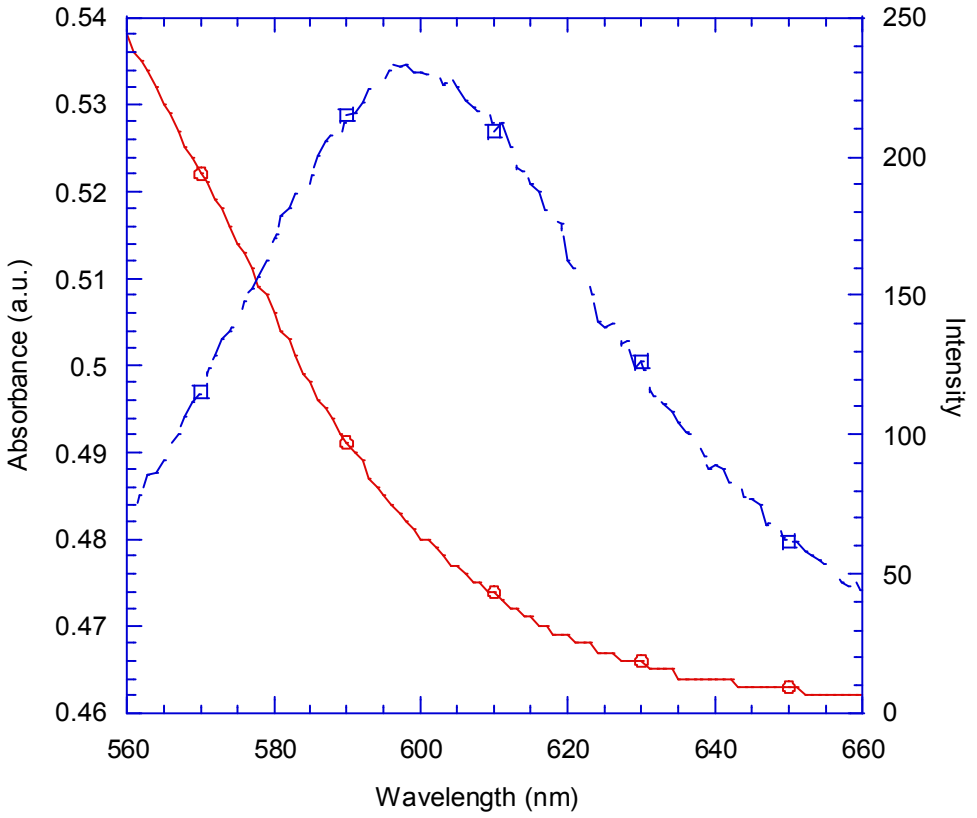


Fig. S9. Spectral overlap of absorption spectrum of Cu_2O NPs and emission spectrum of oxidized species **2**.

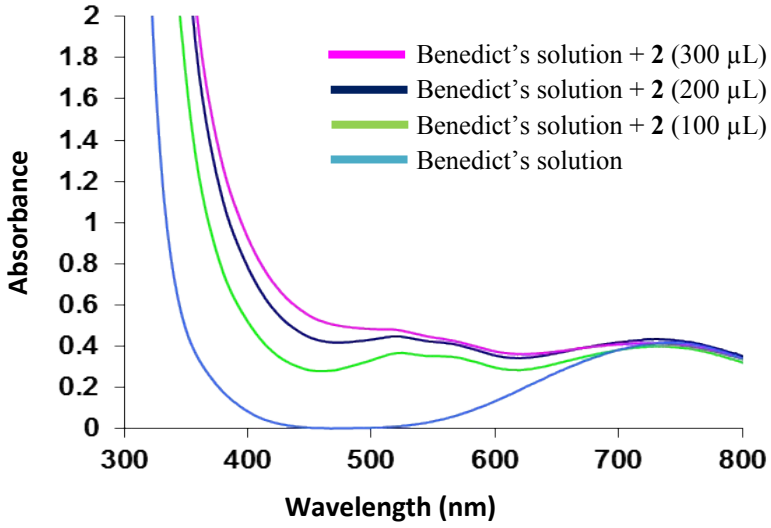


Fig.S10: UV-vis spectra of oxidized species **2** (10 µM) upon addition Benedict's solution (350 µL, 0.04 M).

Table S4.: Catalytic efficiency of supramolecular ensemble 2:Cu_2O for photocatalytic Suzuki coupling reaction of bromobenzene with phenyl boronic acid.

Entry	Catalyst loading	Time (h)	Yield (%)
1	0.02 mmol	8	75
2	0.01 mmol	10	72
3	0.005 mmol	12	68

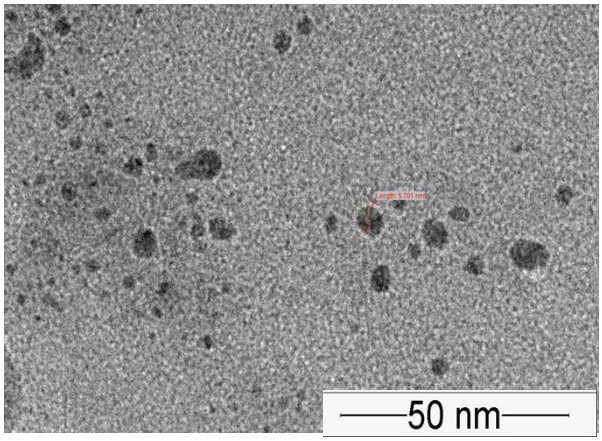


Fig. S11: TEM image of spherical supramolecular ensemble 2:Cu_2O; recovered after photocatalytic Suzuki coupling reaction. Scale bar 50 nm.

SpectrAA Report. **15:22 05-02-2016**

Analyst
Date Started 16:06 02-02-2016 GMT: 10:36 02-02-2016
Worksheet Gurpreet020216
Comment
Methods Cu,Cu
Computer name HP-PC
Serial Number:

Method: Cu (Flame)

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	ISF					
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STANDARD 1	1.000	1.4	0.0009	0.0605		
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	Readings					
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	ISF					
	1.0000					

Fig. S12: Atomic absorption Studies (AAS) of the residual liquid left after the after the recycling of the catalyst and found that only 0.012 mg/lit = 0.012 ppm of copper leached into the solution.

[1]H NMR spectra of products of the photocatalytic Suzuki coupling reactions using different substrates.

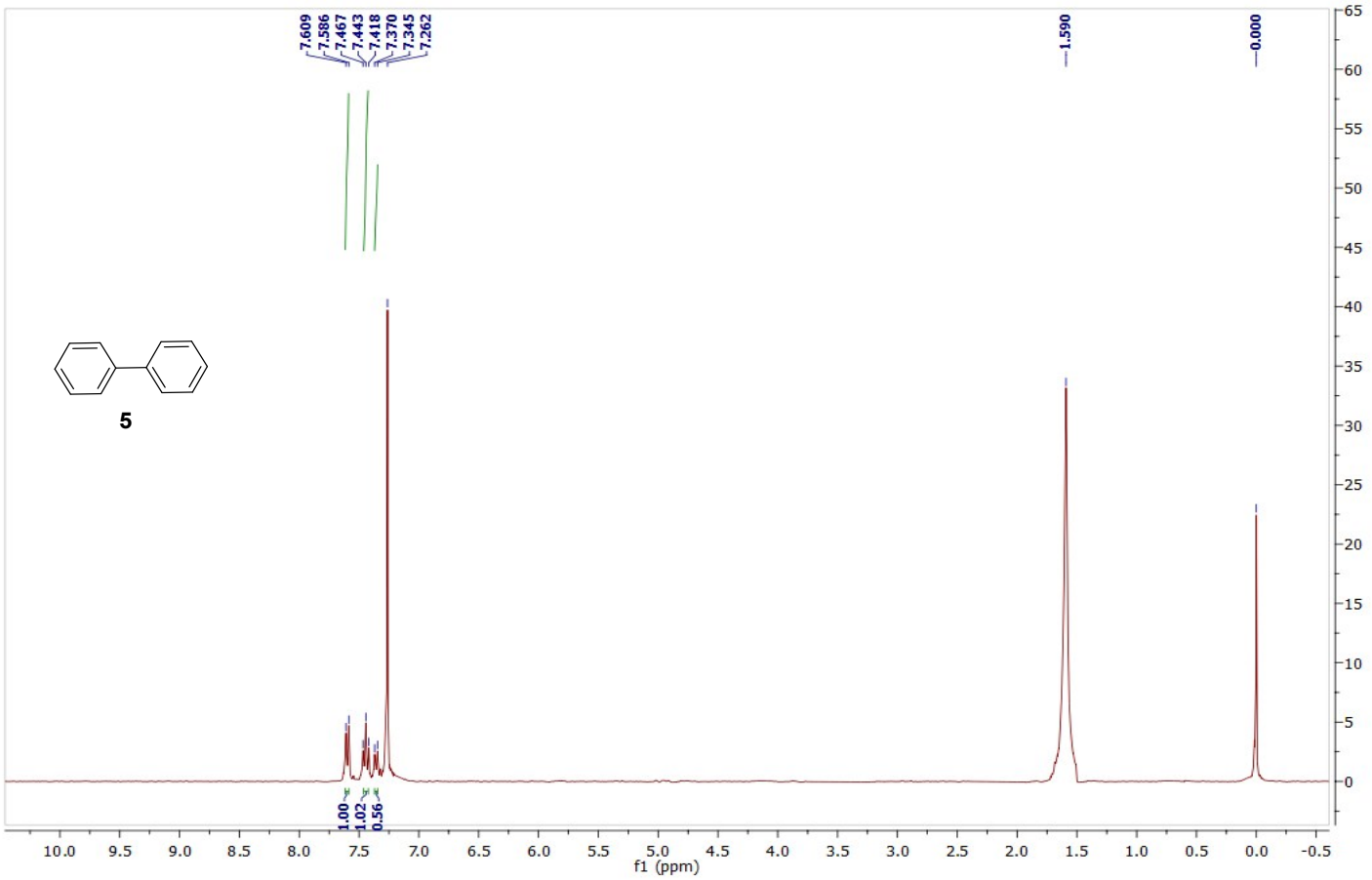

Fig. S13: The 1H NMR spectrum of compound 5 in $CDCl_3$**.**

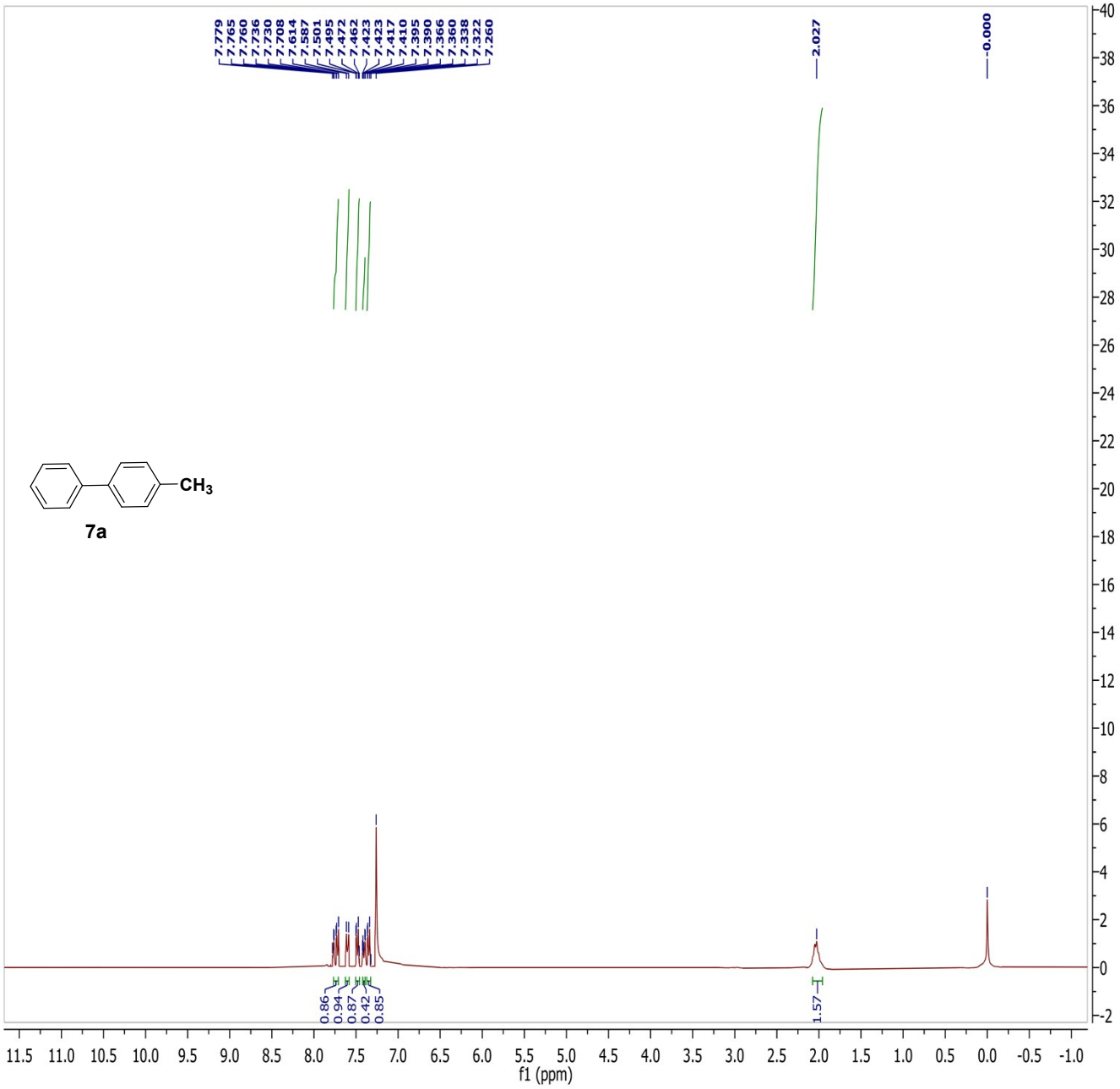

Fig. S14: The ^{1}H NMR spectrum compound 7a in $CDCl_3$**.**

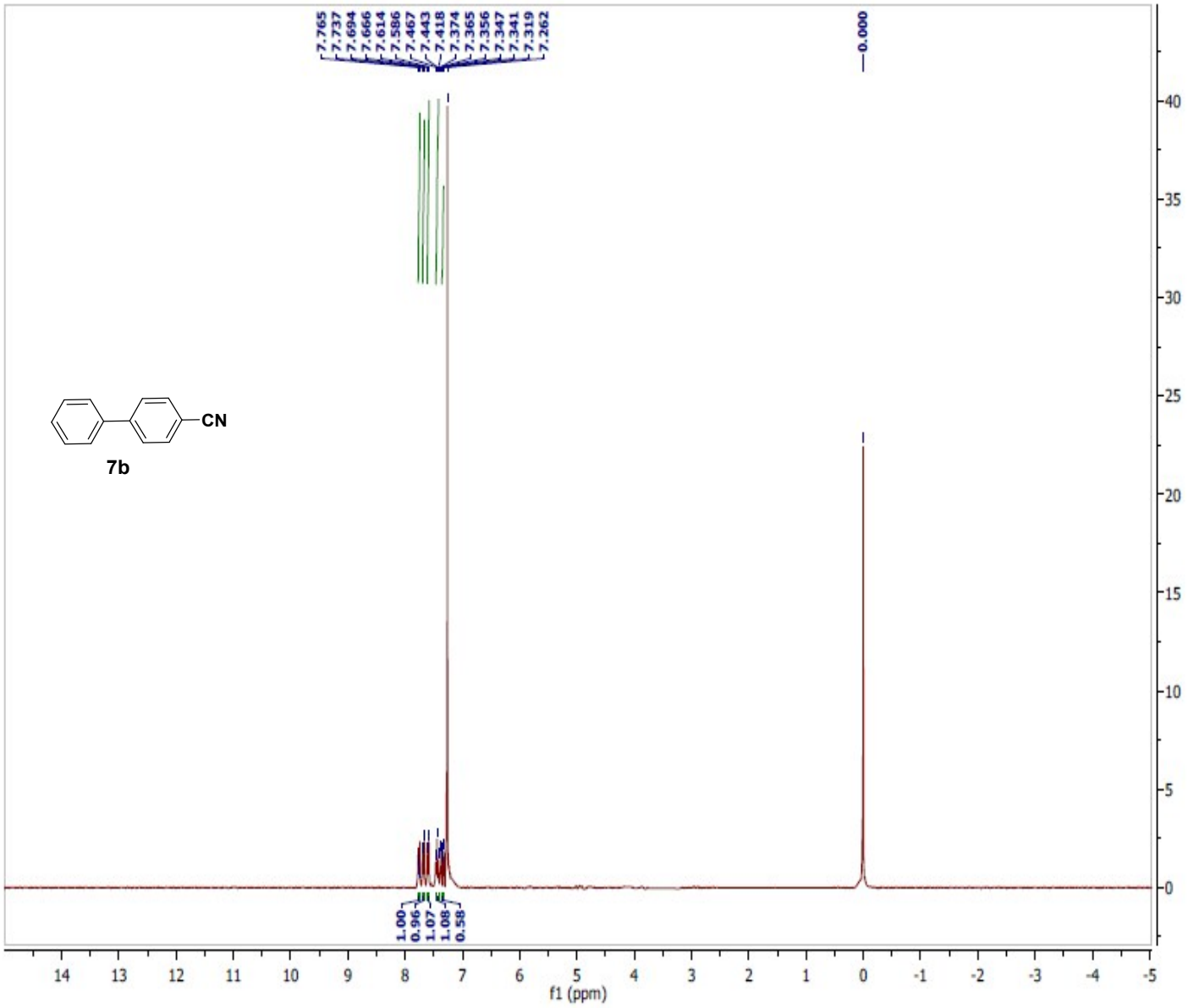

Fig.S15: The ^{1}H NMR spectrum compound 7b in $CDCl_3$**.**

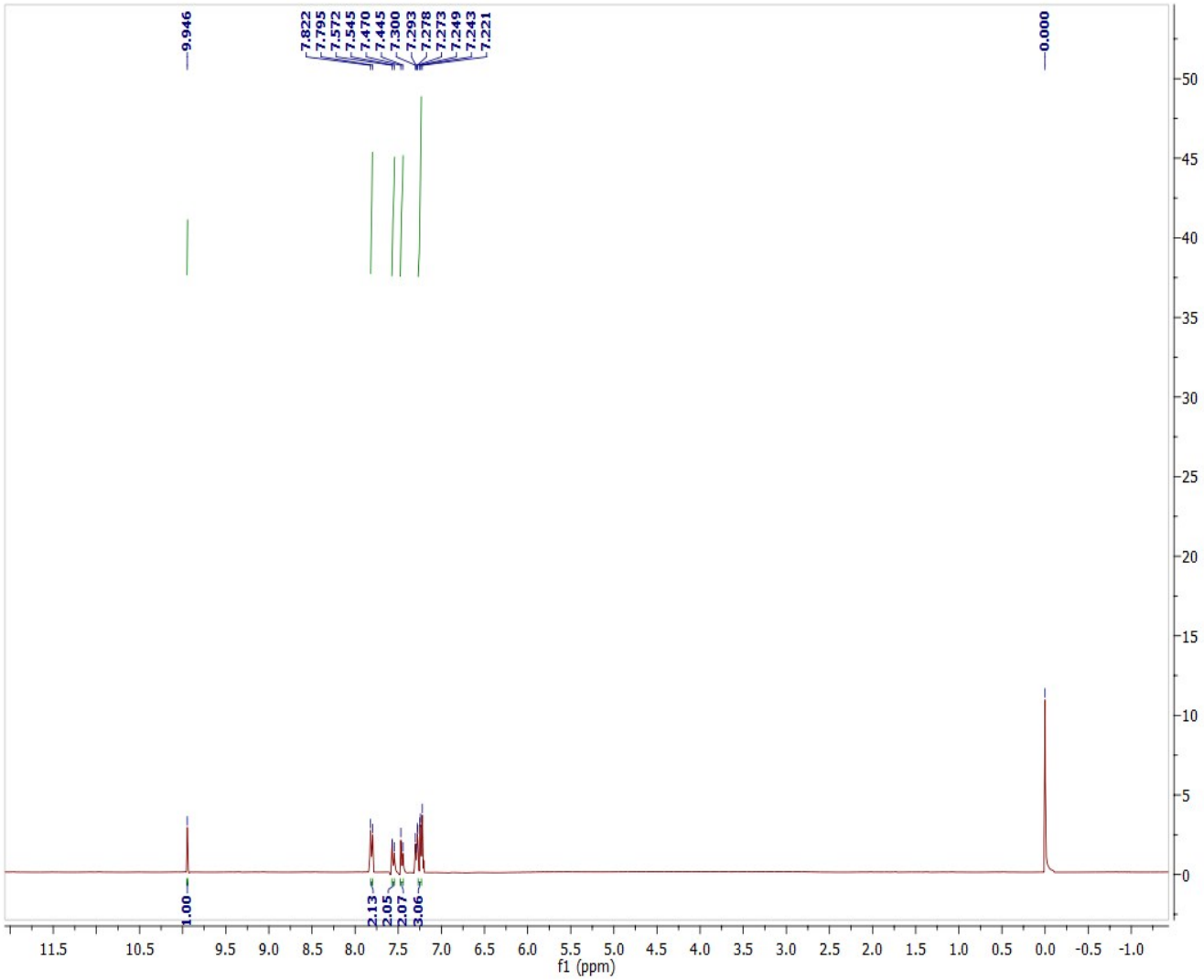

Fig.S16: The ^{1}H NMR spectrum of compound 7c in $CDCl_3$.

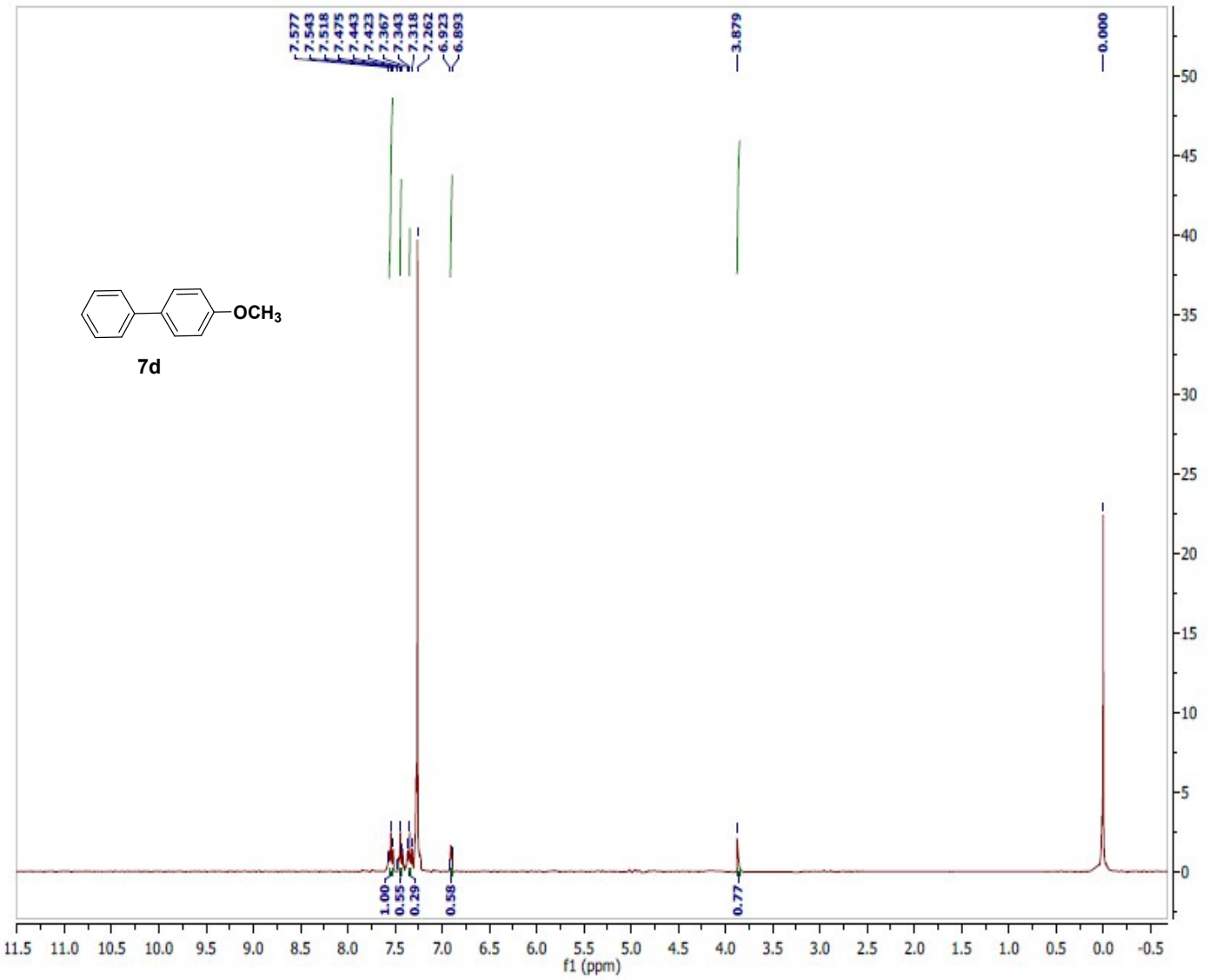

Fig.17 The ^{1}H NMR spectrum of compound **7d** in $CDCl_3$.

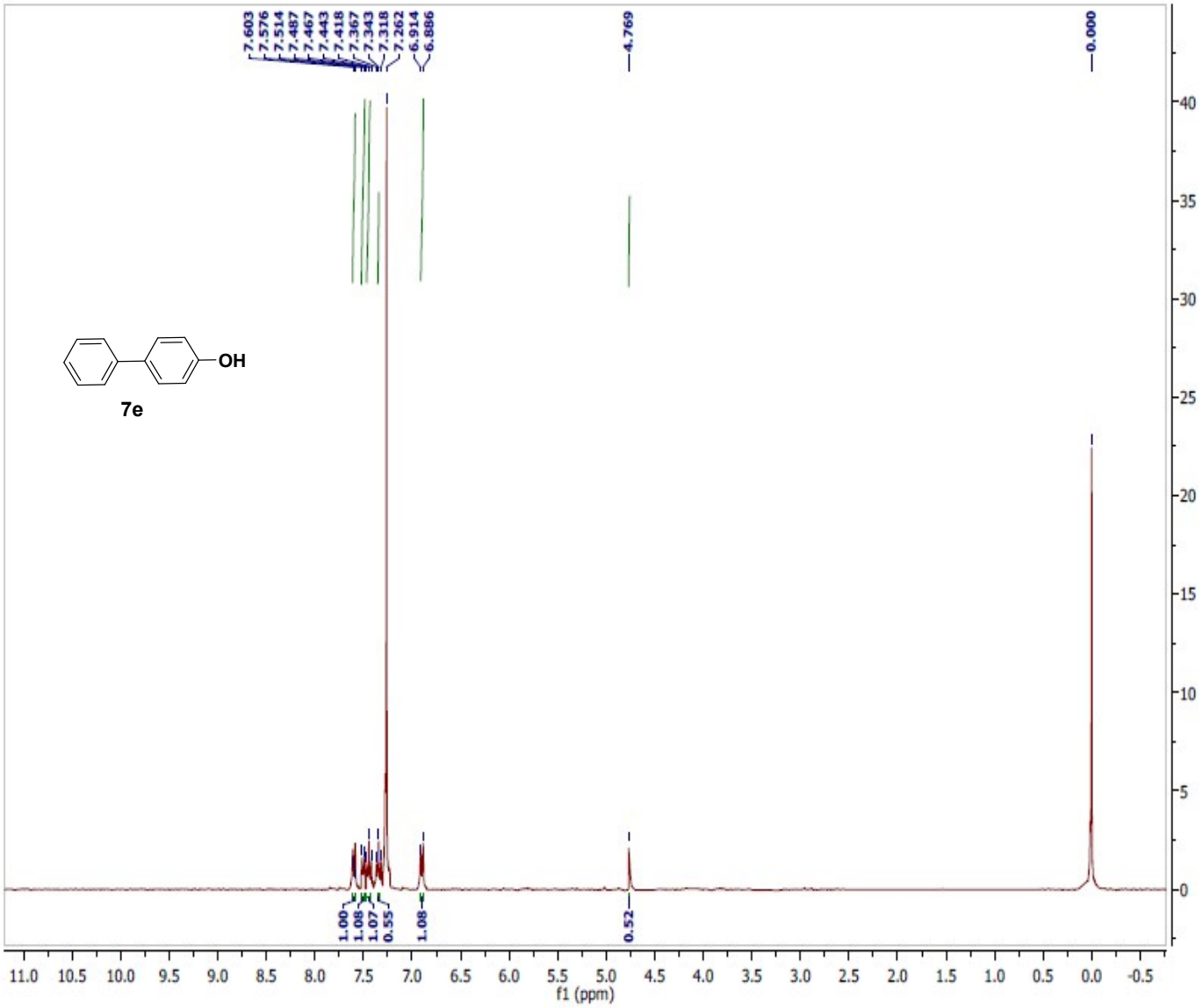

Fig.S18: The ^{1}H NMR spectrum of compound **7a** in $CDCl_3$.

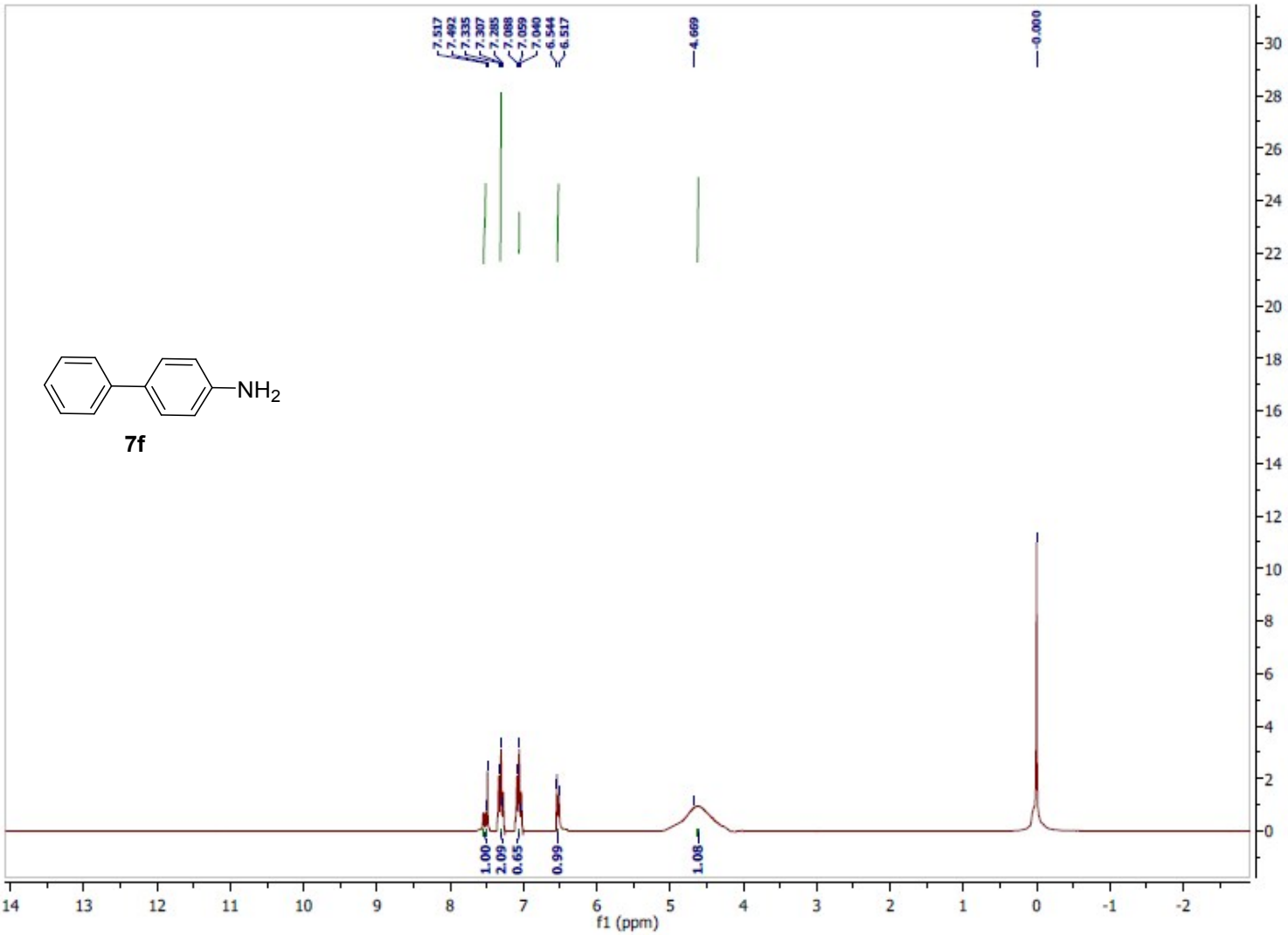

Fig.S19: The 1H NMR spectrum of compound **7f** in $CDCl_3$.

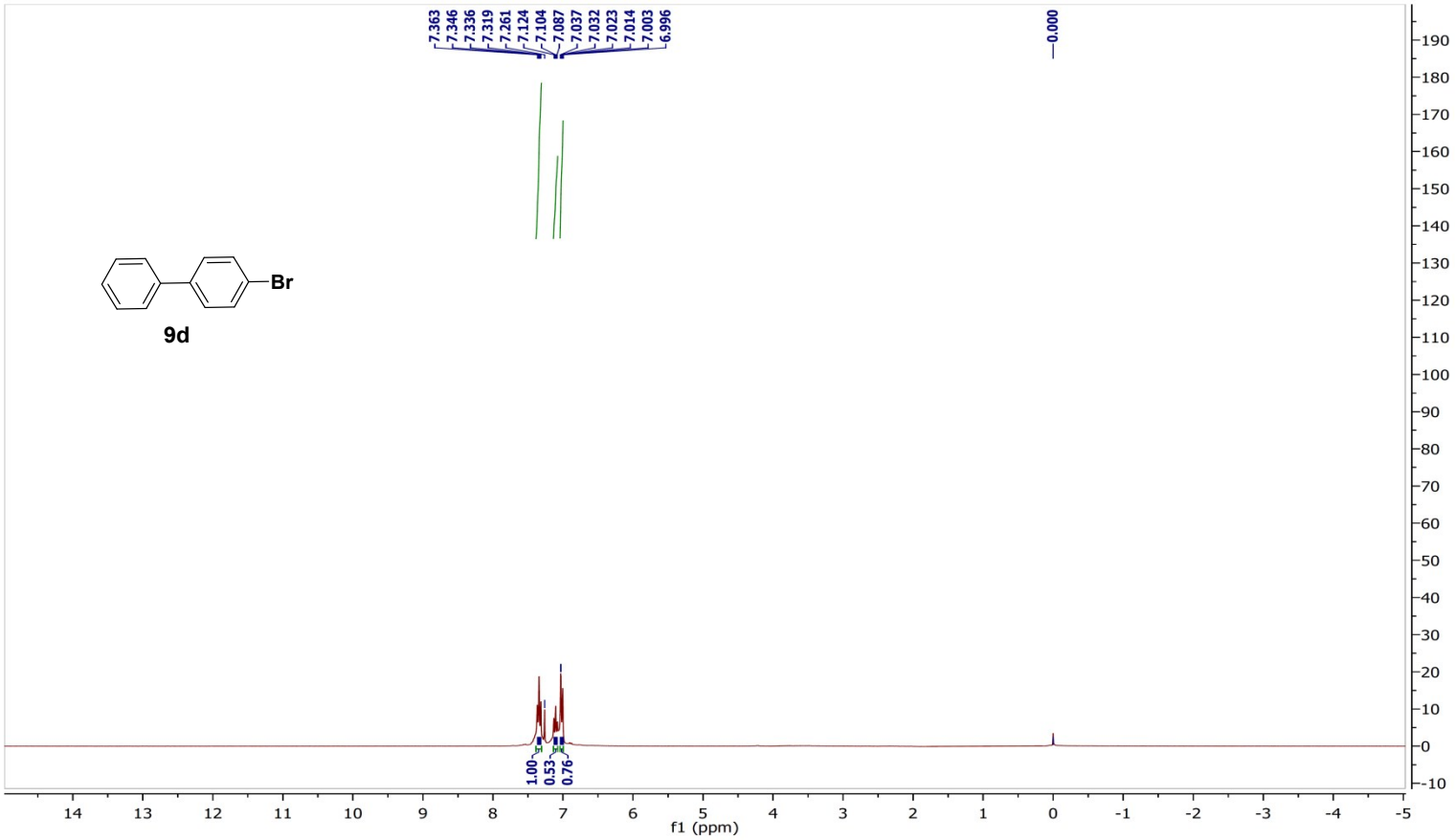

Fig.S20: The ^{1}H NMR spectrum of compound **9d** in $CDCl_3$.

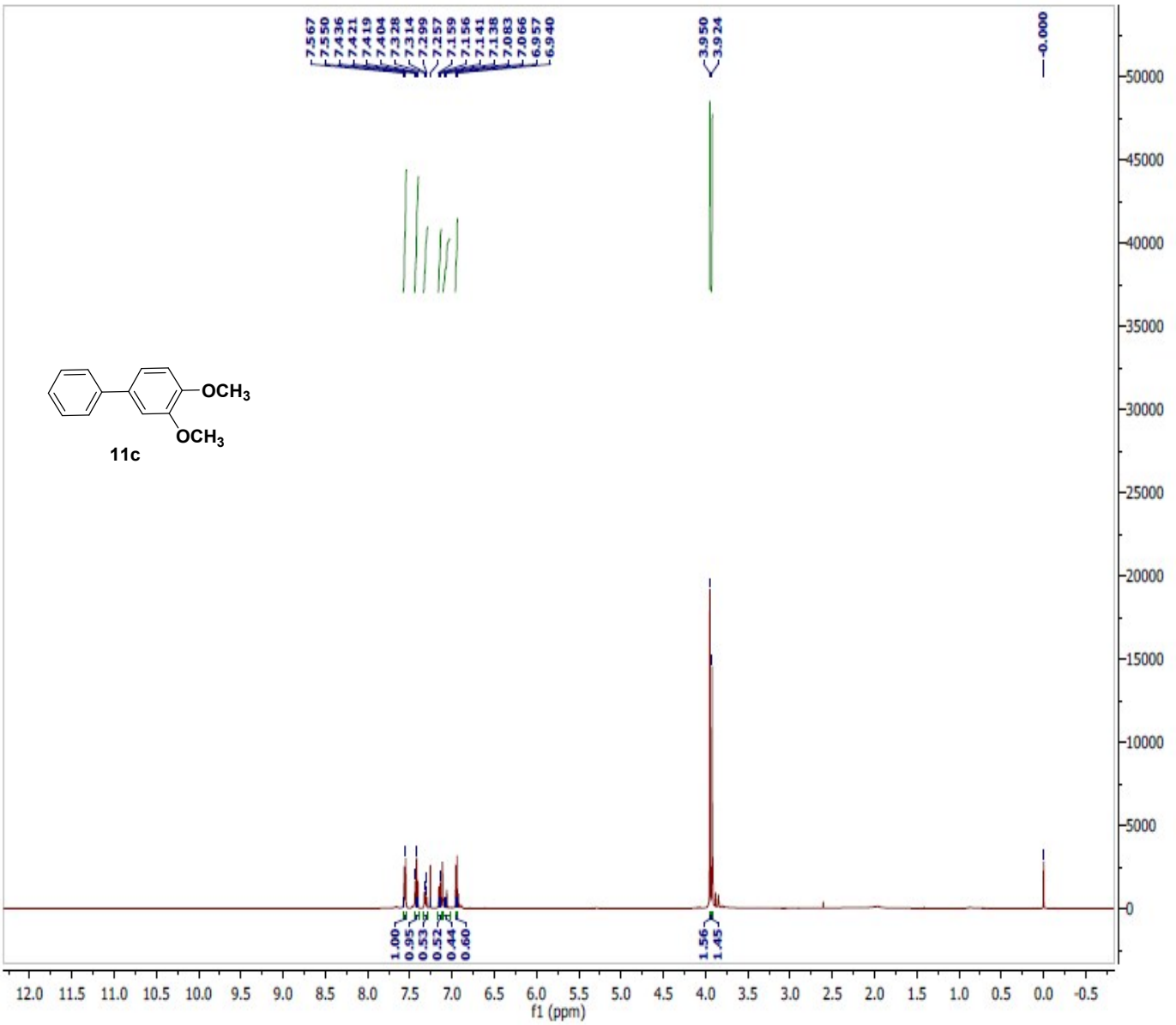

Fig.S21: The ^{1}H NMR spectrum of compound **11c** in $CDCl_3$.

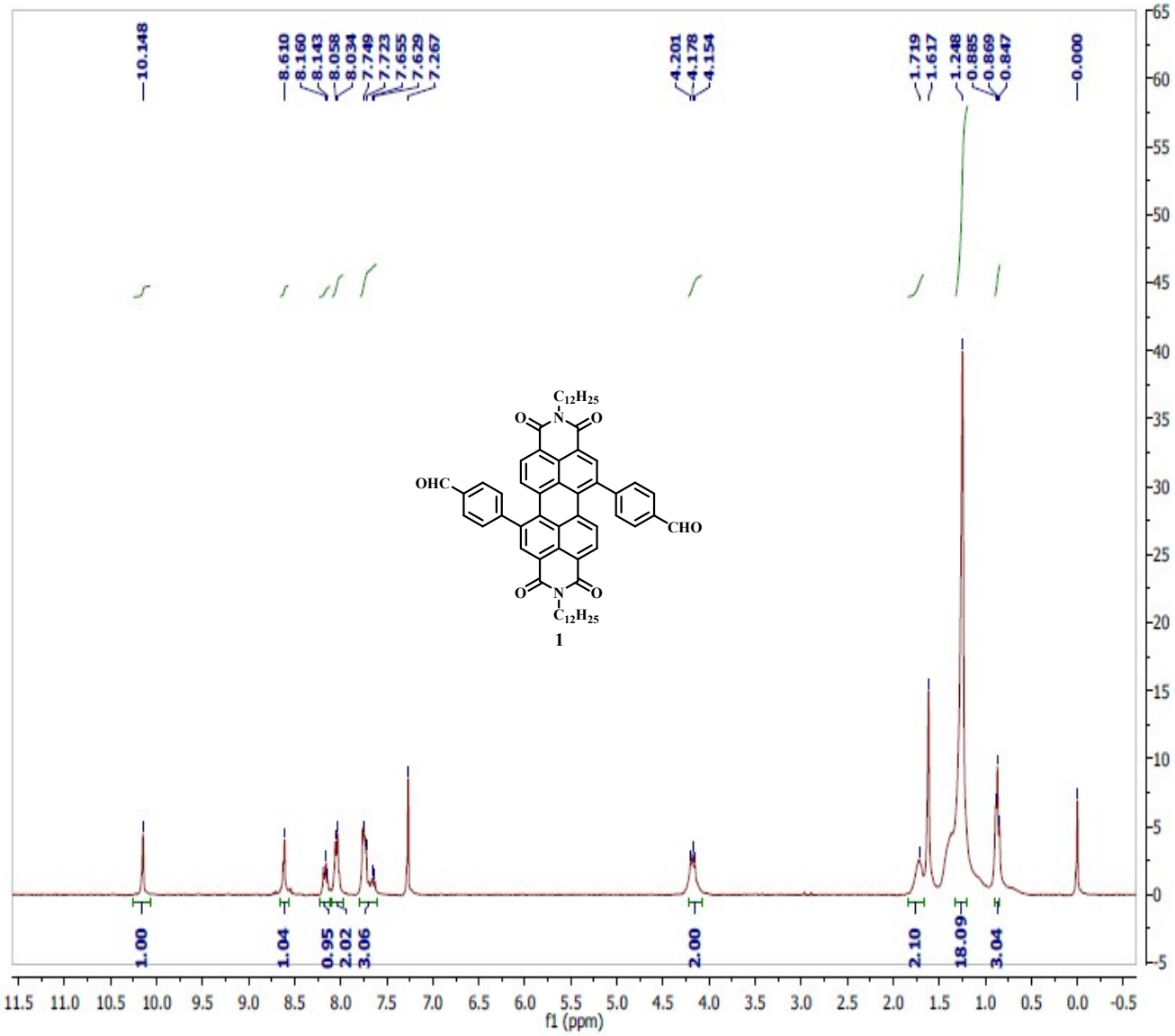

Fig.S22: The ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

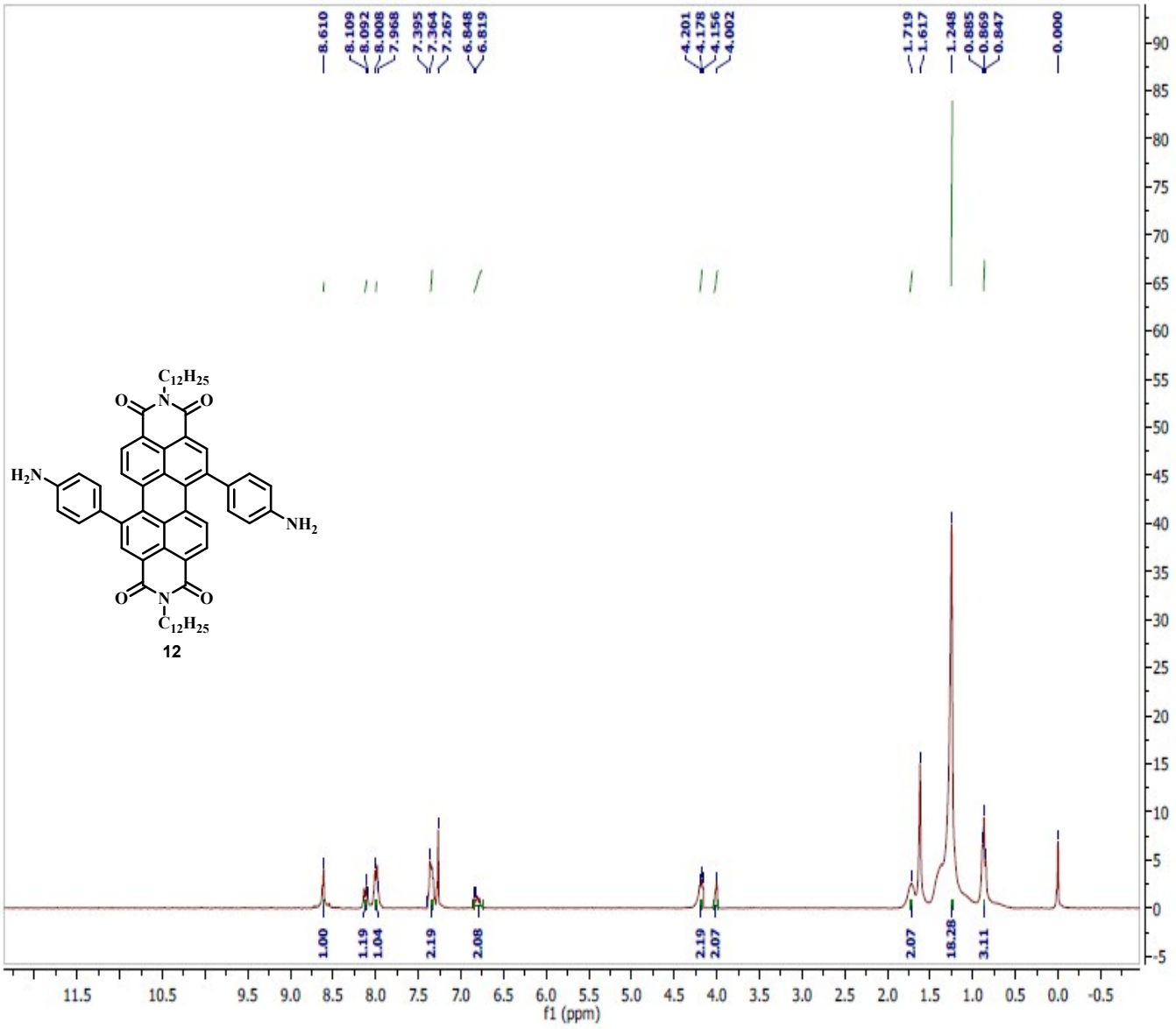

Fig.S23: The ^{1}H NMR spectrum compound **12** in $CDCl_3$.

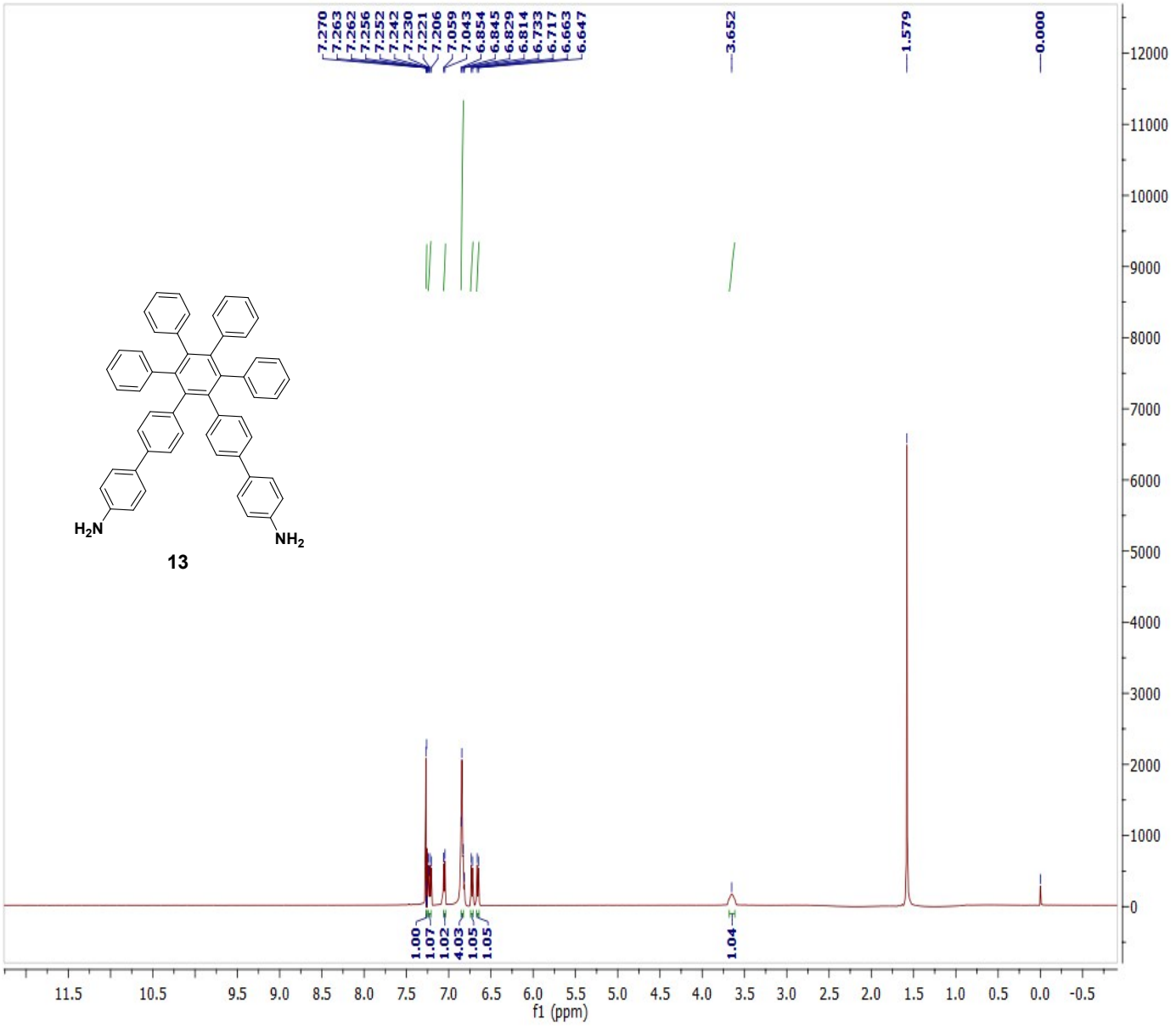

Fig.S24: The ^{1}H NMR spectrum of compound **13** in $CDCl_3$.

^{1}H NMR spectra of products of the photocatalytic Suzuki type coupling reactions using different substrates.

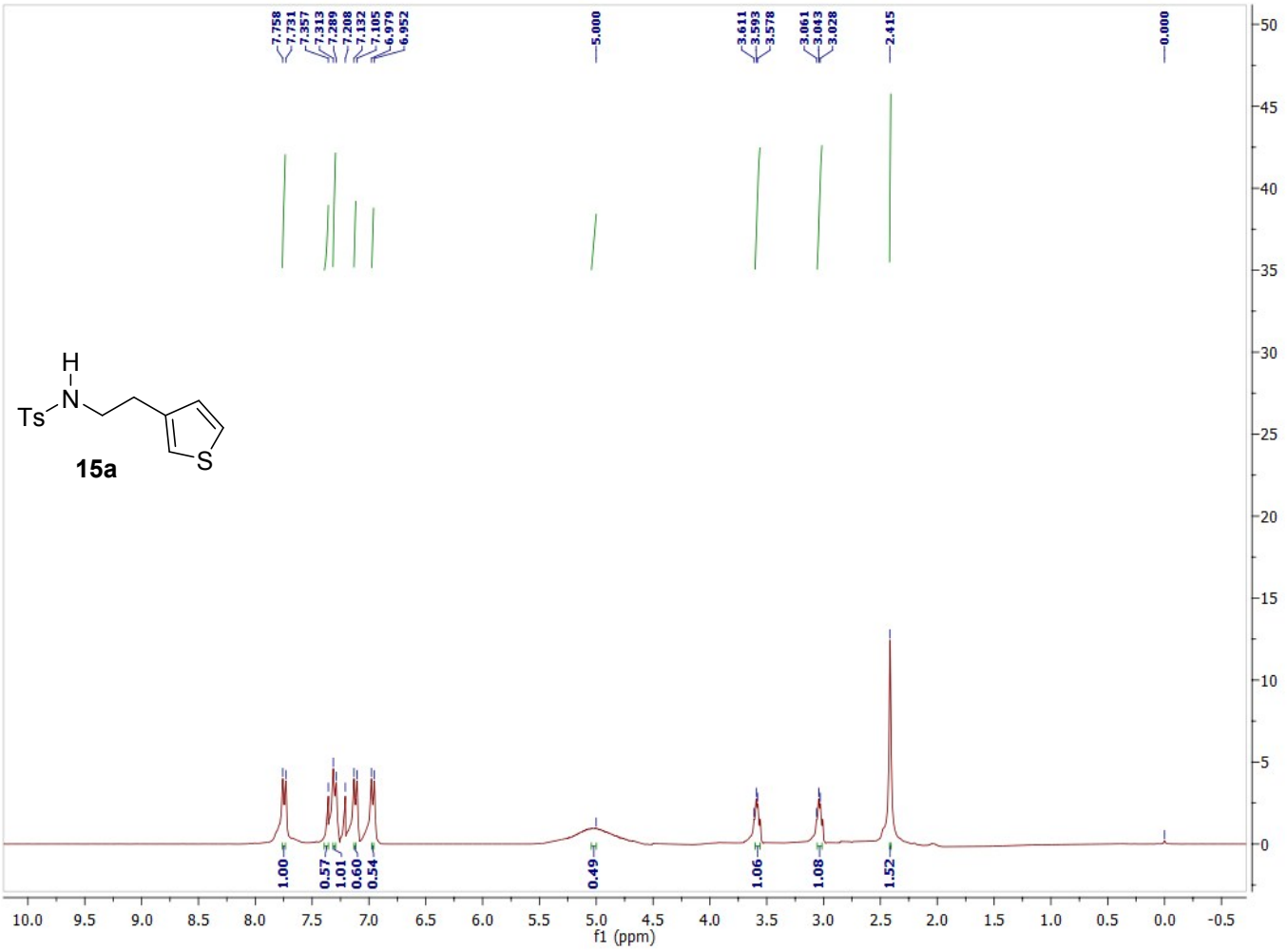

Fig.S25: The ^{1}H NMR spectrum of compound **15a** in $CDCl_3$.

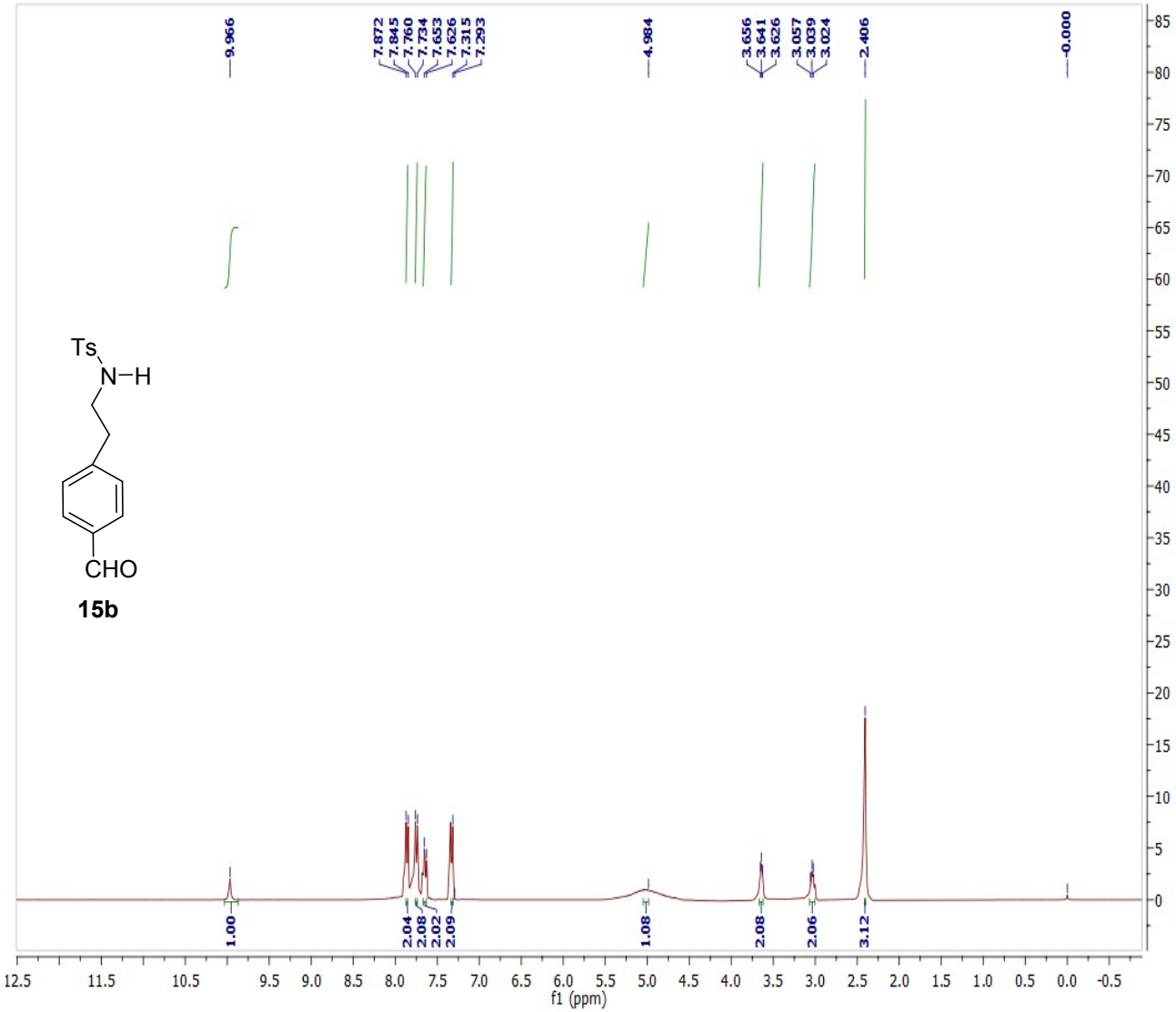

Fig. S26: The ^{1}H NMR spectrum of compound **15b** in $CDCl_3$.

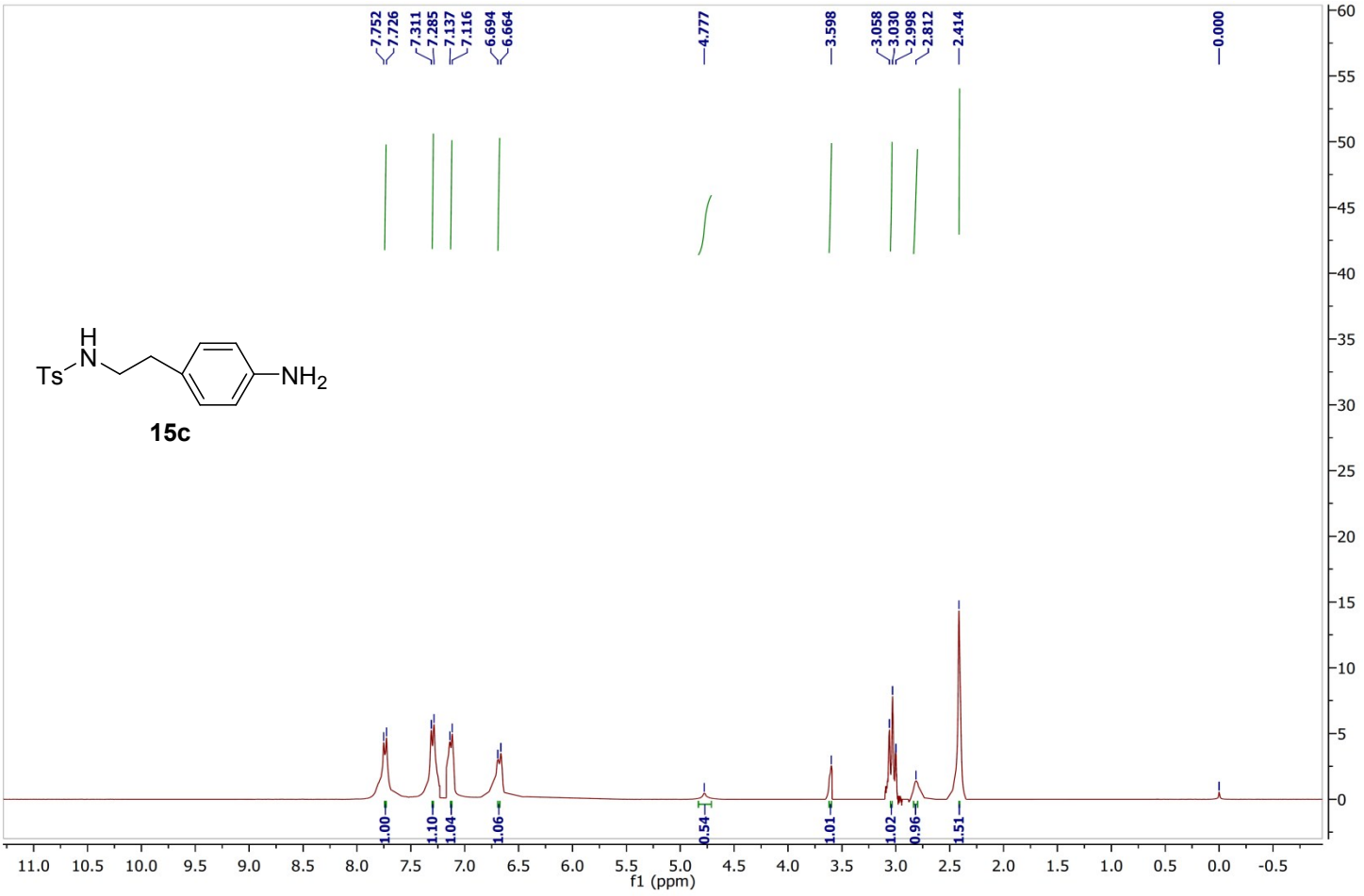

Fig.S27: The ^{1}H NMR spectrum of compound 15c in $CDCl_3$.

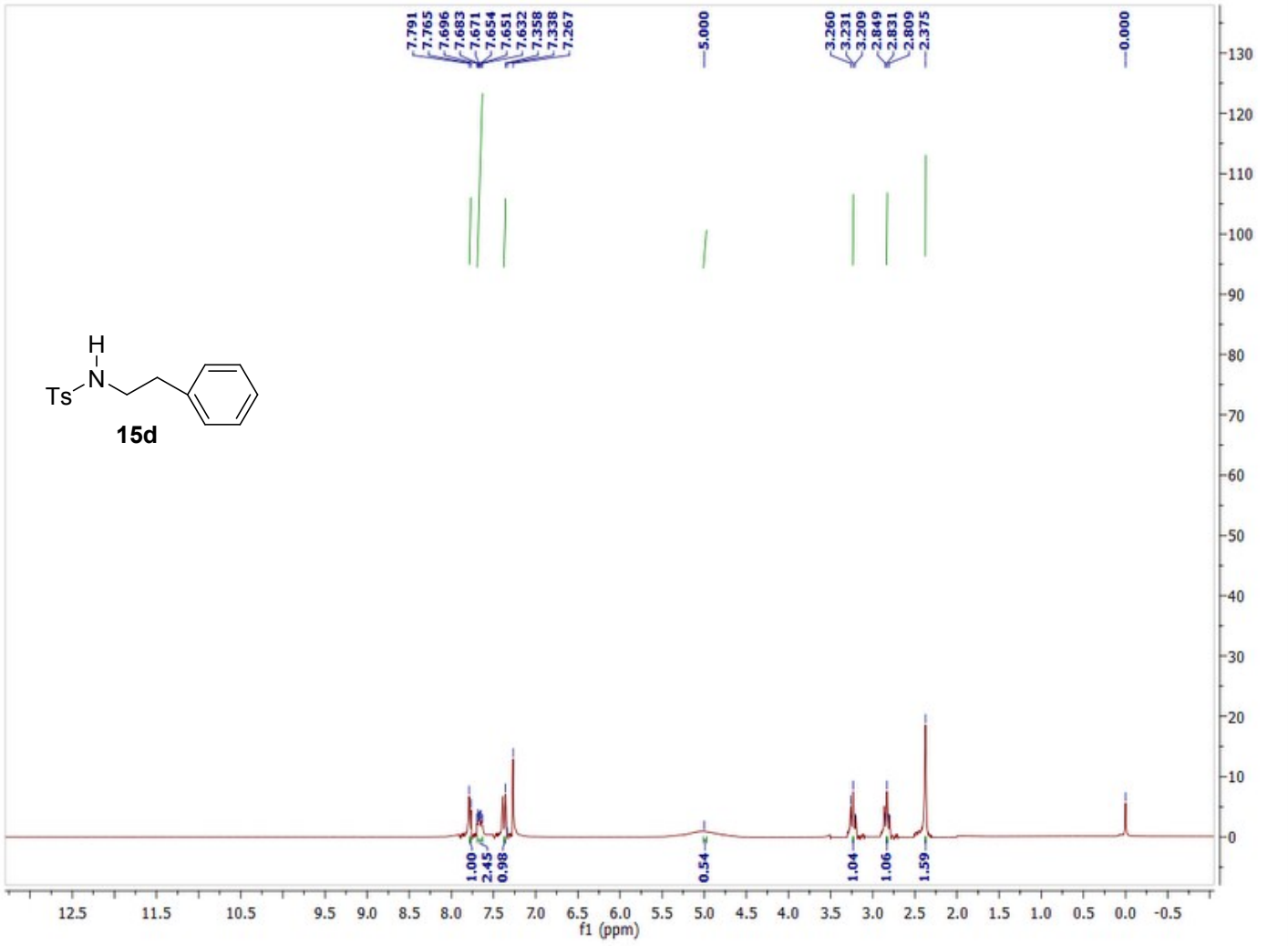

Fig.S28: The ^{1}H NMR spectrum of compound **15d** in $CDCl_3$.

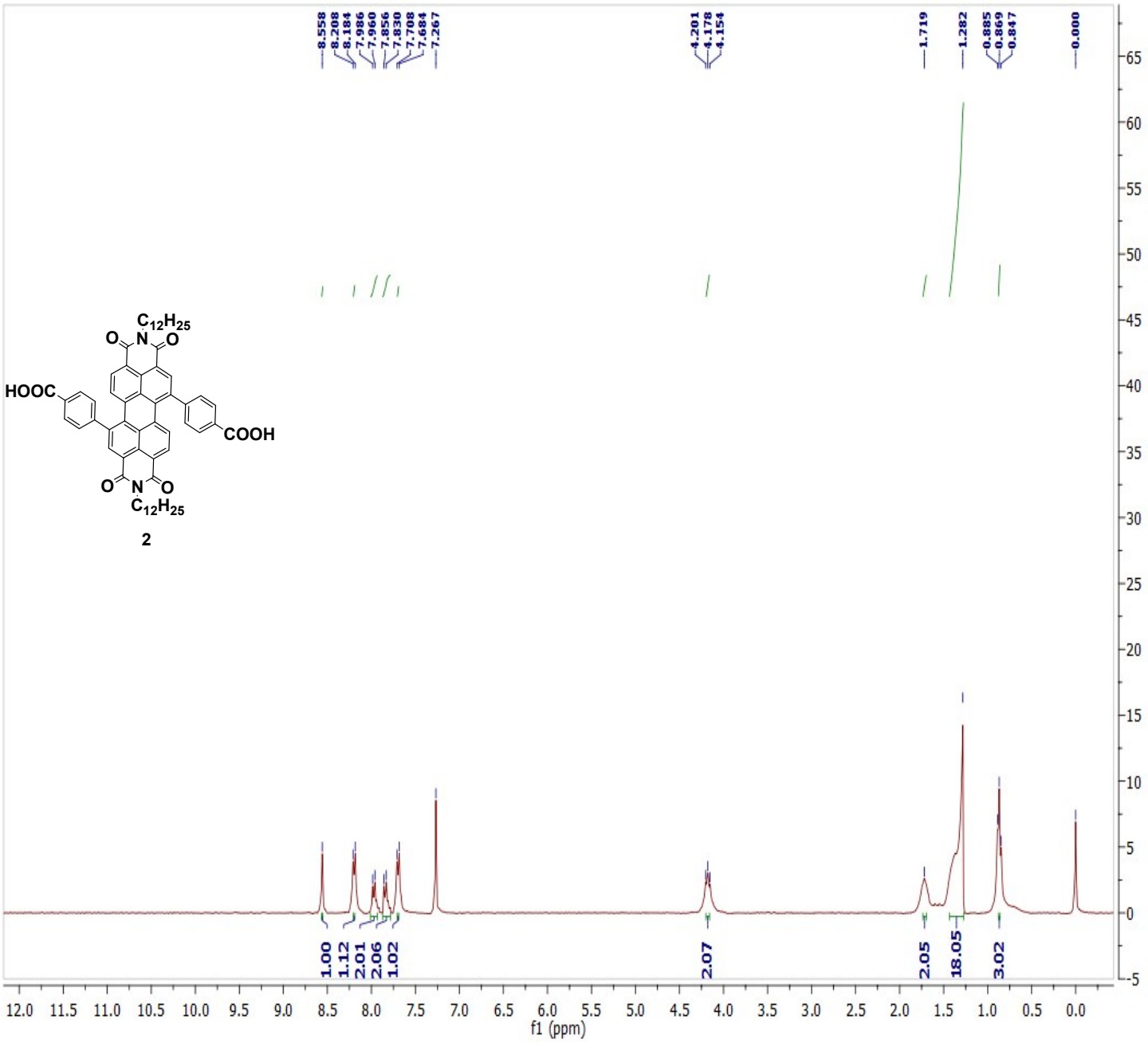

Fig.S29: The ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

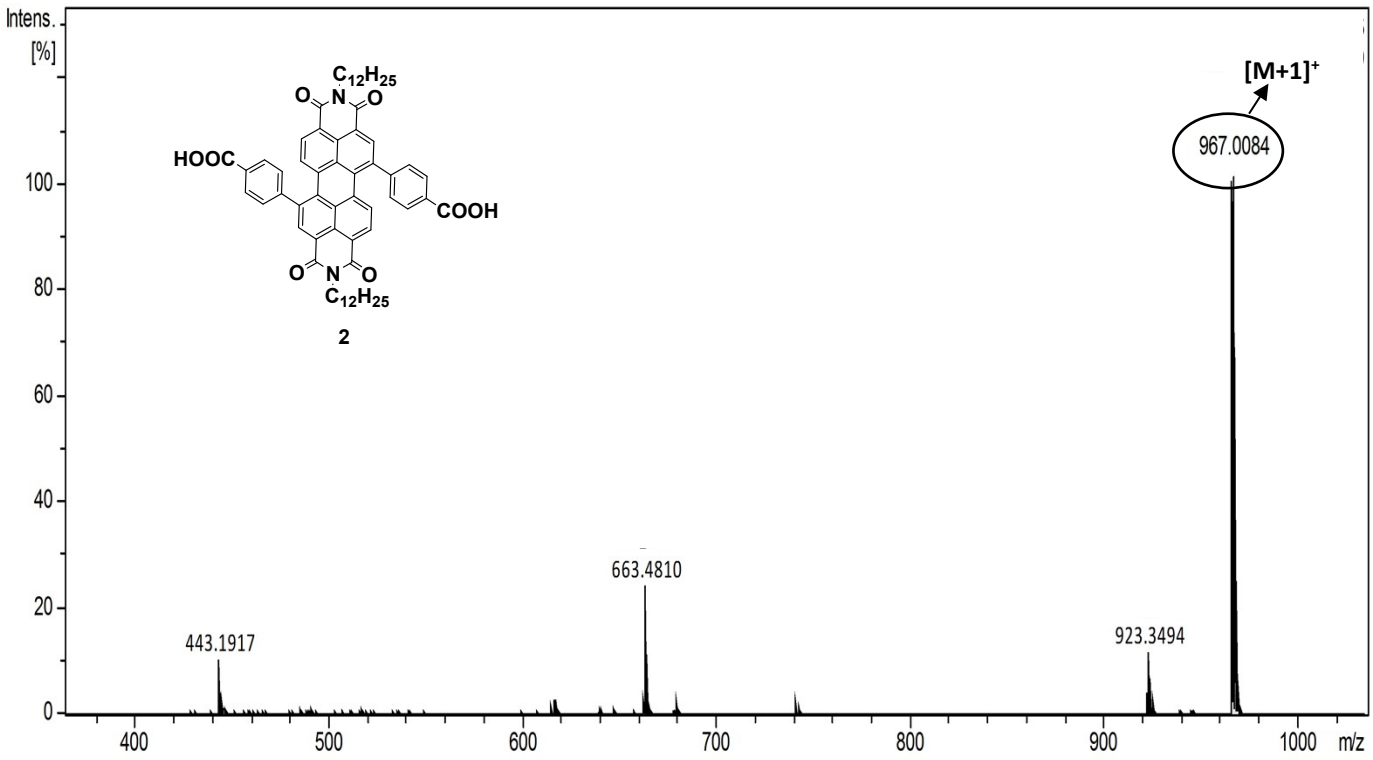

Fig.S30: The mass spectrum of compound **2** in $CDCl_3$.