Supplementary Information (SI) for Catalysis Science & Technology.

Electronic Supplementary Information

Minimizing Radiative and Nonradiative Energy Leakage in Red-Light Absorbing Supramolecular Nanoassemblies to Boost Oxidative Photocatalytic Activity in Water

Aditya Singh, Manoj Kumar and Vandana Bhalla*

Department of Chemistry, UGC Sponsored-Centre of Advance Studies-II, Guru Nanak Dev University, Amritsar–143005, Punjab, India

Email: vanmanan@yahoo.co.in

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GENERAL EXPERIMENTAL SECTION

Materials and Instrumentation: All the reagents were purchased from Sigma-Aldrich and were used as such without further purification. 1,2-Bis(4-((4-bromophenyl)(phenyl)amino)phenyl)ethane-1,2-dione (**1**) was prepared according to our previous literature.[1] THF was dried by the distillation over sodium using benzophenone as an indicator. The UV–vis and fluorescence studies were performed with HPLC grade solvents and double distilled water. The UV–vis studies were performed on SHIMADZU UV–2450 spectrophotometer, with a quartz cuvette (path length, 1 cm). The emission spectra were recorded on Horiba QM-8075-21-C instrument. The High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL JEM-2100 Plus microscope. The dynamic light scattering (DLS) data was recorded with MALVERN Instruments (Nano-ZS). High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) methods on a Waters mass spectrometer (XEVO G2-XS QTOF). Powder X-ray diffraction (PXRD) patterns were acquired on a Rigaku MiniFlex-II instrument in the 2θ range of 5−80°. FE-SEM measurements were performed on a ZEISS SUPRA 55. The electrochemical measurements were performed on room temperature using a computer controlled potentiostat/ galvanostat Autolab PGSTAT204 (Netherlands) Metrohm, equipped with FRA (frequency response analyzer) module. The NOVA software was used to collect, plot and analyze the raw data of CV measurement. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER-AVANCE-II FT-NMR-AL 500 MHz and JEOL 400 MHz spectrophotometer using $CDCl_3$, and DMSO-d_6 as solvent and tetramethylsilane ($SiMe_4$) as internal standards. Data are reported as follows: chemical shifts in ppm, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet), coupling constants *J* (Hz), integration and interpretation. Silica gel 60 (60–120 mesh) was used for column chromatography. EPR spectra was recorded at room temperature using a Bruker A300-9.5/12/S/W X-band spectrometer. **BrTPA-Py** nanoassemblies in H_2O: DMSO (99:1) with 2,2,6,6-tetramethylpiperidine (TEMP) were irradiated in an EPR tube using two 10 W red LEDs (TOORPE-10W, 630 nm, plant growth bulbs, Amazon India). The same LEDs were used for photocatalytic experiments.

Synthesis of BrTPA-Py

Compound **1** (0.50 g, 0.71 mmol) and 5,6-diaminopyrazine-2,3-dicarbonitrile (0.16 g, 0.99 mmol), a trace amount of *p*-toluenesulfonic acid, were dissolved in toluene (30 mL) in a 100 mL round bottom flask and the resulting reaction mixture was refluxed for 4 days. The reaction was then cooled to room temperature, and the solvent was removed under reduced pressure. The residue was dissolved with chloroform and thereafter extracted with chloroform (3 × 30 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and solvent was removed under reduced pressure. The crude product was purified by column chromatography using 8:92 (ethyl acetate: hexane) as an eluent to give compound **BrTPA-Py** as purple-black coloured solid (0.34 g, 58%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 7.61 (d, J = 8.8 Hz, 4H), 7.51 (d, J = 8.9 Hz, 4H), 7.38 (t, J = 7.8 Hz, 4H), 7.21 (t, J = 7.3 Hz, 2H), 7.14 (d, J = 7.7 Hz, 4H), 7.06 (d, J = 8.8 Hz, 4H), 6.91 (d, J = 9.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 161.0, 151.5, 145.8, 145.3, 144.0, 132.9, 132.3, 132.1, 130.0, 128.8, 127.6, 126.4, 125.7, 120.0, 118.0, 113.1. HRMS *m*/*z*: $[M+H]^+$ calcd for $C_{44}H_{26}Br_2N_8$, 827.0700; found, 827.0712.

GENERAL PROCEDURE FOR PHOTOCATALYTIC REACTIONS

General procedure for photocatalyzed oxidation of triaryl phosphines

In a 25 mL round bottom flask, the triaryl phosphines (**3a/3b/3c/3d/3e**) (100 mg, 1 equiv.), and 1 mol% photocatalyst (**BrTPA-Py**, dissolved in 150 μL of DMSO) were added followed by addition of 10 mL of H_2O to the reaction mixture. The reaction mixture was stirred at room temperature for 30 h under air and 2×10 W red LEDs irradiation. The LEDs were placed opposite each other, with the round bottom flask positioned between them at a distance of 3 cm. After the completion of the reaction (TLC), organic part was extracted with ethyl acetate (3× 10 mL). The combined organic layer was dried over anhydrous sodium sulphate and removed under reduced pressure to give a crude product. The crude products (**4a**-**4e**) were purified by column chromatography using ethyl acetate: hexane as an eluent. The product (**4a**) was characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and all other products (**4b**-**4e**) were characterized by ^{1}H and ^{13}C NMR spectroscopy (Pages S18-S23).

General procedure for photocatalyzed oxidative hydroxylation of arylboronic acids

In a 25 mL round bottom flask, the arylboronic acid(**5a/5b/5c/5d/5e/5f/5g/5h**) (100 mg, 1 equiv.) and DIPEA (10 equiv.) and 0.6 mol% photocatalysts (**BrTPA-Py**, dissolved in 100 μL of DMSO) were added followed by addition of 10 mL of H_2O to the reaction mixture. The reaction mixture was stirred at room temperature for 12 h under air and 2×10 W red LEDs irradiation. The LEDs were placed opposite each other, with the round bottom flask positioned between them at a distance of 3 cm. After the completion of the reaction (TLC), organic part was extracted with ethyl acetate (3× 10 mL). The combined organic layer was dried over anhydrous sodium sulphate and removed under reduced pressure to give a crude product. The crude products (**6a-6h**) were purified by column chromatography using ethyl acetate: hexane as an eluent. All the products were identified by ^{1}H and ^{13}C NMR spectroscopy (Pages S24-S31).

Table S1. Comparison of the photocatalytic activity of the **BrTPA-Py** nanoassemblies for photooxidation of triaryl phosphines over other photocatalytic systems reported in the literature.

S.No.	**Publication**	**Photocatalyst (loading)**	**Photocatalyst type**	**Solvent**	**Time**	**Light Source**	**Oxidant/ Temperature**
1.	**This report**	**BrTPA-Py Nanoassemblies (1 mol%)**	**Supramolecular assemblies**	H_2O	30 h	**2 ×10 W RED LEDs**	Air/RT
2.	*J. Colloid Interface Sci.*, 2024, **665**, 871–878	DPQ-TPA (1 mol%)	Supramolecular Photosensitizer	H_2O	30 h	Blue LEDs (450–455 nm)	Air/RT
3.	*ACS Sustainable Chem. Eng.*, 2024, **12**, 4236−4244	TPPB (4 mol%)	Cationic Macrocycle	H_2O	48 h	Blue LEDs (465–475 nm)	Air/RT
4.	*Chem Synth*, 2024**, 4**, 47 (https://dx.doi.org/10.20517/cs.2024.36)	2TPE-Py-I@CB[8] aqueous solution (1.0 mol%, 2.0 mL)	Supramolecular dimer	H_2O	24 h	Purple light (400 nm)	Air/RT
5.	*Org. Lett.*, 2023, **25**, 7984−7989	Butanone (1.0 mL)	Organic compound	Butanone (1.0 mL),	24 h	38 W white LEDs	Air/ 28 °C
6.	*Chem. Commun.*, 2022, **58**, 5001–5004	Dibenzo-fused 1,4-azaborine (DBAB) (1 mol%)	Organic photocatalyst	CH_2Cl_2	8 h	White LED	Air/RT
7.	*Tetrahedron Lett.*, 2018, **59**, 3880 –3883	4-phenylthioxanthone (5 mol%)	Synthetic Organic dye	MeOH or CH_2Cl_2: MeOH (1:5)	1-6 h	23W household lamp	Air/RT
8.	*RSC Adv.*, 2017, **7**, 13240–13243	Eosin Y (1 mol%)	Natural Organic dye	CH_2Cl_2: MeOH (5:1)	3.5 h	23W household lamp	Air/RT
9.	*J. Org. Chem.*, 2005, **70**, 1276-1280	Combination of Biphenyl (1.00×10^{-1} M), and 9,10-dicyanoanthracene (5.00×10^{-5} M) for (1.00×10^{-2} M of triaryl phosphines	Combination of organic photocatalyst and cosensitizer	MeCN	90 s	Xenon arc short lamp through a sharp-cut filter (irradiation at $\lambda >$ 390 nm).	Air/RT

Table S2. Comparison of the photocatalytic activity of the **BrTPA-Py** nanoassemblies in oxidative hydroxylation of arylboronic acids to other photocatalytic systems reported in the literature.

Sr. No.	**Publication**	**Photocatalyst (loading)**	**Solvent**	**Time**	**Light source**	**Base**	**Oxidant**
1.	**Present work**	**BrTPA-Py Nanoassemblies (0.6 mol%)**	10 ml of H_2O : DMSO (99: 1)	12 h	**2× 10 W Red LEDs**	DIPEA (10 equiv.)	Air
2.	*Green Chem.*, 2022, **24**, 9263–9268	**Chlorophyll (2.0 mol%)**	EtOH (2.0 mL)	20 h	**30 W red LEDs**	TEA (1 equiv.)	Air
3.	*J. Am. Chem. Soc.*, 2023, **145**, 4951-4956	Cy-N_3-COF (3.8 mol %),	ACN: H_2O (4:1)	6 h	Blue LED irradiation	DIPEA (5.0 equiv.)	O_2 (1 atm)
4.	*Chem. Mater.*, 2023, **35**, 2782−2789	Rhombic dodecahedra Cu_2O nanoacrystals (2.5 mg)	H_2O (3.0 mL)	12 h	Blue LED (20 W, 390 nm) at **30 ˚C**	DIPEA (2.0 equiv.)	Air
5.	*J. Org. Chem.*, 2023, **88**, 6489−6497	Linker-Assisted CdS-TiO_2 Nanohybrids CdS@MPA-TiO_2 (10 wt %),	H_2O (5.0 mL)	24 h	3 W blue LED (467 nm)	TEA (5 equiv.)	O_2 (saturated atmosphere),
6.	*Chem. Commun.*, 2023, **59**, 635–638	Conjugated microporous polymer PTPA-AQ (5 mg)	ACN (2 mL)	14–24 h	White LED (18 W)	TEA (1.5 equiv.)	O_2 (1 atm)
7.	*Chem. Commun.*, 2023, **59**,2239-2242	Cobaloxime based zirconium metal–organic framework (Zr-TCPCo) (3.0 mg)	DCE (2 mL)	12 h	450 nm LEDs irradiation	TEA (2 equiv.)	O_2 (1 atm)

8.	*ACS Appl. Mater. Interfaces,* 2023, **15**, 9412-9420	Boron Nitride Nanosheets BN−OH (20 mg)	H_2O_2 (100 μL), H_2O (5 mL), 50 °C.	30 min	–	–	–
9.	*ACS Appl. Nano Mater.*, 2023,**6**, 8396-8403	COF catalyst (5 mg)	ACN:H_2O (4:1)	6 h	20 W white LEDs	DIPEA (3.0 equiv.)	Air
10.	*Mater. Adv.*, 2022, **3**, 4699–4706	BTT-BTDDA-COF (2 mg)	ACN (3 ml)	12-26 h	Blue LED (36 W)	TEA (3 equiv.)	Air
11.	*Chem. Sci.*, 2023, **14**, 4532-4537	Cu^{2+}-seamed coordination nanocapsule (10 mg)	H_2O (3.0 mL)	5 h	300 W xenon lamp with visible light ($\lambda >$ 420 nm, 100 mW/cm2),	TEA (2 equiv.)	O_2 (1 atm)
12.	*J. Mater. Chem. A,* 2022, **10**, 7165–7172.	MeO-TBT-COF (5 mg)	ACN:H_2O (4:1)	12 h	20 W white LEDs	DIPEA (3 equiv.)	Air
13.	*Chem. Eur. J.,* 2022, **28**, e202202200	Supramolecular organic framework TM-SOF (0.125 mol%)	D_2O	2.5-6 h	450 nm light	TEOA (2.5 equiv.)	Air
14.	*Angew. Chem.*, 2021, **133**, 9470 –9474	Supramolecular dimer 2MPT-CB[8] (1 mol%)	D_2O	3 h	405 nm Xenon lamp (20 mW/cm^2)	. TEOA (10 equiv).	O_2 (1 atm)
15.	*Asian J. Org. Chem.*, 2021, **10**, 2596-2602	Assemblies of PBI-TPY (0.1 mol%)	ACN:H_2O (7:3)	24 h	Tungsten filament lamp (100W)	TEA (1.5 equiv.)	Air
16.	*Eur. J. Org. Chem.*, 2021, **29**, 3986–3991	COF-JLU25 (5.0 mg)	ACN:D_2O (4: 1)	12-96 h	20 W white LEDs	DIPEA (5 equiv.)	Air
17.	*J. Am. Chem. Soc.*, 2020, **142**, 20763−20771	Porphyrinic COF catalyst (DhaTph-Ni)	ACN	1.5 – 2.5 h	300 W Xe Lamp with visible light ($\lambda >$ 400 nm),	50 µL of TEA	O_2 (1 atm)

18.	*ACS Sustainable Chem. Eng.*, 2020, **8**, 13894-13899	Aminoquinolate Diarylboron (1 mol%)	H_2O	36 h	10W white LED	DIPEA (3.5 equiv.)	Air
19.	*ACS Sustainable Chem. Eng.*, 2020, **8**, 2682-2687	Cu@C_3N_4 (10 mg)	H_2O	6-8 h	Blue LED (460 nm)	NaOH (1 equiv.)	Air
20.	*J. Org. Chem.*, 2020, **85**, 2040−2047	$Rh_2(OAc)_4$ (2 mol%), bpy (4 mol%)	DMF	36 h	10.5 W white LED.	DIPEA (2.0 equiv.)	O_2 (1 atm)
21.	*Macromolecules*, 2019, **52**, 7977−7983	BBO-COF (5 mol%)	ACN:H_2O (4:1)	28-96	18 W white LED	DIPEA (5.0 mmol),	Air
22.	*Adv. Synth. Catal.*, 2019, **361**, 961-964	Phthalocyanine Zinc (0.5 mol%)	THF	1.5-3	Filament lamp (100 W)	DMFU (2 equiv.)	O_2 (1 atm)
23.	*Green Chem.*, 2019, **21**, 4971-4975	-	2-MeTHF	24	UV-Light source (15 W)	TEA (1.5 eqiv.)	O_2 (1 atm)
24.	*Tetrahedron Lett.*, 2019, **60**, 660-663	Thioxanthone derivative (0.5 mol%)	Dimethyl carbonate	12	Purple LED	DIPEA (2 equiv.)	Air (1 atm.)
25.	*J. Am. Chem. Soc.*, 2018, **140**, 4623-4631	LZU-190 (0.075 mol%)	ACN:H_2O (4:1)	48	20 W white LED	DIPEA (5 equiv.)	Air
26.	*Adv. Synth. Catal.*, 2018, **360**, 2013-2019	C_{70}-fullerene (0.05 mol%)	$CHCl_3$ (0.05M)	12	6 W blue LED	DIPEA (2 equiv.)	O_2
27.	*Synlett*., 2018, **29**, 1324-1328	2,2-dimethoxy-2-phenyl acetophenone (20 mol%)	H_2O	72	2 x 80 W lamps	DIPEA (7.5 equiv.)	O_2
28.	*J. Org. Chem.*, 2017, **82**, 5236-5241	N-substituted 3(10H)-Acridones (1 mol%)	H_2O	36	6 W blue LED	DIPEA (5 equiv.)	O_2
29.	*Polymer*, 2017, **126**, 291-295	Porus conjugated polymer (10 mg)	ACN	20-24	White LED lamp(1.2 W/cm^2)	TEA (3 equiv.)	1 atm. O_2

RESULTS AND DISCUSSION

Table S3. The PXRD Peak Assignments and Interpretation for pristine solid sample of BrTPA-Py

The diffraction peaks corresponding to 2θ value of 27° (d ≈ 3.3 Å) and 39.60° (d = 2.27 Å) in PXRD spectra of pristine solid sample of **BrTPA-Py** corresponds to π···π stacking interactions between aromatic rings and indicate presence of short-range aromatic interactions. The peak around 17° (d = 4.97 Å) is most likely associated with long-range molecular packing interactions or weaker halogen-bonding effects whereas the peaks at 9.41° (d ≈ 9.4 Å) and 13.87° (d = 6.38 Å) corresponds to long-range packing or layered arrangements stabilized by van der Waals forces and weaker supramolecular interactions and peak at 57.34° (d = 1.61 Å) represent higher-order reflections or substructures within the crystalline lattice. Together, these noncovalent interactions-especially Type II halogen bonding (Br···Br) and π···π stacking-play a pivotal role in maintaining the material's crystallinity.

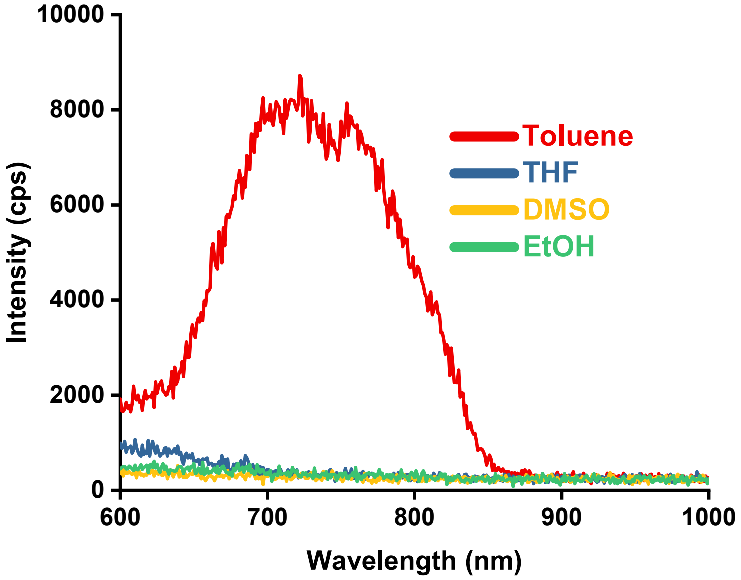


Fig. S1 Fluorescence spectra of **BrTPA-Py** (10 μM) in different solvents. (λ_{ex} = 584 nm (toluene), 565 nm (THF), 568 nm (DMSO, and EtOH), slit width = 3 nm for each).

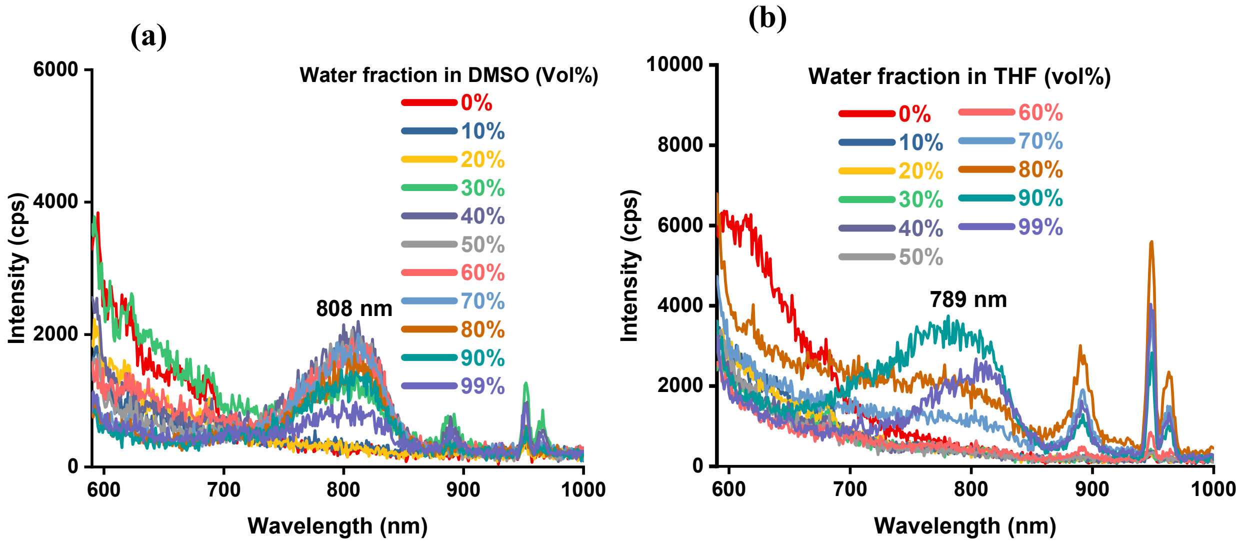


Fig. S2 The fluorescence spectra of **BrTPA-Py** (10 µM) in **(a)** DMSO and **(b)** THF solutions with increasing water fractions. λ_{ex} = 568 nm (DMSO) and 565 nm (THF). **Slit width = 5 nm for each measurement.**

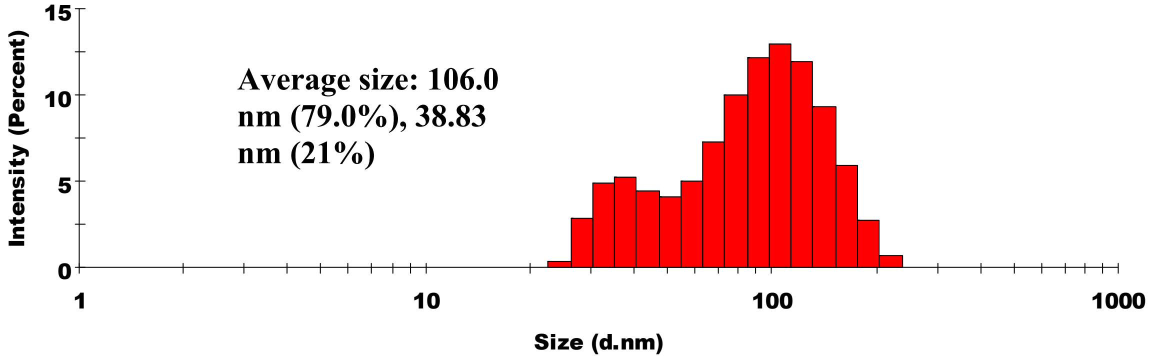


Fig. S3 The DLS studies of **BrTPA–Py** nanoassemblies in H_2O: DMSO (99:1) solvent mixture showing particles size.

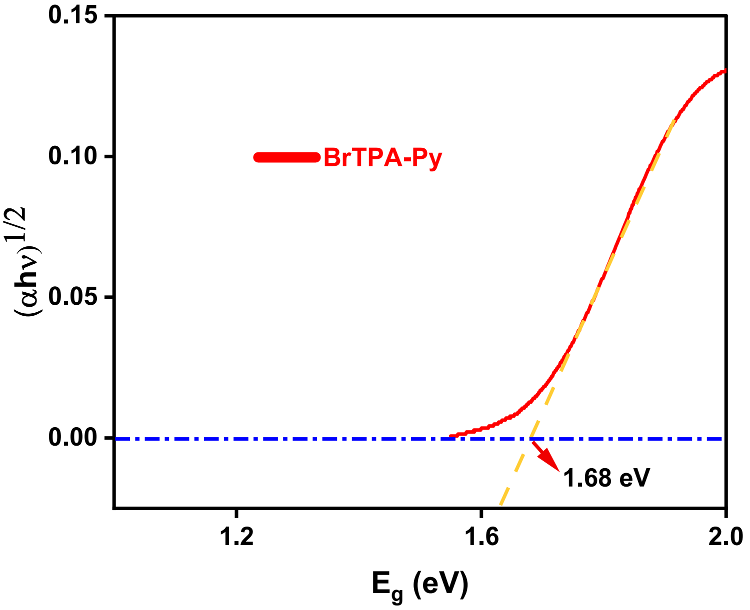


Fig. S4 The Tauc plot for **BrTPA-Py** in DCM.

Determination of Electron Transportation ability.[2] Methyl viologen (MV^{2+}) and triethanolamine (TEOA) were selected as the electron acceptor and sacrificial donor materials, respectively. Upon addition of TEOA (30 mM) to the **BrTPA-Py** nanoassemblies in H_2O: DMSO (99:1) and H_2O: THF (99:1) solvent mixture, a decrease in the intensity of the absorption band was observed. This observation suggests the existence of strong interactions between a sacrificial donor and supramolecular assemblies. Thereafter, we added MV^{2+} (0.1 mM) to the solution and exposed it to the light irradiation of 2× 10 W Red LEDs (placed opposite to each other at a distance of 3 cm from the vial) under an inert atmosphere. The colour of the solution changed to dark blue depending upon potential of nanoassemblies to transport the electrons. The absorption spectrum of the solution in the presence of methyl viologen showed the formation of two new bands at 395 nm and 605 nm, respectively. These two bands are due to the presence of reduced cationic species $MV^{\cdot+}$ of methyl viologen. The intensity of both bands gradually increased upon exposure to light irradiation of 2× 10 W Red LEDs. These observations led us to propose that assemblies of **BrTPA-Py** are reductively quenched by a sacrificial donor to generate radical anion (ex. **BrTPA-Py**$^{*-}$) which in turn transports electron to MV^{2+} and reduce it via single electron transfer (SET).

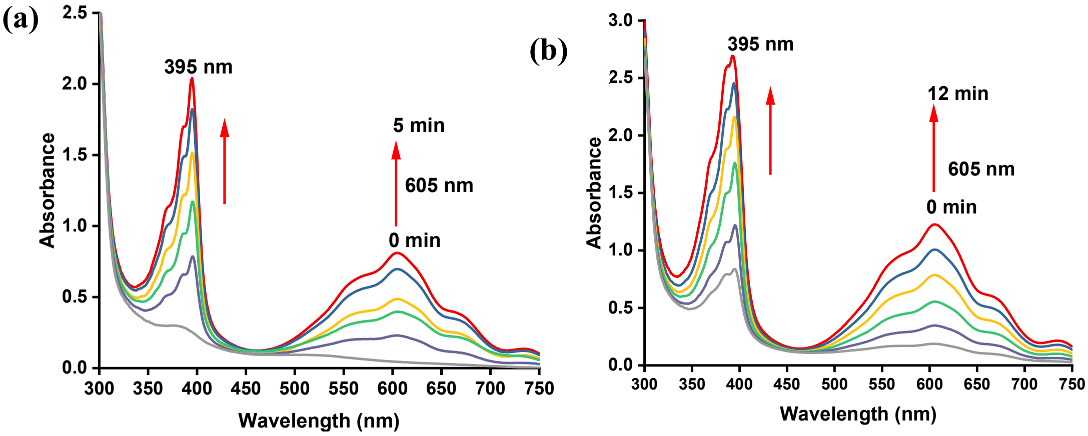
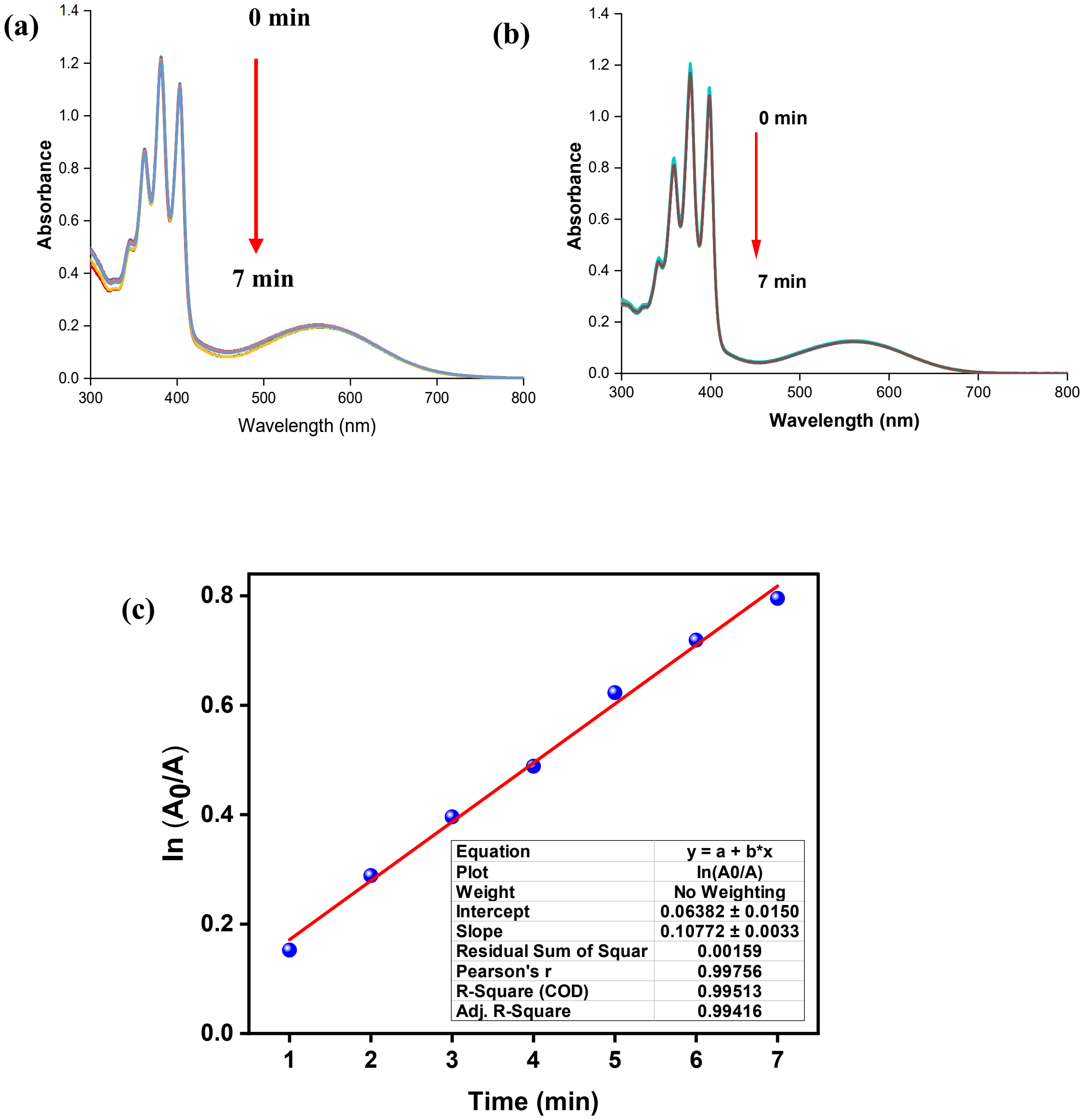


Fig. S5 The absorption spectral changes of **BrTPA-Py** nanoassemblies (10 μM) in the presence of MV^{2+} (0.1 mM) and TEOA (30 mM) in **(a)** H_2O:DMSO (99:1) solvent mixture, and **(b)** H_2O:THF (99:1) solvent mixture under light irradiation of 2×10 W red LEDs and inert atmosphere.

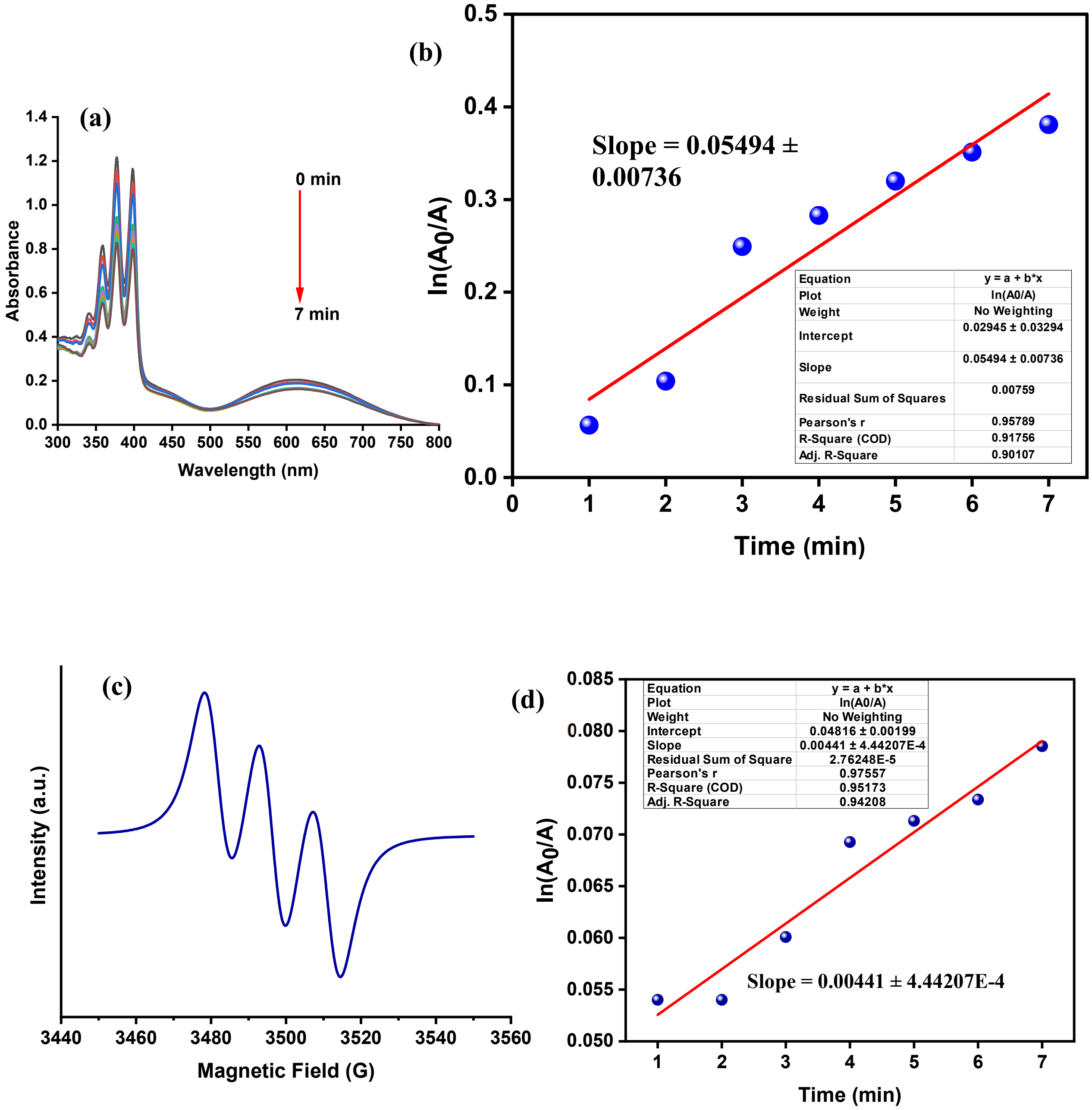
Detection of singlet oxygen ($^1O_2$) in solution[3]

The singlet oxygen generation by **BrTPA-Py** nanoassemblies was determined by UV-vis spectroscopy and 9,10 anthracenediylbis(methylene)dimalonic acid (ABDA) as indicator. The stock solutions of ABDA (in DMSO/ THF) and nanoassemblies (in DMSO /THF) were used for measurement. The absorbance of photosensitizing **BrTPA-Py** nanoassemblies (10 μM) was firstly set as blank and then, 100 μM of ABDA was added to it in dark, and the absorbance of the sample was measured at once. After that, the solution was exposed to light irradiation of 2×10 W red LEDs (placed opposite to each other at a distance of 3 cm from the vial) for 0 to 7 min. The singlet oxygen generation was monitored by measuring the decay of absorbance of ABDA at 398 nm at different irradiation time from the plot between $\ln(A_0/A)$ *vs.* light irradiation time, where A_0 is the initial absorbance at 398 nm, while A represents the final absorbance at 398 nm after 2×10 W red LEDs irradiation.



Equation	y = a + b*x
Plot	ln(A0/A)
Weight	No Weighting
Intercept	0.06382 ± 0.0150
Slope	0.10772 ± 0.0033
Residual Sum of Squar	0.00159
Pearson's r	0.99756
R-Square (COD)	0.99513
Adj. R-Square	0.99416

Fig. S6 The UV–vis spectra of ABDA (100 µM) in the presence of **BrTPA–Py** (10 µM) in **(a)** DMSO, and **(b)** in THF under 2×10 W red LEDs irradiation. **(c)** The decomposition rate constant of ABDA by **BrTPA–Py** nanoassemblies (10 µM) in H_2O: DMSO (99:1) solvent mixture under 2×10 W red LEDs irradiation.



Equation	y = a + b*x
Plot	ln(A0/A)
Weight	No Weighting
Intercept	0.02945 ± 0.03294
Slope	0.05494 ± 0.00736
Residual Sum of Squares	0.00759
Pearson's r	0.95789
R-Square (COD)	0.91756
Adj. R-Square	0.90107

Equation	y = a + b*x
Plot	ln(A0/A)
Weight	No Weighting
Intercept	0.04816 ± 0.00199
Slope	0.00441 ± 4.44207E-4
Residual Sum of Square	2.76248E-5
Pearson's r	0.97557
R-Square (COD)	0.95173
Adj. R-Square	0.94208

Fig. S7 **(a)** The UV–vis spectra of ABDA (100 µM) in the presence of **BrTPA–Py** nanoassemblies (10 µM) in H_2O: THF (99:1) under 2×10 W red LEDs irradiation. The decomposition rate constant of ABDA by **(b)** **BrTPA–Py** nanoassemblies (10 µM) in H_2O: THF (99:1) solvent mixture and **(d)** **RB** (10 µM) in H_2O: DMSO (99:1) solvent mixture under 2×10 W red LEDs irradiation. **(c)** EPR spectra showing singlet oxygen generation by **BrTPA-Py** nanoassemblies in H_2O: DMSO (99:1) under irradiation with two 10 W red LEDs, with TEMP acting as a spin-trapping agent (unprocessed raw data).

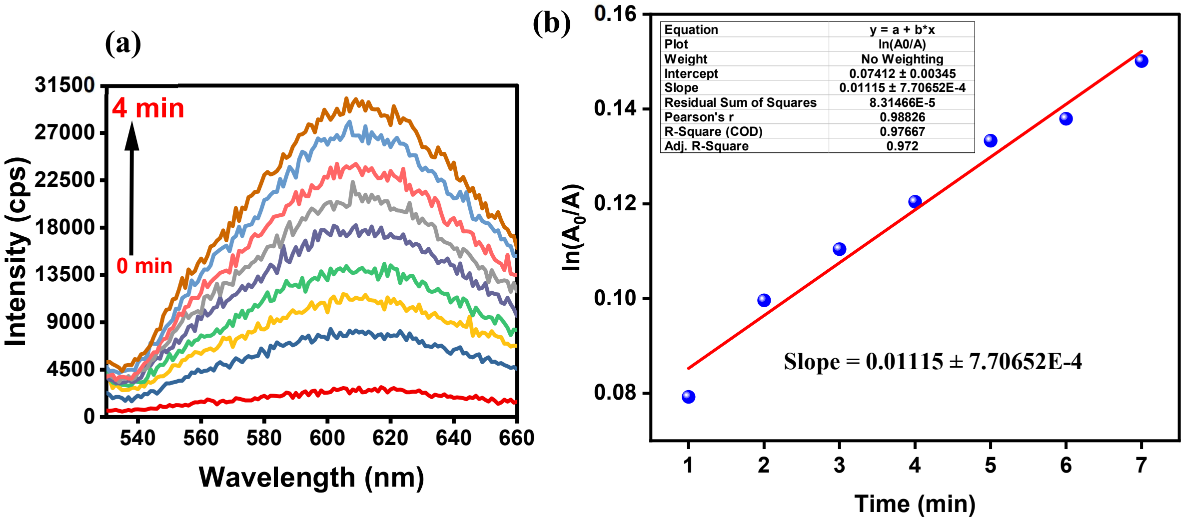


Fig. S8 **(a)** Fluorescence spectra of DHE (50 µM; excitation at 510 nm, emission range 530–660 nm) in the presence of **BrTPA-Py** nanoassemblies (10 µM) in H_2O: DMSO (99:1), recorded from 0 to 4 min of red-light exposure using 2 × 10 W LEDs at 30 s irradiation intervals. **(b)** The decomposition rate constant of ABDA by **TPA–Br** nanoassemblies (10 µM) in H_2O: DMSO (99:1) solvent mixture under 2×10 W red LEDs irradiation.

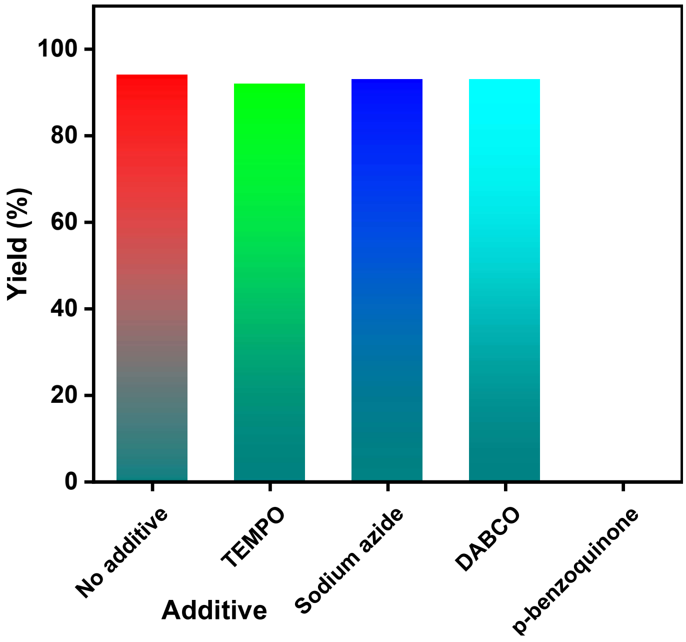


Fig. S9 Controlled experiments in **BrTPA-Py** nanoassemblies catalyzed oxidative hydroxylation of arylboronic acids under optimized reaction conditions in the presence of various quenching agent (1 equiv).

CHARACTERIZATION OF THE PHOTOCATALYSIS PRODUCTS

(A) BrTPA-Py nanoassemblies catalysed oxidation of triaryl phosphines under RED LEDs irradiation

Triphenylphosphine oxide (4a):[4, 5] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.69 – 7.64 (m, 6H), 7.56-7.51 (m, 3H), 7.47-7.43 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 133.2, 132.3, 132.2, 132.1, 132.0, 128.7, 128.6. ^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) = 29.7.

Tris(4-methoxyphenyl)phosphine oxide (4b):[4, 5] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.53 – 7.49 (m, 6H), 6.89 (dd, J = 8.9, 2.3 Hz, 6H), 3.76 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 162.4, 162.3, 133.9, 133.8, 124.7, 123.9, 114.1, 114.0, 55.3.

Tris(4-methylphenyl)phosphine oxide (4c): [4, 5] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.49 (dd, J = 11.9, 7.7 Hz, 6H), 7.17 (d, J = 8.9 Hz, 6H), 2.30 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 142.1 (d, J_{PC}= 2.8 Hz), 132.0, 131.9, 130.0, 129.1, 129.0, 21.5.

Tris(4-fluorophenyl)phosphine oxide (4d[4, 5] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.65 – 7.60 (m, 6H), 7.18 – 7.14 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.4 (d, J = 3.1 Hz), 164.4 (d, J = 3.3 Hz), 134.6 (dd, J = 11.5, 8.8 Hz), 128.6 (d, J = 3.5 Hz), 127.7 (d, J = 3.4 Hz), 116.3 (dd, J = 21.5, 13.3 Hz).

Tris(2-methylphenyl)phosphine oxide (4e): [4, 5] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.41 (t, J = 7.4 Hz, 3H), 7.30 (dd, J = 7.6, 4.0 Hz, 3H), 7.15 – 7.08 (m, 6H), 2.50 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 143.4, 132.9, 132.8, 132.1, 132.0, 131.9 (d, J = 2.7 Hz), 131.0, 130.2, 125.6, 125.5, 22.0 (d, J = 4.0 Hz).

(B) BrTPA-Py nanoassemblies catalysed oxidative hydroxylation of arylboronic acids under RED LEDs irradiation

4-Cyanophenol (6a):[6] ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 7.54 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) = 160.2, 134.5, 119.4, 116.6, 103.6.

4-Nitrophenol (6b):[7] ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 8.17 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 9.2 Hz, 2H), 6.16 (s, 1H). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) = 161.7, 141.8, 126.5, 115.9.

4-Fluorophenol (6c):[6] ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 6.92 (t, J = 8.7 Hz, 2H), 6.78 – 6.76 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) = 158.4, 156.5, 151.8 (d, J = 2.3 Hz), 116.5, 116.4, 116.2, 116.0.

4-Chlorophenol (6d):[6] ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 7.18 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) = 154.3, 129.7, 125.8, 116.8.

4-Acetylphenol (6e):[8] ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 7.90 (d, J = 8.7 Hz, 2H), 7.02 (s, 1H), 6.91 (d, J = 8.7 Hz, 2H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) = 198.5, 161.4, 131.3, 129.9, 115.7, 26.4.

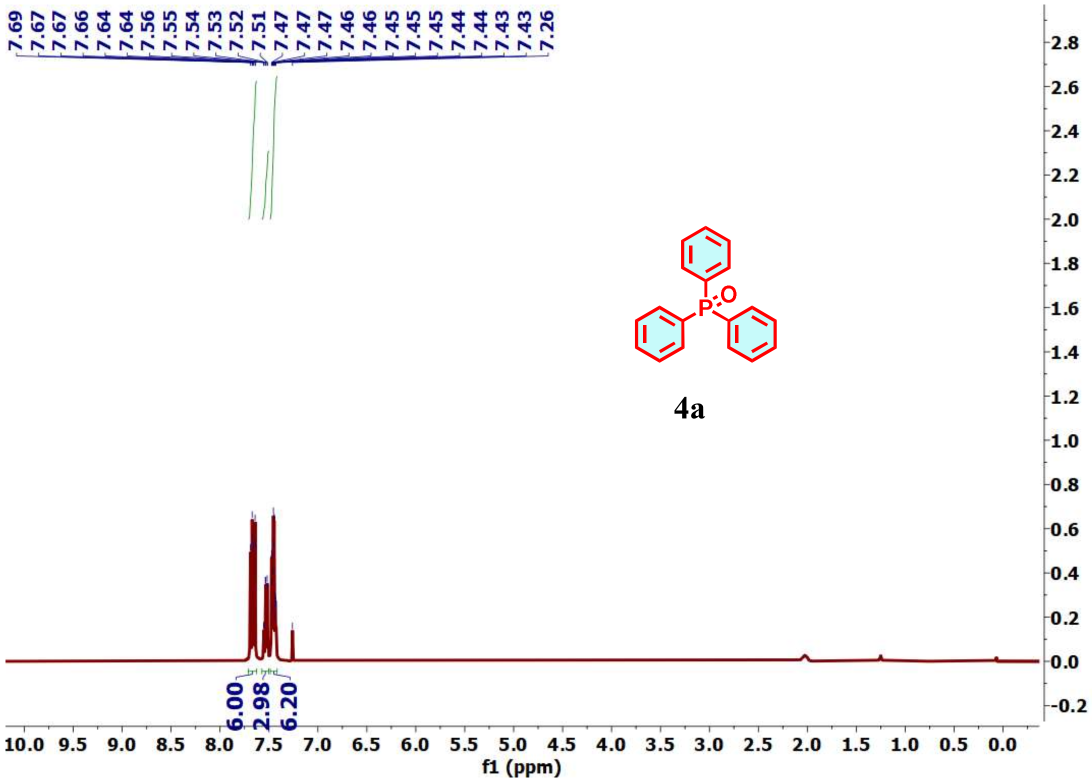
4-Hydroxybenzaldehyde (6f):[6, 8] ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 9.86 (s, 1H), 7.82 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 6.47 (s, 1H). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) = 191.5, 162.0, 132.7, 130.0, 116.2.

Phenol (6g):[8, 9] ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 7.23 – 7.20 (m, 2H), 6.91 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 8.1 Hz, 2H). ^{13}C NMR (15 MHz, CDCl$_3$): δ (ppm) = 155.6, 129.8, 120.9, 115.5.

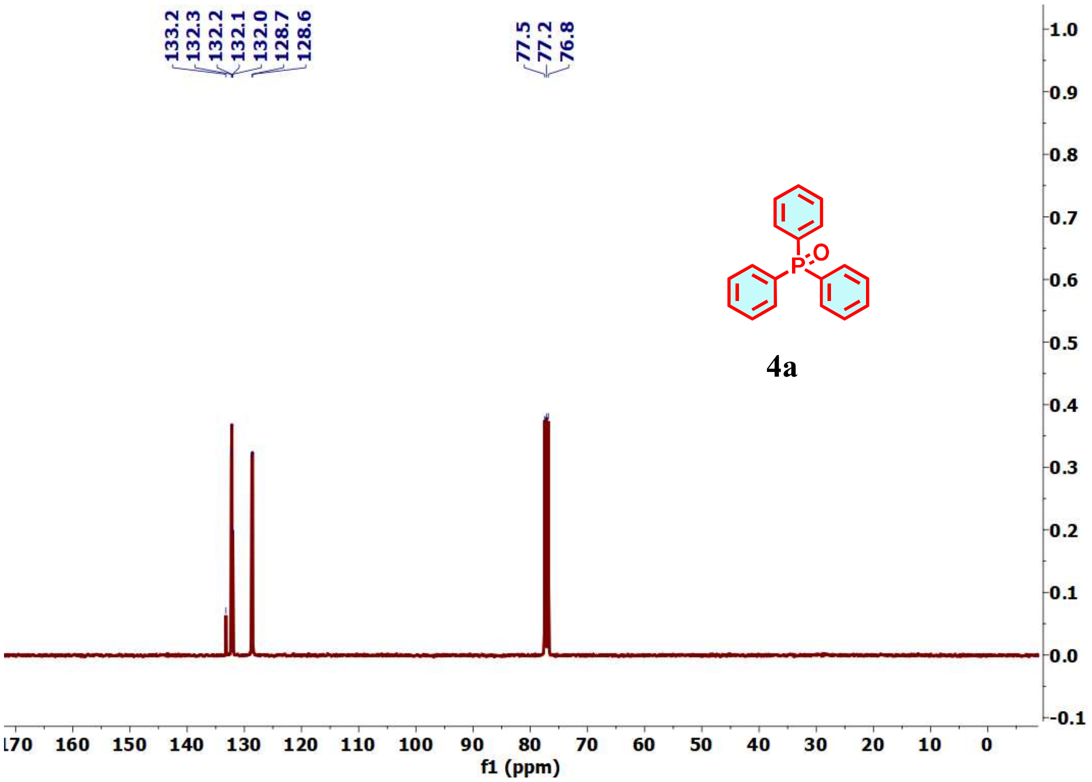
4-(*tert*-butyl)phenol (6h):[6] ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 7.26 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 4.92 (s, 1H), 1.29 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) = 153.4, 143.7, 126.6, 115.0, 34.2, 31.7.

NMR SPECTRA OF THE PHOTOCATALYSIS PRODUCTS

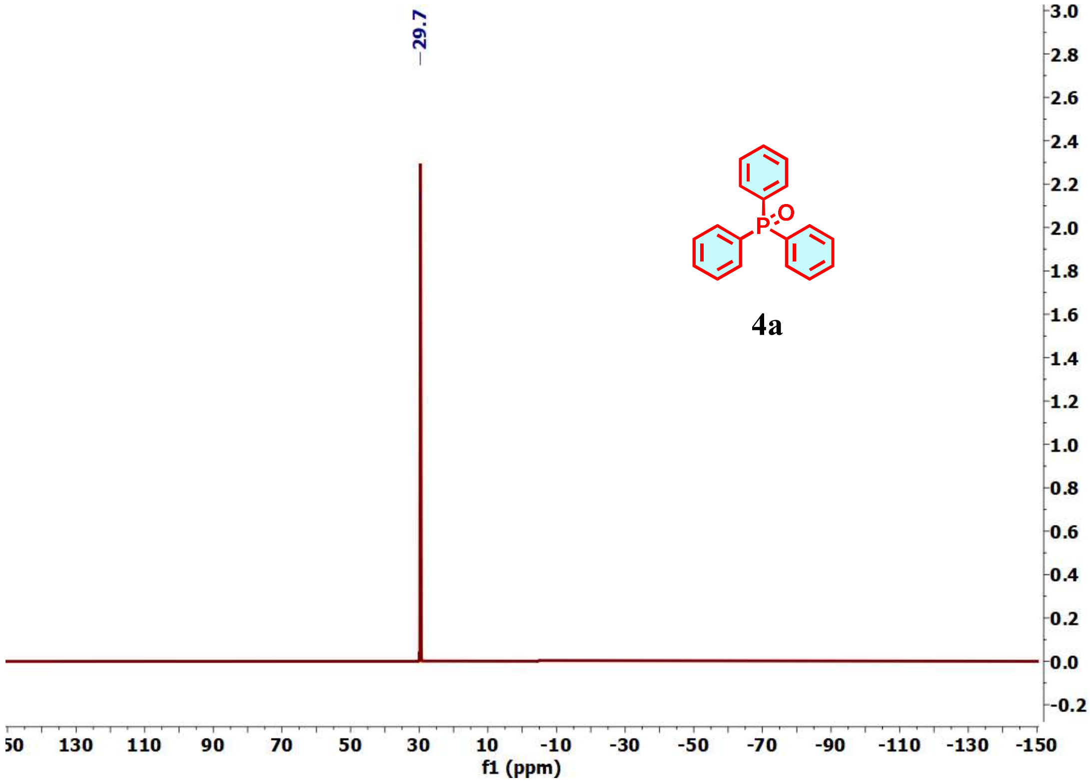
^{1}H NMR (400 MHz, CDCl3) of compound **4a**



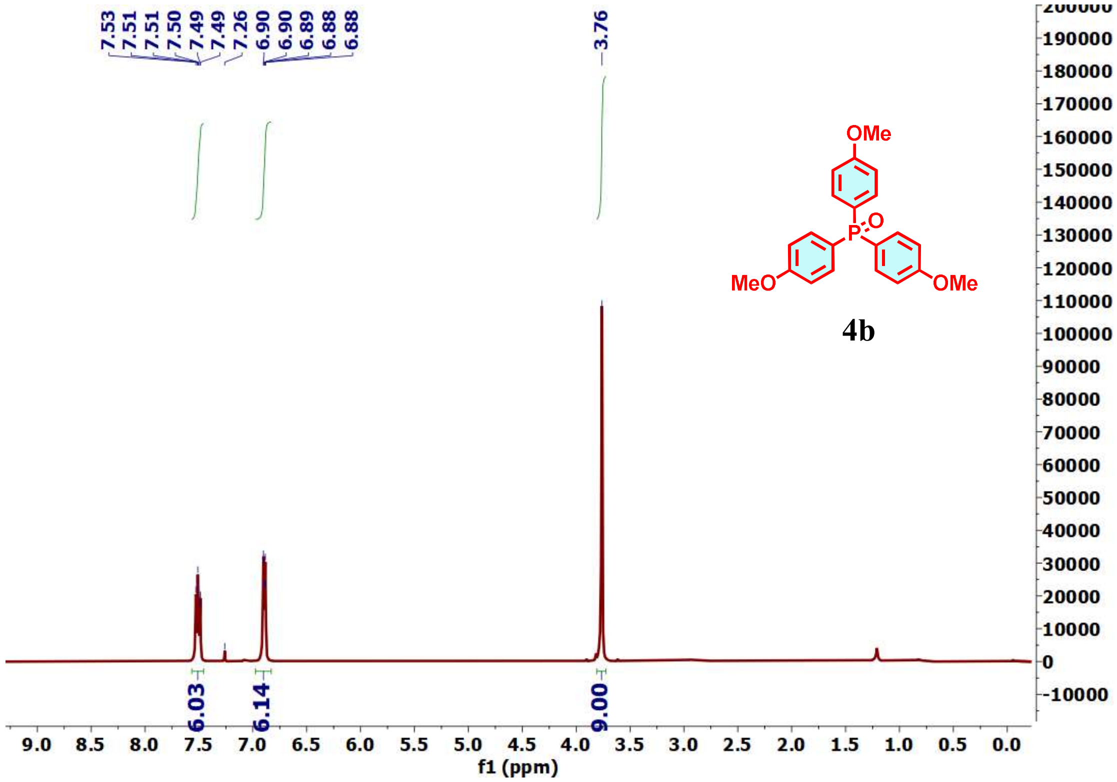
^{13}C NMR (100 MHz, CDCl$_3$) of compound **4a**



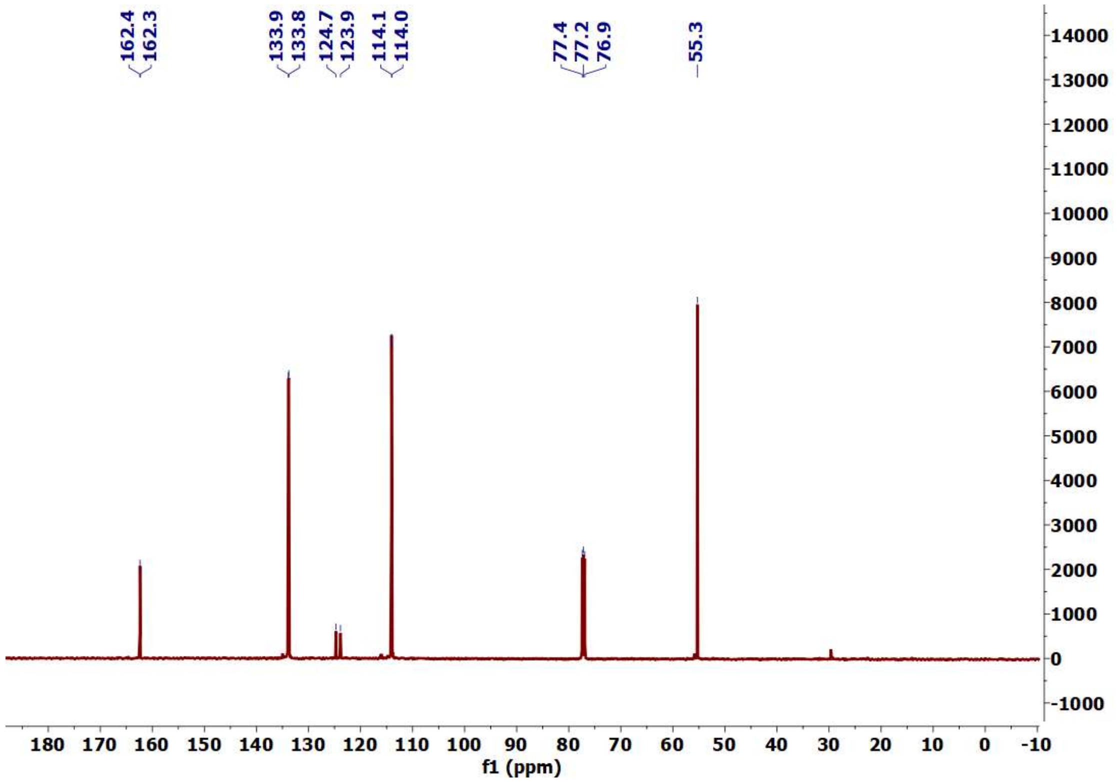
^{31}P NMR (202 MHz, CDCl$_3$) of compound **4a**



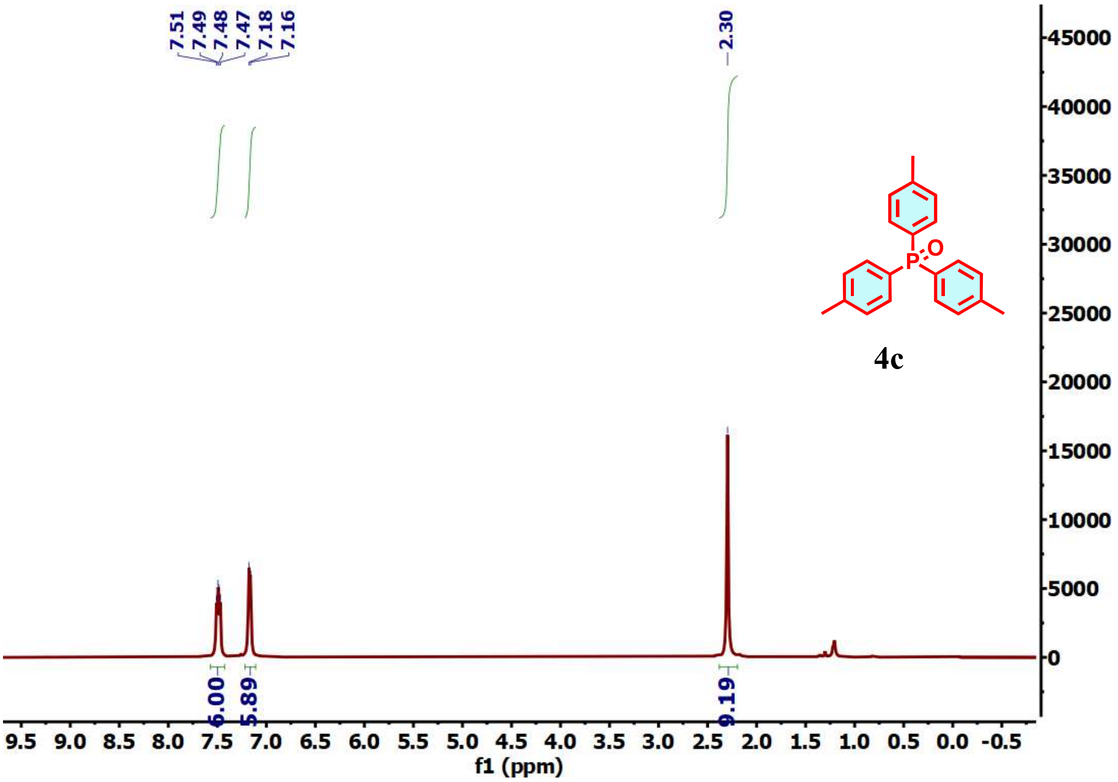
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4b**



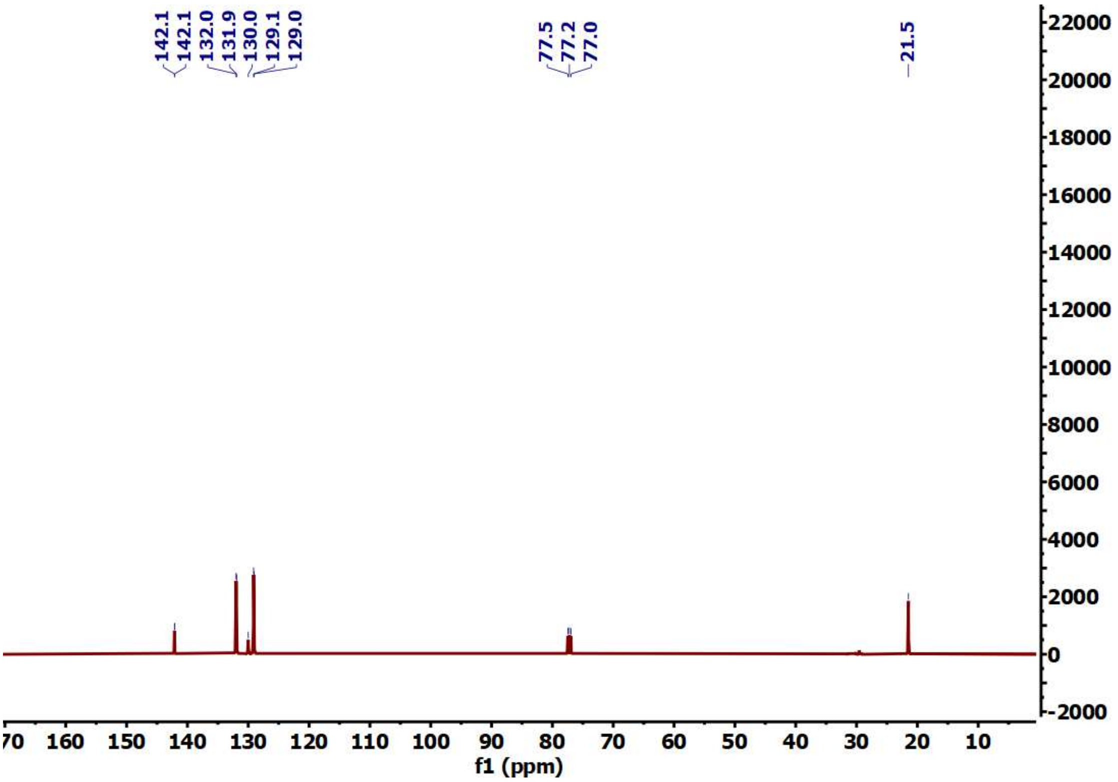
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4b**



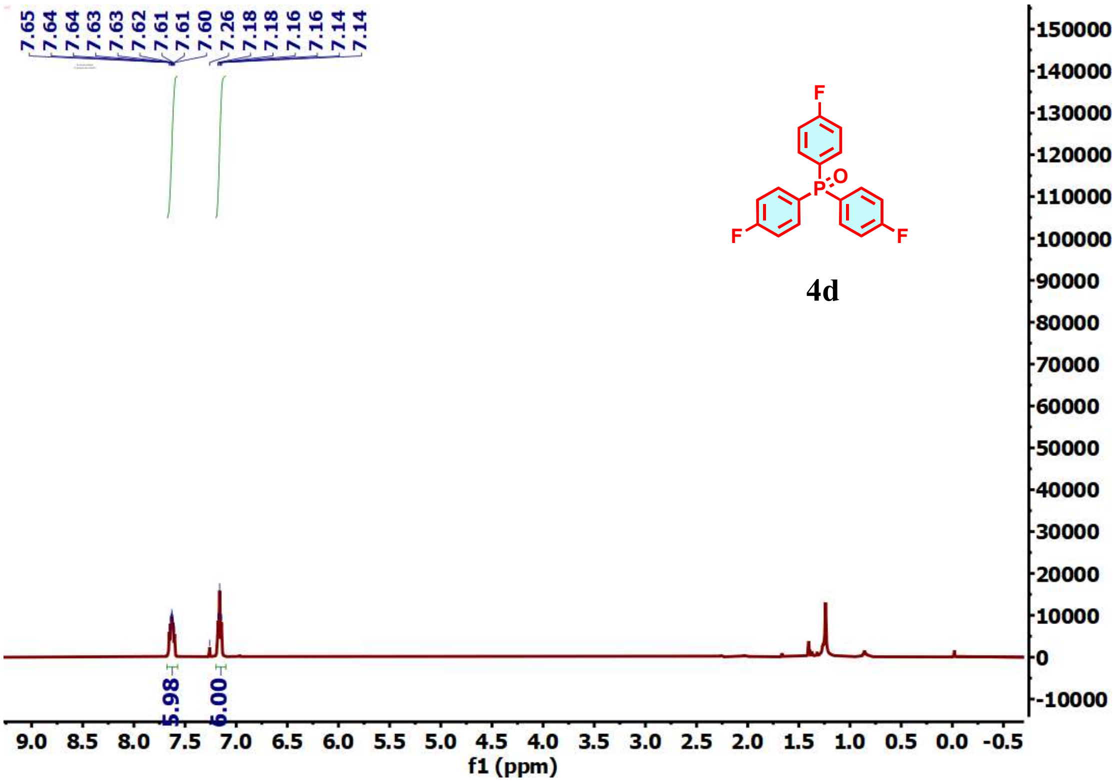
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4c**



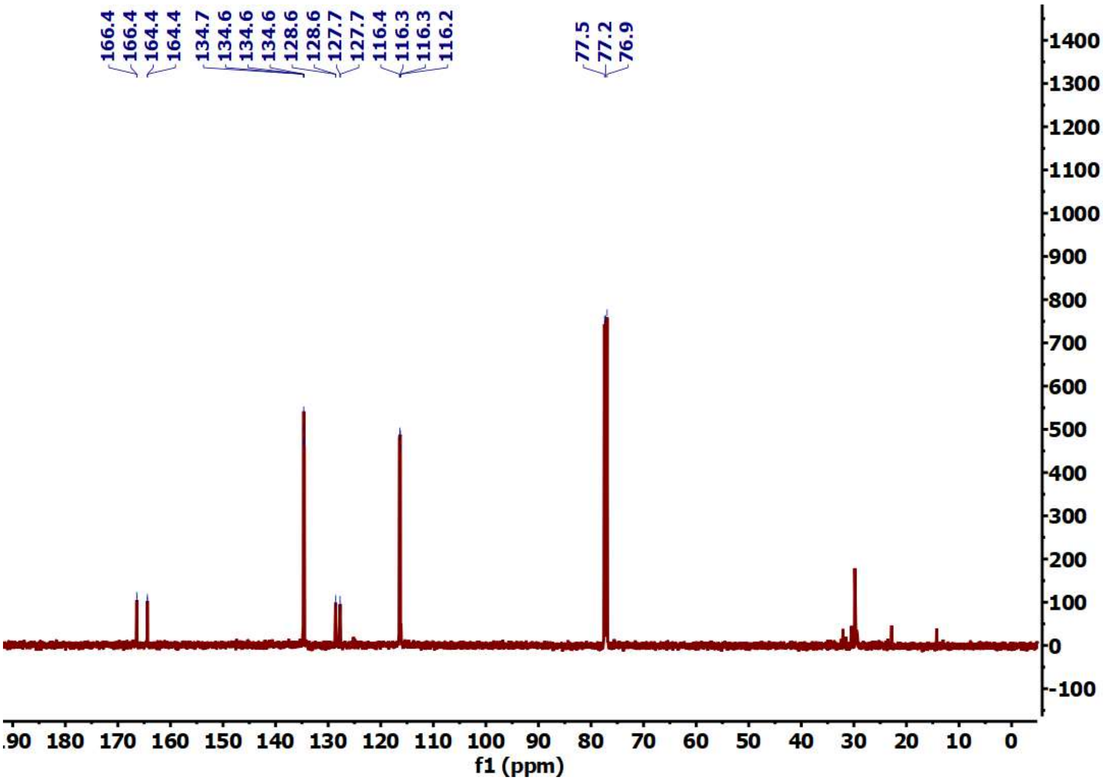
^{13}C NMR (125 MHz, CDCl$_3$) of compound **4c**



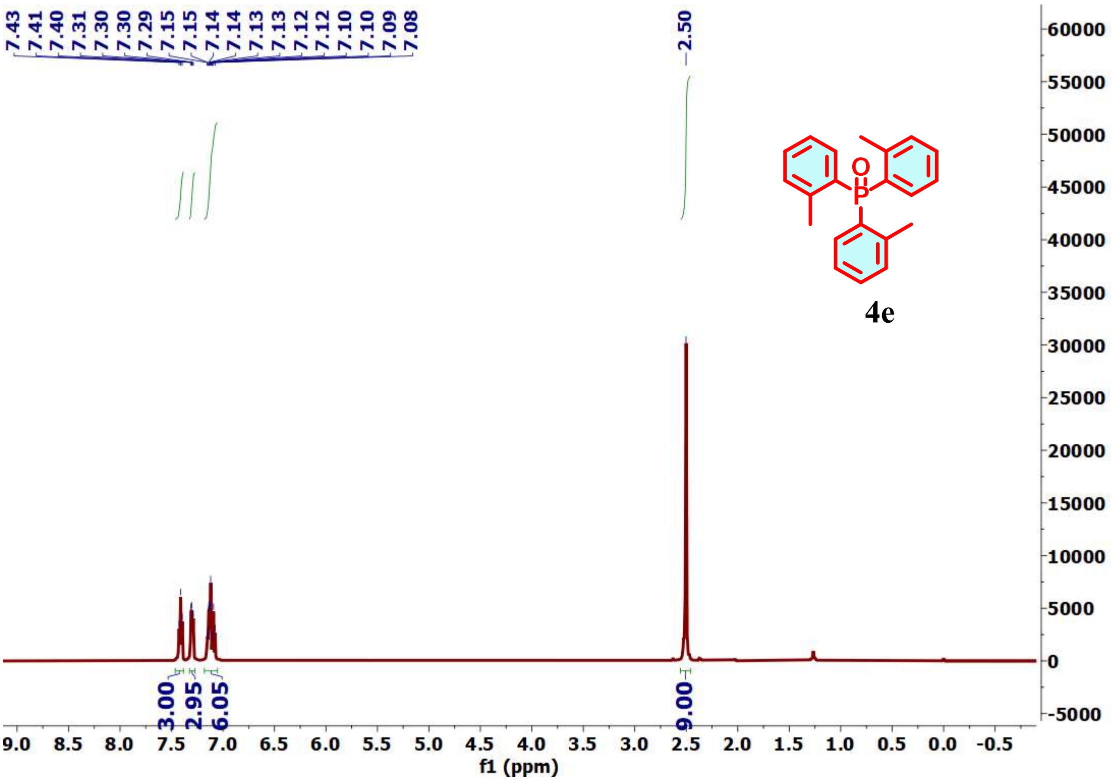
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4d**



^{13}C NMR (125 MHz, CDCl$_3$) of compound **4d**

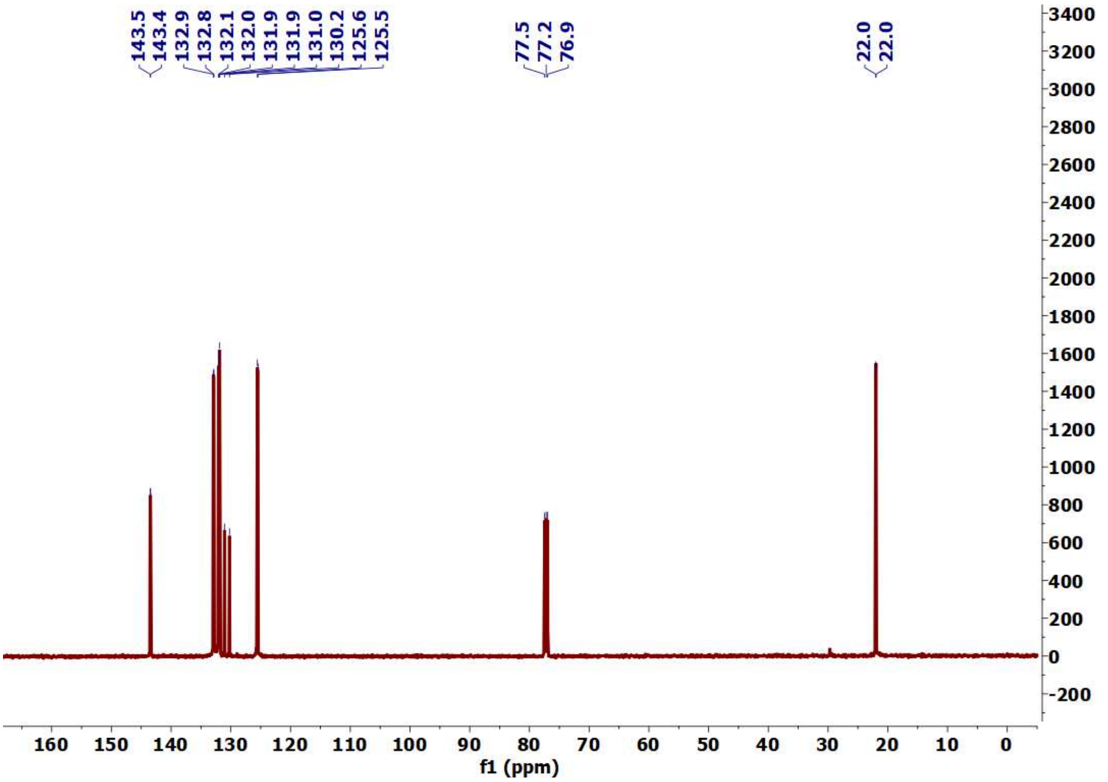


^{1}H NMR (500 MHz, CDCl$_3$) of compound **4e**

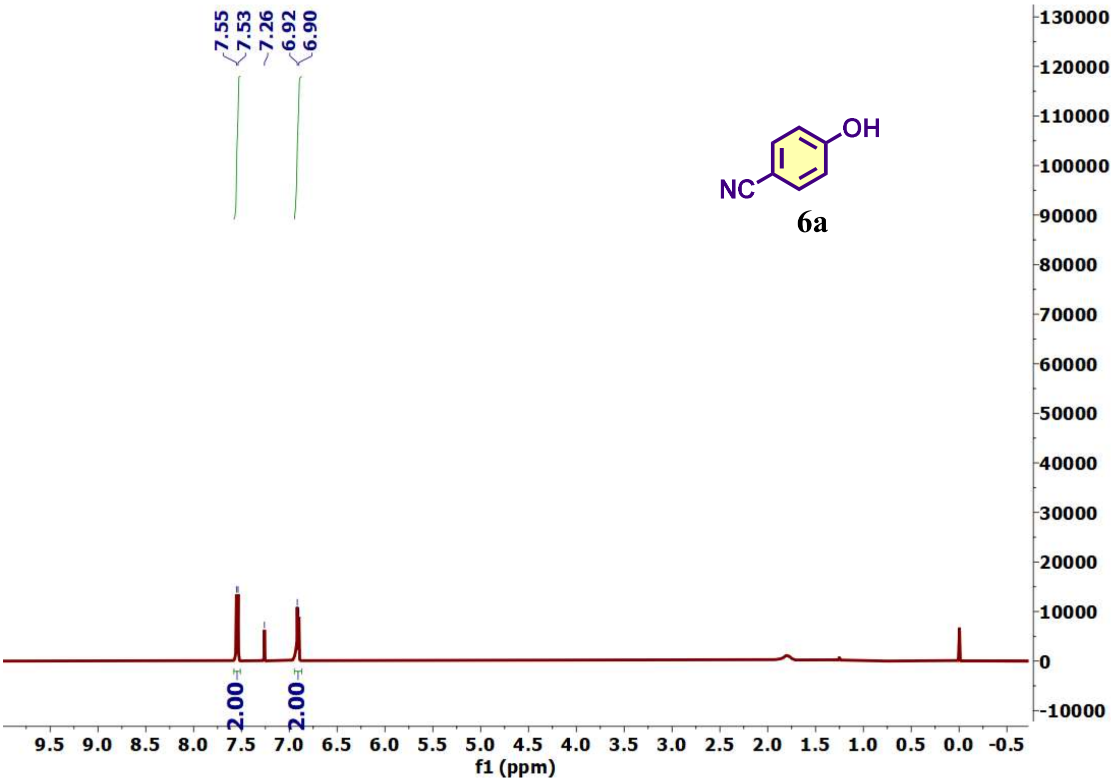


4e

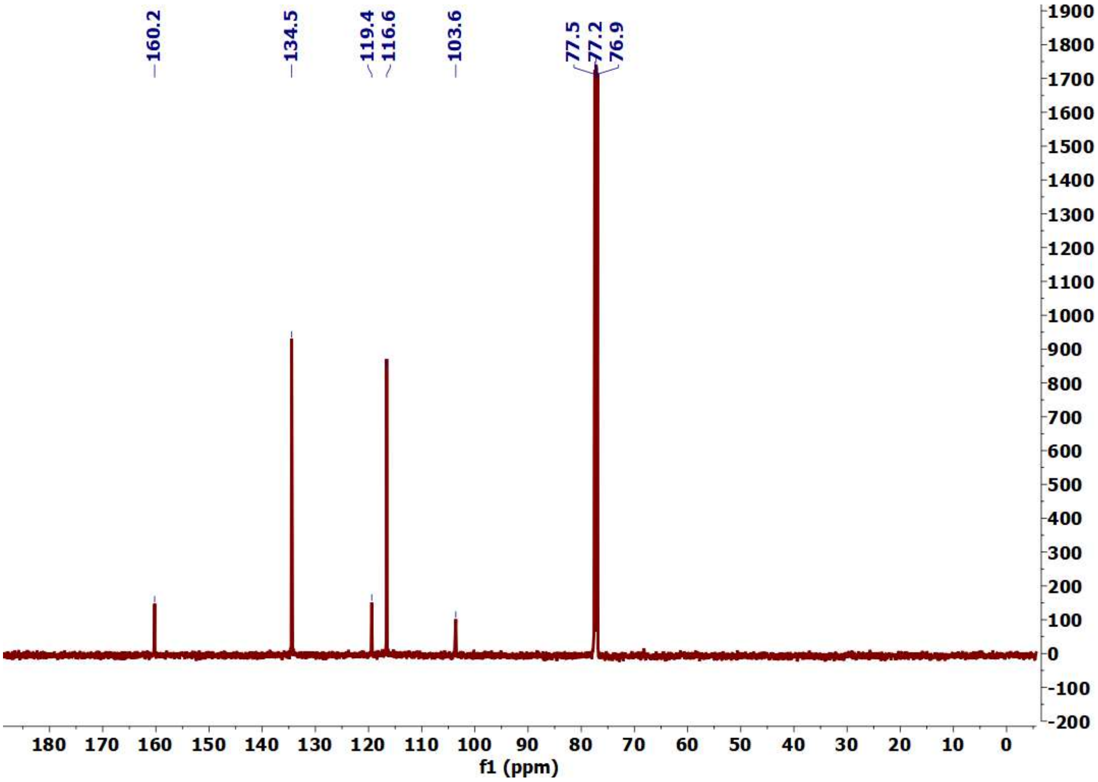
^{13}C NMR (125 MHz, CDCl$_3$) of compound **4e**



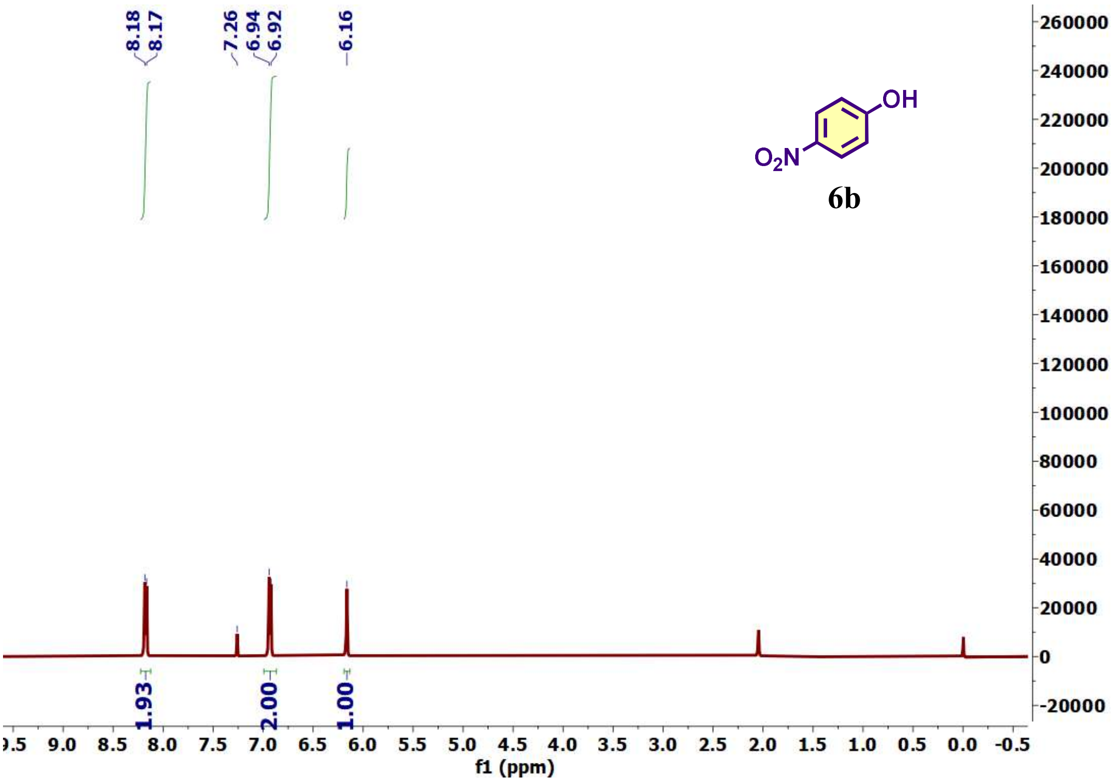
^{1}H NMR (500 MHz, CDCl$_3$) of compound **6a**



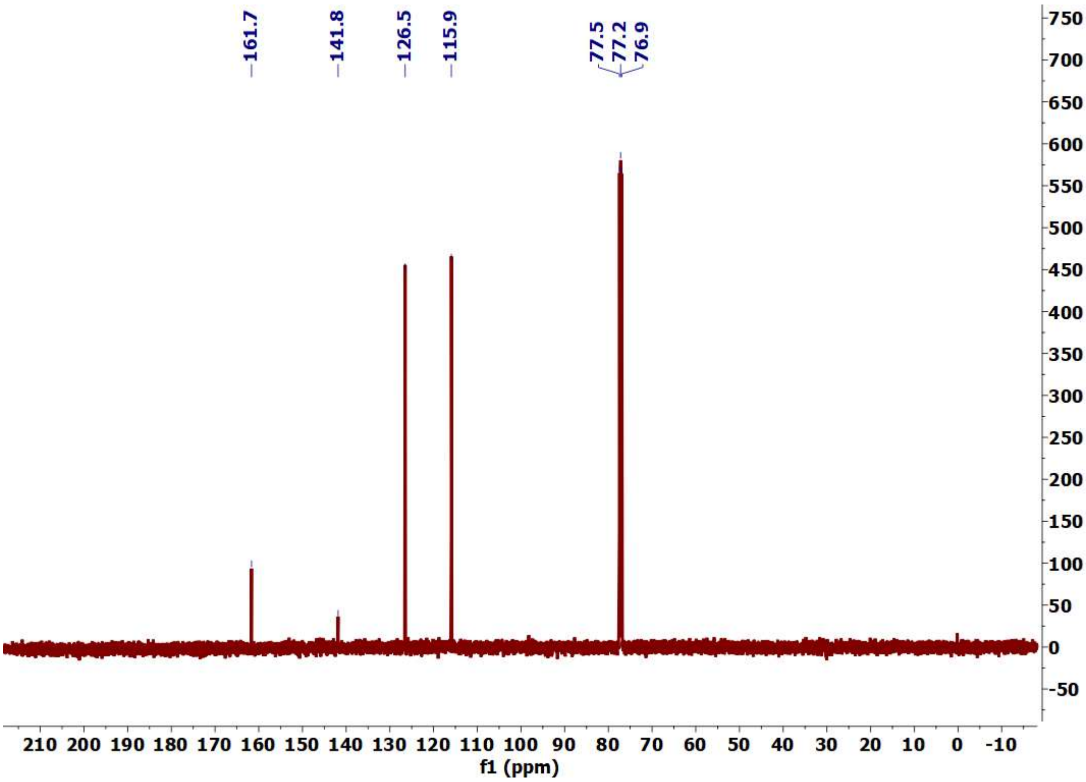
^{13}C NMR (125 MHz, CDCl$_3$) of compound **6a**



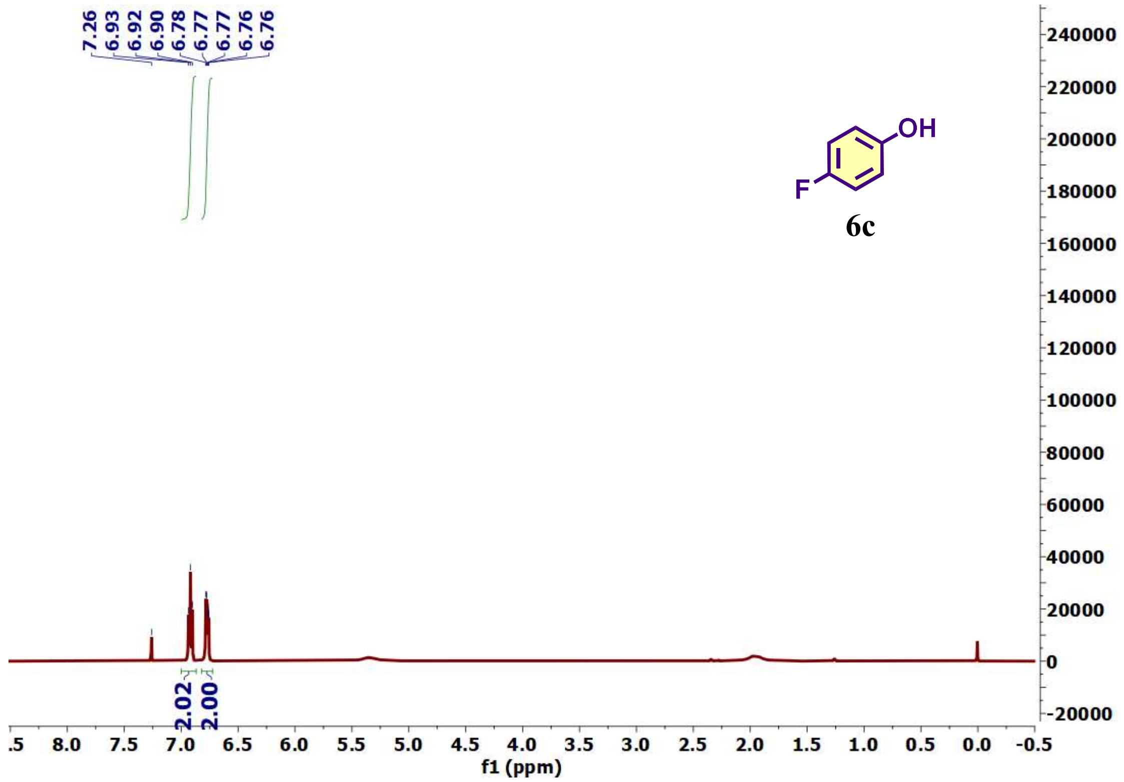
^{1}H NMR (500 MHz, CDCl$_3$) of compound **6b**



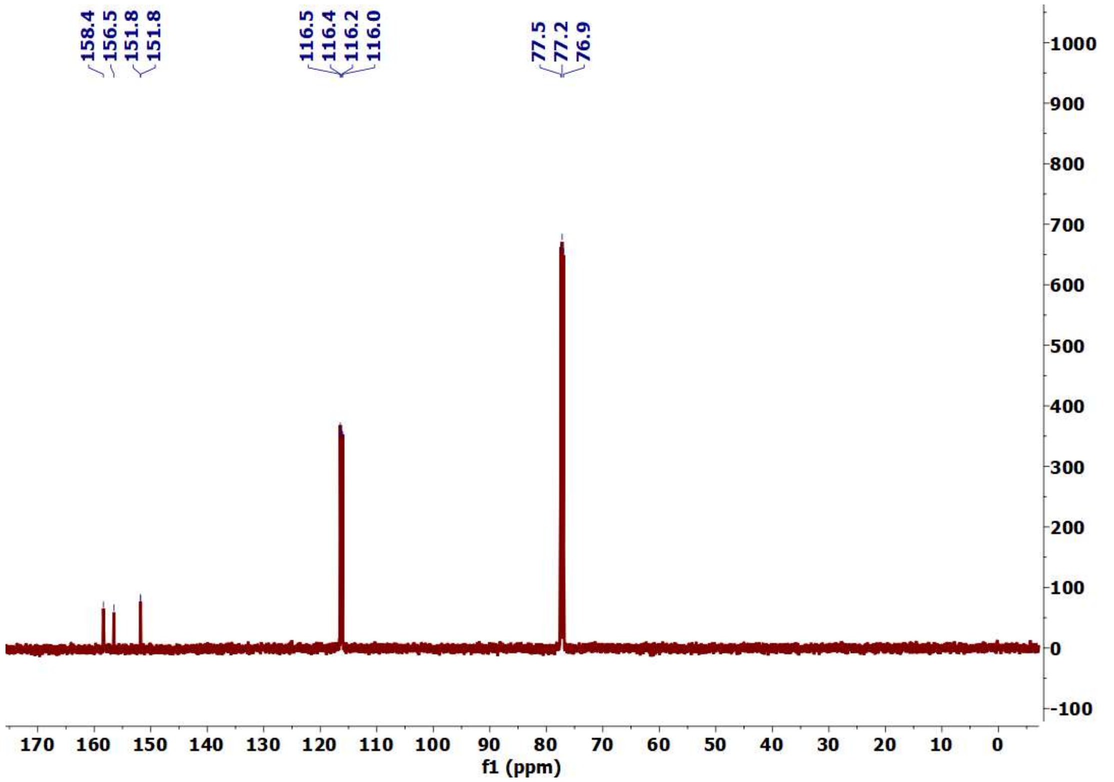
^{13}C NMR (125 MHz, CDCl$_3$) of compound **6b**



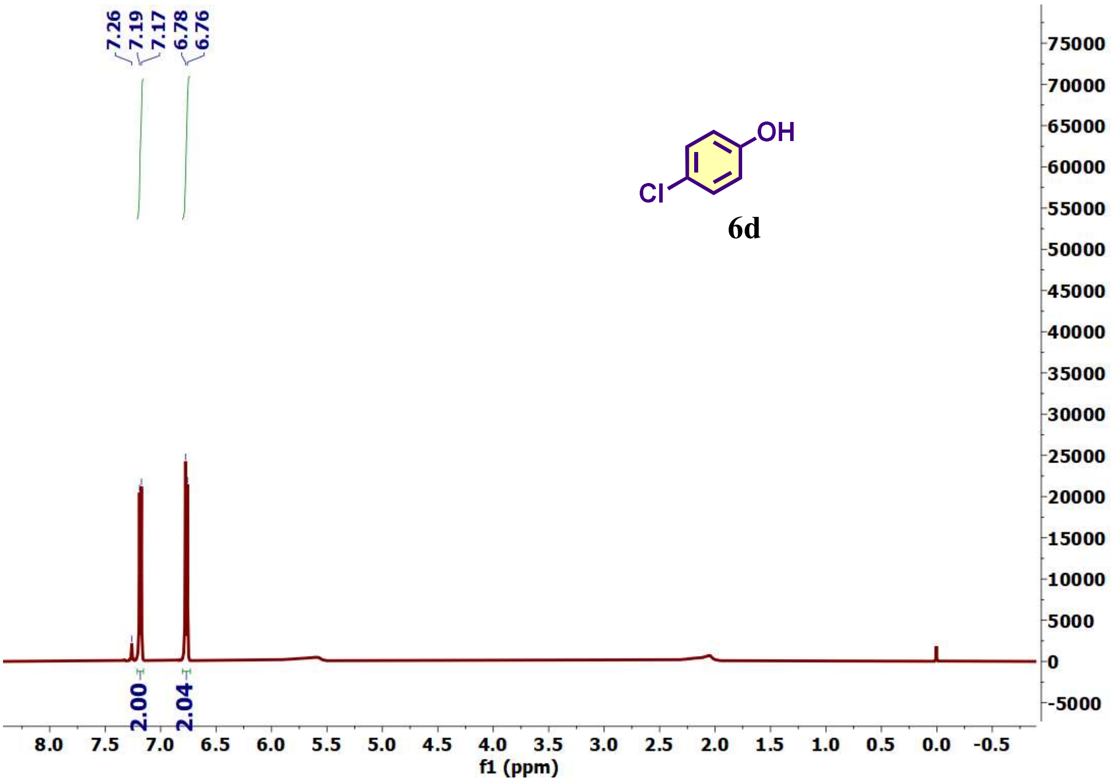
^{1}H NMR (500 MHz, CDCl$_3$) of compound **6c**



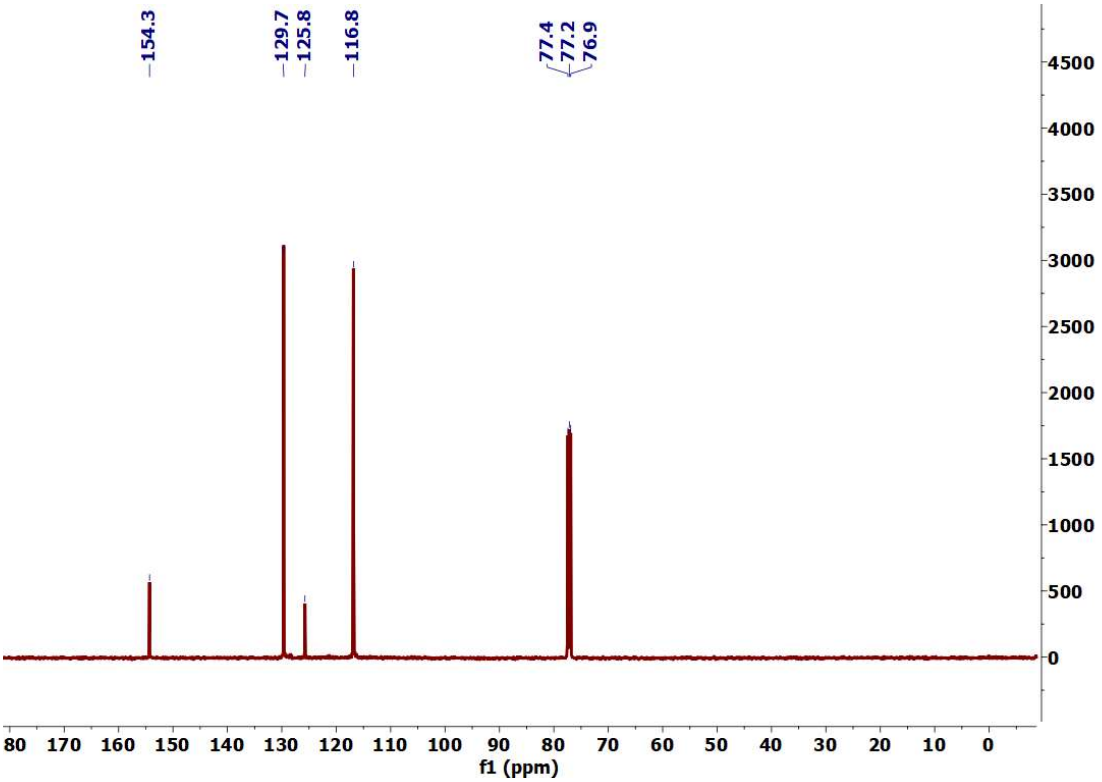
^{13}C NMR (125 MHz, CDCl$_3$) of compound **6c**



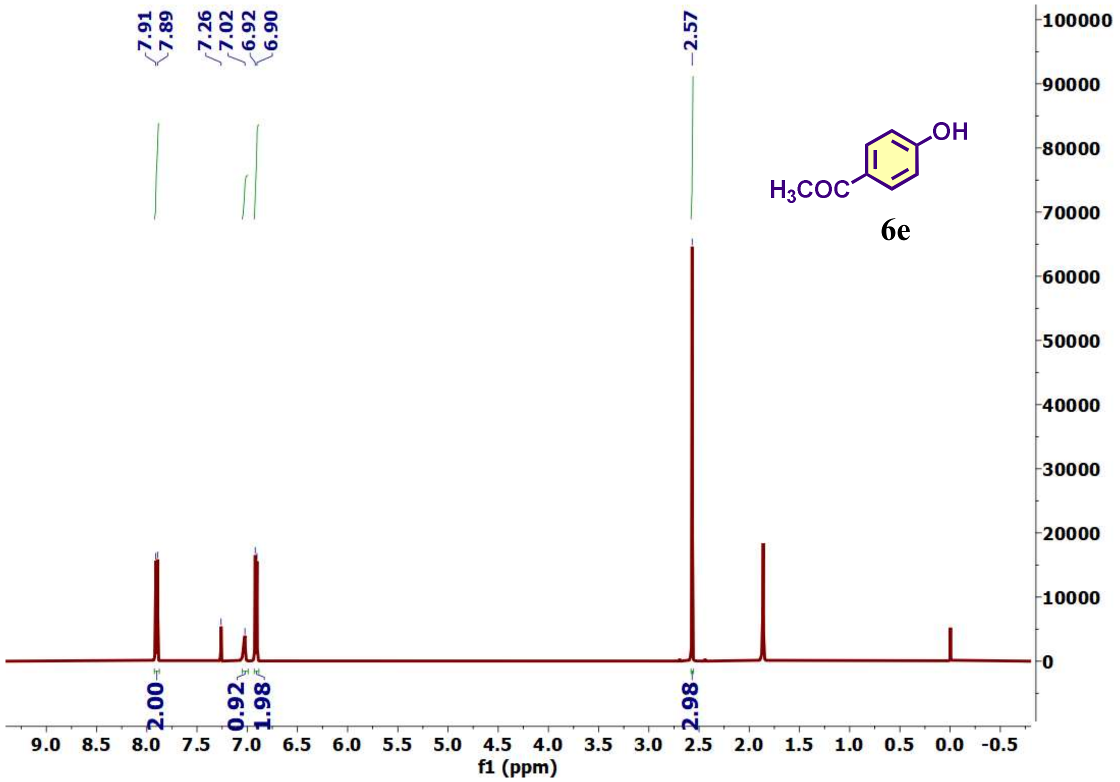
^{1}H NMR (500 MHz, CDCl$_3$) of compound **6d**



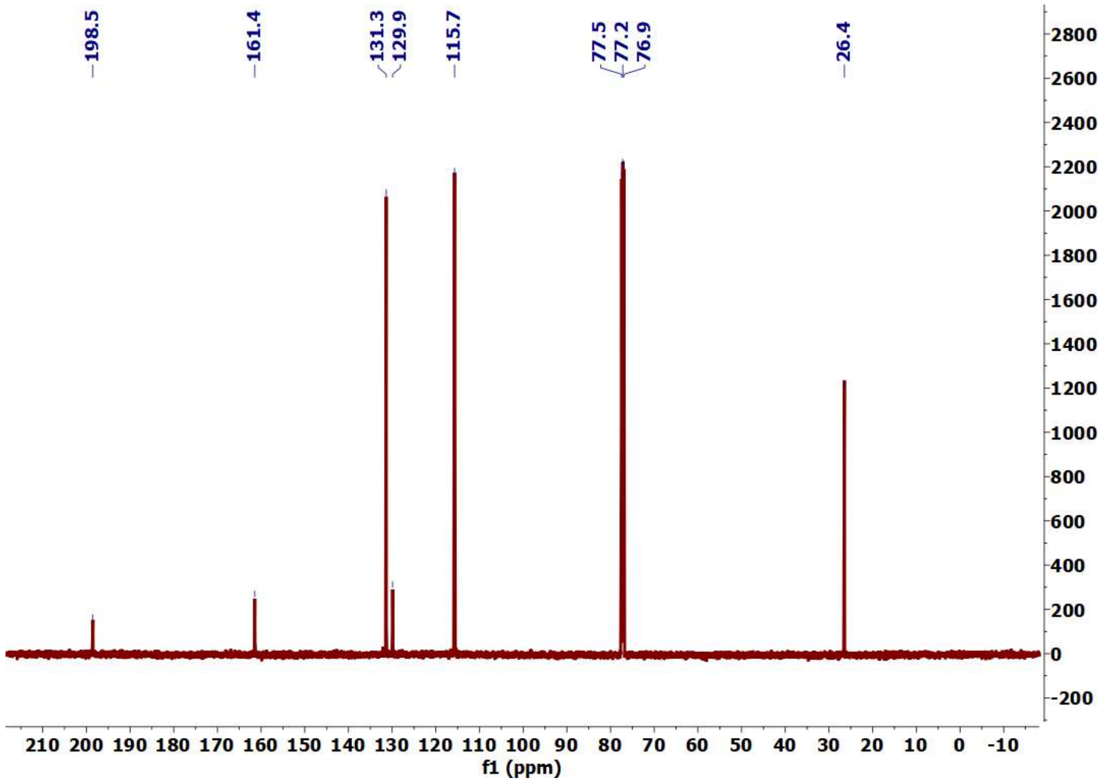
^{13}C NMR (125 MHz, CDCl$_3$) of compound **6d**



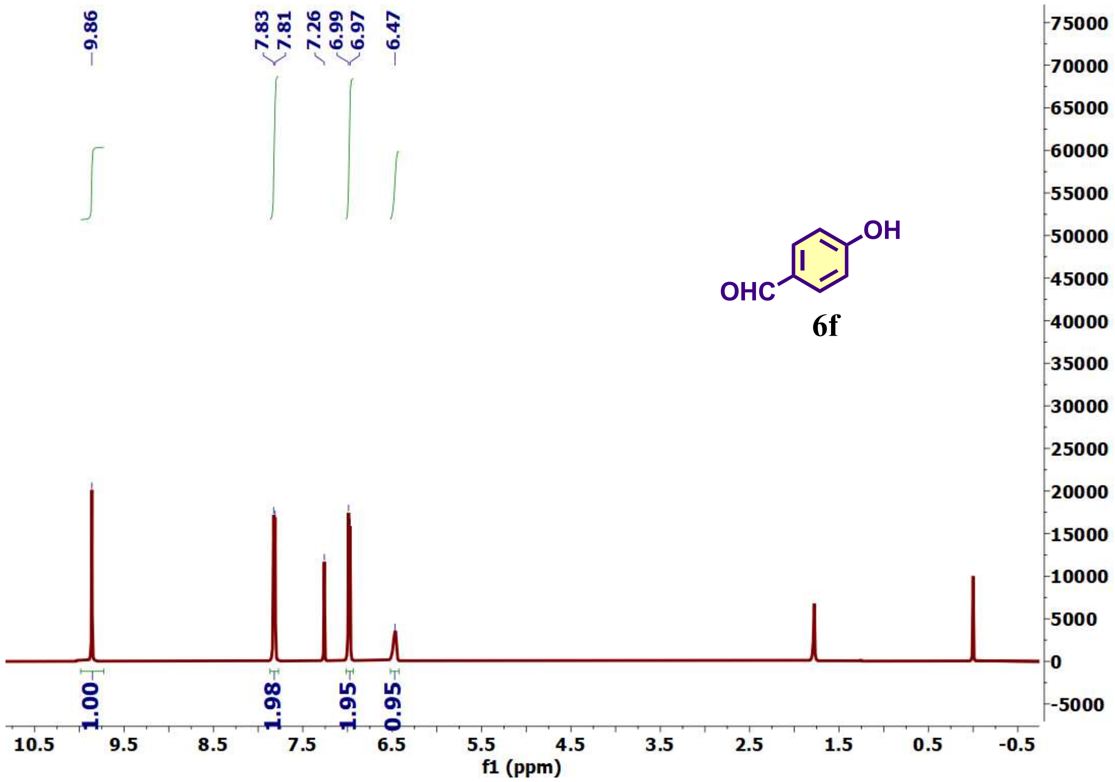
^{1}H NMR (500 MHz, CDCl$_3$) of compound **6e**



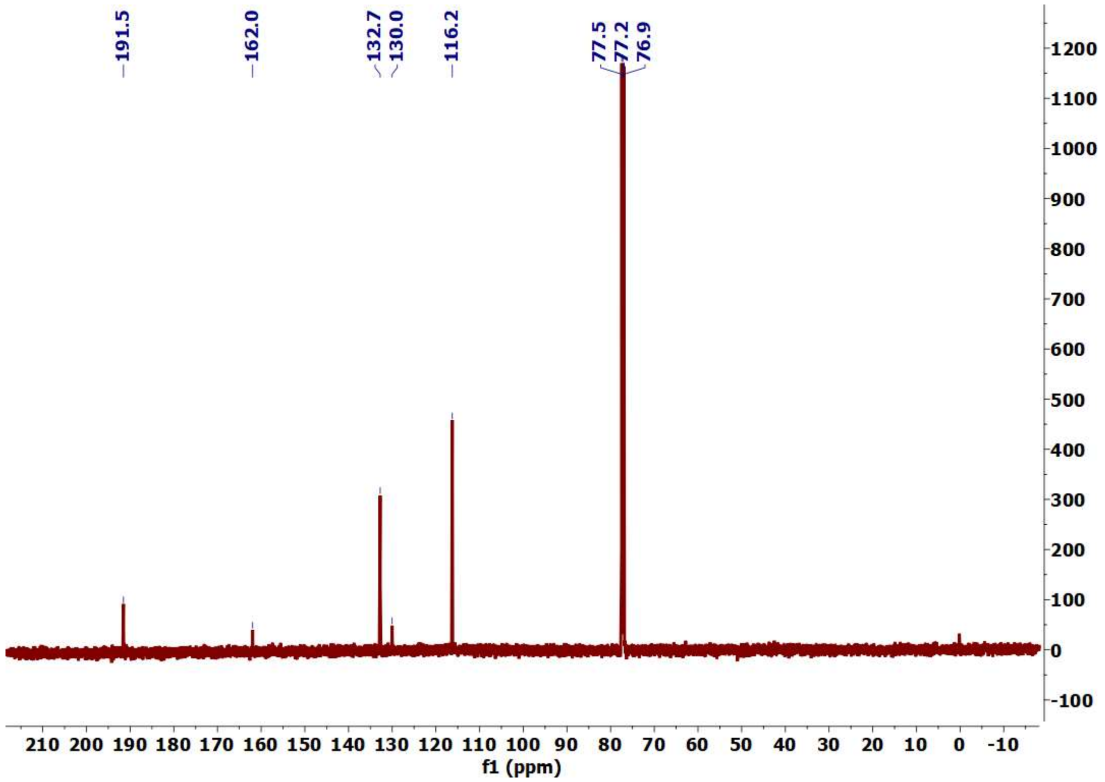
^{13}C NMR (125 MHz, CDCl$_3$) of compound **6e**



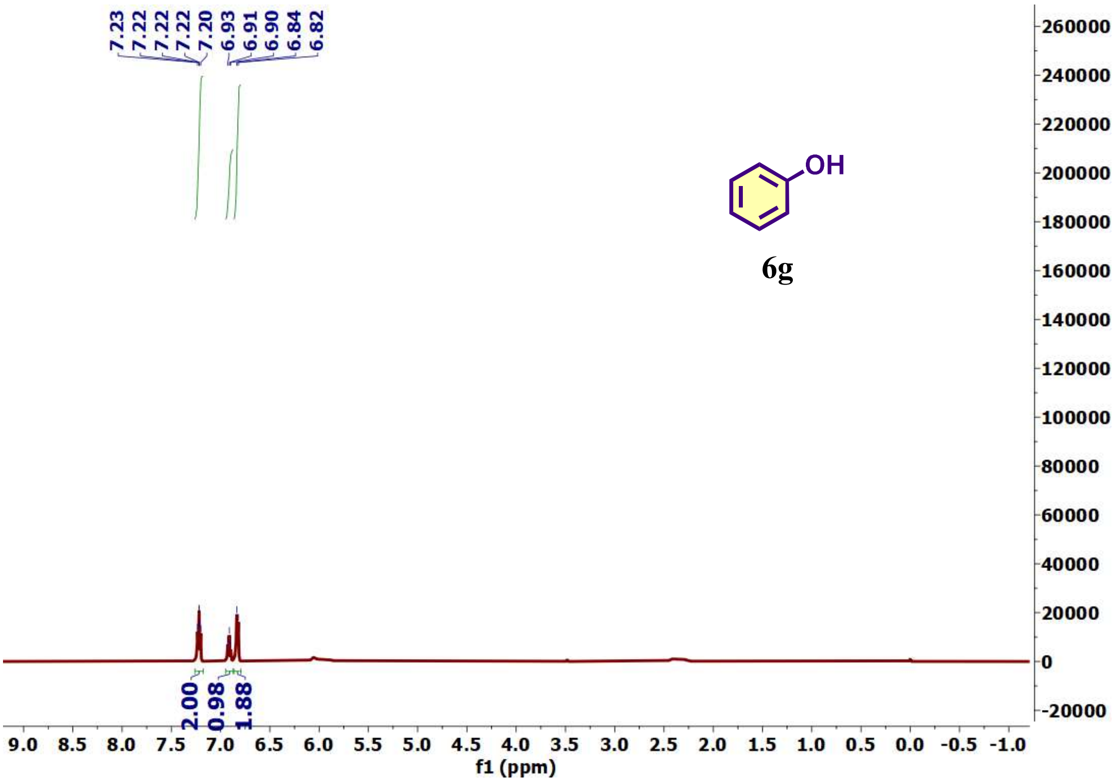
^{1}H NMR (500 MHz, CDCl$_3$) of compound **6f**



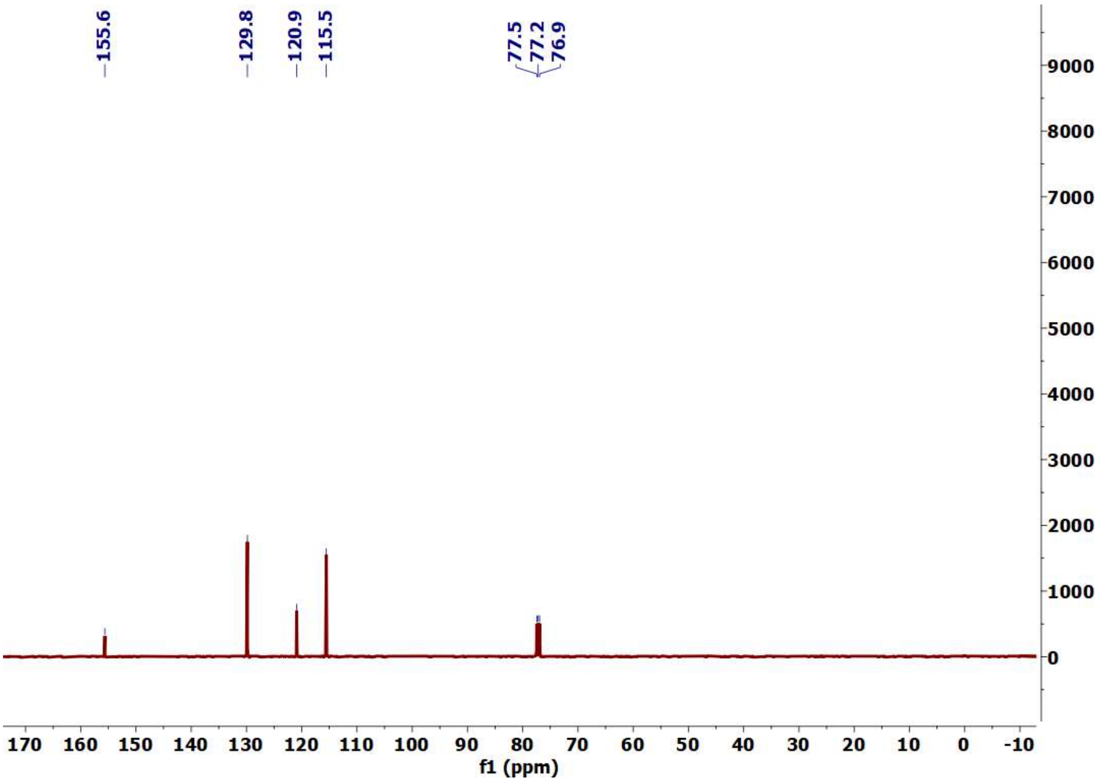
^{13}C NMR (125 MHz, CDCl$_3$) of compound **6f**



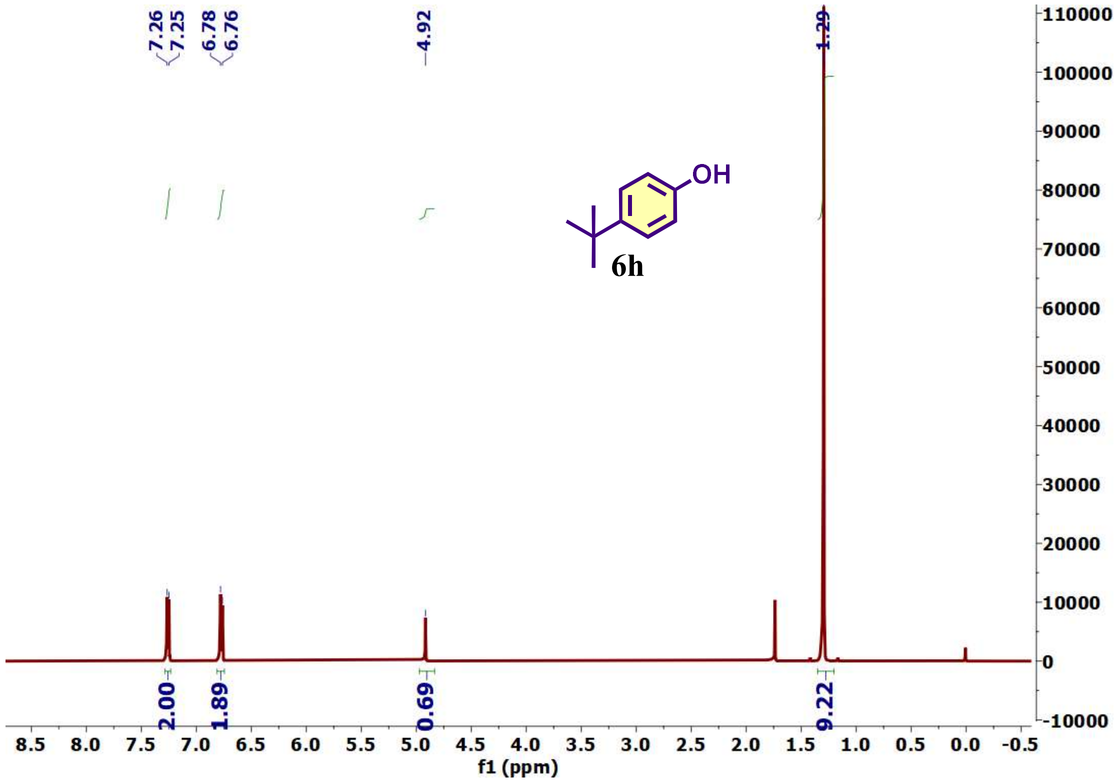
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6g**



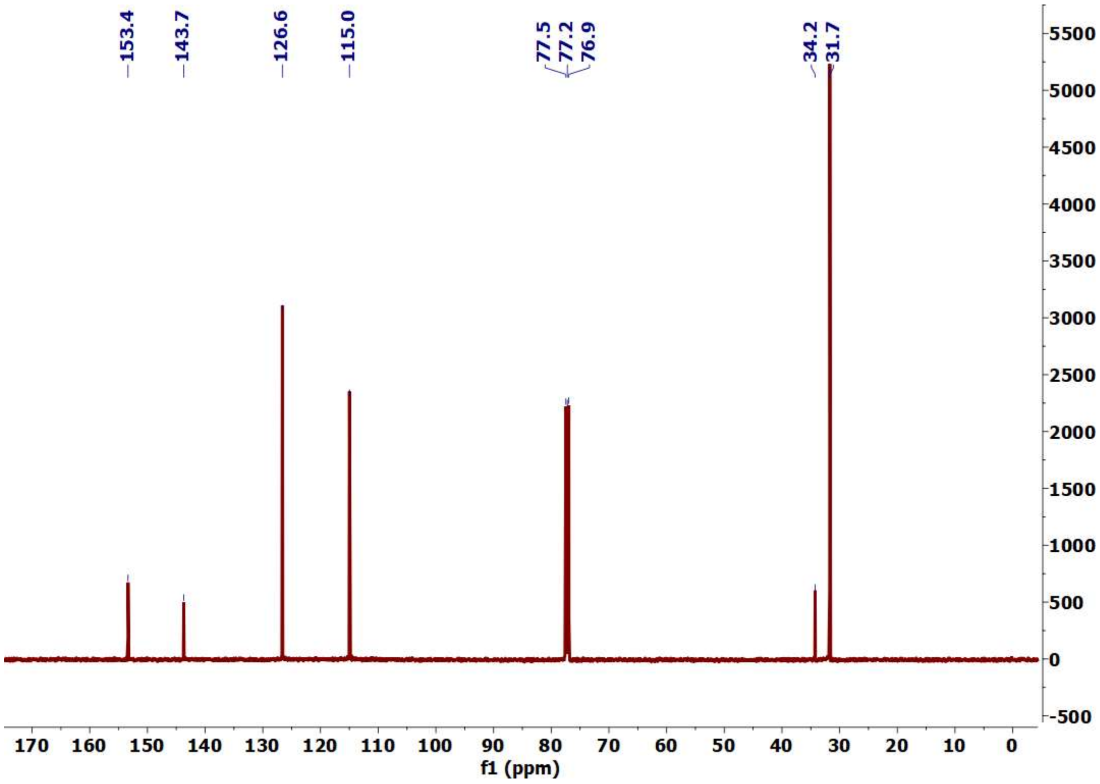
^{13}C NMR (125 MHz, $CDCl_3$) of compound **6g**



^{1}H NMR (500 MHz, CDCl$_3$) of compound **6h**

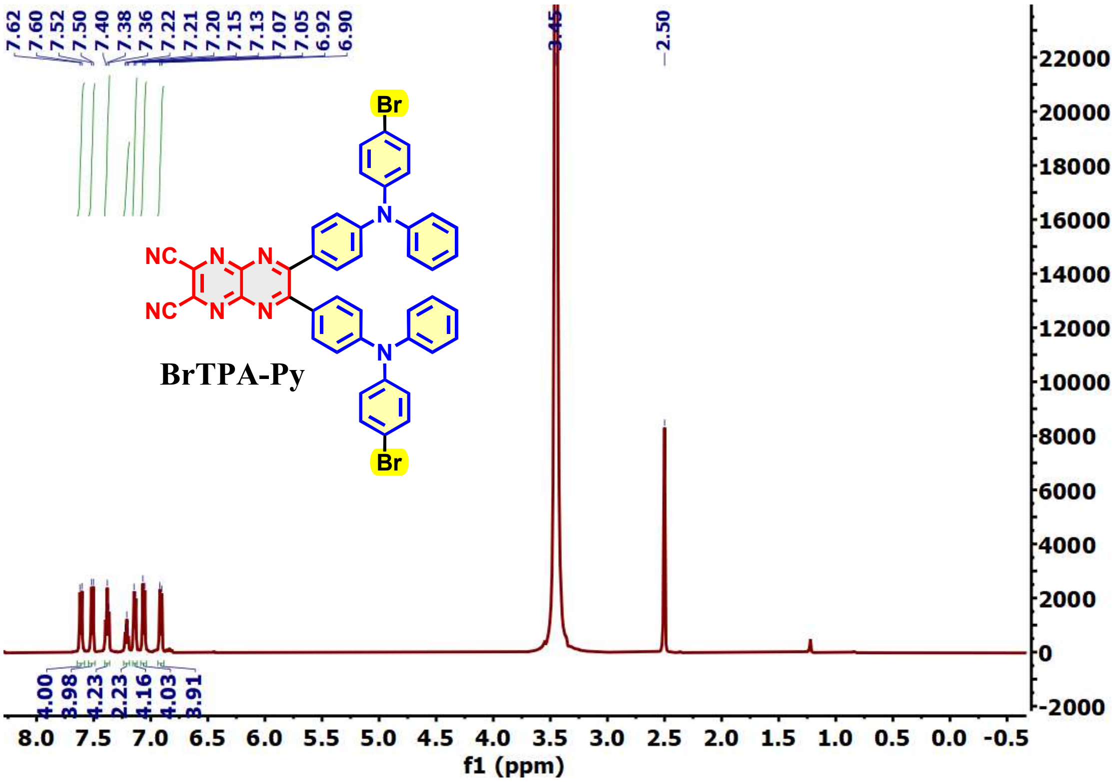


^{13}C NMR (125 MHz, CDCl$_3$) of compound **6h**

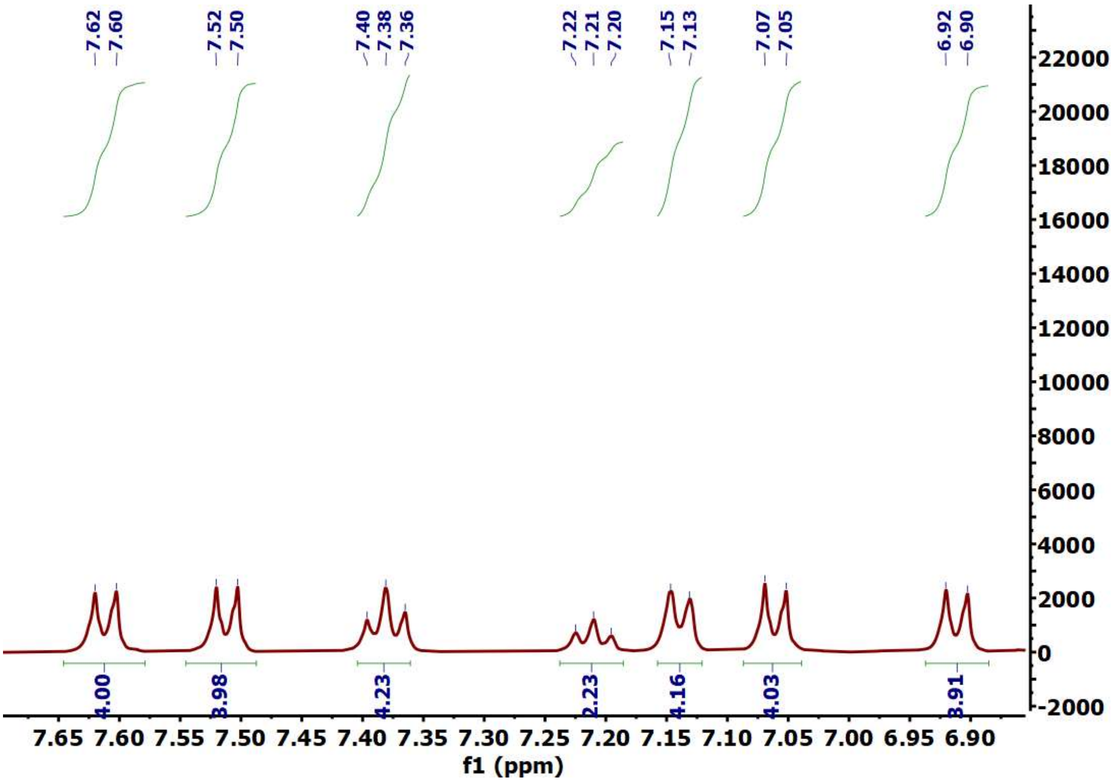


CHARACTERISATION of BrTPA-Py

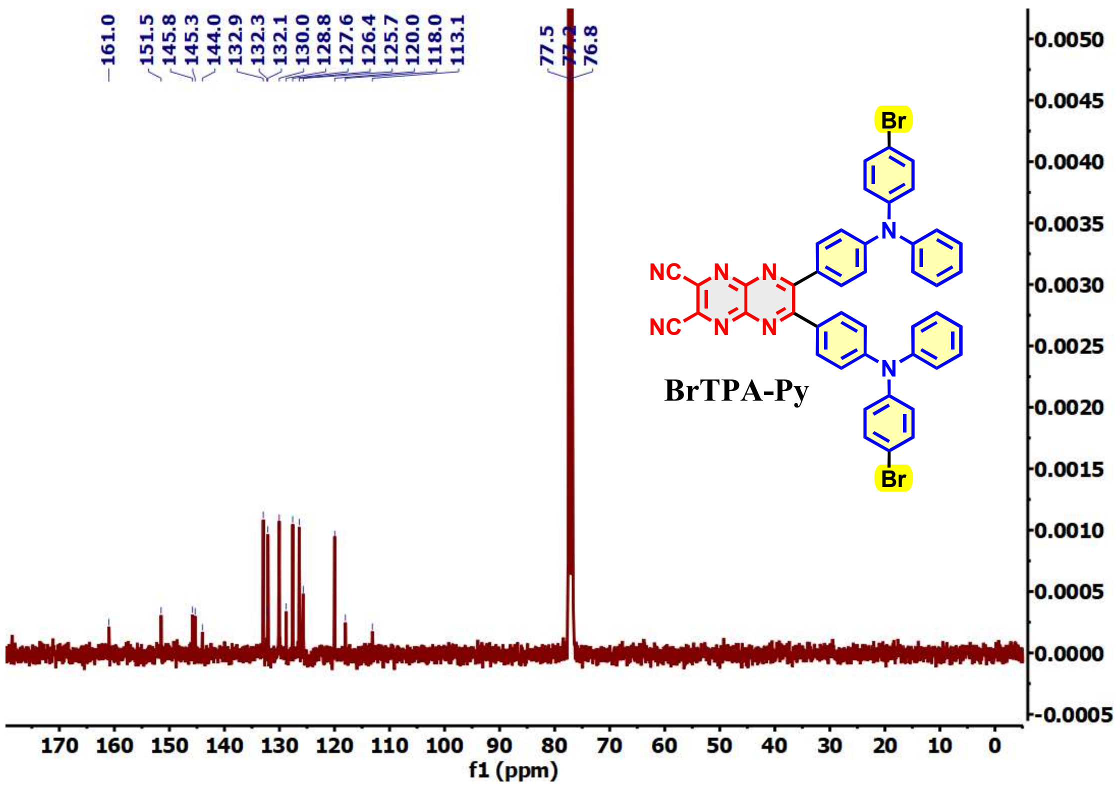
Full ^{1}H NMR (500 MHz, DMSO-d_6) of **BrTPA-Py**



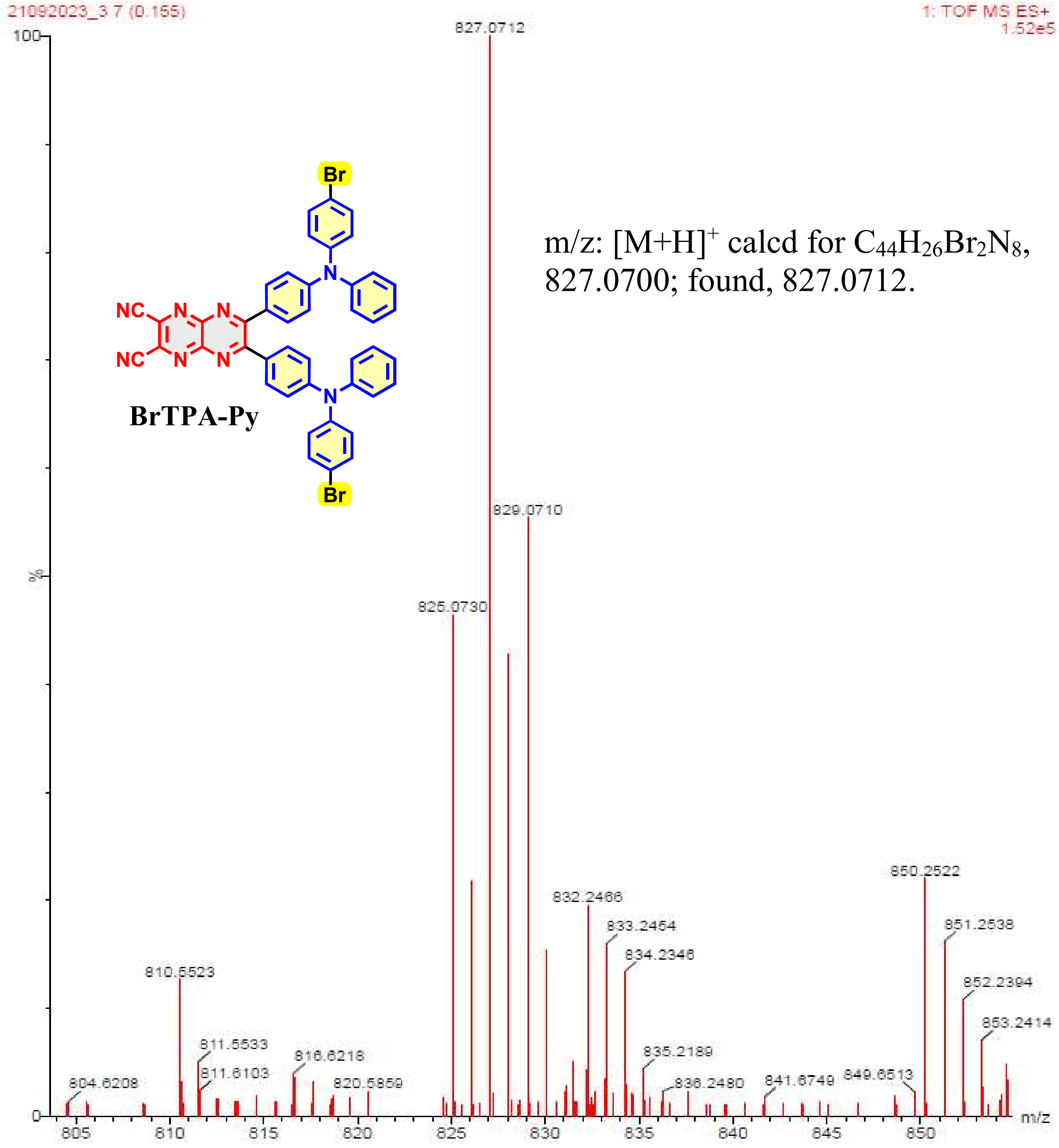
Expanded Aromatic Region of the ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of **BrTPA-Py**



^{13}C NMR (100 MHz, $CDCl_3$) of **BrTPA-Py**



High-resolution mass spectra (HRMS) of **BrTPA-Py**



m/z: $[M+H]^+$ calcd for $C_{44}H_{26}Br_2N_8$, 827.0700; found, 827.0712.

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