Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Acceleration of BODIPY dye-sensitized photocatalytic hydrogen production in aqueous ascorbic acid solutions using alkyl-chain formed second coordination sphere effects

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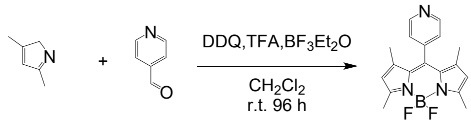
Synthesis of materials

*1-1. Synthesis of 5,5-difluoro-1,3,7,9-tetramethyl-10-(pyridin-4-yl)-5H-4l4,5l4-dipyrrolo [1,2-c:2',1'-f] [1,3,2]diazaborinine **3***

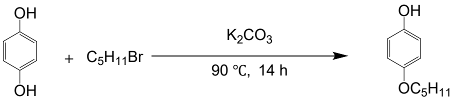


1 **2** **3** (16 %)

A solution of 3,5-dimethyl-2H-pyrrole **1** (4.9 g,51.5 mmol) and 4-Pyridinecarboxaldehyde **2** (2.3 g, 21.5 mmol) in dichloromethane (150 mL) under a nitrogen atmosphere. After added Trifluoroacetic acid (TFA, 8 drops), the solution was heated to reflux for 96 h. Then, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ, 3.2 g,14.1 mmol) was added, and the mixture was stirred for 1 h in ice bath. NEt_3 (20.9 mL, 150 mmol), and $BF_3 \cdot Et_2O$ (27.8 mL, 202.3 mmol) was added and stirred for 98 h at room temperature. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with CH_2Cl_2/ethyl acetate (50:1) to give compound **3** (1.4 g, 19.6 %) as dark green solids.

^{1}H (400 MHz, $CDCl_3$) 1.41 (s, 6H), 2.56 (s, 6H), 6.01 (s,2H), 7.32 (d, J=6.0 Hz, 2H), 8.79 (d, J=5.9 Hz, 2H). ^{13}C (100 MHz, $CDCl_3$) 14.6, 121.8, 123.4, 130.4, 137.6, 142.6, 143.7, 150.5, 156.5.

*1-2. Synthesis of 4-(pentyloxy) phenol **6b***

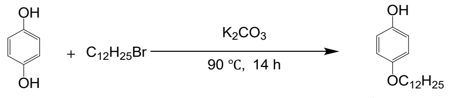


4 **5b** **6b** (48.3 %)

A solution of hydroquinone **4** (3.2 g, 29 mmol), potassium carbonate (10.0 g, 72 mmol) and 1-Bromopentane **5** (3.5 g, 23 mmol, 0.8 eq) in ethanol (80 mL), the solution was heated to reflux for 14 h. Then, ion-exchange water was added, the organic layer was dried by Na_2SO_4, crude product was purified by a silica gel chromatograph eluted with CH_2Cl_2/hexane (2:1) to give compound **6b** (2.0 g, 48.3 %).

^{1}H NMR (400 MHz, $CDCl_3$) 0.92 (t, J=7.1 Hz, 3H), 1.29-1.48 (m, 4H, 1.68-1.85 (m, 2H), 3.89 (t, J=6.6 Hz, 2H), 4.46 (s, 1H), 6.73-6.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) 14.04, 22.50, 28.20, 29.06, 69.00, 115.83, 116.24, 149.66, 152.97.

*1-3. Synthesis of 4-(pentyloxy) phenol **6c***

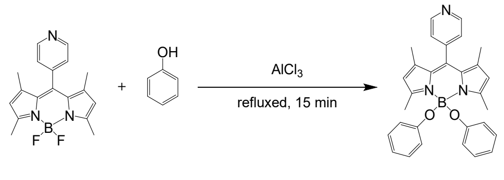


4 **5c** **6c** (28.1 %)

A solution of hydroquinone **4** (3.2 g, 29 mmol), potassium carbonate (10.0 g, 72 mmol) and 1-Bromododecane **5c** (5.7 g, 23 mmol, 0.8 eq) in ethanol (80 mL), the solution was heated to reflux for 14 h. Then, ion-exchange water was added, the organic layer was dried by Na_2SO_4, crude product was purified by a silica gel chromatograph eluted with CH_2Cl_2/hexane (2:1) to give compound **6c** (1.8 g, 28.1 %).

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (t, J=6.8 Hz, 3H), 1.22-1.51 (m, 18H), 1.71-1.83 (m, 2H), 3.91 (t, J=6.6 Hz, 2H), 4.58 (s, 1H), 6.73-6.83 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) 14.10, 22.68, 26.05, 29.34, 29.41, 29.58, 29.63, 29.65, 31.91, 68.75, 115.63, 115.98, 149.33, 153.38.

1-4. Synthesis of 1,3,7,9-tetramethyl-5,5-diphenoxy-10-(pyridin-4-yl)-5H-4l4, 5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine **7a**

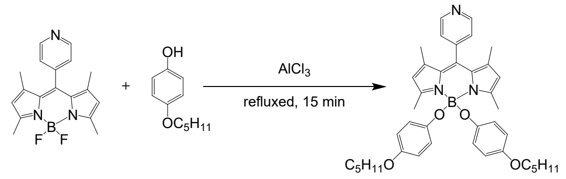


3 **6a** **7a** (30 %)

A solution of **3** (0.4 g, 1.2 mmol) and aluminum chloride (0.4 g, 2.5 mmol) in dried dichloromethane (20 mL) under a nitrogen atmosphere. The solution was heated to reflux for 15 minutes. After that, the mixture was cooled to room temperature, **6a** (0.4 g, 4.8 mmol) was added, and the mixture was stirred for 2 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with dichloromethane to give compound **7a** (171 mg, 30 %).

^{1}H NMR (400 MHz, $CDCl_3$) 1.39 (s, 6H), 2.55 (s, 6H), 5.90 (s, 2H), 6.61 (d, J=8.1 Hz, 4H), 6.80 (t, J=7.2 Hz, 2H),7.04-7.15 (m, 4H), 7.22 (d, J=5.1 Hz, 2H), 8.8 (d, J=4.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) 14.81, 15.29, 115.64, 118.72, 119.91, 122.56, 123.46, 129.57, 130.96, 137.75, 142.41, 143.69, 150.56, 156.51, 157.19.

1-5. Synthesis of 1,3,7,9-tetramethyl-5,5-bis(4-(pentyloxy)phenoxy)-10-(pyridin-4-yl)-5H-4l4, 5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine **7b**

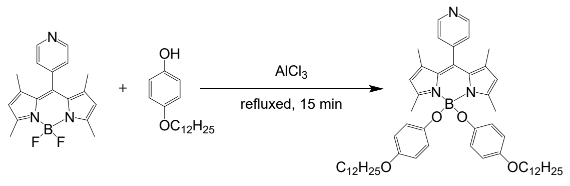


3 **6b** **7b** (22 %)

A solution of **3** (0.4 g, 1.2 mmol) and aluminum chloride (0.4 g, 2.5 mmol) in dried dichloromethane (20 mL) under a nitrogen atmosphere. The solution was heated to reflux for 15 minutes. After that, the mixture was cooled to room temperature, **6b** (0.8 g, 4.8 mmol) was added, and the mixture was stirred for 2 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with dichloromethane to give compound **7b** (173 mg, 22 %).

^{1}H NMR (400 MHz, $CDCl_3$) 0.85-0.95 (m, 3H), 1.37-1.48 (m, 12H), 1.6-1.75 (m, 4H),2.56 (s, 6H), 3.07-3.20 (m, 2H), 3.75-3.91 (m, 4H), 5.92 (s, 2H), 6.48 (d, J=7.7 Hz, 4H), 6.64 (d, J=7.7 Hz, 4H), 7.19 (s, 2H), 8.77 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 8.64, 14.01, 14.75, 15.27, 22.46, 28.25, 29.15, 45.98, 68.46, 115.03, 119.10, 122.40, 123.45, 130.94, 142.16, 150.34, 150.52, 152.59, 157.08.

1-6. Synthesis of 5,5-bis(4-(dodecyloxy)phenoxy)-1,3,7,9-tetramethyl-10-(pyridin-4-yl)-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine ***7c***



3 **6c** **7c** (20 %)

A solution of **3** (0.4 g, 1.2 mmol) and aluminum chloride (0.4 g, 2.5 mmol) in dried dichloromethane (20 mL) under a nitrogen atmosphere. The solution was heated to reflux for 15 minutes. After that, the mixture was cooled to room temperature, **6c** (1.3 g, 4.8 mmol) was added, and the mixture was stirred for 2 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with dichloromethane to give compound **7c** (203 mg, 20 %).

^{1}H NMR (400 MHz, $CDCl_3$) 0.85-0.95 (m, 3H), 1.23-1.32 (m, 32H), 1.37-1.43 (m, 10H), 1.68-1.76 (m, 4H), 2.56 (s, 6H), 3.88 (t, J=6.6 Hz, 4H), 5.91 (s, 2H), 6.48 (d, J=8.9 Hz, 4H), 6.64 (d, J=8.9 Hz, 4H), 7.19 (d, J=5.3 Hz, 2H), 8.77 (d, J=5.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 14.09, 14.75, 15.27, 22.67, 26.10, 29.33, 29.43, 29.48, 29.59, 29.65, 31.91, 68.48, 115.03, 119.09, 122.40, 123.41, 130.95, 143.70, 150.34, 150.57, 152.59, 157.09.

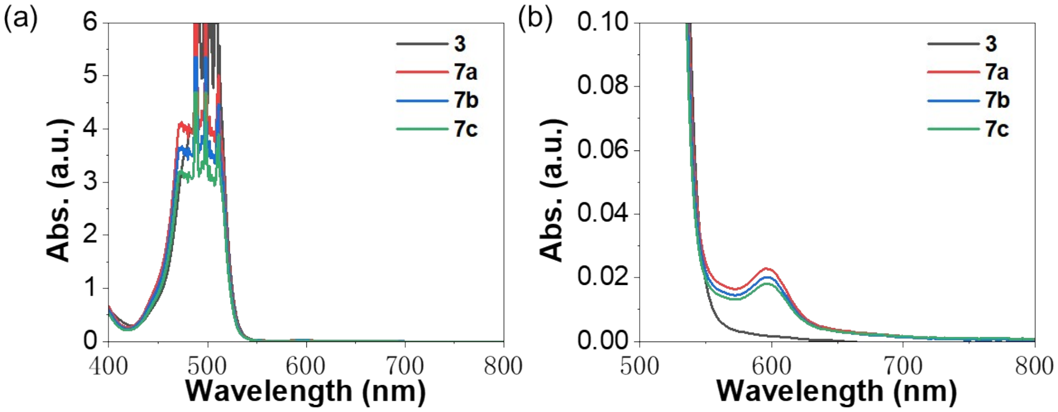


Fig. S1 UV–vis absorption spectra of dye in THF solution (2 × 10^{-4} M): (a) full spectra; (b) The enlarged plot between 500-800 nm.

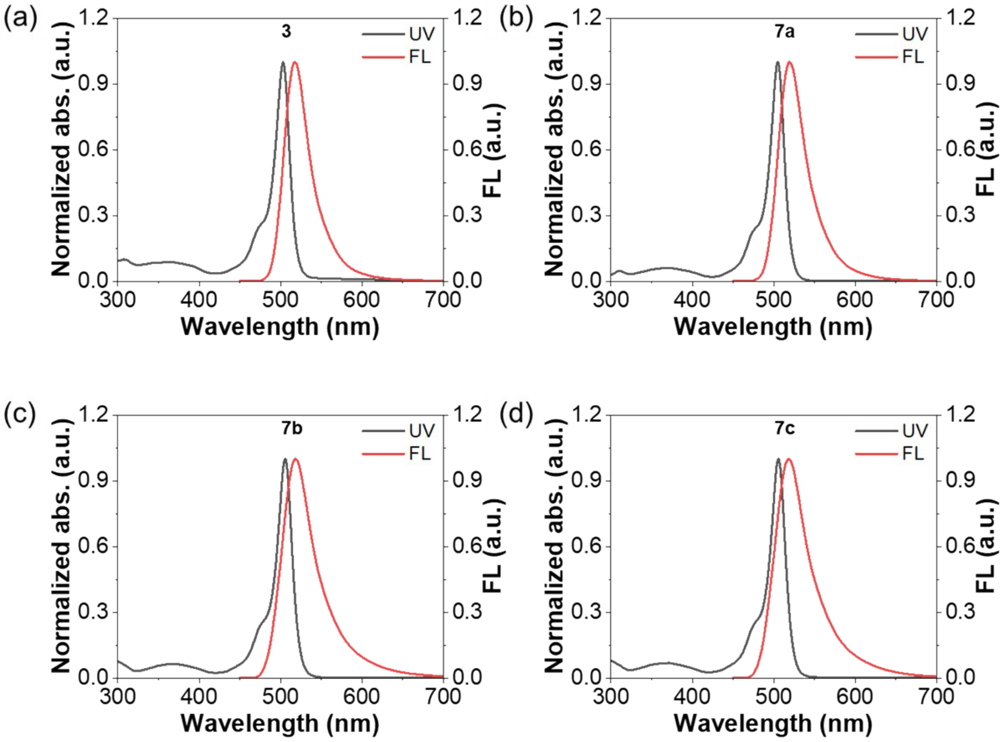
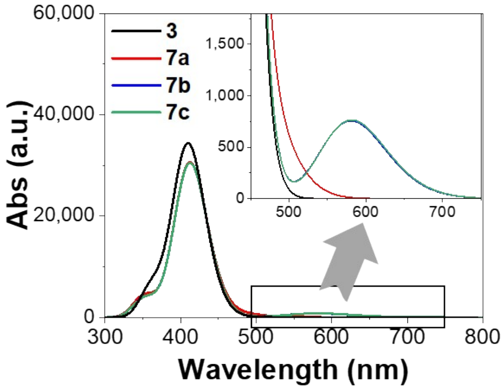
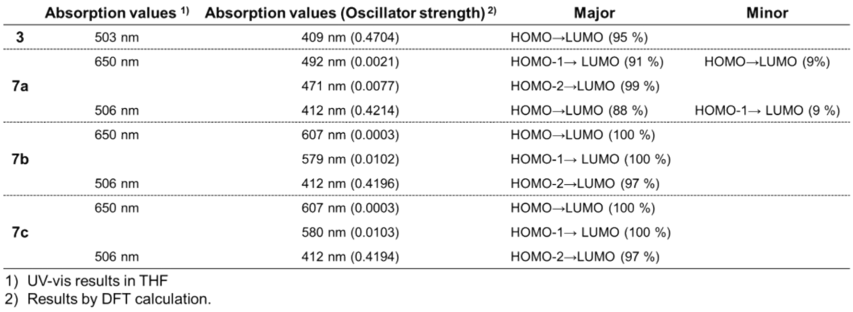


Fig. S2 UV and FL spectra of dye in THF solution: (a) **3**; (b) **7a**; (c) **7b**; (d) **7c**.

(a)



(b)



	Absorption values [1)]	Absorption values (Oscillator strength) [2)]	Major	Minor
3	503 nm	409 nm (0.4704)	HOMO→LUMO (95 %)	
7a	650 nm	492 nm (0.0021)	HOMO-1→ LUMO (91 %)	HOMO→LUMO (9%)
		471 nm (0.0077)	HOMO-2→LUMO (99 %)	
	506 nm	412 nm (0.4214)	HOMO→LUMO (88 %)	HOMO-1→ LUMO (9 %)
7b	650 nm	607 nm (0.0003)	HOMO→LUMO (100 %)	
		579 nm (0.0102)	HOMO-1→ LUMO (100 %)	
	506 nm	412 nm (0.4196)	HOMO-2→LUMO (97 %)	
7c	650 nm	607 nm (0.0003)	HOMO→LUMO (100 %)	
		580 nm (0.0103)	HOMO-1→ LUMO (100 %)	
	506 nm	412 nm (0.4194)	HOMO-2→LUMO (97 %)	

1) UV-vis results in THF
2) Results by DFT calculation.

Fig. S3 (a) TD-DFT caliculated absorption spectra of **3** and **7a-7c** (b) Values of absorption (experimental and theoritical), and molecular orbital contributions to electronic transitions of **3** and **7a**-**7c**.

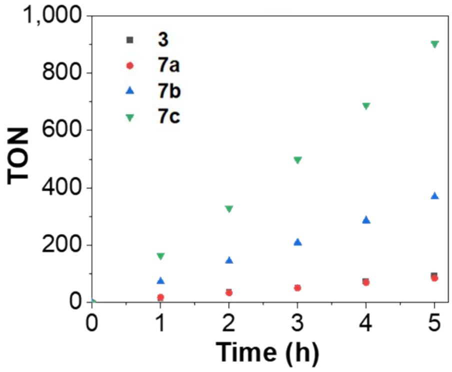


Fig. S4 Turnover number (TON) of the hydrogen production for **3** and **7a**-**7c** /Pt-TiO_2. Conditions: 0.57 M ascorbic acid (pH = 4), Xe lamp (0.15 W cm^{-2}, >420 nm).

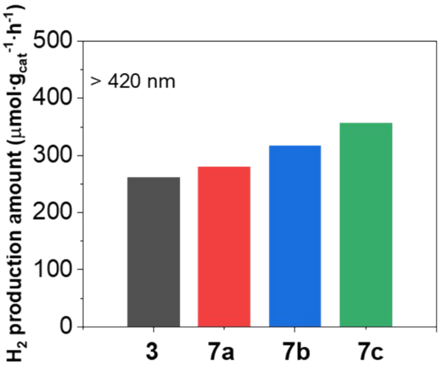


Fig. S5 Photocatalytic hydrogen production results of same loading amount (5.0 μmol/g) **3** and **7a**-**7c** /Pt-TiO_2 in ascorbic acid solution. Conditions: 0.57 M ascorbic acid (pH = 4), Xe lamp (0.08 W cm^{-2}, >420 nm)

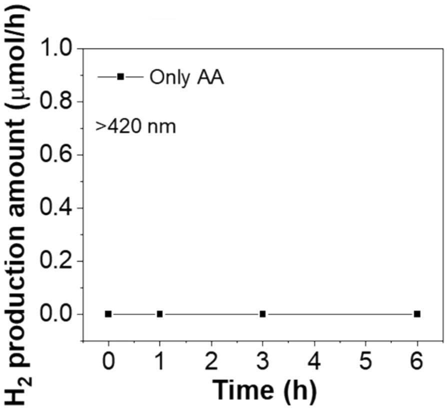


Fig. S6 Photocatalytic hydrogen production results of without photocatalyst. Conditions: 0.57 M ascorbic acid (pH = 4), Xe lamp (0.15 W cm^{-2}, >420 nm).

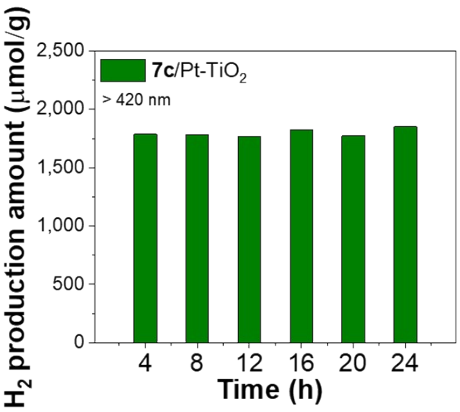


Fig. S7 Cycle stability test of **7c** /Pt-TiO$_2$.Conditions: Xe lamp (0.15 W cm^{-2}, >420 nm), 0.57 M ascorbic acid aq. (pH 4.0).

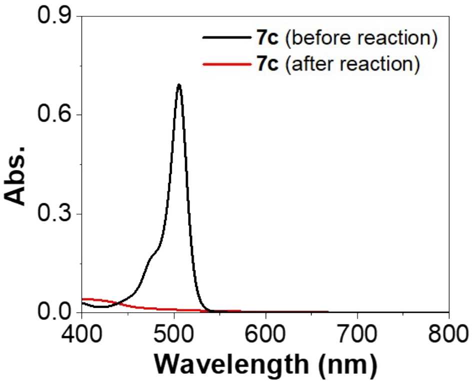


Fig. S8 UV–vis absorption spectrum of (black) **7c** in chloroform solution, and (red) spectrum on the chloroform solution side, where the aqueous solution after the reaction is extracted with chloroform

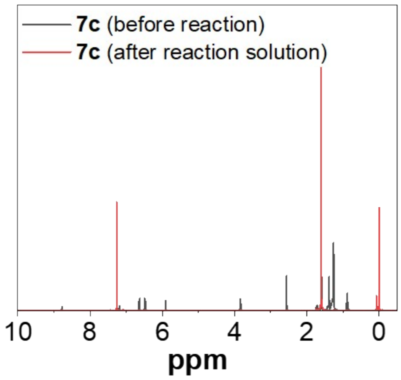


Fig. S9 ^1H NMR spectrum of (black) **7c** in $CDCl_3$ solution, and (red) spectrum on the $CDCl_3$ solution side, where the aqueous solution after the reaction is extracted with $CDCl_3$.

Table S1. AQY results of dye-sensitized photocatalyst

	AQY	Reaction time (Reduction rate of activity)	
BBT/Pt-TiO_2	0.4 % 650 nm	7 h $^{a)}$	[1]
Zn- *tri* -PcNc/gC_3N_4	0.5 % 660 nm	10 h $^{b)}$	[2]
ZnPyd/Pt-C_3N_4	1.1 % 635 nm	30 h (-12%) $^{a)}$	[3]
1 @SWCNT/fullerodendron	1.4 % 650 nm	21 h (-66%) $^{a)}$	[4]
7c/Pt-TiO_2	1.4 % 650 nm	24 h $^{a)}$	This work
1/Pt-HPT (TiO_2)	3.6 % 670 nm	30 h (-22%) $^{a)}$	[5]
SA1/Pt-TiO_2	12.5 % 650 nm	30 h (-10%) $^{a)}$	[6]

a) >420 nm

b) >500 nm

1 H. J. Hou, X. H. Zhang, D. K. Huang, X. Ding, S. Y. Wang, X. L. Yang, S. Q. Li, Y. G. Xiang and H. Chen, *Appl. Catal. B Environ.*, 2017, **203**, 563–571.

2 L. Yu, X. Zhang, C. Zhuang, L. Lin, R. Li and T. Peng, *Phys. Chem. Chem. Phys.*, 2014, **16**, 4106–4114.

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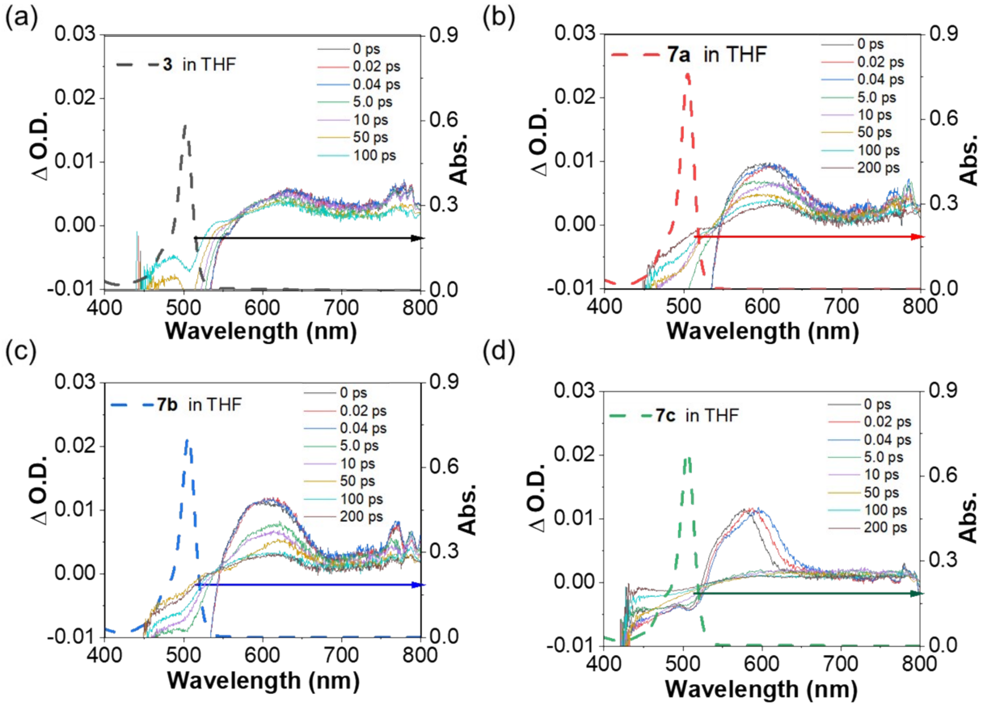

Fig. S10 Time-resolved absorption spectra of **3** and **7a**-**7c** /TiO_2 in 0.57 M ascorbic acid aq. (pH 4.0) for excitation at 400 nm in the 0–200 ps temporal window : (a) **3**; (b) **7a**; (c) **7b**; (d) **7c**.

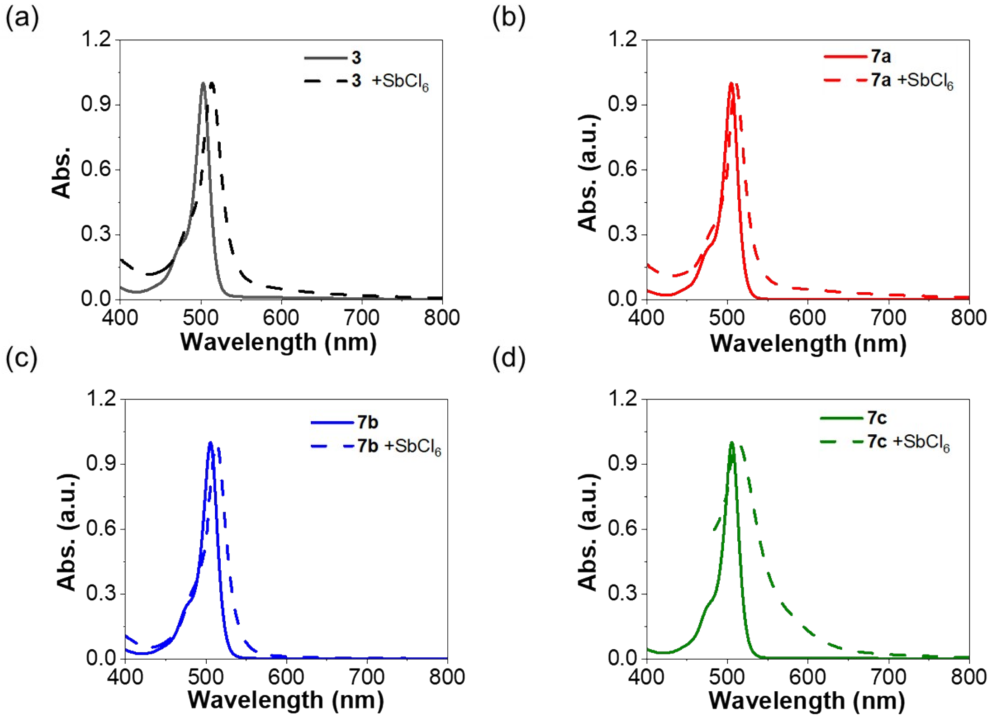

Fig. S11 UV–vis absorption spectra of **dye** and after added $SbCl_6$ in **dye** THF solution: (a) **3**; (b) **7a**; (c) **7b**;

(d) **7c**.

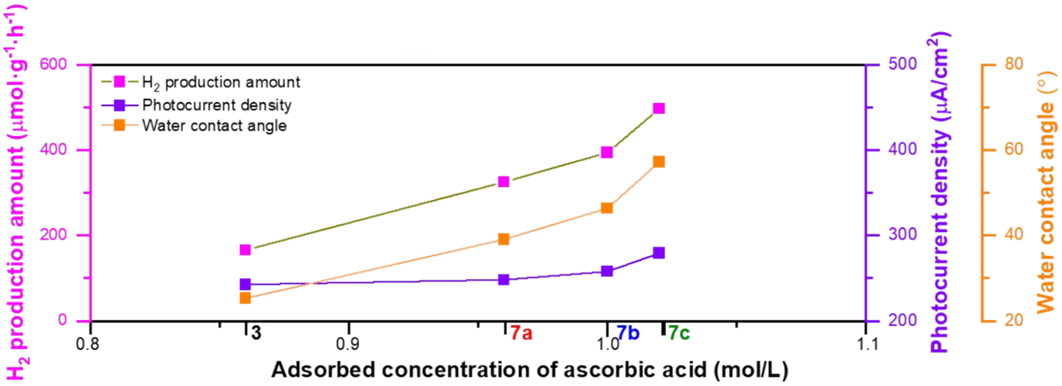

Fig. S12 The relationship between hydrophobicity, photocatalytic activity, photocurrent density and zeta potential differences with ascorbic acid.

Table S2. Different properties of dyes

	3	**7a**	**7b**	**7c**
Water contact angle (°)	25.3	39.1	46.4	57.2
TOF ($\cdot h^{-1}$)	18.6	19.0	73.8	180.5
Photocurrent density ($\mu A\cdot cm^{-2}$)	242.8	248.3	257.9	279.3
Impedance ($\Omega\cdot cm^{-2}$)	74.4	77.3	88.3	106.1
Zeta potential (mV)	-0.3 [a)] -10.5 [b)]	-2.4 [a)] -13.6 [b)]	-3.1 [a)] -14.5 [b)]	-15.3 [a)] -15.2 [b)]
Adsorbed concentration of ascorbic acid ($mol\cdot L^{-1}$)	0.86 [b)]	0.96 [b)]	1.00 [b)]	1.02 [b)]
τ_1 (ns)	84.3	13.9	8.3	0.14
τ_2 (ns)	667.3	356.6	144.1	29.0

a) Saturated loaded amount (amount: please see the main text) in water

b) Same loaded amount (5 $\mu mol\cdot g^{-1}$) in ascorbic acid

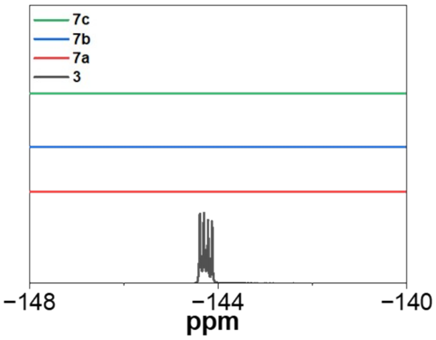

Fig. S13 ^{19}F NMR spectra of **3**, **7a**, **7b** and **7c**.

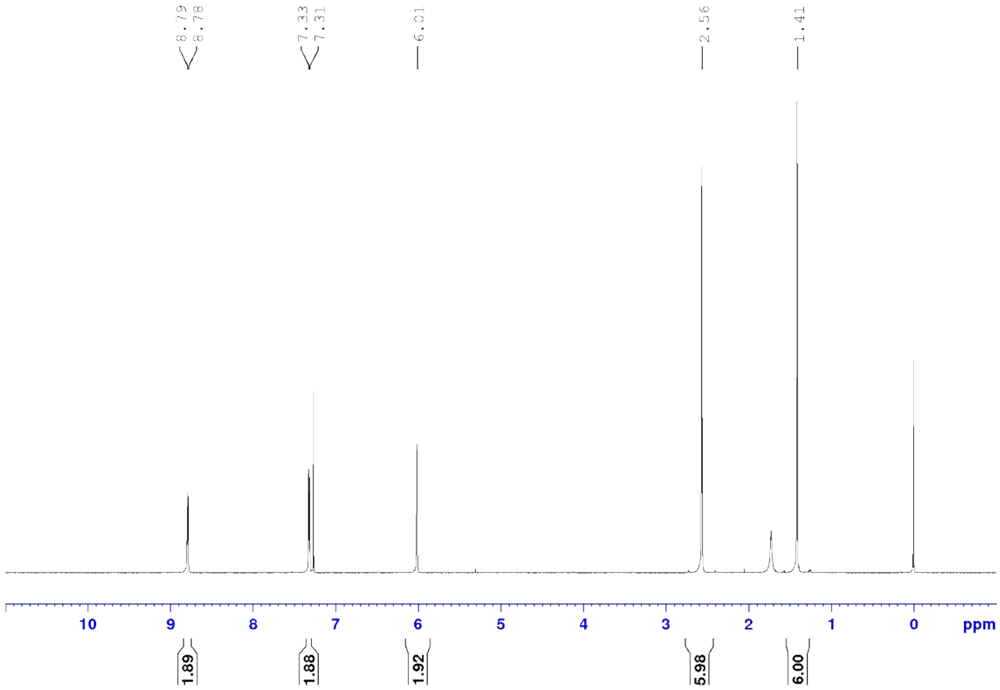

Fig. S14 ^{1}H NMR spectra of **3** (400 MHz).

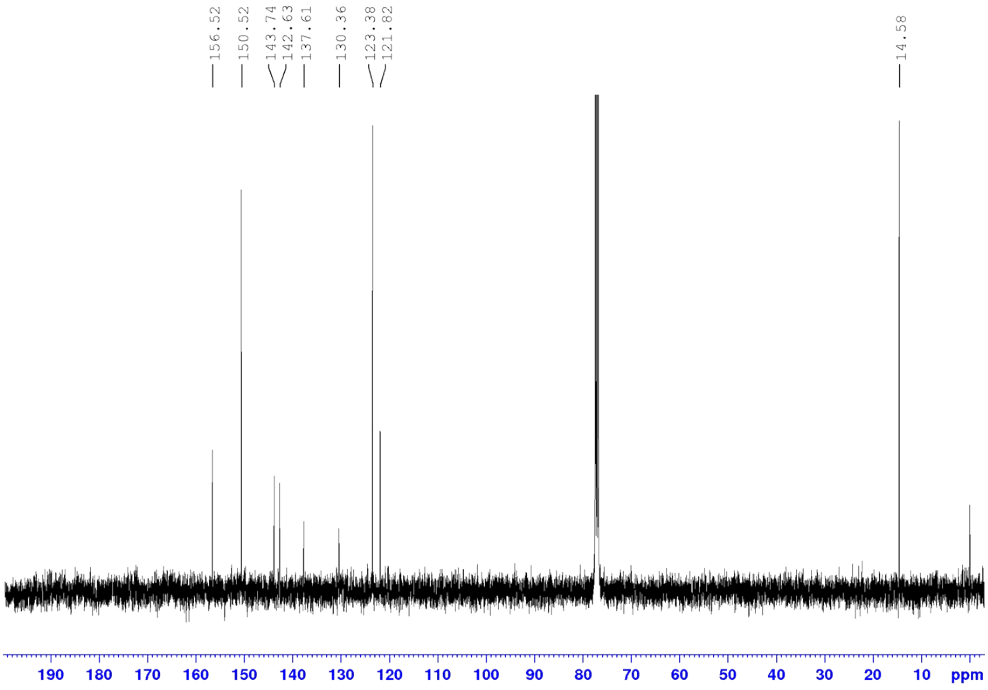

Fig. S15 ^{13}C NMR spectra of **3** (100 MHz).

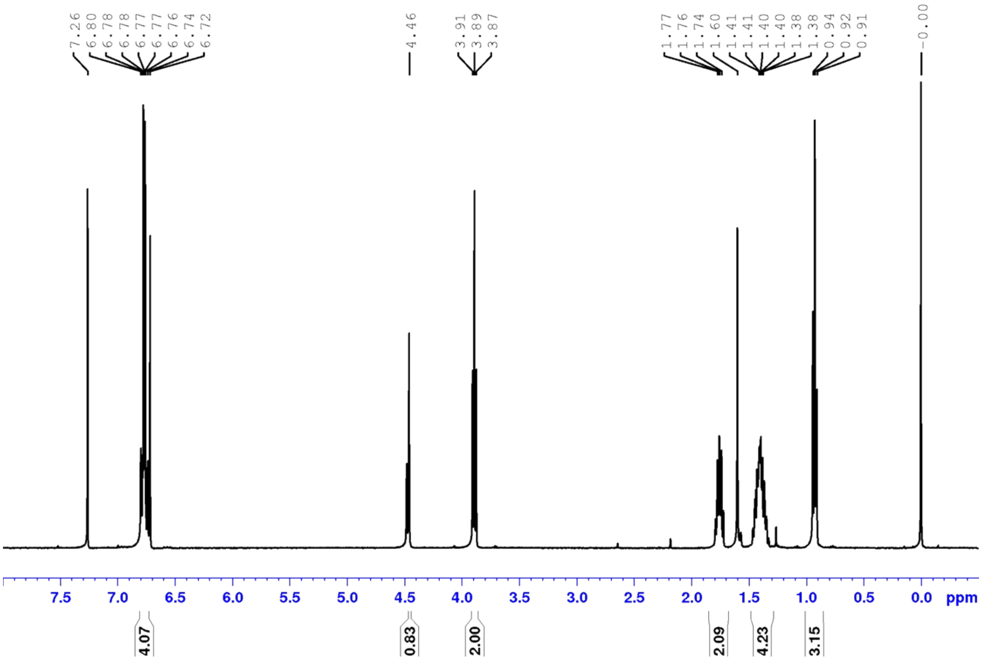

Fig. S16 ^{1}H NMR spectra of **6b** (400 MHz).

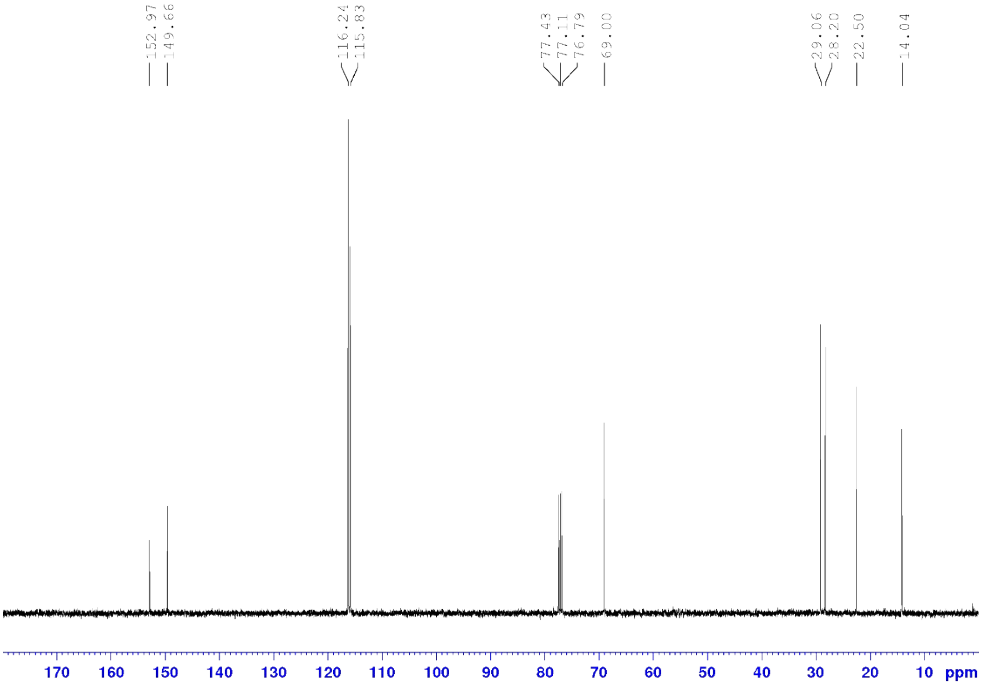

Fig. S17 ^{13}C NMR spectra of **6b** (100 MHz).

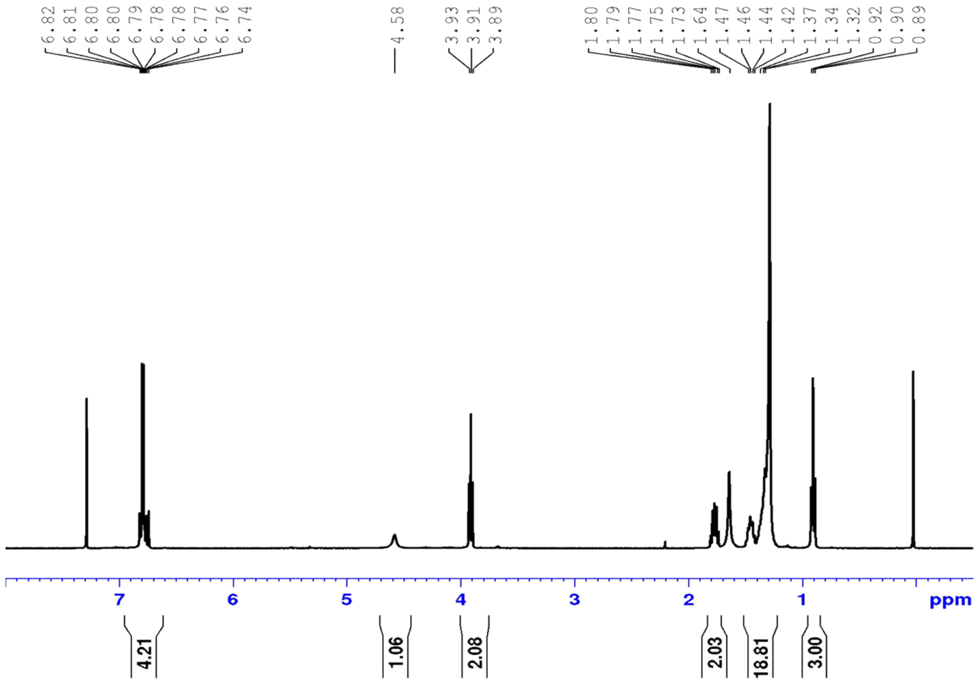

Fig. S18 ^{1}H NMR spectra of **6c** (400 MHz).

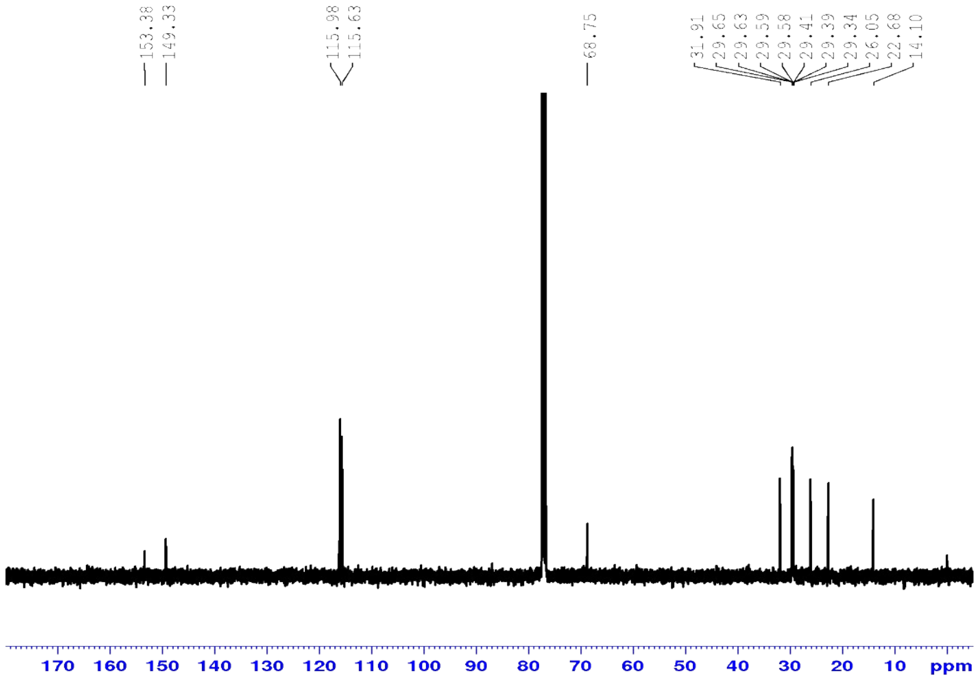

Fig. S19 ^{13}C NMR spectra of **6c** (100 MHz).

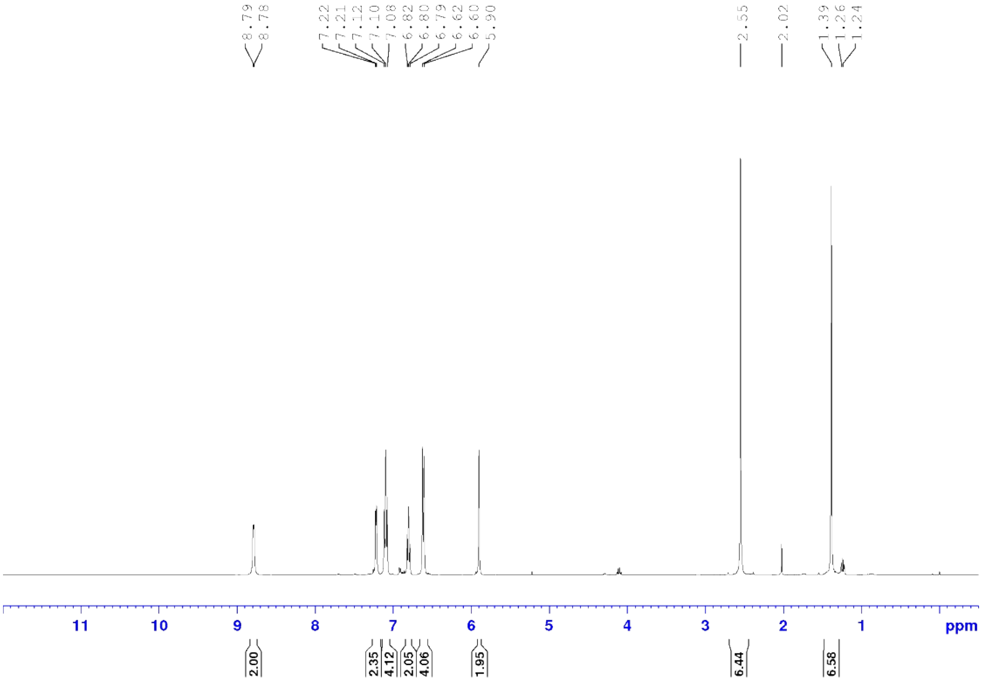

Fig. S20 ^{1}H NMR spectra of **7a** (400 MHz).

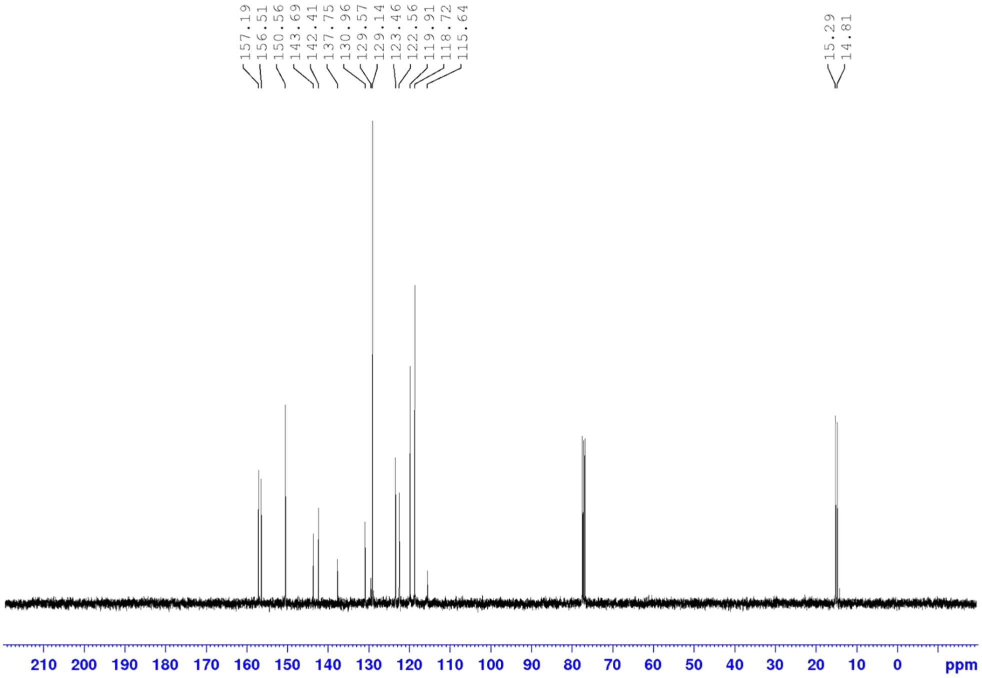

Fig. S21 ^{13}C NMR spectra of **7a** (100 MHz).

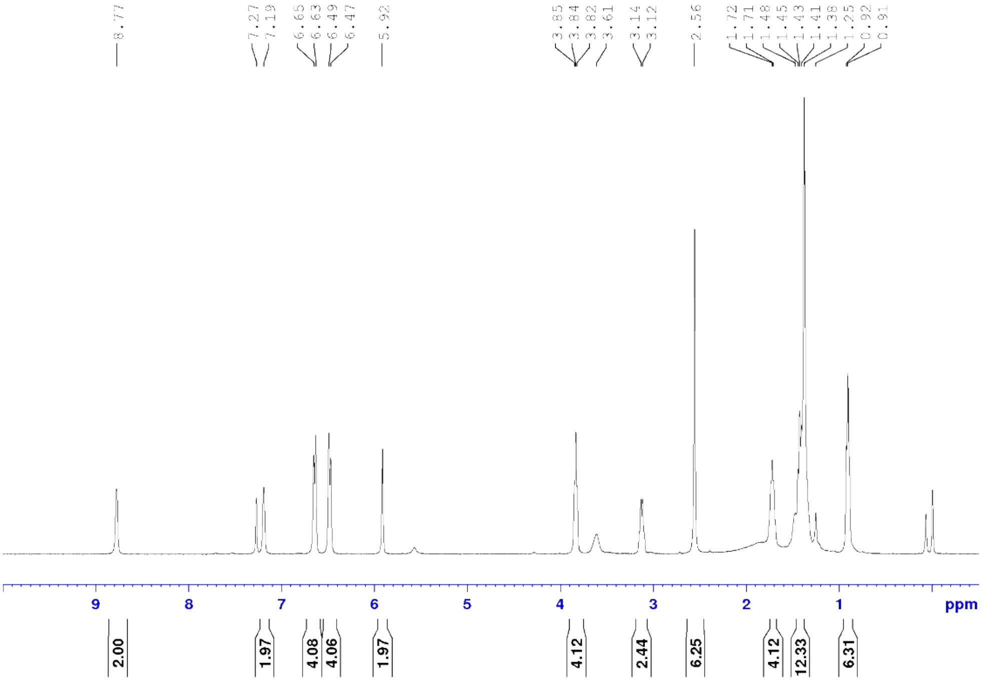

Fig. S22 ^{1}H NMR spectra of **7b** (400 MHz).

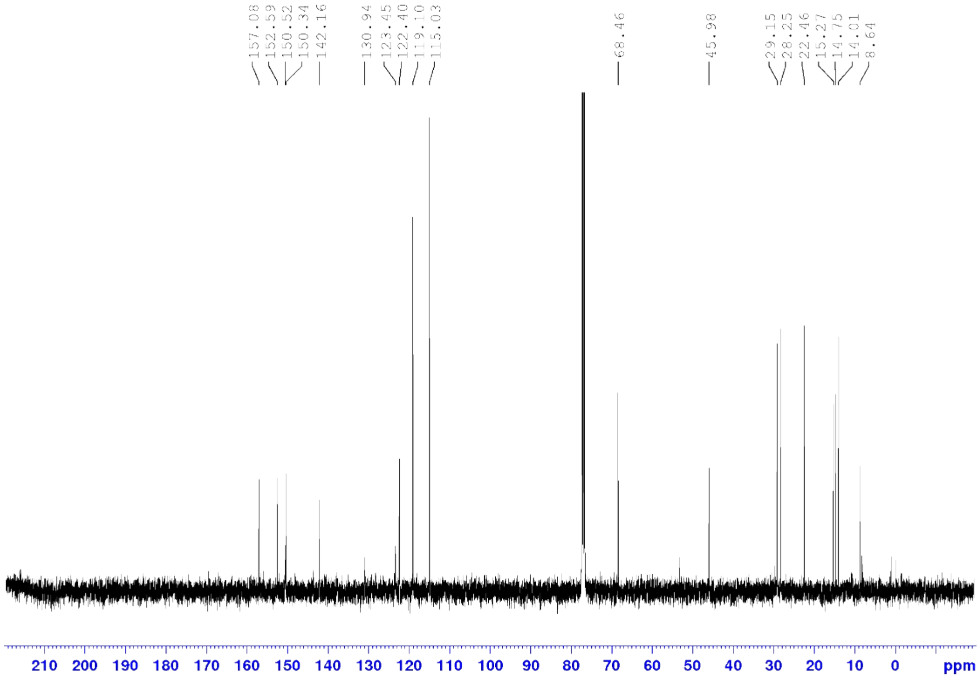

Fig. S23 ^{13}C NMR spectra of **7b** (100 MHz).

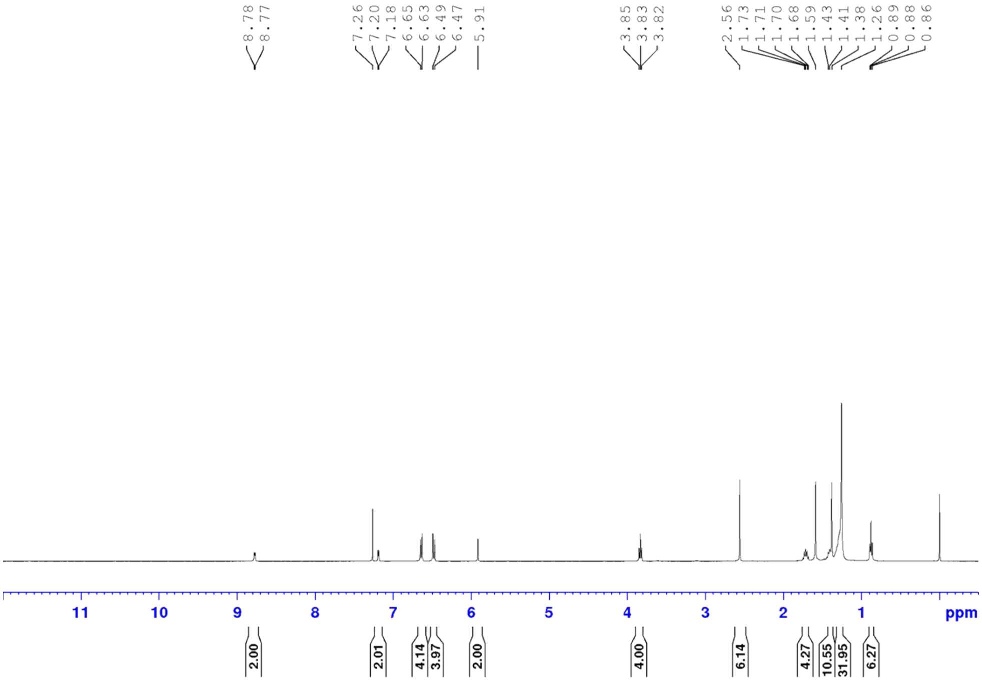

Fig. S24 ^{1}H NMR spectra of **7c** (400 MHz).

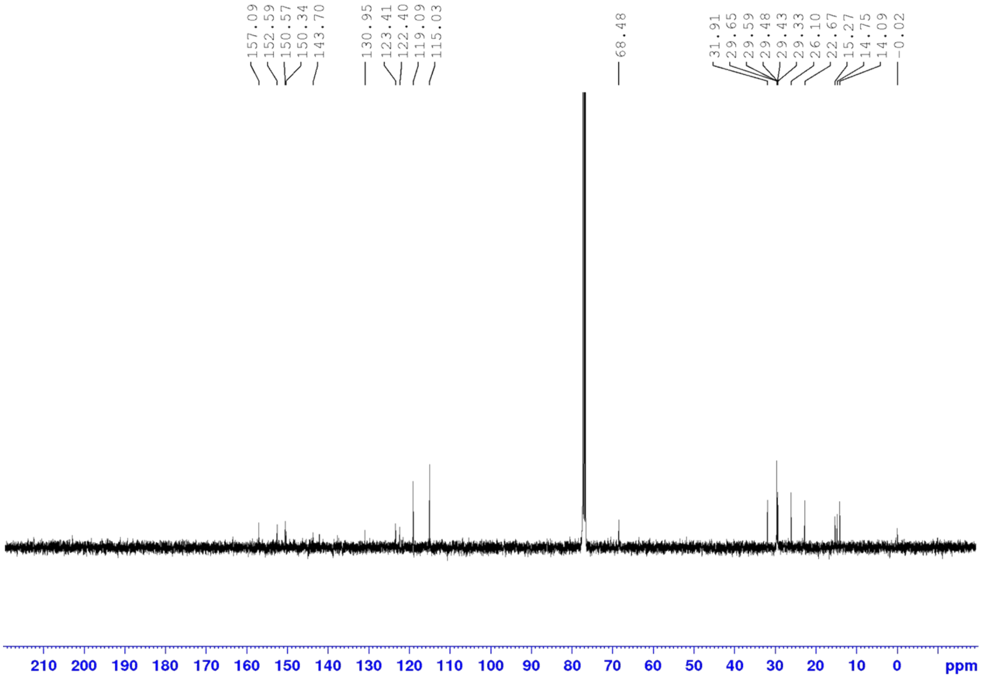

Fig. S25 ^{13}C NMR spectra of **7c** (100 MHz).