Supporting information

Highly efficient stereoscopic phenothiazine dyes with different anchors for dye-sensitized solar cells

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General information

All solvents were treated by standard methods before use and all chemicals were purchased from commercial suppliers and used without further purification unless indicated otherwise. *N*, *N*-Dimethylformamide (DMF) and tetrahydrofuran (THF) were dried and distilled from CaH_2.

The ^1H NMR spectra were recorded on a Bruker DRX NMR spectrometer with tetramethylsilane (TMS) as the internal standard.

Fabrication of DSSCs

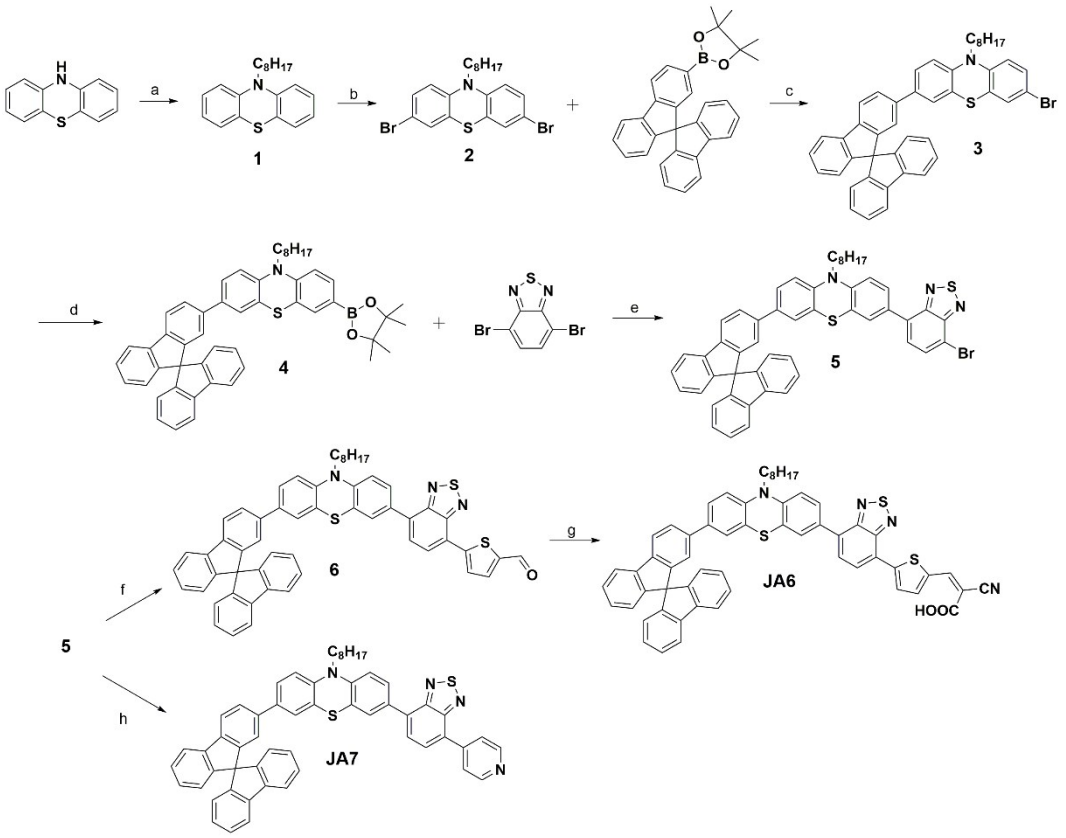
The working electrode (active area is 0.196 cm^2) was prepared by screen printing the TiO_2 paste on Fluorine-doped tin oxide (FTO) glass plates (15 Ω / square). For preparation of a DSSC, FTO glass plates were cleaned in a detergent solution using an ultrasonic bath for 30 min for two times and then rinsed with water and ethanol. Then, the plates were immersed into 40 mM $TiCl_4$ (aqueous) at 70℃ for 30 min and washed with water and ethanol. The TiO_2 paste consisted of 12 μm thick film (particle size, 20 nm, pore size 32 nm). The TiO_2 films were performed with a programmed procedure: (1) 80℃ for 15 min; (2) 135℃ for 10 min; (3) 325℃ for 30 min; (4) 375℃ for 5 min; (5) 450℃ for 15 min, and (6) 500℃ for 15 min. Then the films were treated again with $TiCl_4$ at 70℃ for 30 min and sintered at 500℃ for 30 min. Then the electrode was immersed into 0.3 mM dye (JA0, JA6 and JA7) solution (THF/EtOH=1/4) for 18 h at room temperature. The working electrode and the Pt counter electrode were then sealed with a Surlyn film (25 μm) by heating the sandwich-type cell at 110℃. The electrolyte was introduced through pre-drilled holes in the counter electrode and was driven into the cell via vacuum backfilling, and the hole was sealed with a Surlyn film and a thin glass (0.1 mm thickness) cover by heating. The electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide

(BMII), 50 mM I_2, 50 mM LiI, 0.5 M tert-butylpyridine and 0.1 M guanidiniumthiocyanate (GuNCS) in acetonitrile.

Characterizations of DSSCs

The photocurrent-voltage (*I-V*) curves of the DSSCs were measured on a Keithley 2400 source meter under standard global AM 1.5G solar irradiation supplied by a xenon light source (Oriel). The incident photo-to-electron conversion efficiency (IPCE) spectra of the DSSCs were measured by a DC method. The light source was a 300 W xenon lamp (Oriel 6258) coupled with a flux controller to improve the stability of the irradiance. The single wavelength was selected by a monochromator (Cornerstone 260 Oriel74125). Light intensity was measured by a NREL traceable Si detector (Oriel 71030NS) and the short circuit currents of the DSSCs were measured by an optical power meter (Oriel 70310).

Synthesis of the dyes



Scheme S1 synthesis procedure of **JA6** and **JA7**. Reagents and conditions: a) 1-bromooctane, NaH, DMF; b) NBS, DMF; c) $Pd(PPh_3)_4$, K_2CO_3, H_2O, 1, 4-dioxane, 90℃; d) bis(pinacolato)diboron, $Pd(dppf)Cl_2$, KOAc, DMF, 80℃; e) $Pd(PPh_3)_4$, K_2CO_3, H_2O, 1, 4-dioxane, 90℃; f) 5-formyl-2-thiopheneboronic acid, $Pd(PPh_3)_4$, K_2CO_3, H_2O, 1, 4-dioxane, 90℃; g) cyanoacetic acid, piperidine; h) pyridine-4-boronic acid, $Pd(PPh_3)_4$, K_2CO_3, H_2O, 1, 4-dioxane, 90℃.

Synthesis of compound 1

A mixture of phenothiazine (5.00 g, 25.09 mmol) in DMF (100 mL), and then add NaH (1.20 g, 30.11 mmol, 60%) in batches under an ice bath, after 30 min, the 1-bromooctane (5.81 g, 30.11 mmol) was added in drops, then the mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with H_2O (150 mL) and extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE) to give the compound 1 (6.0 g, 77%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.16-7.49 (m, 4H), 6.88-6.94 (m, 4H), 3.87 (s, 2H), 1.80-1.86 (m, 2H), 1.43-1.47 (m, 2H), 1.29-1.33 (m, 8H), 0.92 (t, J = 7.0Hz, 3H).

Synthesis of compound 2

Compound 1 (6.00 g, 19.26 mmol) was added to DMF (100 mL), and then NBS (6.86 g, 38.52 mmol) was added in one portion, the mixture was stirred for overnight reaction at room temperature. The reaction mixture was quenched with H_2O (200 mL) and extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE) to give the compound 2 (7.10 g, 79%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.23-7.28 (m, 4H), 6.69-6.70 (d, J = 8.7Hz, 2H), 3.77 (s, 2H), 1.72-1.78 (m, 2H), 1.23-1.43 (m, 10H), 0.87-0.89 (t, J = 6.9Hz, 3H).

Synthesis of compound 3

Under an nitrogen, compound 2 (7 g, 14.92 mmol), 2-borate ester-9,9'-spirobifluorene (6.6 g, 14.92 mmol), K_2CO_3 (7.1 g, 51 mmol) and $Pd(PPh_3)_4$ (0.98 g, 0.85 mmol) were dissolved in 1, 4-dioxane (100 mL) and H_2O (20 mL). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and extracted by EtOAc (3×100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA=10/1) to give the compound 3

(5.0 g, 48%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.83-7.86 (m, 4H), 7.52-7.54 (m, 1H), 7.38 (t, *J* = 7.6Hz, 3H), 7.14-7.19 (m, 4H), 7.07-7.12 (m, 3H), 6.85 (s, 1H), 6.70-6.78 (m, 4H), 6.62 (d, *J* = 8Hz, 1H), 3.72 (s, 2H), 1.67-1.74 (m, 2H), 1.23-1.37 (m, 10H), 0.84 (t, *J* = 7.2Hz, 3H).

Synthesis of compound 4

A mixture of compound 3 (2.5 g, 3.55 mmol), bis(pinacolato)diboron (1.35 g, 5.32 mmol) and KOAc (1.04 g, 10.64 mmol) in DMF (40 mL) was added $Pd(dppf)Cl_2$ (0.29 g, 0.35 mmol) under dinitrogen. The mixture was heated under 80℃ for overnight. The reaction mixture was cooled to room temperature and H_2O (150 mL) was added, the mixture was extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA=10/1) to give the compound 4 (2 g, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.84-7.90 (m, 4H), 7.47-7.59 (m, 2H), 7.40 (t, *J* = 6.9Hz, 2H), 7.10-7.20 (m, 4H), 6.92-7.06 (m, 3H), 6.89 (s, 1H), 6.73-6.83 (m, 5H), 3.81 (t, *J* = 6.3Hz, 2H), 1.74-1.78 (m, 2H), 1.26-1.46 (m, 22H), 0.85-0.91 (m, 3H).

Synthesis of compound 5

Under an nitrogen, compound 4 (3.0 g, 3.99 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (1.17 g, 3.99 mmol), K_2CO_3 (7.1 g, 51 mmol) and $Pd(PPh_3)_4$ (0.32 g, 0.28 mmol) were dissolved in 1, 4-dioxane (100 mL) and H_2O (20 mL). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/DCM=4/1) to give the compound 5 (1.64 g, 49%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.85-7.91 (m, 5H), 7.71-7.74 (m, 1H), 7.63-7.64 (m, 1H), 7.57-7.57 (m, 1H), 7.46-7.49 (m, 1H), 7.37-7.40 (m, 3H), 6.92-6.95 (m, 2H), 6.74-6.81 (m, 4H), 3.85 (s, 2H), 1.79-1.84 (m, 2H), 1.43-1.47 (m, 2H), 1.27-1.29 (m, 8H), 0.86-0.91 (m, 3H).

Synthesis of compound 6

Under an nitrogen, compound 5 (1 g, 1.19 mmol), 5-formyl-2-thiopheneboronic acid (0.28 g, 1.19 mmol), K_2CO_3 (0.50 g, 3.58 mmol) and $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol) were dissolved in 1, 4-dioxane (50 mL) and H_2O (10 mL). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and extracted by DCM (3×20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/DCM=4/1) to give the compound 6 as a red solid (0.73 g, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 9.98 (s, 1H), 8.16-8.17 (d, *J* = 3.6Hz, 1H), 7.96-7.99 (d, *J* = 7.2Hz, 1H), 7.86-7.91 (m, 4H), 7.82-7.83 (m, 2H), 7.71 (s, 1H), 7.56-7.65 (m, 2H), 7.38-7.42 (m, 3H), 7.11-7.21 (m, 5H), 6.91 (s, 2H), 6.74-6.82 (m, 4H), 3.88 (s, 2H), 1.73-1.89 (m, 2H), 1.27-1.41 (m, 10H), 0.83-0.91 (m, 3H).

Synthesis of JA6

To a flask containing compound 6 (200 mg, 0.23 mmol) and cyanoacetic acid (39 mg, 0.46 mmol) was added acetonitrile (5.0 mL), piperidine (a drop) and THF (2.0 mL), and the solution was heated at 90℃ for 24 h. The solution was added 1 M HCl solution to quench the reaction. The reaction mixture was then extracted with DCM and H_2O. The organic extracts were collected, dehydrated with anhydrous MgSO4, and filtered, evaporated in vacuo. The residue was purified by silica gel column chromatography (DCM/MeOH=20/1) to give JA 6 as a deep red solid (130 mg, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.27 (s, 1H), 8.13 (s, 1H), 7.83-7.87 (m, 6H), 7.65-7.68 (m, 1H), 7.61 (s, 1H), 7.52-7.55 (m, 2H), 7.35-7.38 (m, 3H), 7.09-7.14 (m, 5H), 6.87 (s, 1H), 6.72-6.78 (m, 4H), 6.64-6.67 (m, 1H), 3.71 (s, 2H), 1.69-1.74 (m, 2H), 1.19-1.23 (m, 8H), 0.82-0.86 (m, 3H).

Synthesis of JA7

Under an nitrogen, compound 5 (200 mg, 0.24 mmol), Pyridine-4-boronic acid (58 mg, 0.48 mmol), K_2CO_3 (0.1 g, 0.72 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol) were dissolved in 1, 4-dioxane (30 mL) and H_2O (5 mL). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and

extracted by DCM (3×20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (DCM/MeOH=50/1) to give JA7 as a red solid (150 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.78-8.79 (d, *J* = 6.0Hz, 2H), 8.23 (s, 1H), 7.96-7.98 (m, 1H), 7.86-7.89 (m, 2H), 7.83-7.84 (m, 1H), 7.78-7.80 (d, *J* = 7.6Hz, 1H), 7.74-7.75 (d, *J* = 2.4Hz, 2H), 7.65-7.70 (m, 2H), 7.52-7.58 (m, 2H), 7.44-7.48 (m, 2H), 7.35-7.39 (m, 3H), 7.21-7.23 (m, 1H), 7.09-7.13 (m, 3H), 6.97-7.00 (m, 1H), 6.87-6.88 (d, *J* = 1.6Hz, 2H)，6.71-6.82 (m, 3H), 3.85-3.89 (d, *J* = 7.2Hz, 2H), 1.78-1.86 (m, 2H), 1.40-1.44 (m, 2H), 1.25-1.37 (m, 8H), 0.83-0.90 (m, 3H).

Table S1 Optical and electrochemical properties of dyes

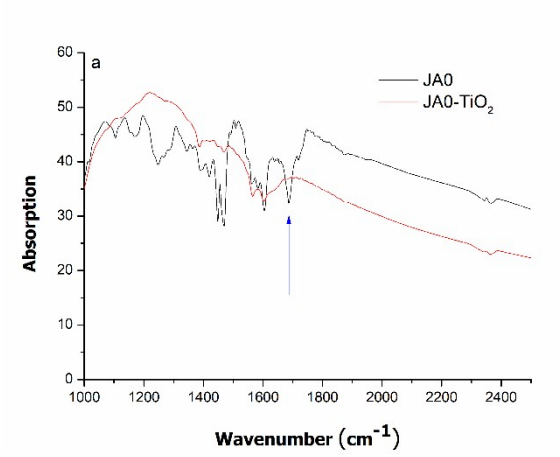
Dye	[a]λ_{max}/nm ($\varepsilon\times10^4$ M^{-1} cm^{-1})	[b]E_{OX}/V (NHE)	[c]$E_{0\text{-}0}$/eV	[d]E^*_{OX}/V (NHE)
JA0	452 (1.08)	0.98	2.10	-1.12
JA6	508 (1.02)	0.95	1.82	-0.87
JA7	454 (0.67)	1.04	2.06	-1.02

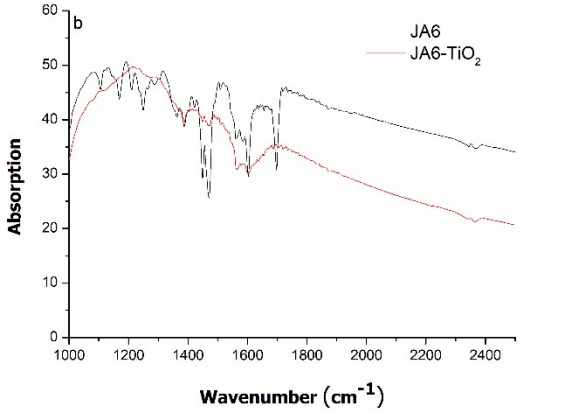
[a]Absorption maximum in DCM solution (1×10^{-5} M), [b]the ground state oxidation potentials, [c]$E_{0\text{-}0}$ was estimated from the absorption spectra, [d]E^*_{OX} was calculated by the formula: $E^*_{OX} = E_{OX}\text{-}E_{0\text{-}0}$.

Table S2 Photovoltaic parameters of the DSSCs obtained from the J-V curves

Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	η (%)
[a] JA0	12.32	0.840	64.63	6.69
[b] JA6	13.93	0.800	65.83	7.34
[b] JA7	7.32	0.615	67.94	3.05

[a]The DSSC based on JA0 was reported in ref. 50, [b]The size of the active area for each cell is 0.196 cm^2, the DSSCs were all measured under standard global AM 1.5G solar irradiation.





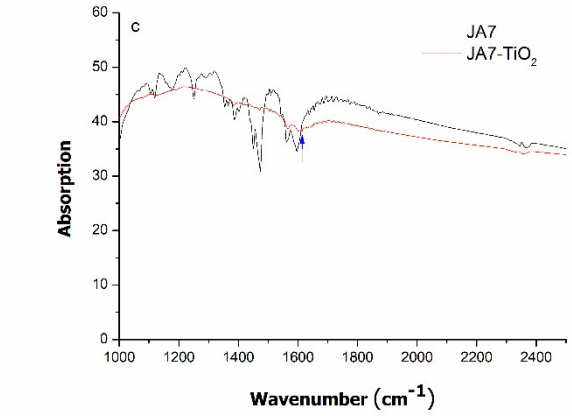


Fig. S1 FTIR spectra of dye powders (black line) and dyes adsorbed on TiO_2 nanoparticles (red

line)

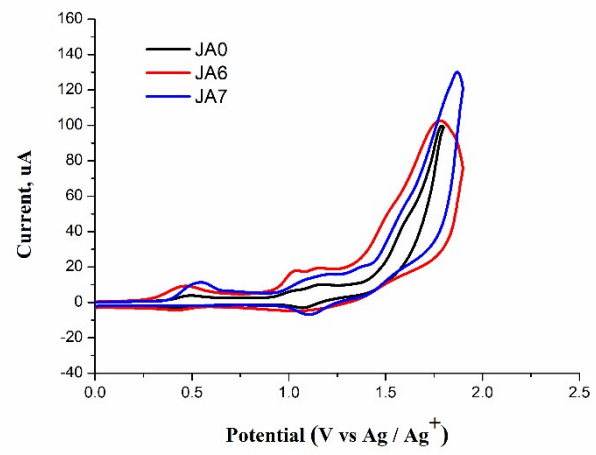


Fig. S2 Cyclic voltammogram of **JA0**, **JA6** and **JA7** in DCM, 0.1 M $TBAPF_6$, glassy carbon electrode as working electrode, Pt as counter electrode, Ag/Ag^+ as reference electrode, scan rate: 100 mV s^{-1}, calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an external reference.

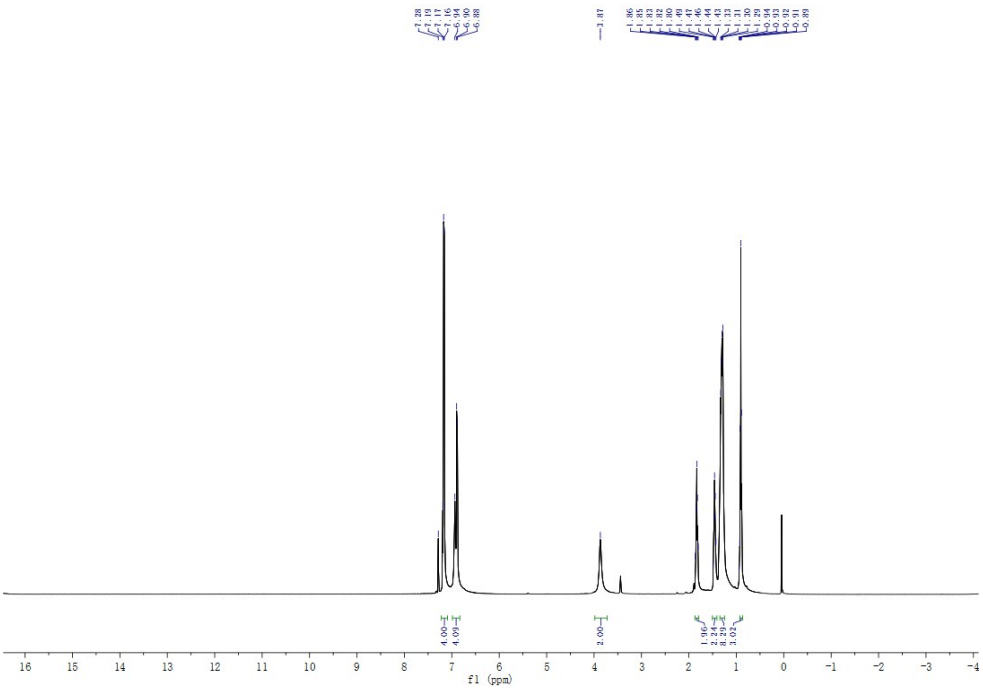


Fig. S3 ^{1}H NMR of compound 1 ($CDCl_3$)

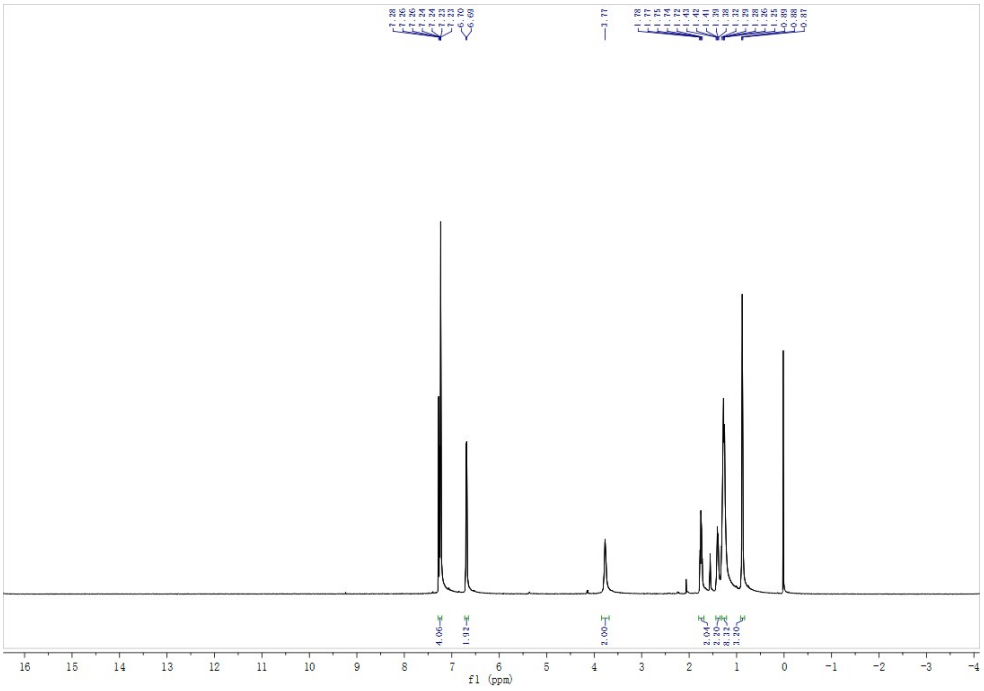


Fig. S4 ^{1}H NMR of compound 2 ($CDCl_3$)

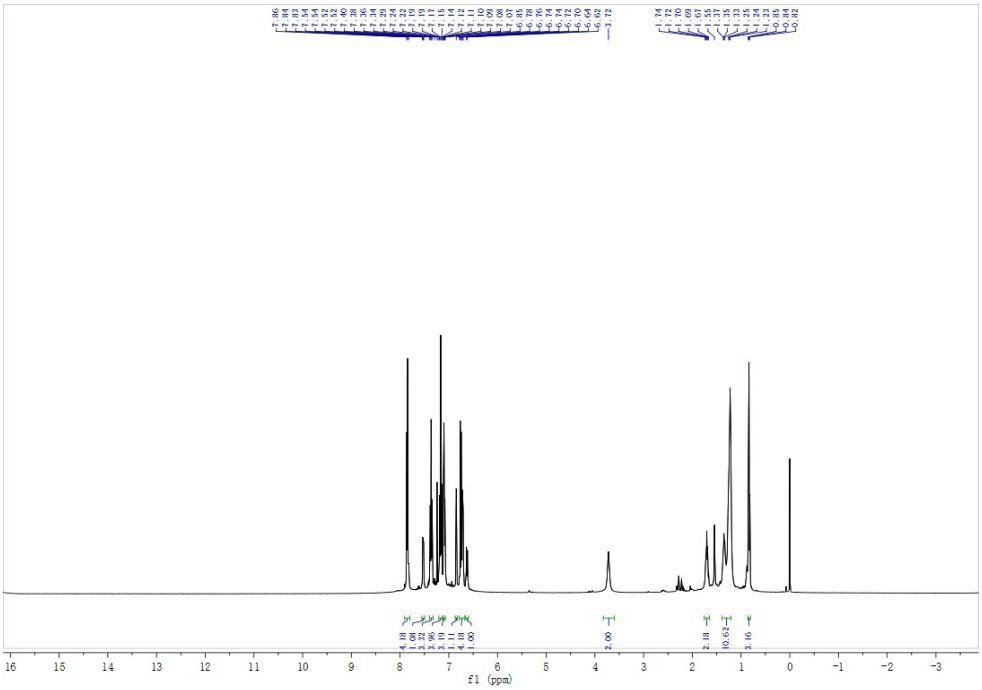


Fig. S5 ^{1}H NMR of compound 3 ($CDCl_3$)

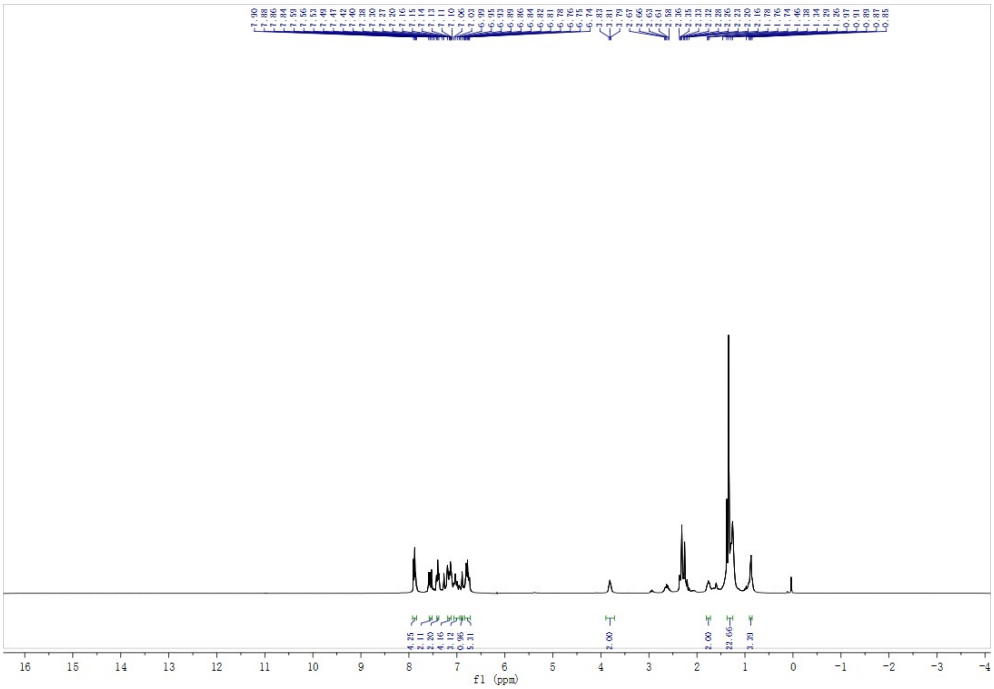


Fig. S6 ^{1}H NMR of compound 4 ($CDCl_3$)

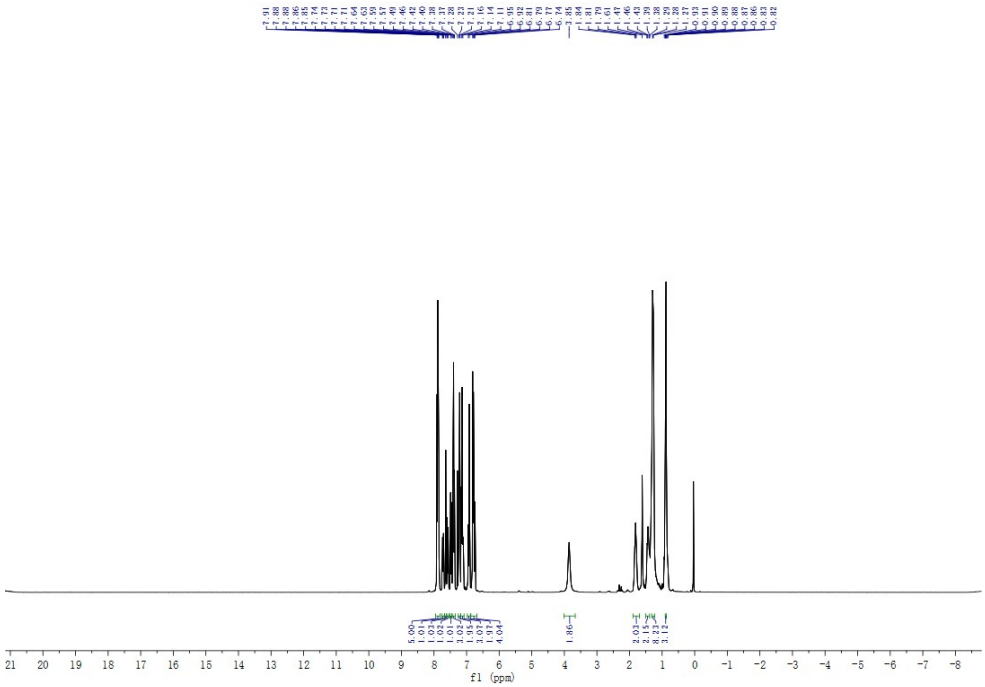


Fig. S7 ^{1}H NMR of compound 5 ($CDCl_3$)

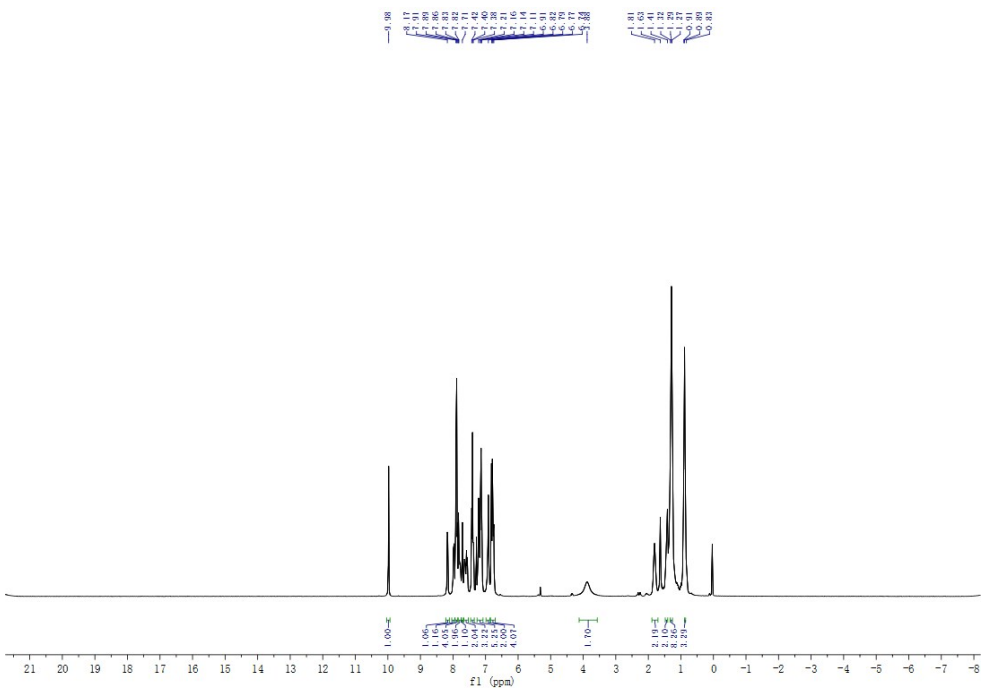


Fig. S8 ^{1}H NMR of compound 6 ($CDCl_3$)

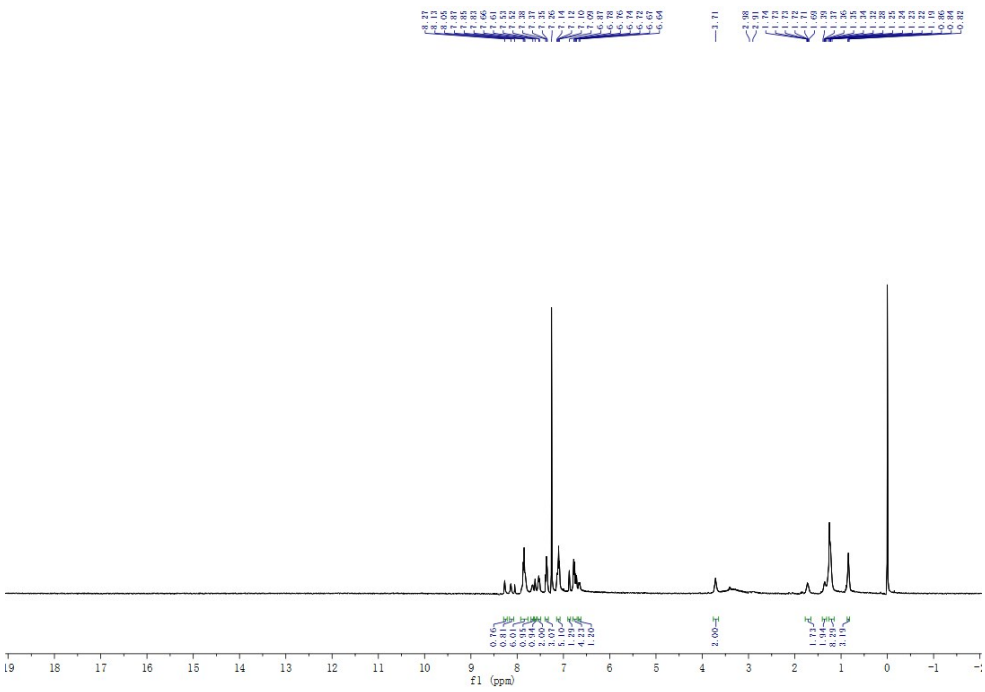


Fig. S9 ^{1}H NMR of JA6 ($CDCl_3$)

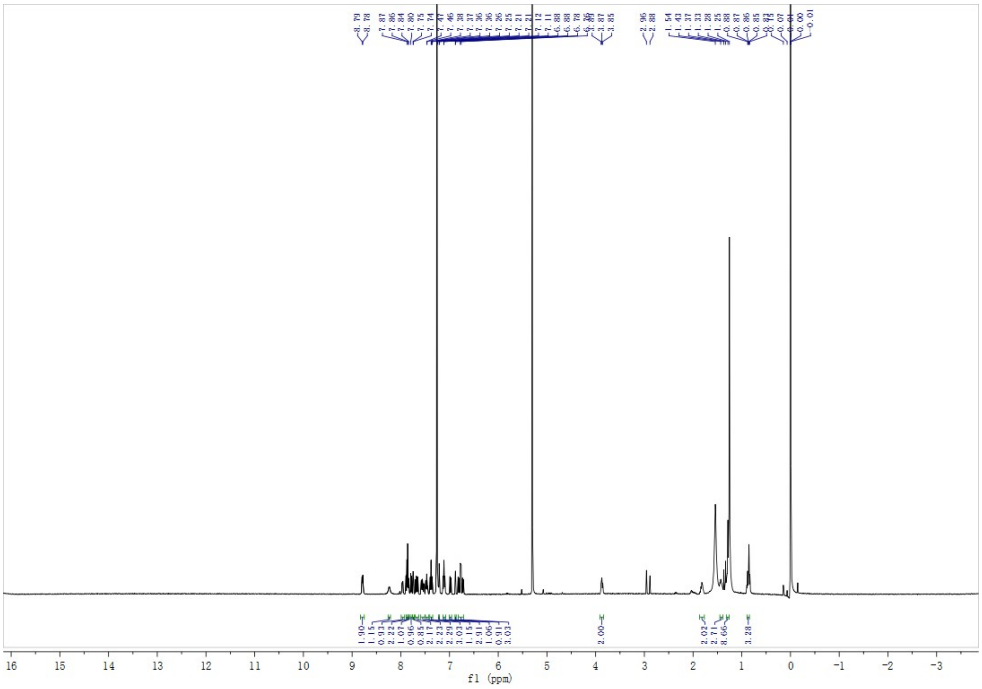


Fig. S10 ^{1}H NMR of JA7 ($CDCl_3$)