

Electronic Supplementary Information

Synthesis of diarylethene covalently bonded boron-dipyrromethene for building a stable photosensitizer with photo-controlled reversibility

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1. Experimental details

1.1 Materials and reagents

All reagents were of the highest available purity and of analytical grade at least. Thiophene-2-carboxaldehyde, 4-bromoacetophenone, ammonium acetate, nitromethane, diethylamine, diisopropylethylamine, phosphine oxychloride, 2-methyl indole, NBS, 5 - methyl - 2 thiophene aldehyde were obtained from Alfa Aesar Ltd., methyl iodide, butyl lithium, triethyl orthoformate and hydroxylamine hydrochloride were obtained from J&K Chemical, sodium hydride, lithium aluminum hydride, boron trifluoride-ether complex and octafluorocyclopentene were obtained from TCI (Shanghai) Development Co., Ltd., methanol, ethanol, petroleum ether, tetrahydrofuran, acetonitrile, dichloromethane, acetone, DMSO and N,N-dimethylformamide were obtained from Concord Chemical Research Institute (Tianjin, China). HCl, KOH and NaOH were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China).

1.2 Characterization

Fourier transform infrared (FT-IR) spectra ($4000\text{-}400\text{ cm}^{-1}$) were collected on a Magna-560 spectrometer (Nicolet, Madison, WI). ^1H -nuclear magnetic resonance (NMR) spectra were recorded on an AV400 NMR spectrometer (Bruker, Switzerland) and Mercury Vx-300 (Varian, USA). Mass spectra were recorded on VG ZAB-HS mass spectrometer (VG Instruments, UK), Varian 7.0T FTMS (Varian, USA) and AutoflexIII LRF200-CID mass spectrometer (Bruker Daltonics, Germany). Absorption spectra were recorded on a UV-3600 UV-vis-NIR spectrophotometer (Shimadzu, Tokyo, Japan). Fluorescence spectra, absolute fluorescence quantum yield and lifetime were measured with a PTI QM/TM/NIR fluorescence spectrometer (Birmingham, NJ, USA). 670 nm light used a DS3-21312-101 Laser Device (0-0.56 amp) (BWT, Beijing, China). 600-900 nm light is achieved by infrared quartz lamp (250 W) with a 600 nm glass cut off filter (Schott).

1.3 Quantification of singlet oxygen generation

The singlet oxygen quantum yield (Φ_{Δ}) is achieved by using the chemical trapping method with DPBF probe. The Φ_{Δ} value was obtained by using methylene blue as the

reference and calculated by using eq. 2:

$$\Phi_{\Delta} = \Phi_{\Delta}^{MB} \cdot \frac{k}{k^{MB}} \cdot \frac{I_a^{MB}}{I_a} \dots\dots\dots (\text{eq. 1})$$

where Φ_{Δ}^{MB} is the singlet oxygen quantum yield for methylene blue (0.52); k and k^{MB} are the DPBF photobleaching rate constants in the presence of sample and methylene blue, respectively; I_a and I_a^{MB} are the rates of light absorption at the irradiation wavelength by sample and methylene blue, respectively.^{1,2}

1.4 Fatigue resistance test of the BODIPY-DAE

5 μmol BODIPY-DAE was dissolved in 10 mL acetonitrile. The open form of the BODIPY-DAE was obtained with 10 min irradiation with 600-900 nm infrared lamp, while the close form of the BODIPY-DAE was obtained with 10 min irradiation of 365 nm UV light. The absorbance (A) is recorded on a UV/vis spectrophotometer.

1.5 Measurement of reversible photosensitivity of BODIPY-DAE

Acetonitrile as the solvent was bubbled with air for 30 min before measurement to ensure the oxygen dissolved in acetonitrile is enough for the BODIPY-DAE to consume during measurement. 3 ml of 34 μM DPBF in acetonitrile were treated with 5 μmol of the close form of BODIPY-DAE obtained via 15-min irradiation with 365 nm light and the open form of BODIPY-DAE obtained via 20-min irradiation with 600-900 nm light, respectively.³ The absorbance of DPBF at 410 nm under 670 nm laser light irradiation was measured every 10 seconds.

1.6 Photocatalyst oxidation of DHN

DHN (1.5×10^{-4} M) and the open form of BODIPY-DAE (5 mol% vs. DHN, obtained via 20-min irradiation with 600-900 nm light) was added into dichloromethane-methanol (9:1, v/v) in a 25 mL round bottom flask. The solution was then irradiated with a 600-900 nm infrared lamp. UV/Vis spectra were recorded every 2 minutes. The consumption of DHN was monitored via the decrease of the UV absorbance at 298 nm, 316 nm and 331nm. The production of juglone was monitored via an increase in the absorbance at 425 nm.

1.7 Synthesis section

All reagents were achieved from commercial suppliers and used without further purification unless otherwise indicated. Air and moisture-sensitive reactions were carried out in a Schlenk vessel under argon or nitrogen atmosphere.

Synthesis of **1**. In a 500 mL three-necked round-bottomed flask thiophene-2-carboxaldehyde (6.72 g, 5.6 mL, 60 mmol, 1.2 eq.) and 4-bromoacetophenone (10.0 g, 50.2 mmol, 1 eq.) dissolved in 250 mL methanol were added. After cooling the mixture solution to 0 °C, an aqueous potassium hydroxide solution (150 mL, 2.5 M) was added dropwise under magnetic stirring. Then, the solution was warmed to room temperature and stirred overnight. After cooling down to 0 °C, the mixture was filtrated and the resulting solid was washed with petroleum ether for 3 times. The crude product was recrystallized in ethanol to yield a light yellow solid (11.70 g, 80%). ¹H NMR (400 MHz CDCl₃) δ: 7.95 (d, *J* = 16 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 4.0 Hz, 1H), 7.38 (d, *J* = 4.0 Hz, 1H), 7.27 (d, *J* = 16 Hz, 1H), 7.11-7.09 (m, 1H); ¹³C NMR (75 MHz CDCl₃) δ: 187.63, 139.70, 137.09, 136.44, 131.65, 131.42, 129.42, 128.54, 127.92, 127.35, 120.00; HRMS (ESI) *m/z* : calcd for: 291.9557, found: 292.9633 [M+H]⁺.

Synthesis of **2**. Nitromethane (6.5 g, 5.6 mL, 102 mmol, 5 eq.), **1** (6.1 g, 20.5 mmol, 1 eq.) and diethylamine (7.5 g, 11 mL, 100 mmol, 5 eq.) were dissolved in methanol (150 mL) and transferred to a 500 mL three-necked round-bottomed flask heated with oil bath until reflux overnight. After cooling down the solution with ice bath to 0 °C, an aqueous solution of hydrochloric acid (2.5 M) was added dropwise until pH 2-3. The solvent methanol was evaporated under reduced pressure and the crude product was dissolved with 150 mL dichloromethane. The organic layer was washed with brine and water, then dried over sodium sulfate and the solvent was evaporated. The crude residue was purified by column chromatography on silica gel (petroleum ether / ether (5/1 v/v)) to get a dark yellow oil (5.3 g, 68%). ¹H NMR (400 MHz CDCl₃) δ: 7.79 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 4.0 Hz, 1H), 6.96-6.93 (m, 2H), 4.85-4.80 (m, 1H), 4.73-4.68 (m, 1H), 4.57-4.50 (m, 1H), 3.47 (t, *J* = 8.0 Hz, 2H); ¹³C NMR (75 MHz CDCl₃) δ: 194.35, 141.10, 134.58, 131.57, 129.01, 128.39, 126.67, 125.11, 124.28, 79.70, 42.61, 35.21; HRMS (ESI) *m/z* : calcd

for: 352.9721, found: 353.9803 [M+H]⁺.

Synthesis of **3**. Ammonium acetate was sublimated under vacuum (7.6 g, 98 mmol, 35 eq.) in a Schlenk vessel. **2** (1.2 g, 2.8 mmol, 1 eq.) and 35 mL anhydrous ethanol was added under argon protection. The solution was heated to reflux for 48 h. The solution was cooled to room temperature and concentrated to half, after cooled to 0 °C the mixture was vacuum filtered. The residue was washed with 3 × 5 mL hexane to afford a dark blue solid **3** (0.24 g, 26 %). ¹H NMR (400 MHz DMSO-d₆) δ: 7.98 (d, *J* = 8.0 Hz, 4H), 7.89 (d, *J* = 4.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 4H), 7.74 (d, *J* = 4.0 Hz, 2H), 7.58 (s, 2H), 7.23-7.21 (m, 2H); HRMS (MALDI) *m/z* : calcd for: 618.921, found: 619.954 [M+H]⁺.

Synthesis of **4**. **3** (1.0 g, 1.6 mmol, 1 eq.) in anhydrous dichloromethane (120 mL) was added in a 250 mL flask in a Schlenk vessel. The mixture was stirred at 0 °C for 20 min and then diisopropylethylamine (1.9 g, 2.4 mL, 15 mmol, 10 eq.) was added dropwise. The mixture solution was kept stirring for 30 min and then boron trifluoride-ether complex (6.4 g, 5.6 mL, 45 mmol, 30 eq.) was added. The solution was stirred at room temperature for 50 h under argon and the solution was washed with 3 × 60 mL brine and water. The organic layer was dried over sodium sulfate and the dichloromethane was evaporated. The crude product was purified by column chromatography on silica gel (petroleum ether / ethyl acetate (4/1 v/v)) to afford a dark blue solid which shinning red with sunshine (0.38g, 35%). ¹H NMR (400 MHz CDCl₃) δ: 7.91 (d, *J* = 4.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 4H), 7.63-7.58 (m, 6H), 7.21-7.19 (m, 2H), 6.87 (s, 2H); ¹³C NMR (75 MHz CDCl₃) δ: 158.14, 145.08, 138.72, 134.62, 131.86, 130.88, 130.55, 129.98, 128.34, 125.85, 116.63; HRMS (MALDI) *m/z* : calcd for: 666.920, found: 666.930 [M]⁺.

Synthesis of **5**. **4** (1.0g, 1.5 mmol, 1 eq.) was dissolved in anhydrous dichloromethane (20 mL) in a 25 mL round bottom flask, and cooled to 0 °C in an ice bath. Anhydrous dimethyl formamide (0.94g, 13 mmol, 1.0 mL, 8 eq.) was added dropwise under magnetic stirring. Then, phosphine oxychloride (1.9 g, 13 mmol, 1.1 mL, 8 eq.) in anhydrous dichloromethane (5 mL) was slowly added through a constant pressure funnel. The solution was warmed to room temperature and refluxed

at 35 °C overnight. The mixture was poured to 200 mL 0 °C saturated sodium acetate solution and stirred for 6 h. The organic layer was washed with 2 × 60 mL saturated sodium bicarbonate solution, 3 × 60 mL brine and water. The organic layer was dried over sodium sulfate and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (petroleum ether / ethyl acetate (3/1 v/v)) to afford a blue solid (0.47 g, 45%). ¹H NMR (400 MHz CDCl₃) δ: 9.71 (s, 1H), 8.49 (d, *J* = 4.0 Hz, 1H), 8.09 (d, *J* = 4.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 4.0 Hz, 1H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.65-7.61 (m, 4H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.29-7.27 (m, 1H), 7.25-7.23 (m, 1H), 7.00 (s, 1H); HRMS (MALDI) *m/z* : calcd for: 694.915, found: 675.976 [M-F]⁺, 694.979 [M]⁺.⁴

Synthesis of **6. 5** (0.86g, 1.2 mmol, 1 eq.) was dissolved in tetrahydrofuran (50 mL) in a 200 mL round bottom flask, then NBS (2.2 g, 12 mmol, 10 eq.) in tetrahydrofuran (40 mL) in a constant pressure funnel was added dropwise. The mixture was stirred and kept away from light at room temperature for 15 h. The organic layer was mixed with 150 mL dichloromethane and washed with 2 × 50 mL saturated sodium thiosulfate solution, 3 × 50 mL brine and water, dried over magnesium sulfate and then the solvent was evaporated. The crude product was purified by column chromatography on silica gel (petroleum ether / dichloromethane / ethyl acetate (10/2/1 v/v/v)) to afford a blue solid (0.85 g, 76%). ¹H NMR (400 MHz CDCl₃) δ: 9.61 (s, 1H), 8.44-8.43 (m, 1H), 7.87 (t, *J* = 8.0 Hz, 2H), 7.72-7.71 (m, 1H), 7.64 (t, *J* = 8.0 Hz, 4H), 7.54-7.51 (m, 2H), 7.29 (d, *J* = 3.6 Hz, 1H), 7.23 (d, *J* = 4.0 Hz, 1H); HRMS (MALDI) *m/z* : calcd for: 932.642, found: 913.619 [M-F]⁺, 932.638 [M]⁺.

Synthesis of **7. 2-methyl indole** (4.0 g, 30 mmol), NBS (5.4 g, 30 mmol) and silica gel (800 mg) were added to 40 mL dichloromethane in a 200 mL round bottom flask and stirred at room temperature under nitrogen protection for 1 h. The organic layer was washed by 2 × 50 mL brine and water and the solvent was evaporated. The crude product dissolved in 50 mL anhydrous tetrahydrofuran in a 250 mL round bottom flask. Sodium hydride (1.44 g, 60 mmol) was slowly added under nitrogen atmosphere and stirred at room temperature for 30 min. Methyl iodide (6.4 g, 2.8 mL,

45 mmol) was added through a syringe and kept stirring overnight. The mixture was washed by 2 × 50 mL brine and water and the solvent was evaporated. Solid crude product was purified by column chromatography on silica gel (petroleum ether / ethyl acetate (5/1 v/v)) to afford a white solid. In a Schlenk vessel 6.72 g white solid was dissolved in 70 mL anhydrous tetrahydrofuran and cooled to -78 °C by liquid nitrogen-acetone system and stirred for 30 min. 20 mL 1.6 M butyl lithium was added through a syringe dropwise and kept stirring for 30 min under nitrogen atmosphere. Then octafluorocyclopentene (9.48g, 6.05 mL, 45 mmol) was added and the reaction mixture was stirred at room temperature overnight. The crude mixture was quenched with 5 ml ethanol and stirred for 10 min and filtered. The filtrate was washed by 2 × 50 mL brine and water and then purified by column chromatography on silica gel (petroleum ether / ethyl acetate (10/1 v/v)) to give **7** as a dark yellow solid (7.49 g, 74 %). ¹H NMR (400 MHz CDCl₃) δ: 7.60 (d, *J*=8.0 Hz, 1H), 7.34 (d, *J*=8.0 Hz, 1H), 7.28 (t, *J*=7.6 Hz, 1H), 7.21 (t, *J*=7.6 Hz, 1H), 3.75 (s, 3H), 2.41 (s, 3H).

Synthesis of **8**. 50 ml glacial acetic acid was added to 5-methyl-2-thiophene aldehyde (10 g, 0.08 mol) in a tinfoil covered 250 mL round bottom flask and stirred for 10 min at room temperature. Liquid bromine (15.5g, 5 mL, 0.09 mol) in 25 mL glacial acetic acid was added dropwise using a constant pressure funnel and stirred overnight. The crude solution poured to 0 °C saturated sodium bicarbonate solution under vigorous stirring and use potassium carbonate to adjust to pH 7. The turbid liquid was filtered under vacuum and the residue was washed with 10 mL ice water and 10 mL petroleum ether to afford an orange solid (10.71 g, 66 %). The orange solid (10.71 g), triethyl orthoformate (45 mL), p-toluenesulfonic acid (100 mg) and ethanol (150 mL) were dissolved in a 250 mL round bottom flask and stirred under nitrogen atmosphere for 24 h. Anhydrous potassium carbonate (500 mg) was added to the solution and stirred for 15 min. The ethanol was evaporated and the organic layer was washed by 3 × 50 mL brine and water and purified by column chromatography on neutral alumina (petroleum ether / ethyl acetate (15/1 v/v)) to afford a light yellow oil (13.11 g, 90 %). The yellow oil (1.2 g, 4.4 mmol) was dissolved in 20 mL anhydrous tetrahydrofuran and cooled to -78 °C by liquid nitrogen-acetone system

and stirred for 30 min. 1.6 M butyl lithium (3.4 mL, 5.4 mmol) was added dropwise through a syringe and kept stirring for 30 min under nitrogen atmosphere. **7** (1.5 g, 4.4 mmol) was quickly added and kept reacting at -78 °C for 2 h and then warmed to room temperature. 400 mg p-toluenesulfonic acid, several drops of 10 % hydrochloric acid and 4 ml water were added to the mixture solution, and stirred at 35 °C for 24 h. After the tetrahydrofuran was evaporated, the crude product was extracted with 100 mL dichloromethane and washed by 3 × 50 mL water. The organic layer was dried over sodium sulfate, then purified by column chromatography on silica gel (petroleum ether / ethyl acetate (first 10/1, then 9/1, last 3/1 v/v)) to give a white solid which turn green with sunlight irradiation (1.2 g, 64 %). ¹H NMR (400 MHz CDCl₃) δ: 9.84 (s, 1H), 7.82 (s, 1H), 7.54 (d, *J*=8.0 Hz, 1H), 7.29 (d, *J*=8.0 Hz, 1H), 7.24 (d, *J*=8.4 Hz, 1H), 7.14 (t, *J*=7.6 Hz, 1H) 3.64 (s, 3H), 2.00 (s, 3H), 1.87 (s, 3H); ¹³C NMR (100 MHz CDCl₃) δ: 181.17, 150.59, 140.24, 138.15, 136.80, 136.09, 135.83, 126.48, 124.22, 121.29, 120.26, 118.38, 118.34, 118.29, 115.55, 115.30, 108.32, 99.57, 29.03, 14.57, 10.45.

Synthesis of **9. 8** (0.44 g, 1.0 mmol) was mixed with hydroxylamine hydrochloride (0.28 g, 4.1 mmol) and dimethylsulfoxide (15 mL) in a 100 mL round bottom flask. The mixture was heated at 100 °C for 4 h. After cooling to room temperature, the mixture was put into 100 mL dichloromethane and washed with 5 × 80 mL brine and water. The organic layer was dried over magnesium sulfate and purified by column chromatography on silica gel (petroleum ether / ethyl acetate (3/1 v/v)) to afford a light blue solid (0.26 g, 59 %). ¹H NMR (400 MHz CDCl₃) δ: 7.66 (s, 1H), 7.48 (d, *J*=8.0 Hz, 1H), 7.29 (d, *J*=8.0 Hz, 1H), 7.23 (d, *J*=8.0 Hz, 1H), 7.15 (t, *J*=8.0 Hz, 1H), 3.66 (s, 3H), 2.02 (s, 3H), 1.87 (s, 3H); ¹³C NMR (100 MHz CDCl₃) δ: 168.06, 147.36, 140.20, 136.79, 136.10, 134.16, 125.85, 124.13, 121.38, 120.33, 118.22, 115.16, 112.42, 108.38, 106.51, 101.74, 99.34, 29.07, 13.76, 10.48; HRMS (MALDI) *m/z* : calcd for: 440.0782, found: 440.0775 [M]⁺.

Synthesis of **10**. LiAlH₄ (0.14 g, 3.8 mmol) was dissolved in 20 mL anhydrous tetrahydrofuran and cooled to 0 °C on an ice bath in a Schlenk vessel. Under nitrogen protection, **9** (0.44g, 1.0 mmol) in 10 mL anhydrous tetrahydrofuran was slowly

added. The mixture was stirred for 4 h and then warm to room temperature. After cooling in an ice bath, 1 mL water was added to the mixture slowly, then 2 mL of 1 mol l⁻¹ NaOH was put into the mixture. The mix solution was vacuum filtered with Celite and the filtrate was evaporated. The residue was purified by column chromatography on silica gel (dichloromethane / methanol / ammonium hydroxide (80/17/ 3 v/v/v)) to afford a yellow oil (0.32 g, 73 %). The yellow oil (0.13 g, 0.28 mmol) and **6** (0.23 g, 0.25 mmol) was dissolved in 50 mL methanol under argon atmosphere. The solution was mixed with 0.1 g 4A molecular sieves and 0.3 mL glacial acetic acid, under hard stirring the mixture was heated at 60 °C for 16 h. After cooling to room temperature the solution was poured to 50 mL tetrahydrofuran and filtered. The filtrate was evaporated and the crude residue was purified by column chromatography on neutral alumina (dichloromethane / methanol (95/5 v/v)) and recrystallized in cold petroleum ether / dichloromethane (9/1 v/v) twice to give a dark blue solid (0.19 g, 57 %). ¹H NMR (400 MHz DMSO-d₆) δ: 8.79 (s, 1H), 8.18 (s, 1H), 7.73-7.70 (m, 3H), 7.68-7.65 (m, 3H), 7.51 (d, *J* =8.0 Hz, 1H), 7.41-7.36 (m, 5H), 7.26 (d, *J* =2.4 Hz, 1H), 7.24 (d, *J* =2.8 Hz, 1H), 7.20 (t, *J* =8.0 Hz, 1H), 7.09 (t, *J* =8.0 Hz, 1H), 5.14 (s, 2H), 3.68 (s, 3H), 2.03 (s, 3H), 1.82 (s, 3H); HRMS (MALDI) *m/z* : calcd for: 1358.742, found: 1358.756 [M]⁺.

2. Supplementary data

2.1 Figures of ¹H NMR, ¹³C NMR and mass spectra

Compound **1**

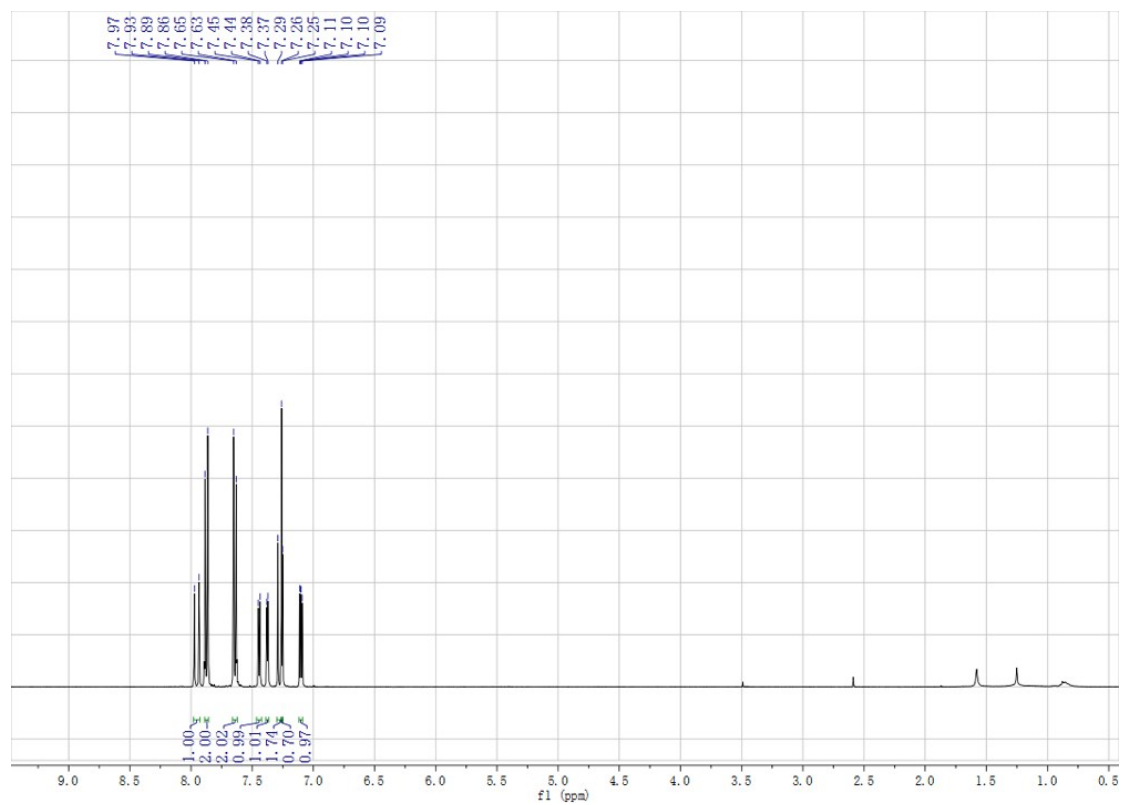


Fig. S1 ^1H NMR spectra of **1**

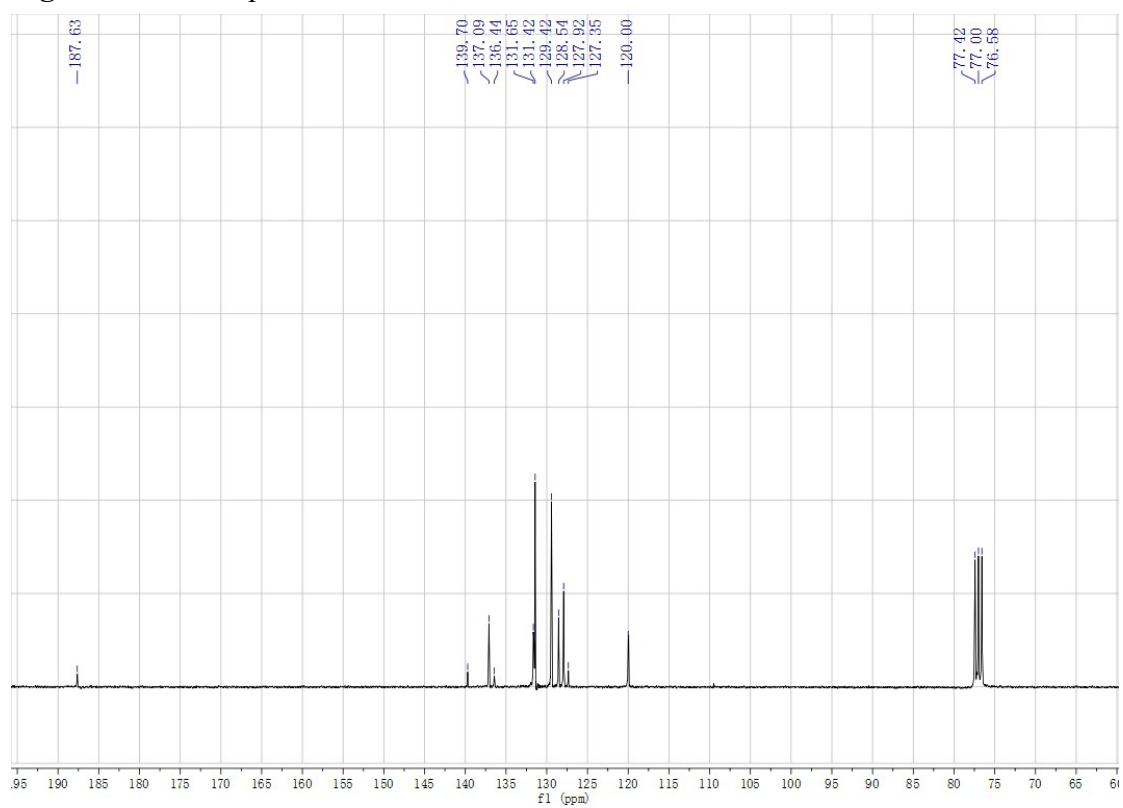


Fig. S2 ^{13}C NMR spectra of **1**

Sample Name	A1	Position	P1-A1	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
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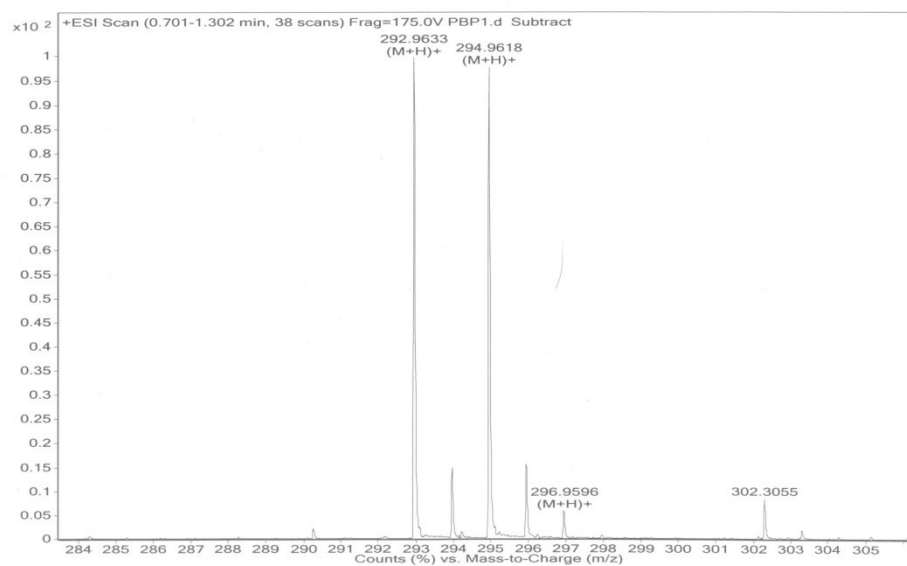


Fig. S3 Mass spectra of **1**

Compound 2

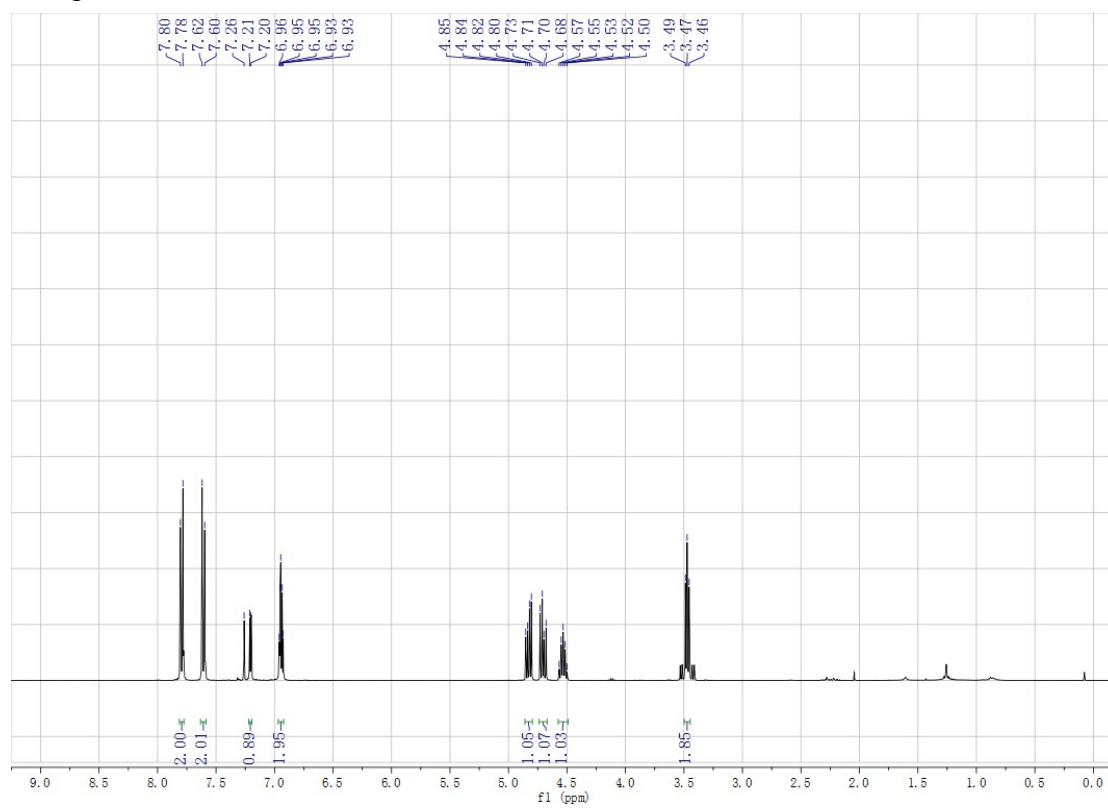


Fig. S4 ¹H NMR spectra of 2

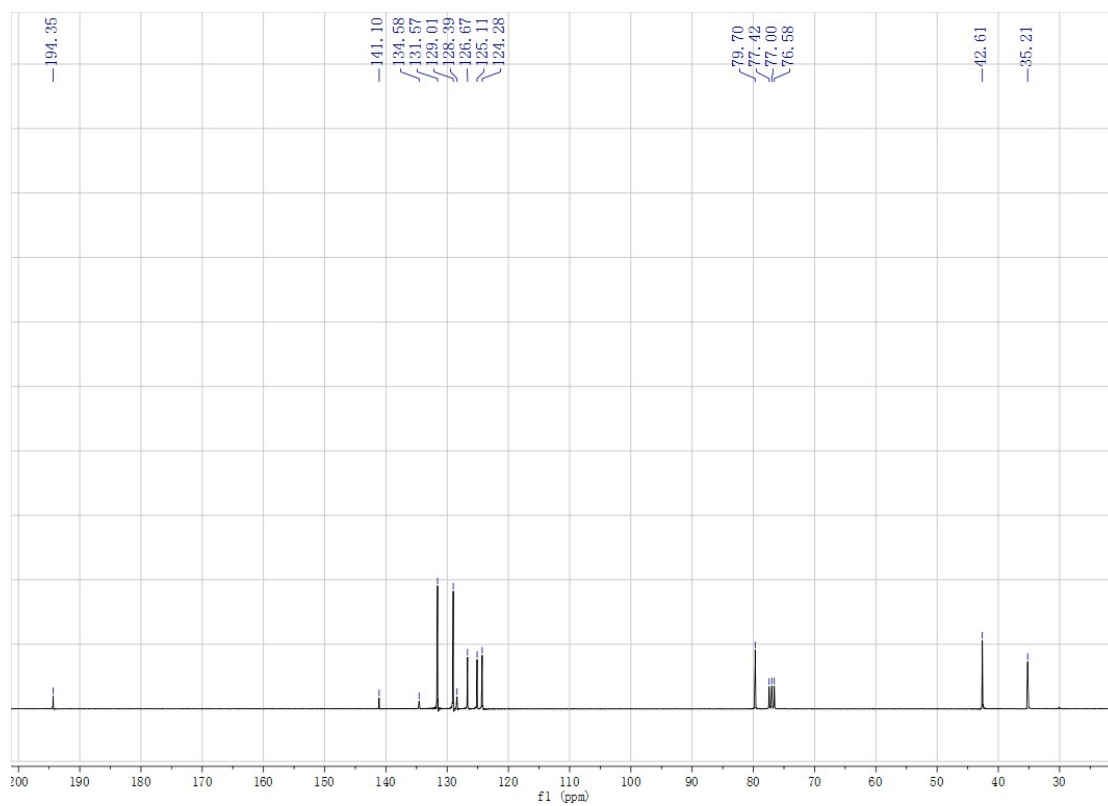


Fig. S5 ¹³C NMR spectra of 2

Sample Name	A2	Position	P1-A2	Instrument Name	Instrument 1	User Name	
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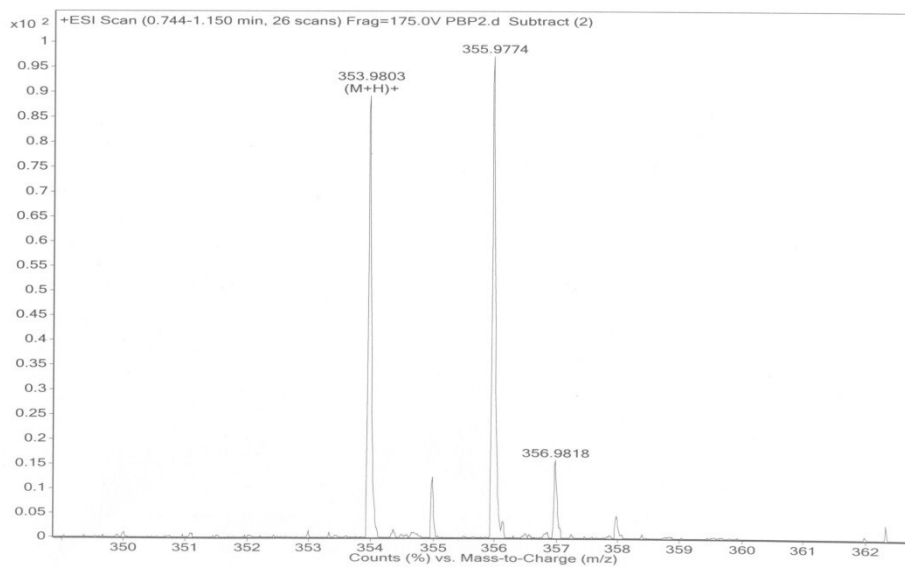


Fig. S6 Mass spectra of **2**

Compound 3

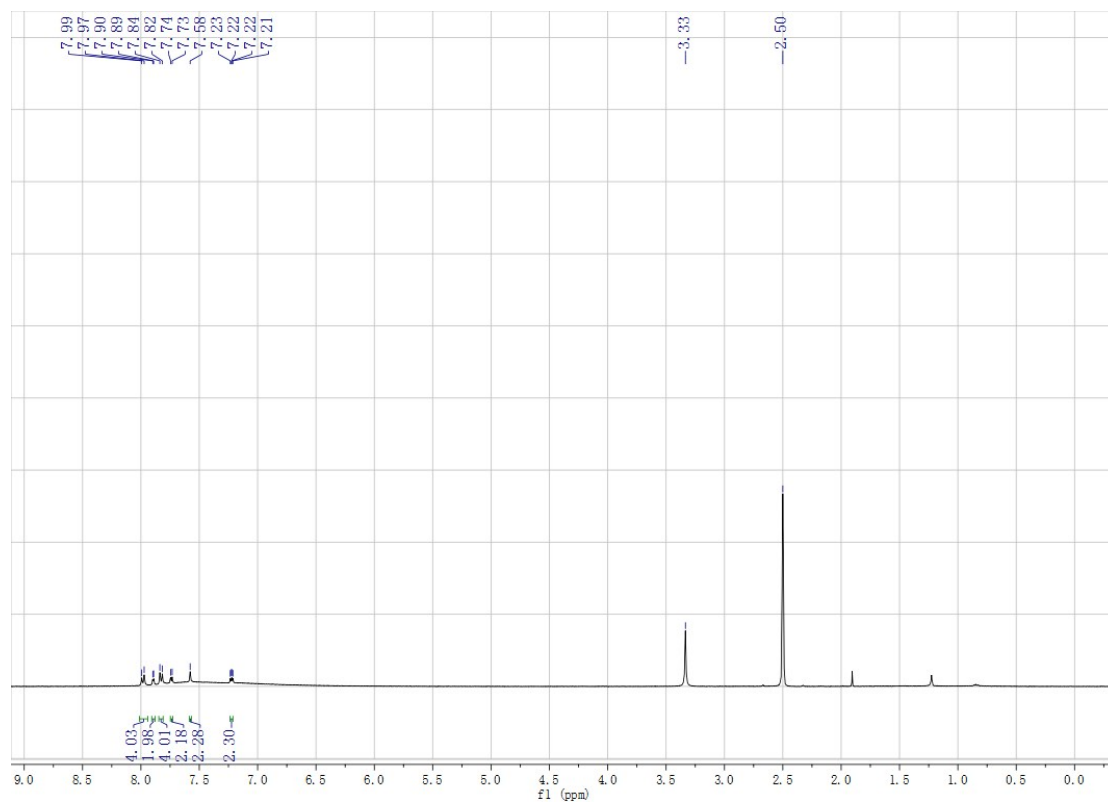


Fig. S7 ¹H NMR spectra of **3**

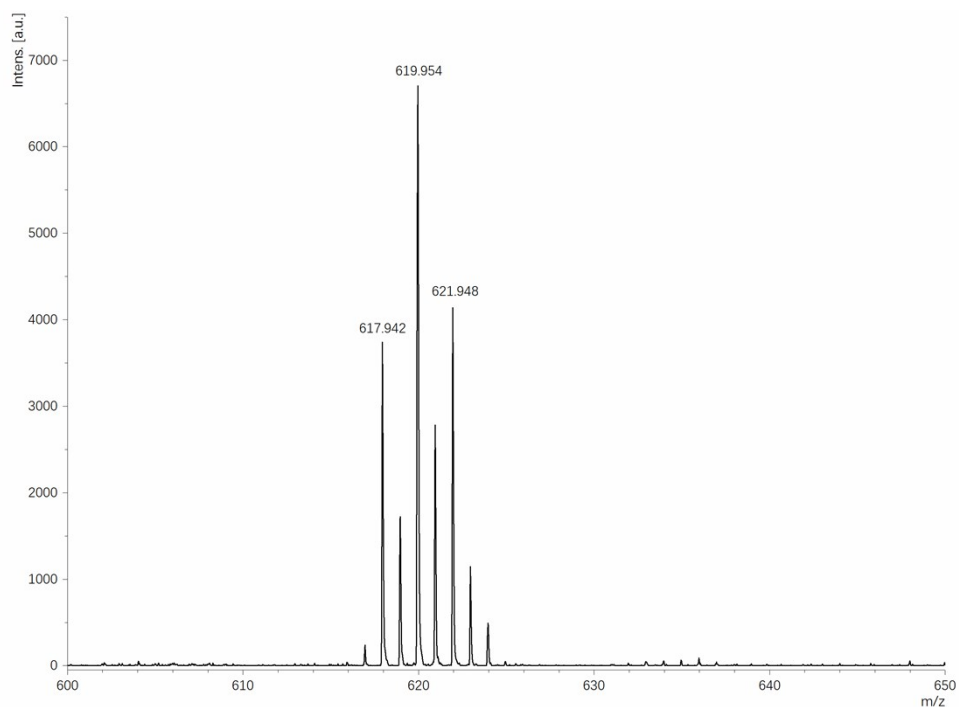


Fig. S8 Mass spectra of **3**

Compound 4

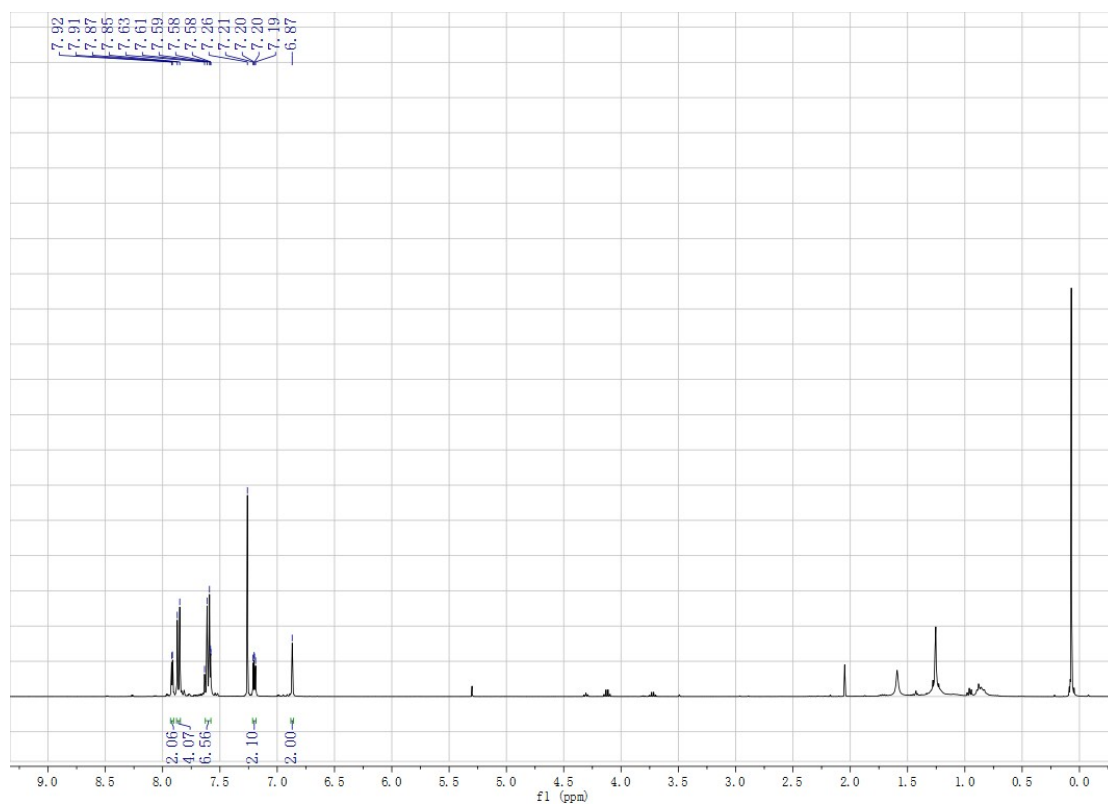


Fig. S9 ¹H NMR spectra of **4** (0.8-1.5 ppm are the solvent peaks of petroleum ether, 2.05, 4.12 and 1.26 ppm are the solvent peaks of ethyl acetate, 1.56 ppm is the solvent peak of water)

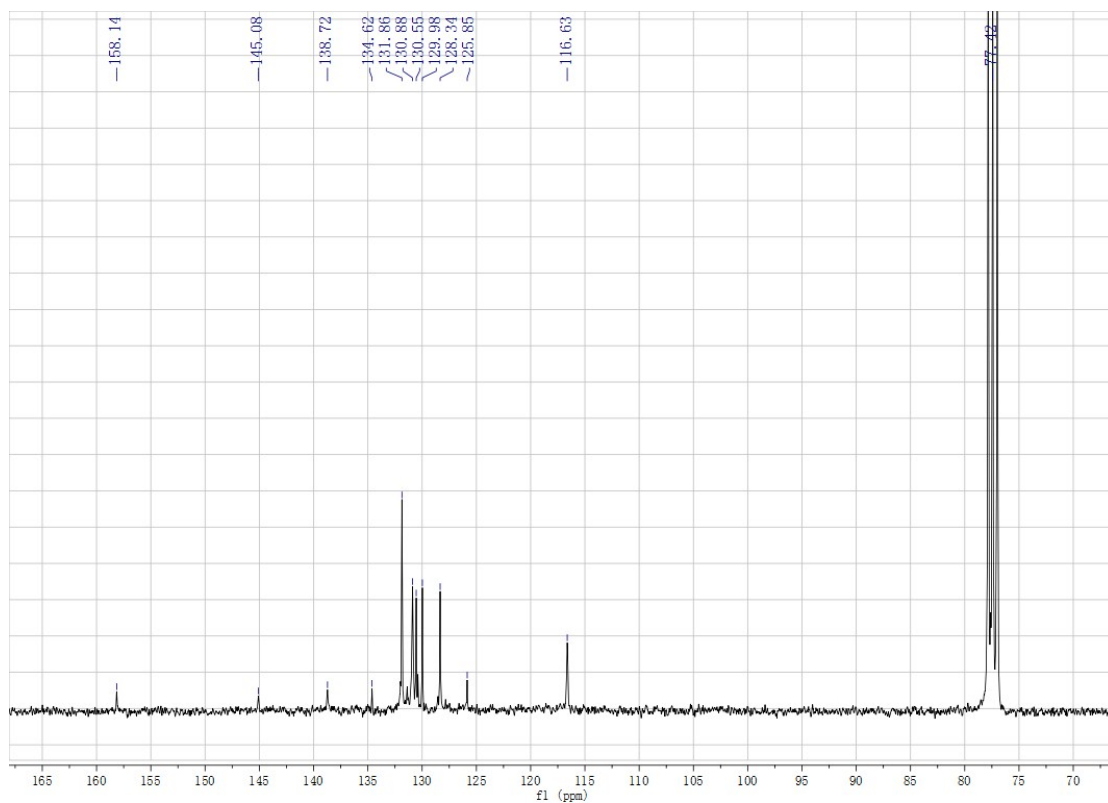


Fig. S10 ^{13}C NMR spectra of **4**

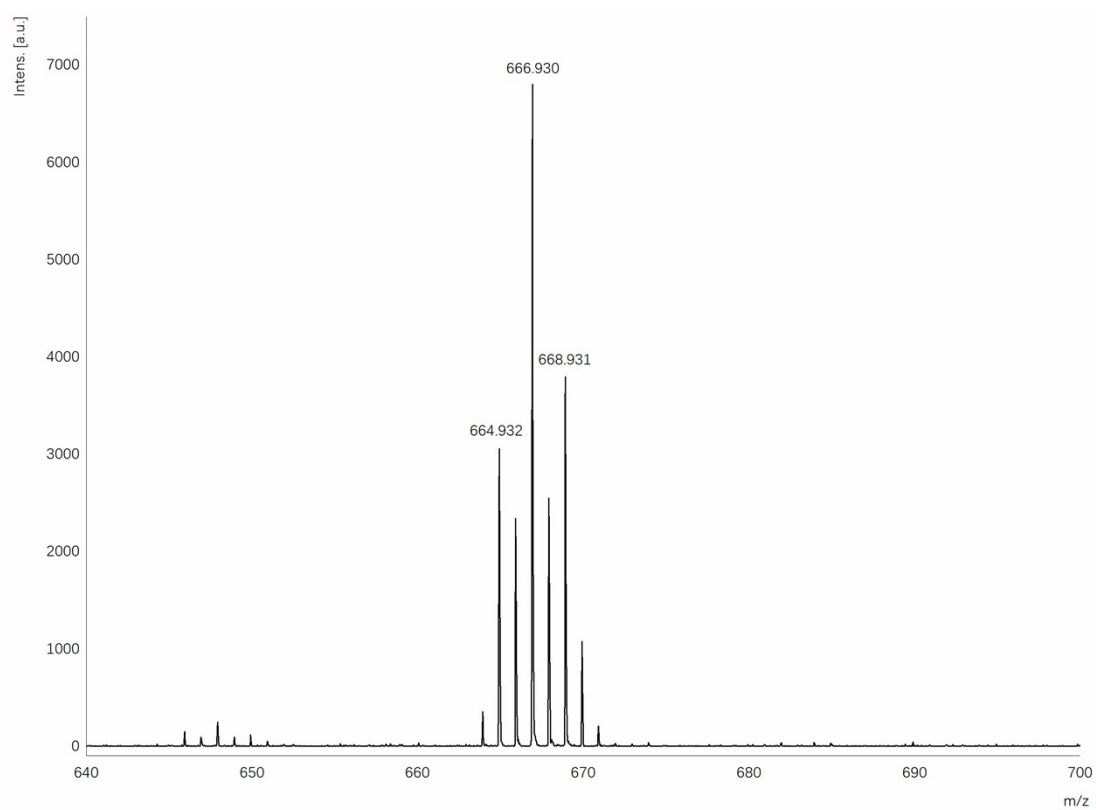


Fig. S11 Mass spectra of **4**

Compound 5

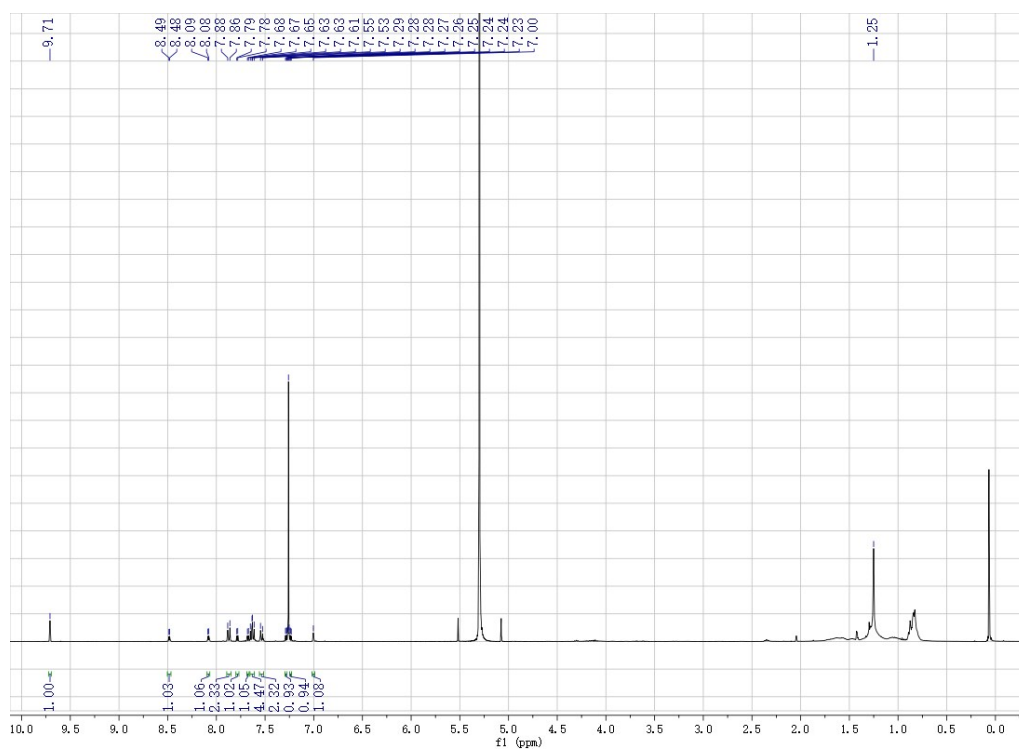


Fig. S12 ^1H NMR spectra of **5** (0.8-1.5 ppm are the solvent peaks of petroleum ether, 5.3 ppm is the solvent peak of dichloromethane)

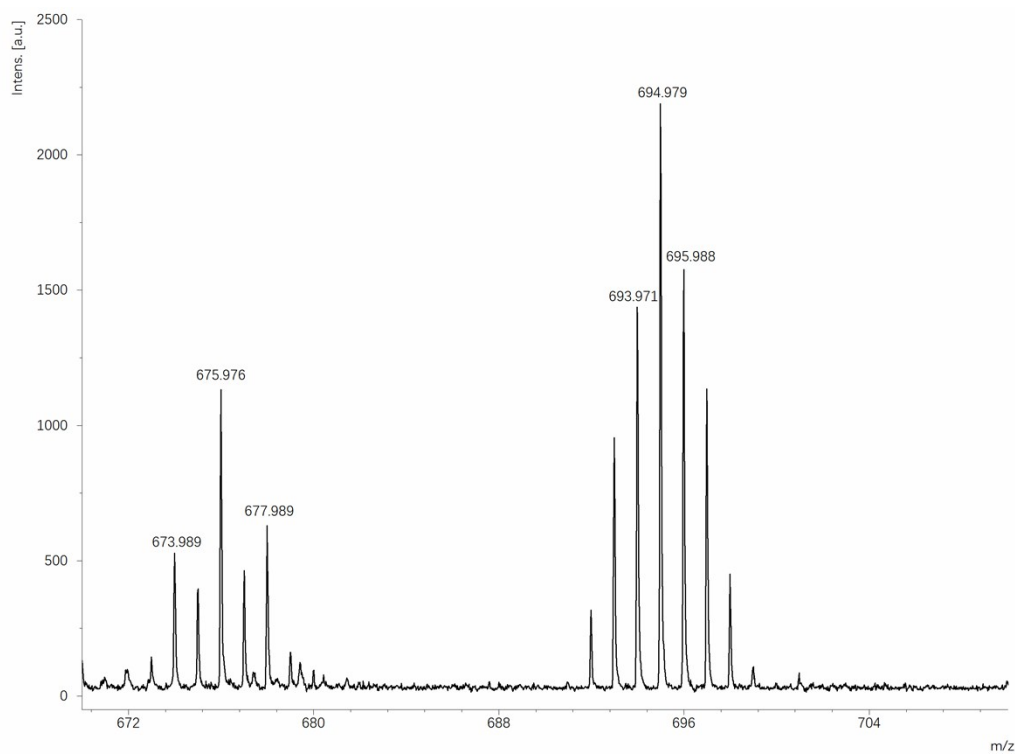


Fig. S13 Mass spectra of **5**

Compound 6

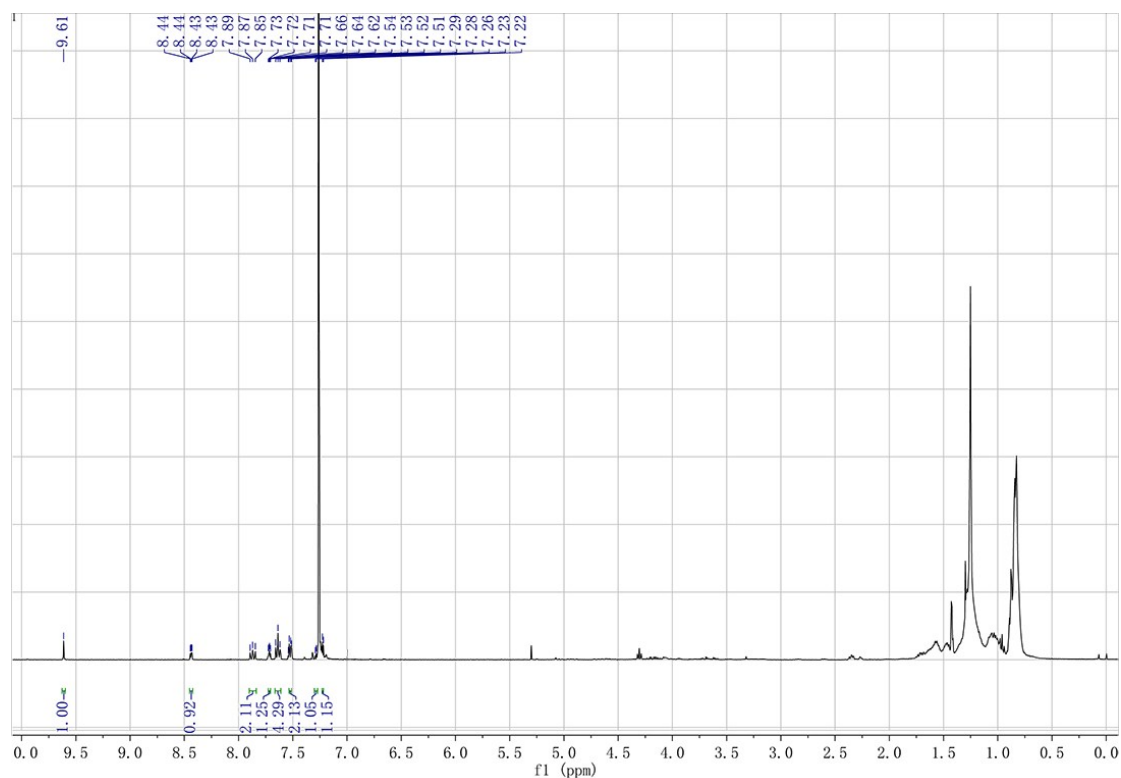


Fig. S14 ^1H NMR spectra of **6** (0.8-1.5 ppm are the solvent peaks of petroleum ether, 1.56 ppm is the solvent peak of water)

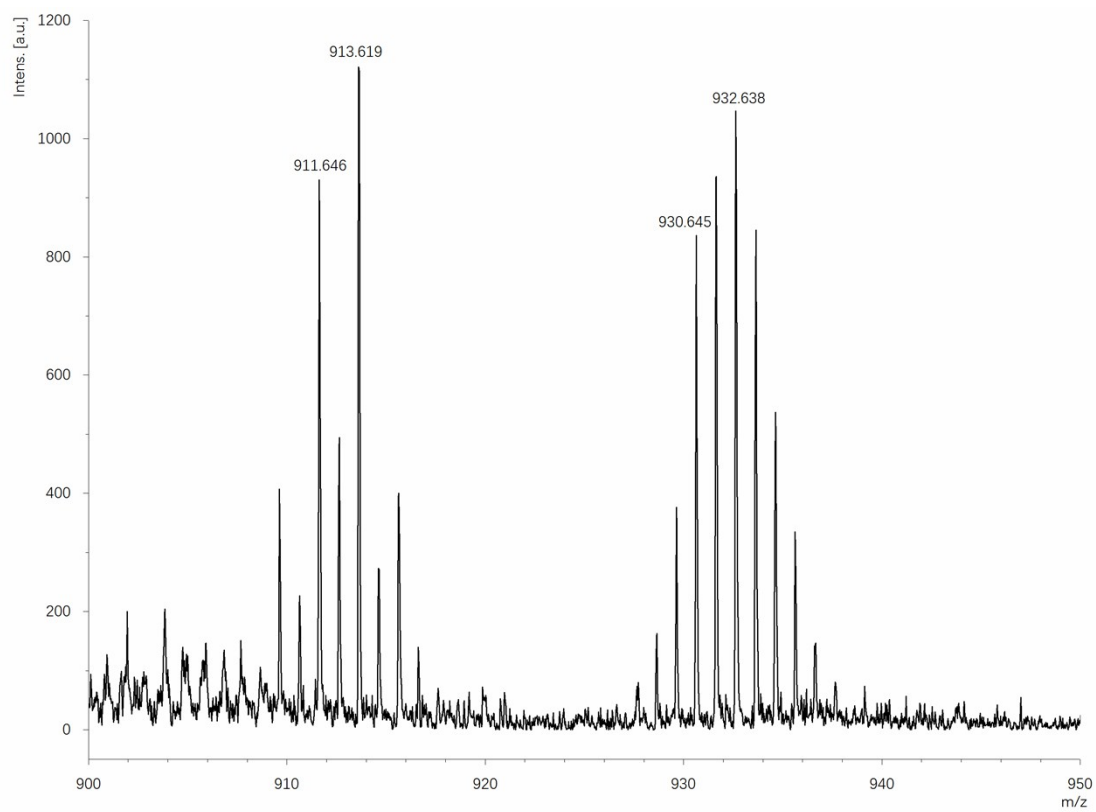


Fig. S15 Mass spectra of **6**

Compound 7

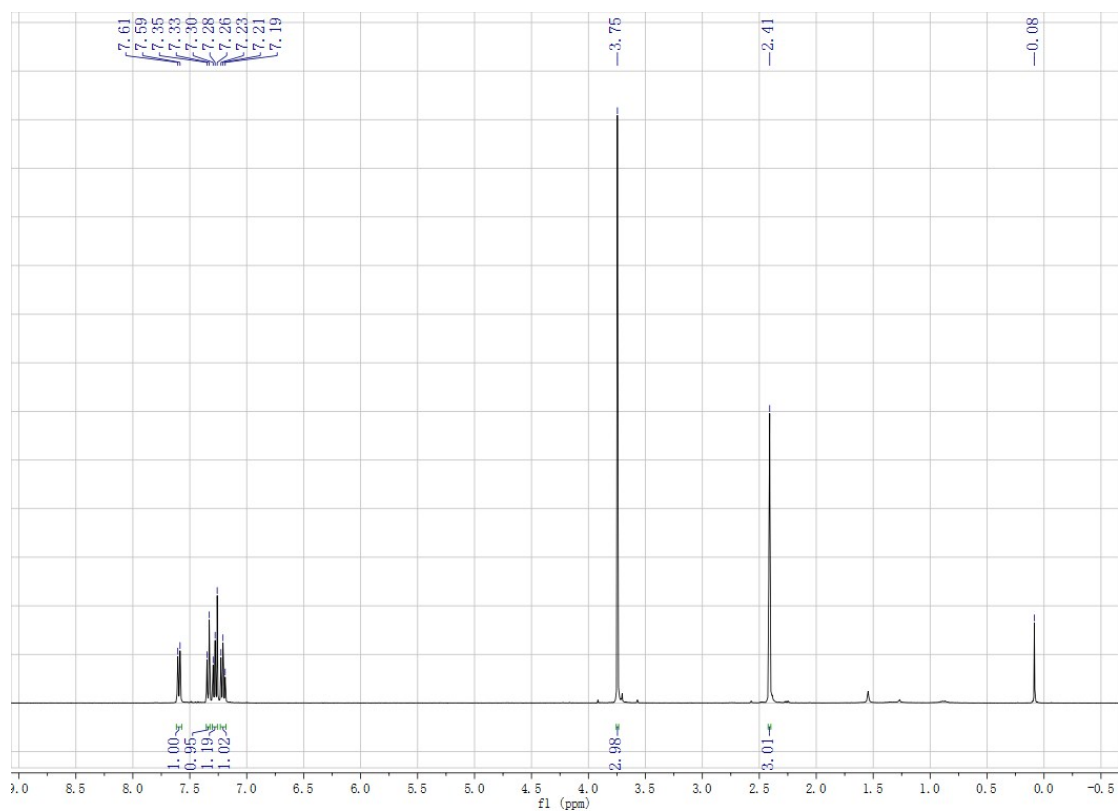


Fig. S16 ¹H NMR spectra of 7

Compound 8

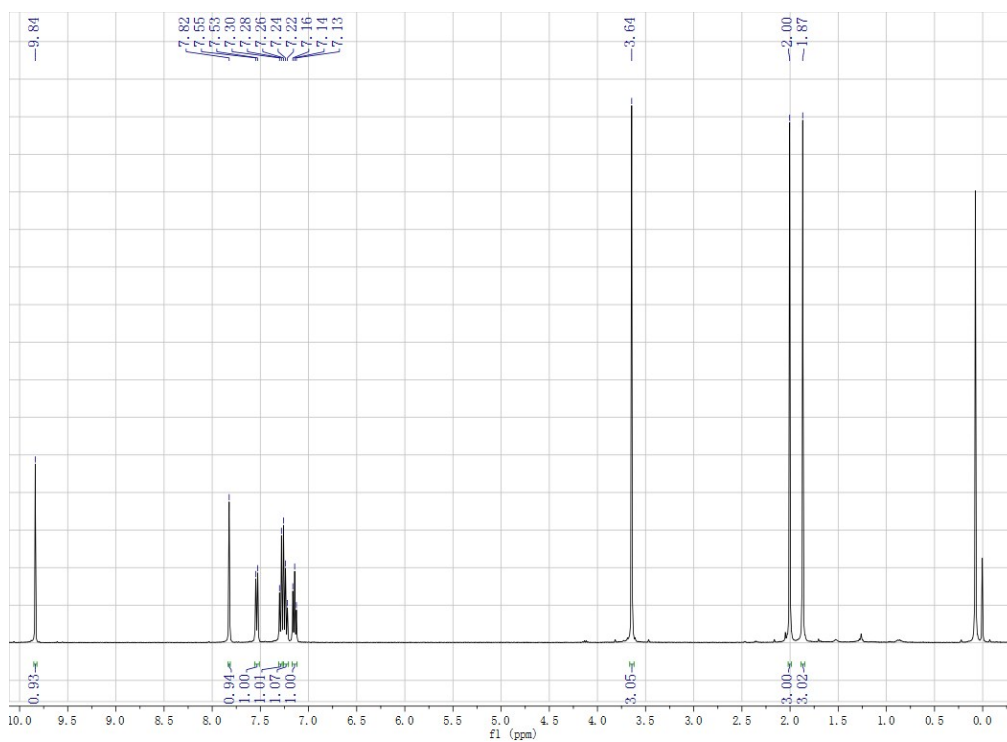


Fig. S17 ¹H NMR spectra of 8

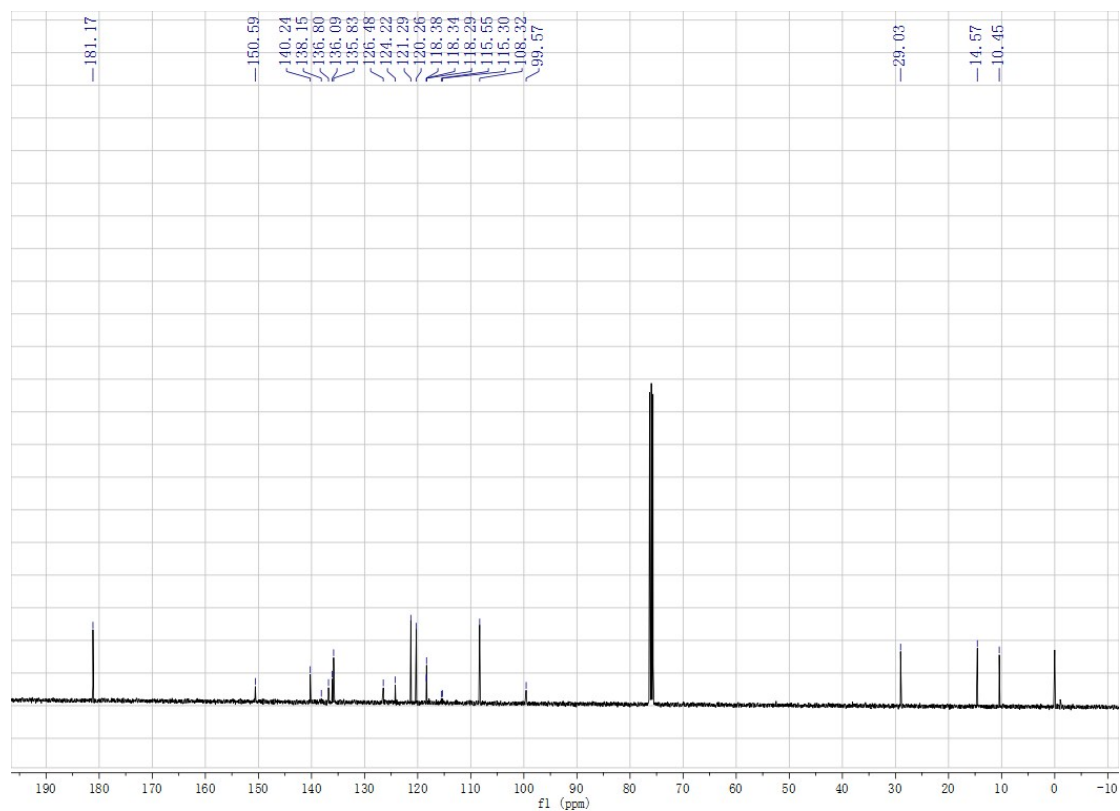


Fig. S18 ^{13}C NMR spectra of **8**
Compound **9**

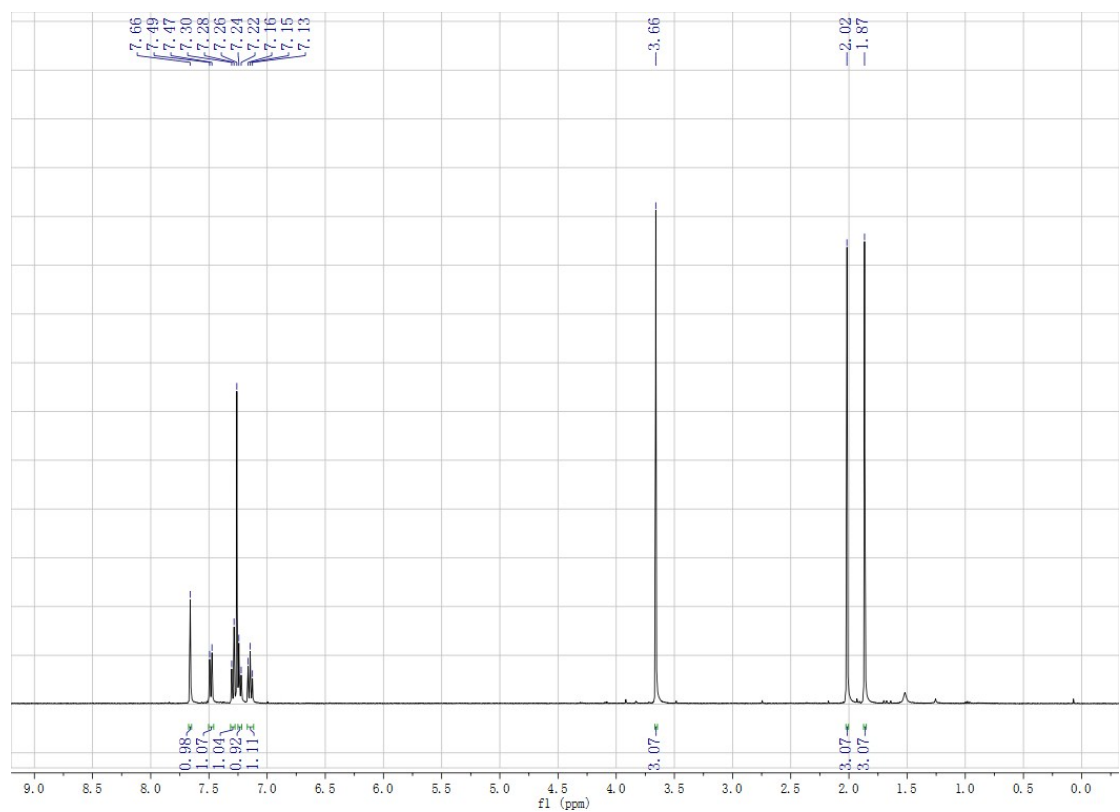


Fig. S19 ^1H NMR spectra of **9**

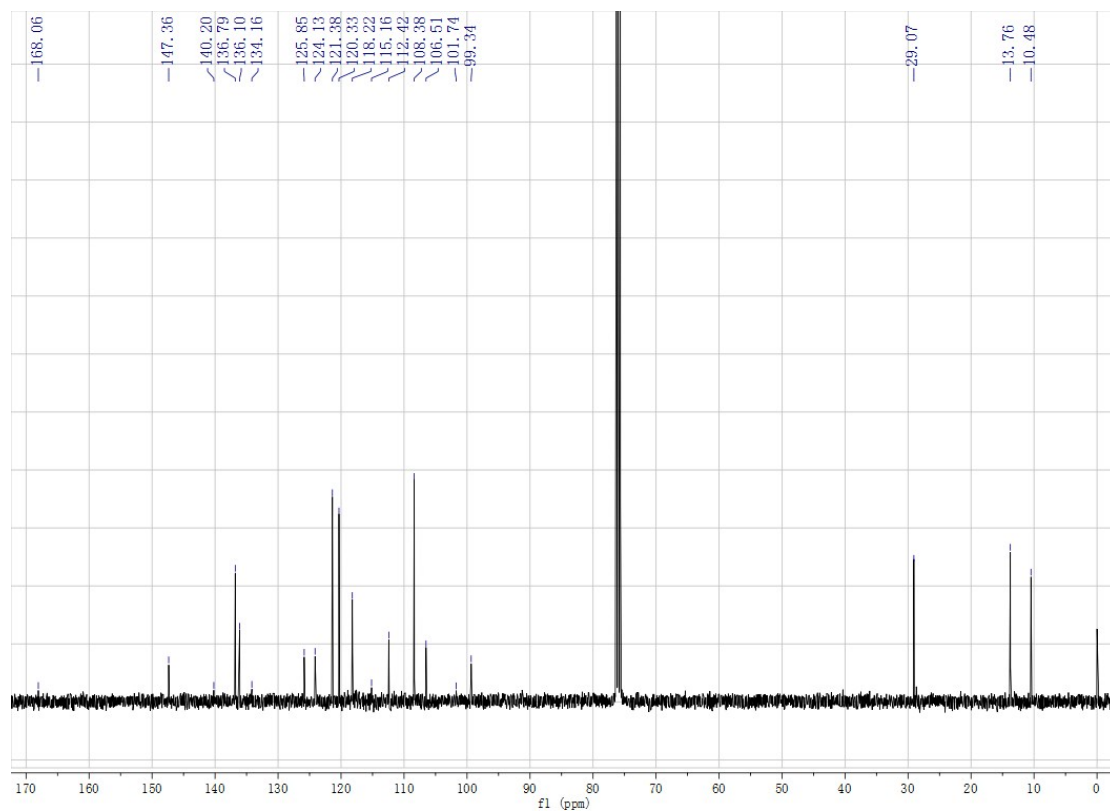


Fig. S20 ^{13}C NMR spectra of **9**

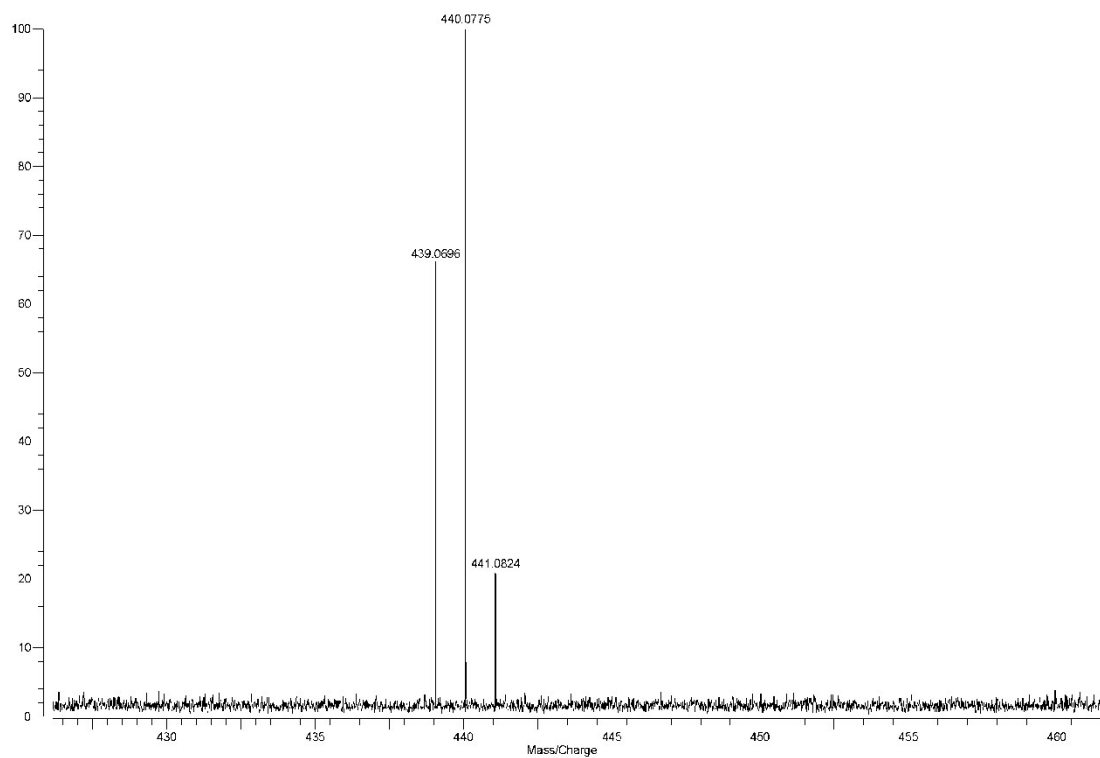


Fig. S21 Mass spectra of **9**

Compound 10

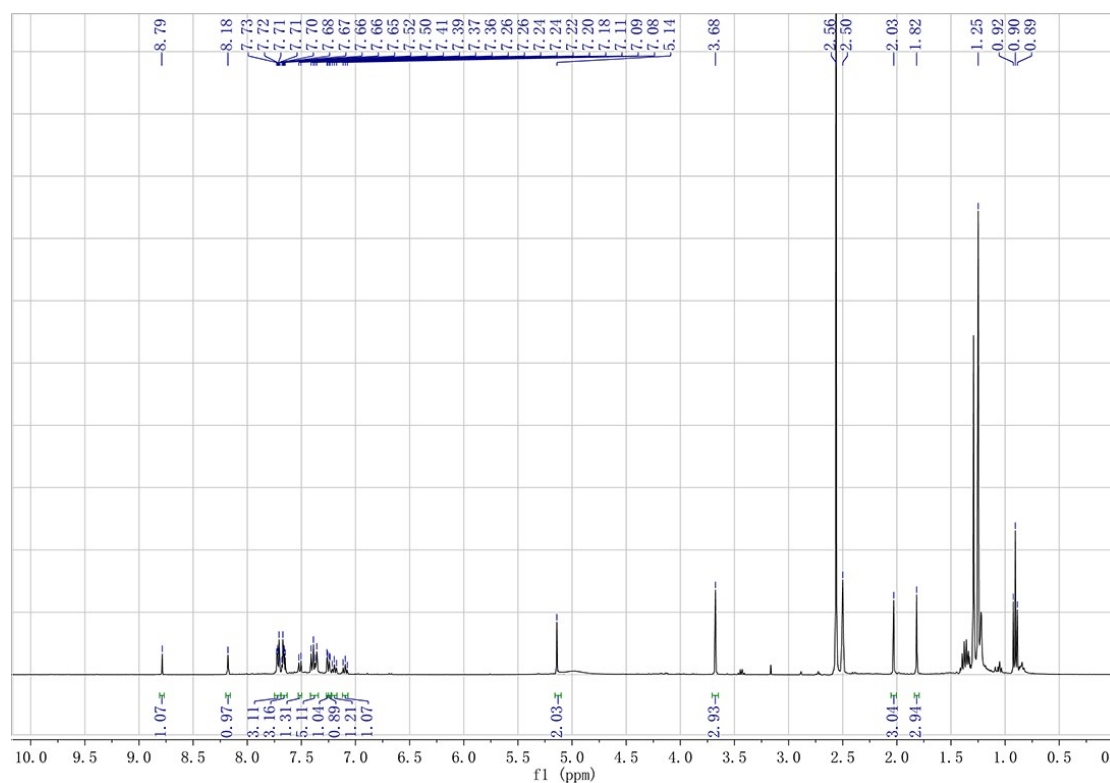


Fig. S22 ¹H NMR spectra of **10** (0.8-1.5 ppm are the solvent peaks of petroleum ether)

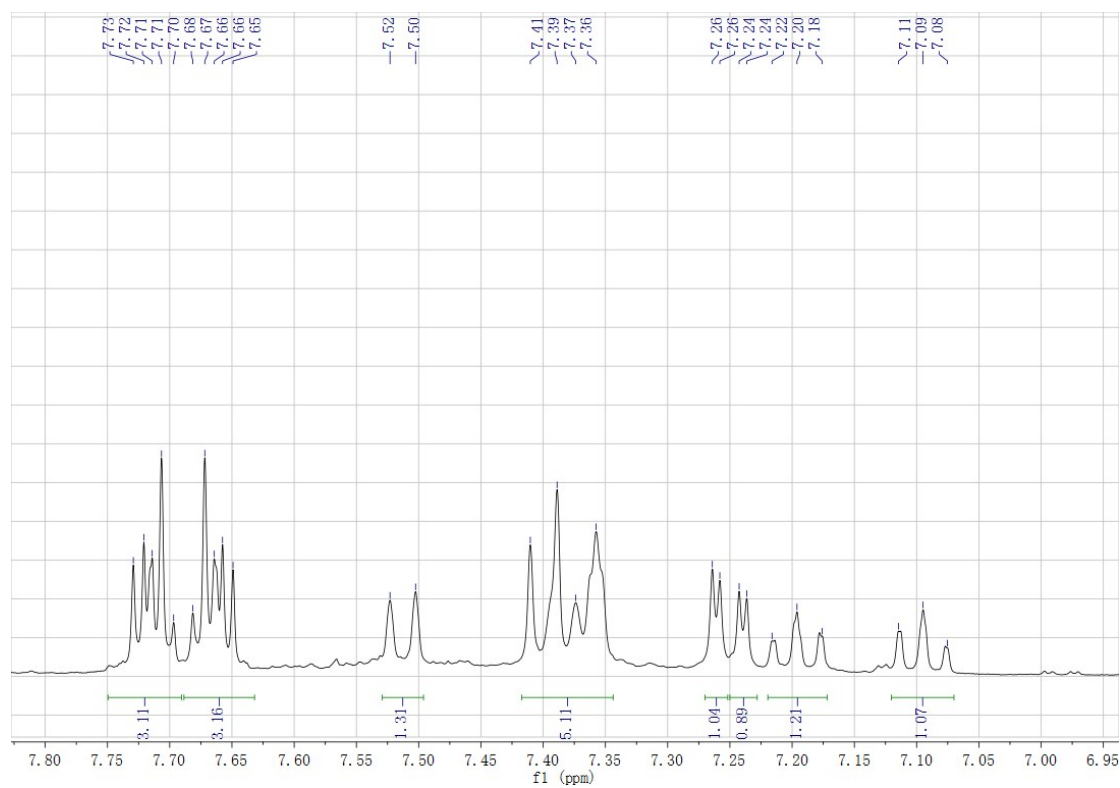


Fig. S23 ¹H NMR spectra of **10** (6.9-7.8 ppm)

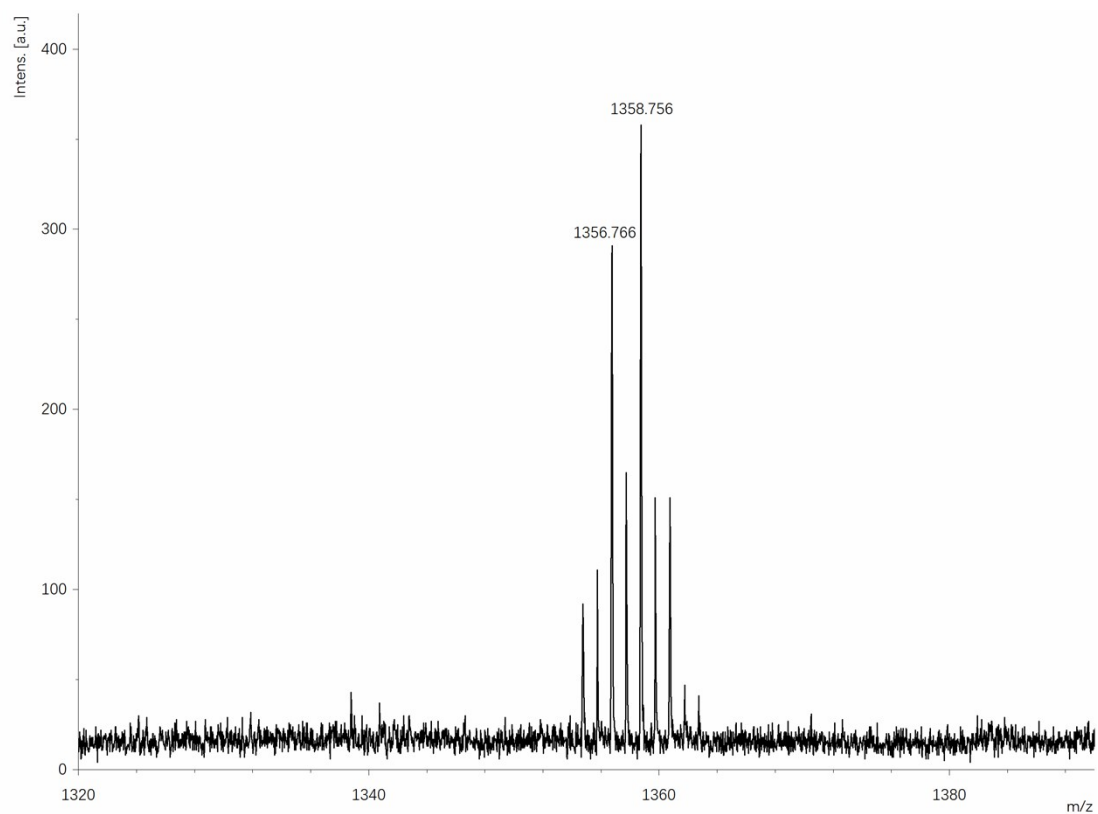


Fig. S24 Mass spectra of **10**

2.2 UV-Vis spectra

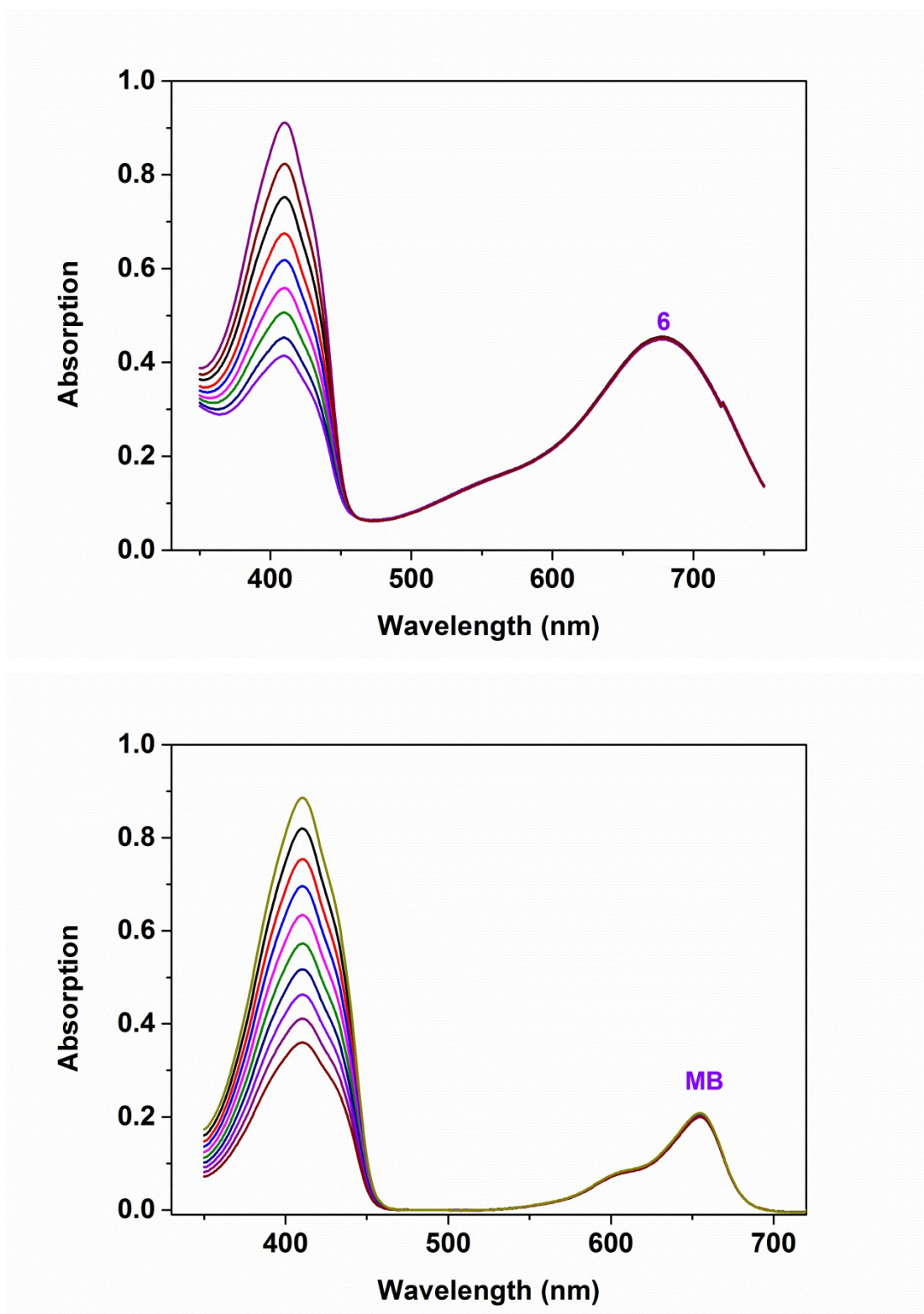


Fig. S25 Change in the absorption spectra of DPBF upon irradiation ($\lambda_{\text{irr}} = 670 \text{ nm}$) with 5 s interval in the presence of **6** and MB.

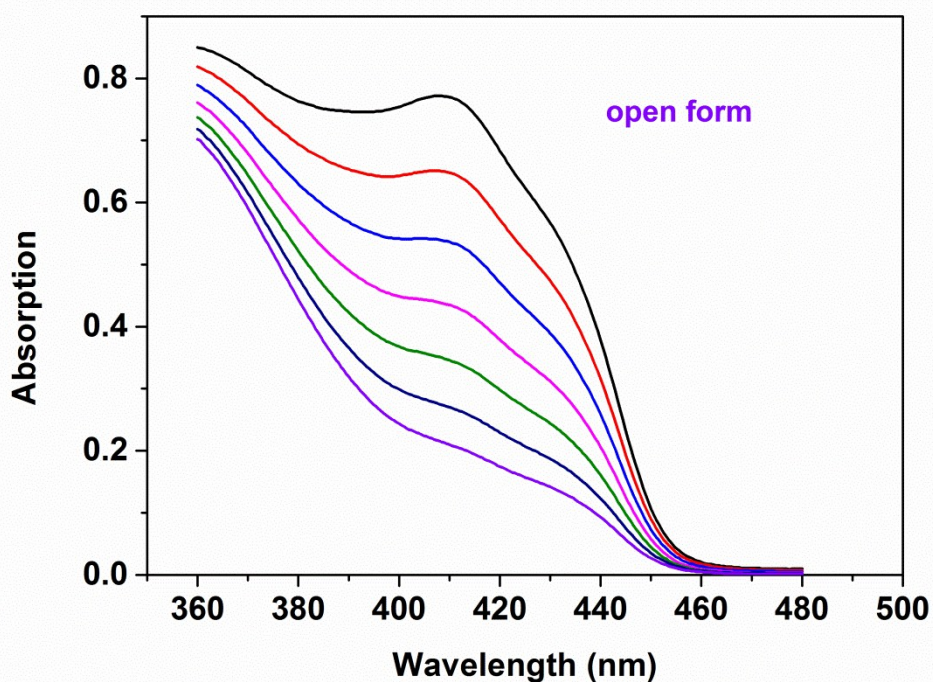
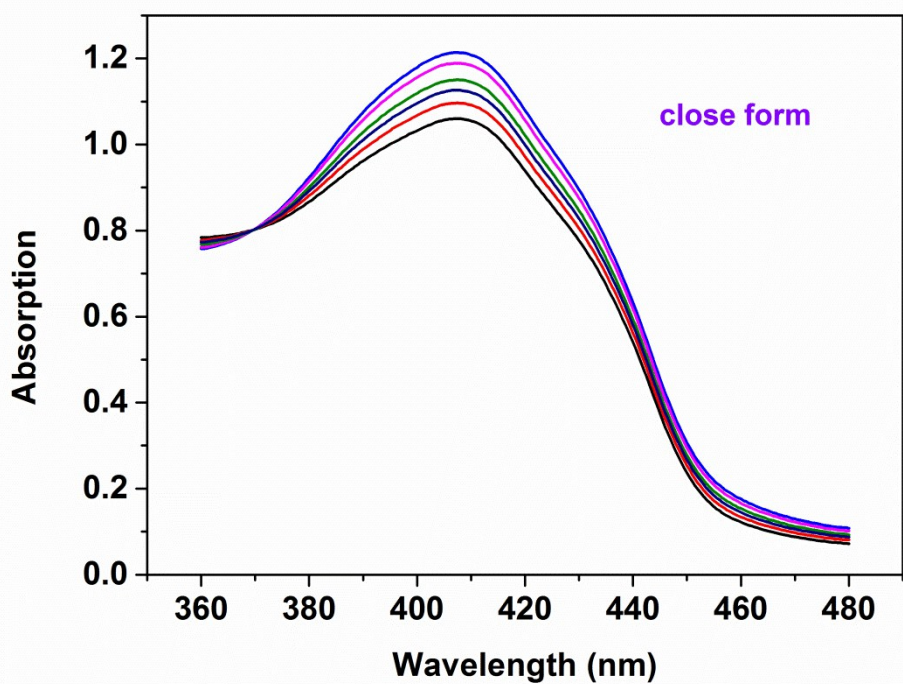


Fig. S26 Change in the absorption spectra of DPBF upon irradiation ($\lambda_{\text{irr}} = 670 \text{ nm}$) with 10 s interval in the presence of close form **10** and open form **10**.

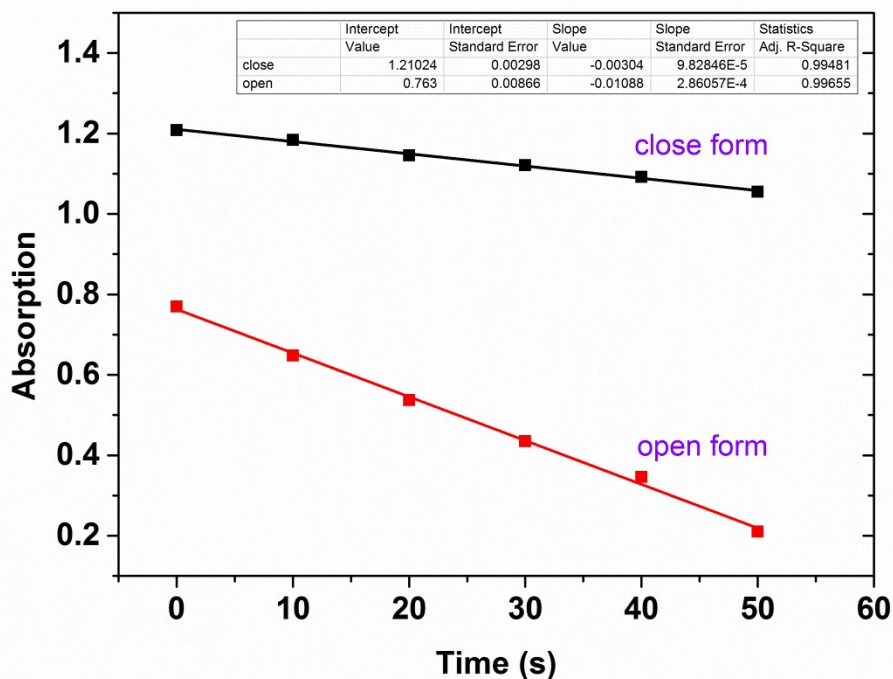


Fig. S27 The plot of DPBF absorbance at 410 nm against time and the linear fitting from 0 s to 50 s in the presence of close form **10** and open form **10**.

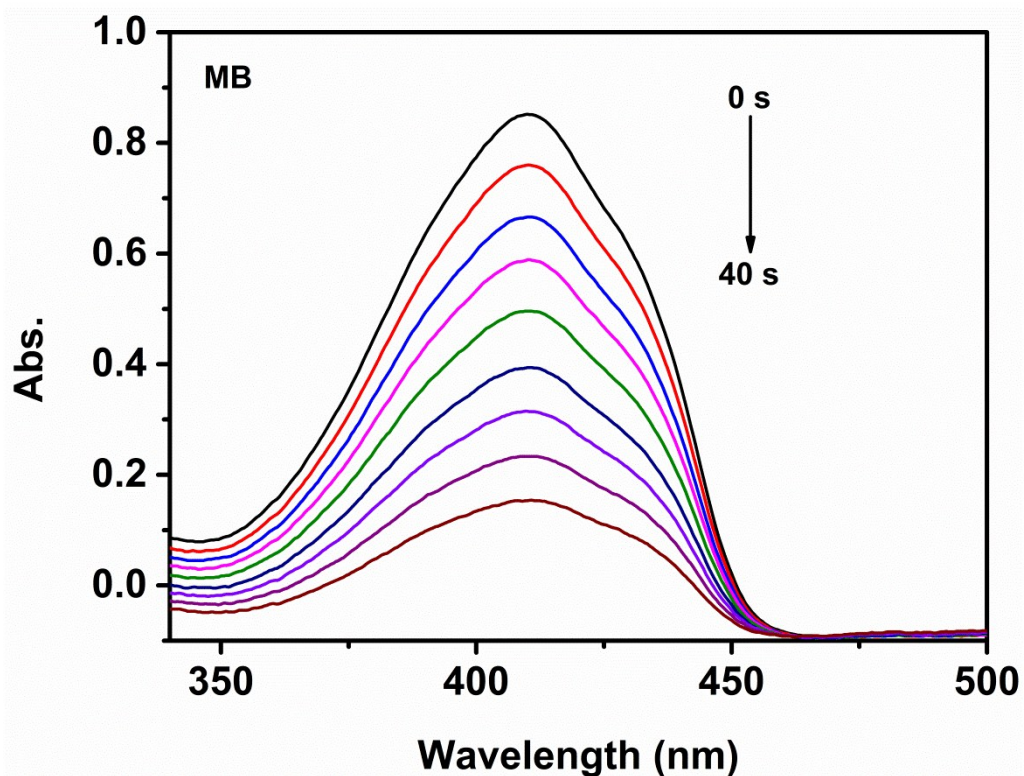


Fig. S28 Change in the absorption spectra of DPBF upon irradiation ($\lambda_{\text{irr}} = 670 \text{ nm}$) with 5 s interval in the presence of MB.

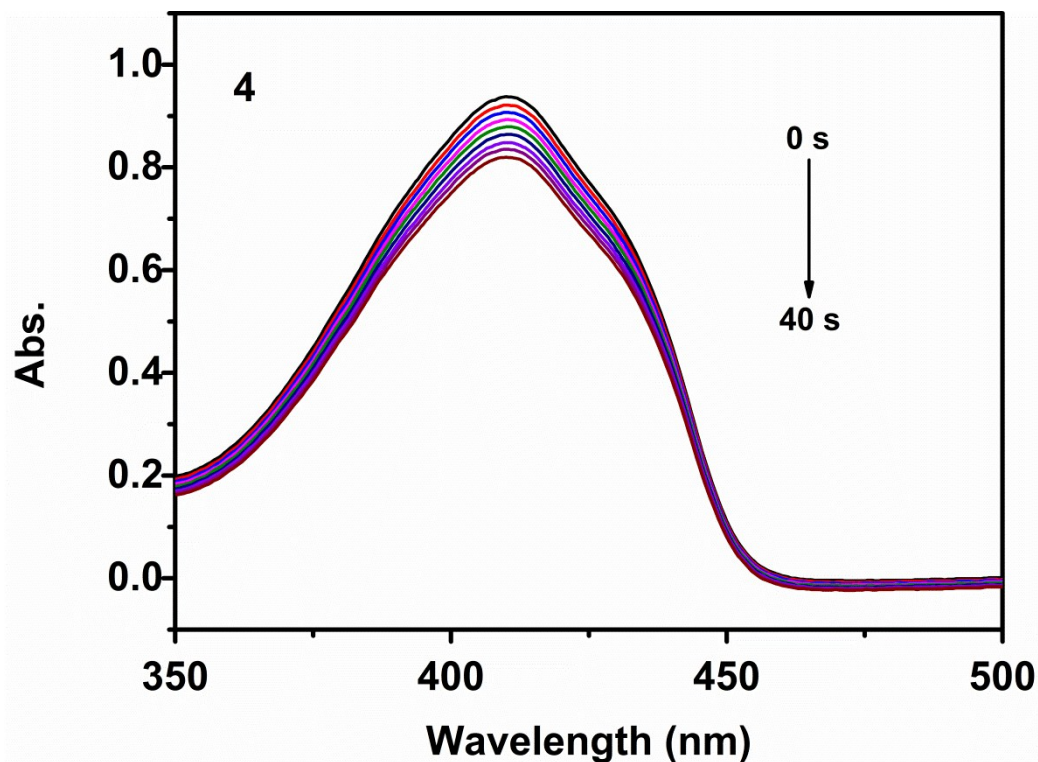


Fig. S29 Change in the absorption spectra of DPBF upon irradiation ($\lambda_{\text{irr}} = 670 \text{ nm}$) with 5 s interval in the presence of 4.

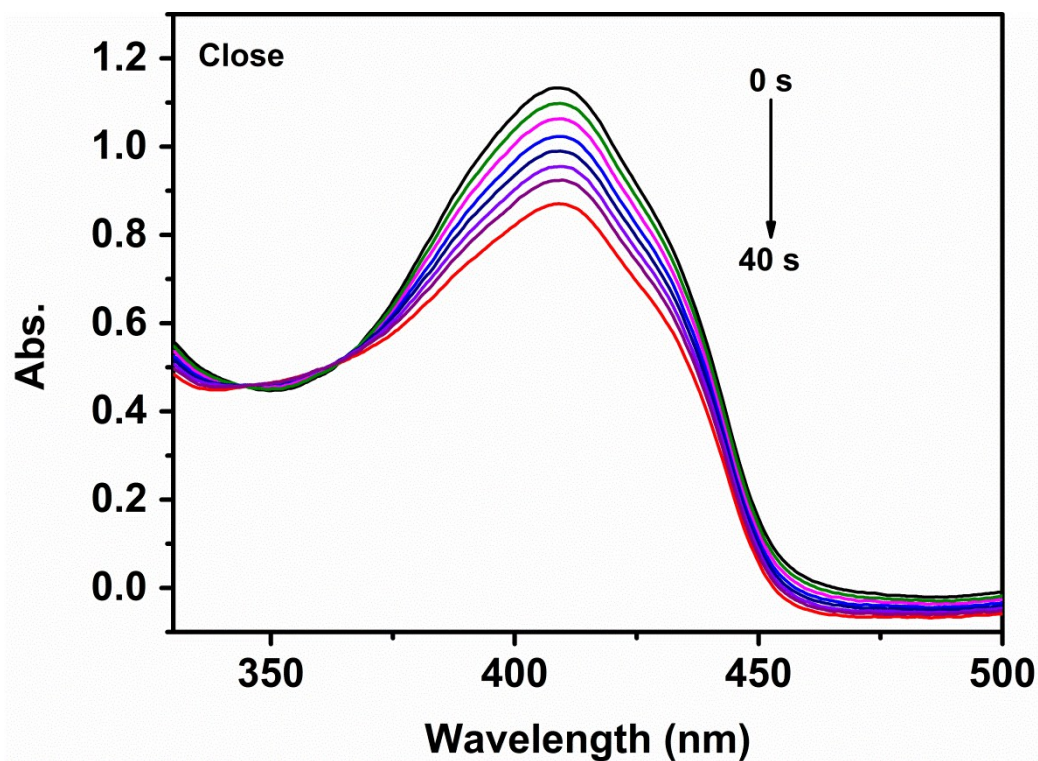


Fig. S30 Change in the absorption spectra of DPBF upon irradiation ($\lambda_{\text{irr}} = 670 \text{ nm}$) with 5 s interval in the presence of close form 10.

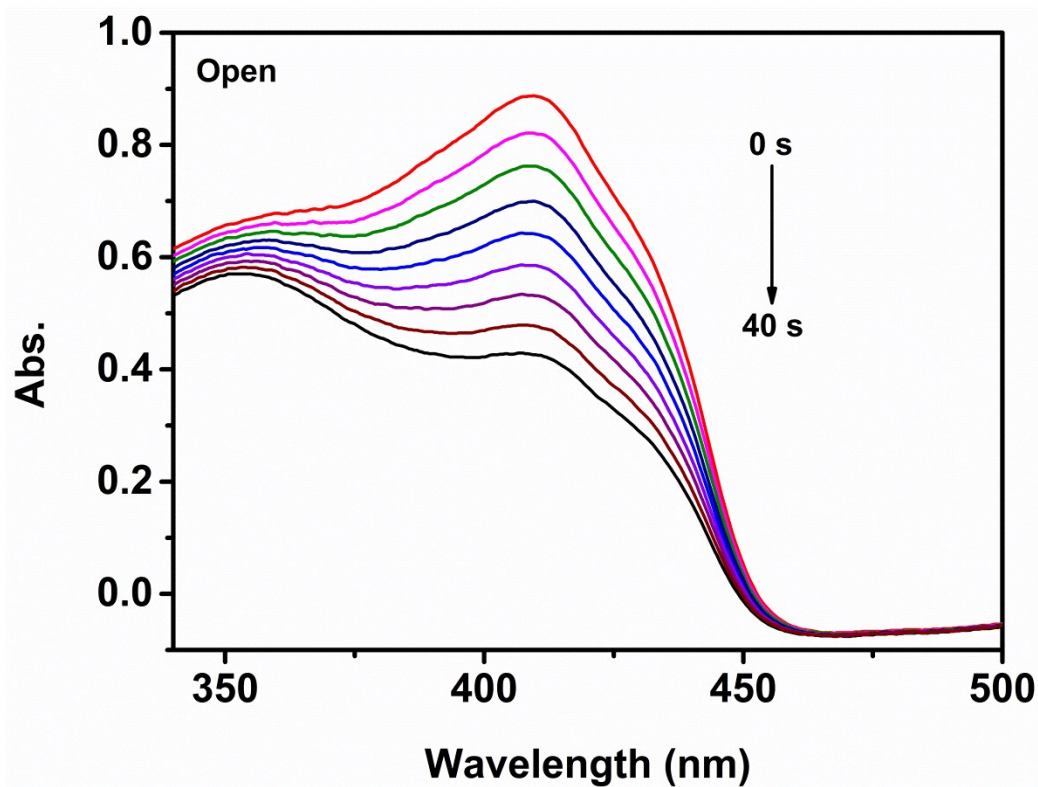


Fig. S31 Change in the absorption spectra of DPBF upon irradiation ($\lambda_{\text{irr}} = 670 \text{ nm}$) with 5 s interval in the presence of open form **10**.

2.3 Figures of fluorescence decay

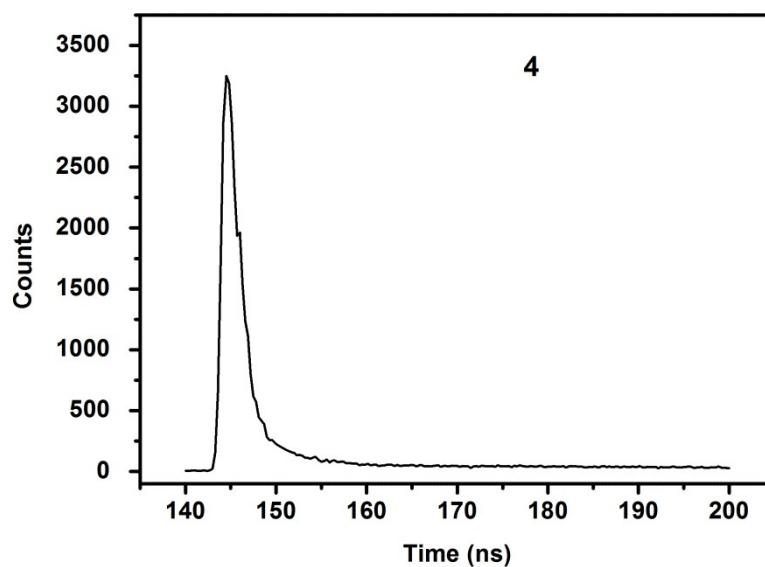


Fig. S32 The fluorescence decay of **4** in dichloroethane with emission was monitored at 730 nm.

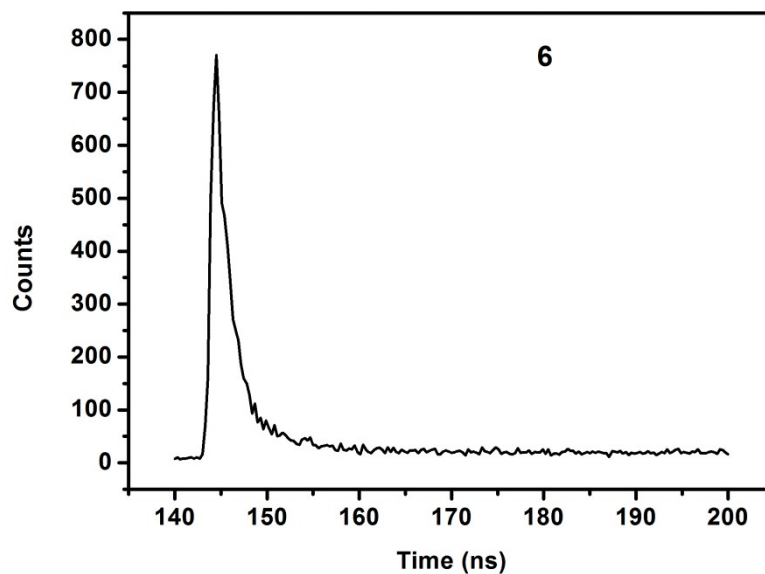


Fig. S33 The fluorescence decay of **6** in dichloroethane with emission was monitored at 780 nm.

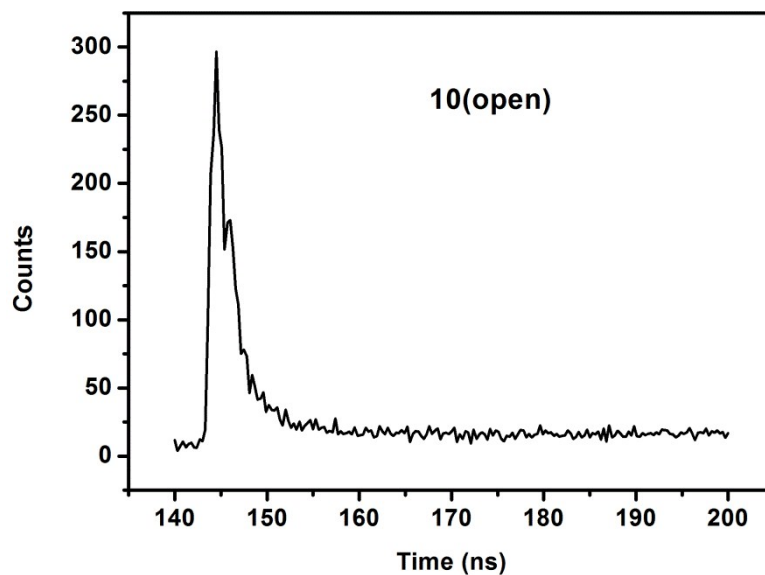


Fig. S34 The fluorescence decay of open form **10** in dichloroethane with emission was monitored at 780 nm.

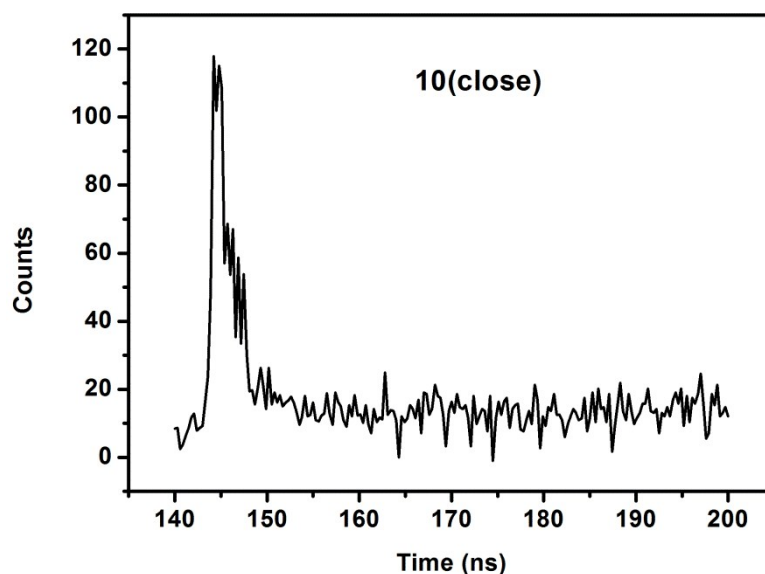


Fig. S35 The fluorescence decay of close form **10** in dichloroethane with emission was monitored at 780 nm.

2.4 Additional table

Table S1 Comparison of the spectroscopic properties of compound **4**, **6** and **10**.

Compounds	Φ_f^a	τ (ns) ^b	Φ_Δ^c
4	0.041	0.72	0.11
6	0.011	0.99	0.37
10(Open)	0.0086	1.13	0.33
10(Close)	0.0026	0.66	0.10

^a Absolute fluorescence quantum yield (Φ_f) in dimethylsulfoxide. ^b Fluorescence lifetime (τ) was determined in dichloromethane. ^c Singlet oxygen quantum yield (Φ_Δ) was determined with respect to methylene blue (0.52 in acetonitrile).

3. References.

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