Electronic Supplementary Information for

Synthesis and solvatochromism of a NIR II emissive amphiphilic Aza-BODIPY dye and its application as a colorimetric and fluorometric probe in sequential detection of Cu^{2+} and PO_4^{3-}

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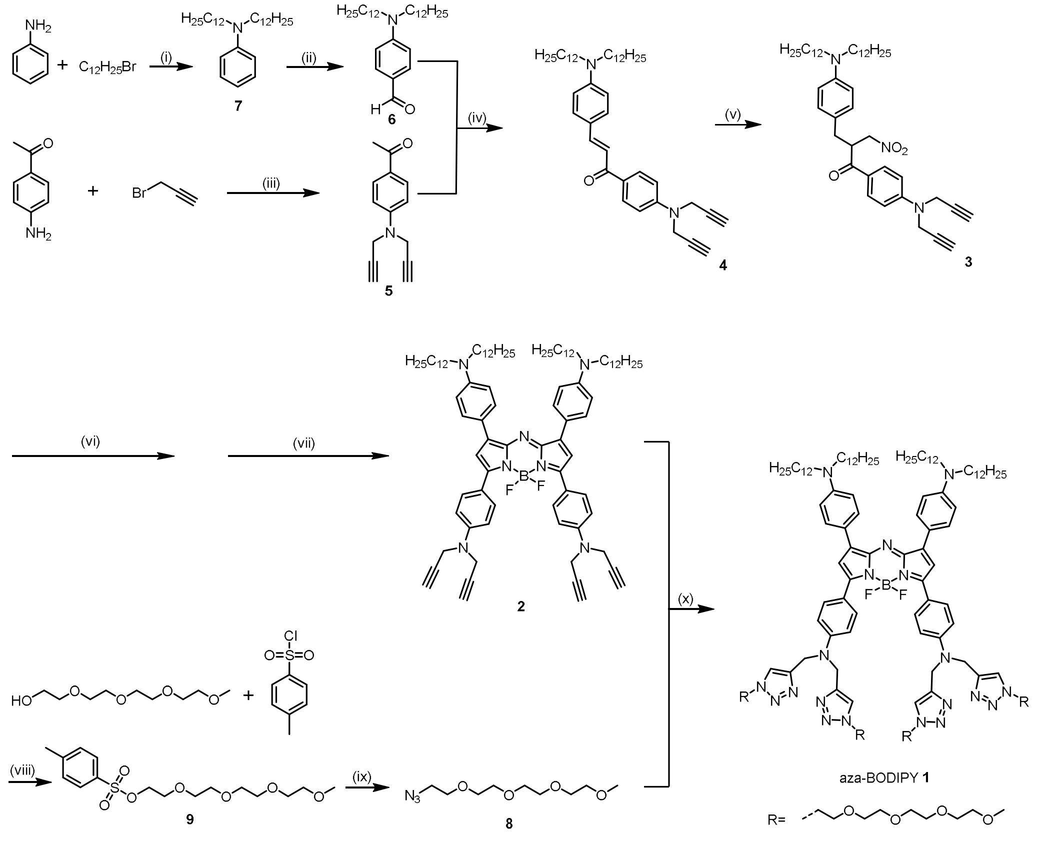
Synthesis and characterization of aza-BODIPY 1



Scheme 1 Synthesis of aza-BODIPY **1**. Reagents and conditions: (i) K_2CO_3, DMF, r.t., 80 °C, 24 h; (ii) $POCl_3$, DMF, r.t.; 79 %; (iii) K_2CO_3, DMF, r.t., 24 h; 43 %; (iv) t-BuOK, ethanol, r.t., 12 h; 41 %; (v) t-BuOK, nitromethane, ethanol, r.t., 80 °C, 24 h; 56 %; (vi) CH_3COONH_4, n-butanol, 110 °C, 12 h; (vii) $BF_3{\cdot}Et_2O$, dry DCM, DIEA, r.t., 12 h; 71 %; (viii) Et_3N, dye DCM, r.t., 24 h; 98 %; (ix) NaN_3, EtOH, r.t., 2.5 h; 97 %; (x) CuI, DIEA, CH_2Cl_2, CH_3CN, 60 °C, 8 h; 82 %.

***N*,*N*-Didodecylaniline (Compound 7)**[1]**:** Aniline (4.66 g, 0.05 mol) and 1-bromododecane (31.16 g, 0.125 mol) were dissolved in 50 mL DMF and then K_2CO_3 (24.19 g, 0.175 mol) was also added. The reaction was carried out at 80 °C for 24 h. After the reaction was completed (monitored by TLC), the solvent was rotary-evaporated. The residue was dissolved in CH_2Cl_2 and washed with water (3 × 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to obtain a crude product. This reaction had a high yield, and the obtained crude product **7** could be directly used in the next step.

4-(Didodecylamino)benzaldehyde (Compound 6): Compound **7** (8.60 g, 0.02 mol) was dissolved in DMF (1.68 g, 0.024 mol) and then, $POCl_3$ (3.68 g, 0.024 mol) was added dropwise to the system under the protection of nitrogen (N_2). After keeping it in an ice-water bath for 30 minutes, the reaction was carried out at 60 °C for 3 h. Finally, 10 mL of 2 M NaOH solution was added to the system and stirred rapidly for hydrolysis at room temperature for 2 h. After the reaction was completed (monitored by TLC), the solvent was rotary-evaporated. The residue was dissolved in CH_2Cl_2 and washed with water (3 × 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. Further purification by column chromatography (silica gel, 300-400 mesh) using DCM/PE (3/1, *v*/*v*) as the eluent gave the yellow oily compound **6** (7.23 g, 79%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ = 9.69 (s, 1H), 7.69 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 3.37 - 3.30 (m, 4H), 1.61 (t, J = 7.7 Hz, 4H), 1.30 (d, J = 25.1 Hz, 36H), 0.89 (d, J = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 189.73, 152.62, 124.65, 110.70, 51.11, 31.92, 29.64, 29.62, 29.60, 29.58, 29.45, 29.34, 27.18, 27.06, 22.67, 14.07. HRMS (ESI): m/z calculated for $C_{31}H_{56}NO$, $[M+H]^+$ = 458.4362, found: 458.4363.

1-(4-(Di(prop-2-yn-1-yl)amino)phenyl)ethan-1-one (Compound 5): 4'-aminoacetophenone (6.76 g, 0.05 mol) and 3-bromopropyne (29.74 g, 0.25 mol) were dissolved in 50 mL DMF. K_2CO_3 (34.55 g, 0.25 mol) was taken to the system and the reaction was carried out at room temperature for 24 h. After the reaction was completed (monitored by TLC), the solvent was rotary-evaporated. The residue was dissolved in CH_2Cl_2 and washed with water (3 × 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. Further purification by column chromatography (silica gel, 300-400 mesh) using DCM/PE (1/1, *v*/*v*) as the eluent gave the yellow solid compound **5** (4.54 g, 43%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.92 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 4.20 (d, *J* = 2.4 Hz, 4H), 2.53 (s, 3H), 2.28 (t, *J* = 2.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ = 196.45, 150.86, 130.37, 128.15, 113.19, 78.45, 72.98, 40.09, 26.12. HRMS (ESI): m/z calculated for $C_{14}H_{13}NONa$, $[M+Na]^+$ = 234.0895, found: 234.0991.

(E)-1-(4-(di(prop-2-yn-1-yl)amino)phenyl)-3-(4-(didodecylamino)phenyl) prop-2-en-1-one (Compound 4): Compound **5** (4.23 g, 0.02 mol) was dissolved in 10 mL EtOH. After it was completely dissolved, *t*-BuOK (1.12 g, 0.01 mol) was added to the system. Finally, compound **6** (10.97 g, 0.024 mol) was added dropwise to the system, and the reaction was carried out at 50 °C for 12 h. After the reaction was completed (monitored by TLC), the solvent was rotary-evaporated. The residue was dissolved in CH_2Cl_2 and washed with water (3 × 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. Further purification by column chromatography (silica gel, 300-400 mesh) using EA/PE (1/5, *v*/*v*) as the eluent gave the yellow solid compound **4** (5.33 g, 41%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ = 8.03 (d, *J* = 8.9 Hz, 2H), 7.77 (d, *J* = 15.4 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 15.4 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 2H), 4.22 (s, 4H), 3.35 – 3.26 (m, 4H), 2.29 (s, 2H), 1.58 (s, 4H), 1.27 (s, 36H), 0.87 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ = 196.49, 150.84, 130.42, 130.38, 130.30, 130.16, 128.12, 113.42, 113.17, 111.37, 72.96, 51.06, 40.09, 31.92, 29.69, 29.66, 29.63, 29.60, 29.54, 29.50, 29.44, 29.34, 27.30, 27.26, 27.20, 27.13, 26.13, 22.69. HRMS (ESI): m/z calculated for $C_{45}H_{67}N_2O$, $[M+H]^+$ = 651.5253, found: 651.5243.

1-(4-(Di(prop-2-yn-1-yl)amino)phenyl)-3-(4-(didodecylamino)phenyl)-4-nitrobutan-1-one (Compound 3): Compound **4** (3.25 g, 5 mmol) was dissolved in 20 mL EtOH. After it was completely dissolved, *t*-BuOK (0.56 g, 5 mmol) and nitromethane (1.53 g, 25 mmol) were added to the system, and the reaction was carried out at 80 °C for 24 h. After the reaction was completed (monitored by TLC), the solvent was rotary-evaporated. The residue was dissolved in CH_2Cl_2 and washed with water (3

× 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. Further purification by column chromatography (silica gel, 300-400 mesh) using DCM/PE (2/1, *v*/*v*) as the eluent gave the yellow oily compound **3** (1.99 g, 56%). ^{1}H NMR (400 MHz, Chloroform-*d*) : δ = 7.79 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.6 Hz, 2H), 6.46 (d, J = 8.5 Hz, 2H), 4.68 (dd, J = 12.2, 6.5 Hz, 1H), 4.56 - 4.48 (m, 1H), 4.08 (d, J = 2.1 Hz, 4H), 3.98 (p, J = 7.3 Hz, 1H), 3.29 - 3.18 (m, 2H), 3.15 - 3.07 (m, 4H), 2.18 (s, 2H), 1.46 (t, J = 7.5 Hz, 5H), 1.19 (s, 37H), 0.80 (t, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ = 195.49, 151.03, 147.65, 130.17, 128.21, 113.17, 111.85, 73.05, 51.06, 41.34, 40.07, 38.77, 31.95, 29.71, 29.69, 29.67, 29.65, 29.57, 29.38, 27.30, 27.22, 22.72, 14.14. HRMS (ESI): m/z calculated for $C_{46}H_{70}N_3O_3$, $[M+H]^+$ = 712.5417, found: 712.5413.

4,4'-(3,7-Bis(4-(di(prop-2-yn-1-yl)amino)phenyl)-5,5-difluoro-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinine-1,9-diyl)bis(N,N-didodecylaniline (Compound 2): Compound **3** (3.56 g, 5 mmol) and ammonium acetate (5.78 g, 75 mmol) were dissolved in 20 mL n-butanol. The mixture was heated to 110 °C and reacted for 12 h. After the reaction was completed (monitored by TLC), the solvent was rotary-evaporated. The residue was dissolved in CH_2Cl_2 and washed with water (3 × 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to obtain a blue-black crude product (1.34 g, 1 mmol). And then 10 mL anhydrous DCM and DIEA (1.55 g, 15 mmol) were added to the above system under the protection of nitrogen (N_2). 30 minutes later, an equal volume of $BF_3\cdot Et_2O$ was added, and the reaction was carried out at room temperature for 24 h. After the reaction was completed (monitored by TLC), the solvent was rotary-evaporated. The residue was dissolved in CH_2Cl_2 and washed with water (3 × 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. Further purification by column chromatography (silica gel, 300-400 mesh) using DCM/PE (3/2, *v*/*v*) as the eluent gave the blue-black solid compound **2** (0.29 g, 21%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ = 8.07 (t, J = 9.1 Hz, 8H), 6.99 (d, J = 8.8 Hz, 4H), 6.83 (s, 2H), 6.69 (d, J = 8.7 Hz, 4H), 4.21 (d, J = 2.4 Hz, 8H), 3.34 (t, J = 7.6 Hz, 8H), 2.28 (d, J = 2.4 Hz, 4H), 1.64 (t, J = 7.5 Hz, 8H), 1.30 (d, J = 30.1 Hz, 72H), 0.88 (t, J = 6.7 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ =

156.02, 148.67, 148.57, 145.15, 130.98, 130.88, 123.04, 120.59, 114.06, 111.34, 78.95, 72.82, 53.48, 51.19, 39.97, 31.98, 29.80, 29.76, 29.71, 29.64, 29.42, 27.47, 27.30, 22.75, 14.18. HRMS (ESI): m/z calculated for $C_{93}H_{131}BF_2N_7$, $[M]^+$ = 1383.0527, found: 1383.0525.

2,5,8,11-Tetraoxatridecan-13-yl 4-methylbenzenesulfonate (Compound 9): Tetraethylene glycol monomethyl ether (0.03 mol, 6.24 g) and triethylamine (0.045 mol, 4.55 g) were dissolved in 50 ml dry DCM, then the mixture was cooled to 0 °C. After stirring for 10 minutes, p-toluenesulfonyl chloride (0.045 mol, 8.58 g) was added slowly to it, and then the mixture was allowed to return to room temperature and reacted for 24 hours. After the reaction was completed (monitored by TLC), the solvent was rotary-evaporated. The residue was dissolved in CH_2Cl_2 and washed with water (3 × 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. Further purification by column chromatography (silica gel, 300-400 mesh) using PE/EA (7/3, *v*/*v*) as the eluent gave the yellow oily compound **9** (10.65 g, 98%). ^{1}HNMR (400 MHz, Chloroform-*d*): δ = 7.80 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 4.20 - 4.11 (m, 2H), 3.70 - 3.52 (m,14H), 3.37 (s, 3H), 2.45 (s, 3H). HRMS (ESI): m/z calculated for $C_{16}H_{27}O_7S$, $[M+H]^+$ = 363.1477, found: 363.1473.

13-Azido-2,5,8,11-tetraoxatridecane (Compound 8): Compound **9** (1.88 mmol, 0.69 g) and sodium azide (3.77 mmol, 0.25 g) were dissolved in 50 mL EtOH, and the mixture was heated to 60 °C for 2.5 hours. After the reaction was completed (monitored by TLC), the solvent was rotary-evaporated. The residue was dissolved in CH_2Cl_2 and washed with water (3 × 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. Further purification by column chromatography (silica gel, 300-400 mesh) using MeOH/DCM (2/98, *v*/*v*) as the eluent gave the yellow oily compound **8** (0.424 g, 97%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ = 3.66 (d, J = 7.8 Hz, 12H), 3.59 - 3.51 (m, 2H), 3.39 (d, J = 3.5 Hz. 5H). HRMS (ESI): m/z calculated for $C_9H_{19}N_3O_4Na$, $[M+Na]^+$ = 256.1273, found: 256.1266.

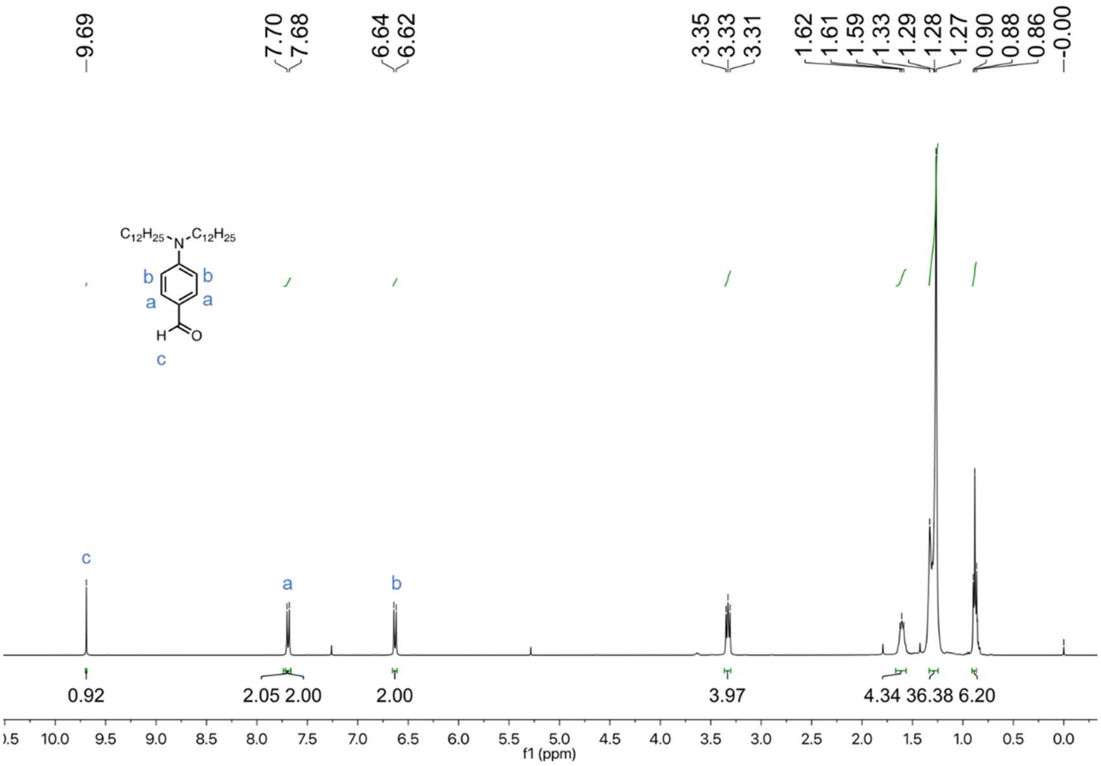


Fig. S1 ^{1}H-NMR spectrum and chemical structure of compound **6** in $CDCl_3$.

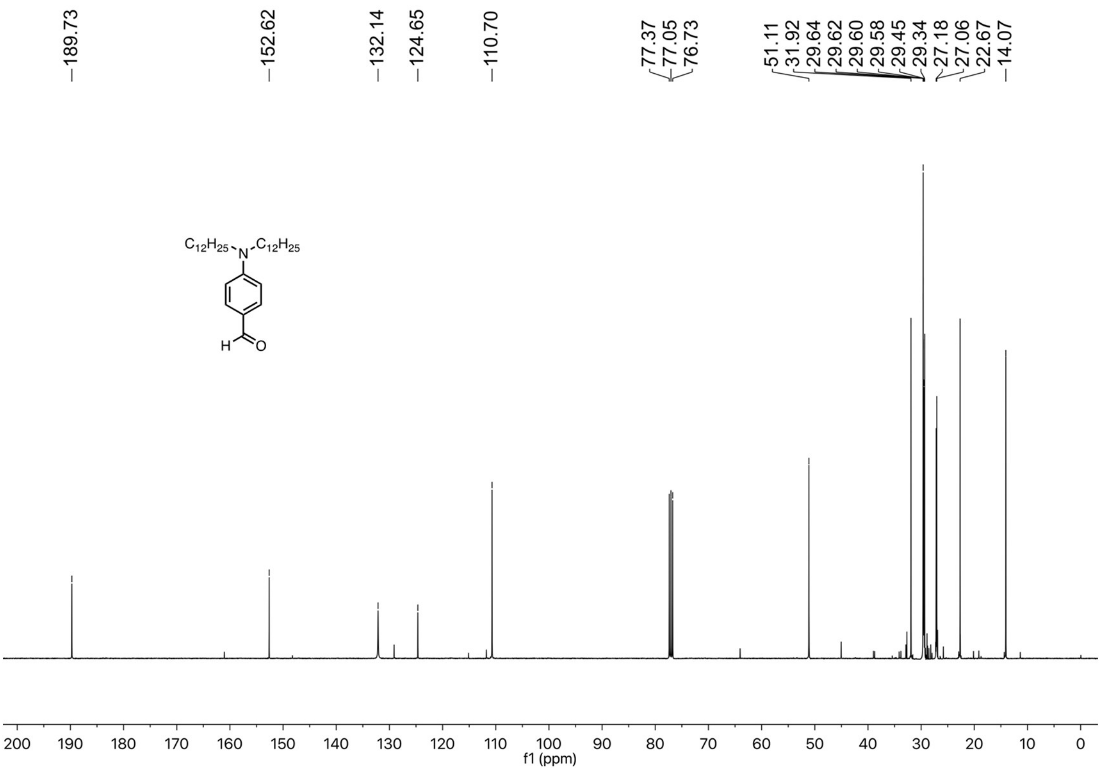


Fig. S2 ^{13}C-NMR spectrum and chemical structure of compound **6** in $CDCl_3$.

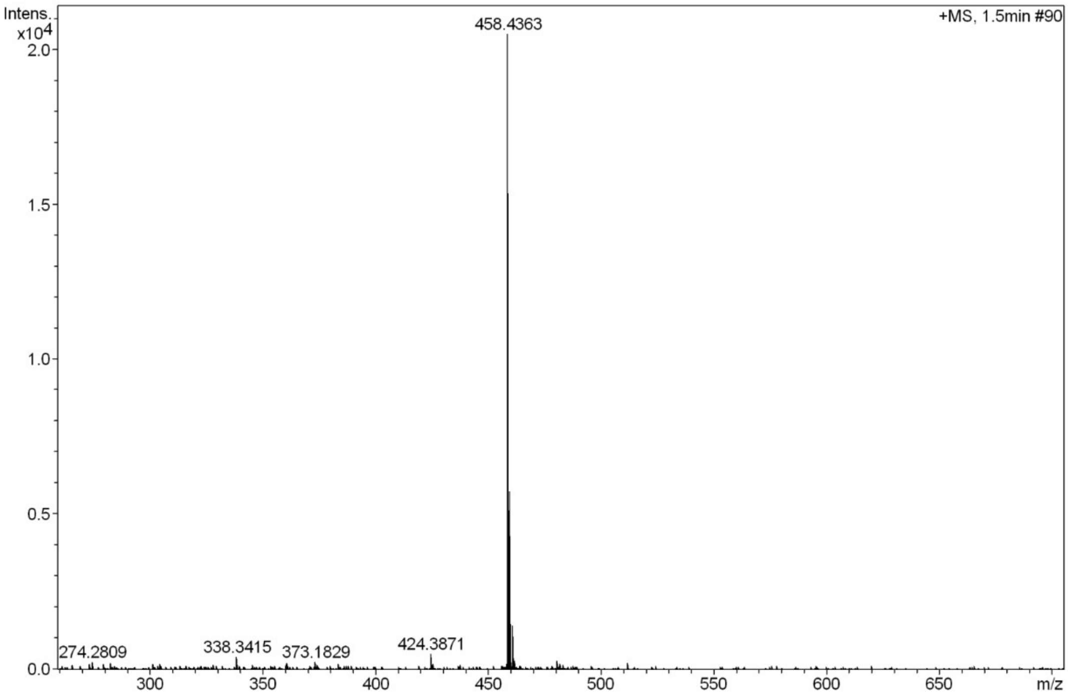


Fig. S3 HRMS spectrum of compound **6**.

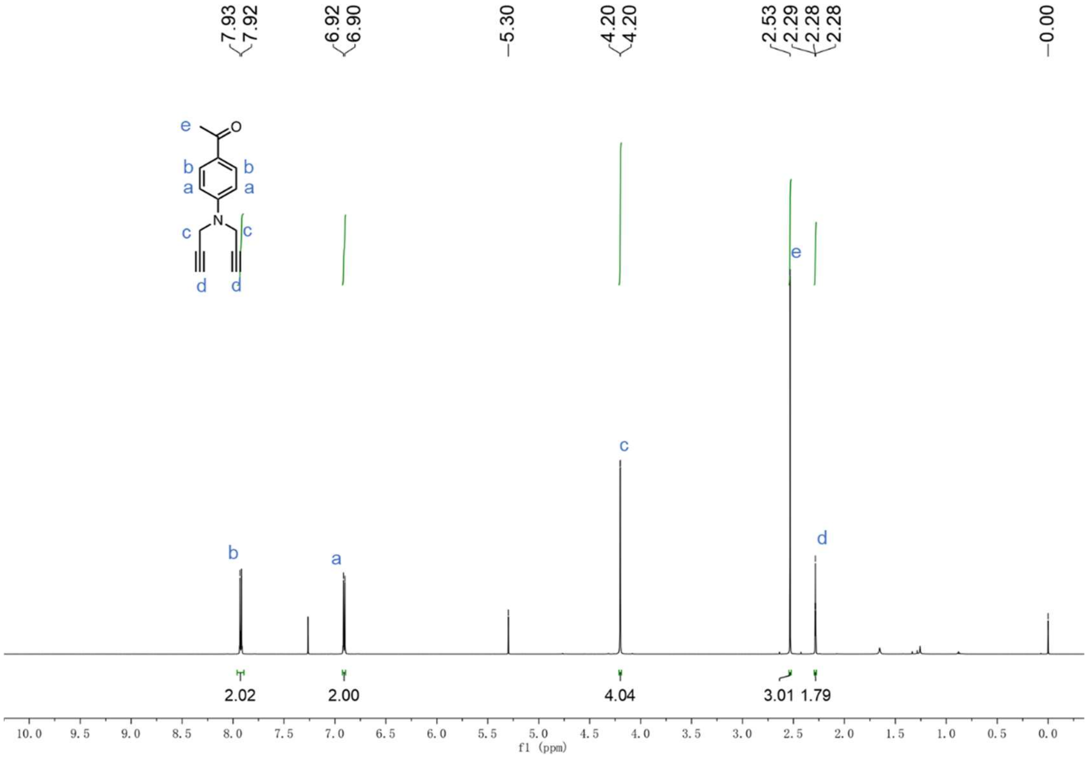


Fig. S4 ^{1}H-NMR spectrum and chemical structure of compound **5** in $CDCl_3$.

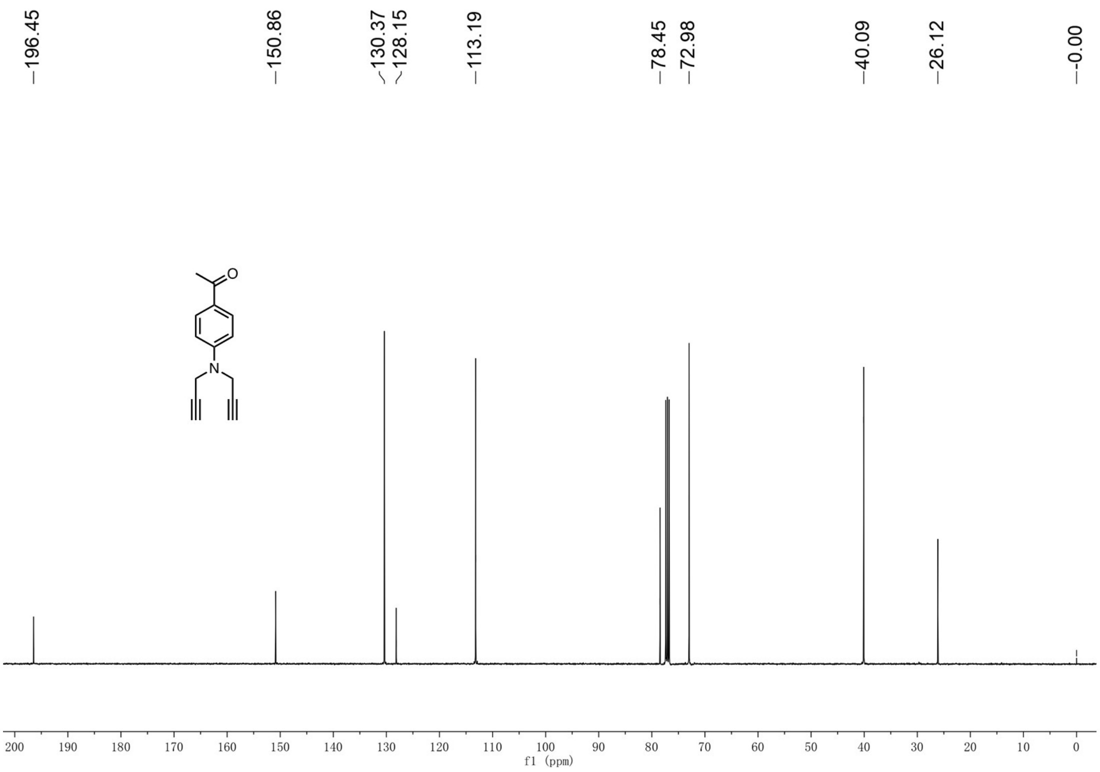


Fig. S5 ^{13}C-NMR spectrum and chemical structure of compound **5** in $CDCl_3$.

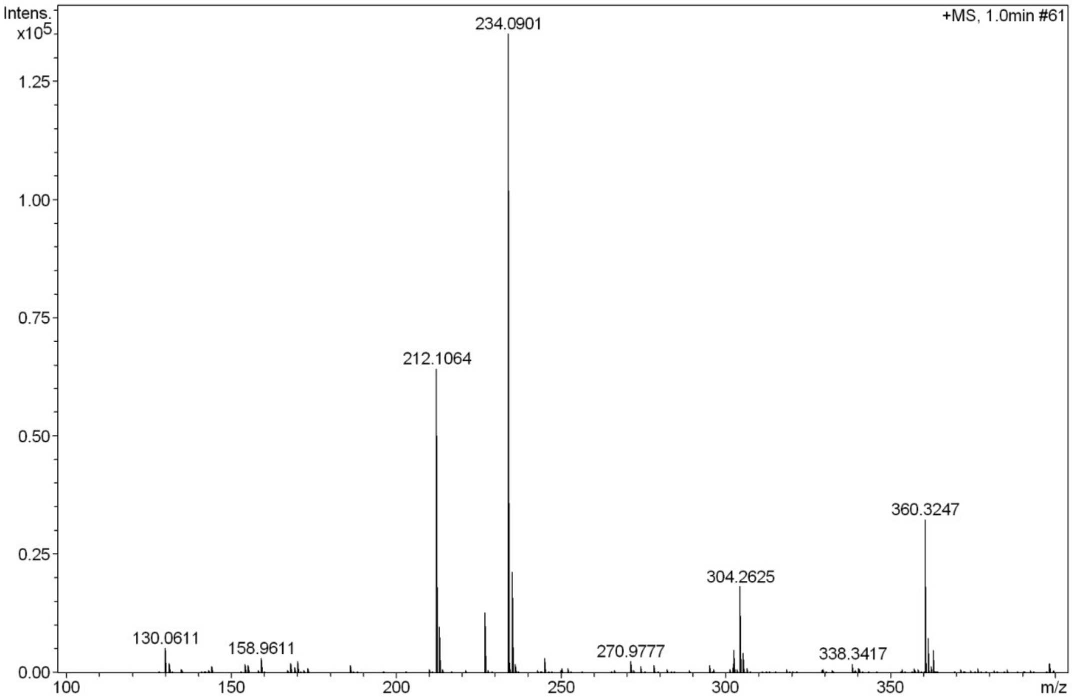


Fig. S6 HRMS spectrum of compound **5**.

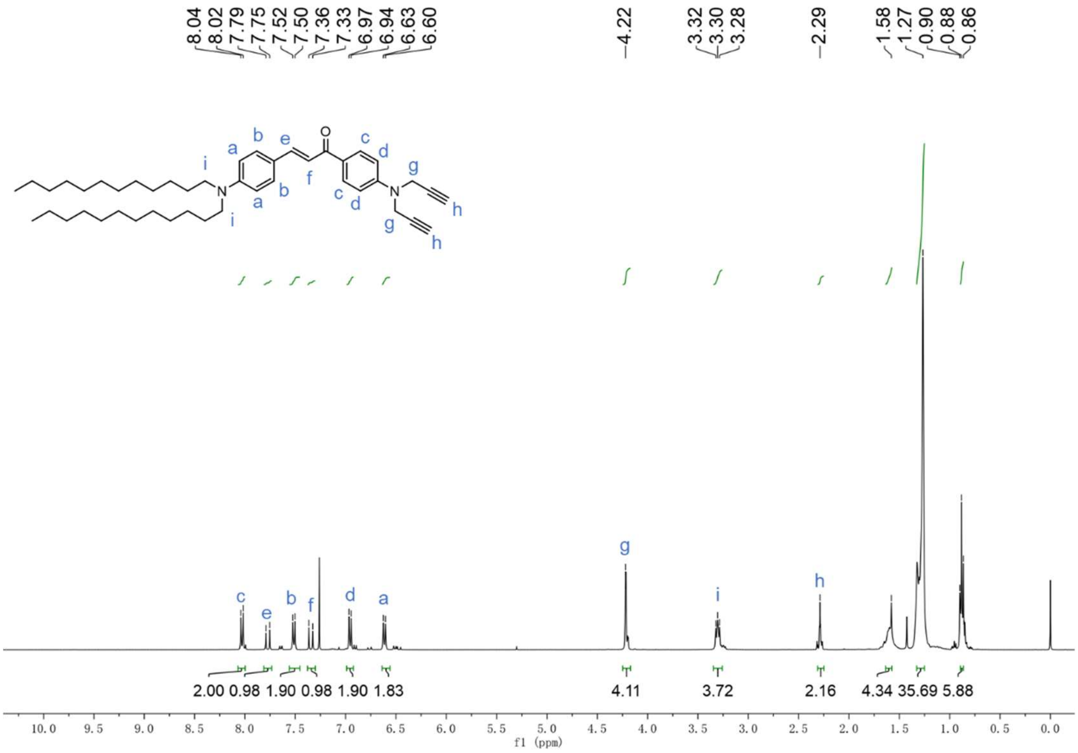


Fig. S7 ^{1}H-NMR spectrum and chemical structure of compound **4** in $CDCl_3$.

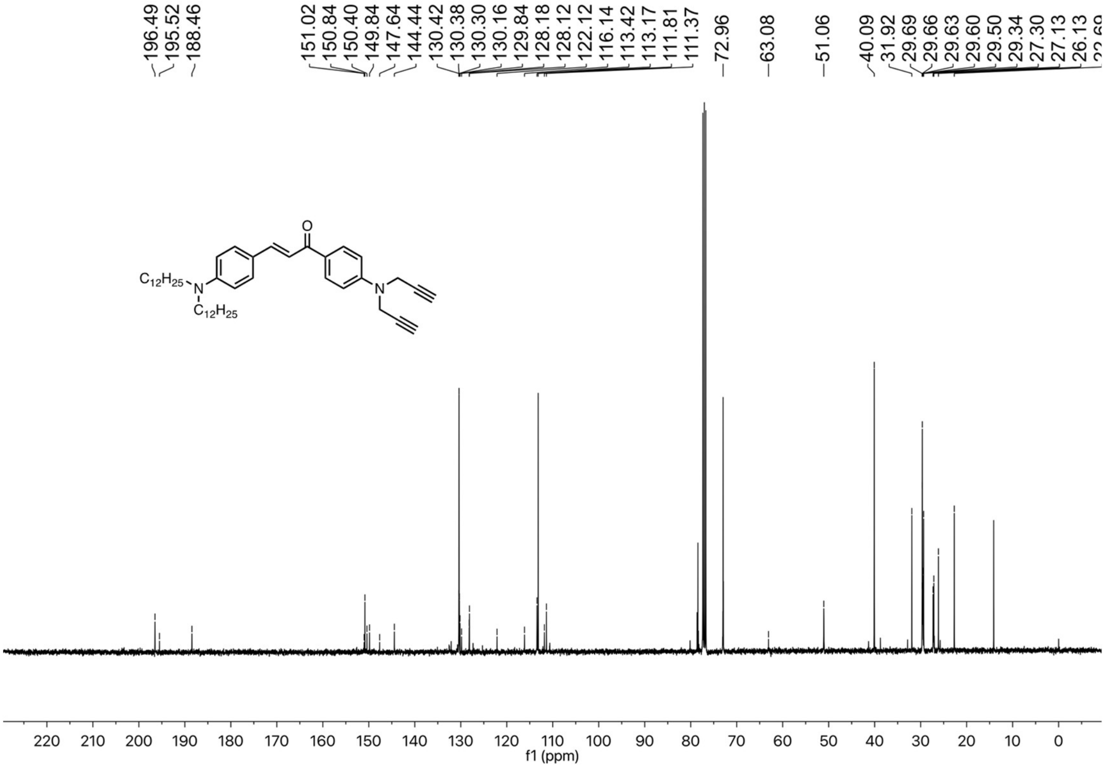


Fig. S8 ^{13}C-NMR spectrum and chemical structure of compound **4** in $CDCl_3$.

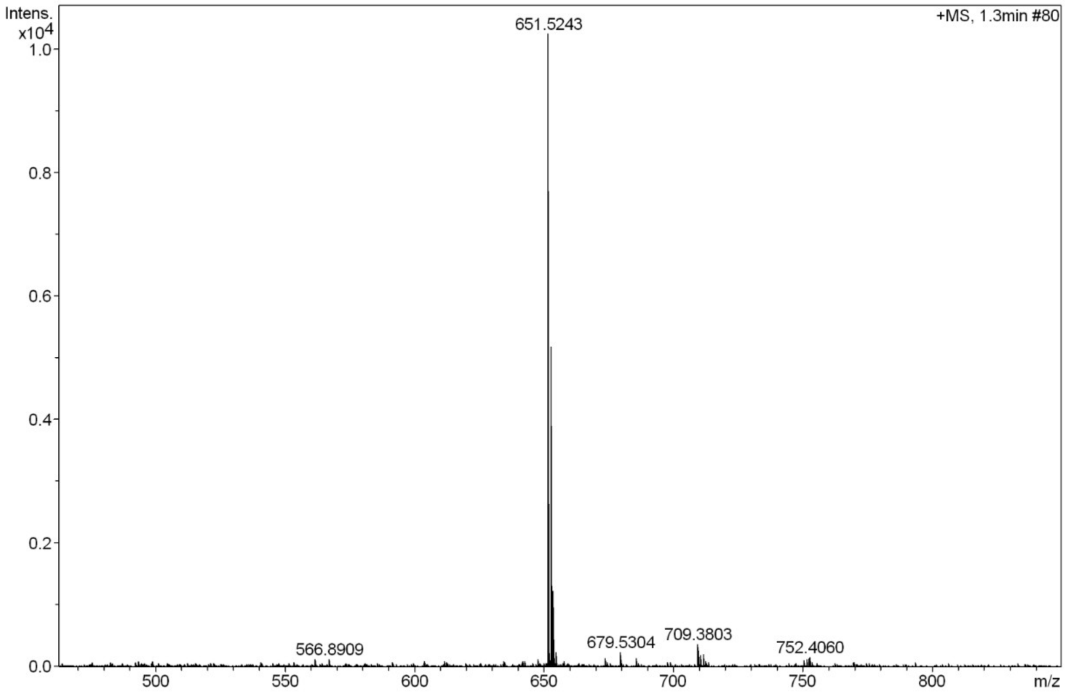


Fig. S9 HRMS spectrum of compound **4**.

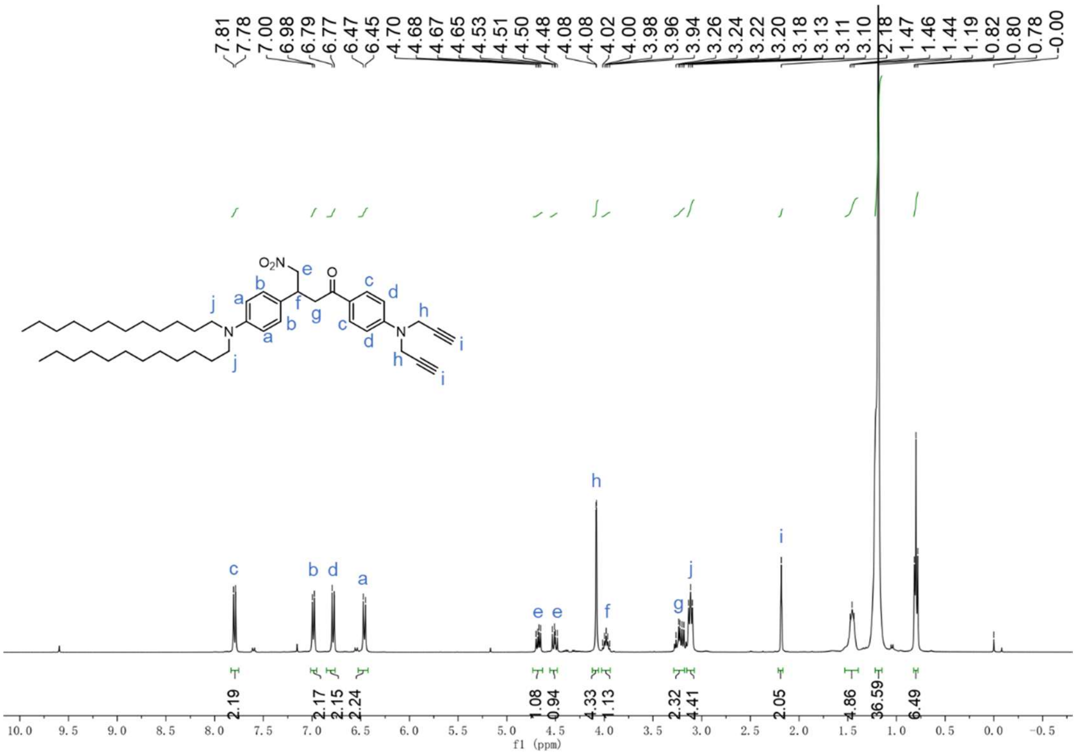


Fig. S10 ^{1}H-NMR spectrum and chemical structure of compound **3** in $CDCl_3$.

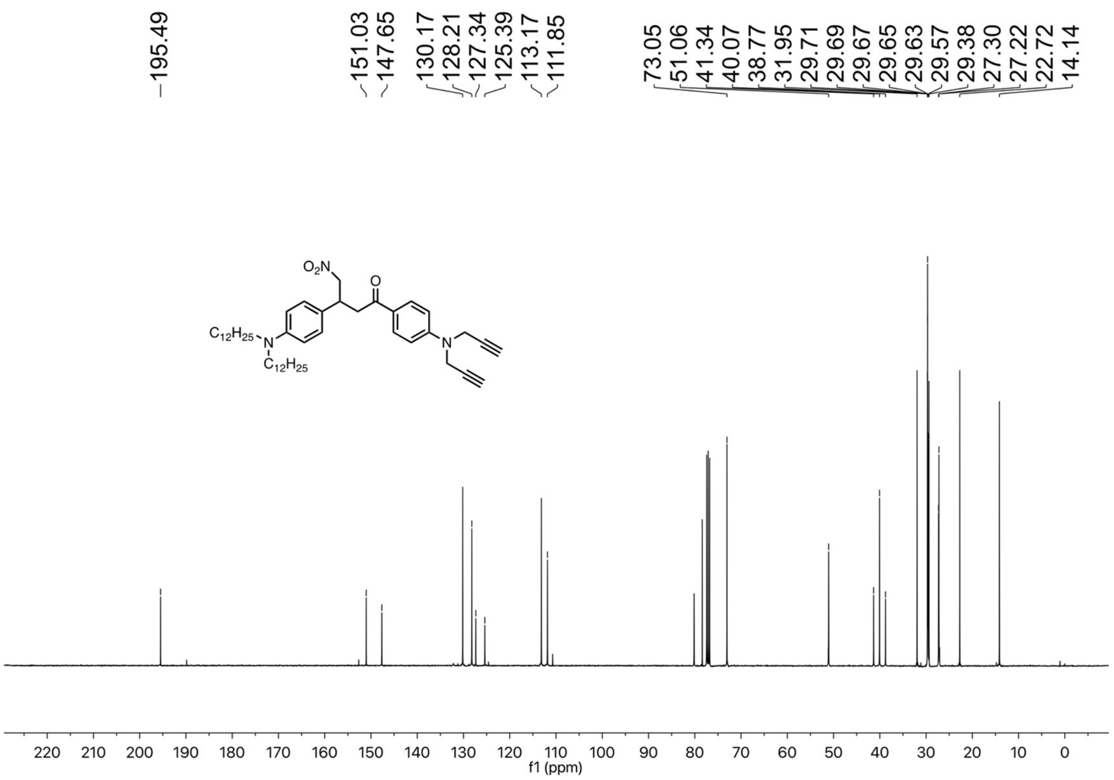


Fig. S11 ^{13}C-NMR spectrum and chemical structure of compound **3** in $CDCl_3$.

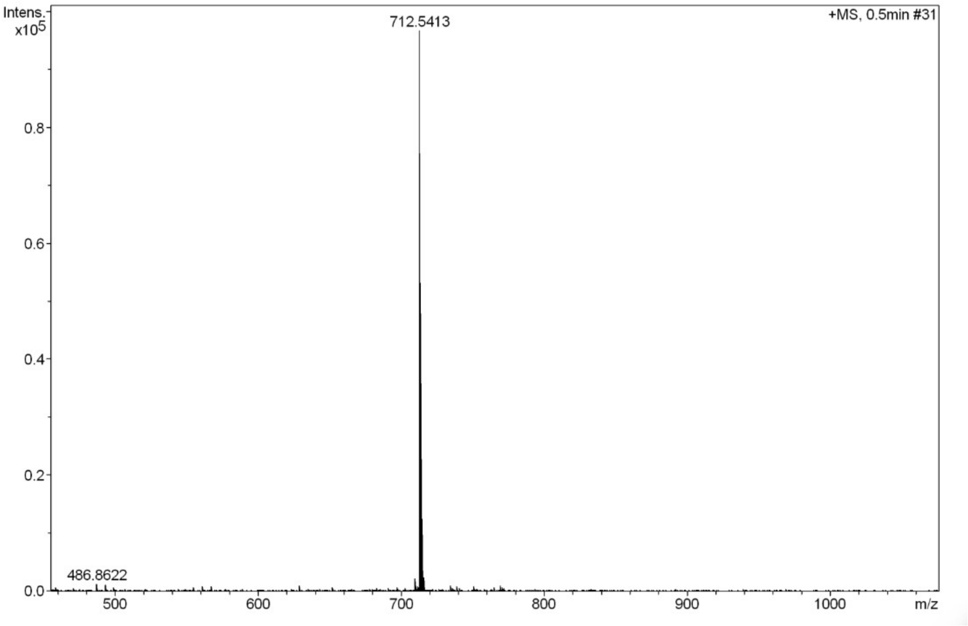


Fig. S12 HRMS spectrum of compound **3**.

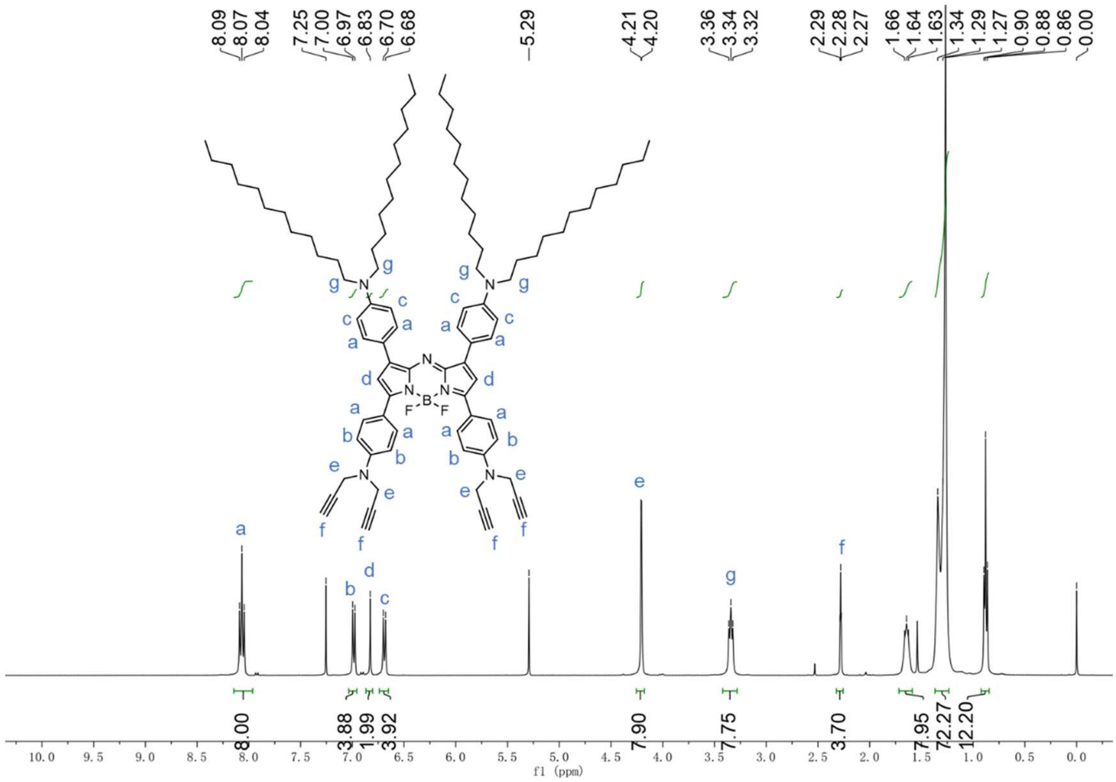


Fig. S13 ^{1}H-NMR spectrum and chemical structure of compound **2** in $CDCl_3$.

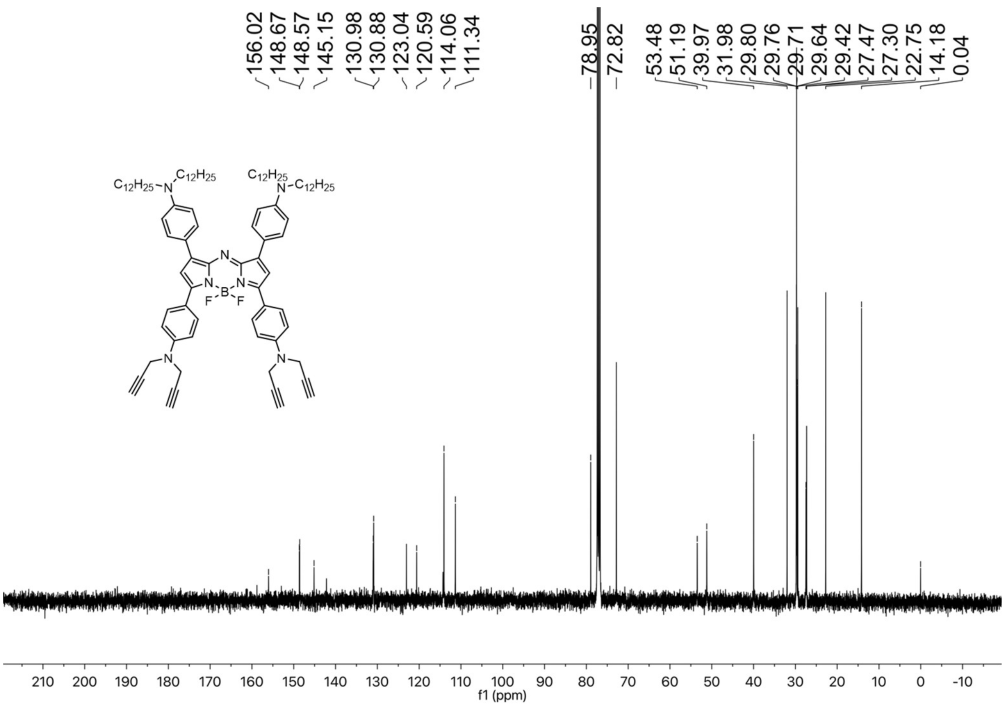


Fig. S14 ^{13}C-NMR spectrum and chemical structure of compound **2** in $CDCl_3$.

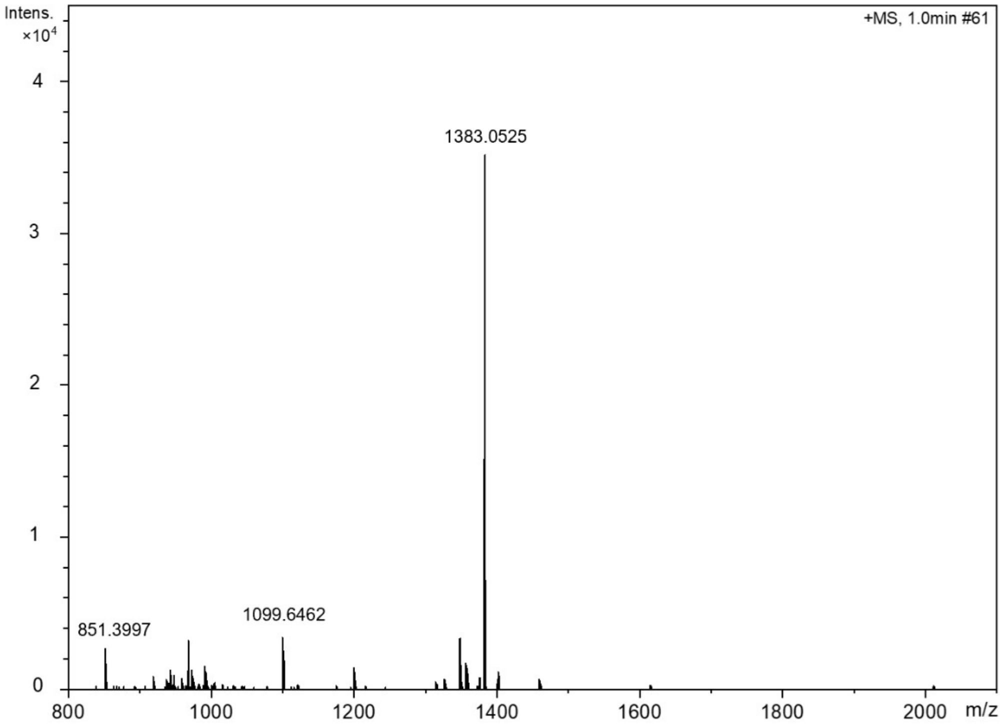


Fig. S15 HRMS spectrum of compound **2**.

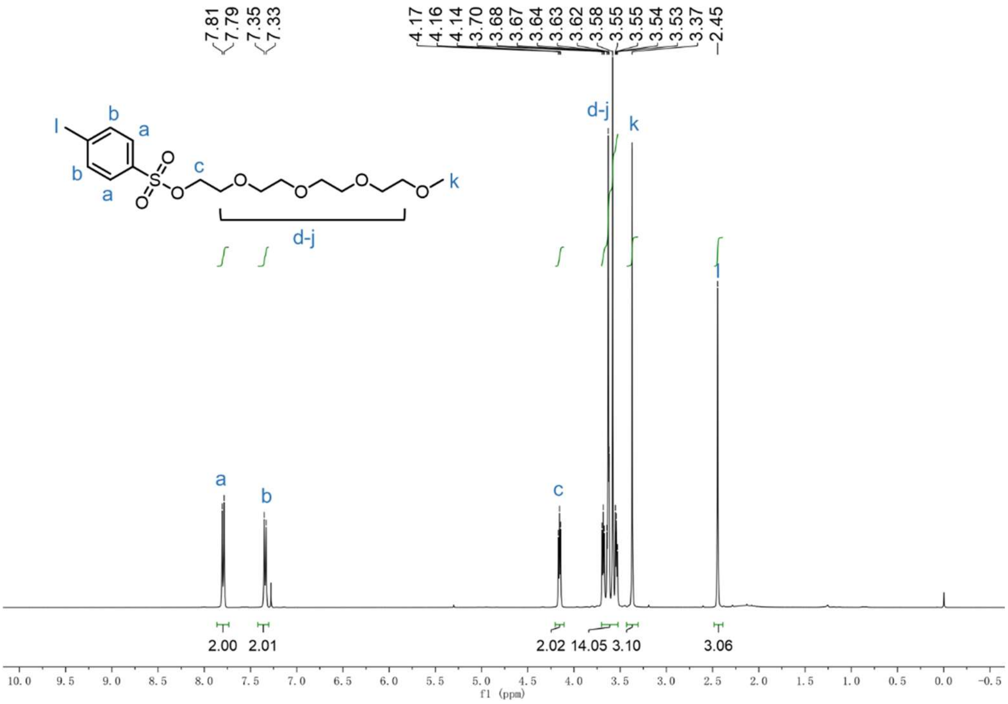


Fig. S16 ^{1}H-NMR spectrum and chemical structure of compound **9** in $CDCl_3$.

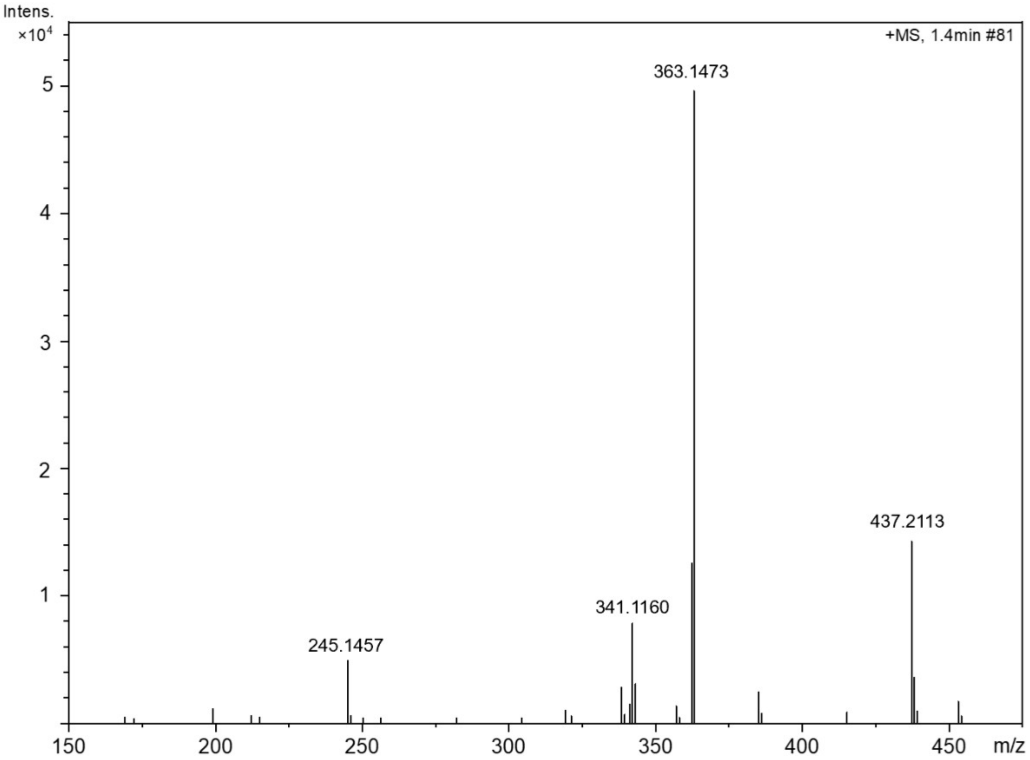


Fig. S17 HRMS spectrum of compound **9**.

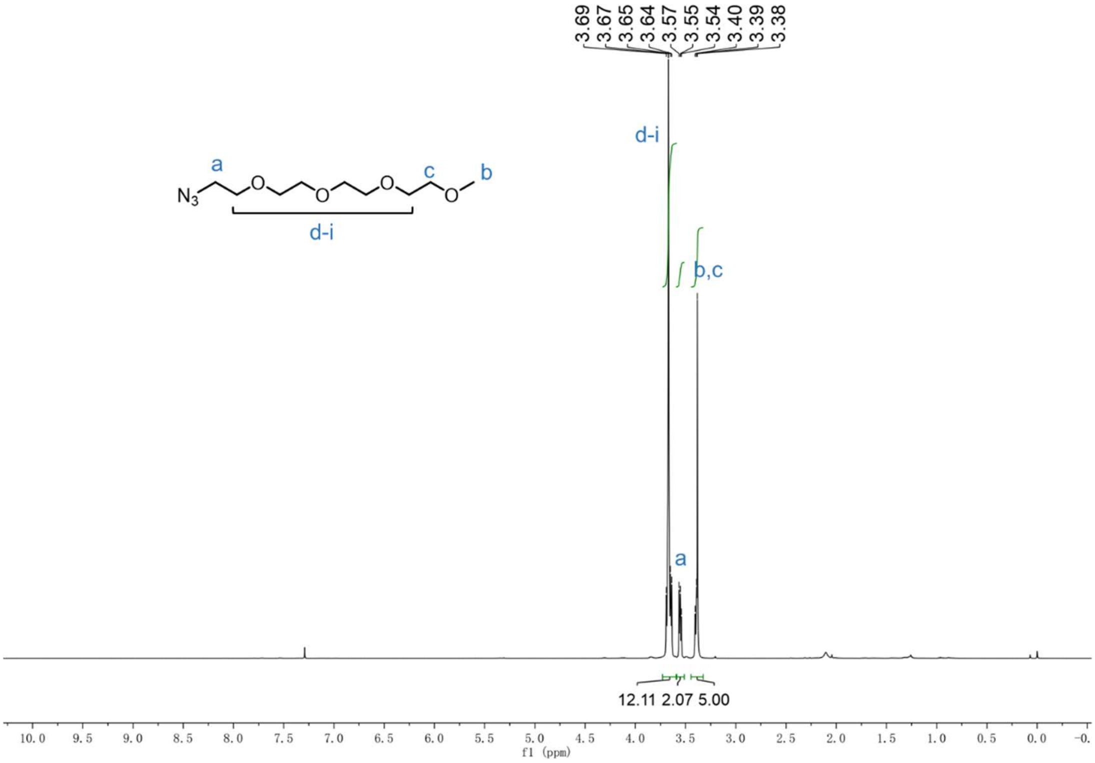


Fig. S18 ^{1}H-NMR spectrum and chemical structure of compound **8** in $CDCl_3$.

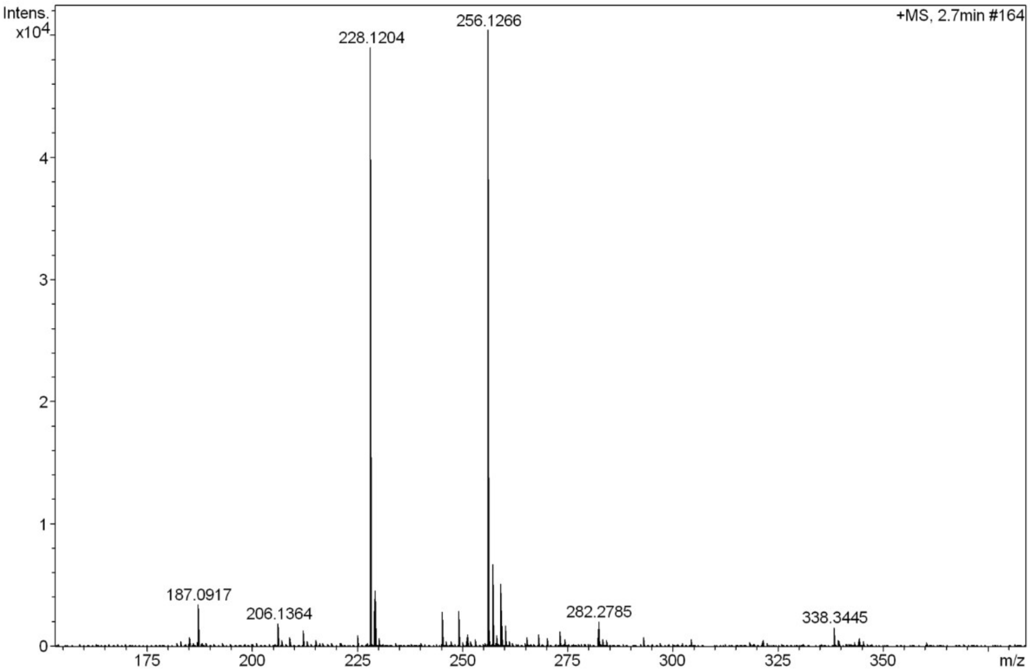


Fig. S19 HRMS spectrum of compound **8**.

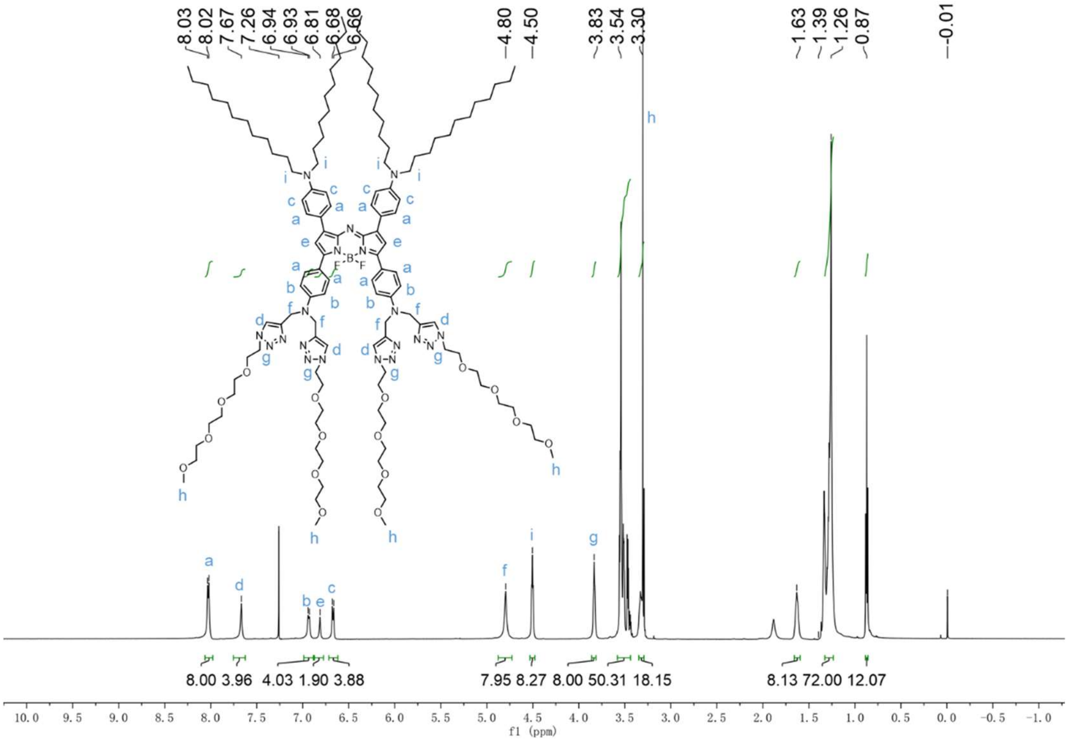


Fig. S20 ^{1}H-NMR spectrum and chemical structure of aza-BODIPY **1** in $CDCl_3$.

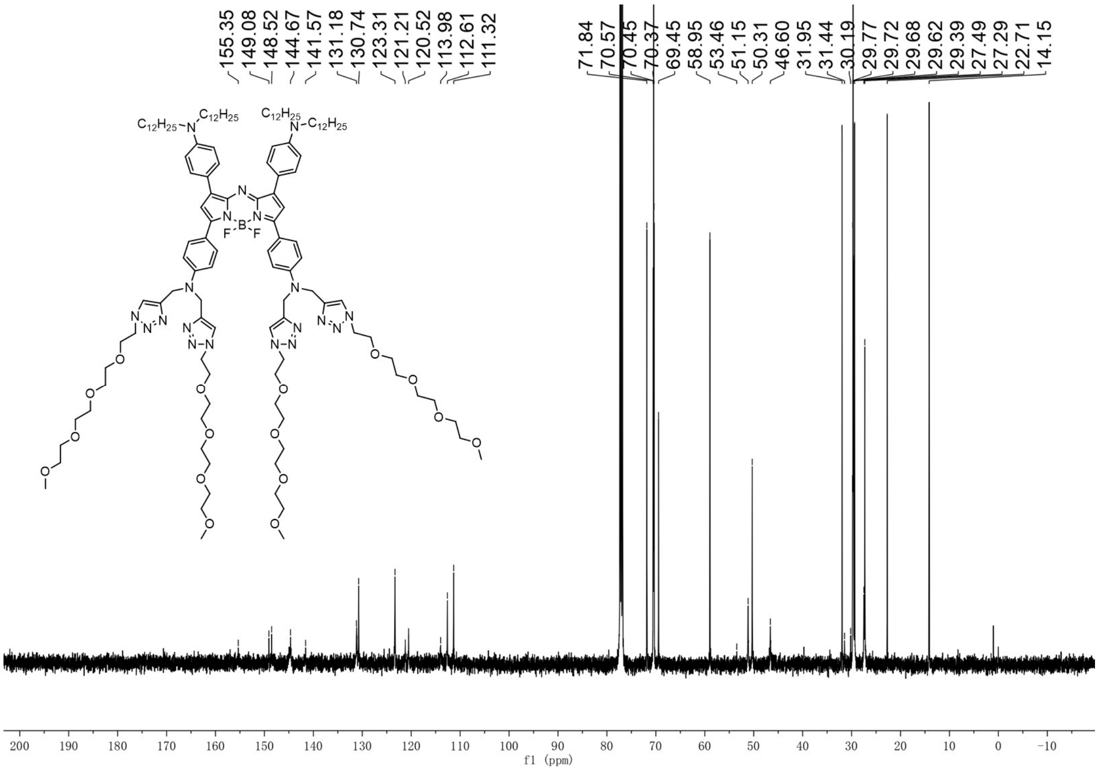


Fig. S21 ^{13}C-NMR spectrum and chemical structure of aza-BODIPY **1** in $CDCl_3$.

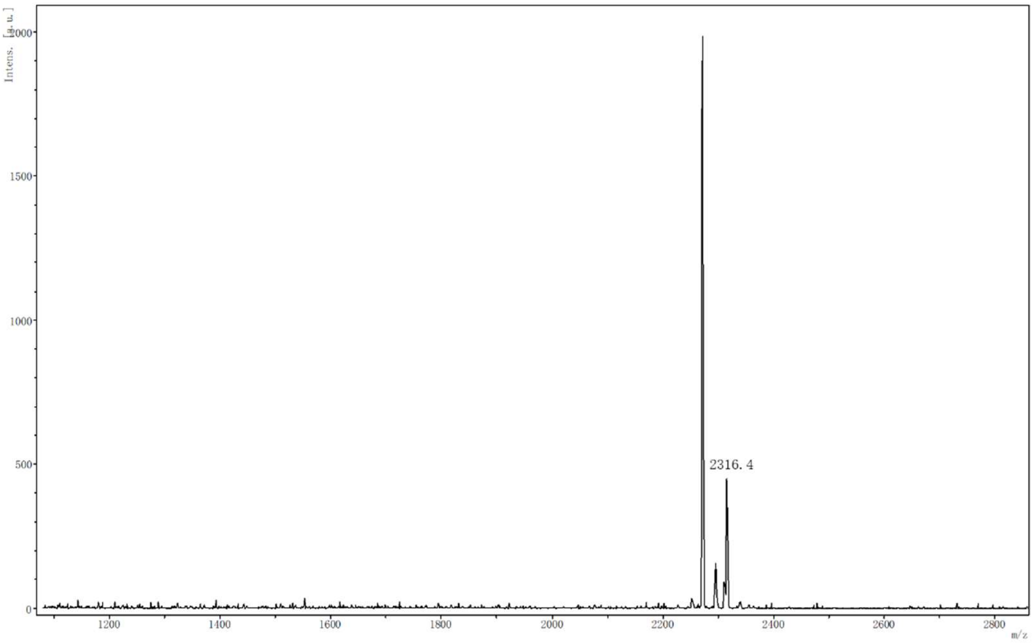


Fig. S22 Mass spectrum (MALDI-TOF) of aza-BODIPY **1**.

Studies on detection of Cu^{2+}

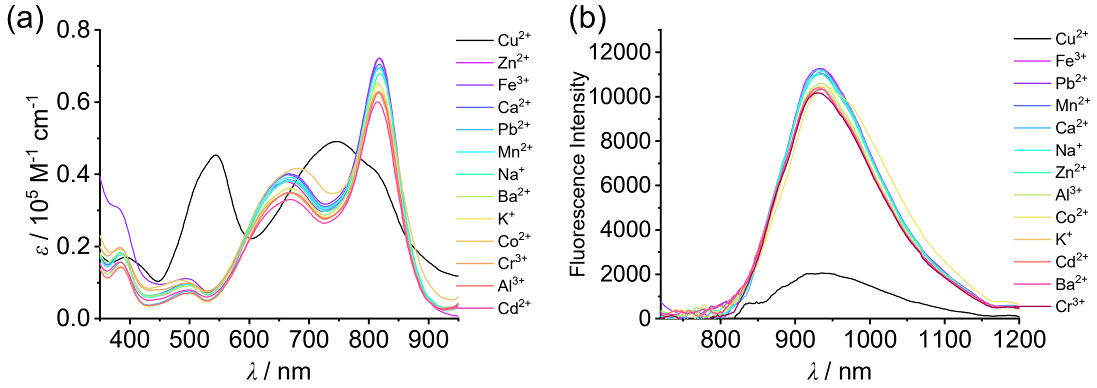


Fig. S23 Change in UV-Vis-NIR absorption spectra (a) and fluorescence spectra (b) of dye **1** after adding 10 equiv. different metal ions. ([**1**] = 1.0×10^{-5} M，[metal]= 1.0×10^{-3} M).

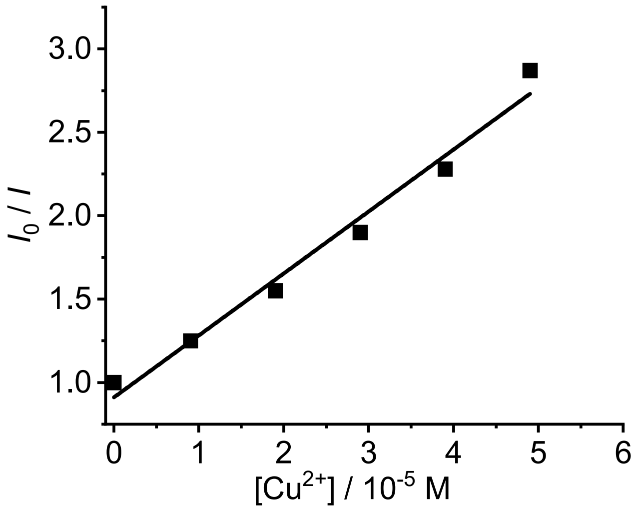


Fig. S24 The data fitting of the Stern-Volmer equation. $I_0/I = 1 + K_{SV} + [Q]$, where I_0 was the initial fluorescence intensity of the dye **1** before the addition of Cu^{2+}, I was the fluorescence intensity of the solution after adding Cu^{2+}, K_{SV} was the Stern-Volmer quenching constant, and [Q] was the concentration of Cu^{2+}.

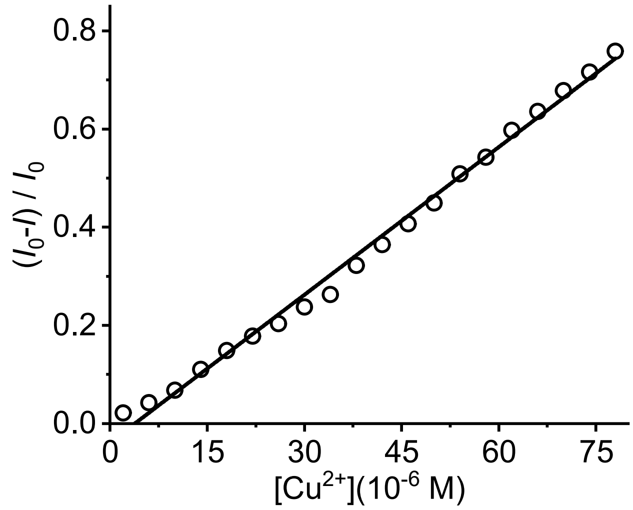


Fig. S25 Calibration curve of change in fluorescence intensity versus concentration of Cu^{2+}.

The LOD could be estimated using the following formula, where the parameter a and b was obtained by the linear fitting of

$$(I_0 - I)/I_0 = a + b[Cu^{2+}]$$

$$LOD = 3\,Sa/b$$

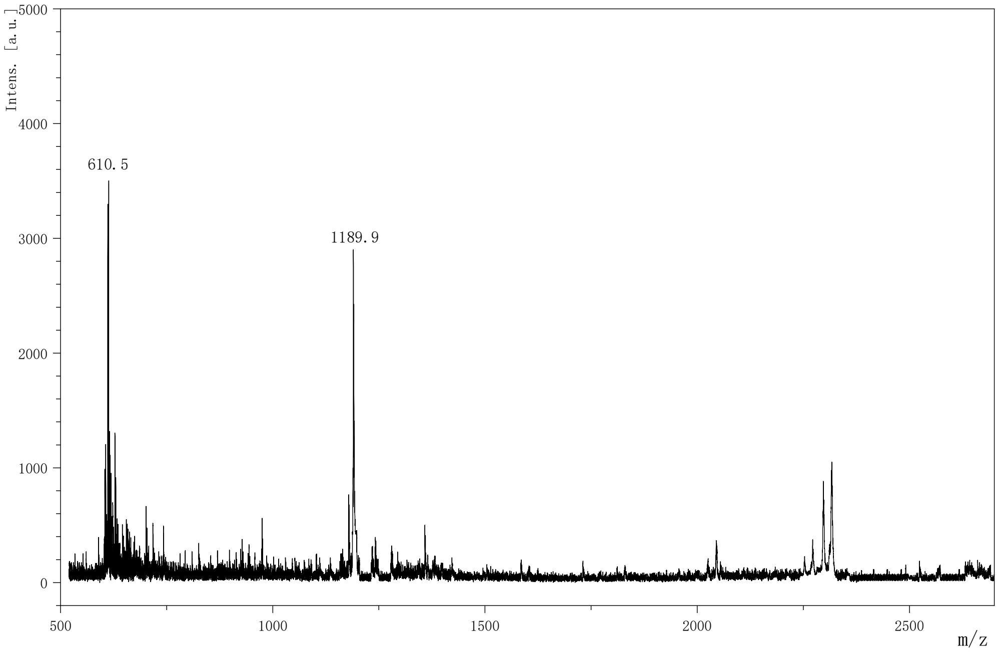


Fig. S26 Mass spectrum (MALDI-TOF) of **1**+2Cu^{2+}. m/z calculated for **1**+2Cu^{2+}, [M]$^{4+}$: 610.4, found: 610.5; m/z calculated for 1+Cu^{2+}, [M]$^{2+}$: 1189.3, found: 1189.9.

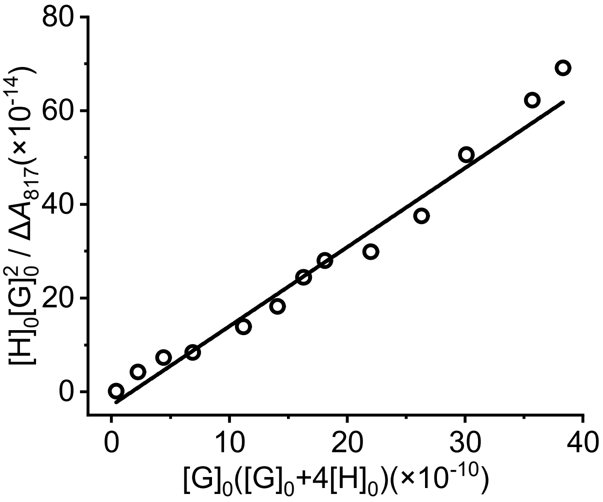


Fig. S27 Linear least squares graph for determining association constants of dye **1** and Cu^{2+}.

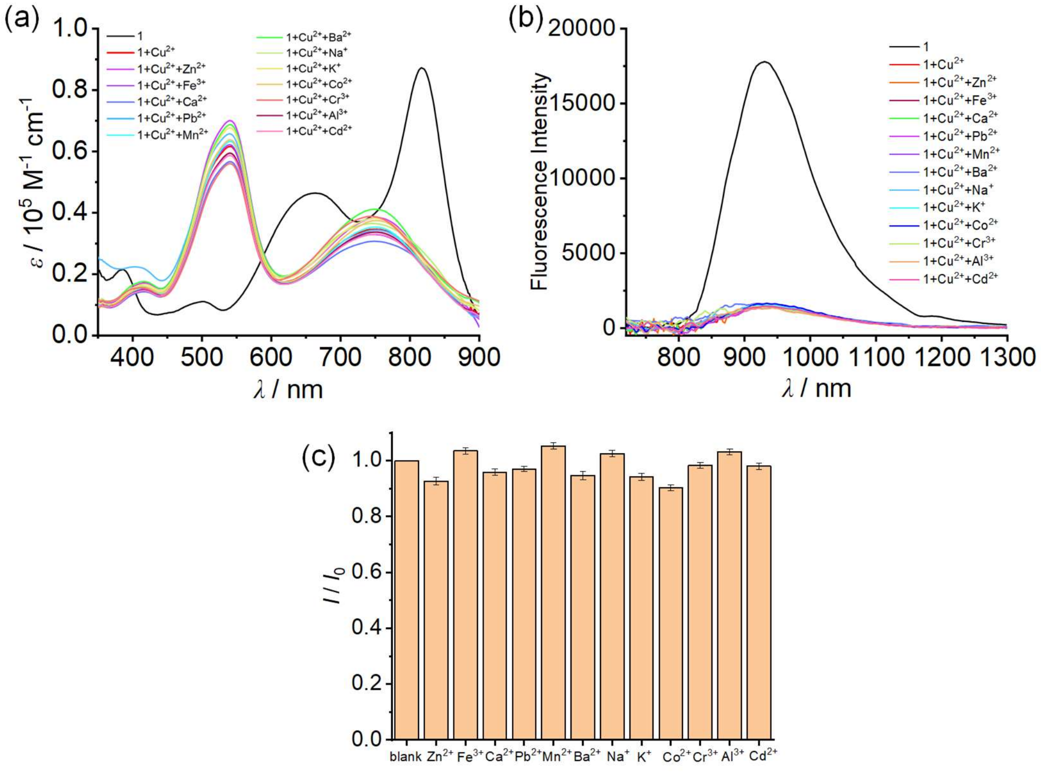


Fig. S28 Absorption spectra (a), fluorescence spectra (b) and fluorescence intensity (c) of the solutions of dye **1**+Cu^{2+} after the addition of other metal ions.

Studies on detection of PO_4^{3-}

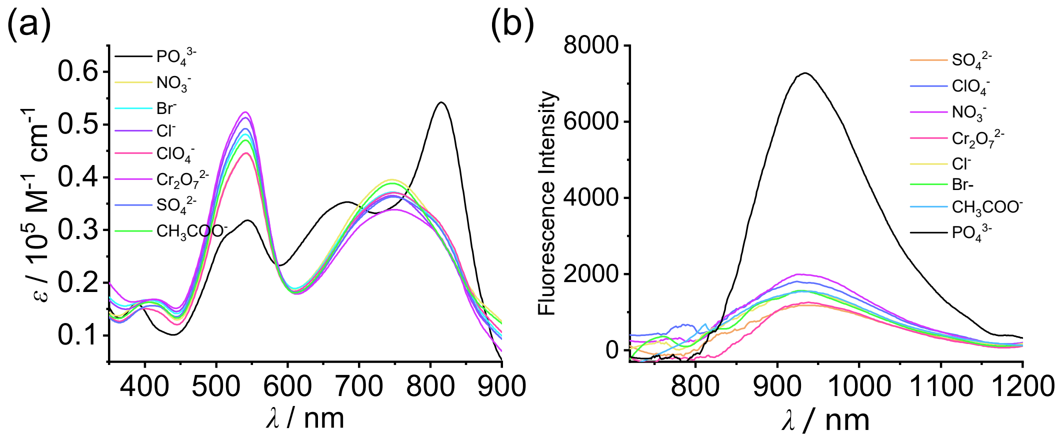


Fig. S29 Changes in UV-Vis-NIR absorption spectra (a) and fluorescence spectra (b) and the colors of **1**+Cu^{2+} after adding 8 equiv. different anions. ([**1**+Cu^{2+}] = 1.0×10^{-5} M, [anions]= 1.0×10^{-3} M).

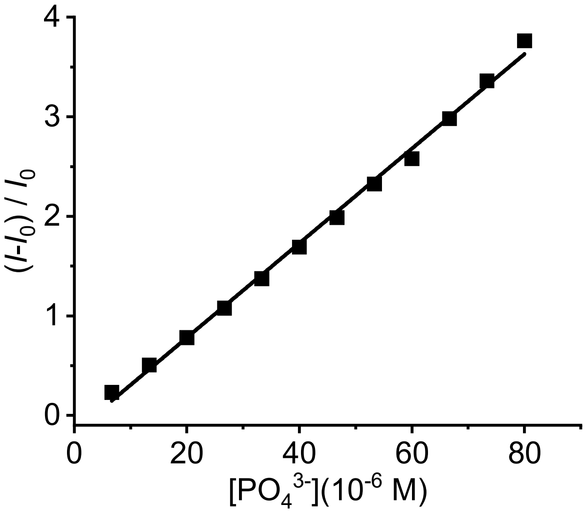


Fig. S30 Calibration curve of change in fluorescence intensity versus concentration of PO_4^{3-}.

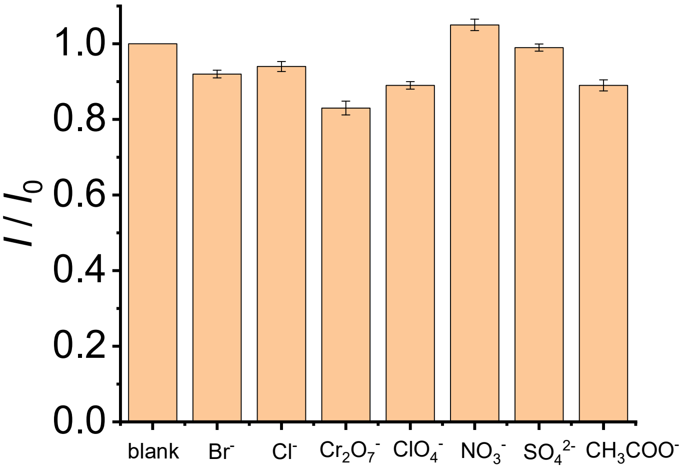


Fig. S31 Fluorescence intensity of the solutions of **1**+Cu^{2+}+PO_4^{3-} after the addition of other anions.

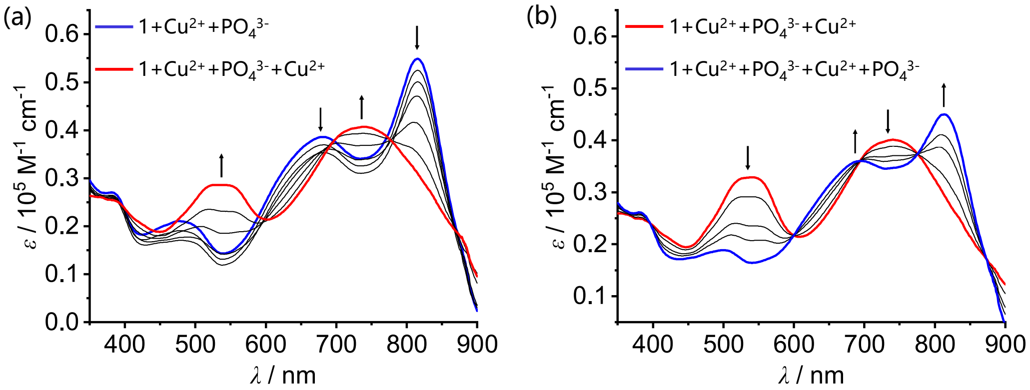
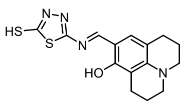
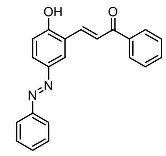


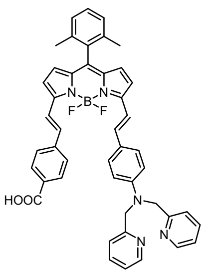
Fig. S32 (a) The absorption spectra of further adding Cu^{2+} to the system of 1+Cu^{2+}+ PO_4^{3-}; (b) The absorption spectra of further adding PO_4^{3-} to the system of 1+Cu^{2+}+ PO_4^{3+}+Cu^{2+}.



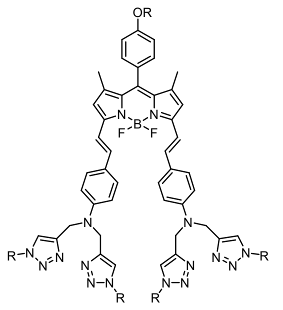
A (Ref.2)



B (Ref.3)

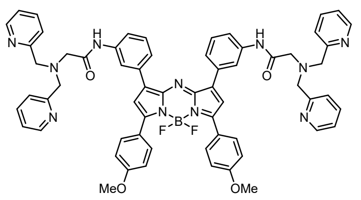


C (Ref.4)

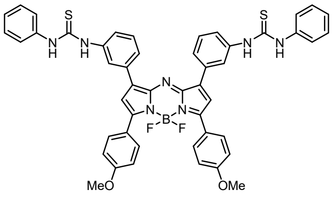


R = —$(CH_2CH_2O)_3Me$

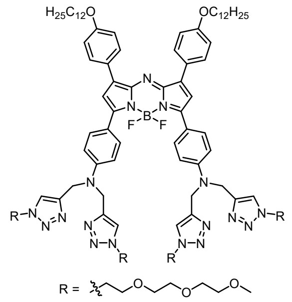
D (Ref.5)



E (Ref.6)



F (Ref.7)



G (Ref.8, our previous work)

Fig. S33 Chemical structures of probe **A-G**.

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