Electronic Supplementary Information

Dialdehyde-Diboronate-Functionalized AIE Luminogen: Design, Synthesis and Application for Detection of Hydrogen Peroxide

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Contents

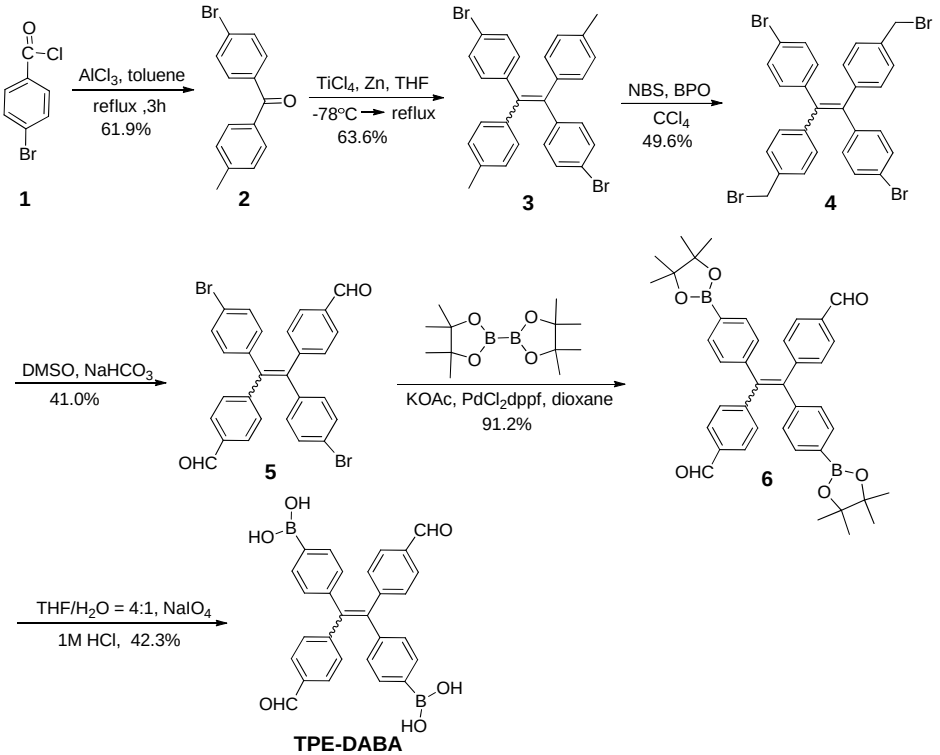
1. General information

All the starting materials were purchased as reagent grade and used without further purification. Reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel F_{254} glass plates and visualized under UV light (254 nm or 365 nm). Flash column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR(400 MHz) and ^{13}C NMR(100 MHz) spectra were measured on a Bruker Avanced III spectrometer. ^{1}H NMR(600 MHz) and ^{13}C NMR(150 MHz) spectra were measured on JEOL's NMR spectrometer. Chemical shifts for ^{1}H were reported in δ-values (ppm) with tetramethylsilane as an internal standard. The δ values for ^{13}C were calibrated with deuterated solvents ($CDCl_3$ δ = 77.16 ppm; MeOD δ = 49.00 ppm). Coupling constants in Hz were calculated from the one-dimensional spectra. Electrospray ionization (ESI) mass spectral analyses were performed on Waters LCT Premier XEmass spectrometer. MALDI-TOF-MS was performed on Bruker autoflex speed. FT-IR data was obtained on an IR Affinity-1 spectrometer (Shimadzu, Japan).

Deionized water was used to prepare all aqueous solutions. Most of spectroscopic measurements were performed in 0.1 M sodium phosphate buffers at pH 7.4. UV−vis spectra were obtained on a Shimadzu UV-2450 spectrophotometer. FL spectra were recorded on a FS5 Spectrofluorometer (Edinburgh Instruments). Samples for absorption and emission measurements were contained in 1-cm × 1-cm quartz cells. Particle size data were obtained through dynamic light scattering (ZetaPLUS, Brookhaven Instruments Corporation). Photographs were taken using a Canon camera. Spectral data were processed in OriginPro 8.0.

2. Syntheses of the compound TPE-DABA and TPE-DAP

(1) Syntheses of the probe TPE-DABA



Scheme S1. Synthetic routes to probe **TPE-DABA**

4-Bromo-4'-methylbenzophenone (2). This compound was synthesized according to the previously published procedure.[1] To a stirred solution of 3.0 g (13.7 mmol) of 4-bromobenzoyl chloride in 4.0 mL of toluene at room temperature was added 2.8 g (21.0 mmol) of $AlCl_3$ in one portion. The solution was refluxed at 110 ºC for 3.5 h. After cooled to rt, the solution was poured over concentrated HCl and ice. Then the mixture was extracted with ethyl acetate (EtOAc) and the organic layer was washed with diluted HCl, saturated NaCl (aq.), saturated $NaHCO_3$ (aq.), saturated NaCl (aq.) sequentially. The extract was dried over $MgSO_4$, filtered, and concentrated to give a white solid which was recrystallized from EtOAc and petroleum ether to give 2.33 g (61.9%) of 4-bromo-4'-methylbenzophenone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m , 6H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). The spectroscopic data coincide with the previous report.[1]

1,2-bis(4-bromophenyl)-1,2-di-*p*-tolylethene (3). 1.35 g of 4-bromo-4'-methylbenzophenone and 1.16 g of Zn power was added to a pre-dried two necked round-bottom flask with a magnetic stirrer and a water condenser. The flask was degassed and flushed with argon three times. 20 mL of anhydrous THF was injected into the flask and the mixture was cooled to -50ºC for 10 min. 0.8 mL of titanium tetrachloride ($TiCl_4$) was injected into the flask and then the mixture was allowed to warm to rt to obtain a black mixture. After stirred for 0.5 h at rt, the black mixture was refluxed overnight. The reaction was quenched with a 10% potassium carbonate (K_2CO_3) aqueous solution and filtered. The filtrate was then extracted with CH_2Cl_2, washed with NaCl (aq.) and the aqueous layer was reextract with CH_2Cl_2. The combined organic fractions were dried over anhydrous $MgSO_4$. After filtration and solvent evaporation, the crude product was purified by silica gel column chromatography to give **3** (0.81 g) as white solid in 63.6% yield. IR (KBr) υ (cm^{-1}): 3023, 2929, 1904, 1583, 1509, 1485, 1392, 1111, 1071, 1010, 826, 817, 802, 769, 736, 495. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.4 Hz, 1H), 6.92 (s, 1H), 6.86 (s, 2H), 2.27 (d, *J* = 4.3 Hz, 2H) ^{13}C NMR (101 MHz, $CDCl_3$) 142.97, 142.88, 140.29, 140.17, 139.92, 139.89, 136.73, 136.60, 133.10, 133.04, 131.27, 131.21, 131.15, 131.00, 128.85, 128.71, 120.69, 120.57, 21.34. MS (MALDI-TOF): calibrated for $C_{28}H_{23}Br_2$ $[M+H]^+$ 519.01, found 518.97.

1,2-bis(4-(bromomethyl)phenyl)-1,2-bis(4-bromophenyl)ethene (4). In a 100 mL round-bottom flask with a reflux condenser was added **3** (1.04 g, 2.0 mmol), *N*-bromosuccinimide (NBS, 0.8 g, 4.5 mmol), benzoyl peroxide (BPO, 12mg), followed by addition of 20 mL of CCl_4. After refluxed for 13 h, the mixture was cooled to room temperature and filtered to remove succinimide. The filtrate was evaporated under reduced pressure and the residue was purified by silica gel column chromatography to give white solid product **4** (1.36 g) in 49.6% yield. IR (KBr) υ (cm^{-1}): 3025, 2922, 2852, 1906, 1583, 1507, 1486, 1410, 1392, 1227, 1202, 1071, 1010, 828, 780, 607, 492. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 4H), 7.18 – 7.11 (m, 4H), 6.97-6.92 (m, 4H), 6.89 – 6.83 (m, 4H), 4.42 (d, *J* = 4.7 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) 143.03, 142.99, 142.02, 141.97, 140.28, 136.68, 136.61, 132.99, 131.68, 131.37, 131.27, 128.92, 128.82, 121.25, 121.20, 33.39, 33.34. MS (MALDI-TOF): calibrated for $C_{28}H_{21}Br_4$ $[M+H]^+$ 675.83, found 675.88.

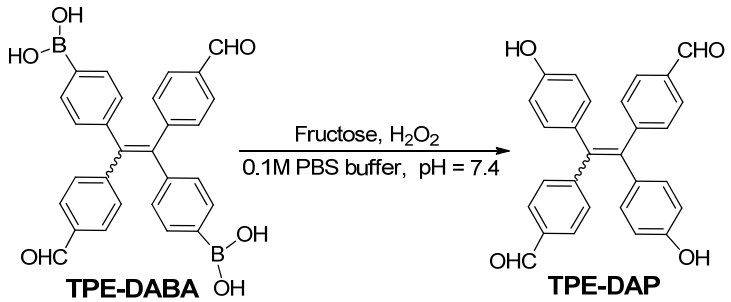
4,4'-(1,2-bis(4-bromophenyl)-1,2-ethenylene)dibenzaldehyde (5). $NaHCO_3$ (0.2 g, 2.4 mmol) was added to a stirred solution of **4** (0.4 g, 0.59 mmol) in DMSO (3.4 mL) and the mixture was stirred at 95 ºC for 4 h. The mixture was cooled back to rt, diluted with water, and extracted twice with EtOAc. The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4). After filtration and solvent evaporation, the crude product was purified by silica gel column chromatography and **5** (133 mg) was obtained as a white solid in 41.0% yield. IR (KBr) υ (cm^{-1}): 2831, 2732, 1701, 1601, 1564, 1485, 1392, 1304, 1211, 1168, 1072, 1011, 822, 786, 742. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 9.92 (s, 2H), 7.64 (d, *J* = 8.1 Hz, 4H), 7.31 (d, *J* = 8.3 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 4H), 6.87 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) 191.64, 148.78, 141.05, 140.89, 135.07, 132.80, 131.90, 131.62, 129.55, 121.92. MS (MALDI-TOF): calibrated for $C_{28}H_{19}Br_2O_2$ $[M+H]^+$ 546.97, found 546.96.

4,4'-(1,2-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) -1,2-ethenylene)dibenzaldehyde (6). 5 (82 mg, 0.15 mmol), bis(pinacolato)diboron (83.8 mg, 0.33 mmol), potassium acetate (92.7 mg, 0.94 mol) and Pd(dppf)Cl_2 (12 mg) were added in a 25 mL pre-dried reaction flask with a reflux condenser before adding anhydrous dioxane (3 mL) by syringe. After the reaction was refluxed for 18 h, the reaction mixture was cooled to room temperature and diluted with CH_2Cl_2, washed with saturated NaCl (aq.). The organic layer was dried over anhydrous $MgSO_4$ and filtered. Afterwards, the filtrate was concentrated under reduced pressure and the obtained residue was purified by silica gel column chromatography to get diboronic ester compound **6** (87.7 mg, 91.2%). IR (KBr) υ (cm^{-1}): 2978, 2830, 2733, 1705, 1603, 1514, 1400, 1359, 1323, 1272, 1212, 1268, 1146, 1089, 1020, 963, 859, 828, 786, 657. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 2H), 7.62 (d, *J* = 7.8 Hz, 4H), 7.57 (d, *J* = 7.7 Hz, 4H), 7.16 (d, *J* = 7.9 Hz, 4H), 7.00 (d, *J* = 7.6 Hz, 4H), 1.33 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) 191.86, 149.58, 145.12, 142.10, 134.93, 134.63, 132.08, 130.64, 129.47, 84.02, 25.05. MS (ESI) calcd for $C_{40}H_{43}B_2O_6$ $[M+H]^+$: 641.32, found: 641.28. MS (MALDI-TOF): calibrated for $C_{40}H_{43}B_2O_2$ $[M+H]^+$ 641.32, found 641.33.

4,4'-(1,2-bis(4-formylphenyl)-1,2-ethenylene)diphenylboronic acid (TPE-DABA). To the solution of **6** (75 mg) in THF (2 mL) and water (0.5 mL) was added $NaIO_4$ (150 mg). The mixture was stirred at rt for 30 min and then HCl solution (1 M, 120 μL) was added. After 12 h, H_2O was added to the reaction and the mixture was extracted with EtOAc. The organic layer was washed with water and saturated NaCl (aq.) and then dried over anhydrous Na_2SO_4. After filtration, solvent evaporation and purification by flash column chromatography. The desired product **TPE-DABA** (23.6 mg) was obtained in 42.3% yield. IR (KBr) υ (cm^{-1}): 3600-3200 (broad), 2928, 2852, 2733 (-CHO), 1698 (C=O), 1601, 1564, 1510, 1403, 1365, 1344, 1306, 1212, 1169, 1103, 1018, 828, 793, 739, 704, 649. ^{1}H NMR (400 MHz, DMSO) δ 9.90 (s, 2H), 7.98 (s, -B(OH)2), 7.70 (d, *J* = 7.9 Hz, 4H), 7.65-7.48 (m, 4H), 7.21 (d, *J* = 7.9 Hz, 4H), 7.08 – 6.94 (m, 4H). ^{1}H NMR (400 MHz, MeOD) δ 9.87 (s, 2H), 7.66 (d, *J* = 7.9 Hz, 4H), 7.55 – 7.35 (m, 4H), 7.23 (d, *J* = 7.3 Hz, 4H), 7.06 – 6.98 (m, 4H). ^{13}C NMR (101 MHz, MeOD) 193.63, 150.96, 136.35, 134.45, 133.01, 131.51, 130.20. HRMS (ESI) calibrated for $C_{28}H_{23}B_2O_6$ $[M+H]^+$ 477.1685, found 477.1682.

(2) Syntheses of the oxidation product TPE-DAP



4,4'-(1,2-bis(4-hydroxyphenyl) -1,2- ethenylene)dibenzaldehyde (TPE-DAP). Fructose (4.31 g, 23.9 mmol) was added to the suspension of TPE-DABA in 0.1 M PBS buffer containing 2 vol% DMSO (120 mL, pH =7.4) at room temperature. After 30min, H_2O_2 (30% in water, 0.4 mmol) was

added dropwise and the resultant mixture was allowed to stand for 3h. Then the mixture was extracted with ether acetate and the organic layer was dried over anhydrous sodium sulfate. After filtration and solvent evaporation, the crude product was purified by silica gel column chromatography. TPE-DAP was obtained in 94% yield (15.7 mg). IR (KBr) υ (cm^{-1}): 3384, 3032, 2843, 2737, 1685, 1598, 1562, 1512, 1435, 1390, 1366, 1306, 1267, 1214, 1169, 1105, 1015, 869, 836, 783, 736, 562, 522. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.91 (d, *J* = 11.3 Hz, 2H, 2-CHO), 7.63 (dd, *J* = 19.8, 8.2 Hz, 4H), 7.19 (dd, *J* = 20.7, 8.1 Hz, 4H), 6.86 (dd, *J* = 24.4, 8.6 Hz, 4H), 6.61 (dd, *J* = 20.0, 8.3 Hz, 4H), 4.88 (s, 2H, 2-OH). ^{13}C NMR (151 MHz, $CDCl_3$) 192.35, 192.21, 155.18, 155.02, 150.64, 150.44, 140.72, 140.62, 135.10, 134.87, 134.64, 134.51, 132.89, 132.81, 132.17, 132.10, 129.52, 129.50, 115.31, 115.21. HRMS (ESI) calibrated for $C_{28}H_{19}O_4$ $[M-H]^-$ 419.1288, found 419.1291.

3. Sample Preparations.

(1) Production of various reactive oxygen species (ROS).[2]

H_2O_2: Hydrogen peroxide was delivered from 30% aqueous solution and the concentration was determined from the absorption at 240 nm with Ɛ = 43.6 $M^{-1}cm^{-1}$

•OH: Hydroxyl radical was generated by Fenton reaction of 1 mM Fe^{2+} with 250 μM H_2O_2.

ClO^-: Hypochlorite was delivered from 5% aqueous solution and the concentration was determined from the absorption at 292 nm (Ɛ = 350 $M^{-1}cm^{-1}$).

$ONOO^-$: The peroxynitrite alkaline stock was prepared following the literature procedure and assayed using UV-Vis spectrophotometer via $Ɛ_{302\ nm}$ =1670 $cm^{-1}.M^{-1}$.[3]

TBHP: tert-Butyl hydroperoxide (TBHP) was prepared from 70% aqueous solutions

O_2^- : Superoxide (O_2^-) was added as a solution of KO_2 in DMSO.

•OBu: tert-Butoxy radical was generated by reaction of 1 mM Fe^{2+} with 250 μM TBHP.

NO_2^- : Nitrite was added as a solution of $NaNO_2$ in water.

NO_3^- : Nitrate was added as a solution of $NaNO_3$ in water.

(2) Preparation of stock solutions.

Buffer solutions: Britton-Robinson buffer solutions were prepared by adding different amount of 0.2 M NaOH to the mixed solution of acids (phosphoric acid, 0.04 M; acetic acid, 0.04 M; boronic acid, 0.04 M). PBS buffer solution (pH 7.40) was prepared by mixing the solution of Na_2HPO_4 (133 mM) and NaH_2PO_4 (133 mM) and the concentration was adjusted to 100 mM before spectroscopic measurements were performed.

Stock solution of TPE-DABA in DMSO: The stock solution of TPE-DABA with a concentration of 2.5 mM was prepared by dissolving TPE-DABA in DMSO and the solution was stored in a refrigerator under 4ºC.

Stock solution of D-fructose in water: The stock solution of D-fructose with a concentration of 160 mM was prepared by dissolving D-fructose in deionized water and the solution was freshly prepared every time before use.

4. General procedure for optical spectrum measurements

pH effect of compound 6 and TPE-DABA. The stock solution of **6** in DMSO and the TPE-DABA in DMSO was diluted to 0.5 mM respectively. Then 80 μL solution was added into 3920 μL Britton-Robinson buffers with different pH values respectively. The resultant solution was allowed to stand for 30 min before fluorescence measurements. All experiments were repeated twice.

Detection of D-fructose. 80 μL Stock solution of TPE-DABA and certain amount of stock solution of D-fructose were added into 3 mL PBS buffer solution. Then the volume of the solution was increased to 4 mL by adding appropriate amount of deionized water. The resultant solution was allowed to stand for 30 min before fluorescence measurements. All experiments were repeated twice.

Detection of H_2O_2. 80 μL Stock solution of TPE-DABA and 750 μL stock solution of D-fructose were added into 3 mL PBS buffer solution. After adding appropriate amount of deionized water, the resultant solution was allowed to stand for 30 min. Then different amount H_2O_2 solution was added and the mixture was shaken for 1 h before optical spectrum measurements. All measurements were repeated twice.

Detection of glucose. 80 μL Stock solution of TPE-DABA, 750 μL stock solution of D-fructose and certain amount of stock solution of glucose (20 mM) were added into 3 mL PBS buffer solution. After adding appropriate amount of deionized water, the resultant solution was allowed to stand for 30 min. Then 4U GOD was added to sample tube. The mixture was shaken for 1 h at 37 ºC before fluorescence measurements. All measurements were repeated twice.

5. Supplementary mass spectra and optical spectra.

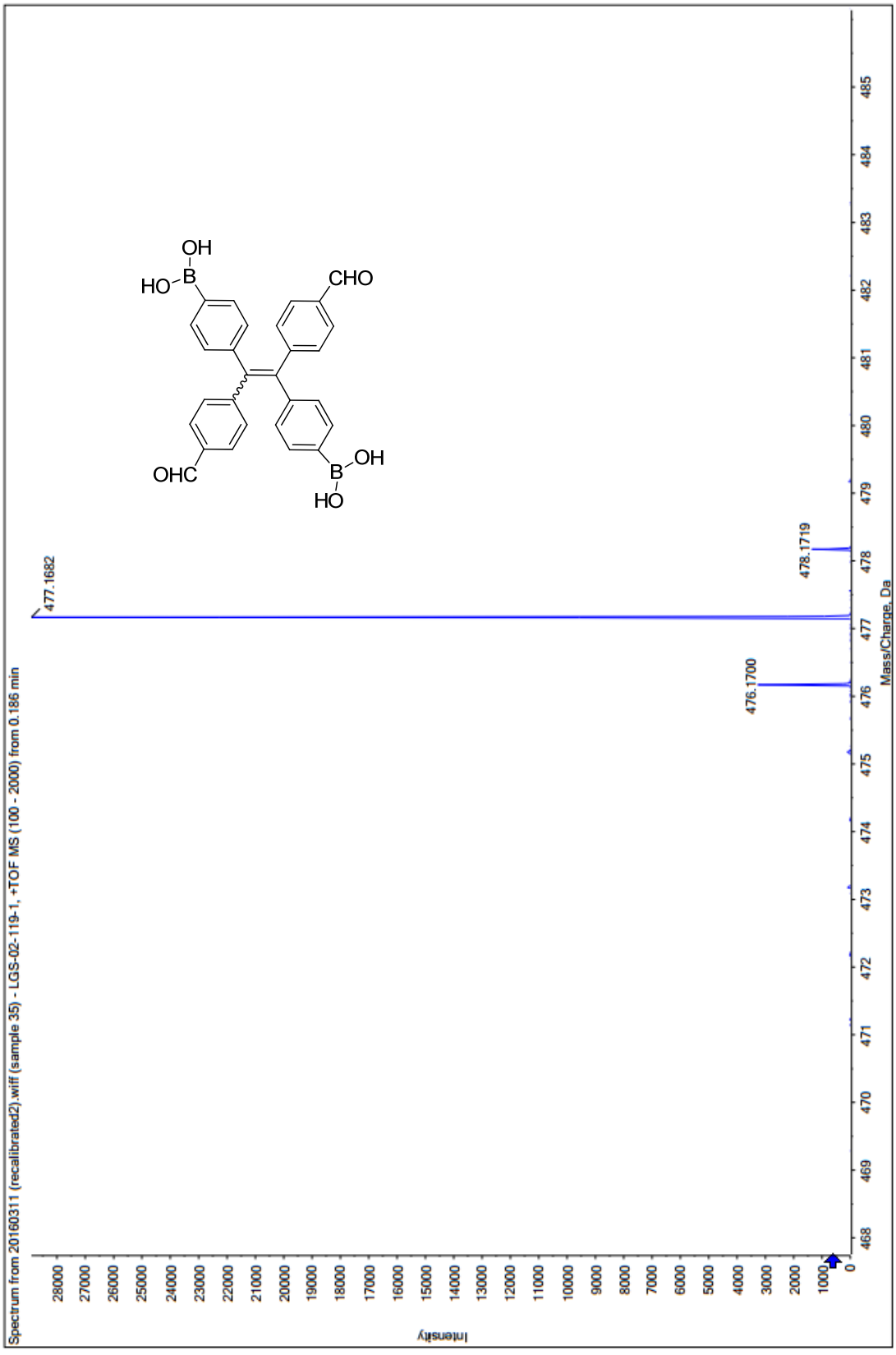


Figure S1. HRMS (ESI) spectrum of **TPE-DABA** in CH_3OH

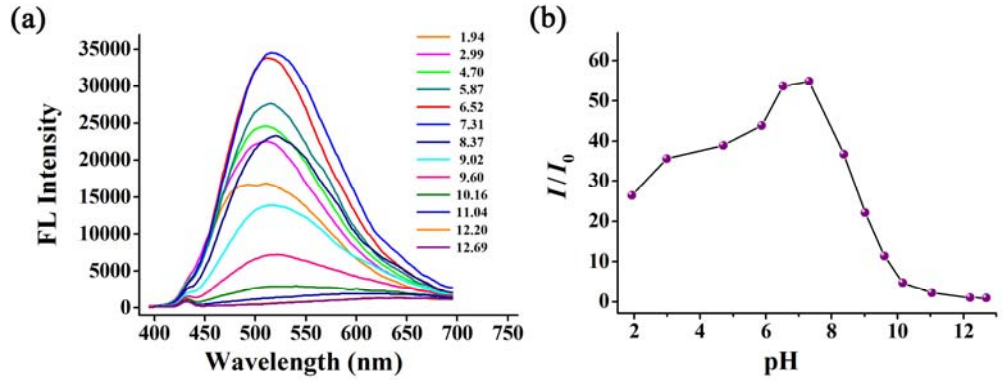


Figure S2. (a) Fluorescence spectra of TPE-DABA (10 μM) in Britton-Robinson buffers containing 2 vol% DMSO at different pH values. (b) pH effect on fluorescence intensity (***I***) of fluorescent probe **TPE-DABA** at 510 nm; $\boldsymbol{I_0}$ is the intensity at pH 12.2. (λ_{ex} = 380 nm).

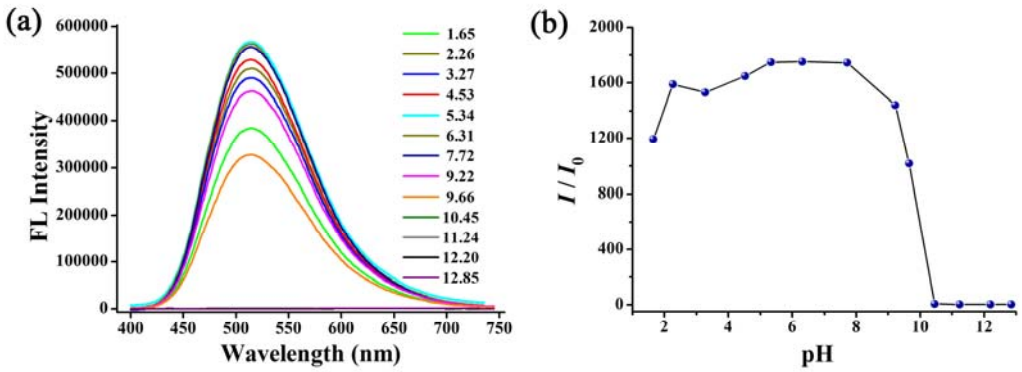


Figure S3. (a) Fluorescence spectra of compound **6** (10 μM) in Britton-Robinson buffers containing 2 vol% DMSO at different pH values. (b) pH effect on fluorescence intensity (***I***) of compound **6** at 510 nm; I_0 is the intensity at pH 12.2. (λ_{ex} = 380nm)

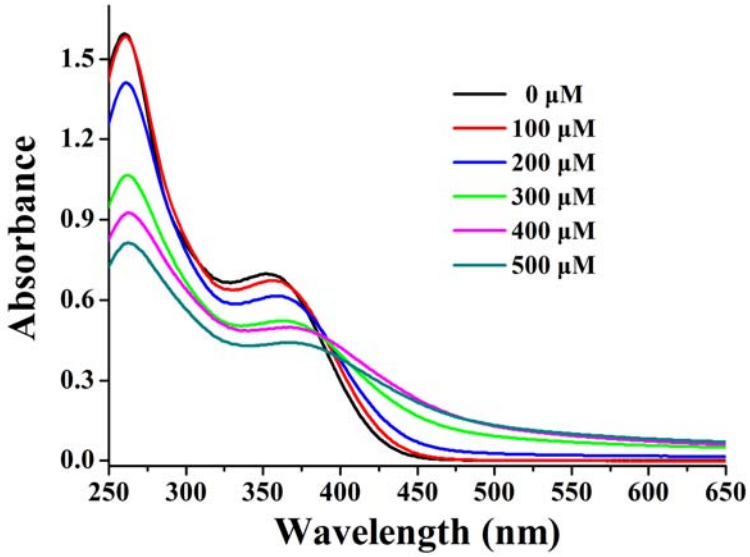


Figure S4. UV-vis absorption spectra of the complex TPE-DABF (TPE-DABA, 50 μM; D-fructose, 30 mM) upon titration of H_2O_2. Data were acquired in PBS buffer 60 min after addition of H_2O_2.

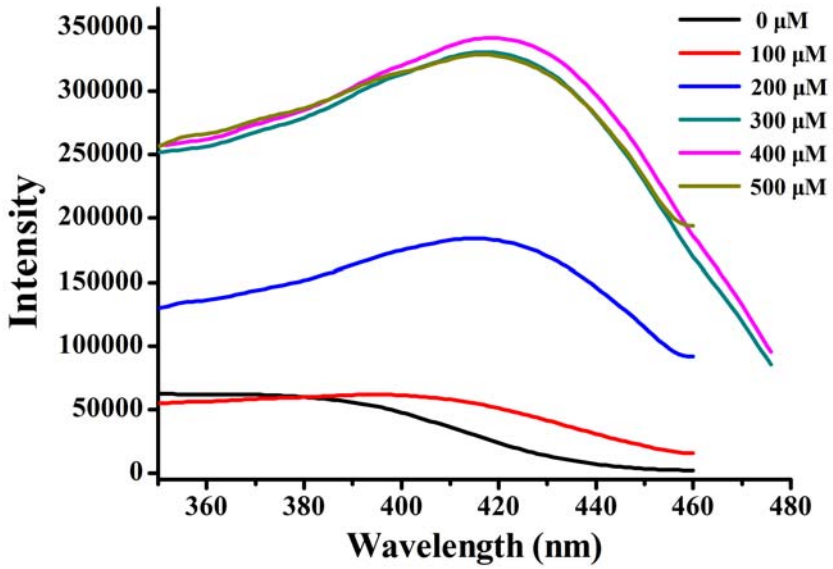


Figure S5. Excitation spectra of the complex TPE-DABF (TPE-DABA, 50 μM; D-fructose, 30 mM) upon titration of H_2O_2. Data were acquired in PBS buffer 60 min after addition of H_2O_2 (λ_{em} = 576 nm).

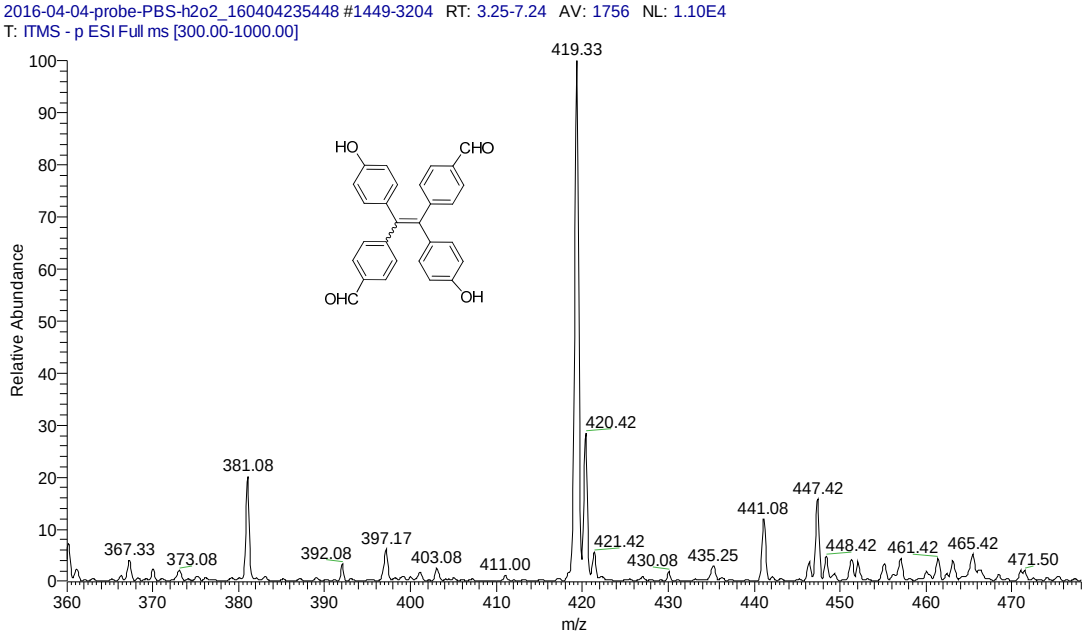


Figure S6. MS spectrum (ESI^-) of the product **TPE-DAP** extracted from the reaction of **TPE-DABF** and hydrogen peroxide. The data was collected in CH_3OH and water.

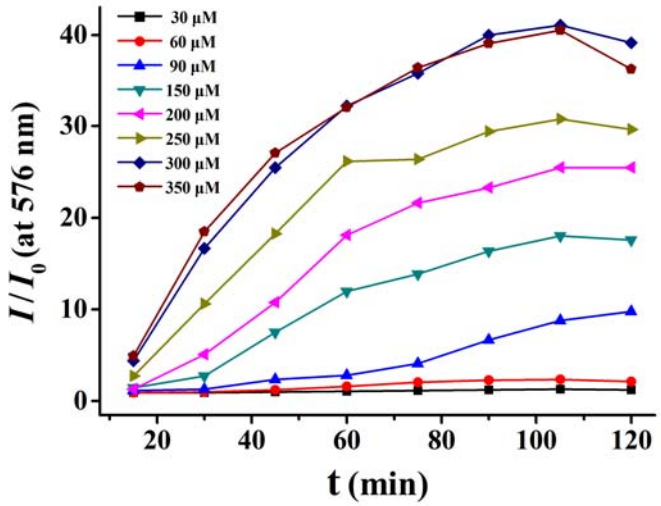


Figure S7. Time dependent relative fluorescence intensity of TPE-DABF complex (TPE-DABA, 50 μM; D-fructose, 30 mM) in PBS buffers (0.1 M, pH 7.40) upon addition of different concentrations of H_2O_2 from 0 to 120 min. These plots show relative emission responses at 576 nm over various time points; $\boldsymbol{I_0}$ is the intensity of the solution of TPE-DABF in the absence of H_2O_2. (λ_{ex} = 430 nm)

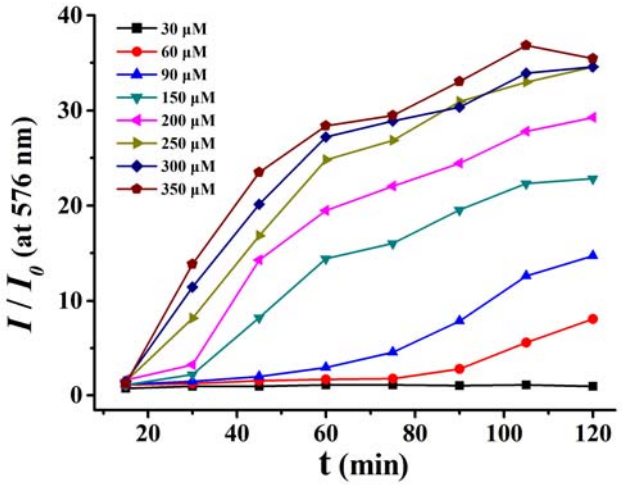


Figure S8. Time dependent relative fluorescence intensity of TPE-DABF complex (TPE-DABA, 50 μM; D-fructose, 30 mM) in PBS buffers (0.1 M, pH 7.40) upon addition of glucose oxidase (1 U/mL) and different concentrations of glucose from 0 to 120 min. These plots show relative emission responses at 576 nm over various time points; $\boldsymbol{I_0}$ is the intensity of the solution of TPE-DABF in the absence of glucose. (λ_{ex} = 430 nm)

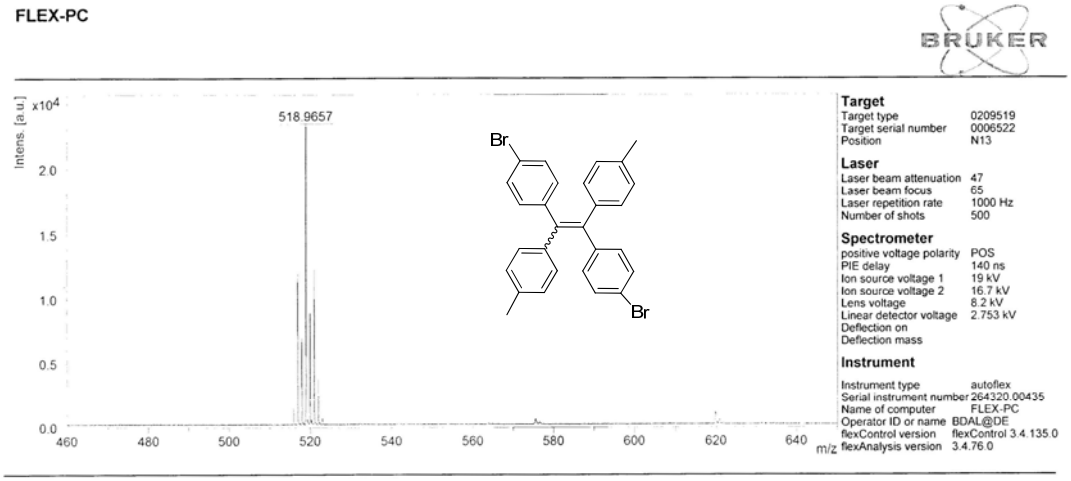


Figure S9. MS (MALDI-TOF) spectrum of compound **3**

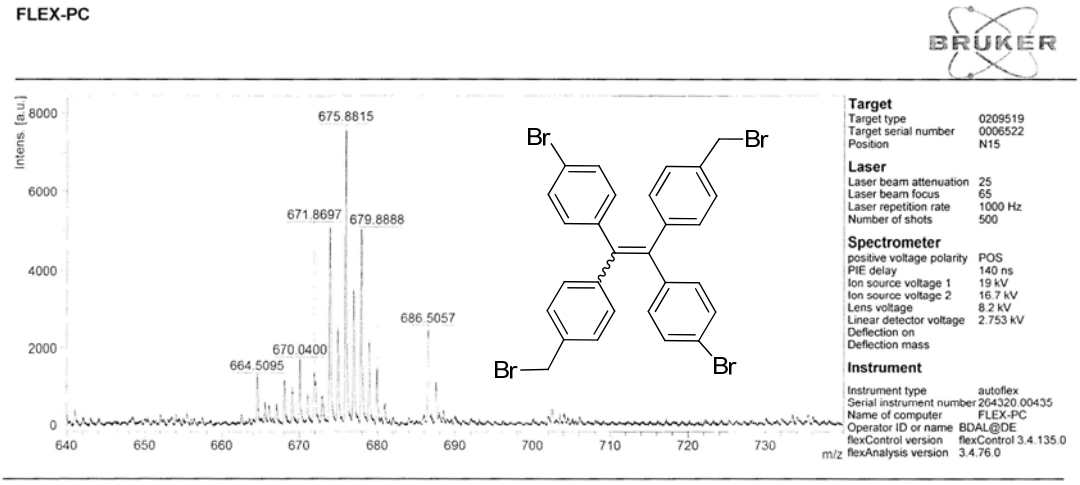


Figure S10. MS (MALDI-TOF) spectrum of compound **4**

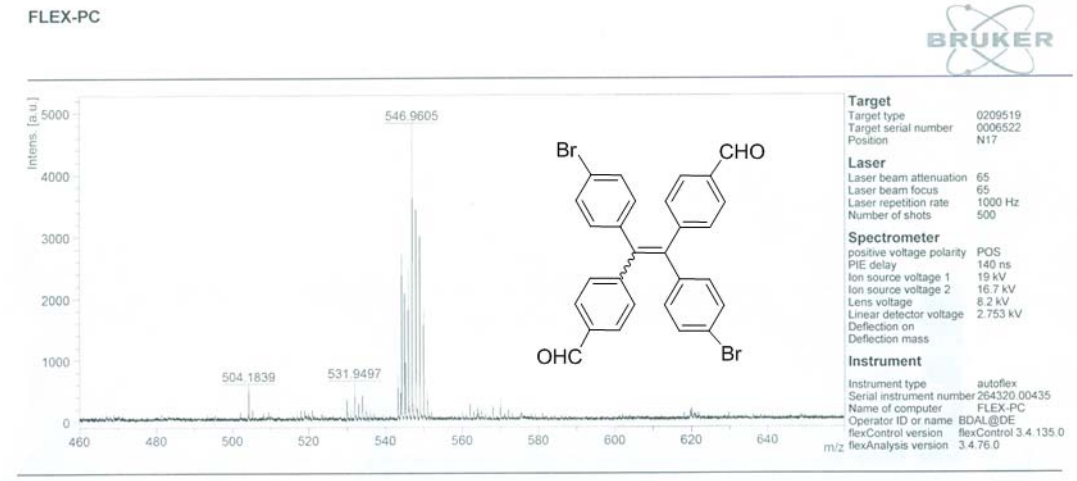


Figure S11. MS (MALDI-TOF) spectrum of compound **5**

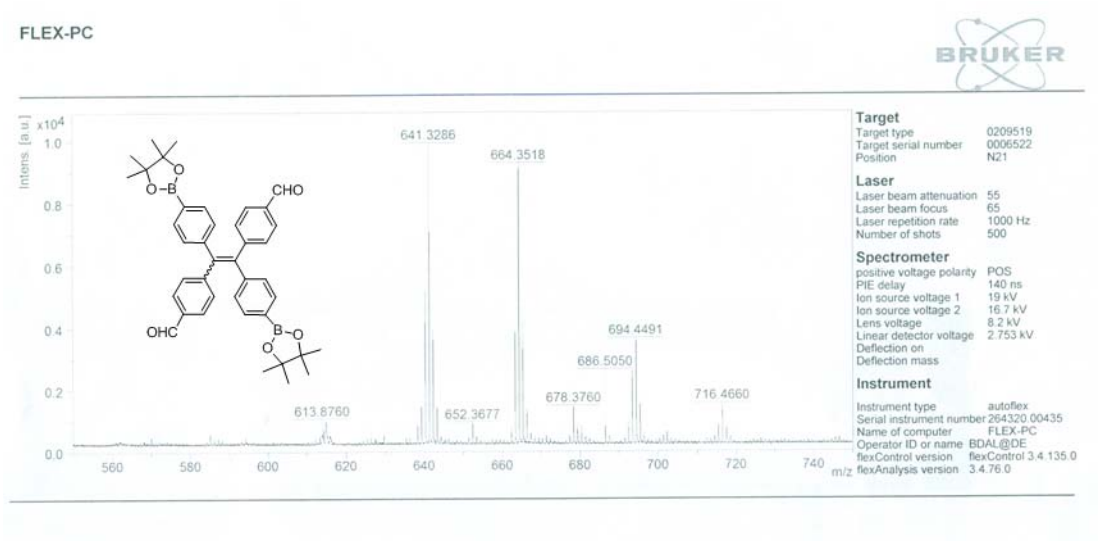


Figure S12. MS (MALDI-TOF) spectrum of compound **6**

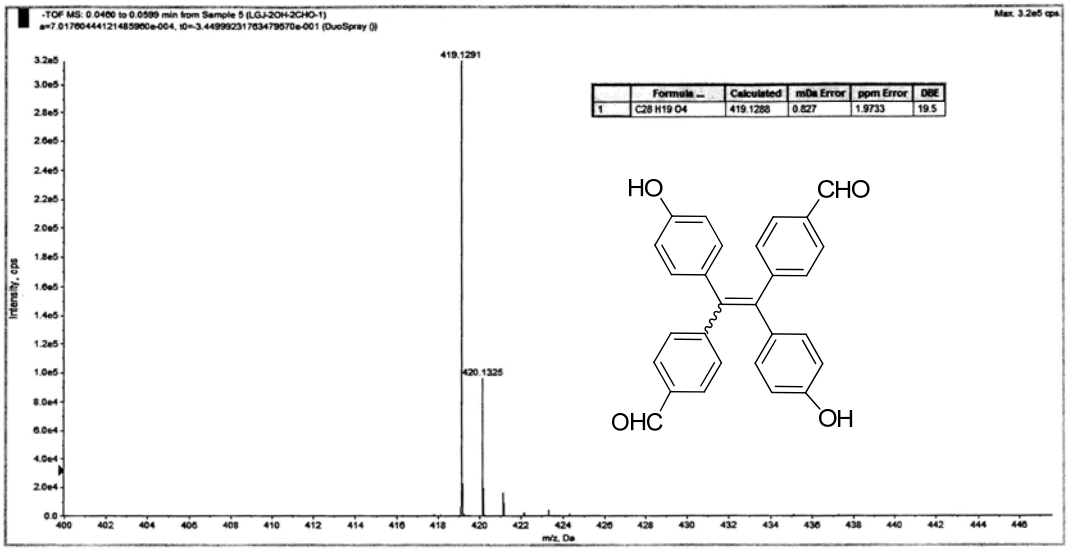
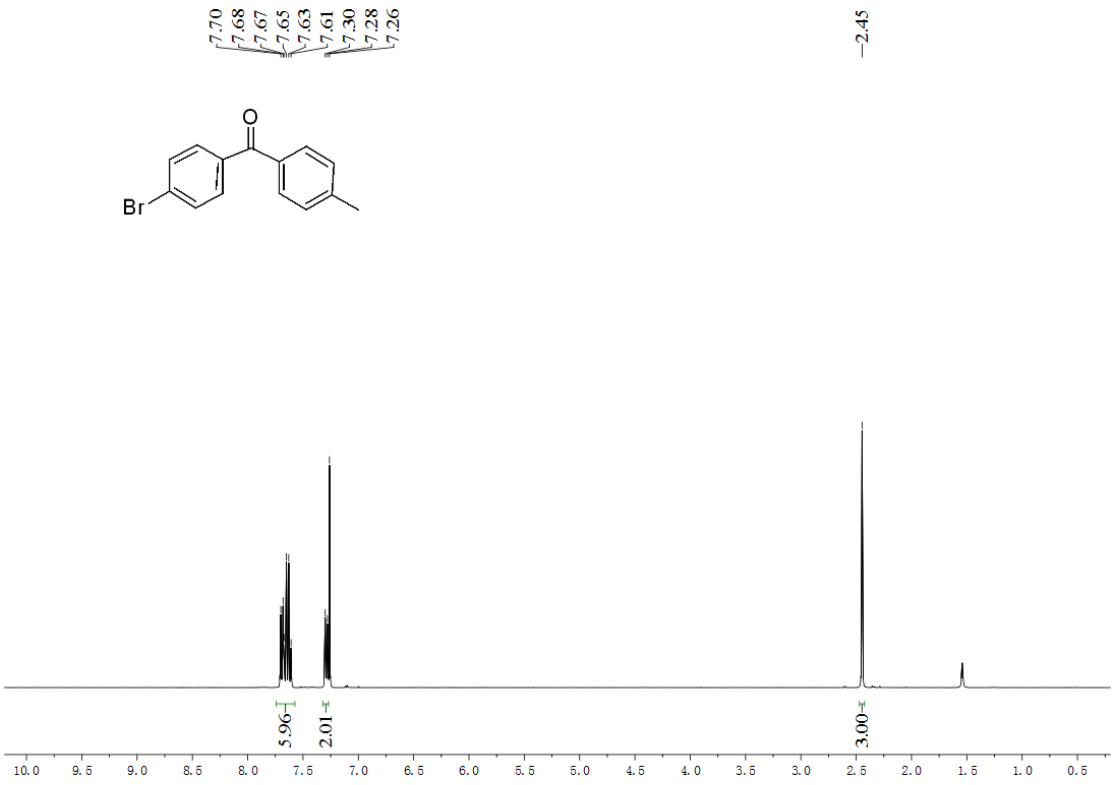
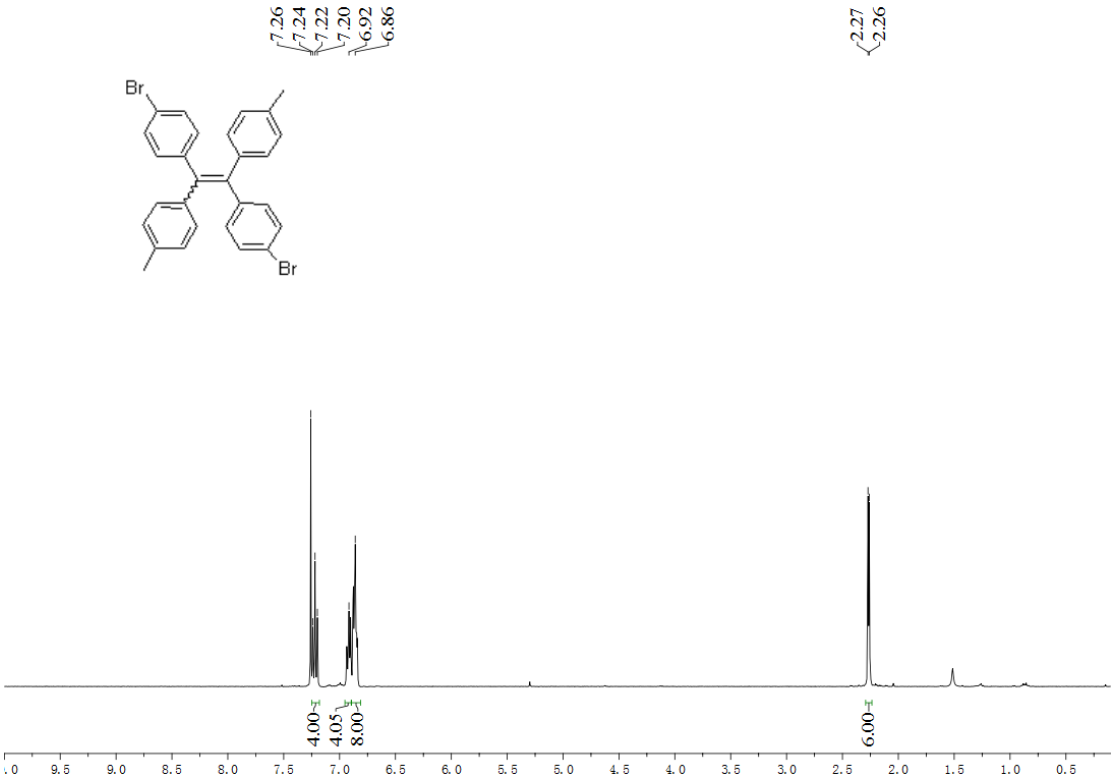
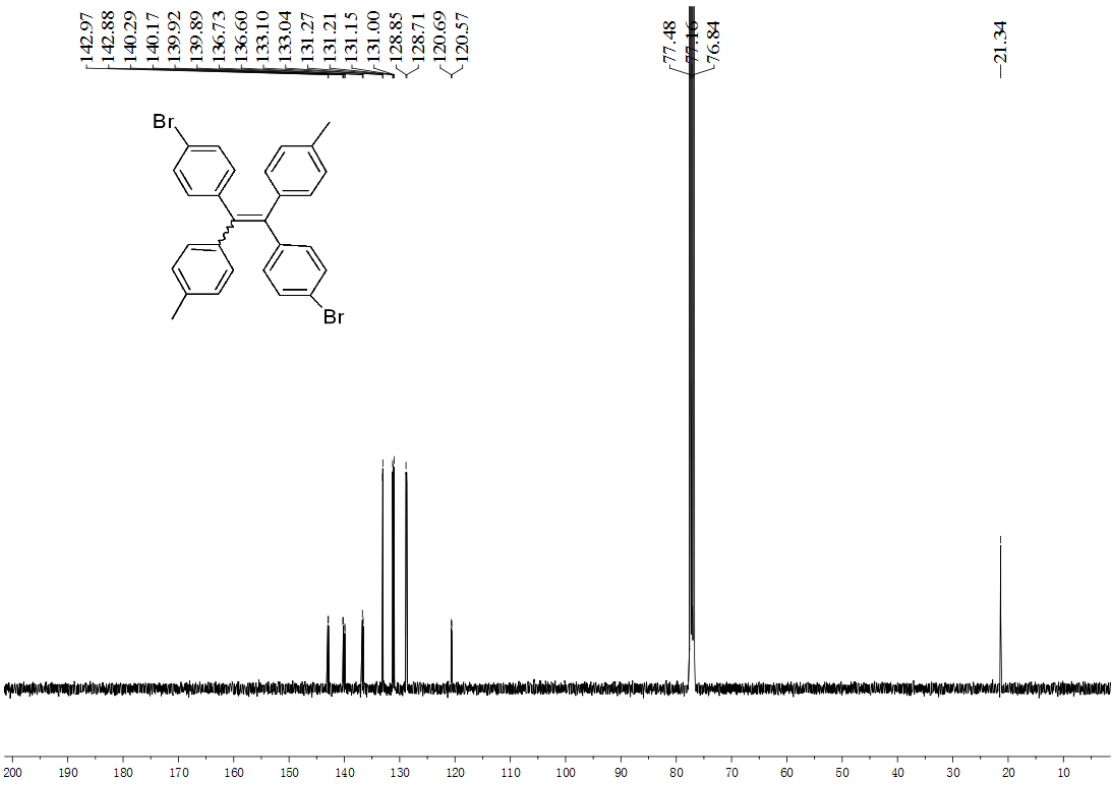


Figure S13. HRMS (ESI$^-$) spectrum of compound **TPE-DAP**

6. NMR spectra



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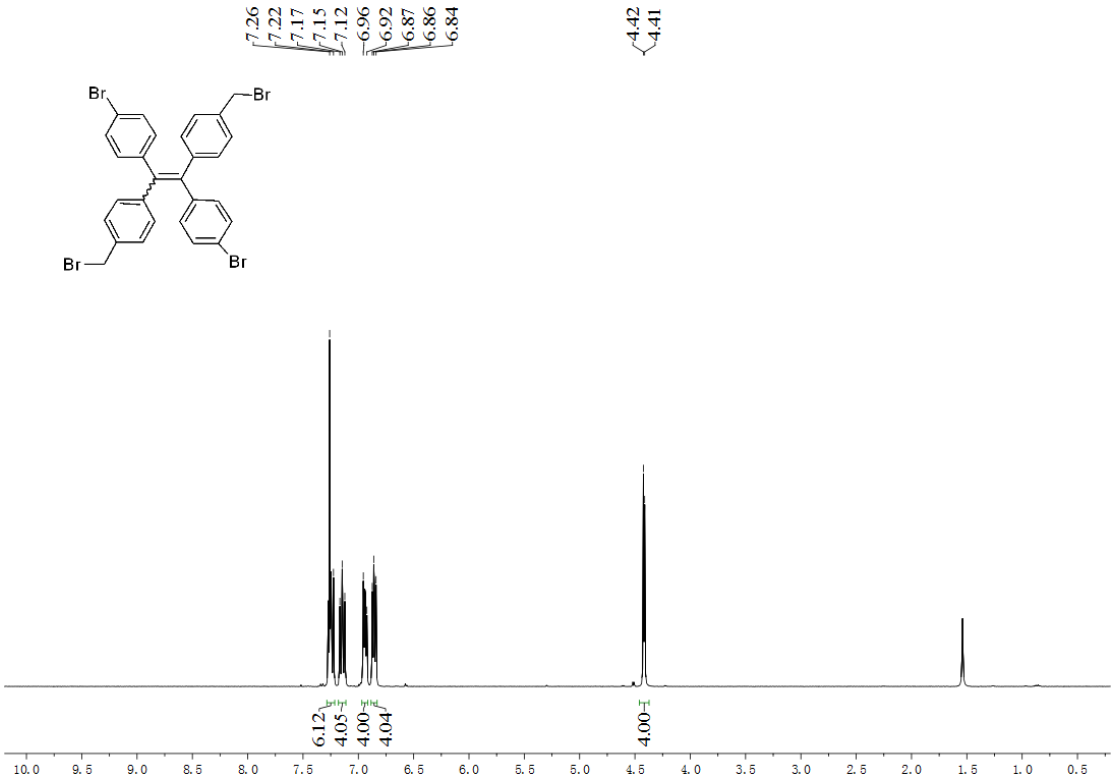
Br
Br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Br
Br
Br
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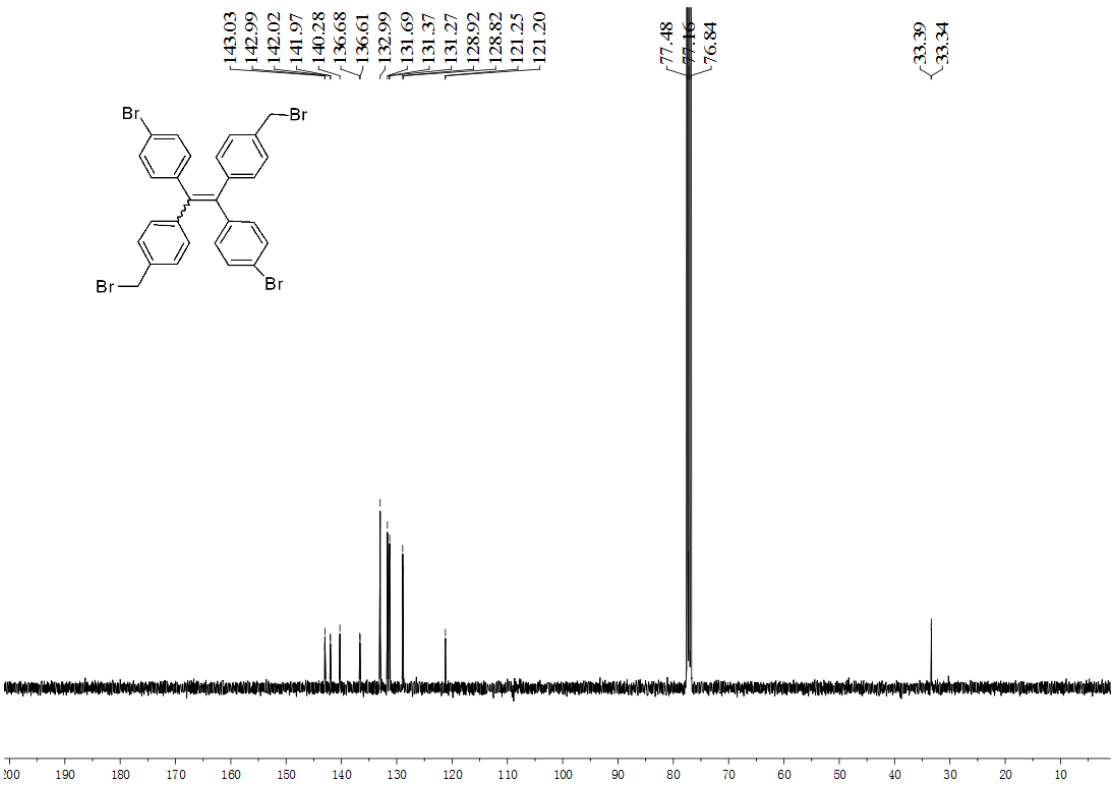
4.00
4.04
4.00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132.99
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76.84
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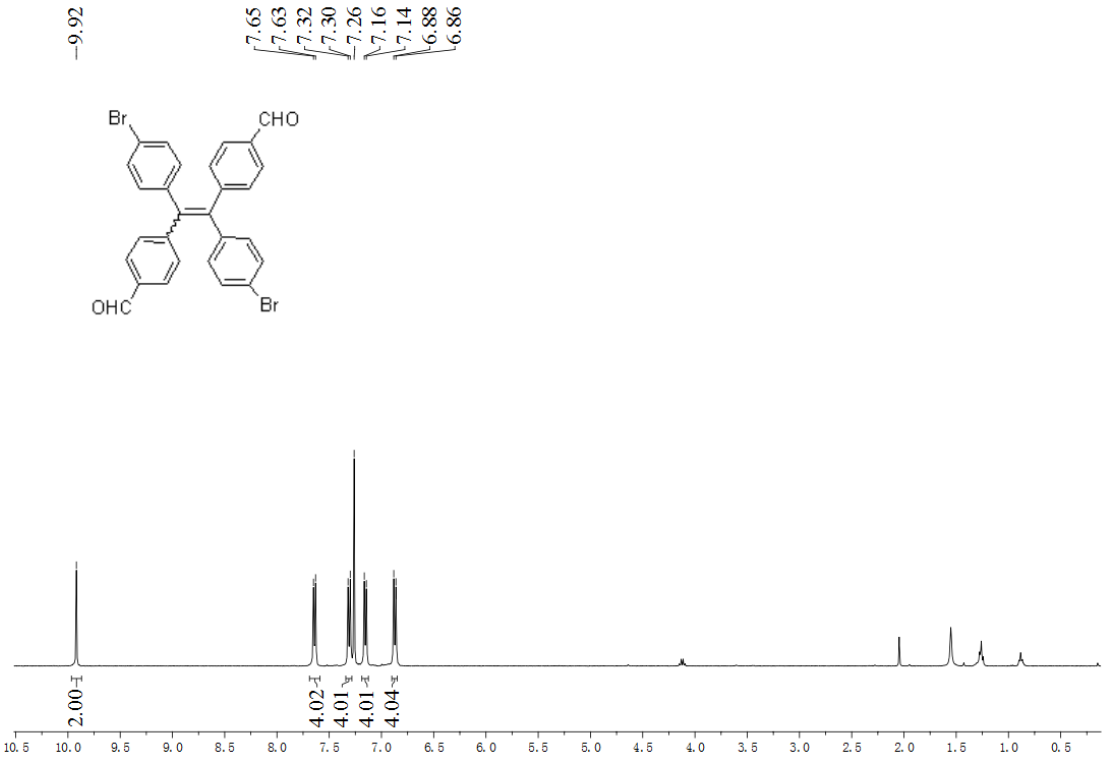
Br
Br
Br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Br
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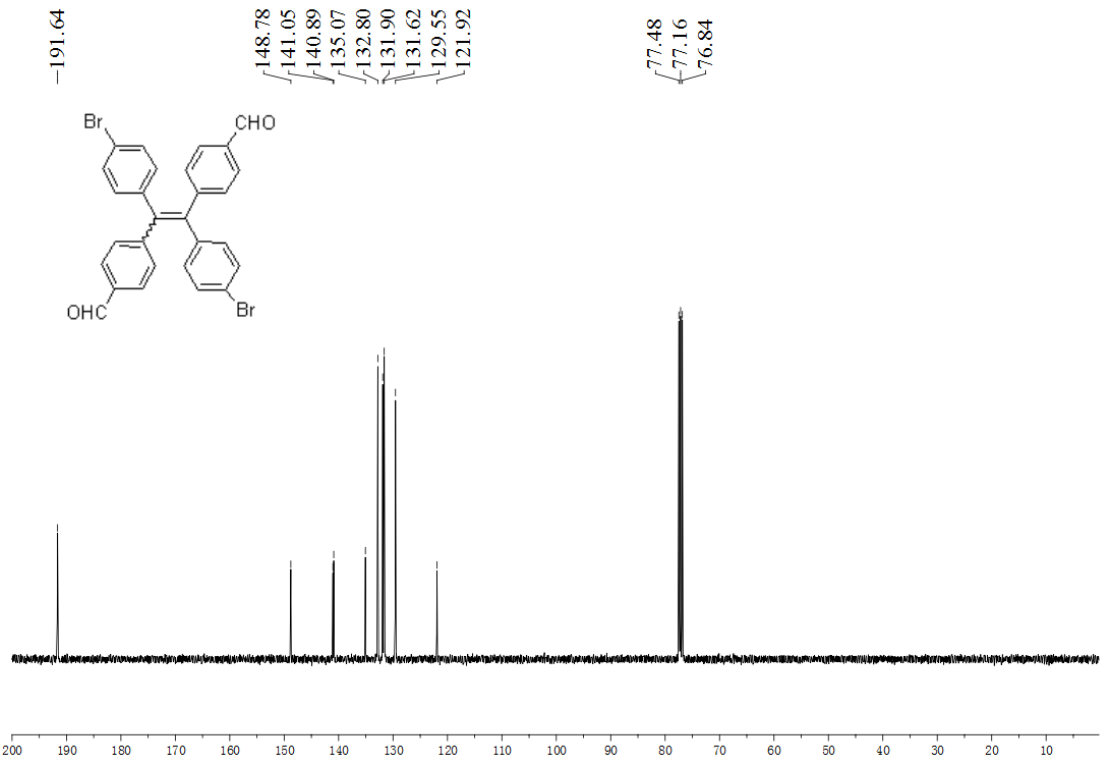
4.02
4.01
4.01
4.04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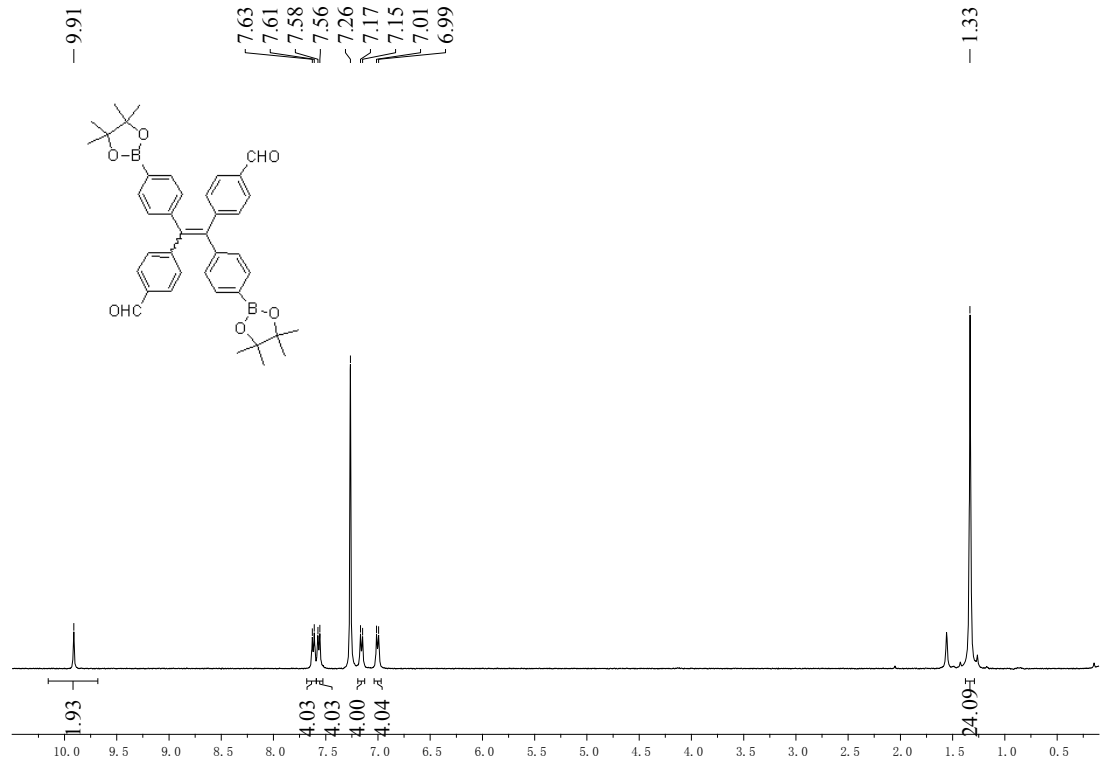
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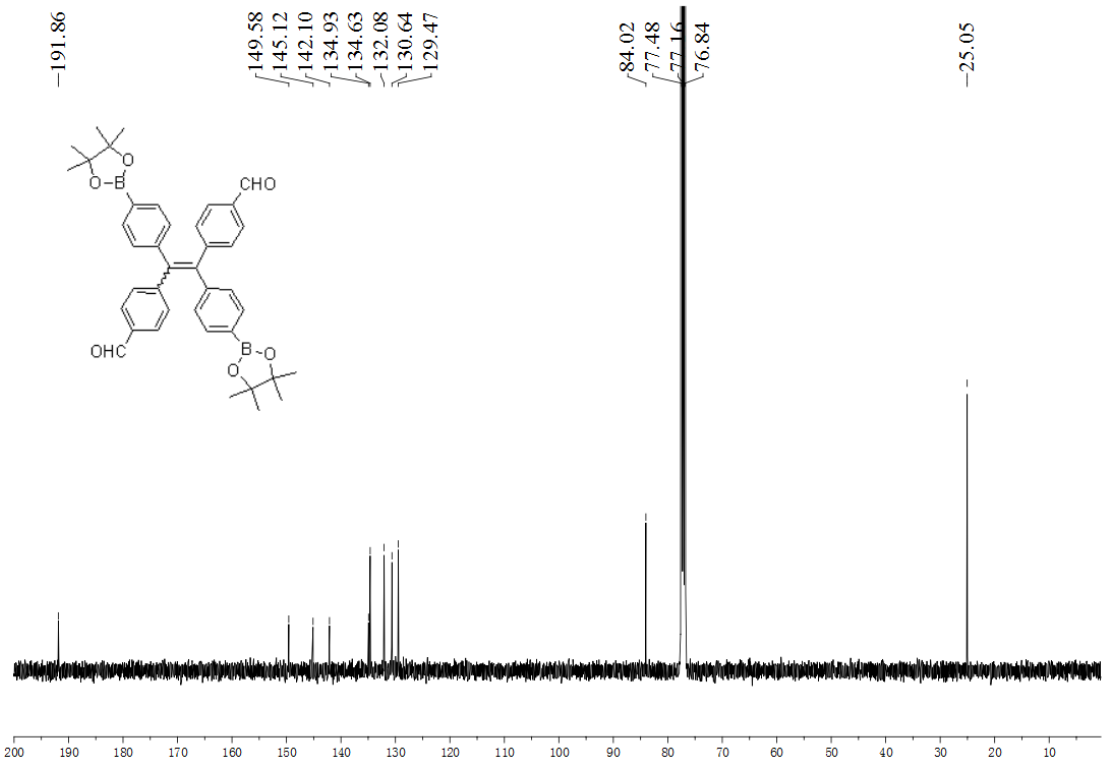
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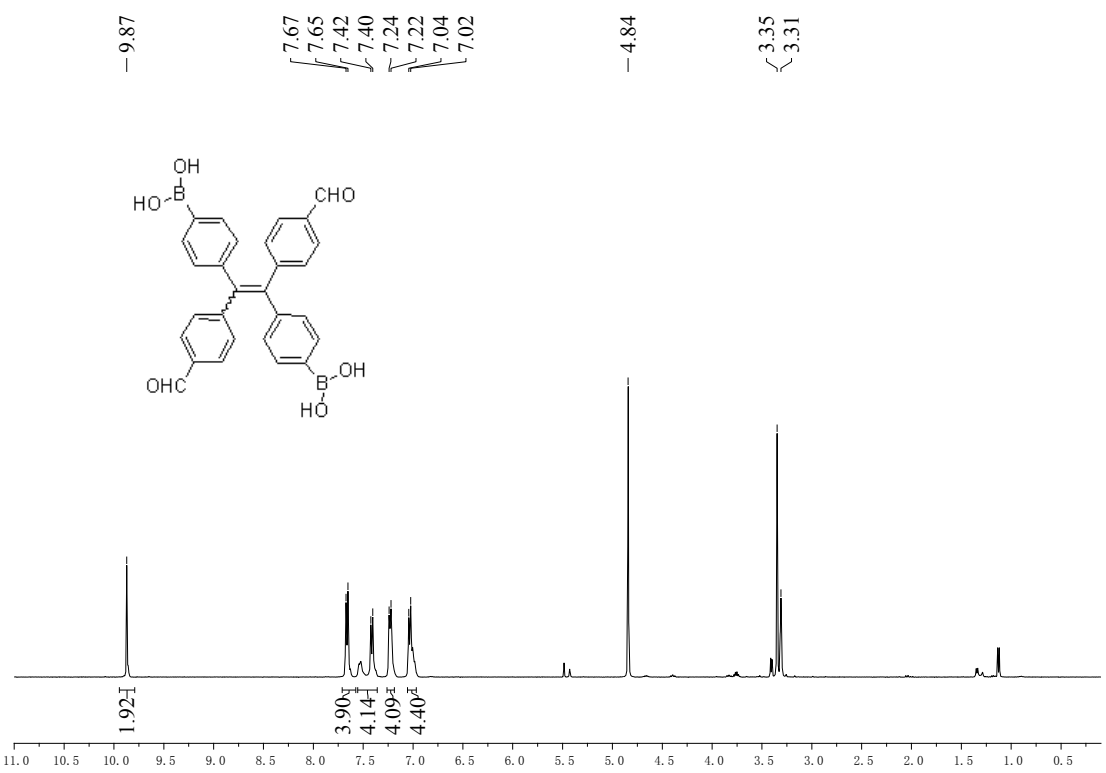
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HO
B
CHO
OHC
1.92
3.90
4.14
4.09
4.40
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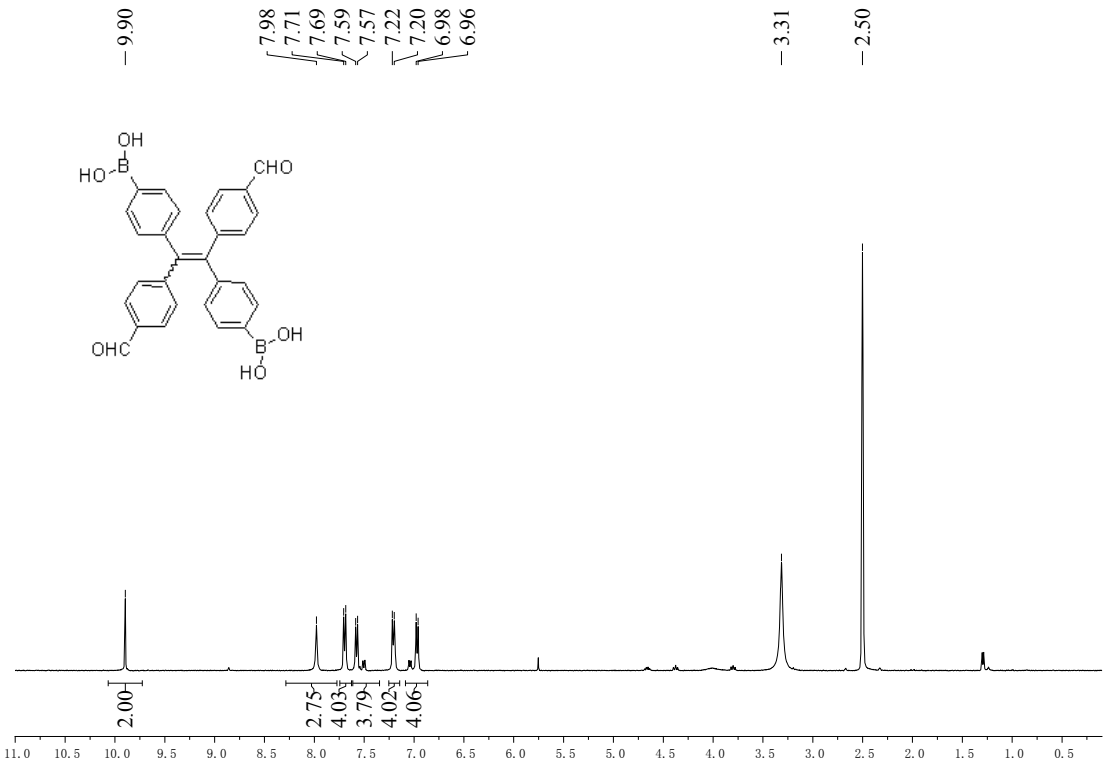
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B
CHO
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B
OH
HO
2.00
2.75
4.03
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4.02
4.06
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10.0
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9.0
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7.0
6.5
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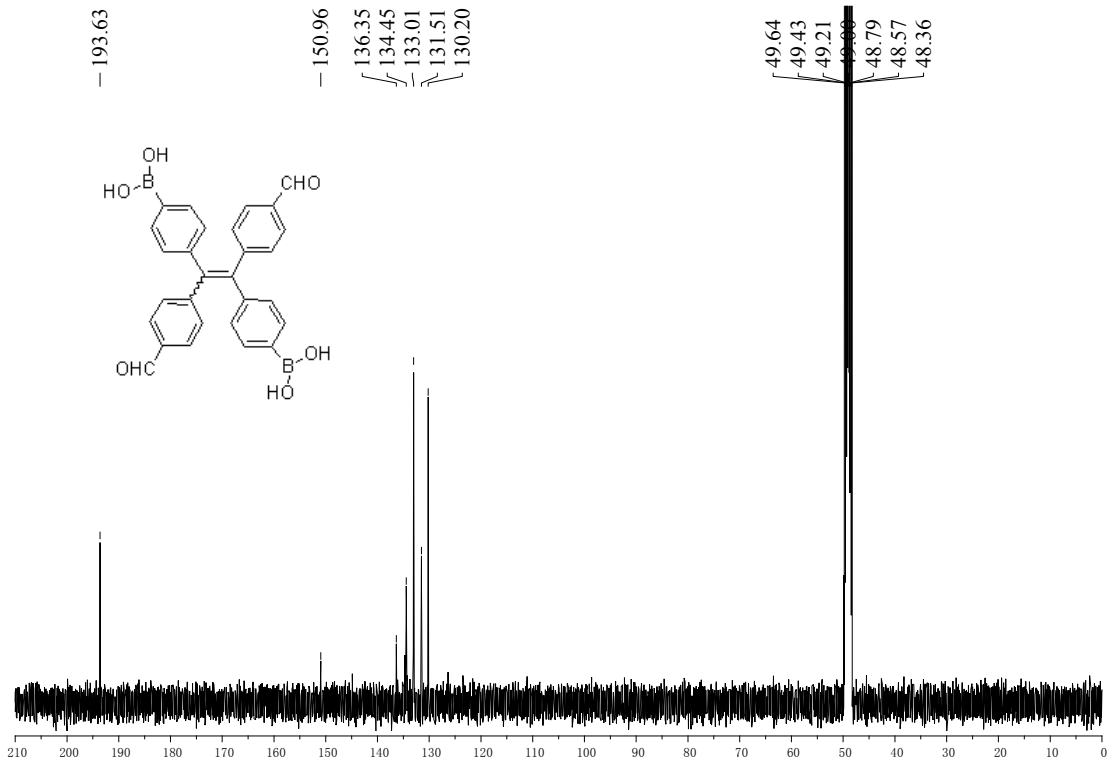
1.0
0.5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HO
B
CHO
OHC
B
OH
HO
210
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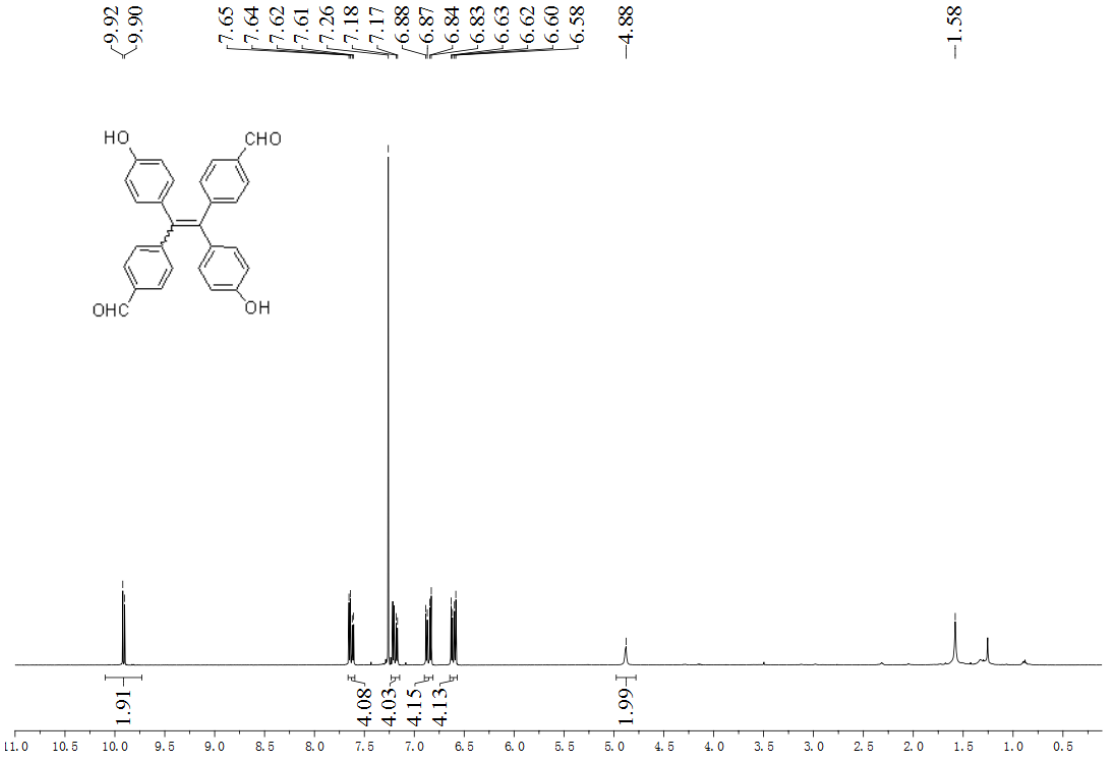
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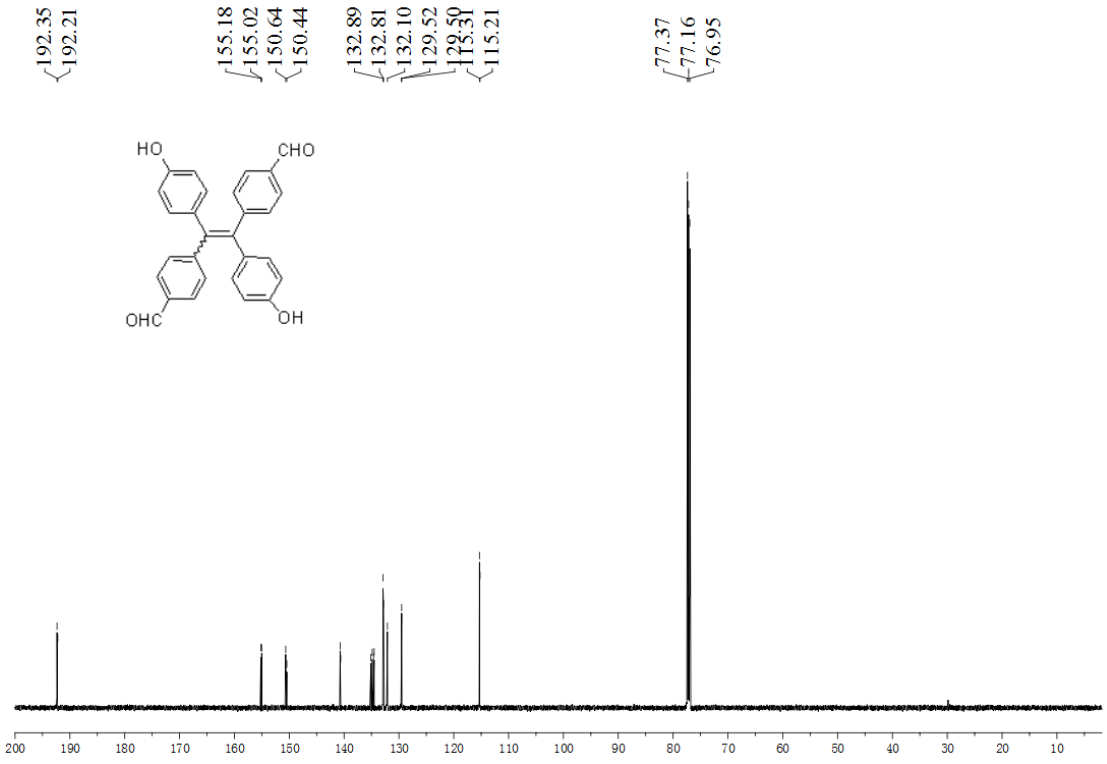
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OHC
OH

References

1. P. Wang, D. H. Blank and T. A. Spencer, *J. Org. Chem.*, 2004, **69**, 2693-2702.
2. X. Sun, Q. Xu, G. Kim, S. E. Flower, J. P. Lowe, J. Yoon, J. S. Fossey, X. Qian, S. D. Bull and T. D. James, *Chem. Sci.*, 2014, **5**, 3368-3373.
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