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Supporting Information

meso-Borneol- and *meso*-Carbazole-Substituted Porphyrins: Multifunctional Chomophores with Tunable Electronic Structures and Antitumor Activities

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Experimental Section

i. Experimental Section

General. ^{1}H NMR spectra were recorded on a Bruker AVANCEIII 600M spectrometer. Chemical shifts for ^{1}H NMR spectra were expressed in parts per million (ppm) relative to $CDCl_3$ (δ = 7.26 ppm) as the internal standard. UV-Vis spectra were recorded on Shimadzu UV-2600 spectrophotometer at ambient temperature with a 1 cm quarts cell. CD spectra were performed on a JASCO-810 spectrometer. Elemental analyses for C, H and N were

performed on a Perkin Elmer 240C elemental analyzer. The High Resolution Mass Spectra (HRMS) data was performed on a LTQ Orbitrap XL spectrometer equipped with an electrospray ionization (ESI) source. Fluorescence spectra, quantum yields and the fluorescence life time of the samples were determined with a FluoroLog-UltraFast (HORIBA Instrument Inc, Edison) spectrometer equipped with a 450 W CW xenon lamp and an Open-Electrode TECooled CCD Detector (Syncerity).

Antitumor Activity Evaluation. The antitumor activities of **4a, 4b**, **7b** and **7c** *in vitro* were evaluated by MTT assay against human hepatoma cells (HepG2). HepG2 cells were transferred into 96-well plates at a concentration of 1×10^3 cells/well, and incubated for 6 h. The cells in the wells were respectively treated with target compounds at various concentration for 68 h. Then, 20 μl MTT (4 mg/mL) was added to each well and incubated for 4 h at 37 ºC. After the supernatant was discarded, 200 μL DMSO was added to each well and the absorbance values were read at 570 nm using a microplate scanning spectrophotometer. All measurements were repeated for three time to

Synthesis of 3,6-dibutylcarbazole 1a[S1]. 20 mL CH_2Cl_2 solution containing 2-bromo-2-methylpropane (4.12 g, 30.00 mmol) dropwise added to the 50 mL dehydrous CH_2Cl_2 solution containing carbazole (2.51 g, 15.00 mmol) and $AlCl_3$ (2.00 g, 15.00 mmol) at 0^{o}C under N_2, then stirred at room temperature about 24h. The reaction was queanched by ice-water,and further extracted by CH_2Cl_2 (30 mL x 3). The organic solvent was removed under reduced pressure. The target compound was finally purified by recrystallization (C_2H_5OH) to give the white solid state compound in 87% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (s, 2H), 7.83 (br s, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H),1.45 (s, 18H)。

Synthesis of 3,6-dichloro-9H-carbazole 1b[S2]. 8.0 g Carbazole was firstly dissolved in 40 mL freshly distilled DMF, and 40 mL DMF solution containing N-chlorosuccinimide (12.80 g, 96.00 mmoL) was slowly added to the same solution. The mixture was continuely stirred and heated at 60 ^{o}C for 3 h and the target compound was finally obtained as the light yellow solid state compound in 81% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (br s, 1H), 7.97 (d, J

= 1.2 Hz, 2H), 7.40- 7.34 (m, 4H).

Synthesis of 4-(3,6-di-tert-butyl-9H-carbazol-9-yl)benzaldehyde 2a[S3]. 3,6-dibutylcarbazole **1a** and t-BuOK was mixted in the freshly distilled DMF, and stirred at 110^{o}C for 0.5 h. Then, a 20 mL DMF solution containing 20.0 mmol *p*-fluorobenzaldehyde (2.48 g mmol) was slowly added and heated at 110^{o}C for 36 h. After cooling to the room temperature, the mixture was directly mixed with ice-water to provide the solid state compound, and underwent filtration by Buchner funnel. The final target compound was obtained through recrystallization with ethanol in 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.16-8.13 (m, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.48 (dd, *J* = 2,4, 9.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 1.47 (s, 18H).

Synthesis of 4-(3,6-dichloro-9H-carbazol-9-yl)benzaldehyde 2b[S4-S5]. The general synthetic procedure is similar with that of **2a**, only 3,6-dichlorocarbazole **1b** was used instead. The target compound was finally obtained through recrystallization with ethanol to give the yellow solid state compound in a 70%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.13 (s, 1H), 8.15 (d, *J* = 7.8 Hz, 2H), 8.05 (d, *J* = 1.2 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.42- 7.39 (m, 4H).

Synthesis of 5-(4 -(3,6--dibutyl-9-(4-N-benzoylphenyl)) carbazole)phenyl)-dipyrromethane 3a[S6-S7]**. Under Ar,** the freshly distilled pyrrole (50 mL, 704.00 mmol, excess amount) and trifluoroacetic acid (0.21 mL, 0.28 mmol) was disolved in 100 mL dry CH_2Cl_2, and 3,6-dibutyl-9-(4 –N-benzoylphenyl))carbazole (0.71 g, 1.84 mmol) was slowly added. The reaction mixture stirred for another 1 h. After the reaction was quenched by saturated NaOH solution, washing with distilled water, extracting with CH_2Cl_2, and distilling to fully remove the excess amount of pyrrole. The residues was finally purified through silica gel column chromatography with CH_2Cl_2 as eluent to give the pure yellow solid state compound in 88% yield. ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 8.13 (d, *J* = 1.2 Hz, 2H), 8.00 (s, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.45 (dd, *J* = 1.8, 7.8 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.75-6.74 (m, 2H), 6.22- 6.20 (m, 2H), 5.99 (s, 2H), 5.57 (s, 1H), 1.48 (s, 18H).

Synthesis of 5-(4-(3,6--dichloro-9-(4-N-benzoylphenyl))carbazole)phenyl)-dipyrromethane 3b. The general synthetic procedure is with that of **3a**, excepting 3,6-dibutylcarbazole **6b** was used instead. The target compound was finally obtained as the organic solid state compound in a 88% yield. ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 8.16 (d, *J* = 1.8 Hz, 2H), 8.01 (s, 2 H), 7.47 (dd, *J* = 1.8, 9.6 Hz, 2H), 7.44-7.39 (m, 4H), 7.24 (d, *J* = 9.0 Hz, 2H), 6.76-6.75 (m, 2 H), 6.22- 6.20 (m, 2H) 5.98 (s, 2 H), 5.58 (s, 1H).

Synthesis of 4-(9H-carbazol-9-yl)benzaldehyde 5a. The general synthetic procedure is similar with that of **2a**, excepting carbazole was used instead. The arget compound was finally obtained as the pure yellow solid state compound in 68%. ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 10.12 (s, 1H), 8.14 (t, *J* = 7.8 Hz, 4H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.45-7.42 (m, 2H), 7.34- 7.32 (m, 2H).

Synthesis of 4-(3,6-dibromo-9H-carbazol-9-yl)benzaldehyde 5b[S8]**.** 5.0 g **4-(9H-carbazol-9-yl)benzaldehyde 5a** was dissolved in 145 mL freshly distilled CH_2Cl_2 solution, and a CH_2Cl_2 solution containing 1.45 mL Br_2 (56.12 mmol) was dropwise added. The reaction was kept at room temperature over 6h, and the excess amount of Br_2 was neutralized by the saturated NaOH solution. After extraction with CH_2Cl_2 and seperation, removal of organic solvent and recrystallization with C_2H_5OH, the target compound was finally obtained as a deep-yellow solid compound in a 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 10.13 (s, 1H), 8.25-8.20 (m, 2H), 8.14 (dd, *J* = 2.4, 8.4 Hz, 2H), 7.74(dd, *J* = 8.4, 19.2 Hz, 2H), 7.55-7.50 (m, 2H), 7.35 (dd, *J* = 8.4,12.6 Hz, 2H).

Synthesis of 4-(3,6-diiodo-9H-carbazol-9-yl)benzaldehyde 5c[S9]**.** 5.0 g **4-(9H-carbazol-9-yl)benzaldehyde 5a** was dissolved in 125 mL CH_3COOH, stirred and heated at 80 ^{o}C. After **5a** was fully dissolved into the solution, KI (4.13 g, 24.83 mmol) and KIO_3(3.00 g, 14.00 mmol) was added, and the reaction mixture was stirred at 80 ^{o}C for 5 h. Then, the mixture was washed by excess amount of 5% $NaHSO_3$ water solution to remove extra I_2 and KIO_3. After extraction with CH_2Cl_2, drying over anhydrous Na_2SO_4, the organic solvent

was removed under reduced pressure. The residues was purified by recrystalization with THF. The target compound was finally obtained as the brown solid state compound in a 84% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.41 (s, 2H), 8.13 (d, *J* = 7.2 Hz, 2H), 7.72 (t, *J* = 9.0 Hz, 4H), 7.22 (d, *J* = 8.4 Hz, 2H).

Synthesis of 5-(4-(9-(4 –N-benzoylphenyl))carbazole)phenyl)-dipyrromethane 6a. The general synthetic procedure is similar with that of **8a**, except 4-(9H-carbazol-9-yl)benzaldehyde **5a** was used instead. The target compound was finally obtained as the yellow solid state compound in a 82.0% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 2H), 7.99 (s, 2H), 7.51- 7.49 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.40- 7.38 (m, 4 H), 7.29-7.26 (m, 2 H), 6.75- 6.74 (m, 2 H), 6.22- 6.20 (m, 2 H), 6.00 (s, 2 H), 5.58(s, 1H).

Synthesis of 5-(4-(3,6-dibromo-9-(4–N-benzoylphenyl))carbazole)phenyl)-dipyrromethane 6b. The general synthetic procedure is similar with that of **3a**, excepting 4-(3,6-dibromo-9H-carbazol-9-yl)benzaldehyde **5b** was used instead. The target compound was finally obtained as the orange solid state one in a 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 8.03 (d, *J* = 1.8 Hz, 4H), 7.46-7.43 (m, 4H), 7.37 (dd, *J* = 1.8, 8.4 Hz, 2H), 7.31 (d, *J* = 9.0 Hz, 2H), 6.78-6.77 (m, 2H), 6.25- 6.23 (m, 2H) 6.00 (s, 2H), 5.60 (s, 1H).

Synthesis of 5-(4-(3,6-diiodo-9-(4–N-benzoylphenyl))carbazole)phenyl)-dipyrromethane 6c. The general synthetic procedure is similar with that of **3a**, excepting 4-(3,6-diiodo-9H-carbazol-9-yl)benzaldehyde **5c** was used instead. The target compound was finally obtained as the orange solid state one in an 88% yield. ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 8.38 (d, *J* = 1.8 Hz, 2H), 8.04 (s, 2H), 7.65 (d, *J* = 9.0 Hz, 2H), 7.45- 7.41 (m, 4H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.78 (s, 2 H), 6.22 (s, 2H), 5.99 (s, 2H), 5.60 (s, 1 H).

ii. [1]HNMR spectra

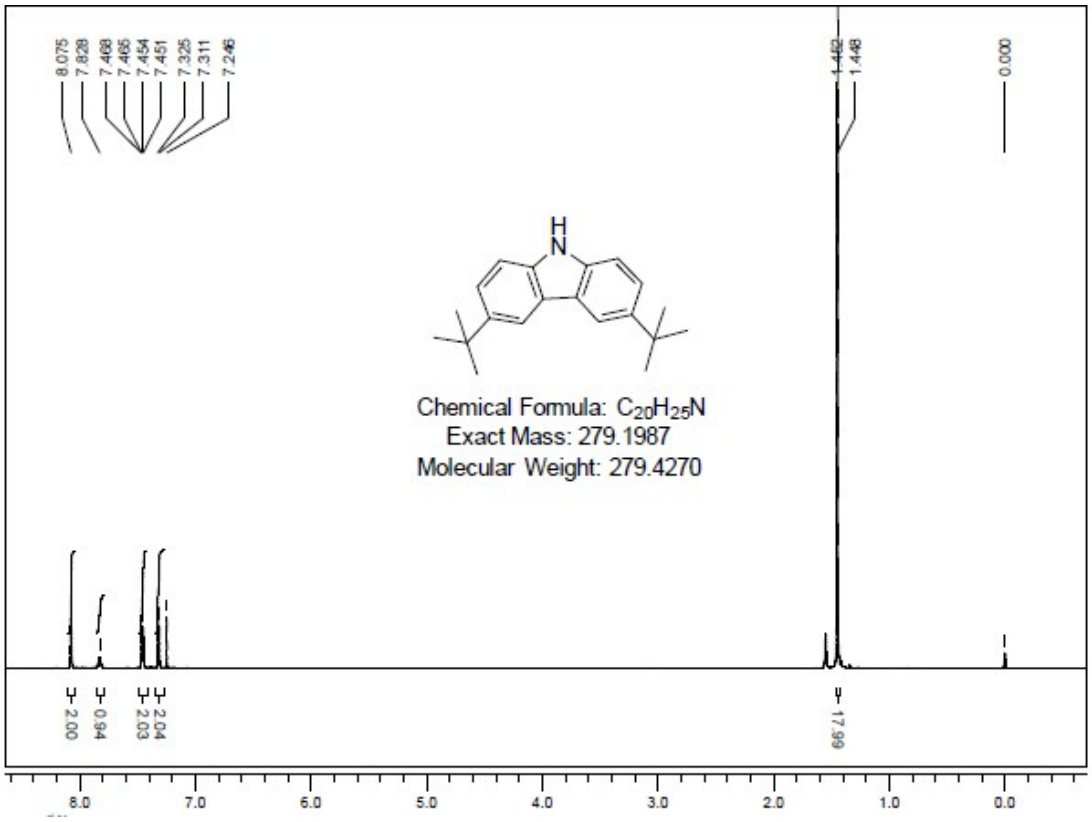

Figure S1 [1]HNMR spectra of **1a**.

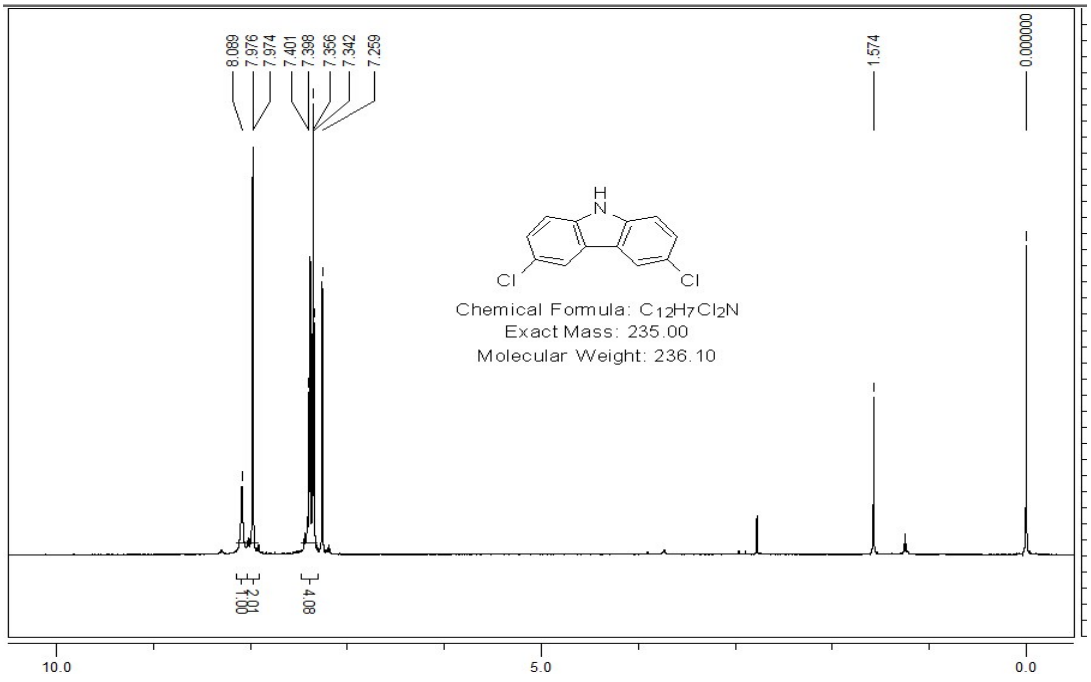

Figure S2 [1]HNMR spectra of **1b**.

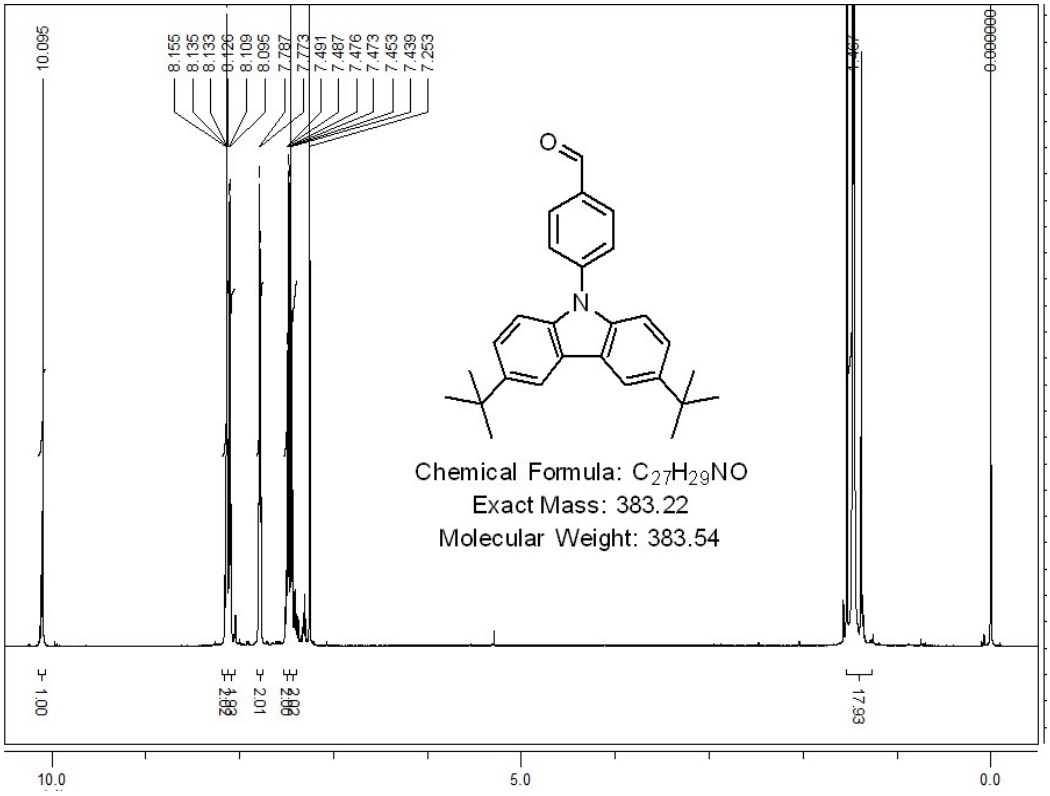

Figure S3 [1]HNMR spectra of **2a**.

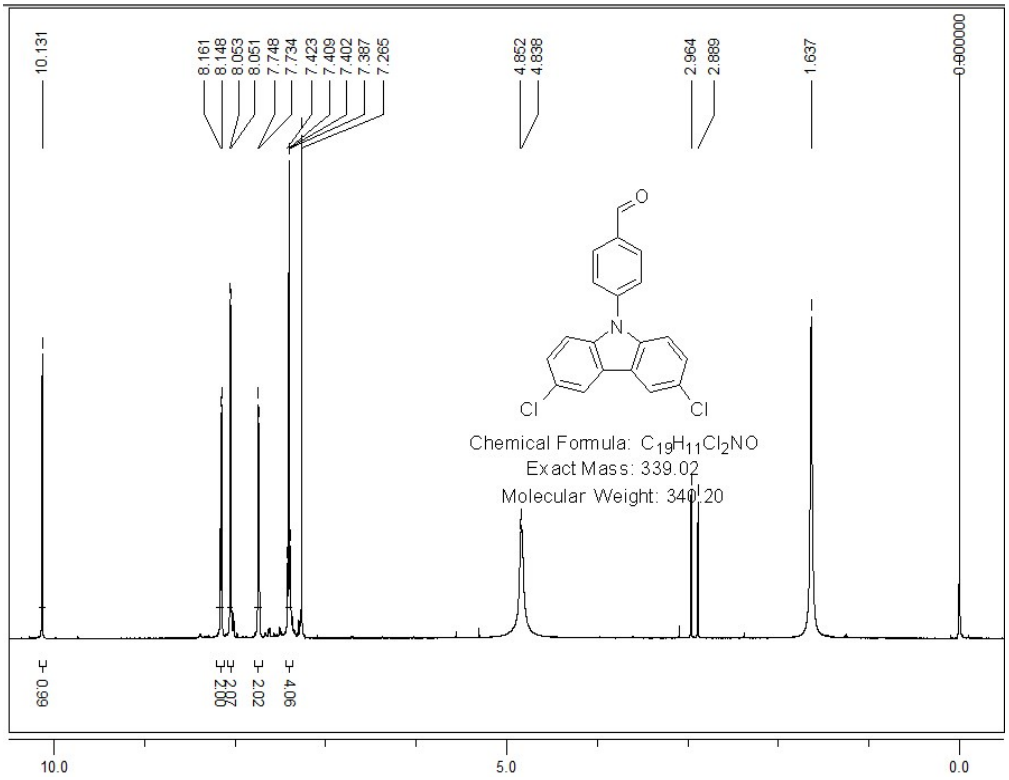

Figure S4 [1]HNMR spectra of **2b**.

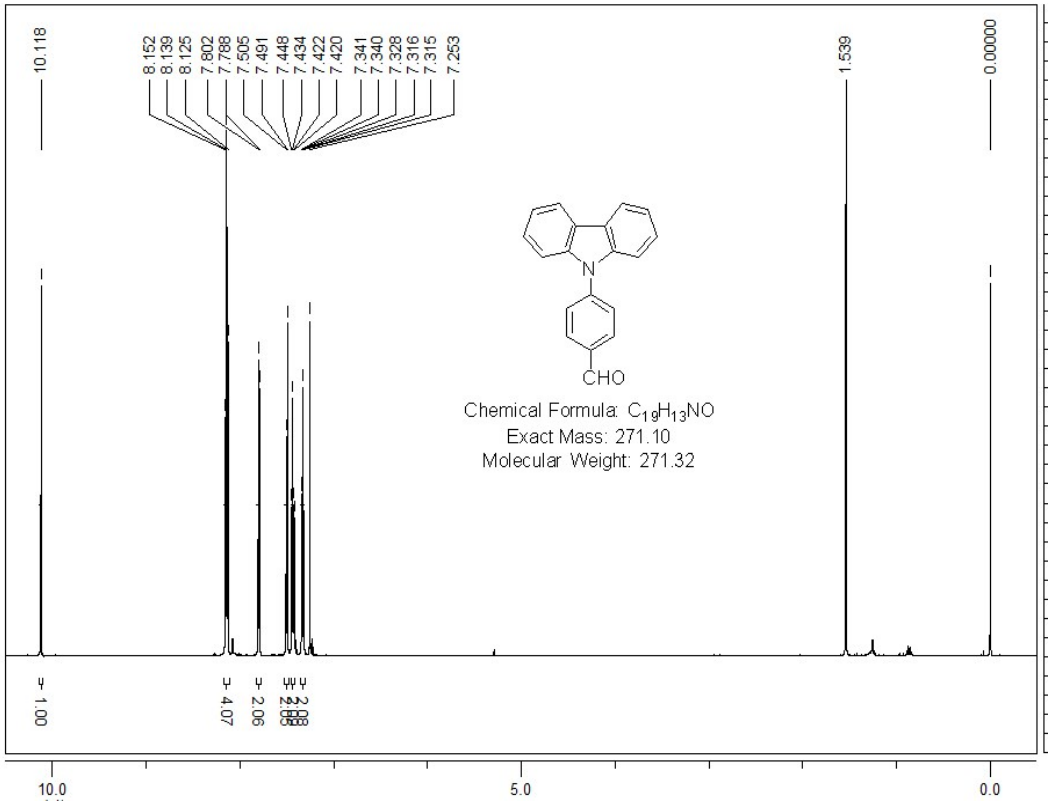

Figure S5 [1]HNMR spectra of **5a**.

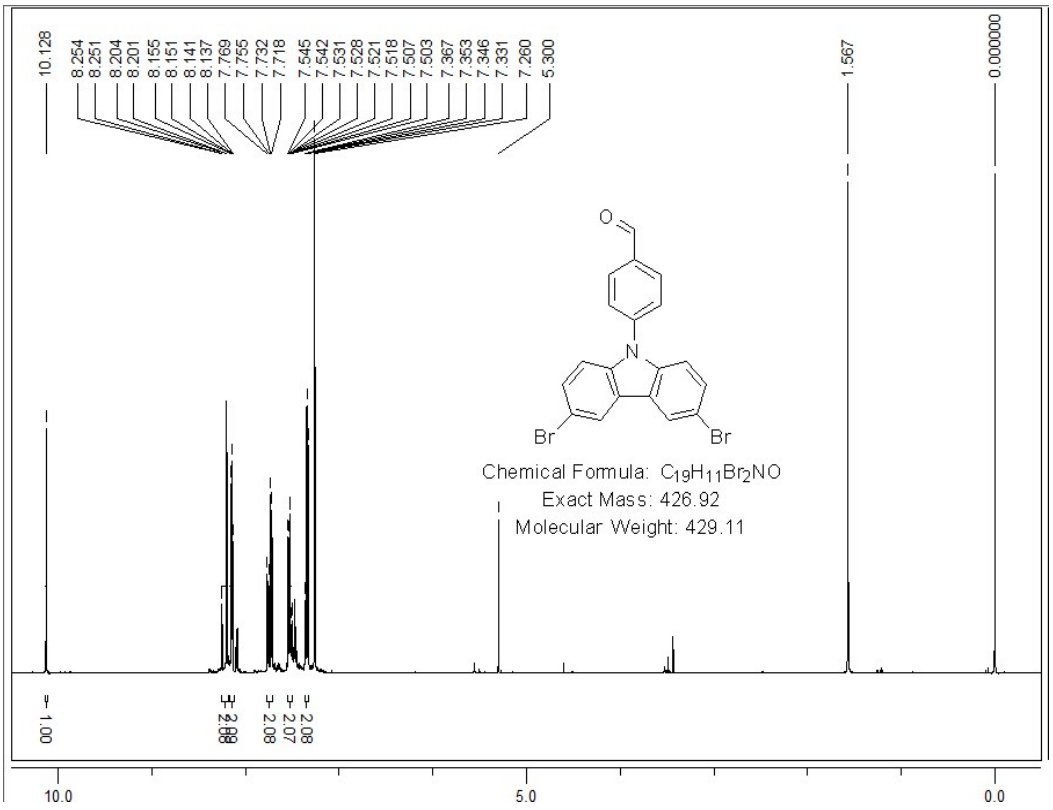

Figure S6 [1]HNMR spectra of **5b**.

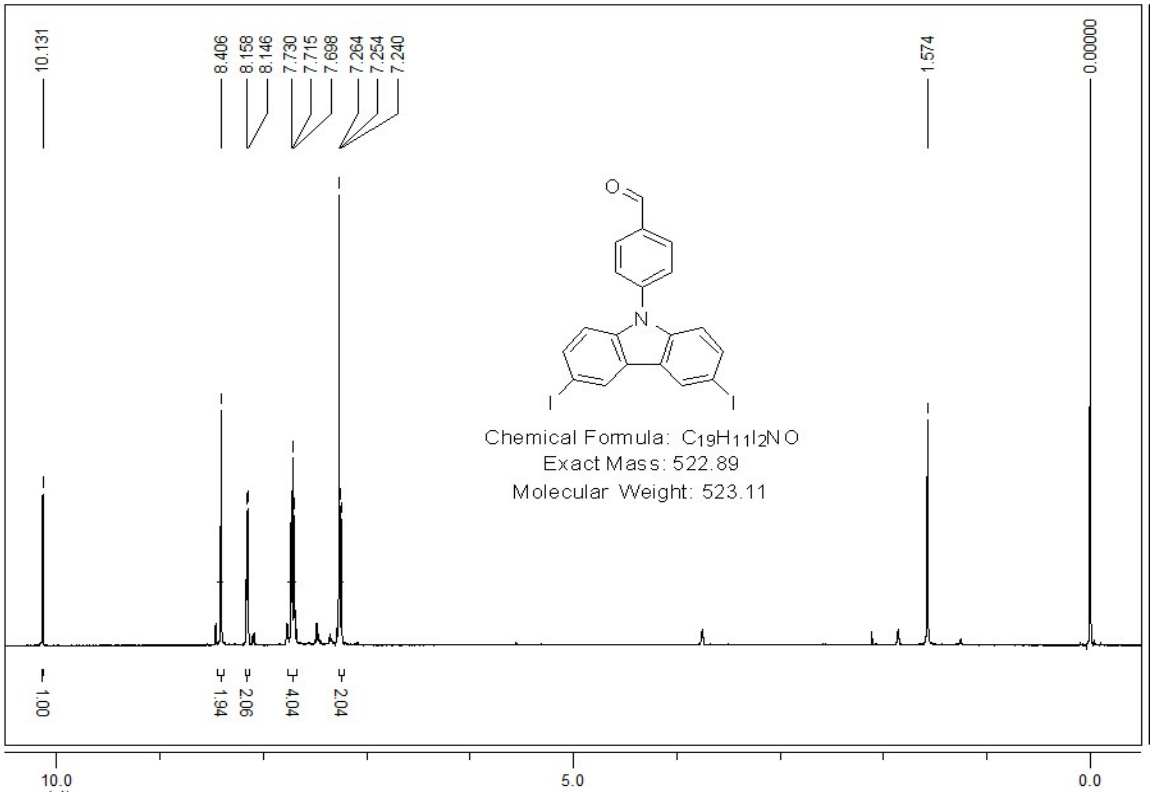

Figure S7 [1]HNMR spectra of **5c**.

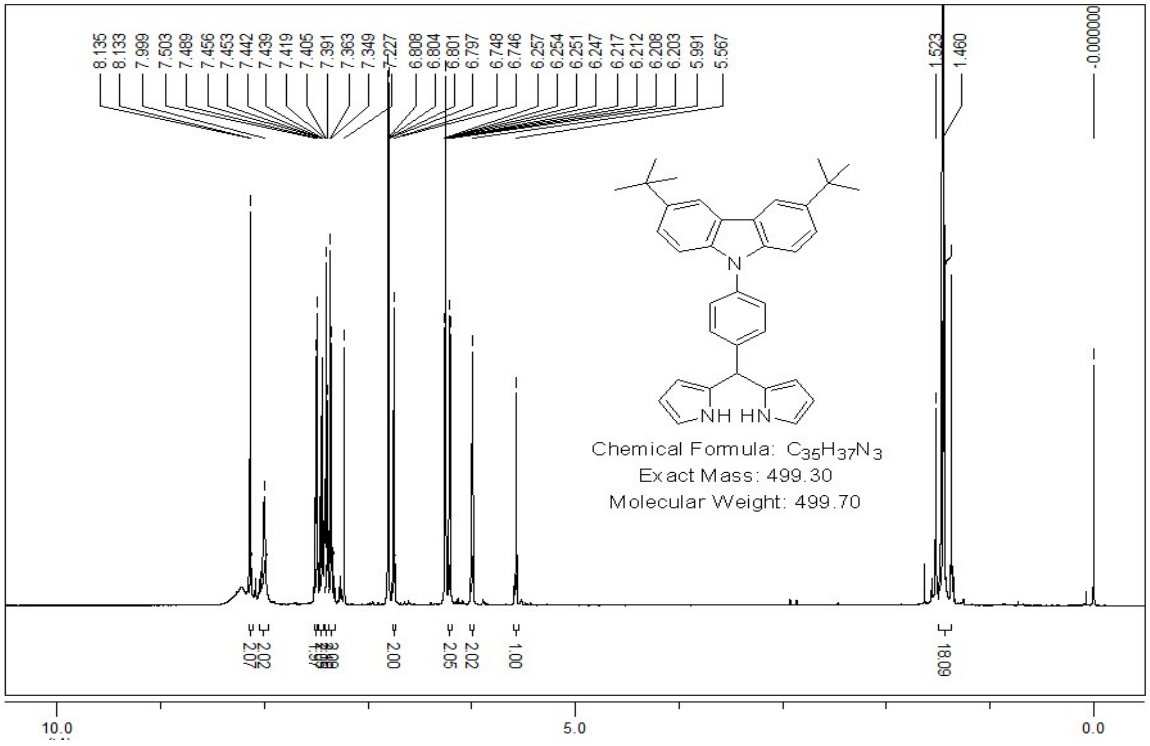

Figure S8 [1]HNMR spectra of **3a**.

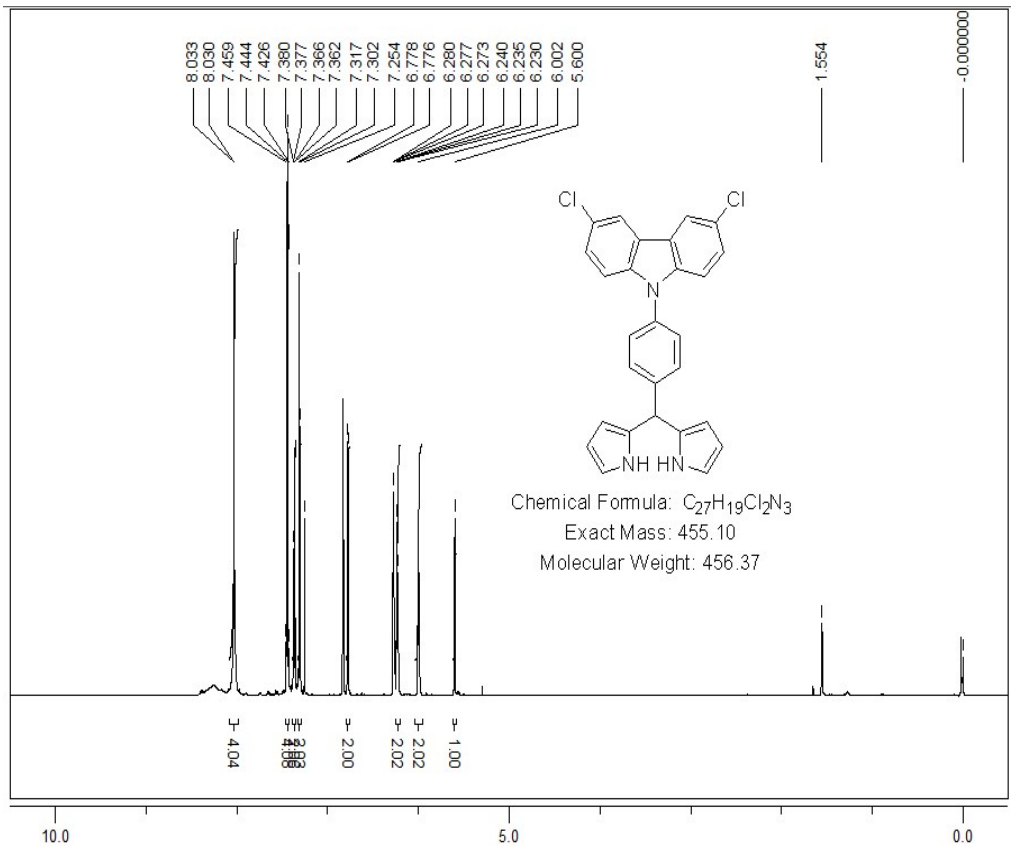

Figure S9 [1]HNMR spectra of **3b**.

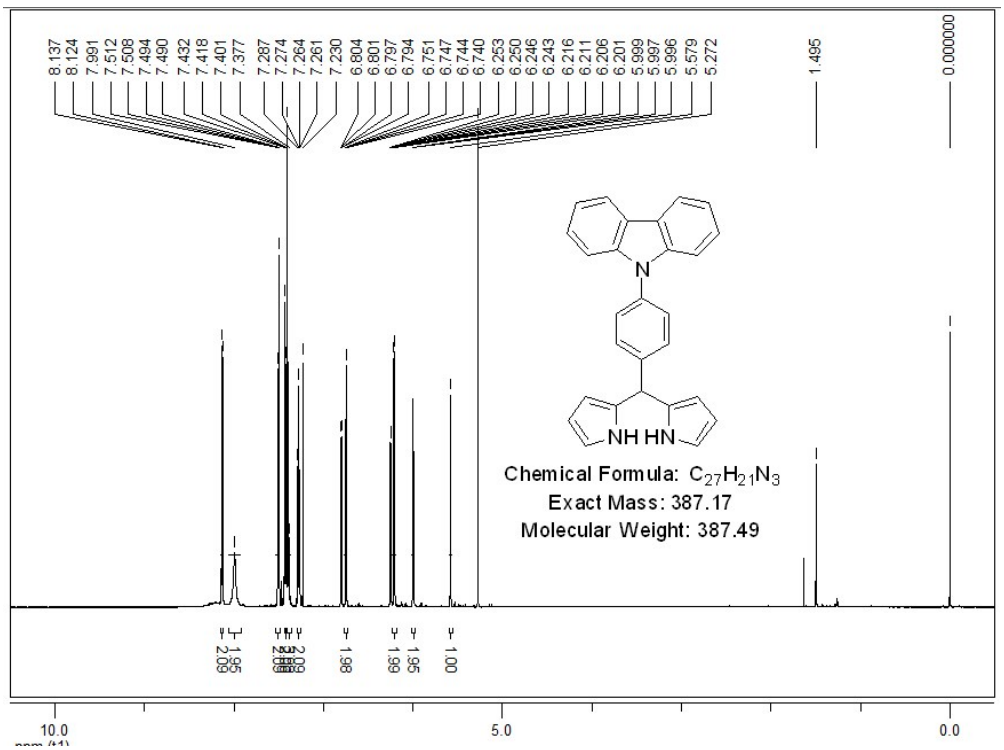

Figure S10 [1]HNMR spectra of **6a**.

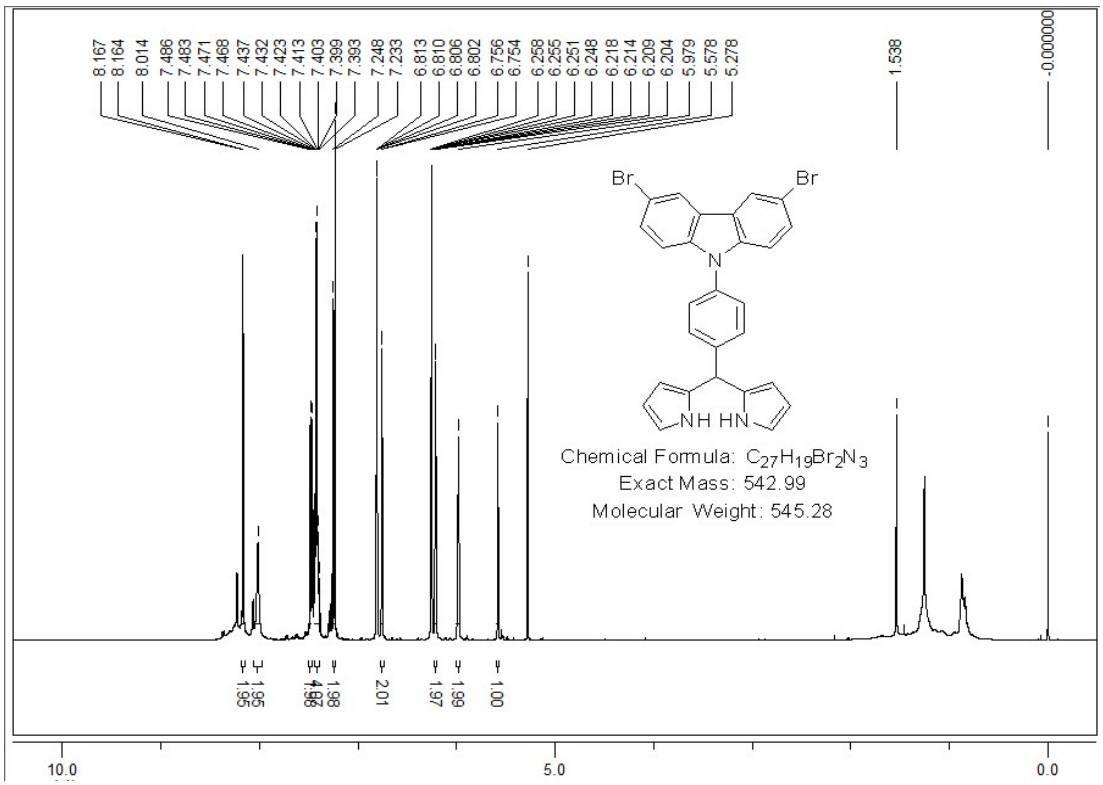

Figure S11 [1]HNMR spectra of **6b**.

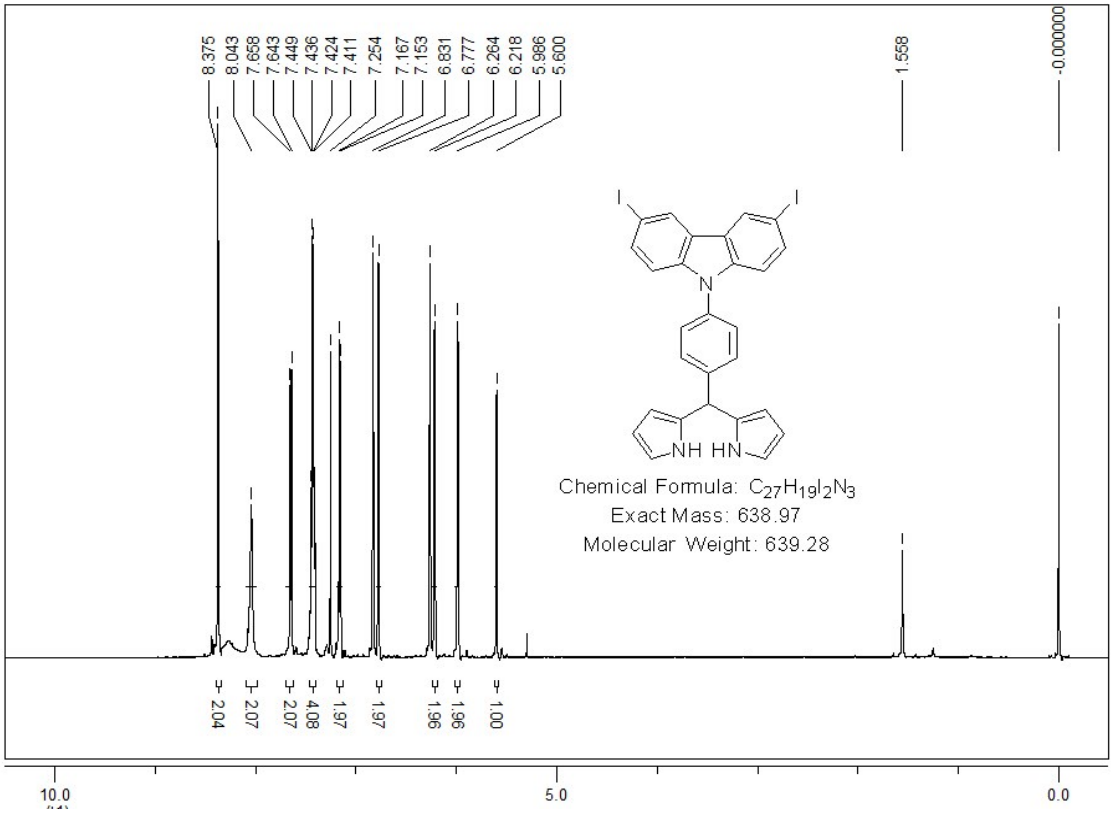

Figure S12 [1]HNMR spectra of **6c**.

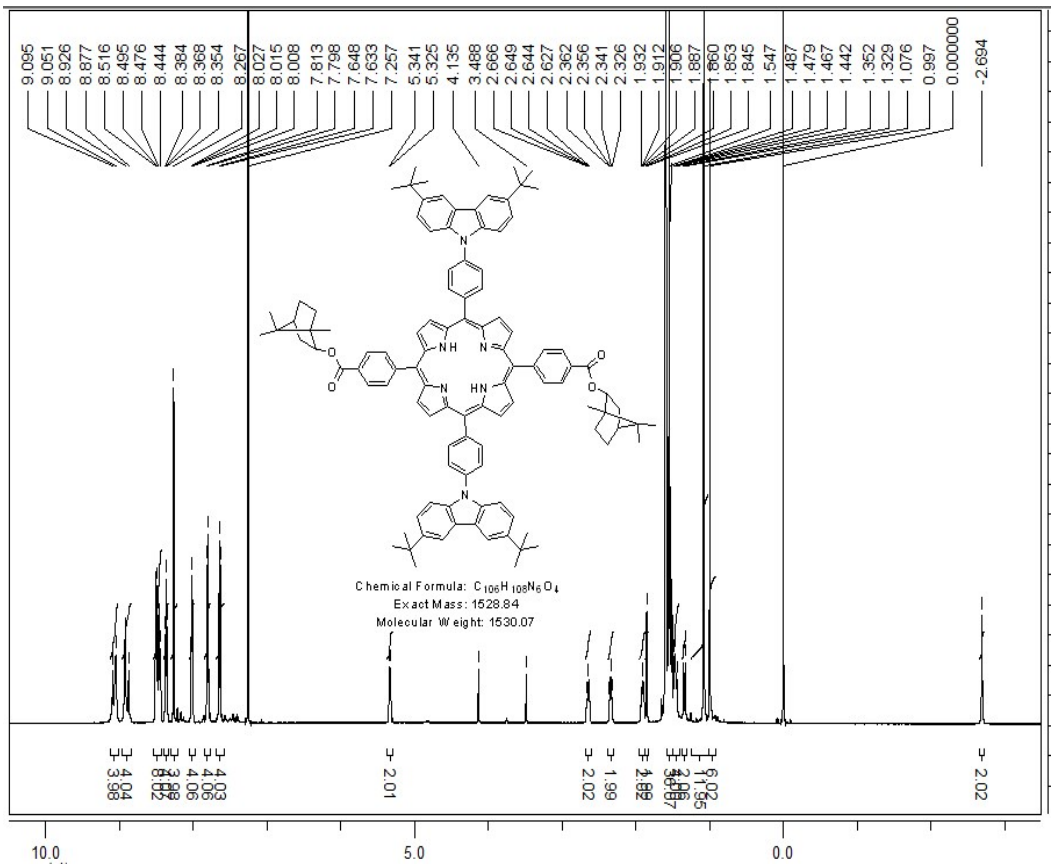

Figure S13 ^{1}HNMR spectra of **4a**.

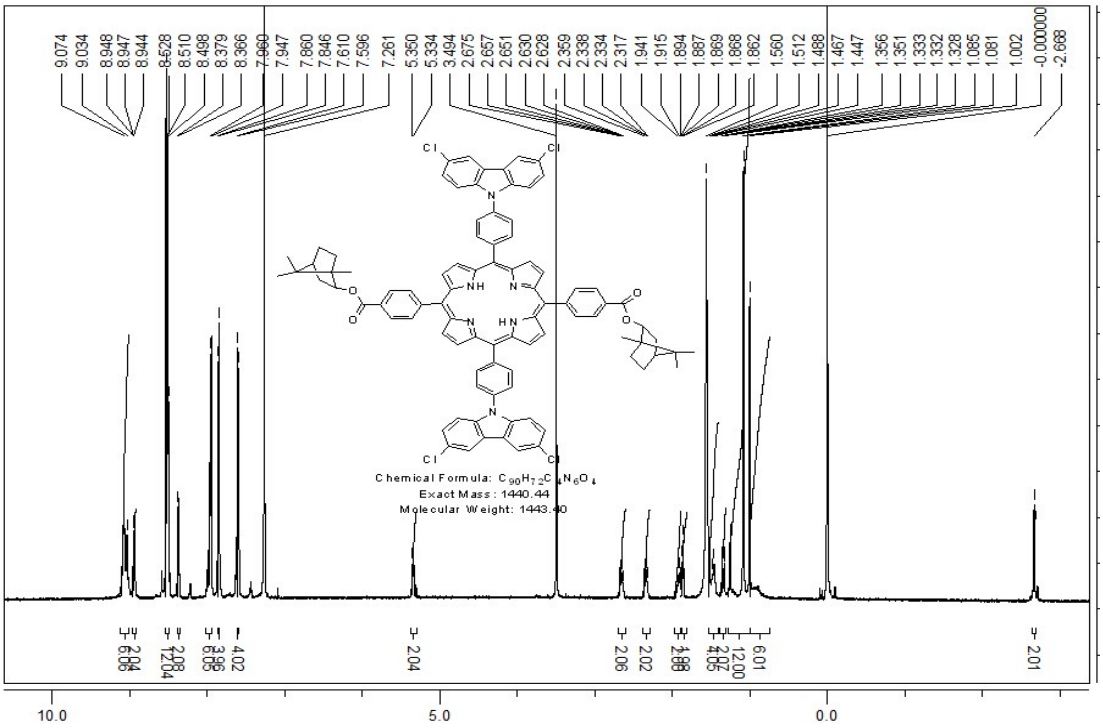

Figure S14 ^{1}HNMR spectra of **4b**.

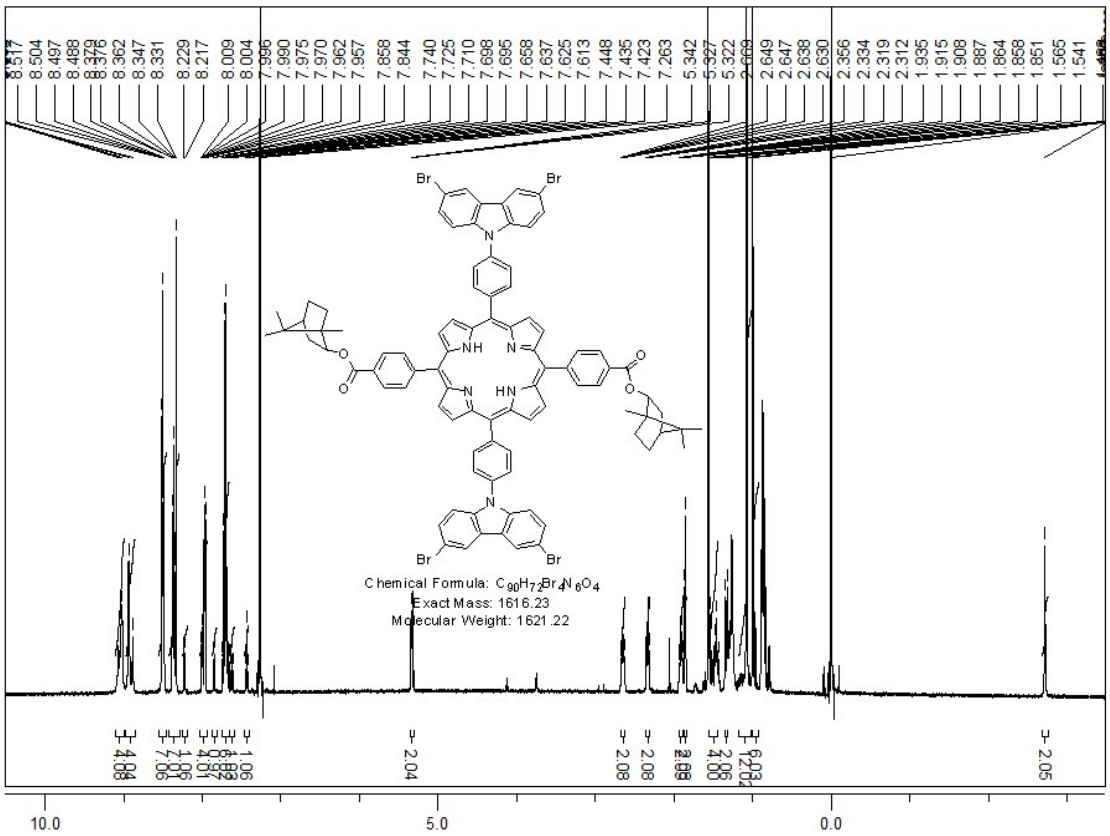

Figure S15 ^{1}HNMR spectra of **7b**.

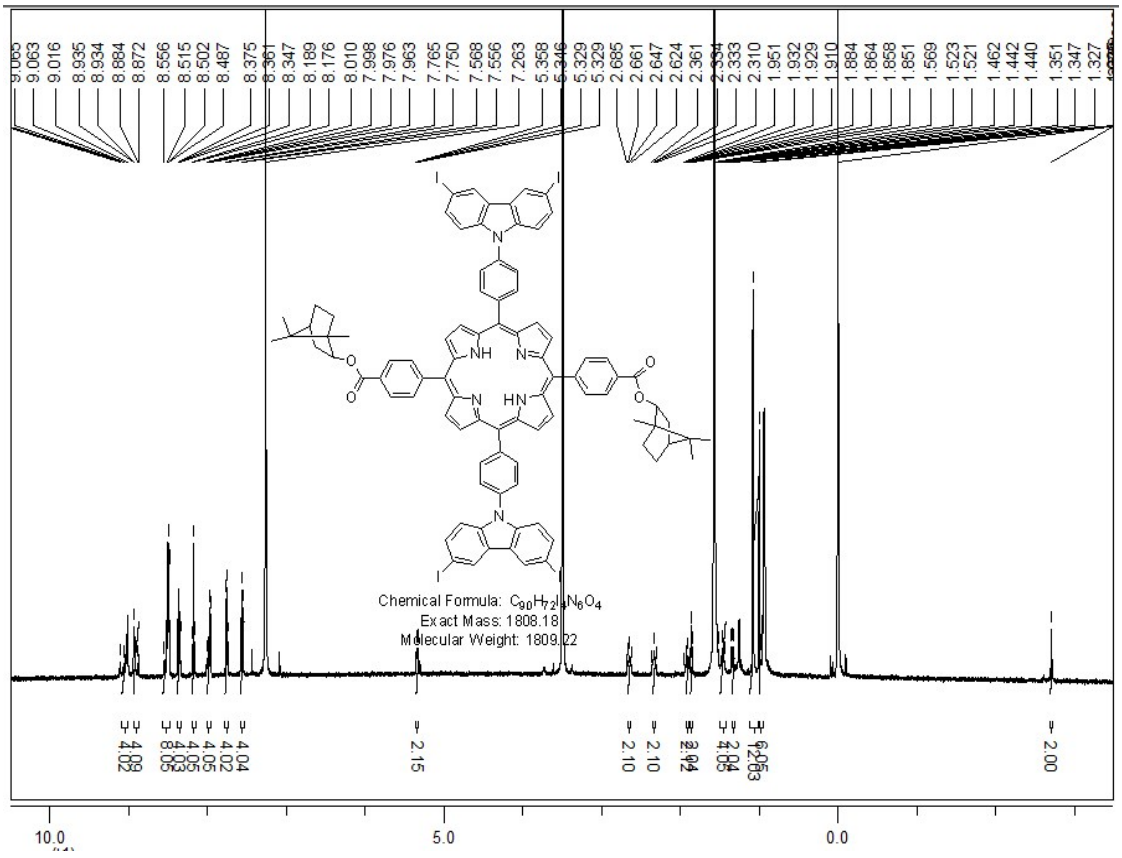

Figure S16 ^{1}HNMR spectra of **7c**.

iii. High-resolution ESI-mass spectra

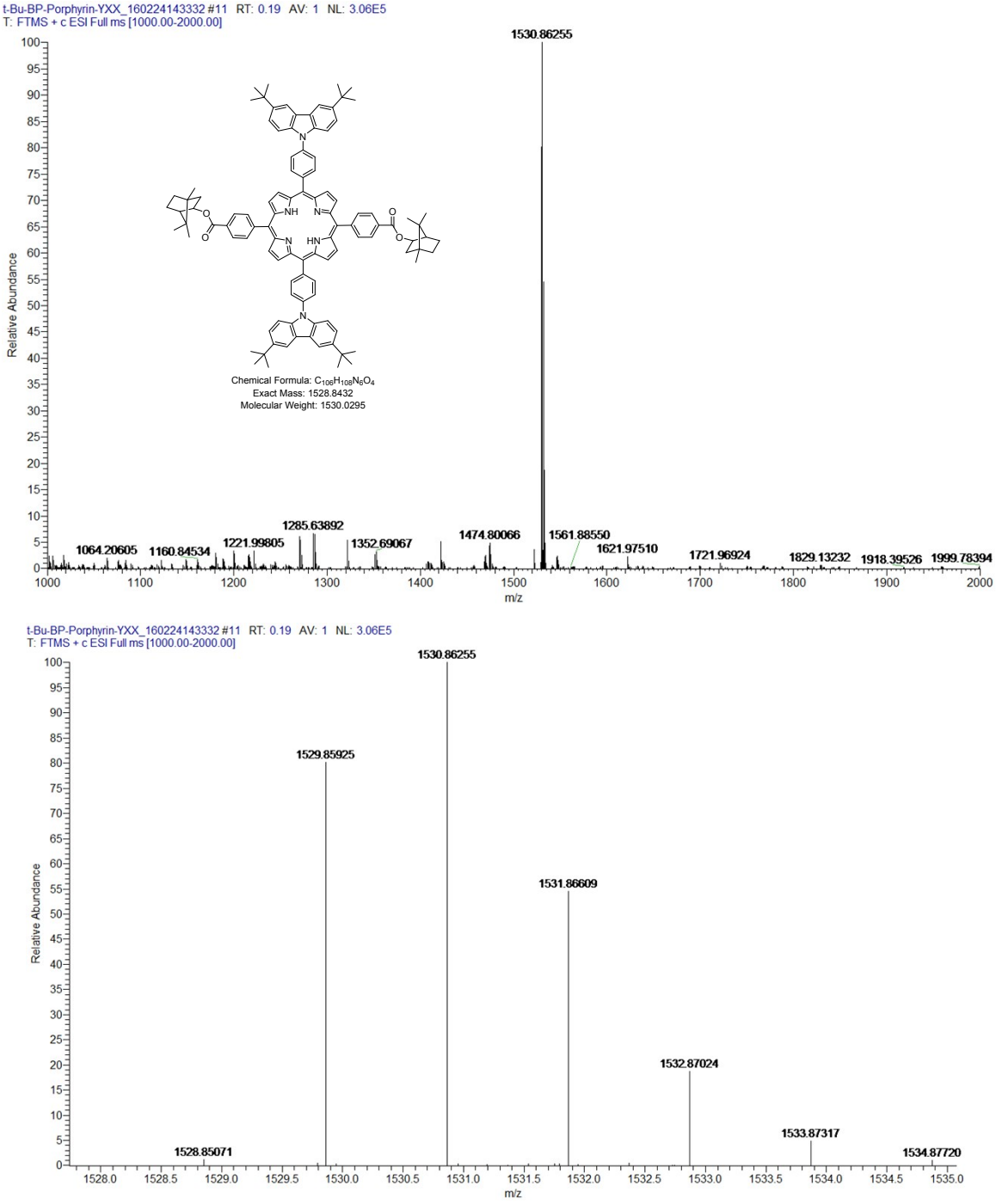

Figure S17 HR-ESI-mass spectra of **4a**.

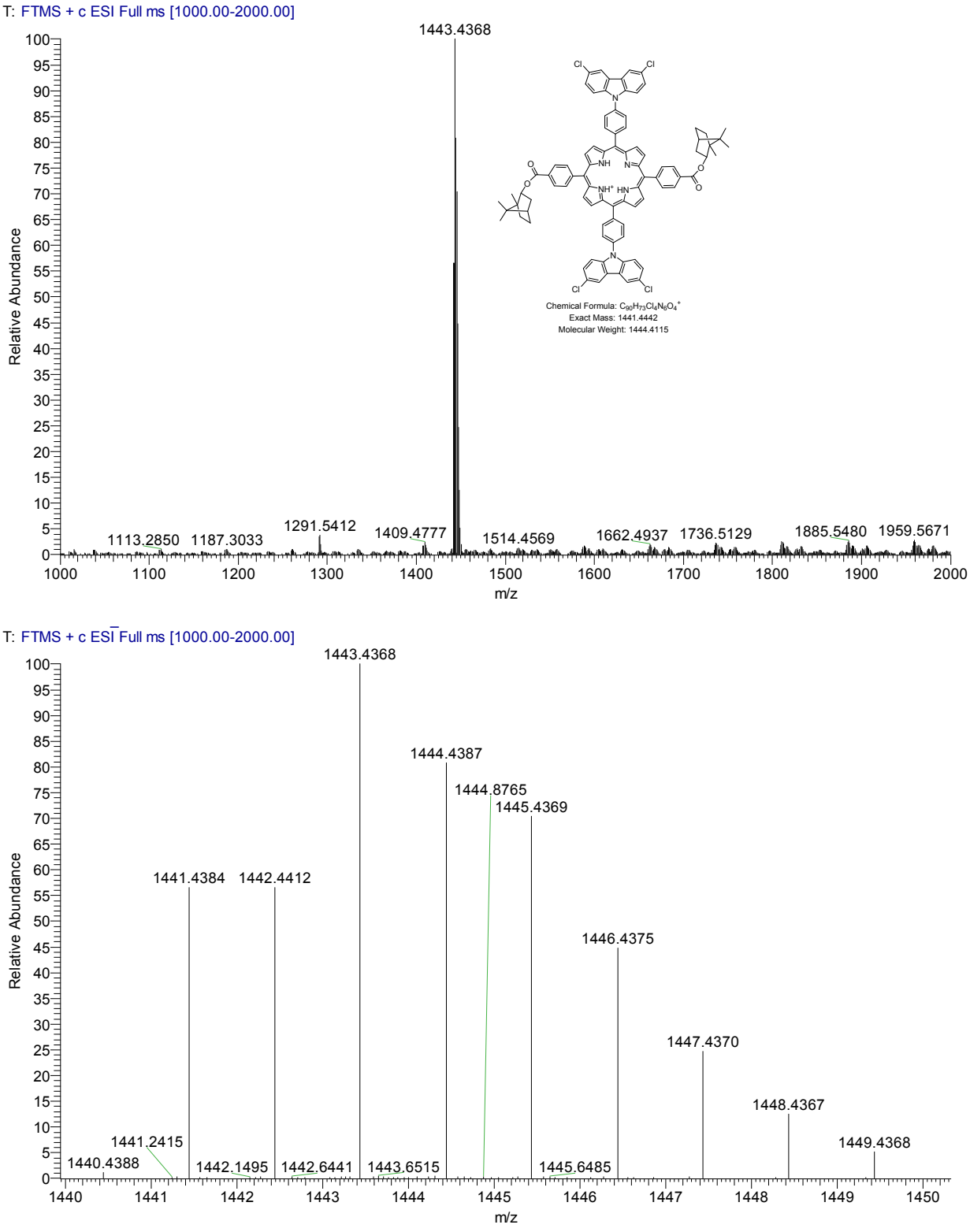

Figure S18 HR-ESI-mass spectra of **4b**.

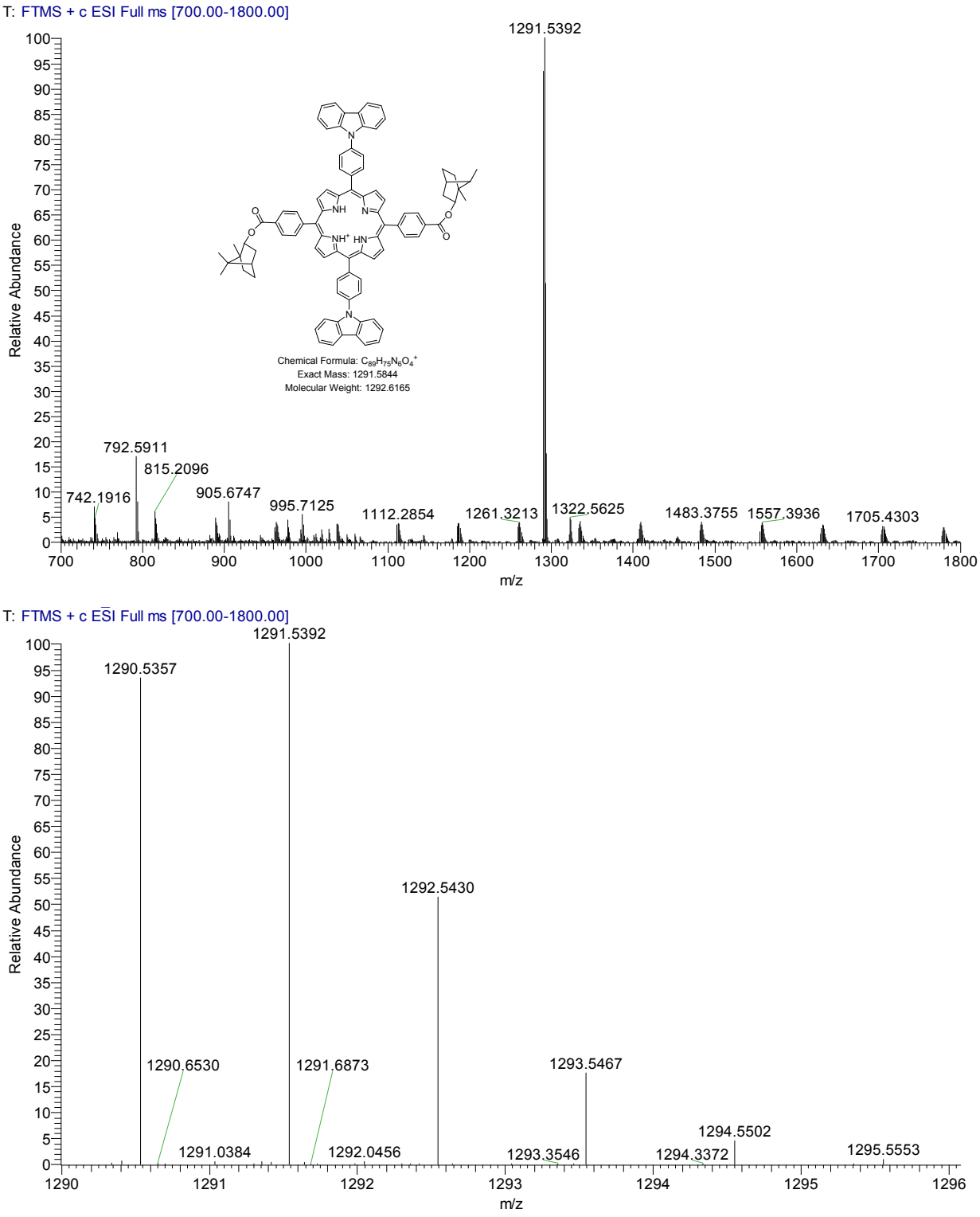

Figure S19 HR-ESI-mass spectra of **7a**.

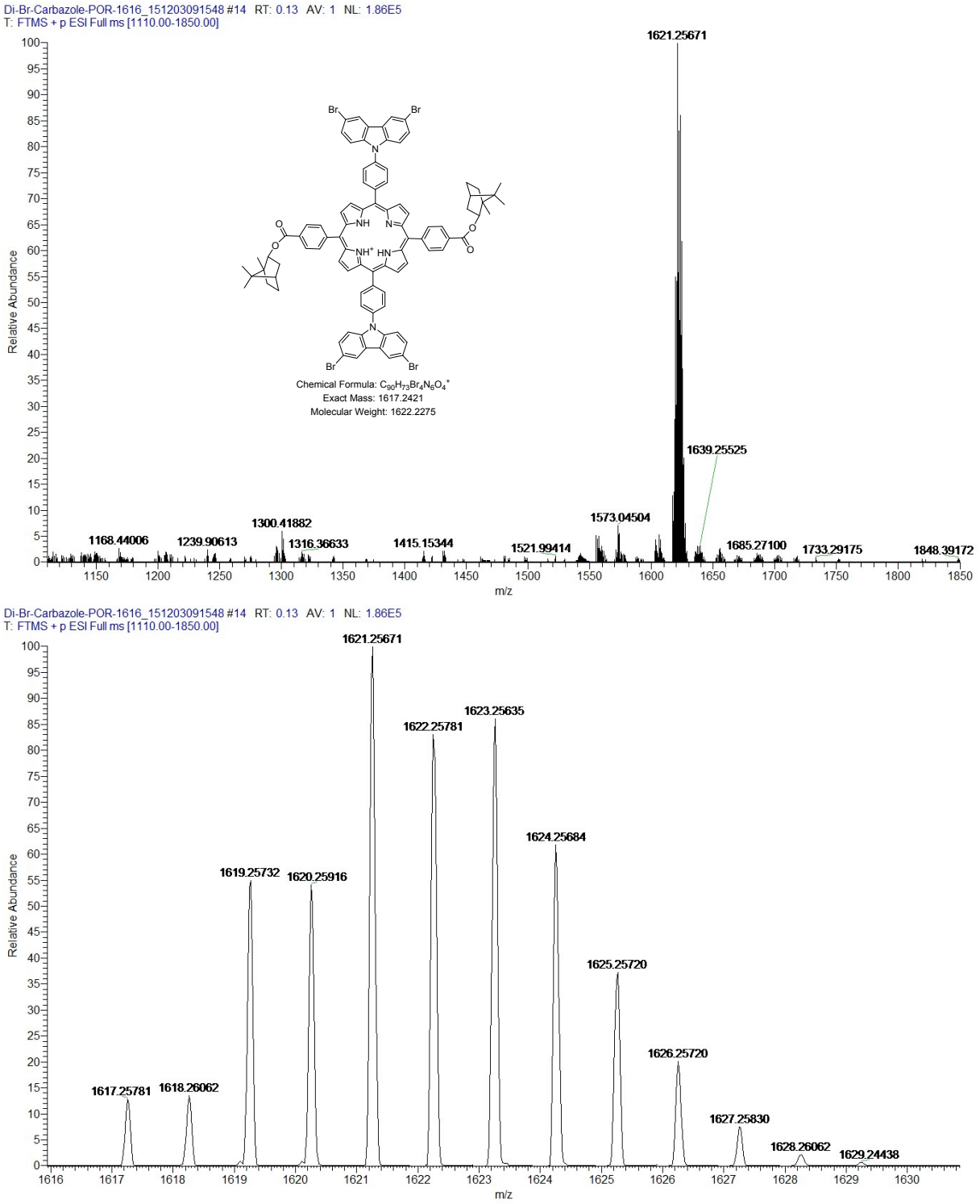

Figure S20 HR-ESI-mass spectra of **7b**.

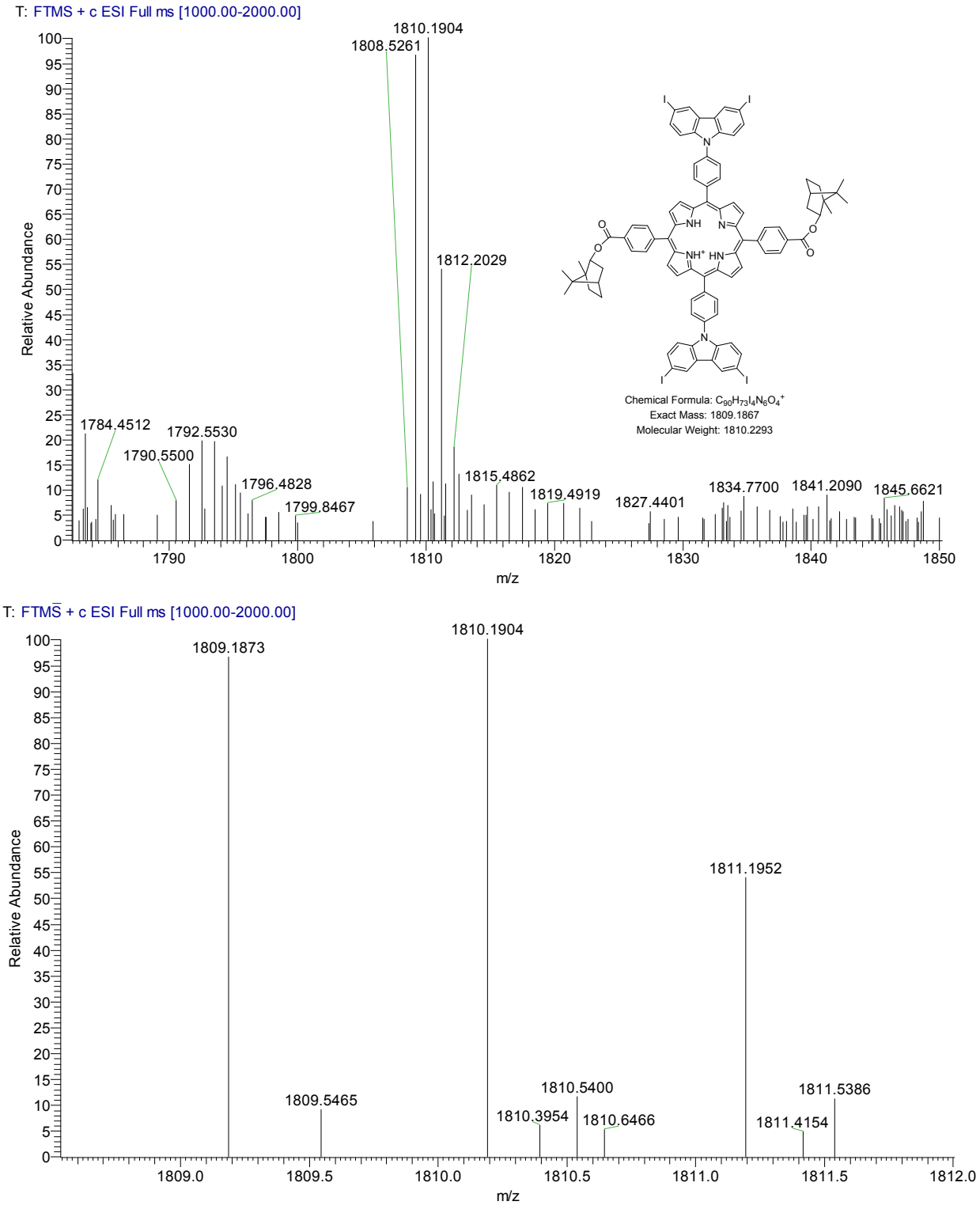

Figure S21 HR-ESI-mass spectra of **7c**.

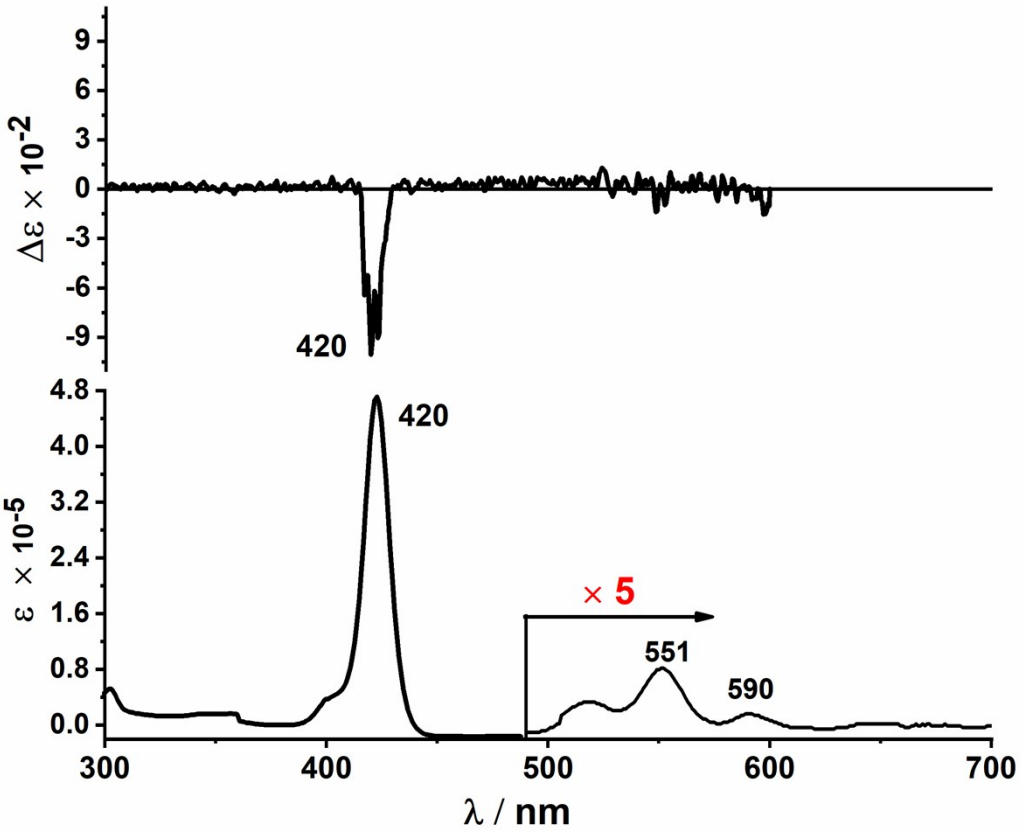

Figure S22 UV-vis (bottom) and circular dichroism spectra (up) of **Zn(II)4b** in CH_2Cl_2..

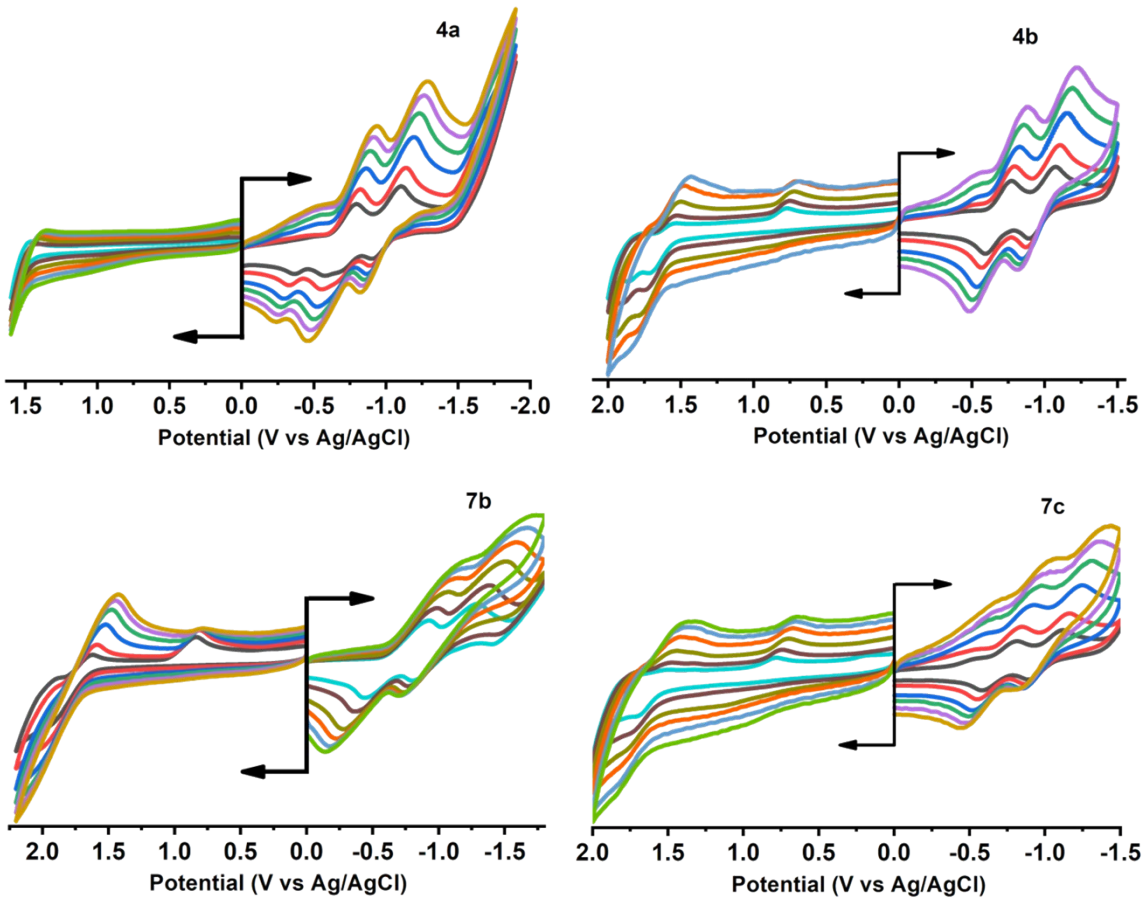

Figure S23 Cyclic voltammetry of **4a-4b** and **7b-c** in o-dichlorobenzene at 10-500 mV/s speeds.

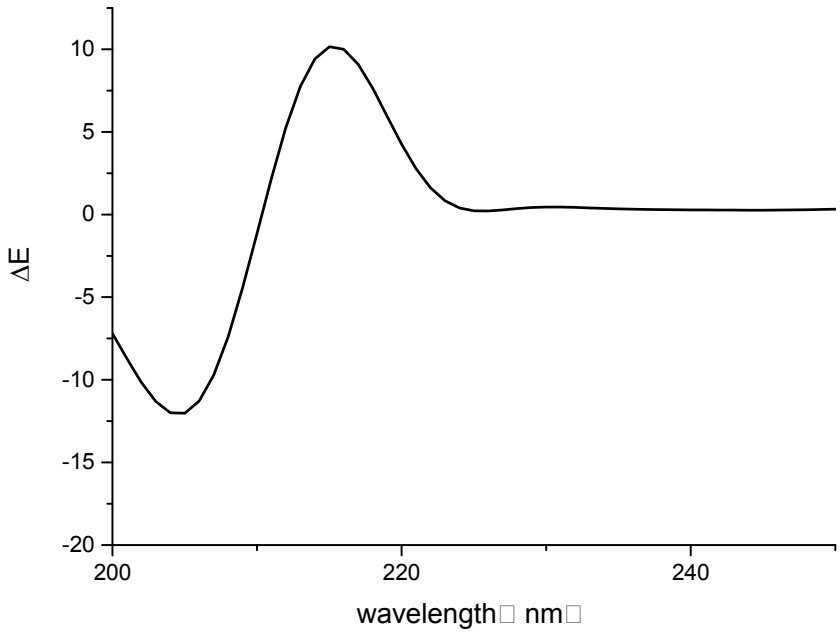

Figure S24 CD spectra of (-)-Bomeol in DCM

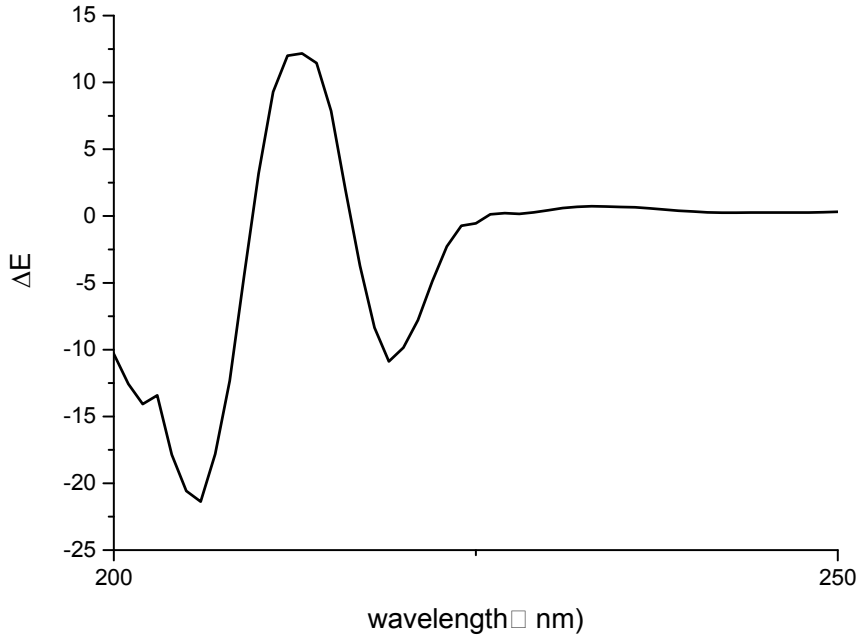

Figure S25 CD spectra of **4a** in DCM

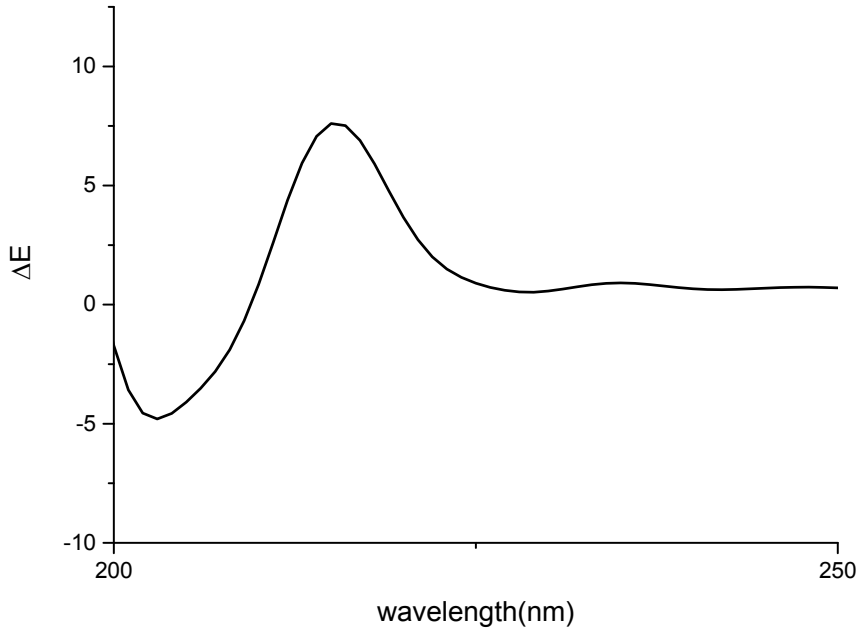

Figure S26 CD spectra of **4b** in DCM

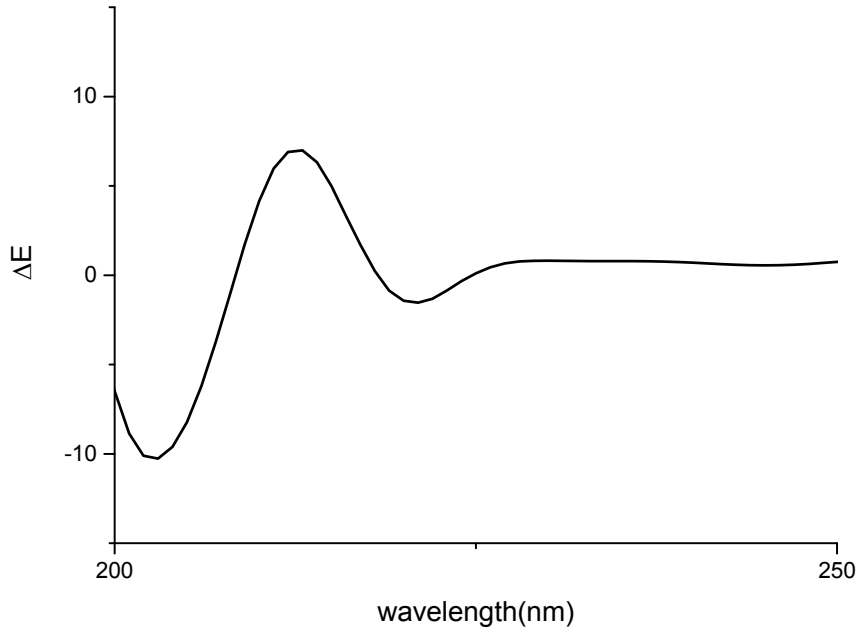

Figure S27 CD spectra of **7b** in DCM

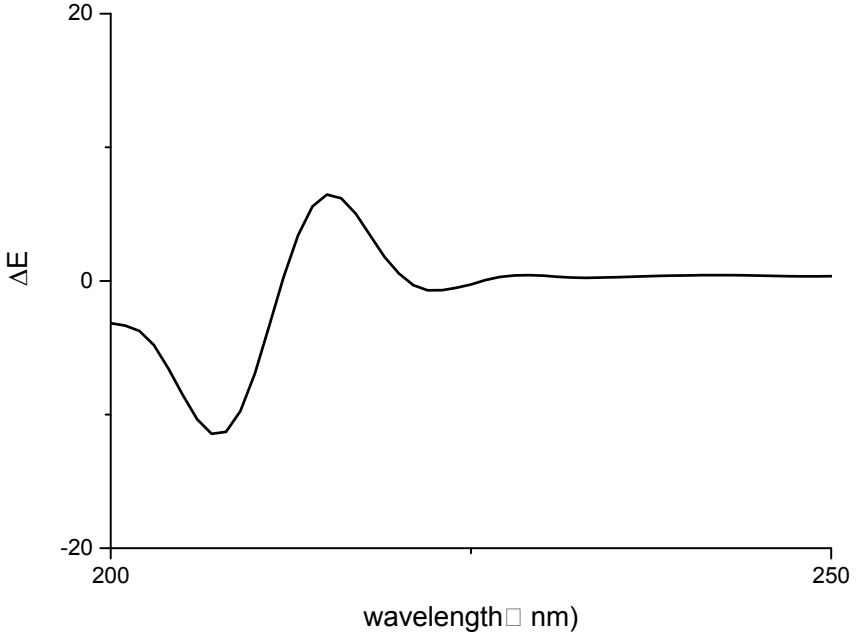

Figure S28 CD spectra of **7c** in DCM

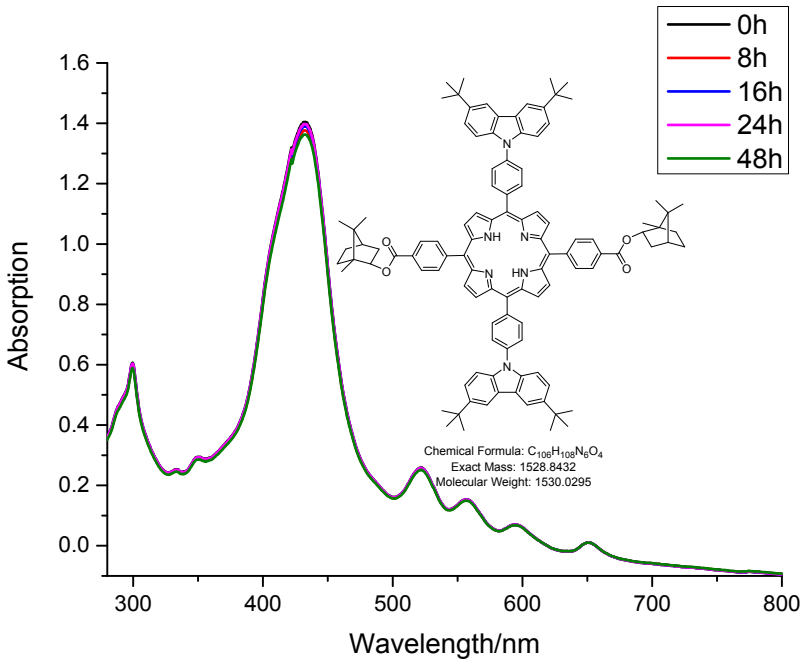

Figure S29 UV-vis spectra of **4a** after 48h in the mixture solvent of DMSO and pH 7.4 PBS from 0h to 48h.

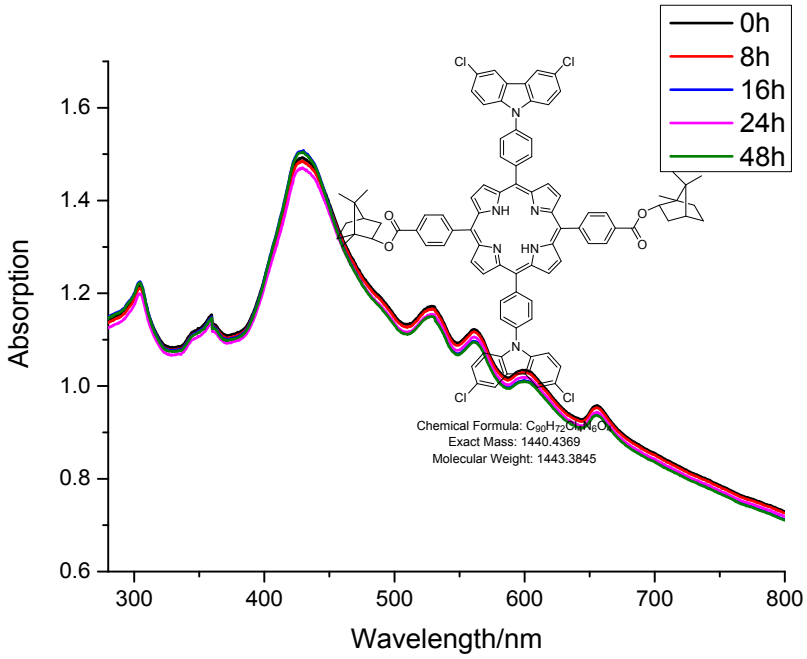

Figure S30 UV-vis spectra of **4b** after 48h in the mixture solvent of DMSO and pH 7.4 PBS from 0h to 48h.

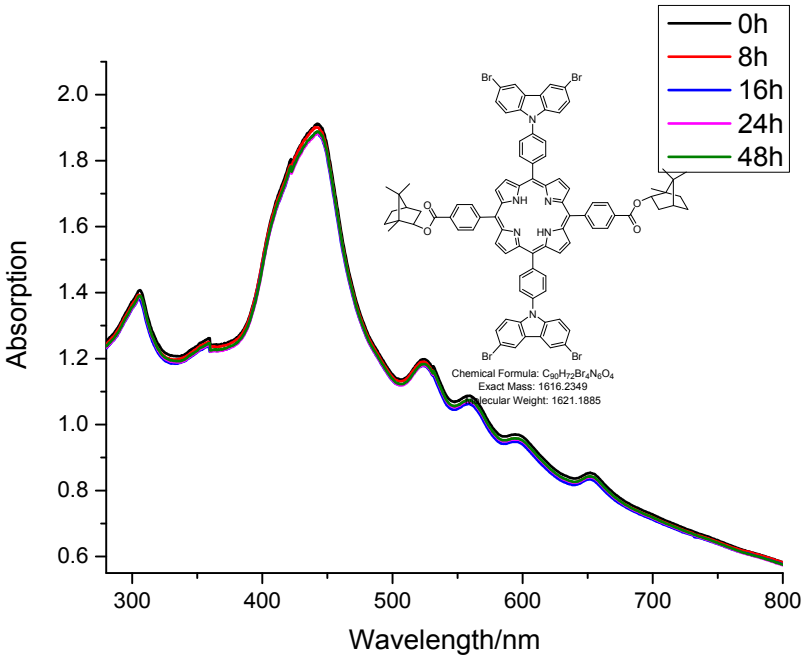

Figure S31 UV-vis spectra of **7b** after 48h in the mixture solvent of DMSO and pH 7.4 PBS from 0h to 48h.

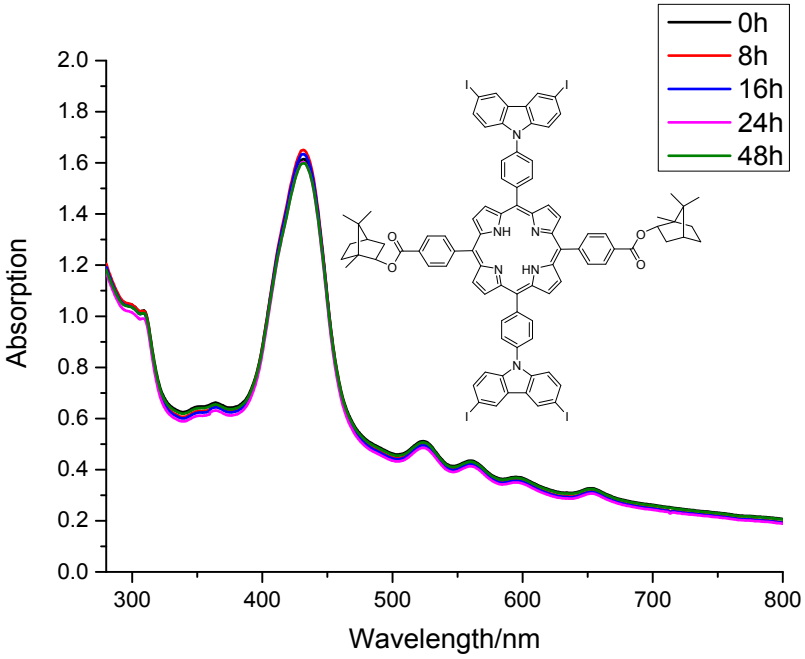

Figure S32 UV-vis spectra of **7c** after 48h in the mixture solvent of DMSO and pH 7.4 PBS from 0h to 48h.

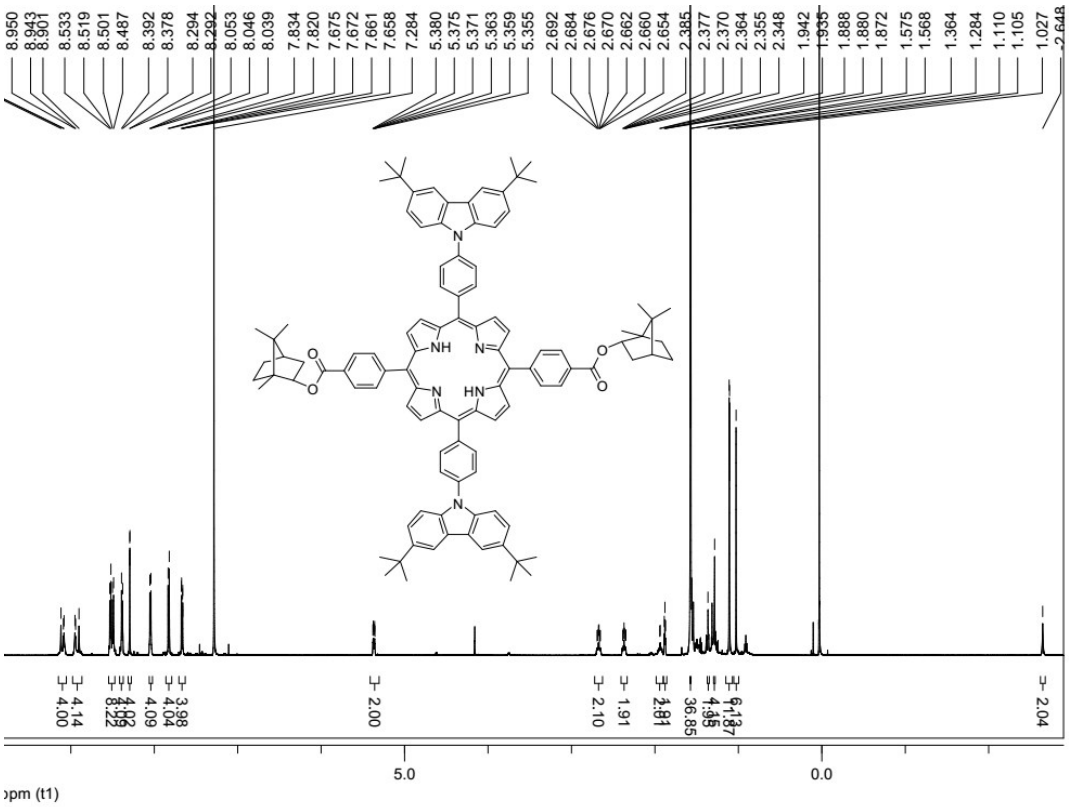

Figure S33 ^{1}HNMR spectra of **4a** in $CDCl_3$ **(**after 48h in the mixture solvent of DMSO and pH 7.4 PBS at 37°C).

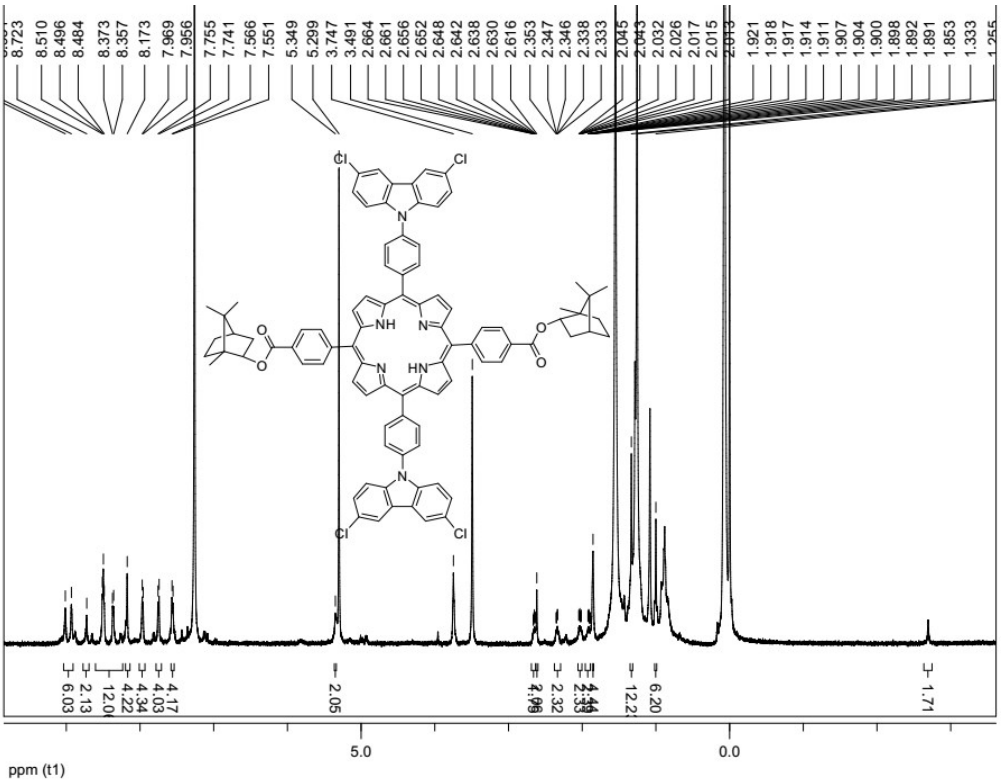

Figure S34 ^{1}HNMR spectra of **4b** in $CDCl_3$ **(**after 48h in the mixture solvent of DMSO and pH 7.4 PBS at 37°C).

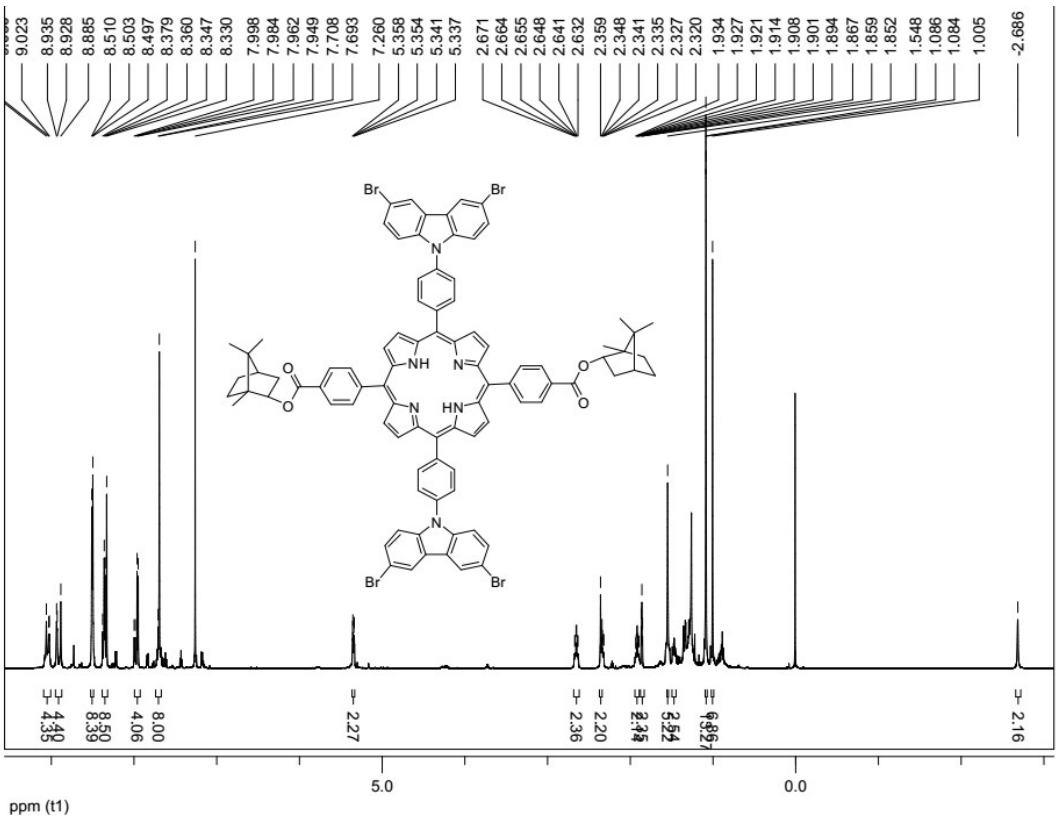

Figure S35 ^{1}HNMR spectra of **7b** in $CDCl_3$ **(**after 48h in the mixture solvent of DMSO and pH 7.4 PBS at 37°C).

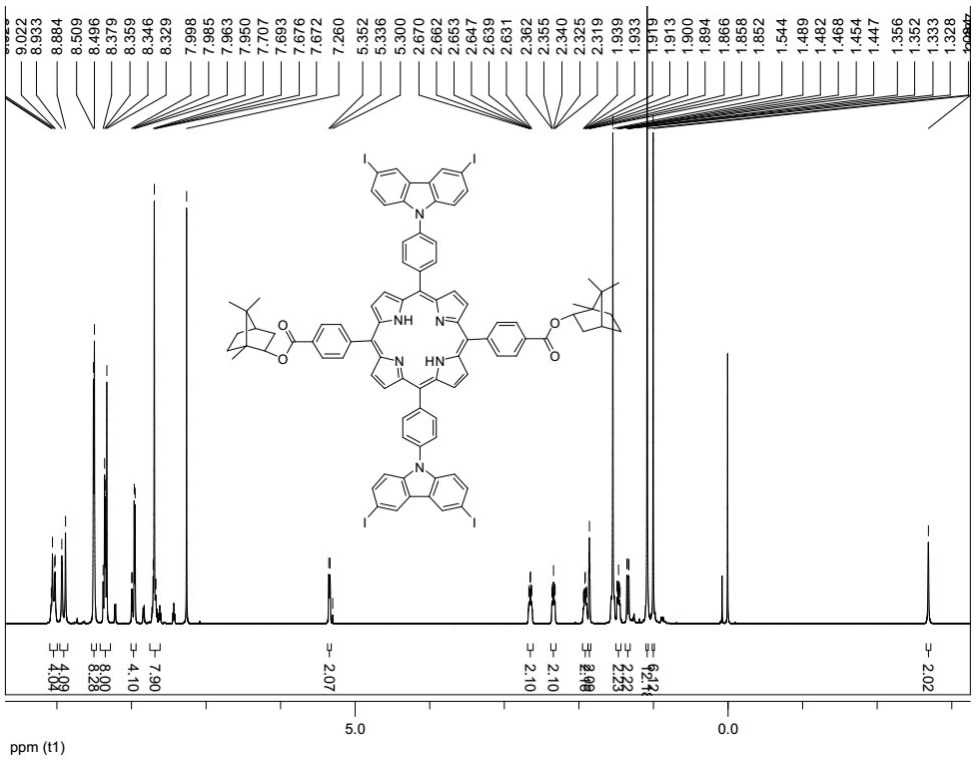

Figure S36 ^{1}HNMR spectra of **7c** in $CDCl_3$ **(**after 48h in the mixture solvent of DMSO and pH 7.4 PBS at 37°C).

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