1. General instrumentation and methods

All reactants were purchased from commercial supplies without purification. Compound **2**[1], **6**[2], **7**[3], **BVM**[3] and photosensitizer **$Na_4Ru(BDC)_3$**[4] were prepared according to the published methods. ^{1}H NMR ,^{13}C NMR and ^{1}H COSY NMR spectra were obtained by Bruker AVANCE III HD 400 Hz instrument. High-resolution mass spectra (HRMS) were recorded on a Bruker mcriOTOF11 analyzer. UV-visible spectra were recorded with a PerkinElmer LAMBDA 650 UV/Vis/NIR spectrometer. Dynamic light scattering (DLS) experiments were conducted on a Malvern Zetasizer Nano ZS90 with a monochromatic coherent He-Ne laser (633 nm) as the light source. The light power density was measured using a radiometer from Beijing Normal University Photoelectric Instrument Factory.

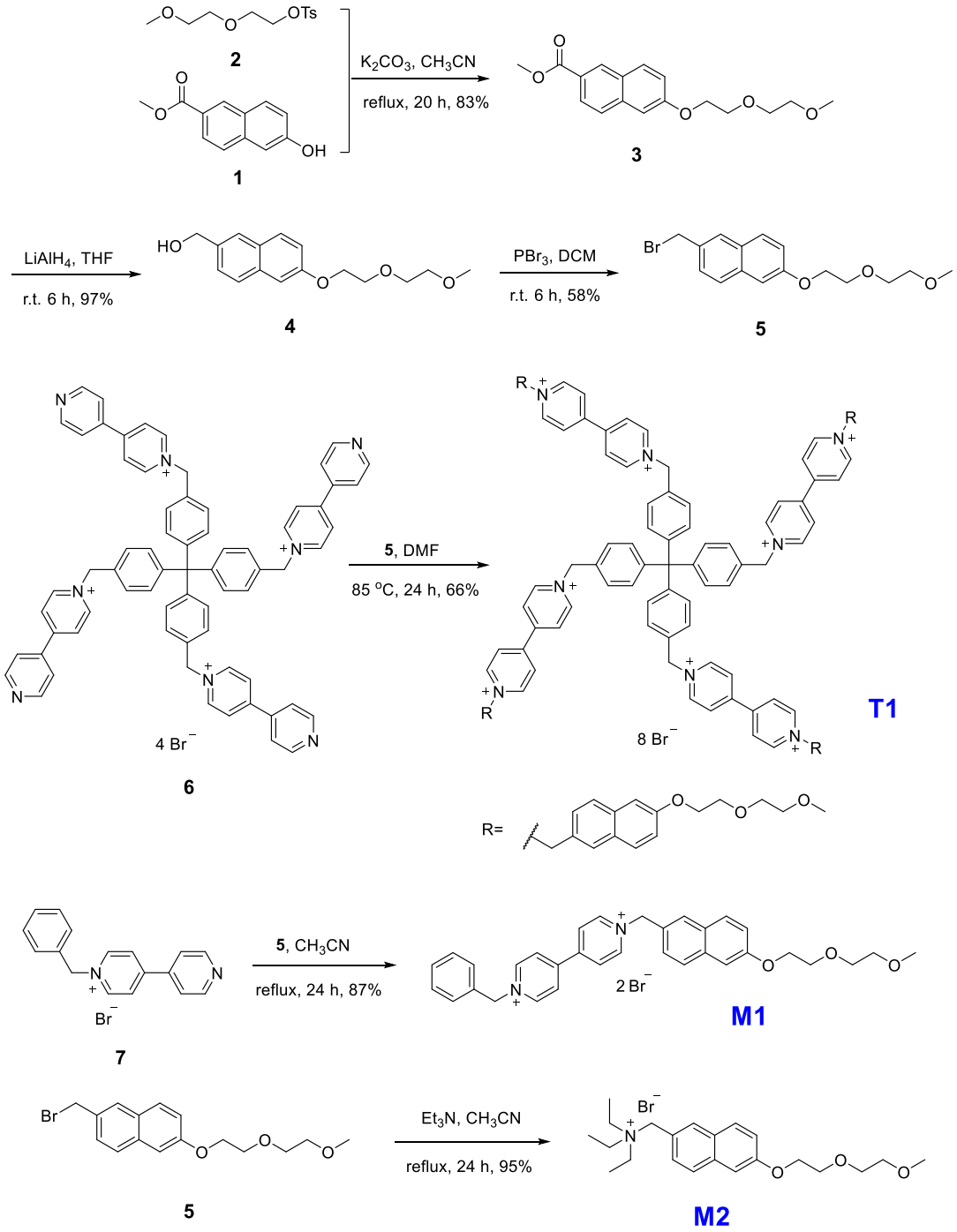
Agilent Technologies 1260 Infinity high performance liquid chromatography (HPLC) instrument were used to analyze the composition of the reaction mixture during photocatalytic aerobic oxidation. All samples were conducted with pre-column derivatization[5,6] before injecting into the HPLC system. The OPA-MCE pre-column derivatization reagent contained 40 mM *o*-phthalaldehyde and 1% (v/v) 2-mercaptoethanol in a saturated solution of $NaBO_2$ with 20% (v/v) methanol. The samples for HPLC analysis were prepared with 10 μL reaction mixture, 25 μL H_2O and 75μL derivatization reagent. Derivatized samples (10 μL) were directly injected into the HPLC system. The column employed was Platisil PH C18 (5 μm, 4.6×150 mm). The HPLC chromatography was performed at 35 °C with a flow rate of 1.00 mL·min^{-1} and a detector at 338 nm. Phase A was composed of NaH_2PO_4/Na_2HPO_4 buffer (40 mM, pH=7.8), and phase B was composed of MeCN: MeOH: H_2O (45: 45: 10 v/v/v). The gradient of phase A and phase B in HPLC analysis was set as shown in Table S1.

Table S1: Gradient of Phase A and Phase B in HPLC analysis

Time	Phase A (%)	Phase B (%)
0	80	20
5	80	20
20	20	80
21	20	80
21.1	80	20
25	80	20

Gas chromatographic analysis was conducted on a Shimadazu GC-2010 instrument to analyze the amount of H_2 during photocatalytic hydrogen generation. The column employed was CARBOXEN-1006 PLOT (30 m×0.53 mm). The temperature was set at 150 °C for the vaporizer and 240 °C for the BDI plasma detector. The gas carrier was helium with a flow rate of 4.3 mL/min. The temperature of column was conducted at 35 °C for H_2 analysis in 10 min and turned to 200 °C later for eight-minute clean of column.

2. Synthesis and Catalysis



Scheme S1. Synthetic route of the compounds.

Compound 3. Methyl 6-hydroxy-2-naphthoate (5.0 g, 24.7 mmol), compound **2** (8.14 g, 29.7 mmol) and K_2CO_3 were mixed in CH_3CN (100 mL) and stirred under nitrogen atmosphere for 24 h at 82 °C. The suspension was cooled to room temperature, filtered and concentrated in vacuo. The resulting crude product was subjected to flash column chromatography on silica gel (hexane/ethyl acetate: 4:1 v/v) to afford compound **3** as a white solid (6.2 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.03 (d, J = 8.5

Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 1H), 7.17 (s, 1H), 4.30 (t, *J* = 4.8 Hz, 2H), 3.97 (s, 3H), 3.95 (t, *J* = 4.6 Hz, 2H), 3.77 (t, *J* = 4.5 Hz, 2H), 3.61 (t, *J* = 4.6 Hz, 2H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.54, 158.89, 137.25, 131.05, 130.99, 128.15, 127.04, 126.08, 125.46, 120.07, 106.77, 72.16, 71.01, 69.83, 67.71, 59.28, 52.25. HRMS (ESI): Calcd for $C_{17}H_{20}O_5Na$: 327.1203 $[M + Na]^+$. Found: 327.1197.

Compound 4. Lithium aluminum hydride (0.62 g, 16.3 mmol) was suspended in dried tetrahydrofuran (15 mL) at 0 °C and compound **3** (2.0 g, 6.6 mmol) in dried tetrahydrofuran (15 mL) was slowly added to the solution. The mixture was stirred for 12 h at room temperature and monitored by TLC (hexane/ethyl acetate: 1:1 v/v). The suspension was cooled to 0 °C and the reaction was then quenched by the dropwise addition of water and then ethyl acetate (100 mL) and water (200 mL) were added. The organic layer was separated, washed with water (100 mL×3) and saturated aq. NaCl (100 mL), dried over anhydrous Na_2SO_4 and evaporated to afford compound **4** as a light yellow oil (1.76 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.9 Hz, 3H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 11.0 Hz, 1H), 7.15 (s, 1H), 4.83 (s, 2H), 4.28 (t, *J* = 4.9 Hz, 2H), 3.94 (t, *J* = 4.9 Hz, 2H), 3.77 (t, *J* = 4.7 Hz, 2H), 3.61 (t, *J* = 4.6 Hz, 2H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.09, 136.31, 134.24, 129.53, 129.08, 127.44, 126.03, 125.73, 119.50, 106.94, 72.17, 70.99, 69.96, 67.63, 65.76, 59.28. HRMS (ESI): Calcd for $C_{16}H_{20}O_4Na$: 299.1254 $[M + Na]^+$. Found: 299.1252.

Compound 5. Compound **4** (1.5 g, 5.4 mmol) was dissolved in dried dichloromethane (15 mL) under nitrogen atmosphere, and then phosphorus tribromide (510 μL, 5.4 mmol) dissolved in dried dichloromethane (15 mL) was added to the solution at 0 °C. The mixture was stirred for 6 h at room temperature and monitored by TLC (hexane/ethyl acetate: 3:1 v/v). The suspension was cooled to 0 °C and the reaction was then quenched by the dropwise addition of water and then ethyl acetate (50 mL) and water (100 mL) were added. The organic layer was separated, washed with water (100 mL×3), 5% aq. $NaHCO_3$ (100 mL) and saturated aq. NaCl (100 mL), dried over anhydrous Na_2SO_4 and evaporated to afford crude product as a light yellow oil. The resulting crude product was subjected to flash column chromatography on silica gel (hexane/ethyl acetate: 3:1 v/v with 1% triethylamine) to afford compound **5** as a white solid (1.07 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.48 (s, 1H), 7.20 (d, *J* = 8.9 Hz, 1H), 7.14 (s, 1H), 4.67 (s, 2H), 4.27 (t, *J* = 4.9 Hz, 2H), 3.94 (t, *J* = 4.9 Hz, 2H), 3.76 (t, *J* = 4.6 Hz, 2H), 3.61 (t, *J* = 4.6 Hz, 2H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.59, 134.47, 133.03, 129.62, 128.85, 127.94, 127.81, 127.49, 119.78, 106.93, 72.15, 70.99, 69.91, 67.64, 59.29, 34.63. HRMS (ESI): Calcd for $C_{16}H_{19}BrO_3Na$: 361.0410 $[M + Na]^+$. Found: 361.0401.

Synthesis of T1. Compounds **5** (0.48 g, 1.4 mmol) and **6** (0.2 g, 0.15 mmol) were mixed with dried N, N-dimethylformamide (15 mL) and stirred under nitrogen atmosphere for 24 h at 85 °C. The suspension was cooled to room temperature and the solvent was evaporated. The solid residue was washed with CH_3CN (100 mL×2) and dried to afford **T1** as a yellow powder (268 mg, 66%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.59 (s, 16H), 8.79 (s, 16H), 8.13 (s, 4H), 7.88 (t, *J* = 9.4 Hz, 8H), 7.67 (d, *J* = 8.4 Hz, 4H), 7.55 (d, *J* = 8.1 Hz, 8H), 7.38 (s, 4H), 7.24 (t, *J* = 10.2 Hz, 12H), 6.10 (s, 8H), 5.93 (s, 8H), 4.21

(t, J = 4.0 Hz, 8H), 3.80 (t, J = 4.1 Hz, 8H), 3.60 (t, J = 4.6 Hz, 8H), 3.46 (t, J = 4.6 Hz, 8H), 3.24 (s, 12H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.74, 149.56, 149.48, 147.37, 146.15, 134.93, 132.37, 131.17, 130.09, 129.55, 129.16, 129.01, 128.49, 128.49, 127.68, 127.63, 126.86, 120.13, 107.17, 71.72, 70.18, 69.26, 67.78, 64.04, 62.82, 58.51. HRMS (ESI): Calcd for $C_{133}H_{132}Br6N_8O_{12}$: 1257.2528 $[M - 2Br]^{2+}$. Found:1257.2508.

Synthesis of M1. Compound **5** (0.31 g, 0.92 mmol) and **7** (0.2 g, 0.61 mmol) were mixed with CH_3CN (20 mL) and stirred under nitrogen atmosphere for 24 h at 82 °C. After cooling to room temperature, the precipitate formed was filtered, washed with CH_3CN (50 mL×2) and dried to afford **M1** as an orange solid (354 mg, 87%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.54 (dd, J_1 = 15.8 Hz, J_2 = 6.8 Hz, 4H), 8.74 (d, J = 6.5 Hz, 4H), 8.11 (s, 1H), 7.87 (t, J = 9.3 Hz, 2H), 7.64 (dd, J_1 = 8.7 Hz, J_2 = 1.5 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.46 (m, 3H), 7.38 (d, J = 2.2 Hz, 1H), 7.25 (dd, J_1 = 8.9 Hz, J_2 = 2.4 Hz, 1H), 6.07 (s, 2H), 5.95 (s, 2H), 4.2 (t, J = 4.5 Hz, 2H), 3.80 (t, J = 4.5 Hz, 2H), 3.60 (t, J = 4.7 Hz, 2H), 3.46 (t, J = 4.7 Hz, 2H), 3.24 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.81, 149.75, 149.69, 146.16, 134.99, 130.13, 130.02, 129.76, 129.54, 129.40, 129.07, 128.54, 128.43, 127.72, 127.67, 126.86, 120.17, 107.27, 71.78, 70.24, 69.32, 67.85, 63.93, 58.55. HRMS (ESI): Calcd for $C_{33}H_{34}BrN_2O_3$: 585.1747 $[M - Br]^+$. Found: 585.1742.

Synthesis of M2. Compound **5** (0.2 g, 0.59 mmol) and dried triethylamine (2 mL, 14.4 mmol) were dissolved in dried CH_3CN (20 mL) and stirred under nitrogen atmosphere for 24 h at 82 °C. The suspension was cooled to room temperature and evaporated to afford crude product as a dark yellow oil. The resulting crude product was subjected to flash column chromatography on silica gel (methanol/water: 3:1 v/v) to afford **M2** as a white solid (247 mg, 95%).^{1}H NMR (400 MHz, D_2O): δ 7.94 (dd, J_1 = 13.8 Hz, J_2 = 4.9 Hz, 3H), 7.52 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.33 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 4.49 (s, 2H), 4.36 (t, J = 4.2 Hz, 2H), 3.98 (t, J = 4.2 Hz, 2H), 3.80 (t, J = 4.4 Hz, 2H), 3.67 (t, J = 4.4 Hz, 2H), 3.40 (s, 3H), 3.24 (q, J = 7.1 Hz, 6H), 1.43 (t, J = 7.1 Hz, 9H). ^{13}C NMR (100 MHz, D_2O): δ 157.26, 134.80, 132.45, 130.09, 129.09, 128.32, 127.67, 122.40, 119.52, 106.96, 70.91, 69.54, 68.91, 67.13, 59.84, 57.98, 52.07, 6.96. HRMS (ESI): Calcd for $C_{22}H_{34}NO_3$: 360.2533 $[M - Br]^+$. Found:360.2547.

Photocatalytic oxidation with L-methionine

Standard condition: 1 mM **T1/CB[8]** aqueous solution (0.5 mL) and 10 mM L-methionine aqueous solution (0.5 mL) were mixed in 20 mL septum-sealed glass vials. Sample vials were capped and bubbled oxygen for 15 min to ensure that it was completely filled with oxygen. The solution was irradiated by blue LEDs strips (18 W, power density was measured as 7 $mW \cdot cm^{-2}$) and stirred for 18 h at room temperature. An aliquot (10 μL) was taken from the reaction mixture and analyzed by high performance liquid chromatography (HPLC) to determine the conversion of L-methionine and the yield of L -methionine sulfoxide. When the control molecules were used as catalysts for comparison, it was necessary to control the concentration of viologen units and naphthyl units to be constant, that was, $[V^{2+}]$ = [NaP] = 2 mM.

Photocatalytic hydrogen evolution reactions

Standard condition: 2 mL solution containing 20 μM **$Na_4Ru(BDC)_3$** and 2 μM **K-**

POM-a (Keggin-type of **POM**, $Na_3PW_{12}O_{40}$) in 100 μM **T1/CB[8]** aqueous solution with 20% methanol (v/v) was injected into 10 mL septum-sealed glass vials. Sample vials were capped and deoxygenated by bubbling nitrogen through them for 30 min to ensure complete air removal. The solution was irradiated by a 300 W (power density was measured as 200 $mW \cdot cm^{-2}$) xenon lamp and the lamp current was controlled at 15 A. The distance between the samples and the lamp was 15 cm and the fans were continuously used to cool the samples. An aliquot (500 μL) from the headspace was taken from the reaction mixture and analyzed by Gas chromatography. As same in photocatalytic oxidation as it was necessary to control the concentration of viologen units and naphthyl units to be constant, that was, $[V^{2+}] = [NaP] = 400$ μM.

3. Supplemental Characterizations

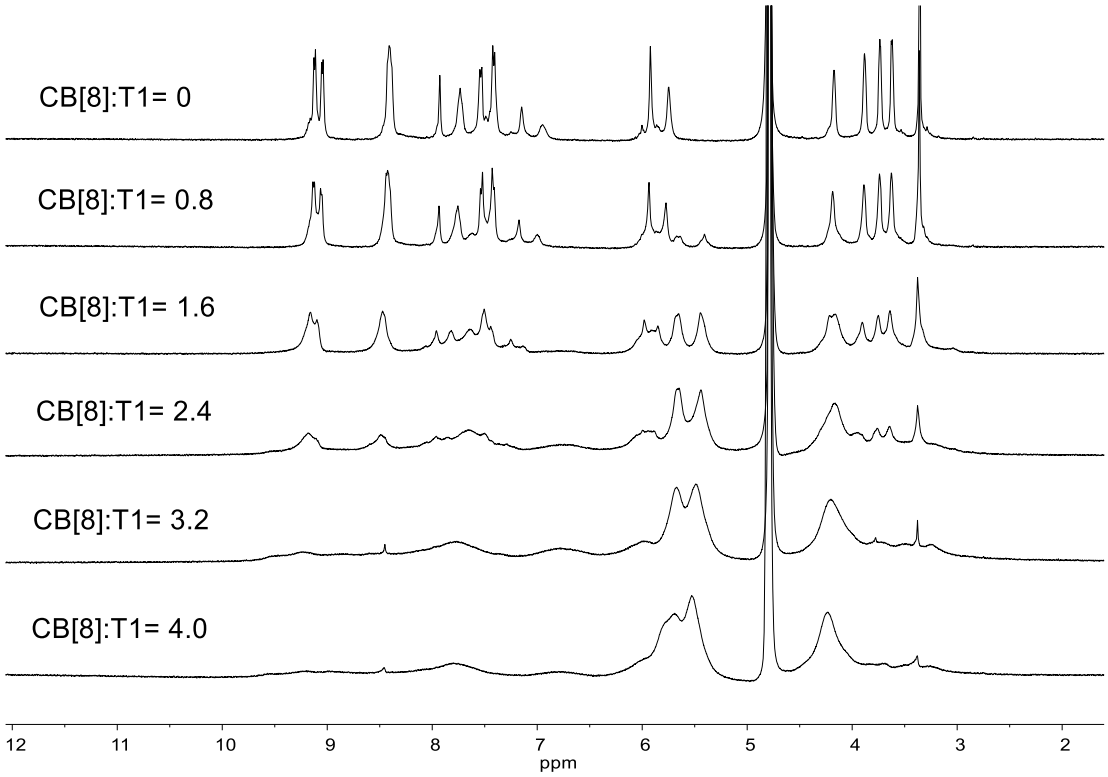


Fig. S1 ^{1}H NMR spectra of the solution of **T1** (1.25 mM) and CB[8] of 0, 0.8, 1.6, 2.4, 3.2 and 4.0 equivalents (from top to bottom) in D_2O.

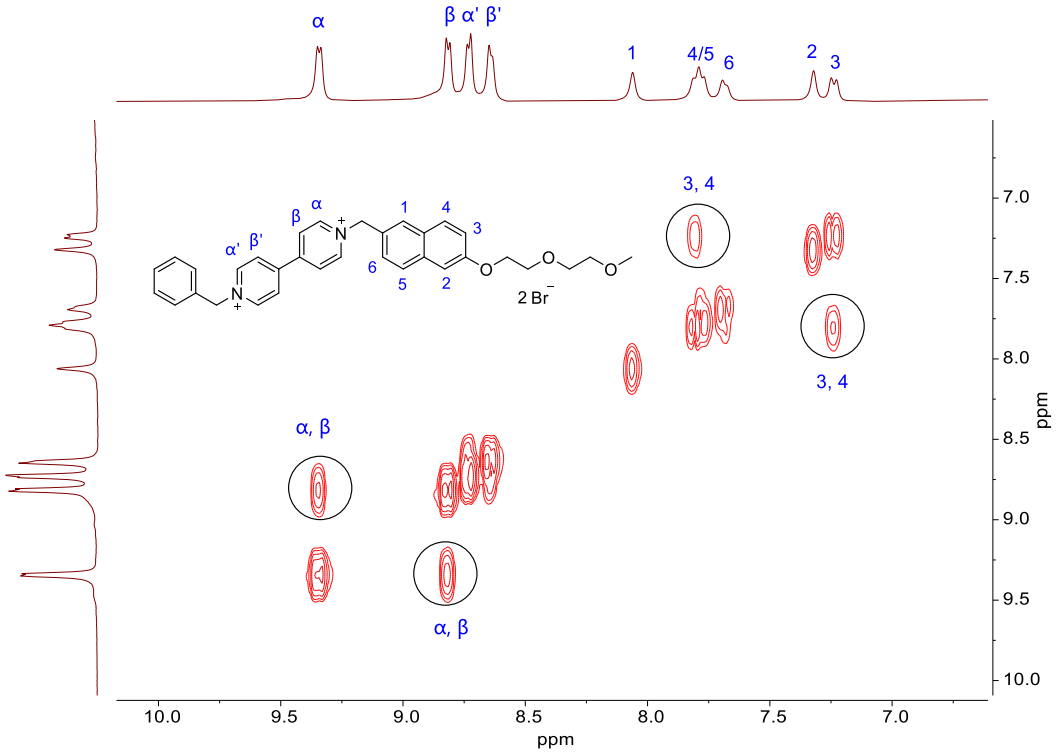


Fig. S2 ^{1}H COSY NMR spectrum (400 MHz) of **M1** (1.0 mM) in D_2O at 25 °C.

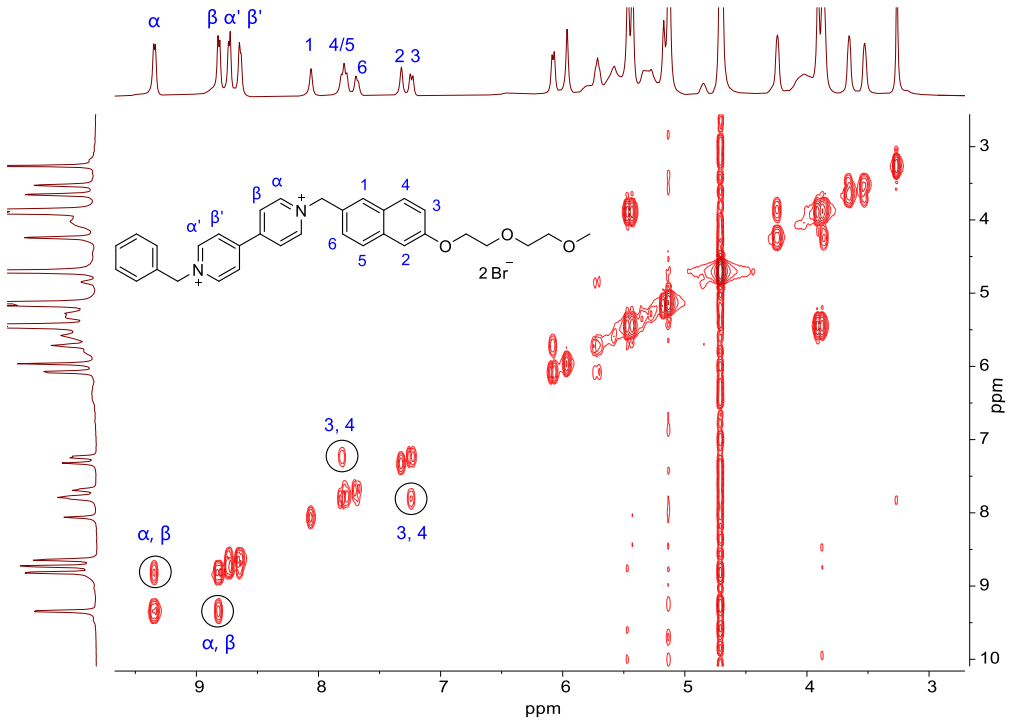


Fig. S3 ^{1}H COSY NMR spectrum (400 MHz) of the mixture of **M1** (1.0 mM) and CB[8] (1.0 mM) in D_2O at 25 °C.

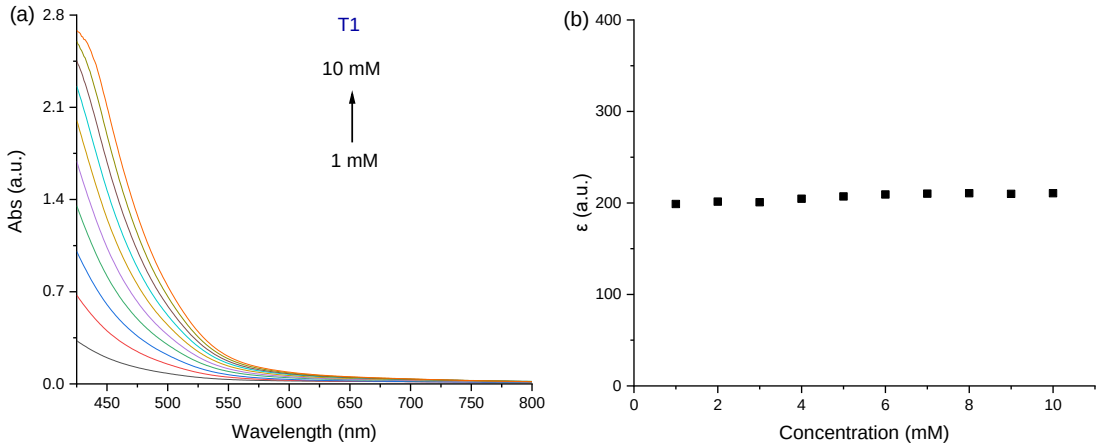


Fig. S4 UV/Vis absorption spectra of **T1** aqueous solutions at different concentrations of viologen units (from 1 mM to 10 mM). (b) Molar absorption coefficient (ε) at 450 nm at different concentrations of viologen units.

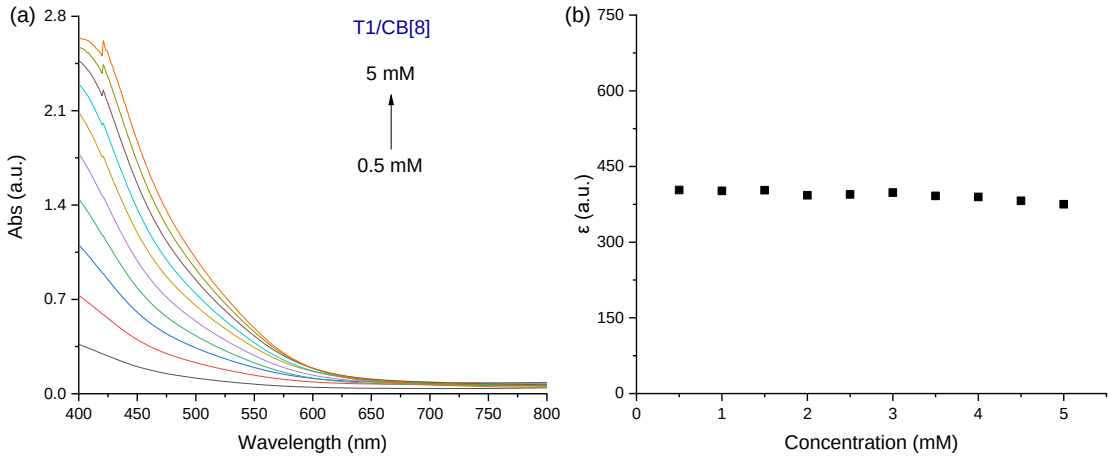


Fig. S5 UV/Vis absorption spectra of **T1/CB[8]** aqueous solutions at different concentrations of viologen units (from 0.5 mM to 5 mM). (b) Molar absorption coefficient (ε) at 450 nm at different concentrations of viologen units.

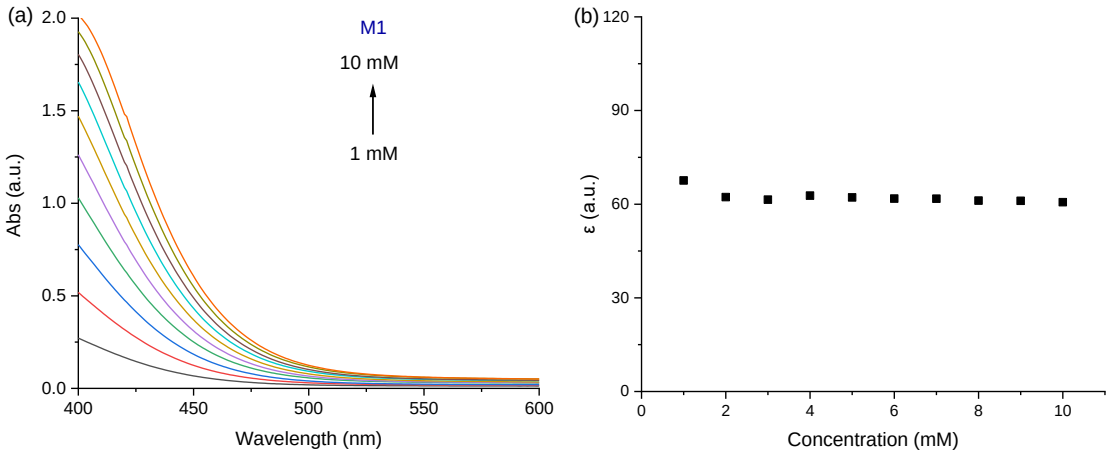


Fig. S6 UV/Vis absorption spectra of **M1** aqueous solutions at different concentrations of viologen units (from 1 mM to 10 mM). (b) Molar absorption coefficient (ε) at 450 nm at different concentrations of viologen units.

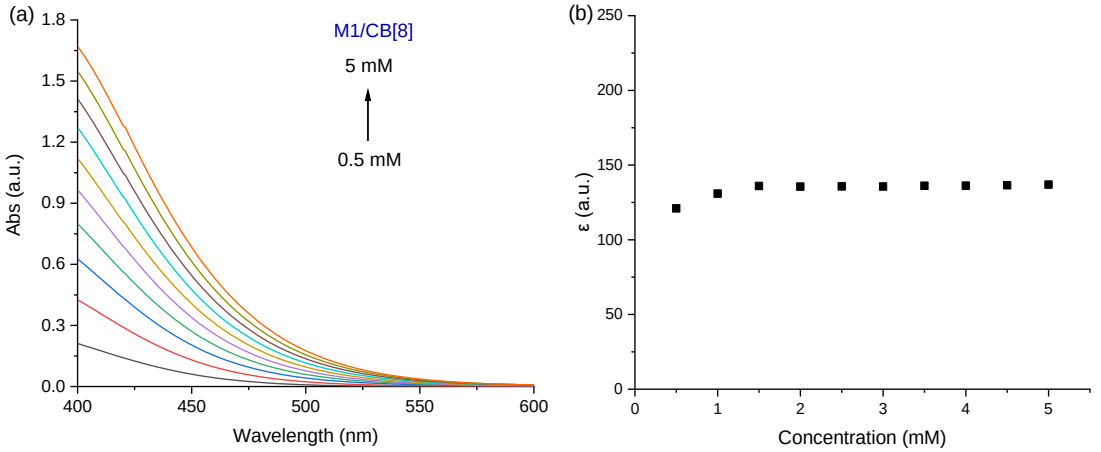


Fig. S7 UV/Vis absorption spectra of **M1/CB[8]** aqueous solutions at different concentrations of viologen units (from 0.5 mM to 5 mM). (b) Molar absorption coefficient (ε) at 450 nm at different concentrations of viologen units.

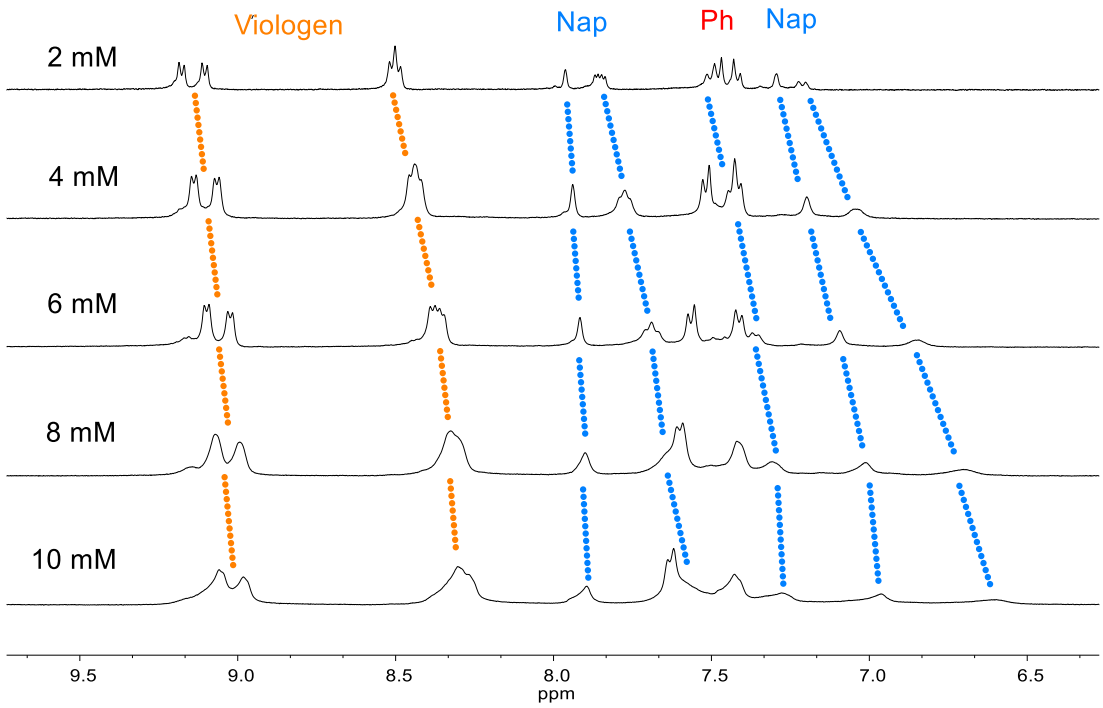


Fig. S8 ^{1}H NMR (400 MHz, D_2O, 298 K) spectra in solution of **T1** with different concentrations of viologen units (from 2 mM to 10 mM).

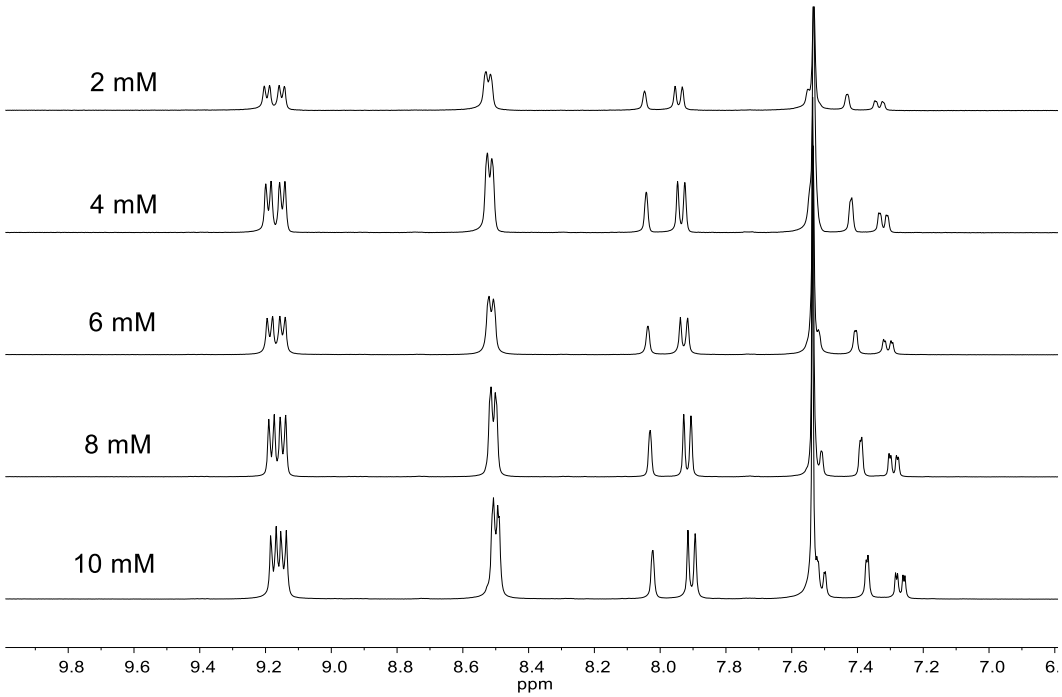


Fig. S9 ^{1}H NMR (400 MHz, D_2O, 298 K) spectra in solution of **M1** with different concentrations of viologen units (from 2 mM to 10 mM).

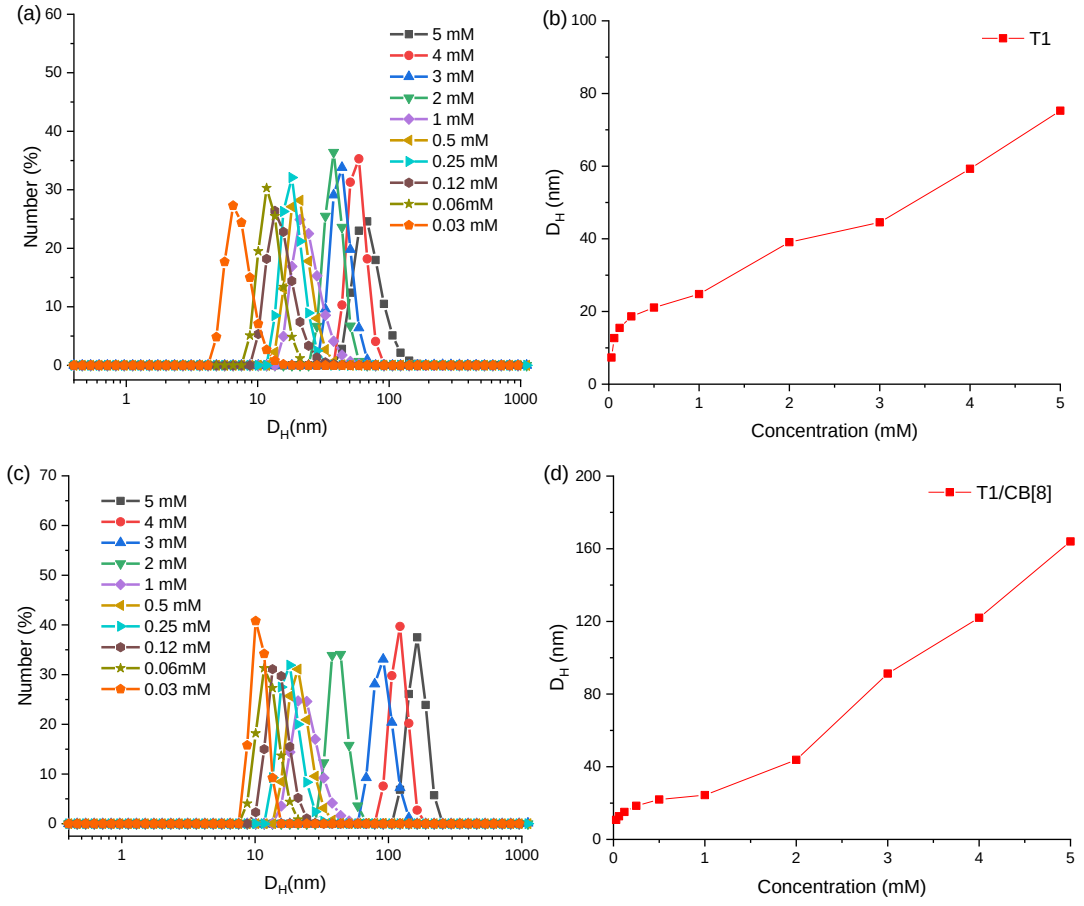


Fig. S10 Dynamic light scattering profile of the solution of **T1** in water and the solution of the 1:1 mixture of **T1** and CB[8] in H_2O at 25 °C.

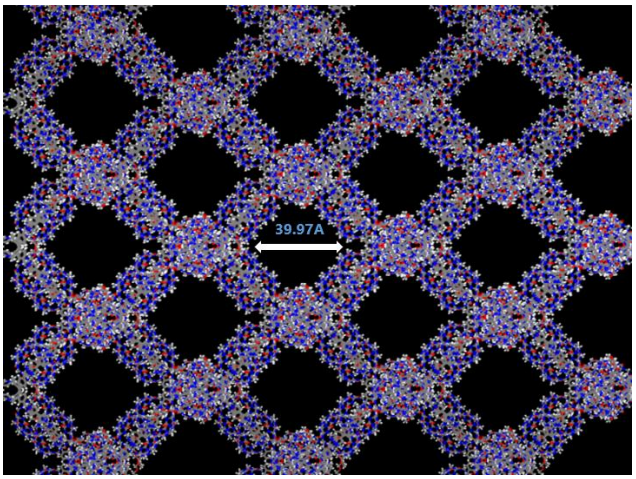


Fig. S11 Modelled porous structure of **CBSP** created by repeating the unit of the monomer molecule. The geometrical structures were optimized by using the Forcite Plus module and the Universal force field in Material Studio 5.5 from Accelrys.[7,8]

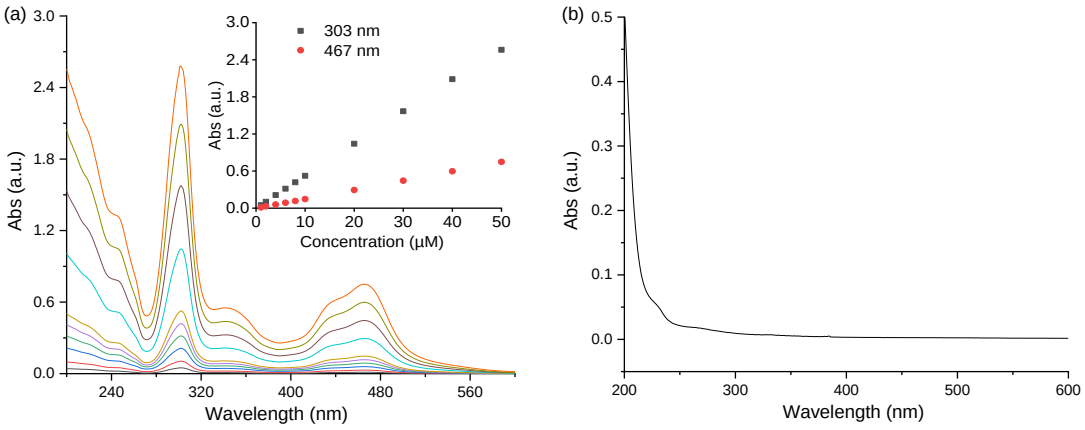


Fig. S12 a) UV-Vis spectrum of **$Na_4Ru(BDC)_3$** by gradually dilution (50 μM to 0.5 μM). Inset: absorbance at 303 and 467 nm at different concentrations of $Na_4Ru(BDC)_3$, b) and the possible leaching of **$Na_4Ru(BDC)_3$** from the **$Na_4Ru(BDC)_3$@CBSP** hybrid after dialysis for 24 h in water. The results indicated that the guest was absorbed by **CBSP** which inhibited the leaching of the guest into the outside water.

4. Characterization of important compounds

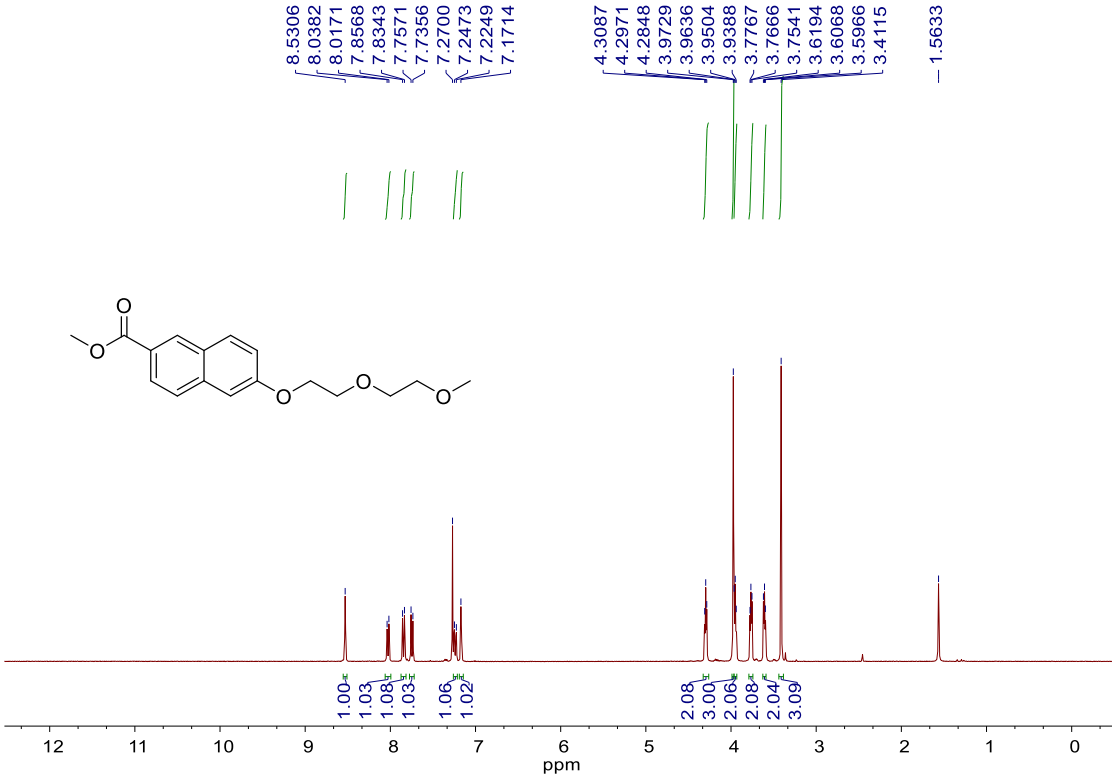


Fig. S13 ^{1}H NMR spectrum of **Compound 3** (400 MHz, $CDCl_3$, 298 K).

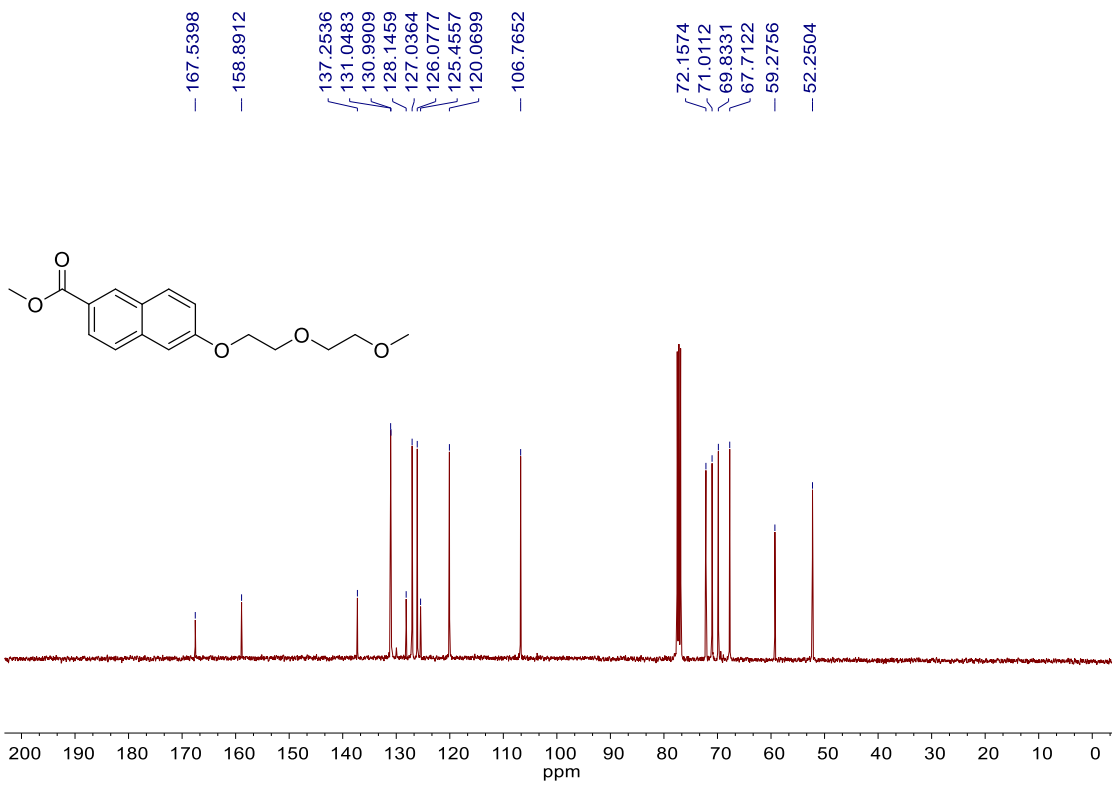


Fig. S14 ^{13}C NMR spectrum of **Compound 3** (100 MHz, $CDCl_3$, 298 K).

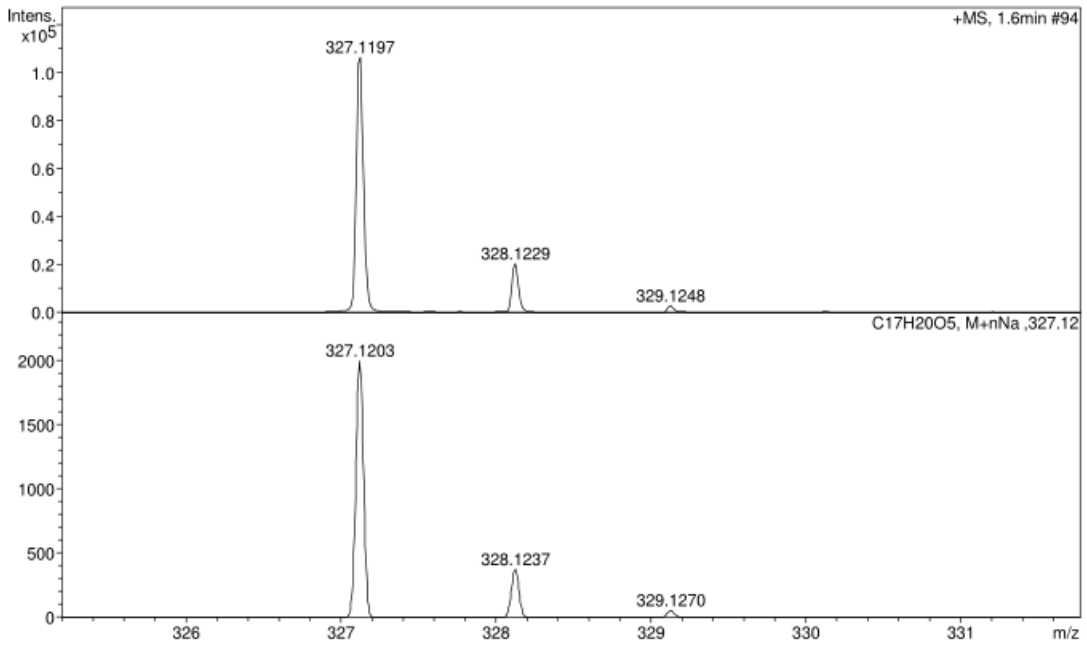


Fig. S15 HR-MS spectrum of **Compound 3**.

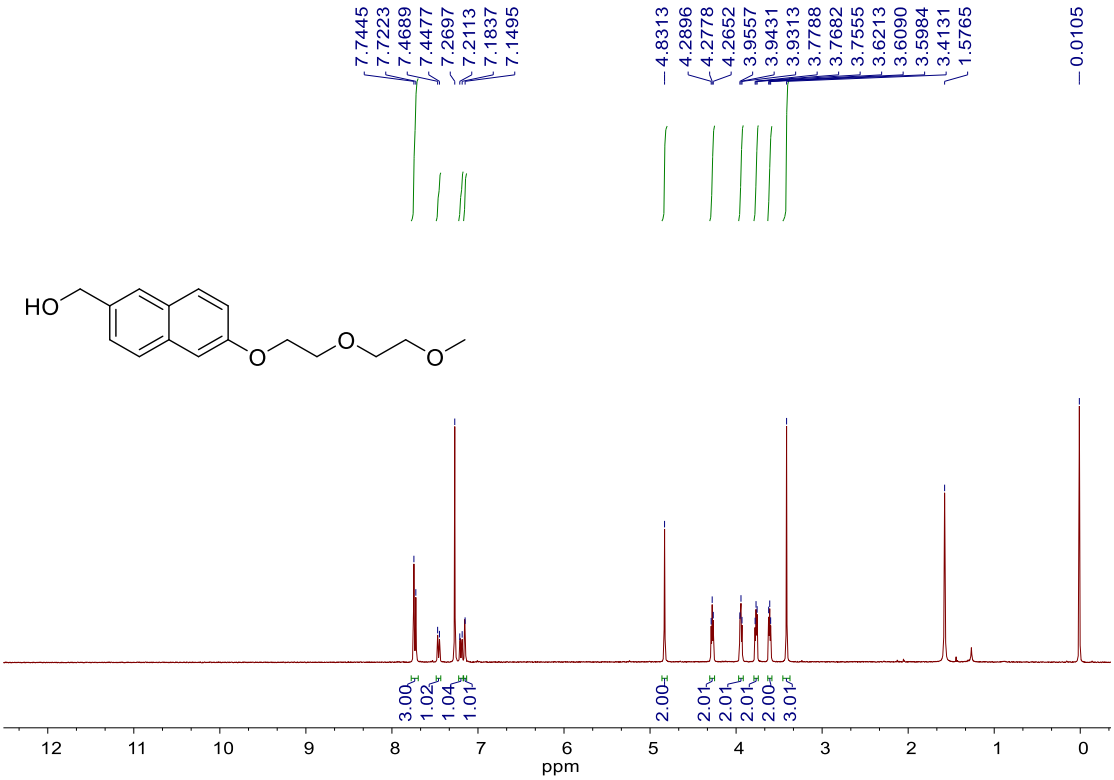


Fig. S16 ^{1}H NMR spectrum of **Compound 4** (400 MHz, $CDCl_3$, 298 K).

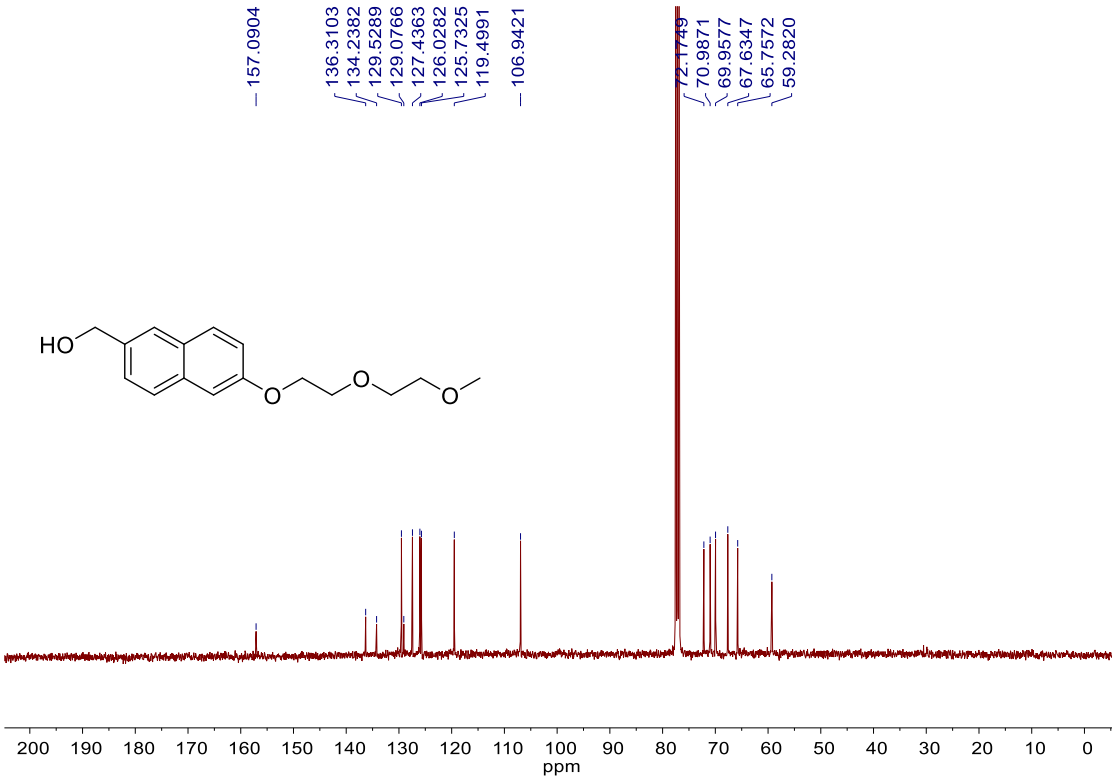


Fig. S17 ^{13}C NMR spectrum of **Compound 4** (100 MHz, $CDCl_3$, 298 K).

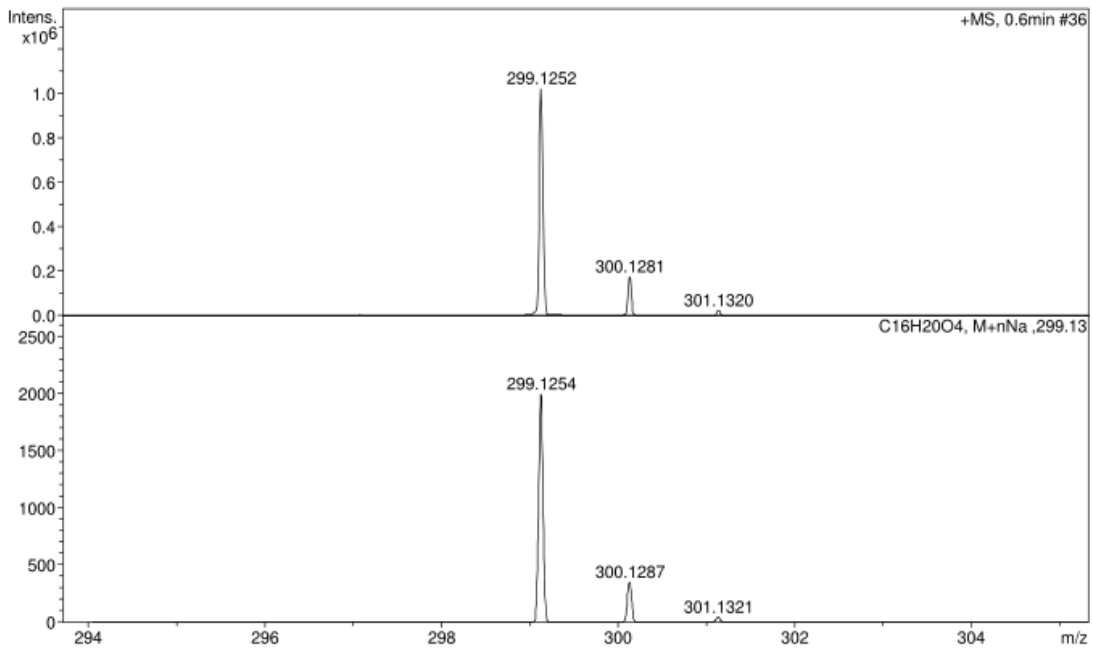


Fig. S18 HR-MS spectrum of **Compound 4**.

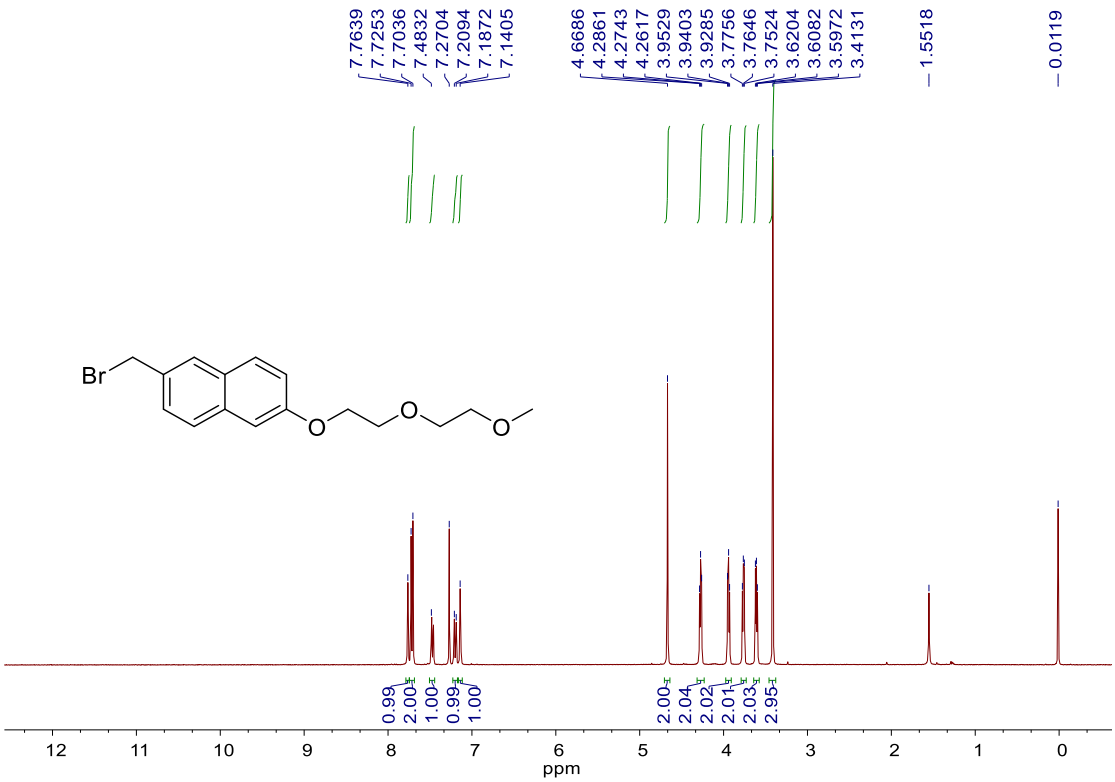


Fig. S19 ^{1}H NMR spectrum of **Compound 5** (400 MHz, $CDCl_3$, 298 K).

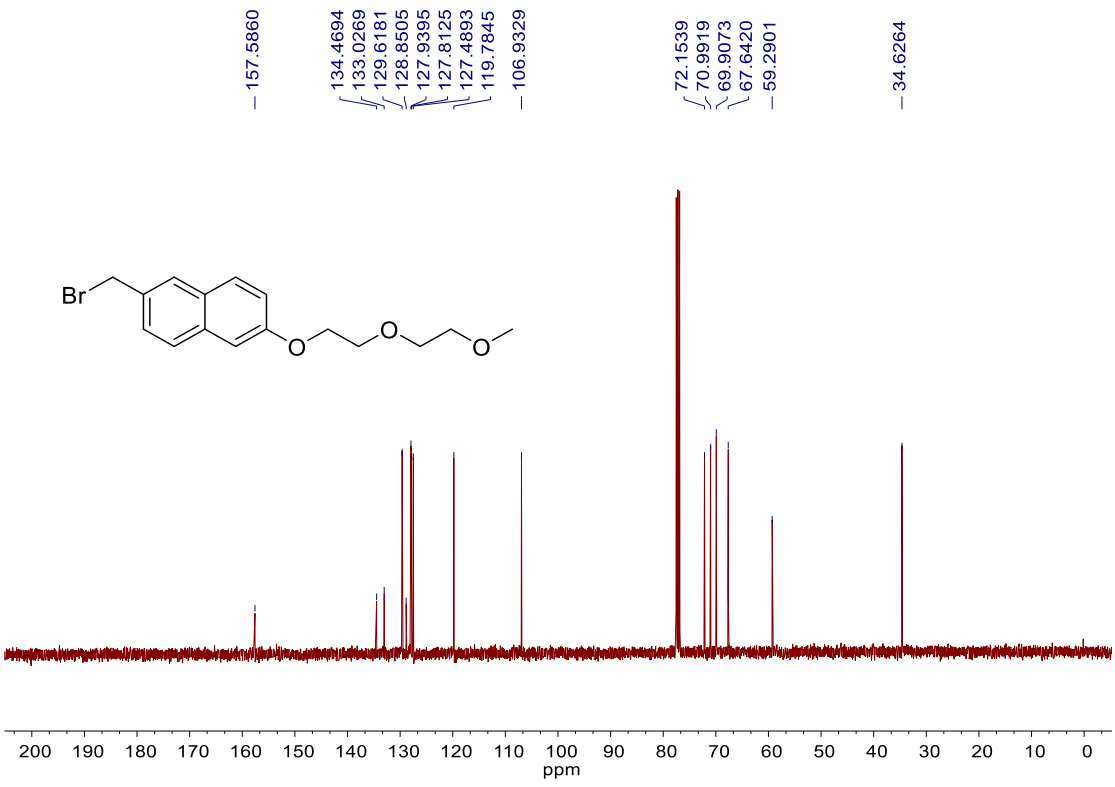


Fig. S20 ^{13}C NMR spectrum of **Compound 5** (100 MHz, $CDCl_3$, 298 K).

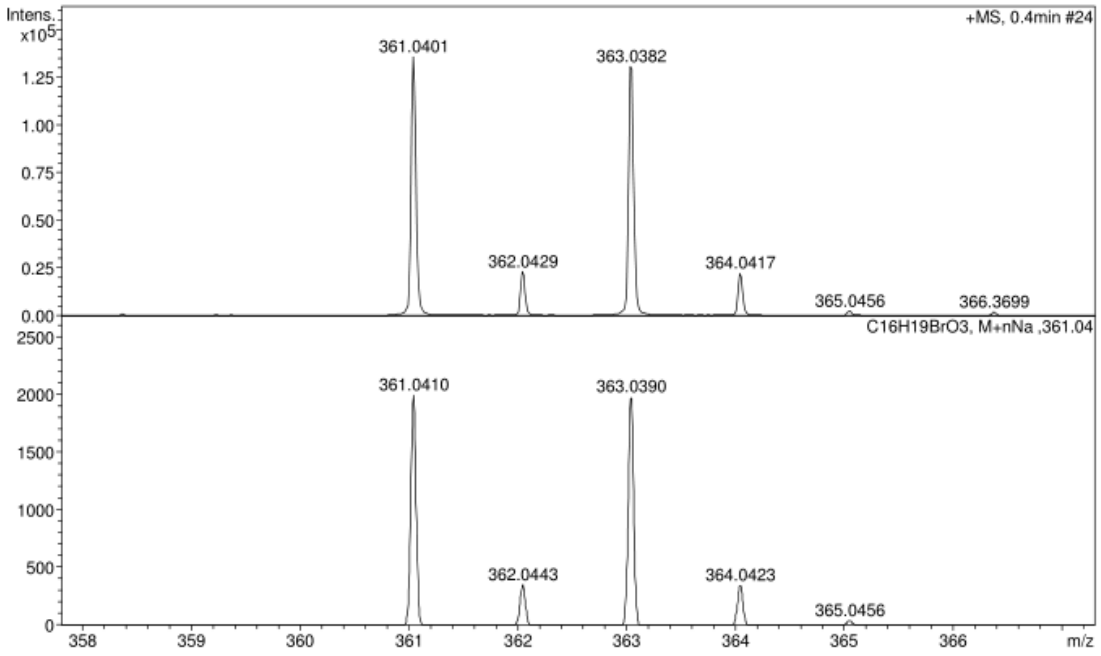


Fig. S21 HR-MS spectrum of **Compound 5**.

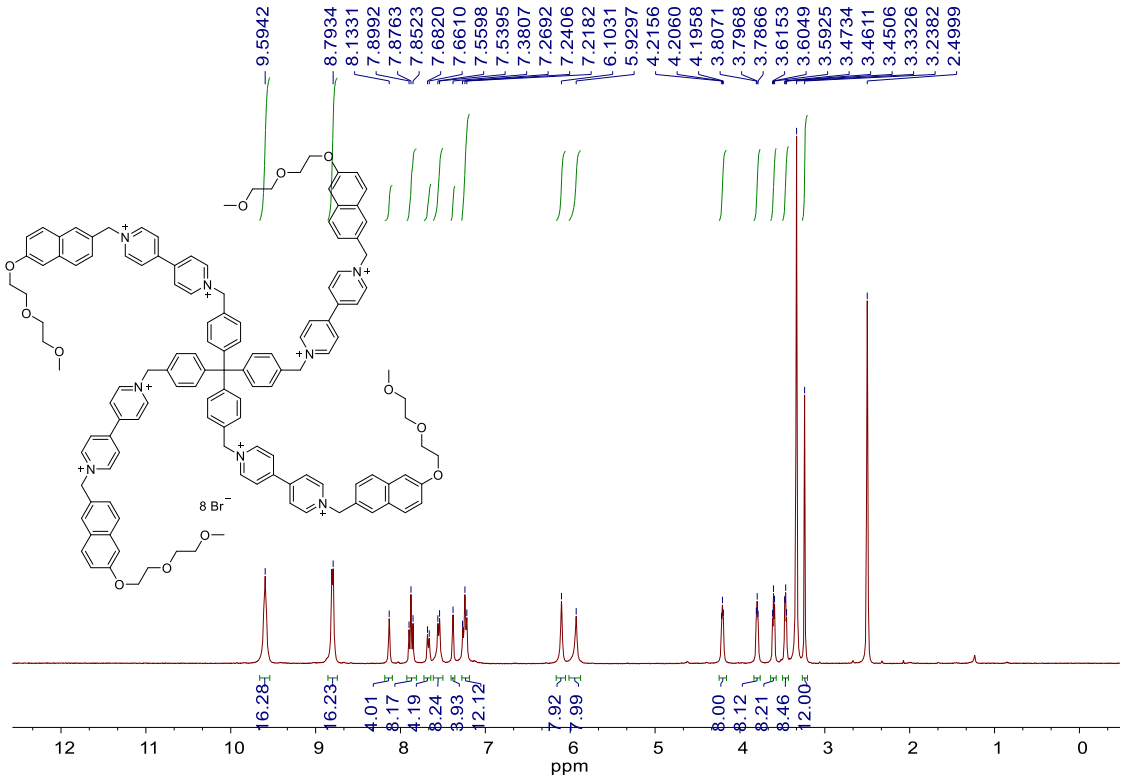


Fig. S22 ^{1}H NMR spectrum of **T1** (400 MHz, DMSO-d_6, 298 K).

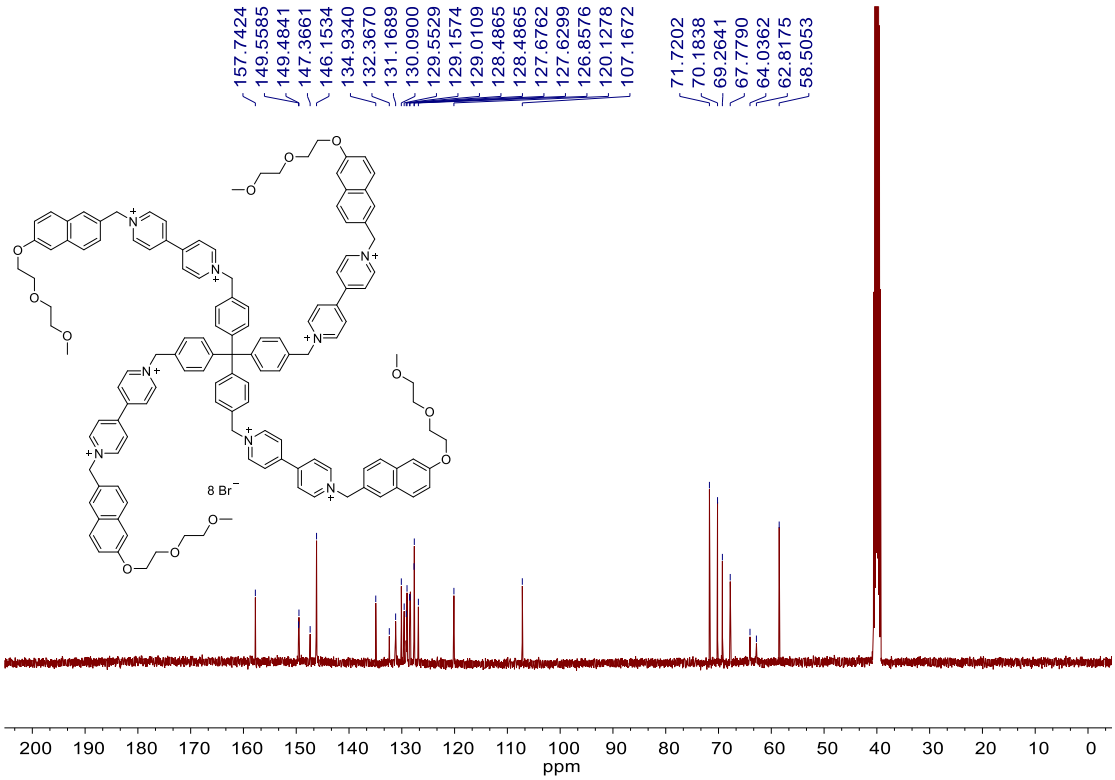


Fig. S23 ^{13}C NMR spectrum of **T1** (100 MHz, DMSO-d_6, 298 K).

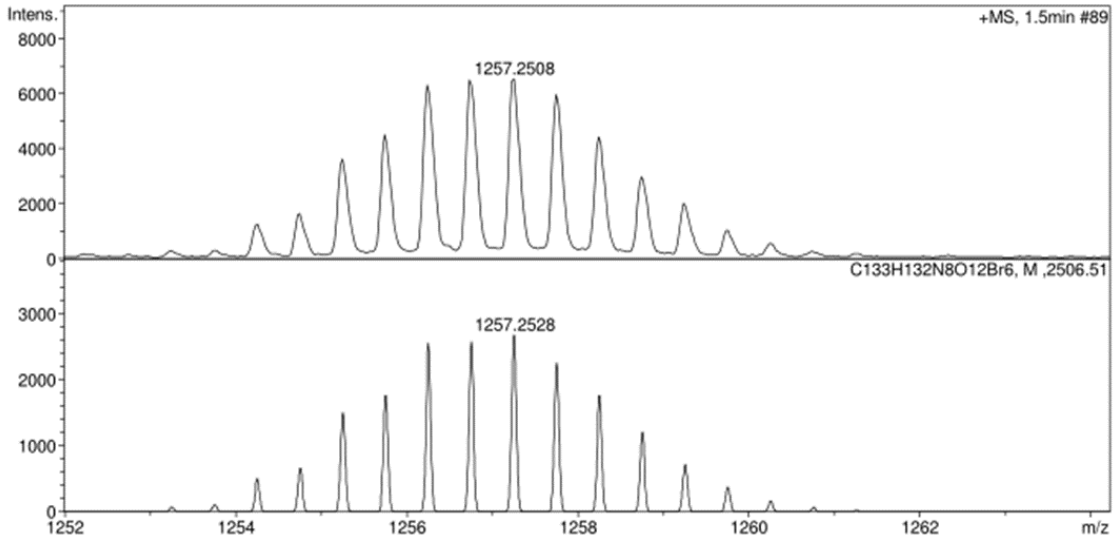


Fig. S24 HR-MS spectrum of **T1**.

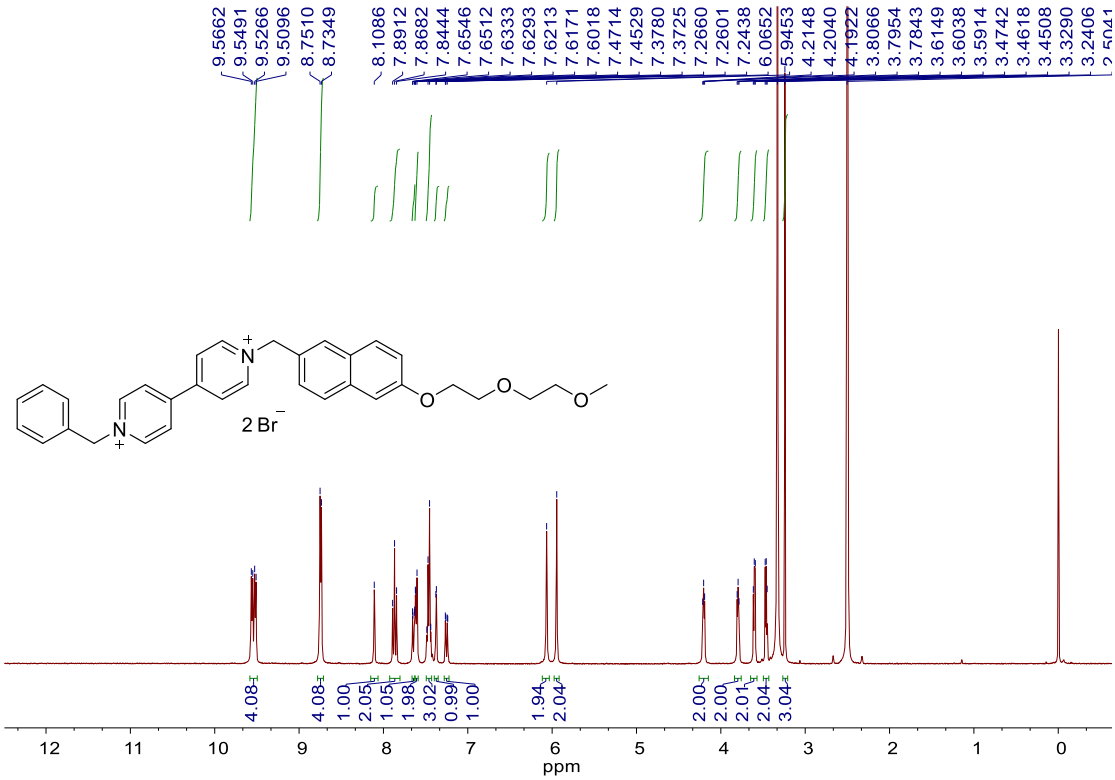


Fig. S25 ^{1}H NMR spectrum of **M1** (400 MHz, DMSO-d_6, 298 K).

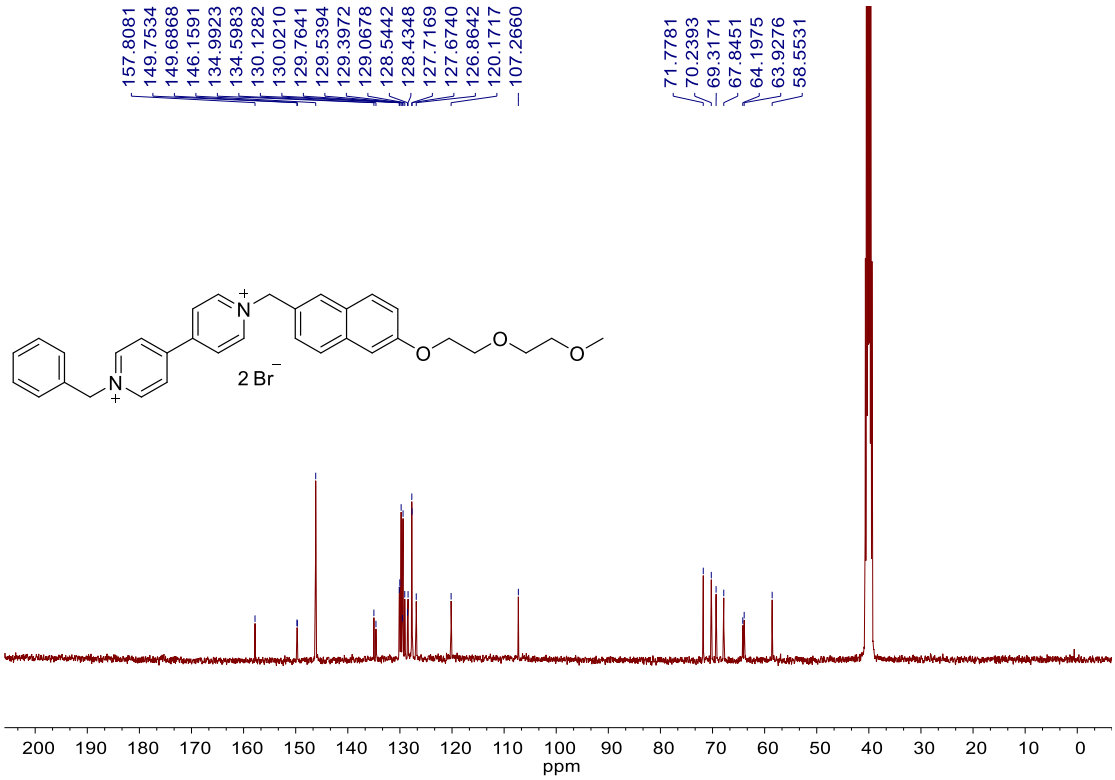


Fig. S26 ^{13}C NMR spectrum of **M1** (100 MHz, DMSO-d_6, 298 K).

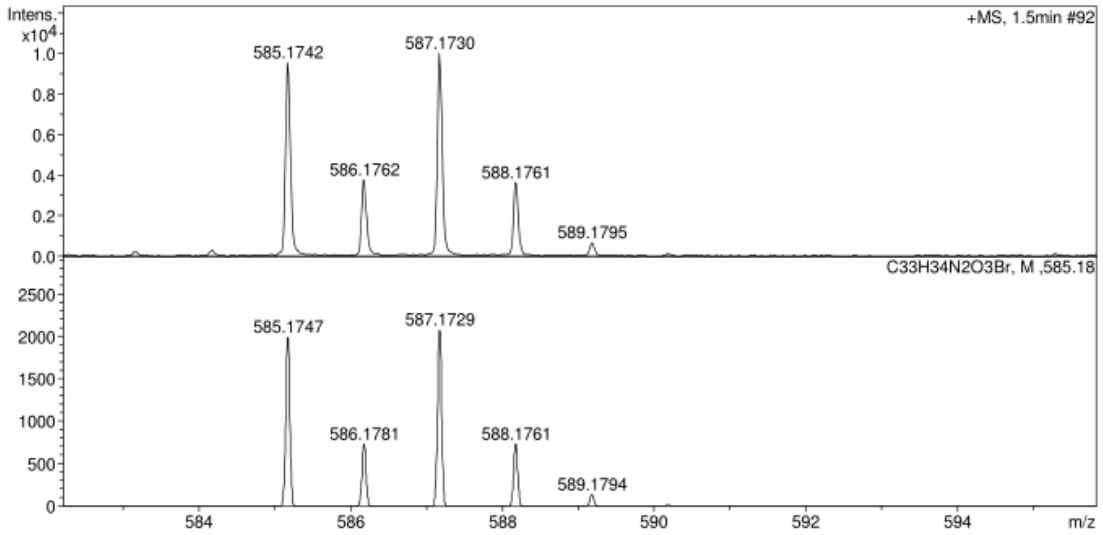


Fig. S27 HR-MS spectrum of **M1**.

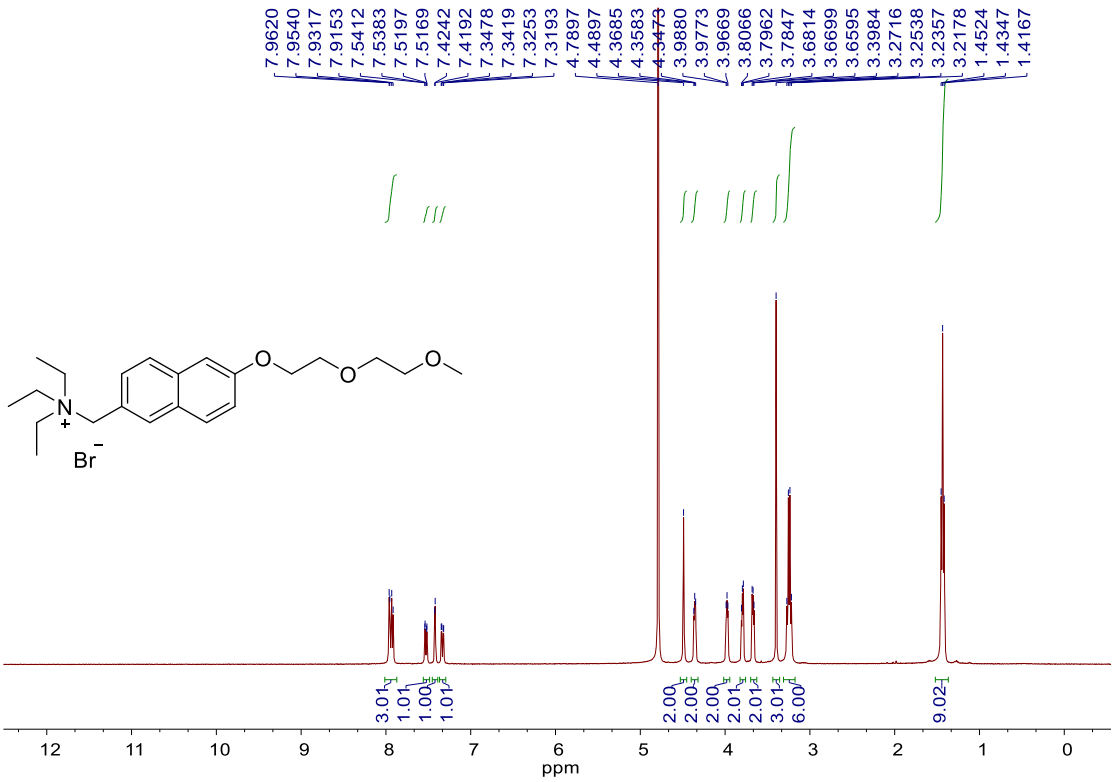


Fig. S28 ^{1}H NMR spectrum of **M2** (400 MHz, D_2O, 298 K).

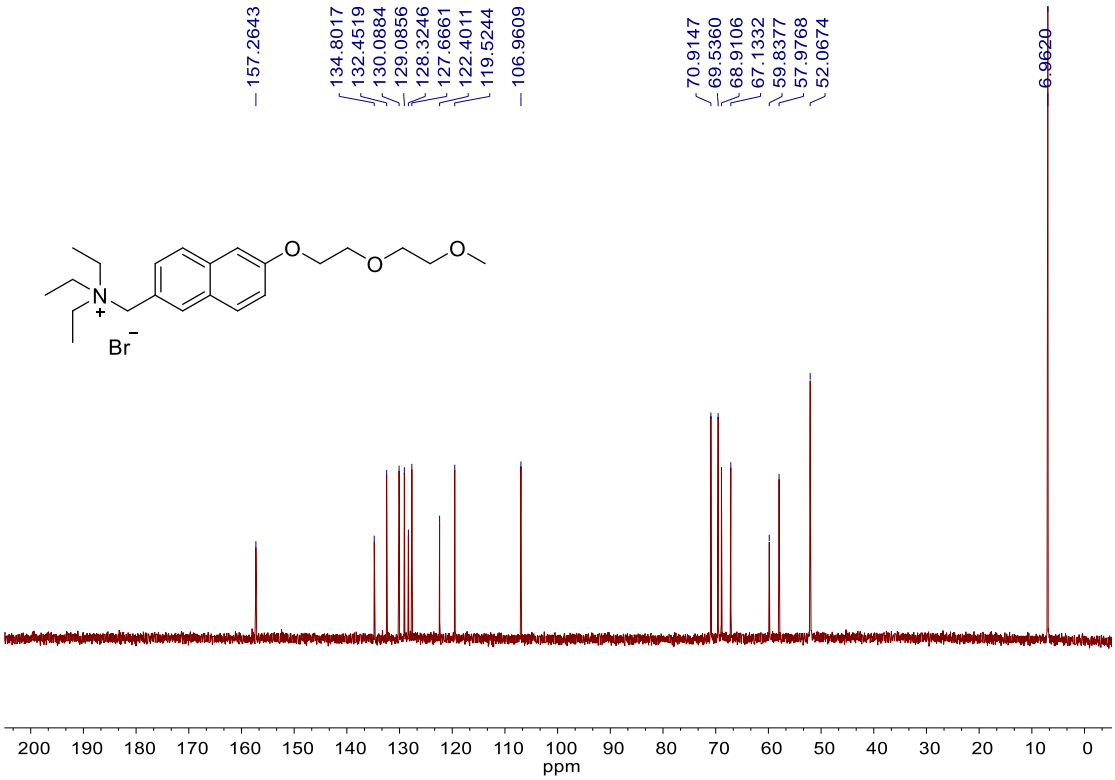


Fig. S29 ^{13}C NMR spectrum of **M2** (100 MHz, D_2O, 298 K).

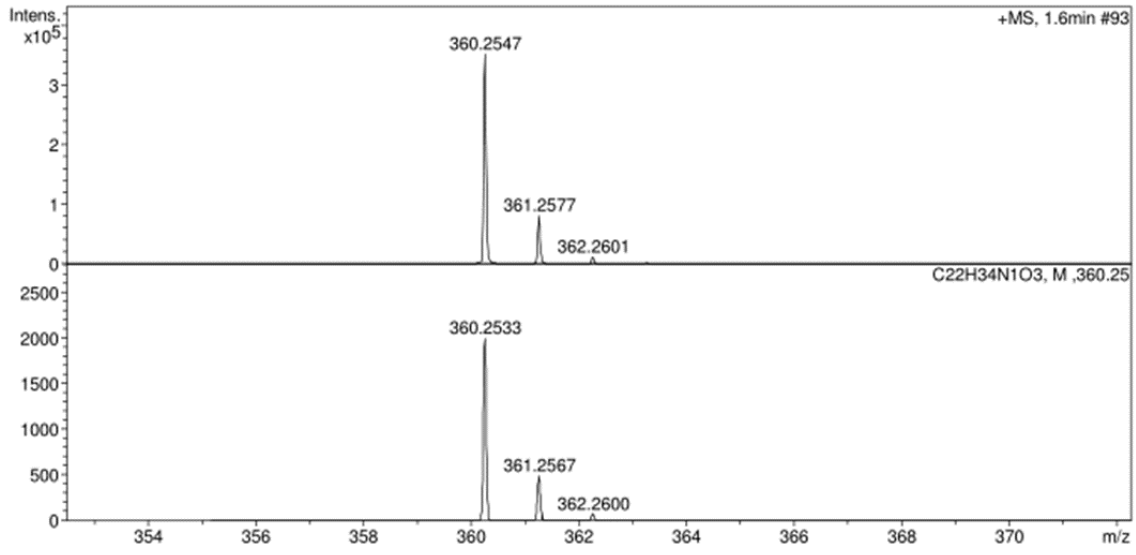


Fig. S30 HR-MS spectrum of **M2**.

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