Electronic Supplementary Information

An orthogonal photo-responsive tristable [3]rotaxane with non-destructive readout

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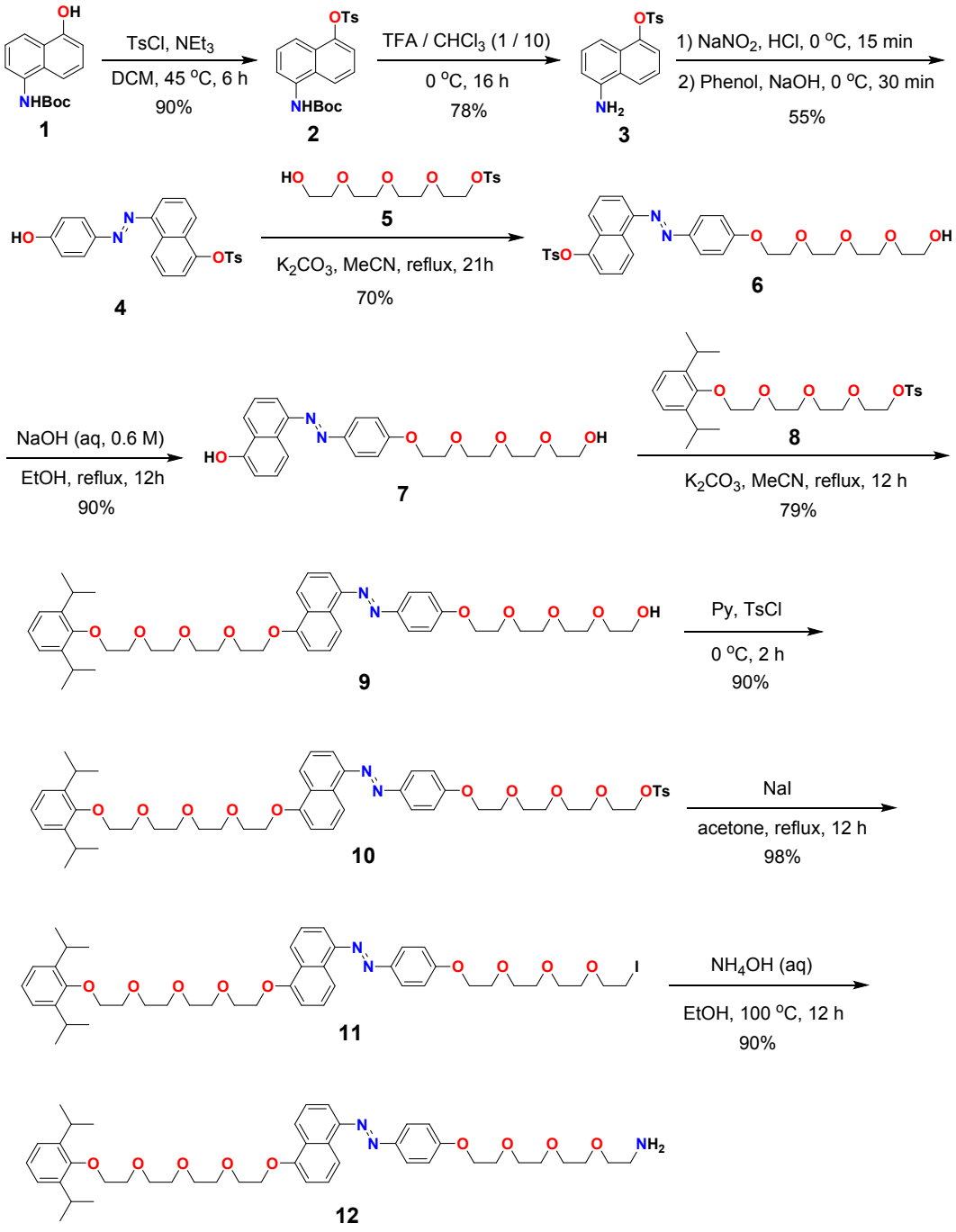
Section 1: General methods and materials

Materials: all the reagents were used as received from the commercial suppliers without further purification, and the intermediate compounds **1**[1], **5**[2], **8**[3], **13**[4] and **18**[4] were synthesized according to the reported procedures with slight modifications.

Nuclear Magnetic Resonance (NMR): the ^{1}H NMR and ^{13}C NMR spectra, as well as the 2D COSY and NOESY NMR spectra of the compounds were recorded on a Bruker AVANCE 600 spectrometer, and the chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard.

UV-Vis Spectroscopy: the UV-Vis absorption spectra were recorded on an Agilent Technologies Cary 60 UV-Vis spectrometer.

Section 2: Synthesis procedures



Scheme S1. Synthetic rout of intermediate compound **12**.

Compound 2. Compound **1**[1] (3.00 g, 12.6 mmol) and *p*-toluenesulfonyl chloride (2.42 g, 12.7 mmol) were dissolved in 30 mL of anhydrous CH_2Cl_2, to the solution of which NEt_3 (1.17 g, 11.5 mol) was added. The resulting mixture was then stirred at 45 °C for 4 hours until the total consumption of starting materials, and the reaction was

quenched by adding 100 mL of water. The mixture was then extracted by acetic acetate (50 mL × 2), and the organic phase was collected and dried by anhydrous Na_2SO_4. The desiccant and solvent were further removed by filtration and concentration, respectively, and the residue was purified by flash column chromatograph using a binary solvent of EtOAc / PE = 1 / 15 as the eluent. After dried under vacuum, compound **2** could be obtained as light purple powdery solid (4.53 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.82 (d, *J* = 5.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.36-7.32 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.93 (s, 1H), 2.37 (s, 3H), 1.53 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 153.47, 146.17, 145.55, 133.07, 132.61, 129.84, 128.40, 128.15, 127.91, 126.62, 125.14, 119.94, 119.87, 118.46, 118.11, 80.87, 28.36, 21.67. MS (ESI) *m/z*: $[M + H]^+$ 414.1. HRMS (ESI) Calcd. for $C_{22}H_{23}NNaO_5S^+$ $[M + Na]^+$ 436.1195, Found: 436.1199.

Compound 3. Compound **2** (11.2 g, 26.8 mmol) was dissolved in a binary solvent of CF_3COOH / $CHCl_3$ = 15 / 150 (v/v), the resulting mixture was then stirred at ice bath for 12 hours until the reaction was completed, and the solvent was removed by evaporation under reduced pressure. The remaining solid was re-dissolved in 50 mL of acetic acetate, and the insoluble residue was discarded by filtration. The filtrate was then washed by 30 mL of saturated $NaHCO_3$ (a.q.), and the collected organic phase was dried with anhydrous Na_2SO_4, which was further removed by filtration. The collected filtrate was concentrated by evaporation under reduced pressure, and the remaining crude product was recrystallized in a binary solvent of EtOAc / PE to give compound **3** as a light pink powdery solid (7.55 g, 78%). ^{1}H NMR (600 MHz, CD_3SOCD_3, 298 K) δ: 8.10 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 8.4 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 5.94 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, CD_3SOCD_3, 298 K) δ: 146.11, 145.73, 145.48, 132.65, 130.61, 128.58, 128.36, 128.32, 124.49, 123.16, 122.35, 118.18, 108.81, 108.78, 21.56. MS (ESI) *m/z*: $[M + H]^+$ 314.1. HRMS (ESI) Calcd. for $C_{17}H_{16}NO_3S^+$ $[M + H]^+$ 314.0851, Found:

314.0857.

Compound 4. Compound **3** (4.16 g, 13.3 mmol) was dissolved in 50 mL of HCl (a.q., 6 M) and 25 mL of water, to which another 25 mL of nitrous acid (574 mM) aqueous solution was added while cooling at ice bath. The mixture was then stirred for another 20 min, after which this reaction mixture was further added dropwise to an aqueous solution (100 mL) containing phenol (1.68 g, 17.8 mmol) and NaOH (12.0 g, 300 mmol). The obtained red solution was stirred at ice bath for 30 min, and then neutralized to pH = 7.0 by adding diluted hydrochloric acid. Deep red precipitates were generated and then collected by filtration, and further purified by flash column chromatograph eluted by a binary solvent of CH_2Cl_2 / PE = 3 /1. After dried under vacuum, compound **4** could be obtained as deep red powdery solid (3.06 g, 55%). ^{1}H NMR (600 MHz, CD_3SOCD_3, 298 K) δ: 10.46 (s, 1H), 8.79 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.67-7.61 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, CD_3SOCD_3, 298 K) δ: 161.92, 147.22, 146.47, 146.44, 145.49, 132.09, 132.04, 130.74, 128.75, 128.01, 127.46, 126.96, 125.90, 123.94, 122.97, 119.48, 116.55, 112.71, 21.61. MS (ESI) *m/z*: $[M + H]^+$ 419.1. HRMS (ESI) Calcd. for $C_{23}H_{19}N_2O_4S^+$ $[M + H]^+$ 419.1066, Found: 419.1073.

Compound 6. Compound **4** (0.900 g, 2.15 mmol) and compound **5**[2] (0.749 g, 2.15 mmol) were dissolved in 30 mL of anhydrous CH_3CN, to which K_2CO_3 (1.78 g, 12.9 mmol) was then added. The obtained mixture was heated with stirring at 90 °C for 10 hours until TLC suggested the total consumption of starting materials. Cooling down to room temperature, and then removing the solvent by evaporation under reduced pressure. The remaining oil residue was re-dissolved using 30 mL of EtOAc and the insoluble solid was discarded by filtration. After washing the filtrate with water (50 mL × 2), the collected organic phase was dried by anhydrous Na_2SO_4, which was then removed by filtration. After concentrating the filtrate by evaporation under reduced

pressure, the residue was subjected to flash column chromatograph for further purification by using a binary solvent of CH_2Cl_2 / MeOH = 200 / 1 as the eluent. Compound **6** could be isolated as orange-yellow oil (0.960 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 8.80 (d, *J* = 8.4 Hz, 1H), 8.00-7.96 (m, 3H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 4.22 (t, *J* = 4.2 Hz, 2H), 3.88 (t, *J* = 4.2 Hz, 2H), 3.75-3.65 (m, 10H), 3.60 (t, *J* = 4.2 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 161.53, 147.64, 147.51, 145.72, 145.53, 132.56, 132.44, 129.83, 128.49, 128.14, 126.50, 125.81, 125.15, 124.14, 122.83, 118.94, 114.94, 112.36, 72.60, 70.82, 70.54, 70.26, 69.57, 67.74, 61.71, 21.69. MS (ESI) *m/z*: $[M + H]^+$ 595.3. HRMS (ESI) Calcd. for $C_{31}H_{32}NO_8S^+$ $[M + H]^+$ 595.2114, Found: 595.2117.

Compound 7. Compound **6** (0.240 g, 0.407 mmol) was dissolved in 14 mL of ethanol, to which 7 mL of NaOH (a.q., 0.60 M) was added, and the mixture was refluxed with stirring for 12 hours. After TLC suggesting the reaction was completed, cooling down to room temperature and the solvent was removed by evaporation. The remaining oil residue was further dissolved in 40 mL of EtOAc, and the insoluble solid was discarded by filtration. The filtrate was washed by water (60 mL × 2), and the organic phase was dried with anhydrous Na_2SO_4. After removing the desiccant and solvent by filtration and evaporation, respectively, the crude product was subjected to flash column chromatograph for further purification by using a binary solvent of CH_2Cl_2 / MeOH = 200 / 1 as the eluent. After dried under vacuum, compound **7** could be obtained as orange-yellow oil (0.160 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 8.55 (s, 1H), 8.37-8.34 (m, 2H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 2H), 4.01 (t, *J* = 4.8 Hz, 2H), 3.75 (t, *J* = 4.8 Hz, 4H), 3.68-3.62 (m, 8H), 3.59-3.57 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 160.92, 152.60, 147.66, 147.60, 132.55, 126.99, 126.00, 124.97, 124.91, 124.57, 115.11, 114.71, 112.04, 109.00, 72.52, 70.60, 70.53, 70.43, 70.08, 69.53, 67.45, 61.60. MS (ESI) *m/z*: [M +

Na]$^+$ 463.2. HRMS (ESI) Calcd. for $C_{24}H_{29}N_2O_6^+$ [M + H]$^+$ 441.2026, Found: 441.2035.

Compound 9. Compound **7** (0.500 g, 1.14 mmol) and compound **8**[3] (0. 597 g, 1.14 mmol) were dissolved in 30 mL of anhydrous CH_3CN, to which K_2CO_3 (0.943 g, 6.84 mmol) was further added, and the resulting mixture was heated at 90 ^{o}C with stirring for 12 hours. When the reaction was completed as suggested by TLC, the reaction mixture was cooled down to room temperature, and the solvent was removed by evaporation under reduced pressure. The obtained oil residue was further dissolved in 50 mL of EtOAc, and the insoluble solid was discarded by filtration. The filtrate was then washed by water (50 mL × 2), and the collected organic phase was dried with anhydrous Na_2SO_4, which was then removed by filtration. After the filtrate was concentrated by evaporation under reduced pressure, the obtained crude product was further purified by flash column chromatograph using a combined eluent of CH_2Cl_2 / MeOH = 250 / 1. After drying under vacuum, compound **9** was obtained as orange-yellow oil (0.620 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 8.47 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 9.0 Hz, 2H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.54-7.49 (m, 2H), 7.09 (br, 3H), 7.07 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.36 (t, *J* = 4.2 Hz, 2H), 4.25 (d, *J* = 4.2 Hz, 2H), 4.04 (d, *J* = 4.8 Hz, 2H), 3.92-3.89 (m, 4H), 3.86-3.83 (m, 4H), 3.78-3.68 (m, 16), 3.62 (t, *J* = 4.2 Hz, 2H), 3.38 (septet, *J* = 7.2 Hz, 2H), 1.21 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 161.21, 154.54, 153.03, 147.79, 147.57, 141.82, 132.38, 126.76, 126.71, 125.03, 124.97, 124.92, 124.64, 124.00, 115.92, 114.90, 112.22, 105.36, 73.86, 72.66, 71.04, 71.00, 70.82, 70.79, 70.78, 70.61, 70.54, 70.51, 70.22, 69.80, 69.58, 67.93, 67.70, 61.65, 26.24, 24.16. MS (ESI) *m/z*: [M + H]$^+$ 777.4. HRMS (ESI) Calcd. for $C_{44}H_{61}N_2O_{10}^+$ [M + H]$^+$ 777.4326, Found: 777.4327.

Compound 10. Compound **9** (0.200 g, 0.257 mmol) and *p*-toluenesulfonyl chloride (0. 245 g, 1.28 mmol) were dissolved in 1.0 mL of anhydrous pyridine and then stirred for 2 hours in an ice bath until the total consumption of starting materials. The

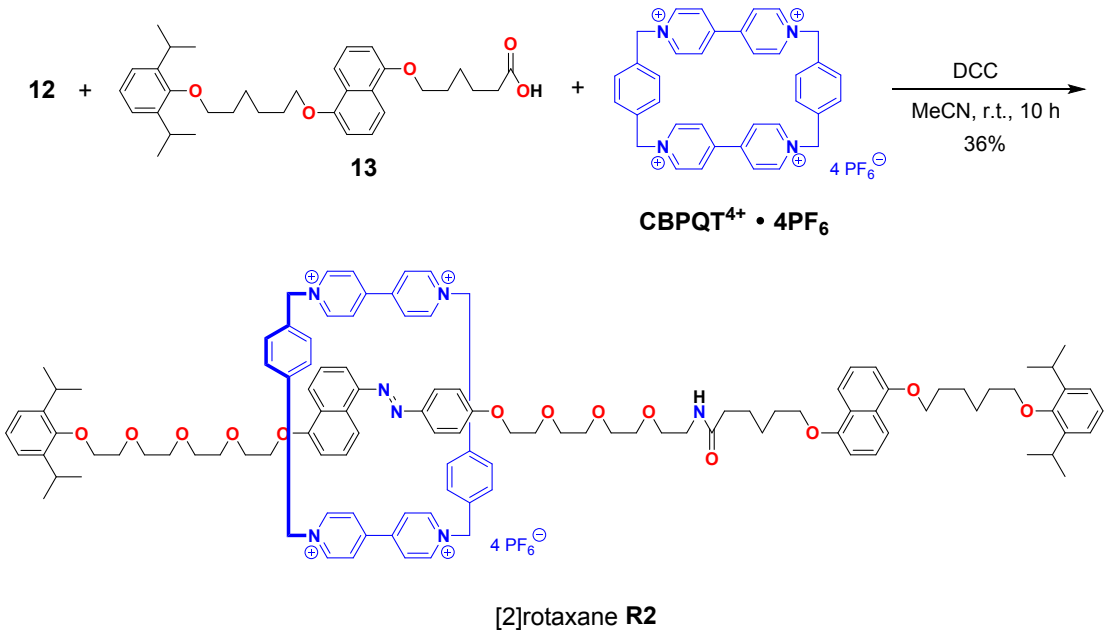
reaction was then quenched by adding 10 mL of water, and aqueous phase was extracted by EtOAc (10 mL × 2), and the organic phase was combined and washed continuously by water (10 mL) and brine (10 mL), respectively, and then dried by anhydrous Na_2SO_4. The desiccant was further removed by filtration, and the filtrate was then concentrated by evaporation under reduced pressure. The remaining residue was purified by flash column chromatograph using a binary solvent of EtOAc / PE = 1 / 2 as the eluent. After drying under vacuum, compound **10** was obtained as orange-yellow oil (0.215 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 8.47 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 9.0 Hz, 2H), 7.80-7.78 (m, 3H), 7.54-7.49 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.09 (br, 3H), 7.06 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 7.8 Hz, 2H), 4.36 (t, *J* = 4.8 Hz, 2H), 4.24 (t, *J* = 4.8 Hz, 2H), 4.16 (t, *J* = 4.8 Hz, 2H), 4.04 (t, *J* = 4.8 Hz, 2H), 4.05 (t, *J* = 4.8 Hz, 4H), 3.91 (t, *J* = 4.8 Hz, 4H), 3.78-3.73(m, 8H), 3.71-3.66 (m, 4H), 3.63-3.59 (m,4H), 3.38 (septet, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.21 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 161.38, 154.59, 153.10, 147.75, 147.54, 144.82, 141.83, 133.02, 132.44, 129.88, 127.95, 126.81, 125.05, 124.93, 124.69, 124.03, 115.91, 114.95, 112.24, 105.41, 73.91, 71.05, 71.02, 70.84, 70.80, 70.72, 70.65, 70.57, 70.54, 69.80, 69.61, 69.36, 68.67, 67.97, 67.80, 26.26, 24.21, 21.62. MS (ESI) *m/z*: $[M + H]^+$ 931.4. HRMS (ESI) Calcd. for $C_{51}H_{67}N_2O_{12}S^+$ $[M + H]^+$ 931.4415, Found: 931.4412.

Compound 11. Compound **10** (0.200 g, 0.215 mmol) was dissolved in 10 mL of acetone, to the solution of which NaI (0.322 g, 2.15 mmol) was then added, and the resulting mixture was heated at 90 °C with stirring for 12 hours until TLC suggested the completion of the reaction. Cooling down and removing the solvent by evaporation under reduced pressure. The remaining oil residue was then re-dissolved in 60 mL of EtOAc and the insoluble solid was discarded via filtration. The collected filtrate was washed by water (60 mL × 2) and then dried with anhydrous Na_2SO_4, which further removed by filtration. After the filtrate was concentrated under reduced pressure, compound **11** could be obtained as orange-yellow oil (0.186 g, 98%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 8.51 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H),

8.04 (d, J = 9.0 Hz, 2H), 7.83 (d, J = 7.8 Hz, 1H), 7.55-7.49 (m, 2H), 7.09 (br, 3H), 7.05 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 7.2 Hz, 1H), 4.31 (t, J = 4.8 Hz, 2H), 4.18 (t, J = 4.8 Hz, 2H), 4.00 (t, J = 4.8 Hz, 2H), 3.91 (t, J = 4.8 Hz, 2H), 3.88-3.80 (m, 8H), 3.77-3.70 (m, 10H), 3.69-3.60 (m, 6H), 3.40 (septet, J = 7.2 Hz, 2H), 3.23 (t, J = 6.6 Hz, 2H), 1.23 (d, J = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 161.34, 154.57, 153.08, 147.75, 147.55, 141.81, 132.43, 126.79, 126.75, 125.04, 124.93, 124.67, 124.02, 115.93, 114.94, 112.25, 105.37, 73.90, 71.95, 71.06, 71.03, 70.90, 70.86, 70.81, 70.72, 70.65, 70.57, 70.22, 69.80, 69.64, 67.95, 67.78, 26.25, 24.22, 3.15. MS (ESI) *m/z*: $[M + H]^+$ 887.3. HRMS (ESI) Calcd. for $C_{44}H_{60}N_2O_9^+$ $[M + H]^+$ 887.3343, Found: 887.3340.

Compound 12. Compound **11** (0.443 g, 0.489 mmol), ethanol (20 mL) and ammonia aqueous (10 mL) were mixed in a Schlenk tube and sealed, and then heated to 100 °C for 12 hours with stirring. After the reaction was completed as suggested by TLC, the solvent was removed by evaporation under reduced pressure. The remaining oil crude was further dissolved in 20 mL of CH_2Cl_2 while discarding the insoluble residue by filtration. The collected filate was then washed by water (20 mL × 2) and the organic phase was dried with anhydrous Na_2SO_4. After removing the desiccant and solvent by filtration and evaporation under reduced pressure, respectively, compound **12** was obtained as orange-yellow oil (0.348 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 8.47 (d, J = 8.4 Hz, 1H), 8.41 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 7.2 Hz, 1H), 7.54-7.49 (m, 2H), 7.09-7.05 (m, 5H), 6.91 (d, J = 7.8 Hz, 1H), 4.36 (t, J = 4.2 Hz, 2H), 4.25 (t, J = 4.2 Hz, 2H), 4.04 (t, J = 4.8 Hz, 2H), 3.93-3.89 (m, 4H), 3.85-3.82 (m, 4H), 3.78-3.74 (m, 8H), 3.72-3.70 (m, 2H), 3.69-3.66 (m, 2H), 3.65-3.63 (m, 2H), 3.53 (t, J = 4.8 Hz, 2H), 3.38 (septet, J = 7.2 Hz, 2H), 2.89 (t, J = 4.8 Hz, 2H), 1.21 (d, J = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 161.30, 154.56, 153.07, 147.76, 147.55, 141.81, 132.41, 126.79, 126.73, 125.03, 124.91, 124.65, 124.01, 115.91, 114.92, 112.23, 105.36, 73.88, 72.83, 71.04, 71.02, 70.80, 70.59, 70.56, 70.22, 69.79, 69.61, 67.94, 67.78, 41.56, 26.24, 24.18. MS (ESI) *m/z*: $[M + H]^+$ 776.5. HRMS (ESI) Calcd. for $C_{44}H_{62}N_3O_9^+$ $[M + H]^+$ 776.4486, Found:

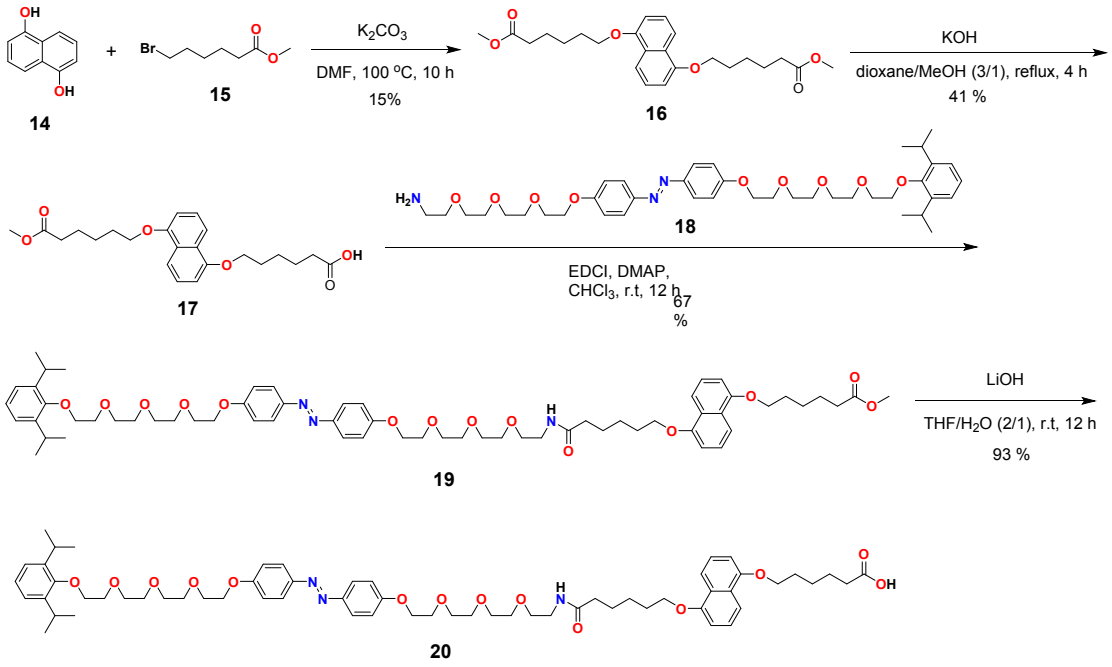
776.4484.



Scheme S2. Synthetic rout of [2]rotaxane **R2**.

[2]rotaxane R2. Compound **12** (0.100 g, 0.129 mmol) and **CBPQT^{4+}•4PF$_6^-$** (0.222 g, 0.202 mmol) were dissolved in 1.5 mL anhydrous CH_3CN, and the obtained mixture was stirred for 15 min at room temperature. Then, compound **13**[4] (0.0690 g, 0.129 mmol) and DCC (0.0443 g, 0.215 mmol) were added, and the resulting reaction mixture was further stirred for another 10 hours at room temperature. After removing the solvent by evaporation under reduced pressure, the remaining residue was subjected to flash column chromatograph for further purification by using the eluent of CH_3OH / NH_4Cl_{aq} (1 M) / CH_3NO_2 = 7 / 2 / 1. Red-brown solid was isolated and dissolved in 30 mL of water, the saturated NH_4PF_6 aqueous solution was further added dropwise to generate red-brown precipitates, which was collected by filtration and washed by another 30 mL of water. After dried under vacuum, [2]rotaxane **R2** was obtained as a red-brown solid (0.112 g, 36%). ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ: 8.75 (d, *J* = 6.0 Hz, 8H), 7.92 (s, 8H), 7.42 (br, 8H), 7.18-7.06 (m, 8H), 7.05-6.45 (m, 9H), 5.74 (s, 8H), 4.42-4.38 (m, 2H), 4.26-4.22 (m, 2H), 4.18-4.13 (m, 4H), 4.08 (t, *J* = 7.2 Hz, 2H), 3.97-3.91 (m, 4H), 3.87-3.74 (m, 10H), 3.72-3.68 (m, 6H),

3.67-3.63 (m, 2H), 3.62-3.59 (m, 2H), 3.42-3.29 (m, 6H), 2.28 (br, 2H), 2.05 (br, 2H), 1.80-1.66 (m, 6H), 1.64-1.56 (m, 2H), 1.23 (d, J = 7.2 Hz, 12H), 1.18 (d, J = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, CD_3CN, 298 K) δ: 173.33, 161.72, 153.45, 153.03, 146.97, 146.94, 145.31, 144.36, 141.86, 141.82, 136.71, 131.18, 126.55, 125.58, 124.79, 124.57, 124.07, 124.03, 114.97, 112.59, 105.25, 74.73, 73.86, 70.86, 70.58, 70.53, 70.42, 70.32, 70.24, 70.06, 69.99, 69.94, 69.52, 69.28, 69.23, 69.18, 68.40, 68.29, 68.22, 68.18, 68.14, 64.91, 64.87, 64.83, 39.03, 35.75, 30.26, 29.16, 28.92, 26.24, 26.22, 25.97, 25.95, 25.79, 25.70, 25.31, 23.43. HRMS (ESI) Calcd. for $C_{114}H_{137}F_{12}N_7O_{13}P_2^{2+}$ [M-2PF_4^-]$^{2+}$ 1050.9779, Found:1050.9798.



Scheme S3. Synthetic rout of intermediate compound **20**.

Compound 16. Compounds **14** (2.00 g, 12.5 mmol) and **15** (6.30 g, 30.0 mmol) were first dissolved in 100 mL of anhydrous DMF, and then K_2CO_3 (10.3 g, 75.0 mmol) was added. The resulting mixture was heated at 100 °C for 10 hours until the reaction was completed. After cooling down to room temperature, the solvent was removed by evaporation under reduced pressure, and the obtained solid was re-dissolved in 20 mL of CH_2Cl_2 while the insoluble residue was discarded by filtration. The collected filtrate was then washed by water (20 mL × 2) and the organic phase was dried using

anhydrous Na_2SO_4 as desiccant, which was then removed by filtration. After concentrating the filtrate by evaporation under reduced pressure, the residue was then purified by flash column chromatograph using a binary solvent of CH_2Cl_2 / PE = 1 / 2 as the eluent. Compound **16** was finally isolated as white solid (0.620 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.85 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 4.09 (t, *J* = 6.6 Hz, 4H), 3.67 (s, 6H), 2.37 (t, *J* = 7.2 Hz, 4H), 1.92 (quintet, *J* = 6.6 Hz, 4H), 1.75 (quintet, *J* = 7.2 Hz, 4H), 1.62-1.56 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 174.02, 154.58, 126.78, 125.09, 114.12, 105.28, 67.77, 51.47, 34.01, 29.01, 25.89, 24.77. MS (ESI) *m/z*: $[M + H]^+$ 417.2. HRMS (ESI) Calcd. for $C_{24}H_{33}O_6^+$ $[M + H]^+$ 417.2277, Found: 417.2278.

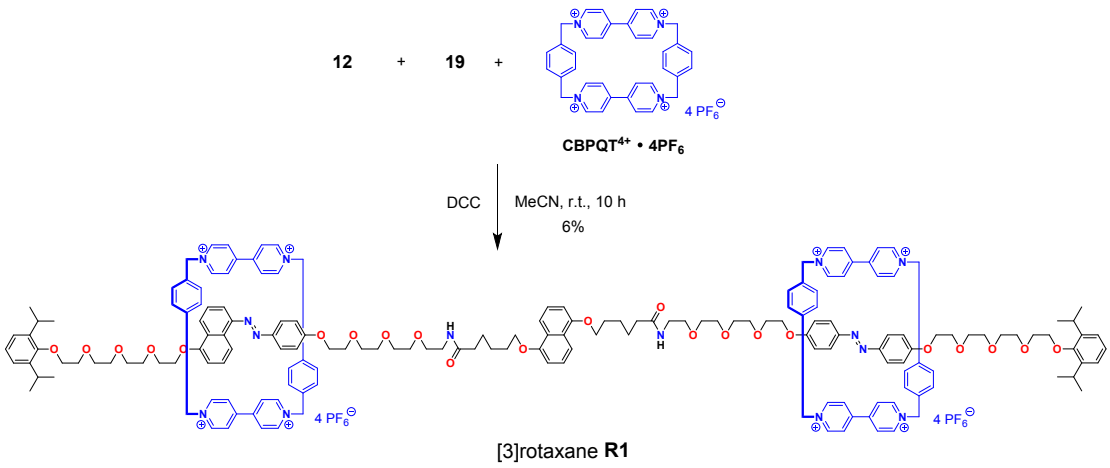
Compound 17. Compound **16** (0.200 g, 4.81 mmol) was first added in 20 mL of anhydrous 1,4-dioxane and heated to 103 °C until completely dissolved, and then 6.7 mL of methanol solution containing KOH (0.270 g, 4.81 mmol) was added. The resulting mixture was heated at 103 °C with stirring for 4 hours until the total consumption of starting material. The reaction mixture was then cooled to room temperature, and the solvent was removed by evaporation under reduced pressure. The remaining solid was re-dissolved in 20 mL of CH_2Cl_2, and the insoluble residue was discarded by filtration. The filtrate was then concentrated via evaporation under reduced pressure, and the obtained solid was suspended in diluted HCl (a.q., 1 M) solution, which was further extracted by CH_2Cl_2 (30 mL × 2). The collected organic phase was dried using anhydrous Na_2SO_4 as desiccant, which was then removed by filtration. After the filtrate was concentrated by evaporation under reduced pressure and dried under vacuum, compound **17** was obtained as white solid (0.800 g, 41%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.82 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 7.8 Hz, 2H), 4.15-4.10 (m, 4H), 3.67 (s, 3H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.96-1.90 (m, 4H), 1.81-1.73 (m, 4H), 1.66-1.57 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 179.91, 174.24, 154.58, 126.79, 125.13, 125.11, 114.16, 105.32, 67.80, 67.79, 51.57, 34.06, 34.03, 29.02, 25.90, 25.83, 24.78, 24.51. MS (ESI) *m/z*: $[M + H]^+$ 403.2. HRMS (ESI) Calcd. for $C_{23}H_{31}O_6^+$ $[M + H]^+$ 403.2121,

Found: 403.2115.

Compound 19. Compounds **17** (0.208 g, 0.517 mmol) and **18**[4] (0.400 g, 0.517 mmol) were dissolved in 20 mL of $CHCl_3$ together with EDCI (0.178 g, 0.931 mmol) and DMAP (0.0032 g, 26 mmol), the resulting mixture was then stirred at room temperature for 10 hours until the reaction was completed. The reaction mixture was continuously washed by water (30 mL), diluted HCl (a.q., 30 mL) and brine (30 mL), respectively, after which the organic phase was collected and dried by anhydrous Na_2SO_4. The desiccant and solvent were then removed by filtration and evaporation under reduced pressure, respectively, and the remaining crude was further purified by flash column chromatograph using the eluent of CH_2Cl_2 / MeOH = 100 /1. Compound **19** was finally isolated as orange-yellow solid (0.397 g, 67%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.85 (d, *J* = 8.4 Hz, 4H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.09 (br, 3H), 7.01-6.97 (m, 4H), 6.81-6.78 (m, 2H), 6.19 (br, 1H), 4.20 (t, *J* = 4.8 Hz, 2H), 4.17 (t, *J* = 4.8 Hz, 2H), 4.13-4.07 (m, 4H), 3.92-3.88 (m, 4H), 3.86-3.84 (m, 4H), 3.78-3.70 (m, 10H), 3.67-3.64 (m, 5H), 3.63-3.59 (m, 4H), 3.54 (t, *J* = 4.8 Hz, 2H), 3.47-3.43 (m, 2H), 3.38 (septet, *J* = 7.2 Hz, 2H), 2.37 (t, *J* = 4.8 Hz, 2H), 2.22 (t, *J* = 4.8 Hz, 2H), 1.96-1.89 (m, 4H), 1.76-1.71 (m, 4H), 1.63-1.55 (m, 4H), 1.21 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 173.95, 173.01, 160.85, 160.69, 154.54, 153.05, 147.13, 147.06, 141.77, 126.73, 125.14, 125.10, 124.65, 124.34, 123.99, 114.81, 114.77, 114.14, 114.08, 105.30, 73.87, 70.98, 70.89, 70.78, 70.74, 70.53, 70.49, 70.46, 70.13, 69.86, 69.59, 69.56, 67.83, 67.76, 67.69, 67.64, 51.45, 39.18, 36.44, 33.97, 29.10, 28.98, 26.22, 26.01, 25.85, 25.50, 24.73, 24.17. MS (ESI) *m/z*: $[M + H]^+$ 1110.6. HRMS (ESI) Calcd. for $C_{63}H_{88}N_3O_{14}^+$ $[M + H]^+$ 1110.6266, Found: 1110.6265.

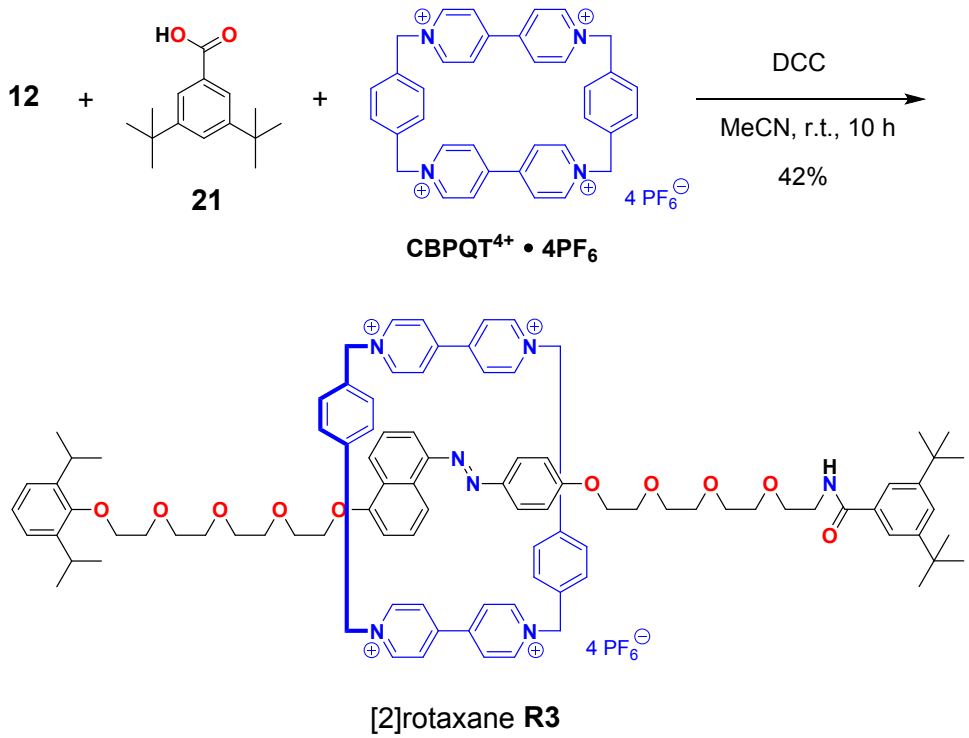
Compound 20. Compound **19** (0.130 g, 0.111 mmol) was dissolved in 15 mL of THF, to which 7 mL of LiOH (0.634 M) aqueous solution was then added, and the resulting mixture was then refluxed with stirring for another 12 hours until TLC suggested the total consumption of starting material. After cooling down, the reaction mixture was

acidified to pH = 3 by adding diluted HCl aqueous solution, and then extracted by CH_2Cl_2 (20 mL × 2). The organic phase was collected and dried using anhydrous Na_2SO_4 as desiccant, which was further removed by filtration. The filtrate was concentrated and the residue crude was subjected to flash column chromatograph for further purification by using a binary solvent of CH_2Cl_2 / MeOH = 50 /1 as the eluent. Finally, compound **20** could be isolated as orange-yellow solid (0.118 g, 93%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.88-7.86 (m, 4H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.36-7.32 (m, 2H), 7.11 (br, 3H), 7.03-6.98 (m, 4H), 6.81-6.79 (m, 2H), 6.31-6.25 (m, 1H), 4.22 (t, *J* = 4.2 Hz, 2H), 4.18 (t, *J* = 4.2 Hz, 2H), 4.12-4.09 (m, 4H), 3.94-3.91 (m, 4H), 3.88-3.86 (m, 4H), 3.80-3.73 (m, 10H), 3.96-3.67 (m, 2H), 3.65-3.60 (m, 4H), 3.56 (t, *J* = 4.8 Hz, 2H), 3.47 (q, *J* = 4.8 Hz, 2H), 3.40 (septet, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.25 (t, *J* = 7.8 Hz, 2H), 1.97-1.90 (m, 4H), 180-1.74 (m, 4H), 1.65-1.57 (m, 4H), 1.24 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 177.09, 173.63, 160.84, 160.65, 154.55, 153.03, 147.16, 147.08, 141.81, 126.76, 125.16, 125.12, 124.67, 124.35, 124.02, 114.83, 144.78, 114.12, 105.30, 73.87, 70.98, 70.89, 70.74, 70.54, 70.44, 70.10, 69.86, 69.62, 69.58, 67.83, 67.81, 67.68, 67.62, 39.27, 36.43, 33.98, 29.09, 29.03, 26.24, 25.99, 25.86, 25.53, 24.67, 24.18. MS (ESI) *m/z*: $[M + H]^+$ 1096.6, HRMS (ESI) Calcd. for $C_{62}H_{86}N_3O_{14}^+$ $[M + H]^+$ 1096.6110, Found: 1096.6099.



Scheme S4. Synthetic rout of [3]rotaxane **R1**.

[3]rotaxane R1. Compound **12** (0.150 g, 0.193 mmol) and **CBPQT^{4+}•4PF$_6^-$** (0.333 g, 0.303 mmol) were dissolved in 1.5 mL anhydrous CH_3CN, and stirred for 15 min at room temperature. Then, compound **20** (0.220 g, 0.193 mmol) and DCC (0.0660 g, 0.322 mmol) were added, and the resulting reaction mixture was further stirred for another 10 hours at room temperature. After removing the solvent by evaporation under reduced pressure, the remaining residue was subjected to flash column chromatograph for further purification using the eluent of CH_3OH / NH_4Cl_{aq} (1M) / CH_3NO_2 = 7 / 2 / 1. Two type of red-brown solids could be isolated, which were then dissolved in 20 mL of water, respectively. The saturated NH_4PF_6 aqueous solution was then added dropwise into both the above solutions, leading to the generation of red-brown precipitates, respectively, which were collected by filtration and washed by another 20 mL of water. After drying under vacuum, [3]rotaxane **R1** could be obtained as red-brown solid (45.0 mg, 6%). ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ: 8.86 (d, *J* = 6.4 Hz, 8H), 8.77 (d, *J* = 6.4 Hz, 8H), 7.91 (s, 8H), 7.90 (s, 8H), 7.70 (br, 8H), 7.44 (br, 8H), 7.15-7.06 (m, 8H), 6.95-6.45 (m, 10H), 6.17-5.90 (br, 2H), 5.85-5.65 (br, 18H), 4.41-4.39 (m, 2H), 4.28-4.25 (m, 2H), 4.18 (br, 2H), 4.14-4.05 (m, 8H), 4.01-3.97 (m, 2H), 3.95-3.90 (m, 6H), 3.85-3.64 (m, 34H), 3.63-3.59 (m, 4H), 3.53-3.47 (m, 4H), 3.40-3.26 (m, 8H), 1.77 (br, 4H), 1.63 (br, 4H), 1.20 (d, *J* = 7.2 Hz, 12H), 1.18 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, CD_3CN, 298 K) δ: 173.34, 161.75, 160.46, 153.01, 146.96, 146.57, 146.35, 144.61, 144.45, 141.84, 141.80, 136.84, 136.71, 131.17, 130.89, 127.28, 126.18, 125.92, 125.66, 124.77, 124.06, 123.76, 123.59, 114.96, 114.30, 114.10, 112.62, 105.14, 73.84, 70.89, 70.39, 70.22, 70.04, 69.91, 69.53, 69.25, 68.41, 68.18, 67.93, 64.88, 64.69, 39.00, 38.93, 35.70, 28.95, 25.93, 25.71, 25.24, 23.38. HRMS (ESI) Calcd. for $C_{178}H_{208}F_{36}N_{14}O_{22}P_6^{2+}$ [M-2PF_4^-]$^{2+}$ 1881.6719, Found: 1881.6729.

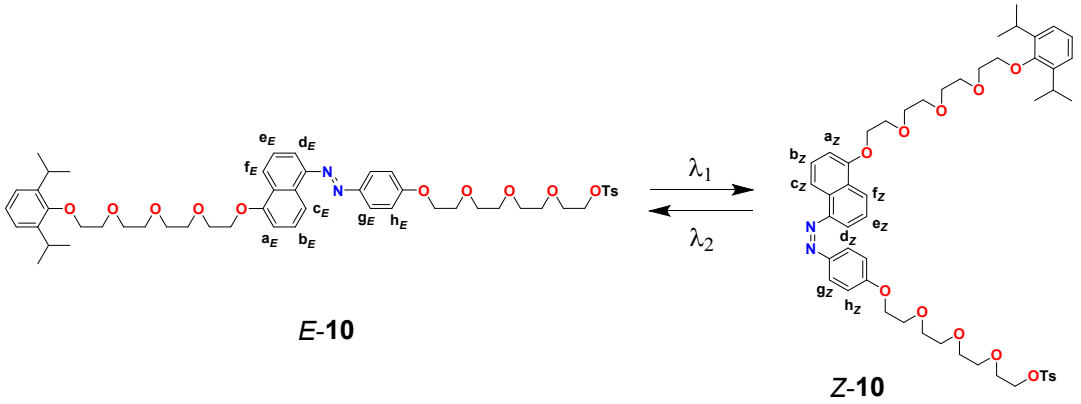


Scheme S5. Synthetic rout of [2]rotaxane **R3**.

[2]rotaxane R3. Compound **12** (0.200 g, 0.258 mmol) and **CBPQT^{4+}•4PF$_6^-$** (0.445 g, 0.404 mmol) were dissolved in 2.0 mL anhydrous CH_3CN, and stirred for 15 min at room temperature. Then, compound **21** (0.0604 g, 0.258 mmol) and DCC (0.0886 g, 0.403 mmol) were added, and the resulting reaction mixture was further stirred for another 10 hours at room temperature. After removing the solvent by evaporation under reduced pressure, the remaining residue was subjected to flash column chromatograph for further purification using the eluent of CH_3OH / H_2O / saturated NH_4Cl_{aq} = 6 / 3 / 1. The isolated red-brown solid was dissolved in 25 mL of water, to which the saturated NH_4PF_6 aqueous solution was then added dropwise to generate red-brown precipitates, which were collected by filtration and washed by another 30 mL of water. After drying under vacuum, [2]rotaxane **R3** could be obtained as red-brown solid (0.230 g, 42%). ^{1}H NMR (600 MHz, CD_3CN, 298 K) δ: 8.80 (d, J = 6.6 Hz, 8H), 7.88 (s, 8H), 7.63 (t, J = 1.8 Hz, 1H), 7.60 (d, J = 7.2 Hz, 2H), 7.52 (br, 8H), 7.20 (t, J = 4.8 Hz, 1H), 7.11-7.04 (m, 3H), 6.89-6.82 (m, 3H), 6.76 (d, J = 7.8 Hz, 1H), 6.71 (t, J = 7.8 Hz, 1H), 6.67 (d, J = 7.2 Hz, 1H), 6.27 (d, J = 8.4 Hz, 2H), 5.75 (br, 8H), 5.16 (d, J = 8.4 Hz, 1H), 4.84 (d, J = 7.8 Hz, 1H), 4.11-4.39 (m, 2H), 4.19-

4.17 (m, 2H), 4.16-4.14 (m, 2H), 3.99-3.97 (m, 2H), 3.90-3.87 (m, 4H), 3.78-3.71 (m, 8H), 3.70-3.62 (m, 8H), 3.57 (t, J = 6.0 Hz, 2H), 3.43 (q, J = 6.0 Hz, 2H), 3.30 (septet, J = 7.2 Hz, 2H), 1.37 (s, 18H), 1.15 (d, J = 7.2 Hz, 12). ^{13}C NMR (150 MHz, CD_3CN, 298 K) δ: 168.12, 161.69, 152.98, 152.52, 151.23, 147.20, 147.06, 145.69, 144.63, 141.78, 136.77, 134.21, 131.19, 129.43, 129.12, 127.31, 125.93, 125.89, 125.67, 125.63, 124.77, 124.07, 121.28, 121.24, 120.15, 114.96, 112.89, 111.03, 105.05, 73.84, 73.79, 73.75, 71.01, 70.70, 70.47, 70.18, 70.00, 69.95, 69.93, 69.62, 69.29, 69.24, 69.19, 68.30, 68.19, 68.14, 68.09, 64.99, 64.94, 64.88, 39.52, 34.71, 30.67, 25.95, 25.93, 23.44, 23.42. HRMS (ESI) Calcd. for $C_{95}H_{113}F_{12}N_7O_{10}P_2^{2+}$ $[M\text{-}2PF_4^-]^{2+}$ 900.8917, Found:900.8940.

Section 3: Photochromic properties of NP-AB and AB contained intermediate compounds



E-**10** *Z*-**10**

Scheme S6. Schematic representation for the *E*/*Z* photoisomerization of compound **10**.

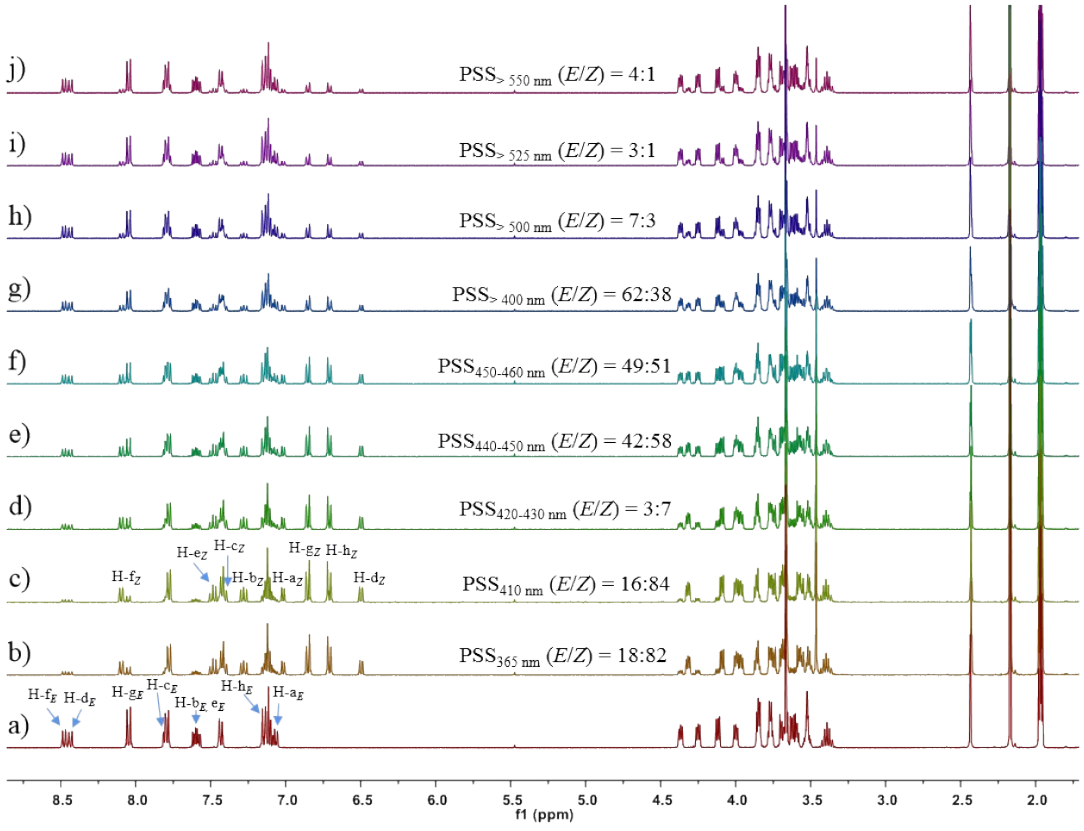
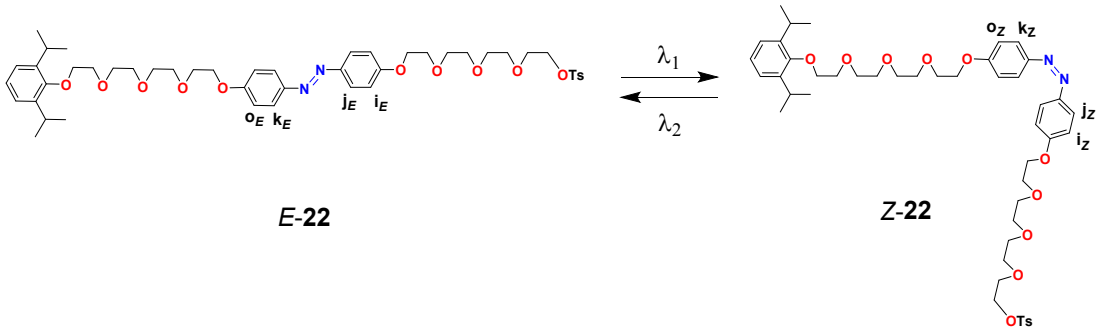


Fig.S1. ^{1}H NMR spectra (400 MHz, CD_3CN, 10 mM, 298K) of compound **10** recorded under conditions of a) before, and b) to j) after irradiation by lights with different wavelengths.



Scheme S7. Schematic representation for the *E*/*Z* photoisomerization of compound **22**.

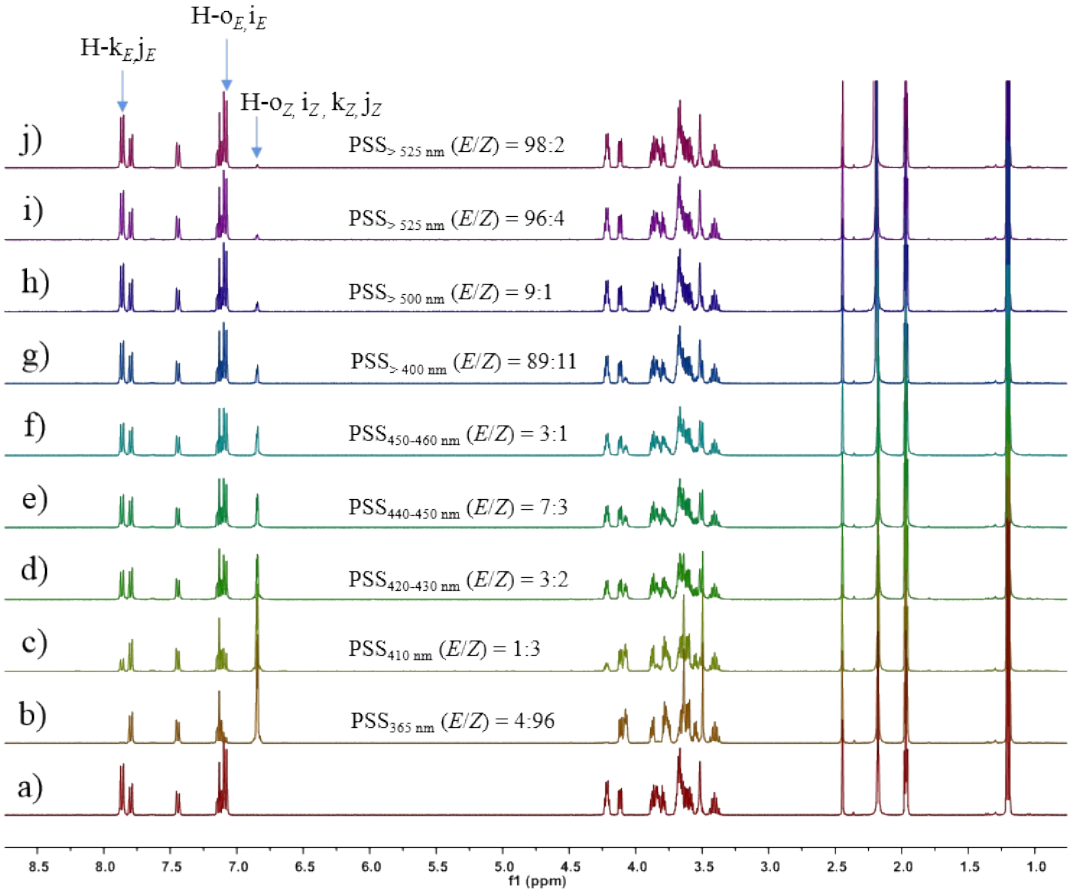


Fig.S2. ^{1}H NMR spectra (400 MHz, CD_3CN, 10 mM, 298K) of compound **22** recorded under conditions of a) before, and b) to j) after irradiation by lights with different wavelengths.

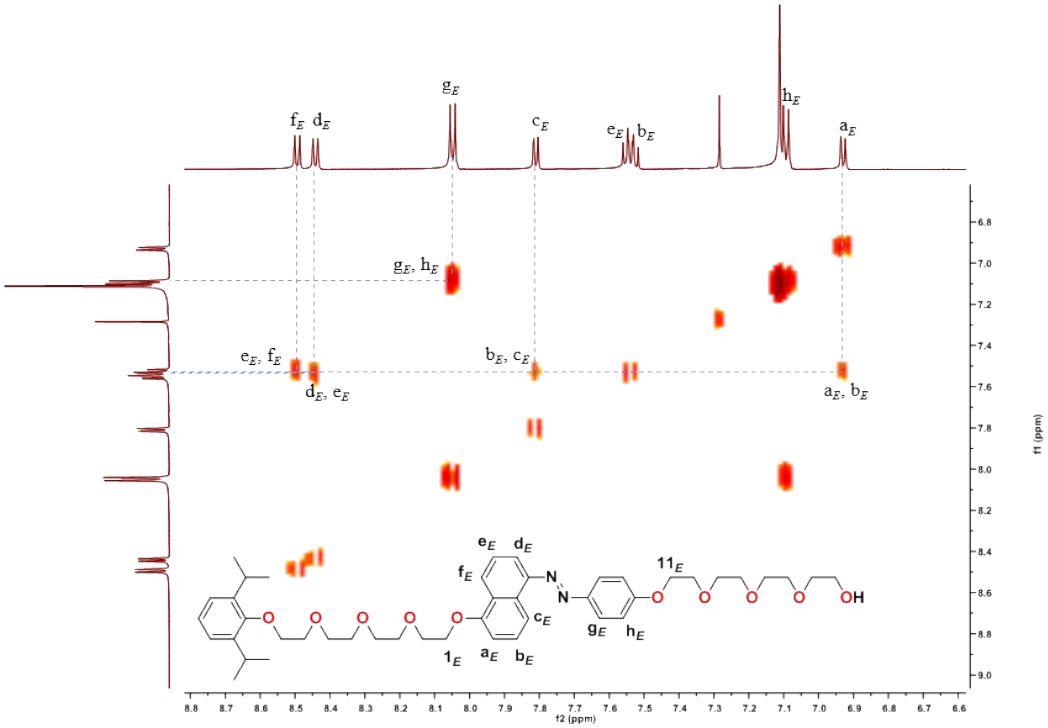


Fig.S3. Partial 2D COSY NMR spectrum (600 MHz, $CDCl_3$, 20 mM, 298K) of compound **9**.

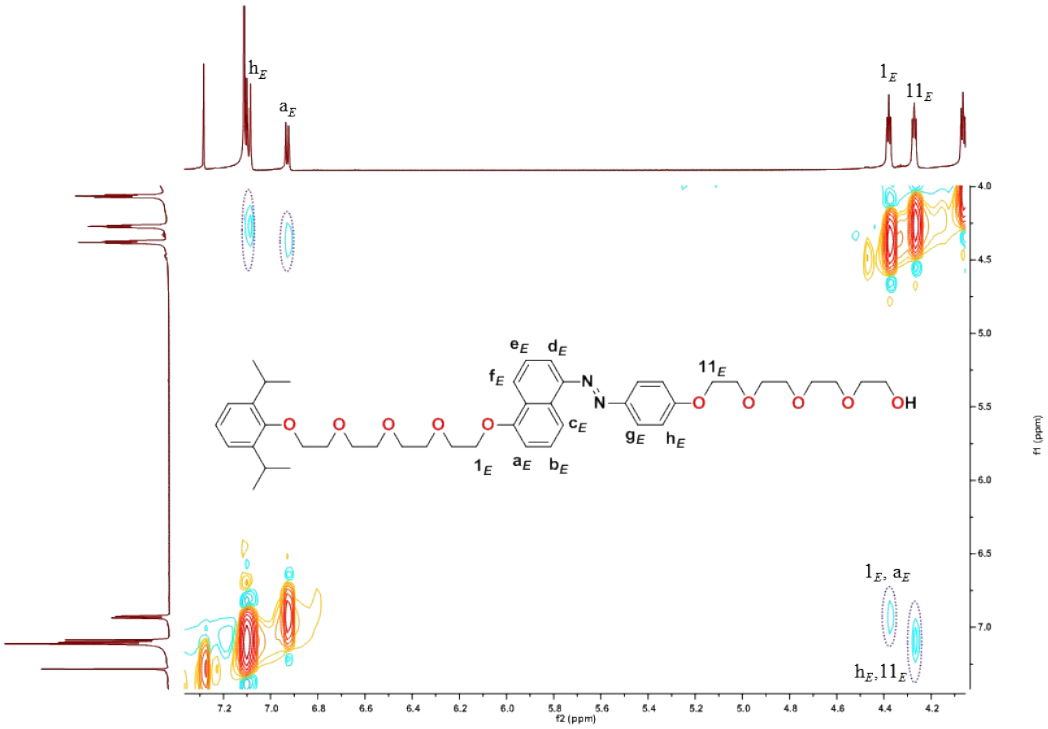


Fig.S4. Partial 2D NOESY NMR spectrum (600 MHz, $CDCl_3$, 20 mM, 298K) of compound **9**.

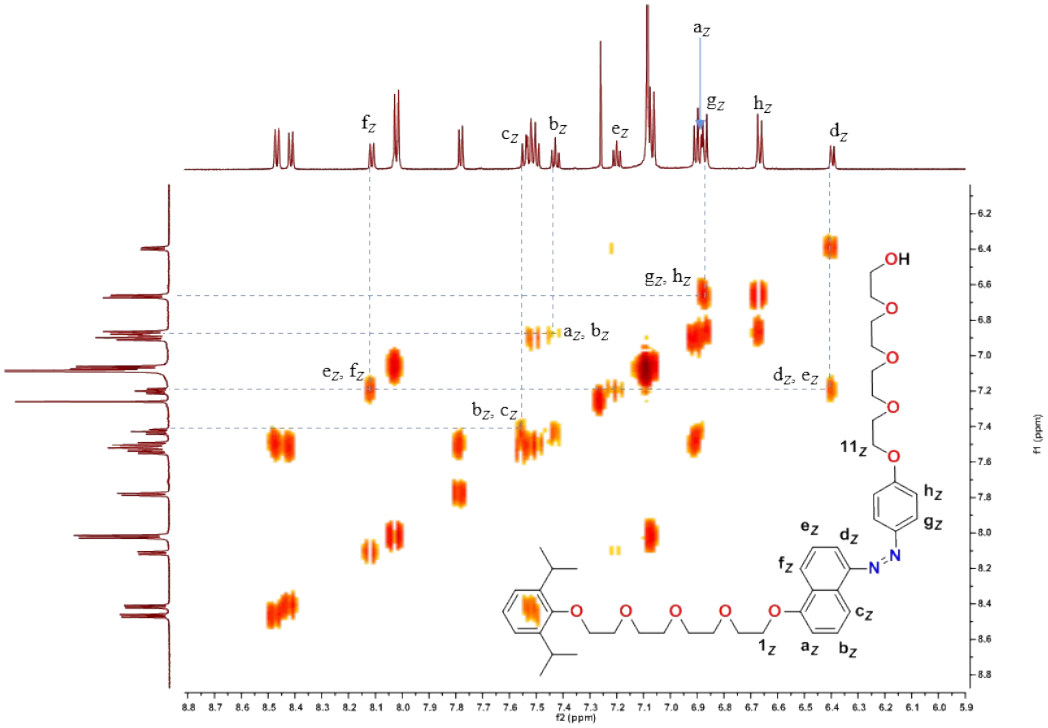


Fig.S5. Partial 2D COSY NMR spectrum (600 MHz, $CDCl_3$, 20 mM, 298K) of compound **9** after irradiation by purple light (410 nm, 2.2 mW / cm^2) for 30 min.

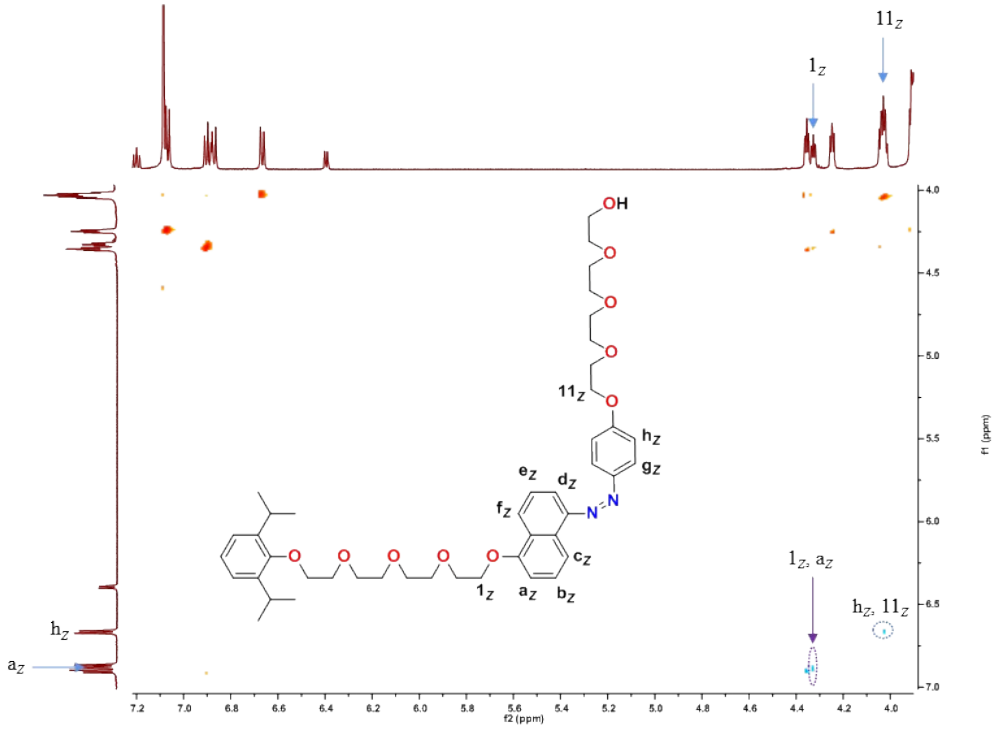


Fig.S5. Partial 2D NOESY NMR spectrum (600 MHz, $CDCl_3$, 20 mM, 298K) of compound **9** after irradiation by purple light (410 nm, 2.2 mW / cm^2) for 30 min.

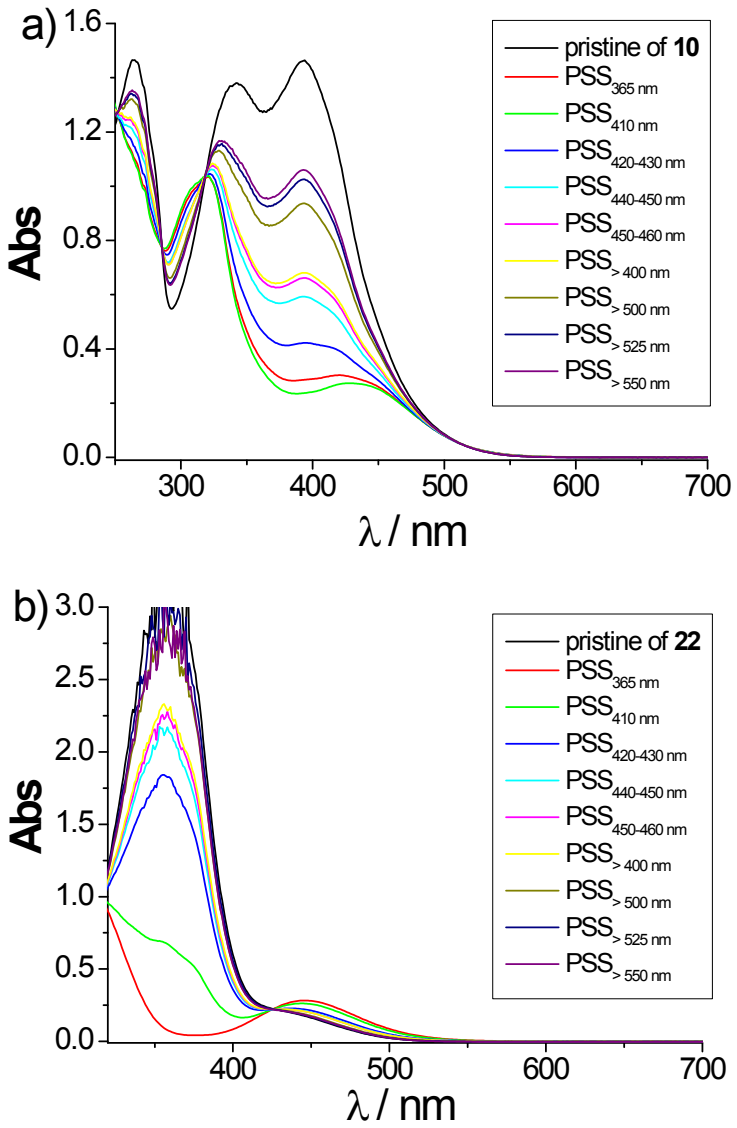
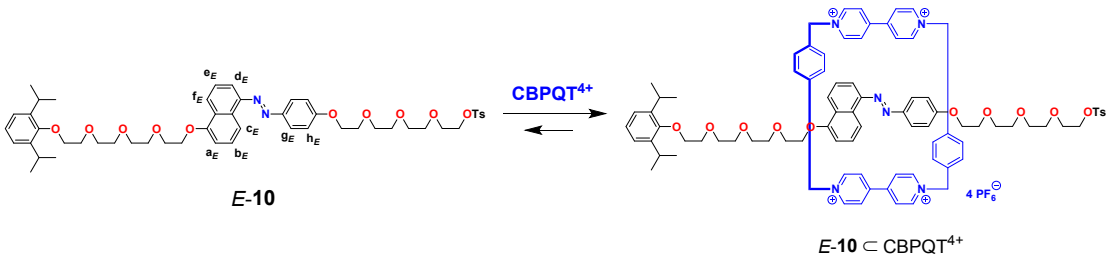


Fig.S6. UV/Vis absorption spectra of (a) compound **10** (0.1 mM) and (b) compound **22** (0.1 mM) before and after irradiation by lights with different wavelengths in MeCN at room temperature.

Section 4: Photochromic behaviors of bistable [2]rotaxane R2



Scheme S8. Schematic representation for the complexation of compound **10** and $CBPQT^{4+}$.

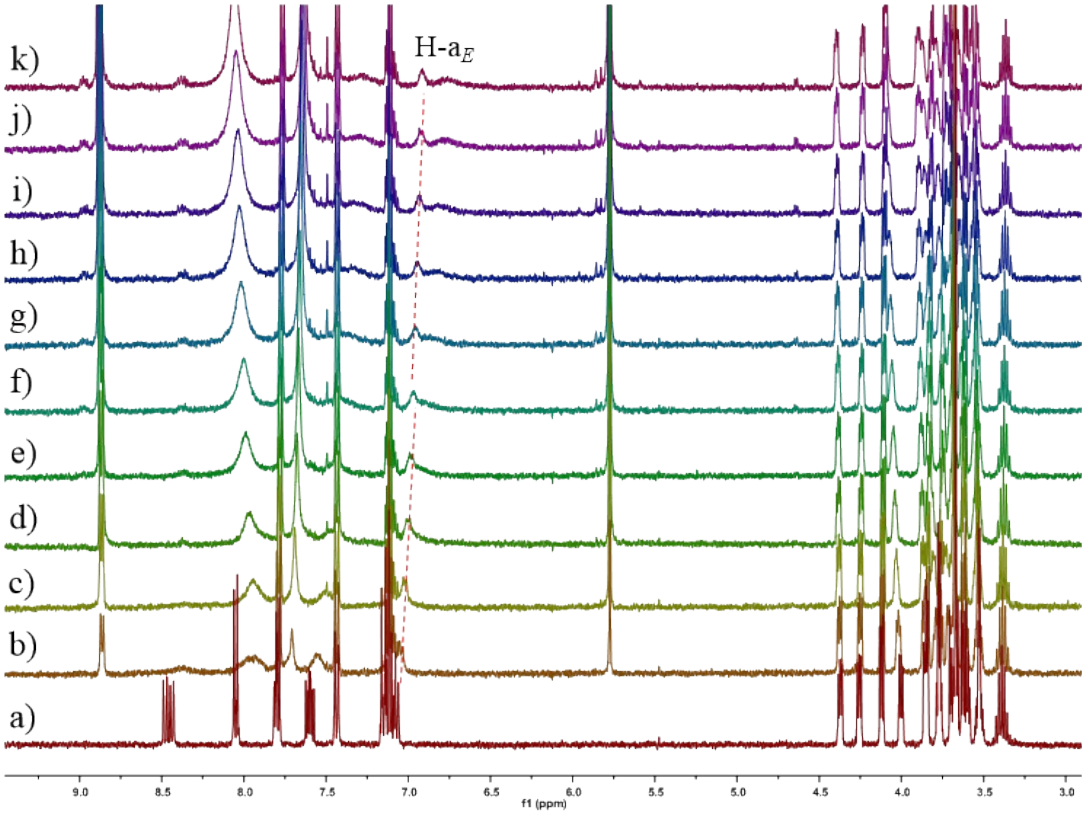


Fig.S7. Partial ^1H NMR spectra (400 MHz, CD_3CN, 298K) of the solution of **10** (2.0 mM) in the presence of a) 0, b) 0.18, c) 0.35, d) 0.50, e) 0.72, f) 0.92, g) 1.1, h) 1.3, i) 1.5, j) 1.7 and k) 1.9 equiv. of $CBPQT^{4+}$•$4PF_6^-$.

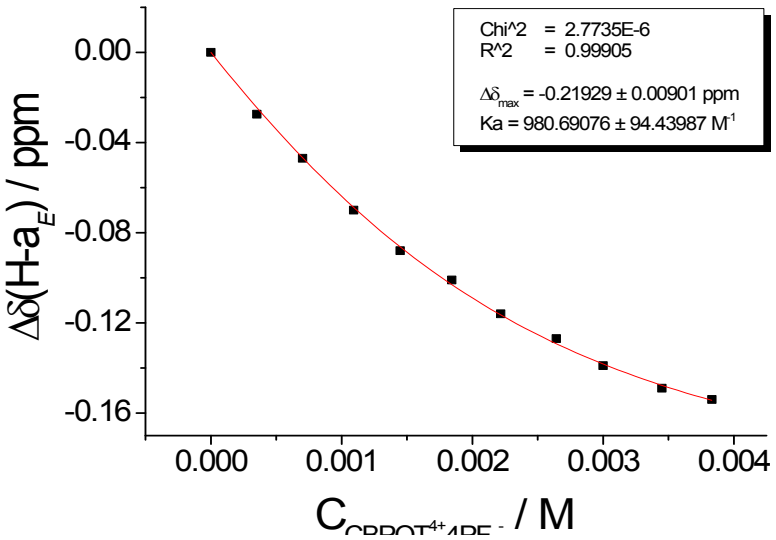
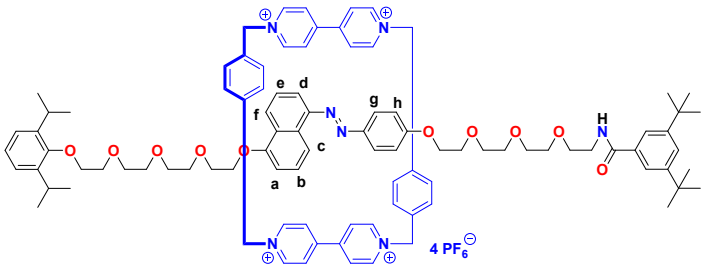


Fig.S8. Plot of the chemical shift changes of proton H-a_E of compound **10** (2.0 mM) versus the concentration of $CBPQT^{4+}$•$4PF_6^-$. The solid line represents the best least-squares fit of the data to a 1:1 binding model (K_a = 980 M^{-1}).



[2]Rotaxane **R3**

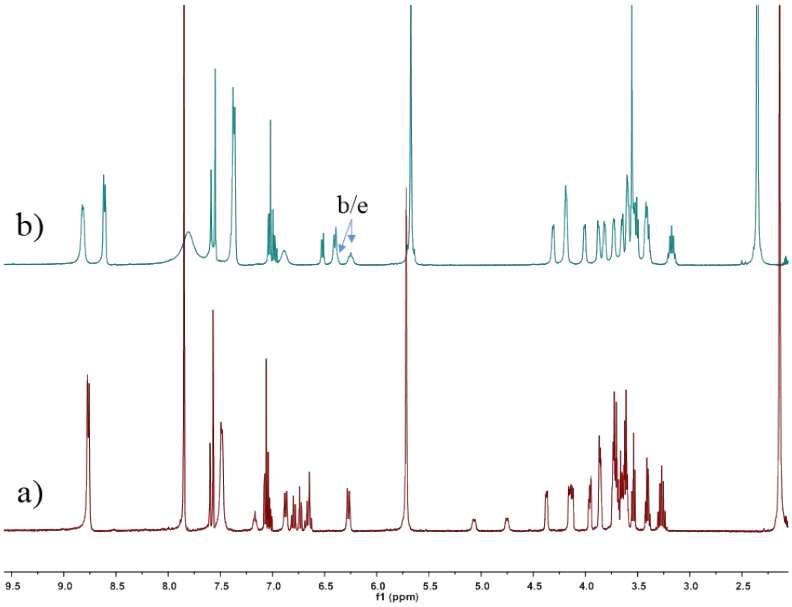
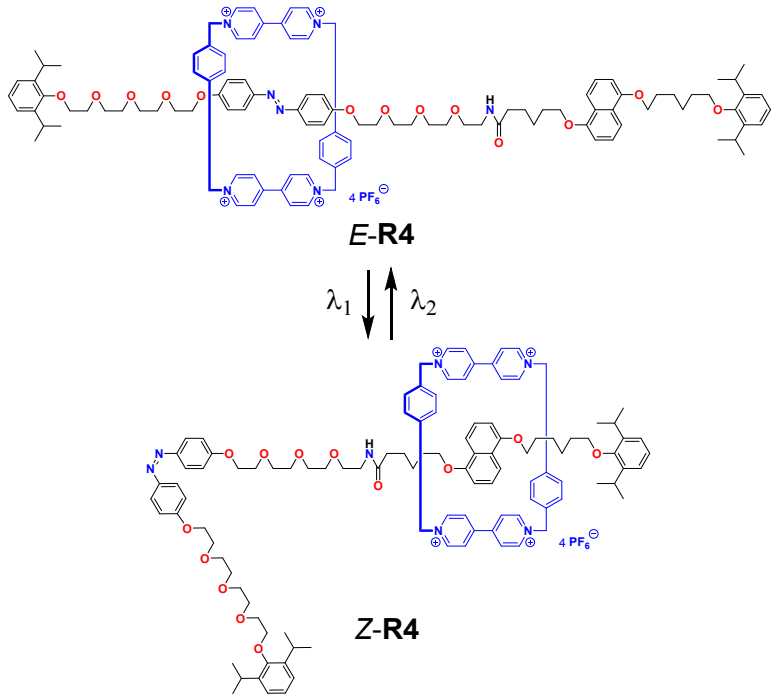


Fig.S9. Variable-temperature ^{1}H NMR spectra (400 MHz, 5 mM) of [2]rotaxane **R3** recorded at (a) 298 K and (b) 233 K in CD_3CN.



Scheme S9. Schematic representation for the phototriggered shuttling of $CBPQT^{4+}$ ring on the axle of [2]rotaxane **R4**.

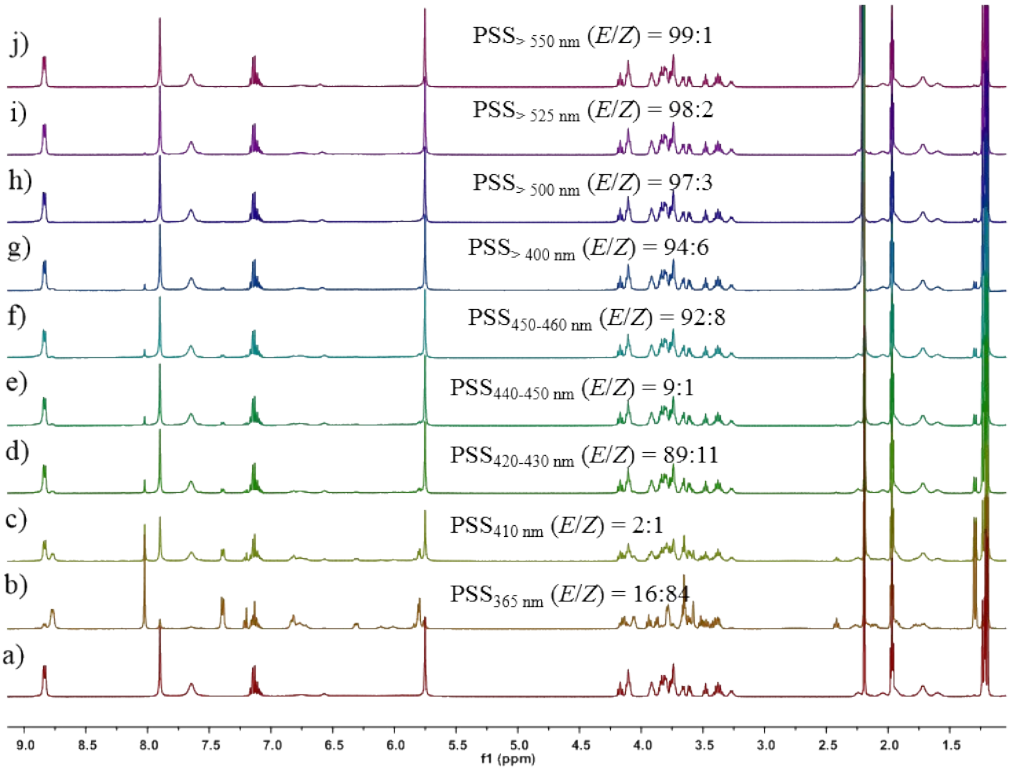


Fig.S10. ^1H NMR spectra (400 MHz, CD_3CN, 10 mM, 298K) of [2]rotaxane **R4** recorded under conditions of a) before and b) to j) after irradiating by lights with different wavelengths at room temperature.

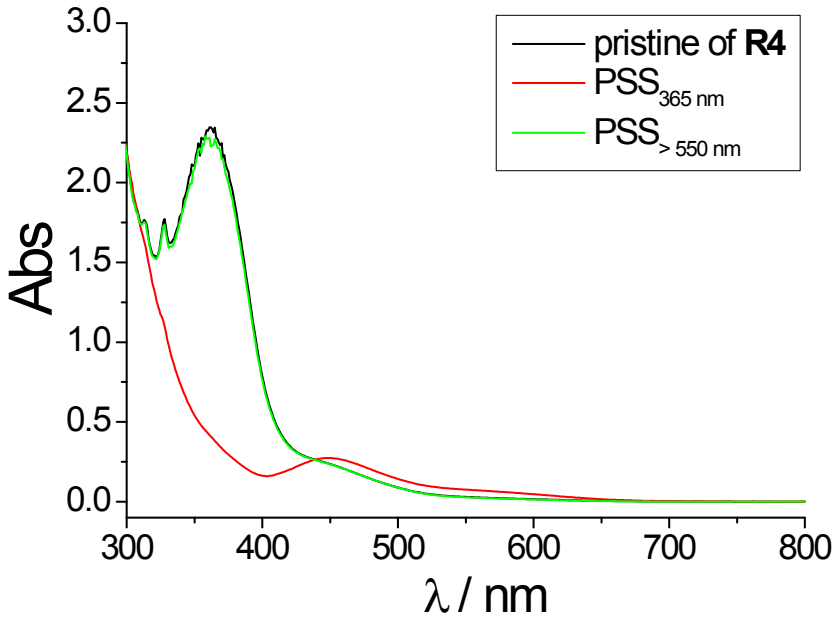
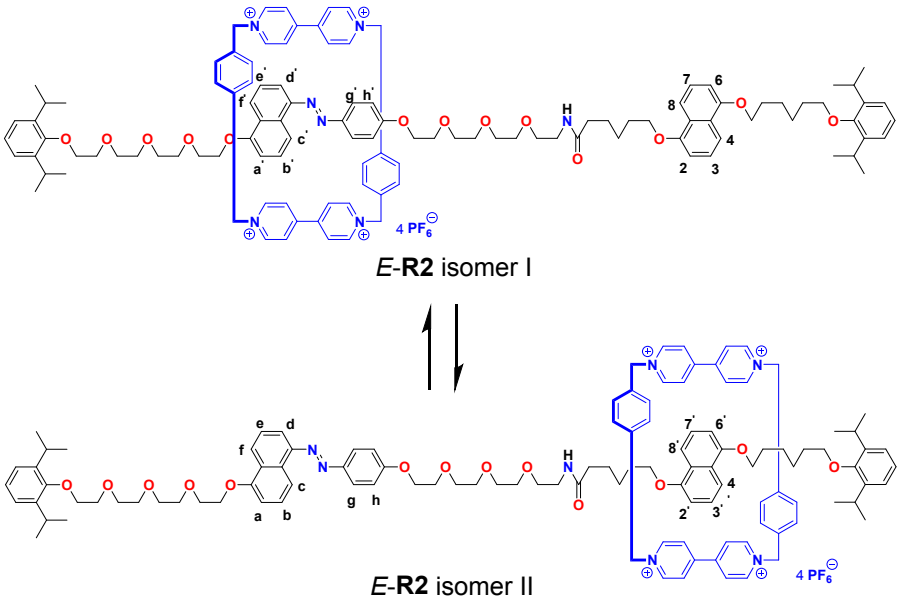


Fig.S11. UV-Vis absorption spectra of [2]rotaxane **R4** (0.1 mM) before and after irradiation with different lights in MeCN at room temperature.



Scheme S10. Schematic representation for the shuttling of $CBPQT^{4+}$ ring on the axle of [2]rotaxane **R2**.

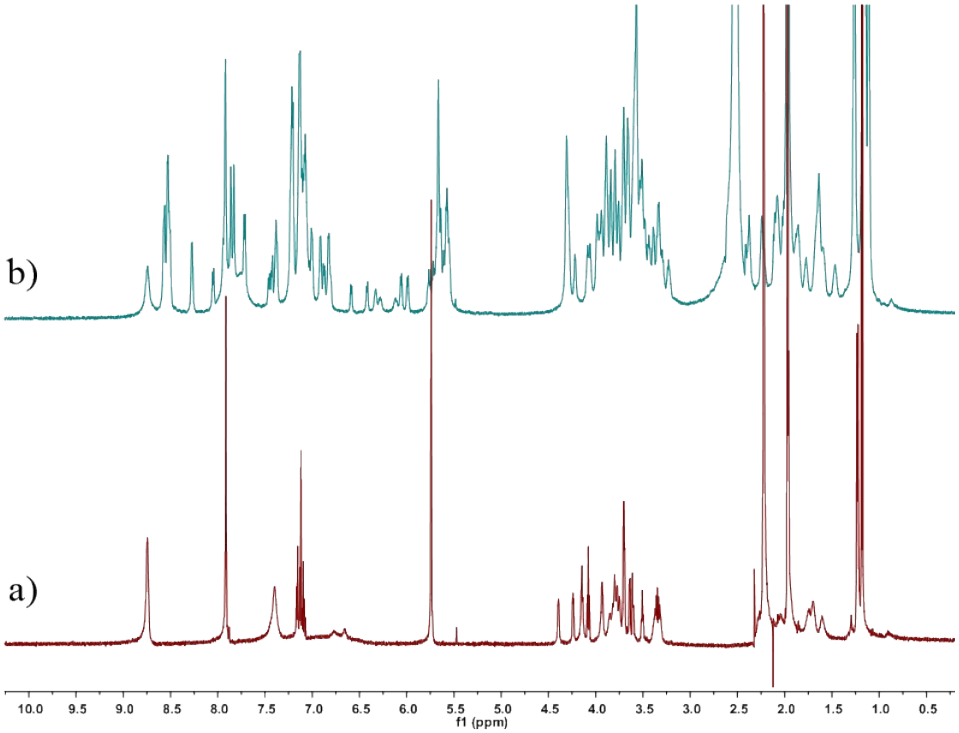


Fig.S12. Variable-temperature ^{1}H NMR spectra (600 MHz, 5 mM) of [2]rotaxane **R2** recorded at (a) 298 K and (b) 233 K in CD_3CN.

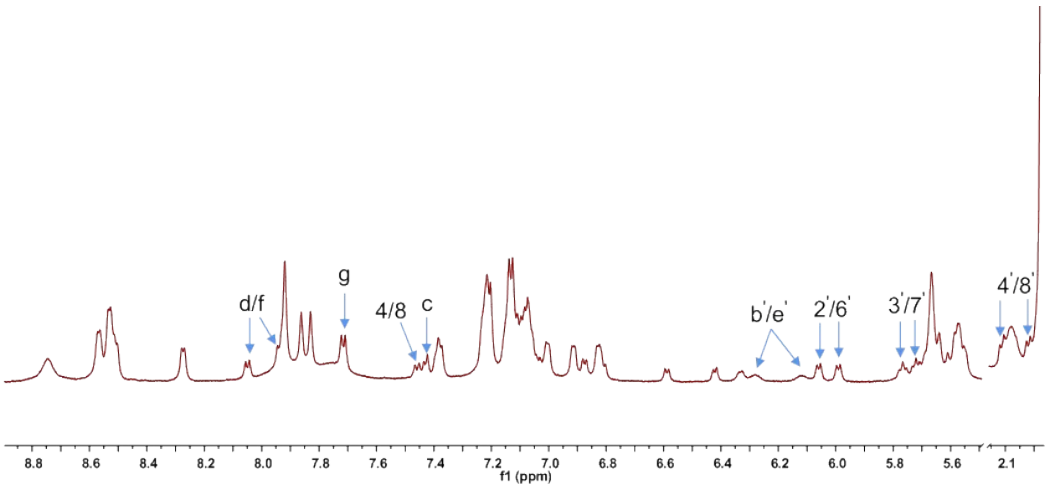


Fig.S13. Partial ^{1}H NMR spectra (600 MHz, 5 mM, CD_3CN) of [2]rotaxane **R2** recorded at 233 K.

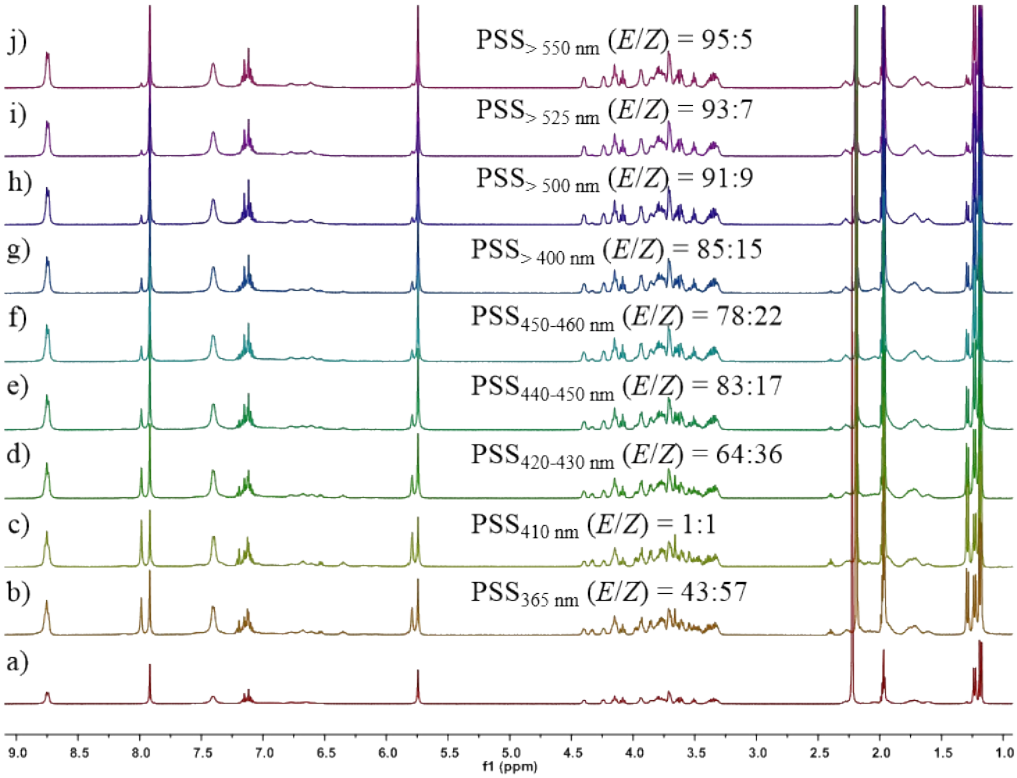


Fig.S14. ^{1}H NMR spectra (400 MHz, CD_3CN, 10 mM, 298K) of [2]Rotaxane **R2** recorded under conditions of a) before, and b) to j) after irradiating by lights with different wavelengths.

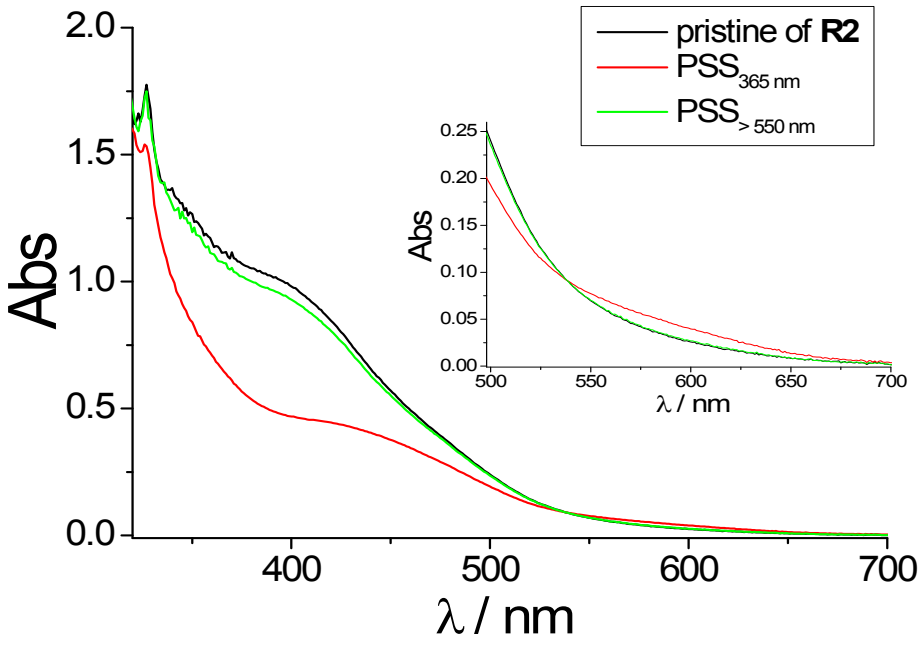
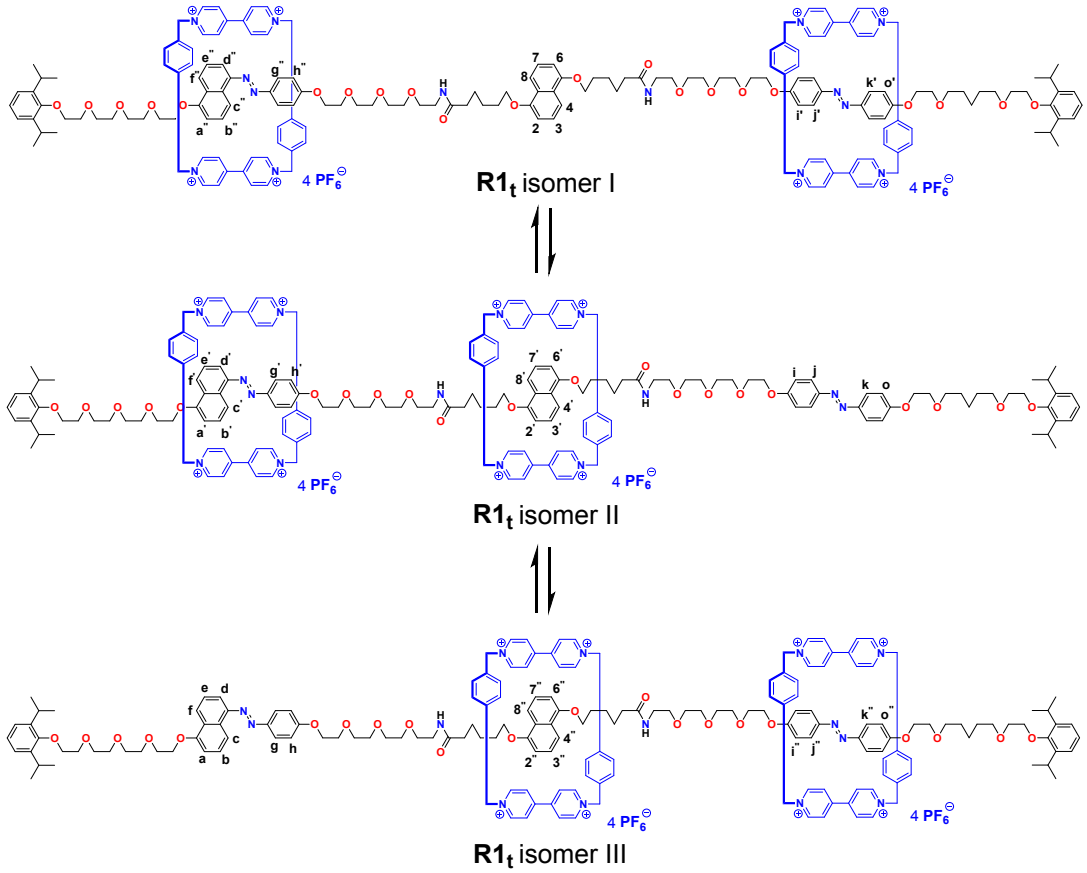


Fig.S15. UV-Vis absorption spectra of [2]Rotaxane **R2** (0.1 mM) before and after irradiation with different light in MeCN at room temperature, and inset shows the CT band changes of the solution before and after light irradiation.

Section 5: Orthogonal photoregulated absorption spectral properties of [3]rotaxane R1



Scheme S11. Schematic representation for the shuttling of $CBPQT^{4+}$ rings on the axle of [3]rotaxane **R1**.

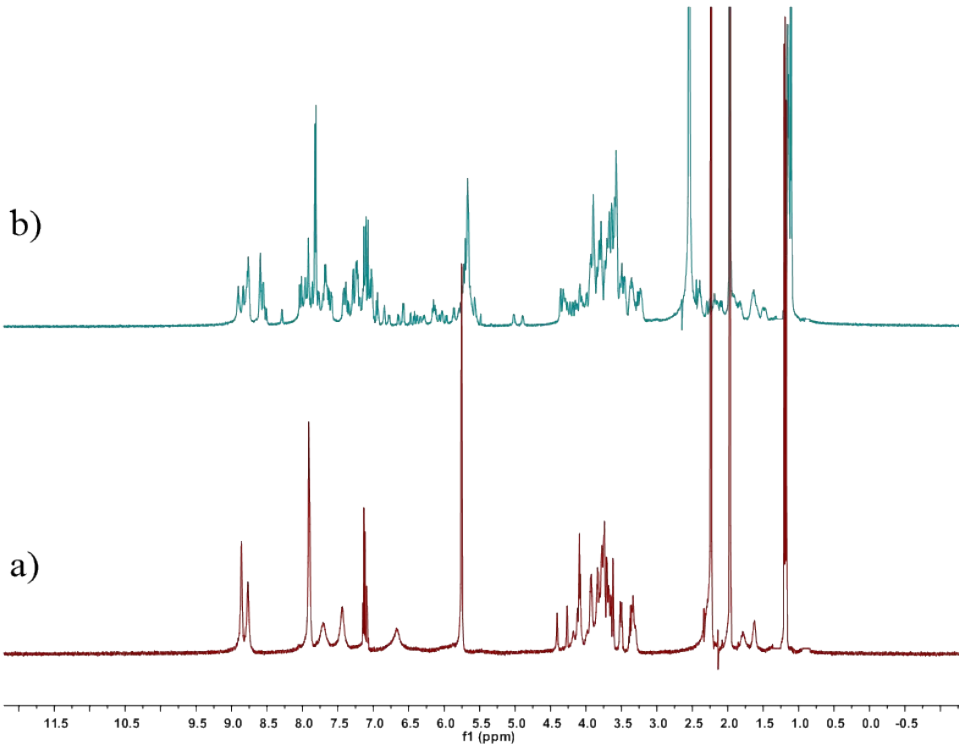


Fig.S16. Variable-temperature ^{1}H NMR spectra (600 MHz, 5 mM, CD_3CN) of the tristable [3]rotaxane **R1** recorded at a) 298 K and b) 233 K.

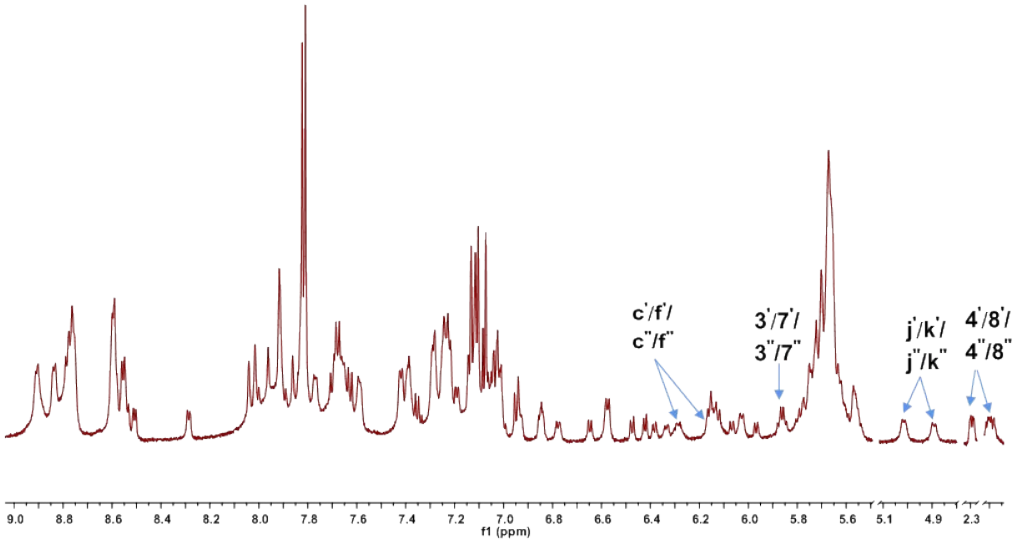


Fig.S17. Partial ^{1}H NMR spectrum (600 MHz, 5 mM, CD_3CN) of the tristable [3]rotaxane **R1** recorded at 233 K.

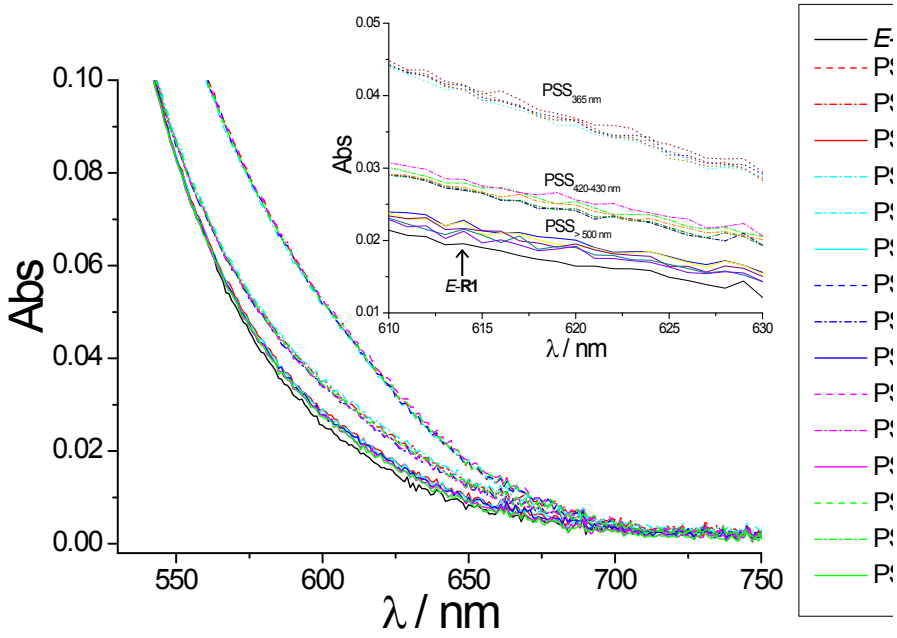


Fig.S18. UV-Vis absorption spectra of [3]rotaxane **R1** (0.1 mM) at different PSSs recorded in MeCN at room temperature during the irradiation cycles: the pure *E*-**R1** was firstly irradiated by UV light (λ = 365 nm), then the UV-irradiated solution of **R1** was irradiated by blue light (λ = 420-430 nm), and the obtained blue light irradiated solution of **R1** was further irradiated by yellow light (λ > 550 nm) before next UV irradiation.

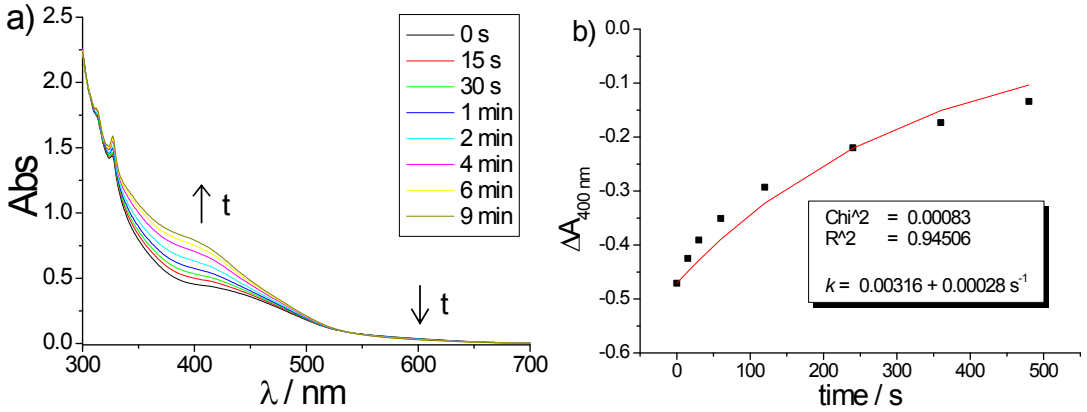


Fig.S19. (a) Time lapse absorption spectra of UV light (λ = 365 nm)-irradiated [2]rotaxane **R2** (0.1 mM) in MeCN at room temperature under yellow light irradiation (λ > 550 nm, 2.0 mW / cm^2), and (b) plot of changes of $\Delta A_{400\ nm} = A_{400\ nm} - A^0_{400\ nm}$ (before irradiation by λ = 365 nm) versus the recording time.

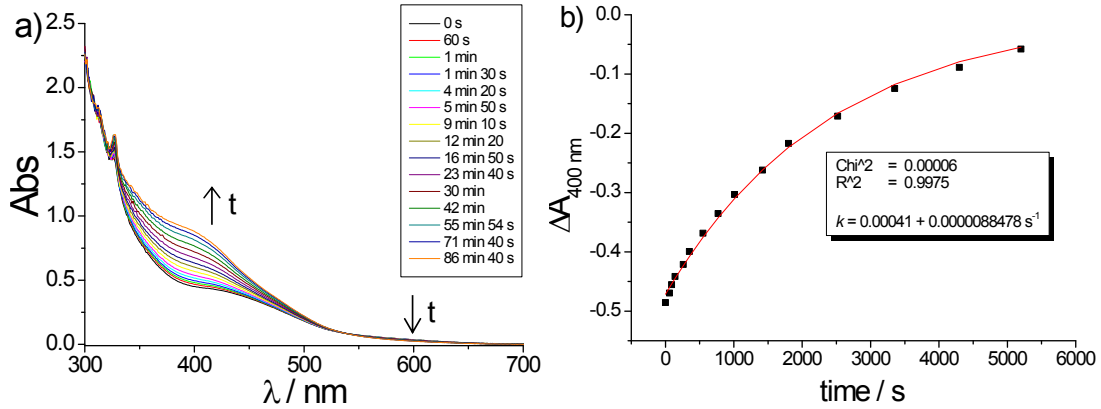


Fig.S20. (a) Time lapse absorption spectra of UV light (λ = 365 nm)-irradiated [2]rotaxane **R2** (0.1 mM) in MeCN at room temperature under red light irradiation (λ = 620 nm, 2.0 mW / cm^2), and (b) plot of changes in $\Delta A_{400\ nm} = A_{400\ nm} - A^0_{400\ nm}$ (before irradiation by λ = 365 nm) versus the recording time.

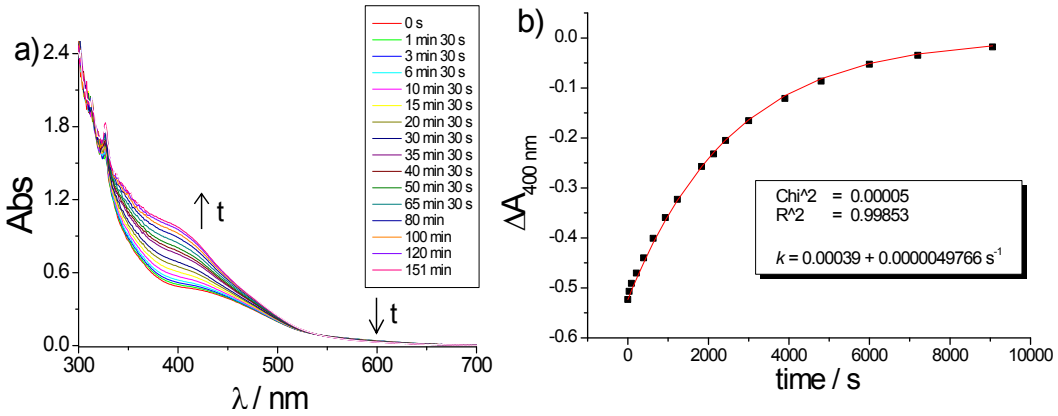


Fig.S21. (a) Time lapse absorption spectra of UV light (λ = 365 nm)-irradiated [2]rotaxane **R2** (0.1 mM) in MeCN at room temperature under dark, and (b) plot of changes in $\Delta A_{400\ nm} = A_{400\ nm} - A^0_{400\ nm}$ (before irradiation by λ = 365 nm) versus the recording time.

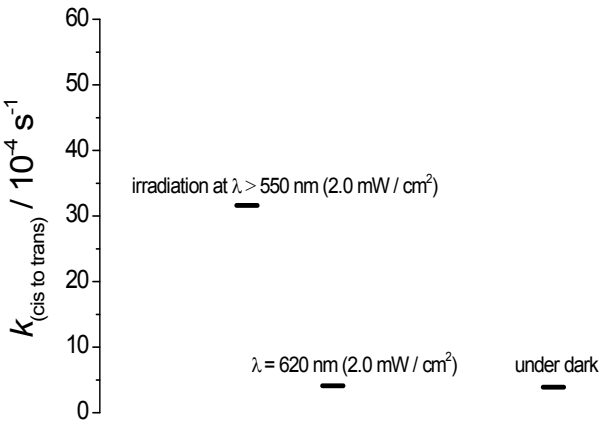
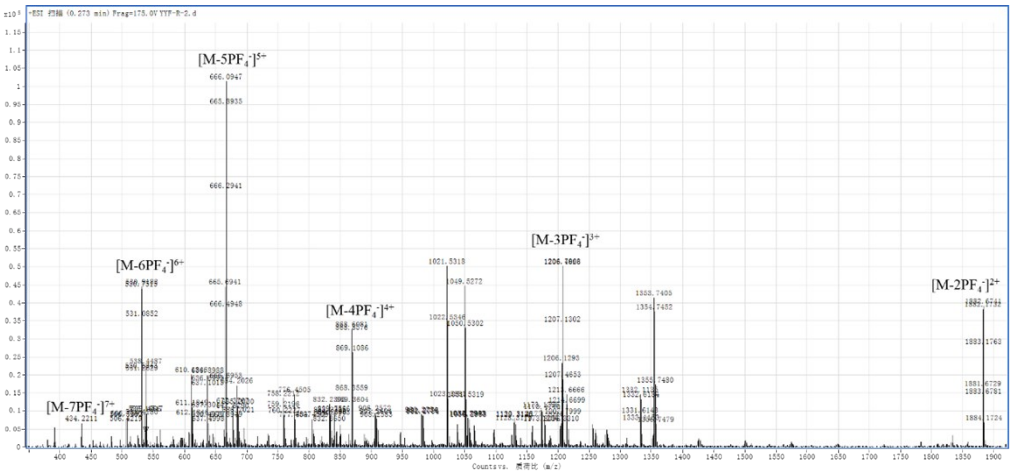
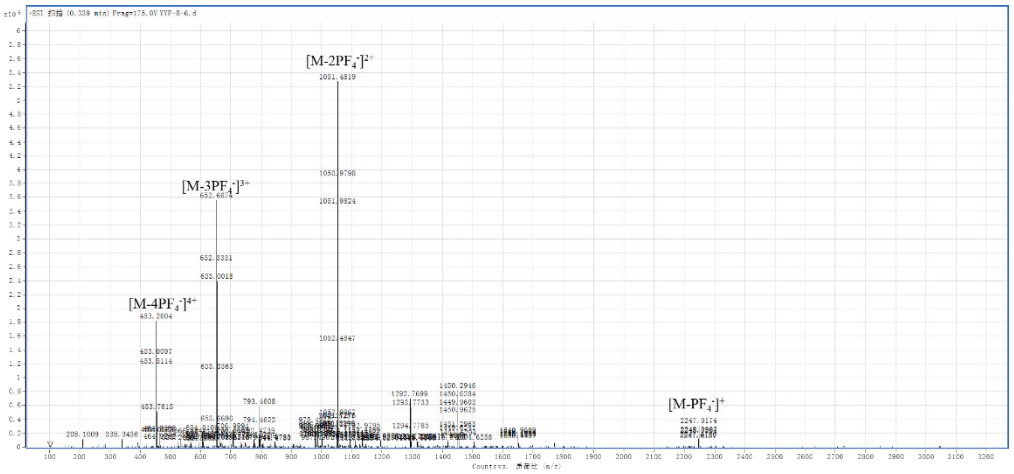


Fig.S22. Diagram of the rate constants for the *cis* → *trans* isomerization of the NP-AB units of **R2**$_c$ under different irradiation conditions.

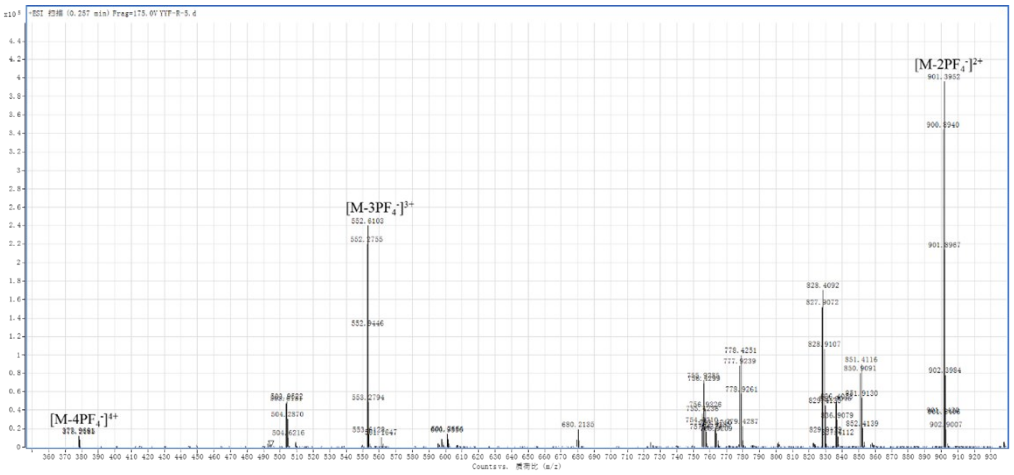
Section 6: HR-MS, ^{1}H and ^{13}C Spectra for New Compounds



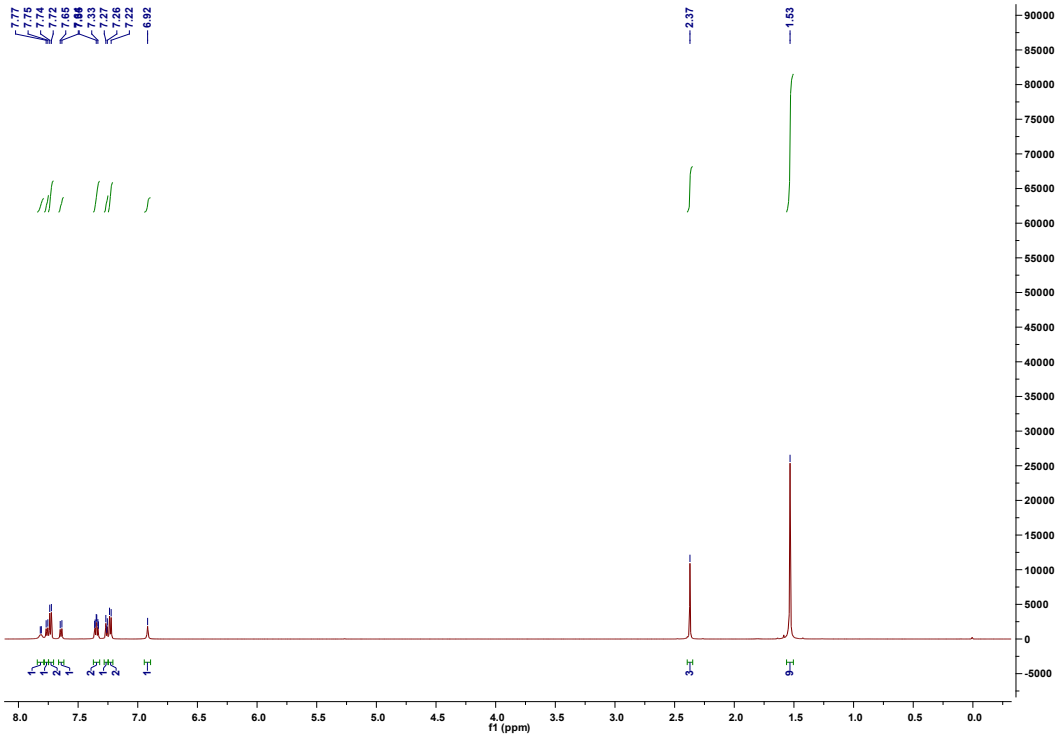
HRMS (ESI)-mass spectrum of [3]rotaxane **R1**.



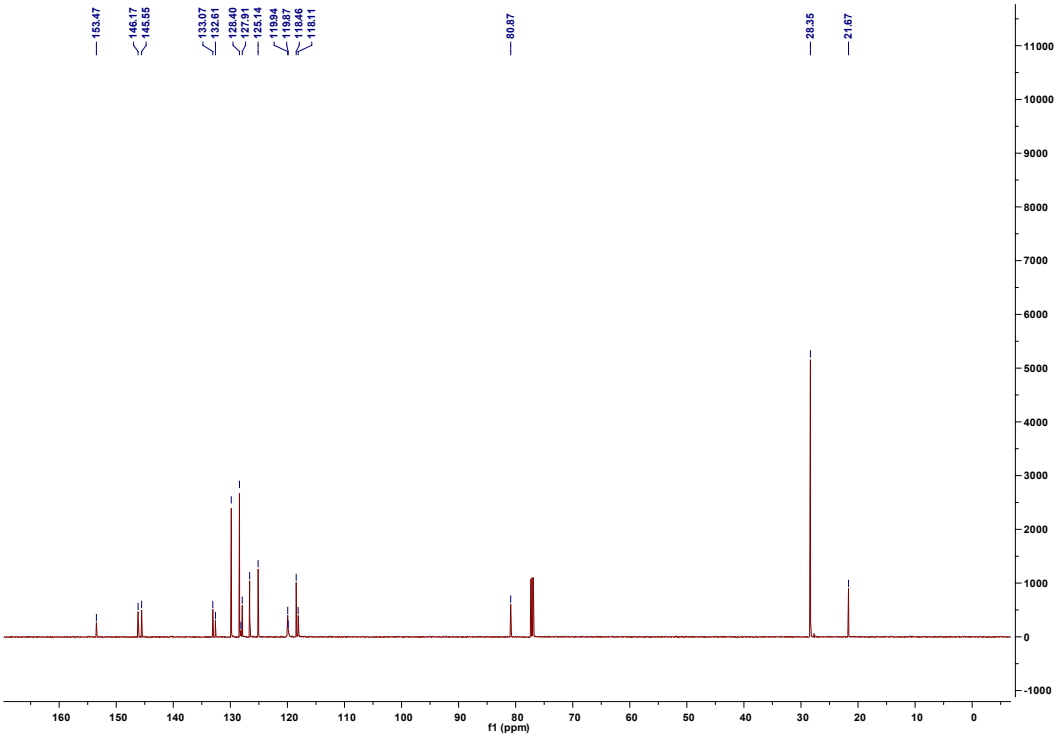
HRMS (ESI)-mass spectrum of [2]rotaxane **R2**.



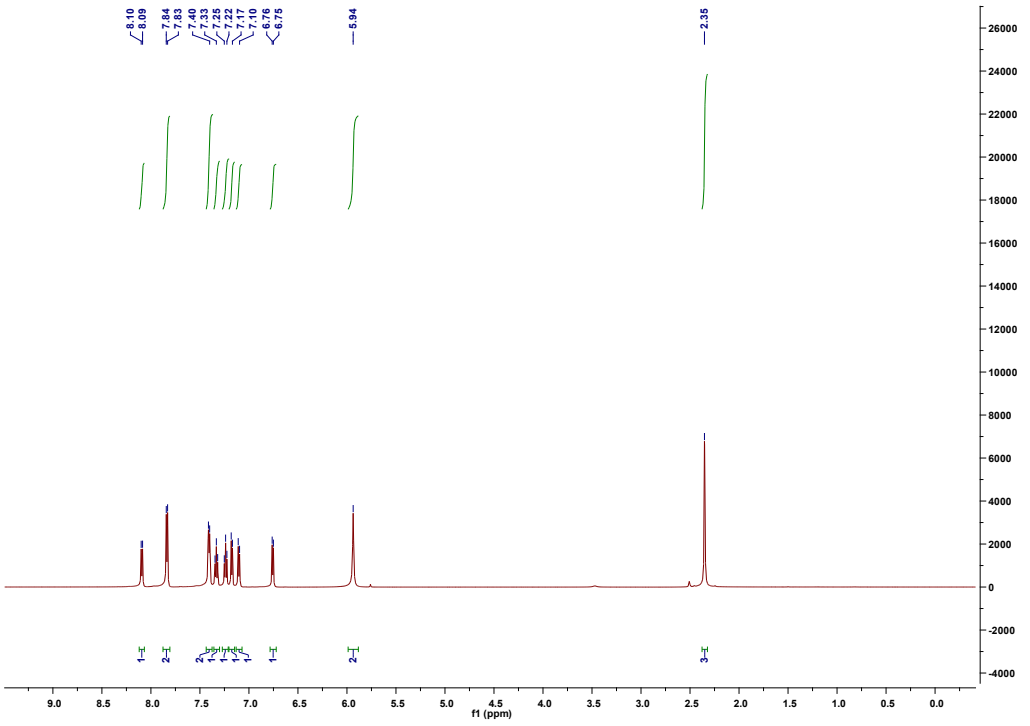
HRMS (ESI)-mass spectrum of [2]rotaxane **R3**.



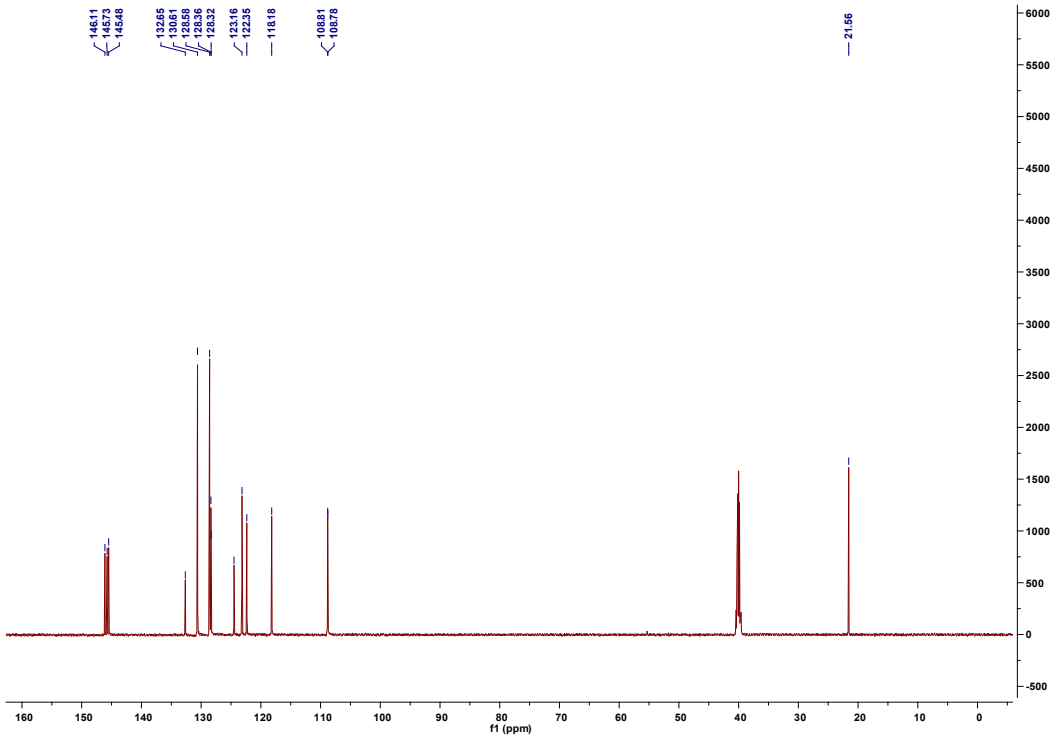
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **2**.



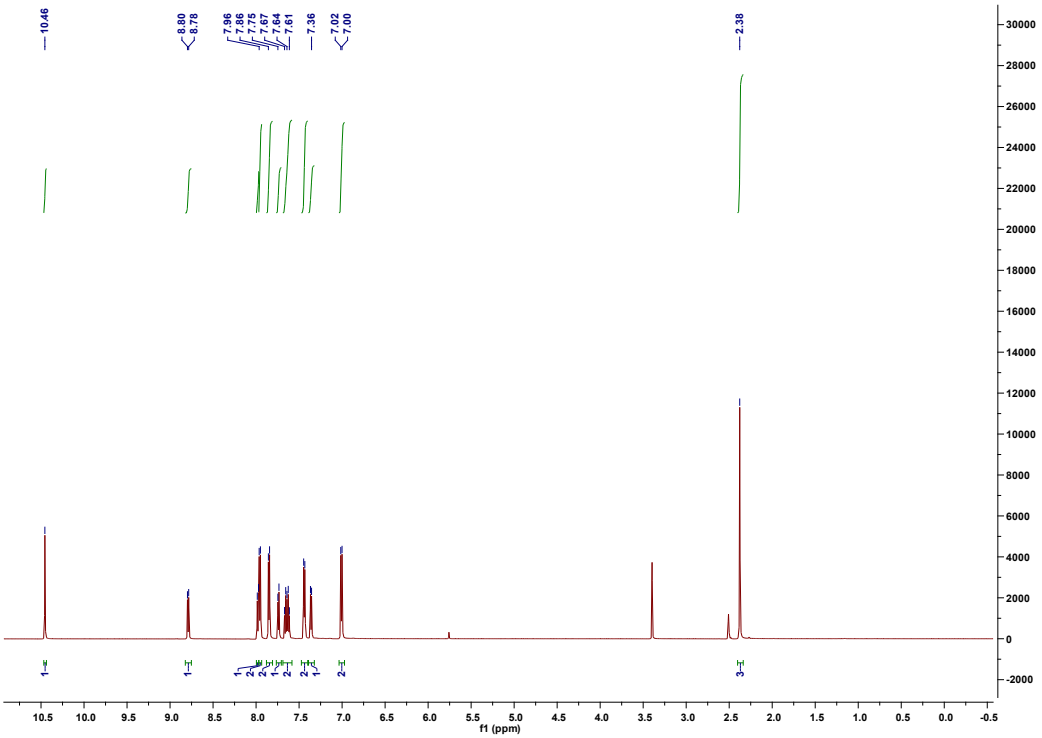
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **2**.



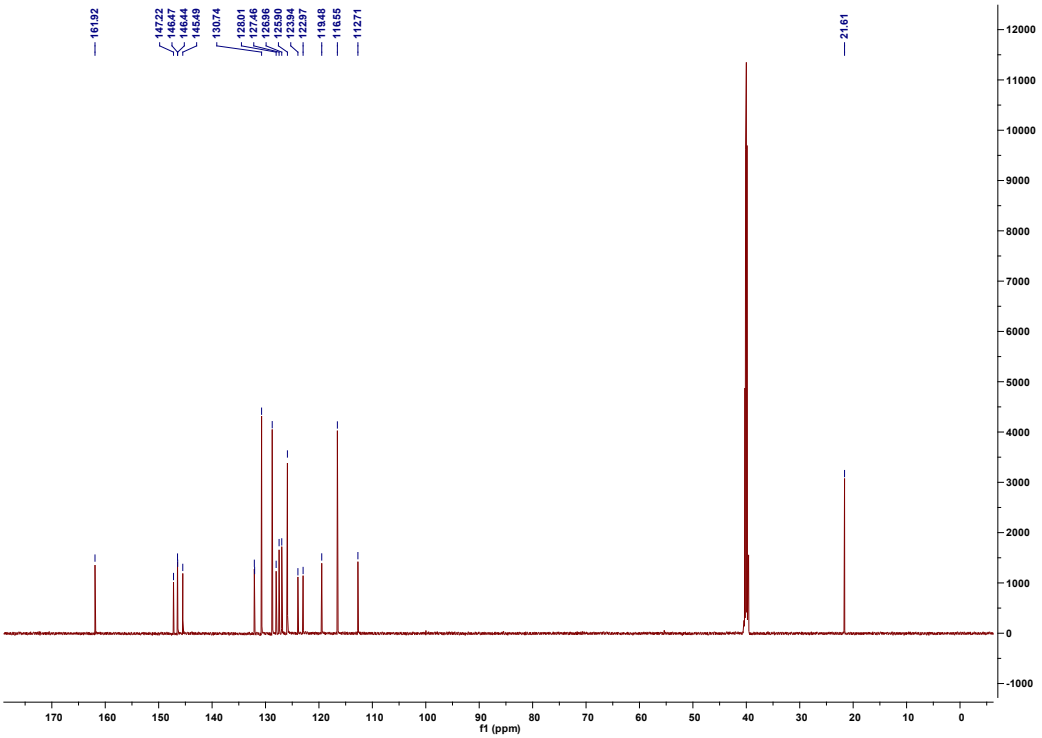
^{1}H NMR spectrum (600 MHz, CD_3SOCD_3, 298 K) of compound **3**.



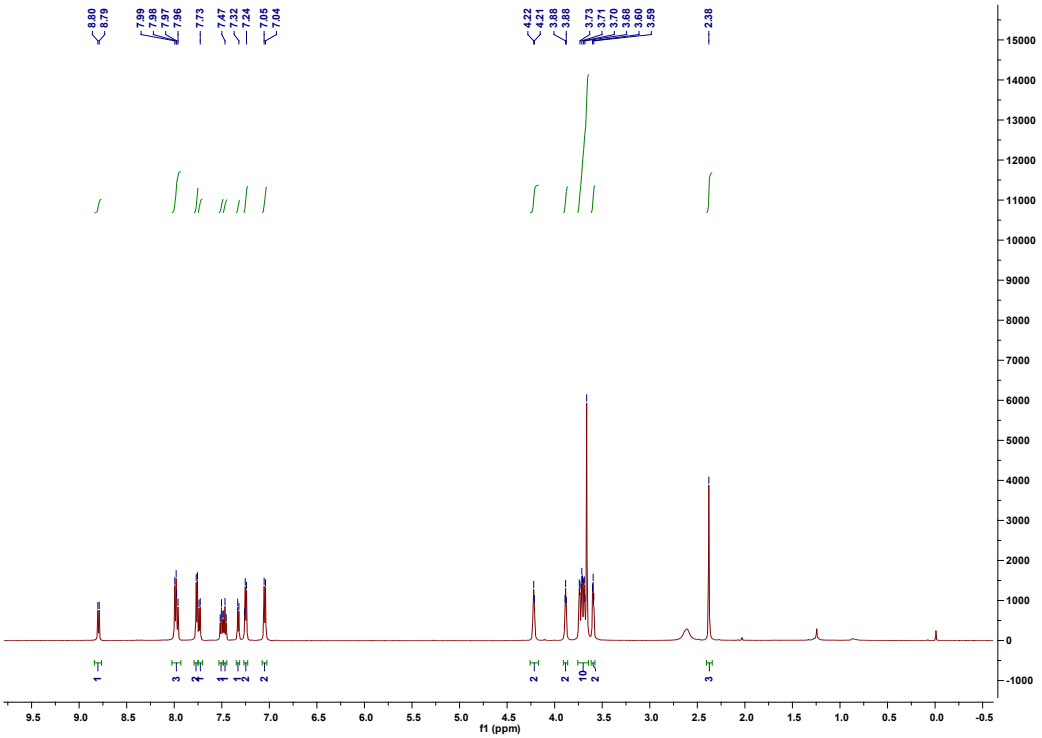
^{13}C NMR spectrum (150 MHz, CD_3SOCD_3, 298 K) of compound **3**.



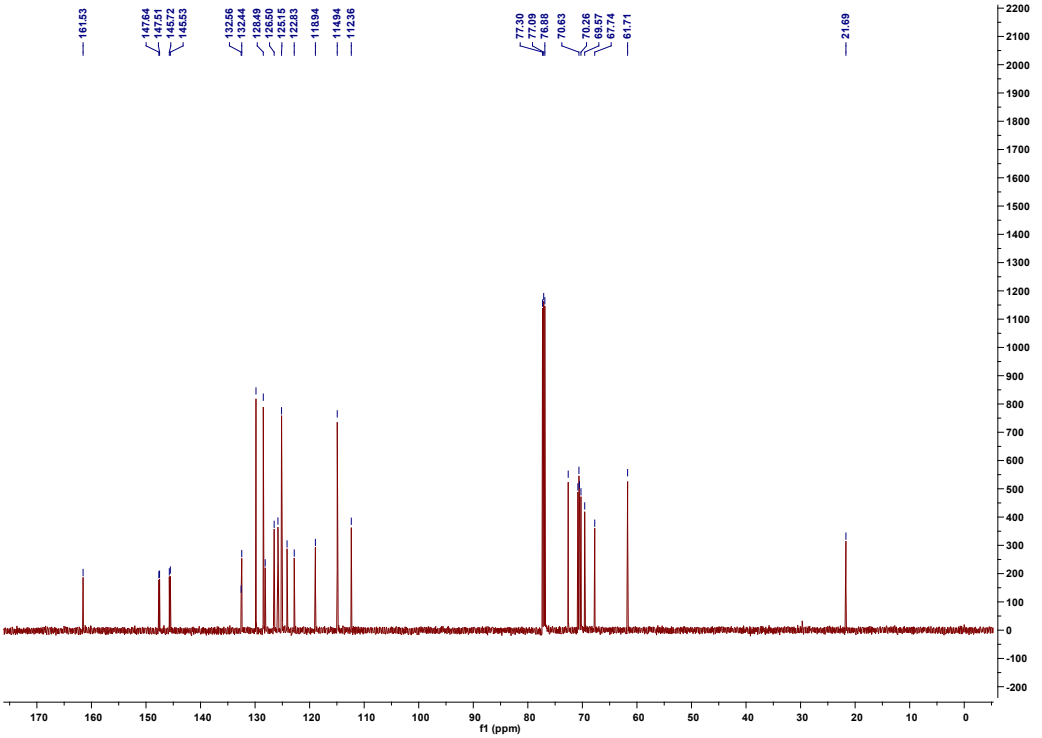
^{1}H NMR spectrum (600 MHz, CD_3SOCD_3, 298 K) of compound **4**.



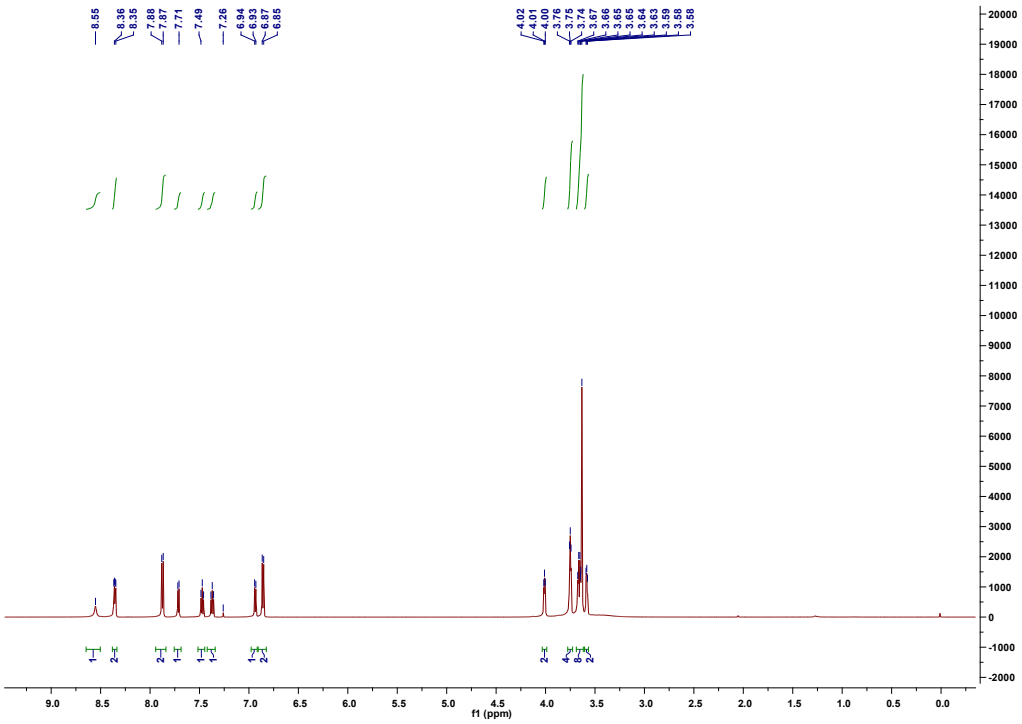
^{13}C NMR spectrum (150 MHz, CD_3SOCD_3, 298 K) of compound **4**.



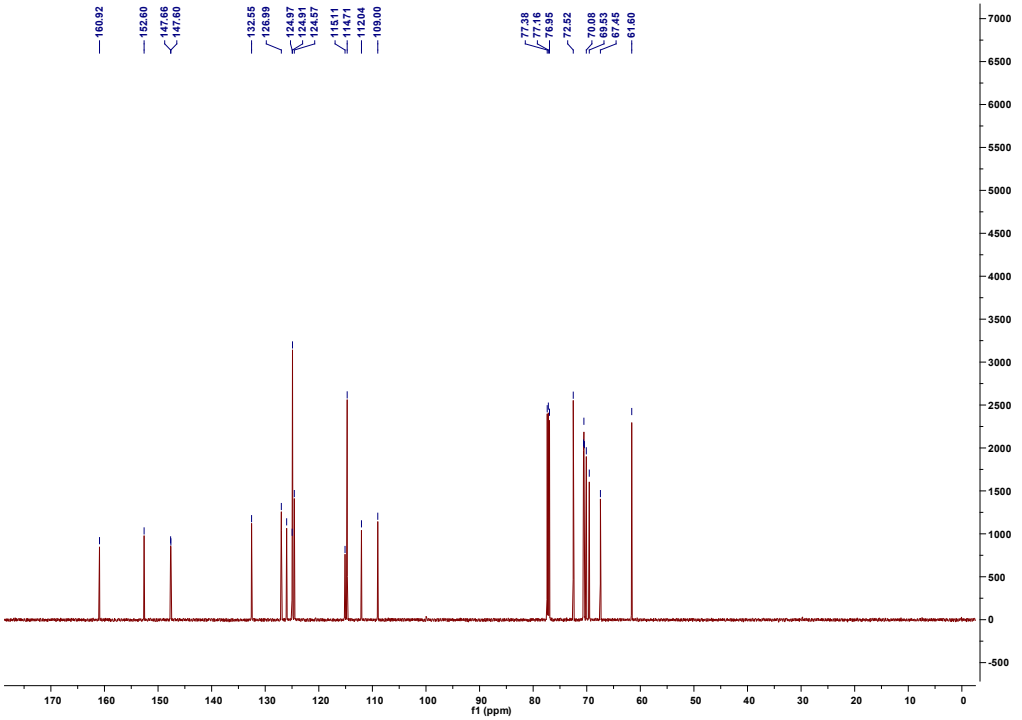
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **6**.



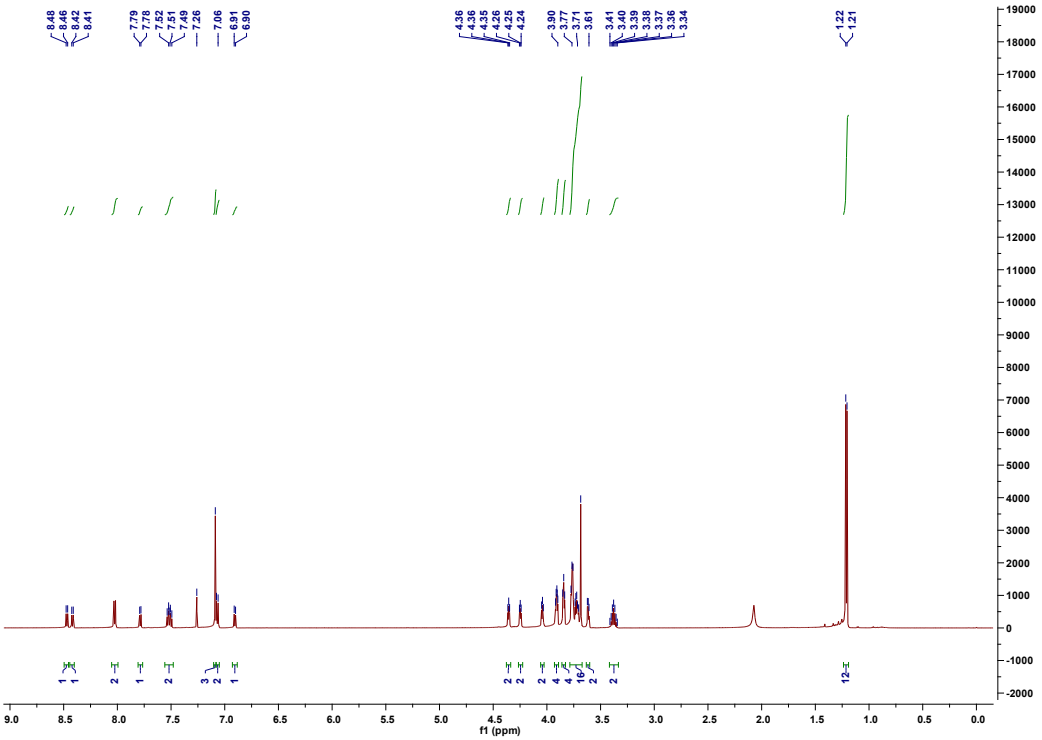
^{13}C NMR spectrum (150 Hz, $CDCl_3$, 298 K) of compound **6**.



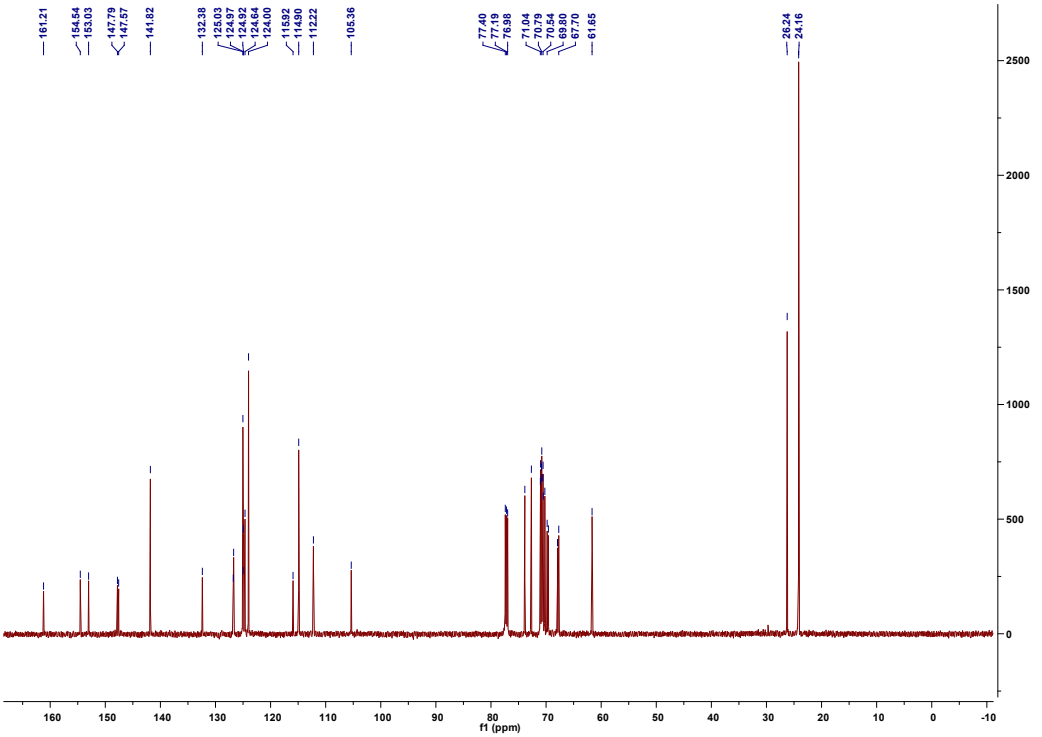
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **7**.



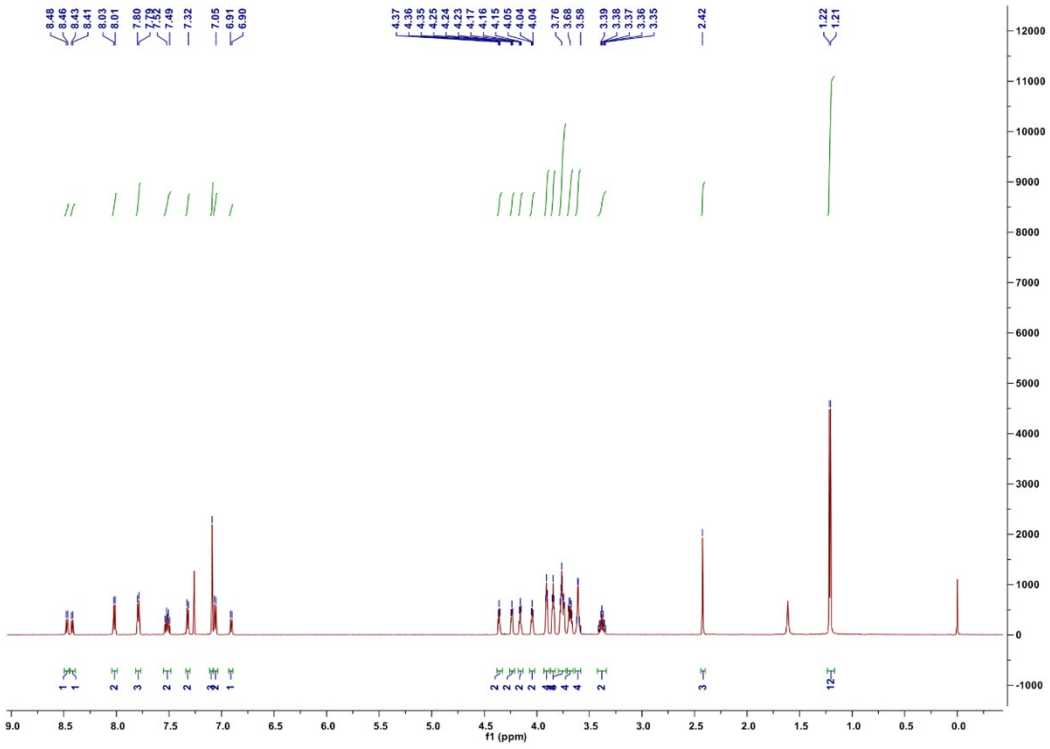
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **7**.



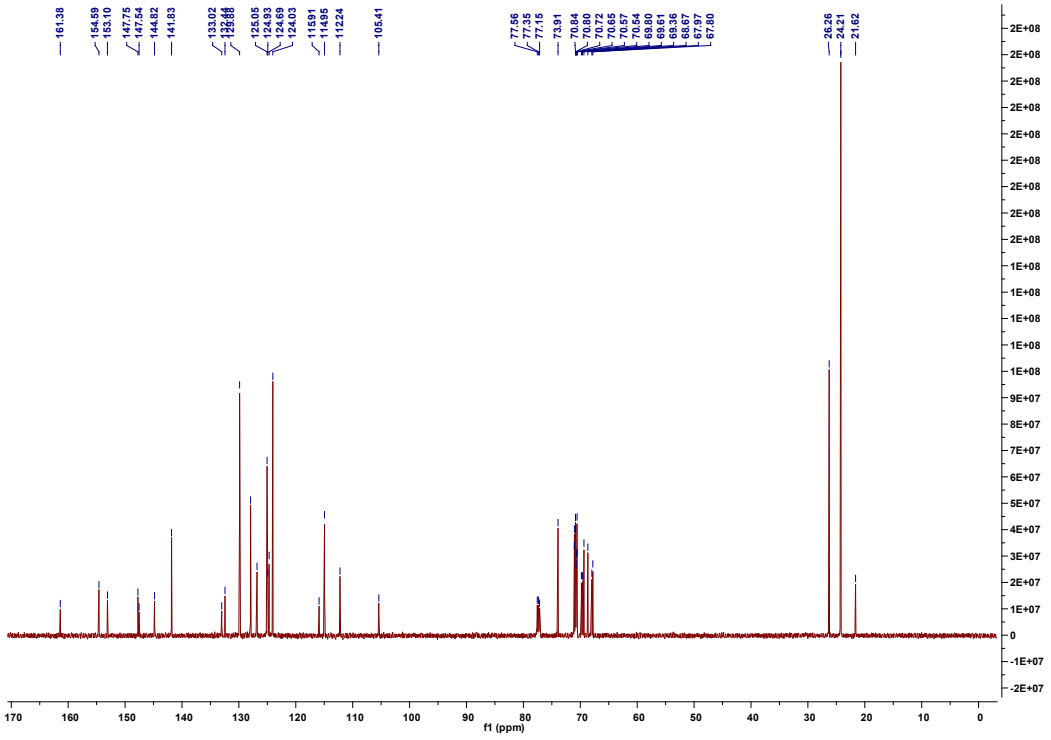
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **9**.



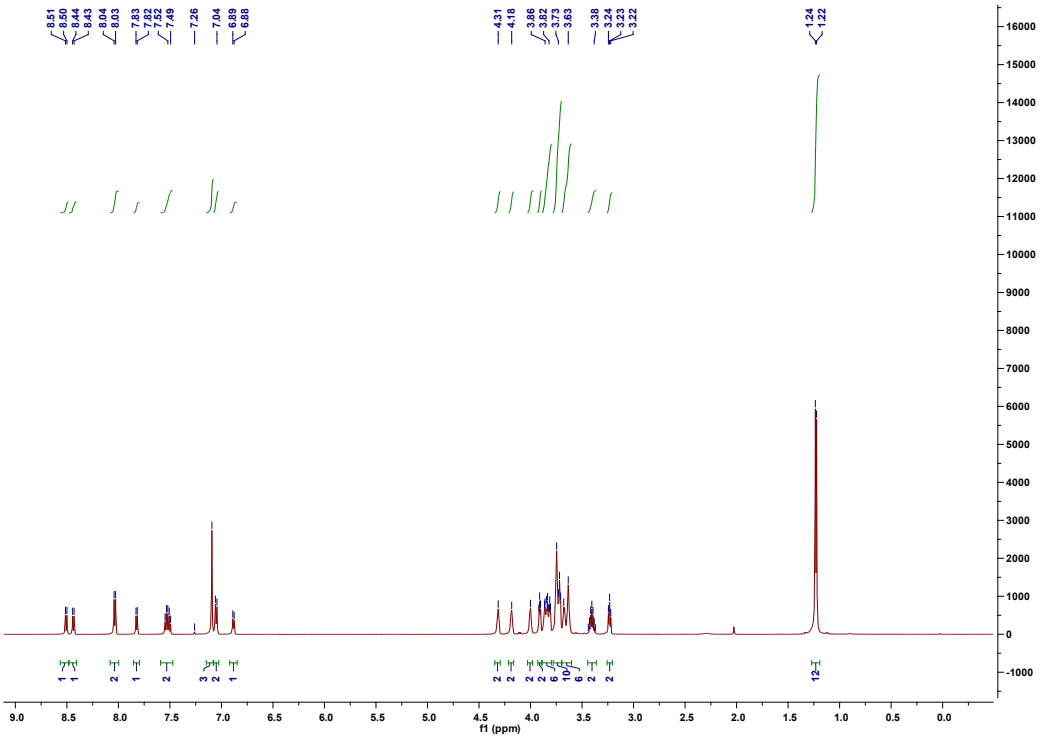
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **9**.



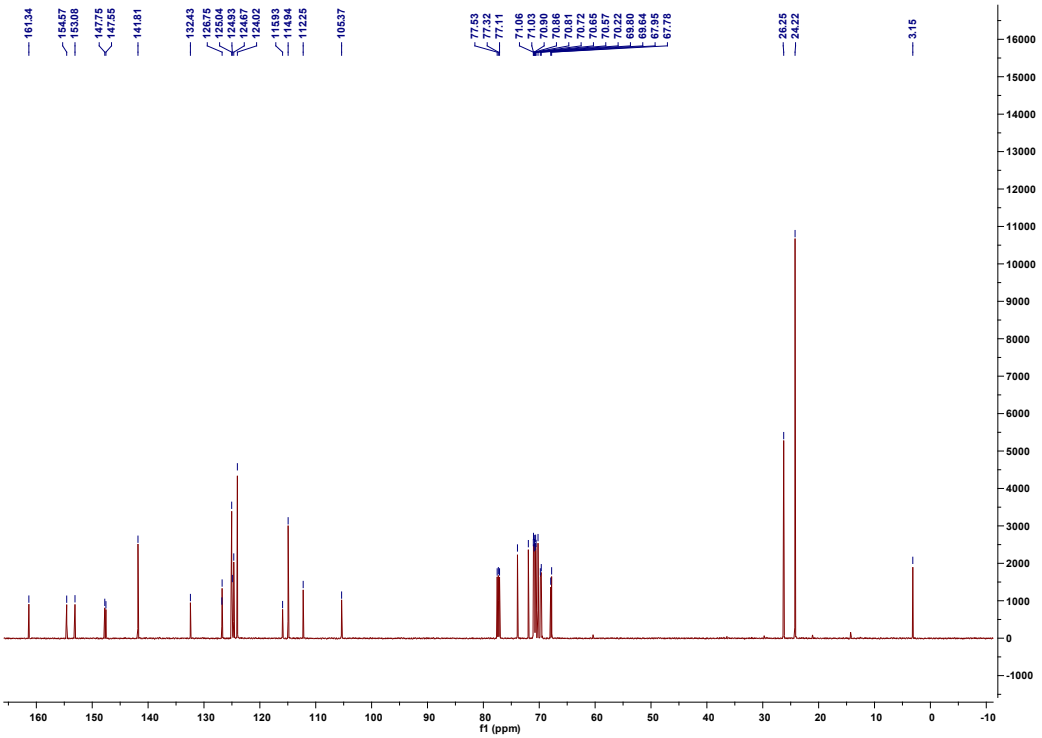
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **10**.



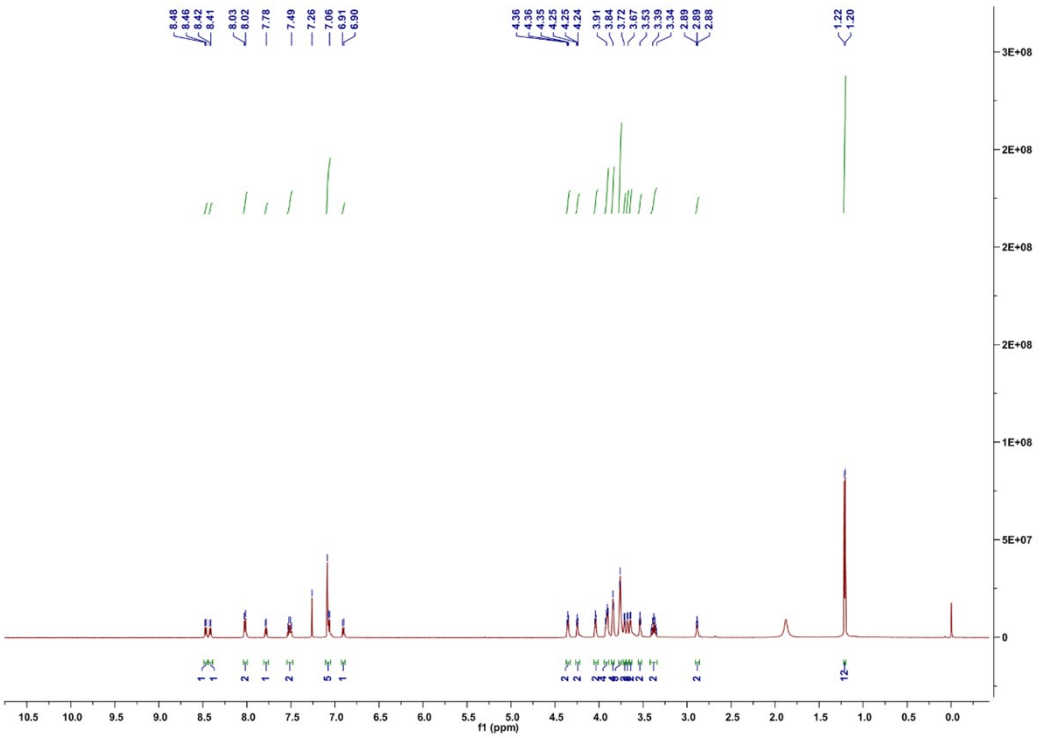
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **10**.



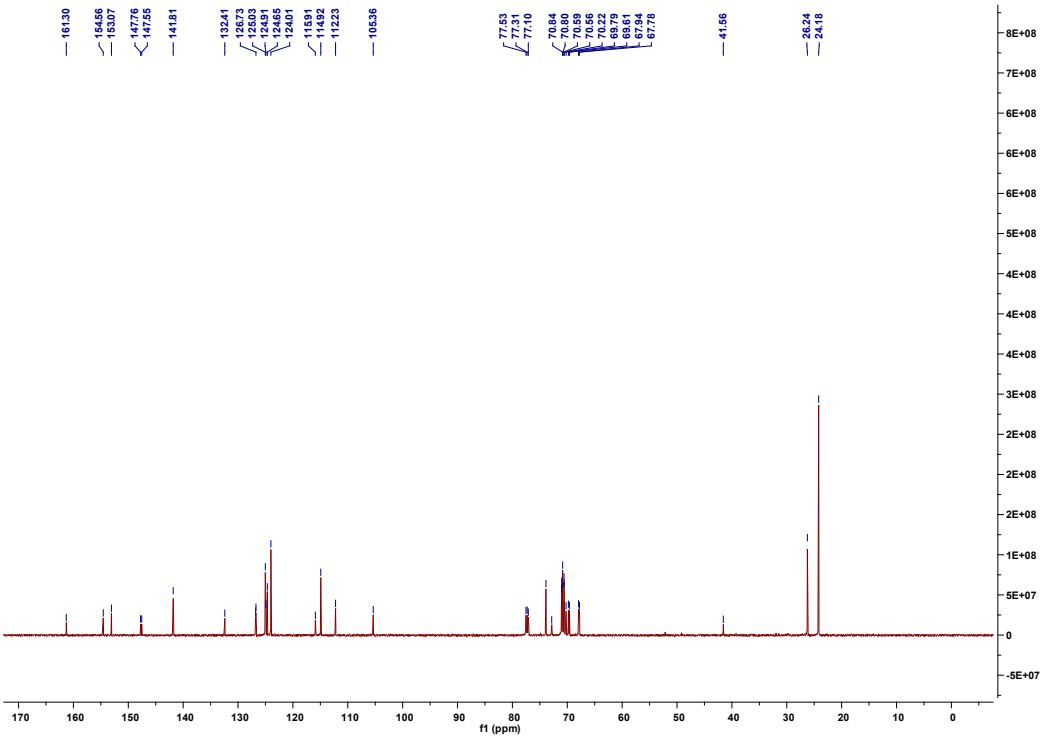
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **11**.



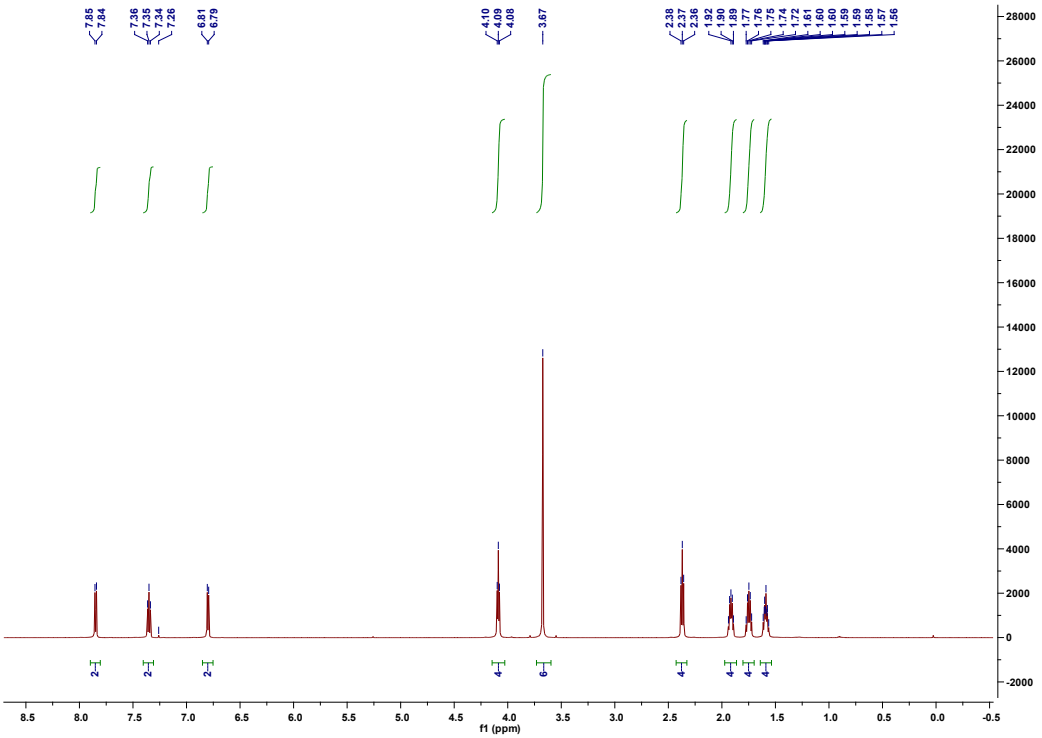
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **11**.



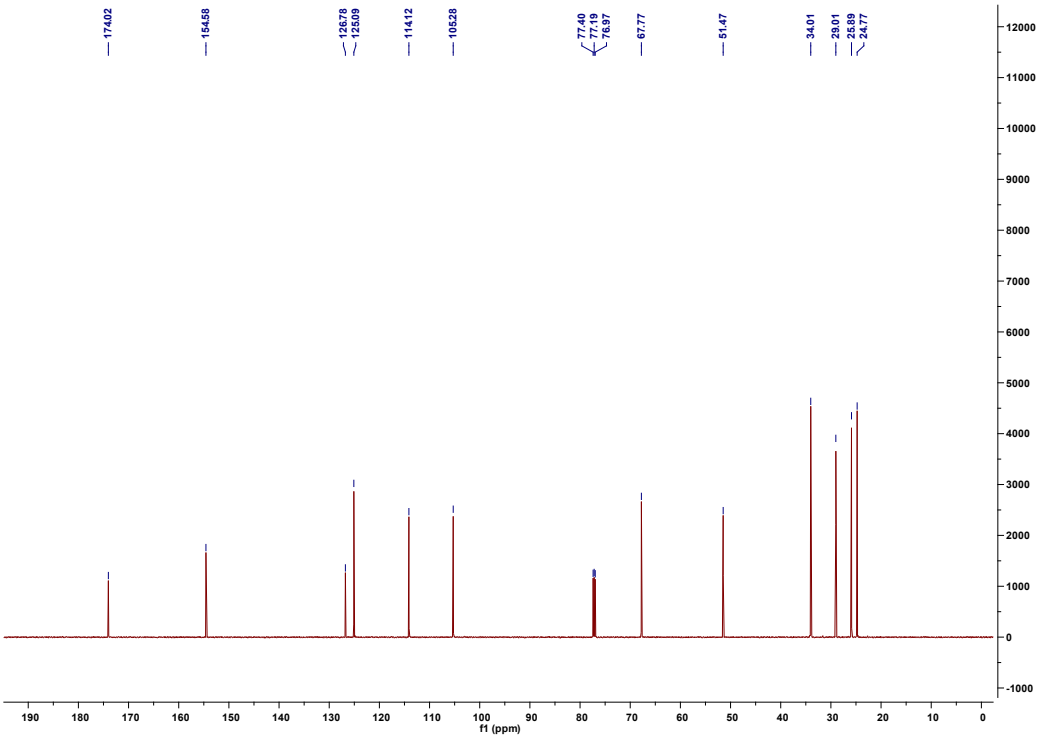
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **12**.



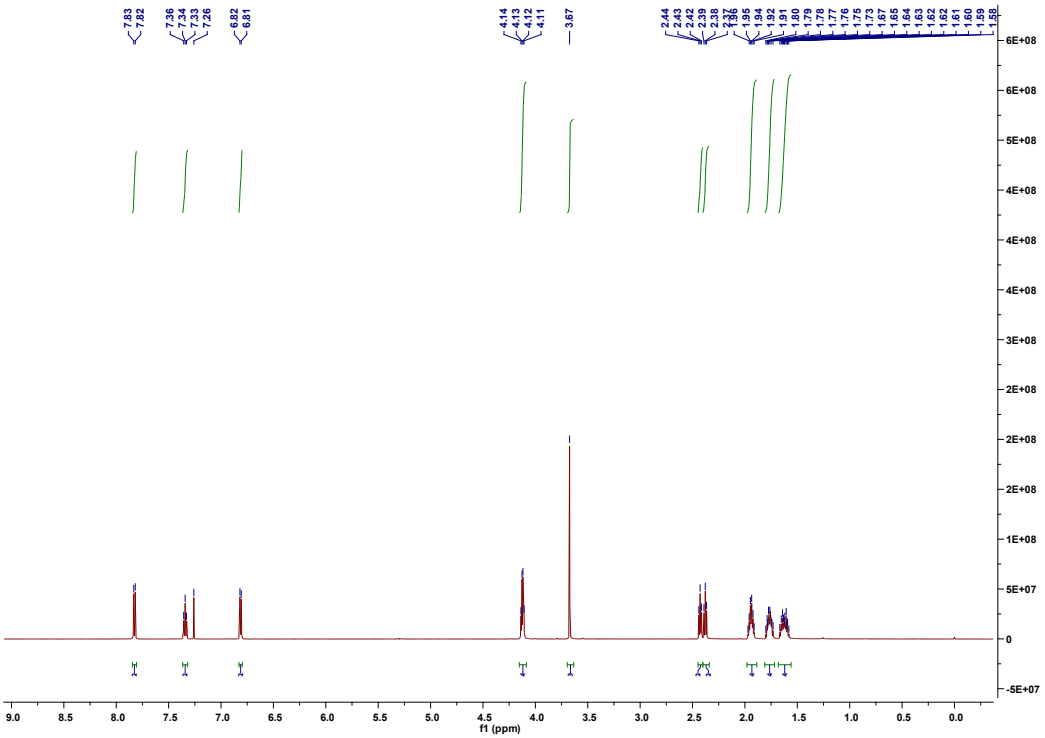
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **12**.



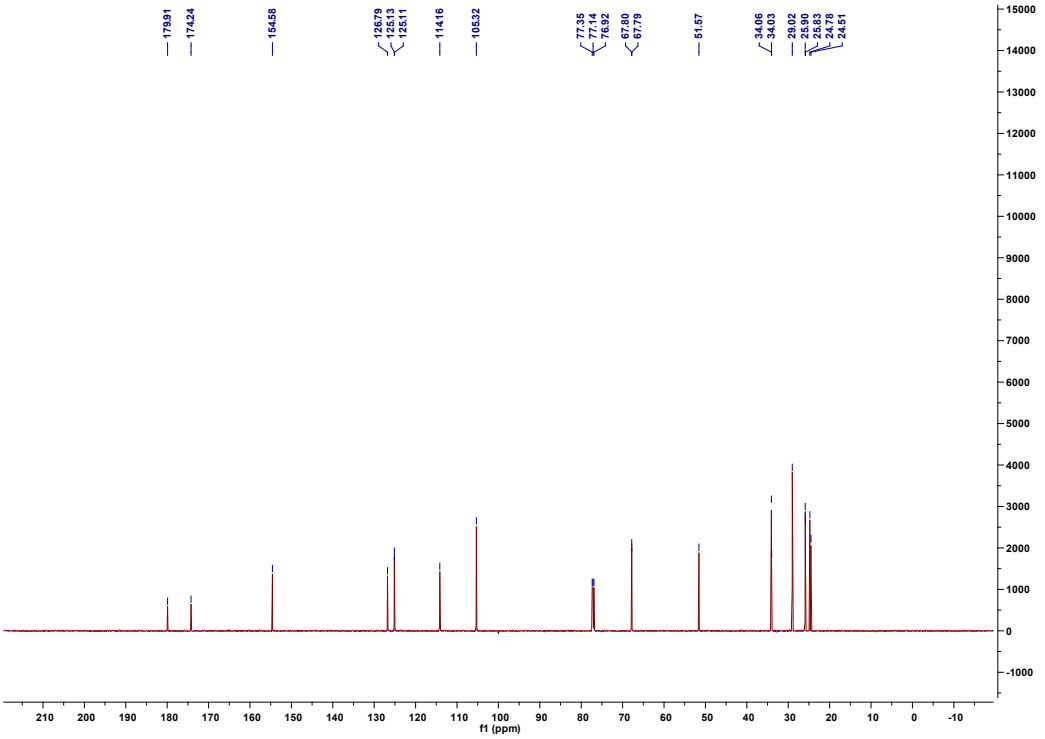
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **16**.



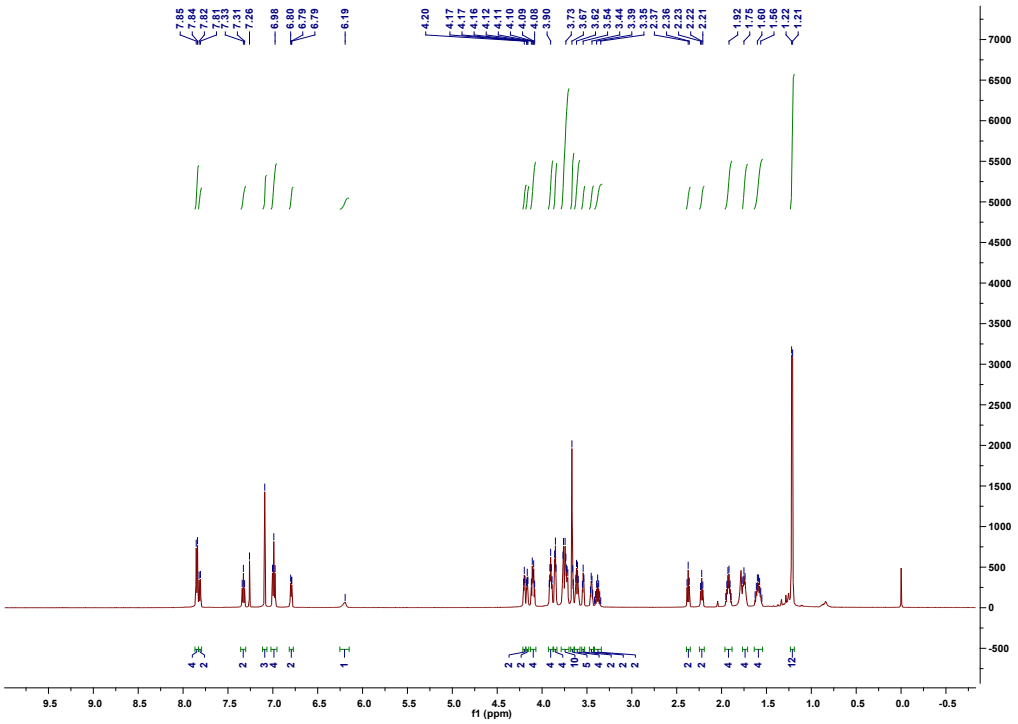
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **16**.



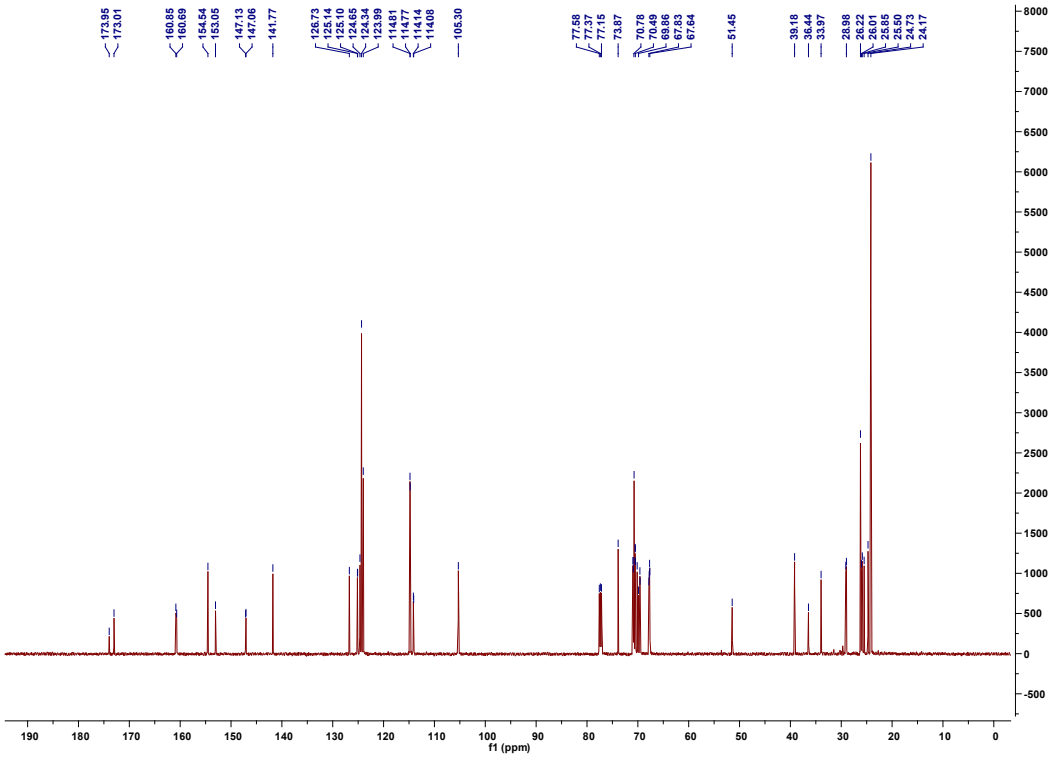
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **17**.



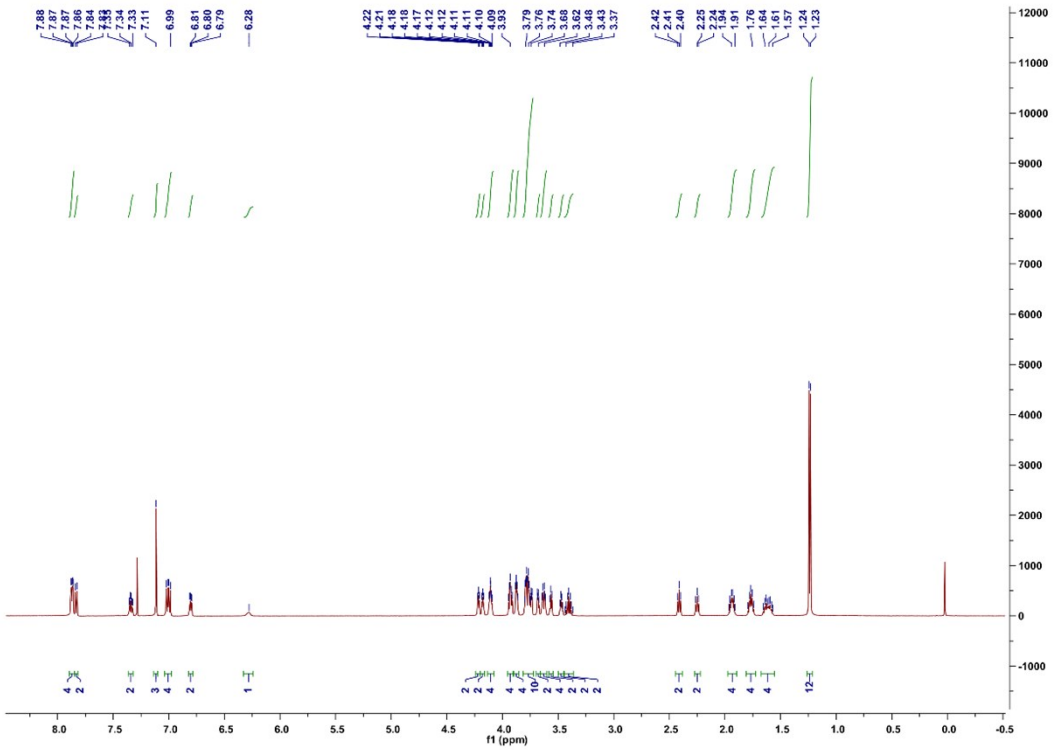
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **17**.



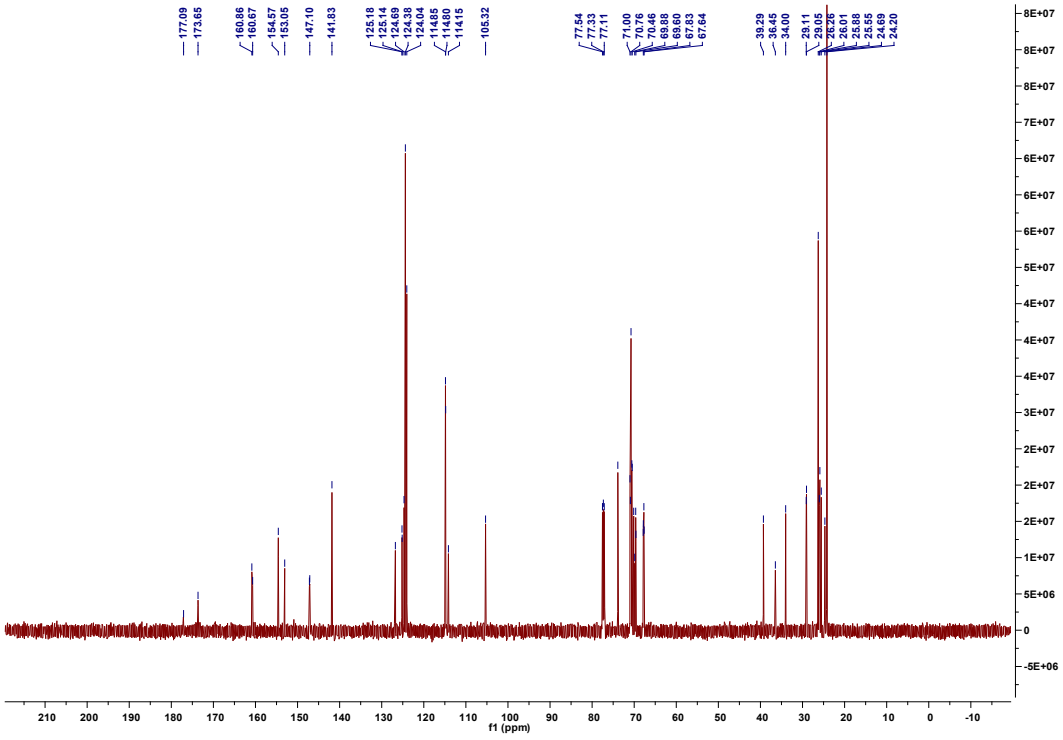
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **19**.



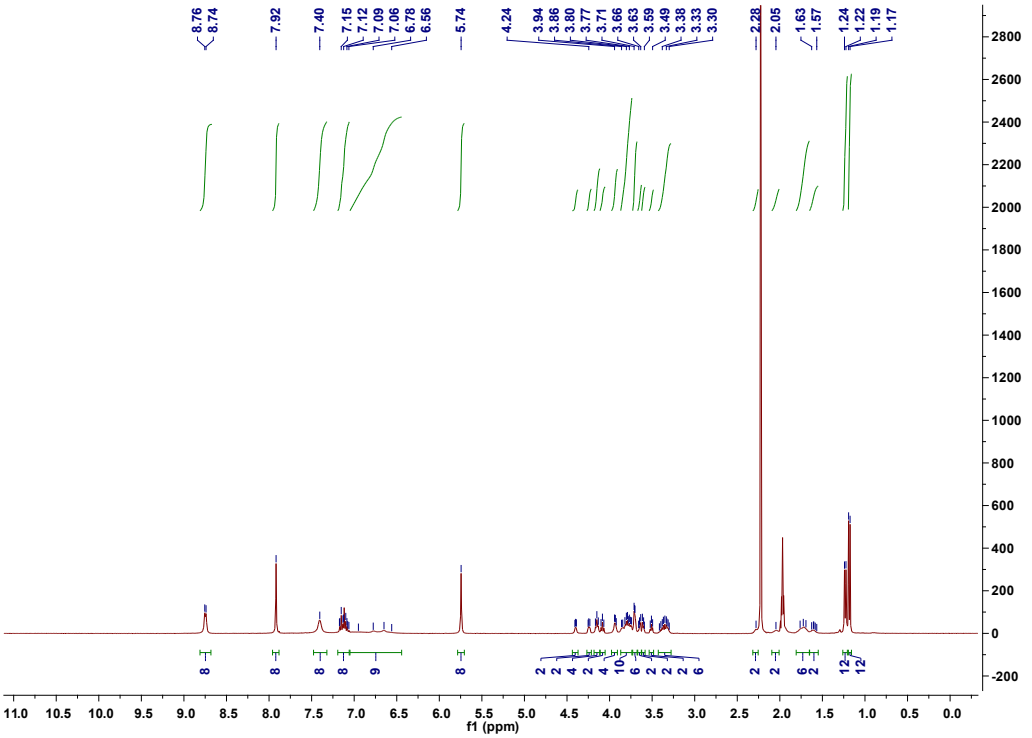
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **19**.



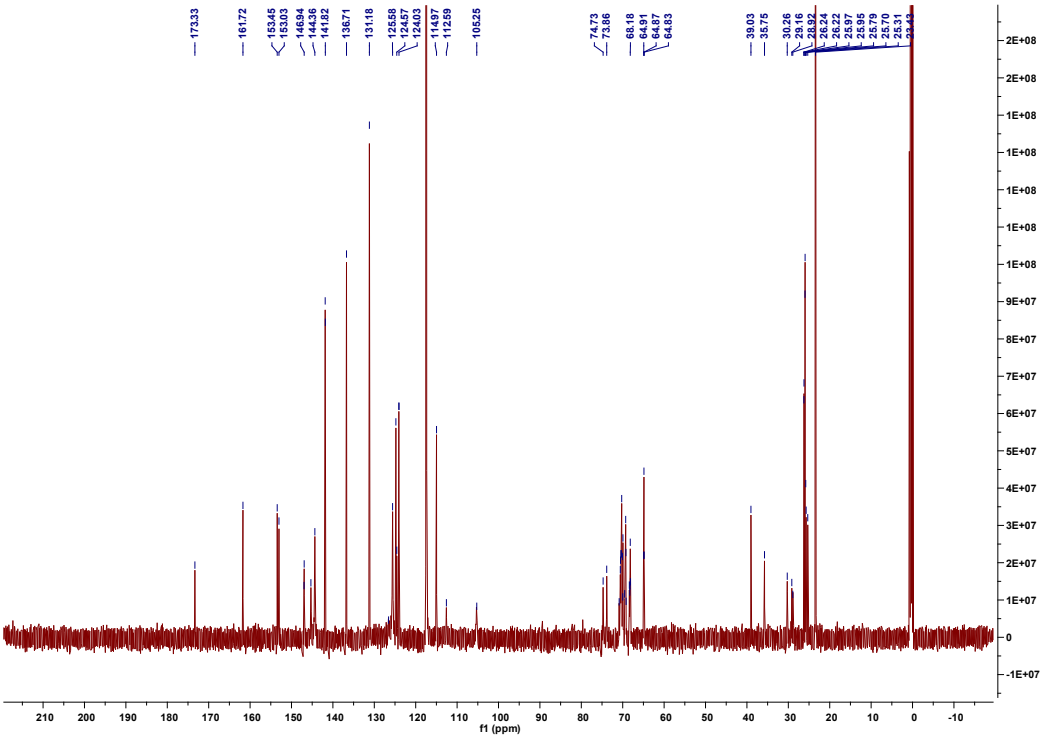
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **20**.



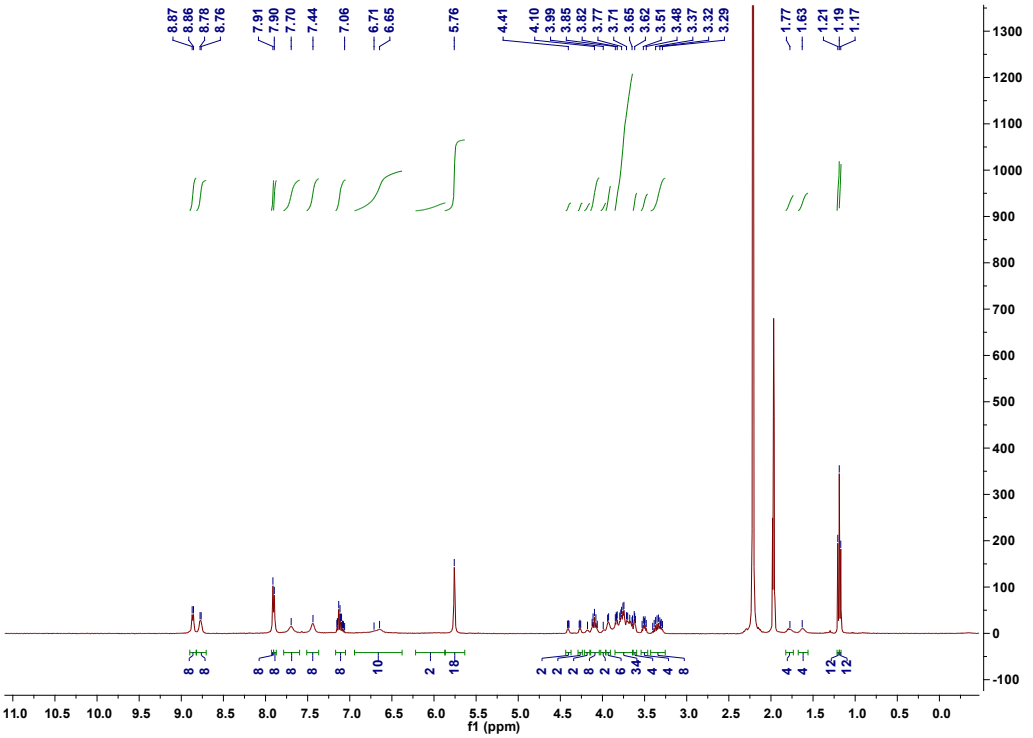
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **20**.



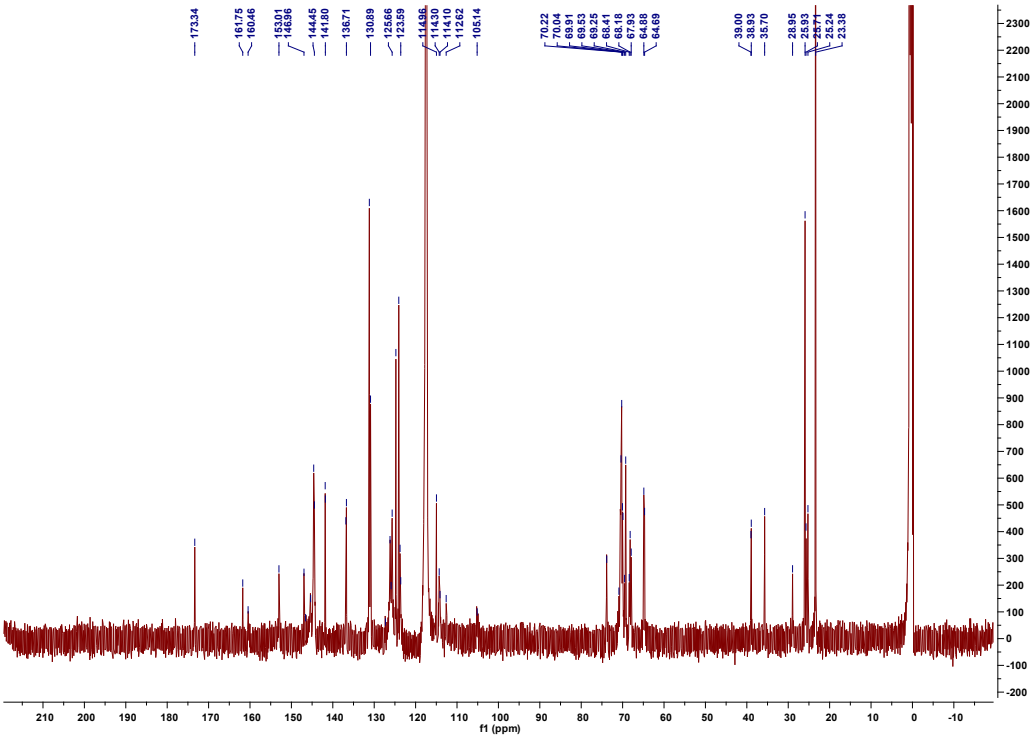
^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of [2]rotaxane **R2**.



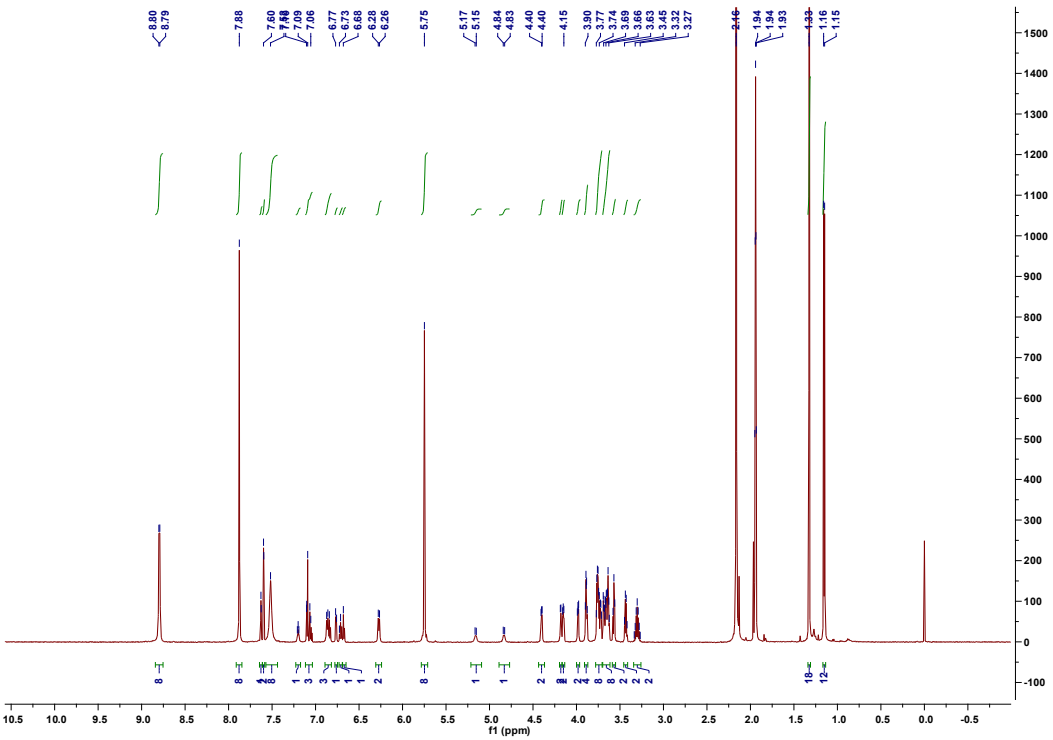
^{13}C NMR spectrum (150 MHz, CD_3CN, 298 K) of [2]rotaxane **R2**.



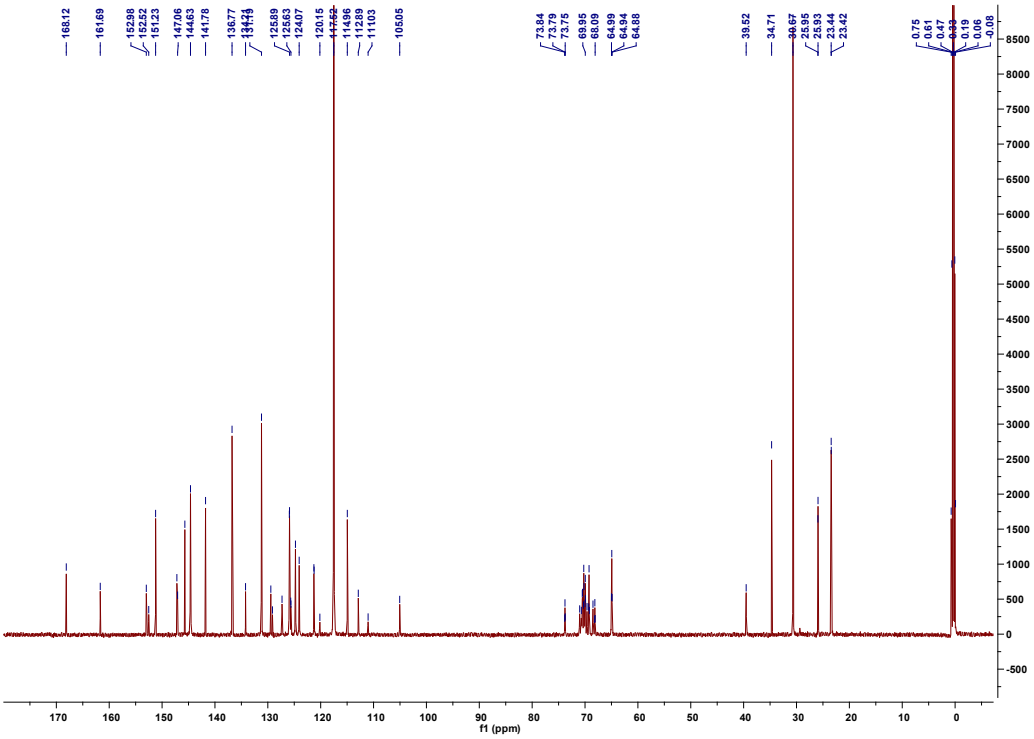
^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of [3]rotaxane **R1**.



^{13}C NMR spectrum (150 MHz, CD_3CN, 298 K) of [3]rotaxane **R1**.



^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of [2]rotaxane **R3**.



^{13}C NMR spectrum (150 MHz, CD_3CN, 298 K) of [2]rotaxane **R3**.

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