# Supporting Information

# Distinct Nanostructures and Organogel Driven by Reversible Molecular Switching of A Tetraphenylethene-Involved Calix[4]arene-Based Amphiphilic [2]Rotaxane

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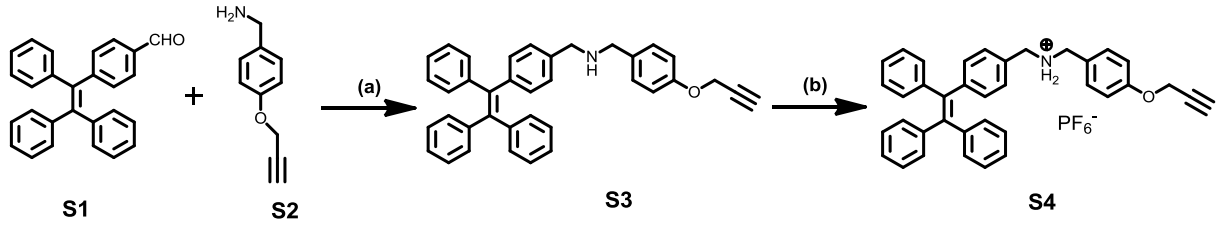
## ■ EXPERIMENTAL SECTION

**Materials and Instrumentations.** All solvents and reagents were purchased from Aldrich and used without further purification. The molecular structures of unknown compounds were confirmed by $^{1}$H NMR, $^{13}$C NMR spectra and HR-ESI mass spectroscopy. $^{1}$H NMR, $^{13}$C NMR spectra were measured on Agilent-NMR400–VNMRs. Chemical shifts (δ) were expressed in parts per million from low to high fields and coupling constants (J) in Hertz. The NMR assignments of target molecules were done with 2D TOCSY and ROESY (Varian Inova 600). UV-vis spectra were measured on a Jasco UV-600 spectrometer (1 cm quartz cell). Fluorescence spectra were recorded on HITACHI 7000 spectrometer (1 cm quartz cell). FTIR spectroscopy data were recorded using Perkin Elmer IR spectrophotometer.

### Synthesis overview

### Preparation of S4

The following compounds of **S1**[1] and **S2**[2] were synthesized according to the reported procedures.




**Scheme S1:** Synthesis of **S4** with reagents and conditions: (a) MeOH, $NaBH_4$, 0$^{o}$C, 24 h, 63%; (b) Con. HCl, MeOH, $NH_4PF_6$, $H_2O$, 70%.

**Synthesis of S3**

A mixture of **S1** (5.6 g, 0.01553 mol), and **S2** (2.5 g, 0.015536 mol) was dissolved in methanol (200 mL) and refluxed for 24 h. After cooled, $NaBH_4$ (5.877 g, 0.1553 mol) was added in portions at 0 ℃. After the suspension was stirred for another 24 h at room temperature, water was added to stop the reaction. After the solvent was reduced under vacuum, the residue was dissolved with $CH_2Cl_2$ (100 mL) and washed with water (50 mL) twice. The organic phase was dried and evaporated off. Then the residue was purified by column chromatography over silica gel (eluent: 100:1 $CH_2Cl_2$/MeOH) to afford **S3** as a yellow oil (5 g, 63%). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.24 (d, 2H, *J* = 8.4 Hz), 7.10–7.07 (m, 10H), 7.05–7.02 (m, 7H), 6.99 (d, 2H, *J* = 8.2 Hz), 6.94 (d, 2H, *J* = 8.6 Hz), 4.68 (d, 2H, *J* = 2.4 Hz), 3.70 (s, 4H), 2.51 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) = 156.60, 143.82, 143.76, 143.74, 142.42, 140.85, 140.77, 138.32, 133.37, 131.38, 131.34, 129.42, 127.67, 127.65, 127.48, 126.42, 126.39, 114.83, 78.69, 75.51, 55.87, 52.81, 52.50. HRMS ($ESI^+$) $[M+H]^+$: calcd for $C_{37}H_{32}NO$ 506.2478, found 506.2507.

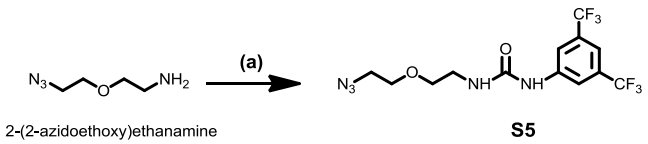
**Synthesis of S4**

To the solution of compound **S3** (3.32 g, 0.00638 mol) in MeOH (25 mL) was added conc. HCl to adjust pH < 2, and the solvent was then evaporated off under reduced pressure. The residue was suspended in acetone (25 mL). A saturated aqueous solution of $NH_4PF_6$ was added until the suspension became clear. The solvent was removed in vacuum, and water (50 mL) was added to the residue and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, yielding a yellow glassy solid **S4** (3 g, 70%) and was pure enough to use without

further purification. $^{1}$H NMR (400 MHz, $CD_3CN$) δ (ppm) = 7.32 (d, 2H, *J* = 8.2 Hz), 7.17–7.14 (m, 11H), 7.09–7.05 (m, 8H), 7.0 (d, 2H, *J* = 8.5 Hz), 4.76 (d, 2H, *J* = 2.0 Hz), 3.92 (s, 2H), 3.90 (s, 2H), 2.83 (s, 1H). $^{13}$C NMR (100 MHz, $CD_3CN$) δ (ppm) = 157.75, 144.10, 143.52, 143.50, 143.45, 141.61, 140.43, 131.24, 130.92, 130.86, 130.82, 128.77, 127.81, 127.76, 126.61, 117.35, 115.01, 78.61, 76.00, 55.59, 51.20, 51.02. HRMS ($ESI^+$) $[M–PF_6^-]^+$: calcd for $C_{37}H_{32}NO$ 506.2478, found 506.2493

**Preparation of S5**

The following compound of 2-(2-azidoethoxy)ethanamine was synthesized according to the reported procedure.[3]




**Scheme S2:** Synthesis of **S5** with reagents and conditions: (a) 3,5-bis(trifluoromethyl)phenyl isocyanate, DCM, rt, overnight, 41%.

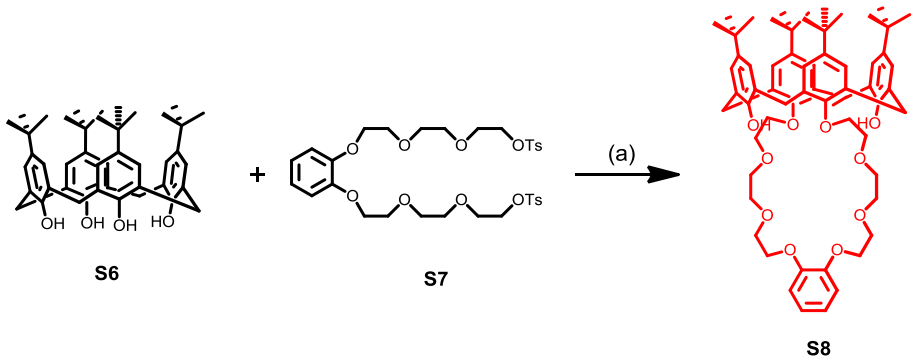
**Synthesis of S5**

A.R-1-5 (3.0 g, 0.0230 mol) was dissolved in dry DCM, and 3,5-bis(trifluoromethyl)phenyl isocyanate (4.0 mL, 0.0230 mol) was added dropwise and stirred at ambient temperature overnight. After the solvent was removed in vacuum, the crude product was purified by column chromatography over silica gel (eluent: Hexane/EA 8:2 ) to afford **S5** yielding a pale yellow solid (3.65 g, 41 %). $^{1}$H NMR (400 MHz, $CD_3CN$) δ (ppm) = 8.01 (s, 2H), 7.87 (s, 1H), 7.53 (s, 1H), 5.65 (br, 1H), 3.67–3.65 (m, 2H), 3.58 (t, 2H, *J* = 4.6 Hz), 3.41–3.37 (m, 4H). $^{13}$C NMR (100 MHz, $CD_3CN$) δ (ppm) = 160.23, 147.35, 136.78, 136.46, 130.19, 127.49, 119.80,

119.76, 119.72, 119.68, 74.91, 74.66, 55.76, 44.80. HRMS ($ESI^+$) $[M+H]^+$: calcd for $C_{13}H_{13}F_6N_5O_2$ 386.1007, found 386.1044

**Preparation of S8**

The following compounds of **S6** and **S7** were synthesized according to the reported procedure.[4,5]



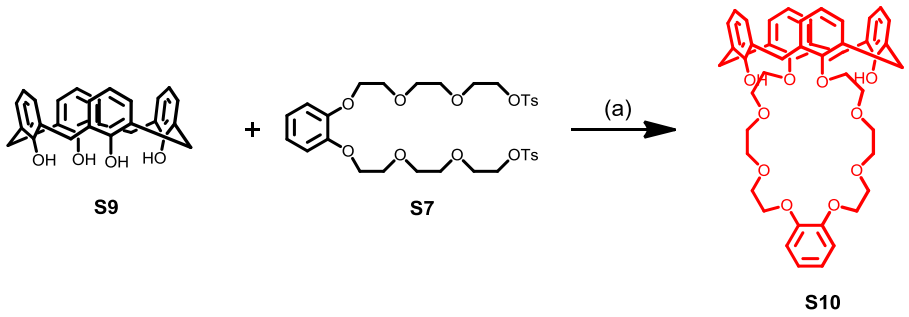

**Scheme S3.** Synthesis of **S8** with reagents and conditions: (a) $K_2CO_3$, ACN, reflux, 3 days, 72%.

**Synthesis of S8**

A mixture of **S6** (4.0 g, 0.006164 mol), **S7** (4.2 g, 0.006164 mol) and $K_2CO_3$ (1.7 g, 0.01232 mol), in dry acetonitrile (150 mL) was refluxed for 3 days. The reaction mixture was filtered and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: DCM/MeOH 9:1) to afford the desired product **S8** as a white solid (4.3 g, 72 % yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.30 (s, 2H), 7.05 (s, 4H), 6.91–6.85 (m, 4H), 6.78 (s, 4H), 4.35 (d, 4H, *J* = 13 Hz) 4.15–4.11 (m, 8H), 4.03–3.98 (m, 4H), 3.94–3.93 (m, 8H), 3.28 (d, 4H, *J* = 13 Hz), 1.29 (s, 18H), 0.95 (s, 18H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) = 150.69, 149.73, 149.00, 146.82, 141.23, 132.62, 127.77, 125.47, 124.99, 121.34, 114.03, 75.96, 71.32, 71.24, 70.20. 69.91. 69.38, 31.71, 31.45, 31.00. HRMS ($ESI^+$) $[M–H]^+$: calcd for $C_{62}H_{81}O_{10}$ 985.5835, found 985.5814.

**Preparation of S10**

The following compounds of **S9** was synthesized according to the reported procedure.[6]

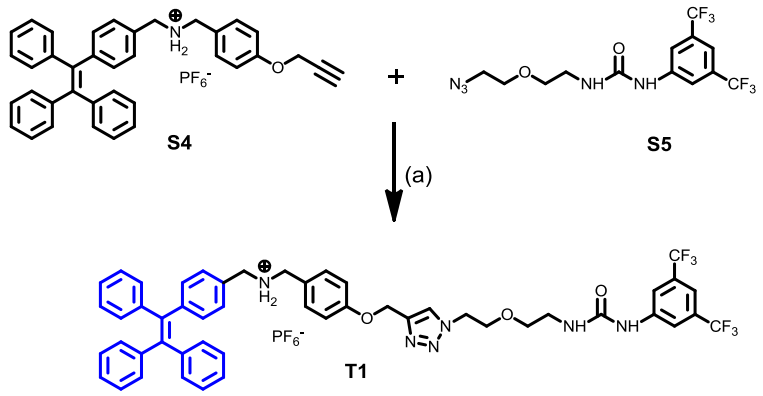



**Scheme S4.** Synthesis of **S10** with reagents and conditions: (a) $K_2CO_3$, ACN, reflux, 3 days, 40%.

**Synthesis of S10**

A mixture of **S9** (3.0 g, 0.0070 mol), **S7** (4.8 g, 0.0070 mol) and $K_2CO_3$ (1.95 g, 0.01414 mol), in dry acetonitrile (150 mL) was refluxed for 3 days. The reaction mixture was filtered and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: DCM/MeOH 9:1) to afford the desired product **S10** as a white solid (1.20 g, 40 % yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.86 (s, 2H), 7.04 (d, 4H, *J* = 7.4 Hz), 6.90–6.86 (m, 8H), 6.71 (t, 2H, *J* = 7.2 Hz), 6.64 (t, 2H, *J* = 7.4 Hz), 4.39 (d, 4H, *J* = 13 Hz), 4.15–4.12 (m, 8H), 4.07–4.06 ( m, 4H), 3.98–3.97 (m, 4H), 3.95–3.92 (m, 8H), 3.35 (d, 4H, *J* = 13 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) = 153.29, 151.78, 148.93, 133.36, 128.94, 128.41, 128.06, 125.35, 121.35, 118.87, 113.91, 75.98, 71.26, 71.19, 70.17, 69.88, 69.33, 31.16. HRMS ($ESI^+$) $[M+H]^+$: calcd for $C_{46}H_{51}O_{10}$ 763.3477, found 763.3485.

**Preparation of thread T1**



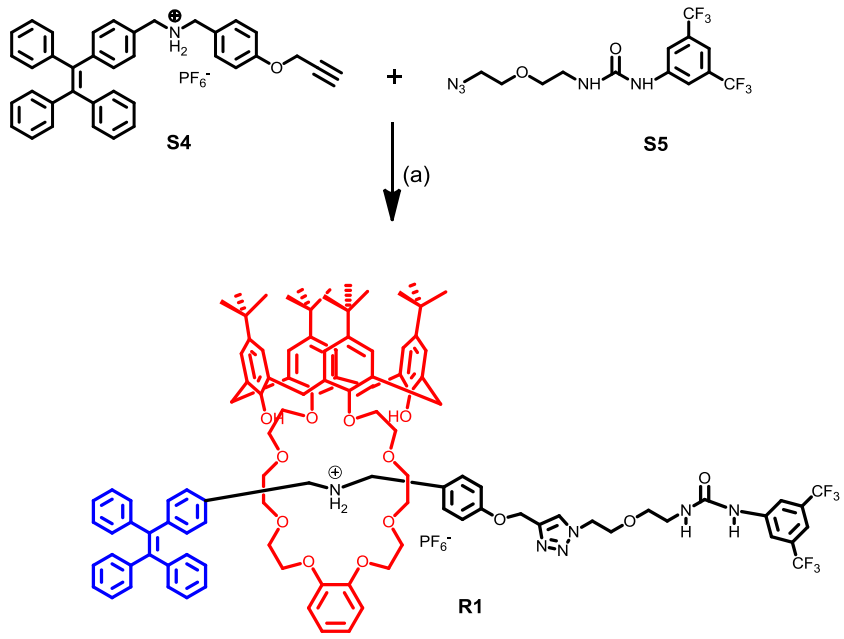

**Scheme S5.** Synthesis of **S4** with reagents and conditions: (a) NaAsc, $CuSO_4 \cdot 5H_2O$, $THF/H_2O$ (3:1), 24 h, 43%.

**Synthesis of thread T1**

To a solution of **S4** (500 mg, 0.76 mmol) and **S5** (305 mg, 0.76 mmol) in $THF/H_2O$ (v:v = 3:1, 60 mL) was added copper (II) sulfate pentahydrate (383 mg, 1.53 mmol) and sodium ascorbate (600 mg, 3.04 mmol). The reaction mixture was stirred for 24 h at room temperature under $N_2$ atmosphere. The THF was removed and the residue was washed twice with $CHCl_3$ (100 ml). Then the organic phase was dried over anhydrous $MgSO_4$, then concentrated. The crude product was purified by column chromatography over silica gel (eluent: 9:1 $CHCl_3$/MeOH) to afford **T1** as a white solid (350 mg, 43%). $^1$H NMR (400 MHz, $CD_3CN$) δ (ppm) = 8.03 (s, 2H), 7.93 (s, 1H), 7.82 (s, 1H), 7.52 (s, 1H), 7.20 (d, 2H, *J* = 8.4 Hz), 7.14–7.03 (m, 17H), 6.99 (d, 2H, *J* = 8 Hz), 6.91 (d, 2H, *J* = 8.4 Hz), 5.61 (s, 1H), 5.11 (s, 2H), 4.55 (t, 2H, *J* = 4.9 Hz), 3.86 (t, 2H, *J* = 2.4 Hz), 3.65 (s, 2H), 3.63 (s, 2H), 3.51 (t, 2H, *J* = 5.3 Hz), 3.30 (q, 2H, *J* = 5.4 Hz). $^{13}$C NMR (100 MHz, $CD_3CN$) δ (ppm) = 157.26, 154.76, 143.78, 143.76, 143.47, 142.21, 142.15, 140.94, 138.69, 130.85, 130.78, 129.39, 127.72, 127.70, 126.43, 117.70,

117.31, 114.49, 114.42, 114.39, 69.56, 68.77, 61.39, 52.06, 51.83, 50.00, 39.32. HRMS ($ESI^+$) $[M–PF_6]^+$: calcd for $C_{50}H_{45}F_6N_6O_3$ 891.3452, found 891.3433.

**Preparation of [2]rotaxane R1**



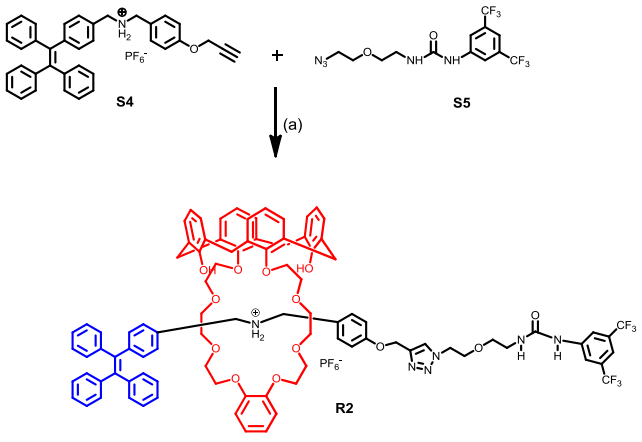

**Scheme S6.** Synthesis of **R1** with reagents and conditions: (a) Dry DCM, S8, Cu $(CH_3CN)_4PF_6$, 2, 6-lutidine, 2 days, 28%.

**Synthesis of [2]rotaxane R1**

To a solution of **S4** (1.0 g, 1.53 mmol), **S5** (600 mg, 1.53 mmol), and **S8** (2.26 g, 2.29 mmol) in dichloromethane (100 mL) was added $Cu(MeCN)_4PF_6$ (1.142 g, 3.06 mmol) and 2,6-lutidine (15 μL). The reaction mixture was stirred for 48 h at room temperature, The solvent was removed, and water (100 mL) was added to the residue. The resulting mixture was then filtered, washed with water, and dried. Then the residue was purified by column chromatography over silica gel (eluent: 9:1 DCM/MeOH) to afford [2]rotaxane **R1** as a

white solid (500 mg, 16%).$^{1}$H NMR (400 MHz, $CD_3CN$) δ (ppm) = 8.20 (s, 1H), 8.03 (s, 2H), 7.97 (s, 1H), 7.89 (s, 1H), 7.80 (br, 2H), 7.53 (s, 2H), 7.24–7.21 (m, 6H), 7.19 (d, 4H, *J* = 5.6 Hz), 7.16–7.14 (m, 11H), 7.13–7.12 (m, 6H),7.11–7.04 (m, 2H), 7.03–7. 01 (m, 2H), 7.00–6. 92 (m, 2H) 6.86–6.69 (m, 2H), 6.59 (d, 2H, *J* = 8.6 Hz), 5.66 (t, 1H, *J* = 5.4 Hz), 4.91 ( s, 2H), 4.59 (t, 2H, *J* = 4.8 Hz), 4.45 (d, 2H, *J* = 12.6 Hz), (d, 4H, *J* = 12.6 Hz), 4.05 (t, 8H, *J* = 8.4 Hz), 3.90 (t, 4H, *J* = 5.1 Hz), 3.80–3.76 (m, 10H), 3.59–3.51 (m, 8H), 3.41–3. 34 (m, 6H), 1.23 (d, 18H, *J* = 1.36 Hz), 1.16 (s, 18H). $^{13}$C NMR (100 MHz, $CD_3CN$) δ (ppm) = 158.86, 154.80, 149.68, 149.00, 148.25, 146.31, 144.17, 143.56, 143.32, 142.65, 142.24, 133.96, 133.93, 131.75, 130.94, 130.80, 130.67, 130.29, 128.00, 127.84, 127.75, 127.72, 127.45, 126.02, 125.26, 123.47, 121.22, 114.34, 111.83, 74.38, 71.09, 69.74, 69.60, 69.57, 69.40, 68.80, 67.95, 61.12, 52.26, 51.70, 50.03, 39.35, 34.00, 33.60, 30.94, 30.87, 30.45. HRMS (ESI$^+$) $[M–PF_6]^+$: calcd for $C_{112}H_{127}F_6N_6O_{13}$ 1877.9360, found 1877.9354.

**Preparation of [2]rotaxane R2**

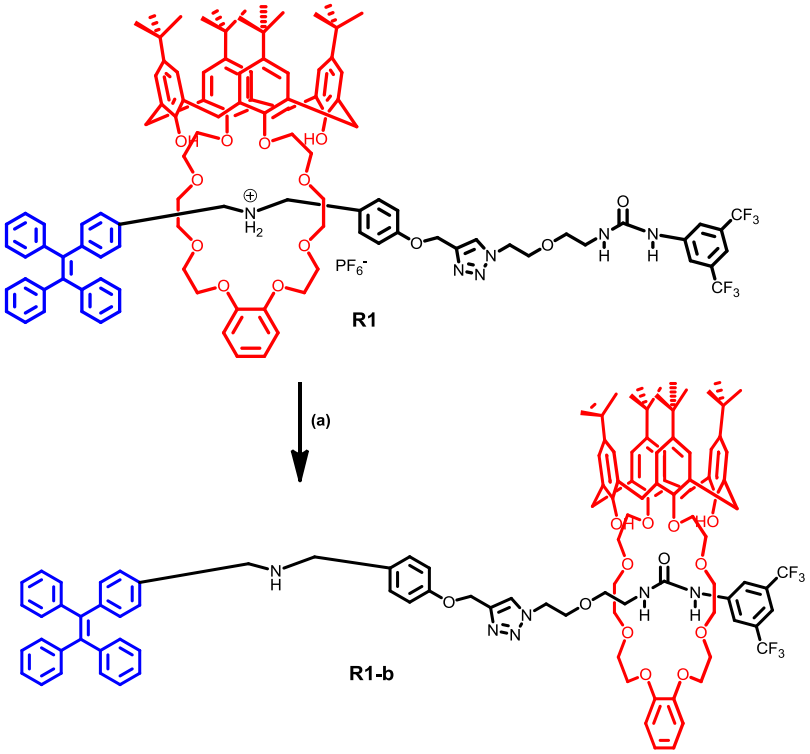



**Scheme S7.** Synthesis of **R2** with reagents and conditions: (a) Dry DCM, S10, $Cu(CH_3CN)_4PF_6$, 2, 6-lutidine, 2 days, 28%.

**Synthesis of [2]rotaxane R2**

To a solution of **S4** (0.75 g, 1.15 mmol), **S5** (443 mg, 1.15 mmol), and **S10** (877 g, 1.15 mmol) in dichloromethane (75 mL) was added $Cu(MeCN)_4PF_6$ (857 mg, 2.3 mmol) and 2,6-lutidine (15 μL,). The reaction mixture was stirred for 48 h at room temperature, The solvent was removed, and water (100 mL) was added to the residue. The resulting mixture was then filtered, washed with water, and dried. Then the residue was purified by column chromatography over silica gel (eluent: 9:1 DCM/MeOH) to afford [2]rotaxane **R2** as a white solid (340 mg, 17%). $^1$H **NMR** (400 MHz, $CD_3CN$) δ (ppm) = 8.03 (s, 2H), 7.97 (s, 1H), 7.82 (s, 1H), 7.72 (br, 2H), 7.64 (s, 1H), 7.53 (s, 1H), 7.15 (d, 2H, *J* = 7.6 Hz), 7.16–7.12 (m, 14H), 7.05–6.95 (m, 12H), 6.85–6.81 (m, 5H), 6.72–6.67 (m, 4H), 6.58 (d, 2H, *J* = 8.24 Hz), 5.64 (s, 1H), 4.92 (s, 1H), 4.68–4.58 (m, 6H), 4.39 (d, 2H, *J* = 13.0 Hz), 4.30 (d, 2H, *J* = 13.0 Hz), 4.17–4.13 (m, 2H), 4.05–3.97 (m, 4H), 3.94–3.89 (m, 4H), 3.80–3.73 (m, 8H), 3.62–3.55 (m, 10H), 3.42 (d, 4H, *J* = 13.0 Hz). 3.35 (q, 2H, *J* = 5.3 Hz). $^{13}$C NMR (100 MHz, $CD_3CN$) δ (ppm) = 158.86. 152.76, 151.69, 146.38, 143.55, 133.80, 133.73, 131.23, 130.88, 130.81, 130.73, 130.68, 129.04, 128.90, 128.70, 127.97, 127.89, 127.85, 127.84, 127.75, 126.69, 126.58, 125.35, 124.61, 123.36, 121.20, 119.46, 114.36, 111.90, 74.80, 70.97, 69.55, 69.41, 69.33, 68.79, 67.92, 61.11, 52.38, 51.95, 50.03, 39.35, 30.42, 30.31. HRMS ($ESI^+$) $[M–PF_6]^+$: calcd for $C_{96}H_{95}F_6N_6O_{13}$ 1653.6856, found 1653.6834.

**Preparation of [2]rotaxane R1-b**



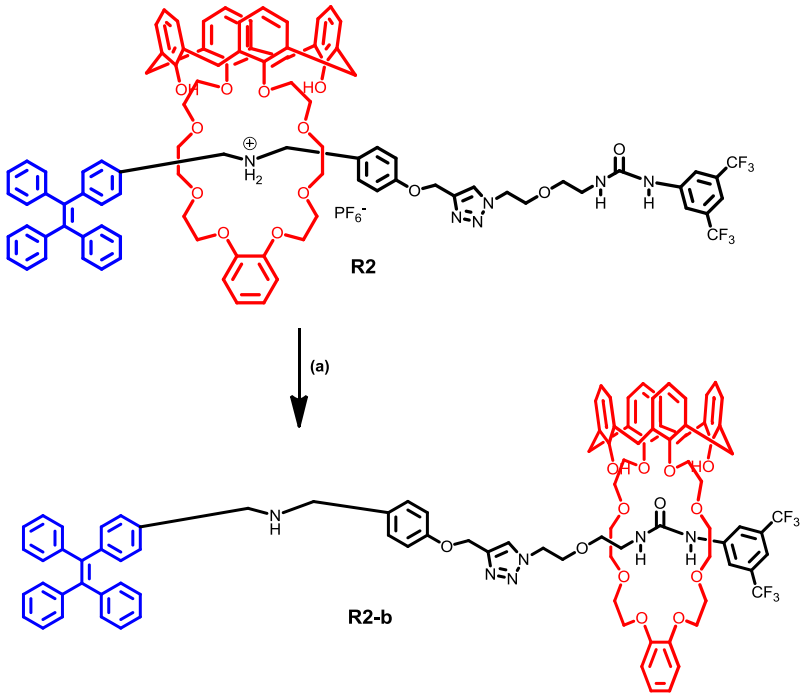

**Scheme S8.** Synthesis of **R1-b** with reagents and conditions: (a) DCM, aq. NaOH (0.1M), 2 hrs, 50%.

**Synthesis of [2]rotaxane R1-b**

**R1** (100 mg) was dissolved in chloroform (10 mL), aq. NaOH solution (0.1 M, 10 mL) was added dropwise, and the mixture was stirred at room temperature for 2 h. Then the solution was extracted with chloroform, the organic layer was combined and dried over $MgSO_4$. Removal of solvent under reduced pressure gave **R1-b** as a white solid. Yield: 50 mg, 50%. $^1$H NMR (400 MHz, $CD_3CN$) δ (ppm) = 8.12 (s, 1H), 7.95 (s,1H), 7.94 (s, 1H), 7.69 (s, 1H), 7.67–7.64 ( m, 3H), 7.55–7.53 (m, 2H), 7.43 (s,1H), 7.23–7.03 (m, 22H), 6.94–6.87 (m, 8H), 5.06 (s,2H), 4.36 (d, 4H, *J* = 12.5 Hz), 4.28 (d, 2H, *J* = 12.8 Hz), 4.16–4.05 (m, 9H), 3.89–3.83 (m, 14 Hz), 3.80–3.51 (m, 10 Hz), 3.36 (d, 2H, *J* = 12.5 Hz), 3.31 (t, 4H, *J* = 5.2 Hz), 1.23–1.19 (m, 18H), 1.17 (d, 9H, *J* = 1.7 Hz), 1.13

(s, 9H). $^{13}$C NMR (100 MHz, $CD_3CN$) δ (ppm) = 162.45, 160.16, 155.22, 155.06, 154.05, 153.25, 149.08, 148.74, 147.61, 147.32, 146.16, 144.59, 139.68, 137.03, 136.94, 136.16, 136.03, 134.54, 134.07, 133.95, 133.54, 132.99, 132.68, 131.71, 130.96, 130.34, 126.47, 119.73, 118.95, 80.58, 75.98, 75.79, 75.03, 74.90, 74.73, 74.06, 66.67, 57.44, 57.21, 55.26, 44.58, 39.27, 38.88, 36.17, 36.05, 35.83, 35.75. HRMS (ESI$^+$) $[M–PF_6]^+$: calcd for $C_{112}H_{127}F_6N_6O_{13}$ 1877.9360, found 1877.9360.

**Preparation of [2]rotaxane R2-b**




**Scheme S9.** Synthesis of **R2-b** with reagents and conditions: (a) DCM, aq. NaOH (0.1 M), 2 h, 50%.

**Synthesis of [2]rotaxane R2-b**

**R2** (100 mg) was dissolved in chloroform (10 mL), aq. NaOH solution (0.1 M, 10 mL) was added dropwise, and the mixture was stirred at room temperature for 2 h. Then the solution was extracted with chloroform, the organic layer was combined and dried over $MgSO_4$. Removal of solvent under reduced pressure gave **R2-b** as a white solid. Yield: 50 mg, 50%. $^1$H NMR (400 MHz, $CD_3CN$) δ (ppm) = 8.08 (s, 2H), 8.05 (s, 2H), 7.93 (s, 1H), 7.52 (s, 1H), 7.42 (br, 1H) 7.20 (d, 2H, *J* = 8.6 Hz), 7.14–7. 08 (m, 15H), 7.06–6.97 (m, 12H), 6.93–6.87 (m, 6H), 6.81 (t, 2H, *J* = 7.2 Hz), 6.65 (t, 2H, *J* = 7.4 Hz), 5.11 (s, 2H), 4.55 (t, 2H, *J* = 4.8 Hz), 4.39 (d, 4H, *J* = 12.9 Hz), 4.15–4.08 (m, 8H), 4.0–3.99 ( m, 4H), 3.89–3.78 (m, 10H), 3.64–3. 59 (m, 8H), 3.51 (t, 2H, *J* = 5.4 Hz), 3.42 (d, 4H, *J* = 13.0 Hz) 3.31 (q, 2H, *J* = 5.4 Hz). $^{13}$C NMR (100 MHz, $CD_3CN$) δ (ppm) = 157.17, 153.00, 152.11, 148.81, 143.81, 143.79, 143.47, 142.04, 141.01, 140.88, 139.29, 134.16, 133.48, 130.88, 130.75, 129. 26, 128.89, 128.56, 127.96, 127.72, 127.70, 127.40, 126.44, 126.42, 125.29, 124.55, 121.22, 119.25, 114.45, 113.80, 75.86, 70.75, 70.70, 69.75, 69.60, 69.49, 68.83, 68.77, 61.39, 52.16, 51.93, 49.98, 39.30, 30.51. HRMS (ESI$^+$) $[M–PF_6]^+$: calcd for $C_{96}H_{95}F_6N_6O_{13}$ 1653.6856, found 1653.6875.

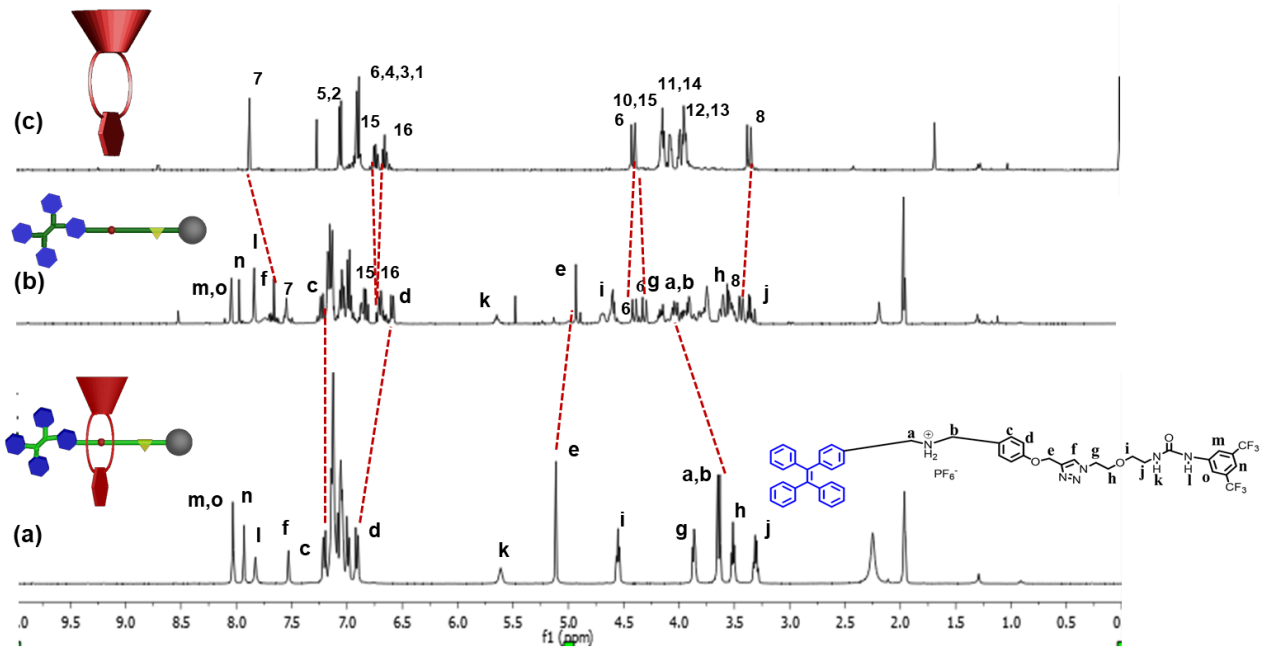



**Figure S1**. $^{1}$H NMR spectra (400 MHz, 298 K, $CD_3CN$) of (a) un-complexed thread **T1**, (b) [2]rotaxane **R2**, and (c) calix[4]arene macrocycle.

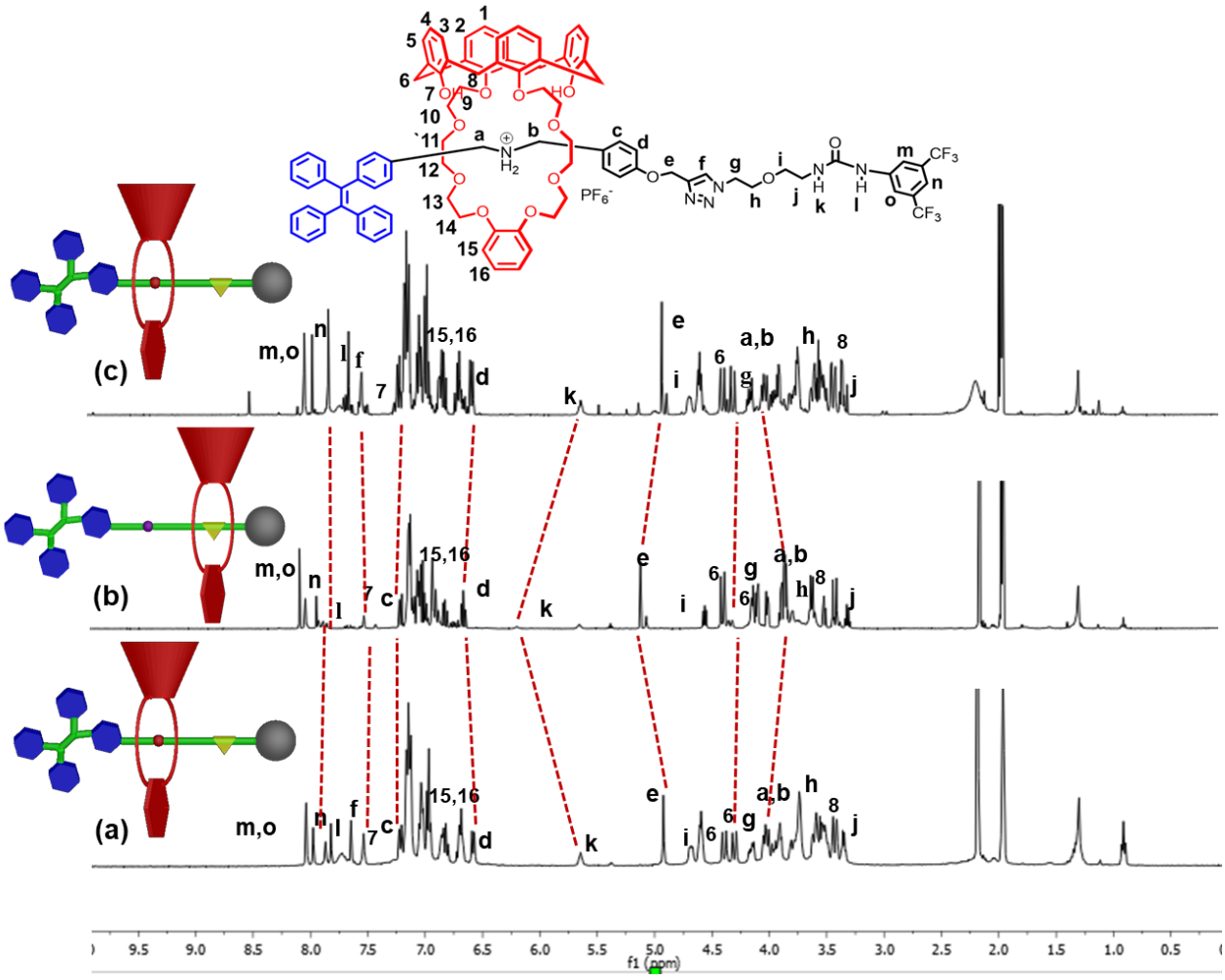



**Figure S2**. $^{1}$H NMR spectra (400 MHz, $CD_3CN$, 293 K) of [2]rotaxane **R2** (a) in its primary state, (b) after the addition of one equiv of base, and (c) further addition of one equiv of TFA to the solution of (b).

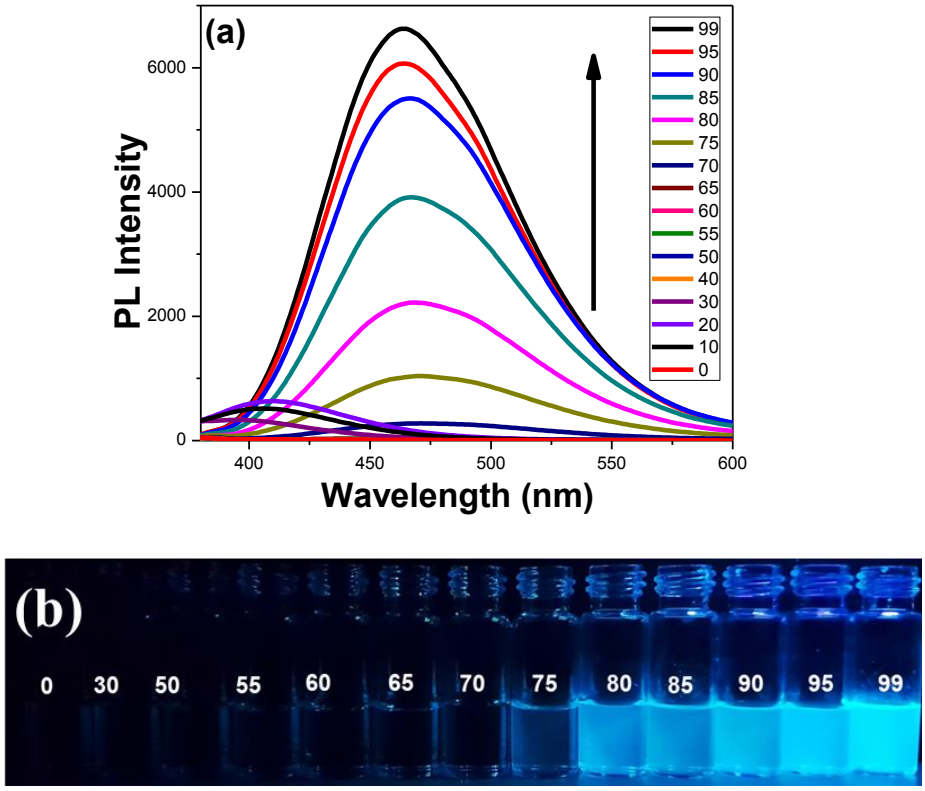



**Figure S3**. (a) Fluorescence spectra and (b) emission photographs of axle **T1** in $CH_3CN$/water mixtures with different water fractions $f_w$ ($\lambda_{ex}$ = 340 nm). The photo was taken under UV light irradiation at 365 nm.

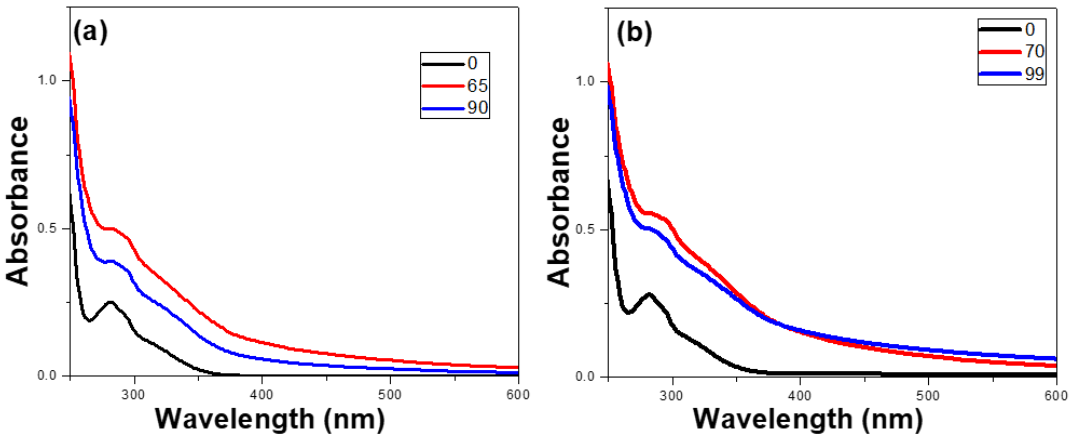



**Figure S4**. UV-vis absorption spectra in $CH_3CN$/water mixtures with different water fractions of (a) [2]rotaxane **R1** and (b) [2]rotaxane **R1-b**.

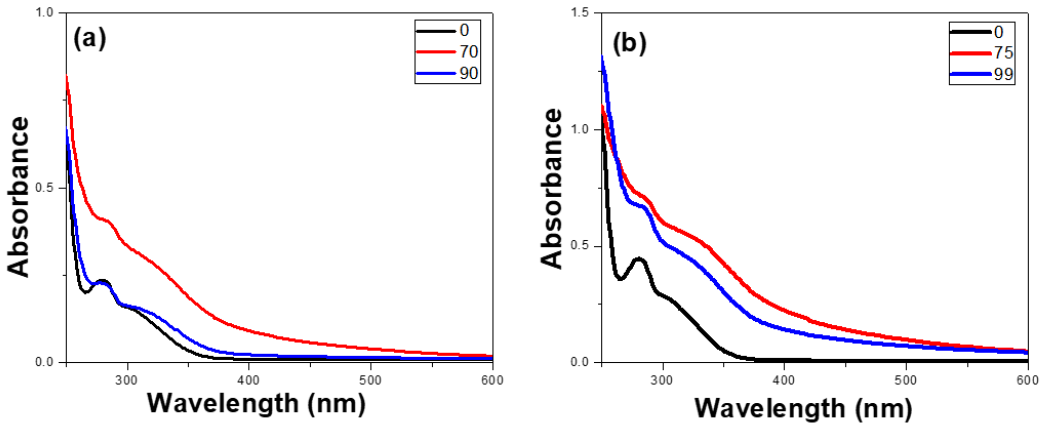



**Figure S5** UV-vis absorption spectra in $CH_3CN$/water mixtures with different water fractions of (a) [2]rotaxane **R2** and (b) [2]rotaxane **R2-b**.

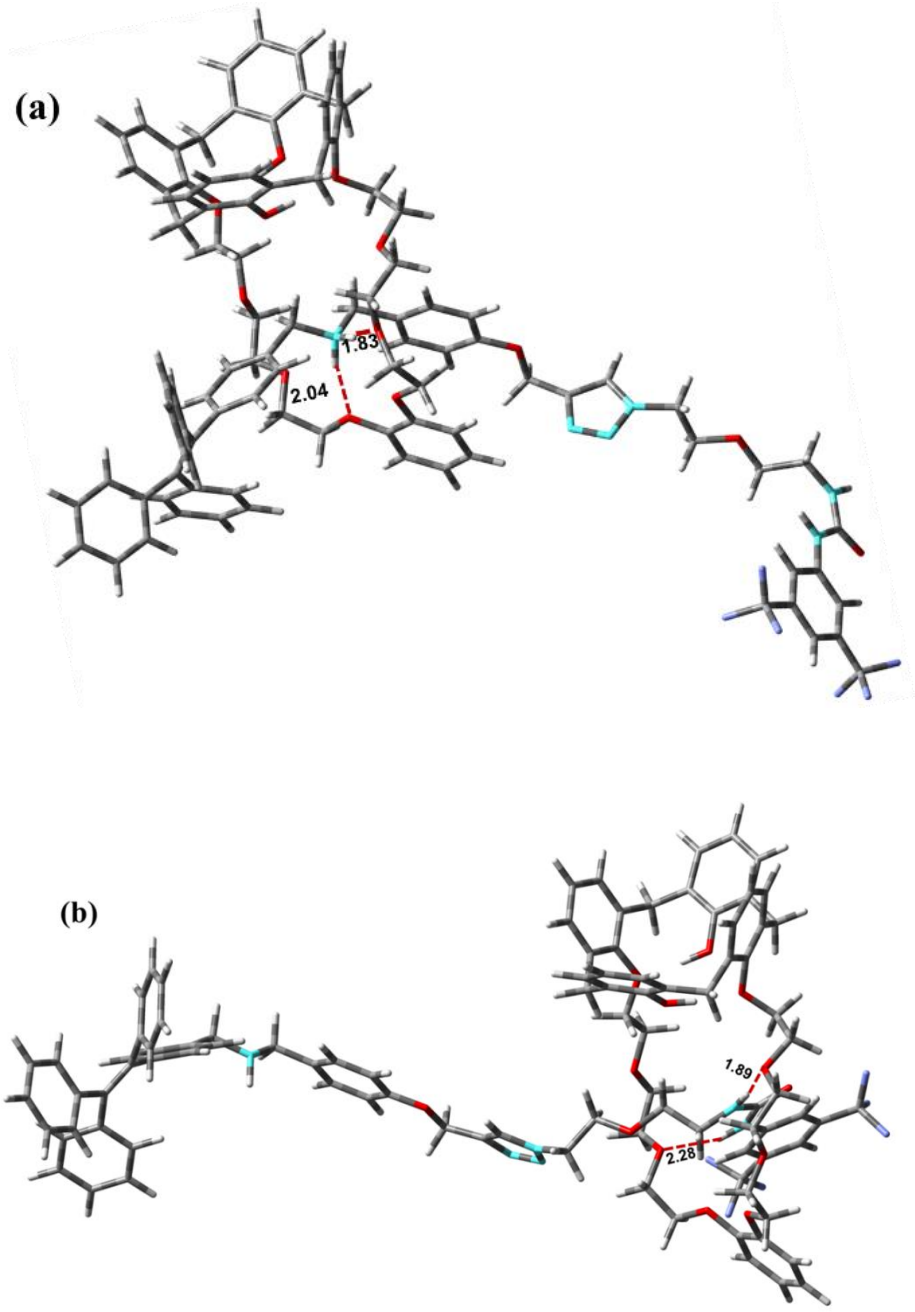



**Figure S6**. Optimized chemical structures of [2]rotaxane **R2** at different states (a) at original state and (b) deprotonated state [2]rotaxane **R2-b** complex at the B3LYP/6-31g level.

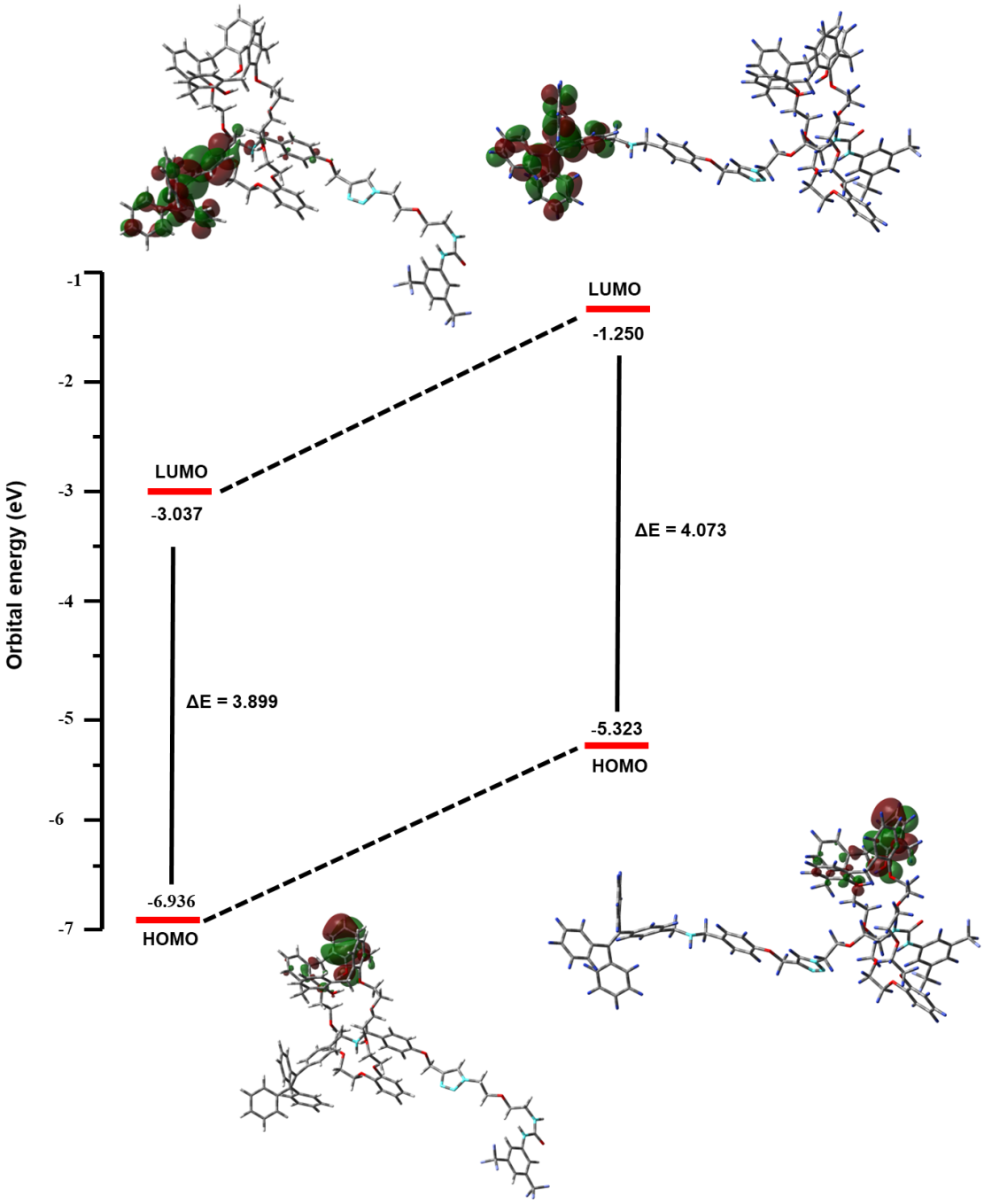



**Figure S7.** Frontier molecular orbital diagram of [2]rotaxane **R2** molecular switching mechanism at the B3LYP/6-31g level

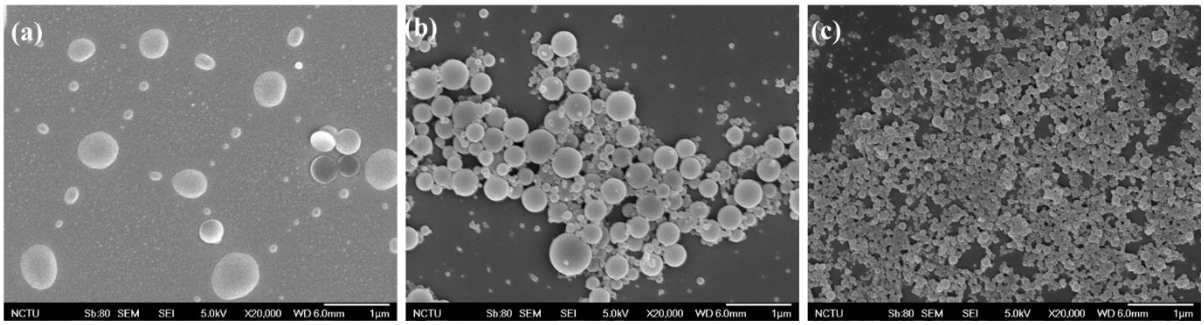



**Figure S8.** FE-SEM images of [2]rotaxane **R2** (10 μM): (a) in $CH_3CN$ only, (b) $CH_3CN$/water ($f_w$ = 70%) (c) $CH_3CN$/water ($f_w$ = 99%). Scale bar was 1 μm for Figures a, b, and c.

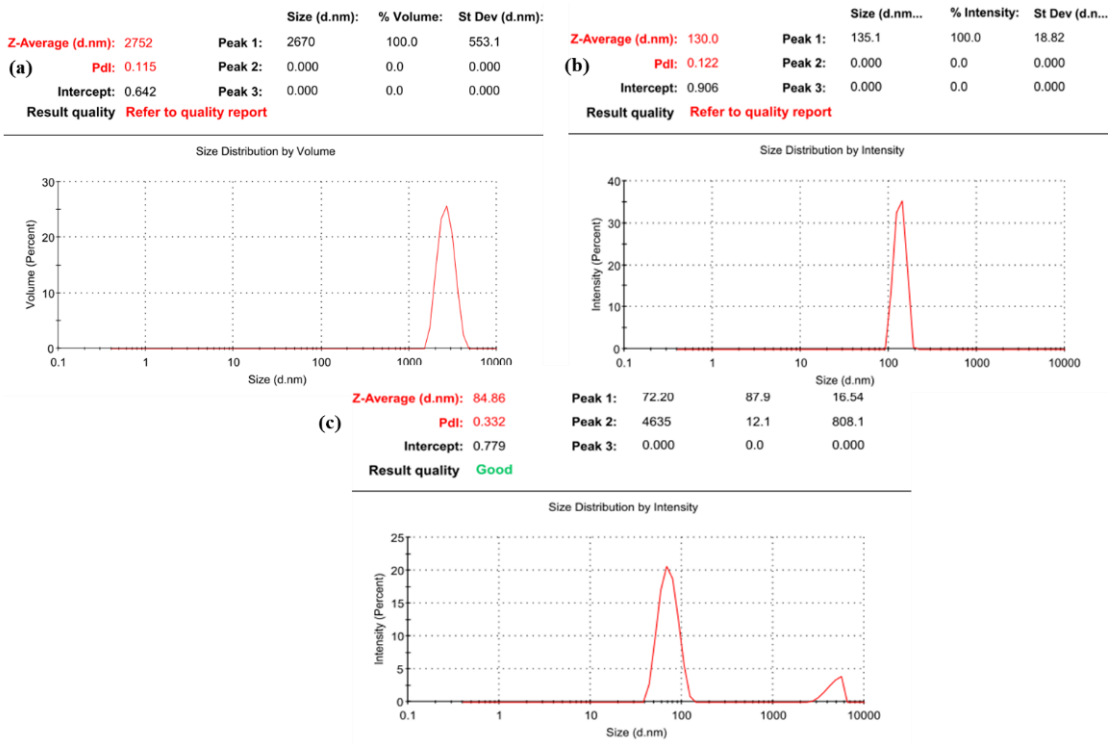



**Figure S9.** The particle size distribution of [2]rotaxane **R1** in $CH_3CN$/water mixed solvent systems (a) in $CH_3CN$ only, (b) at 65 % ($f_w$), and (c) at 90 % ($f_w$).

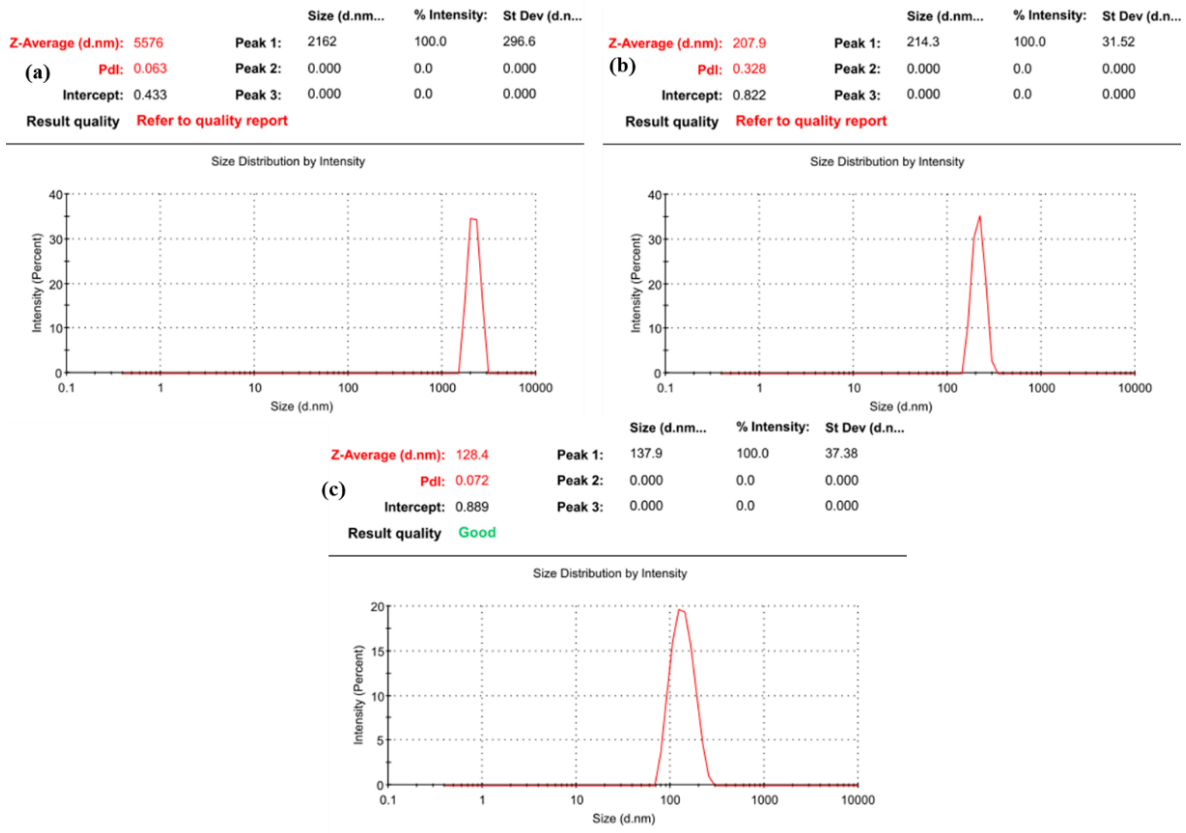



**Figure S10.** The particle size distribution of [2]rotaxane **R2** in $CH_3CN$/water co-solvent system (a) in $CH_3CN$ only, (b) at 70 % ($f_w$), and (c) at 90 % ($f_w$).

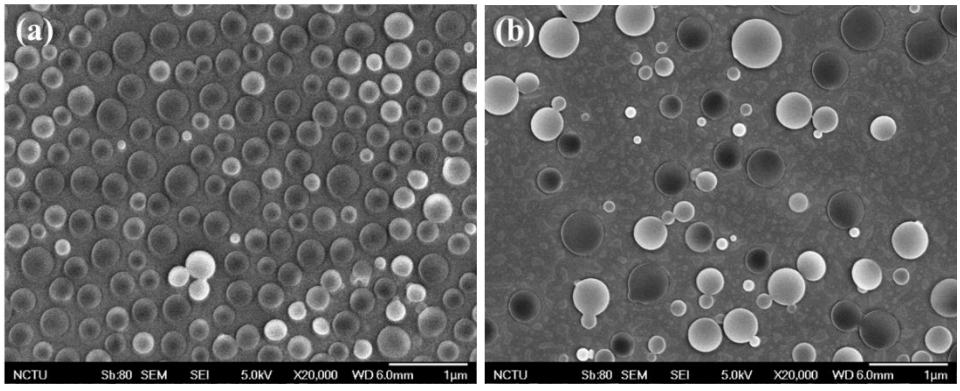



**Figure S11.** FE-SEM images of [2]rotaxane **R1-b** and **R2-b** in pure $CH_3CN$ (10 μM): (a) [2]rotaxane **R1-b** and (b) [2]rotaxane **R2-b**. Scale bar was 1 μm for Figures a and b.

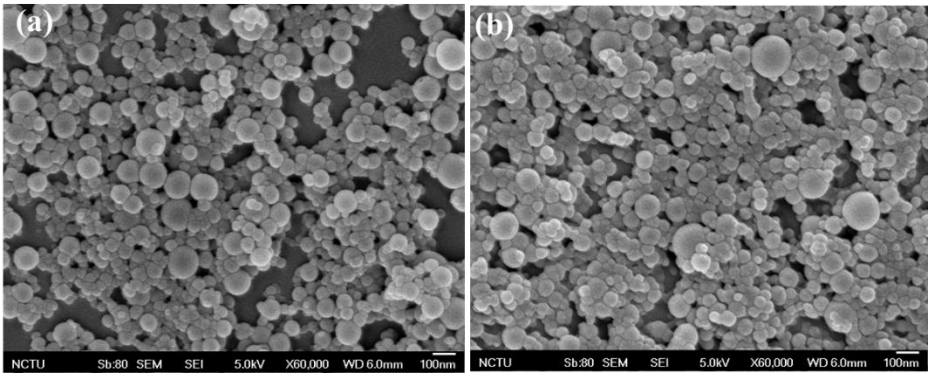



**Figure S12.** FE-SEM images of [2]rotaxane **R1-b and R2-b** in aqueous medium: (a) [2]rotaxane **R1-b** (b) [2]rotaxane **R2-b**. Scale bar was 100 nm for Figures a and b.

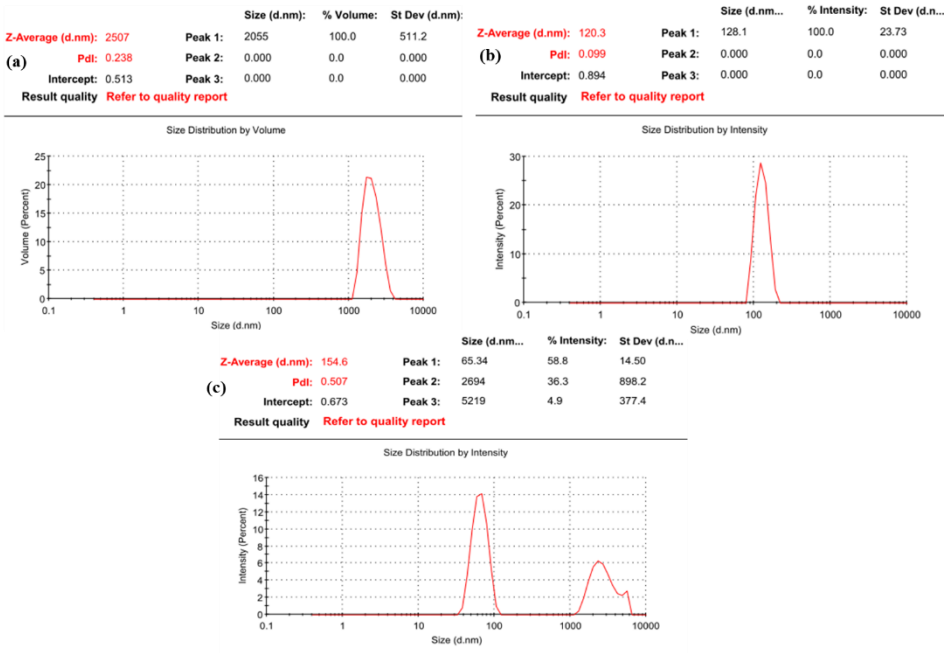



**Figure S13.** The particle size distribution of [2]rotaxane **R1-b** in $CH_3CN$/water mixed solvent systems (a) only in $CH_3CN$ (b) at 70 % ($f_w$) (c) at 99 % ($f_w$).

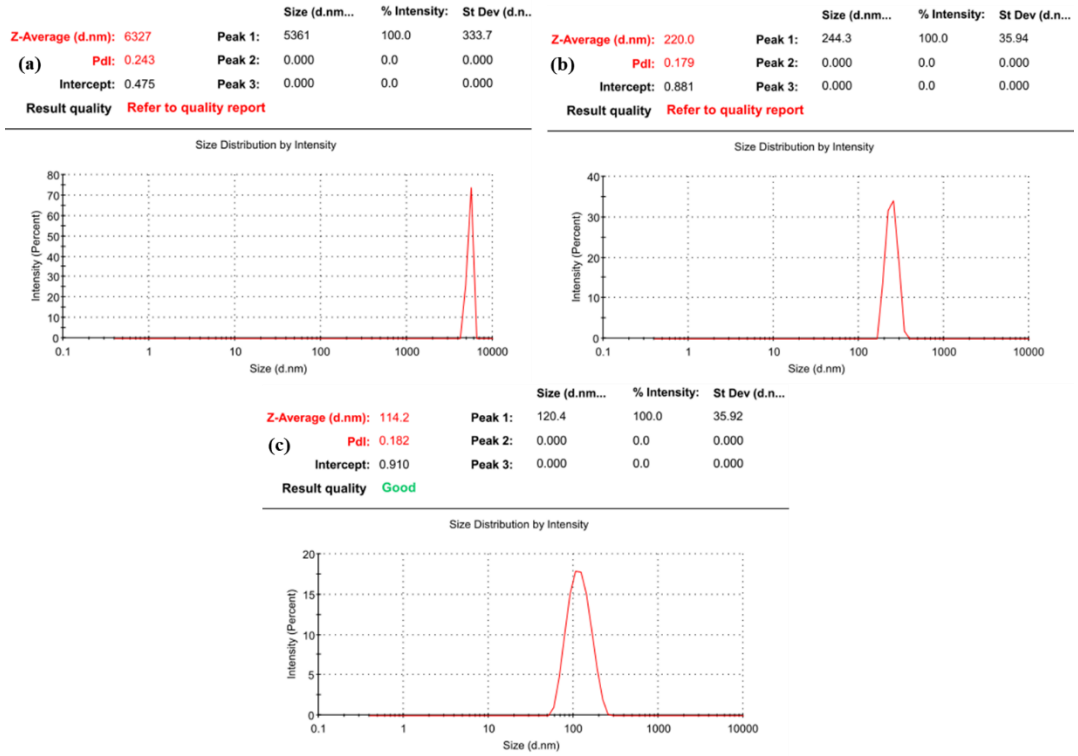



**Figure S14.** The particle size distribution of [2]rotaxane **R2-b** in $CH_3CN$/water mixed solvent systems (a) only in $CH_3CN$ (b) at 75 % ($f_w$) (c) at 99 % ($f_w$).

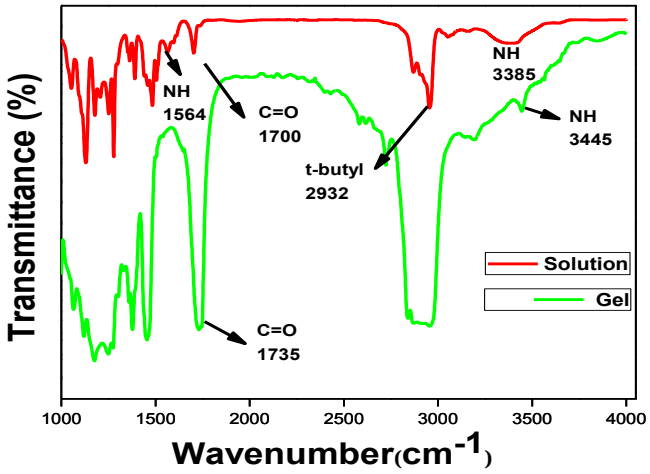



**Figure S15.** FTIR spectra of [2]rotaxane **R1** in their $CH_3CN$ solution (red) and after gelation in MeOH (green).

**Table S1.** The gelation test of [2]rotaxanes **R1**, **R1-b, R2**, and **R2-b** in various solvents.

| Solvent | R1 | R1-b | R2 | R2-b |
|---|---|---|---|---|
| $CH_2Cl_2$ | [a]S | S | S | S |
| $CHCl_3$ | S | S | S | S |
| $C_2H_4Cl_2$ | S | S | S | S |
| DMSO | S | S | S | S |
| DMF | S | S | S | S |
| THF | S | S | S | S |
| Toluene | S | S | S | S |
| P-Xylene | S | S | S | S |
| Ethyl acetate | [c]PG | [b]P | S | P |
| MeOH | [d]G (2.5 w/v%) | P | P | P |
| Ethanol | PG | P | P | P |
| n-propanol | PG | P | P | P |
| Isopropanol | S | S | P | P |
| n-butanol | PG | p | P | S |
| 1- Pentanol | PG | S | P | P |

[a] S = Solution; [b] P = Precipitate; [c] PG = Partial gel; [d] G = Gel ; w/v% = [(g/100 mL) %] = minimum weight volume percent concentration of gel formation.

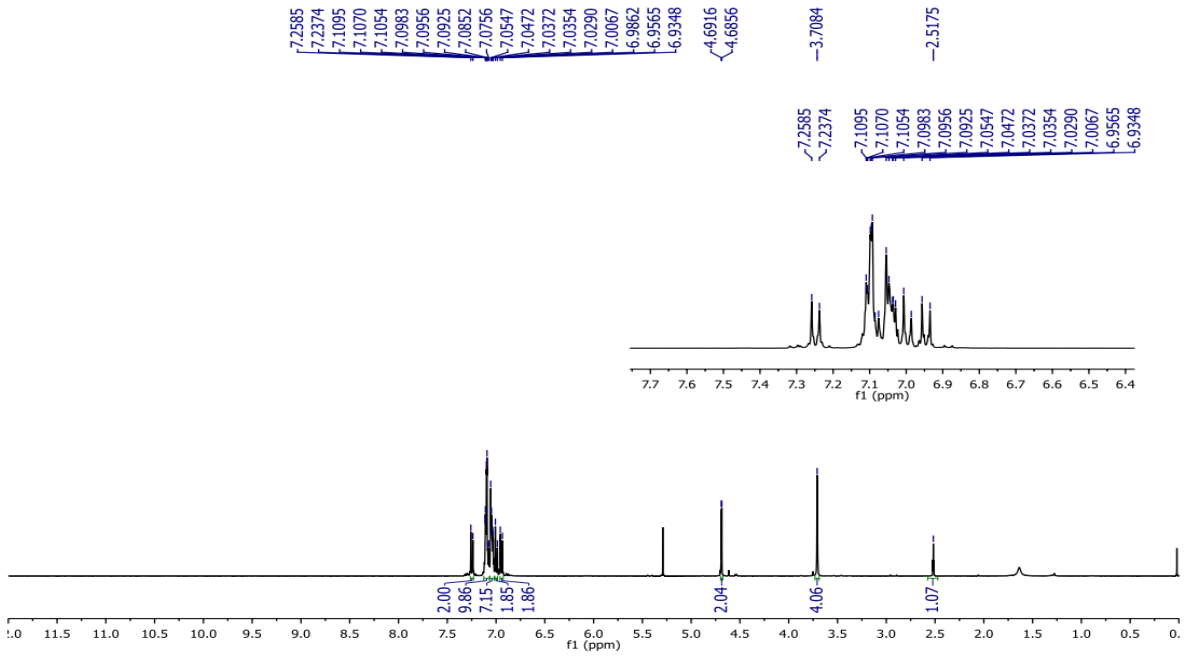



**Figure S16**. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **S3**

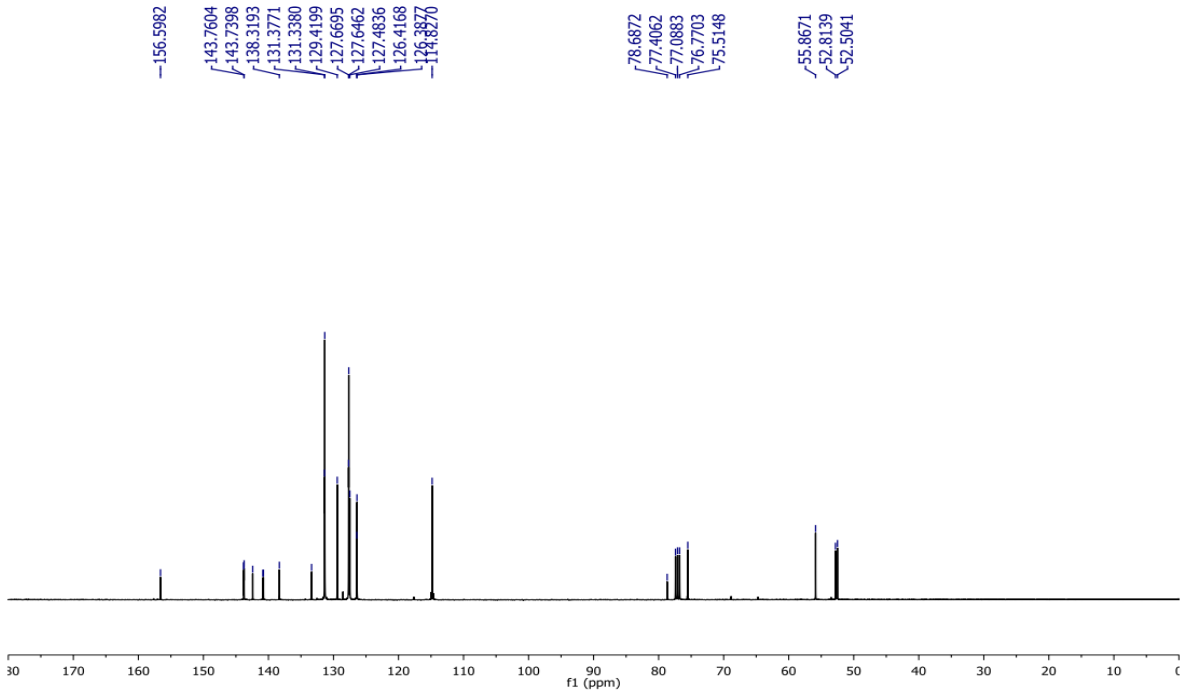



**Figure S17**. $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of compound **S3**.

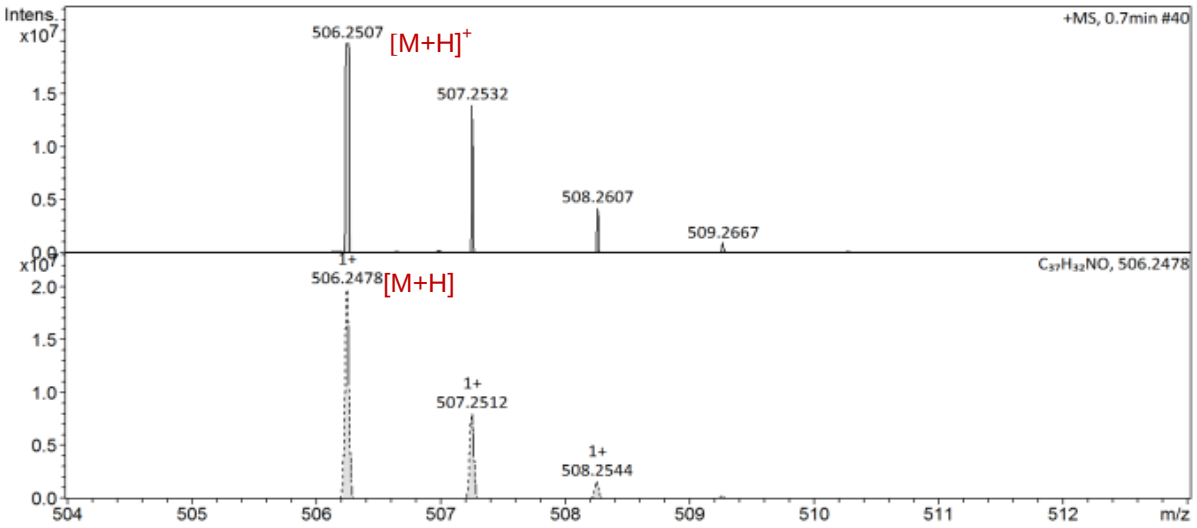



**Figure S18**. HRMS ESI (+)-MS spectrum of compound **S3**.

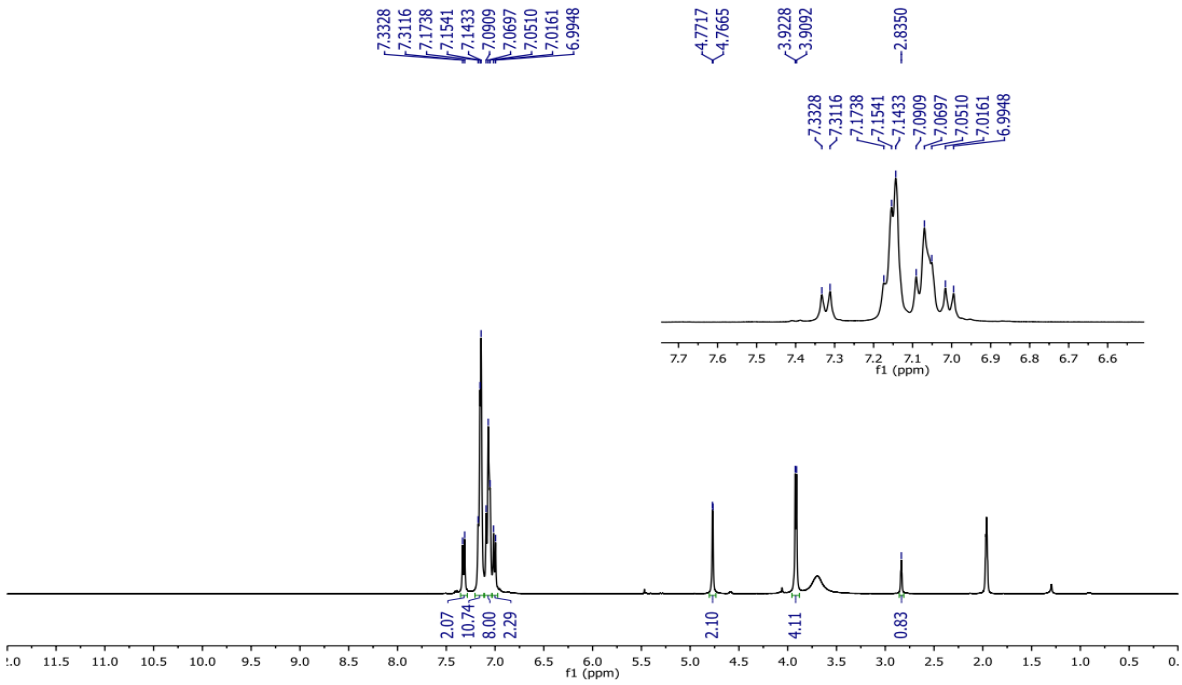



**Figure S19**. $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound **S4**.

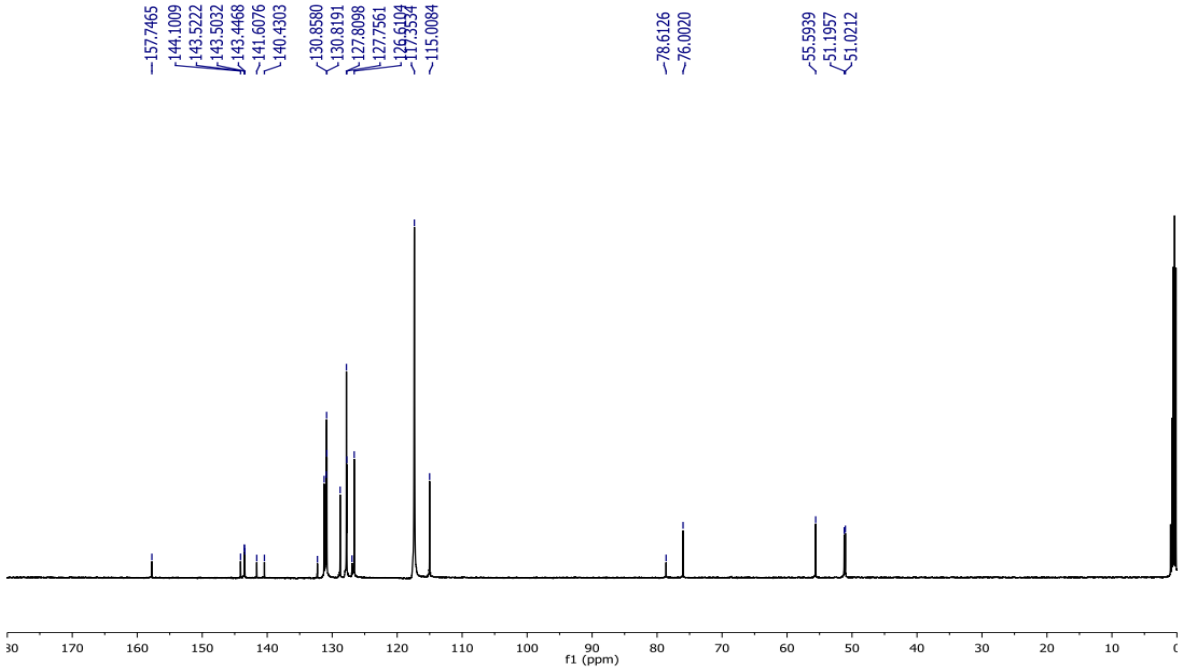



**Figure S20**. $^{13}C$ NMR (100 MHz, $CD_3CN$) spectrum of compound **S4.**

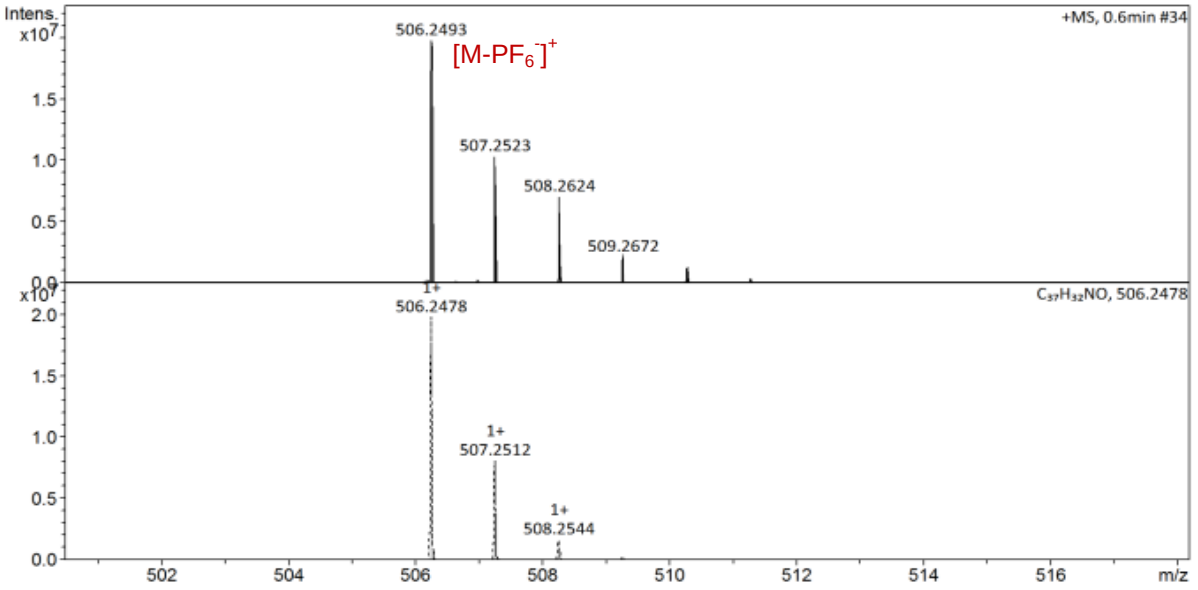



**Figure S21**. HRMS ESI (+)-MS spectrum of compound **S4**.

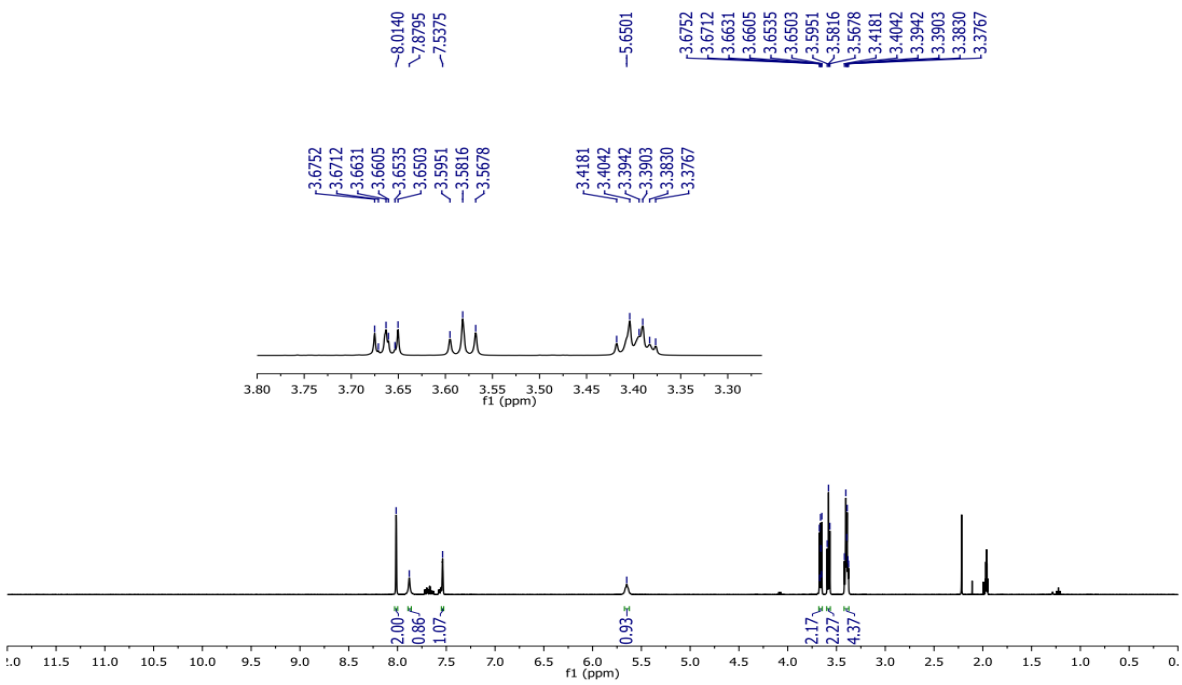



**Figure S22**. $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound **S5**.

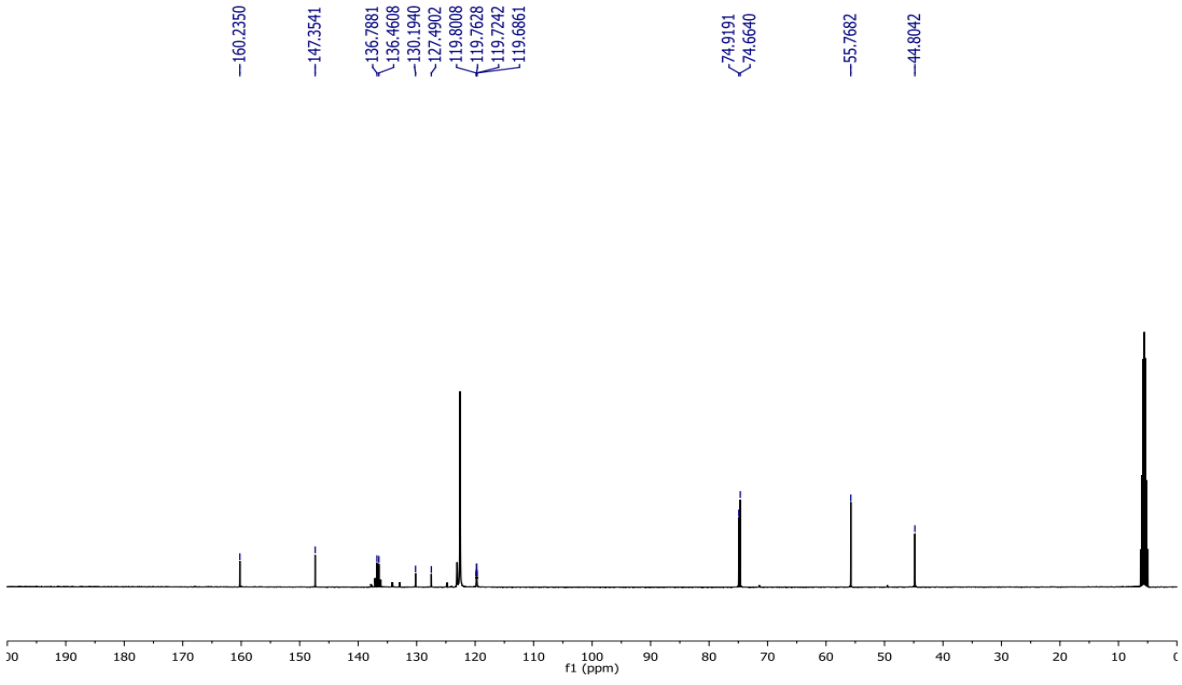



**Figure S23**. $^{13}$C NMR (100 MHz, $CD_3CN$) spectrum of compound **S5**.

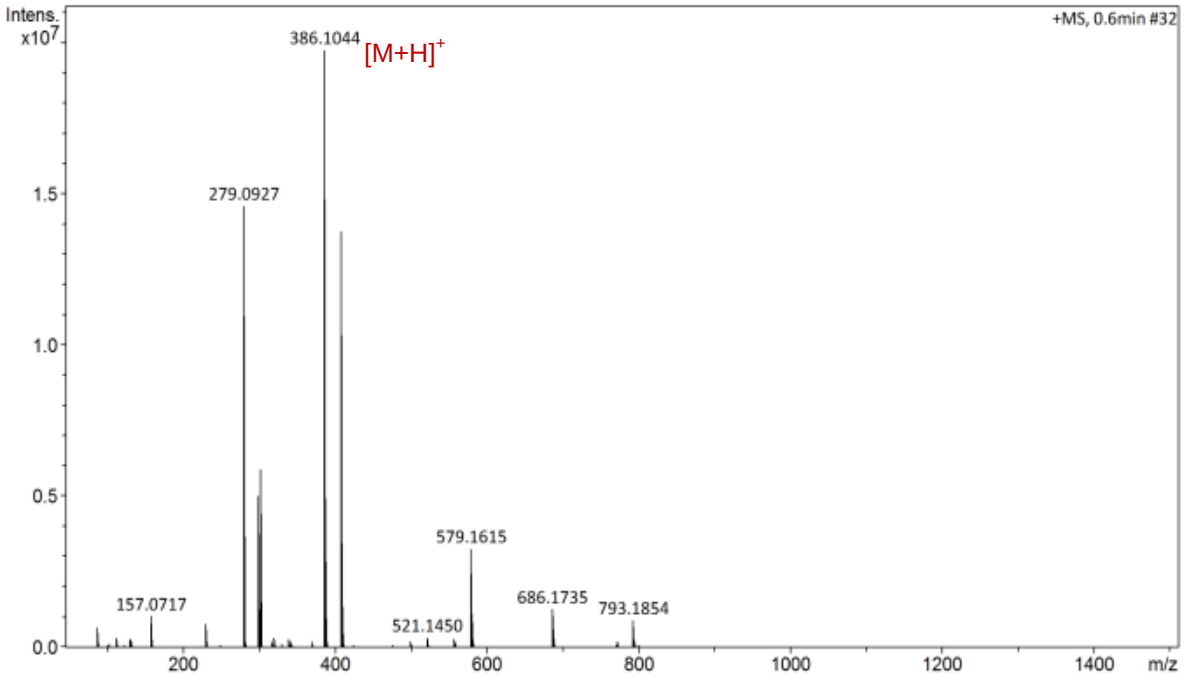



**Figure S24**. HRMS ESI (+)-MS spectrum of compound **S5**.

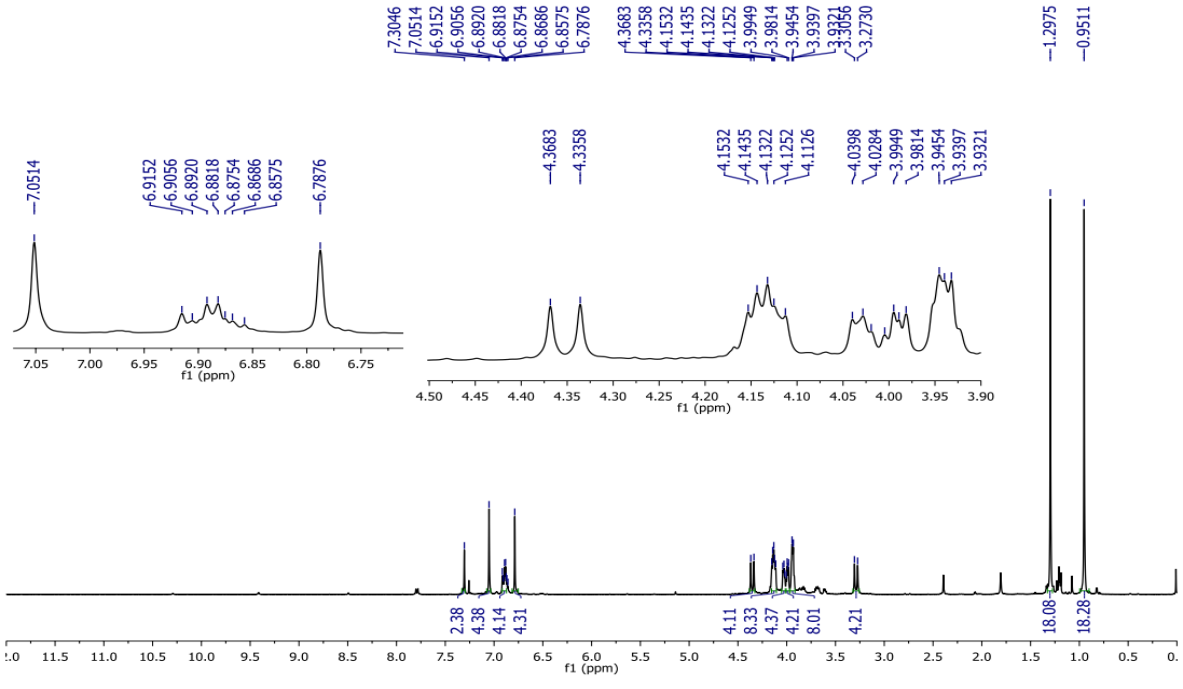



**Figure S25**. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **S8**.

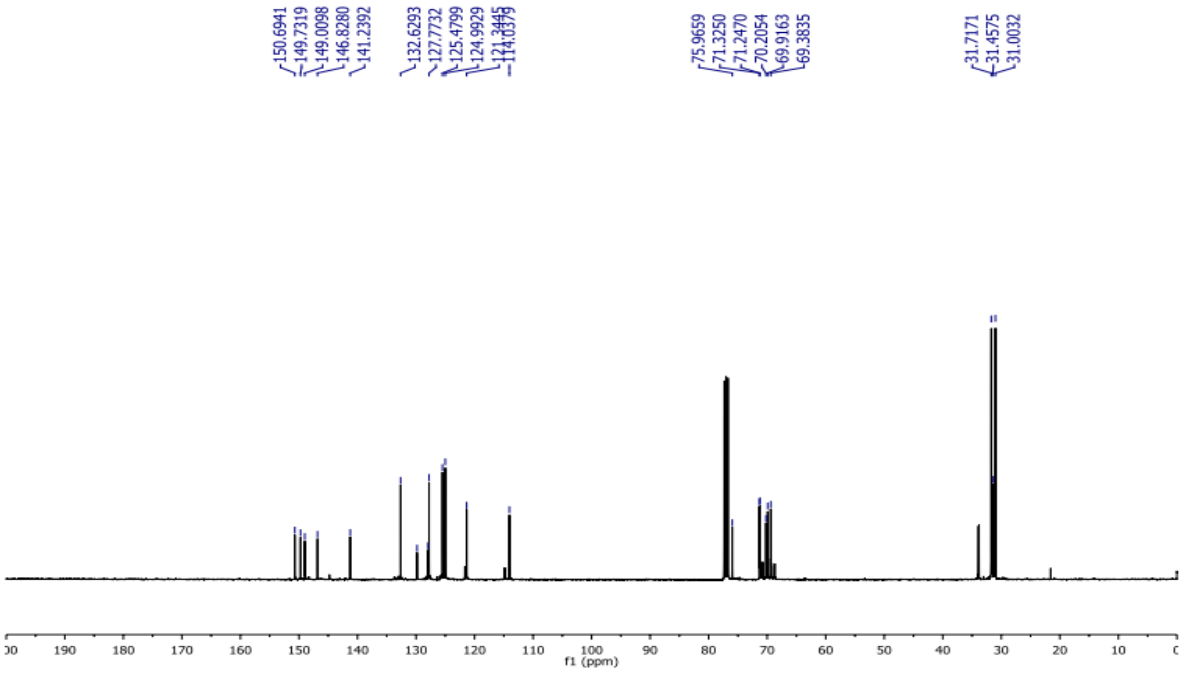



**Figure S26**. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **S8**.

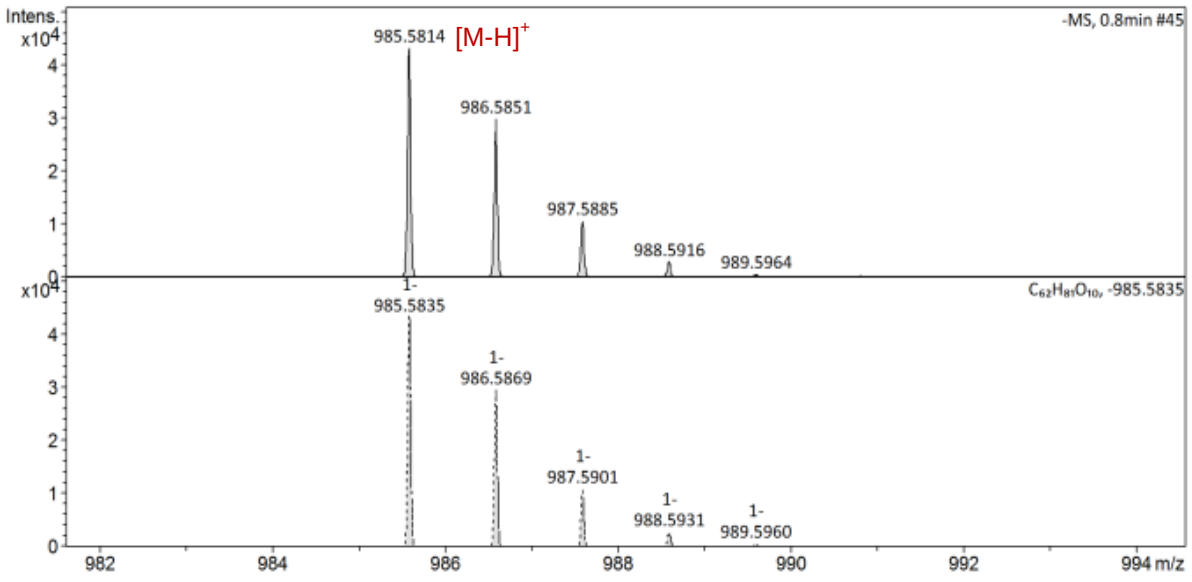



**Figure S27**. HRMS ESI (+)-MS spectrum of compound **S8**.

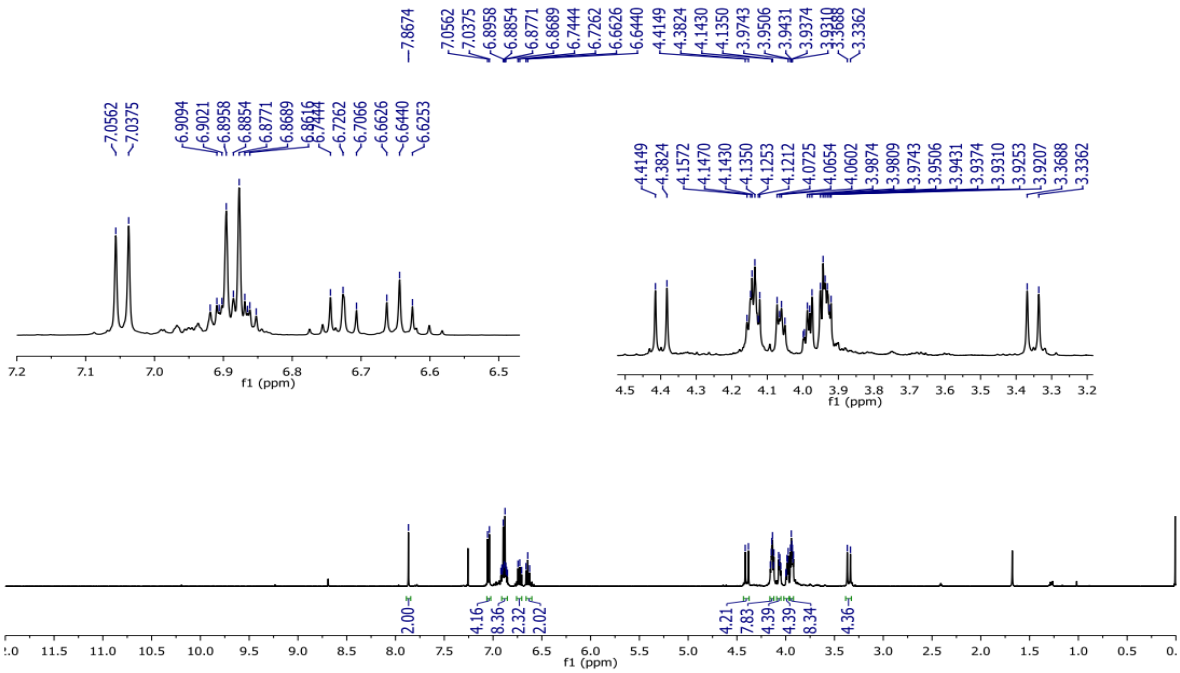



**Figure S28**. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **S10**.

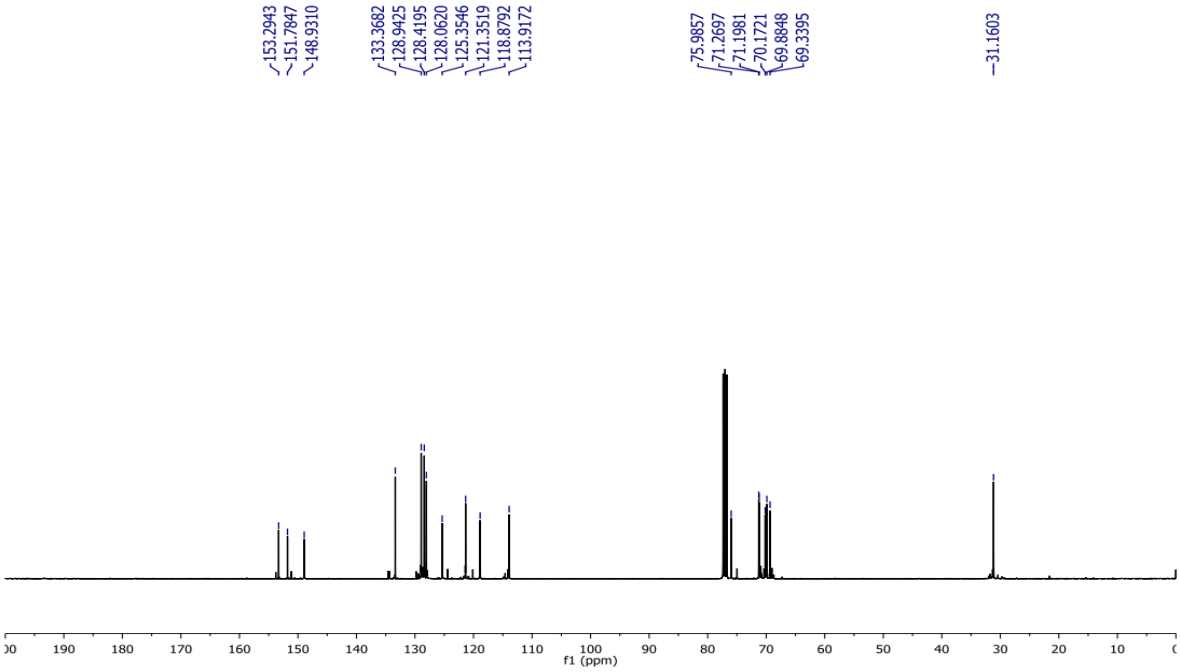



**Figure S29**. $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of compound **S10**.

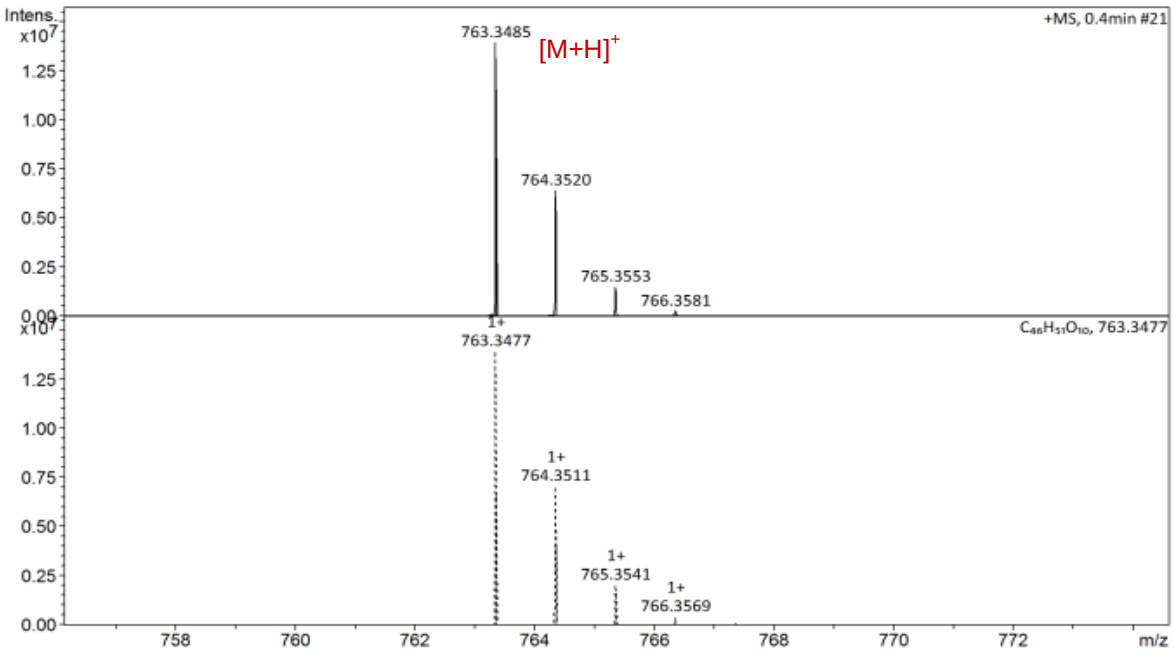



**Figure S30**. HRMS ESI (+)-MS spectrum of compound **S10**.

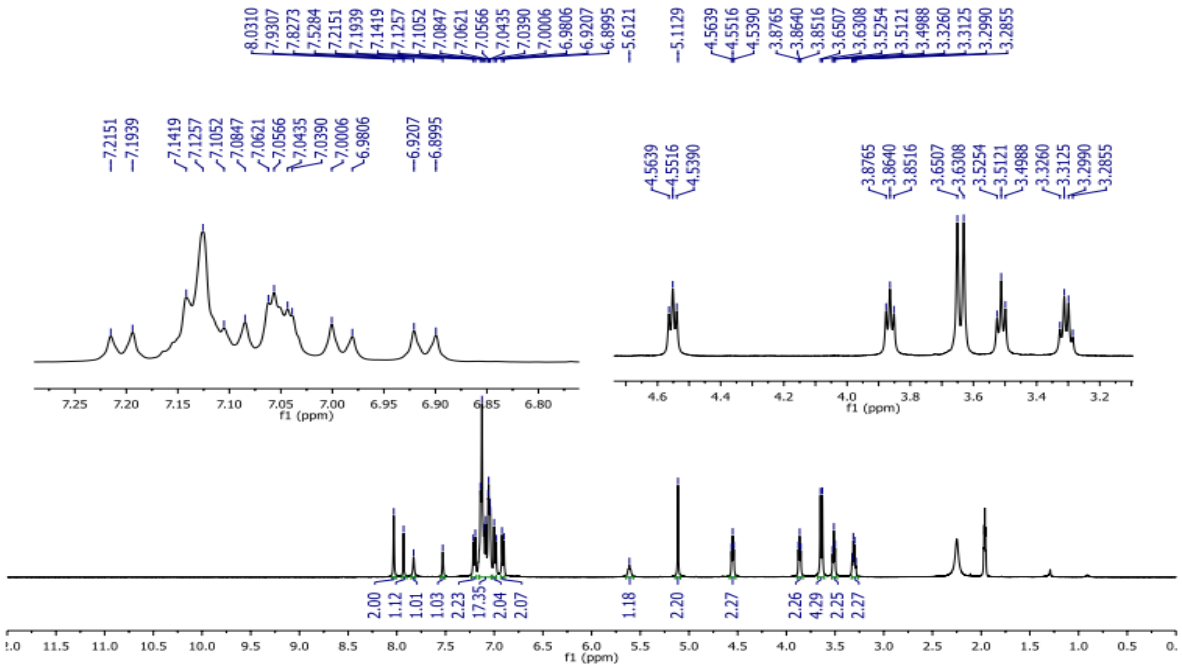



**Figure S31**. $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound **T1**.

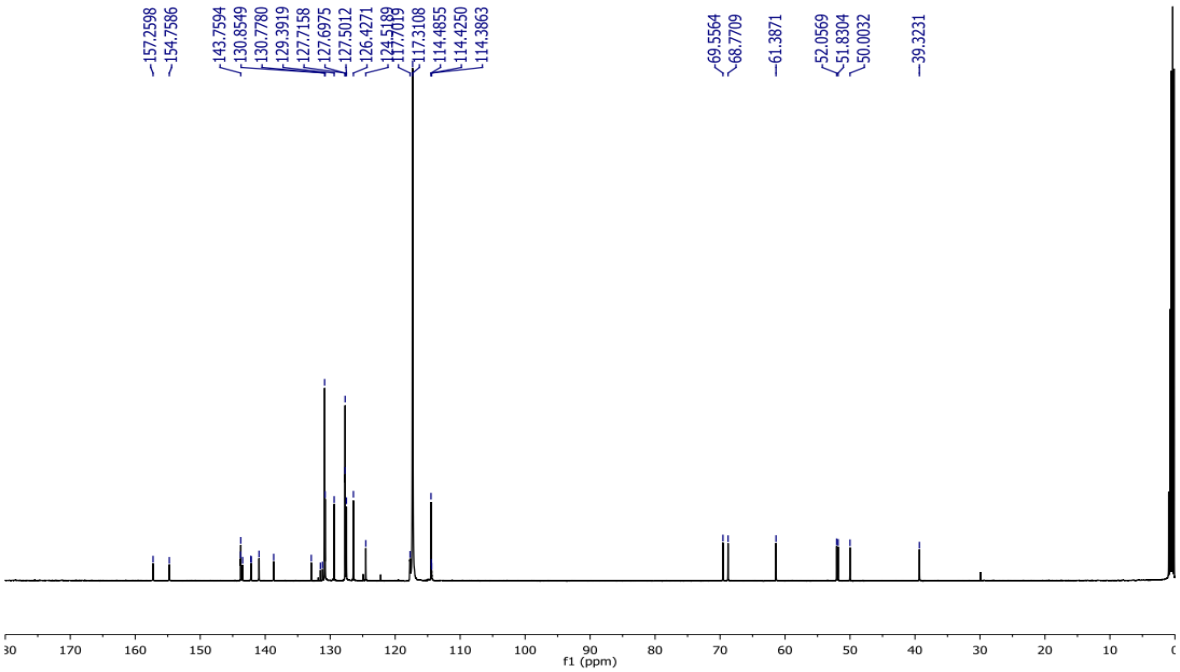



**Figure S32**. $^{13}C$ NMR (100 MHz, $CD_3CN$) spectrum of compound **T1**.

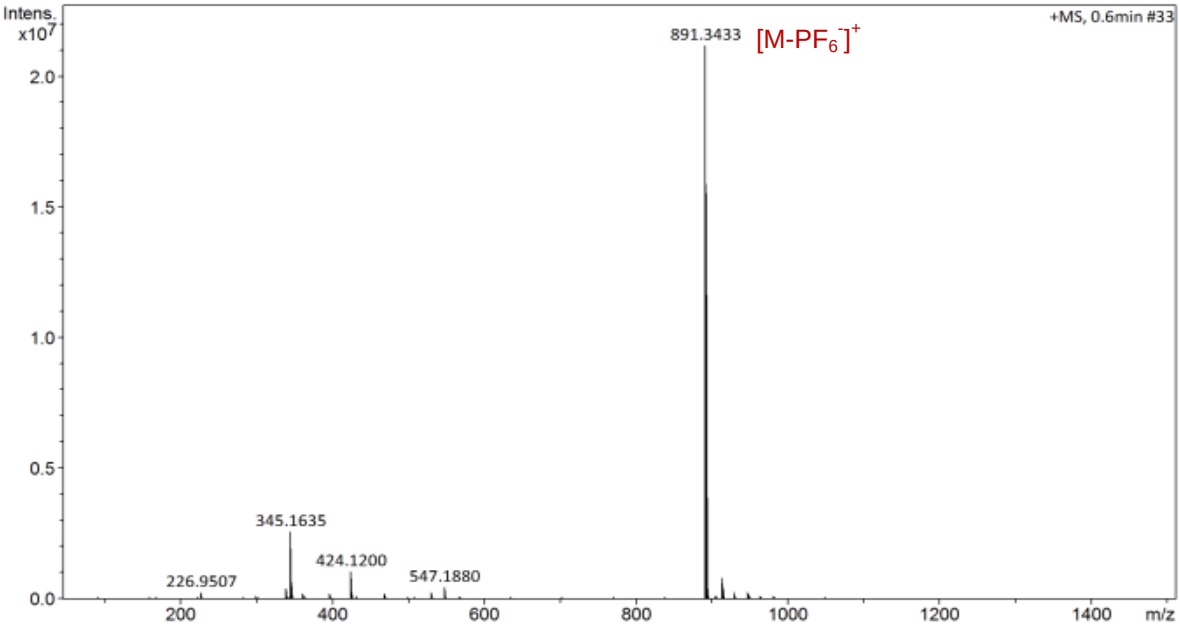



**Figure S33**. HRMS ESI (+)-MS spectrum of compound **T1**.

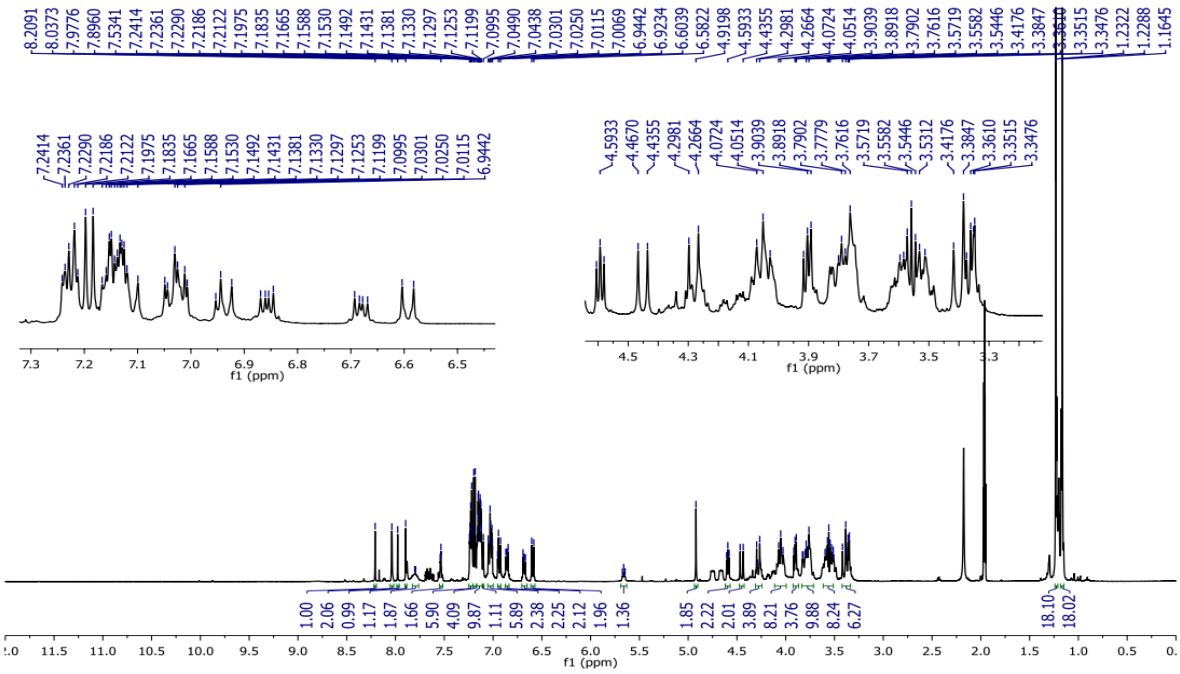


**Figure S34**. $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound [2]rotaxane **R1**.

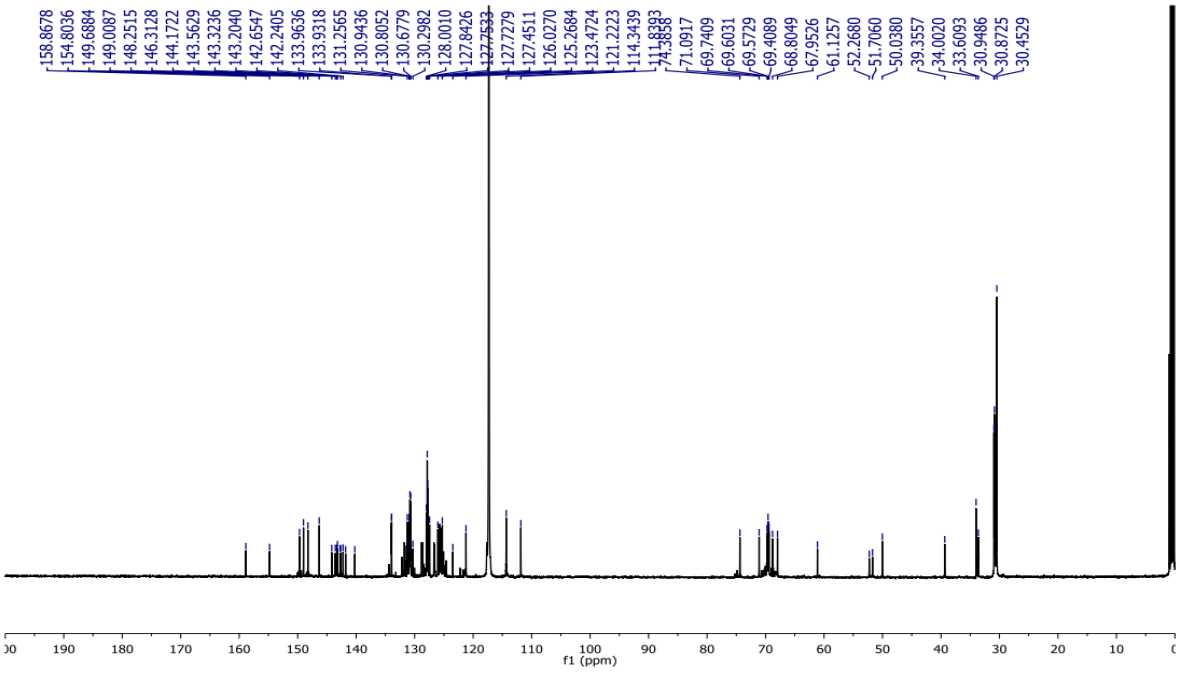


**Figure S35**. $^{13}$C NMR (100 MHz, $CD_3CN$) spectrum of compound [2]rotaxane **R1**.

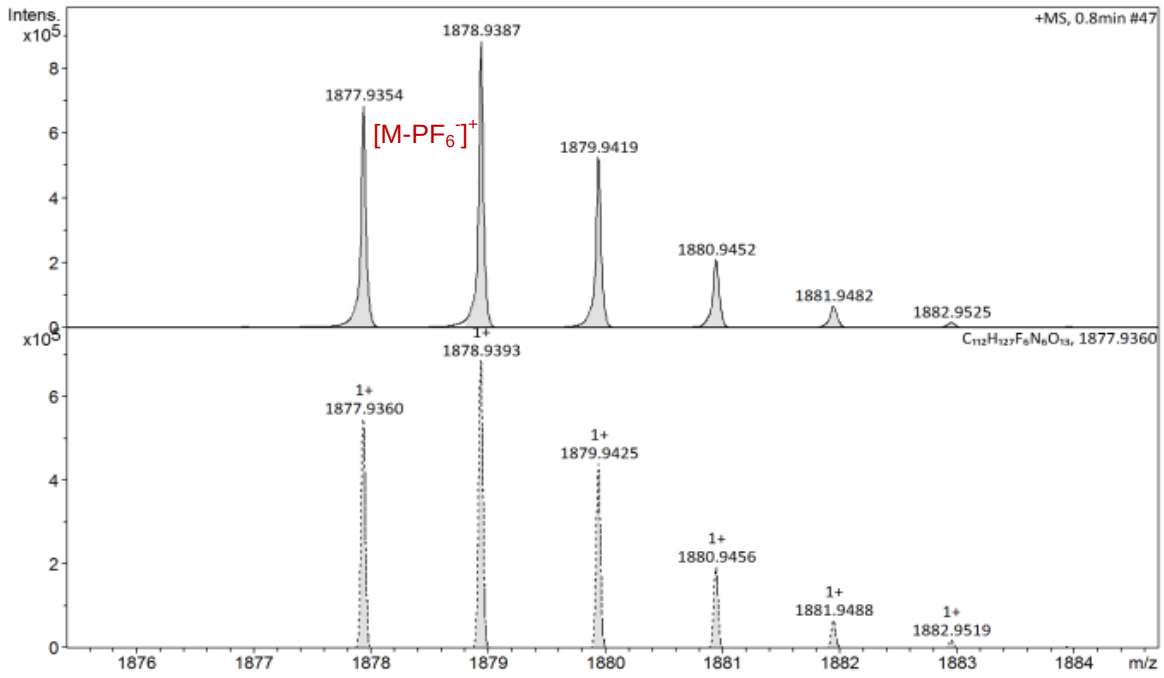



**Figure S36**. HRMS ESI (+)-MS spectrum of compound [2]rotaxane **R1**.

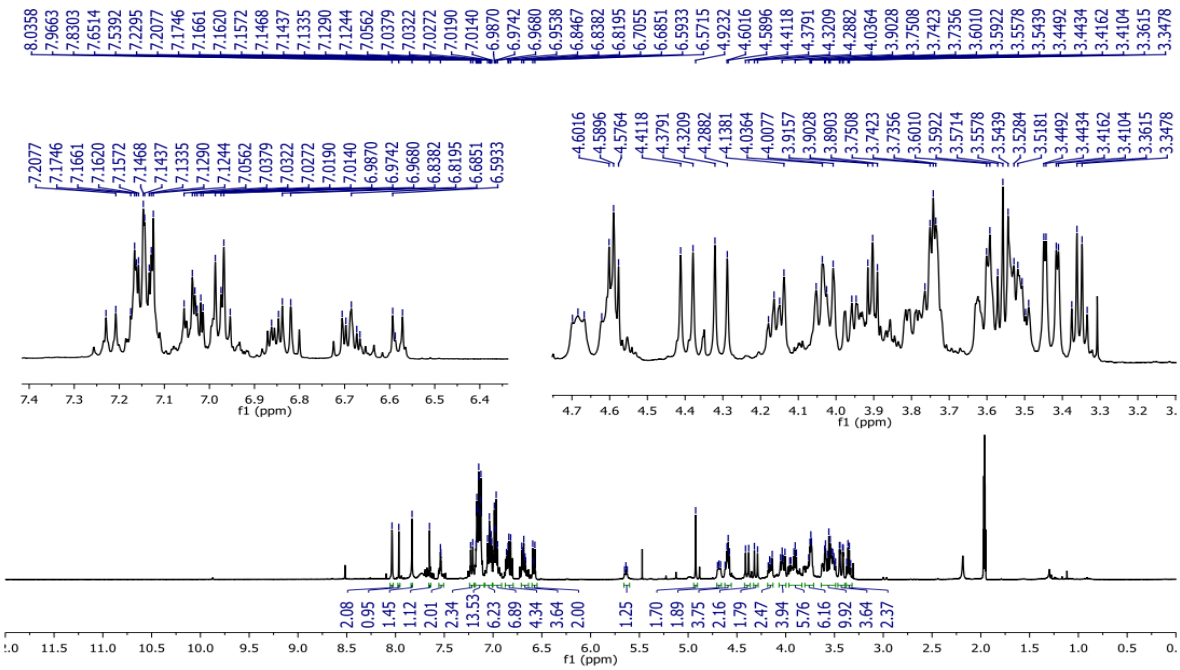



**Figure S37**. $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound [2]rotaxane **R2**.

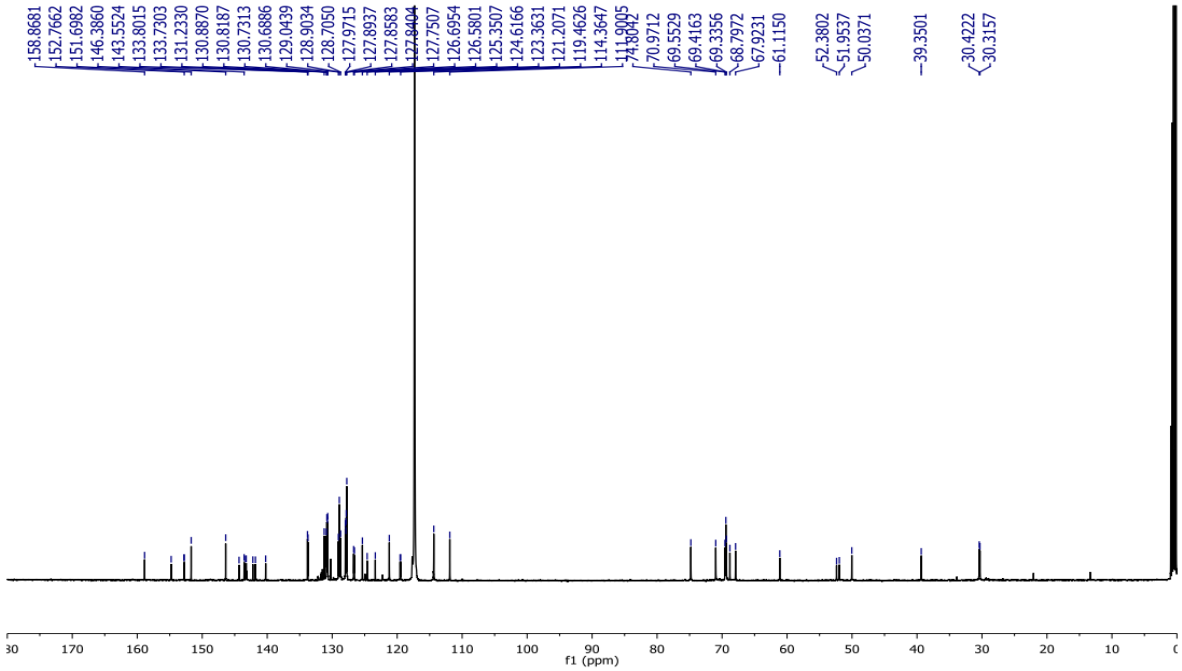



**Figure S38**. $^{13}C$ NMR (100 MHz, $CD_3CN$) spectrum of compound [2]rotaxane **R2**.

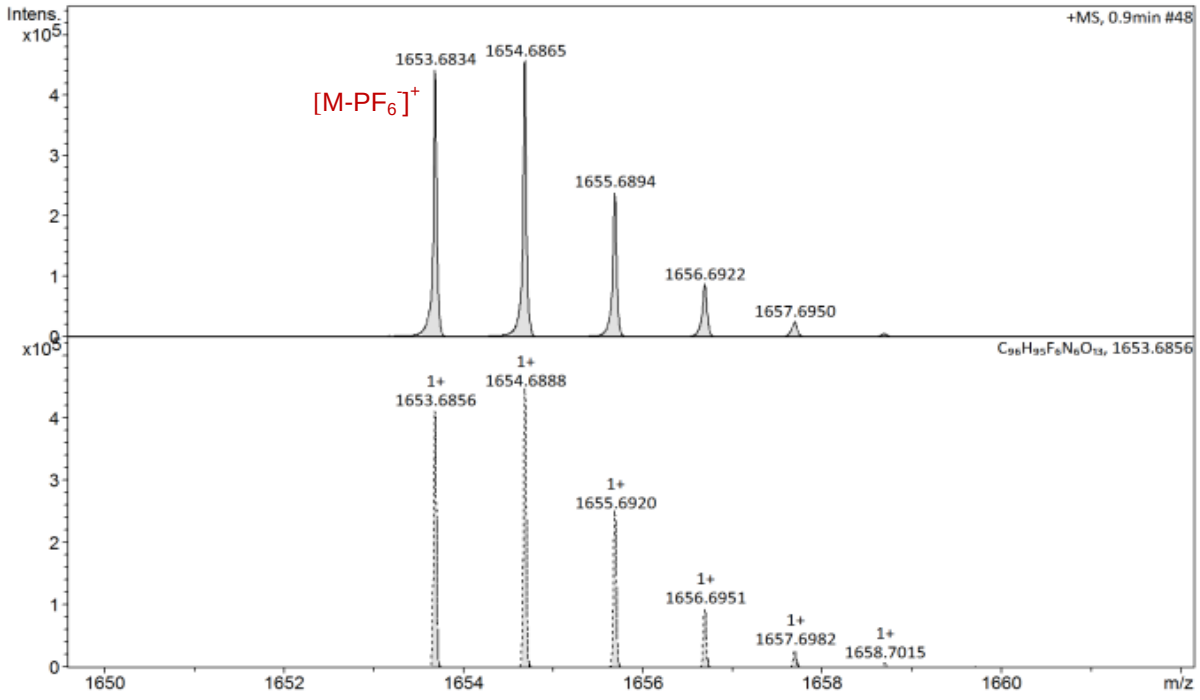



**Figure S39**. HRMS ESI (+)-MS spectrum of compound [2]rotaxane **R2**.

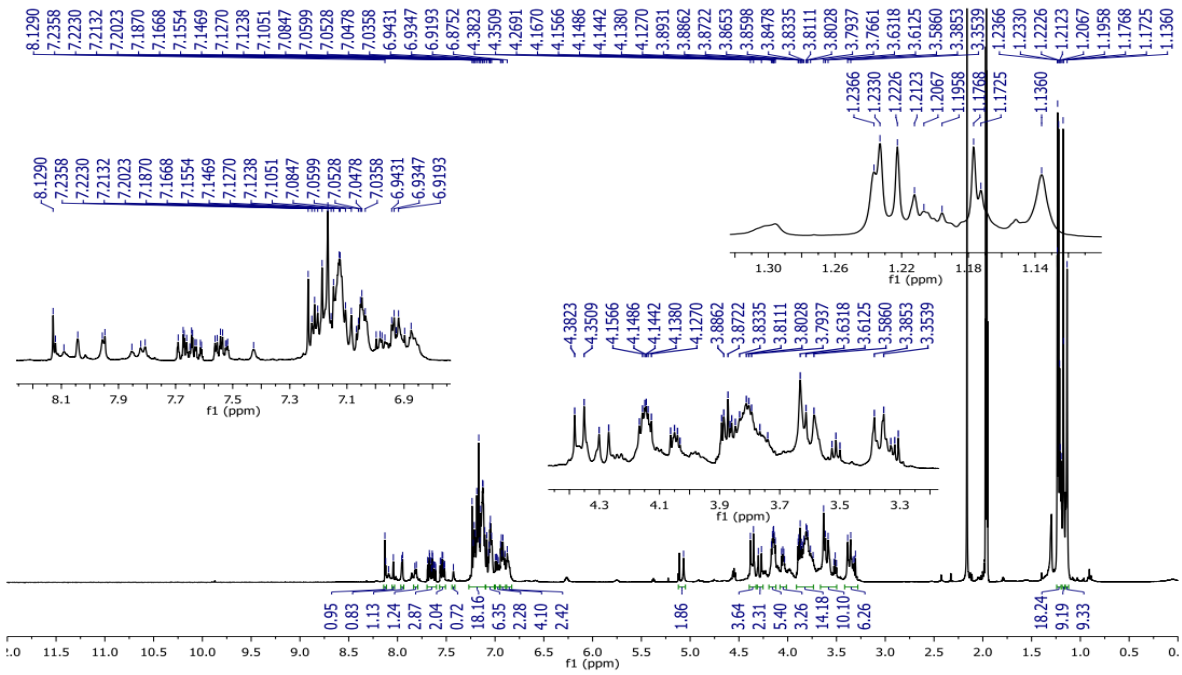


**Figure S40**. $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound [2]rotaxane **R1-b**.

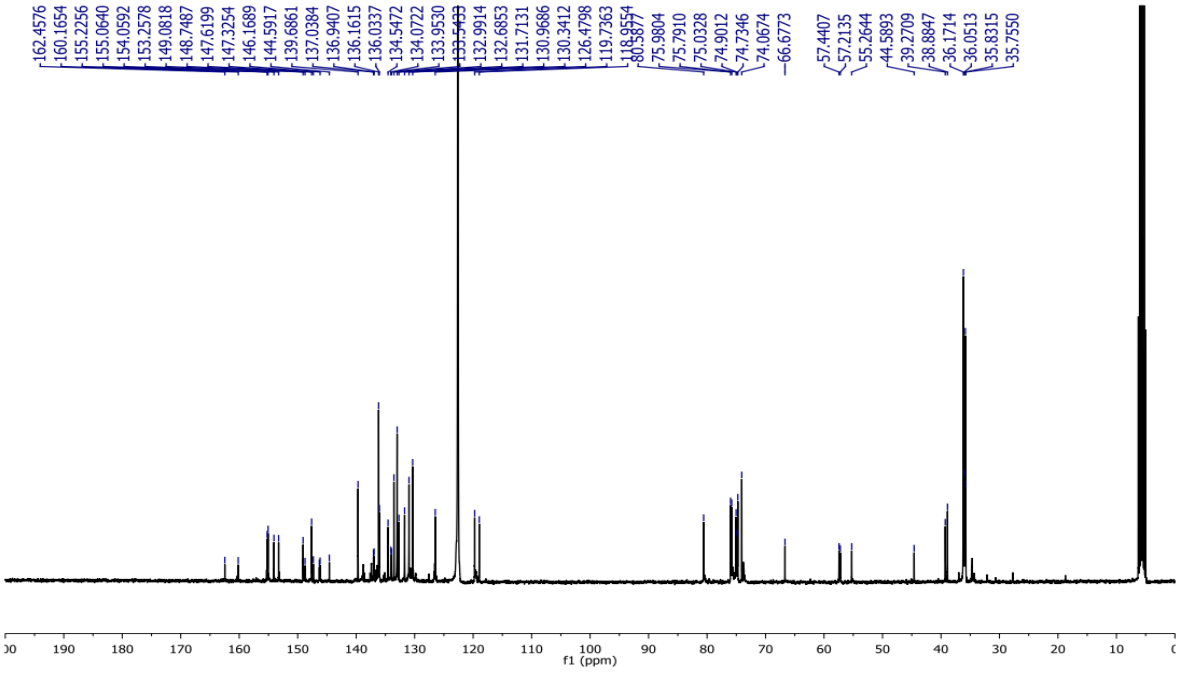


**Figure S41**. $^{13}$C NMR (100 MHz, $CD_3CN$) spectrum of compound [2]rotaxane **R1-b**.

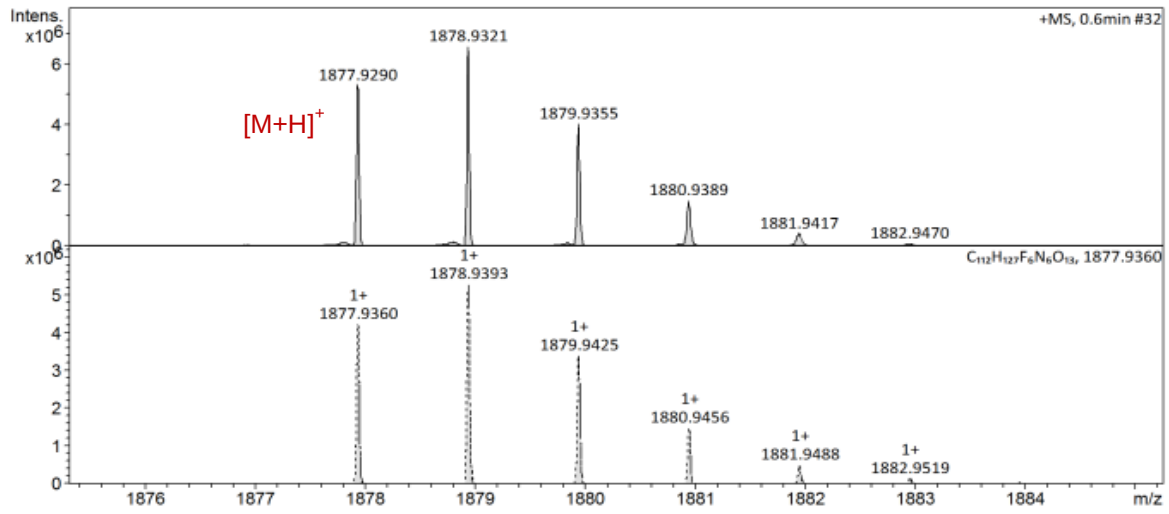



**Figure S42**. HRMS ESI (+)-MS spectrum of compound [2]rotaxane **R1-b**

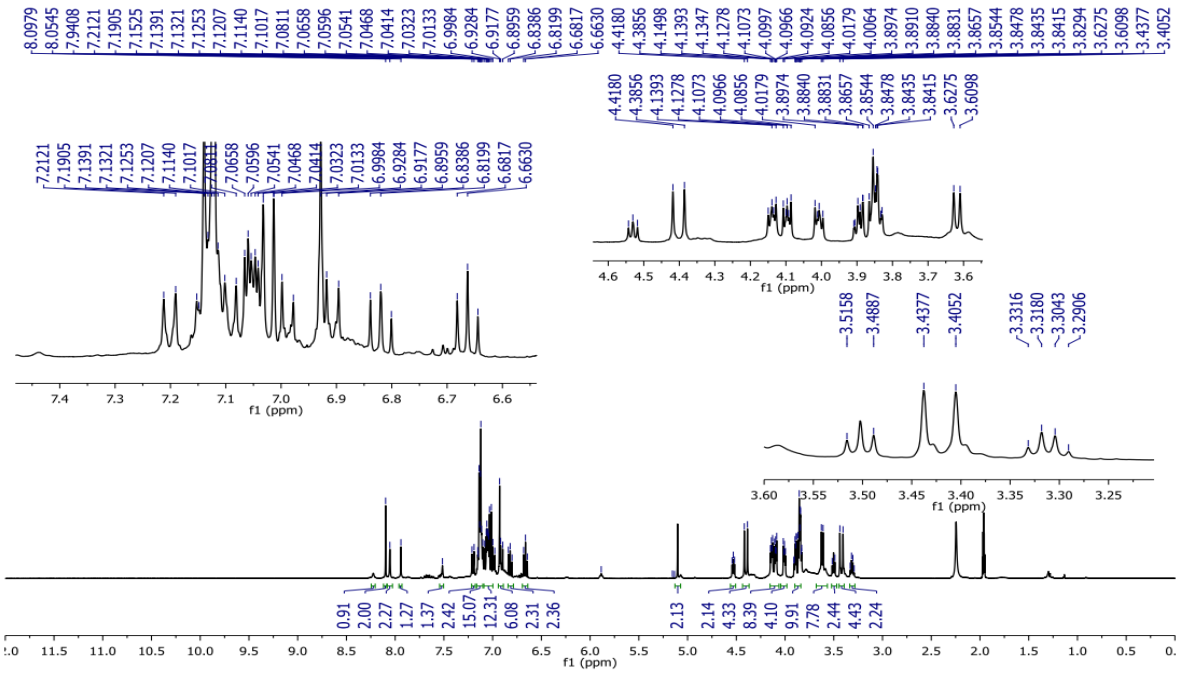



**Figure S43**. $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound [2]rotaxane **R2-b**.

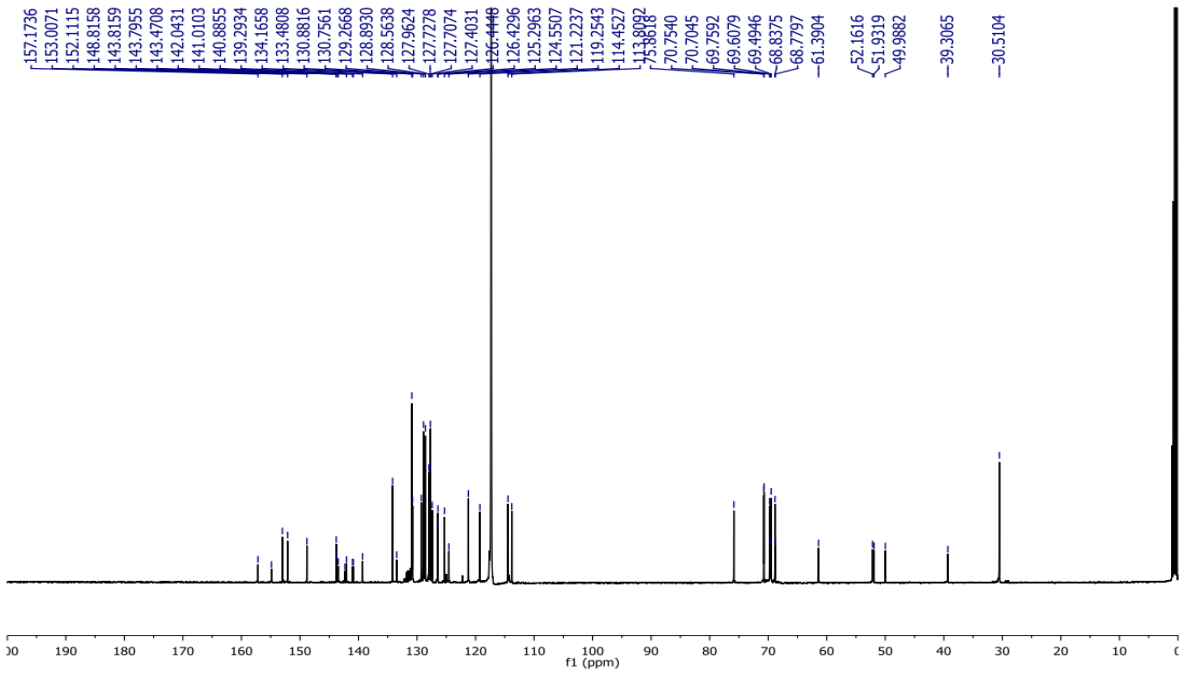



**Figure S44**. $^{13}C$ NMR (100 MHz, $CD_3CN$) spectrum of compound [2]rotaxane **R2-b.**

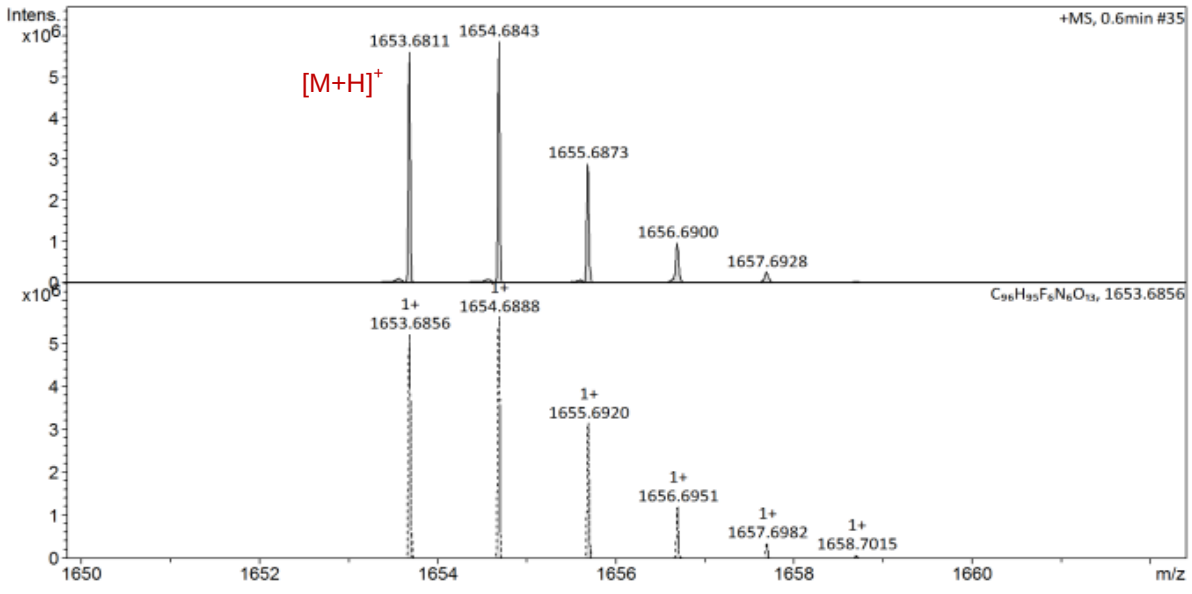



**Figure S45**. HRMS ESI (+)-MS spectrum of compound [2]rotaxane **R2-b**

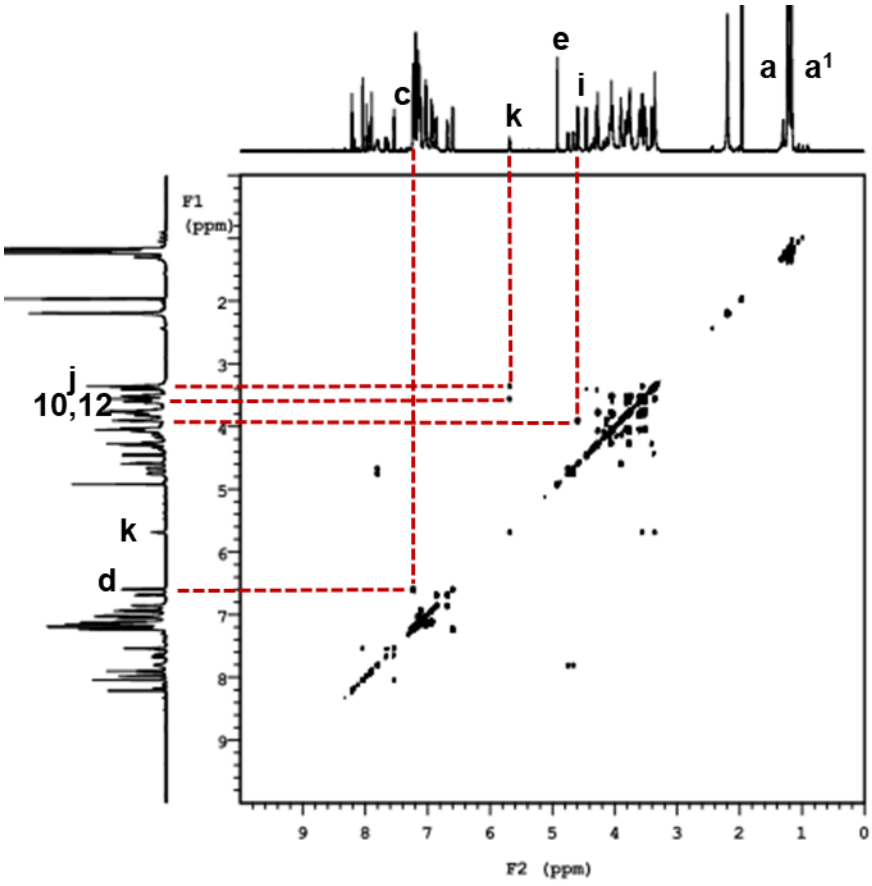



**Figure S46**. 2D TOCSY spectrum (600 MHz, 298 K, $CD_3CN$) of [2]rotaxane **R1**.

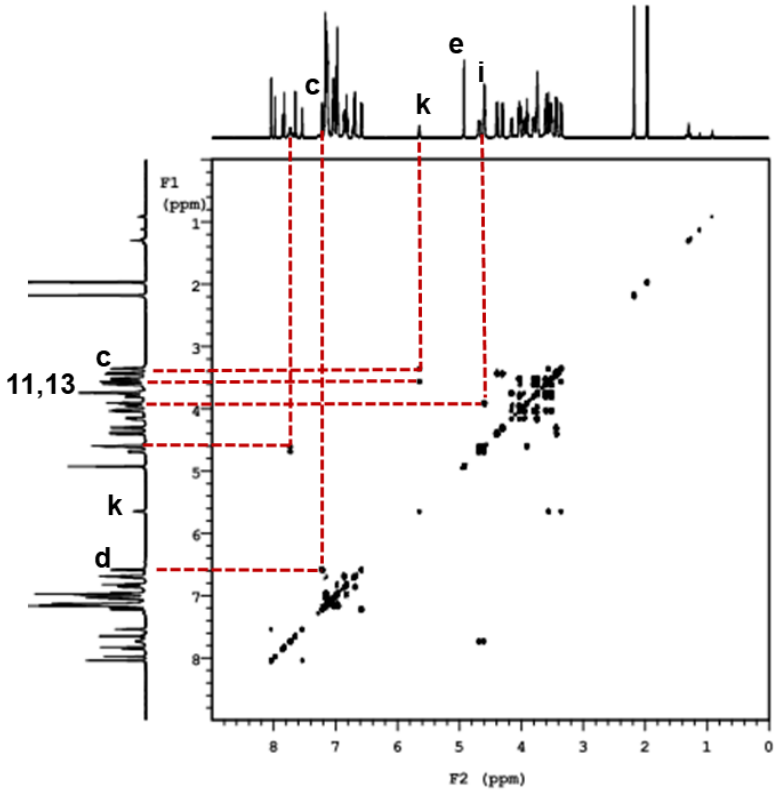



**Figure S47**. 2D TOCSY spectrum (600 MHz, 298 K, $CD_3CN$) of [2]rotaxane **R2**.

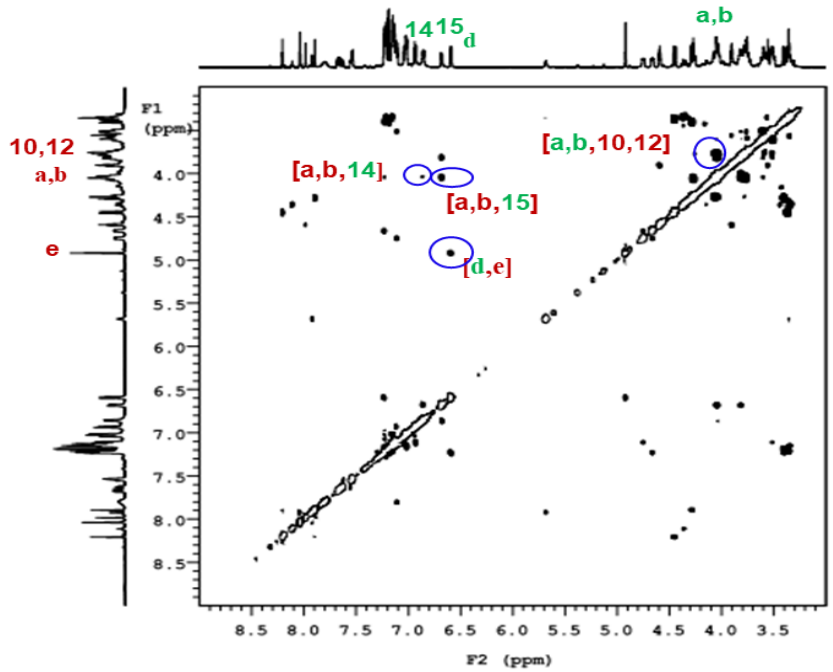



**Figure S48**. 2D ROESY spectrum (600 MHz, 298 K, $CD_3CN$) of [2]rotaxane **R1**.

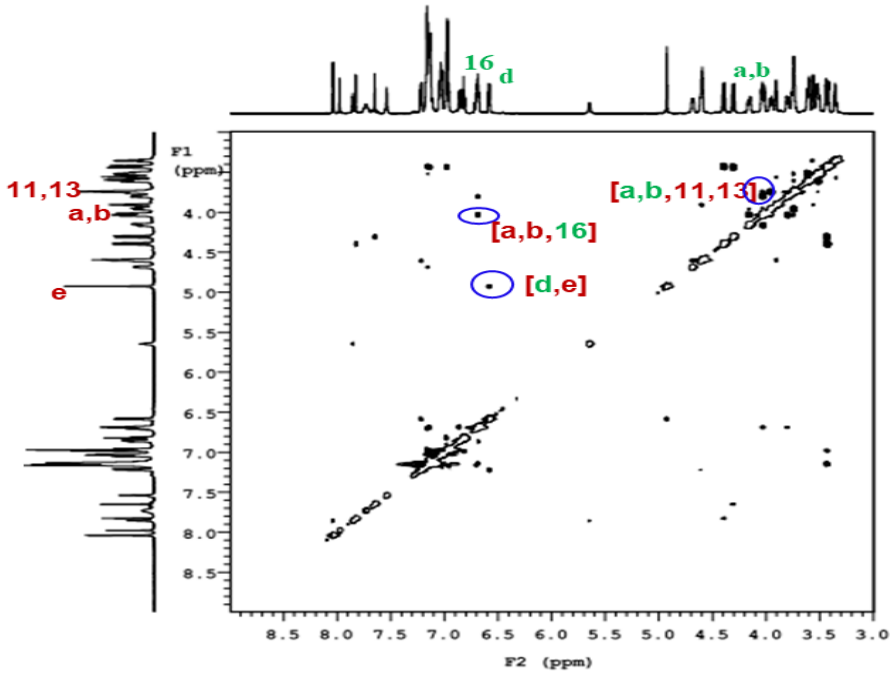



**Figure S49**. 2D ROESY spectrum (600 MHz, 298 K, $CD_3CN$) of [2]rotaxane **R2**.

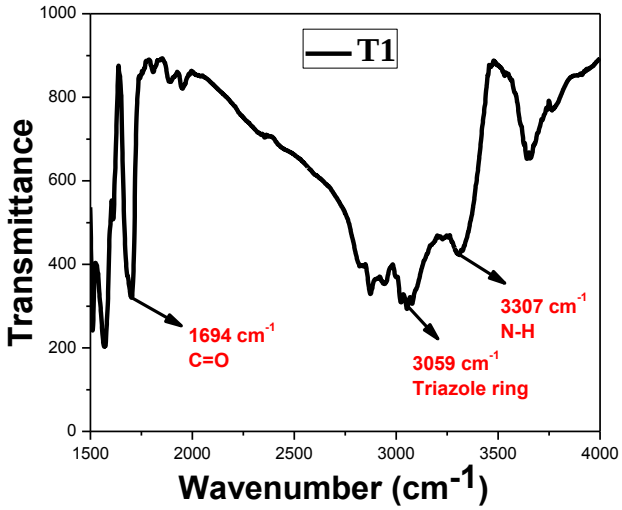



**Figure S50**. FTIR spectra of axle **T1**

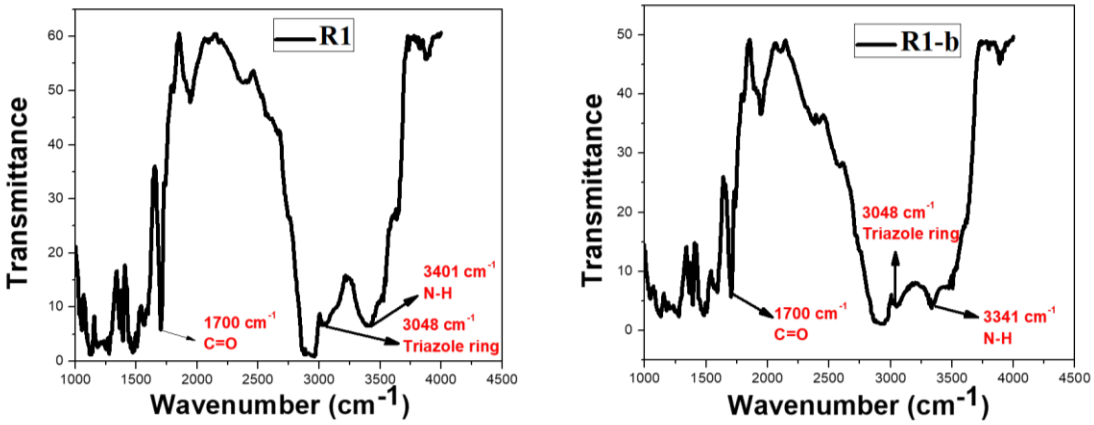



**Figure S51**. FTIR spectra of (a) [2]rotaxane **R1** and (b) [2]rotaxane **R1-b**.

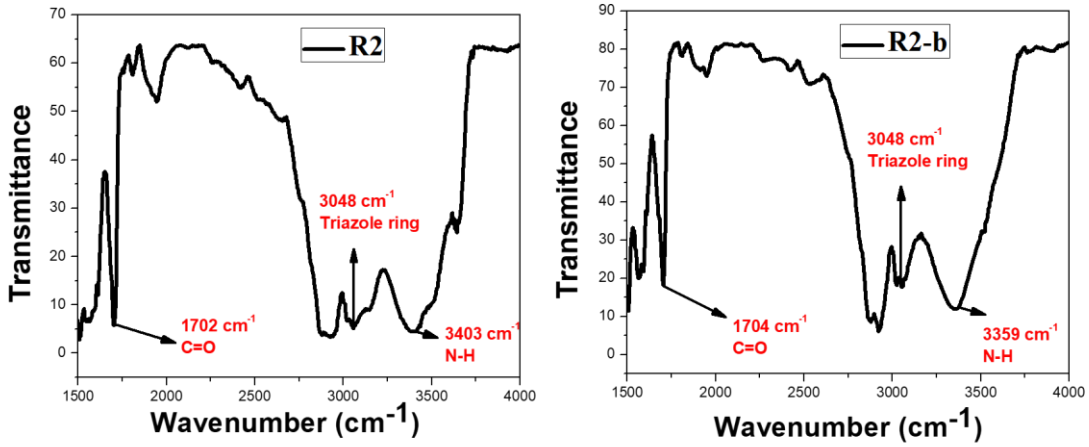



**Figure S52**. FTIR spectra of (a) axle **T1**, (b) [2]rotaxane **R1**, (c) [2]rotaxane **R1-b**, and (d) [2]rotaxane **R2**.

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