Electronic Supplementary Information

A light- and redox-switchable tristable [3]rotaxane with orthogonal controllable shuttling of different wheels

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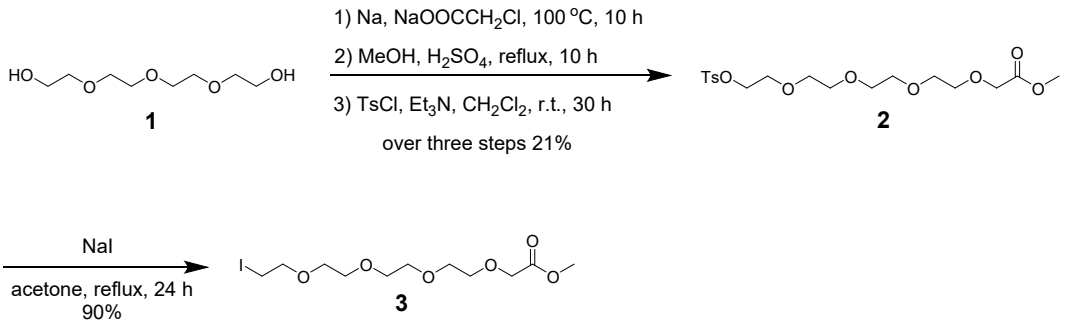
Synthesis



Scheme S1. Synthesis of intermediate compound **3**.

Compound 2. To the liquid tetraethylene glycol (54 mL) was added metallic sodium (2.32 g, 0.101 mol), the resulting mixture was then heated to 100 °C with stirring until the consumption of the sodium. Chloroacetate (11.8 g, 0.101 mol) was further added to the reaction mixture and kept stirring at 100 °C for another 10 hours. After cooling down to room temperature, the excess tetraethylene glycol was removed by evaporation under reduced pressure. The residue was redissolved in water (50 mL), and the solution was acidified by adding concentrated HCl (a.q.) to pH < 1. The mixture was filtrated, and the collected filtrate was concentrated by evaporation under reduced pressure. To the given residue was then added methanol (170 mL) and sulfuric acid (3 mL), respectively, and the resulting mixture was refluxed for 10 hours. after cooling down, the reaction mixture was then concentrated to remove the

methanol, the residue was further dissolved in water (50 mL) and neutralized to pH > 7 with saturated $NaHCO_3$ (a.q.). Then, the mixture was extracted by diethyl ether (30 mL × 3) and CH_2Cl_2 (50 mL × 3), respectively, after which the organic phase was combined and dried by anhydrous Na_2SO_4. The desiccant was discarded *via* filtration, and the filtrate was concentrated to give crude residue as dark brown liquid (9.70 g), which was redissolved in CH_2Cl_2 (160 mL). To this solution, trimethylamine (9.40 mL) and *p*-toluenesulfonyl chloride (10.0 g, 52.4 mmol) were further added. The resulting mixture was stirred at room temperature for 30 hours. After the reaction was completed as suggested by TLC, it was quenched by adding saturated $NaHCO_3$ (a.q., 40 mL) solution. The mixture was extracted with ethyl acetate (50 mL × 3), the combined organic phase was dried by anhydrous Na_2SO_4, which was further removed by filtration. The collected filtrate was concentrated by evaporation under reduced pressure to give a crude residue, which was subsequently submitted to flash silica gel chromatography for purification by using a binary eluent of petroleum /ethyl acetate = 2:1 →1:1→1:4. Compound **2** was isolated as light-yellow oil (8.00 g, 21%).

^{1}H NMR (400 MHz, CDCl3, 298 K) δ: 7.79 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 4.16-4.13 (m, 4 H), 3.75-3.70 (m, 5 H), 3.69-3.66 (m, 4 H), 3.65-3.60 (m, 4 H), 3.58-3.56 (m, 4 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, CDCl3, 298 K) δ: 170.74, 144.76, 132.81, 129.78, 127.79, 70.68, 70.47, 70.42, 70.37, 70.34, 70.32, 69.31, 68.45, 68.34, 51.58, 21.45.

MS (ESI) *m/z*: $[M+Na]^+$ 443.1. HRMS (ESI) Calcd. for $C_{18}H_{28}NaO_9S$ $[M+Na]^+$ 443.1352, Found: 443.1342.

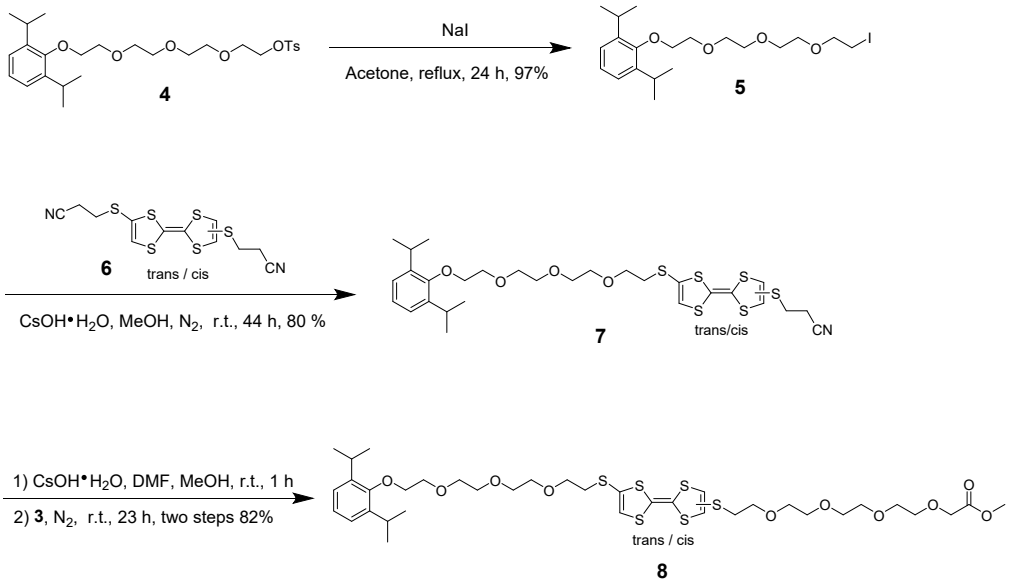
Compound 3. To a stirred solution of **2** (1.00 g, 2.38 mmol) in acetone (30 mL) was added NaI (3.57 g, 23.8 mmol), the resulting mixture was refluxed overnight. After the reaction was completed, the reaction mixture was filtered, and the collected filtrate was concentrated *via* evaporation under reduced pressure. The obtained residue was dissolved in CH_2Cl_2 (25 mL) and washed with water (5 mL × 3), the combined organic layer was then dried over anhydrous Na_2SO_4. The desiccant and solvents were removed by filtration and evaporation *in vacuo*, respectively, to give compound **3** as

yellow oil (0.81 g, 90%).

^{1}H NMR (400 MHz, CDCl3, 298 K) δ: 4.03 (s, 2 H), 3.63-3.57 (m, 7 H), 3.56-3.49 (m, 10 H), 3.12 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl3, 298 K) δ: 170.69, 71.78, 70.75, 70.52, 70.49, 70.46, 70.06, 68.45, 51.68, 3.18.

MS (ESI) *m/z*: $[M+Na]^+$ 339.0. HRMS (ESI) Calcd. for $C_{11}H_{21}INaO_6$ $[M+Na]^+$ 399.0281, Found: 399.0266.



Scheme S2. Synthesis of TTF-containing intermediate compound **8**.

Compound 5. To a solution of compound **4**[1] (6.78 g, 13.3 mmol) in acetone (324 mL) under nitrogen atmosphere was added NaI (20.0 g, 133 mmol), the resulting mixture was then heated at 80 °C for 24 hours until the reaction was completed as suggested by TLC. After cooling down, the mixture was filtered, and the collected filtrate was concentrated by evaporation *in vacuo*. The residue was dissolved in CH_2Cl_2 (80 mL) and washed with water (40 mL × 3), the combined organic layer was then dried over anhydrous Na_2SO_4. The desiccant and solvents were removed by filtration and evaporation *in vacuo*, respectively, to afford compound **5** as yellow oil (6.00 g, 97%).

^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.12 (br, 3 H), 3.95-3.93 (m, 2 H), 3.89-3.87

(m, 2 H), 3.81-3.70 (m, 10 H), 3.40 (heptet, *J* = 7.2 Hz, 2 H), 3.29 (t, *J* = 7.2 Hz, 2 H), 1.24 (d, *J* = 7.2 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 153.04, 141.80, 124.65, 124.01, 73.90, 72.01, 71.06, 70.85, 70.76, 70.60, 70.31, 26.24, 24.21.

MS (ESI) *m/z*: $[M+Na]^+$ 487.1. HRMS (ESI) Calcd. for $C_{20}H_{34}IO_4$ $[M+H]^+$ 465.1502, Found: 465.1496.

Compound 7. To a solution of compounds **5** (0.640 g, 1.38 mmol) and **6**[2] (1.03 g, 2.76 mmol) in the dry DMF (25 mL) under nitrogen atmosphere, was added a solution of cesium hydroxide monohydrate (0.232 g, 1.38 mmol) in methanol (5 mL). The resulting mixture was stirred at room temperature for 44 hours until TLC suggested the completion of the reaction. 58 mL water was added to quench the reaction and the mixture was extracted by ethyl acetate (29 mL × 2). The combined organic phase was then washed by brine (58 mL × 1), and dried over anhydrous Na_2SO_4. The desiccant and solvent were removed by filtration and evaporation under reduced pressure, respectively. The obtained residue was further purified by flash column chromatography eluted with DCM/EtOAc = 50:1, to give compound **7** as brown oil (0.726 g, 80%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.12 (br, 3 H), 6.58/6.57 (s, 1 H), 6.45 (s, 1 H), 3.96-3.92 (m, 2 H), 3.90-3.86 (m, 2 H), 3.81-3.77 (m, 2 H), 3.76-3.66 (m, 8 H), 3.40 (heptet, *J* = 6.8 Hz, 2 H), 3.00-2.94 (m, 4 H), 2.73-2.68 (m, 2 H), 1.24 (d, *J* = 7.2 Hz, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 153.00, 141.85, 126.63, 126.61, 126.40, 126.28, 124.67, 124.04, 123.86, 123.78, 123.07, 123.06, 117.51, 113.94, 113.90, 110.86, 73.86, 71.04, 70.81, 70.68, 70.58, 69.69, 69.68, 35.15, 30.56, 26.24, 24.19, 18.51.

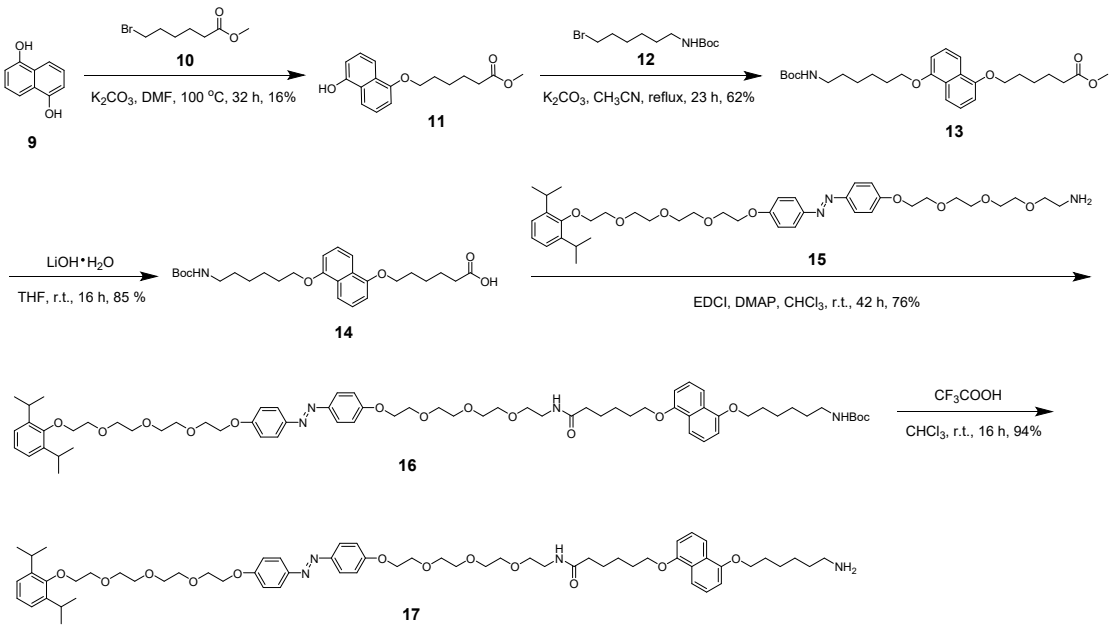
MS (ESI) *m/z*: $[M+Na]^+$ 680.1. HRMS (ESI) Calcd. for $C_{29}H_{39}NNaO_4S_6$ $[M+Na]^+$ 680.1101, Found: 680.1069.

Compound 8. To a solution of **7** (0.240 g, 0.364 mmol) in the dry DMF (8.4 mL) under nitrogen atmosphere, was added a solution of cesium hydroxide monohydrate (0.061 g, 0.364 mmol) in methanol (2.4 mL). The resulting mixture was stirred at room temperature for one hour, after which compound **3** (0.274 g, 0.728 mmol) was added to the reaction solution and kept stirring for another 23 hours. After the reaction was completed as revealed by TLC, it was quenched by adding saturated aqueous ammonium chloride solution (4.2 mL). The mixture was then extracted with ethyl acetate (21 mL × 1), the collected organic phase was washed by saturated $NaHCO_3$ aqueous solution (21 mL × 1) and brine (21 mL × 1), respectively. The combined organic layers were dried over Na_2SO_4, which was further discarded by filtration. The collected filtrate was concentrated, and the obtained crude residue was then purified by silica gel column chromatography (eluent: DCM/EtOAc = 25/3) to afford compound **8** as yellow oil (0.255 g, 82%)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.11 (br, 3 H), 6.45-6.43 (m, 2 H), 4.19 (s, 2 H), 3.96-3.92 (m, 2 H), 3.90-3.86 (m, 2 H), 3.81-3.65 (m, 27 H), 3.40 (heptet, J = 6.8 Hz, 2 H), 2.99-2.93 (m, 4 H), 1.23 (d, J = 6.8 Hz, 12 H).

^{13}C NMR (100 MHz, CDCl3, 298 K) δ: 170.93, 153.01, 141.84, 126.52, 126.46, 124.64, 124.03, 123.13, 123.03, 112.21, 112.17, 73.86, 71.04, 70.93, 70.81, 70.68, 70.65, 70.63, 70.57, 70.54, 70.51, 69.67, 69.65, 68.64, 51.87, 35.14, 26.23, 24.18.

MS (ESI) *m/z*: $[M+H]^+$ 853.3. HRMS (ESI) Calcd. for $C_{37}H_{56}NaO_{10}S_6$ $[M+Na]^+$ 875.2095, Found: 875.2058.



Scheme S3. Synthesis of azo and DNP containing intermediate compound **17**.

Compound 11. To a solution of compounds **9** (9.19 g, 57.4 mmol) and **10** (2.00 g, 9.57 mmol) in anhydrous DMF (50 mL) was added K_2CO_3 (8.61 g, 62.3 mmol), the resulting mixture was stirred at 100 °C for 32 hours under nitrogen atmosphere. After the reaction was completed, the reaction mixture was filtered, and the filtrate was poured into water (300 mL) and ethyl acetate (50 mL) for phase separation. The organic layer was collected and dried over anhydrous Na_2SO_4, which was further discarded by filtration. The filtrate was concentrated by evaporation under reduced pressure to give crude residue, which was further purified by flash column chromatography by using a binary eluent of PE/EtOAc = 25:1, to offer compound **11** as white solid (0.441 g, 16%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.88 (d, J = 8.4 Hz, 1 H), 7.74 (d, J = 8.4 Hz, 1 H), 7.40 (dd, J_1 = 8.0 Hz, J_2 = 7.6 Hz, 1 H), 7.31 (dd, J_1 = 8.4 Hz, J_2 = 7.6 Hz, 1 H), 6.87 (dd, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1 H), 6.84 (d, J = 7.6 Hz, 1 H), 5.25 (s, 1 H), 4.16 (t, J = 6.4 Hz, 2 H), 3.70 (s, 3 H), 2.41 (t, J = 7.2 Hz, 2 H), 2.01-1.94 (m, 2 H), 1.83-1.75 (m, 2 H), 1.68-1.61 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 174.52, 154.67, 151.41, 127.04, 125.42, 125.24, 125.08, 114.57, 113.59, 109.34, 105.16, 67.77, 51.69, 34.10, 28.99, 25.90, 24.76.

MS (ESI) *m/z*: $[M+Na]^+$ 311.1. HRMS (ESI) Calcd. for $C_{17}H_{20}NNaO_6$ $[M+Na]^+$ 311.1259, Found: 311.1243.

Compound 13. To a solution of compounds **11** (0.210 g, 0.728 mmol) and **12** (0.305 g, 1.09 mmol) in anhydrous acetonitrile (7 mL) was added K_2CO_3 (0.402 g, 2.91 mmol), the resulting mixture was then refluxed for 23 hours under nitrogen atmosphere. After the reaction was completed, the mixture was allowed to cool down and filtered. The filtrate was concentrated to give a residue, which was dissolved in CH_2Cl_2 (50 mL), then washed by water (50 mL × 3). The organic phase was dried over anhydrous Na_2SO_4. After the desiccant and solvent were discarded by filtration and evaporation under reduced pressure, respectively, the residue was further purified by flash column chromatography with a binary eluent of DCM/PE = 1:2. Compound **12** was isolated as white solid (0.218 g, 62%).

^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.87-7.84 (m, 2 H), 7.37 (t, *J* = 8.4 Hz, 2 H), 6.83 (d, *J* = 7.8 Hz, 2H), 4.61 (br, 1 H), 4.14-4.44 (m, 4 H), 3.70 (s 1 H), 3.15 (br, 2 H), 2.40 (t, *J* = 7.8 Hz, 2 H), 1.98-1.90 (m, 4 H), 1.80-1.75 (m, 2 H), 1.65-1.52 (m, 6 H), 1.47-1.41 (m, 11 H).

^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 174.13, 156.03, 154.60, 154.54, 126.75, 126.73, 125.11, 125.10, 114.11, 114.03, 105.25, 79.03, 67.95, 67.75, 51.54, 40.57, 34.05, 30.10, 29.25, 29.02, 28.46, 26.64, 26.04, 25.90, 24.77.

MS (ESI) *m/z*: $[M+Na]^+$ 510.3. HRMS (ESI) Calcd. for $C_{28}H_{41}NNaO_6$ $[M+Na]^+$ 510.2832, Found: 510.2807.

Compound 14. To a solution of compound **13** (0.200 g, 0.410 mmol) in THF (10 mL) was added a solution of $LiOH·H_2O$ (0.688 g, 16.4 mmol) in water (2.5 mL). The resulting mixture was stirred at room temperature under argon atmosphere for 16 hours until the reaction was completed. The reaction mixture was concentrated to remove the solution, the residue was further dissolved in CH_2Cl_2 (30 mL). The solution was then acidified to pH = 4.0 by diluted HCl (0.1 M), the organic layers were separated and dried by anhydrous Na_2SO_4. The desiccant was discarded by

filtration, and filtrate was then concentrated by evaporation under reduced pressure to give compound **14** as white solid (0.165 g, 85%), which was further used directly for the next step.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.84-7.81 (m, 2 H), 7.34 (t, *J* = 8.0 Hz, 1 H), 6.81 (d, *J* = 7.6 Hz, 2 H), 4.52 (br, 1 H), 4.14-4.09 (m, 4 H), 3.14 (d, *J* = 6.4 Hz, 2 H), 2.43 (t, *J* = 7.2 Hz, 2 H), 1.98-1.88 (m, 4 H), 1.81-1.74 (m, 2 H), 1.68-1.51 (m, 6 H), 1.46-1.39 (m, 11 H).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 179.27, 156.11, 154.62, 154.57, 126.78, 126.76, 125.15, 125.11, 114.15, 114.08, 105.29, 79.19, 67.98, 67.78, 40.59, 34.08, 30.07, 29.27, 29.05, 28.48, 26.67, 26.05, 25.87, 24.58.

MS (ESI) *m/z*: $[M+H]^+$ 483.2. HRMS (ESI) Calcd. for $C_{27}H_{39}NNaO_6$ $[M+Na]^+$ 496.2675, Found: 496.2664.

Compound 16. To the solution of compounds **14** (0.165 g, 0.348 mmol) and **15**[3] (0.253 g, 0.348 mmol) in chloroform (10 mL) were added EDCI (0.120 g, 0.625 mmol) and DMAP (catalytic amount), the resulting mixture was stirred under nitrogen gas atmosphere at room temperature for 42 hours until TLC suggested the reaction was completed. The reaction mixture was then concentrated by evaporation *in vacuo*, and the residue crude was further purified by silica gel column chromatography (eluent: DCM/MeOH = 20:1) to give compound **16** as yellow solid (0.312 g, 76%).

^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.87 (d, *J* = 9.0 Hz, 4 H), 7.84 (d, *J* = 7.8 Hz, 2 H), 7.37-7.34 (m, 2 H), 7.11 (br, 3 H), 7.03-7.00 (m, 4 H), 6.83-6.81 (m, 2 H), 6.22 (br, 1 H), 4.57 (br, 1 H), 4.22 (t, *J* = 4.8 Hz, 2 H), 4.19 (t, *J* = 4.8 Hz, 2 H), 4.13-4.11 (m, 4 H), 3.94-3.91 (m, 4 H), 3.87 (t, *J* = 5.4 Hz, 4 H), 3.80-3.78 (m, 4 H), 3.77-3.73 (m, 6 H), 3.69-3.67 (m, 2 H), 3.65-3.61 (m, 4H), 3.57 (t. *J* = 4.8 Hz, 2 H), 3.48-3.46 (m, 2 H), 3.41 (heptet, *J* = 7.2 Hz, 2 H), 3.16 (d, *J* = 6.0 Hz, 2 H), 2.25 (t, *J* = 7.2 Hz, 2 H), 1.96-1.91 (m, 4 H), 1.79-1.74 (m, 2 H), 1.63-1.52 (m, 6 H), 1.48-1.41 (m, 11 H), 1.24 (d, *J* = 7.2 Hz, 12 H).

^{13}C NMR (150 MHz, CDCl3, 298 K) δ: 173.10, 160.82, 160.67, 156.03, 154.59, 154.53, 153.01, 147.13, 147.06, 141.82, 126.73, 126.70, 125.14, 125.11, 124.64,

124.33, 124.01, 114.79, 114.75, 114.08, 114.05, 105.25, 79.00, 73.86, 71.01, 70.93, 70.83, 70.77, 70.55, 70.51, 70.50, 70.17, 69.91, 69.64, 69.63, 67.95, 67.81, 67.68, 67.63, 40.55, 39.19, 36.59, 30.07, 29.25, 29.12, 28.47, 26.65, 26.22, 26.04, 26.03, 25.52, 24.17.

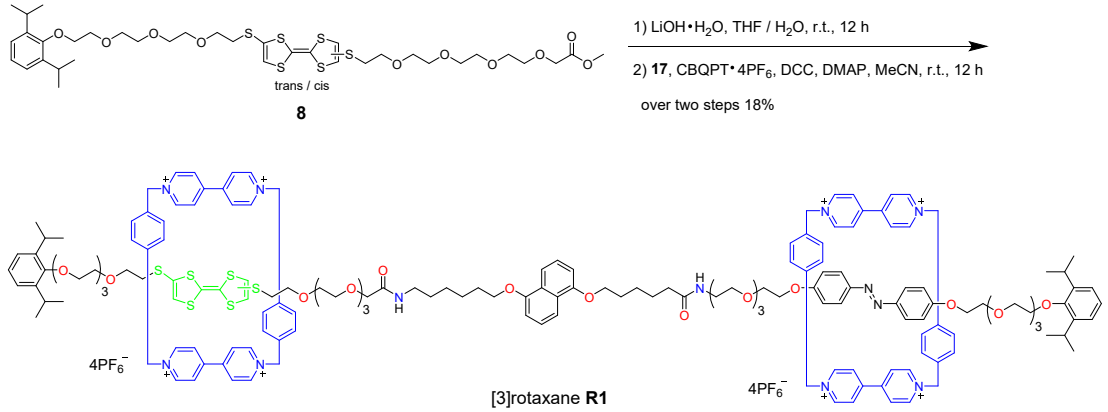
MS (ESI) *m/z*: $[M+Na]^+$ 1203.6. HRMS (ESI) Calcd. for $C_{67}H_{96}N_4NaO_6$ $[M+Na]^+$ 1203.6821, Found: 1203.6743.

Compound 17. To a solution of compound **16** (0.312 g, 0.264 mmol) in chloroform (6.5 mL) was added TFA (0.65 mL), the resulting mixture was stirred in an ice bath under nitrogen gas atmosphere for 16 hours until TLC suggested the reaction was completed. The reaction mixture was concentrated *via* evaporation under reduced pressure, the received residue was dissolved in CH_2Cl_2 (50 mL) and then washed with saturated $NaHCO_3$ aqueous solution (50 mL × 3). The organic phase was dried by anhydrous Na_2SO_4, which was further discarded by filtration. The collected filtrate was evaporation under reduced pressure to afford compound **17** as yellow solid (0.268 g, 94%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.87-7.85 (m, 4 H), 7.83-7.79 (m, 2 H), 7.53-7.29 (m, 2 H), 7.11 (br, 3 H), 7.02-6.98 (m, 4 H), 6.78-6.73 (m, 2 H), 6.30 (t, *J* = 4.2 Hz, 1 H), 4.21 (t, *J* = 5.8 Hz, 2 H), 4.17 (t, *J* =4.8 Hz, 2 H), 4.07 (t, *J* = 6.0 Hz, 2 H), 4.01 (t, *J* = 6.0 Hz, 2 H), 3.94-3.90 (m, 4 H), 3.88-3.85 (m, 4 H), 3.80-3.72 (m, 10 H), 3.68-3.66 (m, 2 H), 3.64-3.60 (m, 4 H), 3.56 (t, *J* = 4.8 Hz, 2 H), 3.47-3.34 (m, 4 H), 2.97 (t, *J* = 7.2 Hz, 2 H), 2.23 (t, *J* = 7.6 Hz, 2 H), 1.94-1.81 (m, 4 H), 1.78-1.71 (m, 4 H), 1.61-1.50 (m, 4 H), 1.47-1.40 (m, 2 H), 1.23 (d, *J* = 6.8 Hz, 12 H).

^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 173.09, 160.83, 160.66, 154.61, 154.56, 153.03, 147.16, 147.09, 141.83, 126.74, 125.14, 124.66, 124.35, 124.03, 114.81, 114.77, 114.07, 105.27, 73.87, 71.01, 70.93, 70.82, 70.77, 70.55, 70.51, 70.16, 69.92, 69.64, 67.96, 67.82, 67.69, 67.63, 41.73, 39.16, 36.55, 32.69, 29.26, 29.12, 26.66, 26.23, 26.12, 26.04, 25.53, 24.18.

MS (ESI) *m/z*: $[M+H]^+$ 1108.7. HRMS (ESI) Calcd. for $C_{62}H_{89}N_4O_{12}$ $[M+H]^+$ 1081.6477, Found: 1081.6503.



Scheme S4. The synthetic route of [3]rotaxane **R1**.

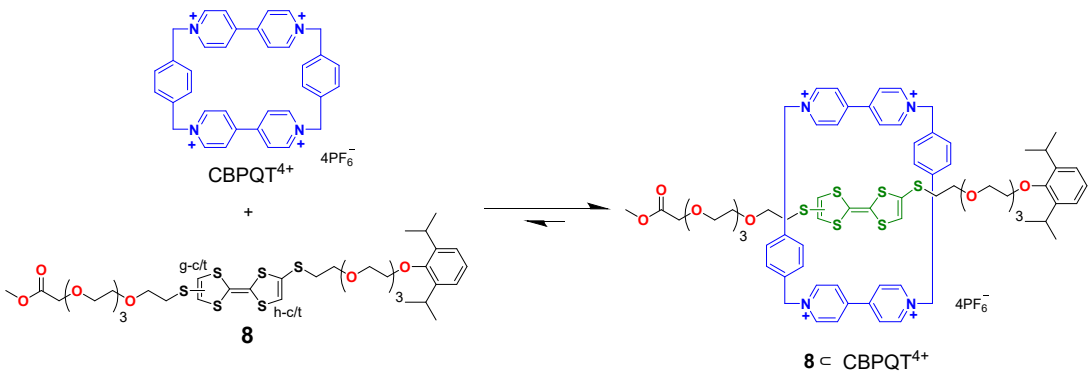
[3]rotaxane R1. To a solution of lithium hydroxide monohydrate (0.482 g, 11.5 mmol) in water (5 mL) was added a solution of compound **8** (0.245 g, 0.287 mmol) in the dry THF (25 mL) under nitrogen atmosphere. The resulting mixture was stirred at room temperature for 12 hours until the reaction was completed, after which the solvent was removed by evaporation under reduced pressure. The reaction mixture was acidified to pH = 4 by using diluted HCl (a.q., 0.1 M), and then extracted with CH_2Cl_2 (50 mL × 3). The combined organic phase was washed by water (50 mL × 3) and dried over anhydrous Na_2SO_4. The desiccant and solvent were discarded by filtration and evaporation *in vacuo*, respectively, to give a yellow oil (0.204 g) which was dissolved in the acetonitrile (2 mL). To this solution, compound **17** (0.263 g, 0.243 mmol) and CBPQT•$4PF_6$ (0.534 g, 0.485 mmol) were added. The resulting mixture was then ultrasonication under nitrogen atmosphere for 15 min, after which DCC (0.085 g, 0.413 mmol) and DMAP (catalytic amount) were added and then stirred at room temperature. After the reaction was completed as monitored by TLC, the reaction mixture was concentrated by evaporation *in vacuo*, and the residue was submitted to silica gel flash column chromatography for purification (eluent: NH_4Cl (a.q.) /MeOH/DMF = 5:4:1), which gave a dark-green solid. This product was further dissolved in water (40 mL), then, the saturated NH_4PF_6 aqueous solution was added to produce dark-green precipitates, which were collected by filtration and washed by water (50 mL). After drying under vacuum, the target [3]Rotaxane **R1** could be

obtained as dark-green solid (0.179 g, 18%).

^{1}H NMR (400 MHz, CD_3CN, 298 K) δ: 9.04 (d, *J* = 4.4 Hz, 8 H), 8.86 (d, *J* = 6.0 Hz, 8 H), 8.02 (br, 8 H), 7.90 (br, 8 H), 7.81-7.59 (m, 16 H), 7.40-7.04 (m, 9 H), 6.93-5.37 (m, 31 H), 4.16-4.05 (m, 8 H), 3.96-3.65 (m, 46 H), 3.63-3.54 (m, 8 H), 3.48 (t, *J* = 6.0 Hz, 2 H), 3.42-3.24 (m, 8 H), 3.14-3.08 (m, 4 H), 2.25 (br, 2 H), 1.77-1.45 (m, 10 H), 1.20 (d, *J* = 7.2 Hz, 24 H).

^{13}C NMR (150 MHz, CD_3CN, 298 K) δ: 173.26, 170.03, 160.46, 150.04, 153.00, 145.75, 144.50, 141.85, 141.83, 136.61, 130.91, 130.87, 126.82, 126.71, 126.64, 126.02, 125.85, 124.79, 124.76, 124.09, 124.07, 123.77, 123.65, 119.78, 119.37, 114.32, 114.24, 108.18, 105.37, 73.88, 70.72, 70.65, 70.54, 70.45, 70.37, 70.35, 70.31, 70.27, 70.21, 70.17, 70.15, 70.07, 70.02, 69.89, 69.81, 69.30, 69.26, 69.21, 69.09, 68.24, 68.13, 67.94, 64.67, 38.94, 38.31, 35.72, 35.19, 35.08, 29.17, 28.85, 28.81, 26.07, 25.95, 25.68, 25.31, 25.25, 23.42, 23.41.

HRMS (ESI) Calcd. for $C_{170}H_{204}F_{30}N_{12}O_{21}P_5S_6$ $[M-3PF_6^-]^{3+}$ 1222.0594, Found: 1222.0599.



Scheme S5. Schematic presentation of complexation behavior between the TTF-containing compound **8** and macrocycle $CBPQT^{4+}$•$4PF_6^-$.

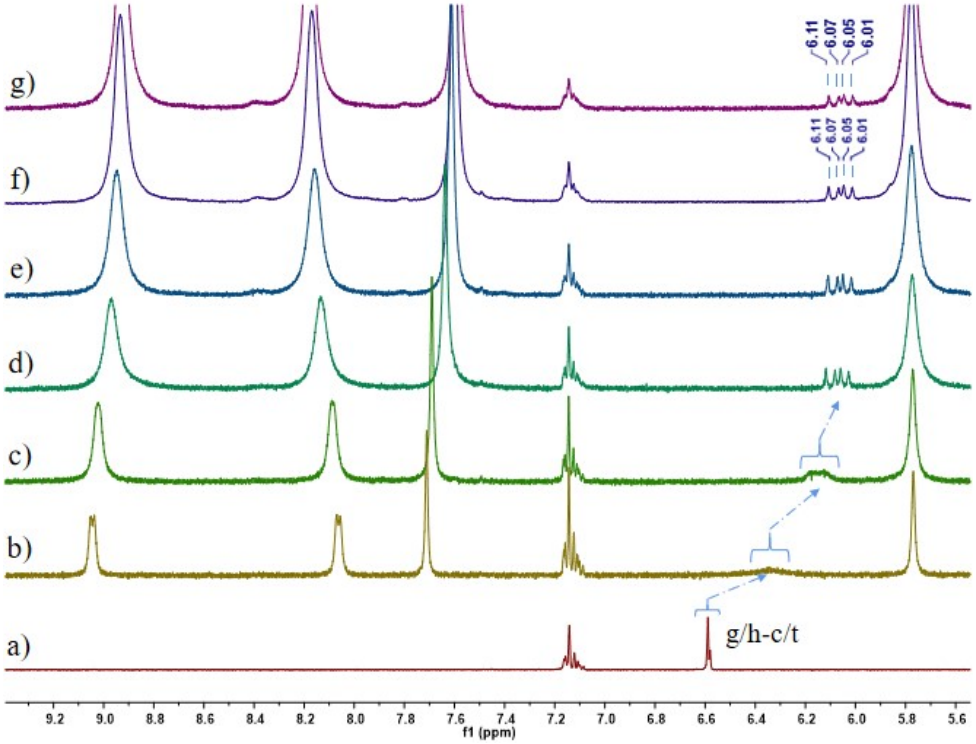
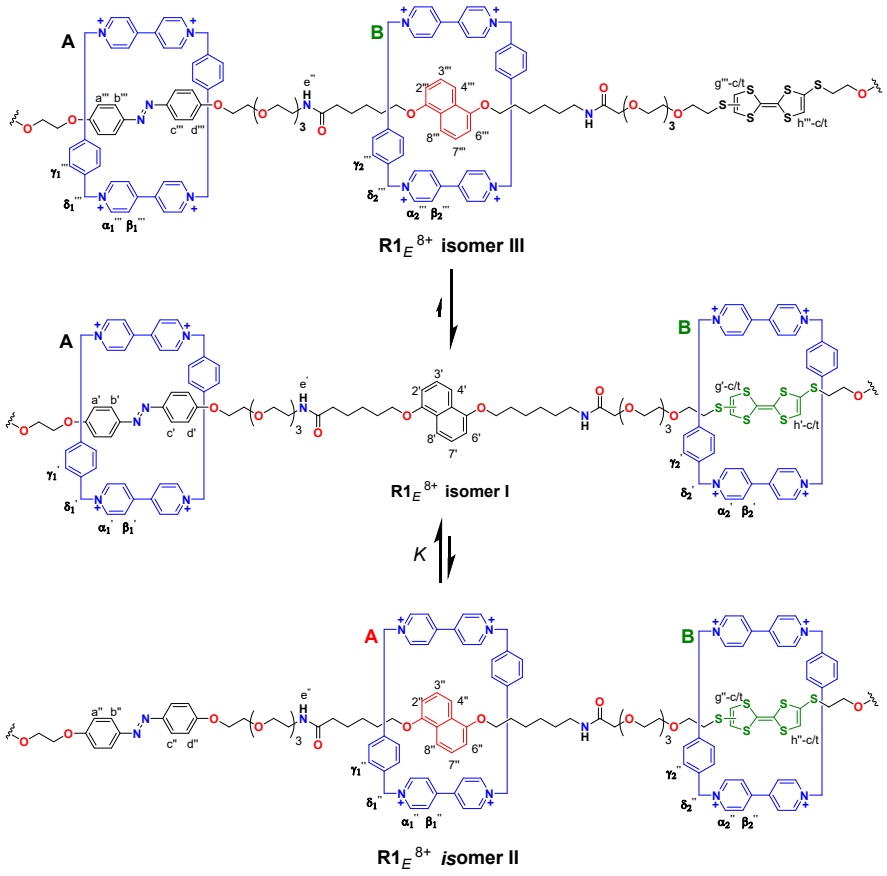


Fig. S1. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298K) for the solution of compound **8** (4.0 mM) in the presence of a) 0, b) 0.5, c) 1.0, d) 2.0, e) 3.0, f) 4.0 and g) 5.0 equiv. of $CBPQT^{4+}\bullet 4PF_6^-$.



Scheme S6. Schematic representation for the shuttling of CBPQT^{4+} rings on the axle of [3]rotaxane **R1**$_E$•8PF$_6$.

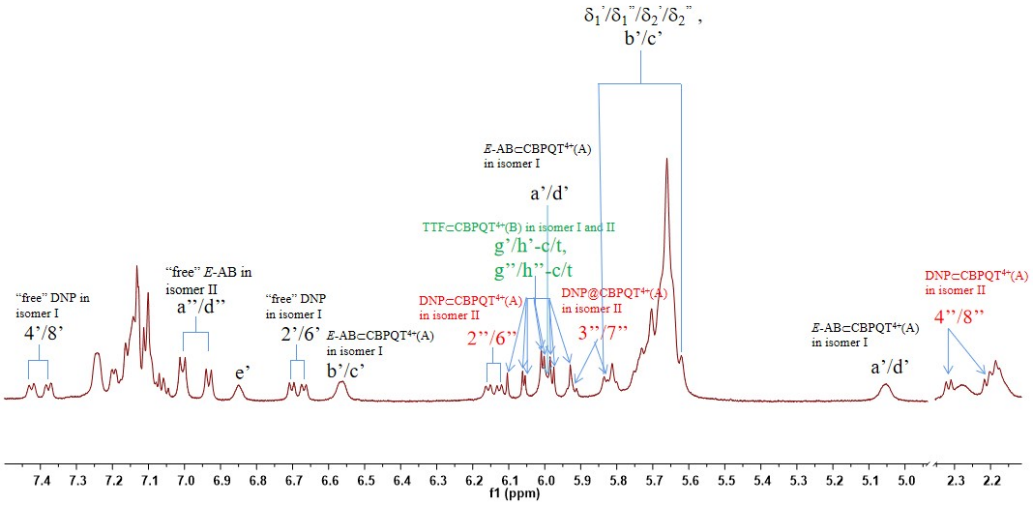


Fig. S2. Partial ^{1}H NMR spectrum (600 MHz, 4.0 mM, CD_3CN) of the tristable [3]rotaxane **R1**$_E$•8PF$_6$ recorded at 233 K. Note: (1) the identifiable ^{1}H NMR signals from the CBPQT^{4+}(A)-encircled *E*-AB unit of **R1**$_E^{8+}$ isomer I, CBPQT^{4+}(A)-encircled DNP unit of **R1**$_E^{8+}$ isomer II and CBPQT^{4+}(B)-encircled TTF unit of **R1**$_E^{8+}$ isomer I and isomer II could be clearly observed at the low temperature of 233 K. However, signals from CBPQT^{4+}(A)-encircled *E*-AB unit, CBPQT^{4+}(B)-encircled DNP unit and "free" TTF unit of **R1**$_E^{8+}$ isomer III could not be observed at 233 K. (2) the signals were assigned by comparing their chemical shifts with those of the corresponding complexations in the reported literatures [4-6].

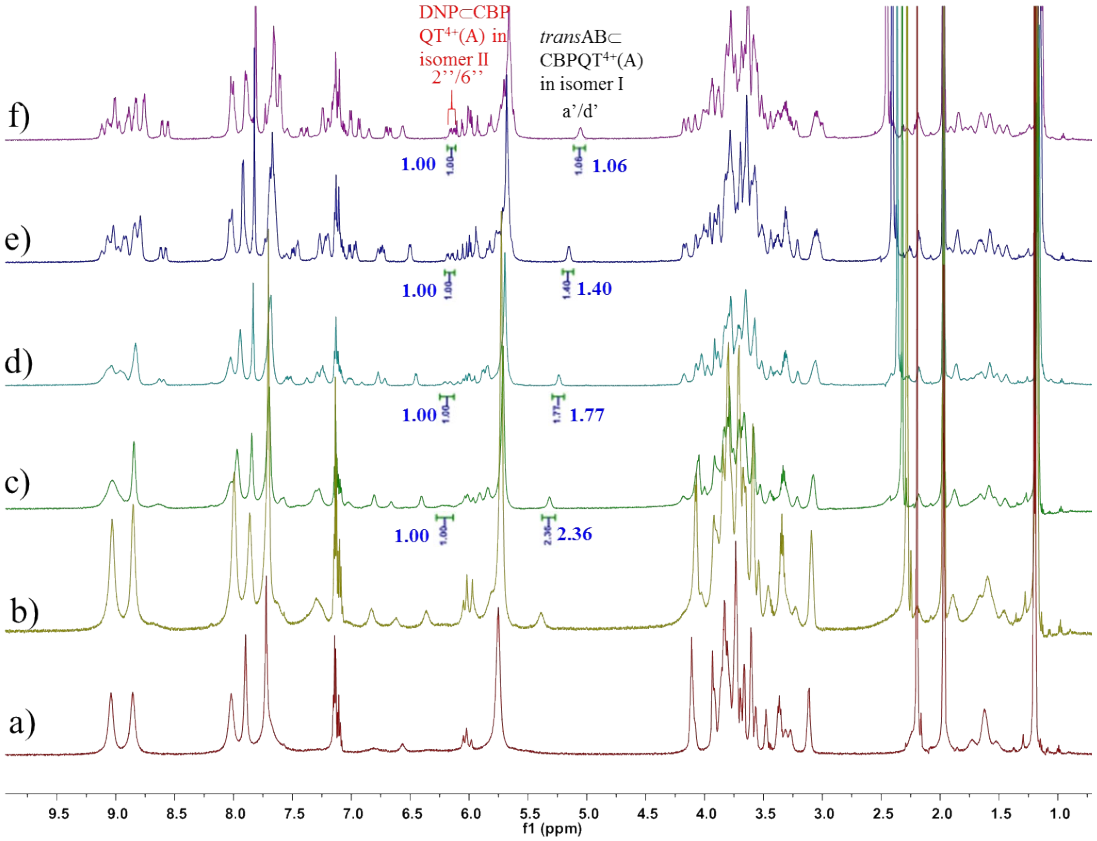


Fig. S3. The temperature-varied ^{1}H NMR spectra (600 MHz, 4.0 mM, CD_3CN) of the [3]rotaxane **R1**$_E$•8PF_6 recorded at a) 298 K; b) 273 K, c) 263 K, d) 253 K, e) 243 K, and f) 233 K, respectively.

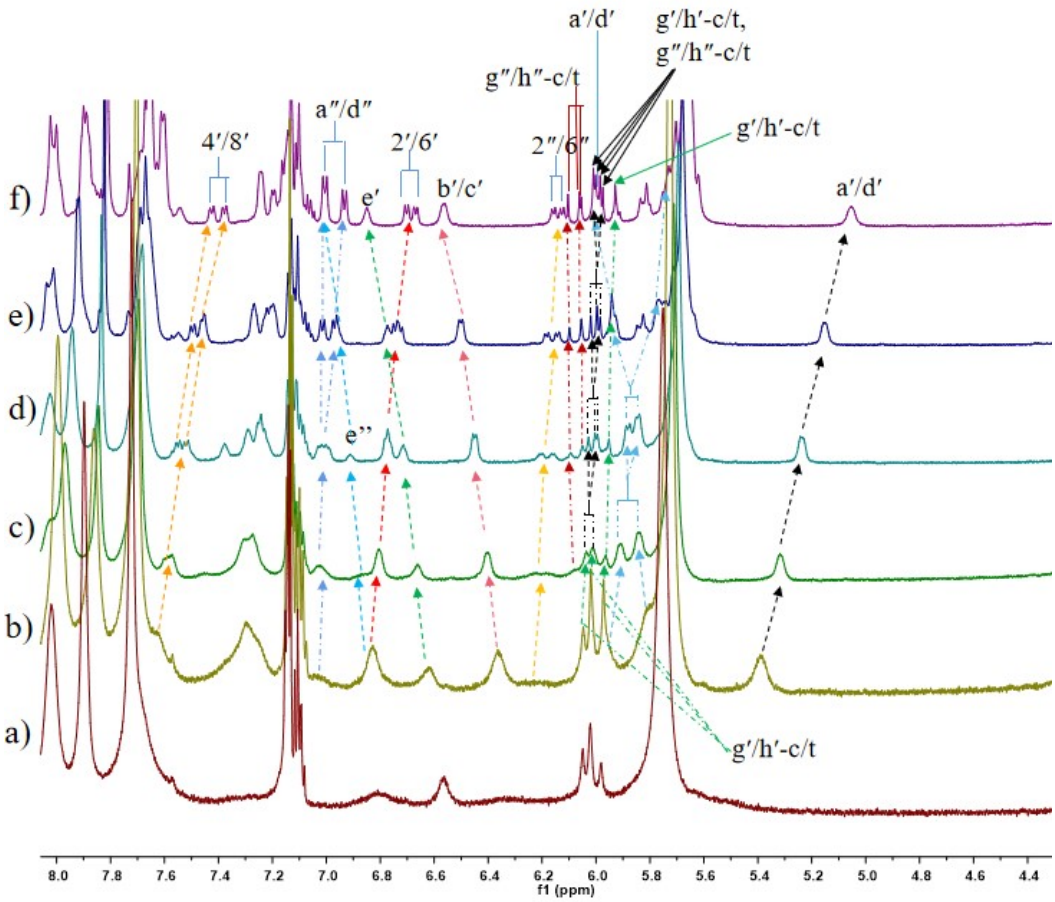
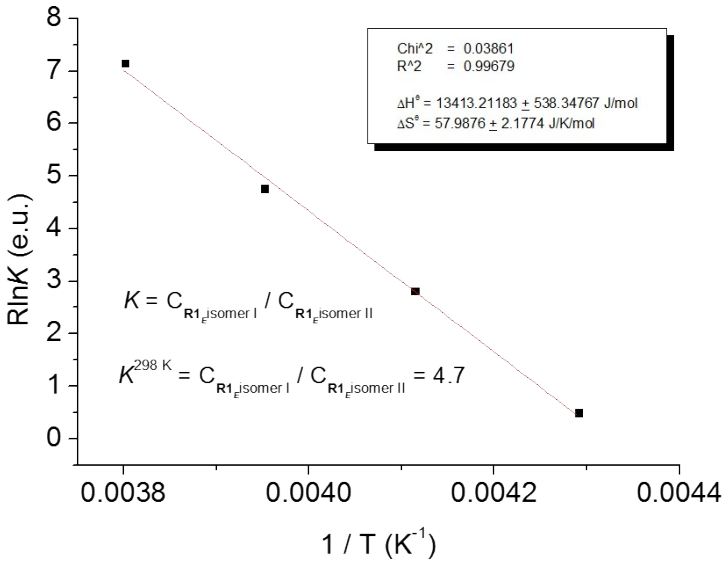


Fig. S4. Partial temperature-varied ^{1}H NMR spectra (600 MHz, 4.0 mM, CD_3CN) of the [3]rotaxane **R1**$_E$•8PF_6 recorded at a) 298 K; b) 273 K, c) 263 K, d) 253 K, e) 243 K, and f) 233 K, respectively.

Note: (1) The VT-NMR study showed that the ratio of **R1**$_E^{8+}$ isomer I to isomer II was changed with decreasing temperature from 273 K to 233 K, while the **R1**$_E^{8+}$ isomer III was not observed (Scheme S6). The chemical shifts of protons H-g/h-c/t (δ = 6.05~5.98 ppm) of TTF unit in **R1**$_E^{8+}$ at 298 K were almost the same with the CBPQT^{4+}-encapsulated TTF unit (δ = 6.05~5.97 ppm) in **R1**$_E^{8+}$ at 273 K, also suggesting almost all the TTF unit was encapsulated by CBPQT^{4+}(B) at 298 K. These results showed that the ratio of **R1**$_E^{8+}$ isomer I to isomer II was temperature dependent in the solution, while **R1**$_E^{8+}$ isomer III was almost nonexistent in solution at temperature from 233 K to 298 K. (2) the signals were assigned by comparing their chemical shifts with those of the corresponding complexations in the reported literatures [4-6].



The van't Hoff equation:

$$\ln K = -\frac{\Delta H^{\Theta}}{RT} + \frac{\Delta S^{\Theta}}{R}$$

Fig. S5. The Van't Hoff plot with best fit straight line for equilibrium between $\mathbf{R1}_E^{8+}$ isomer I and $\mathbf{R1}_E^{8+}$ isomer II in CD_3CN. The equilibrium constant K at 298 K, extrapolated from fitted Van't Hoff plot is 4.7.

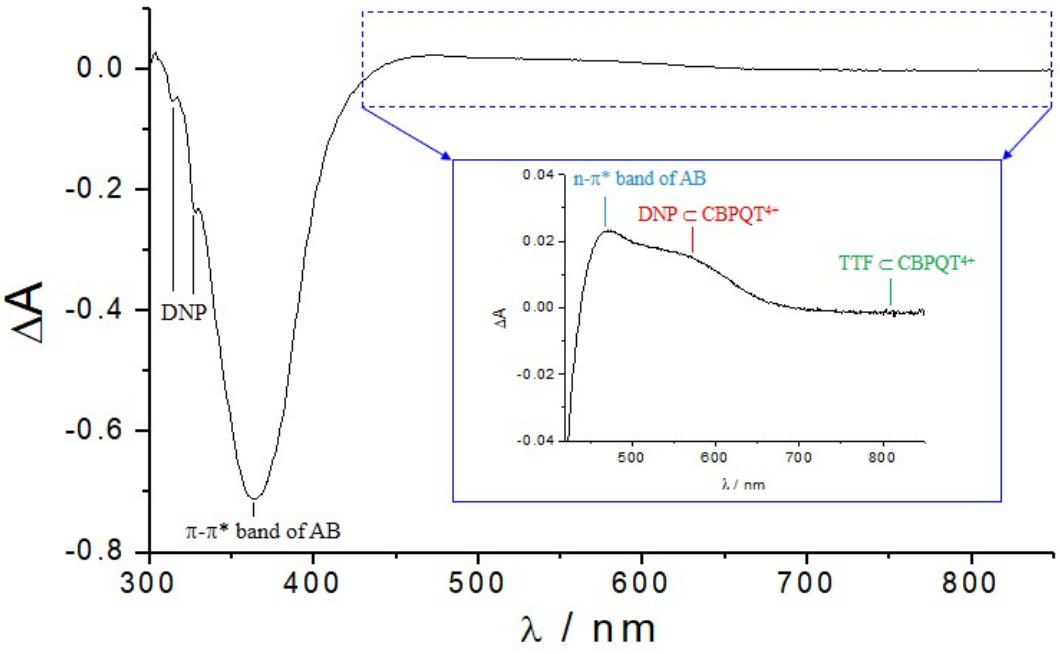


Fig. S6. The difference between the UV/Vis absorption spectra for the solution of $\mathbf{R1}_E \bullet 8PF_6$ (0.04 mM in MeCN at 298 K) before and after irradiation with UV light (365 nm). The differences in absorption ΔA = A (before UV irradiation) – A (after UV irradiation).

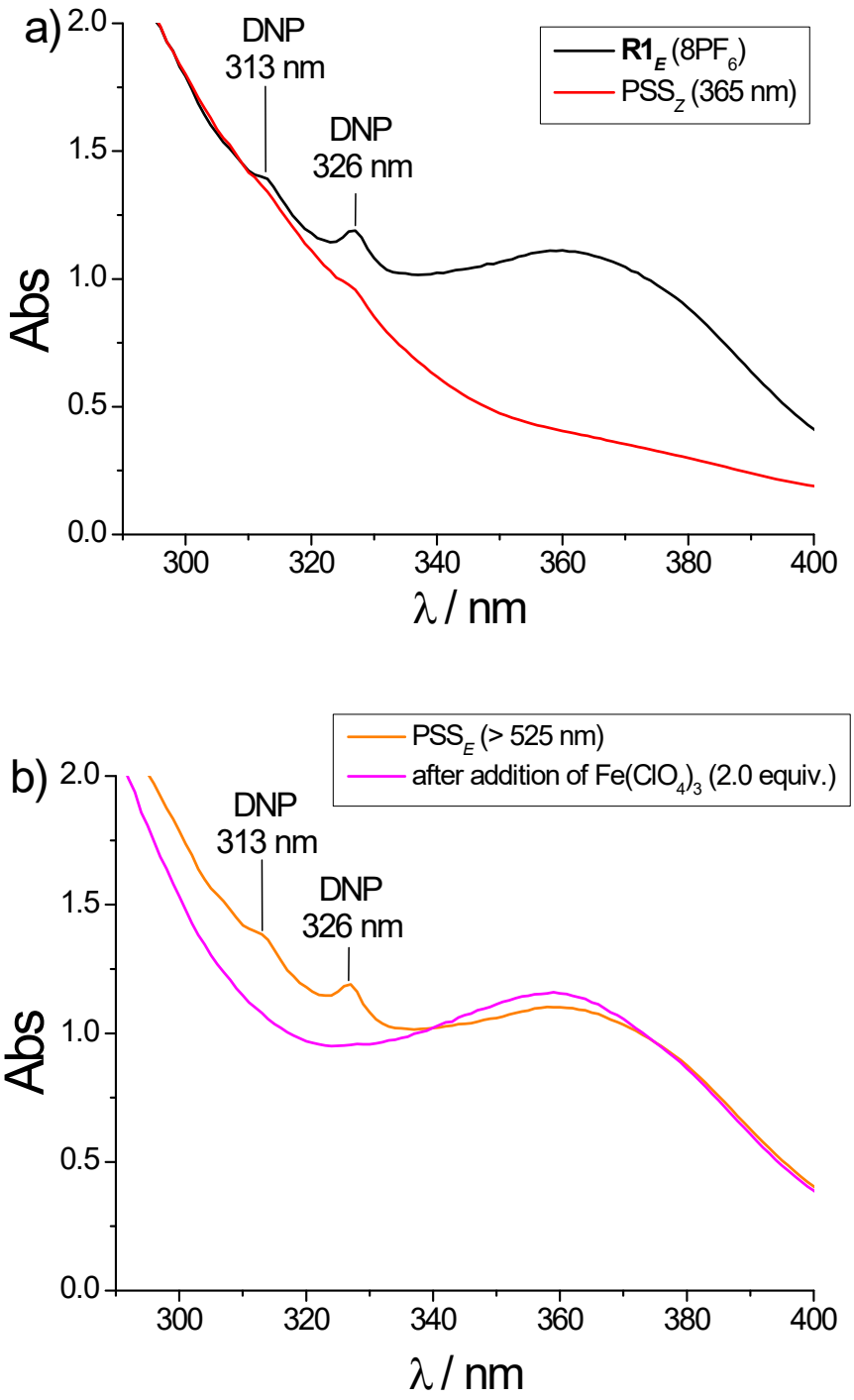
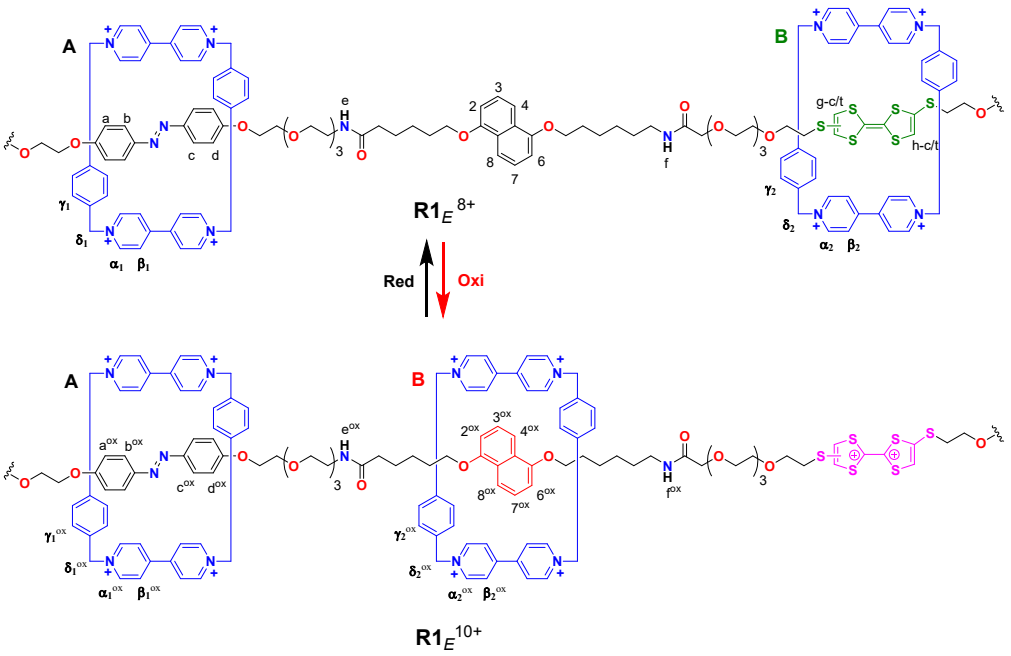


Fig. S7. Partial UV/Vis absorption spectra for the solution of a) **R1**$_E$•8PF$_6$ (0.04 mM in MeCN at 298 K) before (black line) and after (red line) irradiation with UV light (365 nm); b) the PSS$_E$ (> 525 nm) mixtures of **R1** before (purple line) and after (magenta line) 2.0 equiv. of Fe(ClO$_4$)$_3$ was added.



Scheme S7. Schematic presentation of the redox triggered macrocyclic shuttling of [3]rotaxane **R1**.

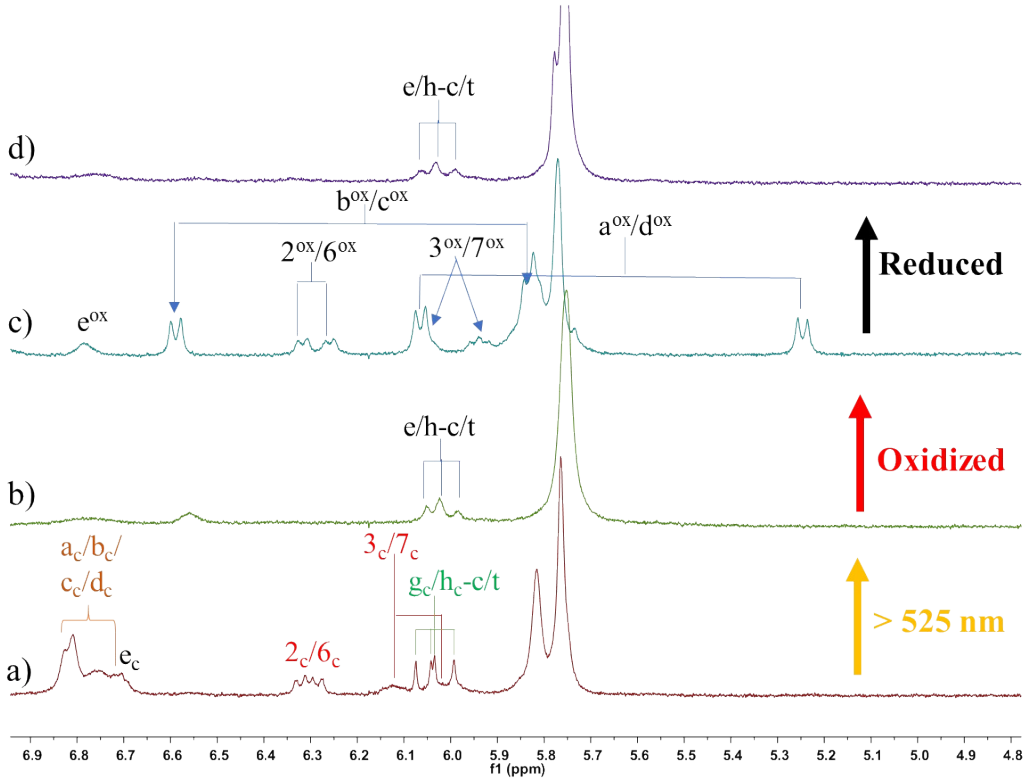
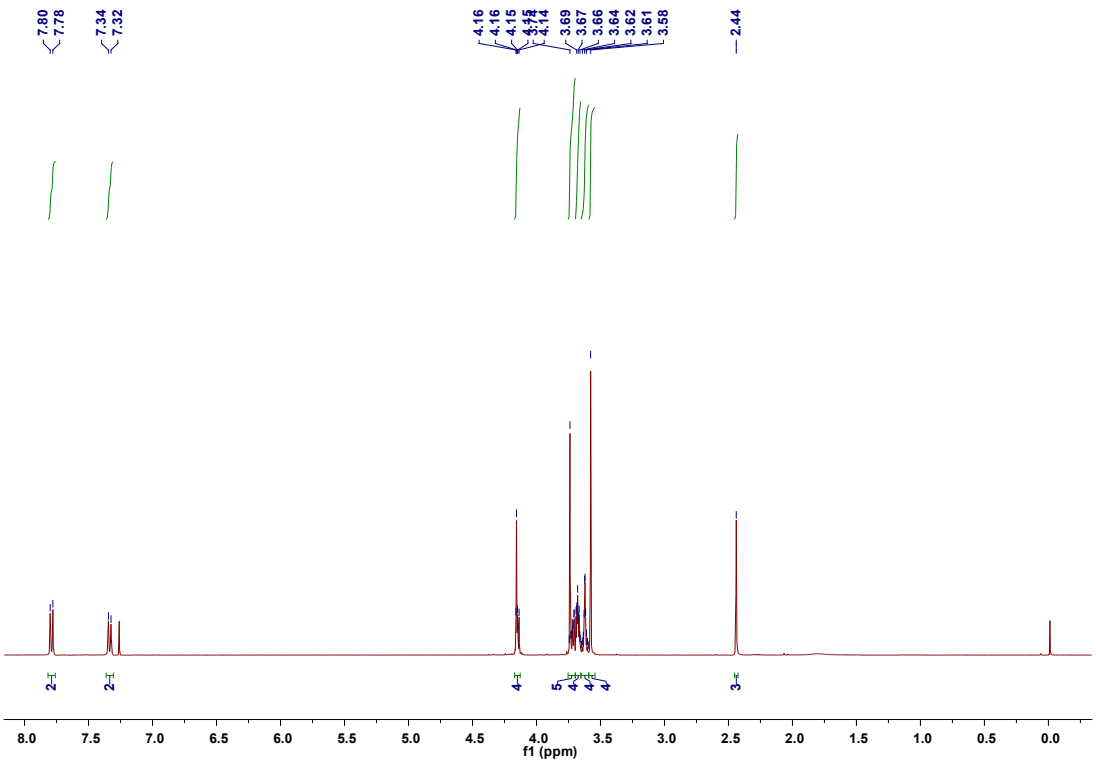
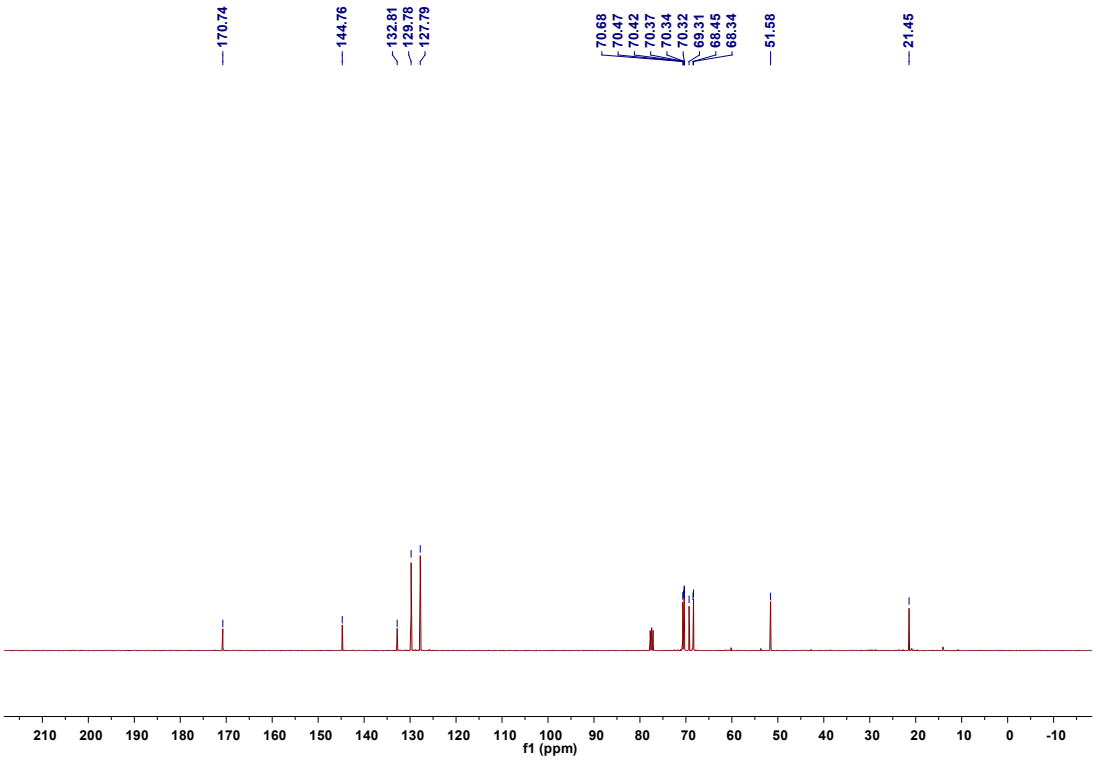


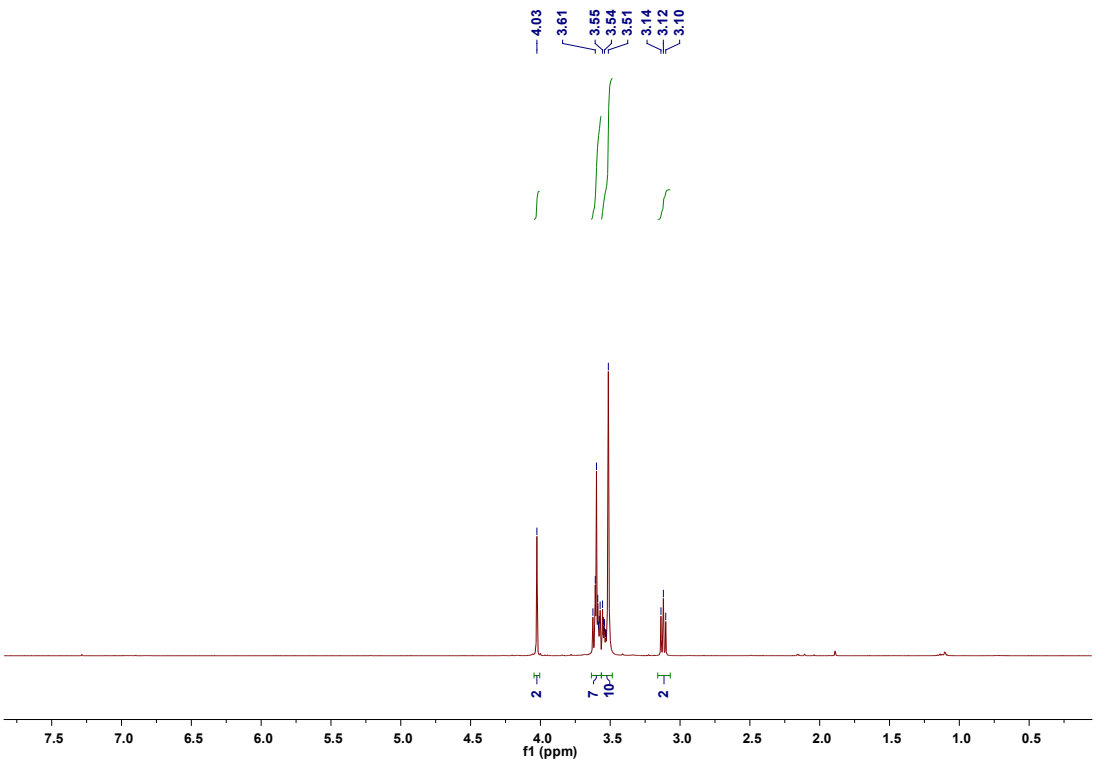
Fig. S8. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 4 mM, 298 K) of a) the PSS_Z (365 nm) mixtures of [3]rotaxane **R1**•8PF_6, b) the PSS_E (> 525 nm) mixtures of [3]rotaxane **R1**•8PF_6, c)) the PSS_E (> 525 nm) mixtures of **R1**•8PF_6 after Magic Blue (2.0 equiv.) was added, and d) after zinc powder (10 equiv.) was added to the above oxidized sample.



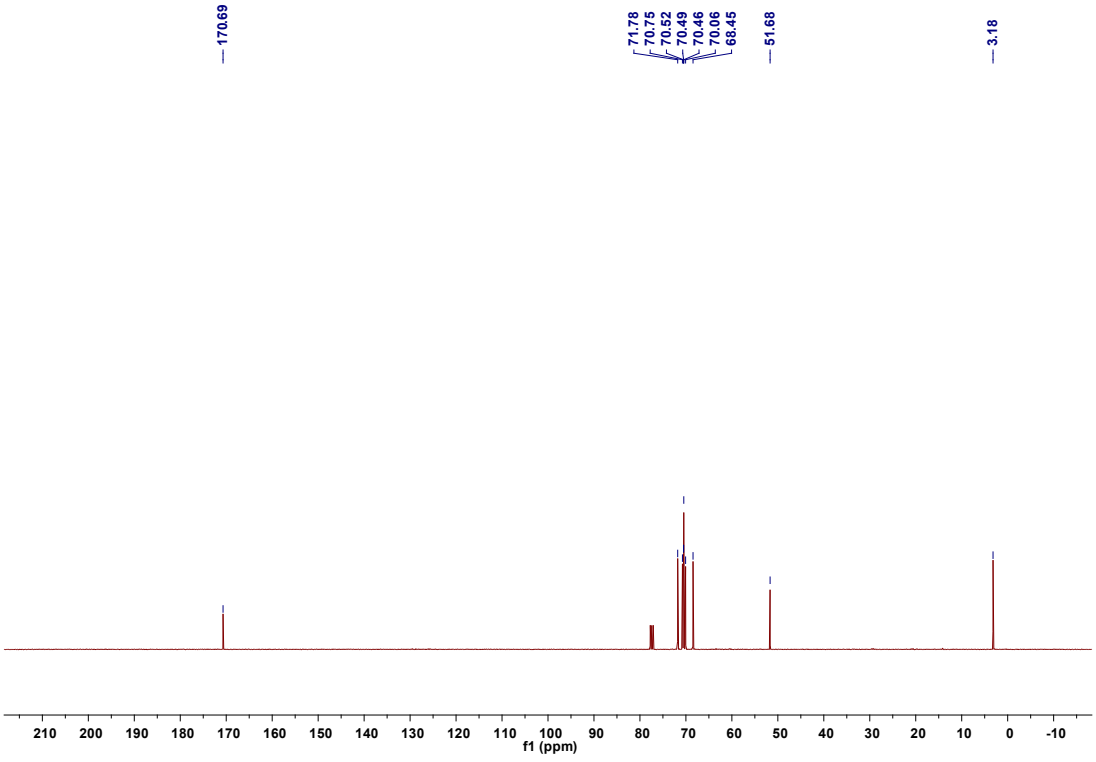
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **2**.



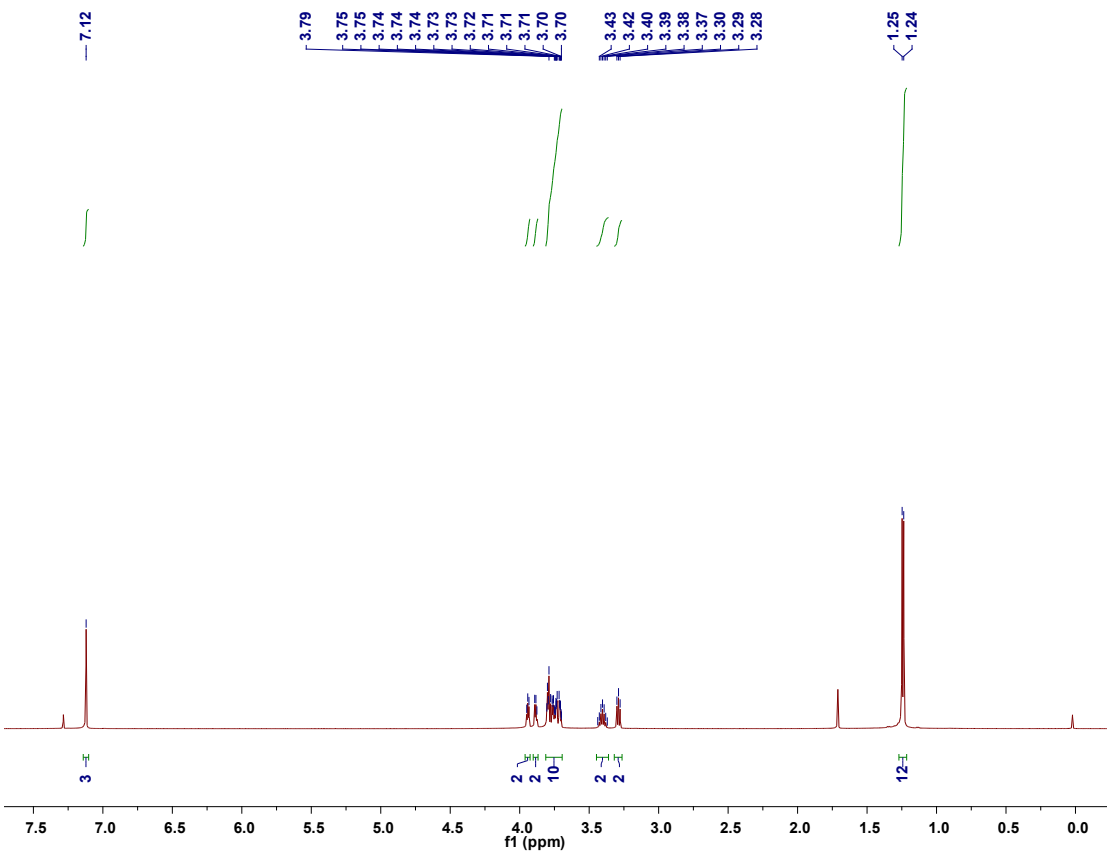
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **2**.



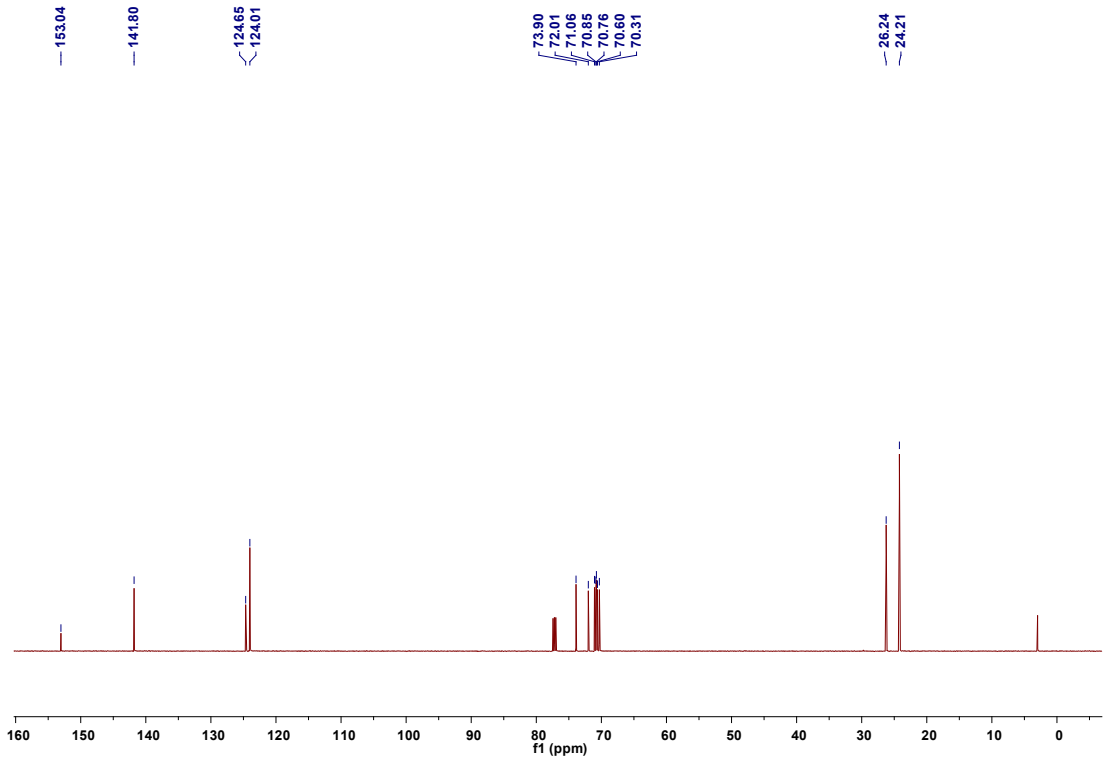
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **3**.



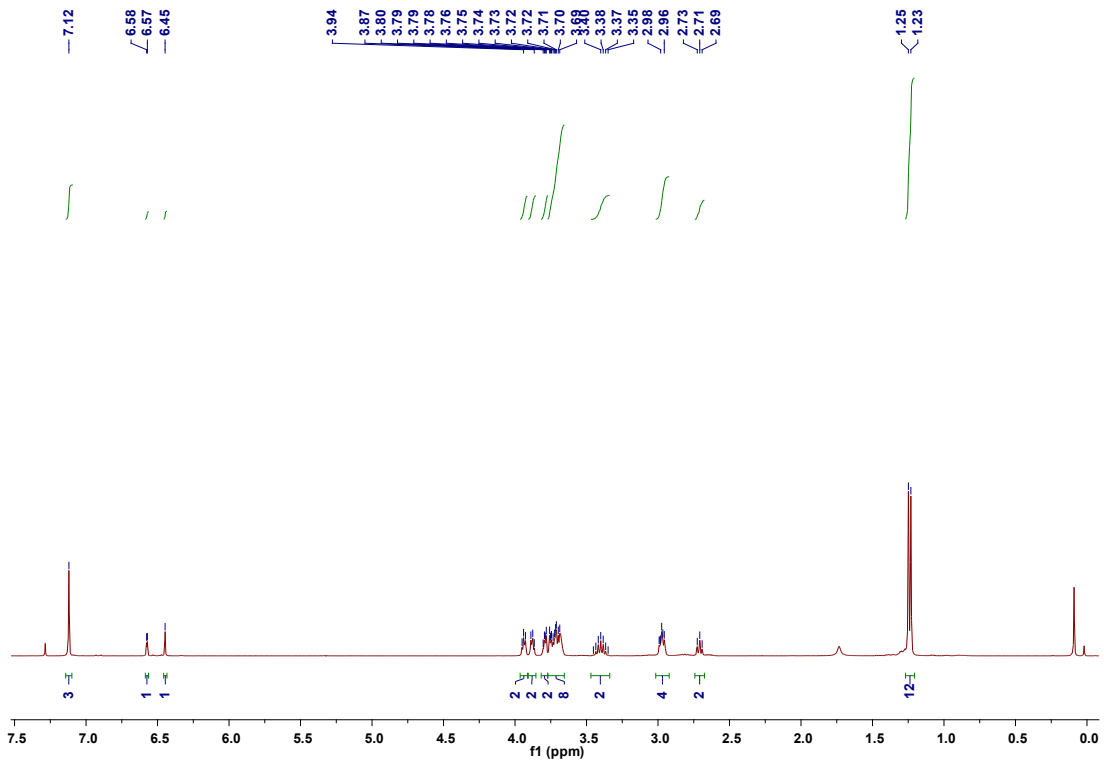
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **3**.



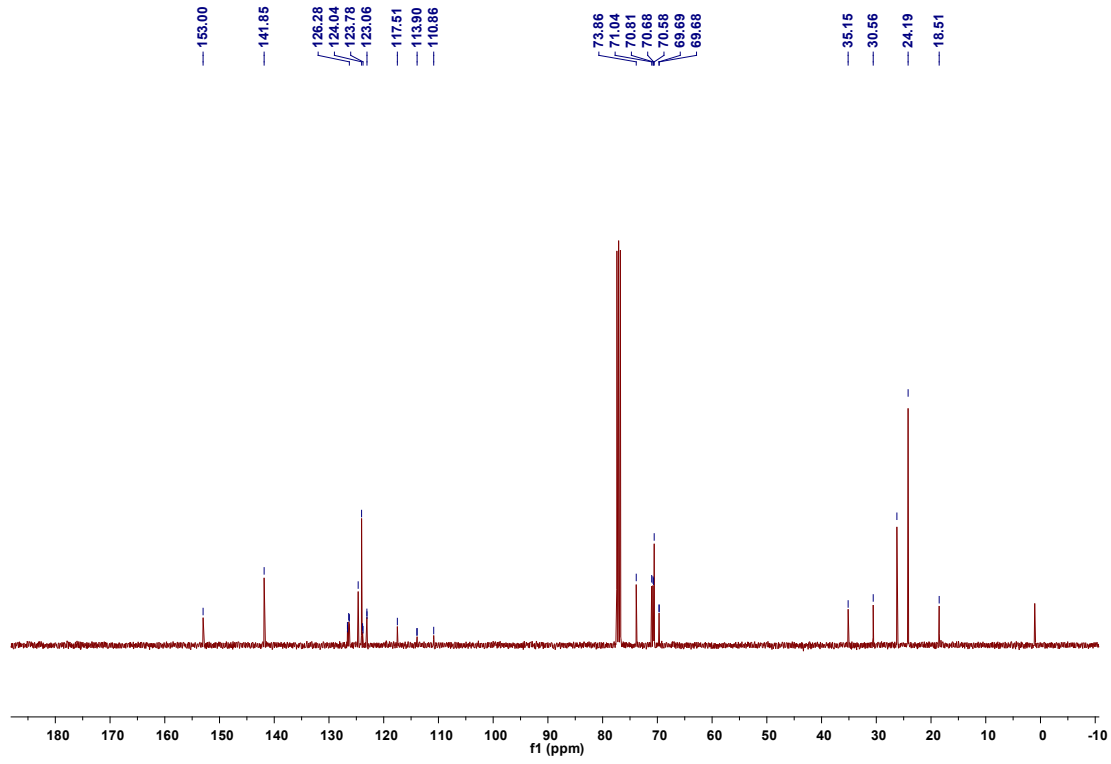
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **5**.



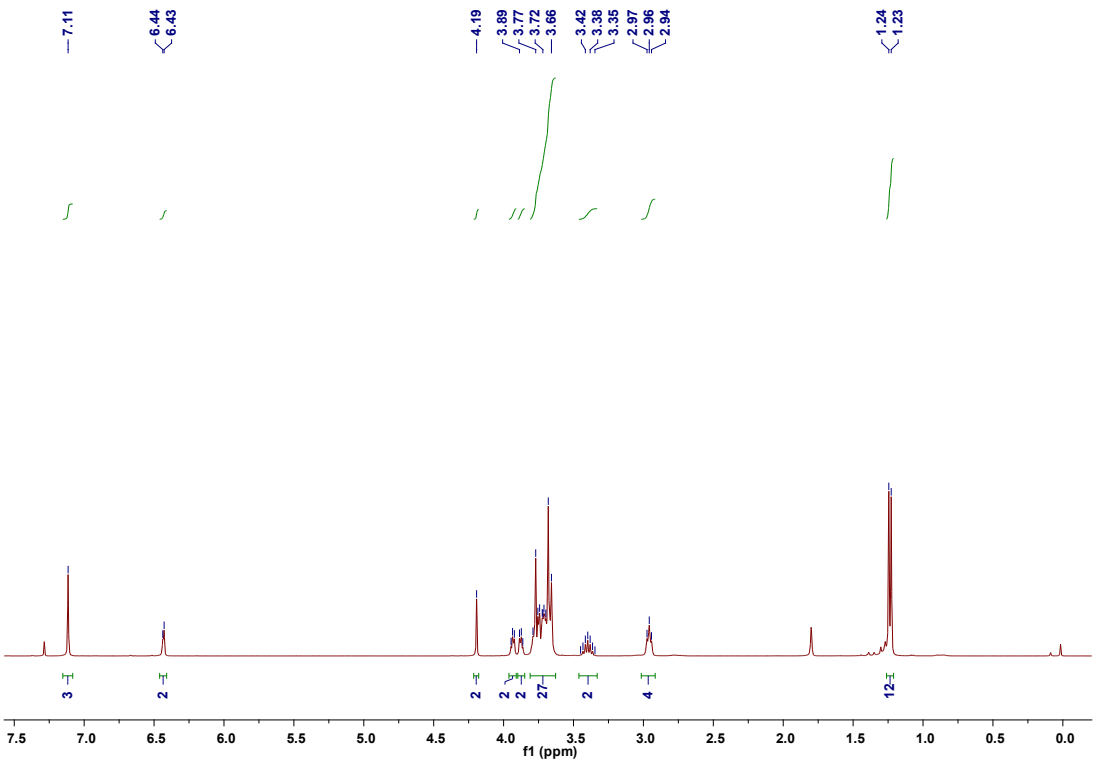
^{13}C NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **5**.



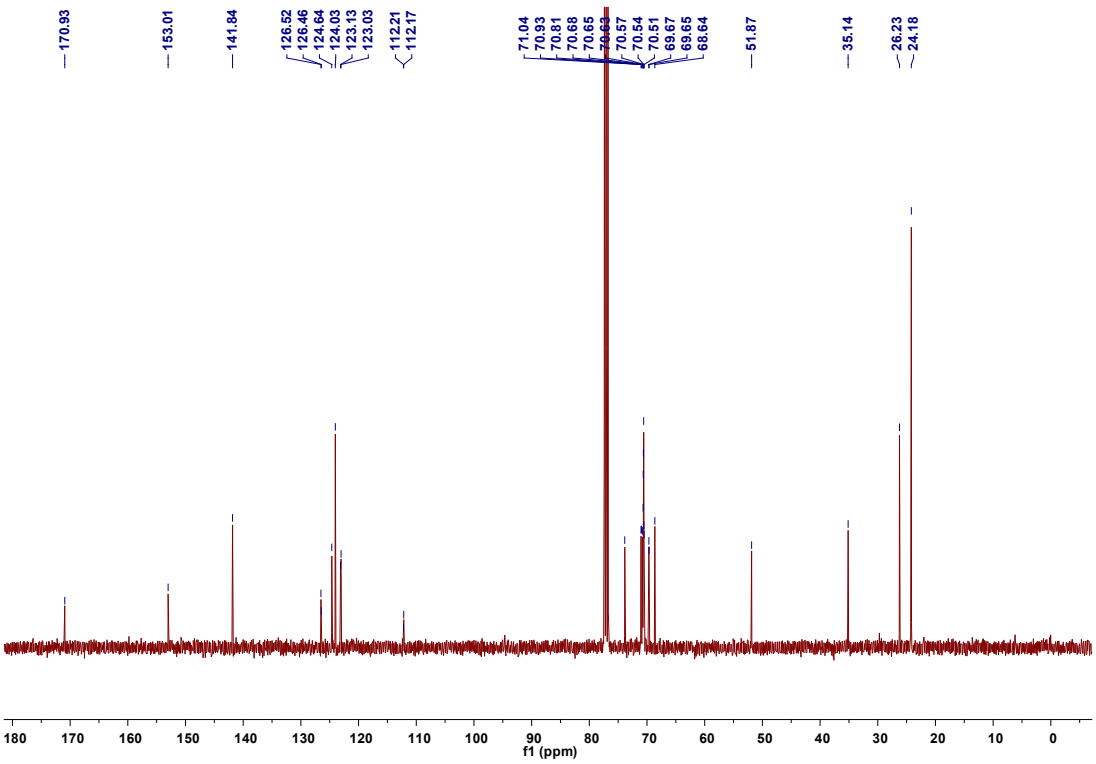
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **7**.



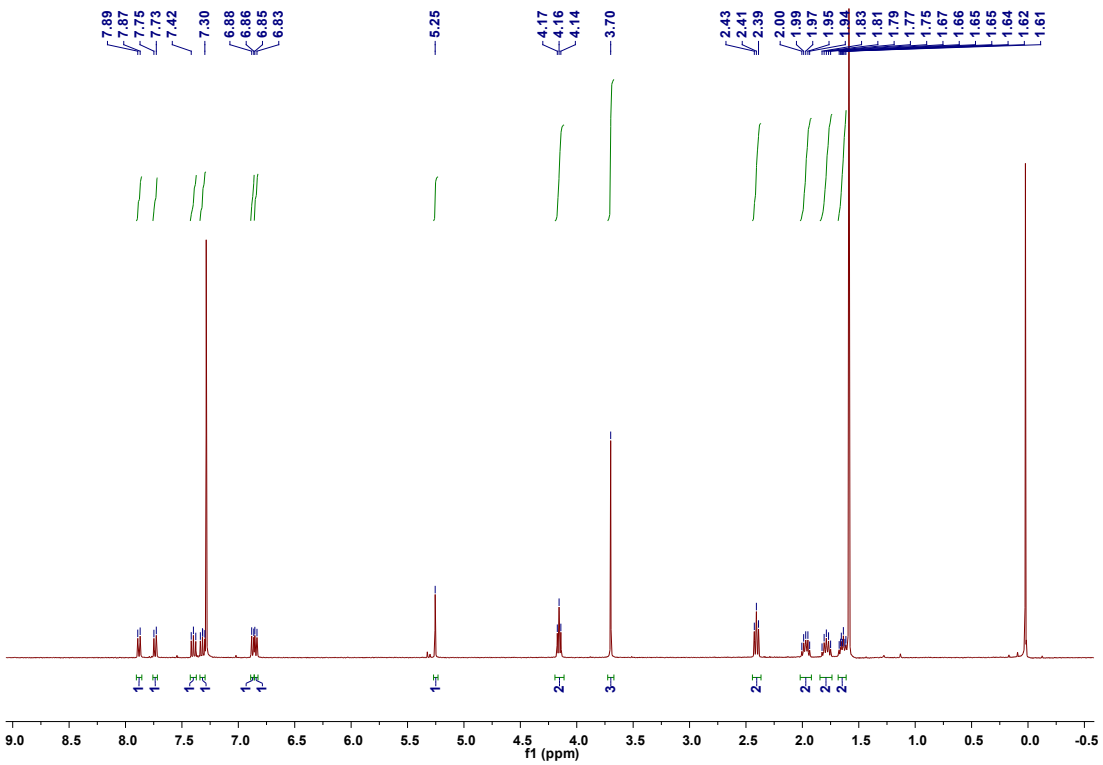
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **7**.



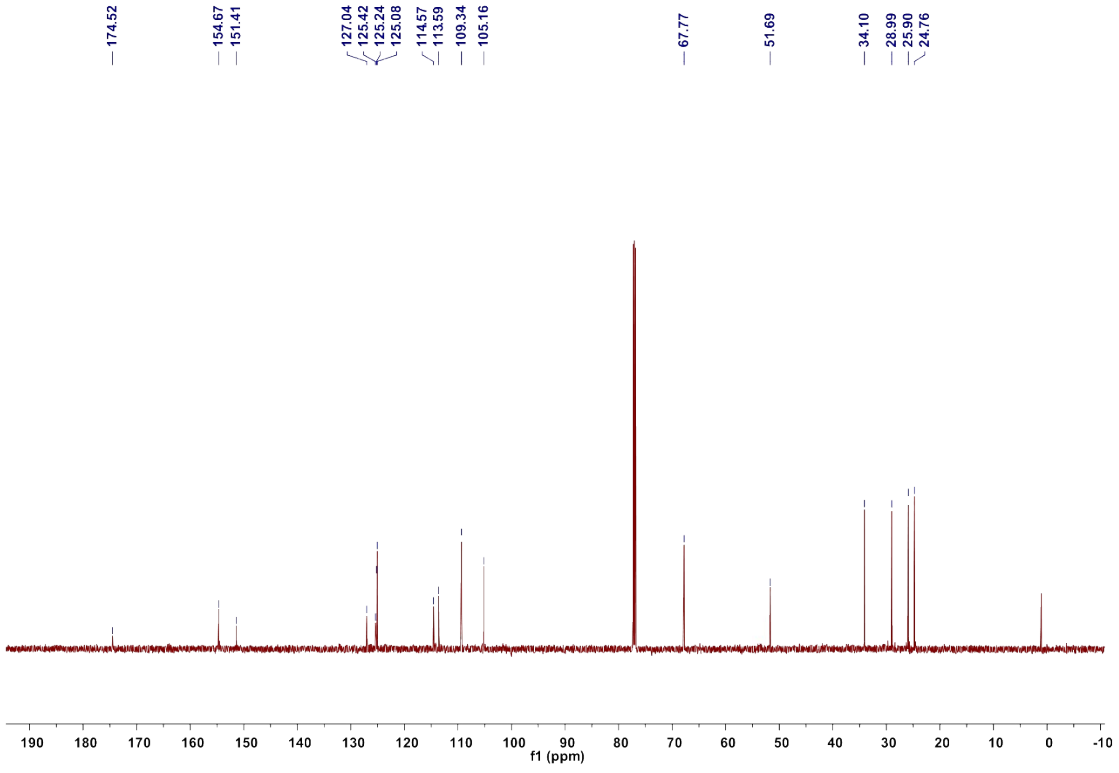
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **8**.



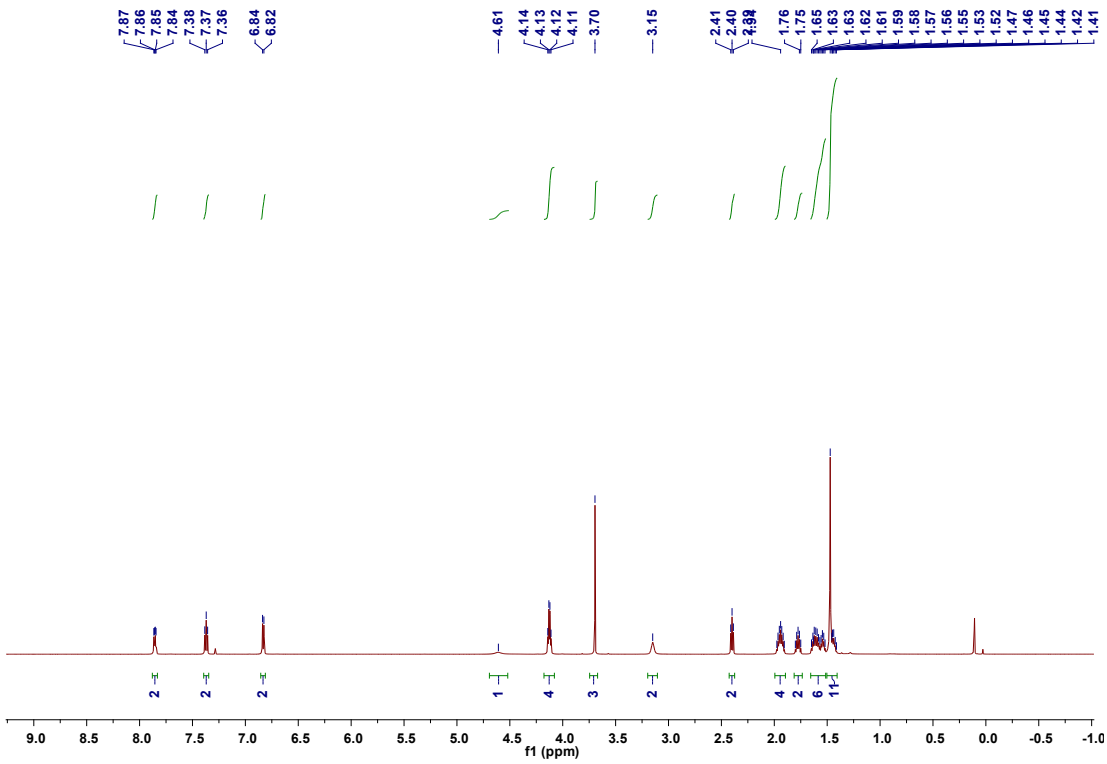
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **8**.



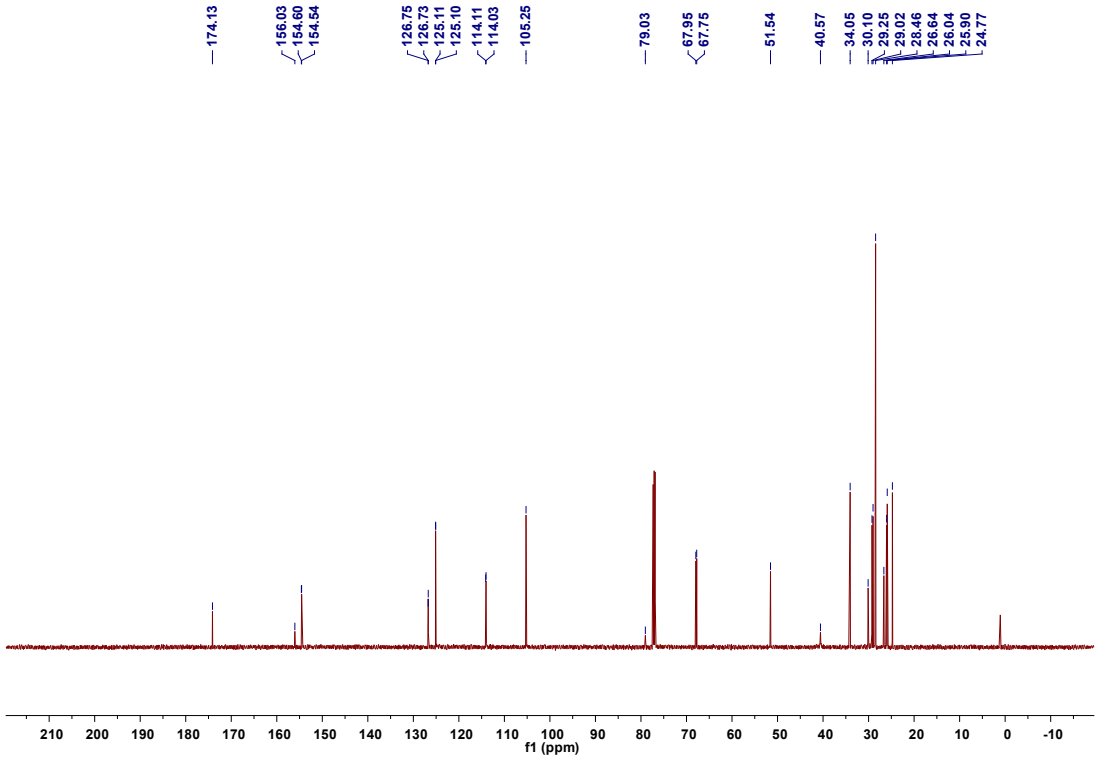
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **11**.



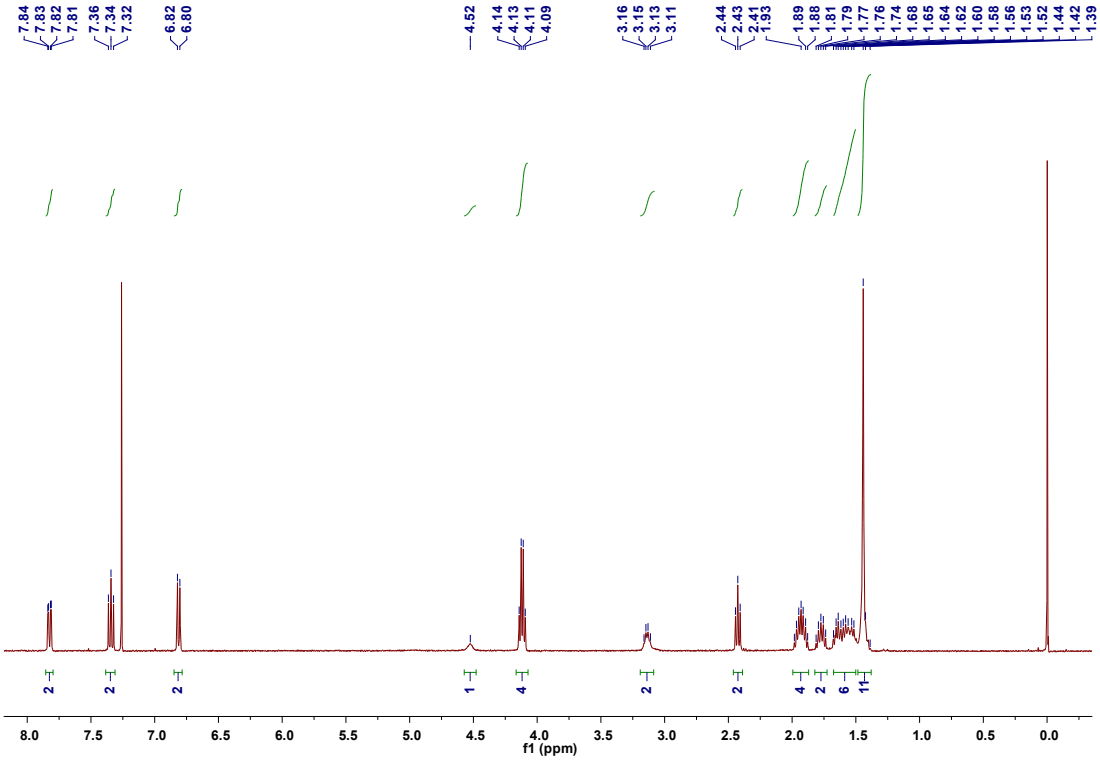
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **11**.



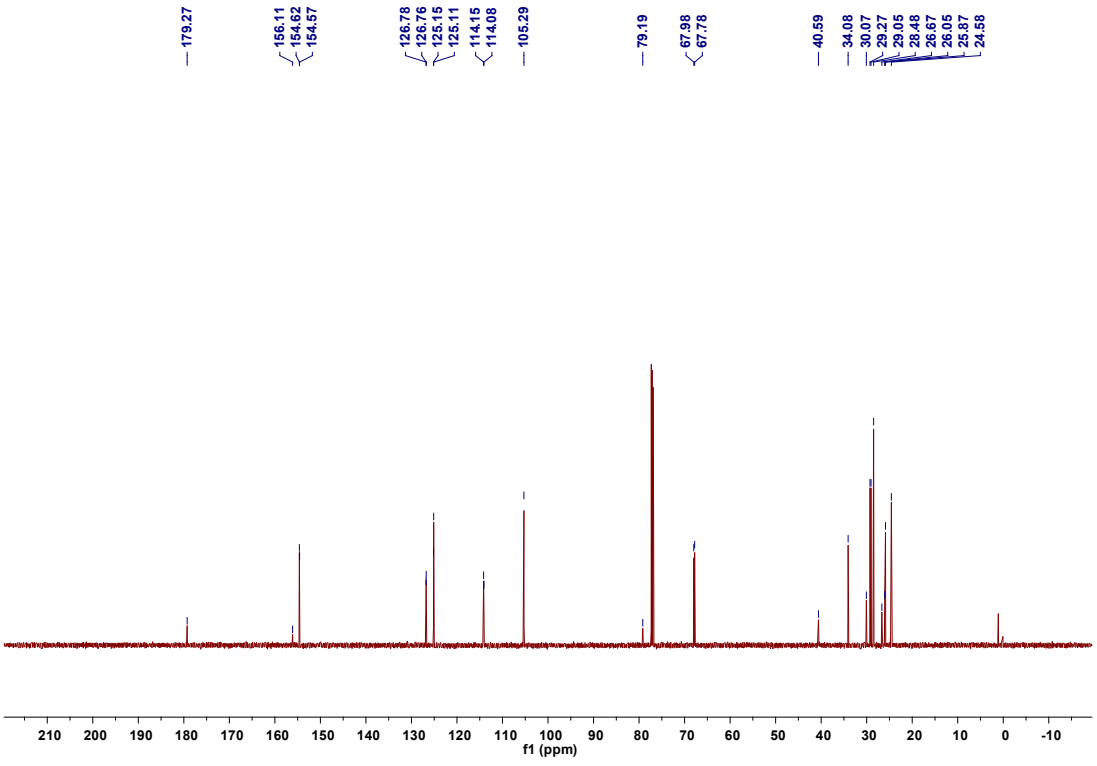
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **13**.



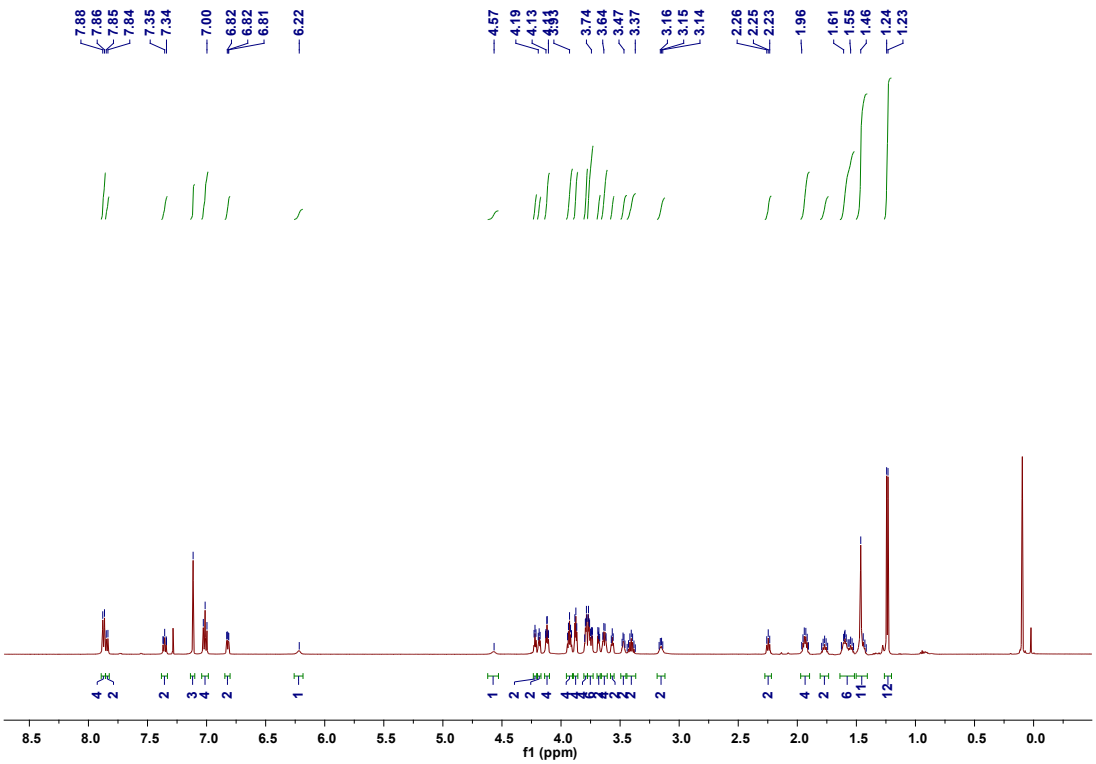
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **13**.



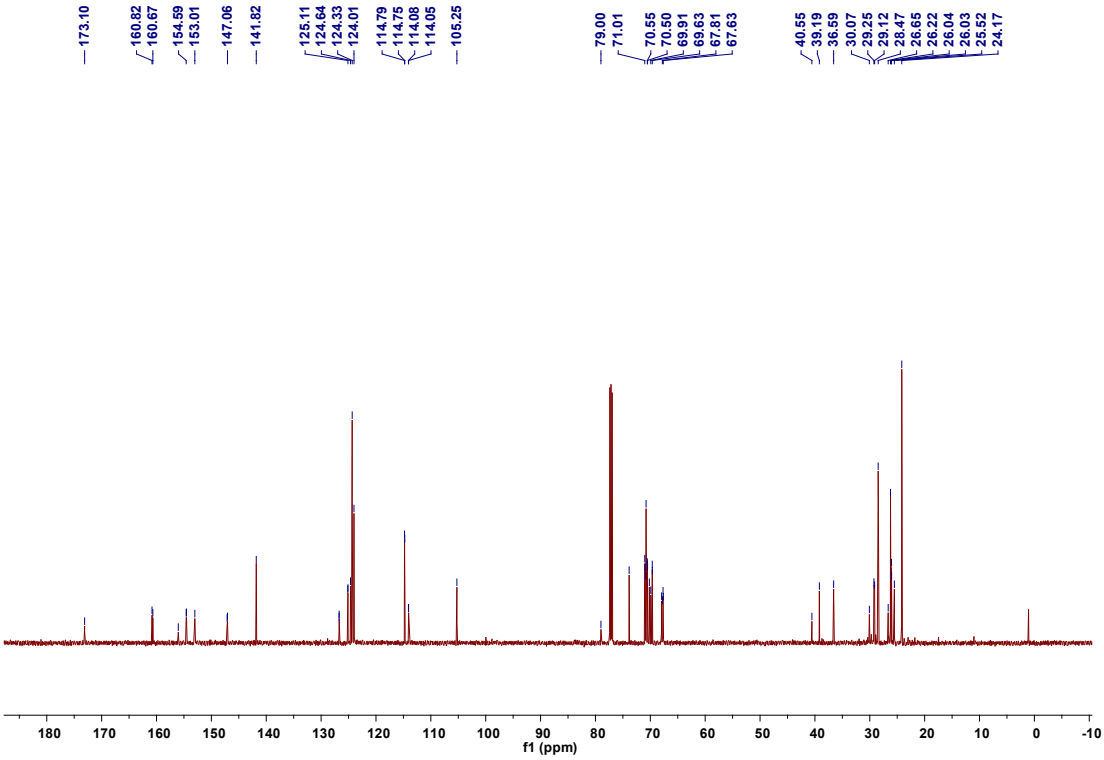
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **14**.



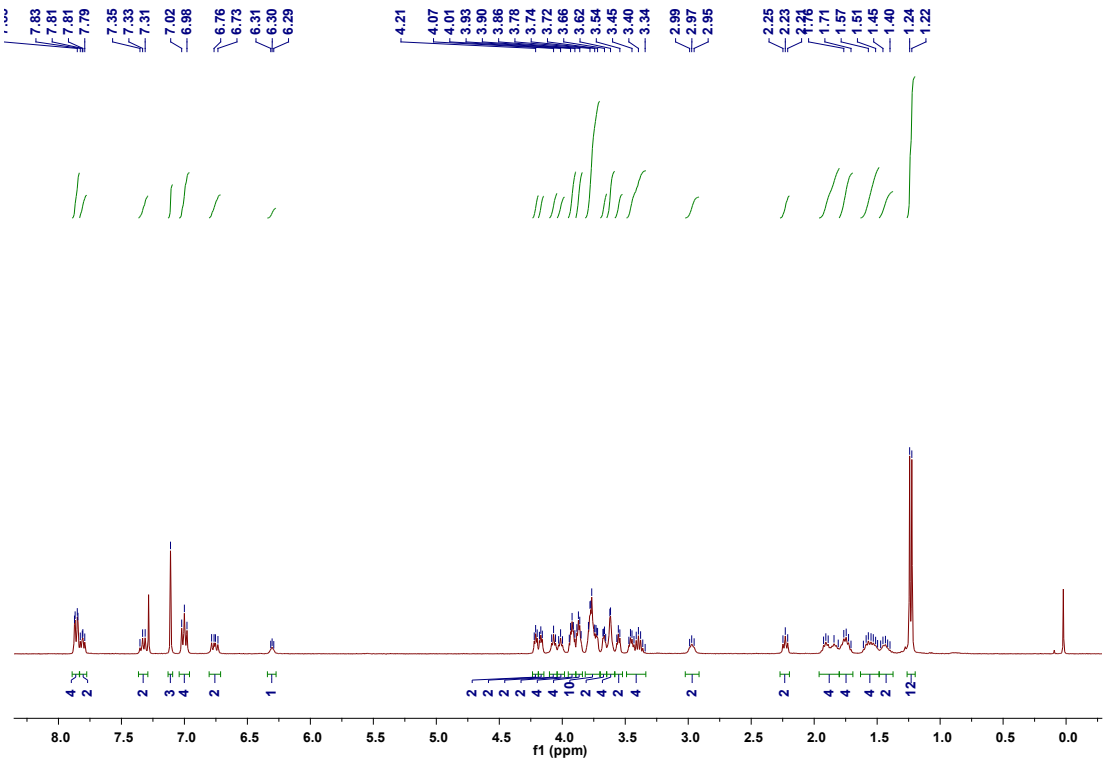
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **14**.



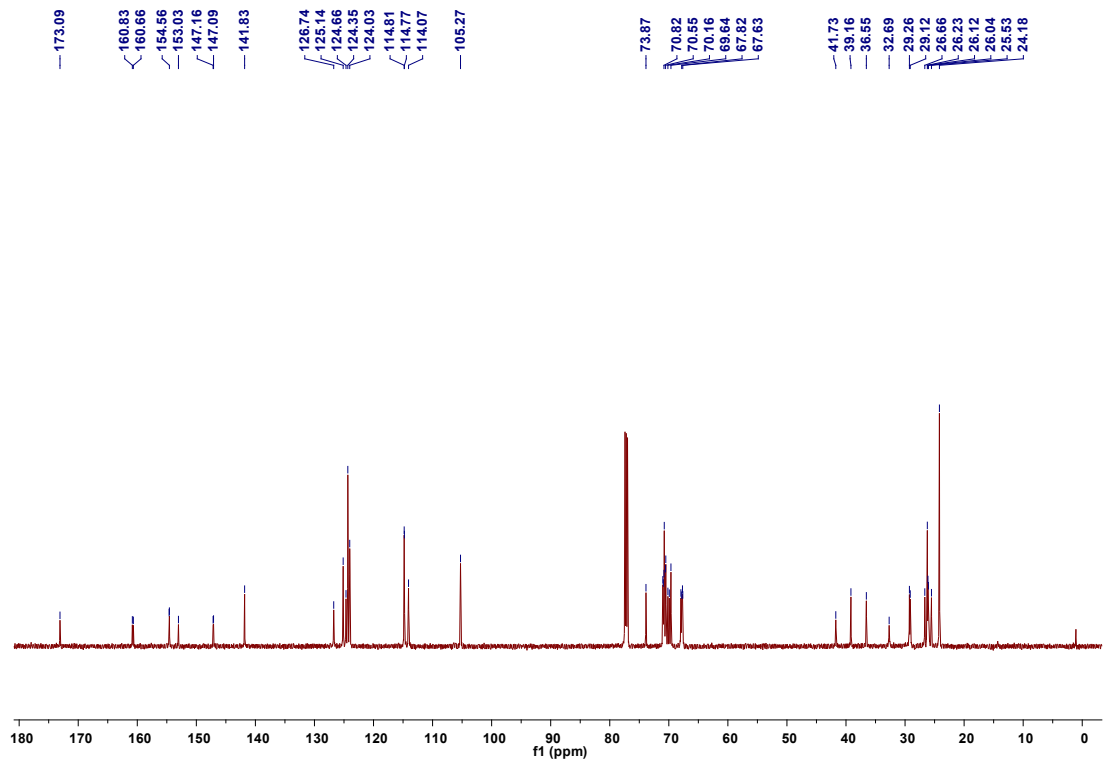
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **16**.



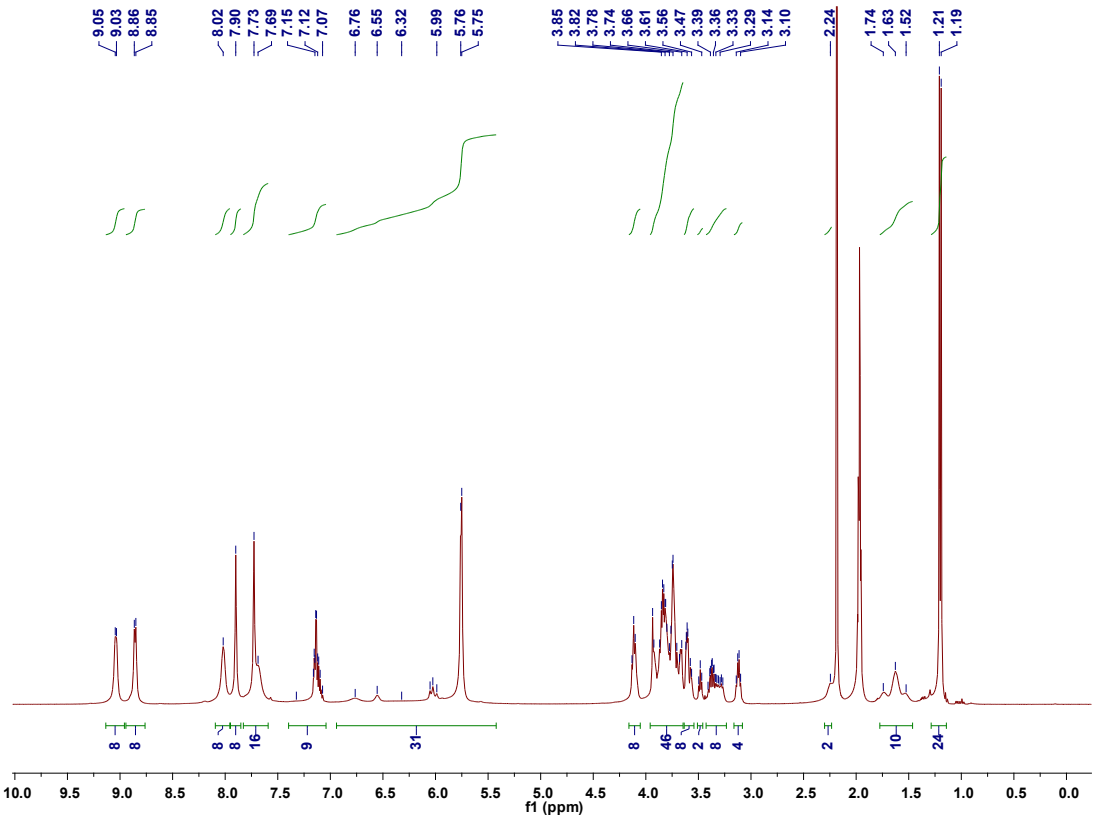
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **16**.



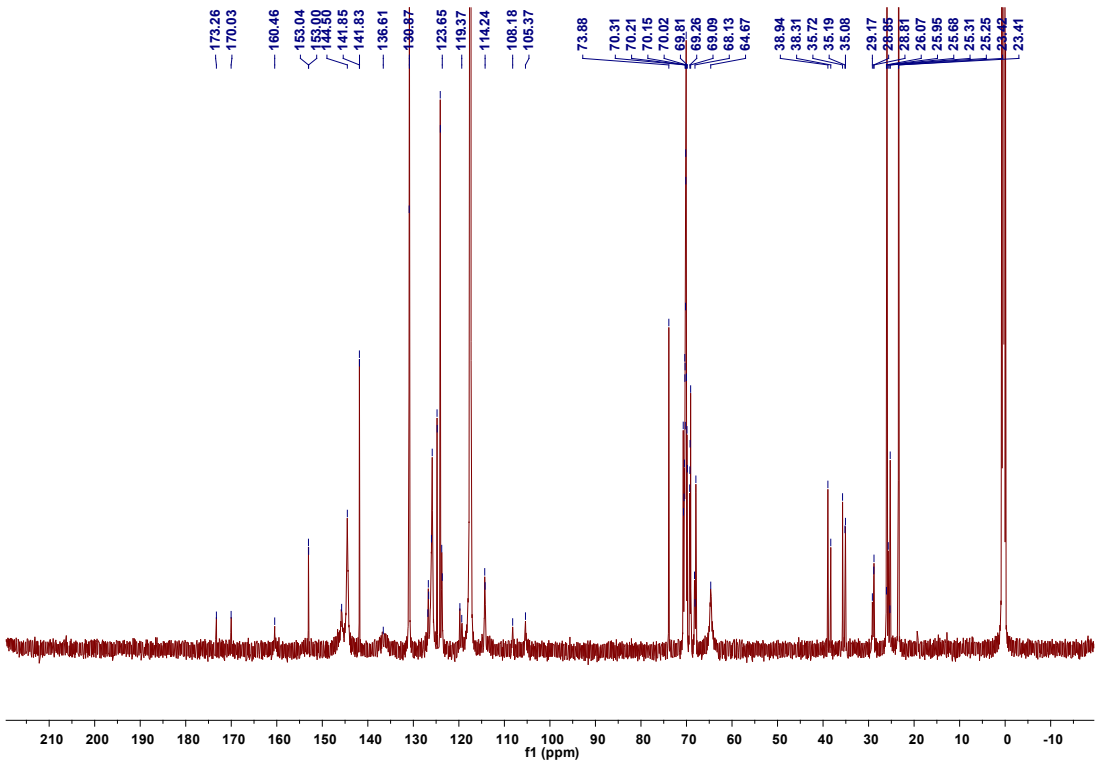
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **17**.



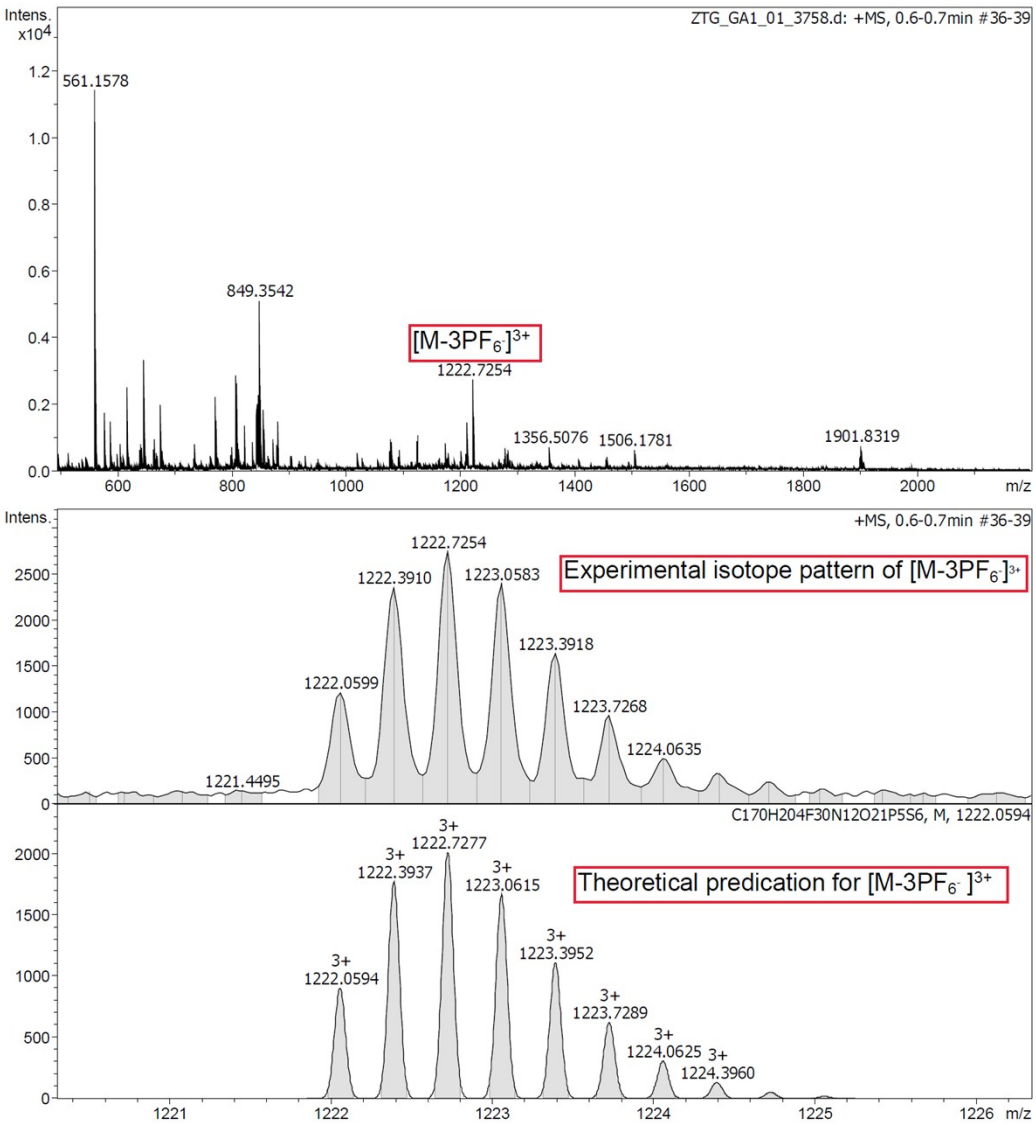
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **17**.



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



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



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

References

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