Supplementary Information

A Thermally Driven Rotaxane-Catenane Interconversion with a Dynamic Bis(Hindered Amino) Disulfide

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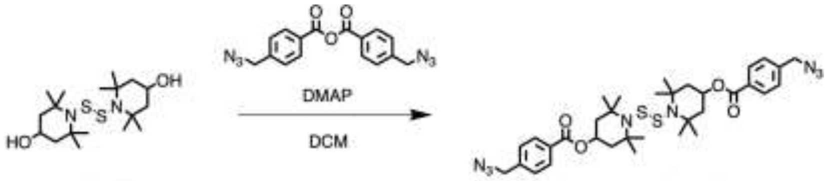
1. General information

All reagents and solvents were purchased from Sigma-Aldrich, FUJIFILM Wako Pure Chemical Corporation, Tokyo Chemical Industries, or Kanto Chemical Co. and used as received. The diol derivative of BiTEMPS prepared following our previous reports.[1,2] Bipyridine macrocycle was synthesized following literatures Goldup et.al. reported.[3] ^{1}H spectra were recorded on a Bruker AVANCE III HD500 spectrometer. The LED method for DOSY measurement was used. Pulse program: ledbpgp2s, Diffusion time: 40 ms, Diffusion gradient length: 2000 μs, Maximum gradient strength: 51 g/cm.[4] ^{13}C{^{1}H} spectra were recorded on a JEOL JNM-ECZ400S/L. Analytical size exclusion chromatography (SEC) measurements were carried out at 40 °C on TOSOH HLC-8320 SEC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a UV-vis detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards (M_n = 4430–3142000; M_w/M_n = 1.03–1.08) were used to calibrate the SEC system. Electrospray ionization mass spectrometry (ESI-TOF-MS) measurements were carried out on Bruker micrOTOF II. FT-IR spectra were recorded using a JEOL FT/IR-4100 Fourier transform infrared spectrometer as thin films embedded in KBr.

2. Synthesis

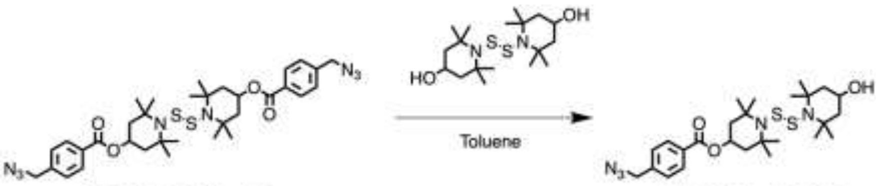
2.1. BiTEMPS(azide)(azide)



BiTEMPS(OH)(OH) BiTEMPS(azide)(azide)

Acid anhydride (1.82 g, 5.41 mmol) was added to a solution of **BiTEMPS(OH)(OH)** (815 mg, 2.16 mmol) and DMAP (661 mg, 5.41 mmol) in dry DCM 50 ml. The reaction mixture was stirred for 24 h at room temperature under inert atmosphere. After the reaction, the solvent was evaporated in vacuo. The residue was purified by silica gel column chromatography with hexane/CH_2Cl_2 (v/v = 100/0 to 0/100) mixture. Obtained elute was evaporated in vacuo to afford **BiTEMPS(azide)(azide)** as a white solid. (1.22 g, 81%). **BiTEMPS(azide)(azide)**;^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 8.05-8.04 (4H, d, Ph), 7.39-7.38 (4H, d, Ph), 5.38-5.32 (2H, m, -O-CH-), 4.42 (4H, s, N_3-CH_2-), 2.12-2.09 (4H, m, -CH-CH_2-C-), 1.71-1.67 (4H, t, -CH-CH_2-C-), 1.50 (12H, s, -CH_3), 1.31 (12H, s, -CH_3), ^{13}C{^{1}H} NMR ($CDCl_3$, TMS), δ (ppm): 165.71, 140.45, 130.53, 130.16, 128.02, 68.02, 59.75, 54.39, 45.79, 34.98, 26.89, FT-IR (KBr, cm^{-1}): 2970, 2930, 2100 (N_3), 1715 (C=O), 1615, 1500, 1415, 1380, 1365, 1315, 1280, 1240, 1195, 1175, 1105, 1020, 1000, 980, 915, 755, MS (ESI): 717.2979 $[M+Na]^+$, calculated for $C_{34}H_{46}N_8NaO_4S_2$ $[M+Na]^+$: 717.2976.

2.2. BiTEMPS(azide)(OH)

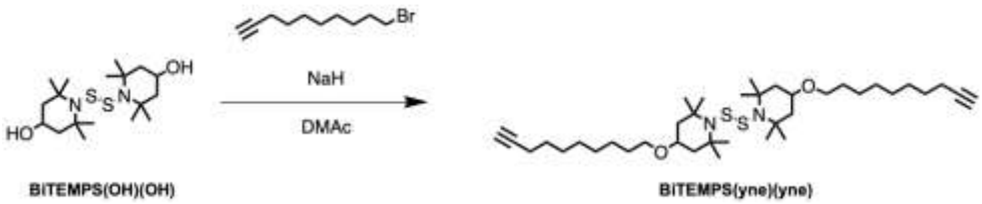


BiTEMPS(azide)(azide) BiTEMPS(azide)(OH)

In a 200 mL flask, **BiTEMPS(OH)(OH)** (5.69 g, 15.1 mmol) and **BiTEMPS(azide)(azide)** (2.10 g, 3.02 mmol) were dissolved in toluene (210 mL) and stirred at reflux for 6 hours. After reaction, the mixture was filtered to remove unreacted **BiTEMPS(OH)(OH)** as a white precipitate (4.31 g, recovered). The filtrate was concentrated in vacuo and purified by silica gel column chromatography with hexane/CH_2Cl_2 / ethyl acetate (v/v/v = 100/0/0 to 0/100/0 to 0/0/100) mixture. Obtained elute was evaporated in vacuo to afford **BiTEMPS(azide)(OH)** as a white solid. (1.76 g, 54%). Another fraction was also evaporated in vacuo to recover **BiTEMPS(azide)(azide)** as a white solid. (567 mg, 27%). **BiTEMPS(azide)(OH)**; ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 8.05-8.04 (2H, d, Ph), 7.40-7.38 (2H, d, Ph), 5.37-5.30 (1H, m, -O-CH-), 4.42 (2H, m, N_3-CH_2-), 4.04-3.97 (1H, m, OH-CH-), 2.11-2.07 (2H, m, -CH-CH_2-C-), 1.95-1.93 (2H, m, -CH-CH_2-C-), 1.70-1.65 (2H, t, -CH-CH_2-C-), 1.52-1.17 (28H, alkyl),

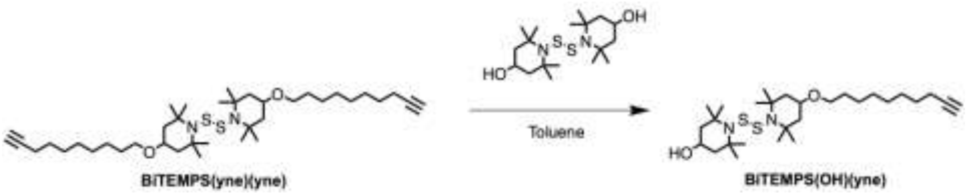
$^{13}C\{^1H\}$ ($CDCl_3$, TMS), δ (ppm): 165.71, 140.44, 130.53, 130.16, 128.01, 68.05, 63.57, 59.71, 59.68, 54.39, 49.73, 45.77, 35.02, 34.94, 26.99, 26.88, FT-IR (KBr, cm^{-1}): 3420, 2970, 2930, 2100 (N_3), 1720 (C=O), 1460, 1380, 1365, 1310, 1280, 1240, 1175, 1105, 1050, 1035, 1020, 1000, 985, 915, 890, 755, MS (ESI): 558.2533 $[M+Na]^+$, calculated for $C_{26}H_{41}N_5NaO_3S_2$ $[M+Na]^+$: 558.2543.

2.3. BiTEMPS(yne)(yne)



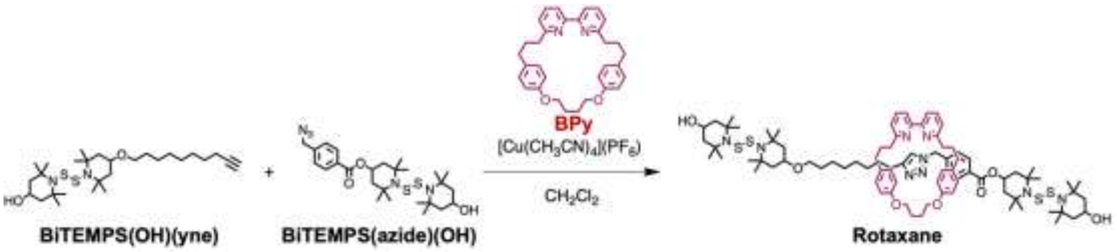
BiTEMPS(OH)(OH) (1.85 g, 4.91 mmol) was dissolved in dehydrated DMAc (15 mL) under N_2 atmosphere. Sodium hydride (60%, dissolved in paraffin liquid, 1.28 g, 32.0 mmol) was added under N_2 flow at 0 °C. After stirring for 20 minutes at 0 °C, **10-bromodec-1-yne** (3.20 g, 14.7 mmol) was slowly added at 0 °C. Then the mixture was stirred for 20 hours at room temperature. The reaction mixture was quenched by excess amount of water at 0 °C and extracted with hexane and ethyl acetate mixture. The organic layer was dried with $MgSO_4$ and concentrated in vacuo. Purification was carried out by silica gel column chromatography with hexane/ethyl acetate (v/v = 100/0 to 5/1) mixture. Obtained elute was evaporated in vacuo to afford **BiTEMPS(yne)(yne)** as a pale-yellow oil. (1.10 g, 35%) Other fraction was also evaporated in vacuo to afford **BiTEMPS(OH)(yne)** as a pale-yellow oil. (541 mg, 21%) **BiTEMPS(yne)(yne)**; ^1H NMR ($CDCl_3$, TMS), δ (ppm): 3.59-3.51 (2H, m, -O-<u>CH</u>-), 3.45-3.42 (4H, t, -O-<u>CH$_2$</u>-), 2.20-2.16 (4H, m, -CH-<u>CH$_2$</u>-C-), 1.96-1.93 (4H, m, -CH-<u>CH$_2$</u>-C-), 1.94 (1H, m, -C≡<u>CH</u>), 1.52-1.17 (52H, alkyl), $^{13}C\{^1H\}$ ($CDCl_3$, TMS), δ (ppm): 84.86, 70.74, 68.25, 68.18, 59.56, 46.62, 35.06, 30.31, 29.46, 29.16, 28.80, 28.57, 27.02, 26.29, 18.51, FT-IR (KBr, cm^{-1}): 3305, 2970, 2935, 2855, 1460, 1430, 1375, 1365, 1280, 1240, 1175, 1100, 630, MS (ESI): 671.4622 $[M+Na]^+$, calculated for $C_{38}H_{68}N_2NaO_2S_2$ $[M+Na]^+$: 671.4614.

2.4. BiTEMPS(OH)(yne)



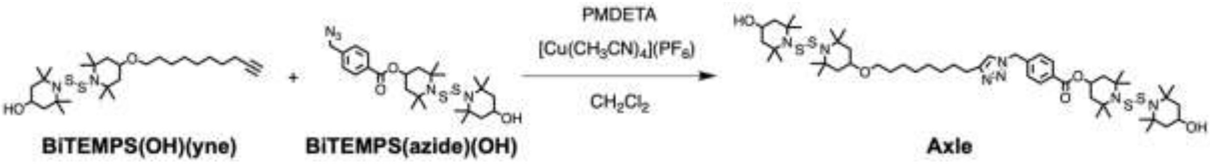
In a 200 mL flask, **BiTEMPS(OH)(OH)** (4.23 g, 11.2 mmol) and **BiTEMPS(yne)(yne)** (1.46 g, 2.25 mmol) were dissolved in toluene (100 mL) and stirred at reflux for 6 hours. After reaction, the mixture was filtered to remove unreacted **BiTEMPS(OH)(OH)** as a white precipitate (3.62 g, recovered). The filtrate was concentrated in vacuo and purified by silica gel column chromatography with hexane/ethyl acetate (v/v = 100/0 to 5/1) mixture. Obtained elute was evaporated in vacuo to afford **BiTEMPS(OH)(yne)** as a slight yellow oil. (1.26 g, 55%) Another fraction was also evaporated in vacuo to recover **BiTEMPS(yne)(yne)** as a white solid. (457 mg, 31%). **BiTEMPS(OH)(yne)**; ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 4.04-3.94 (1H, m, OH-<u>CH</u>-), 3.60-3.52 (1H, m, -O-<u>CH</u>-), 3.45-3.42 (2H, m, -O-<u>CH$_2$</u>-), 2.21-2.16 (2H, m, -CH-<u>CH$_2$</u>-C-), 1.98-1.88, (4H, m, -CH-<u>CH$_2$</u>-C-), 1.94 (1H, m, -C≡<u>CH</u>), 1.52-1.17 (40H, alkyl), ^{13}C{^{1}H} ($CDCl_3$, TMS), δ (ppm): 84.87, 70.73, 68.26, 68.20, 63.58, 59.62, 59.57, 49.72, 46.63, 35.06, 34.99, 30.30, 29.46, 29.16, 28.80, 28.57, 27.02, 26.98, 26.29, 18.51, FT-IR (KBr, cm^{-1}): 3305, 2970, 2930, 2855, 1460, 1430, 1375, 1365, 1240, 1205, 1175, 1090, 1055, 1040, 1000, 985, 910, 890, 830, 640, 620, MS (ESI): 535.3359 $[M+Na]^+$, calculated for $C_{28}H_{52}N_2NaO_2S_2$ $[M+H]^+$: 535.3362.

2.5. [2]Rotaxane



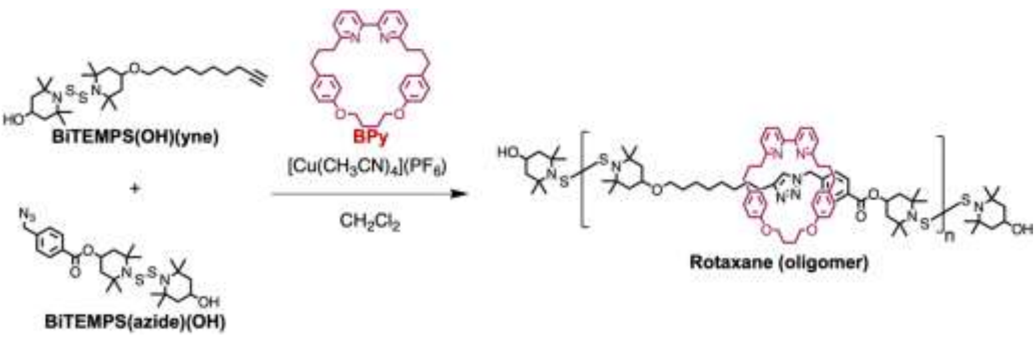
A solution of **BPy** (121 mg, 253 μmol) and $[(CH_3CN)_4Cu]PF_6$ (89.6 mg, 240 μmol) in 10 mL CH_2Cl_2 was added to **BiTEMPS(OH)(yne)** (128 mg, 250 μmol) and **BiTEMPS(azide)(OH)** (134 mg, 250 μmol) under N_2. The orange solution was stirred at 20 °C for 3 days, diluted with CH_2Cl_2 (50 mL) and washed with an EDTA-NH_3 solution (100 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL), then the organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography with hexane/CH_2Cl_2 (v/v = 100/0 to 0/100) mixture. Further purification was carried out by preparative GPC (eluent; $CHCl_3$). Obtained elute was evaporated in vacuo to afford **rotaxane** as a white solid (81 mg, 21%). ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 8.47 (1H, s, -C=<u>CH</u>-N-), 7.66-7.63 (2H, m, Ph), 7.49-7.47 (2H, m, Ph), 7.42-7.41 (2H, d, Ph), 7.09-7.08 (2H, d, Ph), 6.76-6.74 (2H, d, Ph), 6.67-6.62 (8H, m, Ph), 5.31-5.27 (1H, m, -CH$_2$-<u>CH</u>-O-), 4.57 (2H, m, -Ph-<u>CH$_2$</u>-N-), 4.44-4.37 (2H, m, -<u>CH$_2$</u>-O-Ph-), 4.17-4.10 (2H, m, -<u>CH$_2$</u>-O-Ph-), 4.05-3.95 (2H, m, -CH$_2$-<u>CH</u>-OH), 3.55-3.48 (1H, m, -CH$_2$-<u>CH</u>-O-), 3.36-3.31 (2H, t, -CH$_2$-<u>CH$_2$</u>-O-), 2.61-0.96 (alkyl), ^{13}C{^{1}H} ($CDCl_3$, TMS), δ (ppm): 165.74, 162.59, 157.68, 157.36, 147.78, 139.90, 136.71, 133.01, 129.39, 129.25, 129.08, 128.44, 123.50, 121.24, 120.09, 115.13, 70.54, 68.18, 68.12, 67.64, 66.66, 63.47, 61.99, 61.94, 59.62, 59.61, 59.54, 59.48, 52.05, 50.69, 49.66, 47.61, 46.58, 45.73, 36.66, 34.97, 34.93, 34.88, 34.85, 34.40, 31.98, 30.21, 29.33, 29.26, 28.65, 26.92, 26.88, 26.87, 26.79, 26.63, 26.53, 26.15, 25,64, 24.94, FT-IR (KBr, cm^{-1}): 3415, 2970, 2930, 2855, 1715 (C=O), 1610, 1575, 1510, 1460, 1375, 1365, 1310, 1275, 1240, 1205, 1175, 1105, 1040, 1020, 1000, 915, 890, 830, 795, 750, MS (ESI): 1526.8806 $[M+H]^+$, calculated for $C_{86}H_{128}N_9O_7S_4$ $[M+H]^+$: 1526.8814.

2.6. Axle



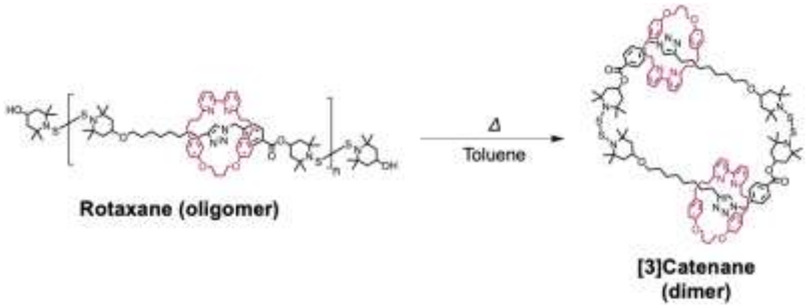
A solution of PMDETA (214 mg, 1.23 mmol) and $[(CH_3CN)_4Cu]PF_6$ (44.0 mg, 118 µmol) in 5 mL CH_2Cl_2 was added to **BiTEMPS(OH)(yne)** (64 mg, 12.5 mmol) and **BiTEMPS(azide)(OH)** (67 mg, 12.5 mmol) under N_2. The orange solution was stirred at 20 °C for 3 hours, diluted with CH_2Cl_2 (100 mL) and washed with an EDTA-NH_3 solution (20 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL), then the organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The mixture was purified by silica gel column chromatography with CH_2Cl_2/ethyl acetate (v/v = 100/0 to 90/10) mixture. Obtained elute was evaporated in vacuo to afford **axle** as a white solid (75 mg, 57%). ^1H NMR ($CDCl_3$, TMS), δ (ppm): 8.03-8.01 (2H, d, Ph), 7.30-7.28 (2H, d, Ph), 7.19 (1H, s, -C=<u>CH</u>-N-), 5.55 (2H, s, -Ph-<u>CH₂</u>-N-), 5.37-5.29 (1H, m, -O-CH-CH_2-), 4.05-3.95 (2H, m, -CH_2-<u>CH</u>-OH), 3.55-3.48 (1H, m, -CH_2-<u>CH</u>-O-), 3.45-3.41 (2H, t, -CH_2-<u>CH₂</u>-O-), 2.70-1.18 (alkyl), $^{13}C\{^1H\}$ ($CDCl_3$, TMS), δ (ppm): 165.44, 149.21, 139.87, 130.87, 130.27, 127.70, 120.56, 70.62, 68.13, 68.09, 63.47, 63.42, 59.61, 59.60, 59.54, 59.49, 53.52, 49.65, 46.55, 45.67, 34.96, 34.91, 34.89, 34.83, 30.20, 29.37, 29.29, 29.21, 26.92, 26.87, 26.75, 26.20, 25.71, FT-IR (KBr, cm^{-1}): 2970, 2930, 2860, 1720 (C=O), 1615, 1460, 1380, 1365, 1310, 1280, 1240, 1170, 1105, 1040, 915, 830, 730, 670, MS (ESI): 1070.6030 $[M+Na]^+$, calculated for $C_{54}H_{93}N_7NaO_5S_4$ $[M+Na]^+$: 1070.6013.

2.7. Mixture ([2]rotaxane and its oligomers)



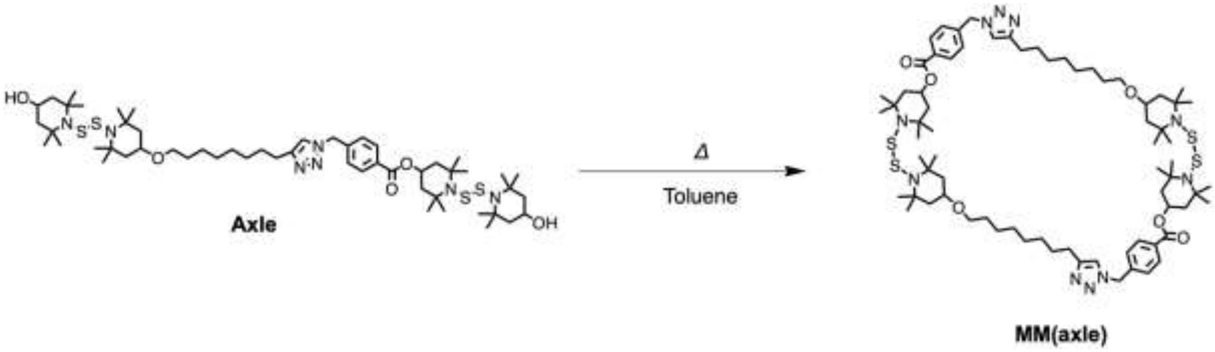
A solution of **BPy** (120 mg, 251 µmol) and $[(CH_3CN)_4Cu]PF_6$ (89.4 mg, 240 µmol) in 10 mL CH_2Cl_2 was added to **BiTEMPS(OH)(yne)** (128 mg, 250 µmol) and **BiTEMPS(azide)(OH)** (134 mg, 250 µmol) mixture under N_2. The orange solution was stirred at 30 °C for 3 days, diluted with CH_2Cl_2 (50 mL) and washed with an EDTA-NH_3 solution (100 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL), then the organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography with hexane/CH_2Cl_2 (v/v = 100/0 to 0/100) mixture. Obtained elute was evaporated in vacuo to afford **rotaxane (oligomer)** as a white solid (261 mg, 68%).

2.8. [3]Catenane



In a 1L flask, **rotaxane** (oligomer) (665 mg) was dissolved in toluene (665 mL) and heated at 100 °C for 9 h. The reaction mixture was evaporated in vacuo. Purification was carried out by silica gel column chromatography with hexane/ethyl acetate (v/v = 100/0 to 50/50) mixture. Obtained elute was evaporated in vacuo to afford **[3]catenane** as a white solid (339 mg, 51% by weight). This product contains two isomers as described in main text. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 8.47 (1H, s, -C=<u>CH</u>-N-), 7.64-7.62 (2H, m, Ph), 7.49-7.44 (2H, m, Ph), 7.43-7.36 (2H, m, Ph), 7.10-7.05 (2H, m, Ph), 6.79-6.71 (2H, m, Ph), 6.70-6.60 (8H, m, Ph), 5.35-5.23 (1H, m, -CH_2-<u>CH</u>-O-), 4.57 (2H, m, -Ph-<u>CH_2</u>-N-), 4.44-4.34 (2H, m, -<u>CH_2</u>-O-Ph-), 4.17-4.10 (2H, m, -<u>CH_2</u>-O-Ph-), 3.58-3.48 (1H, m, -CH_2-<u>CH</u>-O-), 3.38-3.31 (2H, m, -CH_2-<u>CH_2</u>-O-), 2.63-0.96 (alkyl), ^{13}C{^{1}H} ($CDCl_3$), ^{13}C{^{1}H} ($CDCl_3$, TMS), δ (ppm): 165.74, 162.58, 157.66, 157.37, 147.83, 139.90, 136.67, 133.02, 129.40, 129.22, 129.10, 128.49, 123.53, 121.23, 120.09, 115.12, 70.58, 68.20, 68.13, 67.57, 66.64, 61.95, 59.66, 59.55, 59.52, 59.44, 52.10, 47.61, 46.56, 45.73, 36.65, 35.00, 34.93, 34.85, 34.42, 31.96, 30.28, 29.36, 29.26, 29.18, 28.63, 28.31, 26.98, 26.92, 26.87, 26.84, 26.21, 25.64, 24.94, FT-IR (KBr, cm^{-1}): 2930, 2855, 1715 (C=O), 1610, 1575, 1510, 1460, 1380, 1365, 1275, 1240, 1175, 1105, 1045, 1020, 1000, 915, 830, 795, 750, MS (ESI): 2301.3197 $[M+H]^+$, calculated for $C_{136}H_{183}N_{14}O_{10}S_4$ $[M+H]^+$: 2301.3095.

2.9. MM(axle)



In a 500 mL flask, **axle** (60 mg) was dissolved in toluene (300 mL) and heated at 100 °C for 9 h. The reaction mixture was evaporated in vacuo. Purification was carried out by silica gel column chromatography with hexane/ethyl acetate (v/v = 60/40) mixture. Obtained elute was evaporated in vacuo to afford **MM(axle)** as a white solid. A monomer of **MM(axle**) was also collected. The yield of them was not determined because the weight was too small to accurately measure (see **Figure S24** and **Figure S25** for characterization of products).

3. Spectra

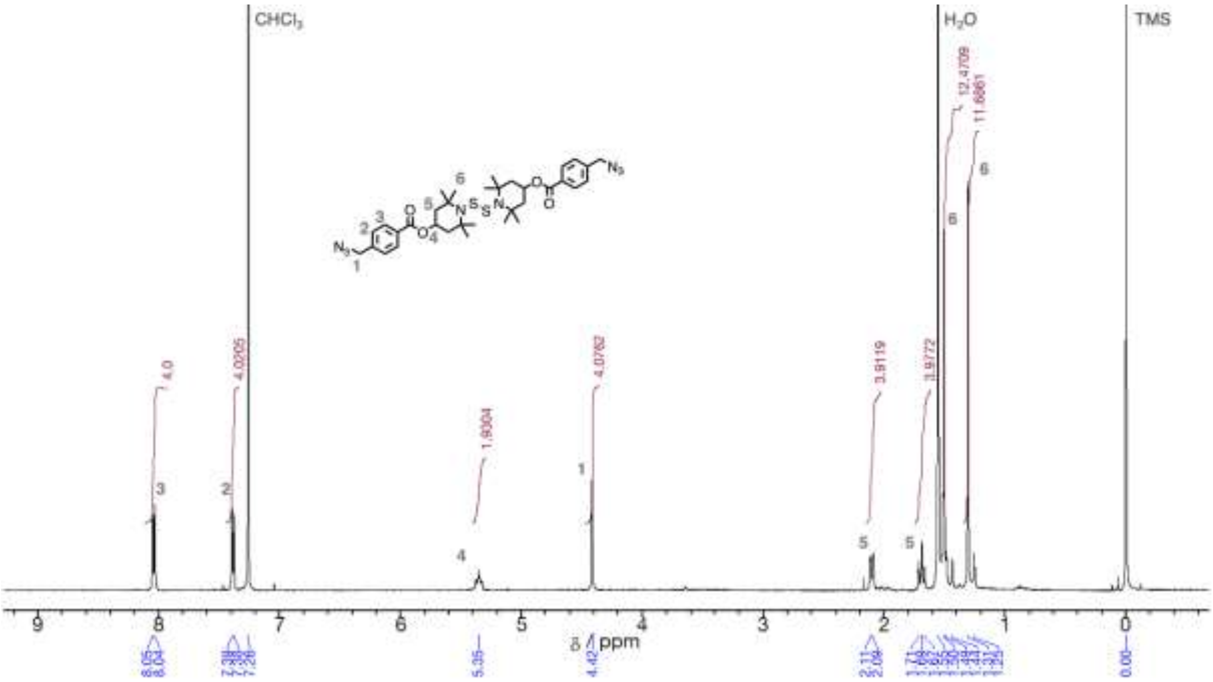


Figure S1. ^{1}H NMR spectrum of **BiTEMPS(azide)(azide)** (500 MHz, 25 °C, $CDCl_3$).

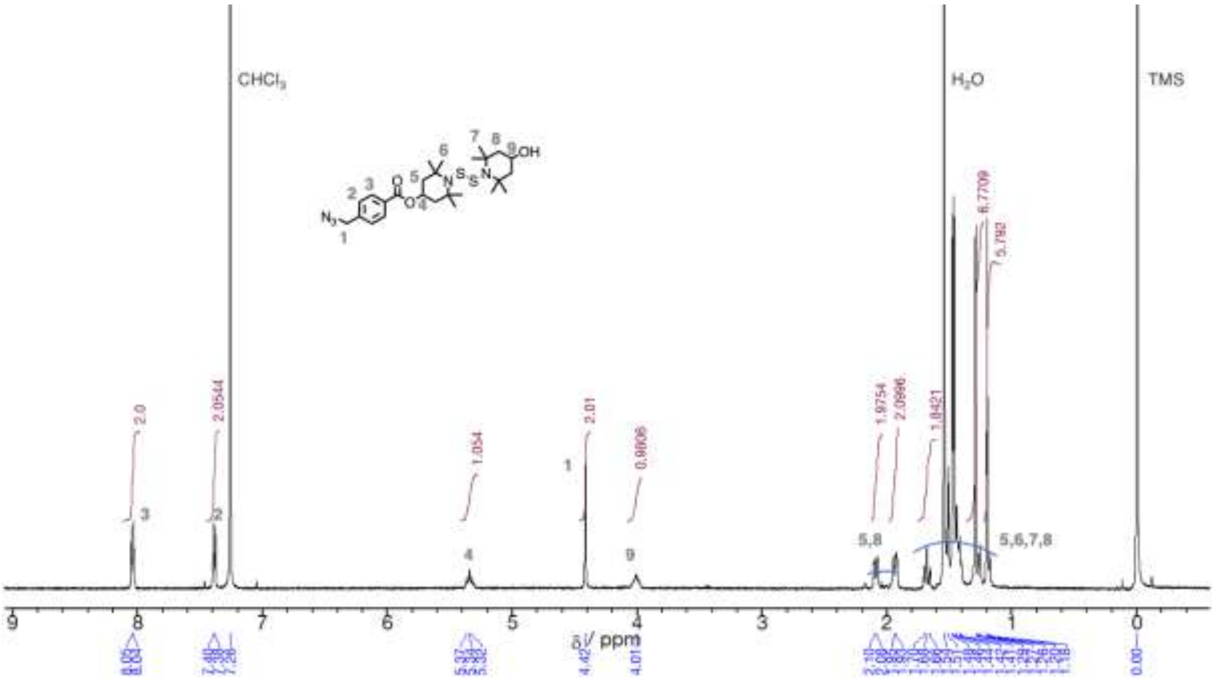


Figure S2. ^{1}H NMR spectrum of **BiTEMPS(azide)(OH)** (500 MHz, 25 °C, $CDCl_3$).

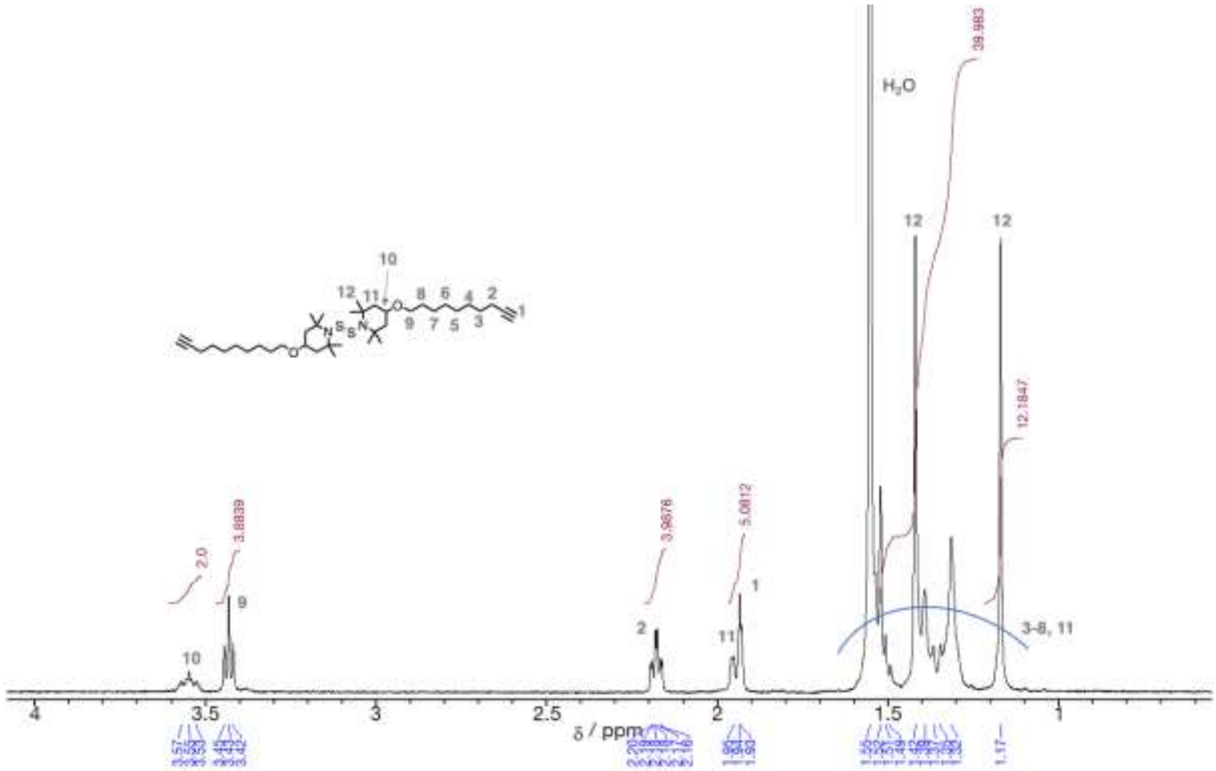


Figure S3. [1]H NMR spectrum of **BiTEMPS(yne)(yne)** (500 MHz, 25 °C, $CDCl_3$).

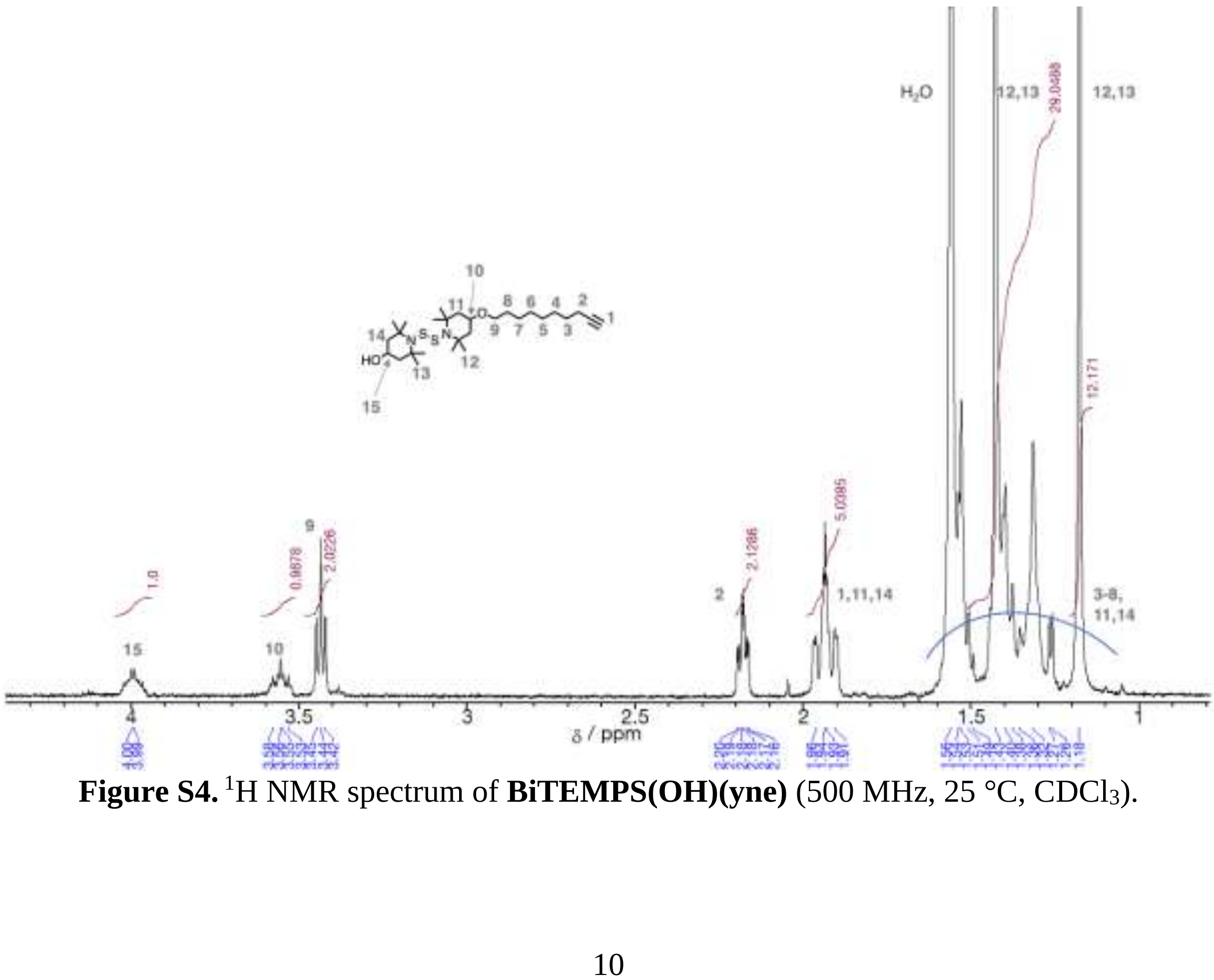


Figure S4. [1]H NMR spectrum of **BiTEMPS(OH)(yne)** (500 MHz, 25 °C, $CDCl_3$).

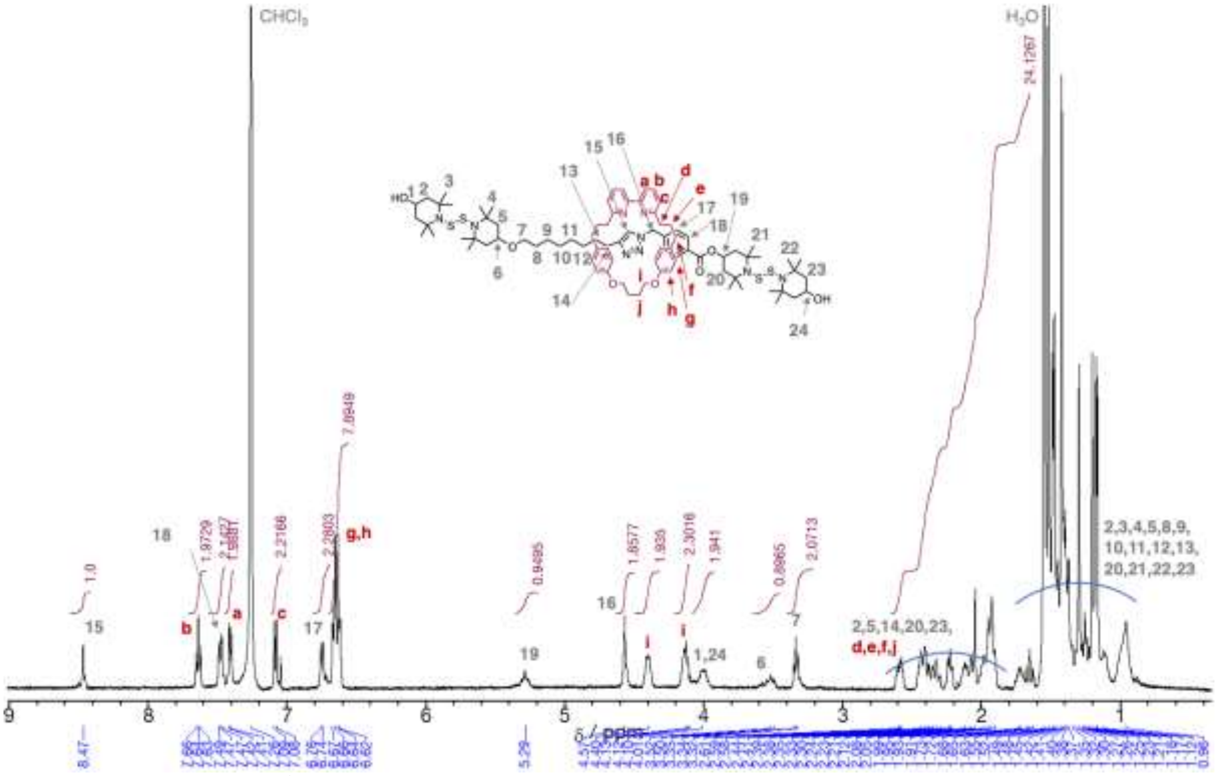


Figure S5. [1]H NMR spectrum of **[2]rotaxane** (500 MHz, 25 °C, $CDCl_3$).

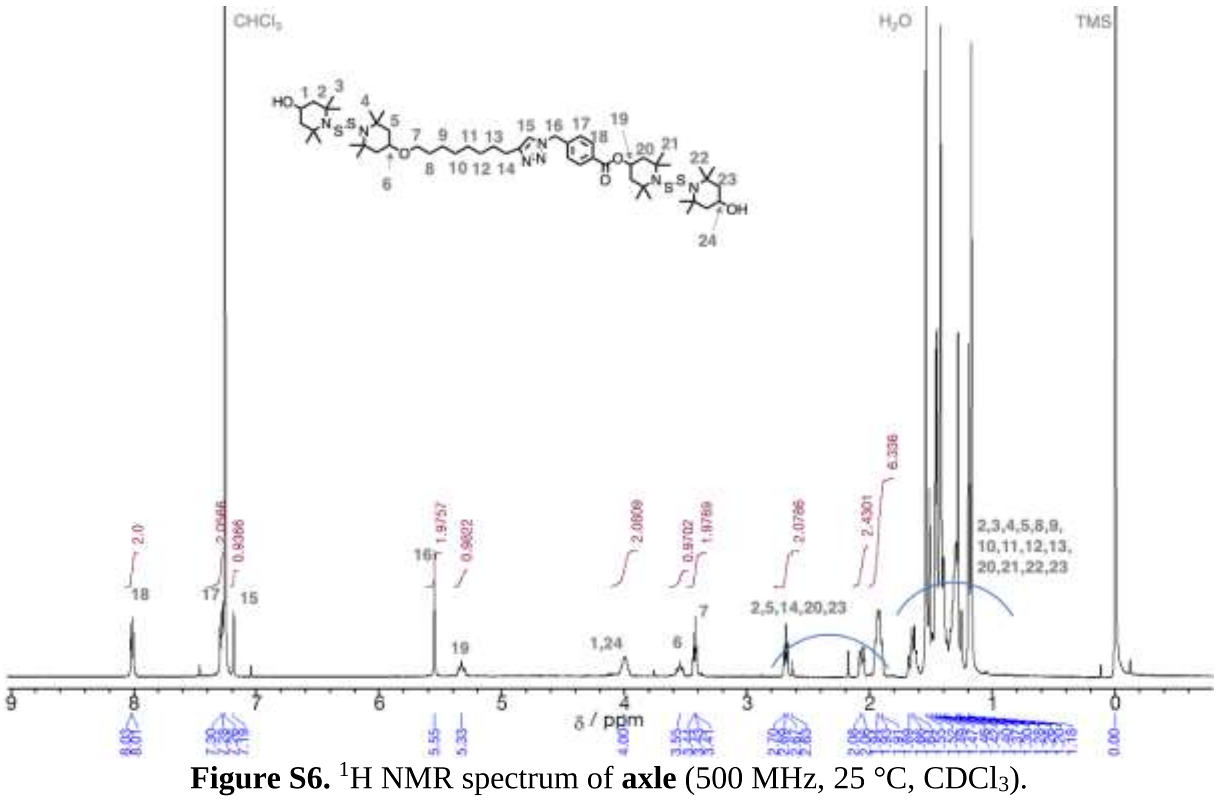


Figure S6. [1]H NMR spectrum of **axle** (500 MHz, 25 °C, $CDCl_3$).

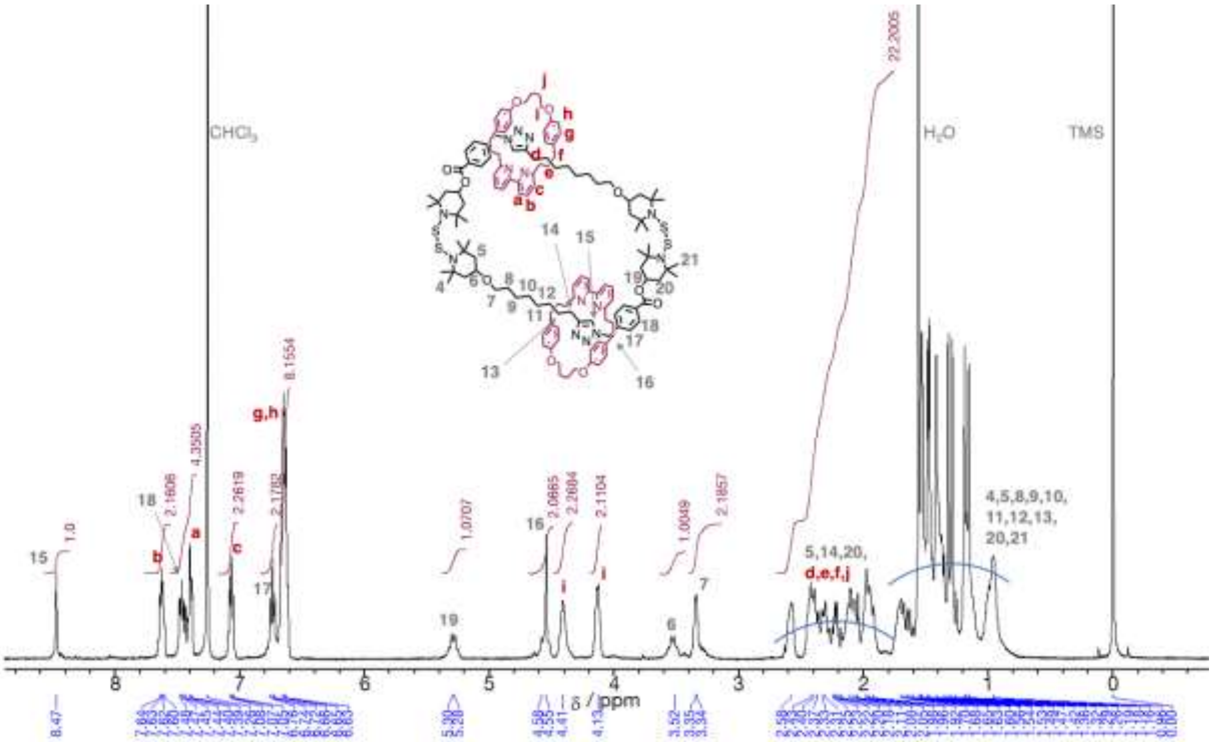


Figure S7. ^{1}H NMR spectrum of **[3]catenane** (500 MHz, 25 °C, $CDCl_3$).

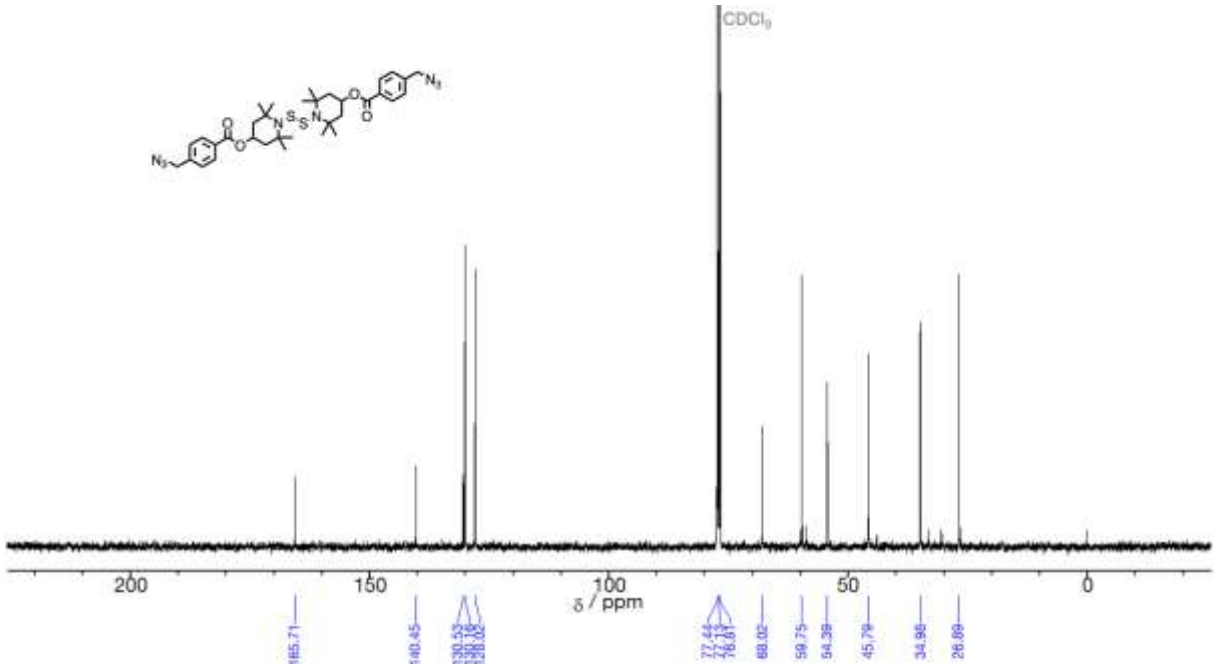


Figure S8. ^{13}C NMR spectrum of **BiTEMPS(azide)(azide)** (100 MHz, 25 °C, $CDCl_3$).

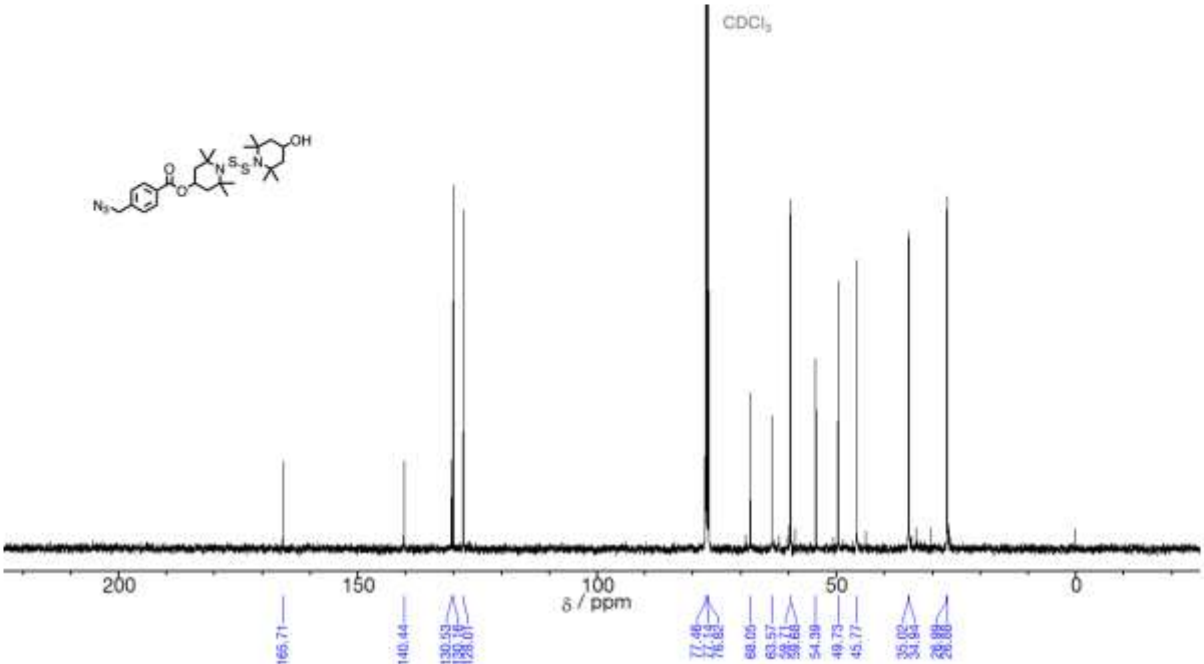


Figure S9. ^{13}C NMR spectrum of **BiTEMPS(azide)(OH)** (100 MHz, 25 °C, CDCl$_3$).

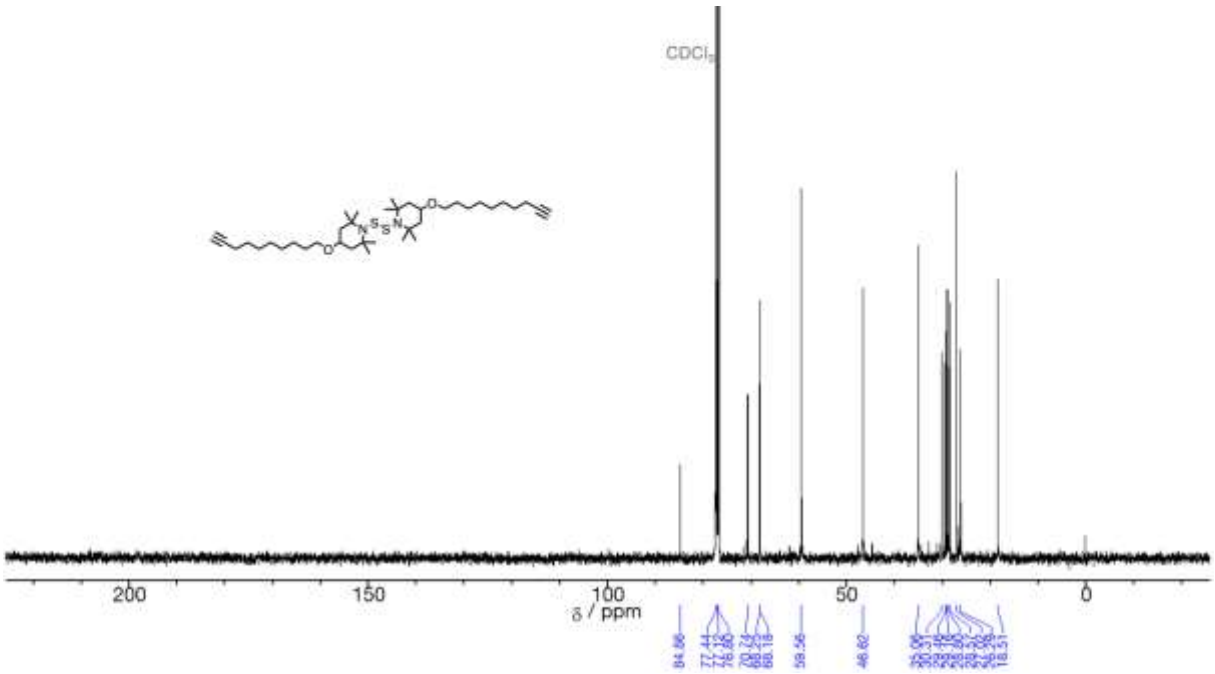


Figure S10. ^{13}C NMR spectrum of **BiTEMPS(yne)(yne)** (100 MHz, 25 °C, CDCl$_3$).

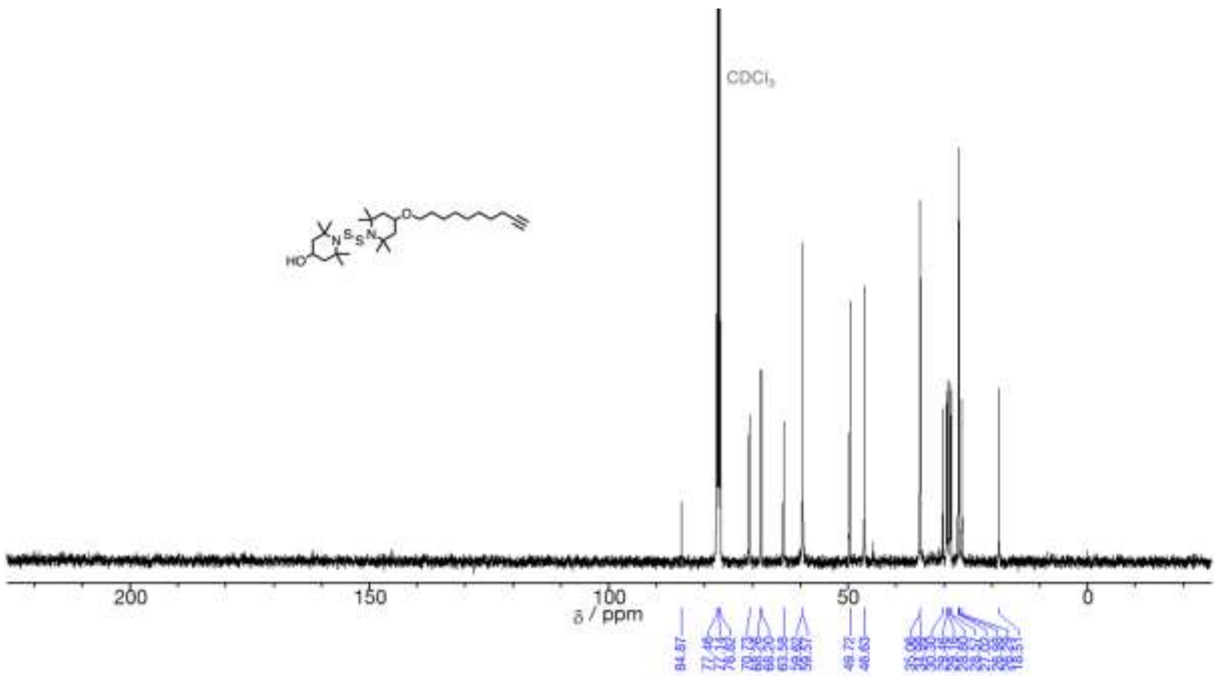


Figure S11. ^{13}C NMR spectrum of **BiTEMPS(OH)(yne)** (100 MHz, 25 °C, $CDCl_3$).

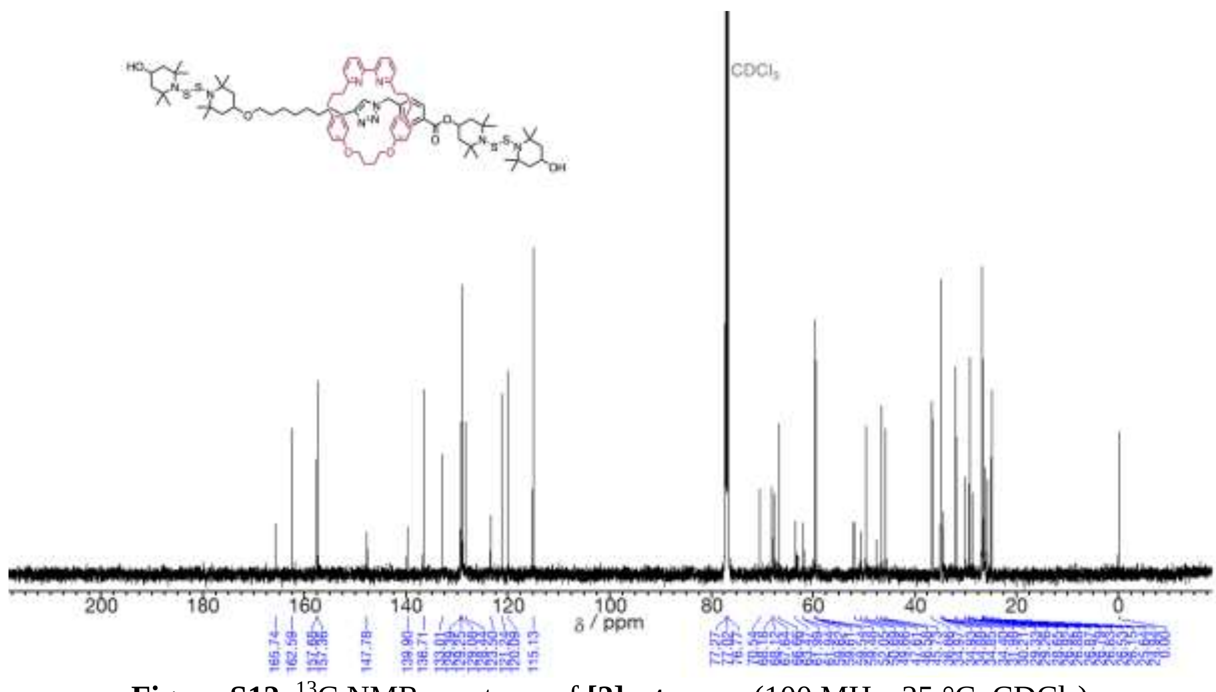


Figure S12. ^{13}C NMR spectrum of **[2]rotaxane** (100 MHz, 25 °C, $CDCl_3$).

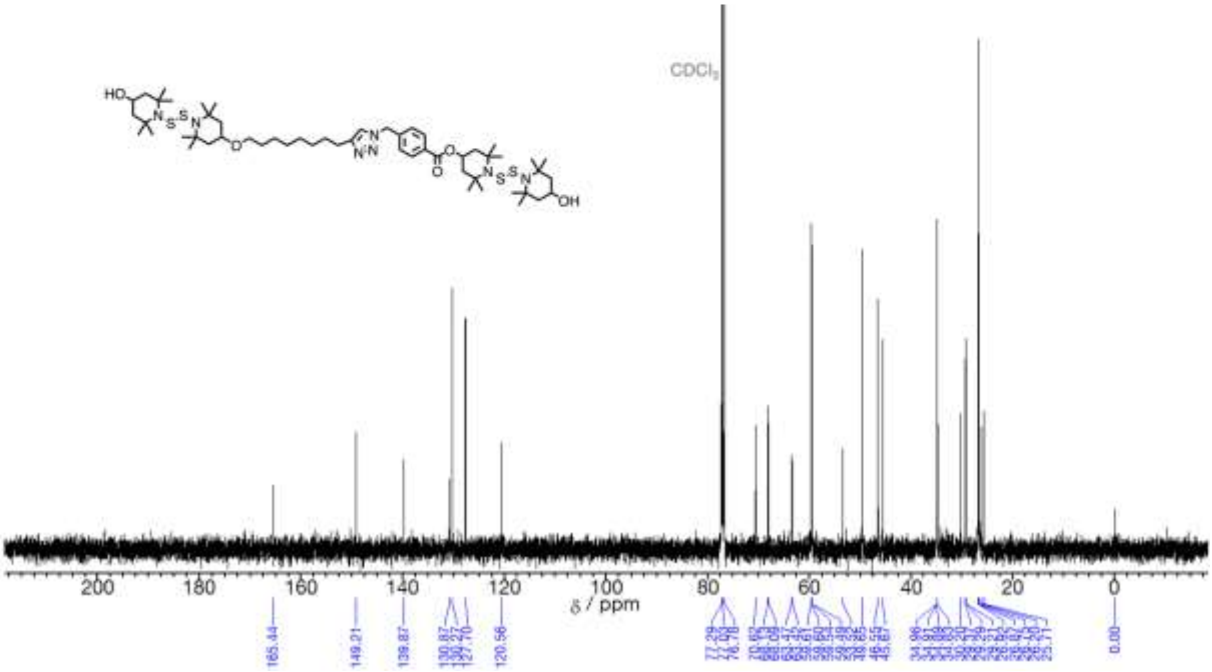


Figure S13. ^{13}C NMR spectrum of **axle** (100 MHz, 25 °C, $CDCl_3$).

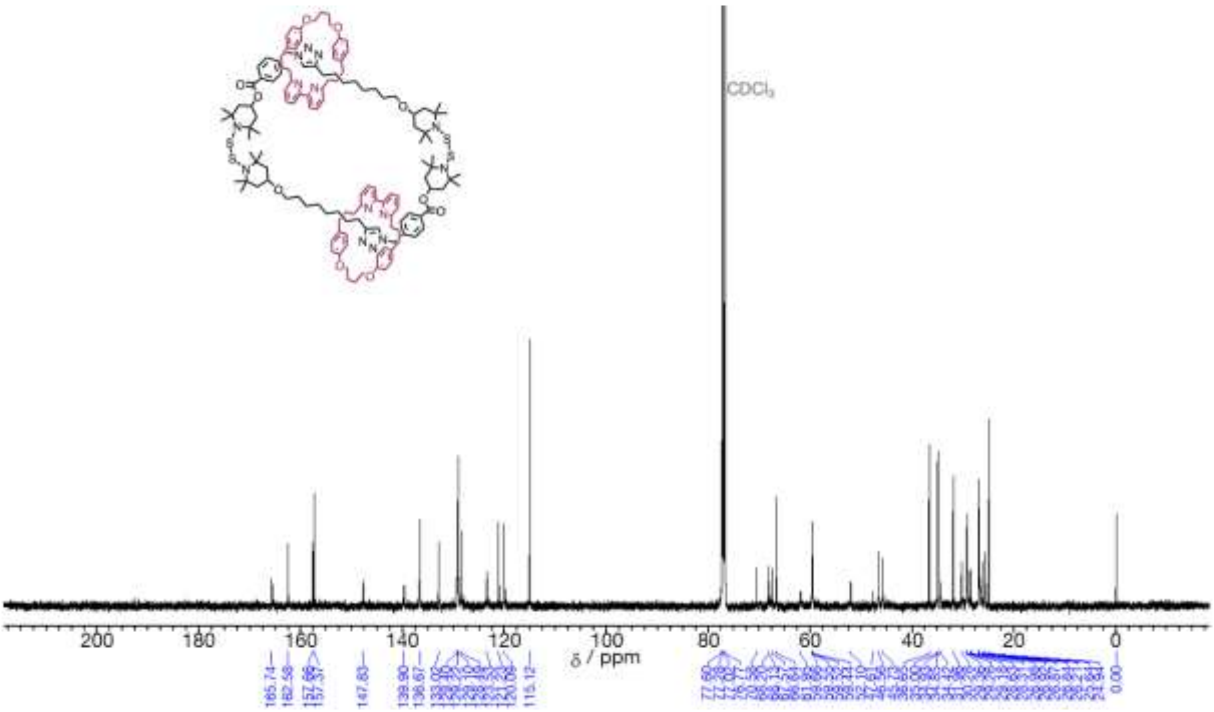


Figure S14. ^{13}C NMR spectrum of **[3]catenane** (100 MHz, 25 °C, $CDCl_3$).

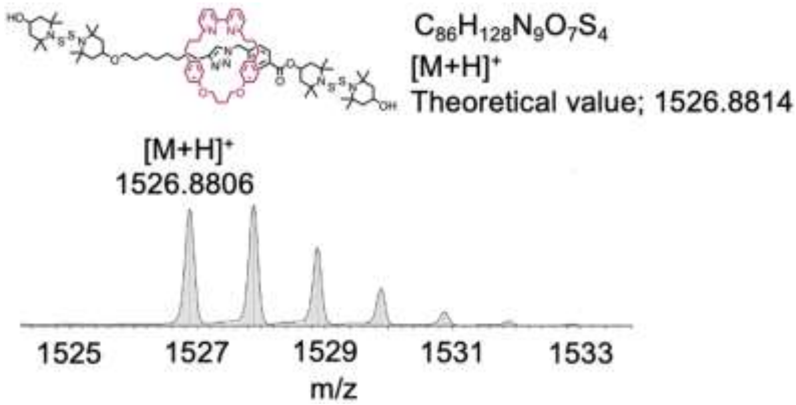


Figure S15. ESI-TOF MS profile of **[2]rotaxane** detected as [M+Na]$^+$.

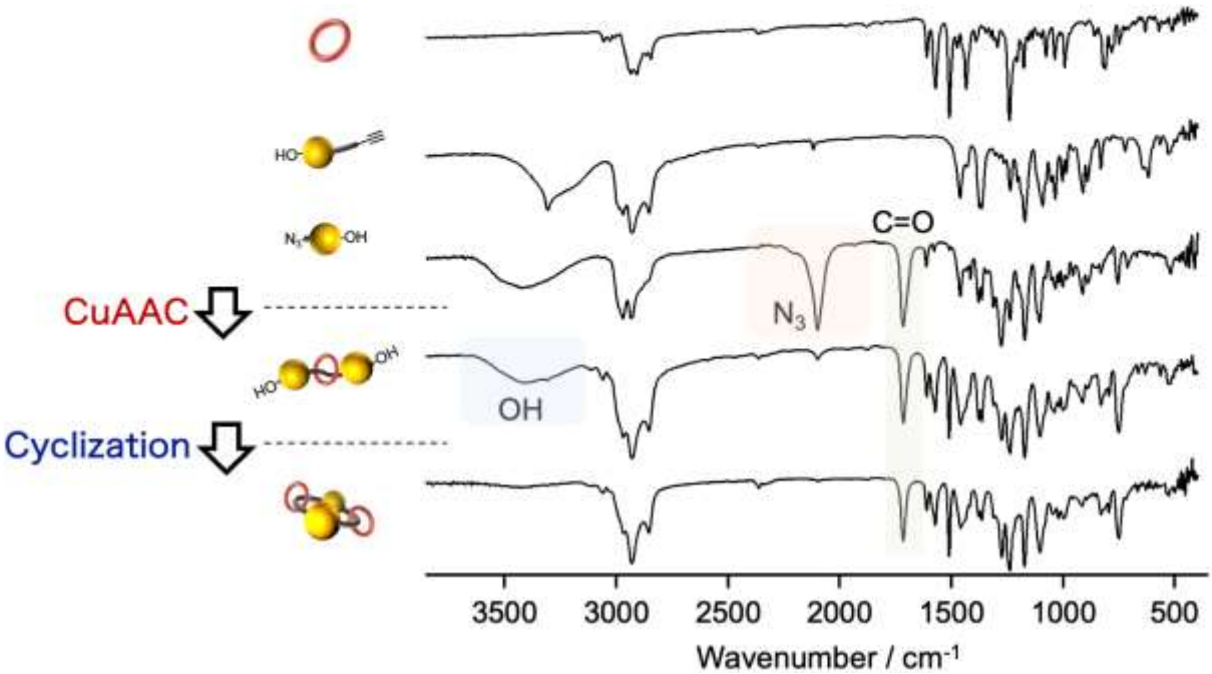


Figure S16. FT-IR spectra of **[3]catenane** and **[2]rotaxane**, and its precursors (KBr).

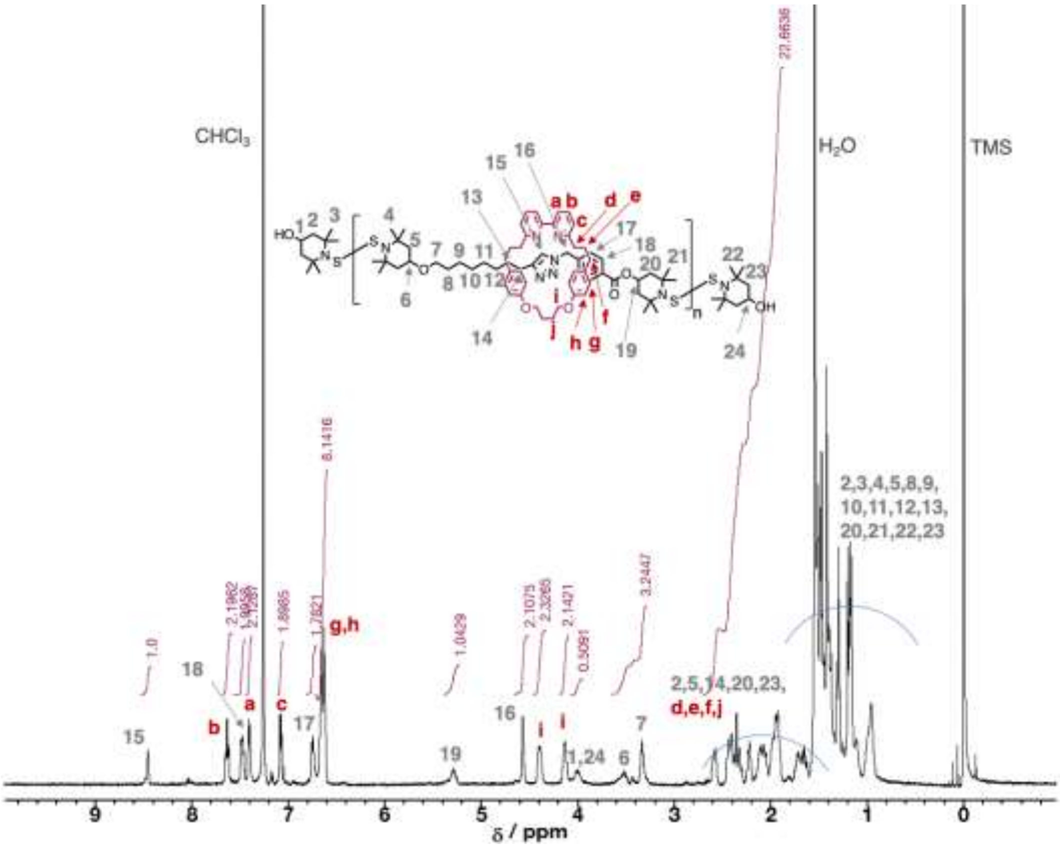


Figure S17. ^{1}H NMR spectrum of rotaxane containing oligomers and its precursors (500 MHz, 25 °C, $CDCl_3$).

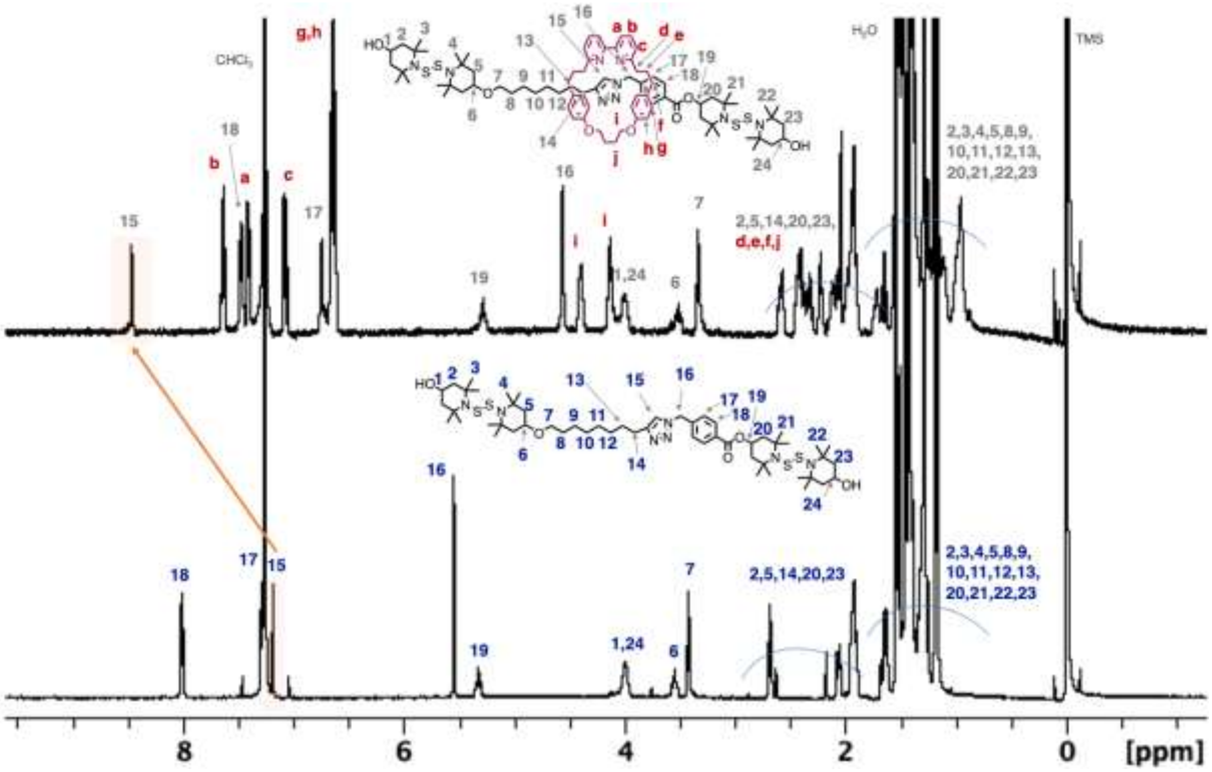


Figure S18. ^{1}H NMR spectra of **[2]rotaxane** and its axle molecule **MM(axle)** (500 MHz, 25 °C, $CDCl_3$).

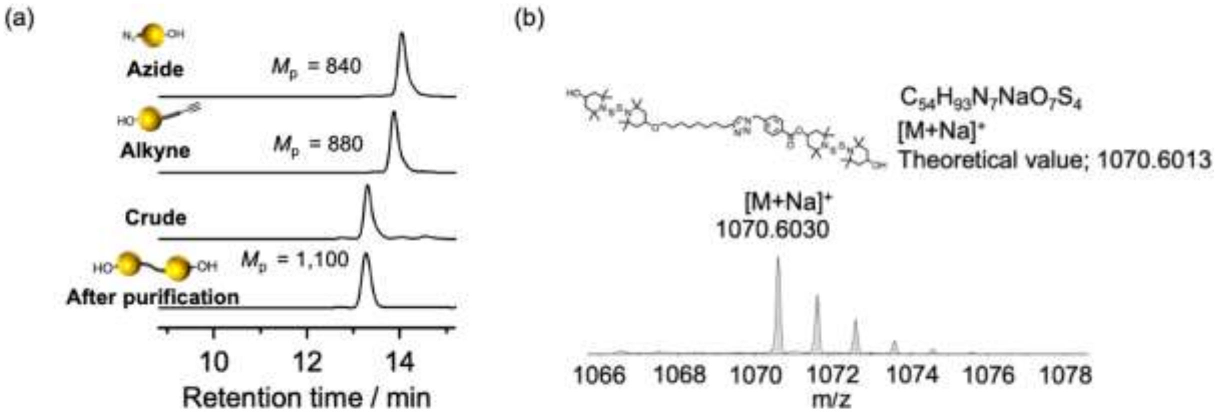


Figure S19. (a) GPC profile of **axle** and its precursors (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV). (b) ESI-TOF MS profile of **axle** detected as [M+Na]$^+$.

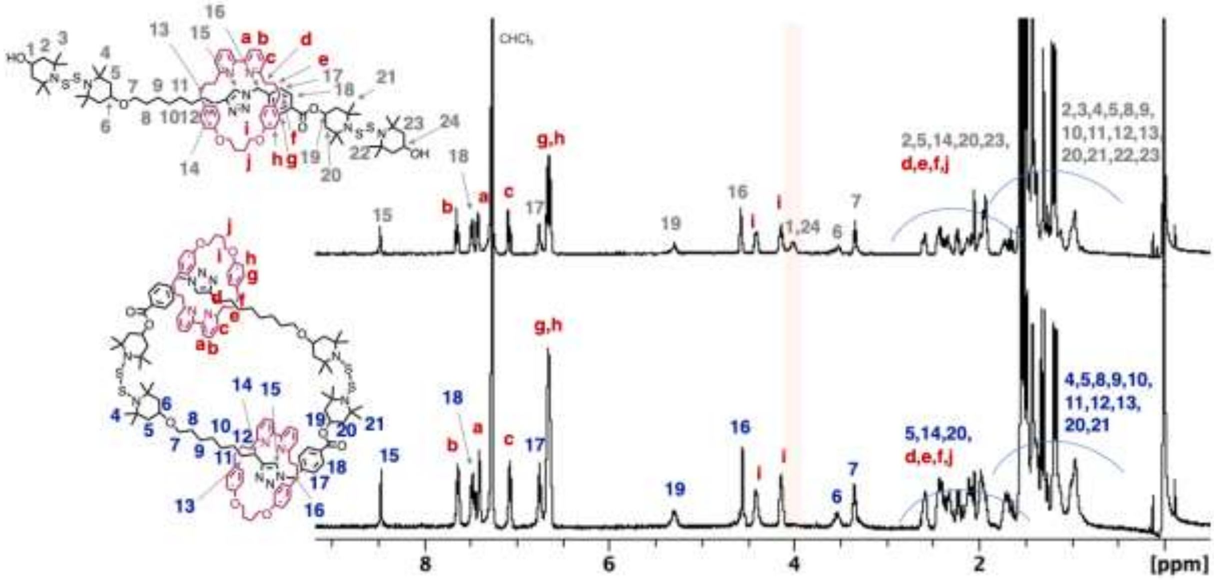


Figure S20. ^{1}H NMR spectra of **[2]rotaxane** and **[3]catenane** (500 MHz, 25 °C, $CDCl_3$).

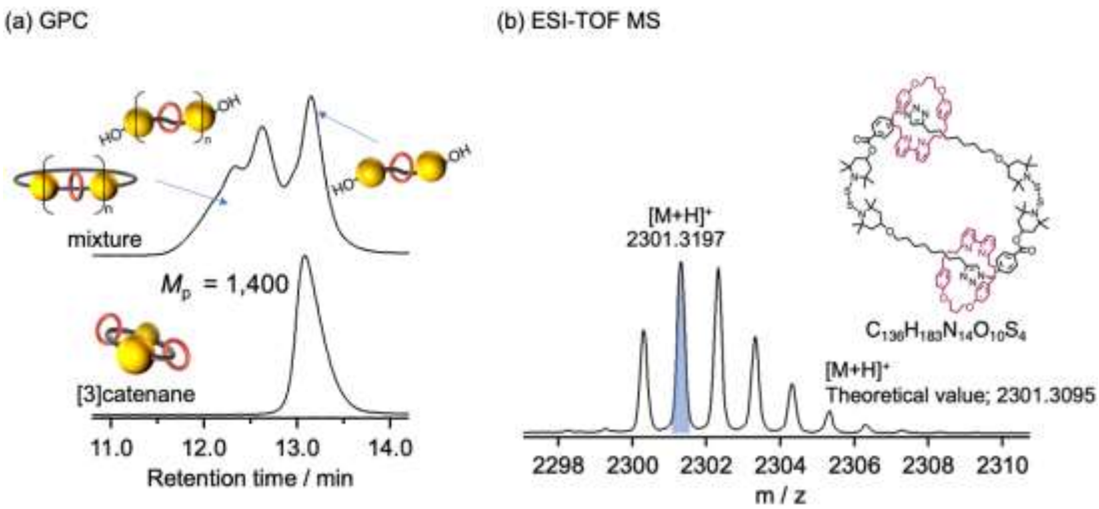


Figure S21. (a) GPC profiles of rotaxane containing oligomers and **[3]catenane** (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV). (b) ESI-TOF MS profile of **[3]catenane** detected as [M+H]$^+$.

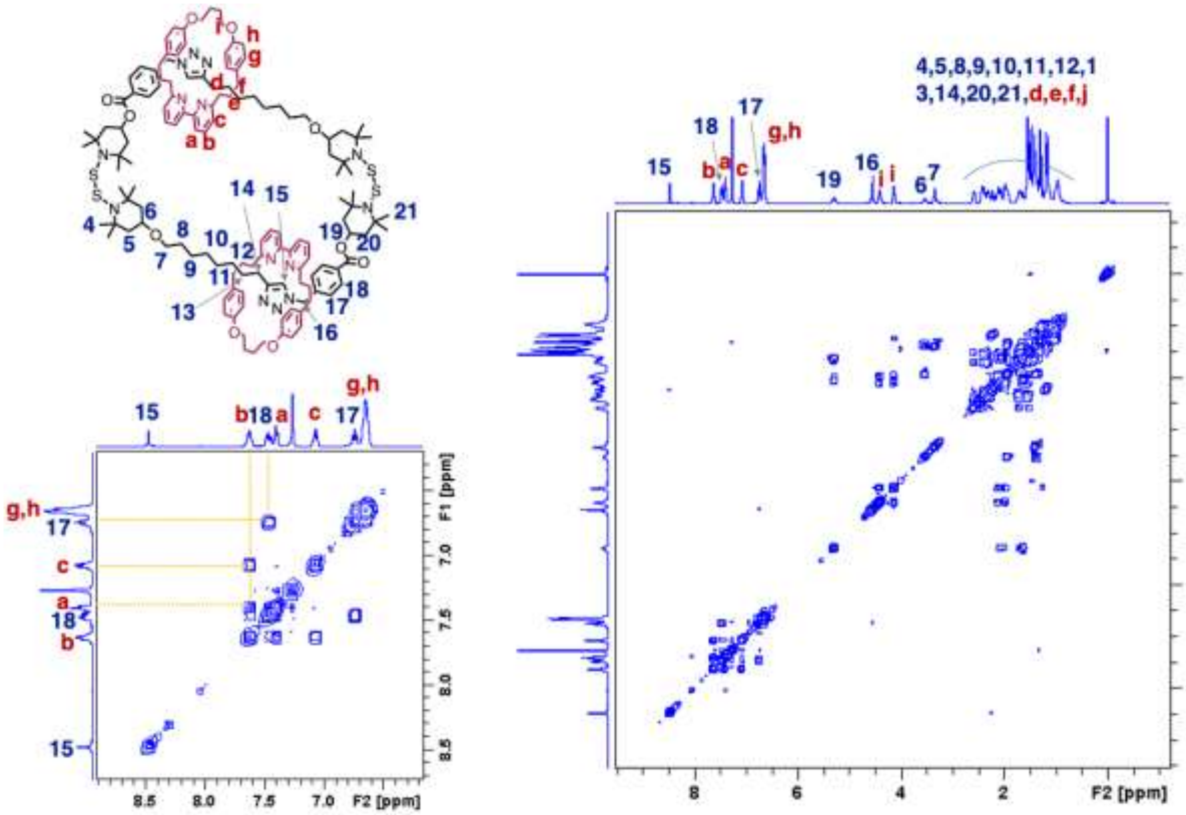


Figure S22. ^{1}H-^{1}H COSY spectrum of **[3]catenane** (500 MHz, 25 °C, $CDCl_3$).

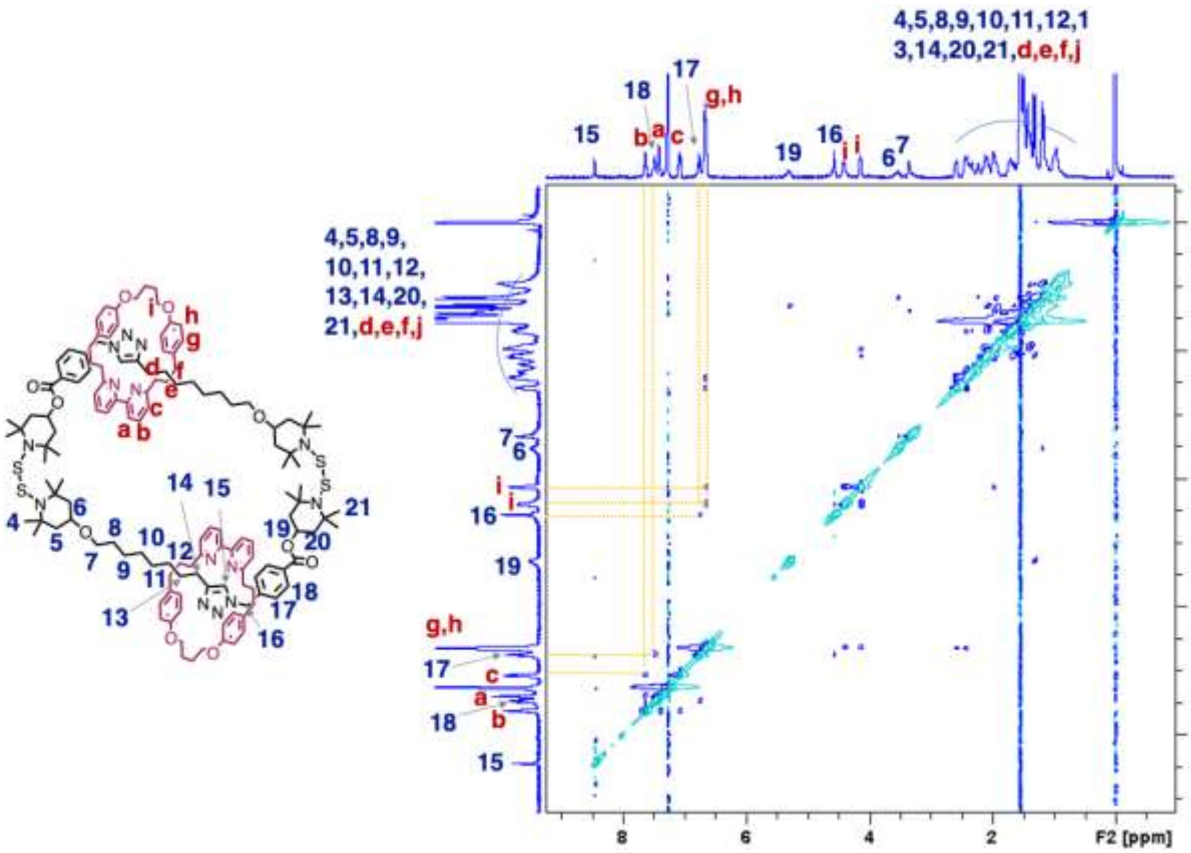


Figure S23. ^{1}H-^{1}H ROESY spectrum of **[3]catenane** (500 MHz, 25 °C, $CDCl_3$).

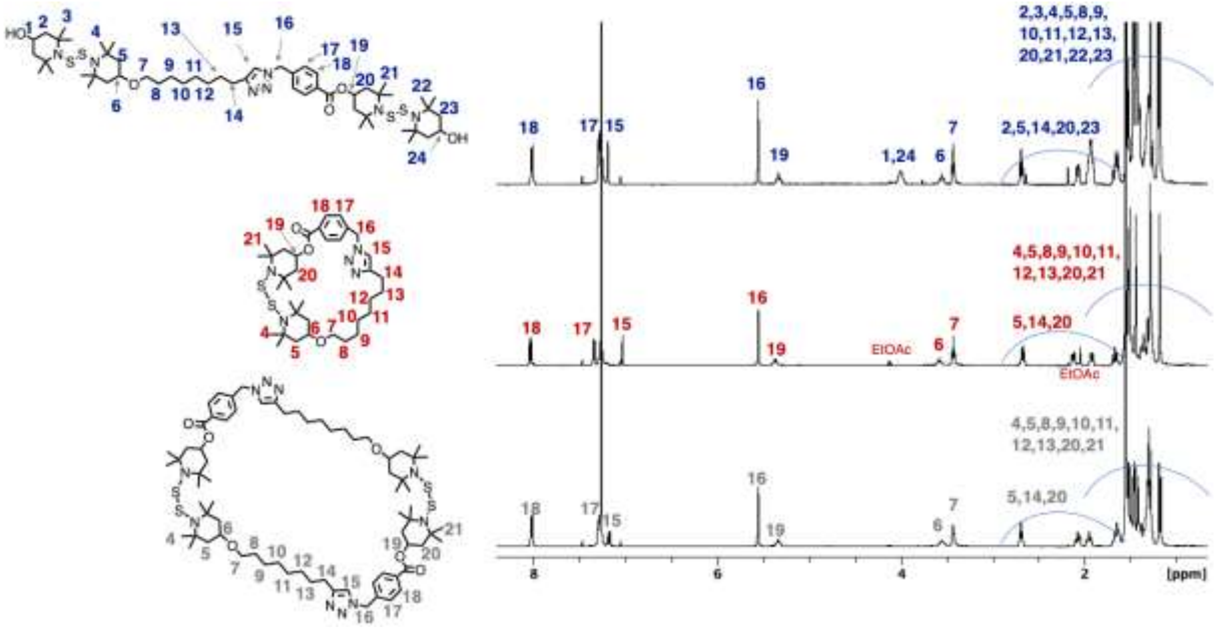


Figure S24. ^{1}H NMR spectra of **axle** and its cyclization products (500 MHz, 25 °C, $CDCl_3$).

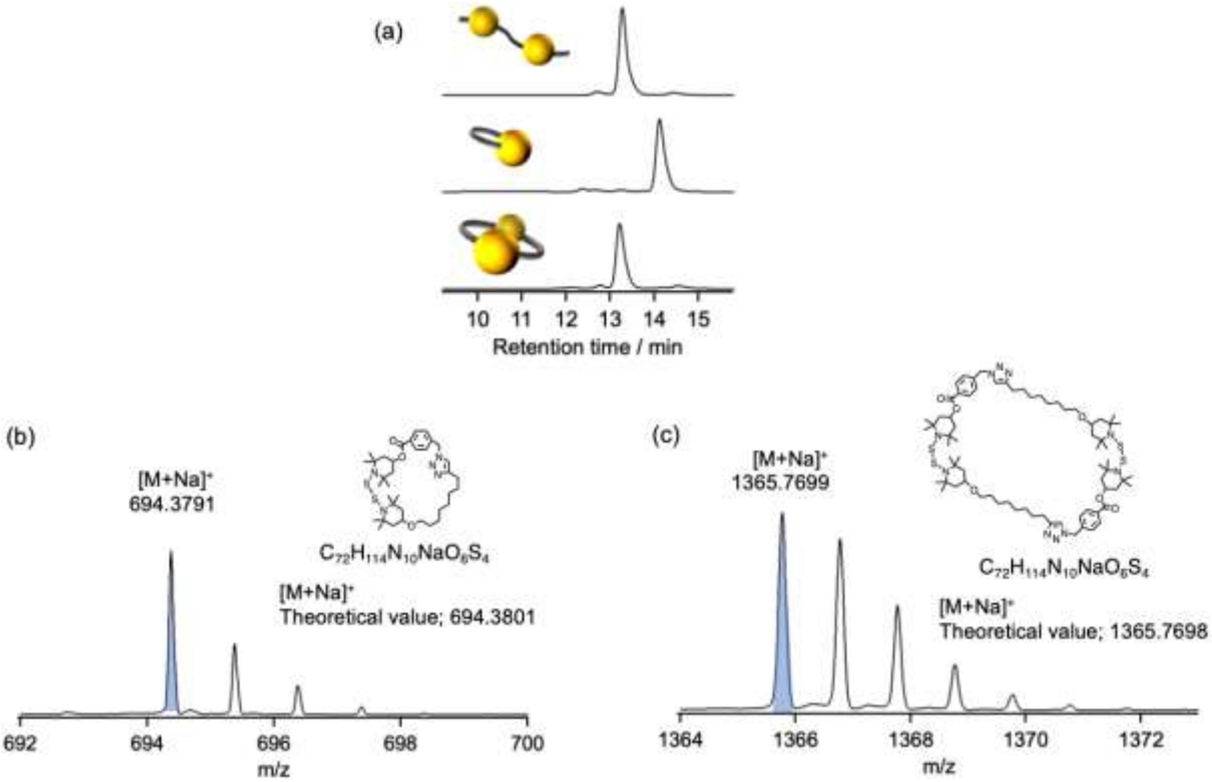


Figure S25. (a) GPC profiles of **MM(axle)** and its monomer (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV). ESI-TOF MS profile of (b) **MM(axle)** and (c) its monomer detected as $[M+Na]^+$.

4. Stability test

(a) Stability of Rotaxane toward Cu catalyst

$[(CH_3CN)_4Cu]PF_6$ and rotaxane were dissolved in CH_2Cl_2 (25 mM in 100 µL). The solution was stirred at 20 °C for 3 days under N_2 atmosphere, diluted with CH_2Cl_2 (1 mL) and washed with an EDTA-NH_3 solution (3 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The product was analyzed by GPC.

(b) Stability of rotaxane

Rotaxane was dissolved in CH_2Cl_2 (25 mM in 100 µL). The solution was stirred at 20 °C for 3 days under N_2 atmosphere, diluted with CH_2Cl_2 (1 mL) and washed with an EDTA-NH3 solution (3 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The product was analyzed by GPC.

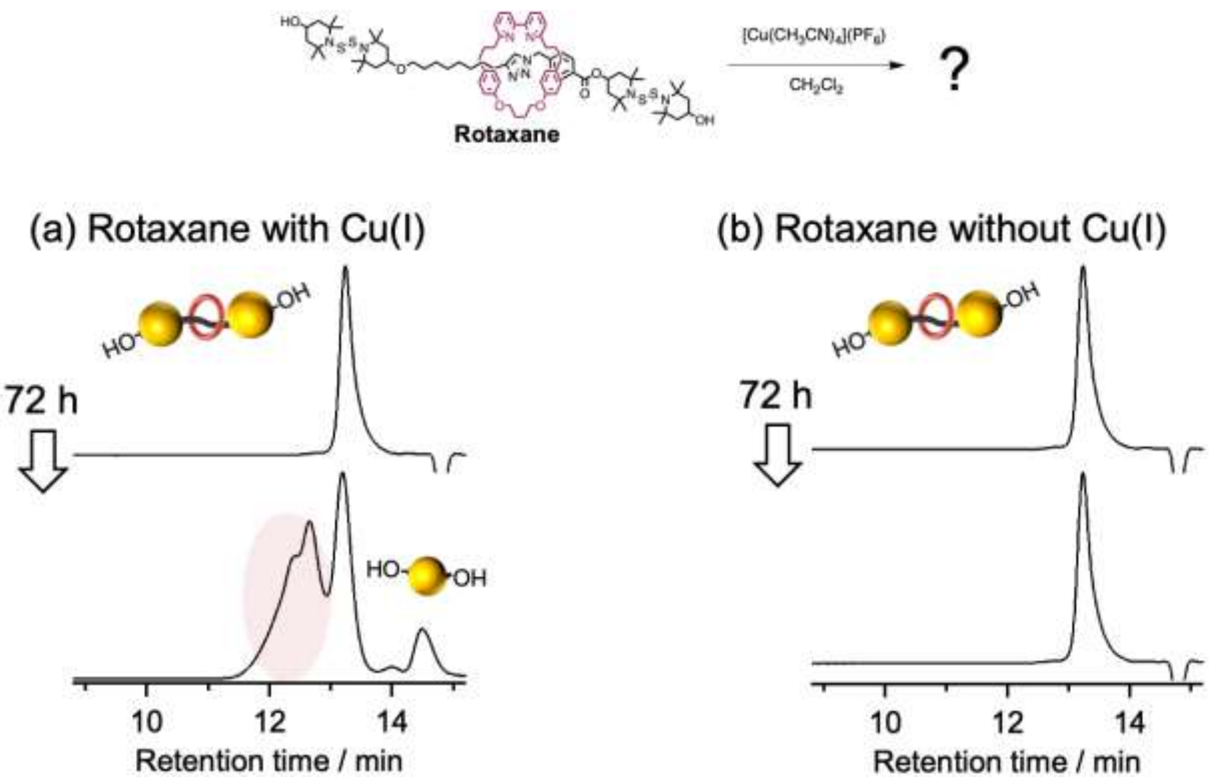
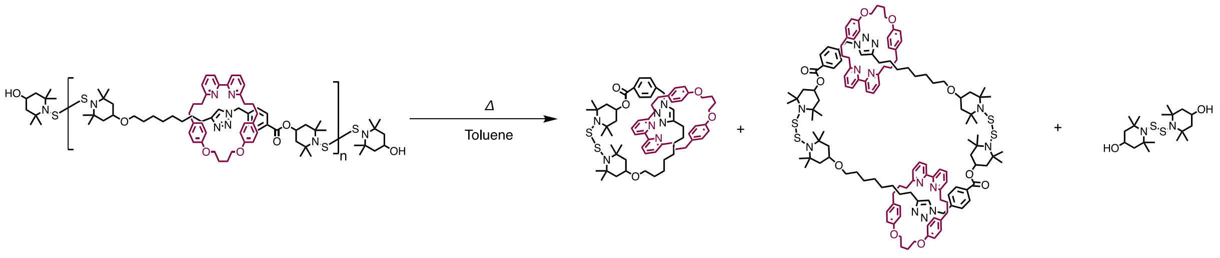


Figure S26. GPC profiles of (a) **[2]rotaxane** before and after stability test with Cu(I) and (b) **[2]rotaxane** before and after stability test without Cu(I). (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV).

5. Cyclization reaction



Rotaxane (oligomer)

In a test tube, rotaxane containing oligomers was dissolved in toluene (1 g/L) and heated at 100 °C for 9 h. We conducted same reaction by using isolated [2]rotaxane and axle (1 mM) as references.

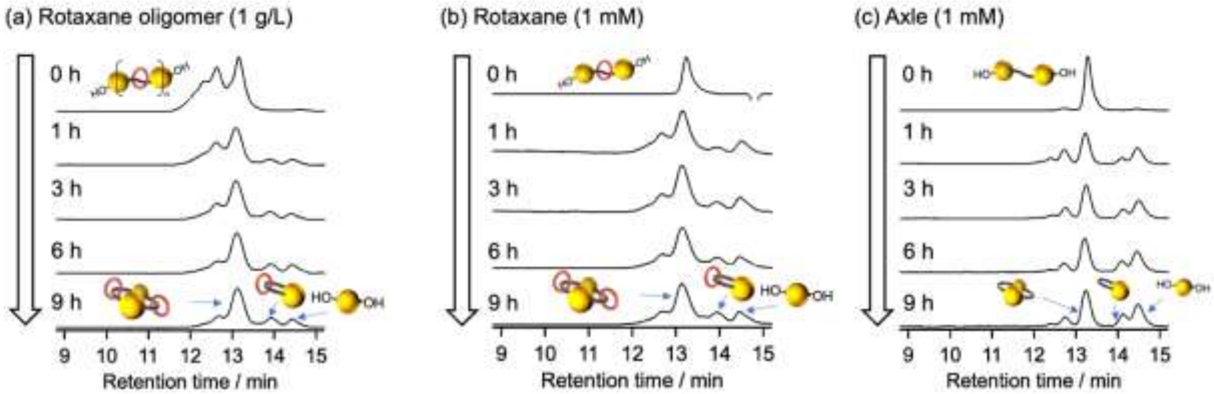


Figure S27. Changes in GPC profiles at cyclization reaction of (a) rotaxane containing oligomers, (b) **[2]rotaxane**, and (c) **axle** (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV).

6. Hydrolysis of [3]catenane

We added excess amounts of KOH (561 mg, 10 mmol) and water (1 mL) to [3]catenane (23 mg, 0.1 mmol) and stirred the mixture at room temperature for 24 h in ethanol solution (9 mL), then, we washed the mixture with toluene without neutralization and collected organic layer.

(Calculation of isomer ratio)

Figure S28 shows ^{1}H NMR of products in the organic layer of the hydrolysate. We observed BiTEMPS(OH)(OH) and bipyridine macrocycle as main products. No other structures containing potassium salts of carboxylic acids were detected in organic layer. As mentioned on **Scheme 2** in the main text, one intermediate would be formed from the head-to-tail isomer and two intermediates would be formed from the head-to-head isomer. We can finally observe two products (i.e., bipyridine rings and diol derivatives of BiTEMPS) from organic layer because bipyridine rings was detached from axile (**Figure S29**). Importantly, BiTEMPS(OH)(OH) can be only formed from the head-to-head isomer. Therefore, our observation of BiTEMPS(OH)(OH) in the organic layer was suggesting contamination of head-to-head isomer before recrystallization. We can also determine the ratio of isomer from the integral ratio of BiTEMPS(OH)(OH) and bipyridine macrocycle in ^{1}H NMR.

The ratio of isomers was calculated as follow. Assume head-tail ratio x, head-head ratio y. The hydrolysis produces (2x+2y) bipyridines and (y) BiTEMPS(OH)(OH) in organic layer as shown in **Figure S29**. Therefore, when we focus on the integrals of the signals (**1** (12H) and **h** (4 h) in **Figure S28**) of the ^{1}H NMR signals originated from the respective compounds, the following equation holds, taking into account the number of their protons.

$$4(2x + 2y) / 12(y) = 4.0763 / 1.8255$$

Namely, the isomer existence ratio, head-to-tail vs head-to-head, was determined as 2.35 to 1. The reasons for this biased generation rate were supported by the DFT calculations described below (**Figure S32**).

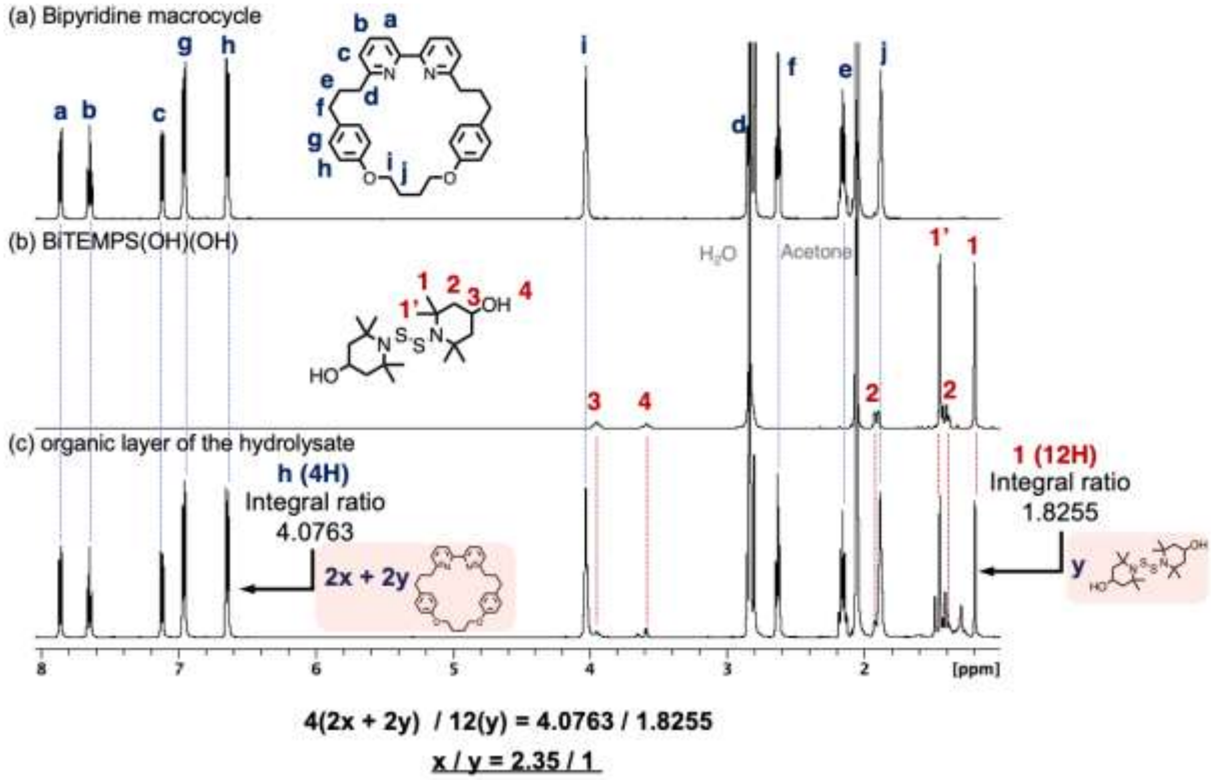


Figure S28. ^{1}H NMR spectra of (a) bipyridine macrocycle, (b) BiTEMPS(OH)(OH), and (c) organic layer of the hydrolysate (500 MHz, 25 °C, Acetone-d_6).

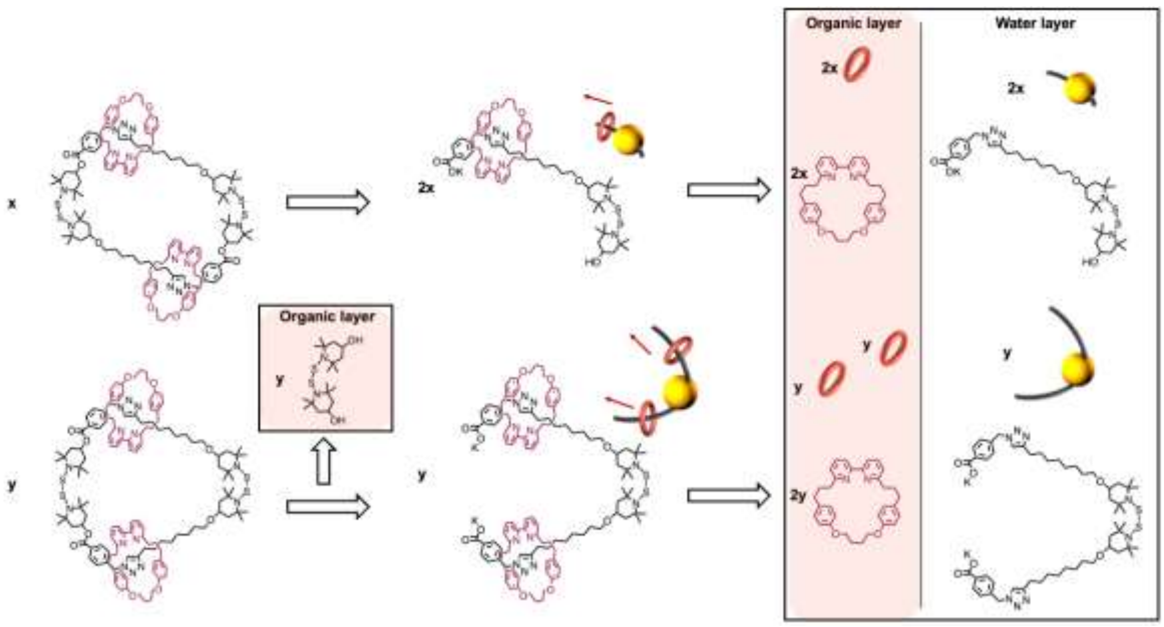
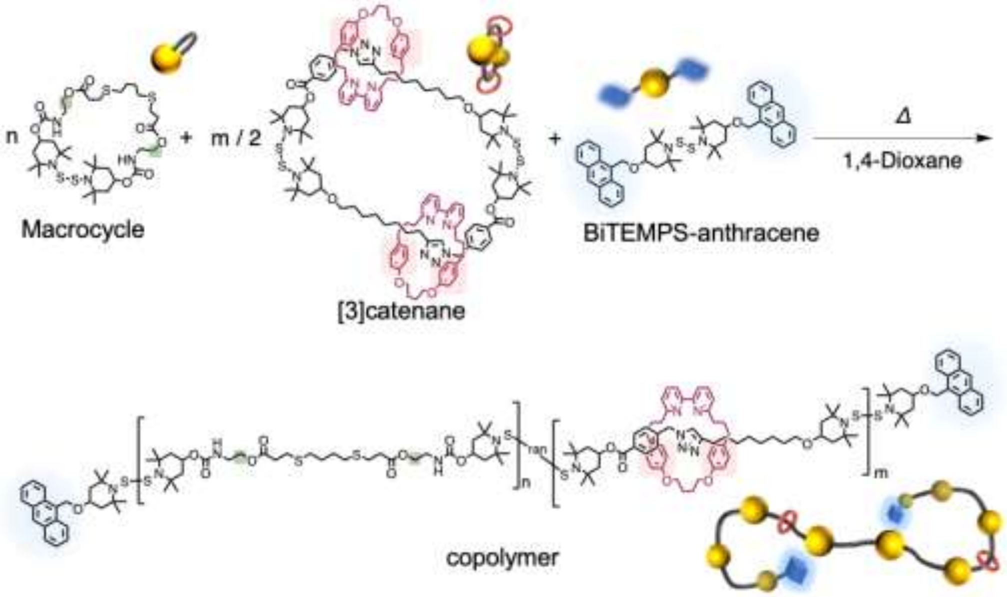


Figure S29. Schematic image of deslipping of bipyridine macrocycles from hydrolysates of [3]catenane and products of in organic and water layers.

7. Polymerization



In a test tube, **macrocycle** (44 mg, 56 μmol), **[3]catenane** (7.2 mg, 3.1 μmol), and **BiTEMPS-anthracene** (4.7 mg, 6.3 μmol) were dissolved in 1,4-dioxane (125 μL) and heated at 100 °C for 6 h. The solution was poured into 20 mL hexane. The precipitate was decanted and dried in vacuo to afford copolymer (56 mg, quant.).

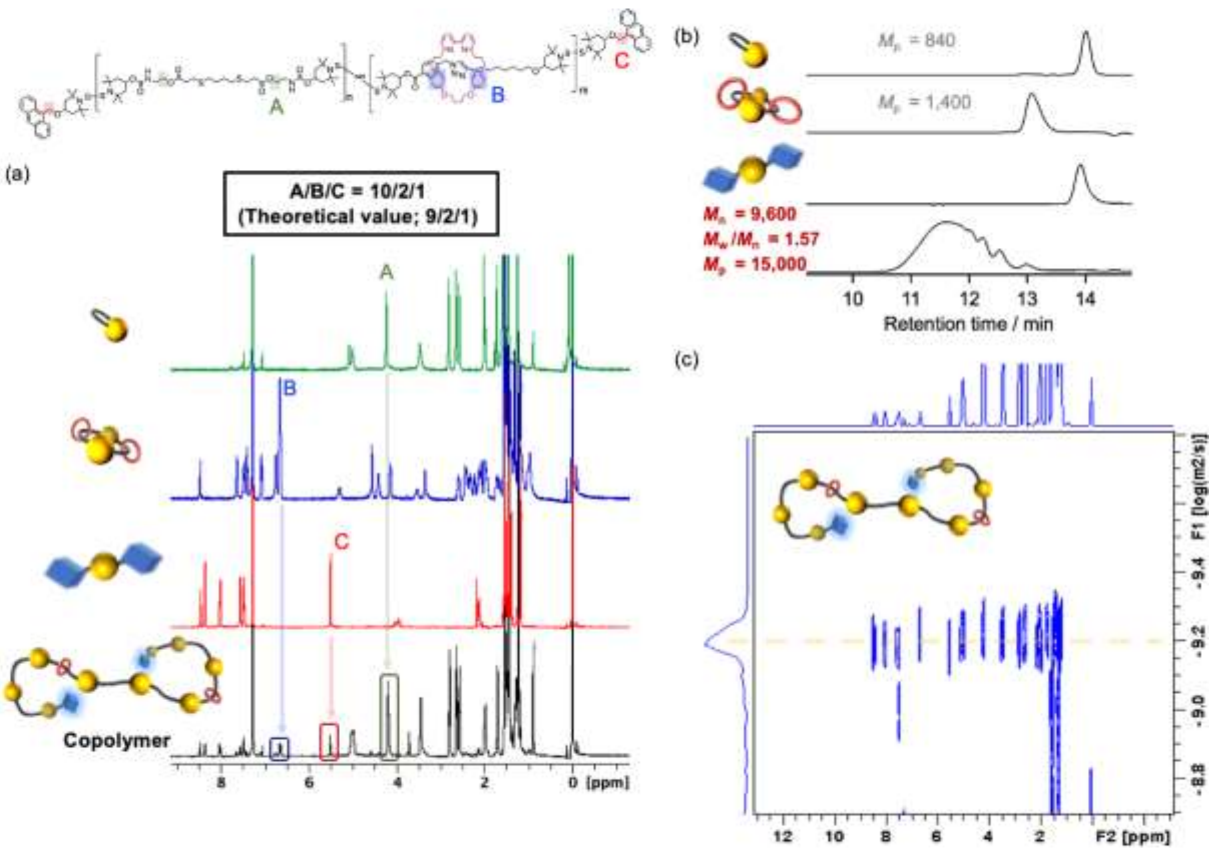


Figure S30. (a) ^{1}H NMR spectra of copolymer and its precursors (500 MHz, 25 °C, $CDCl_3$). (b) DOSY spectrum of copolymer.

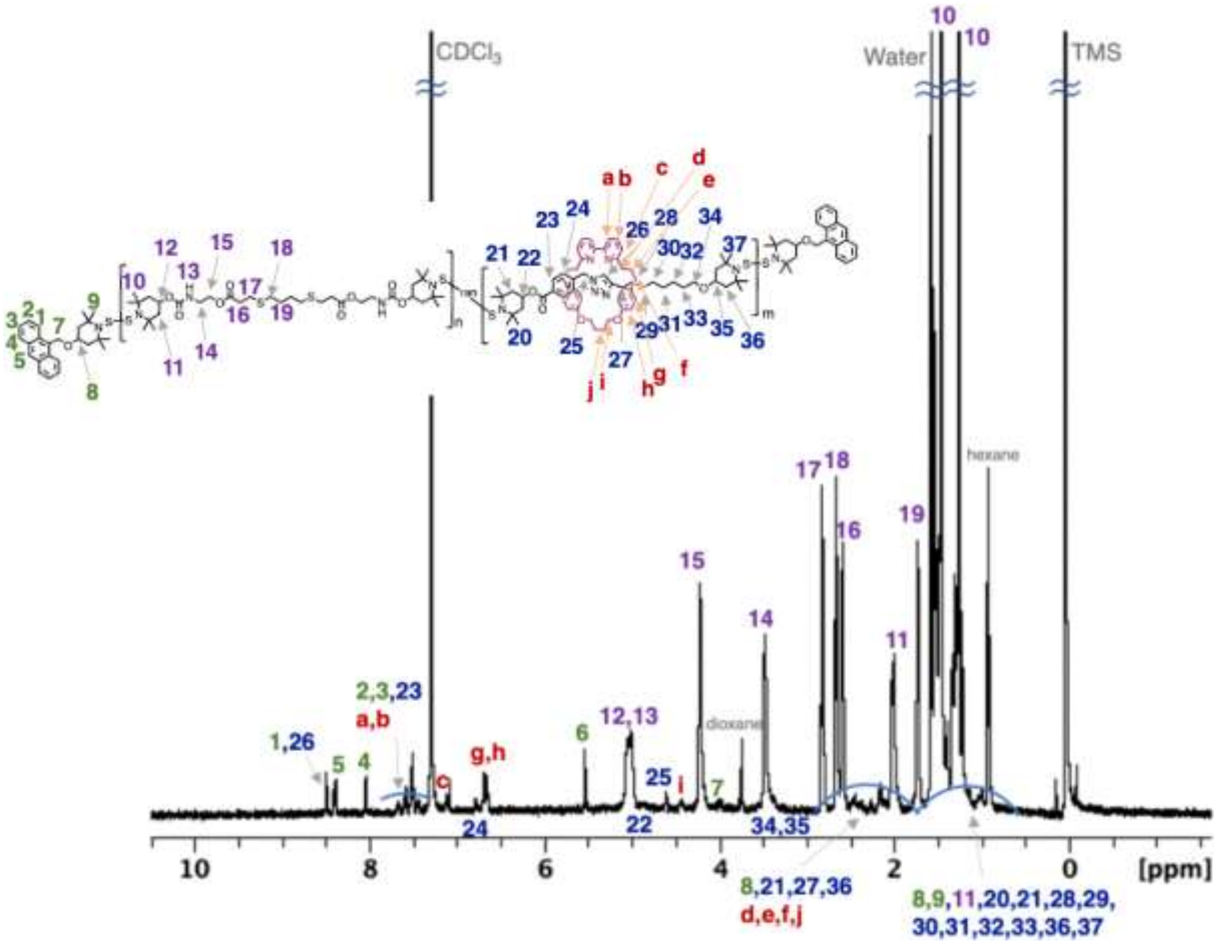


Figure S31. ^{1}H NMR spectrum of copolymer (500 MHz, 25 °C, $CDCl_3$).

8. X-ray analysis

Single clear light colorless block-shaped crystals were obtained by recrystallisation from 1,4-dioxane and hexane mixture. A suitable crystal 0.18×0.12×0.08 mm^3 was selected and mounted on a suitable support on an XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at a steady T = 90 K during data collection.

Data were measured using ω scans of 0.5° per frame for 5.0/15.0 s using Cu Kα radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.42.81a, 2023) The maximum resolution that was achieved was Θ = 76.778° (0.79 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.42.81a, 2023) and the unit cell was refined using CrysAlisPro (Rigaku, V1.171.42.81a, 2023) on 17344 reflections, 38% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.42.81a, 2023). The final completeness is 100.00 % out to 76.778° in Θ. A multi-scan absorption correction was performed using CrysAlisPro 1.171.42.81a (Rigaku Oxford Diffraction, 2023) using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient μ of this material is 1.062 mm^{-1} at this wavelength (λ = 1.542 Å) and the minimum and maximum transmissions are 0.837 and 1.000.

[CCDC-2292612 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

9. DFT calculations

The explanation for preference of head-to-tail was supported by the computation, estimating the free energy (*G*) of head-to-tail dimer and head-to-head dimer. The calculations were conducted by using DFT at the UB3LYP/6-31G(d,p) level. **Figure 2** shows the difference in *G* of molecules between two [3]catenane. The result revealed head-to-head [3]catenane was 63 kJ/mol less stable than head-to-tail [3]catenane. Namely, the result supported head-to-tail [3]catenane was favorable structure and consistent with the experimental result. DFT calculations was carried out using the TSUBAME3.0 supercomputer at Tokyo Institute of Technology.

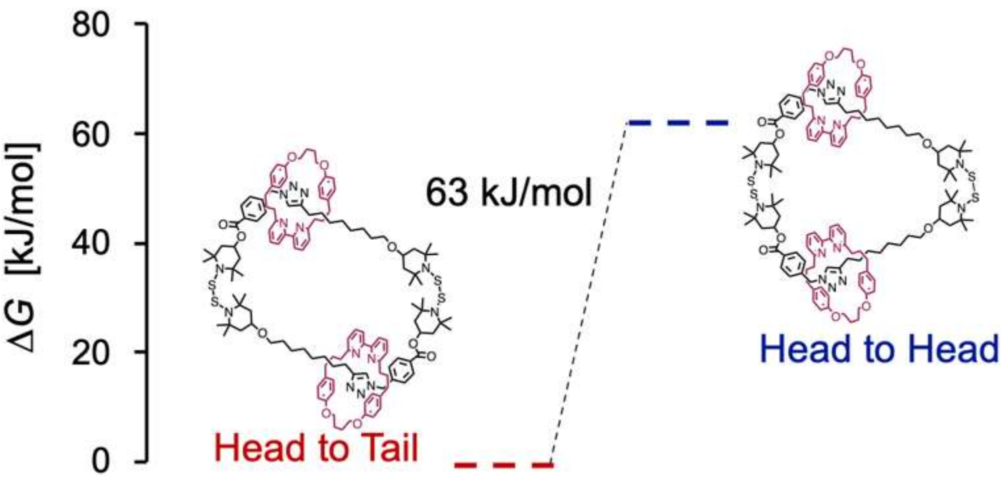
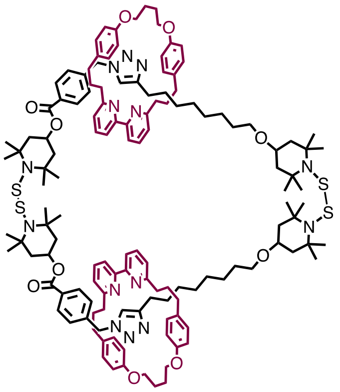


Figure S32. Difference in free energy (*G*) between two [3]catenane. The calculations were conducted by using DFT at the UB3LYP/6-31G(d,p) level.

Optimized geometries from DFT calculations at B3LYP/6-31g(d,p) level



Head-to-Head [3]catenane

atom	X	Y	Z
S	2.53291	-9.92297	3.295
O	-3.37959	-9.57489	2.3083
C	-3.65258	-9.39887	0.91763
C	-4.24946	-8.01249	0.67184
C	-4.74237	-7.77769	-0.76259
C	-5.33176	-6.37012	-0.97332
C	-6.70345	-6.14668	-0.31589
C	-7.08296	-4.6652	-0.19004
N	-8.19563	-0.57976	-1.57648
N	-7.86446	-1.65477	-0.91
C	-8.809	-1.9123	0.04219
C	-9.77426	-0.92625	-0.04372
N	-9.35218	-0.12773	-1.05828
S	-0.95803	8.97893	-0.3216
N	-2.45556	8.24038	-0.05642
C	-3.6862	9.11369	-0.16596
C	-4.95623	8.21568	-0.11841
C	-4.68991	6.90008	-0.83747
C	-3.65311	6.05108	-0.10008
C	-2.55305	6.89839	0.61415
C	-3.65884	9.85417	-1.52003
C	-3.75957	10.15712	0.96498

C	-1.23247	6.12688	0.46682
O	-5.87242	6.10218	-1.14306
C	-2.88151	7.03792	2.12046
C	-9.34643	3.00409	-0.0531
C	-8.556	4.09902	0.27914
C	-7.57147	4.55382	-0.60878
C	-7.40717	3.91104	-1.84354
C	-8.1945	2.80776	-2.16466
C	-9.1602	2.334	-1.26922
C	-9.96644	1.09085	-1.59065
C	-6.66602	5.6482	-0.14935
O	-6.63465	6.05043	1.00004
C	-8.70858	-3.04564	1.02185
N	0.88504	-9.86574	2.75351
C	0.27484	-8.48745	2.90832
C	-1.14258	-8.47997	2.2846
C	-2.02465	-9.62961	2.76105
C	-1.33372	-10.94247	2.41112
C	0.06346	-11.09722	3.05985
C	-8.46915	-4.4528	0.43959
C	1.11019	-7.4622	2.11921
C	0.20854	-8.00771	4.37973
C	0.72714	-12.31799	2.39655
C	6.89451	-9.6142	0.76283
C	5.37544	-8.14053	2.09148
C	3.45843	-11.62968	-0.97364
C	2.51709	-9.31749	-0.96465
C	7.09966	-1.98348	-4.67287
C	5.52801	-8.89515	0.75832
C	5.43807	-7.83847	-0.3639
C	5.44414	-8.38064	-1.79617
C	4.86746	-9.80478	-1.85613
C	3.80913	-10.13983	-0.78079
N	4.41661	-9.89911	0.57399
C	6.4135	-0.80322	-3.95915

O	5.64778	6.89283	2.61968
C	5.32802	6.1841	1.68176
C	8.48525	1.59671	-0.02003
C	7.64795	2.80631	0.36214
C	7.99912	3.5181	1.52345
C	7.24263	4.61029	1.93664
C	6.12033	5.01708	1.19985
C	5.78918	4.32818	0.02735
C	6.5517	3.2381	-0.38576
C	2.28088	9.83833	-0.61352
O	4.20345	6.34651	0.94835
C	3.0891	11.24765	1.27699
C	0.45296	8.08101	3.62841
C	2.51176	9.39175	4.0103
C	2.65588	9.8212	0.88344
C	3.83258	8.81813	1.06827
C	3.26208	7.41471	1.2293
C	2.57633	7.2622	2.5862
C	1.75394	8.54046	2.96148
N	1.4831	9.341	1.71183
N	8.16339	0.98962	-1.30504
C	7.11423	0.1957	-1.64577
C	7.28314	-0.05223	-2.99307
N	8.42347	0.58797	-3.3957
N	8.95214	1.21409	-2.37815
C	7.31723	-3.2222	-3.7956
C	7.90125	-4.40025	-4.58579
C	7.94923	-5.7262	-3.81569
C	8.42208	-6.88743	-4.7009
C	8.38567	-8.28523	-4.06335
C	7.00127	-8.75005	-3.60304
O	6.79627	-8.32525	-2.25935
C	-0.06916	-11.3958	4.57201
S	3.89572	-10.83686	1.86971
S	-0.01654	10.06775	1.42465

H	-4.37617	-10.17362	0.62942
H	-2.75913	-9.55498	0.29898
H	-5.07016	-7.88281	1.38642
H	-3.49941	-7.25234	0.92537
H	-3.90493	-7.92348	-1.45867
H	-5.49356	-8.53537	-1.02818
H	-5.41463	-6.16385	-2.04812
H	-4.61814	-5.6319	-0.57948
H	-6.71178	-6.59226	0.68792
H	-7.47043	-6.68682	-0.88945
H	-7.0366	-4.16681	-1.16413
H	-6.32932	-4.16474	0.43412
H	-10.67569	-0.7137	0.51336
H	-5.27547	8.02461	0.90479
H	-5.77457	8.7517	-0.60947
H	-4.31889	7.12467	-1.8399
H	-3.19127	5.36453	-0.8161
H	-4.1556	5.44185	0.65561
H	-4.55695	10.47261	-1.61526
H	-2.78613	10.5034	-1.59781
H	-3.63126	9.1546	-2.36073
H	-2.91116	10.84557	0.91225
H	-4.67688	10.7485	0.86869
H	-3.76158	9.68751	1.95079
H	-0.41263	6.5898	1.01741
H	-1.38089	5.11366	0.85416
H	-0.93502	6.05492	-0.58259
H	-2.75883	6.07	2.61868
H	-2.21165	7.75714	2.59454
H	-3.90968	7.3582	2.29537
H	-10.10107	2.65319	0.64318
H	-8.67281	4.60378	1.23184
H	-6.64872	4.26443	-2.5321
H	-8.04099	2.28962	-3.1063
H	-10.9639	1.14723	-1.1504

H	-10.06401	0.95898	-2.6713
H	-9.63005	-3.05618	1.61535
H	-7.89486	-2.82646	1.72646
H	-1.61375	-7.52029	2.5227
H	-1.03658	-8.53171	1.19462
H	-2.14004	-9.56468	3.84804
H	-1.96005	-11.78388	2.72641
H	-1.2226	-11.00908	1.3214
H	-8.59378	-5.16728	1.26533
H	-9.25492	-4.6908	-0.28946
H	0.58161	-6.50337	2.10526
H	2.08913	-7.3	2.57287
H	1.25448	-7.79075	1.08839
H	1.20016	-8.0433	4.83941
H	-0.13897	-6.96964	4.41637
H	-0.46995	-8.60265	4.99333
H	1.67432	-12.57827	2.87276
H	0.05928	-13.18153	2.48273
H	0.91392	-12.12933	1.33649
H	7.69773	-8.90184	0.97981
H	6.90286	-10.38509	1.53931
H	7.12212	-10.07954	-0.19682
H	6.1456	-7.3644	2.1506
H	4.39646	-7.66204	2.16867
H	5.50115	-8.80403	2.94895
H	2.64593	-11.94902	-0.32032
H	3.14291	-11.79025	-2.00988
H	4.32583	-12.26594	-0.77527
H	1.80161	-9.58594	-0.18204
H	2.69614	-8.24121	-0.90527
H	2.05866	-9.53146	-1.9369
H	6.4793	-2.26886	-5.53293
H	8.05709	-1.63786	-5.08057
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H	6.27932	-7.14562	-0.26534

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H	4.42224	-9.99696	-2.83804
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H	5.51699	-1.15539	-3.43425
H	8.38473	0.82457	0.74855
H	9.53612	1.89493	-0.06003
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H	4.94545	4.65301	-0.56846
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H	-0.16435	7.50057	2.94401
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H	1.95846	10.31269	4.21856
H	4.45803	9.06933	1.92623
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H	1.91889	6.3869	2.55449
H	3.33095	7.08198	3.35465
H	6.3701	-0.12104	-0.93156
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H	7.80365	-6.90841	-5.6104
H	9.44563	-6.68413	-5.04382
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N	11.26819	3.2293	0.47728
C	11.58937	4.34493	-0.19927
C	12.88024	4.89501	-0.13368
C	13.85273	4.26353	0.6312
C	13.51958	3.0945	1.31305
C	12.20947	2.61298	1.21356
C	10.53333	4.99019	-1.07496
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C	7.91559	3.94423	-4.0336
O	4.27016	4.28228	-3.46762
C	3.86243	2.91344	-3.47334
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C	2.20909	1.42753	-2.24142
C	2.77872	1.41995	-0.82198
O	3.02714	0.0737	-0.39985
C	5.66251	-1.5542	1.52014
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C	11.21843	-0.935	3.30786
C	10.48557	0.24971	3.458
N	10.78058	1.3641	2.76096
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H	9.54294	4.6775	-0.73735
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H	11.77413	4.81614	-2.83753
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N	-12.88222	0.32218	0.463
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C	-13.50825	-0.58303	-2.84426
C	-13.12851	-1.57678	-3.9686
C	-11.65724	-1.93111	-4.04771
C	-11.12123	-3.01794	-3.33743
C	-9.76372	-3.30833	-3.36775
C	-8.88259	-2.51446	-4.11764
C	-9.4029	-1.4618	-4.8809
C	-10.77235	-1.18026	-4.82922
O	-7.5673	-2.85498	-4.02658
C	-6.57027	-2.09635	-4.71614
C	-5.22794	-2.32193	-4.01379
C	-5.02007	-1.36734	-2.82744
C	-3.82806	-1.72936	-1.94256
O	-3.4533	-0.65884	-1.05747
C	-5.86397	1.2792	0.91519
C	-5.00434	0.89574	-0.11321
C	-4.33724	-0.32771	-0.04908
C	-4.51495	-1.14812	1.07038
C	-5.37509	-0.75116	2.09483

C	-6.07809	0.46245	2.0316
C	-7.0617	0.87579	3.11304
C	-8.23519	-0.11123	3.26835
C	-9.35516	0.34487	4.22939
C	-12.17742	1.74168	2.32137
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C	-10.31903	1.36107	3.65149
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H	-12.34807	-1.45786	-1.22558
H	-13.99401	-2.07352	-1.36
H	-14.5439	-0.2572	-3.0069
H	-12.88554	0.31618	-2.9289
H	-13.44279	-1.13775	-4.92315
H	-13.72255	-2.49154	-3.84204
H	-11.78073	-3.64823	-2.74571
H	-9.35416	-4.13842	-2.80302
H	-8.76066	-0.85824	-5.51109
H	-11.15695	-0.35556	-5.42604
H	-6.53602	-2.42336	-5.76518
H	-6.82226	-1.02943	-4.69774
H	-5.19162	-3.37018	-3.69204
H	-4.42164	-2.19135	-4.74761
H	-4.86069	-0.35135	-3.21155
H	-5.92322	-1.34907	-2.21457
H	-4.04115	-2.64278	-1.36905
H	-2.92797	-1.91148	-2.54026
H	-6.38817	2.22729	0.84045
H	-4.8525	1.53212	-0.97853
H	-3.96975	-2.08471	1.13941
H	-5.49414	-1.39833	2.96088

H	-7.44924	1.87253	2.87168
H	-6.54762	0.97112	4.0805
H	-7.84558	-1.06918	3.63147
H	-8.67445	-0.30872	2.28745
H	-9.94798	-0.53327	4.50671
H	-8.91625	0.74307	5.15244
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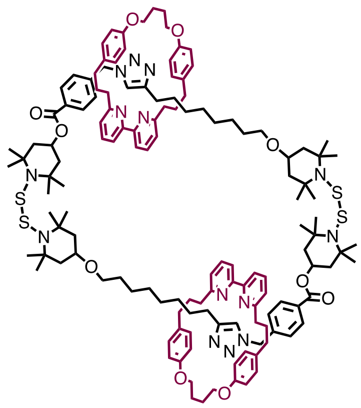

Head-to-Tail [3]catenane

atom	X	Y	Z
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C	-8.37005	8.72104	-3.6834
C	-7.54444	4.02359	-3.79431
C	-9.46897	5.53318	-4.18973
C	-6.60166	0.89887	4.64702
C	-7.81301	7.75247	-2.61253
C	-8.94233	7.45142	-1.5896
C	-8.78789	6.1394	-0.83156
C	-8.70182	4.94821	-1.80687
C	-8.25379	5.2815	-3.26228
N	-7.31971	6.45844	-3.2068

C	-6.46137	-0.63402	4.59096
O	-1.78118	-3.85071	-2.95624
C	-2.20753	-4.59843	-2.09598
C	-7.25786	-3.66254	0.62772
C	-5.93023	-3.90363	-0.06183
C	-5.45065	-3.00395	-1.02476
C	-4.24479	-3.24462	-1.67396
C	-3.49365	-4.3891	-1.36945
C	-3.96797	-5.28883	-0.40755
C	-5.1771	-5.04358	0.23933
C	1.03881	-6.29439	-5.27646
O	-1.56666	-5.71803	-1.68586
C	0.28408	-8.68147	-5.13254
C	2.7202	-7.97086	-1.03931
C	0.74322	-9.30799	-1.71058
C	0.62707	-7.42173	-4.30898
C	-0.64623	-6.98206	-3.54174
C	-0.32884	-6.07716	-2.3632
C	0.55575	-6.77693	-1.32788
C	1.43814	-7.93394	-1.88923
N	1.75396	-7.64984	-3.32984
S	3.1775	-8.3524	-3.97565
N	-7.23107	-2.57262	1.60563
C	-6.49417	-2.45468	2.73641
C	-6.9322	-1.27576	3.31373
N	-7.90164	-0.74808	2.50973
N	-8.08063	-1.53191	1.4782
C	-8.02078	1.39372	4.96743
C	-8.1493	2.92678	4.97255
C	-8.23273	3.55711	3.57397
C	-8.15914	5.09083	3.60596
C	-8.4786	5.78846	2.27364
C	-7.56207	5.36885	1.11709
O	-7.62622	6.25162	0.00135
S	-6.14177	6.6179	-4.44238

C	6.48835	-8.06225	-1.94535
C	7.40486	-7.9898	-4.27346
C	4.04838	-4.5183	-2.87528
C	6.13631	-3.88921	-4.07977
C	7.746	-0.09295	4.18423
C	6.88227	-7.12583	-3.10936
C	8.0377	-6.18792	-2.69238
C	7.69224	-5.11798	-1.64045
C	6.20738	-4.74637	-1.67583
C	5.53369	-4.87901	-3.05539
N	5.70847	-6.29197	-3.55099
C	7.88677	1.41261	3.89713
O	1.89794	7.79713	-1.50774
C	1.9433	6.58286	-1.56286
C	6.81627	3.57596	-0.55018
C	5.53464	4.34689	-0.79063
C	5.50492	5.73984	-0.65198
C	4.33517	6.45312	-0.90578
C	3.17363	5.7785	-1.29875
C	3.19931	4.38345	-1.4413
C	4.37174	3.67666	-1.19521
C	-3.8522	5.01503	-1.1339
O	0.88895	5.79359	-1.8636
C	-3.17521	7.40494	-1.09427
C	-2.14469	6.38001	-5.58715
C	-2.24977	8.33643	-4.06186
C	-2.89184	6.0392	-1.76358
C	-1.44932	5.58058	-1.4433
C	-0.39497	6.41955	-2.14524
C	-0.61346	6.40443	-3.65129
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C	8.62891	-4.84704	2.49432
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H	-7.32378	4.09548	-4.86163
H	-6.61287	3.83611	-3.25689
H	-10.05422	4.61314	-4.2954
H	-10.14425	6.30775	-3.82077
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H	-5.91845	1.28012	5.41759
H	-6.26035	1.3229	3.69518
H	-9.91192	7.42594	-2.098
H	-8.98894	8.28008	-0.87609
H	-9.67065	6.01209	-0.18931
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H	-5.41124	-0.91489	4.73125
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H	3.3516	-7.10094	-1.23152
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H	-0.35346	7.43806	-1.75575
H	0.11194	7.06535	-4.13821
H	-0.41429	5.38413	-3.99961
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H	8.41256	-0.68293	2.22307
H	9.65471	-0.81577	3.45785
H	8.44323	-2.80129	4.44244
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H	9.09712	-6.81678	1.7379
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C	-4.00058	-6.67576	6.12901
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C	-3.69387	-5.26173	4.20949
C	-7.26819	-6.19222	4.24521
C	-8.25064	-5.50945	5.21628
C	-9.73784	-5.74881	4.86694
C	-10.20325	-5.10162	3.578
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C	-10.79079	-5.22905	1.21334
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C	-10.81929	-3.08886	2.33516
C	-10.43315	-3.7221	3.51606

O	-11.29346	-3.31308	-0.05801
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O	-8.12306	0.79146	-2.1177
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C	-6.85235	0.83613	-1.5696
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H	-5.28929	1.21386	1.4186
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H	-1.24478	-0.31783	0.80055
H	-2.27221	-1.09091	-0.40107
H	-3.07149	-0.57688	2.51925
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H	-0.61529	-2.42803	0.9323
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C	13.41112	4.57363	0.18278
C	12.79821	5.0787	1.32712
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C	10.47799	2.67612	-1.32211
C	10.99233	1.22737	-1.43552
C	10.2185	0.35898	-2.45127
C	8.78575	0.01883	-2.08252
C	7.71005	0.34682	-2.92102
C	6.39652	0.00937	-2.59416
C	6.11924	-0.66781	-1.39915
C	7.18267	-1.02278	-0.558
C	8.4892	-0.68045	-0.90559

O	4.80734	-0.95223	-1.13901
C	4.44116	-1.21932	0.22757
C	2.9184	-1.12597	0.36335
C	2.51159	-0.72396	1.79847
C	2.56973	0.79594	1.95898
O	2.64993	1.14025	3.3487
C	4.80691	3.48695	5.11972
C	4.01497	2.37578	4.84099
C	3.30349	2.31099	3.63744
C	3.31467	3.41464	2.78005
C	4.11349	4.51917	3.07531
C	4.90872	4.56453	4.22528
C	5.89119	5.69665	4.48108
C	6.47042	6.32259	3.1994
C	7.68658	7.24424	3.42827
C	10.76624	5.34743	2.7625
C	11.40553	5.25122	4.00789
C	10.78302	5.8061	5.12152
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N	9.57516	5.94754	2.6062
H	13.10781	3.39173	-1.59481
H	14.45542	4.7891	-0.02389
H	13.34664	5.69987	2.02674
H	9.45046	2.67175	-0.95577
H	10.46497	3.12583	-2.32507
H	12.04801	1.23809	-1.73377
H	10.96146	0.75894	-0.44441
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H	6.99878	-1.54725	0.37103
H	9.2942	-0.96843	-0.23385
H	4.78496	-2.22254	0.51637

H	4.93409	-0.49086	0.87709
H	2.55541	-0.37709	-0.35109
H	2.45498	-2.07572	0.07548
H	1.50944	-1.09435	2.04012
H	3.19597	-1.17451	2.527
H	3.44978	1.19203	1.44288
H	1.67703	1.25361	1.50685
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H	2.74578	3.40349	1.85782
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H	5.42223	6.49126	5.08111
H	5.69229	6.90775	2.69693
H	6.76063	5.5301	2.50193
H	7.82952	7.85906	2.53309
H	7.48524	7.9293	4.26068
H	12.35745	4.73888	4.09655
H	11.24473	5.73873	6.10237
H	9.0607	6.92221	5.79649

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