Supporting Information

Impact of mechanical bonding on the redox-switching of tetrathiafulvalene in crown ether-ammonium [2]rotaxanes

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1. Experimental Details

1.1. General methods

All reagents and solvents were obtained from commercial sources and used without further purification. Dry solvents were purchased from Acros Organics. 4-(Prop-2-yn-1-yloxy)phenol,[1] 2,3-bis(2-cyanoethylthio)-6,7-bis(methylthio)tetrathiafulvalene,[2] 2,3-bis(2-(2-(2-iodoethoxy)ethoxy)ethoxy)naphthalene,[3] (4-(prop-2-yn-1-yloxy)phenyl)methanaminium chloride[4] and 2,6-dimethoxybenzonitrile oxide[5] were synthesised according to literature procedures. Thin-layer chromatography was performed on silica gel-coated plates with fluorescent indicator F254 (Merck). For column chromatography, silica gel (0.04-0.063 mm; Merck) was used.

^{1}H and ^{13}C NMR experiments were performed on JEOL ECX 400, JEOL ECP 500, Bruker AVANCE 500 or Bruker AVANCE 700 instruments. Solvent residue signals are abbreviated with an asterisk and were used as internal standard. All shifts are reported in ppm and NMR multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad). Coupling constants *J* are reported in Hertz. Compounds containing the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($BArF_{24}^-$) anion show ^{13}C NMR spectra with ^{19}F, ^{10}B and ^{11}B couplings. These signals were denoted as one signal.

High-resolution ESI mass spectra were measured on an Agilent 6210 ESI-TOF device (Agilent Technologies). HPLC grade solvents were used with a flow rate of 2-4 µL/min. Tandem MS and infrared multiphoton dissociation (IRMPD) experiments were performed on an Ionspec Q FT-7 (Varian Inc.) equipped with a 7 T superconducting magnet and a Micromass Z-spray ESI source.

Fluorescence spectra were obtained on a LS 50 B luminescence spectrometer (PerkinElmer) using excitation and emission slits of 10 nm widths. *Suprasil* fluorescence cuvettes (1 cm x 0.4 cm path-length) were used.

The UV/Vis measurements were performed on a Cary 50 Bio photospectrometer (Varian) equipped with a xenon lamp. Solvents with HPLC grade or better and *Suprasil* glass cuvettes with a path-length of 1 cm were used.

EPR spectra at X-band frequency (ca. 9.5 GHz) were obtained with a Magnettech MS-5000 benchtop EPR spectrometer equipped with a rectangular TE 102 cavity and TC HO4 temperature controller. The measurements were carried out in synthetic quarz glass tubes. Spectra were processed with ESRStudio.

Melting points were determined on a SMP 30 (Stuart) instrument. Melting points are uncorrected.

Electroactive macrocycles and rotaxanes in CH_2Cl_2 solutions were oxidised with $Fe(ClO_4)_3$ by stirring the suspension under argon atmosphere for several minutes. $Fe(ClO_4)_3$ shows very low solubility in CH_2Cl_2 and can be filtered off after oxidation.

1.2. Synthesis of axle 3 and free stoppered axle 5

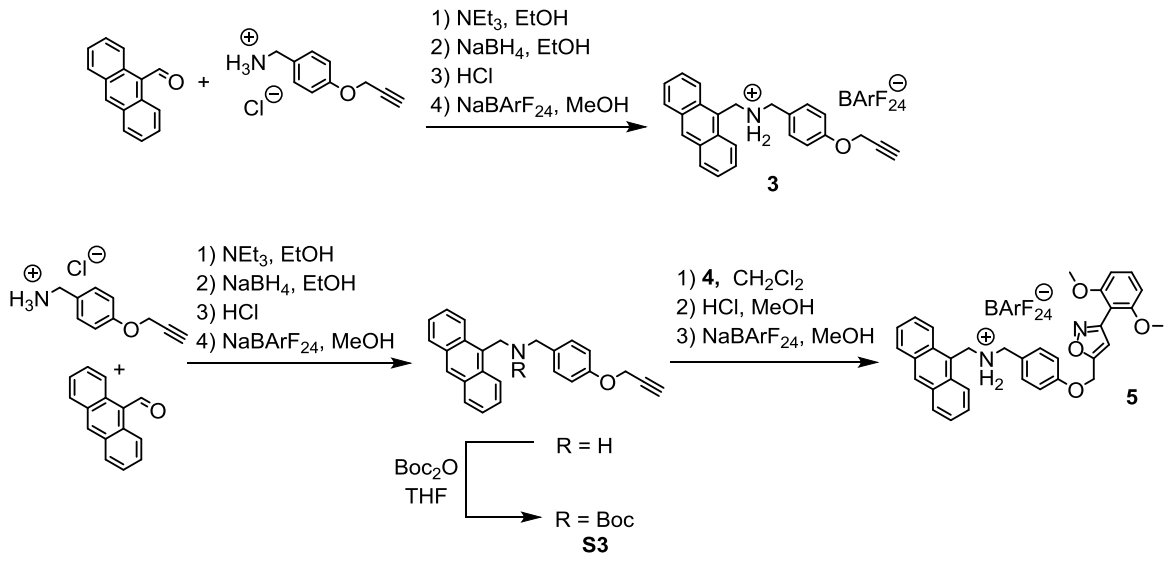
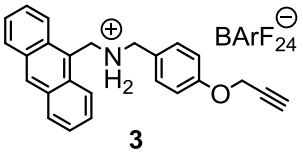


Fig. S1 Synthesis of axle **3** and free stoppered axle **5**

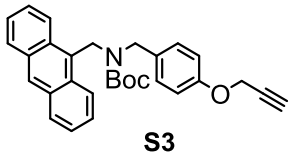
1-(Anthracen-9-yl)-*N*-(4-(prop-2-yn-1-yloxy)benzyl)methanaminium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate



9-Anthracenecarboxaldehyde (413 mg, 2.0 mmol) and (4-(prop-2-yn-1-yloxy)phenyl)-methanaminium chloride (395 mg, 2.0 mmol) were dissolved in dry ethanol (40 mL), treated with NEt_4 (0.2 mL, 1.5 mmol) and the mixture was heated to reflux for 4 h under Ar. After cooling to room temperature, $NaBH_4$ (189 mg, 5.0 mmol) was added at 0 °C and the mixture was stirred overnight under Ar. Afterwards, saturated $NaHCO_3$ solution was added to quench the reaction, the solvent was removed under reduced pressure and CH_2Cl_2 (30 mL) was added. The organic layer was washed with brine (3x30 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting yellow oil was purified by column chromatography (SiO_2, CH_2Cl_2 → CH_2Cl_2/MeOH = 20:1). The amine was obtained as a yellow oil, which was dissolved in Et_2O and precipitated with concentrated aqueous HCl to yield the corresponding hydrochloride (231mg, 0.60 mmol). The hydrochloride (77.6 mg, 0.20 mmol) and $NaBArF_{24}$ (177.2 mg, 0.20 mmol) were dissolved in MeOH (8 mL) and stirred at room temperature for 2 h. The solution was concentrated under reduced pressure and the residue was suspended in water (30 mL) and stirred for another 2 h. The desired product

was obtained through filtration as colourless powder (172.1 mg, 0.14 mmol, 21% over all steps). R_f = 0.50 in CH_2Cl_2/MeOH = 20:1; m.p. 93-95 °C; ^{1}H NMR (700 MHz, CD_2Cl_2): δ = 8.70 (s, 1H, H_{Ar}), 8.16 (d, ^3J = 9.3 Hz, 2H, H_{Ar}), 7.84 (d, ^3J = 9.8 Hz, 2H, H_{Ar}), 7.73 (s, 8H, H_{BArF24}), 7.70-7.65 (m, 2H, H_{Ar}), 7.61-7.58 (m, 2H, H_{Ar}), 7.56 (s, 4H, H_{BArF24}), 7.44 (d, ^3J = 9.3 Hz, 2H, H_{Ar},), 7.17 (d, ^3J = 8.7 Hz, 2H, H_{Ar}), 5.29 (s, 2H, NCH_2), 4.80 (s, 2H, CH_2CCH), 4.45 (s, 2H, NCH_2), 2.61 (s, 1H, CH_2CH) ppm. ^{13}C NMR (176 MHz, CD_2Cl_2): δ = 162.31, 160.24, 135.38, 132.64, 131.93, 131.08, 130.86, 129.60, 129.41, 126.49, 125.20, 121.77, 121.21, 119.24, 118.06, 117.10, 78.21, 76.61, 56.63, 54.00, 53.44, 44.40 ppm; HRMS: *m/z* calcd for $[C_{57}H_{34}BF_{24}NO]$: 352.1696 $[M\text{-}BArF_{24}]^+$, found: 352.1676.

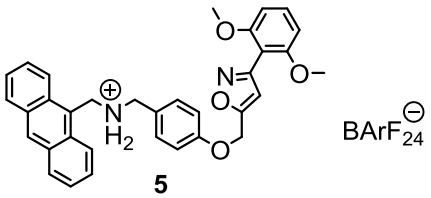
Tert-butyl (anthracen-9-ylmethyl)(4-(prop-2-yn-1-yloxy)benzyl)carbamate



S3

Under argon, the hydrochloride of axle **3** (435 mg, 1.13 mmol), di-*tert*-butyl dicarbonate (296 mg, 1.36 mmol) and NEt_4 (0.24 mL, 1.70 mmol) were dissolved in dry tetrahydrofuran (10 mL) at 0 °C and the mixture was allowed to warm to room temperature while stirring overnight. After removing the volatiles *in vacuo*, the residue was dissolved in CH_2Cl_2 (50 mL) and washed with water (50 mL) and brine (50 mL). The organic phase was dried ($MgSO_4$) and the residue was purified by column chromatography (SiO_2, pentanes/CH_2Cl_2 = 2:1) to give the pure product as a colourless solid (509 mg, 99%). R_f = 0.40 in pentane/CH_2Cl_2 = 2:1; m.p. 66-68 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.43 (s, 1H, H_{Ar}), 8.19 (s, 2H, H_{Ar}), 8.00 (br, 2 H, H_{Ar}), 7.48 – 7.39 (m, 4H, H_{Ar}), 6.81 (br, 4H, H_{Ar}), 5.54 (br, 2H, CH_2), 4.68 (br, 2H, CH_2), 3.98 (br, 2H, CH_2), 2.55 (t, ^3J = 2.4 Hz, 1H, CCH), 1.44 – 1.96 (br, 9H, H_{Boc}) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.53, 131.42, 129.16, 128.46, 128.30, 128.20, 126.15, 125.05, 124.60, 114.71, 80.26, 78.78, 75.56, 55.97, 47.19, 40.79, 28.59 ppm (only 17 of 20 signals for magnetic inequivalent carbons were observed due to strong signal broadening); ESI-HRMS: m/z calcd for $[C_{30}H_{29}NO_3]$: 474.2040 $[M+Na]^+$, found: 474.2050.

1-(Anthracen-9-yl)-N-(4-((3-(2,6-dimethoxyphenyl)isoxazol-5-yl)methoxy)benzyl)-methanaminium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

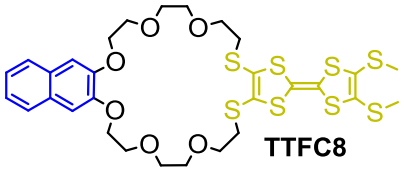


5

Axle **S3** (88 mg, 0.19 mmol), nitrile oxide **4** (36 mg, 0.20 mmol) were dissolved in CH_2Cl_2 (1 mL) and placed into a pressure tube. The mixture was stirred at 38 °C overnight. Purification using column chromatography (SiO_2, CH_2Cl_2) yielded the stoppered axle as a colourless solid (120 mg). Part of the Boc-protected axle (60 mg, 95 µmol) was dissolved in MeOH (10 mL) and concentrated aqueous HCl (1 mL) was added. The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, Et_2O (10 mL) was added and the mixture was suspended by sonication. The mixture was filtered to quantitatively give the hydrochloride as a white solid. Part of the hydrochloride (31 mg, 55 µmol) and $NaBArF_{24}$ (49 mg, 55 µmol) were dissolved in MeOH (3 mL) and the mixture was stirred at room temperature for 5 h. After concentration under reduced pressure, water (5 mL) was added and the mixture was suspended by sonication. Filtration gave the desired product as an off-white solid (57 mg, 41 µmol, 72% over all steps). m.p. 88 °C (decompostion); H NMR (700 MHz, $CDCl_3$) δ = 8.40 (s, 1H, H_{Ar}), 8.16 (br, 2H), 7.95 (m, 2H, H_{Ar}), 7.83 – 7.72 (m, 2H, H_{Ar}), 7.69 – 7.71 (m, 8H, H_{BArF24}), 7.46 (s, 4H, H_{BArF24}), 7.44 – 7.40 (m, 2H, H_{Ar}), 7.23 – 7.18 (m, 2H, H_{Ar}), 7.13 (t, ^3J = 8.3 Hz, 1H), 6.80 (s, 2H, H_{Ar}), 6.44 (s, 1H, H_{isox}), 6.21 (d, ^3J = 8.3 Hz, 2H, H_{Ar}), 5.17 (br, 2H, CH_2), 4.97 (br, 2H, CH_2), 4.31 (br, 2H, CH_2), 3.32 (s, 6H, OCH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ = 165.94, 161.76, 159.36, 157.68, 157.23, 134.92, 132.64, 131.86, 131.51, 131.15, 130.37, 129.05, 128.77, 126.98, 124.69, 122.56, 122.34, 120.97, 118.64, 117.63, 115.95, 107.58, 105.14, 104.87, 77.16, 60.84, 56.26, 52.60, 44.37 ppm. ESI-HRMS: *m/z* calcd for $[C_{66}H_{43}BF_{24}N_2O_4]$ 531.2278 $[M\text{-}BArF_{24}]^+$, found: 531.2282.

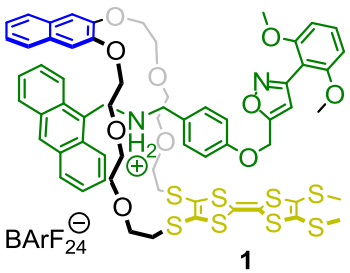
1.3. Synthesis of macrocycle TTFC8 and [2]rotaxanes 1 and 2

Macrocycle TTFC8



A solution of $CsOHxH_2O$ (302 mg, 1.80 mmol) in dry MeOH (5 mL) was added to a solution of 3,3'-((4',5'-bis(methylthio)-[2,2'-bi(1,3-dithiolylidene)]-4,5-diyl)bis(sulfanediyl))di-propane-nitrile (419 mg, 0.90 mmol) in dry dimethylformamide (15 mL) over 30 min. After the colour changed to deep red, this solution was added over 1 h to a solution of 2,3-bis(2-(2-(2-iodoethoxy)ethoxy)ethoxy)naphthalene (582 mg 0.90 mmol) in dry dimethylformamide (75 mL) at 0°C. The solution was stirred over night at room temperature. Afterwards, the solution was concentrated under reduced pressure and the residue was dissolved in CH_2Cl_2 (40 mL). The organic layer was washed with brine (3x30 mL) and dried over $MgSO_4$. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2 → CH_2Cl_2/MeOH = 200:1). The crude product was recrystallized in acetonitrile to yield the desired product (432 mg, 57.7 mmol, 64 %) as an orange solid. R_f = 0.50 in CH_2Cl_2/MeOH = 150:1; m.p. 111-118 °C ; ^{1}H NMR (700 MHz, CD_2Cl_2): δ = 7.67 (AA'XX' spin system, $^3J_{AX}$ = 6.1, 2H, H_{Ar}); 7.32 (AA'XX' spin system, $^3J_{XA}$ = 6.1, 2H, H_{Ar}); 7.14 (s, 2H, H_{Ar}); 4.24 (m, 4H, OCH_2), 3.93-3.92 (m, 4H, OCH_2); 3.79-3.77 (m, 4H, OCH_2); 3.69-3.66 (m, 8 H OCH_2); 3.01 (t, ^3J = 6.3, 4H, SCH_2); 2.41 (s, 6H, SCH_3) ppm. ^{13}C NMR (176 MHz, CD_2Cl_2): δ = 149.63, 129.87, 128.86, 126.79, 124.68, 114.41, 108.44, 71.44, 71.11, 70.35, 70.13, 69.38, 36.34, 30.90 ppm. ESI-HRMS: *m/z* calcd for $[C_{30}H_{36}O_6S_8]$: 771.0169 $[M+Na]^+$, found: 771.0165.

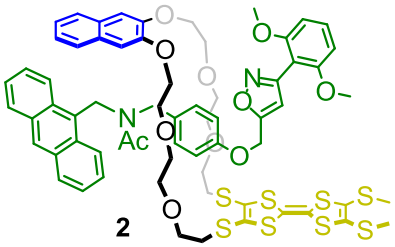
[2]Rotaxane 1



Axle **3** (48.6 mg, 40.0 µmol), macrocycle **TTFC8** (29.9 mg, 40.0 µmol) and nitrile oxide stopper **4** (9.3 mg, 52.0 mmol) were dissolved in CH_2Cl_2 (1 mL). The mixture was heated under argon atmosphere in a pressure tube for 1 d at 38 °C. Afterwards, the solution was directly purified by preparative thin layer chromatography (SiO_2, 2000 microns, CH_2Cl_2) to

yield the desired product as sticky orange oil (67.5 mg, 31.5 µmol, 79%). R_f = 0.80 in CH_2Cl_2; ^{1}H NMR (700 MHz, CD_2Cl_2): δ = 8.34 (d, ^3J = 8.8 Hz, 2H, H_{Ar}), 7.87 (br, 2H, NH_2), 7.74 (s, 8H, H_{BArF24}), 7.69 (d, ^3J = 8.6 Hz, 2H, H_{Ar}), 7.64 (m, 2H, H_{Ar}), 7.58 (s, 4H, H_{Ar}), 7.47 (m, 4H, H_{Ar}), 7.44 (br, 4H, H_{Ar}), 7.39 (t, ^3J = 8.4 Hz, 1H, H_{Ar}), 7.28 (s, 1H, H_{Ar}), 7.20 (d, ^3J = 8.9 Hz, 2H, H_{Ar}), 6.67 (d, ^3J = 8.4 Hz, 2H, H_{Ar}), 6.50 (s, 1H, H_{isox}), 5.83 (s, 2H, H_{Ar}), 5.52 (m, 4H, CH_2), 5.23 (s, 2H, C$\underline{H_2}$CCH), 4.00 (m, 8H, OCH_2), 3.77 (s, 6H, OCH_3), 3.39 (m, 16 H, OCH_2 2.35 (s, 6H, SCH_3) ppm. ^{13}C NMR (700 MHz, CD_2Cl_2): δ = 166.25, 163.06, 162.33, 159.18, 158.93, 157.82, 135.37, 131.95, 131.65, 131.27, 131.02, 130.16, 129.44, 129.38, 128.54, 128.50, 128.12, 128.06, 126.72, 126.04, 125.94, 125.35, 125.01, 123.71, 120.22, 118.04, 115.97, 114.12, 109.15, 107.45, 107.28, 104.67, 104.16, 71.93, 71.76, 71.10, 70.69, 68.67, 61.78, 56.51, 54.00, 53.36, 46.84, 37.49, 19.50 ppm. ESI-HRMS: *m/z* calcd for $[C_{96}H_{79}BF_{24}N_2O_{10}S_8]$: 1279.2556 $[M\text{-}BArF_{24}]^+$, found: 1279.2560.

[2]Rotaxane 2



2

[2]Rotaxane **1** (21.4 mg, 10 µmol) was dissolved in acetonitrile (5 mL) and Ac_2O (200 µmol, 19 µL) and NEt_4 (14 µL, 100 µmol) were added. The mixture was stirred for 1 d at room temperature. Afterwards, the solvent was removed *in vacuo* and the residue was purified by a column chromatography (SiO_2, CH_2Cl_2) to yield the desired product as a sticky orange oil (13.2 mg, 9.9 µmol, 99%). R_f = 0.40 in CH_2Cl_2; ^{1}H NMR (700 MHz, CD_2Cl_2): δ = 8.43 (s, 1H, H_{Ar}), 8.08 (d, ^3J = 8.9 Hz, 2H, H_{Ar}), 7.99 (d, ^3J = 8.3 Hz, 2H, H_{Ar}), 7.62 (m, 2H, H_{Ar}), 7.39 (m, 5H, H_{Ar}), 7.26 (m, 4H, H_{Ar}), 7.12 (s, 2H, H_{Ar}), 6.73 (d, ^3J = 8.2 Hz, 2H, H_{Ar}), 6.66 (s, 1H, H_{isox}), 6.64 (d, ^3J = 8.4 Hz, 2H, H_{Ar}), 5.86 (s, 2H, CH_2), 5.53 (s, 2H, CH_2), 4.32 (m, 2H, OCH_2), 4.22 (m, 2H, OCH_2), 3.97 (m, 2H, CH_2), 3.88 (m, 2H, OCH_2), 3.83 (m, 2H, OCH_2), 3.75 (s, 6H, OCH_3), 3.65 (m, 4H, OCH_2), 3.59 – 3.47 (m, 8H, OCH_2), 3.38 (m, 2H, OCH_2), 3.06 (m, 2H, OCH_2), 2.21 (s, 6H, SCH_3), 2.01 (s, 3H, $OCCH_3$) ppm. ^{3}C NMR (176 MHz, CD_2Cl_2): δ = 171.30, 169.07, 159.26, 158.45, 157.40, 149.32, 132.06, 131.93, 131.46, 129.67, 129.53, 129.10, 128.84, 128.64, 128.23, 127.81, 127.13, 126.82, 126.71, 125.62, 125.08, 124.67, 116.23, 110.99, 110.58, 110.30, 108.29, 107.59, 104.53, 70.41, 70.32, 70.29, 69.84, 68.94, 61.62, 56.47, 54.00, 49.16, 39.47, 35.93, 22.16, 19.30 ppm. ESI-HRMS: *m/z* calcd for $[C_{66}H_{68}N_2O_{11}S_8]$: 1343.2481 $[M+Na]^+$, found: 1343.2502.

4. Synthesis of [2]rotaxane 6

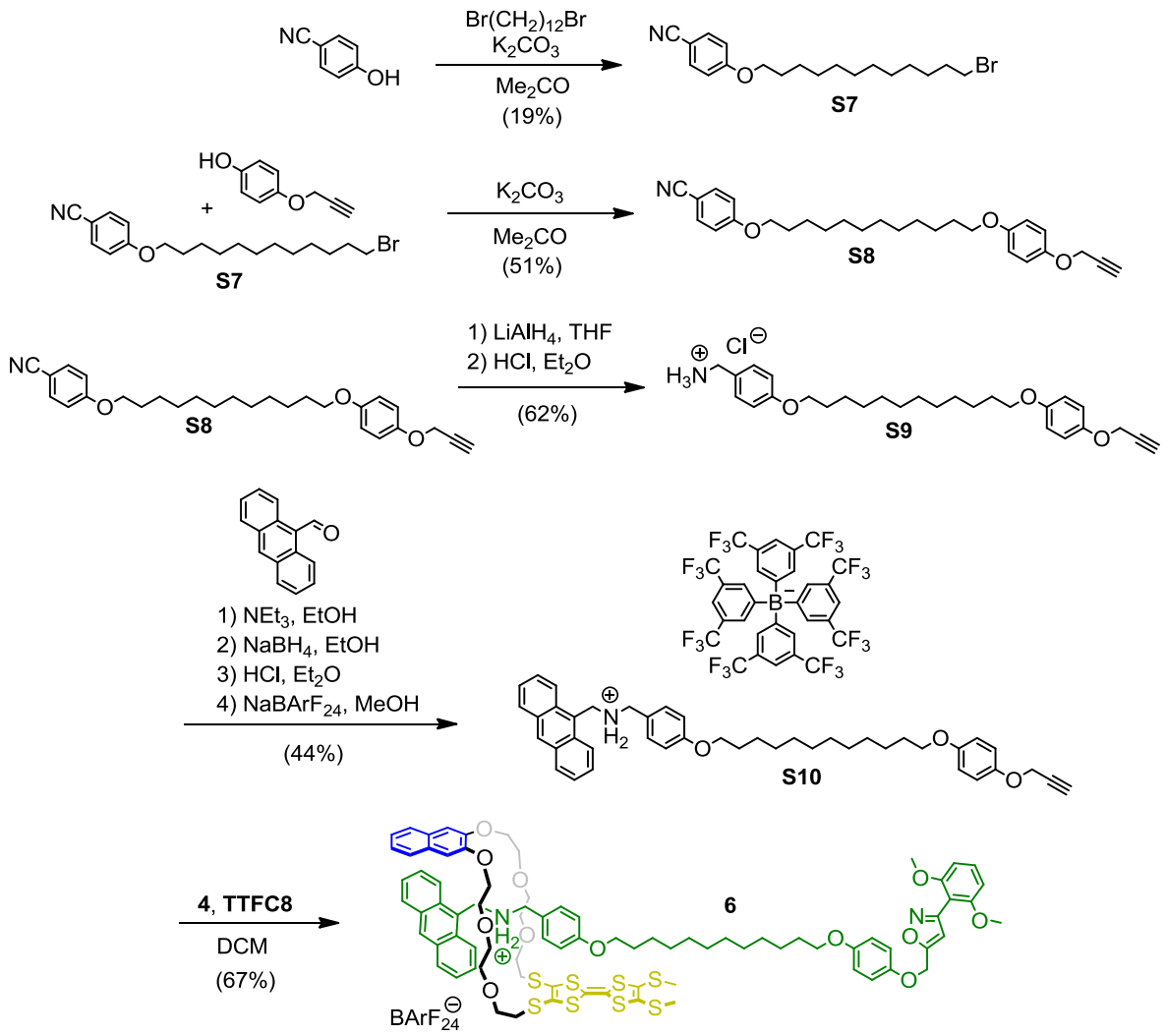
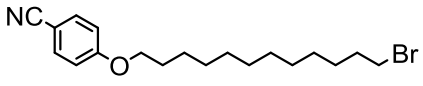


Fig. S2 Synthesis of [2]rotaxane **6**

4-((12-Bromododecyl)oxy)benzonitrile (S7)

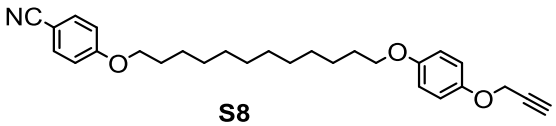


S7

4-Hydroxybenzonitrile (1.58 g, 13.3 mmol), 1,12-dibromododecane (4.35 g, 13.3 mmol) and K_2CO_3 (3.66 g, 26.6 mmol) were refluxed in acetone (100 mL) for 6 h. Afterwards, the mixtures was filtered and concentrated under reduced pressure. The residue was suspended in CH_2Cl_2 (50 mL) and washed with brine (3x50 mL). After the organic layer was dried over $MgSO_4$, the solvent was removed *in vacuo* and the residue was purified by column

chromatography (SiO_2, hexanes/CH_2Cl_2 = 2:1 → 1:1) followed by a recrystallization from MeOH to obtain the desired product as colourless crystals (930 mg, 2.53 mmol, 19%). R_f = 0.30 in hexanes/CH_2Cl_2 = 2:1; m.p. 57-59 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 (AA'XX' spin system, $^3J_{AX}$ = 8.9, 2H, H_{Ar}), 6.93 (AA'XX' spin system, $^3J_{XA}$ = 8.9, 2H, H_{Ar}), 3.99 (t, ^3J = 6.5 Hz, 2H, CH_2), 3.41 (t, ^3J = 6.9 Hz, 2H, CH_2), 1.82 (m, 4H, CH_2), 1.56 – 1.12 (m, 18H, CH_2) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.59, 134.09, 119.47, 103.76, 77.16, 68.54, 34.21, 32.95, 29.63, 29.63, 29.62, 29.54, 29.43, 29.11, 28.88, 28.29, 26.06 ppm. ESI-HRMS: *m/z* calcd for $[C_{19}H_{28}BrNO]$: 404.0986 $[M+K]^+$; found: 404.0967.

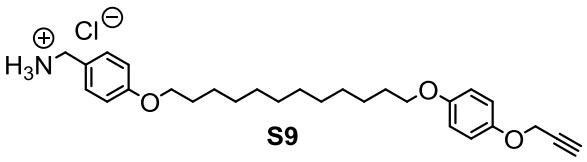
4-((12-(4-(Prop-2-yn-1-yloxy)phenoxy)dodecyl)oxy)benzonitrile (S8)



S8

Bromide **S7** (733 mg, 2.00 mmol), 4-(prop-2-yn-1-yloxy)phenol (593 mg, 4.00 mmol) and K_2CO_3 (553 mg, 4.00 mmol) were refluxed in acetone for 12 h. After cooling to room temperature, the mixture was filtered and concentrated under reduced pressure. The residue was suspended in CH_2Cl_2 (100 mL) and washed with brine (3x100 mL). The organic phase was dried over $MgSO_4$ and solvent was removed *in vacuo*. The residue was purified by column chromatography (SiO_2, pentanes → CH_2Cl_2) to obtain the desired product as a colourless solid (442 mg, 1.02 mmol, 51%). R_f = 0.40 in pentanes/CH_2Cl_2 = 1:1; m.p. 113-114 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (AA'XX' spin system, $^3J_{XA}$ = 8.9, 2H, H_{Ar}), 6.94 – 6.89 (m, 4H, H_{Ar}), 6.83 (AA'XX' spin system, $^3J_{XA}$ = 9.1, 2H, H_{Ar}), 4.64 (d, ^4J = 2.4 Hz, 2H, C$\underline{H_2}$CCH), 3.99 (t, ^3J = 6.5 Hz, 2H, OCH_2), 3.90 (t, ^3J = 6.5 Hz, 2H, OCH_2), 2.50 (t, ^4J = 2.4 Hz, 1H, CCH), 1.83 – 1.71 (m, 4H, CH_2), 1.49 – 1.26 (m, 18H, CH_2) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.60, 154.18, 151.71, 134.10, 119.48, 116.24, 115.44, 115.31, 103.77, 79.07, 77.16, 75.39, 68.68, 68.55, 56.75, 29.69, 29.68, 29.68, 29.65, 29.53, 29.50, 29.45, 29.11, 26.19, 26.07 ppm. ESI-HRMS: *m/z* calcd for $[C_{28}H_{35}NO_3]$: 456.2509; found: 456.2501.

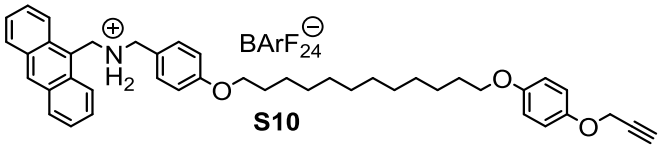
(4-((12-(4-(Prop-2-yn-1-yloxy)phenoxy)dodecyl)oxy)phenyl)methanaminium chloride (S9)



S9

Nitrile **S8** (240 mg, 0.56 mmol) was dissolved in dry THF (8 mL) and slowly dropped into an ice-cooled schlenk flask with dispersed $LiAlH_4$ (105 mg, 2.76 mmol) in dry THF under argon atmosphere. After warming up to room temperature, the mixture was stirred for 1 d. Unreacted $LiAlH_4$ was quenched with dropwise addition of saturated Na_2SO_4 solution. Afterwards, CH_2Cl_2 (50 mL) was added and the mixture was filtered. The filtrate was concentrated under reduced pressure and redissolved in CH_2Cl_2 (50 mL). The clear solution was washed with brine (2x50 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* and a minimum volume of Et_2O/CH_2Cl_2 (1:1) and concentrated aqueous HCl was added to precipitate the desired product as the hydrochloride. Drying *in vacuo* yielded the product as a colourless solid (163 mg, 0.34 mmol, 62%). m.p. 190 °C (decomposition); ^{1}H NMR (500 MHz, DMSO-d6): δ = 8.28 (br, 3H, NH_3), 7.36 (AA'XX' spin system, $^3J_{XA}$ = 8.7, 2H, H_{Ar}), 6.92 (AA'XX' spin system, $^3J_{AX}$ = 8.7, 2H, H_{Ar}), 6.89 – 6.79 (m, 4H, H_{Ar}), 4.68 (d, ^4J = 2.4 Hz, 2H, C$\underline{H}_2$CCH), 3.97 – 3.73 (m, 6H, CH_2), 3.51 (t, ^3J = 2.4 Hz, 1H, CCH), 1.72 – 1.57 (m, 4H, CH_2), 1.30 (m, 16H, CH_2) ppm. ^{13}C NMR (126 MHz, DMSO-d6): δ = 158.80, 153.27, 151.09, 130.50, 125.78, 115.90, 115.16, 114.43, 79.57, 77.97, 67.79, 67.51, 55.89, 41.69, 39.52, 29.02, 29.01, 28.99, 28.97, 28.79, 28.77, 28.63, 25.54, 25.53, 25.50 ppm. ESI-HRMS: *m/z* calcd for $[C_{28}H_{40}ClNO_3]$: 438.3003 $[M\text{-}Cl]^+$, found: 438.3000.

1-(Anthracen-9-yl)-N-(4-((12-(4-(prop-2-yn-1-yloxy)phenoxy)dodecyl)oxy)-benzyl)methanaminium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (S10)

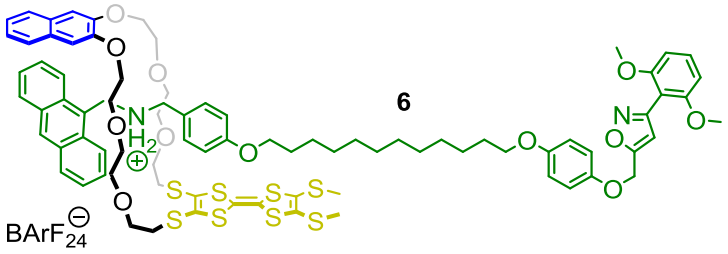


S10

Hydrochloride **S9** (130 mg, 274 µmol), 9-anthracenecarboxaldehyde (56.6 mg, 274 µmol) and NEt_4 (29 µL) were dissolved in dry EtOH (10 mL) and heated at reflux for 6 h under Ar atmosphere. After cooling to room temperature, additional EtOH (15 mL) and $NaBH_4$ (31.1 mg, 822 µmol) was added. The mixture was stirred overnight and quenched with a small volume of saturated $NaHCO_3$ solution. The mixture was concentrated under reduced pressure and redissolved in CH_2Cl_2 (50 mL). The organic phase was washed with saturated $NaHCO_3$ solution (50 mL), brine (50 mL) and dried afterwards over $MgSO_4$. Removing the solvent *in vacuo* yielded the crude amine which was purified by column chromatography (SiO_2, CH_2Cl_2, R_f = 0.15 in CH_2Cl_2). The amine was dissolved in a minimal volume of MeOH/ethyl acetate/concentrated aqueous HCl (10:10:1). Removal of the solvent and drying *in vacuo* yielded the hydrochloride as a colourless solid (115 mg, 173 µmol). The

hydrochloride (50 mg, 75 µmol) and $NaBArF_{24}$ (67 mg, 75 µmol) were dissolved in MeOH and the mixture was stirred for 3 h. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 (5 mL) and washed with water (5 mL). The desired product was obtained as colourless oil (78 mg, 54 µmol, 44% over all steps) after evaporating the solvent. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (s, 1H, H_{Ar}), 8.14 – 8.09 (m, 2H, H_{Ar}), 7.72 (m, 8H, H_{BArF24}), 7.70 – 7.64 (m, 2H, H_{Ar}), 7.60 – 7.52 (m, 4H, H_{Ar}), 7.50 (m, 4H, H_{BArF24}), 7.23 (AA'XX' spin system, $^3J_{XA}$ = 8.7, 2H, H_{Ar}), 7.00 (m, 4 H, H_{Ar} and NH_2), 6.77 – 6.69 (m, 4H, H_{Ar}), 5.22 (m, 2H, CH_2), 4.50 (d, ^4J = 2.4 Hz, 2H, C$\underline{H_2}$CCH), 4.29 (m, 2H, CH_2), 3.99 (t, ^3J = 6.5 Hz, 2H, OCH_2), 3.82 (t, ^3J = 6.5 Hz, 2H, OCH_2), 2.44 (t, ^4J = 2.4, 1H, CCH), 1.82 (m, 4H, CH_2), 1.73 – 1.66 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 1.30 (m, 16H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ = 161.82, 161.80, 154.30, 151.46, 134.95, 132.49, 131.42, 131.14, 130.83, 130.26, 129.48, 128.98, 126.15, 124.66, 120.09, 119.18, 117.90, 117.66, 116.62, 116.34, 115.76, 78.86, 77.16, 75.73, 69.01, 68.63, 57.33, 53.32, 44.01, 29.57, 29.52, 29.52, 29.51, 29.40, 29.37, 29.31, 29.08, 26.06, 25.99 ppm. ESI-HRMS: *m/z* calcd for $[C_{75}H_{62}BF_{24}NO_3]$: 628.3785 $[M\text{-}BArF_{24}]^+$, found: 628.3785.

[2]Rotaxane 6



Ammonium axle **S10** (51.0 mg, 34.1 µmol), macrocycle **TTFC8** (25.5 mg, 34.1 µmol) and nitrile oxide stopper **4** (7.9 mg, 44.3 µmol) were dissolved in CH_2Cl_2 (1 mL) under Ar atmosphere. The solution was heated to 35 °C for 1 d in a pressure tube. Afterwards, the solution was directly purified by column chromatography (SiO_2, pentanes/CH_2Cl_2 = 1:1 → 1:2) to obtain the desired product as an orange oil (55.0 mg, 22.7 µmol, 67%). R_f = 0.50 in CH_2Cl_2; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.34 (d, ^3J = 9.0 Hz, 2H, H_{Ar}), 7.83 (br, 2H, NH_2), 7.73 (m, 12H, H_{Ar} and H_{BArF24}), 7.66 – 7.58 (m, 4H, H_{Ar}), 7.56 (s, 4H, H_{BArF24}), 7.46 (m, 4H, H_{Ar}), 7.43 (m, 4H, H_{Ar}), 7.38 (t, ^3J = 8.4 Hz, 1H, H_{Ar}), 7.28 (s, 1H, H_{Ar}), 7.03 (d, ^3J = 8.8 Hz, 2H, H_{Ar}), 6.93 (AA'XX' spin system, $^3J_{AX}$ = 9.1, 2H, H_{Ar}), 6.83 (AA'XX' spin system, $^3J_{XA}$ = 9.1, 2H, H_{Ar}), 6.66 (d, ^3J = 8.4 Hz, 2H, H_{Ar}), 6.41 (s, 1H, H_{isox}), 5.82 (s, 2H, H_{Ar}), 5.49 (m, 4H, CH_2), 5.11 (s, 2H, CH_2), 4.36 (m, 2H, OCH_2), 4.08 (m, 4H, OCH_2), 3.97 (m, 4H, OCH_2), 3.89 (m, 4H, OCH_2), 3.77 (s, 6H, OCH_3), 3.70 (m, 4H, OCH_2), 3.63 (m, 4H, OCH_2), 3.44 (m, 4H,

OCH_2), 3.29 (m, 4H, OCH_2), 2.98 (m, 2H, OCH_2), 2.35 (m, 6H, SCH_3), 1.76 (m, 4H, CH_2), 1.30 (m, 16H, CH_2) ppm. ^{13}C NMR (176 MHz, CD_2Cl_2): δ = 167.24, 163.08, 162.32, 160.15, 159.23, 157.71, 154.78, 152.61, 145.37, 135.37, 133.14, 131.77, 131.60, 131.27, 131.03, 130.14, 129.46, 129.38, 128.54, 128.08, 127.36, 126.72, 125.50, 125.35, 125.09, 124.51, 123.79, 120.33, 118.04, 116.56, 115.90, 115.44, 107.57, 107.44, 106.90, 104.63, 104.17, 71.95, 71.72, 71.08, 70.70, 69.13, 68.86, 68.67, 62.69, 56.76, 56.52, 54.00, 53.45, 46.79, 37.49, 36.76, 30.13, 30.12, 29.97, 29.95, 29.92, 29.80, 26.59, 19.53, 19.50 ppm. ESI-HRMS: *m/z* calcd for $[C_{114}H_{107}BF_{24}N_2O_{12}S_8]$: 1555.4645 $[M\text{-}BArF_{24}]^+$, found: 1555.4581.

1.5. Synthesis of acetylated [2]rotaxane 7

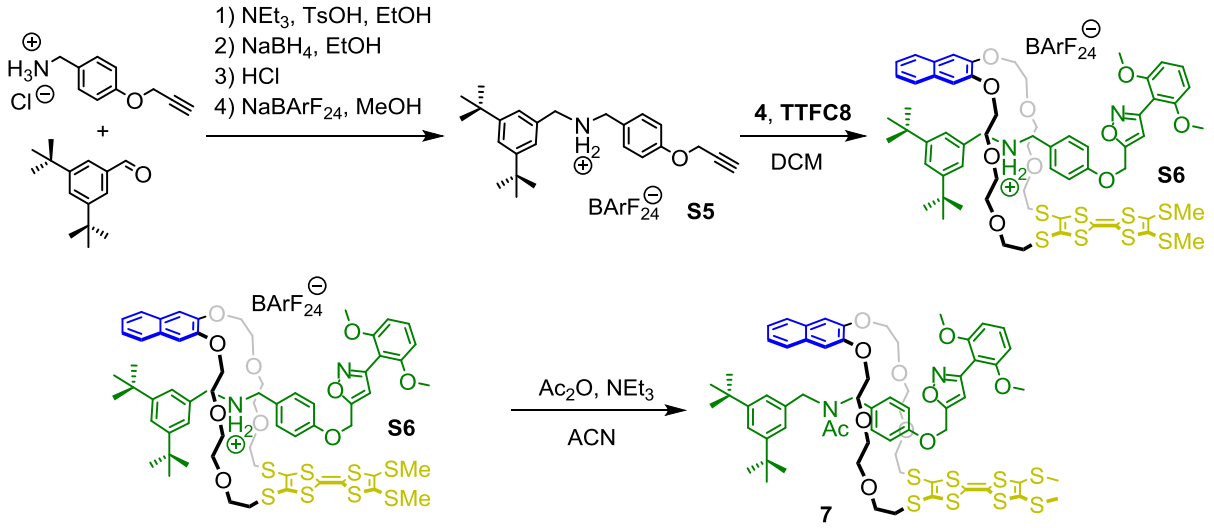
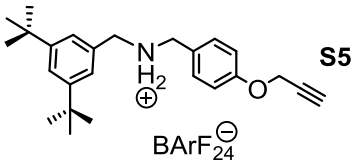


Fig. S3 Synthesis of reference [2]rotaxane **7** and the corresponding axle molecule

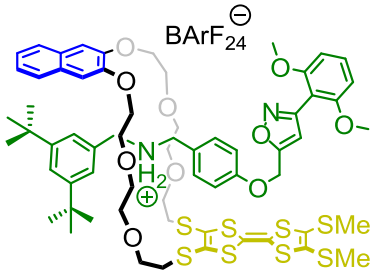
N-(3,5-Di-tert-butylbenzyl)-1-(4-(prop-2-yn-1-yloxy)phenyl)methanaminium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate



(4-(prop-2-yn-1-yloxy)phenyl)methanaminium chloride (594 mg, 3.00 mmol) was dispersed in dry ethanol (100 mL) under Ar atmosphere and NEt_4 was added untill the solution cleared up. Afterwards, $TsOHxH_2O$ (5.7 mg, 0.03 mmol) and 3,5-di-tert-butylbenzaldehyde (688 mg, 3.15 mmol) were added. The mixture was refluxed under Ar for 4 h. After cooling to room

temperature, $NaBH_4$ (567 mg, 15 mmol) was added in portions over 10 min. The solution was stirred over night at RT and quenched with sat. $NaHCO_3$ solution. The solvent was removed under reduced pressure and the remaining aqueous phase was extracted with CH_2Cl_2 (3x100 mL). The combined organic phases were dried over $MgSO_4$ and solvent was removed afterwards. The crude solid was purified by column chromatography (SiO_2, CH_2Cl_2 → CH_2Cl_2/MeOH/ NEt_4 = 200:10:1) and the amine (615 mg, 1.69 mmol) was obtained as a colourless oil. The amine (90.9 mg, 0.25 mmol) was dissolved in ethyl acetate (5 mL) and conc. aqueous HCl (0.3 mL) was added. The mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the hydrochloride was quantitatively obtained as a colourless solid. $NaBArF_{24}$ (221.5 mg, 0.25 mmol, 1 eq.) was added and the solids were dissolved in MeOH (2 mL). The solution was stirred overnight and solvent was evaporated under reduced pressure. The remaining solid was dissolved in CH_2Cl_2 (10 mL) and washed with H_2O (2x5 mL). Drying over $MgSO_4$ and removal of the solvent yielded the desired product (258 mg, 0.21 mmol, 47 % over all steps) as a colourless powder. R_f = 0.40 in CH_2Cl_2/MeOH/NEt_4 = 100:10:1; m.p. 91-93 °C ; ^{1}HNMR (500 MHz, $CDCl_3$): δ = 7.76 – 7.68 (br, 8H, H_{BArF24}), 7.59 (t, ^4J = 1.8 Hz, 1H, H_{Ar}), 7.54 (br, 4H, H_{BArF24}), 7.17 (AA'XX' spin system, $^3J_{AX}$ = 8.7 Hz, 2H, H_{Ar}), 7.11 (d, ^4J = 1.8 Hz, 2H, H_{Ar}), 7.01 (AA'XX' spin system, $^3J_{AX}$ = 8.7 Hz, 2H, H_{Ar}), 4.68 (d, ^4J = 2.4 Hz, 2H, CH2CCH), 4.17 (s, 2H, NCH2), 4.12 (s, 2H, NCH2), 2.49 (t, ^4J = 2.4 Hz, 1H, CCH), 1.29 (s, 18H, H_{tBu}) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.85, 159.76, 153.81, 134.98, 130.91, 129.04, 128.00, 125.71, 124.52, 123.28, 121.50, 117.70, 116.66, 77.54, 77.16, 76.40, 55.99, 53.36, 52.35, 35.14, 31.21 ppm. ESI-HRMS: *m/z* calcd for $[C_{57}H_{46}BF_{24}NO]$: 364.2640 $[M\text{-}BArF_{24}]^+$, found: 364.2647.

[2]Rotaxane S6

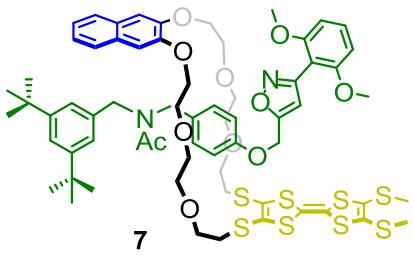


S6

Axle **S5** (45.0 mg, 36.6 µmol) and macrocycle **TTFC8** (27.4 mg, 36.6 µmol) were dissolved in CH_2Cl_2 (0.5 mL) and stirred for 1 h at room temperature. Afterwards, nitrile oxide **4** (7.9 mg, 43.9 µmol) was added and the mixture was heated to 38 °C in a pressure tube for 4 h. The mixture was directly purified by column chromatography (SiO_2, CH_2Cl_2). The desired product (48 mg, 22.3 µmol, 61%) was obtained as an orange sticky solid. R_f = 0.60 in CH_2Cl_2; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 = (m, 8H, H_{BArF24}), 7.63 (AA'XX' spin system, $^3J_{AX}$ = 6.1 Hz,

2H, H_{Ar}), 7.53 (m, 4H, H_{BArF24}), 7.48 (t, ^4J = 1.7 Hz, 1H, HAr), 7.45 (d, ^4J = 1.7 Hz, 2H, H_{Ar}), 7.41 – 7.34 (m, 3H, H_{Ar}), 7.10 (AA'XX' spin system, $^3J_{AX}$ = 8.5 Hz, 2H, H_{Ar}), 6.91 (s, 2H, H_{Ar}), 6.65 (d, ^3J = 8.5 Hz, 2H, H_{Ar}), 6.44 (AA'XX' spin system, $^3J_{AX}$ = 8.5 Hz, 2H, H_{Ar}), 6.34 (s, 1H, H_{isox}), 4.82 – 4.74 (m, 2H, NCH_2), 4.58 (m, 2H, NCH_2), 4.28 (s, 2H, CH_2CC), 4.21 (m, 2H, OCH_2), 4.03 (m, 2H, OCH_2), 3.90 (m, 2H, OCH_2), 3.79 (s, 6H, OCH_3), 3.73 – 3.65 (m, 4H, OCH_2), 3.63 – 3.52 (m, 8H, OCH_2), 3.49 – 3.34 (m, 6H, OCH_2), 1.26 (s, 18H, H_{tBu}) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 165.66, 161.80, 158.89, 158.76, 157.28, 152.43, 134.96, 131.51, 130.84, 130.74, 129.09, 129.03, 127.95, 126.50, 125.79, 125.67, 124.11, 123.62, 123.31, 123.19, 121.45, 117.63, 114.74, 108.03, 106.60, 104.29, 77.16, 71.36, 70.51, 69.91, 68.39, 60.48, 56.16, 53.42, 53.04, 35.15, 31.40 ppm. ESI-HRMS: *m/z* calcd for $[C_{96}H_{91}BF_{24}N_2O_{10}S_8]$: 1291.3495 $[M\text{-}BArF_{24}]^+$, found: 1291.3442.

[2]Rotaxane 7



7

[2]Rotaxane **S6** (10.8 mg, 5.0 µmol) was dissolved in acetonitrile (2 mL) and trimethylamine (6.9 µL, 50 µmol) and Ac_2O (9.5 µL, 100 µmol) were added. The mixture was stirred at room temperature overnight and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2) to obtain the desired product as a yellow oil (5.2 mg, 3.9 µmol, 78%). R_f = 0.15 in CH_2Cl_2; (Because of the *cis-trans* isomerism of the amide bond, two sets of NMR signals are observed.) ^{1}H NMR (700 MHz, CD_2Cl_2): δ = 7.65 (m, 2H, H_{Ar}), 7.39 – 7.27 (m, 5H, H_{Ar}), 7.20 (m, 1H, H_{Ar}), 7.11 (m, 2H, H_{Ar}), 6.99-6.90 (m, 4H, H_{Ar}), 6.67 (m, 1H, H_{isox}), 6.63 (m, 2H, H_{Ar}), 5.84 (s, 2H, CH_2), 4.38 (m, 2H, CH_2), 4.29 (m, 2H, OCH_2), 4.21 (m, 2H, OCH_2), 4.19 (m, 2H, CH_2), 3.83 (m, 4H, OCH_2), 3.74 (m, 6H, OCH_3), 3.65 – 3.59 (m, 4H, OCH_2), 3.54 – 3.45 (m, 6H, OCH_2), 3.42 – 3.32 (m, 2H, OCH_2), 3.03 (m, 2H, OCH_2), 2.03 (m, 3H, $OCCH_3$), 1.30 (m, 18H, H_{tBu}) ppm. ^{13}C NMR (176 MHz, CD_2Cl_2): δ = 171.20, 169.21, 159.28, 158.64, 158.38, 157.41, 151.97, 149.38, 137.39, 131.45, 129.84, 129.69, 129.11, 127.87, 126.72, 124.68, 122.75, 121.93, 121.16, 116.26, 108.36, 107.58, 107.50, 104.56, 104.47, 70.40, 70.29, 69.86, 69.82, 68.96, 61.75, 56.53, 56.49, 54.00, 51.35, 48.76, 47.68, 35.29, 31.79, 21.96 ppm. ESI-HRMS: *m/z* calcd for $[C_{66}H_{80}N_2O_{11}S_8]$: 1333.3601 $[M+H]^+$, found: 1333.3542.

2. Additional NMR Data

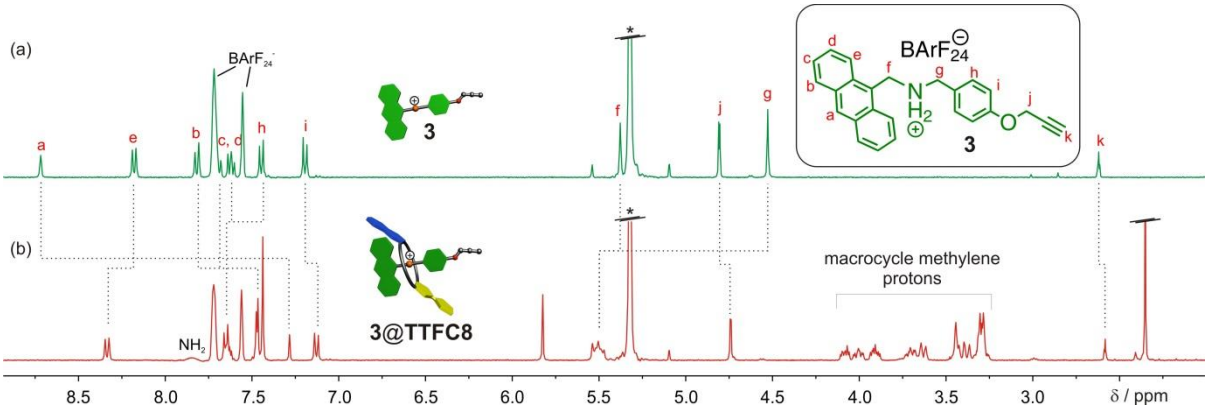


Fig. S4 Stacked ^{1}H NMR spectra (400 MHz, 2.0 mM, CD_2Cl_2, 298 K) of (a) axle **3** and (b) a 1:1 mixture of macrocycle **TTFC8** and axle **3**. Solvent residual signal is marked with an asterisk.

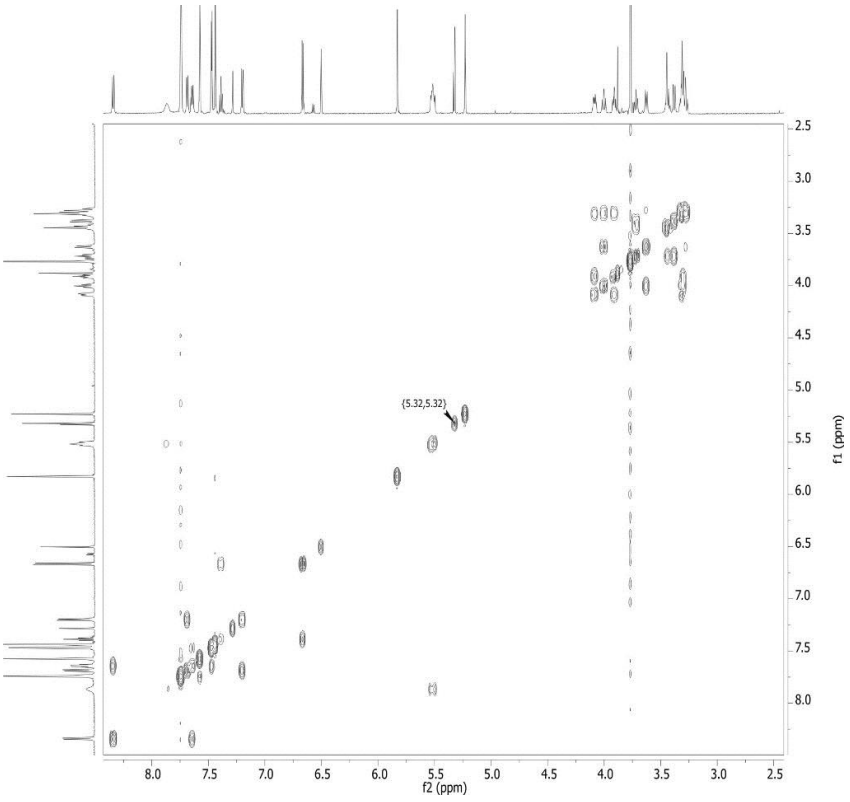


Fig. S5 ^{1}H,^{1}H COSY NMR spectrum (700 MHz, CD_2Cl_2, 298 K) of [2]rotaxane **1**

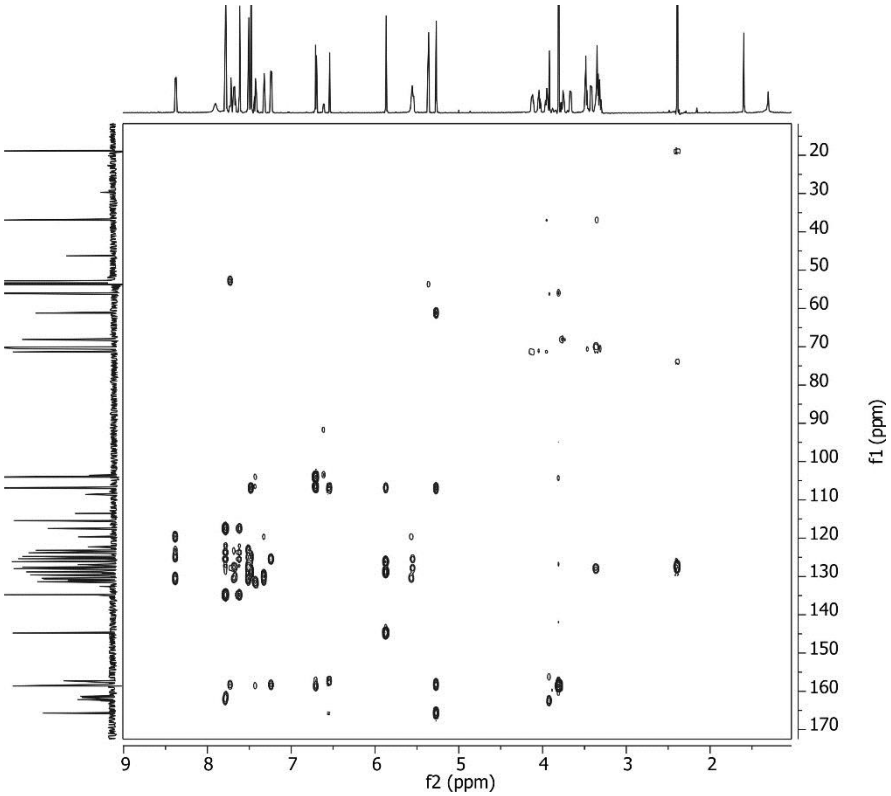


Fig. S6 HMBC spectrum (700 MHz, CD_2Cl_2, 298 K) of [2]rotaxane **1**

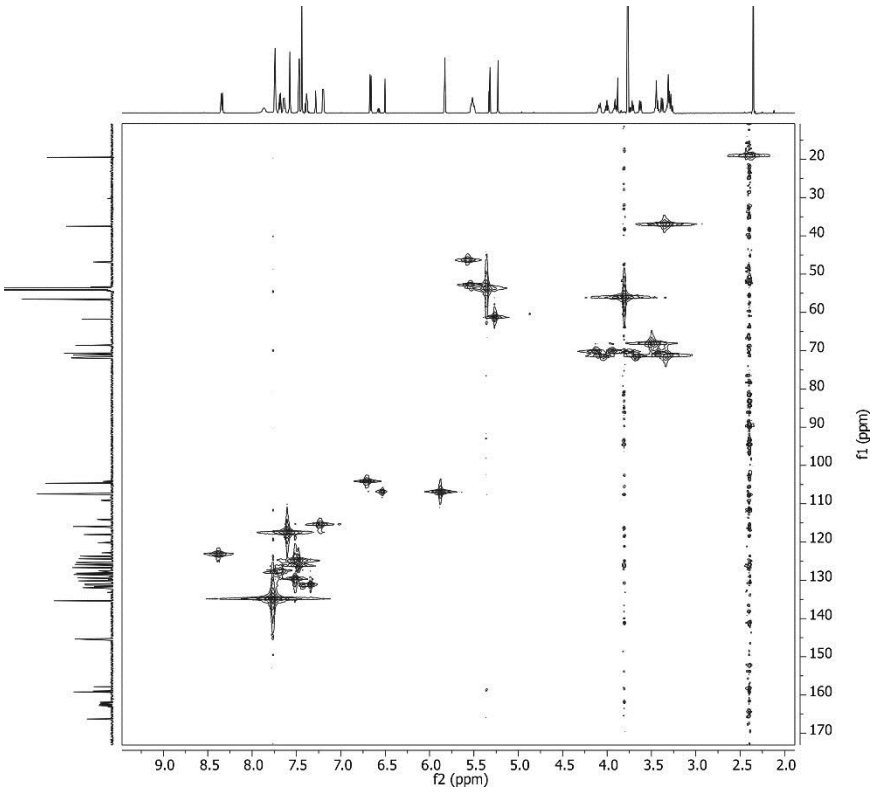


Fig. S7 HMQC spectrum (700 MHz, CD_2Cl_2, 298 K) of [2]rotaxane **1**

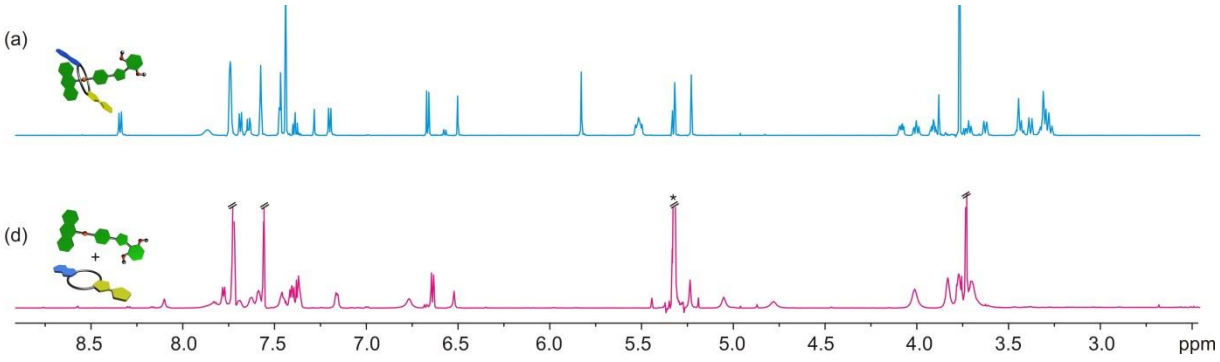


Fig. S8 Stacked ^{1}H NMR spectra (700 MHz, 2.0 mM, CD_2Cl_2, 298 K) of (a) [2]rotaxane **1** and (b) a 1:1 mixture of macrocycle **TTFC8** and free stoppered axle **5**. Clearly, the spectra are not superimposable which confirms the interlocked structure of [2]rotaxane **1**.

3. Mass spectrometric data

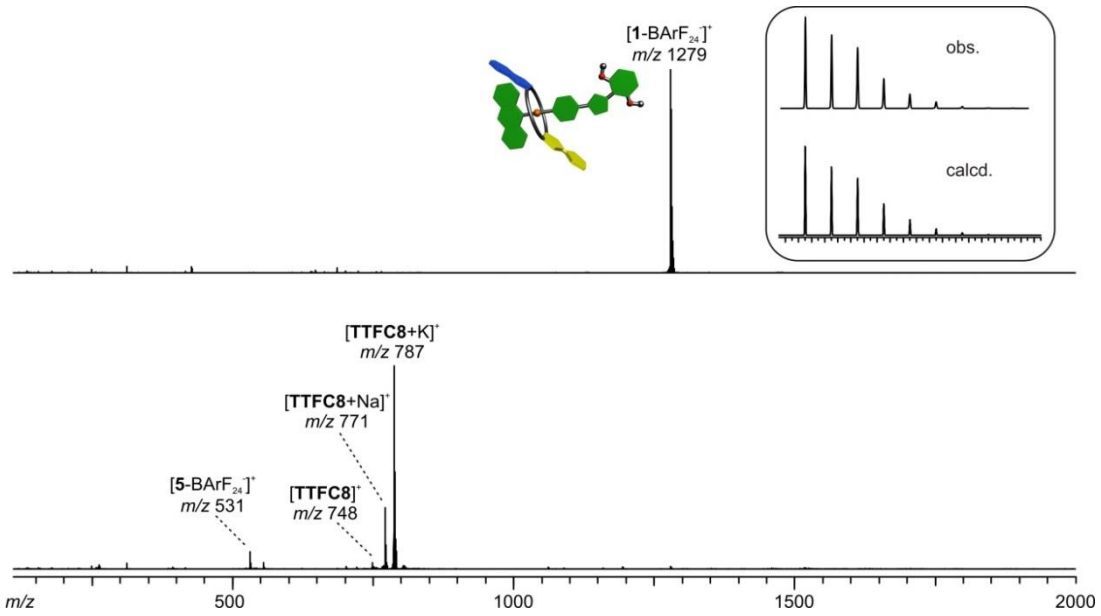


Fig. S9 ESI-FTICR mass spectrum obtained from a MeOH solution (10 µM) of [2]rotaxane **1** (top) and a 1:1 mixture of free stoppered axle **5** and TTF-macrocycle **TTFC8** (bottom). Comparison of both spectra clearly shows [2]rotaxane **1** to be mechanically interlocked and not to dissociate into the two components.

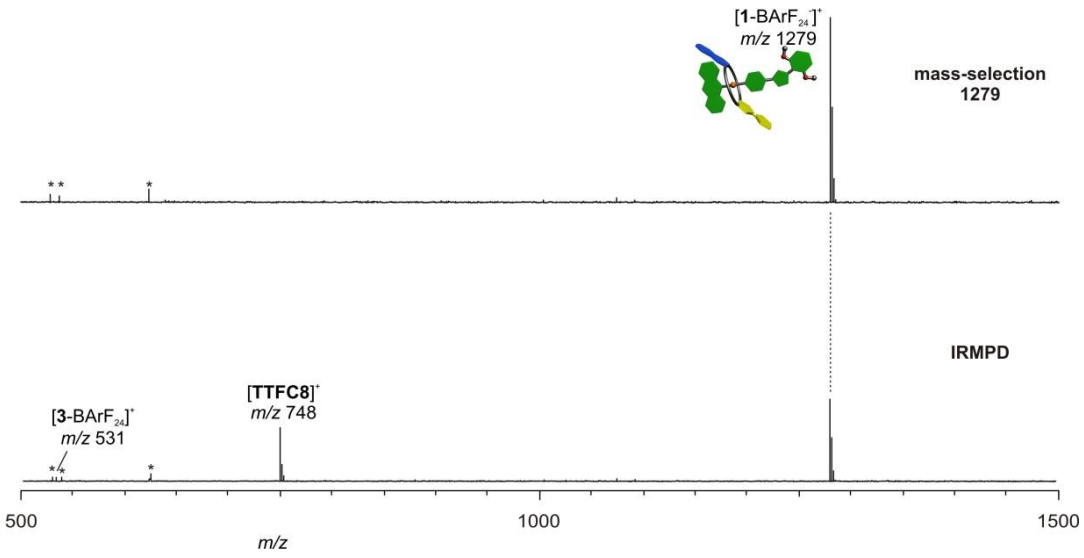


Fig. S10 Infrared multiphoton dissociation (IRMPD) experiment with mass-selected rotaxane ions at m/z 1279 generated from a MeOH solution (10 µM) of [2]rotaxane **1**: (top) after mass-selection; (bottom) after IRMPD experiment. As reported for a similar system, an electron transfer from the macrocycle to the axle occurs and releases the macrocycle cation-radical (*m/z* 748).[3] This fragmentation pathway speaks in favour of a mechanically interlocked structure of [2]rotaxane **1**.

4. Additional fluorescence spectra

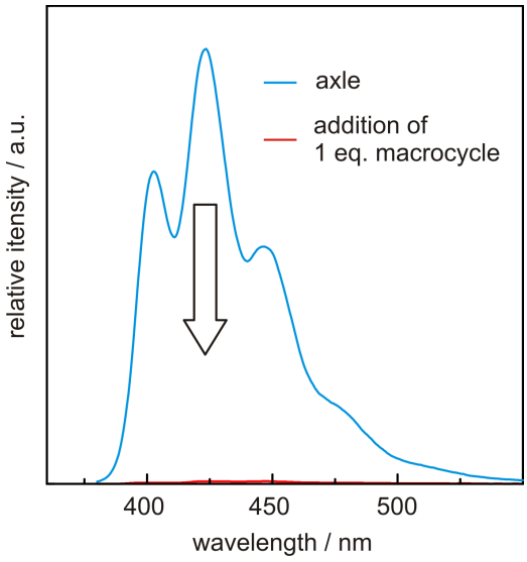


Fig. S11 Fluorescence spectra of axle **3** (blue) and pseudo[2]rotaxane **3@TTFC8** (red) in CH_2Cl_2 (50 µM) at 298 K (λ_{ex} = 370 nm). The fluorescence of axle **3** is strongly quenched due to an electron transfer from the macrocycle to the axle in the pseudo[2]rotaxane **3@TTFC8.**

5. Isothermal titration calorimetry

ITC titrations were carried out in dry 1,2-dichloroethane (DCE) at 298 K on a TAM III microcalorimeter (Waters GmbH, TA Instruments, Eschborn, Germany). A volume of 800 µL of a 1 mM solution of macrocycle **TTFC8** was placed in the sample cell and 250 µL of a solution of the axle **3** (8 mM) in the syringe. The titrations consisted of 32 consecutive injections of 8 µL each with a 20 min interval between injections. Heats of dilution were determined by titration of axle solutions into the sample cell containing blank solvent and were subtracted from each data set. The heat flow generated in the sample cell is measured as a differential signal between sample and reference cells. Hence, an exothermic event results in a positive and an endothermic in a negative heat flow. The data were analysed using the instrument's internal software package and fitted with a 1:1 binding model. Each titration was conducted twice and the measured values for K, ΔG, and ΔH were averaged.

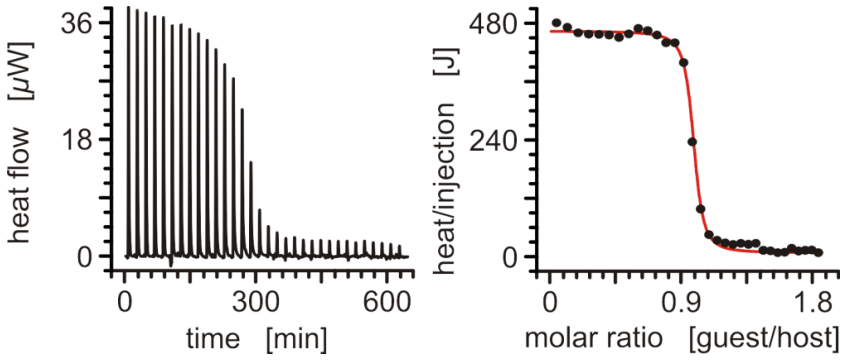


Fig. S12 Titration plots (heat flow over time (left) and heat/volume over guest/host ratio) obtained from ITC experiments conducted with axle **3** and wheel **TTFC8**.

6. Cyclic voltammetry and digital simulations

Redox-potentials reported in this study were obtained by cyclic voltammetry. All measurements were at least conducted twice. Measurements were carried out in dry and degassed CH_2Cl_2 or acetonitrile solutions with 0.1 M electrolyte and 1 mM analyte concentration using a three-electrode configuration (glassy carbon working electrodes, Pt counter electrode, Ag wire as pseudoreference) and an Autolab PGSTAT302N potentiostat. The decamethylferrocene/decamethylferrocenium ($[FeCp_2^*]^{+/0}$) couple was used as the internal reference for all measurements to ensure maximum comparability. Energy differences were calculated according to the equation $\Delta G = n F \Delta E$.

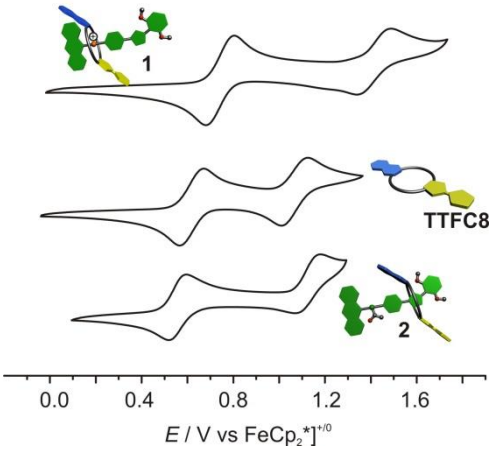


Fig. S13 Stacked cyclic voltammograms (CH_2Cl_2, $TBArF_{24}$ (0.1 M), 298 K) of electro-active species **1**, **TTFC8** and **2** (1 mM) at a scan rate of 100 mV s^{-1} corresponding to the correlation diagram in Fig. 5 in the main text.

Table 1 Electrochemical data obtained by cyclic voltammetry

entry	species	solvent	electrolyte[a]	$E^1_{1/2}$[b] / mV	$E^2_{1/2}$[b] / mV	$\Delta E^1_{1/2}$[c] / mV	$\Delta E^1_{1/2}$[c] / mV
1	**TTFC8**	CH_2Cl_2	$TBABArF_{24}$	610	1060	/	/
2	**TTFC8**	CH_2Cl_2	$TBAClO_4$	600	820	/	/
3	**TTFC8**	CH_2Cl_2	$TBAPF_6$	600	870	/	/
4	**TTFC8**	ACN	$TBABArF_{24}$	600	820	/	/
5	**TTFC8**	ACN	$TBAClO_4$	600	780	/	/
6	**TTFC8**	ACN	$TBAPF_6$	590	810	/	/
7	**1**	CH_2Cl_2	$TBABArF_{24}$	740	1420	130	360
8	**1**	CH_2Cl_2	$TBAClO_4$	640	870	30	50
9	**1**	CH_2Cl_2	$TBAPF_6$	660	960	50	80
10	**1**	ACN	$TBABArF_{24}$	650	930	50	110
11	**1**	ACN	$TBAClO_4$	630	830	40	50
12	**1**	ACN	$TBAPF_6$	640	870	40	70
13	**2**	CH_2Cl_2	$TBABArF_{24}$	560	1140	-50	70
14	**2**	CH_2Cl_2	$TBAClO_4$	540	820	-60	0
15	**2**	CH_2Cl_2	$TBAPF_6$	550	890	-50	20
16	**2**	ACN	$TBABArF_{24}$	570	870	-30	40
17	**2**	ACN	$TBAClO_4$	560	820	-30	50
18	**2**	ACN	$TBAPF_6$	570	840	-20	40
19	**7**	CH_2Cl_2	$TBAPF_6$	540	890	-60	20
20	**6**	CH_2Cl_2	$TBABArF_{24}$	740	1390	130	330
21	**6**	CH_2Cl_2	$TBAPF_6$	650	960	50	80
22	**5 + TTFC8**	CH_2Cl_2	$TBAPF_6$	610	880	10	0

[a] Electrolyte concentration of 0.1 M

[b] Half-wave potential against $[FeCp_2^*]^{+/0}$ at a scan rate of 100 mV s^{-1}. The error is estimated to be ± 5 mV.

[c] Difference of half-wave potentials between measured species and macrocycle **TTFC8**

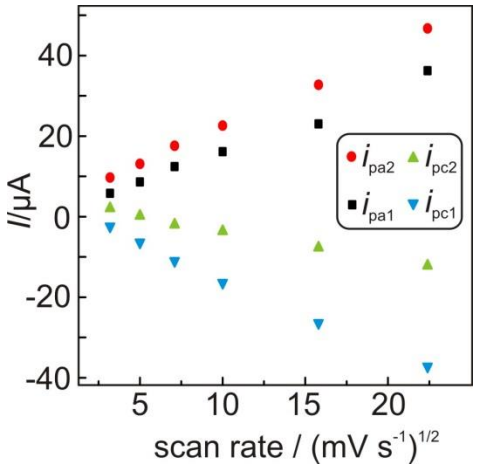


Fig. S14 Peak currents plotted against the square root of scan speed based on cyclic voltammograms of [2]rotaxane **6** (5 mM) in CH_2Cl_2 against $Fe(Cp^*)_2^{0/+}$ with tetrabutylammonium $BArF_{24}^-$ (0.1 M) as electrolyte.

The cyclic voltammogram of **6** was simulated in two segments from 0.30 V to 1.75 V and from 1.75 V to 0.30 V with the software DigiElch Professional[6] by using the Butler-Volmer equation. The surface area of the working electrode was set to 0.02 cm^2 and the starting concentration of **6** was set to 5 mM. The charge transfer coefficients α were left at their initial value of 0.5 and the heterogeneous rate constants k_s were calculated from the peak-to-peak separation[7] and consequently set to $4x10^{-3}$ cm^2 s^{-1}. The diffusion coefficients were left at their initial values of $1x10^{-5}$ cm^2 s^{-1}. The simulated charge-transfer reactions are described by the following equations (E1)-(E4), the E_0 values are given in brackets:

$\mathbf{6}^{2+}$	+	e^-	⇄	$\mathbf{6}^{+\bullet}$	(1.44 V)	(E1)
$\mathbf{6}^{+\bullet}$	+	e^-	⇄	**6**	(0.76 V)	(E2)
$(\mathbf{6}^{2+})^*$	+	e^-	⇄	$(\mathbf{6}^{+\bullet})^*$	(1.14 V)	(E3)
$(\mathbf{6}^{+\bullet})^*$	+	e^-	⇄	**(6)***	(0.61 V)	(E4)

The simulated shuttling mechanism is described by the following equations (C1)-(C3):

(6)*	⇄	**6**	(C1)
$(\mathbf{6}^{+\bullet})^*$	⇄	$\mathbf{6}^{+\bullet}$	(C2)
$(\mathbf{6}^{2+})^*$	⇄	$\mathbf{6}^{2+}$	(C3)

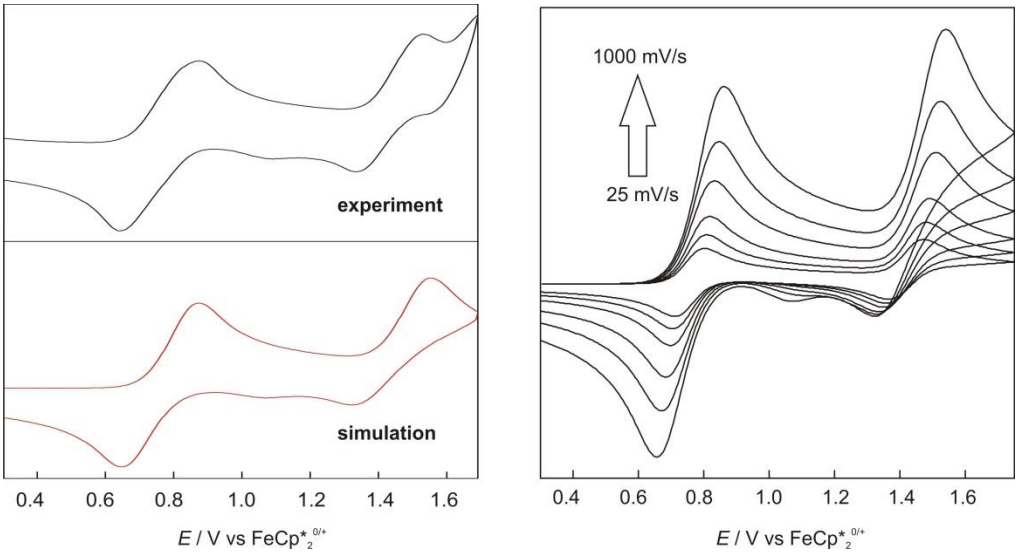


Fig. S15 (left) Comparison of the simulated (red) and experimental cyclic voltammogram (black) of [2]rotaxane **6** measured in CH_2Cl_2 at 298 K with $TBABArF_{24}$ (0.1 M) at 1000 mV s^{-1}. (right) Simulation with the derived parameters from fitting the experimental data for several scan speeds according to the experiment in Fig. 6b.

Table S2. Thermodynamic parameters for chemical reactions C1-C3 derived by fitting the experimental data and used for the simulation of cyclic voltammograms depicted in Fig. S15

reaction	K_{Tn}	k_f / s^{-1}	k_b / s^{-1}
C1	$2.7\ 10^7$	3500	0.00013
C2	$9.4\ 10^4$	80	0.00085
C3	1.0	6	6.2

7. NMR evidence for the switchability [2]rotaxane 6

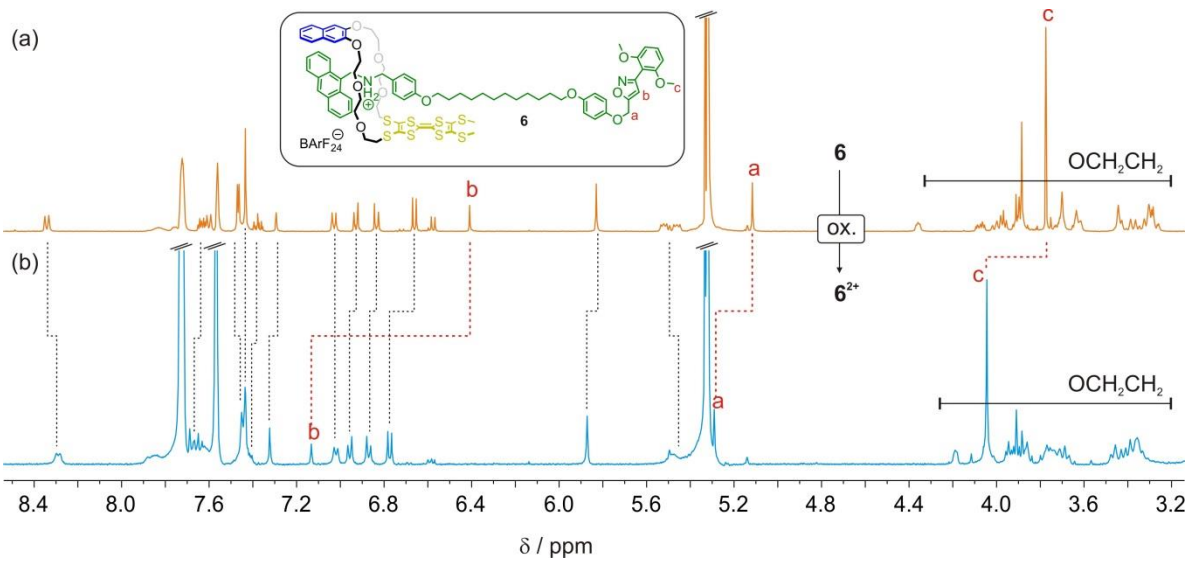


Fig. S16 ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 298 K, 2.0 mM) of [2]rotaxane **6** (a) before and (b) after oxidation by $Fe(ClO_4)_3$ and addition of 5 equiv. $TBABArF_{24}$ as the stabilizing electrolyte. Only small shifts for the aromatic protons of axle and macrocycle are observed which indicates a similar binding situation as in the non-oxidised state. However, the significant downfield shifts of signals a, b and c which belong to the most distant part of the axle, namely the isoxazole/stopper moiety, suggests a major conformational change in the system.

8. ^{1}H and ^{13}C NMR spectra

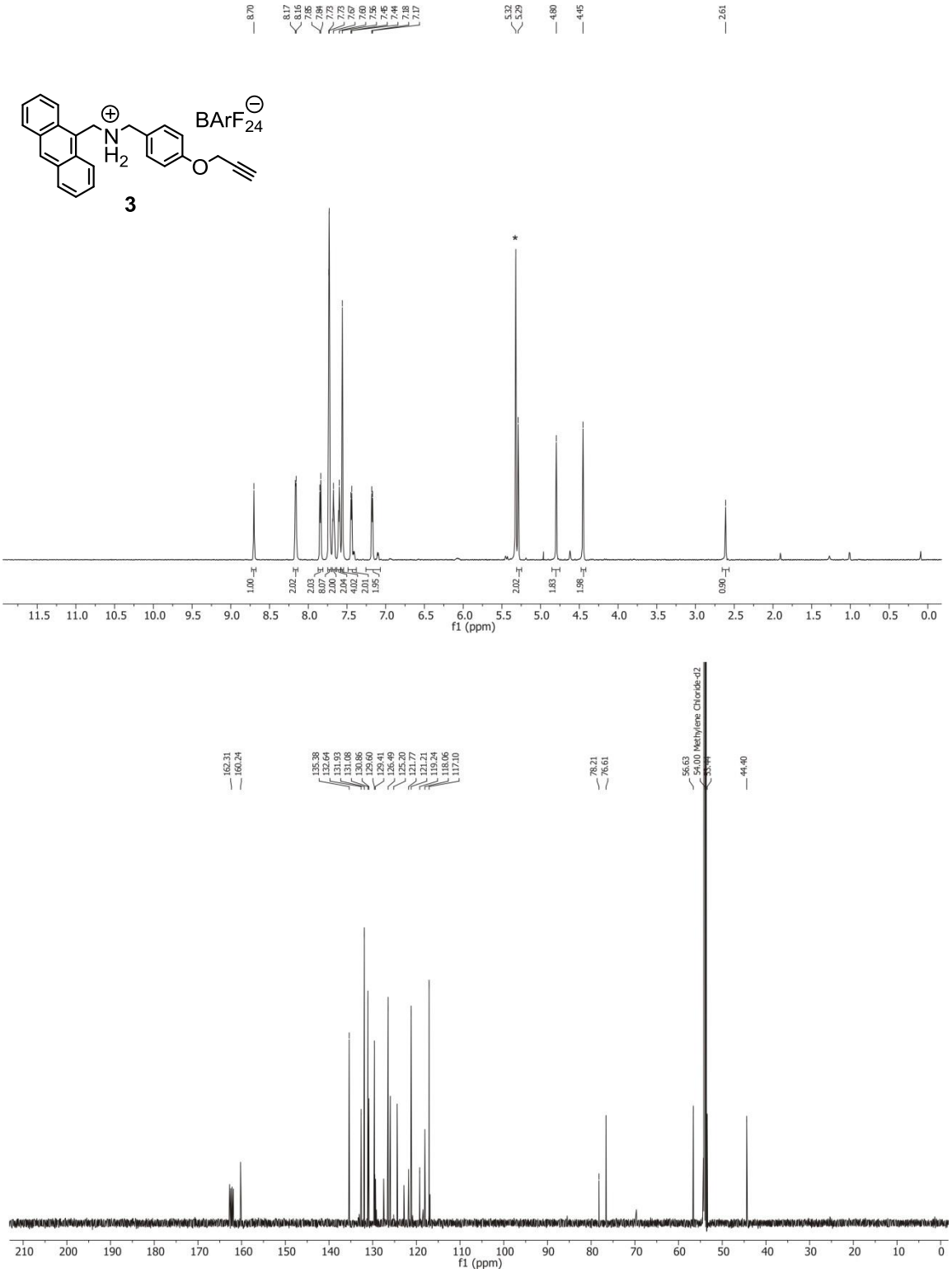


Fig. S17 (top) ^{1}H NMR (700 MHz, CD_2Cl_2, 298 K) spectrum of axle **3**; (bottom) ^{13}C NMR (176 MHz, CD_2Cl_2, 298 K) spectrum of axle **3**.

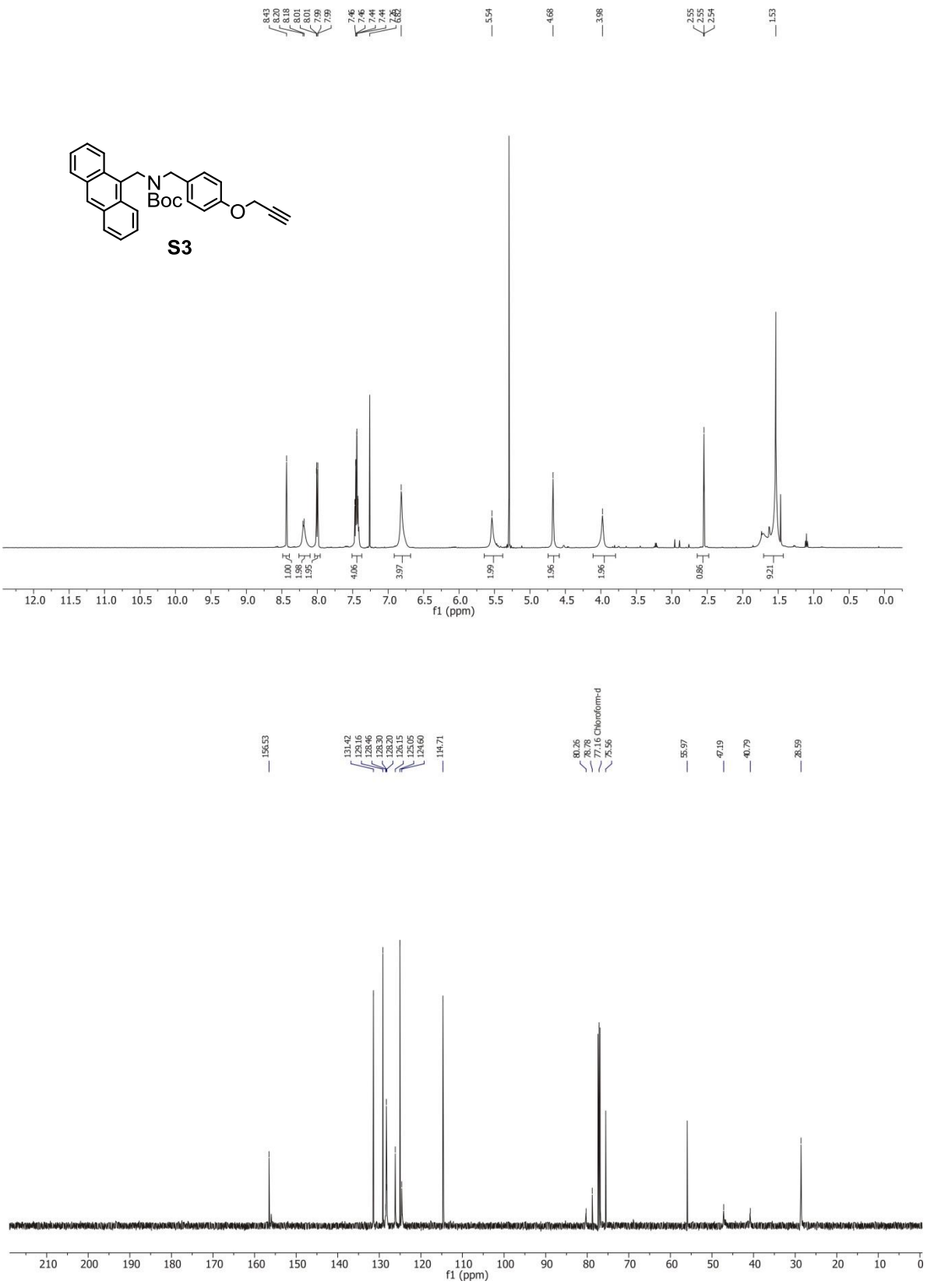


Fig. S18 (top) ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of axle **S3**; (bottom) ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of axle **S3**.

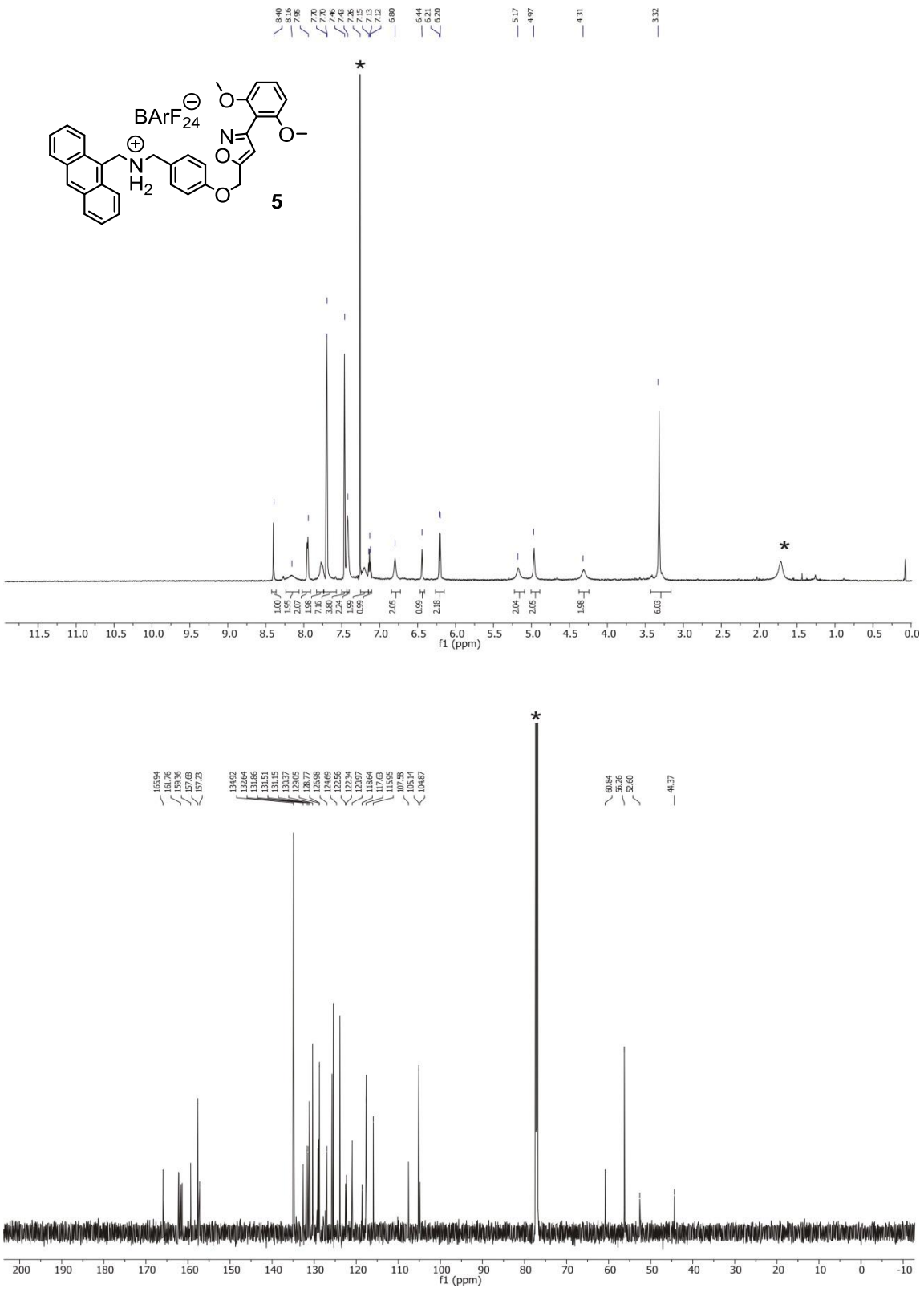


Fig. S19 (top) ^{1}H NMR (700 MHz, $CDCl_3$, 298 K) spectrum of free stoppered axle **5**; (bottom) ^{13}C NMR (176 MHz, $CDCl_3$, 298 K) spectrum free stoppered axle **5**.

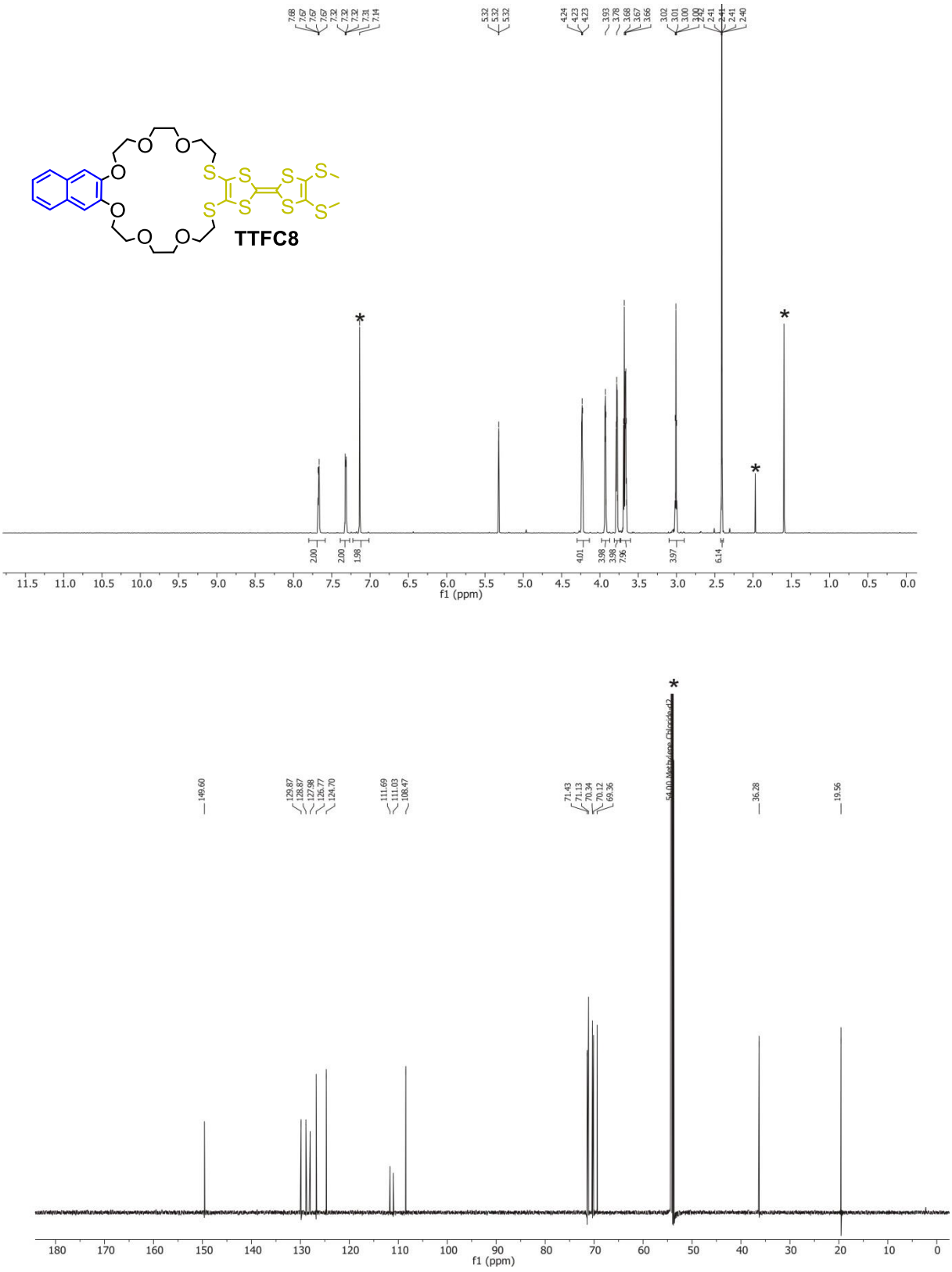


Fig. S20 (top) ^{1}H NMR (700 MHz, CD_2Cl_2, 298 K) spectrum of macrocycle **TTFC8**; (bottom) ^{13}C NMR (176 MHz CD_2Cl_2, 298 K) spectrum of macrocycle **TTFC8**.

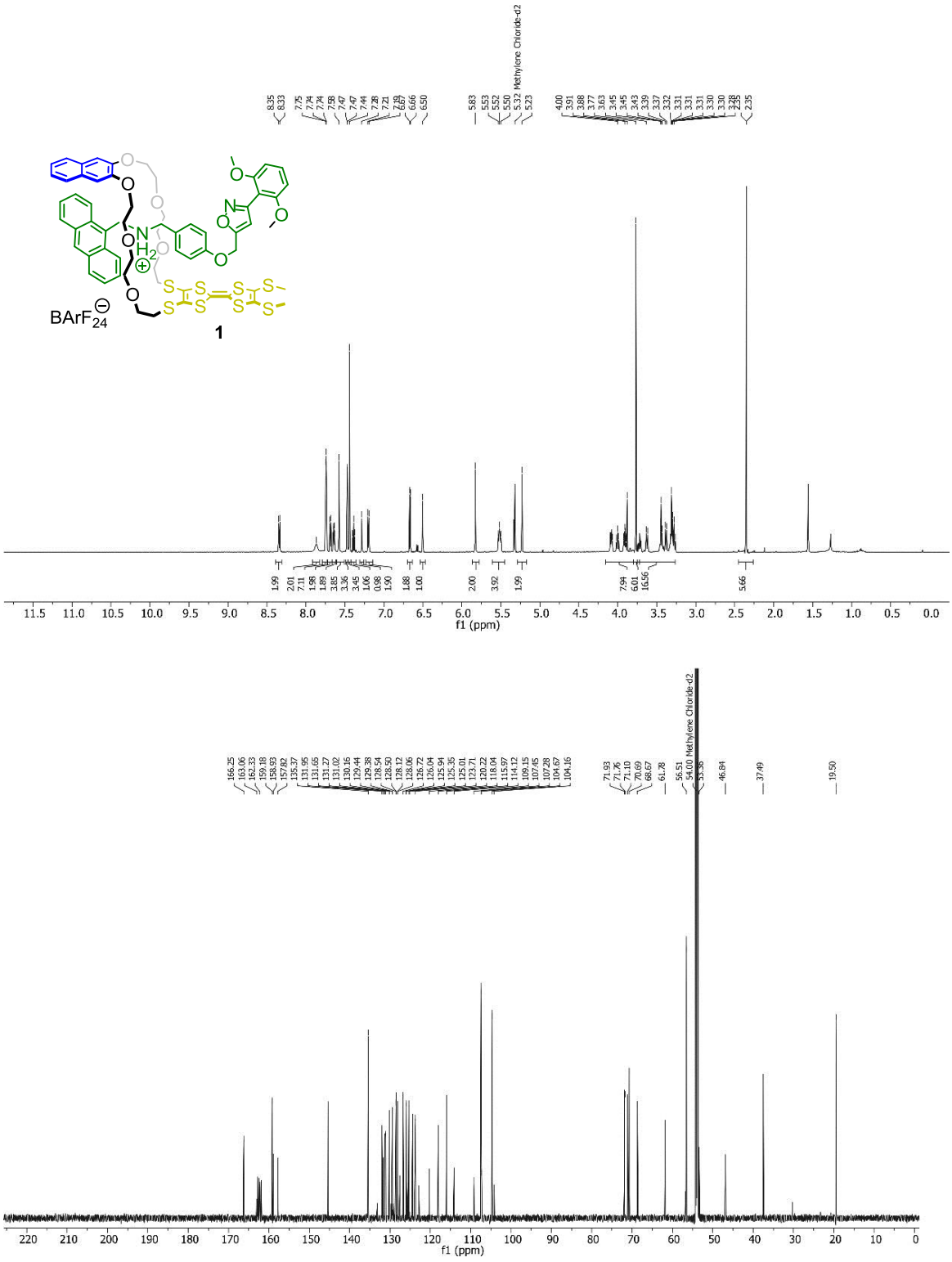


Fig. S21 (top) ^{1}H NMR (700 MHz, CD_2Cl_2, 298 K) spectrum of [2]rotaxane **1**; (bottom) ^{13}C NMR (176 MHz, CD_2Cl_2, 298 K) spectrum of [2]rotaxane **1**

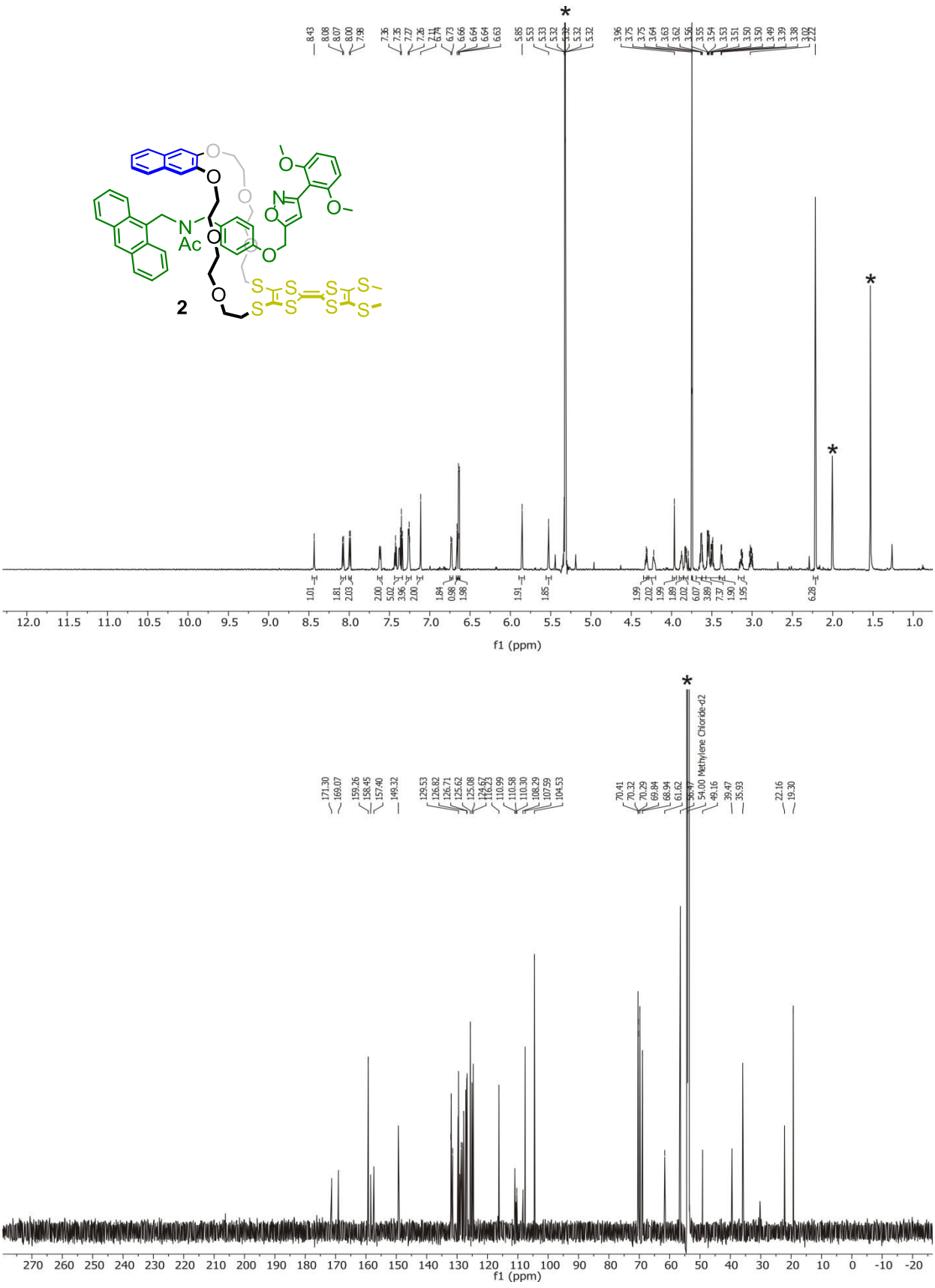


Fig. S22 (top) ^{1}H NMR (700 MHz, CD_2Cl_2, 298 K) spectrum of [2]rotaxane **2**; (bottom) ^{13}C NMR (176 MHz, CD_2Cl_2, 298 K) spectrum of [2]rotaxane 2**.**

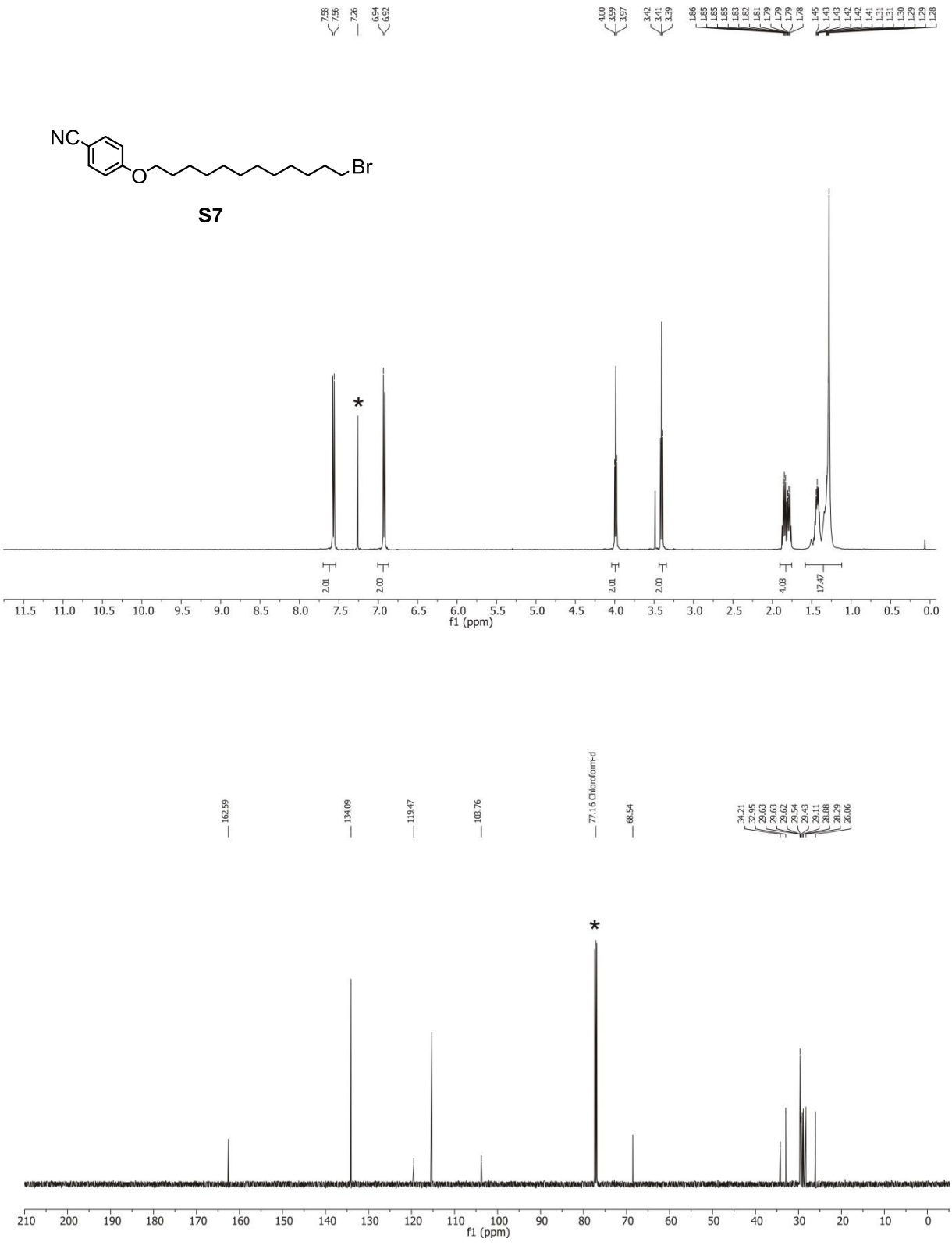


Fig. S23 (top) ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of nitrile **S7**; (bottom) ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of nitrile **S7**.

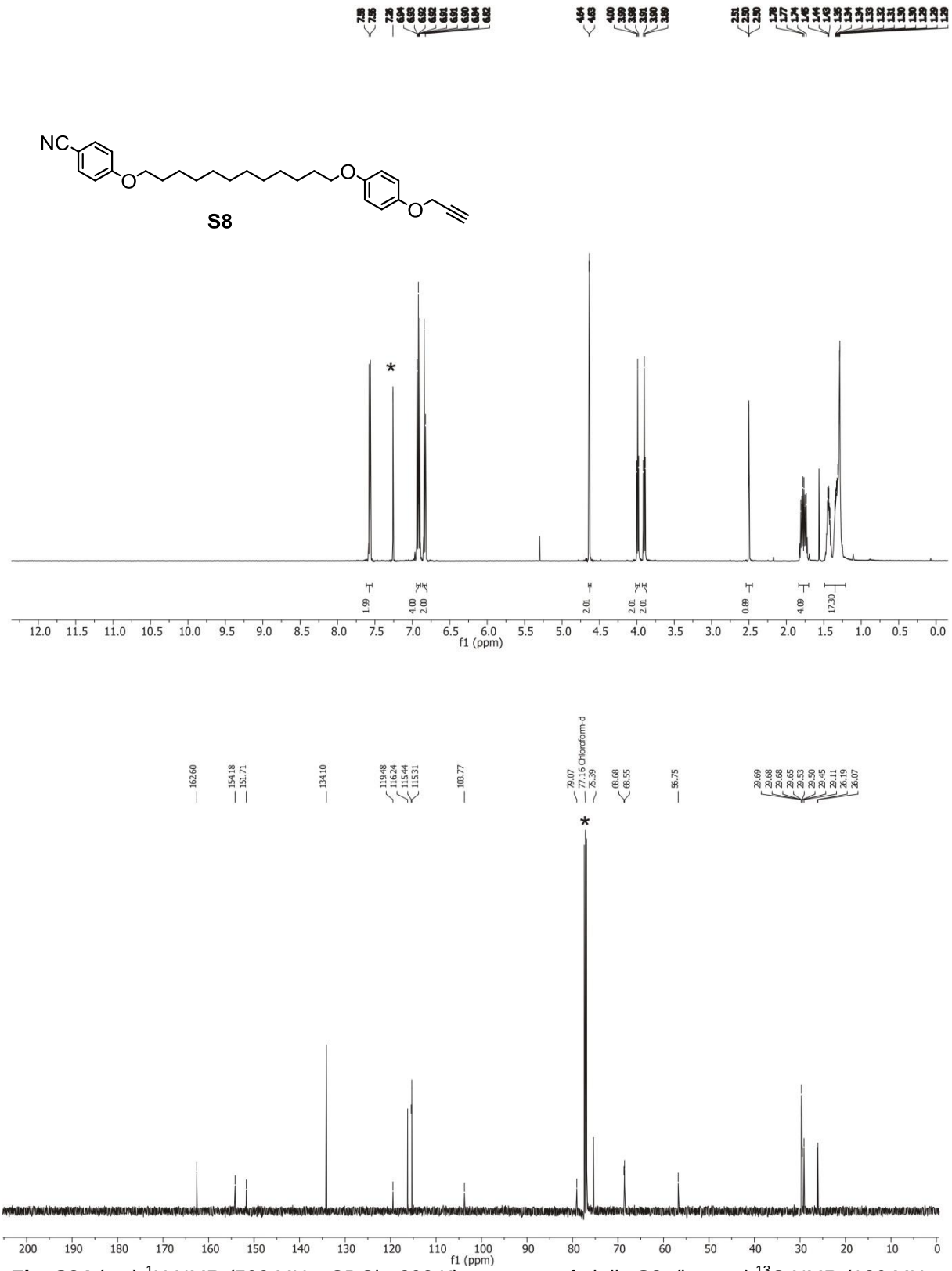


Fig. S24 (top) ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of nitrile **S8**; (bottom) ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of nitrile **S8**.

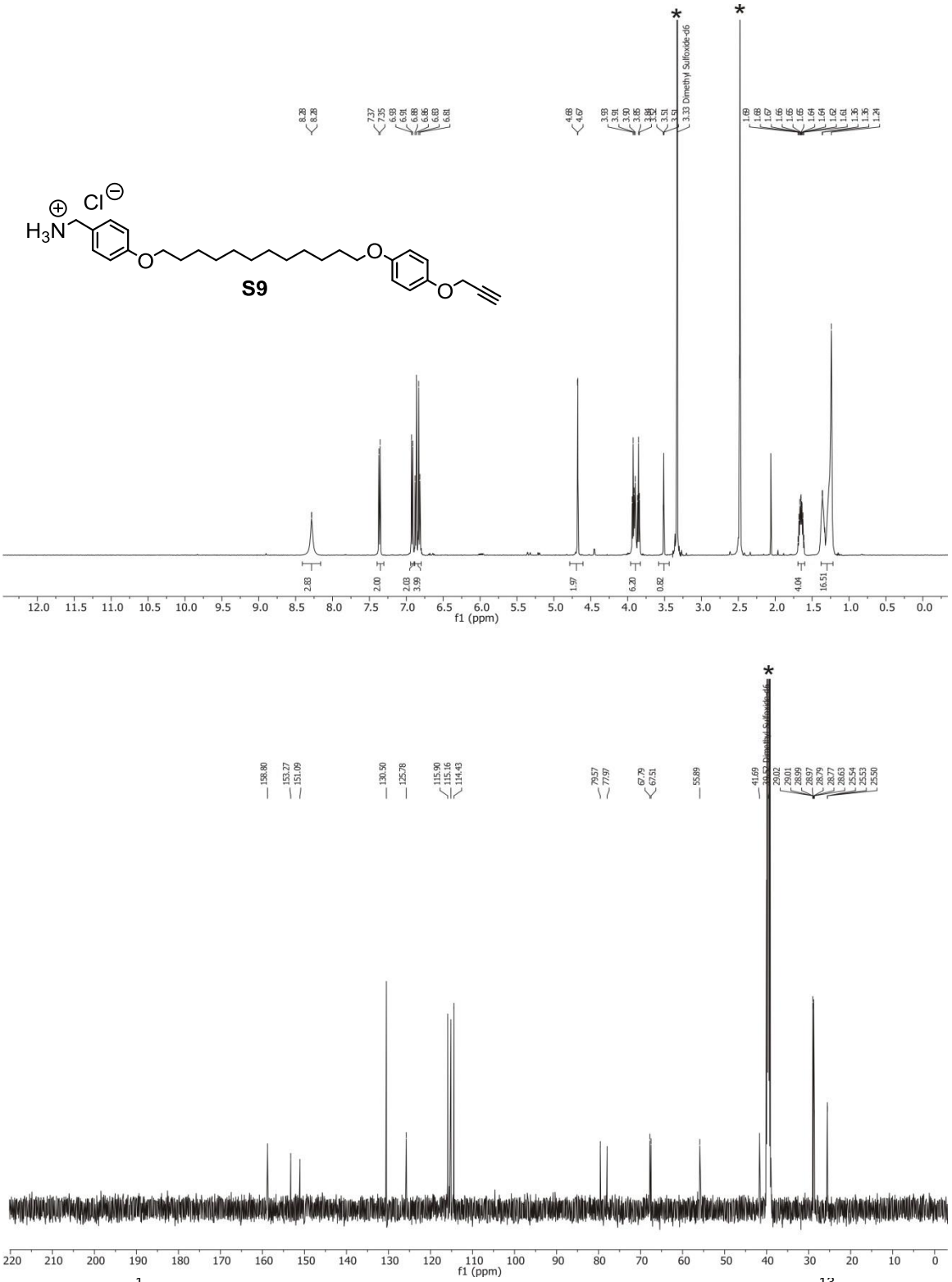


Fig. S25 (top) ^{1}H NMR (500 MHz, DMSO-d6, 298 K) spectrum of amine **S9**; (bottom) ^{13}C NMR (126 MHz, DMSO-d6, 298 K) spectrum of amine **S9**.

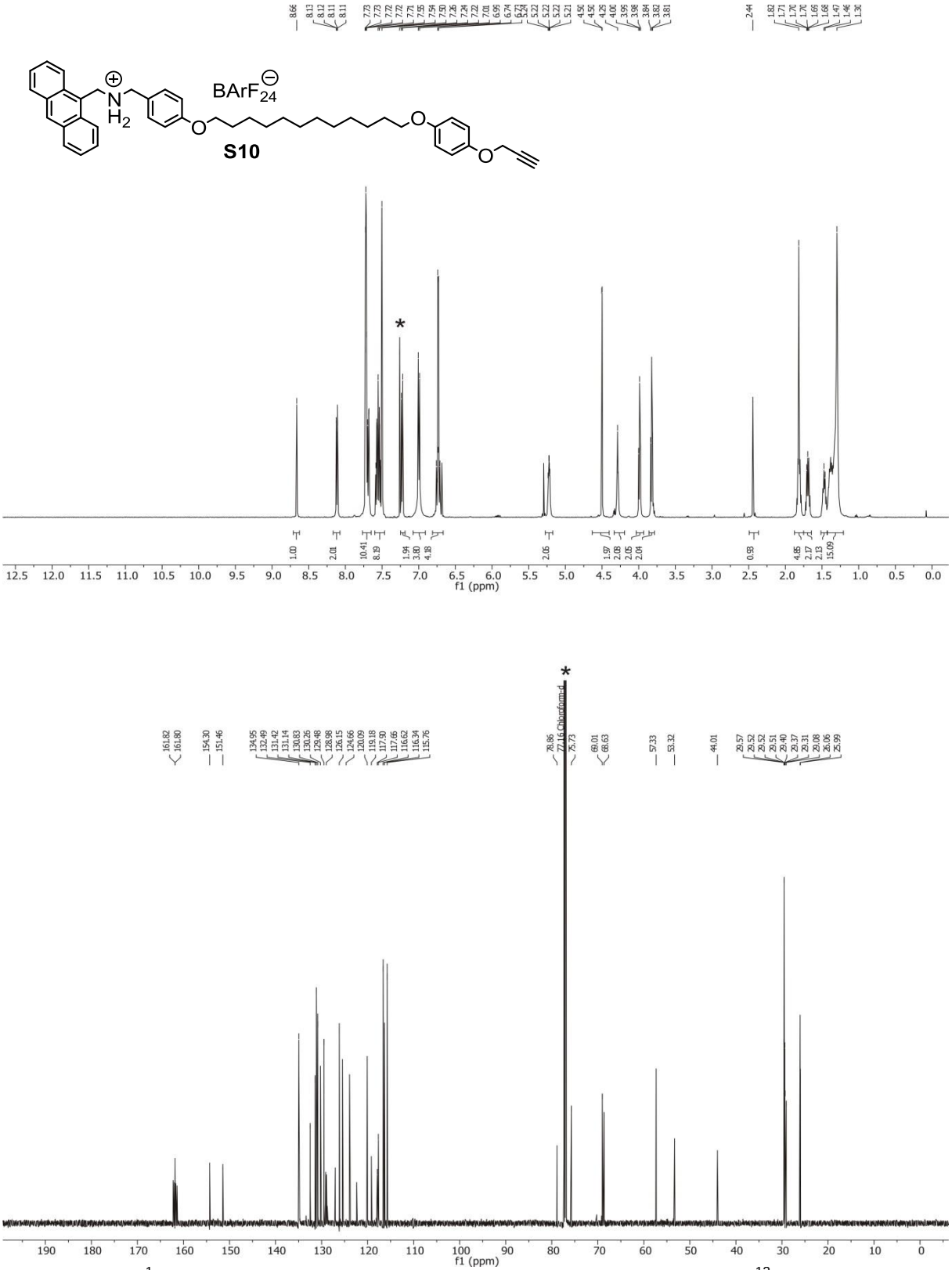


Fig. S26 (top) ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of axle **S10**; (bottom) ^{13}C NMR (176 MHz, $CDCl_3$, 298 K) spectrum of axle **S10**.

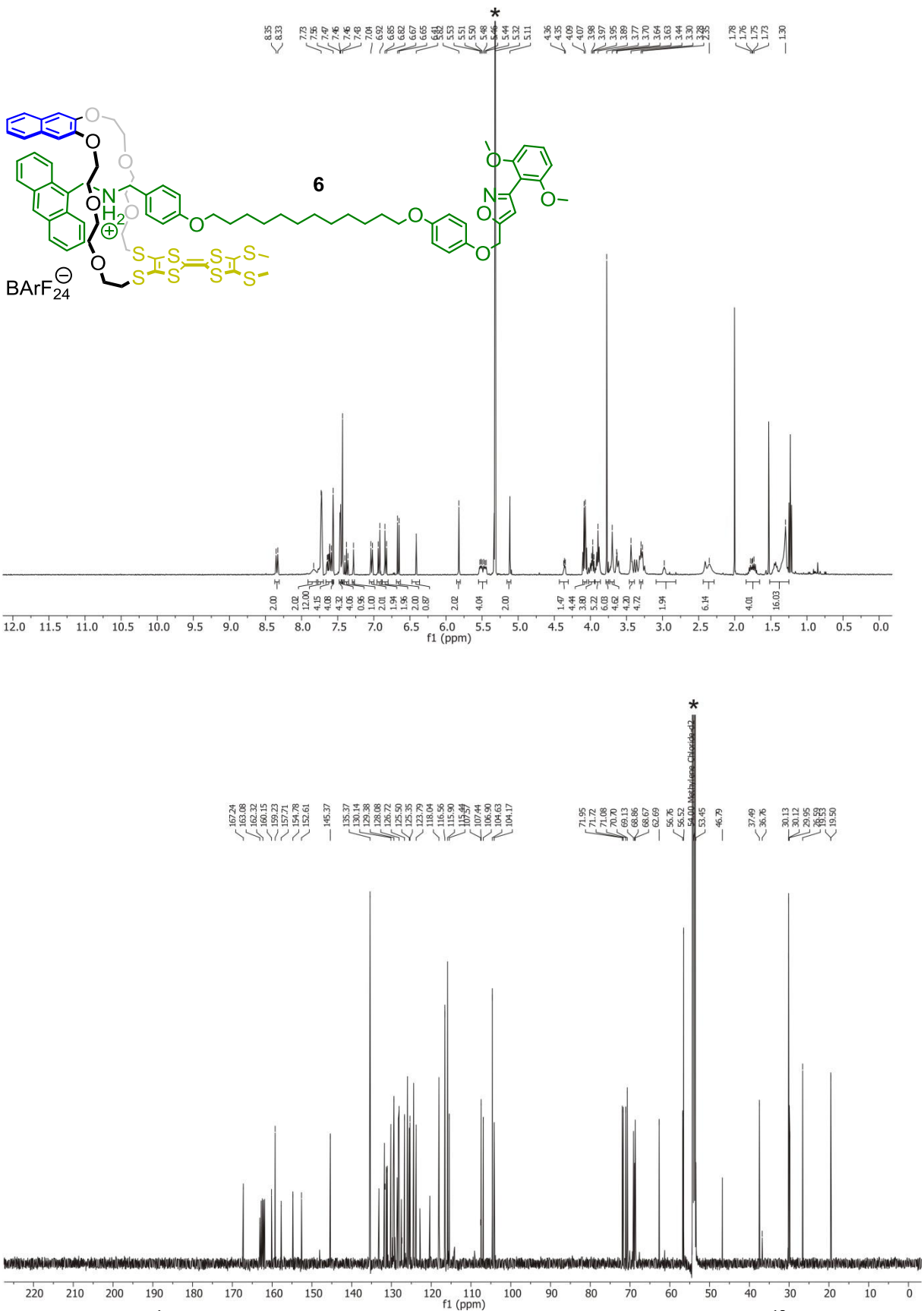


Fig. S27 (top) ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectrum of rotaxane **6**; (bottom) ^{13}C NMR (176 MHz, CD_2Cl_2, 298 K) spectrum of rotaxane **6**.

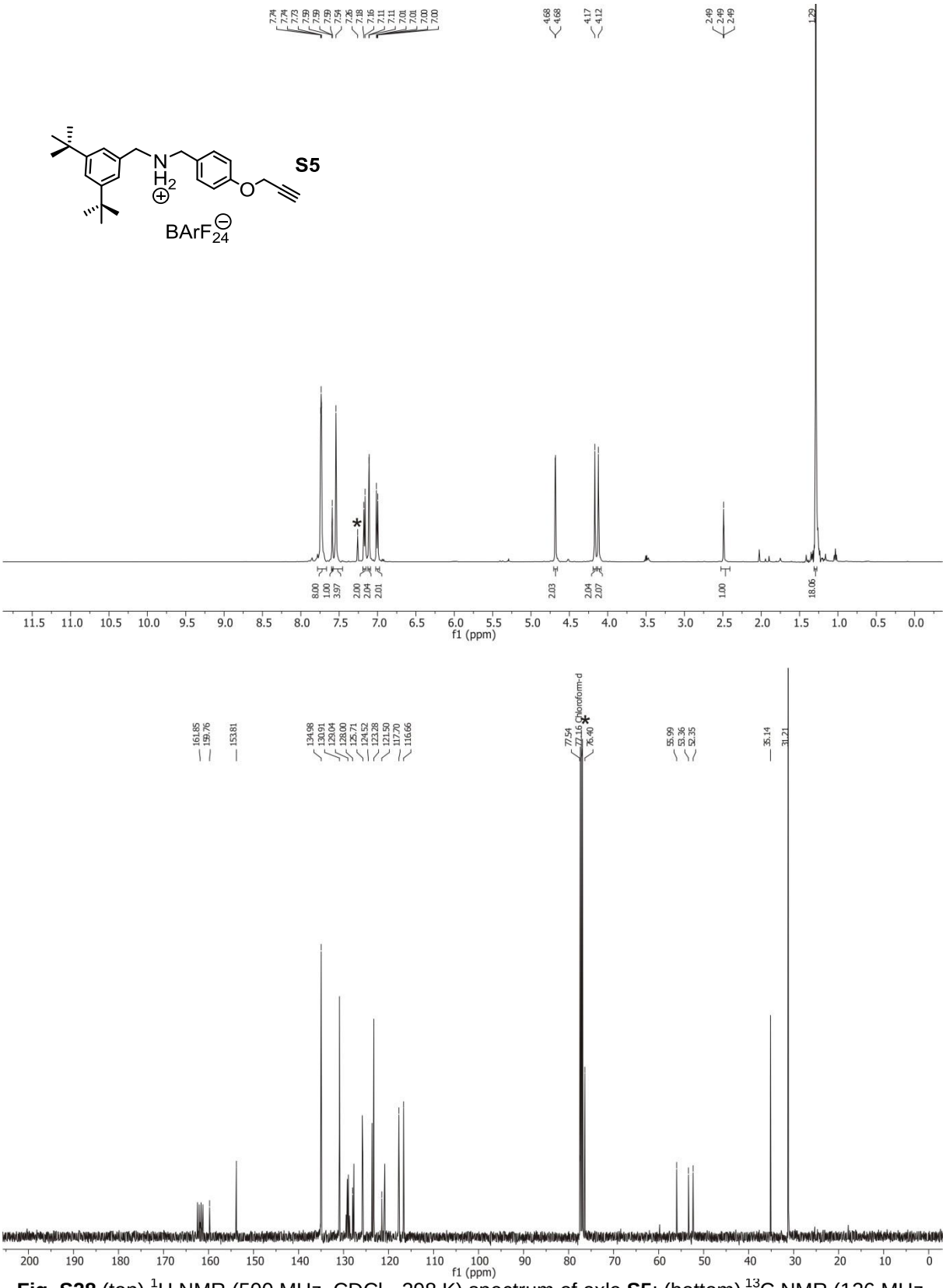


Fig. S28 (top) ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of axle **S5**; (bottom) ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of axle **S5**.

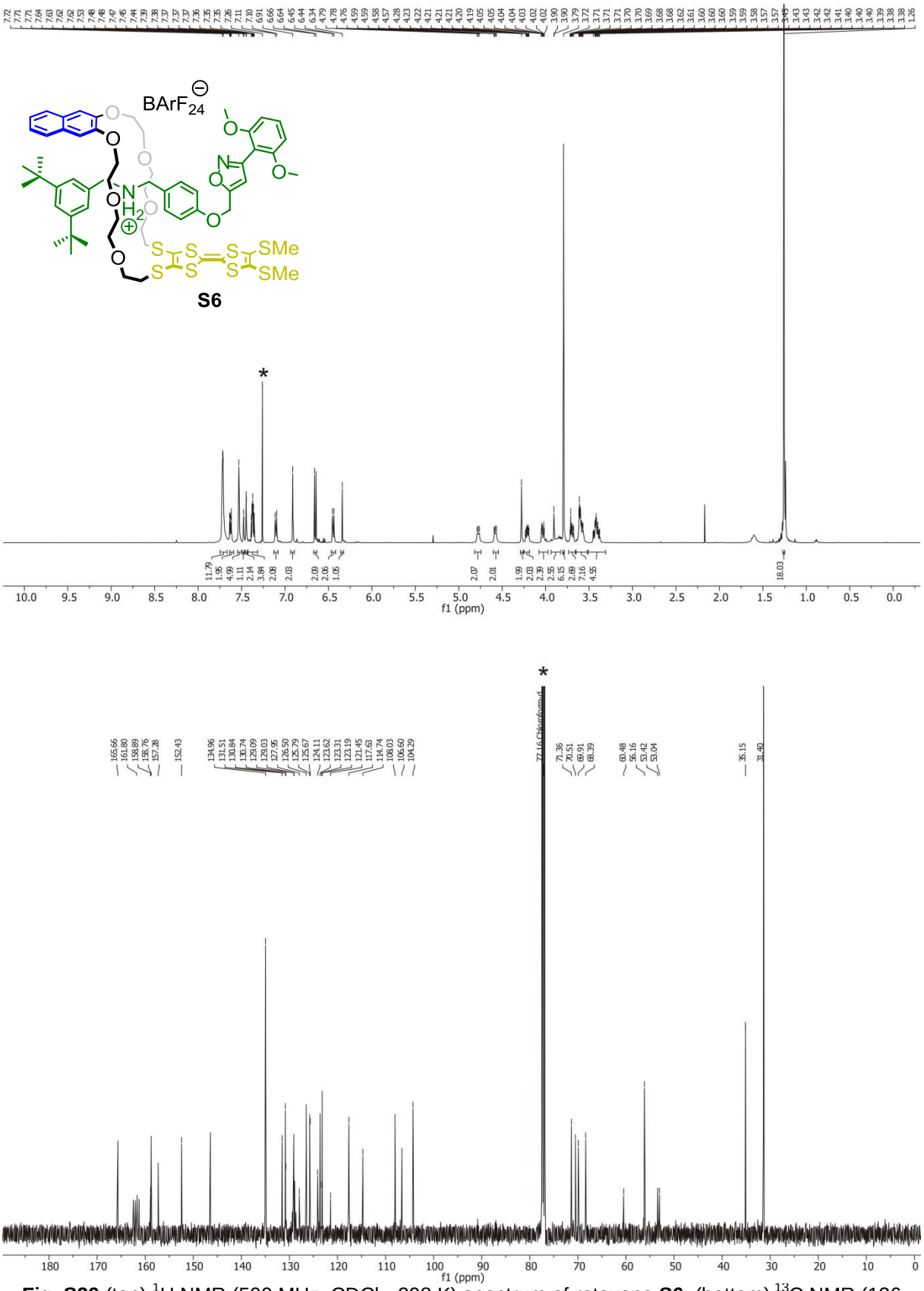


Fig. S29 (top) ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of rotaxane **S6**; (bottom) ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of rotaxane **S6**.

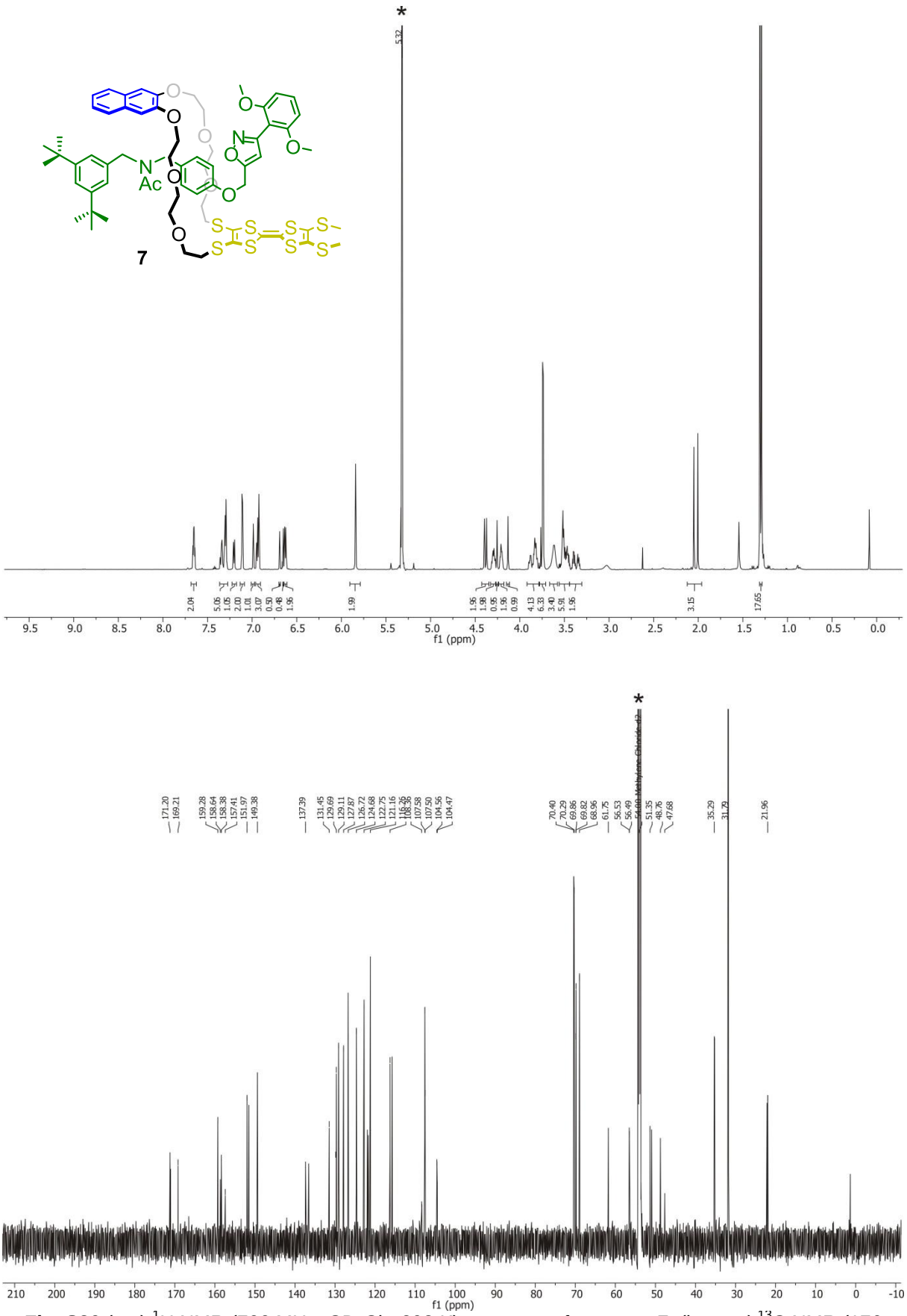


Fig. S30 (top) ^{1}H NMR (700 MHz, CD_2Cl_2, 298 K) spectrum of rotaxane **7**; (bottom) ^{13}C NMR (176 MHz, CD_2Cl_2, 298 K) spectrum of rotaxane **7**.

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