Supplementary Information for

A Compact Chemically Driven Catenane Rotary Motor Operated through Alternate Pumping and Discharging

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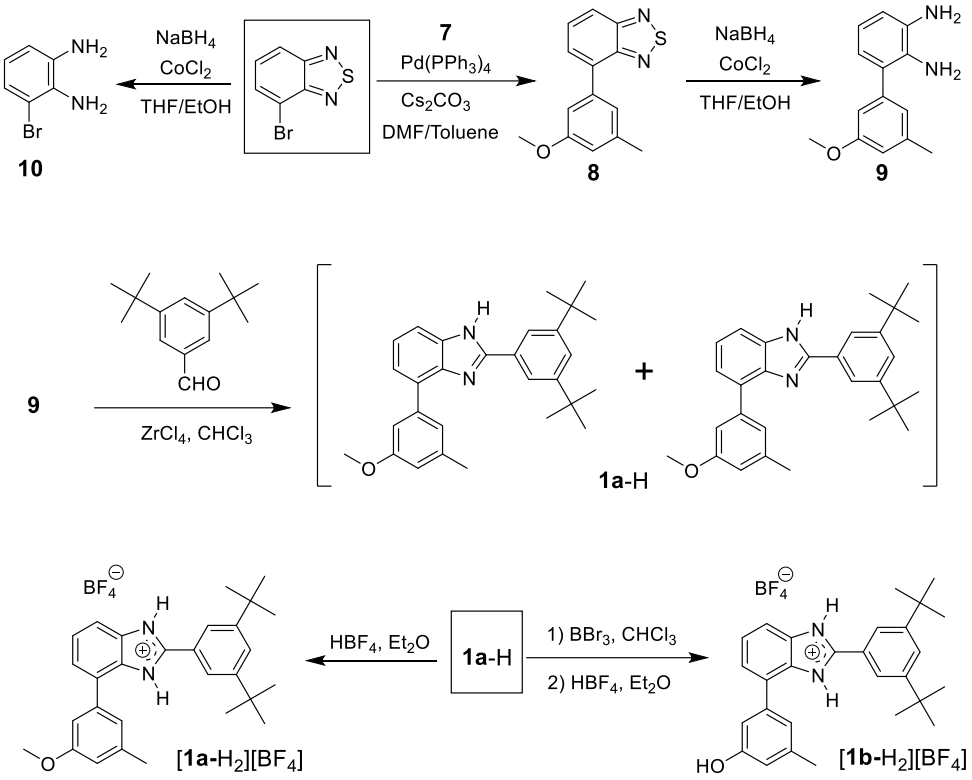
Section A. Materials and general methods

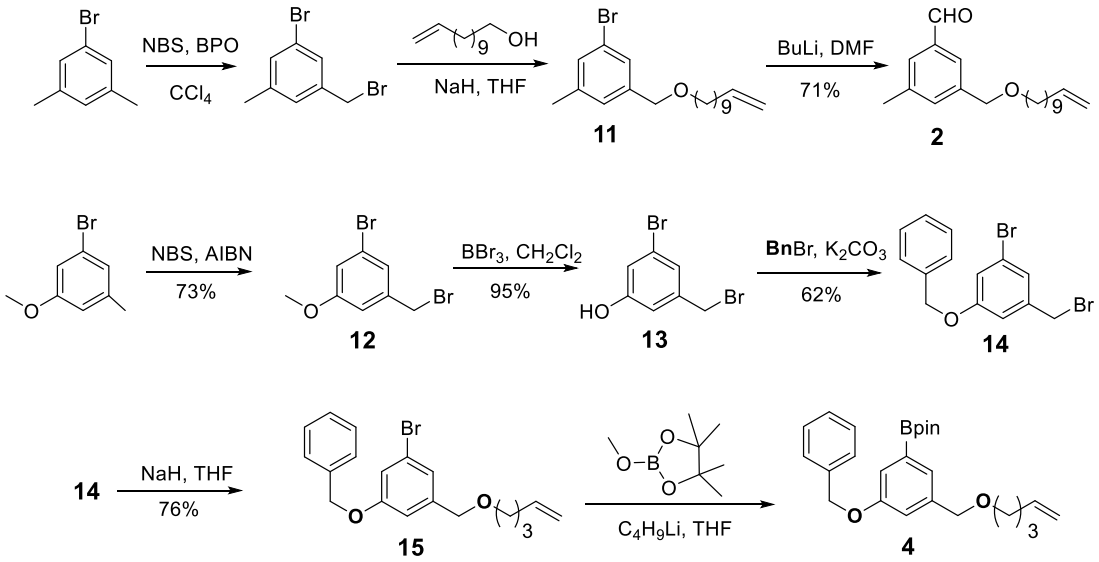
4-Bromo-2,1,3-benzothiadiazole[1], 3-Bromo-1,2-benzenediamine (**10**)[1], 1-Bromo-3-(bromomethyl)-5-methyl-benzene[2], 1-bromo-3-methyl-5-((undec-10-en-1-yloxy)methyl)benzene (**11**)[3], **24C6-pre**[4] and **24C6**[5] were synthesized according to literature. Tetrahydrofuran (THF), dichloromethane (DCM), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), toluene and dioxane were degassed and dried under nitrogen by passing them through a Vigor VSGS-5 Solvent Purification System. 1-Bromo-3-methoxy-5-methylbenzene, 5-bis(trifluoromethyl)phenol, 4-bromobenzaldehyde, 4,7-diphenylbenzo[c][1,2,5]thiadiazole, 3,5-dimethylbenzaldehyde, pentaethylene glycol, bis(pinacolato)diboron, 2-isopropylboronic acid pinacol ester, 11-Bromo-1-undecanol, 10-undecen-1-ol iso-propoxyboronic acid pinacol ester, Grubbs' catalyst 1st generation, tetrakis(triphenylphosphine)-palladium and deuterated solvents were obtained from commercial suppliers and used without further purification unless stated otherwise. Solution ^{1}H, ^{13}C, COSY and NOESY NMR spectra were recorded on a JEOL 400YH instrument or Bruker AVANCE IIIT 400HD instrument. All peak positions are listed in ppm relative to peak of deuterated solvents. Column chromatography was performed using Silicycle Ultra Pure Silica Gel (200–300 mesh). ESI/APCI-MS data were carried out on an Advion Expression^{L} CMS instrument or a Thermo Fisher Scientific LTQ Orbitrap Elite LC/MS (ESI). MALDI-TOF MS experiments were carried out on a Bruker ultraflex matrix assisted laser desorption-ionization TOF mass spectrometer. Single crystal X-ray diffraction analysis was performed on an Agilent Sapphire3 Gemini Ultra diffractometer.

Section B. Synthesis of compounds

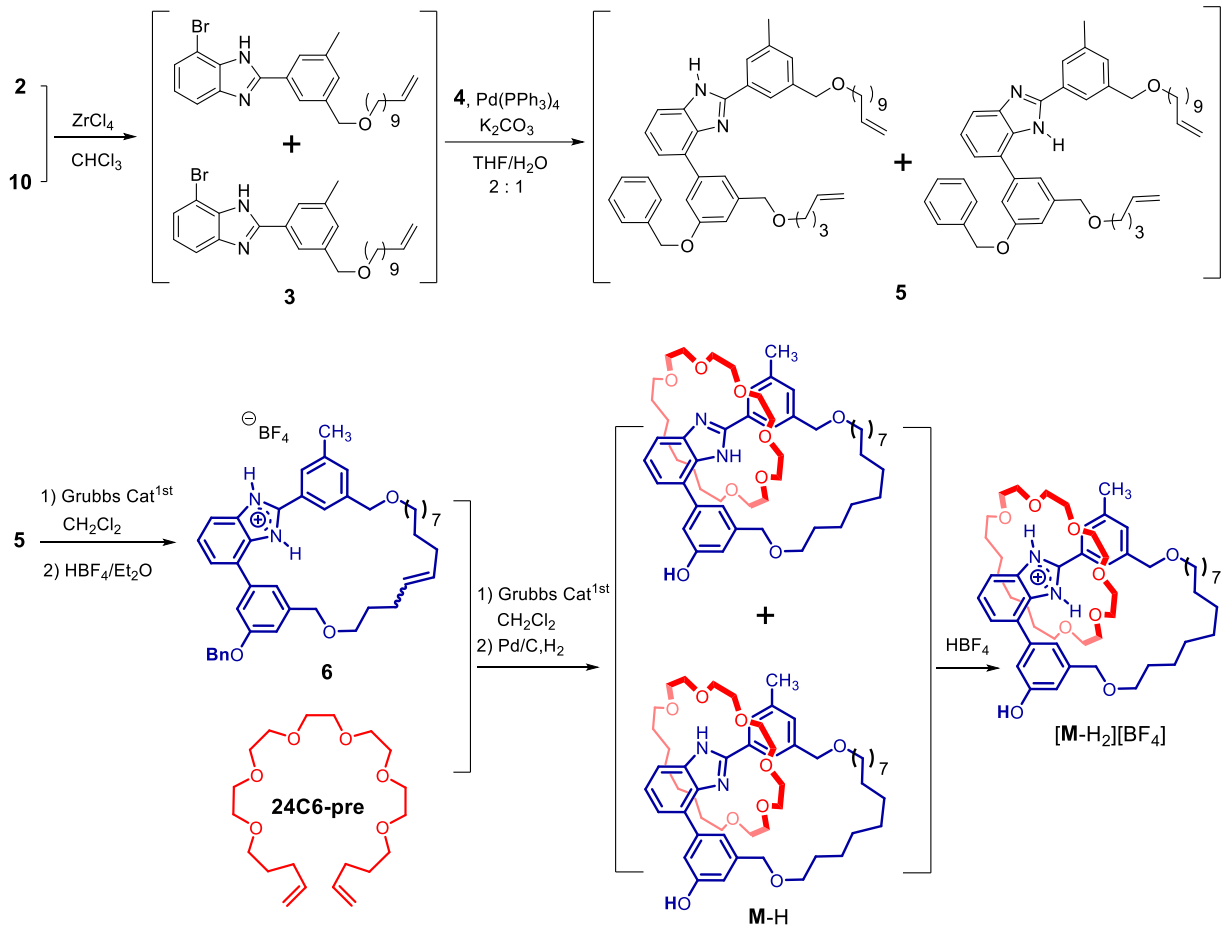
Scheme S1. Synthesis of [**1a**-H][BF_4], [**1b**-H][BF_4] and compound **10**.



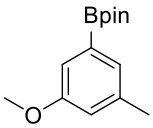
Scheme S2. Synthesis of the key building blocks **2** and **4**.



Scheme S3. Synthesis of the [2]catenane [**M**-H_2][BF_4].



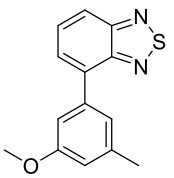
Synthesis of 3-methyl-5-methoxyphenyl(pinacolato)borane (7)



Dioxane was added to a 100-mL Schlenk flask and bubbled with nitrogen for 10 minutes. The mixture of 1-bromo-3-methoxy-5-methylbenzene (1.0 g, 4.97 mmol), bis(pinacolato)diboron (1.4 g, 5.47 mmol) and potassium acetate (1.46 g, 14.92 mmol) were added in solvent under Nitrogen atmosphere. Pd(dppf)Cl_2 dichloromethane complex (203 mg, 0.25mmol) was added and the reaction mixture was heated at 80 ℃ overnight. the reaction mixture was cooled to room temperature and filtered. The combined filtrate was dried on a rotavapor to give a solid mixture which was purified by flash column chromatography with Petroleum ether. Yield: 1.12 g, 91%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.24 (s, 1H), 7.13 (d, J = 2.5 Hz, 1H), 6.83 (s, 1H), 3.82 (s, 3H), 2.33 (s, 3H), 1.35 (s, 13H). ^{13}C NMR (101 MHz, Chloroform-d) δ 159.3, 139.0, 128.1, 118.9, 115.6, 83.9, 77.4, 77.1, 76.8, 55.3, 24.9, 21.3. HR-MS (APCI): calcd for $[M + H]^+$, $[C_{14}H_{22}BO_3 + H]^+$,

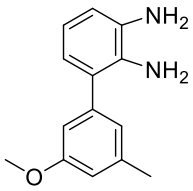
m/z =249.1657, found m/z = 249.1656.

Synthesis of 4-(3-methoxy-5-methylphenyl)benzo[c][1,2,5]thiadiazole (8)



4-Bromo-2,1,3-benzothiadiazole (500 mg, 2.33 mmol), **7** (692 mg, 2.79 mmol), tetra(triphenylphosphine)palladium (134 mg, 5% mmol), Cesium hydrogen carbonate (2.26 g, 6.97 mmol), DMF (10 mL), and toluene (10 mL) were added to a 100-mL Schlenk flask under nitrogen atmosphere. After refluxing overnight, the reaction mixture was cooled to room temperature and filtered. The solvents were taken off under vacuum and the crude product was purified by flash column chromatography (SiO_2, Petroleum ether /dichloromethane, v/v=3:1). The pure product **8** is a yellow solid. Yield: 510 g, 87%. ^{1}H NMR (400 MHz, chloroform-d) δ 7.99 (dd, J = 6.8, 3.1 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.29 (s, 2H), 6.83 (s, 1H), 3.88 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8, 155.7, 153.6, 139.7, 138.6, 134.7, 129.7, 127.8, 122.6, 120.6, 114.9, 112.3, 77.5, 77.1, 76.8, 55.4, 21.9. HR-MS (ESI): calcd for [**M** + H]$^+$, $[C_{14}H_{13}N_2S]^+$, *m*/*z* =257.0743, found *m*/*z* = 257.0742.

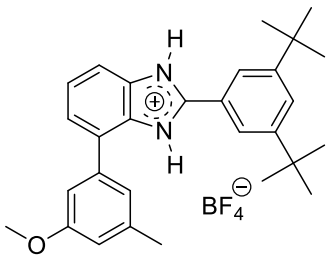
Synthesis of 3'-methoxy-5'-methyl-[1,1'-biphenyl]-2,3-diamine (9)



The compound **8** (509 mg, 1.98 mmol) was dissolved in 60 mL of ethanol/THF (v:v = 3:1) and sodium borohydride (224 mg, 5.94 mmol) was added at room temperature in small portions. $CoCl_2$•$6H_2O$ (47 mg, 10 mol%) was then added and the mixture was stirred at reflux and monitored by TLC. The reaction was completed after 2 h and the mixture was cooled down to room temperature, filtered and concentrated under vacuum. The crude product was extracted twice with ethyl acetate (20 ml) and water (20 ml). The combined organic phases were dried over magnesium sulfate and concentrated to give the crude product, which was purified by flash column chromatography (SiO2, Petroleum ether /dichloromethane, v/v=1:1). The pure product **9** is a pale yellow sticky substance. Yield: 245 mg, 54%. ^{1}H NMR (400 MHz, Chloroform-d) δ 6.85 (s, 1H), 6.79 (s, 1H), 6.73 (p, J = 4.5 Hz, 4H), 3.82 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 140.9, 140.0, 134.8, 132.4, 129.5, 122.5, 121.7, 119.5, 115.9,

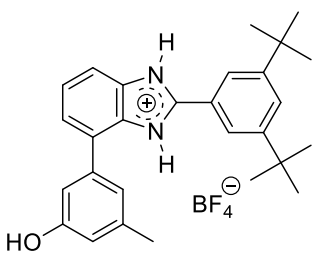
113.9, 111.6, 77.4, 77.12, 76.8, 55.4, 21.7. HR-MS (ESI): calcd for [**M** + H]$^+$, [$C_{14}H_{17}N_2O$]$^+$, *m*/*z* =229.1335, found *m*/*z* = 229.1335.

Synthesis of [**1a**-H_2][BF_4]



The compound **9** (200 mg, 0.88 mmol) and 3,5-di-tert-butylbenzaldehyde (173 g, 0.88 mmol) were dissolved in chloroform (30 mL) and zirconium tetrachloride (31 mg, 0.13 mmol) was added to the solution. The resulted solution was stirred at room temperature for 24 hr and then quenched with triethylamine. The combined filtrate was dried on a rotavapor to give the neutral product which was purified by flash column chromatography (SiO_2, Petroleum ether /dichloromethane, 1:1 v/v). Yield: 344 mg, 89% as a tautomer (**1a**-H). **1a**-H (344 mg, 0.78 mmol) was dissolved in diethyl ether (15 mL) and added with tetrafluoroboric acid diethyl ether complex (86 mg, 0.79 mmol) slowly. After being stirred for 30 min at room temperature, the resulted solid was collected by evaporating the solvent. Yield: 400 mg, 88% for two steps. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.85 (d, *J* = 1.6 Hz, 2H), 7.75 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.01 (s, 1H), 6.91 (s, 1H), 6.87 (s, 1H), 3.87 (s, 3H), 2.45 (s, 3H), 1.37 (s, 19H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.4, 153.6, 150.7, 141.3, 128.1, 127.4, 126.7, 122.5, 121.7, 115.2, 114.7, 111.5, ,77.3, 55.6, 35.4, 31.2, 21.8. HR-MS (APCI): calcd for [**M** – BF_4]$^+$, [$C_{29}H_{35}N_2O$]$^+$, *m/z* = 427.2744, found *m/z* = 427.2742.

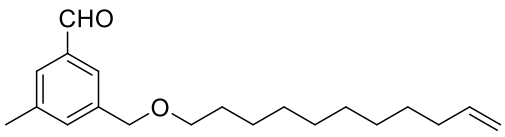
Synthesis of [**1b**-H_2][BF_4]



The compound **1a**-H (150 mg, 0.292 mmol) was dissolved in dichloromethane (15 ml) under nitrogen atmosphere. The reaction system was cooled to 0 °C and stirred for 10 minutes, followed by a dropwise addition of BBr_3 (1.0 mol/L in dichloromethane) (0.35 ml, 0.35 mmol). The reaction mixture was stirred at 0 °C for 30min, then transferred to room temperature and stirred overnight. The reaction was then quenched with water (20 ml), extracted with THF (20 ml), and washed with saturated sodium bicarbonate solution (20 ml) two times. The combined

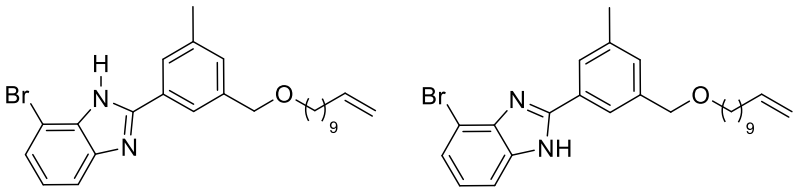
organic phases were dried over magnesium sulfate and concentrated to give pure **1b** as a beige solid. The isolated neutral product (mixture of tautomers) (120 mg, 0.292 mmol) was dissolved in 20 mL of diethyl ether/THF (v: v = 4:1) and added with tetrafluoroboric acid diethyl ether complex (52 mg, 0.321 mmol) slowly. After being stirred for 30 min at room temperature, the resulted solid was filtered and air-dried. Yield: 130 mg, 89%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 2H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.70 (s, 1H), 7.43 (q, *J* = 7.7, 6.5 Hz, 2H), 7.08 (s, 1H), 6.80 (s, 1H), 6.42 (s, 1H), 2.24 (s, 3H), 1.31 (s, 19H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 157.6, 153.0, 151.2, 140.9, 137.0, 131.8, 129.8, 129.3, 128.6, 127.0, 126.4, 123.3, 121.9, 121.2, 117.4, 116.4, 113.0, 112.6, 35.1, 30.4, 20.6. HR-MS (APCI): calcd for [**M** – BF_4]$^+$, $[C_{28}H_{33}N_2O]^+$, *m/z* = 413.2587, found *m/z* = 413.2585.

Synthesis of 3-methyl-5-((undec-10-en-1-yloxy)methyl)benzaldehyde (2)



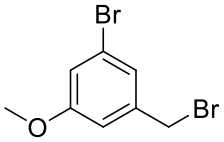
The substrate **11** (3.1 g, 7.65 mmol) was dissolved in dry THF (20 mL) and added to a 100-mL Schlenk flask under nitrogen atmosphere. The reaction system was placed in -78 °C and stirred for 20 minutes. Followed by dropwise addition of N-butyllithium (1.6M in hexane) (8.2 mL, 13.2 mmol). After being stirred for 40 minutes, Dry DMF (1.52 mL, 20.74 mmol) was added slowly. After being stirred for 3 hours, the reaction system was quenched with water under -78 °C. The combined solution was dried under vacuum and the mixture was extracted with dichloromethane and water two times, and the extract was dried over sodium sulfate. The solvent was removed to get crude product which was purified by flash column chromatography (SiO_2, dichloromethane/ hexane, 1/1 v/v). Yield: 1.12g, 41%. 2.2 g, 83%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.64 (s, 1H), 7.60 (s, 1H), 7.43 (s, 1H), 5.80 (td, *J* = 16.9, 6.7 Hz, 1H), 5.02 – 4.89 (m, 2H), 4.52 (s, 2H), 3.49 (t, *J* = 6.7 Hz, 2H), 2.43 (s, 3H), 2.06 – 2.00 (m, 2H), 1.66 – 1.58 (m, 2H), 1.38 – 1.26 (m, 15H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.6, 139.9, 139.3, 139.2, 136.7, 134.4, 129.3, 126.3, 114.2, 77.4, 77.1, 76.8, 72.2, 71.0, 33.9, 29.8, 29.6, 29.5, 29.5, 29.2, 29.0, 26.2, 21.2. HR-MS (APCI): calcd for [**M**]$^+$, $[C_{20}H_{30}O_2]^+$, *m/z* = 302.2251, found *m/z* = 302.2246.

Synthesis of the compound 3



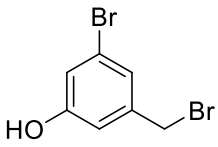
Compound **3** was obtained according to the synthesis method of **1a**-H. Yield: 335 mg, 80%. **NOTE**: compound 3 presents as a mixture of two tautomers. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.78 (s, 1H), 7.61 (s, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.26 (s, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 5.80 (td, *J* = 16.9, 6.7 Hz, 1H), 5.03 – 4.88 (m, 2H), 4.51 (s, 2H), 3.50 (t, *J* = 6.7 Hz, 2H), 2.37 (s, 3H), 2.02 (q, *J* = 8.1, 6.8 Hz, 2H), 1.67 – 1.59 (m, 2H), 1.39 – 1.26 (m, 13H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.1, 139.6, 139.3, 139.2, 130.8, 129.2, 126.9, 125.8, 123.9, 123.1, 114.2, 72.6, 71.1, 33.9, 29.8, 29.6, 29.6, 29.5, 29.2, 29.0, 26.3, 21.4. HR-MS (APCI): calcd for [**M** + H]$^{+}$, $[C_{26}H_{34}BrN_2O]^{+}$, *m/z* =469.1849, found *m/z* = 469.1845.

Synthesis of the compound 1-Bromo-3-(bromomethyl)-5-methoxybenzene (12)



The mixtures of 1-bromo-3-methoxy-5-methylbenzene (5.0 g, 24.87 mmol)，NBS (4.43 g, 24.87 mmol), and AIBN (408 mg, 2.49 mmol) were dissolved in CCl_4 of 60mL. After heating to reflux at 90 ℃ for overnight. the reaction mixture was cooled to room temperature and filtered. The solvent was dried under vacuum. The solid was extracted with dichloromethane and water twice, and the combined filtrate was dried on a rotavapor to give a crude product which was purified by flash column chromatography (SiO_2, Petroleum ether). The pure product is a colorless liquid. Yield: 5.1 g，73%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (t, *J* = 1.6 Hz, 1H), 7.00 – 6.97 (m, 1H), 6.87 – 6.83 (m, 1H), 4.38 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.5, 140.6, 124.4, 123.0, 117.3, 113.9, 55.7, 32.2. HR-MS (APCI): calcd for $[M]^{+}$, $[C_8H_8Br_2O]^{+}$, m/z = 277.8942, found m/z = 277.8940.

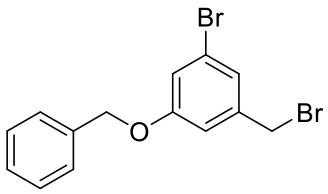
Synthesis of 3-bromo-5-(bromomethyl)phenol (13)



The compound **12** (3.8 g, 21.1 mmol) was dissolved in dichloromethane (60 ml) under nitrogen atmosphere. The reaction system was cooled to 0 °C and stirred for 10 minutes, followed by a dropwise addition of BBr_3 (1.0 mol/L in dichloromethane) (23.2 ml, 23.2 mmol). The reaction mixture was stirred at 0 °C for 30min, then transferred to room

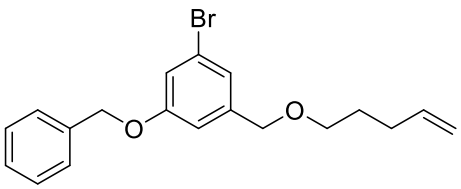
temperature and stirred overnight. The reaction was then quenched with water (20 ml), extracted with THF (20 ml), and washed with saturated sodium bicarbonate solution (20 ml) two times. The combined organic phases were dried over magnesium sulfate and concentrated to give pure compound **13** as a white solid. Yield: 3.62 g, 95%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 (s, 1H), 6.94 (s, 1H), 6.80 (s, 1H), 5.37 (s, 1H), 4.36 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.50, 140.94, 124.60, 122.93, 118.96, 115.08, 31.86. HR-MS (ESI): calcd for [**M** - H]$^{-}$, [$C_7H_5Br_2O$]$^{-}$, *m/z* =262.8713, found *m/z* = 262.8708.

Synthesis of the compound 14



The mixtures of the compound **13** (3.62 g, 13.6 mmol) and (bromomethyl)benzene (13 g, 136 mmol) were dissolved in acetonitrile of 100mL. Then Potassium carbonate (18.8 g, 136 mmol) was added to the mixture. After heating to reflux at 90 ℃ for overnight. the reaction mixture was cooled to room temperature and filtered. The filter residue was washed with acetonitrile, and the solvent was dried under vacuum. The solid was extracted with dichloromethane and water, and the combined filtrate was dried on a rotavapor to give a crude product which was purified by flash column chromatography (SiO_2, Petroleum ether). The pure product is a colorless liquid. Yield: 3.01 g，62%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.32 (m, 5H), 7.15 (s, 1H), 7.08 (s, 1H), 6.94 (s, 1H), 5.04 (s, 2H), 4.38 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.7, 140.7, 136.1, 128.8, 128.4, 127.7, 124.7, 123.0, 118.2, 114.7, 70.4, 32.2. HR-MS (APCI): calcd for [M + H]$^{+}$, [$C_{14}H_{13}BrO$]$^{+}$, m/z = 356.9307, found m/z = 356.9307.

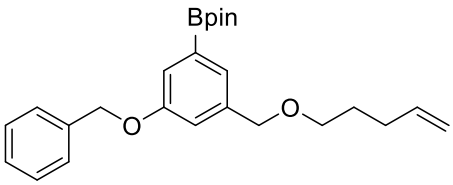
Synthesis of the compound 15



Sodium hydride (610 mg, 15.22 mmol) was added to a Schlenk flash under nitrogen. 40 mL of dry tetrahydrofuran was added and cooled to 0℃. Subsequently, 4-Penten-1-ol (1.1 g, 12.68 mmol) was added. After being stirred for 20 minutes, the reaction mixture was heated to room temperature for 1 hour. Followed by a dropwise addition of **14**

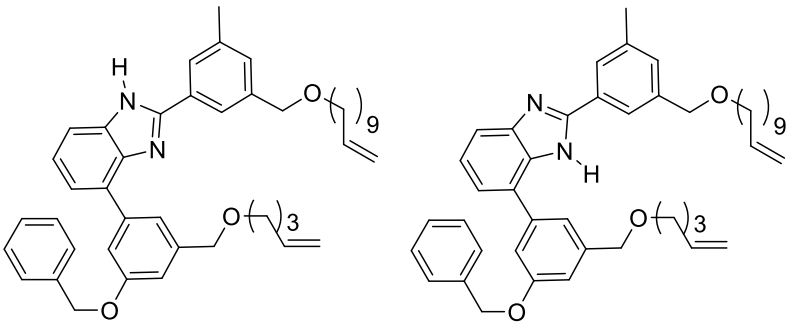
(3.01 g, 8.454 mmol) which was dissolved in 10 mL of dry tetrahydrofuran. The reaction was stirred continuously for 4 hr. Ice water was slowly added to quench excess sodium hydride. the combined solution was dried under vacuum and the mixture was extracted with hexanes, and the extract was dried over sodium sulfate. The solvent was removed to get crude product which was purified by flash column chromatography (SiO_2, hexane). The pure product is light yellow oil. Yield: 2.80 g, 76%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.32 (m, 5H), 7.09 (s, 1H), 7.06 (s, 1H), 6.91 (s, 1H), 5.90 – 5.78 (m, 1H), 5.10 – 4.96 (m, 4H), 4.44 (s, 2H), 3.47 (t, *J* = 6.5 Hz, 2H), 2.19 – 2.12 (m, 2H), 1.80 – 1.69 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.7, 142.1, 138.3, 136.5, 128.8, 128.3, 127.6, 123.1, 122.8, 117.2, 115.0, 112.9, 77.5, 77.1, 76.8, 72.1, 70.3, 70.1, 30.4, 29.0. HR-MS (APCI): calcd for $[M + H]^+$, $[C_{19}H_{22}BrO_2]^+$, m/z = 361.0798, found m/z = 361.0797.

Synthesis of the compound 4



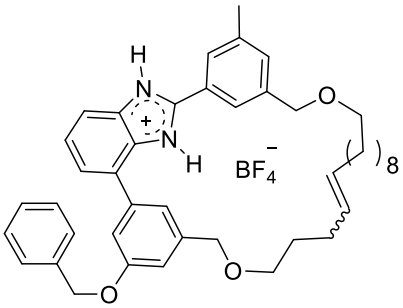
The compound **15** (2.70 g, 7.58 mmol) was dissolved in dry THF (30 mL) and added to a 100-mL Schlenk flask under nitrogen atmosphere. The reaction mixture was placed in a –78 °C cold bath and stirred for 20 minutes, followed by a dropwise addition of *N*-butyllithium (1.6 M in hexane) (7 Ml, 11.2 mmol). After being stirred for 40 minutes, isopropoxyboronic acid pinacol ester (2.5 g, 13.6 mmol) was added slowly. After being stirred for 1 hour, the reaction mixture was raised to room temperature slowly and stirred overnight. After quenched with water, solvents were removed under vacuum and the residue was extracted with dichloromethane and water twice. The extract was dried over sodium sulfate and concentrated to afford the desired product (Yield > 95%) which was subjected to the next step reaction without further purification.

Synthesis of the compound 5



The compound **3** (200 mg, 0.426 mmol), **4** (343 mg, 0.852 mmol), tetra(triphenylphosphine)Palladium (25 mg, 5% mmol), THF (30 mL), and sodium carbonate aqueous solution (15 mL, 2 M) were added to a 100-mL Schlenk flask under nitrogen atmosphere. After refluxing for 4 hours (**NOTE**: reaction time must be strictly controlled to avoid rearrangement of olefins), the reaction mixture was cooled to room temperature and extracted with dichloromethane and water twice. The combined organic phases were dried over magnesium sulfate. Removal of solvent of the filtrate under reduced pressure gave the crude product which was purified by flash column chromatography (SiO_2, CH_2Cl_2/petroleum ether, v/v=1:1). Yield: 245 mg, 86% as a tautomer. **NOTE**: the compound 5 presents as a mixture of two tautomers. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.75 (s, 1H), 7.80 – 7.76 (m, 3H), 7.47 (d, *J* = 7.2 Hz, 3H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.26 (m, 5H), 7.05 (s, 1H), 5.89 – 5.74 (m, 2H), 5.16 (s, 2H), 5.07 – 4.89 (m, 4H), 4.56 (s, 2H), 4.51 (s, 2H), 3.56 (t, *J* = 6.6 Hz, 2H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.41 (s, 3H), 2.21 – 2.11 (m, 2H), 2.08 – 2.00 (m, 2H), 1.76 (q, *J* = 7.0 Hz, 4H), 1.65 – 1.53 (m, 2H), 1.39 – 1.32 (m, 4H), 1.27 (d, *J* = 6.2 Hz, 8H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.16, 139.61, 139.33, 139.09, 138.22, 130.38, 129.80, 128.74, 128.19, 127.64, 126.79, 123.10, 114.99, 114.20, 113.37, 72.93, 72.63, 70.97, 70.30, 33.89, 30.42, 29.81, 29.63, 29.55, 29.53, 29.21, 29.04, 29.01, 26.24, 21.43. HR-MS (APCI): calcd for [**M** + H]$^+$, $[C_{45}H_{55}N_2O_3]^+$, *m/z* =671.4207, found *m/z* = 671.4208.

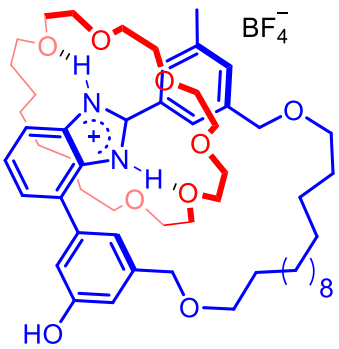
Synthesis of the compound [**6**-H_2][BF_4]



The compound **5** (153 mg, 0.23 mmol) was added to a 100-mL Schlenk flask. The flask was degassed and backfilled with N_2. Dichloromethane (45 mL) was added to the mixture under N_2. After bubbling for 10 min, Grubbs' catalyst^{1st} (19 mg, 10% mmol) was added. The mixture was heated at 43 °C for 24 hr. The reaction mixture was cooled to room temperature. All the solvent was removed on a rotavapor. The oily solid

was purified by flash column chromatography (SiO_2, dichloromethane/ hexane, v/v=1:1). The isolated neutral product (mixture of tautomeras) was dissolved in diethyl ether (20 mL) and added with tetrafluoroboric acid diethyl ether complex (39.2 mg, 0.21 mmol) slowly. After being stirred for 30 min at room temperature, the resulted solid was filtered and air-dried. Yield: 151 mg, 89%. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.85 (s, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.75 (s, 1H), 7.67 (t, J = 7.9 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.49 – 7.45 (m, 3H), 7.38 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.18 (s, 1H), 7.15 (s, 1H), 7.14 (s, 1H), 5.32 (q, J = 5.7 Hz, 2H), 4.53 (s, 4H), 3.52 (t, J = 6.3 Hz, 2H), 3.48 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H), 2.07 – 2.02 (m, 3H), 1.85 (q, J = 6.3, 5.8 Hz, 2H), 1.62 (p, J = 6.7 Hz, 2H), 1.55 (p, J = 6.6 Hz, 2H), 1.35 – 1.26 (m, 2H), 1.21 – 1.12 (m, 8H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 159.6, 140.2, 137.0, 133.9, 131.5, 130.8, 129.8, 128.7, 128.1, 127.8, 127.3, 126.8, 124.8, 122.0, 72.0, 71.3, 70.4, 69.9, 69.8, 67.9, 31.8, 29.3, 28.8, 27.9, 25.8, 22.3, 20.4. HR-MS (APCI): calcd for [**M** + H]$^+$, $[C_{43}H_{51}N_2O_3]^+$, m/z =643.3894, found m/z = 643.389.

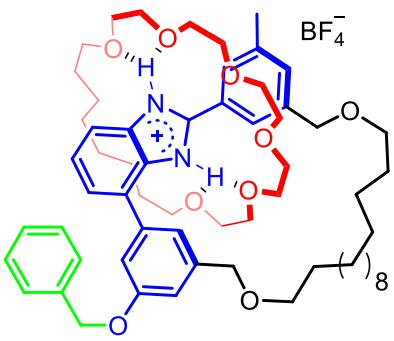
Synthesis of the compound [**M**-H_2][BF_4]



[**6**-H_2][BF_4] (600 mg, 0.82 mmol), pre-crown ether (618 mg, 1.64 mmol) were dissolved in dry dichloromethane under nitrogen atmosphere. After bubbling for 10 min, Grubbs' Catalyst^{1st} (78 mg, 10% mmol) was added. The resulted mixture was heated at 43 °C for 8 hr. Then another 78 mg of catalyst was added. The reaction mixture was heated for another 16 hr. The ^{1}H NMR monitoring shows that the pre-crown ethers were fully consumed. The reaction was stopped and added with triethylamine (5 mL). After the solvent was removed under vacuum, the residue was subjected to reduction directly. The mixture was dissolved in MeOH/THF (15 mL/15 mL) and added to a Schlenk flask charged with 10% Pd/C (100 mg, 15% mmol) under N_2 atmosphere. The flask was degassed and flushed with H_2 gas introduced via a balloon. The mixture was stirred for 4 h at room temperature and filtered through a Celite pad. Removal of the solvent afforded the crude product which was purified by flash column chromatography (SiO_2, dichloromethane/ methanol, v/v=9:1) to give the neutral product (320 mg, 0.323 mmol). After being dissolved in dichloromethane (30 mL), tetrafluoroboric acid diethyl ether complex (57 mg, 0.357

mmol) was slowly added and a precipitate was formed. After being stirred for 30 min, the solid was filtered and air-dried. Yield: 333 mg, 40%. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 13.24 (s, 1H), 12.88 (s, 1H), 9.17 (s, 1H), 8.11 (s, 1H), 8.01 (s, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.64 (t, J = 7.9 Hz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.46 (s, 1H), 7.10 (d, J = 9.0 Hz, 2H), 7.01 (s, 1H), 4.51 (s, 2H), 4.45 (s, 2H), 3.65 – 3.59 (m, 4H), 3.57 – 3.49 (m, 2H), 3.46 – 3.36 (m, 10H), 3.26 (d, J = 9.1 Hz, 4H), 3.17 (dd, J = 9.1, 5.3 Hz, 2H), 3.13 – 3.06 (m, 2H), 3.05 – 2.94 (m, 4H), 2.76 (dd, J = 11.1, 6.3 Hz, 2H), 2.46 (s, 3H), 1.52 (s, 4H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 158.5, 150.6, 141.5, 140.3, 139.2, 137.2, 133.2, 131.5, 129.8, 129.5, 129.0, 126.8, 126.6, 124.0, 72.2, 71.8, 71.5, 70.8, 70.6, 70.4, 70.2, 70.1, 67.4, 29.4, 29.4, 29.3, 28.8, 28.8, 28.6, 28.6, 28.0, 25.8, 25.7, 25.3, 25.0, 20.5. HR-MS (APCI): calcd for [**M** + H]$^{+}$, $[C_{54}H_{83}N_2O_9]^{+}$, *m/z* =903.6093, found *m/z* = 903.610.

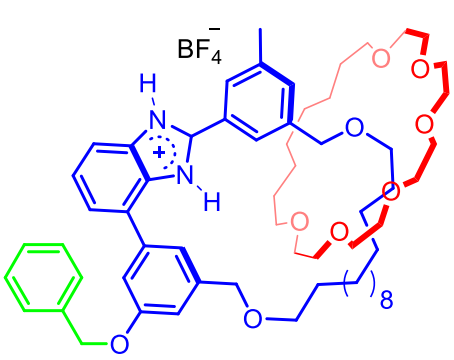
Synthesis of the compound [I-^{Bn}M-H$_2$][BF$_4$]



The mixtures of [**M**-H$_2$][BF$_4$] (190 mg, 0.21 mmol) and (bromomethyl)benzene (180 mg, 1.052 mmol) were dissolved in THF of 20mL. Then excessive Potassium carbonate (290 mg, 2.1 mmol) was added to the mixture. After being heated to reflux at 90 ℃ for overnight. TLC monitoring showed that the [**M**-H$_2$][BF$_4$] was depleted, and the reaction mixture was cooled to room temperature and filtered. The filter residue was washed with THF, and the solvent was dried under vacuum. The solid was extracted with dichloromethane and water, and the organic phase was dried on a rotavapor to give a crude product which was purified by flash column chromatography (SiO$_2$, ethyl acetate/ hexane, v/v=1:2) to give the neutral product (167 mg, 82%). After being dissolved in diethyl ether (30 mL), tetrafluoroboric acid diethyl ether complex (29 mg, 0.177 mmol) was slowly added and a precipitate was formed. After being stirred for 30 min, the solid was filtered and air-dried. Yield: 178 mg, 82%. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 13.11 (s, 1H), 12.53 (s, 1H), 8.36 (s, 1H), 7.88 (s, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.67 (s, 1H), 7.66 – 7.61 (m, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 6.9 Hz, 2H), 7.37 (t, J = 7.2 Hz, 2H), 7.32 (d, J = 8.5 Hz, 1H), 7.18 (s, 1H), 7.07 (s, 2H), 5.13 (s, 2H), 4.75 (s, 2H), 4.51 (s, 2H), 3.63 – 3.38 (m, 17H), 3.34 – 3.09 (m, 17H), 2.83 – 2.78 (m, 2H), 2.45 (s,

3H), 1.59 (dq, *J* = 27.2, 6.7 Hz, 4H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 159.1, 151.2, 142.3, 138.3, 137.1, 136.4, 131.6, 129.6, 129.0, 128.6, 128.1, 127.8, 127.3, 127.1, 126.9, 126.5, 71.8, 71.6, 71.3, 71.1, 70.4, 70.4, 70.3, 70.3, 70.2, 70.1, 70.0, 70.0, 34.9, 29.5, 29.3, 29.1, 28.6, 28.6, 28.4, 28.4, 28.3, 28.3, 25.9, 25.7, 25.5, 20.4. HR-MS (APCI): calcd for [**M** + H]$^+$, $[C_{61}H_{89}N_2O_9]^+$, *m/z* =993.6563, found *m/z* = 993.6562.

Synthesis of the compound [II-^{Bn}M-H_2][BF_4]



[**I-^{Bn}M**-H_2][BF_4] (80 mg, 0.074 mmol) and potassium *tert*-butoxide (5 eq) were dissolved in dry DMSO (10 mL) and heated to 100 °C under nitrogen atmosphere. After being stirred for 4 hours, the reaction mixture was cooled to room temperature. The solvent was removed under vacuum. The residue was extracted with dichloromethane and water twice. The combined organic phase was washed with brine once. Removal of the solvent gave the crude product which was purified by flash column chromatography (SiO_2, ethyl acetate/hexane, v/v=1:5). Acidify the neutral product (60 mg, 0.060 mmol, 81%) with tetrafluoroboric acid diethyl ether complex (13 mg, 0.081 mmol) in diethyl ether afforded the desired product. Yield: 62 mg, 78%. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 13.11 (s, 1H), 12.53 (s, 1H), 8.36 (s, 1H), 7.88 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.67 (s, 1H), 7.66 – 7.61 (m, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 6.9 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.18 (s, 1H), 7.07 (s, 2H), 5.13 (s, 2H), 4.75 (s, 2H), 4.51 (s, 2H), 3.63 – 3.38 (m, 16H), 3.34 – 3.09 (m, 17H), 2.83 – 2.78 (m, 2H), 2.45 (s, 3H), 1.65 – 1.53 (m, 4H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 159.1, 151.2, 142.3, 138.3, 137.1, 136.4, 131.6, 129.6, 129.0, 128.6, 128.1, 127.8, 127.3, 127.1, 126.9, 126.5, 71.8, 71.6, 71.3, 71.1, 70.4, 70.4, 70.3, 70.3, 70.2, 70.1, 70.0, 70.0, 34.9, 29.5, 29.3, 29.1, 28.6, 28.6, 28.4, 28.4, 28.3, 28.3, 25.9, 25.7, 25.5, 20.4. HR-MS (APCI): calcd for [**M** + H]$^+$, $[C_{61}H_{89}N_2O_9]^+$, *m/z* =993.6563, found *m/z* = 993.656.

Section C. Host-guest complexation of L-shaped axles with 24C6.

1. Host-guest complexation between [1a-H_2][BF_4] and 24C6

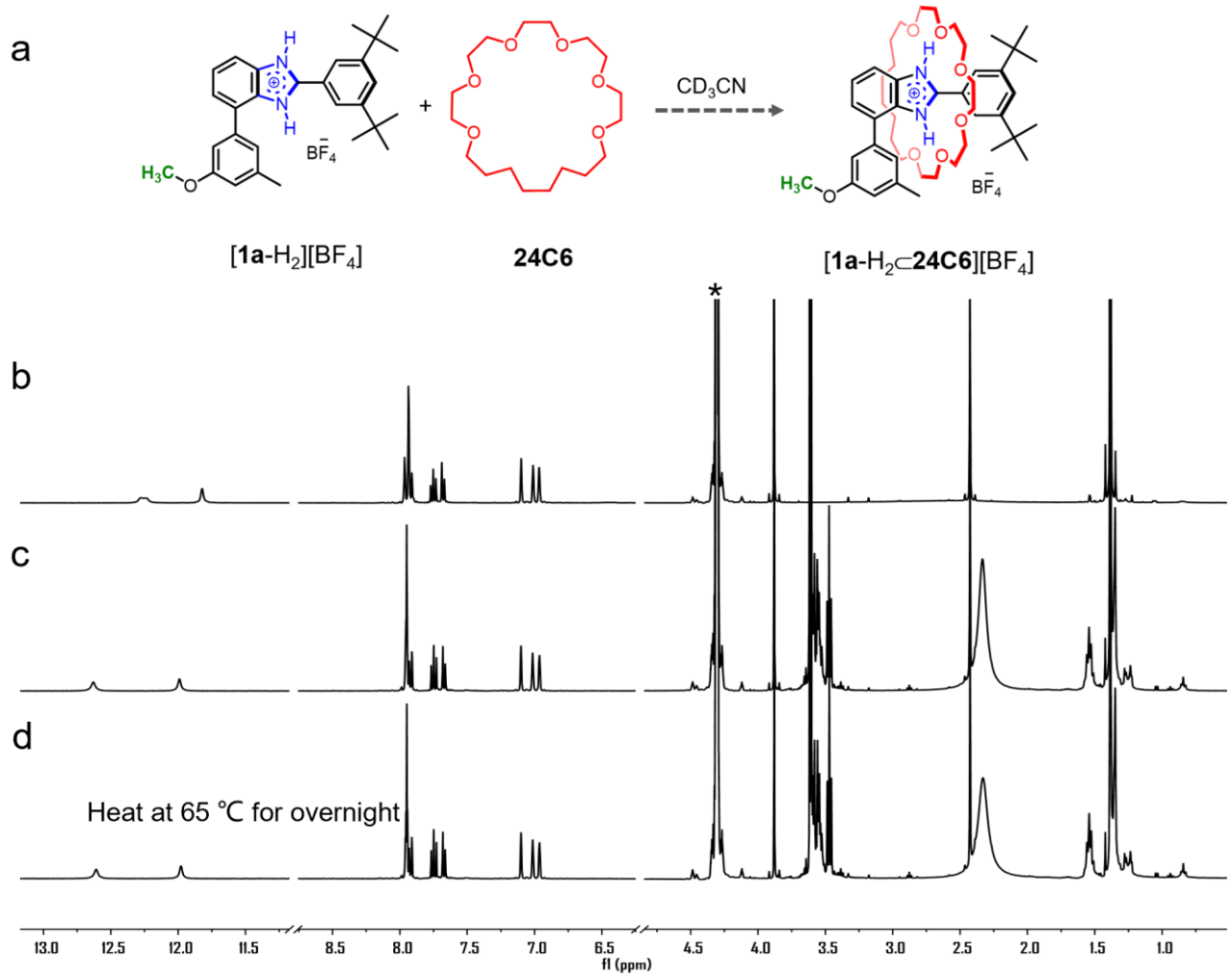


Figure S1. (a) Schematic representation of [2]pseudorotaxane formation between **24C6** and [**1a-H₂**][BF_4]. Partial ^{1}H NMR (400 MHz, CD_3NO_2, 298 K) spectra of [**1a-H₂**][BF_4] (b), an equimolar (2.0 mM) solution of [**1a**-H_2][BF_4] and **24C6** prepared at 25 ℃ (c), and (c) after heating at 65 ℃ overnight (d).

2. Host-guest complexation between [1b-H_2][BF_4] and 24C6

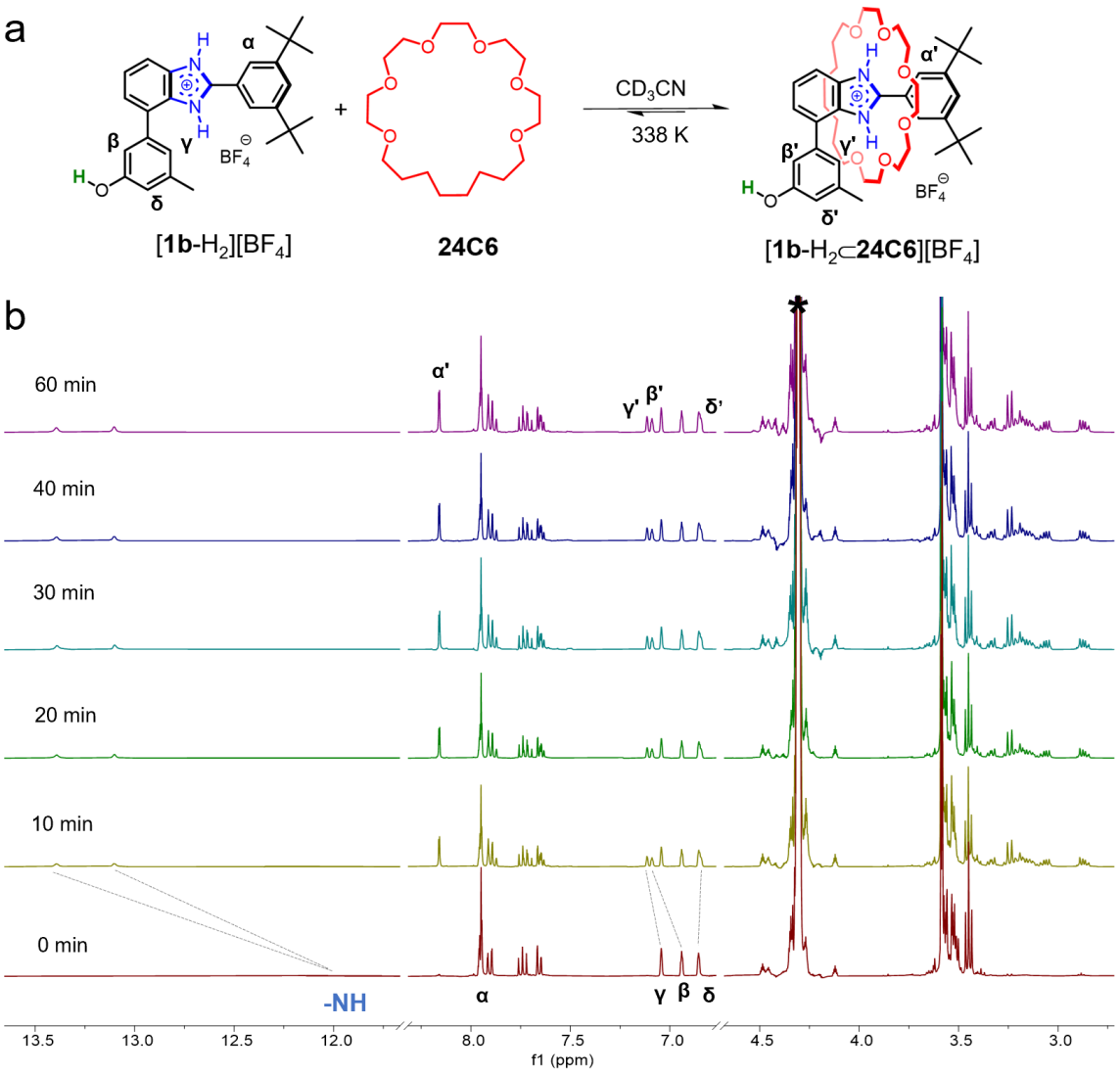


Figure S2. (a) Schematic representation of [2]pseudorotaxane formation between **24C6** and [**1b**-H_2][BF_4]. (b) Partial ^{1}H NMR spectra (400 MHz, 298 K) of an equimolar mixture of [**1b**-H_2]$^+$ and **24C6** in CD_3NO_2-d_3 over time upon heating at 338 K.

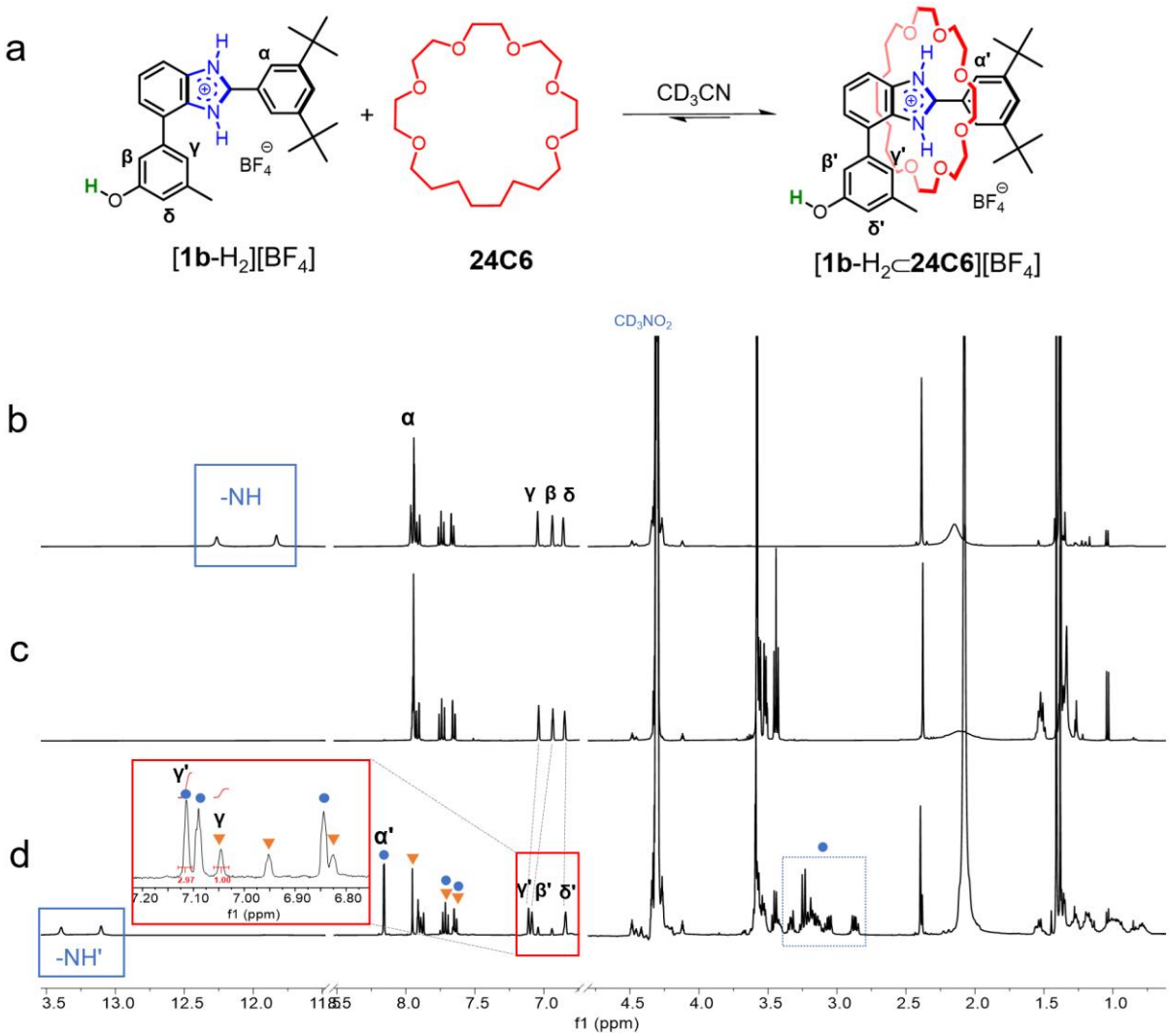


Figure S3. (a) Schematic representation of [2]pseudorotaxane formation between **24C6** and [**1b**-**H2**][BF_4]. Partial ^{1}H NMR (400 MHz, CD_3NO_2, 298 K) spectra of [**1b**-H_2][BF_4] (b), an equimolar (2.0 mM) solution of [**1b**-H_2][BF_4] and **24C6** (c), and (c) after heating at 65 ℃ for 48 hours (d). Resonances peaks of [2]pseudorotaxane [**1b**-H_2⊂**24C6**][BF_4] and free components were marked with circle and triangle, respectively. The association constant (*K*) was determined by a single-point method using the integral ratio of a probe proton. The *K* of [**1b**-H_2⊂**24C6**][BF_4] was calculated from the integral ratio of the H_γ to be 5890 M^{-1}.

Section D. Kinetics for ring translocation in the motor.

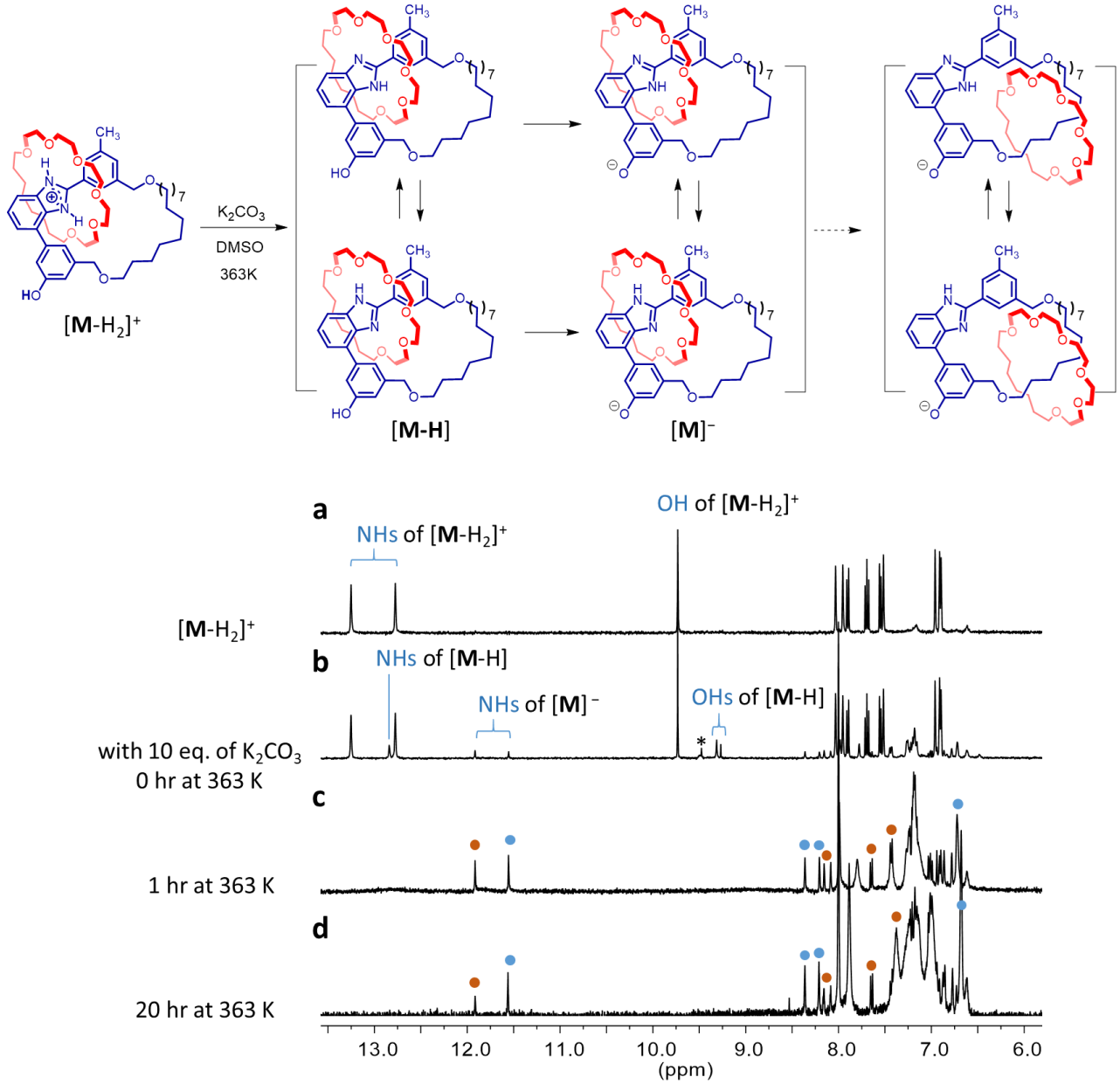


Figure S4. (Top) Schematic representation of deprotonation of [**M**-H_2][BF_4] in the presence of potassium carbonate. (Bottom) ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) spectra of [**M**-H_2][BF_4] (a), a mixture of [**M**-H_2][BF_4] with 10 equiv of potassium carbonate (b), (b) heated at 363K for 1hr (c), and (b) heated at 363K for 20 hr (d). After heating at 363K for 20 hr, the phenolic proton resonance peak disappeared while the benzimidazolium was deprotonated to benzimidazole. The phenolate [**M**]$^-$ presents as a tautomer with two NH proton signal recognizable. Further heating induces no translocation of the wheel but bias the ration of two isomers (orange and blue circles labelled) due to tautomerization. * impurity.

Kinetic analysis for transformation of [I-^{Bn}M]$^{-}$ to [II-^{Bn}M]$^{-}$

A mixture of [**I-^{Bn}M**-H_2][BF_4] and excess potassium *tert*-butoxide (5 eq) was dissolved in DMSO-d_6 (0.6 mL). ^{1}H NMR spectra were recorded after heating at 338 K for various time periods. As drawn from **Figure S6**, upon heating, the resonance signal (**g**) of [**I-^{Bn}M**]$^{-}$ at 8.22 ppm progressively decreases while that of [**II-^{Bn}M**]$^{-}$ at 7.11 ppm (signal **g'**) emerges. From the integral ratio of signal (**g**) to signal (**g'**), the conversion c([**I-^{Bn}M**]$^{-}$)/c_0([**I-^{Bn}M**]$^{-}$) was determined to be **g** / (**g** + **g'**). The reaction rate constant *k* obeys the pseudo-first-order kinetics and was described with the following equation:

$$-\mathrm{d}[c] = -k\,\mathrm{d}[c_0]\mathrm{d}t;$$

$$-\mathrm{d}[c]/\mathrm{d}t = -k\,\mathrm{d}[c_0];$$

$$\ln(c/c_0) = -k\,t.$$

Times *vs* ln(c/c_0) plot was drawn to determine the *k*. The half-life period $\tau_{1/2}$ of [**I-^{Bn}M**]$^{-}$ was estimated from the following equation:

$$\tau_{1/2} = \ln 2/k;$$

The energy barrier for the reaction was determined according to the following equation:

$$\Delta G^{\ddagger} = -RT\ln(kh/k_B T)$$

$\Delta G^{\ddagger}$: activation energy barrier

R: gas constant (8.31 $m^2 kg \cdot s^{-2} K^{-1} mol^{-1}$)

T: absolute temperature

k: reaction rate constant

h: Plank constant (6.63×10^{-34} m^2 kg•s^{-1})

K_B: Boltzmann constant (1.38×10^{-23} m^2 kg•s^{-2} K^{-1}).

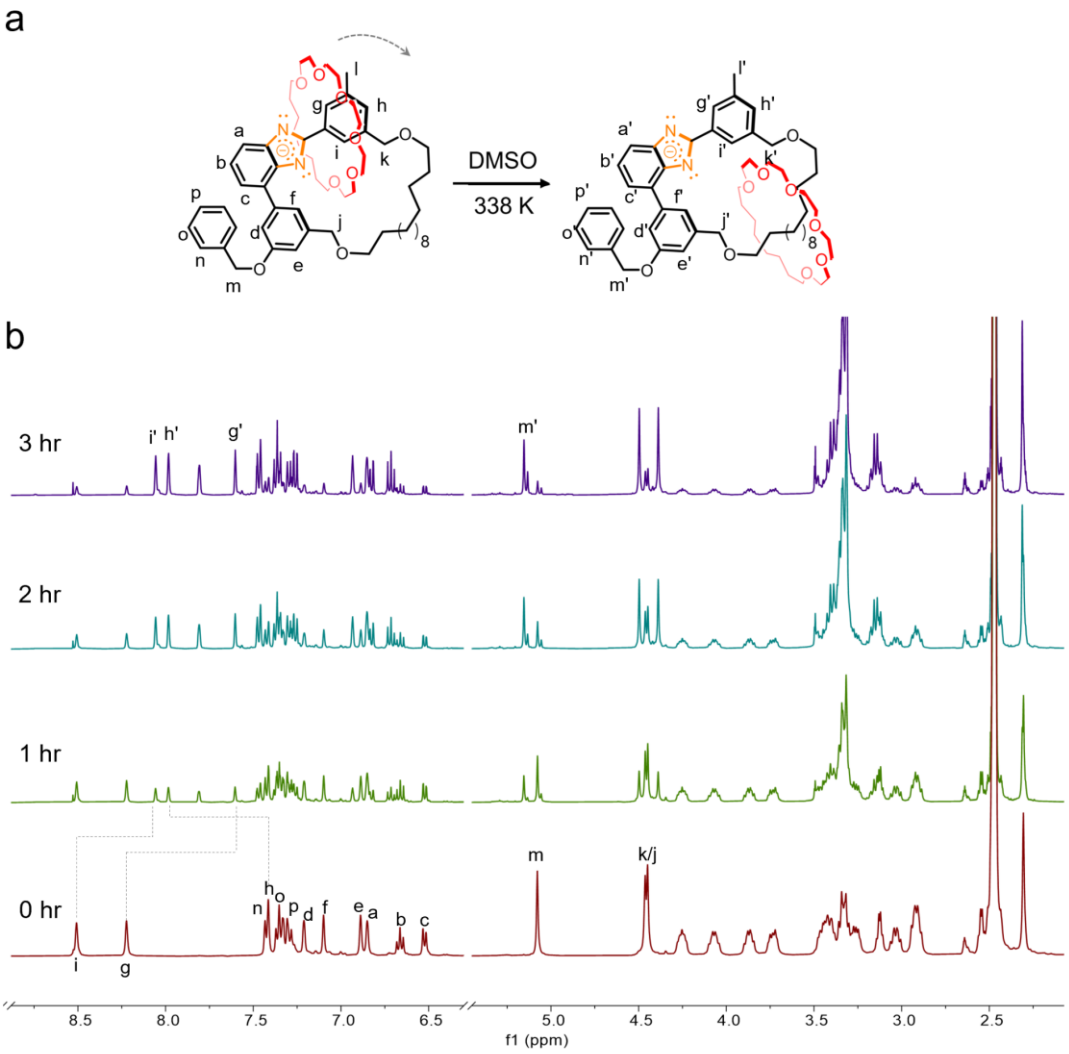


Figure S5. (a) Schematic representation of ring transportation with conversion [**I-^{Bn}M**]$^{-}$ to [**II-^{Bn}M**]$^{-}$. (b) A comparison of ^{1}H NMR spectra (400 MHz, 298 K) of a mixture of [**I-^{Bn}M**-H_2][BF_4] (5 mM) and *t*-BuOK (25 mM) in DMSO-d_6 over time upon heating at 338 K.

Table S1. Kinetic analysis for transformation of [**I**-^{Bn}**M**]$^{-}$ to [**II**-^{Bn}**M**]$^{-}$ (338 K, DMSO-d_6).

Time/h	c/c_0	$-\ln(c/c_0)$
0	1	0
1	0.629	0.464
2	0.340	1.079
3	0.199	1.615

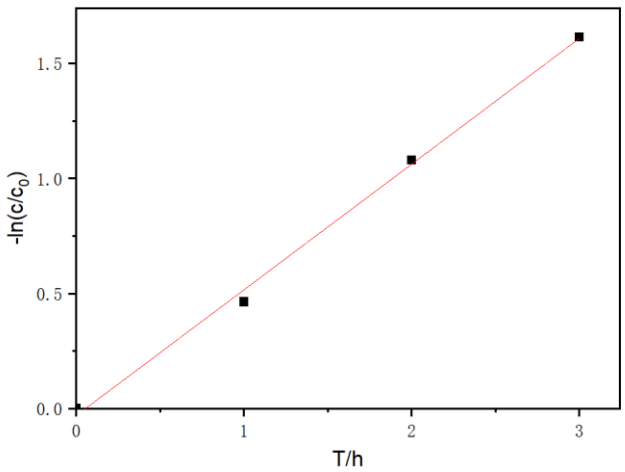


Figure S6. First-order kinetic plot fitting for converting [**I**-^{Bn}**M**]$^{-}$ to [**II**-^{Bn}**M**]$^{-}$ (338 K, DMSO-d_6).

Table S2. Kinetic parameters for converting [**I**-^{Bn}**M**]$^{-}$ to [**II**-^{Bn}**M**]$^{-}$ at 338 K in DMSO-d_6.

[2]Catenane	k/s^{-1}	$\tau_{1/2}$/s	$\Delta G^{\ddagger}$/kcal•mol^{-1}
[**I**-^{Bn}**M**]$^{-}$	1.52×10^{-4}	4560	25.81

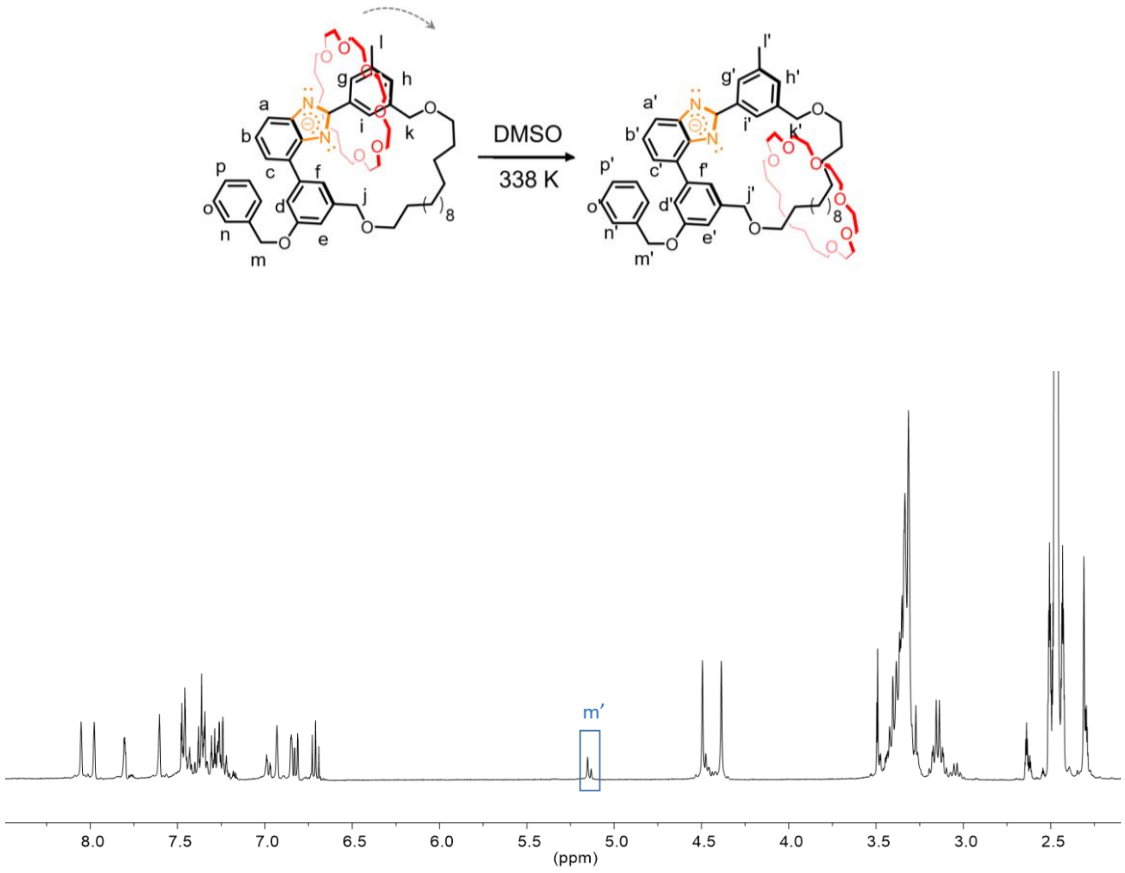


Figure S7. ^{1}H NMR spectrum (400 MHz, 298 K) of a mixture of [**I-^{Bn}M-H$_2$**][BF_4] (5 mM) and *t*-BuOK (25 mM) in DMSO-d_6 after heating at 100 °C for 4 hr. A very similar spectrum to that of heated at 338K for 12 hr indicating the nearly full translocation of the wheel. The significant decreased intensity of the m' proton is attributed to the exchange between deuterated solvent at high temperature in the presence of a strong base.

Section E. De-benzylation of [II-^{Bn}M-H_2][BF_4]

Procedures for debenzylation: [**II-**^{Bn}**M**-H_2][BF_4] (50 mg, 0.046 mmol) was dissolved in MeOH/THF (5 mL/5 mL) and added to a Schlenk flask charged with 10% Pd/C (11 mg, 10% mmol) under N_2 atmosphere. The flask was degassed and flushed with H_2 gas introduced via a balloon. ^{1}H NMR monitoring showed that [**II-**^{Bn}**M**-H_2][BF_4] was completely transformed to [**M**-H_2][BF_4] after stirring for 4 hours at room temperature. The mixture was filtered through a Celite pad. Removal of the solvent afforded the crude product which was washed with ethyl ether to give the pure [**M**-H_2][BF_4]. Yield: 40 mg, 88% (Characterization data see **Section. B**).

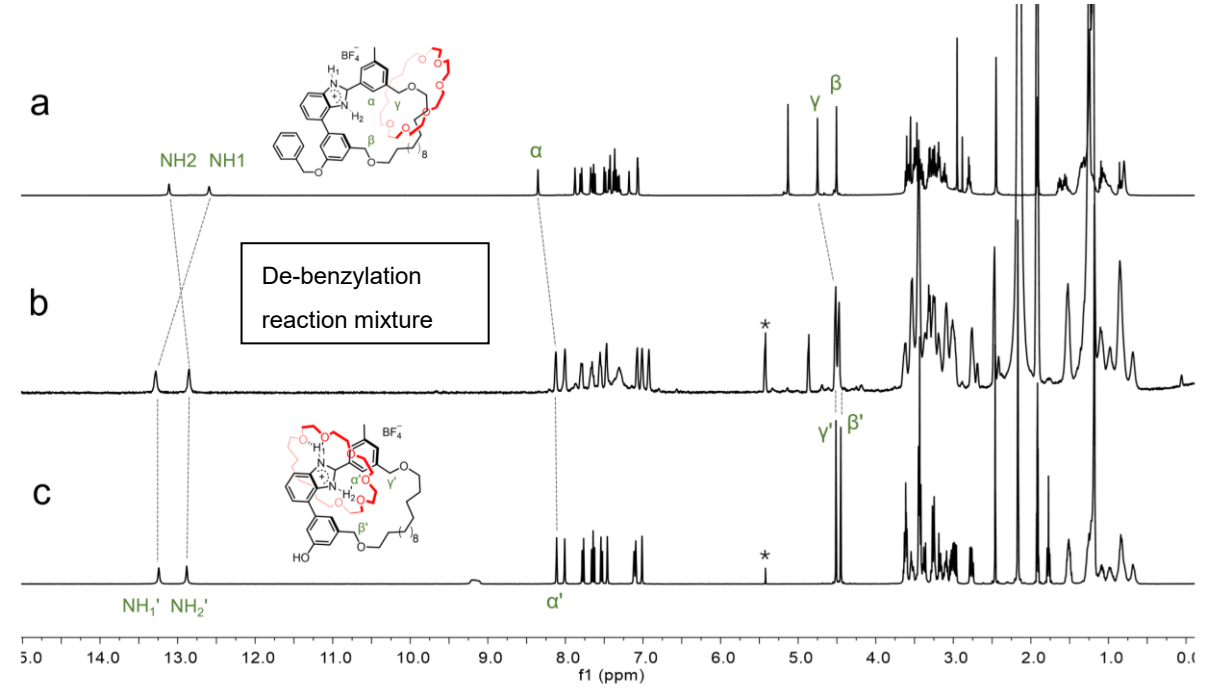


Figure S8. ^{1}H NMR (400 MHz, CD_3NO_2, 298 K) spectra of [**II-**^{Bn}**M**-H_2][BF_4] (a) the reaction mixture after the reduction for 4 hours, and [**M**-H_2][BF_4] (c). *Impurity.

Section F. Details of X-ray crystallography

Crystals of [**1b**-H_2⊂**24C6**][BF_4] were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of [**1b**-H_2][BF_4] and **24C6** (molar ratio = 1:10) at room temperature. Crystals of **M**-H was obtained from slow evaporation of a chloroform/hexane solution of [**M**-H_2][BF_4] at room temperature. Suitable crystals were frozen in paratone oil inside a cryoloop under a cold stream of N_2. Reflection data were collected either on a Rigaku SuperNova, Dual, AtlasS2 diffractometer using monochromatized Cu Kα radiation or on a BRUKER D8 VENTURE PHOTON III diffractometer using Ga Kα radiation. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved using OLEX^2 crystallography software. When practical, non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in idealized positions and refined using a riding model. Figures were drawn with Diamond 4.0. Details can be obtained from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk for CCDC accession numbers 2349580 ([**1b**-H_2⊂**24C6**][BF_4]), 2349579 (**M**-H).

Table S3. Crystal Data, Solution and Refinement Parameters.

	[**1b**-H_2⊂**24C6**][BF_4]
CCDC number	2349580
formula	$C_{46}H_{69}BF_4N_2O_7$
formula weight	848.87
crystal system	Monoclinic
space group	$P2_1$-c
T （K）	293 (2)
a （Å）	9.6885 (6)
b （Å）	16.4051 (11)
c （Å）	29.993 (2)
α （º）	90
β （º）	96.342 (2)
γ （º）	90
V （Å^3）	4738.0 (6)
Z	4
ρ, g cm^{-3}	1.172
μ, mm^{-1}	0.065
reflections used	10861
variables	549
restraints	0
R_1 [$I > 2\sigma(I)$][a]	0.0811
R_1 （all data）	0.1372
wR_2 [$I > 2\sigma(I)$][b]	0.2090
wR_2 （all data）	0.2510
GoF on F^2	1.005

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; [b] $R_2w = [\Sigma[w (F_o^2 - F_c^2)^2] / \Sigma[w (F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2 (F_o^2) + (aP)^2 + bP]^{-1}$

Table S4. Crystal Data, Solution and Refinement Parameters.

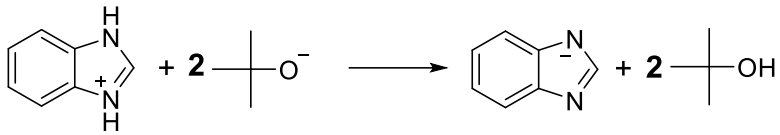
	M-H
CCDC number	2349579
formula	$C_{54}H_{80}N_2O_9$
formula weight	900.93
crystal system	Monoclinic
space group	C_2
T （K）	293（2）
a （Å）	45.143（3）
b （Å）	10.3290（4）
c （Å）	25.3390（7）
α （º）	90
β （º）	98.908（4）
γ （º）	90
V （Å^3）	11672.6（10）
Z	8
ρ, g cm^{-3}	1.025
μ, mm^{-1}	0.603
reflections used	10423
variables	844
restraints	524
R_1 [$I > 2\sigma(I)$][a]	0.0875
R_1 （all data）	0.1147
wR_2 [$I > 2\sigma(I)$][b]	0.2601
wR_2 （all data）	0.2893
GoF on F^2	1.063

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; [b] $R_2w = [\Sigma[w (F_o^2 - F_c^2)^2] / \Sigma[w (F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2 (F_o^2) + (aP)^2 + bP]^{-1}$

Section G. Estimating the chemical energy input to perform each of the 180-degree rotation.

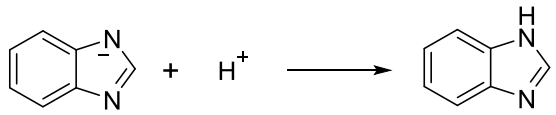
To estimate the chemical energy input required to perform each 180-degree turn, the full rotation of the motor was deconvoluted into 5 model reactions (a~e) as described below. ΔG^* for related model compounds were obtained via density functional theory (DFT) calculations (# opt. freq. b3lyp/6-31g(d)) performed in Gaussian 09W software. The calculated energies were summarized in Table S5 and S6.

1) Chemical reactions associated to the first 180-degree rotation include the deprotonation and re-protonation: Firstly, motor [**I-^{Bn}M**-H_2]$^+$ was deprotonated with 2 equivalents of *t*BuOK to yield the benzimidazolide [**I-^{Bn}M**]$^-$.

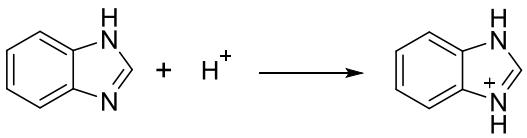
a.  ΔG_1^*

$\Delta G_1^* = \Delta G^*_{(\text{benzimidazolide})} + 2\Delta G^*_{(t\text{BuOH})} - \Delta G^*_{(\text{benzimidazolium})} - 2\Delta G^*_{(t\text{BuO}^-)} = -811.8$ kJ/mol

[**I-^{Bn}M**]$^-$ was re-protonated with 2 equivalents of acid to afford [**I-^{Bn}M**-H_2]$^+$. The energy change for the re-protonation can be estimated according to pK_a:

b.  ΔG_2^*

$\Delta G_2^* = -RTlnK = -RTln(1/K_a) = -75.9$ kJ/mol (pK_a of benzimidazole = 13.3)[6]

c.  ΔG_3^*

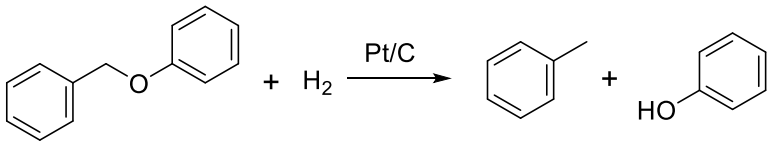
$\Delta G_3^* = -RTlnK = -RTln(1/K_a) = -31.38$ kJ/mol (*pKa* of benzimidazolium = 5.5)[6]

Therefore, the chemical energy input associated to the first 180-degree rotation can be obtained:

$$\Delta G^* = -(\Delta G_1^* + \Delta G_2^* + \Delta G_3^*) = 919.1 \text{ kJ/mol} = 219.5 \text{ kcal/mol}$$

2) Chemical reactions associated the other 180-degree rotation include the debenzylation and re-benzylation. Firstly, [**II-^{Bn}M**-H_2]$^+$ was debenzylated via Pd/C catalyzed hydrogenation to form [**M**-H_2]$^+$.

d.

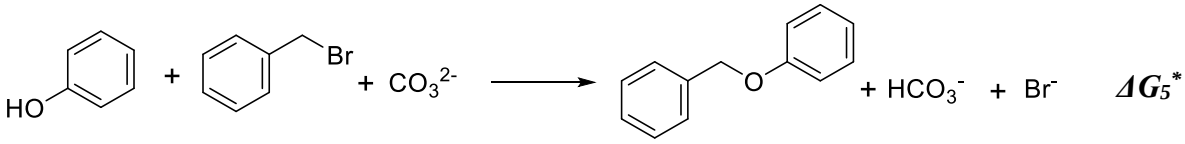


ΔG_4^*

$\Delta G_4^* = \Delta G^*_{(phenol)} + \Delta G^*_{(Toluene)} - \Delta G^*_{(H2)} - \Delta G^*_{(BnOPh)} = -74.9$ kJ/mol

[**M**-H_2]$^+$ was then re-benzylated to yield [**I-^{Bn}M**-H_2]$^+$. The energy change for this transformation can be estimated as follows:

e.



ΔG_5^*

$\Delta G_5^* = \Delta G^*_{(BnOPh)} + \Delta G^*_{(HCO3^-)} + \Delta G^*_{(Br^-)} - \Delta G^*_{(phenol)} - \Delta G^*_{(BnBr)} - \Delta G^*_{(CO3^{2-})} = -743.4$ kJ/mol

Therefore, the chemical energy input associated to the second 180-degree rotation can be obtained:

$\Delta G^* = -(\Delta G_4^* + \Delta G_5^*) = 818.3$ kJ/mol = 195.3 kcal/mol

Table S5. Summary of calculated energies of model compounds in gas phase.

	Benzimid-azolide	**Benzimid-azolium**	***t*BuO$^-$**	***t*BuOH**	**BnOPh**	**Toluene**
Temperature (K)	298.150	298.150	298.150	298.150	298.150	298.150
Pressure (atm)	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
Electronic Energy (EE) (Hartree)	-379.29731	-380.24759	-233.03928	-233.67096	-577.82329	-271.56664
Zero-point Energy Correction (Hartree)	0.104862	0.132582	0.120299	0.136175	0.215065	0.128316
Thermal Correction to Energy (Hartree)	0.110601	0.138689	0.126786	0.142901	0.226217	0.134535
Thermal Correction to Enthalpy (Hartree)	0.111545	0.139633	0.127730	0.143845	0.227162	0.135479
Thermal Correction to Free Energy (Hartree)	0.074908	0.102372	0.091516	0.107174	0.176135	0.097484
EE + Zero-point Energy (Hartree)	-379.19245	-380.11499	-232.91898	-233.53478	-577.60823	-271.43834
EE + Thermal Energy Correction (Hartree)	-379.18671	-380.10890	-232.91249	-233.52806	-577.59708	-271.43211
EE + Thermal Enthalpy Correction (Hartree)	-379.18576	-380.10794	-232.91155	-233.52711	-577.59613	-271.43116
EE + Thermal Free Energy Correction (Hartree)	**-379.22240**	**-380.14520**	**-232.94776**	**-233.56378**	**-577.64716**	**-271.46916**

(1 Hartree = 2625.5 kJ/mol)

Table S6. Summary of calculated energies of model compounds in gas phase.

	Phenol	**H_2**	**BnBr**	**CO_3^{2-}**	**HCO_3^-**	**Br^-**
Temperature (K)	298.150	298.150	298.150	298.150	298.150	298.150
Pressure (atm)	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
Electronic Energy (EE) (Hartree)	-307.458352	-1.175482	-2842.6701	-263.58687	-264.425692	-2571.76134
Zero-point Energy Correction (Hartree)	0.103787	0.010145	0.119422	0.013958	0.026230	0.000000
Thermal Correction to Energy (Hartree)	0.108940	0.012505	0.126549	0.017151	0.029755	0.001416
Thermal Correction to Enthalpy (Hartree)	0.109884	0.013450	0.127493	0.018095	0.030699	0.002360
Thermal Correction to Free Energy (Hartree)	0.074988	-0.001342	0.085257	-0.011623	0.000449	-0.016176
EE + Zero-point Energy (Hartree)	-307.354565	-1.165337	-2842.5507	-263.57291	-264.399463	-2571.76134
EE + Thermal Energy Correction (Hartree)	-307.349412	-1.162977	-2842.5436	-263.56972	-264.395938	-2571.75992
EE + Thermal Enthalpy Correction (Hartree)	-307.348468	-1.162033	-2842.5426	-263.56878	-264.394993	-2571.75898
EE + Thermal Free Energy Correction (Hartree)	**-307.383364**	**-1.176825**	**-2842.5849**	**-263.59850**	**-264.425244**	**-2571.77751**

(1 Hartree = 2625.5 kJ/mol)

Section H. NMR spectra.

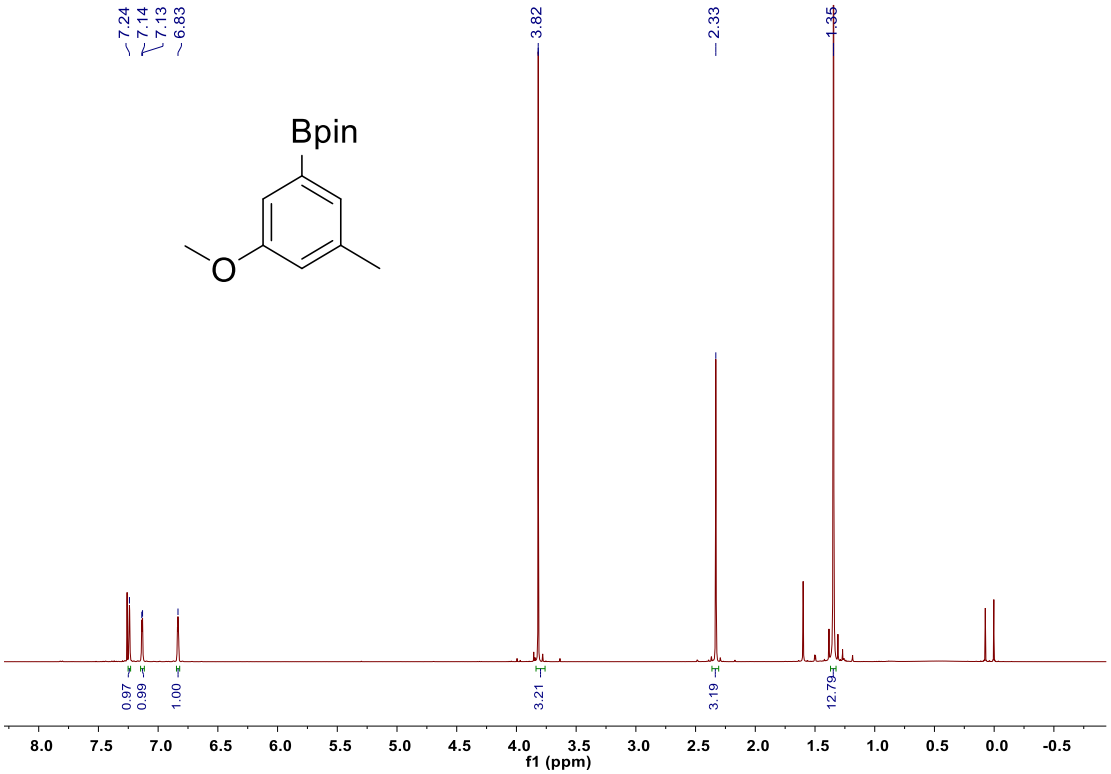


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **7**.

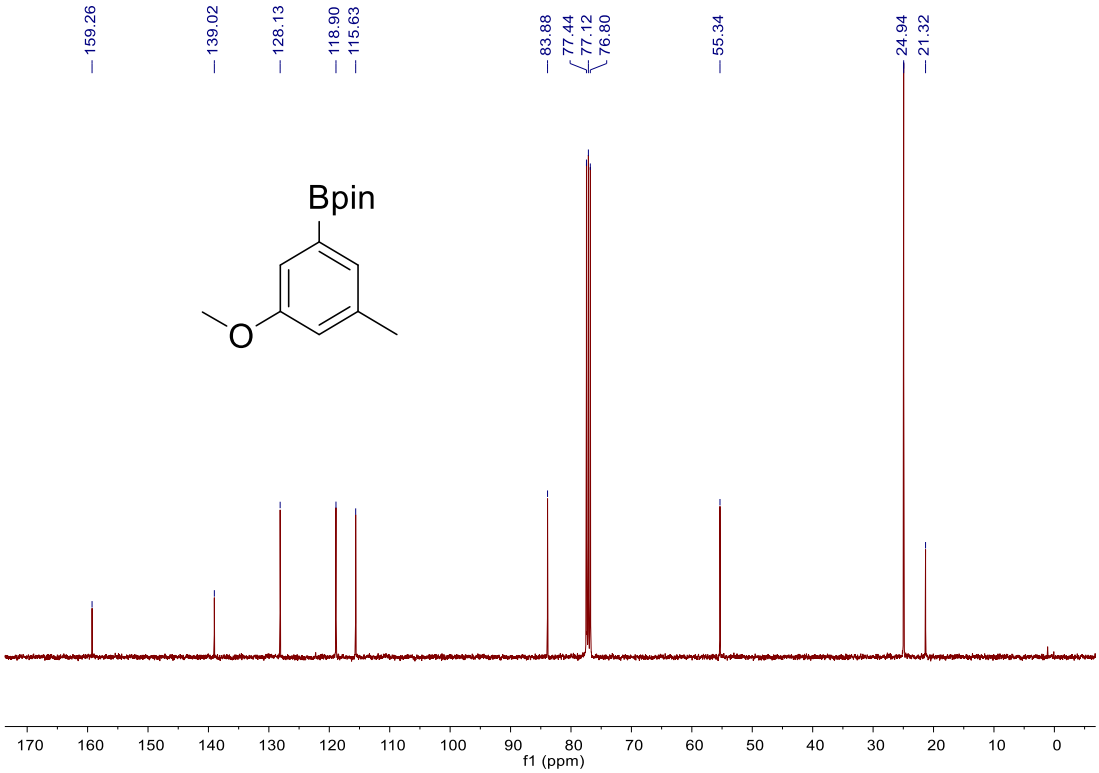


Figure S10. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **7**.

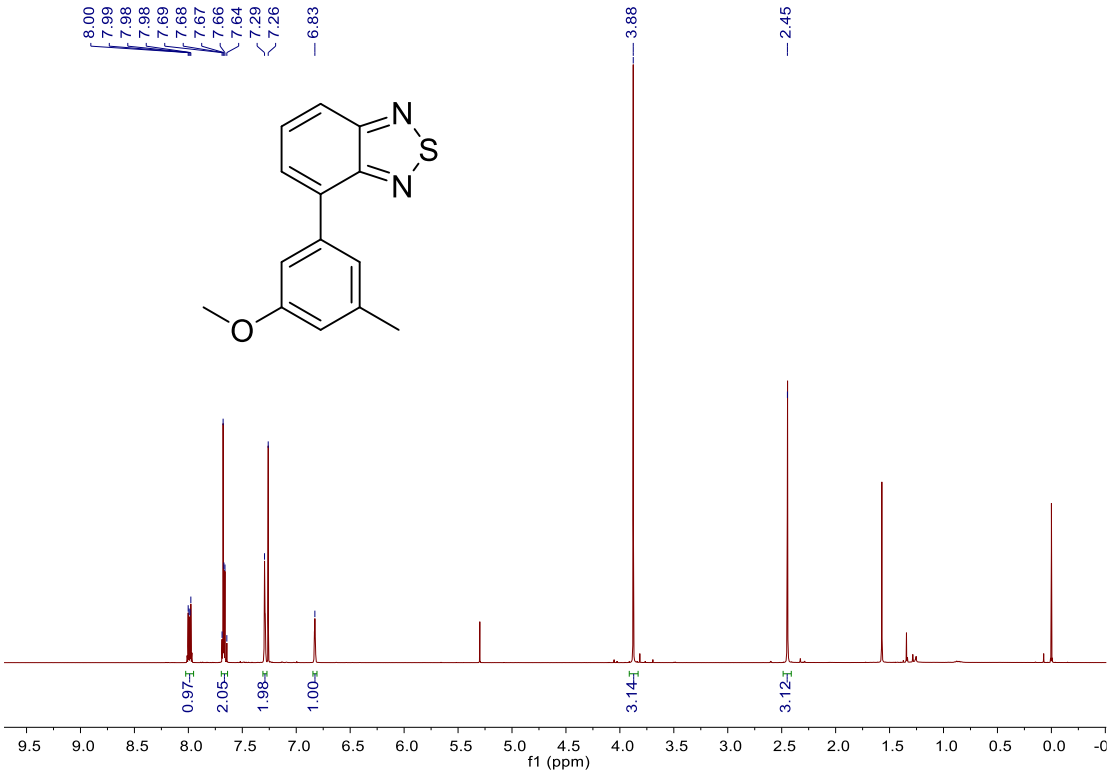


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **8**.

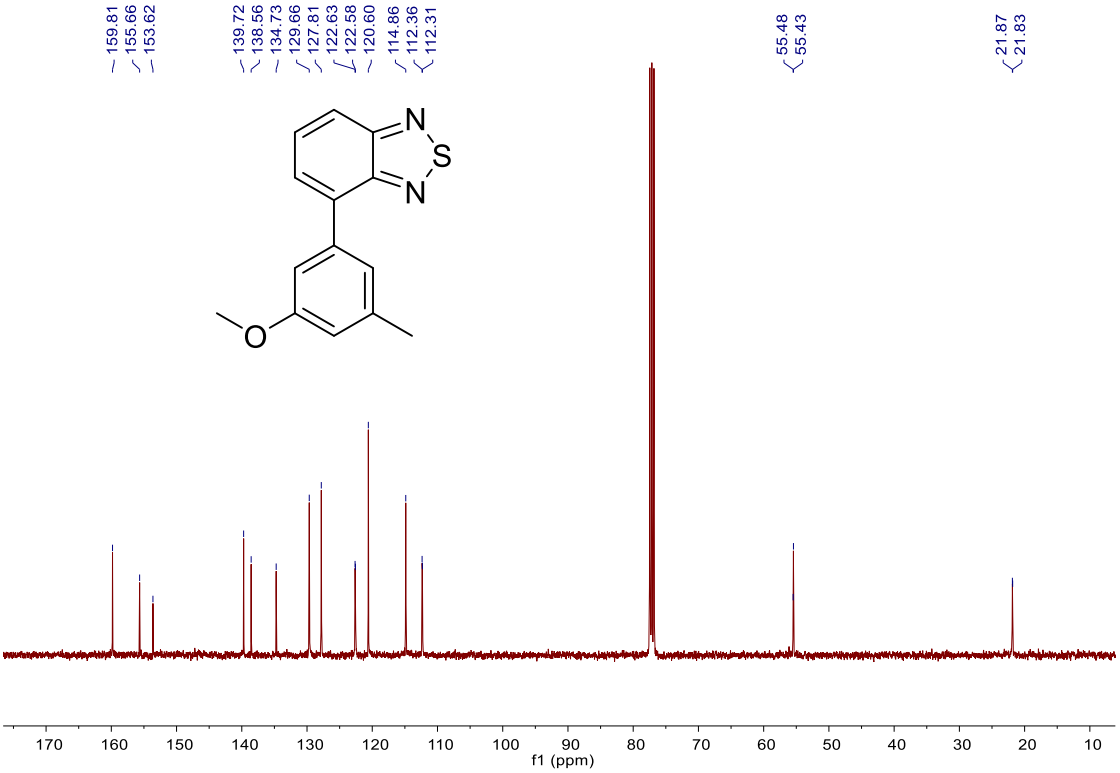


Figure S12. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **8**.

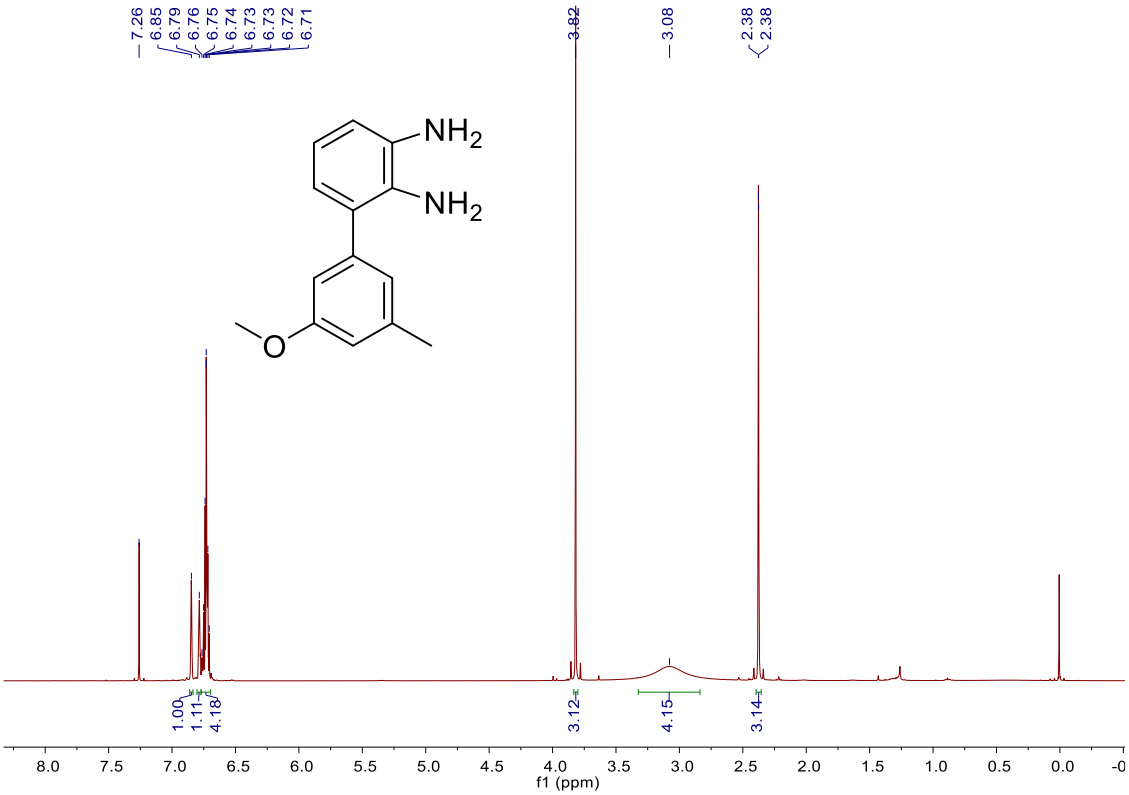


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **9**.

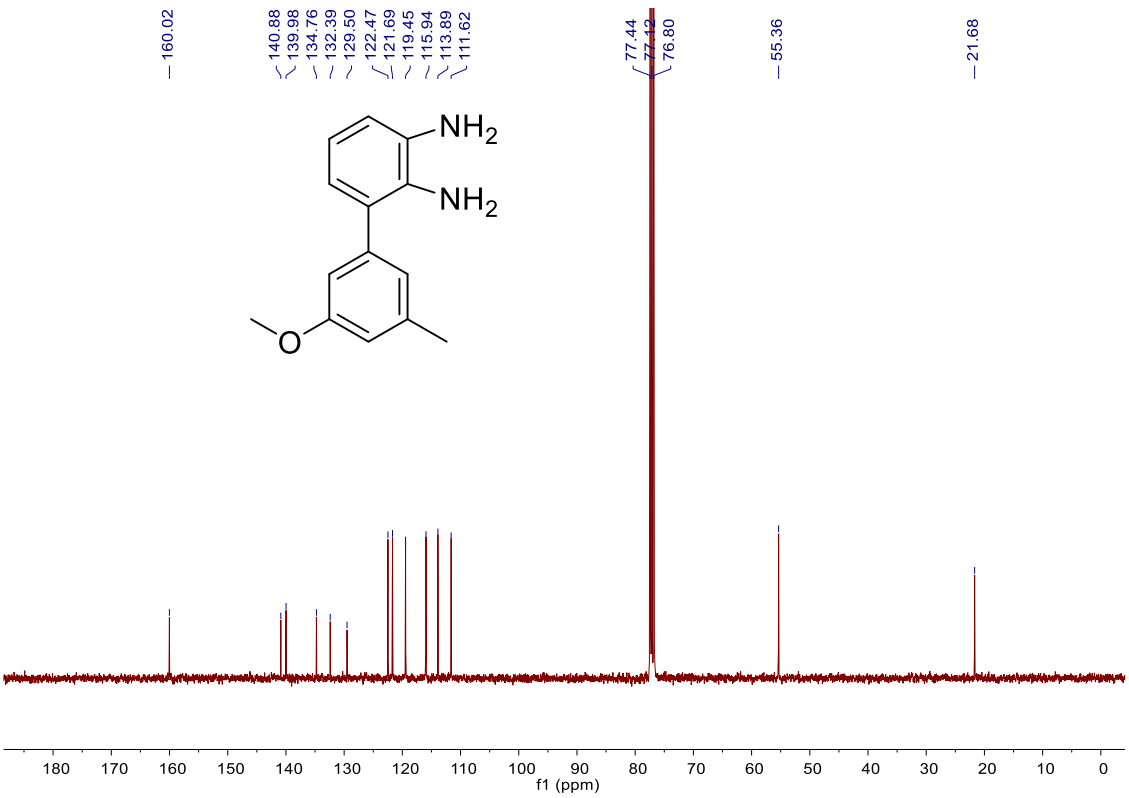


Figure S14. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **9**.

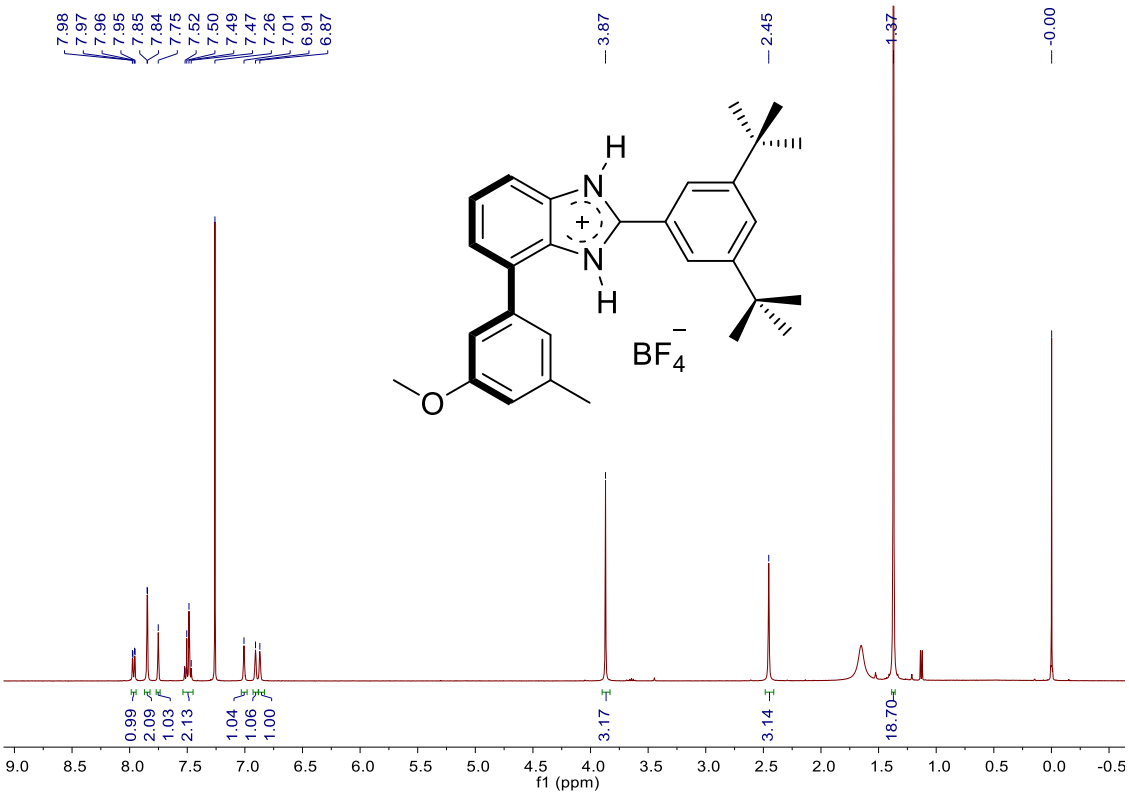


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of [**1a**-H_2][BF_4].

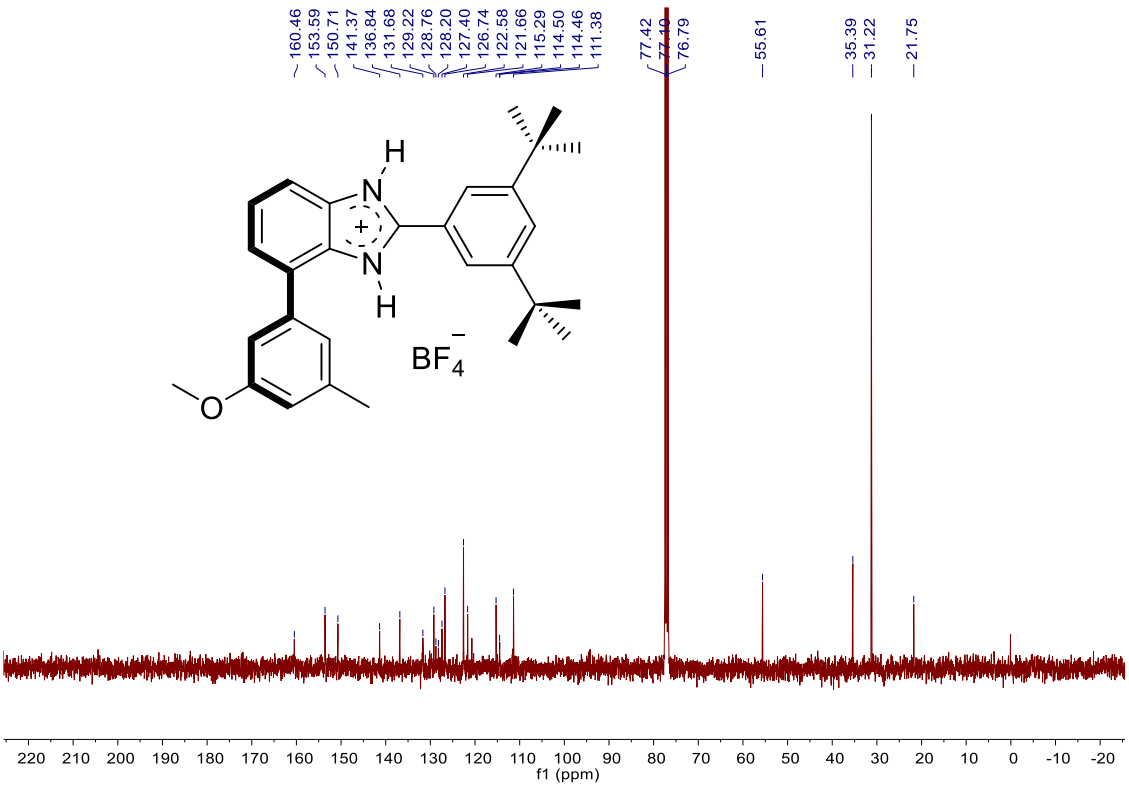


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of [**1a**-H_2][BF_4].

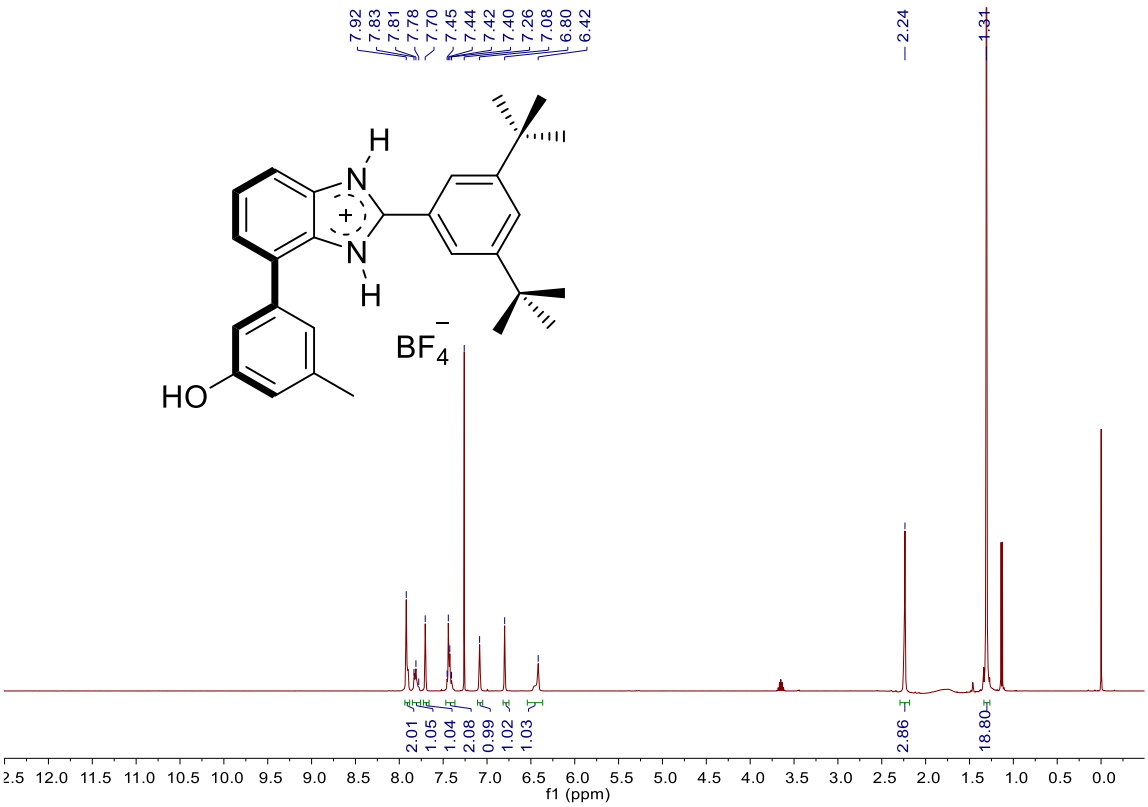


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of [**1b**-H_2][BF_4].

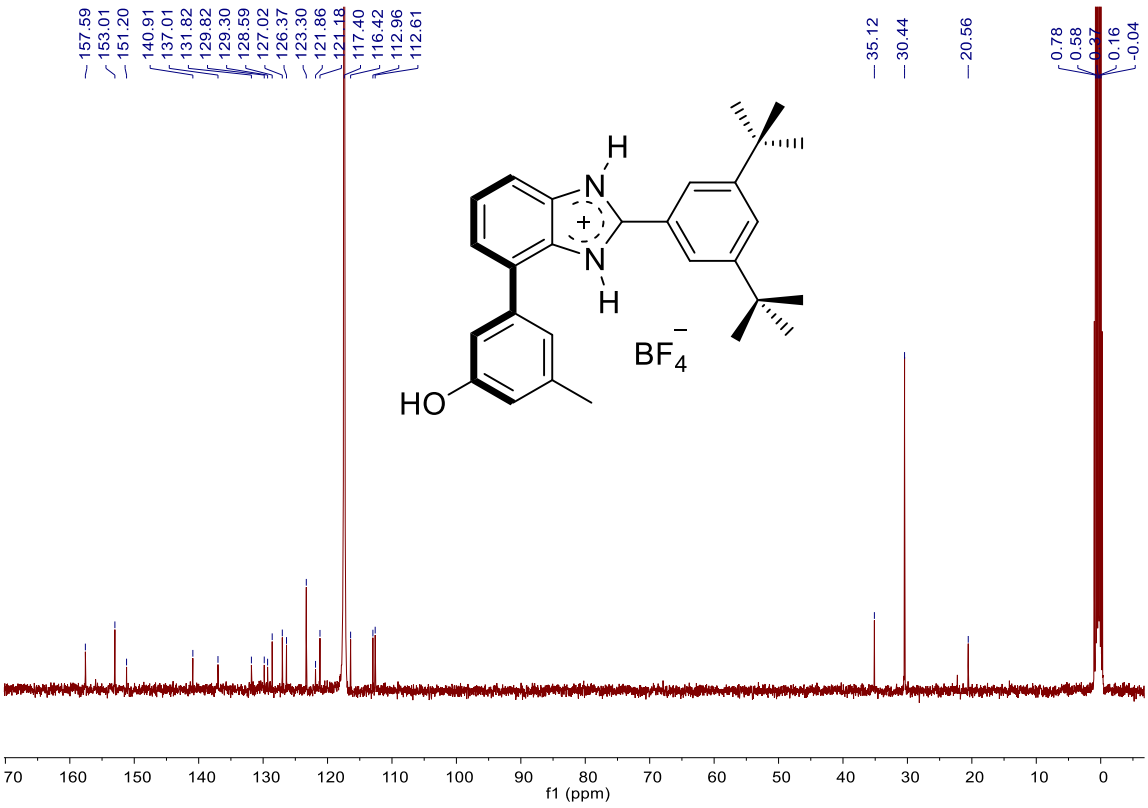


Figure S18. ^{1}H NMR (400 MHz, CD_3NO2, 298 K) spectrum of [**1b**-H_2][BF_4].

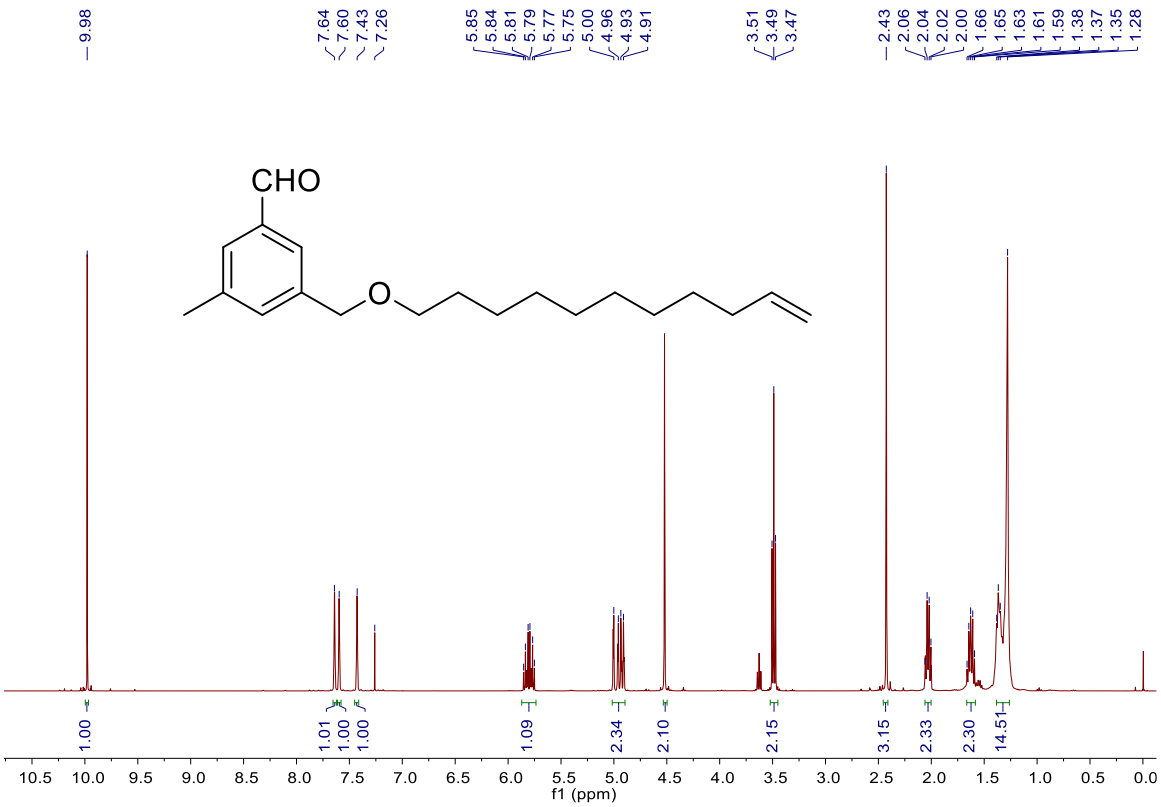


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **2**.

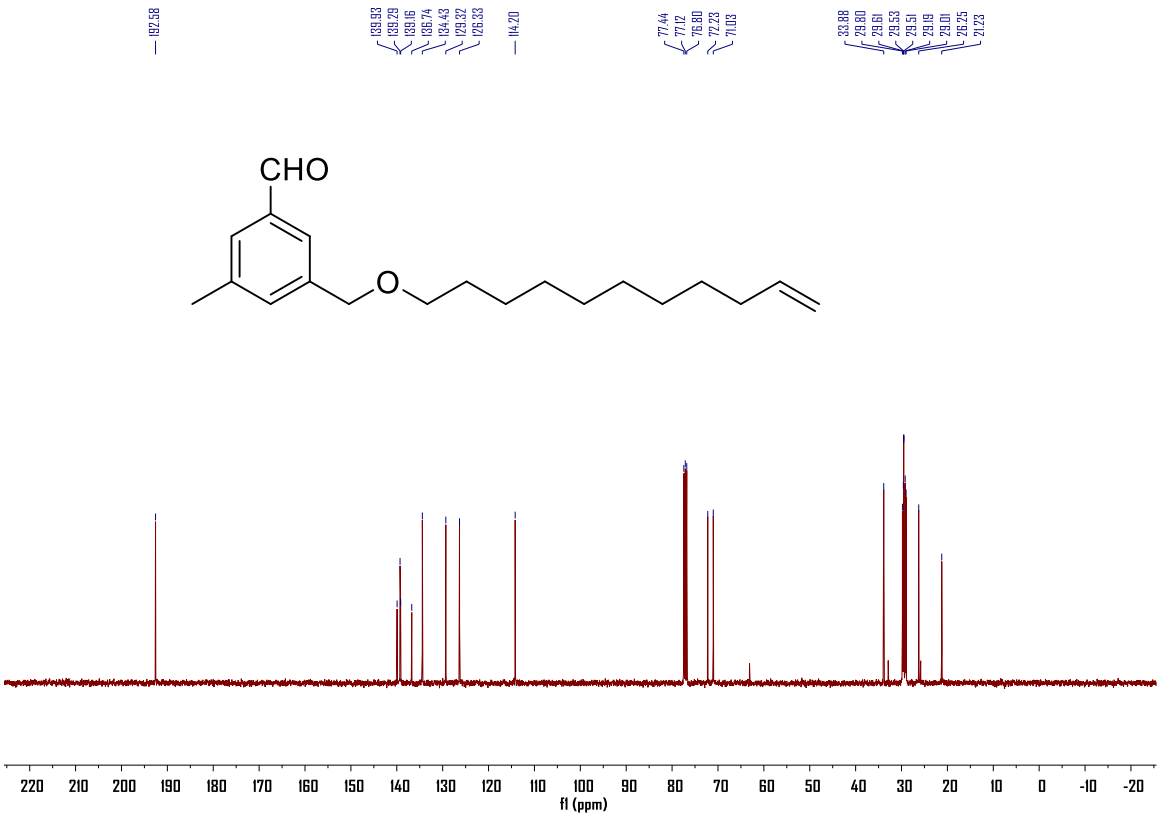


Figure S20. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **2**.

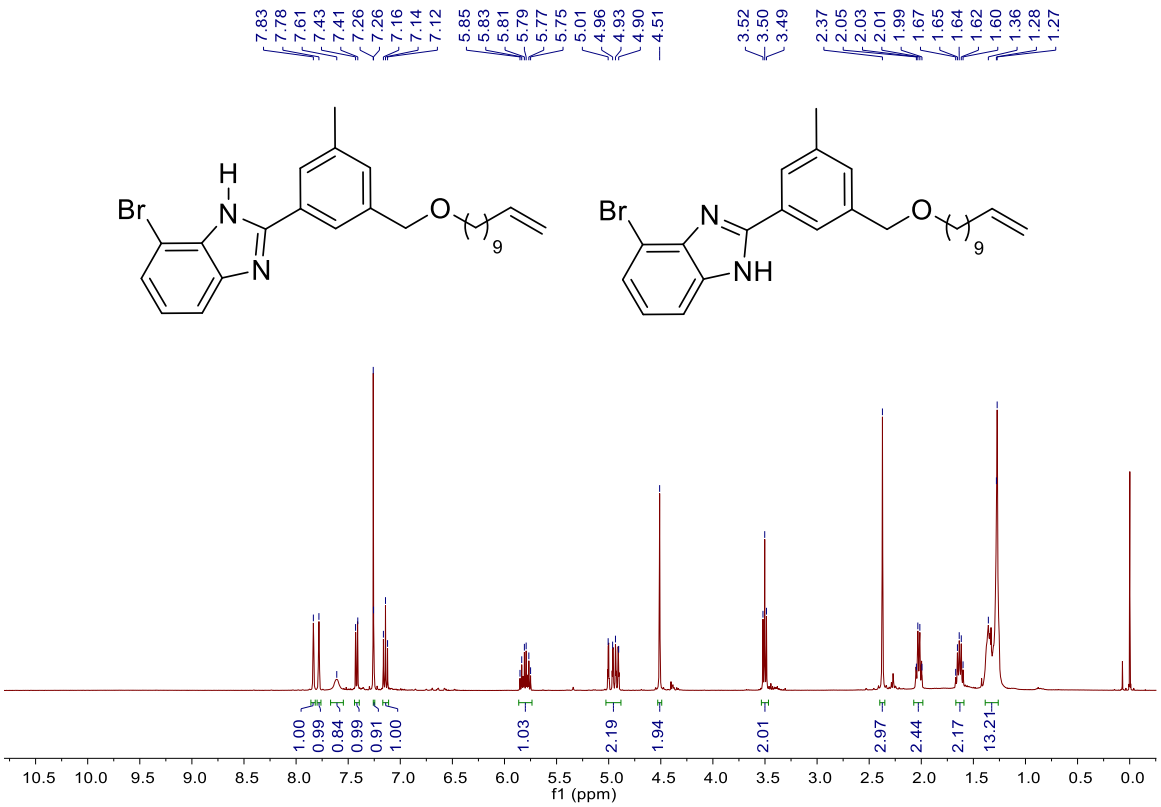


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **3**.

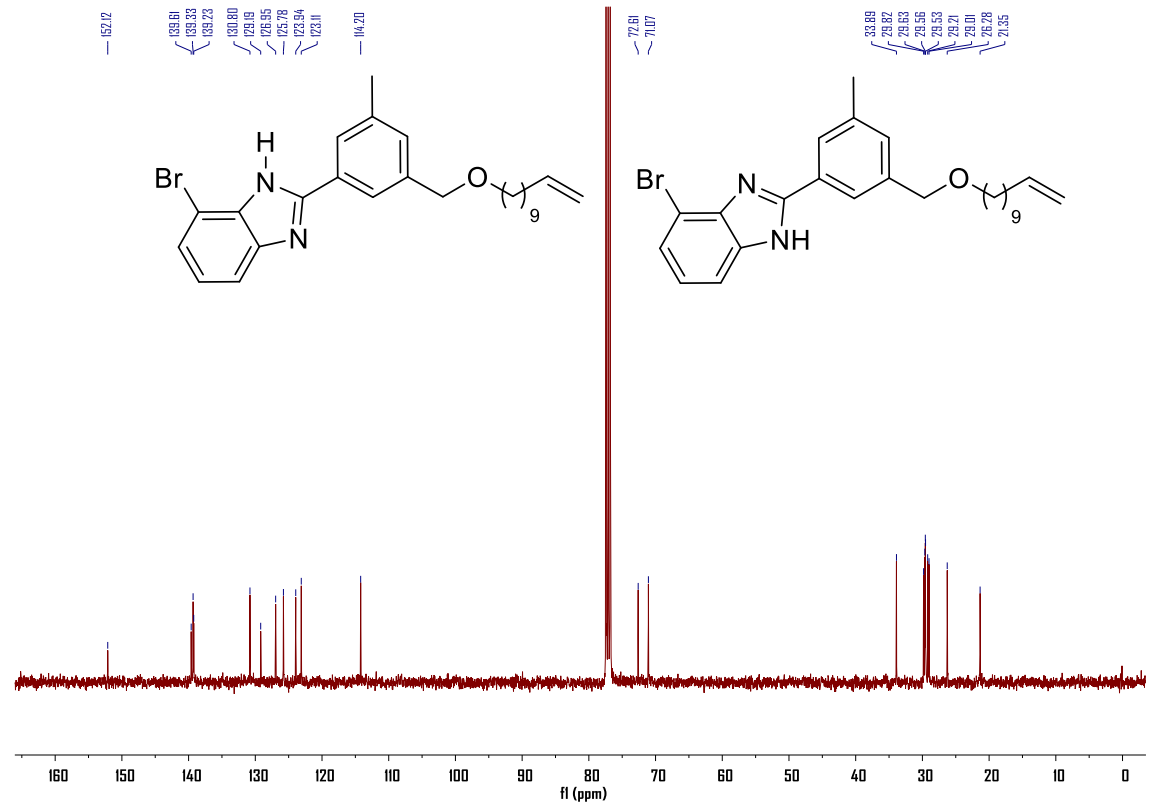


Figure S22. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **3**.

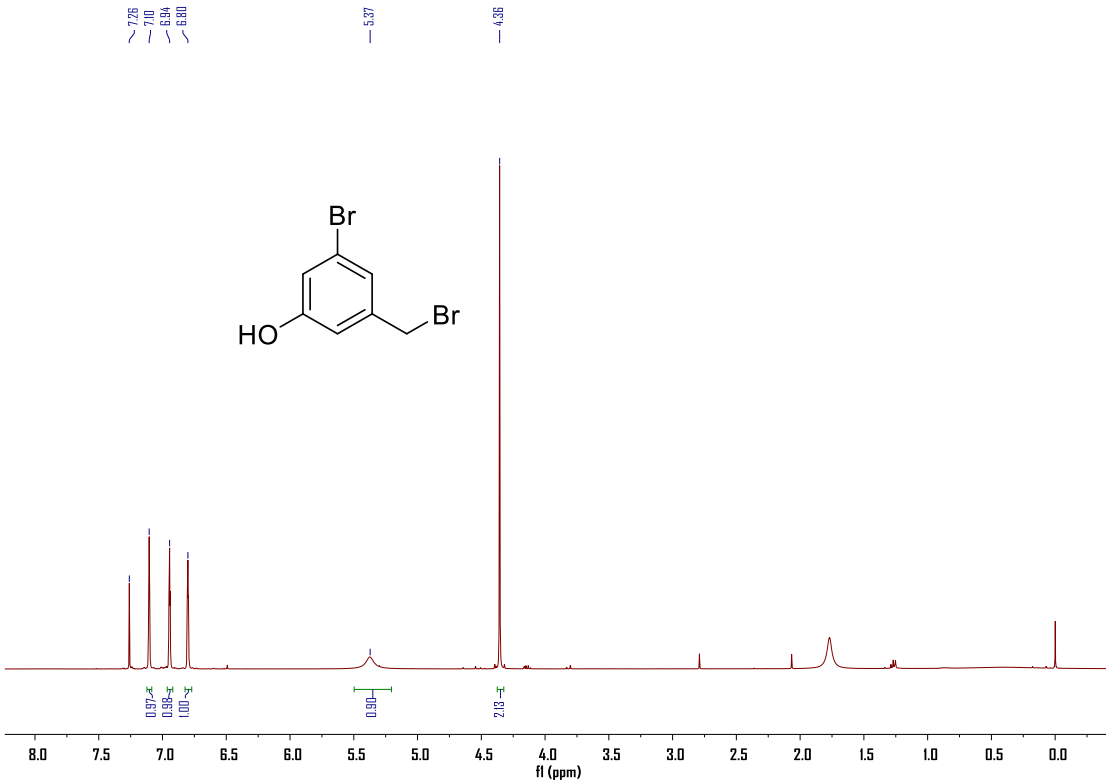


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **13**.

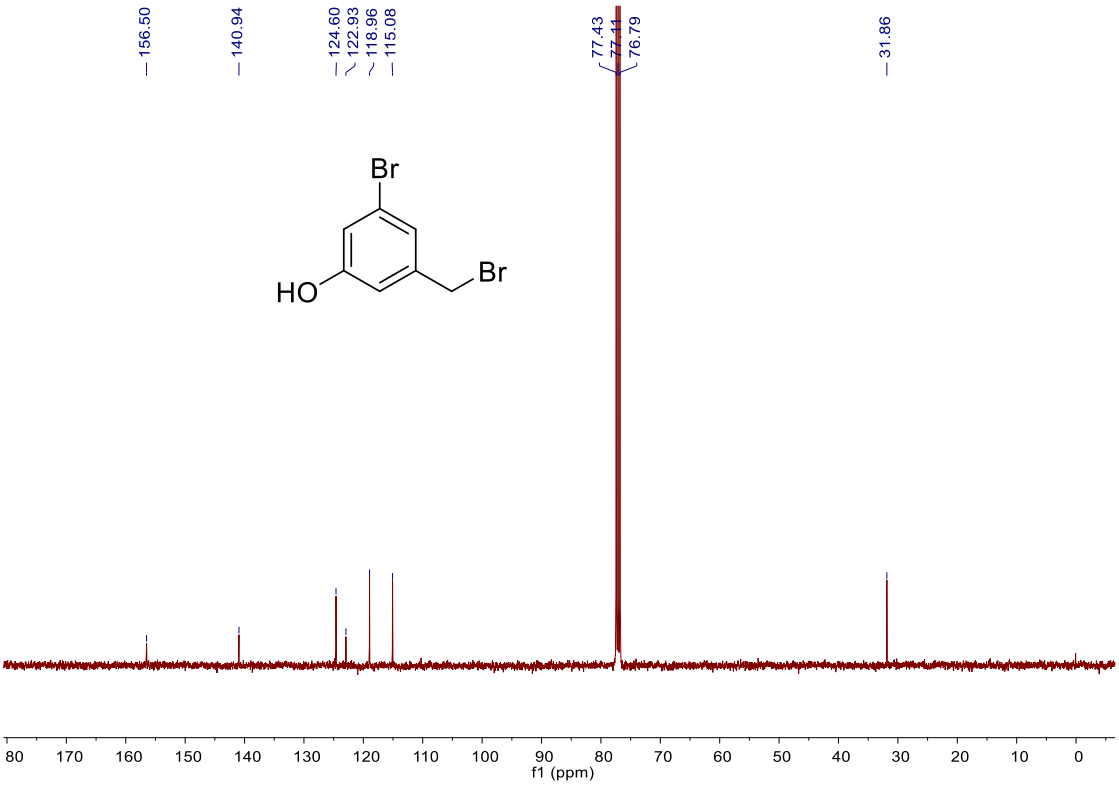


Figure S24. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **13**.

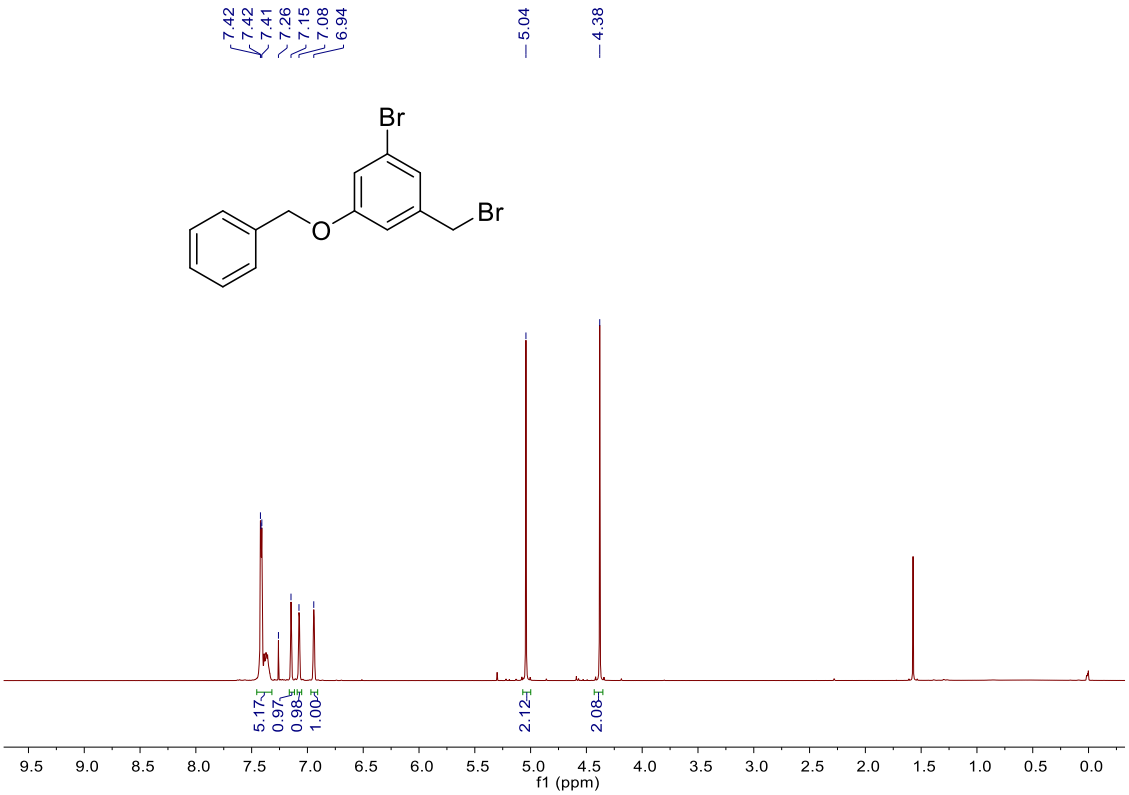


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **14**.

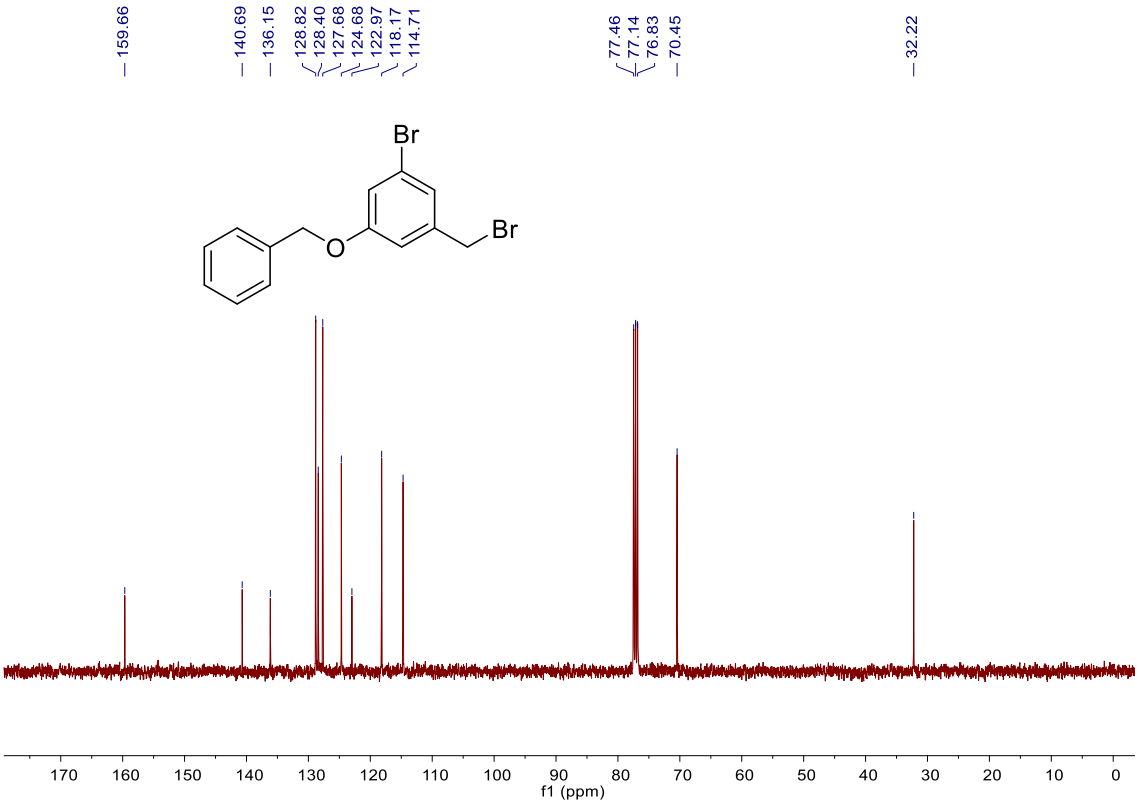


Figure S26. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **14**.

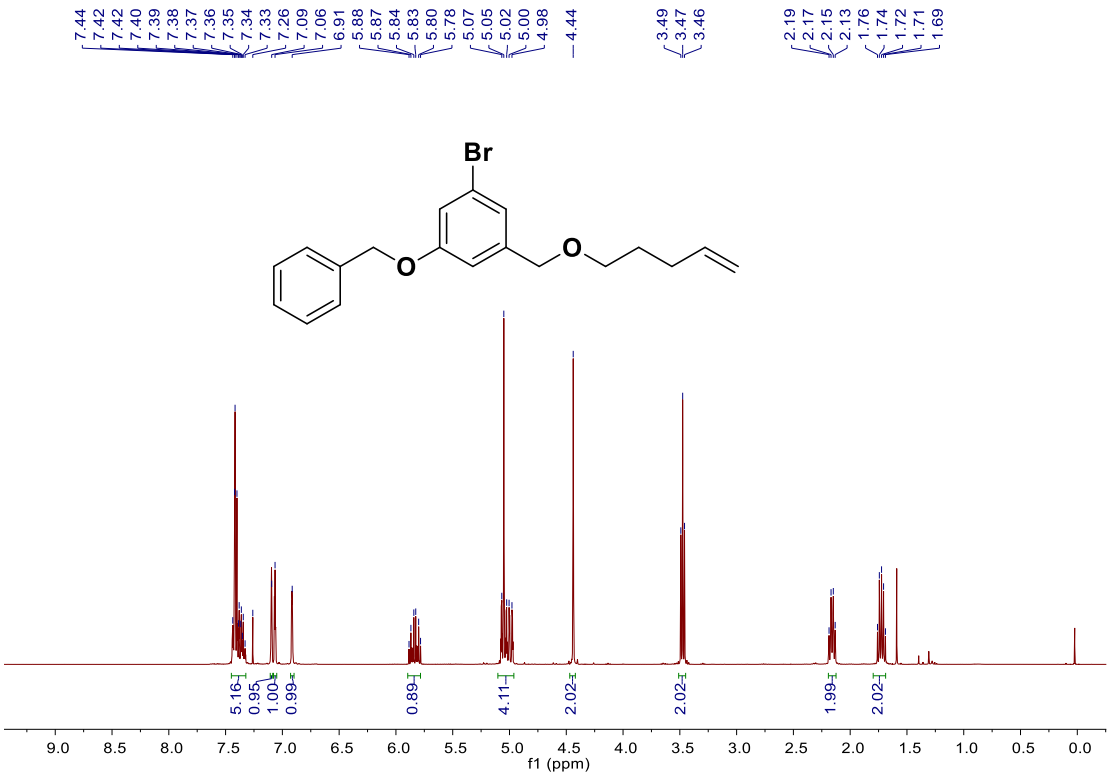


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **15**.

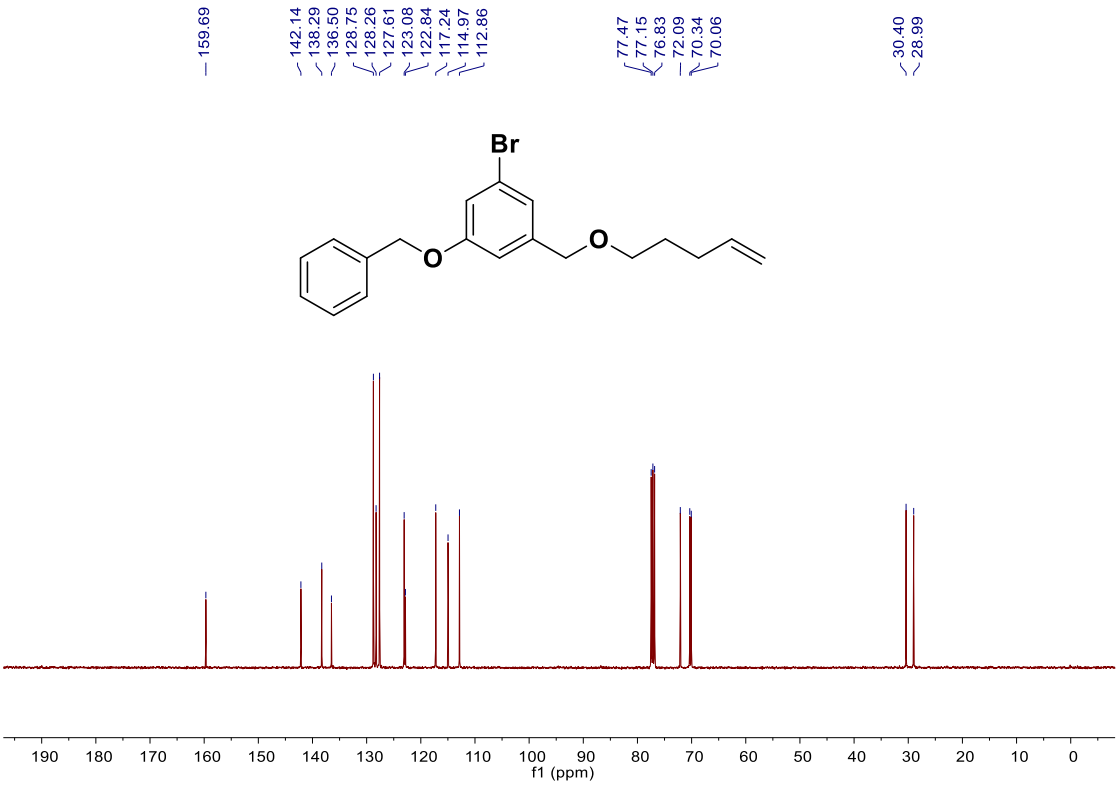


Figure S28. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **15**.

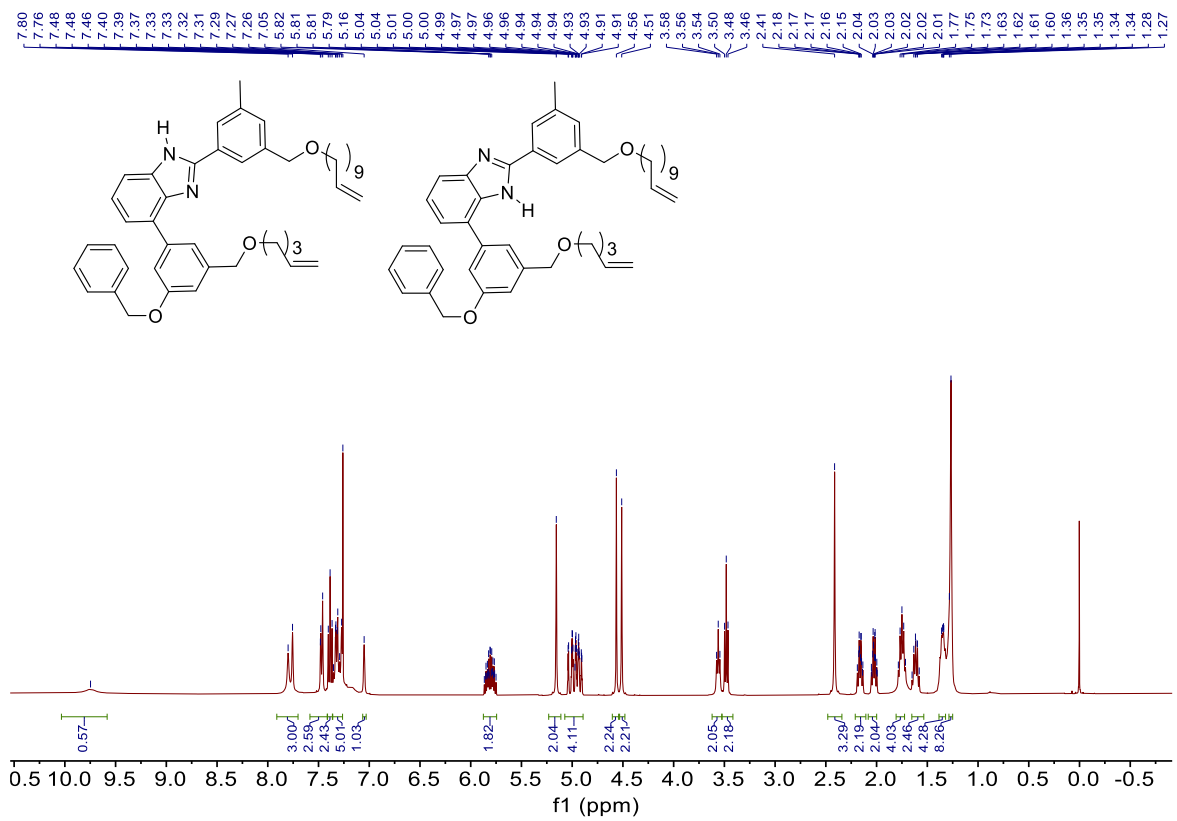


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **5**.

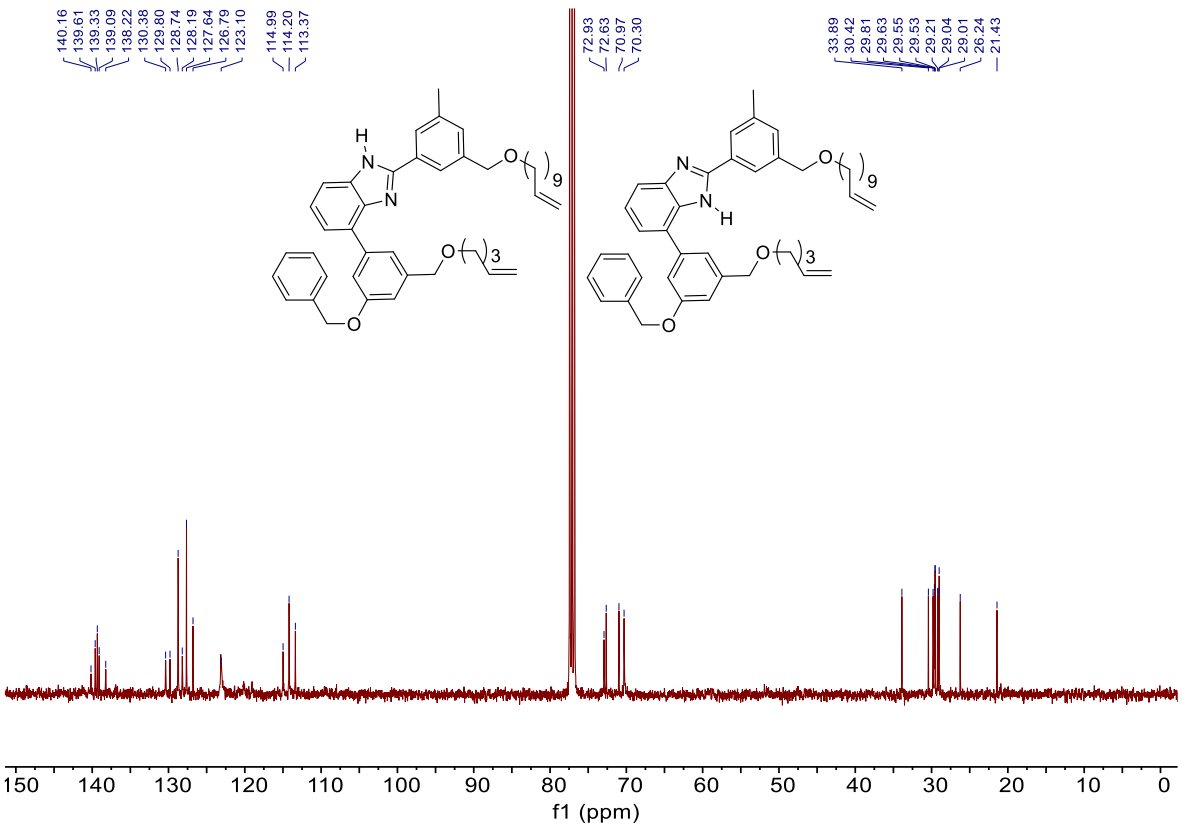


Figure S30. ^{13}C NMR (101 MHz, CD_3CN, 298 K) spectrum of **5**.

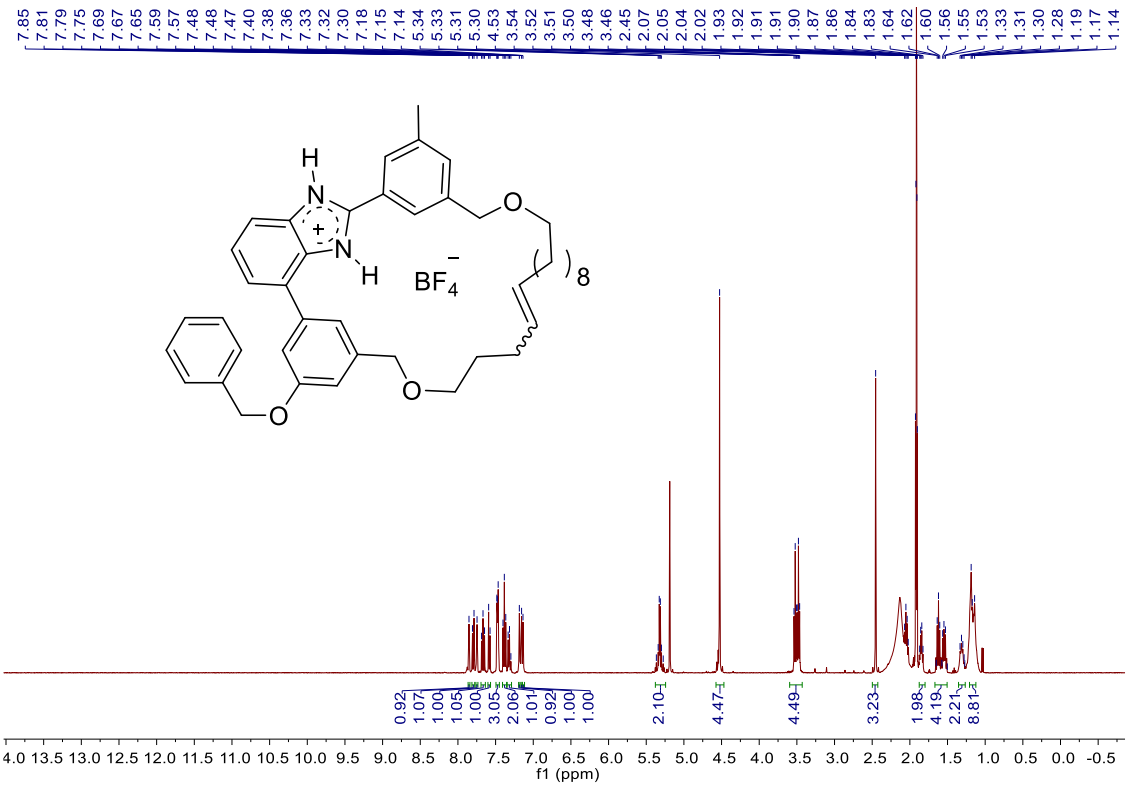


Figure S31. ^{1}H NMR (400 MHz, CD_3CN, 298 K) spectrum of [**6**-H_2][BF_4].

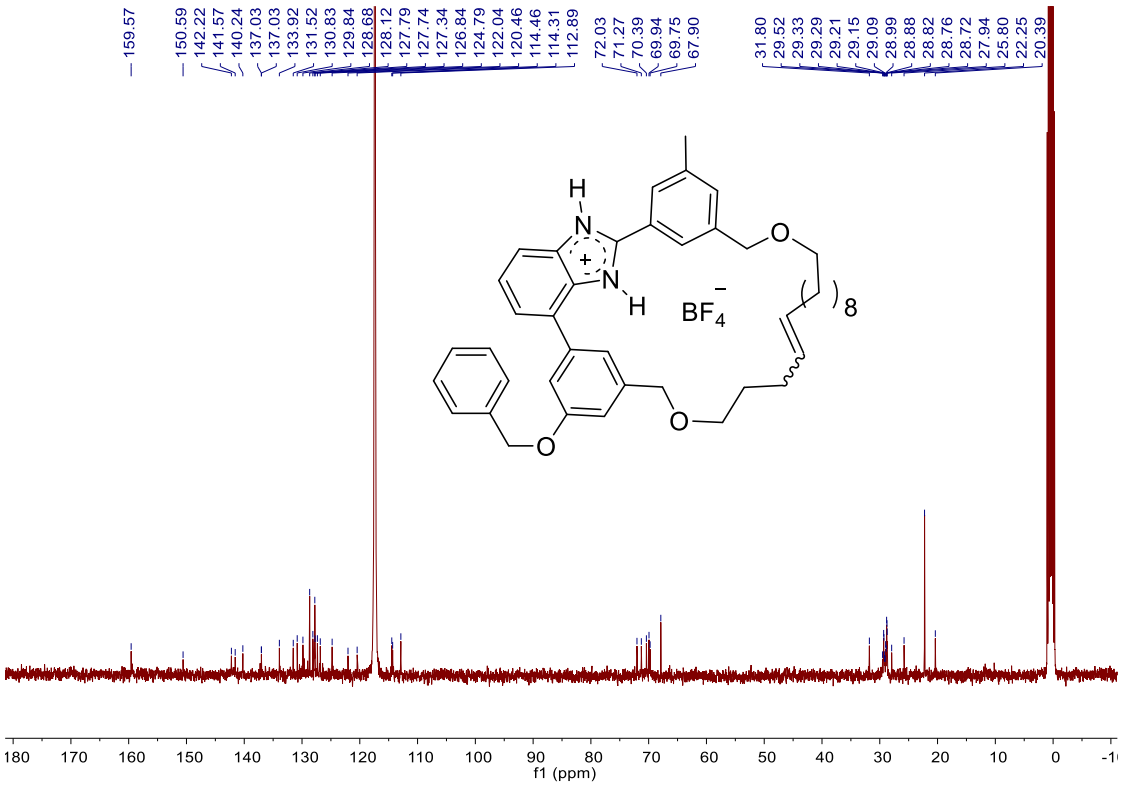


Figure S32. ^{13}C NMR (101 MHz, CD_3CN, 298 K) spectrum of [**6**-H_2][BF_4].

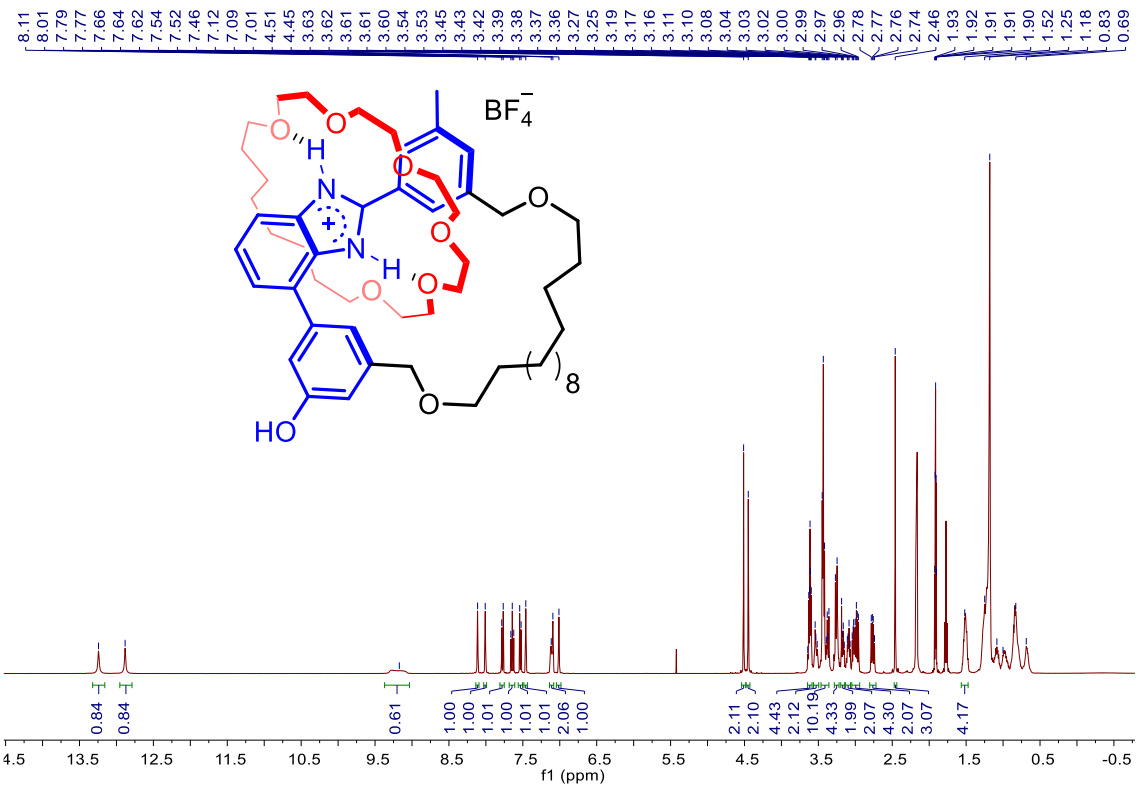


Figure S33. ^{1}H NMR (400 MHz, CD_3CN, 298 K) spectrum of [**M**-H_2][BF_4].

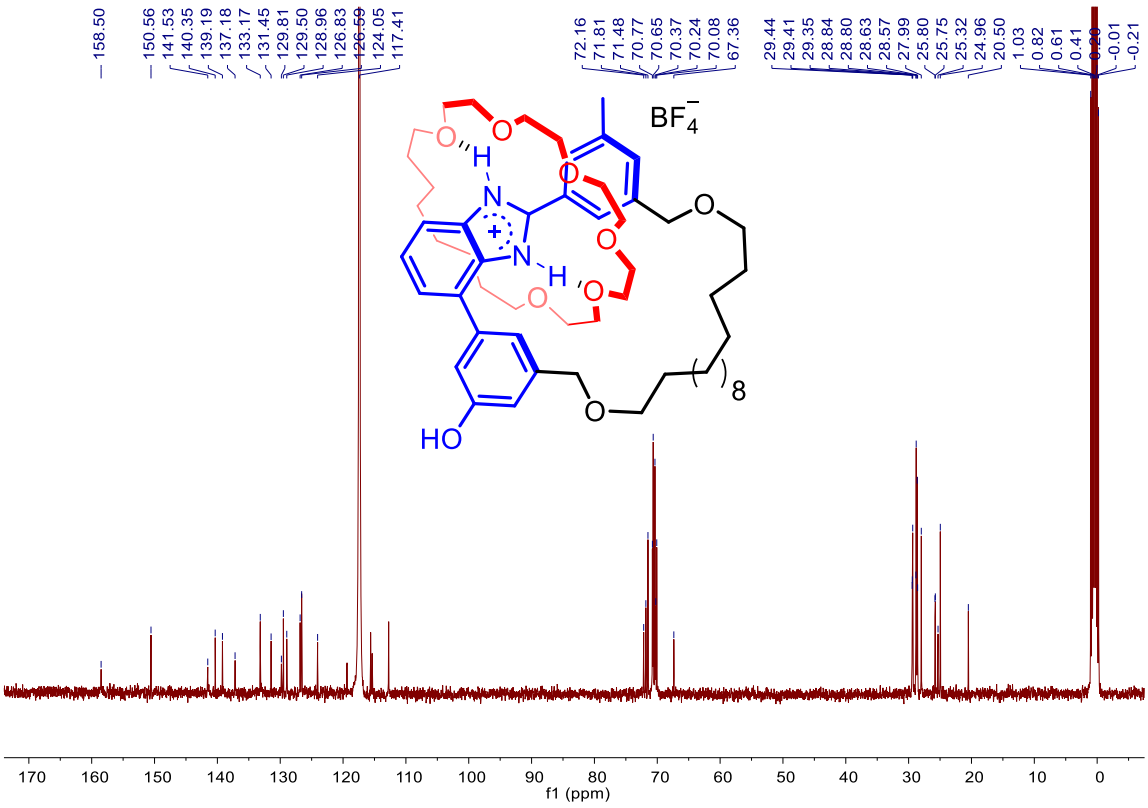


Figure S34. ^{13}C NMR (101 MHz, CD_3CN, 298 K) spectrum of [**M**-H_2][BF_4].

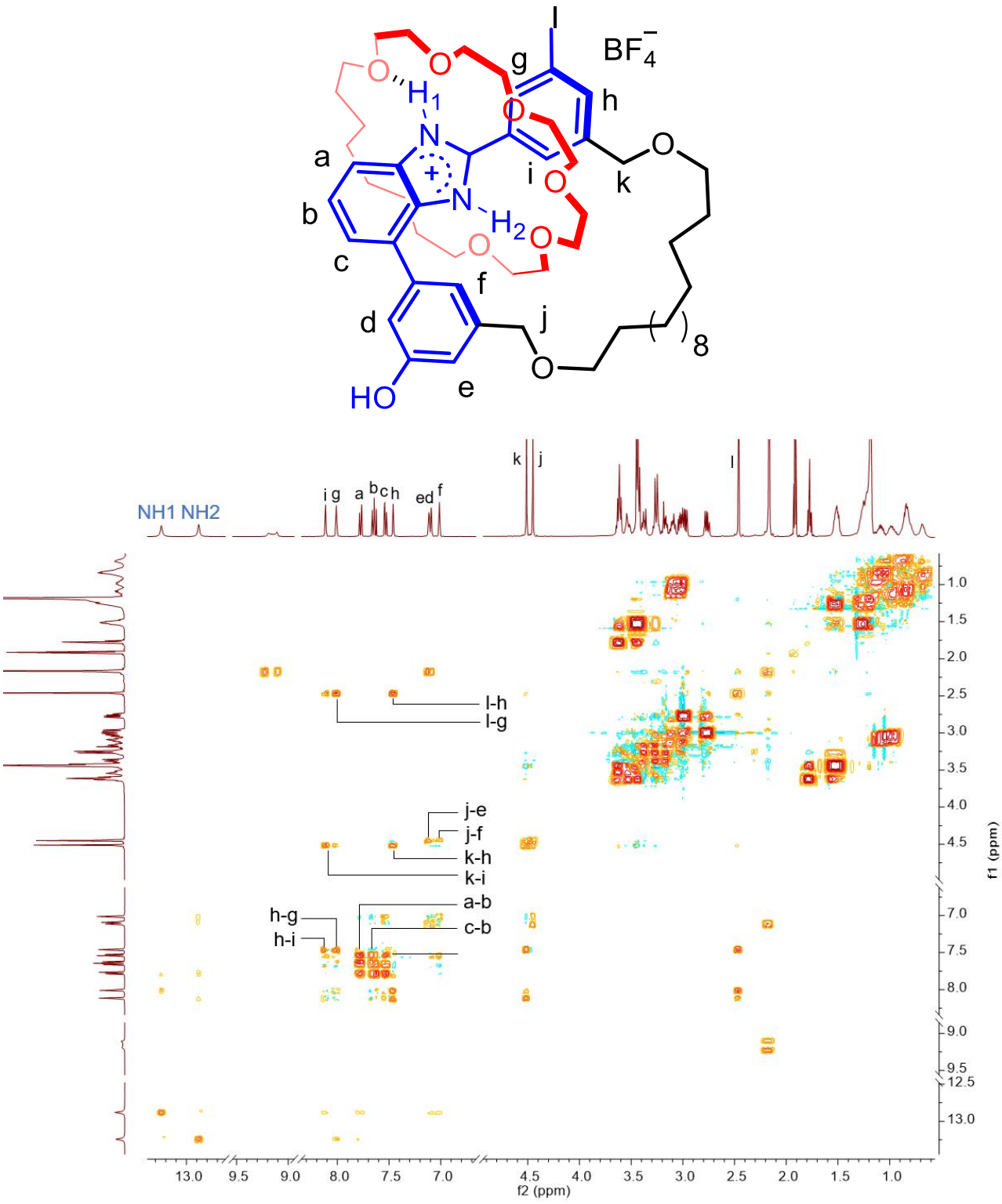


Figure S35. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3CN, 298 K) spectrum of [**M**-H_2][BF_4].

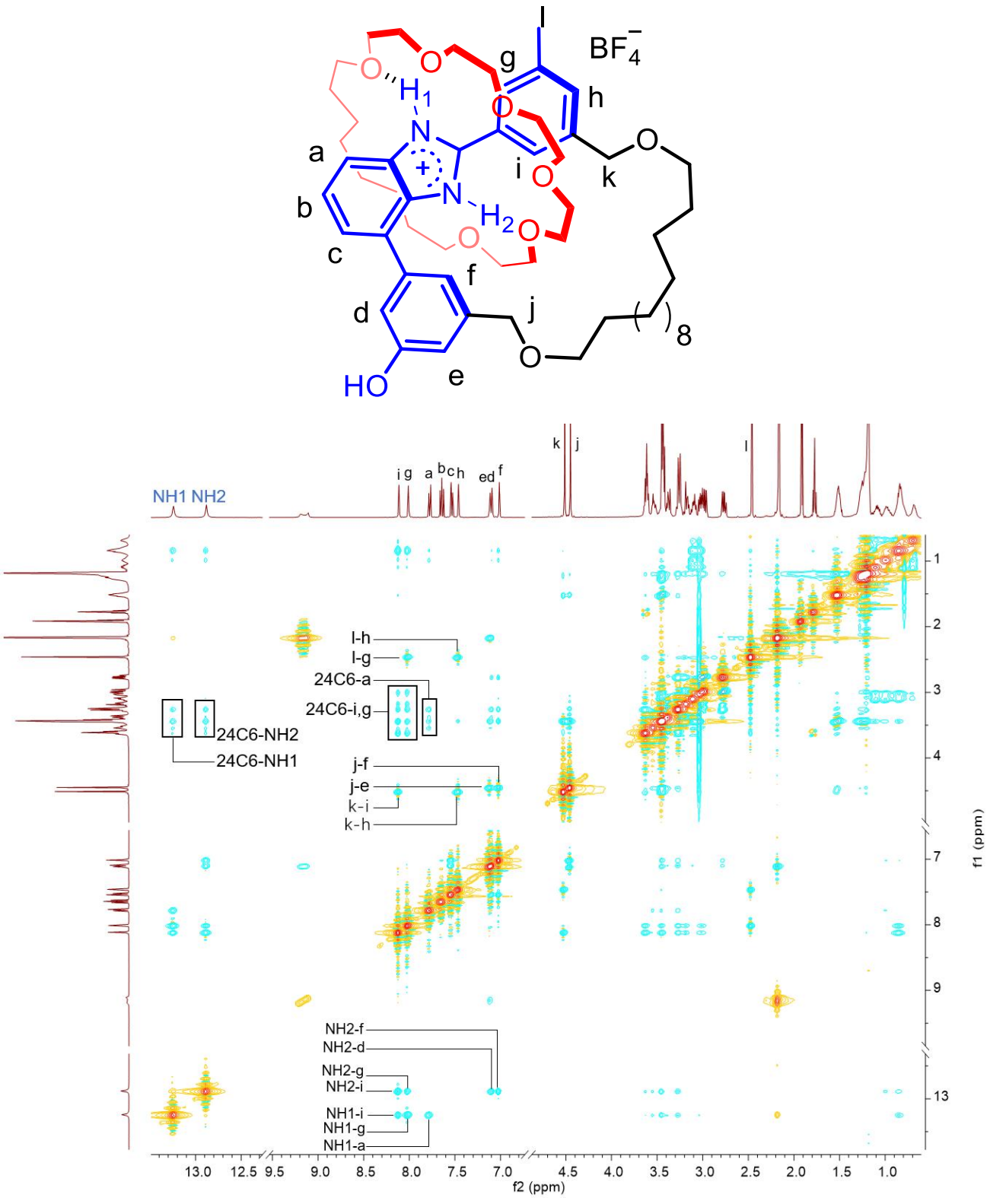


Figure S36. ^{1}H-^{1}H NOESY NMR (400 MHz, CD_3CN, 298 K) spectrum of [**M**-H_2][BF_4].

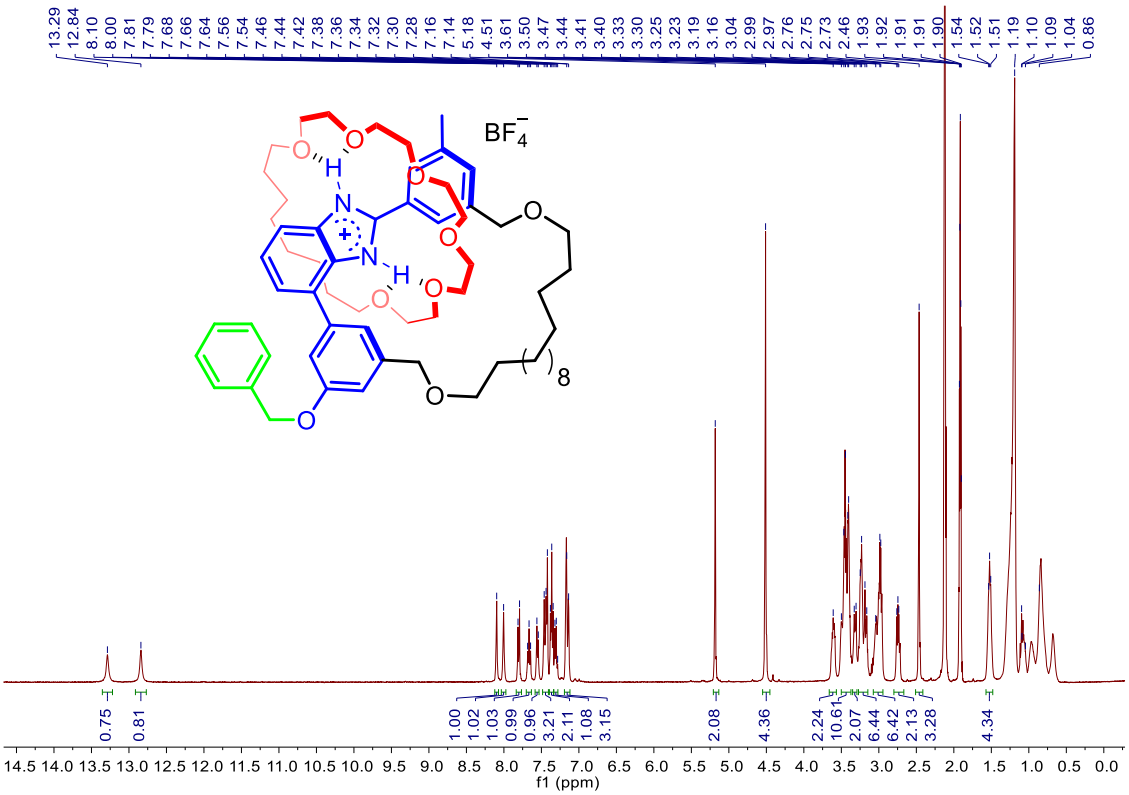


Figure S37. ^{1}H NMR (400 MHz, CD_3CN, 298 K) spectrum of [**I-^{Bn}M**-H_2][BF_4].

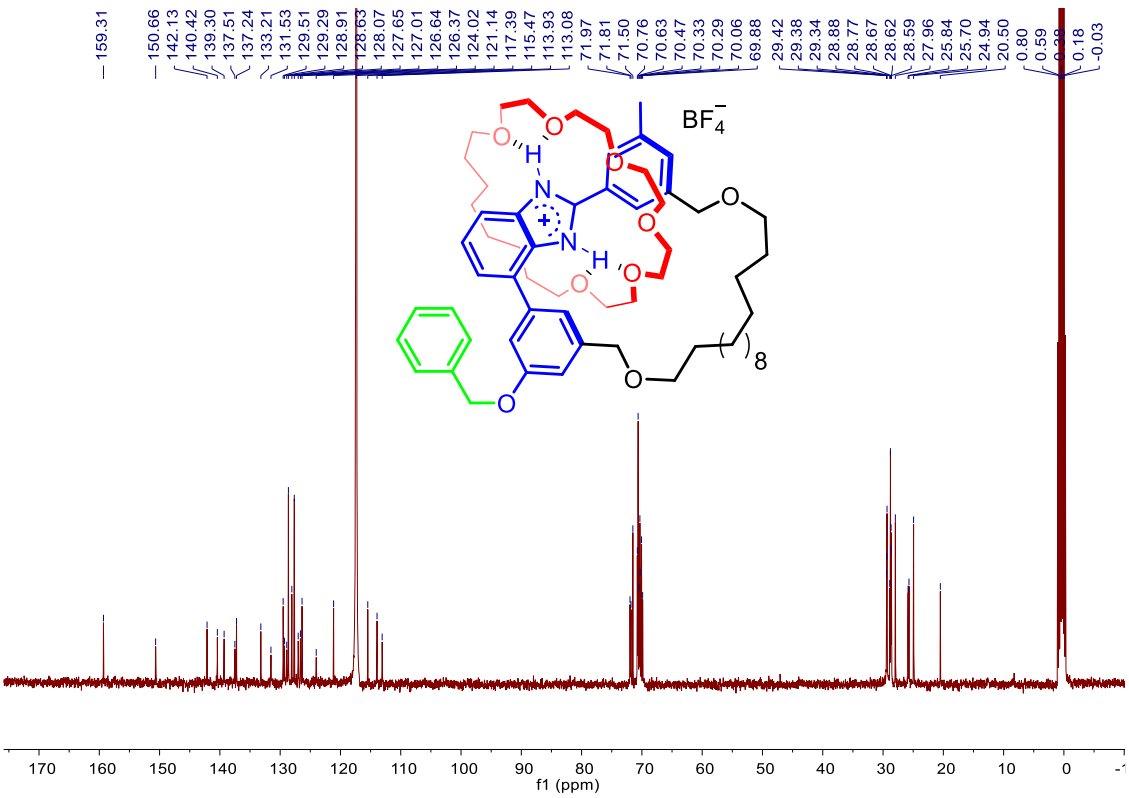


Figure S38. ^{13}C NMR (101 MHz, CD_3CN, 298 K) spectrum of [**I-^{Bn}M**-H_2][BF_4].

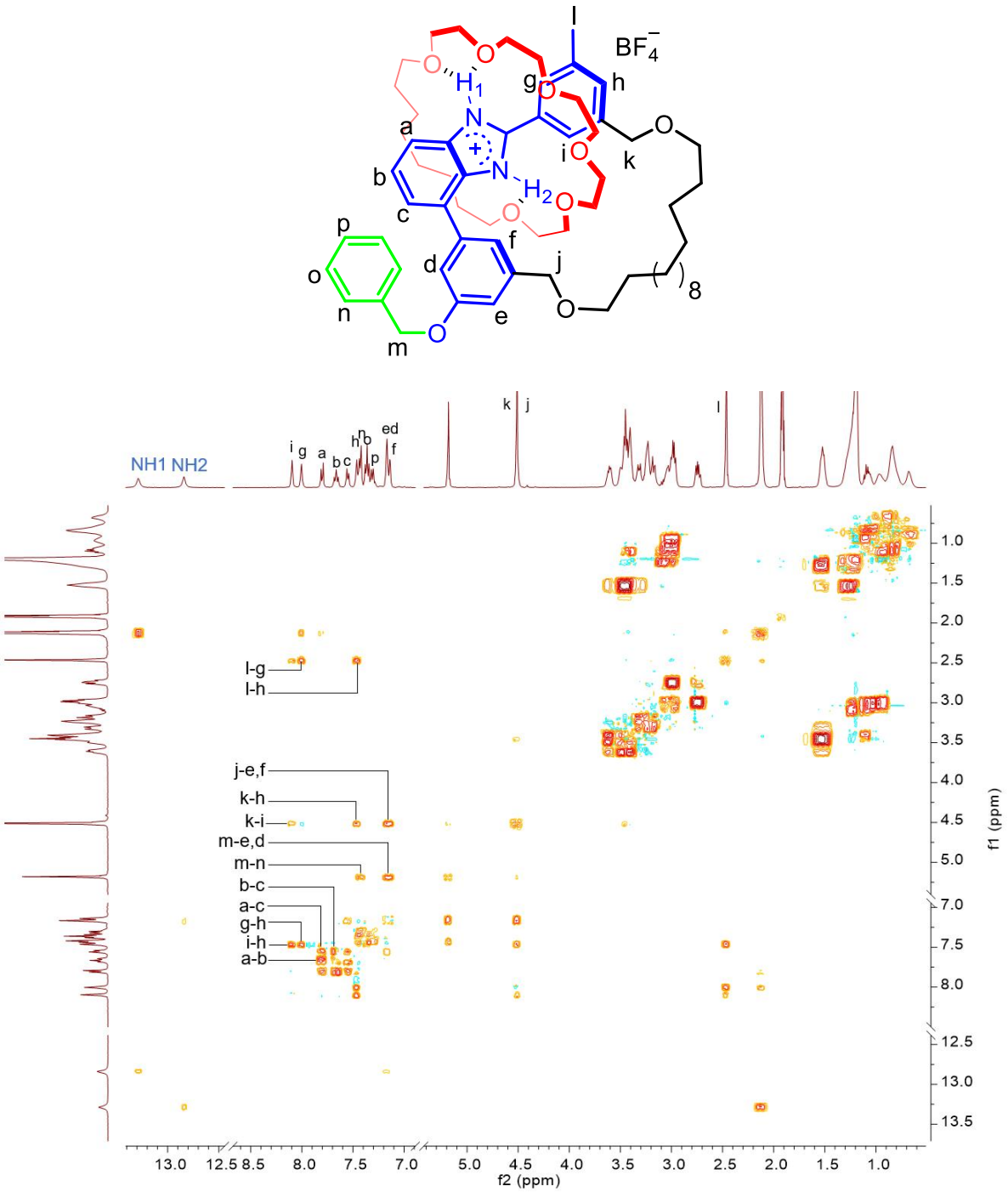


Figure S39. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3CN, 298 K) spectrum of [**I-^{Bn}M**-H_2][BF_4].

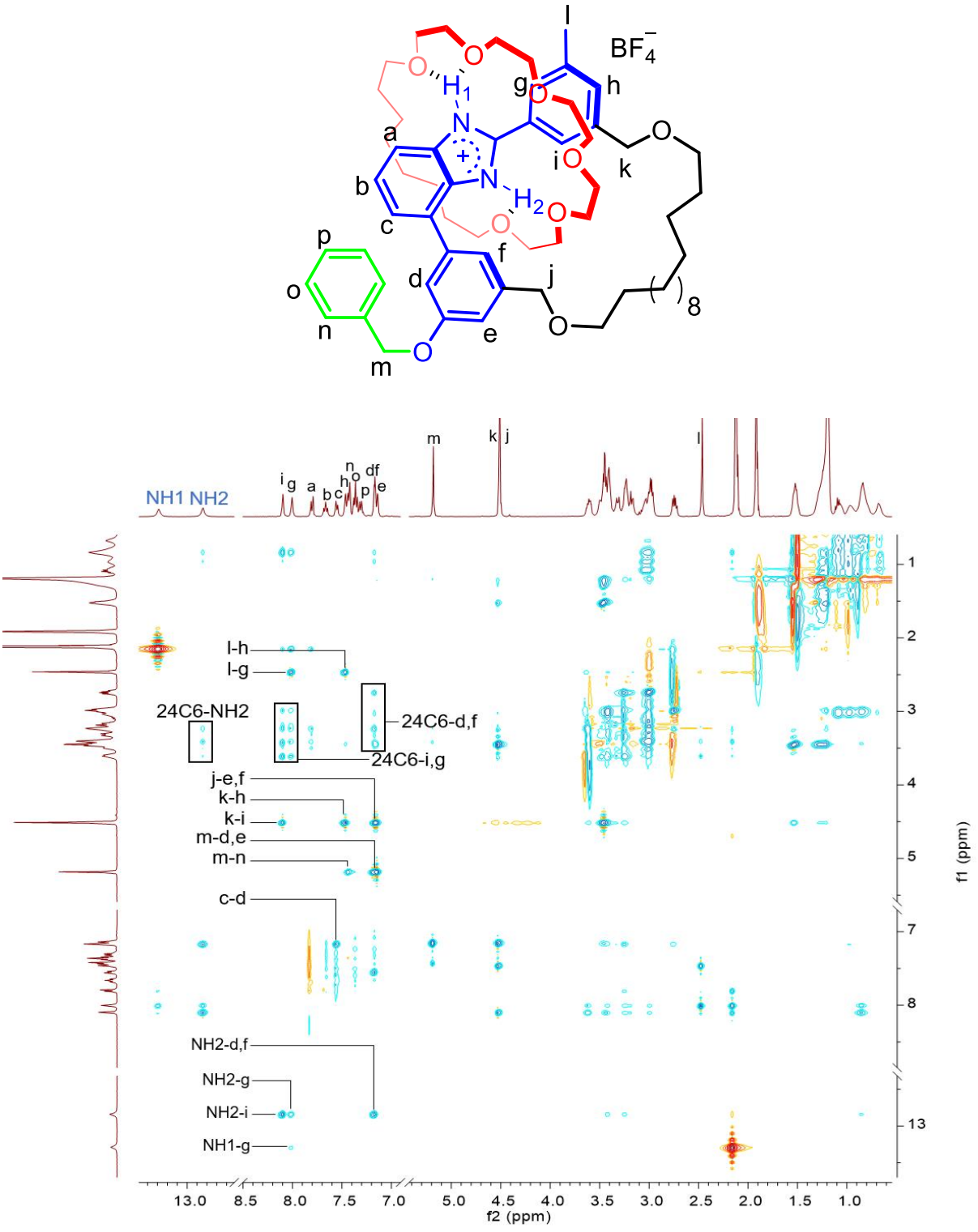


Figure S40. ^{1}H-^{1}H NOESY NMR (400 MHz, CD_3CN, 298 K) spectrum of [**I-**^{Bn}**M**-H_2][BF_4].

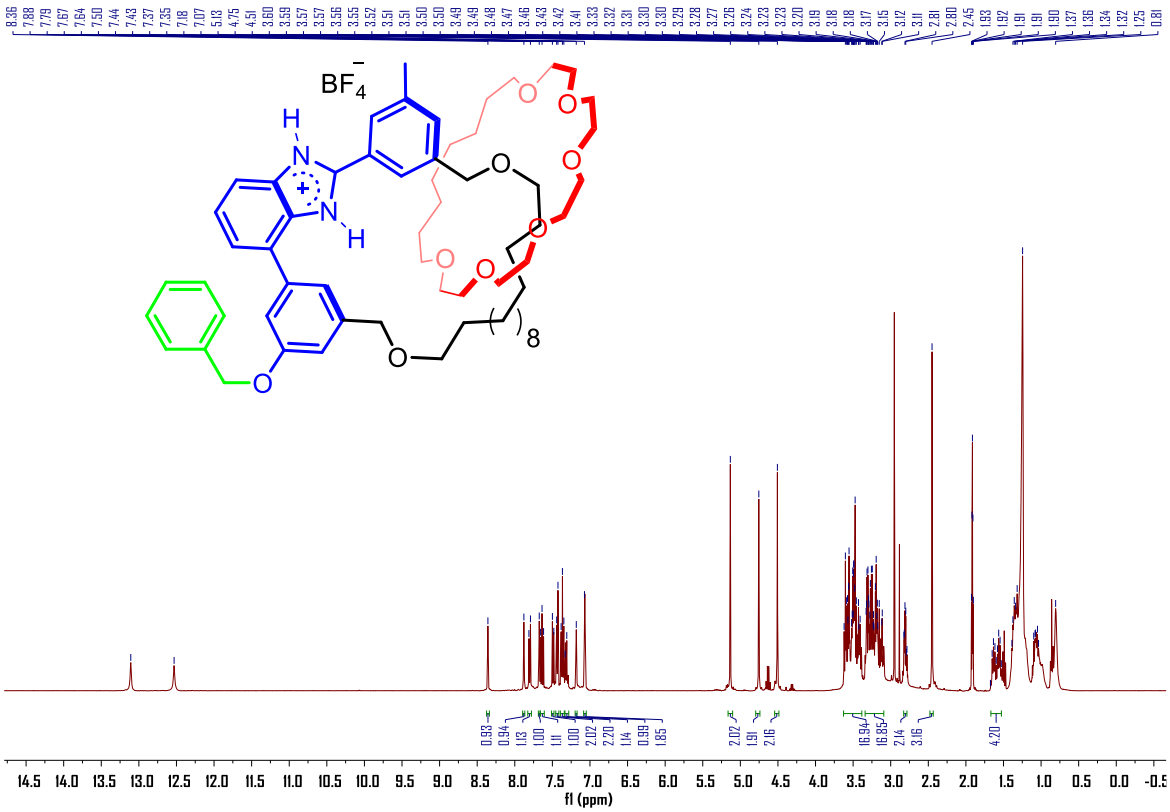


Figure S41. ^{1}H NMR (400 MHz, CD_3CN, 298 K) spectrum of [**II-^{Bn}M**-H_2][BF_4].

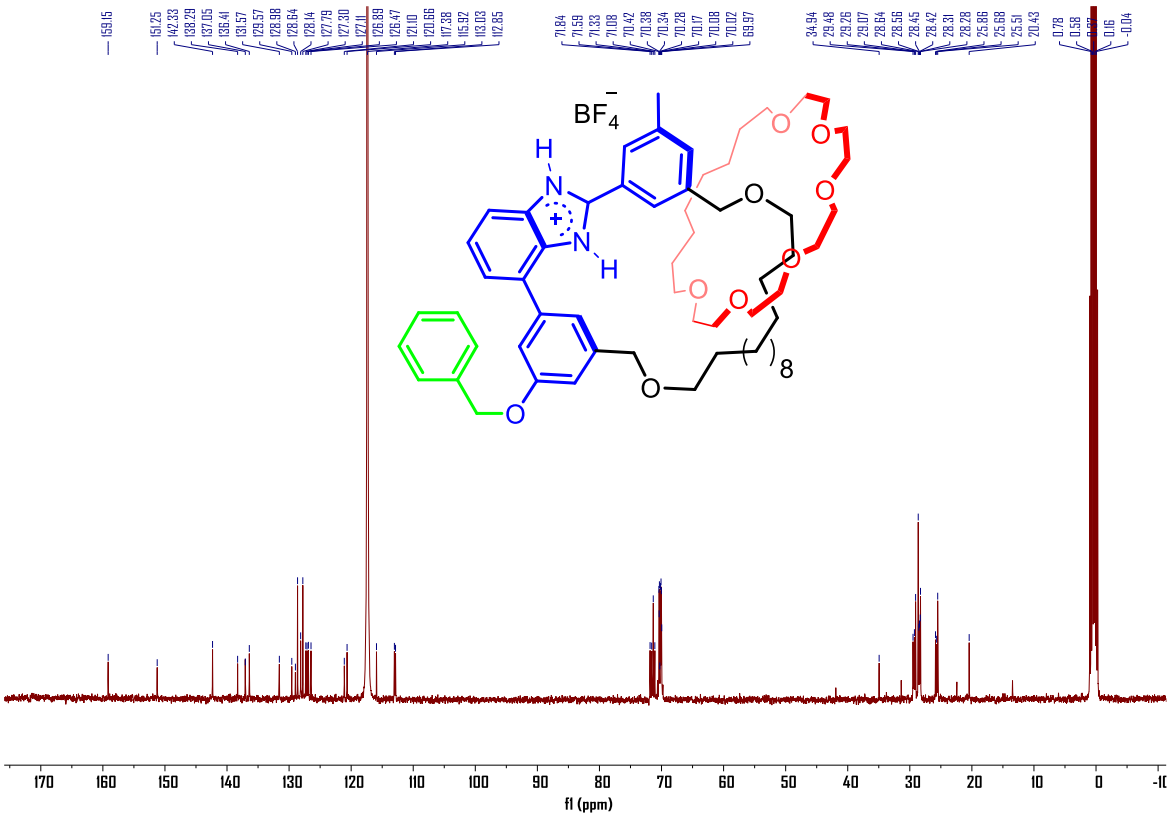


Figure S42. ^{13}C NMR (101 MHz, CD_3CN, 298 K) spectrum of [**II-^{Bn}M**-H_2][BF_4].

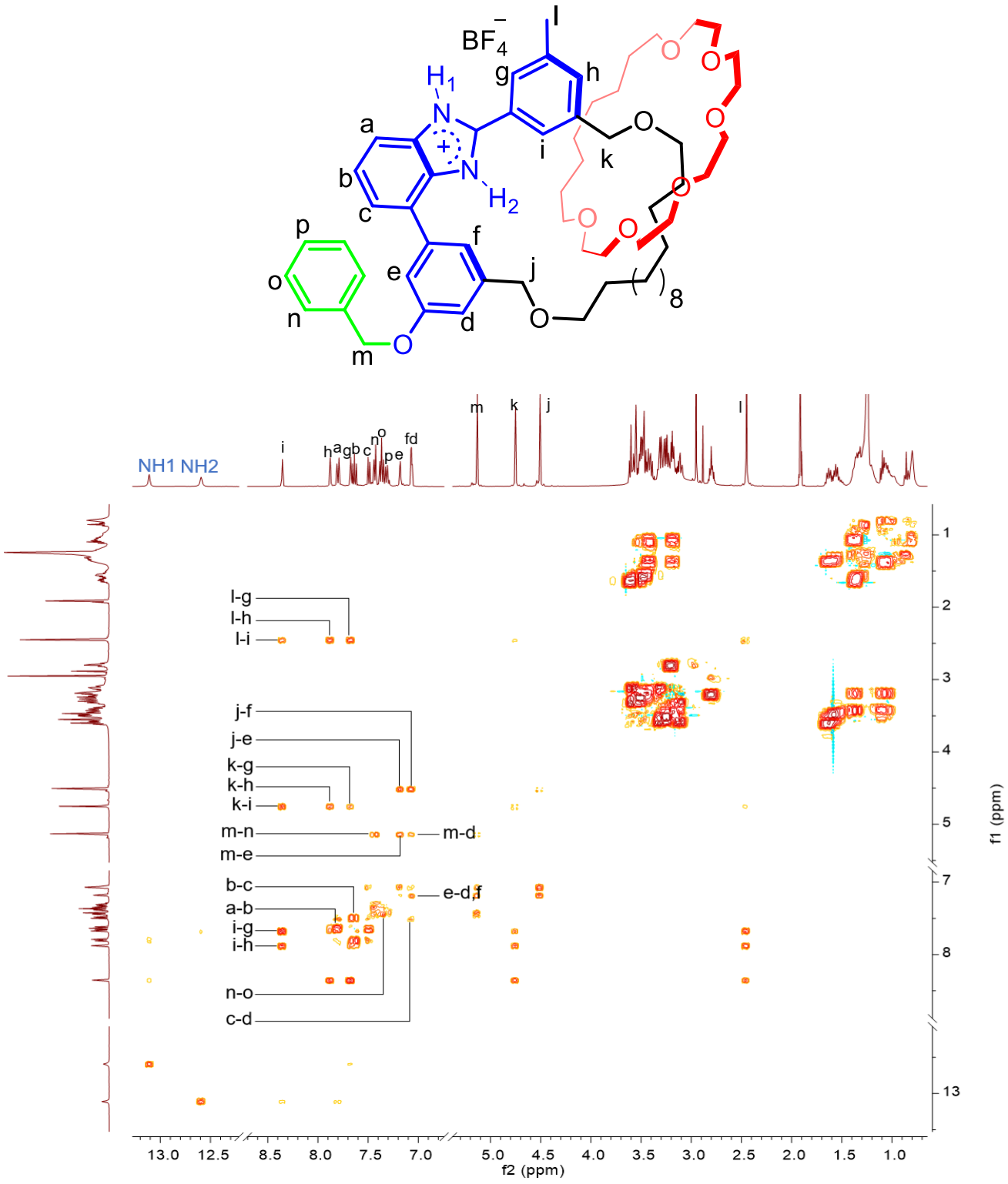


Figure S43. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3CN, 298 K) spectrum of [**II-^{Bn}M**-H_2][BF_4].

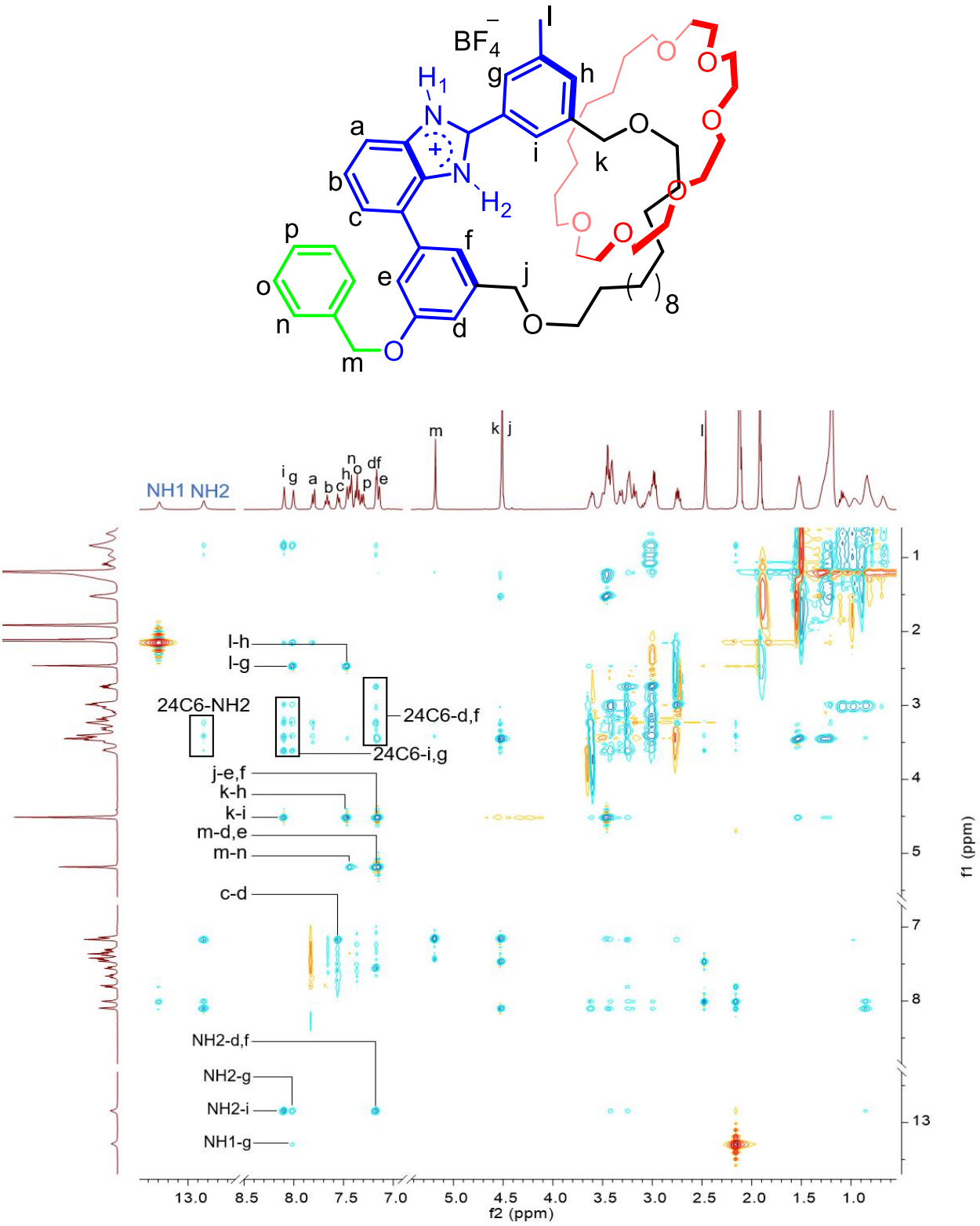


Figure S44. ^{1}H-^{1}H NOESY NMR (400 MHz, CD_3CN, 298 K) spectrum of [**II-^{Bn}M**-H_2][BF_4].

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