Supporting Information

A Novel Pentiptycene Bis(crown ether)-Based [2](2)Rotaxane Whose Two DB24C8 Rings Act as Flapping Wings of Butterfly

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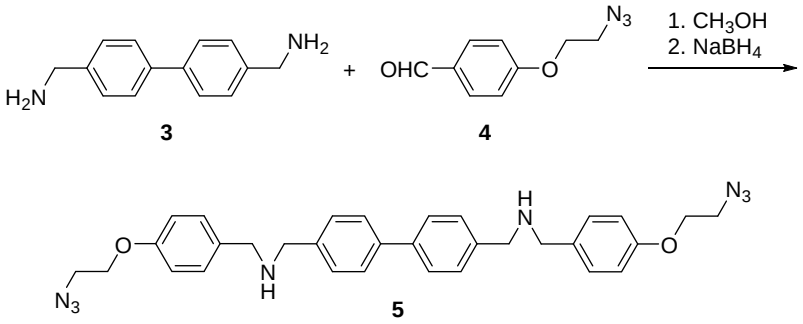
Content

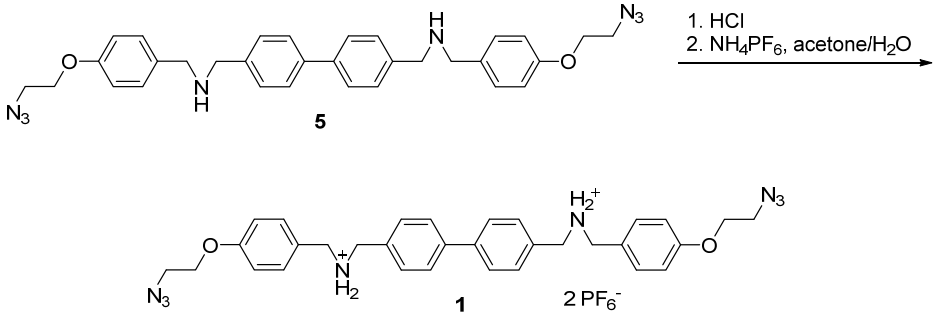
1. Experimental Section

General Methods. NMR spectra were recorded on a Bruker DPX 300 MHz or Bruker AVANCE 600 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. 2D-COSY, ROESY experiments were performed on a Bruker AVANCE 600 MHz spectrometer. Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet), m (multiplet). High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific Exactive^{TM} spectrometer. All reagents, unless otherwise indicated, were obtained from commercial sources without further purification. Compounds 1,3-di-methyl-5-(prop-2-yn-1-yloxy)benzene **2**,[1] [1,1'-biphenyl]-4,4'-diyldimeth-anamine **3**,[2] 4-(2-azidoethoxy)benzaldehyde **4**,[3] and host **H**[4] were synthesized as the literature procedures. Anhydrous CH_2Cl_2, CH_3CN, CH_3OH and DMF were obtained by 4 Å molecular sieves activated under 500 °C for 6 hours. Melting points were determined using a Focus X-4 apparatus and were not corrected. All yields were given as isolated yields.

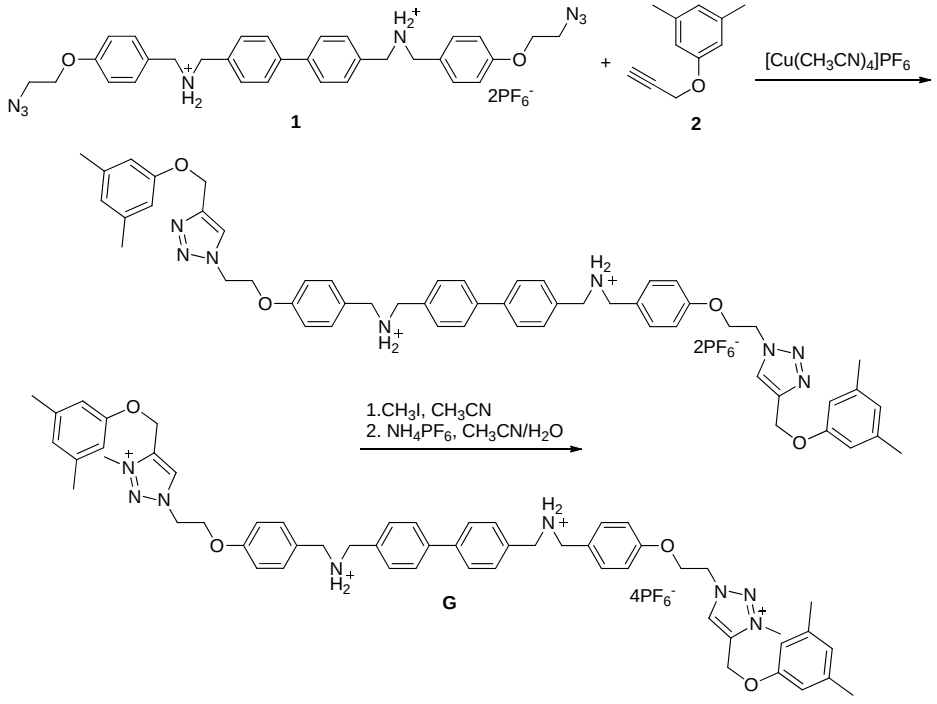


Synthesis of compound 5. A mixture of **3** (1.06 g, 5.0 mmol) and **4** (1.91 g, 10.0 mmol) in dry CH_3OH (100 mL) was stirred for 6 hours. To the solution was then added $NaBH_4$ (5 g, 131.5 mmol) in portion. After the mixture was stirred for overnight, the solvent was removed under vacuum, and the residue was extracted by dichloromethane. The organic layer was washed by brine till clear, dried over anhydrous sodium sulfate, and then concentrated to give the title compound **5** (2.11g, 75% yield) as a white solid. M.p.: 260 °C dec.. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, J = 8.1 Hz, 4H), 7.40 (d, J = 8.1 Hz, 4H), 7.28 (d, J = 8.5 Hz, 4H), 6.89 (d, J = 8.6 Hz, 4H), 4.19–4.10 (m, 4H), 3.83 (s, 4H), 3.78 (s, 4H), 3.59 (d, J = 5.1 Hz, 4H), 1.59 (s, 3H). ^{13}C

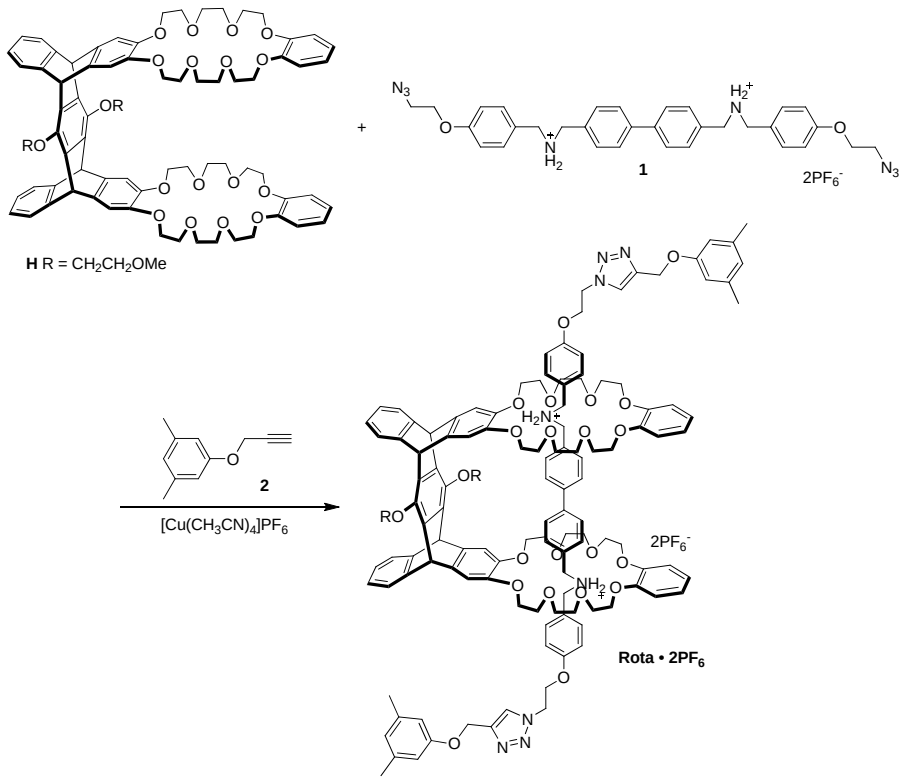
NMR (75 MHz, $CDCl_3$): δ = 157.3, 139.7, 139.5, 133.3, 129.5, 128.6, 127.1, 114.6, 67.1, 52.8, 52.6, 50.2. HRMS (ESI): *m/z* = 563.2869 $[M+H]^+$ (calcd. 562.2804 for $C_{32}H_{35}N_8O_2$).



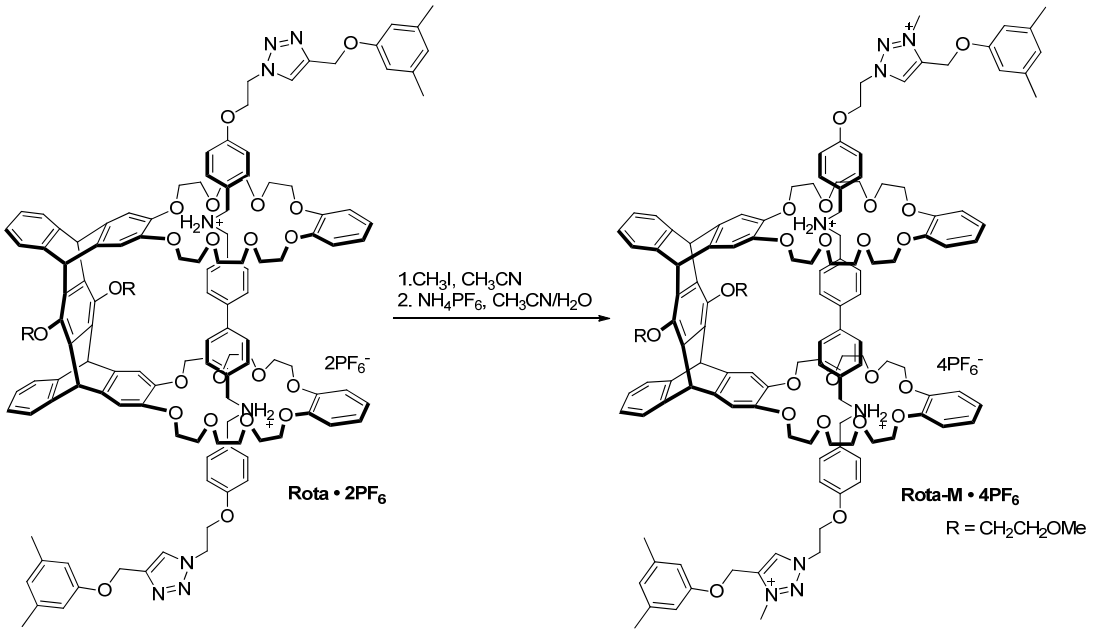
Synthesis of compound 1. To a solution of **5** (2.00 g, 3.6 mmol) in dry DCM (50 mL) was added HCl (10.0 mL) at room temperature. After the mixture was stirred for 2 hours under nitrogen atmosphere, the solvent was removed under vacuum. The residue was dispersed in acetone (20 mL), and then added saturated NH_4PF_6 (2 mL) to yield a white precipitate. After being filtered, washed with H_2O, and dried under vacuum, the title compound **1** (2.94 g) as a pale yellow oil was obtained in 97 % yield. M.p.: 274 °C dec.. ^{1}H NMR (300 MHz, CD_3CN): δ 7.72 (d, *J* = 8.1 Hz, 4H), 7.53 (d, *J* = 8.2 Hz, 4H), 7.40 (d, *J* = 8.6 Hz, 4H), 7.00 (d, *J* = 8.6 Hz, 4H), 4.27–4.11 (m, 12H), 3.67–3.55 (m, 4H). ^{13}C NMR (75 MHz, CD_3CN): δ = 159.1, 140.6, 131.6, 130.5, 130.2, 127.2, 122.9, 114.6, 66.9, 50.8, 50.5, 49.6. HRMS (ESI): *m/z* = 709.2600 $[M-PF_6]^+$ (calcd. 709.2598 for $C_{32}H_{36}N_8O_2P_1F_6$); *m/z* = 282.1477 $[M-2PF_6]^{2+}$ (calcd. 282.1475 for $1/2C_{32}H_{36}N_8O_2$).



Synthesis of compound G. To the mixture of compound **1** (85 mg, 0.1 mmol) and **2** (40 mg 0.25 mmol) in CH_3CN (5 mL) was added $[Cu(CH_3CN)_4]PF_6$ (17 mg, 0.05 mmol). The reaction mixture was stirred for 24 hours under nitrogen atmosphere, the solvent was removed under vacuum. The residue was extracted by dichloromethane, the organic layer was washed by H_2O till clear, dried over anhydrous sodium sulfate to give a white solid. The solid was dissolved in dry CH_3CN (5 mL), and then added iodomethane (3 mL). After the mixture was stirred for 48 hours at 50 °C, the excess iodomethane was evaporated, and the residue was washed with H_2O to give a pale yellow solid. To a suspension of the solid in CH_3CN (5 mL) was added saturated NH_4PF_6. The resulted mixture was vigorously stirred for 2 hours. The aqueous layer was extracted with DCM (5 mL × 3). The combined organic layer was dried over Na_2SO_4, and then concentrated to give **G** (97 mg, 65 %) as a pale yellow solid. M.p.: 267 °C dec.. ^{1}H NMR (300 MHz, $CD_3CN/CDCl_3$ = 1:1): δ 8.56 (s, 2H), 7.82–7.65 (m, 4H), 7.57 (d, *J* = 7.7 Hz, 4H), 7.44 (d, *J* = 6.8 Hz, 4H), 7.00 (t, *J* = 8.4 Hz, 4H), 6.71 (s, 2H), 6.66 (s, 4H), 5.27 (s, 4H), 5.02–4.94 (m, 4H), 4.53–4.16 (m, 14H), 2.28 (s, 12H). ^{13}C NMR (75 MHz, CD3CN/CDCl3 = 1:1): δ = 156.2, 139.2, 138.9, 132.0, 131.2, 130.9, 130.1, 129.4, 127.0, 123.3, 126.8, 114.5, 114.3, 111.6, 57.0, 52.6, 37.9, 28.7, 28.3, 20.0. HRMS (ESI): *m/z* = 602.2231 $[M\text{-}2PF_6]^{2+}$ (calcd. 602.2245 for $C_{56}H_{66}N_8O_4P_2F_{24}$).



Synthesis of Rota•2PF$_6$. To the mixture of host **H** (131.9 mg, 0.1mmol) and **1** (85.5 mg 0.1 mmol) in DCM (10 mL) was added [Cu(CH$_3$CN)$_4$]PF$_6$ (35.5 mg, 0.1 mmol) and compound **2** (96.1 mg, 0.60 mmol). The reaction mixture was stirred for 24 hours at room temperature, and then concentrated. The residue was subjected to silica gel column chromatography with CH$_3$OH/DCM (1:100, v/v) as eluent to give the **Rota•2PF$_6$** (112.3 mg, 45 %) as a pale yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.81 (s, 2H), 7.62 (br, 4H), 7.30 (m, 4H), 7.23 (d, *J* = 8.9 Hz, 4H), 7.14 (d, *J* = 7.9 Hz, 4H), 7.09 (d, *J* = 8.3 Hz, 4H), 6.98–6.88 (m, 8H), 6.80–6.76 (m, 4H), 6.72–6.63 (m, 6H), 6.61 (s, 8H), 5.68 (s, 4H), 5.17 (s, 4H), 4.86–4.78 (m, 4H), 4.74 (t, *J* = 4.9 Hz, 4H), 4.74 (t, *J* = 4.9 Hz, 4H), 4.42–4.33 (m, 4H), 4.30 (t, *J* = 4.4 Hz, 3H), 4.21–4.10 (m, 6H), 4.10–4.00 (m, 8H), 3.9–3.84 (m, 14H), 3.76–3.63 (m, 24H), 3.54–3.43 (m, 6H), 3.42–3.33 (m, 6H), 2.27 (s, 12H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 158.6, 146.9, 146.3, 145.4, 144.8, 144.6, 139.3, 138.4, 136.7, 131.0, 129.1, 127.1, 125.3, 125.0, 123.6, 123.5, 123.2, 123.1, 121.7, 121.6, 114.7, 112.6, 112.1, 109.7, 71.9, 71.8, 70.8, 70.4, 70.0, 69.6, 68.8, 68.3, 67.7, 67.1, 67.0, 59.3, 47.7, 47.6, 21.5. HRMS (ESI): *m/z* = 2349.0107 [M-PF$_6$]$^+$ (calcd. 2349.0120 for C$_{130}$H$_{146}$N$_8$O$_{24}$P$_1$F$_6$); *m/z* = 1102.0222 [M-2PF$_6$]$^{2+}$ (calcd. 1102.0236 for 1/2C$_{130}$H$_{146}$N$_8$O$_{24}$).



Synthesis of Rota-M•4PF$_6$. To **Rota•2PF$_6$** (100.0 mg, 0.04 mmol) in dry CH$_3$CN (5 mL) was added iodomethane (3 mL), and the mixture was stirred for 48 hours at 50 °C. The excess iodomethane was evaporated, and the residue was washed with H$_2$O to give a pale yellow solid. To a suspension of the solid in CH$_3$CN (5 mL) was added saturated NH$_4$PF$_6$, and the resulted

mixture was vigorously stirred for 2 hours. The aqueous layer was extracted with DCM (5 mL × 3). The combined organic layer was dried over Na_2SO_4, and then concentrated to give the title complex **Rota-M•4PF$_6$** (109 mg, 97 %) as a pale yellow solid. ^{1}H NMR (600 MHz, $CDCl_3/CD_3CN$ = 1:1, v/v): δ 8.56 (s, 2H), 7.58 (br, 4H), 7.34 (d, *J* = 8.7 Hz, 4H), 7.32 (dd, *J* = 5.2, 3.3 Hz, 4H), 7.23 (d, *J* = 8.3 Hz, 4H), 7.02 (d, *J* = 8.3 Hz, 4H), 7.00 (s, 4H), 6.93 (dd, *J* = 5.4, 3.1 Hz, 4H), 6.76 (d, *J* = 8.7 Hz, 4H), 6.74 (m, 6H), 6.67 (dd, *J* = 6.1, 3.8 Hz, 8H), 5.70 (s, 4H), 5.31 (s, 4H), 4.96 (dd, *J* = 9.4, 4.6 Hz, 4H), 4.95–4.90 (m, 4H), 4.46–4.41 (m, 4H), 4.40–4.34 (m, 4H), 4.32 (s, 6H), 4.24 (t, *J* = 9.7 Hz, 4H), 4.12–3.98 (m, 14H), 3.97–3.86 (m, 12H), 3.77 (dd, *J* = 15.3, 3.4 Hz, 12H), 3.73–3.62 (m, 12H), 3.60 (d, *J* = 8.6 Hz, 6H), 3.60–3.51 (m, 8H), 2.31 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3/CD_3CN$ = 1:1, v/v): δ = 158.1, 157.1, 146.8, 146.2, 145.4, 144.9, 140.1, 139.8, 138.1, 136.9, 131.8, 131.1, 130.2, 129.5, 126.6, 125.0, 124.5, 124.2, 123.2, 121.3, 114.7, 112.4, 112.0, 109.7, 74.7, 71.7, 71.0, 70.9, 70.3, 69.9, 68.1, 67.9, 64.8, 58.7, 57.9, 53.5, 52.2, 51.9, 47.4, 38.8, 20.9. HRMS (ESI): *m/z* = 1262.0077 $[M\text{-}2PF_6]^{2+}$ (calcd. 2524.0237 for $1/2C_{132}H_{152}N_8O_{24}P_2F_{12}$); *m/z* = 793.0169 $[M\text{-}3PF_6]^{3+}$ (calcd. 2379.0595 for 1/3 $C_{130}H_{146}N_8O_{24}P_1F_6$); *m/z* = 558.5218 $[M\text{-}4PF_6]^{4+}$ (calcd. 2234.0953 for 1/4 $C_{130}H_{146}N_8O_{24}$).

2. ^{1}H NMR and ^{13}C NMR spectra of all new compounds

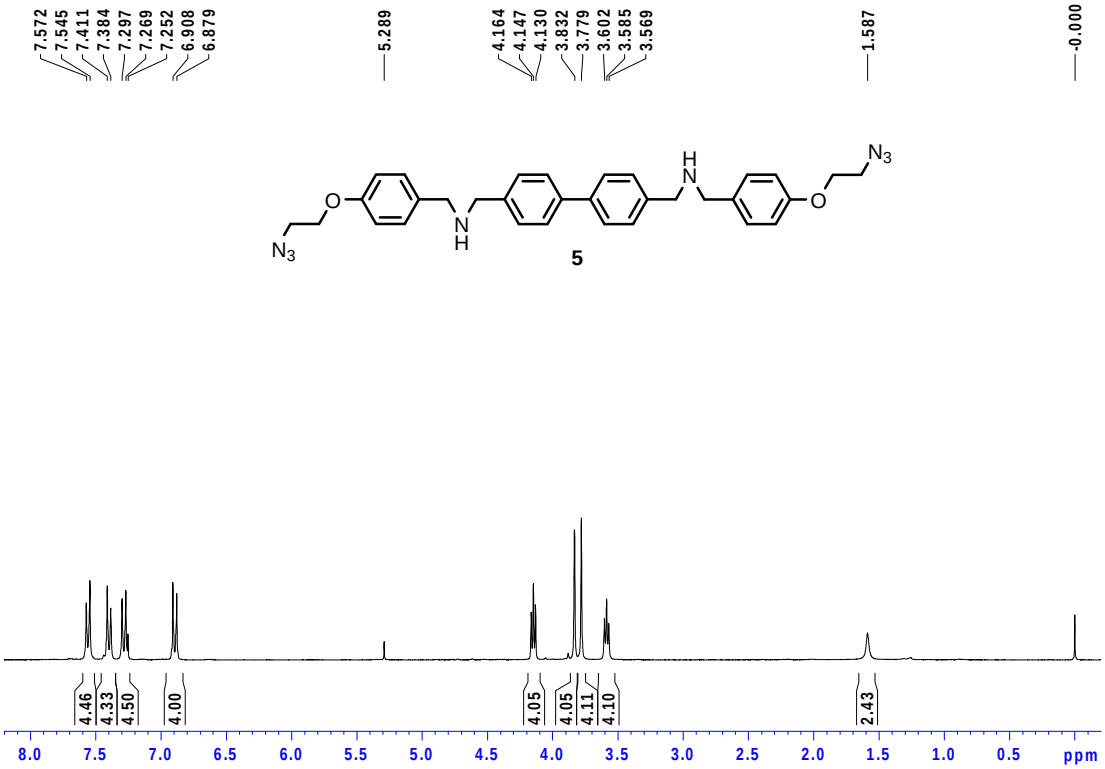


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of **5**.

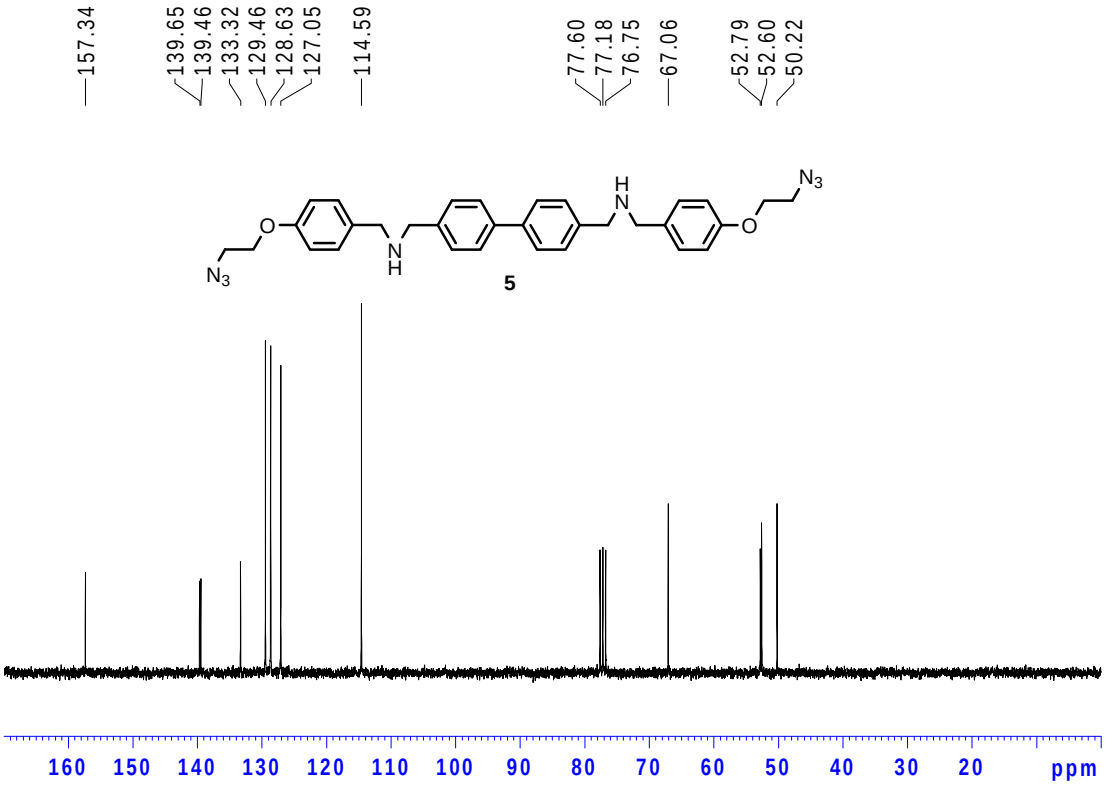


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of **5**.

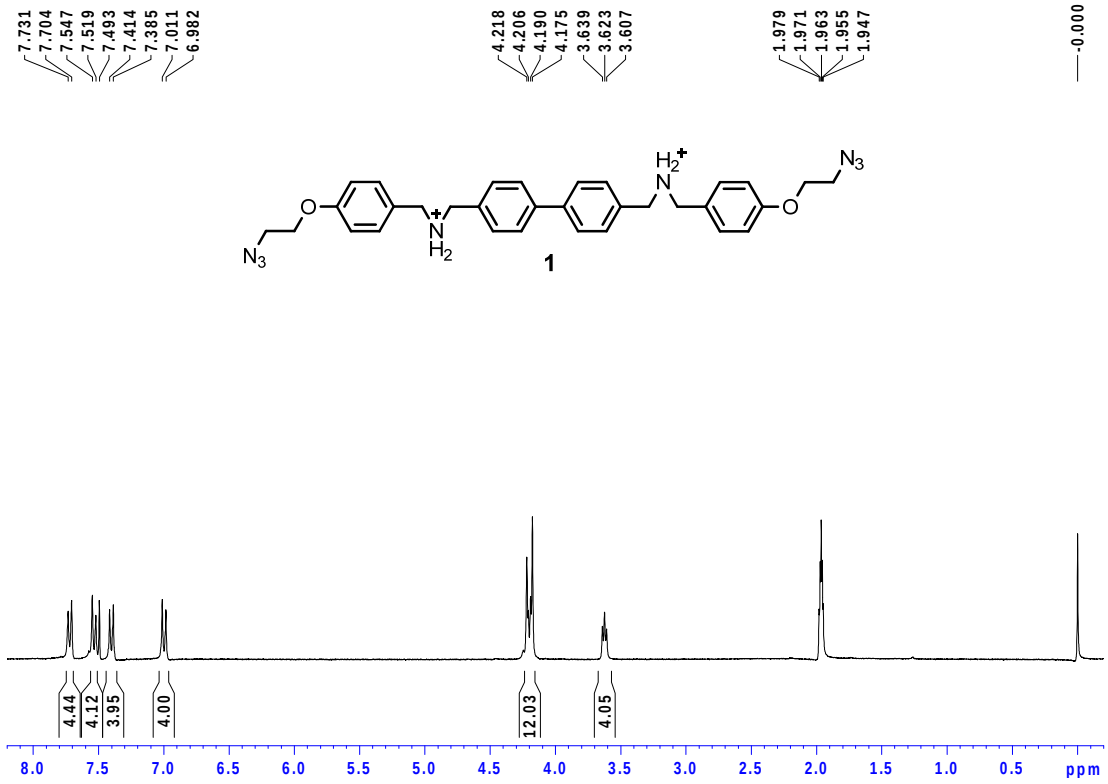


Figure S3. ^{1}H NMR spectrum (CD_3CN, 300 MHz, 298 K) of **1**.

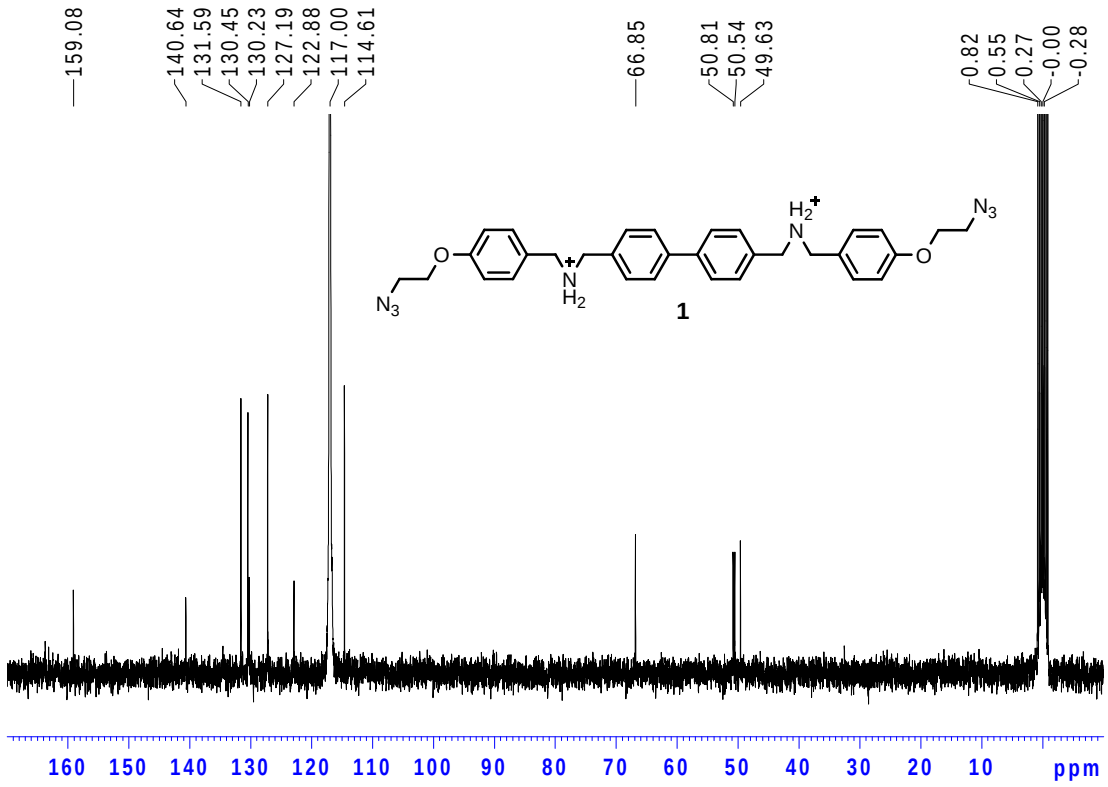


Figure S4. ^{13}C NMR spectrum (CD_3CN, 75 MHz, 298 K) of **1**.

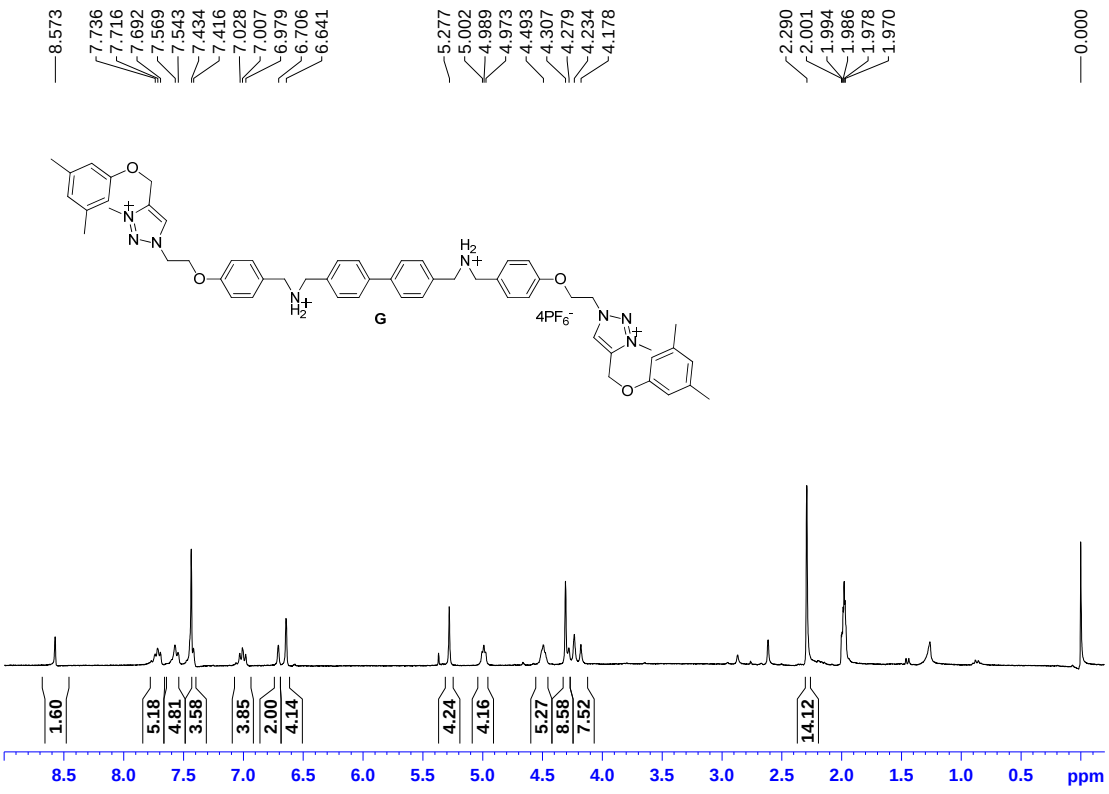


Figure S5. ^{1}H NMR spectrum ($CD_3CN/CDCl_3$ = 1:1, v/v, 300 MHz, 298 K) of **G**.

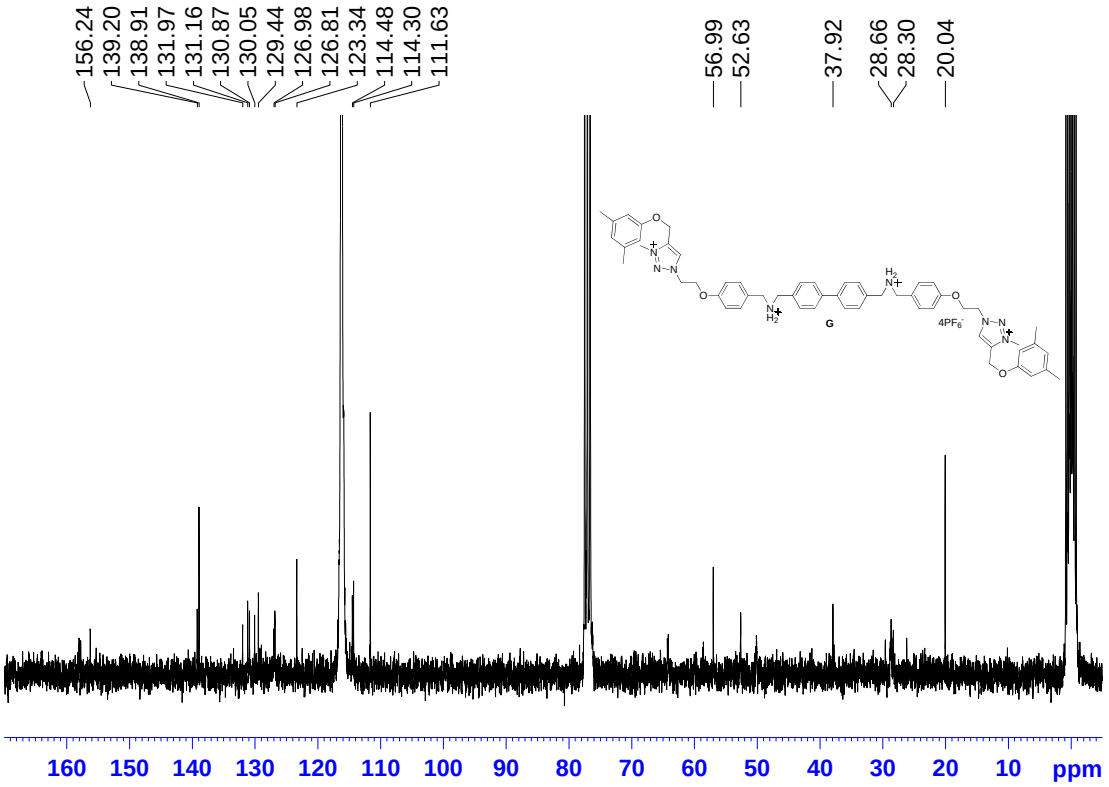


Figure S6. ^{13}C NMR spectrum ($CD_3CN/CDCl_3$ = 1:1, v/v, 75 MHz, 298 K) of **G**.

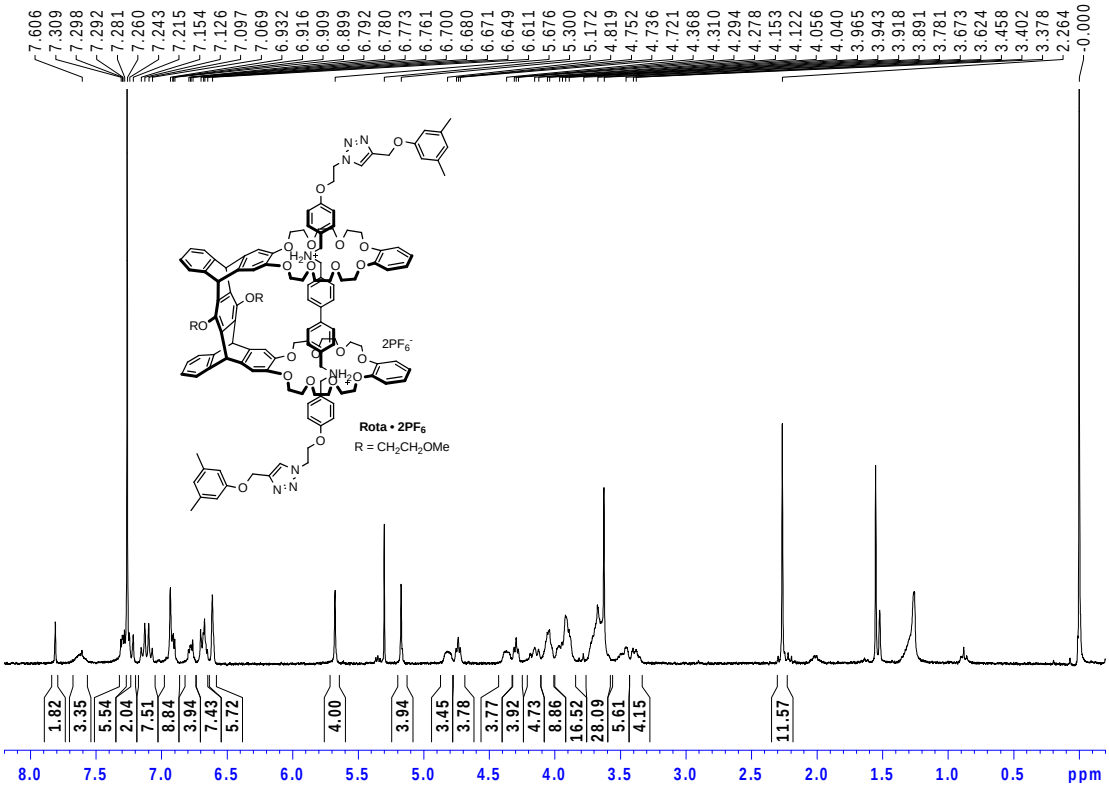


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of **Rota•2PF$_6$**.

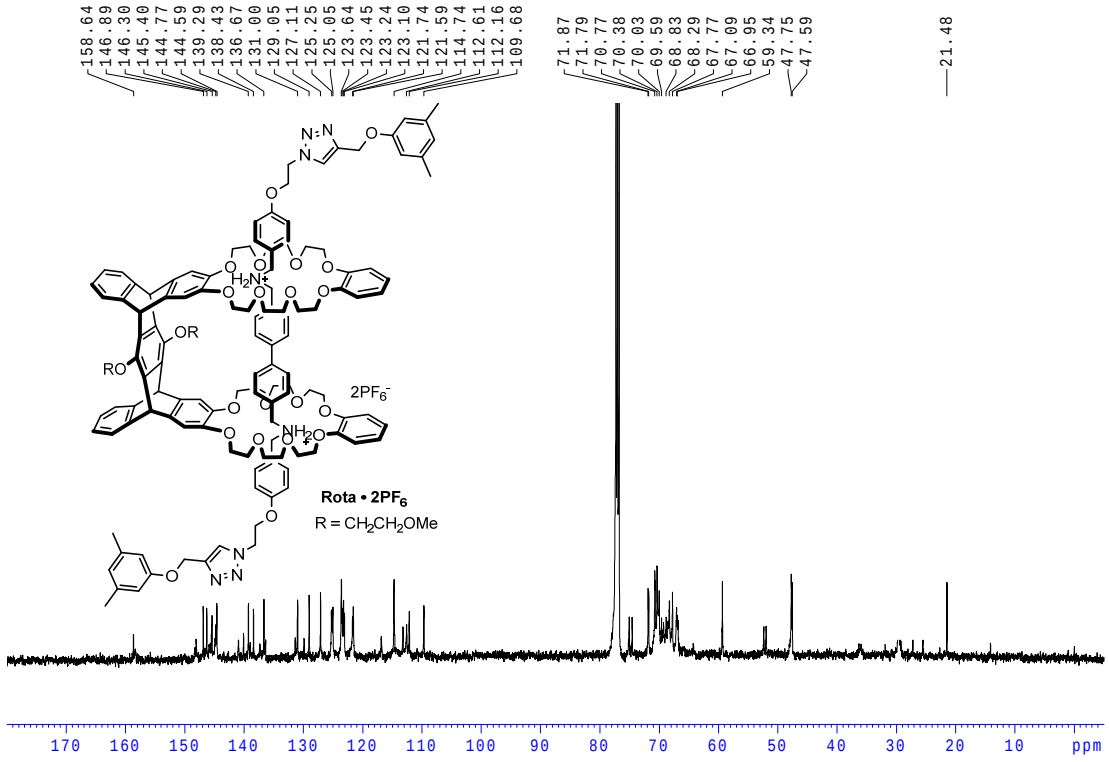


Figure S8. ^{13}C NMR spectrum ($CDCl_3$, MHz, 298 K) of **Rota•2PF$_6$**.

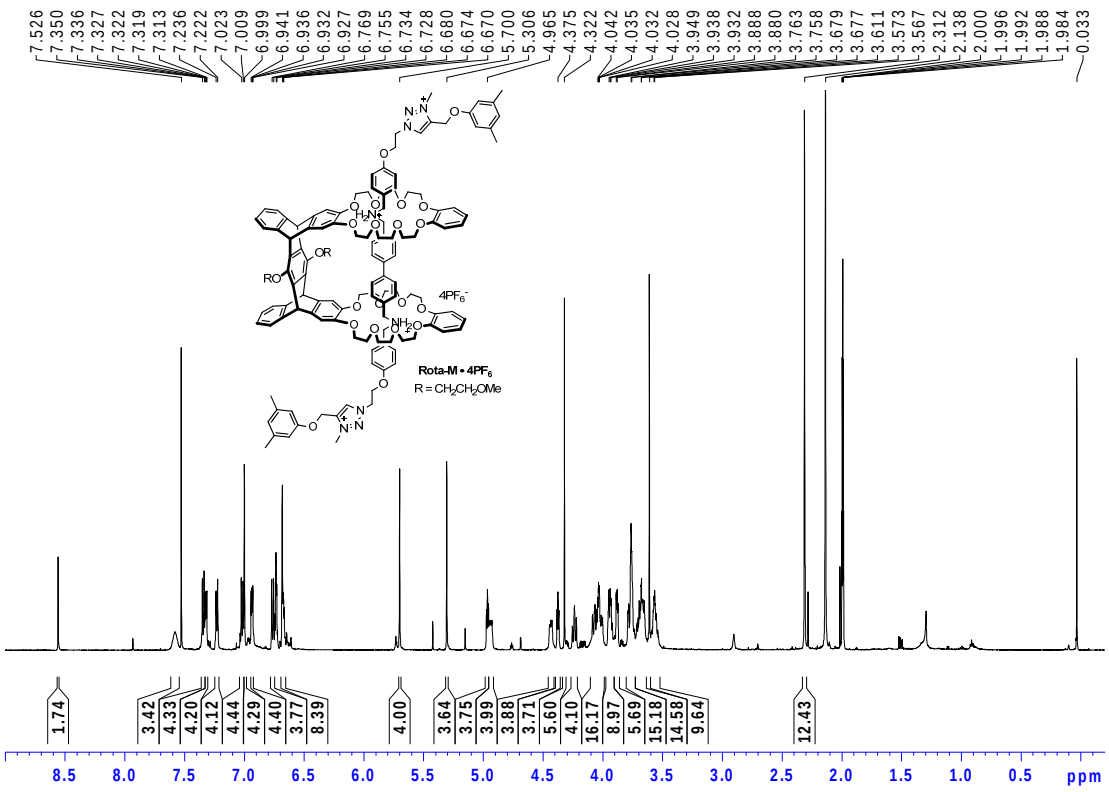


Figure S9. ^{1}H NMR spectrum ($CD_3CN/CDCl_3$ = 1:1, v/v, 600 MHz, 298 K) of **Rota-M•4PF$_6$**.

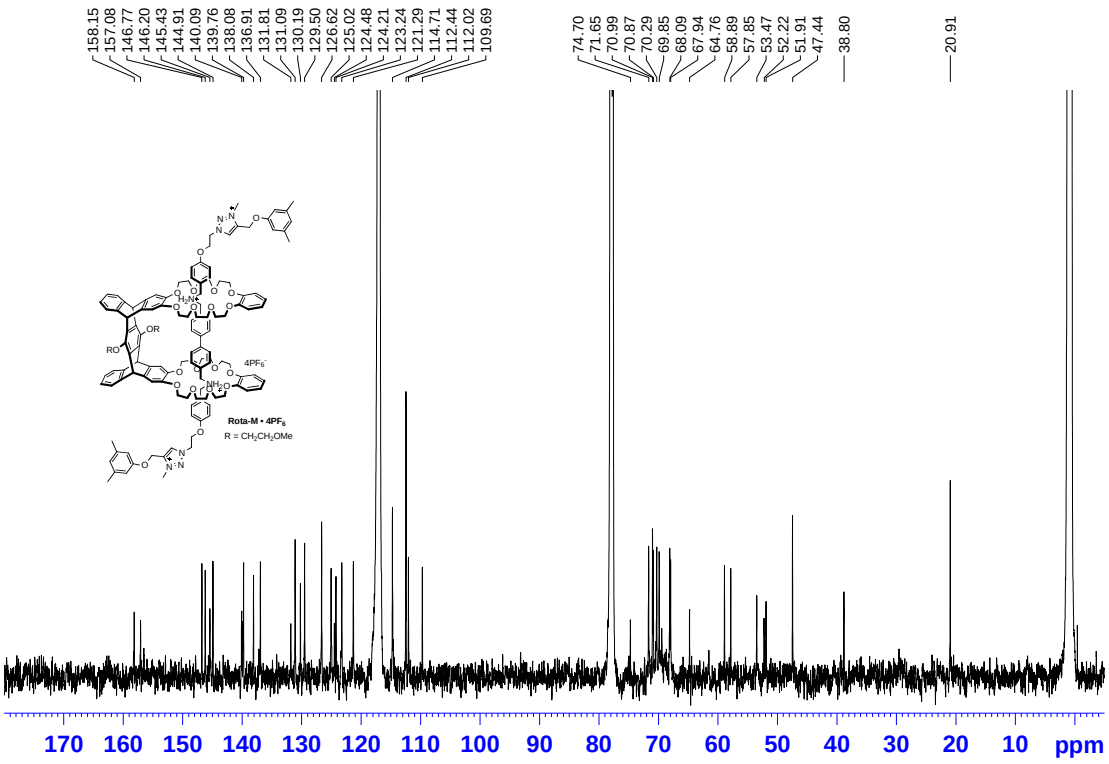
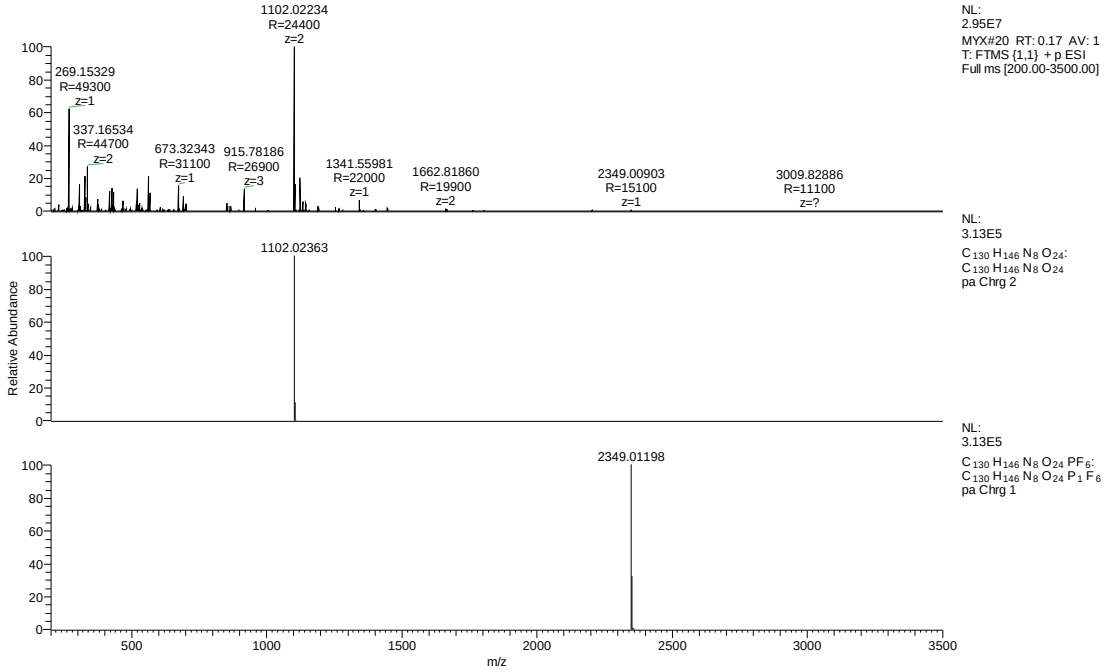
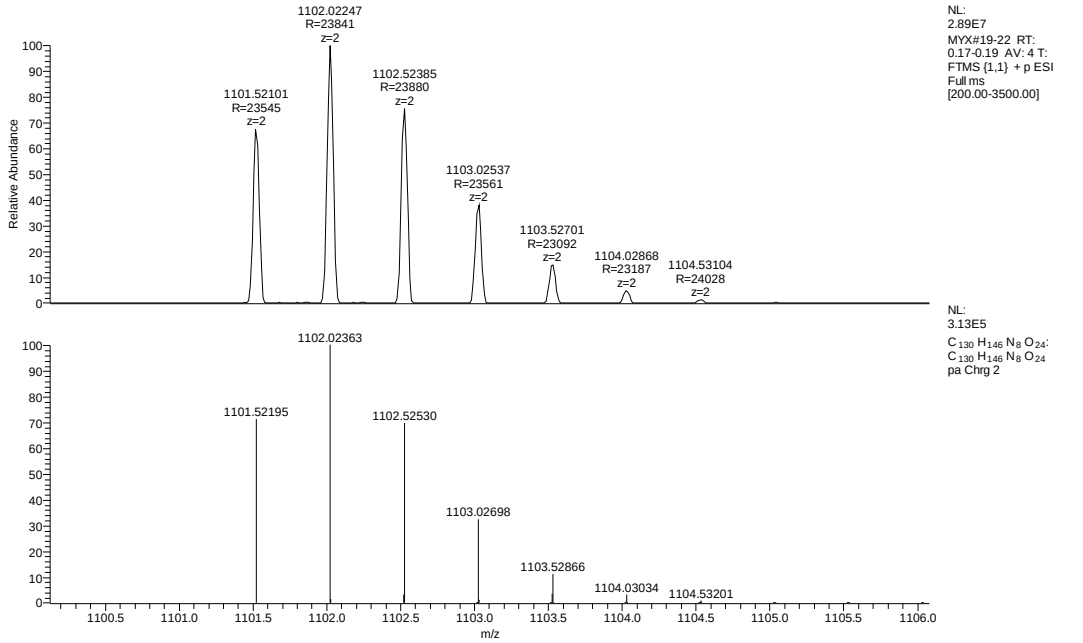


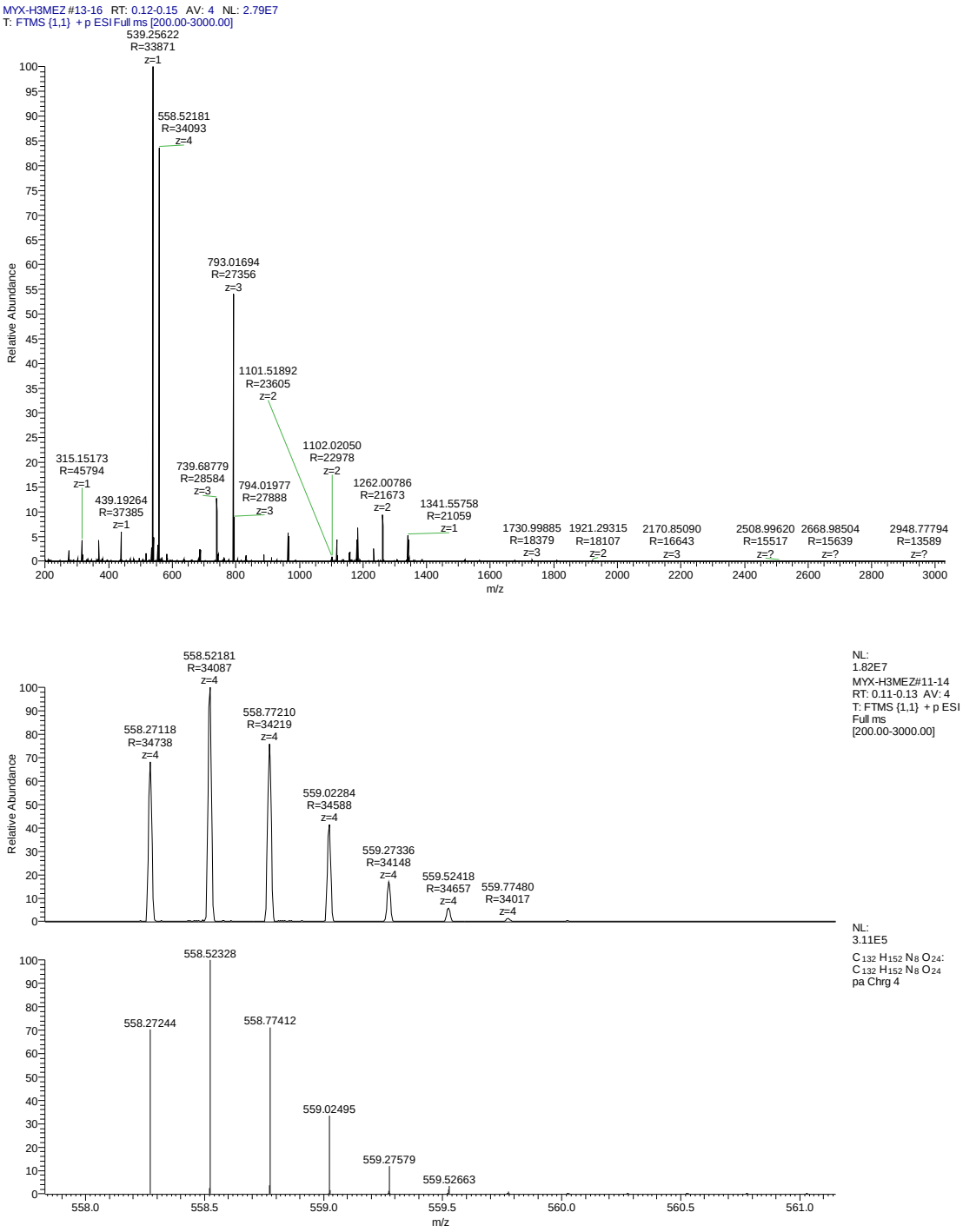
Figure S10. ^{13}C NMR spectrum ($CD_3CN/CDCl_3$ = 1:1, v/v, 151 MHz, 298 K) of **Rota-M•4PF$_6$**.

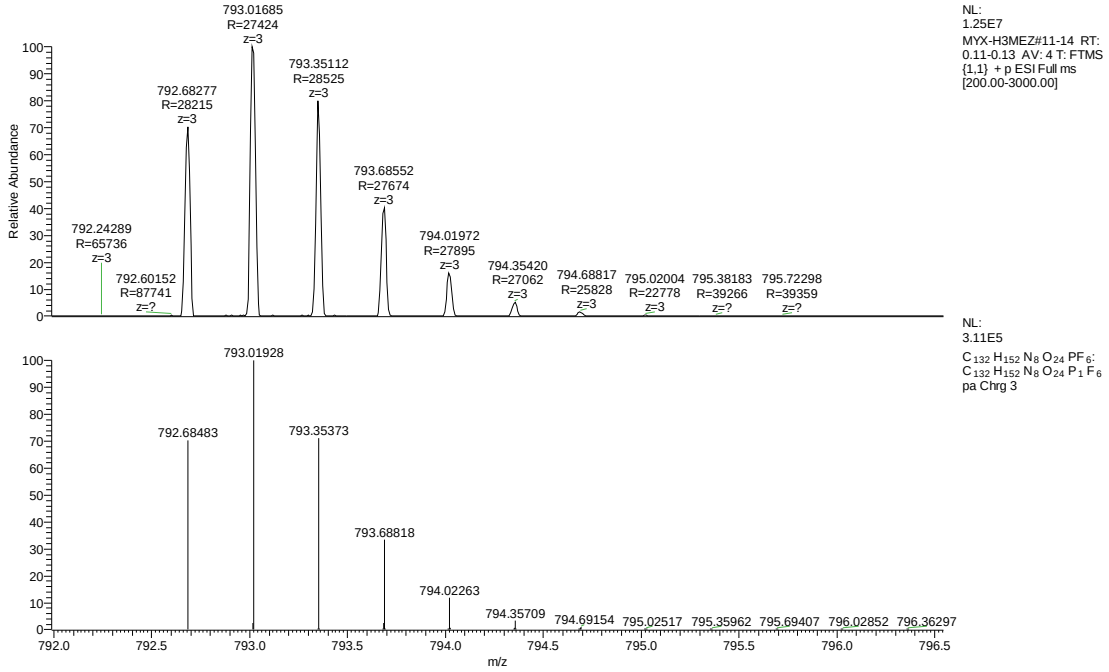
3. HRMS spectrum for Rota•2PF_6





4. HRMS spectrum for Rota-M•4PF_6

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z=?
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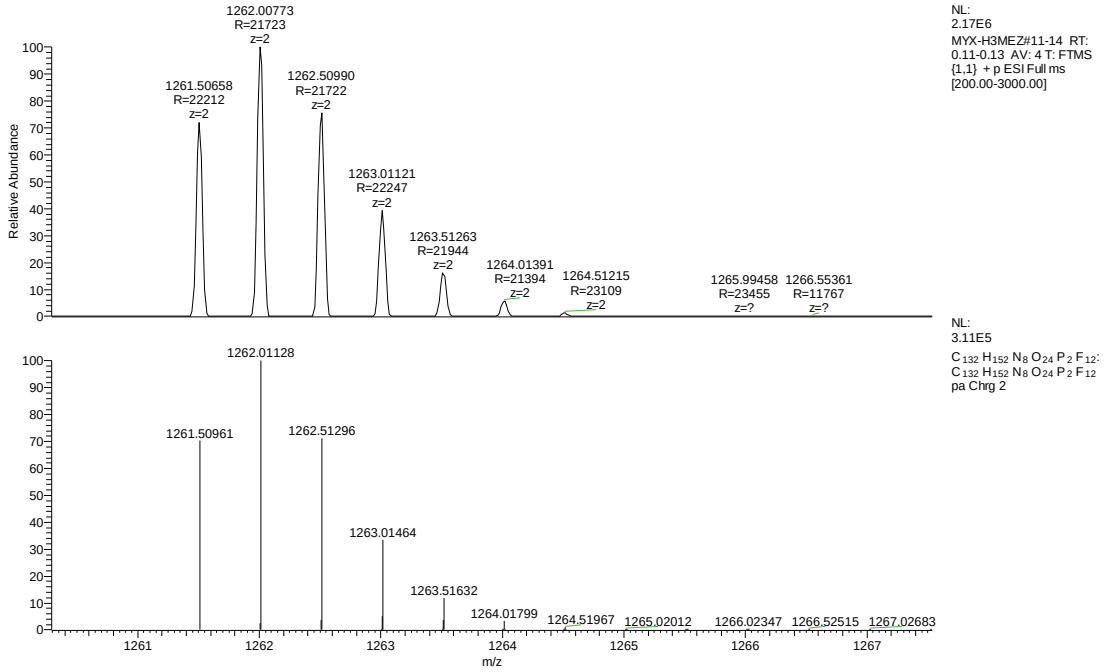
pa Chrg 3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z=?
1266.55361
R=11767
z=?
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m/z
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pa Chrg 2

5. Comparison of partial ^{1}H NMR spectra between H, 1 and complex H•1

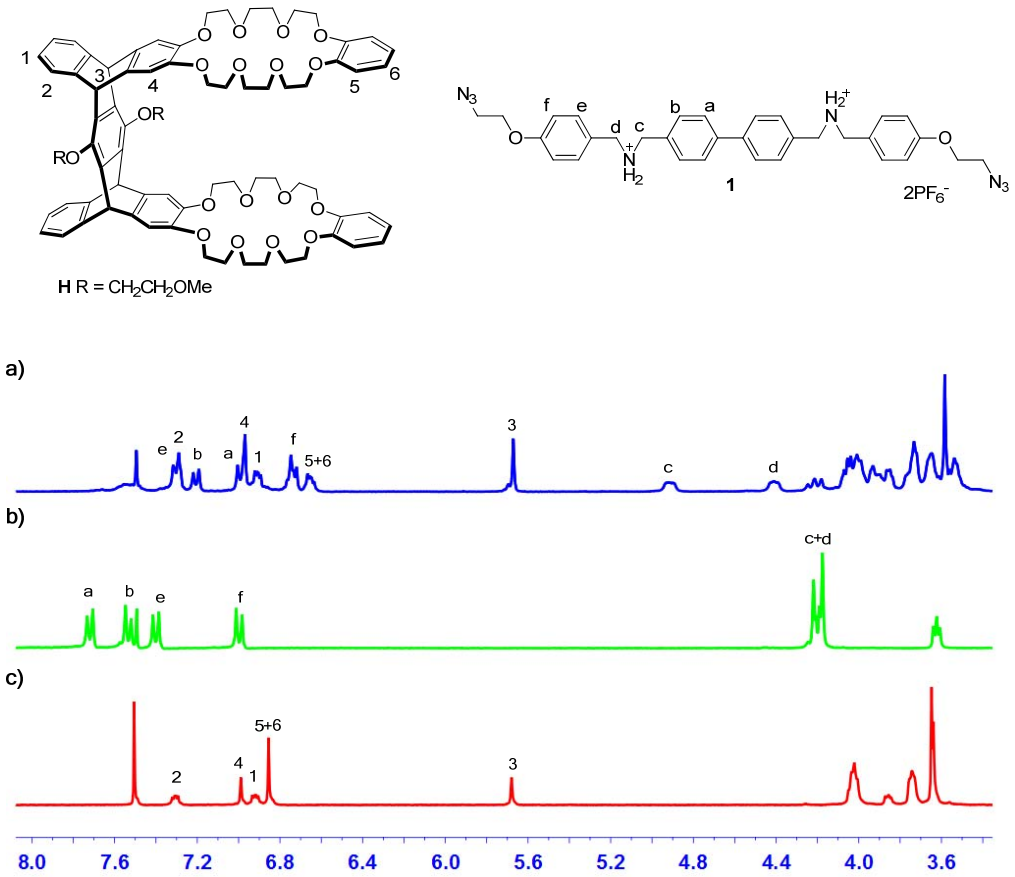


Figure S11. Partial ^{1}H NMR spectra (300 MHz, $CDCl_3$:CD_3CN = 1:1, v/v, 298 K) of (a) **H** and 1.0 equiv. of **1**, (b) **1**, and (c) **H**. $[\mathbf{H}]_0$ = 3.0 mM.

6. Partial ^{1}H-^{1}H COSY and ROESY spectra of Rota-M•4PF$_6$ before and after addition of 2.5 equiv. DBU

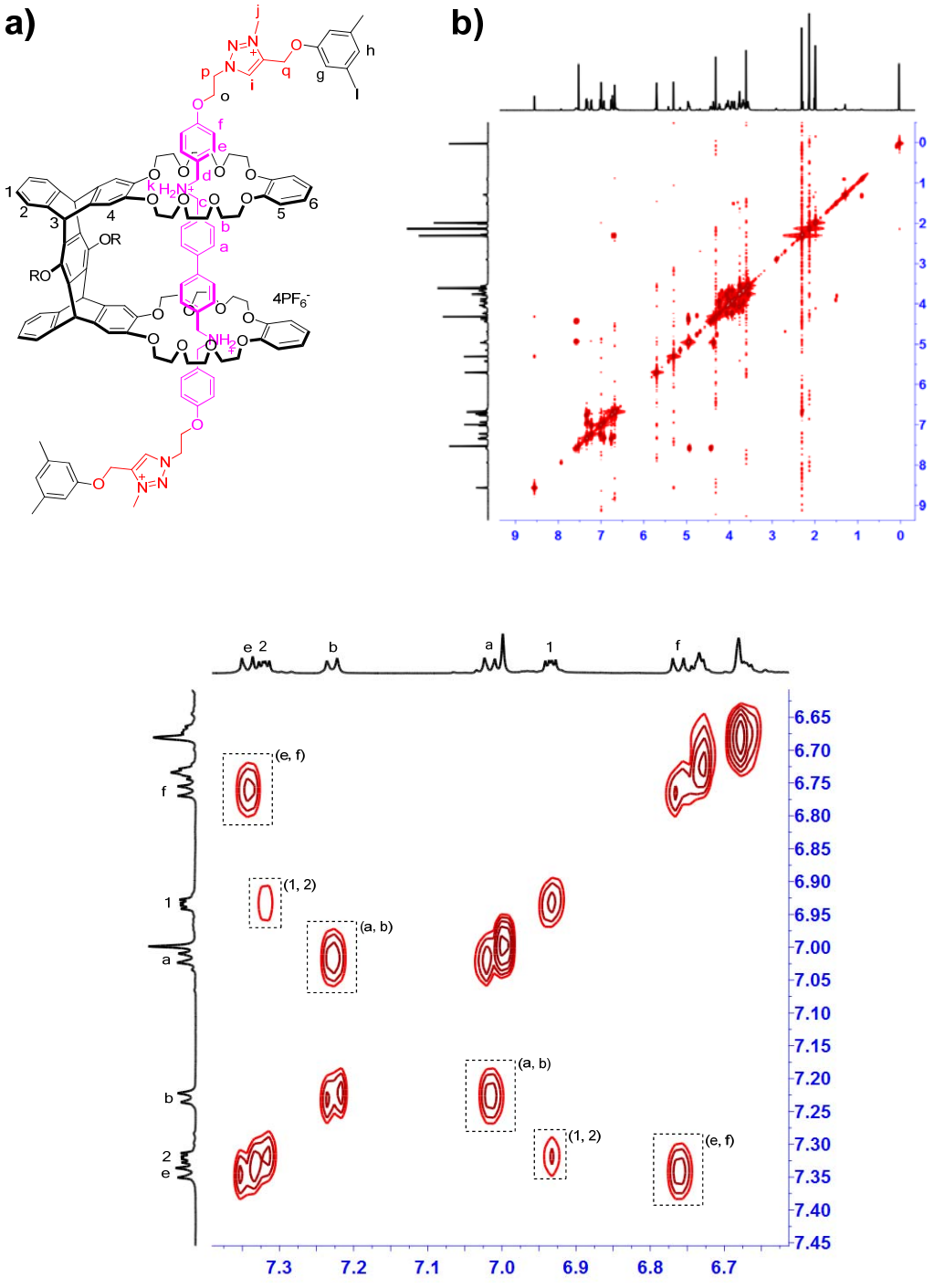


Figure S12. ^{1}H-^{1}H COSY spectrum ($CDCl_3$/CD_3CN=1:1, v/v, 600 MHz, 298 K) of **Rota-M•4PF$_6$**. [**Rota-M•4PF$_6$**]$_0$ = 3.0 mM.

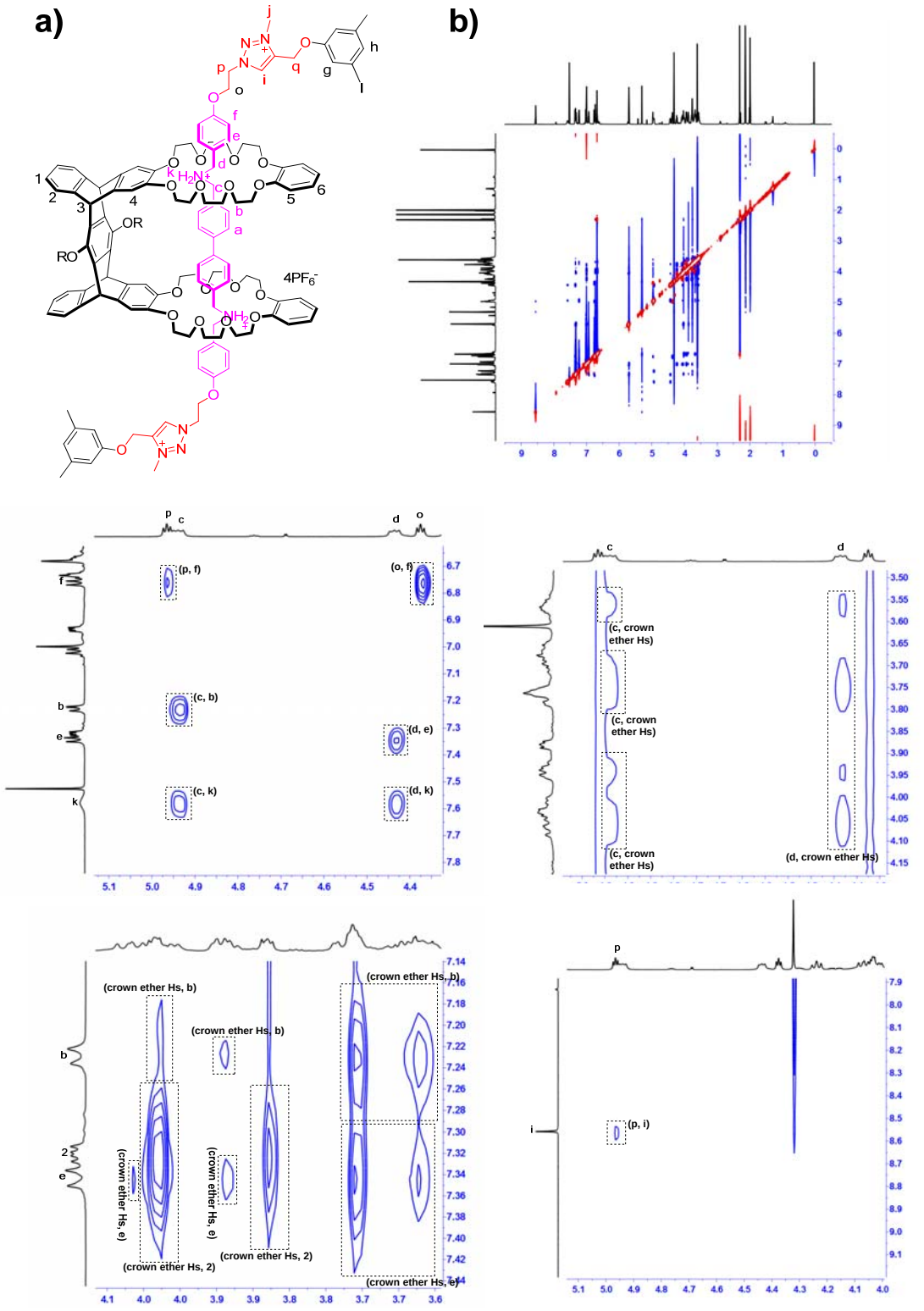


Figure S13. ROESY spectrum ($CDCl_3/CD_3CN$=1:1, v/v, 600 MHz, 298 K) of **Rota-M•4PF$_6$**. [**Rota-M•4PF$_6$**]$_0$ = 3.0 mM.

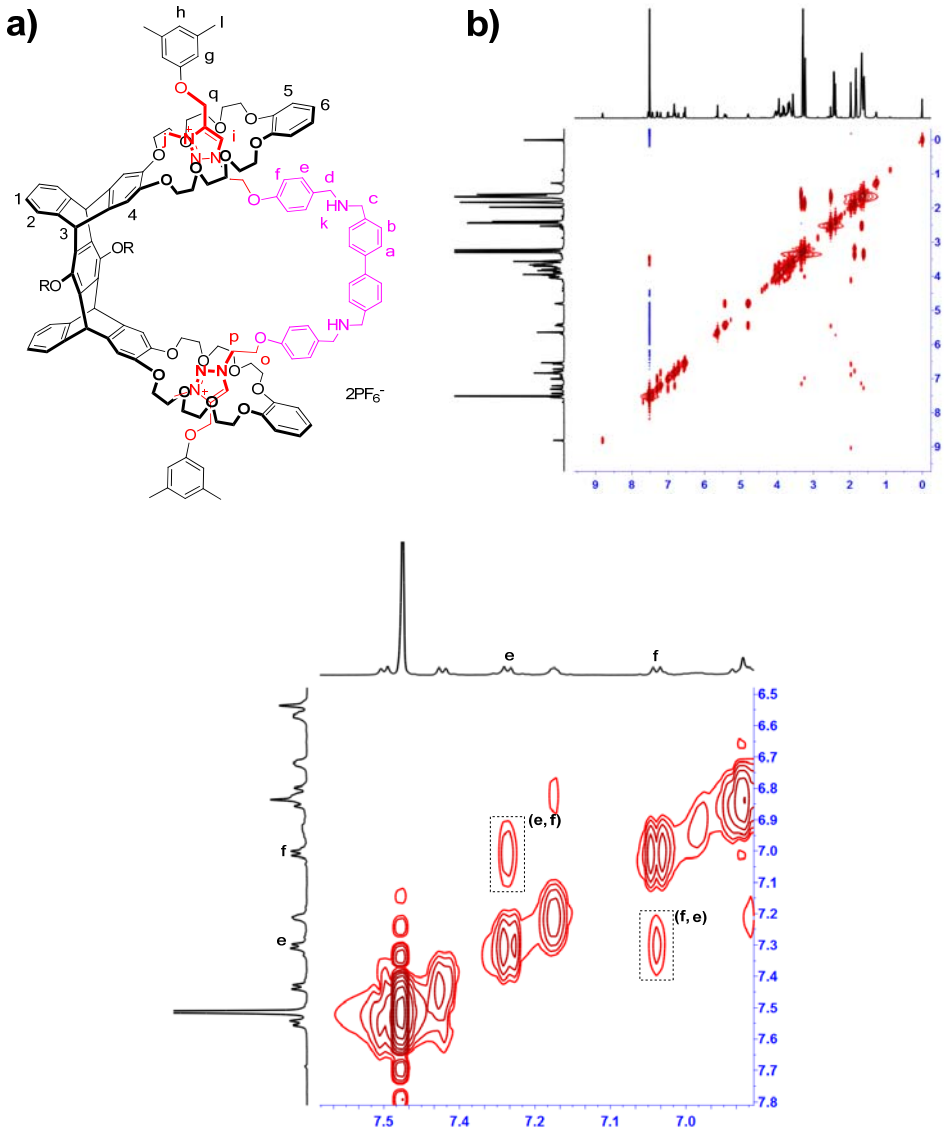
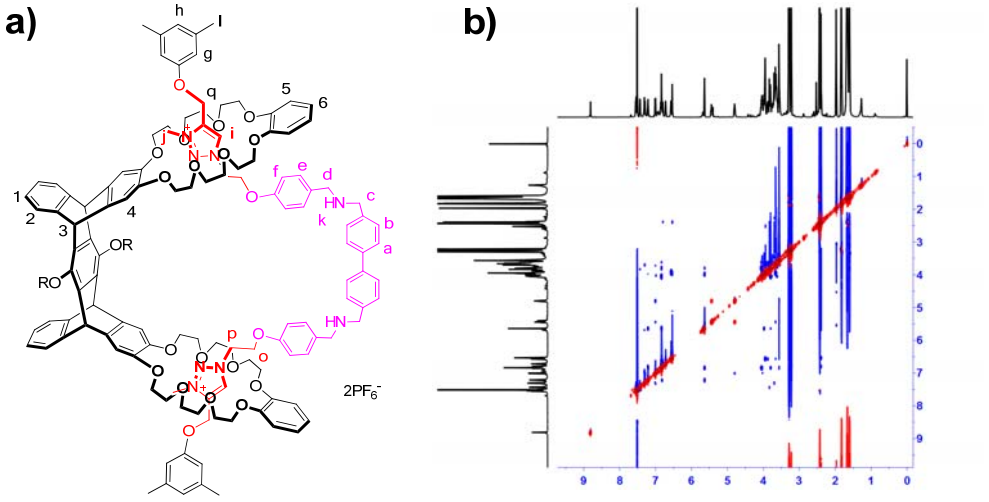


Figure S14. ^{1}H-^{1}H COSY spectrum ($CDCl_3/CD_3CN$=1:1, v/v, 600 MHz, 298 K) of **Rota-M•4PF$_6$** after addition of 2.5 equiv. DBU. [**Rota-M•4PF$_6$**]$_0$ = 3.0 mM.



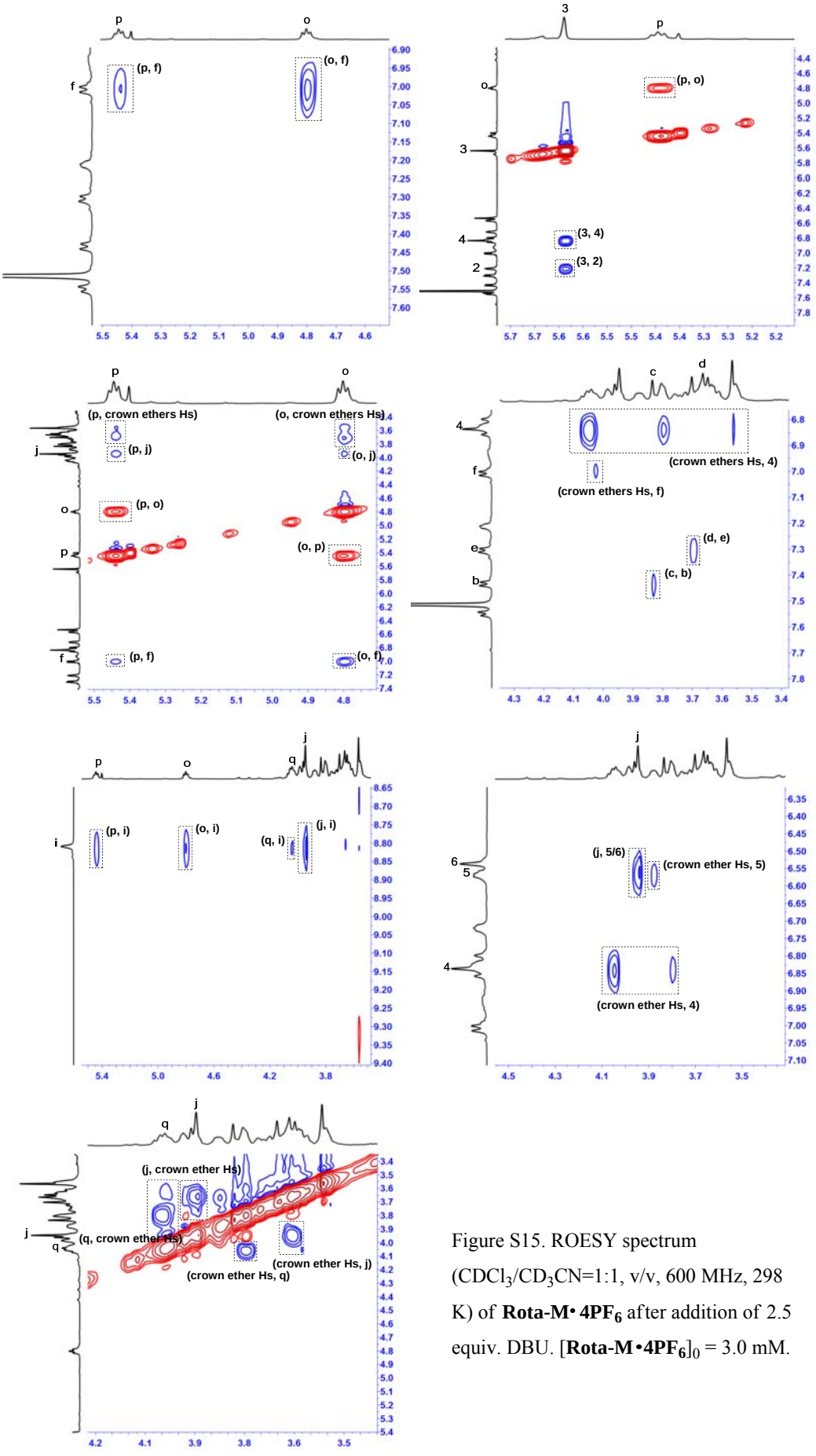


Figure S15. ROESY spectrum ($CDCl_3/CD_3CN$=1:1, v/v, 600 MHz, 298 K) of **Rota-M• 4PF$_6$** after addition of 2.5 equiv. DBU. [**Rota-M•4PF$_6$**]$_0$ = 3.0 mM.

7. Partial ^{1}H NMR spectra for the acid-base regulation cycle of the Rota-M•4PF$_6$

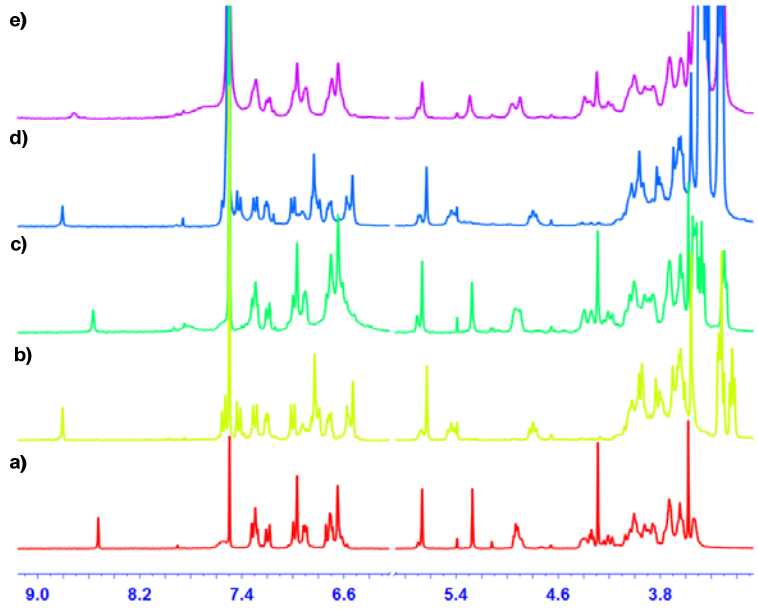


Figure S16. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$= 1:1, v/v, 298K) of (a) free **Rota-M • 4PF$_6$**, (b) to the solution of a was added 2.2 equiv. of DBU, (c) to the solution of b was added 4.0 equiv. of TFA, (d) to the solution of c was added 5.0 equiv. of DBU, and (e) to the solution of d was added 8.0 equiv. of TFA. [**Rota-M•4PF$_6$**]$_0$ = 3.0 mM.

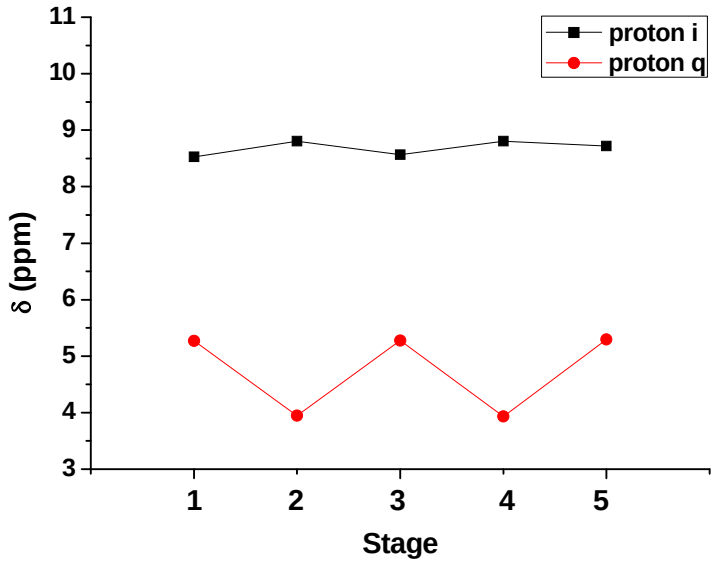


Figure S17. The shift for the protons of **Rota-M•4PF$_6$** in the acid/base control cycle. Stage (1) free **Rota-M•4PF$_6$**, (2) to the solution of stage 1 was added 2.2 equiv. of DBU, (3) to the solution of stage 2 was added 4.0 equiv. of TFA, (4) to the solution of stage 3 was added 5.0 equiv. of DBU, and (5) to the solution of stage 4 was added 8.0 equiv. of TFA. [**Rota-M•4PF$_6$**]$_0$ = 3.0 mM.

8. References

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