Electronic Supplementary Information

Bifunctionalized [3]rotaxane and its incorporation into mechanically interlocked polymer

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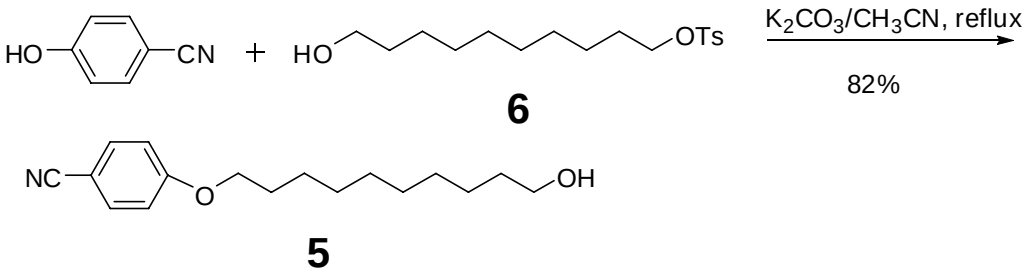
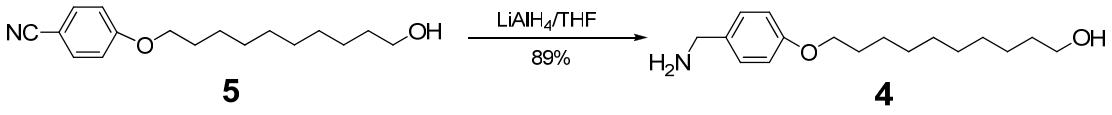
Contents

1. Experimental section

General methods. Melting points, taken on an electrothermal melting point apparatus, are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX300 NMR. MALDI-TOF MS were obtained on a Bruker BIFLEXIII mass spectrometer. Elemental analyses were performed by the Analytical Laboratory of Institute of Chemistry, CAS. Materials obtained commercially were used without further purification.

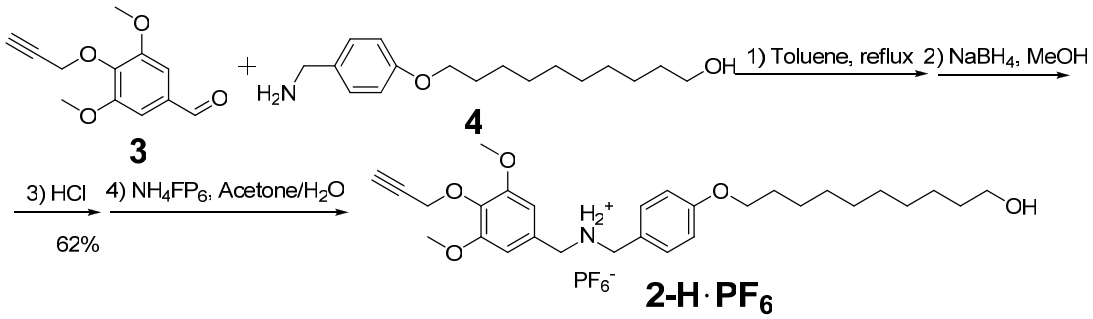


Synthesis of compound 5. Compound **6**[S1] (1.4 g, 4.27 mmol), 4-cyanophenol (0.58 g, 4.87 mmol), and potassium carbonate (0.89 g, 6.45 mmol) were suspended in anhydrous CH_3CN (50 mL). The reaction mixture was heated to 80 °C and stirred for 1 day. The reaction mixture was diluted with water and washed with ethyl acetate three times to give a crude product, which was purified by column chromatography (SiO_2: hexanes:ethyl acetate 9:1) to yield the alkylated product as an orange oil (0.96 g, 82% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.63 (t, J = 6.6 Hz, 2H), 1.84-1.77 (m, 2H), 1.59-1.52 (m, 2H), 1.45-1.25 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.5, 133.9, 119.3, 115.2, 103.6, 68.4, 62.9, 32.7, 29.5, 29.42, 29.37, 29.3, 28.9, 25.9, 25.7. EI-MS: m/z = 275 (calcd. 275 for [M^+]). Anal. Calcd. for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 74.01; H, 9.28; N, 5.01.



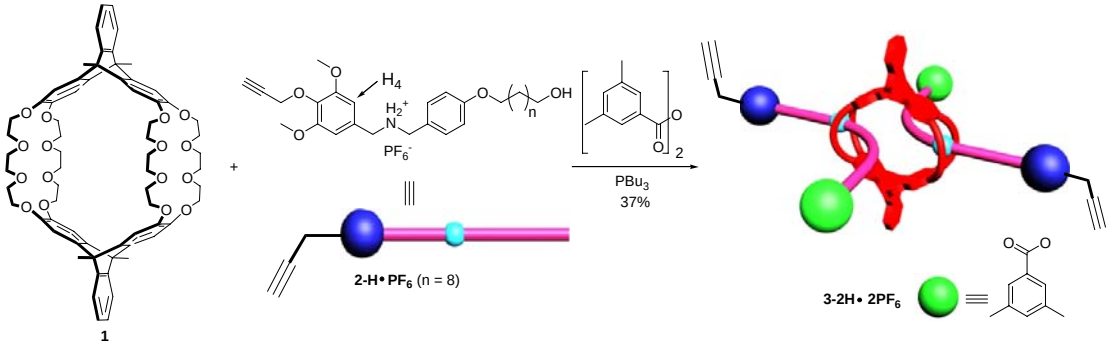
Synthesis of compound 4. Compound **5** (1.0 g, 3.64 mmol) was dissolved in anhydrous THF (40 mL) and cooled to 0 °C. Lithium aluminum hydride (0.42 g, 11

mmol) was then added slowly to the reaction mixture. The reaction mixture was warmed to 60 °C and refluxed under an argon atmosphere for 12 h. The mixture was then quenched by addition of H_2O (5.5 mL), 15% NaOH (aq) (5.5 mL) and H_2O (5 mL), respectively. The organic layer was diluted with ethyl ether, and washed with water three times to yield compound **4** as a yellow oil (0.88 g, 89% yield). No further purification was necessary. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.20 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 3.94 (t, J = 6.5 Hz, 2H), 3.79 (s, 2H), 3.61 (t, J = 6.6 Hz, 2H), 1.81-1.74 (m, 2H), 1.57-1.50 (m, 2H), 1.46-1.26 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.1, 135.2, 128.2, 114.6, 68.0, 62.8, 45.9, 32.8, 29.50, 29.46, 29.41, 29.32, 29.27, 26.0, 25.8. EI-MS: *m/z* = 279 (calcd. 279 for [M^+]). Anal. Calcd. for $C_{17}H_{29}NO_2$: C, 73.07; H, 10.46; N, 5.01. Found: C, 73.18; H, 10.32; N, 4.92.

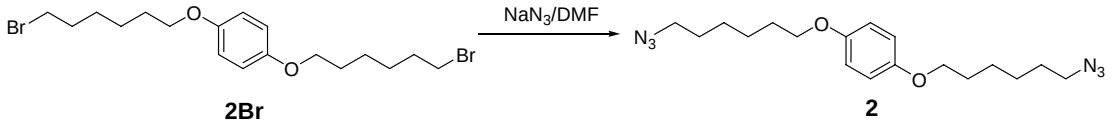


Synthesis of compound 2-H·PF_6. A mixture of **3** (393 mg, 1.79 mmol) and **4** (490 mg, 1.79 mmol) in dry toluene (60 mL) was heated overnight at 145 °C in a Dean-Stark apparatus under nitrogen atmosphere. The solvent was removed under vacuum and the residue was dissolved in MeOH (50 mL), and then $NaBH_4$ (0.70 g, 18.4 mmol) was added in portion. After stirring for overnight, the solvents were 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 the solvent was removed and the residue was purified by column chromatography (silica gel, DCM:MeOH = 100:0 ~ 99:1) to give the free amine compound. To a solution of the amine in dry DCM (20 mL) was added HCl (10.0 mL) at room temperature. After stirring for 2 h under nitrogen atmosphere, the solvent was removed under vacuum. The residue was dissolved in MeOH (2 mL), and saturated NH_4PF_6 (8 mL, aq) was then added to yield a white precipitate. After being filtered,

washed with H_2O and dried under vacuum, the title compound **2-H·PF$_6$** was obtained in 62% yield as a pale yellow solid. Mp = 118-119 °C. ^{1}H NMR (300 MHz, CD_3CN) δ = 7.39 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 8.2 Hz, 2H), 6.75 (s, 2H), 4.67 (s, 2H), 4.17-4.14 (m, 4H), 4.02 (t, J = 6.3 Hz, 2H), 3.85 (s, 6H), 3.47 (t, J = 6.4 Hz, 2H), 2.75 (s, 1H), 1.77 (m, 2H), 1.46-1.31 (m, 14H). ^{13}C NMR (75 MHz, CD_3CN): δ = 159.9, 153.5, 131.5, 126.3, 121.6, 114.5, 106.8, 78.9, 75.1, 67.6, 61.3, 58.9, 55.6, 50.9, 50.5, 32.2, 28.9, 28.83, 28.80, 28.6, 28.5, 25.3. MALDI-TOF MS: *m/z* 484.3 (calcd. 484.3 for [M-PF_6^-]$^+$). Anal. Calcd. for $C_{28}H_{39}F_6NO_5P$: C, 54.72; H, 6.40; N, 2.28. Found: C, 54.51; H, 6.18; N, 2.17.

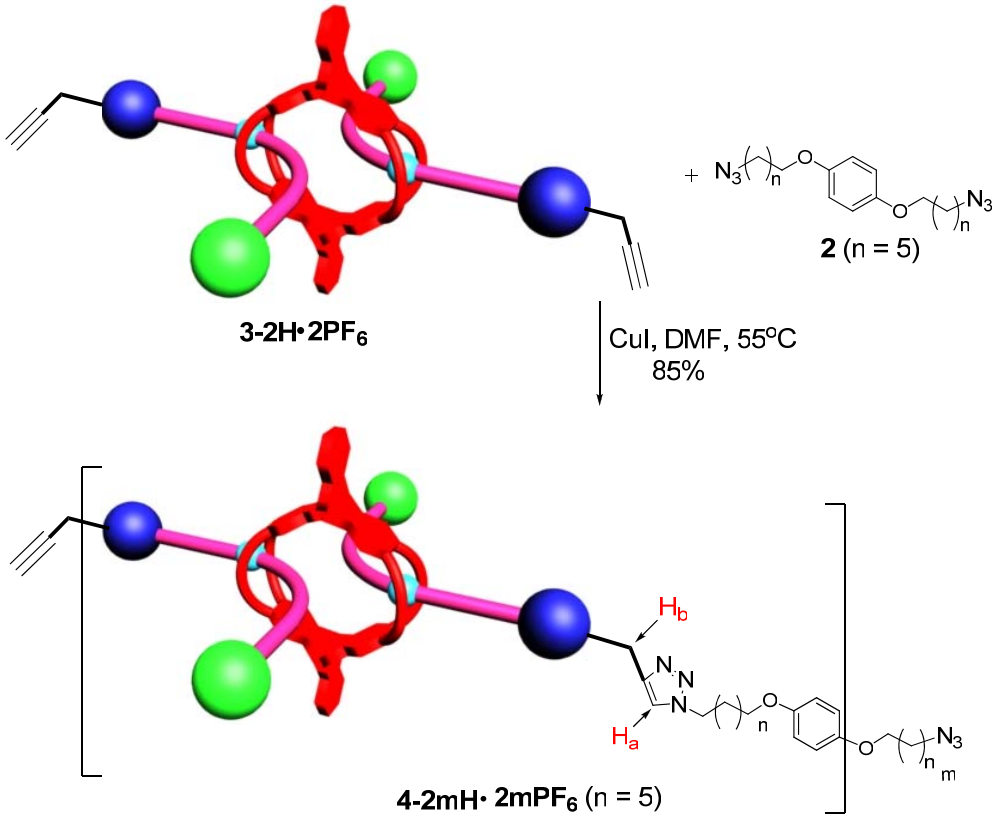


Synthesis of [3]rotaxane 3-2H·2PF$_6$. Host **1** (23 mg, 0.02 mmol) and **2-H·PF$_6$** (33.9 mg 0.05 mmol) was mixed and stirred in 1:1 $CHCl_3$:CH3CN solution (2 mL) for 24 h. To the mixture was added 3,5-dimethyl benzoic anhydride (30 mg, 0.1 mmol) and trimethylphosphine (10.4 μL, 0.150 mmol). The reaction mixture was stirred for 12 h. After evaporation, the residue was subjected to silica gel column chromatography (SiO_2: MeOH:CH_2Cl_2 = 1:100) to give rotaxane **3-2H·2PF$_6$** in 37% yield. ^{1}H NMR (300 MHz, 1:1 $CDCl_3$: CD_3CN): δ = 7.61 (s, 4H), 7.33-7.30 (m, 4H), 7.22 (s, 2H), 7.04-6.99 (m, 12H), 6.71 (s, 4H), 5.58 (d, J = 8.2 Hz, 4H), 5.36 (d, J = 8.2 Hz, 4H), 4.71 (br m, 4H), 4.42-4.26 (m, 8H), 4.10 (brs, 4H), 3.97 (brs, 16H), 3.83 (s, 12H), 3.72-3.63 (m, 8H), 3.53-3.44 (m, 8H), 3.30-3.24 (m, 8H), 3.14 (br m, 4H), 2.86 (br m, 4H), 2.60 (s, 2H), 2.33-2.29 (m, 18H), 1.66-1.26 (m, 32H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 167.1, 158.7, 153.5, 144.1, 138.0, 134.5, 129.3, 124.9, 120.2, 113.9, 107.9, 106.9, 79.2, 70.8, 70.6, 70.2, 69.1, 65.0, 56.3, 53.5, 48.0, 31.9, 29.4, 26.1, 23.8, 21.2, 14.2, 13.5, 13.3. HRMS cald. for [M-2PF_6^-]$^{2+}$: 1191.1216. Found: 1191.1187.



2Br **2**

Synthesis of compound 2. **2Br**[S2] (852 mg, 1.95 mmol) and NaN_3 (635 mg, 9.77 mmol) were mixed in anhydrous DMF (10 mL) and the reaction mixture was stirred under an atmosphere of N_2 for 2 days at room temperature. DMF was then removed under reduced pressure and the residue was dissolved in EtOAc and washed with H_2O (3 × 10 mL). The organic layer was dried and subjected to column chromatography [SiO_2: CH_2Cl_2/hexane (1:1)] to afford the pure diazide **2** as an off-white oil (577 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.81 (s, 4H), 3.90 (t, J = 6.4 Hz, 4H), 3.27 (t, J = 6.9 Hz, 4H), 1.79-1.67 (m, 4H), 1.65-1.58 (m, 4H), 1.52-1.40 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.2, 115.4, 68.3, 51.4, 29.3, 28.8, 26.5, 25.7. EI-MS: *m/z* = 360 (calcd. 360 for $[M]^+$). Anal. Calcd. for $C_{18}H_{28}N_6O_2$: C, 59.98; H, 7.83; N, 23.32. Found: C, 59.88; H, 7.65; N, 23.21.



Synthesis of poly[3]rotaxane 4-2mH·2mPF$_6$. **3-2H·2PF$_6$** (44.0 mg, 0.0165 mmol) and **2** (5.9 mg, 0.0165 mmol) were mixed in 2 mL DMF. After degassing of the

solution with bubbling argon, CuI (2.7 mg) was added. The reaction mixture was heated to 50 ˚C in an oil-bath for 3 days, and then added dropwise into a HPF_6 aqueous solution (100 mL). The resulting precipitate was collected by filtration and washed with H_2O, CH_2Cl_2, and Et_2O, to give a pale yellow powder (42.4 mg, 85%). *Tg* = 108 °C. FT-IR: $\nu_{\equiv C\text{-}H}$ = 3303 cm^{-1}, ν_{N3} = 2091 cm^{-1}, $\nu_{trizole}$ = 1062 cm^{-1}. ^1H NMR (300 MHz, 1:1 $CDCl_3$:CD_3CN): δ = 7.82 (s, 2H), 7.61 (s, 4H), 7.27-7.14 (m, 18H), 7.01 (br m, 8H), 6.76 (s, 4H), 5.56 (d, *J* = 8.4 Hz,, 4H), 5.36 (d, *J* = 8.4 Hz,, 4H), 5.11 (s, 4H), 4.37-4.28 (m, 10H), 4.10-3.16 (brm, 44H), 2.33-2.28 (br m, 18H), 1.87-1.26 (brm, 34H). SEC chromatogram: M_m = ca. 43 KDa, PDI = 1.42.

References:

[1] L. Yi, J. Shi, S. Gao, S. Li, C. Niu and Z. Xi, *Tetrahedron. Lett.*, **2009**, *50*, 759-762.

[2] F. Han, X. He, J. Huang and Z. Li, *J. Phys. Chem. B*, **2004**, *108*, 5256-5262.

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

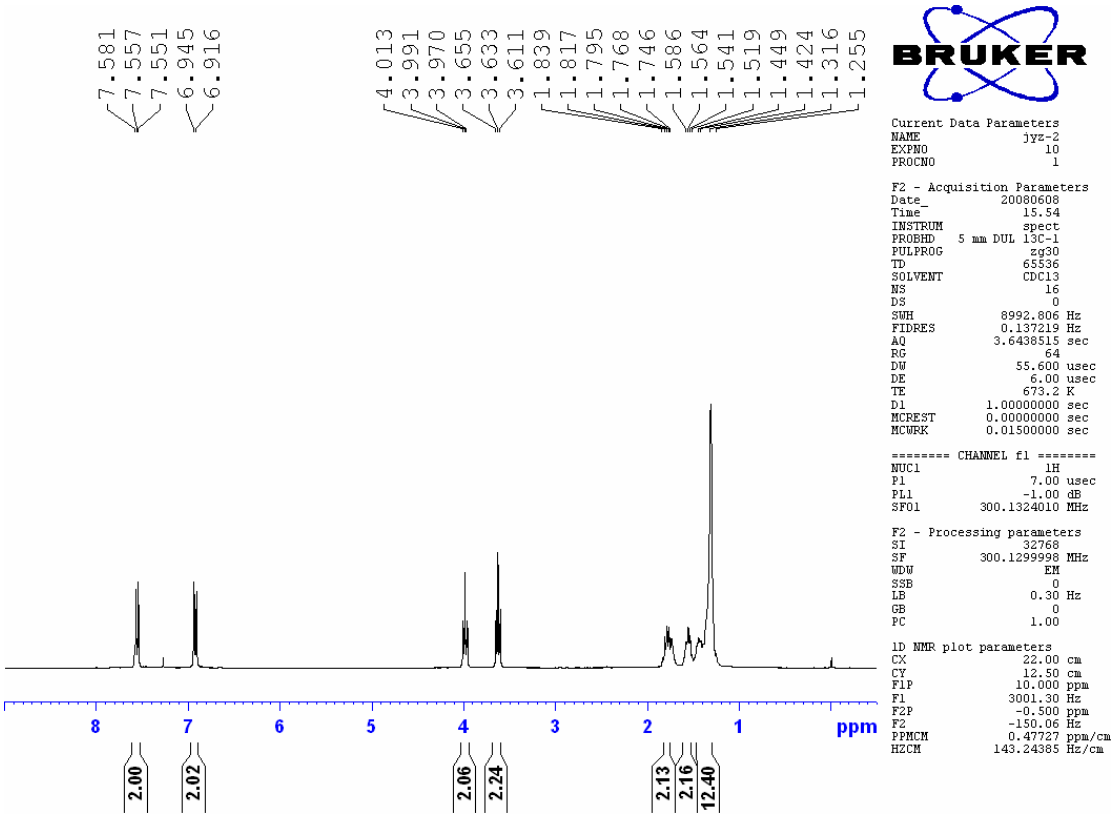


Fig. S1 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **5**.

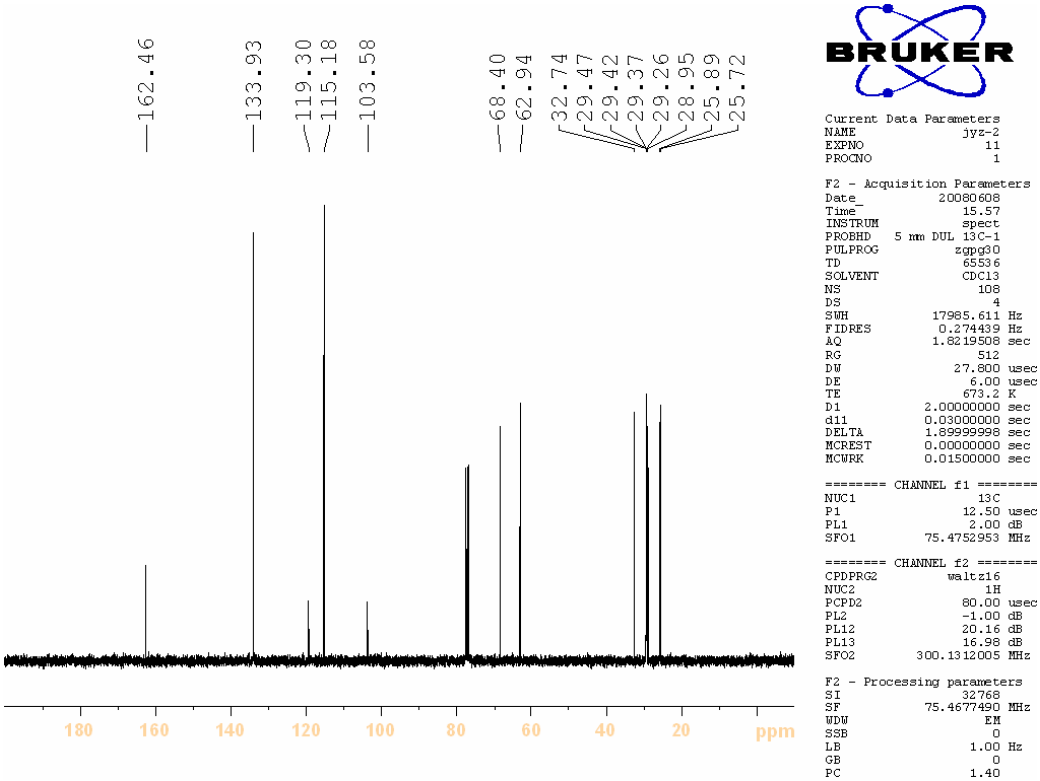


Fig. S2 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **5**.

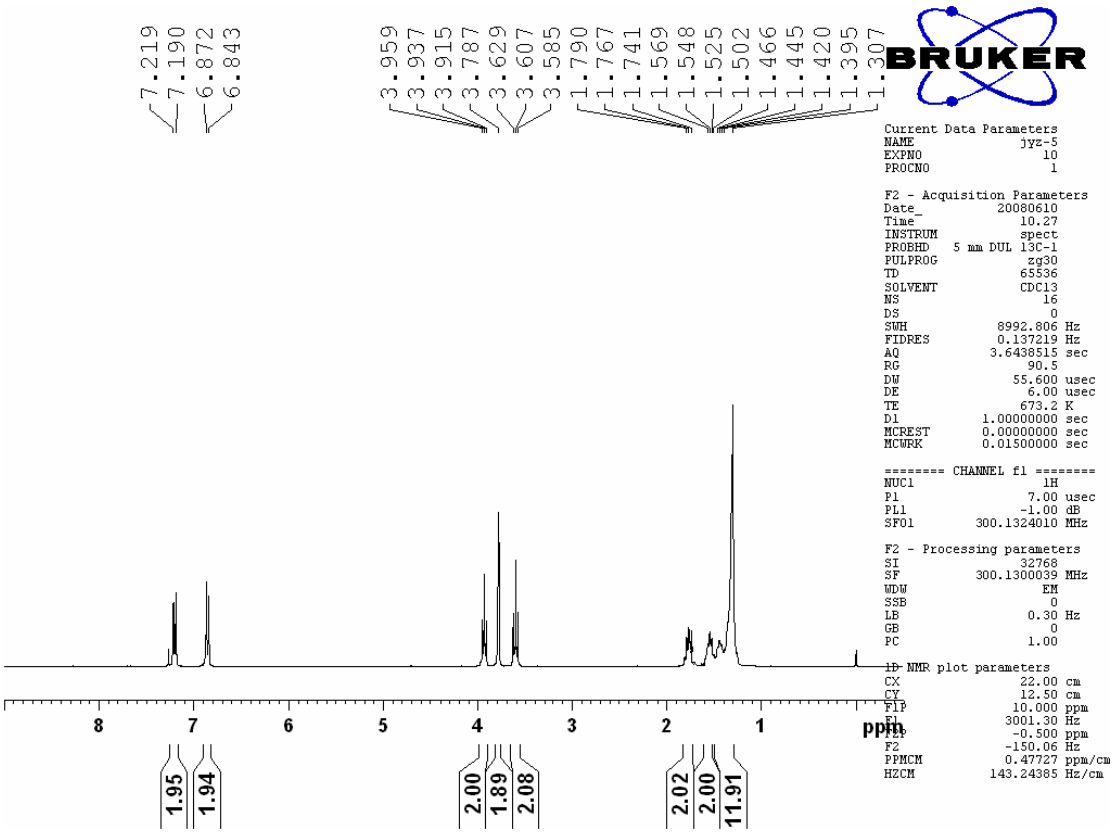


Fig. S3 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4**.

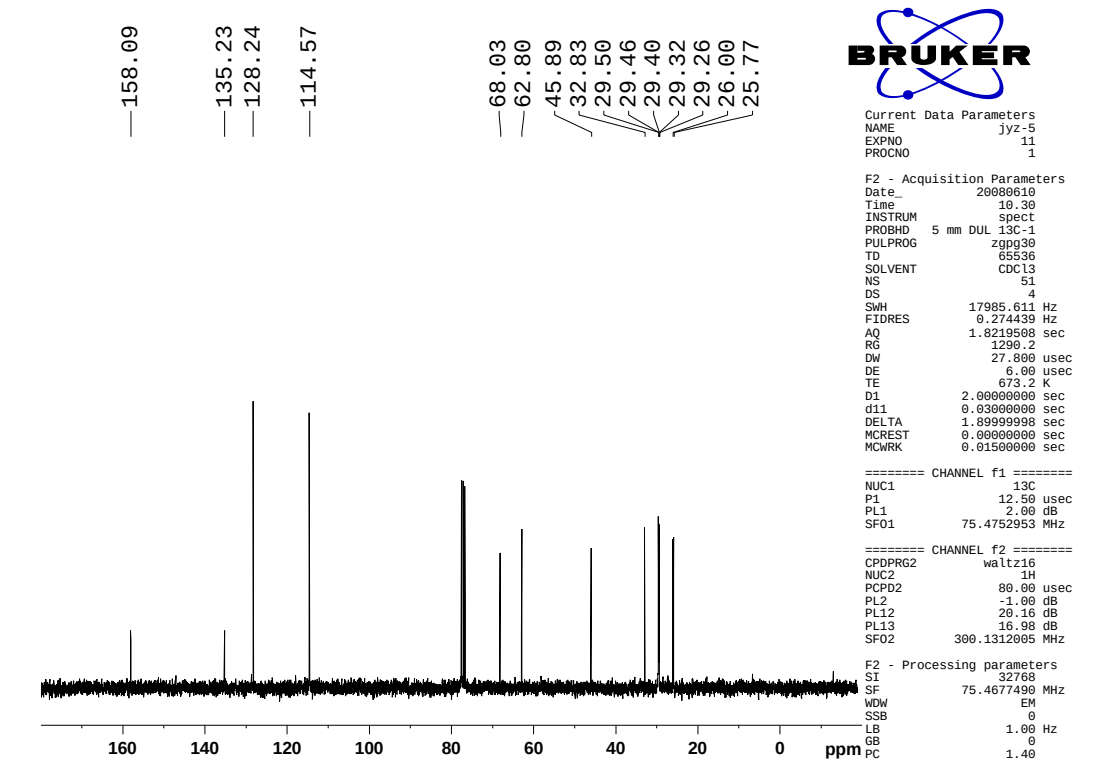


Fig. S4 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **4**.

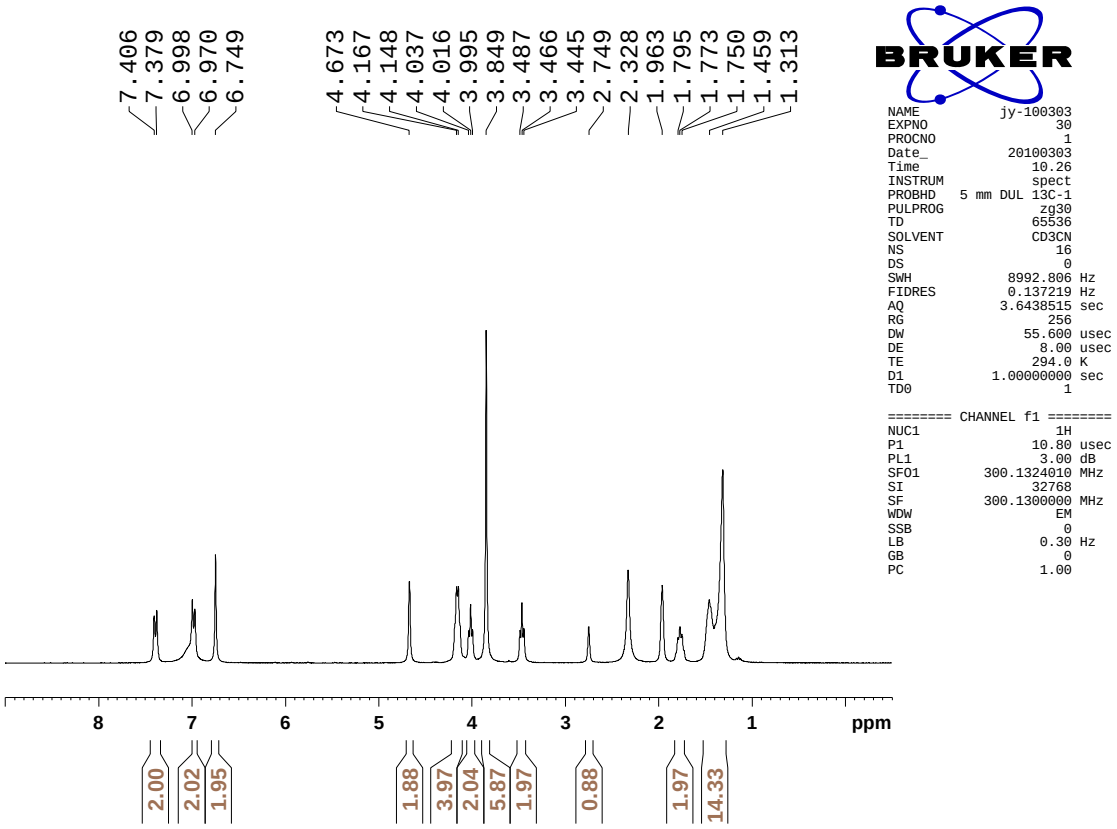


Fig. S5 ^{1}H NMR spectrum (300 MHz, CD_3CN) of **2-H·PF$_6$**.

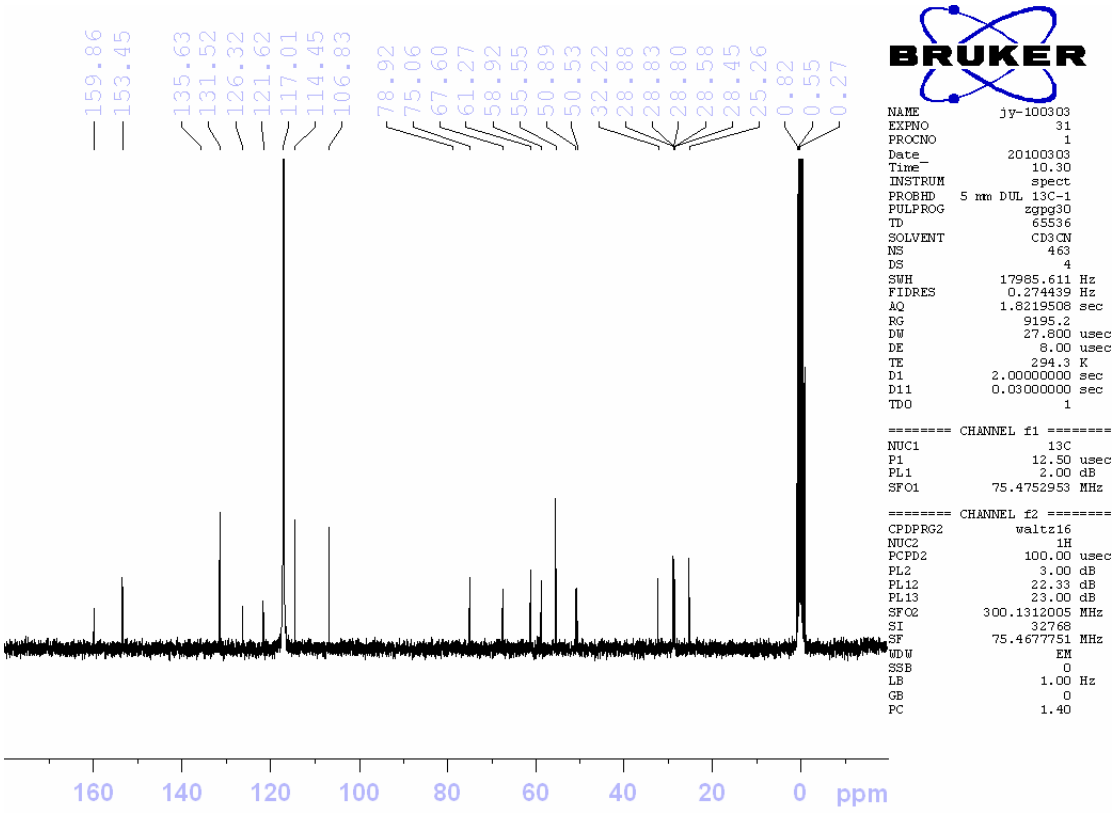


Fig. S6 ^{13}C NMR spectrum (300 MHz, CD_3CN) of **2-H·PF$_6$**.

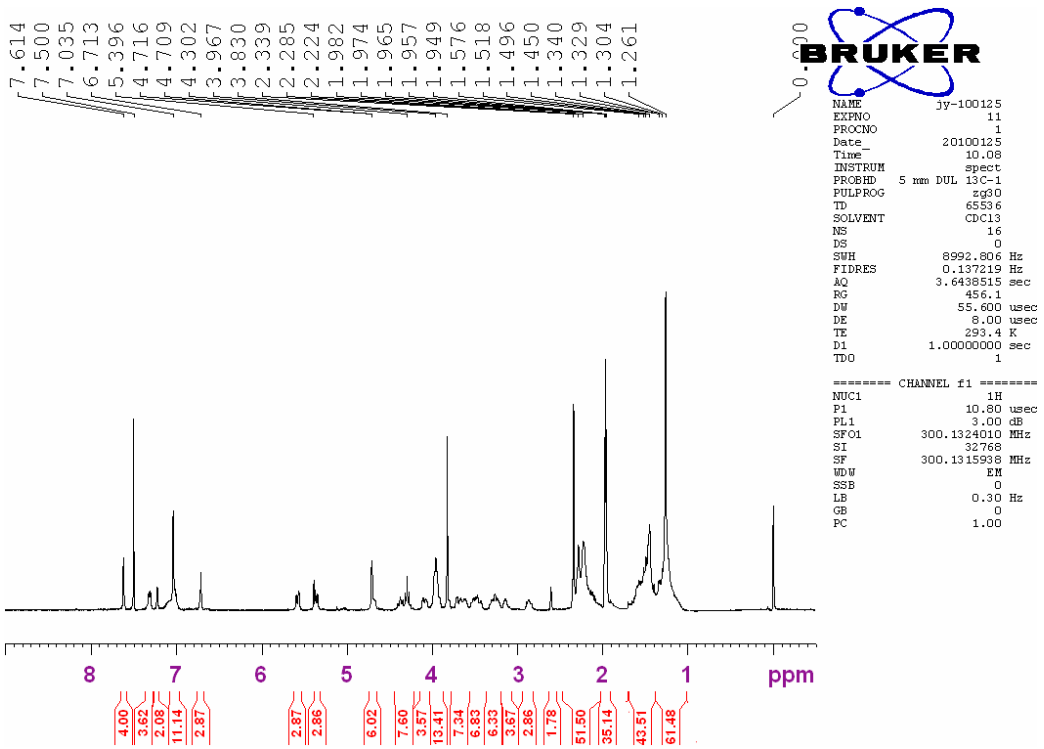


Fig. S7 ^{1}H NMR spectrum (300 MHz, 1:1 $CDCl_3$:CD_3CN) of **3-2H·2PF$_6$**.

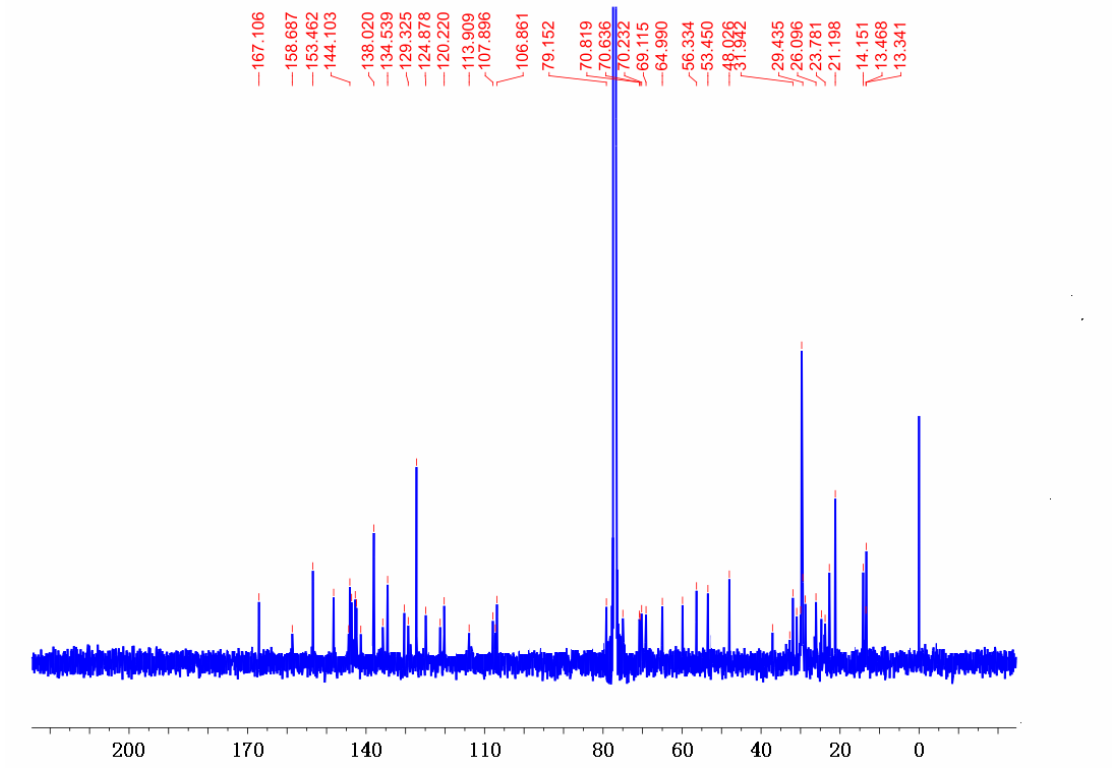


Fig. S8 ^{1}H NMR spectrum (150 MHz, $CDCl_3$) of **3-2H·2PF$_6$**.

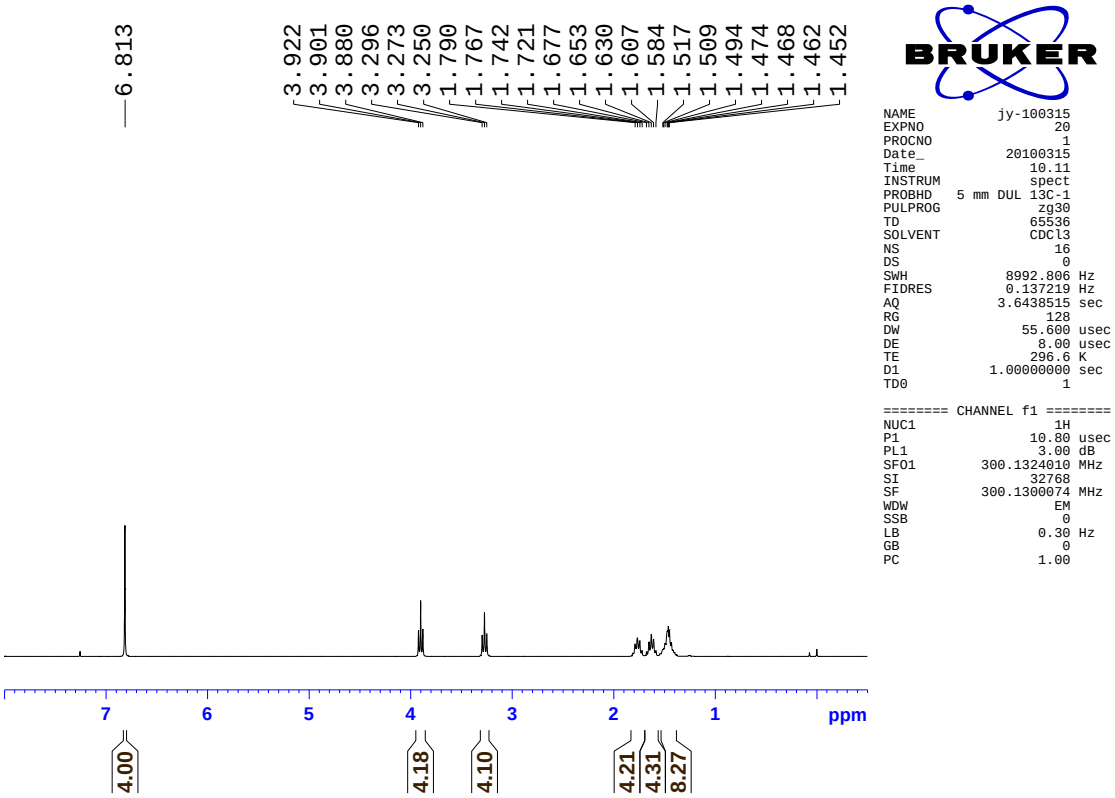



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Fig. S9 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2**.

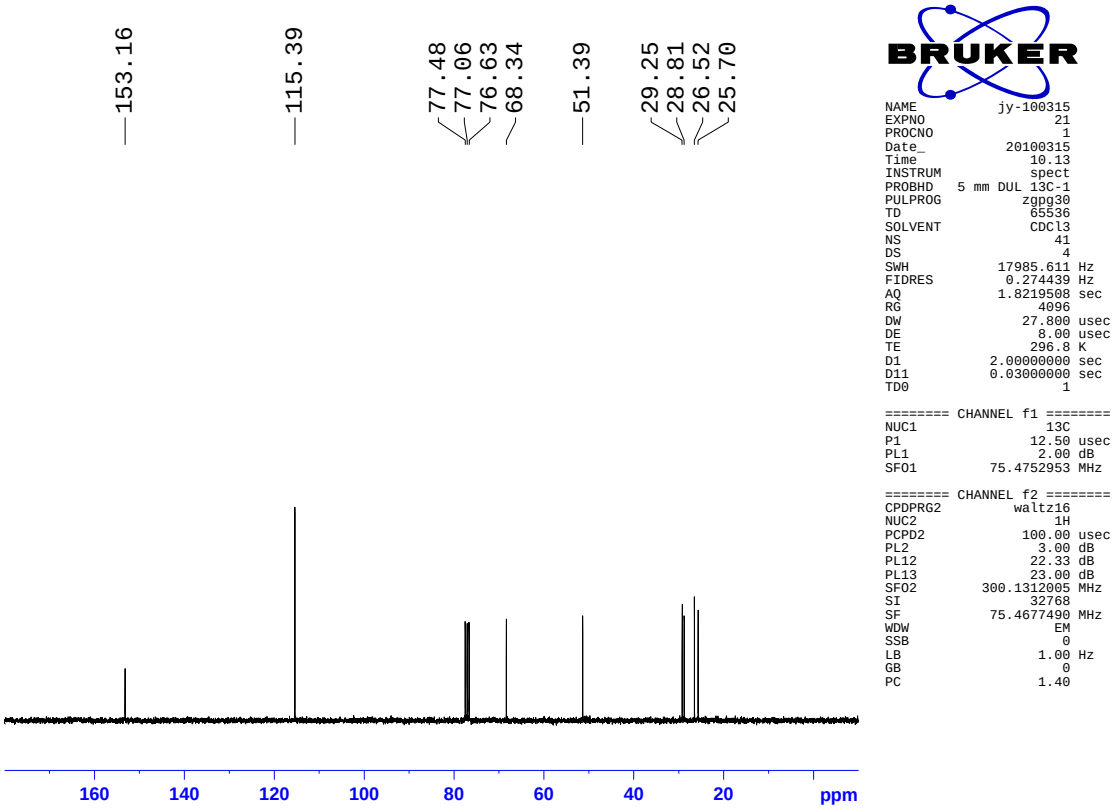


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Fig. S10 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **2**.

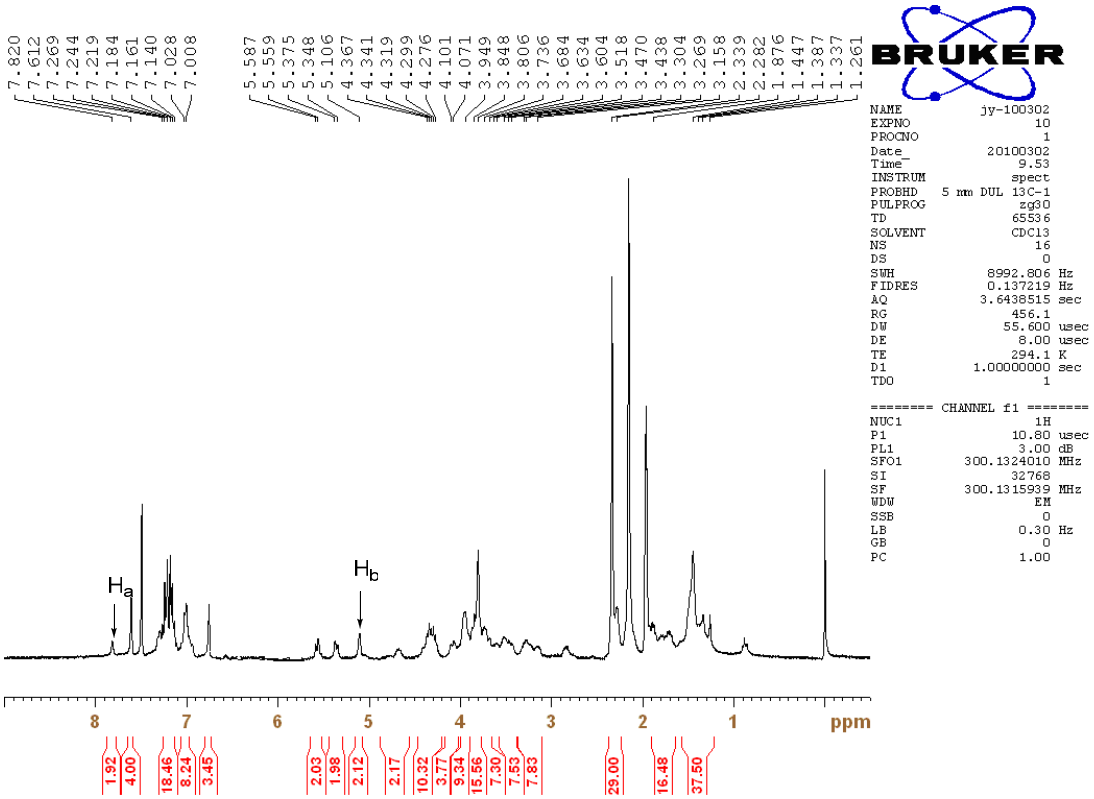

Fig. S11 ^{1}H NMR spectrum (300 MHz, 1:1 $CDCl_3$:CD_3CN) of **4-2mH·2mPF$_6$**.

3. Partial ^{1}H NMR spectra of 1, 2-H·PF_6, and 1 and 2.0 equiv of 2-H·PF_6

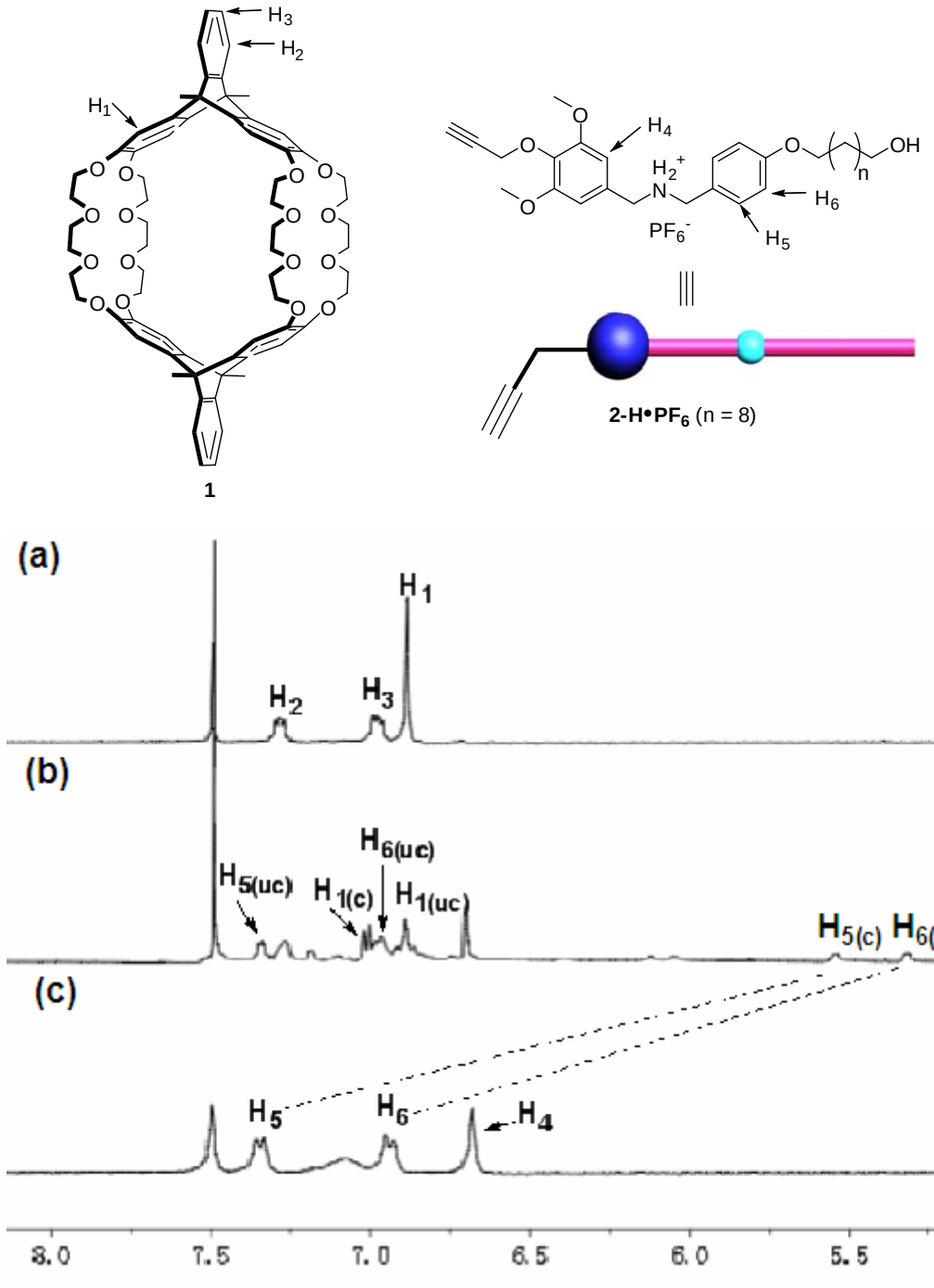

Fig. S12 Partial ^{1}H NMR spectra (300 MHz, $CDCl_3$: CD_3CN = 1 : 1, 298 K) of (a) **2-H·PF_6**, (b) **1** and 2.0 equiv of **2-H·PF_6**, (c) host **1**. $[\mathbf{1}]_0$ = 1.0 mM.

4. ESI-MS spectrum of complex 1·2(2-H·PF_6)

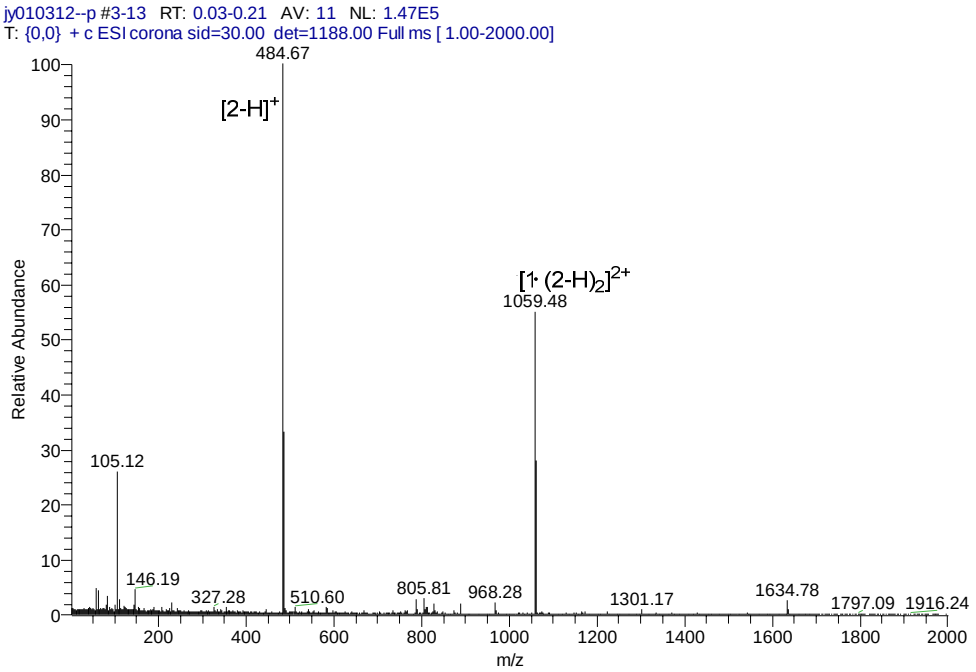

Fig. S13 ESI-MS spectrum of complex **1·2(2-H·PF_6)**.

5. ^{1}H-^{1}H COSY spectrum of 3-2H·2PF_6

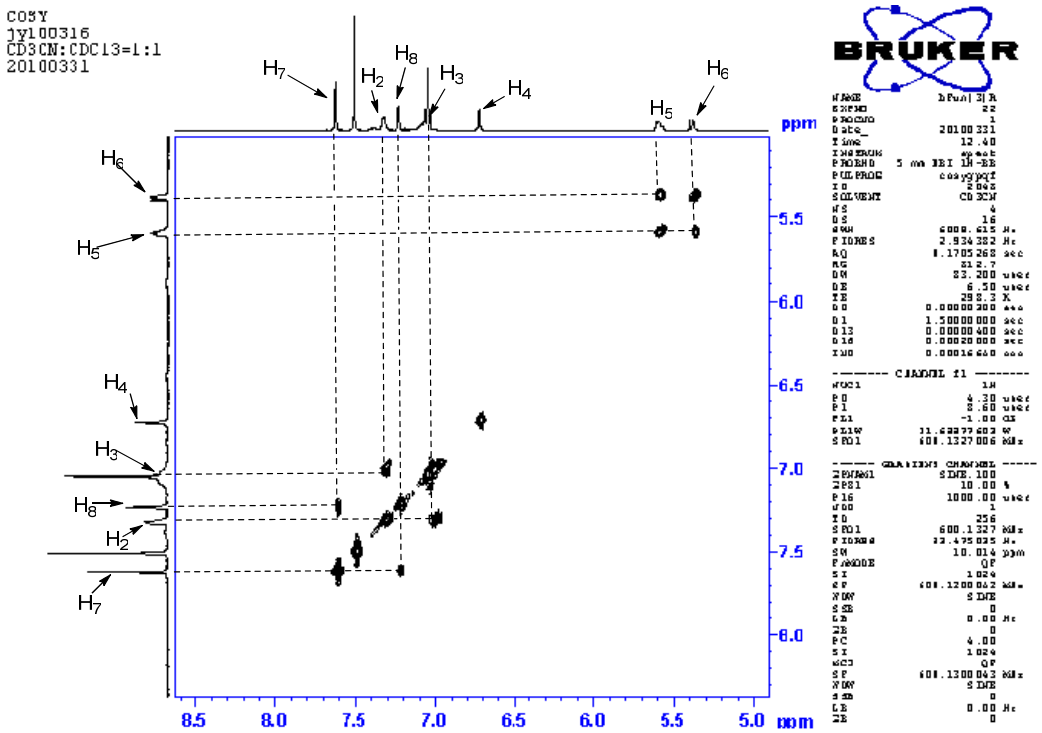

Fig. S14 ^{1}H-^{1}H COSY spectrum of **3-2H·2PF_6** (600 MHz, $CDCl_3$: CD_3CN = 1 : 1, 298 K).

6. HRMS spectrum of [3]rotaxane 3-2H·2PF$_6$

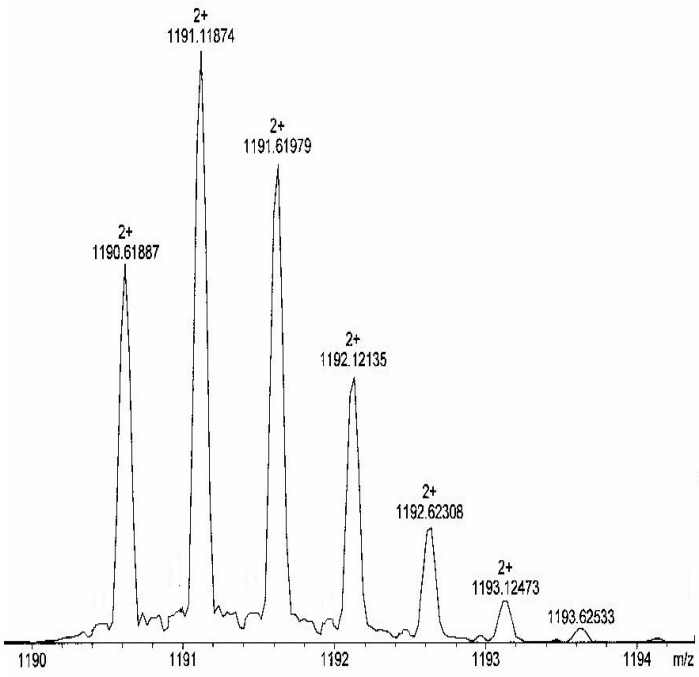

Fig. S15 ESI-HRMS spectrum of [3]rotaxane **3-2H·2PF$_6$**.

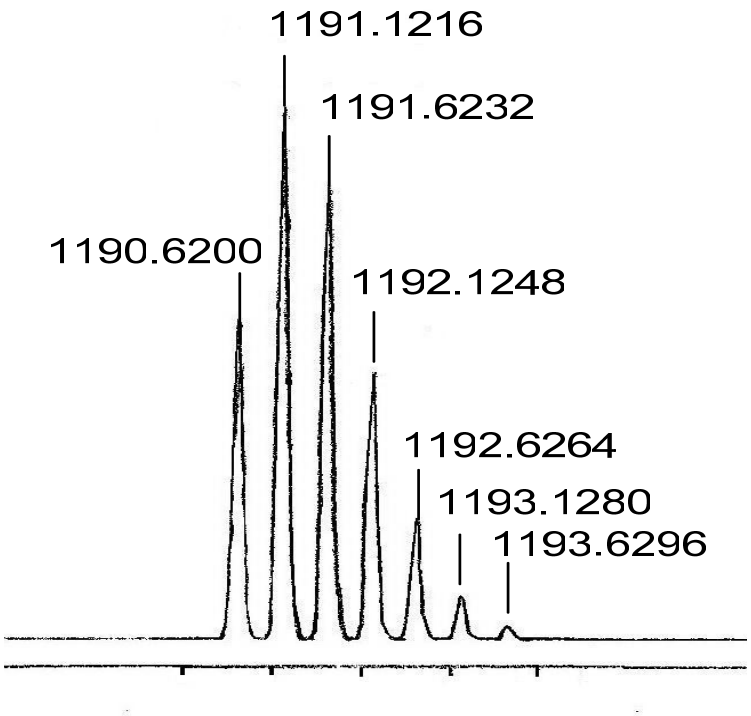

Fig. S16 Calculated HRMS spectrum of [3]rotaxane **3-2H·2PF$_6$**.

7. DSC curve of 4-2mH·2mPF$_6$

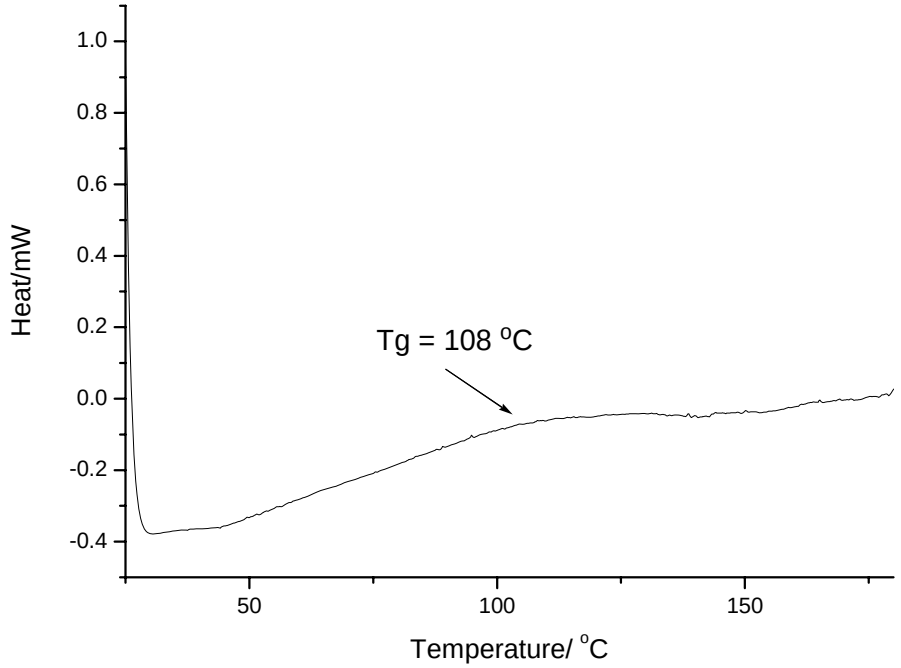

Fig. S17 DSC curve of solid state **4-2mH·2mPF$_6$**.

8. The FT-IR of 4-2mH·2mPF$_6$

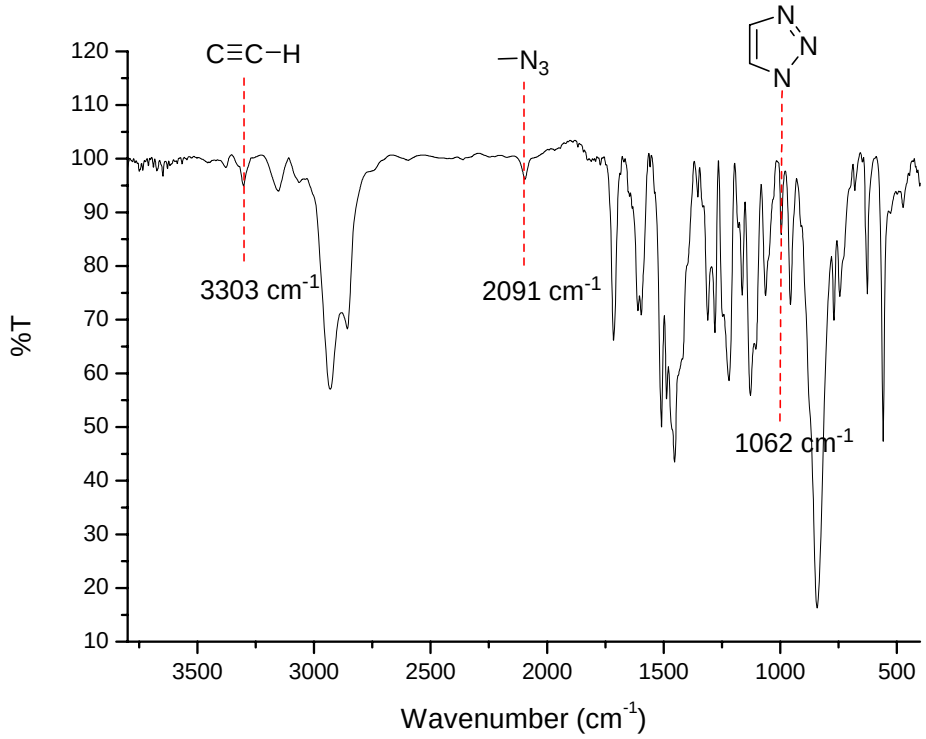

Fig. S18 FT-IR of **4-2mH·2mPF$_6$**.

9. SEC of 3-2H·2PF$_6$ and 4-2mH·2mPF$_6$

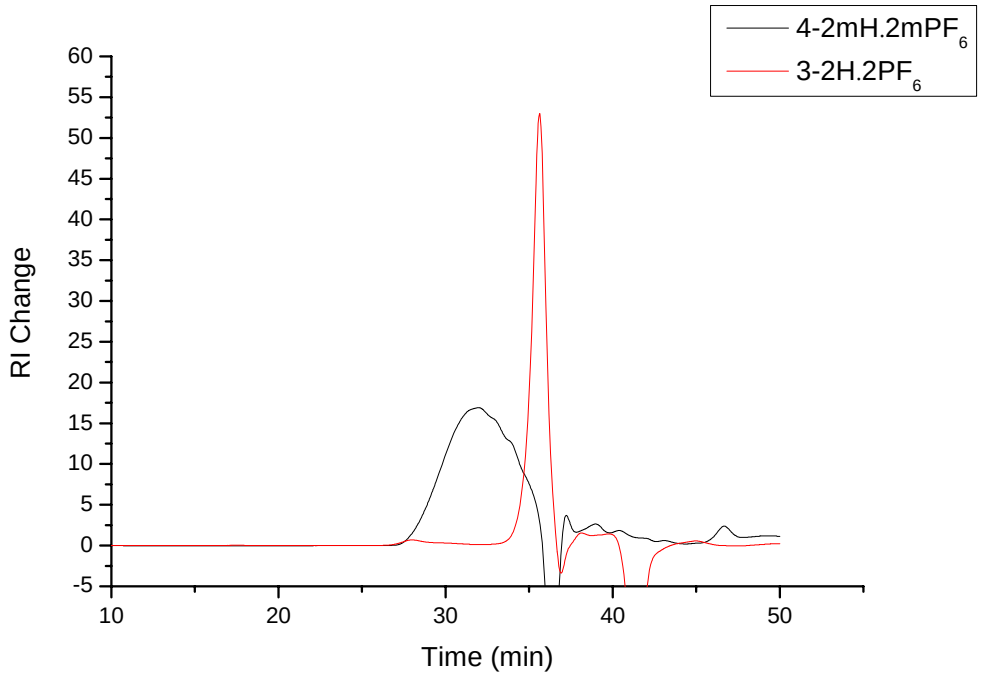

Fig. S19 SEC chromatography of **4-2mH·2mPF$_6$** (black) and **3-2H·2PF$_6$** (red) eluted by pure DMF.