SUPPORTING INFORMATION

Facile synthesis of diverse rotaxanes via successive supramolecular transformations

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1. General Information.

All reagents were of analytical purity and used without further treatment. TLC analyses were performed on silica-gel plates, and flash chromatography was conducted using silica-gel column packages purchased from Qingdao Haiyang Chemical Co., Ltd. (China). The starting material **S1**,[1] $(Ph_3P)_2PtCl_2$,[2] and 1,4-dipropoxypillar[5]arene (DPP[5]A)[3] were prepared according to the established methods.

^1H NMR and ^{31}P NMR spectra were recorded on Bruker 400 MHz Spectrometer (^1H: 400 MHz; ^{31}P: 161.9 MHz) at 298 K. 2-D NOESY spectrum was recorded on Bruker 500 MHz Spectrometer at 298 K. The ^1H and ^{13}C NMR chemical shifts are reported relative to the residual solvent signals, and ^{31}P NMR resonances are referenced to an internal standard sample of 85% H_3PO_4 (δ 0.0). Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. Mass spectra were recorded on a Waters LCT Premier XE spectrometer with acetonitrile or methanol as solvent. UV−vis spectra were recorded in a quartz cell (light path 10 mm) on a Cary 50Bio UV-Visible spectrophotometer.

Synthesis of key [3]rotaxane precursor 1: A Schlenk flask was charged with 186 mg (0.45 mmol) of **S1**, DPPillar[5]arene (2.8 g, 2.72 mmol), and $Pt(PPh_3)_2Cl_2$ (179 mg, 0.23 mmol). The Schlenk flask was then evacuated *via* the reduced pressure and backfilled with N_2. Next, 8.0 mL of the mixture solvent of dry $CHCl_3$ and *i*-Pr_2NH (v/v, 2:1) was added *via* syringe. The resultant solution was stirred for two hours under ice bath. Then CuI (44 mg, 50 mol %) was added to the mixture under N_2 atmosphere, and the mixture was allowed to stirring for 3 days at room temperature. The solvent was then removed by reduced pressure, and the compound was purified by column chromatography (eluent, petroleum ether/dichloromethane, v/v, 2:1 to 1:3): 611 mg (75% yield) of a slight yellow solid was afforded; Mp: 202 °C (dec.); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (m, 12H), 7.39 (m, 18H), 7.02 (t, J = 8.4 Hz, 2H), 6.89 (s, 10H), 6.85 (s, 10H), 6.61 (d, J = 8.8 Hz, 4H), 6.38 (d, J = 8.4 Hz, 4H), 6.26 (d, J = 8.4 Hz, 4H), 3.97 (t, J = 8.4 Hz, 4H), 3.87 (s, 12H), 3.74 (s, 20H), 3.60–3.90 (m, 48H), 2.46 (m, 4H), 1.57–1.93 (m, 40H), 1.31 (m, 4H), 1.10 (t, J = 6.0 Hz , 30H), 0.89 (t, J = 6.0 Hz , 30H), 0.56 (m, 4H), -0.36 (m, 4H), -0.72 (m, 4H), -1.68 (m, 4H), -2.32 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.2, 153.7, 149.6, 149.5, 137.4, 135.3, 131.6, 129.9, 128.2, 128.1, 127.6, 123.5, 114.2, 113.8, 112.7, 106.3, 73.7, 69.7, 69.4, 68.1, 56.0, 31.5, 31.2, 30.8, 30.2, 29.0, 28.4, 28.2, 27.0, 23.2, 23.1, 22.1, 10.7, 10.6; ^{31}P NMR ($CDCl_3$, 161.9 Hz): δ 18.7 ppm ($^1J_{P\text{-}Pt}$ = 2671 Hz); MALDI-TOF-MS: 3599.40 ($[M+H]^+$); Anal. Calcd. for $C_{218}H_{276}O_{28}P_2Pt$: C, 72.70; H, 7.72; Found: C, 72.56; H, 7.68.

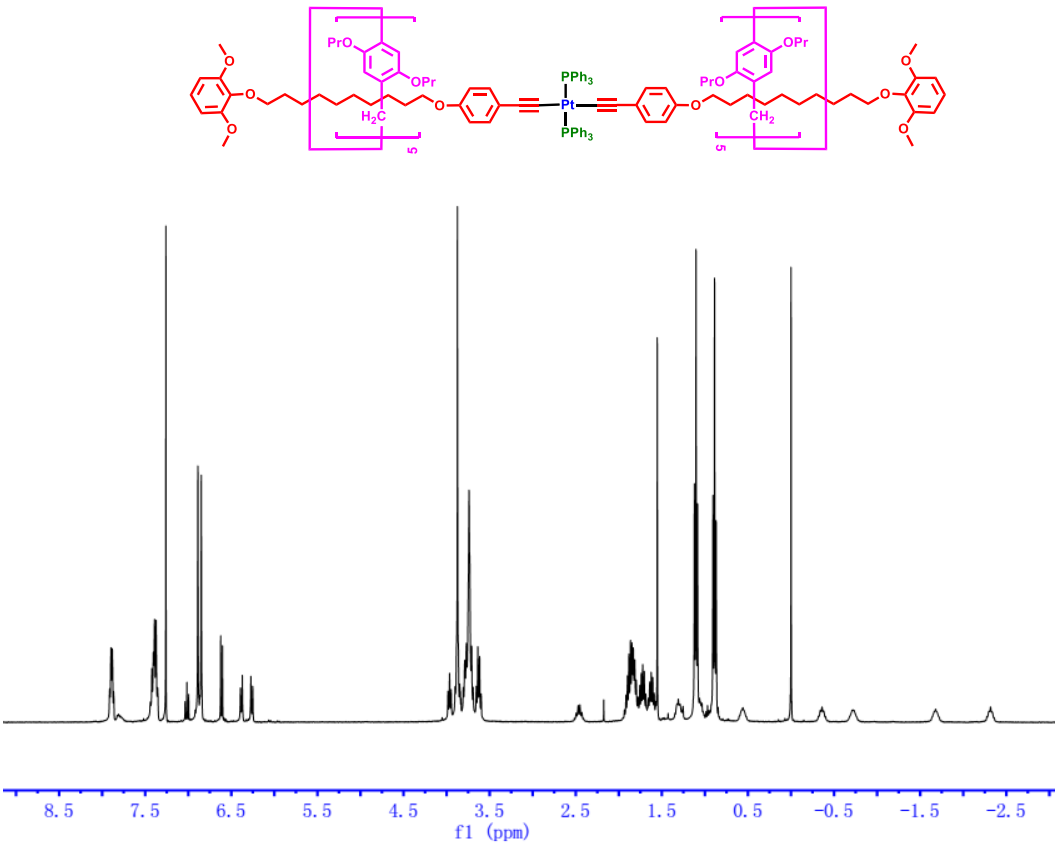


Figure S1: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, room temperature) of **1**.

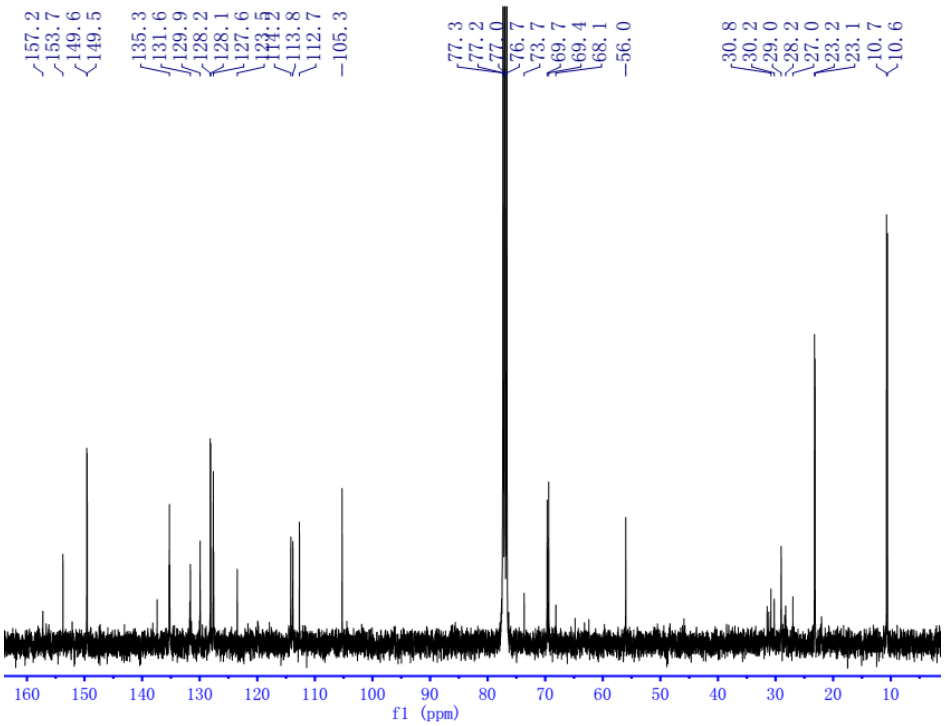


Figure S2: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, room temperature) of **1**.

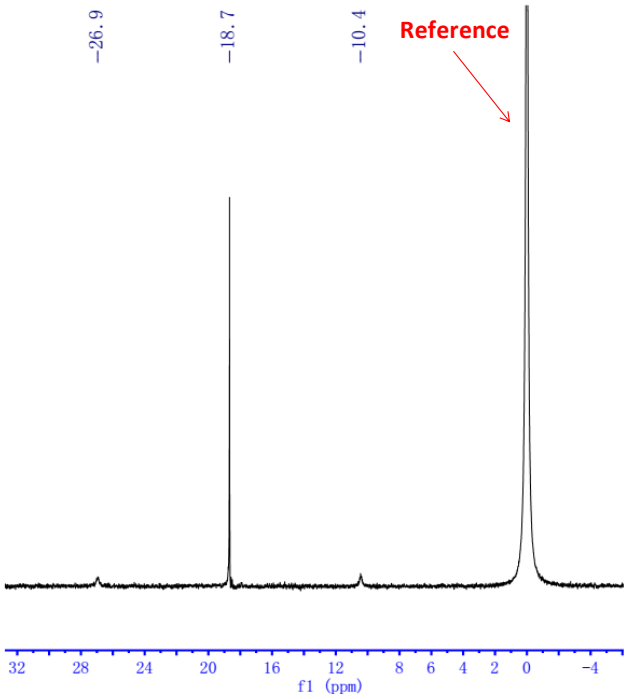


Figure S3: ^{31}P NMR spectrum ($CDCl_3$, 161.9MHz, room temperature) of **1**.

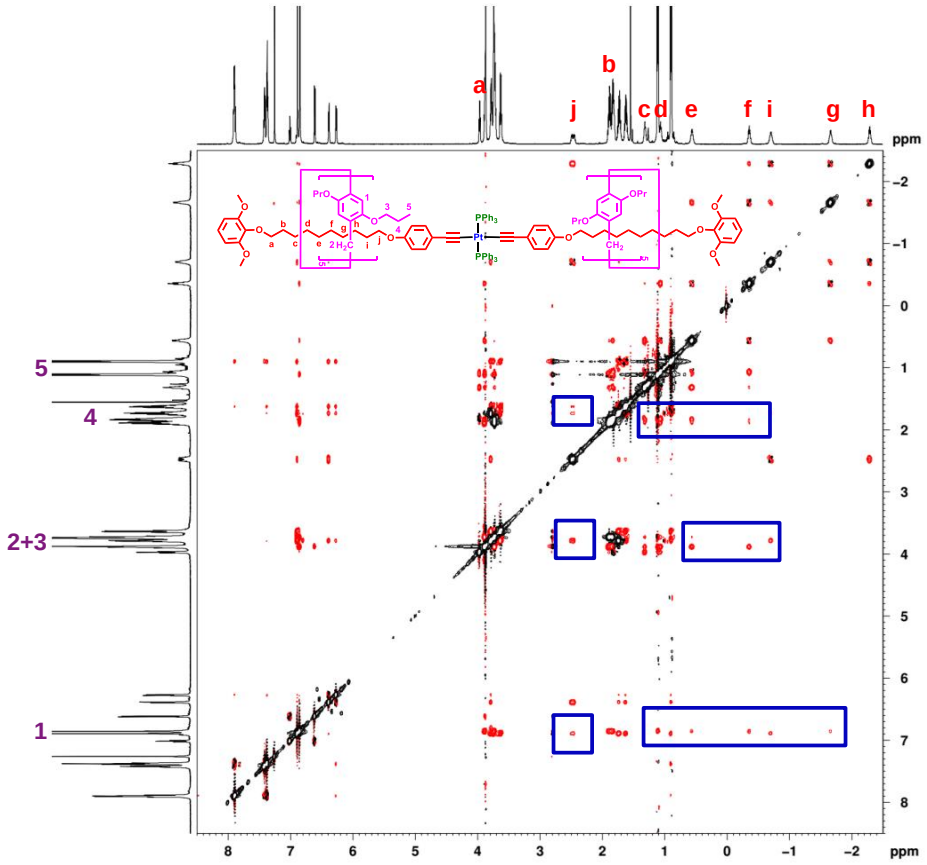


Figure S4: 2-D NOESY spectrum ($CDCl_3$, 500 MHz, room temperature) of **1**.

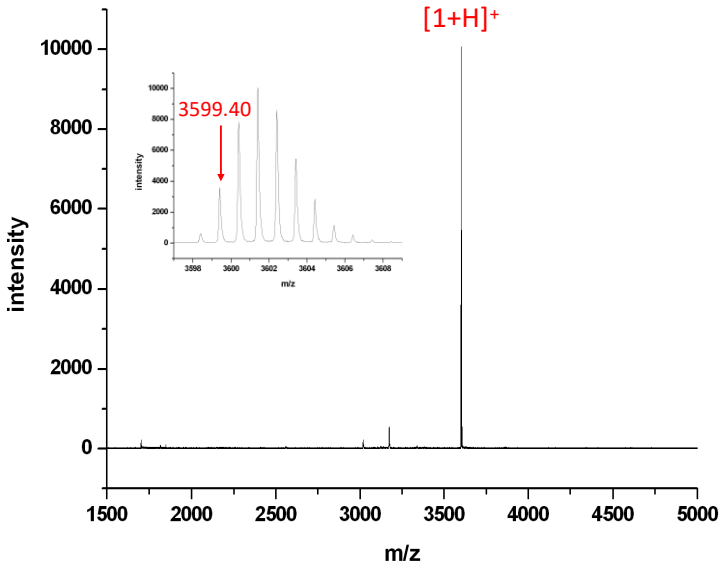


Figure S5: MALDI-TOF-MS spectrum of **1**.

General procedure for the synthesis of V-shaped organometallic [3]rotaxanes 2, 3, 5, and 6 *via* ligand exchange reactions. Chelating diphosphine (2.0 eq.) was added to a solution of **1** (1.0 eq.) in dry CH_2Cl_2. The mixture was then stirred at room temperature for 18 h. Solvent removal followed by purification *via* gradient column chromatography (silica gel, CH_2Cl_2/PE 1:1 to CH_2Cl_2) afforded the corresponding [3]rotaxanes.

For each rotaxane, the ligand used was listed as below:

cis-Bis(diphenylphosphino)ethylene **(DPPEE)**, **2**; 1,3-Bis(diphenylphosphino)propane (**DPPP**), **3**; (*2S*,*3S*)-Bis(diphenylphosphino)butane **(*S*, *S*-CHIRAPHOS)**, **5**; (*2R*,*3R*)-Bis(diphenylphosphino) -butane **(*R*, *R*-CHIRAPHOS)**, **6**.

2: pale yellow solid, Yield: 95%, Mp: 128 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (m, 8H), 7.41–7.49 (m, 14H), 7.19 (d, J = 8.8 Hz, 4H), 7.02 (t, J = 8.4 Hz, 2H), 6.92 (s, 10H), 6.87 (s, 10H), 6.60–6.63 (m, 8H), 3.98 (t, J = 8.4 Hz, 4H), 3.88 (s, 12H), 3.75 (s, 20H), 3.61–3.92 (m, 52H), 2.41 (m, 4H), 1.65–1.94 (m, 36H), 1.31 (m, 4H), 1.11 (t, J = 6.0 Hz , 30H), 0.90 (t, J = 6.0 Hz , 30H), 0.67 (m, 4H), -0.18 (m, 4H), -0.85 (m, 4H), -1.48 (m, 4H), -2.29 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.7, 153.7, 149.7, 149.5, 137.4, 133.6, 133.5, 132.1, 131.1, 128.7, 128.5, 128.2, 128.1, 123.5, 114.3, 113.8, 113.2, 105.3, 73.6, 69.8, 69.4, 68.2, 56.0, 31.4, 31.3, 30.8, 30.4, 29.0, 28.6, 27.9, 27.0, 23.2, 23.1, 22.1, 10.7, 10.5; ^{31}P NMR ($CDCl_3$, 161.9 Hz): δ 52.2 ppm ($^1J_{P\text{-}Pt}$ = 2283 Hz); MALDI-TOF-MS: 3471.47 ($[M+H]^+$); Anal. Calcd. for $C_{208}H_{268}O_{28}P_2Pt$: C, 71.93; H, 7.78; Found: C, 71.85; H, 7.76.

3: white solid, Yield: 90%, Mp: 164 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (m, 8H), 7.38 (m, 12H), 7.01 (t, J = 8.4 Hz, 2H), 6.91 (s, 10H), 6.85 (s, 10H), 6.79 (d, J = 8.8 Hz, 4H), 6.61 (d, J = 8.4 Hz, 4H), 6.48 (d, J = 8.4 Hz, 4H), 3.97 (t, J = 8.4 Hz, 4H), 3.87 (s, 12H), 3.74 (s, 20H),

3.61–3.90 (m, 52H), 2.49 (m, 8H), 2.13 (m, 2H), 1.62–1.92 (m, 36H), 1.32 (m, 4H), 1.11 (t, *J* = 6.0 Hz , 30H), 0.90 (t, *J* = 6.0 Hz , 30H), 0.60 (m, 4H), -0.30 (m, 4H), -0.76 (m, 4H), -1.62 (m, 4H), -2.34 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.5, 153.8, 149.7, 149.5, 137.4, 133.8, 132.3, 130.2, 128.2, 128.1, 128.2, 128.1, 119.7, 114.2, 113.8, 112.7, 105.3, 73.7, 69.7, 69.4, 68.2, 56.0, 31.4, 31.2, 30.8, 30.3, 30.1, 29.7, 29.0, 28.5, 28.1, 27.0, 23.2, 23.1, 22.0, 10.7, 10.5; ^{31}P NMR ($CDCl_3$, 161.9 Hz): δ -5.5 ppm ($^1J_{P\text{-}Pt}$ = 2202 Hz); MALDI-TOF-MS: 3487.40 ($[M+H]^+$); Anal. Calcd. for $C_{209}H_{272}O_{28}P_2Pt$: C, 71.94; H, 7.86; Found: C, 71.59; H, 7.93.

5: white solid, Yield: 55%, Mp: 62 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03–7.90 (m, 8H), 7.38 (m, 12H), 7.04-7.00 (m, 6H), 6.91 (s, 10H), 6.86 (s, 10H), 6.61 (d, *J* = 8.4 Hz, 4H), 6.55 (d, *J* = 8.4 Hz, 4H), 3.98 (t, *J* = 8.4 Hz, 4H), 3.88 (s, 12H), 3.75 (s, 20H), 3.63–3.91 (m, 52H), 2.54–2.42 (m, 6H), 1.61–1.94 (m, 36H), 1.33 (m, 4H), 1.11 (t, *J* = 6.0 Hz , 30H), 1.05 (m, 6H), 0.90 (t, *J* = 6.0 Hz , 30H), 0.62 (m, 4H), -0.27 (m, 4H), -0.77 (m, 4H), -1.57 (m, 4H), -2.30 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.4, 153.7, 149.7, 149.5, 137.4, 136.5, 133.8, 133.6, 133.3, 132.1, 131.2, 130.5, 128.7, 128.5, 128.4, 128.3, 128.20, 128.16, 128.1, 123.5, 119.9, 114.2, 113.8, 112.9, 105.3, 73.7, 69.8, 69.4, 68.2, 56.0, 31.4, 31.2, 30.8, 30.3, 29.7, 29.0, 28.5, 28.0, 27.0, 23.2, 23.1, 22.1, 15.4, 10.7, 10.5; ^{31}P NMR ($CDCl_3$, 161.9 Hz): δ 44.7 ppm ($^1J_{P\text{-}Pt}$ = 2234 Hz); MALDI-TOF-MS: 3504.0 ($[M+H]^+$); Anal. Calcd. for $C_{210}H_{274}O_{28}P_2Pt$: C, 71.99; H, 7.88;; Found: C, 72.38; H, 7.95.

6: white solid, Yield: 65%, Mp: 62 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03–7.90 (m, 8H), 7.38 (m, 12H), 7.04-7.00 (m, 6H), 6.91 (s, 10H), 6.86 (s, 10H), 6.61 (d, *J* = 8.4 Hz, 4H), 6.55 (d, *J* = 8.4 Hz, 4H), 3.98 (t, *J* = 8.4 Hz, 4H), 3.88 (s, 12H), 3.75 (s, 20H), 3.63–3.91 (m, 52H), 2.54–2.42 (m, 6H), 1.61–1.94 (m, 36H), 1.33 (m, 4H), 1.11 (t, *J* = 6.0 Hz , 30H), 1.05 (m, 6H), 0.90 (t, *J* = 6.0 Hz , 30H), 0.62 (m, 4H), -0.27 (m, 4H), -0.77 (m, 4H), -1.57 (m, 4H), -2.30 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.5, 153.8, 149.7, 149.5, 137.5, 136.5, 133.8, 133.6, 133.3, 132.1, 131.2, 130.5, 128.7, 128.5, 128.4, 128.33, 128.30, 128.2, 128.1, 123.4, 119.9, 114.2, 113.9, 113.0, 105.3, 73.7, 69.8, 69.4, 68.2, 56.0, 31.4, 31.2, 30.8, 30.3, 29.7, 29.0, 28.5, 28.0, 27.0, 23.2, 23.1, 22.1, 15.4, 10.7, 10.5; ^{31}P NMR ($CDCl_3$, 161.9 Hz): δ 44.7 ppm ($^1J_{P\text{-}Pt}$ = 2234 Hz); MALDI-TOF-MS: 3504.7 ($[M+H]^+$); Anal. Calcd. for $C_{210}H_{274}O_{28}P_2Pt$: C, 71.99; H, 7.88; Found: C, 72.00; H, 8.09.

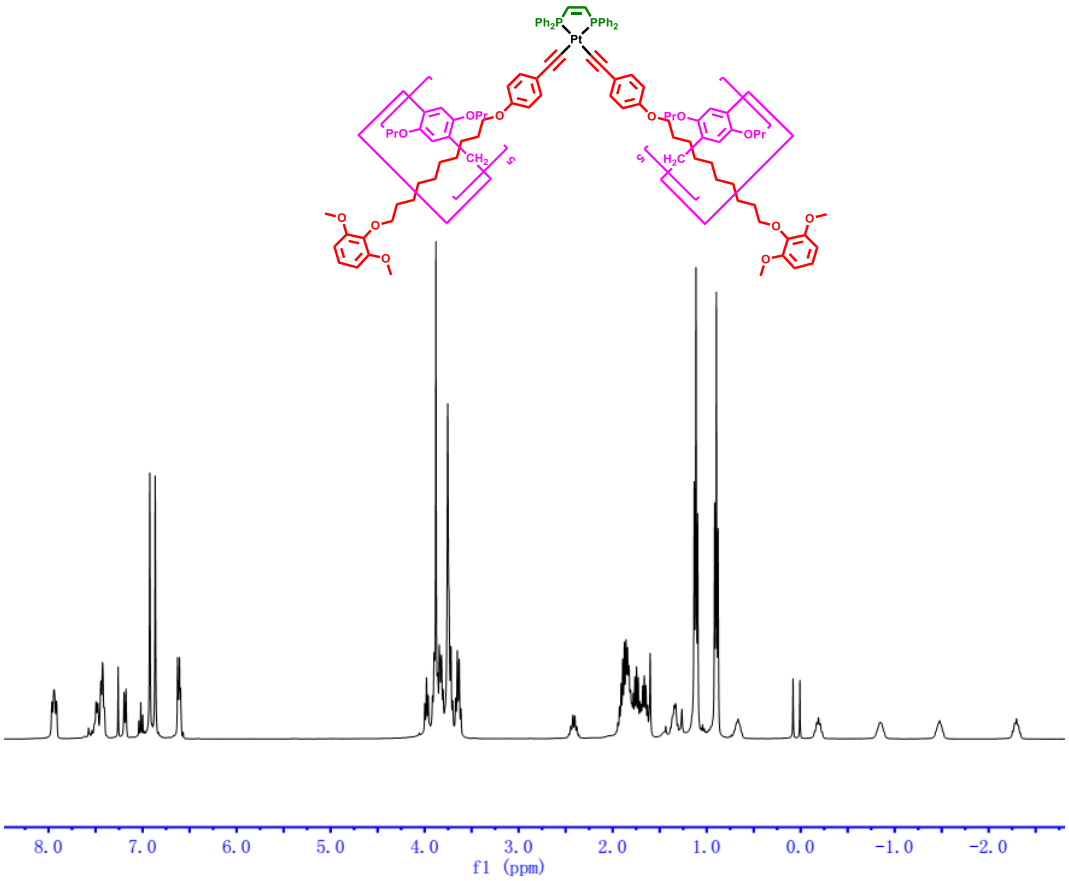


Figure S6: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, room temperature) of **2**.

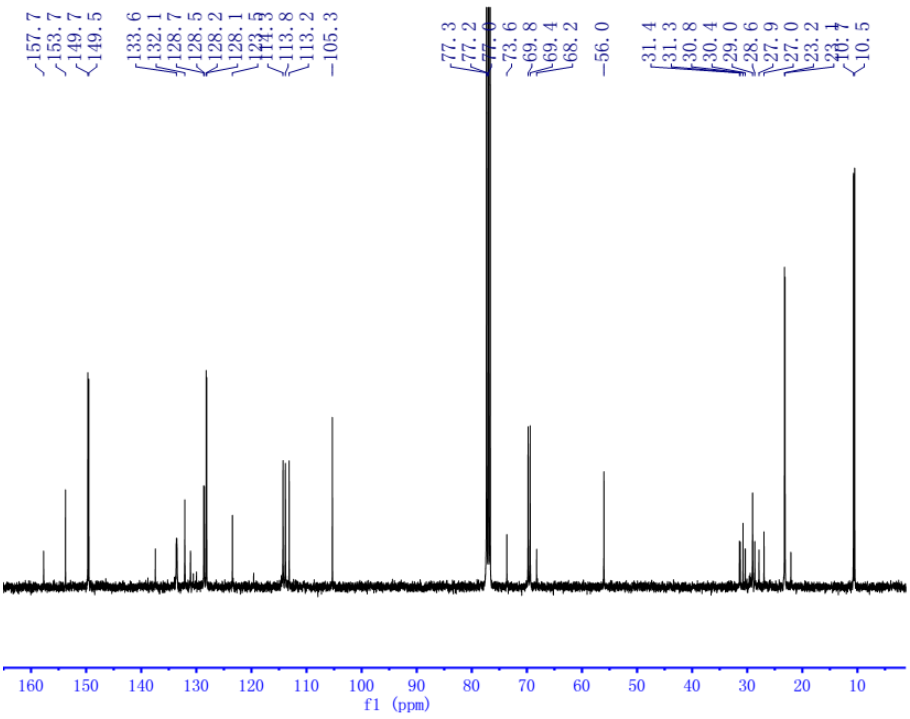


Figure S7: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, room temperature) of **2**.

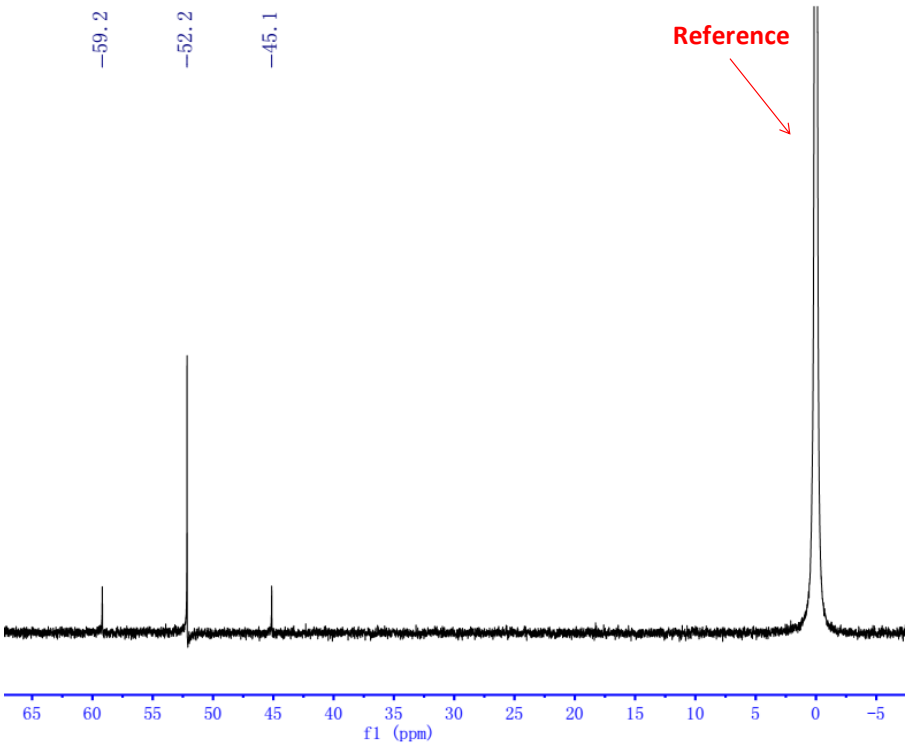


Figure S8: ^{31}P NMR spectrum ($CDCl_3$, 161.9 MHz, room temperature) of **2**.

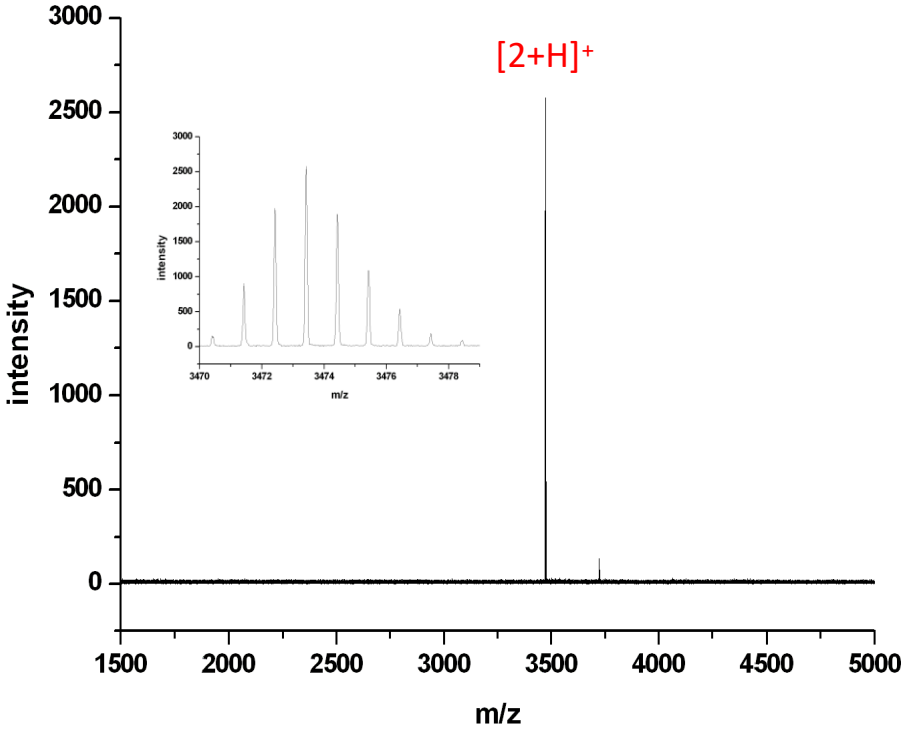


Figure S9: MALDI-TOF-MS spectrum of **2**.

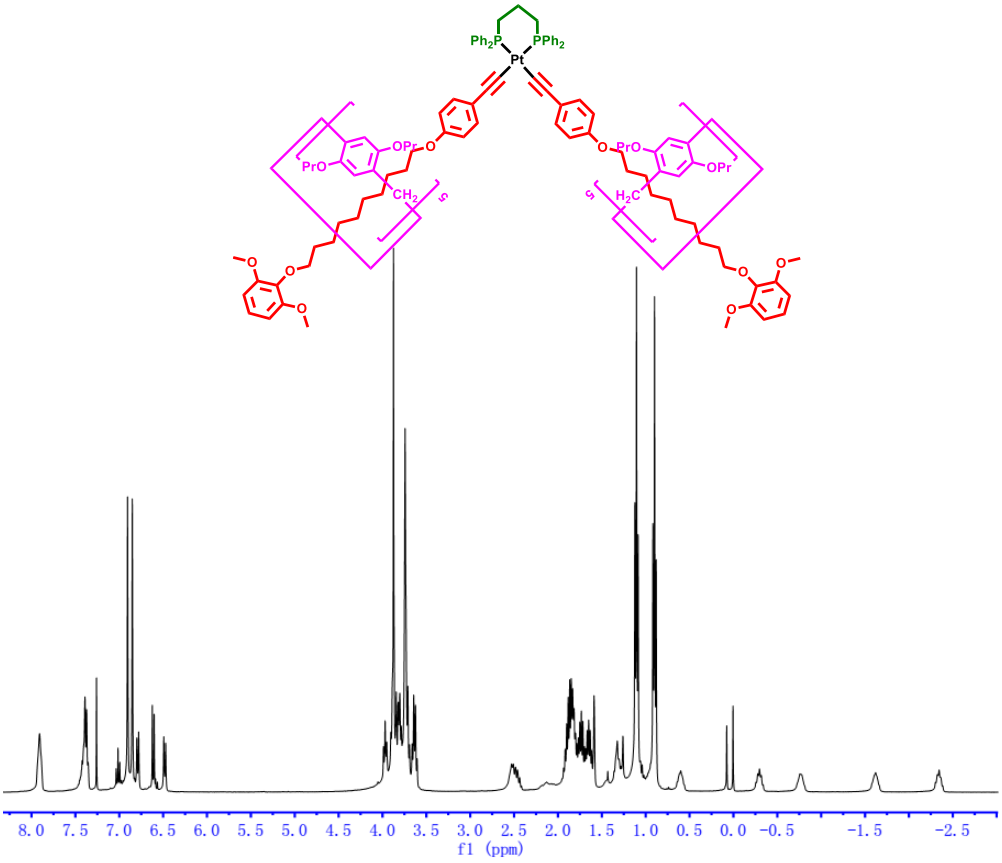


Figure S10: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, room temperature) of **3**.

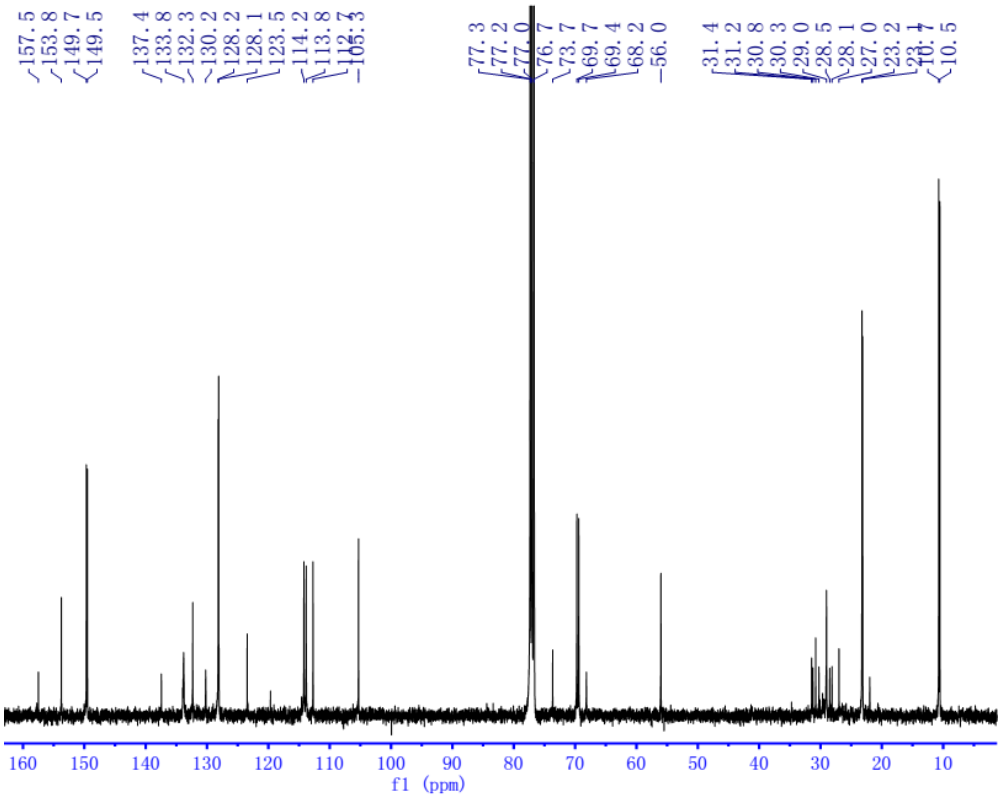


Figure S11: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, room temperature) of **3**.

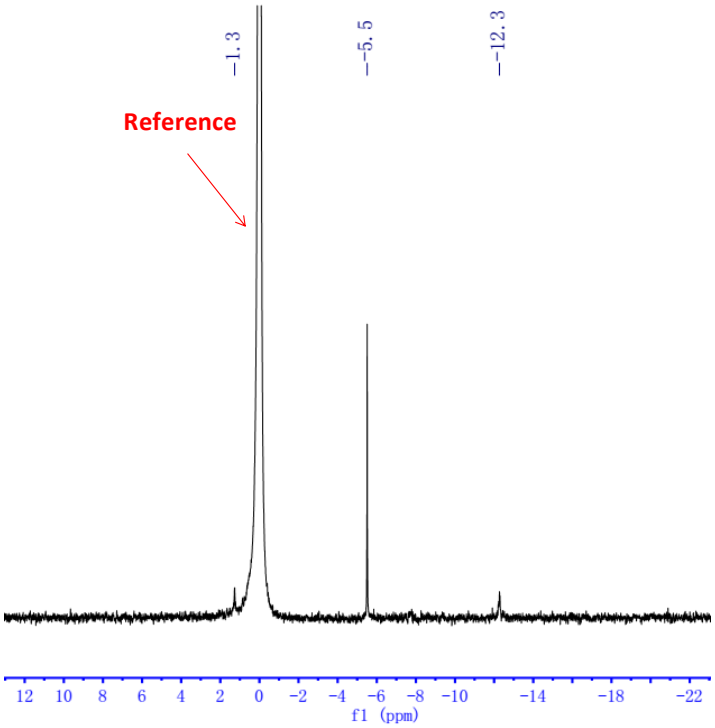


Figure S12: ^{31}P NMR spectrum ($CDCl_3$, 161.9 MHz, room temperature) of **3**.

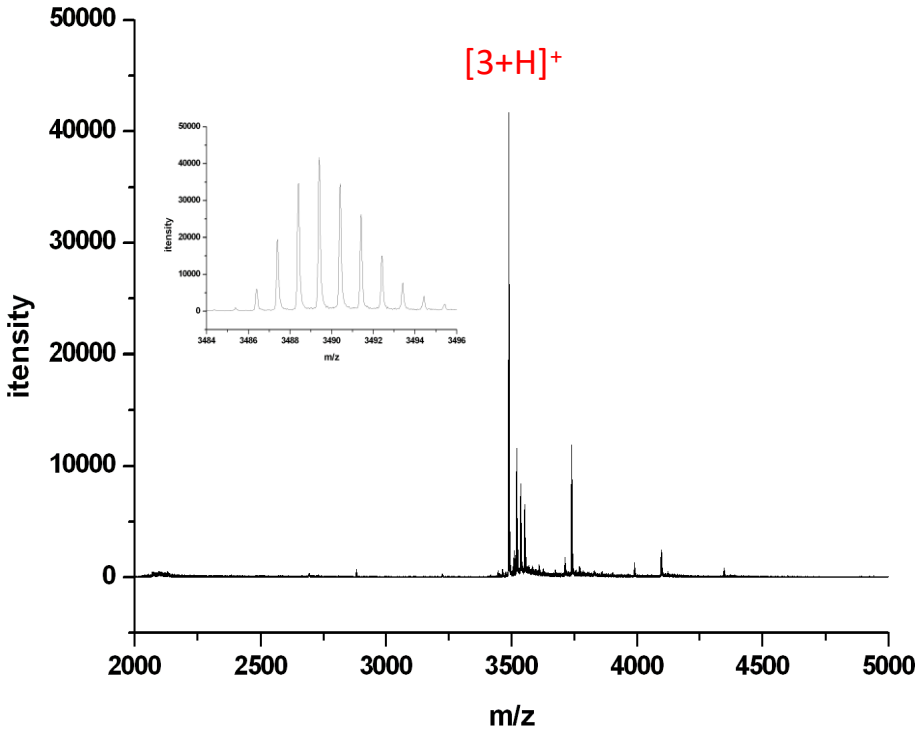


Figure S13: MALDI-TOF-MS spectrum of **3**.

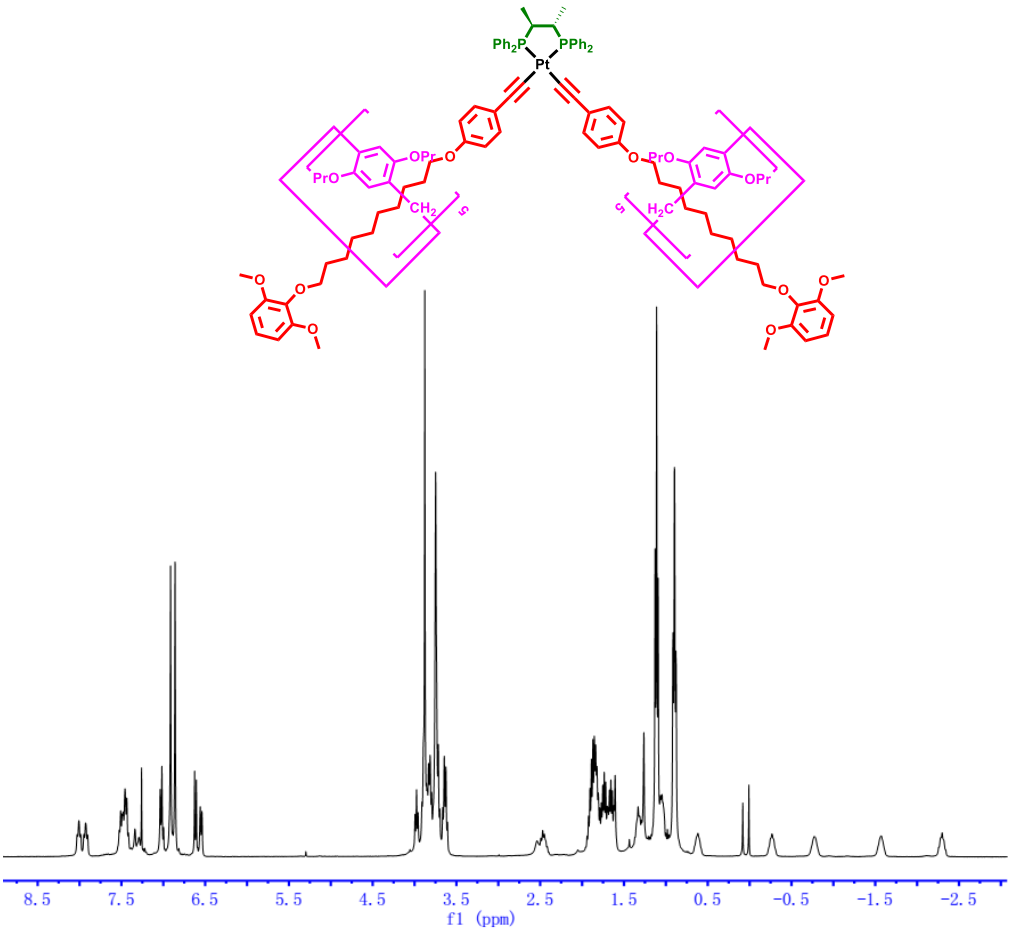


Figure S14: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, room temperature) of **5**.

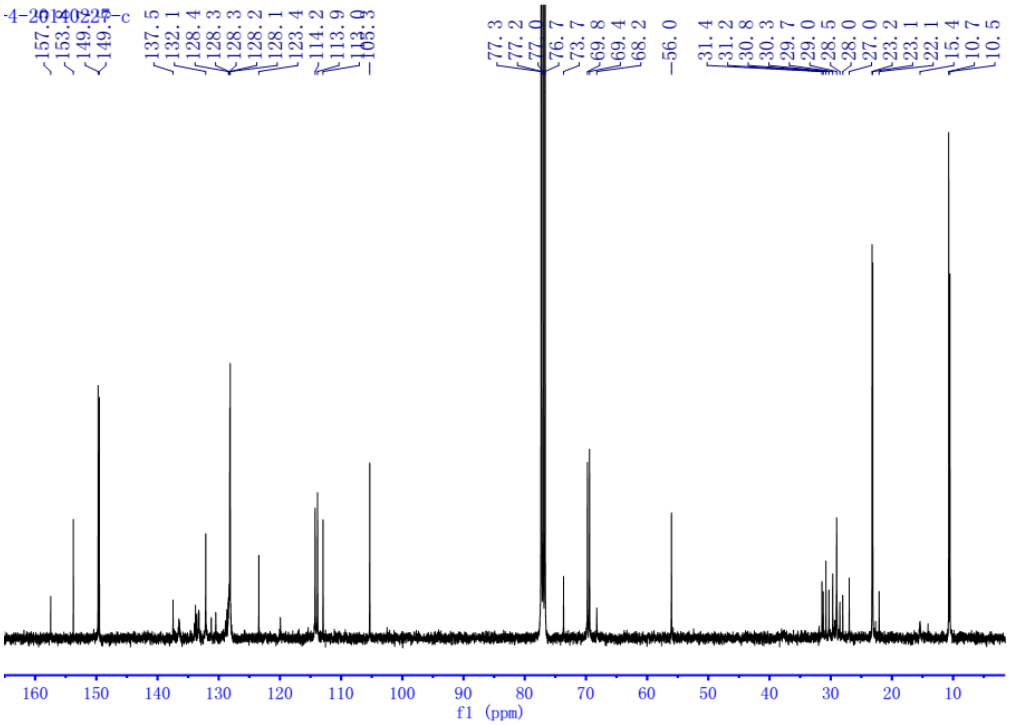


Figure S15: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, room temperature) of **5**.

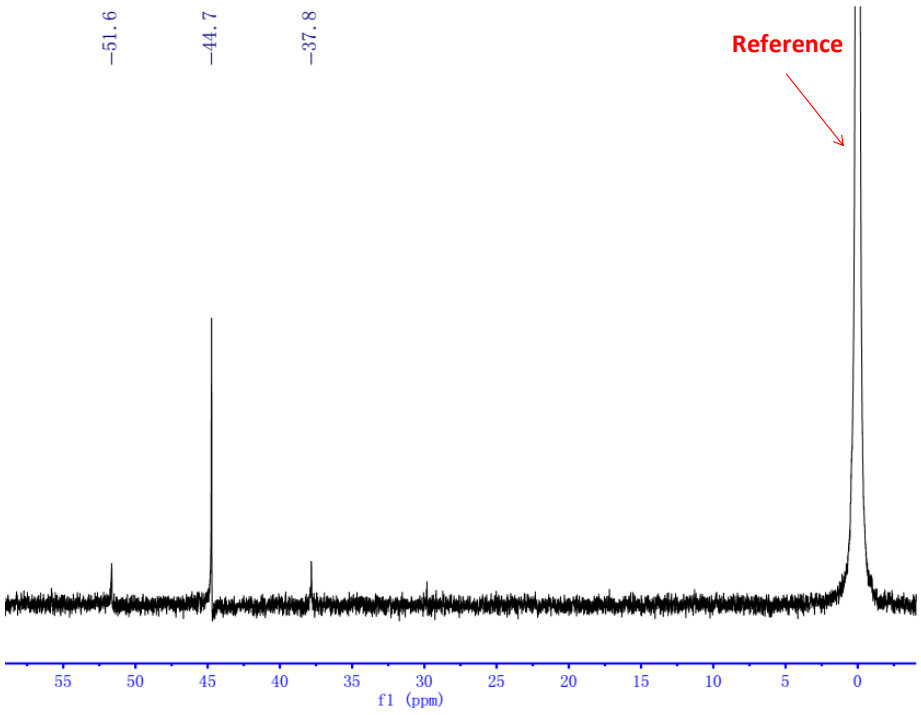


Figure S16: ^{31}P NMR spectrum ($CDCl_3$, 161.9 MHz, room temperature) of **5**.

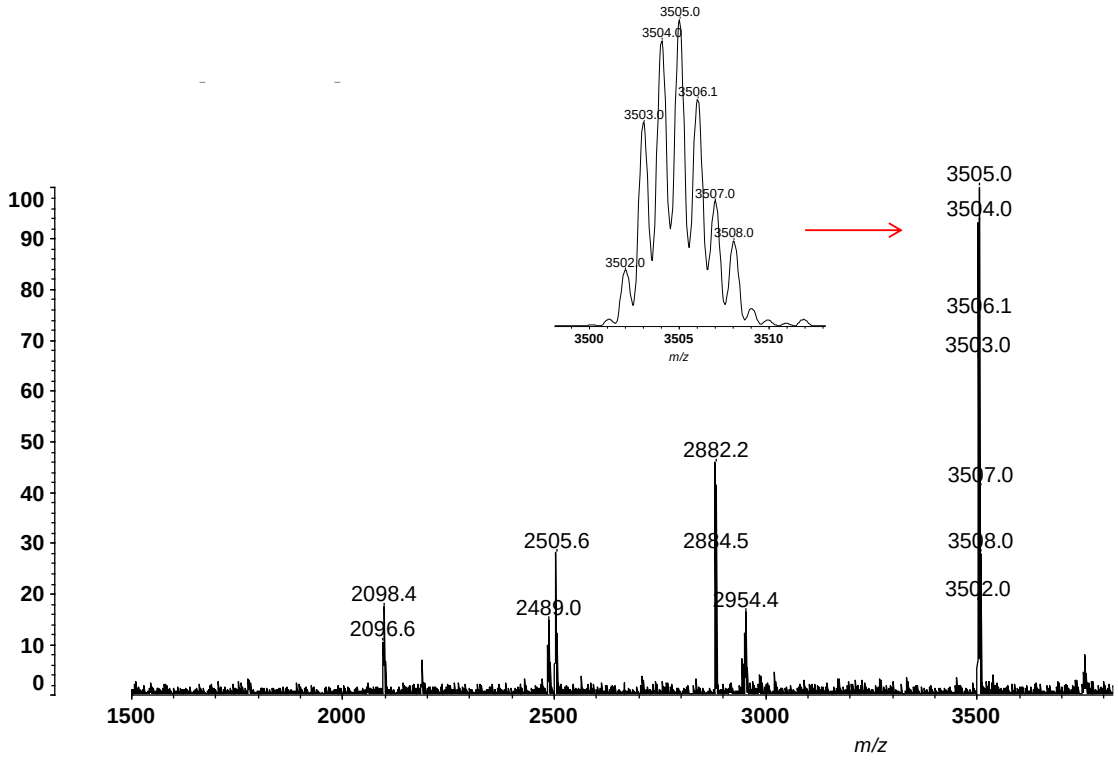


Figure S17: ESI-TOF-MS spectrum of **5**.

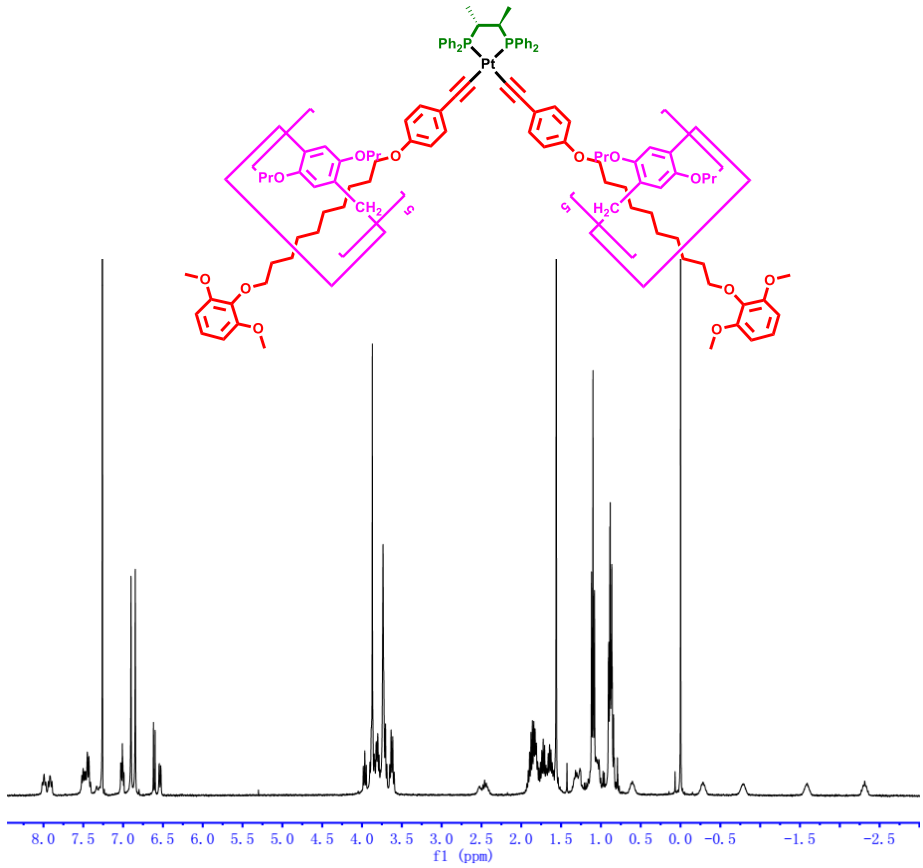


Figure S18: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, room temperature) of **6**.

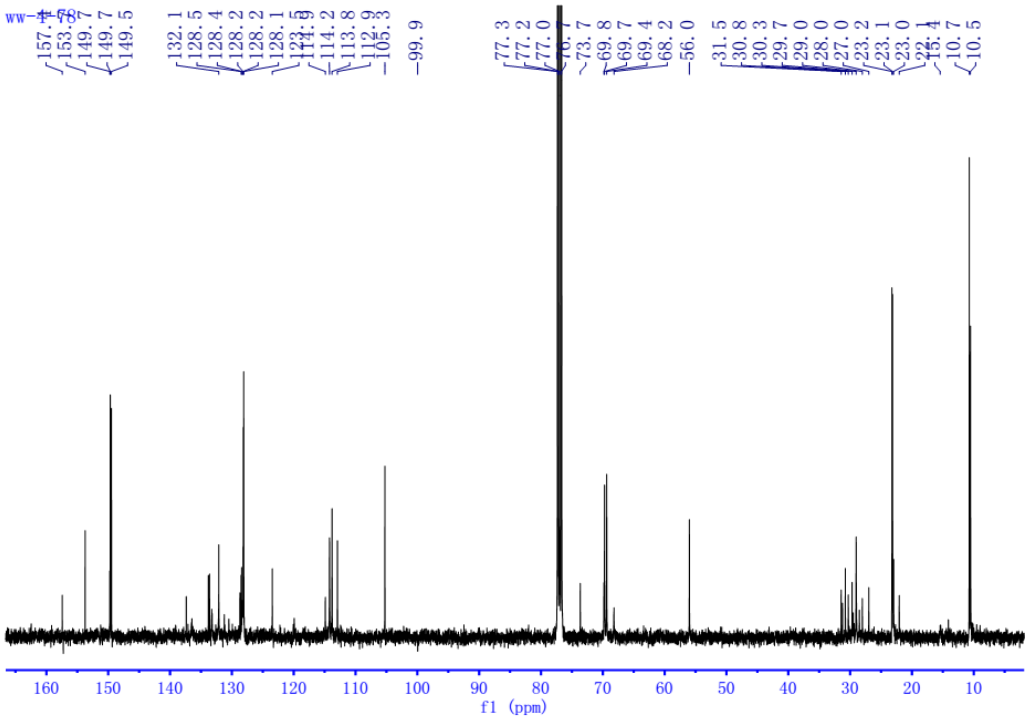


Figure S19: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, room temperature) of **6**.

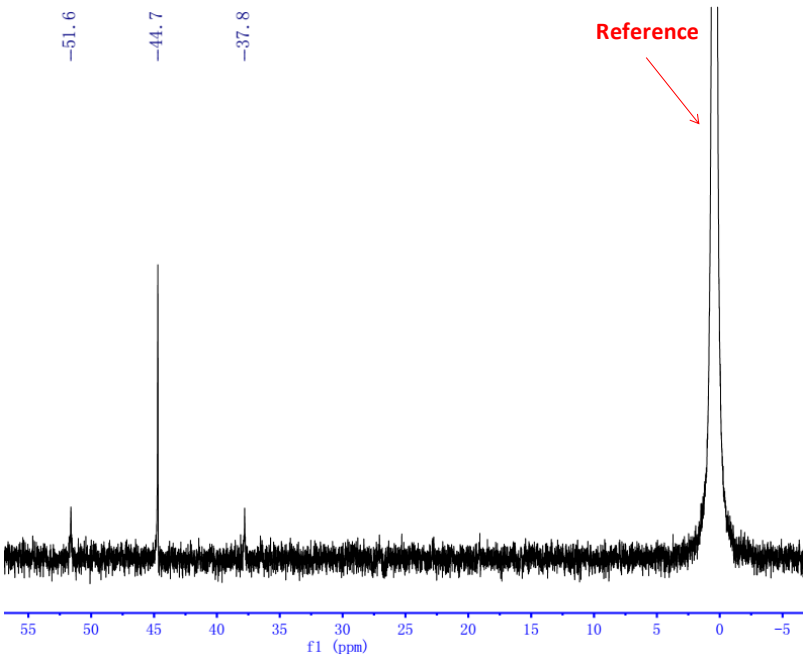


Figure S20: ^{31}P NMR spectrum ($CDCl_3$, 161.9 MHz, room temperature) of **6**.

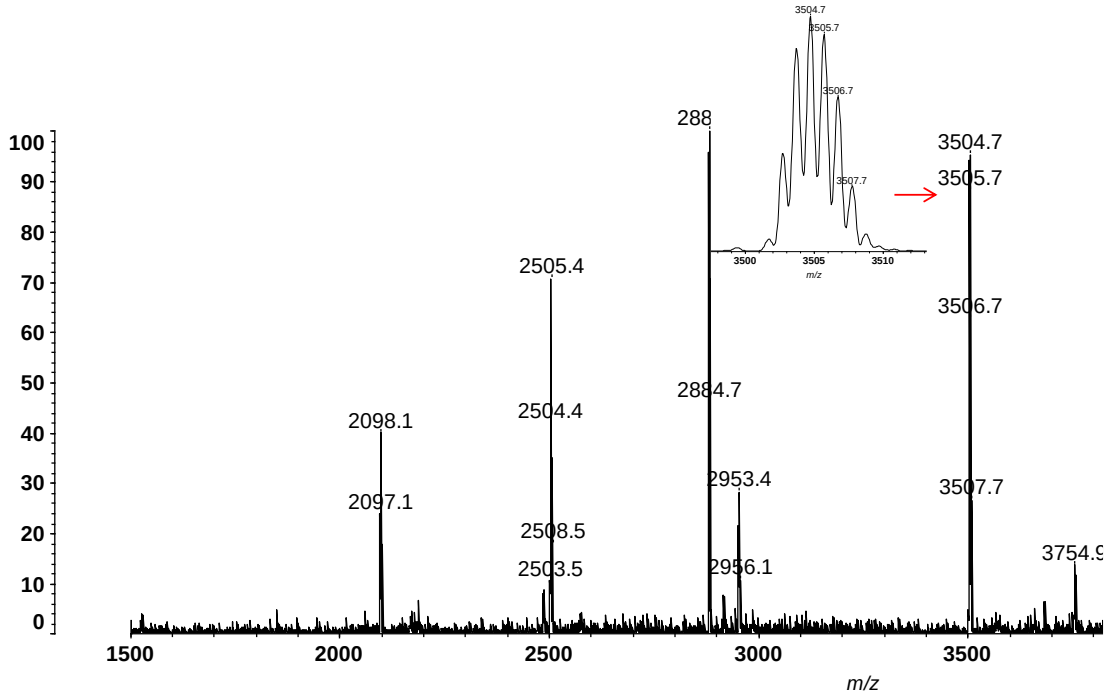


Figure S21: ESI-TOF-MS spectrum of **6**.

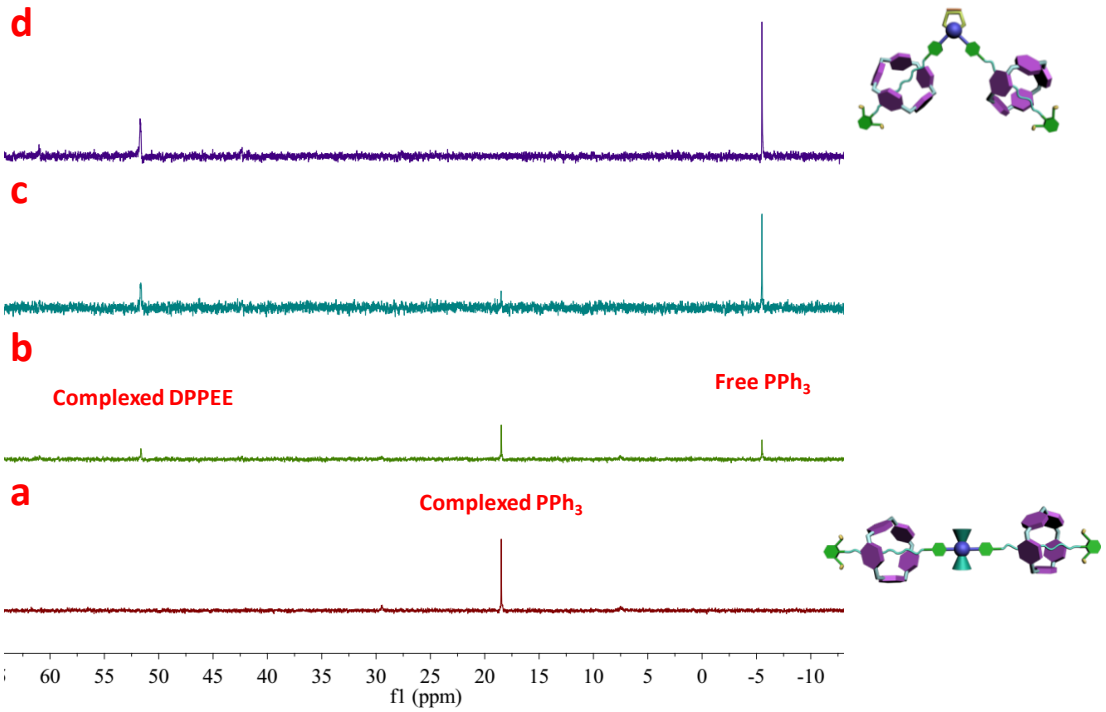


Figure S22. Partial ^{31}P NMR spectra of ligand exchange-induced supramolecular transformation from linear [3]rotaxane **1** to V-shaped [3]rotaxane **2** (196 MHz, CD_2Cl_2, 298 K): (a) [3]rotaxane **1**; (b) titration with 0.33 equiv. of **DPPEE**; (c) 0.66 equiv.of **DPPEE**; (d) 1.00 equiv. of **DPPEE**.

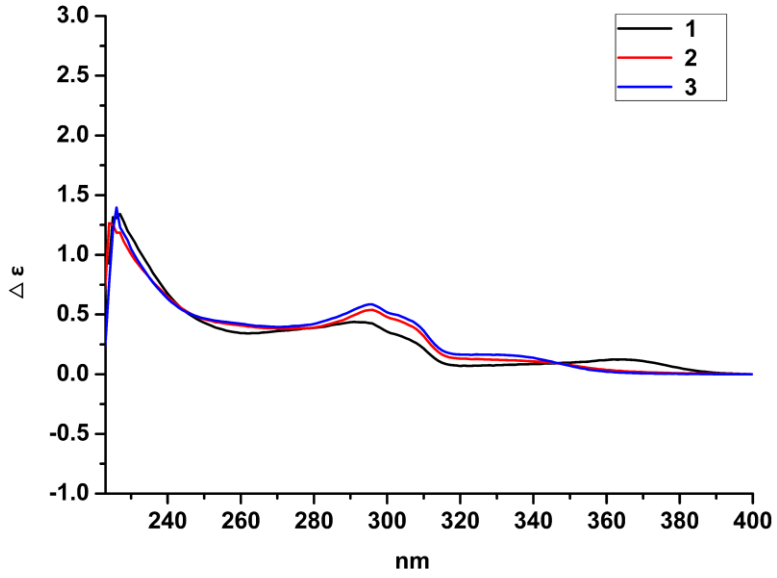


Figure S23: UV-vis spectra of **1, 2** and **3** in CH_2Cl_2 (10^{-5} M^{-1}).

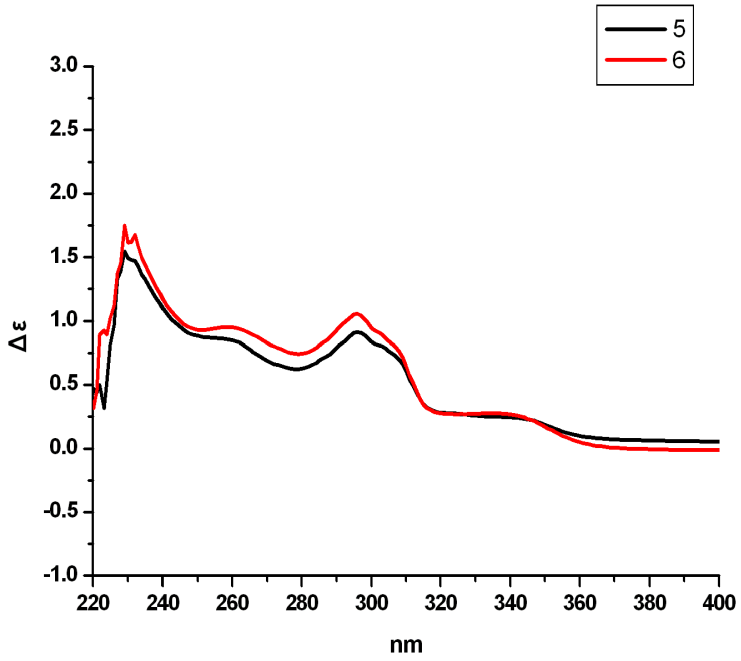


Figure S24: UV-vis spectra of **5** and **6** in CH_2Cl_2 (10^{-5} M^{-1}).

General Procedure for the Synthesis of 4: I_2 (4.0 eq.) was added to a solution of **2** or **3** (1.0 eq.) in dry $CHCl_3$. The mixture was then stirred at room temperature for 12 h until the full conversion of **2** or **3** according to the TLC analysis. Solvent removal followed by purification *via* gradient column chromatography (silica gel, CH_2Cl_2/PE 1:1 to CH_2Cl_2) afforded **4** as a pale yellow solid.

4, Yield: (from **2**, 64%); (from **3**, 59%), Mp: 66 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, J = 8.8 Hz, 4H), 7.02 (t, J = 8.4 Hz, 2H), 6.92 (s, 10H), 6.87 (s, 10H), 6.74 (d, J = 8.4 Hz, 4H), 6.62 (d, J = 8.4 Hz, 4H), 3.98 (t, J = 8.4 Hz, 4H), 3.88 (s, 12H), 3.75 (s, 20H), 3.63–3.92 (m, 52H), 2.19 (m, 4H), 1.65–1.93 (m, 36H), 1.38 (m, 4H), 1.17 (m, 4H), 1.11 (t, J = 6.0 Hz , 30H), 0.96 (t, J = 6.0 Hz , 30H), 0.79 (m, 4H), 0.05 (m, 4H), -0.97 (m, 4H), -1.21 (m, 4H), -2.15 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.6, 153.7, 149.6, 137.3, 133.5, 132.7, 130.2, 128.4, 128.2, 123.5, 114.5, 114.3, 113.8, 113.5, 105.2, 81.8, 73.5, 72.4, 70.0, 69.4, 68.5, 56.0, 31.3, 31.2, 30.7, 30.6, 29.7, 29.0, 28.8, 27.4, 26.8, 23.22, 23.17, 22.2, 10.6, 10.5; MALDI-TOF-MS: 2880.36 ($[M+H]^+$).

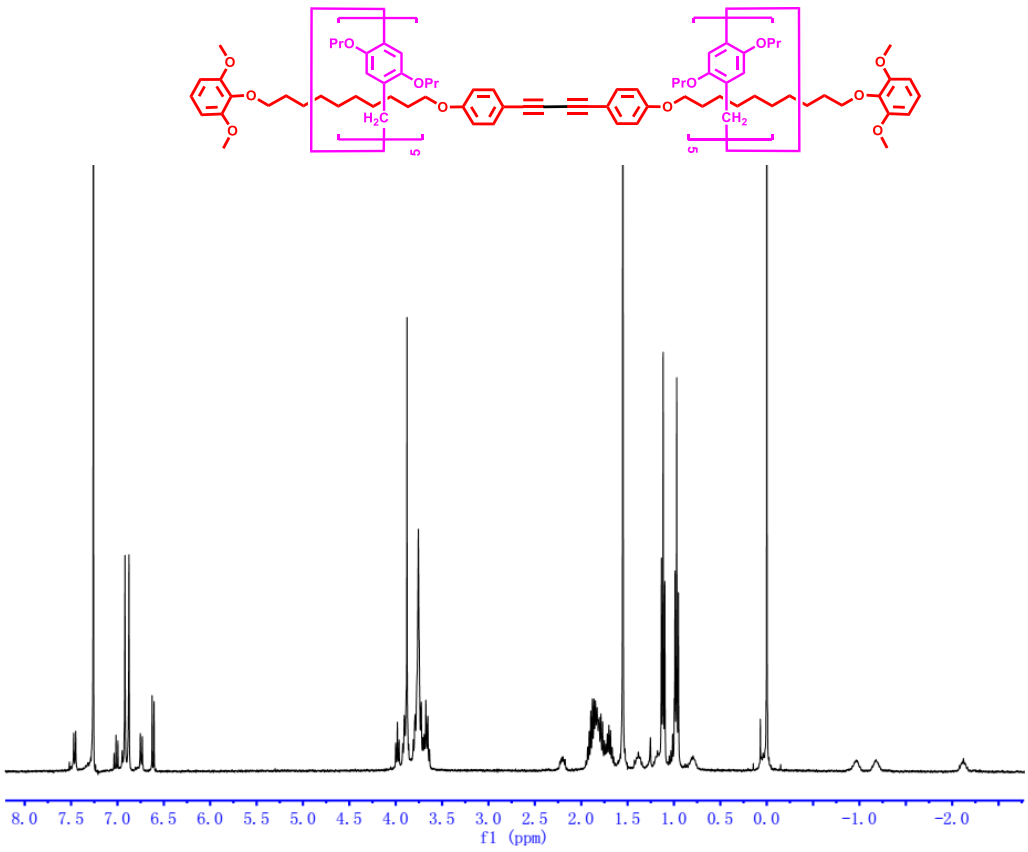


Figure S25: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, room temperature) of **4**.

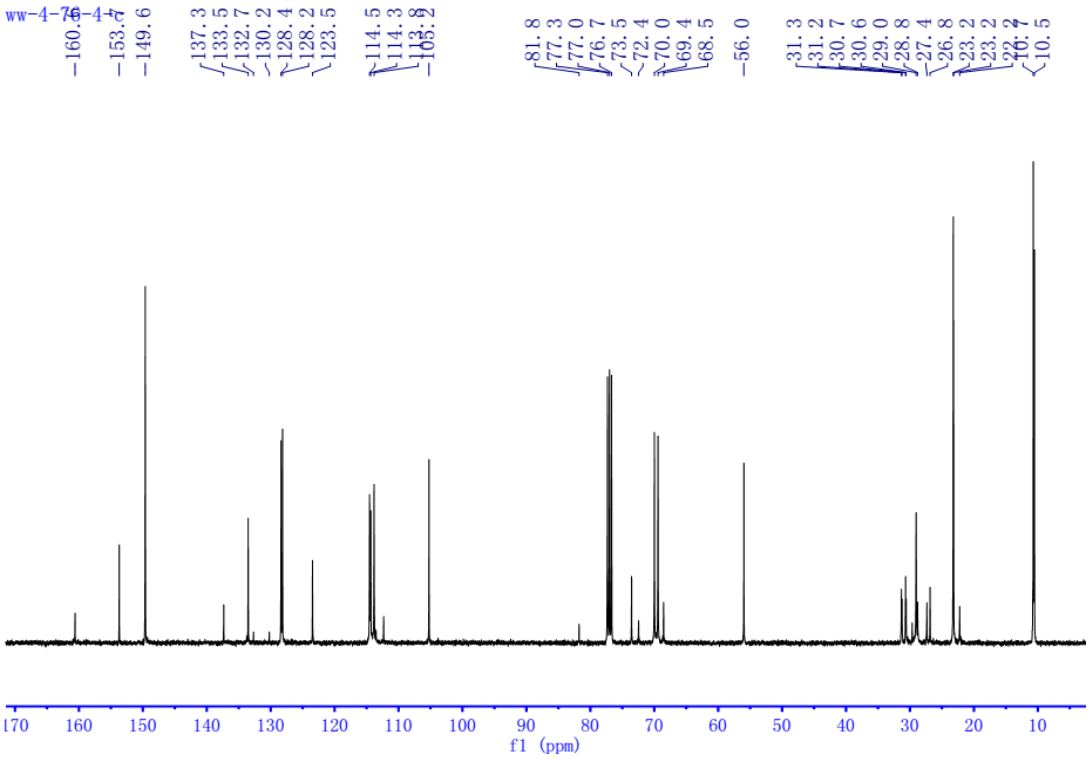


Figure S26: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, room temperature) of **4**.

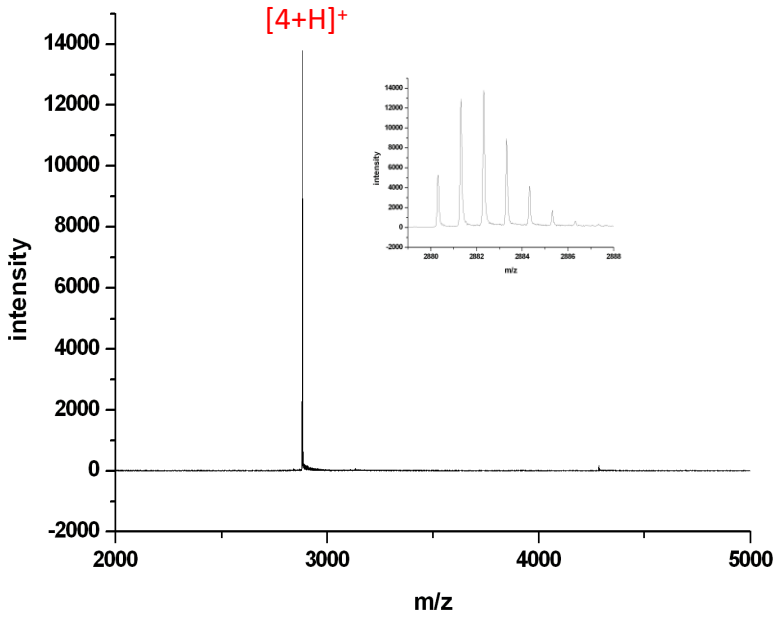
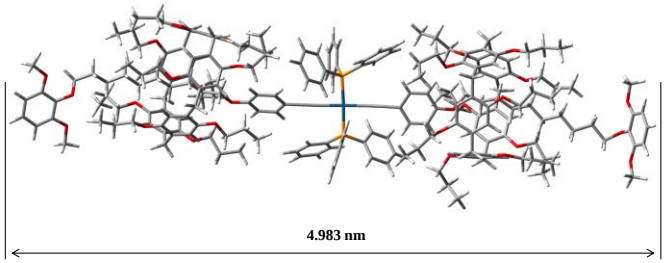
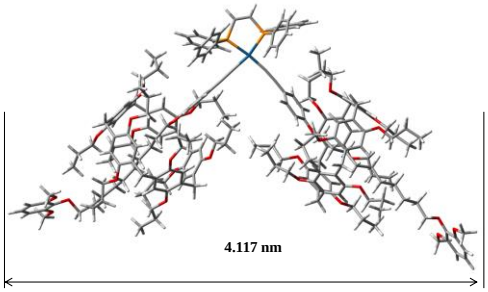


Figure S27: MALDI-TOF-MS spectrum of **4.**

Figure S28: Geometrical structure of rotaxanes **1** - **6** optimized by PM6 semiempirical molecular orbital methods.



1



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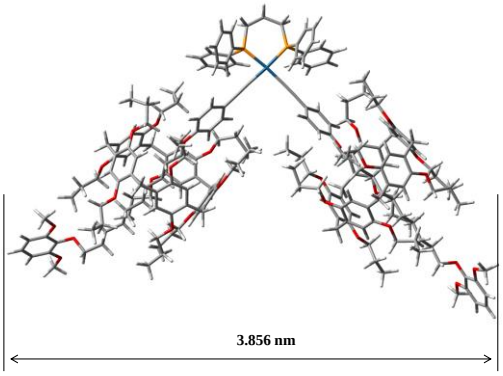

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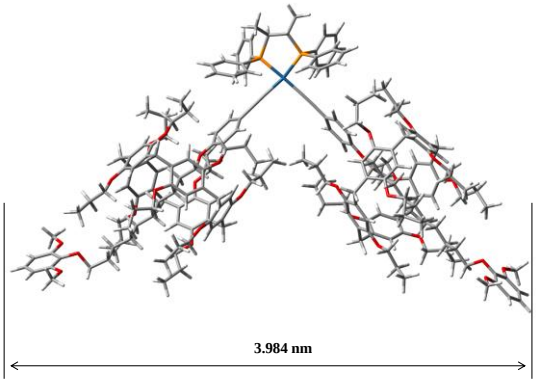

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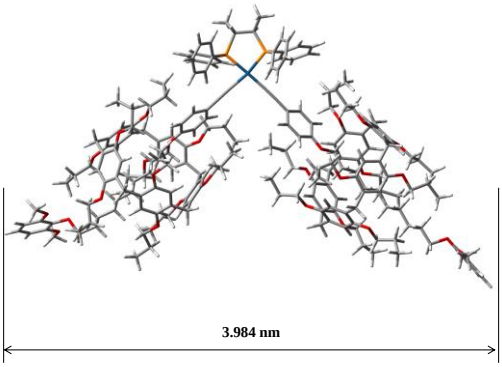

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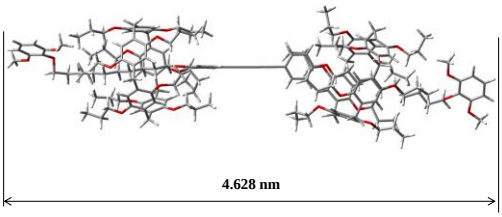

6

Table S1: Lengths of rotaxanes **1** - **6** optimized by PM6 semiempirical molecular orbital methods.

Rotaxane	**Lengths (nm)**
1	4.983
2	4.117
3	3.865
4	3.984
5	3.984
6	4.628

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