Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Towards a Hexa-Branched [7]Rotaxane from a [3]Rotaxane *via* a [2+2+2] Alkyne Cyclotrimerization Process

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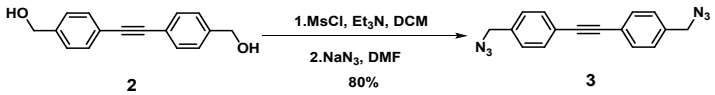
1. General methods and details

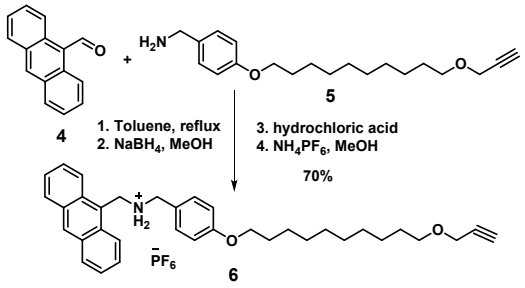
Chemicals were purchased from Adamas-beta®, Aldrich or TCI and used as received unless otherwise stated. Solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. All reactions were carried out under an atmosphere of dry nitrogen unless otherwise stated. The molecular structures were confirmed using ^{1}H NMR, 2D COSY, ^{13}C NMR, and high resolution ESI mass spectroscopy. NMR experiments (^{1}H NMR, ^{13}C NMR, and COSY spectra) were done on a Brüker AV-400 spectrometer (^{1}H, 400MHz; ^{13}C, 100 MHz) and Ascend 600 spectrometer (^{13}C, 150 MHz). The electrospray ionization (ESI) mass spectra were obtained on a LCT Premier XE mass spectrometer.

2. Synthesis of the New Compounds



Scheme S1. Synthetic route of the diazide 3

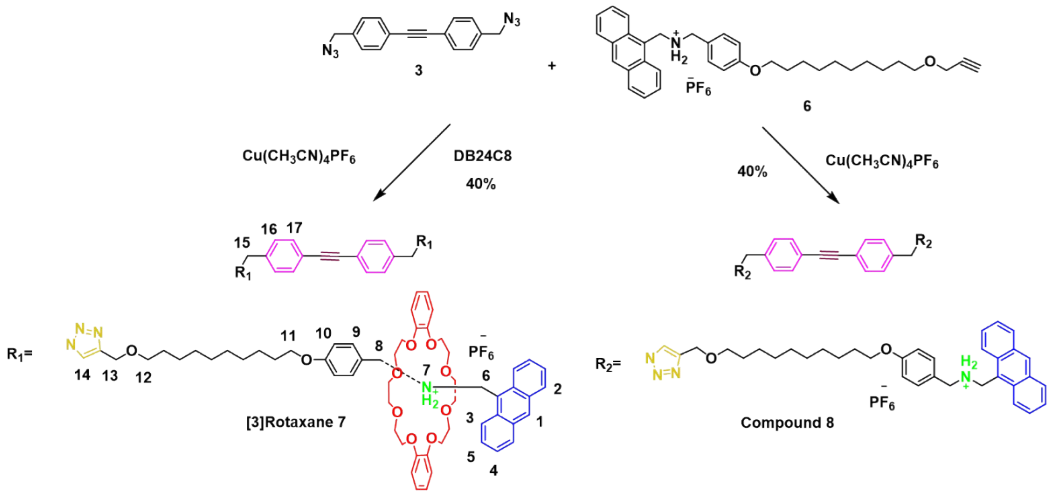
Synthesis of diazide 3. A mixture of dihydroxyl **2**[S1] (1.0 g, 4.2 mmol), mesyl chloride (1.43 g, 12.6 mmol), triethylamine (0.85 g, 8.4 mmol) and CH_2Cl_2 (40 mL) was stirred at room temperature overnight. The crude product was purified only by washing with water (80 mL) and solvent removal. Then, the crude product was mixed with NaN_3 (0.82g, 12.6 mmol) in anhydrous DMF (40 mL), and the reaction mixture under an atmosphere of N_2 was stirred at 80 °C for 16 h. DMF was then removed under reduced pressure, and the residue was dissolved in EtOAc and then washed with H_2O (3 × 40 mL). The organic layer was dried, and subjected to column chromatography to afford the diazide **3** (970mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.55 (d, J = 8 Hz, 4H), 7.31 (d, J = 8 Hz, 4H), 4.37 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6, 132.1, 128.2, 123.1, 89.5, 54.5. HRMS (ESI): m/z calcd for $C_{16}H_{12}N_6K^+$:327.0755; found: 327.0757 $[M+K]^+$.



Scheme S2. Synthetic route of the ammonium salt 6

Synthesis of the ammonium salt 6. A mixture of **4** (1.8g, 8.7 mmol) and **5**[S2](2.5g, 7.9 mmol) in dry toluene (70 mL) was refluxed overnight in a Dean-Stark apparatus under nitrogen atmosphere. The solvent was removed under vacuum, and the residue was dissolved in MeOH (60 mL). To the solution was then added $NaBH_4$ (1.2 g, 31.6 mmol) in portion. After the mixture was stirred 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 free amine compound. To a solution of the amine in MeOH (30 mL) was added concentrated hydrochloric acid (2.0 mL) at room temperature. After the mixture was stirred for 2 h under nitrogen atmosphere, the solvent was removed under vacuum. The residue was dissolved in MeOH (5 mL), and then added saturated NH_4PF_6 (20 mL). After the mixture was stirred 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 subjected to column chromatography to afford the ammonium salt **6** (970mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.39 (s , 1H), 8.19 (d, J = 8 Hz, 2H), 7.99 (d, J = 12 Hz, 2H), 7.43-7.52 (m, 4H), 7.32 (d, J = 8 Hz, 2H), 6.89 (d, J = 8Hz, 2H), 4.69 (s, 2H), 4.13 (d, J = 2.4Hz, 2H), 3.92-3.96 (m, 4H), 3.50 (t, J = 8Hz, 2H), 2.41 (t, J = 4Hz, 1H), 1.74-1.81 (m, 2H), 1.56-1.61 (m, 2H), 1.41-1.47 (m, 2H), 1.27-1.34 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 132.2, 131.7, 131.6, 130.4, 129.6, 129.1, 127.2, 126.0, 125.0, 124.2, 114.5, 80.1, 74.2, 70.3, 68.1, 58.1, 53.7, 44.8, 29.5, 26.1. HRMS (ESI): m/z calcd for $C_{35}H_{42}NO_2^+$: 508.3210; found: 508.3214 $[M\text{-}PF_6]^+$.

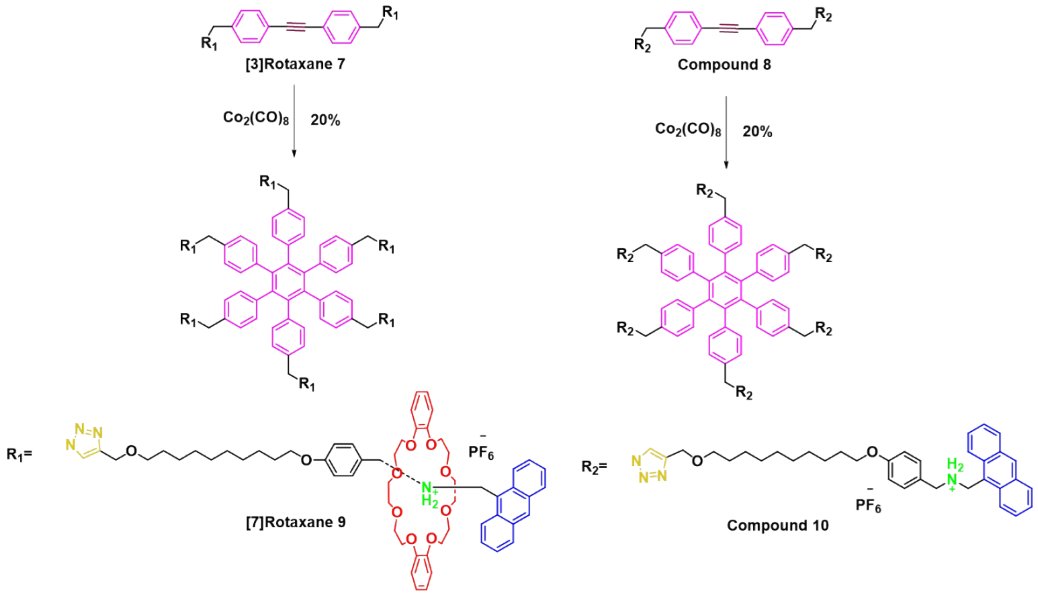


Scheme S3. Synthetic route of [3]rotaxane **7** and compound **8**

Synthesis of [3]rotaxane 7. Compound **6** (500 mg, 0.76 mmol) and DB24C8 **1** (408 mg, 0.91 mmol) were dispersed in dry CH_2Cl_2 (8 ml). The mixture was stirred for 2 hours at room temperature to form pseudorotaxane. Then, $[Cu(CH_3CN)_4]PF_6$ (283 mg, 0.76 mmol) and compound **3** (101 mg, 0.35 mmol) were added to the mixture under nitrogen atmosphere. After being stirred for 2 days, the mixture was washed with saturated NH_4PF_6 (aq, 3 × 10 mL) and water (3 × 10 mL), respectively. The organic layer was separated, and the solvent was removed under reduced pressure. The purification of the product was performed by silica gel chromatography (CH_2Cl_2:CH_3OH = 50:1, v/v) on silica gel to afford [3]rotaxane **7** (350 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.42 (d, J = 12Hz, 4H), 8.08 (s, 2H), 7.80 (d, J = 12Hz, 4H), 7.67 (s, 4H), 7.53-7.57 (m, 4H), 7.52 (s, 2H), 7.46 (d, J = 8Hz, 4H), 7.41-7.45 (m, 4H), 7.36 (d, J = 8Hz, 4H), 7.24 (d, J = 8Hz, 4H), 6.84 (d, J = 8Hz, 4H), 6.63-6.68 (m, 8H), 6.29-6.34 (m, 8H), 5.50 (s, 4H), 5.45-5.48 (m, 4H), 5.16-5.20 (m, 4H), 4.56 (s, 4H), 3.75-3.92 (m, 28H), 3.65-3.70 (m, 8H), 3.57-

3.61 (m, 8H), 3.38-3.46 (m, 12H), 1.71-1.75 (m, 4H), 1.51-1.56 (m, 4H), 1.39-1.42 (m, 4H), 1.21-1.28 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 146.6, 145., 141.6, 135.0, 134.2, 132.2, 130.7, 130.6, 129.4, 128.6, 128.1, 127.2, 125.1, 124.5, 123.7, 123.3, 122.7, 121.3, 114.5, 111.9, 89.5, 71.0, 70.8, 70.3, 68.6, 68.1, 67.9, 65.8, 64.2, 53.6, 52.3, 50.1, 45.2, 29.6, 29.4, 29.2, 26.1, 26.0. HRMS (ESI): m/z calcd for $C_{134}H_{160}N_8O_{20}^{2+}$: 1101.0886; found: 1101.0917 $[M-2PF_6]^{2+}$.

Synthesis of compound 8. A mixture of Compound **6** (500 mg, 0.76 mmol), compound **3** (101 mg, 0.35 mmol) and $[Cu(CH_3CN)_4]PF_6$ (283 mg, 0.76 mmol) were dissolved in dry CH_2Cl_2 (10 ml) under nitrogen atmosphere. After being stirred for 2 days at room temperature, the mixture was washed with saturated NH_4PF_6 (aq, 3 × 10 mL) and water (3 × 10 mL), respectively. The organic layer was separated, and the solvent was removed under reduced pressure. The purification of the product was performed by silica gel chromatography (CH_2Cl_2:CH_3OH = 60:1, v/v) on silica gel to afford compound **8** (220 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.40 (s, 2H), 8.19 (d, J = 8Hz, 4H), 7.98 (d, J = 8Hz, 4H), 7.50 (d, J = 8Hz, 4H), 7.31-7.48 (m, 8H), 7.44 (s, 2H), 7.32 (d, J = 8Hz, 4H), 7.22 (d, J = 8Hz, 4H), 6.88 (d, J = 8Hz, 4H), 5.50 (s, 4H), 4.70 (s, 4H), 4.59 (s, 4H), 3.92-3.97 (m, 8H), 3.49 (t, J = 8Hz, 4H), 1.64-1.74 (m, 32H). ^{13}C NMR (150 MHz, $CDCl_3$): δ =158.3, 146.0, 134.8, 132.2, 131.5, 130.3, 129.5, 129.0, 128.0, 127.2, 126.0, 124.9, 124.1, 123.4, 122.2, 114.4, 89.5, 70.9, 68.0, 64.3, 53.7, 44.6, 29.6, 29.4, 29.3, 26.0. HRMS (ESI): m/z calcd for $C_{86}H_{96}N_8O_4^{2+}$: 652.3772; found: 652.3785 $[M-2PF_6]^{2+}$.

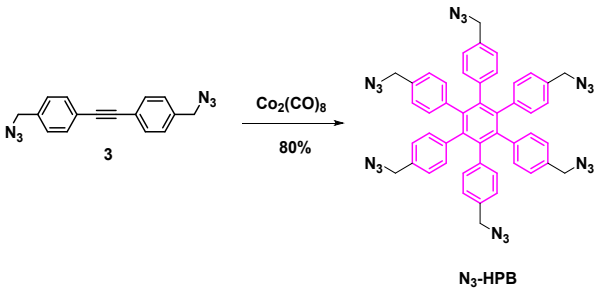


Scheme S4. Synthetic route of [7]rotaxane **9** and compound **10**

Synthesis of [7]rotaxane 9. A mixture of [3]rotaxane **7** (300mg, 0.12mmol) and $Co_2(CO)_8$ (4mg, 0.012mmol)was dissolved in freshly distilled 1,4-dioxane (15 ml) under nitrogen atmosphere. The reaction mixture was stirred at room temperature overnight and then refluxed for 1 day at 110 °C. After cooling to room temperature, the mixture was washed with saturated NH_4PF_6 (aq, 3 × 10 mL) and water (3 × 10 mL), respectively. The organic layer was separated, and the solvent was removed under reduced pressure. The purification of the product was performed by silica gel chromatography (CH_2Cl_2:CH_3OH = 20:1, v/v) on silica gel to afford [7]rotaxane **9** (60 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.43 (d, J = 8Hz, 12H), 8.09 (s, 6H), 7.80 (d, J = 8Hz, 12H), 7.68 (s, 12H), 7.52-7.57

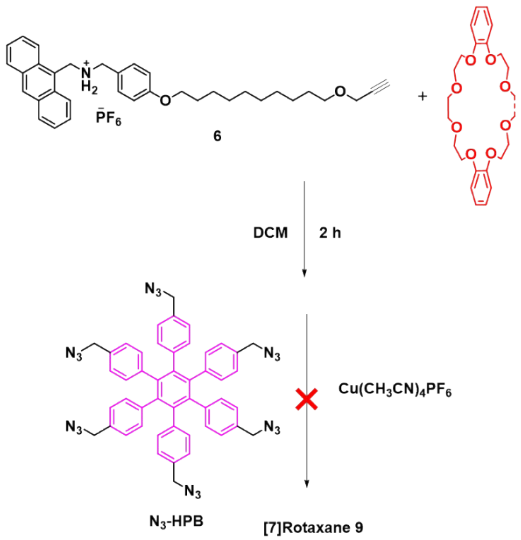
(m, 12H), 7.42-7.45 (m, 12H), 7.37 (d, J = 8Hz, 12H), 7.35 (s, 6H), 6.84 (d, J = 8Hz, 12H), 6.69 (s, 24H), 6.64-6.67 (m, 24H), 6.31-6.33 (m, 24H), 5.46-5.49 (m, 12H), 5.26 (s, 12H), 5.17-5.21 (m, 12H), 4.55 (s, 12H), 3.78-3.92 (m, 72H), 3.67-3.70 (m, 24H), 3.58-3.62 (m, 24H), 3.39-3.49 (m, 48H), 1.24-1.26 (m, 96H). ^{13}C NMR (100 MHz, CD_3CN): δ =171.6, 159.9, 150.2, 147.5, 141.1, 134.5, 132.6, 131.6, 130.3, 129.7, 128.0, 127.4, 125.9, 121.9, 115.2, 112.7, 79.3, 79.0, 78.9, 78.6, 71.8, 71.2, 68.7, 64.5, 60.9, 55.3, 53.2, 46.0, 32.3, 30.2, 26.9, 26.7, 21.1, 14.5. HRMS (ESI): m/z calcd for $C_{402}H_{480}F_6N_{24}O_{60}P^{5+}$: 1350.4999; found:1350.4994 $[M-5PF_6]^{5+}$.

Synthesis of compound 10. A mixture of compound **8** (200mg, 0.12mmol) and $Co_2(CO)_8$ (4mg, 0.012mmol)was dissolved in freshly distilled 1,4-dioxane (15 ml) under nitrogen atmosphere. The reaction mixture was stirred at room temperature overnight and then refluxed for 1 day at 110 °C. After cooling to room temperature, the mixture was washed with saturated NH_4PF_6 (aq, 3 × 10 mL) and water (3 × 10 mL), respectively. The organic layer was separated, and the solvent was removed under reduced pressure. The purification of the product was performed by silica gel chromatography (CH_2Cl_2:CH_3OH = 25:1, v/v) on silica gel to afford [7]rotaxane **9** (40 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.37 (s, 6H), 8.19 (d, J = 8Hz, 12H), 7.97 (d, J = 8Hz, 12H), 7.41-7.49 (m, 24H), 7.31 (d, J = 8Hz, 12H), 7.30 (s, 6H), 6.88 (d, J = 8Hz, 12H), 6.69 (s, 24H), 5.25 (s, 12H), 4.66 (s, 12H), 4.56 (s, 12H), 3.94 (m, 24H), 3.51 (m, 12H), 1.38-1.72 (m, 96H). ^{13}C NMR (150 MHz, $CDCl_3$): δ =183.3, 145.6, 140.4, 139.9, 134.3, 133.6, 132.1, 131.8, 131.6, 130.5, 130.0, 129.3, 127.4, 126.7, 125.1, 124.2, 122.6, 114.9, 114.6, 71.2, 68.5, 68.2, 64.3, 58.6, 53.6, 51.0, 36.0, 32.0, 29.7, 29.4, 27.3, 26.2, 26.0, 25.6, 22.8, 18.6, 14.3. HRMS (ESI): m/z calcd for $C_{258}H_{288}N_{24}O_{12}^{6+}$: 652.7116; found:652.7104 $[M-6PF_6]^{6+}$.



Scheme S5. Synthetic route of N_3-HPB

Synthesis of N_3-HPB. A mixture of compound 3 (500mg, 0.2mmol) and $Co_2(CO)_8$ (7mg, 0.02mmol)was dissolved in freshly distilled 1,4-dioxane (15 ml) under nitrogen atmosphere. The reaction mixture was stirred at room temperature overnight and then refluxed for 1 day at 110 °C. After cooling to room temperature, the mixture was washed with saturated NH_4PF_6 (aq, 3 × 10 mL) and water (3 × 10 mL), respectively. The organic layer was separated, and the solvent was removed under reduced pressure. The purification of the product was performed by silica gel chromatography (CH_2Cl_2:CH_3OH = 200:1, v/v) on silica gel to afford N_3-HPB (400 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 6.80-6.84 (m, 24H), 4.05 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): δ =140.4, 140.1, 132.2, 131.8, 127.3, 54.3. HRMS (ESI): m/z calcd for $C_{48}H_{36}N_{18}Na^+$: 887.3263; found:887.3275.



Scheme S6. Conventional synthetic route of [7]rotaxane **9**

Conventional synthetic route of [7]rotaxane 9. Compound **6** (500 mg, 0.76 mmol) and DB24C8 **1** (408 mg, 0.91 mmol) were dispersed in dry CH_2Cl_2 (8 ml). The mixture was stirred for 2 hours at room temperature to form pseudorotaxane. Then, $[Cu(CH_3CN)_4]PF_6$ (283 mg, 0.76 mmol) and N_3-HPB (104 mg, 0.12 mmol) were added to the mixture under nitrogen atmosphere. After being stirred for 2 days, the mixture was washed with saturated NH_4PF_6 (aq, 3 × 10 mL) and water (3 × 10 mL), respectively. The organic layer was separated, and the solvent was removed under reduced pressure. [7]rotaxane **9** has not been detected with HRMS (ESI).

3. 2D NMR characterization

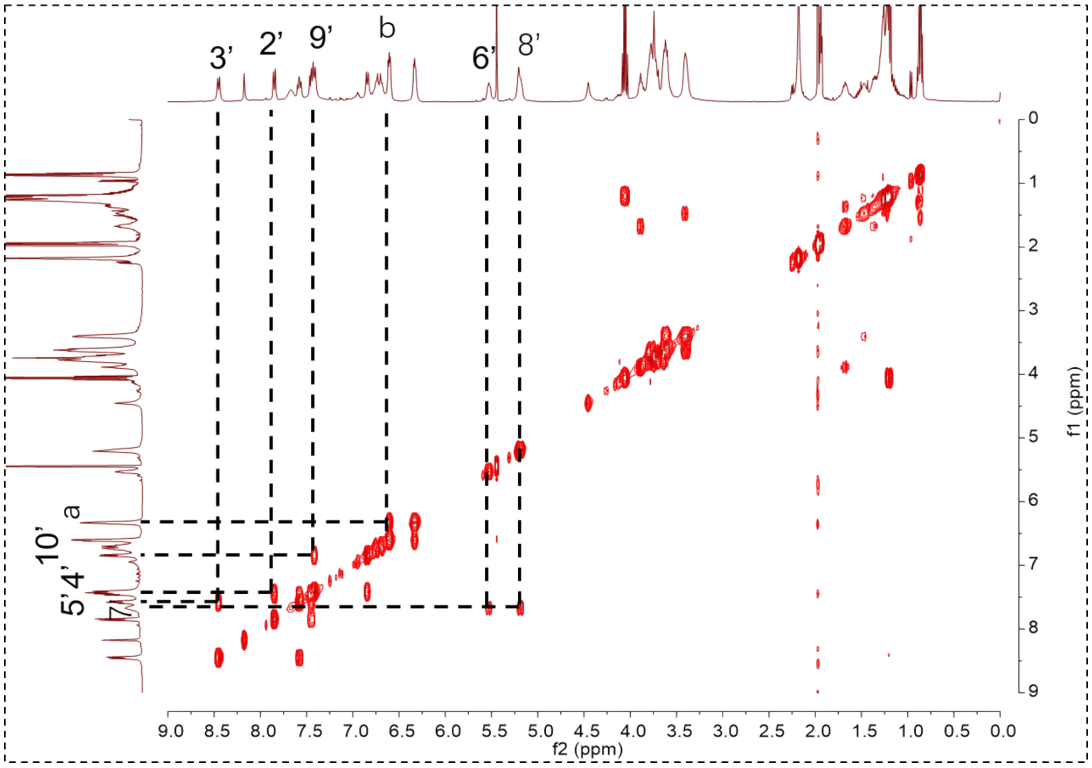
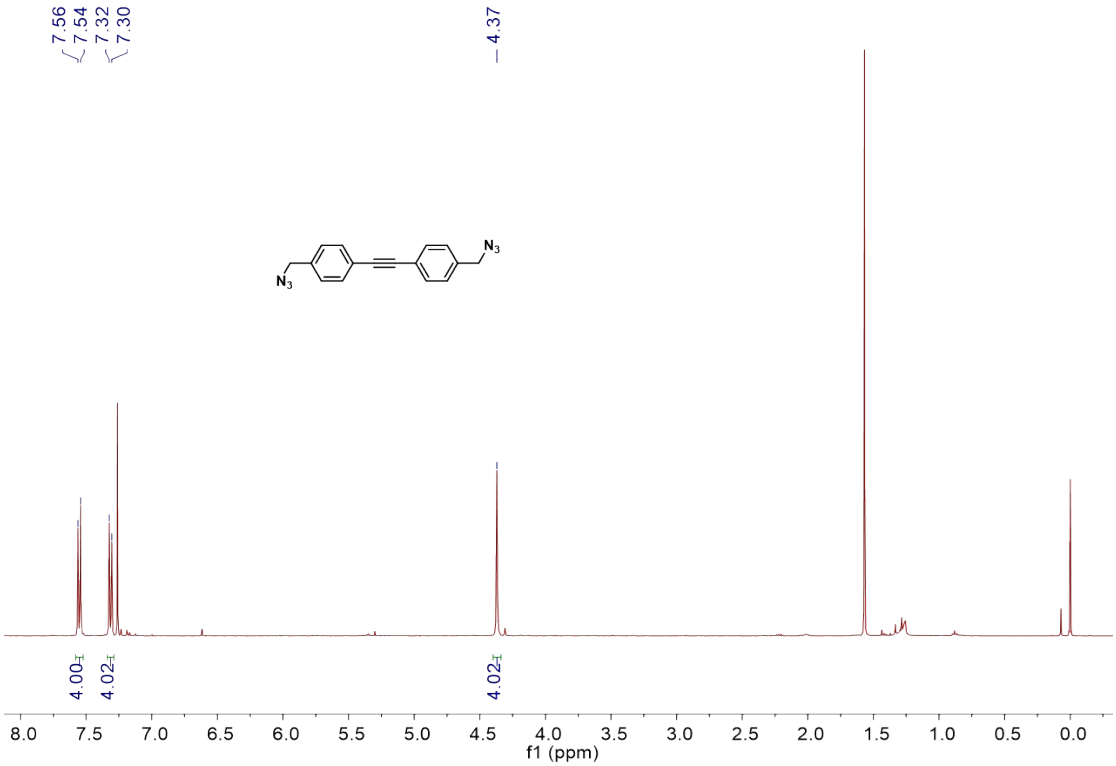
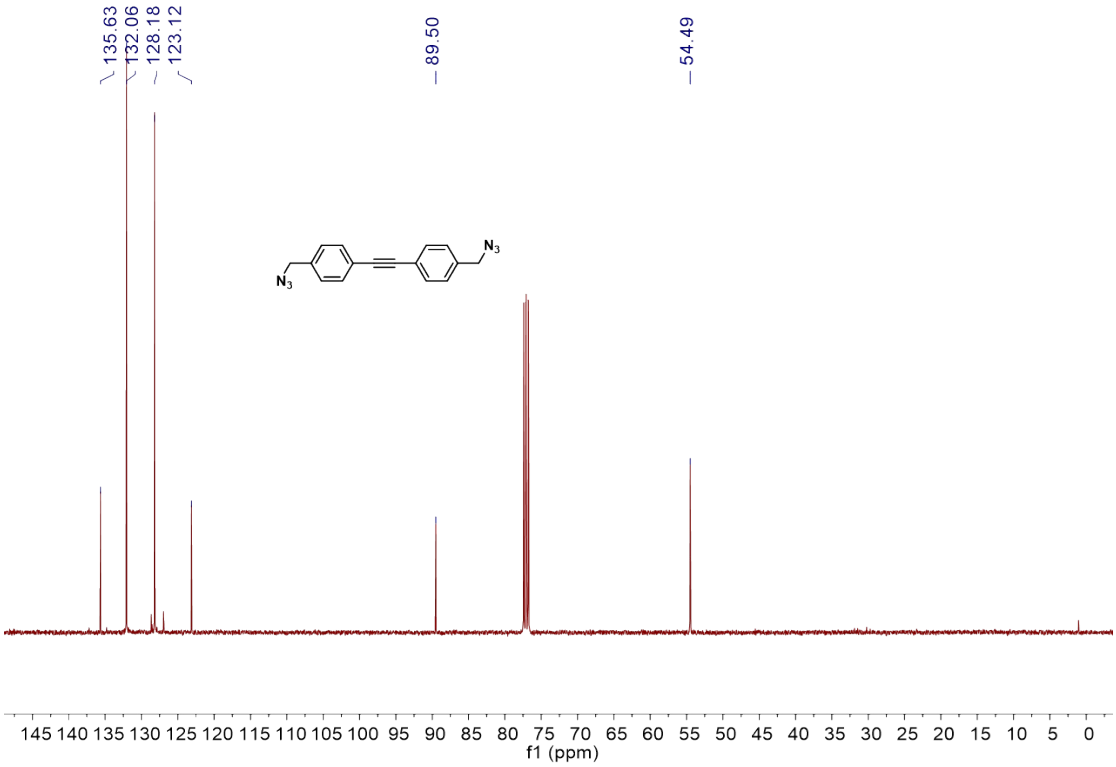


Figure S1. ^{1}H-^{1}H COSY spectrum (CD_3CN, 400 MHz, 298 K) of [7]rotaxane **9**.

4. Additional Spectra



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



^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298K) of **3**

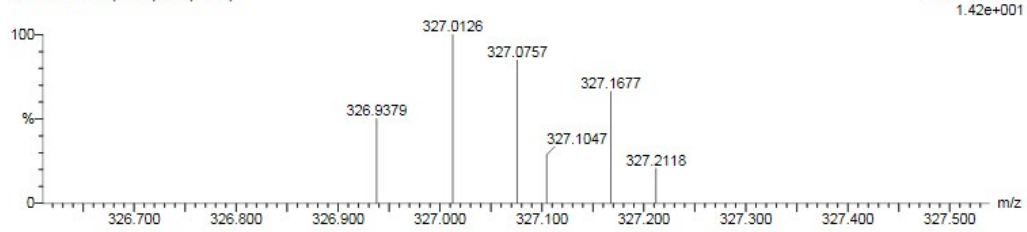
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-16 H: 0-12 N: 0-6 K: 0-1

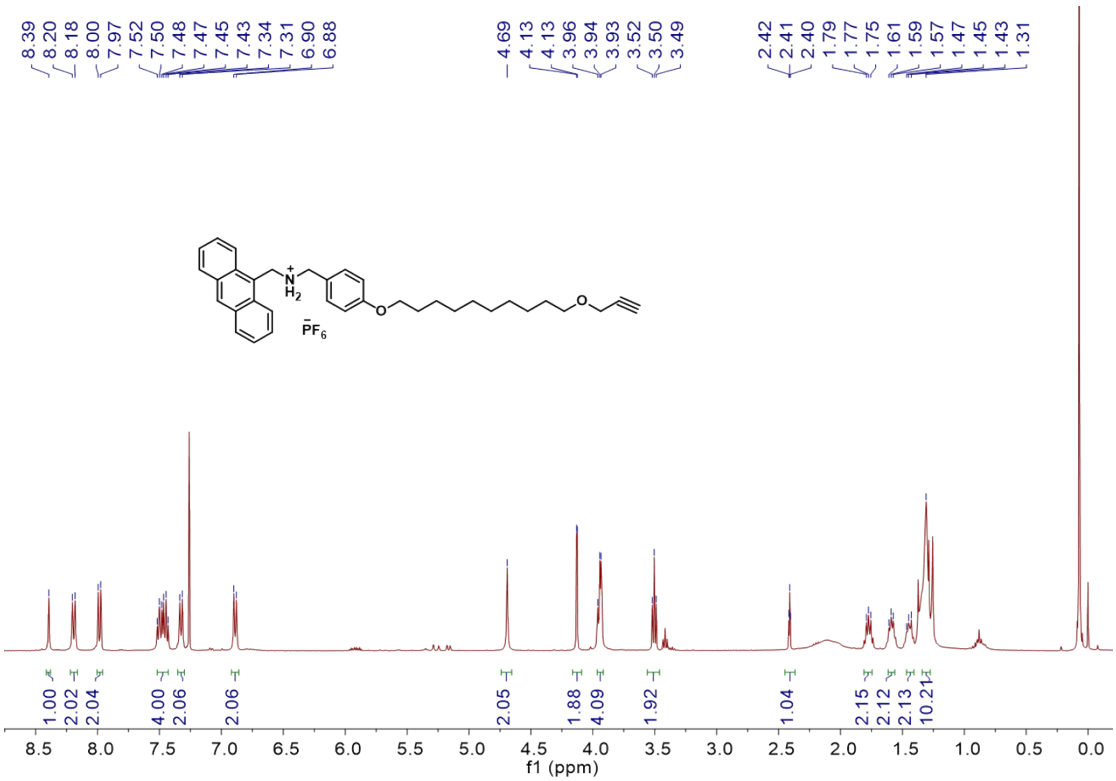
DH-QU
QD-MM-375 80 (0.904) Cm (78:81)

1: TOF MS ES+
1.42e+001

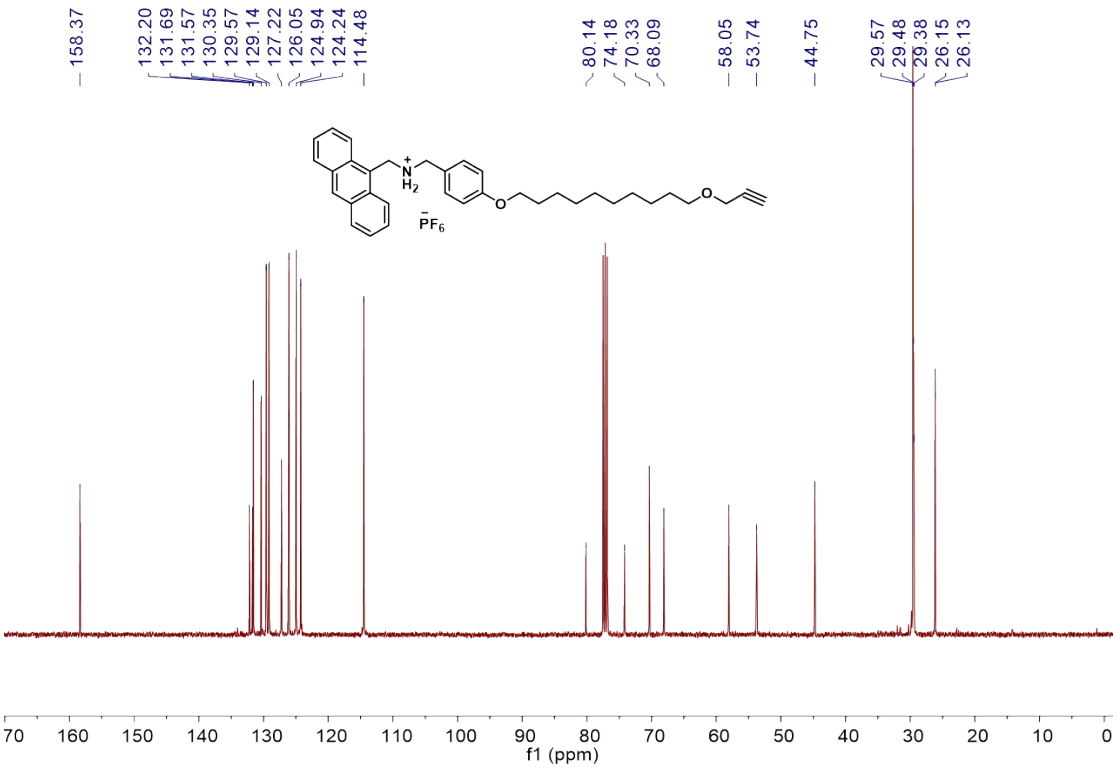


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
327.0757	327.0761	-0.4	-1.2	13.5	22.2	0.0	C16 H12 N6 K

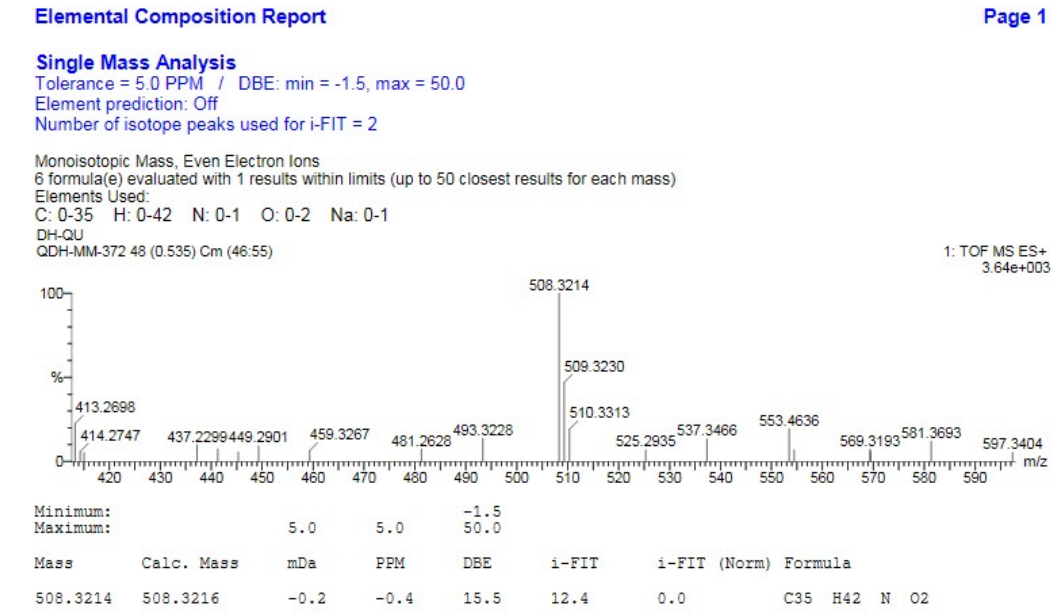
HRMS (ESI): m/z calcd for $C_{16}H_{12}KN_6^+$: 327.0755; found: 327.0757 $[M+K]^+$.



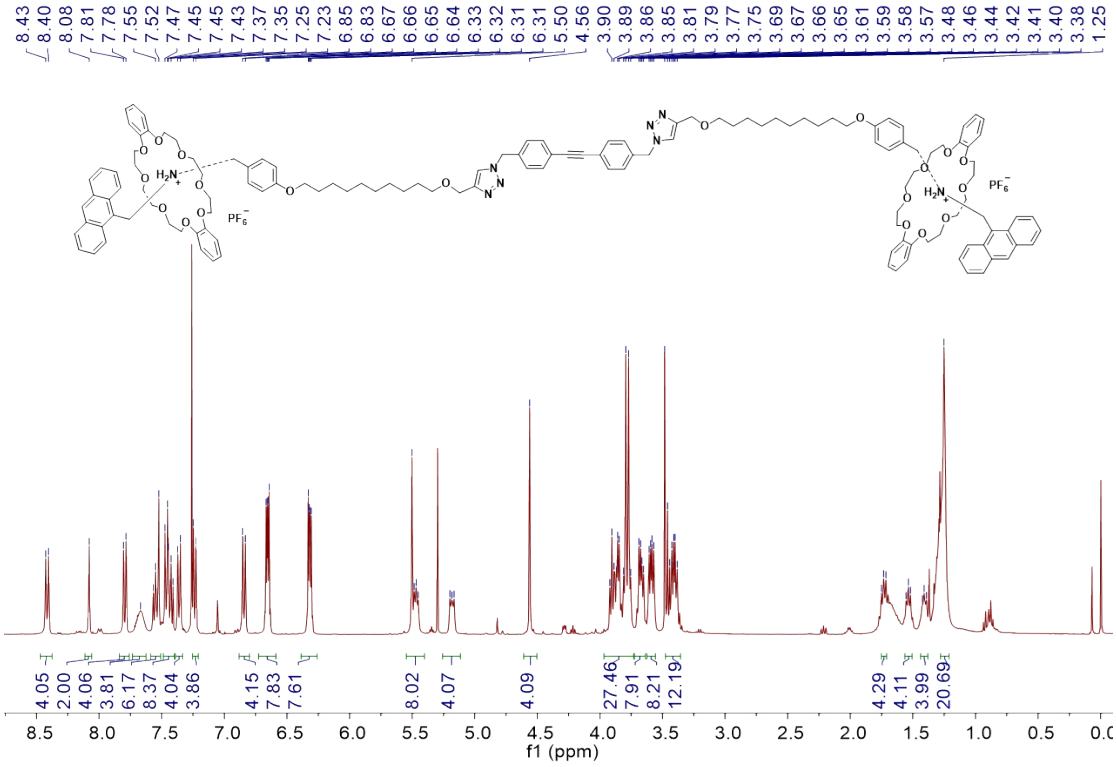
^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of **6**.



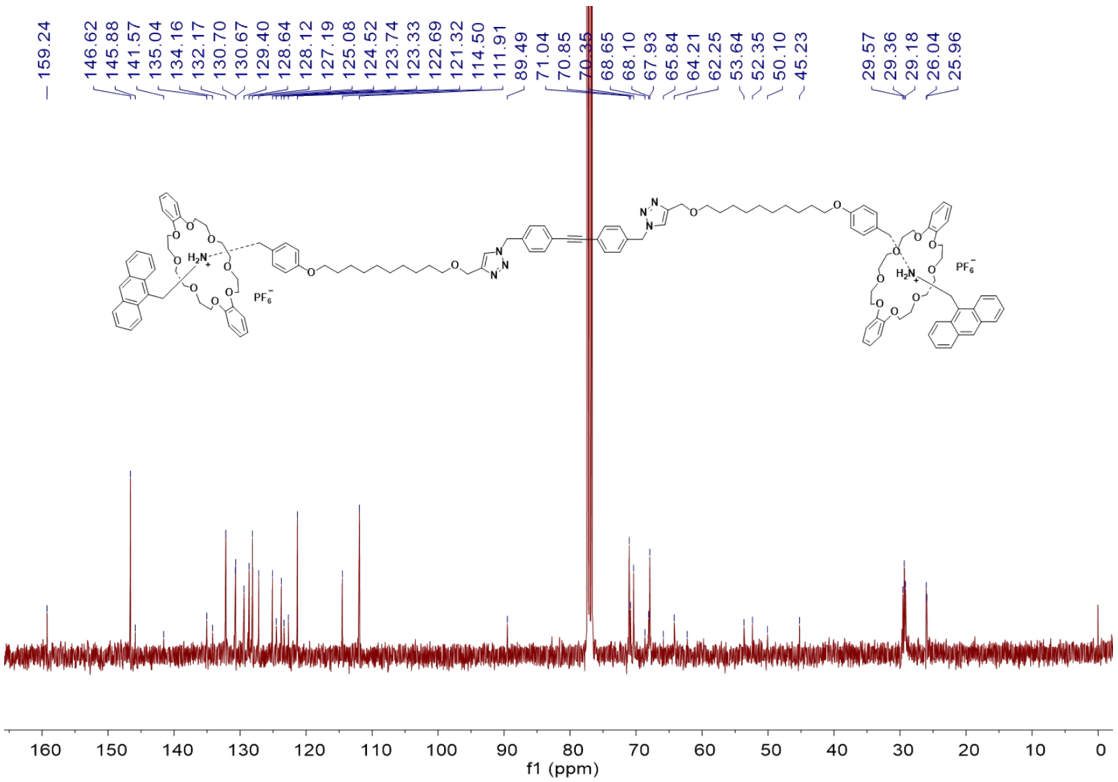
^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298K) of **6**



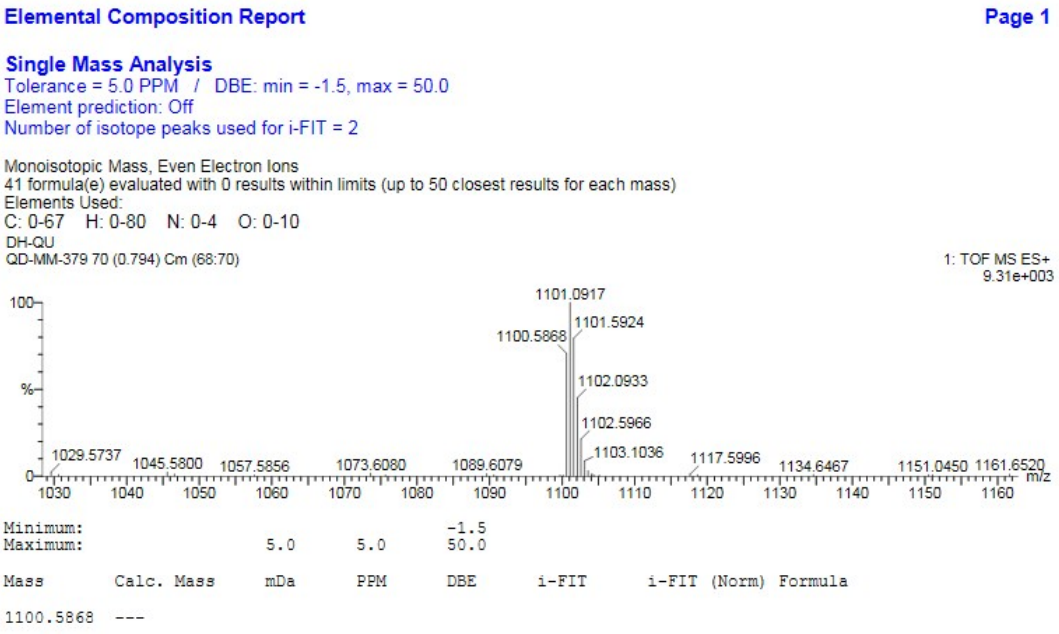
HRMS (ESI): m/z calcd for $C_{35}H_{42}NO_2^+$: 508.3210; found: 508.3214 $[M\text{-}PF_6]^+$.



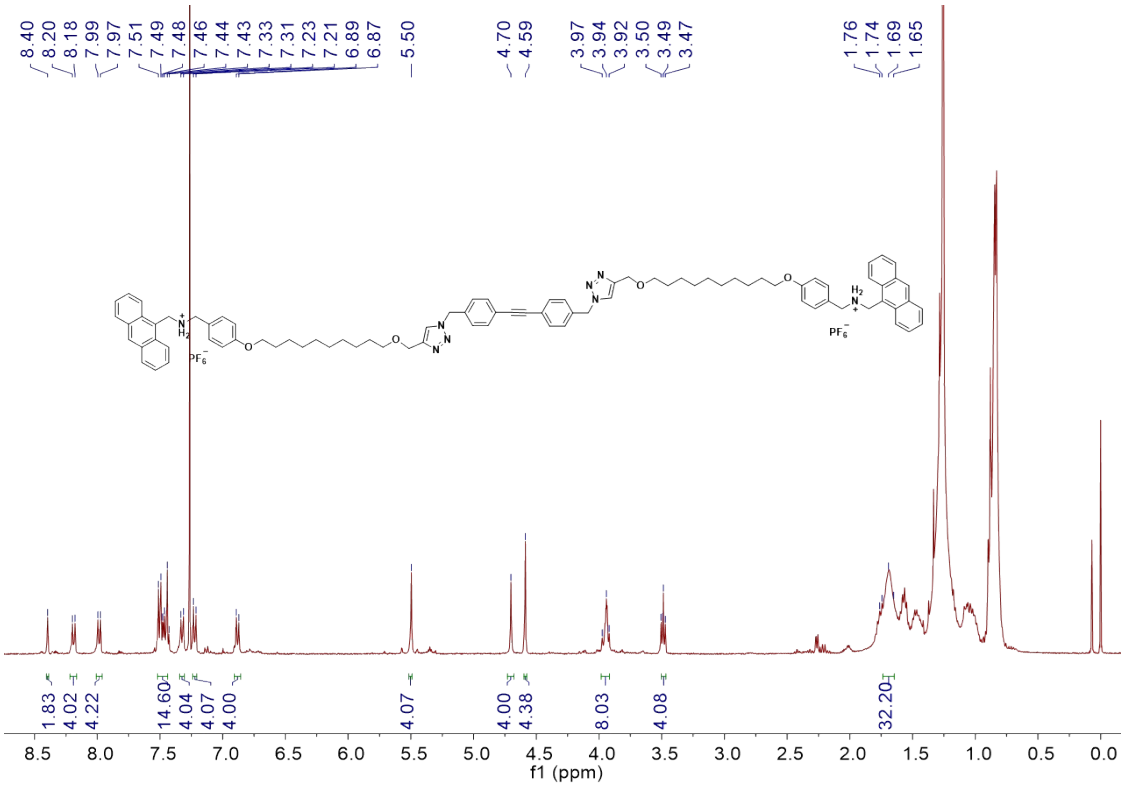
^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of [3]rotaxane **7**.



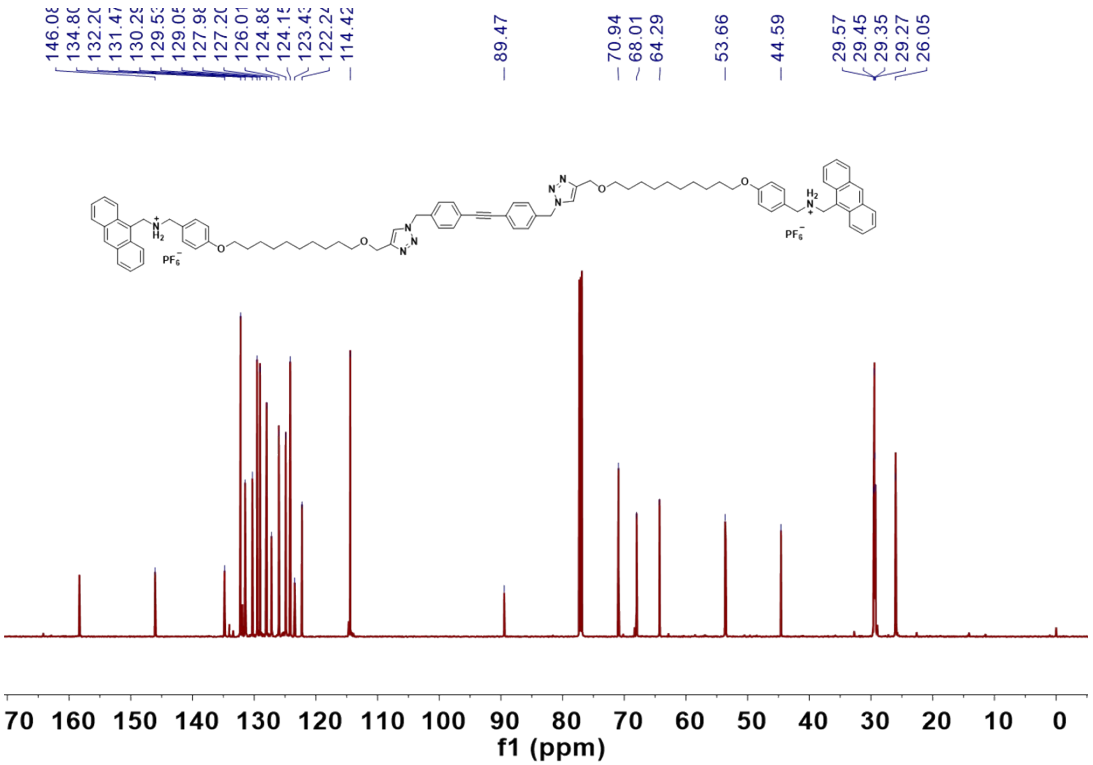
^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298K) of [3]rotaxane **7**.



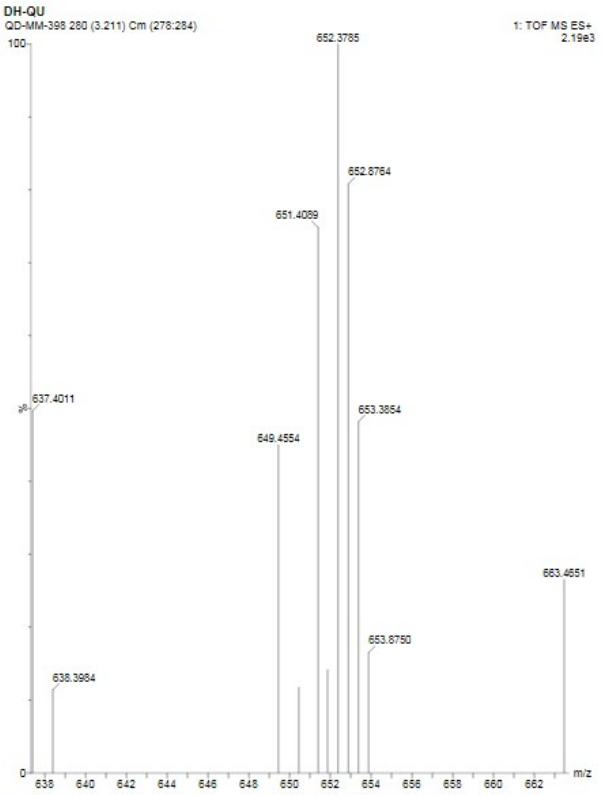
HRMS (ESI): m/z calcd for $C_{134}H_{160}N_8O_{20}^{2+}$: 1101.0886; found: 1101.0917 $[M-2PF_6]^{2+}$.



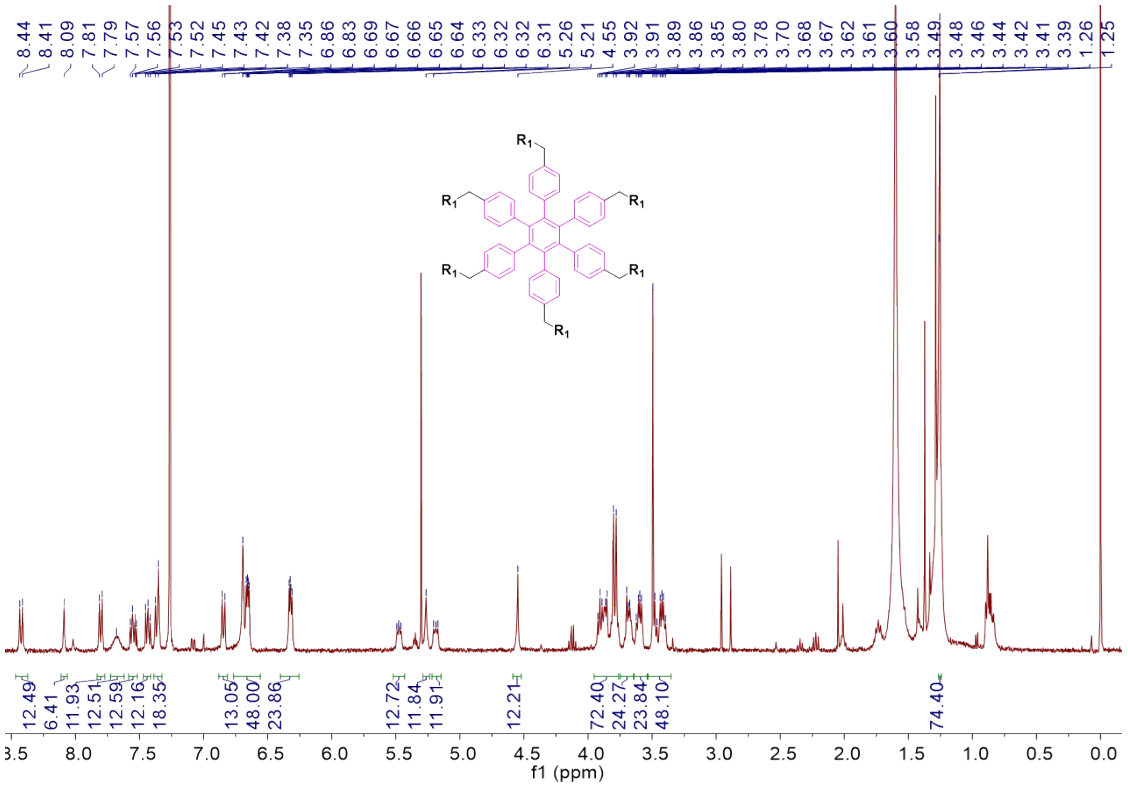
^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of **8**.



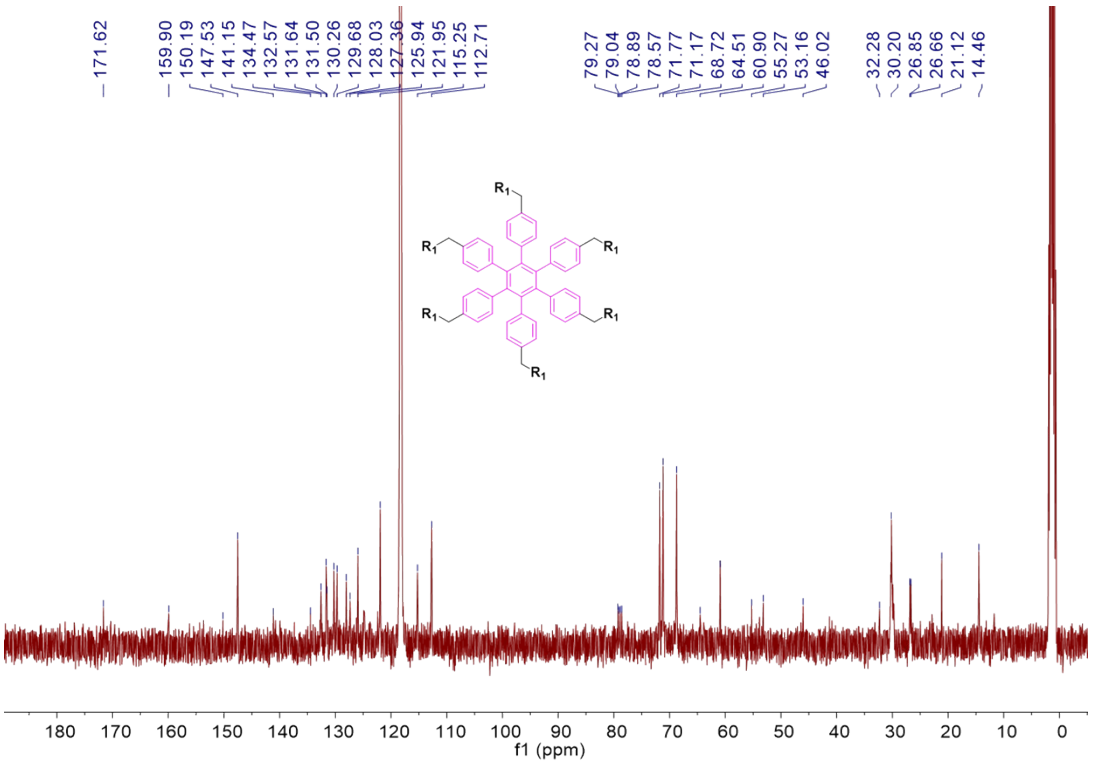
^{13}C NMR spectrum ($CDCl_3$, 150 MHz, 298K) of **8**.



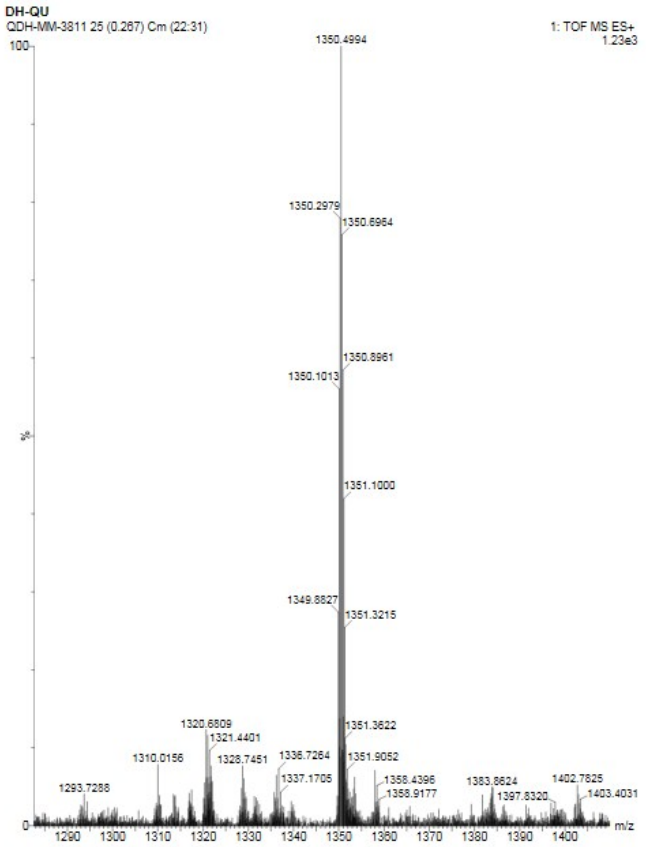
HRMS (ESI): m/z calcd for $C_{86}H_{96}N_8O_4^{2+}$: 652.3772; found: 652.3785 $[M\text{-}2PF_6]^{2+}$.



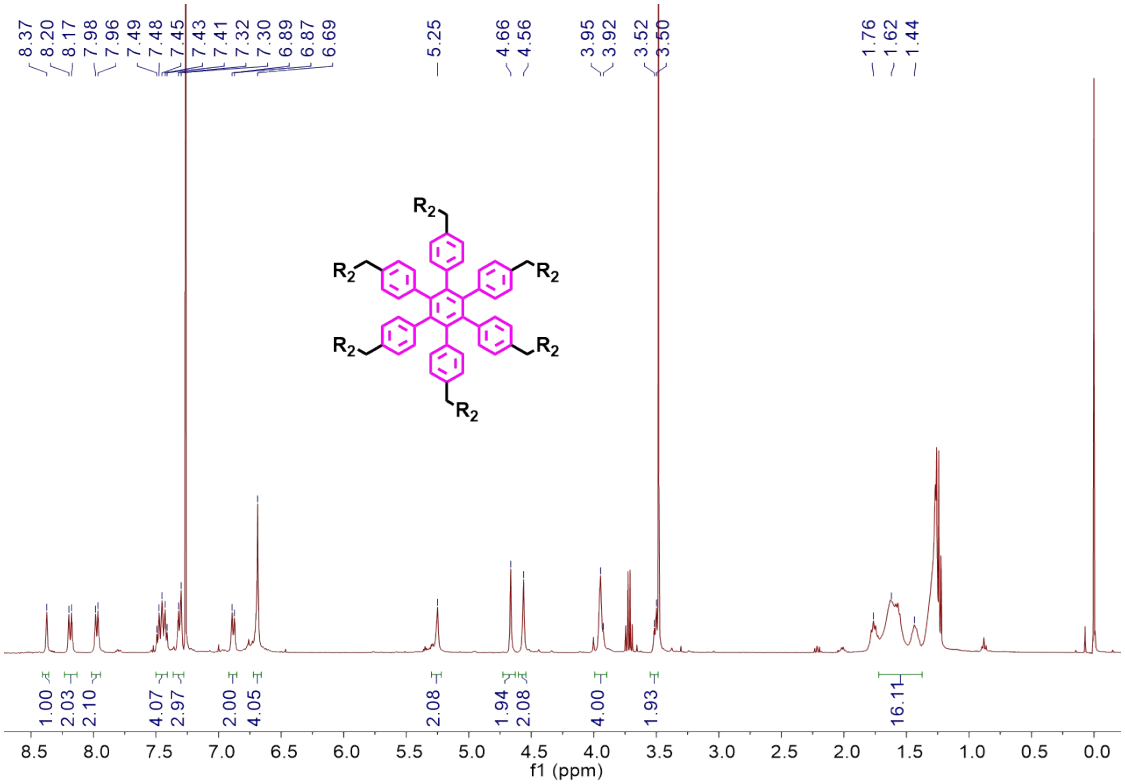
^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of [7]rotaxane **9**.



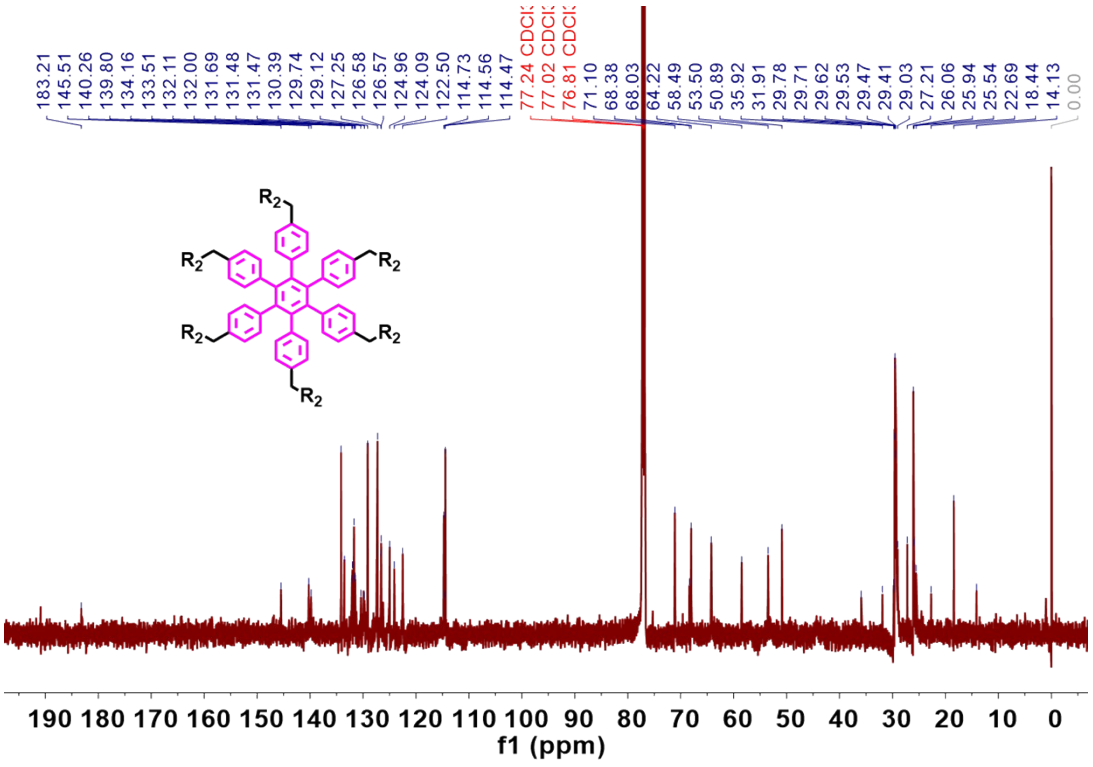
^{13}C NMR spectrum (CD_3CN, 100 MHz, 298K) of [7]rotaxane **9**.



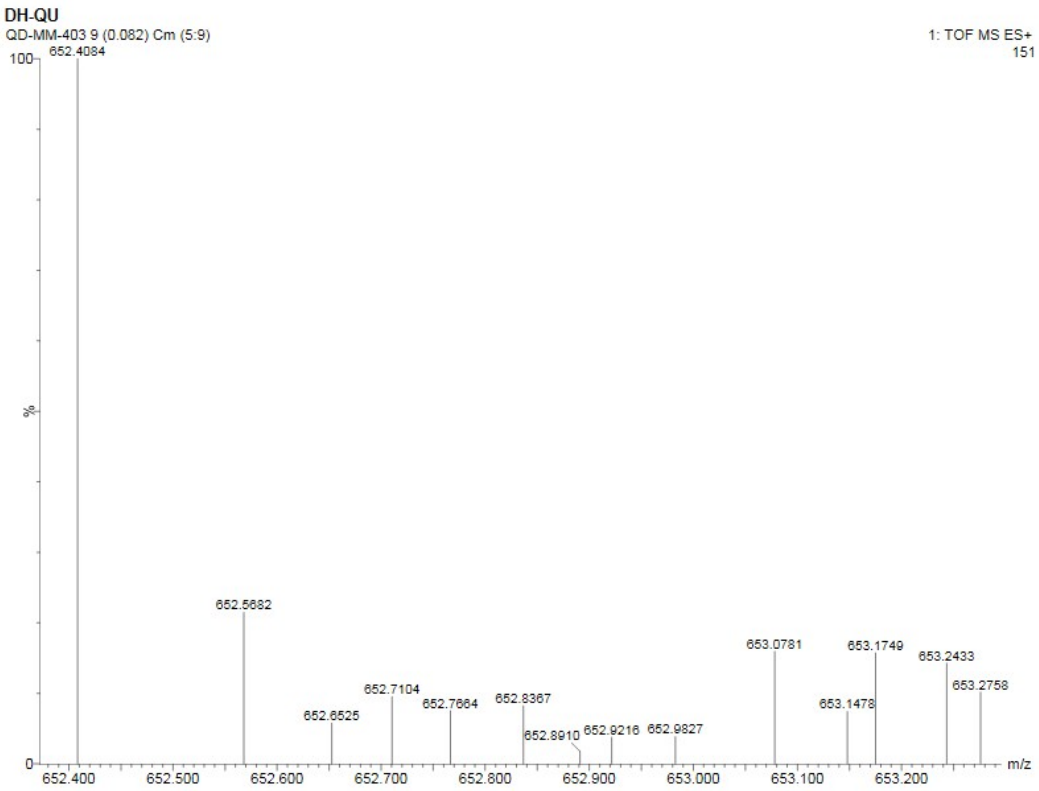
HRMS (ESI): m/z calcd for $C_{402}H_{480}F_6N_{24}O_{60}P^{5+}$: 1350.4999; found:1350.4994 $[M\text{-}5PF_6]^{5+}$.



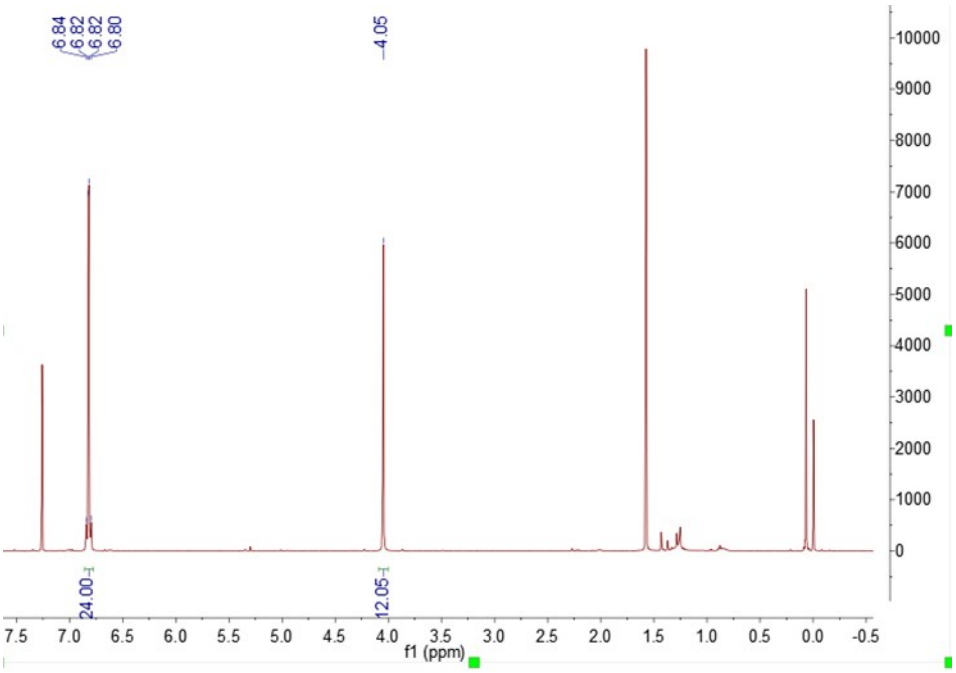
^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of **10**.



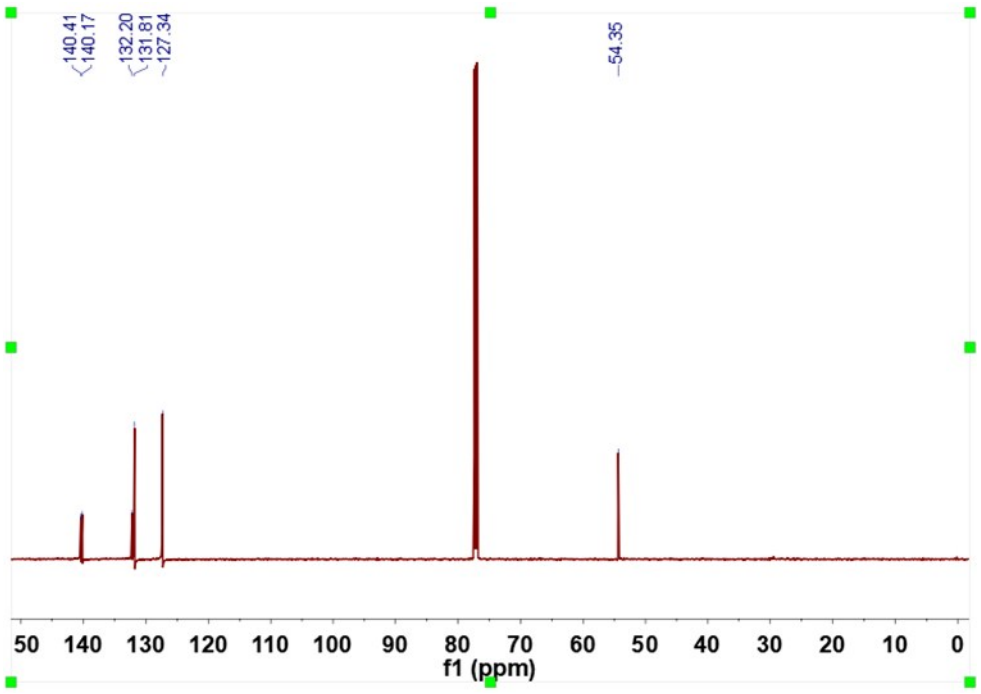
^{13}C NMR spectrum ($CDCl_3$, 150 MHz, 298K) of **10**.



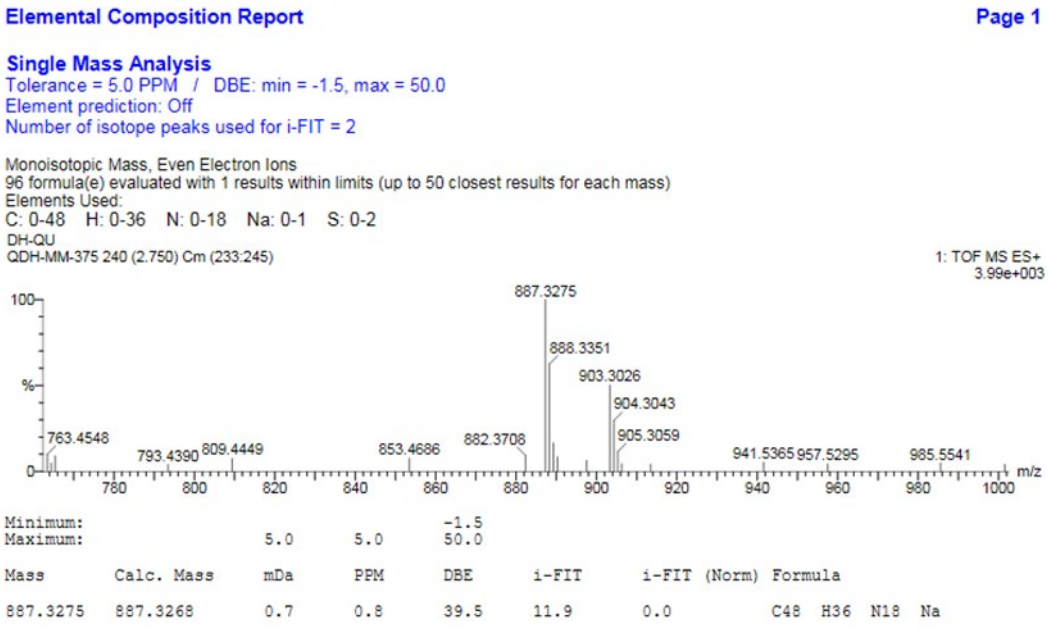
HRMS (ESI): m/z calcd for $C_{258}H_{288}N_{24}O_{12}^{6+}$: 652.7116; found:652.7104 $[M-6PF_6]^{6+}$.



^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of N_3-HPB.



^{13}C NMR spectrum ($CDCl_3$, 150 MHz, 298K) of N_3-HPB.



HRMS (ESI): m/z calcd for $C_{48}H_{36}N_{18}Na^+$: 887.3263; found:887.3275.

5. References

[S1] A. Adam, G. Haberhauer, *Chem. Eur. J.* 2017, **23**, 12190-12197.

[S2] Y. Jiang, J. B. Guo, C. F. Chen, *Org. Lett.* 2010, **12**, 4248-4251.