Electronic Supplementary Information

A molecular pulley based on a triply interlocked [2]rotaxane

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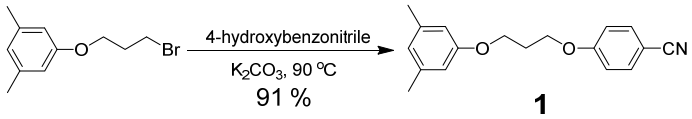
Contents

1. Materials and methods

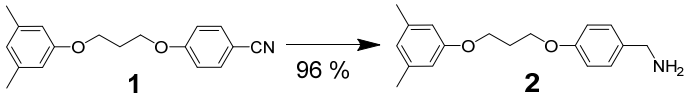
All reagents, unless otherwise indicated, were obtained from commercial sources. Anhydrous solvents (CH_2Cl_2, CH_3OH, DMF, CH_3CN) were obtained by 4 Å molecular sieves activated under 500 °C for 6 hours. Melting points were determined using a Focus X-4 apparatus, and were not corrected. Analytical thin-layer chromatography (TLC) was performed on Merck silicagel 60 F254 plates. 1-(3-Bromopropoxy)-3,5-dimethylbenzene,[1] 4-(2-azidoethoxy)benzaldehyde,[2] (4-(prop-2-yn-1-yloxy)phenyl)methanamine,[3] 4-(2-bromoethoxy)benzaldehyde[4] were synthesized according to the literature procedures. All yields were given as isolated yields. 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-ROESY, 2D-COSY, and HSQC 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.

2. Synthesis of new compounds



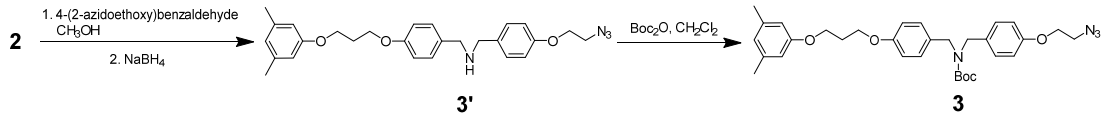
Scheme S1. Synthesis of **1**.

Synthesis of 1. 1-(3-Bromopropoxy)-3,5-dimethylbenzene (5.40 g, 22.2 mmol) and 4-hydroxy-benzonitrile (3.71 g, 31.3 mmol) were dissolved in 60 mL of dry acetonitrile. To this solution, 4.3 g (31.3 mmol) of anhydrous potassium carbonate was added. The mixture was stirred at 90 ^{o}C for twelve hours, then cooled to room temperature and filtrated. The filtered cake was washed with 100 mL of CH_2Cl_2. The filtrate was collected and concentrated, and redissolve in 200 mL of CH_2Cl_2. The obtained solution was successively washed with sodium hydroxide solution (5 M, 100 mL× 3) and water (100 mL× 3). The organic phrase was separated and dried by anhydrous $MgSO_4$, and concentrated in vacuum to give compound **1** as white solid (5.68 g, 91%) without further purification. M.p.: 70–71 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 6.59 (s, 1H), 6.53 (s, 2H), 4.19 (t, J = 6.2 Hz, 2H), 4.11 (t, J = 5.9 Hz, 2H), 2.32–2.18 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ =162.2, 158.8, 139.3, 134.0, 122.7, 119.3, 115.2, 112.2, 104.0, 64.9, 63.8, 29.2, 21.5; HRMS (APCI): m/z =282.1488 $[M+H]^+$ (calcd. 282.1494 for $C_{18}H_{20}O_2N$).



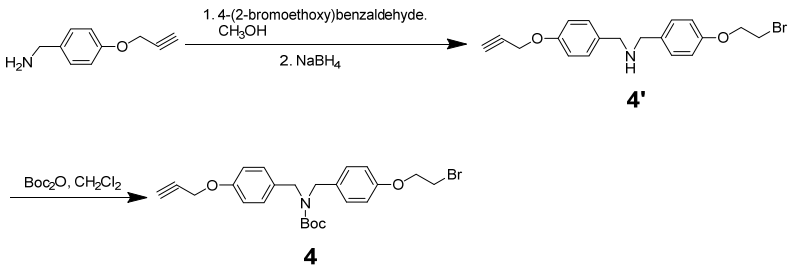
Scheme S2. Synthesis of **2**.

Synthesis of 2. To a solution of **1** (5 g, 18 mmol) in dry THF (150 mL) was added $LiAlH_4$ (2.4 g, 63 mmol) in parts with 3 minutes. After being stirred in room temperature for 6 h, the reaction mixture was quenched with water cautiously, and then extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated off, and the residue was purified by flash chromatography over silica gel (eluent: CH_2Cl_2 :CH_3OH= 15:1) to afford **2** (4.9 g) in 96 % yield as an off-white solid. M.p.: 47–48°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 6.58 (s, 1H), 6.54 (s, 2H), 4.11 (td, J = 6.1, 3.4 Hz, 4H), 3.77 (s, 2H), 2.26 (s, 6H), 2.25-2.15 (m, 6H), 1.52 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 157.9, 139.2, 135.7, 128.3, 122.5, 114.6, 112.3, 68.0, 64.6, 64.3, 46.0, 29.5, 25.7, 21.5; HRMS (ESI): *m/z* =286.1801 $[M+H]^+$ (calcd. 286.1807 for $C_{18}H_{24}O_2N$).



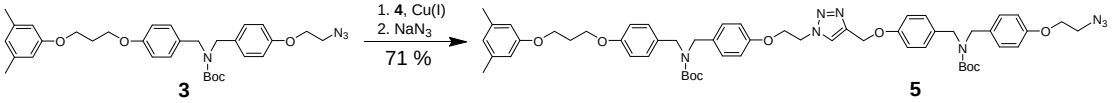
Scheme S3. Synthesis of **3**.

Synthesis of 3. A solution of **2** (4.0 g, 14.1 mmol) and 4-(2-azidoethoxy)benzaldehyde (2.7 g, 14.1 mmol) in 100 mL of CH_3OH was stirred at room temperature for 4 h, and then was added 2.7 g (70 mmol) of $NaBH_4$ in small portions. After the reaction mixture was stirred for 3 h, water was slowly added to quench the reaction, and the mixture was partitioned between water and CH_2Cl_2 (300 mL). The organic extract was washed with water (100 mL×3), and then dried over anhydrous magnesium sulfate. The removal of the solvent afforded **3′** as a slight yellow oil, which could be solidified upon standing. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25 (d, J = 6.9 Hz, 2H), 7.22 (d, J = 7.1 Hz, 2H), 6.88 (d, J = 2.5 Hz, 2H), 6.85 (d, J = 2.5 Hz, 2H), 6.58 (s, 1H), 6.54 (s, 2H), 4.17–4.09 (m, 6H), 3.71 (s, 4H), 3.57 (t, J = 5.0 Hz, 2H), 2.27 (s, 6H), 2.27–2.17 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 158.0, 157.3, 139.2, 133.3, 132.5, 129.4, 129.3, 128.6, 122.5, 114.7, 114.5, 114.4, 112.51, 112.3, 67.0, 64.6, 64.3, 52.5, 52.4, 50.2, 29.4, 21.5. Compound **3′** was then dissolved in CH_2Cl_2 (150 mL), and was added 2.4 g of Boc_2O. After the solution was stirred at room temperature for 12 h, the mixture was evaporated in vacuum, and the residues were purified by silica gel chromatography (petroleum ether to petroleum ether : CH_2Cl_2= 1: 2) to give compound **3** as colorless sticky oil (7.1 g) in a total yield of 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12 (br, 4H), 6.88 (d, J = 2.1 Hz, 2H), 6.85 (d, J = 2.1 Hz, 2H), 6.58 (s, 1H), 6.54 (s, 2H), 4.31 (br, 2H), 4.25 (br, 2H), 4.18–4.08 (m, 6H), 3.56 (t, J = 5.0 Hz, 2H), 2.27 (s, 6H), 2.26–2.17 (m, 2H), 1.50 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 158.2, 157.5, 156.0, 139.2, 131.0, 130.1, 129.4, 128.9, 122.5, 114.9, 114.7, 114.6, 112.3, 80.0, 67.1, 64.6, 64.2, 53.5, 50.2, 29.4, 28.5, 21.5; HRMS (ESI): *m/z* =583.2890 $[M+Na]^+$ (calcd. 583.2896 for $C_{30}H_{40}O_5N_4Na$).



Scheme S4. Synthesis of **4**.

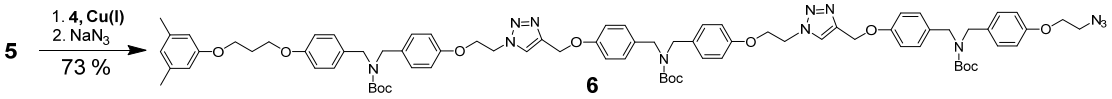
Synthesis of 4. The synthesis of **4** follows the similar procedure as that of compound **3**. A solution of (4-(prop-2-yn-1-yloxy)phenyl)methanamine (3.0 g, 18.78 mmol) and 4-(2-bromoethoxy)-benzaldehyde (4.3 g, 18.78 mmol) in 100 mL of CH_3OH was stirred at room temperature for 4 h. Then, 2.7 g (5.0 equiv.) of $NaBH_4$ was added to reduce the Schiff base. After being stirred for 3 h, water was added to quench the reaction, and the mixture was partitioned between water and CH_2Cl_2 (300 mL). The organic extract was washed with water (100 mL×3), and then dried. The removal of the solvent gave **4'** as a slight yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 4.64 (d, J = 2.4 Hz, 2H), 4.23 (t, J = 6.2 Hz, 2H), 3.69 (s, 4H), 3.59 (t, J = 6.3 Hz, 2H), 2.51 (t, J = 2.4 Hz, 1H), 1.93 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.2, 156.7, 133.0, 132.9, 129.6, 129.5, 114.9, 114.7, 78.7, 75.6, 68.0, 55.9, 52.3, 29.3. After compound **4′** reacted with Boc_2O in CH_2Cl_2 at room temperature for 12 h, the mixture was evaporated in vacuum, and the residues were purified by silica gel chromatography (eluent: petroleum ether: CH_2Cl_2 = 1: 2) to give compound **4** as colorless sticky oil (7.7 g, total yield of 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14 (br, 4H), 6.93 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 4.68 (d, J = 2.4 Hz, 2H), 4.41–4.17 (m, 6H), 3.63 (t, J = 6.3 Hz, 2H), 2.53 (t, J = 2.4 Hz, 1H), 1.50 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.3, 156.8, 155.9, 146.7, 131.1, 131.0, 114.9, 114.8, 85.2, 80.0, 78.6, 75.5, 68.0, 55.9, 29.1, 28.5; HRMS (ESI): *m/z* =496.1094 $[M+Na]^+$ (calcd. 496.1099 for $C_{24}H_{28}O_4NBrNa$).



Scheme S5. Synthesis of **5**.

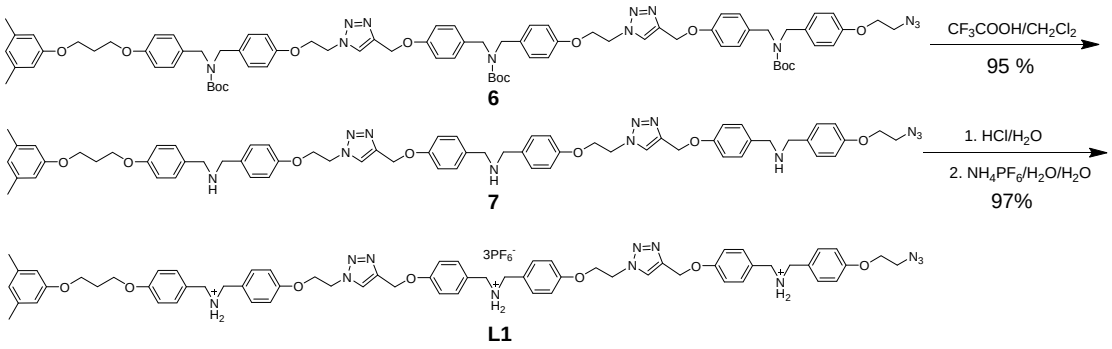
Synthesis of 5. To a solution of **3** (4.22 g, 7.5 mmol) and **4** (3.66 g, 7.5 mmol) in dry and degassed DMF (80 mL) under an Ar atmosphere was added 280 mg (0.75 mmol) of CuI. After the solution was stirred for 24 h at 40 ^{o}C, 1.0 g (15.0 mmol) of NaN_3 was added. And the mixture was then heated to 75 °C for 12 h, cooled to room temperature, and concentrated in vacuo to remove most of the solvent. The residues were subjected to ethyl acetate/H_2O, washed with water (5×50 mL). The organic layer was dried over anhydrous $MgSO_4$, and then concentrated in vacuo to give the crude product, which was further purified by silica-gel column chromatography (CH_2Cl_2→ CH_2Cl_2/CH_3OH = 70:1→CH_2Cl_2/CH_3OH = 30:1) to give **5** as a colorless oily solid (5.3 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (s, 1H), 7.12 (br, 8H), 6.95 (d, J = 8.6 Hz, 2H), 6.92–6.78 (m, 6H), 6.59 (s, 1H), 6.54 (s, 2H), 5.21 (s, 2H), 4.77 (t, J = 5.0 Hz, 2H), 4.36 (t, J = 5.0 Hz, 2H), 4.30 (br, 4H), 4.25 (br, 4H), 4.18–4.08 (m, 6H), 3.59 (t, J = 5.0 Hz, 2H), 2.27 (s, 6H), 2.26–2.19 (m, 2H), 1.49 (s, 9H), 1.49 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 158.2, 157.6, 157.5,

157.1, 155.9, 144.1, 139.1, 131.3, 130.9, 130.1, 129.3, 129.0, 124.1, 122.6, 114.9, 114.7, 114.6, 112.3, 79.9, 79.8, 67.1, 66.4, 64.5, 64.2, 62.0, 53.6, 50.1, 49.7, 48.4, 30.8, 29.4, 28.5, 28.5, 21.5; HRMS (ESI): *m/z* =1019.5000 $[M+Na]^+$ (calcd. 1019.5007 for $C_{56}H_{68}O_9N_8Na$).



Scheme S6. Synthesis of **6**.

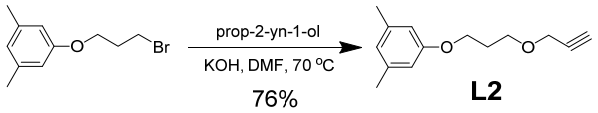
Synthesis of 6. Adopting the modular synthesis strategy in which a Boc-protected amine segment **4** was attached, the synthesis of **6** was simply followed the condition as that of **5**. The resulting crude product was purified by silica-gel column chromatography (CH_2Cl_2/CH_3OH = 60:1→ CH_2Cl_2/CH_3OH = 30:1) to give **6** as white pumiceous solid (3.3 g, 73 %). M.p.: 76–78 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (s, 2H), 7.12 (s, 12H), 6.95 (d, J = 7.6 Hz, 4H), 6.91–6.77 (m, 8H), 6.59 (s, 1H), 6.54 (s, 2H), 5.21 (s, 4H), 4.77 (t, J = 4.7 Hz, 4H), 4.36 (t, J = 4.9 Hz, 4H), 4.31 (br, 6H), 4.25 (br, 6H), 4.19–4.07 (m, 6H), 3.59 (t, J = 5.0 Hz, 2H), 2.27 (s, 6H), 2.26–2.18 (m, 2H), 1.49 (s, 27H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 158.2, 157.6, 157.5, 157.5, 157.0, 157.0, 155.9, 155.9, 139.2, 131.4, 131.3, 130.9, 130.7, 130.7, 130.0, 129.4, 129.0, 122.5, 114.8, 114.6, 114.6, 114.5, 112.3, 80.04, 79.99, 67.0, 66.4, 64.5, 64.2, 62.0, 50.2, 49.9 48.4, 48.2, 29.4, 28.5, 21.5; HRMS (ESI): *m/z* =1455.7103 $[M+Na]^+$ (calcd. 1455.7118 for $C_{80}H_{96}O_{13}N_{12}Na$).



Scheme S7. Synthesis of **L1**.

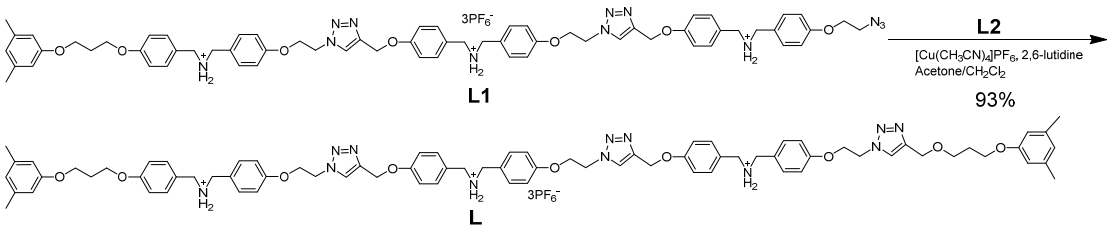
Synthesis of L1. Compound **6** (3.0 g, 2.0 mmol) was dissolved in 30 mL of mixed solvent of CH_2Cl_2/CF_3CO_2H (v/v = 4:1). The reaction mixture was stirred at room temperature for 0.5 h, and then treated with saturated aqueous NaOH solution until a basic pH was reached. The mixture was partion between CH_2Cl_2 and water. The organic layer was collected and evaporated in vacuum to give **7** as white solid in a yield of 95% (2.15 g). M.p.: 107–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (s, 2H), 7.29–7.18 (m, 12H), 6.94 (d, J = 8.3 Hz, 4H), 6.87 (dd, J = 8.6, 3.8 Hz, 4H), 6.80 (d, J = 8.6 Hz, 4H), 6.58 (s, 1H), 6.54 (s, 2H), 5.19 (s, 4H), 4.73 (t, J = 4.9 Hz, 4H), 4.33 (t, J = 4.9 Hz, 4H), 4.18–4.08 (m, 6H), 3.73–3.67 (m, 12H), 3.57 (t, J = 5.0 Hz, 2H), 2.25 (s, 6H), 2.25–2.17 (m, 2H), 1.54 (br, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 157.9, 157.3, 156.8, 144.4, 144.3, 139.2, 133.8, 133.7, 133.3, 133.2, 133.1, 132.5, 129.5, 129.40, 129.37, 129.3, 123.9, 122.5, 114.7, 114.5, 114.5 114.4, 112.3, 67.0, 66.4, 64.5, 64.2, 62.1, 52.5, 52.4, 52.3, 50.2, 49.9, 29.4, 21.5; HRMS (ESI): *m/z* =1133.5718 $[M+H]^+$ (calcd. 1133.5725 for $C_{65}H_{73}O_7N_{12}$). Without further purification, the obtained product was then dissolved in CH_2Cl_2, and added 0.5 mL of

concentrated hydrochloric acid. After being stirred at room temperature for 3 h, the solvent was evaporated to dryness under reduced pressure. The resulting solid was dispersed in acetone (100 mL), and excess saturated aqueous NH_4PF_6 solution was added until a clear solution was obtained. The mixture was stirred at room temperature for 3 h to complete the ion exchange. The acetone was evaporated under reduced pressure to produce a precipitate. It was collected by filtration and wash with deionized water, and then dried to give **L1** as an white solid (2.74 g, 97% yield). M.p.: 117–119 °C; ^{1}H NMR (300 MHz, acetone-d_6): δ = 8.20 (s, 2H), 7.57–7.40 (m, 12H), 7.10–6.93 (m, 12H), 6.53 (s, 3H), 5.54 (br, 6H), 5.13-5.15 (m, 4H), 4.83 (t, J = 4.8 Hz, 4H), 4.54–4.37 (m, 16H), 4.20 (t, J = 6.2 Hz, 2H), 4.16 (t, J = 6.2 Hz, 2H), 4.10 (t, J = 6.2 Hz, 2H), 3.62 (t, J = 5.1 Hz, 2H), 2.19 (s, 6H), 2.18–2.14 (m, 2H); ^{13}C NMR (75 MHz, acetone-d_6): δ = 160.8, 160.3, 160.0, 150.0, 144.4, 140.1, 132.6, 132.5, 132.4, 130.9, 126.9, 126.8, 126.6, 126.2, 125.9, 123.5, 116.3, 116.1, 116.1, 116.0, 113.4, 68.4, 67.8, 65.7, 65.1, 62.6, 52.4, 51.2, 50.6, 21.8; ^{1}H NMR (600 MHz, CD_3CN:$CDCl_3$=1:1): δ = 7.96 (s, 2H), 7.34 (td, J = 8.0, 7.2, 4.5 Hz, 12H), 7.03 (dd, J = 8.7, 2.4 Hz, 4H), 6.99–6.86 (m, 8H), 6.58 (s, 1H), 6.53 (s, 2H), 5.15 (s, 4H), 4.77 (t, J = 4.9 Hz, 3H), 4.40 (t, J = 4.8 Hz, 4H), 4.21–4.02 (m, 18H), 3.72 (br, 6H), 3.64–3.59 (m, 2H), 2.25 (s, 6H), 2.23–2.17 (m, 2H); ^{13}C NMR (150 MHz, CD_3CN:$CDCl_3$=1:1): δ =160.0, 159.4, 159.4, 159.4, 159.1, 159.0, 143.2, 139.2, 131.8, 131.8, 131.7, 124.8, 123.5, 123.3, 123.1, 123.1, 123.0, 122.5, 122.4, 115.3, 115.1, 115.0, 112.3, 67.3, 66.5, 64.7, 64.1, 61.6, 51.0, 50.9, 50.8, 50.1, 49.7, 30.5, 29.2, 21.0; HRMS (ESI): m/z =1425.5143 $[M\text{-}PF_6]^+$ (calcd. 1425.5160 for $C_{65}H_{75}F_{12}N_{12}O_7P_2$).



Scheme S8. Synthesis of **L2**.

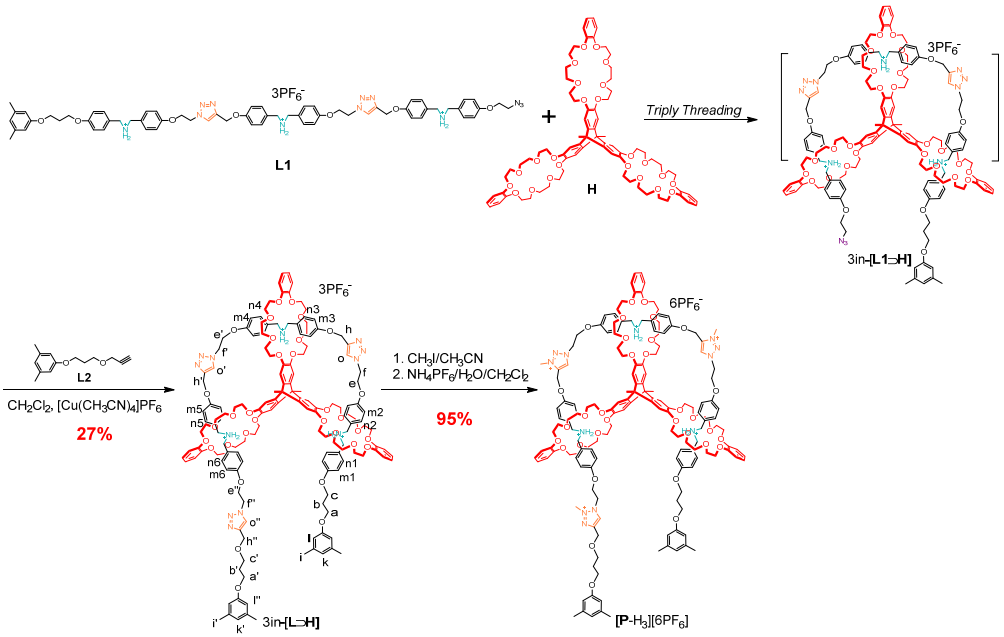
Synthesis of L2. 1-(3-Bromopropoxy)-3,5-dimethylbenzene (1.5 g, 6.2 mmol) and prop-2-yn-1-ol (0.9 mL, 30 mmol) were dissolved in 30 mL of dry DMF. Then, KOH (1.68 g, 30 mmol) was added, and the temperature was gradually raised to 70 ^{o}C. After being stirred for 8 h, the mixture was subjected to H_2O/ethyl acetate. The organic layer was washed with water for 5 times, and further concentrated in vacuum to give the crude product as yellow oil. After purification by flash silica gel chromatography (eluent: petroleum ether: CH_2Cl_2 = 1: 1), product **L2** (1.0 g, 76%) as light yellow oil was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.55 (s, 1H), 6.51 (s, 2H), 4.10 (d, J = 2.2 Hz, 2H), 3.99 (t, J = 6.1 Hz, 2H), 3.66 (t, J = 6.1 Hz, 2H), 2.39 (d, J = 2.3 Hz, 1H), 2.26 (s, 6H), 2.08–1.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 139.1, 122.5, 112.4, 80.0, 74.4, 66.8, 64.5, 58.3, 29.7, 21.5.; HRMS (ESI): m/z =241.1199 $[M\text{-}PF_6]^+$ (calcd. 241.1204 for $C_{14}H_{18}O_2Na$).



Scheme S9. Synthesis of **L**.

Synthesis of L. Under Ar atmosphere, a drop of 2,6-lutidine and 50 mg (0.14 mmol) of $[Cu(CH_3CN)_4]PF_6$ were successively added to a solution of **L1** (106 mg, 0.067 mmol) and **L2** (45 mg, 0.20 mmol) in 20 mL of dry and degassed solvent of acetone/CH_2Cl_2 (v/v = 1:1). The resulting mixture was stirred overnight at room temperature for 18 h, and then washed with EDTA·2Na 0.1 M (aq, 3 ×15 mL), saturated NH_4PF_6 (aq, 3 × 10 mL) and water (3 × 10 mL), respectively. The organic layer was then separated, and the solvent was removed under reduced pressure. The resulting residue was dispersed in 10 mL of petrol ether/EtOAc (v/v = 1:1), and ultrasonically oscillated. The remaining solid was filtrated, and collected to give **L1** as white solid (111 mg, 93%). M.p.: 134–136 °C; ^{1}H NMR (600 MHz, $CD_3CN/CDCl_3$ = 1:1): δ = 7.90 (s, 2H), 7.78 (s, 1H), 7.32–7.15 (m, 12H), 6.93 (d, J = 8.4 Hz, 4H), 6.86 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 7.1 Hz, 6H), 6.61–6.55 (m, 2H), 6.53 (s, 2H), 6.50 (s, 2H), 5.13 (s, 4H), 4.73 (t, J = 4.9 Hz, 4H), 4.68 (t, J = 4.7 Hz, 2H), 4.57 (s, 2H), 4.38–4.28 (m, 6H), 4.11 (q, J = 6.1 Hz, 4H), 3.98 (t, J = 6.2 Hz, 2H), 3.73–3.60 (m, 14H), 2.37 (br, 6H), 2.25 (s, 12H), 2.22–2.15 (m, 2H), 2.02–1.96 (m, 2H); ^{13}C NMR (150 MHz, $CD_3CN/CDCl_3$ = 1:1): δ = 156.0, 159.3, 159.1, 144.9, 143.2, 139.3, 139.2, 131.8, 131.7, 124.9, 124.2, 123.6, 123.5, 123.5, 122.5, 122.4, 115.3, 115.1, 115.0, 112.3, 67.0, 66.5, 64.7, 64.6, 64.1, 63.9, 61.5, 51.0, 50.9, 50.8, 49.8, 49.6, 30.5, 29.6, 29.2, 21.1; HRMS (ESI): m/z =1643.6463 $[M\text{-}PF_6]^+$ (calcd. 1643.6467 for $C_{79}H_{93}F_{12}N_{12}O_9P_2$); m/z = 749.3401 $[M\text{-}2PF_6]^{2+}$ (calcd. 749.3410 for $C_{79}H_{93}F_6N_{12}O_9P$); and m/z = 451.2387 $[M\text{-}3PF_6]^{3+}$ (calcd. 451.2391 for $C_{79}H_{93}N_{12}O_9$).

3. Synthesis of rotaxane 3in-[L⊃H], [P-H$_3$][6PF$_6$]



Scheme S10. Synthesis of **3**in-[**L**⊃**H**] and [**P**-H_3][6PF_6].

Synthesis of 3in-[L⊃H]. **L1** (312 mg, 0.20 mmol) and **H** (254 mg, 0.20 mmol) were dispersed in dry CH_2Cl_2 (50 mL). The mixture was ultrasonic oscillated, and violently stirred until a clear solution was obtained. The solution was then stirred for another 18 h at room temperature to fully form pseudorotaxane **3**in-[**L**⊃**H**]. To the above solution was successively added **L2** (131 mg, 0.60 mmol), a drop of lutidine and $[Cu(CH_3CN)_4]PF_6$ (71 mg, 0.20 mmol) under Ar atmosphere. After

being stirred for two days, the reaction mixture was diluted with CH_2Cl_2 (50 mL), and washed with EDTA·2Na solution (aq, 0.1 M, 2×40 mL) and H_2O (40 mL). The organic fraction was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (CH_2Cl_2/MeOH 50:1 → 30:1) to yield rotaxane **3**in-[**L**⊃**H**] (164 mg, 27%) as white power. M.p.: 182–183 °C; ^{1}H NMR (600 MHz, $CD_3CN/CDCl_3$ = 1:1): δ = 7.82–7.76 (m, 3H), 7.48–7.38 (br, 6H), 7.36 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.0 Hz, 4H), 7.20 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.7 Hz, 3H), 7.01–6.92 (m, 10H), 6.91–6.82 (m, 10H), 6.80–6.75 (m, 4H), 6.74–6.60 (m, 14H), 6.57 (s, 1H), 6.55 (s, 1H), 6.53 (s, 2H), 6.48 (s, 2H), 4.98 (s, 2H), 4.94 (s, 2H), 4.73–4.69 (m, 4H), 4.69–4.65 (m, 2H), 4.59 (s, 2H), 4.52 (dq, J = 22.8, 10.6, 9.0 Hz, 12H), 4.35–4.29 (m, 2H), 4.29–4.12 (m, 21H), 4.12–3.90 (m, 31H), 3.89–3.76 (m, 11H), 3.76–3.61 (m, 34H), 3.61–3.53 (m, 13H), 3.52–3.27 (m, 24H), 2.30 (s, 6H), 2.25 (s, 6H), 2.23 (s, 6H); ^{13}C NMR (150 MHz, $CD_3CN/CDCl_3$ = 1:1): δ = 159.5, 159.03, 158.96, 158.8, 158.6, 158.6, 148.3, 148.0, 147.1, 146.9, 145.0, 144.7, 144.7, 143.5, 143.44, 143.36, 142.4, 142.1, 139.2, 139.1, 131.6, 131.5, 131.1, 131.0, 130.9, 129.9, 125.1, 124.9, 124.6, 124.6, 124.5, 124.4, 123.9, 123.8, 122.5, 122.3, 121.8, 121.7, 121.5, 121.4, 115.2, 114.8, 114.7, 114.6, 114.5, 114.4, 114.1, 113.8, 112.8, 112.3, 112.2, 112.2, 107.3, 107.2, 106.2, 72.0, 71.0, 70.8, 70.7, 70.64, 70.55, 70.52, 70.48, 70.3, 70.14, 70.06, 70.3, 70.0, 69.9, 69.8, 69.7, 69.2, 69.1, 68.7, 68.6, 68.5, 68.4, 68.3, 68.2, 68.14, 68.06, 67.9, 67.0, 66.6, 66.4, 64.5, 64.4, 64.2, 64.1, 64.0, 61.7, 61.5, 60.8, 51.9, 51.8, 51.7, 49.8, 49.5, 47.9, 29.7, 29.61, 29.58, 29.54, 29.49, 29.44, 29.40, 29.3, 29.2, 29.1, 27.1, 25.5, 22.6, 21.0; HRMS (ESI): m/z = 1446.1567 $[M\text{-}2PF_6]^{2+}$ calcd. 1446.1572 for $C_{155}H_{189}F_6N_{12}O_{33}P$); m/z = 915.7829 $[M\text{-}3PF_6]^{3+}$ (calcd. 915.7833 for $C_{155}H_{189}N_{12}O_{33}$).

Synthesis of [P-H$_3$][6PF$_6$]: The solution of rotaxane **3**in-[**L**⊃**H**] (80 mg, 0,025 mmol) in 10 mL of CH_3I/CH_3CN (1:4, v/v) was stirred at 45 °C for two days in a sealed tube. After being cooled to room temperature, the reaction mixture was diluted with CH_2Cl_2 (30 mL), and then washed with saturated aqueous NH_4PF_6 (20 mL×3) and H_2O (20 mL×3). The organic layer was concentrated in vacuo to give the product [**P**-H$_3$][6PF$_6$] as white powder (86 mg, 95%). M.p.: 182–183 °C; ^{1}H NMR (600 MHz, $CD_3CN/CDCl_3$ = 1:1): δ = 8.44 (s, 2H), 8.41 (s, 1H), 7.57–7.45 (br, 6H) 7.42 (s, 2H), 7.39 (s, 3H), 7.37–7.34 (m, 2H), 7.32 (s, 1H), 7.28–7.22 (m, 4H), 7.19 (d, J = 8.5 Hz, 2H), 7.05–6.89 (m, 12H), 6.88–6.79 (m, 8.3 Hz, 10H), 6.77 (d, J = 6.0 Hz, 3H), 6.75–6.62 (m, 10H), 6.57 (s, 2H), 6.54 (s, 2H), 6.48 (s, 2H), 5.16 (s, 2H), 5.10 (s, 2H), 4.91 (dt, J = 9.2, 4.7 Hz, 6H), 4.74 (s, 2H), 4.70 (s, 2H), 4.58 (s, 6H), 4.49 (s, 4H), 4.35 (dd, J = 11.6, 7.1 Hz, 6H), 4.30–4.16 (m, 18H), 4.13–3.90 (m, 28H), 3.83–3.77 (m, 6H), 3.77–3.70 (m, 8H), 3.69–3.58 (m, 18H), 3.58–3.47 (m, 8H), 3.47–3.33 (m, 12H), 3.33–3.22 (m, 5H), 2.29 (d, J = 7.8 Hz, 6H), 2.24 (d, J = 2.8 Hz, 13H), 2.20–2.10 (m, 2H), 2.07–2.00 (m, 2H); ^{13}C NMR (150 MHz, $CD_3CN/CDCl_3$ = 1:1): δ = 159.5 158.9, 158.1, 157.6, 157.3, 147.9, 147.1, 146.8, 144.8, 143.5, 142.50, 142.4, 142.0, 140.9, 140.1, 139.2, 131.7, 131.2, 131.1, 130.9, 130.4, 130.1, 129.8, 125.9, 125.6, 125.0, 123.6, 122.4, 121.5, 121.4, 121.3, 115.2, 114.9, 114.8, 114.5, 114.4, 112.8, 112.2, 107.4, 107.3, 106.4, 71.1, 70.9, 70.8, 70.5, 70.5, 70.3, 70.0, 69.2, 68.7, 68.4, 68.1, 65.0, 64.8, 64.4, 64.04, 64.0, 60.1, 58.2, 53.5, 53.3, 51.6, 47.8, 38.6, 38.4, 29.5, 29.2, 29.1, 21.0; HRMS (ESI): m/z =1686.1393 $[M\text{-}2PF_6]^{2+}$ (calcd. for $C_{158}H_{198}F_{24}N_{12}O_{33}P_4$); m/z = 1075.7709 $[M\text{-}3PF_6]^{3+}$ (calcd. 1075.7709 for $C_{158}H_{198}F_{18}N_{12}O_{33}P_3$); and m/z = 770.5862 $[M\text{-}4PF_6]^{4+}$ (calcd. 770.5870 for $C_{158}H_{198}F_{12}N_{12}O_{33}P_2$).

4. NMR characterization of the [2]rotaxane 3in-[L⊃H], [P-H_3][6PF_6] and [P-H_3][6PF_6] upon the addition of DBU

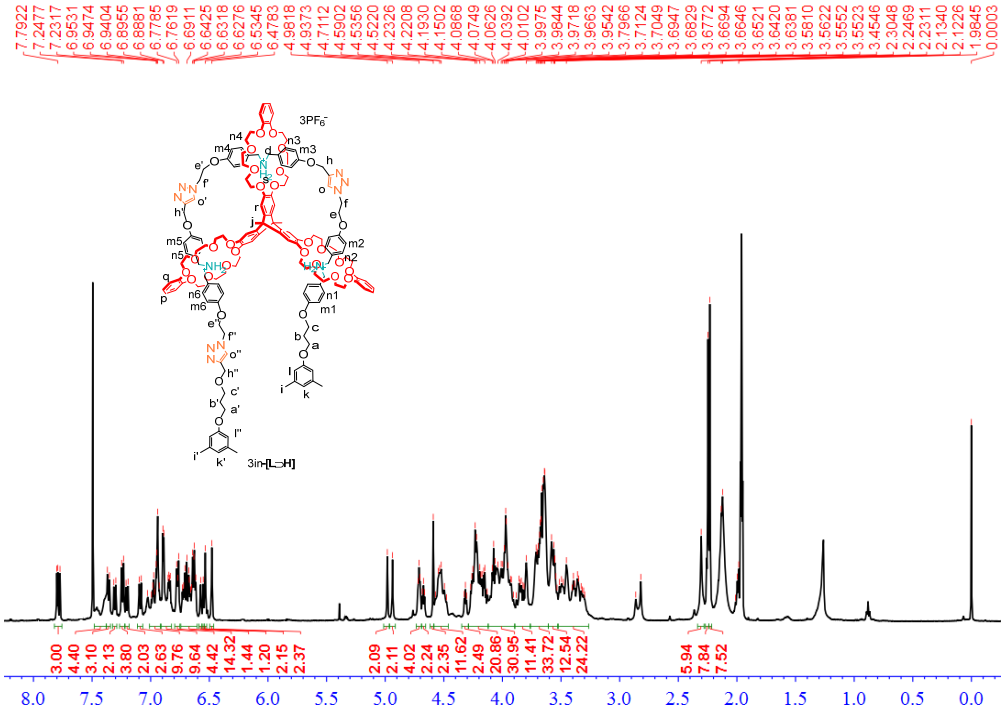


Fig. S1. ^{1}H NMR spectrum ($CDCl_3$/CD_3CN=1:1, 600 MHz, 298 K) of [2]rotaxane **3**in-[**L**⊃**H**].

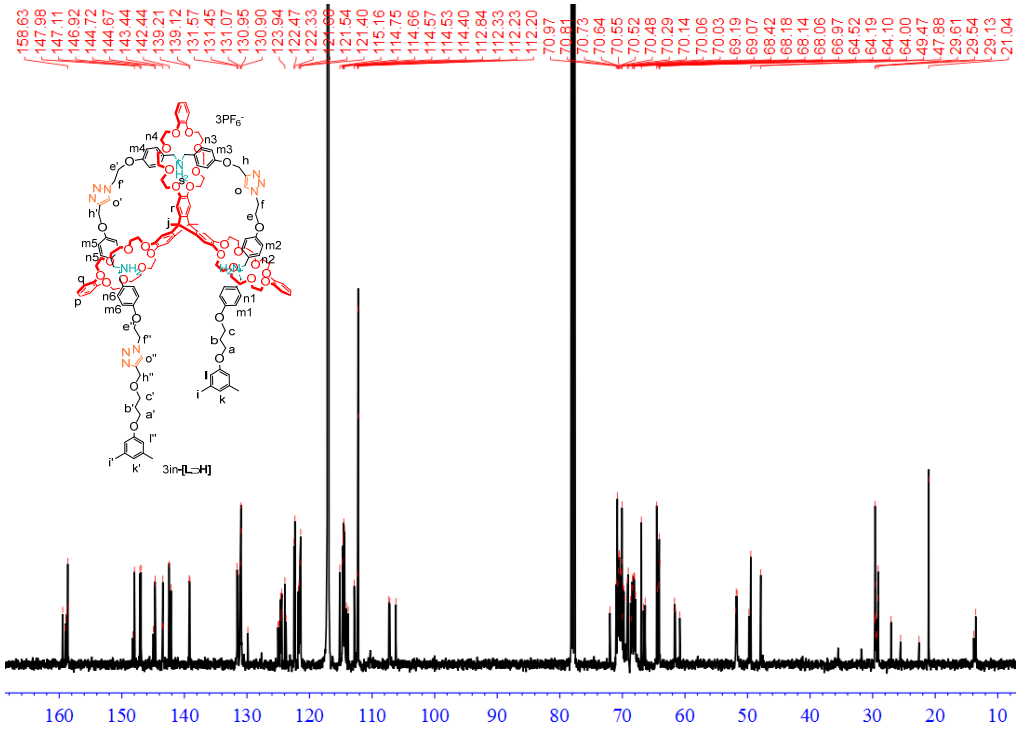


Fig. S2. ^{13}C NMR spectrum ($CDCl_3$/CD_3CN=1:1, 150 MHz, 298 K) of [2]rotaxane **3**in-[**L**⊃**H**].

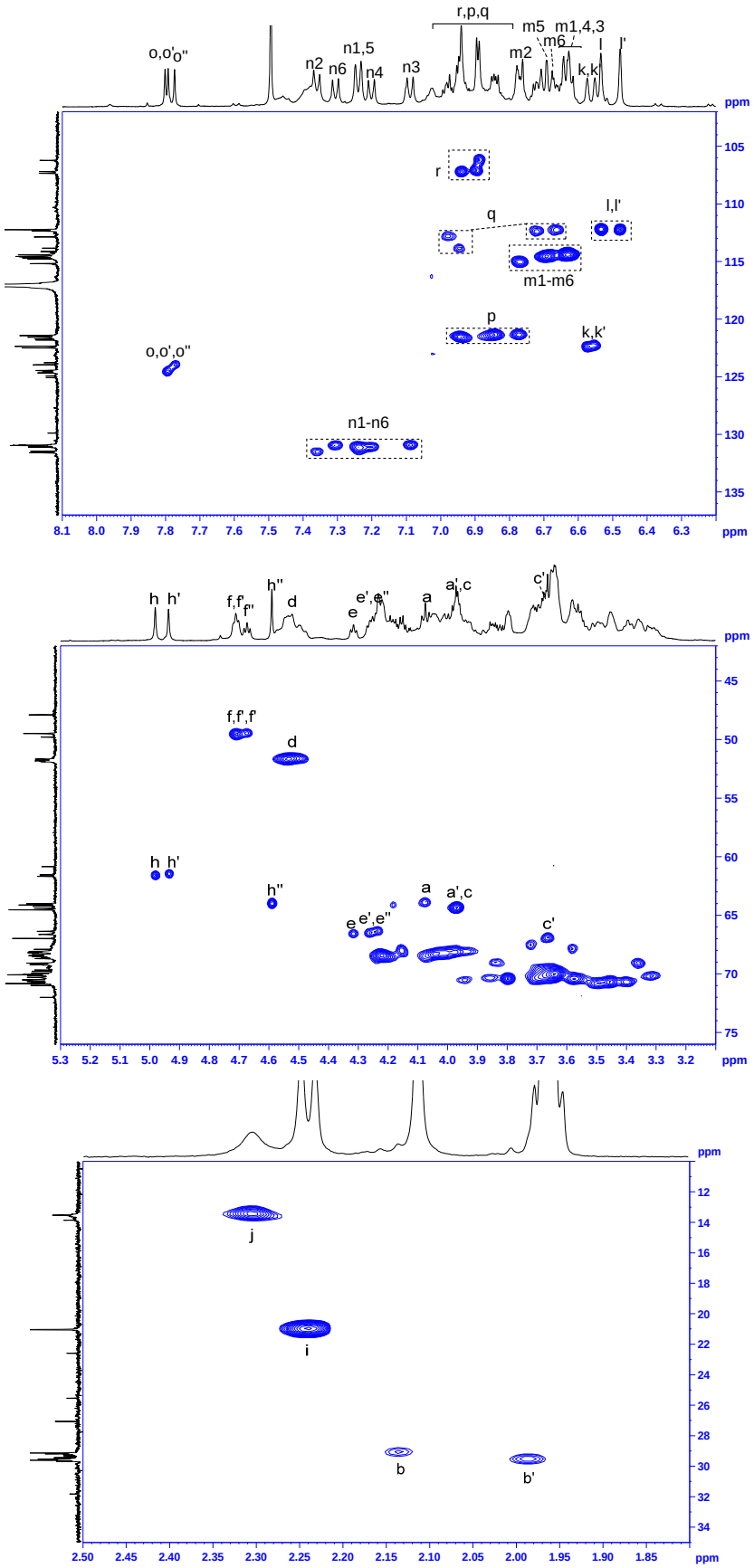


Fig. S3. HSQC spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 298 K) of [2]rotaxane **3**in-[**L**⊃**H**].

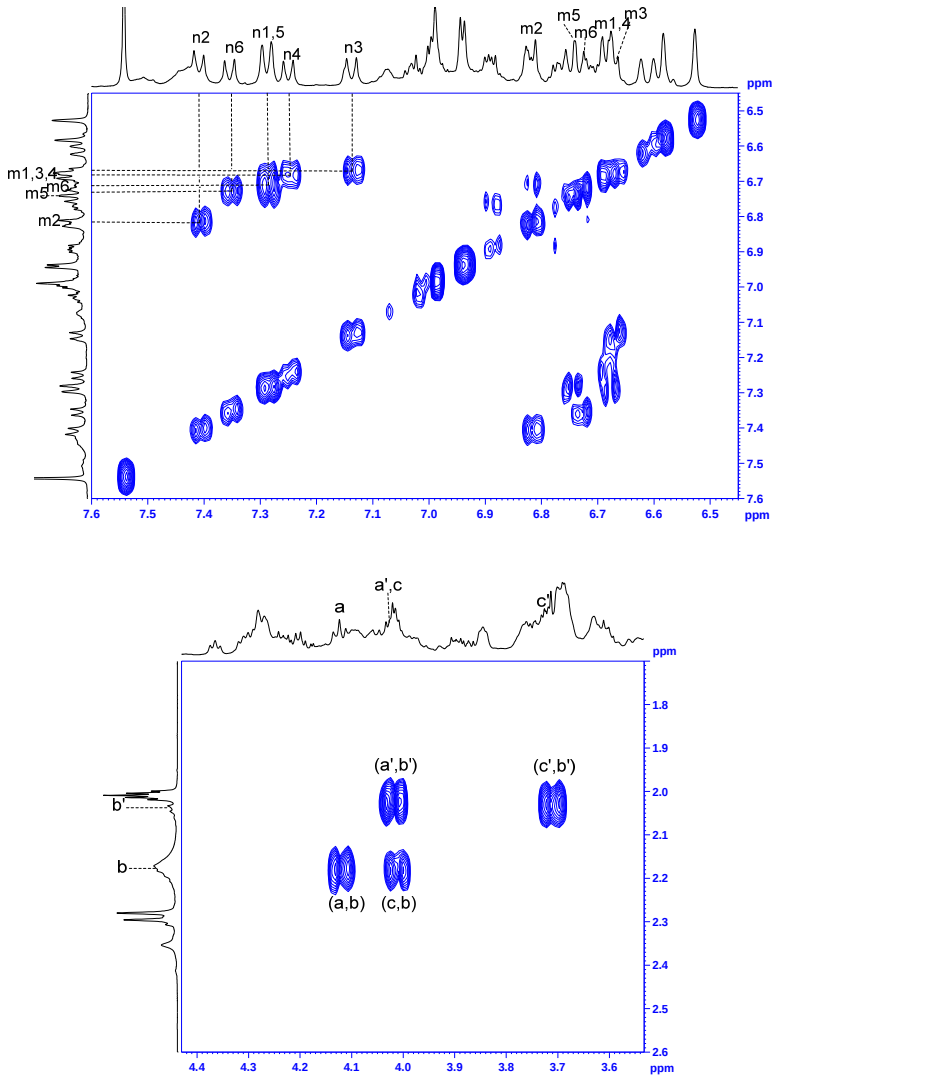


Fig. S4. COSY spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 298 K) of [2]rotaxane **3**in-[**L**⊃**H**].

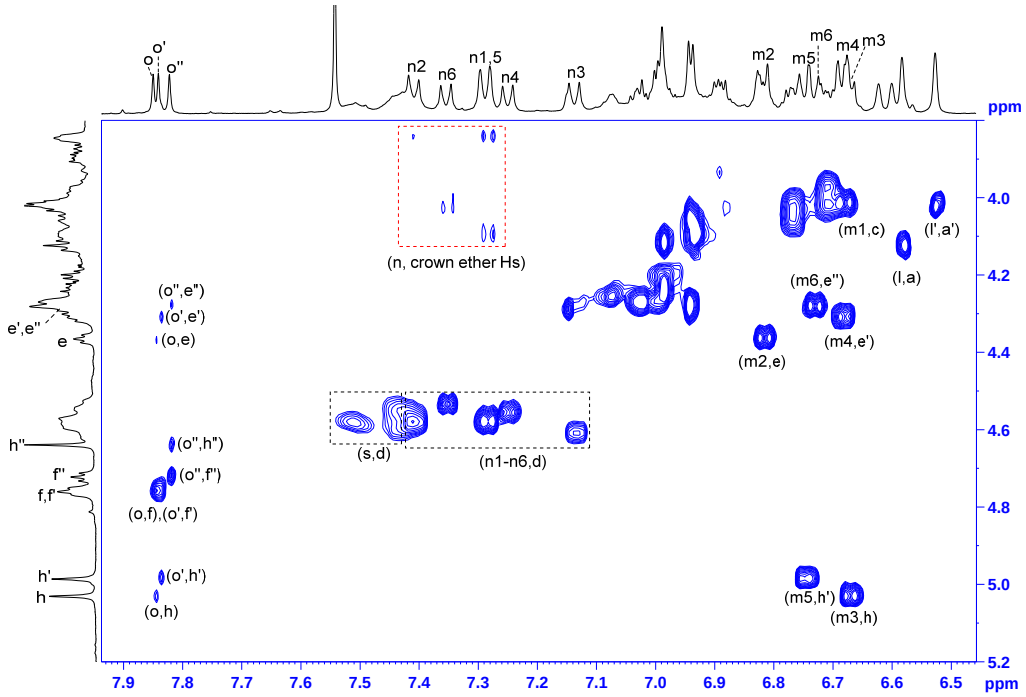


Fig. S5. ROESY spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 298 K) of [2]rotaxane **3**in-[**L**⊃**H**].

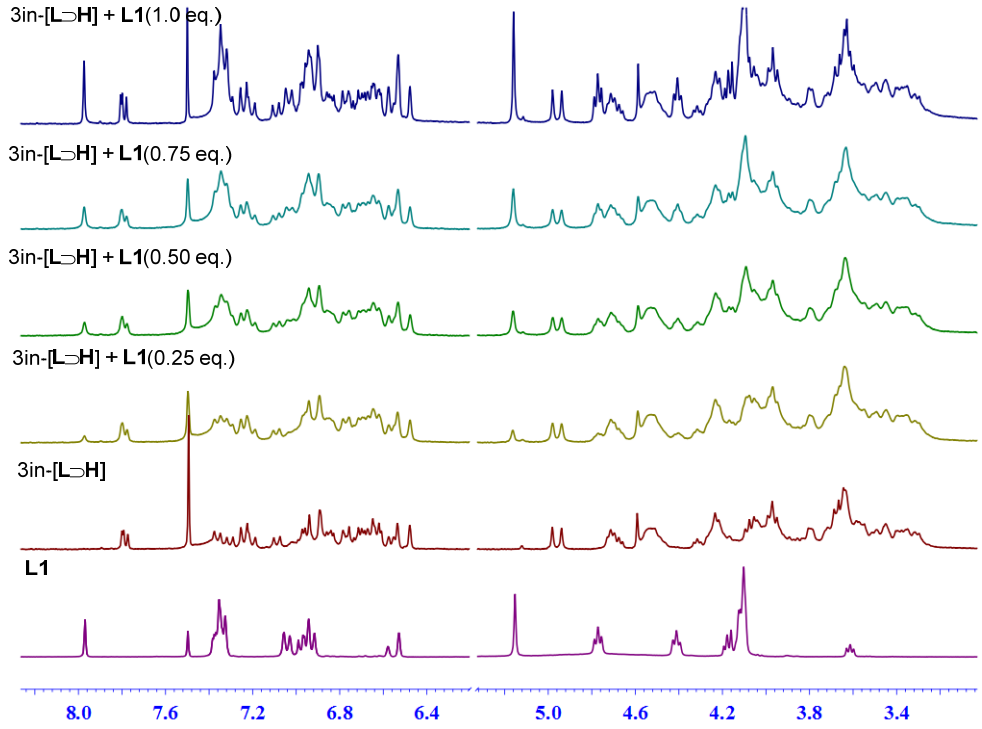


Fig. S6. ^{1}H NMR of spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 298 K) of [2]rotaxane **3**in-[**L**⊃**H**] upon the addition of different amount of **L1**.

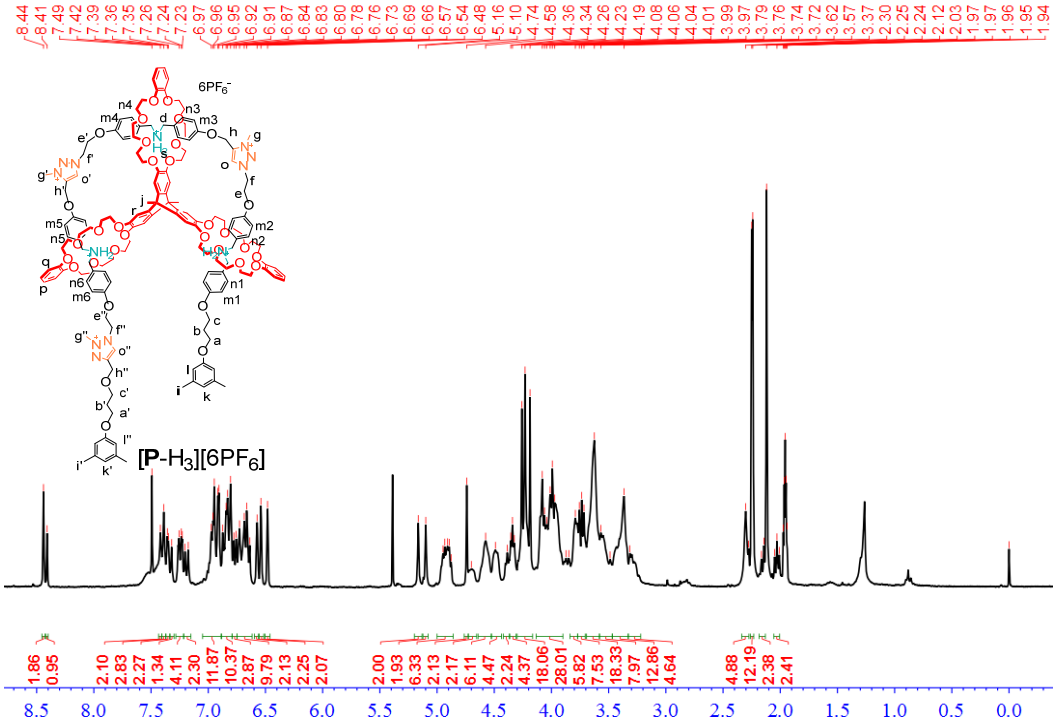


Fig. S7. ^{1}H NMR spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 298 K) of [2]rotaxane [**P**-H_3][$6PF_6$].

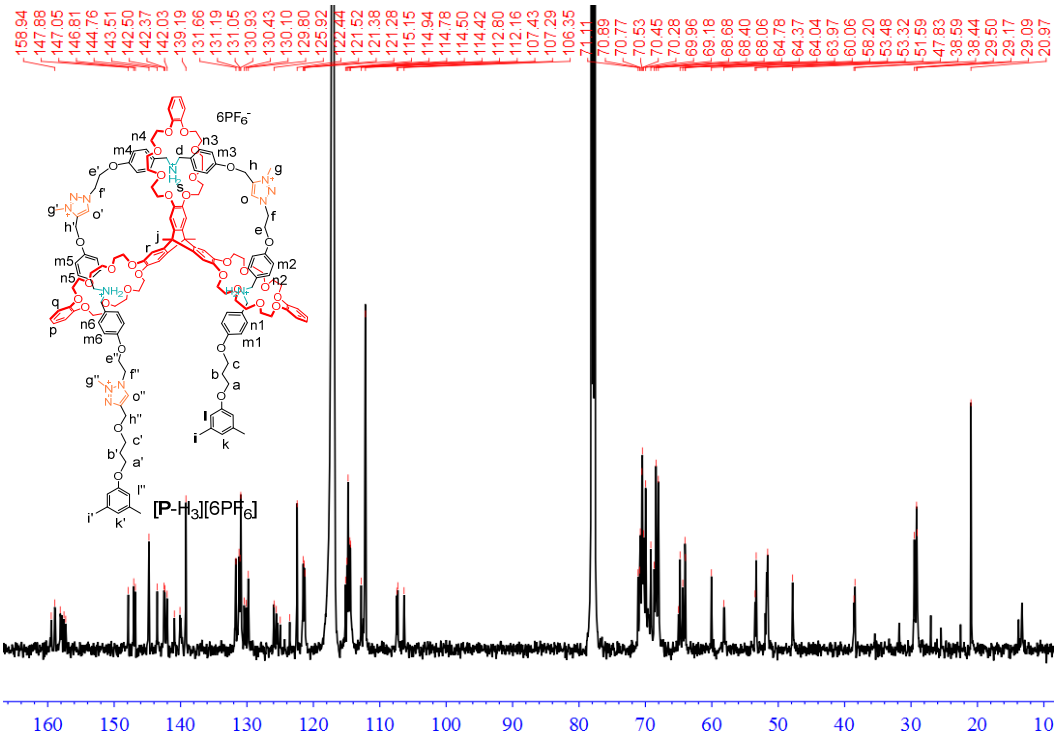


Fig. S8. ^{13}C NMR spectrum ($CDCl_3/CD_3CN$=1:1, 150 MHz, 298 K) of [2]rotaxane [**P**-H_3][$6PF_6$].

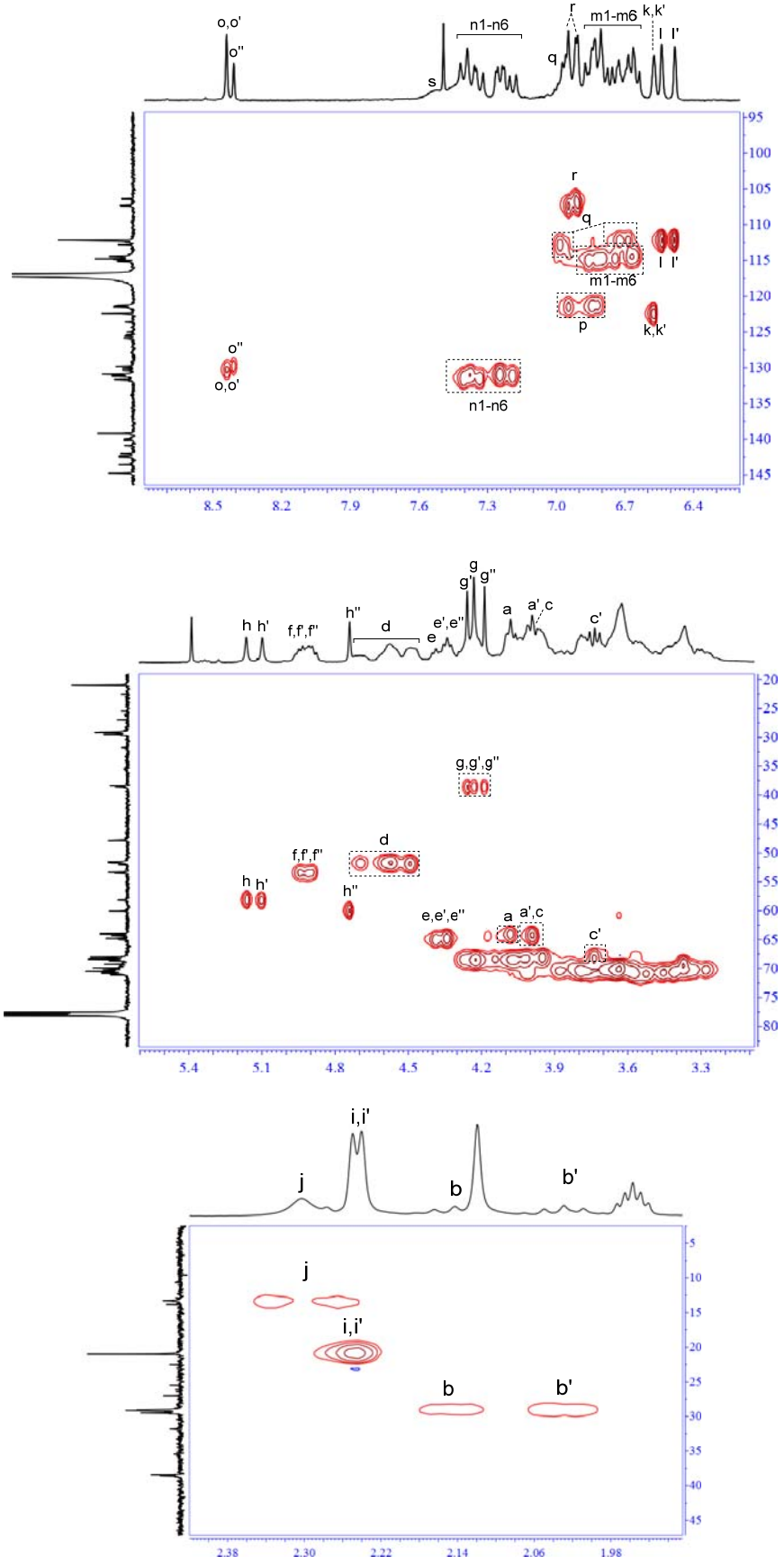


Fig. S9. HSQC spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 298 K) of [2]rotaxane [**P**-H_3][6PF_6].

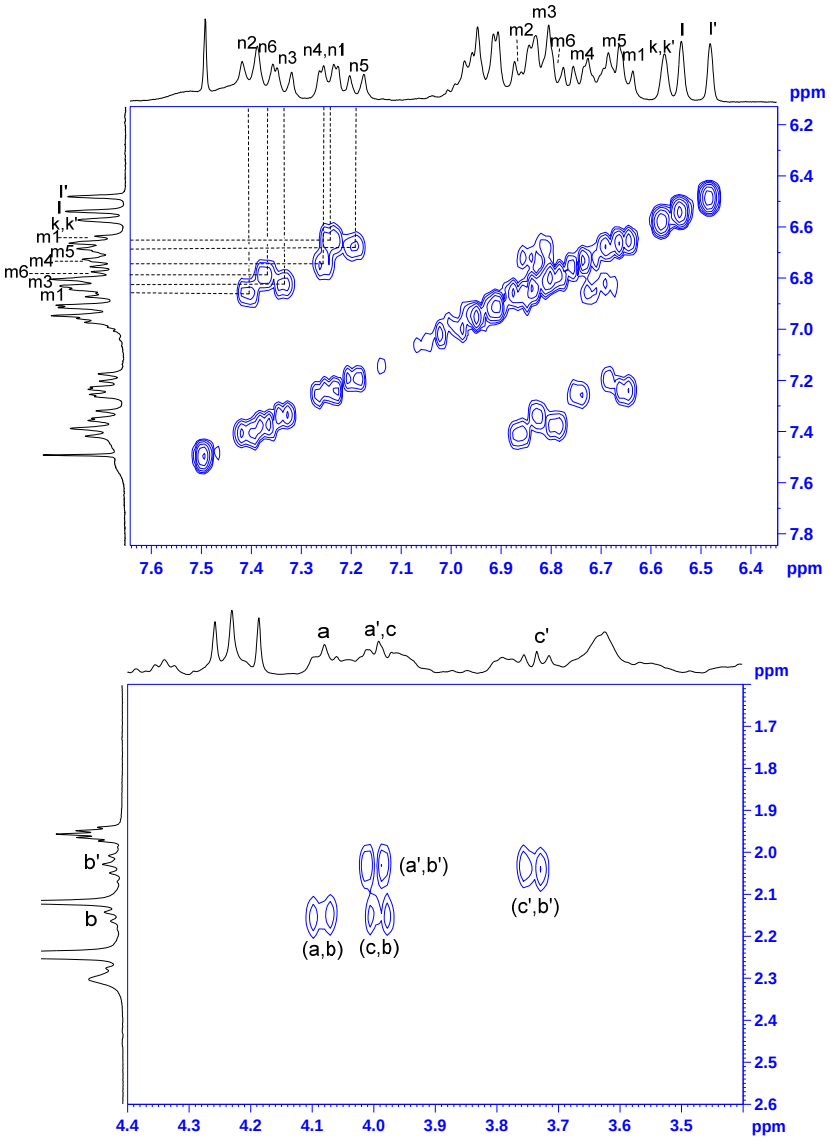


Fig. S10. COSY spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 298 K) of [2]rotaxane [**P**-H_3][6PF_6].

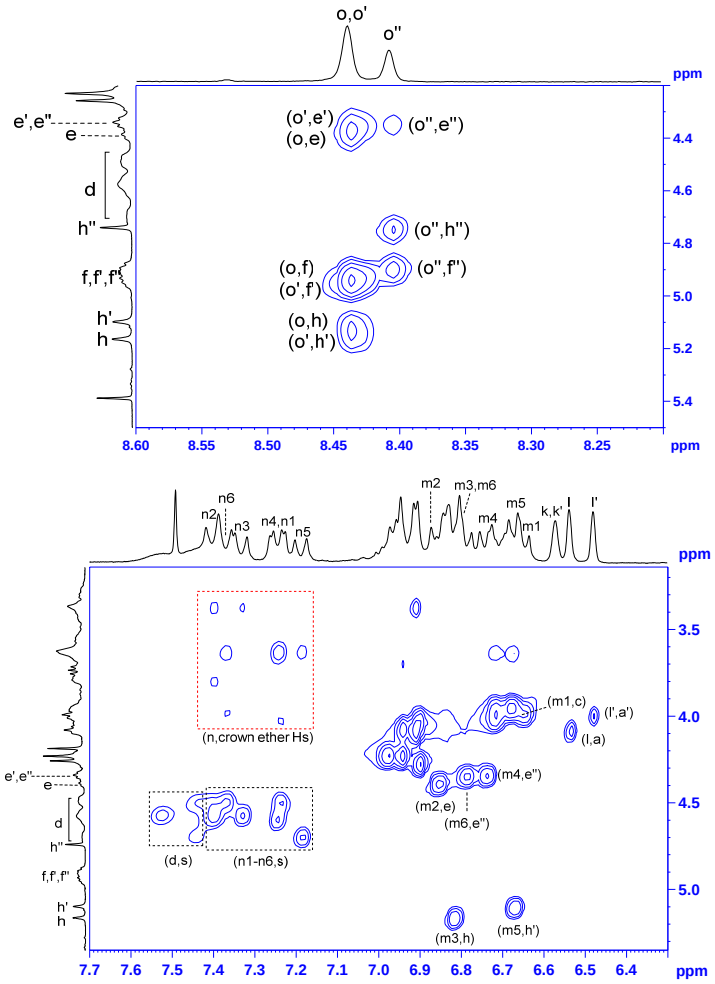


Fig. S11. ROESY spectrum ($CDCl_3/CD_3CN$=1:1, 600MHz) of [2]rotaxane [**P**-H_3][6PF_6].

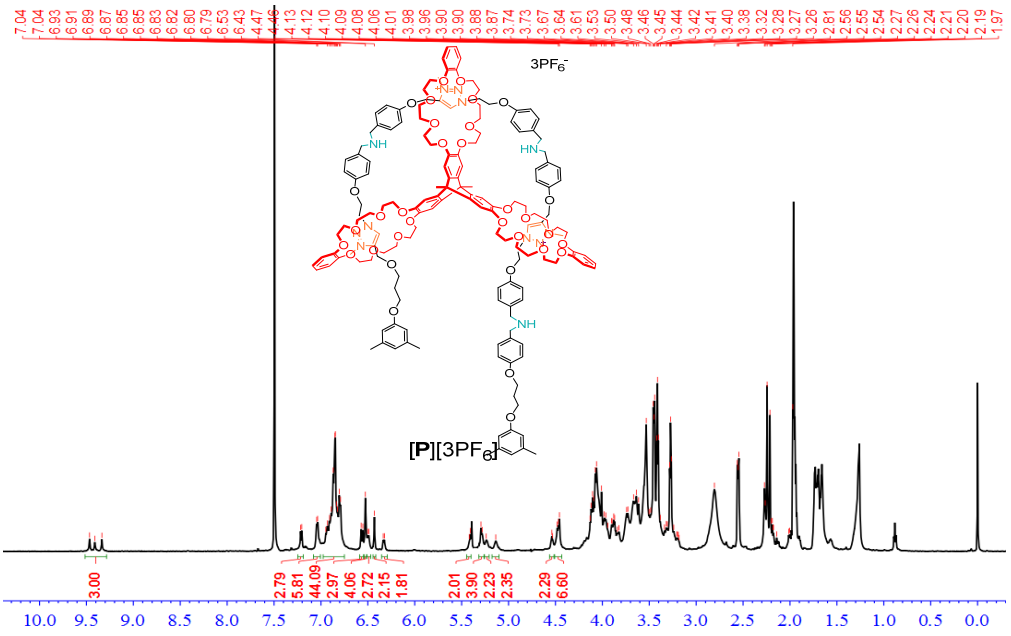


Fig. S12. ^{1}H NMR spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of [2]rotaxane [**P**-H_3][6PF_6] upon the addition of 3.6 equivalents of DBU.

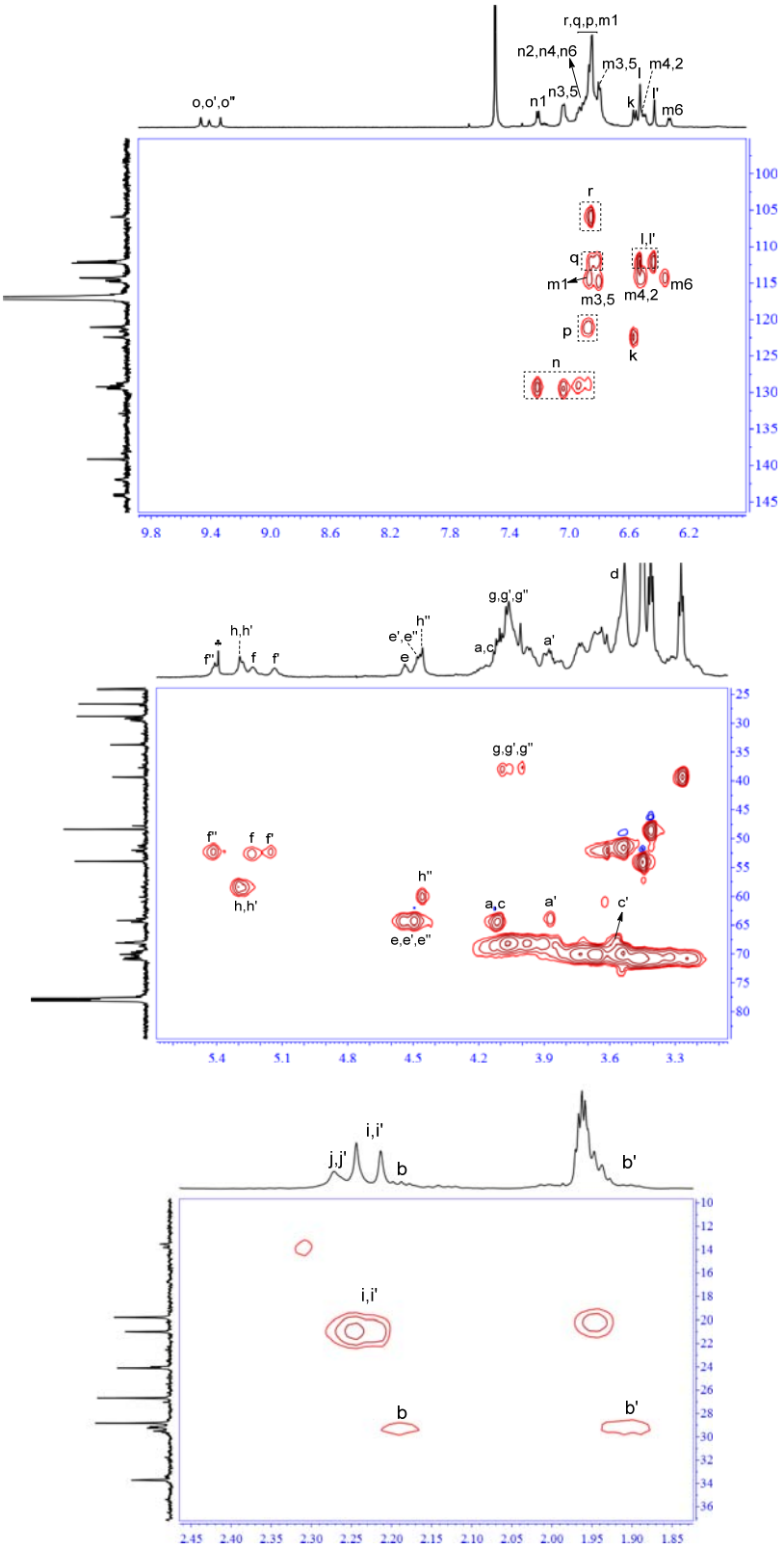


Fig. S13. HSQC spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 298 K) of [2]rotaxane [**P**-H_3][6PF_6] upon the addition of 3.6 equivalents of DBU.

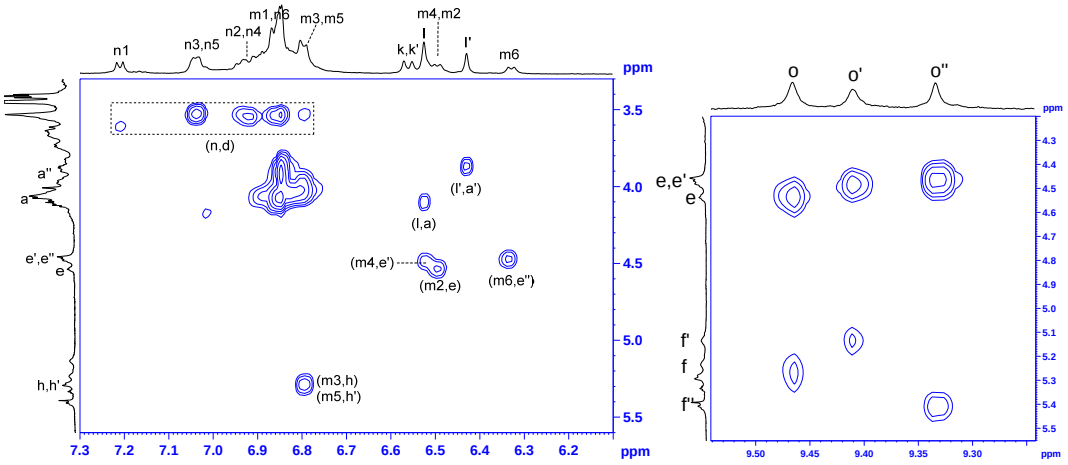


Fig. S14. ROESY spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 298 K) of [2]rotaxane [**P**-H_3][$6PF_6$] upon the addition of 3.6 equivalents of DBU.

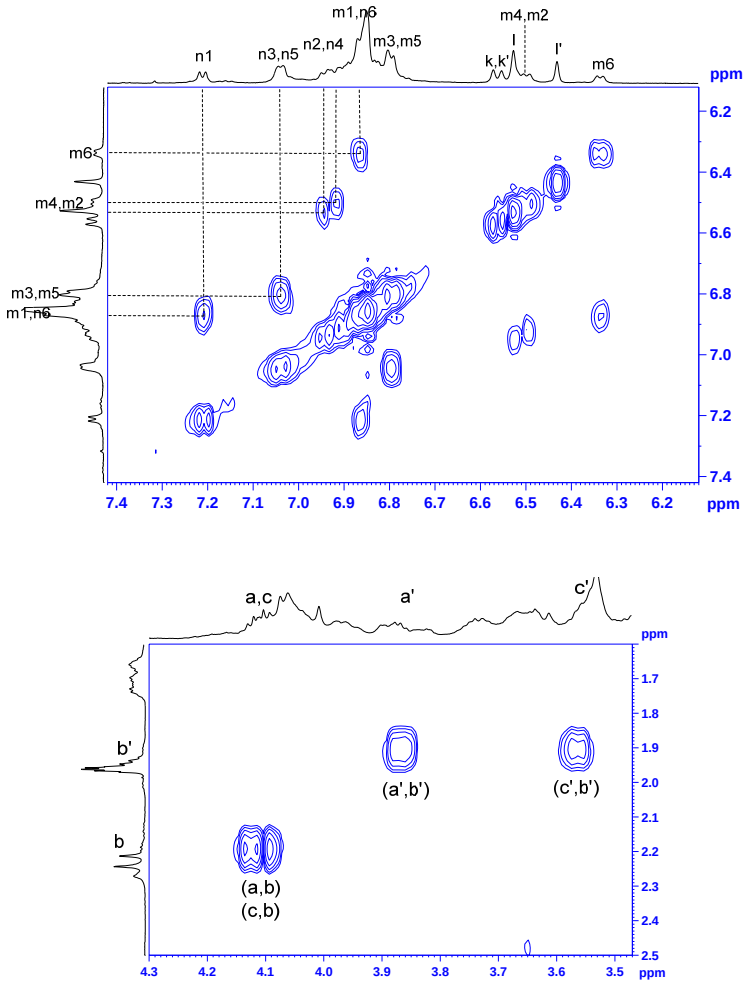


Fig. S15. COSY spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 298 K) of [2]rotaxane [**P**-H_3][$6PF_6$] upon the addition of 3.6 equivalents of DBU.

5. HRMS spectrum of the [2]rotaxane

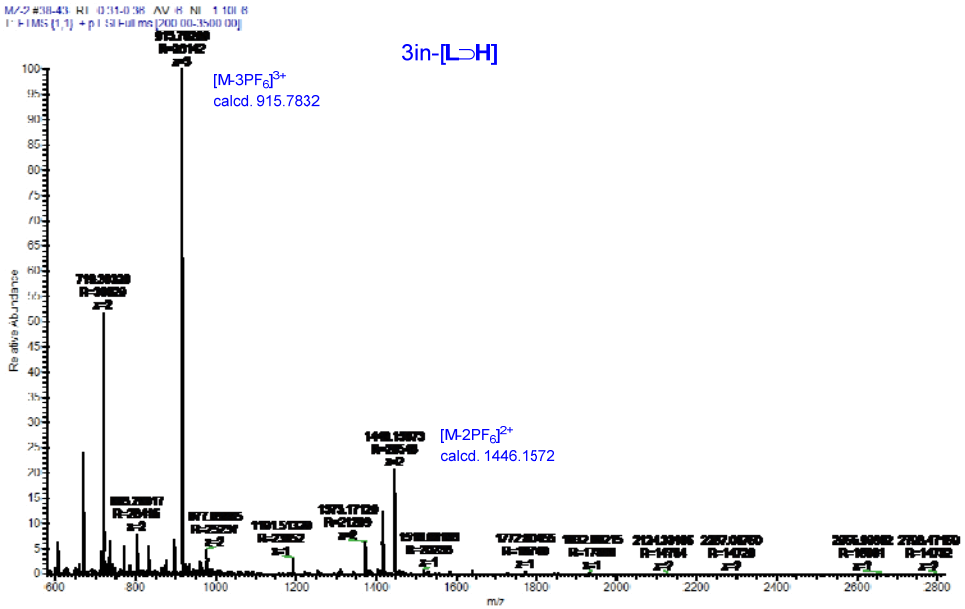


Fig. S16. HRMS spectrum of [2]rotaxane **3**in-[**L**⊃**H**].

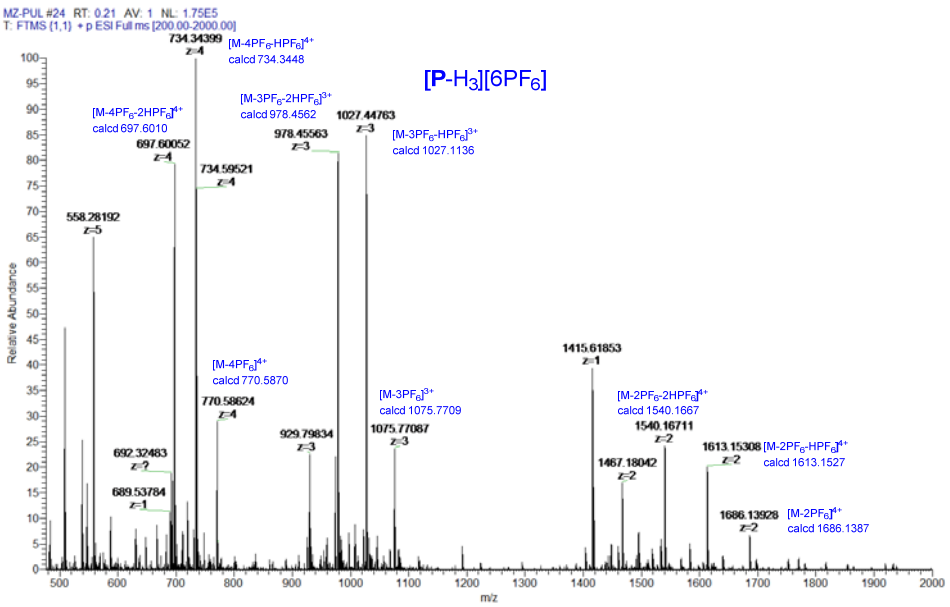


Fig. S17. HRMS spectrum of [2]rotaxane [**P**-H_3][6PF_6].

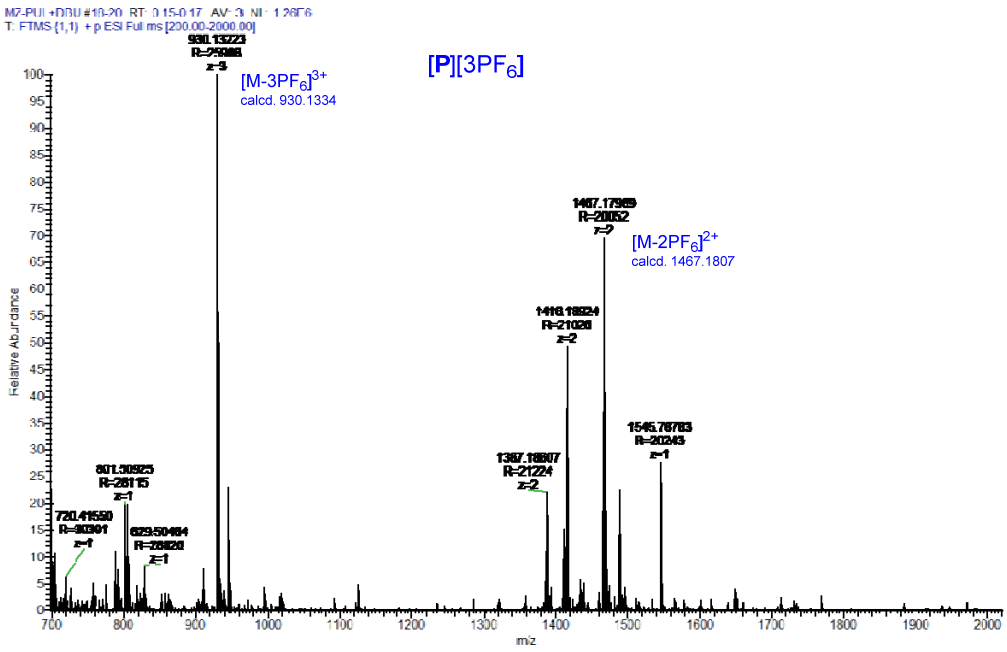


Fig. S18. HRMS spectrum of [2]rotaxane [**P**-H_3][6PF_6] upon the addition 3.6 equivalents of DBU.

6. NMR spectra for other new compounds

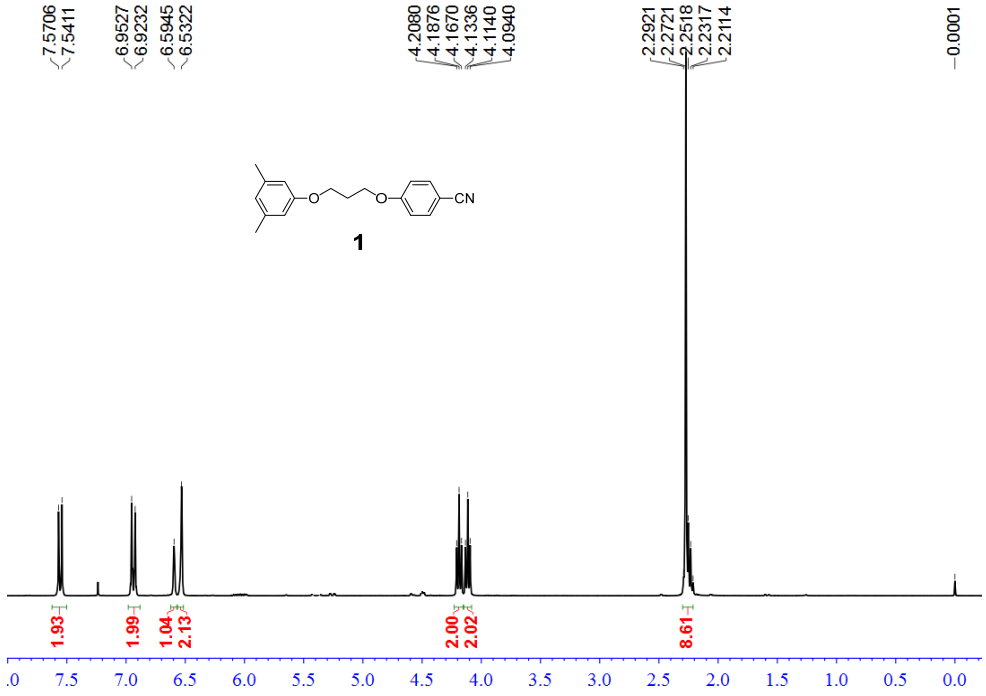


Fig. S19. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of compound **1**.

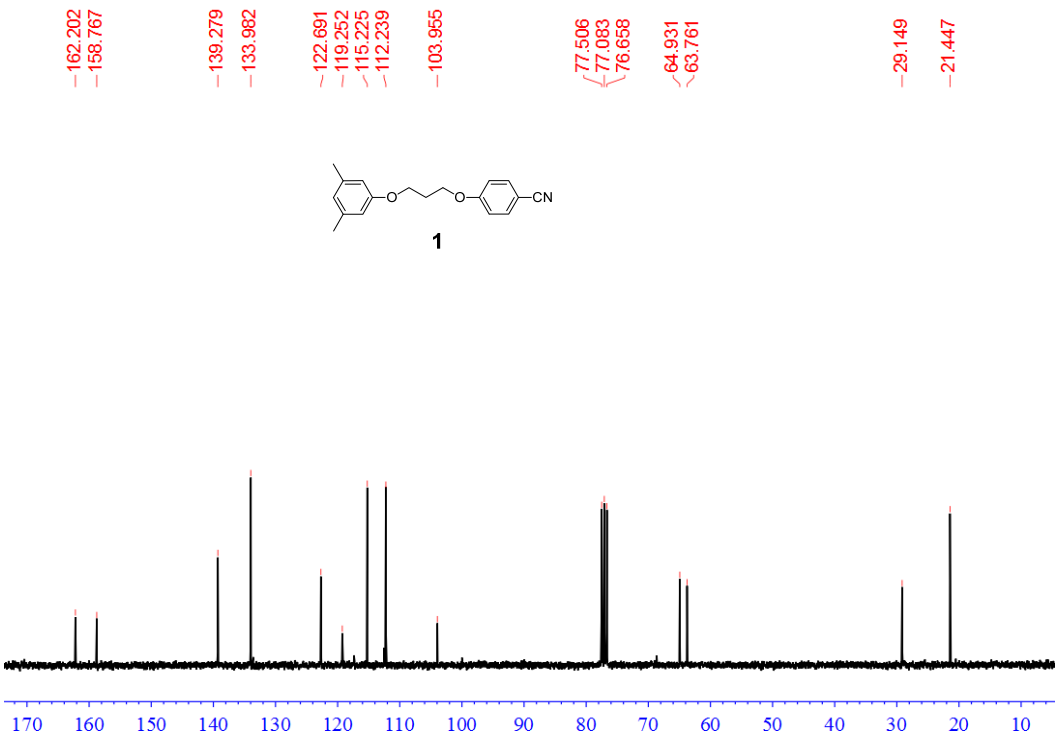


Fig. S20. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of compound **1**.

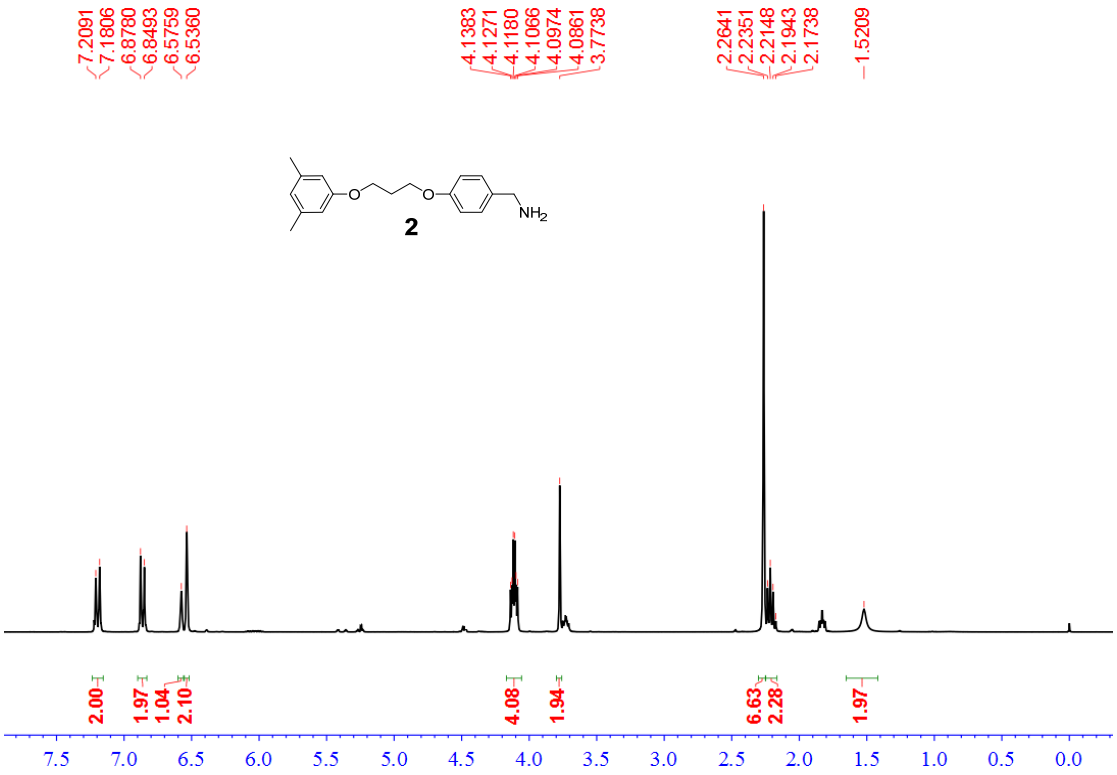


Fig. S21. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of compound **2**.

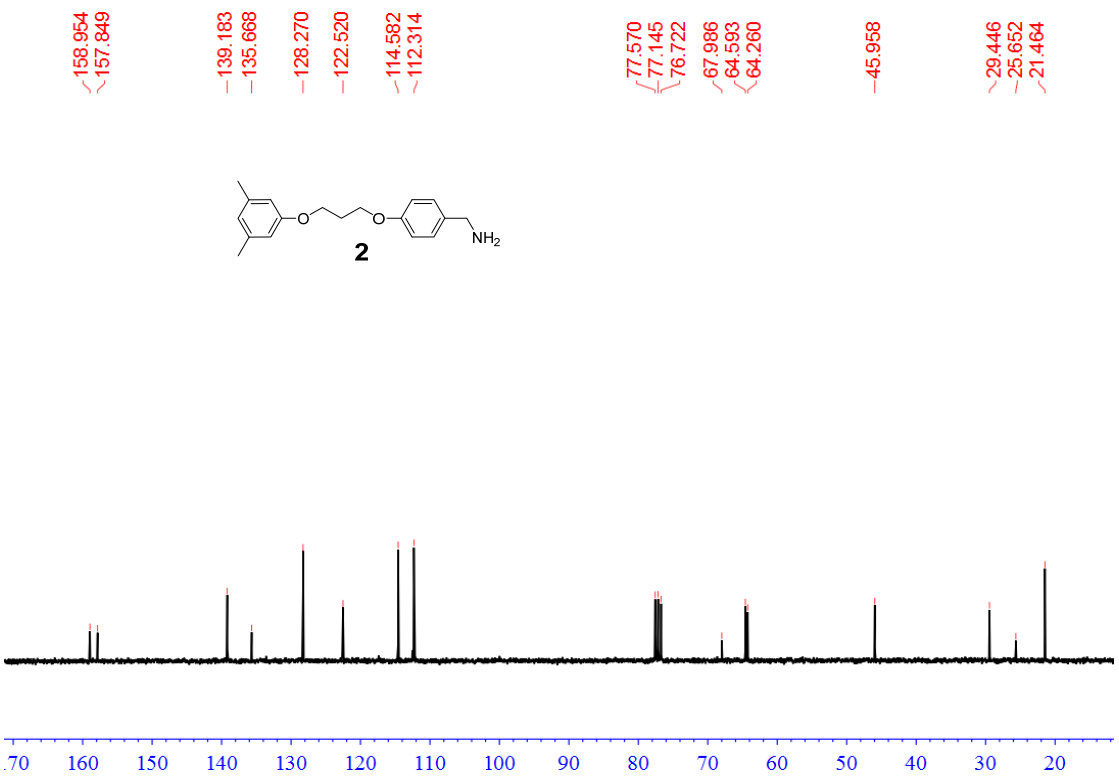


Fig. S22. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of compound **2**.

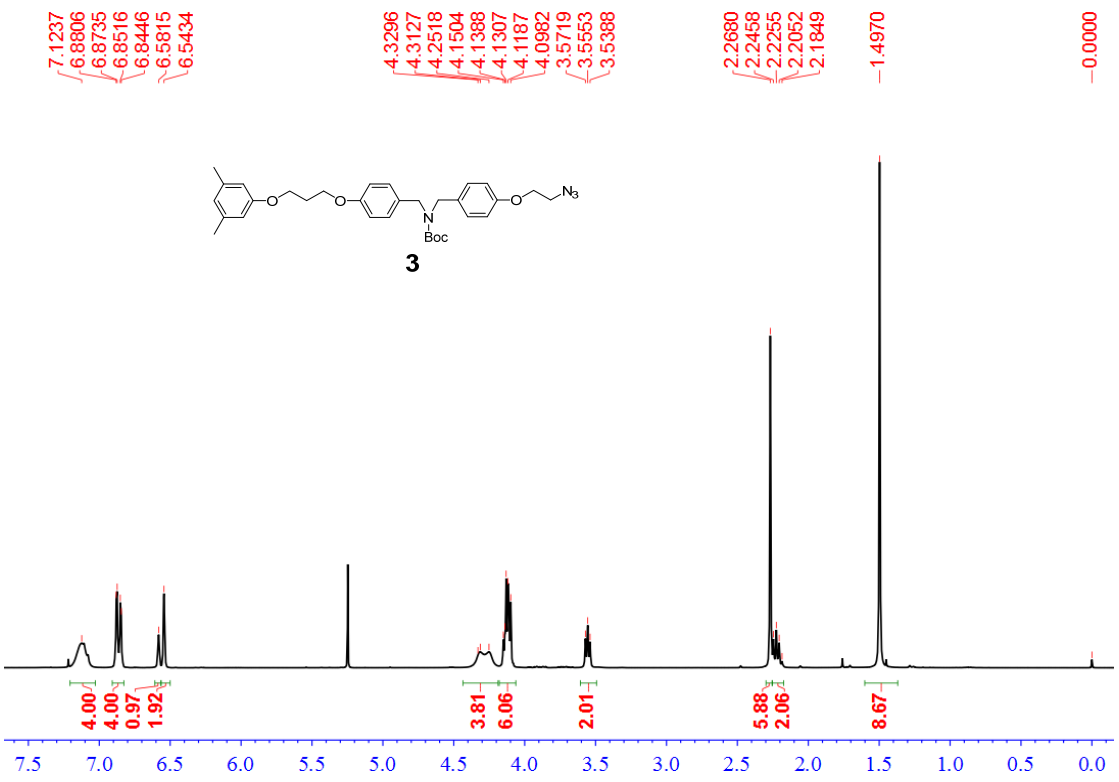


Fig. S23. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of compound **3**.

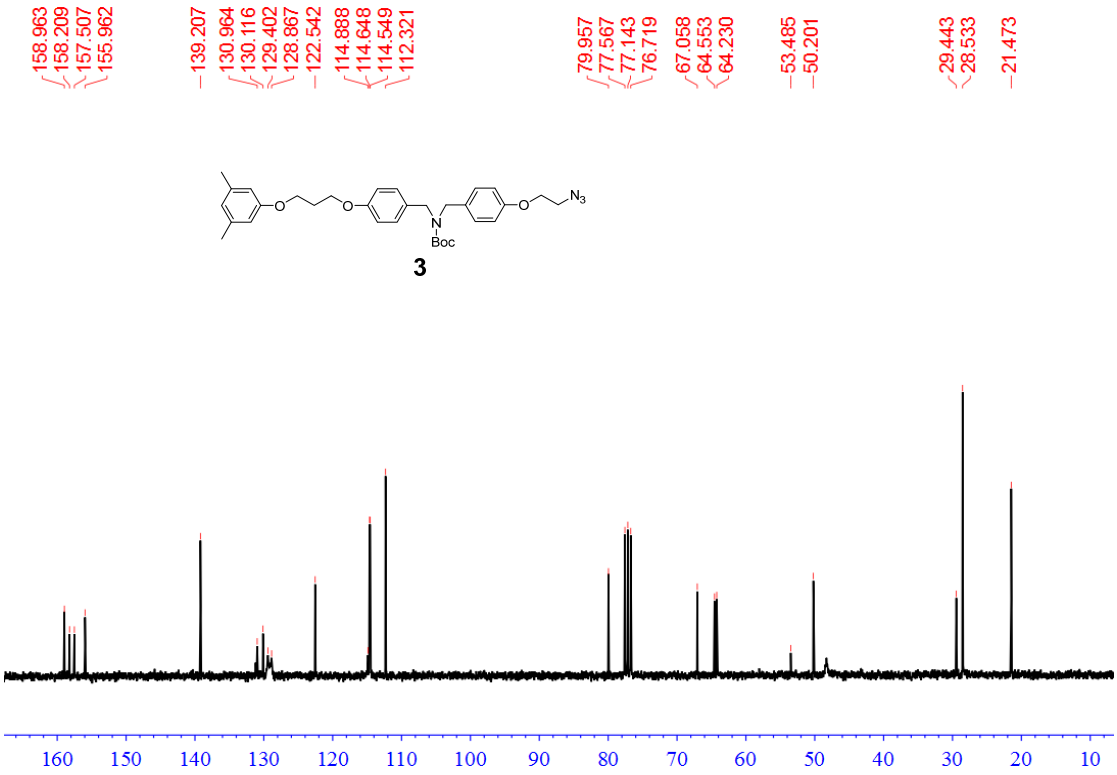


Fig. S24. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of compound **3**.

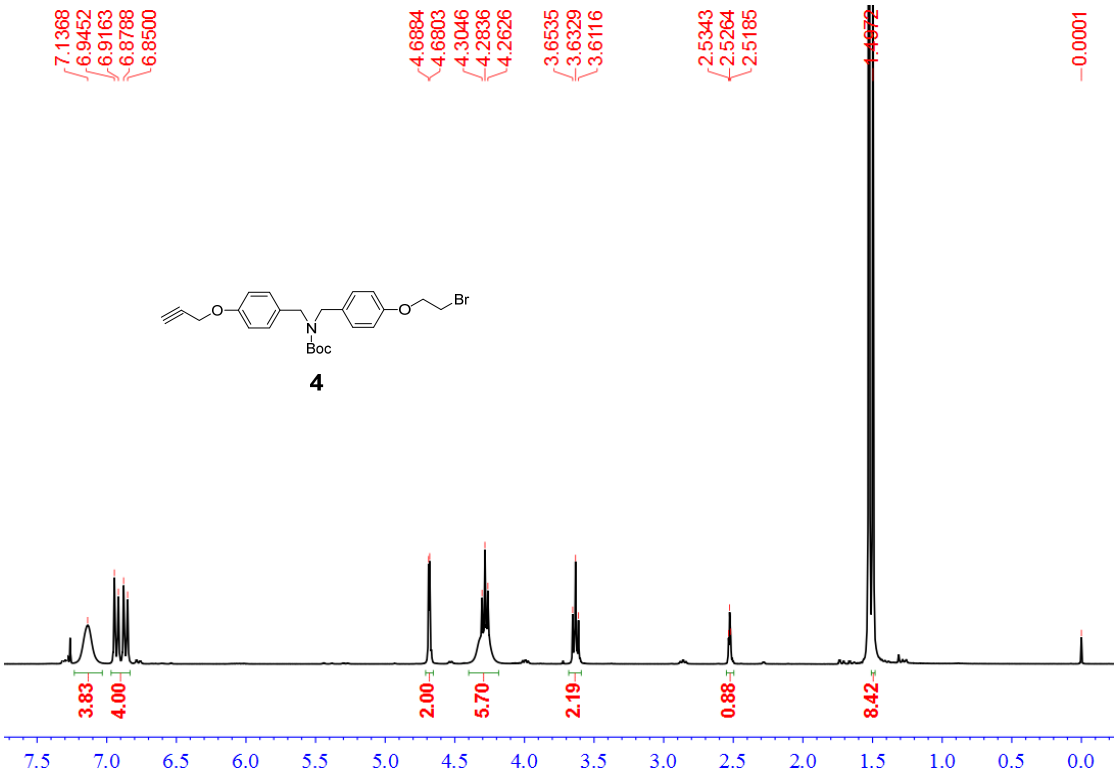


Fig. S25. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of compound **4**.

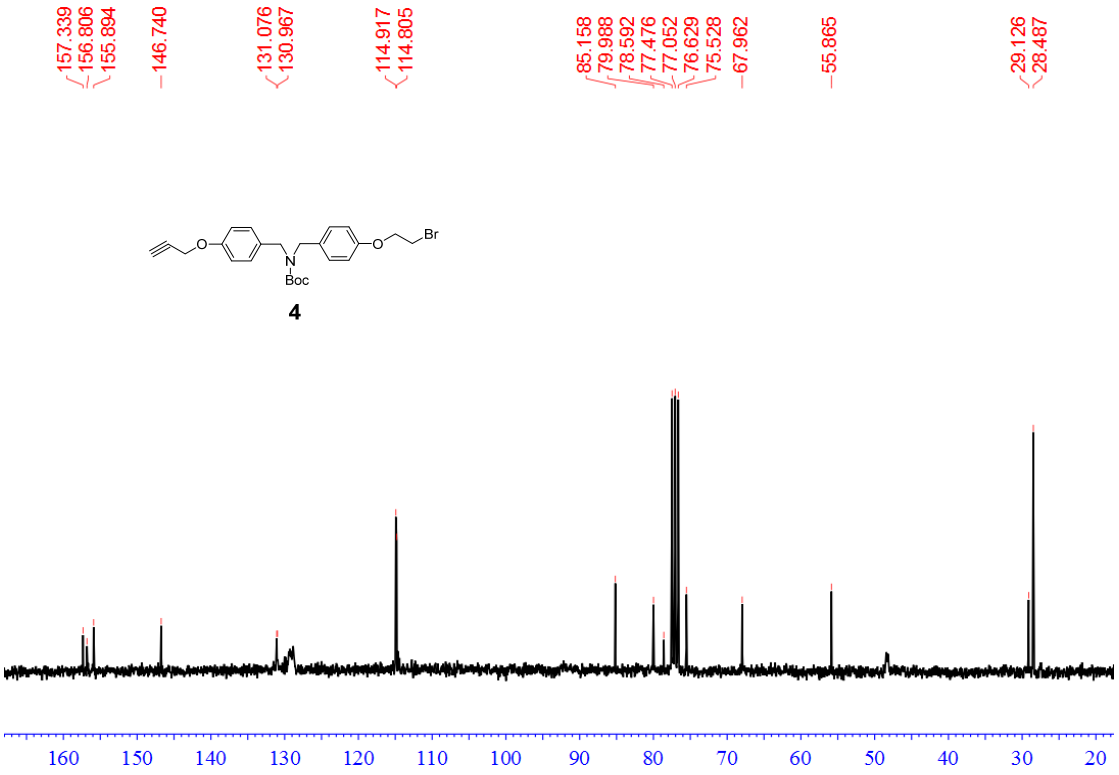


Fig. S26. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of compound **4**.

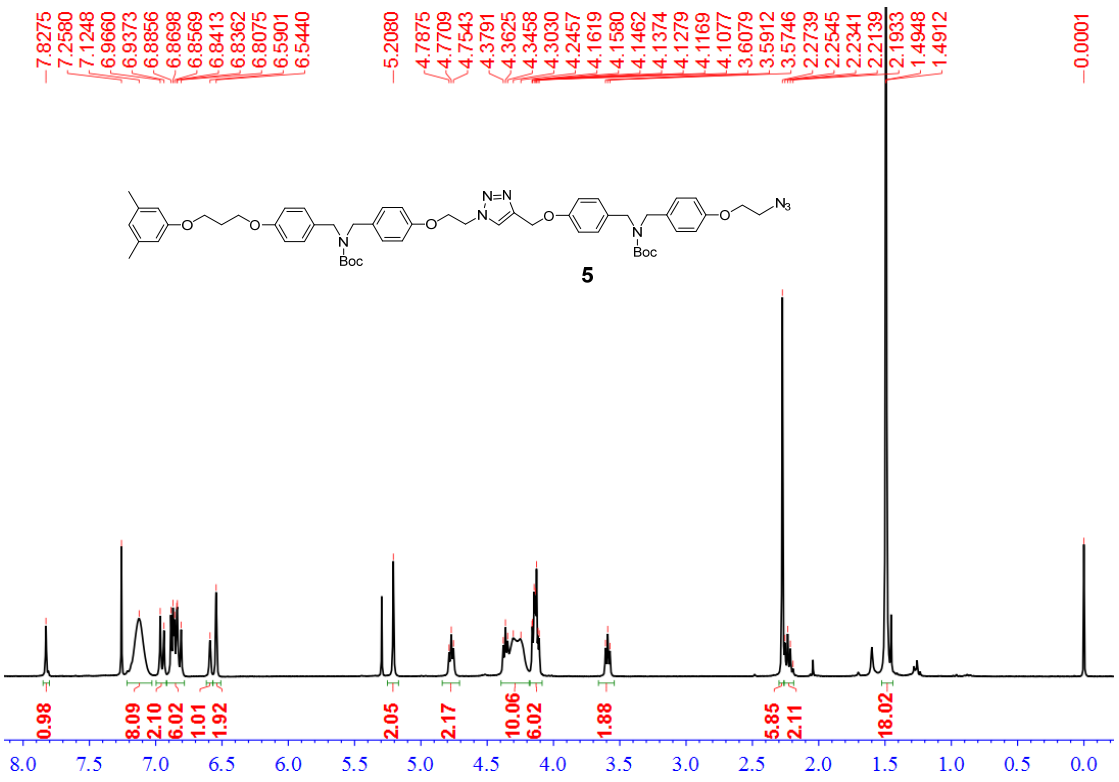


Fig. S27. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of compound **5**.

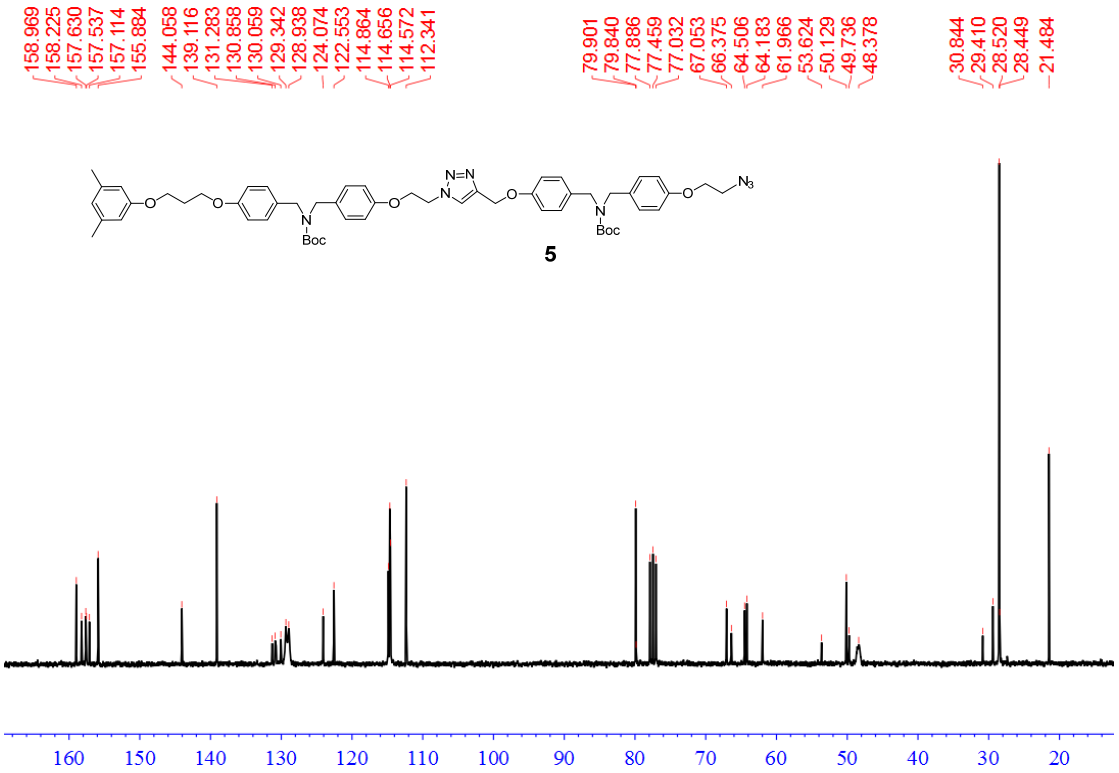


Fig. S28. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of compound **5**.

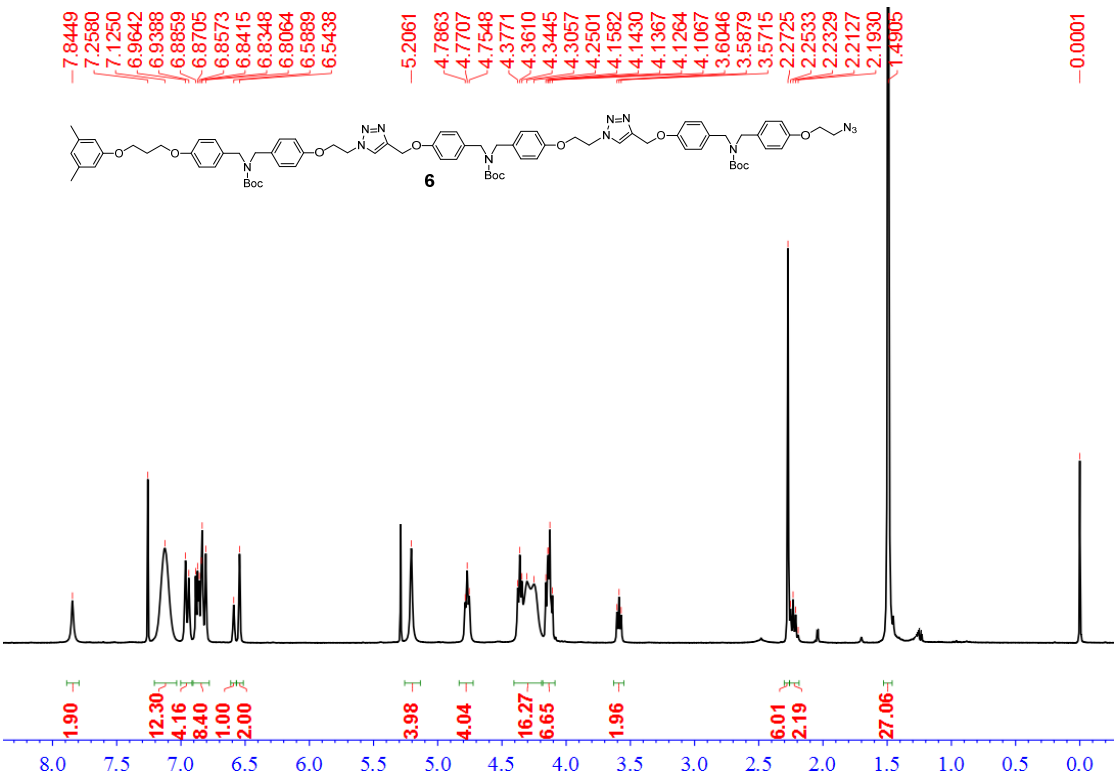


Fig. S29. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of compound **6**.

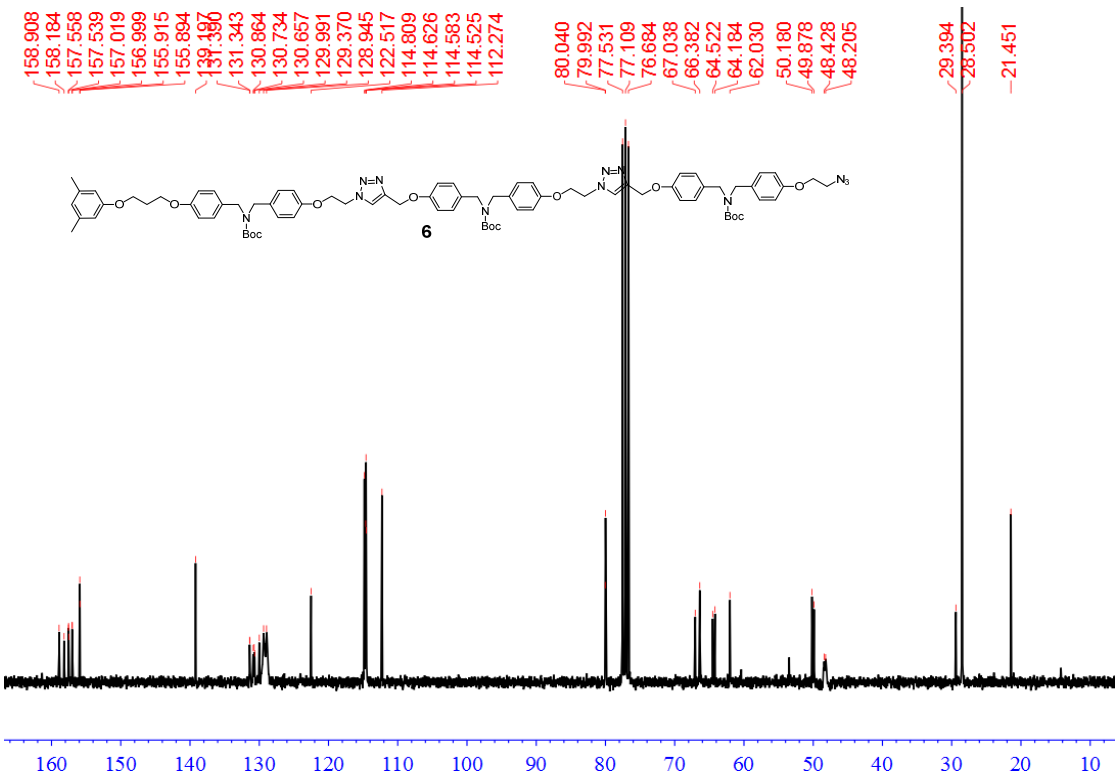


Fig. S30. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of compound **6**.

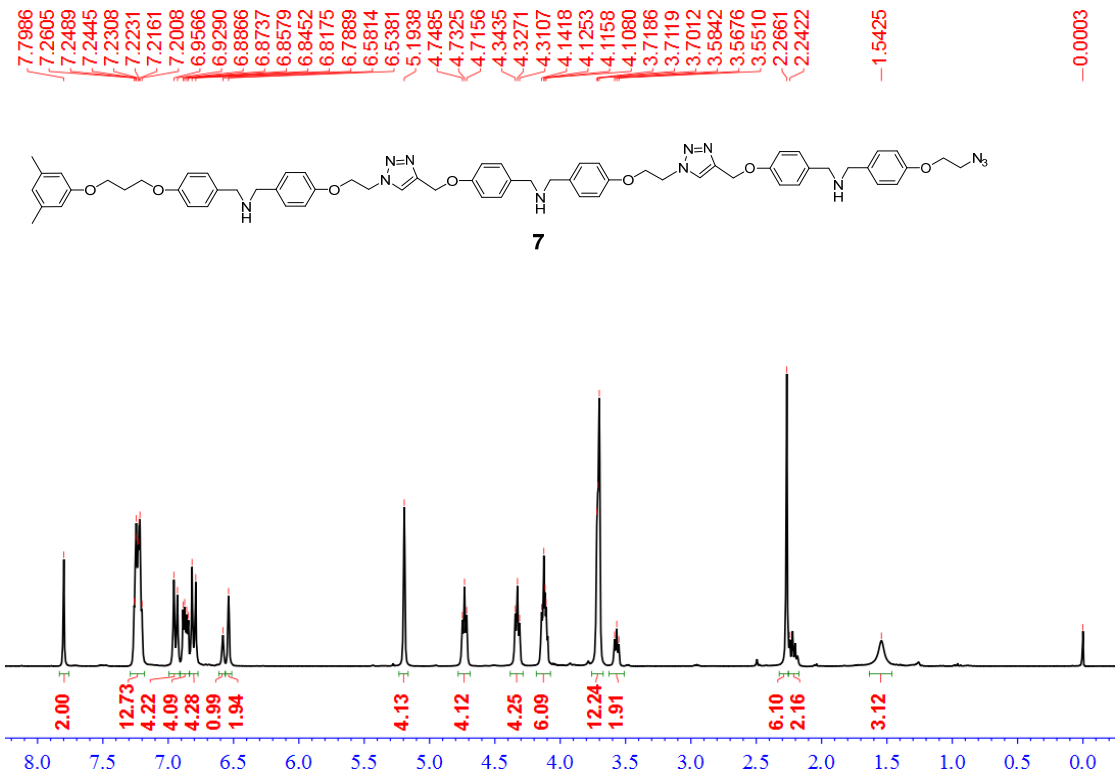


Fig. S31. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of compound **7**.

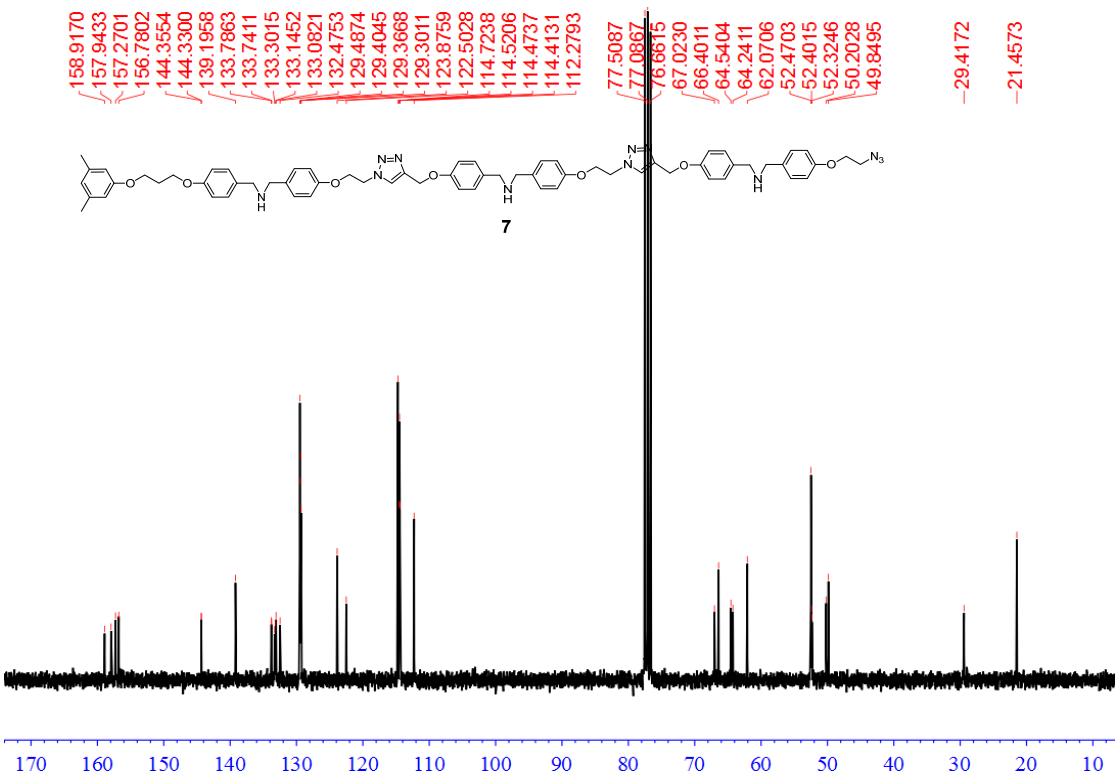


Fig. S32. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of compound **7**.

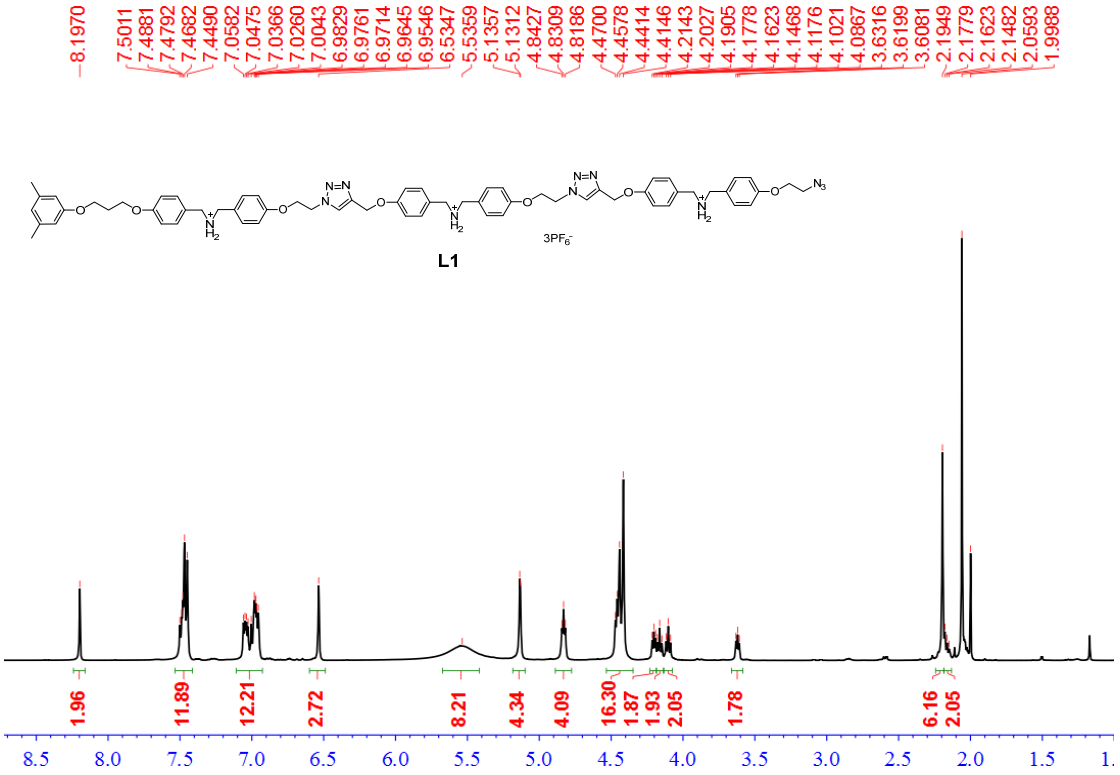


Fig. S33. ^{1}H NMR spectrum (acetone-d_6, 300 MHz, 298 K) of compound **L1**.

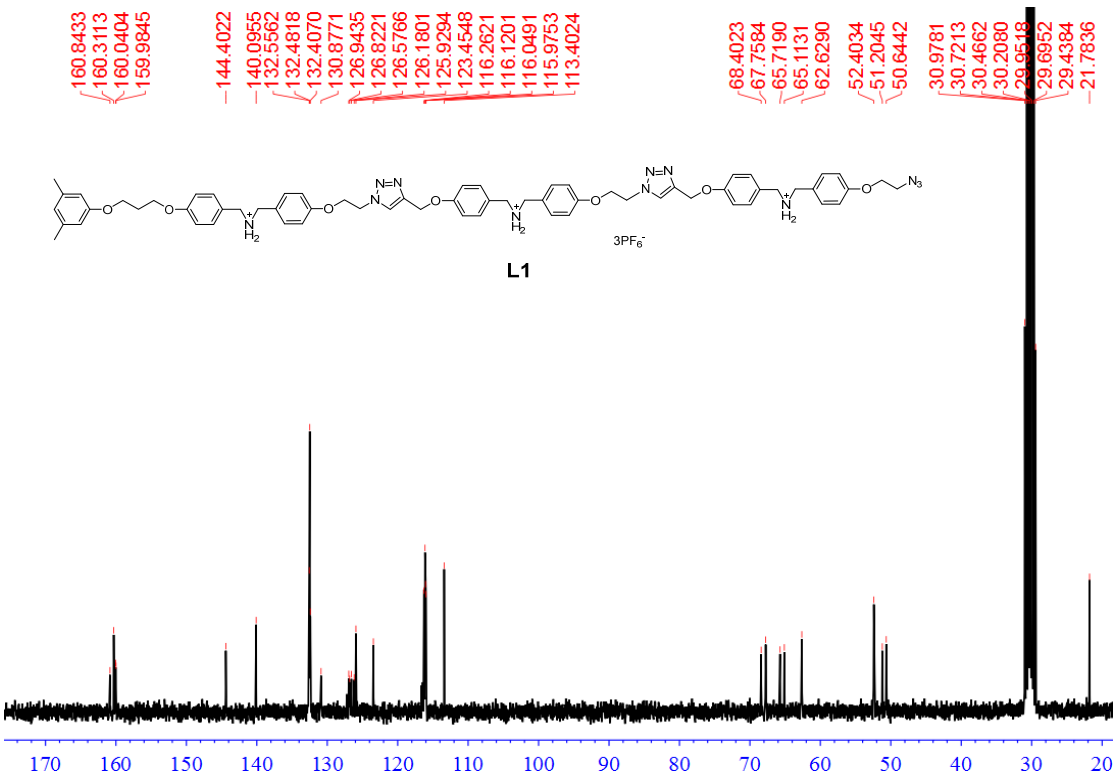


Fig. S34. ^{13}C NMR spectrum (acetone-d_6, 75 MHz, 298 K) of compound **L1**.

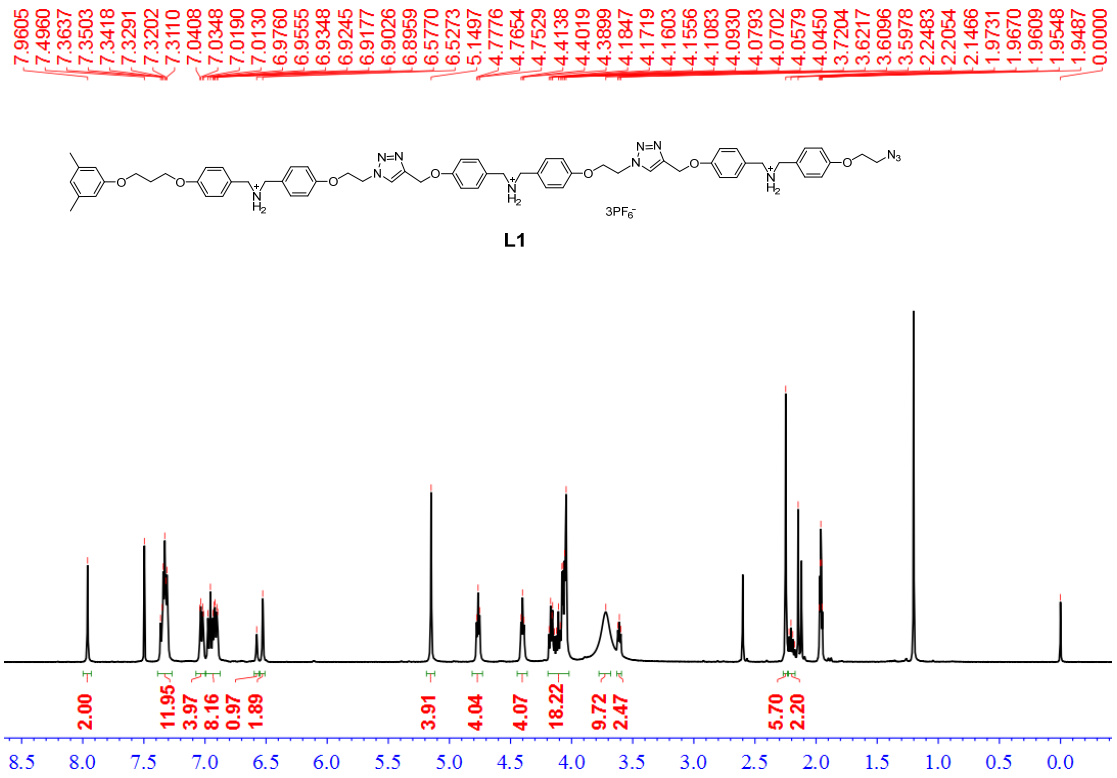


Fig. S35. ^{1}H NMR spectrum ($CDCl_3$:CD_3CN=1:1, 600 MHz, 298 K) of compound **L1**.

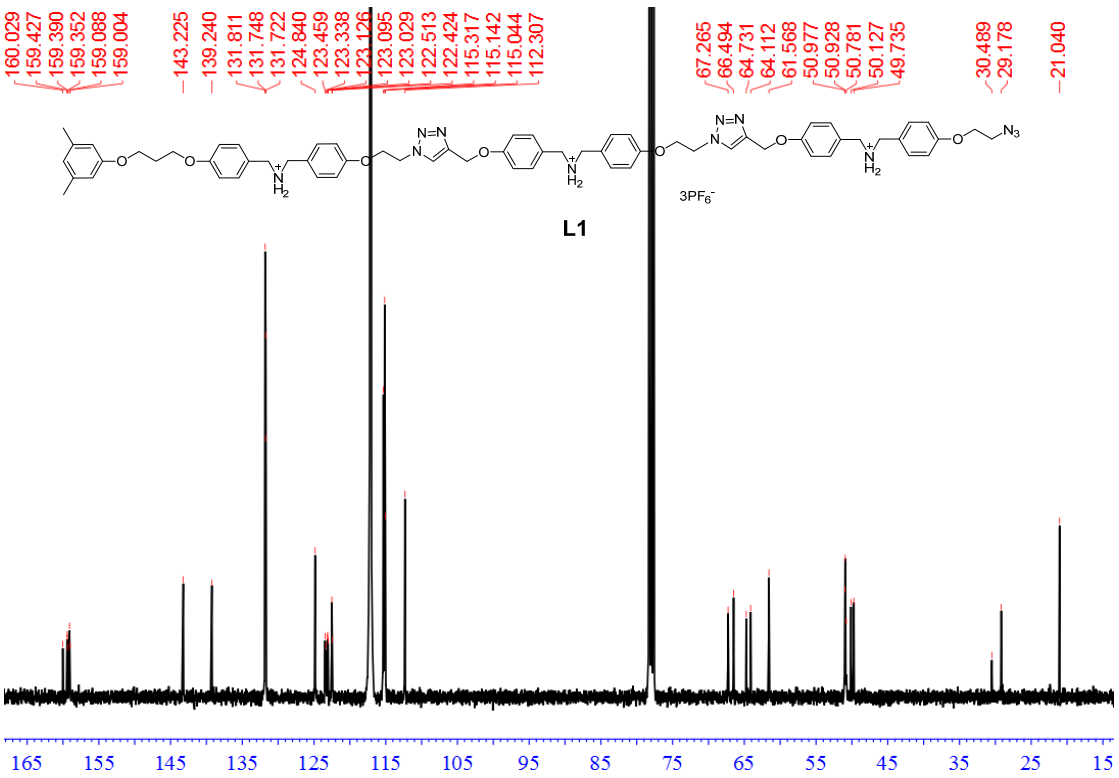


Fig. S36. ^{13}C NMR spectrum ($CDCl_3$:CD_3CN=1:1, 150 MHz, 298 K) of compound **L1**.

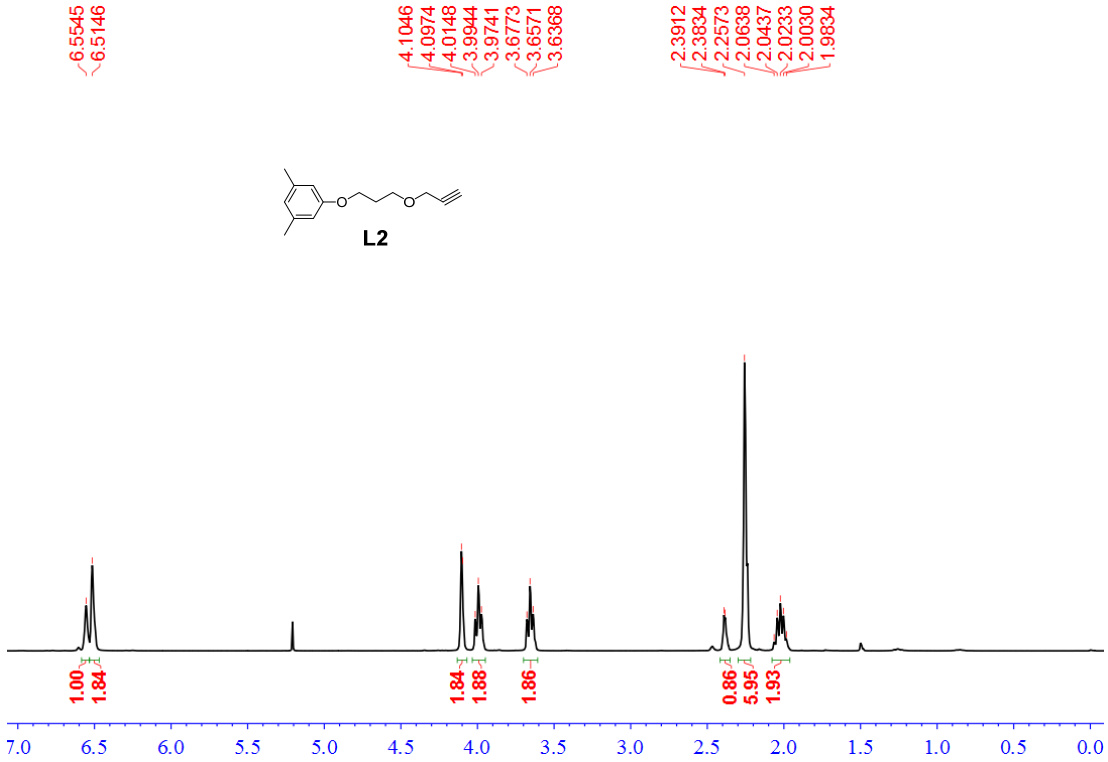


Fig. S37. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of compound **L2**.

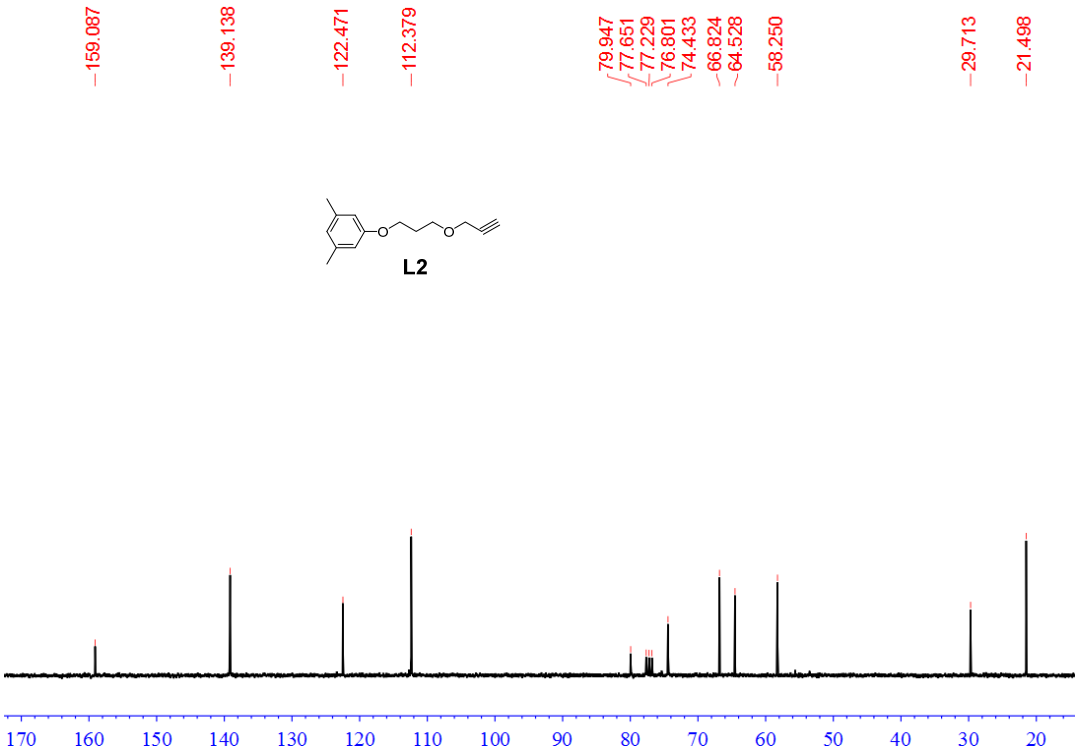


Fig. S38. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of compound **L2**.

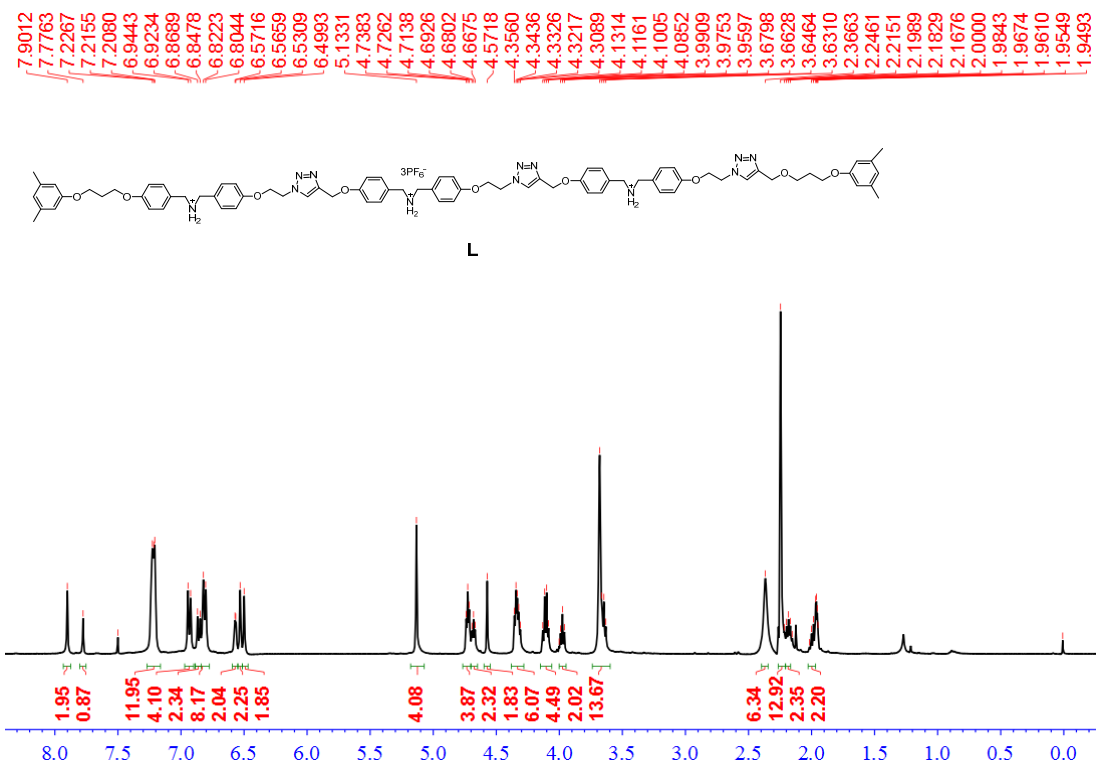


Fig. S39. ^{1}H NMR spectrum ($CDCl_3$:CD_3CN=1:1, 600 MHz, 298 K) of compound **L**.

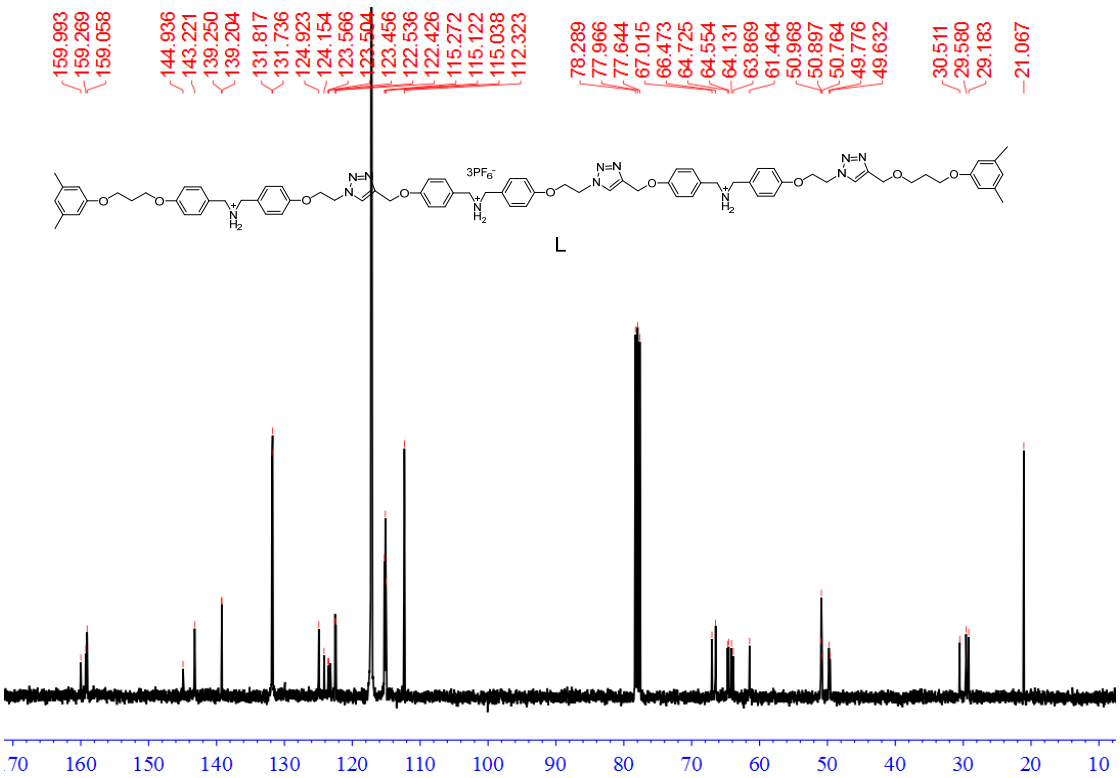


Fig. S40. ^{13}C NMR spectrum ($CDCl_3$:CD_3CN=1:1, 150 MHz, 298 K) of compound **L**.

7. References

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