Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Successive Catalytic Reactions Specific to Pd-Based Rotaxane Complexes as a Result of Wheel Translation along the Axle

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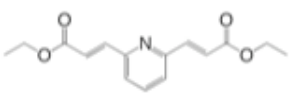
Experimental Section

General Methods. All reactions dealing with air and moisture-sensitive compounds were conducted under an argon atmosphere. Dichloromethane and toluene were dried over freshly activated molecular sieves 4 A (MS 4A). Acetonitrile was dried over freshly activated molecular sieves 3 A (MS 3A).

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL AL-400 spectrometer using $CDCl_3$ and toluene–d_8 as the solvents, calibrated using residual undeuterated solvent or tetramethylsilane as the internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Melting points were measured on a MELTING POINT APPARATUS SMP3 (Stuart Scientific) instrument. FAB HR-MS spectra were recorded on a Nihondensi JMS-700 spectrometer. All measurements for **9** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The structure of **9** was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Methyl alcohol solvent molecule was treated isotropically and the H atom of hydroxyl group of methyl alcohol was not decided due to the data quality.

The compounds **1**, **2**, **3**, **7** and **8** were prepared according to the literature : Y. Furusho, T. Matsuyama, T. Takata, T. Moriuchi, T. Hirao, *Tetrahedron Lett.* **2004**, *45*, 9593. The other chemicals from commercial sources were used without further purification as obtained. All compounds given below bear the same foumula numbers as used in the main text. Compounds unlabeled in the main text are labeled with letters [A–G].

Experimental Procedure.



A

Synthesis of diester **A**. A mixture of 2,6-pyrdinedicarboxydialdehyde (5.00 g, 36.9 mmol) and (carboethoxymethylene)triphenylphosphorane (33.5 mg, 96.1 mmol) in THF (360 mL) was refluxed for 16 h. The mixture was cooled to room temperature and concentrated in vacuo. The crude material was

purified by flash column chromatography on silica gel (CH_2Cl_2) to give diester **A** (7.23 g, 72%) as a white solid. Recrystallization from hexane gave white needles: m.p. 67.7–69.0 ℃ ; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) : δ 7.73 (t, *J* = 8.0 Hz, 1H, py-H), 7.67 (d, *J* = 15.6 Hz, 2H, CH), 7.37 (d, *J* = 8.0 Hz, 2H, OCH_2), 7.04 (d, *J* = 15.6 Hz, 2H, CH), 4.27 (q, *J* = 7.2 Hz, 4H, OCH_2), 1.34 (t, *J* = 7.2 Hz, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 152.8, 142.6, 137.5, 124.5, 123.0, 60.6, 14.1 ppm. IR (KBr) : 3076, 2978,1705, 1644, 1577, 1474, 1452, 1369, 1323, 1303, 1226, 1200, 1169, 1034, 1004, 991, 889, 816, 754, 700, 601 cm^{-1}. FAB HR-MS (matrix : NBA) Calcd for $C_{15}H_{17}NO_4$ $[M + H]^+$, m/z 176.1236, found : 176.1240.

Synthesis of diol **4**. To a solution of diester **A** (4.00 g, 14.5 mmol) in CH_2Cl_2 (70 mL) was added diisobutylaluminium hydride (DIBAL-H) (1.0 M in hexane, 75.5 mL, 76 mmol) at –78 ℃ and stirred for 3 h. The reaction was quenched by the addition of sat. aq. Rochelle salt at 0 ℃, diluted with CH_2Cl_2 and warmed to room temperature. The organic/aqueous layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (x 3). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by recrystallization from $CHCl_3$ to give diol **4** (1.62 g, 58%) as colorless plates : m.p. 67.5–68.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ 7.58 (t, *J* = 8.0 Hz, 1H, py-H), 7.12 (d, *J* = 8.0 Hz, 2H, py-H), 6.92 (dt, *J* = 16, 4.0 Hz, 2H, CHCH), 6.72 (td, *J* = 16, 1.6 Hz, 2H, $CHCH_2$), 4.40 (dd, *J* = 4.0, 1.6 Hz, 4H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 136.9, 134.0, 129.8, 119.9, 62.9 ppm. IR (KBr) : 3272, 3017, 2880, 1802, 1657, 1584, 1563, 1455, 1366, 1311, 1293, 1275, 1224, 1186, 1160, 1083, 994, 961, 906, 833, 764, 612, 525, 457, 439 cm^{-1}. FAB HR-MS (matrix : NBA) Calcd for $C_{11}H_{13}NO_2$ $[M + H]^+$, m/z 192.1025, found : 192.1024.

Synthesis of Rotaxane **6** (pseudorotaxane **5**). A mixture of diol **4** (109 mg, 0.575 mmol) and Pd complex **7** (400 mg, 0.575 mmol) in CH_2Cl_2 (5 mL) was stirred for 2 h at room temperature. The solution was concentrated in vacuo. The crude material was used for the next reaction without further purification. The mixture was dissolved in CH_2Cl_2 (5 mL). After the addition of a solution of endcap **8** (737 mg, 1.39 mmol) in CH_2Cl_2 (5 mL) and dibutyltin dilaurate (DBTDL) (50 μL, 88.0 μmol), the resulting mixture

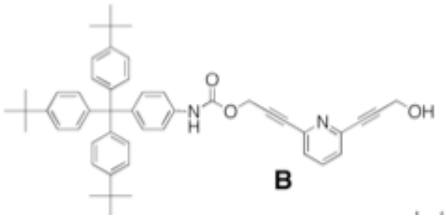
was stirred for 19 h at room temperature. The solution was concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel ($CHCl_3$, MeOH = 30/1) to give rotaxane **6** (901 mg, 83%) as a pale yellow solid. Recrystallization from *i*-PrOH/hexane gave pale yellow plates: m.p. 234.0 ℃ (decomp.) ; ^{1}H NMR (400 MHz, toluene-d_8, 70 ℃) δ 7.95 (s, 2H, -NH), 7.74 (d, J = 16 Hz, 2H, CHCH), 7.57 (d, J = 8.8 Hz, 4H, Ar-H), 7.45 (d, J = 7.6 Hz, 2H, py-H), 7.35 (m, 16H, Ar-H, py-H), 7.18 (d, J = 8.8 Hz, 12H, Ar-H), 6.91 (t, J = 8.0 Hz, 1H, py-H), 6.63 (d, J = 8.0 Hz, 2H, py-H)、6.47 (d, J = 8.8 Hz, 4H, Ar-H), 6.38 (d, J = 8.8 Hz, 4H, Ar-H), 5.85 (dt, J = 16, 5.6 Hz, 2H, $CHCH_2$), 4.51 (d, J = 5.6 Hz, 4H, CH_2), 4.28 (s, 4H, CH_2), 3.68 (br, 4H, CH_2), 3.44-3.36 (m, 12H, CH_2), 1.24 (s, 54H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃) δ 170.9, 157.5, 157.0, 153.2, 152.6, 148.2, 143.9, 142.0, 140.5, 138.1, 135.7, 133.4, 131.7, 130.9, 130.6, 129.6, 128.4, 124.7, 124.3, 124.0, 119.8, 117.0, 113.1, 70.6, 70.6, 69.7, 66.9, 64.0, 63.2, 49.1, 34.6, 34.5, 34.3, 31.6, 31.5, 31.4, 31.2, 25.3, 25.2, 22.6, 20.7, 14.1 ppm. IR (KBr) 3437, 2961, 1733, 1596, 1509. 1465, 1363, 1320, 1217, 1108, 1057, 1018, 953, 822, 763, 676, 581, 507, 429, 420, 411 cm^{-1}. FAB HR-MS (matrix : NPOE) Calcd for $C_{116}H_{130}N_6O_{11}Pd$ $[M + H]^+$, m/z 1889.8943, found : 1889.8932.

Synthesis of Rotaxane **9**: To a solution of rotaxane **3** (4.0 mg, 2.1 μmol) in MeOH–THF (4/1, 2.5 mL) was added dropwise a solution of $Mg(OMe)_2$ in MeOH (6.0 wt%, 73 μL, 42 μmol) was refluxed for 10 min. The mixture was cooled to room temperature, and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel ($CHCl_3$–MeOH = 100/1) to give rotaxane **9** (2.72 mg, 68%) as yellow plates: m.p. 265.0 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ 7.51 (brd, 1H, py-H), 7.41 (brd, 2H, py-H), 7.29 (brd, 12H, Ar-H), 7.26 (m, 4H, Ar-H), 7.22 (3H, py-H), 7.00 (4H, Ar-H), 6.87 (12H, Ar-H), 6.34 (2H, C=CH), 6.20 (4H, Ar-H), 6.14 (4H, Ar-H), 5.10 (4H, CH_2), 4.06 (brd, 4H, CH_3), 3.93 (4H, CH_2O), 3.78 (12H, CH_2O), 1.30 (s, 54H, CH_3) ppm. Anal, calcd for $C_{116}H_{126}N_6O_{11}Pd{\cdot}2H_2O$: C, 72.46; H, 6.81; N, 4.37%, found. C, 72.60; H, 6.99; N, 4.23%. Crystals of **9** suitable for X-ray analysis were obtained by recrystallization from mixed solvent of CH_2Cl_2 and MeOH. Single crystal data of **9**: $C_{116}H_{126}N_6O_{11}Pd{\cdot}5(CH_2Cl_2){\cdot}4(CH_3OH)$ M_w = 2439.54, yellow plate, size: 0.60 ×

0.10 × 0.10 mm, triclinic, space group *P-1*, $Z = 2$, *a* : 14.624 (5) Å, *b* : 19.851 (16) Å, *c* : 23.822 (4) Å, α : 85.30 (3)°, β : 79.42 (3)°, γ : 69.09 (4)°, *V* : 6349 (6) Å^3, $D = 1.276$ Mg m^{-3}, $\mu = 0.418$ mm^{-1}, $T = 223(1)$ K, $F(000) = 2560.0$; 57449 reflections measured, of which 28260 were unique ($R_{int} = 0.068$). 1424 refined parameters, final $R_1 = 0.0924$ for reflections with $I > 2\sigma(I)$, $wR = 0.2820$ (all data), GOF = 1.012. Final largest diffraction peak and hole: 1.57 and –0.98 e Å^3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 756922 for **9**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK. Fax: (+44)-1223-336-033 e-mail: deposit@ccdc.cam.ac.uk http://www.ccdc.cam.ac.uk/deposit

Synthesis of Rotaxane **10 (anti)** and **11 (syn)**. To a solution of rotaxane **6** (150 mg, 79 μmol) in MeOH–THF (4/1, 0.7 mL) was added dropwise a solution of $Mg(OMe)_2$ in MeOH (6.0 wt%, 2.63 mL, 1.6 mmol) was refluxed for 10 min. The mixture was cooled to room temperature, and concentrated *in vacuo* to give a mixture of **10** and **11** in a quantitative yield. The compounds were purified by flash column chromatography on silica gel ($CHCl_3$–MeOH = 100/1) to give rotaxane **10** (36.0 mg, 25%) and rotaxane **11** (63.8 mg, 43%) as pale yellow solids, respectively. Recrystallization from toluene gave pale yellow needles: **10** : m.p. 256.0 ℃ (decomp.) ; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ 7.60 (brd, 3H, py-H), 7.34 (brd, 1H, py-H), 7.28－7.21 (m, 16H, Ar-H), 7.10－7.03 (m, 16H, Ar-H), 6.81 (d, $J = 8.0$ Hz, 2H, py-H), 6.28 (d, $J = 8.0$ Hz, 2H, Ar-H), 6.14 (d, $J = 8.0$ Hz, 2H, Ar-H), 5.89 (d, $J = 8.4$ Hz, 2H, Ar-H), 5.78 (d, $J = 8.4$ Hz, 2H, Ar-H), 4.42 (brd, 4H, CH, CH_2), 4.00 (brd, 6H, CH_2O), 3.91 (brd, 4H, CH_2), 3.75－3.68 (m, 12H, CH_2), 3.07 (brd, 2H, CH_2), 1.27 (s, 54H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃) δ 171.1, 170.9, 159.1, 157.4, 156.9, 155.8, 152.2, 151.9, 148.2, 146.8, 143.5, 140.7, 139.1, 133.0, 132.9, 132.3, 131.8, 130.5, 128.5, 128.2, 125.2, 124.8, 124.4, 123.3, 123.0, 114.6, 114.5, 70.8, 70.6, 70.5, 70.0, 69.8, 69.7, 67.6, 67.2, 66.0, 63.5, 54.6, 50.1, 49.5, 42.0, 34.3, 31.4 ppm. IR (neat): 2961 (C-H), 1761 (C=O), 1606, 1509, 1459, 1401, 1241, 1110, 1019, 823, 759, 676, 580, 420, 410 cm^{-1}. FAB HR-MS (matrix : NPOE) Calcd for $C_{116}H_{130}N_6O_{11}Pd$ $[M + H]^+$, m/z 1889.894, found : 1889.8864.

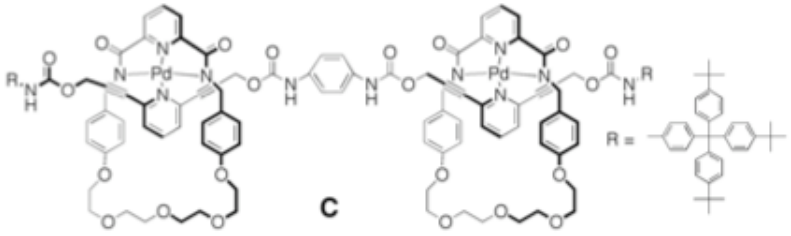
Recrystallization of **11** from toluene gave pale yellow needles: m.p. 280.0 ℃ (decomp.) ; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ 7.77 (t, *J* = 8.0 Hz, 1H, py-H), 7.39 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.31－7.20 (m, 15H, Ar-H, py-H), 7.10－7.00 (m, 14H, Ar-H, py-H), 6.80 (d, *J* = 8.8 Hz, 4H, Ar-H)、6.22 (d, *J* = 8.4 Hz, 4H, Ar-H), 6.07 (d, *J* = 8.4 Hz, 4H, Ar-H), 4.36 (brd, 2H, CH), 4.17－4.11 (m, 6H, CH_2), 4.01－3.91 (m, 8H, CH_2), 3.73－3.65 (m, 12H, CH_2), 2.63 (brd, 2H, CH_2), 1.29 (s, 54H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃) δ 171.2, 159.1, 157.6, 155.5, 151.6, 148.3, 145.6, 143.5, 140.7, 139.3, 137.8, 133.0, 131.4, 130.5, 129.0, 128.5, 128.2, 125.2, 124.9, 124.4, 124.3, 121.6, 114.9, 77.2, 70.4, 70.1, 69.7, 67.5, 65.8, 63.3, 54.4, 49.7, 41.5, 34.3, 31.4, 21.5 ppm. IR (neat): 2960 (C-H), 1761 (C=O), 1606, 1508, 1463, 1400, 1243, 1110, 1053, 1019, 823, 759, 705, 675, 580 cm^{-1}. FAB HR-MS (matrix : NPOE) Calcd for $C_{116}H_{130}N_6O_{11}Pd$ $[M + Na]^+$, m/z 1911.8762, found : 1911.8765.



B

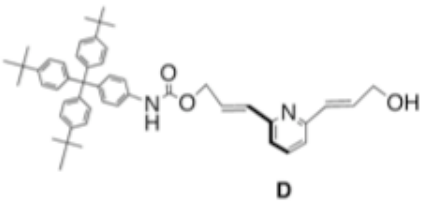
Synthesis of Alcohol **B**. To a solution of 2,6-bis(3-hydroxy-1-propynyl)pyridine **1** (4.10 g, 21.9 mmol) in THF (70 mL) was added DBTDL (327 μL, 0.547 mmol) and dropwise a solution of isocyanate **8** (2.90 g, 5.47 mmol) in THF (60 mL) over 30 min under Ar. The mixture was stirred for 15 h at room temperature. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel with CH_2Cl_2 : MeOH (20 : 1) and then by recrystalization from $CHCl_3$/hexane to give **B** (83%) as a white solid: m.p. 204 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) *δ* 7.63 (t, *J* = 8.1 Hz, 1H), 7.41–7.37 (m, 2H), 7.24–7.07 (m, 16H), 6.67 (s, 1H), 5.00 (s, 2H), 4.50 (d, *J* = 6.5 Hz, 2H), 1.78 (t, *J* = 6.5 Hz, 1H), 1.30 (s, 27 H) ppm; FAB-MS (matrix : *m*-nitrobenzyl alcohol) Calcd for $C_{49}H_{52}N_2O_3$ $[M + H]^+$, m/z 717.3, found : 717.4.

Synthesis of [2]Rotaxanate **12** and [3]Rotaxanate **C**. A mixture of alcohol **B** (211 mg, 0.294 mmol) and macrocyclic palladium complex **7** (200 mg, 0.294 mmol) in CH_2Cl_2 (5.0 mL) was stirred for 1 h at room temperature. The solvent was evaporated under reduced pressure to give the pseudorotaxanate, to which were successively added 4,4'-phenylenediisocyanate (47.0 mg, 0.294 mmol), THF (10mL) and DBTDL (8.80 μL, 14.7 μmol). The mixture was stirred for 0.5 h at room temperature. To it were added a solution of pseudorotaxane (211 mg, 0.294 mmol) in THF (5.0 mL) and DBTDL, and the resulting mixture was stirred for 3 h at room temperature. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel with CH_2Cl_2 : MeOH (50 : 1) and then by preparative HPLC with $CHCl_3$ to give **12** (44%) and **C** (38%). **12**: m.p. 176.0 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ 8.50–8.25 (m, 4H), 7.91 (d, J = 7.1 Hz, 2H), 7.82 (t, J = 7.8 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H) 7.39–7.00 (m, 41H), 6.49 (s, 8H), 4.98 (s, 2H), 4.96 (s, 2H), 4.82 (s, 2H), 4.71 (s, 4H), 4.42–3.45 (m, 16H), 1.29 (s, 27H), 1.28 (s, 27H) ppm; Anal. calcd for $C_{135}H_{139}N_5O_{15}Pd\cdot 2H_2O$: C, 71.43; H, 6.35; N, 5.55%. found: C, 71.33; H, 6.65; N, 5.56%.



C

C: m.p. 172 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ 8.55 (s, 2H), 8.48 (s, 2H), 7.96 (br, 2H), 7.85 (t, J = 7.6 Hz, 2H), 7.78 (d, J = 7.6 Hz), 7.50 (s, 4H), 7.37–7.09 (m, 36H), 6.51–6.49 (m, 16H), 4.82 (s, 4H), 4.77 (s, 4H), 4.25–3.51 (m, 40H) 1.23 (s, 54H) ppm; Anal. calcd for $C_{164}H_{170}N_{12}O_{22}Pd_2\cdot H_2O\cdot CHCl_3$: C, 65.83; H, 5.76; N, 5.58. found: C, 65.80; H, 5.79; N, 5.53.

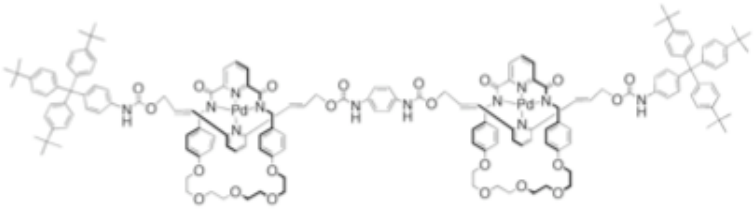


D

Synthesis of axle **D**. To a mixture of diol **4** (700 mg, 3.66 mmol) and DBTDL (50 μL, 88.0 μmol) in CH_2Cl_2 (20 mL) was added dropwise a solution of endcap **8** (485 mg, 0.915 mmol) in CH_2Cl_2 (10 mL) and stirred for 18 h. The solution was concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel ($CHCl_3$–MeOH = 30/1) to give an axle **D** (392 mg, 15 %) as a white solid. Recrystallization from MeOH gave white plates: m.p. 202.0–203.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ 7.58 (t, *J* = 7.6 Hz, 1H, py-H), 7.22 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.13 (brd, 4H, py-H, Ar-H), 7.08 (d, *J* = 8.0 Hz, 6H, Ar-H), 6.95－6.84 (m, 2H, CHCH), 6.75－6.64 (m, 3H, CHCH, -NH), 4.87 (d, *J* = 5.6 Hz, 2H, CH_2), 4.39 (s, 2H, $CHCH_2$), 1.29 (s, 27H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃) δ 154.9, 154.1, 148.2, 143.8, 142.3, 137.0, 135.4, 134.2, 131.9, 131.7, 130.6, 129.3, 128.5, 124.0, 120.2, 119.9, 117.3, 63.2, 62.6, 50.4, 34.2, 31.3 ppm. IR (KBr) : 3433, 2962, 1735, 1609, 1508, 1457, 1215, 1018, 823, 583, 417 cm^{-1}. FAB HR-MS (matrix : NBA) Calcd for $C_{48}H_{53}N_2O_3$ $[M + H]^+$, m/z 721.4369, found : 721.4358.

Synthesis of 2st[2]Rotaxane **13** (2st[3]Rotaxane **E**). A mixture of axle **D** (100 mg, 0.138 mmol) and Pd complex **7** (96.5 mg, 0.138 mmol) in CH_2Cl_2 (5.0 mL) was stirred for 1 h at room temperature. The solution was concentrated in vacuo. The crude material was used for the next reaction without further purification. The mixture was dissolved in THF (5.0 mL). After the addition of 4,4'-diphenylisocyanate (22.1 mg, 0.138 mmol) in THF (5.0 mL) and DBTDL (50 μL, 88.0 μmol), the resulting mixture was stirred for 0.5 h at room temperature. A solution of axle **D** (100 mg, 0.138 mmol) was added to the mixture, and the reaction mixture was stirred overnight at room temperature. The solution was concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel ($CHCl_3$–MeOH = 35/1) to give 2st[2]Rotaxane **13** (61.9 mg, 20 %) and 2st[3]Rotaxane **E** (76.9 mg, 19 %) as pale yellow plates, respectively. **13** : m.p. 217.0 ℃ (decomp.) ; ^{1}H NMR (400 MHz, $CDCl_3$, 67 ℃) δ 7.91 (t, *J* = 8.0 Hz, 1H, py-H), 7.73 (d, *J* = 7.6 Hz, 2H, py-H), 7.68 (t, *J* = 7.6 Hz, 1H, py-H), 7.66－7.55 (m, 3H, olefin, -NH), 7.53 (t, *J* = 7.6 Hz, 2H, py-H), 7.30－7.21 (m, 24H, Ar-H), 7.12－7.06 (m, 20H, Ar-H), 6.86－6.83 (m, 2H, CHCH)、6.75－6.69 (m, *J* = 5.2, 2H, CHCH), 6.39 (d, *J* = 8.8 Hz,

4H, Ar-H), 6.33 (d, J = 8.8 Hz, 4H, Ar-H), 6.15－5.98 (m, 2H, $CHCH_2$), 4.85 (t, J = 4.8 Hz, 4H, CH_2), 4.57 (brd, 4H, CH_2), 3.95 (brd, 6H, CH_2), 3.76 (d, J = 4.0 Hz, 4H, CH_2), 3.65－3.57 (m, 8H, CH_2), 1.29 (s, 27 H, CH_3), 1.28 (s, 27 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃) δ 177.8, 170.9, 157.5, 154.1, 153.28, 152.5, 148.2, 143.9, 143.8, 138.2, 137.1, 133.2, 132.5, 131.7, 130.6, 128.4, 124.9, 124.0, 120.8, 119.8, 117.5, 113.1, 77.2, 70.6, 70.5, 69.7, 66.9, 64.9, 6.40, 63.2, 63.2, 49.2, 34.3, 34.2, 34.0, 31.9, 31.3, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 29.2, 29.1, 24.8, 22.7, 14.1 ppm. IR (KBr) 3399, 3030, 2960, 2867, 1732, 1594, 1509, 1458, 1407, 1362, 1312, 1214, 1099, 1056, 1017, 822, 761, 705, 676, 581, 525, 421 cm^{-1}. FAB HR-MS (matrix : NBA + NaI) Calcd for $C_{135}H_{147}N_9O_{15}Pd$ $[M + Na]^+$, m/z 2262.9984, found : 2262.9970.



E

E : m.p. 228.0 ℃ (decomp.) ; ^1H NMR (400 MHz, $CDCl_3$, 25 ℃) δ 7.86 (t, J = 8.0 Hz, 2H, py-H), 7.73－7.71 (m, 6H, py-H), 7.32－7.07 (m, 36H, Ar-H), 6.40－6.29 (m, 16H, Ar-H), 4.81 (s, 2H), 4.61 (s, 4H, CH_2), 4.56 (s, 4H, CH_2), 3.96 (brd, 12H, CH_2), 3.77 (s, 8H, CH_2), 3.65－3.59 (m, 16H, CH_2), 1.29 (s, 54H, CH_3) ppm. IR (KBr) 3422, 2959, 2363, 1727, 1593, 1509, 1465, 1407, 1362, 1299, 1215, 1099, 1057, 1017, 952, 823, 760, 676, 582, 417 cm^{-1}. FAB HR-MS (matrix : NBA) Calcd for $C_{164}H_{178}N_{12}O_{22}Pd_2$ $[M + H]^+$, m/z 2882.1393, found : 2282.1458.

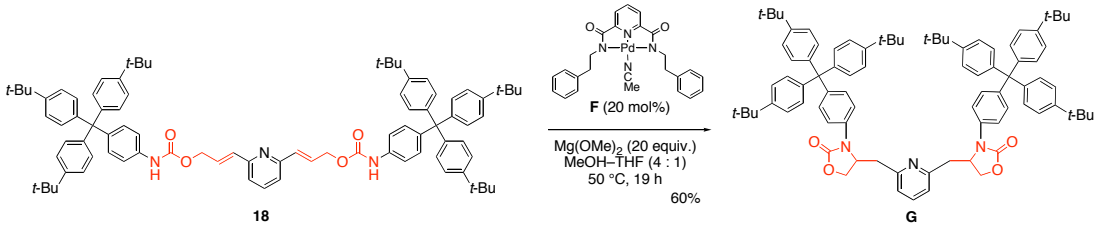
Synthesis of Axle **16**. To a mixture of diol **4** (300 mg, 1.57 mmol) and phenylisocyanate (748 mg, 6.28 mmol) in CH_2Cl_2 (5.0 mL) was added DBTDL (50 μL, 88.0 μmol) and the mixture was stirred for 18 h

at room temperature. The solution was concentrated *in vacuo*. The crude material was purified by recrystallization from *i*-PrOH to give Axle **16** (530 mg, 79 %) as white plates: m.p. 146.6-147.2 ℃ ; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ 7.60 (t, *J* = 8.0 Hz, 1H, py-H), 7.40 (d, *J* = 8.0 Hz, 4 H, Ar-H), 7.31 (t, *J* = 8.0 Hz, 4H, Ar-H), 7.16 (d, *J* = 8.0 Hz, 2H, Py-H), 7.07 (t, *J* = 8.0 Hz, 2H, Ar-H), 6.94－6.87 (m, 2H, CHCH), 6.75 (d, *J* = 16 Hz, 2H, CHCH), 6.69 (s, 2H, -NH), 4.89 (d, *J* = 6.0 Hz, 4H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃) δ 154.1, 153.2, 137.7, 137.0, 132.3, 128.9, 128.3, 123.4, 120.7, 118.6, 64.9 ppm. IR (KBr) : 3320, 1703, 1598, 1534, 1446, 1314, 1233, 1092, 1064, 1026, 966, 842, 766, 691, 509, 417 cm^{-1}. FAB-MS (matrix : NBA) Calcd for $C_{25}H_{23}N_3O_4$ $[M + H]^+$, m/z 430.1767, found : 430.1773.

Synthesis of dumbbell **18**. To a mixture of diol **4** (200 mg, 1.05 mmol) and endcap **8** (1.72 g, 3.14 mmol) in CH_2Cl_2 (5 mL) was added DBTDL (50 μL, 88.0 μmol) and the mixture was stirred for 18 h at room temperature. The solution was concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel ($CHCl_3$–hexane = 5/1) to give dumbbell **18** (1.04 g, 79 %) as a gray solid. Recrystallization from MeOH gave gray plates: m.p. 189.0–191.0 ℃; ^{1}HNMR (400 MHz, $CDCl_3$, 25 ℃) δ 7.66 (brd, 1H, py-H), 7.27－7.20 (m, 18 H, Ar-H), 7.13 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.08 (d, *J* = 6.8 Hz, 6H, Ar-H), 6.90 (brd, 4H, CHCH), 6.76 (brd, 2H, -NH), 4.89 (d, *J* = 3.6 Hz, 4H, CH_2), 1.29 (s, 54H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃) δ 153.4, 153.1, 148.2, 143.8, 142.5, 138.2, 135.3, 131.7, 130.6, 130.3, 124.0, 120.6, 117.4, 64.6, 63.2, 34.2, 31.3 ppm. IR (KBr) 3855, 3434, 2693, 1741, 1609, 1509, 1458, 1406, 1204, 1098, 822, 580 cm^{-1}. FAB HR-MS (matrix : NBA) Calcd for $C_{87}H_{100}N_3O_4$ $[M + H]^+$, m/z 1250.7714, found : 1250.7764.

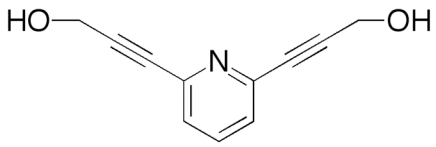
Typical procedure for catalytic reaction. To a mixture of Pd complex **7** (9.73 mg, 13.9 μmol) and axle **16** (30.0 mg, 69.9 μmol) in THF (0.14 mL) was added dropwise a solution of $Mg(OMe)_2$ in MeOH (121 mg, 1.40 mmol, 0.56 mL) was stirred at 50 ℃ for 19 h. The mixture was cooled to room temperature, and concentrated *in vacuo*. The crude material was purified by flash column

chromatography on silica gel ($CHCl_3$–MeOH = 15/1) to give axle **17** (22.0 mg, 73 %) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ 7.56－7.53 (m, 4H, Ph-H), 7.48 (t, J = 7.6 Hz, 1 H, py-H), 7.43－7.38 (m, 4H, Ph-H), 7.20 (t, J = 7.6 Hz, 2H, Ph-H), 6.90 (d, J = 7.6 Hz, 2H, py-H), 4.96 (brd, J = 4.4 Hz, 2H, $CHCH_2$), 4.54 (m, 2H, CH_2O), 4.36 (m, 2H, CH_2O), 3.22 (m, 2H, CH_2), 3.02 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃) δ 156.0, 137.1, 129.2, 125.1, 125.0, 122.3, 121.3, 121.2, 66.7, 55.6, 55.5, 39.4, 39.3 ppm. IR (KBr) : 3434, 2923, 1751, 1637, 1405, 1125, 471 cm^{-1}; FAB HR-MS (matrix : NBA + NaI) Calcd for $C_{25}H_{23}N_3O_4$ $[M + Na]^+$, m/z 452.1586, found : 452.1589.

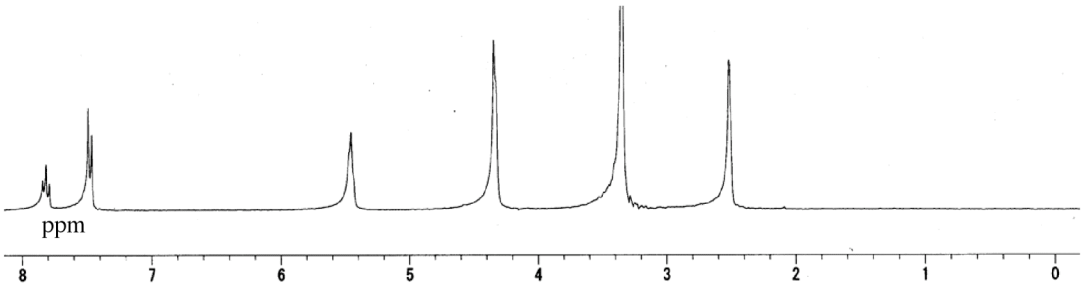


Synthesis of **G**. To a mixture of Pd complex **F** (7.2 mg, 14 μmol) and axle **18** (87.4 mg, 70.0 μmol) in THF (0.14 mL) was added dropwise a solution of $Mg(OMe)_2$ in MeOH (120.7 mg, 1.40 mmol, 0.56 mL). The mixture was stirred at 50 °C for 19 h, cooled to room temperature, and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (Hexane–EtOAc = 2/1) to give axle **G** (52.0 mg, 60 %) as a white foam: ^{1}HNMR (400 MHz, $CDCl_3$, 25 ℃) δ 7.43-7.35 (m, 5H, Ar-H), 7.26-7.20 (m, 16H, Ar-H), 7.09-7.06 (m, 12H, Ar-H), 6.86 (d, J = 7.7 Hz, 2H, Ar-H), 4.92 (brd, 2H, $CHCH_2$), 4.52-4.45 (m, 2H, CH_2O), 4.35-4.32 (m, 2H, CH_2O), 3.26 (brd, J = 14.8 Hz, 2H, CH_2), 3.05-2.98 (m, 2H, CH_2), 1.30 (s, 54H, CH_3) ppm. IR (neat) 3031, 2961, 2867, 1758, 1593, 1575, 1505, 1456, 1395, 1362, 1268, 1209, 1113, 1018, 969, 823, 756, 737, 704, 579 cm^{-1}. MALDI-TOF MS (matrix : CHCα) Calcd for $C_{87}H_{100}N_3O_4$ $[M + H]^+$, m/z 1250.7708, found : 1250.7735.

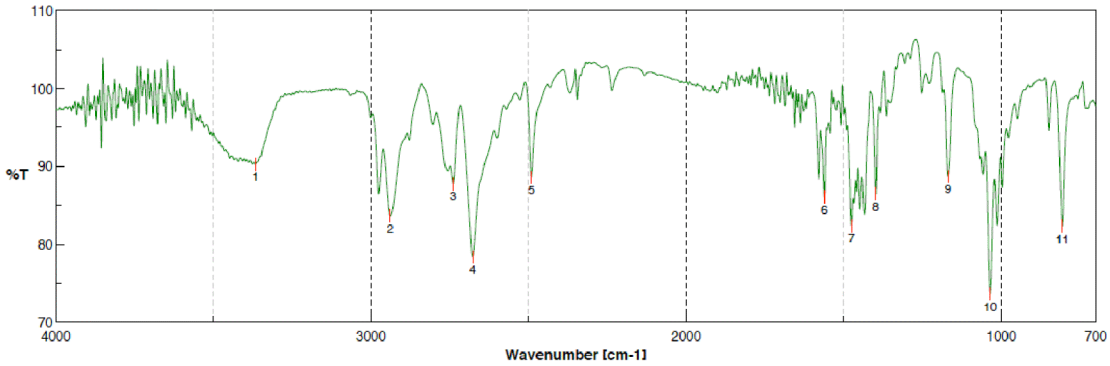
Figure (^{1}H NMR, IR)



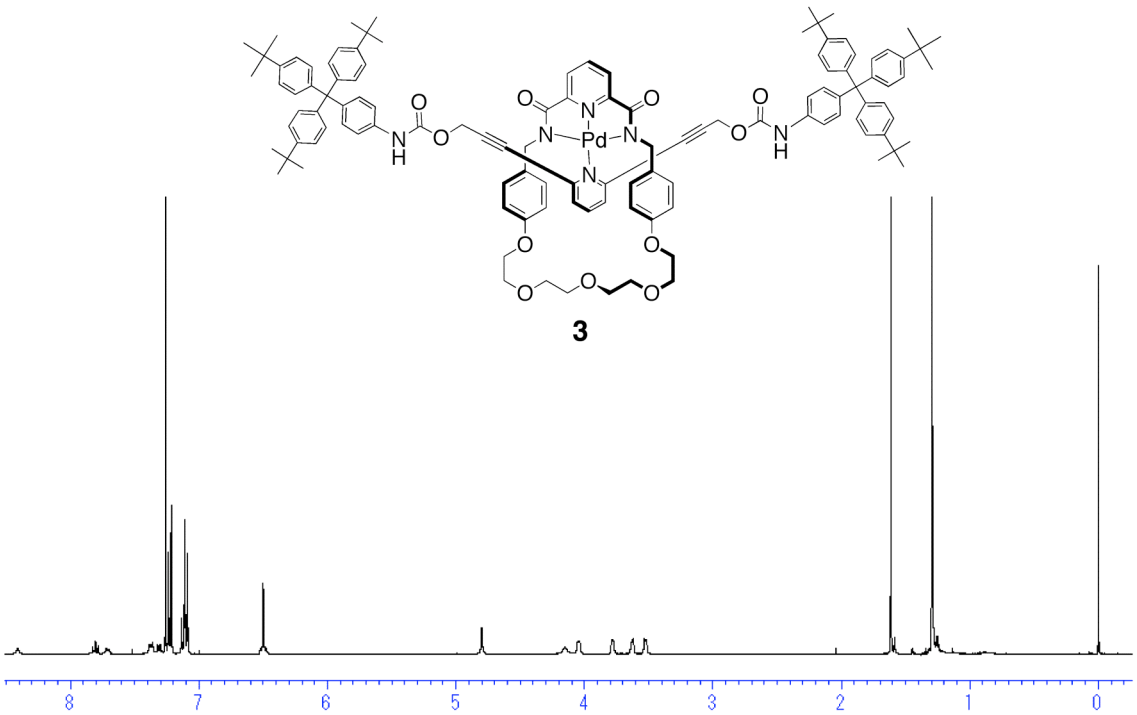
1



^{1}H NMR spectrum (300 MHz, DMSO–d_6, 298 K) of 1

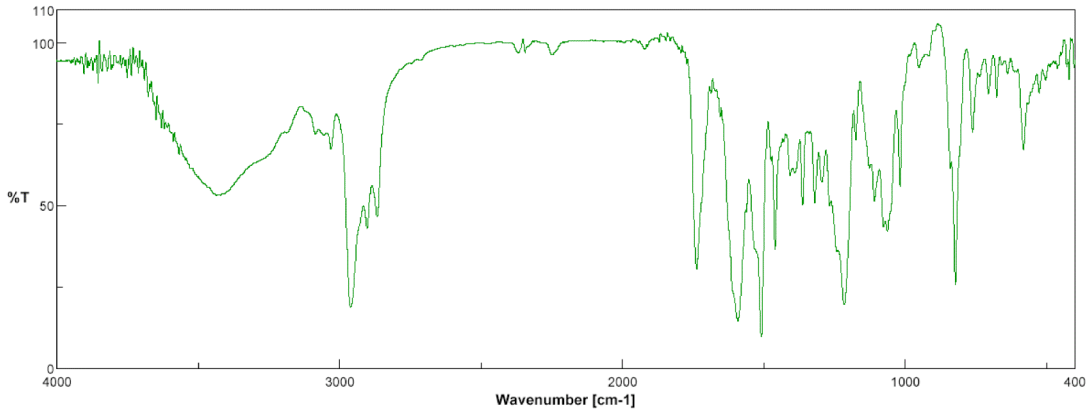


IR spectrum (KBr) of 1

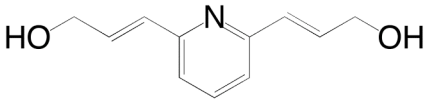


3

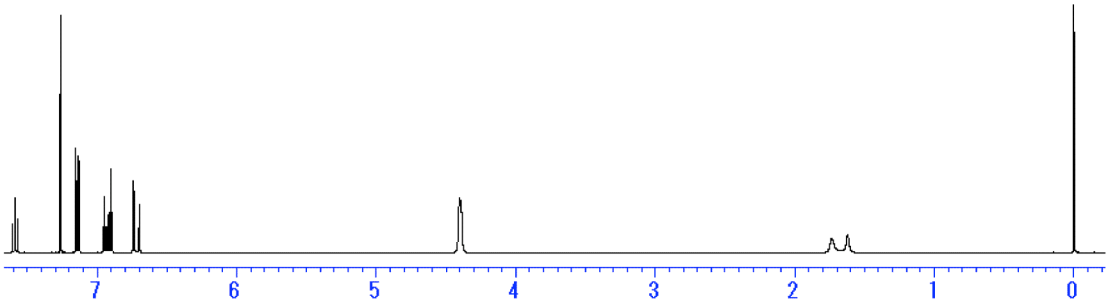
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of Rotaxane 3



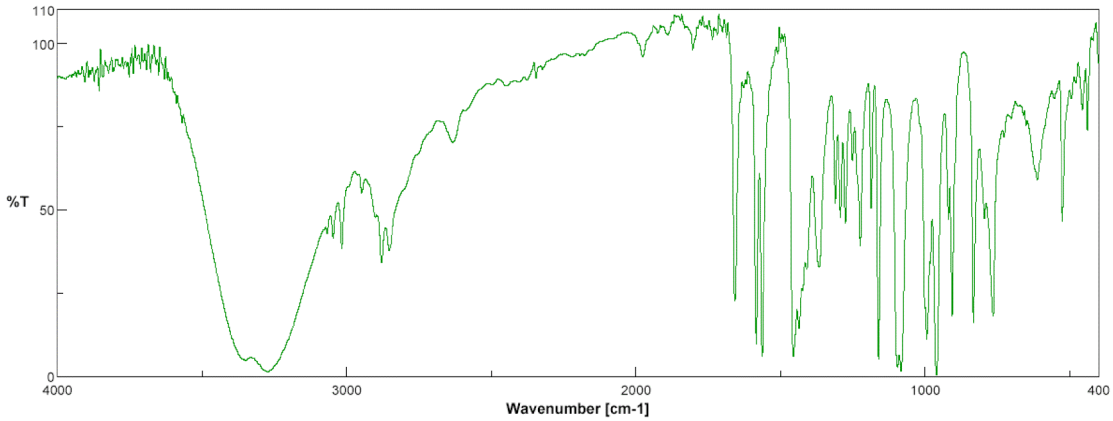
IR spectrum (KBr) of Rotaxane 3



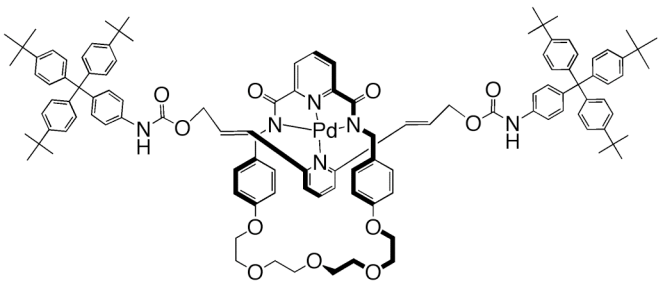
4



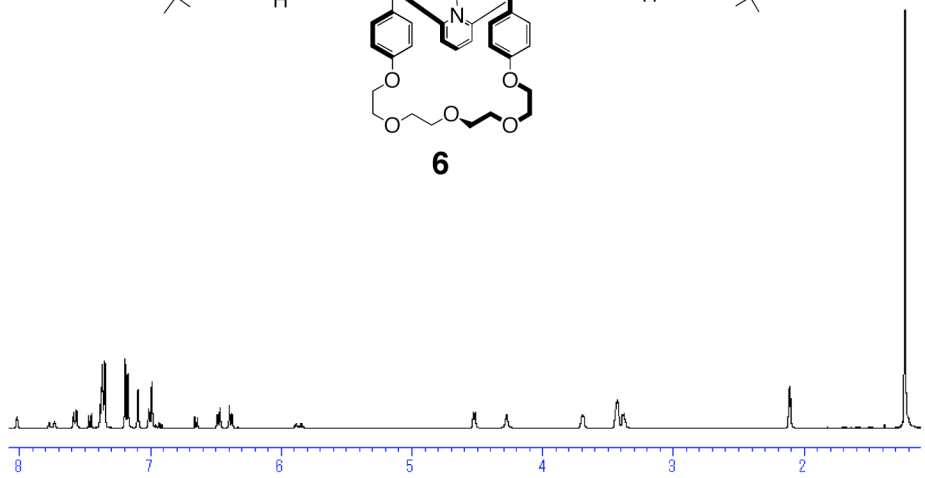
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of dialcohol 4



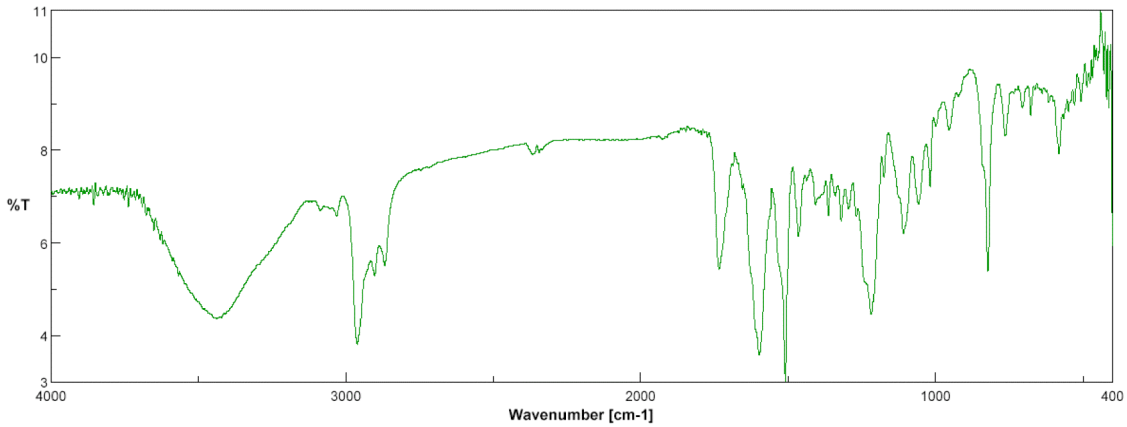
IR spectrum (KBr) of dialcohol 4



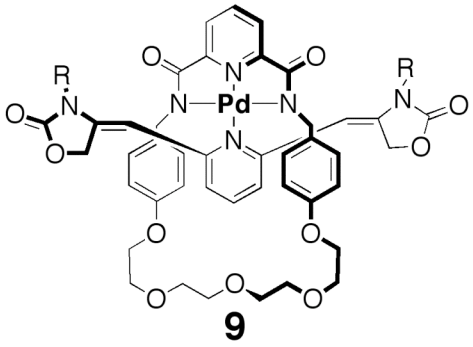
6



^{1}H NMR spectrum (400 MHz, toluene-d_8, 343 K) of Rotaxane 6

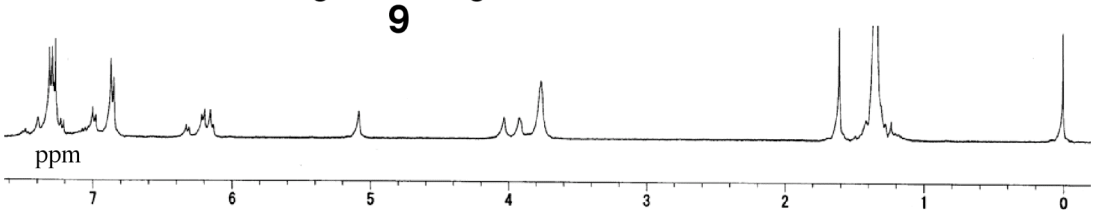


IR spectrum (KBr) of Rotaxane 6

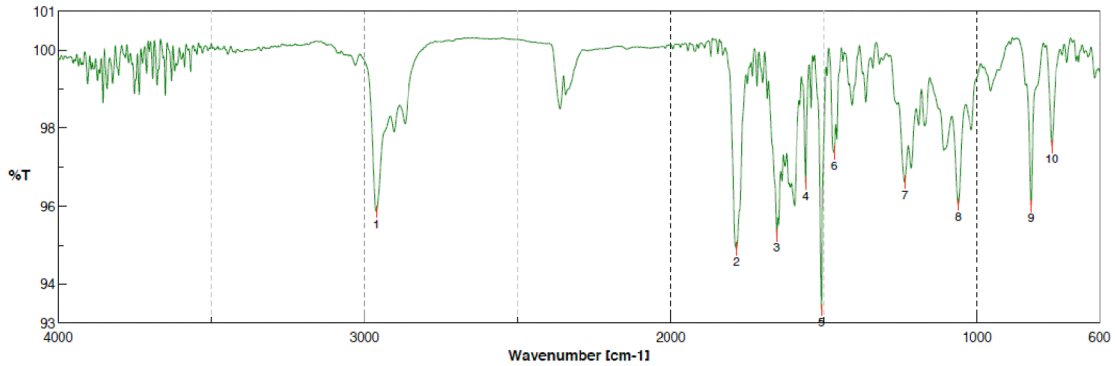


9

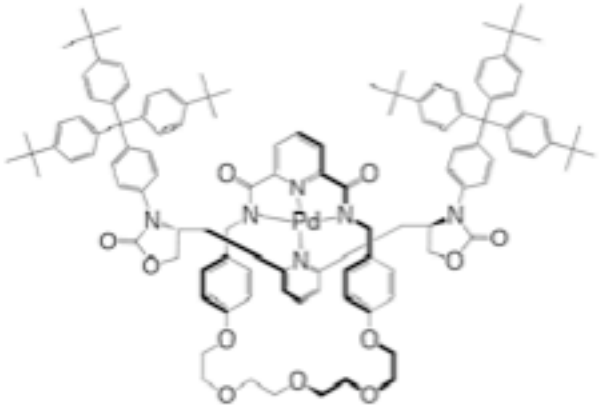
R =



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of rotaxane 9

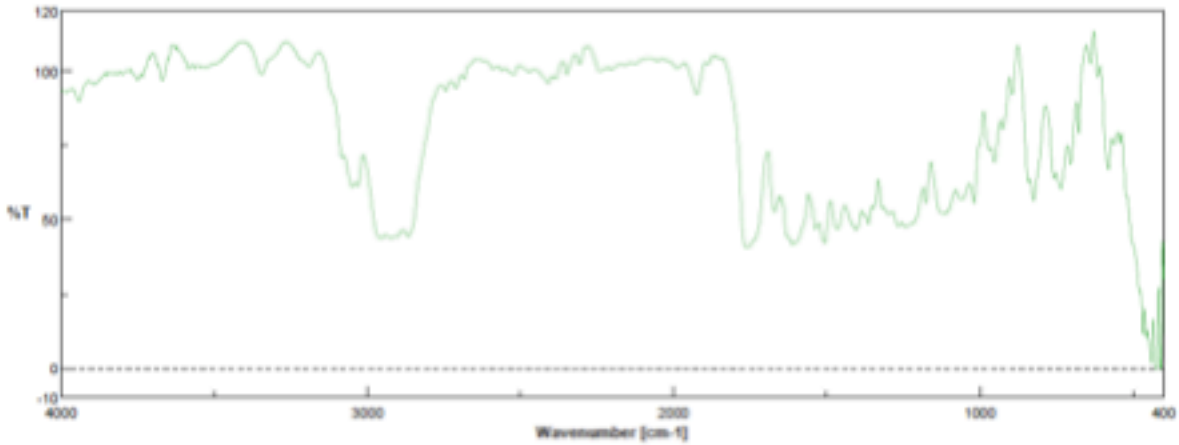


IR spectrum (KBr) of rotaxane 9

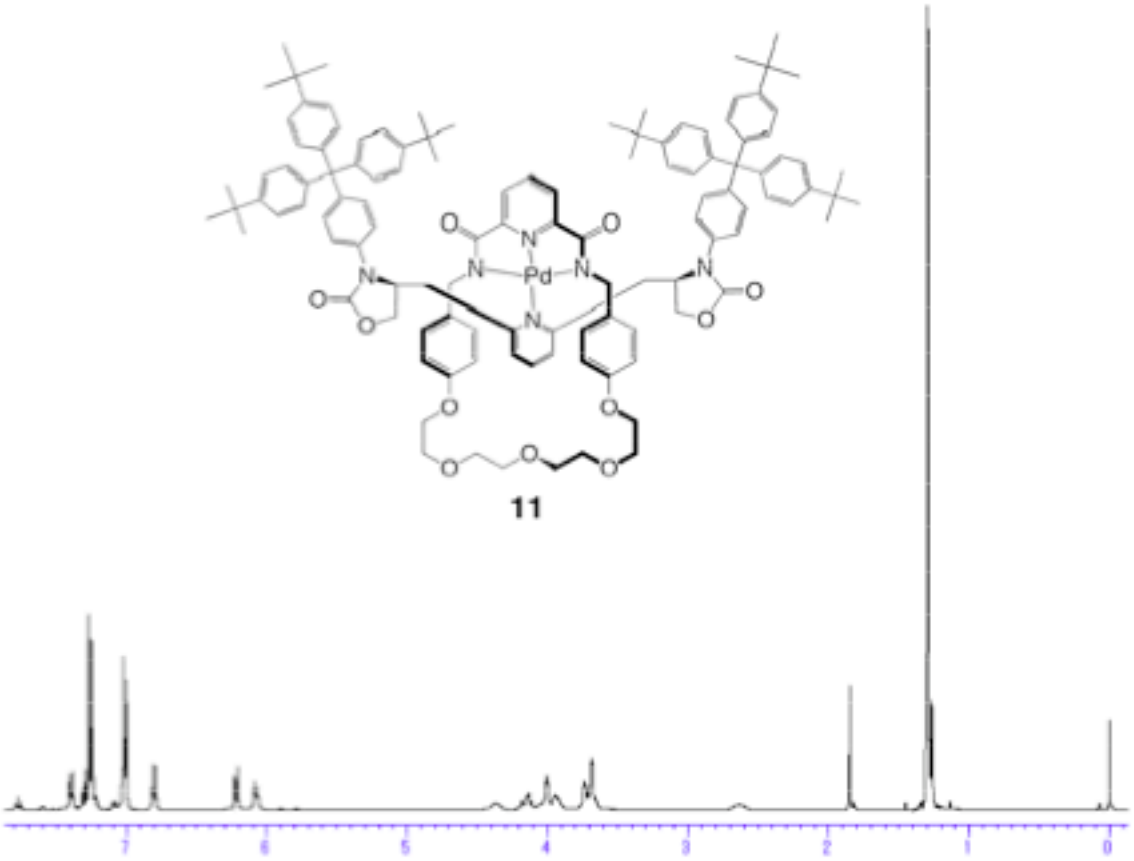


10

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

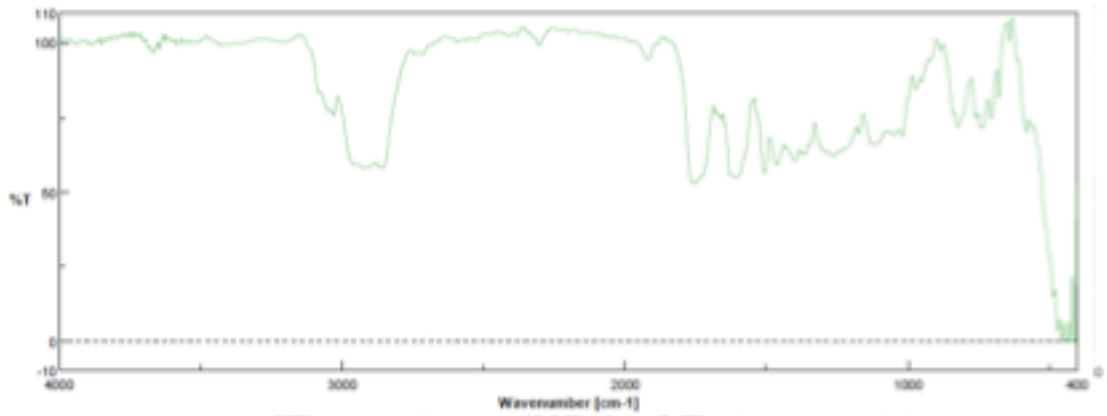


IR spectrum (neat) of Rotaxane 10

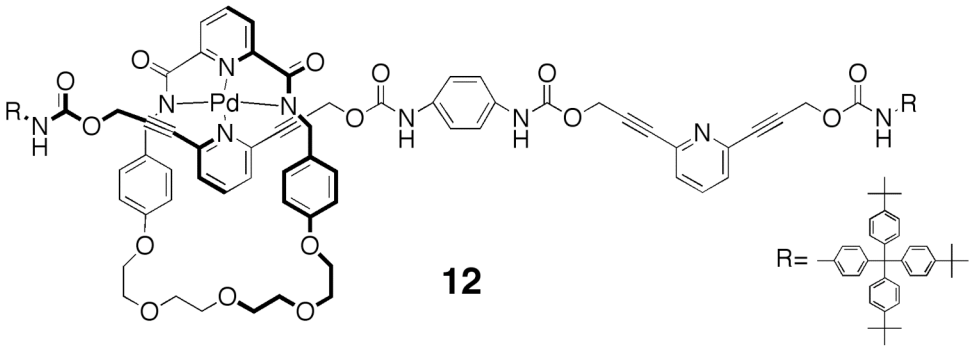


11

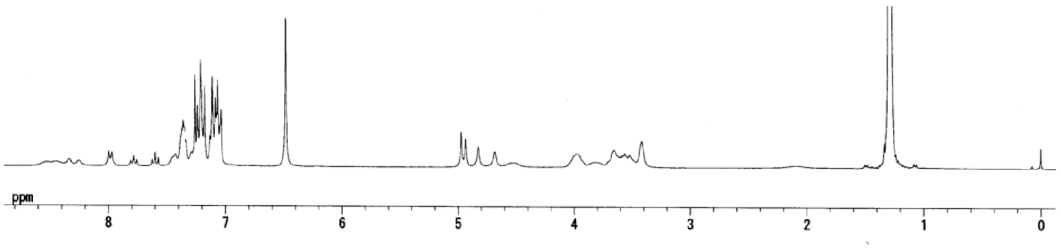
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of Rotaxane 11



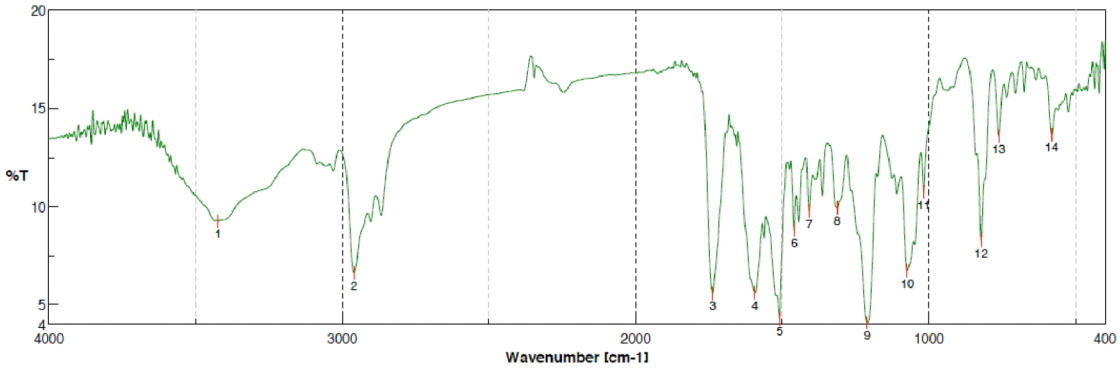
IR spectrum ($\tilde{\nu}$ neat) of Rotaxane 11



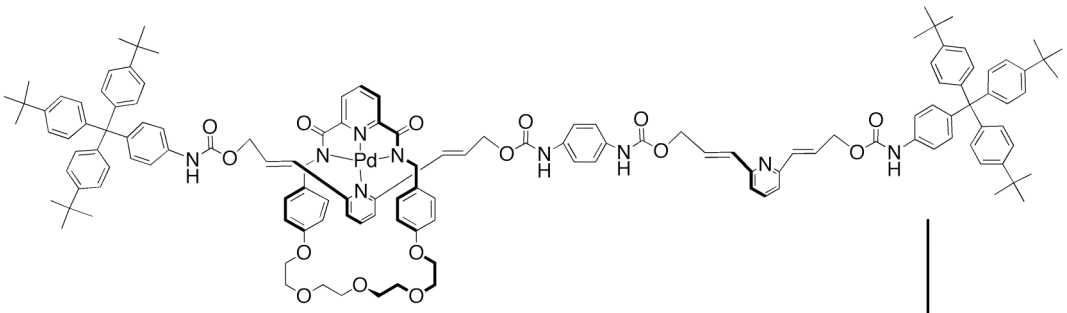
12



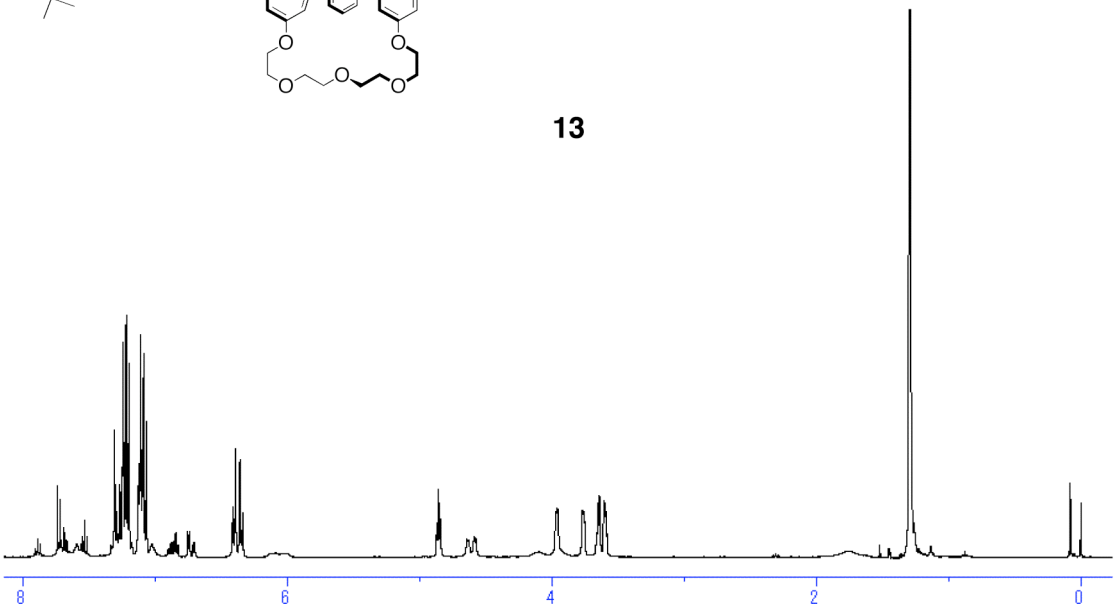
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of rotaxane 12



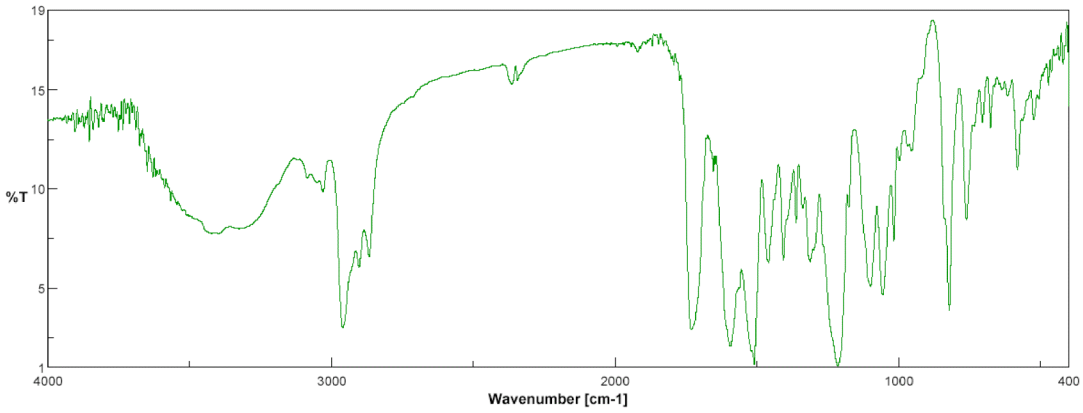
IR spectrum (KBr) of rotaxane 12



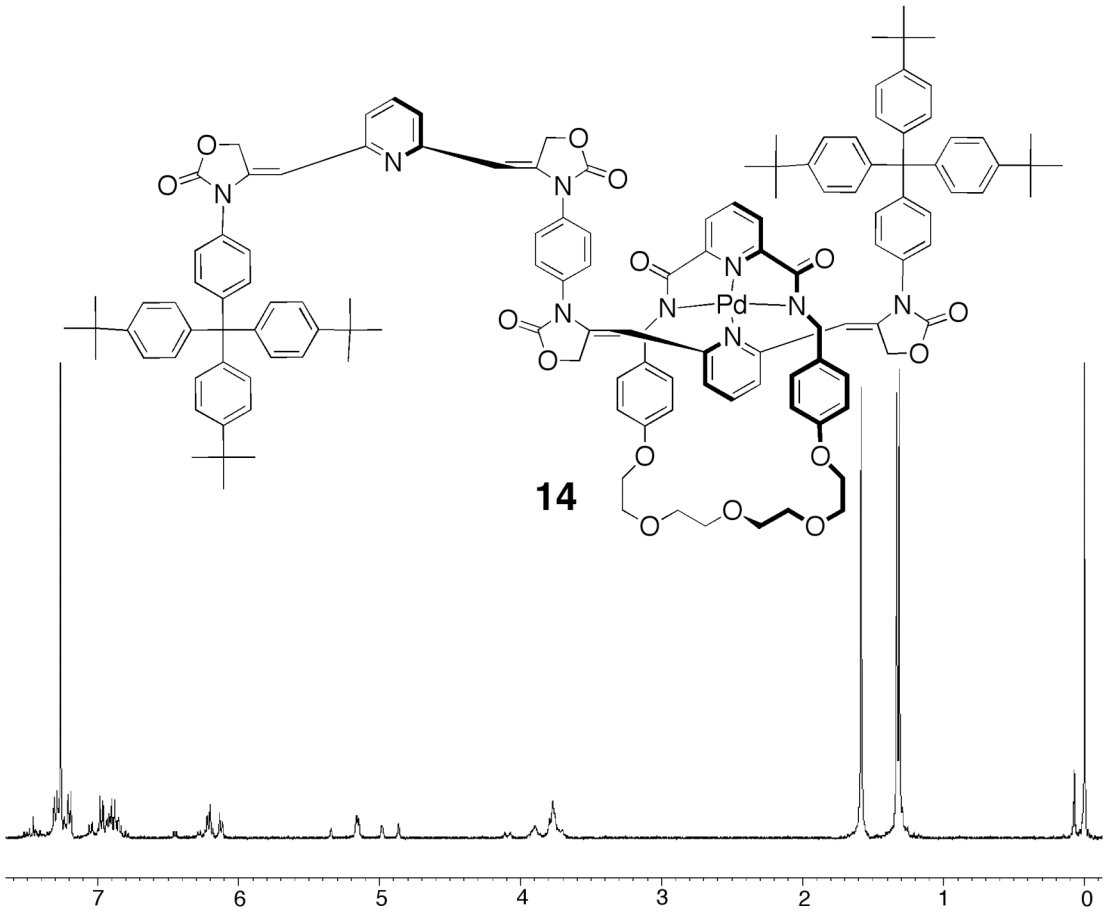
13



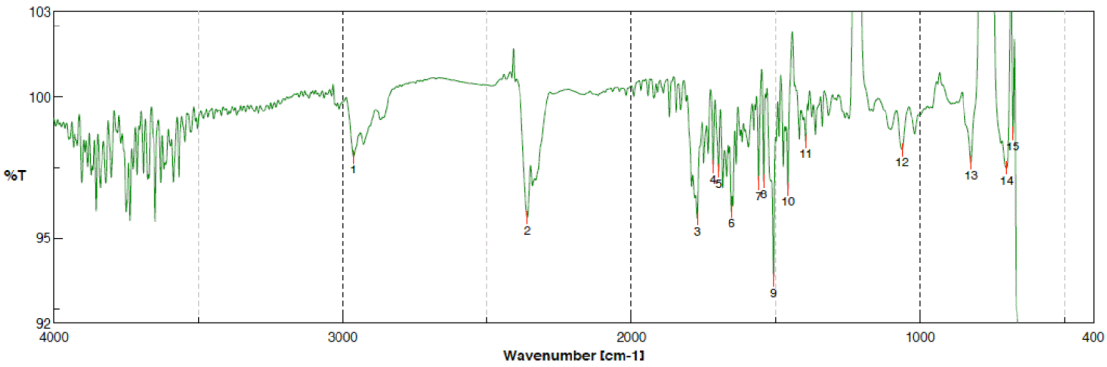
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 340 K) of Rotaxane 13



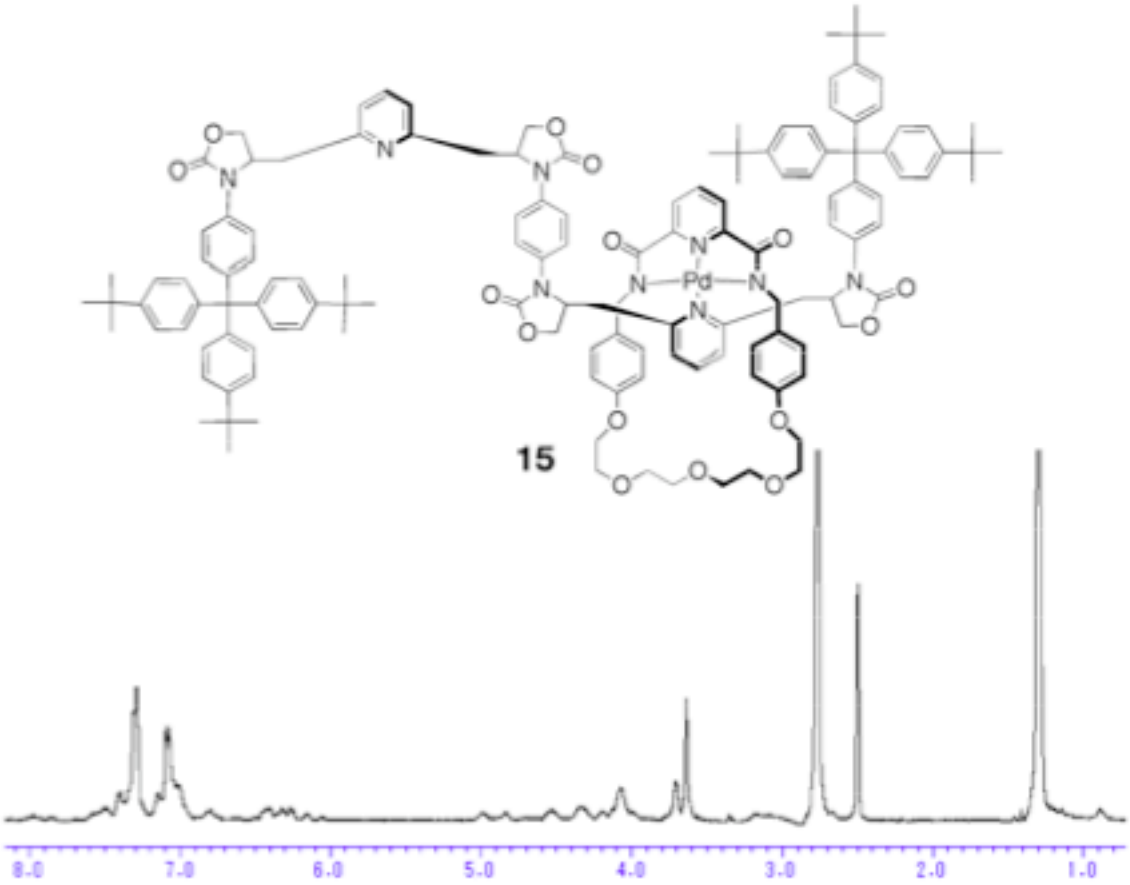
IR spectrum (KBr) of Rotaxane 13



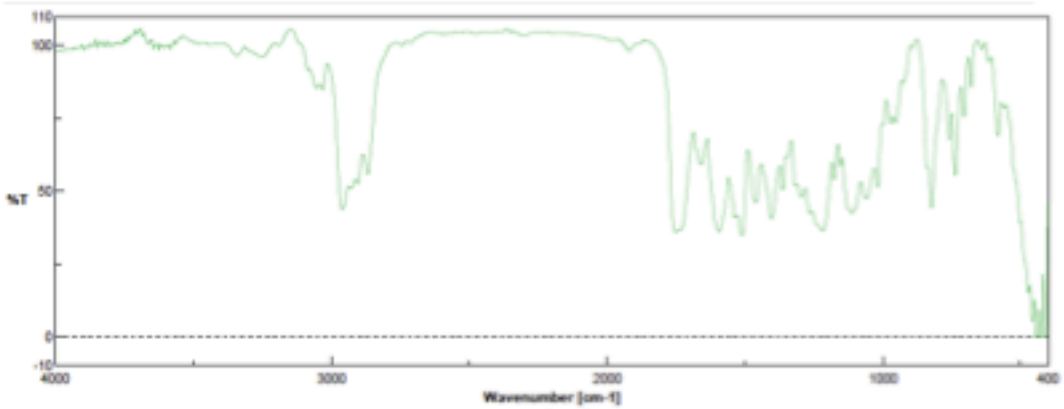
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of rotaxane 14



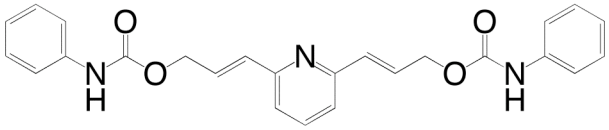
IR spectrum (KBr) of rotaxane 14



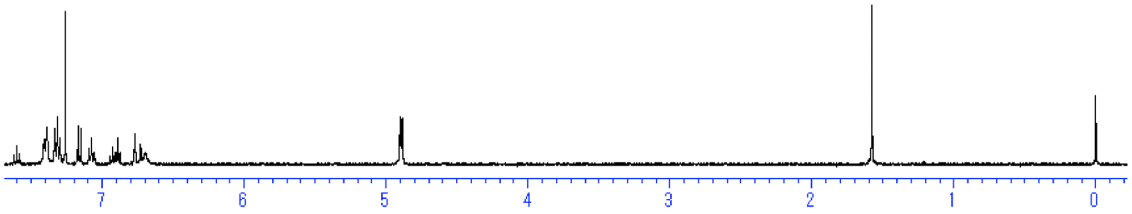
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of rotaxane 15



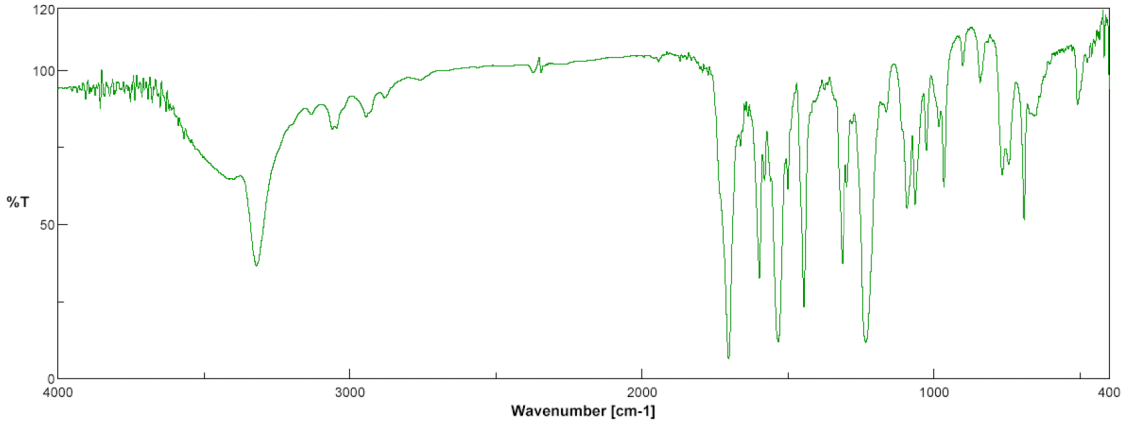
IR spectrum (heat) of rotaxane 15



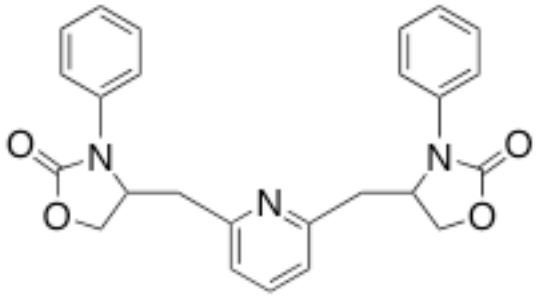
16



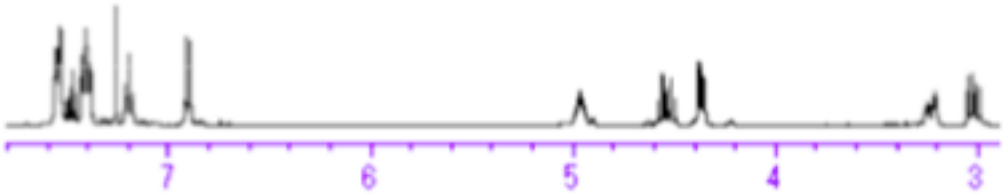
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of diphenyl 16



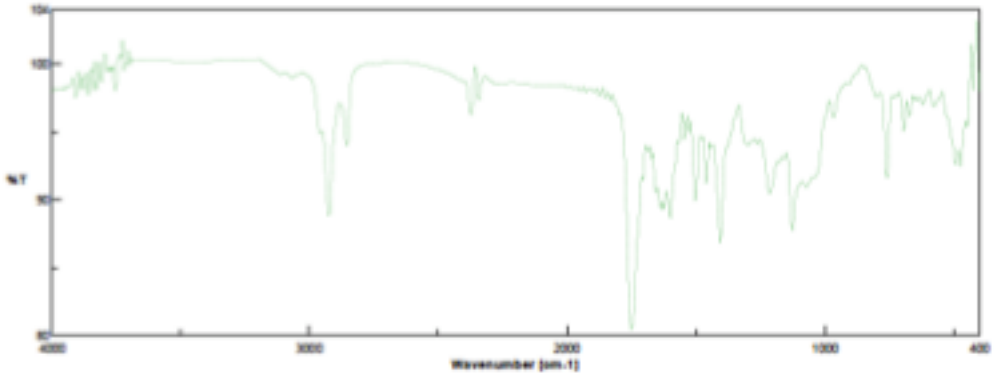
IR spectrum (KBr) of diphenyl 16



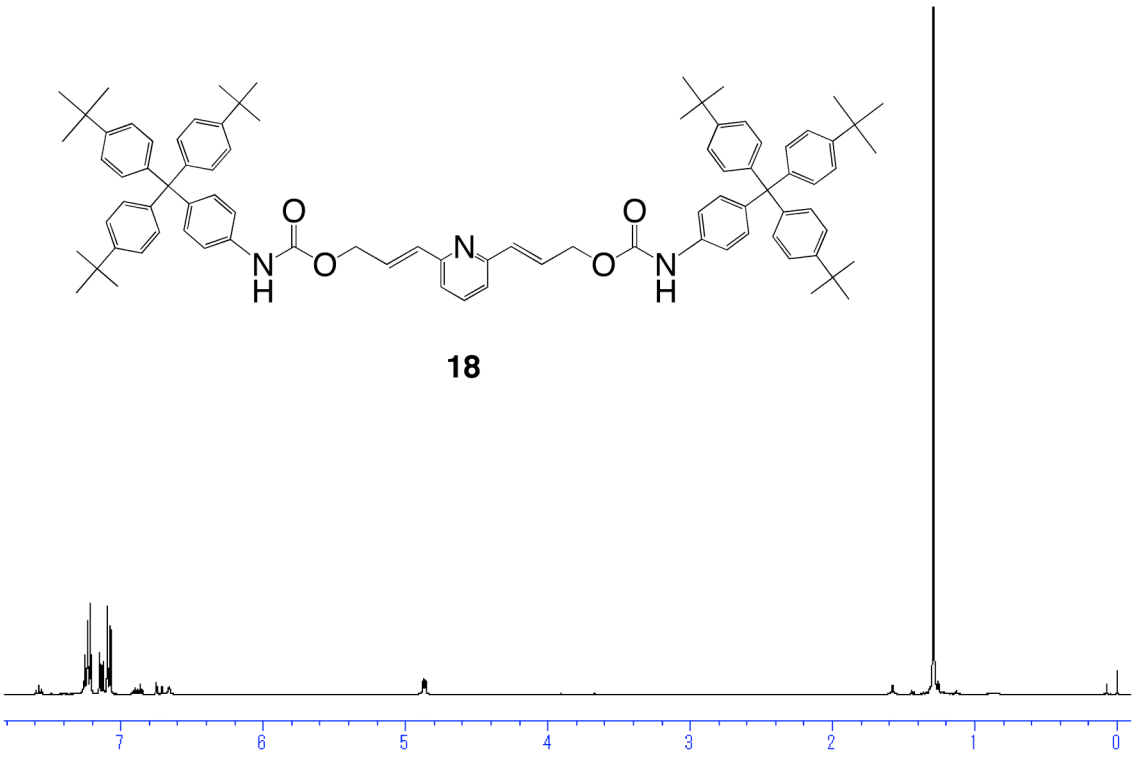
17



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of 17

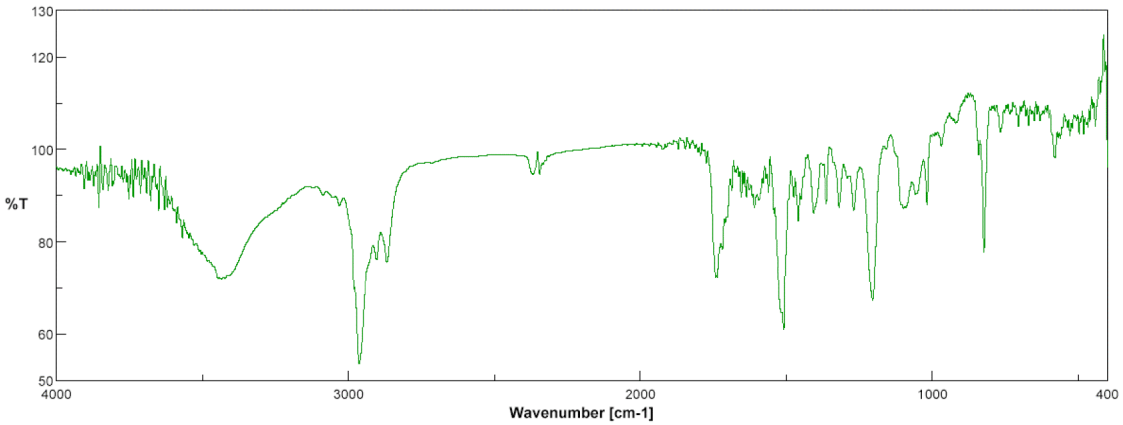


IR spectrum (KBr) of 17

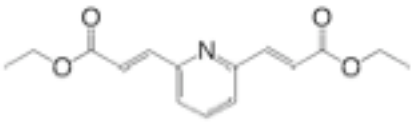


18

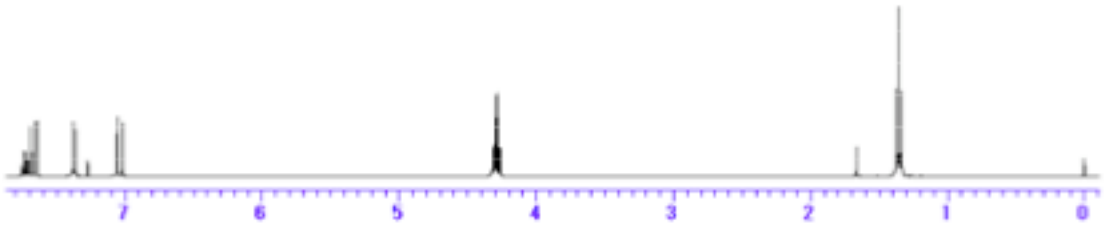
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of dumbbell 18



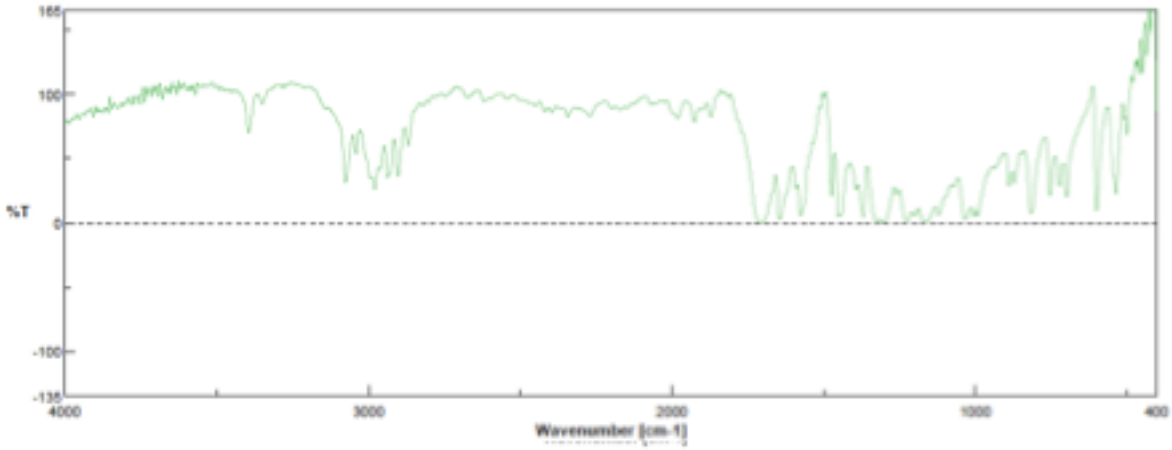
IR spectrum (KBr) of dumbbell 18



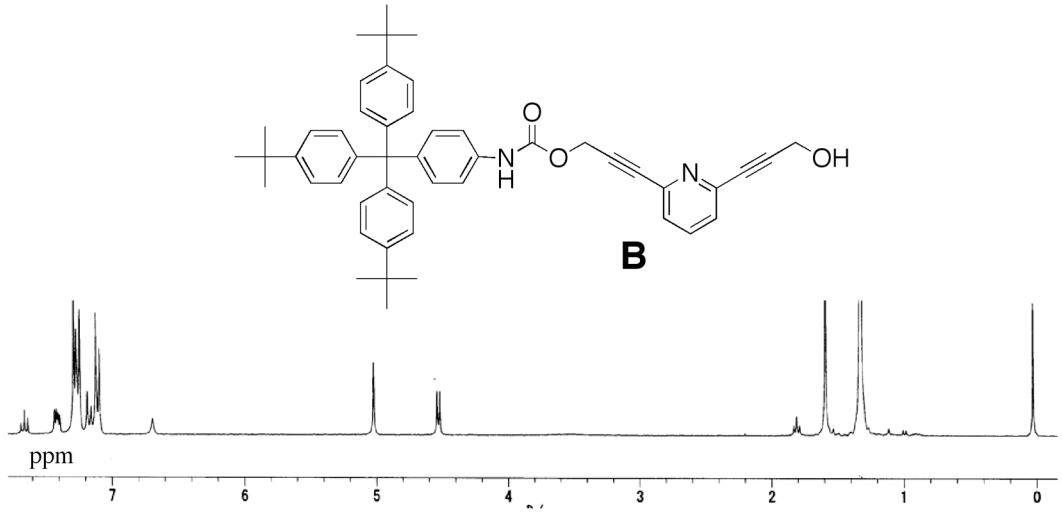
A



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of diester A

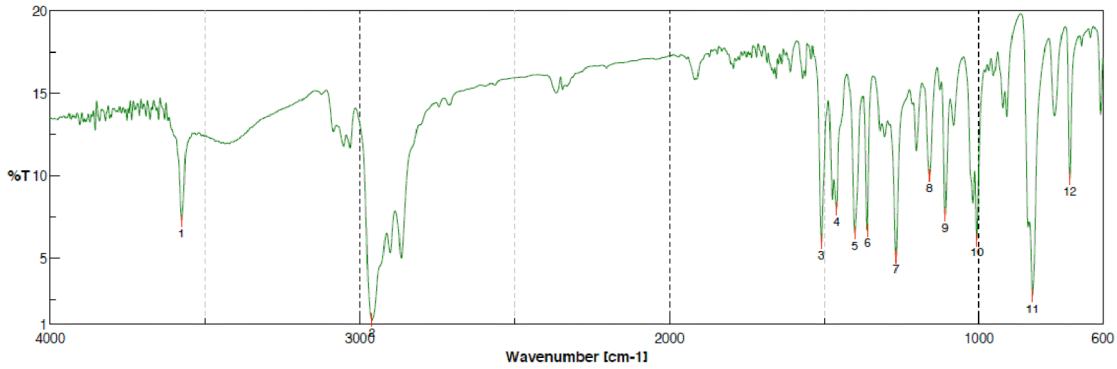


IR spectrum (KBr) of diester A

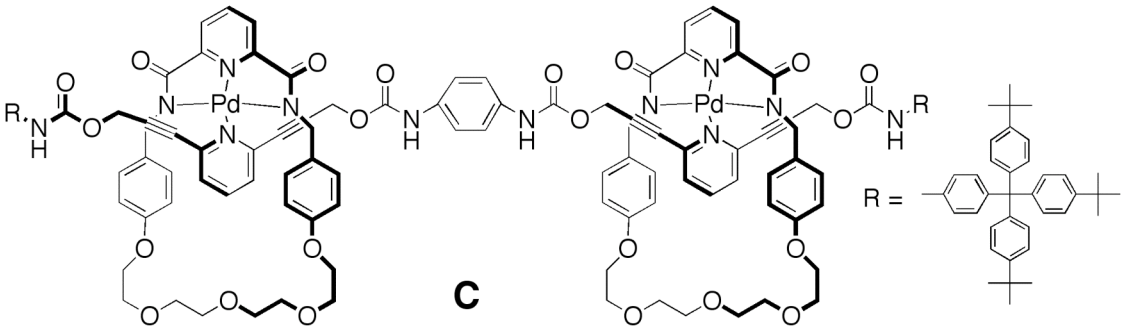


B

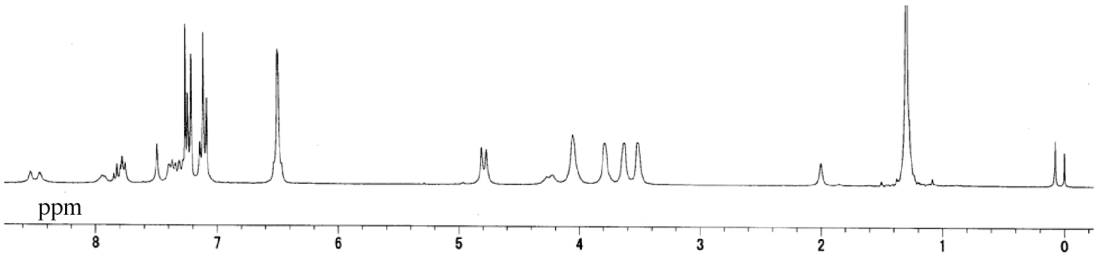
^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of B



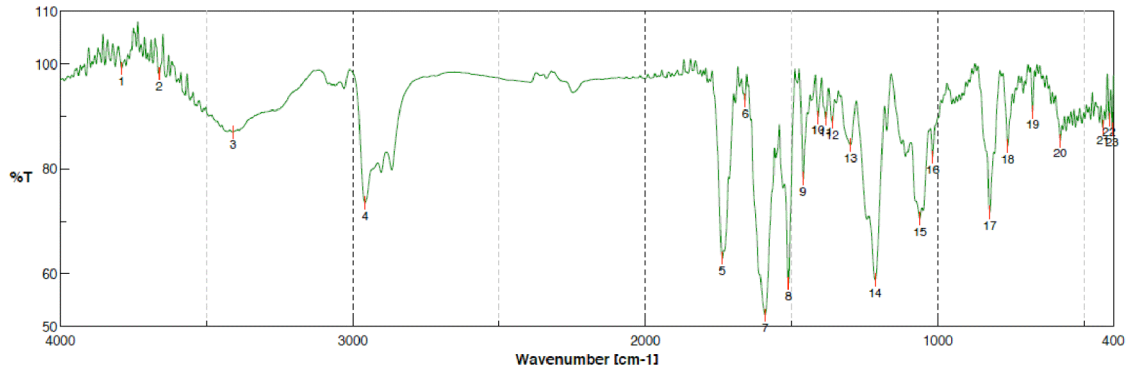
IR spectrum (KBr) of B



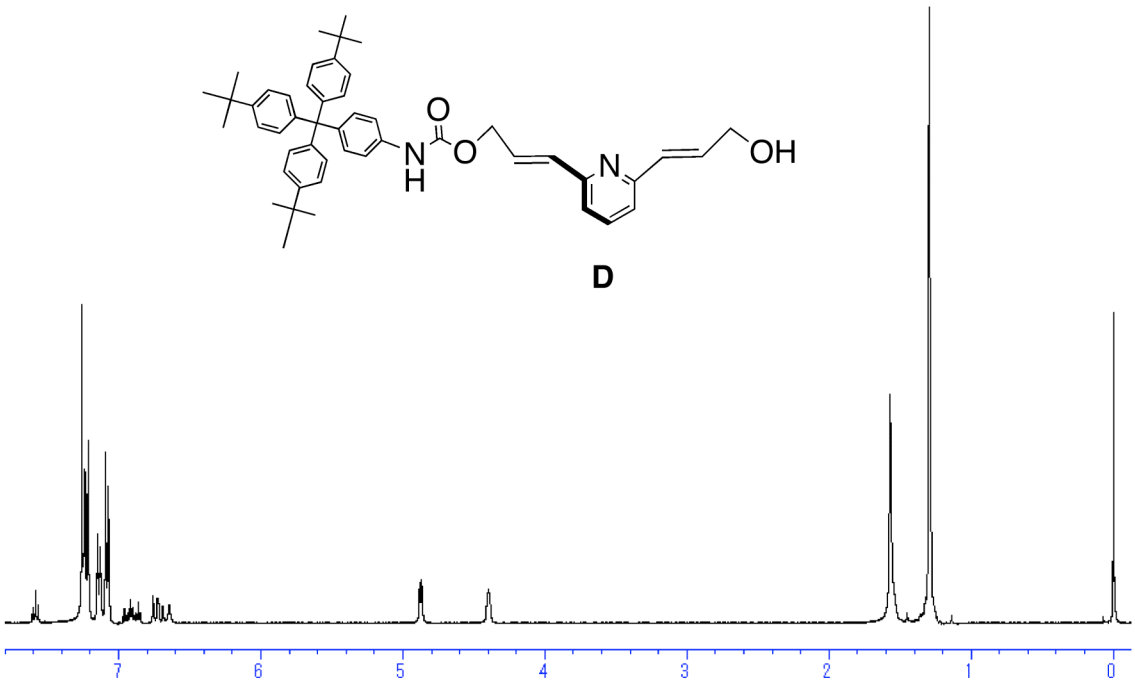
C



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of rotaxane C

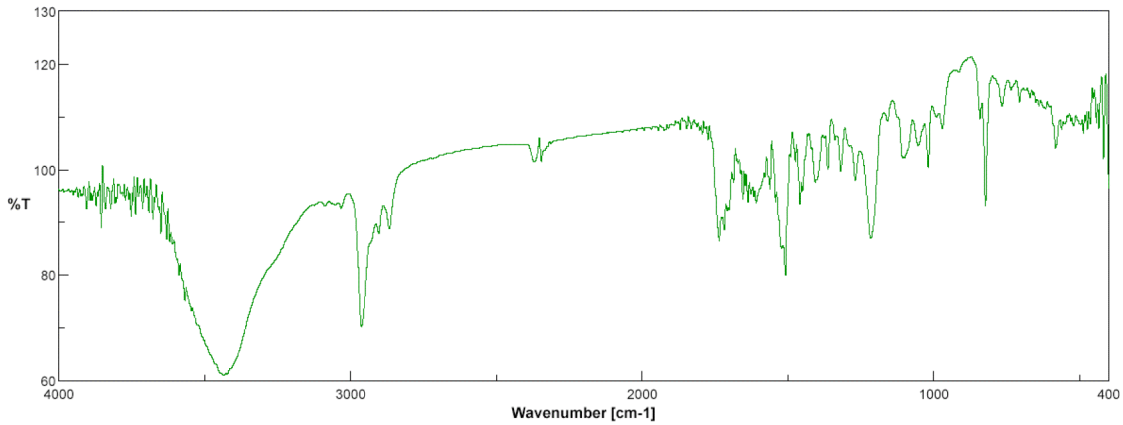


IR spectrum (KBr) of rotaxane C

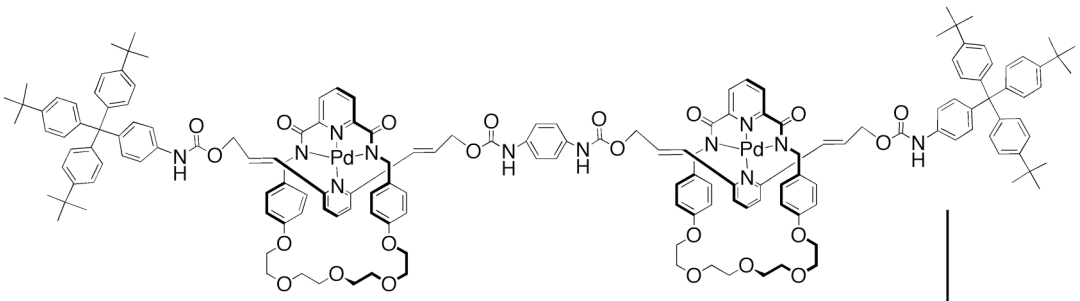


D

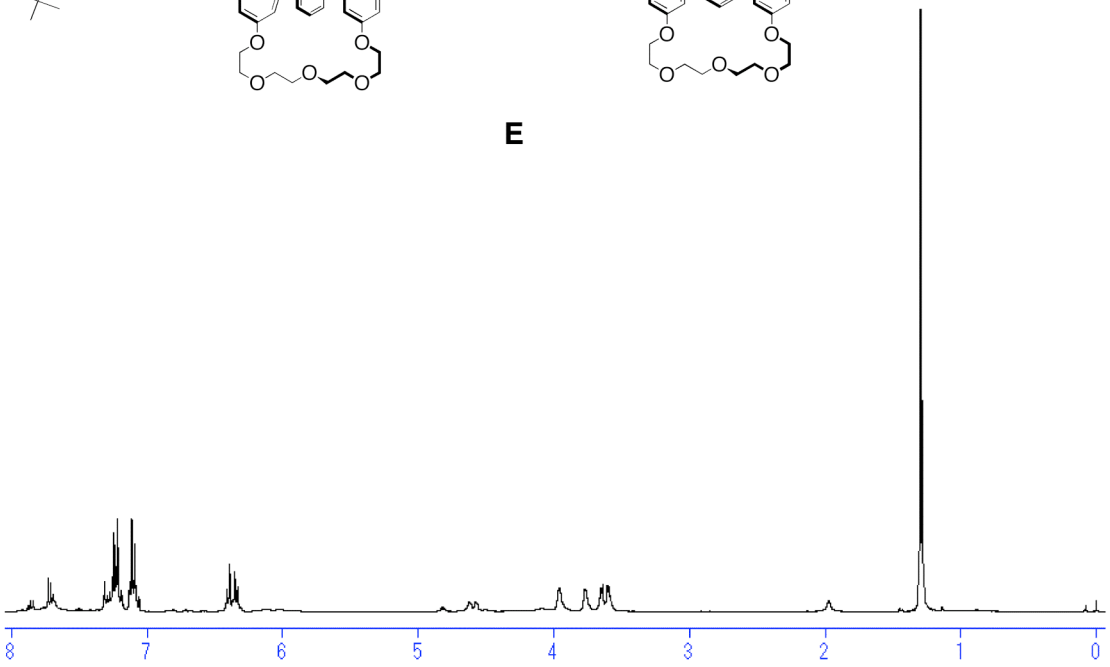
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of alcohol D



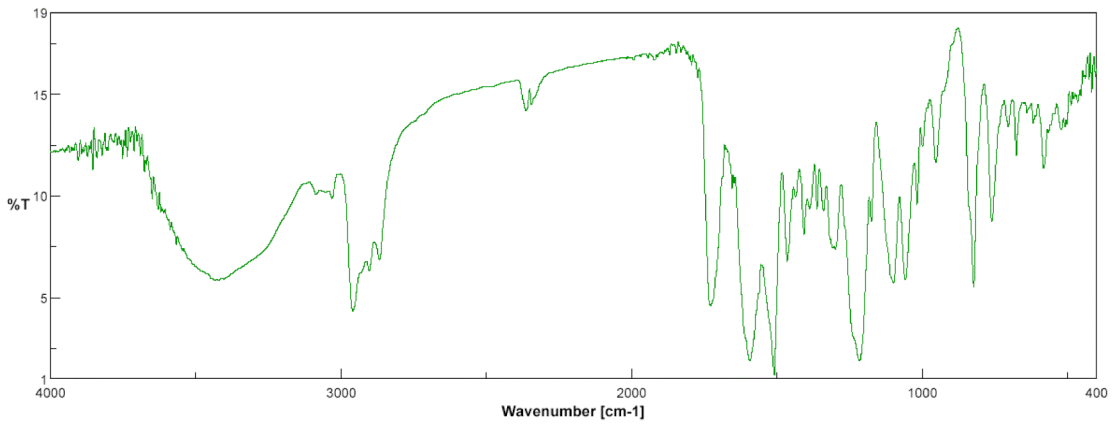
IR spectrum (KBr) of alcohol D



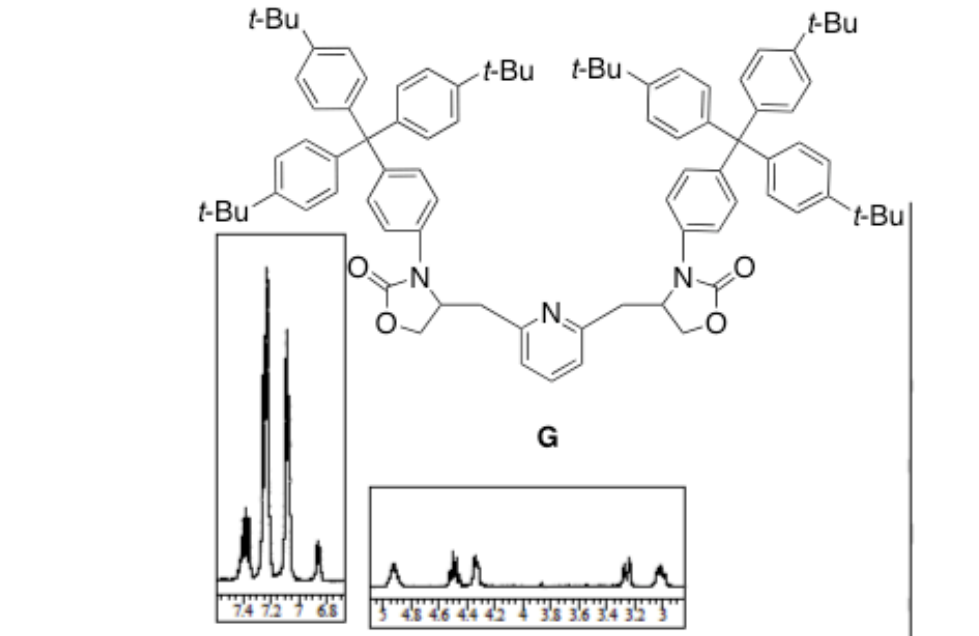
E



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 340 K) of Rotaxane E

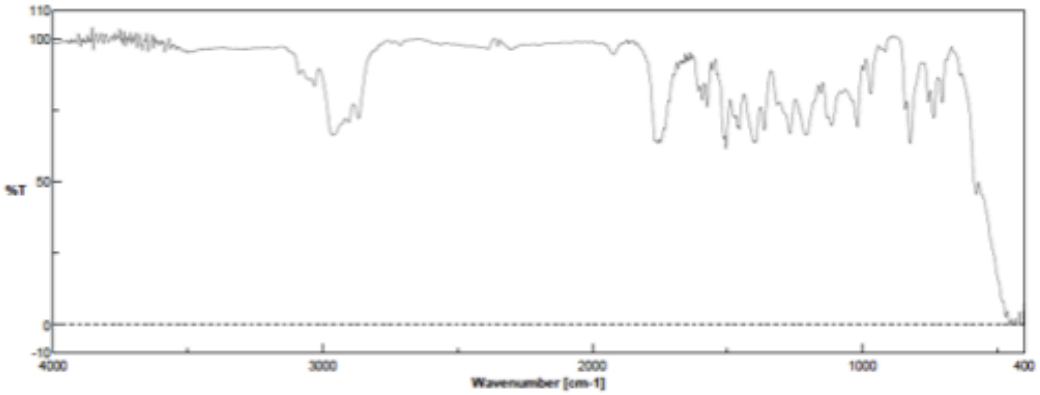


IR spectrum (KBr) of Rotaxane E



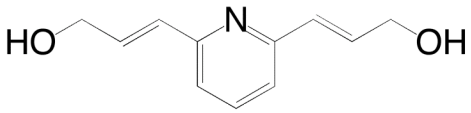
G

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

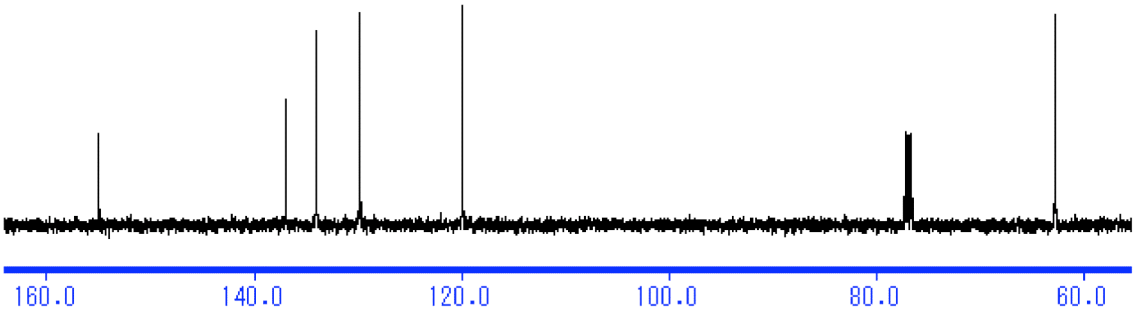


IR spectrum (neat) of G

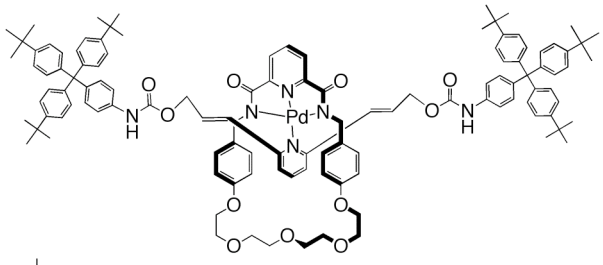
[^{13}C NMR]



4

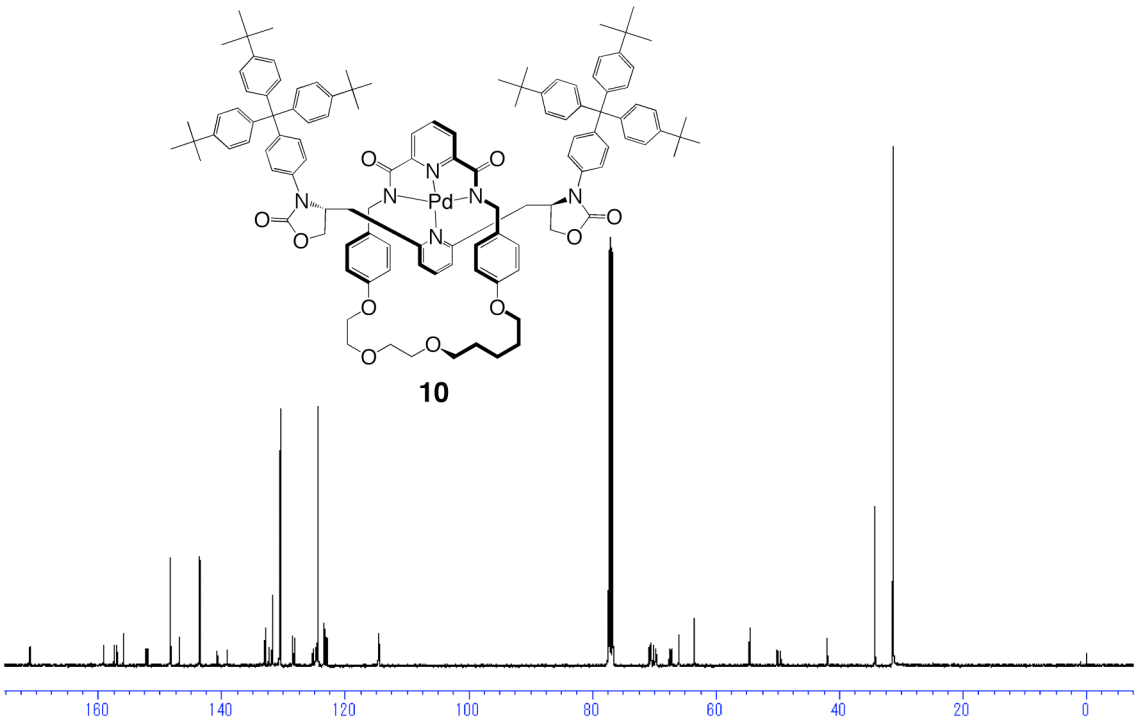


^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of dialcohol 4



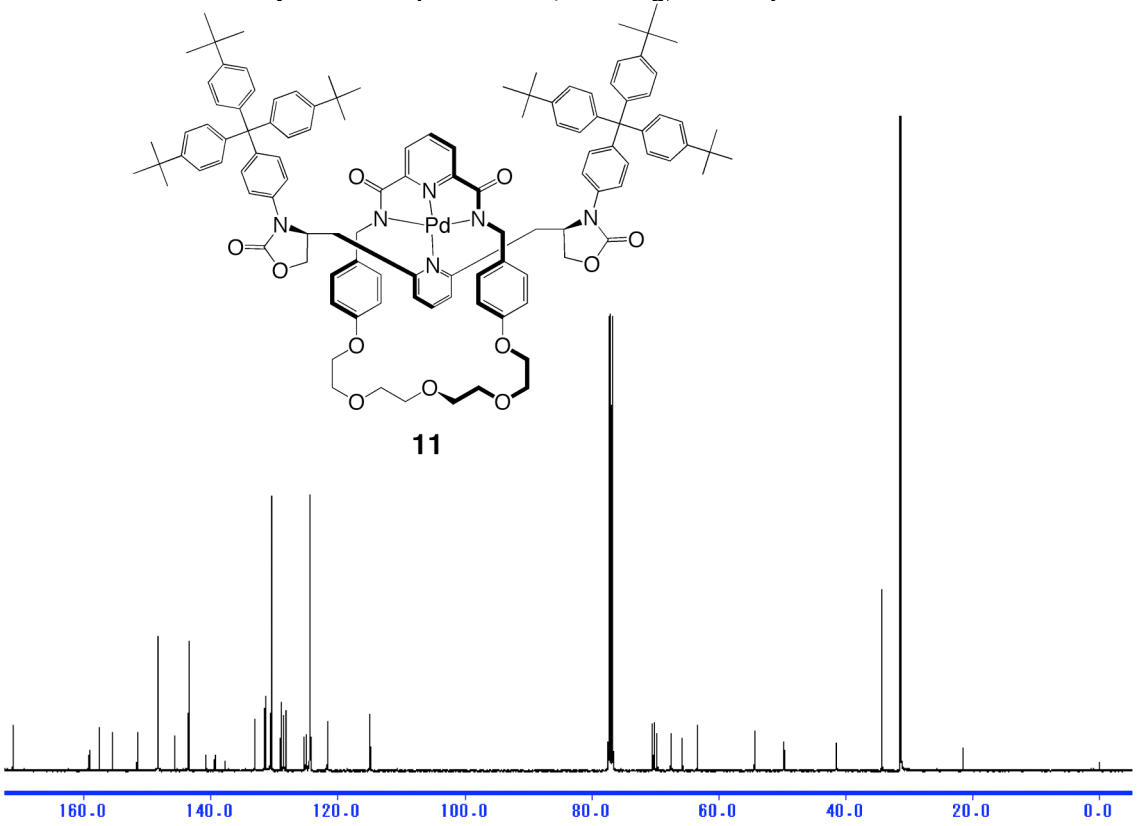
6

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



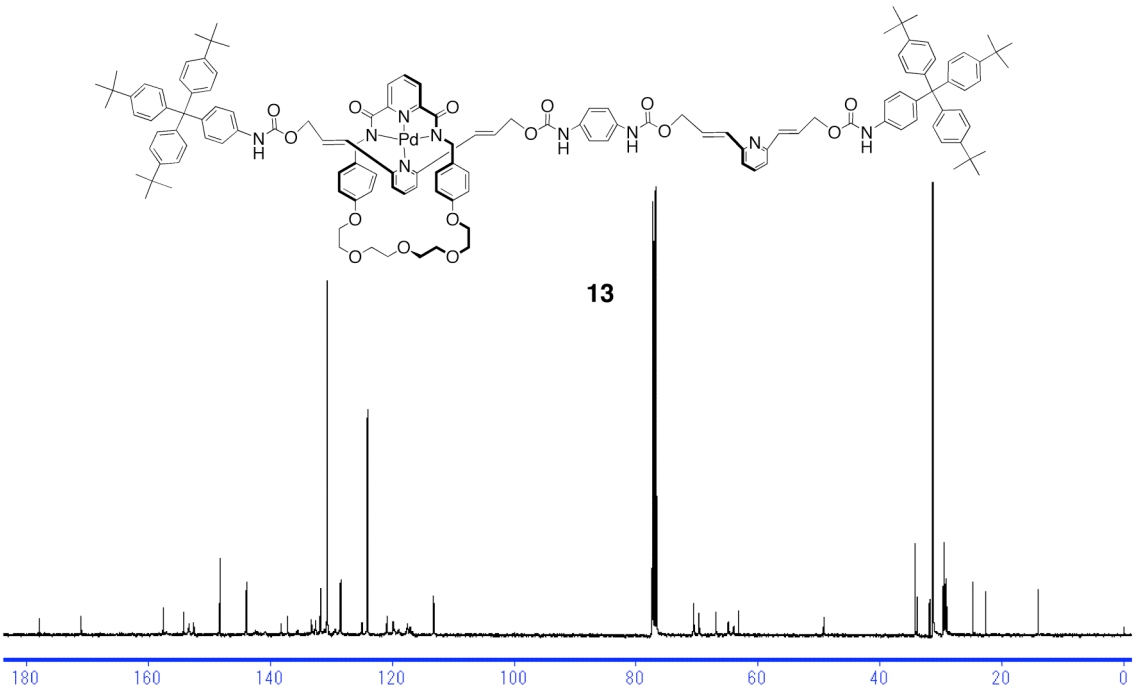
10

^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of Rotaxane 10

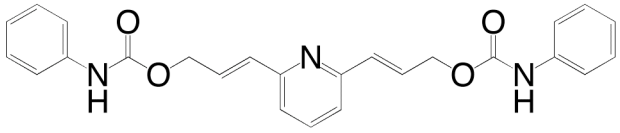


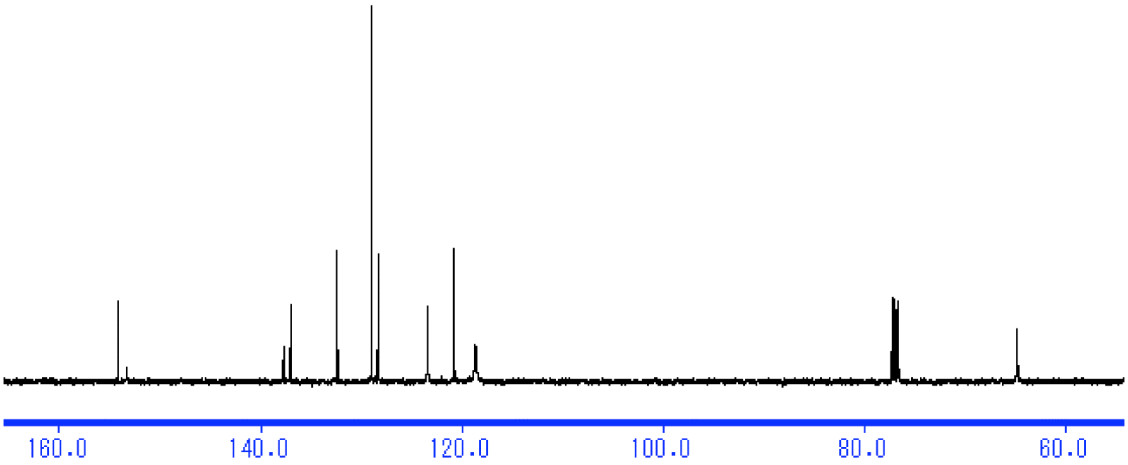
11

^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of Rotaxane 11

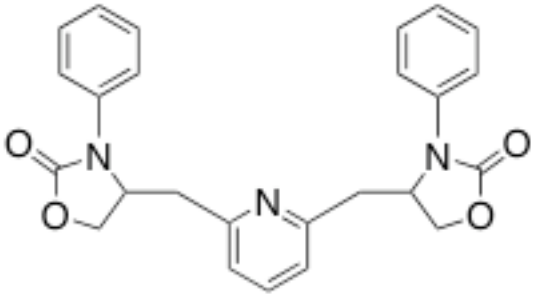


^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of Rotaxane 13

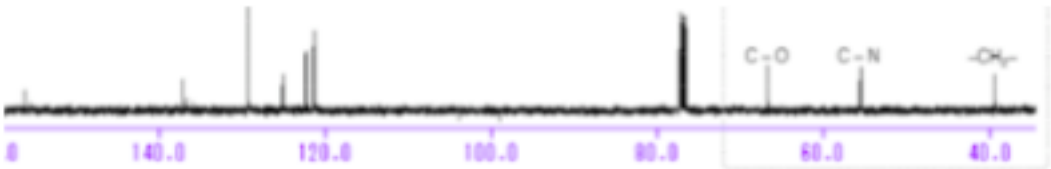




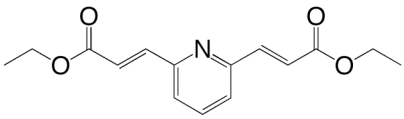
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of diphenyl 16



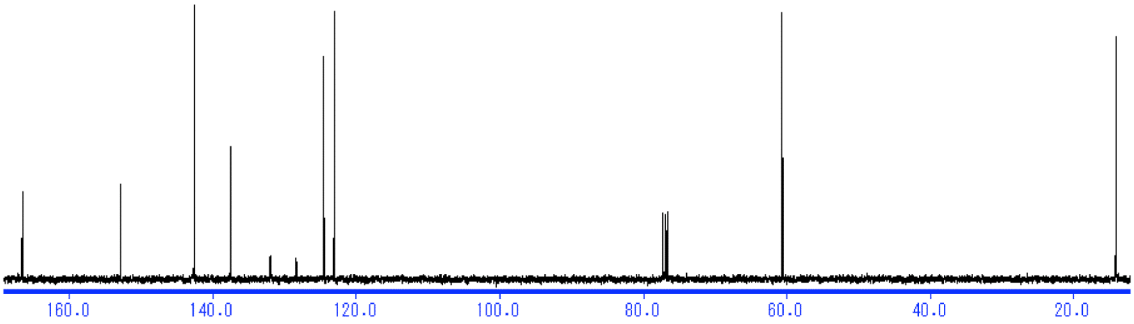
17



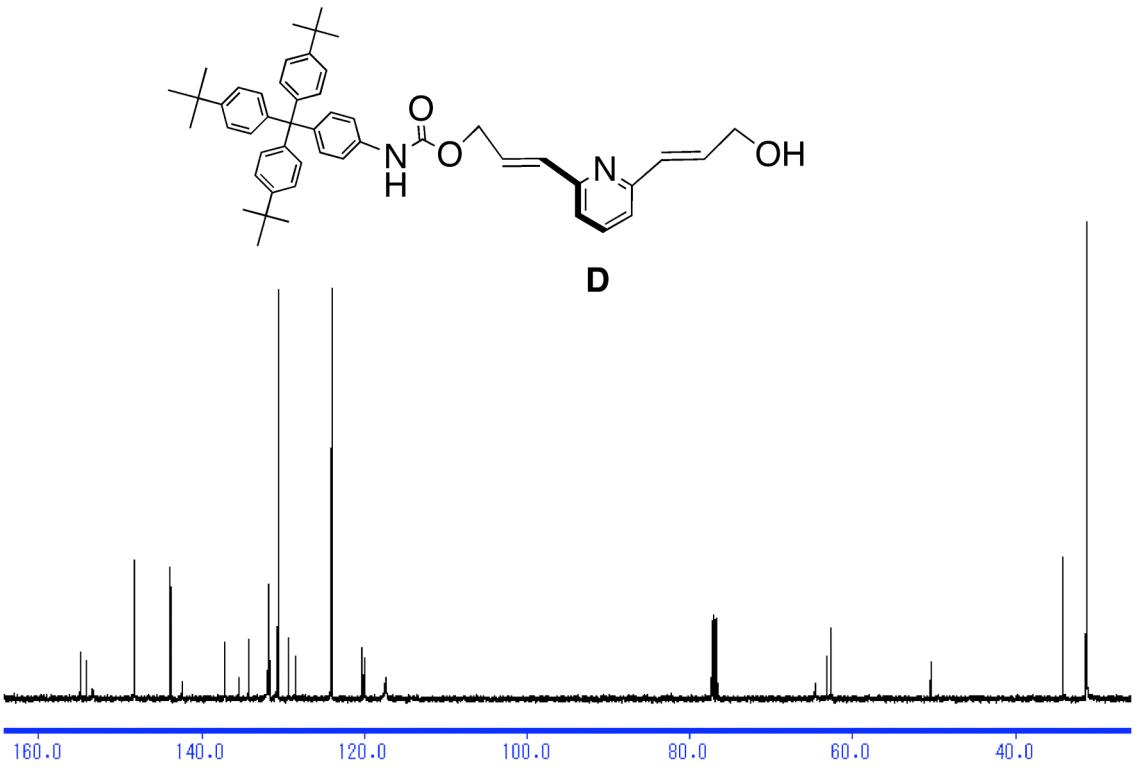
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 293 K) of 17



A



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

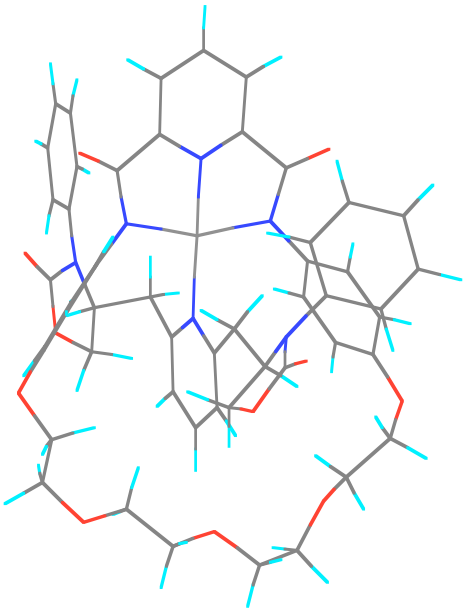


D

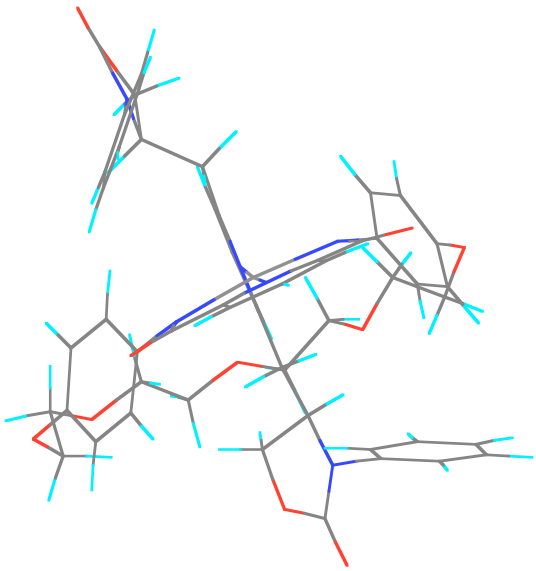
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of alcohol D

Energy Minimized Structures (DFT, B3LYP, 6–31**)

Structures of 10

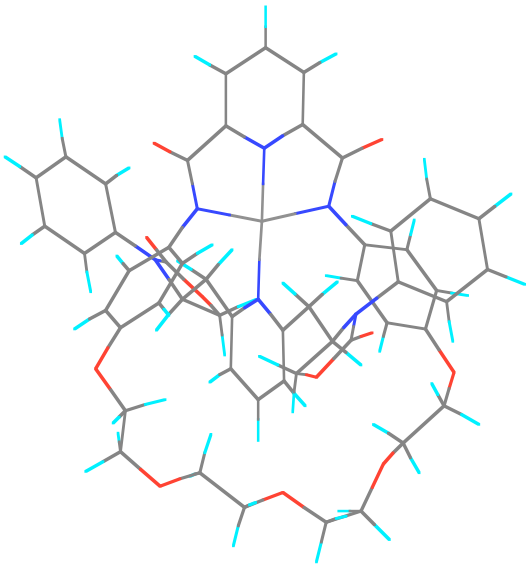


Front view

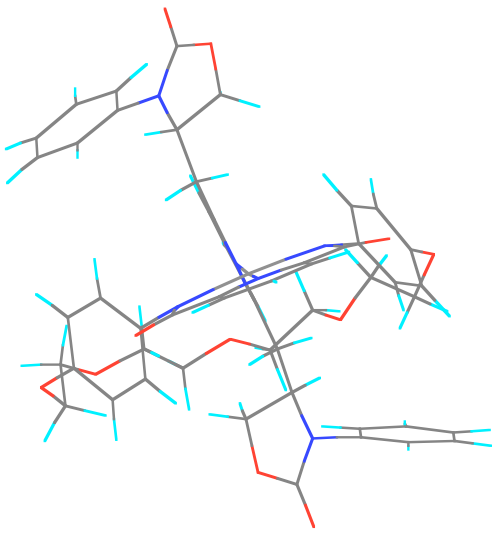


Top view

Structures of 11



Front view



Top view