



Supporting Information

© Wiley-VCH 2006

69451 Weinheim, Germany

# Dynamic Covalent Bonded Rotaxanes Cross-linked by Imine Bonds between Axle and Ring: Inverse Temperature Dependence of Subunit Mobility

Hidetoshi Kawai,\* Takeshi Umehara, Kenshu Fujiwara,  
Takashi Tsuji,\* and Takanori Suzuki

*Division of Chemistry, Graduate School of Science, Hokkaido University,  
Sapporo 060-0810, Japan  
Fax: +81-11-706-2714, e-mail: kawai@sci.hokudai.ac.jp*

## Supporting Information

---

Experimental procedures		--- p. S2
<sup>1</sup> H NMR spectra of <b>1b</b> , <b>1d</b> , <b>1e</b> , <b>5b</b> , <b>5e</b> and <b>7a</b>	(Figure S1)	--- p. S13
Temperature-dependence of equilibrated ratio of <b>1f</b> , <b>9f</b> and <b>2f</b> in the hydrolyzed mixture	(Figure S2)	--- p. S13
ROESY spectrum of hydrolyzed mixture containing <b>1f</b> , <b>9f</b> and <b>2f</b> in 0.08% TFA/CDCl <sub>3</sub> at 253K	(Figure S3)	--- p. S14
References		--- p. S15

## Experimental procedures

**General:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL ECP-300, AL-300 ( $^1\text{H}/300$  MHz,  $^{13}\text{C}/75$  MHz) or  $\alpha 400$  ( $^1\text{H}/400$  MHz,  $^{13}\text{C}/100$  MHz) spectrometer in  $\text{CDCl}_3$  unless otherwise indicated. VT-NMR and ROESY spectra were measured on a  $\alpha 600$  spectrometer at the High-Resolution NMR Laboratory (Hokkaido University). IR spectra were taken on a Hitachi Model 215 grating spectrometer and a JASCO model FT/IR-230 infrared spectrophotometer. Mass spectra were recorded on a JEOL JMS-600H (EI) and JMS-01SG-2 (FD) spectrometers. Column chromatography was performed on silica gel 60 (Merck, particle size 63-200  $\mu\text{m}$ ), silica gel I-6-40 (YMC, size 40-63  $\mu\text{m}$ ) and aluminum oxide 90 (Merck, 63-200  $\mu\text{m}$ ), respectively. Thin-layer chromatography (TLC) was performed on silica gel 60 (Merck) of particle size 5-20  $\mu\text{m}$ . Gel Permeation Chromatography was carried out LC-908 (Japan Analytical Industry) with JAIGEL 1H + 2H or 2H + 2.5H columns. Elemental analyses were taken on a Yanako MT-6 CHN corder at the Center for Instrumental Analysis of Hokkaido University. Reactions were carried out under an argon atmosphere.  $\alpha$ -[4-[Tris(4'-*tert*-butylphenyl)methyl]phenoxy]- $\alpha'$ -bromo-*p*-xylene **8a**<sup>[S1]</sup> was prepared following the known procedure. All commercially available compounds were used without further purification unless otherwise indicated.

**Preparation of 1,2,4,5-Tetrakis(bromomethyl)benzene:** This compound was prepared with some modification of the method reported by Soyer et al.<sup>[S2]</sup> To a mixture of durene (17.0 g, 127 mmol) and NBS (86.2 g, 484 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (400 mL) was irradiated by a 600 W tungsten lamp for 20 h under reflux. After cooling, succinimide which precipitated as a colorless powder was filtered off and washed with  $\text{CH}_2\text{Cl}_2$ . After removal of solvent from the filtrate, the crude product was suspended in MeOH (100 mL) and stirred for 5 min to remove unreacted NBS and byproducts such as perbrominated durene. The resulting suspension was filtered and the insoluble material was washed with MeOH to give the title compound (31.0 g, 54%) as a white solid: The spectral data were identical with those reported in the literature.<sup>[S2]</sup> mp 149-151  $^\circ\text{C}$ ;  $^1\text{H}$  NMR:  $\delta$  7.38 (s, 2H), 4.60 (s, 8H); IR (KBr) 3016, 2976, 1456, 1210, 910, 798, 600  $\text{cm}^{-1}$ .

**Preparation of 2,6-Bis(4-bromophenyl)-1,2,3,5,6,7-hexahydro-s-indacene-2,6-dicarbonitrile (E/Z)-4a:** To a solution of 1,2,4,5-tetrakis(bromomethyl)benzene (4.5 g, 10.0 mmol) and 4-bromophenylacetonitrile (3.92 g, 20.0 mmol) in toluene (900 mL) were added 40% aqueous NaOH (60 mL) and benzyltriethylammonium chloride (10 mg, 0.44 mmol). After vigorously

stirring for 26 h at 65 °C, the reaction mixture was diluted with water (200 mL). The insoluble resin-like material was filtered off and washed with toluene. After combining the filtrate and the washing, the aqueous layer was separated from the organic layer and extracted with toluene. The organic layers were combined and washed successively with 1 M HCl, water and brine, and dried over MgSO<sub>4</sub>. The crude product obtained by evaporation of the solvent was subjected to chromatography on silica gel eluted with toluene to give (*E*)-**4a** (970 mg, 19%) and (*Z*)-**4a** (1274 mg, 28%) as white solids, respectively. Their analytical samples were obtained by recrystallization from benzene: (*E*)-**4a**: *R*<sub>f</sub> = 0.58 (SiO<sub>2</sub>, CHCl<sub>3</sub>); mp 284.0-286.0 °C (dec.); <sup>1</sup>H NMR: δ 7.51 (d, *J* = 8.7 Hz, 4H), 7.35 (d, *J* = 8.7 Hz, 4H), 7.16 (s, 2H), 3.76 (d, *J* = 15.3, 4H), 3.47 (d, *J* = 15.3 Hz, 4H); <sup>13</sup>C NMR: δ 138.99, 138.60, 132.24, 127.50, 123.81, 122.35, 120.79, 47.23, 46.48; IR (KBr): 2956, 2924, 2848, 2228, 1448, 1398, 1074, 1010, 816 cm<sup>-1</sup>; MS (EI) *m/z* (%): 520 (M<sup>+</sup>+4, 52), 518 (M<sup>+</sup>+2, 100), 516 (M<sup>+</sup>, 51), 491 (M<sup>+</sup>+2-HCN, 65); Anal. calcd. for C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>Br<sub>2</sub>: C, 60.26; H, 3.50; N, 5.41; Br, 30.84. Found: C, 60.11; H, 3.67; N, 5.42; Br, 30.63; (*Z*)-**4a**: *R*<sub>f</sub> = 0.33 (SiO<sub>2</sub>, CHCl<sub>3</sub>); mp 239.0-243.0 °C (dec.); <sup>1</sup>H NMR: δ 7.49 (d, *J* = 8.5 Hz, 4H), 7.33 (d, *J* = 8.5 Hz, 4H), 7.16 (s, 2H), 3.78 (d, *J* = 15.4, 4H), 3.46 (d, *J* = 15.4 Hz, 4H); <sup>13</sup>C NMR: δ 138.94, 138.77, 132.12, 127.47, 123.62, 122.25, 120.73, 46.85, 46.38; IR (KBr): 2952, 2908, 2844, 2232, 1448, 1398, 1078, 1012, 826 cm<sup>-1</sup>; MS (EI) *m/z* (%): 520 (M<sup>+</sup>+4, 51), 518 (M<sup>+</sup>+2, 100), 516 (M<sup>+</sup>, 50), 491 (M<sup>+</sup>+2-HCN, 30); Anal. calcd. for C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>Br<sub>2</sub>: C, 60.26; H, 3.50; N, 5.41; Br, 30.84. Found: C, 60.31; H, 3.61; N, 5.36; Br, 31.00.

**Preparation of (*E*)-2,6-Bis[4'-(*tert*-butyldimethylsilyloxy)biphenyl-4-yl]-1,2,3,5,6,7-hexahydro-*s*-indacene-2,6-dicarbonitrile **4b**:** To a mixture of (*E*)-**4a** (188 mg, 0.36 mmol) and 4-(*tert*-butyl dimethylsilyloxy)phenylboronic acid (277 mg, 1.1 mmol) in benzene (15 mL) were added EtOH (5 mL), aqueous Na<sub>2</sub>CO<sub>3</sub> (2 M, 5 mL) and Pd(PPh<sub>3</sub>)<sub>4</sub> (50 mg, 0.043 mmol). The resulting heterogeneous mixture was purged with argon and gently refluxed for 22 h with stirring under an argon atmosphere. After cooling to room temperature, the reaction mixture was poured into 5% aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The aqueous layer was separated from the organic layer and extracted with benzene. The organic layer was combined with the extract, washed with brine, dried over MgSO<sub>4</sub>, and then filtered. The crude obtained by concentrating the filtrate was subjected to chromatography on silica gel eluted with benzene to give (*E*)-**4b** (273 mg, 98%): mp 292.0-293.0 °C (dec.); <sup>1</sup>H NMR: δ 7.57 (d, *J* = 8.4 Hz, 4H), 7.52 (d, *J* = 8.4 Hz, 4H), 7.45 (d, *J* = 8.7 Hz, 4H), 7.20 (s, 2H), 6.91 (d, *J* = 8.7 Hz, 4H), 3.80 (d, *J* = 15.3 Hz, 4H), 3.55 (d, *J* = 15.3 Hz, 4H), 1.00 (s, 18H), 0.23 (s, 12H); <sup>13</sup>C NMR: δ 155.64, 140.86, 139.16, 137.77, 133.13, 128.04, 127.28, 126.16, 124.43, 120.77, 120.45, 47.52, 46.59, 25.69, 18.24, -4.39; IR (KBr): 2930, 2858, 2231, 1607, 1497, 1267, 1253,

1174, 916, 824, 779  $\text{cm}^{-1}$ ; MS (FD)  $m/z$  (%): 774 ( $M^+ + 2$ , 31), 773 ( $M^+ + 1$ , 66), 772 ( $M^+$ , 100); HR-MS (FD) calcd. for  $\text{C}_{50}\text{H}_{56}\text{N}_2\text{O}_2\text{Si}_2$ : 772.3880; found: 772.3857; Anal. calcd. for  $\text{C}_{50}\text{H}_{56}\text{N}_2\text{O}_2\text{Si}_2$ : C, 77.67; H, 7.30; N, 3.62. found: C, 77.66; H, 7.38; N, 3.63.

**Preparation of 2,6-Bis(4-bromophenyl)-1,2,3,5,6,7-hexahydro-s-indacene-2,6-dicarbaldehyde**

**5a:** To a solution of (*E*)-**4a** (518 mg, 1.0 mmol) in dry benzene (500 mL) at 25 °C was added diisobutylaluminum hydride (1.0 M solution in toluene, 2.5 mL, 2.5 mmol) under an argon atmosphere. After stirring for 1 h, the reaction mixture was poured into 5% aqueous  $\text{H}_2\text{SO}_4$ . The aqueous layer was separated from the organic layer and successively extracted with benzene and chloroform. The organic layer was combined with the extracts, washed with water and brine, dried over  $\text{MgSO}_4$  and filtered. The filtrate was concentrated to give (*E*)-**5a** (491 mg, 94%) as a white solid. An analytical sample was obtained by recrystallization from benzene as colorless crystals: mp 248.0-251.0 °C (dec.);  $^1\text{H}$  NMR:  $\delta$  9.43 (s, 2H,  $\text{H}_a$ ), 7.53 (d,  $J = 8.8\text{Hz}$ , 4H,  $\text{H}_f$ ), 7.17 (d,  $J = 8.8\text{Hz}$ , 4H,  $\text{H}_e$ ), 7.14 (s, 2H,  $\text{H}_d$ ), 3.75 (d,  $J = 15.1$ , 4H,  $\text{H}_b$ ), 3.23 (d,  $J = 15.1\text{Hz}$ , 4H,  $\text{H}_c$ );  $^{13}\text{C}$  NMR:  $\delta$  198.85, 139.35, 137.98, 132.20, 129.21, 121.84, 120.67, 63.21, 38.61; IR (KBr): 2900, 2836, 1720, 1488, 1398, 1078, 1010, 882, 818  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 526 ( $M^+ + 4$ , 51), 524 ( $M^+ + 2$ , 100), 522 ( $M^+$ , 49), 495 ( $M^+ + 2\text{-CHO}$ , 65); Anal. calcd. for  $\text{C}_{26}\text{H}_{20}\text{O}_2\text{Br}_2$ : C, 59.57; H, 3.85; Br, 30.48. Found: C, 59.71; H, 3.86; Br, 30.51.

**Preparation of (*E*)-2,6-Bis[4'-(*tert*-butyldimethylsilyloxy)biphenyl-4-yl]-1,2,3,5,6,7-hexahydro-s-indacene-2,6-dicarbaldehyde 5b:**

To a solution of (*E*)-**4b** (221 mg, 0.29 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (10 mL) at room temperature was added diisobutylaluminum hydride (0.95 M solution in hexane, 750  $\mu\text{L}$ , 0.71 mmol) under an argon atmosphere. After stirring for 2 h, the reaction mixture was poured into 5% aqueous  $\text{H}_2\text{SO}_4$ . The aqueous layer was separated from the organic layer and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was combined with the extract, washed with water and brine, dried over  $\text{MgSO}_4$ , and then filtered. The filtrate was concentrated to give **5b** (186 mg, 84%) as a white solid: mp 219.0-220.0 °C (dec.);  $^1\text{H}$  NMR:  $\delta$  9.48 (s, 2H,  $\text{H}_a$ ), 7.58, (d,  $J = 8.4\text{Hz}$ , 4H,  $\text{H}_f$ ) 7.46 (d,  $J = 8.7\text{Hz}$ , 4H,  $\text{H}_g$ ), 7.34 (d,  $J = 8.4\text{Hz}$ , 4H,  $\text{H}_e$ ), 7.18 (s, 2H,  $\text{H}_d$ ), 6.91 (d,  $J = 8.7\text{Hz}$ , 4H,  $\text{H}_h$ ), 3.81 (d,  $J = 15.0\text{Hz}$ , 4H,  $\text{H}_b$ ), 3.31 (d,  $J = 15.0\text{Hz}$ , 4H,  $\text{H}_c$ ), 1.00 (s, 18H, *t*Bu), 0.23 (s, 12H, Me);  $^{13}\text{C}$  NMR:  $\delta$  199.33, 155.51, 140.20, 139.52, 137.20, 133.42, 128.03, 127.91, 127.33, 120.66, 120.42, 63.38, 38.62, 25.70, 18.25, -4.37; IR (KBr): 2957, 2929, 2858, 1729, 1604, 1494, 1253, 1169, 905, 839, 821, 783  $\text{cm}^{-1}$ ; MS (FD)  $m/z$  (%): 779 ( $M^+ + 1$ , 64), 778 ( $M^+$ , 100), 664( $M^+ \text{-TBS} + 1$ , 48); HR-MS (FD) calcd. for  $\text{C}_{50}\text{H}_{58}\text{O}_4\text{Si}_2$ : 778.3874; found: 778.3887; Anal. calcd. for  $\text{C}_{50}\text{H}_{58}\text{O}_4\text{Si}_2 \cdot 0.5\text{H}_2\text{O}$ : C, 76.19; H, 7.54. found: C, 76.14; H, 7.48.

**Preparation of 2,6-Bis[4-(*tert*-butyldimethylsilyloxy)phenyl]aniline 6a:** 4-(*tert*-Butyldimethylsilyloxy)phenylboronic acid (4.46 g, 17.7 mmol) was added to a solution of 2,6-dibromoaniline (1.82 g, 7.3 mmol) in a mixture of benzene (60 mL), EtOH (20 mL) and 2 M aqueous Na<sub>2</sub>CO<sub>3</sub> (30 mL) at room temperature under an argon atmosphere. Pd(PPh<sub>3</sub>)<sub>4</sub> (360 mg, 0.3 mmol, 4 mol%) was then added and the mixture was heated under reflux with stirring for 48 h. After the solution was diluted with benzene, the organic layer was separated from the aqueous layer, washed with 5% aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, water and brine, dried over MgSO<sub>4</sub>, and then filtered. The brown solid obtained by concentrating the filtrate was subjected to chromatography on silica gel eluted with EtOAc/hexane (1:19). The resulting white solid was recrystallized from hexane at -10 °C to give pure **6a** (3.57 g, 97%) as colorless crystals: mp 65.0-66.0 °C; <sup>1</sup>H NMR: δ 7.35 (d, *J* = 8.7 Hz, 4H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 4H), 6.84 (t, *J* = 7.5, 1H), 3.80 (br.s, 2H), 1.00 (s, 18H), 0.24 (s, 12H); <sup>13</sup>C NMR: δ 154.85, 141.05, 132.59, 130.36, 129.43, 127.67, 120.29, 117.98, 25.68, 18.20, -4.37; IR (KBr): 3427, 3347, 2956, 2929, 2858, 1605, 1508, 1463, 1447, 1263, 1169, 907, 853, 781 cm<sup>-1</sup>; MS (EI) *m/z* (%): 506 (M<sup>+</sup>+1, 97), 505 (M<sup>+</sup>, 100); HR-MS (EI) calcd. for C<sub>30</sub>H<sub>43</sub>NO<sub>2</sub>Si<sub>2</sub>: 505.2832, found: 505.2848.

**Preparation of 2,6-Bis[4-(*prop*-2-ynyloxy)phenyl]aniline 6b:** To a solution of **6a** (2.69 g, 5.3 mmol) in dry THF (30 mL) at 25 °C was added tetrabutylammonium fluoride (TBAF, 1.0 M solution in THF, 10.6 mL, 10.6 mmol) under an argon atmosphere. After stirring for 5 min, Cs<sub>2</sub>CO<sub>3</sub> (3.46 g, 26.5 mmol) and propargyl bromide (1.97 mL, 26.5 mmol) were added. The mixture was stirred for 16 h at room temperature and then poured into 5% aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The aqueous layer was separated from the organic layer and extracted with ether. The organic layer was combined with the extract, washed with water and brine, dried over MgSO<sub>4</sub>, and then filtered. The brown solid obtained by concentrating the filtrate was subjected to chromatography on silica gel eluted with benzene to give pure **6b** (1.63 g, 87%). An analytical sample was obtained by gel-permeation-chromatography (GPC; eluted with CHCl<sub>3</sub>) as colorless crystals: mp 123.0-125.0 °C; <sup>1</sup>H NMR: δ 7.44 (d, *J* = 8.7 Hz, 4H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 4H), 6.85 (t, *J* = 7.5 Hz, 1H), 4.74 (d, *J* = 2.7 Hz, 4H), 3.80 (br. s, 2H), 2.55 (t, *J* = 2.7 Hz, 2H); <sup>13</sup>C NMR: δ 156.79, 141.11, 132.94, 130.46, 129.59, 127.42, 118.09, 115.19, 78.57, 75.63, 55.85; IR (KBr): 3417, 3339, 3283, 3165, 2106, 1606, 1509, 1445, 1289, 1213, 1173, 1024, 923, 829, 752 cm<sup>-1</sup>; MS (EI) *m/z* (%): 353 (M<sup>+</sup>, 100), 314 (47); HR-MS (EI) calcd. for C<sub>24</sub>H<sub>19</sub>NO<sub>2</sub>: 353.1416; found: 353.1440; Anal. calcd. for C<sub>24</sub>H<sub>19</sub>NO<sub>2</sub>: C, 81.56; H, 5.42; N, 3.96. found: C, 82.02; H, 5.51; N, 3.71.

**Preparation of Macrocycle 7a:** A solution of **6b** (596 mg, 1.69 mmol) in dry CH<sub>3</sub>CN (50 mL) was added to a refluxing suspension of anhydrous Cu(OAc)<sub>2</sub> (119 mg, 6.59 mmol) in dry CH<sub>3</sub>CN (300 mL) over 25 h using a syringe pump. After the completion of the addition, the mixture was stirred for an additional 2 h and then concentrated in vacuo. The resulting solid was dissolved in a mixture of CHCl<sub>3</sub> and water. The aqueous layer was separated from the organic layer and extracted with CHCl<sub>3</sub>. The organic layer was combined with the extract, washed with brine, and the mixture was extracted with CHCl<sub>3</sub>. The organic layer was washed with water and brine, dried over MgSO<sub>4</sub>, and then filtered. The yellow solid obtained by concentrating the filtrate was subjected to chromatography on silica gel eluted with CHCl<sub>3</sub> to give pure **7a** (465 mg, 79%) as a white solid. An analytical sample was obtained by recrystallization from acetone as colorless crystals: mp 179-181 °C (dec.); <sup>1</sup>H NMR: δ 7.43 (d, *J* = 8.7 Hz, 8H, H<sub>C</sub>), 7.05 (d, *J* = 7.5 Hz, 4H, H<sub>D</sub>), 7.03 (d, *J* = 8.7 Hz, 8H, H<sub>B</sub>), 6.82 (t, *J* = 7.5 Hz, 2H, H<sub>E</sub>), 4.82 (s, 8H, H<sub>A</sub>), 3.82 (br. s, 4H, NH<sub>2</sub>); <sup>13</sup>C NMR: δ 156.47, 141.08, 133.08, 130.48, 129.58, 127.31, 118.06, 115.12, 74.84, 71.18, 55.98; IR (KBr): 3444, 3357, 3036, 2909, 2854, 2114, 1606, 1510, 1448, 1214, 1178, 1018, 832, 748 cm<sup>-1</sup>; MS (FD) *m/z* (%): 703 (M<sup>+</sup>+1, 52), 702 (M<sup>+</sup>, 100); HR-MS (FD) calcd. for C<sub>48</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>: 702.2519; found: 702.2497; Anal. calcd. for C<sub>48</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>·C<sub>3</sub>H<sub>6</sub>O: C, 80.51; H, 4.88; N, 3.99. found: C, 80.90; H, 5.15; N, 3.73.

**Preparation of Macrocycle 7b :** A mixture of **7a** (275 mg, 391 μmol) and 10% Pd/C (3.0 mg) in THF (100 mL) was stirred for 16 h at room temperature under hydrogen atmosphere and then filtrated through celite. The filtrate was concentrated in vacuo to give **7b** (281 mg, >99%) as a white solid: mp 276.0-277.0 °C (dec.); <sup>1</sup>H NMR: δ 7.36 (d, *J* = 8.4 Hz, 8H, H<sub>C</sub>), 7.07 (d, *J* = 7.2 Hz, 4H, H<sub>D</sub>), 6.93 (d, *J* = 8.4 Hz, 8H, H<sub>B</sub>), 6.82 (t, *J* = 7.2 Hz, 2H, H<sub>E</sub>), 4.03 (t, *J* = 6.3 Hz, 8H, H<sub>A</sub>), 3.68 (m, 4H, NH<sub>2</sub>), 1.85 (m, 8H, OCH<sub>2</sub>CH<sub>2</sub>), 1.58 (br. s, 8H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C NMR: δ 158.32, 141.32, 131.85, 130.39, 129.23, 127.60, 117.94, 114.90, 67.62, 28.74, 25.24; IR (KBr): 3464, 3371, 3031, 2939, 2865, 1608, 1510, 1449, 1402, 1284, 1240, 1174, 1108, 1018, 836, 787, 748 cm<sup>-1</sup>; MS (FD) *m/z* (%): 719 (M<sup>+</sup>+1, 54), 718 (M<sup>+</sup>, 100); Anal. calcd. for C<sub>48</sub>H<sub>50</sub>N<sub>2</sub>O<sub>4</sub>: C, 80.19; H, 7.01; N, 3.90. found: C, 80.21; H, 7.05; N, 3.89.

**Preparation of Bromo-terminated Imine-bridged Pseudorotaxane 1a:** To a solution of **5a** (135 mg, 0.26 mmol) and **7a** (217 mg, 0.31 mmol) in benzene (35 mL) was added a catalytic amount of trifluoroacetic acid (one drop, ca. 10 μL, 0.13 mmol). The mixture was refluxed for 35 h under dehydrating conditions (Soxhlet apparatus with a thimble filter containing MS4A), while additional

trifluoroacetic acid (one drop, ca. 10  $\mu$ L, 0.13 mmol) was added to the mixture every 10 h. The solvent was removed in vacuo and the resulting solid was washed with MeOH. GPC separation of the residue gave **1a** (306 mg, >99%) as a white solid. Single crystals for X-ray crystallography was obtained by recrystallization from THF/hexane as colorless crystals: mp 230-233  $^{\circ}$ C (dec.);  $^1$ H NMR:  $\delta$  7.36 (d,  $J$  = 8.7 Hz, 4H, H<sub>f</sub>), 7.15 (d,  $J$  = 8.7 Hz, 2H, H<sub>D1</sub>), 7.14 (d,  $J$  = 6.0 Hz, 2H, H<sub>D2</sub>), 7.09 (s, 2H, H<sub>a</sub>), 7.08 (dd,  $J$  = 8.7 Hz, 6.0 Hz, 2H, H<sub>E</sub>), 6.95 (d,  $J$  = 8.7 Hz, 8H, H<sub>C</sub>), 6.75 (d,  $J$  = 8.7 Hz, 4H, H<sub>e</sub>), 6.69 (s, 2H, H<sub>d</sub>), 6.49 (d,  $J$  = 8.7 Hz, 8H, H<sub>B</sub>), 4.81 (d,  $J$  = 15.3 Hz, 4H, H<sub>A1</sub> or H<sub>A2</sub>), 4.70 (d,  $J$  = 15.3 Hz, 4H, H<sub>A1</sub> or H<sub>A2</sub>), 3.44 (d,  $J$  = 15.0 Hz, 4H, H<sub>b</sub>), 3.29 (d,  $J$  = 15.0 Hz, 4H, H<sub>c</sub>); IR (KBr): 3052, 2910, 2849, 2150, 1657, 1608, 1510, 1459, 1213, 1018, 829  $\text{cm}^{-1}$ ; MS (FD)  $m/z$  (%): 1193 ( $M^+$ +5, 58), 1192 ( $M^+$ +4, 71), 1191 ( $M^+$ +3, 81), 1190 ( $M^+$ +2, 100), 1189 ( $M^+$ +1, 35), 1188 ( $M^+$ , 69); HR-MS (FD) calcd. for  $C_{74}H_{50}N_2O_4Br_2$ : 1188.2137; found: 1188.2164; Anal. calcd. for  $C_{74}H_{50}N_2O_4Br_2 \cdot 2CH_3OH$ : C, 72.73; H, 4.66; N, 2.23. found: C, 72.95; H, 4.39; N, 2.30.

**Preparation of TBSO-terminated Imine-bridged Pseudorotaxane 1b:** Compound **1b** was prepared from **5b** (139 mg, 0.18 mmol) and **7a** (125 mg, 0.18 mmol) following the same protocol as described for **1a** (PhH 50 mL, TFA one drop, ca. 10  $\mu$ L, 0.13 mmol, 10 h). The crude product was purified by GPC separation to give **1b** (244 mg, 95%) as a white solid. An analytic sample was obtained by recrystallization from  $CHCl_3$ /hexane as colorless crystals: mp 242.0-244.0  $^{\circ}$ C (dec.);  $^1$ H NMR:  $\delta$  7.49 (d,  $J$  = 9.0 Hz, 4H, H<sub>g</sub>), 7.45 (d,  $J$  = 8.1 Hz, 4H, H<sub>f</sub>), 7.19 (s, 2H, H<sub>a</sub>), 7.14 (d,  $J$  = 6.0 Hz, 2H, H<sub>D1</sub>), 7.14 (d,  $J$  = 8.7 Hz, 2H, H<sub>D2</sub>), 7.06 (dd,  $J$  = 8.7 Hz, 6.0 Hz, 2H, H<sub>E</sub>), 6.98 (d,  $J$  = 8.1 Hz, 4H, H<sub>e</sub>), 6.95 (d,  $J$  = 9.0 Hz, 8H, H<sub>C</sub>), 6.93 (d,  $J$  = 9.0 Hz, 4H, H<sub>b</sub>), 6.73 (s, 2H, H<sub>d</sub>), 6.51 (d,  $J$  = 9.0 Hz, 8H, H<sub>B</sub>), 4.82 (d,  $J$  = 15.3 Hz, 4H, H<sub>A1</sub> or H<sub>A2</sub>), 4.72 (d,  $J$  = 15.3 Hz, 4H, H<sub>A1</sub> or H<sub>A2</sub>), 3.49 (d,  $J$  = 15.3 Hz, 4H, H<sub>b</sub>), 3.37 (d,  $J$  = 15.3 Hz, 4H, H<sub>c</sub>), 1.01 (s, 18H, *t*Bu), 0.25 (s, 12H, Me);  $^{13}C$  NMR:  $\delta$  170.61, 155.41, 155.17, 149.81, 142.08, 139.70, 138.65, 134.12, 132.96, 132.89, 130.53, 128.53, 127.98, 127.76, 126.70, 123.65, 120.33, 120.11, 114.07, 74.59, 71.39, 56.60, 56.18, 40.11, 25.72, 18.25, -4.34; IR (KBr): 3032, 2955, 2927, 2856, 2153, 1653, 1608, 1511, 1496, 1460, 1434, 1362, 1286, 1255, 1228, 1212, 1176, 1111, 1020, 921, 827  $\text{cm}^{-1}$ ; MS (FD)  $m/z$  (%): 1448 ( $M^+$ +2, 44), 1446 ( $M^+$ , 100); HR-MS (FD) calcd. for  $C_{98}H_{88}N_2O_6Si_2$ : 1444.6181; found: 1444.6154; Anal. calcd. for  $C_{98}H_{88}N_2O_6Si_2$ : C, 81.40; H, 6.13; N, 1.94. found: C, 81.14; H, 6.29; N, 1.61.

**Preparation of Imine-bridged Pseudorotaxane 1c:** A mixture of **1b** (94 mg, 65  $\mu$ mol) and 10% Pd/C (3.0 mg) in THF (100 mL) was stirred for 3 h at room temperature under hydrogen atmosphere and then filtrated though celite. The filtrate was concentrated to give **1c** (95 mg, >99%)

as a white solid: mp >300 °C;  $^1\text{H}$  NMR:  $\delta$  7.42, (d,  $J$  = 8.4 Hz, 4H,  $\text{H}_g$ ), 7.39 (d,  $J$  = 9.0 Hz, 4H,  $\text{H}_f$ ), 7.23 (s, 2H,  $\text{H}_a$ ), 7.19 (d,  $J$  = 7.2 Hz, 4H,  $\text{H}_d$ ), 7.08 (dd,  $J$  = 8.4 Hz,  $J$  = 7.2 Hz, 2H,  $\text{H}_e$ ), 6.99 (d,  $J$  = 8.4 Hz, 8H,  $\text{H}_c$ ), 6.96 (d,  $J$  = 9.0 Hz, 4H,  $\text{H}_e$ ), 6.88 (d,  $J$  = 8.4 Hz, 4H,  $\text{H}_h$ ), 6.82 (s, 2H,  $\text{H}_d$ ), 6.73 (d,  $J$  = 8.4 Hz, 8H,  $\text{H}_b$ ), 4.07 (m, 8H,  $\text{H}_A$ ), 3.24 (d,  $J$  = 15.0 Hz, 4H,  $\text{H}_b$ ), 3.10 (d,  $J$  = 15.0 Hz, 4H,  $\text{H}_c$ ), 1.85 (m, 8H,  $\text{OCH}_2\text{CH}_2$ ), 1.52 (m, 8H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.00 (s, 18H,  $t\text{Bu}$ ), 0.23 (s, 12H,  $\text{Me}$ );  $^{13}\text{C}$  NMR:  $\delta$  169.40, 157.03, 155.32, 148.61, 142.82, 139.32, 139.23, 133.68, 133.36, 132.34, 131.01, 128.58, 128.00, 127.55, 126.77, 123.85, 120.62, 120.33, 114.81, 68.25, 56.52, 40.45, 28.99, 25.86, 25.68, 18.22, -4.38; IR (KBr): 3036, 2932, 2860, 1660, 1607, 1511, 1495, 1254, 1177, 1105, 1007, 918, 831  $\text{cm}^{-1}$ ; MS (FD)  $m/z$  (%): 1463 ( $\text{M}^+ + 1$ , 70), 1462 ( $\text{M}^+$ , 100), 1461 ( $\text{M}^+ - 1$ , 87); Anal. calcd. for  $\text{C}_{98}\text{H}_{104}\text{N}_2\text{O}_6\text{Si}_2$ : C, 80.51; H, 7.17; N, 1.92. found: C, 80.32; H, 7.23; N, 1.86.

**Preparation of Tris(4'-*tert*-butylbiphenyl-4-yl)methanol 9:** To a solution of 4-bromo-4'-*tert*-butylbiphenyl (1.76 g, 6.1 mmol) in THF (100 mL) at -40 °C was added *n*-butyllithium (1.56 M solution in hexane, 4.1 mL, 6.4 mmol) under an argon atmosphere. After 1 h, diethylcarbonate (253  $\mu\text{L}$ , 2.1 mmol) was added and the mixture was stirred for 2 h at -40 °C, before pouring into saturated aqueous  $\text{NH}_4\text{Cl}$ . The aqueous layer was separated from the organic layer and extracted with ether. The extract was combined with the organic layer, washed with brine, dried over  $\text{MgSO}_4$ , and then filtered. The crude obtained by concentrating the filtrate was subjected to chromatography on silica gel eluted with benzene to give **9** (1.07 g, 80%) as a white solid: mp 270.0-271.0 °C (dec.);  $^1\text{H}$  NMR:  $\delta$  7.57, (d,  $J$  = 8.4 Hz, 6H), 7.55 (d,  $J$  = 8.4 Hz, 6H), 7.46 (d,  $J$  = 8.4 Hz, 6H), 7.41 (d,  $J$  = 8.4 Hz, 6H), 2.88 (s, 1H), 1.36 (s, 27H);  $^{13}\text{C}$  NMR:  $\delta$  150.36, 145.56, 139.99, 137.73, 128.31, 126.73, 126.58, 125.73, 81.74, 34.55, 31.37; IR (KBr): 3578, 3447, 3030, 2963, 2905, 2870, 1497, 1392, 1363, 1268, 1112, 1004, 820, 566  $\text{cm}^{-1}$ ; MS (FD)  $m/z$  (%): 658 ( $\text{M}^+ + 2$ , 25), 657 ( $\text{M}^+ + 1$ , 91), 656 ( $\text{M}^+$ , 100); HR-MS (FD) calcd. for  $\text{C}_{49}\text{H}_{52}\text{O}$ : 656.4018; found: 656.3993; Anal. calcd. for  $\text{C}_{49}\text{H}_{52}\text{O}$ : C, 89.59; H, 7.98; found: C, 89.59; H, 8.04.

**Preparation of 4-[Tris(4'-*tert*-butylbiphenyl-4-yl)methyl]phenol 10:** A mixture of **9** (468 mg, 0.71 mmol) and acetyl chloride (15 mL) was stirred for 5 min at room temperature. To a purple solid obtained by concentrating the reaction mixture was added phenol (9.4 g, 0.1 mol). After stirring for 18 h at 100 °C under an argon atmosphere, the reaction mixture was poured into  $\text{CHCl}_3$  (20 mL). The resulting solution was washed with 2 M aqueous NaOH. The washings were combined and extracted with  $\text{CHCl}_3$ . The  $\text{CHCl}_3$  solution was combined with the extract, washed with water and brine, dried over  $\text{MgSO}_4$ , and then filtered. The crude product obtained by concentrating the filtrate was subjected to chromatography on silica gel eluted with benzene to give

**10** (515 mg, 99%) as a white solid: mp >300 °C; <sup>1</sup>H NMR: δ 7.55 (d, *J* = 8.4 Hz, 6H), 7.51 (d, *J* = 8.4 Hz, 6H), 7.45 (d, *J* = 8.4 Hz, 6H), 7.34 (d, *J* = 8.4 Hz, 6H), 7.17 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 4.78 (s, 1H), 1.35 (s, 27H); <sup>13</sup>C NMR: δ 153.52, 150.15, 145.77, 139.25, 138.38, 137.68, 132.44, 131.43, 126.58, 125.92, 125.67, 114.32, 63.63, 34.51, 31.35; IR (KBr): 3538, 3430, 3028, 2963, 2905, 2867, 1494, 1269, 1178, 1113, 1004, 816, 594, 566, 529 cm<sup>-1</sup>; MS (FD) *m/z* (%): 733 (M<sup>+</sup>+1, 47), 732 (M<sup>+</sup>, 100); HR-MS (FD) calcd. for C<sub>55</sub>H<sub>56</sub>O: 732.4331; found: 732.4357; Anal. calcd. for C<sub>55</sub>H<sub>56</sub>O·0.5H<sub>2</sub>O: C, 89.02; H, 7.74; found: C, 89.19; H, 7.77.

**Preparation of α-[4-{Tris(4'-*tert*-butylbiphenyl-4-yl)methyl}phenoxy]-α'-bromo-*p*-xylene **8b**:**

To a solution of **10** (79 mg, 0.11 mmol) in dry THF (30 mL) was added NaH (60% in oil, 12 mg, 0.3 mmol) under an argon atmosphere. After stirring for 20 min at room temperature, α,α'-dibromo-*p*-xylene (420 mg, 1.6 mmol) in dry THF (30 mL) was added to the resulting mixture. After 14 h, the reaction mixture was poured into saturated aqueous NH<sub>4</sub>Cl and extracted with ether. The ethereal extract was washed with brine, dried over MgSO<sub>4</sub>, and then filtered. GPC separation of the residue obtained by concentrating the filtrate gave **8b** (74 mg, 76%) as a white solid: mp 284.0-285.0 °C (dec.); <sup>1</sup>H NMR: δ 7.55, (d, *J* = 8.4 Hz, 6H), 7.51 (d, *J* = 8.4 Hz, 6H), 7.45 (d, *J* = 8.4 Hz, 6H), 7.42 (s, 4H), 7.31 (d, *J* = 8.4 Hz, 6H), 7.22 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 5.05 (s, 2H), 4.51 (s, 2H), 1.35 (s, 27H); <sup>13</sup>C NMR: δ 189.31, 156.75, 150.16, 145.76, 138.38, 137.69, 137.47, 132.28, 131.44, 129.29, 127.91, 126.58, 125.92, 125.67, 113.63, 87.38, 69.51, 63.65, 34.51, 33.16, 31.35; IR (KBr): 3028, 2961, 2901, 2866, 1605, 1579, 1494, 1361, 1268, 1242, 1182, 1112, 1004, 816, 565 cm<sup>-1</sup>; MS (FD) *m/z* (%): 917 (M<sup>+</sup>+3, 45), 916 (M<sup>+</sup>+2, 100), 915 (M<sup>+</sup>+1, 46), 914 (M<sup>+</sup>, 84); HR-MS (FD) calcd. for C<sub>63</sub>H<sub>63</sub>OBr: 914.4062; found: 914.4067; Anal. calcd. for C<sub>63</sub>H<sub>63</sub>OBr: C, 82.60; H, 6.93. found: C, 83.07; H, 7.03.

**Preparation of Imine-bridged Rotaxane **1d****: To a solution of **1b** (32 mg, 22 μmol) in dry THF (1 mL) and dry DMF (4 mL) at room temperature was added TBAF (1.0 M solution in THF, 43 μL, 43 μmol) under an argon atmosphere. After stirring for 5 min, Cs<sub>2</sub>CO<sub>3</sub> (28 mg, 86 μmol) and **8a** (33 mg, 48 μmol) were added. And the mixture was then stirred for 17 h at room temperature, before pouring into water. The aqueous mixture was extracted with CHCl<sub>3</sub> and the extract was washed with water and brine, dried over MgSO<sub>4</sub>, and then filtered. The crude product obtained by concentrating the filtrate was separated by GPC to give **1d** (36 mg, 68%) as a white solid: <sup>1</sup>H NMR: δ 7.55 (d, *J* = 8.4 Hz, 4H, H<sub>g</sub>), 7.48 (s, 8H, H<sub>j,k</sub>), 7.45 (d, *J* = 8.4 Hz, 4H, H<sub>f</sub>), 7.23 (d, *J* = 8.4 Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>), 7.18 (s, 2H, H<sub>a</sub>), 7.14 (d, *J* = 8.7 Hz, 2H, H<sub>D1</sub>), 7.14 (d, *J* = 6.0 Hz, 2H, H<sub>D2</sub>), 7.11-7.07 (m, 6H,

H<sub>E,h</sub>), 7.10 (d,  $J = 9.0$  Hz, 4H, H<sub>n</sub>), 7.08 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>), 6.97 (d,  $J = 8.4$  Hz, 4H, H<sub>e</sub>), 6.96 (d,  $J = 8.4$  Hz, 8H, H<sub>C</sub>), 6.85 (d,  $J = 9.0$  Hz, 4H, H<sub>m</sub>), 6.73 (s, 2H, H<sub>d</sub>), 6.51 (d,  $J = 8.4$  Hz, 8H, H<sub>B</sub>), 5.13 (s, 4H, H<sub>i</sub>), 5.05 (s, 4H, H<sub>j</sub>), 4.82 (d,  $J = 15.3$  Hz, 4H, H<sub>A1</sub> or H<sub>A2</sub>), 4.71 (d,  $J = 15.3$  Hz, 4H, H<sub>A1</sub> or H<sub>A2</sub>), 3.49 (d,  $J = 15.0$  Hz, 4H, H<sub>b</sub>), 3.37 (d,  $J = 15.0$  Hz, 4H, H<sub>c</sub>), 1.30 (s, 54H, *t*Bu); LR-MS (FAB) calcd. for C<sub>176</sub>H<sub>160</sub>N<sub>2</sub>O<sub>8</sub>: 2431.2; found: 2431.9.

**Preparation of Imine-bridged Rotaxane 1e:** Compound **1e** was prepared from **1b** (16.5 mg, 11.4 μmol) and **8b** (23 mg, 25 μmol) following the same protocol as described for **1d** (THF 5.0 mL, DMF 5.0 mL, TBAF 23 μmol, Cs<sub>2</sub>CO<sub>3</sub> 15 mg). The crude product was purified by preparative TLC (silica gel) eluted with benzene to give **1e** (17 mg, 52%) as a white solid: mp 252.0-254.0 °C (dec.); <sup>1</sup>H NMR: δ 7.56-7.43 (2d, 8H, H<sub>f,g</sub>), 7.55 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>), 7.51 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>), 7.47 (s, 8H, H<sub>i,k</sub>), 7.45 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>), 7.32 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>), 7.23 (d,  $J = 9.0$  Hz, 4H, H<sub>n</sub>), 7.18 (s, 2H, H<sub>a</sub>), 7.14 (d,  $J = 8.7$  Hz, 2H, H<sub>D1</sub>), 7.14 (d,  $J = 6.0$  Hz, 2H, H<sub>D2</sub>), 7.07 (d,  $J = 8.4$  Hz, 4H, H<sub>h</sub>), 7.06 (dd,  $J = 8.7$  Hz, 6.0 Hz, 2H, H<sub>E</sub>), 6.97 (d,  $J = 8.4$  Hz, 4H, H<sub>e</sub>), 6.96 (d,  $J = 8.4$  Hz, 8H, H<sub>C</sub>), 6.92 (d,  $J = 9.0$  Hz, 4H, H<sub>m</sub>), 6.73 (s, 2H, H<sub>d</sub>), 6.51 (d,  $J = 8.4$  Hz, 8H, H<sub>B</sub>), 5.14 (s, 4H, H<sub>i</sub>), 5.08 (s, 4H, H<sub>j</sub>), 4.81 (d,  $J = 15.3$  Hz, 4H, H<sub>A1</sub> or H<sub>A2</sub>), 4.71 (d,  $J = 15.3$  Hz, 4H, H<sub>A1</sub> or H<sub>A2</sub>), 3.49 (d,  $J = 15.3$  Hz, 4H, H<sub>b</sub>), 3.37 (d,  $J = 15.3$  Hz, 4H, H<sub>c</sub>), 1.35 (s, 54H, *t*Bu); <sup>13</sup>C NMR; δ 170.55, 158.18, 156.83, 155.39, 150.14, 149.79, 145.77, 142.13, 139.68, 139.31, 138.36, 137.69, 136.88, 136.81, 133.93, 132.92, 132.84, 132.26, 131.44, 130.51, 128.52, 128.08, 127.87, 127.78, 127.71, 127.69, 126.70, 126.58, 125.92, 125.66, 123.66, 120.10, 115.15, 114.03, 113.63, 74.56, 71.37, 69.82, 69.69, 63.64, 56.59, 56.15, 40.09, 34.51, 31.35; IR (KBr): 3030, 2958, 2904, 2866, 1606, 1506, 1495, 1362, 1224, 1174, 1112, 1003, 818 cm<sup>-1</sup>; LR-MS (FAB) calcd. for C<sub>212</sub>H<sub>184</sub>N<sub>2</sub>O<sub>8</sub>: 2887.4, found: 2888.2; Anal. calcd. for C<sub>212</sub>H<sub>184</sub>N<sub>2</sub>O<sub>8</sub>·2H<sub>2</sub>O: C, 87.09; H, 6.48; N, 0.96. found: C, 87.04; H, 6.57; N, 0.94.

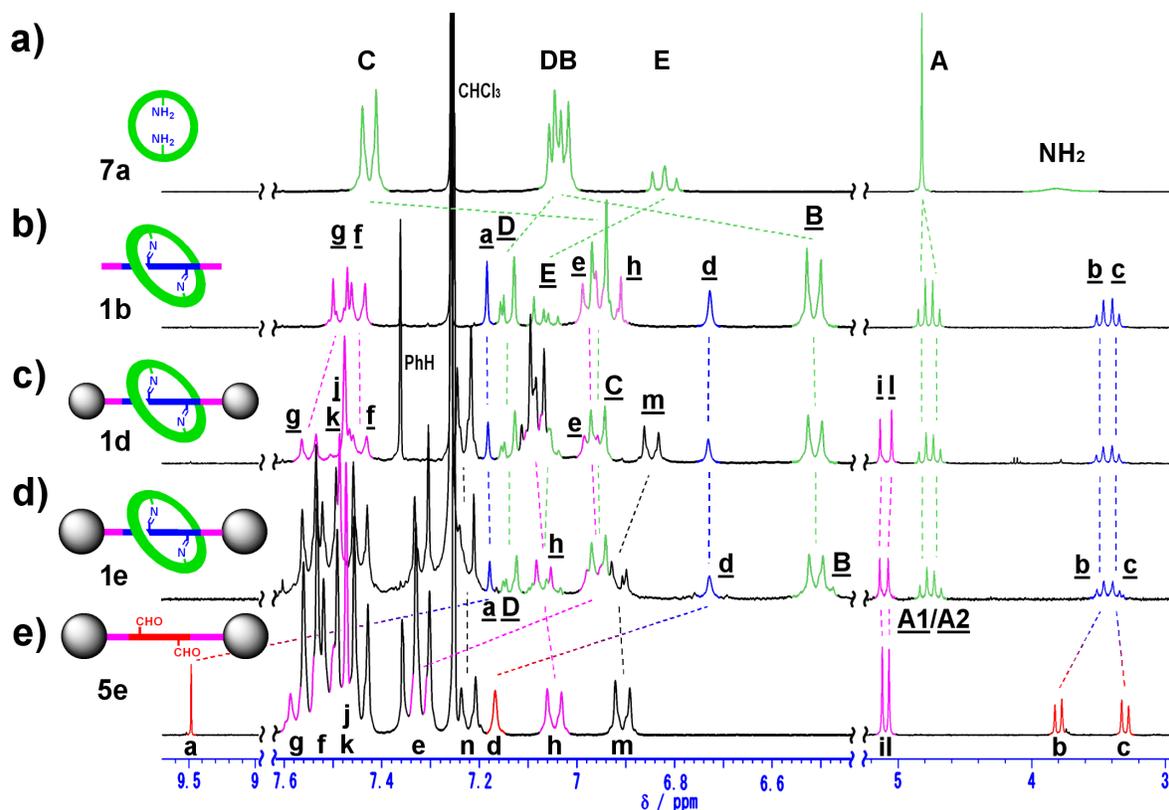
**Preparation of Imine-bridged Rotaxane 1f:** Compound **1e** was prepared from **1c** (95.1 mg, 65.0 μmol) and **8b** (148.9 mg, 163.0 μmol) following the same protocol as described for **1d** (THF 30.0 mL, DMF 3.0 mL, TBAF 130 μmol, Cs<sub>2</sub>CO<sub>3</sub> 15 mg). The crude product was purified by chromatography on silica gel eluted with benzene/hexane (4:1) to give **1f** (131 mg, 69 %) as a white solid: mp 243.0-245.0 °C (dec.); <sup>1</sup>H NMR: δ 7.55 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>), 7.50 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>), 7.47 (s, 8H, H<sub>i,k</sub>), 7.45 (d,  $J = 7.8$  Hz, 4H, H<sub>g</sub>), 7.44 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>), 7.42 (d,  $J = 8.7$  Hz, 4H, H<sub>f</sub>), 7.32 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>), 7.23 (s, 2H, H<sub>a</sub>), 7.22 (d,  $J = 9.0$  Hz, 4H, H<sub>n</sub>), 7.18 (d,  $J = 6.9$  Hz, 4H, H<sub>D1</sub>), 7.08 (dd,  $J = 8.4$  Hz, 6.9 Hz, 2H, H<sub>E</sub>),

7.03 (d,  $J = 8.7$  Hz, 4H, H<sub>h</sub>), 6.98 (d,  $J = 8.4$  Hz, 8H, H<sub>C</sub>), 6.96 (d,  $J = 7.8$  Hz, 4H, H<sub>e</sub>), 6.90 (d,  $J = 9.0$  Hz, 4H, H<sub>m</sub>), 6.82 (s, 2H, H<sub>d</sub>), 6.73 (d,  $J = 8.4$  Hz, 8H, H<sub>B</sub>), 5.12 (s, 4H, H<sub>i</sub>), 5.06 (s, 4H, H<sub>l</sub>), 4.06 (m, 4H, H<sub>A</sub>), 3.24 (d,  $J = 15.3$  Hz, 4H, H<sub>b</sub>), 3.10 (d,  $J = 15.3$  Hz, 4H, H<sub>c</sub>), 1.84 (m, 8H, OCH<sub>2</sub>CH<sub>2</sub>), 1.53 (m, 8H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.35 (s, 54H, *t*Bu); <sup>13</sup>C NMR:  $\delta$  169.37, 158.34, 157.04, 156.85, 150.19, 148.60, 145.78, 139.34, 139.24, 139.17, 138.39, 137.71, 136.93, 136.73, 133.49, 133.36, 132.34, 132.28, 131.45, 131.01, 128.58, 128.08, 127.85, 127.69(2C), 127.60, 126.77, 126.58, 125.92, 125.66, 123.87, 120.62, 115.18, 114.81, 113.65, 69.84, 69.70, 68.25, 63.67, 56.54, 40.45, 34.52, 31.36, 29.00, 25.86; IR (KBr): 3027, 2959, 2865, 1908, 1650, 1607, 1580, 1510, 1495, 1459, 1392, 1363, 1240, 1175, 1112, 1033, 1003, 816 cm<sup>-1</sup>; LR-MS (FD) calcd. for C<sub>212</sub>H<sub>200</sub>N<sub>2</sub>O<sub>8</sub>: 2903.5, found: 2903.9; Anal. calcd. for C<sub>212</sub>H<sub>200</sub>N<sub>2</sub>O<sub>8</sub>·H<sub>2</sub>O: C, 87.15; H, 6.97; N, 0.96. found: C, 86.94; H, 6.99; N, 0.98.

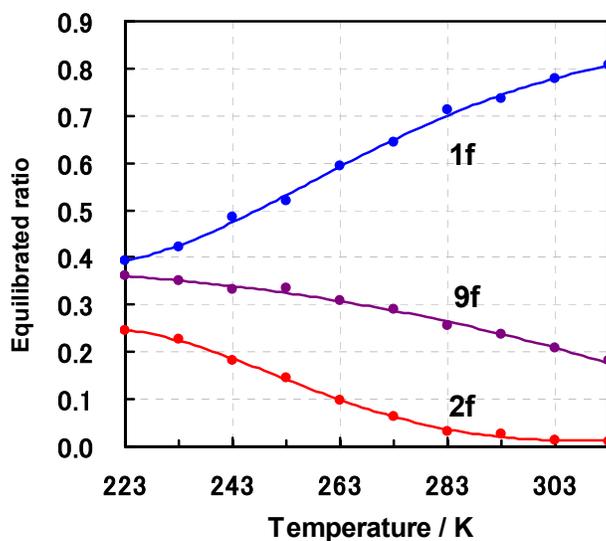
**Preparation of Protected [2]Rotaxane 3f:** To a solution of **1b** (10.0 mg, 3.44  $\mu$ mol) in water-saturated CHCl<sub>3</sub> (3.0 mL) was added trifluoroacetic acid (one drop, ca. 10  $\mu$ L, 0.13 mmol) and ethanedithiol (one drop, ca. 10  $\mu$ L, 0.12 mmol) under an argon atmosphere. After stirring for 14 h at 40 °C, the crude product obtained by concentrating the mixture was purified by preparative TLC (silica gel) eluted with benzene to give **3f** (8.0 mg, 75 %) as a yellow solid: mp 206.0-207.0 °C; <sup>1</sup>H NMR:  $\delta$  7.53 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>), 7.53 (d,  $J = 8.4$  Hz, 4H, H<sub>F</sub>), 7.49 (d,  $J = 8.4$  Hz, 4H, H<sub>e</sub>), 7.47 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>), 7.44 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>), 7.42 (d,  $J = 8.7$  Hz, 4H, H<sub>g</sub>), 7.34 (s, 8H, H<sub>J,K</sub>), 7.28 (d,  $J = 8.4$  Hz, 12H, *t*BuC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>), 7.18 (d,  $J = 8.7$  Hz, 8H, H<sub>C</sub>), 7.16 (d,  $J = 8.4$  Hz, 4H, H<sub>n</sub>), 7.12 (s, 2H, H<sub>d</sub>), 7.01 (d,  $J = 7.8$  Hz, 4H, H<sub>D</sub>), 6.92 (d,  $J = 8.7$  Hz, 4H, H<sub>h</sub>), 6.78 (d,  $J = 8.7$  Hz, 8H, H<sub>B</sub>), 6.75 (t,  $J = 7.8$  Hz, 2H, H<sub>E</sub>), 6.74 (d,  $J = 8.4$  Hz, 4H, H<sub>m</sub>), 5.00 (s, 4H, H<sub>i</sub>), 4.91 (s, 4H, H<sub>l</sub>), 4.77 (s, 2H, H<sub>a</sub>), 3.87 (t,  $J = 6.0$  Hz, 8H, H<sub>A</sub>), 3.48 (d,  $J = 15.6$  Hz, 4H, H<sub>b</sub>), 3.34 (d,  $J = 15.6$  Hz, 4H, H<sub>c</sub>), 3.26 (s, 4H, NH<sub>2</sub>), 2.81 (m, 4H, H<sub>o1</sub>), 2.30 (m, 4H, H<sub>o2</sub>), 1.76 (m, 8H, OCH<sub>2</sub>CH<sub>2</sub>), 1.47 (m, 8H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.35 (s, 54H, *t*Bu); <sup>13</sup>C NMR:  $\delta$  158.19, 158.13, 156.71, 150.16, 145.74, 142.22, 141.44, 139.74, 139.29, 138.57, 138.37, 137.66, 136.81, 136.65, 133.48, 132.20, 131.78, 131.43, 130.32, 129.47, 129.10, 127.91, 127.67, 127.60, 127.26, 126.58, 125.90, 125.67, 125.21, 121.05, 117.60, 115.05, 114.76, 113.53, 69.69, 69.57, 67.61, 63.62, 57.01, 55.55, 44.46, 38.29, 34.51, 31.36, 28.94, 25.41; IR (KBr): 3027, 2950, 2865, 1607, 1510, 1497, 1462, 1446, 1240, 1175, 1111, 1033, 1003, 815 cm<sup>-1</sup>; LR-MS (FD) calcd. for C<sub>216</sub>H<sub>212</sub>N<sub>2</sub>O<sub>8</sub>S<sub>4</sub>: 3091.5, found: 3089.7; Anal. calcd. for C<sub>216</sub>H<sub>212</sub>N<sub>2</sub>O<sub>8</sub>S<sub>4</sub>: C, 83.90; H, 6.91; N, 0.91; S, 4.15. found: C, 83.84; H, 7.02; N, 0.91; S, 4.14.

**Hydrolysis of Imine-bridged Pseudorotaxane 1a:** To a solution of **1a** (7.0 mg, 5.9  $\mu\text{mol}$ ) in water-saturated  $\text{CHCl}_3$  (50 mL) was added trifluoroacetic acid (20  $\mu\text{L}$ , 0.26 mmol) and water (10  $\mu\text{L}$ , 0.56 mmol). Time-course of hydrolysis was monitored by  $^1\text{H}$  NMR. After stirring for 12 h, a few drops of  $\text{Et}_3\text{N}$  were added. The brown solid obtained by concentrating the mixture was subjected to preparative TLC on silica gel eluted with benzene to give (*E*)-**5b** (3.0 mg, 97%) and **7a** (4.0 mg, 97%).

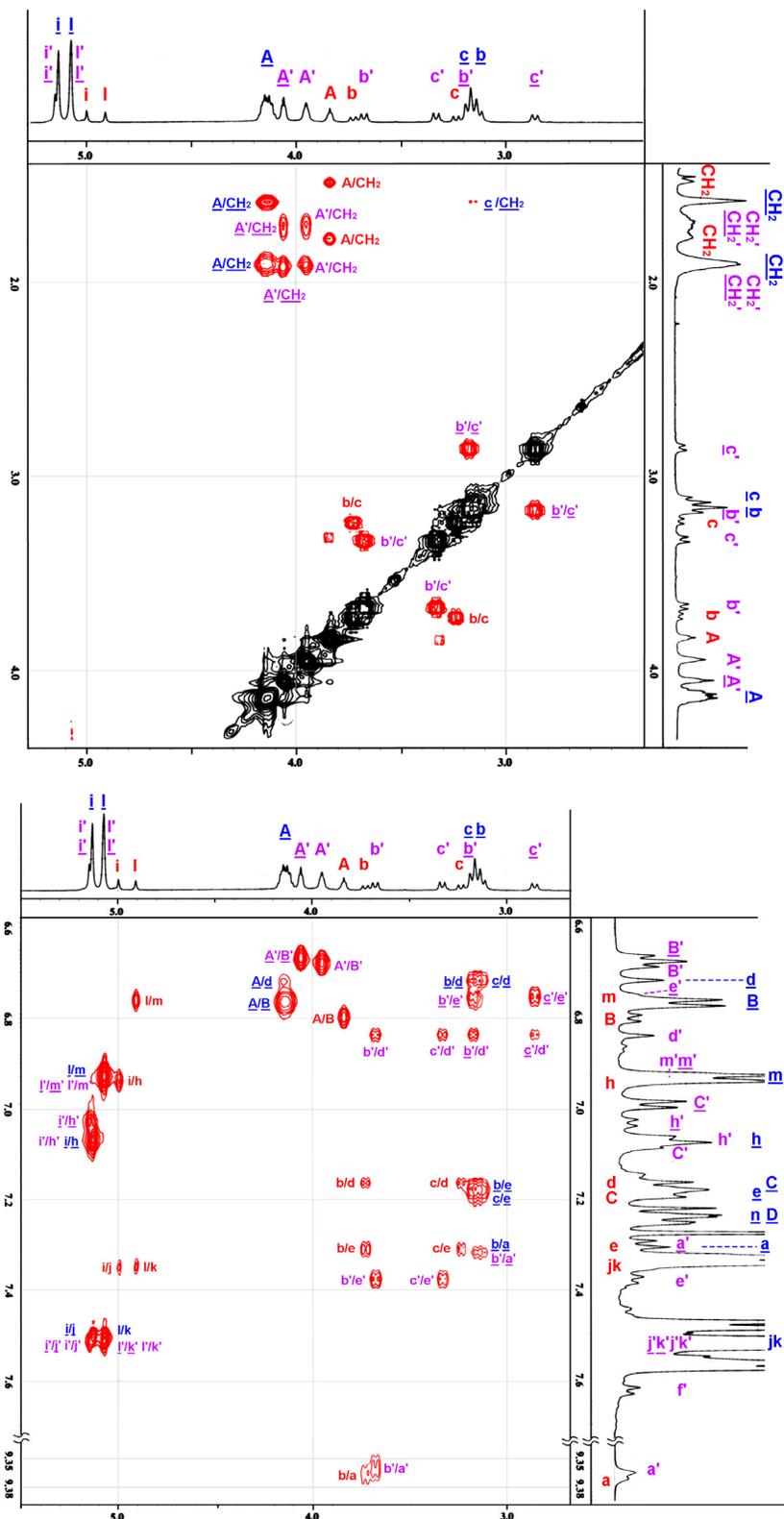
**Hydrolysis of Imine-bridged Rotaxane 1d-f:** To a solution of **1** in water-saturated  $\text{CDCl}_3$  (0.6 mL) in an NMR tube was added 10% TFA in  $\text{CDCl}_3$  (5.0  $\mu\text{L}$ , 6.7  $\mu\text{mol}$ ). Time-course of hydrolysis and attainment of equilibrium were monitored by  $^1\text{H}$  NMR. In the case of **1f**, the equilibrated state was attained just after an addition of TFA. VT NMR analyses and ROESY measurement were conducted for the mixture. Ratio of **1f**, **9f** and **2f** in the equilibrated mixture were estimated by integrating the intensities of macrocyclic methylene proton signals (Figure S2 and S3).



**Figure S1.**  $^1\text{H}$  NMR spectra (300 MHz,  $\text{CDCl}_3$ , 298 K) of (a) macrocycle **7a**, (b) imine-bridged pseudorotaxane **1b**, (c) imine-bridged rotaxane **1d**, (d) imine-bridged rotaxane **1e**, and (e) axle **5e**. The assignments correspond to the lettering shown in Scheme 3.



**Figure S2.** Temperature-dependence of equilibrated ratio of **1f**, **9f** and **2f** in the hydrolyzed mixture, which were estimated by integration of the macrocyclic methylene protons in the  $^1\text{H}$  NMR spectra (600 MHz).



**Figure S3.** ROESY spectra (600 MHz, 0.08% TFA/CDCl<sub>3</sub> (v/v)) of the hydrolyzed mixture containing imine-bridged rotaxane **1f**, mono-imine **9f** and [2]rotaxane **2f** at 253 K. The lettering corresponds to the assignments shown in Scheme 3.

## References

- [s1] H. W. Gibson, S.-H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen, M. Bheda, *J. Org. Chem.* **1993**, *58*, 3748-3756.
- [s2] N. Soyer, M. Kerfanto, D. Raphalen, *Bull. Soc. Chim. Fr.* **1975**, 2121-2127.