Supporting Information for

Reversible Control of Polyacetylene Helix by Pendant Rotaxane Switch

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1. Materials and Methods

Commercially available materials and solvents including $NaBH(AcO)_3$ (Aldrich), paraformaldehyde (Nakalai Tesque, Ltd.), $[RhCl(nbd)]_2$ (Wako Pure Chemical Industries, Ltd.), 1,8-diazabicyclo[5,4,0]undec-7-ene (Aldrich), *N*-methylpyrrolidone (NMP, Wako Pure Chemical Industries, Ltd.), and triethylamine (Wako Pure Chemical Industries, Ltd.) were used without further purification. SiO_2 column chromatography was performed using Wakogel C-400HG (Wako Pure Chemical Industries Ltd.). Al_2O_3 column chromatography was performed using Merck Aluminum Oxide 90 standardized. Rotaxanes **(*R*)-2** and **(*R*)-2Ac** were prepared according to the literature.[1]

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL AL-400 spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. Samples were purified by repeated preparative gel permeation chromatography (GPC) on a JAI Co., Ltd. LC-9204 system (JAIGEL-1H-40) with $CHCl_3$ as the eluent. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Melting points were measured with a Stuart Scientific SMP3 (Bibby Scientific). UV-vis spectra were taken on a JASCO V-550 UV-vis spectrophotometer. CD spectra were taken on a JASCO J-820 spectropolarimeter. Specific optical rotations were measured on a JASCO DIP-1000 digital polarimeter in a 10 cm cuvette. High-resolution mass spectra (HR-MS) data were taken by the National University Corporation, Tokyo Institute of Technology, Center for Advanced Materials Analysis, on request.

2. Experiments

Synthesis of rotaxane **(*R*)-1b**: *N*-Methylation[2] of **(*R*)-2**

A solution of rotaxane **(*R*)-1b** (600 mg, 0.423 mmol), paraformaldehyde (300 mg, 10.0 mmol), $NaBH(AcO)_3$ (600 mg, 2.83 mmol), and triethylamine (1 mL) in NMP (5 mL) was stirred for 8 h at 70 °C under an Ar atmosphere. The reaction mixture was poured into water (500 mL), and the precipitate was collected by filtration. The products were dissolved in EtOAc; washed with H_2O, sat. $NaHCO_3$ (aq.), and brine; dried over $MgSO_4$; and concentrated *in vacuo*. The residue was purified by Al_2O_3 column chromatography (EtOAc) to give rotaxane ***rac*-7** (440 mg, 0.342 mmol, 81%) as a colorless foam. $[\alpha]_D^{25}$: +121.1° (*c* = 0.10, THF), mp 81.4–83.1 °C, ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.09 (s, 1H), 8.04 (s, 1H), 7.90 (d, *J* = 9.1 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 9.1 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.52 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.32–7.30 (m, 3H), 7.28–7.18 (m, 4H), 7.15–7.14 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.75–6.72 (m, 2H), 6.65–6.63 (m, 1H), 6.59–6.57 (m, 1H), 5.38 (s, 2H), 4.39–4.34 (m, 1H), 3.96–3.93 (m, 3H), 3.87–3.81 (m, 2H), 3.71–3.63 (m, 3H), 3.58–3.51 (m, 3H), 3.39–3.06 (m, 14H), 2.89–2.85 (m, 1H), 2.84 (s, 1H), 2.13 (s, 3H), 1.34 (s, 18H), 1.12–1.11 (m, 21H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 154.4, 154.3, 151.6, 146.5, 146.4, 139.66, 136.9, 133.9, 133.6, 133.0, 132.6, 131.0, 130.6, 130.5, 130.2, 130.0, 129.8, 129.7, 128.2, 128.1, 127.9, 126.7, 125.4, 125.0, 124.7, 124.5, 124.3, 123.8, 123.6, 123.0, 122.3, 121.7, 120.7, 117.6, 116.7, 112.1, 112.0, 104.6, 93.4, 81.6, 79.2, 71.3, 71.2, 71.0, 70.9, 70.7, 70.5, 70.3, 69.4, 69.2, 68.1, 67.8, 66.3, 52.8, 52.1, 34.9, 31.3, 18.7, 11.2 ppm, IR (neat) ν 3278, 2949, 2866, 2155, 1731, 1592, 1505, 1457, 1362, 1309, 1221, 1129, 950, 844, 750, 670, 557 cm^{-1}. FAB HR-MS Calc'd for $C_{82}H_{100}NO_{10}Si$ $[M+H]^+$: *m/z* = 1286.7117. Found: *m/z* = 1286.7084.

Synthesis of **(*R*)-1a**:

A solution of rotaxane **(*R*)-1b** (100 mg, 0.078 mmol) in $CHCl_3$ (50 mL) was washed with ca. 10% HPF_6 aq. (15 mL × 3) and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by recycle preparative GPC ($CHCl_3$) to give rotaxane **(*R*)-1a** (111 mg, 0.078 mmol, 100%) as a colorless foam. $[\alpha]_D^{25}$: +119.6° (*c* = 0.15, THF), mp 113.1–115.2 °C, ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 164.8, 153.8, 153.6, 151.8, 151.5, 147.7, 147.5, 147.4, 147.3, 139.7, 136.9, 136.5, 133.6, 133.5, 133.4, 132.95, 132.91, 132.6, 132.2, 132.1, 130.7, 130.6, 130.4, 130.3, 129.9, 129.8, 129.4, 129.1, 128.1, 128.0, 127.8, 127.5, 126.7, 126.5, 126.0, 125.2, 125.1, 125.0, 124.7, 124.6, 124.5, 124.4, 123.9, 123.7, 123.1, 123.0, 121.4, 121.3, 121.2, 121.1, 121.0, 120.5, 120.1, 119.0, 115.5, 115.2, 115.1, 114.4, 112.1, 112.0, 111.8, 111.6, 104.6, 93.5, 81.6, 79.3, 79.2, 71.4, 71.3, 71.2, 71.1, 71.0, 70.9, 70.7, 70.6, 70.5, 70.4, 70.2, 70.1, 69.5, 68.9, 68.0, 67.9, 67.8, 67.6, 66.5, 66.3, 61.1, 60.9, 60.7, 60.4, 53.5, 39.3, 39.2, 34.8, 34.7, 31.4, 31.3, 18.7, 11.2 ppm, IR (KBr) ν 3283, 3064, 2953, 2866, 2154, 1727, 1621, 1591, 1506, 1459, 1363, 1309, 1251, 1221, 1085, 1031, 951, 844, 748, 679, 637 cm^{-1}. FAB HR-MS Calc'd for $C_{82}H_{100}NO_{10}Si$ $[M–HPF_6]^+$: *m/z* = 1286.7117. Found: *m/z* = 1286.7229.

Synthesis of **poly-(*R*)-1a**: Polymerization of **(*R*)-1a**

To a solution of **(*R*)-1a** (200 mg, 0.141 mmol) in $CHCl_3$ (478 μL) was added a solution (82 μL) consisting of $[RhCl(nbd)]_2$ (4.0 mg, 8.7 μmol) and Et_3N (10 μL) in $CHCl_3$ (990 μL). The mixture was stirred for 4 h at room temperature. The solution was poured into Et_2O. The precipitate was collected by filtration to give polyacetylene **poly-(*R*)-1a** (190 mg, 0.134 mmol, 95%) as a red solid. IR (KBr) ν 3062, 2952, 2866, 2155, 1731, 1622, 1593, 1506, 1457, 1248, 1110, 949, 843, 750, 681, 558 cm^{-1}.

3. Spectra

3-1. ^{1}H and ^{13}C NMR spectra, HH COSY correlations

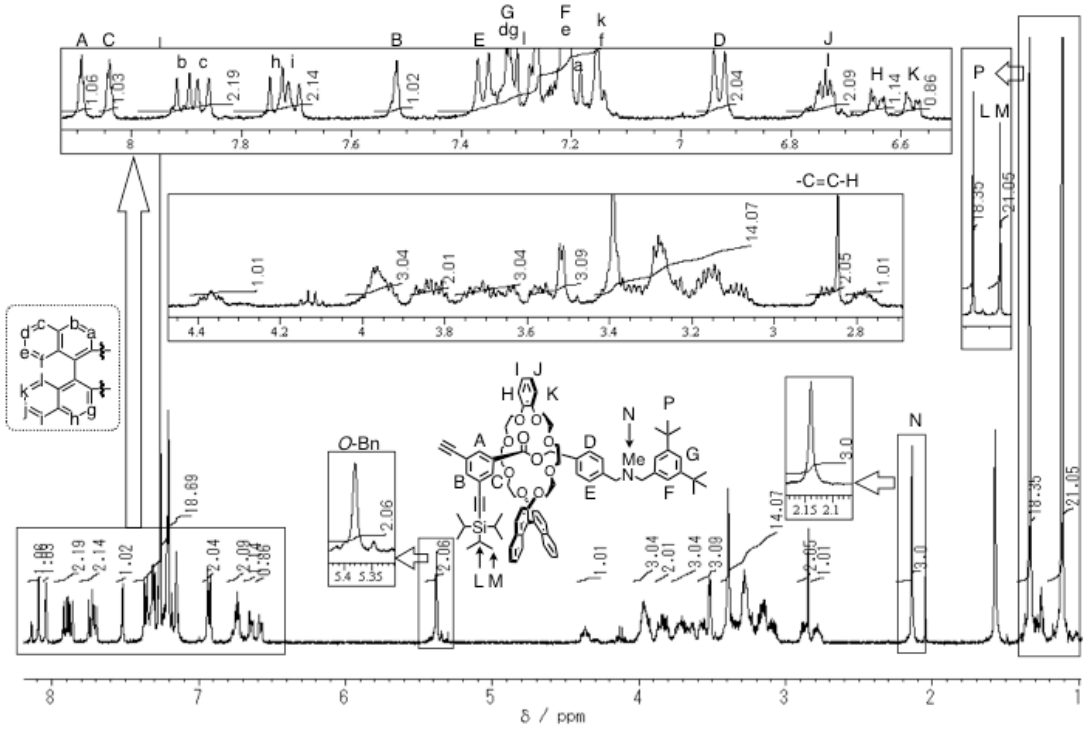

Figure S1. ^{1}H NMR spectrum of **(*R*)-1b** (400 MHz, $CDCl_3$, 298 K)

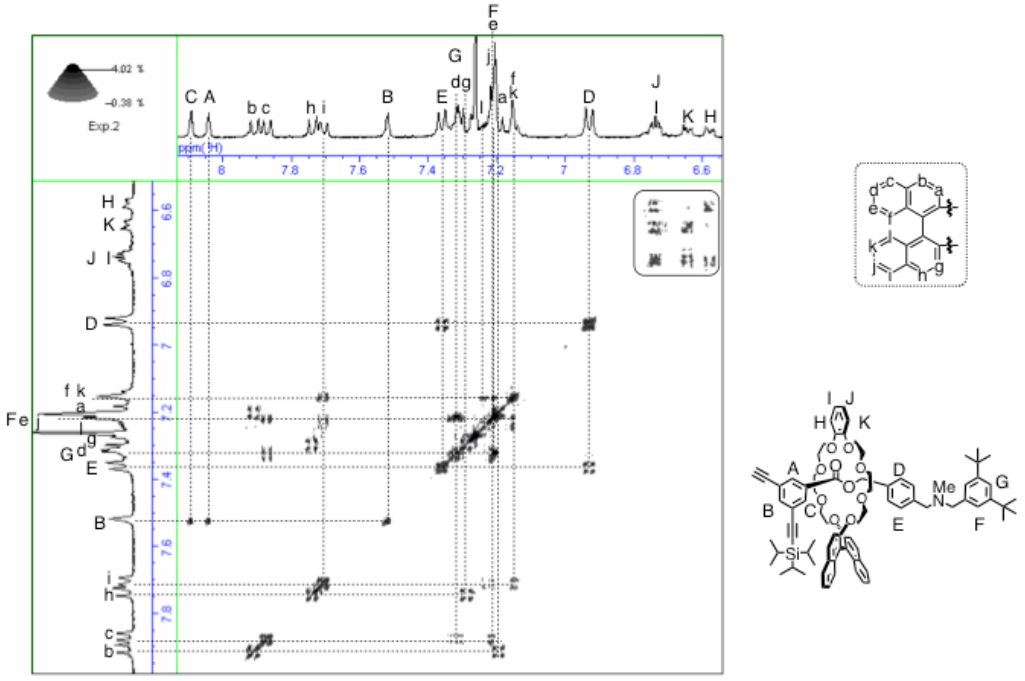

Figure S2. HH COSY correlations of **(*R*)-1b** (400 MHz, $CDCl_3$, 298 K)

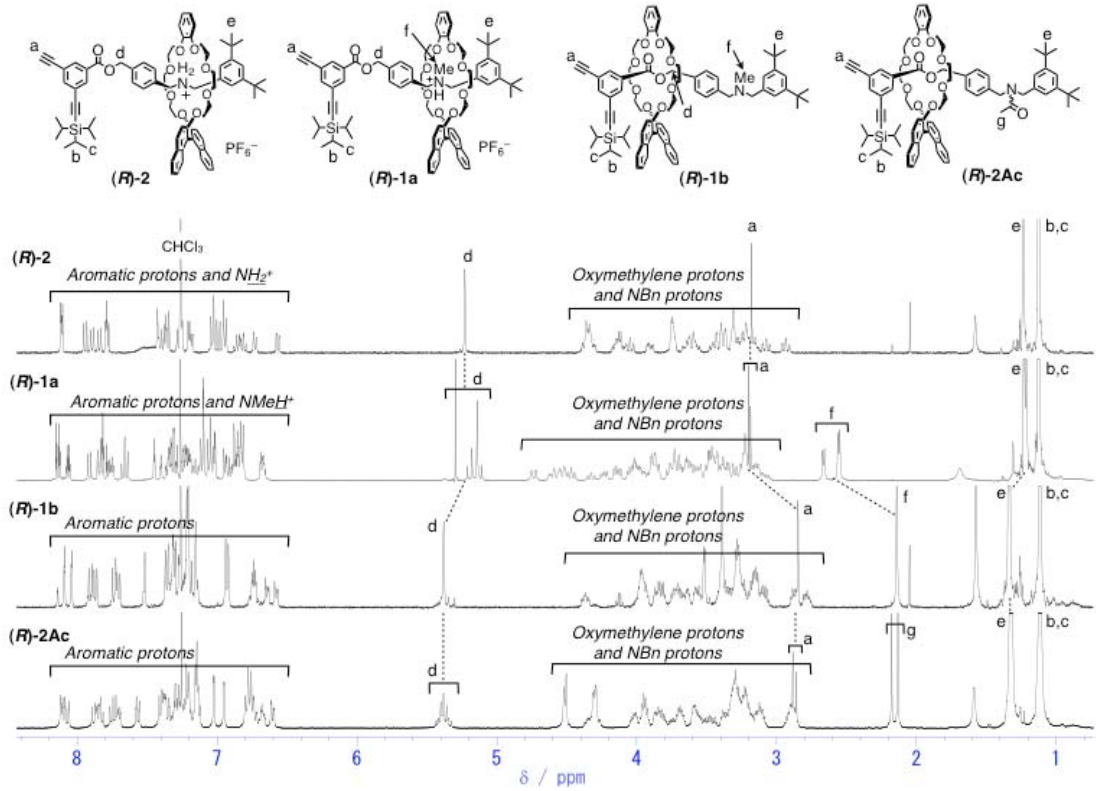

Figure S3. ^{1}H NMR spectra of **(*R*)-2**, **(*R*)-1a**, **(*R*)-1b**, and **(*R*)-2Ac** (400 MHz, $CDCl_3$, 298 K)

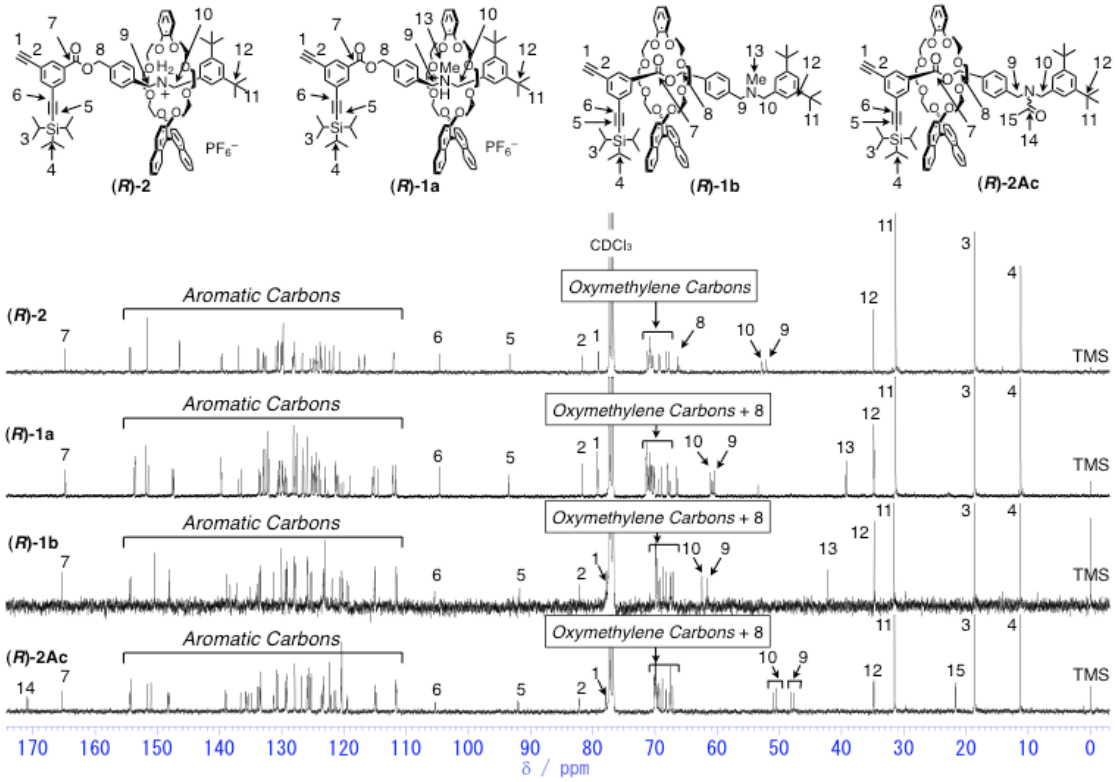

Figure S4. ^{13}C NMR spectra of **(*R*)-2**, **(*R*)-1a**, **(*R*)-1b**, and **(*R*)-2Ac** (100 MHz, $CDCl_3$, 298 K)

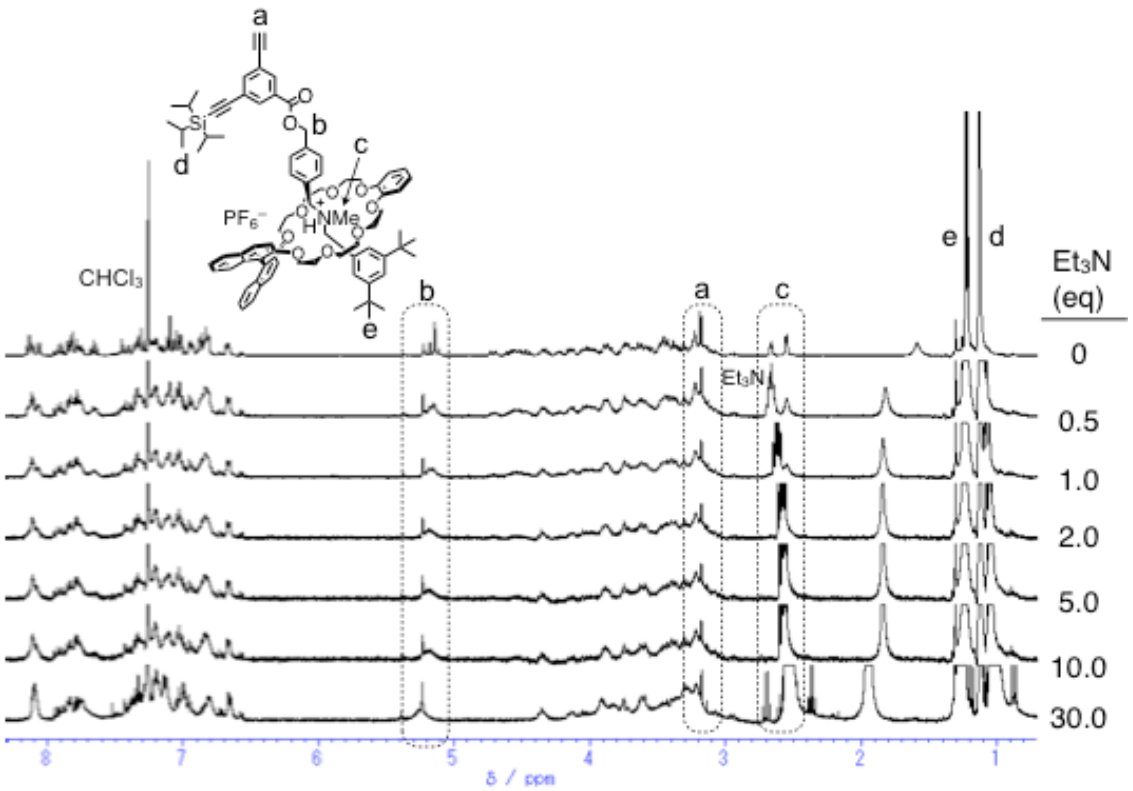

Figure S5. Titration of **(*R*)-1a** by Et_3N (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)

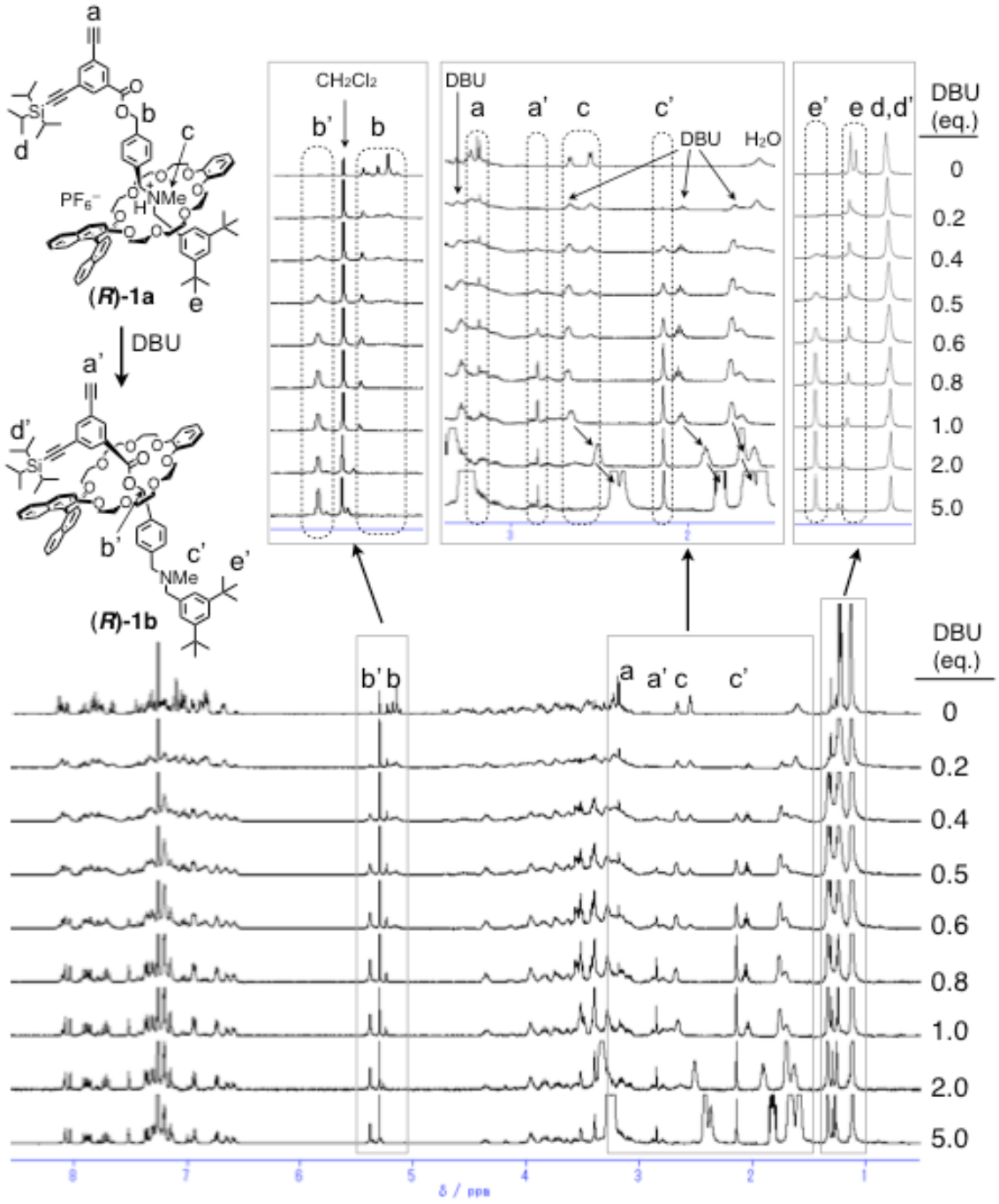

Figure S6. Titration of **(*R*)-1a** by DBU (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)

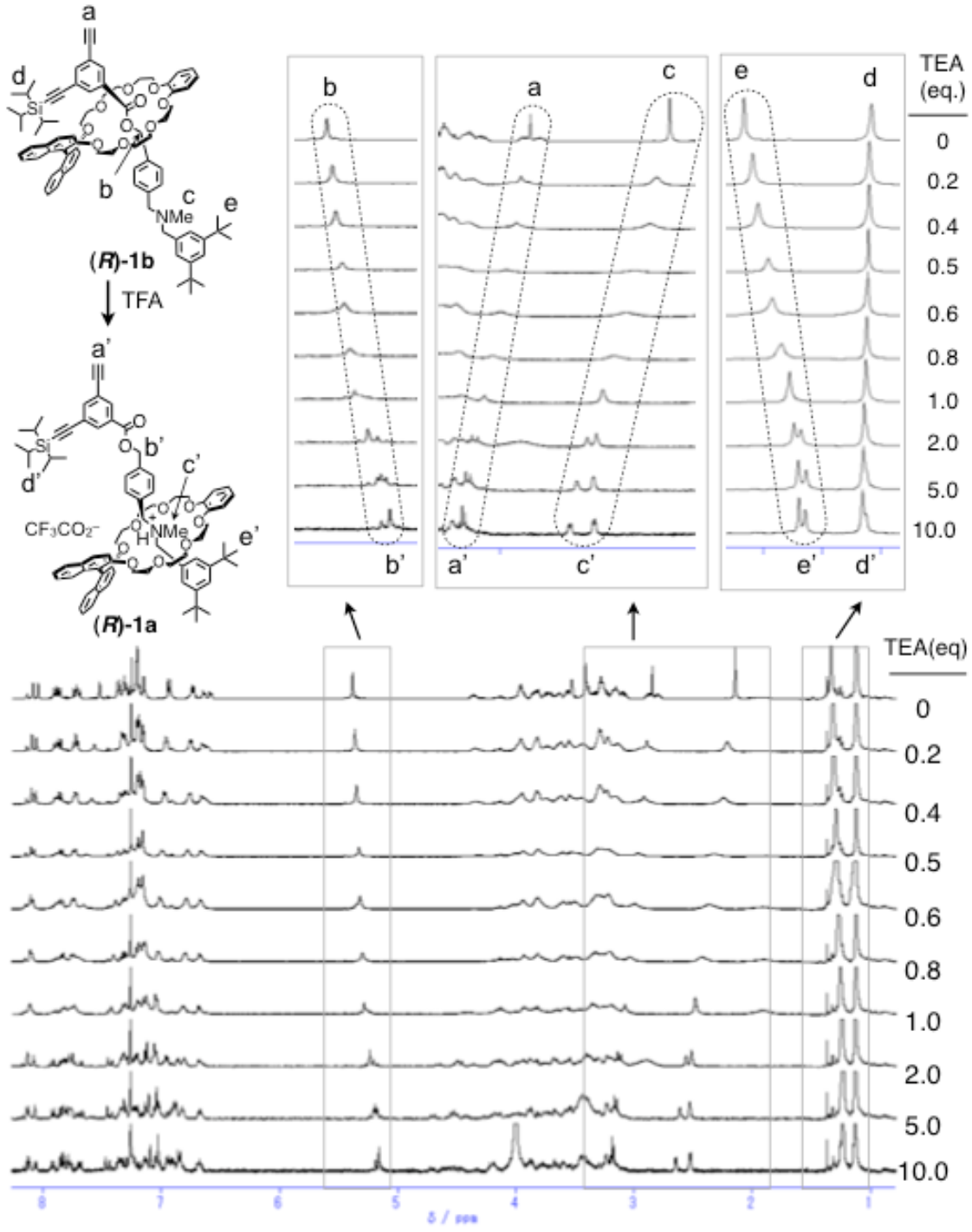

Figure S7. Titration of **(*R*)-1b** by CF_3COOH (^1H NMR, 400 MHz, $CDCl_3$, 298 K)

3-2. High-resolution mass spectra

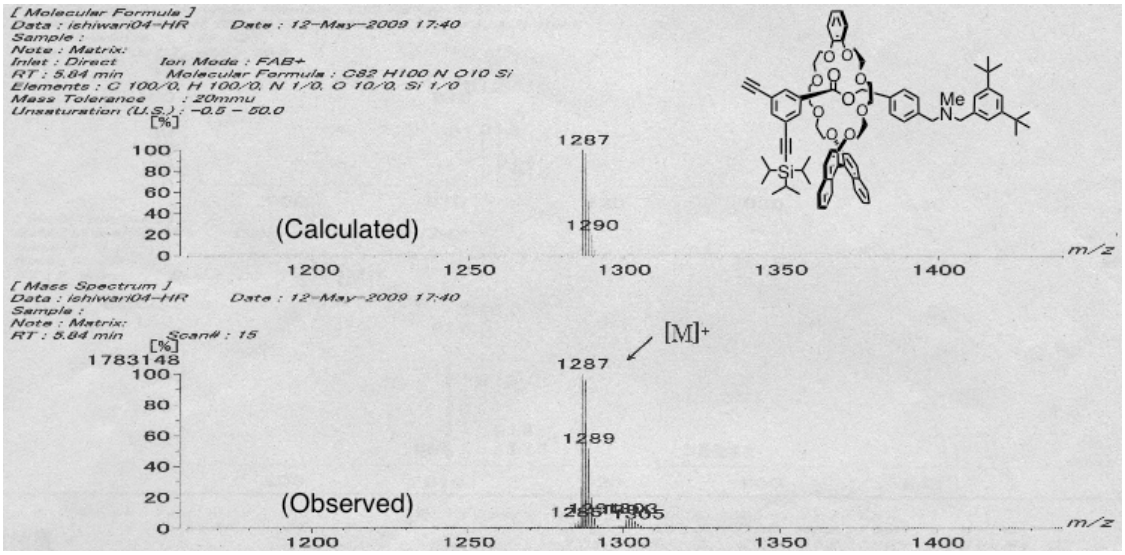

Figure S8. FAB-MS spectrum of **(*R*)-1a** (Ion mode: FAB^+, matrix: NBA, solvent: $CHCl_3$)

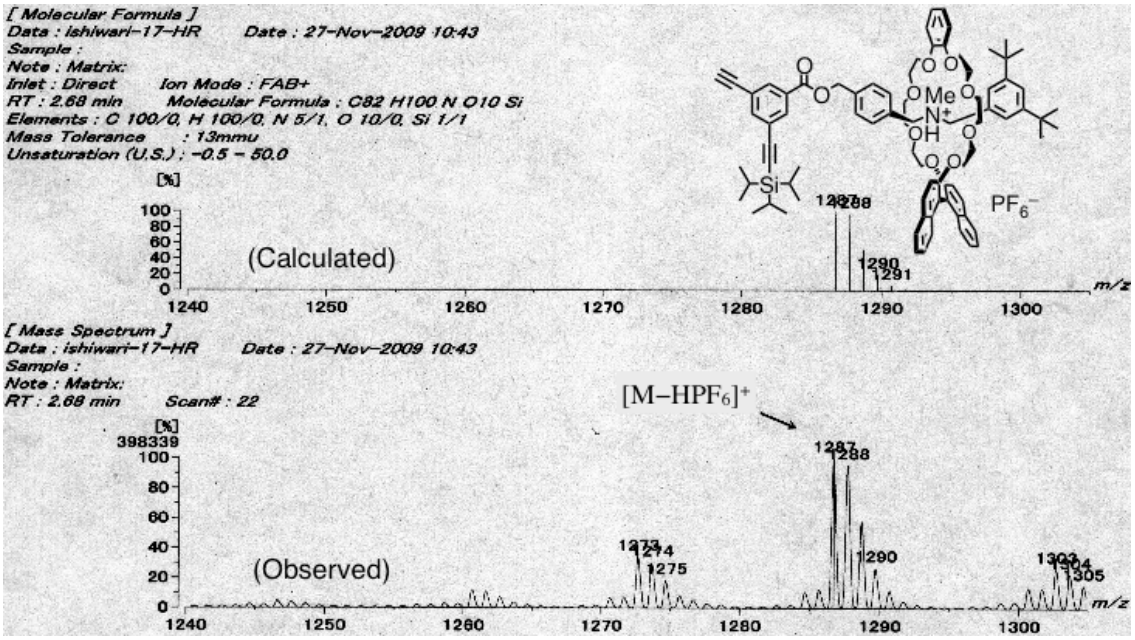

Figure S9. FAB-MS spectrum of **(*R*)-1b** (Ion mode: FAB^+, matrix: NBA, solvent: $CHCl_3$)

3-3. FT-IR spectra

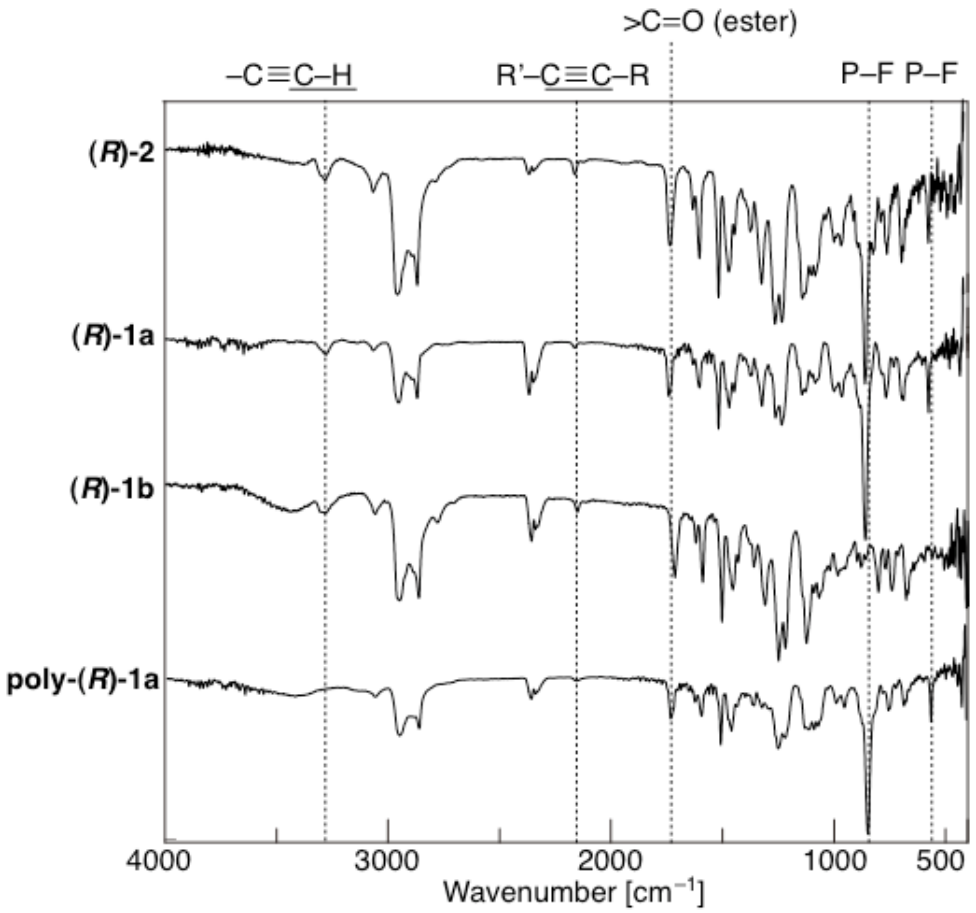

Figure S10. FT-IR spectra of **(*R*)-2**, **(*R*)-1a**, **(*R*)-1b**, and **poly-(*R*)-1a** (KBr)

3-4. CD and UV-vis spectra

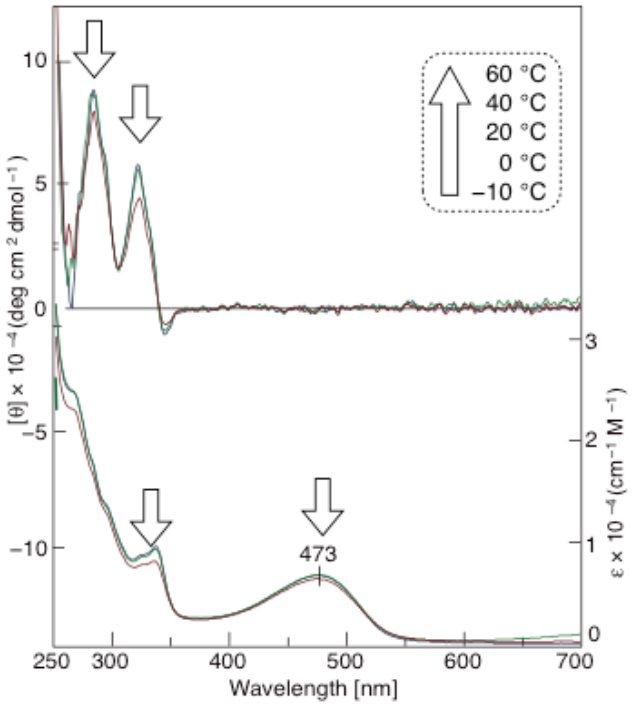

Figure S11. CD and UV-vis spectra of **poly-(*R*)-1a** (THF, 0.10 mM for monomer unit, 263–333 K)

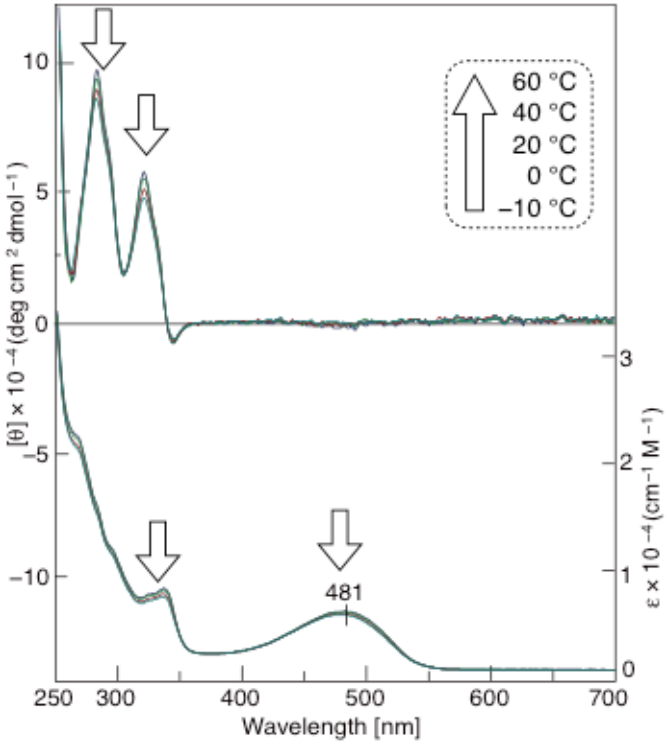

Figure S12. CD and UV-vis spectra of **poly-(*R*)-1a** ($CHCl_3$, 0.10 mM for monomer unit, 263–333 K)

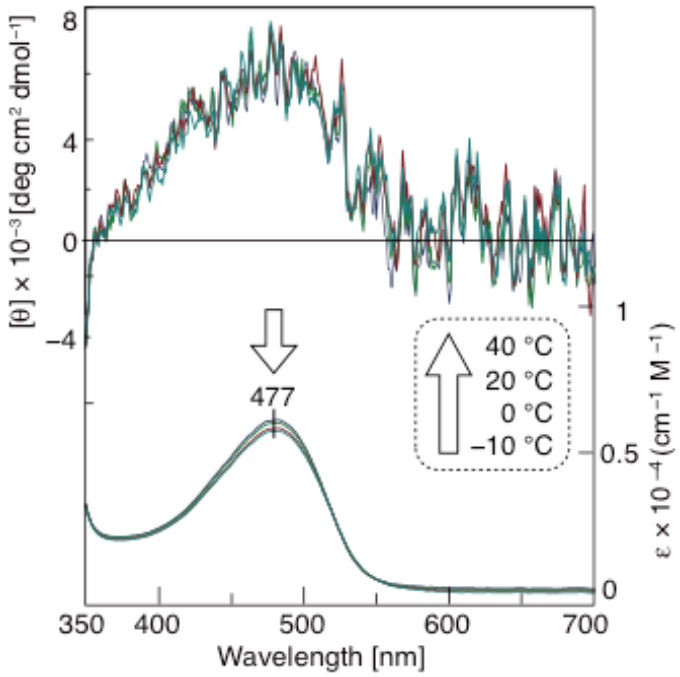

Figure S13. CD and UV-vis spectra of **poly-(*R*)-1a** (Acetone, 0.10 mM for monomer unit, 263–313 K)

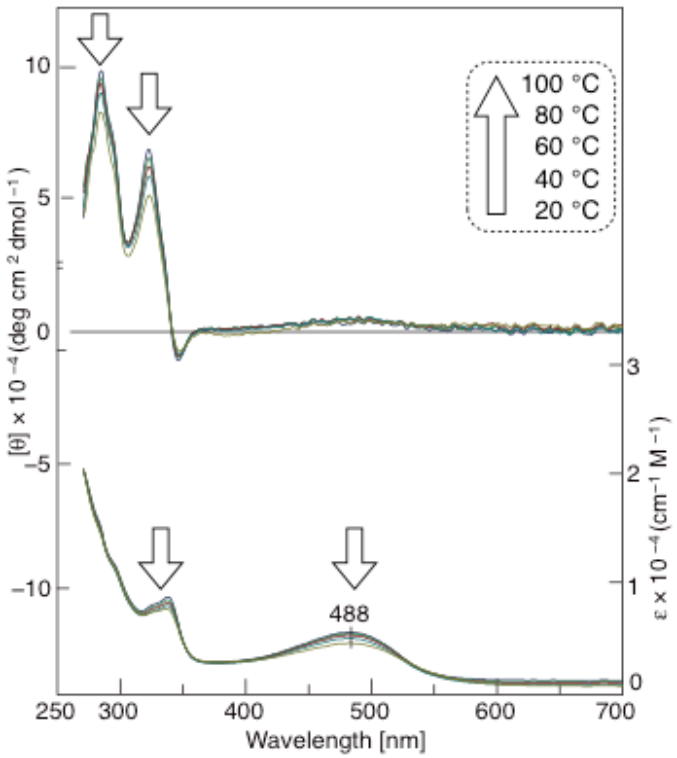

Figure S14. CD and UV-vis spectra of **poly-(*R*)-1a** (DMSO, 0.10 mM for monomer unit, 293–373 K)

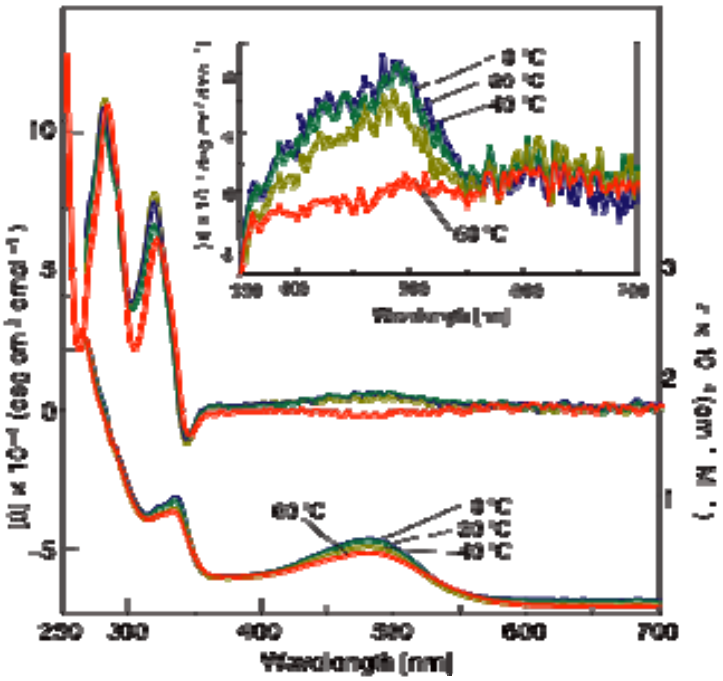

Figure S15. Investigation of helix stability in THF using **poly-(*R*)-1a**. The polymer was prepared by one-handed helix formation in acetone and subsequent removal of acetone. Variable temperature CD and UV-vis spectra of **poly-(*R*)-1a** (THF, 0.14 mM, 273–333 K)

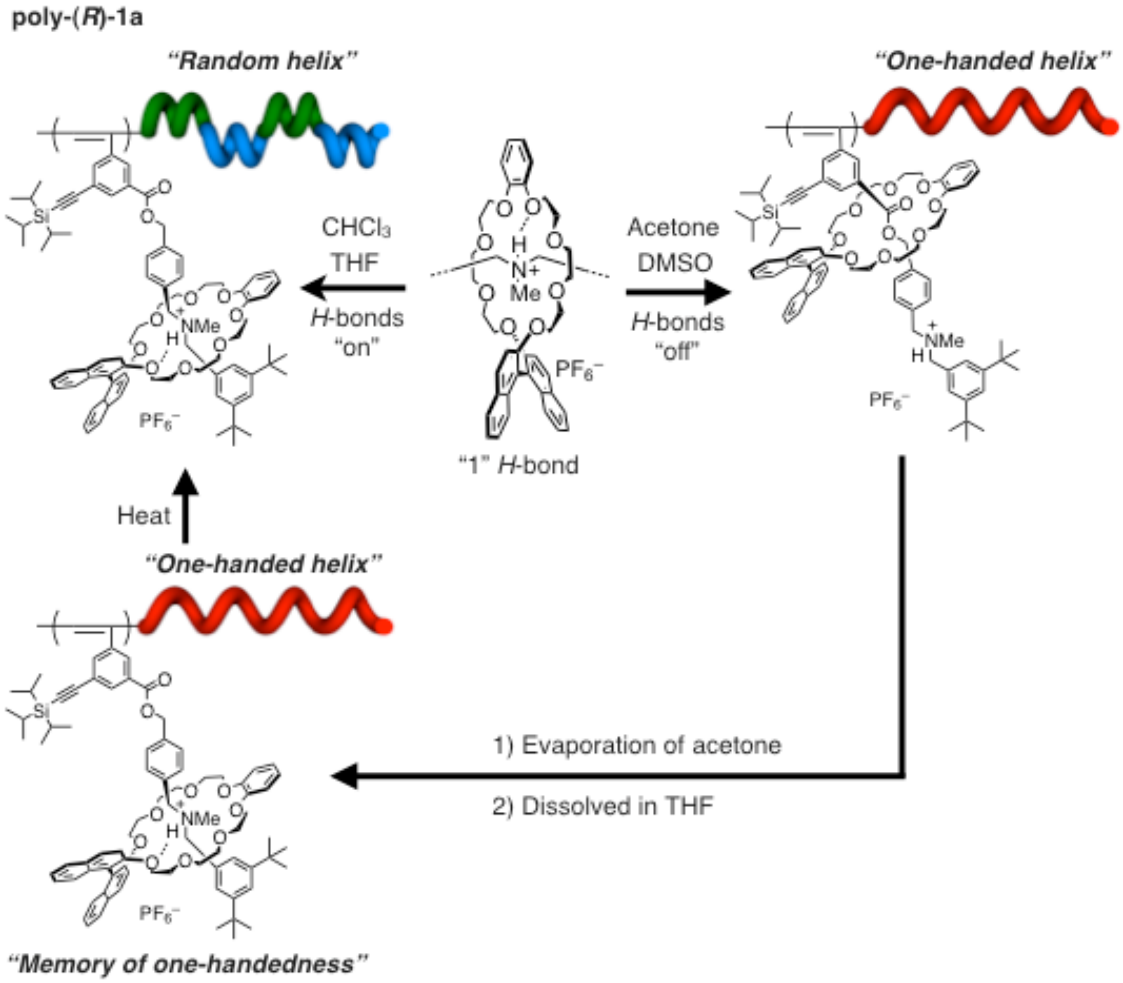

Figure S16. Schematic illustrations of the effect of solvent on **poly-(*R*)-1a**

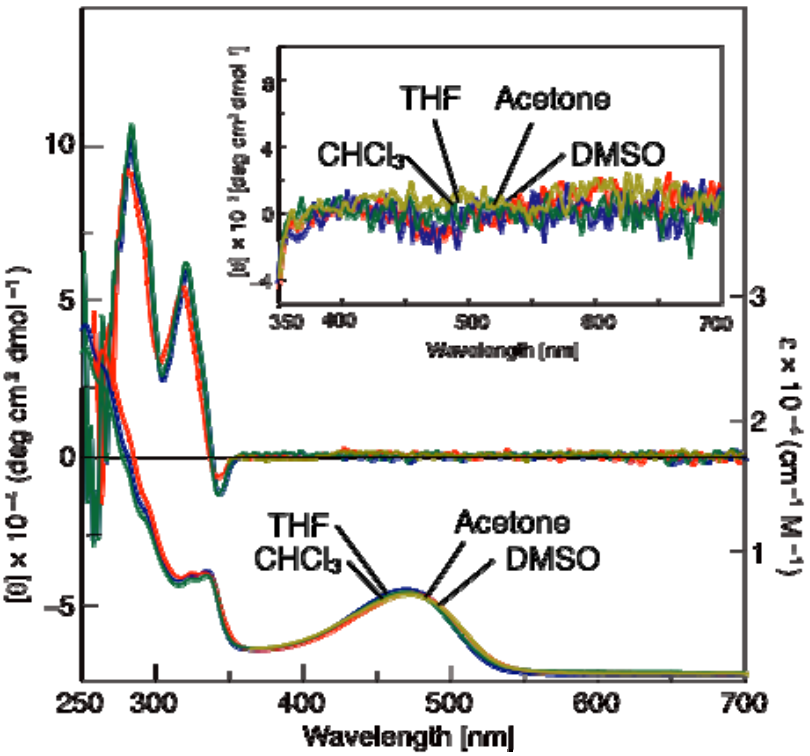

Figure S17. CD and UV-vis spectra of **poly-(*R*)-2** in various solvents ($CHCl_3$, THF, acetone, and DMSO, 293 K, 0.14 mM). Inset shows expanded CD spectra (350–500 nm).

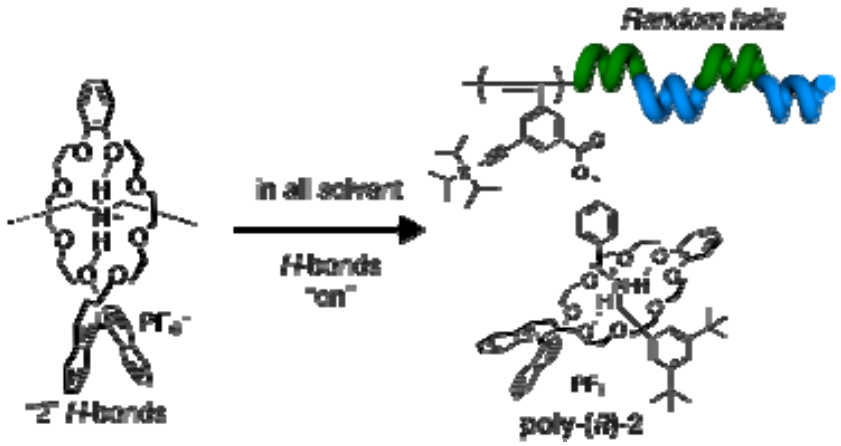

Figure S18. Schematic illustrations of the effect of solvent on **poly-(*R*)-2**

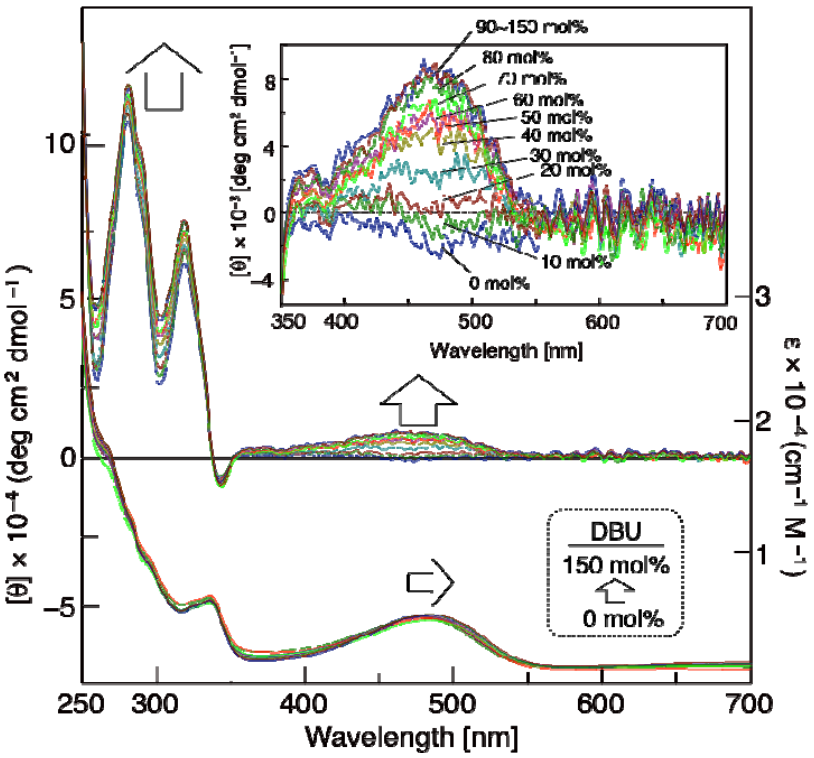

Figure S19. Titration of **poly-(*R*)-1a** by DBU ($CHCl_3$, 293K, 0.14 mM)

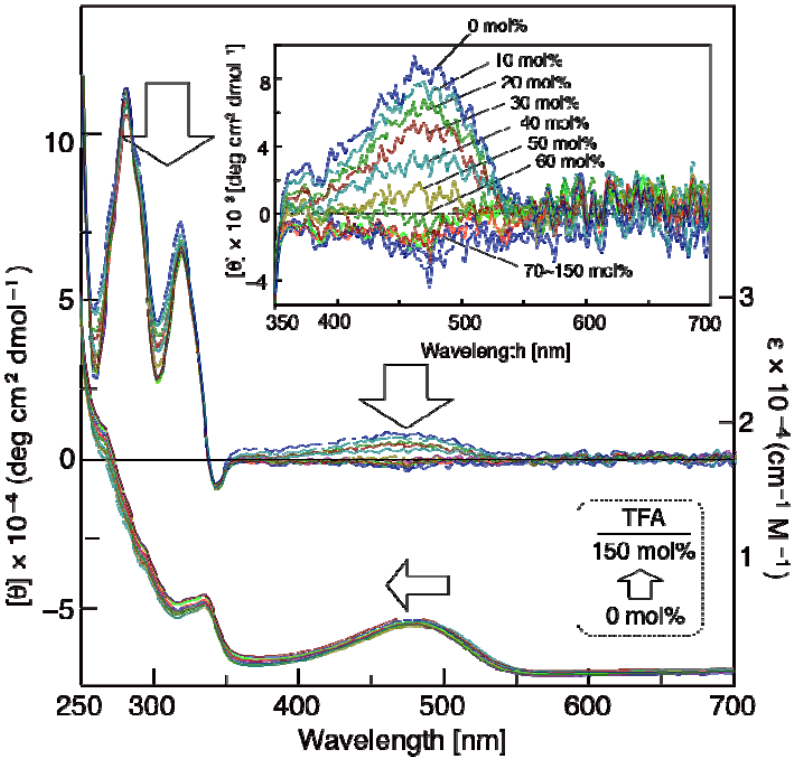

Figure S20. Titration of **poly-(*R*)-1b** by TFA ($CHCl_3$, 293K, 0.14 mM)

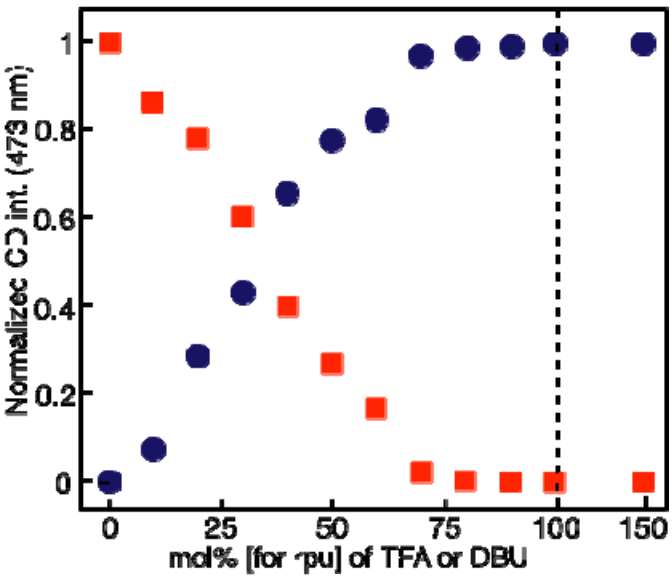

Figure S21. Titration result of DBU to **poly-(*R*)-1a** (blue circle) and titration result of TFA to **poly-(*R*)-1b** (red square) ($CHCl_3$, 293 K, 0.14 mM).

3-5. UV and FP spectra

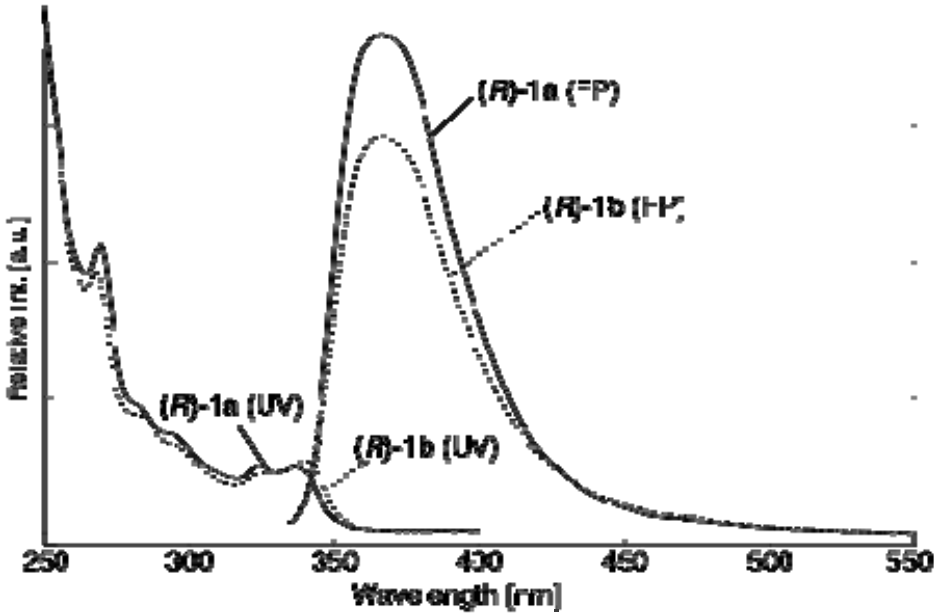

Figure S22. UV and FP spectra of **(*R*)-1a** in **(*R*)-1b** ($CHCl_3$, 293 K, O.D. = 0.10 at 325 nm, λ_{ex} = 325 nm).

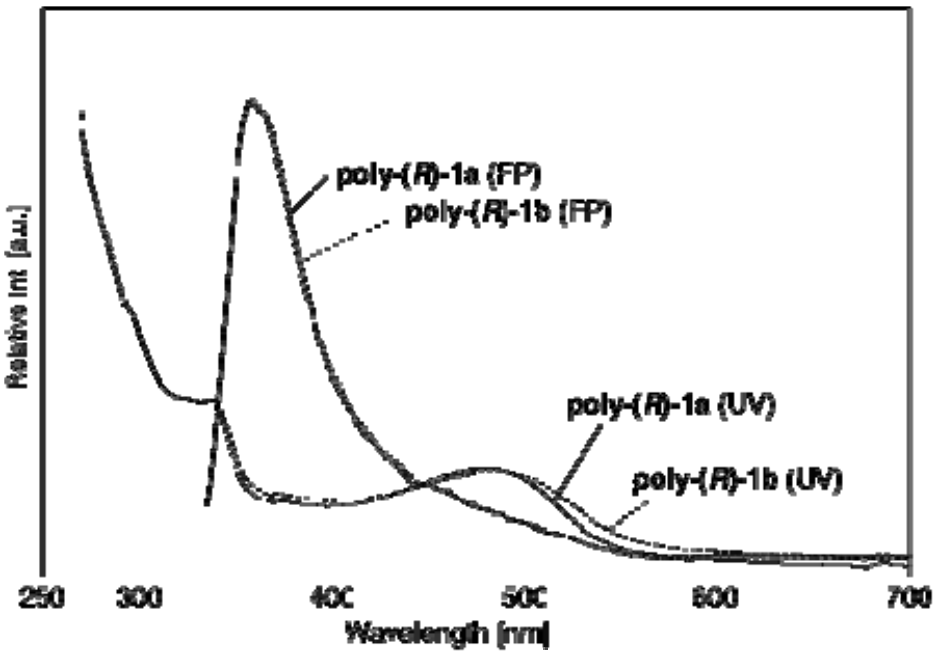

Figure S23. UV and FP spectra of **poly-(*R*)-1a** in **poly-(*R*)-1b** ($CHCl_3$, 293 K, O.D. = 0.10 at 325 nm, λ_{ex}

= 325 nm).

4. References

1) F. Ishiwari, K. Fukasawa, T. Sato, K. Nakazono, Y. Koyama, T. Takata, *Chem. Eur. J.* **2011**, *in press*

2) S. Suzuki, K. Nakazono, T. Takata, *Org. Lett.* **2010**, *12*, 712.