Supplementary Material

Complexation-induced inversion of helicity by an organic guest in a dynamic molecular propeller based on a tristerephthalamide host with a two-layer structure

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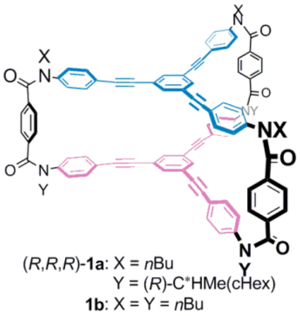
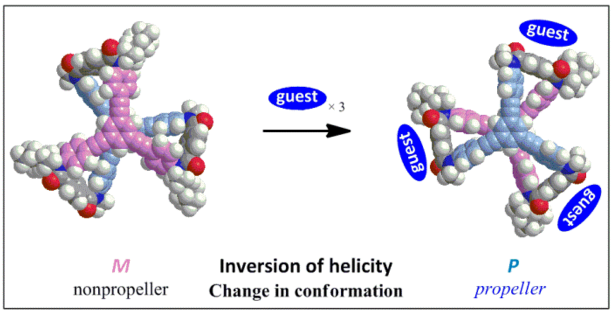




Supplementary Figures

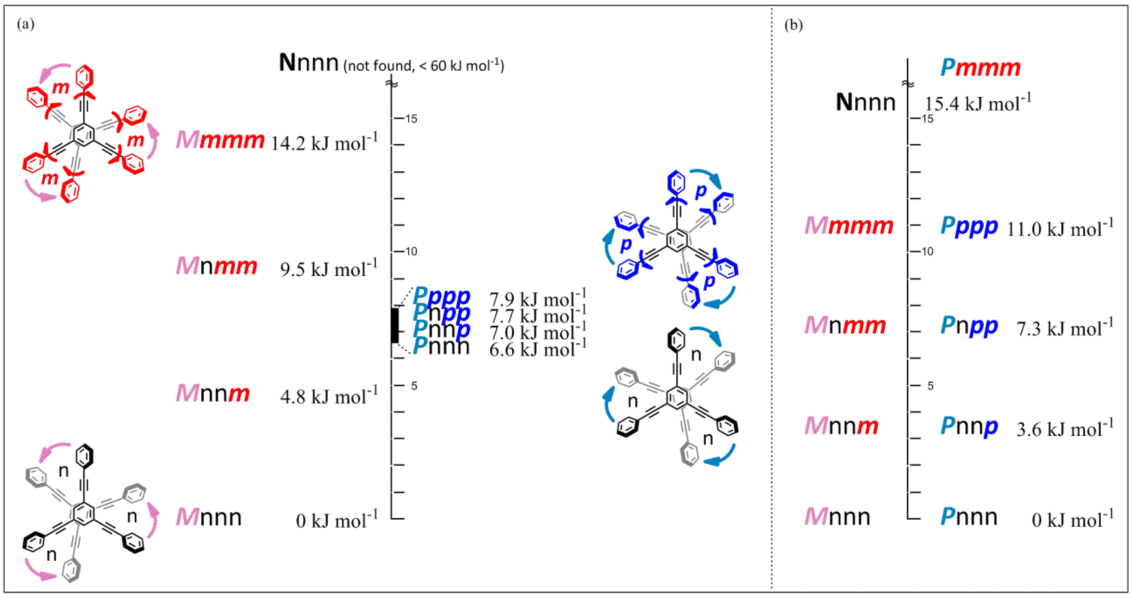


Fig. S1 Energy diagrams for (a) (*R*,*R*,*R*)-**1a'** [X = Me, Y = (*R*)-C*HMe(cHex)], and (b) **1b'** [X = Y = Me], obtained by a conformational search with MacroModel software (v9.9 Monte Carlo Multiple Minimum method, MMFF*, nonsolvated, 50000 steps).

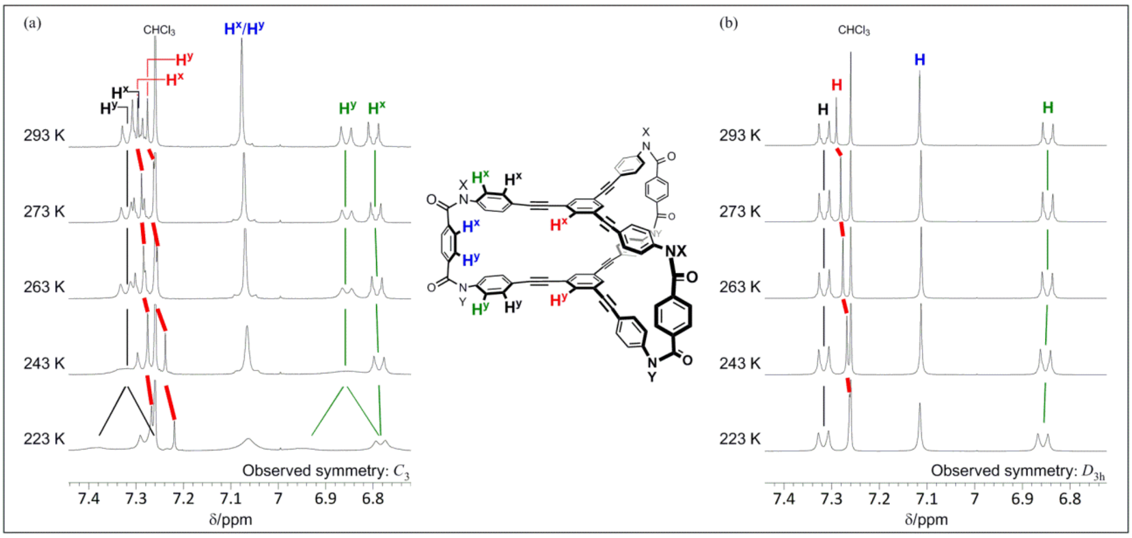


Fig. S2 ^{1}H NMR spectra (400 MHz) of (a) (*R*,*R*,*R*)-**1a**, and (b) **1b**, measured in $CDCl_3$ at 223-293 K.

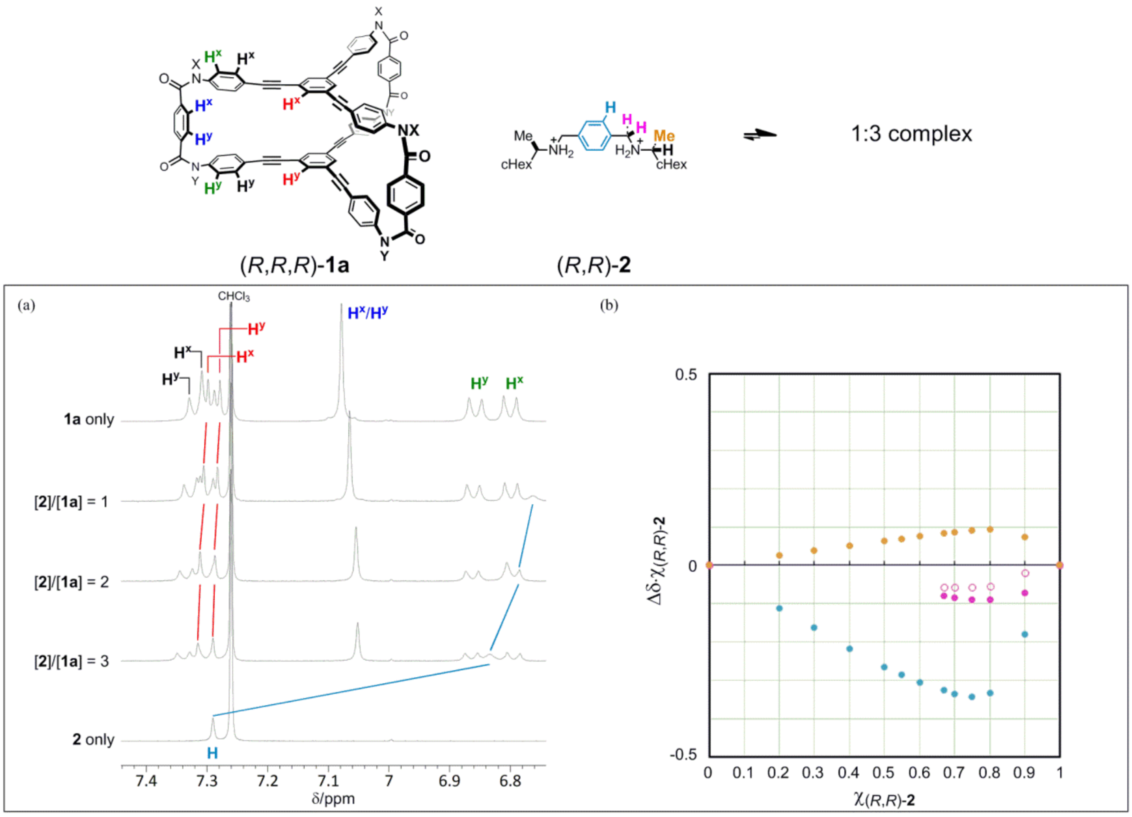


Fig. S3 (a) ^{1}H NMR spectra (400 MHz) of (*R*,*R*,*R*)-**1a** in the presence of (*R*,*R*)-**2** [0 (**1a** only), 1, 2, and 3 equiv.], and ^{1}H NMR spectrum of (*R*,*R*)-**2**; (b) Job plot for the complexation of (*R*,*R*,*R*)-**1a** with (*R*,*R*)-**2**, measured in $CDCl_3$ at 298 K, using continuous changes ($\Delta\delta = \delta_{\mathbf{1a}\cdot\mathbf{2}} - \delta_{\mathbf{2}}$) in the chemical shift for phenylene (pale blue), benzyl (pink), or methyl protons (orange) ([**1**] + [**2**] = 2 mM).

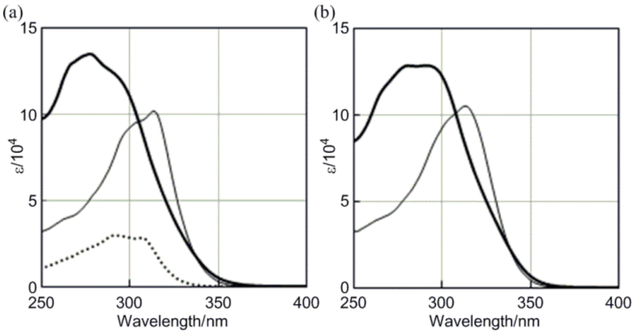


Fig. S4 UV spectra of (a) (*R*,*R*,*R*)-**1a** (bold line), (*R*,*R*,*R*)-**3a** (thin line), and (*R*)-**4** (dashed line), and (b) **1b** (bold line) and **3b** (thin line). All spectra were measured in CH_2Cl_2 at room temperature.

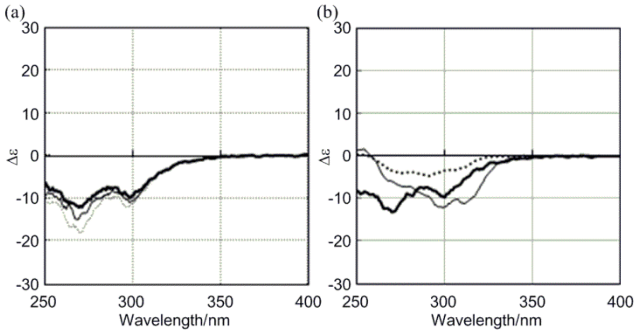


Fig. S5 (a) CD spectra of (*R*,*R*,*R*)-**1a**, measured in CH_2Cl_2 at 303 K (bold line), 283 K (thin line), and 263 K (dashed line); (b) CD spectra of (*R*,*R*,*R*)-**1a** (bold line), (*R*,*R*,*R*)-**3a** (thin line), and (*R*)-**4** (dashed line), measured in CH_2Cl_2 at 293 K.

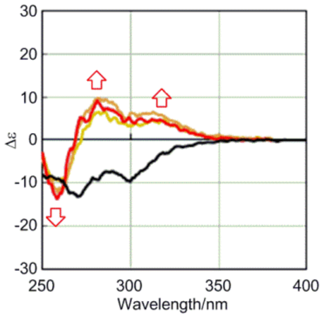


Fig. S6 Continuous change in the CD spectrum of (*R*,*R*,*R*)-**1a** (8.4×10^{-5} M) upon complexation with a ditopic guest (*S*,*S*)-**2** [0 (**1a** only, black line), 3, 6, and 12 equiv.]. All spectra were measured in CH_2Cl_2 at 293 K. The smaller change in the CD spectra does not mean smaller binding affinity.

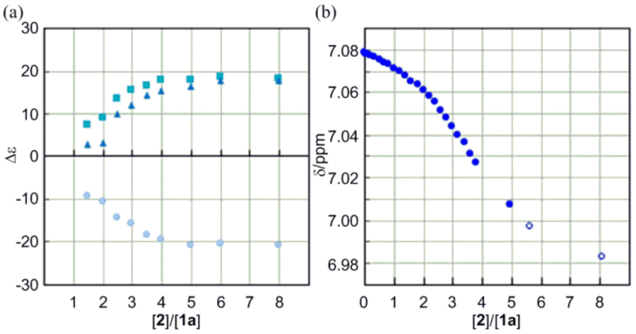
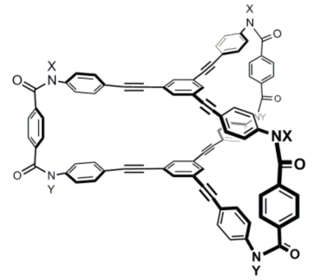


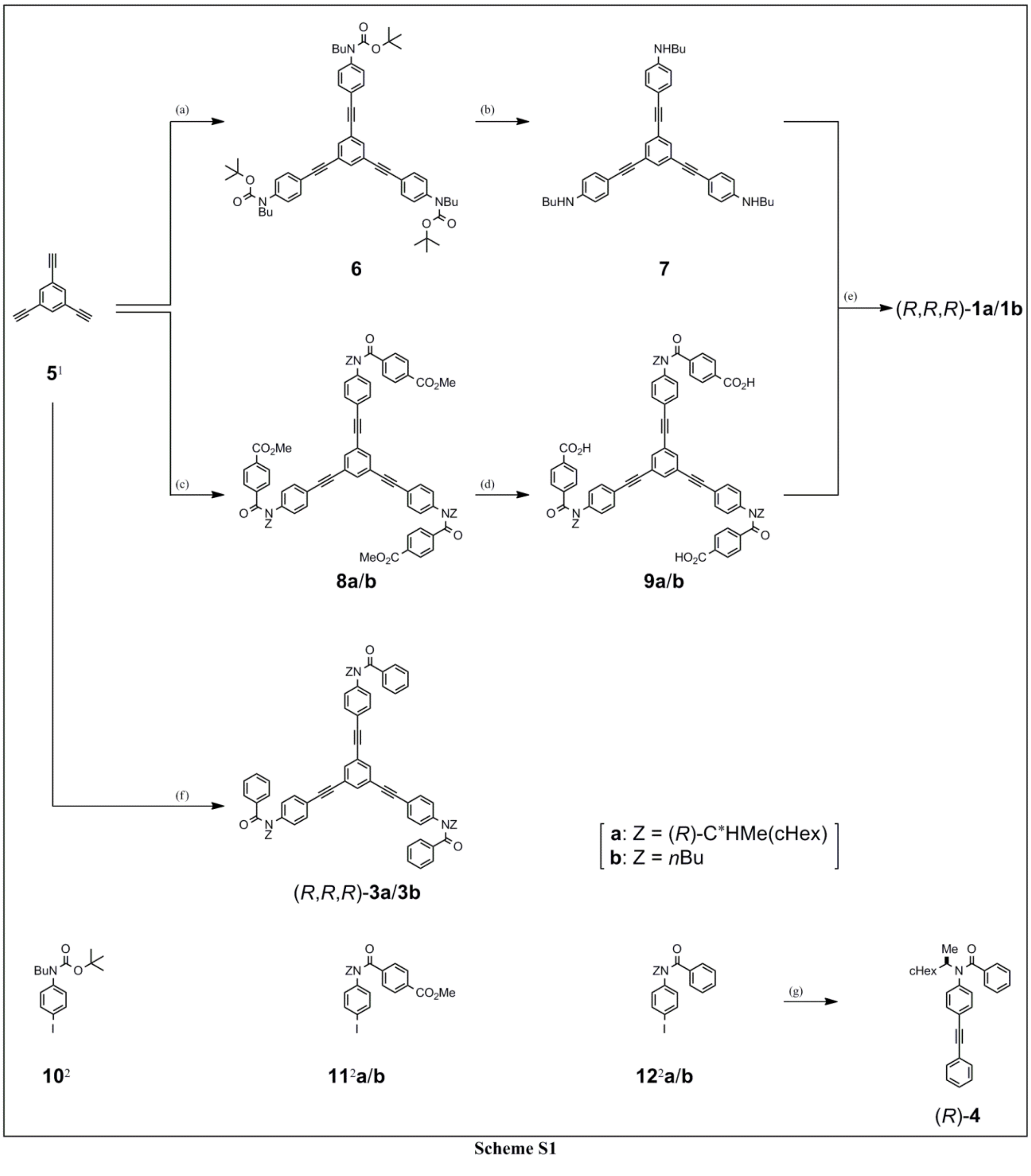
Fig. S7 (a) Continuous changes in the molar CDs at 310 (square), 280 (triangle), and 258 (circle) nm in the CD spectrum of (*R*,*R*,*R*)-**1a** (9.2×10^{-5} M) upon complexation with a ditopic guest (*R*,*R*)-**2** [1.5-8.0 equiv.], measured in CH_2Cl_2 at 293 K; (b) NMR titration curve (phenylene protons in terephthalamide units) for the complexation of (*R*,*R*,*R*)-**1a** with (*R*,*R*)-**2** (●: [**1a**] = 1.02 mM, [**2**] = 0-5.06 mM; ○: [**1a**] = 1.08 mM, [**2**] = 6.03 mM and [**1a**] = 0.76 mM, [**2**] = 6.10 mM, respectively), measured in $CDCl_3$ at 298 K.

Experimental Details of New Compound Preparation



(*R*,*R*,*R*)-**1a**/**1b**

a: X = *n*Bu, Y = (*R*)-C*HMe(cHex)
b: X = Y = *n*Bu



Scheme S1

Scheme S1. Preparation of (*R*,*R*,*R*)-**1a**/**1b**, (*R*,*R*,*R*)-**3a**/**3b**, and (*R*)-**4**. Conditions and yields: (a) **10**[2], Pd(PPh_3)$_4$, CuI, ^{i}Pr$_2$NH, THF (92%); (b) TFA, CH_2Cl_2 (85%); (c) **11**[2]**a**/**b**, Pd(PPh_3)$_4$, CuI, Et_2NH, CH_3CN (86% for **8a**, 92% for **8b**); (d) LiOH, THF, MeOH, H_2O (88% for **9a**, 97% for **9b**); (e) i) **9a**/**b**, $SOCl_2$, $BnNEt_3Cl$, CH_2Cl_2, ii) **7**, **9'a**/**b**, Et_3N, THF, Toluene (50% for (*R*,*R*,*R*)-**1a**, 41% for **1b**); (f) **12**[2]**a**/**b**, Pd(Ph_3)$_4$, CuI, Et_2NH, CH_3CN (80% for (*R*,*R*,*R*)-**3a**, 99% for **3b**); (g) phenylacetylene, Pd(PPh_3)$_4$, CuI, Et_3N, THF (80% from **12a**[2]).

Preparation of 6

To a solution of **10**[2] (7.918 g, 21.1 mmol), Pd(PPh_3)$_4$ (365 mg, 316 μmol) and CuI (95 mg, 0.50 mmol) in ^{i}Pr$_2$NH (70 mL) was added a solution of **5**[1] (880 mg, 5.86 mmol) in THF (70 mL) at 60 °C over a period of 15 min using an addition funnel under an argon atmosphere, and the reaction mixture was further stirred at the temperature for 45 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (4:1 dichloromethane/hexane-dichloromethane) to give **6** (4.808 g) as a white solid in 92% yield.

An analytical sample was obtained as a white solid by further purification through GPC (chloroform, detected by UV 254 nm and RI).

Data of 6

mp 108-109 °C; ^{1}H NMR δ_H(400 MHz, $CDCl_3$, TMS)/ppm 7.64 (3H, s), 7.49 (6H, d, *J* = 8.4 Hz), 7.20 (6H, d, *J* = 8.4 Hz), 3.65 (6H, t, *J* = 7.6 Hz), 1.53 (6H, quint, *J* = 7.6 Hz), 1.45 (9H, s), 1.31 (6H, sext, *J* = 7.6 Hz), 0.90 (9H, t, *J* = 7.6 Hz); ^{13}C NMR δ_C(100 MHz, $CDCl_3$)/ppm 154.4, 142.9, 133.9, 132.0, 126.7, 124.0, 119.9, 90.2, 87.8, 80.4, 49.5, 30.6, 28.3, 19.9, 13.8; IR (KBr) 3049, 2964, 2931, 2873, 2211, 1702, 1678, 1580, 1510 cm^{-1}; FD-LRMS m/z 894.5 ([M+3]$^+$, 4.3%), 893.5 ([M+2]$^+$, 23), 892.5 ([M+1]$^+$, 66), 891.5 (M$^+$, BP); FD-HRMS Calcd. for $C_{57}H_{69}N_3O_6$ 891.51863, Found 891.51809.

Preparation of 8a [Z = (*R*)-CHMe(cHex)]

To a solution of **5** (407 mg, 2.71 mmol) and **11a**[2] (4.749 g, 9.66 mmol) in CH_3CN/Et_2NH (337/67 mL) were added Pd(PPh_3)$_4$ (155 mg, 134 μmol) and CuI (52 mg, 0.27 mmol) at 80 °C under an argon atmosphere, and the reaction mixture was stirred at the temperature for 50 min. After dilution with ethyl acetate, the diluted reaction mixture was washed with 1N HCl. aq and brine. The organic layer was separated, and then dried over $MgSO_4$. Chromatographic separation on SiO_2 (chloroform) gave **8a** (2.903 g) as a white solid in 86% yield.

An analytical sample was obtained as a white solid by further purification through GPC (chloroform, detected by UV 254 nm and RI).

Data of 8a [Z = (*R*)-CHMe(cHex)]

mp 142-143 °C; ^{1}H NMR δ_H(400 MHz, $CDCl_3$, TMS)/ppm 7.83 (6H, br.d), 7.55 (3H, s), 7.83-7.30 (12H, br.d×2), 6.98 (6H, br.d), 4.57-4.45 (3H, br.), 2.14 (3H, br.d), 1.87-1.63 (15H, br.m), 1.34-0.95 (15H, br.m), 1.21 (9H, d, *J* = 6.8 Hz); ^{13}C NMR δ_C(100 MHz, $CDCl_3$)/ppm 169.9, 166.3, 141.5, 134.1, 132.2, 130.5, 129.6, 129.3, 129.1, 128.2, 123.7, 121.6, 89.6, 88.7, 59.2, 52.2, 41.4, 30.9, 30.4, 26.2, 26.1, 26.0, 16.8; IR (KBr) 3044, 2928, 2851, 2210, 1725, 1649, 1579, 1508 cm^{-1}; FD-LRMS m/z 1242.5 ([M+3]$^+$, 15%), 1241.5 ([M+2]$^+$, 42), 1240.5 ([M+1]$^+$, 90), 1239.5 (M$^+$, BP); $[\alpha]_D^{22}$ –120 (*c* 0.218 in $CHCl_3$); FD-HRMS Calcd. for $C_{81}H_{81}N_3O_9$ 1239.59728, Found 1239.60219.

Preparation of 8b [Z = *n*Bu]

To a solution of **5** (589 mg, 3.92 mmol) and **11b**[2] (6.17 g, 14.1 mmol) in CH_3CN/Et_2NH (490/100 mL) were added $Pd(PPh_3)_4$ (338 mg, 0.293 mmol) and CuI (225 mg, 1.18 mmol) at 80 °C under an argon atmosphere, and the reaction mixture was stirred at the temperature for 50 min. After dilution with ethyl acetate, the diluted reaction mixture was washed with 1N HCl. aq., water, and brine. The organic layer was separated, and then dried over $MgSO_4$. Chromatographic separation on SiO_2 (dichloromethane-ethyl acetate/dichloromethane) gave **8b** (3.869 g) as a white solid in 92% yield.

An analytical sample was obtained as a white solid by further purification through GPC (chloroform, detected by UV 254 nm and RI).

Data of 8b [Z = *n*Bu]

mp 102-103 °C; ^{1}H NMR δ_H(400 MHz, $CDCl_3$, TMS)/ppm 7.86 (6H, d, *J* = 8.4 Hz), 7.56 (3H, s), 7.35 (6H, d, *J* = 8.4 Hz), 7.35 (6H, d, *J* = 8.4 Hz), 7.00 (6H, d, *J* = 8.4 Hz), 3.94 (6H, t, *J* = 7.6 Hz), 3.88 (9H, s), 1.62 (6H, quint, *J* = 7.6 Hz), 1.38 (6H, sext, *J* = 7.6 Hz), 0.93 (9H, t, *J* = 7.6 Hz); ^{13}C NMR δ_C(100 MHz, $CDCl_3$)/ppm 169.2, 166.3, 143.1, 140.4, 134.1, 132.5, 130.8, 129.1, 128.5, 127.6, 123.7, 121.2, 89.6, 88.5, 52.2, 50.0, 29.8, 20.1, 13.8; IR (KBr) 3043, 2954, 2931, 2872, 2210, 1725, 1649, 1580, 1510 cm^{-1}; FD-LRMS m/z 1080.4 ([M+3]$^+$, 9.3%), 1079.4 ([M+2]$^+$, 37), 1078.4 ([M+1]$^+$, 85), 1077.4 (M$^+$, BP); FD-HRMS Calcd. for $C_{69}H_{63}N_3O_9$ 1077.45643, Found 1077.45665.

Preparation of 9a [Z = (*R*)-CHMe(cHex)]

A mixture of **8a** (138 mg, 0.111 mmol), $LiOH\cdot H_2O$ (38 mg, 0.91 mmol), THF (5 mL), MeOH (2 mL) and water (2 mL) was stirred at room temperature for 80 min. After removal of the organic solvents by evaporation, the residue was acidified with 1N HCl aq., and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, and then concentrated to give **9a** (117 mg) as a white solid in 88% yield. The product was subjected to the next reaction without purification.

Preparation of 9b [Z = *n*Bu]

A mixture of **8b** (156 mg, 0.145 mmol), $LiOH\cdot H_2O$ (47 mg, 1.1 mmol), THF (5 mL), MeOH (2 mL) and water (2 mL) was stirred at room temperature for 70 min. After removal of the organic solvents by evaporation, the residue was acidified with 1N HCl aq., and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, and then concentrated to give **9b** (145 mg) as a white solid in 97% yield. The product was subjected to the next reaction without purification.

Preparation of (*R*,*R*,*R*)-1a [X = *n*Bu, Y = (*R*)-CHMe(cHex)]

To a refluxed solution of **9a** (580 mg, 0.484 mmol) and $BnNEt_3Cl$ (4 mg, 0.02 mmol) in CH_2Cl_2 (16 mL) was added $SOCl_2$ (0.22 mL, 3.0 mmol), and the mixture was further refluxed for 1 h. After removal of the solvent by evaporation, the resulting solid (**9a'**) was dried *in vacuo* and dissolved in THF (10 mL) [acid chloride preparation].

To a solution of **6** (471 mg, 0.528 mmol) in CH_2Cl_2 (54 mL) was added TFA (5.20 mL), and the mixture was stirred at room temperature for 1 h, and then diluted with CH_2Cl_2 (135 mL). The diluted reaction mixture was quenched by addition of satd. $NaHCO_3$ aq. The organic layer was separated, and then dried over $MgSO_4$. Chromatographic separation on SiO_2 (2:3-1:1 dichloromethane/hexane) gave **7** (266 mg) as a white amorphous in 85% yield [deprotection of BOC].

To a solution of **7** (266 mg, 0.441 mmol) and Et_3N (2.0 mL, 14 mmol) in toluene (21 mL) were added the freshly prepared THF solution (10 mL) containing the acid chloride **9a'** and extra THF (5+5 mL) at 80°C, and the mixture was stirred at the temperature for 50 min. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (chloroform-ethyl acetate/chloroform), followed by GPC (chloroform, UV detected by 254 nm and RI), to give (*R*,*R*,*R*)-**1a** (389 mg) as a white solid in 50% yield.

Data of (*R*,*R*,*R*)-1a [X = *n*Bu, Y = (*R*)-CHMe(cHex)]

mp 251-256 °C (decomp.); ^{1}H NMR δ_H(400 MHz, $CDCl_3$, TMS)/ppm [298 K] 7.32 (6H, d, *J* = 8.4 Hz), 7.30 (6H, d, *J* = 8.4 Hz), 7.30 (3H, s), 7.28 (3H, s), 7.08 (12H, s), 6.86 (6H, d, *J* = 8.4 Hz), 6.80 (6H, d, *J* = 8.4 Hz), 4.45 (3H, dq, *J* = 3.6, 6.8 Hz), 3.90 (3H, ddd, *J* = 8.0, 13.6, 21.6 Hz), 3.85 (3H, ddd, *J* = 7.6, 13.6, 20.8 Hz), 2.07 (3H, br.d), 1.82-1.48 (21H, br.m), 1.37-0.85 (21H, br.m), 1.13 (9H, d, *J* = 6.8 Hz), 0.88 (9H, t, *J* = 7.6 Hz); ^{13}C NMR δ_C(100 MHz, $CDCl_3$)/ppm 170.2, 169.5, 143.4, 141.6, 138.6, 136.8, 134.0, 132.2, 131.9, 129.6, 128.0, 127.4, 127.4, 123.5, 123.4, 121.3, 120.6, 89.2, 89.2, 88.7, 88.3, 59.0, 49.8, 41.4, 30.8, 30.4, 29.7, 26.2, 26.0, 26.0, 20.1, 16.8, 13.7; IR (KBr) 3041, 2928, 2851, 2208, 1657, 1580, 1509 cm^{-1}; FD-LRMS m/z 1737.7 ([M+3]$^+$, 37%), 1736.7 ([M+2]$^+$, 75), 1735.7 ([M+1]$^+$, BP), 1734.7 (M$^+$, 74); UV-Vis λ_{max}(CH_2Cl_2)/nm (logε) 291sh. (5.09), 277 (5.13); CD λ(CH_2Cl_2)/nm ($\Delta\varepsilon$) 300 (–9.6), 271 (–13); $[\alpha]_D^{23}$ –72.6 (*c* 0.357 in $CHCl_3$); FD-HRMS Calcd. for $C_{120}H_{114}N_6O_6$ 1734.87998, Found 1734.87807.

Preparation of 1b [X = Y = *n*Bu]

To a refluxed solution of **9b** (216 mg, 0.208 mmol) and $BnNEt_3Cl$ (9 mg, 0.04 mmol) in CH_2Cl_2 (9 mL) was added $SOCl_2$ (0.12 mL, 1.7 mmol), and the mixture was further refluxed for 2 h. After removal of the solvent by evaporation, the resulting solid (**9b'**) was dried *in vacuo* and dissolved in THF (4.1 mL) [acid chloride preparation].

To a solution of **6** (339 mg, 0.380 mmol) in CH_2Cl_2 (40 mL) was added TFA (3.70 mL), and the mixture was stirred at room temperature for 30 min, and then diluted with CH_2Cl_2 (100 mL). The diluted reaction mixture was quenched by addition of satd. $NaHCO_3$ aq. The organic layer was separated, and then dried over $MgSO_4$. Chromatographic separation on SiO_2 (2:3-3:2 dichloromethane/hexane) gave **7** (122 mg) as a white amorphous in 54% yield [deprotection of BOC].

To a solution of Et_3N (0.43 mL, 3.1 mmol) in toluene (8.2 mL) were added a solution of **7** (122 mg, 0.206 mmol) in THF (4.1 mL) and the freshly prepared THF solution (10 mL) containing the acid chloride **9b'** at 80°C over a period of 12 h using a syringe pump under an argon atmosphere, and the mixture was stirred at the temperature for 2 h. After addition of 1N NaOH aq., the organic layer was separated and washed with water and brine, and then dried over $MgSO_4$. Chromatographic separation on SiO_2 (chloroform-1:3 ethyl acetate/chloroform) and GPC separation (chloroform, UV detected by 254 nm and RI) gave **1b** (133 mg) as a white solid in 41% yield.

An analytical sample was collected as a white solid by filtration after precipitation in ethyl acetate.

Data of 1b [X = Y = *n*Bu]

mp >300 °C; ^{1}H NMR δ_H(400 MHz, $CDCl_3$, TMS)/ppm [293 K] 7.32 (12H, d, *J* = 8.4 Hz), 7.29 (6H, s), 7.12 (12H, s), 6.85 (12H, d, *J* = 8.4 Hz), 3.88 (12H, t, *J* = 7.6 Hz), 1.54 (12H, quint, *J* = 7.6 Hz), 1.33 (12H, sext, *J* = 7.6 Hz), 0.89 (18H, t, *J* = 7.6 Hz); ^{13}C NMR δ_C(75 MHz, $CDCl_3$)/ppm 169.4, 143.4, 137.3, 134.0, 132.2, 128.0, 127.5, 123.4, 120.8, 89.2, 88.4, 49.9, 29.7, 20.1, 13.8; IR (KBr) 3041, 2956, 2930, 2870, 2209, 1656, 1649, 1580, 1509 cm^{-1}; FD-LRMS m/z 1575.8 ([M+3]$^+$, 32%), 1574.8 ([M+2]$^+$, 65), 1573.8 ([M+1]$^+$, BP), 1572.8 (M$^+$, 83); UV-Vis λ_{max}(CH_2Cl_2)/nm (logε) 291 (5.11), 281 (5.11); FD-HRMS Calcd. for $C_{108}H_{96}N_6O_6$ 1572.73913, Found 1572.73951.

Preparation of (*R*,*R*,*R*)-3a [Z = (*R*)-CHMe(cHex)]

To a solution of **5** (22 mg, 0.15 mmol) and **12a**[2] (232 mg, 0.535 mmol) in CH_3CN/Et_2NH (18/3.6 mL) were added $Pd(PPh_3)_4$ (11 mg, 9.5 μmol) and CuI (4.5 mg, 24 μmol) at 77 °C under an argon atmosphere, and the reaction mixture was stirred at the temperature for 75 min. After dilution with ethyl acetate, the diluted reaction mixture was washed with 1N HCl. aq and brine. The organic layer was separated, and then dried over $MgSO_4$. Chromatographic separation on SiO_2 (chloroform-1:19 ethyl acetate/chloroform) gave (*R*,*R*,*R*)-**3a** (125 mg) as a white solid in 80% yield.

An analytical sample was obtained as a white solid by further purification through GPC (chloroform, detected by UV 254 nm and RI).

Data of (*R*,*R*,*R*)-3a [Z = (*R*)-CHMe(cHex)]

mp 128-129 °C; ^{1}H NMR δ_H(400 MHz, $CDCl_3$, TMS)/ppm 7.54 (3H, s), 7.34 (6H, br.d), 7.27-

7.14 (15H, br.m), 7.00 (6H, br.d), 4.57-4.38 (3H, br.), 2.16 (3H, br.d), 1.93-1.55 (15H, br.m), 1.38-0.84 (15H, br.m), 1.21 (9H, d, *J* = 6.8 Hz); ^{13}C NMR δ_C(100 MHz, $CDCl_3$)/ppm 169.9, 166.3, 141.5, 134.1, 132.2, 130.5, 129.6, 129.3, 129.1, 128.2, 123.7, 121.6, 89.6, 88.7, 59.2, 52.2, 41.4, 30.9, 30.4, 26.2, 26.1, 26.0, 16.8; ^{13}C NMR δ_C(100 MHz, $CDCl_3$)/ppm 170.9, 142.4, 137.1, 134.0, 132.0, 129.5, 129.3, 128.4, 127.8, 123.8, 121.1, 89.8, 88.5, 59.4, 41.5, 30.8, 30.5, 26.3, 26.1, 26.0, 16.9; IR (KBr) 3040, 2927, 2850, 2210, 1649, 1579, 1508 cm^{-1}; FD-LRMS m/z 1068.5 ($[M+3]^+$, 9.6%), 1067.5 ($[M+2]^+$, 37), 1066.5 ($[M+1]^+$, 85), 1065.5 (M^+, BP); UV-Vis λ_{max}(CH_2Cl_2)/nm (logε) 313 (5.01), 305sh. (4.98); CD λ(CH_2Cl_2)/nm ($\Delta\varepsilon$) 311 (–11), 299 (–12), 254 (+1.7); $[\alpha]_D^{21}$ –137 (*c* 0.108 in $CHCl_3$); FD-HRMS Calcd. for $C_{75}H_{75}N_3O_3$ 1065.58084, Found 1065.57866.

Preparation of **3b** [Z = *n*Bu]

To a solution of **5** (36 mg, 0.24 mmol) and **12b**[2] (327 mg, 0.862 mmol) in CH_3CN/Et_2NH (30/6.0 mL) were added $Pd(PPh_3)_4$ (16 mg, 0.014 mmol) and CuI (9.4 mg, 0.049 mmol) at 78 °C under an argon atmosphere, and the reaction mixture was stirred at the temperature for 75 min. After dilution with ethyl acetate, the diluted reaction mixture was washed with 1N HCl. aq and brine. The organic layer was separated, and then dried over $MgSO_4$. Chromatographic separation on SiO_2 (chloroform-1:9 ethyl acetate/chloroform) gave **3b** (216 mg) as a white solid in 99% yield.

An analytical sample was obtained as a white solid by further purification through GPC (chloroform, detected by UV 254 nm and RI).

Data of 3b [Z = *n*Bu]

mp 81-82 °C; ^{1}H NMR δ_H(300 MHz, $CDCl_3$, TMS)/ppm 7.55 (3H, s), 7.36 (6H, d, *J* = 8.4 Hz), 7.31-7.15 (15H, m), 7.01 (6H, d, *J* = 8.4 Hz), 3.94 (6H, t, *J* = 7.5 Hz), 1.62 (6H, quint, *J* = 7.5 Hz), 1.37 (6H, sext, *J* = 7.5 Hz), 0.92 (9H, t, *J* = 7.5 Hz); ^{13}C NMR δ_C(75 MHz, $CDCl_3$)/ppm 170.2, 143.9, 136.1, 134.0, 132.4, 129.7, 128.7, 127.9, 127.6, 123.8, 120.7, 89.8, 86.3, 50.2, 29.9, 20.2, 13.8; IR (KBr) 3056, 2956, 2929, 2870, 2209, 1648, 1578, 1508 cm^{-1}; FD-LRMS m/z 906.4 ($[M+3]^+$, 5.7%), 905.4 ($[M+2]^+$, 30), 904.4 ($[M+1]^+$, 78), 903.4 (M^+, BP); UV-Vis λ_{max}(CH_2Cl_2)/nm (logε) 313 (5.02), 305sh. (4.99); FD-HRMS Calcd. for $C_{63}H_{57}N_3O_3$ 903.43999, Found 903.43952.

Preparation of (*R*)-4

To a solution of phenylacetylene (0.10 mL, 0.91 mmol) and **12a** (200 mg, 462 μmol) in THF/Et_3N (11/22 mL) were added $Pd(PPh_3)_4$ (26 mg, 23 μmol) and CuI (7.4 mg, 0.039 mmol), and the mixture was stirred at 40 °C for 15 h. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 ($CHCl_3$) and GPC (chloroform, detected by UV 254 nm) to give (*R*)-**4** (150 mg) as a white solid in 80% yield.

Data of (*R*)-4

mp 68-69 °C; ^{1}H NMR δ_H(300 MHz, CDCl$_3$, TMS)/ppm 7.52-7.46 (2H, m), 7.37-7.31 (5H, m), 7.28-7.11 (5H, m), 6.98 (2H, d, *J* = 8.4 Hz), 4.58-4.40 (1H, br.m), 2.16 (1H, br.d), 1.87-1.62 (5H, br.m), 1.35-0.93 (5H, br.m), 1.20 (3H, d, *J* = 6.9 Hz); ^{13}C NMR δ_C(75 MHz, CDCl$_3$)/ppm 170.9, 141.8, 137.2, 131.9, 131.5, 129.4, 129.2, 128.4, 128.4, 127.7, 122.9, 121.7, 90.3, 88.4, 59.2, 41.5, 30.8, 30.4, 26.3, 26.1, 26.0, 16.8; IR (KBr) 3058, 2927, 2850, 2215, 1645, 1595, 1510 cm^{-1}; FD-LRMS m/z 408.3 ([M+1]$^+$, 34%), 407.3 (M$^+$, BP); UV-vis λ_{max}(CH$_2$Cl$_2$)/nm (logε) 291 (4.47), 307 (4.45); CD λ(CH$_2$Cl$_2$)/nm ($\Delta\varepsilon$) 306 (–3.3), 291 (–4.7), 275 (–4.0); $[\alpha]_D^{25}$ –108 (*c* 0.180 in CHCl$_3$); Anal. Calcd. for $C_{29}H_{29}NO$ C 85.47, H 7.17, N 3.44, Found C 85.62, H 7.20, N 3.28.

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