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Supplementary Information

Planar chiral desymmetrization of a two-layered cyclophane and control of dynamic helicity through the arrangement of two nonstereogenic centers

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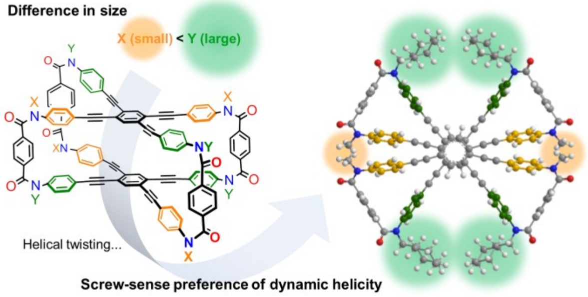
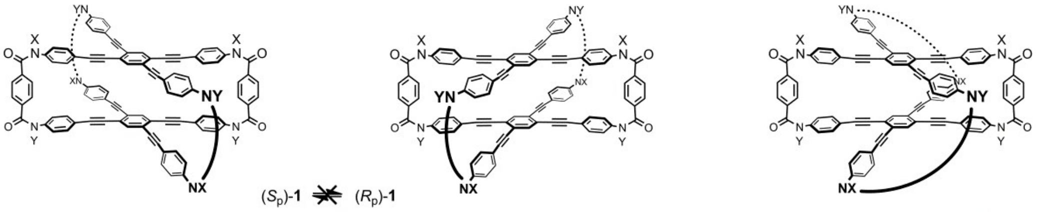


Contents

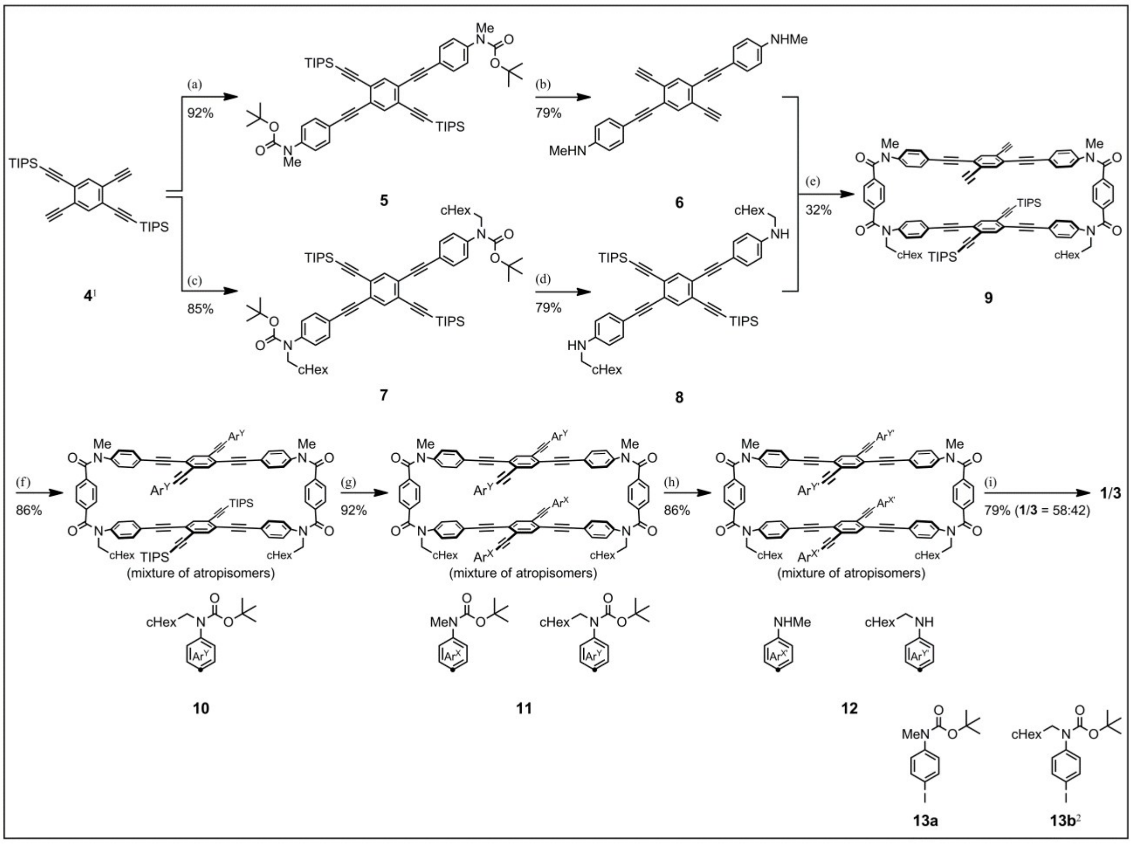
Experimental



(S_p)-**1** $\not\rightleftharpoons$ (R_p)-**1**

1: X = CH_3, Y = CH_2(cHex)

3: X = CH_3, Y = CH_2(cHex)



Scheme S1. Preparation of cyclophanes **1**/**3**. Reagents: (a) **13a**, $Pd(PPh_3)_4$, CuI, *i*Pr_2NH, THF; (b) i) TFA, CH_2Cl_2; ii) TBAF, THF; (c) **13b**, $Pd(PPh_3)_4$, CuI, *i*Pr_2NH, THF; (d) TFA, CH_2Cl_2; (e) terephthaloyl chloride, Et_3N, toluene, THF; (f) **13b**, $Pd(PPh_3)_4$, CuI, *i*Pr_2NH, THF; (g) **13a**, $Pd(PPh_3)_4$, CuI, TBAF, Et_3N, THF; (h) TFA, CH_2Cl_2; (i) terephthaloyl chloride, Et_3N, toluene, THF.

Preparation of **5**

To a solution of **4**[1] (1.44 g, 2.96 mmol) and **13a** (2.56 g, 7.69 mmol) in THF (55 mL) and *i*Pr_2NH (55 mL) were added $Pd(PPh_3)_4$ (206 mg, 0.178 mmol) and CuI (69 mg, 0.36 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 50 ºC for 13 hours. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane–dichloromethane) to give **5** (2.44 g) as a pale yellow solid in 92% yield. An analytical sample was obtained as a white solid by further purification through GPC (chloroform). **5**: mp 185.0-185.5 °C; elemental analyses Found: C, 74.87; H, 8.43; N, 3.13%. Calc. for $C_{56}H_{76}N_2O_4Si_2$: C, 74.95; H, 8.54; N, 3.12%; IR (KBr) ν_{max}/cm^{-1} 2941, 2864, 2220, 2154, 1703, 1513; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.65 (2H, s), 7.48 (4H, d, J = 8.8 Hz), 7.23 (4H, d, J = 8.8 Hz), 3.28 (6H, s), 1.47 (18H, s), 1.16-1.10 (42H, m); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.2, 143.9, 136.1, 131.9, 125.1, 124.7, 119.3, 104.2, 97.3, 94.6, 87.1, 80.6, 36.9, 28.2, 18.6, 11.2; FD-LRMS *m*/*z* 896.56 (M^+, 100%), 897.56 ($[M+1]^+$, 72), 898.56 ($[M+2]^+$, 33), 899.57 ($[M+3]^+$, 12).

Preparation of **6**

To a solution of **5** (491 mg, 0.547 mmol) in CH_2Cl_2 (20 mL) was added TFA (3.6 mL) at room temperature. The mixture was stirred at room temperature for 90 min, neutralized with 1M aq. NaOH, and separated. The organic layer was dried over magnesium sulfate and concentrated. The residue was dissolved in THF (15 mL) and treated with 1M TBAF solution in THF (1.2 mL). After stirring at room temperature for 20 min, the mixture was concentrated. The residue was purified by column chromatography on SiO_2 (dichloromethane) to give **6** as a yellow solid, which was suspended in hexane, collected by filtration as a yellow solid (165 mg) in 79% yield, and immediately subjected to the next reaction.

Preparation of **7**

To a solution of **4** (1.87 g, 3.84 mmol) and **13b**[2] (4.14 g, 9.97 mmol) in THF (77 mL) and *i*Pr_2NH (77 mL) were added $Pd(PPh_3)_4$ (265 mg, 0.229 mmol) and CuI (94 mg, 0.49 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 50 ºC for 12 hours. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **7** (3.45 g) as an off-white solid in 85% yield. An analytical sample was obtained as a white solid by further purification through GPC (chloroform). **7**: mp 209.0-210.0 °C; elemental analyses Found: C, 76.95; H, 9.01; N, 2.62%. Calc. for $C_{68}H_{96}N_2O_4Si_2$: C, 76.93; H, 9.11; N, 2.64%; IR (KBr) ν_{max}/cm^{-1} 2923, 2864, 2223, 2157, 1701, 1514; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.65 (2H, s), 7.48 (4H, d, J = 8.4 Hz), 7.18 (4H, d, J = 8.4 Hz), 3.53 (4H, d, J = 7.2 Hz), 1.73-1.59 (10H, br m), 1.52-1.39 (2H, br m), 1.43 (18H, s), 1.19-0.85 (52H, br m); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.7, 143.2, 136.1, 132.1, 126.7, 125.3, 125.2, 120.0, 104.3, 97.5, 94.6, 87.3, 80.3, 55.5, 36.8, 30.7, 28.3, 26.4, 25.8, 18.7, 11.3; FD-LRMS *m*/*z* 1060.74 (M^+, 100%), 1061.74 ($[M+1]^+$, 88), 1062.74 ($[M+2]^+$, 45), 1063.74 ($[M+3]^+$, 18).

Preparation of **8**

To a solution of **7** (1.57 g, 1.48 mmol) in CH_2Cl_2 (70 mL) was added TFA (9.8 mL) at room temperature. The mixture was stirred at room temperature for 100 min, neutralized with aq. 1M NaOH, and separated. The organic layer was dried over magnesium sulfate, concentrated, and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **8** as a bright yellow solid (1.00 g) in 79% yield, and immediately subjected to the next reaction.

Preparation of **9**

To a solution of terephthaloyl chloride (240 mg, 1.18 mmol) in toluene (75 mL) were added a solution of **8** (488 mg, 0.567 mmol) in THF (8.8 mL) containing Et_3N (0.80 mL, 5.8 mmol) at 51-54 °C over a period of 1 hour, and then additional THF (150 mL). To the diluted mixture were added a solution of **6** (207 mg, 0.538 mmol) in THF (20 mL) and additional THF (60 mL) at that temperature, and the reaction mixture was stirred for 30 min. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, which was washed with 1M aq. NaOH and satd. aq. $NaHCO_3$, dried over magnesium sulfate, and then purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give **9** (259 mg) as a white solid in 32% yield. An analytical sample was suspended in 1:5 ethanol/ethyl acetate, and collected as a white solid. **9**: mp >220 °C (dec); IR (KBr) ν_{max}/cm^{-1} 3294, 2923, 2862, 2221, 2212(sh), 2158, 2143, 1655, 1600, 1510; ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.36 (2H, s), 7.35 (2H, s), 7.33 (4H, d, J = 8.4 Hz), 7.29 (4H, d, J = 8.4 Hz), 7.17 (4H, d, J = 8.4 Hz), 7.15 (4H, d, J = 8.4 Hz), 6.86 (4H, d, J = 8.4 Hz), 6.84 (4H, d, J = 8.4 Hz), 4.00 (2H, dd, J = 8.0, 12.8 Hz) , 3.60 (2H, dd, J = 6.4, 12.8 Hz), 3.46 (6H, s), 3.34 (2H, s), 1.77-1.46 (12H, br m), 1.25-0.90 (52H, m); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 169.8, 169.2, 144.5, 143.3, 137.2, 136.9, 135.1, 134.9, 132.2, 132.2, 128.4, 127.9, 126.9, 126.3, 125.3, 125.1, 125.0, 124.5, 121.1, 120.8, 104.2, 97.1, 94.1, 93.6, 88.3, 87.8, 83.1, 81.0, 55.6, 37.8, 36.2, 30.9, 30.7, 26.3, 25.7, 18.7, 11.2; FD-LRMS *m*/*z* 1504.75 (M^+, 80%), 1505.76 ($[M+1]^+$, 100), 1506.76 ($[M+2]^+$, 69), 1507.76 ($[M+3]^+$, 35), 1508.77 ($[M+4]^+$, 14), 1509.77 ($[M+5]^+$, 5); FD-HRMS Found: 1504.75884. Calc. for $C_{102}H_{104}N_4O_4Si_2$: 1504.75961.

Preparation of **10** (mixture of atropisomers) [X = Me, Y = CH_2(cHex)]

To a solution of **9** (592 mg, 0.393 mmol) and **13b** (499 mg, 1.20 mmol) in THF (9.5 mL) and $i Pr_2NH$ (9.5 mL) were added $Pd(PPh_3)_4$ (46 mg, 0.040 mmol) and CuI (9 mg, 0.05 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 50 °C for 13 hours. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane) to give **10** (705 mg) as a white amorphous solid in 86% yield.

Preparation of **11** (mixture of atropisomers) [X = Me, Y = CH_2(cHex)]

To a solution of **10** (705 mg, 0.339 mmol), **13a** (400 mg, 1.20 mmol), $Pd(PPh_3)_4$ (40 mg, 0.035 mmol) and CuI (8 mg, 0.04 mmol) in THF (6 mL) and Et_3N (17 mL) was added a solution of TBAF (0.72 mmol) in THF (3.2 mL) over a period of 2 hours via a syringe pump at 50 °C under an argon atmosphere, and the mixture was stirred at that temperature for 20 min. After dilution with ethyl acetate, the mixture was washed with aq. $NaHCO_3$, dried over magnesium sulfate, and then purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane) to give **11** (677 mg) as a pale yellow amorphous solid in 92% yield.

Preparation of **12** (mixture of atropisomers) [X = Me, Y = CH_2(cHex)]

To a solution of **11** (677 mg, 0.311 mmol) in CH_2Cl_2 (37 mL) was added TFA (16 mL) at room temperature. The mixture was stirred at room temperature for 1 hour, neutralized with aq. 1M NaOH, and separated. The organic layer was dried over magnesium sulfate, concentrated, and purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane) to give **12** as a yellow solid (475 mg) in 86% yield, and immediately subjected to the next reaction.

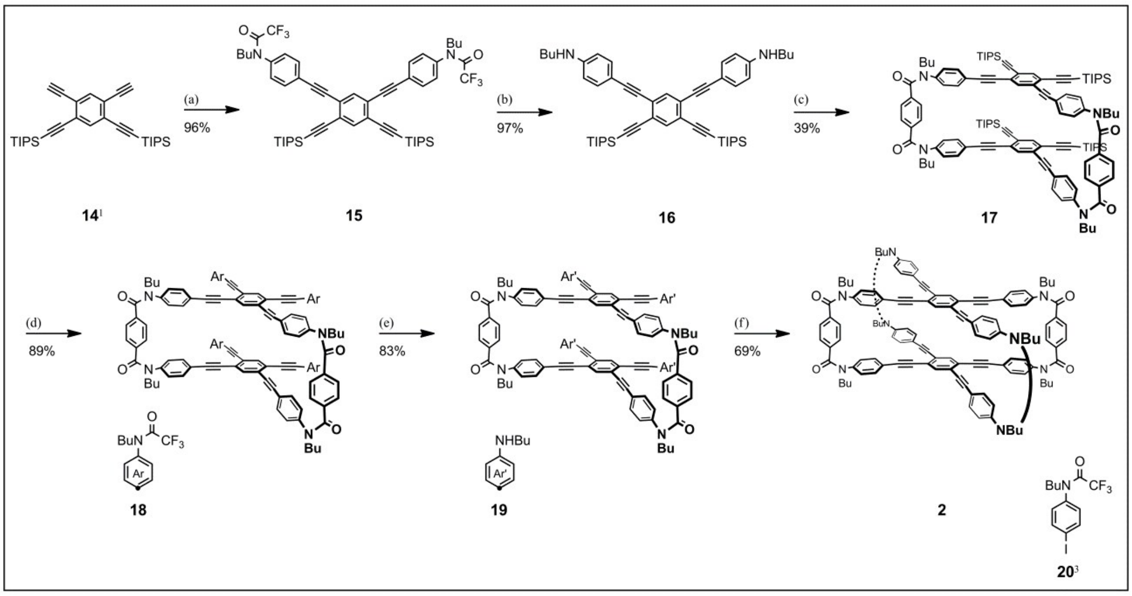
Preparation of **1** [X = Me, Y = CH_2(cHex)]

To a solution of **12** (475 mg, 0.267 mmol) in toluene (105 mL) and THF (50 mL) containing Et_3N (0.80 mL, 5.8 mmol) was added terephthaloyl chloride (121 mg, 0.596 mmol), and the mixture was stirred at 80 °C for 1 hour. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, and which was washed with 1M aq. NaOH and aq. $NaHCO_3$, dried over magnesium sulfate, concentrated, and purified by column chromatography on SiO_2 (tetrahydrofuran/dichloromethane), followed by GPC (chloroform) to give a mixture of **1** and **3** (431 mg) as a pale yellow solid in 79% yield (*See* **Fig. S1B**). HPLC separation (2:8 tetrahydrofuran/dichloromethane; YMC-Pack SIL, SIL-06, YMC Co., Ltd.) gave *rac*-**1** in pure form. Optical resolution (5:95 ethanol/chloroform; CHIRALPAK IF, DAICEL Co.) gave (–)-**1** and (+)-**1**, as the first and second fractions, respectively.

rac-**1**: mp >300 °C; UV $\lambda_{max}(CH_2Cl_2)$/nm 312 (log ε 5.16); IR (KBr) ν_{max}/cm^{-1} 2922, 2849, 2202, 1655, 1600, 1513, 1348, 1101, 838, 725, 581; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.43 (4H, s), 7.29 (8H, d, J = 8.4 Hz), 7.14 (8H, d, J = 8.4 Hz), 7.13 (16H, s), 3.80 (4H, dd, J = 7.2, 13.6 Hz), 3.72 (4H, dd, J = 7.2, 13.6 Hz), 3.44 (12H, s), 1.75-1.51 (24H, br m), 1.21-0.96 (20H, br m); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 169.6, 169.2, 144.5, 143.8, 137.8, 136.3, 135.5, 132.2, 128.3, 127.9, 127.4, 125.7, 125.0, 124.7, 120.8, 120.5, 94.0, 94.0, 88.4, 88.2, 55.8, 37.9, 36.3, 30.9, 30.8, 26.3, 25.7; FD-LRMS *m*/*z* 1018.42 (M^{2+}, 8%), 1018.93 ($[M+1]^{2+}$, 15), 1019.43 ($[M+2]^{2+}$, 15), 1019.93 ($[M+3]^{2+}$, 10), 1020.43 ($[M+4]^{2+}$, 5), 2036.85 (M^+, 63), 2037.86 ($[M+1]^+$, 100), 2038.86 ($[M+2]^+$, 84), 2039.86 ($[M+3]^+$, 47), 2040.87 ($[M+4]^+$, 21), 2041.87 ($[M+5]^+$, 8); FD-HRMS Found: 2036.89518. Calc. for $C_{140}H_{116}N_8O_8$: 2036.89161.

(–)-**1**: $[\alpha]_D^{23}$ –359 (c 4.16 × 10^{-1} in $CHCl_3$); CD $\lambda(CH_2Cl_2)$/nm 358 ($\Delta\varepsilon$ +8.8), 317 (–106) and 265 (+41.1).

(+)-**1**: $[\alpha]_D^{23}$ +365 (c 3.89 × 10^{-1} in $CHCl_3$); CD $\lambda(CH_2Cl_2)$/nm 358 ($\Delta\varepsilon$ –7.9), 317 (+106) and 265 (–38.7).



Scheme S2. Preparation of cyclophane **2**. Reagents: (a) **20**, $Pd(PPh_3)_4$, CuI, *i*Pr_2NH, THF; (b) NaH, MeOH, THF; (c) terephthaloyl chloride, Et_3N, toluene, THF; (d) **20**, $Pd(PPh_3)_4$, CuI, TBAF, Et_3N, THF; (e) NaH, MeOH, THF; (f) terephthaloyl chloride, Et_3N, toluene, THF.

Preparation of **15**

To a solution of **14**[1] (1.65 g, 3.39 mmol) and **20**[3] (3.51 g, 9.45 mmol) in THF (20 mL) and *i*Pr_2NH (20 mL) were added $Pd(PPh_3)_4$ (235 mg, 0.203 mmol) and CuI (79 mg, 0.41 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 49-51 ºC for 16 hours. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **15** (3.26 g) as a pale yellow amorphous solid in 96% yield. An analytical sample was obtained as a white amorphous by further purification through GPC (chloroform). **15**: mp 54-55 °C; elemental analyses Found: C, 69.10; H, 7.24; N, 2.85%. Calc. for $C_{56}H_{70}F_6N_2O_2$: C, 69.10; H, 7.25; N, 2.88%; IR (KBr) ν_{max}/cm^{-1} 2942, 2865, 2218, 2152, 1702, 1512; ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.69 (1H, s), 7.63 (1H, s), 7.58 (4H, d, J = 8.4 Hz), 7.20 (4H, d, J = 8.4 Hz), 3.75 (4H, t, J = 7.6 Hz), 1.59-1.52 (4H, m), 1.35 (4H, sext, J = 7.2 Hz), 1.15-1.08 (42H, m), 0.92 (6H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 156.4 ($\underline{C}(=O)CF_3$), 139.0, 136.4, 135.3, 132.6, 128.3, 125.7, 125.0, 123.8, 116.3 ($\underline{C}F_3$), 103.8, 98.2, 93.5, 88.8, 51.5, 28.9, 19.8, 18.6, 13.6, 11.2; FD-LRMS m/z 972.49 (M^+, 100%), 973.49 ($[M+1]^+$, 75), 974.49 ($[M+2]^+$, 35), 975.49 ($[M+3]^+$, 13).

Preparation of **16**

To an ice-cooled solution of **15** (1.48 g, 1.52 mmol) in THF (40 mL) were added 60% NaH in oil (168 mg, 4.19 mmol) and MeOH (1.5 mL), and the mixture was stirred at that temperature for 10 mim, and then diluted with dichloromethane. The organic layer was washed with aq. $NaHCO_3$, dried over magnesium sulfate, and then purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **16** (1.16 g) as a bright yellow solid in 97% yield, which was immediately subjected to the next reaction.

Preparation of **17**

To a solution of terephthaloyl chloride (303 mg, 1.49 mmol) in toluene (100 mL) and THF (50 mL) were added 5 mL of a solution of **16** (1.05 g, 1.34 mmol) in THF (10 mL) containing Et_3N (0.9 mL, 7 mmol) at room temperature over a period of 1 hour, and then the rest of the solution containing **16** and additional THF (40 mL), and the mixture was stirred at 79 ºC for 40 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give **17** (478 mg) as a white solid in 39% yield. An analytical sample was obtained as colorless crystals by recrystallization from chloroform/acetone. **17**: mp >300 °C; elemental analyses Found: C, 78.93; H, 8.27; N, 2.99%. Calc. for $C_{120}H_{148}N_4O_4Si_4$: C, 79.07; H, 8.18; N, 3.07%; IR (KBr) ν_{max}/cm^{-1} 3041, 2941, 2863, 2213, 2150, 1660, 1650, 1510; ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.87 (2H, s), 7.63 (2H, s), 7.35 (8H, d, J = 8.4 Hz), 7.00 (8H, s), 6.79 (2H, d, J = 8.4 Hz), 3.85 (8H, t, J = 7.2 Hz), 1.53 (8H, quin, J = 7.2 Hz), 1.33 (8H, sext, J = 7.2 Hz), 1.21-1.08 (84H, m), 0.89 (12H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 169.6, 143.0, 137.3, 134.6, 132.4, 127.9, 127.4, 125.6, 124.9, 121.0, 104.1, 97.8, 94.1, 88.3, 77.2, 49.3, 29.6, 20.0, 18.7, 13.7, 11.2; FD-LRMS *m/z* 1821.13 (M^+, 63%), 1822.14 ($[M+1]^+$, 100), 1823.13 ($[M+2]^+$, 86), 1824.13 ($[M+3]^+$, 56), 1825.14 ($[M+4]^+$, 29), 1826.14 ($[M+5]^+$, 13).

Preparation of **18**

To a solution of **17** (227 mg, 0.125 mmol), **20** (285 mg, 0.768 mmol), $Pd(PPh_3)_4$ (33 mg, 0.029 mmol) and CuI (5 mg, 0.03 mmol) in THF (7 mL) and Et_3N (20 mL) was added a solution of TBAF (0.52 mmol) in THF (2.8 mL) over a period of 2 hours via a syringe pump at 46-47 °C under an argon atmosphere, and the mixture was stirred at that temperature for 10 min. After removal of a solid by filtration, the filtrate was concentrated and dissolved in ethyl acetate, which was washed with 0.1M aq. HCl, and brine, dried over magnesium sulfate, and then concentrated. The residue was dissolved in CH_2Cl_2 (10 mL) containing Et_3N (0.1 mL). To the solution was added TFAA (0.14 mL, 0.99 mmol) at room temperature, and the mixture was stirred for 10 min and diluted with dichloromethane, which was washed with satd. aq. $NaHCO_3$, dried over magnesium sulfate, and purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane) to give **18** (240 mg) as a yellowish-white solid in 89% yield, which was further purified by GPC (chloroform). An analytical sample was suspended in refluxed 1-butanol, followed by washing with ethanol, and collected as a pale-yellowish white solid. **18**: mp 291-292 °C (dec); elemental analyses Found: C, 73.03; H, 5.34; N, 5.19%. Calc. for $C_{132}H_{116}F_{12}N_8O_8$: C, 73.05; H, 5.39; N, 5.16%; IR (KBr) ν_{max}/cm^{-1} 3043, 2959, 2933, 2872, 2206, 1701, 1698, 1694, 1655, 1649, 1513, 1204, 1151; ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.87 (2H, br s), 7.77 (2H, s), 7.57 (8H, d, J = 8.0 Hz), 7.40 (8H, d, J = 8.0 Hz), 7.22 (8H, d, J = 8.0 Hz), 7.03 (8H, s), 6.77 (8H, d, J = 8.0 Hz), 3.83 (8H, t, J = 7.6 Hz), 3.77 (8H, t, J = 7.6 Hz), 1.62-1.54 (8H, m), 1.55-1.47 (8H, m), 1.37 (8H, sext, J = 7.6 Hz), 1.30 (8H, sext, J = 7.2 Hz), 0.94 (12H, t, J = 7.2 Hz), 0.87 (12H, t, J = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; CDCl$_3$)/ppm 169.1, 156.2 ($\underline{C}$(=O)CF$_3$), 143.6, 139.5, 137.2, 135.3, 134.3, 132.6, 132.3, 128.6, 127.8, 127.8, 125.5, 125.2, 123.7, 120.9, 116.4 ($\underline{C}$F$_3$), 95.2, 94.1, 89.1, 88.2, 51.7, 49.6, 29.7, 29.0, 20.0, 19.8, 13.7, 13.6; FD-LRMS *m*/*z* 2168.91 (M$^+$, 67%), 2169.91 ([M+1]$^+$, 100), 2170.91 ([M+2]$^+$, 76), 2171.91 ([M+3]$^+$, 40), 2172.90 ([M+4]$^+$, 19), 2173.91 ([M+5]$^+$, 7).

Preparation of **19**

To an ice-cooled solution of **18** (100 mg, 0.0461 mmol) in THF (5 mL) were added 60% NaH in oil (13 mg, 0.33 mmol) and MeOH (0.13 mL), and the mixture was stirred at that temperature for 5 min, and then diluted with dichloromethane. The organic layer was washed with aq. NaHCO$_3$, dried over magnesium sulfate, and then purified by column chromatography on SiO$_2$ (ethyl acetate/dichloromethane) to give **19** (68 mg) as a yellow solid in 83% yield, which was immediately subjected to the next reaction.

Preparation of **2** [X = Y = *n*Bu]

To a solution of **19** (68 mg, 0.038 mmol) in toluene (19 mL) and THF (19 mL) containing Et$_3$N (0.11 mL, 0.79 mmol) was added terephthaloyl chloride (16 mg, 0.078 mmol), and the mixture was stirred at 80 °C for 1 hour. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO$_2$ (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give **2** (54 mg) as a yellow solid in 69% yield. An analytical sample was obtained as a pale yellow solid by reprecipitation in ethyl acetate with hexane. **2**: mp >300 °C; UV λ_{max}(CH$_2$Cl$_2$)/nm 318 (log ε 5.22); IR (KBr) ν_{max}/cm^{-1} 3040, 2955, 2929, 2870, 2204, 1650, 1600, 1513, 1379, 1294, 836, 730; ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.43 (4H, s), 7.25 (16H, d, J = 8.8 Hz), 7.15 (16H, s), 6.77 (16H, d, J = 8.8 Hz), 3.89 (8H, ddd, J = 7.6, 13.6, 21.2 Hz), 3.85 (8H, ddd, J = 7.6, 13.6, 21.2 Hz), 1.55 (16H, quin, J = 7.6 Hz), 1.34 (16H, sext, J = 7.6 Hz), 0.91 (24H, t, J = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; CDCl$_3$)/ppm 168.9, 143.6, 137.1, 135.3, 132.2, 128.2, 127.1, 124.9, 120.9, 94.2, 88.5, 50.0, 29.7, 20.1, 13.8; FD-LRMS *m*/*z* 1022.51 (M^{2+}, 14%), 1023.01 ([M+1]$^{2+}$, 23), 1023.51 ([M+2]$^{2+}$, 19), 1024.01 ([M+3]$^{2+}$, 11), 1024.51 ([M+4]$^{2+}$, 5), 2045.02 (M$^+$, 64), 2046.02 ([M+1]$^+$, 100), 2047.03 ([M+2]$^+$, 84), 2048.03 ([M+3]$^+$, 49), 2049.04 ([M+4]$^+$, 23), 2050.04 ([M+5]$^+$, 9); FD-HRMS Found: 2044.95464. Calc. for $C_{140}H_{124}N_8O_8$: 2044.95421.

Supplementary Figures

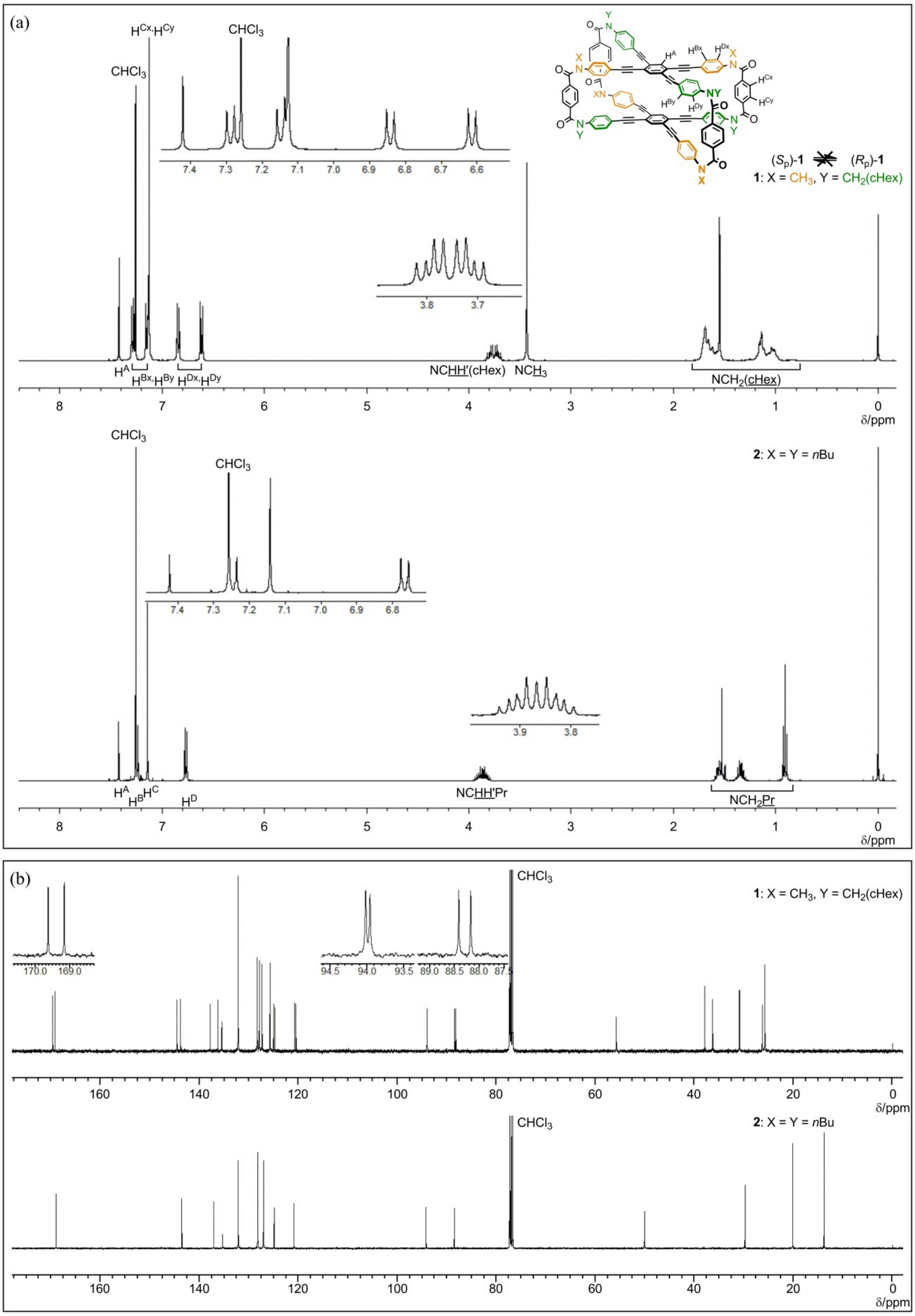


Fig. S1A (a) ^{1}H (400 MHz) and (b) ^{13}C (100 MHz) NMR spectra of *rac*-**1** (upper) and **2** (lower), measured in chloroform-*d* at room temperature.

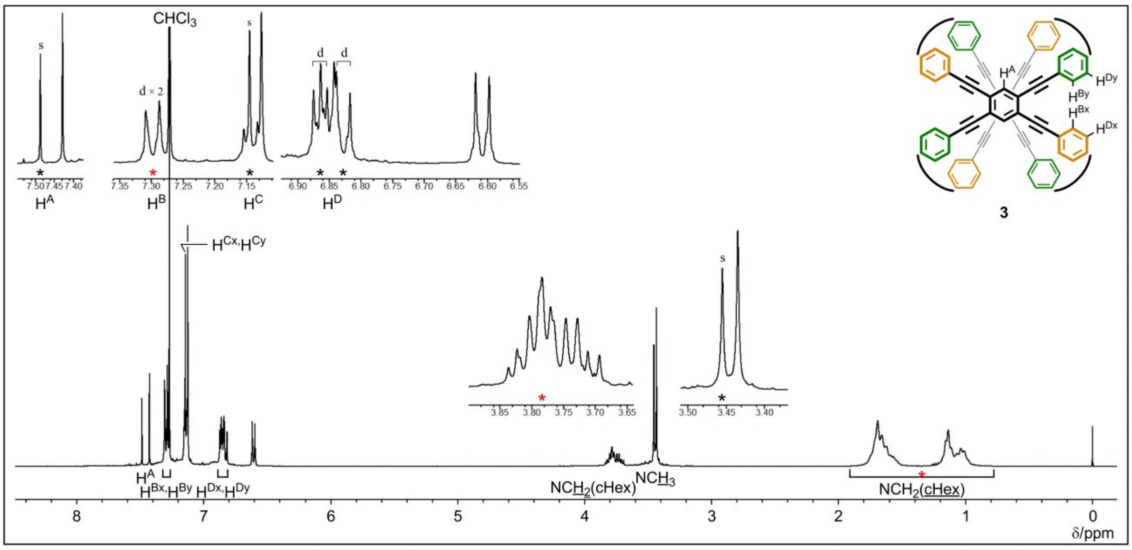


Fig. S1B ^{1}H (400 MHz) NMR spectrum of a purified mixture of *rac*-**1** and **3**, obtained by GPC. The spectrum was measured in chloroform-*d* at room temperature. Asterisk (*) denotes a resonance for **3**. * indicates a resonance(s) superimposed on that for **1** (*See also* **Fig. S1A**).

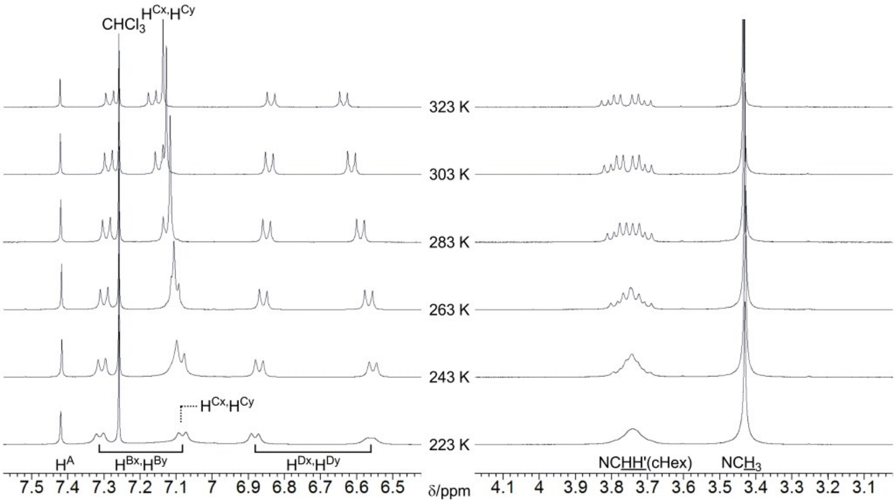


Fig. S2 Partial VT ^{1}H NMR spectra of *rac*-**1**, measured in chloroform-*d* at 223-323 K.

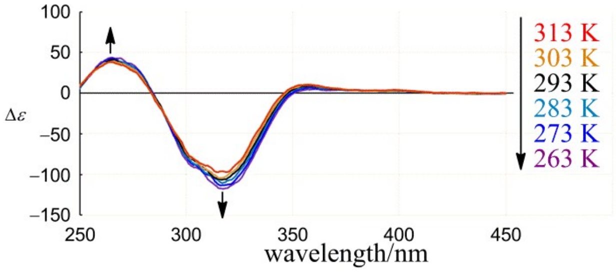


Fig. S3 VT CD spectra of (−)-**1**, measured in dichloromethane at 263-313 K.

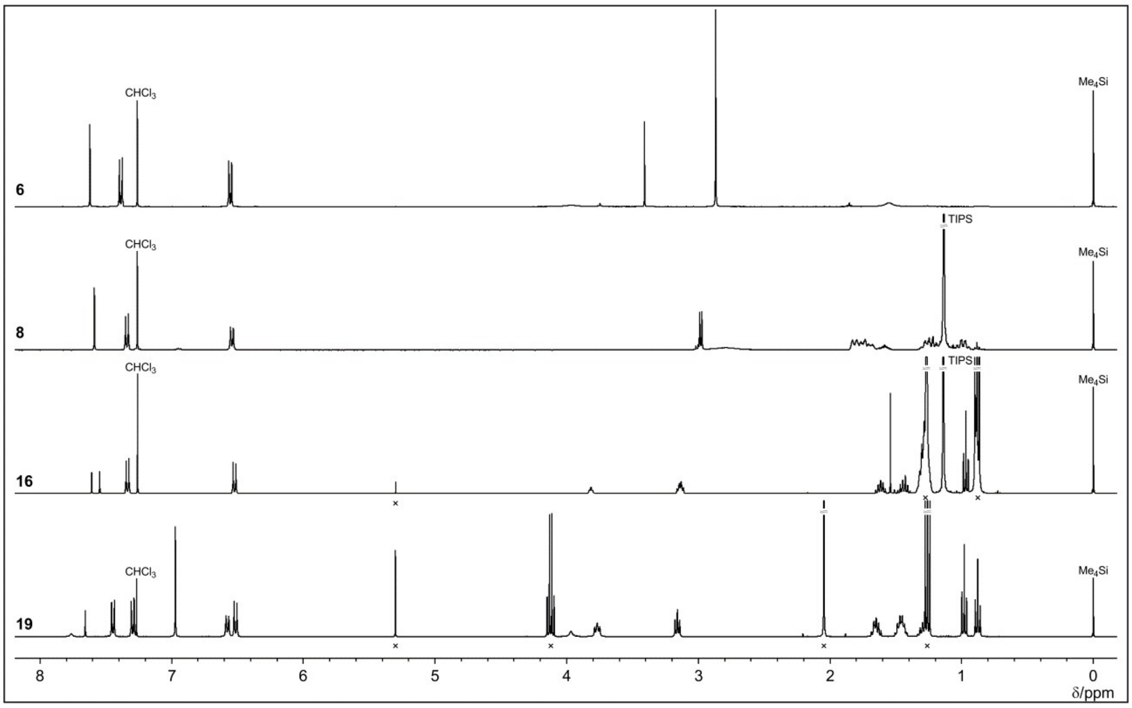


Fig. S4 ^{1}H (400 MHz) NMR spectra of anilines **6**, **8**, **16** and **19**, measured in chloroform-*d* at room temperature. Residual solvents (dichloromethane, ethyl acetate, or hexane) are indicated with a × symbol.

References

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