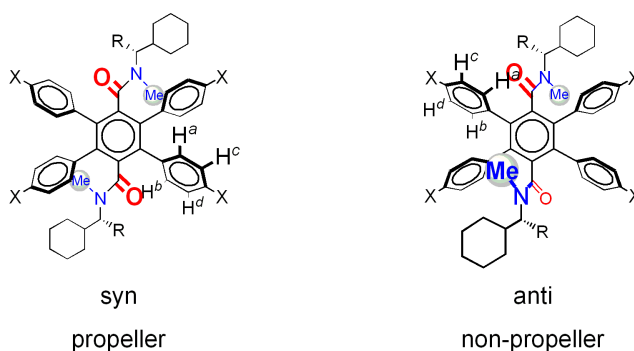


Supplementary Material

Designed Molecular Propellers Based on Tetraaryltetraphthalamide and their Chiroptical Properties Induced by Biased Helicity through Transmission of Point Chirality

by Ryo Katoono, Hidetoshi Kawai, Kenshu Fujiwara and Takanori Suzuki*



[1 : X = OMe, 2 : X = *p*-MeO-C₆H₄, a : R = H, b : R = Me]

Supplementary Figures and Table

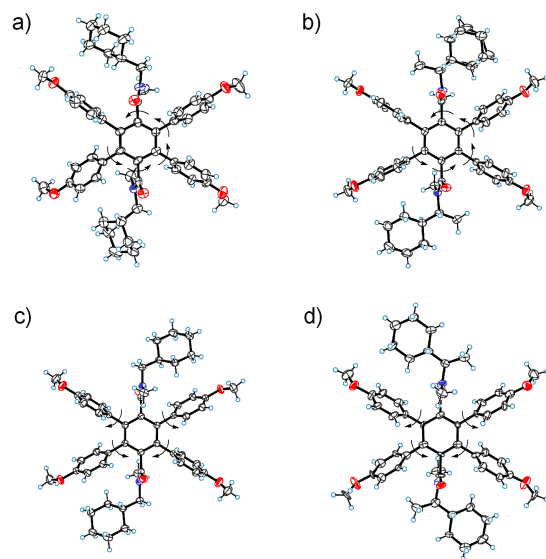


Fig. S1 X-ray structures of a) syn-**1a** ($P-1$, $Z = 2$), b) (R,R)-syn-**1b** ($P1$, $Z = 1$), c) anti-**1a** ($P-1$, $Z = 1$), and d) (R,R)-anti-**1b** ($P1$, $Z = 1$) measured at -120 °C, respectively. One of the aryl blades in a) and b) is almost perpendicular to the central core. The solvated benzene molecule in the crystal in c) is omitted for clarity. Thermal ellipsoids are shown at 50% probability level.

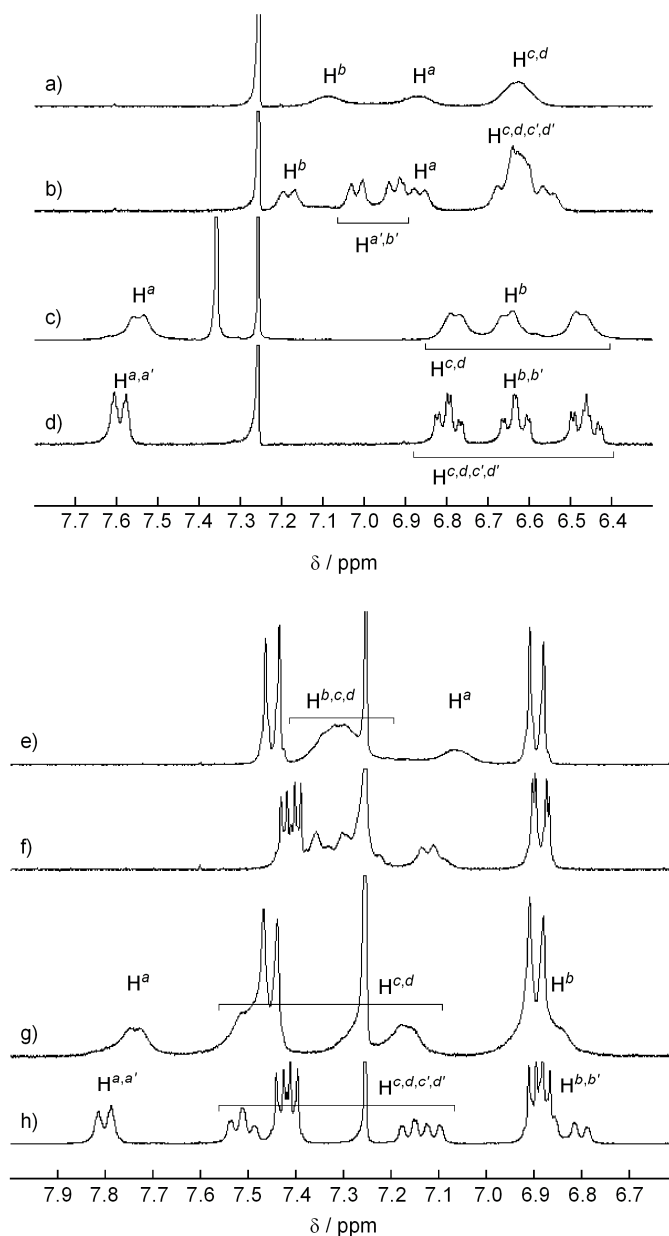


Fig. S2 Aromatic region in ^1H NMR spectra (300 MHz) for a) *syn-1a*, b) *(R,R)*-*syn-1b*, c) *anti-1a*, d) *(R,R)*-*anti-1b*, e) *syn-2a*, f) *(R,R)*-*syn-2b*, g) *anti-2a*, and h) *(R,R)*-*anti-1b* measured in CDCl_3 at room temperature.

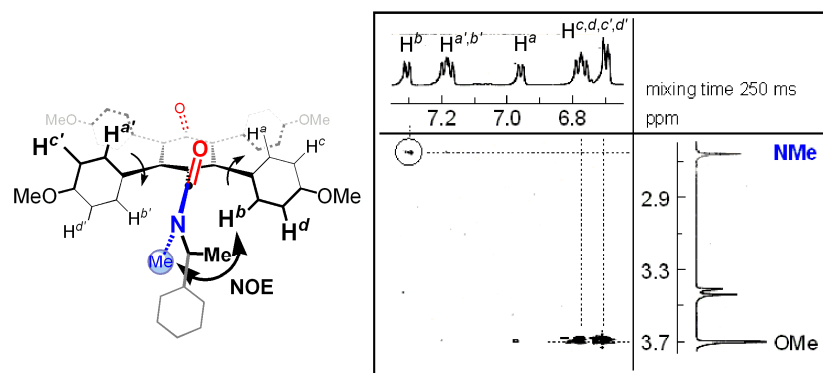


Fig. S3 2D-ROESY spectrum of *(R,R)*-syn-**1b** measured in acetone- d_6 at 223 K (600 MHz).

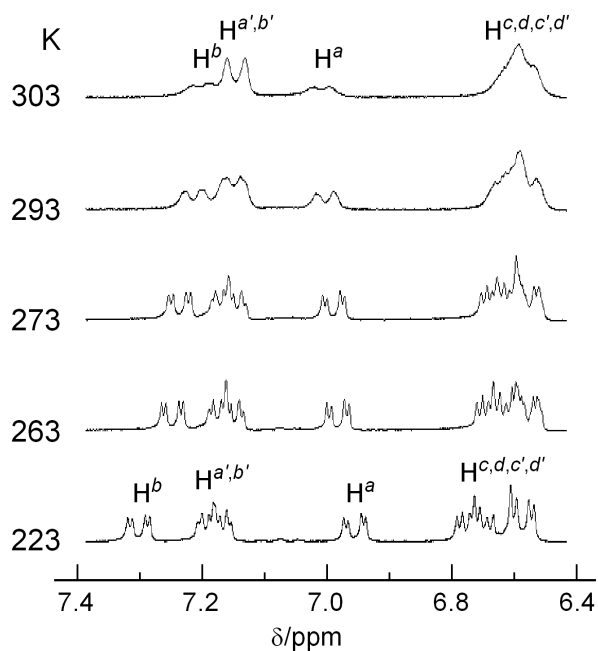


Fig. S4 Aromatic region in 1H NMR spectra (300 MHz) for *(R,R)*-syn-**1b** measured in acetone- d_6 upon raising temperature from 223 to 303 K.

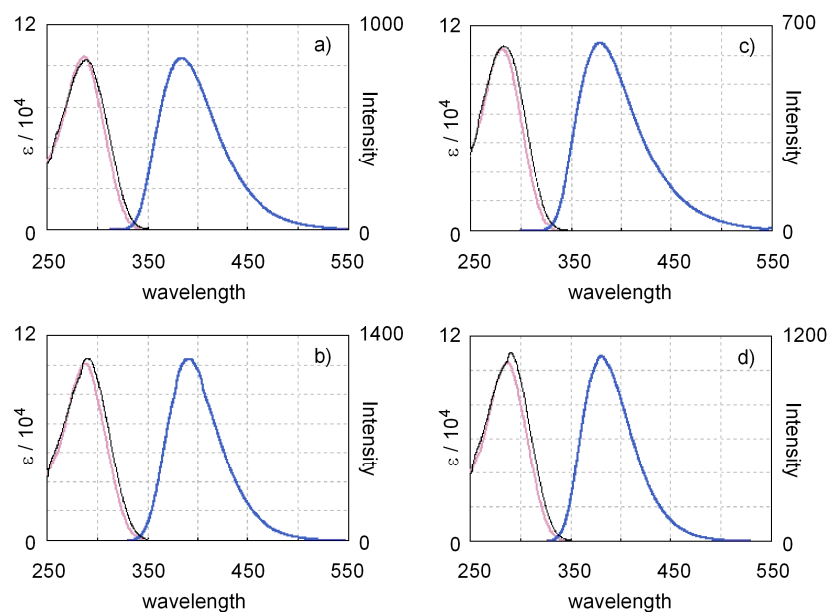


Fig. S5 Absorption (pink), fluorescence emission (blue) and fluorescence excitation (black) spectra of a) *syn-2a*, b) *anti-2a*, c) *(R,R)-syn-2b*, and d) *(R,R)-anti-2b* measured in CH_2Cl_2 at room temperature. The solutions of 10^{-5} M (for UV and CD) and of 10^{-6} M (for fluorescence) were used for the measurement.

Table S1 UV and CD spectral data of **1a/2a** and *(R,R)-5b* in CH_2Cl_2 at room temperature.

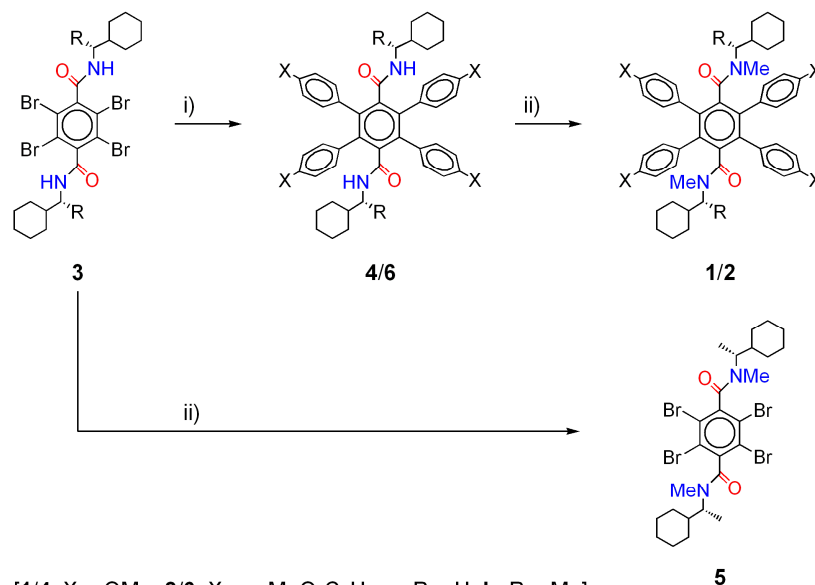
	syn-1a	anti-1a	syn-2a	anti-2a	syn-5b	anti-5b
$\lambda_{\text{max}} / \text{nm}$	256	260	287	289	[250]	[250]
(log ϵ)	(4.62)	(4.60)	(5.00)	(5.01)	(4.16 ^b)	(4.15 ^b)
$\lambda_{\text{max}} / \text{nm}$	-	-	-	-	[250]	[250]
($\Delta\epsilon$)	-	-	-	-	(-3.60 ^c)	(-2.66 ^c)
$\lambda_{\text{max, em}}^{\text{a}} / \text{nm}$	-	-	384	390	-	-

a: Excited at each absorption maximum.

b: The value of log ϵ at 250 nm, it diminishes gradually toward 0 at ca. 310 nm, the end of absorption.

c: The value of $\Delta\epsilon$ at 250 nm, it increases gradually toward 0 at around 280 nm.

Experimental



Reagents i) ArB(OH)₂, Pd(PPh₃)₄, Na₂CO₃ in DME/toluene, ii) NaH, CH₃I in THF.

Preparation of achiral 1a

To a solution of **4a** (160 mg, 0.205 mmol) and iodomethane (380 μ L, 6.10 mmol) in THF (30 mL) was added 60% NaH in oil (50 mg, 1.25 mmol), and the mixture was refluxed for 74 h. The solution was diluted with ethyl acetate, and was washed with 1N HCl aq., sodium thiosulfate aq., and brine. The organic layer was dried over MgSO₄. Chromatographic separation on preparative TLC plates (SiO₂, 1 mm thickness, 10% ethylacetate/CHCl₃) gave 43 mg of syn-**1a** and 86 mg of anti-**1a** in 26% and 52% yields, respectively. Analytical samples of syn-**1a** and anti-**1a** were obtained by recrystallization from ethyl acetate and ethyl acetate/benzene, respectively.

Data of syn-**1a**

mp 280-281 °C; ¹H NMR δ_{H} (300 MHz; CDCl₃; TMS)/ppm 7.16-7.00 (4H, br), 6.94-6.80 (4H, br), 6.73-6.55 (8H, br), 3.708 (12H, s), 2.757 (6H, s), 2.680 (4H, d, *J* = 7.2 Hz), 1.59-1.41 (6H, m), 1.29-1.09 (2H, m), 1.41-0.84 (10H, m), 0.62-0.41 (4H, m); ¹³C NMR δ_{C} (75 MHz; CDCl₃; TMS)/ppm 169.03 (C=O), 158.14 (C_{Ar}-OMe), 138.33 (C_{Ar}-CO), 137.52 (C_{Ar}-Anisyl), 132.29 (C_{Ar}, *meta* position to MeO), 130.68 (C_{Ar}-Core), 130.19 (C_{Ar}, *meta* position to MeO), 112.59 (C_{Ar}, *ortho* position to MeO), 54.91 (MeO), 53.10 (CH₂cHex), 37.89, 35.68, 30.56, 26.31, 25.82 (NMe, cHex×4); IR (KBr) 2921, 2848, 1639, 1629, 1612, 1515, 1247, 1179, 1033, 830, 561 cm⁻¹; FD-MS *m/z* 808 (M⁺, BP), 809 ([M+1]⁺, 60.2%), 810 ([M+2]⁺, 21.0%); UV-Vis λ_{max} (CH₂Cl₂)/nm 256 (log ϵ 4.62); FD-HRMS Calcd. for C₅₂H₆₀N₂O₆ 808.4451, Found 808.4478.

Data of anti-**1a**

mp 282-283 °C; ¹H NMR δ_{H} (300 MHz; CDCl₃; TMS)/ppm 7.65-7.45 (4H, br d), 6.86-6.72 (4H, br d), 6.72-6.56 (4H, br d), 6.55-6.41 (4H, br d), 3.708 (12H, s), 2.611 (4H, d, *J* = 7.5 Hz), 2.338 (6H, s),

1.55-1.30 (6H, m), 1.21-0.79 (12H, m), 0.54-0.31 (4H, m); ^{13}C NMR δ_{C} (75 MHz; CDCl_3 ; TMS)/ppm 169.23 ($\text{C}=\text{O}$), 158.14 ($\text{C}_{\text{Ar}}\text{-OMe}$), 138.72 ($\text{C}_{\text{Ar}}\text{-CO}$), 137.16 ($\text{C}_{\text{Ar}}\text{-Anisyl}$), 132.37, 131.55 (C_{Ar} , *meta* position to $\text{MeO}\times 2$), 130.49 ($\text{C}_{\text{Ar}}\text{-Core}$), 112.75, 112.36 (C_{Ar} , *ortho* position to $\text{MeO}\times 2$), 54.89 (MeO), 52.86 (CH_2cHex), 37.03, 35.46, 30.20, 26.33, 25.77 (NMe , $\text{cHex}\times 4$); IR (KBr) 2930, 2836, 1641, 1609, 1514, 1244, 1175, 1036, 832, 680 cm^{-1} ; FD-MS m/z 808 (M^+ , BP), 809 ($[\text{M}+1]^+$, 36%), 810 ($[\text{M}+2]^+$, 17%); UV-Vis $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 260 ($\log\epsilon$ 4.60); FD-HRMS Calcd. for $\text{C}_{52}\text{H}_{60}\text{N}_2\text{O}_6$ 808.4451, Found 808.4462.

Preparation of (*R,R*)-**1b**

To a solution of (*R,R*)-**4b** (128 mg, 0.158 mmol) and iodomethane (0.30 mL, 4.8 mmol) in THF (23 mL) was added 60% NaH in oil (34 mg, 0.85 mmol), and the mixture was refluxed for 49 h. The solution was diluted with ethyl acetate, and was washed with 1N HCl aq., sodium thiosulfate aq., and brine. The organic layer was dried over MgSO_4 . Chromatographic separation on preparative TLC plates (SiO_2 , 1 mm thickness, 10% ethylacetate/ CHCl_3) gave 55 mg of (*R,R*)-syn-**1b** and 16 mg of (*R,R*)-anti-**1b** in 42% and 12% yields, respectively. An analytical sample of (*R,R*)-syn-**1b** was obtained by slow evaporation from acetone, and that of (*R,R*)-anti-**1b** was obtained by recrystallization from ethyl acetate/hexane, respectively.

Data of (*R,R*)-syn-**1b**

mp > 300 $^{\circ}\text{C}$; ^1H NMR δ_{H} (300 MHz; CDCl_3 ; TMS)/ppm 7.23-7.14 (2H, br d), 7.06-6.98 (2H, br d), 6.97-6.90 (2H, br d), 6.90-6.82 (2H, br d), 6.74-6.49 (8H, br m), 3.854 (2H, dq, $J = 6.6, 10.2$ Hz), 3.689 (6H, s), 3.684 (6H, s), 2.612 (6H, s), 1.63-1.25 (8H, m), 1.07-0.57 (10H, m), 0.423 (6H, d, $J = 6.6$ Hz), 0.31-0.063 (4H, m); ^{13}C NMR δ_{C} (75 MHz; CDCl_3 ; TMS)/ppm 168.91 ($\text{C}=\text{O}$), 158.26, 158.12 ($\text{C}_{\text{Ar}}\text{-OMe}\times 2$), 138.44 ($\text{C}_{\text{Ar}}\text{-CO}$), 137.64, 137.40 ($\text{C}_{\text{Ar}}\text{-Anisyl}\times 2$), 132.41, 132.28, 130.72, 130.57, 130.12 (C_{Ar} , *meta* position to $\text{MeO}\times 4$, $\text{C}_{\text{Ar}}\text{-Core}\times 2$), 115.27, 112.78, 112.63, 112.47 (C_{Ar} , *ortho* position to $\text{MeO}\times 4$), 55.06, 54.85 ($\text{MeO}\times 2$), 52.23 (CHMecHex), 39.53, 30.48, 29.71, 28.68, 26.16, 26.09, 25.70 (NMe , $\text{cHex}\times 6$), 14.31 (CHMecHex); IR (KBr) 2919, 2847, 1614, 1517, 1247, 1177, 1107, 1033, 816, 554 cm^{-1} ; FD-MS m/z 836 (M^+ , BP), 837 ($[\text{M}+1]^+$, 61%), 838 ($[\text{M}+2]^+$, 19%); UV-Vis $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 249sh ($\log\epsilon$ 4.54); CD(CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\Delta\epsilon$) 254 (-4.06), 291 (-7.67); $[\alpha]_{\text{D}}^{23}$ -69.9 (c 0.12 in CHCl_3); FD-HRMS Calcd. for $\text{C}_{54}\text{H}_{64}\text{N}_2\text{O}_6$ 836.4764, Found 836.4736.

Data of (*R,R*)-anti-**1b**

mp > 300 $^{\circ}\text{C}$; ^1H NMR δ_{H} (300 MHz; CDCl_3 ; TMS)/ppm 7.589 (4H, d, $J = 8.4$ Hz), 6.814 (2H, dd, $J = 2.4, 8.4$ Hz), 6.787 (2H, dd, $J = 2.4, 8.4$ Hz), 6.655 (2H, dd, $J = 2.4, 8.4$ Hz), 6.625 (2H, dd, $J = 2.4, 8.4$ Hz), 6.488 (2H, dd, $J = 2.4, 8.4$ Hz), 6.451 (2H, dd, $J = 2.4, 8.4$ Hz), 3.881 (2H, dq, $J = 6.6, 10.2$ Hz), 3.699 (6H, s), 3.686 (6H, s), 2.118 (6H, s), 1.55-1.35 (6H, m), 1.192 (2H, d, $J = 13.2$ Hz), 0.99-0.88 (4H, m), 0.81-0.57 (6H, m), 0.180 (6H, d, $J = 6.6$ Hz), 0.12- -0.1 (4H, m); ^{13}C NMR δ_{C} (75 MHz; CDCl_3 ; TMS)/ppm 169.28 ($\text{C}=\text{O}$), 158.25, 158.20 ($\text{C}_{\text{Ar}}\text{-OMe}\times 2$), 138.95 ($\text{C}_{\text{Ar}}\text{-CO}$), 137.22, 136.94 ($\text{C}_{\text{Ar}}\text{-Anisyl}\times 2$), 132.70, 132.28, 131.68, 131.63, 130.58, 130.40 (C_{Ar} , *meta* position to $\text{MeO}\times 4$, $\text{C}_{\text{Ar}}\text{-Core}\times 2$), 113.19, 112.77, 112.54, 112.16 (C_{Ar} , *ortho* position to $\text{MeO}\times 4$), 55.14, 54.85 ($\text{MeO}\times 2$), 52.13 (CHMecHex), 39.39, 29.74, 29.41,

28.27, 26.15, 26.09, 25.63 (NMe, cHex \times 6), 14.48 (CHMecHex); IR (KBr) 2923, 2850, 1638, 1611, 1516, 1245, 1177, 1104, 1039, 830, 555 cm⁻¹; FD-MS m/z 836 (M⁺, BP), 837 ([M+1]⁺, 65%); UV-Vis λ_{\max} (CH₂Cl₂)/nm 259 (log ϵ 4.59); CD(CH₂Cl₂) λ_{\max} /nm ($\Delta\epsilon$) 261 (-2.56), 291 (-0.608); [α]_D²³ +3.75 (*c* 0.057 in CHCl₃); FD-HRMS Calcd. for C₅₄H₆₄N₂O₆ 836.4764, Found 836.4758.

Preparation of achiral 2a

To a solution of **6a** (109 mg, 0.100 mmol) and iodomethane (380 μ L, 6.10 mmol) in THF (20 mL) was added 60% NaH in oil (54 mg, 1.35 mmol), and the mixture was refluxed for 88 h. The solution was diluted with ethyl acetate, and was washed with 1N HCl aq., sodium thiosulfate aq., and brine. The organic layer was dried over MgSO₄. Chromatographic separation on silica gel (CHCl₃-ethyl acetate/CHCl₃) and preparative TLC plates (SiO₂, 1 mm thickness, 10% ethylacetate/CHCl₃) gave 50 mg of syn-**2a** and 36 mg of anti-**2a** in 45% and 32% yields. Analytical samples of both isomers were obtained by reprecipitation with ethyl acetate and hexane.

Data of syn-**2a**

mp > 300 °C; ¹H NMR δ_{H} (300 MHz; CDCl₃; TMS)/ppm 7.451 (8H, d, *J* = 8.7 Hz), 7.40-7.26 (12H, br), 7.12-6.99 (4H, br), 6.900 (8H, d, *J* = 8.7 Hz), 3.815 (12H, s), 2.842 (6H, s), 2.696 (4H, d, *J* = 6.9 Hz), 1.43-1.14 (8H, m), 0.96 (4H, d, *J* = 11.7 Hz), 0.93-0.74 (6H, m), 0.58-0.42 (4H, m); ¹³C NMR δ_{C} (75 MHz; CDCl₃; TMS)/ppm 168.82 (C=O), 158.98 (C_{Ar}-OMe), 138.75, 137.07, 137.67, 136.54, 133.08, 131.55, 129.65, 127.83, 125.89, 124.58 (C_{Ar} \times 10), 114.02 (C_{Ar}, *ortho* position to MeO), 55.29 (MeO), 53.09 (CH₂cHex), 37.87, 35.49, 30.53, 26.25, 25.74 (NMe, cHex \times 4); IR (KBr) 2921, 2847, 1632, 1610, 1500, 1247, 1178, 1108, 1039, 821, 621 cm⁻¹; FD-MS m/z 1112 (M⁺, BP), 1113 ([M+1]⁺, 87%), 1114 ([M+2]⁺, 37%), 556 (M²⁺, 31%); UV-Vis λ_{\max} (CH₂Cl₂)/nm 287 (log ϵ 5.00); Fluorescence $\lambda_{\max, \text{em}}$ (CH₂Cl₂, excited at 287 nm) 384 nm; FD-HRMS Calcd. for C₇₆H₇₆N₂O₆ 1112.5703, Found 1112.5730.

Data of anti-**2a**

mp > 300 °C; ¹H NMR δ_{H} (300 MHz; CDCl₃; TMS)/ppm 7.84-7.65 (4H, br), 7.59-7.40 (4H, br), 7.455 (8H, d, *J* = 8.7 Hz), 7.23-7.09 (4H, br), 7.01-6.79 (4H, br), 6.900 (8H, d, *J* = 8.7 Hz), 3.815 (12H, s), 2.624 (4H, d, *J* = 7.2 Hz), 2.425 (6H, s), 1.37-1.06 (8H, m), 0.93-0.66 (10H, m), 0.50-0.30 (4H, m); ¹³C NMR δ_{C} (75 MHz; CDCl₃; TMS)/ppm 168.97 (C=O), 159.00 (C_{Ar}-OMe), 138.69, 138.43, 137.40, 136.31, 133.02, 132.02-130.45, 127.81, 125.29-124.24 (C_{Ar} \times 8), 114.03 (C_{Ar}, *ortho* position to MeO), 55.31 (MeO), 52.72 (CH₂cHex), 36.92, 35.27, 30.13, 26.24, 25.71 (NMe, cHex \times 4); IR (KBr) 2920, 2848, 1632, 1609, 1500, 1247, 1178, 1108, 1038, 823, 617 cm⁻¹; FD-MS m/z 1112 (M⁺, BP), 1113 ([M+1]⁺, 85%), 1114 ([M+2]⁺, 40%), 556 (M²⁺, 21%); UV-Vis λ_{\max} (CH₂Cl₂)/nm 289 (log ϵ 5.01); Fluorescence $\lambda_{\max, \text{em}}$ (CH₂Cl₂, excited at 289 nm) 390 nm; FD-HRMS Calcd. for C₇₆H₇₆N₂O₆ 1112.5703, Found 1112.5701.

Preparation of (R,R)-**2b**

To a solution of (R,R)-**6b** (95 mg, 0.085 mmol), iodomethane (160 μ L, 2.56 mmol) in THF (20 mL) was added 60% NaH in oil, and the mixture was refluxed for 52 h. The solution was diluted with ethyl acetate, and was washed with 1N HCl aq., sodium thiosulfate aq., and brine. The organic layer was dried over

MgSO₄. Chromatographic separation on preparative TLC plates (SiO₂, 1 mm thickness, 10% ethyl acetate/CHCl₃) gave 39 mg of (*R,R*)-syn-**2b** and 19 mg of (*R,R*)-anti-**2b** in 40% and 20% yields, respectively.

Data of (*R,R*)-syn-**2b**

mp > 300 °C; ¹H NMR δ_H(300 MHz; CDCl₃; TMS)/ppm 7.419 (4H, d, *J* = 8.7 Hz), 7.406 (4H, d, *J* = 8.7 Hz), 7.38-7.19 (12H, br m), 7.19-7.04 (4H, br), 6.894 (4H, d, *J* = 8.7 Hz), 6.888 (4H, d, *J* = 8.7 Hz), 3.94-3.77 (2H, m), 3.890 (12H, s), 2.701 (6H, s), 1.62-1.22 (6H, br m), 1.17-0.52 (12H, br m), 0.354 (6H, d, *J* = 6.6 Hz), 0.43-0.28 (2H, m), 0.25-0.07 (2H, m); ¹³C NMR δ_C(75 MHz; CDCl₃; TMS)/ppm 168.67 (C=O), 159.00, 158.94 (C_{Ar}-OMe×2), 138.16 (C_{Ar}-CO), 138.94, 138.89, 137.69, 137.44, 136.39, 136.33, 133.37, 133.20, 131.72, 131.54, 130.06, 129.68, 127.92, 127.83, 126.06, 124.60 (C_{Ar}×18), 114.04, 114.01 (C_{Ar}, *ortho* position to MeO×2), 55.32, 55.29 (MeO×2), 52.36 (CHMecHex), 39.50, 30.61, 29.69, 28.69, 26.08, 25.96, 25.71 (NMe, cHex×6), 14.15 (CHMecHex); IR (KBr) 2927, 2848, 1624, 1611, 1500, 1247, 1177, 1109, 1039, 813, 617 cm⁻¹; FD-MS *m/z* 1140 (M⁺, BP), 1141 ([M+1]⁺, 82%), 1142 ([M+2]⁺, 39%), 570 (M²⁺, 22%); UV-Vis λ_{max}(CH₂Cl₂)/nm 282 (logε 5.02); Fluorescence λ_{max,em}(CH₂Cl₂, excited at 282 nm) 379 nm; CD(CH₂Cl₂) λ_{max}/nm (Δε) 286 (-10.0), 312 (+1.04); [α]_D²⁴ -49.4 (*c* 0.050 in CHCl₃); FD-HRMS Calcd. for C₇₈H₈₀N₂O₆ 1140.6016, Found 1140.6033.

Data of (*R,R*)-anti-**2b**

mp > 300 °C; ¹H NMR δ_H(300 MHz; CDCl₃; TMS)/ppm 7.86-7.72 (4H, br d), 7.56-7.50 (2H, br d), 7.53-7.47 (2H, br d), 7.429 (4H, d, *J* = 8.7 Hz), 7.414 (4H, d, *J* = 8.7 Hz), 7.20-7.14 (2H, br d), 7.14-7.06 (2H, br d), 6.902 (4H, d, *J* = 8.7 Hz), 6.886 (4H, d, *J* = 8.7 Hz), 6.92-6.85 (2H, br d), 6.83-6.76 (2H, br d), 3.912 (2H, dq, *J* = 6.6, 9.9 Hz), 3.811 (12H, s), 2.197 (6H, s), 1.59-1.20 (6H, m), 1.00-0.42 (12H, m), 0.20-0.03 (4H, m), 0.127 (6H, d, *J* = 6.6 Hz); ¹³C NMR δ_C(75 MHz; CDCl₃; TMS)/ppm 168.98 (C=O), 159.06, 158.94 (C_{Ar}-OMe×2), 138.93, 138.88, 138.75, 137.43, 137.11, 136.37, 136.21, 133.22, 132.09, 131.70, 130.95, 130.88, 127.86, 127.83, 125.58, 125.52, 125.28, 125.18 (C_{Ar}×19), 114.09, 113.99 (C_{Ar}, *ortho* position to MeO×2), 55.32, 55.28 (MeO×2), 52.19 (CHMecHex), 39.41, 29.74, 29.49, 28.18, 26.02, 25.96, 25.61 (NMe, cHex×6), 14.23 (CHMecHex); IR (KBr) 2930, 2849, 1630, 1610, 1500, 1247, 1178, 1105, 1040, 822, 620 cm⁻¹; FD-MS *m/z* 1140 (M⁺, BP), 1141 ([M+1]⁺, 86%), 1142 ([M+2]⁺, 39%), 570 (M²⁺, 20%); UV-Vis λ_{max}(CH₂Cl₂)/nm 287 (logε 5.02); Fluorescence λ_{max,em}(CH₂Cl₂, excited at 287 nm) 381 nm; CD(CH₂Cl₂) λ_{max}/nm (Δε) 256 (-1.38), 272 (+2.11), 286 (-1.18), 304 (+1.43); [α]_D²³ -1.71 (*c* 0.041 in CHCl₃); FD-HRMS Calcd. for C₇₈H₈₀N₂O₆ 1140.6016, Found 1140.5992.

Preparation of achiral **3a**

A mixture of 2,3,5,6-tetrabromoterephthalic acid (3.20 g, 6.64 mmol), benzyltriethylammonium chloride (36 mg, 0.16 mmol) and thionyl chloride (25 mL) was refluxed for 3.5 h under an argon atmosphere. After removal of thionyl chloride by evaporation, the remaining solid was dissolved in THF (100 mL). To a solution of cyclohexylmethylamine (1.73 mL, 13.3 mmol) and triethylamine (1.86 mL, 13.4 mmol) in THF (10 mL) was added the THF solution of the acid chloride via cannula. The mixture was stirred at room temperature for 22 h and then refluxed for 1 h. After pouring the mixture into water, white

precipitates were collected by filtration to give 4.41 g of **3a** as a white solid in 99% yield.

mp > 300 °C; ¹H NMR δ_H(300 MHz; DMSO-*d*₆; TMS)/ppm 8.67-8.46 (2H, m), 3.13-2.97 (4H, m), 1.87-0.70 (22H, br. m). The low resolution of the spectrum is due to low solubility in organic solvents.; IR (KBr) 3276, 3088, 2919, 2849, 1664, 1642, 1563, 1448, 1328, 1304, 1270, 690, 525 cm⁻¹; FD-MS *m/z* 83 ([C₆H₁₁]⁺, 80%), 670 ([M+2]⁺, 71%), 672 ([M+4]⁺, BP), 674 ([M+6]⁺, 72%); FD-HRMS Calcd. for C₂₂H₂₈Br₄N₂O₂ 667.8884, Found 667.8884.

Preparation of (*R,R*)-**3b**

A mixture of 2,3,5,6-tetrabromoterephthalic acid (3.16 g, 6.56 mmol), benzyltriethylammonium chloride (36 mg, 0.16 mmol) and thionyl chloride (25 mL) was refluxed for 2.5 h under an argon atmosphere. After removal of thionyl chloride by evaporation, the remaining solid was dissolved in THF (60 mL). To a solution of (*R*)-1-cyclohexylethylamine (1.95 mL, 13.1 mmol) and triethylamine (1.90 mL, 13.7 mmol) in THF (10 mL) was added the THF solution of the acid chloride via cannula. The mixture was stirred at 45 °C for 20.5 h. After removal of the solvent, the remaining solid was suspended in water and filtrated to give 4.40 g of (*R,R*)-**3b** as a white solid in 96% yield.

mp > 300 °C; ¹H NMR δ_H(300 MHz; DMSO-*d*₆; TMS)/ppm 8.422 (2H, d, *J* = 8.4 Hz), 3.83-3.64 (2H, m), 1.91-0.91 (24H, m), 1.091 (6H, d, *J* = 6.6 Hz); ¹³C NMR δ_C(75 MHz; DMSO-*d*₆; TMS)/ppm 164.75 (C=O), 143.71 (C_{Ar}-CO), 123.31, 122.87 (C_{Ar}-Br×2), 49.90 (CHMecHex), 42.54, 29.23, 29.13, 26.50, 26.20, 26.15, (cHex×6), 17.35 (CHMecHex); IR (KBr) 3426, 3256, 3071, 2923, 2852, 1649, 1552, 1448, 1328, 1308, 1262, 535 cm⁻¹; FD-MS *m/z* 83 ([C₆H₁₁]⁺, BP), 698 ([M+2]⁺, 33%), 700 ([M+4]⁺, 48%), 702 ([M+6]⁺, 30%); UV-Vis λ_{250nm}(CH₂Cl₂) logε 4.07; CD(CH₂Cl₂) λ₂₅₀ Δε -2.04; [α]_D²¹ -9.12 (*c* 0.024 in CHCl₃); FD-HRMS Calcd. for C₂₄H₃₂Br₄N₂O₂ 695.9197, Found 695.9179.

Preparation of achiral **4a**

To a suspension of **3a** (670 mg, 1.00 mmol), 4-methoxyboronic acid (912 mg, 6.00 mmol) and 2M Na₂CO₃ aq. (12 mL, 24.0 mmol) in dimethoxyethane (DME) (40 mL) and toluene (10 mL) was added Pd(PPh₃)₄ (240 mg, 0.208 mmol) under an argon atmosphere, and the mixture was refluxed for 68 h. After removal of precipitates by filtration with celite and evaporation of the solvent, the remaining solid was dissolved in CHCl₃ and washed with 5% NaOH aq., 10% HCl aq. and satd. NaHCO₃ aq. The organic layer was dried over MgSO₄. Chromatographic separation on silica gel (CHCl₃) gave 695 mg of **4a** as a white solid in 89% yield. An analytical sample was obtained by gel permeation chromatography (GPC, CHCl₃, detected by UV 254 nm) and recrystallization from ethyl acetate.

mp 279-280 °C; ¹H NMR δ_H(300 MHz; CDCl₃; TMS)/ppm 7.046 (8H, d, *J* = 8.4 Hz), 6.647 (8H, d, *J* = 8.4 Hz), 5.082 (2H, t, *J* = 6.3 Hz), 3.702 (12H, s), 1.57-1.36 (6H, br m), 1.17-0.74 (12H, br m), 0.56-0.33 (4H, br m); ¹³C NMR δ_C(75 MHz; CDCl₃; TMS)/ppm 168.46 (C=O), 158.17 (C_{Ar}-OMe), 139.63 (C_{Ar}-CO), 137.85 (C_{Ar}-Anisyl), 131.59, 130.62 (C_{Ar}, *meta* position to MeO, C_{Ar}-Core), 112.73 (C_{Ar}, *ortho* position to MeO), 54.95 (MeO), 45.23 (CH₂cHex), 37.33, 30.34, 26.21, 25.70 (cHex×4); IR (KBr) 3371, 2920, 2850, 1658, 1639, 1612, 1517, 1247, 1178, 1107, 1033, 835, 810, 566, 541 cm⁻¹; FD-MS *m/z* 780 (M⁺, BP), 781

($[M+1]^+$, 47%), 782 ($[M+2]^+$, 17%); UV-Vis $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 260 (log ϵ 4.60); FD-HRMS Calcd. for $\text{C}_{50}\text{H}_{56}\text{N}_2\text{O}_6$ 780.4138, Found 780.4131.

Preparation of (*R,R*)-**4b**

To a suspension of (*R,R*)-**3b** (700 mg, 1.00 mmol), 4-methoxyboronic acid (915 mg, 6.00 mmol) and 2M Na_2CO_3 aq. (12 mL, 24.0 mmol) in DME (50 mL) was added $\text{Pd}(\text{PPh}_3)_4$ (230 mg, 0.200 mmol) under an argon atmosphere, and the mixture was refluxed for 66 h. After removal of precipitates by filtration with celite and evaporation of the solvent, the remaining solid was dissolved in CHCl_3 and washed with 5% NaOH aq., 10% HCl aq. and satd. NaHCO_3 aq. The organic layer was dried over MgSO_4 . Chromatographic separation on silica gel (CHCl_3) gave 734 mg of (*R,R*)-**4b** as a white solid in 91% yield. An analytical sample was obtained by reprecipitation from ethyl acetate and hexane.

mp 286-287 °C; ^1H NMR δ_{H} (300 MHz; CDCl_3 ; TMS)/ppm 7.18-6.95 (8H, br), 6.651 (8H, d, $J = 8.7$ Hz), 4.756 (2H, d, $J = 9.3$ Hz), 3.710 (12H, s), 3.41-3.28 (2H, m), 1.51-1.36 (6H, br m), 1.21-0.68 (12H, br m), 0.43-0.24 (4H, br m), 0.351 (6H, d, $J = 6.6$ Hz); ^{13}C NMR δ_{C} (75 MHz; CDCl_3 ; TMS)/ppm 167.59 ($\text{C}=\text{O}$), 158.25 ($\text{C}_{\text{Ar}}\text{-OMe}$), 139.81 ($\text{C}_{\text{Ar}}\text{-CO}$), 137.74 ($\text{C}_{\text{Ar}}\text{-Anisyl}$), 134.35, 131.82, 130.60 (C_{Ar} , meta position to MeO, $\text{C}_{\text{Ar}}\text{-Core}$), 112.74, 112.67 (C_{Ar} , ortho position to MeO $\times 2$), 55.00 (MeO), 49.02 (CHMecHex), 42.40, 28.56, 27.80, 26.12, 25.99 ($\text{cHex}\times 6$), 17.09 (CHMecHex); IR (KBr) 3435, 3357, 2923, 2848, 1632, 1612, 1516, 1247, 1179, 1106, 1033, 828, 583, 540 cm^{-1} ; FD-MS m/z 808 (M^+ , BP), 809 ($[M+1]^+$, 58%), 810 ($[M+2]^+$, 19%); UV-Vis $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 258 (log ϵ 4.53); CD(CH_2Cl_2) λ_{\max}/nm ($\Delta\epsilon$) 256 (-3.68), 292 (-1.64); $[\alpha]_{\text{D}}^{23}$ -10.9 (c 0.072 in CHCl_3); FD-HRMS Calcd. for $\text{C}_{52}\text{H}_{60}\text{N}_2\text{O}_6$ 808.4451, Found 808.4454.

Preparation of (*R,R*)-**5b**

To a solution of (*R,R*)-**3b** (251 mg, 0.359 mmol) and iodomethane (600 μL , 9.63 mmol) in DMF (6 mL) was added 60% NaH in oil (65 mg, 1.63 mmol), and the mixture was stirred at room temperature for 24.5 h. The mixture was diluted with ethyl acetate, and washed with 1N HCl aq., sodium thiosulfate aq., and brine. The organic layer was separated, and then dried over MgSO_4 . Chromatographic separation on silica gel (CHCl_3) and preparative TLC plates (SiO_2 , 1 mm thickness, CHCl_3) gave 120 mg of (*R,R*)-syn-**5b** and 76 mg of (*R,R*)-anti-**5b** in 46% and 29% yields.

Data of (*R,R*)-syn-**5b**

mp 219-220 °C; ^1H NMR δ_{H} (300 MHz; CDCl_3 ; TMS)/ppm 4.521 (2H, dq, $J = 6.6, 10.2$ Hz), 2.679 (6H, s), 1.96-1.57 (10H, br m), 1.57-1.37 (2H, br m), 1.37-0.94 (10H, br m), 1.229 (6H, d, $J = 6.6$ Hz); ^{13}C NMR δ_{C} (75 MHz; CDCl_3 ; TMS)/ppm 166.24 ($\text{C}=\text{O}$), 142.54 ($\text{C}_{\text{Ar}}\text{-CO}$), 122.96, 122.49 ($\text{C}_{\text{Ar}}\text{-Br}\times 2$), 53.84 (CHMecHex), 40.29, 30.20, 30.00, 29.46, 26.14, 25.98, 25.81 (NMe , $\text{cHex}\times 6$), 14.94 (CHMecHex); IR (KBr) 2925, 2850, 1644, 1482, 1445, 1408, 1305, 1240, 1130, 537 cm^{-1} ; FD-MS m/z 83 ($[\text{C}_6\text{H}_{11}]^+$, 17%), 726 ($[M+2]^+$, 72%), 728 ($[M+4]^+$, BP), 730 ($[M+6]^+$, 69%); UV-Vis $\lambda_{250\text{nm}}(\text{CH}_2\text{Cl}_2)$ log ϵ 4.16; CD(CH_2Cl_2) λ_{250} $\Delta\epsilon$ -3.60; $[\alpha]_{\text{D}}^{22}$ -37.8 (c 0.050 in CHCl_3); FD-HRMS Calcd. for $\text{C}_{26}\text{H}_{36}\text{Br}_4\text{N}_2\text{O}_2$ 723.9510, Found 723.9534.

Data of (*R,R*)-anti-**5b**

mp 257-258 °C; ^1H NMR δ_{H} (300 MHz; CDCl_3 ; TMS)/ppm 4.510 (2H, dq, $J = 6.6, 10.2$ Hz), 2.667 (6H, s), 1.95-1.60 (10H, br m), 1.54-1.37 (2H, br m), 1.36-0.96 (10H, br m), 1.227 (6H, d, $J = 6.6$ Hz); ^{13}C NMR δ_{C} (75 MHz; CDCl_3 ; TMS)/ppm 166.60 ($\text{C}=\text{O}$), 142.56 ($\text{C}_{\text{Ar}}-\text{CO}$), 122.99, 122.78 ($\text{C}_{\text{Ar}}-\text{Br}\times 2$), 53.94 (CHMeHex), 40.28, 30.20, 30.01, 29.60, 26.14, 25.99, 25.81 (NMe, $\text{cHex}\times 6$), 15.00 (CHMeHex); IR (KBr) 2921, 2850, 1647, 1482, 1446, 1411, 1320, 1242, 1132, 731, 532 cm^{-1} ; FD-MS m/z 83 ($[\text{C}_6\text{H}_{11}]^+$, 19%), 726 ($[\text{M}+2]^+$, 73%), 728 ($[\text{M}+4]^+$, BP), 730 ($[\text{M}+6]^+$, 70%); UV-Vis $\lambda_{250\text{nm}}(\text{CH}_2\text{Cl}_2)$ $\log\epsilon$ 4.15; $\text{CD}(\text{CH}_2\text{Cl}_2)$ λ_{250} $\Delta\epsilon$ -2.66; $[\alpha]_{\text{D}}^{21}$ -32.3 (c 0.041 in CHCl_3); FD-HRMS Calcd. for $\text{C}_{26}\text{H}_{36}\text{Br}_4\text{N}_2\text{O}_2$ 723.9510, Found 723.9482.

Preparation of achiral **6a**

To a suspension of **3a** (680 mg, 1.01 mmol), 4'-methoxybiphenyl-4-yl boroxin (1.26 g, 2.00 mmol) and 2M Na_2CO_3 aq. (12 mL, 24.0 mmol) in DME (40 mL), toluene (20 mL) and ethanol (4 mL) was added $\text{Pd}(\text{PPh}_3)_4$ (230 mg, 0.200 mmol) under an argon atmosphere, and the mixture was refluxed for 76 h. After removal of precipitates by filtration with celite and evaporation of the solvent, the remaining solid was dissolved in CHCl_3 and washed with 5% NaOH aq., 10% HCl aq. and satd. NaHCO_3 aq. The organic layer was dried over MgSO_4 . Chromatographic separation on silica gel (CHCl_3) gave 109 mg of **6a** as a white solid in 9.9% yield. An analytical sample was obtained by GPC (CHCl_3 , detected by UV 254 nm) separation.

mp > 300 °C; ^1H NMR δ_{H} (300 MHz; CDCl_3 ; TMS)/ppm 7.460 (8H, d, $J = 8.7$ Hz), 7.343 (8H, d, $J = 8.4$ Hz), 7.242 (8H, d, $J = 8.4$ Hz), 6.910 (8H, d, $J = 8.7$ Hz), 3.819 (12H, s), 2.583 (4H, t, $J = 6.3$ Hz), 1.44-1.30 (6H, br m), 1.17-1.02 (4H, br m), 0.91-0.72 (8H, br m), 0.49-0.32 (4H, br m); ^{13}C NMR δ_{C} (75 MHz; CDCl_3 ; TMS)/ppm 168.18 ($\text{C}=\text{O}$), 159.07 ($\text{C}_{\text{Ar}}-\text{OMe}$), 139.40 ($\text{C}_{\text{Ar}}-\text{CO}$), 138.86, 138.08, 136.51, 133.10, 130.89, 127.88, 125.42 ($\text{C}_{\text{Ar}}\times 7$), 114.08 (C_{Ar} , *ortho* position to MeO), 55.31 (MeO), 45.61 (CH_2cHex), 37.19, 30.33, 26.12, 25.59 ($\text{cHex}\times 4$); IR (KBr) 3358, 2921, 2850, 1665, 1659, 1639, 1633, 1608, 1501, 1249, 1178, 1039, 826, 808, 623 cm^{-1} ; FD-MS m/z 1084 (M^+ , BP), 1085 ($[\text{M}+1]^+$, 81%), 1086 ($[\text{M}+2]^+$, 32%); UV-Vis $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 287 ($\log\epsilon$ 4.99); Fluorescence $\lambda_{\text{max,em}}(\text{CH}_2\text{Cl}_2)$, excited at 287 nm) 389 nm; FD-HRMS Calcd. for $\text{C}_{74}\text{H}_{72}\text{N}_2\text{O}_6$ 1084.5390, Found 1084.5415.

Preparation of (*R,R*)-**6b**

To a suspension of (*R,R*)-**3b** (700 mg, 1.00 mmol), 4'-methoxybiphenyl-4-yl boroxin (1.26 g, 2.00 mmol) and 2M Na_2CO_3 aq. (12 mL, 24.0 mmol) in DME (50 mL) was added $\text{Pd}(\text{PPh}_3)_4$ (220 mg, 0.190 mmol) under an argon atmosphere, and the mixture was refluxed for 89 h. After removal of precipitates by filtration with celite and evaporation of the solvent, the remaining solid was dissolved in CHCl_3 and washed with 5% NaOH aq., 10% HCl aq. and satd. NaHCO_3 aq. The organic layer was dried over MgSO_4 . Chromatographic separation on silica gel (CHCl_3) and reprecipitation from benzene and hexane gave 195 mg of (*R,R*)-**6b** as a white solid in 18% yield. An analytical sample was obtained by GPC (CHCl_3 , detected by UV 254 nm) separation.

mp > 300 °C; ^1H NMR δ_{H} (300 MHz; CDCl_3 ; TMS)/ppm 7.441 (8H, d, $J = 8.7$ Hz), 7.40-7.22 (16H, br

m), 6.903 (8H, d, $J = 8.7$ Hz), 4.843 (2H, d, $J = 9.0$ Hz), 3.813 (12H, s), 3.45-3.27 (2H, m), 1.43-1.23 (6H, br d), 1.18-1.08 (2H, br d), 1.08-0.96 (2H, br d), 0.94-0.63 (8H, br m), 0.42-0.18 (4H, br m), 0.297 (6H, d, $J = 6.6$ Hz); ^{13}C NMR δ_{C} (75 MHz; CDCl_3 ; TMS)/ppm 167.31 ($\underline{\text{C}}=\text{O}$), 159.03 ($\underline{\text{C}}_{\text{Ar}}\text{-OMe}$), 139.58 ($\underline{\text{C}}_{\text{Ar}}\text{-CO}$), 138.94, 137.90, 136.42, 133.19, 131.16, 127.85, 125.41 ($\underline{\text{C}}_{\text{Ar}}\times 7$), 114.06 ($\underline{\text{C}}_{\text{Ar}}$, *ortho* position to MeO), 55.29 ($\underline{\text{MeO}}$), 49.17 ($\underline{\text{CHMecHex}}$), 42.40, 28.70, 27.73, 26.08, 25.91 ($\underline{\text{cHex}}\times 6$), 16.96 ($\underline{\text{CHMecHex}}$); IR (KBr) 3371, 2921, 2848, 1656, 1641, 1609, 1501, 1248, 1178, 1039, 820, 621, 518 cm^{-1} ; FD-MS m/z 1112 (M^+ , BP), 1113 ($[\text{M}+1]^+$, 83%), 1114 ($[\text{M}+2]^+$, 37%); UV-Vis $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 286 ($\log\epsilon$ 4.99); Fluorescence $\lambda_{\text{max,em}}(\text{CH}_2\text{Cl}_2, \text{excited at } 286 \text{ nm})$ 386 nm; $\text{CD}(\text{CH}_2\text{Cl}_2)$ $\lambda_{\text{max}}/\text{nm}$ ($\Delta\epsilon$) 254 (-3.29), 287 (+0.38), 284 (-0.43), 306 (+1.72); $[\alpha]_{\text{D}}^{23}$ -4.78 (c 0.041 in CHCl_3); FD-HRMS Calcd. for $\text{C}_{76}\text{H}_{76}\text{N}_2\text{O}_6$ 1112.5703, Found 1112.5692.

Details of X-ray Analyses

Crystal data of syn-1a: Single-crystalline sample was obtained by recrystallization from ethyl acetate. $\text{C}_{52}\text{H}_{60}\text{N}_2\text{O}_6$, $M = 809.06$, colorless plate, $0.40\times 0.05\times 0.03 \text{ mm}^3$, triclinic $P-1$, $a = 6.200(4)$, $b = 14.073(8)$, $c = 25.764(15) \text{ \AA}$, $\alpha = 74.34(3)^\circ$, $\beta = 84.36(5)^\circ$, $\gamma = 82.62(5)^\circ$, $V = 2142(2) \text{ \AA}^3$, $\rho_{\text{calcd}} (Z = 2) = 1.254 \text{ g cm}^{-3}$. A total of 8329 unique data ($2\theta_{\text{max}} = 54.2$) were measured at $T = 153 \text{ K}$ by a Rigaku Mercury CCD apparatus (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$). Numerical absorption correction was applied ($\mu = 0.81 \text{ cm}^{-1}$). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms are located at the calculated positions. The final R and R_w values are 0.0972 and 0.089 for 2093 reflections with $I > 2\sigma I$ and 602 parameters. Estimated standard deviations for syn-1a are 0.007-0.011 \AA for bond lengths and $0.4\text{-}0.9^\circ$ for bond angles, respectively. CCDC 680695.

Crystal data of anti-1a: Single-crystalline sample was obtained by recrystallization from ethyl acetate/benzene. $\text{C}_{58}\text{H}_{66}\text{N}_2\text{O}_6$, $M = 887.17$, colorless block, $0.25\times 0.15\times 0.15 \text{ mm}^3$, triclinic $P-1$, $a = 9.668(3)$, $b = 11.144(4)$, $c = 11.778(4) \text{ \AA}$, $\alpha = 106.388(5)^\circ$, $\beta = 96.224(5)^\circ$, $\gamma = 100.015(5)^\circ$, $V = 1182.0(7) \text{ \AA}^3$, $\rho_{\text{calcd}} (Z = 1) = 1.246 \text{ g cm}^{-3}$. A total of 5034 unique data ($2\theta_{\text{max}} = 54.2$) were measured at $T = 153 \text{ K}$ by a Rigaku Mercury CCD apparatus (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$). Numerical absorption correction was applied ($\mu = 0.80 \text{ cm}^{-1}$). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms are located at the calculated positions. The final R and R_w values are 0.0723 and 0.2246 for 2795 reflections with $I > 2\sigma I$ and 332 parameters. Estimated standard deviations for anti-1a are 0.002-0.005 \AA for bond lengths and $0.19\text{-}0.4^\circ$ for bond angles, respectively. CCDC 680697.

Crystal data of (R,R)-syn-1b: Single-crystalline sample was obtained by recrystallization from ethyl

acetate/hexane. $C_{54}H_{64}N_2O_6$, $M = 837.11$, colorless block, $0.50 \times 0.30 \times 0.30$ mm³, triclinic $P1$, $a = 6.305(2)$, $b = 13.323(5)$, $c = 13.959(5)$ Å, $\alpha = 86.986(10)^\circ$, $\beta = 81.092(9)^\circ$, $\gamma = 85.727(9)^\circ$, $V = 1154.1(7)$ Å³, ρ_{calcd} ($Z = 1$) = 1.204 g cm⁻³. A total of 7239 unique data ($2\theta_{\text{max}} = 54.2$) were measured at $T = 153$ K by a Rigaku Mercury CCD apparatus (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å). Numerical absorption correction was applied ($\mu = 0.77$ cm⁻¹). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms are located at the calculated positions. One of the cyclohexyl groups exhibits positional disorder by involving 20% of the ring-flipped counter part, whose population was also refined in the middle of least-square method. The final R and R_w values are 0.0430 and 0.1321 for 6810 reflections with $I > 2\sigma I$ and 669 parameters. Estimated standard deviations for (R,R)-syn-**1b** are 0.002-0.02 Å for bond lengths and 0.16-1.9° for bond angles, respectively. The absolute configuration was determined by chemical correlation. The refined Flack parameter is 0.0(9). CCDC 680696.

Crystal data of (R,R)-anti-1b**:** Single-crystalline sample was obtained by recrystallization from acetone. $C_{54}H_{64}N_2O_6$, $M = 837.11$, colorless block, $0.15 \times 0.07 \times 0.03$ mm³, triclinic $P1$, $a = 6.930(4)$, $b = 12.154(7)$, $c = 13.995(9)$ Å, $\alpha = 98.002(14)^\circ$, $\beta = 92.728(12)^\circ$, $\gamma = 93.553(11)^\circ$, $V = 1163.1(12)$ Å³, ρ_{calcd} ($Z = 1$) = 1.195 g cm⁻³. A total of 6376 unique data ($2\theta_{\text{max}} = 55.0$) were measured at $T = 153$ K by a Rigaku Mercury CCD apparatus (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å). Numerical absorption correction was applied ($\mu = 0.77$ cm⁻¹). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms are located at the calculated positions. The final R and R_w values are 0.0699 and 0.1834 for 2736 reflections with $I > 2\sigma I$ and 624 parameters. Estimated standard deviations for (R,R)-anti-**1b** are 0.009-0.018 Å for bond lengths and 0.7-1.6° for bond angles, respectively. The absolute configuration was determined by chemical correlation. The refined Flack parameter is -3(5). CCDC 380698.