Unusual Totally Selective Cyclodimerization of Epoxides: Synthesis of a Pair of Diastereoisomers of Enantiopure 2,5-Disubstituted 1,4-Dioxanes with $C_2$ Symmetry.
General Remarks

No use of dry solvents or inert atmosphere was necessary to carry out the reactions. All reagents were purchased in the higher quality available from Aldrich and were used without further purification. BF₃·OEt₂ was distilled from CaH₂ and stored over activated 4Å molecular sieves. The solvents used in column chromatography, were obtained from commercial suppliers and used without further distillation. TLC’s were performed on aluminium-backed plates coated with silica gel 60 with F₂₅₄ indicator and were purchased from Scharlau. Flash column chromatography was carried out on silica gel 60, 230–240 mesh. ¹H NMR (300, 400 MHz) and ¹³C NMR (75, 100 MHz) spectra were measured at room temperature on a Bruker Ac-300 and AMX-400 instruments, respectively, with tetramethylsilane (δ = 0.0, ¹H NMR) or CDCl₃ (δ = 77.00, ¹³C NMR) as internal standard. Carbon multiplicities were assigned by DEPT techniques. The diastereoisomeric ratios were obtained using ¹H NMR analysis and GC-MS of crude products. GC-MS were made on a HP-5973 chromatograph. Low-resolution electron impact mass spectra were measured at 70 eV or using FAB conditions on a HP 5987 A, and the intensities are reported as a percentage relative to the base peak after the corresponding m/s value. High-resolution mass spectra (HRMS) were determined on a Finigan MAT 95 spectrometer. When HMRS could not be measured on molecular ion the HRMS of a significant fragment is given.
IR spectra were recorded with a Perkin-Elmer 1720-X FTIR spectrometer. Only the most important IR absorptions (cm⁻¹) and the molecular ions and/or base peaks in MS are given.

Analytical and spectroscopic data for products 1 and 2 are given as follows:

**2,5-Bis-[(S)-1-(Dibenzylamino)ethyl]-(2R,5R)-1,4-dioxane (1a):** Colorless oil. [α]²⁰_D = +30.8 (c=1.48 in CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 7.35-7.15 (m, 10 H), 3.74 (d, J = 13.7 Hz, 2 H), 3.54-3.43 (m, 3 H), 3.44 (d, J = 13.7 Hz, 2 H), 2.96 (qt, J = 6.8 Hz, 1 H), 0.91 ppm (d, J = 6.8 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 140.5 (2 × C), 128.8 (4 × CH), 128.0 (4 × CH), 126.6 (2 × CH), 75.5 (CH), 65.1 (CH₂), 54.0 (2 × CH₂), 51.5 (CH), 10.5 (CH₃); MS (70 eV, EI) m/z (%): 534 (M⁺, <1), 224 (100); HRMS (70 eV) calc. for C₃₆H₄₂N₂O₂ (M⁺) 534.3246, found 534.3255; IR (neat): 3414, 3027, 2966, 1602, 1494, 1453, 1365 cm⁻¹; R_f = 0.42 (hexane/EtOAc 10:1).

**2,5,-Bis-[(S)-1-(Dibenzylamino)-3-methylbutyl]-(2R,5R)-1,4-dioxane (1b):** White solid, m.p. 97-8 °C [α]²⁰_D = +4.4 (c=1.74 in CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 7.39-7.23 (m, 10 H), 3.83-3.56 (m, 3 H), 3.80 (d, J = 13.8 Hz, 2 H), 3.64 (d, J = 13.8 Hz, 2 H), 2.95 (apparent q, J = 6.0 Hz, 1 H), 1.85-1.77 (m, 1 H), 1.47-1.39 (m, 1 H), 1.12-1.03 (m, 1 H), 0.88 (d, J = 6.5 Hz, 3 H), 0.68 (d, J = 6.4 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 140.7 (2 × C), 129.0 (4 × CH), 128.0 (4 × CH), 126.6 (2 × CH), 75.7 (CH), 65.8 (CH₂), 54.5 (2 ×
2,5,-Bis-[\((S)\)-1-(Dibenzylamino)-2-phenylethyl]-1,4-dioxane (1c): Colorless oil. \([\alpha]^{20}_{D} = +8.5\ (c=1.30\ \text{in } \text{CHCl}_3);\) \(^1\text{H} \text{NMR (300 MHz, CDCl}_3): \delta\ 7.34-7.00\ (m, 15\ \text{H}),\ 3.98\ (dd, J = 12.0, 5.7\ \text{Hz, 1 H}),\ 3.91\ (d, J = 13.7\ \text{Hz, 2 H}),\ 3.62-3.58\ (m, 1\ \text{H}),\ 3.56\ (d, J = 13.7\ \text{Hz, 2 H}),\ 3.36\ (dd, J = 12.0, 3.1\ \text{Hz, 1 H}),\ 3.21\ (\text{apparent q, } J = 6.8\ \text{Hz, 1 H}),\ 2.88\ (dd, J = 13.7, 6.8\ \text{Hz, 1 H}),\ 2.76\ (dd, J = 13.7, 7.7\ \text{Hz, 1 H});\) \(^{13}\text{C} \text{NMR (75 MHz, CDCl}_3): \delta\ 140.2\ (\text{C}),\ 140.1\ (2\ \times \text{C}),\ 129.3\ (2\ \times \text{CH}),\ 128.7\ (4\ \times \text{CH}),\ 128.2\ (2\ \times \text{CH}),\ 128.0\ (4\ \times \text{CH}),\ 126.6\ (2\ \times \text{CH}),\ 125.8\ (\text{CH}),\ 74.3\ (\text{CH}),\ 66.0\ (\text{CH}_2),\ 58.2\ (\text{CH}),\ 54.7\ (2\ \times \text{CH}_2),\ 32.3\ (\text{CH}_2);\) \text{MS (70 eV, EI) } m/z\ (%): 686\ (M^+, <1),\ 595\ (24),\ 300\ (100),\ 131\ (16);\) \text{HRMS (70 eV) calc. for } C_{48}H_{50}N_{2}O_{2}\ (M^+)\ 686.3872,\ \text{found}\ 686.3856;\) \text{IR (neat): 3402, 3026, 2928, 1602, 1494, 1454, 1365}\ \text{cm}^{-1};\ R_f = 0.41\ (\text{hexane/EtOAc 10:1}).

2,5,-Bis-[\((S)\)-1-(Dibenzylamino)-2-benzyloxyethyl]-1,4-dioxane (1d): Colorless oil. \([\alpha]^{20}_{D} = +50.5\ (c=0.95\ \text{in } \text{CHCl}_3);\) \(^1\text{H} \text{NMR (300 MHz, CDCl}_3): \delta\ 7.38-7.15\ (m, 15\ \text{H}),\ 4.46\ (d, J = 12.1\ \text{Hz, 1 H}),\ 4.41\ (d, J = 12.1\ \text{Hz, 1 H}),\ 3.87\ (d, J = 13.7\ \text{Hz, 2 H}),\ 3.88-3.82\ (m, 1\ \text{H}),\ 3.68-
3.55 (m, 3 H), 3.63 (d, J = 13.7 Hz, 2H), 3.47 (dd, J = 12.0, 3.0 Hz, 1 H), 3.08 (dt, J = 7.5, 4.8 Hz, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 140.6 (2 × C), 138.3 (C), 128.8 (4 × CH), 128.3 (2 × CH), 128.0 (4 × CH), 127.5 (CH), 127.4 (2 × CH), 126.6 (2 × CH), 73.5 (CH), 73.1 (CH$_2$), 68.4 (CH$_2$), 65.3 (CH$_2$), 55.6 (CH), 55.3 (2 × CH$_2$); MS (70 eV, EI) m/z (%) 748 (M$^+$+2, 58), 747 (M$^+$+1, 100), 330 (30), 210 (10); HRMS (70 eV) calc. for C$_{23}$H$_{24}$NO (BnOCH$_2$CHNBn$_2^+$) 330.1858, found 330.1860; IR (neat): 3402, 3026, 2929, 1602, 1494, 1454, 1365 cm$^{-1}$; $R_f$ = 0.27 (hexane/EtOAc 10:1).

2,5-Bis-[((S)-1-(Dibenzylamino)ethyl]-(2S,5S)-1,4-dioxane (2a): Colorless oil. [α]$_D^{20}$ = +31.0 (c=0.96 in CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$): δ 7.26-7.19 (m, 10 H), 3.67 (d, J = 13.7 Hz, 2 H), 3.61-3.54 (m, 2 H), 3.43-3.37 (m, 1 H), 3.36 (d, J = 13.7 Hz, 2 H), 2.79 (apparent qt, J = 6.5 Hz, 1 H), 0.95 (d, J = 6.8 Hz, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 139.8 (2 × C), 128.7 (4 × CH), 128.1 (4 × CH), 126.7 (2 × CH), 74.4 (CH), 64.5 (CH$_2$), 54.2 (2 × CH$_2$), 51.2 (CH), 8.0 (CH$_3$); MS (70 eV, EI) m/z (%) 534 (M$^+$, <1), 224 (100), 181 (13); HRMS (70 eV) calc. for C$_{36}$H$_{42}$N$_2$O$_2$ (M$^+$) 534.3246, found 534.3215; IR (neat): 3426, 3026, 2929, 1603, 1494, 1452, 1366 cm$^{-1}$; $R_f$ = 0.37 (hexane/EtOAc 10:1).

2,5-Bis-[(S)-1-(Dibenzylamino)-3-methylbutyl]-(2S,5S)-1,4-dioxane (2b): Colorless oil. [α]$_D^{20}$ = -10.4 (c=1.68 in CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$): δ 7.18-7.06 (m, 10 H),
3.64-3.44 (m, 3 H), 3.56 (d, J = 13.7 Hz, 2 H), 3.47 (d, J = 13.7 Hz, 2 H), 2.70 (dt, J = 7.4, 4.4 Hz, 1 H), 1.79-1.61 (m, 1 H), 1.47-1.38 (m, 1 H), 1.16-1.02 (m, 1 H), 0.77 (d, J = 6.5 Hz, 3 H), 0.48 (d, J = 6.4 Hz, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 140.1 (2 × C), 128.9 (4 × CH), 128.1 (4 × CH), 126.8 (2 × CH), 74.2 (CH), 65.0 (CH$_2$), 54.3 (2 × CH$_2$), 52.8 (CH), 37.1 (CH$_2$), 25.0 (CH), 23.6 (CH$_3$), 22.2 (CH$_3$); MS (70 eV, EI) m/z (%) 619 (M$^+$ + 1, 100), 292 (35), 266 (34), 210 (64), 91 (60); HRMS (70 eV) calc. for C$_{42}$H$_{54}$N$_2$O$_2$ (M$^+$) 618.4185, found 618.4171; IR (neat): 2954, 2866, 1601, 1494, 1453, 1366 cm$^{-1}$; $R_f$ = 0.34 (hexane/EtOAc 10:1).

2,5,-Bis-[(S)-1-(Dibenzylamino)-2-phenylethyl]-(2R,5R)-1,4-dioxane (2c): Colorless oil. $[\alpha]^{20}_D$ = -3.0 (c=1.06 in CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$): δ 7.31-7.07 (m, 15 H), 3.70-3.59 (m, 2 H), 3.64 (d, J = 13.9 Hz, 2 H), 3.54 (d, J = 13.9 Hz, 2 H), 3.38 (dd, J = 11.0, 2.5 Hz, 1 H), 3.07 (dt, J = 8.3, 4.5 Hz, 1 H), 2.85 (dd, J = 14.3, 8.3 Hz, 1 H), 2.68 (dd, J = 14.3, 4.5 Hz, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 141.4 (C), 139.6 (2 × C), 129.5 (2 × CH), 128.7 (4 × CH), 128.0 (6 × CH), 126.7 (2 × CH), 125.6 (CH), 73.8 (CH), 64.4 (CH$_2$), 57.6 (CH), 54.5 (2 × CH$_2$), 32.9 (CH$_3$); MS (70 eV, EI) m/z (%) 595 (M$^+$ - C$_7$H$_7$, 4), 300 (100); HRMS (70 eV) calc. for C$_{41}$H$_{43}$N$_2$O$_2$ (M$^+$ - C$_7$H$_7$) 595.3325, found 595.3321; IR (neat): 3414, 3028, 2928, 1602, 1494, 1453, 1366 cm$^{-1}$; $R_f$ = 0.38 (hexane/EtOAc 10:1).