

Supporting Information

Absolute Configuration for 1,n-Glycols: A Non-empirical Approach to Long Range Stereochemical Determination

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EXPERIMENTAL:

Materials and general instrumentations:

Anhydrous CH_2Cl_2 was dried and redistilled over CaH_2 . The solvents used for CD measurements were purchased from Aldrich and were spectra grade. All reactions were performed in dried glassware under nitrogen. Column chromatography was performed using SiliCycle silica gel (230-400 mesh). ^1H NMR and ^{13}C NMR spectra were obtained on a Varian Inova 300 MHz or 500 MHz instrument and are reported in parts per million (ppm) relative to the solvent resonances (δ), with coupling constants (J) in Hertz (Hz). IR studies were performed on a Nicolet FT-IR 42 instrument. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 40 spectrophotometer, and are reported as λ_{max} [nm]. CD spectra were recorded on a JASCO J-810 spectropolarimeter, equipped with a temperature controller (Neslab 111) for low temperature studies, and were reported as λ [nm] ($\Delta\epsilon_{\text{max}}$ [$\text{L mol}^{-1} \text{cm}^{-1}$]). Optical rotations were recorded at 20 °C on a Perkin Elemer 341 Polarimeter ($\lambda = 589 \text{ nm}$, 1 dm cell). HRMS analyses were performed on a Q-TOF Ultima system using electrospray ionization in positive mode.

General procedure for CD measurement:

Zinc porphyrin tweezer (2.5 μL of a 1 mM solution in anhydrous CH_2Cl_2) was added to hexane (1 mL) in a 1.0 cm cell to obtain a 2 μM tweezer solution. The background spectrum was recorded from 350 nm to 550 nm with a scan rate of 100 nm/min at 0 °C. Chiral diol (1 to 10 μL of a 10 mM solution in anhydrous CH_2Cl_2) was added into the prepared tweezer solution to afford the host/guest complex. The CD spectra were measured immediately (minimum of 4 accumulations). The resultant ECCD spectra recorded in millidegrees were normalized based on the tweezer concentration to obtain the molecular CD (Mol CD).

Inconclusive ECCD results with Tweezer A

When zinc porphyrin tweezer **A** bearing 5 methylene carbon linker was used for ECCD measurements, complications were observed for diols **2**, **5** (Figure S1-a) and **10** (Figure S1-b) as described in manuscript. Their UV profiles upon complexation with tweezer **A** (Figure S2) are similar to those of other diol substrates. Changing the temperature did not solve this issue as similar ECCD curves were observed albeit with diminished amplitude at higher temperature (25 °C, Figure S3-a) or increased amplitude at lower temperature (-10 °C, Figure S3-b). In other nonpolar solvents such as MCH, fairly poor CD signal was detected. More polar solvents led to no ECCD (competitive binding of solvent with the highly fluorinated zincated porphyrin).

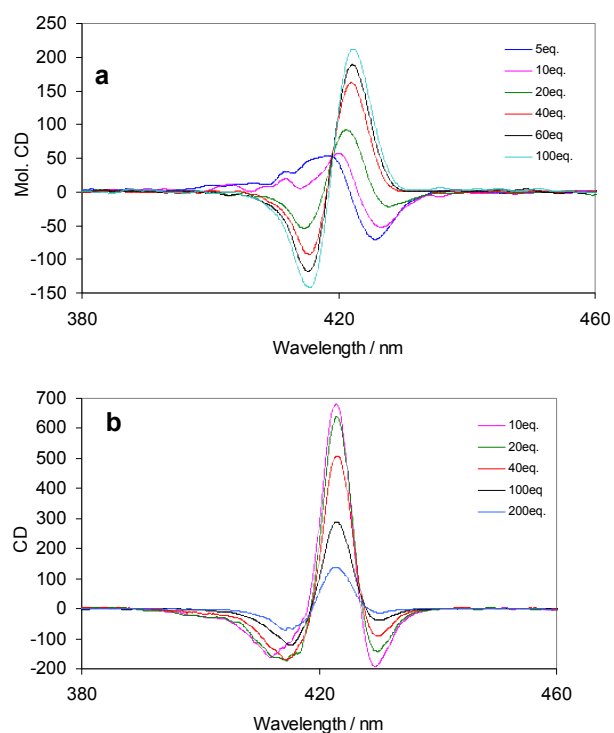


Figure S1. ECD spectra of tweezer **A** (2 μ M in hexane) with **5** (graph **a**) and **10** (graph **b**) at different equivalents at 0°C.

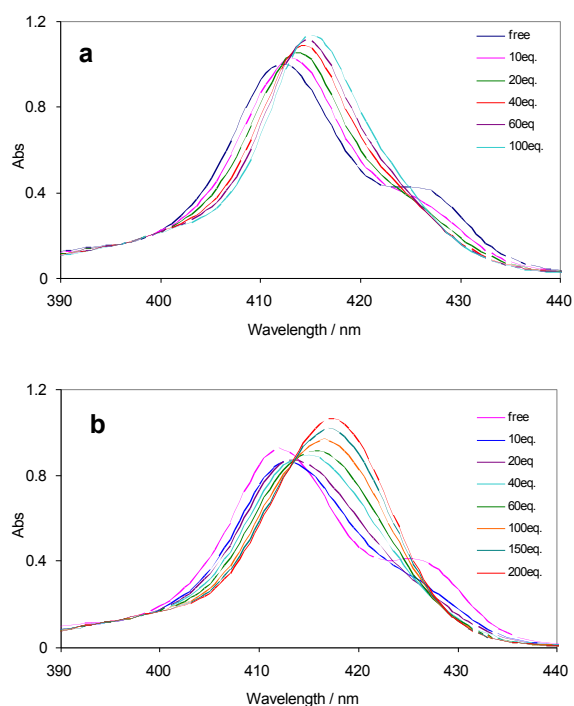


Figure S2. UV-Vis spectra change upon titration of tweezer **A** (1 μ M in hexane) with **5** (graph **a**) and **10** (graph **b**) at different equivalents (only selected curves were shown for clarity).

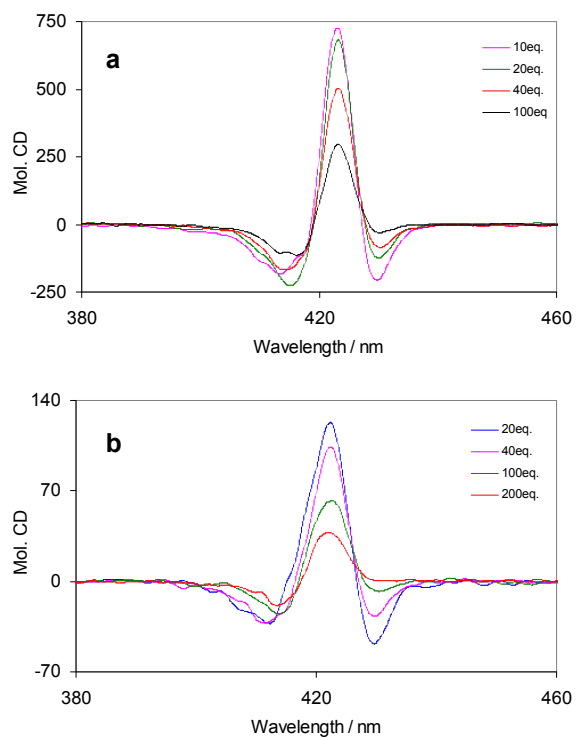


Figure S3. ECCD spectra of tweezer **A** (2 μM in hexane) with 1,12-diol **10** at -10 °C (graph **a**) and 25 °C (graph **b**) at different equivalents.

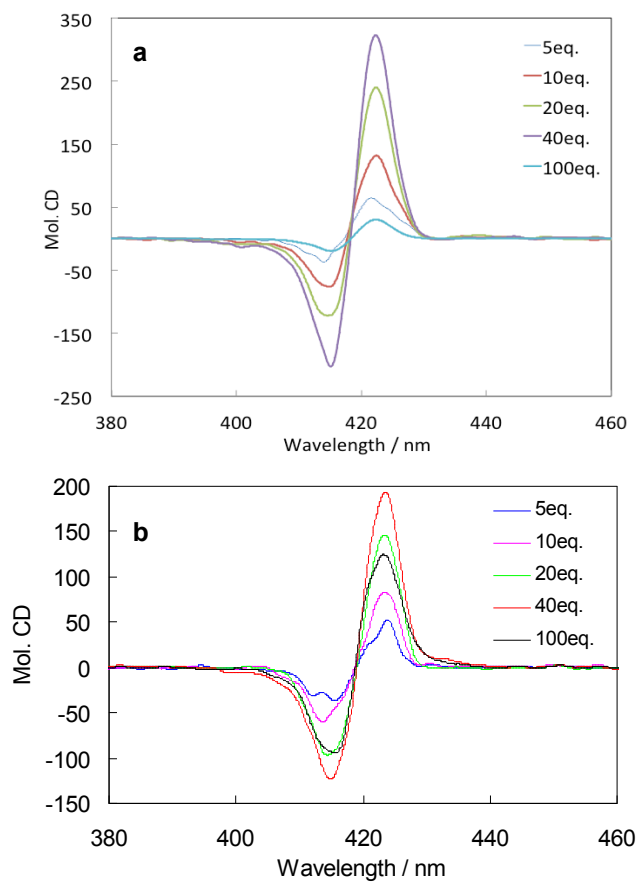


Figure S4. ECCD spectra of tweezer **B** (2 μM in hexane) with **5** (graph **a**) and **10** (graph **b**) at different equivalents at 0 °C.

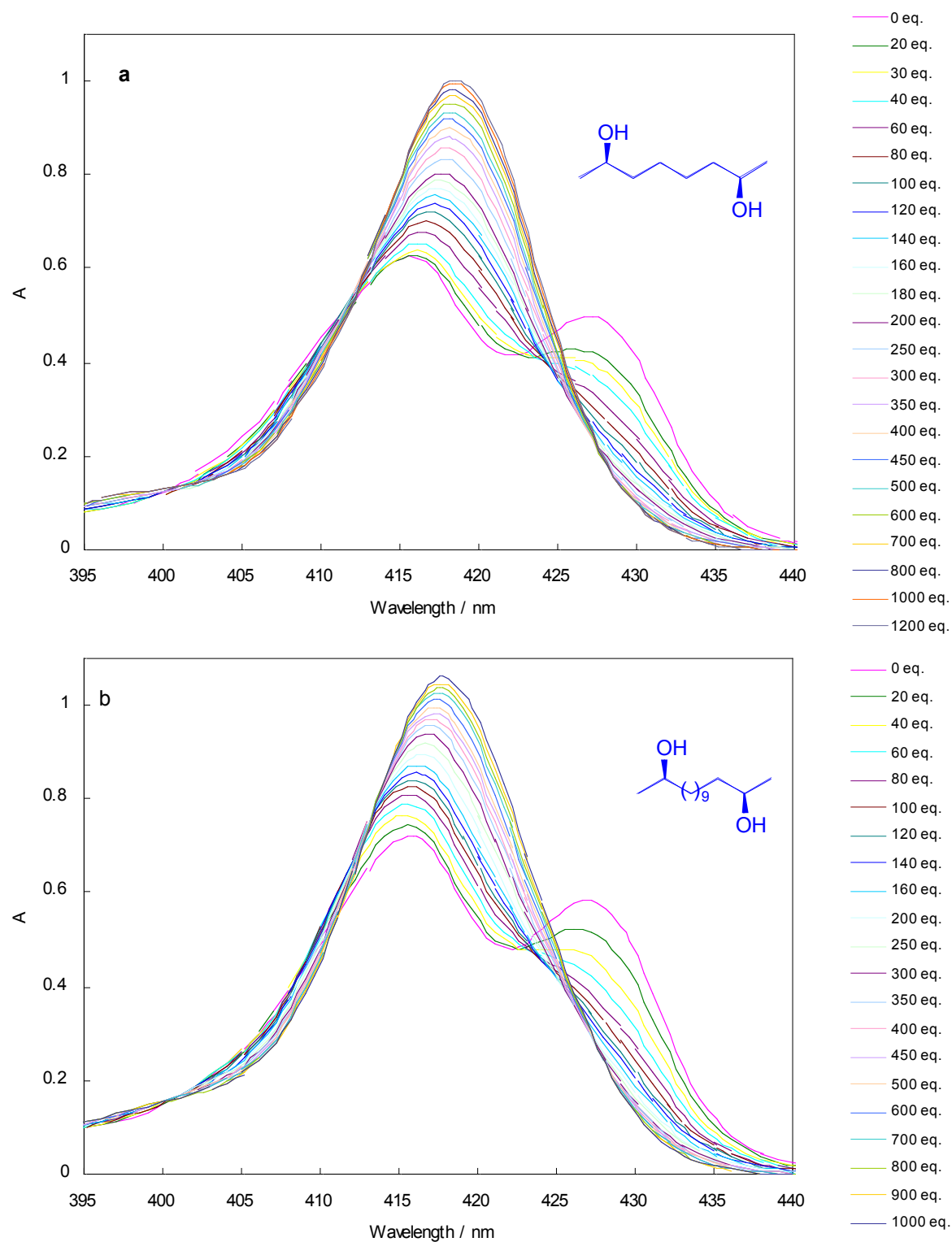


Figure S5. UV-Vis spectra change upon titration of tweezer **B** (1 μ M in hexane) with **5** (10 mM in DCM, graph **a**) and **10** (10 mM in DCM, graph **b**)

Job's Continuous Plot Analysis to Determine Complex Stoichiometry:¹

For each titration, a stock solution of tweezer (10^{-3} M) and a stock solution of diol (10^{-3} M) in dichloromethane were made. To 1 mL of hexanes in a 1 cm UV-Vis cuvette, the tweezer (Tz/1 μ L of the stock solution) and diol (0, 0.2, 0.5, 1, 2, 5, 10, 20 and 50 equivalents) were added and UV-Vis spectrum (350 nm-600 nm) was recorded. The molar fraction of tweezer multiplied by the change in UV-Vis absorbance at the indicated wavelength for each titration point was determined and was plotted against the molar fraction of tweezer. Peaking at 0.5 mol fraction corresponds to a 1:1 tweezer:diol complex. This was observed in all cases as shown in Figures S6-S11.

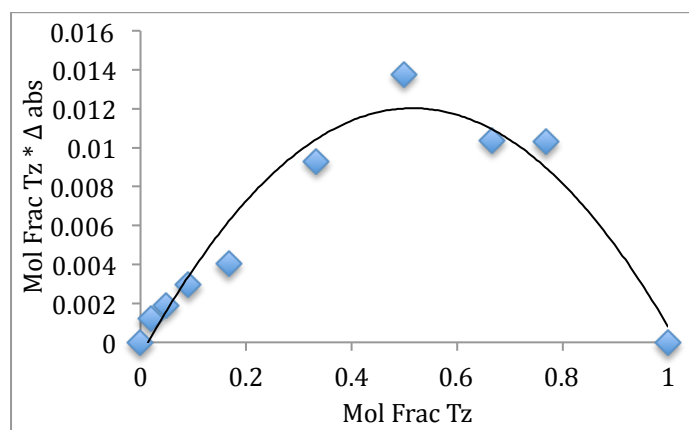


Figure S6. Job's Plot C5 Tweezer (A) with 1,2-*R,R* diol (**1**). Absorbance at 409 nm.

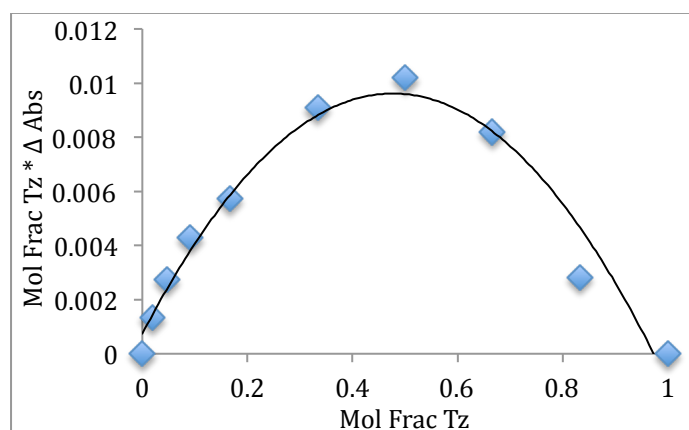


Figure S7. Job's Plot C5 Tweezer (A) with 1,7-*R,R* diol (**6**). Absorbance at 409 nm.

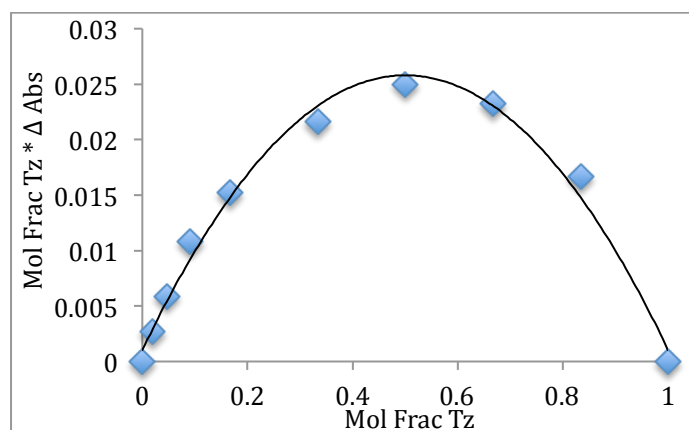


Figure S8. Job's Plot C5 Tweezer (A) with 1,12-*R,R* diol (**10**). Absorbance at 409 nm.

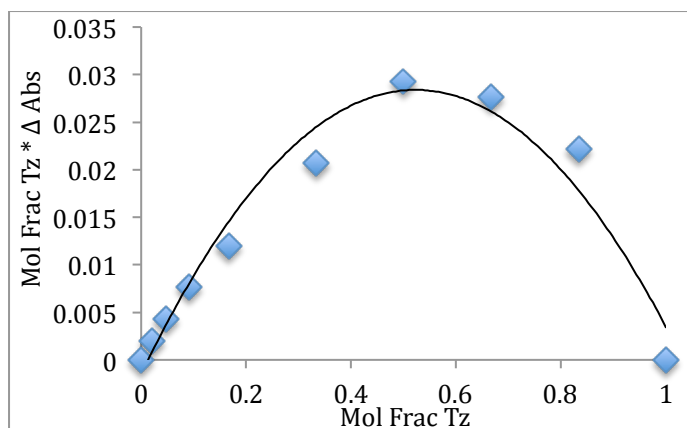


Figure S9. Job's Plot C3 Tweezer (**B**) with 1,2-*R,R* diol (**1**). Absorbance at 426 nm.

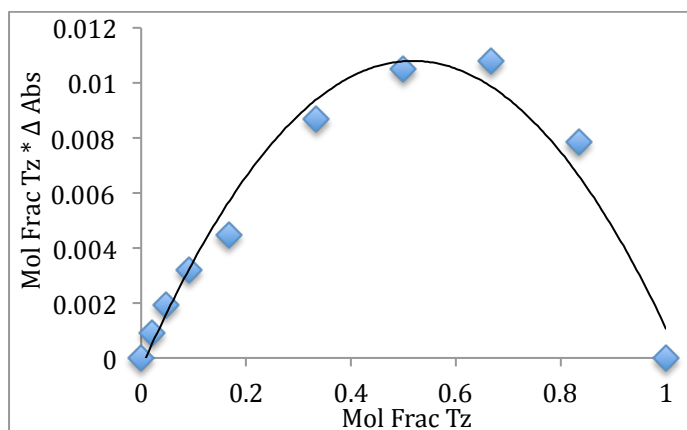


Figure S10. Job's Plot C3 Tweezer (**B**) with 1,7-*R,R* diol (**6**). Absorbance at 426 nm.

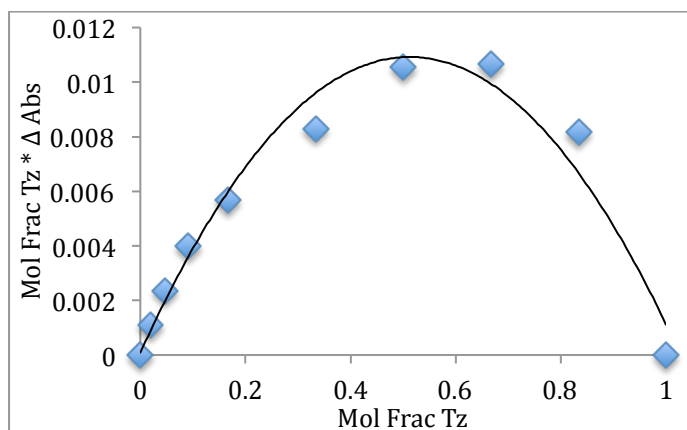


Figure S11. Job's Plot C3 Tweezer (**B**) with 1,12-*R,R* diol (**10**). Absorbance at 426 nm.

***trans*-All staggered conformations of 1,6-diol and 1,7-diol**

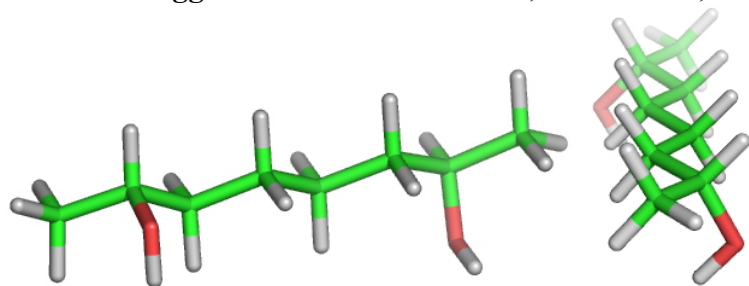


Figure S12. Most stable *trans*-all staggered conformation of 1,6-diol (5)

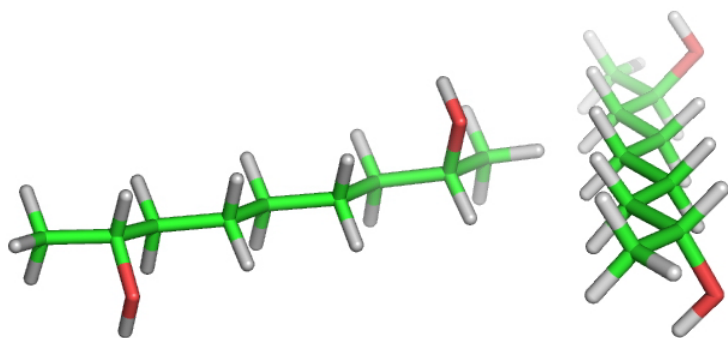


Figure S13. Most stable *trans*-all staggered conformation of 1,7-diol (6)

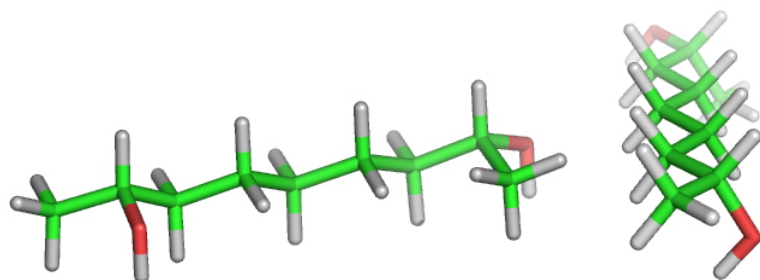


Figure S14. Alternative *trans*-all staggered conformation of 1,7-diol (6)

Crystal structure of diol 10

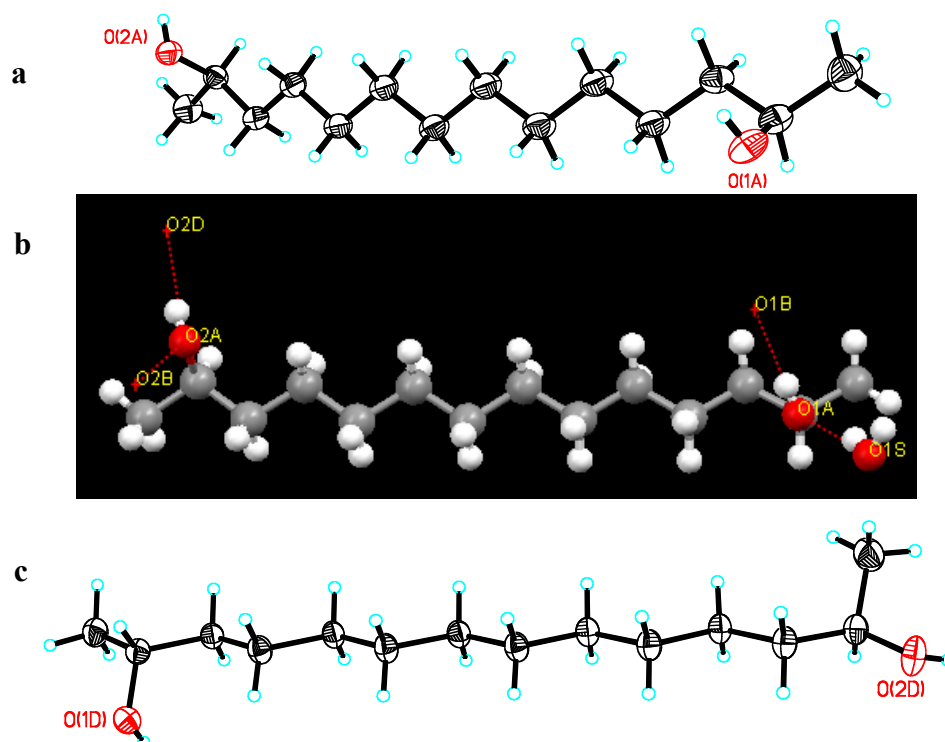


Figure S15. Crystal structure of diol **10** (graph **a** and **c** indicate two formations in the cell), graph **b** illustrates H-bondings involved (red dashed line, O1B, O2B and O2D refer to oxygen atoms of adjacent diol molecules within the cell, note that the H atom on O2B is not shown); d(O1A-O1B): 2.726Å, d(O1A-O1S): 2.737Å, d(O2A-O2B): 2.702Å, d(O2A-O2D): 2.713Å

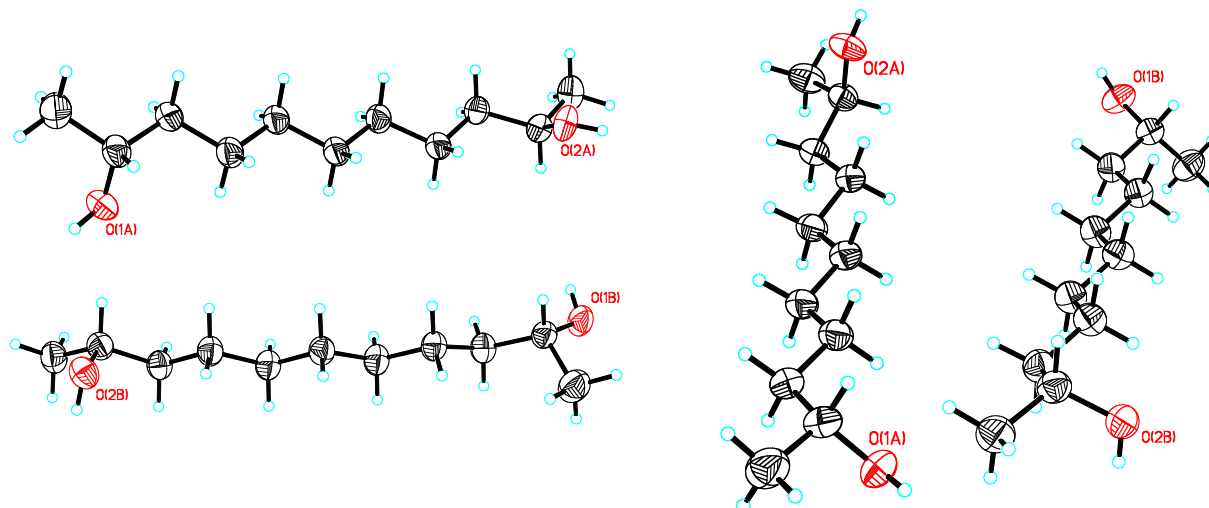


Figure S16. Crystal structure of diol **8**, two conformations were found in one asymmetric unit cell

Table S1. Crystal data and structure refinement for Diol **8**.

Identification code	Diol 8
Empirical formula	C11 H24 O2
Formula weight	188.30
Temperature	173(2) K
Wavelength	0.71073 Å

Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 7.78370(10) Å $\alpha = 90^\circ$. b = 10.9032(2) Å $\beta = 90^\circ$. c = 28.9411(4) Å $\gamma = 90^\circ$.
Volume	2456.15(6) Å ³
Z	8
Density (calculated)	1.018 Mg/m ³
Absorption coefficient	0.067 mm ⁻¹
F(000)	848
Crystal size	0.22 x 0.16 x 0.12 mm ³
Theta range for data collection	1.41 to 25.31°.
Index ranges	-8 ≤ h ≤ 9, -13 ≤ k ≤ 12, -34 ≤ l ≤ 34
Reflections collected	14442
Independent reflections	4434 [R(int) = 0.0363]
Completeness to theta = 25.31°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9922 and 0.9851
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4434 / 0 / 243
Goodness-of-fit on F ²	1.016
Final R indices [I > 2σ(I)]	R1 = 0.0393, wR2 = 0.0808
R indices (all data)	R1 = 0.0555, wR2 = 0.0919
Absolute structure parameter	-0.3(11)
Largest diff. peak and hole	0.110 and -0.167 e.Å ⁻³

Table S2. Crystal data and structure refinement for diol **10**.

Identification code	Dio 10	
Empirical formula	C ₁₄ H _{30.50} O _{2.25}	
Formula weight	234.88	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 9.4357(8) Å	α = 88.3600(10)°.
	b = 10.0619(8) Å	β = 76.6840(10)°.
	c = 17.2986(13) Å	γ = 71.8240(10)°.
Volume	1516.8(2) Å ³	
Z	4	
Density (calculated)	1.029 Mg/m ³	
Absorption coefficient	0.067 mm ⁻¹	
F(000)	530	
Crystal size	1.08 x 0.20 x 0.18 mm ³	
Theta range for data collection	1.21 to 32.04°.	
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -25 ≤ l ≤ 24	
Reflections collected	31513	
Independent reflections	14753 [R(int) = 0.0283]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9881 and 0.9311	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14753 / 3 / 1074	
Goodness-of-fit on F ²	0.983	
Final R indices [I > 2σ(I)]	R1 = 0.0433, wR2 = 0.0965	
R indices (all data)	R1 = 0.0728, wR2 = 0.1106	
Absolute structure parameter	0.6(6)	
Largest diff. peak and hole	0.202 and -0.191 e.Å ⁻³	

Conformational search of the diol-tweezer **10** complex

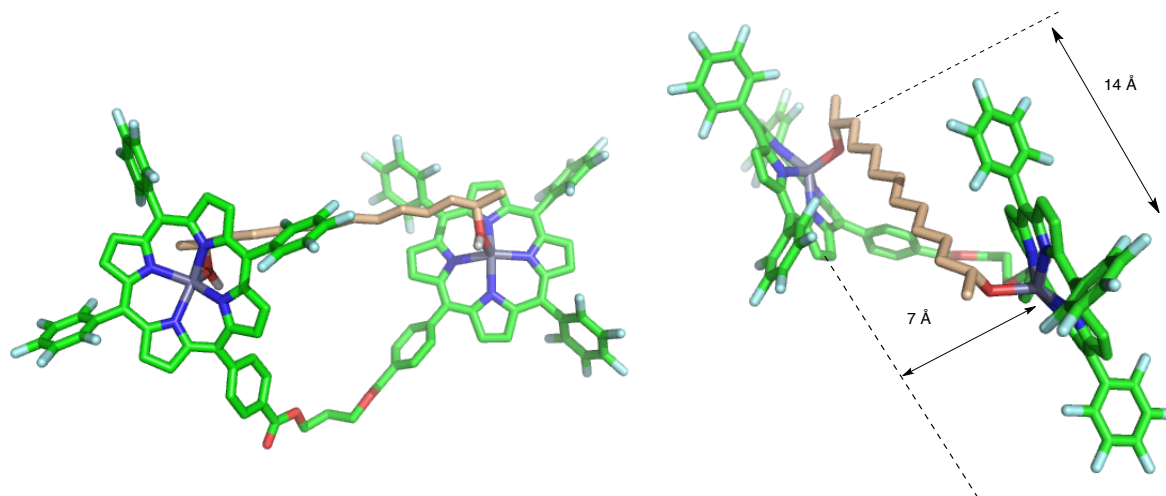


Figure S17. Front view (left) and side view (right) of the ‘side-on’ binding model of diol **10**-tweezer **B** complex (lowest energy conformer by Monte Carlo conformational search using SYBYL force field, hydrogen atoms were omitted for clarity); the chromophore’s center-to-center distance (7 Å) and the distance between carbinol carbons (14 Å) is highlighted

Monte Carlo conformational search of diol-tweezer complex was performed in vacuo with Spartan V 5.1.3 utilizing SYBYL as the force field. The O–Zn distance was constrained at 2.2 Å to avoid dissociation of the complex. Default parameterization was used for metal atoms. All possible torsional angles were varied during each optimization step, except the porphyrin ring dihedral angles. Default convergence criteria was used. After over 1500 fully optimized steps, conformers with 10 kcal / mol were collected for analysis. For all three diols (**5**, **6**, and **10**) complexed with tweezer **B**, the most stable conformers consistently indicated clockwise helicity as proposed (Figure S17-S20). The side-on approach was also clearly revealed in these optimized structures. The center-to-center distance (Zn1-Zn2) of the tweezer host increases accordingly with the increase of diol chain length (ca. 7 Å in **5/B** complex and 16 Å in **10/B** complex). However, the interplanar distance changes only slightly while extending the guest molecular skeleton (ca. 6 Å in **5/B** complex and 7 Å in **10/B** complex), which is in line with the unusually strong CD signals primarily due to intimate chromophoric interaction in the ‘side-on’ binding process (Figure S17). The independence of CD amplitudes on substrate chain length is of particular importance since most bischromophoric methods inevitably suffer from weakened ECCD signal strength when used for long range stereochemical determination.

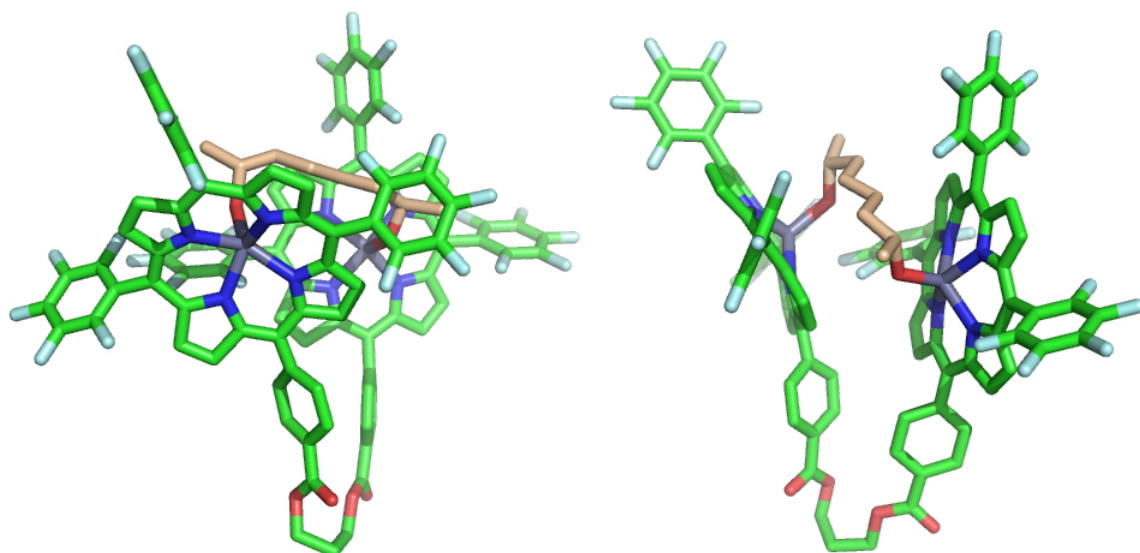


Figure S18. Front view (left) and side view (right) of the 1,6-diol-tweezer **B** complex (hydrogen atoms were omitted for clarity)

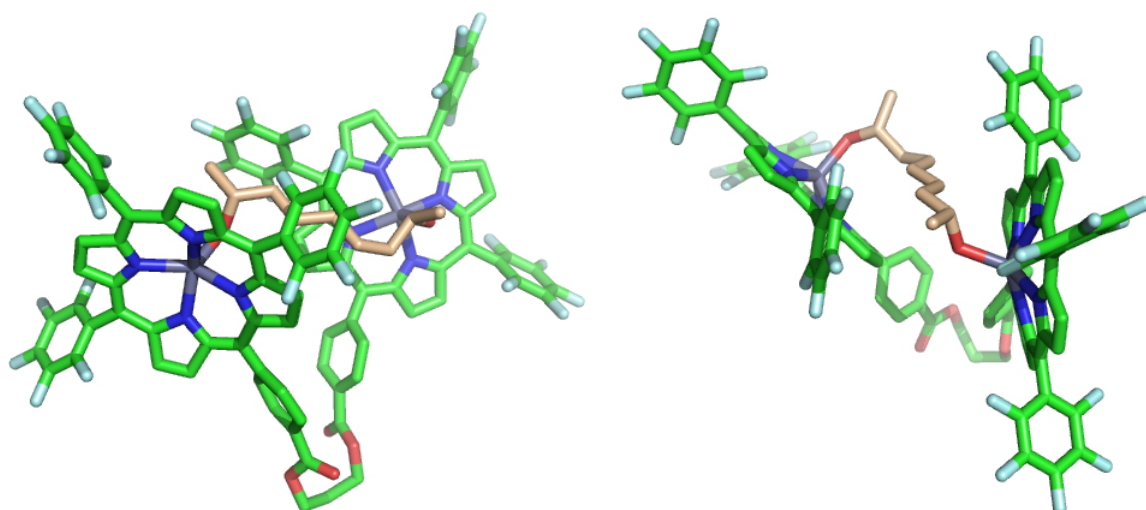


Figure S19. Front view (left) and side view (right) of the 1,7-diol-tweezer **B** complex (hydrogen atoms were omitted for clarity)

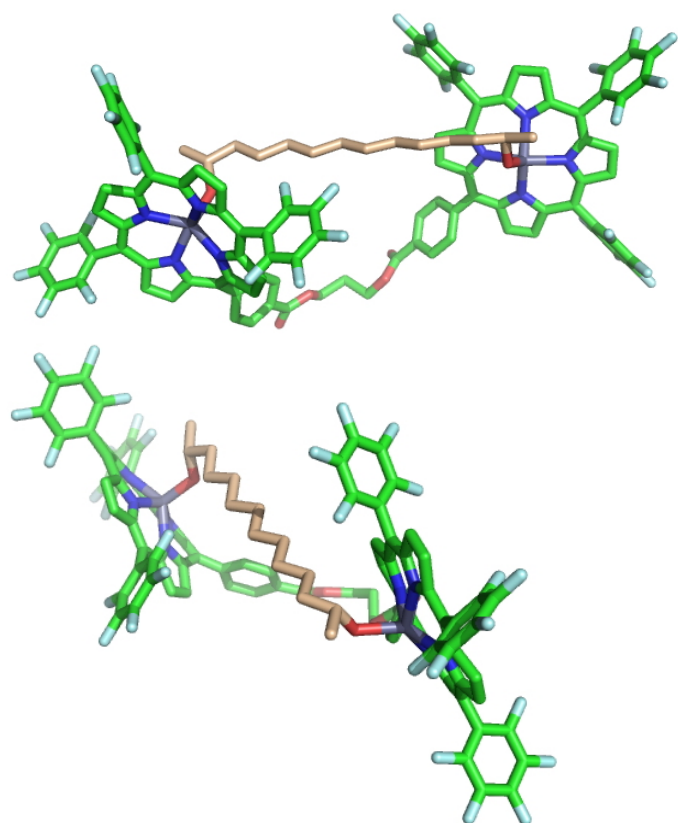


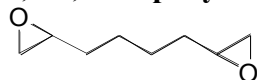
Figure S20. Front view (left) and side view (right) of the 1,12-diol-tweezer **B** complex (hydrogen atoms were omitted for clarity)

Synthesis of chiral diols

Diol **1** was obtained from Sharpless asymmetric dihydroxylation according to known procedures. Diol **2** is commercially available from Acros. Chiral 1,*n*-glycols (**3-9**) were readily accessible through Jacobsen's Hydrolytic Kinetic Resolution (HKR) of terminal dienes and subsequent ring opening of chiral diepoxides by LAH. Diols **10** and **11** were synthesized from (*R*)-propyl epoxide. Diols **12** and **13** were prepared from Grignard mediated ring-opening of (2*S*,3-epoxypropyl)benzene as described below.

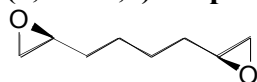
Typical procedure for synthesis of chiral diols using Jacobsen hydrolytic kinetic resolutions² described for the synthesis of **5**:

1,2:7,8-Diepoxyoctane (**S1**)



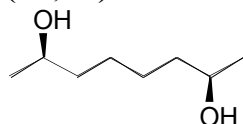
To a solution of 1,7-octanediene (5.0 g, 45.5 mmol) in CH₂Cl₂ (100 mL) at 0 °C was added *m*-CPBA (70%, 13.4 g, 54.5 mmol). The suspension was stirred at room temperature for 2 h monitored by TLC until completion. The reaction was quenched and washed by saturated NaHCO₃ solution (4 × 80 mL) followed by brine (100 mL). The organic layers were then dried (Na₂SO₄) and concentrated. The oil residue was purified by flash chromatography (5-20% EtOAc / hexane) to afford the 1,2:7,8-diepoxyoctane (5.32 g, 83%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 1.52 (s, br, 8H), 2.44 (dd, 2H, *J*₁ = 5.1 Hz, *J*₂ = 2.7 Hz), 2.73 (t, 2H, *J* = 5.1 Hz), 2.88 (s, br, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.5, 32.1, 46.6, 51.8.³

(1,2*S*:7*S*,8)-Diepoxyoctane (**S2**)

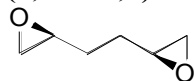


1,2:7,8-Diepoxy-heptane (3.68 g, 25.94 mmol), (*S,S*)-Salen-Co catalyst (157 mg, 0.0259 mmol, 0.01 equiv), THF (0.26 mL) and HOAc (62 mg, 1.04 mmol, 0.04 equiv) were added sequentially to a 50 mL round bottom flask rendering a dark red-brown solution. The mixture was cooled in ice-bath and H₂O (514 mg, 28.53 mmol, 1.1 equiv) was added in one portion. The reaction mixture was stirred for 20 h and then purified by flash chromatography (10-30% EtOAc / hexane) to afford the (1,2*S*:7*S*,8)-diepoxyoctane (552 mg, 15%) as a colorless oil. [α]_D²⁰ = -22.3, (*c* = 2.0, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.52 (s, br, 8H), 2.44 (dd, 2H, *J*₁ = 5.1 Hz, *J*₂ = 2.7 Hz), 2.73 (t, 2H, *J* = 5.1 Hz), 2.88 (s, br, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.5, 32.1, 46.6, 51.8.

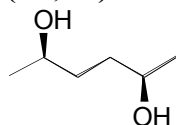
(2*R*,7*R*)-Octanediol (**5**)



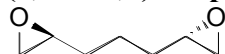
To a solution of (1,2*S*:7*S*,8)-diepoxyoctane (205 mg, 1.44 mmol) in dry THF (10 mL) at 0 °C was added LAH (219 mg, 5.77 mmol, 4.0 equiv). The mixture was stirred for 1 h until completion, then was quenched with Et₂O (20 mL), H₂O (1 mL), and H₂SO₄ (1 mL). After filtration through celite, the organic layer was dried and concentrated. Purification by flash chromatography (30-50% EtOAc / hexane) afforded the (2*R*,7*R*)-octanediol (203 mg, 97%) as a colorless oil. [α]_D²⁰ = -17.5, (*c* = 0.72, CHCl₃); *ee* = 95% (NMR analysis of *R*-MPA diester); ¹H NMR (CDCl₃, 300 MHz) δ 1.14 (d, 6H, *J* = 6.3 Hz), 1.35 (m, 8H), 1.71 (s, 2H), 3.75 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 23.4, 25.6, 39.1, 67.8.³

(1,2*S*:5*S*,6)-Diepoxyhexane (S3)

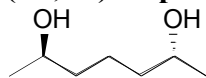
HKR of racemic 1,2:5,6-diepoxyhexane following procedures described above afforded (1,2*S*:5*S*,6)-diepoxyhexane as colorless oil (12%). $[\alpha]_D^{20} = -27.5$, ($c = 1.08$, CHCl_3), lit.⁴ $[\alpha]_D^{26} = -26.4$, ($c = 1.86$, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.69 (m, 4H), 2.48 (dd, 2H, $J_1 = 5.1$ Hz, $J_2 = 2.7$ Hz), 2.76 (t, 3H, $J = 4.8$ Hz), 2.99 (s, br, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 28.6, 29.1, 47.0, 51.5, 51.8.

(2*R*,5*R*)-Hexanediol (3)

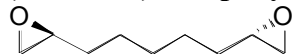
LAH ring opening of **S3** following procedures described above afforded **3** as colorless oil (90%). $[\alpha]_D^{20} = -32.0$, ($c = 1.0$, CHCl_3), lit.^{4b,5} $[\alpha]_D^{25} = -35.7$, ($c = 1.0$, CHCl_3); $ee = 95\%$ (NMR analysis of *R*-MPA diester); ^1H NMR (CDCl_3 , 300 MHz) δ 1.18 (d, 6H, $J = 6.3$ Hz), 1.55 (m, 4H), 3.78 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 23.7, 36.0, 68.3.

(1,2*S*:6*S*,7)-Diepoxyheptane (S4)

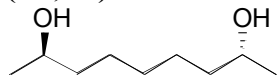
HKR of racemic 1,2:6,7-diepoxyheptane following procedures described above afforded **S4** as colorless oil (12%). $[\alpha]_D^{20} = -23.1$, ($c = 1.0$, CHCl_3), lit.^{4b,6} $[\alpha]_D^{20} = +24.1$, ($c = 1.7$, CHCl_3) for (2*R*,6*R*)-diepoxyheptane; ^1H NMR (CDCl_3 , 300 MHz) δ 1.62 (m, 6H), 2.46 (dd, 2H, $J_1 = 5.1$ Hz, $J_2 = 2.7$ Hz), 2.74 (t, 2H, $J = 4.8$ Hz), 2.91 (s, br, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 22.4, 32.1, 46.9, 52.0.

(2*R*,6*R*)-Heptanediol (4)

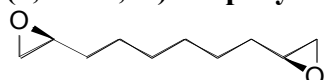
LAH ring opening of **S4** following procedures described above afforded **4** as colorless oil (90%). $[\alpha]_D^{20} = -24.9$, ($c = 1.01$, CHCl_3), lit.^{4b,7} $[\alpha]_D^{25} = -25$, ($c = 0.8$, CHCl_3); $ee = 95\%$ (NMR analysis of *R*-MPA diester); ^1H NMR (CDCl_3 , 300 MHz) δ 1.18 (d, 6H, $J = 6.3$ Hz), 1.44 (m, 6H), 1.63 (s, 2H) 3.78 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 21.8, 23.5, 38.8.

(1,2*S*:8*S*,9)-Bisepoxy-Nonane (S5)

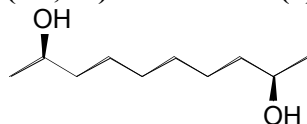
HKR of racemic 1,2:8,9-diepoxy-nonane following procedures described above afforded **S5** as colorless oil (14%). $[\alpha]_D^{20} = -20.3$, ($c = 1.45$, CHCl_3), lit.^{4b,8} $[\alpha]_D^{23} = +20.7$, ($c = 1.03$, CHCl_3) for (1,2*R*:8*R*,9)-diepoxy-nonane; ^1H NMR (CDCl_3 , 300 MHz) δ 1.48 (m, 10H), 2.44 (dd, 2H, $J_1 = 5.1$ Hz, $J_2 = 3.0$ Hz), 2.73 (t, 2H, $J = 4.8$ Hz), 2.88 (s, br, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 25.8, 29.1, 32.3, 47.0, 52.2.

(2*R*,8*R*)-Nonanediol (6)

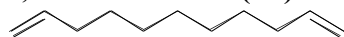
LAH ring opening of **S5** following procedures described above afforded **6** as colorless oil (92%). $[\alpha]_D^{20} = -8.0$, ($c = 1.56$, CHCl_3); $ee = 95\%$ (NMR analysis of *R*-MPA diester); ^1H NMR (CDCl_3 , 300 MHz) δ 1.16 (d, 6H, $J = 6.3$ Hz), 1.38 (m, 10H), 3.76 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 23.5, 25.7, 29.6, 39.2, 68.1.⁹

(1,2*S*:9*S*,10)-Diepoxydecane (S6)

HKR of racemic 1,2:9,10-diepoxydecane following procedures described above afforded **S6** as colorless oil (14%). $[\alpha]_D^{20} = -18.4$, ($c = 1.0$, CHCl_3), lit.^{4b,10} $[\alpha]_D^{27} = -17$, ($c = 0.79$, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.47 (m, 12H), 2.43 (dd, 2H, $J_1 = 5.1$ Hz, $J_2 = 2.7$ Hz), 2.71 (t, 2H, $J = 4.2$ Hz), 2.87 (s, br, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 25.8, 29.3, 32.4, 47.1, 52.3; IR (film) 3046, 2984, 2930 (str.), 2857 (str.), 1466, 1410, 1260, 914, 835 (str.); HRMS (ES+) m/z for $\text{C}_{10}\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$; obs'd 193.1207, calc'd 193.1204.

(2*R*,9*R*)-Decanediol (7)

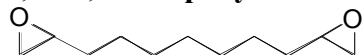
LAH ring opening of **S6** following procedures described above afforded **7** as colorless oil (92%). $[\alpha]_D^{20} = -9.9$, ($c = 1.0$, CHCl_3), $ee = 95\%$ (NMR analysis of *R*-MPA diester); ^1H NMR (CDCl_3 , 300 MHz) δ 1.16 (d, 6H, $J = 6.0$ Hz), 1.36 (m, 12H), 3.74 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 23.5, 25.7, 29.6, 39.3, 68.1.¹¹

1,10-Undecdiene (S7)

To a slurry of PCC (2.4 g, 48.6 mmol) and celite (30 g) in dry CH_2Cl_2 (120 mL) and THF (60 mL) was added 1,9-nonanediol solid powder (3.24 g, 20.3 mmol). The dark brown solution was stirred under N_2 at RT overnight. The mixture was filtered through celite, concentrated and purified by flash chromatography (5-20% EtOAc / hexane) to afford 1,9-nonane dialdehyde (1.93 g, 61%) as a colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ 1.30 (m, 10H), 2.39 (t, 4H, $J = 6.6$ Hz), 9.76 (s, 2H).

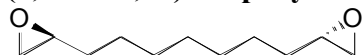
To a solution of triphenylphosphine methyl bromide (10.4 g, 28.5 mmol) in dry THF (80 mL) at 0 °C was added NaHMDS (28.5 mL, 28.5 mmol, 1M in THF) dropwise. The solution was stirred for 1 h before dropwise addition of 1,9-nonane dialdehyde (1.74 g, 11.14 mmol). The resultant yellow slurry was stirred at RT overnight then quenched with saturated NH_4Cl solution. The aqueous layer was extracted by Et_2O (2×60 mL). Organic extracts were dried (Na_2SO_4), concentrated and subjected to flash chromatography (0-5% EtOAc / hexane) to afford 1,10-undecdiene (1.61 g, 95%) as a colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ 1.34 (m, 10H), 2.01 (q, 4H, $J = 6.6$ Hz), 4.94 (m, 4H), 5.78 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 28.9, 29.1, 29.3, 33.8, 114.1, 139.2.¹²

1,2:10,11-Diepoxyundecane (S8)



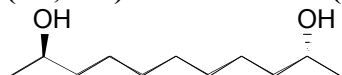
m-CPBA mediated epoxidation of **S7** as described above afforded **S8** as colorless oil (78%). ¹H NMR (CDCl₃, 300 MHz) δ 1.44 (m, 14H), 2.45 (dd, 2H, *J*₁ = 5.1 Hz, *J*₂ = 2.7 Hz), 2.73 (t, 2H, *J* = 4.5 Hz), 2.88 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.8, 29.2, 29.3, 32.4, 47.0, 52.2.

(1,2*S*:10*S*,11)-Diepoxyundecane (S9)



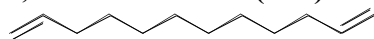
HKR of racemic 1,2:10,11-diepoxyundecane following procedures described above afforded **S9** as colorless oil (13%). [α]_D²⁰ = -15.5, (*c* = 1.19, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.44 (m, 12H), 2.44 (dd, 2H, *J*₁ = 5.1 Hz, *J*₂ = 2.7 Hz), 2.73 (t, 2H, *J* = 4.5 Hz), 2.88 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.9, 29.3, 29.4, 32.4, 47.1, 52.3.; IR (film) 3046, 2982, 2930 (str.), 2859 (str.), 1458, 1410, 1260, 916, 835 (str.) cm⁻¹; HRMS (ES+) *m/z* for C₁₁H₂₁O₂ [M+H]⁺; obs'd 185.1540, calc'd 185.1542.

(2*R*,10*R*)-Undecanediol (**8**)



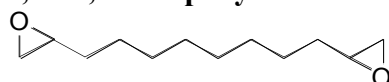
LAH ring opening of **S9** following procedures described above afforded **8** as white solid (89%). [α]_D²⁰ = -10.3, (*c* = 1.0, CHCl₃), *ee* = 95% (NMR analysis of *R*-MPA diester); ¹H NMR (CDCl₃, 300 MHz) δ 1.16 (d, 6H, *J* = 6.0 Hz), 1.36 (m, 14H), 3.75 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 23.4, 25.7, 29.5, 39.3, 68.0.¹³

1,11-Dodecadiene (S10)



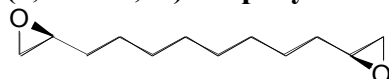
1,11-Dodecadiene was prepared from 1,10-decanediol using procedures described above for **S7** (61% over two steps). ¹H NMR (CDCl₃, 300 MHz) δ 1.31 (m, 12H), 2.00 (q, 4H), 4.94 (m, 4H), 5.78 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 28.9, 29.1, 29.4, 33.8, 114.1, 139.2.¹⁴

1,2:11,12-Diepoxydodecane (S11)

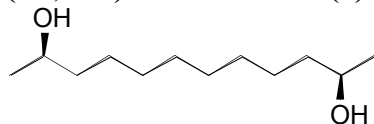


m-CPBA mediated epoxidation of **S10** as described above afforded **S11** as colorless oil (75%). ¹H NMR (CDCl₃, 300 MHz) δ 1.45 (m, 16H), 2.45 (dd, 2H, *J*₁ = 5.1 Hz, *J*₂ = 2.7 Hz), 2.73 (t, 2H, *J* = 4.5 Hz), 2.88 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.8, 29.2, 29.3, 32.3, 46.9, 52.2.⁸

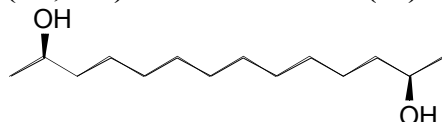
(1,2*S*:11*S*,12)-Diepoxydodecane (S12)



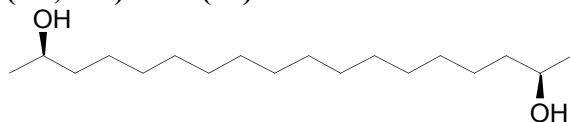
HKR of racemic 1,2:11,12-diepoxydodecane following procedures described above afforded **S12** as colorless oil (20%). [α]_D²⁰ = -14.9, (*c* = 1.0, CHCl₃), lit.^{4b,8} [α]_D²³ = -16.4, (*c* = 0.3, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.45 (m, 16H), 2.45 (dd, 2H, *J*₁ = 5.1 Hz, *J*₂ = 2.7 Hz), 2.73 (t, 2H, *J* = 4.5 Hz), 2.88 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.8, 29.2, 29.3, 32.3, 46.9, 52.2.

(2*R*,11*R*)-Dodecanediol (9)

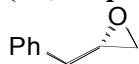
LAH ring opening of **S12** following procedures described above afforded **9** as white solid (93%). $[\alpha]_D^{20} = -8.9$, ($c = 1.0$, CHCl_3), $ee = 95\%$ (NMR analysis of *R*-MPA diester); ^1H NMR (CDCl_3 , 300 MHz) δ 1.17 (d, 6H, $J = 6.0$ Hz), 1.38 (m, 16H), 3.76 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 23.4, 25.7, 29.5, 29.6, 39.3, 68.1.¹¹

(2*R*,11*R*)-Tetradecanediol (10)

To a flame dried 50 mL round bottom flask was added magnesium turnings (514 mg, 21.4 mmol), 1,8-dibromooctane (1.46 g, 5.35 mmol) and dry THF (10 mL). The mixture was stirred under N_2 at 70 °C for 2 h then cooled to room temperature. This solution was added dropwise via syringe into a solution of (*R*)-propyleneoxide (0.62 g, 10.7 mmol) and CuI (0.21 g, 1.07 mmol) in dry THF (15 mL) at -78 °C. The resultant slurry was stirred at -78 °C for 1 h and then warmed to room temperature. After being stirred overnight, the dark blue slurry was quenched by saturated aqueous NH_4Cl and the aqueous layer was extracted by Et_2O (3×20 mL). Organic extracts were dried (Na_2SO_4), concentrated and subjected to flash chromatography (10-30 % EtOAc / hexane) to afford **10** as white solid (849 mg, 69%). $[\alpha]_D^{20} = -9.9$, ($c = 1.29$, CHCl_3), lit.^{4b,15} $[\alpha]_D^{20} = 10$, ($c = 1.04$, CHCl_3) for (2*S*,11*S*)-tetradecanediol, $ee = 95\%$ (NMR analysis of *R*-MPA diester); ^1H NMR (CDCl_3 , 300 MHz) δ 1.16 (d, 6H, $J = 6.6$ Hz), 1.30 (m, 20H), 3.77 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 23.4, 25.7, 29.49, 29.52, 29.57, 39.3, 68.0.

(2*R*,17*R*)-Diol (11)

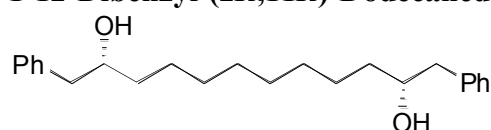
Diol **11** was prepared from 1,12-dibromododecane and (*R*)-propyleneoxide using procedures described above for **10** as white solid (51%). $[\alpha]_D^{20} = -7.4$, ($c = 0.62$, CHCl_3), $ee = 95\%$ (NMR analysis of *R*-MPA diester); ^1H NMR (CDCl_3 , 500 MHz) δ 1.16 (d, 6H, $J = 6.0$ Hz), 1.31 (m, 28H), 3.77 (m, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 23.5, 25.8, 29.57, 29.59, 29.62, 39.4, 68.2.; HRMS (ES^+) m/z for $\text{C}_{18}\text{H}_{39}\text{O}_2$ $[\text{M}+\text{H}]^+$; obs'd 287.2969, calc'd 287.2950.

(2*S*,3-Epoxypropyl)benzene (S14)

To a solution of allylbenzene (5.9 g, 50.0 mmol) in CH_2Cl_2 (90 mL) at 0 °C was added *m*-CPBA (77%, 12.32 g, 55.0 mmol). The white suspension was stirred at room temperature for 4 h monitored by TLC until completion. The reaction was quenched and washed with saturated NaHCO_3 solution (4×80 mL) followed by brine (100 mL). The organic layers were then dried (Na_2SO_4) and concentrated. The oil residue was purified by flash chromatography (5-10% EtOAc / hexane) to afford the (2,3-epoxypropyl)benzene (5.5 g, 82%) as a colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ 2.53 (m, 1H), 2.80 (t, 1H, $J = 4.8$ Hz), 2.82 (d, 1H, $J = 5.7$ Hz), 2.88 (d, 1H, $J = 5.7$ Hz), 3.15 (m, 1H), 7.28 (m, 5H)

(2,3-Epoxypropyl)benzene (5.0 g, 37.3 mmol), (*S,S*)-Salen-Co catalyst (113 mg, 0.187 mmol, 0.005 equiv), THF (0.4 mL) and HOAc (43 μ L, 45 mg, 0.746 mmol, 0.02 equiv) were added sequentially to a 25 mL round bottom flask rendering a dark red-brown solution. The mixture was cooled in ice-bath and H₂O (369 mg, 20.5 mmol, 0.55 equiv) was added in one portion. The reaction mixture was stirred for 20 h and then purified by flash chromatography (10-30% EtOAc / hexane) to afford the (2*S*,3-epoxypropyl)benzene as light brown oil (2.09 g, 42%) and 3-phenyl-1,2*R*-propyldiol as light brown oil (2.31g, 46%). Epoxide **S14**: $[\alpha]_D^{20} = -17.3$, ($c = 1.0$, EtOH), lit. $[\alpha]_D^{25S} = +17.5$, ($c = 1.94$, EtOH) for (2*R*,3-epoxypropyl)benzene, $ee = 98\%$ (comparison of optical rotation); ¹H NMR (CDCl₃, 300 MHz) δ 2.53 (m, 1H), 2.80 (t, 1H, $J = 4.8$ Hz), 2.82 (d, 1H, $J = 5.7$ Hz), 2.88 (d, 1H, $J = 5.7$ Hz), 3.15 (m, 1H), 7.28 (m, 5H)

1-12-Dibenzyl-(2*R*,11*R*)-Dodecanediol (**12**)



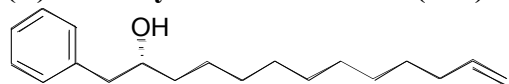
To a flame dried 25 mL round bottom flask was added grounded magnesium turnings (96 mg, 4.0 mmol), 1,6-dibromohexane (244 mg, 1.0 mmol) and dry Et₂O (5 mL). The mixture was stirred under N₂ at 50 °C for 3 h then cooled to room temperature. This solution was added dropwise via syringe into a suspension of CuI (57 mg, 0.3 mmol) in dry THF (5 mL) at -50 °C leading to white slurry. The mixture was warmed to 0 °C over 30 min and then cooled to -10 °C. followed by slow addition of (2*S*,3-epoxypropyl)benzene (268 mg, 2.0 mmol) solution in dry THF (2 mL). The resultant dark brown slurry was stirred overnight while warmed to room temperature, and was quenched by saturated aqueous NH₄Cl (20 mL). The aqueous layer was extracted by EtOAc (3 \times 20 mL). Organic extracts were dried (Na₂SO₄), concentrated and subjected to flash chromatography (5-50 % EtOAc / hexane) to afford **12** as white solid (85 mg, 24%). $[\alpha]_D^{20} = -8.3$, ($c = 0.51$, CHCl₃), $ee = 95\%$ (NMR analysis of *R*-MPA diester); ¹H NMR (CDCl₃, 300 MHz) δ 1.25-1.54 (m, 16H), 2.61 (dd, 2H, $J_1 = 8.4$ Hz, $J_2 = 13.5$ Hz), 2.80 (dd, 2H, $J_1 = 4.2$ Hz, $J_2 = 13.5$ Hz), 3.78 (m, 2H), 7.29 (m, 10H); ¹³C NMR (CDCl₃, 125 MHz) δ 25.7, 29.47, 29.54, 36.7, 44.0, 126.3, 128.4, 129.4, 138.6; HRMS (ES⁺) m/z for C₂₄H₃₄O₂Na [M+Na]⁺; obs'd 377.2445, calc'd 377.2457.

10-Bromodec-1-ene (**S15**)

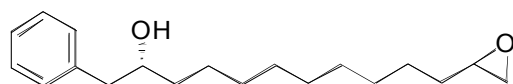


To a solution of 9-decene-1-ol (1.56 g, 10 mmol) and CBr₄ (3.98 g, 12 mmol) in dry CH₂Cl₂ (10 mL) at 0 °C, was added Ph₃P (3.15 g, 12 mmol) portionwise. The resulting brown-orange slurry was stirred for 2 h and warmed to RT. After further stirring for 1 h, TLC indicated completion and the solvent was then removed under reduced pressure. The brown residue was extracted with hexane (4 \times 20 mL) and filtered. Combined filtrates were concentrated and subjected to flash chromatography (hexane) to afford **S15** as light yellow oil in quantitative yield.

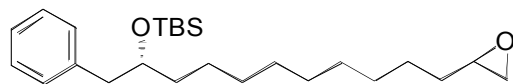
¹H NMR (CDCl₃, 300 MHz) δ 1.24-1.42 (m, 10H), 1.83 (m, 2H), 2.03 (q, 2H, $J_1 = 6.9$ Hz, $J_2 = 7.8$ Hz), 3.39 (d, 2H, $J = 6.9$ Hz), 4.89-5.01 (m, 2H), 5.75-5.84 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 28.4, 29.0, 29.1, 29.2, 29.5, 33.1, 34.0, 34.2, 114.4, 139.3.

(R)-1-Phenyltridec-12-en-2-ol (S16)

To a mixture of **S15** (1.75 g, 8.0 mmol) and magnesium turnings (384 mg, 16.0 mmol) in dry THF (10 mL), was added catalytic amount of I₂ crystals immediately leading to a dark brown solution with gently reflux. The flask was placed in heating mantle after 20 min and heated at 70 °C for 2.5 h. The solution was then cooled down and added to a suspension of CuI (76 mg, 0.4 mmol, 0.15 equiv) in dry Et₂O (10 mL) at -10 °C quickly via syringe. The slurry was stirred for 30 min and a solution of (2*S*,3-epoxypropyl)benzene (357 mg, 2.67 mmol) in dry THF (3 mL) was added at -30 °C. The resultant dark brown solution was stirred for 2 h, and was then slowly warmed to RT over 1 h. The reaction was quenched by addition of aqueous NH₄Cl (sat. 20 mL) and extracted by EtOAc (3 × 20 mL). Organic extracts were dried (Na₂SO₄), concentrated and subjected to flash chromatography (0-10 % EtOAc / hexane) to afford **S16** as colorless oil (497 mg, 68%). [α]_D²⁰ = -7.7, (*c* = 1.0, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.26-1.53 (m, 16H), 2.03 (q, 2H, *J*₁ = 6.9 Hz, *J*₂ = 14.4 Hz), 2.62 (dd, 1H, *J*₁ = 8.4 Hz, *J*₂ = 13.8 Hz), 2.62 (dd, 1H, *J*₁ = 4.2 Hz, *J*₂ = 13.5 Hz), 3.79 (m, 1H), 4.89-5.01 (m, 2H), 5.75-5.86 (m, 1H), 7.28 (m, 5H); ¹³C NMR (CDCl₃, 125 MHz) δ 25.7, 28.9, 29.1, 29.4, 29.51, 29.57, 29.61, 33.8, 36.8, 44.0, 72.7, 114.1, 126.4, 128.5, 129.4, 138.6, 139.2; HRMS (ES⁺) *m/z* for C₂₄H₃₄O₂ [M+H]⁺; obs'd 355.2636, calc'd 355.2627.

S17

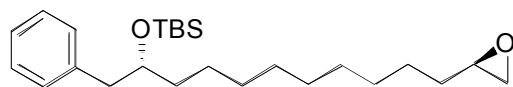
To a solution of **S16** (800 mg, 2.92 mmol) in CHCl₃ (20 mL) at 0 °C was added *m*-CPBA (77%, 786 mg, 3.5 mmol). The white suspension was stirred overnight at room temperature, then was quenched and washed by saturated NaHCO₃ solution (4 × 30 mL) and brine (30 mL). The organic layers were then dried (Na₂SO₄), concentrated and subjected to flash chromatography (0-30 % EtOAc / hexane) to afford **S17** as colorless oil (557 mg, 68%). [α]_D²⁰ = -8.0, (*c* = 1.0, CHCl₃); ¹H NMR (CDCl₃, 500 MHz) δ 1.27-1.52 (m, 18H), 2.44 (q, 1H, *J*₁ = 2.5 Hz, *J*₂ = 5 Hz), 2.63 (dd, 1H, *J*₁ = 8.5 Hz, *J*₂ = 13.5 Hz), 2.72 (t, 1H, *J* = 4.0 Hz), 2.81 (dd, 1H, *J*₁ = 4.0 Hz, *J*₂ = 13.5 Hz), 2.88 (m, 1H), 3.79 (m, 1H), 7.28 (m, 5H); ¹³C NMR (CDCl₃, 125 MHz) δ 25.7, 25.9, 29.36, 29.40, 29.45, 29.50, 29.56, 32.4, 36.8, 44.0, 47.1, 52.3, 72.6, 126.3, 128.5, 129.4, 138.6, 139.2; HRMS (ES⁺) *m/z* for C₁₉H₃₀O₂Na [M+Na]⁺; obs'd 313.2132, calc'd 313.2144.

S18

To a solution of alcohol in epoxy alcohol **S17** (500 mg, 1.72 mmol), DMAP (42 mg, 0.34 mmol) and imidazole (288 mg, 4.30 mmol) in dry CH₂Cl₂ (10 mL) at 0 °C was added TBSCl (285 mg, 1.90 mmol). The mixture was stirred overnight at RT and quenched by saturated NH₄Cl solution (20 mL). The aqueous layer was extracted with CH₂Cl₂ (20 mL) and the combined organic layers were then dried (Na₂SO₄), concentrated and subjected to flash chromatography (0-5 % EtOAc / hexane) to afford **S18** as colorless oil (653 mg, 94%). [α]_D²⁰ = -7.0, (*c* = 0.6, CHCl₃); ¹H NMR (CDCl₃, 500 MHz) δ -0.22 (s, 3H), -0.08 (s, 3H), 0.83 (s, 9H), 1.24-1.52 (m, 18H), 2.44 (dd, 1H, *J*₁ = 2.7 Hz, *J*₂ = 5.1 Hz), 2.69 (dd, 2H, *J*₁ = 4.0 Hz, *J*₂ = 6.5 Hz), 2.72 (t, 1H, *J* = 4.0 Hz), 2.88 (m, 1H), 3.79 (m, 1H), 7.22 (m, 5H); ¹³C

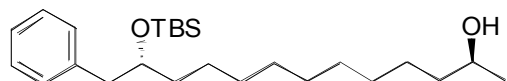
NMR (CDCl₃, 125 MHz) δ -4.9, -4.7, 18.1, 25.2, 25.89, 25.95, 29.42, 29.45, 29.50, 29.56, 29.7, 32.5, 37.0, 44.0, 47.1, 52.4, 73.8, 125.9, 128.0, 129.7, 139.5.

S19



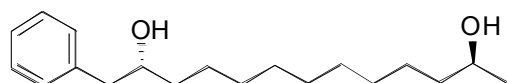
Racemic epoxide **S18** (315 mg, 0.78 mmol), (*R,R*)-Salen-Co catalyst (4.8 mg, 0.0078 mmol, 0.01 equiv), THF (0.2 mL) and HOAc (1.8 μ L, 1.9 mg, 0.0312 mmol, 0.04 equiv) were added sequentially to a 4 mL vial rendering a dark red-brown solution. The mixture was cooled in ice-bath and H₂O (7.7 mg, 0.429 mmol, 0.55 equiv) was added in one portion. The reaction mixture was stirred for 22 h and then purified by flash chromatography (0-5% EtOAc / hexane) to afford the **S19** as colorless oil (162 mg, 51%) with the ring opening diol as colorless oil (150 mg, 47%). Epoxide **S19**: $[\alpha]_D^{20} = -6.1$, ($c = 1.0$, CHCl₃); ¹H NMR (CDCl₃, 500 MHz) δ -0.22 (s, 3H), -0.08 (s, 3H), 0.83 (s, 9H), 1.24-1.52 (m, 18H), 2.44 (dd, 1H, $J_1 = 2.7$ Hz, $J_2 = 5.1$ Hz), 2.69 (dd, 2H, $J_1 = 4.0$ Hz, $J_2 = 6.5$ Hz), 2.72 (t, 1H, $J = 4.0$ Hz), 2.88 (m, 1H), 3.79 (m, 1H), 7.22 (m, 5H); ¹³C NMR (CDCl₃, 125 MHz) δ -4.9, -4.7, 18.1, 25.2, 25.89, 25.95, 29.42, 29.45, 29.50, 29.56, 29.7, 32.5, 37.0, 44.0, 47.1, 52.4, 73.8, 125.9, 128.0, 129.7, 139.5; HRMS (ES⁺) m/z for C₂₅H₄₅O₂Si [M+H]⁺; obs'd 405.3170, calc'd 405.3189.

S20



To a solution of **S19** (45 mg, 0.111 mmol) in dry Et₂O (1 mL) at 0 °C was added LAH (8.5 mg, 0.223 mmol). The mixture was stirred for 2 h until completion, then was quenched with Et₂O (5 mL), H₂O (0.6 mL), and NaOH (2M, 0.2 mL). The mixture was stirred for 30 min and filtered through celite. The organic layer was dried and concentrated to afford the pure **S20** (43.5 mg, 96%) as a colorless oil. $[\alpha]_D^{20} = -4.9$, ($c = 0.44$, CHCl₃); *ee* = 95% (NMR analysis of *R*-MPA diester); ¹H NMR (CDCl₃, 500 MHz) δ -0.22 (d, 3H, $J = 4.0$ Hz), -0.07 (d, 3H, $J = 4.0$ Hz), 0.83 (s, 9H), 1.16 (d, 3H, $J = 6.0$ Hz), 1.24-1.44 (m, 18H), 2.69 (m, 2H), 3.79 (m, 2H), 7.23 (m, 5H); ¹³C NMR (CDCl₃, 125 MHz) δ -4.9, -4.7, 18.1, 23.5, 25.3, 25.76, 25.89, 29.50, 29.57, 29.59, 29.62, 29.8, 37.0, 39.4, 44.0, 68.2, 73.8, 125.9, 128.0, 129.7, 139.5; HRMS (ES⁺) m/z for C₂₅H₄₇O₂Si [M+H]⁺; obs'd 407.3339, calc'd 407.3345.

13

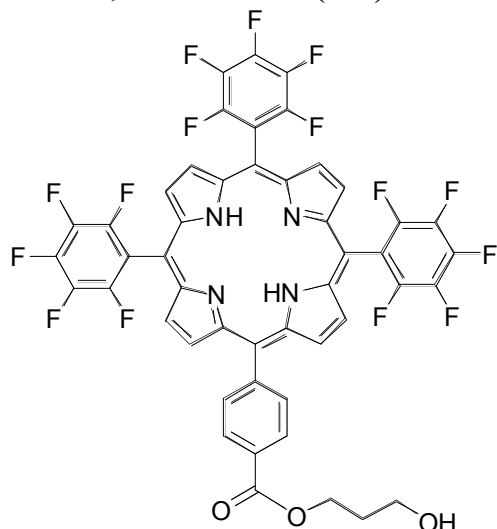


To a solution of **S20** (20 mg, 0.049 mmol) in dry THF (1 mL) at 0 °C was added TBAF (1 M in THF, 59 μ L, 0.059 mmol). The mixture was stirred for 4 h until completion, then was quenched with saturated NH₄Cl solution (3 mL) and CH₂Cl₂ (10 mL). The organic layer was dried (Na₂SO₄), concentrated and subjected to pipette column (10-50 % EtOAc / hexane) to afford **13** as white solid (13 mg, 94%). $[\alpha]_D^{20} = -6.4$, ($c = 0.2$, CHCl₃); ¹H NMR (CDCl₃, 500 MHz) δ 1.16 (d, 3H, $J = 6.0$ Hz), 1.24-1.54 (m, 18H), 2.63 (dd, 1H, $J_1 = 8.5$ Hz, $J_2 = 13.5$ Hz), 2.81 (dd, 1H, $J_1 = 4.0$ Hz, $J_2 = 13.5$ Hz), 3.79 (m, 2H), 7.28 (m, 5H); ¹³C NMR (CDCl₃, 125 MHz) δ 23.5, 25.7, 29.47, 29.55, 29.60, 36.8, 39.4, 44.1, 68.2, 72.7, 126.4, 128.5, 129.4, 138.6; HRMS (ES⁺) m/z for C₁₉H₃₂O₂Na [M+Na]⁺; obs'd 315.2284, calc'd 315.2300.

Synthesis of TFPF porphyrin tweezers **B**

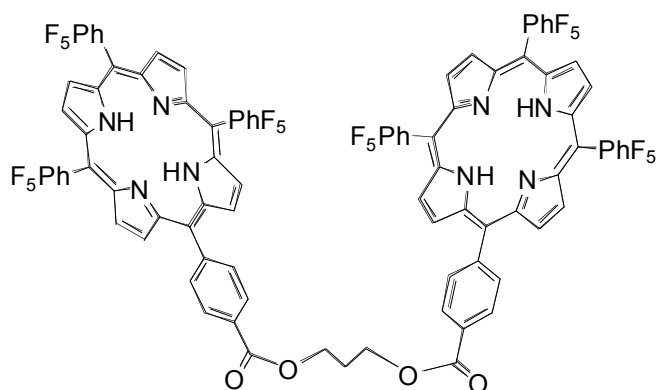
Following literature procedures,¹⁶ TFPF monolinker and tweezer were prepared.

TPFP 1,3-Monolinker (S21)



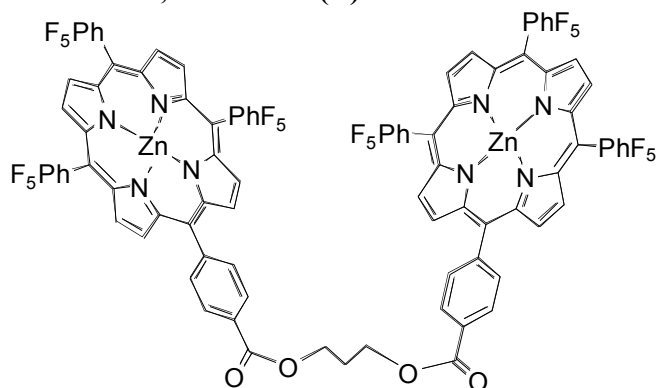
^1H NMR (CDCl_3 , 300 MHz): δ -2.88 (s, 2H), 2.17 (m, 2H), 3.93 (t, 2H, $J = 6.0$ Hz), 4.70 (t, 2H, $J = 6.0$ Hz), 8.29 (d, 2H, $J = 8.4$ Hz), 8.46 (d, 2H, $J = 8.4$ Hz), 8.82-8.91 (m, 8H); IR (film) 3322, 3107, 2930, 1717, 1518 (str.), 1499 (str.), 1402, 1275, 990, 920, 764; HRMS (ES $^+$) m/z for $\text{C}_{48}\text{H}_{22}\text{O}_3\text{N}_4\text{F}_{15}$ $[\text{M}+\text{H}]^+$; obs'd 987.1458, calc'd 987.1452.

TPFP 1,3-Tweezer (S22)



^1H NMR (CDCl_3 , 300 MHz): δ -2.88 (s, 4H), 2.58 (t, 2H, $J = 6.3$ Hz), 4.84 (t, 2H, $J = 6.3$ Hz), 8.34 (d, 4H, $J = 8.4$ Hz), 8.54 (d, 4H, $J = 8.4$ Hz), 8.13-8.94 (m, 16H); IR (film) 3322, 3105, 2928, 1719, 1518 (str.), 1499(str.), 1267, 990, 920, 764; HRMS (ES $^+$) m/z for $\text{C}_{93}\text{H}_{35}\text{O}_4\text{N}_8\text{F}_{30}$ $[\text{M}+\text{H}]^+$; obs'd 1897.2314, calc'd 1897.2302.

TPFP Zn-1,3-Tweezer (B)



^1H NMR (CDCl_3 , 300 MHz): δ 2.17 (t, 2H, $J = 6.3$ Hz), 4.25 (t, 4H, $J = 6.3$ Hz), 8.08 (d, 4H, $J = 8.1$ Hz), 8.22 (d, 4H, $J = 8.1$ Hz), 8.87-8.96 (m, 16H); IR (film) 3104, 2935, 1719, 1696, 1520 (str.), 1491 (str.), 1339, 1269, 988, 939, 768; HRMS (ES+) m/z for $\text{C}_{93}\text{H}_{31}\text{O}_4\text{N}_8\text{F}_{30}\text{Zn}_2$ $[\text{M}+\text{H}]^+$; obs'd 2021.0588, calc'd 2021.0572.

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