Supporting Information

General: Solvents were freshly distilled from Na/benzophenone (THF, toluene), or P₂O₅ (CH₂Cl₂). Reactions were carried under Ar. Optical rotations were measured on a Perkin Elmer 241 digital polarimeter with a path length of 1 dm. Fast Atom Bombardment Mass Spectra (FAB-MS) were obtained with a JMS-700 spectrometer. Elemental analyses were performed by the Service d'Analyse de l'Université Pierre et Marie Curie, 75252 Paris Cedex 05, France. ¹H NMR spectra were recorded with a Bruker DRX 400 for solutions in CDCl₃ at ambient temperature. Assignment were aided by COSY experiments. ¹³C NMR spectra were recorded at 100.6 MHz with a Bruker DRX 400 spectrometer for solutions in CDCl₃ adopting 77.00 ppm for the central line of CDCl₃. Assignments were aided by J-mod technique and HMQC. Reactions were monitored by thin-layer chromatography (TLC) on a precoated plate of silica gel 60 F₂₅₄ (layer thickness 0.2 mm; E. Merck, Darmstadt, Germany) and detection by charring with sulfuric acid. Flash column chromatography was performed on silica gel 60 (230-400 mesh, E. Merck). Diisobutylaluminium was purchased from Aldrich as a 1.5 M solution in toluene.
Deprotection of CD (2)

DIBAL-H (1.5 M in toluene, 1.8 mL, 2.7 μmol) was slowly added to a solution of 2 (230 g, 92 µmol) in toluene (1 mL) under argon at r.t. The reaction mixture was heated at 50°C for 2h, then cooled to r.t. and poured on ice. The aqueous layer was extracted with EtOAc (3* 15 mL). The combined organic layers were dried (MgSO₄), filtered, and concentrated. Silica gel chromatography of the residue (cyclohexane/EtOAc, 3:1 then 2:1) gave 3 (38 mg, 19%), 4 (19 mg, 9%), and diol 1 (113 mg, 51%), as foams.

\[ \alpha \] D²⁰ = +39 (CHCl₃, c = 1.0)

RMN ¹H (400 MHz, CDCl₃) : δ = 3.44 (dd, 3 J₂,₁ = 3.2 Hz, 3 J₂,₃ = 9.9 Hz, 1H, 2-H), 3.51 (dd, 3 J₂,₁ = 3.4 Hz, 3 J₂,₃ = 9.7 Hz, 1H, 2-H), 3.61 (dd, 3 J₁,₂ = 3.9 Hz, 3 J₂,₃ = 9.7 Hz, 1H, 2-H), 3.72 (dd, 3 J₄,₃ = 3 J₄,₅ = 8.9 Hz, 1H, 4-H), 3.78-4.03 (m, 13H, 2*4-H, 3*5-H, 6*6-H, 2* OCH₂CH=CH₂), 4.05 (dd, 3 J₃,₂ = 3 J₃,₄ = 9.1 Hz, 1H, 3-H), 4.15 (dd, 3 J₃,₂ = 3 J₃,₄ = 8.8 Hz, 1H, 3-H), 4.25 (dd, 3 J₃,₂ = 9.6 Hz, 3 J₃,₄ = 7.5 Hz, 1H, 3-H), 4.38 (d, 2 J = 12.8 Hz, 1H, 1*CHPh), 4.41 (d, 2 J = 12.8 Hz, 1H, 1*CHPh), 4.48 (d, 2 J = 12.2 Hz, 1H, 1*CHPh), 4.50 (d, 2 J = 11.9 Hz, 1H, 1*CHPh), 4.54 (d, 2 J = 12.6 Hz, 1H, 1*CHPh), 4.58 (d, 2 J = 12.6 Hz, 1H, 1*CHPh), 4.65 (d, 2 J = 12.2 Hz, 1H, 1*CHPh), 4.72 (d, 3 J₁,₂ = 3.3 Hz, 1H, 1-H), 4.76 (d, 3 J₁,₂ = 3.4 Hz, 1H, 1-H), 4.79 (d, 2 J = 9.8 Hz, 2H, 2*CHPh), 4.82 (d, 2 J = 9.0 Hz, 1H, 1*CHPh), 4.93 (d, 2 J = 11.0 Hz, 1H, 1*CHPh), 5.18 (d, 2 J = 1.0 Hz, J cis = 10.4 Hz, 1H, OCH₂CH=CH₂), 5.22 (d, 2 J = 10.8 Hz, 1H, 1*CHPh), 5.25 (d, 2 J = 1.5 Hz, J trans = 17.3 Hz, 1H, OCH₂CH=CH₂), 5.49 (d, 2 J = 10.3 Hz, 1H, 1*CHPh), 5.79 (d, 3 J₁,₂ = 3.9 Hz, 1H, 1-H), 5.85 (ddt, J cis = 10.8 Hz, J trans = 16.3 Hz, 3 J = 5.8Hz, 1H, OCH₂CH=CH₂), 7.10-7.32 (m, 35H, CH arom.)

RMN ¹³C (100 MHz, CDCl₃) : δ = 61.4, 69.5, 69.9 (3*C-6), 71.2, 71.7, 72.0 (3*C-5), 72.4 (OCH₂CH=CH₂), 72.9 (CH₂Ph), 73.4 (2*CH₂Ph), 73.7 (C-4), 73.9, 76.1, 76.4 (3*CH₂Ph), 77.6 (C-2), 79.0 (C-2), 79.8 (C-2), 80.6 (C-3), 80.9 (C-3), 81.2 (C-4), 81.7 (C-3), 81.9 (C-4), 97.6 (C-1), 97.7 (C-1), 98.4 (C-1), 117.6 (OCH₂CH=CH₂), 126.3-128.3 (35*CH arom.), 134.3 (OCH₂CH=CH₂), 137.8, 137.9, 138.3, 138.6, 139.2 (5*C arom.quat.), 139.25 (2*C arom.quat.)
m/z (FAB): found [M+Na⁺] = 2337.4
[\alpha]_D^{20} = +35 (CHCl_3, c = 1.0)

RMN $^1$H (400 MHz, CDCl$_3$): $\delta = 3.46$ (dd, $^3J_{2,1} = 3.3$ Hz, $^3J_{2,3} = 9.6$ Hz, 1H, 2-H), 3.50 (dd, $^3J_{2,1} = 3.2$ Hz, $^3J_{2,3} = 9.9$ Hz, 1H, 2-H), 3.60 (dd, $^3J_{1,2} = 3.9$ Hz, $^3J_{2,3} = 9.8$ Hz, 1H, 2-Ha), 3.68 (br d, $^2J = 11.4$ Hz, 1H, 6-H), 3.75-4.03 (m, 13H, 3*4-H, 3*5-H, 5*6-H, 2* OCH$_2$CH=CH$_2$), 4.06 (dd, $^3J = 6.9$ Hz, $^3J = 8.4$ Hz, 1H, 3-H), 4.14 (dd, $^3J = 8.0$ Hz, $^3J = 9.3$ Hz, 1H, 3-H), 4.24 (dd, $^3J = 7.0$ Hz, $^3J = 9.6$ Hz, 1H, 3-H), 4.34 (d, $^2J = 12.6$ Hz, 1H, 1*CHPh), 4.40 (d, $^2J = 12.6$ Hz, 1H, 1*CHPh), 4.48 (d, $^2J = 11.9$ Hz, 1H, 1*CHPh), 4.49 (d, $^2J = 12.1$ Hz, 1H, 1*CHPh), 4.56 (d, $^2J = 12.6$ Hz, 1H, 1*CHPh), 4.62 (d, $^2J = 11.9$ Hz, 1H, 1*CHPh), 4.74 (d, $^3J_{1,2} = 3.4$ Hz, 1H, 1-H), 4.76 (d, $^3J_{1,2} = 3.4$ Hz, 1H, 1-H), 4.78 (d, $^2J = 11.7$ Hz, 1H, 1*CHPh), 4.80 (d, $^2J = 11.0$ Hz, 1H, 1*CHPh), 4.81 (d, $^2J = 11.4$ Hz, 1H, 1*CHPh), 4.93 (d, $^2J = 11.9$ Hz, 1H, 1*CHPh), 4.94 (d, $^2J = 10.3$ Hz, 1H, 1*CHPh), 5.20 (d, $^2J = 1.5$ Hz, $J_{cis} = 10.5$ Hz, 1H, OCH$_2$CH=CH$_2$), 5.23 (d, $^2J = 11.0$ Hz, 1H, 1*CHPh), 5.27 (d, $^2J = 1.6$ Hz, $J_{trans} = 17.0$ Hz, 1H, OCH$_2$CH=CH$_2$), 5.51 (d, $^2J = 10.4$ Hz, 1H, 1*CHPh), 5.79 (d, $^3J_{1,2} = 4.0$ Hz, 1H, 1-H), 5.89 (ddt, $J_{cis} = 10.5$ Hz, $J_{trans} = 16.3$ Hz, $^3J = 5.8$ Hz, 1H, OCH$_2$CH=CH$_2$), 7.09-7.33 (m, 35H, CH arom.)

RMN $^{13}$C (100 MHz, CDCl$_3$): $\delta = 61.3, 69.4, 69.7$ (3*C-6), 71.2, 71.6, 72.0 (3*C-5), 72.2, 72.4 (CH$_2$Ph, OCH$_2$CH=CH$_2$), 73.1, 73.3, 73.4 (3*CH$_2$Ph), 73.6 (C-4), 73.8 (CH$_2$Ph), 76.1, 76.5 (2*CH$_2$Ph), 77.6, 79.0, 79.8 (C-2), 80.6 (C-3), 80.9 (C-3), 81.3 (C-4), 81.6 (C-4), 81.65 (C-3), 97.7, 97.8, 98.4 (C-1), 117.6 (OCH$_2$CH=CH$_2$), 126.2-128.4 (35*CH arom.), 134.4 (OCH$_2$CH=CH$_2$), 137.8, 137.9, 138.2, 138.6, 139.2, 139.25, 139.3 (7*C arom. quat.)

m/z (FAB): found [M+Na$^+$] = 2337.1.
Deprotection of CD (5)

DIBAL-H (1.5 M in toluene, 36 mL, 54 mmol) was slowly added to a solution of 5 (4.4g, 1.8 mmol) in toluene (18 mL) under argon at r.t. The reaction mixture was heated at 50°C for 2h, then cooled to r.t. and poured on ice. The aqueous layer was extracted with EtOAc (3*60 mL). The combined organic layers were dried (MgSO₄), filtered, and concentrated. Silica gel flash chromatography of the residue (cyclohexane/EtOAc 2:1) gave 6 (3.43 g, 84%) as 1:1 mixture E:Z compounds and as a white foam.

RMN ¹H (400 MHz, CDCl₃) : δ = 3.32 (dd, J = 7.9 Hz, J = 9.5 Hz, 1H, 2-H), 3.37-3.62 (m, 9H, 5*2-H, 4*6-H), 3.70-3.77 (m, 1H, OCH₃CH=CH-CH₂O), 3.82-4.27 (m, 29H, 6*3-H, 6*4-H, 6*5-H, 8*6-H, 3*OCH₃CH=CH-CH₂O), 4.36 (d, J = 12.5 Hz, 1H, 1*CHPh), 4.43-4.60 (m, 14H, 14*CHPh), 4.62 (d, J = 12.1 Hz, 1H, 1*CHPh), 4.66 (d, J = 12.3 Hz, 1H, 1*CHPh), 4.77 (d, J = 10.4 Hz, 1H, 1*CHPh), 4.78 (d, J = 3.8 Hz, 1H, 1-H), 4.82 (d, J = 3.1 Hz, 1H, 1-H), 4.83 (d, J = 3.3 Hz, 1H, 1-H), 4.86-4.91 (m, 2H, 2*CHPh), 4.92 (d, J = 10.1 Hz, 1H, 1*CHPh), 4.95 (d, J = 10.3 Hz, 1H, 1*CHPh), 4.98 (d, J = 11.8 Hz, 1H, 1*CHPh), 4.99 (d, J = 3.4 Hz, 1H, 1-H), 5.03 (d, J = 11.8 Hz, 1H, 1*CHPh), 5.09 (d, J = 10.9 Hz, 1H, 1*CHPh), 5.27 (d, J = 10.4 Hz, 1H, 1*CHPh), 5.28 (d, J = 11.0 Hz, 1H, 1*CHPh), 5.33 (d, J = 3.9 Hz, 1H, 1-H), 5.44 (d, J = 10.1 Hz, 1H, 1*CHPh), 5.48 (d, J = 3.7 Hz, 1H, 1-H), 5.69 (t, J = 4.3 Hz, 2H, OCH₃CH=CH-CH₂O), 5.95 (t, J = 3.0 Hz, 2H, OCH₃CH=CH-CH₂O), 7.00-7.30 (m, 70H, CH arom.).

RMN ¹³C (100 MHz, CDCl₃) : δ = 66.1, 69.3, 69.4 (6*C-6), 70.8, 71.0 (2*OCH₃CH=CH-CH₂O), 70.7, 70.85, 71.2, 71.7, 71.9, 73.5 (6*C-5), 72.1, 72.4, 72.8, 72.9, 73.05, 73.1, 73.2, 73.3, 74.4, 74.7, 75.6, 75.8, 76.3, 76.4 (14* CH₂Ph), 77.9, 78.1, 78.2, 79.1, 79.15, 79.2 (6*C-2), 79.7, 80.0, 80.4, 80.5, 80.6, 83.0 (6*C-4), 80.7, 80.9, 81.1, 81.6, 81.7, 81.8 (6*C-3), 96.7, 97.1, 98.8, 99.2, 99.3, 99.35 (6*C-1), 126.6-128.3 (70*CH arom.), 129.5, 131.5 (2*OCH₃CH=CH-CH₂O), 137.9, 137.95, 138.0, 138.05, 138.1, 138.2, 138.3, 138.6, 139.15, 139.2, 139.25, 139.3, 139.4, 139.45 (14*C arom.quat.)

m/z (FAB): found [M+Na⁺] = 2309.1, Calcd. for C₁₃₈H₁₄₈O₃₀, C, 72.49; H, 6.52. Found, C, 71.97; H, 6.58
A solution of 6 (145 mg, 63 \( \mu \text{mol} \)), pyridine (41 \( \mu \text{L}, 0.5 \text{ mmol} \)) and tert-butyldimethylsilyltrifluoromethanesulfonate (116 \( \mu \text{L}, 0.5 \text{ mmol} \)) in dichloromethane (2.5 mL) was stirred at r.t. for 2h, diluted with dichloromethane (10 mL), washed with aq. sat. NH\(_4\)Cl (2*5mL), dried (MgSO\(_4\)), filtered and concentrated. Silica gel flash chromatography (cyclohexane/EtOAc 6:1) on silica gel gave a disilylated compound (150 mg, 95\%) directly used in the next step. Grubbs catalyst (9.8 mg, 12 \( \mu \text{mol} \)) was added to stirred solution of this compound (150 mg, 60 \( \mu \text{mol} \)) in degassed dichloromethane (3.6 mL), under ethylene at r.t. The reaction mixture was stirred at r.t. under ethylene atmosphere for 18h, then Grubbs catalyst (9.8 mg, 12 \( \mu \text{mol} \)) was added and the reaction mixture was stirred for additional 30h at r.t., then treated with Pb(OAc)\(_4\) (16 mg, 36 \( \mu \text{mol} \)), stirred under argon for 3h, concentrated and purified by silica gel flash chromatography (cyclohexane/EtOAc 10:1) to give 7 (112 mg, 70\%) as a white foam.

\([\alpha]_D^{20} = +35 \text{ (CHCl}_3, c = 1.1)\]

RMN \(^1\text{H} \text{ (400 MHz, CDCl}_3) : \delta = 0.01 \text{ (s, 6H, CH}_3\text{Si), 0.04 (s, 6H, CH}_3\text{Si), 0.90 (s, 18H, (CH}_3\text{)}_2\text{Si), 3.35-3.50 (m, 6H, 6*2-H), 3.55-4.05 (m,28H, 4*OCH}_2\text{CH=CH}_2, 6*4-H, 6*5-H, 12*6-H), 4.10-4.25}
\( \text{ (m, 6H, 6*3-H), 4.30 (br d, 4H, 4*CHPh), 4.42-4.70 (m, 12H, 12*CHPh), 4.80-4.95 (m, 6H, 6*CHPh), 5.00 (d, 3J}_1,2\text{= 3.2 Hz, 2H, 2*1-H), 5.08-5.30 (m, 16H, 6*CHPh, 4*1-H, 4*OCH}_2\text{CH=CH}_2), 5.74-5.84 (dtt, 3J}_\text{cis} = 10.5 Hz, 3J}_\text{trans} = 16.0 Hz, 2H, 2*OCH}_2\text{CH=CH}_2\text{CH}_2\text{), 7.18-7.31 (m, 70H, CH arom.)} \]

RMN \(^{13}\text{C} \text{ (100 MHz, CDCl}_3) : \delta = -5.1 \text{ (2*CH}_3\text{Si), -4.9 (2*CH}_3\text{Si), 18.3 (2*(H}_3\text{C})_3\text{S}, 25.9}
\( \text{(3*(H}_3\text{C})_3\text{CS), 26.0 (3*(H}_3\text{C})_3\text{CS), 62.4 (2*C-6), 68.85 (2*C-6), 69.0 (2*C-6), 71.3, 71.4, 72.5 (6*C-6), 72.2, 72.4, 72.8, 72.9, 73.3 (2*CH}_2\text{Ph, 2*OCH}_2\text{CH=CH}_2\text{CH}_2\text{), 75.1, 75.4, 75.7 (6*CH}_2\text{Ph), 78.1 (2*C-4), 78.75 (4*C-4), 78.8, 79.0, 79.1 (6*C-2), 80.7, 81.1, 81.2 (6*C-3), 98.0, 98.3, 98.4 (6*C-1), 116.9}
\( \text{(2*OCH}_2\text{CH=CH}_2\text{CH}_2\text{), 126.8-138.6 (70*CH arom.), 132.2 (2* OCH}_2\text{CH=CH}_2\text{CH}_2\text{), 138.1, 138.2, 138.25, 138.3 (8*C arom.quat), 139.25, 139.3, 139.4 (6*C arom.quat.)} \]

m/z (FAB): found [M+Na\(^+\)] = 2565.2, Calcd. for C\(_{152}\)H\(_{180}\)O\(_{30}\)Si\(_{12}\), C, 71.78; H, 7.13. Found, C, 71.81; H, 7.15