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Synthesis of macrocyclic derivatives with di-sucrose scaffold

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Dedicated to Prof. Jacek Młochowski on the occasion of his 80th birthday

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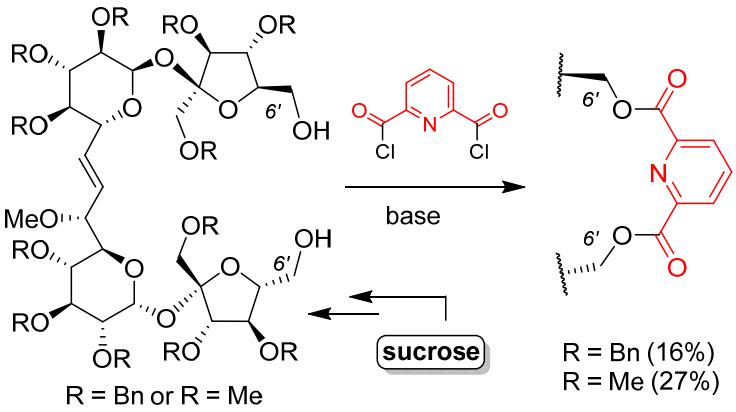
Abstract

Two macrocyclic derivatives with a di-sucrose scaffold were obtained by cyclization of the corresponding di-sucrose diol with pyridine-2,6-dicarboxylic acid. The cyclization step was very sensitive to steric hindrance; the macrocycle with a bulky benzyl groups was formed in only 16% yield, while application of smaller methyl blocking groups afforded the corresponding cyclic derivative in 27% yield.



Keywords: Sucrose, macrocyclization, sugars, Wittig type reaction

Introduction

Chiral crown and aza-crown derivatives are important targets in supramolecular chemistry.[1] Many of them possess interesting complexing properties, being able to enantioselectively recognize guests. Carbohydrates are often used as platforms for the construction of macrocyclic receptors in optically pure form.[2-5] This refers, however, mostly to monosaccharides;[6-11]application of di-saccharides in chiral scaffolds has been rather limited.[12-14]

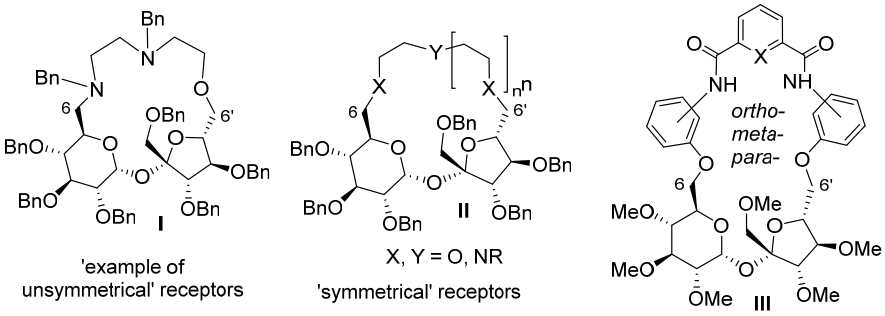


Figure 1. Examples of macrocyclic derivatives with sucrose scaffold.

We have reported that the most common di-saccharide, sucrose, can be efficiently used as a chiral platform for the preparation of crown and aza-crown analogs[15] (see examples: **I** and **II** in Figure 1), able to differentiate chiral ammonium cations.[16-18] More complex structures, such as *e.g.* **III** are also available from sucrose.[19-21]

Looking for a different type of macrocyclic derivative with a sucrose scaffold, we turned our attention to compounds in which the terminal positions of this di-saccharide are connected *via* a carbon bridge (Figure 2). We hoped that this type of derivative may give a new insight into the properties of such sucrose-based macrocycles.

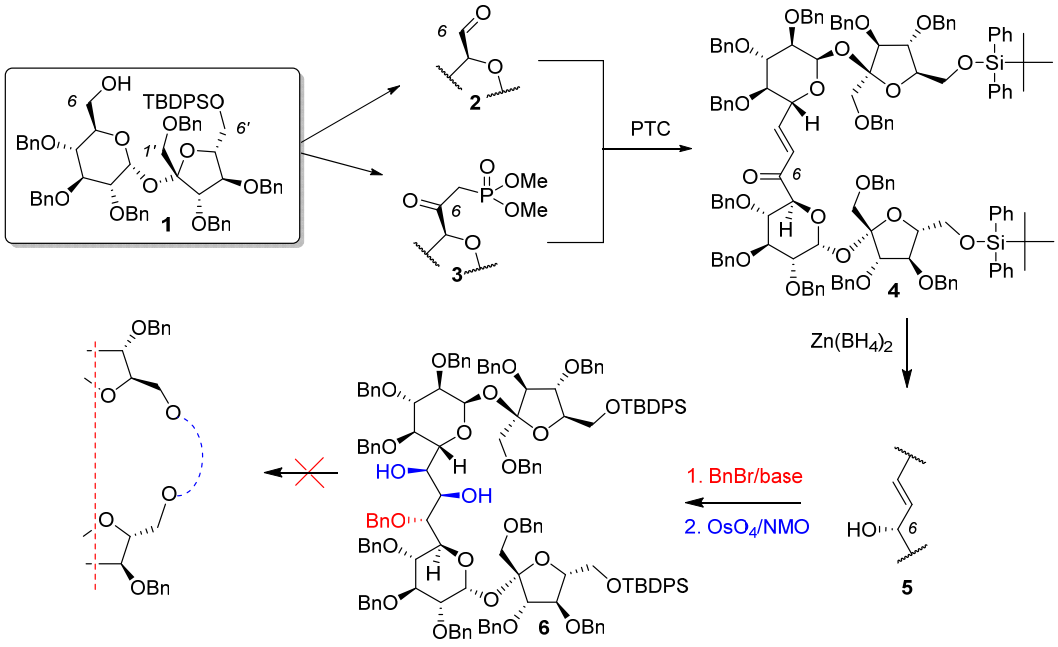


Figure 2. Synthesis of a precursor **6** of complex macrocyclic derivatives with a sucrose scaffold.

Previously, we showed that reaction of aldehyde **2** with phosphonate **3** – both prepared from the selectively protected sucrose **1** – afforded enone **4** with two sucrose units in the molecule.[22] Stereoselective reduction of the enone system in **4** with zinc borohydride[23] afforded allylic alcohol **5** with the expected *R*-configuration at the newly created stereogenic center. Olefin **5** was converted into diol **6** (Figure 2).[22] However, we were not able to connect the terminal positions of **6**.

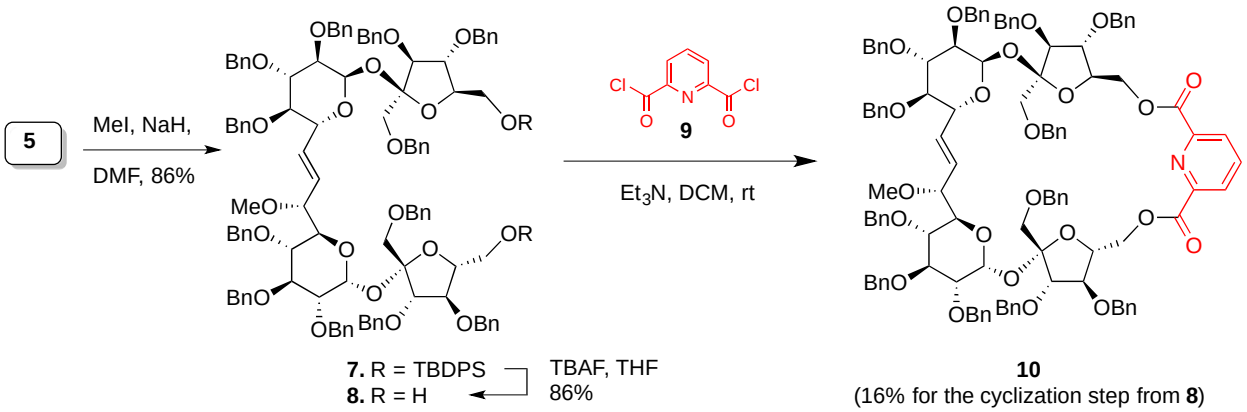
Now, we can present new results on the successful cyclization of such a di-saccharide dimer. The results presented here provide a useful route to the unknown macrocyclic derivatives with sucrose scaffold.

Results and Discussion

The protection of both hydroxyl groups in diol **6**, which was necessary for further functionalization of the terminal positions, was very problematic. The most convenient blocking group for these positions would be a benzyl group; however, all attempts (BnBr/NaH, BnCl/PTC) to introduce benzyl groups failed, most probably for steric reasons.

The strategy was therefore changed. The free hydroxyl group in **5** was protected as a methyl ether (→ **7**) and the silyl blocking groups were removed with fluoride to give diol **8**.

Treatment of this diol with pyridine-2,6-dicarboxylic acid dichloride (**9**) in basic media afforded macrocyclic compound **10** albeit in low yield (16%). Its structure was confirmed by advanced NMR (see supplementary information) and MS data in which an ion at 1926.793 Da, which correspond to structure **10** [($C_{117}H_{117}O_{23}N$) + Na^+], was observed.

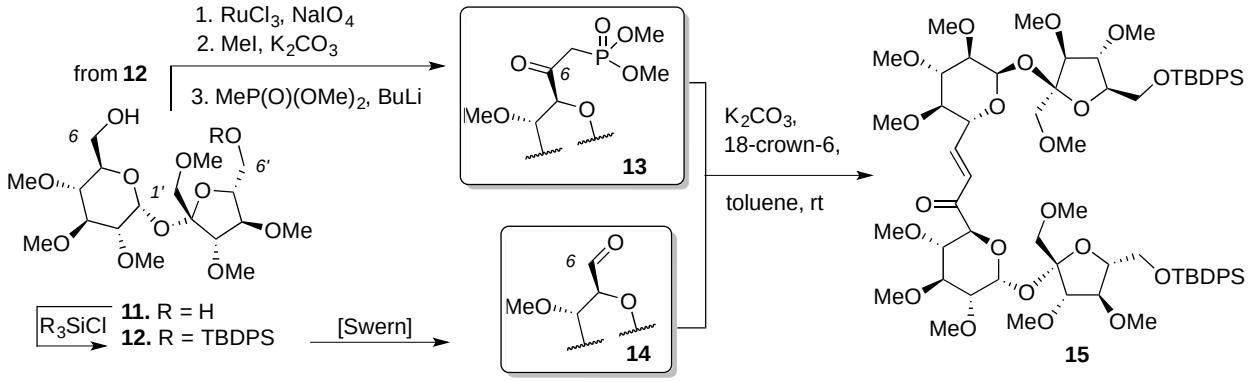


Scheme 1. Preparation of macrocycle **10** with a di-sucrose unit in the molecule

The per-benzylated derivatives could, potentially, be deprotected to hydrosoluble derivatives. However, our goal was to elaborate a route which can provide a macrocycle in reasonable yield. We reasoned that the low yield of the formation of **10** may result from the presence of bulky benzyl groups in the molecule. Thus, replacement of these blocking groups for smaller ones should improve the cyclization step. Methyl groups were, therefore, chosen to test our hypothesis.

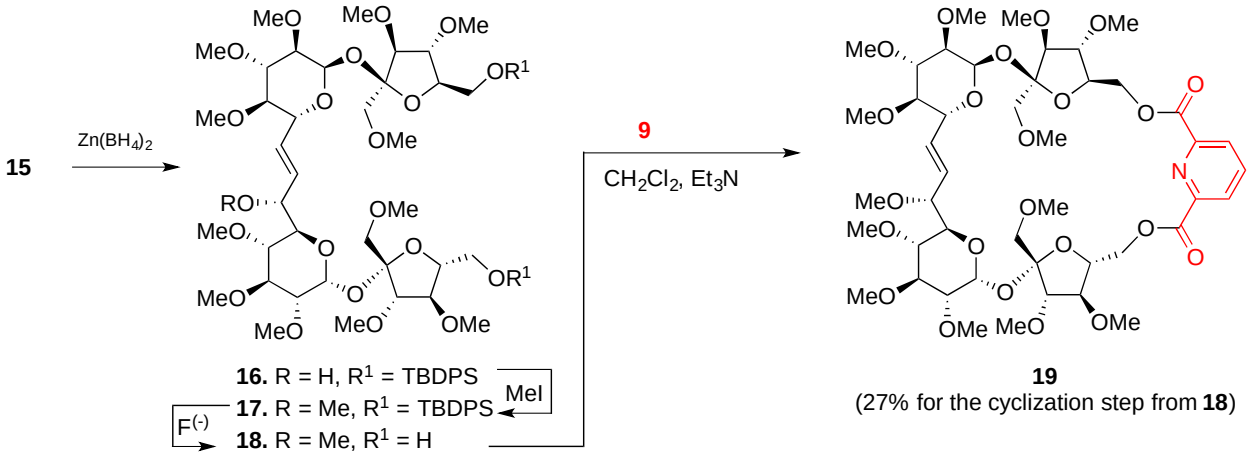
The synthesis of the per-methylated analog was initiated from the known hexa-*O*-methylsucrose[11] (**11**) which was protected at the '*fructose end*' (C-6') with TBDPS-Cl. The resulting alcohol **12** was converted into phosphonate **13** and separately into aldehyde **14** according to the methodology already applied in the

synthesis of the benzylated analog.[22] Reaction between aldehyde **14** and phosphonate **13** under PTC conditions[24,25] afforded enone **15** in good yield (Scheme 2).



Scheme 2. Preparation of enone **15**, based on hexa-*O*-methylsucrose.

Reduction of the carbonyl group in **15** with zinc borohydride, by analogy with the benzylated compound **5**,[22] provided alcohol **16** as a single stereoisomer. Protection of the hydroxyl group as methyl ether (→ **17**) and removal of the silyl blocking groups furnished diol **18**. Treatment of this diol with dichloride **9** led to macrocycle **19** in 27% yield (Scheme 3). The presence of an ion at 1014.4158 Da, clearly pointed at the structure **19** [M($C_{45}H_{69}O_{23}N$) + Na^+]; further confirmation came from advanced NMR experiments (see Experimental Section and supplementary information).

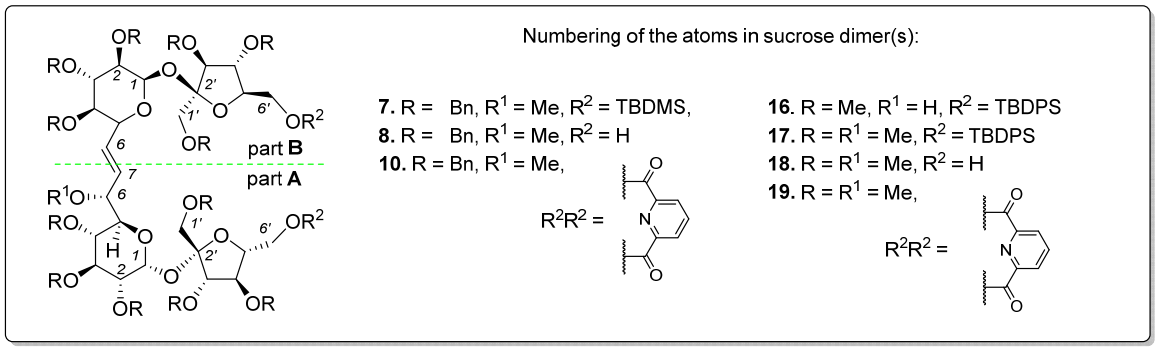


Scheme 3. Preparation of macrocycle **19** with a di-sucrose unit in the molecule.

We have prepared two new macrocyclic derivatives with a di-sucrose scaffold. Their synthesis was realized via a relatively short pathway, starting from the readily available hexa-*O*-benzyl or hexa-*O*-methylsucrose. The latter compounds were converted into di-sucrose open-chain derivatives under rather standard conditions, providing either benzylated diol **8** or methylated analog **18**. Both compounds were reacted with 2,6-pyridine-dicarboxylic acid dichloride to afford macrocyclic derivatives **10** and **19** respectively. The cyclization step was highly dependent on the steric factors. Changing the bulky benzyl protecting groups for methyl groups almost double the yield of the final product (16% for **10** *vs*. 27% for **19**).

Experimental Section

General. NMR spectra were recorded in $CDCl_3$ (internal Me_4Si) with a Varian AM-600 (600 MHz ^1H, 150 MHz ^{13}C) spectrometer at rt. Chemical shifts (δ) are reported in ppm relative to Me_4Si (δ 0.00) for ^1H and residual chloroform (δ 77.00) for ^{13}C. All significant resonances (carbon skeleton) were assigned by COSY (^1H-^1H), HSQC (^1H-^{13}C), and HMBC (^1H-^{13}C) correlations. The aromatic resonances occurring in the typical range were omitted for simplicity. Reagents were purchased from Sigma-Aldrich, Alfa Aesar or ABCR, and used without purification. Commercially available solvents were used without purification. Hexanes (65-80 °C fraction from petroleum) and EtOAc were purified by distillation. TLC was carried out on silica gel 60 F254 (Merck). Chromatography was performed on Buchi glass columns packed with silica gel 60 (230-400 mesh, Merck), or GraceResolv™ (40 μm) columns and Reveleris® from GRACE. Organic solutions were dried over $MgSO_4$. Specific rotation was measured with a Jasco DIP-360 digital polarimeter for solution in CH_2Cl_2 (c = 0.5) at rt.



Compound 7. To a solution of alcohol **5**[22] (2.80 g, 1.25 mmol) in DMF (50 mL), NaH (300 mg of a ~50% suspension in mineral oil) was added followed by MeI (0.78 mL, 12.5 mmol), and the mixture was stirred at rt overnight. The excess of hydride was decomposed by careful addition of H_2O (0.5 mL) and the mixture was partitioned between H_2O (100 mL) and Et_2O (100 mL). The organic phase was separated and the aqueous one extracted with Et_2O (3 × 50 mL). The combined organic solutions were washed with H_2O (5 × 50 mL), dried, and concentrated. Chromatographic purification of the residue (hexane/EtOAc, 9:1) afforded **7** (2.54 g, 90%). $[\alpha]_D$ = 27.8; ^1H-NMR δ: 5.85 (H1-B, *d*, *J* 3.5 Hz, 1H), 5.78 (H7-A, *dd*, *J* 15.9, 9.0 Hz, 1H), 5.59 (H6-B, *dd*, *J* 15.8, 5.9 Hz, 1H), 5.49 (H1-A, *d*, *J* 3.5 Hz, 1H), 4.46 (H5-B, *m*, 1H), 4.43 (H3-B, *m*, 1H), 4.40 (H3'-A, *m*, 1H), 4.29 (H4'-B, *m*, 1H), 4.27 (H4'-A, *m*, 1H), 4.20 (H5-A, *dd*, *J* 10.4, 1.4 Hz, 1H), 4.09 (H5'-A, *m*, 1H), 4.04 (H5'-B, *m*, 1H), 4.03 (H6'-B, *m*, 1H), 3.98 (H6'-B, *m*, 1H), 3.98 (H6'-A, *m*, 1H), 3.93 (H6'-A, *m*, 1H), 3.85 (H3-B, *m*, 1H), 3.79 (H1'-B, m, 1H), 3.74 (H3-A, *m*, 1H), 3.74 (H1'-A, *m*, 1H), 3.52 (H1'-A, *m*, 1H), 3.50 (H1'-B, *m*, 1H), 3.40 (H2-B, *dd*, *J* 9.7, 3.6 Hz, 1H), 3.16 (H4-A, H4-B, *dd*, J 9.7, 9.1 Hz, 2H), 2.94 (OMe, *s*, 3H), 2.92 (H2-A, *dd*, *J* 9.7, 3.5 Hz, 1H), 1.02 [2×$SiPh_2C(\underline{CH_3})_3$, 18H].

^{13}C-NMR δ: 104.42 (C1-A), 104.34 (C1-B), 89.94 (C1-A), 89.83 (C1-B), 84.38 (C3'-B), 84.26 (C3'-A), 84.05 (C4'-A), 83.22 (C4'-B), 82.07 (C5'-A), 82.03 (C6-A), 81.97 (C4-B), 81.64 (C5'-B), 81.63 (C3-B), 81.54 (C3-A), 80.35 (C2-A), 79.91 (C2-B), 78.18 (C4-A), 72.29 (C5-A), 75.60, 75.17, 74.51, 74.10, 73.53, 73.25, 73.14, 72.83, 72.66, 72.62, 71.96, 71.85 (12×OCH_2Ph), 70.88 (C1'-B), 70.23 (C5-B, C1'-A), 66.34 (C6'-B), 65.65 (C6'-A), 56.05 (OMe), 26.90, 26.95 [2×$Si(Ph)_2C(\underline{CH_3})_3$], 19.27, 19.30 (2×$C_{quat}$). MS *m/z*: [$M(C_{142}H_{152}O_{21}Si_2) + Na^+$]; calcd: 2272.0262; found: 2272.0278; Analysis: calcd. for $C_{142}H_{152}O_{21}Si_2$: C, 75.77; H, 6.81; found: C, 75.87; H, 6.89%.

Compound 8. To a solution of compound **7** (403 mg, 0.17 mmol) in THF (10 mL), TBAF (1M solution in THF; 0.37 mL, 2.1 equiv.) was added and the mixture was kept at rt overnight. Then it was partitioned between H_2O (20 mL) and CH_2Cl_2. The organic phase was separated, washed with H_2O, concentrated, and the residue was

purified by chromatography (hexane/EtOAc, 4:1 to 2:1) to afford **8** (273 mg, 86%) as an oil. $[\alpha]_D$ = 31.7; ^{1}H-NMR δ: 5.88 (H7-A, *dd*, *J* 15.6, 8.9 Hz, 1H), 5.65 (H6-B, *dd*, *J* 15.9, 5.3 Hz, 1H), 5.52 (H1-A, *d*, *J* 3.4 Hz, 1H), 5.45 (H1-B, *d*, *J* 3.3 Hz, 1H), 4.48 (H3'-A, *m*, 1H), 4.46 (H5-B, *m*, 1H), 4.36 (H4'-B, *m*, 1H), 4.33 (H4'-A, *m*, 1H), 4.29 (H5-A, *m*, 1H), 3.98 (H3-B, *m*, 1H), 3.97 (H5'-B, *m*, 1H), 3.95 (H3-A, *m*, 1H), 3.94 (H5'-A, *m*, 1H), 3.85 (H6-A, *d*, *J* 9.6 Hz, 1H), 3.79 (H6'-A, *m*, 1H), 3.74 (H1'-A, *m*, 1H), 3.70 (H6'-A, *m*, 1H), 3.68 (H6'-B, *m*, 1H), 3.59 (H1'-B, *m*, 1H), 3.50 (H1'-A, *m*, 1H), 3.48 (H4-A, *m*, 1H), 3.47 (H1'-B, *m*, 1H), 3.47 (H6'-B, *m*, 1H), 3.45 (H2-B, *m*, 1H), 3.29 (H2-A, *dd*, *J* 9.7, 3.4 Hz, 1H), 3.21 (H4-B, *d*, *J* 9.4 Hz, 1H), 3.18 (OCH_3, *s*, 3H), 3.00 (H5'-B, *dd*, *J* 9.6, 2.7 Hz, 1H). ^{13}C-NMR δ: 104.23 (C2'-A), 104.03 (C2'-B), 90.89 (C2-A), 90.63 (C2-B), 84.38 (C4'-B), 83.57 (C5-B), 82.97 (C4-B), 81.84 (C3-B), 81.60 (C3-A), 81.45 (C5'-A), 81.42 (C5'-B), 81.33 (C6-A), 81.24 (C4'-A), 80.70 (C5-A), 79.80 (C2-A), 79.46 (C2-B), 77.54 (C4-A), 75.53, 75.06, 74.82, 74.15 73.50, 73.41, 73.30, 73.27, 72.88, 72.73, 72.51, 72.37 (12×OCH_2Ph), 71.23 (C1'-B), 70.64 (C1'-A), 70.52 (C3'-A), 61.97 (C6') 61.41 (C6'-B), 56.36(OMe). MS *m/z*: [M($C_{110}H_{116}O_{21}$) + 2Na+]; calcd.: 909.3902; found: 909.3887; Analysis: calcd. for $C_{110}H_{116}O_{21}$ (1772.82 Da): C 74.47; H 6.59; found: 74.46; H 6.47%.

Cyclization of compound 8; synthesis of macrocycle 10. *This reaction was carried out under an argon atmosphere with the exclusion of moisture*. To a solution of **8** (100 mg, 0.056 mmol) in dry CH_2Cl_2 (12 mL), Et_3N (0.23 mL, 0.169 mmol) was added followed by solution of di-chloride **9** (13.8 mg, 0.068 mmol in 0.15 mL of CH_2Cl_2). The mixture was stirred for 75 h at rt. (TLC monitoring in hexane/EtOAc, 2:1) and then concentrated in vacuum. The residue was purified by column chromatography (hexane/EtOAc, 4:1 to 1:1) to afford the title product **10** (15 mg, 16%). ^{1}H-NMR δ: 5.88 (H7-A, *dd*, *J* 15.6, 8.9 Hz, 1H), 5.64 (H6-B, *dd*, *J* 15.8, 6.0 Hz, 1H), 5.54 (H1-A, *d*, *J* 3.4 Hz, 1H), 5.33 (H1-B, *d*, *J* 3.4 Hz, 1H), 4.89 (H6'-B, *m*, 2H), 4.85 (H6'-A, *m*, 1H), 4.65 (H6'-A, *m*, 4H), 4.64 (H5-B, *m*, 1H)), 4.37 (H3'-B;H4'-B;H5'-B; H3'-A; H5'-A, *m*, 6H), 4.33 (H6'-B, *m*, 2H), 4.20 (H4'-A, *m*, 1H), 3.99 (H3-A, *m*, 1H), 3.88 (H3-B, *m*, 1H), 3.88 (H6-A, *m*, 1H), 3.62 (H1'-B, *d*, *J* 10.9 Hz, 1H), 3.52 (H1'-B, *d*, *J* 10.9 Hz, 1H), 3.40 (H2-A, m, 1H), 3.40 (H1'-A, *m*, 1H), 3.19 (H4-A, *m*, 1H), 3.18 (H4-B, *m*, 1H), 3.18 (H2-B, *m*, 1H), 3.17 (H1'-A, *m*, 1H). ^{13}C-NMR δ: 165.11 and 164.37 (2×C=O), 104.39 (C2'-B), 103.92(C2'-A), 89.39 (C1-B), 89.35 (C1-A), 83.22 (C3'-B), 83.12 (C3'-A), 83.11 (C5'-B), 83.09 (C5'-A), 82.46 (C2-B), 82.25 (C3-B), 81.73 (C6-A), 81.35 (C3-A), 80.08 (C4-B), 79.56 (C2-A), 78.28 (C4-A), 76.33 (C4'-B), 75.95 (C4'-A), 73.12 (C5-A), 75.48, 75.20, 74.60, 74.18, 73.34, 73.21, 72.92, 72.81, 72.79, 72.62, 72.51, 72.25 (12×OCH_2Ph), 71.86 (C1'-B), 71.40 (C1'-A), 71.00 (C5-B), 66.60 (C6'-A), 64.83 (C6'-B), 55.93 (OCH_3). MS *m/z*: [M($C_{117}H_{117}O_{23}N$) + Na^+]; calcd.: 1926.7914; found: 1926.7930

1',2,3,3',4,4'-Hexa-O-methyl-6'-*O*-*tert*-butyl-diphenylsilylsucrose 12. *This reaction was carried out under an argon atmosphere with the exclusion of moisture*. To a solution of 1',2,3,3',4,4'-hexa-*O*-methylsucrose (**11**; 2.59 g; 6.08 mmol) in dry CH_2Cl_2 (50 mL) containing a catalytic amount of imidazole (12 mg), *tert*-butyldiphenylsilyl chloride (1.98 mL; 7.03 mmol, 1.2 equiv.) and Me_3N (1.27 mL, 9.12 mmol, 1.5 equiv.) were added with a syringe pump within 1 h. The mixture was stirred at rt for 24 h (TLC monitoring in hexane/EtOAc, 4:1), concentrated, and the residue was dissolved in EtOAc. The insoluble material was filtered off, the filtrate was concentrated, and the crude material was purified by column chromatography (hexane/EtOAc, 6:1 to 1:1) to afford the desired product **12** (2.21 g, 54.6%). The disilylated derivative (873 mg) and unreacted diol (296 mg) were also isolated. $[\alpha]_D$ = 50.7; ^{1}H-NMR δ: 5.91 (H1, *d*, *J* 3.6 Hz, 1H), 4.24 (H4', *m*, 1H), 4.09 (H3', *d*, *J* 8.4 Hz, 1H), 4.00 (H6' a/b, *dd*, *J* 11.8, 2.7 Hz, 1H), 3.88 (H5, *m*, 1H), 3.79 (H6 b/a, *m*, 1H), 3.76 (H6' b/a, *dd*, *J* 11.8, 3.5 Hz, 1H), 3.72 (H5', *m*, 1H), 3.61 (H6 a/b, *m*, 1H), 3.59 (OCH_3, *s*, 3H), 3.53 (OCH_3, *s*, 3H), 3.52 (H1'a/b, *m*, 1H), 3.51 (OCH_3, *s*, 3H), 3.47 (H1'b/a, *m*, 1H), 3.45 (OCH_3, *s*, 3H), 3.42 (OCH_3, *s*, 3H), 3.39 (H3, *d*, *J* 4.9 Hz, 1H), 3.37 (OCH_3, *s*, 3H), 2.99 (H2, *dd*, *J* 9.6, 4.0 Hz, 1H), 2.94 (H4, *dd*, *J* 10.1, 9.0 Hz, 1H), 1.07 [$SiPh_2C(\underline{CH_3})_3$, *s*, 9H]. ^{13}C-NMR δ: 135.70, 135.50, 133.19, 132.72, 129.84, 129.76, 127.73, 127,71 (8×Ph), 103.51 (C2'), 87.34 (C1), 85.45 (C3'), 83.21 (C3), 81.13 (C2), 80.58 (C4'), 80.33 (C4), 79.66 (C5'), 75.98 (C1'), 71.43 (C5), 62.86 (C6'), 62.58 (C6),

60.74, 60.54, 59.54, 58.85, 58.59, 57.59 (6×OCH_3), 26.81 [$SiPh_2C(\underline{CH_3})_3$], 19.26 ($C_{quat}$). MS *m/z*: [M($C_{34}H_{52}O_{11}Si$) + Na^+]; calcd.: 687.3177; found: 687.3174; Analysis calcd. for $C_{34}H_{52}O_{11}Si$ (664.33 Da): C, 61.42; H, 7.88; found: C, 61.63; H, 7.84%.

Conversion of alcohol 12 into methyl uronate. To a solution of alcohol **12** (3.57 g, 5.37 mmol) in EtOAc/MeCN/H_2O (v/v 2:3:2 (70 mL), $NaIO_4$ (4.60 g, 21.50 mmol; 4 equiv.) was added followed by $RuCl_3$ (55 mg, 0.05 mmol), and the heterogeneous mixture was stirred for 3 h (TLC monitoring in EtOAc/MeOH/H_2O, 45:5:3). Et_2O (50 mL) was added, the layers were separated, and the aqueous phase was extracted with EtOAc (3 × 30 mL). Combined organic solutions were concentrated to afford crude acid (3.59 g) which was used in the next step without further purification. This crude material was dissolved in DMF (50 mL) to which K_2CO_3 (2.24 g, 16.22 mmol; 3 equiv.) and MeI (1.00 mL, 16.22 mmol, 3 equiv.) were added. The mixture was stirred for 12 h at rt (TLC monitoring, in hexane/EtOAc, 2:1), and partitioned between Et_2O (100 mL) and H_2O (100 mL). The organic phase was separated and the aqueous one extracted with Et_2O (2 x 30 mL). Combined organic solutions were dried and concentrated, and the residue was subjected to column chromatography (hexane/EtOAc, 7:1 to 1:1) to afford the corresponding methyl uronate (2.76 g, 74% over two steps). $[\alpha]_D$ = 43.4; ^{1}H-NMR δ: 5.68 (H1, *d*, *J* 3.8 Hz, 1H), 4.41 (H5, *d*, *J* 10.1 Hz, 1H), 4.04 (H4', m, 1) 4.01 (H3', *d*, *J* 7.8 Hz, 1H), 3.93 (H6' b/a, *m*, 1H), 3.83 (H6' a/b, *m*, 1H), 3.83 (H5', *m*, 1H), 3.67 (OCH_3, *s*, 3H), 3.56 (OCH_3, *s*, 3H), 3.53 (H1' b/a *m*, 1H), 3.49 (OCH_3, *s*, 3H), 3.48 (OCH_3, *s*, 3H), 3.41 (2×OMe, 6H), 3.39 (H1' a/b, *m*, 1H), 3.39 (H3, *m*, 1H), 3.37 (OCH_3, s, 3H), 3.30 (H4, *m*, 1H), 3.04 (H2, *dd*, *J* 9.6, 3.8 Hz, 1H), 1.06 (3×CH_3, *s*, 9H). ^{13}C-NMR δ: 170.50 (C6), 135.53, 133.47, 133.18, 129.67, 129.62, 127.67 (6×Ph), 103.91 (C2'), 88.65 (C1), 85.19 (C3'), 82.83 (C4'), 82.66 (C3), 81.30 (C4), 80.88 (C2), 80.67 (C5'), 74.59 (C1'), 70.15 (C5), 60.79, 60.28, 59.52, 58.67, 58.48, 58.00 (6×OCH_3), 52.03 (COO CH_3), 26.81 [$SiPh_2C(\underline{CH_3})_3$], 19.27 ($C_{quat}$). MS *m/z*: [M(C35H52O12Si) + Na^+]; calcd.: 715,3126; found: 715,3118; Analysis: calcd. for $C_{35}H_{52}O_{12}Si$ (692.33 Da): C, 60.67; H, 7.56; found: C, 60.55; H, 7.46%.

Phosphonate 13. *This reaction was carried out under an argon atmosphere with the exclusion of moisture*. To a cooled to -78 °C solution of dimethyl methylphosphonate (2.09 g, 16.87 mmol) in dry THF (50 mL) BuLi (5.40 mL of a 2.5M solution in hexanes; 13.49 mmol; 4 eqiuv.) was added dropwise within 5 min, and the mixture was stirred at -78 °C for 40 min. Then a solution of the above prepared methyl uronate (2.33 g, 3,37 mmol) in THF (5 mL) was added within 20 min. the mixture was stirred for 2 h (TLC monitoring in EtOAc/MeOH/H_2O, 100:5:3). The mixture was warmed to rt. and partitioned between Et_2O (100 mL) and H_2O (100 mL). The organic phase was separated washed with H_2O, dried, concentrated, and the crude product was purified by column chromatography (hexane/EtOAc, 2:1 to 1:1) to afford phosphonate **13** (5.19 g, 84%) as an oil. $[\alpha]_D$ = 31.2; ^{1}H-NMR δ: 6.00 (H1, *d*, *J* 3.8 Hz, 1H), 4.35 (H5, *d*, *J* 10.0 Hz, 1H), 4.20 (H4', m, 1H), 4.08 (H3', *d*, *J* 8.4 Hz, 1H), 4.01 (H6' a/b, *dd*, *J* 11.8, 2.7 Hz, 1H), 3.78 (OCH_3, *m*, 3H), 3.76 (H6' b/a, *m*, 1H), 3.76 (OCH_3, *m*, 3H), 3.70 (H5', *m*, 1H), 3.57 (OCH_3, *s*, 3H), 3.54 (OCH_3, *s*, 3H), 3.52 (OCH_3, *s*, 3H), 3.51 (H1' a/b, *m*, 1H), 3.46 (OCH_3, *s*, 3H), 3.46 (H1' b/a, *m*, 1H), 3.44 (H3, *m*, 1H), 3.42 (OCH_3, *s*, 3H), 3.41 (H7 a/b, *dd*, *J* 29.8, 14.8 Hz, 1H), 3.38 (H7 b/a, *m*, 1H), 3.34 (OCH_3, *s*, 3H), 3.31 (H4, *m*, 1H), 2.96 (H2, *dd*, *J* 9.7, 3.8 Hz, 1H), 1.06 [$SiPh_2C(\underline{CH_3})_3$], s, 9H). ^{13}C-NMR δ: 198.74 (C6), 135.78, 135.63, 135.58, 135.42, 133.08, 132.59, 129.87, 129.79, 127.78, 127.72 (10×Ph), 103.67 (C2'), 87.98 (C1), 85.43 (C3'), 83.06 (C3), 80.52 (C2), 80.48 (C4'), 79.68 (C5'), 79.54 (C4), 75.57 (C1'), 74.92 (C5), 62.70 (C6'), 60.80, 60.29, 59.53, 59.03, 58.50, 57.66, 52.89, 52.79 (8×OCH_3), 37.32 (C7), 26.82 [$SiPh_2C(\underline{CH_3})_3$], 19.22 ($C_{quat}$). MS *m/z*: [M($C_{37}H_{57}O_{14}PSi$) + Na^+]; calcd.: 807.3153; found: 807.3143; Analysis calcd. for $C_{37}H_{57}O_{14}PSi$ (784.33 Da): C, 56.62; H, 7.32; found: C, 55.99; H, 7.31%.

Aldehyde 14. To a cooled to -78 °C solution of oxalyl chloride (0.60 mL; 7.00 mmol; 5 equiv.) in CH_2Cl_2 (15 mL), DMSO (0.99 mL, 14.0 mmol, 10 equiv.) was added within 5 min followed by a solution of **12** (932 mg, 1.40 mmol) in dry CH_2Cl_2 (2 mL), and the mixture was stirred for 80 min at this temperature. Et_3N (1.56 mL, 11.21

mmol, 8 equiv.) was added in one portion, the mixture was stirred for 5 min. at -78 °C and allowed to reach rt. It was then partitioned between H_2O (50 mL) and Et_2O (50 mL), the organic phase was separated and the aqueous one extracted with Et_2O (2 × 30 mL). Combined organic solutions were washed with diluted sulfuric acid (2 × 15 mL of a ~1M solution), H_2O, dried, and concentrated to give crude aldehyde **14** (951 mg) which was used directly in the next step.

Enone 15. To a solution of phosphonate **13** (1.10 g; 1.40 mmol; 1 equiv.) and crude aldehyde **14** (928 mg; 1.40 mmol; 1 equiv.) in dry toluene (30 mL), K_2CO_3 (387 mg, 2.80 mmol, 2.0 equiv.) was added followed by 18-crown-6 (225 mg), and the mixture was vigorously stirred at rt for 48 h (TLC monitoring in hexane/EtOAc, 1:1). The solid material was filtered off through a short Celite pad, the filtrate was concentrated, and the residue was purified by column chromatography (hexane/EtOAc, 10:1 to 1:1) to afford enone **15** (1.35 g, 73%) as an oil. $[\alpha]_D$ = 50.1; ^{1}H-NMR δ: 7.05 (H7-A, *dd*, *J* 15.8, 4.9 Hz, 1H), 6.73 (H6-A, *dd*, *J* 15.8, 1.5 Hz, 1H), 5.81 (1H-B, *d*, *J* 3.8 Hz, 1H), 5.79 (1H-A, *d*, *J* 3.7 Hz, 1H), 4.57 (H5-B, *d*, *J* 10.2 Hz, 1H), 4.47 (H5-A, *ddd*, *J* 10.2, 4.8, 1.2 Hz, 1H), 4.04 (H5'-AB, *m*, 2H), 3.99 (H3'-AB, *m*, 2H), 3.96 (H6'-AB, *m*, 2H), 3.80 (H4'-AB, *m*, 2H), 3.79 (H6'-AB, *m*, 2H), 3.54 (H1'-AB, *m*, 2H), 3.53 (double intensity), 3.44, 3.42, 3.41, 3.38 (double), 3.38, 3.36 (double), 3.34 double; (12×OMe), 3.39 (H3-B, *m*, 1H), 3.38 (H1'-AB, m, 2H), 3.38 (H3-A, *m*, 1H), 3.15 (H4-B, *dd*, *J* 10.1, 8.9 Hz, 1H), 3.00 (H2-B, *dd*, *J* 9.6, 3.8 Hz, 1H), 2.96 (H2-A, *dd*, *J* 9.7, 3.8 Hz, 1H), 2.77 (H4-A, *dd*, *J* 10.0, 8.9 Hz, 1H), 1.07 [2×$SiPh_2C(\underline{CH_3})_3$]. ^{13}C NMR δ: 196.09 (CO), 144.14, 135.58, 133.36, 132.99, 129.71, 127.70, 126.78 (Ph), 103.90 (C2'-AB), 88.63 (C1-A), 88.31 (C1-B), 85.56 (C4'-A/B), 83.73 (C4-B), 82.95 (C3-AB), 82.49 (C5'-AB), 81.91 (C4-A), 81.23 (C2-B), 80.96 (C2-A), 80.41 (C4'-B/A), 74.77 (C1'-AB), 73.75 (C5-A), 70.03 (C5-B), 64.10 (C6'-AB), 60.82, 60.74, 60.49, 60.16, 59.55, 59.52, 58.74, 58.63, 58.48, 58.45, 57.83, 57.76 (12×OCH_3), 26.87 [2×$Si(Ph)_2C(\underline{CH_3})_3$], 19.28 (2×$C_{quat}$). MS *m/z*: [M($C_{69}H_{100}O_{21}Si_2$) + Na^+]; calcd.: 1343.6190; found: 1343.6183; Analysis: calcd. for $C_{69}H_{100}O_{21}Si_2$ (1320.64 Da): C, 62.70; H, 7.63; found: C, 62.78; H, 7.73%.

Stereoselective reduction of enone 15. *This reaction was carried out under an argon atmosphere with the exclusion of moisture*. To a cooled to -30 °C solution of **15** (100 mg; 0.076 mmol) in dry Et_2O (3 ml), zinc borohydride (1 mL of ~0.5M solution in Et_2O) was added, and the mixture was allowed to reach rt. After 3 h (TLC monitoring, in hexane/EtOAc, 1:1) H_2O (5 mL) was added, the organic phase was separated, dried, concentrated, and the crude product was purified by column chromatography (hexane/EtOAc, 2:1 to 1:1) to afford alcohol **17** (67 mg, 67%) as amorphous solid. $[\alpha]_D$ = 32.5; ^{1}H-NMR δ: 5.96 (H1-A, *d*, *J* 3.9 Hz, 1H), 5.93 (H6-B, *dd*, *J* 15.2, 7.2 Hz, 1H), 5.64 (H1-B, *d*, *J* 3.9 Hz, 1H), 5.64 (H7-A, *m*, 1H), 4.34 (H6-A, H5-B, *m*, 2H), 4.27 (H4'-A, *m*, 1H), 4.11 (H3'-A, *m*, 1H), 4.01 (H6'-A, *m*, 1H), 4.01 (H5-A, *m*, 1H), 4.01 (H3'-A, *m*, 1H), 4.01 (H4'-B, *m*, 1H), 4.01 (H3'-B, *m*, 1H), 3.95 (H6'-B, *dd*, *J* 10.3, 4.0 Hz, 1H), 3.85 (H6'-B, *m*, 1H), 3.84 (H5'-B, *m*, 1H), 3.77 (H6'-A, *dd*, *J* 12.0, 3.1 Hz, 1H), 3.65 (H5'-A, *m*, 1H), 3.53 (OCH_3, s, 3H), 3.53 (OCH_3, *s*, 3H), 3.50 (OCH_3, *s*, 3H), 3.50 (OCH_3, *s*, 3H), 3.50 (OCH_3, *s*, 3H), 3.48 (H1'-A, *m*, 1H), 3.47 (H1'-A, *m*, 1H), 3.45 (OCH_3, *s*, 3H), 3.42 (OCH_3, *s*, 3H), 3.39 (OCH_3, *s*, 3H), 3.38 (2×OCH_3, *s*, 6H), 3.37 (OCH_3, *s*, 3H), 3.36 (H3-B, *m*, 1H), 3.35 (H3-A, *m*, 1H), 3.29 (OCH_3, *s*, 3H), 2.99 (H2-B, *dd*, *J* 9.7, 3.8 Hz, 1H), 2.95 (H4-A, *dd*, *J* 10.2, 8.9 Hz, 1H), 2.90 (H2-A, *m*, 1H), 2.83 (H4-B, *m*, 1H). ^{13}C-NMR δ: 131.77 (C6-B), 131.03 (C7-A), 103.85 (C2'-A), 103.42 (C2'-B), 88.45 (C1-B), 87.29 (C1-A), 85.71 (C3'-B), 85.58 (C3'-A), 83.77 (C4-B), 83.52 (C3-A), 83.46 (C4'-B), 82.97 (C3-B), 81.64 (C2-B), 80.98 (C2-A), 80.94 (C5'-B), 80.01 (C4-A), 79.78 (C4'-A), 79.17 (C5'-A), 76.05 (C1'-A), 74.22 (C1'-B), 73.25 (C5-A), 71.99 (C5-B), 70.38 (C6-A), 65.03 (C6-B), 62.25 (C6'-A), 60.61, 60.56, 60.17, 60.02, 59.61, 59.54, 59.11, 58.60, 58.59, 58.52, 57.75, 57.30 (12×OCH_3), 26.87 [$SiPh_2C(\underline{CH_3})_3$], 19.27 ($C_{quat}$).MS *m/z*: [M($C_{69}H_{102}O_{21}Si_2$) + Na^+]; calcd.: 1345,6350; found: 1345,6337; Analysis: calcd. for $C_{69}H_{102}O_{21}Si_2$ (1322.65 Da): C, 62.61; H, 7.77; found: C, 62.77; H, 7.84%.

Synthesis of 17. To a solution of **16** (399 mg; 0.256 mmol) in dry DMF (10 mL) NaH (50% suspension in mineral oil, 40.9 mg) was added, and the mixture was stirred for 10 min at rt. MeI (0.16 mL, 2.56 mmol, 10 equiv.) was added, stirring was continued for 14 h (TLC monitoring in hexane/EtOAc, 1:1), and then the mixture was

partitioned between H_2O (10 mL) and Et_2O (20 mL). The organic phase was separated, washed with H_2O, dried, concentrated, and the crude material was purified by column chromatography (hexane/EtOAc, 8:1 to 1:1) to give **17** (202 mg, 59%) and unreacted alcohol **16** (68 mg). ^{1}H-NMR δ: 5.75 (H7-A, *dd*, *J* 15.4, 8.4 Hz, 1H), 5.71 (H1-A, *d*, *J* 3.8 Hz, 1H), 5.61 (H6-B, *dd*, *J* 15.7, 6.3 Hz, 1H), 5.52 (H1-B, *d*, *J* 3.7 Hz, 1H), 4.33 (H5-B, *dd*, *J* 9.8, 6.3 Hz, 1H), 4.02 (H3'-B, *m*, 1H), 4.02 (H4'-B, *m*, 1H), 4.02 (H5'-B, *m*, 1H), 4.01 (H5'-A, *m*, 1H), 3.95 (H5'-A, m, 1H), 3.93 (H6'-B, *m*, 1H), 3.92 (H6'-A, *m*, 1H), 3.92 (H6'-B, *m*, 1H), 3.88 (H4'-A, *m*, 1H), 3.86 (H3'-A, *m*, 1H), 3.84 (H6'-A, *m*, 1H), 3.72 (H6-A, *d*, *J* 9.1 Hz, 1H), 3.55 (OCH_3, *s*, 3H), 3.55 (H1'-A, *m*, 1H), 3.54 (H1'-B, *m*, 1H), 3.49 (OCH_3, *s*, 3H), 3.47 (OCH_3, *s*, 3H), 3.45 (OCH_3, *s*, 3H), 3.43 (OCH_3, *s*, 3H), 3.42 (OCH_3, *s*, 3H), 3.42 (2×OCH_3, *s*, 6H), 3.41 (OCH_3, *s*, 3H), 3.39 (OCH_3, *s*, 3H), 3.37 (OCH_3, *s*, 3H), 3.36 (OCH_3, *s*, 3H), 3.35 (H1'-A, *m*, 1H), 3.35 (H1'-B, *m*, 1H), 3.13 (OCH_3, *s*, 3H), 3.02 (H4-A, *m*, 1H), 3.01 (H2-B, *m*, 1H), 2.89 (H2-A, *dd*, *J* 9.6, 3.7 Hz, 1H), 2.81 (H4-B, m, 1H). ^{13}C-NMR δ: 132.57 (C6-B), 129.63 (C7-A), 103.75 (C2'-B), 103.71 (C2'-A), 88.51 (C1-A), 88.05 (C1-B), 85.43 (C5'-B), 85.38 (C4'-B), 84.11 (C4-B), 83.60 (C3'-B), 83.36 (C3-A), 82.87 (C3-B), 82.54 (C6-A), 82.54 (C5'-A), 81.55 (C2-A), 81.47 (C2-B), 81.01 (C4'-A), 80.63 (C3'-A), 79.61 (C4-A), 74.82 (C1'-A), 74.10 (C1'-B), 72.35 (C5-A), 70.31 (C5-B), 65.11 (C6'-A), 64.47 (C6'-B), 60.66, 60.55, 60.35, 59.56, 59.54, 59.45, 58.53, 58.51, 58.43, 58.40, 57.90, 57.75, 56.39 (13×OCH_3), 26.82 [2×$SiPh_2C(\underline{CH_3})_3$], 19.24 ($C_{quat}$). $[\alpha]_D$ = 42.7; MS *m/z*: [M($C_{70}H_{104}O_{21}Si_2$) + NH_4^+] calcd.: 1354.6952; found: 1354,6953. Analysis: calcd. for $C_{70}H_{104}O_{21}Si_2$ (1336.66 Da): C, 62.85; H, 7.84; found: C, 62.76; H, 8.01%.

Synthesis of diol 18. To a solution of **17** (170 mg, 0.127 mmol) in THF (50 mL), an aq. solution of TBAF (1 mL) was added, the mixture was stirred for 13 h (TLC monitoring in Me_2CO/EtOAc 1:3), and partitioned between H_2O (20 mL) and CH_2Cl_2 (30 mL). The organic phase was separated, dried, concentrated, and the crude product was isolated by column chromatography (Me_2CO/EtOAc, 1:6 to 1:1) to give **18** (90.4 mg, 84%). $[\alpha]_D$ = 42.5; ^{1}H-NMR: 5.85 (H7-A, *dd*, *J* 16.0, 8.7 Hz, 1H), 5.78 (H6-B, *dd*, *J* 15.8, 5.9 Hz, 1H), 5.48 (H1-A, *d*, *J* 3.5 Hz, 1H), 5.46 (H1-B, *d*, *J* 3.6 Hz, 1H), 4.36 (H5-B, *dd*, *J* 9.8, 5.8 Hz, 1H), 4.09 (H5-A, *m*, 1H), 4.07 (H4'-B, *m*, 1H), 4.03 (3'-A, *m*, 1H), 4.03 (H5'-A, *m*, 1H), 3.92 (H4'-A, *m*, 1H), 3.92 (H5'-B, *m*, 1H), 3.89 (H3'-B, *m*, 1H), 3.88 (H6-A, *m*, 1H), 3.82 (H6'-A, *dd*, *J* 12.6, 2.4 Hz, 1H), 3.77 (H6'-B, *dd*, *J* 12.2, 2.5 Hz, 1H), 3.70 (H6'-A, *dd*, *J* 12.7, 4.3 Hz, 1H), 3.62 (OCH_3, *s*, 3H), 3.60 (H1'-A, *m*, 1H), 3.60 (H6'-B, *m*, 1H), 3.57 (OCH_3, *s*, 3H), 3.55 (H1'-B, *m*, 1H), 3.54 (OCH_3, *s*, 3H), 3.52 (OCH_3, *s*, 3H), 3.50 OCH_3, *s*, 3H), 3.50 (OCH_3, *s*, 3H), 3.50 (H3-B, *m*, 1H), 3.48 (OCH_3, *s*, 3H), 3.47 (H3-A, *m*, 1H), 3.47 (2×OCH_3, *s*, 6H), 3.45 (OCH_3, *s*, 3H), 3.42 (OCH_3, *s*, 3H), 3.40 (OCH_3, *s*, 3H), 3.40 (H1'-B, *m*, 1H), 3.40 (H1'-A, m, 1H), 3.32 (OCH_3, s, 3H), 3.16 (H4-A, *dd*, *J* 10.1, 9.0 Hz, 1H), 3.11 (H2-B, *dd*, *J* 9.7, 3.6 Hz, 1H), 3.08 (H2-A, *dd*, *J* 9.7, 3.6 Hz, 1H), 2.86 (H4-B, *m*, 1H). ^{13}C-NMR (150 MHz, $CDCl_3$): 132.64 (C7-A), 129.48 (C6-B), 103.65 (C2'-A), 103.64 (C2'-B), 90.03 (C1-B), 89.86 (C1-A), 85.65 (C5'-A), 85.15 (C4'-B), 84.54 (C4-B), 83.16 (C3-A), 82.90 (C3-B), 82.17 (C5'-B), 81.84 (C3'-A), 81.72 (C2-A), 81.59 (C3'-B), 81.52 (C2-B), 81.44 (C4'-A), 81.32 (C3'-B), 79.33 (C4-A), 74.19 (C1'-B), 73.97 (C1'-A), 73.04 (C-A), 70.71 (C5-B), 62.01 (C6'-A), 61.91 (C6'-B), 60.71, 60.68, 60.55, 59.77, 59.48, 59.40, 59.20, 58.65, 58.50, 58.44, 58.33, 58.31, 56.45 (13×OCH_3). MS *m/z*: [M($C_{38}H_{68}O_{21}$) + Na^+]; calcd.: 883.4150; found: 883.4146; Analysis calcd. for $C_{38}H_{68}O_{21}$ (860.43 Da): C, 53.01; H, 7.96; found: C, 53.24; H, 7.84%.

Macrocyclization of diol 18. Synthesis of 19. *This reaction was carried out under an argon atmosphere with the exclusion of moisture*. To a solution of **18** (90 mg, 0.105 mmol) in CH_2Cl_2 (5 mL), Me_3N (0.043 ml, 0.314 mmol, 3 equiv.) and dichloride **9** (20.90 mg, 0.102 mmol, 0.98 equiv.) were added, the mixture was stirred for rt for 96 h (TLC monitoring in hexane/EtOAc, 6:1), and concentrated. Chromatographic purification of the residue (hexane/EtOAc, 6:1) afforded macrocycle **19 (**28 mg, 27%) as an oil. ^{1}H-NMR: 8.22 (2 protons from pyridine, *m*), 7.96 (1 proton from pyridine, *t*, *J* 7.8 Hz), 5.77 (H7-A, *dd*, *J* 16.1, 8.8 Hz, 1H), 5.69 (H6-B, *dd*, *J* 15.8, 4.9 Hz, 1H), 5.48 (H1-B, *d*, *J* 3.7 Hz, 1H), 5.41 (H1-A, *d*, *J* 3.6 Hz, 1H), 4.95 (H6'-B, *dd*, *J* 11.5, 5.1 Hz, 1H), 4.87 (H6'-A, *dd*, *J* 11.7, 7.2 Hz, 1H), 4.63 (H6'-A, *dd*, *J* 11.7, 4.6 Hz, 1H), 4.44 (H6'-B, *dd*, *J* 11.5, 6.0 Hz, 1H), 4.40 (H5-

B, *dd*, *J* 10.0, 4.8 Hz, 1H), 4.30 (H5'-A, *m*, 1H), 4.10 (H5'-B, m, 1H), 4.07 (H5-A, *m*, 1H), 4.04 (H3'-A, *m*, 1H), 4.02 (H3'-B, *m*, 1H), 4.02 (H4'-A, *m*, 1H), 4.02 (H4'-B, *m*, 1H), 3.84 (H6-A, *m*, 1H), 3.64 (OCH_3, *s*, 3H), 3.60 (OCH_3, *s*, 3H), 3.56 (OCH_3, *s*, 3H), 3.56 (OCH_3, *s*, 3H), 3.52 (OCH_3, *s*, 3H), 3.51 (OCH_3, *s*, 3H), 3.48 (OCH_3, *s*, 3H), 3.48 (OCH_3, *s*, 3H), 3.47 (OCH_3, *s*, 3H), 3.44 (OCH_3, *s*, 3H), 3.42 (H3-B, H3-A, *m*, 6H), 3.41 (OCH_3, *s*, 3H), 3.39 (OCH_3, *s*, 3H), 3.27 (OCH_3, *s*, 3H), 3.04 (H2-A, *dd*, *J* 9.7, 3.6 Hz, 1H), 3.00 (H2-B, *m*, 1H), 2.96 (H4-A, *dd*, J 10.2, 9.0 Hz, 1H), 2.73 (H4-B, *dd*, *J* 9.8, 9.1 Hz, 1H). ^{13}C-NMR: 165.28 (CO-A), 164.33 (CO-B), 148.73 (C_{py}), 147.84 (C_{py}), 137.69 (C_{py}), 133.11 (C6-B), 128.32 (C7-A), 127.60 (2xC_{py}), 104.09 (C2'-B), 103.70 (C2'-A), 88.94 (C1-A), 88.18 (C1-B), 84.69 (C3'-B), 84.55 (C3'-A), 84.47 (C4-B), 83.74 (C5'-B), 83.63 (C4'-A), 83.59 (C3-A), 82.77 (C3-B), 81.91 (C6-A), 81.75 (C2-A), 81.50 (C2-B), 80.03 (C4-A), 77.11 (C5'-A), 76.23 (C5'-A), 74.74 (C1'-B), 74.21 (C1'-A), 72.80 (C5-A), 70.27 (C5-B), 66.68 (C6'-A), 64.57 (C6'-B), 60.70, 60.63, 60.47, 59.89, 59.53, 59.41, 59.39, 58.84, 58.81, 58.60, 58.37, 57.82, 56.07 (13×OCH_3). MS *m/z*: [M($C_{45}H_{69}O_{23}N$) + Na^+]; calcd.: 1014.4158; found: 1014.4197.

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