Supporting Information

for

Flexible synthesis of anthracycline aglycone mimics
via domino carbopalladation reactions

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Experimental details and analytical data of all new compounds as well as their \(^1\)H and \(^{13}\)C NMR spectra

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General experimental

**Preparative methods**

All solvents for column chromatography were distilled before use unless otherwise stated. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium/benzophenone under an argon atmosphere. Dichloromethane (CH₂Cl₂) and toluene were distilled from CaCl₂ under an argon atmosphere. All other solvents were used as analytical grade and were stored over suitable molecular sieves (3 Å or 4 Å). Air and moisture sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated.

Microwave: A Biotage® microwave oven with adjustable temperature in the range of 40-250 °C has been used to apply microwave irradiation. Pressures of 20 bar are possible inside the reaction vessel. The power of the magnetron at 2.45 GHz is regulated between 0-400 W. The reaction volumes are available in four different dimensions (0.2–0.5 mL, 0.5–2.0 mL, 2.5–5.0 mL and 10.0–20.0 mL). The device was run with the software version 2.3 build 6250. Exact reaction conditions are given in the respective procedure.

**Chromatography**

Thin-layer chromatography (TLC): Analytical TLC was performed on Merck silica gel plates (60 F₂₅₄, 0.25 mm). The compounds were visualized under UV irradiation (254 nm and 350 nm). As common coloration reagent were used cerium ammonium molybdate in solution [5 g (NH₄)₄Ce(SO₄)₄, 30 g Mo₇(NH₄)₆·4H₂O, 30 mL conc. H₂SO₄ and 600 mL H₂O] and elementary iodine for the detection of alkynes.

Column Chromatography: Preparative purification of the products was achieved by flash column chromatography on Merck silica gel (grade 60, 0.063–0.200 mm, 70–230 mesh ASTM) with elevated pressure. Difficult purifications were accomplished by middle pressure liquid chromatography (MPLC) by Biotage® Isolera™ One. As stationary phase Biotage® SNAP cadridges KPSIL (10-250 g silica gel, 30 or 50 µm) were used.

**Instrumental analytics**

NMR spectra: Proton (^1H) and carbon (^13C) NMR spectra were recorded on 300, 500 and 600 MHz instruments (Varian Unity-300, Varian Mecury-300, Varian Inova-500 and Varian Inova-600), respectively, using the residual signals from CHCl₃: δ = 7.26 ppm and δ = 77.0 ppm; DMSO: δ = 2.54 ppm and δ = 40.5 ppm; acetone: δ = 2.09 ppm and δ = 30.9 ppm and δ = 207.1 ppm and methanol: δ = 4.87 ppm and δ = 49.2 ppm, as internal references for ^1H and ^13C chemical shifts, respectively. Assignments of the respective signals were made by the combination of H,H-COSY, HSQC, NOE and HMBC experiments. The
splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; sbr, broad singlet; m, multiplet and as combination of that kind. Undefined assignments of hydrogen and carbon atoms are marked by * sign.

Mass spectra: ESIMS and HRMS–ESI mass spectrometry was carried out on a FTICR instrument by Finnigan LCQ and on an APEX IV 7T FTICR by Bruker Daltonic. EIMS and HRMS–EI mass spectrometry was performed on an EI-TOF (Accu TOF) by Jeol and a sector instrument (MAT 95) by Finnigan.

IR (ATR) and UV Spectra: IR (ATR) spectra were measured on a conventional ATR spectrometer (FT/IR-4100) by JASCO. UV spectra were measured with a common photometer (V630) by JASCO in acetonitrile or methanol as solvent.

Optical rotation values were measured at 20 °C using a polarimeter by Perkin-Elmer 241 in respective suitable solvents (e.g. chloroform, methanol and dimethyl sulfoxide).

X-ray analysis: For the X-ray crystal structures a single crystal was mounted in an inert oil. The data was collected from cooled crystals at 100 K on a Bruker Smart ApexII with Incoatec micro focus source using monochromatic MoKα radiation, λ = 0.71073 Å. Data reduction was done with SAINT,1 and an empirical absorption correction with SADABS2 or TWINABS3 was applied. The structure was solved by direct methods (SHELXS-97)4 and refined by full-matrix least-squares methods against F² (SHELXL-97).5 All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their Uiso values constrained to 1.5 times the Ueq of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms.

Literature
1. Bruker, SAINT V7.68A, Bruker AXS Inc., Madison (WI, USA), 2005.
2. Sheldrick, G. M.; SADABS 2008/2, Göttingen, 2008.
3. Sheldrick, G. M.; TWINABS 2008/4, Göttingen, 2008.
4. Sheldrick, G. M. Acta Crystallogr. Sect. A 2008, 64, 112-122.
5. Flack, H. D. Acta Crystallogr. Sect. A 1983, 39, 876-881.
Synthesis and analytical data of the compounds

General procedures

Common aqueous workup:

The reaction was stopped by addition of saturated aq. \( \text{NH}_4\text{Cl} \) solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution, dried over \( \text{Na}_2\text{SO}_4 \) and the solvent was removed by rotary evaporation.

GP1: Appel reaction

The alcohol (1.0 equiv), triphenylphosphine (1.5–2.0 equiv) and imidazole (1.5–2.0 equiv) were dissolved in a mixture of \( \text{Et}_2\text{O} \) and MeCN and cooled to 0 °C. Iodine (1.5–2.0 equiv) was added portionwise over a period of 45 min and the reaction was allowed to stir for further 15 min (monitored by TLC). After completion of the reaction, the mixture was poured into pentane and was immediately purified by silica gel column chromatography (pentane) to afford the desired product.

GP2: Silylacetylene coupling

To a solution of silylacetylene (2.0–3.0 equiv) in THF was added ethyl magnesium bromide (3.0 mol/L in \( \text{Et}_2\text{O} \)) at room temperature. The solution was heated to reflux for 2 h and then cooled to ambient temperature. \( \text{CuCl} \) (25–40 mol %) and the corresponding iodide (1.0 equiv), dissolved in THF, were successively added to the reaction mixture and heated to 75 °C for 16 h. The reaction was stopped by addition of saturated aq. \( \text{NH}_4\text{Cl} \) solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over \( \text{Na}_2\text{SO}_4 \). The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography to afford the desired product.

GP3: TBS-cleavage

The protected alcohol (1.0 equiv) was dissolved in MeOH at 0 °C and AcCl was added dropwise. The reaction mixture was stirred for 3 h and then stopped by slow addition of \( \text{NaHCO}_3 \) solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over \( \text{Na}_2\text{SO}_4 \). The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography to afford the desired product.

GP4: Silyl ether formation

Dialkyne (1.0–1.2 equiv) was dissolved in dry \( \text{CCl}_4 \) and cooled to 0 °C. A freshly prepared solution of bromine in dry \( \text{CCl}_4 \) (0.976 mol/L, 1.0–1.2 equiv) was added over a period of 1 h
via syringe pump and stirred for further 2 h at 0 °C. To a solution of glycal (1.0 equiv), NEt₃ (2.0 equiv) and DMAP (10 mol %) in dry CCl₄ and dry Et₂O was added the solution of the alkyne at 0 °C over a period of 30 min via syringe pump. The reaction was stirred for at least 2 h and stopped by the addition of saturated aq. NH₄Cl solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na₂SO₄. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography to afford the desired product.

GP5: Domino reaction

The alkynylated bromoglycal (1.0 equiv) was dissolved in a mixture of DMF/MeCN/NMP (8:8:1). Pd(PPh₃)₄ (10 mol %), t-Bu₃PHBF₄ (20 mol %) and diisopropylamine (5.0 equiv) were added. The reaction was stirred in a microwave reactor for 3–5 h at 120 °C. The absorption level was set as very high and the prestirring time at 10 s. The reaction was stopped by the addition of saturated aq. NH₄Cl solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution, dried over Na₂SO₄. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography to afford the desired product.
### Analytical data

**Compound 20**

Alcohol 19 (3.34 g, 13.3 mmol, 1.0 equiv), triphenylphosphine (6.95 g, 26.5 mmol, 2.0 equiv), imidazole (1.80 g, 26.5 mmol, 2.0 equiv) and iodine (6.73 g, 26.5 mmol, 2.0 equiv), dissolved in Et₂O (100 mL) and MeCN (25 mL) were brought to reaction according to GP1. Purification by silica gel column chromatography (pentane) afforded 4.44 g (93%) of compound 20 as an orange oil: Rᵢ: 0.53 (hexane/EtOAc = 20:1). **¹H-NMR** (300 MHz, CDCl₃): δ = 0.14 (s, 6 H, Me₆TBS), 0.96 (s, 9 H, fBu₆TBS), 4.51 (s, 2 H, 1-H), 4.79 (s, 2 H, 8-H), 7.17–7.34 (m, 3 H, 3-H*, 4-H*, 5-H*), 7.38–7.42 (m, 1 H, 6-H*). **¹³C-NMR** (125 MHz, CDCl₃): δ = –5.1 (C-8), 3.3 (Me₆TBS), 18.4 (C₄TBS), 26.0 (fBu₆TBS), 62.5 (C-1), 127.5, 127.6, 128.2, 129.7 (C-3, C-4, C-5, C-6), 135.9, 139.1 (C-2, C-7). IR (ATR): ν (cm⁻¹) = 3271, 2852, 1918, 1455, 1368, 1185. UV (CH₃CN): λ max [nm] (lg ε) = 241 (4.03), 360 (2.77). MS (ESI): m/z (%) = 385.1 (32) [M+Na]+. C₁₄H₂₃OSi (362.32), calc.: 385.0455, found: 385.0453, [M+Na]+ (ESI-HRMS).

**Compound 22a**

Trimethylsilylacetylene (542 mg, 5.52 mmol, 2.0 equiv) in THF (30 mL), ethyl magnesium bromide (3.0 mol/L in diethyl ether, 1.84 mL, 5.52 mmol, 2.0 equiv), CuCl (69 mg, 0.69 mmol, 25 mol %) and 20 (1.00 g, 2.76 mmol, 1.0 equiv) in THF (10 mL) were brought to reaction according to GP5.2. Purification by silica gel column chromatography (pentane/EtOAc = 100:1) afforded 807 mg (88%) of compound 22a as a pale yellow oil: Rᵢ: 0.53 (hexane/EtOAc = 20:1). **¹H-NMR** (300 MHz, CDCl₃): δ = 0.10–0.11 (m, 6 H, Me₆TBS), 0.18–0.20 (m, 9 H, Me₆TMS), 0.94–0.96 (s, 9 H, fBu₆TBS), 3.64 (s, 2 H, 1-H), 4.78 (s, 2 H, 8-H), 7.24–7.29 (m, 2 H, H₆), 7.41–7.46 (m, 2 H, H₆). **¹³C-NMR** (125 MHz, CDCl₃): δ = –5.2 (Me₆TBS), 0.2 (Me₆TMS), 18.5 (C₄TBS), 23.5 (C-8), 62.0 (fBu₆TBS), 63.0 (C-1), 87.0, 103.7 (C-9, C-10), 126.7, 126.8, 127.2, 128.4 (C-3, C-4, C-5, C-6), 133.5, 138.6 (C-2, C-7). IR (ATR): ν (cm⁻¹) = 2955, 2856, 2175, 1471, 1249. UV (CH₃CN): λ max [nm] (lg ε) = 194 (4.82). MS (ESI): m/z (%) = 355.2 (100) [M+Na]+. C₁₉H₃₂OSi₂ (332.63), calc.: 355.1884, found: 355.1885, [M+Na]+ (ESI-HRMS).
Compound 23a

![Chemical Structure](image)

The protected alcohol 22a (4.80 g, 14.4 mmol, 1.0 equiv), dissolved in MeOH (45 mL), and AcCl (6.0 mL) were brought to reaction according to GP5.3. Purification by silica gel column chromatography (pentane/EtOAc = 10:1) afforded 2.71 g (86%) of compound 23a as a slightly yellow oil: Rf: 0.21 (hexane/EtOAc = 5:1). ^1H-NMR (300 MHz, CDCl₃): δ = 0.17 (s, 9 H, Me₃Si), 3.71 (s, 2 H, 8-H), 4.74 (s, 2 H, 1-H), 7.25–7.31 (m, 2 H, H₉), 7.36–7.45 (m, 2 H, H₈). ^13C-NMR (125 MHz, CDCl₃): δ = -0.03 (C-Me₃Si), 23.7 (C-8), 63.3 (C-1), 87.3, 104.5 (C-9, C-10), 127.3, 128.3, 128.7, 129.1 (C-3, C-4, C-5, C-6), 134.8, 138.3 (C-2, C-7).

IR (ATR): v (cm⁻¹) = 3321, 2958, 2174, 1455, 1412, 1248, 1016. UV (CH₃CN): λ_max [nm] (lg ε) = 194 (4.74). MS (EI, 70 eV): m/z (%)= 217.1 (5) [M-H]⁺. C₁₃H₁₈OSi (218.37), calc.: 217.1049, found: 217.1058, [M-H]⁺ (EI-HRMS).

Compound 24a

![Chemical Structure](image)

Alcohol 23a (2.67 g, 12.2 mmol, 1.0 equiv), triphenylphosphine (4.81 g, 18.3 mmol, 1.5 equiv), imidazole (1.25 g, 18.3 mmol, 1.5 equiv) and iodine (4.66 g, 18.3 mmol, 1.5 equiv), dissolved in Et₂O (100 mL) and MeCN (25 mL) were brought to reaction according to GP1. Purification by silica gel column chromatography (pentane) afforded 3.96 g (99%) of compound 24a as an orange oil: Rf: 0.68 (hexane/EtOAc = 10:1). ^1H-NMR (300 MHz, CDCl₃): δ = 0.17 (s, 9 H, Me₃Si), 3.68 (s, 2 H, 8-H), 4.48 (s, 2 H, 1-H), 7.16–7.33 (m, 3 H, H₉), 7.42–7.47 (m, 1 H, H₈). ^13C-NMR (125 MHz, CDCl₃): δ = -0.1 (Me₃Si), 3.5 (C-1), 23.5 (C-8), 87.9, 102.9 (C-9, C-10), 127.5, 128.7, 129.4, 129.8 (C-3, C-4, C-5, C-6), 134.8, 136.5 (C-2, C-7). IR (ATR): v (cm⁻¹) = 2957, 2174, 1488, 1454, 1248, 1152, 837. UV (CH₃CN): λ_max [nm] (lg ε) = 240 (3.91). MS (ESI): m/z (%) = 279.1 (6) [M-TMS+Na]⁺. C₁₃H₁₇ISi (328.26).

Compound 16a

![Chemical Structure](image)

Silylacetylene 25 (1.50 g, 10.7 mmol, 3.0 equiv) in THF (50 mL), ethyl magnesium bromide (3.0 mol/L in diethyl ether, 3.55 mL, 10.7 mmol, 3.0 equiv), CuCl (141 mg, 1.42 mmol,
40 mol %) and 24a (1.17 g, 3.55 mmol, 1.0 equiv) in THF (15 mL) were brought to reaction according to GP5.2. Purification by silica gel column chromatography (pentane/CH₂Cl₂ = 150:1) afforded 1.15 g (95%) of compound 16a as a yellow oil: Rf: 0.32 (hexane/CH₂Cl₂ = 10:1). ¹H-NMR (300 MHz, CDCl₃): δ = 0.17–0.18 (m, 9 H, Me₃Si), 1.04–1.10 (m, 14 H, iPr-H), 3.64 (s, 2 H, 3-H*), 3.69 (s, 2 H, 10-H*), 3.72 (s, 1 H, SiH), 7.23–7.29 (m, 2 H, Hα), 7.42–7.53 (m, 2 H, Hα). ¹³C-NMR (125 MHz, CDCl₃): δ = 0.0 (Me₃Si), 10.9, 18.3, 18.5 (C₆H₅), 23.9, 24.0 (C₃, C-10), 81.1, 87.4 (C-2, C-11), 103.3, 106.1 (C-1, C-12), 127.2, 127.2, 128.6, 128.7 (C-5, C-6, C-7, C-8), 134.1, 134.1 (C-4, C-9). IR (ATR): ʋ (cm⁻¹) = 2942, 2863, 2174, 2116, 1455, 1249. UV (CH₃CN): λmax [nm] (lg ε) = 260 (2.45), 193 (4.72). MS (ESI): m/z (%) = 363.3 (33) [M+Na]⁺. C₂₁H₂₂Si₂ (340.65), calc.: 363.1935, found: 363.1936, [M+Na]⁺ (ESI-HRMS).

**Compound 14a**

Dialkyne 16a (582 mg, 1.71 mmol, 1.2 equiv) was dissolved in dry CCl₄ (20.0 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry CCl₄ (0.976 mol/L, 1.75 mL, 1.71 mmol, 1.2 equiv) was added over a period of 1 h via syringe pump and stirred for further 2 h at 0 °C. The resulting solution was added to a mixture of glacial 15a (378 mg, 1.42 mmol, 1.0 equiv), NEt₃ (395 µL, 2.85 mmol, 2.0 equiv) and DMAP (18 mg, 0.142 mmol, 10 mol %) in dry CCl₄ (20.0 mL) and dry Et₂O (2.5 mL) at 0 °C over a period of 30 min via syringe pump. The reaction was stirred overnight and stopped by the addition of saturated aq. NH₄Cl solution. The aqueous layer was extracted three times with CH₂Cl₂. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na₂SO₄. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc = 100:1) to afford 754 mg (88%) of compound 14a as a colorless oil: Rf: 0.62 (hexane/EtOAc = 6:1). [α]D²⁰ = +52.7° (c = 0.33, CHCl₃). ¹H-NMR (300 MHz, CDCl₃): δ = 0.18 (s, 9 H, Me₃Si), 1.07–1.14 (m, 14 H, iPr), 1.38 (s, 3 H, 8-H), 1.48 (s, 3 H, 9-H), 3.65 (s, 2 H, 3'-H), 3.71 (s, 2 H, 10'-H), 3.75–3.83 (m, 2 H, 4-H*, 6-Hα), 3.89–3.97 (m, 2 H, 5-H*, 6-Hβ), 4.57 (dd, J = 1.4, 7.1 Hz, 1 H, 3-H), 6.56 (d, J = 1.4 Hz, 1 H, 1-H), 7.24–7.31 (m, 2 H, Hα), 7.41–7.47 (m, 1 H, Hα), 7.55–7.59 (m, 1 H, Hα). ¹³C-NMR (125 MHz, CDCl₃): δ = 0.1 (Me₃Si), 13.3, 14.0, 17.2, 17.3, 17.6, 17.7 (C₆H₅), 18.7, 28.9 (C-8, C-9), 23.9, 24.0 (C-3', C-10'), 61.3 (C-6), 70.3, 71.6, 73.2 (C-3, C-4, C-5), 82.8, 87.5, 103.3, 106.1 (C-1', C-2', C-11', C-12'), 99.6 (C-7), 103.7 (C-2), 127.2, 127.2, 128.6, 128.7 (C-5', C-6', C-7', C-8'), 134.0,

S8
134.1 (C-4', C-9'), 143.6 (C-1). IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 2944, 2865, 2173, 1631, 1462, 1249, 1171. UV (CH\(_3\)CN): \( \lambda_{\text{max}} \) [nm] (lg \( \varepsilon \)) = 193 (4.69). MS (ESI): \( m/z \) (%) = 627.2 (100) [M+Na]\(^+\). C\(_{30}\)H\(_{43}\)O\(_4\)Si\(_2\)Br (603.74), calc.: 627.1757, found: 627.1765, [M+Na]\(^+\) (ESI-HRMS).

**Compound 13a**

The alkynylated bromoglycal 14a (300 mg, 0.497 mmol, 1.0 equiv), Pd(PPh\(_3\))\(_4\) (58 mg, 0.050 mmol, 10 mol %), t-Bu\(_3\)PH-BF\(_4\) (29 mg, 0.099 mmol, 20 mol %) and diisopropylamine (352 \( \mu \)L, 2.48 mmol, 5.0 equiv), dissolved in DMF/MeCN/NMP (9.0 mL, 9.0 mL, 1.1 mL) were brought to reaction according to GP5. Purification by silica gel column chromatography (pentane/EtOAc = 30:1) afforded 210 mg (81%) of compound 13a as a white solid: \( R_f \): 0.41 (hexane/EtOAc = 10:1). [\( \alpha \)]\(_D\)\(^{20} \) = +27.2\(^\circ\) (c = 0.16, CHCl\(_3\)).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)):

\( \delta \) = 0.41 (s, 9 H, Me\(_{\text{TMS}}\)), 0.93 (d, \( J = 7.5 \) Hz, 3 H, CH\(_{3,iPr}\)), 0.99 (d, \( J = 7.4 \) Hz, 3 H, CH\(_{3,Pi}\)), 1.13 (d, \( J = 7.3 \) Hz, 3 H, CH\(_{3,\text{in}}\)), 1.20 (d, \( J = 7.5 \) Hz, 3 H, CH\(_{3,Pi}\)), 1.23-1.47 (m, 2 H, CH\(_{3,iPr}\)), 1.53 (s, 3 H, 8-H), 1.55 (s, 3 H, 9-H), 3.71-4.16 (m, 8 H, 4-H, 5-H, 6-H, 12-H, 19-H), 5.09 (d, \( J = 9.1 \) Hz, 1 H, 13-H), 7.15-7.31 (m, 4 H, 14-H, 15-H, 16-H, 17-H). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)):

\( \delta \) = 2.7 (Me\(_{\text{TMS}}\)), 12.9, 13.8, 17.2, 17.4, 17.4, 17.7 (C\(_{Pi}\)), 19.1, 29.1 (C-8, C-9), 37.3, 39.2 (C-12, C-19), 62.3 (C-6), 70.2, 72.5, 78.1 (C-3, C-4, C-5), 100.0 (C-7), 123.8 (C-21), 126.0, 126.1, 126.3, 126.8 (C-14, C-15, C-16, C-17), 130.1, 133.5, 135.2, 137.6, 137.6, 144.6 (C-2, C-10, C-11, C-13, C-18, C-20), 154.1 (C-1). IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 2941, 2862, 1538, 1538, 1380, 1246, 1091. UV (CH\(_3\)CN): \( \lambda_{\text{max}} \) [nm] (lg \( \varepsilon \)) = 306 (3.70), 300 (3.68), 263 (3.41), 212 (4.62). MS (ESI): \( m/z \) (%) = 545.3 (100) [M+Na]\(^+\). C\(_{80}\)H\(_{82}\)O\(_8\)Si\(_2\) (522.82), calc.: 545.2514, found: 545.2522, [M+Na]\(^+\) (ESI-HRMS).

**Compound 26a**

To a solution of 13a (130 mg, 0.249 mmol, 1.0 equiv) in MeOH (10 mL) was added dropwise Ac\(_2\)Cl (1.0 mL) at 0 °C. The reaction mixture was stirred at 60 °C for 2 h and then stopped by slow addition of saturated aq. NaHCO\(_3\) solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na\(_2\)SO\(_4\). The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography to afford 98 mg (96%) of
compound 26a as a white solid: \( R_t: 0.30 \) (CH\(_2\)Cl\(_2\)/MeOH = 10:1). [\( \alpha \)]\(_D\)\(^{20}\) = +38.7° (c = 0.15, CHCl\(_3\)). \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 0.86 \) (d, \( J = 7.4 \) Hz, 3 H, Me\(_{26}\)), 1.01 (d, \( J = 7.4 \) Hz, 3 H, Me\(_{26}\)), 1.14 (d, \( J = 7.3 \) Hz, 3 H, Me\(_{26}\)), 1.19 (d, \( J = 7.5 \) Hz, 3 H, Me\(_{26}\)), 1.20–1.34 (m, 1 H, CH\(_{26}\)), 1.38–1.50 (m, 1 H, CH\(_{26}\)), 3.72–3.82 (m, 2 H, 9-H\(_{a}\), 4-H\(^*\)), 3.83–3.96 (m, 3 H, 9-H\(_{b}\), 16-H), 3.95–4.08 (m, 2 H, 6-H), 4.14 (dt, \( J = 9.6 \), 3.7 Hz, 1 H, 5-H\(^*\)), 5.05 (d, \( J = 9.1 \) Hz, 1 H, 3-H), 6.79 (s, 1 H, 18-H), 7.16–7.31 (m, 4 H, 11-H, 12-H, 13-H, 14-H). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \( \delta = 12.7\), 13.8, 17.1, 17.3, 17.3, 17.6 (C\(_{26}\)), 36.6, 38.0 (C-9, C-16), 62.6 (C-6), 70.5, 78.9 (C-4, C-5), 80.2 (C-3) 115.0 (C-18), 126.2, 126.2, 126.9, 127.3 (C-11, C-12, C-13, C-14), 130.8, 132.8, 132.9, 136.6, 136.8, 138.6 (C-2, C-7, C-8, C-10, C-15, C-17), 149.4 (C-1). IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3377, 2941, 2863, 2360, 1586, 1447, 1261. UV (CH\(_3\)CN): \( \lambda_{\text{max}} \) [nm] (lg \( e \)) = 260 (4.23). MS (ESI): \( m/z \) (%) = 433.2 (62) [M+Na]\(^+\). C\(_{24}\)H\(_{30}\)O\(_4\)Si (410.58), calc.: 433.1806, found: 433.1802, [M+Na]\(^+\) (ESI-HRMS).

**Compound 12a**

![Diagram of Compound 12a](image)

To a solution of 26a (20 mg, 0.049 mmol, 1.0 equiv) in THF (0.1 mL) was added TBAF (1.0 mol/L in THF, 146 µL, 0.146 mmol, 3.0 equiv). The mixture was stirred for 70 min and directly poured on a packed silica gel column (CH\(_2\)Cl\(_2\)/MeOH = 10:1). 14 mg (96%) of compound 12a were obtained as a yellow solid after chromatographic purification: \( R_t: 0.23 \) (CH\(_2\)Cl\(_2\)/MeOH = 10:1). [\( \alpha \)]\(_D\)\(^{20}\) = +62.7° (c = 0.11, DMSO). \(^1\)H-NMR (300 MHz, DMSO-d\(_6\)): \( \delta = 3.44–3.55 \) (m, 1 H, 4-H), 3.59–3.71 (m, 1 H, 6-H\(_{a}\)), 3.73–3.83 (m, 2 H, 5-H, 6-H\(_{b}\)), 3.80 (s, 4 H, 9-H, 16-H), 4.40 (t, \( J = 7.1 \) Hz, 1 H, 3-H), 4.69 (t, \( J = 5.7 \) Hz, 1 H, O\(_{C-6}\)), 5.28 (d, \( J = 5.2 \) Hz, 1 H, O\(_{C-4}\)), 5.50 (d, \( J = 6.3 \) Hz, 1 H, O\(_{C-3}\)), 6.69 (s, 1 H, 18-H), 7.11–7.18 (m, 2 H, 12-H, 13-H), 7.22–7.32 (m, 2 H, 11-H, 14-H), 7.28 (s, 1 H, 7-H). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \( \delta = 34.5\), 36.0 (C-9, C-16), 60.7 (C-6), 68.5 (C-4), 70.1 (C-3), 79.7 (C-5), 113.8 (C-18), 123.3 (C-2), 125.7, 125.8, 126.5, 127.0 (C-11, C-12, C-13, C-14), 127.0 (C-7), 128.1 (C-17), 136.4, 136.6 (C-10, C-15), 137.0 (C-8), 151.5 (C-1). IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3319, 2879, 1494, 1429, 1255, 1049. UV (CH\(_3\)CN): \( \lambda_{\text{max}} \) [nm] (lg \( e \)) = 261 (3.67), 283 (3.55). MS (ESI): \( m/z \) (%) = 321.1 (100) [M+Na]\(^+\). C\(_{18}\)H\(_{18}\)O\(_4\) (298.33), calc.: 321.1097, found: 321.1097, [M+Na]\(^+\) (ESI-HRMS).

**Compound 27a**

![Diagram of Compound 27a](image)
Compound 12a (40 mg, 0.136 mmol, 1.0 equiv), TBSCI (309 mg, 2.05 mmol, 15.0 equiv), imidazole (418 mg, 6.13 mmol, 45.0 equiv) and DMAP (17 mg, 0.136 mmol, 1.0 equiv) were dissolved in DMF (8.0 mL). The reaction mixture was heated in a sealed vial at 90 °C for 24 h. Then additional TBSCI (100 mg, 0.681 mmol, 20 mol %) was added. The reaction was heated at 90 °C for further 14 h and stopped by the addition of saturated aq. NH₄Cl solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed three times with saturated aq. NaCl solution and dried over Na₂SO₄. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc = 100:1) to afford 69 mg (79%) of compound 27a as a colorless oil: \( R_f \): 0.49 (hexane/EtOAc = 10:1). [\( \alpha \)]D²⁰ = +45.0° (c = 0.08, CHCl₃). ¹H-NMR (300 MHz, CDCl₃): \( \delta \) = 0.00 (s, 3 H, MeTBS), 0.05 (s, 3 H, MeTBS), 0.08 (s, 3 H, MeTBS), 0.09 (s, 3 H, MeTBS), 0.16 (s, 3 H, MeTBS), 0.19 (s, 3 H, MeTBS), 0.19 (s, 3 H, MeTBS), 0.81 (s, 9 H, tBuTBS), 0.88 (s, 9 H, tBuTBS), 0.89 (s, 9 H, tBuTBS), 3.81–3.93 (m, 6 H, 4-H+, 6-Ha, 9-H, 16-H), 4.04 (dd, \( J = 2.4, 0.7 \) Hz, 1 H, 6-Hb*), 4.23–4.29 (m, 1 H, 5-H*), 4.40–4.42 (m, 1 H, 3-H*), 6.80 (s, 1 H, 18-H), 7.02 (s, 1 H, 7-H), 7.17–7.23 (m, 2 H, Ha), 7.23–7.31 (m, 2 H, Ha). ¹³C-NMR (125 MHz, CDCl₃): \( \delta = -5.3, -5.2, -4.6, -4.6, -4.2, -4.2 \) (MeTBS), 17.9, 18.0, 18.3 (C₄TBS), 25.7, 25.7, 25.9 (tBuTBS), 35.2, 36.0 (C-9, C-16), 62.6 (C-6), 68.7, 69.5, 80.7 (C-3, C-4, C-5, C-), 115.5 (C-18), 119.9, 127.9, 136.6, 137.1, 137.5 (C-2, C-8, C-10, C-15, C-17), 125.9, 125.9, 127.3, 1274, 129.3 (C-7, C-11, C-12, C-13, C-14), 150.3 (C-1). IR (ATR): \( \tilde{\nu} \) (cm⁻¹) = 2928, 2856, 2360, 1471, 1251. UV (CH₅CN): \( \lambda_{\text{max}} \) [nm] (lg e) = 261 (4.35). MS (ESI): \( m/z \) (%) = 663.4 (77) [M+Na]+. C₉₆H₆₀O₄Si₃ (641.12), calc.: 664.3722, found: 664.3694, [M+Na]+ (ESI-HRMS).

**Compound 28a**

Compound 27a (64 mg, 0.100 mmol, 1.0 equiv), FeCl₃·6H₂O (6 mg, 0.020 mmol, 20 mol %) and t-BuOOH (5.5 mol/L in decane, 182 μL, 0.998 mmol, 10.0 equiv) were dissolved in dry pyridine (4.0 mL). The reaction mixture was aerated with molecular oxygen and heated in a sealed vial at 80 °C for 4 h. After common aqueous workup (general procedures) the residue was purified by silica gel column chromatography (pentane/EtOAc = 25:1) to afford 47 mg (70%) of compound 28a as a yellow solid: \( R_f \): 0.43 (hexane/EtOAc = 10:1). [\( \alpha \)]D²⁰ = -11.4° (c = 0.14, CHCl₃). ¹H-NMR (300 MHz, CDCl₃): \( \delta = 0.01 \) (s, 3 H, MeTBS), 0.06 (s, 3 H, MeTBS), 0.08 (s, 3 H, MeTBS), 0.11 (s, 3 H, MeTBS), 0.19 (s, 3 H, MeTBS), 0.23 (s, 3 H, MeTBS), 0.78 (s, 9 H, tBuTBS), 0.87 (s, 9 H, tBuTBS), 0.89 (s, 9 H, tBuTBS), 3.89 (dd, \( J = 5.3, 11.3 \) Hz, 1 H, 6-Ha), 3.97 (dd, \( J = 7.4, 11.3 \) Hz, 1 H, 6-Hb), 4.14 (dd, \( J = 1.8, 3.2 \) Hz, 1 H, 4-H*), 4.40–4.46 (m,
To a solution of 28a (43 mg, 0.098 mmol, 1.0 equiv) in MeOH (8.0 mL) and water (0.8 mL) was added HCl (0.3 mol/L, 0.8 mL). The mixture was stirred for 14 h at 75 °C and stopped by the addition of saturated aq. NaHCO₃ solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na₂SO₄. The solvent was removed by rotary evaporation and the residue was filtered over a small plug of celite (CH₂Cl₂: 50 mL and CH₂Cl₂/MeOH = 5:1: 250 mL). The product-containing fractions were collected, the solvent was removed by rotary evaporation and the residue was washed with water (250 mL). 26 mg (82%) of compound 11a were obtained as a shiny yellow solid: yield: 82% (99% for small scale reactions). Rₜ: 0.34 (CH₂Cl₂/MeOH = 7:1). [α]培育° = +74.6° (c = 0.13, DMSO). ¹H-NMR (600 MHz, DMSO-d₆): δ = 3.65 (t, J = 9.1 Hz, 1 H, 4-H), 3.77 (dt, J = 12.0, 4.9 Hz, 1 H, 6-H₆), 3.86 (dd, J = 12.0, 2.4 Hz, 1 H, 6-H₄), 4.10 (ddd, J = 9.1, 4.9, 2.4 Hz, 5 H), 4.60 (d, J = 8.3, 3.6 Hz, 1 H, 3-H), 4.86 (t, J = 5.9 Hz, 1 H, OH₃), 5.66 (sbr, 1 H, OH₂), 6.10 (d, J = 5.7 Hz, 1 H, OH₁), 7.41 (s, 1 H, 18-H), 7.86–7.94 (m, 2 H, 12-H, 13-H), 8.16–8.21 (m, 2 H, 11-H, 14-H), 8.30 (s, 1 H, 7-H). ¹³C-NMR (125 MHz, DMSO-d₆): δ = 60.2 (C-6), 66.8 (C-4), 69.4 (C-3), 80.9 (C-5), 112.9 (C-18), 125.9, 126.6, 126.6, 134.5 (C-11, C-12, C-13, C-14) 128.1 (C-7), 132.7, 133.1, 133.2, 133.8, 134.0, (C-2, C-8, C-10, C-15, C-17), 158.5(C-1), 181.1, 182.0 (C-9, C-16). IR (ATR): ν (cm⁻¹) = 3498, 3398, 3323, 2953, 1672, 1584, 1364. UV (MeOH): λmax [nm] (lg ε) = 275 (3.92). MS (ESI): m/z (%) = 325.2 (100) [M-H]. C₁₈H₁₄O₆ (326.3), calc.: 325.0718, found: 325.0715, [M-H]⁺ (ESI-HRMS).
To a solution of dimethylphenylsilylacetylene (3.32 g, 20.7 mmol, 1.5 equiv) in THF (120 mL) was added ethyl magnesium bromide (3.0 mol/L in diethyl ether, 6.90 mL, 20.7 mmol, 1.5 equiv) at room temperature. The solution was heated to reflux for 2 h and then cooled to ambient temperature. CuCl (342 mg, 3.45 mmol, 25 mol %) and 20 (5.00 g, 13.8 mmol, 1.0 equiv) were added to the reaction mixture and heated to 75 °C for 16 h. The reaction was stopped by addition of saturated aq. NH₄Cl solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na₂SO₄. The solvent was removed by rotary evaporation. The crude product was dissolved in MeOH (60 mL) at 0 °C and AcCl (6.0 mL) was added dropwise. The reaction mixture was stirred for 3 h and then stopped by slow addition of NaHCO₃ solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na₂SO₄. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc = 7:1) to afford 2.83 g (73% over two steps) of compound 23b as a yellow oil: \( R_f \): 0.14 (hexane/EtOAc = 5:1).

**1H-NMR** (300 MHz, CDCl₃): \( \delta = 0.44 \) (s, 6 H, MeDMPS), 1.88 (s, 1 H, OMe), 3.78 (s, 2 H, 8-H), 4.74 (s, 2 H, 1-H), 7.25–7.32 (m, 2 H, HA), 7.47–7.52 (m, 1 H, HA), 7.62–7.66 (m, 2 H, HAr). \n
**13C-NMR** (125 MHz, CDCl₃): \( \delta = -0.7 \) (MeDMPS), 23.8 (C-8), 63.2 (C-1), 85.4, 106.1 (C-9, C-10), 127.2, 127.7, 128.2, 128.4, 129.0, 129.3, 133.5 (C-3, C-4, C-5, C-6, CPh,DMPS), 134.4, 137.0, 138.1 (C-2, C-7, Cq,DMPS). IR (ATR): \( \tilde{\nu} \) (cm⁻¹) = 3363, 2957, 2893, 1604, 1488, 1427, 1249, 1113. **UV** (CH₃CN): \( \lambda_{max} \) [nm] (lg \( \varepsilon \)) = 193 (4.89), 253 (3.03). **MS** (ESI): \( m/z \) (%) = 303.1 (100) [M+Na]⁺. \n
**Compound 24b**

Alcohol 23b (1.26 g, 4.48 mmol, 1.0 equiv), triphenylphosphine (1.76 g, 6.72 mmol, 2.0 equiv), imidazole (0.46 g, 6.72 mmol, 2.0 equiv) and iodine (1.71 g, 6.72 mmol, 2.0 equiv), dissolved in Et₂O (40 mL) and MeCN (10 mL) were brought to reaction according to GP1. Purification by silica gel column chromatography (pentane) afforded 1.71 g (98%) of compound 24b as an orange oil: \( R_f \): 0.53 (hexane/EtOAc = 10:1). **1H-NMR** (300 MHz, CDCl₃): \( \delta = 0.44 \) (s, 6 H, MeDMPS), 3.77 (s, 2 H, 8-H), 4.50 (s, 2 H, 1-H), 7.18–7.35 (m, 3 H,
H₆), 7.35–7.41 (m, 3 H, H₆), 7.47–7.51 (m, 1 H, H₆), 7.61–7.67 (m, 2 H, H₆).

**13C-NMR** (125 MHz, CDCl₃): δ = 0.6 (C-1), 3.6 (MeDMPS), 23.7 (C-8), 85.9, 104.8 (C-9, C-10), 127.5, 127.8, 128.7, 129.3, 129.4, 133.6 (C-3, C-4, C-5, C-6, CₚₕDMPS), 134.6, 136.4, 137.1 (C-2, C-7, CₗₕDMPS). **IR** (ATR): v (cm⁻¹) = 3551, 2956, 1715, 1427, 1247, 1112. **UV** (CH₃CN): λmax [nm] (lg ε) = 241 (3.90). **MS** (ESI): m/z (%) = 413 (57) [(M+Na)+].

**Compound 16b**

![Diagram of Compound 16b](image)

Silylacetylene 25 (70% in THF, 1.47 g, 7.33 mmol, 2.0 equiv) in THF (40 mL), ethyl magnesium bromide (3.0 mol/L in diethyl ether, 2.50 mL, 7.33 mmol, 2.0 equiv), CuCl (91 mg, 0.916 mmol, 25 mol %) and 24b (1.43 g, 3.66 mmol, 1.0 equiv) in THF (20 mL) were brought to reaction according to GP5.2. Purification by silica gel column chromatography (pentane/CH₂Cl₂ = 50:1 → 20:1) afforded 1.08 g (73%) of compound 16b as a yellow oil: Rf: 0.26 (hexane/CH₂Cl₂ = 10:1).

**1H-NMR** (300 MHz, CDCl₃): δ = 0.42–0.44 (m, 6 H, MeDMPS), 1.05–1.12 (m, 14 H, iPr), 3.71 (s, 2 H, 3-H), 3.72 (s, 2 H, 10-H), 3.73 (br, 1 H, SiH), 7.25–7.30 (m, 2 H, H₆), 7.36–7.40 (m, 3 H, H₆), 7.46–7.53 (m, 2 H, H₆), 7.62–7.67 (m, 2 H, H₆).

**13C-NMR** (125 MHz, CDCl₃): δ = –0.6 (MeDMPS), 11.0 (CH₃Pr), 18.4, 18.6 (CH₃Ph), 24.1, 24.1 (C-3, C-10), 81.2, 85.4, 105.2, 106.0 (C-1, C-2, C-11, C-12), 127.1, 127.2, 127.8, 128.6, 128.6, 129.2, 133.6 (C-5, C-6, C-7, C-8, CₚₕDMPS), 133.8, 134.0, 137.2 (C-4, C-9, CₗₕDMPS). **IR** (ATR): v (cm⁻¹) = 2941, 2863, 2173, 2115, 1489, 1428, 1248, 1113. **UV** (CH₃CN): λmax [nm] (lg ε) = 244 (2.98), 259 (2.95). **MS** (ESI): m/z (%) = 425.2 (100) [M+Na]+. C₂₆H₃₄Si₂ (402.72), calc.: 425.2091, found: 425.2083, [M+Na]+ (ESI-HRMS).

**Compound 14b**

![Diagram of Compound 14b](image)

Dialkyne 16b (100 mg, 0.245 mmol, 1.0 equiv) was dissolved in dry Et₂O (10 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry Et₂O (0.976 mol/L, 267 µL, 0.261 mmol, 1.05 equiv) was added slowly and stirred for 2 h at 0 °C. The resulting solution was added to a mixture of glucal 15a (66 mg, 0.738 mmol, 1.0 equiv), NEt₃ (45 µL, 0.319 mmol, 1.3 equiv) and DMAP (3 mg, 0.025 mmol, 10 mol %) in dry Et₂O (10 mL) at 0 °C over a period of 20 min. The reaction was stirred over night and stopped by the addition of saturated aq.
NH₄Cl solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na₂SO₄. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc = 30:1) to afford 106 mg (65%) of compound 14b as a colorless oil: Rf: 0.26 (hexane/EtOAc = 20:1). [α]₂⁰ D = +23.2° (c = 0.10, CHCl₃). ¹H-NMR (300 MHz, CDCl₃): δ = 0.42 (s, 6 H, Me₂DMPS), 1.06–1.16 (m, 14 H, ′Pr), 1.38 (s, 3 H, 8-H), 1.48 (s, 3 H, 9-H), 3.72 (s, 2 H, 3′-H), 3.72 (s, 2 H, 10′-H), 3.76–3.84 (m, 2 H, 5-H, 6-H₂*), 3.88–3.96 (m, 2 H, 4-H*, 3-H*), 4.57 (dd, J = 1.4, 7.0 Hz, 1 H, 6-Hb), 6.56 (s, 1 H, 1-H) 7.24–7.29 (m, 2 H, Hₙ), 7.35–7.39 (m, 3 H, Hₐ), 7.46–7.50 (m, 1 H, Hₗ), 7.55–7.59 (m, 1 H, Hₜ), 7.62–7.66 (m, 2 H, Hₙ), 13C-NMR (125 MHz, CDCl₃): δ = −0.6 (Me₂DMPS), 13.4, 14.1, 17.3, 17.4, 17.7, 17.8 (Cₚ), 18.8 (C-8), 24.0, 24.2 (C-3′, C-10′), 28.9 (C-9), 61.3, 70.3, 71.6, 73.2 (C-3, C-4, C-5, C-6), 82.8, 85.5, 105.1, 105.9 (C-1′, C-2′, C-11′, C-12′), 99.5 (C-7), 103.6 (C-2), 127.2, 127.8, 128.6, 128.7, 129.2, 133.6 (C-5′, C-6′, C-7′, C-8′, CₚDMPS), 133.8, 133.9, 137.1 (C-4′, C-9′, CₚDMPS), 143.5 (C-1).MS (ESI): m/z (%) = 689.2 (29) [M+Na]⁺. C₃₅H₄₅BrO₅Si₂ (665.80), calc.: 689.1914, found: 689.1901, [M+Na]⁺ (ESI-HRMS).

**Compound 13b**

![Compound 13b](SI5)

The alkylnylated bromoglycal 14b (200 mg, 0.300 mmol, 1.0 equiv), Pd(PPh₃)₄ (35 mg, 0.030 mmol, 10 mol %), t-Bu₃PH-BF₄ (18 mg, 0.060 mmol, 20 mol %) and diisopropylamine (213 μL, 1.50 mmol, 5.0 equiv), dissolved in DMF/MeCN/NMP (8.0 mL, 8.0 mL, 1.0 mL), were brought to reaction according to GP5. Purification by silica gel column chromatography (pentane/EtOAc = 35:1) afforded 157 mg (89%) of compound 13b as a white solid: Rf: 0.43 (hexane/EtOAc = 6:1). [α]₂⁰ D = 17.2° (c = 0.11, CHCl₃). ¹H-NMR (300 MHz, CDCl₃): δ = 0.64 (s, 3 H, Me₂DMPS), 0.64 (s, 3 H, Me₂DMPS), 0.93 (d, J = 7.5 Hz, 3 H, CH₃,P), 1.00 (d, J = 7.4 Hz, 3 H, CH₃,P), 1.15 (d, J = 7.4 Hz, 3 H, CH₃,P), 1.21 (d, J = 7.4 Hz, 3 H, CH₃,P), 1.24–1.33 (m, 1 H, CH₃,P), 1.42–1.49 (m, 1 H, CH₃,P), 1.52 (s, 3 H, 8-H), 1.54 (s, 3 H, 9-H), 3.57–3.87 (m, 6 H, 4-H, 6-Hₙ, 12-H, 19-H), 3.87–4.01 (m, 2 H, 5-H, 6-Hₙ), 5.10 (d, J = 9.0 Hz, 1 H, 3-H), 6.78 (d, J = 7.2 Hz, 1 H, 14*-H), 7.03–7.20 (m, 3 H, Hₐ), 7.30–7.38 (m, 2 H, Hₐ), 7.49–7.54 (m, 2 H, Hₐ), 13C-NMR (125 MHz, CDCl₃): δ = 1.5, 1.9 (Me₂DMPS), 13.0, 13.9, 17.3, 17.5, 17.5, 17.8 (Cₚ), 19.1, 29.2 (C-8, C-9), 37.6, 39.2 (C-12, C-19), 62.1 (C-6), 70.2 (C-5), 72.4 (C-4), 78.1 (C-3), 99.9 (C-7), 121.4 (C-21), 125.7, 125.9, 126.0, 126.7, 127.8, 128.6, 133.5, 137.4 (C-14, C-15, C-16, C-17, C-20, CₚDMPS, CₚDMPS), 130.1, 133.7, 135.7 (C-10, C-13, C-18), 140.8 (C-11), 145.1 (C-2), 154.4 (C-1). IR (ATR): v (cm⁻¹) = 2941, 2862, 1538, 1381, 1247,
1091. UV (CH$_3$CN): $\lambda_{\text{max}}$ [nm] (lg $\varepsilon$) = 307 (3.72), 211 (4.68). MS (ESI): m/z (%) = 607.3 (100) [M+Na$^+$]. C$_{35}$H$_{44}$O$_4$Si$_2$ (584.89), calc.: 607.2651, found: 607.2670, [M+Na$^+$] (ESI-HRMS).

**Compound 22c**

To a solution of dimethylbenzylsilylacetylene (433 mg, 2.48 mmol, 2.0 equiv) in THF (16 mL) was added ethyl magnesium bromide (3.0 mol/L in diethyl ether, 0.83 mL, 2.48 mmol, 2.0 equiv) at room temperature. The solution was heated to reflux for 2 h and then cooled to ambient temperature. CuCl (62 mg, 0.621 mmol, 50 mol%) and 20 (450 mg, 1.24 mmol, 1.0 equiv) were added to the reaction mixture and heated to 75 °C for 16 h. The reaction was stopped by addition of saturated aq. NH$_4$Cl solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na$_2$SO$_4$. The solvent was removed by rotary evaporation to afford 22c as crude product.

**Yield:** not determined. $R_f$: 0.54 (hexane/EtOAc = 10:1). $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 0.10 (s, 3 H, Me), 0.10 (s, 3 H, Me), 0.13 (s, 3 H, Me$_{\text{TBS}}$), 0.14 (s, 3 H, Me$_{\text{TBS}}$), 0.94–0.95 (m, 9 H, tBu$_{\text{TBS}}$), 2.20 (s, 2 H, CH$_2$Br), 3.64 (s, 2 H, 8-H), 4.76 (s, 2 H, 1-H), 7.02–7.12 (m, 3 H, H$_{\text{Ar}}$), 7.16–7.23 (m, 2 H, H$_{\text{Ar}}$), 7.25–7.29 (m, 2 H, H$_{\text{Ar}}$), 7.39–7.45 (m, 2 H, H$_{\text{Ar}}$). $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ = –5.3 (Me$_{\text{TBS}}$), 2.0 (Me), 18.4 (C$_8$-$\text{TBS}$), 23.3 (C-8), 26.0 (tBu$_{\text{TBS}}$), 26.4 (CH$_2$Br), 63.1 (C-1), 85.5 (C-9), 105.2 (C-10), 124.3, 126.8, 127.0, 127.4, 128.1, 128.3, 128.5 (C-3, C-4, C-5, C-6, CH$_{\text{Bn}}$), 133.5, 138.6, 139.1 (C-2, C-7, C$_{\text{q,Bn}}$). IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2942, 2863, 2174, 2066, 1601, 1492, 1453, 1249. UV (CH$_3$CN): $\lambda_{\text{max}}$ [nm] (lg $\varepsilon$) = 194 (5.06). MS (ESI): m/z (%) = 431.2 (100) [M+Na$^+$]. C$_{25}$H$_{36}$OSi$_2$ (408.72), calc.: 431.2197, found: 431.2191, [M+Na$^+$] (ESI-HRMS).

**Compound 23c**

The crude product 22c was dissolved in MeOH (8 mL) at 0 °C and AcCl (0.8 mL) was added dropwise. The reaction mixture was stirred for 3 h and then stopped by slow addition of saturated aq. NaHCO$_3$ solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na$_2$SO$_4$. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc = 7:1) to afford 224 mg (62% over two steps) of compound 23c as a colorless oil: $R_f$: 0.08 (hexane/EtOAc = 8:1). $^1$H-NMR
(300 MHz, CDCl₃): δ = 0.13 (s, 6 H, Me), 2.19 (s, 2 H, CH₂,Bn), 3.71 (s, 2 H, 8-H), 4.72 (d, J = 5.8 Hz, 2 H, 1-H), 7.00−7.12 (m, 3 H, H₆), 7.13−7.25 (m, 2 H, H₅), 7.25−7.35 (m, 2 H, H₄), 7.35−7.44 (m, 2 H, H₃). ¹³C-NMR (125 MHz, CDCl₃): δ = −2.0 (Me), 23.6 (CH₂,Bn), 26.3 (C-8), 63.2 (C-1), 85.7 (C-9), 105.7 (C-10), 124.3, 137.2, 128.2, 128.5, 129.1 (C-3, C-4, C-5, C-6, CH₃), 128.1, 128.3 (CH₃), 134.5, 138.2, 139.0 (C-2, C-7, C₆,Bn). IR (ATR): ν (cm⁻¹) = 3317, 3059, 2889, 2173, 1559, 1492, 1248. UV (CH₂CN): λmax [nm] (lg ε) = 197 (4.78), 260 (3.20). MS (ESI): m/z (%) = 317.1 (100) [M+Na]⁺. C₁₉H₂₂OSi (294.46), calc.: 295.1513, found: 295.1511, [M+Na]⁺ (ESI-HRMS).

**Compound 24c**

Alcohol 23c (540 mg, 1.83 mmol, 1.0 equiv), triphenylphosphine (962 mg, 3.67 mmol, 2.0 equiv), imidazole (250 mg, 3.67 mmol, 2.0 equiv) and iodine (932 mg, 3.67 mmol, 2.0 equiv), dissolved in Et₂O (16 mL) and MeCN (4.0 mL), were brought to reaction according to GP1. Purification by silica gel column chromatography (pentane) afforded 722 mg (97%) of compound 24c as a yellow oil: Rf: 0.72 (hexane/EtOAc = 10:1). ¹H-NMR (300 MHz, CDCl₃): δ = 0.17 (s, 6 H, Me), 2.23 (s, 2 H, CH₂,Bn), 3.71 (s, 2 H, 8-H), 4.48 (s, 2 H, 1-H), 7.05−7.14 (m, 3 H, H₆), 7.19−7.27 (m, 3 H, H₅), 7.29−7.36 (m, 2 H, H₄), 7.40−7.44 (m, 1 H, H₃). ¹³C-NMR (125 MHz, CDCl₃): δ = −2.0 (Me), 3.6 (C-1), 23.6 (CH₂,Bn), 26.3 (C-8), 86.2 (C-9), 104.4 (C-10), 124.3, 127.5, 128.7, 129.5, 129.8 (C-3, C-4, C-5, C-6, CH₃), 128.1, 128.3 (CH₃), 134.7, 136.5, 139.0 (C-2, C-7, C₆,Bn). IR (ATR): ν (cm⁻¹) = 3022, 2956, 2172, 1599, 1491, 1451, 1248. UV (CH₂CN): λmax [nm] (lg ε) = 197 (4.96). MS (ESI): m/z (%) = 427.0 (42) [M+Na]⁺. C₁₉H₂₂OSi (404.36), calc.: 427.0349, found: 427.0344, [M+Na]⁺ (ESI-HRMS).

**Compound 16c**

Silylacetylene 25 (490 mg, 3.49 mmol, 2.0 equiv) in THF (25 mL), ethyl magnesium bromide (3.0 mol/L in diethyl ether, 1.2 mL, 3.49 mmol, 2.0 equiv), CuCl (87 mg, 0.872 mmol, 50 mol %) and 24c (705 g, 1.73 mmol, 1.0 equiv) in THF (7 mL) were brought to reaction according to GP5.2. Purification by silica gel column chromatography (pentane/CH₂Cl₂ = 100:1) afforded 170 mg (23%) of compound 16c as clear oil: Rf: 0.54 (hexane/EtOAc = 20:1). ¹H-NMR (300 MHz, CDCl₃): δ = 0.14 (s, 6 H, Me), 1.01−1.14 (m, 14, H₅), 2.19 (s, 2 H, CH₂,Bn), 3.64 (s, 2 H, 3-H⁺), 3.67 (s, 2 H, 10-H⁺), 3.72 (s, 1 H, SiH), 7.02−
7.12 (m, 3 H, H₆), 7.16–7.30 (m, 4 H, H₈), 7.38–7.42 (m, 1 H, H₉), 7.49–7.53 (m, 1 H, H₇).

**13C-NMR** (125 MHz, CDCl₃): δ = −2.0 (Me), 10.9, 18.3, 18.5 (C₆Pr), 24.0, 24.0 (C-3, C-10), 26.4 (CH₂-Bn), 81.2, 85.8 (C-2, C-11), 104.7, 106.1 (C-1, C-12), 124.3, 127.2, 127.2, 128.1, 128.3, 128.6, 128.8 (C-5, C-6, C-7, C-8, CH₃Bn), 133.9, 134.1, 139.0 (C-4, C-9, C₆Bn). IR (ATR): ν (cm⁻¹) = 2941, 2862, 1600, 1492, 1453, 1249. UV (CH₃CN): λ_max [nm] (lg ε) = 194 (5.06), 266 (3.33). MS (ESI): m/z (%) = 434.3 (100) [M+Na⁺]. C₂₇H₃₆Si₂ (416.75), calc.: 434.2694, found: 434.2695, [M+Na⁺] (ESI-HRMS).

**Compound 14c**

Dialkyne 16c (100 mg, 0.240 mmol, 1.0 equiv) was dissolved in dry CCl₄ (4.0 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry CCl₄ (0.976 mol/L, 369 µL, 0.360 mmol, 1.5 equiv) was added over a period of 1 h via a syringe pump and stirred for further 2 h at 0 °C. The resulting solution was added to a mixture of glucal 15a (77 mg, 0.288 mmol, 1.0 equiv), NEt₃ (67 µL, 0.480 mmol, 2.0 equiv) and DMAP (3 mg, 0.024 mmol, 10 mol %) in dry CCl₄ (4.0 mL) and dry Et₂O (1.0 mL) at 0 °C over a period of 30 min via syringe pump. The reaction was stirred for 2 h and stopped by the addition of saturated aq. NH₄Cl solution. The aqueous layer was extracted three times with CH₂Cl₂. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na₂SO₄. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc = 100:1) to afford 56 mg (35%) of compound 14c as a colorless oil: Rf: 0.46 (hexane/EtOAc = 6:1). [α]D ≈ +33.6° (c = 0.25, CHCl₃). **1H-NMR** (300 MHz, CDCl₃): δ = 0.13 (s, 6 H, Me), 1.03–1.18 (m, 14 H, iPr), 1.38 (s, 3 H, 8-H), 1.48 (s, 3 H, 9-H), 2.19 (s, 2 H, CH₂-Bn), 3.65 (s, 2 H, 3'-H*), 3.69 (s, 2 H, 10'-H*), 3.74–3.84 (m, 2 H, 4'-H*, 6'-H*), 3.86–3.99 (m, 2 H, 5-H*, 6-H*), 4.58 (dd, J = 1.3, 7.2 Hz, 1 H, 3-H), 6.56 (s, 1 H, 1-H), 7.20–7.42 (m, 8 H, H₆), 7.55–7.62 (m, 1 H, H₇). **13C-NMR** (125 MHz, CDCl₃): δ = −2.0 (Me), 13.3, 14.0, 17.2, 17.3, 17.6, 17.7 (C₆Pr), 18.7, 28.9 (C-8, C-9), 23.9, 24.0 (C-3', C-10'), 26.3 (CH₂-Bn), 61.3 (C-6), 70.3, 71.6, 73.2 (C-3, C-4, C-5), 82.8, 85.9 (C-2', C-11'), 99.6 (C-7), 103.7 (C-2), 104.7, 106.1 (C-1', C-12'), 124.3, 127.2, 127.2, 128.1, 128.3, 128.7 (C-5', C-6', C-7', C-8', CH₃Bn), 133.9, 134.0, 139.0 (C-4', C-9', C₆Bn), 143.6 (C-1). IR (ATR): ν (cm⁻¹) = 2942, 2864, 2173, 1631, 1600, 1492. UV (CH₃CN): λ_max [nm] (lg ε) = no absorption between 190–350 nm. MS (ESI): m/z (%) = 703.2 (46) [M+Na⁺]. C₉₈H₄₇BrO₄Si₂ (679.83), calc.: 679.2269, found: 679.2254, [M+H⁺] (ESI-HRMS).
**Compound 13c**

The alkynylated bromoglycal 14c (54 mg, 0.079 mmol, 1.0 equiv), Pd(PPh₃)₄ (10 mg, 0.008 mmol, 10 mol %), t-Bu₃PH·BF₄ (5 mg, 0.016 mmol, 20 mol %) and diisopropylamine (57 μL, 0.397 mmol, 5.0 equiv), dissolved in DMF/MeCN/NMP (1.5 mL, 1.5 mL, 0.2 mL) were brought to reaction according to GP5. Purification by silica gel column chromatography (pentane/EtOAc = 50:1) afforded 33 mg (70%) of compound 13c as a white solid: Rf: 0.49 (hexane/EtOAc = 4:1). [α]D⁰⁺ = +19.6° (c = 0.26, CHCl₃).

1H-NMR (300 MHz, CDCl₃): δ = 0.39 (s, 3 H, Me), 0.44 (s, 3 H, Me), 0.92 (d, J = 7.4 Hz, 3 H, CH₃,Pr), 1.00 (d, J = 7.3 Hz, 3 H, CH₃,Pr), 1.15 (d, J = 7.3 Hz, 3 H, CH₃,Pr), 1.21 (d, J = 7.4 Hz, 3 H, CH₃,Pr), 1.25–1.50 (m, 2 H, CH₂,Pr), 1.52 (s, 3 H, 8-H), 1.53 (s, 3 H, 9-H), 2.40 (s, 2 H, CH₂,Pr), 3.65–3.86 (m, 4 H, 4-H*, 6-Ha, 12-H), 3.86–4.01 (m, 4 H, 5-H*, 6-Ha, 19-H), 5.07 (d, J = 9.1 Hz, 1 H, 3-H), 6.82 (d, J = 7.3 Hz, 2 H, Ha), 6.97–7.13 (m, 3 H, Ha), 7.16–7.27 (m, 4 H, Ha).

13C-NMR (125 MHz, CDCl₃): δ = 12.2, 1.6 (Me), 12.8, 12.8, 17.1, 17.3, 17.4, 17.7 (C₃), 19.0, 29.1 (C₈, C₉), 27.1 (CH₂,Pr), 37.4, 39.2 (C₁₂, C₁₉), 62.2 (C₆), 70.1, 72.4, 78.1 (C₃, C₄, C₅), 100.0 (C₇), 122.3, 130.2, 133.6, 135.7, 137.3, 137.4, 140.4, 144.7 (C₂, C₁₀, C₁₁, C₁₃, C₁₈, C₂₀, C₂₁, C₄,Pr), 123.9, 126.0, 126.2, 126.3, 127.0 (C₁₄, C₁₅, C₁₆, C₁₇, CH₂,Pr), 127.9, 128.3 (CH₂,Pr), 154.3 (C-1).

IR (ATR): ν (cm⁻¹) = 2942, 2863, 1382, 1248. UV (CH₃CN): λ_{max} [nm] (lg ε) = 211 (4.69), 306 (3.70). MS (ESI): m/z (%) = 621.3 (74) [M+Na]⁺. C₂₆H₂₆O₂Si₂ (598.92), calc.: 621.2827, found: 621.2820, [M+Na]⁺ (ESI-HRMS).

**Compound 22d**

Diisopropylsilylacetylene (1.13 g, 8.05 mmol, 2.9 equiv) in THF (40 mL), ethyl magnesium bromide (3.0 mol/L in diethyl ether, 2.68 mL, 8.05 mmol, 2.9 equiv), CuCl (110 mg, 1.10 mmol, 40 mol %) and 20 (1.00 g, 2.76 mmol, 1.0 equiv) in THF (10 mL) were brought to reaction according to GP5.2. Purification by silica gel column chromatography (pentane/EtOAc = 100:1) afforded 821 mg (80%) of compound 22d as a pale yellow oil: Rf: 0.60 (hexane/EtOAc = 8:1).

1H-NMR (300 MHz, CDCl₃): δ = 0.10 (s, 6 H, Me₃TBS), 0.94 (s, 9 H, fBuTBS), 1.03–1.12 (m, 14 H, iPr), 3.68 (s, 2 H, 8-H), 3.72 (s, 1 H, SiH), 4.77 (s, 2 H, 1-H), 7.24–7.28 (m, 2 H, Ha), 7.39–7.43 (m, 1 H, Ha), 7.48–7.52 (m, 1 H, Ha).

13C-NMR (125 MHz, CDCl₃): δ = −5.3 (Me₃TBS), 10.9, 18.3, 18.4 (C₃), 18.4 (C₄,Pr), 23.4 (C₈, C₉), 25.9 (fBuTBS), 25.9 (fBuTBS).
Compound 23d

The protected alcohol 22 (810 mg, 2.162 mmol, 1.0 equiv), dissolved in MeOH (8.0 mL), and AcCl (0.8 mL) were brought to reaction according to GP5.3. Purification by silica gel column chromatography (pentane/EtOAc = 10:1) afforded 464 mg (83%) of compound 23 as a colorless oil: Rf: 0.20 (hexane/EtOAc = 8:1). H-NMR (300 MHz, CDCl3): δ = 0.97–1.16 (m, 14 H, iPr), 3.71 (s, 1 H, SiH), 3.76 (s, 2 H, H-8), 4.74 (d, J = 5.8 Hz, 2 H, H-1), 7.24–7.32 (m, 2 H, HAr), 7.31–7.42 (m, 1 H, HAr), 7.46–7.55 (m, 1 H, HAr). C16H24OSi (260.45), calc.: 283.1489, found: 283.1491, [M+Na]+ (ESI-HRMS).

Compound 23d-2

Alkyne 23d (248 mg, 1.708 mmol, 1.2 equiv) and MeOH (1.2 mL) were dissolved in dry CCl4 (15 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry CCl4 (0.976 mol/L, 975 µL, 0.952 mmol, 1.0 equiv) was added over a period of 30 min via syringe pump and stirred for further 15 min at 0 °C. To this solution NEt3 (221 µL, 1.589 mmol, 2.0 equiv) was added and stirred for 1 h. The reaction was stopped by the addition of saturated aq. NH4Cl solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na2SO4. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc = 10:1) to afford 201 mg (87%) of compound 23d-2 as a colorless oil: Rf: 0.14 (hexane/EtOAc = 8:1). H-NMR (300 MHz, CDCl3): δ = 1.00–1.40 (m, 14 H, iPr), 3.55 (s, 3 H, OCH3), 3.80 (s, 2 H, H-8), 7.78 (d, J = 6.0 Hz, 2 H, H-1), 7.23–7.39 (m, 3 H, HAr), 7.50–7.57 (m, 1 H, HAr). C16H22OSi (260.45), calc.: 283.1489, found: 283.1491, [M+Na]+ (ESI-HRMS).
C-4, C-5, C-6), 134.6, 138.1 (C-2, C-7). IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3350, 2941, 2864, 2172, 1461, 1094. UV (CH\(_3\)CN): \( \lambda_{\text{max}} \) [nm] (lg \( \varepsilon \)) = 193 (4.70), 261 (2.24). MS (ESI): \( m/z \) (%) = 313.2 (100) [M+Na]+. \( \text{C}_{17}\text{H}_{26}\text{O}_{2}\text{Si} \) (290.47), calc.: 313.1594, found: 313.1596, [M+Na]+ (ESI-HRMS).

**Compound 24d**

Alcohol 23d-2 (440 mg, 1.51 mmol, 1.0 equiv), triphenylphosphine (596 mg, 2.27 mmol, 1.5 equiv), imidazole (155 mg, 2.27 mmol, 1.5 equiv) and iodine (577 mg, 2.27 mmol, 1.5 equiv), dissolved in Et\(_2\)O (12 mL) and MeCN (3.0 mL) were brought to reaction according to GP1. Purification by silica gel column chromatography (pentane) afforded 403 mg (67%) of compound 24d as a pale yellow oil: \( R_f \): 0.67 (hexane/EtOAc = 20:1). \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta \) = 1.00–1.10 (m, 14 H, iPr), 3.56 (s, 3 H, OMe), 3.75 (s, 2 H, 8-H), 4.49 (s, 2 H, 1-H), 7.16–7.33 (m, 3 H, H\(_{\text{Ar}}\)), 7.48–7.53 (m, 1 H, H\(_{\text{Ar}}\)). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \( \delta \) = 3.4 (C-1), 12.9, 17.1, 17.3 (C\(_{\text{iPr}}\)), 23.4 (C-8), 52.3 (OMe), 82.4, 104.8 (C-9, C-10), 127.5, 128.8, 129.3, 129.8 (C-3, C-4, C-5, C-6), 134.6, 136.3 (C-2, C-7). IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 2940, 2863, 2172, 1461, 1151. UV (CH\(_3\)CN): \( \lambda_{\text{max}} \) [nm] (lg \( \varepsilon \)) = 241 (3.90). MS (ESI): \( m/z \) (%) = 423.1 (100) [M+Na]+. \( \text{C}_{17}\text{H}_{25}\text{IOSi} \) (400.37), calc.: 423.0612, found: 423.0604, [M+Na]+ (ESI-HRMS).

**Compound 16d**

Silylacetylene 25 (400 mg, 2.884 mmol, 3.0 equiv) in THF (18 mL), ethyl magnesium bromide (3.0 mol/L in diethyl ether, 0.96 mL, 2.884 mmol, 3.0 equiv) and 24d (385 g, 0.962 mmol, 1.0 equiv) in THF (6.0 mL) were brought to reaction according to GP5.2. Purification by silica gel column chromatography (pentane/CH\(_2\)Cl\(_2\) = 150:1) afforded 173 mg (43%) of compound 16d as a pale yellow oil: \( R_f \): 0.39 (hexane/EtOAc = 20:1). \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta \) = 0.99–1.12 (m, 28 H, iPr), 3.57 (s, 3 H, OMe), 3.71 (s, 2 H, 3-H*), 3.71 (s, 1 H, SiH), 3.73 (s, 2 H, 10-H*), 7.22–7.31 (m, 2 H, H\(_{\text{Ar}}\)), 7.44–7.56 (m, 2 H, H\(_{\text{Ar}}\)). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \( \delta \) = 10.9, 12.9, 17.0, 17.2, 18.2, 18.5 (C\(_{\text{iPr}}\)), 23.8, 24.0 (C-3, C-10), 52.3 (OMe), 81.2, 82.0, 105.2, 105.0 (C-1, C-2, C-11, C-12), 127.2, 127.2, 128.6, 128.7 (C-5, C-6, C-7, C-8), 133.9, 134.0 (C-4, C-9). IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 2941, 2863, 2172, 2117, 1461, 1095. UV (CH\(_3\)CN): \( \lambda_{\text{max}} \) [nm] (lg \( \varepsilon \)) = 193 (4.75), 253 (2.55). MS (ESI): \( m/z \) (%) = 435.3 (100) [M+Na]+. \( \text{C}_{25}\text{H}_{49}\text{OSi}_2 \) (412.76), calc.: 435.2510, found: 435.2503, [M+Na]+ (ESI-HRMS).
Compound 14d

Dialkyne 16d (165 mg, 0.396 mmol, 1.2 equiv) was dissolved in dry CCl₄ (6.0 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry CCl₄ (0.976 mol/L, 406 µL, 0.396 mmol, 1.2 equiv) was added over a period of 1 h via syringe pump and stirred for further 2 h at 0 °C. The resulting solution was added to a mixture of glucal 15a (88 mg, 0.330 mmol, 1.0 equiv), NEt₃ (92 µL, 0.660 mmol, 2.0 equiv) and DMAP (5 mg, 0.040 mmol, 10 mol %) in dry CCl₄ (4.0 mL) and dry Et₂O (0.5 mL) at 0 °C over a period of 30 min via syringe pump. The reaction was stirred overnight and stopped by the addition of saturated aq. NH₄Cl solution. The aqueous layer was extracted three times with CH₂Cl₂. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na₂SO₄. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc = 100:1) to afford 78 mg (30%) of compound 14d as a colorless oil: \(R_f: 0.35\) (hexane/EtOAc = 10:1). \(\Delta H_{\text{fus}} = +60.3^\circ\) (c = 0.32, CHCl₃). 

**1H-NMR** (300 MHz, CDCl₃): \(\delta = 1.00–1.15\) (m, 28 H, \(i\)-Pr), 1.38 (s, 3 H, 8-H), 1.47 (s, 3 H, OMe), 3.57 (s, 3 H, OMe), 3.73 (s, 2 H, 3'-H*), 3.74 (s, 2 H, 10'-H*), 3.75–3.86 (m, 2 H, 4'-H*, 6'-Hₐ), 3.88–3.97 (m, 2 H, 5'-H*, 6'-Hₐ), 4.56 (dd, \(J = 1.3, 7.0\) Hz, 1 H, 3-H), 6.56 (d, \(J = 1.3\) Hz, 1 H, 1-H), 7.22–7.33 (m, 2 H, Hₐ), 7.47–7.60 (m, 2 H, Hₐ). 

**13C-NMR** (150 MHz, CDCl₃): \(\delta = 13.0, 13.3, 14.1, 17.1, 17.3, 17.3, 17.3, 17.6, 17.7\) (C₈), 18.8, 28.9 (C-8, C-9), 24.0, 24.0 (C-3', C-10'), 52.3 (OMe), 61.3 (C-6), 70.3, 71.6, 73.2 (C-3, C-4, C-5), 82.1, 82.8, 105.2, 105.8 (C-1', C-2', C-11', C-12'), 99.6 (C-7), 103.6 (C-2), 127.2, 127.2, 128.5, 128.7 (C-5', C-6', C-7', C-8'), 133.8, 133.8 (C-4', C-9'), 143.6 (C-1). \(\lambda_{\text{max}}\) (cm⁻¹) = 3419, 2942, 2864, 2172, 1632, 1462, 1171. **UV** (CH₃CN): \(\lambda_{\text{max}}\) [nm] (lg e) = 194 (5.13). **MS** (ESI): \(m/z\) (%) = 694.3 (100) [M+NH₄]+. 

**Compound 13d**

The alkynylated bromoglycal 14d (70 mg, 0.104 mmol, 1.0 equiv), Pd(PPh₃)₄ (12 mg, 0.010 mmol, 10 mol %), \(t\)-Bu₃PH-BF₄ (6 mg, 0.021 mmol, 20 mol %) and diisopropylamine (74 µL, 0.518 mmol, 5.0 equiv), dissolved in DMF/MeCN/NMP (2.3 mL, 2.3 mL, 0.3 mL) were...
brought to reaction according to GP5. Purification by silica gel column chromatography (pentane/ EtOAc = 50:1) afforded 53 mg (86%) of compound 13d as a pale yellow solid: \( R_t: 0.29 \) (hexane/EtOAc = 10:1). \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 0.88 \) (d, \( J = 7.5 \) Hz, \( 3 \) H, Me\(_{\beta\beta}\)), 0.92 (d, \( J = 7.5 \) Hz, 3 H, Me\(_{\beta\mu}\)), 0.96 (d, \( J = 7.4 \) Hz, 3 H, Me\(_{\beta\mu}\)), 1.04 (d, \( J = 7.4 \) Hz, 3 H, Me\(_{\beta\mu}\)), 1.05 (d, \( J = 7.5 \) Hz, 3 H, Me\(_{\beta\mu}\)), 1.10 (d, \( J = 7.3 \) Hz, 3 H, Me\(_{\beta\mu}\)), 1.14 (d, \( J = 7.3 \) Hz, 3 H, Me\(_{\beta\mu}\)), 1.21 (d, \( J = 7.4 \) Hz, 3 H, Me\(_{\beta\mu}\)), 1.24–1.48 (m, 4 H, CH\(_{\beta\mu}\)), 1.50 (s, 3 H, 8-H), 1.53 (s, 3 H, 9-H), 3.66 (s, 3 H, OMe), 3.70 (d, \( J = 7.4 \) Hz, 3 H, 1-H). 

**Compound 24e**

Alcohol 23e (328 mg, 2.24 mmol, 1.0 equiv), triphenylphosphine (1832 mg, 4.49 mmol, 2.0 equiv), imidazole (305 mg, 4.49 mmol, 2.0 equiv) and iodine (1140 mg, 4.49 mmol, 2.0 equiv) dissolved in Et\(_2\)O (30 mL) and MeCN (7.5 mL) were brought to reaction according to GP1. Purification by silica gel column chromatography (pentane) afforded 533 mg (93%) of compound 24e as a pale yellow oil.

**yield:** 93 %. \( R_t: 0.57 \) (hexane/EtOAc = 4:1). \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 2.21 \) (t, \( J = 2.7 \) Hz, 1 H, 10-H), 3.65 (d, \( J = 2.7 \) Hz, 2 H, 8-H), 4.49 (s, 2 H, 1-H), 7.16–7.33 (m, 3 H, H\(_{\alpha\alpha}\)), 7.43–7.47 (m, 1 H, H\(_{\alpha\beta}\)). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \( \delta = 3.43 \) (C-1), 22.1 (C-8), 71.3 (C-10), 80.8 (C-9), 127.6, 128.8, 129.5, 129.9 (C-3, C-4, C-5, C-6), 134.6, 136.5 (C-2, C-7). 

**IR (ATR):** \( \tilde{\nu} \) (cm\(^{-1}\)) = 3275, 3258, 1635, 1484, 1145. **UV (CH\(_3\)CN):** \( \lambda_{\text{max}} \) [nm] (lg \( e \)) = 193 (4.45), 238 (3.90). **MS (ESI):** m/z (%) = 279.1 (16) [M+Na]\(^+\). \( \text{C}_{10}\text{H}_{9}\text{I} \) (256.08).

**Compound 16e**

Silylacetylene 25 (838 mg, 5.97 mmol, 3.0 equiv) in THF (35 mL), ethyl magnesium bromide (3.0 mol/L in diethyl ether, 2.0 mL, 5.97 mmol, 3.0 equiv), CuCl (79 mg, 0.796 mmol,
40 mol %) and 24e (510 g, 1.99 mmol, 1.0 equiv) in THF (12 mL) were brought to reaction according to GP5.2. Purification by silica gel column chromatography (pentane/CH₂Cl₂ = 50:1) afforded 292 mg (55%) of compound 16e as a yellow oil: R₉: 0.61 (hexane/EtOAc = 10:1). ¹H-NMR (300 MHz, CDCl₃): δ = 1.00–1.14 (m, 14 H, iPr), 2.19 (t, J = 2.7 Hz, 1 H, 12'-H), 3.62 (d, J = 2.7 Hz, 2 H, 10'-H), 3.71 (s, 2 H, 3-H), 3.72 (s, 1 H, SiH), 7.24–7.29 (m, 2 H, Ha), 7.44–7.53 (m, 2 H, Ha). ¹³C-NMR (125 MHz, CDCl₃): δ = 10.9, 18.3, 18.5 (C₆Pr), 22.5, 24.0 (C-3, C-10), 70.9 (C-12), 81.1, 81.2 (C-2, C-11), 106.0 (C-1), 127.3, 127.4, 128.7, 128.7 (C-5, C-6, C-7, C-8), 133.8, 134.0 (C-4, C-9). IR (ATR): ν (cm⁻¹) = 3307, 2941, 2862, 2174, 2113. UV (CH₃CN): λ_max [nm] (log ε) = 193 (4.71), 260 (2.25). MS (ESI): m/z (%) = 291.2 (22) [M+Na]⁺. C₁₈H₂₆Si (268.47), calc.: 291.1539, found: 291.1538, [M+Na]⁺ (ESI-HRMS).

**Compound 14e**

Dialkyne 16e (284 mg, 1.06 mmol, 1.1 equiv) was dissolved in dry CCl₄ (12 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry CCl₄ (0.976 mol/L, 1.1 mL, 1.06 mmol, 1.1 equiv) was added over a period of 1 h via syringe pump and stirred for further 2 h at 0 °C. To a solution of glucal 15a (255 mg, 0.961 mmol, 1.0 equiv), NEt₃ (267 µL, 1.922 mmol, 2.0 equiv) and DMAP (12 mg, 0.096 mmol, 10 mol %) in dry CCl₄ (6.0 mL) and dry Et₂O (1.5 mL) was added the solution of 16e at 0 °C over a period of 30 min via syringe pump. The reaction was stirred for 2 h and stopped by the addition of saturated aq. NH₄Cl solution. The aqueous layer was extracted three times with CH₂Cl₂. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na₂SO₄. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc = 60:1) to afford 285 mg (56%) of compound 14e as a yellow oil: R₉: 0.42 (hexane/EtOAc = 6:1). [α]D⁰ = +57.1° (c = 0.52, CHCl₃). ¹H-NMR (300 MHz, CDCl₃): δ = 1.06–1.14 (m, 14 H, iPr), 1.38 (s, 3 H, 8-H), 1.48 (s, 3 H, 9-H), 2.19 (t, J = 2.7 Hz, 1 H, 12'-H), 3.62 (d, J = 2.7 Hz, 2 H, 10'-H), 3.73 (s, 2 H, 3'-H), 3.76–3.83 (m, 2 H, 4-H⁺, 6-H₂), 3.88–3.96 (m, 2 H, 5-H⁺), 4.57 (dd, J = 1.4, 7.1 Hz, 1 H, 3-H), 6.56 (d, J = 1.4 Hz, 1 H, 1'-H), 7.24–7.29 (m, 2 H, Ha), 7.42–7.48 (m, 1 H, Ha), 7.54–7.59 (m, 1 H, Ha). ¹³C-NMR (125 MHz, CDCl₃): δ = 13.3, 14.0, 17.2, 17.3, 17.6, 17.7 (C₆Pr), 18.7, 28.8 (C-8, C-9), 22.6, 23.9 (C-3', C-10'), 61.3 (C-6), 70.3, 71.6, 73.2 (C-3, C-4, C-5), 71.0 (C-12'), 81.1, 82.8 (C-2', C-11'), 99.6 (C-7), 103.7 (C-2), 106.0 (C-1'), 127.3, 127.4, 128.6, 128.8 (C-5', C-6', C-7', C-8'), 133.8, 133.9 (C-4', C-9'), 143.6 (C-1). IR (ATR): ν (cm⁻¹) = 3297, 2942, 2864, 2173, S24
UV (CH\textsubscript{3}CN): \(\lambda_{\text{max}}\) [nm] (lg \(\varepsilon\)) = 193 (5.04). MS (ESI): \(m/z\) (%) = 555.1 (83) [M+Na]\textsuperscript{+}. \(\text{C}_{27}\text{H}_{35}\text{BrO}_{4}\text{Si}\) (531.55), calc.: 555.1361, found: 555.1353, [M+Na]\textsuperscript{+} (ESI-HRMS).

**Compound 13e**

The alkynylated bromoglycal 14e (265 mg, 0.498 mmol, 1.0 equiv), \(\text{Pd(PPh}_{3}\text{)}_{4}\) (58 mg, 0.050 mmol, 10 mol %), \(t\text{-Bu}_{3}\text{PH-BF}_{4}\) (29 mg, 0.100 mmol, 20 mol %) and diisopropylamine (353 \(\mu\text{L}, 2.49 \text{mmol, 5.0 equiv}) dissolved in DMF/MeCN/NMP (9.5 mL, 9.5 mL, 1.2 mL) were brought to reaction according to GP5. Purification by silica gel column chromatography (pentane/EtOAc = 50:1) afforded 150 mg (67%) of compound 13e as a white solid: \(R_{f}\): 0.31 (hexane/EtOAc = 10:1). \([\alpha]_{D}^{20} = +58.0^\circ\) (c = 0.25, CHCl\textsubscript{3}). \(^1\text{H-NMR}\) (600 MHz, CDCl\textsubscript{3}): \(\delta\) = 0.87 (d, \(J = 7.5 \text{ Hz, 3 H, CH}_{3}\text{, iPr}\)), 0.96 (d, \(J = 7.4 \text{ Hz, 3 H, CH}_{3}\text{, iPr}\)), 1.13 (d, \(J = 7.4 \text{ Hz, 3 H, CH}_{3}\text{, iPr}\)), 1.19 (d, \(J = 7.5 \text{ Hz, 3 H, CH}_{3}\text{, iPr}\)), 1.22–1.29 (m, 1 H, CH\text{ipr}), 1.51 (s, 3 H, 8-H), 1.53 (s, 3 H, 9-H), 3.85 (m, 6 H, 4-H, 6-H\(_a\), 12-H, 19-H), 4.01–4.13 (m, 2 H, 5-H, 6-H\(_b\)), 5.10 (d, \(J = 9.1 \text{ Hz, 1 H, 3-H}\)), 6.71 (s, 1 H, 21-H), 7.15–7.19 (m, 2 H, \(H_A\)), 7.21–7.23 (m, 1 H, \(H_B\)), 7.25–7.28 (m, 1 H, \(H_A\)). \(^{13}\text{C-NMR}\) (125 MHz, CDCl\textsubscript{3}): \(\delta\) = 12.8, 13.8, 17.1, 17.3, 17.4, 17.6 (C\text{ipr}), 19.0, 29.1 (C-8, C-9), 36.6 (C-19), 38.0 (C-12), 62.3 (C-6), 70.5 (C-5), 72.7 (C-4), 77.7 (C-3), 100.0 (C-7), 114.8 (C-21), 126.1, 126.2 (C-15, C-16), 127.0, 127.2 (C-14, C-17), 131.3 (C-2), 133.2 (C-18), 133.8 (C-20\textsuperscript{*}), 136.5 (13), 136.8 (C-11\textsuperscript{*}), 138.7 (C-10), 149.2 (C-1). IR (ATR): \(\tilde{\nu}\) (cm\textsuperscript{-1}) = 2941, 2863, 2360, 2341, 1585, 1575, 1445, 1253. UV (CH\textsubscript{3}CN): \(\lambda_{\text{max}}\) [nm] (lg \(\varepsilon\)) = 263 (3.54), 294 (3.65), 309 (4.61). MS (ESI): \(m/z\) (%) = 473.2 (100) [M+Na]\textsuperscript{+}. \(\text{C}_{27}\text{H}_{34}\text{BrO}_{4}\text{Si}\) (450.64), calc.: 473.2119, found: 473.2117, [M+Na]\textsuperscript{+} (ESI-HRMS).

**Compound 14f**

Dialkyne 16a (177 mg, 0.520 mmol, 1.0 equiv) was dissolved in dry CCl\textsubscript{4} (5.0 mL) and cooled to 0 \textdegree C. A freshly prepared solution of bromine in dry CCl\textsubscript{4} (0.976 mol/L, 559 \(\mu\text{L}, 0.546 \text{mmol, 1.05 equiv}) was added over a period of 1 h via syringe pump and stirred for further 2 h at 0 \textdegree C. The resulting solution was added to a mixture of glucal 15c (179 mg, 0.572 mmol, 1.1 equiv), NEt\textsubscript{3} (159 \(\mu\text{L}, 1.14 \text{mmol, 2.0 equiv}) and DMAP (7 mg, 0.052 mmol, 10 mol %) in
dry CCl₄ (5.0 mL) and dry Et₂O (1.0 mL) at 0 °C over a period of 30 min via syringe pump. The reaction was stirred for 2 h and stopped by the addition of saturated aq. NH₄Cl solution. The aqueous layer was extracted three times with CH₂Cl₂. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na₂SO₄. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc = 80:1 → 30:1) to afford 229 mg (68%) of compound 14f as a slightly yellow oil: Rᵣ: 0.43 (hexane/EtOAc = 6:1). [α]ᵢ₀ = +88.4° (c = 0.25, CHCl₃). ¹H-NMR (300 MHz, CDCl₃): δ = 0.18 (s, 9 H, MeTMS), 0.96–1.06 (m, 7 H, CH₃(Pri), CH(Pri)), 1.11–1.18 (m, 7 H, CH₃(Pri), CH(Pri)), 3.63–3.77 (m, 6 H, 4-H*, 6-Ha, 3'-H, 10'-H), 4.15–4.27 (m, 2 H, 5-H*, 6-Hb), 4.73 (dd, J = 2.0, 5.0 Hz, 1 H, 3-H), 5.31 (s, 1 H, 7-H), 6.65 (d, J = 2.0 Hz, 1 H, 1-H), 7.24–7.36 (m, 5 H, Ha), 7.40–7.54 (m, 4 H, Hb). ¹³C-NMR (125 MHz, CDCl₃): δ = 0.0 (MeTMS), 13.0, 13.8, 16.9, 17.0, 17.2, 17.3 (C(Pri)), 23.8, 24.0 (C-3', C-10'), 67.6, 68.8, 69.2, 73.5 (C-3, C-4, C-5, C-6), 82.1, 88.1 (C-2', C-11'), 101.3 (C-7), 101.4 (C-2), 102.9, 106.1 (C-1', C-12'), 126.4, 127.4, 127.6, 128.0, 128.8, 128.9 (C-5', C-6', C-7', C-8', CH(Pri)), 134.1, 134.2, 137.4 (C-4', C-9', C₆(Pri)), 143.4 (C-1). IR (ATR): ν (cm⁻¹) = 2944, 2864, 2171, 1645, 1454, 1247, 1192. UV (CH₃CN): λₘₐₓ [nm] (lg ε) = no absorption between 190–350 nm. MS (ESI): m/z (%) = 674.2 (45) [M+Na]+. C₃₅H₄₃Br₄O₄Si₂ (651.78), calc.: 674.1808, found: 674.1840, [M+Na]+ (ESI-HRMS).

**Compound 13f**

The alkynylated bromoglycal 14f (218 mg, 0.334 mmol, 1.0 equiv), Pd(PPh₃)₄ (39 mg, 0.034 mmol, 10 mol %), t-Bu₃PH-BF₄ (20 mg, 0.067 mmol, 20 mol %) and diisopropylamine (237 µL, 1.67 mmol, 5.0 equiv), dissolved in DMF/MeCN/NMP (8.8 mL, 8.8 mL, 1.1 mL) were brought to reaction according to GP5. Purification by silica gel column chromatography (pentane/EtOAc = 20:1) afforded 141 mg (74%) of compound 13f as a white solid: Rᵣ: 0.22 (hexane/EtOAc = 10:1). [α]ᵢ₀ = +14.6° (c = 0.13, CHCl₃). ¹H-NMR (300 MHz, CDCl₃): δ = 0.47 (s, 9 H, MeTMS), 0.84 (d, J = 7.4 Hz, 3 H, CH₃(Pri), 0.84 (d, J = 7.4 Hz, 3 H, CH₃(Pri), 1.13 (d, J = 7.3 Hz, 3 H, CH₃(Pri), 1.13 (d, J = 7.4 Hz, 3 H, CH₃(Pri), 1.16–1.43 (m, 2 H, CH(Pri), 3.80 (s, 2 H, 10'-H*), 4.02–4.06 (m, 2 H, 17'-H*), 4.10–4.16 (m, 2 H, 5-H, 6-Ha), 4.48 (dd, J = 1.9, 12.5 Hz, 1 H, 6-Hb), 4.56 (dd, J = 1.6, 3.2 Hz, 1 H, 4-H), 5.19 (d, J = 3.2 Hz, 1 H, 3-H), 5.60 (s, 1 H, 7-H), 7.13–7.23 (m, 8 H, Ha), 7.27–7.31 (m, 1 H, Hb). ¹³C-NMR (125 MHz, CDCl₃): δ = 2.7 (MeTMS), 13.2, 13.9, 17.1, 17.3, 17.4, 17.7 (C(Pri)), 37.3, 39.2 (C-10, C-17), 68.8, 70.0, 73.1, 76.1 (C-3, C-4, C-5, C-6), 100.7 (C-7), 123.5, 128.3, 132.5, 133.7, 137.7,
137.8, 137.9, 143.7 (C-2, C-8, C-9, C-11, C-16, C-18, C-19, C_q(PPh)), 125.9, 126.0, 126.4, 126.9, 127.7, 128.6 (C-12, C-13, C-14, C-15, CH_PPh), 154.9 (C-1). IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 2942, 2862, 1542, 1458, 1384, 1247. UV (CH\(_3\)CN): \( \lambda_{\text{max}} \) [nm] (lg \( \varepsilon \)) = 209 (4.70), 305 (3.70). MS (ESI): \( m/z \) (%) = 593.3 (100) [M+Na]*. \( \text{C}_{34}\text{H}_{42}\text{O}_{4}\text{Si}_{2} \) (570.87), calc.: 593.2514, found: 593.2510, [M+Na]* (ESI-HRMS).

**Compound 26b**

To a solution of 13f (130 mg, 0.228 mmol, 1.0 equiv) in MeOH (10 mL) was added dropwise AcCl (1.0 mL) at 0 °C. The reaction mixture was stirred at 60 °C for 3.5 h and then stopped by slow addition of saturated aq. NaHCO\(_3\) solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na\(_2\)SO\(_4\). The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography to afford 78 mg (83%) of compound 26b as a white solid: \( R_f \) = 0.47 (CH\(_2\)Cl\(_2\)/MeOH = 8:1). [\( \alpha \)\(_D\)]\(^{20}\) = +34.7° (c = 0.15, CHCl\(_3\)). \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta \) = 0.92 (d, \( J \) = 7.5 Hz, 3 H, C_H\(_{3(iPr)}\)), 1.09 (d, \( J \) = 7.4 Hz, 3 H, C_H\(_{3(iPr)}\)), 1.14 (d, \( J \) = 7.4 Hz, 3 H, C_H\(_{3(iPr)}\)), 1.20 (d, \( J \) = 7.4 Hz, 3 H, C_H\(_{3(iPr)}\)), 1.23–1.51 (m, 2 H, C_H\(_{iPr}\)), 2.06 (s, 1 H, O_H), 2.38 (s, 1 H, O_H), 3.80–3.95 (m, 4 H, 12-H, 19-H), 4.02 (dd, \( J \) = 4.7, 11.7 Hz, 1 H, 6-H\(_a\)), 4.11 (dd, \( J \) = 5.9, 11.7 Hz, 1 H, 6-H\(_b\)), 4.24–4.30 (m, 1 H, 5-H), 4.40 (d, \( J \) = 3.2 Hz, 1 H, 3-H*), 5.18 (d, \( J \) = 3.2 Hz, 1 H, 4-H*), 6.83 (s, 1 H, 21-H), 7.16–7.32 (m, 4 H, 14-H, 15-H, 16-H, 17-H). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \( \delta \) = 13.0, 13.9, 17.2, 17.3, 17.6, 17.6 (C_PPh), 36.7, 38.0 (C-12, C-19), 63.6, 67.1, 76.2, 76.8 (C-3, C-4, C-5, C-6), 115.1 (C-21), 126.1, 126.1, 126.9, 127.3 (C-14, C-15, C-16, C-17), 129.2, 132.9, 133.5, 136.7, 136.8, 138.7 (C-2, C-10, C-11, C-13, C-18, C-20), 149.7 (C-1). IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3385, 2940, 2862, 1587, 1447, 1261, 1070. UV (CH\(_3\)CN): \( \lambda_{\text{max}} \) [nm] (lg \( \varepsilon \)) = 262 (3.62), 289 (3.65). MS (ESI): \( m/z \) (%) = 433.2 (23) [M+Na]*. \( \text{C}_{34}\text{H}_{42}\text{O}_{4}\text{Si}_{2} \) (410.58), calc.: 433.1806, found: 433.1800, [M+Na]* (ESI-HRMS).

**Compound 12b**

To a solution of 26b (73 mg, 0.178 mmol, 1.0 equiv) in THF (0.1 mL) was added TBAF (1.0 mol/L in THF, 711 µL, 0.711 mmol, 3.0 equiv). The mixture was stirred for 4 h and directly poured on a packed silica gel column (CH\(_2\)Cl\(_2\)/MeOH = 10:1). 55 mg (99%) of
compound 12b was obtained as a yellow solid after chromatographic purification: \( R_t = 0.26 \) (CH\(_2\)Cl\(_2\)/MeOH = 10:1). \([\alpha]_D^{20} = +67.0^\circ \) (c = 0.10, DMSO). \(^1\)H-NMR (300 MHz, DMSO-\(d_6\)): \( \delta = 3.61–3.76 \) (m, 2 H, 6-H\(_a\), 6-H\(_b\)), 3.81 (s, 4 H, 9-H, 16-H), 3.93 (dt, \( J = 1.1, 3.8 \) Hz, 1 H, 3-H), 4.01 (t, \( J = 6.3 \) Hz, 1 H, 5-H), 4.57 (d, \( J = 3.9 \) Hz, 1 H, O-H\(_{C-3}\)), 4.70 (dd, \( J = 3.8, 7.5 \) Hz, 1 H, 4-H), 4.78 (t, \( J = 5.6 \) Hz, 1 H, O-H\(_{C-4}\)), 5.08 (d, \( J = 7.6 \) Hz, 1 H, O-H\(_{C-4}\)), 6.65 (s, 1 H, 18-H), 7.13–7.19 (m, 2 H, 12-H, 13-H), 7.25–7.30 (m, 2 H, 11-H, 14-H), 7.31 (s, 1 H, 7-H).

\(^{13}\)C-NMR (125 MHz, DMSO-\(d_6\)): \( \delta = 34.5, 35.0 \) (C-9, C-16), 60.6 (C-6), 64.7 (C-3), 66.3 (C-4), 77.5 (C-5), 113.3 (C-18), 122.7, 127.7, 136.0, 136.4, 137.0 (C-2, C-8, C-10, C-15, C-17), 125.7, 125.7, 126.3, 127.0, 127.0 (C-7, C-11, C-12, C-13, C-14), 151.7 (C-1). IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3255, 2919, 2344, 1672, 1295. UV (CH\(_3\)CN): \( \lambda_{\text{max}} \) [nm] (lg \( e \)) = 261 (4.22). MS (ESI): \( m/z \) (%) = 321.1 (15) [M+Na]\(^+\). \( C_{18}H_{18}O_{4} \) (298.33), calc.: 321.1097, found: 321.1096, [M+Na]\(^+\) (ESI-HRMS).

**Compound 28b**

![Diagram](image)

Compound 12b (29 mg, 0.099 mmol, 1.0 equiv), TBSCI (224 mg, 1.48 mmol, 15.0 equiv), imidazole (303 mg, 4.45 mmol, 45.0 equiv) and DMAP (19 mg, 0.148 mmol, 1.0 equiv) were dissolved in DMF (8.0 mL). The reaction mixture was heated in a sealed vial at 90 °C for 68 h. TLC still showed no complete conversion. The mixture of products was purified and the crude product was again set to reaction according the described procedure for 18 h. The reaction was stopped by the addition of saturated aq. NH\(_4\)Cl solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed three times with saturated aq. NaCl solution and dried over Na\(_2\)SO\(_4\). The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc = 100:1) to afford 18 mg (30%) of compound 27b as a colorless oil.

Compound 27b (18 mg, 0.028 mmol, 1.0 equiv), FeCl\(_3\)-6H\(_2\)O (2 mg, 0.006 mmol, 20 mol %) and t-BuOOH (5.5 mol/L in decane, 52 µL, 0.281 mmol, 10.0 equiv) were dissolved in dry pyridine (2.0 mL). The reaction mixture was aerated with molecular oxygen and heated in a sealed vial at 80 °C for 3 h. After common aqueous workup (general procedures) the residue was purified by silica gel column chromatography (pentane/EtOAc = 25:1) to afford 11 mg (59%) of compound 28b as a yellow solid: \( R_t = 0.21 \) (hexane/EtOAc = 20:1). \([\alpha]_D^{20} = -20.0^\circ \) (c = 0.10, CHCl\(_3\)). \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 0.01 \) (s, 3 H, Me\(_{\text{TBS}}\)), 0.09 (s, 3 H, Me\(_{\text{TBS}}\)), 0.11 (s, 3 H, Me\(_{\text{TBS}}\)), 0.13 (s, 3 H, Me\(_{\text{TBS}}\)), 0.24 (s, 3 H, Me\(_{\text{TBS}}\)), 0.27 (s, 3 H, Me\(_{\text{TBS}}\)), 0.68 (s, 9 H, \( t\)Bu\(_{\text{TBS}}\)), 0.93 (s, 9 H, \( t\)Bu\(_{\text{TBS}}\)), 1.07 (s, 9 H, \( t\)Bu\(_{\text{TBS}}\)), 3.87–3.92 (m, 2 H, 5-H\(^*\), 6-H\(_a\)\(^*\)),
4.29–4.36 (m, 2 H, 4-H*, 6-Hb*), 4.96 (s, 1 H, 3-H*), 7.57 (s, 1 H, 18-H), 7.73–7.78 (m, 2 H, 12-H, 13-H), 8.25–8.31 (m, 2 H, 11-H, 14-H), 8.33 (s, 1 H, 7-H). $^{13}$C-NMR (125 MHz, CDCl$_3$):

δ = −5.3, −5.2, −4.9, −4.4, −3.9 (Me$_{3}$TBS), 18.2, 18.3, 18.8 (C$_{q}$TBS), 25.7, 25.8, 26.3 (tBu$_{3}$TBS), 61.5, 67.5, 70.9, 80.2 (C-3, C-4, C-5, C-6), 113.0 (C-18), 126.5, 133.8, 133.9, 134.6, 134.6 (C-2, C-8, C-10, C-15, C-17), 127.0, 127.0, 133.5, 133.9 (C-11, C-12, C-13, C-14), 131.7 (C-7), 159.0 (C-1), 182.1, 183.2 (C-9, C-16). IR (ATR): ν (cm$^{-1}$) = 2927, 2855, 1674, 1592, 1292.

UV (CH$_3$CN): λ$_{max}$ [nm] (lg ε) = 276 (3.91). MS (ESI): m/z (%) = 692.3 (65) [M+Na]$^+$. C$_{36}$H$_{56}$O$_6$Si$_3$ (669.08), calc.: 691.3277, found: 691.3266, [M+Na]$^+$ (ESI-HRMS).

**Compound 11b**

To a solution of 28b (8 mg, 0.012 mmol, 1.0 equiv) in MeOH (1.0 mL) and water (0.1 mL) was added HCl (0.3 mol/L, 0.4 mL). The mixture was stirred for 17 h at 75 °C and stopped by the addition of saturated aq. NaHCO$_3$ solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na$_2$SO$_4$. The solvent was removed by rotary evaporation and the residue was filtered over a small plug of celite (CH$_2$Cl$_2$: 20 mL and CH$_2$Cl$_2$/MeOH = 5:1: 250 mL). The product-containing fractions were collected, the solvent was removed by rotary evaporation and the residue was washed with water (50 mL). 3.5 mg (90%) of compound 11b were obtained as a yellow solid: $R_f$: 0.16 (CH$_2$Cl$_2$/MeOH = 10:1). [α]$^2_0$ = −10.0° (c = 0.30, DMSO).

$^1$H-NMR (300 MHz, DMSO-d$_6$): δ = 3.72 (s$_{br}$, 2 H), 4.06 (s$_{br}$, 1 H), 4.31 (s$_{br}$, 1 H), 4.84 (s$_{br}$, 1 H), 5.08 (s$_{br}$, 1 H), 5.08 (s$_{br}$, 1 H), 5.30 (s$_{br}$, 1 H), 5.94 (s$_{br}$, 1 H), 7.31 (s, 1 H, 18-H), 7.88 (s$_{br}$, 2 H, 12-H, 13-H), 8.15 (s$_{br}$, 2 H, 11-H, 14-H), 8.28 (s, 1 H, 7-H). $^{13}$C-NMR (125 MHz, DMSO-d$_6$): δ = 60.2, 64.1, 66.5, 79.2 (C-3, C-4, C-5, C-6), 112.1 (C-18), 125.7, 133.1, 133.1, 133.2, 133.6 (C-2, C-8, C-10, C-15, C-17), 126.5, 126.6, 127.7, 134.0, 134.4 (C-7, C-11, C-12, C-13, C-14), 159.0 (C-1), 181.2, 182.1 (C-9, C-16). IR (ATR): ν (cm$^{-1}$) = 3281, 2922, 1667, 1588, 1565, 1332, 1287. UV (MeOH): λ$_{max}$ [nm] (lg ε) = 239 (3.99), 276 (4.21). MS (ESI): m/z (%) = 349.1 (89) [M+Na]$^+$. C$_{18}$H$_{14}$O$_6$ (326.30), calc.: 325.0718, found: 325.0714, [M-H]$^-$ (ESI-HRMS).
$^1$H and $^{13}$C NMR spectra of the compounds

Compound 20
Compound 22a
Compound 14a
Compound 12a

mLS-177_3h
MLB-177 DMSO
Lebeling / Wenz

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mLS-177_3c
MLB-177 dmso-06
Lebeling / Wenz
Compound 27a

![Chemical Structure](image)

**NMR Spectroscopy**

- **Compound 27a**
- **NMR Spectra**
  - **1H NMR**
  - **13C NMR**

**S39**
Compound 28a

TBSO
TBSO

OTBS

137.94
127.11
127.34
128.32
133.38
133.92
133.89
133.98
135.56
135.80
5.17
4.70
4.62
4.29
5.31
5.39
17.88
17.63
15.63
12.37
80.98
80.98
18.42
18.42

Compound 24b
Compound 16b
Compound 14b

mZT-224_3b
MLT-224 CDCl3
Leiteng / Wenz
Compound 13b
Compound 13c
Compound 24d
Compound 16d

mILB 38_3h
MLR 38 CDC13
Lebeling / Wenz

[Diagram of chemical structure]

mILB 38_3c
MLR 38 cdc3
Lebeling / Wenz

[Graphs of NMR spectra with chemical shifts]
Compound 13d

nMR-40.3h
ML8-40 cdcd3
Leibeling / Venz / PE

Si(Pr)₉OMe

O-Si(Pr)₂

mMR-40.5c
ML8-40 cdcd3
Leibeling / Venz / mw
Compound 24e
Compound 16e

mIB-46_3h
ML8-46 CDCl3
Lebeling / Wenz

[Chemical structure image]

[1H NMR spectrum]

mIB-46_5c
ML8-46 cdcd3
Lebeling / Wenz / msw
Compound 14e
Compound 13f
Compound 12b
