# **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 <sup>1</sup>H and <sup>13</sup>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 ( $Et_2O$ ) were distilled from sodium/benzophenone under an argon atmosphere. Dichloromethane ( $CH_2CI_2$ ) and toluene were distilled from  $CaCI_2$  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*<sup>®</sup> 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  $F_{254}$ , 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 (NH<sub>4</sub>)<sub>4</sub>Ce(SO<sub>4</sub>)<sub>4</sub>, 30 g Mo<sub>7</sub>(NH<sub>4</sub>)<sub>6</sub>·4H<sub>2</sub>O, 30 mL conc. H<sub>2</sub>SO<sub>4</sub> and 600 mL H<sub>2</sub>O] and elementary iodine for the detection of alkynes.

Colum 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*<sup>®</sup> Isolera<sup>TM</sup> One. As stationary phase *Biotage*<sup>®</sup> SNAP cadridges KPSIL (10-250 g silica gel, 30 or 50 µm) were used.

## Instrumental analytics

NMR spectra: Proton (<sup>1</sup>H) and carbon (<sup>13</sup>C) 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 CHCl<sub>3</sub>:  $\delta$  = 7.26 ppm and  $\delta$  = 77.0 ppm; DMSO:  $\delta$  = 2.54 ppm and  $\delta$  = 40.5 ppm; acetone:  $\delta$  = 2.09 ppm and  $\delta$  = 30.9 ppm and  $\delta$  = 207.1 ppm and methanol:  $\delta$  = 4.87 ppm and  $\delta$  = 49.2 ppm, as internal references for <sup>1</sup>H and <sup>13</sup>C 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; s<sub>br</sub>, 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 MoK<sub>a</sub> radiation,  $\lambda = 0.71073$  Å. Data reduction was done with SAINT,<sup>1</sup> and an empirical absorption correction with SADABS<sup>2</sup> or TWINABS<sup>3</sup> was applied. The structure was solved by direct methods (SHELXS-97)<sup>4</sup> and refined by full-matrix least-squares methods against  $F^2$  (SHELXL-97).<sup>5</sup> 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  $U_{iso}$  values constrained to 1.5 times the  $U_{eq}$  of their pivot atoms for terminal sp<sup>3</sup> 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.  $NH_4CI$  solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution, dried over  $Na_2SO_4$  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  $Et_2O$  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 Et<sub>2</sub>O) at room temperature. The solution was heated to reflux for 2 h and then cooled to ambient temperature. 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. NH<sub>4</sub>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<sub>2</sub>SO<sub>4</sub>. 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 NaHCO<sub>3</sub> 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<sub>2</sub>SO<sub>4</sub>. 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  $CCI_4$  and cooled to 0 °C. A freshly prepared solution of bromine in dry  $CCI_4$  (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), NEt<sub>3</sub> (2.0 equiv) and DMAP (10 mol %) in dry CCl<sub>4</sub> and dry Et<sub>2</sub>O 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. NH<sub>4</sub>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<sub>2</sub>SO<sub>4</sub>. 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(PPh<sub>3</sub>)<sub>4</sub> (10 mol %), *t*-Bu<sub>3</sub>PH·BF<sub>4</sub> (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. NH<sub>4</sub>Cl solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aq. NaCl solution, dried over Na<sub>2</sub>SO<sub>4</sub>. 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 Et<sub>2</sub>O (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: **R**<sub>f</sub>: 0.53 (hexane/EtOAc = 20:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.14 (s, 6 H, Me<sub>TBS</sub>), 0.96 (s, 9 H, *t*Bu<sub>TBS</sub>), 4.51 (s, 2 H, 1-H), 4.79 (s, 2 H, 8-H), 7.17–7.34 (m, 3 H, 3-H<sup>\*</sup>, 4-H<sup>\*</sup>, 5-H<sup>\*</sup>), 7.38–7.42 (m, 1 H, 6-H<sup>\*</sup>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = -5.1 (C-8), 3.3 (Me<sub>TBS</sub>), 18.4 (C<sub>q,TBS</sub>), 26.0 (*t*Bu<sub>TBS</sub>), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 3271, 2852, 1918, 1455, 1368, 1185. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg ε) = 241 (4.03), 360 (2.77). **MS** (ESI): *m/z* (%) = 385.1 (32) [M+Na]<sup>+</sup>. **C**<sub>14</sub>**H**<sub>23</sub>**IOSi** (362.32), calc.: 385.0455, found.: 385.0453, [M+Na]<sup>+</sup> (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: R<sub>f</sub>: 0.53 (hexane/EtOAc = 20:1). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.10–0.11 (m, 6 H, Me<sub>TBS</sub>), 0.18–0.20 (m, 9 H, Me<sub>TMS</sub>), 0.94–0.96 (s, 9 H, *t*Bu<sub>TBS</sub>), 3.64 (s, 2 H, 8-H), 4.78 (s, 2 H, 1-H), 7.24–7.29 (m, 2 H, H<sub>Ar</sub>), 7.41–7.46 (m, 2 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta = -5.2$ (Me<sub>TBS</sub>), 0.2 (Me<sub>TMS</sub>), 18.5 (C<sub>a.TBS</sub>), 23.5 (C-8), 26.0 (*t*Bu<sub>TBS</sub>), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 2955, 2856, 2175, 1471, 1249. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 194 (4.82). **MS** (ESI): m/z(%) = 355.2(100)  $[M+Na]^+$ . **C**<sub>19</sub>**H**<sub>32</sub>**OSi**<sub>2</sub> (332.63), calc.: 355.1884, found: 355.1885, [M+Na]<sup>+</sup> (ESI-HRMS).

#### **Compound 23a**



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: **R**<sub>f</sub>: 0.21 (hexane/EtOAc = 5:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.17 (s, 9 H, Me<sub>TMS</sub>), 3.71 (s, 2 H, 8-H), 4.74 (s, 2 H, 1-H), 7.25–7.31 (m, 2 H, H<sub>Ar</sub>), 7.36–7.45 (m, 2 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = -0.03 (C-Me<sub>TMS</sub>), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 3321, 2958, 2174, 1455, 1412, 1248, 1016. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (Ig  $\varepsilon$ ) = 194 (4.74). **MS** (EI, 70 eV): *m/z* (%) = 217.1 (5) [M-H]<sup>+</sup>. **C**<sub>13</sub>H<sub>18</sub>OSi (218.37), calc.: 217.1049, found: 217.1058, [M-H]<sup>+</sup> (EI-HRMS).

#### **Compound 24a**



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 Et<sub>2</sub>O (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: **R**<sub>f</sub>: 0.68 (hexane/EtOAc = 10:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.17 (s, 9 H, Me<sub>TMS</sub>), 3.68 (s, 2 H, 8-H), 4.48 (s, 2 H, 1-H), 7.16–7.33 (m, 3 H, H<sub>Ar</sub>), 7.42–7.47 (m, 1 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = -0.1 (Me<sub>TMS</sub>), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 2957, 2174, 1488, 1454, 1247, 1152, 837. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg ε) = 240 (3.91). **MS** (ESI): *m/z* (%) = 279.1 (6) [M-TMS+Na]<sup>+</sup>. **C**<sub>13</sub>**H**<sub>17</sub>**ISi** (328.26).

#### **Compound 16a**



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 Purification according to GP5.2. by silica gel column chromatography (pentane/CH<sub>2</sub>Cl<sub>2</sub> = 150:1) afforded 1.15 g (95%) of compound **16a** as a yellow oil:  $\mathbf{R}_{f}$ : 0.32 (hexane/CH<sub>2</sub>Cl<sub>2</sub> = 10:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.17–0.18 (m, 9 H, Me<sub>TMS</sub>), 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, H<sub>Ar</sub>), 7.42–7.53 (m, 2 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta = 0.0$  (Me<sub>TMS</sub>), 10.9, 18.3, 18.5 (C<sub>iPr</sub>), 23.9, 24.0 (C-3, 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): v (cm<sup>-</sup> <sup>1</sup>) = 2942, 2863, 2174, 2116, 1455, 1249. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 260 (2.45), 193 (4.72). **MS** (ESI): m/z (%) = 363.3 (33) [M+Na]<sup>+</sup>. **C**<sub>21</sub>**H**<sub>32</sub>**Si**<sub>2</sub> (340.65), calc.: 363.1935, found: 363.1936, [M+Na]<sup>+</sup> (ESI-HRMS).

#### Compound 14a



Dialkyne 16a (582 mg, 1.71 mmol, 1.2 equiv) was dissolved in dry CCl<sub>4</sub> (20.0 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry CCl<sub>4</sub> (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 glucal **15a** (378 mg, 1.42 mmol, 1.0 equiv), NEt<sub>3</sub> (395 µL, 2.85 mmol, 2.0 equiv) and DMAP (18 mg, 0.142 mmol, 10 mol %) in dry CCl<sub>4</sub> (20.0 mL) and dry Et<sub>2</sub>O (2.5 mL) at 0 °C over a period of 30 min via syringe pump. The reaction was stirred over night and stopped by the addition of saturated aq. NH<sub>4</sub>Cl solution. The aqueous layer was extracted three times with  $CH_2CI_2$ . The combined organic layers were washed with saturated aq. NaCl solution and dried over Na<sub>2</sub>SO<sub>4</sub>. 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: R<sub>f</sub>: 0.62 (hexane/EtOAc = 6:1).  $[\alpha]_{D}^{20} = +52.7^{\circ}$  (c = 0.33, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.18 (s, 9 H, Me<sub>TMS</sub>), 1.07–1.14 (m, 14 H, *i*Pr), 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-H<sub>a</sub>), 3.89–3.97 (m, 2 H, 5-H\*, 6-H<sub>b</sub>), 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,  $H_{Ar}$ ), 7.41–7.47 (m, 1 H,  $H_{Ar}$ ), 7.55–7.59 (m, 1 H,  $H_{Ar}$ ). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta = 0.1$ (Me<sub>TMS</sub>), 13.3, 14.0, 17.2, 17.3, 17.6, 17.7 (C<sub>iPr</sub>), 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,

134.1 (C-4', C-9'), 143.6 (C-1). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 2944, 2865, 2173, 1631, 1462, 1249, 1171. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 193 (4.69). **MS** (ESI): m/z (%) = 627.2 (100) [M+Na]<sup>+</sup>. **C**<sub>30</sub>**H**<sub>43</sub>**O**<sub>4</sub>**Si**<sub>2</sub>**Br** (603.74), calc.: 627.1757, found: 627.1765, [M+Na]<sup>+</sup> (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<sub>3</sub>PH·BF<sub>4</sub> (29 mg, 0.099 mmol, 20 mol %) and diisopropylamine (352 µL, 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<sub>f</sub>: 0.41 (hexane/EtOAc = 10:1).  $[\alpha]_{D}^{20} = +27.2^{\circ}$  (c = 0.16, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.41$  (s, 9 H, Me<sub>TMS</sub>), 0.93 (d, J = 7.5 Hz, 3 H, CH<sub>3,Pr</sub>), 0.99 (d, J = 7.4 Hz, 3 H, CH<sub>3,Pr</sub>), 1.13 (d, J = 7.3 Hz, 3 H, CH<sub>3.Pr</sub>), 1.20 (d, J = 7.5 Hz, 3 H, CH<sub>3.Pr</sub>), 1.23–1.47 (m, 2 H, CH<sub>Pr</sub>), 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, 3-H), 7.15–7.31 (m, 4 H, 14-H, 15-H, 16-H, 17-H). <sup>13</sup>C-NMR (125 MHz,  $CDCI_3$ ):  $\delta = 2.7$  (Me<sub>TMS</sub>), 12.9, 13.8, 17.2, 17.4, 17.4, 17.7 (C<sub>iPr</sub>), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 2941, 2862, 1538, 1459, 1380, 1246, 1091. UV (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 306 (3.70), 300 (3.68), 263 (3.41), 212 (4.62). **MS** (ESI): m/z (%) = 545.3 (100) [M+Na]<sup>+</sup>. **C**<sub>30</sub>**H**<sub>42</sub>**O**<sub>4</sub>**Si**<sub>2</sub> (522.82), calc.: 545.2514, found: 545.2522, [M+Na]<sup>+</sup> (ESI-HRMS).

#### **Compound 26a**



To a solution of **13a** (130 mg, 0.249 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 2 h and then stopped by slow addition of saturated aq. NaHCO<sub>3</sub> 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<sub>2</sub>SO<sub>4</sub>. 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**<sub>f</sub>: 0.30 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 10:1).  $[\alpha]_D^{20} = +38.7^{\circ}$  (c = 0.15, CHCl<sub>3</sub>). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.86$  (d, J = 7.4 Hz, 3 H, Me<sub>Pr</sub>), 1.01 (d, J = 7.4 Hz, 3 H, Me<sub>Pr</sub>), 1.14 (d, J = 7.3 Hz, 3 H, Me<sub>Pr</sub>), 1.19 (d, J = 7.5 Hz, 3 H, Me<sub>Pr</sub>), 1.20–1.34 (m, 1 H, CH<sub>Pr</sub>), 1.38–1.50 (m, 1 H, CH<sub>Pr</sub>), 3.72–3.82 (m, 2 H, 9-Ha, 4-H\*), 3.83–3.96 (m, 3 H, 9-Hb, 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). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 12.7$ , 13.8, 17.1, 17.3, 17.3, 17.6 (C<sub>Pr</sub>), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 3377, 2941, 2863, 2360, 1586, 1447, 1261. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 260 (4.23). **MS** (ESI): *m*/*z* (%) = 433.2 (62) [M+Na]<sup>+</sup>. **C**<sub>24</sub>H<sub>30</sub>O<sub>4</sub>Si (410.58), calc.: 433.1806, found: 433.1802, [M+Na]<sup>+</sup> (ESI-HRMS).

#### Compound 12a



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<sub>2</sub>Cl<sub>2</sub>/MeOH = 10:1). 14 mg (96%) of compound **12a** were obtained as a yellow solid after chromatographic purification: **R**<sub>f</sub>: 0.23 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 10:1).  $[\alpha]_D^{20} = +62.7^{\circ}$  (c = 0.11, DMSO). <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta = 3.44-3.55$  (m, 1 H, 4-H), 3.59–3.71 (m, 1 H, 6-H<sub>a</sub>), 3.73–3.83 (m, 2 H, 5-H, 6-H<sub>b</sub>), 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,  $OH_{C-6}$ ), 5.28 (d, J = 5.2 Hz, 1 H,  $OH_{C-4}$ ), 5.50 (d, J = 6.3 Hz, 1 H,  $OH_{C-3}$ ), 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). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 34.5$ , 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 3319, 2879, 1494, 1429, 1255, 1049. UV (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (Ig  $\epsilon$ ) = 261 (3.67), 283 (3.55). MS (ESI): m/z (%) = 321.1 (100) [M+Na]<sup>+</sup>. C<sub>18</sub>H<sub>18</sub>O<sub>4</sub> (298.33), calc.: 321.1097, found: 321.1097, [M+Na]<sup>+</sup> (ESI-HRMS).

#### Compound 27a



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. NH<sub>4</sub>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<sub>2</sub>SO<sub>4</sub>. 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).  $[\alpha]_D^{20} = +45.0^\circ$  (c = 0.08, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.00 (s, 3 H, Me<sub>TBS</sub>), 0.05 (s, 3 H, Me<sub>TBS</sub>), 0.08 (s, 3 H, Me<sub>TBS</sub>), 0.09 (s, 3 H, Me<sub>TBS</sub>), 0.16 (s, 3 H, Me<sub>TBS</sub>), 0.19 (s, 3 H, Me<sub>TBS</sub>), 0.81 (s, 9 H, *t*Bu<sub>TBS</sub>), 0.88 (s, 9 H, *t*Bu<sub>TBS</sub>), 0.89 (s, 9 H, *t*Bu<sub>TBS</sub>), 3.81–3.93 (m, 6 H, 4-H\*, 6-H<sub>a</sub>, 9-H, 16-H), 4.04 (dd, *J* = 2.4, 0.7 Hz, 1 H, 6-H<sub>b</sub>\*), 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, H<sub>Ar</sub>), 7.25–7.31 (m, 2 H, H<sub>Ar</sub>).<sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta = -$ 5.3, -5.2, -4.6, -4.6, -4.2, -4.2 (Me<sub>TBS</sub>), 17.9, 18.0, 18.3 (C<sub>g.TBS</sub>), 25.7, 25.7, 25.9 (*t*Bu<sub>TBS</sub>), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 2928, 2856, 2360, 1471, 1251. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 261 (4.35). **MS** (ESI): m/z (%) = 663.4 (77) [M+Na]<sup>+</sup>. **C**<sub>36</sub>**H**<sub>60</sub>**O**<sub>4</sub>**Si**<sub>3</sub> (641.12), calc.: 664.3722, found: 664.3694, [M+Na]<sup>+</sup> (ESI-HRMS).

#### Compound 28a



Compound **27a** (64 mg, 0.100 mmol, 1.0 equiv), FeCl<sub>3</sub>·6H<sub>2</sub>O (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:  $\mathbf{R}_{f}$ : 0.43 (hexane/EtOAc = 10:1).  $[\alpha]_{D}^{20} = -11.4^{\circ}$  (c = 0.14, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.01$  (s, 3 H, Me<sub>TBS</sub>), 0.06 (s, 3 H, Me<sub>TBS</sub>), 0.78 (s, 9 H, *t*Bu<sub>TBS</sub>), 0.87 (s, 9 H, *t*Bu<sub>TBS</sub>), 0.89 (s, 9 H, *t*Bu<sub>TBS</sub>), 3.89 (dd, *J* = 5.3, 11.3 Hz, 1 H, 6-H<sub>a</sub>), 3.97 (dd, *J* = 7.4, 11.3 Hz, 1 H, 6-H<sub>b</sub>), 4.14 (dd, *J* = 1.8, 3.2 Hz, 1 H, 4-H\*), 4.40–4.46 (m,

1 H, 5-H), 4.55 (dd, J = 1.8, 3.2 Hz, 1 H, 3-H\*), 7.72 (s, 1 H, 18-H), 7.74–7.79 (m, 2 H, 11-H, 14-H), 8.15 (s, 1 H, 7-H), 8.26–8.31 (m, 2 H, 12-H, 13-H). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta = -5.3$ , -5.2, -4.7, -4.6, -4.3 (Me<sub>TBS</sub>), 17.9, 18.0, 18.3 (C<sub>q,TBS</sub>), 25.6, 25.7, 25.9 (*t*Bu<sub>TBS</sub>), 62.6 (C-6), 68.4, 68.4, 82.4 (C-3, C-4, C-5), 115.6 (C-18), 126.4, 128.5, 133.8, 133.9, 135.1 (C-2, C-8, C-10, C-15, C-17), 127.0, 127.1, 131.4, 133.6, 134.0 (C-7, C-11, C-12, C-13, C-14), 157.9 (C-1), 182.1, 183.0 (C-9, C-16). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 2928, 2856, 1674, 1462, 1289. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 247 (4.32), 275 (4.53). MS (ESI): m/z (%) = 691.6 (82) [M+Na]<sup>+</sup>. **C<sub>36</sub>H<sub>56</sub>O<sub>6</sub>Si<sub>3</sub>** (669.08), calc.: 692.3308, found: 692.3288, [M+Na]<sup>+</sup> (ESI-HRMS).

#### **Compound 11a**



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 HCI (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. NaHCO<sub>3</sub> solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated ag. NaCl solution and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was filtered over a small plug of celite (CH<sub>2</sub>Cl<sub>2</sub>: 50 mL and CH<sub>2</sub>Cl<sub>2</sub>/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). R<sub>f</sub>: 0.34  $(CH_2CI_2/MeOH = 7:1)$ .  $[\alpha]_D^{20} = +74.6^{\circ}$  (c = 0.13, DMSO). <sup>1</sup>H-NMR (600 MHz, DMSO- $d_6$ ):  $\delta$  = 3.65 (t, J = 9.1 Hz, 1 H, 4-H), 3.77 (dt, J = 12.0, 4.9 Hz, 1 H, 6-H<sub>a</sub>), 3.86 (dd, J = 12.0, 2.4 Hz, 1 H, 6-H<sub>b</sub>), 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,  $OH_{C-6}$ ), 5.66 (s<sub>br</sub>, 1 H,  $OH_{C-4}$ ), 6.10 (d, J = 5.7 Hz, 1 H,  $OH_{C-3}$ ), 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). <sup>13</sup>**C-NMR** (125 MHz, DMSO- $d_6$ ):  $\delta = 60.2$  (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):  $\tilde{v}$  (cm<sup>-1</sup>) = 3498, 3398, 3323, 2953, 1672, 1584, 1364. UV (MeOH):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 275 (3.92). **MS** (ESI): m/z (%) = 325.2 (100) [M-H]<sup>-</sup>. **C**<sub>18</sub>**H**<sub>14</sub>**O**<sub>6</sub> (326.3), calc.: 325.0718, found: 325.0715, [M-H]<sup>-</sup> (ESI-HRMS).

#### Compound 23b



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. NH<sub>4</sub>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<sub>2</sub>SO<sub>4</sub>. 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 NaHCO<sub>3</sub> 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<sub>2</sub>SO<sub>4</sub>. 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**<sub>f</sub>: 0.14 (hexane/EtOAc = 5:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.44 (s, 6 H, Me<sub>DMPS</sub>), 1.88 (s<sub>br</sub>, 1 H, O*H*), 3.78 (s, 2 H, 8-H), 4.74 (s, 2 H, 1-H), 7.25–7.32 (m, 2 H, H<sub>Ar</sub>), 7.36–7.41 (m, 4 H, H<sub>Ar</sub>), 7.47–7.52 (m, 1 H, H<sub>Ar</sub>), 7.62–7.66 (m, 2 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = -0.7 (Me<sub>DMPS</sub>), 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, C<sub>Ph,DMPS</sub>), 134.4, 137.0, 138.1 (C-2, C-7, C<sub>q,DMPS</sub>). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 3363, 2957, 2893, 1604, 1488, 1427, 1249, 1113. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 193 (4.89), 253 (3.03). **MS** (ESI): *m/z* (%) = 303.1 (100) [M+Na]<sup>+</sup>. **C<sub>18</sub>H<sub>20</sub>OSi** (280.44), calc.: 303.1176, found: 303.1163, [M+Na]<sup>+</sup> (ESI-HRMS).

#### **Compound 24b**

$$4 \underbrace{5}_{6} \underbrace{7}_{8} \underbrace{9}_{10} \operatorname{SiMe}_{2} \operatorname{Ph}$$

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 Et<sub>2</sub>O (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:  $\mathbf{R}_{f}$ : 0.53 (hexane/EtOAc = 10:1). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.44 (s, 6 H, Me<sub>DMPS</sub>), 3.77 (s, 2 H, 8-H), 4.50 (s, 2 H, 1-H), 7.18–7.35 (m, 3 H,

H<sub>Ar</sub>), 7.35–7.41 (m, 3 H, H<sub>Ar</sub>), 7.47–7.51 (m, 1 H, H<sub>Ar</sub>), 7.61–7.67 (m, 2 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.6 (C-1), 3.6 (Me<sub>DMPS</sub>), 23.7 (C-8), 85.9, 104.8 (C-9, C-10), 127.5, 127.8, 128.7, 129.3, 129.4, 129.8, 133.6 (C-3, C-4, C-5, C-6, C<sub>Ph,DMPS</sub>), 134.6, 136.4, 137.1 (C-2, C-7, C<sub>q,DMPS</sub>). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 3551, 2956, 1715, 1427, 1247, 1112. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 241 (3.90). **MS** (ESI): *m/z* (%) = 413 (57) [M+Na]<sup>+</sup>. **C**<sub>18</sub>H<sub>19</sub>ISi (390.33).

#### Compound 16b



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/CH<sub>2</sub>Cl<sub>2</sub> = 50:1  $\rightarrow$  20:1) afforded 1.08 g (73%) of compound **16b** as a yellow oil: **R**<sub>f</sub>: 0.26 (hexane/CH<sub>2</sub>Cl<sub>2</sub> = 10:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.42–0.44 (m, 6 H, Me<sub>DMPS</sub>), 1.05–1.12 (m, 14 H, *I*Pr), 3.71 (s, 2 H, 3-H), 3.72 (s, 2 H, 10-H), 3.73 (s<sub>br</sub>, 1 H, Si*H*), 7.25–7.30 (m, 2 H, H<sub>Ar</sub>), 7.36–7.40 (m, 3 H, H<sub>Ar</sub>), 7.46–7.53 (m, 2, H<sub>Ar</sub>), 7,62-7,67 (m, 2 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = -0.6 (Me<sub>DMPS</sub>), 11.0 (CH<sub>*i*Pr</sub>), 18.4, 18.6 (CH<sub>3,*i*Pr</sub>), 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, C<sub>Ph,DMPS</sub>), 133.8, 134.0, 137.2 (C-4, C-9, C<sub>q,DMPS</sub>). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 2941, 2863, 2173, 2115, 1489, 1428, 1248, 1113. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 244 (2.98), 259 (2.95). **MS** (ESI): *m/z* (%) = 425.2 (100) [M+Na]<sup>+</sup>. **C**<sub>26</sub>H<sub>34</sub>**Si**<sub>2</sub> (402.72), calc.: 425.2091, found: 425.2083, [M+Na]<sup>+</sup> (ESI-HRMS).

#### **Compound 14b**



Dialkyne **16b** (100 mg, 0.245 mmol, 1.0 equiv) was dissolved in dry  $Et_2O$  (10 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry  $Et_2O$  (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), NEt<sub>3</sub> (45 µL, 0.319 mmol, 1.3 equiv) and DMAP (3 mg, 0.025 mmol, 10 mol %) in dry  $Et_2O$  (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.

NH<sub>4</sub>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<sub>2</sub>SO<sub>4</sub>. 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: **R**<sub>f</sub>: 0.26 (hexane/EtOAc = 20:1).  $[\alpha]_{D}^{20}$  = +23.2° (c = 0.10, CHCl<sub>3</sub>). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.42 (s, 6 H, Me<sub>DMPS</sub>), 1.06–1.16 (m, 14 H, *i*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-H<sub>a</sub>\*), 3.88–3.96 (m, 2 H, 4-H\*, 3-H\*), 4.57 (dd, *J* = 1.4, 7.0 Hz, 1 H, 6-H<sub>b</sub>), 6.56 (s, 1 H, 1-H) 7.24–7.29 (m, 2 H, H<sub>Ar</sub>), 7.35–7.39 (m, 3 H, H<sub>Ar</sub>), 7.46–7.50 (m, 1 H, H<sub>Ar</sub>), 7.55–7.59 (m, 1 H, H<sub>Ar</sub>), 7.62–7.66 (m, 2 H, H<sub>Ar</sub>), 1<sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = -0.6 (Me<sub>DMPS</sub>), 13.4, 14.1, 17.3, 17.4, 17.7, 17.8 (C<sub>*i*Pr</sub>), 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', C<sub>Ph,DMPS</sub>), 133.8, 133.9, 137.1 (C-4', C-9', C<sub>q,DMPS</sub>), 143.5 (C-1).**MS** (ESI): *m*/*z* (%) = 689.2 (29) [M+Na]<sup>+</sup>. **C**<sub>35</sub>**H**<sub>45</sub>**BrO**<sub>4</sub>**Si**<sub>2</sub> (665.80), calc.: 689.1914, found: 689.1901, [M+Na]<sup>+</sup> (ESI-HRMS).

#### Compound 13b



The alkynylated bromoglycal **14b** (200 mg, 0.300 mmol, 1.0 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.030 mmol, 10 mol %), t-Bu<sub>3</sub>PH·BF<sub>4</sub> (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: R<sub>f</sub>: 0.43 (hexane/EtOAc = 6:1).  $[\alpha]_{D}^{20} = 17.2^{\circ}$  (c = 0.11, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.64$ (s, 3 H, Me<sub>DMPS</sub>), 0.64 (s, 3 H, Me<sub>DMPS</sub>), 0.93 (d, J = 7.5 Hz, 3 H, CH<sub>3,Pr</sub>), 1.00 (d, J = 7.4 Hz, 3 H, CH<sub>3,Pr</sub>), 1.15 (d, J = 7.4 Hz, 3 H, CH<sub>3,Pr</sub>), 1.21 (d, J = 7.4 Hz, 3 H, CH<sub>3,Pr</sub>), 1.24–1.33 (m, 1 H, CH<sub>Pr</sub>), 1.42–1.49 (m, 1 H, CH<sub>Pr</sub>), 1.52 (s, 3 H, 8-H), 1.54 (s, 3 H, 9-H), 3.57–3.87 (m, 6 H, 4-H, 6-H<sub>a</sub>, 12-H, 19-H), 3.87–4.01 (m, 2 H, 5-H, 6-H<sub>b</sub>), 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, H<sub>Ar</sub>), 7.30–7.38 (m, 2 H, H<sub>Ar</sub>), 7.49–7.54 (m, 2 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.5, 1.9 (Me<sub>DMPS</sub>), 13.0, 13.9, 17.3, 17.5, 17.5, 17.8 (C<sub>iPr</sub>), 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, C<sub>Ph.DMPS</sub>, C<sub>a.Ph.DMPS</sub>), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 2941, 2862, 1538, 1381, 1247,

1091. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 307 (3.72), 211 (4.68). **MS** (ESI): m/z (%) = 607.3 (100) [M+Na]<sup>+</sup>. **C**<sub>35</sub>H<sub>44</sub>**O**<sub>4</sub>Si<sub>2</sub> (584.89), calc.: 607.2651, found: 607.2670, [M+Na]<sup>+</sup> (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<sub>4</sub>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<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation to afford **22c** as crude product.

**Yield**: not determined. **R**<sub>f</sub>: 0.54 (hexane/EtOAc = 10:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>): δ = 0.10 (s, 3 H, Me), 0.10 (s, 3 H, Me), 0.13 (s, 3 H, Me<sub>TBS</sub>), 0.14 (s, 3 H, Me<sub>TBS</sub>), 0.94–0.95 (m, 9 H, *t*Bu<sub>TBS</sub>), 2.20 (s, 2 H, CH<sub>2,Bn</sub>), 3.64 (s, 2 H, 8-H), 4.76 (s, 2 H, 1-H), 7.02–7.12 (m, 3 H, H<sub>Ar</sub>), 7.16–7.23 (m, 2 H, H<sub>Ar</sub>), 7.25–7.29 (m, 2 H, H<sub>Ar</sub>), 7.39–7.45 (m, 2 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>): δ = -5.3 (Me<sub>TBS</sub>), 2.0 (Me), 18.4 (C<sub>q,TBS</sub>), 23.3 (C-8), 26.0 (*t*Bu<sub>TBS</sub>), 26.4 (*C*H<sub>2,Bn</sub>), 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<sub>Bn</sub>), 133.5, 138.6, 139.1 (C-2, C-7, C<sub>q,Bn</sub>). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 2942, 2863, 2174, 2066, 1601, 1492, 1453, 1249. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg ε) = 194 (5.06). **MS** (ESI): *m*/*z* (%) = 431.2 (100) [M+Na]<sup>+</sup>. **C**<sub>25</sub>H<sub>36</sub>**OSi**<sub>2</sub> (408.72), calc.: 431.2197, found: 431.2191, [M+Na]<sup>+</sup> (ESI-HRMS).

#### **Compound 23c**



The crude product **22c** was dissolved in MeOH (8 mL) at 0 °C and AcCI (0.8 mL) was added dropwise. The reaction mixture was stirred for 3 h and then stopped by slow addition of saturated aq. NaHCO<sub>3</sub> 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<sub>2</sub>SO<sub>4</sub>. 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**<sub>f</sub>: 0.08 (hexane/EtOAc = 8:1). <sup>1</sup>H-NMR

(300 MHz, CDCl<sub>3</sub>): δ = 0.13 (s, 6 H, Me), 2.19 (s, 2 H, CH<sub>2,Bn</sub>), 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, H<sub>Ar</sub>), 7.13–7.25 (m, 2 H, H<sub>Ar</sub>), 7.25–7.35 (m, 2 H, H<sub>Ar</sub>), 7.35–7.44 (m, 2 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>): δ = -2.0 (Me), 23.6 (CH<sub>2,Bn</sub>), 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, CH<sub>Bn</sub>), 128.1, 128.3 (CH<sub>Bn</sub>), 134.5, 138.2, 139.0 (C-2, C-7, C<sub>q,Bn</sub>). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 3317, 3059, 2889, 2173, 1559, 1492, 1248. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg ε) = 197 (4.78), 260 (3.20). **MS** (ESI): *m*/*z* (%) = 317.1 (100) [M+Na]<sup>+</sup>. **C**<sub>19</sub>H<sub>22</sub>**OSi** (294.46), calc.: 295.1513, found: 295.1511, [M+Na]<sup>+</sup> (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 Et<sub>2</sub>O (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: **R**<sub>f</sub>: 0.72 (hexane/EtOAc = 10:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.17 (s, 6 H, Me), 2.23 (s, 2 H, CH<sub>2,Bn</sub>), 3.71 (s, 2 H, 8-H), 4.48 (s, 2 H, 1-H), 7.05–7.14 (m, 3 H, H<sub>Ar</sub>), 7.19–7.27 (m, 3 H, H<sub>Ar</sub>), 7.29–7.36 (m, 2 H, H<sub>Ar</sub>), 7.40–7.44 (m, 1 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = -2.0 (Me), 3.6 (C-1), 23.6 (CH<sub>2,Bn</sub>), 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, CH<sub>Bn</sub>), 128.1, 128.3 (CH<sub>Bn</sub>), 134.7, 136.5, 139.0 (C-2, C-7, C<sub>q,Bn</sub>). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 3022, 2956, 2172, 1599, 1491, 1451, 1248. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg ε) = 197 (4.96). **MS** (ESI): *m/z* (%) = 427.0 (42) [M+Na]<sup>+</sup>. **C**<sub>19</sub>H<sub>21</sub>**ISi** (404.36), calc.: 427.0349, found: 427.0344, [M+Na]<sup>+</sup> (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/CH<sub>2</sub>Cl<sub>2</sub> = 100:1) afforded 170 mg (23%) of compound **16c** as clear oil:  $R_f$ : 0.54 (hexane/EtOAc = 20:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.14 (s, 6 H, Me), 1.01–1.14 (m, 14, H<sub>Pr</sub>), 2.19 (s, 2 H, CH<sub>2.Bn</sub>), 3.64 (s, 2 H, 3-H\*), 3.67 (s, 2 H, 10-H\*), 3.72 (s<sub>br</sub>, 1 H, SiH), 7.02-S17

7.12 (m, 3 H, H<sub>Ar</sub>), 7.16–7.30 (m, 4 H, H<sub>Ar</sub>), 7.38–7.42 (m, 1 H, H<sub>Ar</sub>), 7.49–7.53 (m, 1 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta = -2.0$  (Me), 10.9, 18.3, 18.5 (C<sub>*i*Pr</sub>), 24.0, 24.0 (C-3, C-10), 26.4 (*C*H<sub>2,Bn</sub>), 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, *C*H<sub>Bn</sub>), 133.9, 134.1, 139.0 (C-4, C-9, C<sub>q,Bn</sub>). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 2941, 2862, 1600, 1492, 1453, 1249. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 194 (5.06), 266 (3.33). **MS** (ESI): m/z (%) = 434.3 (100) [M+Na]<sup>+</sup>. **C**<sub>27</sub>H<sub>36</sub>Si<sub>2</sub> (416.75), calc.: 434.2694, found: 434.2695, [M+Na]<sup>+</sup> (ESI-HRMS).

#### Compound 14c



Dialkyne 16c (100 mg, 0.240 mmol, 1.0 equiv) was dissolved in dry CCI<sub>4</sub> (4.0 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry CCl<sub>4</sub> (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), NEt<sub>3</sub> (67 µL, 0.480 mmol, 2.0 equiv) and DMAP (3 mg, 0.024 mmol, 10 mol %) in dry CCl<sub>4</sub> (4.0 mL) and dry Et<sub>2</sub>O (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. NH<sub>4</sub>Cl solution. The aqueous layer was extracted three times with  $CH_2CI_2$ . The combined organic layers were washed with saturated aq. NaCl solution and dried over Na<sub>2</sub>SO<sub>4</sub>. 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: R<sub>f</sub>: 0.46 (hexane/EtOAc = 6:1).  $[\alpha]_{D}^{20}$  = +33.6° (c = 0.25, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 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, CH<sub>2 Bn</sub>), 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<sub>a</sub>), 3.86–3.99 (m, 2 H, 5-H\*, 6-H<sub>b</sub>), 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, H<sub>Ar</sub>), 7.55–7.62 (m, 1 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta = -2.0$  (Me), 13.3, 14.0, 17.2, 17.3, 17.6, 17.7 (C<sub>Pr</sub>), 18.7, 28.9 (C-8, C-9), 23.9, 24.0 (C-3', C-10'), 26.3 (CH<sub>2.Bn</sub>), 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, 128.3, 128.7 (C-5', C-6', C-7', C-8', CH<sub>Bn</sub>), 133.9, 134.0, 139.0 (C-4', C-9', C<sub>q,Bn</sub>), 143.6 (C-1). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 2942, 2864, 2173, 1631, 1600, 1492. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = no absorption between 190– 350 nm. **MS** (ESI): m/z (%) = 703.2 (46) [M+Na]<sup>+</sup>.  $C_{36}H_{47}BrO_4Si_2$  (679.83), calc.: 679.2269, found: 679.2254, [M+H]<sup>+</sup> (ESI-HRMS).

#### Compound 13c



The alkynylated bromoglycal **14c** (54 mg, 0.079 mmol, 1.0 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg, 0.008 mmol, 10 mol %), t-Bu<sub>3</sub>PH·BF<sub>4</sub> (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: R<sub>f</sub>: 0.49 (hexane/EtOAc = 4:1).  $[\alpha]_{D}^{20}$  = +19.6° (c = 0.26, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.39 (s, 3 H, Me), 0.44 (s, 3 H, Me), 0.92 (d, J = 7.4 Hz, 3 H,  $CH_{3Pr}$ ), 1.00 (d, J = 7.3 Hz, 3 H,  $CH_{3,Pr}$ , 1.15 (d, J = 7.3 Hz, 3 H,  $CH_{3,Pr}$ ), 1.21 (d, J = 7.4 Hz, 3 H,  $CH_{3,Pr}$ ), 1.25–1.50 (m, 2 H, CH<sub>IPr</sub>), 1.52 (s, 3 H, 8-H), 1.53 (s, 3 H, 9-H), 2.40 (s, 2 H, CH<sub>2,Bn</sub>), 3.65-3.86 (m, 4 H, 4-H\*,  $6-H_a$ , 12-H), 3.86–4.01 (m, 4 H, 5-H<sup>\*</sup>,  $6-H_b$ , 19-H), 5.07 (d, J = 9.1 Hz, 1 H, 3-H), 6.82 (d, J = 7.3 Hz, 2 H, H<sub>Ar</sub>), 6.97–7.13 (m, 3 H, H<sub>Ar</sub>), 7.16–7.27 (m, 4 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>): δ = 1.2, 1.6 (Me), 12.8, 12.8, 17.1, 17.3, 17.4, 17.7 (C<sub>*P*r</sub>), 19.0, 29.1 (C-8, C-9), 27.1 (CH<sub>2.Bn</sub>), 37.4, 39.2 (C-12, C-19), 62.2 (C-6), 70.1, 72.4, 78.1 (C-3, C-4, C-5), 100.0 (C-7), 122.3, 130.2, 133.6, 135.7, 137.3, 137.4, 140.0, 144.7 (C-2, C-10, C-11, C-13, C-18, C-20, C-21, C<sub>a.Bn</sub>), 123.9, 126.0, 126.2, 126.3, 127.0 (C-14, C-15, C-16, C-17, CH<sub>Bn</sub>), 127.9, 128.3 (CH<sub>Bn</sub>), 154.3 (C-1). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 2942, 2863, 1382, 1248. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm]  $(\lg \varepsilon) = 211$  (4.69), 306 (3.70). **MS** (ESI): m/z (%) = 621.3 (74)  $[M+Na]^+$ .  $C_{36}H_{46}O_4Si_2$ (598.92), calc.: 621.2827, found: 621.2820, [M+Na]<sup>+</sup> (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: **R**<sub>f</sub>: 0.60 (hexane/EtOAc = 8:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.10 (s, 6 H, Me<sub>TBS</sub>), 0.94 (s, 9 H, *t*Bu<sub>TBS</sub>), 1.03–1.12 (m, 14 H, *i*Pr), 3.68 (s, 2 H, 8-H), 3.72 (s, 1 H, Si*H*), 4.77 (s, 2 H, 1-H), 7.24–7.28 (m, 2 H, H<sub>Ar</sub>), 7.39–7.43 (m, 1 H, H<sub>Ar</sub>), 7.48–7.52 (m, 1 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = -5.3 (Me<sub>TBS</sub>), 10.9, 18.3, 18.4 (C<sub>Pr</sub>), 18.4 (C<sub>g,TBS</sub>), 23.4 (C-8), 25.9 (*t*Bu<sub>TBS</sub>),

80.7, 106.5 (C-9, C-10), 126.8, 126.9, 127.4, 128.4 (C-3, C-4, C-5, C-6), 133.5, 138.5 (C-2, C-7). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 2928, 2861, 2174, 2116, 1460, 1254, 1074. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 193 (4.73), 252 (2.74). **MS** (ESI): m/z (%) = 397.2 (100) [M+Na]<sup>+</sup>. **C**<sub>22</sub>**H**<sub>38</sub>**OSi**<sub>2</sub> (374.71), calc.: 397.2353, found: 397.2354, [M+Na]<sup>+</sup> (ESI-HRMS).

#### Compound 23d



The protected alcohol 22d (810 mg, 2.162 mmol, 1.0 equiv), dissolved in MeOH (8.0 mL), and AcCI (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 23d as a colorless oil:  $R_f$ : 0.20 (hexane/EtOAc = 8:1). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.97–1.16 (m, 14 H, *i*Pr), 3.71 (s, 1 H, Si*H*), 3.76 (s, 2 H, 8-H), 4.74 (d, *J* = 5.8 Hz, 2 H, 1-H), 7.24–7.32 (m, 2 H, H<sub>Ar</sub>), 7.31–7.42 (m, 1 H, H<sub>Ar</sub>), 7.46–7.55 (m, 1 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta = 10.9, 18.3, 18.5 (C_{Pr}), 23.7 (C-8), 63.3 (C-1), 81.1, 106.9 (C-9, C-10), 127.2, 128.2,$ 128.4, 128.9 (C-3, C-4, C-5, C-6), 134.6, 138.1 (C-2, C-7). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 3307, 2940, 2862, 2175, 2115, 1457. UV (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 259 (2.86). MS (ESI): m/z(%) = 283.2(100)[M+Na]<sup>+</sup>.  $C_{16}H_{24}OSi$ (260.45),calc.: 283.1489, found: 283.1491, [M+Na]<sup>+</sup> (ESI-HRMS)

#### Compound 23d-2

$$\int_{6}^{4} \int_{7}^{2} \int_{8}^{1} OH Si(iPr)_{2}OMe$$

Alkyne **23d** (248 mg, 1.708 mmol, 1.2 equiv) and MeOH (1.2 mL) were dissolved in dry CCl<sub>4</sub> (15 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry CCl<sub>4</sub> (0.976 mol/L, 975  $\mu$ L, 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 NEt<sub>3</sub> (221  $\mu$ L, 1.589 mmol, 2.0 equiv) was added and stirred for 1 h. The reaction was stopped by the addition of saturated aq. NH<sub>4</sub>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<sub>2</sub>SO<sub>4</sub>. 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: **R**<sub>f</sub>: 0.14 (hexane/EtOAc = 8:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.00–1.40 (m, 14 H, *i*Pr), 3.55 (s, 3 H, OC*H*<sub>3</sub>), 3.80 (s, 2 H, 8-H), 7.78 (d, *J* = 6.0 Hz, 2 H, 1-H), 7.23–7.39 (m, 3 H, H<sub>Ar</sub>), 7.50–7.57 (m, 1 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 12.9, 17.0, 17.2 (C<sub>*i*Pr</sub>), 23.4 (C-8), 52.3 (OMe), 63.3 (C-1), 81.9, 106.0 (C-9, C-10), 127.2, 128.3, 128.4, 128.9 (C-3, 2.4 (C-8), 52.3 (OMe), 63.3 (C-1), 81.9, 106.0 (C-9, C-10), 127.2, 128.3, 128.4, 128.9 (C-3, 2.4 (C-8), 52.3 (OMe), 63.3 (C-1), 81.9, 106.0 (C-9, C-10), 127.2, 128.3, 128.4, 128.9 (C-3, 2.4 (C-8), 52.3 (OMe), 63.3 (C-1), 81.9, 106.0 (C-9, C-10), 127.2, 128.3, 128.4, 128.9 (C-3, 2.4 (C-8), 52.3 (OMe), 63.3 (C-1), 81.9, 106.0 (C-9, C-10), 127.2, 128.3, 128.4, 128.9 (C-3, 2.4 (C-8), 52.3 (OMe), 63.3 (C-1), 81.9, 106.0 (C-9, C-10), 127.2, 128.3, 128.4, 128.9 (C-3, 2.4 (C-8), 52.3 (OMe), 63.3 (C-1), 81.9, 106.0 (C-9, C-10), 127.2, 128.3, 128.4, 128.9 (C-3, 2.4 (C-8), 52.3 (OMe), 63.3 (C-1), 81.9, 106.0 (C-9, C-10), 127.2, 128.3, 128.4, 128.9 (C-3, 2.4 (C-8), 52.3 (OMe), 63.3 (C-1), 81.9, 106.0 (C-9, C-10), 127.2, 128.3, 128.4, 128.9 (C-3, 2.4 (C-8), 52.3 (OMe), 63.3 (C-1), 81.9, 106.0 (C-9, C-10), 127.2, 128.3, 128.

C-4, C-5, C-6), 134.6, 138.1 (C-2, C-7). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 3350, 2941, 2864, 2172, 1461, 1094. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 193 (4.70), 261 (2.24). **MS** (ESI): m/z (%) = 313.2 (100) [M+Na]<sup>+</sup>. **C**<sub>17</sub>**H**<sub>26</sub>**O**<sub>2</sub>**Si** (290.47), calc.: 313.1594, found: 313.1596, [M+Na]<sup>+</sup> (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<sub>2</sub>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:  $\mathbf{R}_{f}$ : 0.67 (hexane/EtOAc = 20:1). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 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<sub>Ar</sub>), 7.48–7.53 (m, 1 H, H<sub>Ar</sub>). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.4 (C-1), 12.9, 17.1, 17.3 ( $C_{IPr}$ ), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 2940, 2863, 2172, 1461, 1151. UV (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 241 (3.90). MS (ESI): *m/z* (%) = 423.1 (100) [M+Na]<sup>+</sup>. C<sub>17</sub>H<sub>25</sub>IOSi (400.37), calc.: 423.0612, found: 423.0604, [M+Na]<sup>+</sup> (ESI-HRMS).

#### Compound 16d

$$\begin{cases} 5 & 3 & \frac{2}{-1} \\ 7 & 9 & \frac{1}{10 & 11 & 12} \\ 8 & 9 & 10 & 11 & 12 \\ \end{array} Si(iPr)_2OMe$$

Silvlacetylene 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), CuCl (39 mg, 0.385 mmol, 40 mol %) and 24d (385 g, 0.962 mmol, 1.0 equiv) in THF (6.0 mL) were brought to reaction to GP5.2. Purification silica gel column according by chromatography (pentane/CH<sub>2</sub>Cl<sub>2</sub> = 150:1) afforded 173 mg (43%) of compound **16d** as a pale yellow oil:  $\mathbf{R}_{f}$ : 0.39 (hexane/EtOAc = 20:1). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.99–1.12 (m, 28 H, *i*Pr), 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,  $H_{Ar}$ ), 7.44–7.56 (m, 2 H,  $H_{Ar}$ ). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.9, 12.9, 17.0, 17.2, 18.2, 18.5 (C<sub>iPr</sub>), 23.8, 24.0 (C-3, C-10), 52.3 (OMe), 81.2, 82.0, 105.2, 106.0 (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):  $\tilde{v}$  (cm<sup>-1</sup>) = 2941, 2863, 2172, 2117, 1461, 1095. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 193 (4.75), 253 (2.55). **MS** (ESI): m/z (%) = 435.3 (100) [M+Na]<sup>+</sup>. **C**<sub>25</sub>**H**<sub>40</sub>**OSi**<sub>2</sub> (412.76), calc.: 435.2510, found: 435.2503, [M+Na]<sup>+</sup> (ESI-HRMS).

#### Compound 14d



Dialkyne 16d (165 mg, 0.396 mmol, 1.2 equiv) was dissolved in dry CCl<sub>4</sub> (6.0 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry CCl<sub>4</sub> (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), NEt<sub>3</sub> (92 µL, 0.660 mmol, 2.0 equiv) and DMAP (5 mg, 0.040 mmol, 10 mol %) in dry CCl<sub>4</sub> (4.0 mL) and dry Et<sub>2</sub>O (0.5 mL) at 0 °C over a period of 30 min via syringe pump. The reaction was stirred over night and stopped by the addition of saturated aq. NH<sub>4</sub>Cl solution. The aqueous layer was extracted three times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na<sub>2</sub>SO<sub>4</sub>. 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<sub>f</sub>: 0.35 (hexane/EtOAc = 10:1).  $[\alpha]_{D}^{20} = +60.3^{\circ}$  (c = 0.32, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.00–1.15 (m, 28 H, *i*Pr), 1.38 (s, 3 H, 8-H), 1.47 (s, 3 H, 9-H), 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-H<sub>a</sub>), 3.88–3.97 (m, 2 H, 5-H\*, 6-H<sub>b</sub>), 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,  $H_{Ar}$ ), 7.47–7.60 (m, 2 H,  $H_{Ar}$ ). <sup>13</sup>**C-NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.0, 13.3, 14.1, 17.1, 17.3, 17.3, 17.3, 17.6, 17.7 (C<sub>Pr</sub>), 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). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 3419, 2942, 2864, 2172, 1632, 1462, 1171. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 194 (5.13). **MS** (ESI): m/z (%) = 694.3 (100) [M+NH<sub>4</sub>]<sup>+</sup>. **C**<sub>34</sub>**H**<sub>51</sub>**BrO**<sub>5</sub>**Si**<sub>2</sub> (675.84), calc.: 694.2782, found: 694.2772, [M+NH<sub>4</sub>]<sup>+</sup> (ESI-HRMS).

#### Compound 13d



The alkynylated bromoglycal **14d** (70 mg, 0.104 mmol, 1.0 equiv),  $Pd(PPh_3)_4$  (12 mg, 0.010 mmol, 10 mol %), *t*-Bu<sub>3</sub>PH·BF<sub>4</sub> (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 S22

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**<sub>f</sub>: 0.29 (hexane/EtOAc = 10:1). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.88$  (d, J = 7.5 Hz, 3 H, Me<sub>Pr</sub>), 0.92 (d, J = 7.5 Hz, 3 H, Me<sub>Pr</sub>), 0.96 (d, J = 7.4 Hz, 3 H, Me<sub>Pr</sub>), 1.04 (d, J = 7.4 Hz, 3 H, Me<sub>Pr</sub>), 1.05 (d, J = 7.5 Hz, 3 H, Me<sub>Pr</sub>), 1.10 (d, J = 7.3 Hz, 3 H, Me<sub>Pr</sub>), 1.14 (d, J = 7.3 Hz, 3 H, Me<sub>Pr</sub>), 1.21 (d, J = 7.4 Hz, 3 H, Me<sub>Pr</sub>), 1.24–1.48 (m, 4 H, CH<sub>Pr</sub>), 1.50 (s, 3 H, 8-H), 1.53 (s, 3 H, 9-H), 3.66 (s, 3 H, OMe), 3.70–3.91 (m, 4 H, 4-H\*, 6-H<sub>a</sub>, 12-H), 3.92–4.05 (m, 2 H, 5-H\*, 6-H<sub>b</sub>), 4.11 (d, J = 16.4 Hz, 1 H, 19-H<sub>a</sub>), 4.28 (d, J = 16.6 Hz, 1 H, 19-H<sub>b</sub>), 5.08 (d, J = 9.0 Hz, 1 H, 3-H), 7.14–7.30 (m, 4 H, H<sub>Ar</sub>).<sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta = 12.9$ , 13.8, 14.4, 14.4, 17.1, 17.3, 17.4, 17.6, 17.6, 17.7, 18.1, 18.2 ( $C_{Pr}$ ), 19.0, 29.1 (C-8, C-9), 35.6, 39.6 (C-12, C-19), 51.9 (OMe), 62.1 (C-6), 70.4, 72.5, 78.0 (C-3, C-4, C-5), 100.0 (C-7), 119.2, 129.5, 134.6, 135.8, 137.9, 138.6, 146.7 (C-2, C-10, C-11, C-13, C-18, C-20, C-21), 153.8 (C-1). **MS** (ESI): m/z (%) = 617.3 (100) [M+Na]<sup>+</sup>. **C<sub>34</sub>H<sub>50</sub>O<sub>5</sub>Si**<sub>2</sub> (594.93), calc.: 617.3089, found: 617.3085, [M+Na]<sup>+</sup> (ESI-HRMS).

#### 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  $Et_2O$  (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**<sub>f</sub>: 0.57 (hexane/EtOAc = 4:1). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 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<sub>Ar</sub>) 7.43–7.47(m, 1 H, H<sub>Ar</sub>). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 3275, 3258, 1635, 1484, 1145. UV (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 193 (4.45), 238 (3.90). **MS** (ESI): *m/z* (%) = 279.1 (16) [M+Na]<sup>+</sup>. C<sub>10</sub>H<sub>9</sub>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 GP5.2. Purification according to by silica gel column chromatography (pentane/CH<sub>2</sub>Cl<sub>2</sub> = 50:1) afforded 292 mg (55%) of compound **16e** as a yellow oil:  $\mathbf{R}_{f}$ : 0.61 (hexane/EtOAc = 10:1). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 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, H<sub>Ar</sub>), 7.44–7.53 (m, 2 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.9, 18.3, 18.5 (C<sub>iPr</sub>), 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-, C-5, C-6, C-7, C-8), 133.8, 134.0 (C-4, C-9). IR (ATR): v (cm<sup>-</sup> <sup>1</sup>) = 3307, 2941, 2862, 2174, 2116, 1455. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 193 (4.71), 260 (2.25). **MS** (ESI): m/z (%) = 291.2 (22) [M+Na]<sup>+</sup>. **C**<sub>18</sub>**H**<sub>24</sub>**Si** (268.47), calc.: 291.1539, found: 291.1538, [M+Na]<sup>+</sup> (ESI-HRMS).

#### Compound 14e



Dialkyne 16e (284 mg, 1.06 mmol, 1.1 equiv) was dissolved in dry CCl<sub>4</sub> (12 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry CCl<sub>4</sub> (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), NEt<sub>3</sub> (267 µL, 1.922 mmol, 2.0 equiv) and DMAP (12 mg, 0.096 mmol, 10 mol %) in dry CCl<sub>4</sub> (6.0 mL) and dry Et<sub>2</sub>O (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. NH<sub>4</sub>Cl solution. The aqueous layer was extracted three times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na<sub>2</sub>SO<sub>4</sub>. 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:  $\mathbf{R}_{f}$ : 0.42 (hexane/EtOAc = 6:1).  $[\alpha]_{D}^{20} = +57.1^{\circ}$  (c = 0.52, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.06–1.14 (m, 14 H, *I*Pr), 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-H<sub>a</sub>), 3.88–3.96 (m, 2 H, 5-H\*, 6-H<sub>b</sub>), 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, H<sub>Ar</sub>), 7.42–7.48 (m, 1 H, H<sub>Ar</sub>), 7.54–7.59 (m, 1 H, H<sub>Ar</sub>). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.3, 14.0, 17.2, 17.3, 17.6, 17.7 (C<sub>Pr</sub>), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 3297, 2942, 2864, 2173, S24

1632, 1461, 1171. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 193 (5.04). **MS** (ESI): *m*/*z* (%) = 555.1 (83) [M+Na]<sup>+</sup>. **C**<sub>27</sub>**H**<sub>35</sub>**BrO**<sub>4</sub>**Si** (531.55), calc.: 555.1361, found: 555.1353, [M+Na]<sup>+</sup> (ESI-HRMS).

#### **Compound 13e**



The alkynylated bromoglycal **14e** (265 mg, 0.498 mmol, 1.0 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (58 mg, 0.050 mmol, 10 mol %), t-Bu<sub>3</sub>PH·BF<sub>4</sub> (29 mg, 0.100 mmol, 20 mol %) and diisopropylamine (353 µL, 2.49 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<sub>f</sub>: 0.31 (hexane/EtOAc = 10:1).  $[\alpha]_{D}^{20} = +58.0^{\circ}$  (c = 0.25, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 0.87$  (d, J = 7.5 Hz, 3 H, CH<sub>3,Pr</sub>), 0.96 (d, J = 7.4 Hz, 3 H, CH<sub>3,Pr</sub>), 1.13 (d, J = 7.4 Hz, 3 H, CH<sub>3,Pr</sub>), 1.19 (d, J = 7.5 Hz, 3 H, CH<sub>3,Pr</sub>), 1.22–1.29 (m, 1 H, CH<sub>Pr</sub>), 1.40–1.48 (m, 1 H, CH<sub>Pr</sub>), 1.51 (s, 3 H, 8-H), 1.53 (s, 3 H, 9-H), 3.85 (m, 6 H, 4-H, 6-H<sub>a</sub>, 12-H, 19-H), 4.01–4.13 (m, 2 H, 5-H, 6-H<sub>b</sub>), 5.10 (d, J = 9.1 Hz, 1 H, 3-H), 6.71 (s, 1 H, 21-H), 7.15–7.19 (m, 2 H,  $H_{Ar}$ ), 7.21–7.23 (m, 1 H,  $H_{Ar}$ ), 7.25–7.28 (m, 1 H,  $H_{Ar}$ ). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 12.8, 13.8, 17.1, 17.3, 17.4, 17.6 (C<sub>Pr</sub>), 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\*), 136,5 (13), 136.8 (C-11\*), 138,7 (C-10), 149.2 (C-1). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 2941, 2863, 2360, 2341, 1585, 1575, 1445, 1253. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 263 (3.54), 294 (3.65), 309 (4.61). **MS** (ESI): m/z (%) = 473.2 (100) [M+Na]<sup>+</sup>. **C**<sub>27</sub>**H**<sub>34</sub>**O**<sub>4</sub>**Si** (450.64), calc.: 473.2119, found: 473.2117,  $[M+Na]^+$  (ESI-HRMS).

#### Compound 14f



Dialkyne **16a** (177 mg, 0.520 mmol, 1.0 equiv) was dissolved in dry CCl<sub>4</sub> (5.0 mL) and cooled to 0 °C. A freshly prepared solution of bromine in dry CCl<sub>4</sub> (0.976 mol/L, 559  $\mu$ L, 0.546 mmol, 1.05 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 **15c** (179 mg, 0.572 mmol, 1.1 equiv), NEt<sub>3</sub> (159  $\mu$ L, 1.14 mmol, 2.0 equiv) and DMAP (7 mg, 0.052 mmol, 10 mol %) in

dry CCl<sub>4</sub> (5.0 mL) and dry Et<sub>2</sub>O (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. NH<sub>4</sub>Cl solution. The aqueous layer was extracted three times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with saturated aq. NaCl solution and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (pentane/EtOAc =  $80:1 \rightarrow 30:1$ ) to afford 229 mg (68%) of compound **14f** as a slightly yellow oil:  $\mathbf{R}_{f}$ : 0.43 (hexane/EtOAc = 6:1).  $[\alpha]_{D}^{20} = +88.4^{\circ}$  (c = 0.25, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.18 (s, 9 H, Me<sub>TMS</sub>), 0.96–1.06 (m, 7 H, CH<sub>3,Pr</sub>, CH<sub>Pr</sub>), 1.11–1.18 (m, 7 H, CH<sub>3,Pr</sub>, CH<sub>IPr</sub>), 3.63–3.77 (m, 6 H, 4-H\*, 6-H<sub>a</sub>, 3'-H, 10'-H), 4.15–4.27 (m, 2 H, 5-H\*, 6-H<sub>b</sub>), 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, H<sub>Ar</sub>), 7.40–7.54 (m, 4 H, H<sub>Ar</sub>). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.0 (Me<sub>TMS</sub>), 13.0, 13.8, 16.9, 17.0, 17.2, 17.3 (C<sub>Pr</sub>), 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, 128.0, 128.8, 128.9 (C-5', C-6', C-7', C-8', CH<sub>Ph</sub>), 134.1, 134.2, 137.4 (C-4', C-9', C<sub>a.Ph</sub>), 143.4 (C-1). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 2944, 2864, 2171, 1645, 1454, 1247, 1192. UV (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = no absorption between 190–350 nm. MS (ESI): m/z (%) = 674.2 (45) [M+Na]<sup>+</sup>.  $C_{34}H_{43}B_4O_4Si_2$  (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),  $Pd(PPh_3)_4$  (39 mg, 0.034 mmol, 10 mol %), *t*-Bu<sub>3</sub>PH·BF<sub>4</sub> (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: **R**<sub>f</sub>: 0.22 (hexane/EtOAc = 10:1).  $[\alpha]_D^{20} = +14.6^{\circ}$  (c = 0.13, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.47$  (s, 9 H, Me<sub>TMS</sub>), 0.84 (d, J = 7.4 Hz, 3 H,  $CH_{3,Pr}$ ), 0.84 (d, J = 7.4 Hz, 3 H,  $CH_{3,Pr}$ ), 1.16–1.43 (m, 2 H,  $CH_{3,Pr}$ ), 1.13 (d, J = 7.3 Hz, 3 H,  $CH_{3,Pr}$ ), 1.13 (d, J = 7.4 Hz, 3 H,  $CH_{3,Pr}$ ), 1.16–1.43 (m, 2 H,  $CH_{Pr}$ ), 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-H<sub>a</sub>), 4.48 (dd, J = 1.9, 12.5 Hz, 1 H, 6-H<sub>b</sub>), 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, H<sub>Ar</sub>), 7.27–7.31 (m, 1 H, H<sub>Ar</sub>). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 2.7$  (Me<sub>TMS</sub>), 13.2, 13.9, 17.1, 17.3, 17.4, 17.7 (C<sub>Pr</sub>), 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,  $C_{q,Ph}$ ), 125.9, 126.0, 126.4, 126.4, 126.9, 127.7, 128.6 (C-12, C-13, C-14, C-15, CH<sub>Ph</sub>), 154.9 (C-1). **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 2942, 2862, 1542, 1458, 1384, 1247. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 209 (4.70), 305 (3.70). **MS** (ESI): m/z (%) = 593.3 (100) [M+Na]<sup>+</sup>. **C**<sub>34</sub>H<sub>42</sub>**O**<sub>4</sub>**Si**<sub>2</sub> (570.87), calc.: 593.2514, found: 593.2510, [M+Na]<sup>+</sup> (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<sub>3</sub> 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<sub>2</sub>SO<sub>4</sub>. 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<sub>2</sub>Cl<sub>2</sub>/MeOH = 8:1).  $[\alpha]_D^{20} = +34.7^\circ$  (c = 0.15, CHCl<sub>3</sub>). <sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.92$  (d, J = 7.5 Hz, 3 H,  $CH_{3,Pr}$ ), 1.09 (d, J = 7.4 Hz, 3 H, CH<sub>3.Pr</sub>), 1.14 (d, J = 7.4 Hz, 3 H, CH<sub>3,Pr</sub>), 1.20 (d, J = 7.4 Hz, 3 H, CH<sub>3,Pr</sub>), 1.23–1.51 (m, 2 H, CH<sub>Pr</sub>), 2.06 (s<sub>br</sub>, 1 H, OH), 2.38 (s<sub>br</sub>, 1 H, OH), 3.80–3.95 (m, 4 H, 12-H, 19-H), 4.02 (dd,  $J = 4.7, 11.7 \text{ Hz}, 1 \text{ H}, 6 \text{-H}_{a}$ , 4.11 (dd,  $J = 5.9, 11.7 \text{ Hz}, 1 \text{ H}, 6 \text{-H}_{b}$ ), 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). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.0, 13.9, 17.2, 17.3, 17.6, 17.6 (C<sub>Pr</sub>), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 3385, 2940, 2862, 1587, 1447, 1261, 1070. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 262 (3.62), 289 (3.65). **MS** (ESI): m/z (%) = 433.2 (23) [M+Na]<sup>+</sup>. **C**<sub>24</sub>**H**<sub>30</sub>**O**<sub>4</sub>**Si** (410.58), calc.: 433.1806, found: 433.1800, [M+Na]<sup>+</sup> (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  $\mu$ L, 0.711 mmol, 3.0 equiv). The mixture was stirred for 4 h and directly poured on a packed silica gel column (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 10:1). 55 mg (99%) of

compound **12b** was obtained as a yellow solid after chromatographic purification: **R**<sub>f</sub>: 0.26 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 10:1).  $[\alpha]_D^{20}$  = +67.0° (c = 0.10, DMSO). <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>): δ = 3.61–3.76 (m, 2 H, 6-H<sub>a</sub>, 6-H<sub>b</sub>), 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, OH<sub>C-3</sub>), 4.70 (dd, *J* = 3.8, 7.5 Hz, 1 H, 4-H), 4.78 (t, *J* = 5.6 Hz, 1 H, OH<sub>C-6</sub>), 5.08 (d, *J* = 7.6 Hz, 1 H, OH<sub>C-4</sub>), 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). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>): δ = 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<sup>-1</sup>) = 3255, 2919, 2344, 1672, 1295. UV (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\epsilon$ ) = 261 (4.22). MS (ESI): *m*/*z* (%) = 321.1 (15) [M+Na]<sup>+</sup>. **C**<sub>18</sub>H<sub>18</sub>**O**<sub>4</sub> (298.33), calc.: 321.1097, found: 321.1096, [M+Na]<sup>+</sup> (ESI-HRMS).

#### **Compound 28b**



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.  $NH_4CI$  solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed three times with saturated aq. NaCI solution and dried over  $Na_2SO_4$ . 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<sub>3</sub>·6H<sub>2</sub>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:  $\mathbf{R}_{f}$ : 0.21 (hexane/EtOAc = 20:1). [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -20.0° (c = 0.10, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.01 (s, 3 H, Me<sub>TBS</sub>), 0.09 (s, 3 H, Me<sub>TBS</sub>), 0.11 (s, 3 H, Me<sub>TBS</sub>), 0.13 (s, 3 H, Me<sub>TBS</sub>), 0.24 (s, 3 H, Me<sub>TBS</sub>), 0.27 (s, 3 H, Me<sub>TBS</sub>), 0.68 (s, 9 H, *t*Bu<sub>TBS</sub>), 0.93 (s, 9 H, *t*Bu<sub>TBS</sub>), 1.07 (s, 9 H, *t*Bu<sub>TBS</sub>), 3.87–3.92 (m, 2 H, 5-H\*, 6-H<sub>a</sub>\*),

4.29–4.36 (m, 2 H, 4-H\*, 6-H<sub>b</sub>\*), 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). <sup>13</sup>**C-NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta = -5.3, -5.2, -4.9, -4.4, -3.9$  (Me<sub>TBS</sub>), 18.2, 18.3, 18.8 (C<sub>q,TBS</sub>), 25.7, 25.8, 26.3 (*t*Bu<sub>TBS</sub>), 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 2927, 2855, 1674, 1592, 1292. **UV** (CH<sub>3</sub>CN):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 276 (3.91). **MS** (ESI): *m/z* (%) = 692.3 (65) [M+Na]<sup>+</sup>. **C<sub>36</sub>H<sub>56</sub>O<sub>6</sub>Si<sub>3</sub>** (669.08), calc.: 691.3277, found: 691.3266, [M+Na]<sup>+</sup> (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 HCI (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<sub>3</sub> solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated ag. NaCl solution and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was filtered over a small plug of celite (CH<sub>2</sub>Cl<sub>2</sub>: 20 mL and CH<sub>2</sub>Cl<sub>2</sub>/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<sub>2</sub>Cl<sub>2</sub>/MeOH = 10:1).  $[\alpha]_D^{20}$  = -10.0° (c = 0.30, DMSO). <sup>1</sup>**H-NMR** (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 3.72 (s<sub>br</sub>, 2 H), 4.06 (s<sub>br</sub>, 1 H), 4.31 (s<sub>br</sub>, 1 H), 4.84 (s<sub>br</sub>, 1 H), 5.08 (s<sub>br</sub>, 1 H), 5.08 (s<sub>br</sub>, 1 H), 5.30 (s<sub>br</sub>, 1 H), 5.94 (s<sub>br</sub>, 1 H), 7.31 (s, 1 H, 18-H), 7.88  $(s_{br}, 2 H, 12-H, 13-H), 8.15 (s_{br}, 2 H, 11-H, 14-H), 8.28 (s, 1 H, 7-H).$  <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 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):  $\tilde{v}$  (cm<sup>-1</sup>) = 3281, 2922, 1667, 1588, 1565, 1332, 1287. **UV** (MeOH):  $\lambda_{max}$  [nm] (lg  $\varepsilon$ ) = 239 (3.99), 276 (4.21). **MS** (ESI): m/z (%) = 349.1 (89) [M+Na]<sup>+</sup>.  $C_{18}H_{14}O_6$  (326.30), calc.: 325.0718, found: 325.0714, [M-H]<sup>-</sup> (ESI-HRMS).

## <sup>1</sup>H and <sup>13</sup>C NMR spectra of the compounds

## Compound 20



## Compound 22a



## Compound 23a



## Compound 24a



## **Compound 16a**



S34

#### **Compound 14a**



S35

## Compound 13a



## **Compound 26a**



## Compound 12a



160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104 102 100 f1 (ppm)

## Compound 27a



## Compound 28a



S40

## Compound 11a



## Compound 23b



## Compound 24b

ml7-217\_3h ML7-217 CDCl3 Leibeling / Werz



## **Compound 16b**

ml7-221\_3h ML7-221 CDCl3 Leibeling / Werz





#### **Compound 14b**

ml7-224\_3h ML7-224 CDCl3 Leibeling / Werz



#### **Compound 13b**





## Compound 22c



## Compound 23c



## Compound 24c



## **Compound 16c**



#### Compound 14c

ml8-169\_3h ML8-169 CDCl3 Leibeling / Werz

<del>)</del>0



## Compound 13c

ml8-149\_3h ML8-149 CDCl3 Leibeling / Werz



## Compound 22d



f1 (ppm) <del>)</del>0 -10

## Compound 23d



S54

## Compound 24d



f1 (ppm)

0 180

-10

## Compound 16d



### Compound 14d



## Compound 13d



## Compound 24e



## **Compound 16e**



## Compound 14e



## Compound 13e



S62

#### Compound 14f





#### Compound 13f



## **Compound 26b**



## Compound 12b



## Compound 28b



## **Compound 11b**

