Supporting Information

A Palladium-Catalyzed Carbo-Oxygenation: the Bielschowskysin Case

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Material and Methods

All moisture and oxygen sensitive reactions were carried out in flame-dried glassware under a slight argon overpressure. All reactions were stirred magnetically. Reactions were monitored by thin-layer chromatography (TLC) or NMR of the crude mixture. Evaporations were conducted under reduced pressure at temperatures less than 40 °C, unless otherwise noted. Further dryings of the residues were accomplished using a high vacuum pump.

All solvents (except dichloromethane and methanol) were purchased at highest available grade from Sigma-Aldrich, Acros-Organics or Fischer-Chemicals. Anhydrous dichloromethane was purified by filtration through alumina under argon immediately before use. Methanol was heated at reflux for several hours over sodium before being distilled. NEt₃, iPr₂NEt and 2,6-lutidine were distilled over CaH₂ before use. All other reagents were used as received from Sigma-Aldrich, Acros-Organics, Fischer-Chemicals, TCI or ABCR unless otherwise stated.

Thin-layer chromatographies (TLC) were carried out on pre-coated Merk silica gel 60 F254 to monitor all reactions. The detection was first performed using UV (254 nm) as a visualizing agent followed by SI-2 immersion in an aqueous solution of phosphomolybdic acid (20 g), ceric(IV) sulfate (0.4 g) and 22 mL of H₂SO₄. Treatment with a heat-gun eventually revealed the state of the reaction. Preparative column chromatography was performed with silica gel 60 from Merk (0.040-0.063 μm, 240-400 mesh). The columns were packed with a suspension of gel in hexane and eluted with an appropriate solvent combination using a hand-pump overpressure.

All NMR spectra were measured on a Bruker AV400, DRX400 or DRX600. Chemical shifts are given in ppm and referenced to the solvent residual peaks (CDCl₃; ¹H, δ = 7.26 ppm, ¹³C, δ = 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d =
**Experimental Procedures**

(25,4S)-4-methylhex-5-yne-1,2,4-triol

Alkyne 12 (2.40 g, 13.0 mmol) was digested in AcOH (27 mL) and H2O (1.4 mL) at room temperature. The resulting colorless solution was stirred overnight and concentrated under reduced pressure. The remaining pale yellow gum was evaporated with toluene (3 x 10 mL) till the smell of acetic acid was gone. Purification by flash column chromatography (SiO2, Hex/EtOAc 2/1 → 0/1) afforded the corresponding triol as a colorless gum (1.67 g, 89%).

\[ \text{H NMR} \quad (\text{CDCl}_3, 400 MHz) : \delta = 4.40 \text{ (m, 1H)}, \ 4.05 \text{ (br s, 1H)}, \ 3.68 \text{ (dd, } J = 11.1, 2.9 \text{ Hz, 1H)}, \ 3.51 \text{ (dd, } J = 10.7, 6.9 \text{ Hz, 1H)}, \ 3.33 \text{ (br s, 1H)}, \ 2.51 \text{ (s, 1H)}, \ 2.11 \text{ (br s, 1H)}, \ 1.85 \text{ (dd, } J = 14.4, 10.6 \text{ Hz, 1H)}, \ 1.70 \text{ (dd, } J = 14.4, 2.1 \text{ Hz, 1H)} \ 1.55 \text{ (s, 3H).} \]

\[ \text{C NMR} \quad (\text{CDCl}_3, 400 MHz) : \delta = 87.0, 72.3, 71.3, 68.3, 66.8, 43.9, 31.2. \]

**HRMS** (ESI) (m/z): calculated for C7H12O3 [M]+ 144.0786, found 144.0791.

**IR** (cm\(^{-1}\)): \( \tilde{\nu} = 3298, 2983, 2359, 1418, 1133, 1109, 1058, 1036, 1016, 908. \)

\[ [\alpha]_D^{20} = -7.9, \quad (\text{CHCl}_3, c = 1.0). \]

\[ R_f: \] (Hex/EtOAc 1/2) 0.19.
(S)-2-methyl-1-((S)-oxiran-2-yl)but-3-yn-2-ol (14).

To a suspension of NaH (5.2 g, 132 mmol) in THF (100 mL) at 0 °C was added a solution of the aforementioned triol (3.8 g, 26.4 mmol) in THF (40 mL). The resulting suspension was stirred at 0 °C for 30 min, allowed to stir at room temperature for 30 min before being re-cooled to 0 °C. Trisylimidazole 13 (11.5 g, 34.3 mmol) was then added as a solid in three portions under a constant stream of argon and the resulting reaction mixture was vigorously stirred at 0 °C for 1 h. The resulting thick suspension was quenched with H₂O (50 mL) and brine (20 mL). The aqueous phase was extracted with CH₂Cl₂ (4 × 20 mL), the combined organic phases were dried with MgSO₄, filtered and evaporated to give a brown oil. Purification by flash column chromatography (SiO₂, Hex/EtOAc 1/1 → 1/2) afforded epoxide 14 as a colorless oil (2.36 g, 78%).

¹H NMR (CDCl₃, 400 MHz): δ = 3.31 (m, 1H), 3.07 (s, 1H), 2.81 (dd, J = 4.8, 4.2 Hz, 1H), 2.53 (dd, J = 4.9, 2.8 Hz, 1H), 2.50 (s, 1H), 2.02 (dd, J = 4.2, 14.2 Hz, 1H), 1.71 (dd, J = 14.2, 7.6 Hz, 1H), 1.52 (s, 3H).

¹³C NMR (CDCl₃, 400 MHz): δ = 87.0, 72.1, 67.2, 49.5, 46.7, 45.5, 30.2.

HRMS (EI) (m/z): calculated for C₆H₇O₂ [M−CH₃]⁺ 111.0446, found 111.0441.

IR (cm⁻¹): ν = 3408, 3283, 2985, 2926, 1450, 1410, 1304, 1165, 1135, 1047.

[α]D²⁰ = −20.5, (CHCl₃, c = 1.0).

Rf: (Hex/EtOAc 1/2) 0.58.

2-(ethyl oxycarbonyl)-γ-butyrolactone

Under a constant stream of argon Na (1.08 g, 46.8 mmol) was added to EtOH (100 mL). After the disappearance of all solids, diethylmalonate (14.2 mL, 94 mmol) was added dropwise. After stirring at room temperature for 15 min, a solution of epoxide 14 (2.36 g, 18.7 mmol) in EtOH (100 mL) was added. The reaction mixture was stirred at room temperature for 16 h and quenched with sat. aq. NH₄Cl (50 mL) and H₂O (50 mL). The aqueous phase was
extracted with CH₂Cl₂ (4 × 10 mL) and the combined organic phases were dried with MgSO₄, filtered and evaporated to give a pale yellow oil. Purification by flash column chromatography (SiO₂, Hex/EtOAc 4/1 → 3/1 → 2/1 → 1/1) afforded a (1:1.45) diastereoisomeric mixture of the desired malonate as colorless oil (3.86 g, 86%).

¹H NMR (CDCl₃, 400 MHz):

**major diastereomer:** δ = 4.98-4.91 (m, 1H), 4.28 (dd, J = 7.12, 1.3 Hz, 1H), 4.24 (dd, J = 7.1, 1.2 Hz, 1H), 3.61 (dd, J = 11.2, 9.1 Hz, 1H), 2.68 (dd, J = 9.1, 6.1 Hz, 1H), 2.65 (dd, J = 9.1, 6.1 Hz, 1H), 2.52 (s, 1H), 2.43 (dd, J = 11.2, 9.8 Hz, 1H), 2.18 (dd, J = 14.8, 8.7 Hz, 1H), 2.05 (m, 1H), 1.56 (s, 3H), 1.31 (t, J = 1.4 Hz, 3H).

**minor diastereomer:** δ = 5.19-5.12 (m, 1H), 4.27 (d, J = 7.1 Hz, 1H), 4.23 (d, J = 7.1 Hz, 1H), 3.57 (dd, J = 9.6, 4.1 Hz, 1H), 2.80 (dd, J = 6.7, 4.1 Hz, 1H), 2.77 (dd, J = 6.7, 4.1 Hz, 1H), 2.54 (s, 1H), 2.39 (dd, J = 11.2, 9.8 Hz, 1H), 2.20 (m, 1H), 2.03 (m, 1H), 1.55 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H).

¹³C NMR (CDCl₃, 400 MHz):

**major diastereomer:** δ = 171.2, 167.7, 86.5, 76.9, 72.8, 66.6, 62.4, 48.0, 46.8, 32.9, 30.5, 14.2.

**minor diastereomer:** δ = 171.2, 167.7, 86.4, 77.9, 72.9, 66.6, 62.5, 48.1, 46.5, 32.9, 30.5, 14.2.

HRMS (EI): (m/z) calculated for C₁₁H₁₃O₅ [M-CH₃]⁺ 225.0763, found 225.0765.

IR (cm⁻¹): ν = 3473, 2984, 1767, 1450, 1371, 1260, 1156, 1095, 1035, 1008.

[α]D²⁰ = −33.5, (CHCl₃, c = 1.0).

Rf: (Hex/EtOAc 1/1) 0.51.

(R)-5-((S)-2-hydroxy-2-methylbut-3-ynyl)dihydrofuran-2(3H)-one (15)

A solution of the malonate (3.8 g, 15.83 mmol) and LiCl (1.33 g, 31.66 mmol) in DMSO (32 mL) and water (1 mL) was heated to 155 °C and stirred at this temperature for 5 h. The resulting brown mixture was cooled to room temperature and quenched with sat. aq. NH₄Cl (10 mL) and H₂O (30 mL). The aqueous phase was extracted with CH₂Cl₂ (7 × 10 mL) and the combined organic phases were dried with MgSO₄, filtered and evaporated to give a viscous
brown oil. Purification by flash column chromatography (SiO₂, Hex/EtOAc 3/1 → 2/1 → 1/1) afforded alcohol 15 as colorless oil (2.5 g, 94%).

**1H NMR** (CDCl₃, 400 MHz): δ = 5.0 (m, 1H), 2.72 (br s, 1H), 2.54 (dd, J = 9.9, 1.7 Hz, 1H), 2.53 (d, J = 9.6 Hz, 1H) 2.52 (s, 1H), 2.43 (m, 1H), 2.09–1.89 (m, 3H), 1.55 (s, 3H).

**13C NMR** (CDCl₃, 400 MHz): δ = 176.3, 86.6, 78.5, 72.7, 66.9, 48.2, 30.5, 28.9, 28.3.

**HRMS** (ESI) (m/z): calculated for C₈H₉O₃ [M-CH₃]+ 153.0552, found 153.0557.

**IR** (cm⁻¹): ν = 3430, 3280, 2985, 2934, 1760, 1357, 1173, 1124, 1035, 1008.

[α]D₂₀ = −67.2, (CHCl₃, c = 1.0).

**Rf:** (Hex/EtOAc 1/2) 0.41.

(R)-5-((S)-2-hydroxy-2-methylpenta-3,4-dienyl)dihydrofuran-2(3H)-one

A solution of alcohol 15 (2.5 g, 14.9 mmol), paraformaldehyde (1.29 g, 44.6 mmol), iPr₂NH (3.2 mL, 22.32 mmol) and CuBr (1.07 g, 7.45 mmol) in 1,4-dioxane (30 mL) was heated to 125 °C and stirred at this temperature for 6 h. The resulting greenish suspension was cooled to room temperature, filtered through a pad of Celite and sat. aq. NH₄Cl (10 mL) and H₂O (30 mL) were added. The aqueous phase was extracted with CH₂Cl₂ (5 × 10 mL) and the combined organic phases were washed with sat. aq. NaCl (10 mL), dried with MgSO₄, filtered and evaporated to give a brown oil. Purification by flash column chromatography (SiO₂, Hex/EtOAc, 2/1 → 1/1 → 1/2) afforded the desired allene as colorless oil (1.9 g, 86%).

**1H NMR** (CDCl₃, 400 MHz): δ = 5.31 (t, J = 6.6 Hz, 1H), 4.90 (d, J = 6.6 Hz, 2H), 4.79 (m, 1H), 2.51 (d, J = 9.7 Hz, 1H), 2.49 (d, J = 9.7 Hz, 1H), 2.36 (m, 1H), 2.24 (br s, 1H), 2.02 (dd, J = 14.7, 8.5 Hz, 1H), 1.94–1.82 (m, 2H), 1.38 (s, 3H).

**13C NMR** (CDCl₃, 400 MHz): δ = 205.5, 176.9, 99.4, 79.1, 78.1, 70.4, 47.7, 29.4, 28.9, 28.7.

**HRMS** (EI) (m/z): calculated for C₁₀H₁₂O₂ [M]+ 164.0839, found 164.0837.

**IR** (cm⁻¹): ν = 3423, 2978, 2934, 1956, 1760, 1727, 1457, 1419, 1357, 1289, 1223, 1179, 1114, 1075, 1012, 986, 917, 850.

[α]D₂₀ = −49.3, (CHCl₃, c = 1.0).

**Rf:** (Hex/EtOAc 1/1) 0.18.
(R)-5-((S)-2-methyl-2-(trimethylsilyloxy)penta-3,4-dienyl)dihydrofuran-2(3H)-one (16)

To a solution of the tertiary allenic alcohol (4.2 g, 23.0 mmol) in THF (50 mL) were sequentially added 2,6-lutidine (8.0 mL, 69.1 mmol) and TMSOTf (6.3 mL, 34.6 mmol) at 0 °C. The cooling bath was removed and the reaction was quenched after 30 min with sat. aq. NH₄Cl (50 mL). The aqueous phase was extracted with hexanes (10 mL) and the combined organic phases were washed with sat. aq. NaCl (20 mL), dried with MgSO₄, filtered and evaporated to give a crude colorless oil. Purification by flash column chromatography (SiO₂, Hex/EtOAc 4/1) afforded lactone 16 as colorless oil (5.1 g, 87%).

1H NMR (CDCl₃, 400 MHz): δ = 5.25 (t, J = 6.6 Hz, 1H), 4.82 (d, J = 6.6 Hz, 2H), 4.73 (m, 1H), 2.50 (dd, J = 8.4, 2.5 Hz, 1H), 2.48 (d, J = 9.7 Hz, 1H), 2.36 (sext., J = 6.5 Hz, 1H), 1.99−1.84 (m, 3H), 1.39 (s, 3H), 0.10 (s, 9H).

13C NMR (CDCl₃, 400 MHz): δ = 206.3, 177.4, 99.8, 78.1, 77.9, 72.8, 49.4, 29.8, 29.0, 27.7, 2.4 (3C).

HRMS (ESI) (m/z): calculated for C₁₃H₂₂O₃SiNa [M+Na]⁺ 277.1233, found 277.1236.

IR (cm⁻¹): ν = 2955, 1956, 1773, 1249, 1154, 1110, 1078, 1001, 982, 916, 836.

[α]D²⁰ = −42.3, (CHCl₃, c = 1.0).

Rf: (Hex/EtOAc 1/1) 0.64.

2-phenylselenyl-γ-butyrolactone 10

To a solution of lactone 16 (1.50 g, 5.9 mmol) in THF (30 mL) at −78 °C was added LiHMDS (1.0 M in toluene, 6.5 mL, 64.9 mmol) and TMSCl (0.83 mL, 64.9 mmol). The resulting mixture was stirred at −78 °C for 2 h before a solution of PhSeCl (1.24 g, 64.9 mmol) in THF (30 mL) was added within 10 min. After 30 min of stirring at −78 °C, the reaction was quenched with sat. aq. NH₄Cl (40 mL). The aqueous phase was extracted with Et₂O (3 x...
20 mL) and the combined organic phases were washed with sat. aq. NaCl (40 mL), dried with MgSO₄, filtered and evaporated to give a colorless oil. Purification by flash column chromatography (SiO₂, Hex/EtOAc 20/1 → 15/1 → 10/1) afforded a (1:1.5) diastereoisomeric mixture of lactone 10 as colorless oil (2.0 g, 83%).

**¹H NMR** (CDCl₃, 400 MHz): δ = 7.71–7.63 (m, 3H), 7.41–7.29 (m, 4.6H), 5.20 (t, J = 6.6 Hz, 1H), 5.19 (t, J = 6.6 Hz, 0.5H), 4.81 (d, J = 6.6 Hz, 3H), 4.70–4.62 (m, 0.5H), 4.57–4.48 (m, 1H), 4.02 (dd, J = 10.1, 9.1 Hz, 0.5H), 3.91 (dd, J = 6.4, 4.0 Hz, 1H), 2.79–2.69 (m, 0.5H), 2.41–2.35 (m, 2H), 2.01 (dt, J = 13.3, 10.0 Hz, 0.5H), 1.92 (dd, J = 14.3, 6.3 Hz, 1H), 1.86–1.76 (m, 1.5H), 1.70 (dd, J = 14.4, 5.1 Hz, 1H), 1.35 (s, 1.5H), 1.32 (s, 3H), 0.09 (s, 9H), 0.08 (s, 4.5H).

**¹³C NMR** (CDCl₃, 400 MHz): δ = 206.1, 175.8, 136.0, 135.9, 135.6, 128.7, 127.1, 126.8, 99.6, 99.6, 77.8, 76.6, 76.4, 72.6, 49.2, 48.9, 38.3, 37.0, 27.5, 2.2 (3C).

**HRMS** (ESI) (m/z): calculated for C₁₉H₂₆O₃SeSiNa [M+Na]⁺ 433.0709, found 433.0715.

**IR** (cm⁻¹): ν = 2956, 1956, 1769, 1483, 1251, 1112, 1022, 840, 740.

[α]D²⁰ = −53.5, (CHCl₃, c = 1.0).

**Rf:** (Hex/EtOAc 8/1) 0.27 (major), 0.32 (minor).

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α-D-ribofuranose 17

Available from D-(+)-glucose in six reaction steps.¹

**¹H NMR** (CDCl₃, 400 MHz): δ = 5.82 (d, J = 3.6 Hz, 1H), 4.78 (dd, J = 4.3, 3.8 Hz, 1H), 4.22-4.11 (m, 2H), 3.90-3.85 (m, 2H), 3.59-3.54 (m, 1H), 2.70 (dd, J = 16.5, 8.1 Hz, 1H), 2.48-2.41 (m, 1H), 2.38 (dd, J = 16.5, 5.4Hz, 1H), 2.04 (sbr, 1H), 1.50 (s, 3H), 1.32 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H).

**¹³C NMR** (CDCl₃, 400 MHz): δ = 172.4, 111.9, 104.9, 81.8, 81.5, 61.6, 61.0, 39.8, 30.0, 26.8, 26.5, 14.3.

**HRMS** (ESI) (m/z): calculated for C₁₂H₂₀O₆Na [M+Na]⁺ 283.1158, found 283.1153.

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¹ (a) Rosenthal, A.; Nguyen, L. B. *J. Org. Chem.* 1969, 34, 1029-1034. (b) Xie, M.; Berges, D. A.; Robins, M. *J. Org. Chem.* 1996, 61, 5178-5179 and references cited therein.

SI-7
IR (cm⁻¹): \( \tilde{\nu} = 3474, 2985, 2937, 1731, 1374, 1214, 1167, 1112, 1013, 874 \).

\([\alpha]_D^{25} = +62.9\), (CHCl₃, c = 1.0).

Rᵣ: (Hex/EtOAc 1/1) 0.33.

A solution of \( \alpha \)-D-ribofuranose 17 (9.8 g, 37.7 mmol) in MeOH (370 mL) and trifluoroacetic acid (60 mL) was heated to reflux for 16 h. The resulting pale yellow solution was concentrated in vacuo and the remaining yellow oil was co-evaporated with toluene (3 x 50 mL). Purification by flash column chromatography (SiO₂, Hex/EtOAc 1/1 → 1/2) afforded the desired lactone as pale yellow oil (5.7 g, 81%).

\(^1\)H NMR (CDCl₃, 400 MHz): \( \delta = 5.08\) (s, 1H), 4.89 (d, \( J = 6.8\) Hz, 1H), 4.23 (dd, \( J = 3.8\) Hz, 1H), 3.73 (dd, \( J = 12.2\), 2.9 Hz, 1H), 3.57 (dd, \( J = 12.2\), 4.2 Hz, 1H), 3.46 (s, 3H), 3.22 (m, 1H), 2.86 (dd, \( J = 18.4\), 9.9 Hz, 1H), 2.52 (dd, \( J = 18.4\), 3.9 Hz, 1H), 1.25 (br s, 1H).

\(^{13}\)C NMR (CDCl₃, 400 MHz): \( \delta = 175.5, 107.8, 89.6, 87.7, 64.7, 55.9, 38.1, 34.1 \).

HRMS (ESI) (m/z): calculated for C₈H₁₂O₅Na [M+Na]⁺ 211.0582, found 211.0582.

IR (cm⁻¹): \( \tilde{\nu} = 3412, 2923, 1776, 1454, 1377, 1161, 1106, 1049, 959, 813 \).

\([\alpha]_D^{25} = -40.3\), (CHCl₃, c = 1.0).

Rᵣ: (Hex/EtOAc 1/4) 0.29.

**lactone 18**

To a solution of the primary alcohol (4.1 g, 21.8 mmol) in CH₂Cl₂ (200 mL) was added imidazole (3.6 g, 52.3 mmol) as a solid in one portion under a stream of argon at room temperature. As the solids were dissolved, tert-butyldimethylsilyl chloride (3.9 g, 26.1 mmol) was added as a solid in three portions under an argon stream. After stirring at room temperature for 2 h the resulting pale yellow reaction mixture was quenched by the addition
of water (100 mL). The aqueous layer was separated and extracted with CH$_2$Cl$_2$ (3 x 50 mL). The combined organic phases were washed with water (100 mL) and aq. sat. NaCl (100 mL), dried with MgSO$_4$ and filtered. After evaporation of all volatiles flash column chromatography (SiO$_2$, Hex/EtOAc 3/1) of the residue gave lactone 18 (6.0 g, 91%) as colorless oil.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 5.06 (s, 1H), 4.81 (d, $J$ = 6.4 Hz, 1H), 4.00 (ddd, $J$ = 8.3, 5.1, 4.7 Hz, 1H), 3.74 (dd, $J$ = 9.8, 5.3 Hz, 1H), 3.52 (dd, $J$ = 9.8, 8.3 Hz, 1H), 3.34 (s, 3H), 3.03 (m, 1H), 2.82 (dd, $J$ = 18.1, 9.3 Hz, 1H), 2.48 (dd, $J$ = 18.1, 2.0 Hz, 1H), 0.88 (s, 9H), 0.59 (s, 6H).

$^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ = 175.8, 107.4, 88.1, 87.3, 65.8, 55.0, 40.3, 34.5, 25.9 (3C), 18.3, -5.2, -5.3.

HRMS (ESI) (m/z): calculated for C$_{14}$H$_{26}$O$_5$SiNa [M+Na]$^+$ 325.1447, found 325.1448.

IR (cm$^{-1}$): $\tilde{\nu}$ = 2953.6, 2930.1, 2857.2, 1787.9, 1471.8, 1254.4, 1154.0, 1106.7, 1004.4, 837.7.

$[\alpha]_D^{20}$ = -88.3, (CHCl$_3$, c = 0.6).

R$_f$: (Hex/EtOAc 1/2) 0.73.

diol

To a suspension of freshly powdered lithium aluminium hydride pellets (2.5 g, 66.1 mmol) in anhydrous diethylether (100 mL) at 0 °C was added a solution of lactone 18 (11.7 g, 38.8 mmol) in diethylether (200 mL) within 30 min under vigorous stirring in a 1 L round-bottomed flask. After 1 h sat. aq. NH$_4$Cl (200 mL) was carefully added at 0 °C followed by the addition of sat. aq. Na/K tartrate (200 mL). The resulting turbid biphasic system was stirred for 2 h and allowed to warm to room temperature. The aqueous phase was separated and extracted with diethylether (5 x 100 mL). The combined organic phases were washed with sat. aq. NaCl (200 mL) and dried with MgSO$_4$. After evaporation of all volatiles under reduced pressure the desired diol was isolated as colorless sticky oil (11.9 g, quant.) which was used without further purification in the next reaction.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 4.83 (s, 1H), 4.18 (d, $J$ = 4.6 Hz, 1H), 3.95 (dt, $J$ = 8.6, 5.5 Hz, 1H), 3.84 (m, 1H), 3.74 (dd, $J$ = 10.3, 5.2 Hz, 1H), 3.70 (m, 1H), 3.62 (dd, $J$ = 10.3, 5.8 Hz, 1H),
3.33 (s, 3H), 3.00 (br s, 1H), 2.29 (br s, 1H), 2.19 (m, 1H), 1.92-1.74 (m, 2H), 0.90 (s, 9H), 0.07 (s, 6H).

**13C NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 109.0, 84.3, 77.2, 66.8, 62.0, 54.6, 43.9, 28.9, 26.1 (3C), 18.5, -5.24, -5.26.

**HRMS** (ESI) (m/z): calculated for C<sub>14</sub>H<sub>30</sub>O<sub>5</sub>SiNa [M+Na]<sup>+</sup> 329.1760, found 329.1749.

**IR** (cm<sup>-1</sup>): ν = 3394, 2929, 2857, 1471, 1254, 1103, 1061, 1036, 951, 837.

[α]<sub>D</sub><sup>20</sup> = -28.2, (CHCl<sub>3</sub>, c = 1.1).

**Rf:** (Hex/EtOAc 1/1) 0.19.

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**1-methoxy tetrahydrofuran 19**

To a solution of the crude diol (10.9 g, 35.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (150 mL) was added imidazole (9.7 g, 142.5 mmol) as a solid in one portion under a stream of argon at room temperature. As the solids were dissolved triethylsilyl chloride (13.1 mL, 78.2 mmol) was added within 15 min via syringe through a rubber septum. The resulting pale yellow solution was aged at room temperature for 2 h during which a white precipitate formed. Sat. aq. NH<sub>4</sub>Cl (100 mL) was added and stirring was continued for another 30 min. The aqueous layer was separated and extracted with diethylether (3 x 50 mL). The combined organic phases were washed with water (100 mL), sat. aq. NaCl (100 mL) and dried with MgSO<sub>4</sub>. After removal of all volatiles a pale yellow oil was obtained which yielded tetrahydrofuran 19 (17.3 g, 91%) as colorless oil after flash column chromatography (SiO<sub>2</sub>, Hex/EtOAc 20/1).

**1H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 4.67 (s, 1H), 4.04 (d, J = 4.4 Hz, 1H), 3.93 (ddd, J = 9.3, 5.4, 3.9 Hz, 1H), 3.71 (dd, J = 10.8, 3.8 Hz, 1H), 3.67-3.55 (m, 3H), 3.32 (s, 3H), 2.13 (m, 1H), 1.85 (m, 1H), 1.57 (m, 1H), 0.96 (dt, J = 8.1, 4.3Hz, 18H), 0.91 (s, 9H), 0.61 (m, 12H), 0.07 (s, 6H).

**13C NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 109.3, 84.8, 77.3, 66.3, 61.8, 54.5, 40.2, 28.9, 26.1 (3C), 18.6, 6.9 (6C), 5.1 (3C), 4.6 (3C), -5.2 (2C).

**HRMS** (ESI) (m/z): calculated for C<sub>26</sub>H<sub>58</sub>O<sub>5</sub>Si<sub>3</sub>Na [M+Na]<sup>+</sup> 557.3490, found 557.3477.

**IR** (cm<sup>-1</sup>): ν = 2953, 2877, 1461, 1251, 1102, 1041, 1003, 958, 834, 775.

SI-10
\[ \alpha \]_D^{20} = +6.9, \ (\text{CHCl}_3, \ c = 1.2).

Rf: (Hex/EtOAc 10/1) 0.36.

aldehyde 11

A flame dried 100 mL round-bottomed flask with a rubber septum was charged with CH\_2\_Cl\_2 (20 mL) and oxalyl chloride (2.0 mL, 23.4 mmol) and cooled to -78 °C in a dry ice/acetone cooling bath under argon atmosphere. A bubbler was installed and dimethylsulfoxide (3.4 mL, 48.1 mmol) was added to the above solution within 5 min. After the evolution of gas had ceased the bubbler was removed and stirring was continued for further 10 min at -78 °C. To the resulting reaction mixture was added dropwise tetrahydrofuran 19 (2.5 g, 4.7 mmol) dissolved in CH\_2\_Cl\_2 (20 mL) via syringe within 10 min. The resulting solution was allowed to warm to -50 °C within 4 h. As TLC-analysis indicated full consumption of the starting material and formation of an intermediate (Hex/EtOAc 3/1, Rf = 0.18) the reaction mixture was cooled to -78 °C, followed by the dropwise addition of Et\_3N (6.5 mL, 46.7 mmol). After stirring for 2 h the reaction mixture was quenched by the addition of sat. aq. NaHCO\_3 (20 mL) and was warmed to room temperature. The aqueous layer was separated and extracted with diethylether (3 x 20 mL). The combined organic phases were washed with water (30 mL) and sat. aq. NaCl (30 mL) and dried with MgSO\_4. Removal of the volatiles under reduced pressure and flash column chromatography (SiO\_2, Hex/EtOAc 20/1) of the remaining residue gave aldehyde 11 (1.9 g, 97%) as pale yellow oil.

\[^1\text{H} \text{NMR} \ (\text{CDCl}_3, \ 400 \text{ MHz}) : \ \delta = 9.79 \ (s, \ 1 \text{H}), \ 4.69 \ (s, \ 1 \text{H}), \ 4.22 \ (d, \ J = 4.4 \text{ Hz}, \ 1 \text{H}), \ 3.94 \ (\text{ddd}, \ J = 8.4, \ 5.5, \ 0.7 \text{ Hz}, \ 1 \text{H}), \ 3.74 \ (\text{dd}, \ J = 10.3, \ 4.9 \text{ Hz}, \ 1 \text{H}), \ 3.59 \ (\text{dd}, \ J = 10.3, \ 6.1 \text{ Hz}, \ 1 \text{H}), \ 3.32 \ (s, \ 3 \text{H}), \ 2.79 \ (\text{ddd}, \ J = 17.3, \ 8.6, \ 1.0 \text{ Hz}, \ 1 \text{H}), \ 2.60 \ (m, \ 1 \text{H}), \ 2.56 \ (m, \ 1 \text{H}), \ 0.94 \ (t, \ J = 8.0 \text{ Hz}, \ 9 \text{H}), \ 0.89 \ (s, \ 9 \text{H}), \ 0.58 \ (\text{ddd}, \ J = 17.3, \ 7.5, \ 0.9 \text{ Hz}, \ 6 \text{H}), \ 0.06 \ (s, \ 3 \text{H}), \ 0.06 \ (s, \ 3 \text{H}).

\[^{13}\text{C} \text{NMR} \ (\text{CDCl}_3, \ 400 \text{ MHz}) : \ \delta = 201.2, \ 109.5, \ 83.3, \ 77.1, \ 66.4, \ 54.7, \ 41.0, \ 39.4, \ 26.1 (3 \text{C}), \ 18.5, \ 6.9 (3 \text{C}), \ 4.9 (3 \text{C}), \ -5.3 (2 \text{C}).

HRMS (ESI) (m/z): calculated for C\_20H\_42O\_5Si\_2Na [M+Na]^+ 441.2468, found 441.2476.
IR (cm⁻¹): ν = 2955, 2929, 2879, 1728, 1462, 1254, 1127, 1108, 1039, 837.

[α]D²⁰ = +1.4, (CHCl₃, c = 1.2).

Rf: (Hex/EtOAc 8/1) 0.68.

butenolide 20 and 21

To a solution of butyrolactone 10 (267 mg, 0.6 mmol) in THF (3 mL) was added LiHMDS (720 µL, 1.0 M in toluene, 0.72 mmol) at -40 °C within 5 min. After 30 min of stirring at that temperature a solution of aldehyde 11 (250 mg, 0.7 mmol) in THF (3 mL) was dropwise added within 10 min. After 2 h at -40 °C the reaction mixture was quenched by the addition of sat. aq. NH₄Cl (10 mL) and CH₂Cl₂ (10 mL). The aqueous phase was separated and extracted with CH₂Cl₂ (3 x 10 mL). The combined organic phases were washed with water (10 mL) and sat. aq. NaCl (10 mL), dried with MgSO₄, filtered and concentrated under reduced pressure. NMR analysis of the crude pale yellow oil indicated consumption of butyrolactone 10 and showed a complex mixture of four diastereomers (480 mg, 0.58 mmol, Hex/EtOAc 4/1, Rf = 0.55).

The complex mixture was digested in a mixture of CH₂Cl₂ (6 mL) and pyridine (0.6 mL) in a round-bottomed flask equipped with a stirring bar and cooled to 0 °C. Under vigorous stirring H₂O₂ (0.4 mL, 3.5 mmol) was added and the resulting biphasic mixture was aged at this temperature for 1 h. The reaction was quenched by the addition of sat. aq. Na₂S₂O₃ (8 mL) and stirring was continued for additional 30 min. The aqueous phase was separated and extracted with CH₂Cl₂ (3 x 10 mL). After the combined organic phases have been washed with water (10 mL) and sat. aq. NaCl (10 mL) MgSO₄ was added followed by filtration. Evaporation of the volatiles and flash column chromatography (SiO₂, Hex/EtOAc 20/1) of the remaining oil yielded the desired butenolides 20 and 21 as an inseparable 1:1 mixture (384 mg, 0.6 mmol) as pale yellow oil.

¹H NMR (CDCl₃, 400 MHz):
Diastereomer 1  δ = 7.30 (t, J = 1.5 Hz, 1H), 5.26 (t, J = 6.7 Hz, 1H), 5.21 (m, 1H), 4.84 (d, J = 6.5 Hz, 1H), 4.69 (s, 1H), 4.49 (m, 1H), 4.16 (d, J = 4.6 Hz, 1H), 4.12 (d, J = 7.1 Hz, 1H), 4.06 (dt, J = 8.7, 5.3 Hz, 1H), 3.77 (t, J = 4.7 Hz, 1H), 3.68 (m, 1H), 3.67 (m, 1H), 3.31 (s, 3H), 2.39 (m, 1H), 1.98-1.90 (m, 2H), 1.81 (dd, J = 14.3, 7.3 Hz, 1H), 1.65 (m, 1H), 1.47 (s, 3H), 0.95 (t, J = 7.9 Hz, 9H), 0.91 (s, 9H), 0.73 (q, J = 7.7 Hz, 6H), 0.14 (s, 9H), 0.1 (br s, 6H).

Diastereomer 2  δ = 7.31 (t, J = 1.4 Hz, 1H), 5.26 (t, J = 6.7 Hz, 1H), 5.21 (m, 1H), 4.85 (d, J = 6.7 Hz, 1H), 4.67 (s, 1H), 4.49 (m, 1H), 4.13 (d, J = 12.6 Hz, 1H), 4.10 (d, J = 4.4 Hz, 1H), 4.00 (dt, J = 9.0, 4.8 Hz, 1H), 3.79 (t, J = 4.8 Hz, 1H), 3.69 (m, 1H), 3.40 (d, J = 5.2 Hz, 1H), 3.31 (s, 3H), 2.33 (m, 1H), 2.20 (dd, J = 7.9, 2.6 Hz, 1H), 2.17 (dd, J = 7.9 Hz, 2.5 Hz, 1H), 1.94 (m, 1H), 1.79 (dd, J = 14.3, 7.2 Hz, 1H), 1.47 (s, 3H), 0.96 (t, J = 7.9 Hz, 9H), 0.90 (s, 9H), 0.63 (q, J = 7.8 Hz, 6H), 0.14 (s, 9H), 0.1 (br s, 6H).

13C NMR (CDCl3, 400 MHz):

Diastereomer 1  δ = 172.7, 150.1, 136.0, 109.0, 99.7, 83.9, 79.0, 78.6, 78.2, 78.0, 72.8, 66.7, 66.2, 54.7, 47.1, 41.7, 32.1, 27.8, 26.1 (3C), 18.6, 6.9 (3C), 5.0 (3C), 2.4 (3C), -5.3 (2C).

Diastereomer 2  δ = 172.8, 150.2, 135.9, 109.2, 99.7, 83.9, 78.9, 78.6, 78.2, 78.0, 72.8, 66.5, 66.1, 54.8, 47.2, 41.1, 32.3, 27.8, 26.1 (3C), 18.6, 6.9 (3C), 5.0 (3C), 2.4 (3C), -5.3 (2C).

HRMS (ESI) (m/z): calculated for C33H62O8Si3Na [M+Na]+ 693.3650, found 693.3650.

Rf: (Hex/EtOAc 3/1) 0.57.

cage-shaped lactones 22 and 23 (+ 24 and 25)

A mixture of butenolides 20 and 21 (dr = 1:1, 490 mg, 0.7 mmol) was dissolved in freshly degassed cyclohexane (four pump-freeze-thaw cycles, 80 mL). The resulting solution was split in 8 equal parts which were transferred to quartz tubes of a diameter of 1 cm and a total height of 18 cm which were equipped with a magnetic stirring bar. Each of the charged quartz vials was placed 0.5 cm in front of a UV-C lamp (SYLVANIA G8W T5, 8W) in a home-made reactor and irradiated for 2 h while stirring. The contents of all vials were combined
and the volatiles were removed under reduced pressure. The remaining slightly yellow oil was subjected to flash column chromatography (SiO₂, Hex/EtOAc 20/1) yielding undesired [4.2.0]ring systems 24 and 25 (76 mg, 15% combined yield) as well as the desired caged [2+2]-photocyclization products 22 (170 mg, 35%) and 23 (169 mg, 34%) as colorless oils.

analytical data for 22

1H NMR (CDCl₃, 400 MHz): δ = 5.40 (dd, J = 2.7, 1.2 Hz, 1H), 5.20 (dd, J = 2.1, 1.1 Hz, 1H), 5.16 (td, J = 7.9, 5.2 Hz, 1H), 4.69 (s, 1H), 4.14 (d, J = 4.5 Hz, 1H), 4.02 (dt, J = 9.0, 5.5 Hz, 1H), 3.98 (dt, J = 9.7, 2.9 Hz, 1H), 3.75 (dd, J = 10.4, 5.3 Hz, 1H), 3.71 (d, J = 2.2 Hz, 1H), 3.66 (dd, J = 10.4, 5.7 Hz, 1H), 3.33-3.29 (m, 4H), 3.13 (m, 1H), 2.45 (qd, J = 12.4, 1.7 Hz, 1H), 2.40 (m, 1H), 1.94 (dd, J = 14.7, 5.3 Hz, 1H), 1.79-1.67 (m, 2H), 1.43 (s, 3H), 0.96 (t, J = 7.9 Hz, 9H), 0.91 (s, 9H), 0.62 (q, J = 8.2 Hz, 6H), 0.11 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H).

13C NMR (CDCl₃, 400 MHz): δ = 177.7, 144.0, 115.1, 109.0, 84.9, 84.1, 83.7, 77.5, 70.4, 67.0, 57.8, 57.7, 54.6, 49.6, 44.8, 41.4, 27.9, 26.2 (3C), 23.4, 18.6, 7.0 (3C), 5.1 (3C), 2.4 (3C), -5.2, -5.3.

HRMS (ESI) (m/z): calculated for C₃₃H₆₂O₈Si₃Na [M+Na]+ 693.3650, found 693.3629.

IR (cm⁻¹): ν ≈ 3500, 2954, 1767, 1462, 1375, 1301, 1251, 1186, 1104, 988.

[α]D²⁰ = -38.7, (CHCl₃, c = 1.1).

Rf: (Hex/EtOAc 4/1) 0.45.

analytical data for 23

1H NMR (CDCl₃, 400 MHz): δ = 5.27 (dd, J = 2.7, 1.4 Hz, 1H), 5.19 (td, J = 8.0, 5.3 Hz, 1H), 5.15 (dd, J = 2.0, 1.5 Hz, 1H), 4.66 (s, 1H), 4.17 (d, J = 4.8 Hz, 1H), 4.12 (ddd, J = 11.7, 5.7, 2.2 Hz, 1H), 3.96 (ddd, J = 8.1, 5.9, 4.7 Hz, 1H), 3.79 (dd, J = 10.5, 4.6 Hz, 1H), 3.66 (dd, J = 10.6, 6.1 Hz 1H), 3.43 (dd, J = 8.2, 6.3 Hz, 1H), 3.31 (s, 3H), 3.11 (m, 1H), 3.05 (d, J = 5.7 Hz, 1H), 2.45 (qd, J = 12.4, 1.6 Hz, 1H), 2.41 (m, 1H), 1.93 (dd, J = 14.8, 5.3 Hz, 1H), 1.87 (ddd, J = 14.1, 8.7, 2.3 Hz, 1H), 1.67 (ddd, J = 14.0, 11.7, 5.7 Hz, 1H), 1.42 (s, 3H), 0.97 (t, J = 7.9 Hz, 9H), 0.91 (s, 9H), 0.63 (q, J = 8.2 Hz, 6H), 0.12 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H).

13C NMR (CDCl₃, 400 MHz): δ = 176.8, 145.4, 114.5, 109.2, 85.0, 84.0, 83.6, 79.1, 70.2, 67.1, 59.6, 57.7, 54.7, 49.8, 43.5, 41.6, 28.9, 26.2 (3C), 23.6, 18.7, 6.9 (3C), 5.1 (3C), 2.4 (3C), -5.3 (2C).

HRMS (ESI) (m/z): calculated for C₃₃H₆₂O₈Si₃Na [M+Na]+ 693.3650, found 693.3647.
IR (cm$^{-1}$): $\tilde{\nu} = 3484, 2954, 1768, 1462, 1348, 1251, 1187, 1106, 1040, 991.$

$[\alpha]_D^{20} = -26.7$, (CHCl$_3$, C = 0.6).

$R_F$: (Hex/EtOAc 4/1) 0.39.

**analytical data for 24**

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 5.75$ (m, 1H), 4.75 (dt, $J = 8.7$, 1.8 Hz, 1H), 4.66 (s, 1H), 4.13 (m, 1H), 4.09 (d, $J = 4.9$ Hz, 1H), 3.91 (m, 2H), 3.84 (dd, $J = 10.1$, 4.5 Hz, 1H), 3.61 (dd, $J = 10.1$, 7.2 Hz, 1H), 3.50 (m, 1H), 3.29 (s, 3H), 3.26 (m, 1H), 2.74 (dd, $J = 13.4$, 1.1 Hz, 1H), 2.31 (m, 2H), 2.53 (dd, $J = 15.4$, 5.9 Hz, 1H), 1.95 (dd, $J = 15.4$, 1.8 Hz, 1H), 1.77 (dd, $J = 6.0$, 4.1 Hz, 2H), 1.36 (s, 3H), 0.96 (t, $J = 7.9$ Hz, 9H), 0.91 (s, 9H), 0.62 (q, $J = 7.7$ Hz, 6H), 0.10 (s, 6H), 0.06 (s, 9H).

$^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta = 179.1, 137.9, 127.9, 108.8, 83.1, 78.3, 76.6, 71.1, 70.1, 67.0, 55.6, 54.5, 47.9, 44.8, 42.8, 38.8, 31.2, 29.2, 25.9 (3C), 18.4, 6.7 (3C), 4.8 (3C), 2.2 (3C), -5.5 (2C).

HRMS (ESI) (m/z): calculated for C$_{33}$H$_{62}$O$_8$Si$_3$Na [M+Na]$^+$ 693.3650, found 693.3650.

IR (cm$^{-1}$): $\tilde{\nu} = 3476, 2955, 2930, 1768, 1462, 1251, 1111, 1042, 1005, 839.$

$[\alpha]_D^{20} = -44.1$, (CHCl$_3$, c = 2.0).

$R_F$: (Hex/EtOAc 4/1) 0.28.

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**epoxide**

A round-bottomed flask was charged with alcohol 22 (10 mg, 0.07 mmol) and a magnetic stirring bar and cooled to 0 °C. A freshly prepared solution of DMDO (0.4 mL, 0.08 M, 0.03 mmol) was added and the resulting colorless reaction mixture was allowed to warm to room temperature overnight. Additional DMDO (0.4 mL, 0.08 M, 0.03 mmol) was added and the reaction was aged at room temperature for 24 h. As TLC-analysis (Hex/EtOAc 4/1) still indicated remaining starting material DMDO (0.4 mL, 0.08 M, 0.03 mmol) was added again and the reaction was stirred for additional 24 h. The volatiles were removed under reduced pressure in a cold water bath (15 °C). The resulting colorless residue was purified by flash...
column chromatography (SiO2, Hex/EtOAc 12/1) yielding the desired epoxide (9 mg, 85%) as colorless oil.

$^1$H NMR (CDCl3, 400 MHz): $\delta = 5.19$ (m, 1H), 4.68 (s, 1H), 4.11 (d, $J = 4.5$ Hz, 1H), 4.03 (dt, $J = 8.6$, 5.4 Hz, 1H), 3.95 (t, $J = 6.6$ Hz, 1H), 3.76 (dd, $J = 10.3$, 5.2 Hz, 1H), 3.67 (dd, $J = 10.3$, 5.7 Hz, 1H), 3.56 (t, $J = 7.7$ Hz, 1H), 3.31 (s, 3H), 3.25 (sbr, OH), 3.07 (dd, $J = 7.3$, 1.8 Hz, 1H), 2.97 (d, $J = 4.4$ Hz, 1H), 2.78 (d, $J = 4.4$ Hz, 1H), 2.57 (ddd, $J = 14.7$, 7.5, 1.9 Hz, 1H), 2.37 (m, 1H), 1.93 (dd, $J = 14.7$, 5.1 Hz, 1H), 1.66 (t, $J = 6.7$ Hz, 2H), 1.32 (s, 3H), 0.95 (t, $J = 8.0$ Hz, 9H), 0.92 (s, 9H), 0.63 (q, $J = 7.8$ Hz, 6H), 0.10 (m, 15H).

$^{13}$C NMR (CDCl3, 400 MHz): $\delta = 176.2$, 109.1, 83.9, 83.5, 82.9, 77.6, 67.5, 67.0, 62.9, 58.0, 56.9, 54.6, 50.7, 47.7, 42.1, 41.7, 27.9, 26.2 (3C), 23.4, 18.9, 6.9 (3C), 5.0 (3C), 2.4 (3C), -5.2, -5.3.

HRMS (ESI) (m/z): calculated for C$_{33}$H$_{62}$O$_9$Si$_3$Na [M+Na]$^+$ 709.3555, found 709.3598.

IR (cm$^{-1}$): $\tilde{\nu} = 2955$, 2930, 1768, 1462, 1376, 1252, 1143, 1040, 991, 840.

$[\alpha]_D^{20}$ = -32.0, (CHCl$_3$, c = 1.0).

R$_f$: (Hex/EtOAc 4/1) 0.53.

epoxide 26

The epoxide (21 mg, 0.03 mmol) was dissolved in CH$_2$Cl$_2$ (0.5 mL) and cooled to 0 °C. Pyridine (7 µL, 0.09 mmol), acetic anhydride (6 µL, 0.06 mmol) and DMAP (1 mg, 0.01 mmol) were sequentially added to the reaction mixture. The round-bottomed flask was sealed with a stopper and the reaction mixture was allowed to warm to room temperature overnight. Diethyl ether (5 mL) and sat. aq. NH$_4$Cl (5 mL) were added. The aqueous phase was separated and extracted with diethyl ether (3 x 5 mL). The combined organic phases were washed with sat. aq. CuSO$_4$ (10 mL), water (10 mL) and sat. aq. NaCl (10 mL), dried with MgSO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (SiO$_2$, Hex/EtOAc 12/1) of the residue gave the desired acylated epoxide 26 (22 mg, quant.) as needle-shaped crystals which were subjected to X-ray analysis.
\(^1\)H NMR (CDCl\(_3\), 600 MHz): \(\delta = 5.31\) (dd, \(J = 11.1, 3.2\) Hz, 1H), 5.19 (dt, \(J = 7.9, 5.3\) Hz, 1H), 4.65 (s, 1H), 4.23 (d, \(J = 4.2\) Hz, 1H), 3.83 (dt, \(J = 9.4, 5.1\) Hz, 1H), 3.71 (dd, \(J = 10.3, 4.9\) Hz, 1H), 3.57 (dd, \(J = 10.3, 5.8\) Hz, 1H), 3.54 (dd, \(J = 8.7, 7.4\) Hz, 1H), 3.27 (s, 3H), 3.02 (dd, \(J = 7.1, 1.8\) Hz, 1H), 2.88 (d, \(J = 4.6\) Hz, 1H), 2.70 (d, \(J = 4.6\) Hz, 1H), 2.58 (dq, \(J = 2.5, 2.0\) Hz, 1H), 2.14 (s, 3H), 2.00 (m, 1H), 1.91 (dd, \(J = 14.7, 5.3\) Hz, 1H), 1.84-1.75 (m, 2H), 1.31 (s, 3H), 0.97 (t, \(J = 8.0\)Hz, 9H), 0.92 (s, 9H), 0.69 (q, \(J = 8\) Hz, 6H), 0.12 (s, 9H), 0.08 (s, 6H).

\(^{13}\)C NMR (CDCl\(_3\), 600 MHz): \(\delta = 174.9, 170.3, 109.5, 83.5, 83.4, 82.6, 76.4, 68.2, 66.3, 62.2, 57.9, 55.8, 54.6, 50.2, 47.0, 42.4, 40.7, 26.1\) (3C), 25.7, 23.1, 21.3, 18.5, 7.0 (3C), 4.9 (3C), 2.4 (3C), -5.3 (2C).

HRMS (ESI) (m/z): calculated for C\(_{35}\)H\(_{64}\)O\(_{10}\)Si\(_{3}\)Na [M+Na]\(^+\) 751.3705, found 751.3704.

mp = 93 - 95 °C.

IR (cm\(^{-1}\)): \(\nu = 2955, 2928, 1768, 1744, 1231, 1124, 1041, 991, 843, 776\).

[\(\alpha\)]\(_D\)\(^{20}\) = -23.1, (CHCl\(_3\), c = 0.4).

Rf: (Hex/EtOAc 4/1) 0.53.

X-ray see cif-file

acetate intermediate

Alcohol 22 (250 mg, 0.37 mmol) was dissolved in CH\(_2\)Cl\(_2\) (4.0 mL) and cooled to 0 °C. Pyridine (90 \(\mu\)L, 1.12 mmol), acetic anhydride (70 \(\mu\)L, 0.70 mmol) and DMAP (5 mg, 0.04 mmol) were sequentially added to the reaction mixture. The round-bottomed flask was sealed with a stopper and the reaction mixture was allowed to warm to room temperature overnight. Diethylether (20 mL) and sat. aq. NH\(_4\)Cl (20 mL) were added. The aqueous phase was separated and extracted with diethylether (3 x 20 mL). The combined organic phases were washed with sat. aq. CuSO\(_4\) (20 mL), water (20 mL) and sat. aq. NaCl (20 mL), dried with MgSO\(_4\), filtered and concentrated under reduced pressure. The desired acetylated product (266 mg, quant.) was isolated as a colorless amorphous solid and was used in the next reaction without further purification.
**1H NMR** (CDCl₃, 400 MHz): δ = 5.48 (dd, J = 11.0, 3.1 Hz, 1H), 5.34 (dd, J = 2.6, 1.6 Hz, 1H), 5.20 (dd, J = 2.2, 1.6 Hz, 1H), 5.13 (dt, J = 8.0, 5.3 Hz, 1H), 4.66 (s, 1H), 4.14 (d, J = 4.1 Hz, 1H), 3.87 (dt, J = 9.1, 5.1 Hz, 1H), 3.69 (dd, J = 10.4, 4.8 Hz, 1H), 3.60 (dd, J = 10.4, 5.4 Hz, 1H), 3.40 (dd, J = 8.2, 6.5 Hz, 1H), 3.27 (s, 3H), 3.13 (m, 1H), 2.47 (dd, J = 14.8, 7.7, 1.7 Hz, 1H), 2.08 (s, 3H), 2.01-1.88 (m, 4H), 1.41 (s, 3H), 0.99 (t, J = 7.9 Hz, 9H), 0.92 (s, 9H), 0.69 (q, J = 7.8 Hz, 6H), 0.12 (s, 9H), 0.08 (s, 6H).

**13C NMR** (CDCl₃, 400 MHz): δ = 174.2, 170.7, 144.1, 115.8, 109.4, 84.8, 83.7, 82.9, 76.5, 71.0, 66.1, 57.6, 57.2, 54.6, 49.6, 44.7, 40.5, 26.1 (3C), 25.5, 23.6, 21.0, 18.5, 7.0 (3C), 5.0 (3C), 2.4 (3C), -5.3 (2C).

**HRMS** (ESI) (m/z): calculated for C₃₅H₆₄O₉Si₃Na [M+Na]^+ 735.3756, found 735.3769.

**IR** (cm⁻¹): ν = 2954, 1772, 1747, 1462, 1372, 1251, 1150, 1040, 991, 840.

[α]₀²⁰ = -15.8, (CHCl₃, c = 0.7).

**Rf**: (Hex/EtOAc 5/1) 0.52.

**acetate 27**

The acylated substrate was digested in an AcOH/THF/H₂O = 2/1/1 mixture (2.8 mL) and stirred at room temperature for 24 h. The resulting pale yellow solution was concentrated under reduced pressure and subsequently coevaporated with toluene (3 x 20 mL) till the smell of acetic acid was gone.

To the resulting crude colorless amorphous solid (144 mg) was added CH₂Cl₂ (4.0 mL) at room temperature. Under vigorous stirring imidazole (600 mg, 8.75 mmol) was added and the mixture was stirred till all solids were dissolved. Chlorotriethylsilane (650 µL, 3.85 mmol) was added to the resulting pale yellow solution within 5 min. After 16 h of stirring at room temperature diethylether (20 mL) and sat. aq. NH₄Cl (20 mL) were added to the resulting suspension. The aqueous layer was separated and extracted with diethylether (3 x 20 mL). The combined organic phases were washed with water (20 mL) and sat. aq. NaCl (20 mL)
before being dried with MgSO₄. The solids were removed by filtration and the filtrate was concentrated under reduced pressure. Flash column chromatography (SiO₂, Hex/EtOAc 10/1) gave desired globally TES-protected acetate 27 (265 mg, 94%) as colorless oil.

\[ ^1H \text{ NMR} (\text{CDCl}_3, 400 \text{ MHz}): \delta = 5.48 (dd, J = 10.2, 3.6 \text{ Hz, 1H}), 5.34 (dd, J = 2.6, 1.6 \text{ Hz, 1H}), 5.19 (dd, J = 2.1, 1.6 \text{ Hz, 1H}), 5.14 (dt, J = 8.0, 5.3 \text{ Hz, 1H}), 4.64 (s, 1H), 4.14 (d, J = 3.8 \text{ Hz, 1H}), 3.89 (dt, J = 8.6, 5.2 \text{ Hz, 1H}), 3.69 (dd, J = 10.3, 5.2 \text{ Hz, 1H}), 3.60 (dd, J = 10.3, 5.4 \text{ Hz, 1H}), 3.39 (dd, J = 8.2, 6.5 \text{ Hz, 1H}), 3.28 (s, 3H), 3.09 (m, 1H), 2.44 (ddd, J = 14.7, 7.8, 1.6 \text{ Hz, 1H}), 2.08 (s, 3H), 1.97-1.87 (m, 4H), 1.41 (s, 3H), 1.01-0.90 (m, 27H), 0.69 (q, J = 8.0 \text{ Hz, 6H}), 0.65-0.55 (m, 12H). \]

\[ ^{13}C \text{ NMR} (\text{CDCl}_3, 400 \text{ MHz}): \delta = 174.3, 170.6, 144.3, 115.7, 109.4, 84.4, 83.7, 83.0, 76.5, 71.0, 66.1, 57.8, 57.2, 54.6, 49.7, 44.8, 40.8, 25.5, 23.4, 21.0, 7.1 (3C), 7.0 (3C), 6.9 (3C), 6.6 (3C), 5.1 (3C), 4.5 (3C). \]

HRMS (ESI) (m/z): calculated for C_{38}H_{70}O_{9}Si_{3}Na [M+Na]^+ 777.4225, found 777.4195.

IR (cm⁻¹): \( \tilde{\nu} = 2954, 2877, 1772, 1371, 1230, 1150, 1040, 991, 807, 743. \)

\( [\alpha]_D^{22} = -17.8 \), (CHCl₃, c = 0.7).

\( R_f: (\text{Hex/EtOAc 3/1}) 0.59. \)

acetate 28

Alcohol 23 (284 mg, 0.42 mmol) was subjected to the identical procedure as alcohol 22 (see above) giving the corresponding globally TES-protected acetate 28 (278 mg, 87%) as a colorless oil.

analytical data for the intermediate:

\[ ^1H \text{ NMR} (\text{CDCl}_3, 400 \text{ MHz}): \delta = 5.48 (dd, J = 11.1, 2.4 \text{ Hz, 1H}), 5.32 (dd, J = 2.7, 1.6 \text{ Hz, 1H}), 5.22 (dd, J = 2.1, 1.7 \text{ Hz, 1H}), 5.18 (dt, J = 8.1, 5.4 \text{ Hz, 1H}), 4.67 (s, 1H), 3.96 (d, J = 4.5 \text{ Hz, 1H}), 3.91 (m, 1H), 3.73 (dd, J = 10.9, 3.7 \text{ Hz, 1H}), 3.62 (dd, J = 10.9, 6.0 \text{ Hz, 1H}), 3.42 (dd, J = 8.3, 6.4 \text{ Hz, 1H}), 3.30 (s, 3H), 3.15 (m, 1H), 2.47 (ddd, J = 14.7, 7.8, 1.7 \text{ Hz, 1H}), 2.11 (dd, J = 14.2, 10.2 Hz, 1H). \]
6.0 Hz, 1H), 2.07 (m, 1H), 2.03 (s, 3H), 1.92 (dd, J = 14.7, 5.4 Hz, 1H), 1.84 (m, 1H), 1.42 (s, 3H), 0.98 (t, J = 7.9 Hz, 9H), 0.91 (s, 9H), 0.63 (q, J = 8.13 Hz, 6H), 0.11 (s, 9H), 0.08 (s, 6H).

$^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ = 174.7, 170.1, 144.4, 115.6, 109.2, 85.1, 84.9, 83.1, 77.9, 71.9, 66.8, 58.1, 58.0, 54.8, 49.4, 44.2, 40.9, 26.2 (3C), 26.1, 23.4, 21.2, 18.6, 6.9 (3C), 5.1 (3C), 2.4 (3C), -5.1, -5.2.

HRMS (ESI) (m/z): calculated for C$_{35}$H$_{64}$O$_9$Si$_3$Na [M+Na]$^+$ 735.3756, found 735.3759.

IR (cm$^{-1}$): $\tilde{\nu}$ = 2954, 2878, 1774, 1748, 1461, 1372, 1250, 1149, 1040, 991.

$[\alpha]_D^{20}$ = -46.6, (CHCl$_3$, c = 1.5).

R$_f$: (Hex/EtOAc 5/1) 0.48.

**analytical data for acetate 28:**

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 5.49 (dd, J = 11.2, 2.2 Hz, 1H), 5.32 (dd, J = 2.6, 1.6 Hz, 1H), 5.22 (dd, J = 2.1, 1.6 Hz, 1H), 5.19 (dt, J = 8.1, 5.4 Hz, 1H), 4.67 (s, 1H), 3.95 (d, J = 4.4 Hz, 1H), 3.93 (m, 1H), 3.73 (dd, J = 10.8, 3.7 Hz, 1H), 3.60 (dd, J = 10.8, 6.4 Hz, 1H), 3.42 (dd, J = 8.2, 6.4 Hz, 1H), 3.30 (s, 3H), 3.12 (m, 1H), 2.45 (dd, J = 14.7, 7.9, 1.6 Hz, 1H), 2.09 (m, 1H), 2.03 (s, 3H), 2.02 (m, 1H), 1.92 (dd, J = 14.7, 5.4 Hz, 1H), 1.85 (dd, J = 14.4, 5.4, 2.4 Hz, 1H), 1.42 (s, 3H), 0.98 (t, J = 7.9 Hz, 9H), 0.97 (t, J = 7.8 Hz, 9H), 0.94 (t, J = 7.9 Hz, 9H), 0.63 (q, J = 7.9 Hz, 12 H), 0.58 (q, J = 7.9 Hz, 6H).

$^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ = 174.7, 170.1, 144.5, 115.5, 109.2, 85.2, 84.6, 83.2, 76.9, 72.0, 66.6, 58.19, 58.16, 54.7, 49.5, 44.2, 41.1, 26.1, 23.3, 21.2, 7.1 (3C), 6.9 (3C), 6.9 (3C), 6.6 (3C), 6.1 (3C), 4.5 (3C).

HRMS (ESI) (m/z): calculated for C$_{38}$H$_{70}$O$_9$Si$_3$Na [M+Na]$^+$ 777.4225, found 777.4232.

IR (cm$^{-1}$): $\tilde{\nu}$ = 2955, 2877, 1775, 1749, 1229, 1150, 1108, 1077, 1042, 1001.

$[\alpha]_D^{23}$ = -45.9, (CHCl$_3$, c = 0.7).

R$_f$: (Hex/EtOAc 3/1) 0.52.

![aldehyde](image-url)
A flame dried 50 mL round-bottomed flask with a rubber septum was charged with CH₂Cl₂ (8 mL) and oxalyl chloride (660 µL, 7.7 mmol) and cooled to -78 °C in a dry ice/acetone cooling bath under argon atmosphere. A bubbler was installed and dimethylsulfoxide (1.1 mL, 15.5 mmol) was added to above solution within 5 min. After the evolution of gas had ceased the bubbler was removed and stirring was continued for further 10 min at -78 °C. To the resulting reaction mixture was dropwise added acetate 27 (1.16 g, 1.5 mmol) dissolved in CH₂Cl₂ (8 mL) via syringe within 10 min. The resulting solution was stirred at -78 °C for 3 h whereupon an intermediate formed (TLC, Hex/EtOAc 2/1, Rf = 0.23). Et₃N (2.2 mL, 15.5 mmol) was dropwise added to the reaction mixture. After stirring for 4 h the turbid solution was quenched by the addition of sat. aq. NaHCO₃ (15 mL) and warmed to room temperature. The aqueous layer was separated and extracted with diethylether (3 x 15 mL). The combined organic phases were washed with water (20 mL) and sat. aq. NaCl (20 mL) and dried with MgSO₄. Removal of the volatiles under reduced pressure and flash column chromatography (SiO₂, Hex/EtOAc 8/1) of the remaining residue gave the corresponding aldehyde (666 mg, 67%, 89% brsm) as pale yellow oil.

**¹H NMR** (CDCl₃, 400 MHz): δ = 9.57 (d, J =3.1 Hz, 1H), 5.50 (dd, J = 11.6, 2.4 Hz, 1H), 5.31 (dd, J = 2.7, 1.7 Hz, 1H), 5.19 (dd, J = 3.8, 2.0 Hz, 1H), 5.17 (dt, J = 7.9, 5.4 Hz, 1H), 4.81 (s, 1H), 4.21 (d, J =4.2 Hz, 1H), 4.05 (dd, J = 9.7, 3.0 Hz, 1H), 3.43 (dd, J = 8.2, 6.4 Hz, 1H), 3.39 (s, 3H), 3.08 (m, 1H), 2.45 (ddd, J =14.7, 7.8, 1.7 Hz, 1H), 2.17 (m, 1H), 2.07 (s, 3H), 1.98-1.79 (m, 3H), 1.41 (s, 3H), 1.00 (t, J = 7.9 Hz, 9H), 0.94 (t, J = 7.9 Hz, 9H), 0.71 (q, J = 7.8Hz, 6H), 0.58 (q, J = 7.9Hz, 6H).

**¹³C NMR** (CDCl₃, 400 MHz): δ = 202.4, 174.2, 170.7, 144.3, 115.6, 110.6, 86.5, 84.4, 83.2, 75.7, 70.6, 58.0, 57.4, 55.2, 49.7, 44.5, 40.4, 25.2, 23.5, 21.0, 7.1 (3C), 6.9 (3C), 6.6 (3C), 5.0 (3C).

**HRMS** (ESI) (m/z): calculated for C₃₃H₅₃O₁₀Si₂Na [M+MeOH+Na]^+ 693.3466, found 693.3467.

**IR** (cm⁻¹): ν = 2955, 2877, 1770, 1745, 1459, 1373, 1231, 1151, 1038, 808.

**[α]D²⁰ = -39.3, (CHCl₃, c = 0.6).**

**Rf**: (Hex/EtOAc 2/1) 0.50.
To a solution of the aldehyde (207 mg, 0.3 mmol) in CH$_2$Cl$_2$ (3.5 mL) was added NaHCO$_3$ (82 mg, 0.1 mmol) at 0 °C. mCPBA (111 mg, 0.7 mmol), which was purified by extraction of a solution in diethylether with pH 7.5 buffer, was added as a solid in one portion to the vigorously stirred suspension. The resulting heterogeneous mixture was stirred at 0 °C for 2 h after which dimethyl sulfide (300 µL, 4 mmol) was added. After additional 30 min diethylether (10 mL) and sat. aq. NH$_4$Cl (10 mL) were added. The aqueous phase was separated and extracted with diethylether (3 x 10 mL). The combined organic extracts were washed with sat. aq. NaHCO$_3$ (15 mL), water (15 mL) and sat. aq. NaCl (15 mL). After drying with MgSO$_4$ and filtration of the solids the volatiles were removed under reduced pressure. Purification of the remaining residue by flash column chromatography (SiO$_2$, Hex/EtOAc 8/1) gave desired formate 29 (169 mg, 79%) as colorless oil.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 8.11 (s, 1H), 6.14 (d, $J = 4.6$ Hz, 1H), 5.49 (dd, $J = 10.5$, 3.1 Hz, 1H), 5.33 (dd, $J = 2.6$, 1.8 Hz, 1H), 5.21 (dd, $J = 2.1$, 1.8 Hz, 1H), 5.17 (dt, $J = 8.0$, 5.4 Hz, 1H), 4.79 (s, 1H), 4.26 (dd, $J = 5.0$, 0.3 Hz, 1H), 3.40 (dd, $J = 8.2$, 6.4 Hz, 1H), 3.35 (s, 3H), 3.10 (m, 1H), 2.45 (dd, $J = 14.7$, 7.8, 1.7 Hz, 1H), 2.36 (m, 1H), 2.08 (s, 3H), 2.04-1.94 (m, 2H), 1.90 (dd, $J = 14.6$, 5.3 Hz, 1H), 1.41 (s, 3H), 0.98 (t, $J = 7.9$ Hz, 9H), 0.94 (t, $J = 7.9$ Hz, 9H), 0.67 (q, $J = 7.9$ Hz, 6H), 0.58 (q, $J = 7.9$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ = 174.3, 170.7, 160.7, 144.1, 115.9, 110.9, 102.4, 84.5, 83.2, 76.2, 71.2, 57.8, 57.4, 55.6, 49.6, 44.9, 44.7, 25.0, 23.4, 21.1, 7.1 (3C), 6.9 (3C), 6.6 (3C), 4.9 (3C).

HRMS (ESI) (m/z): calculated for C$_{33}$H$_{54}$O$_{10}$Si$_2$Na [M+Na]$^+$ 677.3153, found 677.3136.

IR (cm$^{-1}$): $\tilde{\nu}$ = 2955, 2877, 1769, 1740, 1227, 1152, 1111, 1039, 1017, 990.

$[\alpha]_D^{25}$ = -9.3, (CHCl$_3$, c = 0.8).

$R_f$: (Hex/EtOAc 3/1) 0.55.
Formate 30

Acetate 28 (284 mg, 0.42 mmol) was subjected to the identical two step procedure as acetate 27 (see above) giving the corresponding formate 30 (278 mg, 87%) as colorless oil.

Analytical data for the intermediary aldehyde

$^1$H NMR (CDCl₃, 400 MHz): $\delta$ = 9.57 (d, $J$ = 3.1 Hz, 1H), 5.38 (t, $J$ = 6.4 Hz, 1H), 5.36 (dd, $J$ = 2.7, 1.7 Hz, 1H), 5.26 (t, $J$ = 2.0 Hz, 1H), 5.20 (td, $J$ = 8.1, 5.4 Hz, 1H), 4.80 (s, 1H), 4.11 (dd, $J$ = 8.7, 3.0 Hz, 1H), 4.00 (d, $J$ = 4.6 Hz, 1H), 3.42 (dd, $J$ = 8.3, 6.3 Hz, 1H), 3.39 (s, 3H), 3.13 (m, 1H), 2.50-2.42 (m, 2H), 2.04 (s, 3H), 2.03 (t, $J$ = 6.6 Hz, 2H), 1.92 (dd, $J$ = 14.7, 5.4 Hz, 1H), 1.42 (s, 3H), 0.98 (t, $J$ = 8.0 Hz, 9H), 0.94 (t, $J$ = 8.2 Hz, 9H), 0.64 (q, $J$ = 8.2 Hz, 6H), 0.58 (q, $J$ = 8.3 Hz, 6H).

$^{13}$C NMR (CDCl₃, 400 MHz): $\delta$ = 201.4, 174.6, 170.3, 144.1, 116.0, 110.3, 87.2, 84.7, 83.3, 77.6, 71.4, 58.2 58.1, 55.2, 49.5, 44.1, 40.6, 26.5, 23.3, 21.1, 7.1 (3C), 6.9 (3C), 6.6 (3C), 5.02 (3C).

HRMS (ESI) (m/z): calculated for C$_{33}$H$_{53}$O$_{10}$Si$_2$Na [M+MeOH+Na]$^+$ 693.3466, found 693.3458.

IR (cm$^{-1}$): $\tilde{\nu}$ = 2955, 2912, 2877, 1773, 1748, 1231, 1150, 1040, 1017.

$[\alpha]_{D}^{23}$ = -50.0, (CHCl₃, c = 0.6).

Rf: (Hex/EtOAc 3/1) 0.43.

Analytical data for formate 30

$^1$H NMR (CDCl₃, 400 MHz): $\delta$ = 8.09 (s, 1H), 6.25 (dd, $J$ = 3.8, 0.4 Hz, 1H), 5.41 (dd, $J$ = 11.0, 2.2 Hz, 1H), 5.35 (dd, $J$ = 2.7, 1.7 Hz, 1H), 5.26 (dd, $J$ = 2.1, 1.7 Hz, 1H), 5.21 (dt, $J$ = 8.1, 5.5 Hz, 1H), 4.81 (d, $J$ = 1.1 Hz, 1H), 4.20 (dd, $J$ = 5.6, 1.3 Hz, 1H), 3.41 (dd, $J$ = 8.2, 6.4 Hz, 1H), 3.36 (s, 3H), 3.12 (m, 1H), 2.45 (ddd, $J$ = 14.7, 8.0, 1.7 Hz, 1H), 2.43 (m, 1H), 2.04 (s, 3H), 2.01 (dd, $J$ = 11.0, 2.2 Hz, 1H), 1.97 (dd, $J$ = 11.0, 3.9 Hz, 1H), 1.92 (dd, $J$ = 14.7, 5.5 Hz, 1H), 1.42 (s, 3H), 0.97 (t, $J$ = 8.0 Hz, 9H), 0.94 (t, $J$ = 7.9 Hz, 9H), 0.63 (q, $J$ = 8.0 Hz, 6H), 0.57 (q, $J$ = 7.9 Hz, 6H).
$^{13}$C NMR (CDCl₃, 400 MHz): $\delta = 174.6, 170.1, 160.5, 144.1, 115.9, 111.0, 101.5, 84.6, 83.3, 77.3, 70.4, 58.2, 58.0, 55.7, 49.4, 44.3, 44.2, 26.1, 23.3, 21.1, 7.1 (3C), 6.8 (3C), 6.6 (3C), 4.8 (3C).

HRMS (ESI) (m/z): calculated for C$_{32}$H$_{54}$O$_{10}$Si$_2$Na [M+Na]$^+$ 677.3153, found 677.3142.

IR (cm$^{-1}$): $\tilde{\nu} = 2956, 2877, 1772, 1229, 1150, 1111, 1018, 1002, 944, 908.$

$[\alpha]_D^{23} = -4.5$, (CHCl$_3$, c = 0.2).

$R_f$: (Hex/EtOAc 3/1) 0.65.

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**vinyl bromide 31**

Formate 29 (186 mg, 0.28 mmol) and bromoallylsilane 9 (112 µL, 0.65 mmol) were dissolved in CH$_2$Cl$_2$ (5.6 mL) and cooled to -78 °C. To the resulting slightly turbid mixture was dropwise added SnCl$_4$ (454 µL, 0.45 mmol) via syringe at -78 °C. After complete addition the reaction was stirred till TLC-analysis (Hex/EtOAc 6/1) indicated full consumption of the starting aldehyde. In the following, MeOH/sat. aq. NaHCO$_3$ 2/1 (4 mL) and diethylether (6 mL) were sequentially added. The resulting heterogenic mixture was allowed to warm to room temperature and water was added till all solids were dissolved. The resulting clear aqueous phase was extracted with diethylether (3 x 10 mL). The combined organic extracts were washed with Na/K tartrate (15 mL), water (15 mL) and sat. aq. NaCl (15 mL). After drying with MgSO$_4$ the solids were removed by filtration and the filtrate was concentrated under reduced pressure giving a colorless oil. The residue was taken up in a minimum amount of Hex/EtOAc 6/1 and purified by filtration over a short pad of silica (Hex/EtOAc, 6/1) yielding desired vinyl bromide 31 (194 mg, 94%) after removal of the volatiles as colorless oil.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 5.64$ (s, 1H), 5.52 (dd, $J = 11.5, 2.7$ Hz, 1H), 5.50 (s, 1H), 5.33 (dd, $J = 2.5, 1.8$ Hz, 1H), 5.21 (dd, $J = 1.9, 1.8$ Hz, 1H), 5.17 (dt, $J = 8.0, 5.4$ Hz, 1H), 4.72 (s, 1H), 4.40 (ddd, $J = 10.3, 8.5, 2.6$ Hz, 1H), 4.07 (d, $J = 4.2$ Hz, 1H), 3.39 (dd, $J = 8.2, 6.5$ Hz, 1H), 3.31 (s, 3H), 3.11 (m, 1H), 2.79 (dd, $J = 14.6, 10.5$ Hz, 1H), 2.48-2.36 (m, 3H), 2.11 (s, 3H), 1.90
(dd, J = 14.8, 5.3 Hz, 1H), 1.89-1.77 (m, 2H), 1.41 (s, 3H), 0.98 (t, J = 7.9 Hz, 9H), 0.94 (t, J = 7.8 Hz, 9H), 0.66 (q, J = 7.9 Hz, 6H), 0.58 (q, J = 7.9 Hz, 6H).

$^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ = 174.4, 170.7, 144.2, 131.8, 118.7, 115.8, 108.5, 84.4, 83.2, 77.9, 77.1, 71.5, 57.7, 57.3, 55.0, 49.6, 45.5, 44.8, 40.0, 23.8, 23.4, 21.1, 7.1 (3C), 6.9 (3C), 6.6 (3C), 4.9 (3C).

HRMS (ESI) (m/z): calculated for C$_{36}$H$_{64}$BrN$_2$O$_8$Si$_2$ [M+H$_3$CCN+NH$_4$]$^+$ 789.3364, found 789.3349.

IR (cm$^{-1}$): $\nu$ ~ = 2954, 2877, 1770, 1747, 1459, 1372, 1226, 1151, 1049, 990.

$[\alpha]_D^{25}$ = -50.1, (CHCl$_3$, c = 1.5).

R$_f$: (Hex/EtOAc 3/1) 0.55.

![Vinyl bromide 32](image)

Vinyl bromide 32

Formate 30 (37 mg, 0.42 mmol) was subjected to the identical procedure as formate 29 (see above) giving the corresponding vinyl bromide 32 (30 mg, 73%, 89% brsm) as colorless oily about 1:1 mixture of diastereomers, which was used as such in the Heck reactions. Furthermore starting material (7 mg, 18%) could be recovered from this reaction as a mixture of diastereomers.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 5.70 (br s, 1H), 5.52 (br s, 1H), 5.44 (dd, J = 11.5, 1.5 Hz, 1H), 5.38 (dd, J = 2.7, 1.8 Hz, 1H), 5.29 (dd, J = 2.1, 1.8 Hz, 1H), 5.23 (dt, J = 8.1, 5.5 Hz, 1H), 4.72 (s, 1H), 4.60 (ddd, J = 10.6, 7.8, 2.1 Hz, 1H), 3.95 (d, J = 4.4 Hz, 1H), 3.45 (ddd, J = 8.3, 6.3 Hz, 1H), 3.32 (s, 3H), 3.12 (m, 1H), 2.80 (dd, J = 15.3, 10.6 Hz, 1H), 2.47 (ddd, J = 14.7, 7.9, 1.6 Hz, 1H), 2.42-2.35 (m, 1H), 2.33-2.27 (m, 1H), 2.06 (s, 3H), 2.02 (m, 1H), 1.93 (dd, J = 14.7, 5.5 Hz, 1H), 1.79 (ddd, J = 14.8, 11.5, 3.3 Hz, 1H), 1.43 (s, 3H), 0.98 (t, J = 7.9 Hz, 9H), 0.94 (t, J = 7.9 Hz, 9H), 0.62 (q, J = 7.8 Hz, 6H), 0.58 (q, J = 7.8 Hz, 6H).

$^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ = 174.5, 170.5, 143.9, 131.4, 118.3, 116.2, 108.6, 83.0, 82.6, 79.0, 77.8, 70.6, 58.4, 57.5, 55.0, 48.6, 45.0, 44.0, 39.9, 25.1, 24.1, 21.1, 6.9 (6C), 5.0 (6C).

HRMS (ESI) (m/z): calculated for C$_{34}$H$_{56}$BrNaO$_8$Si$_2$ [M+Na]$^+$ 751.2673, found 751.2653.

SI-25
IR (cm⁻¹):  ν = 2923, 2853, 1773, 1749, 1463, 1375, 1214, 1152, 1050, 1017.

[α]D²⁵ = -32.0, (CHCl₃, c = 0.2).

Rf: (Hex/EtOAc 3/1) 0.45.

Heck macrocyclization

| No. | Substrate | Conditions | Product | Yield |
|-----|-----------|------------|---------|-------|
| 1   | 32        | Pd(OAc)₂ (0.6 eq.), PPh₃ (1.4 eq.), K₂CO₃ (20 eq.), DMF (0.02 M), 100 °C, 1 h | decomposition | -     |
| 2   | 32        | Pd₂(dba)₃ (0.1 eq.), Et₃N (15.0 eq., toluene (0.04 M), 110 °C, 24 h | Starting material recovered | -     |
| 3   | 32        | Pd(PPh₃)₄ (0.5 eq.), Ag₂CO₃ (3.0 eq.), CH₃CN (0.01 M), 90 °C, 24 h | Starting material recovered | -     |
| 4   | 31        | Pd(PPh₃)₄ (0.5 eq.), Ag₂CO₃ (3.0 eq.), CH₃CN (0.01 M), 4 Å MS, 90 °C, 24 h | Starting material recovered | -     |
| 5   | 31        | Pd(OAc)₂ (0.1 eq.), PPh₃ (0.2 eq.), Ag₂CO₃ (3.0 eq.), 4 Å MS, toluene (0.01 M), 80 °C, 3 d | 33 traces |       |
| 6   | 32        | Pd(OAc)₂ (0.1 eq.), KOAc (5.0 eq.), Bu₄NCl (2.0 eq.), 4 Å MS, DMF (0.05 M), 80 °C, 3 h | 36 | 59%   |
| 7   | 31        | Pd(OAc)₂ (0.5 eq.), DIPEA (15.0 eq.), Bu₄NCl (10.0 eq.), 4 Å MS, DMF (0.02 M), 110 °C, 1 h | 34 | 41%   |
| 8   | 31        | Pd(OAc)₂ (0.5 eq.), PPh₃ (1.0 eq.), K₂CO₃ (10.0 eq.), 4 Å MS, DMF (0.004 M), 125 °C, 3 h | Complex mixture | 50%   |
| 9   | 31        | [PdCl₂(PPh₃)₂] (0.1 eq.), Et₂NH (0.4 eq.), Et₃N (5.0 eq.), DMF (0.004 M), 100 °C, 4 h | Complex mixture | 37%   |
| 10  | 31        | Pd(OAc)₂ (0.1 eq.), Bu₄NCl (2.0 eq.), Ag₂CO₃ (3.0 eq.), 4 Å MS, DMF (0.004 M), 80 °C, 5 d | Complex mixture | 35%   |
| 11  | 31        | Pd(OAc)₂ (0.2 eq.), KOAc (1.5 eq.), K₂CO₃ (5.0 eq.), Bu₄NCl (2.5 eq.), CH₃CN (0.01) | 34 | 16%   |
General procedure A: “standard” Heck reaction

A round bottomed flask was charged with the vinyl bromide, a phosphine ligand, base and crushed 4 Å molecular sieves (where stated) were added. Freshly degassed solvent was added at room temperature under an argon atmosphere. The palladium species was added to the reaction mixture as a solid, the flask was sealed with a plastic stopper and immediately heated in an oil bath under vigorous stirring. The reaction was monitored by TLC-analysis (Hex/EtOAc 3/1). The reaction mixture was allowed to cool to room temperature at which diethylether and water were added. The resulting heterogeneous mixture was filtered through a short pad of Celite. The aqueous phase was separated and extracted with diethylether three times. The combined organic phases were washed with water and sat. aq. NaCl followed by drying with MgSO₄. Filtration of the solids, removal of the volatiles under reduced pressure and flash column chromatography (SiO₂, Hex/EtOAc 8:1 → 4:1) of the residue gave the depicted product.

**Table 1:**

| Entry | Reaction Conditions | Products | Conversion (%) |
|-------|---------------------|----------|----------------|
| 12    | Pd(OAc)₂ (0.2 eq.), K₂CO₃ (5.0 eq.), Bu₄NCl (2.5 eq.), CH₃CN (0.01 M), 120 °C, 0.5 h | traces | 34 |
| 13    | Pd(PPh₃)₄ (0.2 eq.), Et₃N (0.1 eq.), CH₃CN (0.01 M), 120 °C, 0.5 h | Complex mixture | - |
| 14    | Pd(OAc)₂ (0.3 eq.), PPh₃ (0.6 eq.), Cs₂CO₃ (3.0 eq.), DMF (0.01 M), 130 °C, 1.5 h | traces | 34 |
| 15    | Pd(OAc)₂ (0.1 eq.), KOAc (5.0 eq.), Bu₄NCl (2.0 eq.), 4 Å MS, DMF (0.01 M), 85 °C, 4 h | Complex mixture | 54% |
| 16    | Pd(OAc)₂ (0.1 eq.), NaOAc (5.0 eq.), Bu₄NCl (2.0 eq.), 4 Å MS, DMF (0.01 M), 85 °C, 1.5 h | Complex mixture | 55% |
| 17    | [Pd(dppf)Cl₂] (0.4 eq.), Cs₂CO₃ (3.0 eq.), nBu₄NCl (3.0 eq.), 4 Å MS, DMF (0.01 M), 90 °C, 2 h | Complex mixture | - |
| 18    | [Pd(dppf)Cl₂] (0.4 eq.), PBu₃ (0.8 eq.), Cs₂CO₃ (3.0 eq.), 4 Å MS, DMF (0.01 M), 90 °C, 16 h | Complex mixture | - |
| 19    | [Pd(dppf)Cl₂] (0.4 eq.), PPh₃ (0.8 eq.), Cs₂CO₃ (3.0 eq.), 4 Å MS, DMF (0.01 M), 90 °C, 24 h | Complex mixture | - |
| 20    | 37 (0.4 eq.), Cs₂CO₃ (3.0 eq.), toluene (0.01 M), 90 °C, 24 h | Complex mixture | - |

**Notes:**
a) Microwave assisted heating was used instead of conventional heating in an oil bath, b) based on recovered starting material.
**General procedure B: phosphine free Heck reaction**

A round bottomed flask was charged with the vinyl bromide, base and crushed 4 Å molecular sieves (where stated) were added. Freshly degased solvent was added at room temperature under an argon atmosphere. The palladium species was added to the reaction mixture as a solid and the flask was sealed with a plastic stopper and immediately heated in an oil bath under vigorous stirring. The reaction was monitored by TLC-analysis (Hex/EtOAc 3/1). The reaction mixture was allowed to cool to room temperature at which diethylether and water were added. The resulting heterogeneous mixture was filtered through a short pad of Celite. The aqueous phase was separated and extracted with diethylether three times. The combined organic phases were washed with water and sat. aq. NaCl followed by drying with MgSO₄. Filtration of the solids, removal of the volatiles under reduced pressure and flash column chromatography (SiO₂, Hex/EtOAc 8:1 → 4:1) of the residue gave the depicted product.

**General procedure C: Jeffery Heck reaction**

A round bottomed flask was charged with the vinyl bromide, base, tetrabutylammonium chloride and crushed 4 Å molecular sieves (where stated) were added. Freshly degased solvent was added at room temperature under an argon atmosphere. The palladium species was added to the reaction mixture as a solid and the flask was sealed with a plastic stopper and immediately heated in an oil bath under vigorous stirring. The reaction was monitored by TLC-analysis (Hex/EtOAc 3/1). The reaction mixture was allowed to cool to room temperature at which diethylether and water were added. The resulting heterogeneous mixture was filtered through a short pad of Celite. The aqueous phase was separated and extracted with diethylether three times. The combined organic phases were washed with water and sat. aq. NaCl followed by drying with MgSO₄. Filtration of the solids, removal of the volatiles under reduced pressure and flash column chromatography (SiO₂, Hex/EtOAc 8:1 → 4:1) of the residue gave the depicted product.

**General procedure D: microwave assisted Heck reaction**

A microwave tube was charged with the vinyl bromide, base and tetrabutylammonium chloride (where stated) were added. Freshly degased solvent was added at room
temperature under an argon atmosphere. The palladium species was added to the reaction mixture as a solid and the tube was sealed with a plastic stopper and immediately heated with a Biotage Initiator™ Microwave Synthesizer under stirring. The reaction was monitored by TLC-analysis (Hex/EtOAc 3/1). At room temperature diethylether and water were added. The resulting heterogeneous mixture was filtered through a short pad of Celite. The aqueous phase was separated and extracted with diethylether three times. The combined organic phases were washed with water and sat. aq. NaCl followed by drying with MgSO₄. Filtration of the solids, removal of the volatiles under reduced pressure and flash column chromatography (SiO₂, Hex/EtOAc 8:1 → 4:1) of the residue gave the depicted product.

Table 1, Entry 1
A mixture of diastereomers of vinyl bromide 32 (10 mg, 0.014 mmol) was subjected to general procedure A using Pd(OAc)₂ (2 mg, 0.008 mmol), triphenylphosphine (5 mg, 0.019 mmol) and K₂CO₃ (40 mg, 0.27 mmol) in DMF (0.8 mL) as solvent. After 1 h at 100 °C no starting material was left. Purification of the residue did not result in isolation of desired product 35.

Table 1, Entry 2
A mixture of diastereomers of vinyl bromide 32 (25 mg, 0.034 mmol) was subjected to general procedure B using Pd(dba)₃ (3 mg, 0.003 mmol) and Et₃N (40 mg, 0.27 mmol) in toluene (5.8 mL) as solvent. After 1 h at 110 °C no reaction was observed and starting material was recovered.

Table 1, Entry 3
A mixture of diastereomers of vinyl bromide 32 (30 mg, 0.04 mmol) was subjected to general procedure B using Pd(PPh₃)₄ (24 mg, 0.02 mmol) and Ag₂CO₃ (34 mg, 0.12 mmol) in acetonitrile (5.0 mL) as solvent. After 24 h at 90 °C no reaction was observed and starting material was recovered.

Table 1, Entry 4
Vinyl bromide 31 (20 mg, 0.03 mmol) was subjected to general procedure B using Pd(PPh₃)₄ (16 mg, 0.01 mmol) and Ag₂CO₃ (23 mg, 0.8 mmol) in acetonitrile (4.0 mL) as solvent. After 24 h at 90 °C no reaction was observed and starting material was recovered.

![Structure](TESO, OTES)

Table 1, Entry 5

Vinyl bromide 31 (14 mg, 0.02 mmol) was subjected to general procedure A using Pd(OAc)₂ (0.5 mg, 0.002 mmol), triphenylphosphine (1 mg, 0.004 mmol), Ag₂CO₃ (16 mg, 0.058 mmol) and crushed 4 Å molecular sieves (100 mg) in toluene (0.8 mL) as solvent. After 3 d at 80 °C no starting material was left. Purification of the residue and mass analysis of the collected fractions indicated the formation of desired macrocycle 33.

HRMS (ESI) (m/z): calculated for C₃₆H₆₃N₂O₈Si₂ [M+H₃CN+NH₄]⁺ 707.4117, found 707.4108.

Table 1, Entry 6: tricyclo[8.2.0.0²,⁹]tridecane ring system 36

A mixture of diastereomers of vinyl bromide 32 (21 mg, 0.03 mmol) was subjected to general procedure C using Pd(OAc)₂ (0.6 mg, 0.003 mmol), KOAc (14 mg, 0.14 mmol), Bu₄NCl (16 mg, 0.06 mmol) and crushed 4 Å molecular sieves (70 mg) in DMF (0.8 mL) as solvent. After 3 h at 80 °C no starting material was left. Purification of the residue resulted in isolation of carbo-oxygenation product 36 (12 mg, 59%) as a mixture of diastereomers.

¹H NMR (CDCl₃, 600 MHz): δ = 5.41 (dd, J = 2.6, 2.0 Hz, 1H), 5.39 (d, J = 10.9 Hz, 1H), 5.27 (t, J = 2.0 Hz, 1H), 5.22 (dt, J = 8.0, 5.6 Hz, 1H), 4.83 (s, 1H), 4.82 (s, 1H), 4.72 (s, 1H), 4.47 (ddd, J = 10.5, 8.0, 1.9 Hz, 1H), 3.93 (d, J = 4.4 Hz, 1H), 3.46 (dd, J = 8.3, 6.3 Hz, 1H), 3.32 (s, 3H), 3.09 (m, 1H), 2.52 (dd, J = 14.9, 10.8 Hz, 1H), 2.46 (ddd, J = 14.8, 7.9, 1.6 Hz, 1H), 2.42 (br d, J = 14.8 Hz, 1H), 2.31 (m, 2H), 2.21 (s, 3H), 2.04 (s, 3H), 2.01 (m, 1H), 1.92 (dd, J = 14.7, 14.7 Hz, 1H).
5.5 Hz, 1H), 1.74 (ddd, \( J = 14.7, 11.8, 3.0 \) Hz, 1H), 1.42 (s, 3H), 0.97 (t, \( J = 7.9 \) Hz, 9H), 0.94 (t, \( J = 7.9 \) Hz, 9H), 0.62 (dq, \( J = 7.9, 1.9 \) Hz, 6H), 0.58 (q, \( J = 7.9 \) Hz, 6H).

\( ^{13}\text{C} \) NMR (CDCl\(_3\), 600 MHz): \( \delta = 175.2, 170.5, 169.8, 153.8, 116.0, 108.7, 103.4, 84.2, 83.5, 79.1, 77.5, 70.3, 58.3, 58.2, 55.0, 49.5, 43.6, 39.7, 37.9, 37.4, 25.2, 23.1, 21.2, 21.1, 7.1 (3C), 6.9 (3C), 6.6 (3C), 4.9 (3C).

HRMS (ESI) (m/z): calculated for C\(_{36}\)H\(_{60}\)NaO\(_{10}\)Si\(_{2}\) [M+Na]\(^+\) 731.3623, found 731.3591.

IR (cm\(^{-1}\)): \( \tilde{\nu} \approx 2955, 2925, 2854, 1773, 1745, 1259, 1226, 1153, 1105, 1017. \)

\([\alpha]\)\(_{D}^{25} = -46.0\), (CHCl\(_3\), c = 0.1).

R\(_f\): (Hex/EtOAc 3/1) 0.35.

Table 1, Entry 7: tricyclo[8.2.0.0\(^2,9\)]tridecane ring system 34

Vinyl bromide 31 (20 mg, 0.027 mmol) was subjected to general procedure C using Pd(OAc)\(_2\) (3.0 mg, 0.014 mmol), DIPEA (70 \( \mu \)L, 0.41 mmol), Bu\(_4\)NCl (78 mg, 0.27 mmol) and crushed 4 Å molecular sieves (70 mg) in DMF (0.8 mL) as solvent. After 1 h at 110 °C no starting material was left. Purification of the residue resulted in isolation of carbo-oxygenation product 34 (8 mg, 41%) as a single diastereomer.

\(^{1}\text{H} \) NMR (CDCl\(_3\), 600 MHz): \( \delta = 5.50 \) (dd, \( J = 11.3, 2.6 \) Hz, 1H), 5.33 (dd, \( J = 2.7, 1.8 \) Hz, 1H), 5.21 (t, \( J = 1.92 \) Hz, 1H), 5.18 (dt, \( J = 5.4, 8.0 \) Hz, 1H), 4.83 (s, 2H), 4.73 (s, 1H), 4.25 (ddd, \( J = 10.8, 8.3, 2.7 \) Hz, 1H), 4.09 (d, \( J = 4.3 \) Hz, 1H), 3.40 (dd, \( J = 8.2, 6.5 \) Hz, 1H), 3.31 (s, 3H), 3.10 (m, 1H), 2.55 (dd, \( J = 15.1, 10.8 \) Hz, 1H), 2.45 (ddd, \( J = 14.7, 7.8, 1.7 \) Hz, 1H), 2.34 (m, 1H), 2.33 (m, 1H), 2.15 (s, 3H), 2.08 (s, 3H), 1.90 (dd, \( J = 14.6, 5.4 \) Hz, 1H), 1.88-1.79 (m, 2H), 1.41 (s, 3H), 0.99 (t, \( J = 8.0 \) Hz, 9H), 0.94 (t, \( J = 7.9 \) Hz, 9H), 0.67 (q, \( J = 8.0 \) Hz, 6H), 0.58 (q, \( J = 7.9 \) Hz, 6H).

\(^{13}\text{C} \) NMR (CDCl\(_3\), 600 MHz): \( \delta = 174.4, 170.6, 169.3, 154.0, 144.2, 115.8, 108.8, 103.4, 84.4, 83.2, 77.6, 76.8, 71.4, 57.7, 57.3, 55.1, 49.6, 44.8, 40.1, 37.7, 23.7, 23.4, 21.3, 21.0, 7.2 (3C), 6.9 (3C), 6.6 (3C), 6.4 (3C).

HRMS (ESI) (m/z): calculated for C\(_{36}\)H\(_{60}\)NaO\(_{10}\)Si\(_{2}\) [M+H\(_3\)CCN+NH\(_4\)]\(^+\) 731.3623, found 731.3628.
IR (cm\(^{-1}\)): \(\tilde{\nu} = 2955, 2915, 1769, 1371, 1226, 1207, 1101, 1051, 1018, 990\).

\([\alpha]_D^{15} = -50.8\), (CHCl\(_3\), c = 0.4).

\(R_f\): (Hex/EtOAc 4/1) 0.27.

**Table 1, Entry 8**

Vinyl bromide 31 (15 mg, 0.021 mmol) was subjected to **general procedure A** using Pd(OAc)\(_2\) (2.0 mg, 0.009 mmol), triphenylphosphine (5 mg, 0.021 mmol), K\(_2\)CO\(_3\) (28 mg, 0.21 mmol) and crushed 4 Å molecular sieves (100 mg) in DMF (5.3 mL) as solvent. After 3 h at 125 °C no starting material was left. Purification of the residue did not result in isolation of desired product.

**Table 1, Entry 9**

Vinyl bromide 31 (15 mg, 0.021 mmol) was subjected to **general procedure B** using [PdCl\(_2\)(PPh\(_3\))\(_2\)] (1.5 mg, 0.002 mmol), Et\(_2\)NH (1 \(\mu\)L, 0.008 mmol) and Et\(_3\)N (28 mg, 0.21 mmol) in DMF (5.0 mL) as solvent. After 4 h at 100 °C no starting material was left. Purification of the residue lead to a complex mixture of products.

**Table 1, Entry 10**

Vinyl bromide 31 (14 mg, 0.020 mmol) was subjected to **general procedure C** using Pd(OAc)\(_2\) (0.5 mg, 0.002 mmol), Ag\(_2\)CO\(_3\) (16 mg, 0.57 mmol), Bu\(_4\)NCl (11 mg, 0.38 mmol) and crushed 4 Å molecular sieves (70 mg) in DMF (5.0 mL) as solvent. After 5 d at 80 °C the reaction was quenched. Purification of the residue lead to a complex mixture of products.

**Table 1, Entry 11: tricyclo[8.2.0.0\(^2\,9\)]tridecane ring system 34**

Vinyl bromide 31 (20 mg, 0.027 mmol) was subjected to **general procedure D** using Pd(OAc)\(_2\) (1.0 mg, 0.005 mmol), KOAc (4 mg, 0.041 mmol), K\(_2\)CO\(_3\) (19 mg, 0.137 mmol) and Bu\(_4\)NCl (19 mg, 0.068 mmol) in acetonitrile (2.7 mL) as solvent. After 1 h at 140 °C no starting material was left. Purification of the residue resulted in isolation of carbo-oxygenation product 34 (3 mg, 16%) as colorless oil.
Table 1, Entry 12: tricyclo[8.2.0.0^2,9]tridecane ring system 34
Vinyl bromide 31 (20 mg, 0.027 mmol) was subjected to general procedure D using Pd(OAc)_2 (1.0 mg, 0.005 mmol), K_2CO_3 (19 mg, 0.137 mmol) and Bu_4NCl (19 mg, 0.068 mmol) in acetonitrile (2.7 mL) as solvent. After 30 min at 120 °C no starting material was left. Purification of the residue and mass- as well as NMR-analysis of the collected fractions indicated the formation of carbo-oxygenation product 34.

Table 1, Entry 13
Vinyl bromide 31 (20 mg, 0.027 mmol) was subjected to general procedure D using Pd(PPh_3)_4 (6.3 mg, 0.005 mmol), Et_3N (38 µL, 0.273 mmol) in acetonitrile (2.7 mL) as solvent. After 30 min at 120 °C no starting material was left. Purification of the residue did not lead to isolation of any previously described products.

Table 1, Entry 14
Vinyl bromide 32 (20 mg, 0.027 mmol) was subjected to general procedure A using Pd(OAc)_2 (2 mg, 0.008 mmol), triphenylphosphine (4 mg, 0.016 mmol) and Cs_2CO_3 (27 mg, 0.082 mmol) in DMF (3.0 mL) as solvent. After 1.5 h at 130 °C no starting material was left. Purification of the residue and mass- as well as NMR-analysis of the collected fractions indicated the formation of carbo-oxygenation product 36.

Table 1, Entry 15: tricyclo[8.2.0.0^2,9]tridecane ring system 34
Vinyl bromide 31 (32 mg, 0.044 mmol) was subjected to general procedure C using Pd(OAc)_2 (1.0 mg, 0.004 mmol), KOAc (22 mg, 0.22 mmol), Bu_4NCl (25 mg, 0.088 mmol) and crushed 4 Å molecular sieves (150 mg) in DMF (1.8 mL) as solvent. After 4 h at 85 °C no starting material was left. Purification of the residue resulted in isolation of carbo-oxygenation product 34 (16 mg, 54%) as a single diastereomer.

Table 1, Entry 16: tricyclo[8.2.0.0^2,9]tridecane ring system 34
Vinyl bromide 31 (20 mg, 0.027 mmol) was subjected to general procedure C using Pd(OAc)_2 (0.6 mg, 0.003 mmol), NaOAc (11 mg, 0.13 mmol), Bu_4NCl (15 mg, 0.053 mmol) and crushed 4 Å molecular sieves (150 mg) in DMF (2.7 mL) as solvent. After 1.5 h at 85 °C no starting
material was left. Purification of the residue resulted in isolation carbo-oxygenation product 34 (10 mg, 55%).

**Table 1, Entry 17**

Vinyl bromide 31 (20 mg, 0.027 mmol) was subjected to general procedure C using [Pd(dppf)2Cl2] (7 mg, 0.011 mmol), Cs2CO3 (27 mg, 0.082 mmol), Bu4NCl (15 mg, 0.053 mmol) and crushed 4 Å molecular sieves (100 mg) in DMF (2.7 mL) as solvent. After 2 h at 90 °C no starting material was left. Purification of the residue lead to a complex mixture of products.

**Table 1, Entry 18**

Vinyl bromide 31 (20 mg, 0.027 mmol) was subjected to general procedure A using [Pd(dppf)2Cl2] (7 mg, 0.011 mmol), tributylphosphine (5.5 µL, 0.022 mmol), Cs2CO3 (27 mg, 0.082 mmol) in DMF (2.7 mL) as solvent. After 16 h at 90 °C no starting material was left. Purification of the residue lead to a complex mixture of products.

**Table 1, Entry 19**

Vinyl bromide 31 (20 mg, 0.027 mmol) was subjected to general procedure A using [Pd(dppf)2Cl2] (7 mg, 0.011 mmol), triphenylphosphine (6 mg, 0.022 mmol), Cs2CO3 (27 mg, 0.082 mmol) and crushed 4 Å molecular sieves (100 mg) in DMF (2.7 mL) as solvent. After 24 h at 90 °C no starting material was left. Purification of the residue lead to a complex mixture of products.

**Table 1, Entry 20**

Vinyl bromide 33 (20 mg, 0.027 mmol) was subjected to general procedure B using allyl palladium catalyst 37 (6 mg, 0.011 mmol) and Cs2CO3 (27 mg, 0.082 mmol) in toluene (2.7 mL) as solvent. After 24 h at 90 °C no starting material was left. Purification of the residue lead to a complex mixture of products.
$^1$H NMR: CDCl$_3$, 400 MHz
$^\text{13}C\text{ NMR: } CDCl_3, 400 MHz$
$^1$H NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
NMR: CDCl₃, 400 MHz

1H NMR: CDCl₃, 400 MHz
NMR: $\text{CDCl}_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
$^1$H NMR: CDCl$_3$, 400 MHz

NMR spectrum with chemical shifts and peaks labeled.
$^{1}H$ NMR: CDCl$_3$, 400 MHz
\[ ^{13}C\text{ NMR: CDCl}_3, 400 \text{ MHz} \]
$^1$H NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
$^{1}H$ NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
$^1$H NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
$^1$H NMR: CDCl$_3$, 400 MHz

SI-53
SI-54

$^1$C NMR: CDCl$_3$, 400 MHz

![Chemical structure with spectrum]
$^{1}H$ NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz

![Chemical Structure](image)
$^1$H NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz

SI-60
\textbf{$^{1}$H NMR: CDCl$_3$, 400 MHz}

\begin{itemize}
  \item \textbf{20} $R^1 = \text{OH}, R^2 = H$
  \item \textbf{21} $R^1 = H, R^2 = \text{OH}$
\end{itemize}

\begin{align*}
  &\text{OTES} \\
  &\text{OMe} \\
  &\text{OTBS} \\
  &\text{TMSO}
\end{align*}

\begin{align*}
  &R^1 = \text{OH, } R^2 = H \\
  &R^1 = H, \text{ } R^2 = \text{OH}
\end{align*}
$^{13}$C NMR: CDCl$_3$, 400 MHz

20 $R^1 = \text{OH}, R^2 = \text{H}$

21 $R^1 = \text{H}, R^2 = \text{OH}$
| No. | $^{13}$C [ppm] | $^1$H [ppm] |
|-----|---------------|-------------|
| 1   | 177.7         | -           |
| 2   | 144.0         | -           |
| 3   | 115.1         | 5.40, 5.20  |
| 4   | 109.0         | 4.69        |
| 5   | 84.9          | -           |
| 6   | 84.1          | 4.02        |
| 7   | 83.7          | 5.16        |
| 8   | 77.5          | 4.14        |
| 9   | 70.4          | 3.98        |
| 10  | 67.0          | 3.75, 3.66  |
| 11  | 57.8          | 3.13        |
| 12  | 57.7          | -           |
| 13  | 54.6          | 3.33-3.29   |
| 14  | 49.6          | 2.45, 1.94  |
| 15  | 44.8          | 3.33-3.29   |
| 16  | 41.4          | 2.40        |
| 17  | 27.9          | 1.79-1.67   |
| 18  | 26.2          | 0.91        |
| 19  | 23.4          | 1.43        |
| 20  | 18.6          | -           |
| 21  | 7.0           | 0.96        |
| 22  | 5.1           | 0.62        |
| 23  | 2.4           | 0.11        |
| 24  | -5.2          | 0.08        |
| 25  | -5.3          | 0.09        |
| 26  | -             | 3.71 (OH)   |
$^1$H NMR: CDCl$_3$, 400 MHz
C NMR: CDCl₃, 400 MHz
| No. | $^{13}$C [ppm] | $^1$H [ppm] |
|-----|----------------|-------------|
| 1   | 176.8          | -           |
| 2   | 145.4          | -           |
| 3   | 114.5          | 5.27, 5.15  |
| 4   | 109.2          | 4.69        |
| 5   | 85.0           | -           |
| 6   | 84.0           | 3.96        |
| 7   | 83.6           | 5.19        |
| 8   | 79.1           | 4.17        |
| 9   | 70.2           | 4.12        |
| 10  | 67.1           | 3.79, 3.65  |
| 11  | 59.6           | -           |
| 12  | 57.7           | 3.11        |
| 13  | 54.7           | 3.31        |
| 14  | 49.8           | 2.45, 1.93  |
| 15  | 43.5           | 3.43        |
| 16  | 41.6           | 2.41        |
| 17  | 28.9           | 1.87, 1.67  |
| 18  | 26.2           | 0.91        |
| 19  | 23.6           | 1.42        |
| 20  | 18.7           | -           |
| 21  | 6.9            | 0.97        |
| 22  | 5.1            | 0.63        |
| 23  | 2.4            | 0.12        |
| 24  | -5.3           | 0.11, 0.12  |
| 25  | -              | 3.05 (OH)   |
NMR: CDCl₃, 400 MHz
| No. | $^{13}$C [ppm] | $^1$H [ppm] |
|-----|----------------|-------------|
| 1   | 179.1          | -           |
| 2   | 137.9          | -           |
| 3   | 127.9          | 5.75        |
| 4   | 108.8          | 4.66        |
| 5   | 83.1           | 4.13        |
| 6   | 78.3           | 4.09        |
| 7   | 76.6           | 4.75        |
| 8   | 71.1           | 3.91        |
| 9   | -              | 3.91 (OH)   |
| 10  | 70.1           | -           |
| 11  | 67.0           | 3.84, 3.61  |
| 12  | 55.6           | -           |
| 13  | 54.5           | 3.29        |
| 14  | 47.9           | 3.50        |
| 15  | 44.8           | 2.53, 1.95  |
| 16  | 42.8           | 2.31        |
| 17  | 38.8           | 3.26, 2.74  |
| 18  | 31.2           | 1.36        |
| 19  | 29.2           | 1.77        |
| 20  | 25.9           | 0.91        |
| 21  | 18.4           | -           |
| 22  | 6.7            | 0.96        |
| 23  | 4.8            | 0.62        |
| 24  | 2.2            | 0.10        |
| 25  | -5.5           | 0.06        |
H NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
| No. | $^{13}$C [ppm] | $^1$H [ppm] |
|-----|---------------|-------------|
| 1   | 174.9         | -           |
| 2   | 170.3         | -           |
| 3   | 109.5         | 4.65        |
| 4   | 83.5          | -           |
| 5   | 83.4          | 3.83        |
| 6   | 82.6          | 5.19        |
| 7   | 76.4          | 4.23        |
| 8   | 68.2          | 5.31        |
| 9   | 66.3          | 3.71, 3.57  |
| 10  | 62.2          | -           |
| 11  | 57.9          | 3.02        |
| 12  | 55.8          | -           |
| 13  | 54.6          | 3.27        |
| 14  | 50.2          | 2.58, 1.91  |
| 15  | 47.0          | 2.88, 2.70  |
| 16  | 42.4          | 3.54        |
| 17  | 40.7          | 2.00        |
| 18  | 26.1          | 0.92        |
| 19  | 25.7          | 1.84-1.75   |
| 20  | 23.1          | 1.31        |
| 21  | 21.3          | 2.14        |
| 22  | 18.5          | -           |
| 23  | 7.0           | 0.97        |
| 24  | 4.9           | 0.69        |
| 25  | 2.4           | 0.12        |
| 26  | -5.3          | 0.08        |
$\text{H NMR: CDCl}_3, 600 \text{ MHz}$
$^{13}$C NMR: CDCl$_3$, 600 MHz

![Chemical Structure](image)
$^1$H NMR: CDCl₃, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
$\text{H NMR: CDCl}_3, 400 \text{ MHz}$
$^{13}$C NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
$^1$H NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
### NOE-Correlation

![Chemical Structure](image)

#### Table: 

| No. | $^13$C [ppm] | $^1$H [ppm] |
|-----|--------------|-------------|
| 1   | 174.3        | -           |
| 2   | 170.7        | -           |
| 3   | 160.7        | 8,11        |
| 4   | 144.1        | -           |
| 5   | 115.9        | 5.33$^a$, 5.21$^b$ |
| 6   | 110.9        | 4,79        |
| 7   | 102.4        | 6,14        |
| 8   | 84.5         | -           |
| 9   | 83.2         | 5,17        |
| 10  | 76.2         | 4,26        |
| 11  | 71.2         | 5,49        |
| 12  | 57.8         | 3,1         |
| 13  | 57.4         | -           |
| 14  | 55.6         | 3,35        |
| 15  | 49.6         | 2.45$^a$, 1.90$^b$ |
| 16  | 44.9         | 2,36        |
| 17  | 44.7         | 3,4         |
| 18  | 25.0         | 2.04-1.94   |
| 19  | 23.4         | 1,41        |
| 20  | 21.1         | 2,08        |
| 21  | 7.1          | 0,94        |
| 22  | 6.9          | 0,98        |
| 23  | 6.6          | 0,58        |
| 24  | 4.9          | 0,67        |
$^{13}$C NMR: CDCl$_3$, 400 MHz
$^1$H NMR: CDCl$_3$, 400 MHz
| No. | $^{13}$C [ppm] | $^1$H [ppm] |
|-----|----------------|-------------|
| 1   | 174.6          | -           |
| 2   | 170.1          | -           |
| 3   | 160.5          | 8.09        |
| 4   | 144.1          | -           |
| 5   | 115.9          | 5.35<sup>a</sup>, 5.26<sup>b</sup> |
| 6   | 111.0          | 4.81        |
| 7   | 101.5          | 6.25        |
| 8   | 84.6           | -           |
| 9   | 83.3           | 5.21        |
| 10  | 77.3           | 4.20        |
| 11  | 70.4           | 5.41        |
| 12  | 58.2           | 3.12        |
| 13  | 58.0           | -           |
| 14  | 55.7           | 3.36        |
| 15  | 49.4           | 2.45<sup>a</sup>, 1.92<sup>b</sup> |
| 16  | 44.3           | 2.43        |
| 17  | 44.2           | 3.42        |
| 18  | 26.1           | 2.01<sup>a</sup>, 1.97<sup>b</sup> |
| 19  | 23.3           | 1.42        |
| 20  | 21.1           | 2.04        |
| 21  | 7.1            | 0.94        |
| 22  | 6.8            | 0.97        |
| 23  | 6.6            | 0.57        |
| 24  | 4.8            | 0.63        |
$^1$H NMR: CDCl$_3$, 400 MHz
$^{13}$C NMR: CDCl$_3$, 400 MHz
| No. | $^{13}$C [ppm] | $^1$H [ppm] |
|-----|---------------|------------|
| 1   | 174.4         | -          |
| 2   | 170.7         | -          |
| 3   | 144.2         | -          |
| 4   | 131.8         | -          |
| 5   | 118.7         | 5.64<sup>a</sup>, 5.50<sup>b</sup> |
| 6   | 115.8         | 5.33, 5.21 |
| 7   | 108.5         | 4.72       |
| 8   | 84.4          | -          |
| 9   | 83.2          | 5.17       |
| 10  | 77.9          | 4.40       |
| 11  | 77.1          | 4.07       |
| 12  | 71.5          | 5.52       |
| 13  | 57.7          | 3.11       |
| 14  | 57.3          | -          |
| 15  | 55.0          | 3.31       |
| 16  | 49.6          | 2.45<sup>a</sup>, 1.90<sup>b</sup> |
| 17  | 45.5          | 2.79, 2.44 |
| 18  | 44.8          | 3.39       |
| 19  | 40.0          | 2.4        |
| 20  | 23.8          | 1.89, 1.82 |
| 21  | 23.4          | 1.41       |
| 22  | 21.1          | 2.11       |
| 23  | 7.1           | 0.94       |
| 24  | 6.9           | 0.98       |
| 25  | 6.6           | 0.58       |
| 26  | 4.9           | 0.66       |
$^1$H NMR: CDCl$_3$, 400 MHz

![NMR Spectrogram](image_url)
$^{13}$C NMR, CDCl$_3$, 400 MHz
NOE-Correlation

6^b 14 18 10 17^a
21 20 8

HMBC-Correlation

8 4 8 20 8 3
6 15 6^a 5 5 13

| No. | \(^{13}\text{C} [\text{ppm}]| | \(^{1}\text{H} [\text{ppm}]| |
|-----|-----------------|-----------------|
| 1   | 174.4           | -               |
| 2   | 170.6           | -               |
| 3   | 169.3           | -               |
| 4   | 154.0           | -               |
| 5   | 144.2           | -               |
| 6   | 115.8           | 5.33^a, 5.21^b |
| 7   | 108.8           | 4.73           |
| 8   | 103.4           | 4.83           |
| 9   | 84.4            | -               |
| 10  | 83.2            | 5.18           |
| 11  | 77.6            | 4.25           |
| 12  | 76.8            | 4.09           |
| 13  | 71.4            | 5.50           |
| 14  | 57.7            | 3.10           |
| 15  | 57.3            | -               |
| 16  | 55.1            | 3.31           |
| 17  | 49.6            | 2.45^a, 1.90^b |
| 18  | 44.8            | 3.40           |
| 19  | 40.1            | 2.34           |
| 20  | 37.7            | 2.55^a, 2.33^b |
| 21  | 23.7            | 1.84           |
| 22  | 23.4            | 1.41           |
| 23  | 21.3            | 2.15           |
| 24  | 21.0            | 2.08           |
| 25  | 7.2             | 0.94           |
| 26  | 6.9             | 0.98           |
| 27  | 6.6             | 0.58           |
| 28  | 6.4             | 0.67           |
$^{13}$C NMR: CDCl$_3$, 600 MHz
COSY, CDCl₃, 600 MHz

![Chemical structure diagram](image)

**34**
HSQC, CDCl₃, 600 MHz

SI-100
HMBC, CDCl₃, 600 MHz
NOESY, CDCl₃, 600 MHz
| ppm | 7.32 | 6.83 | 11.33 | 3.94 | 4.22 | 3.97 | 1.75 | 5.46 | 0.96 | 2.99 | 1.07 | 1.54 | 0.87 | 2.15 | 1.28 | 2.13 | 1.00 |

**1H NMR:** CDCl$_3$, 600 MHz

![Chemical Structure](attachment:image.png)
$^{13}$C NMR: CDCl$_3$, 600 MHz
HSQC, CDCl₃, 600 MHz

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HMBC, CDCl₃, 600 MHz
NOESY, CDCl₃, 600 MHz