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C(1→4)-linked disaccharides through carbonylative Stille cross-coupling

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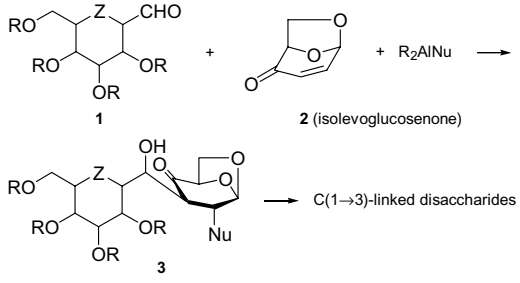
Abstract—A tinglucal tributyl[4,6-*O*-bis(t-butyl)silylidene-3-*O*-tris(isopropyl)silyl]tin **7** and a triflate derived from isolevoglucosenone (1*R*,4*R*,5*R*)-4-benzyloxy-6,8-dioxabicyclo[3.2.1]oct-2-en-2-yl trifluoromethanesulfonate **10** undergo the carbonylative Stille condensation under special conditions requiring $AsPh_3$, LiCl, and powdered charcoal as co-catalysts to give a cross-conjugated dienone **6** in which the bicyclic alkene moiety is more reactive than the glucal alkene moiety. This allows the regio- and stereoselective hydrogenation of the bicyclic alkene moiety giving an enone **21** that can be reduced stereoselectively to an allylic alcohol **22**. Hydroboration of the glucal and bicyclic acetal opening generates a C(1→4) linked disaccharide **25** in which a protected form of β-D-glucopyranose is attached at position C(4) of a α-D-3-deoxy-*ribo*-hexopyranoside derivative via a (*S*)-hydroxymethano linker.

1. Introduction

Carbohydrates regulate the sociology of cells and play a crucial role in the construction of multicellular organs and organisms.[1] With a improved understanding of the functions that cell-surface carbohydrates play in disorders such as inflammation, viral, and bacterial infections, to cancer, etc., numerous carbohydrate analogs have entered clinical studies. Disaccharides containing them offer the advantage of being resistant to acidic and enzymatic hydrolysis.[2,3] They can also be inhibitors of glycosidases and glycosyltransferases.[1m] Since the first syntheses of methylene bridged analogs of maltose (α-D-Glc*p*-*C*(1→4)-α-D-Glc*p*-OMe) and cellobiose (β-D-Glc*p*-*C*(1→4)-α-D-Glc*p*-OMe) by Kishi et al. in 1987,[4] several approaches have been proposed for the preparation of C(1→4)-linked disaccharides.[5,6]

We have shown that the Oshima–Nozaki[7] condensation of monosaccharide-derived carbaldehydes **1** and isolevoglucosenone **2** allows quick access to C(1→3)-linked disaccharides[8,9] and C(1→3)-imino-disaccharides[9] (Scheme 1). A convergent synthesis of C(1→2)- and C(1→4)-linked imino-disaccharides was realized by applying Takai–Oshima–Nozaki–Kishi coupling of



Scheme 1.

hydroxyproline-derived carbaldehydes with levoglucosenone[11] and isolevoglucosenone-derived triflates.[10,11] Witczak et al.[12] have shown that levoglucosenone undergoes Michael addition of glycosylnitromethanes. Through this reaction they prepared C-linked analogs of β-D-glucopyranosyl-(1→4)-3-deoxy-D-*ribo*-hexopyranose.

2. Results and discussion

In 1997 our group showed that C-glycosides and advanced C(1→1)-disaccharide precursors can be obtained in one step through carbonylative Stille cou-

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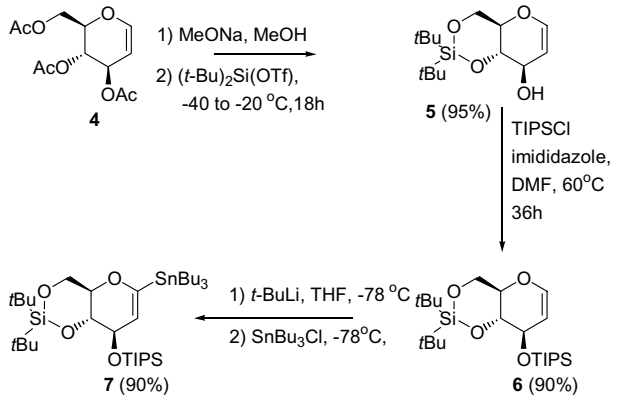
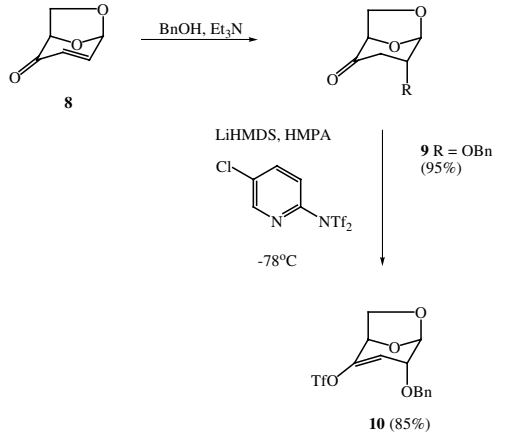


Scheme 2.

pling reactions.[13] We report here that tinglucal derivative **7**[14] and isolevoglucosenone-derived triflate **10** can also be coupled in a carbonylative Stille reaction.[15] Tinglucal **7** was obtained by deprotecting the fully acetylated glucal **4** with MeONa/MeOH. The 4- and 6-hydroxyl-positions were protected by $(t\text{-Bu})_2Si(OSO_2CF_3)_2$ in anhydrous DMF (−40 to −20 °C, over 18 h), to give **5** in 95% yield. Finally the last free hydroxyl group was silylated with TIPSCl/imidazole (DMF, 50 °C, 36 h) giving **6**. Treatment of **6** with *t*-BuLi, followed by Bu_3SnCl furnished the tinglucal derivative **7** in 90% yield (Scheme 2).

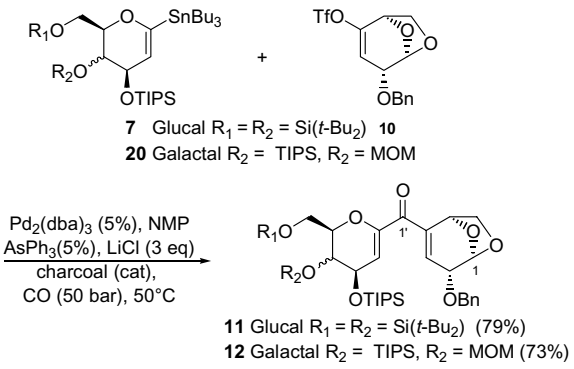
Triflate **10**[10] was synthesized starting from isolevoglucosenone, which undergoes a 1,4-addition of BnOH in the presence of Et_3N. By deprotonation with LDA, followed by quenching of the resulting enolate with 2-*N*,*N*-[bis(trifluoromethanesulfonyl)amino]-5-chloropyridine triflate **10** was obtained in 85% yield (Scheme 3).



Scheme 3.

The carbonylative Stille cross-coupling[16,17] of tinglucal **7** with triflate **10**[11] was possible using $Pd_2(dba)_3$ in the presence of Ph_3As (5 mol %), LiCl (3 equiv), powdered charcoal, and 50 bar atmosphere of CO and heating to 50 °C (Scheme 4).

At higher temperatures only direct coupling between the tinglucal **7** and triflate **10** was observed. At lower temperatures no reaction took place and the starting materials were recovered (Table 1). The temperature range under which the reaction can be carried out varies from 45 to 55 °C.



Scheme 4.

Table 1. Attempted carbonylative Stille cross-coupling of **7** and **10**

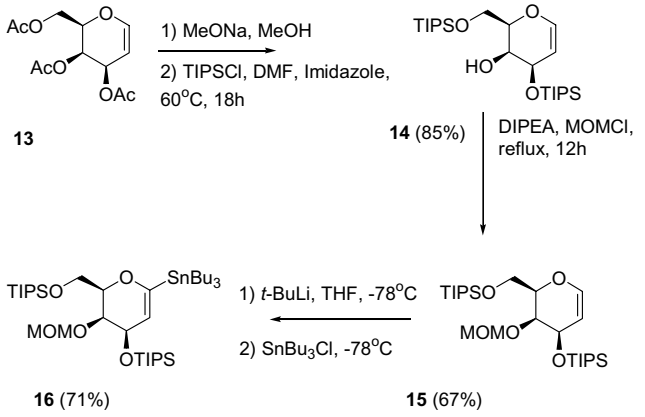
Entry	Conditions[a]	Yield of **11** (%)
1	CO (50 bar), 50 °C, LiCl (1 equiv) charcoal (powder), NMP	23
2	CO (50 bar), 50 °C, LiCl (2 equiv) C (powder), NMP	35
3	CO (50 bar), 50 °C, LiCl (3 equiv) C (powder), NMP	79
4	CO (50 bar), 50 °C, LiCl (4 equiv) C (powder, catalytic), NMP	57
5	CO (50 bar), 50 °C, LiCl (3 equiv) C (solid), NMP	0
6	CO (50 bar), 50 °C, LiCl (3 equiv) C (powder), THF	0
7	CO (50 bar), 50 °C, LiCl (3 equiv) C (powder), THF	45
8	CO (50 bar), 50 °C, C (powder), THF	0
9	CO (50 bar), 60 °C, LiCl (3 equiv) C (powder), NMP	0[b]
10	CO (40 bar), 40 °C, LiCl (3 equiv) C (powder), NMP	0
11	CO (60 bar), 50 °C, LiCl (1 equiv) C (powder), NMP	0

[a] Pd_2dba_3 (5 mol wt %), $AsPh_3$ (5 mol wt %).
[b] Only self-coupled product obtained.

We investigated also the influence of CO-pressure on the outcome of the reaction. The optimum working pressure appears to be 50 bar (Table 1, entries 1–4, 7), above 60 bar (entry 11) no reaction took place and the starting materials decomposed, below 40 bar (entry 10) no reaction took place. The yield was the best (79%, entry 3) using *N*-methylpyrrolidone (NMP) as solvent. The amount of LiCl is crucial for success. With a Pd/LiCl ratio of 1:1 the yield is rather low (23% entry 1). Optimal Pd/LiCl ratio is 1:3 and for Pd(0)/Ph_3As the ratio must be 1:1. Replacement of Ph_3As for Ph_3P or the use of solid charcoal instead of powdered charcoal failed to give product of carbonylative coupling! This is explained by the property of powdered charcoal to disperse metallic palladium and to allow efficient resolubilization into active catalytical species. Other protected glucal (4,6-*O*-

isopropylidene-3-*O*-methoxymethyl, 4,6-*O*-isopropylidene-3-*O*-tri(isopropyl) and 3-*O*-[(*t*-butyl)dimethylsilyl]-tinglucal) than **7** also undergo carbonylative Stille couplings with triflate **10** under our optimal conditions, but with lower yields. Moreover, the subsequent conversions of the corresponding cross-conjugated dienones were lower yielded than those described here.

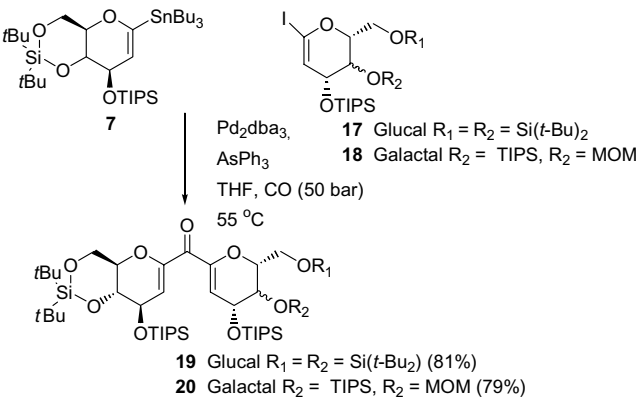
It was also possible to couple triflate **10** with stannylated galactal **16**. This galactal was synthesized starting from fully acetylated galactal **13**. Methanolysis (MeONa/MeOH) of **13** followed by silylation with $(i\text{-Pr})_3SiCl$/imidazole in DMF provided the silylated ether **14**. The sterically hindered HO–C(2) moiety was then protected as a methoxymethyl ether with $MeOCH_2Cl$/Hünig's base under heating. Finally, **15** was stannylated by treatment with *t*-BuLi and subsequent reaction with $SnBu_3Cl$ (Scheme 5). The tin-galactal **16** has been cross-coupled with CO and triflate **10** giving **12** in 73% yield. The yield of this coupling is somewhat lower than for the reaction **7**+**10**+CO→**11** (79%), perhaps because of greater steric hindrance with **16** than with **7**. With these new conditions for the Stille coupling we examined whether it could be applied to the carbonylative cross-coupling of two glucal derivatives, a logical approach for the preparation of C(1→1)-linked disaccharide precursors.[13]



Scheme 5.

Thus, the iodinated glucal derivative **17** was made by iodination of the tinglucal **7**. Reaction of **17**+CO+**7** under our optimized conditions (Table 1) led to dienone **19** that was isolated in 81% yield (Scheme 6). This is a significant improvement compared to our preliminary work.[13] Also cross-coupling of **7**+**18**+CO under the same conditions led to dienone **20** in 79%. To our surprise however, when tin-galactal derivative **16** was combined with the corresponding iodogalactal **18** and CO, no product of cross-coupling could be detected. This failure is probably due to the greater bulk of **20** and its iodo-analog than in the glucal derivatives **7** and **17** (Scheme 6).

The cross-conjugated dienone **11** has been converted into a C(1→4)-linked disaccharide glycosyl donor (Scheme 7). Which combines β-D-glucopyranosyl unit with a 3-deoxy-D-*ribo*-hexopyranosyl moiety through a

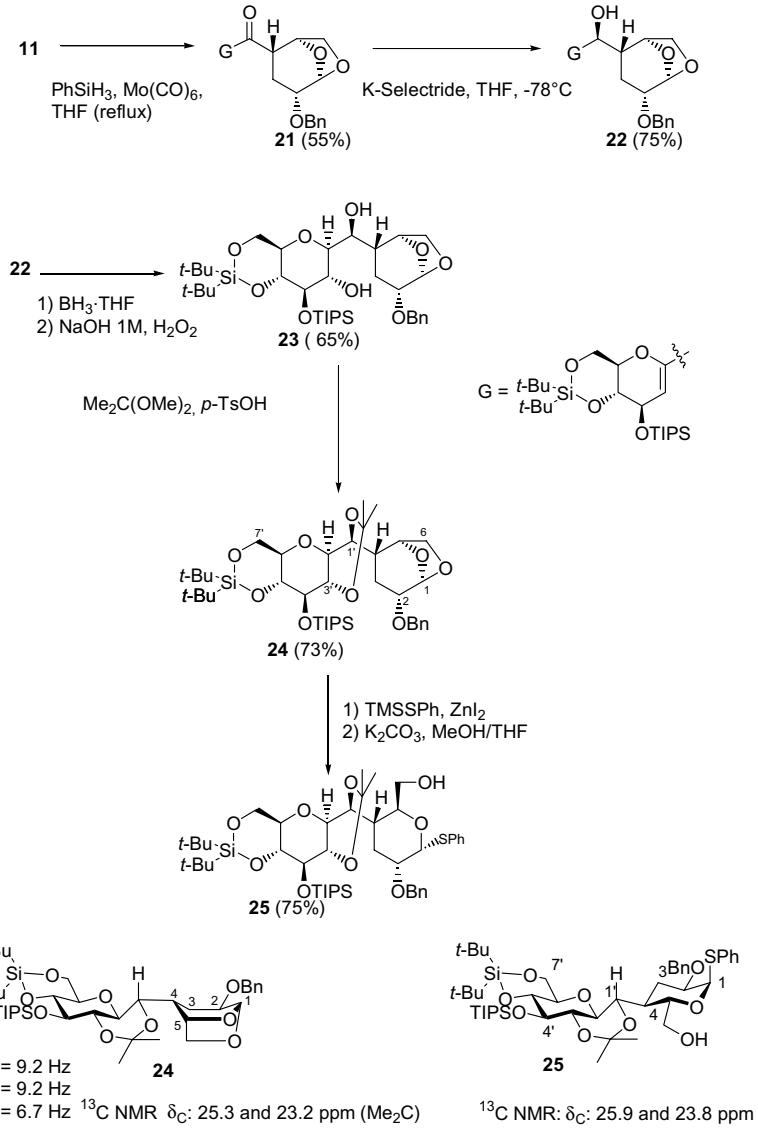


Scheme 6.

(*S*)-hydroxymethano linker. Probably because of the ring-strain of the 1,6-anhydrohexose unit of **11** its C(2,3)-double bond is more reactive than the double bond of the glucal moiety. For instance, chemo- and stereoselective hydrogenation of the bicyclic alkene could be carried with $PhSiH_3$ in the presence of $Mo(CO)_6$ as catalyst, giving enone **21** in 55% yield. The structure of **21** was deduced from its ^1H NMR ($^3J_{3a,4} = 1.2$, $^3J_{3b,4} = 6.7$, and $^3J_{4,5} = 0.6$) and 2D-NOESY-^1H NMR spectrum. Reduction of **21** with $(i\text{-Bu})_2AlH$ gave a 2:1 mixture of allylic alcohol **22** and its diastereomer in 85% yield. With K-Selectride only **22** was formed and isolated in 75% yield. Hydroboration (BH_3·THF) of **22** gave diol **23** (65%) with high diastereoselectivity, probably because the α-face of the glucal alkene moiety is less sterically hindered then its β-face. The β-C-D-glucopyranosyl configuration was confirmed by the vicinal coupling constants $^3J_{2',3'} = 10.4$ and $^3J_{3',4'} = 9.2$ Hz and by the 2D-NOESY-^1H NMR spectrum of **23**. Protection of diol **23** as an acetonide under standard conditions ($Me_2C(OMe)_2$, *p*-TsOH) produced **24** (73%). Its ^1H NMR spectrum displays typical coupling constants for proton pairs H-4/H-5 (1.2 Hz), H-2′/H-3′ (9.2 Hz), H-3′/H-4′ (9.2 Hz). The (1′*S*)-configuration was indicated by $^3J_{1',2'} = 6.7$ Hz and confirmed by the ^{13}C NMR spectrum: δ_C (Me_2C) = 25.3 and 23.2 ppm.[18] Although the 1,6-anhydrohexose **24** is a potential glycosyl donor, we converted it into the thioglycoside **25**, another potential glycosyl donor. Thus treatment of **24** with Me_3SiSPh and ZnI_2 provided **25** in 75% yield, after work up with K_2CO_3/MeOH. The ^1H NMR spectrum of **25** proved its structure, in particular $^3J_{1,2} = 4.9$ Hz, indicated α-thioglycosylation, and $^3J_{1',2'} = 6.7$, $^3J_{2',3'} = 9.4$, and $^3J_{3',4'} = 7.6$ Hz proved the β-glucopyranosyl structure. The (1′*S*)-configuration was confirmed by the ^{13}C NMR spectrum[18] which showed δ_C (Me_2C) = 25.9 and 23.7 Hz (Scheme 7).

3. Conclusion

Since our first report on the application of the carbonylative Stille cross-coupling reaction generating C(1→1)-disaccharide precursors, better conditions have been developed that allow one to create readily advanced precursors for C(1→4)-disaccharides. The method condenses adequately protected tinglucal derivatives



Scheme 7.

with a triflate derived from isolevoglucosenone and carbon monoxide. For one of the cross-conjugated dienones so obtained **11** we demonstrated interesting chemo- and stereoselectivity in its reduction reaction with $PhSiH_3/Mo(CO)_6$ first, and then with K-Selectride. After hydroboration of the allylic alcohol and standard transformations a protected C(1→4) disaccharide in which a β-D-glucopyranosyl group is C-linked at C(4) of a phenylthio-3-deoxy-α-D-ribopyranoside via a linker has been prepared for the first time.

4. Experimental

4.1. General remarks

Commercial reagents (Fluka, Aldrich) were used without purification. Solvents were distilled prior to use: THF from Na and benzophenone. Sulfur dioxide was dried by passing through a column filled with P_2O_5, Al_2O_3 for drying (Fluka 06400), Al_2O_3 basic activated Type 5016A Brockman I (Aldrich 19,944-3). Light petroleum ether used refers to the fraction boiling at 40–60 °C. Solutions after reactions and extractions were evaporated in a rotatory evaporator under reduced pressure. Liquid/solid flash chromatography (FC): columns of silica gel (0.040–0.63 mm, Merck no 9385 silica gel 60, 240–400 mesh). TLC for reaction monitoring: Merck silica gel $60F_{254}$ plates; detection by UV light; Pancaldi reagent [$(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O] or $KMnO_4$. IR spectra: Perkin-Elmer-1420 spectrometer. ^1H NMR spectra: Bruker-ARX-400 spectrometer (400 MHz); δ (H) in parts per million relative to the solvent's residual ^1H signal [$CHCl_3$, δ (H) 7.27] as internal reference; all ^1H assignments were confirmed by 2D-COSY-45 spectra. ^{13}C NMR spectra: same instrument as above (100.6 MHz); δ (C) in parts per million relative to solvent C-signal [$CDCl_3$, δ (C) 77.0] as internal reference; coupling constants J in hertz. MS: Nermag R-10-10C, chemical ionization (NH_3) mode m/z (amu) [% relative base peak (100%)], HRMS: Jeol AX-505. Elemental analyses: Ilse Beetz, D-96301 Kronach, Germany.

4.2. (−)-4,6-*O*-Bis(*tert*-butylsilylidene)-3-*O*-tris(isopropyl)silyl-D-glucal 6

Compound **5**[16] (3.4 g, 11.91 mmol) was dissolved in anhyd DMF (68 mL) and a mixture of imidazole (2.0 g, 29.58 mmol), and tri(isopropyl)chlorosilane (4.5 mL, 21.34 mmol) was added dropwise under stirring at 20 °C. After stirring at 60 °C for 36 h, the mixture was cooled to 20 °C and hexane (300 mL) was added. The solution was washed with water (120 mL, three times) and brine (120 mL). The water phase was extracted with hexane (100 mL, two times). The organic phases were combined, dried over $MgSO_4$, and concentrated in vacuo. FC (AcOEt/light petroleum ether, 0.2:10) 5.1 g (90%), colorless oil. $[\alpha]_{589}^{25} = -54$, $[\alpha]_{577}^{25} = -57$, $[\alpha]_{546}^{25} = -65$, $[\alpha]_{435}^{25} = -115$, $[\alpha]_{405}^{25} = -139$ (*c* 1.21, $CHCl_3$); IR (film): *v* 2940, 2860, 1650, 1470, 1390, 1360, 1300, 1240, 1170, 1130, 1080, 1070, 1000, 940, 880, 830, 770; ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 6.24 (dd, $^3J_{1,2} = 6.1$, $^4J_{1,3} = 1.5$, H-1), 4.69 (dd, 1H $^3J_{2,3} = 1.9$, H-2), 4.43 (dd, 1H, $^3J_{3,4} = 6.9$, H-3), 4.16 (dd, 1H, $^2J_{6,6} = 10.3$, $^3J_{5,6} = 5.0$, H-6), 4.01 (dd, 1H, $^3J_{4,5} = 10.3$, H-4), 3.97 (dd, 1H, $^3J_{5,6} = 10.2$, H-6), 3.81 (ddd, 1H, H-5); 1.20–1.10 (m, 21H, TIPS); 0.99, 1.06 (2s, 18H, $(t\text{-Bu})_2$Si); ^{13}C NMR ($CDCl_3$, 100.6 MHz): *δ* 142.7 (d, 189, C-1), 105.3 (d, 165, C-2), 77.5, 72.7, 70.7 (3d, 145, C-3, C-4, C-5), 65.9 (t, 145, C-6), 27.4, 26.9 (2q, 125, (CH$_3$CSi)), 22.7, 19.8 (2s, $(CH_3)_3C$Si), 18.1 (q, 125, $(C$H$_3)_2$CHSi), 12.4 (d, 120, (CH_3CSi)), CI-MS (NH_3): 442 ($[M]^+$, 1), 399 (5), 317 (11), 269 (36), 229 (2), 119 81 (100); Anal. Calcd for $C_{35}H_{72}O_4Si_2Sn$: C, 62.39; H, 10.47. Found: C, 62.26; H, 10.38.

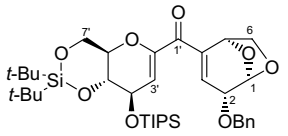
4.3. (−)-4,6-*O*-[Di(*tert*-butylsilylidene)]-1-tributylstannyl-3-*O*-tris(isopropyl)-D-glucal 7

tert-Butyllithium (1.5 M in THF, 25 mL, 40.5 mmol) was added dropwise to a stirred solution of (27 g, 6.11 mmol) in anhyd THF (135 mL), cooled to −78 °C. After stirring at 0 °C for 1 h, it was cooled to −78 °C and tributyltin chloride (11 mL, 40.80 mmol) was added dropwise under stirring. After additional stirring at −78 °C for 30 min, the mixture was quenched by water (270 mL). The water phase was extracted by light petroleum ether (270 mL, three times). The organic phases were combined, dried over $MgSO_4$, and concentrated in vacuo. FC (AcOEt/light petroleum ether, 8/1000) 4.0 g (90%), colorless oil. $[\alpha]_{589}^{25} = -31$, $[\alpha]_{577}^{25} = -34$, $[\alpha]_{546}^{25} = -39$, $[\alpha]_{435}^{25} = -68$, $[\alpha]_{405}^{25} = -82$ (*c* 1.15, $CHCl_3$); IR (film): *v* 3580, 3360, 2930, 2890, 2860, 1605, 1460, 1360, 1250, 1160, 1100, 1080, 1060, 1010, 990, 885, 820, 770, 680; ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 4.69 (dd, 1H $^3J_{2,3} = 1.9$, H-2), 4.39 (dd, 1H, $^3J_{3,4} = 7.0$, H-3), 4.11 (dd, 1H, $^2J_{6,6} = 10.3$, $^3J_{5,6} = 5.0$, H-6); 3.96 (dd, 1H, $^3J_{4,5} = 10.3$, H-4), 3.90 (dd, 1H, $^3J_{5,6} = 5.2$, H-6), 7,31 (ddd, 1H, H-5); 1.55–1.49, 1.35–1.21, 0.94–0.86 (3m, 27H, Bu_3Sn), 1.20–1.10 (m, 21H, TIPS), 0.99, 1.06 (2s, 18H, $(t\text{-Bu})_2$Si); ^{13}C NMR ($CDCl_3$, 100.6 MHz): *δ* 162.1 (s, C-1), 116.1 (d, 164, C-2), 77.7, 73.0, 71.5 (3d, 145, C-3, C-4, C-5), 66.2 (t, 145, C-6), 28.8, 27.1 (2t, 130 and 1t, 166 (CH_3CH$_2C$H$_2C$H$_2)_3$Sn), 27.4, 26.9 (2q, 145, (CH$_3$CSi)), 22.7, 19.8 (2s, $(CH_3)_3$CSi), 18.1 (q, 125, $(CH_3)_2$CHSi), 13.7 (q, 125, (CH$_3$CH$_2$CH$_2$CH$_2)_3$Sn), 12.3 (d, 125, (CH_3CSi)); CI-MS (NH_3): 675 ($[M-t\text{-Bu}]^+$, 21), 441 (11), 369 (8), 291 (16), 235 (22), 119 (38), 81 (100); Anal. Calcd for $C_{23}H_{46}O_4Si_2C$: 62.39, H, 10.47. Found: C, 62.26; H, 10.38.

4.4. (−)-1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-4-*O*-[(trifluoromethyl)sulfonyl]-β-D-*erythro*-hex-3-eno-pyranose 10

n-BuLi (1.6 M in hexane, 1.00 mL, 1.6 mmol) was added dropwise to a solution of $(Me_3Si)_2$NH (0.34 mL, 1.63 mmol) in 6 mL of THF at 0 °C. The mixture was stirred at 0 °C for 15 min and cooled to −78 °C. HMPA (0.080 mL) was added followed by a solution of **9** (190 mg, 0.236 mmol) in 1.0 mL of THF. Stirring was continued at this temperature for 2 h. 2-[*N*,*N*-Bis(trifluoromethylsulfonyl)amin]-5-chloropyridine (640 mg, 1.63 mmol) was then added in one portion. The mixture was stirred for 2 h and warmed to 20 °C. Water (1 mL) was added. The solution was extracted with Et_2O (5 mL, three times). The combined organic phases were dried (anhyd Na_2SO_4) and the solvent was removed in vacuo. FC (3:97 EtOAc/light petroleum ether) 258 mg (85%), colorless oil. $[\alpha]_{589}^{25} = -71$, $[\alpha]_{577}^{25} = -73$, $[\alpha]_{546}^{25} = -85$, $[\alpha]_{435}^{25} = -154$, $[\alpha]_{405}^{25} = -185$ (*c* 1.5, $CHCl_3$); IR (film): *v* 2965, 1672, 1452, 1362, 1214, 1138, 1069; ^{13}C NMR ($CDCl_3$, 100.6 MHz): *δ* 7.45–7.22 (m, 5H, Ph), 5.75 (dt, $^3J_{2,3} = 4.2$, $^4J_{1,3} = {}^4J_{3,5} = 1.2$, H-3), 5.60 (s, H-1), 4.78 (d, $^3J_{5,6} = 4.2$, H-5), 4.66 (s, 2H, PhCH$_2$O), 3.95 (d, $^2J = 7.3$, Ha-6), 3.83 (d, $^3J_{2,3} = 4.2$, H-2), 3.76 (dd, $^3J_{5,6b} = 4.2$, Hb-6); ^{13}C NMR ($CDCl_3$): *δ* 149.9 (s, C-4), 137.3 (s, Ph), 128.6 (d, 161, Ph), 128.2 (d, 161, Ph), 127.9 (d, 158, Ph), 113.2 (d, 170, C-3), 100.5 (d, 181, C-1), 73.0 (d, 149, C-2), 71.8 (t, 141, PhCH$_2$O), 71.6 (d, 149, C-2), 68.9 (t, 152, C-6); CI-MS (NH_3): 384 ($[M+NH_4]^+$, 2), 178 (2), 97 (12), 91 (100), 90 (2), 89 (1), 77 (2); Anal. Calcd for $C_{14}H_{13}O_6F_3S$: C, 45.90; H, 3.58; S, 8.75. Found: C, 45.99; H, 3.62; S, 8.57.

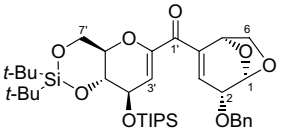
4.5. (−)-((1*S*,4*R*,5*S*)-4-(Benzyloxy)-6,8-dioxabicyclo[3.2.1]-oct-2-en-yl)((4a*R*,8*R*,8a*R*)-2,2-di-*tert*-butyl-8-((triisoprop- ylsilyl)oxy)-4,4a,8,8a-tetrahydropyrano-[3,2-*d*] [1.3.2]dioxasilin-6-yl)methanone 11



In a reaction tube dried under vacuum were placed, under argon, $Pd_2(dba)_3$ (225 mg, 0.25 mmol) and triphenylarsine (80 mg, 0.25 mmol). The flask was degassed, on the vacuum line and filled with argon (three times). The catalyst was dissolved in NMP (10 mL) and lithium chloride (140 mg, 0.75 mmol) and a small amount of activated charcoal were added (weighted in a glove box). Then the organostannane **7** (1.2 g, 1.25 mmol) in NMP (10 mL) and triflate **10** (450 mg, 1.25 mmol) in NMP (10 mL) were added. The reaction mixture was placed in a stainless steel autoclave and stirred for

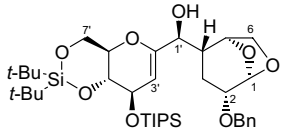
18 h under CO (50 bar) at 50 °C. After releaving pressure, the reaction was quenched by 5 mL of aqueous KF (1 M) solution and stirred for 5 min. Then the solution was filtered through a pad of Celite and rinsed with ether. The aqueous layer was extracted again with ether. The organic phases were combined, dried ($MgSO_4$), and concentrated in vacuo. FC (light petroleum ether/EtOAc 95:5) 600 mg (79%), colorless oil. $[\alpha]_{589}^{25} = -14$, $[\alpha]_{577}^{25} = -11$, $[\alpha]_{546}^{25} = -12$, $[\alpha]_{435}^{25} = -24$, $[\alpha]_{405}^{25} = -34$ (*c* 3.5, $CHCl_3$); IR (film): *v* 2924, 1740, 1652, 1471, 1364, 1234, 1012, 902, 828, 772, 651; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.3–7.2 (m, 5H, C_6H_5), 6.75 (m, $^3J_{2,3}$ 2.4, H-3), 5.73 (d, 1H, $^3J_{2',3'} = 2.4$, H-3′), 5.58 (s, 1H, H-1), 5.14 (d, $^3J_{5,6b} = 4.0$, H-5), 4.50 (s, 2H, CH_2Ph), 4.56 (dd, 1H, 2,4, $^3J_{4',5'} = 7.1$, H-4′), 4.27 (q, 1H, $^2J_{6,6} = 10.3$, $^3J_{5,6}$ 4.9, H-7′a), 4.1–4.0 (m, 2H, H-5′, 7′b), 3.95 (m, 1H, H-6′), 3.74 (1H, $^2J_{6a,6b} = 4.0$, H-6a), 3.7-3.6 (m, 2H, H-2, H-6b), 1.2–0.9 (m, TIPS, Si(*t*-Bu)$_2$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 186.4 (s, C-1′), 148.9 (s, C-2′), 140.1 (s C-4), 135.2 (CH_2–*Ph*) 128.5–127.8 (Ph), 134.0 (d, 160, C-3′) 115.0 (d, 160, C-3) 100.2 (d, 170, C-1), 73.7 (d, 140, C-4′), 72.1 (d, 140, C-5′), 70.9 (C-5), 70.3 (d, 140, C-2), 69.9 (d, 140, C-6′), 71.5 (t, 150, *C*$_2$Ph), 68.8 (t, 150, C-6), 66.0 (t, 150, C-7′), 27.6, 27.0 (2q, 130, Si(C(*C*H$_3$)$_3$)$_2$), 22.8 (s, Si(*C*(CH$_3$)$_3$)$_2$), 18.1 (q, 12.2 (d, 120, Si*C*H(CH$_3$)$_2$)); CI-MS (NH_3): 704 ([M+18]$^+$, 100), 687 (M+1, 55), 643 (16), 613 (5), 513 (14), 461 (22), 384 (42), 286 (12), 235 (22), 201 (86); HRMS: Calcd for $C_{37}H_{58}O_8Si_2Na$: 709.35679. Found: 709.35251 ([M+Na$^+$]).

4.6. (−)-((1*S*,4*R*,5*S*)-4-(Benzyloxy)-6,8-dioxabicyclo[3.2.1]-oct-2-yl)((4a*R*,8*R*,8a*R*)-2,2-di-*tert*-butyl-8-((triisopropylsilyl)oxy)-4,4a,8,8a-tetrahydropyrano[3,2-*d*] [1.3.2]dioxasilin-6-yl)methanone 21



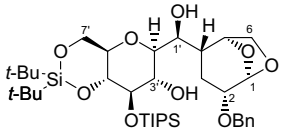
Compound **11** (1.3 g, 8.56 mmol) was dissolved in THF (10 mL), degassed by argon, and placed under argon atmosphere. Afterwards $Mo(CO)_6$ (84 mg, 0.32 mmol) together with phenylsilane (1.2 mL, 9.6 mmol equiv) were added. The mixture was heated under reflux for 4 h, and quenched by slow addition of water (0.01 mL). The reaction mixture was concentrated, water was added, and the mixture was extracted with ether (10 mL, five times). The organic solution was dried ($MgSO_4$) and the solvent evaporated in vacuo. FC (Florisil, light petroleum ether/EtOAc 9:1), 750 mg (55%) colorless oil. $[\alpha]_{589}^{25} = -57$ $[\alpha]_{577}^{25} = -47$, $[\alpha]_{546}^{25} = -27$, $[\alpha]_{435}^{25} = -26$, $[\alpha]_{405}^{25} = -33$ (*c* 0.55, $CHCl_3$); IR (film): *v* 2943, 2865, 1710, 1637, 1471, 1365, 1192, 1111, 1064, 1017, 921, 891, 846, 826; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.80 (d, $^3J_{1,2} = 2.4$, H-1), 5.30 (s, 1H, H-3′), 4.80 (d, $^3J_{4,5} = 0.6$, H-5), 4.55 (dd, $^2J_{H,H} = 10.2$, CH_2Ph) 4.47 (dd, $^3J_{3',4'} = 2.4$, H-4′), 4.09 (dd, 1H, $3J_{7',7b'} = 0.6$, H-7′), 3.99 (m, 1H, H-5′), 4.75 (d, 1H $^3J_{6,7} = 8.0$, H-6), 3.95 (t, 1H, $^3J_{6,7}$ 10.0 H-7′), 3.9–3.8 (m 2H, H-6,6′), 3.75 (dd, $^2J_{6,6} = 2.4$, H-6), 3.45 (d, 1H, $^3J_{3b,4} = 1.2$, H-4), 2.11 (m, 1H, H-2′), 1.90, 1.85 (2dd, 2H, $^3J_{3b,4} = 6.7$, H-3 and H-3′), 1.1–0.9 (m, 41H, 2TIPS, Si(*t*-Bu)$_2$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 194.3 (s, C-1′), 148.6 (s, C-2′), 138.1, 128.6–125.8 (s, 2d 135, Ph), 111.4 (d, 160, C-3′), 101.4 (d, 170, C-1), 77.3 (d, 150, C-6′), 73.3 (t, 145, C-7), 72.1 (t, 140, *C*H_2Ph), 71.8 (d, 140, C-5), 70.9 (d, 135, C-4′), 67.8,(d, 140, C-5′), 65.8 (t, 140, C-7′), 44.8 (d, 145, C-4), 39.1 (t, 145, C-3), 27.6, 27.0 (2q, 130, Si(C(*C*H$_3$)$_3$)$_2$), 22.8 (s, Si(*C*(CH$_3$)$_3$)$_2$), 18.1 (q, 125, SiCH(*C*H$_3$)$_2$), 12.4 (d, 120, Si*C*H(CH$_3$)$_2$); CI-MS (NH_3): 706 ([M+1]$^+$, 5), 645 (1), 513 (15), 455 (25), 430 (10), 258 (8), 83 (100); HRMS: Calcd for Calcd for $C_{37}H_{60}O_8Si_2Na$: 711.3724. Found: 711.3706 ([M+Na$^+$]).

4.7. (−)-(*S*)-((1*S*,4*R*,5*S*)-4-(Benzyloxy)-6,8-dioxabicyclo-[3.2.1]oct-2-yl)((4a*R*,8*R*,8a*R*)-2,2-di-*tert*-butyl-8-((triisopropylsilyl)oxy)-4,4a,8,8a-tetrahydropyrano[3,2-*d*] [1.3.2]dioxasilin-6-yl)methanol 22



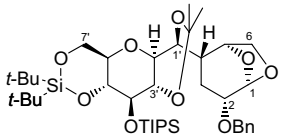
To a solution of **21** (150 mg, 0.26 mmol) in THF (5 mL), cooled at −78 °C, was added dropwise K-Selectride (0.20 mL, 0.3 mmol). The reaction mixture was stirred overnight, allowing the temperature to rise to 20 °C. Then methanol (2 mL) and a satd solution of NH_4Cl in methanol (2 mL) were added. After stirring at 20 °C for 1 h, the mixture was filtered over a pad of Celite. The reaction mixture was concentrated in vacuo. FC (light petroleum ether/EtOAc 8:2) 115 mg (75%), colorless oil. $[\alpha]_{589}^{25} = -43$, $[\alpha]_{577}^{25} = -35$, $[\alpha]_{546}^{25} = -20$, $[\alpha]_{435}^{25} = -18$, $[\alpha]_{405}^{25} = -16$ (*c* 0.5, $CHCl_3$); IR (film): *v* 3434, 2941, 2864, 1668, 1668, 1470, 1388, 1335, 1151, 1107, 1065, 1014, 917, 882, 826, 769, 652; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.3–7.2 (m, 5H, C_6H_5), 5.38 (s, 1H, H-1), 5.05 (s, 1H, H-3′), 4.85 (m, 1H, H-1′), 4.63 (2d, 2H, $^2J_{1,2} = 10.2$, CH_2Ph), 4.54 (d, 2H, $^3J_{3,4}$ 3.6, H-4′), 4.15 (q, 1H, $^2J_{7,7b} = 8.6$, $^3J_{6,7} = 4.8$, H-7′), 3.91–3.51 (m, 4H, H-6′,6, H-5′, H-7′), 3.50 (s, 1H, H-2), 2.07 (d, 1H $^2J_{3,3b} = 12.1$, H-3), 1.88 (m, 2H, H-4, H-3b), 1.2–0.9 (m, TIPS, Si(*t*-Bu)$_2$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 153.9 (s, C-2′) 137.8, 128.5, 127.8 (2d, 120, CH_2*Ph*), 102 (t, 65, C-3′), 100 (d, 160, C-1), 77.9 (d, 150, C-5′), 76.2 (d, 145, C-4′), 73.1 (d, 125, C-1′), 72.4 (d, 150, C-5), 71.4, (d, 145, C-6′), 71.3, 71.0 (t, 150, CH_2Ph, d, 150, C-2), 68.3 (d, 145, C-6), 66.0 (t, 135, C-7′), 38.2 (C-4) 27.4, 27.0 (2q, 130, Si(C(*C*H$_3$)$_3$)$_2$), 22.8 (s, Si(C(*C*H$_3$)$_3$)$_2$), 19.8 (t, 135, C-3) 18.1 (q, 125, SiCH(*C*H$_3$)$_2$), 12.2 (d, 120, Si*C*H(CH$_3$)$_2$); CI-MS (NH_3): 708 ([M+1]$^+$ 3) 647 (1), 517 (5), 477 (1), 415 (1), 258 (8), 83 (100); MALDI-HRMS: Calcd for $C_{37}H_{62}O_8Si_2Na$: 713.3881. Found: 713.3806 ([M+Na$^+$]).

4.8. (−)-(4a*R*,7*S*,8*R*,8a*R*)-6-((1*S*,4*R*,5*S*)-4-(Benzyloxy)-6,8-dioxabicyclo[3.2.1]oct-2-yl)-2,2-di-*tert*-butyl-8-((triisopropylsilyl)oxy)hexahydropyrano[3,2-*d*][1.3.2]dioxasilin-7-ol 23



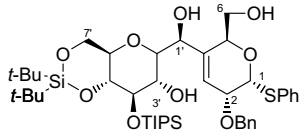
A solution of **22** (150 mg, 0.25 mmol) in dry THF (5 mL) at 0 °C was treated with a borane–THF solution in THF (2 M, 1.5 mL) and stirred at 20 °C overnight. A 10% aq NaOH solution (3 mL) was added, followed by 3 mL of a 30% aq H_2O_2 solution. After stirring at 25 °C for 1 h, the mixture was poured into water and extracted with ethyl ether. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. FC (light petroleum ether/EtOAc 75:25) 100 mg (65%), colorless oil. $[\alpha]_{589}^{25} = -1.4$, $[\alpha]_{577}^{25} = -1.16$, $[\alpha]_{546}^{25} = -0.69$, $[\alpha]_{435}^{25} = -0.69$, $[\alpha]_{405}^{25} = -0.58$ (*c* 0.075, $CHCl_3$); IR (film): *v* 3445, 2923, 2765, 1704, 1695, 1475, 1390, 1317, 1201, 1105, 1077, 1015, 918, 883, 825, 770, 655. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.3–7.2 (m, 5H, C_6H_5), 5.41 (s, 1H, H-1), 4.72 (2d, 2H, $^2J_{1,2} = 10.2$, CH_2Ph), 4.54 (m, 2H, H-1′, H-5), 4.10 (m, 1H, H-7′), 3.91–3.60 (m, 7H, H-6, H-6b, H-5′, H-7′, H-4′, H-2′), 3.51 (dd, 1H, $^3J_{2',3'}$ 10.4, $^3J_{3',4'}$ 9.2, H-3′), 3.36 (m, 1H, H-2), 2.25 (d, 1H $^2J_{3,3} = 12.1$, H-3), 1.94 (m, 1H, H-4), 1.83 (m, 1H, H-3b), 1.2–0.9 (m, TIPS, Si(*t*-Bu)$_2$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 137.8, 128.5, 127.8 (s and 2d, 130, CH_2*Ph*), 100.7 (d, 140, C-1), 79.9 (d, 140, C-2′), 79.5 (t, 145, C-3′), 77.4 (d, 135, C-1′), 75.0 (d, 140, C-4′), 72.4 (t, 135, *C*H$_2$Ph), 71.3,(d, 145, C-2), 71.0 (d, 140, C-5′), 69.2 (d, 140, C-6′), 67.5 (t, 145, C-6), 66.4 (t, 140, C-7′), 39.2 (d, 140, C-4), 27.4, 27.0 (2q, 130 Si(C(*C*H$_3$)$_3$)$_2$), 22.8 (s, Si(*C*(CH$_3$)$_3$)$_2$), 19.8 (t, 135, C-3), 18.1 (q, 125, SiCH(*C*H$_3$)$_2$), 12.2 (d, 120, Si*C*H(CH$_3$)$_2$); CI-MS (NH_3): 726 ([M+1]$^+$, 5), 665 (3) 391 (1), 286 (7), 91 (100) 83 (56); MALDI-HRMS: Calcd for $C_{37}H_{64}O_8Si_2Na$: 713.3881. Found: 713.3856 ([M+Na$^+$]).

4.9. (−)-(4a*R*,6*S*,9a*S*,10*R*,10a*R*)-6-((1*S*,4*R*,5*S*)-4-(Benzyloxy)-6,8-dioxabicyclo[3.2.1]oct-2-yl)-2,2-di-*tert*-butyl-8-((triisopropylsilyl)oxy)hexahydro-4*H*-[1,3]dioxino[4′,5′:5,6]pyrano[3,2-*d*][1.3.2]dioxasiline 24



A solution of **23** (60 mg, 0.08 mmol) in 2,3-dimethoxypropane (5 mL) was treated with *p*-toluenesulfonic acid (pH 3) and stirred at 20 °C under a dry atmosphere of argon. Once TLC showed full conversion satd aq soln of $NaHCO_3$ (10 mL) was added and the organic phase washed with brine (10 mL), water (10 mL), dried ($MgSO_4$), and concentrated in vacuo. FC (light petroleum ether/EtOAc 9:1) 55 mg (73%), colorless oil. $[\alpha]_{589}^{25} = -30$, $[\alpha]_{577}^{25} = -20$, $[\alpha]_{546}^{25} = -12$, $[\alpha]_{435}^{25} = -10$, $[\alpha]_{405}^{25} = -9.9$ (*c* 0.33, $CHCl_3$); IR (film): *v* 2855, 1730, 1470, 1380, 1330, 1220, 1100, 925, 880, 825, 760, 655; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.5–7.2 (m, 10H, *s*-C_6H_5, C_6H_5), 5.75 (d, 1H, $^3J_{1,2} = 4.9$, H-1), 4.65 (dd, 1H, $^3J_{1',2'} = 6.7$, $^3J_{1',4'} = 10.2$, H-1′), 4.60 (dd, $^2J = 11.7$, CH_2Ph), 4.20 (m, 1H, H-7′a), 4.06 (dd, 1H, $^3J_{3',4'} = 9.2$, $^3J_{4',5} = 2.4$, H-4′), 3.9–3.8 (m, 2H, H-6′, H-7′b), 3.75–3.65 (m, 3H, H-5, H-6a, H-5′), 3.56–3.47 (m, 2H, H-3′, H-6b), 3.45 (dd, $^3J_{2',3'} = 9.2$, 1H, H-2′), 3.37 (m, 1H, H-2), 2.13 (m, H-3a), 2.02 (dd, $^3J_{3a,4} = 10.5$, $^3J_{4,5} = 1.2$, 1H, H-4), 1.53 (m, 1H, H-3b), 1.37, 1.30 (2s, 3H, CH_3–C–CH_3), 1.2–0.9 (m, TIPS, Si(*t*-Bu)$_2$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 138.6 (s, CH_2*Ph*), 128.5, 127.8 (2d, 120, CH_2*Ph*), 101 (d, 140, C-1), 100 (s, CH_3–*C*–CH_3), 79.8 (d, 130, C-5), 77.8 (d, 130, C-2′), 76.5 (t, 135, C-3′), 76.4 (d, 140, C-6′), 73.6 (d, 145, C-1′), 72.6 (d, 135, C-2), 71.0 (t, 150, CH_2Ph), 69.5 (t, 140, C-6), 68.2 (d, 125, C-4′), 67.6 (d, 130, C-5), 66.6 (t, 125, C-7′), 35.8 (d, 135, C-4), 27.4, 27.0 (2q, 130, Si(C(*C*H$_3$)$_3$)$_2$), 25.3, 23.2 (2q, 130, C*H*$_3$–C–*C*H$_3$), 22.8 (s, Si(C(CH$_3$)$_3$)$_2$), 19.9 (t, 130, C-3), 18.1 (q, 125, SiCH(*C*H$_3$)$_2$), 12.2 (d, 120, Si*C*H(CH$_3$)$_2$); CI-MS (NH_3): 766 ([M+1]$^+$, 1), 749 (10), 647 (3), 517 (8), 409 (1), 266 (3), 201 (6), 91 (100); HRMS: Calcd for $C_{40}H_{68}O_9Si_2Na$: 771.42996. Found 771.43494 ([M+Na$^+$]).

4.10. (−)-((2*S*,5*R*,6*S*)-5-(Benzyloxy)-3-((4a*R*,6*S*,9a*S*,10*R*,10a*R*)-2,2-di-*tert*-butyl-8,8-dimethyl-10-((triisopropylsilyl)oxy)hexahydro-4*H*-[1,3]dioxino[4′,5′:5,6]pyrano[3,2-*d*][1.3.2]dioxasilin)-6-(phenylthio)tetrahydro-2*H*-pyran-2-yl)methanol 25



To a solution of **24** (30 mg, 0.045 mmol) and TMSSPh (0.05 mL, 0.135 mmol) in CH_2Cl_2 was added portionwise under argon atmosphere ZnI_2 (0.3 mg, 0.045 mmol). The resulting suspension was stirred at 20 °C for 1 h, diluted with EtOAc and filtered through a Celite pad. The filtrate was washed successively with satd aq soln of $NaHCO_3$ (10 mL) and water (10 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue was dissolved in dry THF/MeOH (1:1, 2 mL) containing K_2CO_3. The mixture was stirred for 10 min at 20 °C, diluted with EtOAc (5 mL), washed successively with brine (10 mL) and water (10 mL), dried ($MgSO_4$), and concentrated. FC (light petroleum ether/EtOAc 8:2) 20 mg (75%), colorless oil. $[\alpha]_{589}^{25} = -112$, $[\alpha]_{577}^{25} = -8.6$, $[\alpha]_{546}^{25} = -13$, $[\alpha]_{435}^{25} = -9.8$, $[\alpha]_{405}^{25} = -36$ (*c* 2.9, $CHCl_3$); IR (film): *v* 3444, 2863, 1715, 1581, 1470, 1456, 1396, 1386, 1096, 921, 884, 921, 884, 828, 740, 684, 654; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.3–7.2 (m, 5H, C_6H_5), 5.38 (s, 1H, H-1), 4.64 (m, 1H, H-5), 4.63 (d, 2H, $^2J = 11.1$, CH_2Ph), 4.58 (dd, 1H, $^3J_{1',2'} = 6.8$, $^3J_{1',4} = 10.8$, H-1′), 4.10 (dd, 1H, $^2J_{7a',7b'} = 9.6$,

$^{3}J_{6',7'}$ = 4.8, H-7a′), 3.85–3.75 (m, 4H, H-6′, H-6a, H-7b′, H-5′), 3.72 (dd, 1H, $^{3}J_{2',3'}$ = 9.2, H-2′), 3.65 (dd, 1H, $^{3}J_{3',4'}$ = 9.2, H-3′), 3.39 (m, 2H, H-6b, H-4′), 3.26 (dd, 1H, $^{3}J_{2,3}$ = 4.9, $^{3}J_{1,2}$ = 2.4, H-2), 2.15 (d, 1H $^{2}J_{3a,3b}$ = 13.1, H-3a), 1.84 (m, 1H, H-4), 1.73 (m, 1H, H-3b), 1.34, 1.23 (2s, 3H, CH_3–C–CH_3), 1.2–0.9 (m, TIPS, Si(*t*-Bu)$_2$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 137.8, 128.4, 127.8 (s, 2d, 130, CH_2*Ph*, S*Ph*), 88.1 (s, C-1), 87.6 (s, CH_3–*C*–CH_3), 78.9 (d, 120, C-5), 77.3 (d, 123, C-3′), 77.2 (d, 125, C-5′), 74.3 (t, 130, C-6′), 73.6 (C-2), 72.6 (d, 125, C-1′), 71.5 (d, 140, C-2′), 71.3 (t, 140, *C*H_2Ph), 66.9 (d, 130, C-4′), 66.7 (d, 140, C-7′), 64.6 (t, 145, C-6), 40.8 (d, 125, C-4), 27.5, 27.0 (2q, 130, Si(C(*C*H_3)$_3$)$_2$), 25.9, 23.8 (2q, 140, C*H*$_3$–C–*CH*$_3$), 22.8 (s, Si(C(CH$_3$)$_3$)$_2$), 19.9 (t, 130, C-3), 18.1 (q, 125, SiCH(*C*H$_3$)$_2$), 12.2 (d, 120, Si*C*H(CH$_3$)$_2$); CI-MS (NH_3): 592 ([M+18]$^+$, 25), 575 ([M+1]$^+$, 5), 592 (25), 564 (41), 485 (63), 438 (10), 409 (5), 348 (5), 291 (2), 201 (3), 91 (100); MALDI-HRMS: Calcd for $C_{46}H_{74}O_9SSi_2Na$: 881.4489. Found: 881.4409 ([M+Na$^+$]).

4.11. (−)-3,6-*O*-Bis(triisopropylsilyl)-D-galactal 14

To a solution of tri(*O*-acetyl)-D-galactal **13** (4.0 g, 14.69 mmol) in methanol (60 mL) was added a solution of MeONa in methanol (5.4 M, 300 μL, 1.62 mmol). After stirring at 20 °C for 1 h the solvent was evaporated in vacuo. The crude oil was dissolved in anhyd DMF (10 mL) and the solvent was evaporated in vacuo. After having redissolved the crude oil in DMF (65 mL), imidazole was added (8.0 g, 117.5 mmol), followed by a dropwise addition of triisopropylsilyl chloride (13.0 mL, 61.36 mmol). The mixture was stirred at 60 °C for 18 h, then pentane (500 mL) was added and the solution washed with water (140 mL, five times) and brine (140 mL). The water phase was extracted with pentane (100 mL, twice). The combined organic phases were dried ($MgSO_4$), and concentrated in vacuo. FC (Et_2O/light petroleum ether, 1/9) 5.3 g (85%), colorless oil. $[\alpha]_{589}^{25} = -34$, $[\alpha]_{577}^{25} = -37$, $[\alpha]_{546}^{25} = -41$, $[\alpha]_{435}^{25} = -79$, $[\alpha]_{405}^{25} = -97$ (*c* 1.28, $CHCl_3$); IR (film): *v* 3550, 3070, 2940, 2860, 1640, 1460, 1380, 1240, 1160, 1140, 1090, 1010, 995, 880, 850, 810, 680; ^{1}H NMR (C_6D_6): δ 6.34 (dd, 1H, $^{3}J_{1,2}$ = 6.3, $^{4}J_{1,3}$ 1.5, H-1), 4.56 (dd, 1H, $^{3}J_{2,3}$ = 1.9, $^{4}J_{2,4}$ 1.9, H-2), 4.49 (dd, 1H, $^{3}J_{3,4}$ = 4.7, H-3), 4.34 (dd, $^{2}J_{6,6}$ = 9.6, $^{3}J_{5,6}$ = 7.7, H-6), 4.16 (dd, $^{3}J_{4,5}$ = 2.0, $^{4}J_{2,4}$ = 1.9, H-4), 4.15 (dd, 1H, H-6), 3.98 (dd, 1H, H-5) 1.20–1.10, 1.09–0.90 (2m, 42H, 2TIPS); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 145.2 (d, 187, C-1), 102.8 (d, 166 C-2), 77.8, 66.2, 65.3 (3d, 140, C-3, C-4, C-5), 62.9 (t, 139, C-6), 18.6, 18.5 (2q, 125, Si*C*H(*C*H$_3$)), 12.9, 12.8 (2d, 120, Si*C*H(CH$_3$)$_2$); CI-MS (NH_3): 241 (10), 173 (5), 131 (35), 103 (46), 75 (100); Anal. Calcd for $C_{24}H_{50}O_4Si_2$: C, 62.83; H, 10.98. Found: C 62.80. H 10.95.

4.12. (−)-3,6-Di-*O*-(isopropylsilyl)-4-*O*-methoxymethoxy-D-galactal 15

A stirred solution of **14** (1.7 g, 3.7 mmol) was cooled to 0 °C and methoxymethyl chloride (5 mL, 65.8 mmol) was added dropwise. Then diisopropylethylamine (10 mL, 33.3 mmol) and a catalytic amount of tetrabutylammonium iodide were added. The reaction mixture was heated to 60 °C until TLC showed the reaction to be complete (R_f 0.25 light petroleum ether/Et_2O 10:0.5). The mixture was allowed to cool to 20 °C and quenched with aq HCl (1 M, 30 mL). The organic phase was extracted with pentane (50 mL, three times) then washed with satd aq soln of $NaHCO_3$, dried ($MgSO_4$), and concentrated in vacuo. FC (light petroleum ether/Et_2O 10:0.5) 1.3 g (67%), colorless oil. $[\alpha]_{589}^{25} = -68$, $[\alpha]_{577}^{25} = -71$, $[\alpha]_{546}^{25} = -81$, $[\alpha]_{435}^{25} = -141$, $[\alpha]_{405}^{25} = -172$ (*c* 1.6, $CHCl_3$); IR (film): *v* 2943, 2866, 1641, 1464, 1389, 1236, 1153, 1099, 1044, 964, 919, 883, 828, 736, 680; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.32 (dd, 1H, $^{3}J_{1,2}$ = 6.0, $^{3}J_{1,3}$ = 1.2, H-1), 5.03 (d, 1H ^{1}J = 6.8, C*H*$_2$–O–CH$_3$), 4.75 (d, 1H, C*H*$_2$–O–CH$_3$), 4.71 (dd, 1H, $^{3}J_{2,3}$ = 1.9, $^{3}J_{2,4}$ = 1.9, H-2), 4.58 (s, 1H, H-4), 4.08–3.97 (m, 4H, H-3, H-5, H-6, H-6′), 3.74 (s, 3H, CH$_2$–O–C*H*$_3$), 1.07 (m, 42H, 2TIPS); ^{13}C NMR ($CDCl_3$, 100.6 MHz): 143.1 (d, 190, C-1), 103.7 (d, 170, C-2), 97.2 (t, 164, *C*H$_2$–O–CH$_3$), 77.9, 70.6, 66.2 (3 d, 140, C-3,4,5), 62.1 (t, 140, C-6), 55.9 (q, 142, CH$_2$–O–*C*H$_3$), 18.0, 17.9, 17.8 (3q, 120, SiCH(*C*H$_3$)$_2$), 12.2, 11.9 (2d, 120, Si*C*H(CH$_3$)$_2$); CI-MS (NH_3): 520 ([M+18]$^+$, 60), 459 (38), 427 (10), 329 (100), 273 (40), 213 (6), 162 (14), 81 (20); HRMS: Calcd for $C_{26}H_{54}O_5Si_2$: 501.3421. Found: 501.3422 ([M$^+$]).

4.13. (−)-3,6-Di-*O*-(isopropylsilyl)-4-*O*-methoxymethoxy-1-tributylstannyl-D-galactal 16

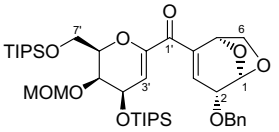
To a stirred solution of **15** (1.3 g, 2.6 mmol) in anhyd THF at −78 °C was added dropwise a 1.5 M soln of *t*-butyllithium in pentane (10 mL, 15 mmol). The mixture was stirred at 0 °C for 30 min and then cooled to −78 °C. Then tributyltin chloride was added dropwise and the reaction mixture was stirred for 30 min at this temperature and allowed to warm to 20 °C. After the addition of aq 1 M HCl (50 mL), the phases were separated and the aq phase was extracted with pentane (100 mL, twice). The combined organic phases were washed with aq satd soln of $NaHCO_3$ (50 mL), dried ($MgSO_4$), and concentrated in vacuo. FC (light petroleum ether/Et_2O 99:1) 1.4 g (71%), colorless oil. $[\alpha]_{589}^{25} = -55$, $[\alpha]_{577}^{25} = -57$, $[\alpha]_{546}^{25} = -66$, $[\alpha]_{435}^{25} = -118$, $[\alpha]_{405}^{25} = -145$, (*c* 2.0, $CHCl_3$); IR (film): *v* 2957, 2867, 2360, 1600, 1464, 1417, 1378, 1248, 1215, 1152, 1098 1042, 974, 919, 882, 832; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.98 (d, 1H, $^{2}J_{H,H}$ = 6.6, C*H*$_2$–O–CH$_3$), 4.73 (d, 1H, C*H*$_2$–O–CH$_3$), 4.70 (d, 1H, $^{3}J_{2,3}$ = 2.0, H-2), 4.59 (s, 1H, H-4), 4.0–3.4, (m, 4H, H-3, H5, Ha-6, Hb-6), 3.43 (s, 3H, CH$_2$–O–C*H*$_3$), 1.58 1.30 (m, 27H, SnBu$_3$), 1.07, 1.06 (m, 42H, 2TIPS); ^{13}C NMR ($CDCl_3$, 100.6 MHz): 162.5 (s, C-1), 114.8 (d, 160, C-2), 96.9 (t, 160, *C*H$_2$–O–CH$_3$) 78.3, 71.4, 66.1 (3d, 150, C-3, C-4, C-5), 55.7 (q, 142, CH$_2$–O–*C*H$_3$), 28.9, 27.8, 27.2, 26.8 (4d, 150, Sn(CH$_2$*C*H$_2$*C*H$_2$CH$_3$)$_3$), 18.1, 18.0, 17.9 (3q, 120, SiCH(*C*H$_3$)$_2$), 12.1, 11.9 (2d, 120, Si*C*H(CH$_3$)$_2$), 13.6 (q, 125, Sn(CH$_2$CH$_2$CH$_2$*C*H$_3$)$_3$), 9.6 (t, 128, Sn(*C*H$_2$CH$_2$CH$_2$CH$_3$)$_3$); CI-MS (NH_3): 791 ([M+1]$^+$, 100), 750 (9), 618 (32), 501 (30), 462 (22), 308 (35), 250

(6), 148 (9), 76 (9); HRMS: Calcd for $C_{38}H_{80}O_5Si_2Sn$ 791.4560. Found: 791.4559 ([M^+]).

4.14. (−)-1-[1′,5′-Anhydro-3′,5′-di-*O*-(isopropylsilyl)-4′-*O*-methoxymetyl-D-*ribono*-hex-1′-en-2′-yl]-2,6-anhydro-5,7-bis(*tert* butylsilylidene)-4-*O*-(isopropylsilyl)-D-*arabino*-hept-2-en-1-one 20

A solution of **16** (100 mg, 0.14 mmol) and I_2 (34 mg, 0.134 mmol) in CH_2Cl_2 (2 mL) was stirred at 20 °C for 30 min and then concentrated in vacuo. The residue was dissolved in THF (2 mL) and added to a solution of Pd_2dba_3 (30 mg, 0.033 mmol) and triphenylarsine (30 mg, 0.1 mmol) in anhyd THF (2 mL). Then a solution of **7** in THF (2 mL) was added and the reaction mixture was placed under CO atmosphere (50 bar autoclave). The mixture was warmed to 50 °C and stirred for 15 h. After releaving pressure, the reaction was quenched by 5 mL of aqueous KF (1 M) solution and stirred for 5 min. Then the solution was filtered through a pad of Celite and rinsed with ether. The aqueous layer was extracted again twice with ether. The organic phases were combined, dried ($MgSO_4$), and concentrated. FC (EtOAc/light petroleum ether: 95:5) 96 mg (79%), colorless oil. $[\alpha]^{25}_{589} = -6.8$, $[\alpha]^{25}_{577} = -6.7$, $[\alpha]^{25}_{546} = -8.0$, $[\alpha]^{25}_{435} = -18$, $[\alpha]^{25}_{405} = -26$ (*c* 2.9, $CHCl_3$); IR (film): *v* 2943, 2866, 1679, 1631, 1464, 1387, 1364, 1245, 1215, 1155, 1112 1106, 1104, 1026, 919, 883, 826, 772, 681, 654; ^{1}H NMR ($CDCl_3$, 400 MHz): 5.83 (d, 1H, $^3J_{3,4} = 2.5$, H-3), 5.81 (d, 1H, $^3J_{2',3'} = 2.0$, H-2′), 5.07 (1H, $^2J_{H,H'} = 6,5$, CH_2–O–CH_3), 4.77 (m, 1H, H-3′), 4.73 (d, 1H, CH_2–O–CH_3), 4.56 (dd, 1H, $^3J_{3,4} = 2.4$, $^3J_{4,5} = 7.2$, H-4), 4.27 (q, 1H, $^2J_{7,7b} = 10.0$, $^3J_{6,7} = 4.8$, H-7), 4.20 (m, 1H, $^3J_{3,4} = 2.0$, $^3J_{4,5} = 3.5$, H-4′), 4.1–4.0 (m, 5H, H-4, Ha-6, H-5′, H-6′, Hb-6), 3.88 (m, 1H, $^3J_{5,6} = 10.3$, H-5), 3.41 (s, 3H, CH_2–O–CH_3), 1.2–0.9 (m, TIPS, Si(*t*-Bu)$_2$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): 182.8 (s, CO), 148.6, 148.5 (2s, C-2, C-1′), 115.2, 115.1 (2d, 165, C-3, C-2′), 97.2 (t, 163, *C*H_2–O–CH_3), 78.3, 76.5, 73.1, 71.2, 68.0, 67.9 (6d, 145, C-4, C-5, C-6 C-3, C-′4, C-5′), 61.1, 65.7 (2 t, 145, C-7, C-6′), 55.9 (q, 140, CH_2–O–*C*H_3), 27.3, 26.8 (2q, 125, Si(C(*C*H_3)$_3$)$_2$), 2.7, 19.7 (2s, Si(*C*(CH$_3$)$_3$)$_2$), 22.8, 19.9 (s, Si(*C*(CH$_3$)$_3$)$_2$), 18.1, 18.0, 17.9, 17.8 (4q, 125, SiCH(*C*H$_3$)$_2$), 12.4, 12.1, 11.8 (3d, 120, Si*C*H(CH$_3$)$_2$); CI-MS (NH_3): 988 ([M+18]$^+$, 1), 984 (22), 924 (24), 796 (27), 624 (14), 550 (51), 492 (100), 399 (26); HRMS: Calcd for $C_{50}H_{98}O_{10}Si_4Na$: 993.6135. Found: 993.6055 ([M+Na$^+$]).

4.15. (−)-((1*S*,4*R*,5*R*)-4-(Benzyloxy)-6,8-dioxabicyclo[3.2.1]-oct-2-en-2-yl)((2*R*,3*S*,4*R*)-2-(((diisopropylsilyl)oxy)-methyl-3-(methoxymethoxy)-4-(8-triisopropylsilyl)oxy)-3,4-dihydro-2*H*-pyran-6-yl)methanone 12



In a reaction tube dried under vacuum were placed, under argon, $Pd_2(dba)_3$ (225 mg, 0.25 mmol), and triphenylarsine (80 mg, 0.25 mmol). The flask was degassed, on the vacuum line and filled with argon (three times). The catalyst was dissolved in NMP (10 mL) and lithium chloride (140 mg, 0.75 mmol) and a small amount of activated charcoal were added (weighted in a glove box). Then the organostannane **16** (1.4 g, 1.25 mmol) in NMP (10 mL) and triflate **11** (450 mg, 1.25 mmol) in NMP (10 mL) were added. The reaction mixture was placed in a stainless steel autoclave and stirred for 18 h under CO (50 bar) at 50 °C. After releaving pressure, the reaction was quenched by 5 mL of aqueous KF (1 M 20 mL) solution and stirred for 5 min. Then the solution was filtered through a pad of Celite and rinsed with ether. The aqueous layer was extracted again with ether. The organic phases were combined, dried ($MgSO_4$), and concentrated in vacuo. FC (light petroleum ether/EtOAc 95:5) 650 mg (73%), colorless oil.

$[\alpha]^{25}_{589} = -0.3$, $[\alpha]^{25}_{577} = -0.7$, $[\alpha]^{25}_{546} = -2.5$, $[\alpha]^{25}_{435} = -36$, $[\alpha]^{25}_{405} = -77$ (*c* 2.9, $CHCl_3$); IR (film): *v* 3120, 3094, 3030, 3010, 2910, 1640, 1470, 1320, 1240, 1180, 1130, 950, 940, 800, 760; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.4 (m, 5H, *Ph*CH_2–O), 6.90 (m, 1H, $^3J_{2,3} = 0.4$, H-3), 5.70 (s, 1H, H-3′), 5.62 (s, 1H, H-1), 5.22 (d, 1H, $^3J_{5,6} = 4.0$, H-5), 5.07 (d, 1H, $^2J_{H,H} = 5.2$, OCH_2OCH$_3$), 4.79 (d, 1H, OCH_2OCH$_3$), 4.47 (s, 1H, H-4′), 4.67 (dd, 2H, $^2J_{H,H} = 12$, PhCH_2), 4.0–4.2 (m, 2H, H-7′, H-7′), 3.66, 3.76 (m, 2H, H-6a, H-6b), 3.34 (s, 3H, OCH$_2$O*C*H$_3$), 1.2–0.9 (m, 42H, TIPS); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 186.4 (s, C-1′), 148.9 (s, C-2′), 140.1 (s, C-4), 135.2 (CH_2–*Ph*), 128.5–127.8 (Ph), 134.7 (d, 160, C-3′), 113.3 (d, 160, C-3), 101.1 (d, 170, C-1), 100.3 (t, 163, *C*H_2–O–CH_3) 78.8 (d, 140, C-4′), 73.4 (d, 140, C-5′), 72.6 (C-5), 70.3 (d, 140, C-2), 69.9 (d, 140, C-6′), 71.6, (t, 150, *C*H_2Ph), 69.4 (t, 150, C-6), 69.0 (t, 150, C-7′), 56.0 (q, 140, CH_2–O–*C*H_3), 18.0, 17.9, 17.8 (3q, 120, SiCH(*C*H$_3$)$_2$), 12.2, 11.9 (2d, 120, Si*C*H(CH$_3$)$_2$); CI-MS (NH_3): 774 ([M+18]$^+$), 755 (M+1, 50), 623 (15), 605 (5), 531 (14), 442 (22), 383 (42), 296 (22), 235 (22), 207 (76); HRMS: Calcd for $C_{40}H_{66}O_9Si_2Na$:769.4143. Found: 769.4235 ([M+Na$^+$]).

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