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Organotransition-metal-modified sugars☆ Part 17. Glucal-derived carbene complexes: synthesis and diastereoselective benzannulation

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

The addition of triisopropylsilyl and/or isopropylidene-protected 1-lithio-D-glucals prepared in situ from stannylated precursors **5** and **6** to hexacarbonyl chromium followed by methylation affords D-*arabino*-hex-1-enopyranosylcarbene complexes **7** and **8**. They undergo a diastereoselective benzannulation upon reaction with tolan and 3-hexyne to give polyoxygenated chromans **9** to **12** in good yields and moderate diastereomeric excess values. The conformation of the glucal moiety in the carbene ligand and in the chroman skeleton is controlled by the nature of the protective groups. ^{1}H-NMR studies and single crystal X-ray analyses indicate a $^5H_4$-conformation of the sugar moiety for the triisopropylsilyl compounds **7**, **9a**,**b**, **10a**,**b** and **11** and $^4H_5$-conformation for the isopropylidene derivatives **8** and **12a**–**c** in solution, and further for **8** and **12a** in the solid state.

1. Introduction

Carbohydrates are ubiquitous naturally occurring compounds and play an eminent role in chemistry and biology [1]. They are involved in molecular recognition at cell walls [2], intracellular enzyme transport [3], infections [4] and cell adhesion [5]. In addition, polysaccharides serve as materials for the storage and supply of energy and for construction [6]. A major area of synthetic carbohydrate chemistry concentrates on glycosidation reactions. Although a variety of powerful *O*-glycosidation methods have been developed [7], the elaboration of stereoselective protocols remains an ongoing challenge [8]. In contrast to *O*-glycosides, their *C*-analogues are inherently stable towards hydrolysis [9] and, thus, they are promising candidates for therapeutic applications. Since organometallic reagents have a great potential in stereoselective synthesis, we focused on an organometallic modification of the multifunctional carbohydrates [10]. Prior to our work, the activation of the anomeric center towards *C*-glycosidation by transition metals has been mainly restricted to samarium and palladium [11]. Glycosyl complexes of iron [12] and manganese [13] have been synthesized, but their application in *C*-glycosidation was hampered by the low reactivity or by the high-pressure conditions required. Recently, a tungsten-carbonyl-catalyzed cycloisomerization of highly functionalized alkynes has been applied to the synthesis of *O*-glycosides [14].

Recently, we have elaborated complementary synthetic routes to metal-carbene-functionalized carbohydrates based on a metal carbonyl electrophile–sugar nucleophile combination or vice versa [10], and demonstrated their application in diastereoselective Diels–Alder [15] and *C*-glycosidation reactions [16], as well as in the formation of iminoglycosylidenes [17]. Chromium aryl- and vinyl-carbenes are known to un-

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dergo benzannulation upon reaction with alkynes [18]. We have used this methodology in the synthesis of chromium-labeled polyoxygenated chromans, and report now on the synthesis of glucal-derived chromium carbenes and their diastereoselective benzannulation.

2. Results and discussion

2.1. Synthesis of chromium glucal carbenes

The Fischer route, based on the sequential addition of an organolithium nucleophile and an alkylative electrophile across a metal carbonyl ligand, is the most general access to metal carbenes [19]. Along this approach the hydroxy substituents of D-glucal **1** have to be suitably protected by isopropylidene and/or triisopropylsilyl groups compatible with the subsequent organometallic protocol. A clean anomeric lithiation is best performed by a metalation/transmetalation sequence [11,20,21a,b]; lithiation of the protected glucal with *tert*-butyl lithium followed by stannylation with tri-*n*-butyl tin chloride afforded excellent yields of the stannylated glucals **5** and **6**, which can be stored for several months at 2°C. Tin–lithium exchange occurs at −78°C with *n*-butyl lithium; addition of the resulting lithioglucals to hexacarbonyl chromium at −40°C generated the acyl chromate intermediates, which were alkylated with trimethyloxonium tetrafluoroborate to give glucal carbene complex **7** as a red oil or **8** as a red solid.

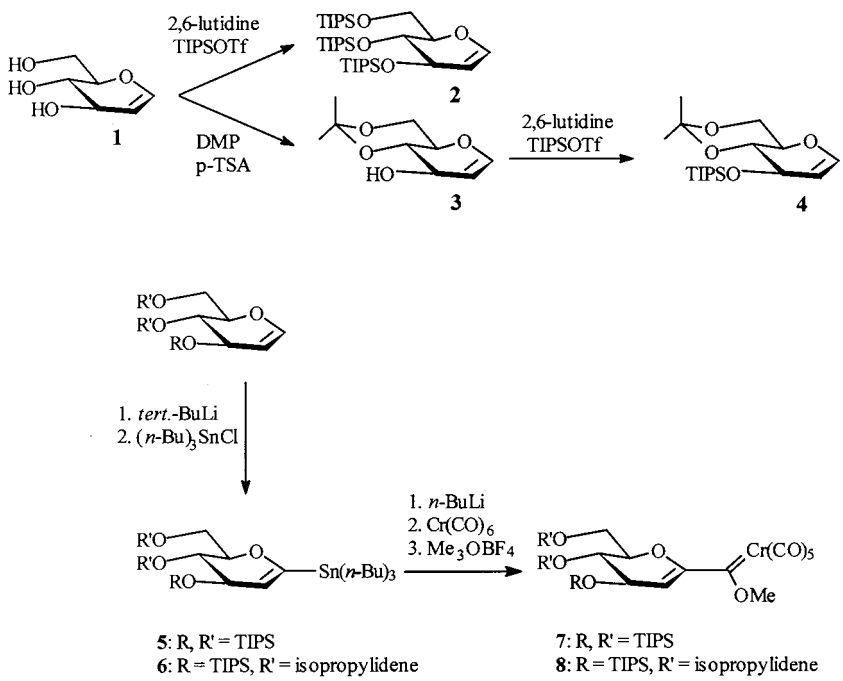
The choice of protective groups is crucial and limited by the basic conditions applied in the stannylation step. The 4,6-*O*-isopropylidene acetal [21b,22] and 3-triisopropylsilyl groups [21] are compatible with the excess of *tert*-butyl lithium required for C-1 deprotonation of the glucal and with the subsequent trapping of the glucal anion by tri-*n*-butyl tin chloride [21a] (Scheme 1).

The conformation of the glucals **2**–**8** depends on the nature of the protective group [23]. The coupling pattern in the ^{1}H-NMR spectrum indicates a $^5H_4$-conformation for the *tri*-TIPS-protected compounds **2**, **5**, and **7** (smaller coupling constants of ca. 1.5–2.0 Hz for $^3J_{H\text{-}3,H\text{-}4}$, $^3J_{H\text{-}4,H\text{-}5}$, $^4J_{H\text{-}2,H\text{-}4}$, and $^4J_{H\text{-}3,H\text{-}5}$ and a medium coupling constant of ca. 5.0–5.5 Hz for $^3J_{H\text{-}3,H\text{-}2}$) and a $^4H_5$-conformation for the 4,6-*O*-isopropylidene-protected glucal derivatives **3**, **4**, **6**, and **8** (smaller coupling constant of ca. 1.9–2.4 Hz for $^3J_{H\text{-}2,H\text{-}3}$ and larger coupling constants of ca. 7.0–8.0 Hz and ca. 10.5 Hz for $^3J_{H\text{-}3,H\text{-}4}$ and $^3J_{H\text{-}4/H\text{-}5}$; no ^4J couplings observable) (Table 1).

The molecular structure of the TIPS/isopropylidene-protected glucal carbene complex **8** has been established by single crystal X-ray analysis (Fig. 1). It reveals a similar $^4H_5$-conformation in the solid state as observed for it and its precursors **3**, **4**, and **6** in solution. The carbene complex adopts a *Z*-configuration for the carbene–oxygen bond and a transoid conformation across the vinylcarbene chromium moiety.

2.2. Diastereoselective benzannulation

We wanted to take advantage of the chiral information provided by the sugar skeleton of chromium glucals **7** and **8** and aimed at a diastereoselective benzannula-



Scheme 1. Syntheses of the carbene complexes **7** and **8** starting from D-glucal.

Table 1
Coupling constants and conformations of the prepared glucal derivatives **2**–**8**

Compound	$^3J_{H\text{-}2,H\text{-}3}$ (Hz)	$^3J_{H\text{-}3,H\text{-}4}$ (Hz)	$^3J_{H\text{-}4,H\text{-}5}$ (Hz)	$^4J_{H\text{-}2,H\text{-}4}$ (Hz)	$^4J_{H\text{-}3,H\text{-}5}$ (Hz)	Conformation
2	5.36	–	–	1.78	–	$^5H_4$
3	1.96	–	–	absent	absent	$^4H_5$
4	1.84	7.01	10.43	absent	absent	$^4H_5$
5	5.07	–	~2	1.69	–	$^5H_4$
6	1.89	7.35	10.44	absent	absent	$^4H_5$
7	5.47	–	~2	1.49	–	$^5H_4$
8	2.35	7.82	–	absent	absent	$^4H_5$

tion in order to generate an additional chiral plane upon coordination of the $Cr(CO)_3$ fragment to the newly formed hydroquinone ring. The diastereoselectivity of the benzannulation is expected to be controlled by the conformation of the glucal, which is known to depend on the nature of the protective groups [23].

First, we studied the reaction of carbene complex **7** with 3-hexyne. The $^5H_4$-conformation of the glucal part combined with the bulky TIPS-groups was supposed to direct the benzannulation in a highly stereoselective way. After chromatographic workup we obtained a 39% yield of a diastereopure chroman–$Cr(CO)_3$ complex along with a 31% yield of the uncoordinated chroman. The benzannulation of **7** with tolan gave an increased yield of the chroman–$Cr(CO)_3$ complex. In addition to the expected benzannulation product **10a** (46%) and a minor amount of uncoordinated chroman **10b** (7%), another chroman–$Cr(CO)_3$ complex **11** (13%) was obtained but could not be isolated as a pure compound (Scheme 2). IR and NMR spectroscopic data suggest the formation of an isomer of **10a** in which the $Cr(CO)_3$ fragment is attached to one of the phenyl rings originating from tolan. So far, we cannot decide whether it is formed via an intermolecular decomplexation/recomplexation sequence or an intramolecular haptotropic metal migration across the biaryl bond. Chromatographic workup afforded the chroman complexes **9a** and **10a** as single diastereomers; within the accuracy of NMR spectroscopy, no minor diastereomers bearing the $Cr(CO)_3$ fragment attached to the opposite face of the arene could be detected.

The reaction of the 4,6-*O*-isopropylidene-protected glucal carbene complex **8** with 3-hexyne carried out in *tert*-butyl methyl ether at 55°C afforded a 79% overall yield of benzannulation products. Along with the uncoordinated chroman **12c** (33%), the diastereomeric chroman complexes **12a** and **12b** were isolated after chromatographic workup in 35% and 11% yields respectively, indicating a diastereomeric excess (d.e.) of 54% as determined by integration of the ^{1}H-NMR spectrum and high performance liquid chromatography (HPLC) (Scheme 3).

The conformation and the configuration of the benzannulation products have been analyzed by ^{1}H-NMR spectroscopy. The coupling patterns of the glucal protons of **9a**,**b**, **10a**,**b**, and **12a**–**c** resemble those observed for carbene complexes **7** and **8**, suggesting that the $^4H_5$-conformation did not change upon benzannulation. The configuration as defined by the coordination of the chromium fragment to the arene was first tentatively assigned on the basis of coordination shifts. As a consequence of the anisotropic effect arising from the $Cr(CO)_3$-tripod glucal, protons located at the same face of the chiral plane as the chromium fragment are expected to resonate at lower field compared with those in the demetalated benzannulation product (Table 2) [24].

The tentative assignment of the configuration concerning the chiral plane on the basis of NMR-coordination shifts was further supported by a study of the molecular structure of the major diastereomer **12a** in the solid state. Cubic crystals, grown from an *n*-hexane solution cooled to −30°C, allowed for an unambiguous assignment of the configuration and the conformation by a single-crystal X-ray analysis. This confirmed that the $^4H_5$-conformation favored in solution is also

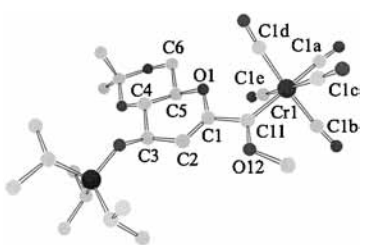
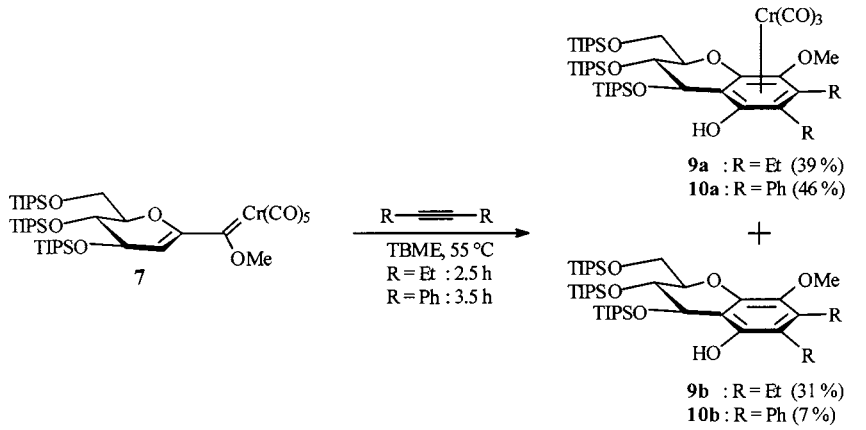
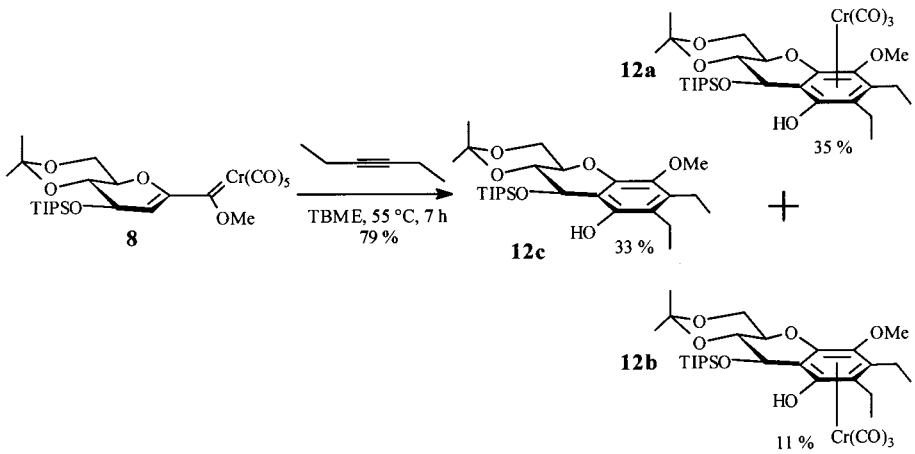


Fig. 1. Molecular structure of carbene complex **8**. Selected bond lengths (Å): C1–C2, 1.331(5); C1–C11, 1.507(5); C11–Cr1, 2.032(4); C1–O1, 1.380(4); C11–O12, 1.320(4); Cr1–C1a, 1.874(5); Cr1–C1b, 1.879(6); Cr1–C1c, 1.889(6); Cr1–C1d, 1.900(6); Cr1–C1e, 1.874(6); selected bond angles (°): C1–C2–C3, 125.1(4); C2–C1–C11, 125.9(4); C1–C11–Cr1, 123.6(3); C1a–Cr1–C11, 175.5(2); C1b–Cr1–C11, 93.8(2); C1c–Cr1–C11, 89.5(2); C1d–Cr1–C11, 90.4(2); C1e–Cr1–C11, 96.1(2); selected torsion angles (°): O1–C1–C2–C3, 0.9(9); C1–C2–C3–C4, −8.5(7); C2–C3–C4–C5, 38.5(6); C3–C4–C5–O1, −63.3(5); C1–O1–C5–C4, 53.3(5); C5–O1–C1–C2, −21.4(8); C2–C1–C11–Cr1, 167.3(5); O1–C1–C11–Cr1, −9.7(7); C1a–Cr1–C11–C1, −43(3); C1b–Cr1–C11–C1, −131.2(4); C1c–Cr1–C11–C1, −41.3(5); C1d–Cr1–C11–C1, 50.5(5); C1e–Cr1–C11–C1, 138.4(4).



Scheme 2. Benzannulation of the TIPS-protected glucal carbene complex **7** with 3-hexyne and tolan.



Scheme 3. Benzannulation of the isopropylidene-protected glucal carbene complex **8** with 3-hexyne.

Table 2
Chemical shifts (ppm) of the glucal protons of the benzannulation products, **9a**,**b** and **10a**,**b** in CD_2Cl_2; **12a**–**c** in $CDCl_3$ (H-1, H-1′ for the *tri*-TIPS-protected compounds and H-1e, H-1a for the TIPS/isopropylidene-protected compounds)

Proton	H-1 (H-1e)	H-1′ (H-1a)	H-2	H-3	H-4
δ(**9a**)	4.31	4.26	4.47	4.42	4.93
δ(**9b**)	4.11	4.00	4.41	4.35	5.03
δ(**9a**)−δ(**9b**)	0.20	0.26	0.06	0.07	−0.10
δ(**10a**)	4.41	4.41	4.60	4.52	5.09
δ(**10b**)	4.21	4.10	4.52	4.44	5.13
δ(**10a**)−δ(**10b**)	0.20	0.31	0.08	0.8	−0.04
δ(**12a**)	4.04	3.98	3.90	4.49	5.23
δ(**12b**)			4.22	–	5.48
δ(**12c**)	4.09	3.95	3.83	4.12	5.26
δ(**12a**)−δ(**12c**)	−0.05	0.03	0.07	0.37	−0.03
δ(**12b**)−δ(**12c**)	–	–	0.39	–	−0.02

preferred in the solid state, as demonstrated by the torsion angles within the glucal moiety, and further established that the $Cr(CO)_3$ fragment is coordinated to the same face of the arene as the bulky TIPSO group at C-4 (Fig. 2). As known for comparable naphthohydroquinone complexes [25], the chromium atom is not coordinated symmetrically to the center of the arene ring but is shifted towards the periphery away from the adjacent pyran ring. The distances of the Cr atom to the bridging ring carbon atoms C4a (2.2478(17) Å) and C8a (2.2640(16) Å) exceed those to C6 (2.2335(16) Å) and C7 (2.2039(16) Å). The $Cr(CO)_3$-tripod deviates

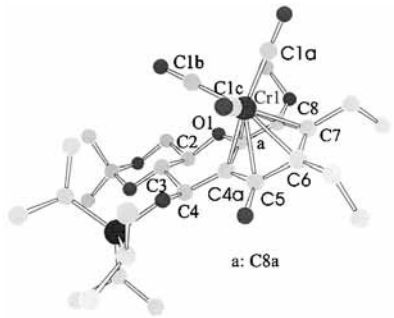
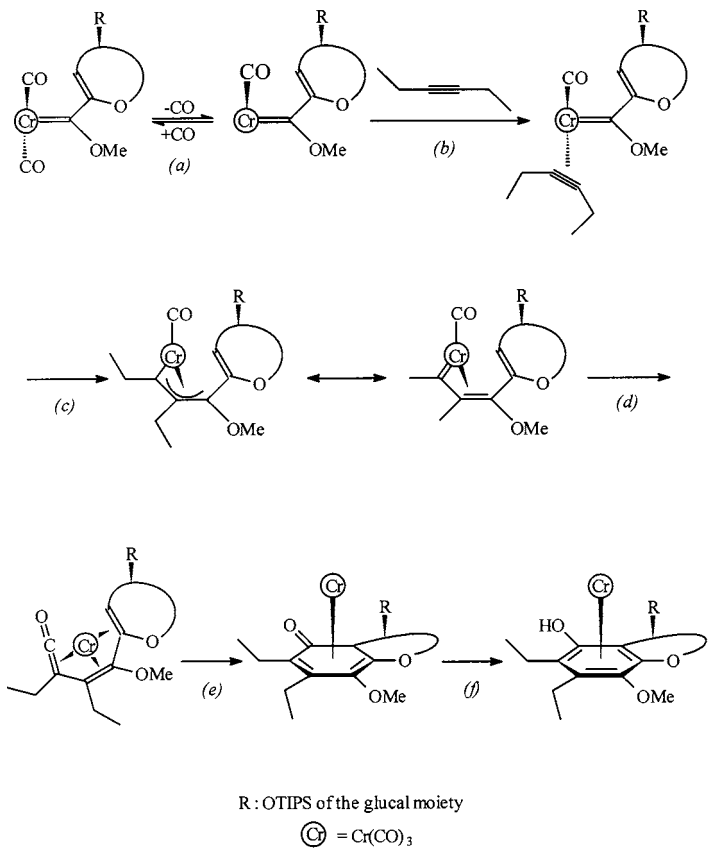


Fig. 2. Molecular structure of the major diastereomer **12a**. Selected bond lengths (Å): C4a–C5, 1.415(2); C4a–C8a, 1.432(2); C8–C8a, 1.405(2); C7–C8, 1.420(2); C6–C7, 1.407(2); C5–C6, 1.431(2); Cr1–C4a, 2.2478(17); Cr1–C8a, 2.2640(16); Cr1–C5, 2.2516(16); Cr1–C8, 2.2306(15); Cr1–C6, 2.2335(16); Cr1–C7, 2.2039(16); Cr1–ZAr, 1.7321(7); selected bond angles (°): ZAr–Cr1–C1a, 125.7(1); ZAr–Cr1–C1b, 126.9(1); ZAr–Cr1–C1c, 125.1(1); C4a–C8a–Cr1, 37.00(6); C8a–C8–Cr1, 36.41(6); C8–C7–Cr1, 37.36(6); C7–C6–Cr1, 36.96(6); C6–C5–Cr1, 37.20(6); C5–C4a–Cr1, 36.65(6); C4a–Cr1–C1b, 95.09(7); C8a–Cr1–C1b, 89.45(7); C6–Cr1–C1c, 92.19(7); C7–Cr1–C1a, 87.29(7); selected torsion angles (°): C4–C4a–C8a–O1, 1.1(2); C3–C4–C4a–C8a, −20.6(2); C2–C3–C4–C4a, 51.12(17); O1–C2–C3–C4, −67.76(17); C8a–O1–C2–C3, 47.79(18); C2–O1–C8a–C4a, −14.7(2); C7–C8–C8a–C4a, 1.4(2); C5–C4a–C8a–C8, −5.4(2); C8a–C4a–C5–C6, 6.2(2); C4a–C5–C6–C7, −2.8(2); C5–C6–C7–C8, −1.5(2); C6–C7–C8–C8a, 2.1(2).

from coplanarity with the coordinated arene ring and is tilted away from the pyran ring, as indicated by the bond angles C4a–Cr1–C1b (95.09(7)°) and C8a–Cr1–C1b (89.45(7)°) versus C6–Cr1–C1c (92.19(7)°) and C7–Cr1–C1a (87.29(7)°). The orientation of the $Cr(CO)_3$-tripod in the solid state is turned about 45° compared with that usually found for $Cr(CO)_3$ complexes of naphthalene and naphthohydroquinones [26]; one CO group of compound **12a** lies above the pyran ring, securing a minimization of steric interaction between the bulky TIPS group at C-4 and the carbonyl ligands.

The preferred coordination of the metal fragment from the more crowded face is surprising at first sight, but may be addressed in terms of the mechanism of the [3 + 2 + 1] benzannulation, as supported by experimental and theoretical evidence [18,27] (Scheme 4). The reaction is believed to start with loss of a cis-carbonyl ligand (a) followed by coordination of the alkyne at the vacant coordination site [28] (b). The C–C bond formation is initiated by the insertion of the alkyne into the chromium–carbene bond, which generates a σ,π-allyl complex (equivalent to a vinylcarbene complex) bearing the metal fragment above or below the allyl plane (c). Since the bulky glucal moiety is expected to favor the coordination of the alkyne from the less-congested side



Scheme 4. Supposed mechanism of the [3 + 2 + 1]-benzannulation.

opposite the bulky TIPSO substituent, the alkyne insertion places the chromium fragment towards the TIPSO group. Provided that no further inversion of configuration occurs associated with the subsequent carbonyl insertion (d), electrocyclization at the chromium template (e) and rearomatization (f) [29], the configuration at the chiral plane observed in the final benzannulation product is determined by the alkyne insertion, which — along these lines — is to be regarded as the stereodifferentiating step of the reaction sequence.

3. Conclusions

Glucals serve as valuable chiral information for the diastereoselective benzannulation of α,β-unsaturated chromium carbene complexes upon reaction with alkynes. The conformation of the pyranose ring is controlled by the nature of the protective groups irrespective of stannylation or metal carbene functionalization at C-1 and of benzannulation to give polyoxygenated chroman $Cr(CO)_3$ complexes. The conformation in solution is determined as $^5H_4$ for the TIPS substitution pattern while the more rigid 4,6-*O*-isopropylidene protection favors the $^4H_5$ conformation, and is unchanged in the solid state as established for the 4,6-*O*-isopropylidene glucal carbene complex and its annulation product with 3-hexyne. The benzannulation proceeds under mild conditions with good overall chemical yields and considerable to excellent diastereoselective excess. Mechanistic considerations based on a stereodifferentiating alkyne insertion into the chromium carbene bond may rationalize the preferred formation of the sterically more congested diastereomeric chroman complexes. The diastereoselective benzannulation of glycal chromium carbenes provides a straightforward access to the skeleton of polyoxygenated chromans as present in cryptosporins, which exhibit a weak antibiotic activity [30].

4. Experimental

4.1. General reaction conditions

All reactions were carried out under argon. The solvents used for reactions and chromatography were dried (dried and distilled over lithium aluminum chloride: diethyl ether, *tert*-butyl methyl ether, petroleum ether, methylene chloride; dried and distilled over potassium: tetrahydrofuran). Chromatography was performed with silica gel (Merck type 60, 0.63–0.200 mm). D.e. values were determined by ^{1}H-NMR spectroscopy and HPLC.

4.2. Instrumentation

IR: Nicolet Magna 550 FT-IR. NMR: Bruker DRX 500 and AM-400. MS (FAB, EI): Kratos MS-50 and Concept 1H. Elemental analysis: Elementar Analysensysteme Vario EL. HPLC: Knauer Wellchrom injection valve A0258, pump K-1001, solvent organizer K-1500, UV-detector K-2600, column Knauer Eurospher 100 RP-18 100 Si.

4.3. X-ray crystallographic studies of **8** and **12a**

Crystallization from *n*-hexane at −30°C provided red crystals of **8** and yellow crystals of **12a** which were subjected to single-crystal X-ray analysis. Data were collected on a Nonius KappaCCD at 123 K. The structures were solved by direct methods (SHELXS-97) [31]. The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-97) [32]. H atoms were refined isotropically using a riding model. The absolute structure was determined by refinement of Flack's parameter *x* [33]. An empirical absorption correction was applied (**8**: $T_{max/min} = 0.9758/0.8439$; **12a**: $T_{max/min} = 0.9533/0.8676$). Further details are given in Table 3. Atomic coordinates and equivalent isotropic displacement parameters are given in Tables 4 and 5 respectively.

4.4. Reagents

4.4.1. Synthesis of glucals **2**–**6**

*4.4.1.1. 1,5-Anhydro-2-desoxy-3,4,6-tri-O-triisopropylsilyl-D-arabino-hex-1-enitol (**2**).* 30.2 ml (112.50 mmol) of TIPSOTf were added dropwise at 0°C to a solution of 3.65 g (25.00 mmol) of D-glucal and 19.2 ml (165.00 mmol) of 2,6-lutidine in 25 ml of CH_2Cl_2. The mixture was stirred for 60 min at room temperature (r.t.) and then diluted with 50 ml CH_2Cl_2. After quenching the reaction with 50 ml of water, the aqueous layer was extracted three times with 50 ml of CH_2Cl_2. Washing the combined organic layers three times with water and once with a saturated solution of brine gives **2**; drying over $MgSO_4$ and removal of the solvent afforded a crude product which was purified by column chromatography with petroleum ether–dichloromethane (1:1) as eluent to give 6.65 g (19.41 mmol, 78%) of a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 6.33$ (d, $^3J_{H\text{-}1,H\text{-}2} = 6.36$ Hz, 1H, H-1), 4.78 (ddd, $^3J_{H\text{-}2,H\text{-}1} = 6.36$ Hz, $^3J_{H\text{-}2,H\text{-}3} = 5.36$ Hz, $^4J_{H\text{-}2,H\text{-}4}$ 1.78 Hz, 1H, H-2), 4.22 (m, 1H, H-5), 4.06 (dd, $^2J_{H\text{-}6,H\text{-}6'} = 11.33$ Hz, $^3J_{H\text{-}6,H\text{-}5} = 7.95$ Hz, 1H, H-6), 4.03 (m, 1H, H-4), 3.93 (m, 1H, H-3), 3.83 (dd, $^2J_{H\text{-}6',H\text{-}6} = 11.33$ Hz, $^3J_{H\text{-}6',H\text{-}5} = 3.77$ Hz, 1H, H-6′), 0.11–0.09 (m, 63H, –Si[C*H*(CH_3)$_2$]$_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 142.9$ (C-1), 100.3 (C-2), 80.7, 70.2, 65.0, 62.0, (4C, C-3, C-4, C-5, C-6),

Table 3
Crystallographic data and summary of data collection and refinement of **8** and **12a**

	8	**12a**
Formula	$C_{25}H_{36}CrO_{10}Si$	$C_{30}H_{46}CrO_9Si$
M_r	576.63	630.76
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a (Å)	11.1512(7)	8.8866(2)
b (Å)	11.2972(8)	17.6827(4)
c (Å)	23.0370(17)	20.4121(3)
α, β, γ (°)	90, 90, 90	90, 90, 90
V (Å^3)	2902.1(3)	3207.54(11)
Z	4	4
Crystal size (mm^3)	$0.25\times0.15\times0.03$	$0.25\times0.25\times0.10$
ρ_{calc} (g cm^{-3})	1.32	1.30
μ (mm^{-1})	0.486	0.443
F(000)	1216	1344
Diffractometer	Nonius KappaCCD	Nonius KappaCCD
Radiation	Mo–K_α	Mo–K_α
λ (Å)	0.710 73	0.710 73
T (K)	123(2)	123(2)
Max. 2Θ (°)	50.0	56.6
Index range	$-13\le h\le13$, $-13\le k\le13$, $-27\le l\le27$	$-11\le h\le11$, $-23\le k\le23$, $-27\le l\le26$
No. of data	34 244	44 382
No. of unique data	5045	7934
Parameters	334/0	373/1
x	0.01(4)	−0.01(1)
$R(F)$ for $I>2\sigma(I)$	0.054	0.031
$wR_2(F^2)$ for all data	0.101	0.075
Goodness of fit on F^2	0.92	0.99

18.1–18.0 (18C, –Si[CH(CH$_3$)$_2$]$_3$), 12.5–12.0 (9C, –Si[CH(CH$_3$)$_2$]$_3$) ppm. EI-MS (70 eV): m/z (%) = 571.5 (100) [M$^+$ − C$_3$H$_7$], 397.2 (67) [M$^+$ − C$_3$H$_7$ − C$_9$H$_{21}$SiOH], 385.2 (62) [M$^+$ − C$_{13}$H$_{29}$SiO].

*4.4.1.2. 1,5-Anhydro-2-desoxy-4,6-O-isopropylidene-D-arabino-hex-1-enitol (**3**).* A solution of 4.24 g (22.17 mmol) D-glucal and 13.0 ml 2,2-dimethoxypropane in 40 ml DMF was adjusted to pH 3 by addition of p-toluene sulfonic acid. The solution was stirred for 45 min at 0°C (control by TLC, ethyl acetate–diethyl ether 1:1). The reaction was quenched with 100 ml of aqueous NaHCO$_3$. The aqueous layer was extracted three times with 100 ml of diethyl ether; the combined organic layers were washed three times with 100 ml water and dried over MgSO$_4$. Chromatography (same eluent as used for TLC) gave 2.07 g (11.12 mmol, 50%) of **3** as a colorless oil.

^{1}H-NMR (500 MHz, CDCl$_3$): δ = 6.15 (dd, $^3J_{H\text{-}1,H\text{-}2}$ = 6.08 Hz, $^4J_{H\text{-}1,H\text{-}3}$ = 1.96 Hz, 1H, H-1), 4.60 (dd, $^3J_{H\text{-}2,H\text{-}1}$ = 6.08 Hz, $^3J_{H\text{-}2,H\text{-}3}$ = 1.96 Hz, 1H, H-2), 4.19 (m, 1H, H-3), 3.83–3.55 (m, 4H, H-4, H-5, H-6a, H-6e), 3.47 (d, ^3J = 4.69 Hz, 1H, –OH), 1.40, 1.38 (s, 6H, (CH_3)$_2$C–) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 143.5 (C-1), 103.9 (C-2), 99.5 [(CH$_3$)$_2$$C$–]; 73.2, 69.0, 66.4, 61.2 (4C, C-3, C-4, C-5, C-6), 28.7, 18.8 (2C, (CH$_3$)$_2$C–) ppm. EI-MS (70 eV): m/z (%) = 186.0 (21) [M$^+$], 171.0 (31) [M$^+$ − CH$_3$], 114.0 (54) [M$^+$ − C$_3$H$_4$O$_2$].

*4.4.1.3. 1,5-Anhydro-2-desoxy-4,6-O-isopropylidene-3-O-(triisopropylsilyl-D-arabino-hex-1-enitol (**4**).* 4 ml (14.90 mmol) TIPSOTf were added dropwise to a solution of 1.83 g (9.83 mmol) of glucal **3** and 2.5 ml of 2,6-lutidine in 11 ml of CH$_2$Cl$_2$. The solution was stirred for 30 min at r.t. before the reaction was

Table 4
Atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters (Å$^2\times10^3$) for **8**

	x	y	z	U_{eq} [a]
Cr1	2444(1)	8086(1)	2114(1)	35(1)
C1a	2566(5)	7728(3)	1322(2)	40(1)
O1a	2700(4)	7534(3)	835(2)	63(1)
C1b	3656(5)	9208(5)	1978(3)	36(2)
O1b	4390(4)	9863(4)	1848(2)	59(1)
C1c	3622(5)	3906(6)	2226(2)	40(2)
O1c	4351(3)	6177(4)	2266(2)	62(2)
C1d	1185(5)	6964(6)	2189(3)	40(2)
O1d	413(3)	6295(4)	2204(2)	63(2)
C1e	1278(5)	9217(6)	1926(3)	40(2)
O1e	556(3)	9883(4)	1768(2)	53(1)
O1	2323(3)	6301(2)	3180(1)	36(1)
C1	2456(5)	7403(4)	3430(2)	31(1)
C2	2651(4)	7541(4)	3996(2)	31(1)
C3	2736(4)	6553(3)	4430(2)	31(1)
C4	2378(5)	5408(3)	4136(2)	33(1)
C5	2843(4)	5375(4)	3531(2)	33(1)
C6	2551(6)	4205(3)	3248(2)	38(1)
O7	3032(3)	3271(3)	3597(1)	43(1)
C8	2677(6)	3295(4)	4192(2)	44(1)
C9	3509(5)	2455(5)	4491(3)	58(2)
C10	1354(5)	2948(5)	4267(3)	56(2)
O11	2886(3)	4435(3)	4447(1)	40(1)
C11	2414(4)	8379(3)	2984(2)	31(1)
O12	2407(3)	9374(2)	3285(1)	39(1)
C12	2487(5)	10 529(3)	3010(2)	43(1)
O3	1993(2)	6787(3)	4917(1)	32(1)
Si1	2326(1)	7150(1)	5596(1)	32(1)
C13	2448(5)	8813(3)	5646(2)	30(1)
C14	1348(4)	9439(5)	5393(2)	45(2)
C15	3594(4)	9308(6)	5387(3)	45(2)
C16	959(4)	6632(5)	5983(3)	34(2)
C17	912(4)	6918(6)	6632(3)	52(2)
C18	670(4)	5308(5)	5896(3)	44(2)
C19	3782(4)	6486(5)	5840(3)	39(2)
C20	3852(5)	5147(5)	5824(3)	59(2)
C21	4180(4)	6916(6)	6455(3)	55(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **12a**

	x	*y*	*z*	U_{eq} [a]
Cr1	3320(1)	6066(1)	6137(1)	18(1)
C1a	1767(2)	5600(1)	5703(1)	24(1)
O1a	834(2)	5295(1)	5416(1)	35(1)
C1b	3480(2)	5196(1)	6629(1)	26(1)
O1b	3606(2)	4642(1)	6930(1)	38(1)
C1c	1934(2)	6471(1)	6717(1)	26(1)
O1c	1070(2)	6741(1)	7055(1)	43(1)
O1	6690(1)	5329(1)	5869(1)	20(1)
C2	7819(2)	5353(1)	6375(1)	19(1)
C3	7127(2)	5577(1)	7025(1)	18(1)
C4	6619(2)	6394(1)	6978(1)	17(1)
C4a	5656(2)	6479(1)	6362(1)	17(1)
C5	4723(2)	7117(1)	6262(1)	17(1)
O5	4656(1)	7674(1)	6717(1)	22(1)
C6	3793(2)	7196(1)	5694(1)	18(1)
C61	2795(2)	7890(1)	5657(1)	23(1)
C62	3630(2)	8588(1)	5413(1)	29(1)
C7	3862(2)	6635(1)	5206(1)	19(1)
C71	2916(2)	6671(1)	4587(1)	23(1)
C72	3717(2)	7045(1)	4014(1)	32(1)
C8	4867(2)	6016(1)	5277(1)	19(1)
O8	5012(1)	5521(1)	4758(1)	23(1)
C81	4734(3)	4738(1)	4878(1)	33(1)
C8a	5763(2)	5941(1)	5840(1)	18(1)
C9	8477(2)	4565(1)	6431(1)	22(1)
O10	9552(1)	4576(1)	6949(1)	25(1)
C11	8947(2)	4789(1)	7567(1)	24(1)
C111	7864(2)	4199(1)	7830(1)	33(1)
C112	10 296(2)	4900(1)	8008(1)	36(1)
O12	8244(1)	5519(1)	7520(1)	20(1)
O4	5766(1)	6646(1)	7529(1)	19(1)
Si4	6288(1)	6836(1)	8309(1)	18(1)
C41	8292(2)	7171(1)	8310(1)	23(1)
C411	8476(2)	7934(1)	7955(1)	32(1)
C412	9036(2)	7207(1)	8988(1)	35(1)
C42	6043(2)	5953(1)	8817(1)	25(1)
C421	4722(2)	5450(1)	8594(1)	33(1)
C422	5917(3)	6107(1)	9558(1)	38(1)
C43	4920(2)	7618(1)	8506(1)	25(1)
C431	5225(3)	8054(1)	9143(1)	37(1)
C432	3276(2)	7363(1)	8480(1)	38(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

quenched by addition of 100 ml of water. Extraction of the aqueous layer with CH_2Cl_2 and purification by chromatography (petroleum ether–CH_2Cl_2 1:1) afforded 2.42 g (7.06 mmol, 72%) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 6.23$ (dd, $^3J_{H\text{-}1,H\text{-}2} = 6.16$ Hz, $^4J_{H\text{-}1,H\text{-}3} = 1.65$ Hz, 1H, H-1), 4.65 (dd, $^3J_{H\text{-}2,H\text{-}1} = 6.16$ Hz, $^3J_{H\text{-}2,H\text{-}3} = 1.84$ Hz, 1H, H-2), 4.39 (ddd, $^3J_{H\text{-}3,H\text{-}4} = 7.01$ Hz, $^3J_{H\text{-}3,H\text{-}2} = 1.84$ Hz, $^4J_{H\text{-}3,H\text{-}1} = 1.65$ Hz, 1H, H-3), 3.90 (dd, $^2J_{H\text{-}6e,H\text{-}6a} = 10.81$ Hz, $^3J_{H\text{-}6e,H\text{-}5} = 5.57$, 1H, H-6e), 3.79 (dd, $J_{H\text{-}4,H\text{-}5} = 10.43$ Hz, $^3J_{H\text{-}4,H\text{-}3} = 7.01$ Hz, 1H, H-4), 3.78 (dd, $^2J_{H\text{-}6a,H\text{-}6e} = 10.81$ Hz, $^3J_{H\text{-}6a,H\text{-}5} = 10.33$ Hz, 1H, H-6a), 3.68 (ddd, $^3J_{H\text{-}5,H\text{-}4} = 10.43$ Hz, $^3J_{H\text{-}5,H\text{-}6a} = 10.33$ Hz, $^3J_{H\text{-}5,H\text{-}6e} = 5.57$ Hz, 1H, H-5), 1.48, 1.38 (s, 6H, $(CH_3)_2C$–), 1.15–0.90 (m, 21H, –Si[$CH(CH_3)_2]_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 143.1$ (C-1), 105.8 (C-2), 99.5 [$(CH_3)_2C$–], 73.3, 69.7, 67.7, 61.8 (4C, C-3, C-4, C-5, C-6), 28.9, 18.9 (2C, $(CH_3)_2C$–), 18.0, 17.9 (6C, –Si[$CH(CH_3)_2]_3$), 12.2 (3C, –Si[$CH(CH_3)_2]_3$) ppm. EI-MS (70 eV): m/z (%) = 327.2 (3.6) [$M^+ - CH_3$], 299.2 (100) [$M^+ - C_3H_7$], 241.1 (97) [$M^+ - C_3H_7 - C_3H_6O$], 197.0 (21) [$C_{10}H_{11}$], 185.1 (61) [$M^+ - C_9H_{21}Si$].

4.4.1.4. Synthesis of stannyl glucals *5* and *6*

General procedure. At −78°C 17.5 ml (28.53 mmol) of *tert*-butyllithium were added slowly to a solution of 6.19 mmol (3.81 g of **2** or 2.12 g of **4**) in 25 ml of THF. After stirring for 28 min at 0°C, the mixture was cooled again to −78°C. 5.0 ml (18.47 mmol) of tri-*n*-butylstannyl chloride were added, the mixture was stirred for 22 min before the reaction was quenched with 100 ml of water. Extraction of the product with three portions of Et_2O, washing of the combined organic layers with water and saturated NaCl solution, drying with $MgSO_4$, evaporation and chromatographic purification with petroleum ether–CH_2Cl_2 (8:1) containing 1‰ NEt_3 as additive afforded the pure products as colorless oils (2.97 g, 4.83 mmol, 78% of **5** and 1.89 g, 5.51 mmol, 89% of **6**).

1,5-Anhydro-2-desoxy-3,4,6-O-triisopropylsilyl-1-(tri-n-butyl-stannyl)-D-arabino-hex-1-enitol (***5***). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 4.81$ (dd, $^3J_{H\text{-}2,H\text{-}3} = 5.07$ Hz, $^4J_{H\text{-}2,H\text{-}4} = 1.69$ Hz, 1H, H-2), 4.10–4.03 (m, 2H, H-4, H-5), 3.94 (dd, $^2J_{H\text{-}6,H\text{-}6'} = 10.83$ Hz, $^3J_{H\text{-}6,H\text{-}5} = 6.95$ Hz, 1H, H-6), 3.89 (dd, $^2J_{H\text{-}6',H\text{-}6'} = 10.83$ Hz, $^3J_{H\text{-}6',H\text{-}5} = 4.97$ Hz, 1H, H-6′), 3.83 (pt, $^3J_{H\text{-}3,H\text{-}2} = 5.07$ Hz, $^3J_{HH} = 2$ Hz, 1H, H-3), 1.6–1.4 (m, 6H, –Sn($CH_2CH_2CH_2CH_3)_3$), 1.4–1.2 (6H, –Sn($CH_2CH_2CH_2CH_3)_3$), 1.0–0.8 (m, 78H, 3 –Si[$CH(CH_3)_2$], –Sn($CH_2CH_2CH_2CH_3)_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 162.3$ (C-1), 111.3 (C-2), 80.6 (C-3), 70.2 (C-4), 65.1 (C-5), 62.4 (C-6), 29.0 (3C, –Sn($CH_2CH_2CH_2CH_3)_3$), 27.3 (3C, –Sn($CH_2CH_2CH_2CH_3)_3$), 18.2–18.0 (18C, –Si[$CH(CH_3)_2]_3$), 13.7 (3C, –Sn($CH_2CH_2CH_2CH_3)_3$), 12.6–12.0 (9C, –Si[$CH(CH_3)_2]_3$), 9.49 (3C, –Sn($CH_2CH_2CH_2CH_3)_3$) ppm. FAB-MS (mNBA): m/z (%) = 903.5 (1.0) [$M^+ - H$], 847.5 (5.6) [$M^+ - C_4H_9$], 729.4 (2.2) [$M^+ - C_9H_{21}SiOH - H$], 687.4 (3.8) [$M^+ - C_9H_{21}SiOH - C_3H_7$], 613.4 (1.3) [$M^+ - SnC_{12}H_{27} - H$], 569.4 (3.5) [$M^+ - C_3H_7 - SnC_{12}H_{27} - H$], 543.2 (3.4) [$M^+ - 2C_9H_{21}SiO - CH_3$], 397.2 (5.9) [$M^+ - C_9H_{21}SiO - SnC_{12}H_{27} - C_3H_7$], 291.1 (20) [$(SnC_{12}H_{27})^+$].

1,5-Anhydro-2-deoxy-4,6-O-isopropylidene-3-O-triisopropylsilyl-1-(tri-n-butyl-stannyl)-D-arabino-hex-1-enitol (***6***). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 4.66$ (d, $^3J_{H\text{-}2,H\text{-}3} = 1.89$ Hz, 1H, H-2), 4.36 (dd, $^3J_{H\text{-}3,H\text{-}4} = 7.35$, $^3J_{H\text{-}3,H\text{-}2} = 1.89$ Hz, 1H, H-3), 3.86 (dd, $^2J_{H\text{-}6e,H\text{-}6a} =$

10.88 Hz, $^3J_{H\text{-}6e,H\text{-}5} = 5.69$ Hz, 1H, H-6e), 3.77 (dd, $^3J_{H\text{-}4,H\text{-}5} = 10.44$ Hz, $^3J_{H\text{-}4,H\text{-}3} = 7.35$ Hz, 1H, H-4), 3.74 (dd, $^2J_{H\text{-}6a,H\text{-}6e} = 10.88$ Hz, $^3J_{H\text{-}6a,H\text{-}5} = 10.44$ Hz, 1H, H-6a), 3.58 (ptd, $^3J_{H,H} = 10$ Hz, $^3J_{H\text{-}5,H\text{-}6e} = 5.69$ Hz, 1H, H-5), 1.47, 1.37 (s, 6H, $(CH_3)_2C$–), 1.6–0.8 (m, 48H, –Si[C*H*$(CH_3)_2]_3$, –Sn($C_4H_9)_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 162.7$ (C-1), 116.5 (C-2), 99.3 ($(CH_3)_2C$–), 73.7 (C-3), 70.0 (C-4), 68.6 (C-5), 62.1 (C-6), 29.0, 19.0 (2C, $(CH_3)_2C$–), 28.9, 27.2, 13.7, 9.7, (12C, –Sn($C_4H_9)_3$), 17.9, 18.0, 12.3, (9C, –Si[C*H*$(CH_3)_2]_3$ ppm. FAB-MS (mNBA): m/z (%) = 631.2 (6.3) [M^+], 589.1 (8.0) [$M^+ - C_3H_6$], 575.1 (28) [$M^+ - C_3H_6O$], 531.1 (5.6) [$M^+ - C_4H_9 - C_3H_7$].

4.4.2. Preparation of the carbene complexes 7 and 8

4.4.2.1. General procedure. To a solution of 855 mg (1.35 mmol) of **6** in 14 ml of THF was added 0.93 ml (1.48 mmol) of *n*-BuLi dropwise at −78°C. After stirring for 30 min the solution was combined with a suspension of 357 mg of $Cr(CO)_6$ (1.62 mmol) in 2 ml of THF at −78°C. Warming up to −37°C over a period of 60 min generated the acyl chromate. After changing the solvent to 40 ml of CH_2Cl_2, addition of 240 mg of $Me_3O^+BF_4^-$, stirring for 90 min at 0°C and chromatography with petroleum ether–CH_2Cl_2 (4:3), 472.8 mg (0.82 mmol, 61%) of **8** were obtained as a red solid. For the synthesis of complex **7**, 3.52 g (3.89 mmol) of stannyl glucal **5** were applied to the synthesis of the lithium acyl chromate intermediate. After stirring for 90 min at −40°C, methylation and chromatography with petroleum ether–CH_2Cl_2 (15:1), 2.31 g (2.72 mmol, 70%) of **7** were obtained as a red oil.

4.4.2.2. Pentacarbonyl[2-desoxy-3,4,6-tri-O-triisopropylsilyl-D-arabino-hex-1-enopyranosyl(methoxy)carbene]-chromium (7). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 5.32$ (dd, $^3J_{H\text{-}2,H\text{-}3} = 5.47$ Hz, $^4J_{H\text{-}2,H\text{-}4} = 1.49$ Hz, 1H, H-2), 4.77 (s, 3H, C*H*$_3$O-), 4.55 (ptt, $^3J_{H\text{-}5,H\text{-}6} = 7$ Hz, $^3J_{H\text{-}5,H\text{-}6'} = 6.56$ Hz, $^3J_{H\text{-}5,H\text{-}4} = 2$ Hz, $^4J_{H\text{-}5,H\text{-}3} = 2$ Hz, 1H, H-5), 4.20 (pdd, $^3J_{H\text{-}4,H\text{-}3} = 3$ Hz, $^3J_{H\text{-}4,H\text{-}5} = 2$ Hz, $^4J_{H\text{-}4,H\text{-}2} = 1.49$ Hz, 1H, H-4), 4.18 (pdt, $^3J_{H\text{-}3,H\text{-}2} = 5.47$ Hz, $^3J_{H\text{-}3,H\text{-}4} = 3$ Hz, $^4J_{H\text{-}3,H\text{-}5} = 2$ Hz, 1H, H-3), 4.01 (dd, $^2J_{H\text{-}6,H\text{-}6'} = 10.63$ Hz, $^3J_{H\text{-}6,H\text{-}5} = 7.00$ Hz, 1H, H-6), 3.94 (dd, $^2J_{H\text{-}6',H\text{-}6} = 10.63$ Hz, $^3J_{H\text{-}6',H\text{-}5} = 6.56$ Hz, 1H, H-6′), 1.1–0.9 (m, 63H, –Si[C*H*$(CH_3)_2]_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 337.9$ (Cr=C), 225.1 (*trans*-CO), 216.4 (4C, *cis*-CO), 156.6 (C-1), 96.9 (C-2), 81.7 (C-3), 68.9 (C-4), 66.8 (C-5), 66.3 (–CH_3O), 61.0 (C-6), 18.1–17.9 (18C, –Si[CH($CH_3)_2]_3$), 12.3–11.9 (3C, –Si[C*H*$(CH_3)_2]_3$) ppm. FAB-MS (mNBA): m/z (%) = 708.4 (100) [$M^+ - 5CO$], 665.3 (32) [$M^+ - 5CO - C_3H_7$], 621.2 (13) [$M^+ - 2C_3H_7 - 5CO - H$], 535.2 (25) [$M^+ - C_9H_{21}SiO - 5CO$], 307.0 (35) [$M^+ - 2C_9H_{21}SiOH - Cr(CO)_5 - H$]. IR (petroleum ether): $\nu_{(C=O)} = 2064$ (m, A_1^1), 1996 (w, B_1), 1965. (s, E), 1948 (vs, A_1^2) cm^{-1}.

4.4.2.3. Pentacarbonyl[2-desoxy-4,6-O-isopropylidene-3-O-triisopropylsilyl-D-arabino-hex-1-enopyranosyl-(methoxy)carbene]chromium (8). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 5.25$ (d, $^3J_{H\text{-}2,H\text{-}3} = 2.35$ Hz, 1H, H-2), 4.82 (s, 3H, C*H*$_3$O–), 4.52 (dd, $^3J_{H\text{-}3,H\text{-}H\text{-}4} = 7.82$ Hz, $^3J_{H\text{-}3,H\text{-}2} = 2.35$ Hz, 1H, H-3), 4.15 (dd, $^3J_{H\text{-}6e,H\text{-}6a} = 10.96$ Hz, $^2J_{H\text{-}6e,H\text{-}5} = 5.09$ Hz, 1H, H-6e), 4.03 (m, 1H, H-6a), 3.86 (ptd, $^3J_{H,H} = 10$ Hz, $^3J_{H\text{-}5,H\text{-}6e} = 5.47$ Hz, 1H, H-5), 3.82 (dd, br, 1H, H-4), 1.50, 1.40 (s, 6H, $(CH_3)_2C$–), 1.2–1.0 (m, 21H, –Si[C*H*$(CH_3)_2]_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 333.8$ (Cr=C), 224.7 (*trans*-CO), 216.6 (*cis*-CO), 157.3 (C-1), 102.2 (C-2), 99.7 ($(CH_3)_2C$–), 72.2, 70.5, 68.4, 66.8, 61.4 (5C, C-3, C-4, C-5, C-6, CH_3O–), 28.9, 18.8, (2C, $(CH_3)_2C$–), 18.0, 17.9 (2C, –Si[CH($CH_3)_2]_3$), 12.3, (–Si[C*H*$(CH_3)_2]_3$) ppm. EI-MS (70 eV): m/z (%) = 576.3 (1.0) [M^+], 548.3 (2.8) [$M^+ - CO$], 534.2 (< 1.0) [$M^+ - C_3H_6$], 464.2 (3.1) [$M^+ - 4CO$], 436.2 (26) [$M^+ - 5CO$], 394.2 (8.6) [$M^+ - C_3H_6 - 5CO$], 219.9 (72) [$M^+ - C_3H_6 - C_9H_{21}SiOH - 5CO - H$]. HR-MS: calc. for $C_{25}H_{36}CrO_{10}Si$ 576.1538; found: 576.1478. IR (petroleum ether): $\nu_{(C=O)} = 2064$ (m, A_1^1), 1994 (w, B_1), 1965 (s, E), 1950 (vs, A_1^2) cm^{-1}. Anal. Found: C, 52.27; H, 6.34. Calc.: C, 57.13; H, 6.29%.

4.4.3. Benzannulation of the glucal carbene complexes 7 and 8

4.4.3.1. General procedure for benzannulation of 7 and 8 with 3-hexyne. A solution of 0.94 mmol (789.3 mg of **7** and 542.0 mg of **8**) of the carbene complex and 1.1 ml (9.4 mmol) of 3-hexyne in 14 ml of *tert*-butyl methyl ether was saturated with argon by three pump–freeze–thaw cycles and warmed under reflux (3.5 h for complex **7** and 7 h for complex **8**). Subsequent chromatography (petroleum ether–diethyl ether, 8:1, for the benzannulation of **7** and petroleum ether–diethyl ether, 4:1, for the benzannulation of **8**) gave first the uncoordinated chromans **9b** (benzannulation of **7**, 168.4 mg, 0.29 mmol, 31%) and **12c** (benzannulation of **8**, 162.5 mg, 0.31 mmol, 33%) as colorless solids and then the $Cr(CO)_3$-coordinated chromans **9a** (benzannulation of **7**, 334.0 mg, 0.37 mmol, 39%), **12a** (benzannulation of **8**, 207.4 mg, 0.33 mmol, 35%) and **12b** (benzannulation of **8**, 66.1 mg, 0.10 mmol, 11%) as yellow solids.

Tricarbonyl{4a-8a-η⁶-[6,7-diethyl-5-hydroxy-8-methoxy-2(R)-triisopropylsilyloxymethyl-3(S),4(R)-bis-(triisopropylsilyloxy)chroman]}chromium (9a). ^{1}H-NMR (500 MHz, CD_2Cl_2): $\delta = 4.93$ (dd, $^3J_{H\text{-}4,H\text{-}3} = 3.28$ Hz,

$^4J_{H\text{-}4,H\text{-}2} = 1.69$ Hz, 1H, H-4), 4.81 (s, 1H, OH), 4.47 (m, 1H, H-2), 4.42 (dd, $^3J_{H\text{-}3,H\text{-}4} = 3.28$ Hz, $^3J_{H\text{-}3,H\text{-}2} = 1.14$ Hz, 1H, H-3), 4.31 (dd, $^2J_{H\text{-}1',H\text{-}1} = 11.23$ Hz, $^3J_{H\text{-}1,H\text{-}2} = 6.71$ Hz, 1H, H-1), 4.26 (dd, $^2J_{H\text{-}1',H\text{-}1} = 11.23$ Hz, $^3J_{H\text{-}1',H\text{-}2} = 5.86$ Hz, 1H, H-1′), 3.77 (s, 3H, –OMe), 2.35–2.89 (m, 4H, $-CH_2-CH_3$), 0.90–1.38 (m, 69H, $-CH_2CH_3$, –Si–[CH–(CH_3)]$_3$) ppm. ^{13}C-NMR (125 MHz, CD_2Cl_2): $\delta = 234.8$ (3C, $Cr(CO)_3$), 134.9, 133.4, 118.8, 112.5, 90.2, 87.5 (6C, C-4a, C-5, C-6, C-7, C-8, C-8a), 83.8 (C-2), 67.9 (C-3), 65.5 (–OMe), 64.8 (C-4), 62.6 (C-1), 22.1, 19.8 (2C, $ArCH_2CH_3$), 18.4–17.7 (18C, –Si[CH(CH_3)$_2$]$_3$), 16.0, 14.9 (2C, $ArCH_2CH_3$), 13.2, 12.6, 12.1 (9C, –Si[CH(CH_3)$_2$]$_3$) ppm. FAB-MS (mNBA): m/z (%) = 902.4 (30) [M^+], 859.5 (7.9) [$M^+ - CH_3 - CO$], 818.5 (17) [$M^+ - 3CO$], 729.3 (4.8) [$M^+ - C_9H_{21}SiO$], 644.3 (100) [$M^+ - C_9H_{21}SiOH - 3CO$], 601.0 (29) [$M^+ - 2C_9H_{21}SiO - 3CO - H$], 592.3 (14) [$M^+ - C_9H_{21}SiOH - Cr(CO)_3$], 549.3 (4.8) [$M^+ - C_3H_7 - C_9H_{21}SiOH - Cr(CO)_3$], 471.2 (7.1) [$M^+ - 2C_9H_{21}SiO - 3CO - H$], 405.3 (55) [$M^+ - CH_3 - 2C_9H_{21}SiO - Cr(CO)_3$]. IR (petroleum ether): $\nu_{(C=O)} = 1960$ (vs, A_1), 1888 (s, E), 1881 (s, E) cm^{-1}.

*6,7-Diethyl-5-hydroxy-8-methoxy-2(R)-triisopropylsilyloxymethyl-3(S),4(R)-bis(triisopropylsilyloxy)chroman (**9b**).* ^{1}H-NMR (500 MHz, CD_2Cl_2): $\delta = 5.03$ (pq, $^3J_{H\text{-}4,H\text{-}3} = 3.13$ Hz, $^4J_{H,H} \approx 1.5$ Hz, 1H, H-4), 4.72 (m, 1H, –OH), 4.41 (m, 1H, H-3), 4.35 (pq, $^3J_{H\text{-}3,H\text{-}4} = 3.13$ Hz, $^4J_{H,H} \approx 1.2$ Hz, 1H, H-2), 4.11 (ddd, $^2J_{H\text{-}1,H\text{-}1'} = 11.00$ Hz, $^3J_{H\text{-}1,H\text{-}2} = 7.65$ Hz, $^4J_{H\text{-}1,H\text{-}3} = 1.05$ Hz, 1H, H-1), 4.00 (ddd, $^2J_{H\text{-}1',H\text{-}1} = 11.00$ Hz, $^3J_{H\text{-}1',H\text{-}2} = 4.67$ Hz, $^4J_{H\text{-}1',H\text{-}3} = 1.29$ Hz, 1H, H-1′), 3.77 (s, 3H, CH_3O–), 2.48–2.67 (m, 4H, $ArCH_2CH_3$), 1.3–0.8 (m, 69H, –Si[CH(CH_3)$_2$]$_3$, $ArCH_2C_3$) ppm. ^{13}C-NMR (125 MHz, CD_2Cl_2): $\delta = 148.2$, 144.4, 140.4, 135.6, 117.9, 110.3 (6C, C-4a, C-5, C-6, C-7, C-8, C-8a), 82.4 (C-2), 70.0 (C-3), 64.6 (C-4), 64.2 (C-1), 60.7 (–OMe), 20.0, 19.1 (2C, $ArCH_2CH_3$), 18.3–17.9 (18C, –Si[CH(CH_3)$_2$]$_3$), 15.7, 14.6 (2C, $ArCH_2CH_3$), 12.9, 12.6, 12.2 (9C, –Si[CH(CH_3)$_2$]$_3$) ppm. FAB-MS (mNBA): m/z (%) = 766.5 (1.6) [M^+], 723.4 (3.5) [$M^+ - C_3H_7$], 592.3 (39) [$M^+ - C_9H_{21}SiOH$], 549.3 (9.2) [$M^+ - C_3H_7 - C_9H_{21}SiOH$], 523.3 (7.6) [$M^+ - 2C_3H_7 - C_9H_{21}Si$], 435.2 (4.4) [$M^+ - C_9H_{21}Si - C_9H_{21}SiOH$], 419.3 (27) [$M^+ - C_9H_{21}SiO - C_9H_{21}SiOH$], 405.3 (100) [$M^+ - CH_3 - 2C_9H_{21}SiO$].

*Tricarbonyl{4a-8a-η^6-[6,7-diethyl-5-hydroxy-8-methoxy-2(R),3(S)-(buta-3,3-dimethyl-2,4-O-1,4-diyl)-4(R)-(triisopropylsilyloxy)chroman]}chromium (**12a**,**b**).* Major diastereomer **12a**: ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 8.38$ (s, 1H, –OH), 5.23 (d, $^3J_{H\text{-}4,H\text{-}3} = 8.79$ Hz, 1H, H-4), 4.49 (dd, $^3J_{H\text{-}3,H\text{-}2} = 9.83$ Hz, $^3J_{H\text{-}1,H\text{-}4} = 8.79$ Hz, 1H, H-3), 4.04 (dd, $^2J_{H\text{-}1e,H\text{-}1a} = 10.72$ Hz, $^3J_{H\text{-}1e,H\text{-}2} = 5.76$ Hz, 1H, H-1e), 3.98 (pt, $^3J_{H,H} = 10$ Hz, 1H, H-1a), 3.90 (ptd, $^3J_{H,H} = 10$ Hz, $^3J_{H\text{-}1,H,\text{-}1e} = 5.76$ Hz, 1H, H-2), 3.65 (s, 3H, CH_3O–), 2.74 (m, 1H, $ArCH_2CH_3$), 2.53 (m, 1H, $ArCH_2CH_3$), 2.44–2.32 (m, 2H, $ArCH_2CH_3$), 1.57, 1.45 (s, 6H, $(CH_3)_2C$–), 1.22–1.10 (m, 27H, –Si[CH(CH_3)$_2$]$_3$, $ArCH_2CH_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 234.6$ (3C, $Cr(CO)_3$), 136.0, 132.3, 129.0, 128.2, 125.3, 118.5 (6C, C-4a, C-5, C-6, C-7, C-8, C-8a), 100.4 (1C, $(CH_3)_2C$–), 113.0, 95.7, 81.9, 66.2, 61.0 (5C, C-4, C-3, C-2, C-1‘, CH_3O–), 28.8, 21.7 (2C, $(CH_3)_2C$–), 19.2, 18.5 (2C, $ArCH_2CH_3$), 18.3, 18.0 (6C, –Si[CH(CH_3)$_2$]$_3$), 16.8, 14.8 (2C, $ArCH_2CH_3$), 13.9 (1C, –Si[CH(CH_3)$_2$]$_3$) ppm. EI-MS (70 eV): m/z (%) = 630.2 (48) [M^+], 615.1 (12) [$M^+ - CH_3$], 546.2 (13) [$M^+ - 3CO$], 503.1 (7.5) [$M^+ - C_3H_7 - 3CO$], 458.2 (73) [$M^+ - CH_3 - C_9H_{21}Si$], 445.0 (100) [$M^+ - C_9H_{21}Si - CO$], 430.1 (20) [$M^+ - C_3H_7 - C_9H_{21}Si$], 403.0 (25) [$M^+ - C_3H_6 - C_9H_{21}Si - CO$], 372.0 (18) [$M^+ - C_9H_{21}SiOH - 3CO$], 342.0 (66) [$M^+ - C_3H_6O - C_9H_{21}SiOH - 2CO$], 320.1 (30) [$M^+ - C_9H_{21}SiOH - Cr(CO)_3$], 284.0 (67) [$M^+ - CH_3 - C_3H_6O_2 - C_9H_{21}SiO - 3CO$]. HR-MS: Found: 630.2312. $C_{30}H_{46}CrO_9Si$. Calc.: 630.2316. Anal. Found: C, 57.09; H, 7.27; $C_{30}H_{46}CrO_9Si$ (630.2). Calc.: C, 57.13; H, 7.35%. IR (petroleum ether): $\nu_{(C=O)} = 1962$ (vs, A_1), 1896 (s, E), 1877 (s, E) cm^{-1}.

Minor diastereomer **12b**: ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 8.58$ (s, –OH), 5.48 (d, $^3J_{H\text{-}4,H\text{-}3} = 8.55$ Hz, H-4), 4.22 (ptd, $^3J_{H,H} = 10$ Hz, $^3J_{H,H} = 6$ Hz 1H, H-2), 3.68 (s, CH_3O–), 1.50 (s, 3H, $(CH_3)_2C$–) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 234.0$ (3C, $Cr(CO)_3$) ppm.

*6,7-Diethyl-5-hydroxy-8-methoxy-2(R),3(S)-(buta-3,3-dimethyl-2,4-O-1,4-diyl)-4(R)-(triisopropylsilyloxy)chroman (**12c**).* ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 7.92$ (s, 1H, –OH), 5.26 (d, $^3J_{H\text{-}4,H\text{-}3} = 8.30$ Hz, 1H, H-4), 4.12 (dd, $^3J_{H\text{-}3,H\text{-}2} = 10.13$ Hz, $^3J_{H\text{-}3,H\text{-}4} = 8.30$ Hz, 1H, H-3), 4.09 (dd, $^2J_{H\text{-}1e,H\text{-}1a} = 10.98$ Hz, $^3J_{H\text{-}1e,H\text{-}2} = 5.76$ Hz, 1H, H-1e), 3.95 (pt, $^3J_{H,H} = 10$ Hz, 1H, H-1a), 3.83 (ptd, $^3J_{H,H} = 10$ Hz, $^3J_{H\text{-}1,H\text{-}1e} = 5.76$ Hz, 1H, H-2), 3.70 (s, 3H, CH_3O–), 2.63–2.54 (m, 4H, $ArCH_2CH_3$), 1.52, 1.45 (s, 6H, $(CH_3)_2C$–), 1.14–1.08 (27H, –Si[CH(CH_3)$_2$]$_3$, $ArCH_2CH_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 150.8$, 144.6, 138.7, 137.0, 122.9, 108.3 (6C, C-4a, C-5, C-6, C-7, C-8, C-8a), 99.7 (1C, $(CH_3)_2C$–), 72.7, 72.1, 69.3, 61.6, 61.1 (5C, C-4, C-3, C-2, C-1′, $–OCH_3$), 29.0, 19.7 (2 C, $(CH_3)_2C$–), 19.1, 18.8 (2C, $ArCH_2CH_3$), 18.4, 18.1 (6C, –Si[CH(CH_3)$_2$]$_3$), 15.5, 14.7 (2C, $ArCH_2CH_3$), 13.6 (3C, –Si[CH(CH_3)$_2$]$_3$) ppm. EI-MS (70 eV): m/z (%) = 494.3 (7.3) [M^+], 451.3 (7.5) [$M^+ - C_3H_6$-H], 419.2 (2.3) [$M^+ - C_3H_6O_2 - H$], 393.2 (5.7) [$M^+ - C_3H_7 - C_3H_6O$], 337.2 (11) [$M^+ - C_9H_{21}Si$], 320.2 (100) [$M^+ - C_9H_{21}SiOH$], 262.1 (33) [$M^+ - C_3H_6O - C_9H_{21}SiOH$].

*4.4.3.2. General procedure for benzannulation of **7** with tolan.* A solution of 534.7 mg (0.63 mmol) of carbene

complex **7** and 1.7 g (1.26 mmol) of tolan was saturated with argon by three pump–freeze–thaw cycles. Warming under reflux for 2.5 h and chromatographic workup using petroleum ether–diethyl ether (4:1) gave first 7% (38.4 mg, 0.045 mmol) of uncoordinated chroman **10b** as a colorless solid and then 46% (285.4 mg, 0.29 mmol) of chroman complex **10a** as a yellow solid. As by-product, 80.7 mg (0.08 mmol, 13%) of **11** can be obtained as a yellow solid.

*Tricarbonyl{4a-8a-η⁶-[6,7-diphenyl-6-hydroxy-8-methoxy-2(R)-triisopropylsilyloxymethyl-3(S),4(R)-bis(triisopropylsilyloxy)chroman]}chromium (**10a**).* ^{1}H-NMR (500 MHz, CD_2Cl_2): $\delta = 7.36–7.0$ (m, 10H, Ar–H), 5.09 (dd, $^3J_{H\text{-}4,H\text{-}3} = 3{,}48$ Hz, $^4J_{H\text{-}4,H\text{-}2} = 1.79$ Hz, 1H, H-4), 4.82 (s, 1H, OH), 4.60 (m, 1H, H-2), 4.54 (dd, $^3J_{H\text{-}3,H\text{-}4} = 3.48$ Hz, $^3J_{H\text{-}3,H\text{-}2} = 1.29$ Hz, 1H, H-3), 4.41 (dd, $^2J_{H\text{-}1',H\text{-}1} = 6.36$ Hz, $^3J_{H\text{-}1,H\text{-}2} = 2.98$ Hz, 2H, H-1, H-1′), 1.4–0.8 (m, 63 H, –Si[CH(CH$_3$)$_2$]$_3$) ppm. ^{13}C-NMR (125 MHz, CD_2Cl_2): $\delta = 234.4$ (3C, Cr(CO)$_3$), 131.8, 131.3, 130.8, 130.6, 129.7, 129.2, 128.9, 127.9, 127.3, 127.2, 126.2, 123.3 (12C, aromatic C-atoms of phenyl substituents), 134.7, 132.6, 117.1, 93.0, 89.3, 87.3 (6C, C-4a, C-5, C-6, C-7, C-8, C-8a), 84.6 (C-2), 67.8 (C-3), 65.3 (–OMe), 64.6 (C-4), 62.7 (C-1), 18.4–17.7 (18C, –Si[CH(*C*H$_3$)$_2$]$_3$), 13.2, 12.5, 12.1 (9C, –Si[*C*H(CH$_3$)$_2$]$_3$) ppm. FAB-MS (mNBA): m/z (%) = 914.5 (1.5) [M$^+$], 862.5 (3.7) [M$^+$ − Cr], 818.5 (1.6) [M$^+$ − Cr − C$_3$H$_7$], 740.3 (2) [M$^+$ − C$_9$H$_{21}$SiOH], 688.3 (14) [M$^+$ − C$_9$H$_{21}$SiOH − Cr], 645.3 (12) [M$^+$ − C$_9$H$_{21}$SiOH − Cr − CH$_3$], 515.1 (24) [M$^+$ − C$_9$H$_{21}$SiO − C$_9$H$_{21}$SiOH − Cr], 501.1 (100) [M$^+$ − 2C$_9$H$_{21}$SiO − Cr − CH$_3$]. IR (petroleum ether): $\nu_{(C\equiv O)} = 1961$ (vs, A$_1$), 1891 (s, E), 1884 (s, E) cm^{-1}.

*Tricarbonyl{11-16-η⁶-[6,7-diphenyl-5-hydroxy-8-methoxy-2(R)-triisopropylsilyloxymethyl-3(S),4(R)-bis-(triisopropylsilyloxy)chroman]}chromium (**11**).* ^{1}H-NMR (500 MHz, CD_2Cl_2): $\delta = 7.40–6.90$ (m, 5H, Ar–H), 5.51 (pt, $J_{H,H} = 6{,}25$ Hz, $^4J_{H\text{-}4,H\text{-}2} = 1{,}79$ Hz, 1H, [Cr(CO)$_3$]Ar–H), 5.29 (pdt, $J_{H,H} = 6.59$ Hz, $J_{H,H} = 1.24$ Hz, 1H, [Cr(CO)$_3$]Ar–H), 5.21 (ptd, $J_{H,H} = 6.46$ Hz, $J_{H,H} = 1.29$ Hz, 1H, [Cr(CO)$_3$]Ar–H), 5.14 (m, 1H, [Cr(CO)$_3$]Ar–-H), 5.17 (dd, $^3J_{H\text{-}3,H\text{-}3} = 3.33$ Hz, $^4J_{H\text{-}4,H\text{-}2} = 1.59$ Hz, 1H, H-4), 5.06 (ptd, $J_{H,H} = 6.51$ Hz, $J_{H,H} = 1.09$ Hz, 1H, [Cr(CO)$_3$]Ar–H), 4.94 (s, 1H, OH), 4.58 (m, 1H, H-2), 4.47 (dd, $^3J_{H\text{-}3,H\text{-}4} = 3.33$ Hz, $^3J_{H\text{-}3,H\text{-}2} = 1.20$ Hz, 1H, H-3), 4.24 (dd, $^2J_{H\text{-}1,H\text{-}1'} = 11.00$ Hz, $^3J_{H\text{-}1,H\text{-}2} = 5.61$ Hz, 1H, H-1), 4.12 (dd, $^2J_{H\text{-}1',H\text{-}1} = 11.00$ Hz, $^3J_{H\text{-}1',H\text{-}2} = 4.77$ Hz, 1H, H-1′), 3.58 (s, 3H, OMe), 1.4–0.8 (m, 63H, –Si[CH(CH$_3$)$_2$]$_3$) ppm. ^{13}C-NMR (125 MHz, CD_2Cl_2): $\delta = 231.5$ (3C, Cr(CO)$_3$), 147.7, 147.5, 146.4, 137.3, 136.6, 135.8, 131.8, 130.9, 127.7, 126.9, 112.4, 110.6 (12C, aromatic C-atoms phenyl and chroman), 103.6, 99.7, 98.3, 94.8, 91.3, 90.7, (6C, aromatic C-atoms of the Cr(CO)$_3$-complexed phenyl ring), 83.1 (C-2), 69.5 (C-3), 64.1 (2C, C-1, OMe), 62.7 (C-4), 18.3–17.9 (18C, –Si[CH(*C*H$_3$)$_2$]$_3$), 12.9, 12.5, 12.1 (9C, –Si[*C*H(CH$_3$)$_2$]$_3$) ppm. IR (petroleum ether): $\nu_{(C\equiv O)} = 1984$ (vs, A$_1$), 1922 (s, E), 1913 (s, E) cm^{-1}.

*6,7-Diphenyl-5-hydroxy-8-methoxy-2(R)-triisopropylsilyloxymethyl-3(S),4(R)-bis(triisopropylsilyloxy)-chroman (**10b**).* ^{1}H-NMR (500 MHz, CD_2Cl_2): $\delta = 7.6–7.0$ (m, 10H, Ar–H), 5.13 (dd, $^3J_{H\text{-}4,H\text{-}3} = 3.43$ Hz, $^4J_{H\text{-}4,H\text{-}2} = 1.54$ Hz, 1H, H-4), 4.90 (s, 1H, OH), 4.52 (m, 1H, H-2), 4.44 (dd, $^3J_{H\text{-}3,H\text{-}4} = 3.43$ Hz, $^3J_{H\text{-}3,H\text{-}2} = 1.29$ Hz, 1H, H-3), 4.21 (dd, $^2J_{H\text{-}1',H\text{-}1} = 10.95$ Hz, $^3J_{H\text{-}1,H\text{-}2} = 7.55$ Hz, 1H, H-1), 4.10 (dd, $^2J_{H\text{-}1',H\text{-}1} = 10.95$ Hz, $^3J_{H\text{-}1',H\text{-}2} = 4.82$ Hz, 1H, H-1′), 3.55 (s, 3H, –OMe), 1.3–0.9 (m, 63H, –Si[CH(CH$_3$)$_2$]$_3$) ppm. ^{13}C-NMR (125 MHz, CD_2Cl_2): $\delta = 147.4$, 146.4, 137.3, 135.4, 135.1, 131.6, 131.2, 130.6, 128.8, 127.3, 127.1, 126.2, 118.7, 111.6 (18C, aromatic C), 83.1 (C-2), 69.6 (C-3), 64.3 (C-1), 64.0 (C-4), 60.7 (OMe), 18.3–17.9 (18C, –Si[CH(*C*H$_3$)$_2$]$_3$), 12.8, 12.5, 12.1 (9C, –Si[*C*H(CH$_3$)$_2$]$_3$) ppm. FAB-MS (mNBA): m/z (%) = 863.5 (2) [M$^+$], 819.5 (1.5) [M$^+$ − C$_3$H$_7$], 688.3 (15.0) [M$^+$ − C$_9$H$_{21}$SiOH − H], 645.3 (12) [M$^+$ − C$_3$H$_7$ − C$_9$H$_{21}$SiOH − H], 515.1 (27) [M$^+$ − C$_9$H$_{21}$SiOH], 501.1 (100) [M$^+$ − C$_9$H$_{21}$SiOH − C$_9$H$_{21}$SiO − C$_9$H$_{21}$SiOH − CH$_3$].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos CCDC-148674 (**8**) and CCDC-148675 (**12a**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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References

[1] (a) D. Voet, J.G. Voet, Biochemistry, Wiley, Chichester, 1999. (b) A.E. Stütz, Iminosugars as Glycosidase Inhibitors, Wiley, Chichester, 1999. (c) H. van Bekkum, H. Röper, A.G.J. Vorhagen, Carbohydrates as Organic Raw Materials III, Wiley, Chichester, 1996.
[2] K.-A. Karlsson, Trends Biochem. Sci. 12 (1991) 265.
[3] G.N. Sando, E.F. Neufeld, Cell 12 (1977) 619.

[4] K.A. Karlsson, Annu. Rev. Biochem. 58 (1989) 309.
[5] H. Ogura, A. Hasegawa, T. Suami, Carbohydrates: Synthetic Methods and Application in Medicinal Chemistry, VCH, Weinheim, 1992.
[6] P. Collins, R. Ferrier, Monosaccharides: Their Chemistry and their Roles in Natural Products, Wiley, Chichester, 1995.
[7] P. Sinaÿ, Pure Appl. Chem. 63 (1991) 519.
[8] (a) R.R. Schmidt, Pure Appl. Chem. 61 (1989) 1257. (b) H.P. Seeberger, M.T. Bilodeau, S.J. Danishefsky, Aldrichim. Acta 30 (1997) 75.
[9] (a) M.H.D. Postema, Tetrahedron 48 (1992) 8545. (b) M.H.D. Postema, C-Glycoside Synthesis, CRC Press, London, 1995. (c) J.-M. Beau, T. Gallagher, Top. Curr. Chem. 189 (1997) 1. (d) F. Nicotra, Top. Curr. Chem. 187 (1997) 55.
[10] (a) K.H. Dötz, R. Ehlenz, Chem. Eur. J. 6 (1997) 1751. (b) K.H. Dötz, C. Jäkel, W.C. Haase, J. Organomet. Chem. 617–618 (2001) 119.
[11] (a) I. Frappa, D.J. Sinou, Carbohydr. Chem. 16 (1997) 255. (b) O. Jarreton, T. Skrydstrup, J.-F. Espinosa, J. Jiménez-Barbero, J.-M. Beau, Chem. Eur. J. 5 (1999) 430.
[12] G.L. Trainor, B.E. Smart, J. Org. Chem. 48 (1983) 2447.
[13] P. DeShong, E.D. Soli, G.A. Slough, D.R. Sidler, V. Elango, P.J. Rybczynski, L.J.S. Vosejpka, T.A. Lessen, T.X. Le, G.B. Anderson, W. von Philipsborn, M. Vöhler, D. Rentsch, O. Zerbe, J. Organomet. Chem. 593 (2000) 49.
[14] (a) F.E. McDonald, Chem. Eur. J. 5 (1999) 3103. (b) F.E. McDonald, K.S. Reddy, Y. Díaz, J. Am. Chem. Soc. 122 (2000) 4304.
[15] B. Weyershausen, M. Nieger, K.H. Dötz, J. Org. Chem. 64 (1999) 4206.
[16] K.H. Dötz, M. Klumpe, M. Nieger, Chem. Eur. J. 5 (1999) 691.
[17] W.-C. Haase, M. Nieger, K.H. Dötz, Chem. Eur. J. 5 (1999) 2014.
[18] K.H. Dötz, P. Tomuschat, Chem. Soc. Rev. 28 (1999) 187.
[19] E.O. Fischer, A. Maasböl, Angew. Chem. 76 (1964) 645; Angew. Chem. Int. Ed. Engl. 76 (1964) 645.
[20] P. Lesimple, J.M. Beau, P. Sinaÿ, Carbohydr. Res. 171 (1987) 289.
[21] (a) R.W. Friesen, C.F. Sturino, A.K. Daljeet, A. Kolaczewska, J. Org. Chem. 56 (1991) 1944. (b) K.H. Dötz, C. Jäkel, Tetrahedron 56 (2000) 167. (c) J.R. Bearder, M.L. Dewis, D.A. Whiting, J. Chem. Soc. Perkin Trans. I (1995) 227. (d) E.J. Corey, H. Cho, C. Rücker, D.H. Hua, Tetrahedron Lett. 22 (1981) 3455. (e) For a review, see: C. Rücker, Chem. Rev. 95 (1995) 1009.
[22] (a) B. Fraser-Raid, D.L. Walker, Y.-K. Tam, N.L. Holder, Can. J. Chem. 51 (1973) 3950. (b) O. Kjølberg, K. Neumann, Acta Chem. Scand. 47 (1993) 843.
[23] (a) R.J. Abraham, H. Gottschalck, H. Paulsen, W.A. Thomas, J. Chem. Soc. (1965) 6268. (b) J.R. Durig, R.O. Carter, L.A. Carreira, J. Chem. Phys. 60 (1974) 3098. (c) R.C. Lord, T.C. Rounds, T. Ueda, J. Chem. Phys. 57 (1972) 2572. (d) S.H. Mahmoud, L. Somsák, I. Farkas, Carbohydr. Res. 254 (1994) 91.
[24] (a) D.E.F. Gracey, W.R. Jackson, W.B. Jennings, S.C. Rennison, R. Spratt, J. Chem. Soc. B (1969) 1210. (b) M. Uemura, K. Take, Y. Hayashi, J. Org. Chem. 48 (1983) 3855. (c) R.P. Hsung, W.D. Wulff, C.A. Challener, Synthesis (1996) 773.
[25] K.H. Dötz, R. Dietz, A. von Imhof, H. Lorenz, G. Huttner, Chem. Ber. 109 (1976) 2033.
[26] (a) V. Kunz, W. Nowacki, Helv. Chim. Acta 50 (1967) 1052. (b) K.H. Dötz, O. Kretschik, M. Nieger, Organometallics 15 (1996) 3625. (c) K.H. Dötz, C. Stinner, M. Nieger, J. Chem. Soc. Chem. Commun. (1995) 2535.
[27] (a) P. Hofmann, M. Hämmerle, Angew. Chem. 101 (1989) 940; Angew. Chem. Int. Ed. Engl. 28 (1989) 908. (b) P. Hofmann, M. Hämmerle, G. Unfried, New J. Chem. 15 (1991) 769. (c) M. Gleichmann, B.A. Heß, K.H. Dötz, J. Am. Chem. Soc. 118 (1996) 10 551. (d) M. Torrent, M. Duran, M. Solà, J. Am. Chem. Soc. 121 (1999) 1309. (e) H. Fischer, P. Hofmann, Organometallics 18 (1999) 2590.
[28] K.H. Dötz, T. Schäfer, F. Knoll, K. Harms, Angew. Chem. 104 (1992) 1257; Angew. Chem. Int. Ed. Engl. 31 (1992) 1236.
[29] K.H. Dötz, J. Mühlemeier, Angew. Chem. 94 (1982) 2023; Angew. Chem. Int. Ed. Engl. 21 (1982) 929.
[30] (a) A. Closse, H.-P. Sigg, Helv. Chim. Acta 56 (1973) 619. (b) K. Khron, G. Brückner, H.-P. Tietjen, Chem. Ber. 111 (1978) 1284. (c) W. Brade, A. Vasella, Helv. Chim. Acta 72 (1989) 1649.
[31] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[32] G.M. Sheldrick, SHELXL-97, Universität Göttingen, Germany, 1997.
[33] H.D. Flack, Acta Crystallogr. Sect. A 39 (1983) 876.