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Organotransition metal-modified sugars Part 25. Spiro-*C*-glycosidation and C_2-homologization of carbohydrates via Fischer glycosylidene complexes: a strategy to novel organometallic disaccharides and a rare example of atropisomerism☆

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Abstract

Fischer-type glycosylidene complexes are shown to bear considerable potential for the synthesis of *C*-glycosidic compounds. Insertion of nucleophilic alkynes into the chromium glycosylidene bond as shown for mannosylidene complex **2** affords C_2-homologuous carbohydrates still bearing the metal carbene functionality. The insertion of *O*-ethynyl-carbohydrates leads to novel organometallic disaccharides in which the sugar moieties are linked by a chromium carbene spacer. Ynamine insertion proceeds with virtually complete *E*-selectivity, and the insertion products reveal a remarkable irreversible atropisomerism. The sugar metal carbenes also serve as glycosylidene sources as demonstrated by the cyclopropanation of electron-deficient alkenes. The mannosylidene complex **2** is further applied to the diastereoselective synthesis of anomeric spirocyclopropyl-*C*-glycosides which bear a conformationally rigid scaffold.

Keywords: Alkyne insertion; Atropisomerism; Carbene complexes; Carbohydrates; Spirocyclopropanation; Disaccharides

1. Introduction

The need for glycosidase-resistant carbohydrate mimetics has stimulated intense research during the past decade, and a variety of synthetic methodologies have been established for the access to *C*-glycosides [2]. The application of Fischer glycosylidene complexes to carbohydrate chemistry [3] has provided various non-conventional routes to annulated or spirocyclic *C*-glycosides [4], iminoheptonic acid derivatives [5], iminosugars [6] and novel glycoconjugates [6b]. Additional synthetic potential of Fischer carbene complexes [7] is based on stereoselective aldol- [8] and Michael-type [9] reactions, cyclopropanation [10], benzannulation [9,11], Diels-Alder reaction [12] or photoinduced β-lactam and β-lactone formation [13]. We now report on template reactions occurring at the anomeric center of readily accessible furanosylidene complexes which we applied to C_2-homologization of carbohydrates as well as to the synthesis of novel organometallic disaccharides and anomeric spirocyclic carbohydrate scaffolds.

2. Results and discussion

Glycosylidene complexes such as chromium mannosylidene (**2**) are synthesized in good yield on a multigram scale via stoichiometric olefin metathesis from the *exo*-glycal precursors (Scheme 1). They show the typical

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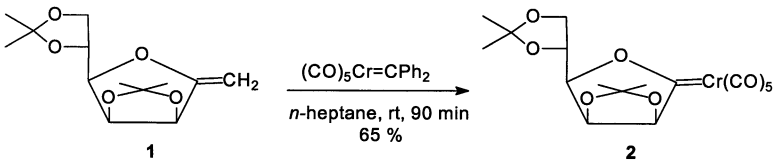


Scheme 1. Synthesis of furanosylidene complex **2**.

spectroscopic and structural features of Fischer-type metal carbenes; they are stable at room temperature, insensitive to water and can be handled shortly in air [6].

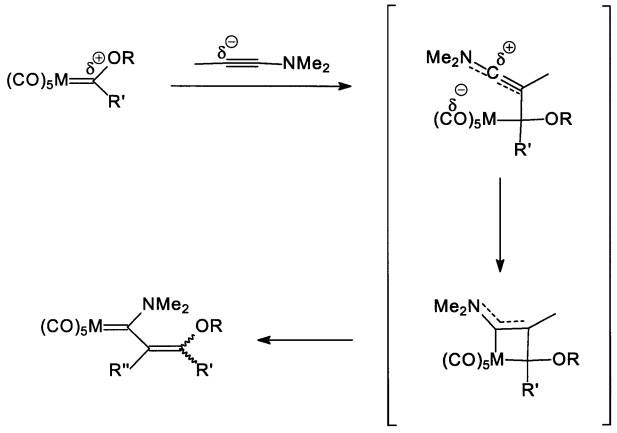
2.1. Insertion reactions

Nucleophilic alkynes are known to insert into the metal–carbene bond of Fischer alkoxycarbene complexes to result in a C_2-elongated α,β-unsaturated carbene complex. This type of insertion reactions have been mostly described with the commercially available 1-*N*,*N*-diethylamino-2-propyne [14] which affords (amino)vinyl carbene complexes; however, similar insertion processes also occur with less nucleophilic alkynes and heteroatom triple bond analogues such as ynethers [15], cyanamides [16], organocyanates and alkylthiocyanates [17].

Kinetic studies on the ynamine insertion suggest that the insertion starts with a nucleophilic attack of the alkyne β-carbon atom at the electrophilic carbene center [18]. Rearrangement to the α,β-unsaturated carbene complex may involve a zwitterionic or metallacyclobutene-type intermediate which, in turn, opens in cycloreversion to give the metal vinyl carbene (Scheme 2).

2.1.1. Insertion of alkynolethers

The reaction of mannofuranosylidene complex **2** with an excess of ethoxyacetylene proceeded slowly at room temperature as monitored by TLC and IR spectroscopy (Scheme 3). It was completed after 86 h to yield an approximate 1:1 mixture of diastereomers *E*/*Z*-**3** which could be isolated and separated by column chromatography [19].



Scheme 2. Proposed mechanism for the insertion of ynamines into the metal–carbene bond of alkoxycarbene complexes [18].

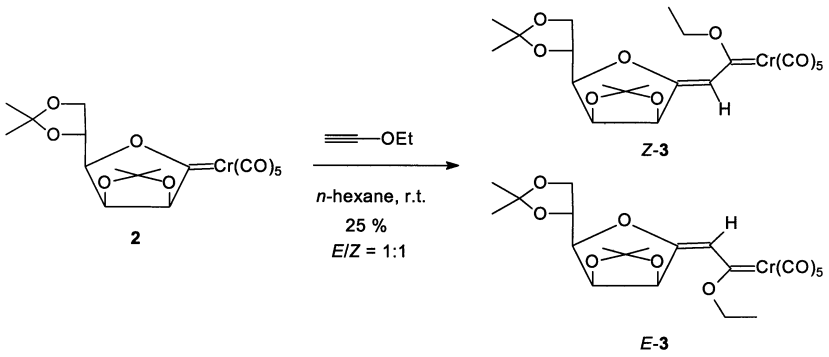
The configuration of the exocyclic double bond was established by X-ray crystallography of *E*-**3** (Fig. 1). The crystal structure of *E*-**3** exhibits a marked push-pull character [20]: the chromium–carbene bond is lengthened to 2.07 Å as compared to 1.98 Å in complex **2** [6a], whereas the carbene carbon–oxygen bond is basically unchanged. The relatively short C3–O2 (1.36 Å) and C1–C2 (1.46 Å) single bonds and the slight lengthening of the C2–C3 double bond (1.35 Å) indicate a contribution of the alkenyl chain in the stabilization of the strongly electrophilic carbene center. The furanose ring adopts an ^{O}E-conformation.

The insertion of *O*-ethynyl sugars is expected to result in novel organometallic disaccharides bearing the versatile α,β-unsaturated Fischer carbene complex functionality [21]. The starting materials 3-*O*-ethynyl-fructopyranose (**4**) and 6-*O*-ethynyl-galactopyranose (**5**) were prepared in good yields following a modified straightforward one-pot-procedure developed by Greene and coworkers (Scheme 4) [22].

Upon reaction of an excess of the secondary alkynolether **4** with mannofuranosylidene complex **2** only traces of an impure diastereomeric mixture of *E*/*Z*-**6** could be obtained. However, when complex **2** was reacted with an excess of the primary galactose-derived alkyne **5** at room temperature for 48 h, an approximate 2.7:1 *E*/*Z* mixture (46% de) of disaccharide complex **7** was obtained in 38% yield. The diastereomers were separated by chromatography and their configuration was determined by NOE experiments (Scheme 5).

2.1.2. Insertion of *N*,*N*-diethylamino-2-propyne

The addition of *N*,*N*-diethylamino-2-propyne to a solution of mannofuranosylidene complex **2** in dichloromethane–light petroleum at −78 °C resulted in an instantaneous color change from orange to yellow, and the reaction was completed within minutes as indicated by TLC and IR spectroscopy. Upon chromatographic work up below −27 °C two isomers were isolated with a d.r. of 15:1 (88% de) in an isolated overall yield of 85% (Scheme 6). At temperatures above 10 °C the major isomer rearranges virtually quantitatively and irreversibly to the minor isomer. No reisomerization was observed when a solution of the stable isomer was cooled again to 233 K.



Scheme 3. Insertion of ethoxyethyne.

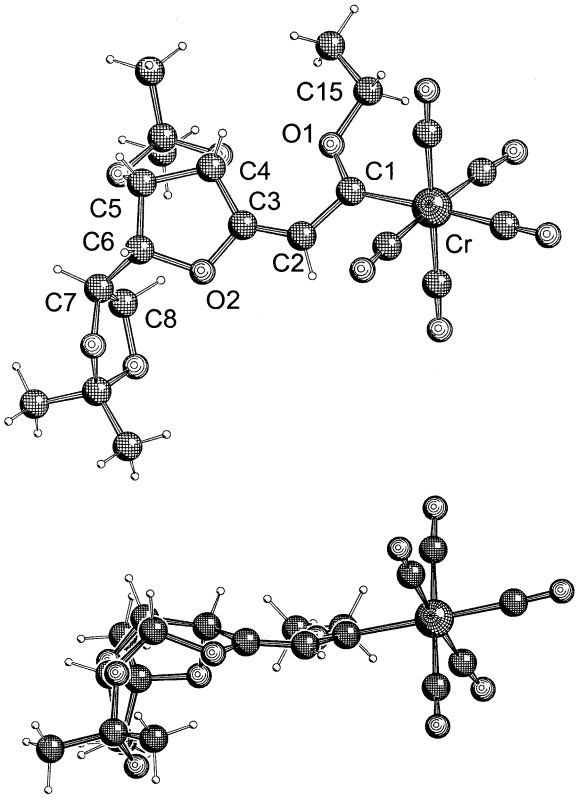
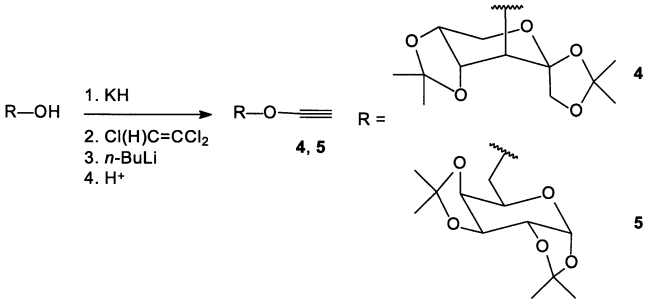


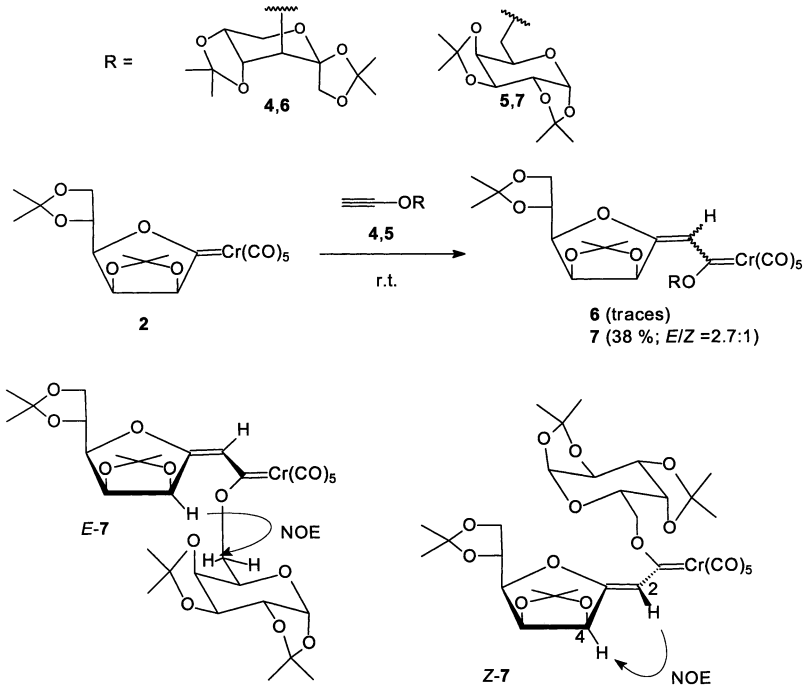
Fig. 1. Schakal plots of the molecular structure of complex *E*-**3**. Selected bond lengths (Å) and angles (°): Cr–C1: 2.070(2); C1–C2: 1.458(3); C2–C3: 1.350(3); C3–C4: 1.501(3); C3–O2: 1.358(3); C1–O1: 1.314(2); O1–C1–Cr: 131.20(14); C2–C1–Cr: 121.17(15); O1–C1–C2: 107.62(18); C1–O1–C15: 123.06(17); C3–C4–C5–C6: −0.5(2); O2–C3–C4–C5: 10.7(2); Cr–C1–O1–C15: −1.0(5); Cr–C1–C2–C3: 162.4(2). (The crystallographic atom numbering is not necessarily identical with the numbering used in the experimental part.)



Scheme 4. Synthesis of the sugar ynethers **4** and **5**.

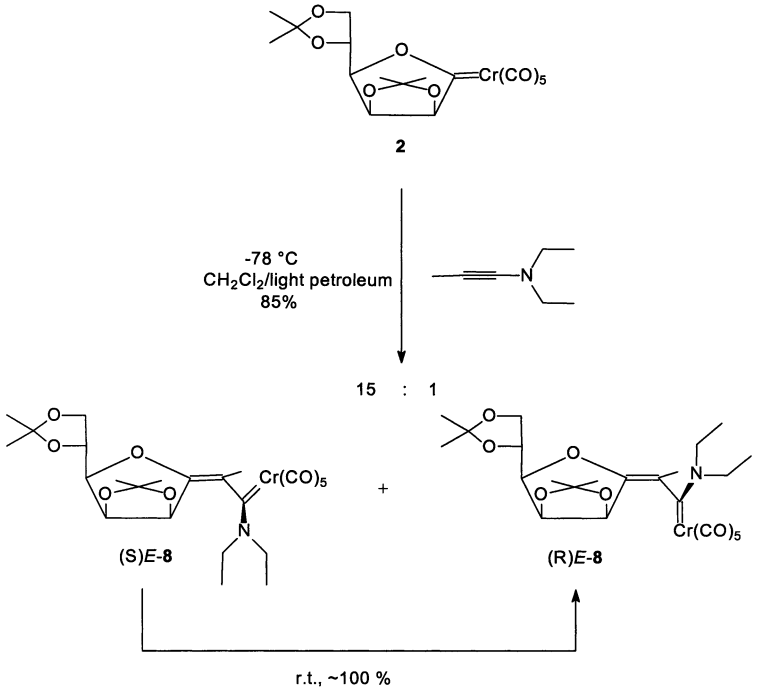
The rearrangement of the thermolabile major isomer of complex **8** to the stable isomer in $CDCl_3$ was monitored by NMR at various temperatures with comparable concentrations of starting materials. At 10 °C no reaction was observed after 16 h; at 30, 40 and 45 °C the reaction followed a first-order kinetics from which the activation energy barrier for the rearrangement could be estimated as ca. 22 kcal mol^{-1} (Fig. 2).

We had first addressed this rearrangement in terms of an *E*/*Z*-isomerization [23] of the insertion products, assuming a similar push-pull character as found in *E*-**3**. Several β-amino-α,β-unsaturated aminocarbene chromium complexes have been shown to exhibit strong push-pull behavior [24,25] which is expected to increase the barrier of rotation around the C1–C2 bond, eventually resulting in a coalescence temperature near 20 °C [25]. X-ray structure analyses of isomerizing systems show a pronounced conjugation and averaged bond lengths [24–26]. To gain insight into the bonding properties of complexes **8**, we grew single crystals of the thermolabile major isomer. An X-ray analysis established both the *E*-configuration around the double bond (Fig. 3) and a $^{O}T_1$-conformation of the furanose ring. In addition, the major isomer was identified as the (*S*)-rotamer around the C1–C2 bond. Presumably for steric reasons, the long chromium–carbene bond (2.13 Å) tends to the upper end of the range of Fischer-type carbene complexes. Comparing the bond lengths of C3–O1 (1.39 Å), C2–C3 (1.32 Å) and C1–C2 (1.50 Å) with those of complex *E*-**3**, and given the orthogonality between the carbene and the double bond plane, there is obviously no conjugation between the two π-systems—a feature of which only one single X-ray crystallographic evidence has been available so far [26].



Scheme 5. Insertion of the sugar ynethers **4** and **5** into the metal–carbene bond of mannofuranosylidene complex **2**.

A rationale for these observation is provided by an atropisomerism [27] around the C1–C2 bond defining (*S*)-*E*-**8** as the kinetically and (*R*)-*E*-**8** as the thermodynamically favored isomer. The kinetic preference of the thermodynamically disfavored rotamer can easily be understood on the basis of the proposed mechanism (Scheme 7) [18]: avoiding steric interactions between the C-2 substituents and the methyl group adjacent to the nucleophilic alkyne carbon atom, the orientation of the approaching ynamine is likely to lead to an *E*-configuration in the product. Furthermore, the ynamine attacks from the sterically less hindered side (i.e. from



Scheme 6. Insertion of *N*,*N*-diethylamino-2-propyne.

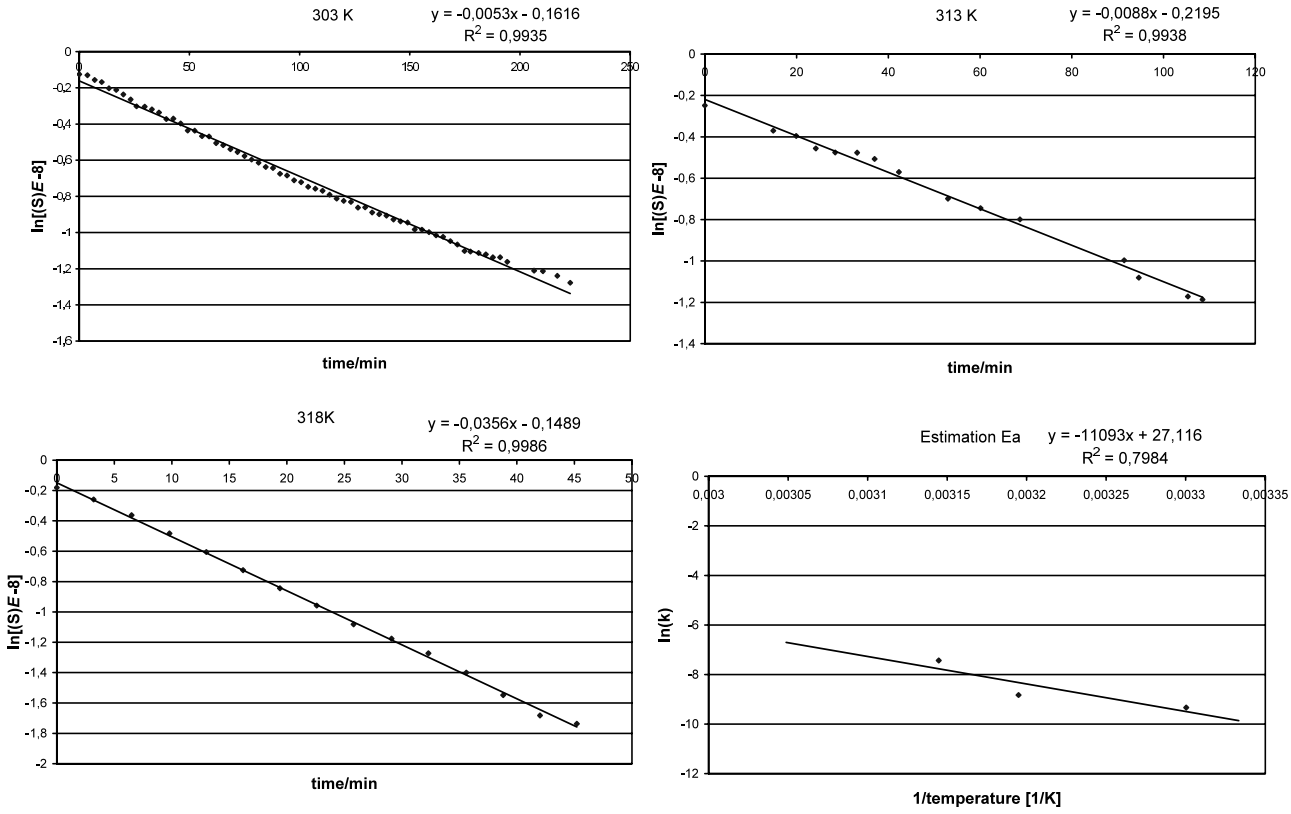


Fig. 2. Kinetic studies of the rearrangement (*S*)-*E*-**8** into (*R*)-*E*-**8**.

below) placing the pentacarbonylchromium fragment fixed on the disfavored side until the rotation barrier can be matched.

3. Cyclopropanation reactions

Carbohydrates with cyclopropane moieties, such as the natural antibiotic ambruticidin [28] bearing a cyclopropyl-functionalized side chain or annulated carbohydrate cyclopropanes, have occasionally been described [29]. Particularly interesting, however, are spirocyclopropanes as synthetic building blocks [30], glycosidase inhibitors, or useful scaffolds for carbohydrate mimics. Thus, a number of 1- [31], 2- [32], 3- [33], 4- [34b] and 5-spirocyclopropyl glycosides [34] have been synthesized, mainly by addition of dihalocarbenes or diazoalkanes to *exo*-glycals. Donor- and acceptor-functionalized anomeric *C*-spiroglycosides which serve as precursors in the synthesis of glycosidase inhibitors [31b] have been synthesized via cyclopropanation of activated alkenes by in situ-generated free glycosylidenes from azides [35], diazirines [36] or glyconolactone toluenesulfonylhydrazone precursors [37]. With a single exception, these reactions suffer from either poor selectivity as observed for pyranosylidenes or from moderate yields as encountered in the furanosylidene series.

Fischer-type metal carbenes are known as useful carbene sources for the synthesis of donor–acceptor substituted cyclopropanes [38]. In addition to the stoichiometric protocol [39], its catalytic variant [40] as well as cascade reactions including insertion and olefin metathesis steps [10b,41] have increased the scope and attractivity of this type of reaction.

Two different mechanisms are being discussed for the attack of the olefin to the carbene center depending on both the reaction conditions and the electrophilic nature of the carbene complex. An associative mechanism is supposed to govern the cyclopropanation of nucleophilic alkenes, proceeding without prior thermal decarbonylation. The nucleophilic terminus of the alkene adds to the carbene center followed by a backside ring closure leading to the cyclopropane skeleton. This model is supported by kinetic and theoretical studies as well as by deuteration experiments and is preferred to occur with pronounced electrophilic carbene complexes such as pentacarbonyl (benzylidene)tungsten [42]. Cyclopropanation reactions employing less electrophilic alkoxycarbene complexes, however, are commonly carried out at higher temperatures and are initiated by substitution of a *cis*-carbonyl ligand by the olefin. The resulting tetracarbonyl (alkene)carbene complex is supposed to lead to a cyclopropane via a metallacyclobutane-like intermediate. In the presence of electron-rich alkenes, the latter pathway competes with the formation of a

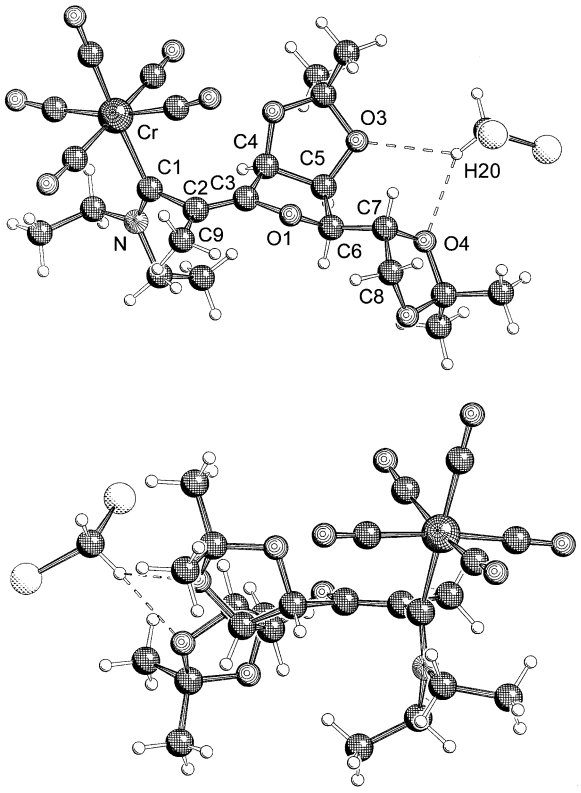


Fig. 3. Schakal plots of the molecular structure of complex *E*-**8**. The compound cocrystallizes with one molecule of CD_2Cl_2. Selected bond lengths (Å) and angles (°): Cr–C1: 2.1314(19); C1–N1: 1.319(2); C1–C2: 1.495(3); C2–C3: 1.317(2); C3–C4: 1.496(2); C3–O1: 1.393(2); Cr–C1–C2–C3: −94.31(19); N1–C1–Cr: 131.84(14); C2–C1–Cr: 115.36(13); N1–C1–C2: 112.67(16); C1–C2–C3–C4: 0.0(3); O4–H20: 2.35; O5a–H20′: 2.30. (The crystallographic atom numbering is not necessarily identical with the numbering used in the experimental part.)

metathesis product [39b,44,45] according to the Chauvin mechanism [43].

Typically, cyclopropanation reactions are carried out over 1 or a few days at 80–90 °C in non-polar solvents such as cyclohexane or octane [46,47]. The focus of these studies has hitherto been on alkoxy(aryl)carbene complexes as a result of the lower reactivity and increased CH-acidity of their alkoxy(alkyl)carbene counterparts [47c]. To our knowledge, stoichiometric cyclopropanation using oxacycloalkylidene complexes has not been studied so far [48]. This fact stimulated us to examine the potential of Fischer-type glycosylidene complexes for the construction of *C*-glycosidic anomeric spirocyclopropanes.

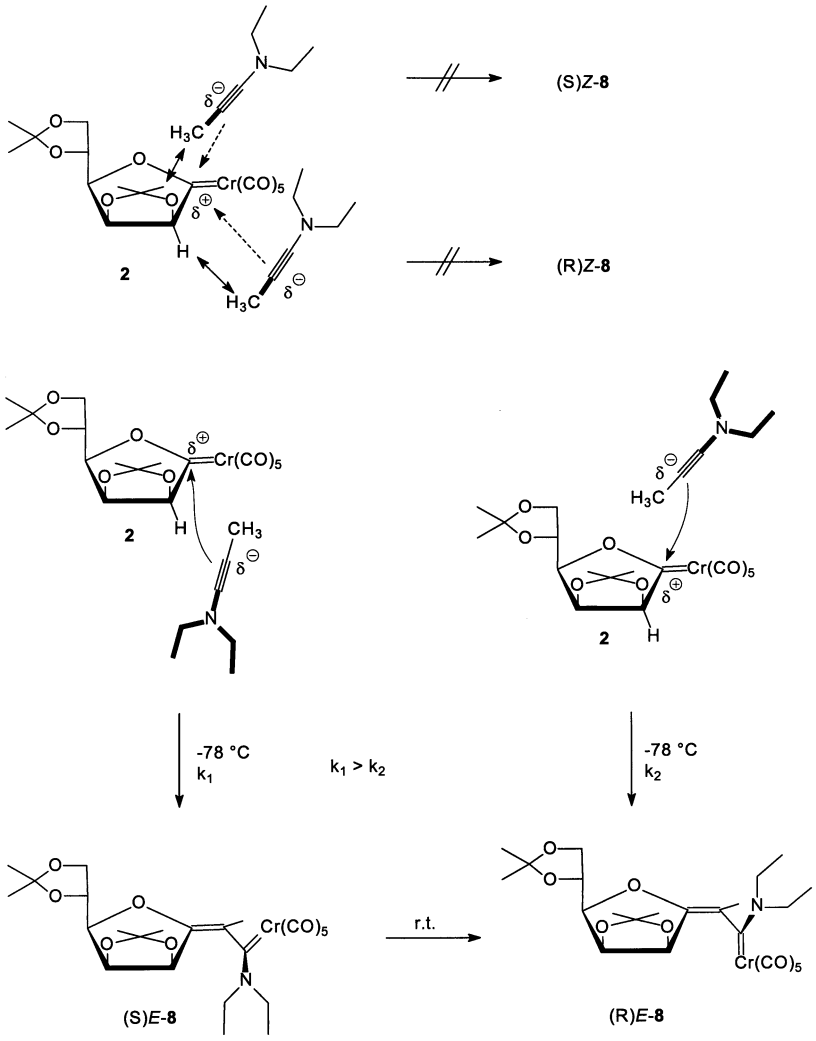
The thermal reaction of mannofuranosylidene complex **2** with *n*-butyl vinyl ether in *n*-heptane afforded *exo*-enol glycal **1** in 46% yield as the main product along with traces of cyclopropanation product (Scheme 8). This result is in accord with earlier observations along similar reactions of alkoxy(aryl)carbene complexes with enol ethers [39].

The reaction of mannofuranosylidene complex **2** with electron-deficient alkenes, however, afforded the desired cyclopropanes. Thus, glycosylidene transfer to alkyl crotonates afforded spirocyclopropanes **9** and **10** in excellent diastereoselectivity and in 84 and 45% yield, respectively. The configuration of the alkene was retained upon cycloaddition; only traces of a minor diastereomer were detected in the cyclopropanation of ethyl crotonate. These examples demonstrate the potential of glycosylidene complexes in stereoselective formation of spirocyclopropyl-*C*-glycosides. Most notably, furano-spirocyclopropanes have been obtained by this methodology in synthetically useful yields (Scheme 9). This type of spirocyclopropanes may serve as useful carbohydrate scaffolds bearing an ester group available for further functionalization. In contrast to crotonates, diethyl fumarate or maleate reacted with complex **2** to give mixtures of spirocyclopropanes **11**–**13** (Scheme 10). The yields were considerably lower, but still similar to those reported for different carbene sources in the furanosylidene series [37b].

The stereochemistry of spirocyclopropanes **9**–**13** as determined by NOE experiments was independently confirmed by an X-ray structural analysis of compound **10** (Fig. 4). The diastereoselective formation of **9** and **10** occurring under complete retention of alkene configuration may be rationalized in terms of an orthogonal "downside" face attack of the alkene followed by a frontside ring closure of the puckered chromacyclobutane intermediate. The formation of three diastereomers **11**–**13**, however, requires a modification of this rationale. The preference of *cis*-cyclopropanation product **12** formed from diethyl maleate as well as the formation of the complementary *trans*-products **11** and **13** originating from diethyl fumarate indicate that a "downside" face attack of the alkene is still favored to secure a minimized steric congestion in the transition state. However, the concomitant formation of spirocyclopropane diastereomers revealing an inversion of alkene configuration (**11** and **13** from diethyl maleate; **12** from diethyl fumarate) suggests a configurational lability of the presumed chromacyclobutane intermediates resulting in partial equilibration of configuration under identical reaction conditions as applied for the cyclopropanation of the crotonates (Scheme 11).

4. Conclusion

The insertion of ynethers and ynamines into the metal–carbene bond provides a non-conventional route for the C_2-elongation of glycosylidene skeletons and leads to novel organometallic mono- and disaccharides bearing an α,β-unsaturated metal carbene spacer. These



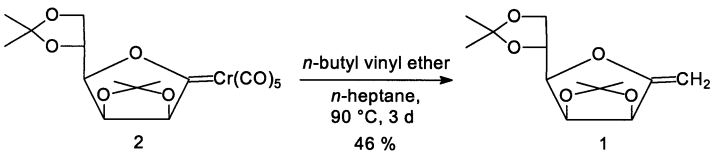
Scheme 7. Mechanistic rationale for the selectivity of the ynamine insertion into the metal–carbene bond of mannofuranosylidene complex **2**.

complexes reveal a temperature-dependent atropisomerism and represent interesting candidates for the elaboration of more complex *C*-saccharides. Furthermore, acceptor-substituted furanosylidene-derived spirocyclopropanes could be synthesized in high yield, demonstrating that glycosylidene complexes may serve as powerful carbene equivalents in the diastereoselective spirocyclopropanation of electron-poor alkenes, a route which may be exploited in novel, conformationally rigid carbohydrate scaffolds.

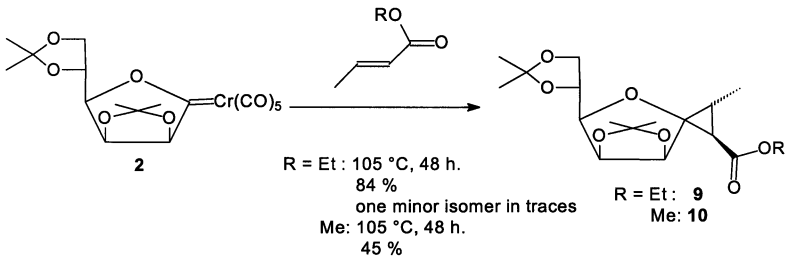
5. Experimental

5.1. General reaction conditions

All operations involving organometallic compounds were performed under argon atmosphere. Reaction mixtures were degassed in three cycles (freeze, pump, thaw) prior to the start of the reaction. Solvents used for organometallic compounds were dried according to standard procedures: THF over sodium–potassium or



Scheme 8. Metathesis reaction of mannofuranosylidene complex **2** with *n*-butyl vinyl ether.



Scheme 9. Diastereoselective spirocyclopropanation of alkyl crotonates with mannofuranosylidene complex **2**.

LAH, diethyl ether over sodium hydride, dichloromethane and light petroleum (40–60 °C) over calcium hydride, and acetone over calcium chloride. If not mentioned otherwise, column chromatography was carried out using degassed solvents and silica gel (Merck Type 60, 0.063–0.200 mm).

5.2. Instruments

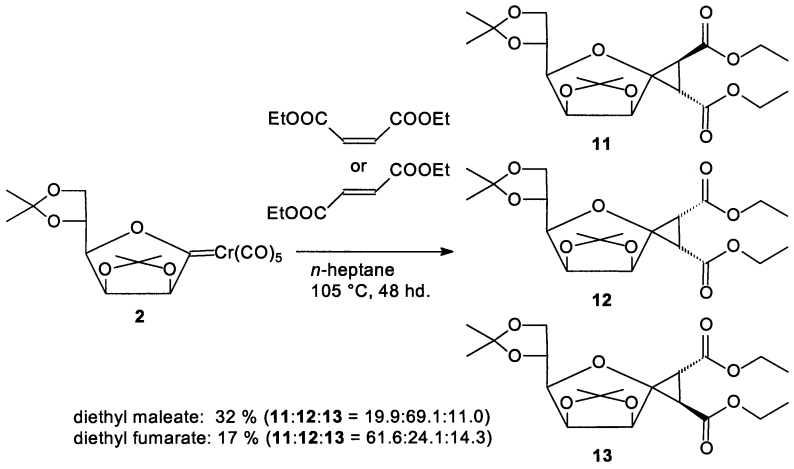
FTIR: Nicolet Magna 550. MS (EI): Kratos (MS 50) and Hewlett-Packard (Series 5972 Mass Detector). MS (+FAB): Kratos (1 H Concept). m.p.: Büchi SMP 20, uncorrected. Elemental analyses: Heraeus CHN-O-Rapid. NMR: Bruker AM 250, Bruker AM 400, Bruker DRX 500. Chemical shifts refer to those of residual solvent signals based on $\delta_{TMS} = 0.00$.

5.3. Insertion of ethoxyethyne

0.5 ml of a 5 M solution of ethoxyethyne in *n*-hexane was added dropwise at −30 °C to a solution of 982 mg (2.26 mmol) mannofuranosylidene complex **2** in 20 ml *n*-hexane, and the solution was stirred at room temperature (r.t.). Over 73 h a total of 5 ml of the ethoxyethyne solution (25 mmol, 11.06 equivalent) was added in portions of 0.5 ml each. The reaction was stopped after 86 h; work up by column chromatography on silica gel (light petroleum–diethyl ether–dichloromethane, 10:5:1) afforded 70 mg (0.16 mmol) of recovered starting material (93% conversion) from the first orange band. The second orange fraction gave 260 mg (0.52 mmol, 25% of converted material) of an approximate 1:1 mixture of *E*-**3** and *Z*-**3**. The diastereomers were separated by a second chromatography on silica gel (light petroleum–dichloromethane–diethyl ether, 70:1:10).

5.3.1. *E*-3,6-Anhydro-2-deoxy-1-ethoxy-4,5:7,8-di-*O*-isopropylidene-D-manno-oct-2-enitol-1-ylidene(pentacarbonyl)chromium (*E*-**3**)

Dark orange, crystalline solid. Crystals for X-ray structural analysis were grown from *n*-pentane. $R_F =$ 0.45 (light petroleum–dichloromethane–diethyl ether, 70:1:10)—IR (light petroleum): $\nu = 2056$ cm^{-1} (s, $^1A_1$; C=O), 1950 cm^{-1} (sh, $^2A_1$/E; C=O), 1940 cm^{-1} (vs, E/$^2A_1$; C=O)—^{1}H-NMR (500.13 MHz, $CDCl_3$): $\delta =$ 1.36 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.61 (t*, $^3J_{HH} = 7.06$ Hz, 3H, CH_3-10), 4.05 (dd, $^2J_{HH} = 8.9$ Hz, $^3J_{HH} = 4.2$ Hz, 1H, H-8a), 4.13 (dd, $^2J_{HH} = 8.9$ Hz, $^3J_{HH} = 6.4$ Hz, 1H, H-8b), 4.21 (dd, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 3.9$ Hz, 1H, H-6), 4.44 (t*d, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 4.57$ Hz, 1H, H-7), 4.79 (t*, $^3J_{HH} = 4.8$ Hz, 1H, H-5), 4.96 (dq, $^2J_{HH} = 10.33$ Hz, $^3J_{HH} = 7.12$ Hz, 1H, H-9a), 5.00 (dq, $^2J_{HH} = 10.03$ Hz, $^3J_{HH} = 7.02$ Hz, 1H, H-9b), 5.33 (d, $^3J_{HH} = 5.77$ Hz, 1H, H-4), 7.12 (s, 1H, H-2)—^{13}C-NMR (62.9 MHz, $CDCl_3$):



Scheme 10. Spirocyclopropanation of diethyl fumarate and maleate with mannofuranosylidene complex **2**.

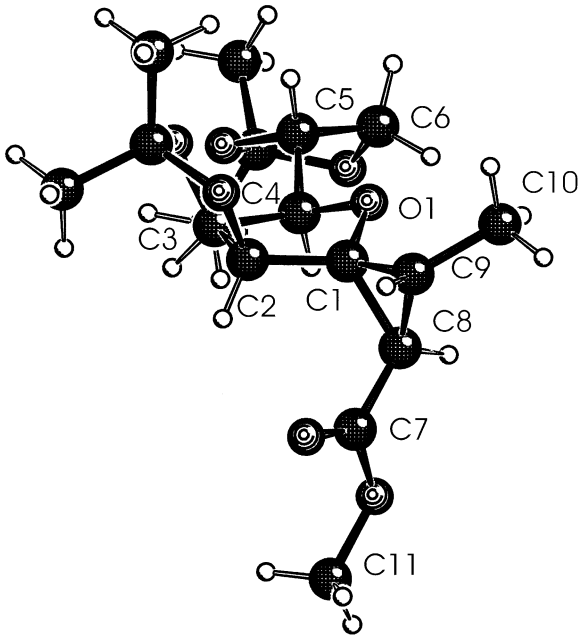


Fig. 4. Schakal plot of the molecular structure of spirocyclopropane **10**. Selected bond lengths (Å) and angles (°): C1–C2: 1.5083(15); C2–C3: 1.5470(16); C3–C4: 1.5296(15); C4–O1: 1.4418(12); O1–C1: 1.4148(13); C1–C9: 1.4746(16); C1–C8: 1.5401(16); C7–C8: 1.4769(17); C8–C9: 1.5314(16); C9–C10: 1.5082(17); O1–C1–C2: 107.65(9); C9–C1–C8: 61.01(7); C1–C9–C8: 61.60(7); C1–C8–C9: −57.38(7); C1–C2–C3–C4: 0.75(10); O1–C1–C2–C3: 22.23(11); C2–C3–C4–O1: −22.76(10); O1–C1–C9–C10: 2.53(16); C2–C1–C8–C7: −9.82(16); C7–C8–C9–C10: 134.61(11). (The crystallographic atom numbering is not necessarily identical with the numbering used in the experimental part.)

$\delta = 15.2$ (1 C, CH_3-10), 25.9, 26.3, 27.5, 27.7 (4 C, CH_3), 67.2 (1 C, C-8), 73.5, 78.4, 82.1, 84.3 (4 C, C-4, C-5, C-6, C-7), 76.9 (1 C, C-9), 110.2, 113.6 (2 C, $C_{acetalic}$), 121.8 (1 C, C-2), 162.1 (1 C, C-3), 218.4 (4 C, CO_{cis}), 224.8 (1 C, CO_{trans}), 324.9 (1 C, C-1). (125.76 MHz, $CDCl_3$): $\delta =$ 14.8 (1 C, CH_3-10), 25.0, 25.7, 26.7, 26.9 (4 C, CH_3), 66.3, 72.7, 76.1, 77.5, 81.2, 83.3 (6 C, C-4, C-5, C-6, C-7, C-8, C-9), 109.7, 113.3 (2 C, $C_{acetalic}$), 121.0 (1 C, C-2), 159.9 (1 C, C-3), 217.0 (4 C, CO_{cis}), 223.9 (1 C, CO_{trans}), 324.3 (1 C, C-1)—MS (EI); *m/z* (%): 504 (1) [M^+], 476 (2) [M^+-CO], 420 (2) [M^+-3 CO], 392 (1) [M^+-4 CO], 364 (5) [M^+-5 CO], 313 (10) [$M+H^+$-5 CO–Cr]—HRMS for $^{12}C^{1}_{16}H^{16}_{24}O^{52}_{6}Cr$ [M^+-5 CO] Calc.: 364.0978. Found: 364.0985.

5.3.1.1. Crystal data for E-3. $C_{21}H_{24}CrO_{11}$, $M = 504.40$, monoclinic, space group $P2_1$ (No. 4), red crystals, dimensions $0.25 \times 0.06 \times 0.04$ mm^3, $a = 9.7860(3)$ Å, $b = 9.2270(5)$ Å, $c = 13.7270(7)$ Å, $\beta = 108.432(5)°$, $V = 1175.90(9)$ Å^3, $D_c = 1.425$ mg m^{-3}, $Z = 2$, μ(Mo–K_α) = 0.543 mm^{-1}, $T = 123(2)$ K, $F(0\,0\,0) = 524$; 8526 reflections were collected on a Nonius KappaCCD diffractometer (4.51–28.29°; $-12 \le h \le 12$, $-11 \le k \le 11$, $-17 \le l \le 17$), 4761 symmetry independent reflections ($R_{int} = 0.0553$) were used for the structure solution (direct methods) [49] and refinement (full-matrix least-squares on F^2 [50], 299 parameters, one restraint), non-hydrogen atoms were refined anisotropically, H atoms localized by difference electron density and refined using a "riding" model; $wR_2 = 0.0992$ [$R_1 = 0.0362$ for $I > 2\sigma(I)$]. The absolute configuration was determined by refinement of Flack's x-parameter ($x = 0.040(15)$) [51]. An extinction correction was applied.

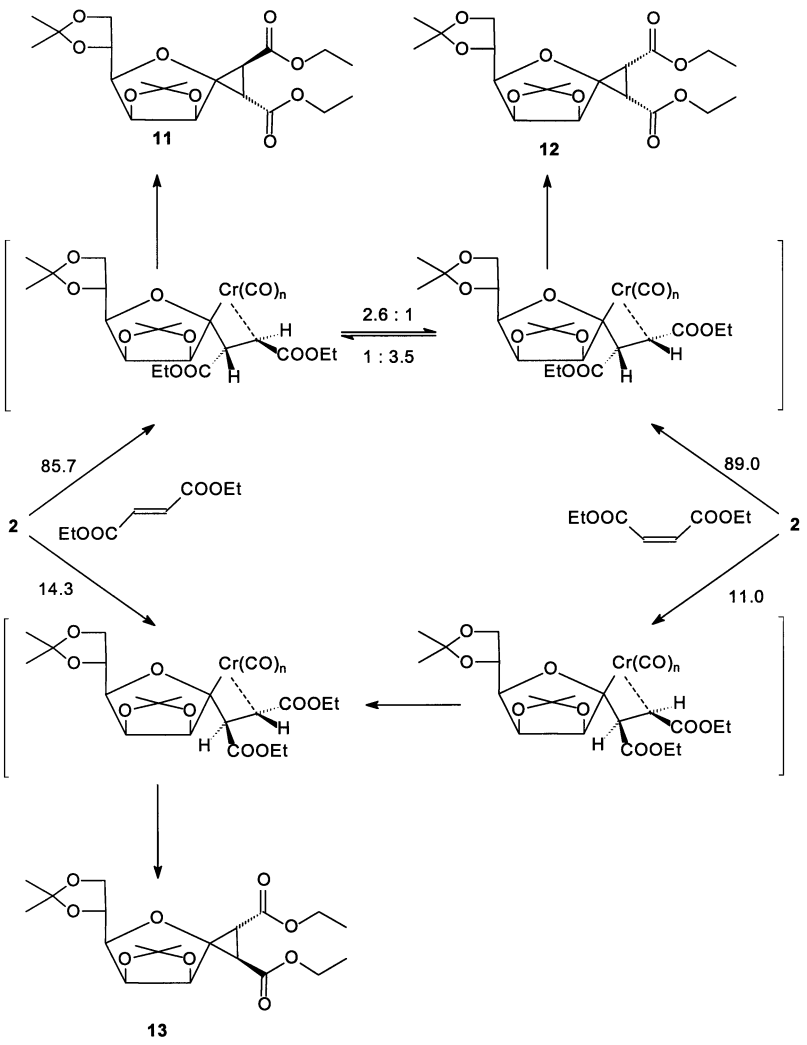
5.3.2. Z-3,6-Anhydro-2-deoxy-1-ethoxy-4,5:7,8-di-O-isopropylidene-D-manno-oct-2-enitol-1-ylidene(pentacarbonyl)chromium (Z-3)

Dark orange oil. $R_F = 0.31$ (light petroleum–dichloromethane–diethyl ether, 70:1:10)—IR (light petroleum): $\nu = 2056$ cm^{-1} (s, $^1A_1$; C=O), 1950 cm^{-1} (sh, $^2A_1$/E; C=O), 1940 cm^{-1} (vs, E/$^2A_1$; C=O)—^{1}H-NMR (500.13 MHz, $CDCl_3$): $\delta = 1.38$ (s, 3H, CH_3-a), 1.40 (s, 3H, CH_3-b), 1.44 (s, 3H, CH_3-c), 1.46 (s, 3H, CH_3-d), 1.56 (t, 3H, $^3J_{HH} = 7.06$ Hz, 3H, CH_3-10), 4.08 (dd, $^2J_{HH} = 8.9$ Hz, $^3J_{HH} = 3.93$ Hz, 1H, H-8a), 4.16 (dd, $^2J_{HH} = 8.9$ Hz, $^2J_{HH} = 6.2$ Hz, 1H, H-8b), 4.40 (dd, $^3J_{HH} = 8.3$ Hz, 3.38 Hz, 1H, H-6), 4.47 (ddd, $^3J_{HH} = 8.3$ Hz, $^3J_{HH} = 6.0$ Hz, $^3J_{HH} = 3.93$ Hz, 1H, H-7), 4.75 (dd, $^3J_{HH} = 5.26$ Hz, $^3J_{HH} = 3.48$ Hz, 1H, H-5), 4.88 (q, $^3J_{HH} = 7.05$ Hz, 2H, CH_2-9), 5.16 (d, $^3J_{HH} = 5.27$ Hz, 1H, H-4), 6.63 (s, 1H, H-2)—^{13}C-NMR (125.76 MHz, $CDCl_3$): $\delta = 15.3$ (1 C, CH_3-10), 25.0 (1 C, CH_3-a), 26.2 (1 C, CH_3-b), 27.0 (1 C, CH_3-d), 27.3 (1 C, CH_3-c), 66.5 (1 C, C-8), 72.3 (1 C, C-7), 75.5 (1 C, C-9), 76.2 (1 C, C-5), 82.1 (1 C, C-4), 85.8 (1 C, C-6), 110.0, 114.6 (2 C, $C_{acetalic}$), 117.4 (1 C, C-2), 217.2 (4 C, CO_{cis}), 224.1 (1 C, CO_{trans}), 322.4 (1 C, C-1), C-3 n.o.—MS (EI); *m/z* (%): 504 (3) [M^+], 420 (6) [M^+-3 CO], 392 (10) [M^+-4 CO], 364 (27) [M^+-5 CO], 313 (28) [$M+H^+$-5 CO–Cr], 248 (22) [M^+-5 CO–2 $(CH_3)CO$]—HRMS for $^{12}C^{1}_{16}H^{16}_{24}O^{52}_{6}Cr$ [M^+-5 CO] Calc.: 364.0978. Found: 364.0980.

5.4. Synthesis of ethynyl sugars 4 and 5

5.4.1. 2,6-Anhydro-3-O-ethinyl-1,2:4,5-di-O-isopropylidene-D-fructose (4)

A solution of 9.72 g (37.4 mmol) 2,6-anhydro-1,2:4,5-di-*O*-isopropylidene-D-fructose [52] in 75 ml THF was added dropwise to a suspension of 3.05 g (75.95 mmol) oil-free potassium hydride in 75 ml THF, and the mixture was stirred at r.t. until the gas evolution stopped. The brown mixture was cooled to −50 °C, and a solution of 3.4 ml (4.90 g. 37.4 mmol) trichloroethylene in 45 ml THF was added. The mixture was warmed to r.t. and stirred for 1 h until the starting material had disappeared as indicated by TLC (3-OH-fructose: $R_F = 0.50$, light petroleum–diethyl ether, 2:1; vinyl ether intermediate: $R_F = 0.94$, light petroleum–diethyl ether, 2:1). The mixture was cooled to −78 °C, and 56.1 ml (90 mmol) *n*-butyllithium (1.6 M in *n*-



Scheme 11. Mechanistic rationale for the product distribution observed for the reaction of complex **2** with diethyl fumarate and maleate.

hexane) was added. After 45 min at −50 °C the vinyl ether intermediate was consumed as indicated by TLC. The mixture was quenched with 20 ml methanol and poured into an ice-cooled saturated aqueous solution of ammonium chloride. The organic layer was extracted with diethyl ether, dried over magnesium sulfate and submitted to silica column chromatography (light petroleum–diethyl ether, 5:1; column and eluent containing 1% of triethylamine; $R_F = 0.65$) to yield 5.97 g (21.00 mmol, 56%) of **4** as a yellowish, waxy solid; m.p.: 46–49 °C—$[\alpha]_D^{25} = -149°$ (584 nm, $CHCl_3$, 2.95 mM)—IR (KBr): $\nu = 3312$ cm^{-1} (m, ≡C–H), 2156 cm^{-1} (s, C≡C)—^{1}H-NMR (400.13 MHz, C_6D_6): $\delta = 1.21$ (s, 3H, CH_3-a), 1.42 (s, 3H, CH_3-b), 1.43 (s, 3H, CH_3-c), 1.50 (s, 3H, CH_3-d), 1.53 (s, 1H, H-2′), 3.70 (ddd, $^3J_{HH} = 5.58$ Hz, $^3J_{HH} = 2.74$ Hz, $^3J_{HH} = 0.35$ Hz, 1H, H-5), 3.78 (dd, $^2J_{HH} = 13.3$ Hz, $^3J_{HH} = 2.74$ Hz, 1H, H-6a), 3.87 (d, br, $^2J_{HH} = 13.3$ Hz, 1H, H-6b), 3.98 (d, $^2J_{HH} = 9.00$ Hz, 1H, H-1a), 4.16 (d, $^3J_{HH} = 7.82$ Hz, 1H, H-3), 4.38 (d, $^2J_{HH} = 9.00$ Hz, 1H, H-1b), 4.47 (dd, $^3J_{HH} = 7.82$ Hz, $^3J_{HH} = 5.48$ Hz, 1H, H-4)—^{13}C-NMR (62.9 MHz, C_6D_6): $\delta = 26.11$ (1 C, CH_3-c), 26.18 (1 C, CH_3-a), 26.7 (1 C, CH_3-b), 27.6 (1 C, C-2′), 28.3 (1 C, CH_3-d), 60.3 (1 C, C-6), 71.8 (1 C, C-1), 74.3 (1 C, C-5), 74.7 (1 C, C-4), 85.7 (1 C, C-3), 90.5 (1 C, C-1′), 103.7, 109.5, 112.9 (3 C, C-2, $C_{acetalic}$)—MS (EI); *m/z* (%): 269 (24) [M^+-CH_3], 243 (28), 185 (71)—HRMS for $^{12}C^1_{13}H^{16}_{17}O_6$ [M^+-CH_3] Calc.: 269.1026. Found: 269.1022.

5.4.2. 1,5-Anhydro-6-O-ethinyl-1,2:3,4-di-O-isopropylidene-D-galactose (5)

A solution of 12.43 g (47.75 mmol) 1,5-anhydro-1,2:3,4-di-*O*-isopropylidene-D-galactose [53] in 100 ml THF was added dropwise to a suspension of 3.82 g (95.1 mmol) oil-free potassium hydride in 50 ml THF, and the mixture was stirred at r.t. until the gas evolution stopped. The brown mixture was cooled to −50 °C, and a solution of 4.2 ml (6.13 g, 46.6 mmol) trichloroethylene in 50 ml THF was added. The mixture was warmed to r.t. and stirred for 1 h until the starting

material had disappeared as indicated by TLC (6-OH-galactose: $R_F = 0.17$, light petroleum–diethyl ether, 2:1; vinyl ether intermediate: $R_F = 0.75$, light petroleum–diethyl ether, 2:1). The mixture was cooled to −78 °C, and 70.1 ml (112 mmol) *n*-butyllithium (1.6 M in *n*-hexane) was added. The mixture was warmed to −35 °C and stirred for 30 min until the vinyl ether intermediate was consumed as indicated by TLC. The mixture was quenched with 33 ml methanol and poured into an ice-cooled saturated aqueous solution of ammonium chloride. The organic layer was extracted with diethyl ether, dried over magnesium sulfate and submitted to silica column chromatography (light petroleum–diethyl ether, 5:1; column and eluent containing 1% of triethylamine; $R_F = 0.43$) to yield 10.68 g (37.60 mmol, 79%) of **5** as a yellowish oil—$[\alpha]_D^{25} = -37°$ (584 nm, $CHCl_3$, 2.44 mM)—IR (film): $\nu = 3310$ cm^{-1} (s, ≡C–H), 2154 cm^{-1} (vs, C≡C)—^{1}H-NMR (500.13 MHz, C_6D_6): $\delta =$ 1.06 (s, 3H, CH_3-a), 1.08 (s, 3H, CH_3-b), 1.32 (s, 3H, CH_3-c), 1.45 (s, 3H, CH_3-d), 1.51 (s, 1H, H-2′), 3.76 (dd, $^3J_{HH} = 7.85$ Hz, $^3J_{HH} = 1.7$ Hz, 1H, H-4), 4.10 (dd, $^2J_{HH} = 10.58$ Hz, $^2J_{HH} = 4.6$ Hz, 1H, H-6a), 4.11 (dd, $^3J_{HH} = 5.0$ Hz, $^3J_{HH} = 2.36$ Hz, 1H, H-2), 4.16 (dd, $^2J_{HH} = 10.58$ Hz, $^3J_{HH} = 7.3$ Hz, 1H, H-6b), 4.24 (ddd, $^3J_{HH} = 7.1$ Hz, $^3J_{HH} = 4.6$ Hz, $^3J_{HH} = 1.9$ Hz, 1H, H-5), 4.39 (dd, $^3J_{HH} = 7.90$ Hz, $^3J_{HH} = 2.34$ Hz, 1H, H-3), 5.40 (d, $^3J_{HH} = 5.06$ Hz, 1H, H-1)—^{13}C-NMR (125.76 MHz, C_6D_6): $\delta = 25.0$, 25.6 (2 C, CH_3-a, CH_3-b), 26.7 (1 C, CH_3-c), 26.8 (1 C, CH_3-d), 28.3 (1 C, C-2′), 66.5 (1 C, C-6), 71.4 (1 C, C-2), 71.68 (1 C, C-4), 71.71 (1 C, C-3), 77.9 (1 C, C-5), 91.7 (1 C, C-1′), 97.2 (1 C, C-1), 109.5, 110.2 (2 C, $C_{acetalic}$)—MS (EI); *m*/*z* (%): 269 (30) [M^+-CH_3], 243 (2), 211 (6) [M^+-$(CH_3)_2CO$], 185 (15)—HRMS for $^{12}C_{13}^1H_{17}^{16}O_6$ [M^+-CH_3] Calc.: 269.1025. Found: 269.1029—$C_{23}H_{31}NO_9Cr$ (545.51): Calc.: C, 59.14; H, 7.09. Found: C, 58.86; H, 7.07%.

5.5. Synthesis of disaccharides 6 and 7

5.5.1. Insertion of fructose-derived ynether 4

5.5.1.1. E/Z-3,6-Anhydro-2-deoxy-1-(2′,6′-anhydro-1′,2′:4′,5′-di-O-isopropylidene-D-fructos-3′-yl)-4,5:7,8-di-O-isopropylidene-D-manno-oct-2-enitol-1-ylidene(pentacarbonyl)chromium (E/Z-6).

429 mg (1.51 mmol) fructose-derived alkyne **4** was dissolved in 14 ml light petroleum and added to 242 mg (0.56 mmol) mannofuranosylidene complex **2** at −55 °C. The mixture was stirred and warmed to r.t. Over 72 h a total of 1.84 g (6.47 mmol, 11.6 equivalent) of ynether **4** was added until IR monitoring indicated complete conversion of the starting material. Chromatographic work up on silica gel (light petroleum–diethyl ether–dichloromethane, 10:5:1; $R_F = 0.23$) yielded ca. 10 mg of a diastereomeric mixture of *E*/*Z*-**6** as red oil—IR (light petroleum): $\nu = 2058$ cm^{-1} (s, $^1A_1$; C=O), 1958 cm^{-1} (vs, E, $^2A_1$; C=O)—^{13}C-NMR (125.76 MHz, C_6D_6): $\delta = 217.5$ (4 C, CO_{cis}, isomer A), 217.1 (4 C, CO_{cis}, isomer B)—MS (+FAB); *m*/*z* (%): 718 (1) [M^+], 660 (1) [M^+-$(CH_3)_2CO$], 578.2 (22) [M^+-5 CO], 527 (6) [M+H^+-5 CO–Cr], 521 (16) [M+H^+-5 CO-$(CH_3)_2CO$], 391.3 (58).

5.5.2. Insertion of galactose-derived ynether 5

A solution of 3.12 g (10.97 mmol, 6.6 equivalent) galactose-derived ynether **5** in 40 ml light petroleum was added to 0.72 g (1.66 mmol) mannofuranosylidene complex **2**, and the mixture was stirred for 48 h at r.t. Chromatographic work up on silica gel (light petroleum–diethyl ether–dichloromethane, 15:5:1) yielded 453 mg (0.63 mmol, 38%) of a 2.7:1 mixture of *E*/*Z*-**7**. Pure diastereomers were obtained after repeated chromatography (light petroleum–dichloromethane, 1:4; gradient light petroleum–dichloromethane–ethyl acetate, 1:4:0–0:10:1).

5.5.2.1. E-3,6-Anhydro-2-deoxy-1-(1′,5′-anhydro-1′,2′:3′,4′-di-O-isopropylidene-D-galactos-6′-yl)-4,5:7,8-di-O-isopropylidene-D-manno-oct-2-enitol-1-ylidene(pentacarbonyl)chromium (E-7).

Red, crystalline solid; $R_F = 0.35$ (light petroleum–diethyl ether–dichloromethane, 10:5:1); 0.08 (light petroleum–dichloromethane, 1:4); m.p.: 80–82 °C—IR (KBr): $\nu = 2056$ cm^{-1} (s, $^1A_1$; C=O), 1981 cm^{-1} (s, B_1; C=O), 1935 cm^{-1} (vs, br, E, $^2A_1$; C=O)—^{1}H-NMR (500.13 MHz, C_6D_6): $\delta = 1.04$ (s, 3H, CH_3-a), 1.10 (s, 3H, CH_3-b), 1.16 (s, 3H, CH_3-c), 1.22 (s, 3H, CH_3-d), 1.25 (s, 3H, CH_3-e), 1.35 (s, 3H, CH_3-f), 1.40 (s, 3H, CH_3-g), 1.49 (s, 3H, CH_3-h), 3.16 (dd, $^3J_{HH} = 8.64$ Hz, $^3J_{HH} = 3.18$ Hz, 1H, H-6), 3.74 (dd, $^2J_{HH} = 8.8$ Hz, $^3J_{HH} = 4.92$ Hz, 1H, H-8a), 3.79 (dd, $^3J_{HH} = 7.85$ Hz, $^3J_{HH} = 2.1$ Hz, 1H, H-4′), 3.84 (dd, $^2J_{HH} = 8.8$ Hz, $^3J_{HH} = 6.16$ Hz, 1H, H-8b), 4.17 (dd, $^3J_{HH} = 5.12$ Hz, $^3J_{HH} = 2.54$ Hz, 1H, H-2′), 4.32 (ddd, $^3J_{HH} = 8.64$ Hz, $^3J_{HH} = 6.16$ Hz, $^3J_{HH} = 4.97$ Hz, 1H, H-7), 4.40 (dd, $^3J_{HH} = 5.3$ Hz, $^3J_{HH} = 3.18$ Hz, 1H, H-5), 4.44 (dd, $^3J_{HH} = 7.85$ Hz, $^3J_{HH} = 2.59$ Hz, 1H, H-3′), 4.53 (dt*, $^3J_{HH} = 9.1$ Hz, $^3J_{HH} = 2.3$ Hz, 1H, H-5′), 5.09 (dd, $^2J_{HH} = 11.2$ Hz, $^3J_{HH} = 2.58$ Hz, 1H, H-6′a, NOE upon decoupling of H-4), 5.43 (d, $^3J_{HH} = 5.17$ Hz, 1H, H-1′), 5.50 (dd, $^2J_{HH} = 11.2$ Hz, $^3J_{HH} = 9.19$ Hz, 1H, H-6′b), 5.57 (dd, $^3J_{HH} = 5.4$ Hz, $^4J_{HH} = 1.5$ Hz, 1H, H-4), 7.46 (d, $^4J_{HH} = 1.4$ Hz, 1H, H-2)—^{13}C-NMR (62.9 MHz, C_6D_6): $\delta = 24.0$ (1 C, CH_3-b), 24.2 (1 C, CH_3-a), 24.8 (1 C, CH_3-d), 25.6 (1 C, CH_3-h), 25.9 (1 C, CH_3-g), 26.57 (1 C, CH_3-f), 26.63 (1 C, CH_3-c), 27.1 (1 C, CH_3-e), 66.3 (1 C, C-5′), 66.6 (1 C, C-8), 70.1 (1 C, C-2′), 70.75, 70.80 (2 C, C-3′, C-4′), 72.2 (1 C, C-7), 77.8 (1 C, C-5), 79.1 (1 C, C-6′), 81.7 (1 C, C-4), 83.4 (1 C, C-6), 96.5 (1 C, C-1′), 107.9, 109.2, 109.6, 112.5 (4 C, $C_{acetalic}$), 120.9 (1 C, C-2), 162.5 (1 C, C-3), 217.2 (4 C, CO_{cis}), 223.8 (1 C, CO_{trans}), 323.9 (1 C, C-1)—MS (+FAB); *m*/*z* (%): 718 (1) [M^+], 606 (1) [M^+-4 CO], 578 (12) [M^+-5

CO], 520 (100) [M^+-5 CO–$(CH_3)_2CO$]—$C_{31}H_{38}O_{16}Cr$ (718.63): Calc.: C, 51.81; H, 5.33. Found: C, 51.85; H, 5.80%.

5.5.2.2. Z-3,6-Anhydro-2-deoxy-1-(1′,5′-anhydro-1′,2′:3′,4′-di-O-isopropylidene-D-galactos-6′-yl)-4,5:7,8-di-O-isopropylidene-D-manno-oct-2-enitol-1-ylidene(pentacarbonyl)chromium (Z-7). Red powder, $R_F = 0.27$ (light petroleum–diethyl ether–dichloromethane, 10:5:1); 0.05 (light petroleum–dichloromethane, 1:4); m.p.: ~60 °C—IR (light petroleum): $\nu = 2056$ cm^{-1} (s, $^1A_1$; C=O), 1971 cm^{-1} (s, B_1; C=O), 1942 cm^{-1} (vs, E, $^2A_1$; C=O)—^{1}H-NMR (400.13 MHz, C_6D_6): $\delta = 1.01$ (s, 3H, CH_3-a), 1.04 (s, 3H, CH_3-b), 1.14 (s, 3H, CH_3-c), 1.21 (s, 3H, CH_3-d), 1.26 (s, 3H, CH_3-e), 1.40 (s, 3H, CH_3-f), 1.45 (s, 6H, CH_3-g, CH_3-h), 3.85 (dd, $^3J_{HH} = 8.96$ Hz, $^3J_{HH} = 3.30$ Hz, 1H, H-6), 4.09 (dd, $^3J_{HH} = 5.13$ Hz, $^3J_{HH} = 3.30$ Hz, 2H, H-5), 4.16 (dd, $^3J_{HH} = 5.06$ Hz, $^3J_{HH} = 2.53$ Hz, 1H, H-2′), 4.19 (dd, $^2J_{HH} = 9.04$ Hz, $^3J_{HH} = 6.14$ Hz, 1H, H-8a), 4.25 (dd, $^3J_{HH} = 5.13$ Hz, $^4J_{HH} = 0.87$ Hz, 1H, H-4, strong NOE upon decoupling of H-2), 4.30 (dd, $^2J_{HH} = 9.04$ Hz, $^3J_{HH} = 4.44$ Hz, 1H, H-8b), 4.33 (dd, $^3J_{HH} = 7.79$ Hz, $^3J_{HH} = 2.10$ Hz, 1H, H-4′), 4.45 (ddd, $^3J_{HH} = 6.72$ Hz, $^3J_{HH} = 6.56$ Hz, $^3J_{HH} = 2.10$ Hz, 1H, H-5′), 4.52 (ddd, $^3J_{HH} = 8.96$ Hz, $^3J_{HH} = 6.14$ Hz, $^3J_{HH} = 4.44$ Hz, 1H, H-7), 4.54 (dd, $^3J_{HH} = 7.79$ Hz, $^3J_{HH} = 2.53$ Hz, 1H, H-3′), 4.85 (dd, $^2J_{HH} = 10.16$ Hz, $^3J_{HH} = 6.56$ Hz, 1H, H-6′a), 5.10 (dd, $^2J_{HH} = 10.16$ Hz, $^3J_{HH} = 6.72$ Hz, 1H, H-6′b), 5.47 (d, $^3J_{HH} = 5.06$ Hz, 1H, H-1′), 6.57 (d, br, $^4J_{HH} = 0.87$ Hz, 1H, H-2)—^{13}C-NMR (125.76 MHz, C_6D_6): $\delta = 25.2$ (1 C, CH_3-c), 25.4 (1 C, CH_3-a), 25.8 (1 C, CH_3-d), 26.65 (1 C, CH_3-b), 26.76 (1 C, CH_3-g), 26.83 (1 C, CH_3-h), 27.8 (1 C, CH_3-f), 28.0 (1 C, CH_3-e), 67.7 (1 C, C-5′), 68.2 (1 C, C-8), 71.4 (1 C, C-2′), 71.8 (1 C, C-3′), 71.9 (1 C, C-4′), 73.1 (1 C, C-7), 77.0 (2 C, C-5, C-6′), 83.0 (1 C, C-4), 87.6 (1 C, C-6), 97.4 (1 C, C-1′), 109.4, 110.5, 114.8, 116.9 (4 C, $C_{acetalic}$), 121.9 (1 C, C-2), 218.6 (4 C, CO_{cis}), 225.4 (1 C, CO_{trans}), 323.6 (1 C, C-1), C-3 not observed—MS (+FAB); *m/z* (%): 578 (11) [M^+-5 CO], 520 (6) [M^+-5 CO–$(CH_3)_2CO$].

5.5.3. Insertion of N,N-diethylamino-2-propyne

0.1 ml (100 mg, 0.90 mmol) *N*,*N*-diethylamino-2-propyne was added at −78 °C to a solution of 391 mg (0.90 mmol) mannofuranosylidene complex **2** in a mixture of 5 ml dichloromethane and 10 ml light petroleum. The mixture was stirred for 5 min at −78 °C and concentrated below −40 °C. Column chromatography on silica gel at −27 °C (light petroleum–diethyl ether–dichloromethane, 10:5:1) afforded pure isomers of (*R*)-*E*-**8** ($R_F = 0.50$) and (*S*)-*E*-**8** (0.13) in a diastereomeric ratio of 1:15 (≙ 88% de) and in a total yield of 85%. During the work up procedure the temperature must be kept below 0 °C to avoid rearrangement of the major isomer into the minor isomer.

5.5.3.1. (R)-E-1-N,N-Diethylamino-3,6-anhydro-2-deoxy-4,5:7,8-di-O-isopropylidene-2-methyl-D-manno-oct-2-enitol-1-ylidene(pentacarbonyl)chromium ((R)-E-8). 26 mg, 5.3%, yellow oil—IR (light petroleum): $\nu = 2052$ cm^{-1} (s, $^1A_1$; C=O), 1929 cm^{-1} (vs, E/$^2A_1$; C=O), 1920 cm^{-1} (sh, $^2A_1$/E; C=O)—^{1}H-NMR (250.13 MHz, $CDCl_3$, 253 K, selected data): $\delta = 3.76$ (dd, $^3J_{HH} = 4.27$ Hz, $^3J_{HH} = 8.4$ Hz, 1H, H-6), 4.08 (dd, $^2J_{HH} = 9.0$ Hz, $^3J_{HH} = 6.83$ Hz, 1H, H-8a), 4.12 (dd, $^2J_{HH} = 9.0$ Hz, $^3J_{HH} = 3.0$ Hz, 1H, H-8b), 4.39 (ddd, $^3J_{HH} = 8.4$ Hz, $^3J_{HH} = 6.83$ Hz, $^3J_{HH} = 3.0$ Hz, 1H, H-7), 4.77 (dd, $^3J_{HH} = 6.38$ Hz, $^3J_{HH} = 4.27$ Hz, 1H, H-5), 4.82 (d, $^3J_{HH} = 6.38$ Hz, 1H, H-4). (500.13 MHz, $CDCl_3$, 293 K): $\delta = 1.20$ (t, $^3J_{HH} = 7$ Hz, 3H, CH_3-12), 1.28 (s, 3H, CH_3-a), 1.36 (s, 3H, CH_3-b), 1.38 (s, 3H, CH_3-c), 1.39 (t, $^3J_{HH} = 7$ Hz, 3H, CH_3-13), 1.43 (s, 3H, CH_3-d), 1.82 (s, 3H, CH_3-9), 3.42 (dq, $^2J_{HH} = 14$ Hz, $^3J_{HH} = 7$ Hz, 1H, H-11a), 3.83 (dd, $^3J_{HH} = 7.55$ Hz, $^3J_{HH} = 4.28$ Hz, 1H, H-6), 3.99 (dq, $^2J_{HH} = 14$ Hz, $^3J_{HH} = 7$ Hz, 1H, H-11b), 4.02 (dq, $^2J_{HH} = 13.8$ Hz, $^3J_{HH} = 7$ Hz, 1H, H-10a), 4.10 (d, $^3J_{HH} = 5.4$ Hz, 2H, CH_2-8), 4.39 (dt, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 5.2$ Hz, 1H, H-7), 4.40 (dq, $^2J_{HH} = 13.8$ Hz, $^3J_{HH} = 7$ Hz, 1H, H-10b), 4.79 (dd, $^3J_{HH} = 6.16$ Hz, 1H, H-5), 4.90 (d, $^3J_{HH} = 6.26$ Hz, 1H, H-4)—^{13}C-NMR (125.76 MHz, $CDCl_3$, 233 K): $\delta = 14.0$, 14.1, 14.3 (3 C, CH_3-9, CH_3-12, CH_3-13), 23.9, 24.8, 25.7, 27.0 (4 C, CH_3), 48.2, 53.2 (2 C, CH_2-10, CH_2-11), 66.3, 72.6, 77.3, 78.6, 81.2 (5 C, C-4, C-5, C-6, C-7, C-8), 109.4, 112.2 (2 C, $C_{acetalic}$), 123.4 (1 C, C-2), 137.4 (1 C, C-3), 217.4 (4 C, CO_{cis}), 223.0 (1 C, CO_{trans}), 266.0 (1 C, C-1). (125.76 MHz, $CDCl_3$, 293 K): $\delta = 14.0$ (qt, $^1J_{CH} = 128$ Hz, $^2J_{CH} = 3.6$ Hz, 1 C, C-13), 14.23 (qt, $^1J_{CH} = 129$ Hz, $^2J_{CH} = 3$ Hz, 1 C, C-12), 14.24 (q, $^1J_{CH} = 129$ Hz, 1 C, C-9), 24.5 (qq, $^1J_{CH} = 127.8$ Hz, $^3J_{CH} = 2.6$ Hz, 1 C, CH_3-a), 25.2 (qq, $^1J_{CH} = 126.6$ Hz, $^3J_{CH} = 2.7$ Hz, 1 C, CH_3-b), 26.0 (qq, $^1J_{CH} = 125.9$ Hz, $^3J_{CH} = 2.7$ Hz, 1 C, CH_2-c), 26.9 (qq, $^1J_{CH} = 127.7$ Hz, $^3J_{CH} = 2.5$ Hz, 1 C, CH_3-d), 48.6 (t, $^1J_{CH} = 141.5$ Hz, 1 C, C-11), 53.5 (t, $^1J_{CH} = 140.5$ Hz, 1 C, C-10), 66.6 (td, $^1J_{CH} = 149.4$ Hz, $^2J_{CH} = 3.1$ Hz, 1 C, C-8), 73.1 (dd, $^1J_{CH} = 152.6$ Hz, $^2J_{CH} = 4$ Hz, 1 C, C-7), 77.9 (d, $^1J_{CH} = 157.3$ Hz, 1 C, C-4), 79.2 (d, $^1J_{CH} = 160.0$ Hz, 1 C, C-5), 82.1 (dq, $^1J_{CH} = 149.2$ Hz, $^2J_{CH} = 2.5$ Hz, 1 C, C-6), 109.4 (m, 1 C, $C_{acetalic}$), 112.5 (m, 1 C, $C_{acetalic}$), 123.8 (q, $^2J_{CH} = 6.4$ Hz, 1 C, C-2), 138.2 (quin*, $^{2/3}J_{CH} = 4.7$ Hz, 1 C, C-3), 217.8 (s, 4 C, CO_{cis}), 222.9 (s, 1 C, CO_{trans}), 268.8 (s, 1 C, C-1)—MS (EI); *m/z* (%): 517 (2) [M^+-CO], 502 (1) [M^+-CO–CH_3], 489 (2) [M^+-2 CO], 461 (6) [M^+-3 CO], 405 (23) [M^+-5 CO], 347 (8) [M^+-5 CO–$(CH_3)_2CO$], 289 (20) [M^+-5 CO–2 $(CH_3)_2CO$]—HRMS for $^{12}C^1_{23}H^{14}_{31}N^{16}O^{52}_9Cr$ [M^+-CO] Calc.: 517.1404. Found: 517.1405—$C_{23}H_{31}NO_9Cr$ (545.51):

Calc.: C, 54.24; H, 5.88; N, 2.57. Found: C, 53.78; H, 6.19; N, 3.63%.

*5.5.3.2. (S)-E-1-N,N-Diethylamino-3,6-anhydro-2-deoxy-4,5:7,8-di-O-isopropylidene-2-methyl-D-manno-oct-2-enitol-1-ylidene(pentacarbonyl)chromium ((S)-E-**8**).* 391 mg (0.72 mmol, 80%), yellowish crystalline solid. Single crystals for X-ray structural analysis were grown from CD_2Cl_2—IR (light petroleum): $\nu = 2054$ cm^{-1} (s, $^1A_1$; C=O), 1975 (m, B_1; C=O), 1938 cm^{-1} (vs, E/$^2A_1$; C=O), 1932 (sh, $^2A_1$/E; C=O)—^{1}H-NMR (500.13 MHz, CD_2Cl_2, 253 K): $\delta = 1.10$ (t, $^3J_{HH} = 7$ Hz, 3H, CH_3-12), 1.20 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.38 (t, $^3J_{HH} = 7$ Hz, 3H, CH_3-13), 1.40 (s, 3H, CH_3), 1.85 (s, 3H, CH_3-9), 3.49 (dq, $^2J_{HH} = 13.2$ Hz, $^3J_{HH} = 6.5$ Hz, 1H, H-10a), 3.59 (dq, $^2J_{HH} = 13.2$ Hz, $^3J_{HH} = 6.5$ Hz, 1H, H-10b), 3.75 (dd, $^3J_{HH} = 7.45$ Hz, $^3J_{HH} = 3.80$ Hz, 1H, H-6), 3.98 (dq, $^2J_{HH} = 13.6$ Hz, $^3J_{HH} = 6.8$ Hz, 1H, H-11a), 4.06 (dd, $^2J_{HH} = 8.5$ Hz, $^3J_{HH} = 5.1$ Hz, 1H, H-8a), 4.07 (dd, $^2J_{HH} = 8.5$ Hz, $^3J_{HH} = 5.1$ Hz, 1H, H-8b), 4.11 (dq, $^2J_{HH} = 13.6$ Hz, $^3J_{HH} = 6.8$ Hz, 1H, H-11b), 4.37 (dt, $^3J_{HH} = 7.45$ Hz, $^3J_{HH} = 5.10$ Hz, 1H, H-7), 4.69 (d, $^3J_{HH} = 6.46$ Hz, 1H, H-4), 4.70 (dd, $^3J_{HH} = 6.46$ Hz, $^3J_{HH} = 3.80$ Hz, 1H, H-5)—^{1}H-NMR (250.13 MHz, $CDCl_3$, 253 K, selected data): $\delta = 3.70$ (dd, $^3J_{HH} = 8.1$ Hz, $^3J_{HH} = 4.36$ Hz, 1H, H-6), 4.05–4.20 (m, 2H, H-8a, H-8b), 4.43 (ddd, $^3J_{HH} = 8.2$ Hz, $^3J_{HH} = 5.1$ Hz, $^3J_{HH} = 3.5$ Hz, 1H, H-7), 4.67 (d, $^3J_{HH} = 6.0$ Hz, 1H, H-4), 4.73 (dd, $^3J_{HH} = 6.2$ Hz, $^3J_{HH} = 4.36$ Hz, 1H, H-5). (500.13 MHz, $CDCl_3$, 263 K): $\delta = 1.15$ (t, $^3J_{HH} = 6.95$ Hz, 3H, CH_3-12), 1.22 (s, 3H, CH_3-a), 1.34 (s, 3H, CH_3-b), 1.41 (t, $^3J_{HH} = 7.05$ Hz, 3H, CH_3-13), 1.42 (s, 3H, CH_3-c), 1.45 (s, 3H, CH_3-d), 1.86 (s, 3H, CH_3-9), 3.50 (dq, $^2J_{HH} = 13$ Hz, $^3J_{HH} = 7$ Hz, 1H, H-10a), 3.65 (dq, $^2J_{HH} = 13.0$ Hz, $^3J_{HH} = 7.1$ Hz, 1H, H-10b), 3.72 (dd, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 4.5$ Hz, 1H, 6), 4.05 (dq, $^2J_{HH} = 13.2$ Hz, $^3J_{HH} = 7$ Hz, 1H, H-11a), 4.08–4.11 (m, 2H, H-8a, H-8b), 4.13 (dq, $^2J_{HH} = 13.7$ Hz, $^3J_{HH} = 7$ Hz, 1H, H-11b), 4.43 (ddd, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 5.3$ Hz, $^3J_{HH} = 3.6$ Hz, 1H, H-7), 4.67 (d, $^3J_{HH} = 6.1$ Hz, H-4), 4.73 (dd, $^3J_{HH} = 6.1$ Hz, $^3J_{HH} = 4.6$ Hz, 1H, H-5)—^{13}C-NMR (125.76 MHz, $CDCl_3$, 233 K): $\delta = 13.9$, 14.6, 15.2 (3 C, CH_3-9, CH_3-12, CH_3-13), 23.6, 24.7, 25.4, 27.1 (4 C, CH_3), 48.4, 53.1 (2 C, CH_2-10, CH_2-11), 66.1, 66.4, 72.7, 77.7, 81.8 (5 C, C-4, C-5, C-6, C-7, C-8), 109.3, 113.0 (2 C, $C_{acetalic}$), 126.0 (1 C, C-2), 137.6 (1 C, C-3), 217.4 (4 C, CO_{cis}), 224.4 (1 C, CO_{trans}), 272.4 (1 C, C-1). (125.76 MHz, $CDCl_3$, 263 K): $\delta = 13.8$ (1 C, CH_3-13), 14.5 (1 C, CH_3-12), 15.4 (1 C, CH_3-9), 23.8 (1 C, CH_3-a), 24.9 (1 C, CH_3-b), 25.5 (1 C, CH_3-d), 26.9 (1 C, CH_3-c), 48.2 (1 C, CH_2-10), 53.3 (1 C, CH_2-11), 66.3 (1 C, C-8), 73.0 (1 C, C-7), 77.2 (1 C, C-5), 78.0 (1 C, C-4), 82.0 (1 C, C-6), 109.2, 113.2 (2 C, $C_{acetalic}$), 125.8 (1 C, C-2), 137.6 (1 C, C-3), 217.5 (4 C, CO_{cis}), 224.3 (1 C, CO_{trans}), 273.6 (1 C, C-1). (62.9 MHz, $CDCl_3$, 293 K): $\delta = 13.7$, 14.5, 15.2 (3 C, CH_3-9, CH_3-12, CH_3-13), 24.1, 25.6, 26.2, 26.8 (4 C, CH_3), 48.1, 53.6 (2 C, CH_2-10, CH_2-11), 65.8, 66.4, 73.3, 78.4, 82.3 (5 C, C-4, C-5, C-6, C-7, C-8), 109.2, 113.5 (2 C, $C_{acetalic}$), 125.8 (1 C, C-2), 137.7 (1 C, C-3), 217.6 (4 C, CO_{cis}), 224.1 (1 C, CO_{trans}), 275.4 (1 C, C-1).

*5.5.3.3. Kinetic study of the rearrangement (S)-E-**8** to (R)-E-**8**.* ^{1}H-NMR samples were prepared at low temperature. The relative total concentrations were determined by the intensities of the H-4 and H-5 signals relative to the signal of non-deuterated solvent at the start of the reaction. The reaction was monitored by the change of the ratio (*S*)-*E*-**8** to the total concentration of (*R*/*S*)-*E*-**8** as indicated by the integrals over the H-4 and H-5 signals of both isomers. The reaction was studied at 283 K (CH_2Cl_2/total concentration of (*R*/*S*)-*E*-**8** = 1:7.28; no reaction over 1041 min), 303 K (CH_2Cl_2/total concentration of (*R*/*S*)-*E*-**8** = 1:7.38), 313 K (CH_2Cl_2/total concentration of (*R*/*S*)-*E*-**8** = 1:9.74) and 318 K (CH_2Cl_2/total concentration of (*R*/*S*)-*E*-**8** = 1:8.40).

*5.5.3.4. Crystal data for (S)-E-**8**.* $C_{24}H_{31}CrNO_{10}$—CH_2Cl_2, $M = 630.42$, orthorhombic, space group $P2_12_12_1$ (No. 19), yellow prisms, dimensions $0.60 \times 0.50 \times 0.40$ mm^3, $a = 12.3401(6)$ Å, $b = 15.5182(8)$ Å, $c = 15.9610(6)$ Å, $V = 3056.5(2)$ Å^3, $D_c = 1.370$ mg m^{-3}, $Z = 4$, μ(Mo–K$_\alpha$) = 0.601 mm^{-1}, $T = 123(2)$ K, $F(0\,0\,0) = 1312$; 11 300 reflections were collected on a Nonius KappaCCD diffractometer (2.63–25.00°; $-11 \le h \le 14$, $-18 \le k \le 15$, $-18 \le l \le 14$), 5364 symmetry independent reflections ($R_{int} = 0.0349$) were used for the structure solution (direct methods) [49] and refinement (full-matrix least-squares on F^2 [50], 353 parameters, zero restraints), non-hydrogen atoms were refined anisotropically, H atoms localized by difference electron density and refined using a "riding" model; $wR_2 = 0.0454$ [$R_1 = 0.0254$ for $I > 2\sigma(I)$]. The absolute configuration was determined by refinement of Flack's *x*-parameter ($x = -0.009(12)$) [51].

5.6. Cyclopropanation reactions

5.6.1. Cyclopropanation of alkyl crotonates

*5.6.1.1. (1*l*′R,2′R,3′R)2′-ethoxycarbonyl-3′-methyl-2,3:5,6-di-O-isopropylidene spiro[1,4-anhydro-D-mannitol-1,1′-cyclopropane] (**9**).* A solution of 300 mg (0.69 mmol) mannofuranosylidene complex **2** and 790 mg (6.90 mmol) ethyl crotonate in 7 ml *n*-heptane was stirred at 105 °C for 48 h. Column chromatography on silica gel (light petroleum–diethyl ether–dichloromethane, 10:5:1; $R_F = 0.48$) afforded 200 mg (0.58 mmol, 84%) of **9** as a waxy colorless solid and traces of a minor diastereomer ($R_F = 0.30$). Major isomer—m.p.: 55–58 °C—[α_D] ($CHCl_3$, c0.0720): +120°—IR (KBr): $\nu = 1714$ cm^{-1} (s, C=O)—^{1}H-NMR (500.13

MHz, $CDCl_3K$): $\delta = 1.23$ (d, $^3J_{HH} = 6.36$ Hz, 3H, CH_3-3′′), 1.24 (t, $^3J_{HH} = 7.15$ Hz, 3H, CH_3-2′′), 1.31 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.45 (d, $^3J_{HH} = 6.85$ Hz, 1H, H-2′), 1.47 (s, 3H, CH_3), 1.88 (quint*, $^3J_{HH} = 6.5$ Hz, 1H, H-3′), 3.66 (dt, $^3J_{HH} = 7.65$ Hz, $^{3/4}J_{HH} = 1.6$ Hz, 1H, H-4), 3.97 (dd, $^2J_{HH} = 8.8$ Hz, $^3J_{HH} = 4.4$ Hz, 1H, H-6a), 4.06 (dd, $^2J_{HH} = 8.74$ Hz, $^3J_{HH} = 6.16$ Hz, 1H, H-6b), 4.08 (dq, $^2J_{HH} = 11$ Hz, $^3J_{HH} = 7.2$ Hz, 1H, H-1′′a), 4.14 (dq, $^2J_{HH} = 11$ Hz, $^3J_{HH} = 7.2$ Hz, 1H, H-1′′b), 4.40 (ddd, $^3J_{HH} = 7.65$ Hz, $^3J_{HH} = 6.2$ Hz, $^3J_{HH} = 4.4$ Hz, 1H, H-5), 4.76 (d, $^{3/4}J_{HH} = 1.6$ Hz, 2H, H-2, H-3)—^{1}H-NMR (500.13 MHz, C_6D_6; NOE experiments: 250.13 MHz, C_6D_6): $\delta = 0.97$ (t, $^3J_{HH} = 7.10$ Hz, 3H, CH_3-2′′, NOE 4.0% upon irradiation on H-3′), 1.12 (d, $^3J_{HH} = 6.41$ Hz, 3H, CH_3-3′′), 1.18 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.58 (d, $^3J_{HH} = 6.71$ Hz, 1H, H-2′, NOE 0.8% upon irradiation on CH_3-3′′), 2.14 (quint*, $^3J_{HH} = 6.45$ Hz, 1H, H-3′, NOE 1.1% upon irradiation on H-2), 3.66 (dd, $^3J_{HH} = 6.87$ Hz, $^3J_{HH} = 3.21$ Hz, 1H, H-4, NOE 3.4% upon irradiation on H-2′), 3.96 (dq, $^2J_{HH} = 10.9$ Hz, $^3J_{HH} = 7.1$ Hz, 1H, H-1′′a), 4.03 (dd, $^2J_{HH} = 8$ Hz, $^3J_{HH} = 6$ Hz, 1H, H-6a), 4.04 (dq, $^2J_{HH} = 11.2$ Hz, $^3J_{HH} = 7.0$ Hz, 1H, H-1′′b), 4.06 (dd, $^2J_{HH} = 8.62$ Hz, $^3J_{HH} = 5.72$ Hz, 1H, H-6b), 4.39 (dd, $^3J_{HH} = 6.1$ Hz, $^3J_{HH} = 3.2$ Hz, 1H, H-3), 4.54 (q*, $^3J_{HH} = 6.3$ Hz, 1H, H-5), 5.00 (d, $^3J_{HH} = 5.95$ Hz, 1H, H-2, NOE 3.1% upon irradiation on H-3′)—^{13}C-NMR (62.9 MHz, $CDCl_3$): $\delta = 11.5$ (qt, $^1J_{CH} = 128$ Hz, $^2J_{CH} = 5.7$ Hz, 1 C, C-3′′/C-2′′), 14.2 (qt, $^1J_{CH} = 127$ Hz, $^2J_{CH} = 2$ Hz, 1 C, C-2′′/C-3′′), 22.2 (dq, $^1J_{CH} = 160.5$ Hz, $^2J_{CH} = 5$ Hz, 1 C, C-3′), 25.2 (qd, $^1J_{CH} = 126.3$ Hz, $^3J_{CH} = 3.0$ Hz, 1 C, CH_3), 25.4 (qd, $^1J_{CH} = 126.3$ Hz, $^3J_{CH} = 2.7$ Hz, 1 C, CH_3), 26.2 (qd, $^1J_{CH} = 126.7$ Hz, $^3J_{CH} = 2.7$ Hz, 1 C, CH_3), 26.8 (qd, $^1J_{CH} = 126.7$ Hz, $^3J_{CH} = 3.0$ Hz, 1 C, CH_3), 32.6 (d, $^1J_{CH} = 164.4$ Hz, 1 C, C-2′), 60.5 (tq, $^1J_{CH} = 147$ Hz, $^3J_{CH} = 4$ Hz, 1 C, CH_2-1′′), 66.7 (td, $^1J_{CH} = 152$ Hz, $^3J_{CH} = 3$ Hz, 1 C, CH_2-6), 73.0 (dd, $^1J_{CH} = 151.6$ Hz, $^3J_{CH} = 3.9$ Hz, 1 C, C-2/C-3/C-4), 76.9 (s, 1 C, C-1/1′), 80.2 (dd, $^1J_{CH} = 160.5$ Hz, $^3J_{CH} = 3.0$ Hz, 1 C, C-5), 80.7 (dt, $^1J_{CH} = 158.5$ Hz, $^3J_{CH} = 2.0$ Hz, 1 C, C-2/C-3/C-4), 81.6 (dt, $^1J_{CH} = 154.2$ Hz, $^3J_{CH} = 3$ Hz, 1 C, C-2/C-3/C-4), 109.1 (s, 1 C, $C_{acetalic}$), 112.6 (s, 1 C, $C_{acetalic}$), 171.4 (s, 1 C, COOEt)—MS (EI); *m/z* (%): 356 (1) [M^+], 341 (8) [M^+-CH_3], 298 (21) [M^+-$(CH_3)_2CO$], 283 (25) [M^+-CH_3-$(CH_3)_2CO$], 225 (14) [M^+-CH_3–2 $(CH_3)_2CO$]—HRMS for $^{12}C_{18}^{1}H_{28}^{16}O_7$ [M^+] Calc.: 356.1835. Found: 356.1843—$C_{18}H_{28}O_7$ (356.42): Calc.: C, 60.66; H, 7.82. Found: C, 60.13; H, 7.45%—Minor isomer—^{1}H-NMR (250.13 MHz, $CDCl_3$): $\delta = 1.23$ (d, $^3J_{HH} = 6.59$ Hz, 3H, CH_3-3′′), 1.33 (s, 6H, 2 CH_3), 1.39 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 2.21 (quint*, $^3J_{HH} = 6.5$ Hz, 1H, H-3′), 3.30 (dd, $^2J_{HH} = 8.4$ Hz, $^3J_{HH} = 3.30$ Hz, 1H, H-6a), 3.86 (dd, $^3J_{HH} = 8.7$ Hz, $^3J_{HH} = 3.5$ Hz, 1H, H-4), 3.95–4.20 (m, 3H, CH_2-1′′, H-6b), 4.38 (ddd, $^3J_{HH} = 8.6$ Hz, $^3J_{HH} = 5.8$ Hz, $^3J_{HH} = 3.2$ Hz, 1H, H-5), 4.53 (d, $^3J_{HH} = 6.10$ Hz, 1H, H-2), 4.86 (dd, $^3J_{HH} = 5.7$ Hz, $^3J_{HH} = 3.5$ Hz, 1H, H-3), H-2′ and CH_3-2′′ hidden.

*5.6.1.2. (1/1′R,2′R,3′R)-2′-methoxycarbonyl-3′-methyl-2,3:5,6-di-O-isopropylidenespiro[1,4-anhydro-D-mannitol-1,1′-cyclopropane] (**10**).* A solution of 550 mg (1.266 mmol) mannofuranosylidene complex **2** and 1.268 g (12.66 mmol) methyl crotonate in 12.8 ml *n*-heptane was stirred at 105 °C for 48 h. Column chromatography on silica gel (light petroleum–diethyl ether–dichloromethane, 10:5:1; $R_F = 0.44$) afforded 195 mg (0.569 mmol, 45%) of **10** as a waxy colorless solid. Crystals for X-ray structural analysis were grown from $CDCl_3$—m.p.: 71–73 °C—$[\alpha_D]$ ($CHCl_3$, c0.0376): −598°—IR (KBr): $\nu = 1721$ cm^{-1} (s, C=O)—^{1}H-NMR (500.13 MHz, C_6D_6; NOE experiments: 250.13 MHz, C_6D_6): $\delta = 1.11$ (d, br, $^3J_{HH} \sim 5$ Hz, 3H, H-3′′), 1.17 (s, 3H, CH_3-a), 1.30 (s, 3H, CH_3-b), 1.41 (s, 6H, CH_3-c, CH_3-d), 1.54 (d, $^3J_{HH} = 6.71$ Hz, 1H, CH_3-2′), 2.09 (quint*, $^3J_{HH} = 6.4$ Hz, 1H, H-3′, NOE 2.7% upon irradiation on H-2), 3.38 (s, 3H, OCH_3), 3.64 (dd, $^3J_{HH} = 6.9$ Hz, $^3J_{HH} = 3.2$ Hz, 1H, H-4, NOE 0.5% upon irradiation on H-2), 4.03 (d, $^3J_{HH} = 5.98$ Hz, 2H, CH_2-6), 4.38 (dd, $^3J_{HH} = 6.11$ Hz, $^3J_{HH} = 3.18$ Hz, 1H, H-3), 4.51 (q*, $^3J_{HH} = 6.3$ Hz, 1H, H-5), 4.91 (d, $^3J_{HH} = 5.98$ Hz, 1H, H-2, NOE 3.2% upon irradiation on H-3′)—^{13}C-NMR (125.76 MHz, C_6D_6): $\delta = 11.3$ (1 C, C-2′), 22.5 (1 C, C-3′), 25.3, 25.4 (2 C, CH_3-a, CH_3-b), 26.3 (1 C, CH_3-c), 26.7 (1 C, CH_3-d), 32.5 (1 C, CH_3-3′′), 51.1 (1 C, OCH_3), 66.8 (1 C, C-6), 73.2 (1 C, C-5), 77.5 (1 C, C-1/1′), 80.5 (1 C, C-2), 80.9 (1 C, C-3), 82.3 (1 C, C-4), 108.8, 112.3 (2 C, $C_{acetalic}$), 171.4 (1 C, COOMe)—MS (+FAB); *m/z* (%): 343 (24) [M^+ +H], 285 (67) [M^+ + H–$(CH_3)_2CO$], 227 (70) [M^+ +H–2 $(CH_3)_2CO$]—(EI); *m/z* (%): 342 (7) [M^+], 327 (21) [M^+-CH_3], 284 (37) [M^+-$(CH_3)_2CO$], 269 (34) [M^+-$(CH_3)_2CO$–CH_3]—HRMS for $^{12}C_{17}^{1}H_{26}^{16}O_7$ [M^+] Calc.: 342.1678. Found: 342.1683—$C_{17}H_{26}O_7$ (342.32): Calc.: C, 59.64; H, 7.65. Found: C, 59.16; H, 7.79%.

*5.6.1.3. Crystal data for **10**.* $C_{17}H_{26}O_7$, $M = 342.38$, orthorhombic, space group $P2_12_12_1$ (No. 19), colorless crystals, dimensions $0.45 \times 0.30 \times 0.25$ mm^3, $a = 10.2621(3)$ Å, $b = 10.9781(4)$ Å, $c = 16.0784(5)$ Å, $V = 1811.37(10)$ $Å^3$, $D_c = 1.255$ mg m^{-3}, $Z = 4$, μ(Mo–K_α) = 0.097 mm^{-1}, $T = 123(2)$ K, $F(0\,0\,0) = 736$; 26 546 reflections were collected on a Nonius KappaCCD diffractometer (3.00–28.34°; $-13 \le h \le 13$, $-14 \le k \le 14$, $-21 \le l \le 21$), 4478 symmetry independent reflections ($R_{int} = 0.0385$) were used for the structure solution (direct methods) [49] and refinement (full-matrix least-squares on F^2 [50], 219 parameters, zero restraints), non-hydrogen atoms were refined anisotropically, H atoms localized by difference electron density and refined using a ''riding'' model; $wR_2 = 0.0767$ [R_1 =

0.0318 for $I > 2\sigma(I)$]. The absolute configuration was not determined reliably by refinement of Flack's x-parameter ($x = 0.6(6)$) [52].

5.6.2. Cyclopropanation of diethyl maleate

A solution of 320 mg (0.737 mmol) mannofuranosylidene complex **2** and 0.25 ml (254 mg, 1.48 mmol) diethyl maleate in 4 ml *n*-heptane was stirred at 105 °C for 48 h. Column chromatography on silica gel (light petroleum–diethyl ether–dichloromethane, 10:5:1; $R_F = 0.17$) afforded 96 mg (0.23 mmol, 32%) of an inseparable mixture of three diastereomeric cyclopropanes **11** (20%), **12** (69%) and **13** (11%) as a colorless oil.

5.6.3. Cyclopropanation with diethyl fumarate

A solution of 210 mg (0.484 mmol) mannofuranosylidene complex **2** and 0.32 ml (333 mg, 1.94 mmol) diethyl fumarate in 3 ml *n*-heptane was stirred at 105 °C for 48 h. Column chromatography on silica gel (light petroleum–diethyl ether–dichloromethane, 10:5:1; $R_F = 0.17$) afforded 34 mg (0.08 mmol, 17%) of an inseparable mixture of three diastereomeric cyclopropanes **11** (62%), **12** (24%) and **13** (14%) as a colorless oil.

*5.6.3.1. (2′S,3′S)-2′,3′-di-ethoxycarbonyl-2,3:5,6-di-O-isopropylidene spiro[1,4-anhydro-D-mannitol-1,1′-cyclopropane] (**11**).* ^{1}H-NMR (500.13 MHz, $CDCl_3$): $\delta = 1.239$ (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3-2″a), 1.243 (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3-2″b), 1.30 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 2.55 (d, $^3J_{HH} = 6.41$ Hz, 1H, H-3′, NOE 11.2% upon irradiation on H-2), 2.91 (d, $^3J_{HH} = 6.41$ Hz, 1H, H-2′), 3.46 (dd, $^3J_{HH} = 8.4$ Hz, $^3J_{HH} = 3.3$ Hz, 1H, H-4), 3.85 (dd, $^2J_{HH} = 8.85$ Hz, $^3J_{HH} = 3.7$ Hz, 1H, H-6a), 4.04 (dd, $^2J_{HH} = 8.85$ Hz, $^3J_{HH} = 6.1$ Hz, 1H, H-6b), 4.08–4.24 (m, 4H, CH_2-1″), 4.38 (ddd, $^3J_{HH} = 8.4$ Hz, $^3J_{HH} = 6.1$ Hz, $^3J_{HH} = 3.7$ Hz, 1H, H-5), 4.72 (d, $^3J_{HH} = 5.95$ Hz, 1H, H-2, NOE 9.8% upon irradiation on H-3′), 4.86 (dd, $^3J_{HH} = 5.95$ Hz, $^3J_{HH} = 3.4$ Hz, 1H, H-3)—^{13}C-NMR (125.76 MHz, $CDCl_3$): $\delta = 14.0$, 14.24 (2 C, CH_3-2″), 25.1, 25.4, 26.0, 27.0 (4 C, CH_3), 27.5 (1 C, C-2′), 32.5 (1 C, C-3′), 61.28, 61.35 (2 C, CH_2-1″), 67.0 (1 C, CH_2-6), 72.5 (1 C, C-5), 75.2 (1 C, C-1/1′), 79.9 (1 C, C-3), 82.6 (1 C, C-4), 83.3 (1 C, C-2), 109.5, 113.2 (2 C, $C_{acetalic}$), 166.57, 168.6 (2 C, COOEt)—MS (EI); *m/z* (%): 414 (3) [M^+], 399 (17) [M^+-CH_3], 368 (41) [M^+-C_2H_5OH], 341 (17) [M^+-CH_3–$(CH_3)_2CO$], 310 (14) [M^+-C_2H_5OH-$(CH_3)_2CO$]—HRMS for $^{12}C^1_{20}H^{16}_{30}O_9$ [M^+] Calc.: 414.1890. Found: 414.1899.

*5.6.3.2. (2′R,3′S)-2′,3′-diethoxycarbonyl-2,3:5,6-di-O-isopropylidene spiro[1,4-anhydro-D-mannitol-1,1′-cyclopropane] (**12**).* ^{1}H-NMR (500.13 MHz, $CDCl_3$; NOE experiments: 400.13 MHz, $CDCl_3$): $\delta = 1.22$ (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3-2″a), 1.26 (t, $^3J_{HH} = 7.3$ Hz, 3H, CH_3-2″b), 1.34 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 2.62 (d, $^3J_{HH} = 7.02$ Hz, 1H, H-2′, NOE 1.7% upon irradiation on H-2), 2.71 (d, $^3J_{HH} = 7.02$ Hz, 1H, H-3′, NOE 7.5% upon irradiation on H-2), 3.75 (dd, $^3J_{HH} = 7.8$ Hz, $^3J_{HH} = 3.2$ Hz, 1H, H-4), 3.95 (dd, $^2J_{HH} = 8.9$ Hz, $^3J_{HH} = 4.2$ Hz, 1H, H-6a), 4.02 (dd, $^2J_{HH} = 8.9$ Hz, $^3J_{HH} = 6.2$ Hz, 1H, H-6b), 4.08–4.24 (m, 4H, CH_2-1″), 4.36 (ddd, $^3J_{HH} = 7.93$ Hz, $^3J_{HH} = 4.43$ Hz, $^3J_{HH} = 6.10$ Hz, 1H, H-5), 4.71 (d, $^3J_{HH} = 5.86$ Hz, 1H, H-2), 4.80 (dd, $^3J_{HH} = 5.86$ Hz, $^3J_{HH} = 3.2$ Hz, 1H, H-3)—^{13}C-NMR (125.76 MHz, $CDCl_3$): $\delta = 14.16$, 14.18 (2 C, CH_3-2″), 25.2, 25.9, 26.3, 26.9 (4 C, CH_3), 29.1 (1 C, C-3′), 31.3 (1 C, C-2′), 61.24, 61.25 (2 C, CH_2-1″), 66.7 (1 C, CH_2-6), 72.9 (1 C, C-5), 76.1 (1 C, C1/1′), 80.0 (1 C, C-2), 80.4 (1 C, C-3), 81.9 (1 C, C-4), 109.3, 113.7 (2 C, $C_{acetalic}$), 166.60, 169.2 (2 C, COOEt).

*5.6.3.3. (2′R,3′R)-2′,3′-diethoxycarbonyl-2,3:5,6-di-O-isopropylidene spiro[1,4-anhydro-D-mannitol-1,1′-cyclopropane] (**13**).* ^{1}H-NMR (500.13 MHz, $CDCl_3$): $\delta = 1.24$ (t, $^3J_{HH} = 7$ Hz, 3H, CH_3-2″a, NOE 28.2% upon irradiation on H-2), 1.29 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.81 (d, $^3J_{HH} = 7.17$ Hz, 1H, H-3′), 1.91 (d, $^3J_{HH} = 7.17$ Hz, 1H, H-2′), 3.59 (dd, $^2J_{HH} = 8.70$ Hz, $^3J_{HH} = 4.1$ Hz, 1H, H-6a), 3.65 (dd, $^3J_{HH} = 8.4$ Hz, $^3J_{HH} = 3.2$ Hz, 1H, H-4), 3.92 (dd, $^2J_{HH} = 8.70$ Hz, $^3J_{HH} = 6.3$ Hz, 1H, H-6b), 4.08–4.24 (m, 4H, CH_2-1″), 4.34 (ddd, $^3J_{HH} = 8.4$ Hz, $^3J_{HH} = 6.6$ Hz, $^3J_{HH} = 4.2$ Hz, 1H, H-5), 4.45 (d, $^3J_{HH} = 5.95$ Hz, 1H, H-2, NOE 1.7% upon irradiation on H-2′), 4.83 (dd, $^3J_{HH} = 5.95$ Hz, $^3J_{HH} = 3.4$ Hz, 1H, H-3), CH_3-2″b, 2 CH_3 hidden.

6. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 205612, 205613 and 205614. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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