# Synthesis of Hydroquinoid *C*- and *O*-Biphenyl Disaccharides by Chromium-Templated Benzannulation Reactions[‡]

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*Dedicated to Professor R. W. Hoffmann on the occasion of his 70th birthday*

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Organometallic monosaccharides **6**–**10** containing a chromium styrylcarbene skeleton have been synthesized in quantitative yield from *O*-glycoside methylcarbene complexes **1**–**5** bearing diisopropylidene-protected glucose, mannose, galactose, or fructose in a *trans*-selective aldol condensation with benzaldehyde. These compounds undergo a chromium-templated benzannulation upon reaction with ethynyl glucoside to give diastereoisomeric mixtures of $Cr(CO)_3$ complexes. The differences in their thermodynamic stability was exploited in a diastereoselective synthesis of hydroquinoid biphenyl disaccharides **12**–**16** in 67–88% yields.



## Introduction

Carbohydrates are of eminent importance in nature and biological chemistry. Beside their long-known functions as structural backbones or energy-storing molecules, they play an important role in intercellular molecular recognition processes such as infection, tumor-cell growth, and cell adhesion.[1] Since the chemistry of sugars is dominated by the reactivity of the glycosidic bond, especially of the anomeric center[2] or *O*-glycosidation,[3] a great deal of effort has gone into the synthesis and study of *C*-glycosides in which the acetal linkage has been replaced by a hydrolytically stable carbon−carbon bond. The synthesis of *C*-glycosides has become a well-established area of carbohydrate chemistry,[4] and several *C*-glycosides are potent carbohydrate mimics[5] in antitumor, antibiotic, antiviral, or antibacterial therapy.[6]

Recently, *O*- and *C*-aryl glycosides[7] have received increasing attention because they often exhibit unique antibiotic and/or antitumor activity.[5] They bear a carbon−oxygen or a carbon−carbon bond as the key structural unit that links the carbohydrate skeleton to an aromatic fragment such as biphenyl,[8] hydroquinone,[9] quinone,[10] and heteroaryl[11] systems.

In the past two decades, metal carbenes have been developed to valuable reagents for stereoselective organic synthesis.[12] Their role as a novel functional group in carbohydrates is still limited, but is increasing.[13] The first example of a sugar-modified carbene complex was based on the addition of carbohydrates to isocyanide complexes of gold and platinum to form (glycosyl)aminocarbene and neomycin B complexes.[14] Transition metal functionalization of the anomeric center is known for glycosyl complexes of cobalt,[15] iron,[16] and manganese,[17] which represent nucleophilic sugar synthons. It was only recently that electrophilic synthons, such as sugar metal carbenes of the Fischer carbene type, have also been synthesized.[18] These complexes have been applied to diastereoselective ligand- or metal-centered cycloaddition, such as Diels−Alder[19] and [3+2+1]-benzannulation[20] reactions, as well as to *O*- and *C*-glycosidation.[21] Glycal carbene complexes undergo chromium-templated benzannulation reactions to form novel aryl carbohydrate compounds.[22] We extended this methodology to organometallic *O*- and *C*-disaccharides in which both sugar moieties are linked by a metal vinylcarbene spacer,[23] as well as to organometallic *C*-glycosides formed by aldol condensation.[24] We now describe a synthetic route to hydroquinoid biphenyl disaccharides that are accessible by benzannulation reactions of an *O*-glycosidic α,β-unsaturated chromium carbene complex with an alkynyl *C*-glycoside.

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## Results and Discussion

### Aldol Condensation

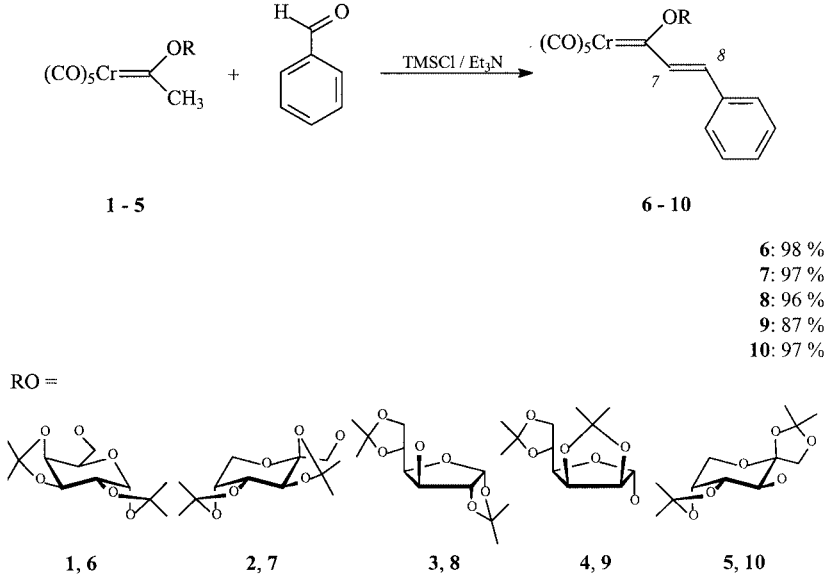
The aldol condensation of methylcarbene complexes is a convenient route to alkenyl carbene complexes.[25] It was first applied to reactive non-enolizable aldehydes, such as benzaldehyde in the presence of triethylamine and trimethylsilyl chloride, where it resulted in quantitative yields.[26] We utilized this approach to the synthesis of α,β-unsaturated chromium carbene complexes also by using carbohydrates as chiral alkoxycarbene groups at the carbene carbon atom.

*O*-Glycosidated carbene complexes have been obtained by addition of suitably protected monodeprotonated carbohydrates to cationic carbyne complexes of manganese and rhenium.[27] Another route was based on the conjugate addition of the sugar moiety to alkynylcarbene complexes of chromium and tungsten to give *O*-glycoside vinylcarbene complexes.[28] We aimed to introduce the carbohydrate at the chromium carbene center, and applied a combined acylation/alcoholysis protocol previously used in the chiral modification of carbene ligands by amines[29] and terpene alcohols.[30,31] Following this route, organometallic monosaccharides have been synthesized from tetramethylammonium acetyl(pentacarbonyl)chromate(−1) applying diisopropylidene-protected 3-glucofuranose, 1-mannofuranose, 6-galactopyranose, 1-fructopyranose, and 3-fructopyranose to give *O*-glycosidic methylcarbene complexes **1**−**5** in 29−84% yields.[23]

These compounds reacted at room temperature in *tert*-butyl methyl ether with an excess of benzaldehyde, trimethylsilyl chloride, and triethylamine in a *trans*-selective aldol condensation leading to styrylcarbene complexes **6**−**10** in 87−98% yields (Scheme 1). The main part of the reaction takes place in the first three hours, but it is only after 12 h that the aldol condensation affords the high yields reported.

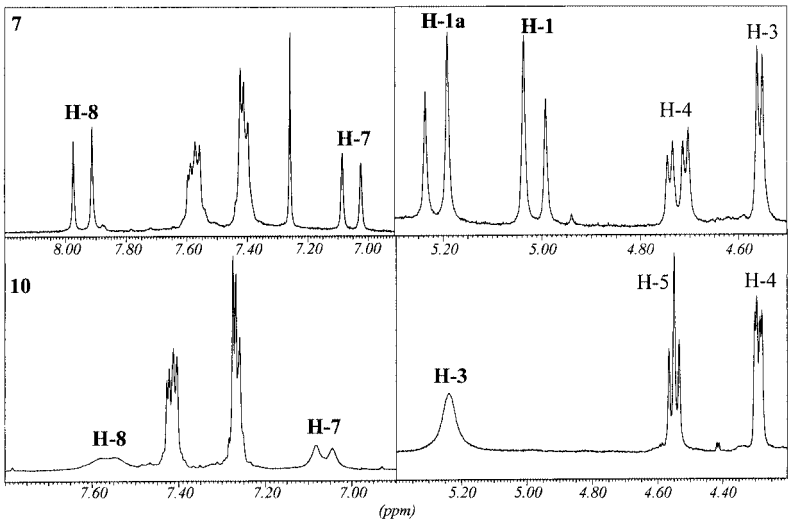
NMR spectroscopy and HPLC indicated the formation of a single diastereoisomer bearing an *E*-vinylcarbene double bond, as established by a coupling constant of $^3J_{H,H}$ = 15−16 Hz. The structural elucidation of the products **6**−**10** was mainly achieved based on their $^1$H and $^{13}$C NMR spectra. The glycosidic region of the spectra does not reveal any significant difference between the starting materials **1**−**5** and the products **6**−**10**, which indicates that the styryl spacer has no major influence on the conformation of the carbohydrates. An interesting phenomenon results when comparing the complexes **7** and **10** containing the fructopyranose in either a boat form with a primary alcohol **7**, or in a chair conformation with a secondary alcohol **10**. The 3-fructopyranosyloxy styrylcarbene complex **10** shows a similar fluctional behavior as previously discussed for the fructose methylcarbene complex **5**.[23] At room temperature, the equatorially linked fructose skeleton in **10** reveals a restricted rotation around the carbene−oxygen bond, as was outlined previously for carbene complex **5**. In the $^1$H NMR spectra of **10**, the signal for 3-H appears as a broad singlet; a similar broadening is also observed for the resonances 7-H and 8-H that appear as doublets reflecting the *E*-vicinal coupling across the olefinic double bond. In contrast to this observation, the $^1$H NMR signals of the complex **7** − like all other styrylcarbene complexes − gave only sharp resonances (Scheme 2).

The same phenomenon − the hindered rotation at room temperature − is also evident from the $^{13}$C NMR signals for C-3, C-7, C-8 and the carbene carbon signal of 3-fructopyranosyloxy styrylcarbene complex **10**. The chromium carbenes **6**−**9**, which bear either a smaller axial combined furanose (**8**, **9**) or one $CH_2$-containing boat conformational pyranose (**6**, **7**) *O*-glycoside component, do not reveal broadened signals. Another peculiar feature of α,β-unsaturated carbene complexes **6**−**10** is that the carbene signals

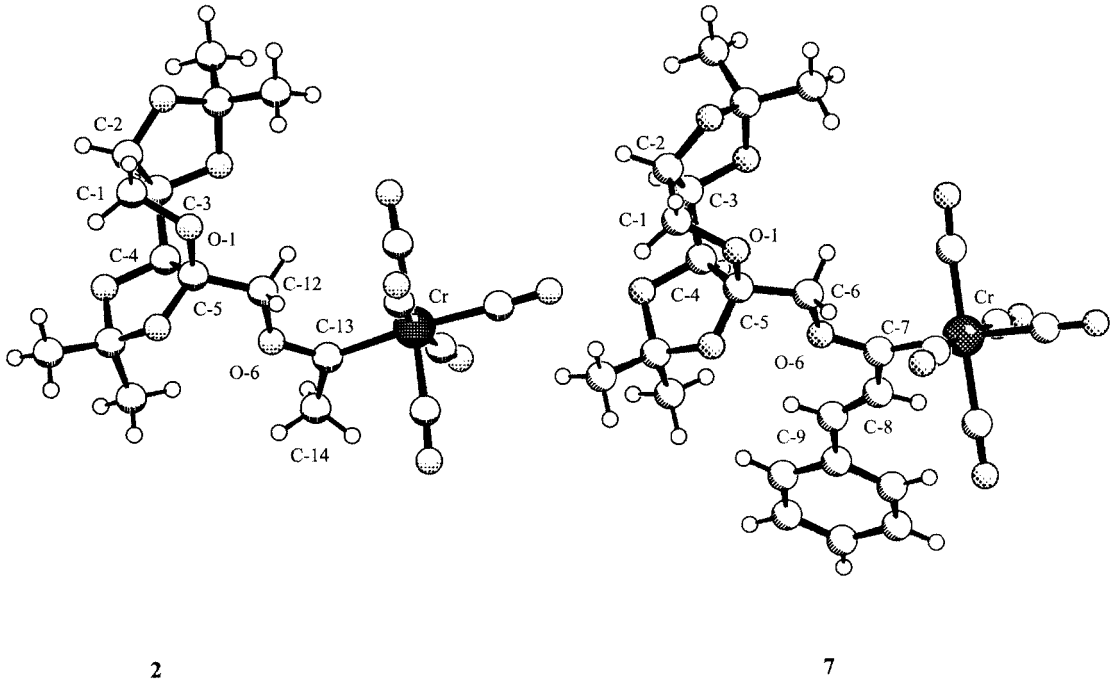



Scheme 1. Synthesis of styrylcarbene glycoside complexes **6**−**10** by aldol condensation




Scheme 2. Comparison of the $^1$H NMR spectra of pentacarbonyl[(2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranosyloxy)-(*E*)-styrylcarbene]chromium (**7**) and pentacarbonyl[(1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranosyloxy)-(*E*)-styrylcarbene]chromium (**10**)




**2** **7**

Figure 1. Molecular structures of fructopyranose-derived complexes **2** and **7** (one of the two in the asymmetric unit of **7**). The numbering of atoms does not correspond with the numbering used in the NMR spectra. Selected distances [pm] and angles [°] for **2**: Cr−C13 2.0238(18), C13−O6 1.321(2), C13−C14 1.510(3), O6−C12 1.442(2), Cr−C13−O6 131.72(14), Cr−C13−C14 122.92(14), O6−C13−C14 105.35(15); for **7**: Cr−C7 2.052(7), C7−O6 1.321(8), C7−C8 1.469(10), O6−C6 1.435(7), C8−C9 1.269(11), Cr−C7−O6 133.2(5), Cr−C7−C8 118.1(5), O6−C7−C8 108.6(6)

reveal a downfield shift of ca. 27 ppm relative to their saturated methyl analogs **1**−**5**.[23]

The incorporation of the styryl linker into the metal carbene *O*-glycoside did not result in any significant variation of the chemical shifts in the sugar skeleton. This fact suggests a similar steric arrangement of the carbohydrate skeleton in methylcarbene complexes **1**−**5** and styrylcarbene complexes **6**−**10**, as is demonstrated by comparing the X-ray crystal structures of complexes **2** and **7** (Figure 1).

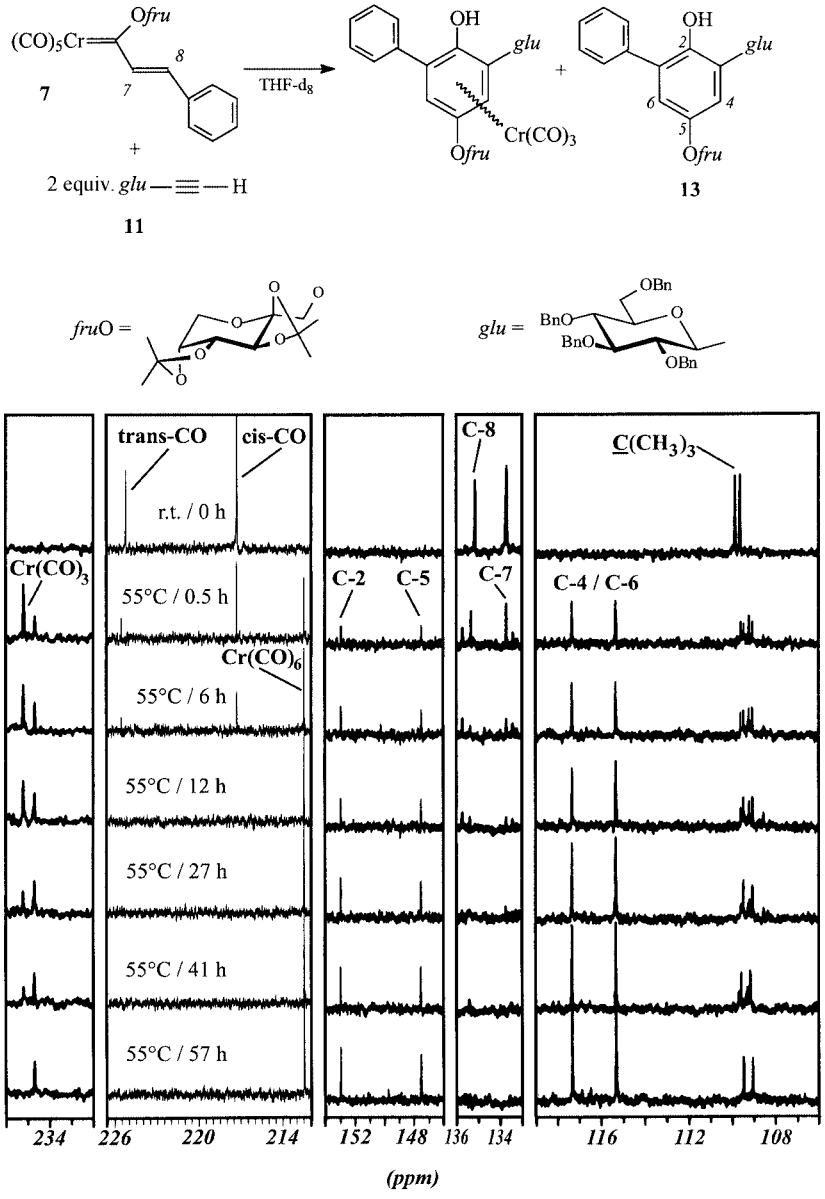
## Benzannulation Reaction

The [3+2+1]-benzannulation reaction of chromium carbene complexes with alkynes provides a straightforward access to densely substituted aromatic compounds.[32] The benzene skeleton results from the assembly of the vinylcarbene chain, the alkyne and one carbonyl ligand, which are interlinked by a sequential C−C bond formation occurring within the coordination sphere of the chromium template.

Most benzannulation reactions reported in the literature so far have been carried out with alkoxycarbene complexes affording $Cr(CO)_3$-coordinated hydroquinoid products; moreover, some examples document that aminophenols also are accessible from aminocarbene complexes.[12,32] As a result of the unsymmetrical substitution pattern, the $Cr(CO)_3$ arene complexes contain a plane of chirality. High levels of chiral induction have been observed with chiral alkynes in special cases.[33] Similarly, incorporating chiral centers into the carbon side chain of the carbene may result in considerable diastereoselection.[34]

We focused on a more general strategy that is based on incorporating chiral alcohol and amine auxiliaries into the heteroatom side chain of the carbene.[31,35] Our first studies indicated that typical carbohydrate-based O-auxiliaries alone, when attached to the carbene carbon atom, did not result in a considerable diastereoselection in the benzannulation reaction.[36] Reactions involving *O*-glycosidic alkoxy(phenyl)carbene complexes and terminal non-chiral aliphatic or aromatic alkynes gave only very moderate *de* values between 14 and 56%.[36,37] We speculated that more bulky alkynes providing additional chiral information would be appropriate candidates for increasing the diastereoselectivity. In this context, we extended the range of alkynes to sugar alkynes and focused on the per-benzyl-protected ethynyl glucopyranose **11**. At our standard conditions (55 °C in *tert*-butyl methyl ether), the benzannulation of *O*-glycosidic styrylcarbene complexes **6**−**10** with sugar alkyne **11** turned out to be rather slow. After 12 hours, chromatographic workup and analytical characterization of the reaction mixtures indicated, in each case, the presence of virtually a single diastereoisomer and of the $Cr(CO)_3$-coordinated




Scheme 3. Benzannulation of pentacarbonyl[(2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranosyloxy)-(*E*)-styrylcarbene]chromium (**7**) by ethynyl glucoside **11** monitored by $^{13}C$ NMR spectroscopy

benzannulation product. Concomitant NMR spectroscopic analyses, however, revealed additional signals characteristic of demetalated hydroquinoid biphenyl disaccharides. To elucidate the origin of these products, we monitored the course of the benzannulation by in situ $^{13}C$ NMR spectroscopy. A solution of *O*-glycosidic styrylcarbene complex **7** in deuterated THF was placed into an NMR tube and was combined with an excess of ethynyl *C*-glycoside **11**; the solution was warmed and kept at 55 °C for 66 h while $^{13}C$ NMR spectra were continually recorded, initially every 30 min and then, after three hours, every 180 min (Scheme 3).

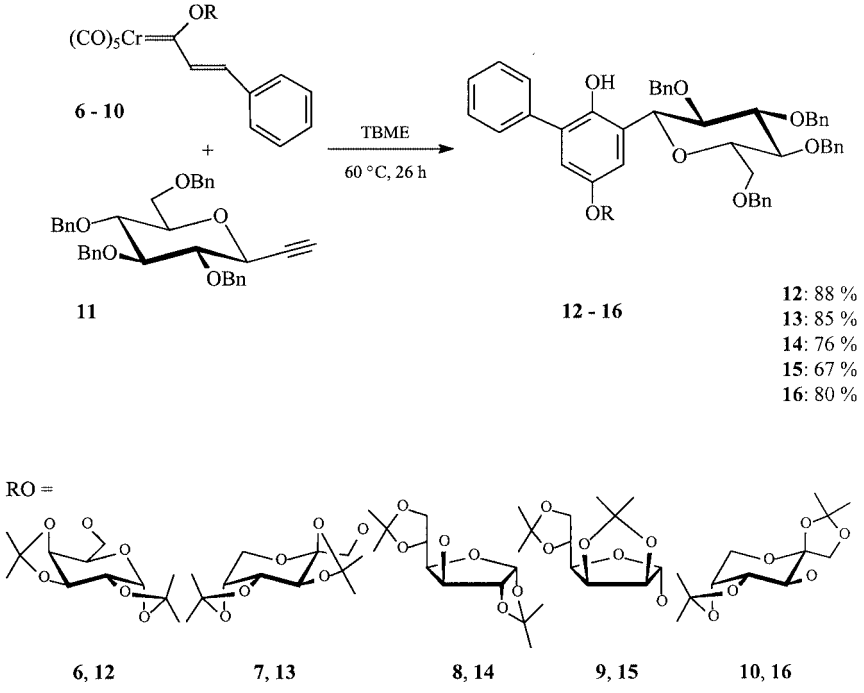
Initially, the $^{13}C$ NMR spectrum is dominated by the signals of the starting carbene complex **7**, which is best identified by its signals for the *cis*- and *trans*-CO ligands at δ = 217.1 and 225.0 ppm, respectively, and for the alkene carbon atoms C-7 and C-8 at δ = 132.2 and 140.5 ppm, respectively. After 30 min, $Cr(CO)_3$ complex formation is indicated by an increasing signal at δ = 234.7 ppm, which is accompanied by a neighboring less-intense, up-field signal (δ = 234.5 ppm). As the reaction proceeds, the ratio of these two signals interconverts, while four additional signals gain in intensity at δ = 152.3, 146.9, 117.0, and 115.2 ppm that are characteristic for an uncoordinated hydroquinone ring (C-2, C-5, C-4, and C-6). These results demonstrate that the formation of one single diastereoisomer (**A**) is kinetically favored; in the early stage of the reaction its concentration increases faster than that of the other diastereoisomer (**B**). The kinetically favored diastereoisomer **A**, however, is more thermolabile than diastereoisomer **B** and, thus, decomposes to give the demetalated hydroquinoid disaccharide, while the concentration of diastereoisomer **B** increases as the reaction proceeds. When the starting carbene complex is consumed, the thermodynamic diastereoisomer **B** is detected in the reaction mixture virtually as a single diastereoisomer along with the uncoordinated disaccharide.

Since we could not achieve a chromatographic separation of the diastereoisomeric benzannulation products **A** and **B** and the demetalated disaccharide, we decided to speed up the demetalation of the kinetic diastereoisomer **A** by increasing the reaction temperature to 58 °C for 15 h and to analyze the mixture of diastereoisomer **B** and demetalated disaccharide. Since the chromatographic workup procedure of these mixtures turned also out to be redious, we focused on the synthesis of the demetalated aryl disaccharides **12**−**16** by increasing the reaction temperature to 60 °C for 26 h, conditions that resulted in overall yields of 67−88% for the uncoordinated hydroquinoid disaccharides **12**−**16** (Scheme 4).

The structures of disaccharides **12**−**16** were analyzed on the basis of their NMR and FAB-mass spectra, which demonstrate the combination of different protected *O*- and *C*-glycosidic moieties within one compound. Moreover, the $^{1}H$ NMR spectral signals of 4-H and 6-H resonating at δ = 6.80−7.10 ppm, as well as the $^{13}C$ NMR spectral absorptions for C-2, C-5, and C-4/C-6 at δ = 150−153, 147−148, and 115 −120 ppm, respectively, indicate the formation of the novel biphenyl-2-ol aglycon.

## Conclusion

The results demonstrate that benzannulation of *O*-glycosidic chromium vinylcarbene complexes by a *C*-glycosidic alkyne leads to novel *O*- and *C*-aryl disaccharides in decent yields. This method is very flexible to different glycosides




Scheme 4. Synthesis of hydroquinoid *C*- and *O*-biphenyl disaccharides by benzannulation reactions

and permits the synthesis of rare or unnatural disaccharides that are frequently employed as chiral building blocks in carbohydrate mimics.

The chromium-templated benzannulation of carbene complexes with carbohydrate-based O-auxiliaries alone gave only unsatisfactory diastereoselections.[36,37] The combination, however, of carbene complexes bearing a sterically hindered *O*-alkoxy unit and a vinyl side-chain group with a bulky alkyne resulted in virtually complete diastereoselectivity. NMR spectroscopic monitoring of the benzannulation reaction indicated that initially one $Cr(CO)_3$ complex is formed preferentially as the kinetically favored benzannulation product. In the course of the reaction, it undergoes a more-rapid decomposition than the other thermodynamic benzannulation product, which, at the end of the reaction, is revealed as the predominant diastereoisomer along with its demetalated analog. The difficulties arising from the chromatographic separation of the mixture may be reduced by the use of other protecting groups at the ethynyl glycoside, conditions that may allow the isolation of the thermodynamic diastereoisomer. Preliminary studies, by the substitution of the styrene moiety by a vinyl glycosidic moiety in the *C*-carbene side chain, have demonstrated that *C*-glycosidic alkynes bearing ketal protective groups are similarly suited for the benzannulation.[37]

## Experimental Section

**General Remarks:** All reactions were carried out under dry argon by using Schlenk techniques. The solvents used for reactions and chromatography were dried by distillation from calcium hydride and saturated with argon. Silica gel (E. Merck, type 60, 0.63−0.200 mm) was degassed at high vacuum and stored under argon prior to use for chromatography.

IR: Nicolet Magna 550 FT-IR. NMR: Bruker DRX-500, AM-400, AM-250. MS (FAB, EI): Kratos Instruments Concept 1H and MS 50 (70 eV). HPLC: Knauer Wellchrom, Injection valve A0258, pump K-1001, solvent organizer K-1500, UV detector K-2600, column Knauer Eurospher 100 Si (250 × 4 ø), EUROCHROM 2000 for Windows.

The following reagents were prepared according to literature procedures: Tetramethylammonium [acetyl(pentacarbonyl)]chromate,[38] pentacarbonyl[1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranosyloxy(methyl)carbene]chromium (**1**),[23] pentacarbonyl-[1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyloxy(methyl)-carbene]chromium (**3**),[23] pentacarbonyl[2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranosyloxy(methyl)carbene]chromium (**4**),[23] pentacarbonyl[1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranosyloxy(methyl)carbene]chromium (**5**),[23] and 2,3,4,6-tetra-*O*-benzyl-1-deoxy-1-ethynyl-β-D-glucopyranose (**11**).[39]

**Synthesis of Pentacarbonyl[2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranosyloxy(methyl)carbene]chromium (2):** Acetyl bromide (1 equiv.) was added at −35 °C to a solution of tetramethylammonium [acetyl(pentacarbonyl)]chromate (2.95 g, 10 mmol) in dichloromethane (100 mL). The mixture was stirred for 30 min at this temperature, and then a solution of 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose[40] (1.5 equiv.) in dichloromethane (30 mL) was added dropwise. After 3 h at −30 °C the solvent was evaporated, and the residue was purified by chromatography at −15 °C by using dichloromethane as eluent to give an orange oil. Yield: 3.90 g (8.16 mmol, 82%); $R_f$ = 0.66 ($CH_2Cl_2$). $^1$H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.35 (s, 3 H, $CH_3$), 1.42 (s, 3 H, $CH_3$), 1.46 (s, 3 H, $CH_3$), 1.57 (s, 3 H, $CH_3$), 2.99 (s, 3 H, $CH_3$), 3.82 (d, $^2J_{H,H}$ = 12.9 Hz, 1 H, 6-H), 3.99 (d, $^2J_{H,H}$ = 12.5 Hz, 1 H, 6a-H), 4.28 (d, $^3J_{H,H}$ = 7.94 Hz, 1 H, 5-H), 4.47 (d, $^3J_{H,H}$ = 2.44 Hz, 1 H, 3-H), 4.68 (dd, $^3J_{H,H}$ = 7.81, 2.56 Hz, 1 H, 4-H), 4.85 (br. d, $^3J_{H,H}$ = 10.9 Hz, 1 H, 1-H), 5.01 (br. d, $^3J_{H,H}$ = 10.9 Hz, 1 H, 1a-H) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$, 25 °C): δ = 23.9, 25.4, 25.7, 26.5 (4 $CH_3$), 48.8 (br., $CH_3$), 61.5 (C-6), 69.8, 70.2, 70.7 (C-3, C-4, C-5), 79.4 (br., C-1), 101.0 (C-2), 109.3, 109.4 [$C(CH_3)_2$], 215.9 (*cis*-CO), 223.1 (*trans*-CO), 360.8 (Cr=C) ppm. IR ($CH_2Cl_2$): ν = 2065, 1943 $cm^{-1}$ (C=O). MS (70 eV, EI): *m/z* (%) = 478 (10) [$M^+$], 463 (6) [$M^+ - CH_3$], 435 (10) [$M^+ - CO - CH_3$], 394 (16) [$M^+ - 3$ CO], 366 (33) [$M^+ - 4$ CO], 338 (18) [$M^+ - 5$ CO], 323 (16) [$M^+ - 5$ CO − $CH_3$], 296 (100) [$M^+ - 5$ CO − $CH_3$ − $C_2H_3$], 245 (38) [$FruO^+ - CH_3$]. HR-MS: calcd. for $M^+$ 478.0567; found 478.0571. Elemental analysis calcd. (%) for $C_{19}H_{22}CrO_{11}$ (478.0): C 47.71, H 4.64; found C 47.61, H 4.70.

**Preparation of the Styrylcarbene Complexes 6−10:** An excess of freshly distilled benzaldehyde (3 equiv.) was added to a solution of the *O*-glycosidic methylcarbene complex **1**−**5** (2.40 g, 5 mmol) in *tert*-butyl methyl ether (30 mL) and after a few minutes *tert*-butyldimethylsilyl chloride (5 equiv.) and of triethylamine (5 equiv.) were added. The dark-red solution was stirred for 12 h at room temperature. The reaction was monitored by IR spectroscopy and TLC. The solvent was evaporated after the reaction reached completion. The residue was purified by chromatography at −15 °C by using dichloromethane as the eluent to give a dark-red oil that (like the methylcarbene complex precursors **3**−**5**) could not be freed completely from traces of solvent, a situation that hampered correct elemental analyses.

**Pentacarbonyl{(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranosyloxy)[(*E*)-styryl]carbene}chromium (6):** Yield: 2.77 g (4.89 mmol, 98%); $R_f$ = 0.78 ($CH_2Cl_2$). $^1$H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.38 (s, 3 H, $CH_3$), 1.39 (s, 3 H, $CH_3$), 1.49 (s, 3 H, $CH_3$), 1.56 (s, 3 H, $CH_3$), 4.42−4.39 (m, 3 H, 2-H, 4-H, 5-H), 4.72 (dd, $^3J_{H,H}$ = 7.69, 2.56 Hz, 1 H, 3-H), 5.16 (d, $^3J_{H,H}$ = 6.60 Hz, 2 H, 6-H, 6a-H), 5.62 (d, $^3J_{H,H}$ = 5.00 Hz, 1 H, 1-H), 7.03 (d, $^3J_{H,H}$ = 15.3 Hz, 1 H, 7-H), 7.42−7.39 (m, 4 H, PhH), 7.60−7.57 (m, 2 H, PhH), 7.95 (d, $^3J_{H,H}$ = 15.3 Hz, 1 H, 8-H) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$, 25 °C): δ = 25.3, 25.7, 26.6, 26.7 (4 $CH_3$), 67.7 (C-5), 71.2, 71.5, 71.7 (C-2, C-3, C-4), 78.7 (C-6), 97.1 (C-1), 103.5 (C-2), 109.6, 110.8 [2 $C(CH_3)_2$], 129.7 (*meta*-PhCH), 130.2 (*ortho*-PhCH), 131.5 (*para*-PhCH), 131.8 (C-7), 135.3 (*ipso*-PhC), 140.2 (C-8), 217.2 (*cis*-CO), 225.1 (*trans*-CO), 333.1 (Cr=C) ppm. IR ($CH_2Cl_2$): $\tilde{\nu}$ = 2058, 1986, 1944 $cm^{-1}$ (C=O). MS (70 eV, EI): *m/z* (%) = 566 (6) [$M^+$], 551 (3) [$M^+ - CH_3$], 523 (3) [$M^+ - C_3H_7$], 482 (7) [$M^+ - 3$ CO], 454 (32) [$M^+ - 4$ CO], 426 (58) [$M^+ - 5$ CO], 80 (100) [$CrCO^+$]. HR-MS: calcd. for $C_{21}H_{26}CrO_6$: 426.1134; found 426.1134.

**Pentacarbonyl{(2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranosyloxy)[(*E*)-styryl]carbene}chromium (7):** Yield: 2.76 g (4.87 mmol, 97%); $R_f$ = 0.76 ($CH_2Cl_2$). $^1$H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.38 (s, 3 H, $CH_3$), 1.42 (s, 3 H, $CH_3$), 1.50 (s, 3 H, $CH_3$), 1.60 (s, 3 H, $CH_3$), 3.87 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, 6-H), 4.04 (dd, $J_{H,H}$ = 13.2, 1.84 Hz, 1 H, 6a-H), 4.32 (br. d, $^3J_{H,H}$ = 7.82 Hz, 1 H, 5-H), 4.56 (d, $^3J_{H,H}$ = 2.68, 1 H, 3-H), 4.72 (dd, $J_{H,H}$ = 7.81, 2.69 Hz, 1 H, 4-H), 5.02 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, 1-H), 5.21 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, 1a-H), 7.06 (d, $^3J_{H,H}$ = 15.4 Hz, 1 H, 7-H), 7.42−7.39 (m, 3 H, PhH), 7.59−7.56 (m, 2 H, PhH), 7.94 (d, $^3J_{H,H}$ = 15.4 Hz, 1 H, 8-H) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$,

25 °C): δ = 26.5, 26.6, 27.3, 27.7 (4 $CH_3$), 62.4 (C-6), 70.8, 71.5, 71.5 (C-3, C-4, C-5), 80.5 (C-1), 102.3 (C-2), 110.1, 110.2 [2 $C(CH_3)_2$], 129.8 (*meta*-PhCH), 129.9 (*ortho*-PhCH), 131.5 (*para*-PhCH), 132.2 (C-7), 135.1 (*ipso*-PhC), 140.5 (C-8), 217.1 (*cis*-CO), 225.0 (*trans*-CO), 334.9 (Cr=C) ppm. IR ($CH_2Cl_2$): ṽ = 2059, 1984, 1948 $cm^{-1}$ (C=O). MS (70 eV, EI): *m*/*z* (%) = 566 (21) [$M^+$], 551 (17) [$M^+ - CH_3$], 516 (16) [$M^+ - C_4H_2$], 482 (13) [$M^+ - 3$ CO], 467 (14) [$M^+ - 3$ CO $- CH_3$], 454 (48) [$M^+ - 4$ CO], 426 (36) [$M^+ - 5$ CO], 411 (2) [$M^+ - 5$ CO $- CH_3$], 375 (4) [$M^+ - 2$ CO $- (CH_3)_2CO - C_6H_5$], 361 (2) [$M^+ - 2$ CO $- (CH_3)_2CO - C_7H_7$], 317 (8) [$M^+ - Cr(CO)_5 - H_2O - C_3H_3$], 252 (7) [$M^+ - Cr(CO)_5 - 3$ $CH_3 - C_6H_5$], 245 (100) [$Fru^+ - CH_3$]. HR-MS: calcd. for $C_{26}H_{26}O_{11}Cr$: 566.0880; found 566.0880.

**Pentacarbonyl{(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyloxy)-[(*E*)-styryl]carbene}chromium (8):** Yield: 2.71 g (4.79 mmol, 96%); $R_f$ = 0.69 ($CH_2Cl_2$). $^1H$ NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.36 (s, 3 H, $CH_3$), 1.42 (s, 3 H, $CH_3$), 1.43 (s, 3 H, $CH_3$), 1.52 (s, 3 H, $CH_3$), 4.16 (ptd, $J_{H,H}$ = 6.95, 3.78 Hz, 1 H, 5-H), 4.34 (d, $^3J_{H,H}$ = 3.90 Hz, 1 H, 2-H), 4.56 (d, $^3J_{H,H}$ = 7.45, 3.78, 1 H, 4-H), 4.65 (d, $^3J_{H,H}$ = 3.78 Hz, 1 H, 3-H), 5.08 (dd, $J_{H,H}$ = 10.9, 4.52 Hz, 1 H, 6-H), 5.14 (dd, $J_{H,H}$ = 10.9, 6.35 Hz, 1 H, 6a-H), 6.08 (d, $J_{H,H}$ = 3.66 Hz, 1 H, 1-H), 7.07 (d, $^3J_{H,H}$ = 15.3 Hz, 1 H, 7-H), 7.39−7.42 (m, 3 H, PhH), 7.56−7.60 (m, 2 H, PhH), 7.93 (d, $^3J_{H,H}$ = 15.3 Hz, 1 H, 8-H) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$, 25 °C): δ = 24.5, 24.6, 27.2, 27.9 (4 $CH_3$), 71.5 (C-5), 75.9 (C-4), 79.3 (C-6), 80.4 (C-2), 84.6 (C-3), 102.1 (C-1), 107.3, 113.1 [2 $C(CH_3)_2$], 129.8 (*meta*-PhCH), 130.2 (*ortho*-PhCH), 131.6 (*para*-PhCH), 132.3 (C-8), 135.2 (*ipso*-PhC), 139.8 (C-7), 217.2 (*cis*-CO), 225.0 (*trans*-CO), 333.4 (Cr=C) ppm. IR ($CH_2Cl_2$): ṽ = 2058, 1985, 1944 $cm^{-1}$ (C=O). MS (FAB): *m*/*z* (%) = 566 (1) [$M^+$], 500.1 (2) [$M^+ - CH_3 - C_4H_2$], 470 (1) [$M^+ - 3$ $CH_3 - C_4H_2$], 426 (46) [$M^+ - 5$ CO], 333 (23) [$M^+ - 5$ CO $- H - CH_3$], 307 (7) [$M^+$ − Glu], 275 (13) [$M^+ - 2$ CO $- (CH_3)_2CO - C_6H_5 - C_5H_8O_2$], 259 (8) [$Glu^+$], 243 (16) [$C_{12}H_{19}O_5^+$], 185 (100) [$C_9H_{13}O_4^+$].

**Pentacarbonyl{(2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranosyloxy)[(*E*)-styryl]carbene}chromium (9):** Yield: 2.47 g (4.37 mmol, 87%); $R_f$ = 0.60 ($CH_2Cl_2$). $^1H$ NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.39 (s, 3 H, $CH_3$), 1.42 (s, 3 H, $CH_3$), 1.45 (s, 3 H, $CH_3$), 1.57 (s, 3 H, $CH_3$), 4.04 (dd, $J_{H,H}$ = 9.03, 4.65 Hz, 1 H, 6-H), 4.13 (dd, $J_{H,H}$ = 9.03, 6.10 Hz, 1 H, 6′-H), 4.22 (dd, $^3J_{H,H}$ = 7.57, 3.18, 1 H, 4-H), 4.48 (m, 1 H, 5-H), 5.08 (dd, $^3J_{H,H}$ = 5.86, 3.18 Hz, 1 H, 3-H), 5.12 (d, $^3J_{H,H}$ = 5.86 Hz, 1 H, 2-H), 6.51 (s, 1 H, 1-H), 7.07 (d, $^3J_{H,H}$ = 15.3 Hz, 1 H, 7-H), 7.39−7.45 (m, 3 H, PhH), 7.59−7.63 (m, 2 H, PhH), 7.91 (d, $^3J_{H,H}$ = 15.3 Hz, 1 H, 8-H) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$, 25 °C): δ = 25.4, 25.9, 26.6, 27.6 (4 $CH_3$), 67.4 (C-6), 73.5 (C-5), 80.3 (C-3), 83.9 (C-4), 86.1 (C-2), 110.2 (C-1), 111.3, 114.4 [2 $C(CH_3)_2$], 129.9 (*meta*-PhCH), 130.2 (*ortho*-PhCH), 132.0 (*para*-PhCH), 135.0 (C-7), 136.3 (*ipso*-PhC), 139.2 (C-8), 217.0 (*cis*-CO), 225.8 (*trans*-CO), 335.2 (Cr=C) ppm. IR ($CH_2Cl_2$): ṽ = 2059, 1987, 1946 $cm^{-1}$ (C=O). MS (FAB): *m*/*z* (%) = 566 (1) [$M^+$], 500 (3) [$M^+ - CH_3 - C_4H_2$], 470 (8) [$M^+ - 3$ $CH_3 - C_4H_2$], 426 (39) [$M^+ - 5$ CO], 366 (13) [$M^+ - C_5H_7O_2 - C_5H_9O_2$], 317 (44) [$M^+ - Cr(CO)_5 - H_2O - C_3H_3$], 259 (30) [$Man^+$], 171 (100) [$C_8H_{11}O_4^+$].

**Pentacarbonyl{(1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranosyloxy)[(*E*)-styryl]carbene}chromium (10):** Yield: 2.75 g (4.86 mmol, 97%); $R_f$ = 0.80 ($CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.23 (s, 3 H, $CH_3$), 1.27 (s, 3 H, $CH_3$), 1.39 (s, 3 H, $CH_3$), 1.40 (s, 3 H, $CH_3$), 3.83 (d, $^2J_{H,H}$ = 9.00 Hz, 1 H, 1-H), 3.94 (d, $^2J_{H,H}$ = 9.00 Hz, 1 H, 1a-H), 3.95 (d, $^3J_{H,H}$ = 13.3 Hz, 1 H, 6-H), 4.14 (dd, $J_{H,H}$ = 13.3, 3.13 Hz, 1 H, 6a-H), 4.29 (dd, $^3J_{H,H}$ = 6.26, 2.35 Hz, 1 H, 4-H), 4.55 (t, $^3J_{H,H}$ = 6.26 Hz, 1 H, 5-H), 5.24 (br. s, 1 H, 3-H), 7.06 (br. d, $^3J_{H,H}$ = 15.3 Hz, 1 H, 7-H), 7.27 (m, 2 H, PhH), 7.40−7.42 (m, 3 H, PhH), 7.57 (br. d, $^3J_{H,H}$ = 15.3 Hz, 1 H, 8-H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 26.0, 26.8, 27.2, 28.3 (4 $CH_3$), 62.0 (C-6), 72.7 (C-1), 73.7 (C-5), 75.4 (C-4), 85.8 (br., C-3), 103.8 (C-2), 110.6, 113.0 [2 $C(CH_3)_2$], 129.6 (*meta*-PhCH), 129.8 (*ortho*-PhCH, *para*-PhCH), 131.7 (C-7), 135.1 (*ipso*-PhC), 138.8 (br., C-8), 217.0 (*cis*-CO), 225.1 (*trans*-CO), 338.4 (Cr=C) ppm. IR ($CH_2Cl_2$): ṽ = 2059, 1986, 1946 $cm^{-1}$ (C=O). MS (70 eV, EI): *m*/*z* (%) = 566 (1) [$M^+$], 510 (4) [$M^+ - 2$ CO], 454 (2) [$M^+ - 4$ CO], 426 (43) [$M^+ - 5$ CO], 375 (7) [$M^+ - 2$ CO $- (CH_3)_2CO$ − Ph], 355 (7) [$M^+ - 5$ CO $- C_4H_7O$], 245 (30) [$M^+ - 5$ CO $- 2(CH_3)_2CO - C_5H_5$], 131 (87) [$M^+ - Cr(CO)_5$ − Fru], 59 (100) [$C_2H_3O_2^+$]. HR-MS: calcd. for $C_{21}H_{26}O_6Cr$: 426.1134; found 426.1157.

**Preparation of Biphenyl Disaccharides 12−16:** A solution of 2 equiv. of 2,3,4,6-tetra-*O*-benzyl-1-deoxy-1-ethynyl-β-D-glucopyranose (**11**) in *tert*-butyl methyl ether (10 mL) was added to a solution of the *O*-glycosidic styrylcarbene complex **6**−**10** in *tert*-butyl methyl ether (5 mL). The resulting solution was degassed in three cycles and heated under reflux at 60 °C for 26 h. The reaction was monitored by IR spectroscopy and TLC. After cooling to room temperature, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography at −20 °C by using *tert*-butyl methyl ether/dichloromethane (1:50) as eluent to give an orange-yellow oil that (like the complex precursors **3**−**10**) could not be completely freed from traces of solvent, a situation that hampered obtaining correct elemental analyses.

**3-(2′,3′,4′,6′-Tetra-*O*-benzyl-1′-deoxy-β-D-glucopyranosyl)-5-(1′′,2′′:3′′,4′′-di-*O*-isopropylidene-α-D-galactopyranosyloxy)-biphenyl-2-ol (12):** Reaction of **6** (1.31 g, 2.31 mmol) yielded **12** (1.93 g, 2.03 mmol, 88%); $R_f$ = 0.69 ($CH_2Cl_2$). $^1H$ NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.37 (s, 6 H, 2 $CH_3$), 1.49 (s, 3 H, $CH_3$), 1.56 (s, 3 H, $CH_3$), 3.64 (d, $^3J_{H,H}$ = 10.2 Hz, 1 H, 2′-H), 3.74−3.83 (m, 5 H, 4′-H, 5′-H, 6′-H, 6a′-H, PhC$H_2$), 3.98 (br. d, $^3J_{H,H}$ = 10.2 Hz, 1 H, 1′-H), 4.14−4.10 (m, 1 H, 3′-H), 4.21 (m, 1 H, 5′′-H), 4.38 (m, 1 H, 2′′-H), 4.62−4.49 (m, 4 H, 4′′-H, 6′′-H, 6a′′-H, PhC$H_2$), 4.68 (d, $^3J_{H,H}$ = 7.83 Hz, 1 H, 3′′-H), 4.87 (d, $^2J_{H,H}$ = 10.6 Hz, 2 H, 2 PhC$H_2$), 4.92 (d, $^2J_{H,H}$ = 10.2 Hz, 1 H, PhC$H_2$), 4.95 (d, $^2J_{H,H}$ = 11.3 Hz, 2 H, 2 PhC$H_2$), 5.02 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, PhC$H_2$), 5.62 (d, $^3J_{H,H}$ = 2.35 Hz, 1 H, 1′′-H), 6.87 (s, 1 H, 4-H), 7.02 (s, 1 H, 6-H), 7.04 (br. s, *para*-Ph*H*), 7.38−7.20 (m, 20 H, Bn*H*), 7.51−7.43 (m, 2 H, *meta*-Ph*H*), 7.59 (d, $^3J_{H,H}$ = 7.04 Hz, 2 H, *ortho*-Ph*H*) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$, 25 °C): δ = 25.1, 25.5, 26.6, 26.7 (4 $CH_3$), 67.2 (C-6′′), 67.9 (C-5′′), 68.8 (C-6′), 71.2, 71.3, 71.7 (C-2′′, C-3′′, C-4′′), 74.0, 75.8, 76.1, 76.2 (4 $CH_2$Ph), 78.0 (C-1′), 79.4 (C-2′), 81.4 (C-4′), 82.3 (C-3′), 86.9 (C-5′), 97.0 (C-1′′), 109.3, 110.0 [2 $C(CH_3)_2$], 115.2, 117.8 (C-4, C-6), 125.4 (C-3), 127.7 (*para*-*C*HPh), 129.0−130.0 (*C*HBn), 129.7 (*meta*-*C*HPh), 130.1 (*ortho*-*C*HPh), 131.5 (C-1), 137.7, 138.6, 138.8, 139.0 (*ipso*-*C*Bn), 139.2 (*ipso*-*C*Ph), 146.9 (C-5), 152.6 (C-2) ppm. MS (FAB): *m*/*z* (%) = 950 (16) [$M^+$], 560 (2) [$M^+ - 3$ $C_7H_7 - C_5H_5 - C_4H_4$], 517 (2) [$M^+ - 2$ $OC_7H_7 - 2$ $C_6H_5 - C_5H_5$], 465 (3) [$M^+ - 3$ $OC_7H_7 - C_7H_7 - (CH_3)_2CO - CH_3$], 181 (100) [$C_9H_9O_4^+$].

**3-(2′,3′,4′,6′-Tetra-*O*-benzyl-1′-deoxy-β-D-glucopyranosyl)-5-(2′′,3′′:4′′,5′′-di-*O*-isopropylidene-β-D-fructopyranosyloxy)biphenyl-2-ol (13):** Reaction of **7** (1.45 g, 2.56 mmol) yielded **13** (2.07 g, 2.18 mmol, 85%); $R_f$ = 0.63 ($CH_2Cl_2$). $^1H$ NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.33 (s, 3 H, $CH_3$), 1.41 (s, 3 H, $CH_3$), 1.47 (s, 3 H, $CH_3$), 1.53 (s, 3 H, $CH_3$), 3.62 (d, $^2J_{H,H}$ = 10.7 Hz, 2 H, 2 C$H_2$Ph), 3.72 (d, $^2J_{H,H}$ = 10.8 Hz, 2 H, 2 C$H_2$Ph), 3.74−3.85 (m, 3 H, 3′-H, 4′-H, 5′-H), 3.91 (d, $^2J_{H,H}$ = 12.8 Hz, 2 H, 6′′-H, 6a′′-

H), 3.97 (d, $^2J_{H,H}$ = 10.0 Hz, 1 H, 1′′-H), 4.01 (d, $^2J_{H,H}$ = 10.0 Hz, 1 H, 1a′′-H), 4.12 (d, $^2J_{H,H}$ = 10.2 Hz, 1 H, C$H_2$Ph), 4.21 (d, $^3J_{H,H}$ = 7.55 Hz, 1 H, 2′-H), 4.25 (d, $^3J_{H,H}$ = 7.95 Hz, 1 H, 5′′-H), 4.39 (d, $^3J_{H,H}$ = 2.28 Hz, 1 H, 3′′-H), 4.43−4.67 (m, 4 H, 1′-H, 4-H, 6′-H, C$H_2$Ph), 4.83 (dd, $J_{H,H}$ = 10.8, 2.98 Hz, 1 H, 6a′-H), 4.91 (d, $^2J_{H,H}$ = 10.3 Hz, 1 H, C$H_2$Ph), 4.98 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C$H_2$Ph), 6.83 (d, $^4J_{H,H}$ = 2.68 Hz, 1 H, 4-H), 6.95 (d, $^4J_{H,H}$ = 2.58 Hz, 1 H, 6-H), 7.15 (d, $^3J_{H,H}$ = 5.47 Hz, 1 H, *para*-PhC*H*), 7.20−7.34 (m, 20 H, BnC*H*), 7.40−7.43 (m, 2 H, *meta*-PhC*H*), 7.56 (d, $^3J_{H,H}$ = 7.35 Hz, 2 H, *ortho*-PhC*H*) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 24.4, 26.0, 26.3, 27.1 (4$CH_3$), 61.5 (C-6′′), 64.1 (C-1′′), 69.8 (C-6′), 70.4, 70.7, 71.6 (C-3′′, C-4′′, C-5′′), 73.9, 75.7, 75.9, 76.0 (4 *C*$H_2$Ph), 77.9 (C-1′), 79.3 (C-2′), 81.2 (C-4′), 82.6 (C-3′), 86.7 (C-5′), 102.8 (C-2′′), 109.3, 109.5 [2 *C*$(CH_3)_2$], 115.2, 117.0 (C-4, C-6), 125.4 (C-3), 127.6 (*para*-*C*HPh), 129.0−130.0 (*C*HBn), 129.2 (*meta*-*C*HPh), 130.0 (*ortho*-*C*HPh), 131.4 (C-1), 137.5, 138.3, 138.5, 138.6 (*ipso*-*C*Bn), 139.1 (*ipso*-*C*Ph), 146.9 (C-5), 152.3 (C-2) ppm. MS (FAB): *m/z* (%) = 950 (21) [$M^+$], 861 (2) [$M^+ - 2\ CH_3 - CH_3CO_2H$], 560 (3) [$M^+ - 3\ C_7H_7 - C_5H_5 - C_4H_4$], 481 (2) [$M^+ - 3\ OC_7H_7 - C_7H_6 - (CH_3)_2CO$], 465 (3) [$M^+ - 3\ OC_7H_7 - C_7H_7 - (CH_3)_2CO - CH_3$], 415 (2) [$M^+ - 3\ OC_7H_7 - C_7H_7 - (CH_3)_2CO - C_5H_5$], 229 (8) [$C_{11}H_{17}O_5^+$], 181.1 (100) [$C_{10}H_{13}O_3^+$].

**3-(2′,3′,4′,6′-Tetra-*O*-benzyl-1′-deoxy-β-D-glucopyranosyl)-5-(1′′,2′′:5′′,6′′-di-*O*-isopropylidene-α-D-glucofuranosyloxy)biphenyl-2-ol (14):** Reaction of **8** (0.99 g, 1.04 mmol) yielded **14** (0.75 g, 0.79 mmol, 76%); $R_f$ = 0.79 ($CH_2Cl_2$/TBME, 4:1). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.29 (s, 3 H, $CH_3$), 1.35 (s, 3 H, $CH_3$), 1.37 (s, 3 H, $CH_3$), 1.46 (s, 3 H, $CH_3$), 3.56−3.80 (m, 2 H, 2′-H, 6′-H), 3.84 (dd, $^3J_{H,H}$ = 6.95, 2.75 Hz, 1 H, 5′-H), 4.02−3.91 (m, 3 H, 3′-H, 4′-H, PhC$H_2$), 4.07 (dd, $^3J_{H,H}$ = 10.4, 2.65 Hz, 1 H, 1′-H), 4.22 (dd, $J_{H,H}$ = 12.6, 3.92 Hz, 1 H, 6a′-H), 4.38 (dd, $^3J_{H,H}$ = 7.20, 3.79 Hz, 1 H, 5′′-H), 4.57−4.41 (m, 4 H, 1′′-H, 2′′-H, 3′′-H, 4′′-H), 4.69(d, $^2J_{H,H}$ = 10.9 Hz, 1 H, PhC$H_2$), 4.76(d, $^2J_{H,H}$ = 10.6 Hz, 1 H, PhC$H_2$), 4.79 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, PhC$H_2$), 4.86 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, PhC$H_2$), 4.90 (d, $^2J$H,H = 11.0 Hz, 1 H, PhC$H_2$), 4.92 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, 6′′-H), 4.97 (d, $^2J_{H,H}$ = 10.5 Hz, 2 H, 2 PhC$H_2$), 5.99 (dd, $J_{H,H}$ = 10.7, 3.79 Hz, 1 H, 6a′′-H), 6.79 (d, $^4J_{H,H}$ = 3.03 Hz, 1 H, 4-H), 6.93 (d, $^4J_{H,H}$ = 3.03 Hz, 1 H, 6-H), 6.97−6.94 (m, 1 H, *para*-Ph*H*), 7.08−7.35 (m, 20 H, Bn*H*), 7.35−7.39 (m, 2 H, *meta*-Ph*H*), 7.52 (d, $^3J_{H,H}$ = 8.46 Hz, 2 H, *ortho*-Ph*H*) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 24.6, 27.2, 27.6, 27.8 (4 $CH_3$), 68.8 (C-6′′), 69.5 (C-6′), 70.3, 71.7 (C-4′′, C-5′′), 74.2, 75.0, 76.0, 76.2 (4 *C*$H_2$Ph), 77.9 (C-1′), 78.3, 79.9, 81.7 (C-2′′, C-2′, C-3′′), 82.7 (C-4′), 84.7 (C-3′), 86.6 (C-5′), 101.7 [*C*$(CH_3)_2$], 107.0 (C-1′′), 112.8 [*C*$(CH_3)_2$], 115.2, 118.2 (C-4, C-6), 125.5 (C-3), 127.7 (*para*-*C*HPh), 128.0−130.0 (*C*HBn), 129.2 (*meta*-*C*HPh), 130.2 (*ortho*-*C*HPh), 131.6 (C-1), 137.8, 138.6, 138.7, 139.1 (*ipso*-*C*Bn), 139.3 (*ipso*-*C*Ph), 147.1 (C-5), 152.8 (C-2) ppm. MS (FAB): *m/z* (%) = 950 (4) [$M^+$], 924 (5) [$M^+ - C_6H_6$], 315 (10) [*GluBn*$^+ - C_7H_7 - C_5H_5 - C_4H_4$], 243 (6) [$C_{11}H_{15}O^+$], 215 (7) [GluBn$^+ - 4C_6H_5$], 181 (100) [$C_9H_9O_4^+$].

**3-(2′,3′,4′,6′-Tetra-*O*-benzyl-1′-deoxy-β-D-glucopyranosyl)-5-(2′′,3′′:5′′,6′′-di-*O*-isopropylidene-α-D-mannofuranosyloxy)-biphenyl2-ol (15):** Reaction of **9** (1.10 g, 1.94 mmol) yielded **15** (1.23 g, 1.30 mmol, 67%); $R_f$ = 0.73 ($CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.26 (s, 3 H, $CH_3$), 1.28 (s, 3 H, $CH_3$), 1.38 (s, 3 H, $CH_3$), 1.48 (s, 3 H, $CH_3$), 3.60−3.79 (m, 6 H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H, 6a′-H), 3.96 (d, $^3J_{H,H}$ = 9.53 Hz, 1

Table 1. Crystal data and structure refinement parameters of **2** and **7**

| | **2** | **7** |
|---|---|---|
| Empirical formula | $C_{19}H_{22}CrO_{11}$ | $C_{26}H_{26}CrO_{11}$ |
| Molecular mass | 478.37 | 566.47 |
| Temperature [K] | 123(2) | 123(2) |
| Wavelength [Å] | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | *P*2(1)2(1)2(1) (no.19) | *P*2(1) (no.4) |
| Unit cell dimensions | | |
| *a* [Å] | 9.5906(1) | 8.0613(3) |
| *b* [Å] | 10.8884(2) | 14.1451(5) |
| *c* [Å] | 20.8864(3) | 23.1087(9) |
| α [°] | 90 | 90 |
| β [°] | 90 | 91.279(2) |
| γ [°] | 90 | 90 |
| *V* [A$^3$] | 2181.09(6) | 2634.38(17) |
| *Z* | 4 | 4 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.457 | 1.428 |
| μ [mm$^{-1}$] | 0.581 | 0.494 |
| *F*(000) | 992 | 1176 |
| Crystal size [mm] | 0.30 × 0.30 × 0.10 | 0.30 × 0.20 × 0.10 |
| Diffractometer | Nonius−Kappa CCD | Nonius−Kappa CCD |
| Radiation | Mo-$K_\alpha$ | Mo-$K_\alpha$ |
| θ range for data collection [°] | 2.11 to 25.00 | 2.53 to 25.04 |
| Index ranges | $-11 \le h \le 11$ | $-9 \le h \le 9$ |
| | $-12 \le k \le 12$ | $-16 \le k \le 16$ |
| | $-23 \le l \le 24$ | $-27 \le l \le 27$ |
| Collected reflections | 18535 | 24527 |
| Unique reflections | 3822 | 8965 |
| Parameters/restraints | 281/0 | 685/1 |
| *R* (*F*) for $I > 2\sigma(I)$ | 0.0236 | 0.0681 |
| *wR*2 ($F^2$) for all data | 0.0586 | 0.1940 |
| Goodness-of-fit on $F^2$ | 1.038 | 1.035 |

H, 6′′-H), 4.01 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, PhC$H_2$), 4.04 (dd, $^3J_{H,H}$ = 8.98, 1.83 Hz, 1 H, 1′-H), 4.48 (dd, $^3J_{H,H}$ = 9.53, 3.78 Hz, 1 H, 6a′′-H), 4.51−4.56 (m, 2 H, 4′′-H, 5′′-H), 4.61 (d, $^2J_{H,H}$ = 12.2 Hz, 1 H, PhC$H_2$), 4.70−4.73 (m, 1 H, PhC$H_2$), 4.80 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, PhC$H_2$), 4.81 (d, $^2J_{H,H}$ = 10.4 Hz, 1 H, PhC$H_2$), 4.83 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, PhC$H_2$), 4.86 (d, $^3J_{H,H}$ = 5.89 Hz, 1 H, 3′′-H), 4.91 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, PhC$H_2$), 4.96−4.98 (m, 1 H, 2′′-H), 5.00 (d, $^2J_{H,H}$ = 10.4 Hz, 1 H, PhC$H_2$), 5.52 (d, $^3J_{H,H}$ = 5.33 Hz, 1 H, 1′′-H), 6.98 (d, $^4J_{H,H}$ = 2.80 Hz, 1 H, 4-H), 7.12 (m, 2 H, 6-H, *para*-Ph*H*), 7.13−7.38 (m, 20 H, Bn*H*), 7.39−7.44 (m, 2 H, *meta*-Ph*H*), 7.52−7.56 (m, 2 H, *ortho*-Ph*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 25.4, 26.0, 26.7, 27.6 (4 $CH_3$), 67.7 (C-6′′), 69.6 (C-6′), 70.4 (C-5′′), 74.3, 75.8, 76.2, 76.4 (4 *C*$H_2$Ph), 78.4 (C-1′), 79.9 (C-2′), 80.4 (C-4′′), 81.0, 81.8, 82.8 (C-3′′, C-3′, C-4′), 86.3 (C-2′′), 86.7 (C-5′), 106.5 (C-1′′), 110.0, 113.7 [2 *C*$(CH_3)_2$], 116.8, 117.3 (C-4, C-6), 125.6 (C-3), 127.7 (*para*-*C*HPh), 127.8−130.0 (*C*HBn, *meta*-*C*HPh), 130.4 (*ortho*-*C*HPh), 131.7 (C-1), 137.8, 138.6, 138.8, 139.2 (*ipso*-*C*Bn), 139.3 (*ipso*-*C*Ph), 148.1 (C-5), 150.4 (C-2) ppm. MS (FAB): *m*/*z* (%) = 950 (9) [$M^+$], 924 (6) [$M^+ - C_6H_6$], 648 (2) [$M^+ - OC_7H_7 - 3\ C_5H_5$], 479 (1) [$M^+$ − Man − $OC_7H_7$ − $OC_8H_9$], 315 (8) [*GluBn*$^+$ − $C_7H_7$ − $C_5H_5$ − $C_4H_4$], 181.1 (100) [$C_9H_9O_4^+$].

**3-(2′,3′,4′,6′-Tetra-*O*-benzyl-1′-deoxy-β-D-glucopyranosyl)-5-(1′′,2′′:4′′,5′′-di-*O*-isopropylidene-β-D-fructopyranosyloxy)biphenyl-2-ol (16):** Reaction of **10** (1.20 g, 2.12 mmol) yielded **16** (1.61 g, 1.69 mmol, 80%); $R_f$ = 0.83 ($CH_2Cl_2$/TBME, 4:1). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.30 (s, 3 H, $CH_3$), 1.44 (s, 3 H, $CH_3$), 1.48 (s, 3 H, $CH_3$), 1.52 (s, 3 H, $CH_3$), 3.69−3.64 (m, 1 H, 2′-H), 3.75−3.73 (m, 2 H, 6′-H, 6a′-H), 3.78 (d, $^3J_{H,H}$ = 9.47 Hz, 1 H, 1′-H), 3.82 (d, $^3J_{H,H}$ = 8.59 Hz, 1 H, 1′′-H), 4.02−3.97 (m, 3 H, 4′-H, 6′′-H, PhC$H_2$), 4.10 (d, $^3J_{H,H}$ = 7.33 Hz, 1 H, 5′-H), 4.15 (dd, $J_{H,H}$ = 13.3, 2.53 Hz, 1 H, 6a′′-H), 4.23 (dd, $^3J_{H,H}$ = 5.56, 2.40 Hz, 1 H, 4′′-H), 4.57−4.39 (m, 3 H, 3′-H, 5′′-H, PhC$H_2$), 4.75 (d, $^3J_{H,H}$ = 2.65 Hz, 1 H, 3′′-H), 4.78 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, PhC$H_2$), 4.80 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, PhC$H_2$), 4.85 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, PhC$H_2$), 4.86 (d, $^3J_{H,H}$ = 10.9 Hz, 1 H, PhC$H_2$), 4.92 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C$H_2$Ph), 4.96 (d, $^2J_{H,H}$ = 10.4 Hz, 1 H, C$H_2$Ph), 7.00−6.95 (m, 2 H, 4-H, *para*-Ph*H*), 7.10−7.31 (m, 21 H, 6-H, Bn*H*), 7.34−7.38 (m, 2 H, *meta*-Ph*H*), 7.51 (d, $^3J_{H,H}$ = 7.20 Hz, 2 H, *ortho*-Ph*H*) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 26.7, 26.8, 27.4, 28.8 (4 $CH_3$), 60.9 (C-6′′), 68.8 (C-6′), 70.2 (C-5′′), 72.3 (C-1′′), 73.9 (*C*$H_2$Ph), 74.5 (C-4′′), 75.7, 76.1, 76.3 (3 *C*$H_2$Ph), 77.3 (C-1′), 79.4 (C-2′), 81.2, 82.1, 82.6 (C-3′′, C-3′, C4′), 86.9 (C-5′), 105.0 (C-2′′), 109.7, 112.9 [*C*$(CH_3)_2$], 117.9, 119.8 (C-4, C-6), 125.6 (C-3), 127.7 (*para*-*C*HPh), 128.0−130.0 (*C*HBn), 128.6 (*meta*-*C*HPh), 130.1 (*ortho*-*C*HPh), 131.5 (C-1), 137.8, 138.4, 138.5, 138.5, 139.2 (*ipso*-*C*Bn, *ipso*-*C*Ph), 147.7 (C-5), 153.4 (C-2) ppm. MS (FAB): *m*/*z* (%) = 950 (14) [$M^+$], 318 (6) [$GluBn^+ - 2\ C_6H_5 - C_4H_3$], 243.1 (20) [$C_{11}H_{15}O_6^+$], 181.1 (100) [$C_9H_9O_4^+$].

**X-ray Crystallographic Study:** Yellow crystals of **2** and dark-red crystals of **7** were grown from diethyl ether at −25 °C. Crystallographic data were collected with a Nonius−Kappa CCD diffractometer at 123 K. The molecular structures have been solved by direct methods (SHELXS-97).[41] The non-hydrogen atoms were refined anisotropically on $F^2$ (SHELXL-97);[42] hydrogen atoms were refined by using a riding model. Details are presented in Table 1.

CCDC-202770 (**2**) and CCDC-202771 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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