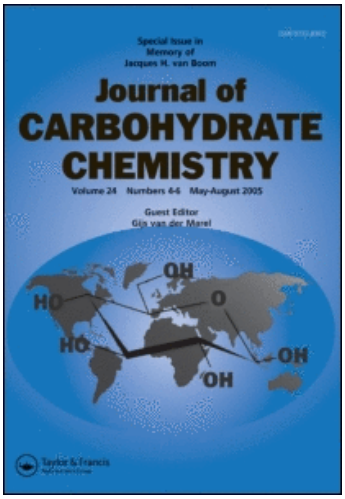

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APPLICATION OF THE KECK RADICAL COUPLING REACTION TO THE PREPARATION OF ALLYLATED C5 FURANOSIDES AND C6 PYRANOSIDES

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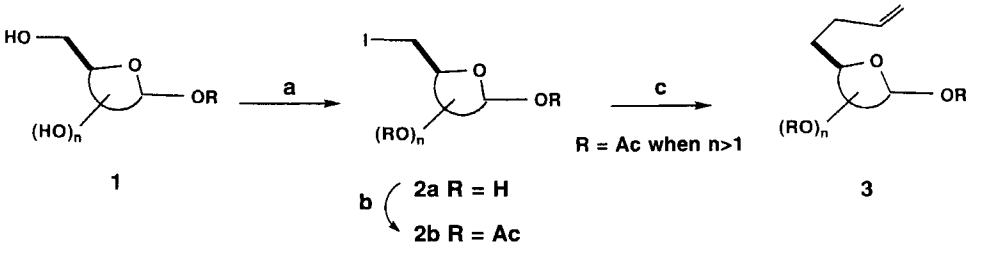
ABSTRACT

Allylated C5 furanosides and C6 pyranosides were prepared from known monosaccharide diol or polyol derivatives via a reaction sequence involving the initial selective formation of the primary iodide followed by application of the Keck allyl radical coupling reaction. Although the yields of the products in the coupling reaction were somewhat modest (usually 55-65%), the protocol was applicable to a variety of substrates, including sterically crowded cases, is experimentally simple and suitable for large scale preparations.

INTRODUCTION

In connection with the exploration of a novel methodology for the synthesis of substituted tetrahydrofuran derivatives,[1] we required a general method for the preparation of large quantities of allylated C6 pyranosides and C5 furanosides from simple monosaccharide precursors. A nucleophilic substitution based approach was deemed unacceptable in view of the side reactions that compete with the S_N2 pathway. E2 type eliminations usually predominate for more hindered systems, and β-elimination can also

be a prevalent side reaction for the reactions of primary halides with Grignard or cuprate reagents. Furthermore, the starting materials for such a plan require lengthy procedures, involving selective activation of the primary alcohol and protection of the secondary alcohols with base stable groups. Since radical coupling reactions are less sensitive to steric and electronic effects, and may be carried out in the presence of free hydroxyl groups, a radical based strategy appeared to be a reasonable alternative. Such methodologies for C-C bond formation have been successfully utilized in the carbohydrate field, notably in the work of the Giese[2] and Keck[3] laboratories.



(a) $PhCH_3$ - CH_3CN, Ph_3P, I_2, Imidazole; (b) Ac_2O, DMAP, pyridine, EtOAc; (c) allyltributyltin, AIBN, PhH, 80 °C;

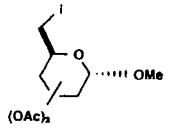
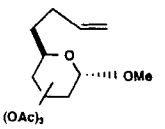
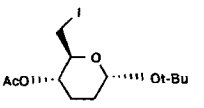
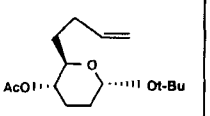
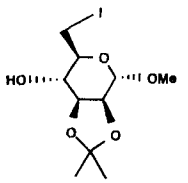
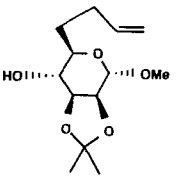
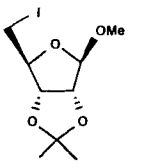
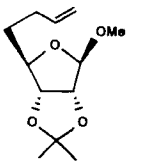
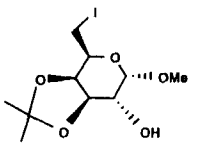
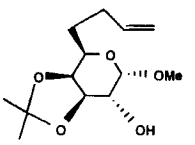
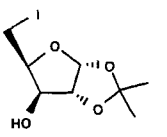
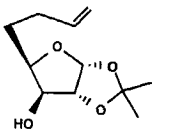
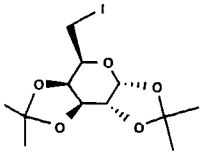
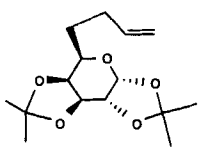
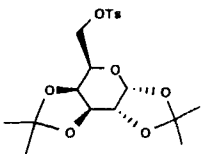
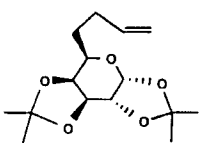
Scheme 1 : Preparation of Allylated Monosaccharide from Primary Alcohol Derivative

Accordingly, a monosaccharide alkene **3** may be prepared by the reaction of allyl tributyltin and a primary iodide precursor **2**, which could be obtained via the selective iodination of a starting polyol **1**. Indeed, several of the iodides suitable for our study were known compounds, previously obtained in this way.

RESULTS AND DISCUSSION

The results obtained for the preparation of several allylated monosaccharides are shown in Table 1. The required iodide precursors were obtained via the Garegg selective iodination procedure on known dihydroxy or polyol monosaccharide derivatives.[4] While the monohydroxy-iodide precursors obtained from the iodination of monosaccharide diols were usually used directly in the radical coupling step, the polyol iodide compounds were first derivatized as their peracetates, due to solubility considerations in their isolation and

Table 1: Preparation of Allylated Monosaccharides

Precursor	Allyl Product. (% Yield)	Precursor	Allyl Product. (% Yield)
			
4 Gluco[4a] **5** Manno[4a] **6** Galacto[4b]	**14** (64) **15** (58) **16** (60)	**10**	**20** (51)
			
7[5]	**17** (53)	**11**[4a]	**21** (64)
			
8[6]	**18** (57)	**12**[7]	**22** (55)
			
9[4a]	**19** (65)	**13**[8]	**19** (12)

under the conditions of the radical reaction. The radical coupling reactions were carried out under thermally promoted conditions similar to those employed by the Keck group.[3] Although the yields obtained were somewhat modest, the protocol is applicable to a wide variety of structural types, is experimentally simple, and suitable for large scale preparations. The major side product in the radical reaction was the reduced product arising from hydrogen abstraction. It should be mentioned that generally higher yields were reported in the original literature; this might be related to the smaller scale on which these reactions were performed.[3]

An important limitation of the radical coupling reaction concerns the use of substrates containing benzyl protecting groups. Thus the reactions of the perbenzylated derivatives corresponding to **4-6**, led to significant amounts of recovered starting compounds along with several other products. A similar observation was made by the Keck group, and appears to be linked to the ability of benzyl groups to act as hydrogen donors, leading to radical quenching.

In view of the successes achieved in the reaction of alkyl cuprates with primary tosylates of less hindered monosaccharides,[9] the reaction of 6-deoxy-1,2-di-*O*-isopropylidene-6-tolyl-α-D-galactopyranose **13** with the allylmagnesium bromide-copper(I) iodide reagent was investigated. This reaction yielded the desired alkene **19**, in very low yield (ca. 12%), with the major products being 1,2-di-*O*-isopropylidene-α-D-galactopyranose and 6-deoxy-6-bromo-1,2-di-*O*-isopropylidene-α-D-galactopyranose. This result was not unexpected since **13** is noted for its slow reactivity in nucleophilic substitution reactions.[10]

In conclusion it has been shown that the combination of the Garegg iodination and Keck allylation procedures provides a practical route for the preparation of large scale quantities of allylated C5 furanosides or C6 pyranosides, from a variety of structurally diverse monosaccharides. In addition to their utility as synthons in natural product synthesis, these derivatives might be useful in the preparation of biopolymers containing non-glycosidic attached oligosaccharides.[11]

EXPERIMENTAL

General Procedures. TLC was performed on aluminum sheets precoated with silica gel 60 (HF-254, E. Merck) to a thickness of 0.25 mm. Flash column chromatography was performed using Kieselgel 60 (230-400 mesh, E. Merck) and usually employed a stepwise solvent polarity gradient, correlated with TLC mobility. Melting points are reported uncorrected. Specific rotations were determined with a Rudolph Research

AUTOPOL III automatic polarimeter, and IR spectra were recorded with a Perkin Elmer 1310 Infrared spectrophotometer. ^{1}H NMR spectra were recorded with a GE QE 300 instrument, with $CHCl_3$ as internal standard.

Preparation of Iodide Precursors. Iodides **4-6**, **7**, **9** and **11** were prepared according to the identical procedure previously reported for these compounds.[4,5] This method was modified for the preparation of **8**, **10** and **12**.

Methyl 6-deoxy-6-iodo-3,4-*O*-isopropylidene-α-D-galactopyranoside (**8**). A solution of methyl 3,4-*O*-isopropylidene-α-D-galactopyranoside[12] (5.0 g, 22.2 mmol), triphenylphosphine (5.90 g, 22.5 mmol), imidazole (3.06 g, 45.0 mmol) and iodine (5.7 g, 22.5 mmol) in anhydrous toluene: acetonitrile (2:1, 100 mL) was heated at reflux for 1 h. The mixture was then cooled, diluted with ether (500 mL), filtered through a bed of celite, and the filtrate concentrated. Purification of the oily residue by column chromatography afforded **8** (5.5 g, 73%) as a white solid: R_f 0.40 (50% ethyl acetate-petroleum ether); needles (ethyl acetate-petroleum ether), mp 84-86 °C; $[\alpha]_D^{26}$ 118° (*c* 1.0, $CHCl_3$). ^{1}H NMR was identical to the previously reported data.[6]

Anal. Calcd for $C_{10}H_{17}IO_5$: C, 34.90; H, 4.98; I, 36.88. Found: C, 35.00; H, 5.02; I, 36.88.

tert-Butyl 4-*O*-acetyl-2,3,6-trideoxy-6-iodo-α-D-glucopyranoside (**10**). A solution of *tert*-butyl 2,3-dideoxy-α-D-glucopyranoside[13] (9.46 g, 46.4 mmol), triphenylphosphine (13.4 g, 51.1 mmol), imidazole (3.74 g, 55.0 mmol) and iodine (12.9 g, 50.8 mmol) in anhydrous benzene (250 mL), was subjected to the procedure described for the preparation of **8**. Purification of the crude reaction mixture by column chromatography afforded **10** (8.44 g, 58%) as an oil: R_f 0.65 (50% ethyl acetate-petroleum ether); $[\alpha]_D^{26}$ 71° (*c* 1.0, $CHCl_3$); IR (neat) 3360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9H), 1.60-2.00 (m, 5H), 3.44 (m, 4H), 5.18 (bs, 1H).

The material (8.4 g, 27 mmol) obtained in the previous step was dissolved in ethyl acetate (100 mL) and treated with 4-dimethylaminopyridine (0.5 g, 4.1 mmol) and acetic anhydride (5.0 mL, 53 mmol) at room temperature for 1 h. Methanol (1 mL) was then added and the solvent evaporated. Column chromatography of the residue afforded iodide **10** (8.7 g, 55%) as a syrup: R_f 0.40 (30% ethyl acetate-petroleum ether); $[\alpha]_D^{26}$ 80° (*c* 1.6, $CHCl_3$); IR (neat) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9H), 1.60-2.00 (m, 4H), 2.15 (s, 3H), 3.20 (dd, J = 7.1, 10.5 Hz, 1H), 3.35 (dd, J = 2.6, 10.5 Hz, 1H), 3.85 (m, 1H), 4.60 (m, 1H), 5.18 (bs, 1H).

Anal. Calcd for $C_{12}H_{21}IO_4$: C, 40.45; H, 5.95. Found: C, 40.45; H, 5.65.

5-Deoxy-5-iodo-1,2-*O*-isopropylidene-α-D-xylofuranose (**12**). A solution of 1,2-*O*-isopropylidene-α-D-xylofuranose[14] (5.0 g, 26.3 mmol), triphenylphosphine (6.9 g, 26.3 mmol), imidazole (3.6g, 52.9 mmol) and iodine (6.7 g, 26.4 mmol) in anhydrous toluene:

acetonitrile (2:1, 280 mL) was subjected to the procedure described for the preparation of **8**. Purification of the crude reaction mixture by column chromatography gave **12** (7.4 g, 94%) as a white solid: Rf 0.50 (50% ethyl acetate-petroleum ether); needles (ethyl acetate-petroleum ether), mp 107-108 °C; $[\alpha]^{26}_D$ -42° (*c* 1.1, $CHCl_3$); IR (Nujol) 3400 cm^{-1}. Lit:[11] mp 108 - 109 °C. $[\alpha]_D^{26}$ -40° (*c* 2, $CHCl_3$).

Anal. Calcd for $C_8H_{13}IO_4$: C, 32.02; H, 4.37; I, 42.29. Found: C, 32.30; H, 4.24; I, 42.01.

General allylation procedure. A solution of the monosaccharide iodide, allyl tributyltin[3] (2.0 equivalents) and 2,2'-azobis(2-methylpropionitrile) (AIBN, 15 mol %) in dry benzene (2 mL/mmol of iodide) was degassed then heated at reflux for 18 h, unless otherwise stated. (If the reaction was incomplete as evidenced by TLC, an additional amount of AIBN was added and heating continued for 5 h.) The solvent was removed, and the residue dissolved in ether and stirred with a saturated, aqueous solution of potassium fluoride for 0.5 h. The aqueous layer was extracted with ether and the combined organic fraction was dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by flash column chromatography.

Methyl 2,3,4-tri-*O*-acetyl-6,7,8,9-tetradeoxy-α-D-*gluco*-non-8-enopyranoside (**14**). Iodide **4**[4a] (2.94 g, 6.84 mmol) was treated according to the general allylation procedure. After column chromatography, alkene **14** (1.52 g, 64%) was obtained as an oil: Rf 0.35 (30% ethyl acetate-petroleum ether); $[\alpha]_D^{26}$ 126° (*c* 1.3, $CHCl_3$); IR (neat) 1735, 1634 cm^{-1}; ^1H NMR ($CDCl_3$) 1.58-1.65 (m, 2H), 1.94, 2.00, 2.10 (all s, 3H each), 2.10 - 2.22 (m, 1H), 2.25 (m, 1H) 3.42 (s, 3H), 3.80 (dt, J = 4.6, 9.4 Hz, 1H), 4.84 - 4.98 (m, 3H), 5.00-5.13 (m, 2H), 5.46 (t, J = 9.6 Hz, 1H), 5.84 (m, 1H).

Anal. Calcd for $C_{16}H_{24}O_8$: C, 55.81; H, 7.03. Found: C, 55.92; H, 7.00.

Methyl 2,3,4-tri-*O*-acetyl-6,7,8,9-tetradeoxy-α-D-*manno*-non-8-enopyranoside (**15**). Iodide **5**[4a] (4.17 g, 9.7 mmol) was treated according to the general allylation procedure. After column chromatography, alkene **15** (1.92 g, 58%) was obtained as an oil: Rf 0.35 (30% ethyl acetate-petroleum ether); $[\alpha]_D^{26}$ 50.4° (*c* 1.0, $CHCl_3$); IR (neat) 1735, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) 1.52-1.67 (m, 2H), 1.95, 2.00, 2.05 (all s, 3H each), 2.05 - 2.15 (m, 1H), 2.22 -2.35 (m, 1H), 3.38 (s, 3H), 3.75 (m, 1H), 4.63 (s, 1H), 4.95 - 5.15 (m, 3H), 5.20-5.34 (m, 2H), 5.80 (m, 1H).

Anal. Calcd for $C_{16}H_{24}O_8$: C, 55.81; H, 7.03. Found: C, 55.77; H, 6.98.

Methyl 2,3,4-tri-*O*-acetyl-6,7,8,9-tetradeoxy-α-D-*galacto*-non-8-enopyranoside (**16**). Iodide **6**[4b] (3.93 g, 9.14 mmol) was treated according to the general allylation procedure. After column chromatography, alkene **16** (1.88 g, 60%) was obtained as an oil: Rf 0.35 (30% ethyl acetate-petroleum ether); $[\alpha]_D^{26}$ 120° (*c* 1,1, $CHCl_3$); IR (neat) 1735, 1632 cm^{-1}; ^1H NMR ($CDCl_3$) 1.53 - 1.62 (m, 2H), 1.97, 2.06, 2.15 (all s, 3H each),

2.10 - 2.22 (m, 2H), 3.38 (s, 3H), 3.95 (dd, J = 5.2, 10.7 Hz, 1H), 4.92 - 5.05 (m, 3H), 5.14 (dd, J = 4.6, 12.6 Hz, 1H), 5.32 (m, 2H), 5.69 (m, 1H).

Anal. Calcd for $C_{16}H_{24}O_8$: C, 55.81; H, 7.03. Found: C, 55.65; H, 6.74.

Methyl 6,7,8,9-tetradeoxy-2,3-*O*-isopropylidene-α-D-*manno*-non-8-enopyranoside (17). Iodide **7**[5] (4.8 g, 13.9 mmol) was treated according to the general procedure. After column chromatography, alkene **17** (1.9 g, 53%) was obtained as a clear syrup: R_f 0.25 (15% ethyl acetate-toluene); $[\alpha]_D^{26}$ 35° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) 1.28 (s, 3H), 1.45 (s, 3H), 1.48 - 1.56 (m, 1H), 1.90 (m, 1H), 2.11 (m, 1H), 2.29 (m, 1H), 2.65 (bd, J = 4.0 Hz, 1H), 3.32 (s, 3H), 3.34-3.48 (m, 2H), 3.98 - 4.06 (m, 2H), 4.80 (s, 1 H), 4.91 (dd, J = 1.6, 10.2 Hz, 1H), 4.98 (dd, J = 1.6, 16.4 Hz, 1H), 5.75 - 5.82 (m, 1H).

Anal. Calcd for $C_{13}H_{22}O_5$: C, 60.45; H, 8.59. Found: C, 60.56; H, 8.53.

Methyl 6,7,8,9-tetradeoxy-3,4-*O*-isopropylidene-α-D-*galacto*-non-8-enopyranoside (18). Iodide **8**[6] (3.78 g, 11.0 mmol) was treated according to the general procedure. After column chromatography, alkene **18** (1.57 g, 57%) was obtained as an oil: R_f 0.20 (15% ethyl acetate-toluene,); $[\alpha]_D^{26}$ 123° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) 1.36, 1.51(both s, 3H each), 1.72, 1.88, (both m, 1H each), 2.20 (m, 2H), 2.28 (bd, J = 6.3 Hz, 1H) 3.44 (s, 3H), 3.79 (m, 1H), 3.90 (m, 1H) 4.06 (dd, J = 2.1, 6.0 Hz, 1H), 4.19 (t. J = 6.3 Hz, 1H) 4.71(d, J = 3.9 Hz, 1H), 4.98 (dd, J = 0.9, 10.5 Hz, 1H), 5.08 (dd, J = 0.9, 17.1 Hz, 1H), 5.86 (m, 1H).

HRMS Calcd for $C_{13}H_{22}O_5$ (M^+): 258.1467. Found: 258.1458

1,2,3,4-Di-*O*-isopropylidene-α-D-*galacto*-non-8-enopyranose (19). Iodide **9**[4a] (1.8 g, 3.8 mmol) was treated according to the general allylation procedure. After purification by column chromatography, alkene **19** (0.70 g, 65%) was obtained as an oil: R_f 0.30 (5% ethyl acetate-toluene); $[\alpha]_D^{26}$ 54.7° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$): 1.29, 1.31, 1.43, 1.47 (all s, 3H each), 1.58, 1.76 (both m, 1H each), 2.03-2.30 (m, 2H), 3.70 (m, 1H), 4.08 (dd, J = 2.0, 7.9 Hz, 1H), 4.26 (m, 1H), 4.55 (dd, J = 2.0, 87.8, 1H), 4.95 (d, J = 9.8 Hz, 1H), 5.04 (d, J = 17.1 Hz, 1H), 5.50 (d, J = 7.0 Hz, 1H), 5.80 (m, 1H).

Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.38; H, 8.45. Found: C, 63.42; H, 8.52.

tert-Butyl 4-*O*-acetyl-2,3,6-trideoxy-α-D-*gluco*-non-8-enopyranoside (20). Iodide **10** (2.30 g, 6.46 mmol) was treated according to the general allylation procedure, for 5 h. After purification by column chromatography, alkene **20** (0.89 g, 51%) was obtained as an oil: R_f 0.35 (5% ethyl acetate-toluene); $[\alpha]_D^{26}$ 122° (*c* 1.2, $CHCl_3$); IR (neat) 1730, 1640 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.30 (s, 9H), 1.55-2.16 (m, 7H), 2.15 (s, 3H), 2.28 (m, 1H), 3.90 (dt, J = 3.8, 11.2 Hz, 1H), 4.55 (m, 1H), 5.08 (m, 3H), 5.85 (m, 1H).

Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.62; H, 9.71. Found: C, 66.69; H, 9.78.

Methyl 5,6,7,8,-tetradeoxy-2,3-*O*-isopropylidene-β-D-*ribo*-oct-7-enofuranoside (21). Iodide **11**[4a] (7.44 g, 23.7 mmol) was treated according to the general allylation

procedure. After purification by column chromatography, alkene **21** (3.43 g, 64%) was obtained as an oil: R_f 0.35 (10% ethyl acetate-petroleum ether); $[\alpha]_D^{26}$ -43.7° (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$) 1.38, 1.54 (both s, 3H each), 1.58-1.80 (m, 2H), 2.17-2.32 (m, 2H), 3.40 (s, 3H), 4.20 (t, J = 6.7 Hz, 1H), 4.57 (d, J = 6.7 Hz, 1H), 4.64 (d, J = 6.7 Hz, 1H), 4.98 (s, 1H), 5.03 (dd, J = 1.5, 9.8 Hz, 1H), 5.12 (dd, J = 1.5, 17.1 Hz, 1H), 5.87 (m, 1H).

HRMS Calcd for $C_{11}H_{17}O_4$ (M^+ - CH_3): 213.1127. Found: 213.1124.

5,6,7,8,-Tetradeoxy-1,2-*O*-isopropylidene-α-D-*xylo*-oct-7-enofuranose (22). Iodide **12**[7] (7.40 g, 24.7 mmol) was treated according to the general allylation procedure. After purification by column chromatography, alkene **22** (2.9 g, 55%) was obtained as a clear oil: R_f 0.20 (15% ethyl acetate:toluene); $[\alpha]_D^{26}$ -23.7° (*c* 1.1, $CHCl_3$); IR (Nujol) 3400, 1640 cm^{-1}; ^1H NMR ($CDCl_3$): 1.31, 1.49 (both s, 3H each), 1.59,(br s, 1H), 1.70 (m, 1 H), 1.85 (m, 1 H), 2.20 (m, 2 H), 4.05 (m, 1H), 4.13 (dt, J = 2.4, 8.8 Hz, 1H), 4.51 (d, J = 3.0 Hz, 1H) 5.00 (d, J = 10.2 Hz, 1H), 5.10 (d, J = 17.6 Hz, 1H), 5.86 (m, 1H), 5.88 (d, J = 3.6 Hz, 1H).

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.76; H, 8.59.

Reaction of 13 with Allylmagnesium Bromide/Copper(I) Iodide. Allylmagnesium bromide (15.0 mL of a 1M solution in ether, 15.0 mmol) was added to a mixture of **13**[8] (1.29 g, 3.12 mmol) and copper iodide (1.80 g, 9.47 mmol) in diethyl ether (15 mL) at room temperature under an atmosphere of argon. The reaction mixture was stirred at this temperature for 48 h, then carefully poured into a saturated aqueous ammonium chloride (50 mL). The mixture was extracted with diethyl ether (3 x 25 mL), the organic phase dried over sodium sulfate, filtered, and concentrated. Column chromatography (ethyl acetate-petroleum ether) of the residue afforded 1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranose[8] (0.260 g, 32%), together with an inseparable mixture of desired alkene **19** and iodide **9** (0.250 g, ca. 24%, ca.1:1 as determined from ^1H NMR).

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