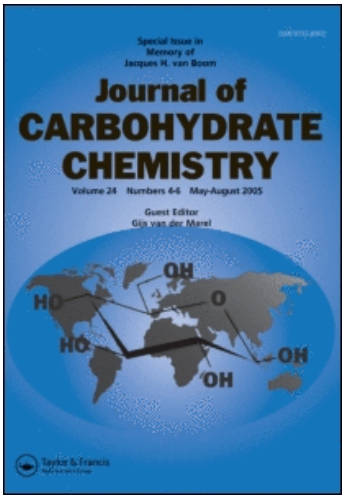

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RHODIUM(I)-CATALYZED REGIO- AND STEREOSELECTIVE CHLOROESTERIFICATION OF FURANOSE-DERIVED TERMINAL ALKYNES WITH ETHYL CHLOROFORMATE

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RHODIUM(I)-CATALYZED REGIO- AND STEREOSELECTIVE CHLOROESTERIFICATION OF FURANOSE-DERIVED TERMINAL ALKYNES WITH ETHYL CHLOROFORMATE

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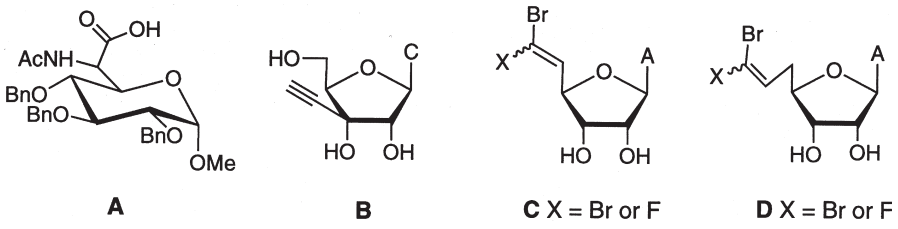
ABSTRACT

Treatment of ribose-, xylose- and homologated ribose-derived terminal alkynes with ethyl chloroformate in the presence of a catalytic amount of $RhCl(CO)(PPh_3)_2$ in toluene effected *syn* chloroalkoxycarbonylation to give doubly functionalized vinylic derivatives.

INTRODUCTION

Sugar acetylenes are valuable chiral precursors with wide applications in organic synthesis.[1-4] The stereocontrolled synthesis of the alkynyl C-glycosides and their reactivities[1a] and the free radical cycloisomerization of optically active alkyne-precursors derived from carbohydrates[1b] have been reviewed. Chromium-mediated benzannulation,[3a] Pauson-Khand [2 + 2 + 1] cyclization,[3b] and oxidative dimerization[3c] of sugar acetylenes were recently reported. Glycosylacetylene-phenylalanine building blocks were used in the synthesis of neoglycopeptide templates,[4a] and diastereoselective ethynylation of methyl 2,3,4-tri-*O*-benzyl-α-D-*gluco*-hexodialdo-1,5-pyranoside was utilized in the construction of the C-glycosyl amino acid backbone **A** of miharamycin antibiotic.[4b] Moreover, various nucleosides with acetylenic functions in the sugar moieties have been prepared,[5-7] and several have potent antitumor (e.g., **B**[5]) and biosynthetic inhibitory activities (Figure 1).[5-7]

Acetylenic sugars have been prepared by: (a) Grignard addition of acetylide anions to the corresponding hemiacetal,[1b,8] lactone[4a] or aldehyde/keto deriva-



A **B** **C** X = Br or F **D** X = Br or F

Figure 1.

tives;[4b,5] (b) reaction of the glycals with silylacetylenes in acidic media;[1a,3b] (c) condensation of sugar aldehydes with the Wittig-dibromomethylene reagents[2a,6b,7] (or diazomethylphosphonate[2a,7a]) and dehydrobromination; and (d) oxidative destannylation of vinyl stannane derivatives.[6a]

The enzyme *S*-adenosyl-L-homocysteine (AdoHcy) hydrolase effects hydrolytic cleavage of AdoHcy to adenosine (Ado) and L-homocysteine (Hcy).[9] Owing to its central role in the regulation of biological methylation reactions, the inhibition of AdoHcy hydrolase represents an attractive target for developing the mechanism-based chemotherapy of cancer and viral diseases.[10] Moreover, elevated plasma levels of Hcy in humans have been shown to be a risk factor in coronary artery diseases.[11]

The (dihalohomovinyl)adenosine derivatives, **C**, inhibit AdoHcy hydrolase and are enzymatically hydrolyzed to give the homoAdo 6′-carboxyl halides at the active site.[12] Nucleophilic attack by proximal amino acid functionalities was shown to produce covalent inhibition.[12b] The X-ray crystallographic determination of AdoHcy hydrolase revealed a unique role for a catalytic water molecule at the active site.[13] We recently prepared "doubly homologated" vinyl halides, **D**, and acetylenic adenine nucleosides with greater conformational flexibility at C5′.[14] The 7′-dihalovinyl nucleosides **D** were prepared from sugar precursors because homoAdo 6′-aldehyde, which was the obvious intermediate for the synthesis of **D** via the Wittig approach, is known to be unstable.[6a] We now report a one-step conversion of ribo- and xylofuranose acetylenes into vinylic derivatives functionalized with chloro and ethoxycarbonyl groups as precursors for the synthesis of the corresponding adenine nucleosides which may interact with AdoHcy hydrolase.

RESULTS AND DISCUSSION

Ribo-, **1a**,**b**, and xylofuranose, **1c**, acetylene precursors were prepared by a modified[6b] Tronchet procedure.[2a] Thus, sequential[15] (one-flask), selective hydrolysis of the 5,6-*O*-isopropylidene acetal from 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose and oxidative cleavage of the exposed glycol with periodic acid gave dehomologated 5-aldehyde. Wittig-type olefination with dibromomethylene reagent (Ph_3P/CBr_4) followed by treatment of the resulting dibromovinyl intermediate with BuLi[16] afforded 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hex-5-

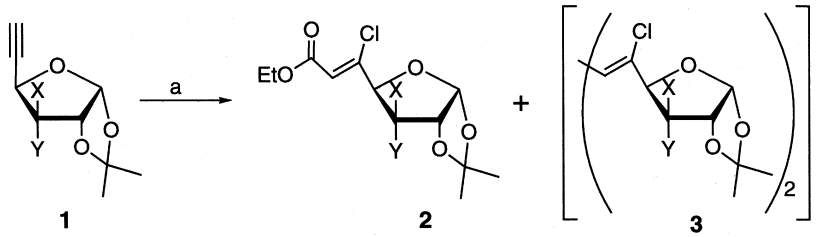
ynofuranose[6b] (**1**; X = H, Y = OH; Scheme 1). Silylation or benzoylation of O3 gave **1a** and **1b**[6b] in good yield.

Treatment of **1a** with ethyl chloroformate in toluene (110 °C/7 h) in the presence of a catalytic amount of carbonylchlorobis(triphenylphosphine)rhodium(I) [$RhCl(CO)(PPh_3)_2$] (0.01 equiv.)[17] effected *syn* chloroesterification to give a single isomer **2a** (82%). Analogous treatment of **1b** and column chromatography gave **2b** (71%) and minor quantity of a second product, tentatively assigned as dimer **3b** (10%). The xylofuranose acetylene **1c**[2a] also gave the desired alkene **2c** (68%) and a dimer **3c** (11%). Formation of traces of dimers under these conditions were also observed by Tanaka and coworkers.[17]

The structure of products **2** and **3** were confirmed by ^1H and ^{13}C NMR as well NOE, DEPT, and HETCOR experiments in addition to MS and elemental analyses. For example, NOE difference spectroscopy experiments showed an 8% enhancement of the allylic proton (H4) signal at δ 4.87 for **2b** upon irradiation of the vinylic proton H6 at δ 6.51 thus verifying *syn* addition[17] to a triple bond. The diene-type dimer **3b** had a singlet for H6 at δ 6.95 and ^{13}C DEPT experiment showed the quaternary C5 at δ 135.07 and C6 at δ 124.24. These data are in agreement with the literature values for the 1,4-dichloro-1,3-butadienes.[18]

The generality of the rhodium-catalyzed chloroesterification of alkynes was further illustrated with ribofuranoside acetylene **4**. Treatment of **4**[2a] with ethyl chloroformate and purification gave **5**(72%, Scheme 2) plus minor byproducts which were not isolated.

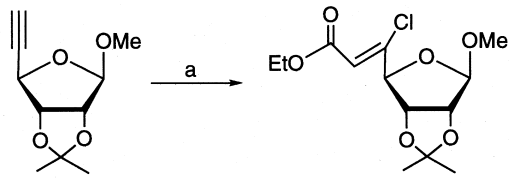
Recently, we reported the synthesis of dibromovinylheptofuranose **6** from 1,2-*O*-isopropylidene-α-D-glucose.[14] The key steps involved regioselective oxidation to the 5-ketone, deoxygenation via its tosylhydrazone, and inversion of configuration at C3. Moffatt oxidation of the resulting ribohexofuranose and treatment of the crude 6-aldehyde with (dibromomethylene)triphenylphosphorane gave **6**.[14] Treatment of **6** with excess BuLi effected dehydrobromination to give acetylenic homologated ribose **7** (Scheme 3). Rhodium-catalyzed *syn* chloroethoxycarbonylation of **7** gave single isomer **8** (69 %).



Series: **a** X = H, Y = OTBDMS
b X = H, Y = OBz
c X = OMe, Y = H

[a] Key: (a) $ClCO_2C_2H_5/RhCl(CO)(PPh_3)_2$/toluene/110 °C/7h

Scheme 1.



4 5

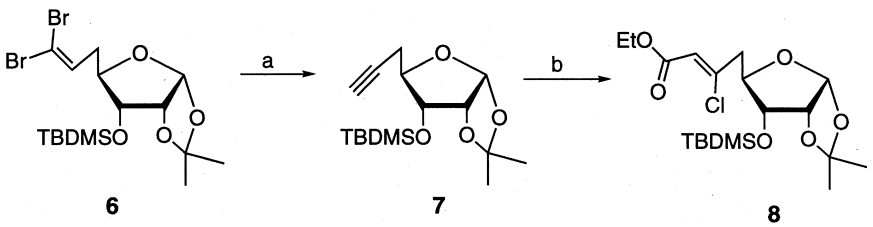
[a] Key: (a) $ClCO_2C_2H_5/RhCl(CO)(PPh_3)_2$/toluene/110 °C/5h

Scheme 2.

EXPERIMENTAL

Uncorrected melting points were determined with a capillary tube apparatus. ^1H (Me_4Si) NMR spectra were determined at 400 MHz and ^{13}C (Me_4Si) at 100.6 MHz in $CDCl_3$ solution. Mass spectra (MS and HRMS) were obtained by atmospheric pressure chemical ionization (APCI), chemical ionization (CI, CH_4), or fast atom bombardment (FAB, 5% trifluoroacetic acid/thioglycerol matrix) techniques. Reagent grade chemicals were used and solvents were dried by reflux over and distillation from CaH_2 under an argon atmosphere. TLC was performed on Merck kieselgel 60-F_{254} with EtOAc/hexane (1:4) as a developing system; and products were detected with 254 nm light or by development of color with $Ce(SO_4)_2/(NH_4)_6Mo_7{\cdot}O_{24}4H_2O/H_2SO_4/H_2O$. Merck kieselgel 60 (230-400 mesh) was used for column chromatography. Elemental analyses were determined by Galbraith Laboratories, Knoxville, TN.

3-*O*-(*tert*-Butyldimethylsilyl)-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hex-5-ynofuranose **(1a)**. *tert*-Butyldimethylsilyl (TBDMS) chloride (188 mg, 1.25 mmol) was added to a solution of 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hex-5-ynofuranose[6b] (**1**; X = H, Y = OH; 368 mg, 2mmol) in dried pyridine (5 mL) and stirring was continued for 24 h at ambient temperature. Volatiles were evaporated *in vacuo* and toluene was added (2 × 3 mL) and evaporation was continued. The residue was partitioned ($EtOAc/H_2O$) and the organic phase was washed (H_2O, brine), dried (Na_2SO_4), and filtered. Volatiles were evaporated and the residue was column chromatographed (5 → 20% EtOAc/hexane) to give **1a**



6 7 8

Scheme 3.

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(263 mg, 88%) as a syrup: ^{1}H NMR δ 0.12 (s, 6H, 2 × Me), 0.91 (s, 9H, *t*-Bu), 1.30 and 1.51 (2 × s, 2 × 3H, 2 × Me), 2.51 (d, 1H, $J_{6,4}$ = 2.0 Hz, H-6), 4.02 (dd, 1H, $J_{3,4}$ = 8.8 Hz, $J_{3,2}$ = 4.4 Hz, H-3), 4.43 ("t", 1H, J = 4.1 Hz, H-2), 4.49 (dd, 1H, H-4), 5.77 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1); ^{13}C NMR δ −4.32, −4.20 (2 × Me), 18.68 (*C*Me$_3$), 26.15 (C*Me*$_3$), 26.93 and 27.10 (C*Me*$_2$), 69.95 (C-4), 75.08 (C-6), 77.81 (C-3), 79.23 (C-2), 80.86 (C-5), 104.23 (C-1), 113.32 (*C*Me$_2$). HRMS (CI) Calcd for $C_{15}H_{26}O_4Si$ + H: 299.1678. Found: 299.1682.

Anal. Calcd for $C_{15}H_{26}O_4Si$ (298.45): C, 60.37; H, 8.78. Found: C, 60.41; H, 8.81.

Ethyl (*Z*)-3-*O*-(*tert*-Butyldimethylsilyl)-5-chloro-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hept-5-enofuranuronate **(2a).** Procedure A. Argon was bubbled through a solution of **1a** (75 mg, 0.25 mmol) and $ClCO_2Et$ (0.12 mL, 135 mg, 1.25 mmol) in dried toluene (2 mL) for 30 min at ambient temperature. $RhCl(CO)(PPh_3)_2$ (1.7 mg, 0.0025 mmol) was then quickly added and the resulting mixture was heated in a pressure tube (Ace glass, 15 mL) at 110 °C for 7 h. After cooling, volatiles were evaporated and the residue was partitioned (EtOAc//$NaHCO_3$/H_2O), and the aqueous layer was extracted (EtOAc). The combined organic phase was washed (brine) and dried ($MgSO_4$). Volatiles were evaporated and the residue was column chromatographed (5 → 20 % EtOAc/hexane) to give **2a** (83 mg, 82%) as a syrup: ^{1}H NMR δ 0.10 and 0.12 (2 × s, 2 × 3H, 2 × Me), 0.91 (s, 9H, *t*-Bu), 1.30 (t, 3H, J = 7.1 Hz, CH_3), 1.35 and 1.60 (2 × s, 2 × 3H, 2 × Me), 4.08 (dd, 1H, $J_{3,4}$ = 8.3 Hz, $J_{3,2}$ = 4.4 Hz, H-3), 4.25 (q, 2H, J = 7.1 Hz, CH_2), 4.45 (d, 1H, H-4), 4.50 ("t", 1H, J = 3.8 Hz, H-2), 5.86 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1), 6.37 (s, 1H, H-6); ^{13}C NMR δ −4.50, −4.41 (2 × Me) 14.54 (CH_3), 18.53 (*C*Me$_3$), 26.05 (C*Me*$_3$), 26.99 and 27.27 (C*Me*$_2$), 61.02 (CH_2), 76.04 (C-3), 79.75 (C-2), 83.35 (C-4), 104.52 (C-1), 113.69(*C*Me$_2$), 119.70 (C-6), 145.43 (C-5), 163.80 (C-7). HRMS (FAB) Calcd for $C_{18}H_{31}{}^{35}ClO_6Si$ + Na: 429.1476. Found: 429.1502.

Anal. Calcd for $C_{18}H_{31}ClO_6Si$ (406.98): C, 53.12; H, 7.68. Found: C, 53.18; H, 7.76.

Ethyl (*Z*)-3-*O*-Benzoyl-5-chloro-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hept-5-enofuranuronate **(2b).** Treatment of **1b**[6b] (100 mg, 0.35 mmol) by procedure A [TLC indicated complete consumption of **1b** (R_f 0.61) with formation of more polar components: **2b** (R_f 0.58, major) and **3b** (R_f 0.49)] gave **2b** (98g, 71%): mp 117-118 °C (MeOH); ^{1}H NMR δ 1.31 (t, 3H, J = 7.1 Hz, CH_3), 1.38 and 1.60 (2 × s, 2 × 3H, 2 × Me), 4.25 (q, 2H, J = 7.1 Hz, CH_2), 4.87 (d, 1H, $J_{4,3}$ = 8.4 Hz, H-4), 5.04 ("t", 1H, J = 4.2 Hz, H-2), 5.09 (dd, 1H, $J_{3,2}$ = 4.6 Hz, H-3), 6.00 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 6.51 (s, 1H, H-6), 7.47-8.12 (m, 5H, C_6H_5); ^{13}C NMR δ 14.54 (CH_3), 27.07 and 27.21 (C*Me*$_2$), 61.25 (CH_2), 76.19 (C-3), 78.07 (C-2), 80.87 (C-4), 104.91 (C-1), 114.23 (*C*Me$_2$), 119.27 (C-6), 128.93, 129.38, 130.39, 134.00 (Ph), 144.23 (C-5), 163.78 (C-7), 165.87 (Bz); MS (FAB) *m/z* 399 (3, $MH^+[^{37}Cl]$), 397 (9, $MH^+[^{35}Cl]$), 341 (36, M^+ - 57, $[^{37}Cl]$), 339 (100, M^+ - 57, $[^{35}Cl]$).

Anal. Calcd for $C_{19}H_{21}ClO_7$ (396.82): C, 57.51; H, 5.33. Found: C, 57.49; H, 5.58.

Further elution of the column gave dimer **3b** (23 mg, 10%): mp 166-169 °C; ^{1}H NMR δ 1.39 and 1.62 (2 × s, 2 × 3H, 2 × Me), 4.91 (d, 1H, $J_{4,3}$ = 8.6 Hz, H-4), 5.02 ("t", 1H, J = 4.2 Hz, H-2), 5.12 (dd, 1H, $J_{3,2}$ = 4.8 Hz, H-3), 5.99 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 6.95 (s, 1H, H-6), 7.44-8.08 (m, 5H, C_6H_5); ^{13}C NMR δ 27.04 and 27.20 (C*Me*$_2$), 75.25 (C-3), 77.86 (C-2), 81.22 (C-4), 104.84 (C-1), 113.98 (*C*Me$_2$), 124.24 (C-6), 128.88, 129.45, 130.34, 133.89 (Ph), 135.07 (C-5), 165.99 (Bz); MS (FAB) *m/z* 673 (11, MNa$^+$[^{37}Cl$_2$]), 671 (65, MNa$^+$[^{37}Cl, ^{35}Cl]), 669 (100, MNa$^+$[^{35}Cl$_2$]).

Anal. Calcd for $C_{32}H_{32}Cl_2O_{10}$ (647.51): C, 59.35; H, 4.98. Found: C, 59.71; H, 5.35.

Ethyl (*Z*)-5-Chloro-3-*O*-methyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hept-5-enofuranuronate **(2c).** Treatment of **1c**[2a] (149 mg, 0.75 mmol) by procedure A [5 h; TLC indicated complete consumption of **1c** (R_f 0.55) with formation of **2c** (R_f 0.62) and **3b** (R_f 0.53)] gave **2c** (156 mg, 68%) as a solidified syrup: mp 61-62 °C; ^{1}H NMR δ 1.28 (t, 3H, J = 7.2 Hz, CH_3), 1.33 and 1.51 (2 × s, 2 × 3H, 2 × Me), 3.40 (s, 3H, OMe), 4.02 (d, 1H, $J_{3,4}$ = 3.2 Hz, H3), 4.19 (q, 2H, J = 7.1 Hz, CH_2), 4.60 (d, 1H, $J_{2,1}$ = 3.6 Hz, H-2), 4.78 (dd, 1H, $J_{4,6}$ = 1.6 Hz, H-4), 5.96 (d, 1H, H-1), 6.49 (d, 1H, H-6); ^{13}C NMR δ 14.54 (CH_3), 26.65 and 27.33 (C*Me*$_2$), 59.16 (OMe), 60.81 (CH_2), 81.66 (C-2), 83.35 (C-4), 84.23 (C-3), 105.72 (C-1), 112.84 (*C*Me$_2$), 117.20 (C-6), 142.53 (C-5), 164.15 (C-7); MS (APCI) *m/z* 309 (43, MH$^+$[^{37}Cl]), 307 (100, MH$^+$[^{35}Cl]).

Anal. Calcd for $C_{13}H_{19}ClO_6$ (306.75): C, 50.90; H, 6.24. Found: C, 51.27; H, 6.32.

Further elution of the column gave **3c** (38 mg, 11%): mp 91-93 °C; ^{1}H NMR δ 1.33 and 1.51 (2 × s, 2 × 3H, 2 × Me), 3.40 (s, 3H, OMe), 3.97 (d, 1H, $J_{3,4}$ = 3.1 Hz, H3), 4.61 (d, 1H, $J_{2,1}$ = 3.6 Hz, H-2), 4.81 (d, 1H, H-4), 6.02 (d, 1H, H-1), 6.91 (s, 1H, H-6); ^{13}C NMR δ 26.72 and 27.33 (C*Me*$_2$), 59.16 (OMe), 81.96 (C-2), 82.81 (C-4), 84.41 (C-3), 105.60 (C-1), 112.64 (*C*Me$_2$), 120.43 (C-6), 130.95 (C-5); MS (APCI) *m/z* 471 (12, MH$^+$[^{37}Cl$_2$]), 469 (68, M$^+$[^{37}Cl, ^{35}Cl]), 467 (100, MH$^+$[^{35}Cl$_2$]).

Anal. Calcd for $C_{20}H_{28}Cl_2O_8$ (467.35): C, 51.40; H, 6.04. Found: C, 51.01; H, 6.25.

Ethyl [Methyl (*Z*)-5-Chloro-5,6-dideoxy-2,3-*O*-isopropylidene-β-D-*ribo*-hept-5-enofuranosid]uronate **(5).** Treatment of **4**[2a] (149 mg, 0.75 mmol) by procedure A (5 h) gave **5** (165 mg, 72%) as a syrup: ^{1}H NMR δ 1.28 (t, 3H, J = 7.2 Hz, CH_3), 1.33 and 1.51 (2 × s, 2 × 3H, 2 × Me), 3.47 (s, 3H, OMe), 4.19 ("dq", 2H, J = 2.2 Hz, J = 7.2 Hz, CH_2), 4.57 (d, 1H, $J_{2,3}$ = 6.1 Hz, H-2), 4.73 ("t", 1H, J = 1.8 Hz, H-4), 4.89 (dd, 1H, $J_{3,4}$ = 2.1 Hz, H-3), 5.10 (s, 1H, H-1), 6.43 (d, 1H, $J_{6,4}$ = 1.6 Hz, H-6); ^{13}C NMR δ 14.58 (CH_3), 25.49 and 27.08 (C*Me*$_2$), 56.62 (OMe), 61.04 (CH_2), 83.66 (C-3), 85.01 (C-2), 90.44 (C-4), 111.41 (C-1), 113.64 (*C*Me$_2$), 116.42 (C-6), 146.51 (C-5), 164.15 (C-7); MS (APCI) *m/z* 309 (43,MH$^+$[^{37}Cl]), 307 (100, MH$^+$[^{35}Cl]).

Anal. Calcd for $C_{13}H_{19}ClO_6$ (306.75): C, 50.90; H, 6.24. Found: C, 50.52; H, 6.23.

3-*O*-(*tert*-Butyldimethylsilyl)-5,6,7-trideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hept-6-ynofuranose **(7).** BuLi/hexane (1.6 M; 8.1 mL, 13 mmol) was added dropwise to a solution of **6**[14] (875 mg, 1.85 mmoL) in dried THF (15 mL) at −78 °C and stirring was continued for 1 h with the temperature slowly increasing to ~ −60 °C. The mixture was neutralized (AcOH, pH ~6.5) and was partitioned (EtOAc//$NaHCO_3$/H_2O), and the aqueous layer was extracted (EtOAc). The combined organic phase was washed (brine) and dried ($MgSO_4$). Volatiles were evaporated and the residue was column chromatographed (15 → 30% hexane/EtOAc) and fractions containing pure **7** [TLC: R_f 0.71; R_f 0.78 (**6**)] were evaporated to give **7** (300 mg, 52%): ^{1}H NMR δ 0.14 and 0.15 (2 × s, 2 × 3H, 2 × Me), 0.94 (s, 9H, *t*-Bu), 1.35 and 1.56 (2 × s, 2 × 3H, 2 × Me), 2.04 (t, 1H, $J_{7\text{-}5,5'}$ = 2.6 Hz, H-7), 2.47 (ddd, 1H, $J_{5',5}$ = 17.4 Hz, $J_{5',4}$ = 4.4 Hz, H-5′), 2.71 (dt, 1H, $J_{5\text{-}7,4}$ = 3.2 Hz, H-5), 3.92 (dd, 1H, $J_{3,4}$ = 8.7 Hz, $J_{3,2}$ = 4.5 Hz, H-3), 4.00 (“quint”, 1H, J = 4.2 Hz, H-4), 4.46 (t, 1H, $J_{2\text{-}1,3}$ = 4.1 Hz, H-2), 5.79 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1); ^{13}C NMR δ −4.37, −4.14 (2 × Me) 18.59 (*C*Me$_3$), 21.01 (C-5), 26.17 (C*Me*$_3$), 26.99 and 27.27 (C*Me*$_2$), 71.05 (C-7), 75.07 (C-3), 77.03 (C-4), 79.48 (C-2), 80.02 (C-6), 104.35 (C-1), 113.00 (*C*Me$_2$); MS (APCI) *m/z* 313 (6, MH^+), 255 (100, M^+ - 57).

Anal. Calcd for $C_{16}H_{28}O_4Si$ (312.48): C, 61.50; H, 9.03. Found: C, 61.66; H, 9.27.

Ethyl (*Z*)-3-*O*-(*tert*-Butyldimethylsilyl)-6-chloro-5,6,7-trideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-oct-6-enofuranuronate **(8)**. Treatment of **7** (172 mg, 0.55 mmol) by procedure A (5 h) gave unchanged **7** (19 mg, 11%) followed by **8** (160 mg, 69%): ^{1}H NMR δ 0.11 and 0.15 (2 × s, 2 × 3H, 2 × Me), 0.91 (s, 9H, *t*-Bu), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 1.33 and 1.55 (2 × s, 2 × 3H, 2 × Me), 2.57 (dd, 1H, $J_{5',5}$ = 15.1 Hz, $J_{5',4}$ = 8.7 Hz, H-5′), 2.76 (dd, 1H, $J_{5,4}$ = 2.4 Hz, H-5), 3.65 (dd, 1H, $J_{3,2}$ = 4.5 Hz, $J_{3,4}$ = 8.8 Hz, H-3), 4.17-4.23 (m, 3H, H-4 & CH_2), 4.43 (“t”, 1H, J = 4.1 Hz, H2), 5.72 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-1), 6.38 (s, 1H, H-7); ^{13}C NMR δ −4.39, −3.98 (2 × Me), 14.61 (CH_3), 26.12 (C*Me*$_3$), 27.06 (C*Me*$_2$), 44.19 (C-5), 60.76 (CH_2), 76.68 (C-4), 76.74 (C-3), 79.19 (C-2), 104.21 (C-1), 113.16 (*C*Me$_2$), 118.70 (C-7), 146.32 (C-6), 164.16 (C-8); MS (APCI) *m/z* 365 (42, M^+ - 57, [^{37}Cl]), 363 (100, M^+ - 57, [^{35}Cl]).

Anal. Calcd for $C_{19}H_{33}ClO_6Si$ (421.01): C, 54.21; H, 7.90. Found: C, 54.01; H, 8.09.

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