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A straightforward synthesis of *glyco*-2,7- and 2,8-dienes

Franck Dolhem, Nicolas Smiljanic, Catherine Lièvre* and Gilles Demailly

Laboratoire des Glucides, UMR 6219, Université de Picardie Jules Verne, 33 rue Saint-Leu, F-80 039 Amiens, France

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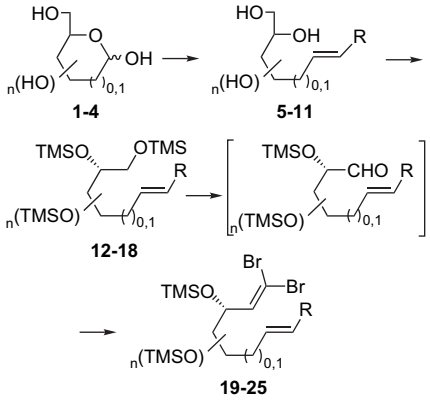
Abstract—In this paper, we report the efficient preparation of carbohydrate-derived 2,7- and 2,8-dienes. By our synthetic approach, we have quickly converted D-glucose **1** to (*E*)-ethyl-2,3-dideoxy-D-*gluco*-oct-2-enoate **5**, which led to the desired (*E*)-ethyl-9,9-dibromo-2,3,8,9-tetradeoxy-4,5,6,7-tetra-*O*-trimethylsilyl-D-*gluco*-nona-2,8-dienoate **19** with satisfying yield.

1. Introduction

Synthesis of well-defined polyhydroxylated chiral building blocks remains of interest in synthetic chemistry.[1] Toward this goal, the chiral pool is an attractive and economic source of enantiomerically pure starting materials. The main task remains to convert efficiently and rapidly these chiral materials into useful synthetic scaffolds for the construction of useful ring systems.[2] Part of our studies is to start from carbohydrates to achieve the synthesis of chain-elongated sugars. A few years ago, we tuned a Wittig type reaction that allowed us to work on free carbohydrates.[3] When aldoses were reacted with methyl bromoacetate, tri-*n*-butylphosphine, and zinc, they gave the corresponding *E*-unsaturated Wittig products in good yields and high stereoselectivity. Moreover this procedure suppressed classical side reactions. As a result of these studies, we conclude that it would be of great value to transpose such smooth conditions to the reaction with dibromotriphenylphosphonium bromide. This goal was achieved by overcoming some difficulties, and we have reported the synthesis of 1,1-dibromo-1-alkenes from partially protected and unprotected aldoses.[4] These compounds were interesting scaffolds that can be used in many transformations.[5] Here we report the efficient synthesis of (*E*)-alkyl-9,9-dibromo-D-*glyco*-nona-2,8-dienoates, (*E*)-9,9-dibromo-D-*gluco*-nona-2,8-dienonitrile, and (*E*)-ethyl-8,8-dibromo-D-*ribo*-octa-2,7-dienoate in a few steps from commercially available monosaccharides. As shown in Scheme 1, these 2,7- and 2,8-dienes were readily obtained from aldoses. Our strategy is based on the prior transformation of the hemiacetal position from which we generated a carbon–carbon double bond (**5**–**11**) by a Wittig type reaction and in a second time on the creation of the second unsaturated bond (**19**–**25**) from the primary hydroxyl group via a Corey–Fuchs reaction. In this strategy, we used TMS group as protecting groups for hydroxyls because a transformation can be carried out by a one-pot procedure to selectively deprotect and then oxidize the primary alcohol.[6]



Scheme 1.

2. Results and discussion

2.1. Synthesis of olefins 5–11

The reaction of D-glucose **1** with ethyl bromoacetate, *tert*-butyl bromoacetate, methyl bromoacetate or bromoacetonitrile, and tri-*n*-butylphosphine in the presence of zinc in refluxing 1,4-dioxane afforded mainly *E*-unsaturated Wittig products **5**–**8** with yields ranging from 52% to 70%. NMR and mass spectrometry experiments were used to establish the structure of olefins **5**–**8**. Indeed, as example, the NMR spectra of **5** exhibited two characteristic peaks 148.2 and 121.6 ppm attributed, respectively, to C-3 and C-2 and 7.06 (dd) and 6.15 (dd) attributed, respectively, to H-3 and H-2 and with J=15.7 Hz. So, the mildness of our conditions

Keywords: Carbohydrate-derived 2,7- and 2,8-dienes; Oxidation; Wittig type reaction; Corey–Fuchs reaction.
* Corresponding author. Tel.: +33 32 282 7661; fax: +33 32 282 7561; e-mail: catherine.lievre@u-picardie.fr

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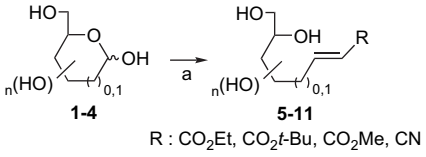
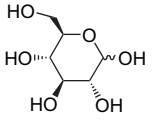
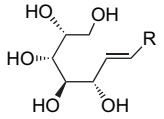
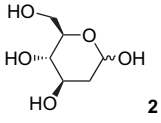
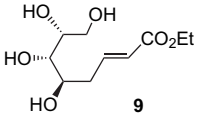
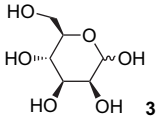
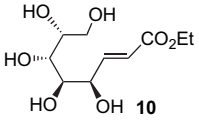
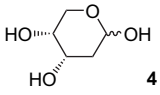
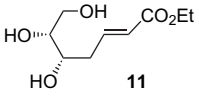
allowed us to form *E*-olefin on naked aldoses, preventing formation of C-glycosides. 2-Deoxy-D-glucose **2** treated with ethyl bromoacetate, tri-*n*-butylphosphine in the presence of zinc in refluxing 1,4-dioxane led to the desired compound **9** in 80% yield. It appears that from 2-deoxy-D-glucose **2** the yield was better than the one for D-glucose **1** in this Wittig type reaction. When these conditions were applied to D-mannose **3** and 2-deoxy-D-ribose **4**, the expected olefins **10** and **11** were obtained in 70% and 73% yields, respectively (Scheme 2, Table 1).



Scheme 2. Synthesis of olefins **5**–**11**. Reagents and conditions: (a) $BrCH_2R$ (2 equiv), *n*-Bu_3P (2 equiv), Zn (2 equiv), 1,4-dioxane, reflux.

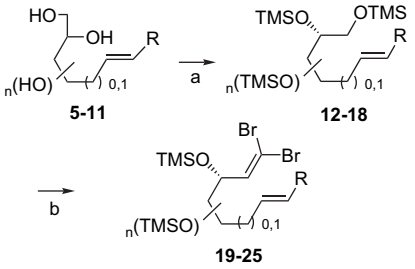
Table 1. Synthesis of olefins **5**–**11**

Aldoses **1**–**4**	Olefins **5**–**11**	Yields[a] (%)
 **1**	 **5** : R = CO_2Et **6** : R = CO_2t-Bu **7** : R = CO_2Me **8** : R = CN	69 52 70 70
 **2**	 **9**	80
 **3**	 **10**	70
 **4**	 **11**	73

[a] Yield represents isolated yield.

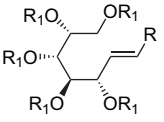
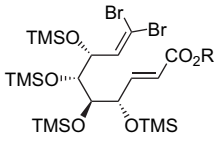
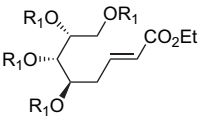
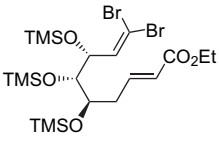
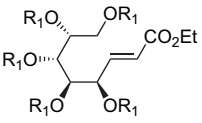
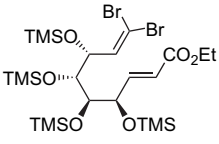
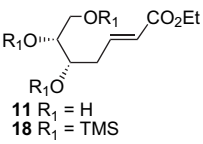
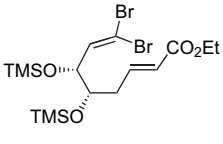
2.2. Synthesis of 2,7- and 2,8-dienes 19–25

The activated DMSO reagents, well-known for oxidizing alcohol to the corresponding carbonyl compounds under mild conditions, can also oxidize trimethyl and triethylsilyl ethers.[5] Furthermore, primary trimethyl and triethylsilyl ethers are more reactive than their secondary analogues, allowing the selective oxidation of the former in the presence of the latter by the Swern reagent, oxalyl chloride, a good activator for DMSO.[7] So, in a three-step procedure on olefin **5**, we carried out a standard silylation (trimethylsilyl chloride, triethylamine in dichloromethane at room temperature) followed by a Swern oxidation and an addition of dibromotriphenylphosphonium bromide, *t*-BuOK in THF. Unfortunately we could not recover more than 30% of the desired diene **19**. TLC monitoring of the reaction showed that the silylation step was neither clean nor complete. Reaction with HMDS as the silylating reagent leaded to the same kind of results. The prior isolation of the persilylated compound **12** was not a positive solution either, due to the relative instability of the TMS groups on silica gel and use of fluorisil as a separative agent was not practicable enough on a reasonable scale. We then searched for a powerful silylating reagent, which would in the same time create only easily removable by-products. We turned our focus to *N*,*O*-bis-(trimethylsilyl)carbamate, and indeed BSC was the reactant of choice since the only by-products of silylation are the gases NH_3 and CO_2 and the products can be used in subsequent reactions without any treatment but a simple removal of the solvent.[8] (Scheme 3, Table 2)



Scheme 3. Synthesis of dienes **19**–**25**. Reagents and conditions: (a) BSC (1.2 equiv per OH), TBAF (0.01 equiv), NMP, rt. (b) (i) $(COCl)_2$ (3 equiv), DMSO (6 equiv), CH_2Cl_2, −70 °C then Et_3N, (ii) Ph_3PCHBr_3 (2.2 equiv), *t*-BuOK (2.1 equiv), THF, rt.

Table 2. Synthesis of dienes **19**–**25**

Olefins **5**–**11**	Dienes **19**–**25**	Yields[a] (%)
 **5** R_1 = H, R = CO_2Et **6** R_1 = H, R = CO_2t-Bu **7** R_1 = H, R = CO_2Me **8** R_1 = H, R = CN **12** R_1 = TMS, R = CO_2Et **13** R_1 = TMS, R = CO_2t-Bu **14** R_1 = TMS, R = CO_2Me **15** R_1 = TMS, R = CN	 **19** R = CO_2Et **20** R = CO_2t-Bu **21** R = CO_2Me **22** R = CN	59 69 56 49
 **9** R_1 = H **16** R_1 = TMS	 **23**	59
 **10** R_1 = H **17** R_1 = TMS	 **24**	50
 **11** R_1 = H **18** R_1 = TMS	 **25**	57

[a] Yield represents isolated yield from persylilated olefins **12**–**18**.

We have tested these silylation conditions (BSC, TBAF in catalytic quantity in 1-methyl-2-pyrrolidinone (NMP) at room temperature). So the starting material **5** was successfully converted into **19** (59% yield) by this sequence involving silylation with BSC followed by Swern oxidation and an addition of dibromotriphenylphosphonium bromide, *t*-BuOK in THF. The structure of **19** was confirmed by NMR spectroscopy experiments, with the characteristic resonances observed at δ=149.2, 139.7, 120.0, 89.8 ppm attributed to C-3, C-8, C-2, C-9, respectively, and those at δ=7.23, 6.60, 5.97 ppm attributed to H-3, H-8, H-2, respectively. We then extended this three-step procedure to the other olefins (**6**–**11**) described above, converting them into their corresponding 2,7- and 2,8-dienes. These conditions on olefins derived from D-glucose **6**–**9** afford the desired compounds **20**–**23** with satisfying yields. When the reaction is performed on olefins **10** and **11** derived from D-mannose and D-ribose, respectively, the corresponding dienes are isolated with 50% and 57% yields, respectively.

In summary, several polyhydroxylated 2,7- and 2,8-dienes were prepared in a versatile manner in four steps from commercially available monosaccharides with satisfying yields. The quickness and efficiency of this methodology to prepare functionalized chiral polyols is noticeable. Such compounds are interesting scaffolds, in particular for the obtaining of polyhydroxylated carbocycles and for the construction of bridged and fused bicyclic systems. Indeed, a study toward their cyclization is currently in progress in our laboratory and any interesting result will be reported in due course. As well, we are pursuing our study on conversion of carbohydrates in interesting polyhydroxylated chiral scaffold derivatives.

3. Experimental

3.1. General

Unless otherwise specified, materials were purchased from commercial suppliers and used without further purification. THF was distilled from lithium aluminum hydride immediately before use. CH_2Cl_2 was distilled from calcium chloride under argon. Moisture sensitive reactions were conducted in oven-dried glassware under an argon atmosphere. Flash chromatography was carried out on Kieselgel 60 (230–400 mesh, Merck) and analytical thin-layer chromatography (TLC) was performed on E. Merck glass-backed silica gel sheets (Silica Gel 60 F254). Melting points are uncorrected. Optical rotations were measured using a sodium lamp (λ=589 nm) and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Spectra were recorded in $CDCl_3$, C_5D_5N, D_2O, or CD_3OD and chemicals shifts (δ) were expressed in parts per million relative to residual $CHCl_3$ or an internal standard. All signals in ^{13}C NMR spectra were assigned through C,H-correlated spectra. IR spectra were recorded as neat films (NaCl cell) and KBr pellets (for solids). Infusion electrospray mass spectra in the positive-ion mode were obtained with an updated (3.6 GHz TDC) Q-TOF hybrid quadrupole-time-of-flight instrument, equipped with a pneumatically assisted electrospray ion source (Z-spray).

3.1.1. Preparation of olefins 5–11. General procedure 1: To an anhydrous 1,4-dioxane solution (3.6 mL, 1 mmol) of zinc (2 equiv) were successively added tri-*n*-butylphosphine (2 equiv), ethyl bromoacetate or *tert*-butyl bromoacetate or bromonitrile (2 equiv), and starting material (**1**–**4**). The reaction was stirred under an argon atmosphere and allowed to reflux. The reaction was monitored by TLC, and after completion the mixture was cooled to room temperature and filtered on sintered glass. After concentration, the crude residue was purified by flash chromatography.

3.1.1.1. (*E*)-Ethyl-2,3-dideoxy-D-*gluco*-oct-2-enoate (5). The compound **5** was prepared by general procedure 1 from D-glucose **1** (1.37 g, 7.65 mmol). The reaction was completed after 1 h. The crude residue was purified by flash chromatography (CH_2Cl_2/MeOH 95:5, 90:10, and then 85:15), and **5** was obtained as a colorless oil (1.32 g, 69%). R_f=0.44 (CH_2Cl_2/MeOH 80:20); $[\alpha]_D^{27}$ −90 (*c* 1.0, MeOH); IR: ν_{max} 3300, 1780, 1640, 1250, 1150, and 960 cm^{-1}; ^{1}H NMR (CD_3OD): δ 7.06 (dd, 1H, *J*=5.3, 15.7 Hz, 3-H), 6.15 (dd, 1H, *J*=1.6, 15.7 Hz, 2-H), 4.50 (dt, 1H, *J*=1.6, 5.3, 5.3 Hz, 4-H), 4.20 (q, 2H, OCH_2CH_3), 3.80 (m, 2H, 5-H, 8a-H), 3.61 (m, 3H, 6-H, 7-H, 8b-H), 1.20 (t, 3H, OCH_2CH_3); ^{13}C NMR (CD_3OD): δ 167.2, 148.2, 121.6, 72.9, 72.9, 72.7, 71.6, 63.7, 60.7, 13.6; Anal. Calcd for $C_{10}H_{18}O_7$: C, 48.00; H, 7.25. Found: C, 48.29; H, 7.37; MS: *m*/*z* 273.2 [M+Na]$^+$.

3.1.1.2. (*E*)-*tert*-Butyl-2,3-dideoxy-D-*gluco*-oct-2-enoate (6). The compound **6** was prepared by general procedure 1 from D-glucose **1** (1 g, 5.55 mmol). The reaction was completed after 1 h. The crude residue was purified by flash chromatography (CH_2Cl_2/MeOH 90:10), and **6** was obtained as a colorless oil (0.8 g, 52%). R_f=0.4 (CH_2Cl_2/MeOH 80:20); $[\alpha]_D^{24}$ −39 (*c* 1.0, MeOH); IR: ν_{max} 3300, 1760, 1630, 1250, 1150, and 960 cm^{-1}; ^{1}H NMR (CD_3OD): δ 7.01 (dd, 1H, *J*=5.5, 15.6 Hz, 3-H), 6.03 (dd, 1H, *J*=1.6, 15.6 Hz, 2-H), 4.39 (ddd, 1H, *J*=1.6, 5.5, 6.2 Hz, 4-H), 3.78 (dd, 1H, *J*=1.7, 4.2 Hz, 8a-H), 3.68 (m, 1H, 5-H), 3.63 (m, 3H, 6-H, 7-H, 8b-H), 1.52 (s, 9H, $OC(CH_3)_3$); ^{13}C NMR (CD_3OD): δ 167.0, 147.0, 123.3, 81.7, 73.9, 73.8, 72.9, 72.7, 64.8, 28.4; Anal. Calcd for $C_{12}H_{22}O_7$: C, 51.79; H, 7.97. Found: C, 51.89; H, 8.11; MS: *m*/*z* 301.3 [M+Na]$^+$.

3.1.1.3. (*E*)-Methyl-2,3-dideoxy-D-*gluco*-oct-2-enoate (7). The compound **7** was prepared by general procedure 1 from D-glucose **1** (1 g, 5.55 mmol). The reaction was completed after 1 h. The crude residue was purified by flash chromatography (CH_2Cl_2/MeOH 85:15), and **7** was obtained as a colorless oil (0.91 g, 70%). R_f=0.38 (CH_2Cl_2/MeOH 80:20); $[\alpha]_D^{27}$ −60 (*c* 1.0, MeOH); IR: ν_{max} 3300, 1780, 1640, 1250, 1150, and 960 cm^{-1}; ^{1}H NMR (D_2O): δ 7.01 (dd, 1H, *J*=5.7, 15.5 Hz, 3-H), 6.17 (dd, 1H, *J*=1.6, 15.5 Hz, 2-H), 4.48 (ddd, 1H, *J*=1.5, 1.6, 5.7 Hz, 4-H), 3.85 (dd, 1H, *J*=1.5, 1.8 Hz, 5-H), 3.82 (dd, 1H, *J*=2.0, 11.7 Hz, 8b-H), 3.73 (ddd, 1H, *J*=2.2, 6.1, 6.5 Hz, 7-H), 3.63 (dd, 1H, *J*=6.1, 11.7 Hz, 8a-H), 2.69 (dd, 1H, *J*=1.8, 6.5 Hz, 6-H), 3.80 (s, 3H, OCH_3); ^{13}C NMR (D_2O): δ 172.0, 150.4, 124.8, 73.9, 73.7, 72.8, 72.3, 64.6, 53.9; Anal. Calcd for $C_9H_{16}O_7$: C, 45.76; H, 6.83. Found: C, 45.89; H, 6.98; MS: *m*/*z* 259.2 [M+Na]$^+$.

3.1.1.4. (*E*)-2,3-Dideoxy-D-*gluco*-oct-2-enonitrile (8). The compound **8** was prepared by general procedure 1

from D-glucose **1** (1 g, 5.55 mmol). The reaction was completed after 1 h. The crude residue was purified by flash chromatography (CH_2Cl_2/MeOH 95:5), and **8** was obtained as a colorless oil (0.796 g, 70%). R_f=0.33 (CH_2Cl_2/MeOH 80:20); $[\alpha]_D^{25}$ −11 (*c* 0.9, MeOH); IR: ν_{max} 3300, 2250, 1600, 1250, 1150, and 960 cm^{-1}; ^1H NMR (C_5D_5N): δ 7.03 (dd, 1H, *J*=4.3, 16.3 Hz, 3-H), 5.82 (dd, 1H, *J*=2.0, 16.3 Hz, 2-H), 4.50 (dt, 1H, *J*=2.0, 4.3, 5.3 Hz, 4-H), 3.81 (m, 2H, 5-H, 8a-H), 3.62 (m, 3H, 6-H, 7-H, 8b-H); ^{13}C NMR (C_5D_5N): δ 158.5, 120.0, 100.2, 74.9, 73.8, 72.8, 63.8; Anal. Calcd for $C_8H_{13}NO_5$: C, 47.29; H, 6.45; N, 6.89. Found: C, 47.42; H, 6.59; N, 6.91; MS: *m/z* 226.2 $[M+Na]^+$.

3.1.1.5. (*E*)-Ethyl-2,3,4-trideoxy-D-*gluco*-oct-2-enoate (9). The compound **9** was prepared by general procedure 1 from 2-deoxy-D-glucose **2** (1 g, 6.1 mmol). The reaction was completed after 1 h. The crude residue was purified by flash chromatography (CH_2Cl_2/MeOH 95:5), and **9** was obtained as a solid (1.14 g, 80%). R_f=0.43 (CH_2Cl_2/MeOH 85:15); $[\alpha]_D^{23}$ +17 (*c* 1.4, MeOH); mp=114–117 °C; IR: ν_{max} 3300, 1770, 1640, 1250, 1150, and 960 cm^{-1}; ^1H NMR (CD_3OD): δ 7.06 (dt, 1H, *J*=3.2, 3.2, 15.7 Hz, 3-H), 6.00 (dt, 1H, *J*=1.5, 1.5, 15.7 Hz, 2-H), 4.20 (q, 2H, OCH_2CH_3), 3.98 (ddd, 1H, *J*=1.7, 5.5, 7.4 Hz, 5-H), 3.80 (dd, 1H, *J*=3.0, 10.6 Hz, 8a-H), 3.69 (ddd, 1H, *J*=3.0, 5.6, 8.1 Hz, 7-H), 3.63 (dd, 1H, *J*=5.6, 10.6 Hz, 8b-H), 3.37 (dd, 1H, *J*=1.7, 8.1 Hz, 6-H), 2.49 (m, 2H, 4a-H, 4b-H), 1.30 (t, 3H, OCH_2CH_3); ^{13}C NMR (CD_3OD): δ 167.0, 147.0, 123.0, 73.1, 71.9, 69.5, 64.0, 60.4, 36.8, 13.5; Anal. Calcd for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75. Found: C, 51.43; H, 7.99; MS: *m/z* 257.3 $[M+Na]^+$.

3.1.1.6. (*E*)-Ethyl-2,3-dideoxy-D-*manno*-oct-2-enoate (10). The compound **10** was prepared by general procedure 1 from D-mannose **3** (1.5 g, 8.3 mmol). The reaction was completed after 40 min. The crude residue was purified by flash chromatography (CH_2Cl_2/MeOH 95:5, 90:10, and then 85:15), and **10** was obtained as a colorless oil (1.45 g, 70%). R_f=0.42 (CH_2Cl_2/MeOH 85:15); $[\alpha]_D^{28}$ +20 (*c* 1.0, MeOH); IR: ν_{max} 3300, 1780, 1640, 1250, 1150, and 960 cm^{-1}; ^1H NMR (CD_3OD): δ 8.02 (dd, 1H, *J*=4.0, 15.7 Hz, 3-H), 6.70 (dd, 1H, *J*=1.8, 15.7 Hz, 2-H), 5.18 (ddd, 1H, *J*=1.8, 4.0, 8.3 Hz, 4-H), 4.85 (dd, 1H, *J*=2.0, 8.2 Hz, 6-H), 4.60 (m, 1H, 7-H), 4.68 (dd, 1H, *J*=2.0, 8.3 Hz, 5-H), 4.50 (dd, 1H, *J*=3.8, 10.9 Hz, 8a-H), 4.35 (dd, 1H, *J*=2.9, 10.9 Hz, 8b-H), 4.20 (q, 2H, OCH_2CH_3), 1.20 (t, 3H, OCH_2CH_3); ^{13}C NMR (CD_3OD): δ 167.1, 153.0, 120.9, 74.0, 73.7, 72.0, 72.0, 61.8, 60.4, 14.5; Anal. Calcd for $C_{10}H_{18}O_7$: C, 48.00; H, 7.25. Found: C, 48.23; H, 7.39; MS: *m/z* 273.3 $[M+Na]^+$.

3.1.1.7. (*E*)-Ethyl-2,3,4-trideoxy-D-*ribo*-hept-2-enoate (11). The compound **11** was prepared by general procedure 1 from 2-deoxy-D-ribose **4** (1 g, 7.45 mmol). The reaction was completed after 1 h. The crude residue was purified by two consecutive flash chromatographies (CH_2Cl_2/MeOH 98:2, 97:3, 95:5, and then EtOAc), and **11** was obtained as a colorless oil (1.13 g, 73%). R_f=0.63 (CH_2Cl_2/MeOH 90:10); $[\alpha]_D^{26}$ −7 (*c* 1.8, $CHCl_3$); IR: ν_{max} 3300, 1780, 1650, 1250, 1150, and 960 cm^{-1}; ^1H NMR (CD_3OD): δ 7.08 (dt, 1H, *J*=7.4, 7.4, 15.7 Hz, 3-H), 5.94 (dt, 1H, *J*=1.5, 1.5, 15.7 Hz, 2-H), 4.18 (q, 2H, OCH_2CH_3), 3.75 (dd, 1H, 3.9, 11.3 Hz, 7a-H), 3.60 (ddd, 1H, *J*=3.3, 7.1, 8.8 Hz, 5-H), 3.59 (dd, 1H, 6.2, 11.3 Hz, 7b-H), 3.47 (ddd, 1H, *J*=3.9, 6.2, 7.1 Hz, 6-H), 2.63 (dddd, 1H, *J*=1.5, 3.3, 7.4, 14.7 Hz, 4a-H), 2.37 (dddd, 1H, *J*=1.5, 7.4, 8.8, 14.7 Hz, 4b-H), 1.30 (t, 3H, OCH_2CH_3); ^{13}C NMR (CD_3OD): δ 167.2, 147.0, 123.2, 74.8, 71.2, 63.7, 60.3, 36.2, 13.6; Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 52.99; H, 8.09; MS: *m/z* 227.3 $[M+Na]^+$.

3.1.2. Preparation of persilylated compounds 12–18. General procedure 2: To the starting material (**5**–**11**) dissolved in 1-methyl-2-pyrrolidinone (NMP) (1 g/10 mL) were successively added *N*,*O*-bis-(trimethylsilyl)carbamate (1.2 equiv per OH) and dropwise tetra-*n*-butylammonium fluoride (TBAF 1 M solution in THF) (0.01 equiv). The reaction was stirred under an argon atmosphere for 24 h at room temperature as monitored by TLC. Methanol was added (3 mL) and the mixture was concentrated, and the residue was diluted in hexane (3 mL hexane/1 mL NMP) and washed with water. The combined organic layers were dried (Na_2SO_4) and concentrated. The residue (**12**–**18**) was used in subsequent reactions without further treatment.

3.1.2.1. (*E*)-Ethyl-2,3-dideoxy-4,5,6,7,8-penta-*O*-trimethylsilyl-D-*gluco*-oct-2-enoate (12). The compound **12** was prepared by general procedure 2 from **5** (1.32 g, 5.27 mmol). The reaction was treated after 24 h. Compound **12** was obtained as a colorless oil. R_f=0.8 (Hexane/EtOAc 95:5); ^1H NMR ($CDCl_3$): δ 7.30 (dd, 1H, *J*=3.2, 15.7 Hz, 3-H), 6.00 (dd, 1H, *J*=2.0, 15.7 Hz, 2-H), 4.45 (ddd, 1H, *J*=2.0, 3.2, 5.6 Hz, 4-H), 4.20 (q, 2H, OCH_2CH_3), 3.92 (ddd, 1H, *J*=3.1, 5.2, 7.7 Hz, 7-H), 3.69 (dd, 1H, *J*=3.1, 10.4 Hz, 8a-H), 3.60 (dd, 2H, 5-H, 6-H), 3.53 (dd, 1H, *J*=7.7, 10.4 Hz, 8b-H), 1.20 (t, 3H, OCH_2CH_3), 0.08–0.15 (s, 45H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 167.0, 149.0, 121.0, 77.0, 77.0, 75.9, 74.0, 64.3, 60.5, 14.7, −0.1–1.4.

3.1.2.2. (*E*)-*tert*-butyl-2,3-dideoxy-4,5,6,7,8-penta-*O*-trimethylsilyl-D-*gluco*-oct-2-enoate (13). The compound **13** was prepared by general procedure 2 from **6** (0.8 g, 2.88 mmol). The reaction was treated after 24 h. Compound **13** was obtained as a colorless oil. R_f=0.8 (Hexane/EtOAc 95:5); ^1H NMR ($CDCl_3$): δ 7.01 (dd, 1H, *J*=5.5, 15.6 Hz, 3-H), 6.03 (dd, 1H, *J*=1.6, 15.6 Hz, 2-H), 4.39 (ddd, 1H, *J*=1.6, 5.5, 6.2 Hz, 4-H), 3.78 (dd, 1H, *J*=1.7, 4.2 Hz, 8a-H), 3.68 (m, 1H, 5-H), 3.63 (m, 3H, 6-H, 7-H, 8b-H), 1.52 (s, 9H, $OC(CH_3)_3$), 0.30–1.12 (s, 45H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 166.7, 147.2, 122.7, 80.4, 77.8, 77.3, 75.3, 74.0, 64.1, 28.5, 0.1–0.2.

3.1.2.3. (*E*)-Methyl-2,3-dideoxy-4,5,6,7,8-penta-*O*-trimethylsilyl-D-*gluco*-oct-2-enoate (14). The compound **14** was prepared by general procedure 2 from **7** (0.91 g, 3.88 mmol). The reaction was treated after 24 h. Compound **14** was obtained as a colorless oil. R_f=0.85 (Hexane/EtOAc 95:5); ^1H NMR ($CDCl_3$): δ 7.26 (dd, 1H, *J*=3.5, 15.7 Hz, 3-H), 5.95 (dd, 1H, *J*=2.6, 15.7 Hz, 2-H), 4.40 (ddd, 1H, *J*=1.4, 2.6, 3.5 Hz, 4-H), 3.86 (m, 2H, 7-H, 8b-H), 3.60 (s, 3H, OCH_3), 3.58 (dd, 1H, *J*=1.7, 6.4 Hz, 6-H), 3.50 (dd, 1H, *J*=1.4, 1.7 Hz, 5-H), 3.48 (dd, 1H, *J*=6.0, 11.6 Hz, 8a-H), −0.9–0.1 (s, 45H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 167.0, 149.1, 120.1, 76.8, 76.8, 75.7, 73.9, 64.1, 51.4, −0.3–1.6.

3.1.2.4. (*E*)-2,3-Dideoxy-4,5,6,7,8-penta-*O*-trimethylsilyl-D-*gluco*-oct-2-enonitrile (15). The compound **15** was prepared by general procedure 2 from **8** (0.79 g, 3.9 mmol). The reaction was treated after 24 h. Compound **15** was obtained as a colorless oil. R_f=0.8 (Hexane/EtOAc 95:5); ^{1}H NMR ($CDCl_3$): δ 7.30 (dd, 1H, J=4.3, 15.9 Hz, 3-H), 5.80 (dd, 1H, J=2.0, 15.9 Hz, 2-H), 4.45 (ddd, 1H, J=2.0, 4.3, 5.6 Hz, 4-H), 3.92 (ddd, 1H, J=3.3, 5.0, 7.7 Hz, 7-H), 3.81 (dd, 1H, J=3.3, 10.7 Hz, 8a-H), 3.72 (m, 2H, 5-H, 6-H), 3.62 (dd, 1H, J=7.7, 10.7 Hz, 8b-H), 0.08–0.15 (s, 45H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 157.0, 120.2, 100.4, 77.0, 77.0, 76.0, 74.3, 63.9, 0.1–1.4.

3.1.2.5. (*E*)-Ethyl-2,3,4-trideoxy-5,6,7,8-tetra-*O*-trimethylsilyl-D-*gluco*-oct-2-enoate (16). The compound **16** was prepared by general procedure 2 from **9** (1.06 g, 4.53 mmol). The reaction was treated after 24 h. Compound **16** was obtained as a colorless oil. R_f=0.9 (Hexane/EtOAc 95:5); ^{1}H NMR ($CDCl_3$): δ 6.95 (m, 1H, J=1.0, 15.7 Hz, 3-H), 5.85 (dt, 1H, J=1.0, 1.0, 15.7 Hz, 2-H), 4.21 (q, 2H, J=8.0 Hz, OCH_2CH_3), 3.75 (m, 2H, 5-H, 7-H), 3.71 (dd, 1H, J=4.0, 10.4 Hz, 8b-H), 3.58 (dd, 1H, J=3.1, 5.4 Hz, 6-H), 3.40 (dd, 1H, J=6.8, 10.4 Hz, 8a-H), 2.45 (m, 2H, 4a-H, 4b-H), 1.30 (t, 3H, OCH_2CH_3), 0.1–1.1 (s, 36H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 167.7, 146.9, 123.6, 78.6, 73.6, 74.7, 64.2, 60.5, 37.1, 14.7, 0.1–1.4.

3.1.2.6. (*E*)-Ethyl-2,3-dideoxy-4,5,6,7,8-penta-*O*-trimethylsilyl-D-*manno*-oct-2-enoate (17). The compound **17** was prepared by general procedure 2 from **10** (1.45 g, 5.79 mmol). The reaction was treated after 24 h. Compound **17** was obtained as a colorless oil. R_f=0.6 (Hexane/EtOAc 95:5); ^{1}H NMR ($CDCl_3$): δ 7.11 (dd, 1H, J=4.6, 15.6 Hz, 3-H), 6.01 (dd, 1H, J=1.8, 15.6 Hz, 2-H), 4.50 (m, 1H, 4-H), 4.22 (q, 2H, J=8.1 Hz, OCH_2CH_3), 3.90 (m, 1H, 5-H), 3.80 (m, 1H, 7-H), 3.78 (m, 1H, 6-H), 3.72 (dd, 1H, J=4.7, 10.1 Hz, 8a-H), 3.48 (dd, 1H, J=6.4, 10.1 Hz, 8b-H), 1.18 (t, 3H, OCH_2CH_3), 0.1–0.3 (s, 45H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 167.1, 149.3, 120.9, 77.4, 76.7, 74.5, 74.2, 63.4, 60.5, 14.7, 0.1–1.4.

3.1.2.7. (*E*)-Ethyl-2,3,4-trideoxy-5,6,7-tri-*O*-trimethylsilyl-D-*ribo*-hept-2-enoate (18). The compound **18** was prepared by general procedure 2 from **11** (1.03 g, 5.04 mmol). The reaction was treated after 24 h. Compound **18** was obtained as a colorless oil. R_f=0.7 (Hexane/EtOAc 95:5); ^{1}H NMR ($CDCl_3$): δ 6.94 (dt, 1H, J=7.7, 7.7, 15.6 Hz, 3-H), 5.82 (dt, 1H, J=0.5, 0.5, 15.6 Hz, 2-H), 4.20 (q, 2H, J=8.1 Hz, OCH_2CH_3), 3.77 (dt, 1H, J=4.7, 4.7, 7.2 Hz, 5-H), 3.58 (dt, 1H, J=4.7, 4.7, 12.0 Hz, 6-H), 3.48 (m, 2H, 7a-H, 7b-H), 2.35 (m, 2H, 4a-H, 4b-H), 1.20 (t, 3H, OCH_2CH_3), 0.1–0.2 (s, 27H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 167.0, 147.0, 123.7, 77.0, 72.7, 64.3, 60.5, 36.4, 14.7, 0.1–1.4.

3.1.3. Preparation of 2,7- and 2,8-dienes 19–25. General procedure 3: To a CH_2Cl_2 (10 mL) solution of oxalyl chloride (3 equiv) was added dropwise dry methyl sulfoxide (6 equiv) at −70 °C under an argon atmosphere. After 5 min under stirring, a solution of substrate (**12**–**18**) in CH_2Cl_2 (5 mL) was added. The reaction was monitored by TLC. After 30 min, triethylamine (9 equiv) was then carefully added. After being stirred at low temperature for 20 min, the reaction mixture was warmed to room temperature, and a saturated solution of NH_4Cl was added. The mixture was extracted and the combined organic layers were washed with water, dried (Na_2SO_4), and concentrated. The residue was diluted in dry THF. The flask was then immersed in a water bath. Dibromomethylenetriphenylphosphorane, prepared from dibromomethyltriphenylphosphonium bromide[4] (2.2 equiv) and *t*-BuOK (2.1 equiv) in THF (10 mL) at room temperature under an argon atmosphere for 15 min, was then added dropwise. After filtration with Buchner, the mixture was concentrated and the residue (**19**–**25**) was purified by flash chromatography.

3.1.3.1. (*E*)-Ethyl-9,9-dibromo-2,3,8,9-tetradeoxy-4,5,6,7-tetra-*O*-trimethylsilyl-D-*gluco*-nona-2,8-dienoate (19). The compound **19** was prepared by general procedure 3 from **12** (1.32 g, 5.27 mmol). The crude residue was purified by two consecutive flash chromatographies (Hexane/CH_2Cl_2 75:25 and Hexane/$CHCl_3$ 75:25), and **19** was obtained as a colorless oil (2.14 g, 59%). R_f=0.8 (Hexane/EtOAc 90:10); $[\alpha]_D^{23}$ +119 (c 1.0, CH_2Cl_2); IR ($CHCl_3$): ν_{max} 1730, 840, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.23 (dd, 1H, J=4.1, 15.7 Hz, 3-H), 6.60 (d, 1H, J=8.7 Hz, 8-H), 5.97 (dd, 1H, J=1.8, 15.7 Hz, 2-H), 4.46 (m, 1H, 4-H), 4.41 (dd, 1H, J=2.6, 8.7 Hz, 7-H), 4.20 (q, 2H, J=7.1 Hz, OCH_2CH_3), 3.72 (dd, 1H, J=2.6, 6.3 Hz, 6-H), 3.44 (t, 1H, J=6.3, 6.3 Hz, 5-H), 1.28 (t, 3H, OCH_2CH_3), 0.09–0.14 (s, 36H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 167.0, 149.2, 139.7, 120.0, 89.8, 76.5, 76.0, 75.5, 73.9, 60.5, 14.7, 0.6–0.7; Anal. Calcd for $C_{23}H_{48}Br_2O_6Si_4$: C, 39.88; H, 6.98. Found: C, 40.11; H, 6.75; MS: m/z 713.7 $[M+Na]^+$.

3.1.3.2. (*E*)-*tert*-Butyl-9,9-dibromo-2,3,8,9-tetradeoxy-4,5,6,7-tetra-*O*-trimethylsilyl-D-*gluco*-nona-2,8-dienoate (20). The compound **20** was prepared by general procedure 3 from **13** (0.80 g, 2.88 mmol). The crude residue was purified by flash chromatography (Hexane/CH_2Cl_2 60:40), and **20** was obtained as a colorless oil (1.42 g, 69%). R_f=0.8 (Hexane/EtOAc 90:10); $[\alpha]_D^{27}$ +29 (c 1.0, CH_2Cl_2); IR ($CHCl_3$): ν_{max} 1730, 840, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.05 (dd, 1H, J=4.3, 15.7 Hz, 3-H), 6.63 (d, 1H, J=8.8 Hz, 8-H), 5.88 (dd, 1H, J=1.8, 15.7 Hz, 2-H), 4.40 (m, 1H, 7-H), 4.39 (m, 1H, 4-H), 3.72 (dd, 1H, J=2.7, 6.2 Hz, 6-H), 3.43 (t, 1H, J=6.2 Hz, 5-H), 1.52 (s, 9H, $OC(CH_3)_3$), 1.2–0.3 (s, 36H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 166.3, 147.6, 139.5, 122.7, 80.4, 80.3, 77.8, 77.4, 75.3, 74.0, 28.5, 0.0–0.2; Anal. Calcd for $C_{25}H_{52}Br_2O_6Si_4$: C, 41.66; H, 7.27. Found: C, 41.79; H, 7.57; MS: m/z 743.8 $[M+Na]^+$.

3.1.3.3. (*E*)-Methyl-9,9-dibromo-2,3,8,9-tetradeoxy-4,5,6,7-tetra-*O*-trimethylsilyl-D-*gluco*-nona-2,8-dienoate (21). The compound **21** was prepared by general procedure 3 from **14** (0.91 g, 3.88 mmol). The crude residue was purified by flash chromatography (Hexane/CH_2Cl_2 60:40), and **21** was obtained as a colorless oil (1.47 g, 56%). R_f=0.8 (Hexane/EtOAc 95:5); $[\alpha]_D^{25}$ +89 (c 1.0, $CHCl_3$); IR ($CHCl_3$): ν_{max} 1730, 840, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.25 (dd, 1H, J=4.2, 15.7 Hz, 3-H), 6.63 (d, 1H, J=8.7 Hz, 8-H), 5.97 (dd, 1H, J=1.7, 15.7 Hz, 2-H), 4.44 (m, 2H, 4-H, 7-H), 3.70 (m, 4H, 6-H, OCH_3), 3.44 (t, 1H, J=6.0, 6.0 Hz, 5-H), −0.9–0.1 (s, 36H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 167.4, 149.7, 144.0, 120.0, 89.8, 76.5, 76.1, 75.5, 73.9, 51.7, 0.0; Anal. Calcd for $C_{22}H_{46}Br_2O_6Si_4$: C,

38.93; H, 6.83. Found: C, 39.00; H, 6.78; MS: *m/z* 701.7 $[M+Na]^+$.

3.1.3.4. (*E*)-9,9-dibromo-2,3,8,9-tetradeoxy-4,5,6,7-tetra-*O*-trimethylsilyl-D-*gluco*-nona-2,8-dienonitrile (22). The compound **22** was prepared by general procedure 3 from **15** (0.79 g, 3.90 mmol). The crude residue was purified by flash chromatography (Hexane/CH_2Cl_2 75:25), and **22** was obtained as a colorless oil (1.23 g, 49%). R_f=0.75 (Hexane/EtOAc 90:10); $[\alpha]_D^{23}$ +49 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): ν_{max} 2230, 1730, 840, and 750 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.03 (dd, 1H, *J*=4.2, 15.7 Hz, 3-H), 6.48 (d, 1H, *J*=8.8 Hz, 8-H), 6.00 (dd, 1H, *J*=1.9, 15.7 Hz, 2-H), 4.61 (dd, 1H, *J*=2.5, 8.8 Hz, 7-H), 4.45 (m, 1H, 4-H), 3.73 (dd, 1H, *J*=2.5, 6.1 Hz, 6-H), 3.47 (t, 1H, *J*=6.1, 6.1 Hz, 5-H), 0.09–0.14 (s, 36H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 158.2, 140.1, 120.0, 100.0, 90.0, 75.0, 74.9, 73.5, 72.9, 0.6–0.7; Anal. Calcd for $C_{21}H_{43}Br_2NO_4Si_4$: C, 39.06; H, 6.71; N, 2.17. Found: C, 39.33; H, 6.57; N, 2.23; MS: *m/z* 668.7 $[M+Na]^+$.

3.1.3.5. (*E*)-Ethyl-9,9-dibromo-2,3,4,8,9-pentadeoxy-5,6,7-tri-*O*-trimethylsilyl-D-*gluco*-nona-2,8-dienoate (23). The compound **23** was prepared by general procedure 3 from **16** (1.06 g, 4.53 mmol). The crude residue was purified by flash chromatography (Cyclohexane/EtOAc 99:1), and **23** was obtained as a colorless oil (1.6 g, 59%). R_f=0.5 (Cyclohexane/EtOAc 95:5); $[\alpha]_D^{23}$ +9 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$): ν_{max} 1730, 840, and 750 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.90 (ddd, 1H, *J*=7.7, 7.9, 15.7 Hz, 3-H), 6.53 (d, 1H, *J*=9.0 Hz, 8-H), 5.82 (d, 1H, *J*=15.7 Hz, 2-H), 4.41 (dd, 1H, *J*=3.4, 9.0 Hz 7-H), 4.16 (q, 2H, *J*=7.1 Hz, OCH_2CH_3), 3.68 (m, 1H, 5-H), 3.57 (dd, 1H, *J*=3.4, 5.1 Hz, 6-H), 2.48 (m, 1H, 4a-H), 2.31 (m, 1H, 4b-H), 1.19 (t, 3H, OCH_2CH_3), 0.08–0.11 (s, 27H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 166.3, 146.8, 139.3, 123.5, 90.6, 78.6, 73.8, 73.2, 60.0, 36.4, 14.2, 0.5–0.6; Anal. Calcd for $C_{20}H_{40}Br_2O_5Si_3$: C, 39.73; H, 6.67. Found: C, 39.98; H, 6.83; MS: *m/z* 627.6 $[M+Na]^+$.

3.1.3.6. (*E*)-Ethyl-9,9-dibromo-2,3,8,9-tetradeoxy-4,5,6,7-tetra-*O*-trimethylsilyl-D-*manno*-nona-2,8-dienoate (24). The compound **24** was prepared by general procedure 3 from **17** (1.45 g, 5.79 mmol). The crude residue was purified by flash chromatography (Hexane/CH_2Cl_2 7:3), and **24** was obtained as a colorless oil (2 g, 50%). R_f=0.7 (Hexane/EtOAc 95:5); $[\alpha]_D^{23}$ +9 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): ν_{max} 1730, 840, and 750 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.05 (dd, 1H, *J*=4.1, 15.7 Hz, 3-H), 6.57 (d, 1H, *J*=8.7 Hz, 8-H), 6.00 (dd, 1H, *J*=1.8, 15.7 Hz, 2-H), 4.31 (ddd, 1H, *J*=1.8, 4.1, 6.3 Hz, 4-H), 4.28 (dd, 1H, *J*=2.6, 8.7 Hz, 7-H), 4.20 (q, 2H, *J*=7.1 Hz, OCH_2CH_3), 3.67 (dd, 1H, *J*=2.6, 6.3 Hz, 6-H), 3.56 (t, 1H, *J*=6.3 Hz, 5-H), 1.28 (t, 3H, OCH_2CH_3), 0.09–0.14 (s, 36H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 167.0, 148.6, 138.9, 122.1, 91.7, 76.6, 74.6, 73.8, 60.3, 14.5, 0.9–1.1; Anal. Calcd for $C_{23}H_{48}Br_2O_6Si_4$: C, 39.88; H, 6.98. Found: C, 40.11; H, 6.75; MS: *m/z* 713.7 $[M+Na]^+$.

3.1.3.7. (*E*)-Ethyl-8,8-dibromo-2,3,4,7,8-pentadeoxy-5,6-di-*O*-trimethylsilyl-D-*ribo*-octa-2,7-dienoate (25). The compound **25** was prepared by general procedure 3 from **18** (1.03 g, 5.04 mmol). The crude residue was purified by flash chromatography (Pentane/Et_2O 98:2), and **25** was obtained as a colorless oil (1.44 g, 57%). R_f=0.8 (Hexane/EtOAc 95:5); $[\alpha]_D^{23}$ −13 (*c* 0.9, $CHCl_3$); IR ($CHCl_3$): ν_{max} 1728, 840, and 750 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.95 (ddd, 1H, *J*=7.2, 7.8, 15.7 Hz, 3-H), 6.35 (d, 1H, *J*=8.0 Hz, 7-H), 5.85 (d, 1H, *J*=15.7 Hz, 2-H), 4.20 (m, 3H, 6-H, OCH_2CH_3), 3.70 (m, 1H, 5-H), 2.35 (m, 2H, 4a-H, 4b-H), 1.20 (t, 3H, OCH_2CH_3), 0.49–0.76 (s, 18H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 166.4, 145.8, 139.0, 124.0, 90.6, 76.8, 75.1, 60.3, 36.9, 14.6, 0.4–0.7; Anal. Calcd for $C_{16}H_{30}Br_2O_4Si_2$: C, 38.25; H, 6.02. Found: C, 38.33; H, 6.31; MS: *m/z* 525.4 $[M+Na]^+$.

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