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A convenient synthesis of *S*-glycosyl donors of sialic acid and their use for *O*-glycosylation*

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ABSTRACT

Sialic acid *S*-glycosyl donors were prepared efficiently in one step by use of *S*,*S*′-bis(1-phenyl-1*H*-tetrazol-5-yl) dithiocarbonate (**2**) and used for *O*-glycosylation. The reaction of **2** with methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate gave methyl [1-phenyl-1*H*-tetrazol-5-yl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-*glycero*-α- (**4**) and -β-D-*galacto*-2-nonulopyranosid]onate (**5**), and 1-phenyl-1*H*-tetrazol-5-yl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranoside)thionate. Compounds **4** and **5** could be applied to the synthesis of a sialosyl-(2→6′)-lactose derivative and cholester-3-yl sialoside, respectively.

INTRODUCTION

Preparation of *S*-glycosides as stable donors for *O*-glycosylation has been reported many times[2–17]. Usually, glycosyl halides and, in rare cases, 1-*O*-acetyl sugars[2] have been used as starting materials to prepare *S*-glycosides which were subsequently converted into *O*-glycosyl compounds by various activating methods. Recently, we reported the use of the coupling reagent, *S*,*S*′-bis(1-phenyl-1*H*-tetrazol-5-yl) dithiocarbonate (**2**) for the formation of esters, macrolids, and peptides[18]. This reagent could also be applied to a single-step synthesis of allylic sulfides having the 1-phenyltetrazole-5-thio group starting from allylic alcohols[1]. Apparently, this reagent is able to react with hydroxy groups of allylic, benzylic, and propargyl alcohols, and hemiacetals, which easily generate stable carbenium intermediates. The aforementioned results prompted us to apply this reagent to the *S*-glycosylation of anomeric hydroxy groups of sugars, particularly to sialic acid. We report herein the preparation of *S*-glycosyl donors from methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate (**1**) by use of **2**, and demonstrate that the *S*-glycosyl donors **4**, **5** derived from sialic acid, could be applied to the *O*-glycosylation of suitable promoters.

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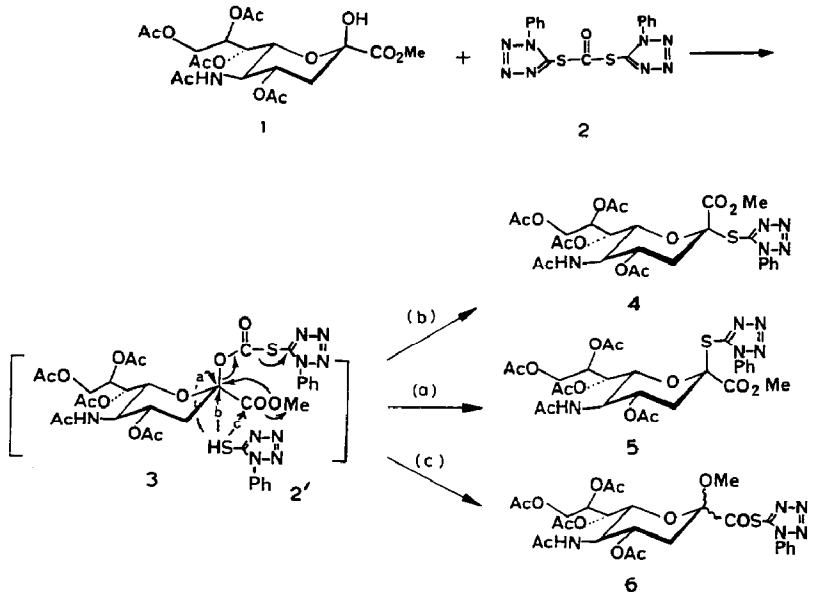
TABLE I

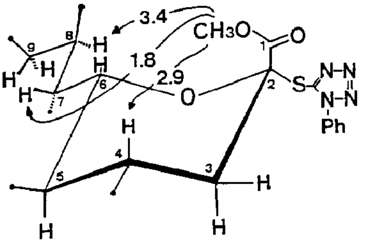
Yields of formation of **4**, **5**, and **6** in various solvents

Product	*Yield* (%)	
	Triethylamine	*4-Dimethylaminopyridine*
4	28	23
5	18	53
6	28	10

RESULTS AND DISCUSSION

Treatment of **1** with **2** in acetonitrile in the presence of triethylamine or 4-dimethylaminopyridine afforded the stable *S*-glycosides, methyl [1-phenyl-1*H*-tetrazol-5-yl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-*glycero*-*α*- (**4**) and -*β*-D-*galacto*-2-nonulopyranosid]onate (**5**), and 1-phenyl-1*H*-tetrazol-5-yl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranoside)thionate (**6**) in fair yield (Table I). When 4-dimethylaminopyridine was used as a base, the *β*-D anomer **5** was the main product. In ^{1}H-n.m.r. spectroscopy, **4** showed the presence of a signal at δ 3.26 due to H-3*e*, whereas **5** showed the presence of a signal at δ 2.89 due to H-3*e*. The coupling constant $J_{7,8}$ was 2.3 for **4**, and 8.0 Hz for **5**. These values are quite different from those for *N*-acetylneuraminic acid derivatives[19,20] (H-3*e* doublets of doublets at the lower field δ 2.6–2.9 for the *α*-D-glycoside and at higher field δ 2.1–2.5 for the *β*-D-glycoside, $J_{7,8}$ value of 7–9 Hz for the *α*-D-glycoside and of 2–3 Hz for the *β*-D-glycoside). The configuration at the anomeric center was not clear from these data





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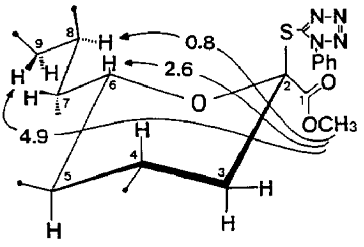


5

alone. One of the most notable differences between **4** and **5** was revealed by an n.O.e difference of 2.9% between the ester methyl protons and H-4*a* of **4**. On the other hand, an n.O.e value was not observed between the ester methyl protons and H-4*a* of **5**. Therefore, we concluded that the anomeric configuration of **4** is *α*-D and that of **5** is *β*-D. The signal due to OMe-2 of **6** appeared at δ 3.23 and that due to H-3*e* was shifted to δ 2.56. From the ^{1}H-n.m.r. data, the anomeric configuration of **6** could not be determined because the coupling constant $J_{7,8}$ was not observed.

In the reaction of **1** with **2**, OH-2 of **1** attacks the carbonyl group of reagent **2** while the sulfur atom of the eliminated 1-phenyltetrazol-5-thio residue (**2'**) attacks C-2 from the *α* (b) or *β* (a) side. Thus, derivatives **4** and **5** were obtained with liberation of carbon dioxide. On the other hand, **6** is formed by nucleophilic attack of **2'** on the methoxy carbonyl group (c), and by subsequent attack of the eliminated methoxyl anion at the anomeric center from the *α* or *β* side.

The usefulness of these sialic acid *S*-glycosyl donors for *O*-glycosylation of sialic acids was demonstrated by glycosylation of **4** and **5** with methanol in the presence of dimethyl(methylthio)sulfonium triflate [$Me_2S(SMe)Tf$], silver triflate (AgOTf), or mercury(II) triflate [$Hg(OTf)_2$][21] as promoters (Table II). In the reaction of **5** with dimethyl-(methylthio)sulfonium triflate as a promoter, the polarity of the solvent may exert

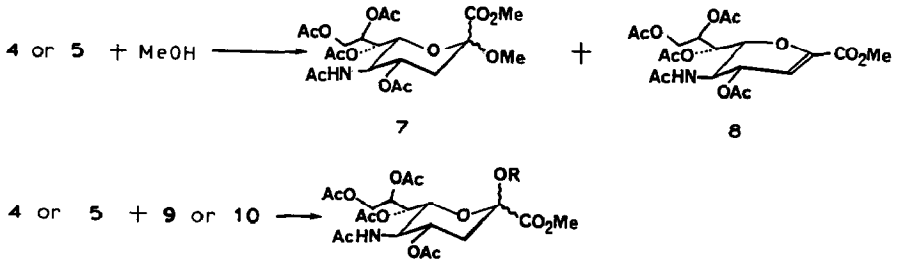
TABLE II

Glycosylation of **4** and **5** with methanol

S-Donor	*Promoter (Molar equiv.)*	*Solvent*	*Time (h)*	*Products (%)*	
				7 (α:β)[a]	**8**
4	$Me_2S(SMe)Tf$ (10)	CH_3CN	24	92 (5:6)	3.2
	AgOTf (20)	CH_2Cl_2	96	56 (1:1)	11.2
	$Hg(OTf)_2$ (20)	CH_3NO_2	1	85 (5:14)	
5	$Me_2S(SMe)Tf$ (10)	CH_3CN	48	66 (9:5)	[b]
	$Me_2S(SMe)Tf$ (10)	CH_2Cl_2	80	10 (10:47)	68
	AgOTf (20)	CH_3CN	24	66 (12:5)	5.1
	AgOTf (20)	CH_2Cl_2	24	87 (10:23)	9.8
	$Hg(OTf)_2$ (20)	CH_3NO_2	1	63 (11:10)	

[a] In parantheses, ratio of *α* to *β* anomer, as estimated from ^{1}H-n.m.r. spectra. [b] Trace.

significant effect on yield, product distribution, and anomeric ratio. In dichloromethane solution, the yield of methyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-nonulopyranosid)onate (**7**) was low, and that of methyl *N*-acetyl-4,7,8,9-tetra-*O*-acetyl-2-deoxy-2,3-dehydro-D-neuraminate[19] (**8**) increased on prolonged reaction time. Although acetonitrile was the best solvent for converting **5** into **7** in the presence of silver triflate by an α-predominant process, the yield of **7** was lower in acetonitrile than in dichloromethane solution. In the case of the reaction of **4** or **5** with methanol in the presence of mercury(II) triflate, the reaction did not require prolonged reaction time. In this instance, the formation of the comparatively short-lived anomeric carbonium ion was diminished. Although the ratios of α to β anomer of **7** in the reaction of **4** in the presence of dimethyl(methylthio)sulfonium triflate or silver triflate were almost the same, the yield was high. From these results, it was concluded that the solvent effect was very important for the α-predominant process. It may be considered that the reaction using silver and mercury(II) triflate occurs *via* an SN2-like mechanism because α-products were favored in the reactions of **5** rather than in those of **4**. These results agree with those of Mukaiyama *et al.*[4] and Hanessian *et al.*[6] who showed that metals promote an SN2-like reaction by remote activation. Furthermore, the ability of polar solvents to circumvent the anomeric effect may favor the α-predominant reaction.



11 R = *O*-(2,3,4-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(1,6-anhydro-2,3-di-*O*-benzyl-β-D-glucopyranosyl)

12 R = cholester-3-yl

Finally, the *S*-glycosyl donors **4** and **5** were used for the synthesis of a sialosyl-(2→6′)-lactose derivative[22] (**11**) and cholester-3-yl sialoside derivative[23] (**12**) under the conditions described above[23] (Table III). In the reaction of **5** with 5 equiv. of *O*-(2,3,4,-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-1,6-anhydro-2,3-di-*O*-benzyl-β-D-glucopyranose (**9**) in the presence of silver triflate, although the solvent acetonitrile exerted a considerable effect in favor of the formation of the α-D anomer, the total yield was lower than in dichloromethane solution. Similar results were obtained in the reaction of **4** with the lactose derivative. On the other hand, the yield of **10** was better when **5** rather than **4** was used as the starting material under the same conditions. The reaction of cholesterol (**10**) with a mixture of **4** and **5** gave only a single product (**12**) in fair yield. In these reactions, the ratios of anomers and yields would be affected by the bulk of the reactant alcohol, solvent effects, and anomeric effect. In conclusion, **2** is a versatile reagent for the

TABLE III

Glycosylation of *O*-(2,3,4-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-1,6-anhydro-2,3-di-*O*-benzyl-β-D-glucopyranose (**9**) and cholesterol (**10**) with **4** and **5**

S-*Donor*	*Acceptor*	*Promoter*	*Solvent*	*Time (h)*	*Product*[a]	*Yield (%)*	*Ratio of α to β anomer*[b]
4	**9**	AgOTf	CH_3CN	96	**11**	10	21:10
4	**9**	AgOTf	CH_2Cl_2	24	**11**	34	10:28
4	**10**	AgOTf	CH_2Cl_2	72	**12**	23	β[c]
4,5	**10**	AgOTf	CH_2Cl_2	24	**12**	64	β[d]
5	**9**	AgOTf	CH_3CN	24	**11**	21	15:10
5	**9**	AgOTf	CH_2Cl_2	24	**11**	54	1:5
5	**10**	$Hg(OTf)_2$	CH_3NO_2	1	**12**	6	1:2
5	**10**	AgOTf	CH_2Cl_2	24	**12**	70	10:85

[a] The structure of the compounds was confirmed by comparison with authentic samples[22,23]. [b] Estimated from the ^{1}H-n.m.r. spectra. [c] Trace of α anomer. [d] Only β anomer.

synthesis of *S*-glycosyl donors, and *O*-glycosylation with these *S*-glycosyl donors were performed in the presence of several promoters.

EXPERIMENTAL

General methods. — Melting points were determined with a Yamato melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO-JIP-4 digital polarimeter. Field-desorption mass spectra (f.d.m.s.), fast atom bombardment mass spectra (f.a.b.-m.s.), and infrared (i.r.) spectra were recorded with JEOL JMS-DX300, JMS-3100, and JASCO IR-A2 instruments, respectively. The ^{1}H-n.m.r. spectra were recorded for solutions in (^{2}H)chloroform containing tetramethylsilane (Me_4Si) as an internal standard with Varian XL-300 and XL-400 spectrometers. Thin-layer chromatography (t.l.c.) was performed on Silica Gel GE_{254} (Merck) plates, and the spots were detected by ultraviolet (u.v.) irradiation and with 5% H_2SO_4 solution. Mercury(II) triflate was prepared *in situ* by the reaction of an equimolar mixture of triflic anhydride and dry mercuric(II) oxide (yellow) at 50° and 1.3 Pa for 5 h in dry nitromethane with stirring overnight under Ar atmosphere[21].

Reaction of methyl 5-acetamido-4,7,8,9-tetra-O-*acetyl-3,5-dideoxy*-D-glycero-β-D-galacto-*2-nonulopyranosonate* (**1**) *with* S,S′-*bis(1-phenyl*-1H-*tetrazol-5-yl) dithiocarbonate* (**2**). — A typical experimental procedure was as follows. A solution of 4-dimethylaminopyridine (33 mg, 0.27 mmol) in acetonitrile (1 mL) was added to **2** (105 mg, 0.28 mmol) and **1** (123 mg, 0.25 mmol) in acetonitrile (10 mL) under stirring at room temperature. After 24 h, the solvent was evaporated and ethyl acetate was added to the residue. The organic layer was washed with 4% aq. $NaHCO_3$, 0.5M HCl, and saturated NaCl, and dried (Na_2SO_4). The residue was subjected to t.l.c. on silica gel (in 1:1 benzene–ethyl acetate or 1:1:3 ether–ethyl acetate–chloroform) to afford **4**, **5**, and **6**.

Compound **4**. Foam (38 mg, 23%), $[\alpha]_D^{27}$ −23° (*c* 0.91, chloroform); υ_{max}^{film} 3300, 3000, 1750, and 1670 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$, 400 MHz): δ 1.82, 1.97, 1.99, 2.04 [4s, 4 ×

3 H, $(COCH_3)_4$], 2.16 (s, 3 H, NHCOCH_3), 2.38 (dd, 1 H, *J* 11.4, 13.8 Hz, H-3*a*), 3.86 (s, 3 H, CO_2CH_3), 3.26 (dd, 1 H, *J* 5.0, 13.8 Hz, H-3*e*), 3.90 (dd, 1 H, *J* 2.3, 1.5 Hz, H-6), 4.16 (dd, 1 H, *J* 7.5, 12.8 Hz, H-9a), 4.33 (q, 1 H, *J* 10.5, 10.5, 10.5 Hz, H-5), 4.70 (dd, 1 H, *J* 2.3, 12.8 Hz, H-9b), 5.14 (dt, 1 H, *J* 2.3, 2.3, 7.5 Hz, H-8), 5.37 (t, 1 H, *J* 2.3, 2.3 Hz, H-7), 5.61 (dt, 1 H, *J* 5.0, 11.4, 10.5 Hz, H-4), 5.69 (d, 1 H, *J* 10.5 Hz, N*H*COCH$_3$), 7.46–7.56 (m, 3 H, Ph), and 7.88–7.94 (m, 2 H, Ph); f.a.b.-m.s.: *m/z* 652 (M + 1).

Anal. Calc. for $C_{27}H_{33}N_5O_{12}S{\cdot}H_2O$: C, 48.42; H, 5.26; N, 10.45. Found: C, 48.68; H, 5.00; N, 10.39.

Compound **5**. Foam (87 mg, 53%), $[\alpha]_D^{27}$ +45° (*c* 0.97, chloroform); υ_{max}^{film} 3350, 3000, 1750, and 1670 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$, 400 MHz); δ 1.86, 1.98, 2.02, 2.03 [4s, 4 × 3 H, $(COCH_3)_4$], 2.07 (s, 3 H, NHCOCH_3), 2.47 (dd, 1 H, *J* 12.0, 13.0 Hz, H-3*a*), 2.89 (dd, 1 H, *J* 4.9, 13.0 Hz, H-3*e*), 3.90 (dd, 1 H, *J* 5.5, 13.0 Hz, H-9a), 3.91 (q, 1 H, *J* 10.0, 10.5, 11.0 Hz, H-5), 4.06 (dd, 1 H, *J* 3.0, 13.0 Hz, H-9b), 4.20 (dd, 1 H, *J* 2.0, 11.0 Hz, H-6), 4.88 (ddd, 1 H, *J* 3.0, 5.5, 8.0 Hz, H-8), 4.90 (dt, 1 H, *J* 4.9, 10.5, 12.0 Hz, H-4), 5.18 (dd, 1 H, *J* 2.0, 8.0 Hz, H-7), 5.38 (d, 1 H, *J* 10.0 Hz, N*H*COCH$_3$), 3.78 (s, 3 H, CO_2CH_3), 7.52–7.60 (m, 3 H, Ph), and 7.70–7.75 (m, 2 H, Ph); f.a.b.-m.s.: *m/z* 652 (M + 1).

Anal. Calc. for $C_{27}H_{33}N_5O_{12}S{\cdot}0.5H_2O$: C, 49.08; H, 5.18; N, 10.6. Found: C, 48.93; H, 5.06; N, 10.37.

Compound **6**. Foam (16 mg, 10%), $[\alpha]_D^{24}$ −195° (*c* 1.1, chloroform); υ_{max}^{film} 3350, 3000, 1740, and 1670 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$, 400 MHz): δ 1.93, 1.94, 2.09, 2.11 [4s, 4 × 3 H, $(COCH_3)_4$], 2.12 (s, 3 H, NHNOCH_3), 2.15 (dd, 1 H, *J* 11.0, 14.6 Hz, H-3*a*), 2.56 (dd, 1 H, *J* 4.8, 14.6 Hz, H-3*e*), 3.23 (s, 3 H, OCH_3), 7.52–7.58 (m, 3 H, Ph), 3.86 (dd, 1 H, *J* 9.0, 12.1 Hz, H-9a), 4.23 (q, 1 H, *J* 10.5, 10.5, 10.5 Hz, H-5), 4.57 (dd, 1 H, *J* 2.1, 12.1 Hz, H-9b), 4.97 (dd, 1 H, *J* 2.0, 10.5 Hz, H-6), 5.24 (dt, 1 H, *J* 4.8, 11.0, 10.5 Hz, H-4), 5.70–5.75 (m, 2 H, H-7,8), 6.56 (d, 1 H, *J* 10.5 Hz, N*H*COCH$_3$), 7.52–7.58 (m, 3 H, Ph), and 7.60–7.66 (m, 2 H, Ph); f.a.b.-m.s.: *m/z* 652 (M + 1).

Anal. Calc. for $C_{27}H_{33}N_5O_{12}S{\cdot}H_2O$: C, 48.42; H, 5.26; N, 10.45. Found: C, 48.80; H, 4.98; N, 9.97.

*Glycosylation of methanol with methyl [1-phenyl-1*H*-tetrazol-5-yl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-*D-glycero-α- (**4**) *or* -β-D-galacto-*2-nonulopyranosid]onate* (**5**). — A typical experiment was as follows. Silver triflate (514 mg, 2 mmol) was added to a mixture of **5** (65.1 mg, 0.1 mmol), methanol (32 mg, 1 mmol), and molecular sieves 4A (400 mg) in dichloromethane (6 mL) under Ar at 0°. After 4 h, the mixture was stirred for 20 h at room temperature, and neutralized with triethylamine. Insoluble materials were removed by filtration, the filtrate was concentrated, and the residue was purified by t.l.c. on silica gel in 2:1 benzene–acetone to give **7** (44 mg, 87%) and **8** (4.6 mg, 9.8%). The ^{1}H-n.m.r. spectra of **7** and **8** were in agreement with previous reports[24,19]. The ratio of α to β anomers of **7** was estimated by integration of the H-3*e* signal in the ^{1}H-n.m.r. spectrum; α anomer: δ 2.55 (dd, *J* 4.5, 12.5 Hz, H-3*e*); β anomer: δ 2.41 (dd, *J* 5.0, 13.0 Hz, H-3*e*).

Condensation of O-*(2,3,4-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-1,6-anhydro-2,3-di-*O*-benzyl-β-D-glycopyranose* (**9**) *or cholesterol* (**10**) *with methyl [1-phenyl-1*H*-tetrazol-5-yl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-*D-glycero-α- (**4**) *or*

-β-D-galacto-*2-nonulopyranosid]onate* (**5**). — A typical glycosylation was as follows. Silver triflate (514 mg, 2 mmol) was added to the mixture of **5** (65.1 mg, 0.1 mmol), **9** (382 mg, 0.5 mmol), and molecular sieves 4A (400 mg) in dichloromethane (10 mL) under Ar at 0°. After 4 h, the mixture was stirred for 20 h at room temperature, and then neutralized with triethylamine. Insoluble materials were removed by filtration, the filtrate was concentrated, and the residue purified by t.l.c. on silica gel in 19:1 chloroform–methanol to give **11** (69 mg, 54%). The t.l.c. value and ^{1}H-n.m.r. spectrum of **11** were in agreement with those of an authentic sample. The ratio of *α* to *β* anomer of **11** was estimated by integration of the H-3*e* signal in the ^{1}H-n.m.r. spectrum; *α* anomer of **11**: *δ* 2.57 (dd, *J* 4.8, 12.8 Hz, H-3*e*); *β* anomer of **11**: *δ* 2.29 (dd, *J* 4.8, 12.8 Hz, H-3*e*); *α* anomer of **12**: *δ* 2.59 (dd, *J* 5.2, 13.0 Hz, H-3*e*); and *β* anomer of **12**: *δ* 2.52 (dd, *J* 4.9, 13.1 Hz, H-3*e*).

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