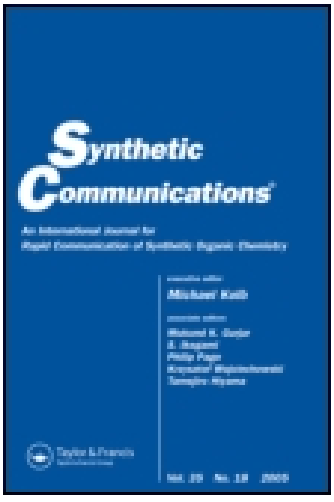

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Microwave-Enhanced Ferrier Reaction: A Facile Synthesis of 2,3-Unsaturated-O-Glycosides Under Solvent-Free Conditions

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Microwave-Enhanced Ferrier Reaction: A Facile Synthesis of 2,3-Unsaturated-*O*-Glycosides Under Solvent-Free Conditions

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Abstract: A variety of 2,3-unsaturated-*O*-glycosides have been prepared by the Ferrier rearrangement of acetyl protected glycals under microwave irradiation using silica gel as an acid catalyst. Environmental friendliness, high yields, and short reaction times are the key features of this method. Furthermore, the method was applicable not only to the Ferrier reaction of 3,4,6-tri-*O*-acetyl glucal and 3,4,6-tri-*O*-acetyl galactal but also to the Ferrier reaction of 3,4-di-*O*-acetyl arabinal.

Keywords: Ferrier rearrangement, glycosylation, microwave, 2,3-unsaturated-*O*-glycosides

2,3-Unsaturated-*O*-glycosides or pseudoglycals obtained by Ferrier rearrangement represent versatile chiral intermediates toward the synthesis of biologically active compounds such as glycopeptide building blocks, oligosaccharides, and modified carbohydrates. They have also been employed in the synthesis of some important antibiotics and nucleosides.

Since Ferrier discovered that 2,3-unsaturated-*O*-glycosides **3** could be obtained from the reaction of corresponding glycal derivatives **1** with various alcohols **2** in the presence of $BF_3 \cdot Et_2O$ in 1969, a number of Lewis acids such as $BF_3 \cdot Et_2O$,[1] $ZnEt_2$,[2] $FeCl_3$,[3] $Sc(OTf)_3$,[4] $LiBF_4$,[5] $InCl_3$,[6]

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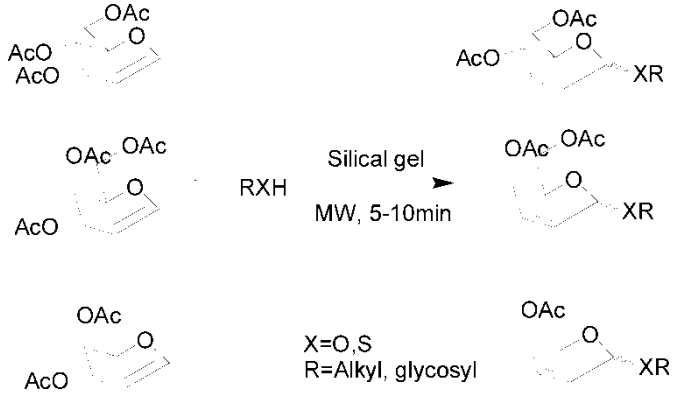
$Yb(OTf)_3$,[7] montmorillonite K10,[8] $BiCl_3$,[9] $InBr_3$,[10] $Dy(OTf)_3$,[11] $CeCl_3 \cdot 7H_2O$,[12] $ZnCl_2$,[13] and $ZrCl_4$[14] were employed in this reaction. Other catalysts used for this include iodonium dicollidinium perchlorate,[15] DDQ,[16] $Ce(NH_4)_2(NO_3)_6$,[17] $Bi(NO_3)_3 \cdot 5H_2O$, and $Ce(NH_4)_2(NO_3)_6$.[18] Very recently, $HClO_4 \cdot SiO_2$ was found to be effective for the Ferrier rearrangement.[19] Despite their usefulness, many of these methods require harsh reaction conditions, such as strong acidity, longer reaction times, higher temperature, unsatisfactory yields, and low stereoselectivity.

Another common method for the Ferrier reaction is microwave irradiation using montmorillonite K10 as a catalyst,[8] but a great quantity of the catalyst and chlorobenzene as a solvent are required in the procedure, both of which are dangerous and pollute the environment. Hotha also reported the Ferrier reaction under microwave irradiation, but still a metal catalyst $NbCl_5$ was necessary.[20] In the view of this, there is a need to develop an economical and green method to yield 2,3-unsaturated-*O*-glycosides.

Herein we report a method for the synthesis of 2,3-unsaturated-*O*-glycosides under solvent-free and microwave irradiation conditions using silica gel as a catalyst which is environment-friendly than any of the previous catalysts used for Ferrier rearrangement.

RESULTS AND DISCUSSION

The method reported in this article allows the reaction of several alcohols, including primary, secondary, allylic, benzylic, and monosaccharide alcohols, with three kinds of glycals to yield the corresponding 2,3-unsaturated-*O*-glycosides in high yields with good to high α-selectivity. Thiol was successfully used instead of alcohols to give 2,3-unsaturated thioglycosides (Scheme 1).



Scheme 1.

The application of microwave irradiation and silica gel as a catalyst improved the safety aspects, avoided poisonous solvents, and made the reaction times much shorter. Also it was more environmentally friendly than previous methods. The silica gel catalyst could be removed from the reaction mixture by simple filtration and recycled. The drawback of our method was that a large excess of alcohols **2** was needed to dissolve glycals, but they could be reclaimed according to the procedure.

In the first set of experiments, 3,4,6-tri-*O*-acetyl glucal was treated with a batch of alcohols in the presence of silica gel under microwave irradiation to afford the corresponding 2,3-unsaturated-*O*-glycosides in high yields. All the reactions were complete in less than 10 min. In addition, in the case of 3,4,6-tri-*O*-acetyl galactal and 3,4-di-*O*-acetyl arabinal, the reactions went smoothly under these conditions. Though the yields were a bit inferior to its glucal counterpart, the α-selectivity increased remarkably (entries m–s, Table 1). A limitation of the procedure was that α-selectivity of some 2,3-unsaturated-*O*-glycosides was not higher than that in the previous study.[8] We are unable to explain this lack of stereoselectivity at present; such results may have arisen from the different reaction conditions such as catalyst, microwave power, and solvent.

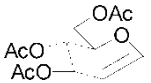
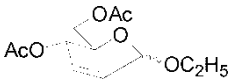
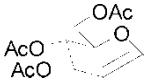
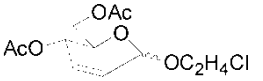
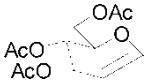
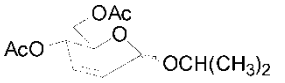
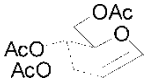
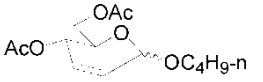
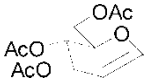
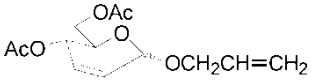
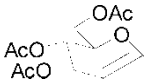
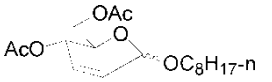
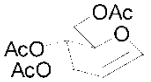
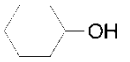
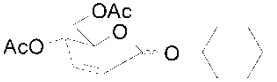
We also investigated the influence of microwave power on these reactions and found that a power of 650 W was most appropriate. When the microwave power was dropped, the reaction times were prolonged and the yields were decreased. But interestingly, the α-selectivity increased moderately (entries t–v, Table 1). Reactions were not processed if the microwave power was less than 260 W.

Untill now, not many methods are available for the Ferrier reaction of 3,4,6-tri-*O*-acetyl galactal and as far as we know, nobody has reported the Ferrier reaction of 3,4-di-*O*-acetyl arabinal. To extend the type of reaction, we developed our approach for the glycosidation of 3,4,6-tri-*O*-acetyl galactal and 3,4-di-*O*-acetyl arabinal. The result revealed that the method was applicable not only to hexose but also to pentaose.

A mixture of two anomers of 2,3-unsaturated-*O*-glycosides (α and β) were obtained, the ratio of which was determined by comparing the integration values of the peaks in ^{1}H NMR analysis (Table 1). The α-configuration of the major product was confirmed from the positions of the anomeric protons in the ^{1}H NMR data, compared with the literature data.[19,21] For further confirmation of α-configuration, NOE analysis was carried out for the major products, in which NOE was observed between H-1 and H-4 in all 2,3-unsaturated-*O*-glucosides and no nuclear overhauser effect (NOE) was observed between H-1 and H-4 of 2,3-unsaturated-*O*-galactosides and arabinosides. From the NOE analysis, a conclusion could be drawn that in the case of 2,3-unsaturated-*O*-glucosides, H-1 and H-4 are on the same side, and in the case of 2,3-unsaturated-*O*-galactosides and arabinosides, H-1 and H-4 are on the opposite side, which is possible only in the case of α-configuration.

In conclusion, we explored a simple, economical, rapid, green method for the synthesis of 2,3-unsaturated-*O*-glycosides by the Ferrier reaction in high

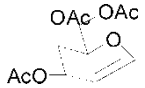
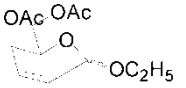
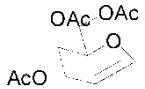
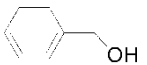
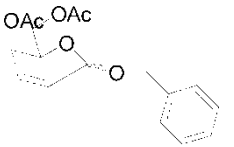
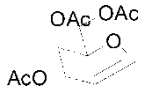
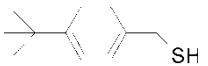
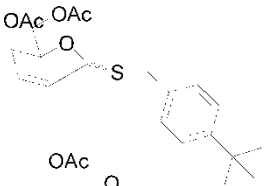
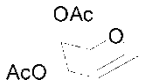
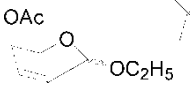
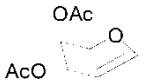
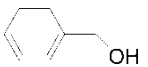
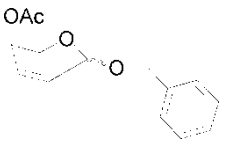
Table 1. Synthesis of 2,3-unsaturated-*O*-glycosides by the Ferrier reaction

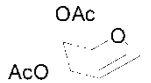
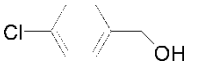
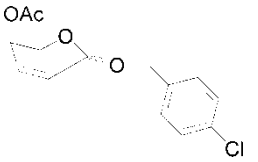
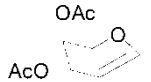
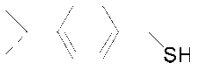
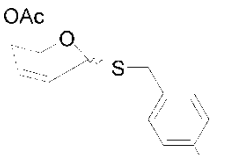
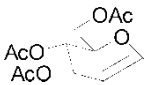
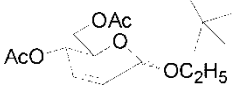
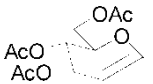
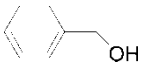
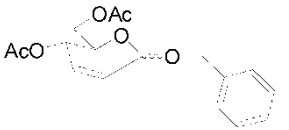
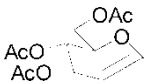
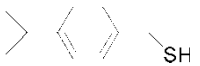
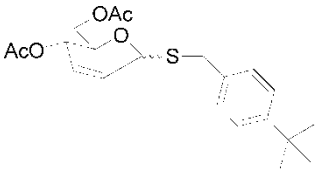
Entry	Glycals (**1**)	Acceptors (**2**)	Products (**3**)	Time (min)	Yield (%)[a]	α/β[b]	Power (W)
a		C_2H_5OH		5	87	3/1	650
b		ClC_2H_4OH		5	25	5/1	650
c		$(CH_3)_2CHOH$		8	91	4/1	650
d		$n\text{-}C_4H_9OH$		8	82	5/1	650
e		$CH_2{=}CHCH_2OH$		8	71	5/1	650
f		$n\text{-}C_8H_{17}OH$		8	85	3/1	650
g				10	81	4/1	650

h				10	92	5/1	650
i				10	91	6/1	650
j				10	93	5/1	650
k				8	90	3/1	650
l				10	63	2/1	650

(*continued*)

Table 1. Continued

Entry	Glycals (**1**)	Acceptors (**2**)	Products (**3**)	Time (min)	Yield (%)[a]	α/β[b]	Power (W)
m		C_2H_5OH		10	78	11/1	650
n				10	87	14/1	650
o				8	80	>20/1	650
p		C_2H_5OH		10	60	5/1	650
q				10	70	9/1	650

r				10	64	8/1	650
s				8	71	>20/1	650
t		C_2H_5OH		10	74	5/1	280
u				25	70	6/1	280
v				55	63	3/1	280

[a]All yields are isolated yields after column chromatography.
[b]The α/β ratio were determined by comparing the integration values of the peaks in ^{1}H NMR analysis.

yields with good to high α selectivity. Furthermore, the method was applicable not only to the Ferrier reaction of 3,4,6-tri-*O*-acetyl glucal and 3,4,6-tri-*O*-acetyl galactal but also to the Ferrier reaction of 3,4-di-*O*-acetyl arabinal.

EXPERIMENTAL

The Ferrier reactions were carried out using microcomputer microwave reactor LWMC 201. The silica gel (200–300 mesh, reagent grade) was obtained commercially (Qingdao, China) and was not pretreated. Infrared spectra were recorded on a Bruck Vector 200 spectrophotometer. NMR spectra were recorded on a Brucker Advance DMX 400-MHz spectrometer with TMS as the internal standard. Chemical shifts are expressed in parts per million (ppm). Elemental analysis was carried out on Carlo ERBA-1108 analyzer.

General Procedure for the Preparation of 2,3-Unsaturated-*O*-Glycosides (3)

All reactions were carried out in an open vessel, sealed with a piece of film. Silica gel (100 mg) was added to a mixture of glycal (1 mmol) and alcohol (8–10 mmol). The mixture was irradated with microwaves for the specified period of time. The process was monitored by TLC. After completion of the reaction, the excessive alcohol was recycled. The reaction mixture was diluted with ethanol and filtered. The combined organic extract was concentrated under vacuum. All the products were purified by column chromatography over silica gel (using different ratios of ethyl acetate and petroleum ether as eluent according to different products).

All known compounds gave NMR spectra that matched data reported in the cited references. New compounds are characterized according to identity and purity. Spectral data of products that are not reported are listed next.

Data

Cyclohexyl 4,6-di-O-acetyl-2,3-dideoxy-erythro-hex-2-eno-D-glucopyranoside (3 g): Colorless oil. IR (neat): 2933, 2858, 1744, 1450, 1370, 1231, 1038, 911, 734 cm^{-1}; ^1H NMR ($CDCl_3$) α-configuration. δ 5.92–5.80 (m, 2 H, H-2, H-3), 5.29 (d, 0.80 H, $J = 9.6$ Hz, H-4), 5.17 (s, 0.80 H, H-1), 4.24–3.97 (m, 3 H, α, H-5, H-6), 3.70–3.59 (m, 1 H, OCH) 2.09, 2.08 (2 × s, 6 H, 2 × $COCH_3$), 1.56–1.18 (m, 10 H, cyclohexanol-H); β-configuration. δ 5.92–5.80 (m, 2 H, H-2, H-3), 5.25 (br s, 0.20 H, H-4), 5.21 (br s, 0.20 H, H-1), 4.24–3.97 (m, 3 H, α, H-5, H-6), 3.70-3.59 (m, 1 H, OCH) 2.09, 2.08 (2 × s, 6 H, 2 × $COCH_3$), 1.56–1.18 (m, 10 H, cyclohexanol-H); ^{13}C NMR ($CDCl_3$): δ 170.66 (C, CO), 170.20 (C, CO), 128.67 (C, Gly-C), 128.50 (C, Gly-C), 92.80 (C, Gly-C), 72.60 (C, Gly-C), 66.70 (C, Gly-C),

65.39 (C, Gly-C), 63.10 (C, cyclohexanol-C), 33.60 (2 C, cyclohexanol-C), 29.60 (C, cyclohexanol-C), 25.51 (2 C, cyclohexanol-C) 24.31 (C, CH3CO), 20.91 (C, CH_3CO). Anal. calcd. for $C_{16}H_{24}O_6$ (312): C, 61.52; H, 7.74. Found: C, 61.77; H, 7.98.

Ethyl 4,6-di-O-acetyl-2,3-dideoxy-threo-hex-2-eno-D-galactopyranoside (3 m): Colorless oil. IR (neat): 2926, 1741, 1370, 1230, 1104, 1049 cm^{-1}; ^1H NMR ($CDCl_3$) α-configuration. δ 6.11 (dd, 1 H, $J = 10.0$, 5.6 Hz, H-3), 6.04 (dd, 0.92 H, $J = 10.0$, 3.2 Hz, H-2), 5.12–5.02 (m, 2 H, H-4, H-1), 4.39–4.36 (m, 1 H, H-5), 4.25–4.22 (m, 2 H, H-6), 3.86–3.81 (m, 0.92 H, OCH_2CH_3), 3.63–3.56 (m, 1 H, OCH_2CH_3), 2.08, 2.07 (2 × s, 6 H, 2 × $COCH_3$), 1.25 (t, 3 H, OCH_2CH_3); β-configuration. δ 6.11 (dd, 1 H, $J = 10.0$, 5.6 Hz, H-3), 5.97 (d, 0.09 H, $J = 10.0$ Hz, H-2), 5.12–5.02 (m, 2 H, H-4, H-1), 4.39–4.36 (m, 1 H, H-5), 4.25–4.22 (m, 2 H, H-6), 3.97–3.90 (m, 0.08 H, OCH_2CH_3), 3.63–3.56 (m, 1 H, OCH_2CH_3), 2.08, 2.07 (2 × s, 6 H, 2 × $COCH_3$), 1.25 (t, 3 H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 170.43 (C, CO), 170.19 (C, CO), 130.55 (C, Gly-C), 124.92 (C, Gly-C), 93.56 (C, Gly-C), 70.70 (C, Gly-C), 66.48 (C, Gly-C), 63.77 (C, Gly-C), 62.66 (C, OCH_2), 20.59 (2C, CH_3CO), 15.05 (C, OCH_2CH_3). Anal. calcd. for $C_{12}H_{18}O_6$ (258): C, 55.81; H, 7.02. Found: C, 56.02; H, 7.28.

para-t-Butylbenzyl 4,6-Di-O-acetyl-2,3-dideoxy-threo-hex-2-eno-1-thio-α-D-galactopyranoside (3o): Colorless oil. IR (neat): 2960, 1741, 1515, 1368, 1231, 1052, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34–7.27 (m, 4 H, Ar-H), 6.13–6.10 (m, 1 H, H-3), 5.99 (dd, 1 H, $J = 9.6$, 1.2 Hz, H-2), 5.19 (d, 1 H, $J = 1.2$ Hz, H-1), 5.10–5.08 (m, 1 H, H-4), 4.28–4.26 (m, 2 H, H-6), 3.99–3.95 (m, 2 H, H-5, $PhCH_2$), 3.77 (d, 1 H, $J = 13.2$ Hz, $PhCH_2$), 2.16, 2.09 (2 × s, 6 H, 2 × $COCH_3$), 1.31–1.26 (m, 9 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 170.40 (2 C, CO), 149.94 (C, Ar-C), 134.22 (C, Ar-C), 133.03 (2 C, Ar-C), 128.64 (C, Gly-C), 125.27 (2 C, Ar-C), 124.66 (C, Gly-C), 77.63 (C, Gly-C), 73.79 (C, Gly-C), 63.24 (C, Gly-C), 62.88 (C, Gly-C), 34.31 (C, $PhCH_2$), 32.73 [C, $C(CH_3)_3$], 31.14 [3 C, $C(CH_3)_3$], 20.70 (2 C, CH3CO). Anal. calcd. for $C_{21}H_{28}O_5S$ (392): C, 64.26; H, 7.19. Found: C, 64.49; H, 7.38.

Ethyl 4-O-acetyl-2,3-dideoxy-threo-hex-2-eno-L-arabinopyranoside (3p): Colorless oil. IR (neat): 2977, 1736, 1372, 1237, 1053, 959 cm^{-1}; ^1H NMR ($CDCl_3$) α-configuration. δ 6.05–6.01 (m, 1.68 H, H-2, H-3), 5.01 (d, 0.84 H, $J = 2.4$ Hz, H-1), 4.96–4.94 (m, 0.84 H, H-4), 4.17 (dd, 1 H, $J = 13.2$, 2.8 Hz, H-5), 3.85–3.81 (m, 2 H, H-5, OCH_2CH_3), 3.59–3.52 (m, 1 H, OCH_2CH_3), 2.08 (s, 3 H, $COCH_3$), 1.24 (t, 3 H, OCH_2CH_3); β-configuration. δ 5.96–5.85 (m, 0.32 H, H-2, H-3), 5.29–5.26 (m, 0.16 H, H-4), 4.95 (br s, 0.16 H, H-1), 3.87–3.81 (m, 3 H, H-5, OCH_2), 3.57–3.52 (m, 1 H, OCH_2), 2.08 (s, 3 H, $COCH_3$), 1.24 (t, 3 H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 170.43 (C, CO), 170.19 (C, CO), 130.55 (C, Gly-C), 124.92 (C, Gly-C), 93.56 (C, Gly-C), 70.70 (C, Gly-C), 66.48 (C, Gly-C), 63.77

(C, Gly-C), 62.66 (C, OCH_2), 20.59 (2 C, CH_3CO), 15.05 (C, OCH_2CH_3). Anal. calcd. for $C_9H_{14}O_4$ (186): C, 58.05; H, 7.58. Found: C, 58.31; H, 7.79.

Benzyl 4-O-acetyl-2,3-dideoxy-threo-hex-2-eno-L-arabinopyranoside (3q): Colorless oil. IR (neat): 3032, 2924, 1739, 1455, 1371, 1235, 1041, 958, 911, 733, 698 cm^{-1}; ^1H NMR ($CDCl_3$) α-configuration. δ 7.36–7.29 (m, 5 H, Ar-H), 6.07–5.86 (m, 2 H, H-2, H-3), 5.09 (d, 0.90 H, $J = 2.8$ Hz, H-1), 4.96–4.95 (m, 0.90 H, H-4), 4.78 (d, 0.90 H, $J = 12.0$ Hz, $PhCH_2$), 4.58 (d, 1 H, $J = 12.0$ Hz, $PhCH_2$), 3.89–3.85 (m, 2 H, H-5), 2.07 (s, 3 H, $COCH_3$); β-configuration. δ 7.36–7.29 (m, 5 H, Ar-H), 6.07–5.86 (m, 2 H, H-2, H-3), 5.33–5.30 (m, 0.10 H, H-4), 5.04 (br s, 0.10 H, H-1), 4.82 (d, 0.10 H, $J = 12.0$ Hz, $PhCH_2$), 4.58 (d, 1 H, $J = 12.0$ Hz, $PhCH_2$), 3.89–3.85 (m, 2 H, H-5), 2.07 (s, 3 H, $COCH_3$); ^{13}C NMR ($CDCl_3$): δ 169.44 (C, CO), 136.56 (C, Ar-C), 129.02–126.64 (5 C, Ar-C), 127.98 (C, Gly-C), 127.33 (C, Gly-C), 92.17 (C, Gly-C), 68.95 (C, Gly-C), 63.94 (C, Gly-C), 59.00 (C, $PhCH_2$), 19.88 (2 C, CH_3CO). Anal. calcd. for $C_{14}H_{16}O_4$ (248): C, 67.73; H, 6.50. Found: C, 67.52; H, 6.21.

para-Chlorobenzyl 4-O-acetyl-2,3-dideoxy-threo-hex-D-eno-L-arabinopyranoside (3r): Colorless oil. IR (neat): 2884, 2361, 1738, 1492, 1371, 1236, 1038, 960, 895, 744, 608 cm^{-1}; ^1H NMR ($CDCl_3$) α-configuration. δ 7.33–7.27 (m, 4 H, Ar-H), 6.09–6.02 (m, 1.78 H, H-2, H-3), 5.07 (d, 0.89 H, $J = 3.2$ Hz, H-1), 4.97–4.95 (m, 0.89 H, H-4), 4.74 (d, 0.89 H, $J = 12.0$ Hz, $PhCH_2$), 4.55 (d, 0.89 H, $J = 12.0$ Hz, $PhCH_2$), 3.88–3.79 (m, 2 H, H-5), 2.09–2.07 (m, 3 H, $COCH_3$); β-configuration. δ 7.33–7.27 (m, 4 H, Ar-H), 5.9–5.85 (m, 0.22 H, H-2, H-3), 5.33–5.28 (m, 0.11 H, H-4), 5.02 (s, 0.11 H, H-1), 4.77 (d, 0.11 H, $J = 12.0$ Hz, $PhCH_2$), 4.54 (d, 0.11 H, $J = 12.0$ Hz, $PhCH_2$), 3.88–3.79 (m, 2 H, H-5), 2.09–2.07 (m, 3 H, $COCH_3$); ^{13}C NMR ($CDCl_3$): δ 170.48 (C, CO), 136.22 (C, Ar-C), 133.52 (C, Ar-C), 129.30–128.86 (4 C, Ar-C), 129.28 (C, Gly-C), 128.57 (C, Gly-C), 93.39 (C, Gly-C), 69.22 (C, Gly-C), 64.59 (C, Gly-C), 60.13 (C, $PhCH_2$), 20.95 (2 C, CH_3CO). Anal. calcd. for $C_{14}H_{15}ClO_4$ (283): C, 59.48; H, 5.35. Found: C, 59.73; H, 5.58.

para-t-Butylbenzyl 4-O-acetyl-2,3-dideoxy-threo-hex-2-eno-1-thio-α-L-arabinopyranoside (3s): Colorless oil. IR (neat): 2962, 1738, 1513, 1369, 1234, 1058, 956, 842, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33–7.23 (m, 4 H, Ar-H), 5.97–5.82 (m, 2 H, H-2, H-3), 5.39 (d, 1 H, $J = 2.4$ Hz, H-1), 5.38–4.96 (m, 1 H, H-4), 4.01–3.66 (m, 4 H, H-5, $PhCH_2$), 2.06 (s, 3 H, $COCH_3$), 1.29–1.26 (m, 9 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 170.39 (C, CO), 149.87 (C, Ar-C), 134.78 (C, Ar-C), 129.69 (2 C, Gly-C), 128.59 (2 C, Ar-C), 125.40 (2 C, Ar-C), 77.82 (C, Gly-C), 64.88 (C, Gly-C), 60.16 (C, Gly-C), 34.62 (C, $PhCH_2$), 34.40 (C, $C(CH_3)_3$), 31.27 [3 C, $C(CH_3)_3$], 20.88 (C, CH_3CO). Anal. calcd. for $C_{18}H_{24}O_3S$ (320): C, 67.47; H, 7.55. Found: C, 67.71; H, 7.80.

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