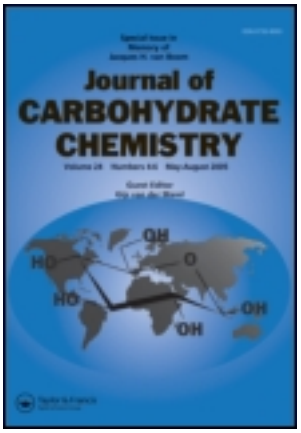

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A Facile H_2SO_4-SiO_2-Catalyzed Ferrier Rearrangement of 3,4,6-Tri-O-benzyl-d-glucal

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A Facile H_2SO_4-SiO_2–Catalyzed Ferrier Rearrangement of 3,4,6-Tri-*O*-benzyl-D-glucal

Jianbo Zhang,[1] Bo Zhang,[1] Jiafen Zhou,[1] Heshan Chen,[1] Juan Li,[1] Guofang Yang,[1] Zhongfu Wang,[2] and Jie Tang[1]

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Sulfuric acid immobilized on silica gel (H_2SO_4-SiO_2) was used as an efficient and convenient promoter for Ferrier-type rearrangement of 3,4,6-tri-*O*-benzyl-D-glucal in CH_2Cl_2, which is a difficult donor for this type of reaction. The acceptors include primary alcohols, secondary alcohols, pentanol, halogenated alcohol, sterols, thiol, and 2-naphthol. Thus, 2,3-unsaturated glycosides were obtained rapidly (<2 h) and efficiently (>62%) in good α-selectivity (α/β>4.2:1) under mild conditions.

Keywords Immobilized sulfuric acid; Silica gel; 3,4,6-Tri-*O*-benzyl-D-glucal; Glycosylation; Ferrier rearrangement

INTRODUCTION

Since R. J. Ferrier et al. reported that 3,4,6-tri-*O*-acetyl-D-glucal catalyzed by Lewis acid in the presence of an alcohol could afford 2,3-unsaturated glycosides,[1] the Ferrier reaction has received extensive attention in organic synthesis for many decades.[2] The products 2,3-unsaturated glycosides as chiral intermediates[3] have played an important role in the synthesis of many bioactive compounds, such as glycopeptide building blocks,[4] oligosaccharides,[5] uronic acids,[6] modified carbohydrates,[7] and some useful antibiotics[8] and nucleosides.[9] To facilitate these conversions, a diversity of catalysts have been employed, such as $SnCl_4$,[10] $InBr_3$,[11] TMSOTf,[12] $Dy(OTf)_3$,[13] $BiCl_3$,[14] $Sc(OTf)_3$,[15] $LiBF_4$,[16] $InCl_3$,[17] $ZnCl_2$,[18] $HClO_4$-SiO_2,[19] $ZrCl_4$,[20] $NbCl_5$,[21]

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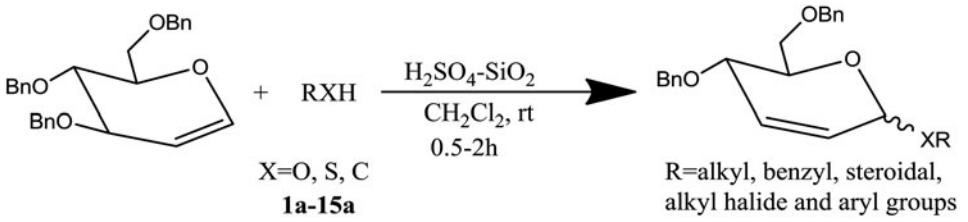
$Er(OTf)_3$,[22] $Fe_2(SO_4)_3 \cdot \chi H_2O$,[23] H_2SO_4,[24] $NaHSO_4$-SiO_2,[25] and CF_3SO_3H-SiO_2.[26] Despite these achievements with different acyl glycals, Ferrier rearrangement of glycals having ether protection at position 3 is hardly ever attained,[23,27] since many side reactions would occur more favorably, such as intramolecular rearrangement and 2-deoxy-glycoside formation.[28–31] Besides, the known catalysts often suffer from disadvantages including narrow scope of acceptors, low yields, high catalyst loading, long reaction times, stringent conditions, and the usage of toxic agents.

In the search for an alternative and green procedure for Ferrier rearrangement of ether-protected substrates, we examined sulfuric acid immobilized on silica (H_2SO_4-SiO_2) that has been utilized well in organic reactions.[32] This handy and metal-free catalyst has shown many advantages such as being inexpensive and safe, rapid reactions, high yields of products, and simple workup procedure. In our previous research, we found that this convenient reagent can catalyze the typical Ferrier rearrangement of tri-*O*-acetyl-D-glucal[33] and peracetylation of carbohydrates.[34] We expect that this mild approach will find more applications in glycoside syntheses. This report describes the Ferrier rearrangement of 3,4,6-tri-*O*-benzyl-D-glucal using H_2SO_4-SiO_2 as a catalyst under mild conditions (Sch. 1).



Scheme 1: H_2SO_4-SiO_2-catalyzed Ferrier rearrangement of 3,4,6-tri-*O*-benzyl-D-glucal.

RESULTS AND DISCUSSION

Initially, H_2SO_4, an efficient catalyst for Ferrier rearrangement of acyl-protected glycosyl donors, was applied directly in the reaction of 3,4,6-tri-*O*-benzyl-D-glucal.[24] Unfortunately, no desired products were obtained. However, when 3,4,6-tri-*O*-benzyl-D-glucal was treated with solid acid, H_2SO_4-SiO_2, we found that the intramolecular Ferrier product was formed quickly with or without external benzyl alcohol. In the literature, P. Nagaraj et al. also witnessed the similar phenomenon with $InCl_3$ catalyst.[35] Therefore, we changed the model acceptor for the Ferrier reaction into *n*-butyl alcohol to distinguish the intermolecular rearrangement. At the same time, to eliminate the possible intramolecular Ferrier rearrangement and other side reactions with benzyl alcohol generated in situ, more than 1 equivalent of the alcohol acceptor

Table 1: H_2SO_4-SiO_2–catalyzed Ferrier rearrangement of 3,4,6-tri-*O*-benzyl-D-glucals in CH_2Cl_2

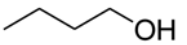
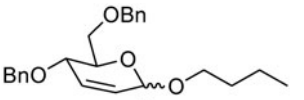
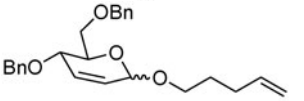
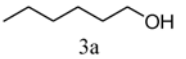
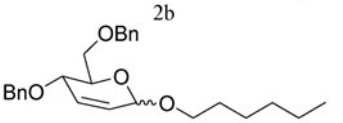
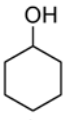
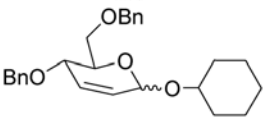
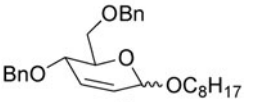
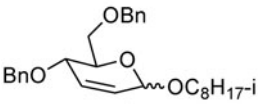
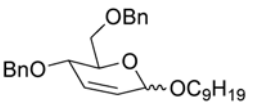
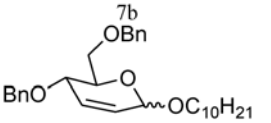
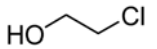
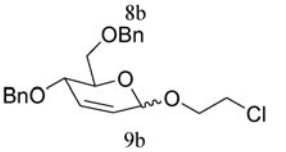
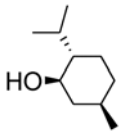
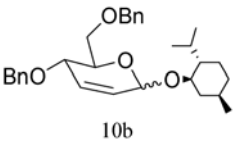
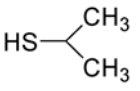
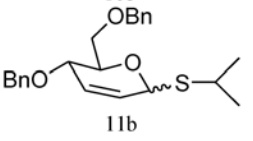
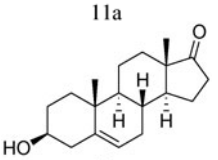
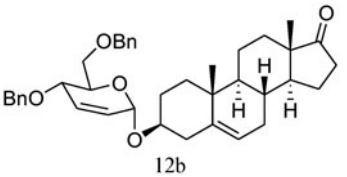
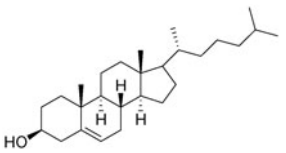
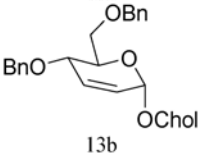
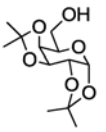
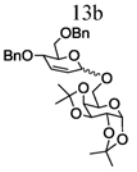
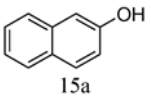
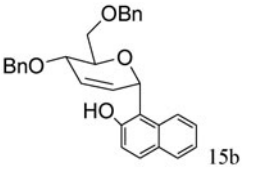
Entry	Acceptors	Products	Time (h)	Yield[a] (%)	α:β[b]
1	 1a	 1b	1.2	87	7.1:1
2	 2a	 2b	1	86[32]	8.5:1
3	 3a	 3b	1	88	4.2:1
4	 4a	 4b	2	81[23]	11:1
5	n-$C_8H_{17}OH$ 5a	 5b	0.5	91[25b]	5.9:1
6	i-$C_8H_{17}OH$ 6a	 6b	0.5	90	7.4:1
7	n-$C_9H_{19}OH$ 7a	 7b	0.5	93	6.7:1
8	n-$C_{10}H_{21}OH$ 8a	 8b	0.5	94	5.6:1
9	 9a	 9b	1	81	10:1

Table 1: H_2SO_4-SiO_2–catalyzed Ferrier rearrangement of 3,4,6-tri-*O*-benzyl-D-glucals in CH_2Cl_2 *(Continued)*

Entry	Acceptors	Products	Time (h)	Yield[a] (%)	α:β[b]
10	 10a	 10b	1	90[32]	10:1
11	 11a	 11b	0.5	93[25b]	8.7:1
12	 12a	 12b	1	87	>19:1
13	 13a	 13b	1	81	>19:1
14	 14a	 14b	1	71[33]	5.6:1
15	 15a	 15b	1	62	>19:1

[a]Isolated yields.
[b]Anomeric ratios were determined by 500 MHz ^{1}H NMR.

was applied and 4 equivalent of the alcohol was found to be optimal, while 0.4 equivalent of H_2SO_4-SiO_2 was found to promote the reaction well in CH_2Cl_2. We also examined acetonitrile as the reaction solvent, which led to reduced yields.[33]

To examine whether or not this novel method had generality, a variety of acceptors were tested. As summarized in Table 1, the desired reactions were completed in 0.5–2 h at rt with high to excellent yields (81%–93%, entries 1–11) for primary, secondary, benzyl, pentenyl, and halogenated alcohols

and thiol. Good α-stereoselectivities as determined by NMR spectroscopy were in the range observed previously with other catalysts on similar donors.[36,37] The complex sterols, such as cholesterol and sterone dehydroisoandrosterone (DHEA), were able to give high yields, 81% and 87%, respectively, with excellent α-selectivity and without the formation of 2-deoxy hexopyranosides as side products (entries 12 and 13). Furthermore, we obtained disaccharide **14b** smoothly with the the acid-sensitive ketal group intact when diacetone-D-galactose **14a** was used as the acceptor (entry 14), which demonstrated the potential application of our method in oligosaccharide synthesis.

It should be noted that the reaction failed with phenol,[38] however, when the donor reacted with 2-naphthol, and a 2,3-unsaturated aryl C-glycoside (**15b**) was obtained. The structure of **15b** was confirmed by spectral analysis. From the ^{1}H NMR spectrum, the peak at the chemical shift value of 9.12 (s, 1H) is typical for the hydroxyl group of 2-naphthol, and the absorption peak at 3308 cm^{-1} in the IR spectrum further indicates the presence of the free hydroxyl group (see supplementary file for more information). In addition, from the ^{13}C NMR spectrum, there were no peaks between 90 and 100 ppm, the typical range for anomeric carbon of *O*-glycosides. Instead, the anomeric carbon of **15b** appeared at 77.65 ppm. All of this indicates that the glycoside must be a *C*-glycoside rather than an *O*-glycoside. The C_1 of the 2-naphtol is more reactive than other positions of the acceptor, which is in agreement with the previous report.[39] The successful synthesis of 15b establishes an alternative synthetic approach for aryl C-glycoside (entry 15).[40,41]

CONCLUSION

In summary, as a convenient and green catalyst, H_2SO_4-SiO_2 can be efficiently utilized to promote Ferrier rearrangement of glycals with benzyl ether protection. The acceptors are widely available, and the catalyst could be simply filtered off after the reaction. We can synthesize glycosides, oligosaccharides, and *C*-glycosides from glycals via this new approach easily. It is a simple, clean, efficient, and environmentally benign method with excellent yields and dominant α-selectivity. Thus, we expect that this methodology will find widespread use in glycoside and oligosaccharide syntheses. Further exploration of this methodology is currently under way in our laboratory.

EXPERIMENTAL

General Experimental Methods

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker DRX-500MHz spectrometer using tetramethylsilane as internal standard and

$CDCl_3$ as solvent. Mass spectra were determined on an LTQ-XL (Thermo Scientific, USA) with an (ESI) ion trap mass spectrometer. Fourier transform infrared (FT-IR) spectra were collected on a Nicolet-Nexus 670 FI-IR Spectrometer. Silica gel (10–40 μm, Yantai, China) was used for column chromatography. TLC plates (10–40 μm, Yantai, China) were applied to monitor the reactions.

General Synthetic Procedure

Typically, 10 mg of H_2SO_4-SiO_2 (0.04 mmol) was added to the solution of 3,4,6-tri-*O*-benzyl-D-glucal (0.10 mmol, 40 mg) in dichloromethane (3 mL), and then was added *n*-butyl alcohol (1a, 36 μL, 0.40 mmol). The reaction mixture was stirred for 1.2 h at rt. After the reaction was completed, the reaction mixture was filtered and the catalyst was washed with dichloromethane. The organic phase was combined and condensed under vacuum to get crude product, which was purified by silica gel column chromatography (petroleum ether/EtOAc = 20/1) to get 1b as yellow syrup in an 87% yield (32.0 mg, α:β = 7.1:1). All new compounds were fully characterized by NMR and MS. Spectral and analytical data were in good agreement with the desired structures.

Butyl 4,6-di-*O*-benzyl-2,3-dideoxy-D-erythro-hex-2-enopyranoside (1b)

α:β = 7.1:1, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.36–7.24 (m, 10H), 6.08 (d, J = 10.2 Hz, 1H), 5.78 (d, J = 10.2, 1H), 5.11 (br s, 1H, H-1β), 5.02 (br s, 1H, H-1α), 4.66 (d, J = 12.1 Hz, 1H), 4.61 (d, J = 11.6 Hz, 1H), 4.51 (d, J = 12.1 Hz, 1H), 4.45 (d, J = 11.6 Hz, 1H), 4.18 (d, J = 9.3 Hz,1H), 3.98 (d, J = 7.5, 1H), 3.82–3.70 (m, 3H), 3.52–3.47 (m, 1H), 1.60–1.56 (m, 2H), 1.40–1.35 (m, 2H), 0.93–0.89 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 138.14, 138.02, 130.42, 128.36, 128.32, 128.27, 127.92, 127.79, 127.68, 127.64, 127.54, 126.68, 95.95 (β-isomer), 94.52 (α-isomer), 73.29, 70.97, 70.29, 69.02, 68.78, 68.25, 31.79, 19.34, 13.82. MS (ESI): m/z = 405.23 ($M + Na^+$).

Isooctyl 4,6-di-*O*-benzyl-2,3-dideoxy-D-erythro-hex-2-enopyranoside (6b)

α:β = 7.4:1 ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.35–7.22 (m, 10H), 6.06 (d, J = 10.2 Hz, 1H), 5.77 (d, J = 10.2 Hz, 1H), 5.08 (br s, 1H, H-1β), 4.98 (br s, 1H, H-1α), 4.67 (d, J = 12.2 Hz, 1H), 4.60 (d, J = 11.5 Hz, 1H), 4.51 (d, J = 12.2 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.19 (d, J = 11.5 Hz, 1H), 3.94 (d, J = 11.5 Hz, 1H), 3.76–3.72 (m, 1H), 3.71–3.67 (m, 2H), 3.36–3.34 (m, 1H), 1.58–1.56 (m, 1H), 1.33–1.25 (m, 8 H), 0.88–0.82 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 138.15, 137.99, 130.26, 128.34, 128.30, 128.26, 127.93, 127.86, 127.82, 127.72, 127.61, 127.54, 126.75, 94.82 (β-isomer), 94.72

(α-isomer), 73.31, 71.17, 71.09, 70.32, 69.12, 68.73, 39.44, 30.30, 28.89, 23.68, 23.05, 14.11, 10.77. MS (ESI): m/z = 461.25 ($M + Na^+$).

Nonyl 4,6-di-O-benzyl-2,3-dideoxy-D-erythro-hex-2-enopyranoside (7b)

α:β = 6.7:1, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.35–7.25 (m, 10H), 6.09 (d, J = 10.2 Hz, 1H), 5.79 (d, J = 10.2 Hz, 1H), 5.12 (br s, 1H, H-1β), 5.03 (br s, 1H, H-1α), 4.68 (d, J = 12.2 Hz, 1H), 4.60 (d, J = 11.5 Hz, 1H), 4.54 (d, J = 12.2 Hz, 1H), 4.47 (d, J = 11.5 Hz, 1H), 4.19 (d, J = 9.3 Hz, 1H), 3.99 (d, J = 7.8 Hz, 1H), 3.82–3.71 (m, 3H), 3.52–3.47 (m, 1H), 1.61–1.56 (m, 2H), 1.27 (br, 12H), 0.91–0.88 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 138.19, 138.07, 130.45, 128.36, 128.32, 128.27, 127.78, 127.68, 127.63, 127.53, 126.72, 95.11 (β-isomer), 94.55 (α-isomer), 73.31, 70.98, 70.35, 69.06, 68.85, 68.63, 31.85, 29.77, 29.53, 29.40, 29.25, 26.19, 22.64, 14.09. MS (ESI): m/z = 475.33 ($M + Na^+$).

Decyl 4,6-di-O-benzyl-2,3-dideoxy-D-erythro-hex-2-enopyranoside (8b)

α:β = 5.6:1, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.35–7.23 (m, 10H), 6.07 (d, J = 10.5 Hz, 1H), 5.78 (d, J = 10.5 Hz, 1H), 5.10 (br s, 1H, H-1β), 5.01(br s, 1H, H-1α), 4.67 (d, J = 12.2 Hz, 1H), 4.61 (d, J = 11.5 Hz, 1H), 4.52 (d, J = 12.2 Hz, 1H), 4.45 (d, J = 11.5 Hz, 1H), 4.18 (d, J = 9.5 Hz, 1H), 3.97 (d, J = 8 Hz, 1H), 3.78–3.69 (m, 3H), 3.49–3.47 (m, 1H), 1.59–1.56 (m, 2H), 1.32–1.25 (m, 14H), 0.89–0.86 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 138.18, 138.06, 130.45, 128.36, 128.32, 128.27, 127.91, 127.78, 127.68, 127.63, 127.53, 126.72, 95.11 (β-isomer), 94.55 (α-isomer), 73.31, 70.98, 70.35, 69.06, 68.86, 68.63, 31.86, 29.77, 29.71, 29.57, 29.55, 29.40, 29.30, 26.19, 22.65, 14.10. MS (ESI): m/z = 489.58 ($M + Na^+$).

2-Chloroethanyl 4,6-di-O-benzyl-2,3-dideoxy-α,β-D-erythro-hex-2-enopyranoside (9b)

α:β = 10:1, ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.23 (m, 10H), 6.10 (d, J = 10.2 Hz, 1H), 5.78 (d, J = 10.2 Hz, 1H), 5.12 (br s, 1H, H-1β), 5.06 (br s, 1H, H-1α), 4.65 (d, J = 12.2 Hz, 1H), 4.60 (d, J = 11.5 Hz, 1H), 4.55 (d, J = 12.2 Hz, 1H), 4.48 (d, J = 11.5 Hz, 1H), 4.17 (d, J = 9.3 Hz, 1H), 4.04–3.97 (m, 2H), 3.82–3.77 (m, 1H), 3.72–3.64 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): 138.08, 137.96, 131.06, 128.37, 128.33, 127.93, 127.81, 127.76, 127.62, 125.99, 95.03, 73.39, 71.06, 70.20, 69.35, 68.83, 68.62, 43.10. MS (ESI): m/z = 411.25 ($M + Na^+$).

Dehydroepiandrosteronyl 4,6-di-*O*-benzyl-2,3-dideoxy-D-erythro-hex-2-enopyranoside (12b)

mp = 146–149°C; $[\alpha]_D^{20}$ = +140 (c 0.89, CH_2Cl_2); α only, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.35–7.23 (m, 10H), 6.09 (d, J = 10.2 Hz, 1H), 5.77 (m, 1H), 5.27 (m, 1H), 5.17 (s, 1H), 4.67 (d, J = 12.2 Hz, 1H), 4.62 (d, J = 11.5 Hz, 1H), 4.52 (d, J = 12.2 Hz, 1H), 4.45 (d, J = 11.5 Hz, 1H), 4.17 (d, J = 9.3 Hz, 1H), 4.04–4.02 (m, 1H), 3.75–3.68 (m, 2H), 3.60–3.56 (m, 1H), 2.45–2.30 (m, 3H), 2.11–2.05 (m, 2H), 1.87–1.83 (m, 4H), 1.65–1.62 (m, 2H), 1.57 (s, 3H), 1.54–1.48 (m, 2H), 1.30–1.25 (m, 2H), 1.03–1.02 (m, 1H), 1.00 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 221.08, 141.11, 138.20, 138.11, 130.39, 128.33, 128.27, 127.81, 127.75, 127.67, 127.50, 127.08, 120.81, 92.89, 73.34, 70.90, 70.44, 69.10, 68.99, 51.76, 50.22, 47.52, 40.29, 37.11, 36.77, 35.82, 31.48, 31.43, 30.79, 28.19, 21.18, 20.31, 19.32, 13.52. IR (film, cm^{-1}): 3065, 3030, 2940, 2861, 1728, 1455,1374, 1095, 1015, 754, 705; MS (ESI): m/z = 619.33 (M + Na^+); ESI-HRMS: Calcd for $C_{39}H_{48}NaO_5$(M + Na^+) 619.3394, found 619.3415.

Cholesteryl 4,6-di-*O*-benzyl-2,3-dideoxy-D-erythro-hex-2-enopyranoside (13b)

mp = 129–132°C; $[\alpha]_D^{20}$ = +82 (c 0.66, CH_2Cl_2); α only, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.36–7.24 (m, 10H), 6.09 (d, J = 10.2 Hz, 1H), 5.77–5.74 (m, 1H), 5.26–5.25 (m, 1H), 5.17 (s, 1H), 4.67 (d, J = 12.2 Hz, 1H), 4.62 (d, J = 11.5 Hz, 1H), 4.52 (d, J = 12.2 Hz, 1H), 4.45 (d, J = 11.5 Hz, 1H), 4.18 (d, J = 9.3 Hz, 1H), 4.04–4.02 (m, 1H), 3.76–3.70 (m, 2H), 3.59–3.57 (m, 1H), 2.42–2.31 (m, 2H), 2.02–1.83 (m, 5H), 1.57 (s, 3H), 1.51–1.29 (m, 6H), 1.26 (s, 3H), 1.15–1.00 (m, 6H), 0.98 (s, 3H), 0.87 (s, 3H), 0.92–0.86 (m, 9H), 0.67 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 140.86, 138.20, 138.15, 130.39, 128.36, 128.32, 128.28, 127.82, 127.74, 127.65, 127.51, 127.15, 121.60, 92.84, 77.48, 73.34, 70.88, 70.43, 69.03, 68.95, 56.75, 56.14, 50.11, 42.30, 40.35, 39.77, 39.50, 37.17, 36.64, 36.17, 35.77, 31.92, 31.87, 28.22, 27.99, 24.27, 23.80, 22.80, 22.54, 21.03, 19.30, 18.70, 11.84. IR (film, cm^{-1}): 3060, 3030, 2935, 2861, 1454, 1382, 1297, 1096, 1014, 752, 702; (ESI): m/z = 717.50 (M + Na^+); ESI-HRMS: Calcd for $C_{47}H_{66}NaO_4$(M + Na^+) 717.4853, found 717.4882.

1-(4,6′-di-*O*-benzyl-2′,3′-dideoxy-α,β-D-hex-2′-enopyranosyl-(1->6)-1,2; 3,4-di-*O*-isopropylidene-α-D-galactopyranoside (14b)

α:β = 5.6:1, ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm): 7.33–7.23 (m, 10H), 6.07 (d, J = 10 Hz, 1H), 5.78–5.76 (m, 1H), 5.51 (d, J = 5 Hz, 1H), 5.29 (d, J = 1 Hz, 1H, H-1β), 5.08 (s, 1H, H-1α), 4.66–4.54 (m, 3H), 4.50 (d, J = 12.2 Hz, 1H), 4.44

(d, $J = 11.5$ Hz, 1H), 4.32–4.29 (m, 2H), 4.24–4.20 (m, 1H), 4.04–3.99 (m, 1H), 3.97–3.93 (m, 1H), 3.88–3.84 (m, 1H), 3.82–3.70 (m, 3H), 1.51 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H). MS (ESI): m/z = 591.20 ($M + Na^+$).

1-(4′,6′-di-O-benzyl-2′, 3′-dideoxy-α-D-erythro-hex-2′-enopyranosyl)-2-naphthol (15b)

α only, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 9.09 (s, 1H), 7.77–7.66 (m, 3H), 7.35–7.25 (m, 12H), 7.14–7.12 (m, 1H), 6.27 (s, 1H), 6.06 (d, $J = 10.5$ Hz, 1H), 5.91 (d, $J = 10.5$ Hz, 1H), 4.69 (dd, $J = 5$ Hz, 11.5 Hz, 2H), 4.54–4.49 (m, 3H), 3.91–3.89 (m, 1H), 3.85–3.80 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 154.21, 137.97, 137.82, 130.96, 129.85, 129.00, 128.82, 128.50, 128.44, 128.06, 127.97, 127.80, 127.71, 126.76, 125.81, 122.90, 120.80, 120.24, 113.57, 77.65, 75.12, 73.46, 71.65, 69.13, 68.20. IR (film, cm^{-1}): 3308, 2962, 2925, 2854, 1262, 1094, 1026, 802; MS (ESI): m/z = 475.33 ($M + Na^+$), ESI-HRMS: Calcd for $C_{30}H_{28}NaO_4$($M + Na^+$) 475.1880, found 475.1893.

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