Supporting Information

**ZNBr₂-CATALYZED AND MICROWAVE-ASSISTED SYNTHESIS OF 2,3-UNSATURATED
GLUCOSIDES OF HINDERED PHENOLS AND ALCOHOLS**

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Contents	Page Number
General Experimental Methods	4
Spectral information	4-17
Spectra data of Compound 3a	18-20
Spectra data of Compound 3b	21-23
Spectra data of Compound 3c	24-26
Spectra data of Compound 3d	27-29
Spectra data of Compound 3e	30-43
Spectra data of Compound 3f	44-58
Spectra data of Compound 3g	59-61
Spectra data of Compound 3h	62-64
Spectra data of Compound 3i	65-67
Spectra data of Compound 3j	68-70
Spectra data of Compound 5a	71-73
Spectra data of Compound 5b	74-76
Spectra data of Compound 5c	77-79
Spectra data of Compound 5d	80-82
Spectra data of Compound 5e	83-85
Spectra data of Compound 5f	86-88
Spectra data of Compound 5g	89-91

Spectra data of Compound 5h	92-94
Spectra data of Compound 5i	95-97
Spectra data of Compound 5j	98-100
Spectra data of Compound 7a	101-103
Spectra data of Compound 7b	104-106
Spectra data of Compound 7c	107-109
Spectra data of Compound 7d	110-112
Spectra data of Compound 7e	113-115
Spectra data of Compound 7f	116-118
Spectra data of Compound 7g	119-121
Spectra data of Compound 9a	122-124
Spectra data of Compound 9b	125-127
Spectra data of Compound 9c	128-130
Spectra data of Compound 9d	131-133
Spectra data of Compound 9e	134-136
Spectra data of Compound 9f	137-139
Spectra data of Compound 9g	140-142
Spectra data of Compound 9h	143-145

General Experimental Methods

ZnBr₂, 3, 4, 6-tri-*O*-acetylglucal, alcohols and phenols employed in the study were procured from Sigma Aldrich (St. Louis, MO, USA). Chloroform used for the reaction was distilled, stored over molecular sieves (5 Å) and passed over anhydrous sodium sulfate prior to use. All reactions were performed in a microwave reactor (Milestone lab-station, model START S, Italy). ¹H and ¹³C NMR spectra were recorded on a 500 MHz NMR spectrometer (Bruker Avance, Reinstetten, Germany) using CDCl₃ solvent. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) as the internal standard, and coupling constants (*J*) in Hz. Multiplicities are reported as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), *bs*(broad singlet) and *sp* (septet). IR Spectra was recorded on FT Raman Nicolet 5700 spectrometer as a sample smear on KBr prism for liquid samples or as a KBr pellet for solid samples. Mass spectral analyses of compounds were carried out using MS (Waters Q-Tof Ultima, Manchester, UK) in the ESI positive mode. Specific rotations of compounds were calculated from observed optical rotations recorded for methanolic solutions of compounds on a Perkin-Elmer 243 model polarimeter. Melting points were measured on a Gallenkamp apparatus using glass capillary tubes and are uncorrected. Thin-layer chromatographic (TLC) analysis was performed on silica gel 60 F₂₅₄ (Merck, Germany) coated on alumina sheet with 5% and 20% ethyl acetate in petroleum ether (60-80⁰ C) as the developing solvent. The compounds were visualized by UV light (254nm and/or 366nm) and/or by staining with Iodine and phosphomolybdic acid.

Spectral Information

1. *Phenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (3a)*²¹. White Solid; mp=48-50⁰ C (lit.47-48⁰C)²¹; [α]_D +128.70⁰ (c = 2.16, CH₃OH, α:β=10:1); IR (KBr, cm⁻¹): 3469,

3058, 2930, 2897, 1760, 1653, 1597, 1380, 1261, 758, 690; ^1H NMR (500 MHz, CDCl_3): δ 7.33-7.28(m, 2H), 7.12(d, $J=8.6$ Hz, 2H), 7.06(t, $J=7.5$ Hz, 1H), 6.06-6.03(bs, 2H), 5.72(s, 1H), 5.41(dd, $J=9.6, 1.2$ Hz, 1H), 4.33-4.25(m, 2H), 4.15(dd, $J=11.50, 1.7$ Hz, 1H), 2.13(s, 3H), 2.0(s, 3H); ^{13}C -NMR (125 MHz, CDCl_3): δ 170.41, 169.95, 156.78, 129.80, 129.17, 126.81, 122.18, 116.77, 92.65, 67.48, 64.77, 62.36, 20.65, 20.35; HRMS (ESI) m/z : $[\text{M}^+ + \text{Na}]$ calcd for $\text{C}_{16}\text{H}_{18}\text{O}_6\text{Na}$ 329.0996; found 329.1020.

2. *2-Methylphenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (3b).*
 Colourless viscous liquid; $[\alpha]_{\text{D}} +108.49^0$ ($c = 2.12$, CH_3OH , $\alpha:\beta=8:1$); IR (film, cm^{-1}): 3432, 2955, 1750, 1590, 1493, 1370, 1229, 1186, 1094, 786, 761; ^1H NMR (500 MHz, CDCl_3): δ 7.22-7.15(m, 3H), 6.98(dt, $J=7.3, 1.3$ Hz, 1H), 6.05(bs, 2H), 5.69(s, 1H), 5.41(d, $J=9.4$ Hz, 1H), 4.34-4.26(m, 2H), 4.17(dd, $J=11.6, 1.5$ Hz, 1H), 2.26(s, 3H), 2.14(s, 3H), 2.02(s, 3H). ^{13}C -NMR (125 MHz, CDCl_3): δ 170.41, 169.93, 155.20, 130.48, 129.63, 127.59, 126.99, 126.60, 122.07, 115.30, 93.05, 67.51, 64.86, 62.44, 20.65, 20.36, 15.98; HRMS (ESI) m/z : $[\text{M}^+ + \text{Na}]$ calcd for $\text{C}_{17}\text{H}_{20}\text{O}_6\text{Na}$ 343.1152; found 343.1167.

3. *3-Methylphenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (3c).*
 Colourless viscous liquid; $[\alpha]_{\text{D}} +95.56^0$ ($c = 2.03$, CH_3OH , $\alpha:\beta=10:1$); IR (film, cm^{-1}): 3462, 3028, 2959, 2923, 2871, 1760, 1650, 1609, 1583, 1368, 1263, 866, 771, 690; ^1H NMR (500 MHz, CDCl_3): δ 7.18(t, $J=7.7$ Hz, 1H), 6.94-6.91(m, 2H), 6.87(d, $J=7.5$ Hz, 1H), 6.00(m, 2H), 5.70 (s, 1H), 5.40(dd, $J=9.58, 1.0$ Hz, 1H), 4.30-4.21(m, 2H), 4.15(dd, $J=12.0, 2.0$ Hz, 1H), 2.35(s, 3H), 2.12(s, 3H), 2.01(s, 3H); ^{13}C -NMR (125 MHz, CDCl_3): δ 170.41, 169.95, 156.81, 139.24, 129.68, 128.90, 126.90, 123.0, 117.49, 113.73, 92.68, 67.46, 64.78, 62.39, 21.16, 20.64, 20.34. HRMS (ESI) m/z : $[\text{M}^+ + \text{Na}]$ calcd for $\text{C}_{17}\text{H}_{20}\text{O}_6\text{Na}$ 343.1152; found 343.1139.

4. *4-Methylphenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (3d)*. White Solid; mp=70-72°C; $[\alpha]_D^{25} +133.16^0$ (c = 1.99, CH₃OH, $\alpha:\beta=1:0$); IR (KBr, cm⁻¹): 3455, 3062, 3028, 2959, 2931, 2899, 1763, 1726, 1651, 1612, 1584, 1432, 1376, 1215, 855, 809, 772. ¹H NMR (500 MHz, CDCl₃): δ 7.10 (d, $J=8.50$ Hz, 2H), 7.02(d, $J=8.5$ Hz, 2H), 6.02(bs,2H), 5.64(s, 1H), 5.40(d, $J=9.4$ Hz, 1H), 4.33-4.24(m, 2H), 4.15(dd, $J=11.6, 1.5$ Hz, 1H), 2.31(s, 3H), 2.11(s, 3H), 2.00(s, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.37, 169.92, 154.69, 131.61, 129.65, 129.59, 126.94, 116.86, 93.03, 67.38, 64.80, 62.41, 20.62, 20.35, 20.25; HRMS (ESI) m/z: $[M^+ + Na]$ calcd for C₁₇H₂₀O₆Na 343.1152; found 343.1135.

5. *5-Isopropyl-2-methylphenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (3e)*. Colourless viscous liquid; $[\alpha]_D^{25} +126.02^0$ (c = 1.96, CH₃OH, $\alpha:\beta=8.5:1$), IR (film, cm⁻¹): 3471, 3054, 3023, 2961, 2928, 2871, 1759, 1651, 1613, 1579, 1456, 1369, 1336, 1236, 868, 790, 763; ¹H NMR (500 MHz, CDCl₃): δ 7.06 (m, 2H), 6.84(dd, $J=7.66, 1.3$ Hz, 1H), 6.01(bs, 2H), 5.67 (bs, 1H), 5.39(d, $J=9.50$ Hz, 1H), 4.33-4.26(m, 2H), 4.16(dd, $J=11.5, 1.5$ Hz, 1H), 2.87(sp, $J=6.89$ Hz, 1H), 2.20(s, 3H), 2.12 (s, 3H), 2.01(s, 3H), 1.23 (d, $J= 6.89$ Hz, 6H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.46, 169.98, 155.26, 147.88, 130.26, 129.61, 127.10, 124.84, 119.83, 113.67, 93.31, 67.51, 64.83, 62.59, 33.68, 23.79, 20.68, 20.40, 15.62; HRMS (ESI) m/z: $[M^+ + Na]$ calcd for C₂₀H₂₆O₆Na 385.1620; found 385.1594.

6. *2-Isopropyl-5-methylphenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (3f)*. Colourless viscous liquid; $[\alpha]_D^{25} +103.26^0$ (c = 1.53, CH₃OH, $\alpha:\beta=13:1$); IR (film, cm⁻¹): 3471, 3059, 2962, 2927, 2870, 1757, 1613, 1577, 1369, 1339, 1235, 791, 767; ¹H NMR (500 MHz, CDCl₃): δ 7.13(d, $J=7.71$ Hz, 1H), 7.06(s, 1H), 6.85(d, $J=7.63$ Hz, 1H), 6.04(bs, 2H), 5.68(bs, 1H), 5.43 (dd, $J=9.70, 1.0$ Hz, 1H), 4.36-4.24(m, 2H), 4.17(dd, $J=12.0, 2.17$ Hz, 1H), 3.28(sp, $J=6.9$ Hz, 1H), 2.34(s, 3H), 2.14(s, 3H), 2.04(s, 3H), 1.23(d, $J=6.90$ Hz, 3 H), 1.22(d, $J=6.90$ Hz, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.44, 169.96,

154.19, 136.23, 134.69, 129.50, 127.04, 125.68, 122.92, 115.92, 93.13, 67.61, 64.82, 62.46, 26.46, 22.71, 22.54, 20.93, 20.66, 20.36; HRMS (ESI) m/z : $[M^+ + Na]$ calcd for $C_{20}H_{26}O_6$ 385.1620; found 385.1635.

7. *4-Ethylphenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (3g)*. White Solid; mp=56-58 $^{\circ}$ C; $[\alpha]_D +116.58^0$ (c = 2.11, CH₃OH, α : β =7:1); IR (KBr, cm⁻¹): 3458, 3099, 3033, 2966, 2931, 2873, 1760, 1731, 1651, 1610, 1584, 1433, 1372, 1223, 830; ¹H NMR (500 MHz, CDCl₃): δ 7.11(d, J =8.0 Hz, 2H), 7.05(d, J =8.40 Hz, 2H), 6.01(bs, 2H), 5.65(s, 1H), 5.38(d, J =9.30 Hz, 1H), 4.30-4.23(m, 2H), 4.13(d, J =11.5 Hz, 1H), 2.59(q, J = 7.50 Hz, 2H), 2.10(s, 3H), 1.99(s, 3H), 1.20(t, J =7.60 Hz, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.44, 169.98, 154.82, 138.15, 129.35, 125.12, 115.97, 114.79, 92.97, 67.37, 64.80, 63.08, 27.76, 20.66, 20.38, 15.51; HRMS (ESI) m/z : $[M^+ + Na]$ calcd for $C_{18}H_{22}O_6Na$ 357.1308; found 357.1330.

8. *3, 4-Dimethylphenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (3h)*. White Solid; mp = 90-92 $^{\circ}$ C; $[\alpha]_D +106.77^0$ (c = 0.59, CH₃OH, α : β =1:0); IR (KBr, cm⁻¹): 3490, 3387, 3028, 2960, 2926, 2883, 1738, 1710, 1573, 1458, 1415, 1372, 1225, 1191, 1126, 893, 860, 818, 767; ¹H NMR (500 MHz, CDCl₃): δ 6.96(s,1H), 6.79(s, 1H), 6.73(s, 1H), 6.27(dd, J =9.86, 2.59 Hz, 1H), 6.02(dt, J =10.2, 2.56 Hz, 1H), 5.45 (bs,1H), 5.25(dd, J =6.92, 3.40 Hz,1H), 4.20(d, J =5.56 Hz, 2H), 3.93(m, 1H), 2.20(s, 3H), 2.17(s, 3H), 2.08(s, 6H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.46, 169.98, 153.40, 138.43, 130.77, 129.24, 127.87, 124.47, 118.02, 87.82, 64.71, 64.38, 61.94, 20.65, 20.39, 19.28, 18.47; HRMS (ESI) m/z : $[M^+ + Na]$ calcd for $C_{18}H_{22}O_6Na$ 357.1308; found 357.1324.

9. *4-Methoxyphenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (3i)*²¹. White Solid; mp = 60-62 $^{\circ}$ C (69-70 $^{\circ}$ C)²¹; $[\alpha]_D +127.31$ (c = 2.16, CH₃OH, α : β =1:0); IR (KBr, cm⁻¹): 3454, 3054, 3025, 3002, 2955, 2929, 2838, 1760, 1723, 1650, 1619, 1437, 1374, 1334,

1248, 1052, 822; ^1H NMR (500 MHz, CDCl_3): δ 7.06(d, $J=9.08$ Hz, 2H), 6.85(d, $J=9.12$ Hz, 2H), 6.03(bs, 2H), 5.58(s, 1H), 5.39(d, $J=9.10$ Hz, 1H), 4.31-4.27(m, 2H), 4.20(m, 1H), 3.79(s, 3H), 2.13(s, 3H), 2.04(s, 3H); ^{13}C -NMR (125 MHz, CDCl_3): δ 170.51, 170.03, 154.91, 150.82, 129.63, 126.95, 118.35, 114.24, 93.73, 67.31, 64.85, 62.51, 55.36, 20.65, 20.42; HRMS (ESI) m/z : $[\text{M}^+ + \text{Na}]$ calcd for $\text{C}_{17}\text{H}_{20}\text{O}_7\text{Na}$ 359.1101; found 359.1122.

10. *4-Nitrophenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (3j)*²¹. Light Yellow Solid; mp=80-82 $^{\circ}\text{C}$ (94-95 $^{\circ}\text{C}$)²¹; $[\alpha]_{\text{D}} +141.87^0$ ($c = 1.6$, CH_3OH , $\alpha:\beta=1:0$); IR (KBr, cm^{-1}): 3471, 3111, 3076, 3016, 2958, 2927, 2841, 1759, 1649, 1592, 1517, 1442, 1372, 1341, 1229, 849, 817; ^1H NMR (500 MHz, CDCl_3): δ 8.20 (d, $J=9.20$ Hz, 2H), 7.18(d, $J=9.20$ Hz, 2H), 6.10(d, $J=9.93$ Hz, 1H), 6.01(d, $J=9.93$ Hz, 1H), 5.81(bs, 1H), 5.41(d, $J=9.5$ Hz, 1H), 4.26-4.15(m, 3H), 2.12(s, 3H), 1.97(s, 3H); ^{13}C -NMR (125 MHz, CDCl_3): δ 170.30, 169.87, 161.55, 142.25, 130.81, 125.53, 125.39, 116.31, 92.32, 68.06, 64.43, 62.08, 20.57, 20.29; HRMS (ESI) m/z : $[\text{M}^+ + \text{Na}]$ calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_8\text{Na}$ 374.0846; found 374.0880.

11. *n-Butyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (5a)*. Colourless liquid; $[\alpha]_{\text{D}}^{30} + 93.82$ ($c = 0.81$, CH_3OH , $\alpha:\beta=2:1$), IR (film, cm^{-1}): 3056, 2959, 2934, 2873, 1745, 1700, 1680, 1651, 1436, 1371, 1232, 1105, 1042, 906, 668; ^1H -NMR (500 MHz, CDCl_3): δ 5.85(m, 2H), 5.30(d, $J=9.80$ Hz, 1H), 5.01(s, 1H), 4.25-4.22(m, 1H), 4.17(dd, $J=2.0, 12.0$ Hz, 1H), 4.11-4.09(m, 1H), 3.78-3.75(m, 1H), 3.53-3.50(m, 1H), 2.09(s, 3H), 2.07(s, 3H), 1.55 – 1.61(m, 2H), 1.36 – 1.41(m, 2H), 0.92(t, $J= 6.87$ Hz, 3H); ^{13}C -NMR (125 MHz, CDCl_3): δ 174.42, 169.93, 128.62, 127.66, 94.06, 68.30, 66.57, 65.02, 62.72, 31.43, 20.62, 20.43, 19.05, 13.47; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_6\text{Na}$ 309.1314; found 309.1341.

12. *2-Methylpentyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (5b).*

Colourless liquid; $[\alpha]_D^{20} + 78.60$ ($c = 1.73$, CH_3OH , $\alpha:\beta=7:1$); IR (film, cm^{-1}): 3471, 2958, 2928, 2872, 2728, 1758, 1650, 1456, 1370, 1240, 1039, 908, 738, 688; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.79(dd, $J=10.0, 18.0$ Hz, 2H), 5.24(d, $J=10.0$ Hz, 1H), 4.94(s, 1H), 4.18(dd, $J=4.0, 12.0$ Hz, 1H), 4.12(d, $J=10.6$ Hz, 1H), 4.02-4.05(m, 1H), 3.61- 3.48(m, 1H), 3.32-3.20(m, 1H), 2.03(s, 3H), 2.02(s, 3H), 1.70- 1.67(m, 1H), 1.34-1.28(m, 2H), 1.08-1.02(m, 2H), 0.88-0.83(m, 6H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 170.20, 169.70, 128.60, 127.60, 94.20, 74.03, 66.61, 65.01, 62.71, 35.46, 32.70, 20.51, 20.31, 19.62, 16.80, 13.90; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{26}\text{O}_6\text{Na}$ 337.1627; found 337.1660.

13. *Hexyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (5c).*

Colourless liquid; $[\alpha]_D^{20} + 62.06$ ($c = 2.03$, CH_3OH , $\alpha:\beta=7:1$), IR (film, cm^{-1}): 3471, 3053, 2960, 2932, 2869, 1757, 1650, 1455, 1370, 1236, 1105, 1035, 908, 734; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.87(d, $J=10.7$ Hz, 1H), 5.83(dt, $J=1.96, 10.3$ Hz, 1H), 5.30(dd, $J=1.5, 9.10$ Hz, 1H), 5.02(s, 1H), 4.24(dd, $J=5.5, 12.1$ Hz, 1H), 4.17(dd, $J=2.1, 12.1$ Hz, 1H), 4.12-4.08(m, 1H), 3.79-3.74(m, 1H), 3.52-3.48(m, 1H), 2.09(s, 3H), 2.08(s, 3H), 1.62-1.59(m, 2H), 1.34-1.29(m, 6H), 0.88(t, $J=7.0$ Hz, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 170.42, 169.93, 128.63, 127.67, 94.07, 68.66, 66.57, 65.03, 62.74, 31.27, 29.35, 25.56, 22.25, 20.61, 20.42, 13.67; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{26}\text{O}_6\text{Na}$ 337.1627, found 337.1660.

14. *2-Ethylhexyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (5d).*

Colourless liquid; $[\alpha]_D^{20} + 55.11$ ($c = 2.25$, CH_3OH , $\alpha:\beta=6:1$), IR (film, cm^{-1}): 3476, 2959, 2929, 2873, 1757, 1650, 1460, 1370, 1234, 1043, 908, 738; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.82(d, $J=10.5$ Hz, 1H), 5.79(dt, $J=2.0, 10.2$ Hz, 1H), 5.25(d, $J=9.6$ Hz, 1H), 4.95(s, 1H), 4.20(dd, $J=5.9, 11.5$ Hz, 1H), 4.13(dd, $J=1.9, 12.0$ Hz, 1H), 4.06-4.02(m, 1H), 3.69-3.63(m, 1H), 3.34-3.30 (m, 1H), 2.05(s, 3H), 2.04(s, 3H), 1.50-1.47(m, 2H), 1.39-1.28(m, 6H), 0.86(d, $J = 1.7$ Hz, 2H), 0.85(t, $J = 1.7$ Hz, 3H), 0.83(d, $J = 2.4$ Hz, 3H); $^{13}\text{C-NMR}$ (125

MHz, CDCl₃): δ 170.79, 170.29, 128.86, 128.07, 94.65, 71.55, 66.99, 65.40, 63.14, 39.70, 30.61, 30.44, 23.80, 23.38, 20.98, 20.79, 14.10, 11.03; HRMS (ESI) m/z : [M+Na]⁺ Calcd for C₁₈H₃₀O₆Na 365.1940; found 365.1932.

15. *Tetrahydrogeranyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (5e).*

Colourless liquid; $[\alpha]_D^{20} + 52.45$ ($c = 2.04$, CH₃OH, $\alpha:\beta=6:1$); IR (film, cm⁻¹): 3555, 3475, 2954, 2927, 2871, 1746, 1464, 1370, 1230, 1186, 1136, 1104, 1040, 975, 686; ¹H-NMR (500 MHz, CDCl₃): δ 5.84(d, $J=10.4$ Hz, 1H), 5.80(dd, $J=1.60, 10.5$ Hz, 1H), 5.28(d, $J=9.4$ Hz, 1H), 4.99(s, 1H), 4.18(dt, $J=2.6, 12.20$ Hz, 1H), 4.06-4.09(m, 1H), 3.82-3.78(m, 1H), 3.52-3.46(m, 1H), 2.07(s, 3H), 2.05(s, 3H), 1.60-1.65(m, 1H), 1.48-1.53(m, 1H), 1.34-1.39(m, 2H), 1.28-1.22(m, 3H), 1.13-1.08(m, 3H), 0.84(s, 3H), 0.86(dd, $J=1.7, 6.5$ Hz 3H), 0.83(s, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.76, 170.26, 128.94, 128.04, 94.52, 67.15, 66.95, 65.37, 63.12, 39.29, 37.45, 36.69, 29.92, 27.96, 24.68, 22.70, 22.60, 20.96, 20.78, 19.68, 19.43; HRMS (ESI) m/z : [M+Na]⁺ Calcd for C₂₀H₃₄O₆Na 393.2253; found 393.2234.

16. *β -Citronellyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (5f)^{45a}.*

Colourless liquid; $[\alpha]_D^{20} + 50$ ($c = 2.0$, CH₃OH, $\alpha:\beta=7:1$); IR (film, cm⁻¹): 3555, 3479, 3055, 2959, 2923, 2723, 1746, 1655, 1446, 1372, 1231, 1104, 1038, 907, 687; ¹H-NMR (500 MHz, CDCl₃): δ 5.88(d, $J=10$ Hz, 1H), 5.83(dt, $J=1.80, 10.1$ Hz, 1H), 5.31(dd, $J = 1.36, 9.5$ Hz, 1H), 5.12-5.07(m, 1H), 5.02(s, 1H), 4.25(dd, $J=5.0, 12$ Hz, 1H), 4.17(dd, $J = 2.3, 12.1$ Hz, 1H), 4.08-4.11(m, 1H), 3.85-3.80(m, 1H), 3.56-3.51(m, 1H), 2.10(s, 3H), 2.08(s, 3H), 2.02-1.93 (m, 3H), 1.68(s, 3H), 1.60(s, 3H), 1.38-1.33(m, 3H), 1.15-1.20(m, 1H), 0.91(d, $J=7$ Hz, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.40, 169.90, 130.87, 128.60, 127.67, 124.38, 94.16, 66.88, 66.60, 65.03, 62.78, 36.91, 39.50, 36.25, 29.15, 25.30, 25.10, 20.60, 20.40, 19.10, 18.90, 17.29; HRMS (ESI) m/z : [M+Na]⁺ Calcd for C₂₀H₃₂O₆Na 391.2096; found 391.2123.

17. *Decyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (5g).* Colourless liquid; $[\alpha]_D^{20} + 52.94$ ($c = 2.04$, CH_3OH , $\alpha:\beta=7:1$); IR (film, cm^{-1}): 3472, 2926, 2855, 1743, 1650, 1462, 1370, 1233, 1041, 980, 908, 726; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.86(d, $J=10.6$ Hz, 1H), 5.83(dt, $J=2.1, 10.3$ Hz, 1H), 5.30(dd, $J=1.5, 9.7$ Hz, 1H), 5.01(s, 1H), 4.24(dd, $J=5.4, 12.1$ Hz, 1H), 4.16(dd, $J=2.4, 12.1$ Hz, 1H), 4.11-4.07(m, 1H), 3.76(dt, $J=2.7, 9.4$ Hz, 1H), 3.49(dt, $J=3.0, 9.7$ Hz, 1H), 2.09(s, 3H), 2.07(s, 3H), 1.61-1.55(m, 2H), 1.25(brs, 14H), 0.87(t, $J=7$ Hz, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 170.41, 169.94, 128.64, 127.67, 94.07, 68.68, 66.57, 65.04, 62.73, 31.51, 29.40, 29.24, 29.08, 28.96, 25.91, 25.77, 22.32, 20.61, 20.42, 13.74; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{34}\text{O}_6\text{Na}$ 393.3153; found 393.3130.

18. *Trans-Hex-3-enyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (5h).* Colourless liquid; $[\alpha]_D^{20} + 67.07$ ($c = 1.64$, CH_3OH , $\alpha:\beta=10:1$); IR (film, cm^{-1}): 3470, 3032, 2961, 2931, 2876, 1756, 1650, 1437, 1370, 1235, 1105, 1044, 973, 908; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.83(d, $J=10.4$ Hz, 1H), 5.80(dt, $J=2.1, 10.2$ Hz, 1H), 5.53-5.48(m, 1H), 5.39-5.33(m, 1H), 5.27(dd, $J=1.2, 9.60$ Hz, 1H), 4.99(s, 1H), 4.21(dd, $J=5.5, 12.2$ Hz, 1H), 4.13(dd, $J=2.0, 12.2$ Hz, 1H), 4.08-4.05(m, 1H), 3.73(dt, $J=2.40, 9.67$ Hz, 1H), 3.50(dt, $J=2.60, 9.60$ Hz, 1H), 2.29-2.23(m, 2H), 2.05(s, 3H), 2.04(s, 3H), 2.0-1.94(m, 2H), 0.92(t, $J=7.40$ Hz, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 170.40, 169.93, 134.08, 128.70, 127.59, 124.60, 94.08, 68.42, 66.59, 65.02, 62.69, 32.60, 25.30, 20.60, 20.42, 13.43; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_6\text{K}$ 351.1210; found 351.1204.

19. *Cis-Hex-3-enyl 4, 6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (5i).* Colourless liquid; $[\alpha]_D^{20} + 72.43$ ($c = 1.85$, CH_3OH , $\alpha:\beta=5:1$); IR (film, cm^{-1}): 3458, 3009, 2962, 2931, 2871, 1745, 1651, 1455, 1371, 1232, 1105, 1039, 976, 687; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.86-5.79(m, 2H), 5.47-5.42(m, 1H), 5.34-5.27(m, 2H), 5.01(s, 1H), 4.24-4.20(m, 1H), 4.15(dd, $J=2.2, 12.0$ Hz, 1H), 4.09-4.07(m, 1H), 3.74-3.71(m, 1H), 3.52-3.48(m, 1H),

2.34(q, $J = 6.9\text{Hz}$, 2H), 2.06(s, 3H), 2.05(s, 3H), 2.0-1.94(m, 2H), 0.97(t, $J = 7.5\text{ Hz}$, 3H); ^{13}C -NMR (125 MHz, CDCl_3): δ 170.42, 169.93, 133.57, 128.70, 127.58, 124.27, 94.07, 68.17, 66.62, 65.01, 62.71, 27.51, 20.61, 20.42, 20.31, 13.89; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_6\text{Na}$ 335.1471; found 335.1511.

20. *β -Phenylethyl 4, 6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (5j)*^{23d}. Colourless liquid; $[\alpha]_{\text{D}}^{20} + 69.20$ ($c = 1.92$, CH_3OH , $\alpha:\beta=7:1$); IR (film, cm^{-1}): 3476, 3088, 3060, 3028, 2928, 2876, 1742, 1726, 1650, 1603, 1496, 1451, 1370, 1235, 1039, 908, 749, 701; ^1H -NMR (500 MHz, CDCl_3): δ 7.22 -7.32(m, 5H), 5.88(dd, $J=10.5\text{ Hz}$, 1H), 5.82(dt, $J=2.3, 10.2\text{ Hz}$, 1H), 5.30(dd, $J=1.3, 9.8\text{ Hz}$, 1H), 5.03(s, 1H), 4.06(dd, $J=2.9, 12.0\text{ Hz}$, 1H), 4.03-3.96 (m, 2H), 3.77(dd, $J=2.8, 6.8, 9.8\text{ Hz}$, 1H), 2.94(t, $J=6.8\text{ Hz}$, 2H), 2.09(s, 3H), 2.08(s, 3H); ^{13}C -NMR (125 MHz, CDCl_3): δ 170.30, 169.96, 138.48, 128.80, 128.70, 128.06, 127.46, 125.89, 94.13, 69.21, 66.63, 64.93, 62.59, 36.03, 20.64, 20.44; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_6\text{Na}$ 357.1314; found 357.1308.

21. *Isopropyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (7a)*³⁵. Colourless liquid; $[\alpha]_{\text{D}}^{30} + 92.98$ ($c = 1.14$, CH_3OH , $\alpha:\beta=6:1$); IR (film, cm^{-1}): 3734, 3639, 3457, 3052, 2975, 2926, 2900, 1760, 1728, 1653, 1452, 1371, 1312, 1236, 1192, 1048, 936, 681; ^1H -NMR (500 MHz, CDCl_3): δ 5.79(d, $J=9.30\text{ Hz}$, 1H), 5.73(d, $J=9.90\text{ Hz}$, 1H), 5.24(d, $J=9.30\text{ Hz}$, 1H), 5.06(brs, 1H), 4.19-4.06(m, 3H), 3.91(sp, $J=6.20\text{ Hz}$, 1H), 2.02(s, 3H), 2.01(s, 3H), 1.19(d, $J=6.0\text{ Hz}$, 3H), 1.11(d, $J=6.20\text{ Hz}$, 3H); ^{13}C -NMR (125 MHz, CDCl_3): δ 170.23, 169.80, 128.37, 128.11, 92.44, 70.31, 66.42, 64.96, 62.75, 23.11, 21.60, 20.51, 20.30; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{20}\text{O}_6\text{Na}$ 295.1158; found 295.1153.

22. *Sec-Butyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (7b)*⁴⁶. Colourless liquid; $[\alpha]_{\text{D}}^{30} + 88.42$ ($c = 1.21$, CH_3OH , $\alpha:\beta=20:1$); IR (film, cm^{-1}): 3465, 3052, 2968, 2930, 2880, 1744, 1652, 1372, 1230, 1140, 1035, 988, 968; ^1H -NMR (500 MHz,

CDCl₃): δ 5.80-5.70(m, 2H), 5.21(dd, $J=1.30, 9.50$ Hz, 1H), 5.04(d, $J=7.50$ Hz, 1H), 4.17-4.06(m, 3H), 3.70-3.63(m, 1H), 2.01(s, 3H), 2.0(s, 3H), 1.53- 1.38(m, 2H), 1.17(d, $J=6.30$ Hz, 2H), 1.07(d, $J=6.30$ Hz, 1H), 0.89-0.81(m, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ 167.79, 167.34, 125.81, 125.56, 91.43, 74.21, 64.09, 62.56, 60.28, 27.20, 18.25, 18.03, 17.81, 7.38; HRMS (ESI) m/z : [M+Na]⁺Calcd for C₁₄H₂₂O₆Na 309.1314; found 309.1340.

23. *2-Pentyl 4,6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (7c)*. Colourless liquid; $[\alpha]_D^{20} + 79.38$ ($c = 1.94$, CH₃OH, $\alpha:\beta=12:1$); IR (film, cm⁻¹): 3469, 2961, 2932, 2874, 1743, 1649, 1453, 1371, 1231, 1035, 907, 728; ¹H-NMR (500 MHz, CDCl₃): δ 5.86-5.71(m, 2H), 5.29–5.26(m, 1H), 5.10(d, $J=11.85$ Hz, 1H), 4.24-4.11(m, 3H), 3.85-3.75(m, 1H), 2.07(s, 6H), 1.55-1.52(m, 1H), 1.43-1.31(m, 3H), 1.24(d, $J=6.2$ Hz, 2H), 1.13(d, $J=6$ Hz, 2H), 0.91(q, $J= 7.20$ Hz, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.53, 170.0, 128.08, 94.20, 91.43, 72.86, 66.42, 65.09, 62.83, 39.24, 38.87, 21.40, 20.67, 20.46, 19.25, 18.84, 18.47, 13.80; HRMS (ESI) m/z : [M+Na]⁺Calcd for C₁₅H₂₄O₆Na 323.1471; found 323.1461.

24. *1-Penten-3-yl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (7d)* Colourless liquid; $[\alpha]_D^{30} +114.52$ ($c = 1.17$, CH₃OH,); IR (film, cm⁻¹):3469, 3079, 3052, 2966, 2934, 2880, 1757, 1649, 1450, 1428, 1370, 1234, 1036, 984, 910; ¹H-NMR (500 MHz,CDCl₃): δ 5.87-5.82(m, 1H), 5.79-5.76(m, 1H), 5.68-5.61(m, 1H), 5.31-5.09(m, 3H), 5.06(s, 1H), 4.24-4.09(m, 3H), 4.04-4.00(m, 1H), 2.08(s, 3H), 2.06(s, 3H), 0.94(t, $J=7.0$ Hz, 3H), 0.90-0.83(m, 2H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.42, 169.93, 137.53, 128.64, 127.86, 117.29, 90.88, 79.16, 66.76, 65.08, 62.80, 28.15, 20.61, 20.42, 9.82; HRMS (ESI) m/z : [M+Na]⁺Calcd for C₁₅H₂₂O₆Na 321.1314; found 321.1349.

25. *(1R,2S,5R)(-) Menthyl 4, 6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (7e)^{45b}*. Colourless liquid; $[\alpha]_D^{20} + 33.08$ ($c = 2.69$, CH₃OH, $\alpha:\beta=1:0$); IR (film, cm⁻¹): 3740, 3535, 3479, 3051, 2955, 2927, 2875, 1750, 1655, 1453, 1370, 1317, 1232, 1183, 1036, 911,

688; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.86(s, 2H), 5.32(d, $J=9.4$ Hz, 1H), 5.04(s, 1H), 4.27-4.22(m, 2H), 4.18-4.13(m, 1H), 3.87(d, $J=9.8$ Hz, 1H), 2.29-2.24(m, 1H), 2.10(s, 6H), 1.99-1.96(m, 1H), 1.74-1.68(m, 2H), 1.63(t, $J=4.2$ Hz, 1H), 1.31-1.23(m, 2H), 1.15(dd, $J=3.2$, 13.1 Hz, 1H), 0.99-0.97(m, 1H), 0.94-0.91(m, 1H), 0.89-0.83(m, 9H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 170.47, 169.97, 128.16, 128.0, 95.88, 85.51, 66.49, 65.22, 62.84, 49.10, 44.76, 37.30, 27.94, 26.37, 20.66, 20.47, 19.39, 18.46, 13.36; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{32}\text{O}_6\text{Na}$ 391.2096; found 391.2104.

26. (+)-Bornyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (**7f**)^{45a}. Colourless liquid; $[\alpha]_{\text{D}}^{20} + 48.76$ ($c = 1.66$, CH_3OH , $\alpha:\beta=1:0$); IR (film, cm^{-1}): 3740, 3638, 3544, 3470, 3052, 2952, 2884, 1758, 1652, 1453, 1370, 1333, 1232, 1186, 1043, 908, 689; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.86(s, 2H), 5.31(d, $J=9.68$ Hz, 1H), 5.03(s, 1H), 4.24(dd, $J=5.73$, 12.1 Hz, 1H), 4.18-4.13(m, 2H), 3.87(dt, $J=2.5$, 9.8 Hz, 1H), 2.27-2.26(m, 1H), 2.10(m, 6H), 1.98-1.94(m, 1H), 1.74-1.67(m, 2H), 1.63(t, $J=4.4$ Hz, 1H), 1.21-1.26(m, 2H), 0.87(s, 3H), 0.86(s, 3H), 0.85(s, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 170.48, 169.98, 128.37, 128.16, 95.87, 85.50, 66.47, 65.19, 62.83, 49.90, 47.05, 44.74, 37.29, 27.94, 26.22, 20.66, 20.47, 19.39, 18.57, 13.36; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_6\text{Na}$ 389.1940; found 389.1908.

27. (+)-endo-Fenchyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (**7g**)^{45b}. White solid; mp=68-70 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{20} + 78.4$ ($c = 2.18$, CH_3OH , $\alpha:\beta=1:0$); IR (KBr, cm^{-1}): 3461, 3048, 2954, 2872, 2720, 1745, 1660, 1464, 1379, 1227, 1052, 909; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.88(s, 2H), 5.31(d, $J=9.6$ Hz, 1H), 5.00(s, 1H), 4.26(dd, $J=5.2$, 12.2 Hz, 1H), 4.18-4.15(m, 2H), 3.47(s, 1H), 2.10(s, 6H), 1.75-1.66(m, 3H), 1.61(s, 1H), 1.50(d, $J=10$ Hz, 1H), 1.44-1.41(m, 1H), 1.13(s, 3H), 1.06(s, 3H), 1.00(m, 1H), 0.89(s, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 170.56, 169.96, 128.26, 127.68, 93.89, 89.90, 65.54, 675.02, 62.86,

48.57, 48.86, 41.08, 39.13, 31.53, 25.67, 20.83, 20.67, 20.48, 19.42; HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{20}H_{30}O_6Na$ 389.1940; found 389.1920.

28. *Allyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (9a)*³⁵. Colourless liquid; $[\alpha]_D^{20} +81.29$ ($c = 1.39$, CH_3OH , $\alpha:\beta=5:1$); IR (film, cm^{-1}): 3457, 3087, 3023, 2952, 2898, 2864, 1745, 1651, 1430, 1372, 1233, 1133, 1043, 976, 912; 1H -NMR (500 MHz, $CDCl_3$): δ 5.96-5.90(m, 2H), 5.88-5.82(m, 1H), 5.32-5.28(m, 2H), 5.20(dd, $J=1.06$, 10.50 Hz, 1H), 5.07(brs, 1H), 4.28-4.23(m, 2H), 4.17(dd, $J= 2.3$, 12 Hz, 1H), 4.13-4.05(m, 2H), 2.09(s, 3H), 2.07(s, 3H); ^{13}C -NMR (125 MHz, $CDCl_3$): δ 170.37, 169.90, 133.81, 128.93, 127.45, 117.13, 93.32, 68.93, 66.68, 65.00, 62.65, 20.59, 20.42. HRMS (ESI) m/z : $[M + K]^+$ Calcd for $C_{13}H_{18}O_6K$ 309.0740; found 309.0773.

29. *R (+) Perillyl 4, 6- di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (9b)*. Colourless liquid; $[\alpha]_D^{20} +83.60$ ($c = 1.10$, CH_3OH , $\alpha:\beta=1:0$); IR (film, cm^{-1}): 3741, 3470, 3078, 2920, 2843, 1758, 1727, 1644, 1437, 1369, 1238, 1187, 1142, 1034, 971, 890, 820, 690; 1H -NMR (500 MHz, $CDCl_3$): δ 5.86(d, $J= 10.6$ Hz, 1H), 5.82(dt, $J=2.3$, 10.4 Hz, 1H), 5.73(brs, 1H), 5.30(dd, $J=1.5$, 12.4 Hz, 1H), 5.03(brs, 1H), 4.69(d, $J = 8.5$ Hz, 2H), 4.23(dd, $J=5.6$, 12.4 Hz, 2H), 4.16(d, $J=2.2, 11.9$ Hz, 1H), 4.15-4.14(m, 1H), 3.91(d, $J=11.4$ Hz, 1H), 2.16-2.11(m, 5H), 2.08(s, 3H), 2.06(s, 3H), 1.84-1.81(m, 2H), 1.71(s, 3H), 1.50-1.46(m, 1H); ^{13}C -NMR (125 MHz, $CDCl_3$): δ 170.40, 169.90, 149.34, 133.60, 128.80, 127.62, 125.0, 108.40, 93.01, 72.53, 66.65, 65.02, 62.71, 40.60, 30.17, 27.09, 26.38, 20.64, 20.47, 20.43; HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{20}H_{28}O_6Na$ 387.1783; found 387.1820.

30. *S (-) Perillyl 4, 6-di-O- acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (9c)*. Colourless liquid; $[\alpha]_D^{20} + 34.13$ ($c = 2.08$, CH_3OH , $\alpha:\beta=1:0$); IR (film, cm^{-1}): 3470, 3078, 2919, 2835, 1759, 1727, 1675, 1644, 1437, 1369, 1237, 1186, 1142, 1100, 1032, 975, 890, 823, 687 ; 1H -NMR (500 MHz, $CDCl_3$): δ 5.87(d, $J=10.3$ Hz, 1H), 5.82(dt, $J=2.2$, 10.3 Hz,

1H), 5.74(bris, 1H), 5.30(dd, J=1.16, 9.5 Hz, 1H), 5.02(bris, 1H), 4.70(d, J=8.3 Hz, 2H), 4.24(dd, J=5.7, 12.2 Hz, 1H), 4.18(d, J=2.2, 11.9 Hz, 1H), 4.12-4.10(m, 2H), 3.93(d, J=11.6 Hz, 1H), 2.16-2.10(m, 5H), 2.09(s, 3H), 2.07(s, 3H), 1.85-1.81(m, 1H), 1.72(s, 3H), 1.49-1.47(m, 1H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.40, 169.90, 149.32, 133.63, 128.78, 127.67, 125.12, 108.40, 92.83, 72.06, 66.69, 65.04, 62.72, 40.67, 30.18, 27.11, 26.11, 20.63, 20.46, 20.42; HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₂₈O₆Na 387.1783; found 387.1777.

31. *Benzyl 4, 6-di-O-acetyl-2, 3-dideoxy- α-D-erythro-hex-2-enopyranoside (9d)*³⁵. Colourless liquid; ; [α]_D²⁰ +58.64 (c = 2.66, CH₃OH, α:β=3:1); IR (film, cm⁻¹): 3465, 3030, 2951, 2900, 1745, 1651, 1496, 1452, 1371, 1234, 1040, 909, 699; ¹H-NMR (500 MHz, CDCl₃): δ 7.37-7.35(m, 3H), 7.32-7.28(m, 2H), 5.90(d, J=10.4 Hz, 2H), 5.34(d, J=9.5 Hz, 1H), 5.14(bris, 1H), 4.81(d, J=11.6 Hz, 1H), 4.60(d, J=11.6 Hz, 1H), 4.25(dd, J=5.0, 11.6 Hz, 1H), 4.18-4.12(m, 2H), 2.10(s, 3H), 2.08(s, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.38, 169.90, 137.33, 129.00, 128.16, 127.71, 127.54, 127.48, 93.38, 69.18, 66.82, 65.03, 62.63, 20.61, 20.45; HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₇H₂₀O₆Na 343.1157; found 343.1129.

32. *tert-Butyl 4, 6-di-O-acetyl-2, 3-dideoxy- α -D-erythro-hex-2-enopyranoside (9e)*⁴⁶. Colourless liquid; [α]_D³⁰ +89.37 (c = 1.60, CH₃OH, α:β=1:0); IR (film, cm⁻¹): 3640, 3544, 3467, 3052, 2976, 2944, 1745, 1652, 1472, 1454, 1436, 1369, 1336, 1232, 1196, 1136, 1100, 1044, 1020, 981, 671; ¹H-NMR (500 MHz, CDCl₃): δ 5.80(d, J=9.90 Hz, 1H), 5.70(d, J=10.20 Hz, 1H), 5.28(s, 1H), 5.22(d, J=9.40 Hz, 1H), 4.19-4.09(m, 3H), 2.03(s, 6H), 1.25(s, 9H); ¹³C-NMR (125 MHz, CDCl₃): δ 170.34, 169.91, 129.26, 127.78, 88.63, 66.25, 65.02, 62.93, 64.34, 28.39, 20.58, 20.38; HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₄H₂₂O₆Na 309.1314; found 309.1312.

33. *tert-Amyl 4, 6-di-O-acetyl-2, 3-dideoxy-α-D-erythro-hex-2-enopyranoside (9f)*²⁷. Colourless liquid; [α]_D²⁰ + 57.76 (c =1.61, CH₃OH, α:β=1:0); IR (film, cm⁻¹): 3470, 3052,

2971, 2932, 2884, 1741, 1725, 1660, 1436, 1370, 1231, 1096, 1036, 910, 645; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.79(d, $J=10$ Hz, 1H), 5.70(dt, $J=2.4$, 10 Hz, 1H), 2.03(s, 6H), 5.25(s, 1H), 5.21(dd, $J=0.93$, 9.6 Hz, 1H), 4.19-4.09(m, 3H), 1.53(m, 2H), 1.20(s, 3H), 1.19(s, 3H), 0.85(t, $J=7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 170.37, 169.92, 129.24, 127.72, 88.41, 66.38, 64.99, 63.29, 62.94, 33.88, 25.79, 25.32, 20.59, 20.39, 8.04; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{24}\text{O}_6\text{Na}$ 323.1470; found 323.1471.

34. *α -Terpinyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (9g)*²⁷. Colourless liquid; ; $[\alpha]_{\text{D}}^{28}=109.8$ ($c=0.51$, CH_3OH , $\alpha:\beta=1:0$) $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.83(d, $J=9.85$ Hz, 1H), 5.74(dt, $J=2.0$, 10.2 Hz, 1H), 5.39(brs, 1H), 5.33(s, 1H), 5.25(m, 1H), 4.24-4.15(m, 4H), 2.096(s, 3H), 2.094(s, 3H), 1.65(s, 3H), 1.34-1.24(m, 5H), 1.23(s, 6H), 1.19(d, $J=8.7$ Hz, 2H), 0.88(m, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 170.51, 170.04, 133.68, 129.38, 127.67, 120.23, 88.20, 78.93, 66.60, 65.11, 63.06, 43.54, 31.25, 30.68, 26.44, 23.44, 20.66, 20.46; IR (film, cm^{-1}): 3450, 2978, 2931, 2901, 2874, 1744, 1652, 1451, 1373, 1234, 1109, 1048, 1012, 981, 833, 675; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_6\text{Na}$ 389.1940; found 389.1929.

35. *Terpin-1-en-4-yl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (9h)*²⁷. Colourless liquid; $[\alpha]_{\text{D}}^{30}+90.90$ ($c=0.33$, CH_3OH , $\alpha:\beta=1:0$); IR (film, cm^{-1}): 3458, 2964, 2928, 1756, 1721, 1656, 1599, 1445, 1371, 1247, 1128, 1100, 1022; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.85(d, $J=9.54$ Hz, 1H), 5.77(dt, $J=2.0$, 10.26 Hz, 1H), 5.33(s, 1H), 5.31(bs, 1H), 4.29(dd, $J=3.58$, 12.0 Hz, 1H), 4.24-4.06(m, 3H), 2.09(s, 3H), 2.07(s, 3H), 1.88-1.81(m, 2H), 1.67(s, 3H), 1.44-1.24(m, 5H), 0.92(m, 6H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 170.53, 170.00, 132.39, 130.53, 128.87, 128.15, 118.73, 87.95, 79.05, 67.27, 66.67, 64.67, 62.48, 38.43, 33.11, 30.05, 27.13, 22.83, 20.66, 17.36, 17.05; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_6\text{Na}$ 389.1940; found 389.1957.

¹H NMR Spectral Chart of Compound **3a**

^{13}C NMR Spectral Chart of Compound **3a**

HRMS Spectral Chart of Compound **3a**

¹H NMR Spectral Chart of Compound **3b**

¹³C NMR Spectral Chart of Compound **3b**

HRMS Spectral Chart of Compound **3b**

^1H NMR Spectral Chart of Compound **3c**

¹³C NMR Spectral Chart of Compound **3c**

^1H NMR Spectral Charts of Compound **3d**

¹³C NMR Spectral Charts of Compound **3d**

HRMS Spectral Charts of Compound **3d**

^1H NMR Spectral Charts of Compound **3e**

¹³C NMR Spectral Charts of Compound **3e**

¹³C NMR Spectral Charts of Compound **3e**

HRMS Spectral Chart of Compound **3e**

HSQC Spectral Chart of Compound **3e**

HSQC Spectral Chart of Compound **3e**

HSQC Spectral Chart of Compound **3e**

COSY Spectral Chart of Compound 3e

COSY Spectral Chart of Compound **3e**

COSY Spectral Chart of Compound **3e**

HMBC Spectral Chart of Compound **3e**

HMBC Spectral Chart of Compound **3e**

HMBC Spectral Chart of Compound **3e**

^1H NMR Spectral Chart of Compound **3f**

^1H NMR Spectral Chart of Compound **3f**

^{13}C NMR Spectral Chart of Compound **3f**

HRMS Spectral Chart of Compound **3f**

HSQC Spectral Chart of Compound **3f**

HSQC Spectral Chart of Compound **3f**

COSY Spectral Chart of Compound **3f**

COSY Spectral Chart of Compound **3f**

COSY Spectral Chart of Compound **3f**

HMBC Spectral Chart of Compound **3f**

HMBC Spectral Chart of Compound **3f**

HMBC Spectral Chart of Compound **3f**

^1H NMR Spectral Chart of Compound **3g**

^{13}C NMR Spectral Chart of Compound **3g**

HRMS Spectral Chart of Compound **3g**

^1H NMR Spectral Chart of Compound **3h**

3h

¹³C NMR Spectral Chart of Compound **3h**

^1H NMR Spectral Chart of Compound **3i**

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¹³C NMR Spectral Chart of Compound **3i**

HRMS Spectral Chart of Compound **3i**

¹H NMR Spectral Chart of Compound **3j**

¹³C NMR Spectral Chart of Compound **3j**

HRMS Spectral Chart of Compound **3j**

¹H NMR Spectral Chart of Compound **5a**

n-Butyl glucosi

¹³C NMR Spectral Chart of Compound **5a**

HRMS Spectral Chart of Compound **5a**

^1H NMR Spectral Chart of Compound **5b**

^{13}C NMR Spectral Chart of Compound **5b**

HRMS Spectral Chart of Compound **5b**

^1H NMR Spectral Chart of Compound **5c**

^{13}C NMR Spectral Chart of Compound **5c**

HRMS Spectral Chart of Compound **5c**

¹H NMR Spectral Chart of Compound **5 d**

HRMS Spectral Chart of Compound **5d**

¹H NMR Spectral Chart of Compound **5 e**

¹³C NMR Spectral Chart of Compound **5e**

HRMS Spectral Chart of Compound **5e**

¹H NMR Spectral Chart of Compound **5f**

¹³C NMR Spectral Chart of Compound **5f**

¹H NMR Spectral Chart of Compound **5g**

¹³C NMR Spectral Chart of Compound **5 g**

HRMS Spectral Chart of Compound **5g**

¹H NMR Spectral Chart of Compound **5h**

¹³C NMR Spectral Chart of Compound **5h**

HRMS Spectral Chart of Compound **5h**

¹H NMR Spectral Chart of Compound **5i**

¹³C NMR Spectral Chart of Compound **5i**

HRMS Spectral Chart of Compound **5i**

5j

¹H NMR Spectral Chart of Compound **5j**

5j

¹³C NMR Spectral Chart of Compound **5j**

HRMS Spectral Chart of Compound **5j**

¹H NMR Spectral Chart of Compound **7a**

¹³C NMR Spectral Chart of Compound **7a**

HRMS Spectral Chart of Compound **7a**

¹H NMR Spectral Chart of Compound **7b**

¹³C NMR Spectral Chart of Compound **7b**

HRMS Spectral Chart of Compound **7b**

^1H NMR Spectral Chart of Compound **7c**

^{13}C NMR Spectral Chart of Compound **7c**

HRMS Spectral Chart of Compound **7c**

¹H NMR Spectral Chart of Compound **7d**

¹³C NMR Spectral Chart of Compound **7d**

HRMS Spectral Chart of Compound **7d**

^1H NMR Spectral Chart of Compound **7e**

HRMS Spectral Chart of Compound **7e**

¹H NMR Spectral Chart of Compound **7f**

¹³C NMR Spectral Chart of Compound **7f**

HRMS Spectral Chart of Compound **7f**

¹H NMR Spectral Chart of Compound **7g**

^{13}C NMR Spectral Chart of Compound **7g**

HRMS Spectral Chart of Compound **7g**

¹³C NMR Spectral Chart of Compound **9a**

¹H NMR Spectral Chart of Compound **9b**

^{13}C NMR Spectral Chart of Compound **9b**

HRMS Spectral Chart of Compound **9b**

¹H NMR Spectral Chart of Compound 9c

¹³C NMR Spectral Chart of Compound **9c**

HRMS Spectral Chart of Compound **9c**

¹H NMR Spectral Chart of Compound **9d**

¹³C NMR Spectral Chart of Compound **9d**

HRMS Spectral Chart of Compound **9d**

¹H NMR Spectral Chart of Compound **9e**

¹³C NMR Spectral Chart of Compound **9e**

^1H NMR Spectral Chart of Compound **9f**

¹³C NMR Spectral Chart of Compound **9f**

HRMS Spectral Chart of Compound **9f**

¹H NMR Spectral Chart of Compound **9g**

¹³C NMR Spectral Chart of Compound **9g**

HRMS Spectral Chart of Compound **9g**

¹H NMR Spectral Chart of Compound **9h**

¹³C NMR Spectral Chart of Compound **9h**

HRMS Spectral Chart of Compound **9h**