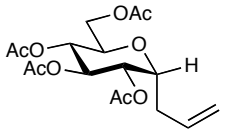
Studies on the Stereoselective Synthesis of *C*-Allyl Glycosides

Glenn J. McGarvey,* Christopher A. LeClair, and Bahar A. Schmidtmann

Supporting Information



3-(2', 3', 4', 6'-Tetra-*O*-acetyl-α-D-glucopyranosyl)-1-propene.[1] To a stirred suspension of D-glucopyranose (2.55 g, 14.16 mmol, 1equiv) in Ac_2O (12.8 mL, 5 mL of Ac_2O/g of substrate) at rt under N_2 was added I_2 (0.13 g, 50 mg I_2/g of substrate). After stirring at rt for 30 min, the reaction mixture was diluted with CH_2Cl_2, washed with dilute aq. $Na_2S_2O_3$ soln. (1x), and then sat. aq. Na_2CO_3 soln. (1x). The organic layer was diluted with an equal volume of sat. aq. $NaHCO_3$ soln. and the biphasic solution was vigorously stirred for 45 min, separated, dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave α-D-glucopyranose pentaacetate (5.53 g, quant.) as a white solid which was taken on without further purification. To a stirred solution of the pentaacetate in MeCN (71 ml, 0.2M) at rt under N_2 was added BF_3•OEt_2 (17.9 mL, 20.10 g, 0.14 mol, 10 equiv) and allyl-$SiMe_3$ (22.5 mL, 16.18 g, 0.14 mol, 10 equiv) then heated to 80 °C. After stirring at 80 °C for 8 h, the reaction mixture was cooled to 0 °C, quenched with sat. aq. $NaHCO_3$ soln., and extracted with EtOAc (3x). The combined organic extracts were washed with H_2O (2x), brine (2x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (3:1) as the eluent to give peracetylated α-*C*-allyl glucopyranoside (2.12 g, 40%) as a white solid.

R_f = 0.58 (hexanes/EtOAc 1:1).

m.p. 107-108 °C.

$[\alpha]_D^{23}$ 75.6 (c 1.14, CH_2Cl_2).

IR (film, NaCl) 3068, 3019, 2995, 2978, 2950, 2905, 1740 br, 1642, 1454, 1426, 1409, 1385, 1368, 1332, 1246 br, 1156, 1136, 1115, 1095, 1082, 1037, 1005, 984, 935, 919, 911, 890, 817, 739, 719, 662, 657, 608, 588, 568 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71 (dddd, 1H, ^3J = 6.2, 7.3, 10.2, and 17.1 Hz, $CH_2C\boldsymbol{H}$=CH_2), 5.30 (t, 1H, ^3J = 9.1 Hz), 5.04-5.13 (m, 2H, CH_2CH=C$\boldsymbol{H_2}$), 5.05 (dd, 1H, ^3J = 5.7, 9.5 Hz), 4.94 (t, 1H, ^3J = 9.3 Hz), 4.24 (m, 1H, H1′), 4.17 (dd, 1H, ^3J = 5.4 Hz, ^2J = 12.2 Hz, H6′a), 4.04 (dd, 1H, ^3J = 2.6 Hz, ^2J = 12.1 Hz, H6′b), 3.82 (ddd, 1H, ^3J = 2.6, 5.3, and 9.4 Hz, H5′), 2.46-2.58 (m, 1H, C$\boldsymbol{H_{(3a)}}$HCH=CH_2), 2.25-2.35 (m, 1H, CH$\boldsymbol{H_{(3b)}}$CH=CH_2), 2.04 (s, 3H, OAc), 2.01 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.99 (s, 3H, OAc).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.3, 169.8, 169.7, 133.1, 117.9, 72.0, 70.5, 70.4, 68.9, 62.3, 30.7, 20.8 (2C).

HRMS (+FAB, *m/z*): calcd for $C_{17}H_{25}O_9$ (MH^+), 373.1498; found, 373.1501.

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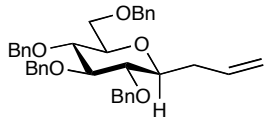
[1] Horton, D.; Miyake, T. *Carbohydr. Res.* **1988**, *184*, 221-229.



3-(2′, 3′, 4′, 6′-Tetra-*O*-benzyl-β-D-glucopyranosyl)-1-propene.[2] To a stirred solution of 2, 3, 4, 6-tetra-*O*-benzyl-D-glucopyranose (6.04 g, 11.18 mmol, 1equiv) in CH_2Cl_2 (160 mL, 0.07M) at rt under N_2 was added 4Å molecular sieves (11.20 g, 1 g/mmol substrate) and PCC (11.08 g, 51.41 mmol) in one portion. After stirring at rt for 2 h, the dark suspension was diluted with EtOAc/hexanes (2:1) and filtered through a dry-packed silica gel column which was flushed with EtOAc/hexanes (2:1). Removal of the combined filtrates under reduced pressure gave corresponding gluconolactone (**4**, 5.77 g, 96%) as a colorless, viscous oil, which was used without further purification.[2,3] To a stirred solution of 2, 3, 4, 6-tetra-*O*-benzyl-D-gluconolactone (5.64 g, 10.46 mmol, 1equiv) in THF (131 mL, 0.08M) at -78 °C under argon was added allyl-MgCl (2.0M in THF) (6.3 mL, 12.56 mmol, 1.2 equiv) slowly dropwise. After stirring at -78 °C for 4 h, the reaction was quenched by addition of sat. aq. NH_4Cl soln., extracted with EtOAc (3x), washed with brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave the expected lactol as an oil which was dissolved in CH_2Cl_2 (105 mL, 0.1M) and cooled to -78 °C under argon. Et_3SiH (5.0 mL, 3.65 g, 31.39 mmol, 3 equiv) and $BF_3{\bullet}OEt_2$ (2.7 mL, 2.97 g, 20.93 mmol, 2 equiv) were added then the reaction was stirred at -78 °C for 2 h before warming to -20 °C. After stirring at -20 °C for 10 h, the reaction mixture was quenched by addition of sat. aq. $NaHCO_3$ soln., extracted with CH_2Cl_2 (3x), washed with brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a crude oil, which was purified by column chromatography on silica gel using hexanes/EtOAc (95:5) as the eluent to give perbenzylated β-*C*-allyl glucopyranoside (4.68 g, 79%) as a white solid.

R_f = 0.47 (hexanes/EtOAc 85:15); 0.72 (hexanes/EtOAc 7:3).

m.p. 89-90 °C.

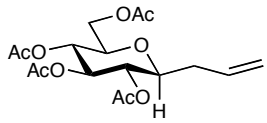
$[\alpha]_D^{23}$ 15.6 (c 1.11, CH_2Cl_2).

IR (film, NaCl) 3064, 3027, 2978, 2909, 2868, 2811, 1642, 1605, 1585, 1495, 1479, 1450, 1430, 1401, 1364, 1319, 1303, 1274, 1230, 1217, 1197, 1152, 1123, 1111, 1099, 1054, 1025, 997, 952, 911, 829, 756, 735, 698, 653, 633 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.40 (m, 20H, PhH), 5.86 (dddd, 1H, ^3J = 6.5, 7.2, 10.2, and 17.2 Hz, CH_2CH=CH_2), 5.09-5.19 (m, 2H, CH_2CH=C***H*$_2$**), 4.94 (ABq, 2H, ^2J = 11.1, 13.0 Hz, benzylic CH_2), 4.81 (ABq, 2H, ^2J = 10.8, 70.6 Hz, benzylic CH_2), 4.74 (ABq, 2H, ^2J = 10.8, 71.0 Hz, benzylic CH_2), 4.64 (ABq, 2H, ^2J = 12.3, 21.3 Hz, benzylic CH_2), 3.62-3.80 (m, 4H), 3.45 (ddd, 1H, ^3J = 2.2, 3.9, and 9.5 Hz, H5′), 3.34-3.41 (m, 2H), 2.59-2.69 (m, 1H, C***H*$_{(3a)}$**HCH=CH_2), 2.30-2.42 (m, 1H, CH***H*$_{(3b)}$**CH=CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 138.5, 138.4, 138.3, 135.0, 128.6 (2C), 128.5, 128.1 (2C), 128.0, 127.9 (2C), 127.8, 127.7, 117.2, 87.5, 81.7, 79.2, 78.9, 78.8, 75.7, 75.3, 75.2, 73.6, 69.2, 36.2.

HRMS (+FAB, *m/z*): calcd for $C_{37}H_{41}O_5$ (MH^+), 565.2954; found, 565.2951.



3-(2′, 3′, 4′, 6′-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1-propene. To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-benzyl-β-D-glucopyranosyl)-1-propene (3.05 g, 5.51 mmol, 1 equiv) in liquid NH_3/THF (4:1) (225 mL, 0.024M) at -78 °C under argon was added small pieces of Na°. Before addition of each new piece of Na°, the solution was allowed to decolorize until a deep blue color persisted for 15 min. Solid NH_4Cl was cautiously added until the blue color was discharged then the solvent was allowed to evaporate. The white powdery residue was suspended in CH_2Cl_2 (90 mL, 0.06M) and Ac_2O (90 mL, 97.38 g, 0.95

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[2] Brenna, E.; Fuganti, C.; Grasselli, P.; Serra, S.; Zambotti, S. *Chem. Eur. J.* **2002**, *8*, 1872-1878.

[3] (a) Kuzuhara, H.; Fletcher, Jr., H.G. *J. Org. Chem.* **1967**, *32*, 2531-2534. (b) Lewis, M.D.; Cha, J.K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976-4978.

mol), pyridine (90 mL, 88.02 g, 1.11 mol), and DMAP (2.25 g, 18.39 mmol, 3.4 equiv) were introduced. After stirring at rt for 4 h, the mixture was filtered through Celite™. The filtrate was concentrated to 1/3 of the original volume, diluted with CH_2Cl_2, washed with sat. aq. $CuSO_4$ soln. (3x), H_2O (2x), brine (2x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a crude oil, which was purified by column chromatography on silica gel using hexanes/EtOAc (3:1) as the eluent to give peracetyl β-*C*-allyl glucopyranoside (1.81 g, 90%) as a white solid.

R_f = 0.61 (hexanes/EtOAc 1:1).

m.p. 75-76 °C.

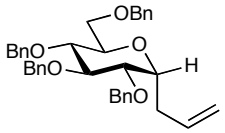
$[\alpha]_D^{23}$ -7.4 (c 1.39, CH_2Cl_2).

IR (film, NaCl) 3081, 3015, 2978, 2950, 2868, 1753, 1642, 1605, 1540, 1434, 1368, 1328, 1225 br, 1144, 1103, 1033, 997, 980, 907, 784, 702, 600 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (ddt, 1H, ^3J = 6.8, 9.5, and 17.8 Hz, CH_2CH=CH_2), 5.13 (t, 1H, ^3J = 9.3 Hz), 4.99-5.08 (m, 2H, CH_2CH=CH_2), 5.01 (t, 1H, ^3J = 9.5 Hz), 4.88 (t, 1H, ^3J = 9.6 Hz), 4.20 (dd, 1H, ^3J = 5.0 Hz, ^2J = 12.3 Hz, H6′a), 4.05 (dd, 1H, ^3J = 2.2 Hz, ^2J = 12.3 Hz, H6′b), 3.60 (ddd, 1H, ^3J = 2.3, 5.0, and 9.8 Hz, H5′), 3.47 (ddd, 1H, ^3J = 4.4, 6.9, and 9.7 Hz, H1′), 2.17-2.36 (m, 1H, CH_2CH=CH_2), 2.04 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.96 (s, 3H, OAc).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.5, 169.7, 169.6, 133.1, 117.8, 77.3, 75.8, 74.5, 71.8, 68.8, 62.4, 36.0, 20.9, 20.8 (2C).

HRMS (+FAB, *m/z*): calcd for $C_{17}H_{25}O_9$ (MH^+), 373.1498; found, 373.1497.



3-(2′, 3′, 4′, 6′-Tetra-*O*-benzyl-α-D-glucopyranosyl)-1-propene.[4] To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-α-D-glucopyranosyl)-1-propene (268 mg, 0.72 mmol, 1equiv) in anhyd. MeOH (4.8 mL, 0.15M) at rt under N_2 was added NaOMe (15.5 mg, 0.29 mmol, 40 mol %) in anhyd. MeOH (1.2 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). To a stirred suspension of the resulting tetrol in DMF (4.8 mL, 0.15M) at 0 °C under N_2 was added NaH (60% in oil) (460 mg, 11.50 mmol, 16 equiv) in portions. After stirring for 15 min, BnBr (1.4 mL, 1.97 g, 11.50 mmol, 16 equiv) was added dropwise over 30 min followed by TBAI (cat.). After warming to rt and stirring for 16 h, the reaction mixture was poured into ice-water and extracted with CH_2Cl_2 (3x). The combined organic extracts were washed with sat. aq. $NaHCO_3$ soln. (2x), brine (2x), dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (9:1) as the eluent to give perbenzylated α-*C*-allyl glucopyranoside (351 mg, 86%) as a white solid.

R_f = 0.42 (hexanes/EtOAc 85:15).

m.p. 59-60 °C.

$[\alpha]_D^{23}$ 37.5 (c 1.24, CH_2Cl_2).

IR (film, NaCl) 3085, 3064, 3027, 3007, 2917, 2864, 1642, 1605, 1585, 1495, 1454, 1397, 1364, 1328, 1262, 1209, 1156, 1091 br, 1025, 1001, 915, 821, 735, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.39 (m, 18H, PhH), 7.14-7.18 (m, 2H, PhH), 5.86 (ddt, 1H, ^3J = 6.6, 10.2, and 17.1 Hz, CH_2CH=CH_2), 5.08-5.18 (m, 2H, CH_2CH=CH_2), 4.91 (ABq, 2H, ^2J = 11.0, 38.9 Hz, benzylic CH_2), 4.69 (ABq, 2H, ^2J =

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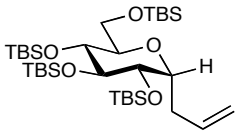
[4] (a) Gurjar, M. K.; Mainkar, A. S.; Syamala, M. *Tetrahedron: Asymmetry* **1993**, *4*, 2343-2346. (b) Hosomi, A.; Sakata, Y.; Sakurai, H. *Carbohydr. Res.* **1987**, *171*, 223-232.

11.6, 21.7 Hz, benzylic CH_2), 4.68 (ABq, 2H, ^2J = 10.6, 103.1 Hz, benzylic CH_2), 4.58 (ABq, 2H, ^2J = 12.3, 47.3 Hz, benzylic CH_2), 4.17 (m, 1H, H1′), 3.61-3.87 (m, 6H), 2.47-2.61 (m, 2H, C***H*****$_2$**CH=CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 138.4 (2C), 138.2, 134.9, 128.6, 128.5, 128.2, 128.1 (2C), 128.0 (2C), 127.9, 127.8 (2C), 117.1, 82.6, 80.2, 78.3, 75.6, 75.3, 73.9, 73.6, 73.3, 71.3, 69.1, 30.0.

HRMS (+FAB, *m/z*): calcd for $C_{37}H_{41}O_5$ (MH^+), 565.2954; found, 565.2950.



3-(2′, 3′, 4′, 6′-Tetra-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranosyl)-1-propene. To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-α-D-glucopyranosyl)-1-propene (260 mg, 0.70 mmol, 1 equiv) in anhyd. MeOH (4.8 mL, 0.15M) at rt under N_2 was added NaOMe (15.1 mg, 0.28 mmol, 40 mol %) in anhyd. MeOH (1.2 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). To a stirred suspension of the resulting tetrol in CH_2Cl_2 (10.0 mL, 0.07M) at 0 °C under N_2 was added 2,6-lutidine (0.81 mL, 0.75 g, 6.99 mmol, 10 equiv) and TBSOTf (1.3 mL, 1.48 g, 5.59 mmol, 8 equiv) then warmed to rt. After stirring at rt for 8 h, the reaction mixture was diluted with CH_2Cl_2, washed with sat. aq. $CuSO_4$ soln. (2x), H_2O (2x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (95:5) as the eluent to give TBS protected α-*C*-allyl glucopyranoside (424 mg, 92%) as a colorless, viscous oil.

R$_f$ = 0.51 (hexanes/EtOAc 9:1).

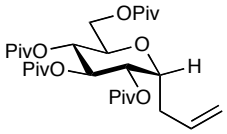
[α]$_D^{23}$ 21.5 (c 1.40, CH_2Cl_2).

IR (film, NaCl) 3077, 2954, 2929, 2884, 2856, 2803, 2774, 2741, 2709, 1642, 1471, 1462, 1405, 1389, 1360, 1323, 1258, 1217, 1189, 1095 br, 1005, 976, 939, 911, 882, 837, 813, 776, 670 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (dddd, 1H, ^3J = 6.1, 7.4, 10.3, and 17.2 Hz, CH_2C***H***=CH_2), 5.10 (ddd, 1H, ^2J = 1.6 Hz, $J_{H1trans,H3}$ = 3.4 Hz, ^3J = 17.3 Hz, CH_2CH=CH***H*****$_{trans}$**), 5.03 (ddt, 1H, ^2J = 1.0 Hz, $J_{H1cis,H3}$ = 2.0 Hz, ^3J = 10.2 Hz, CH_2CH=CH***H*****$_{cis}$**), 3.72-3.88 (m, 5H), 3.70 (m, 1H), 3.47 (m, 1H), 2.44 (dddt, 1H, $J_{H1,H3}$ = 1.5 Hz, ^3J = 6.0, 8.4 Hz, ^2J = 14.5 Hz, C***H*****$_{(3a)}$**HCH=CH_2), 2.04-2.16 (m, 1H, CH***H*****$_{(3b)}$**CH=CH_2), 0.93 (s, 9H, ^{t}Bu), 0.90 (s, 9H, ^{t}Bu), 0.88 (s, 18H, 2 ^{t}Bu), 0.11 (s, 6H, 2 SiMe), 0.09 (s, 3H, SiMe), 0.08 (s, 6H, 2 SiMe), 0.07 (s, 3H, SiMe), 0.04 (s, 6H, 2 SiMe).

^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 116.3, 78.2, 74.6, 71.8, 70.9, 69.6, 62.6, 36.1, 26.5, 26.3, 26.2, 26.0, 18.6, 18.4, 18.1, -3.2, -3.9, -4.0, -4.4, -4.8, -4.9, -5.1.

HRMS (+FAB, *m/z*): calcd for $C_{33}H_{73}O_5Si_4$ (MH^+), 661.4535; found, 661.4538.



3-(2′, 3′, 4′, 6′-Tetra-*O*-pivaloyl-α-D-glucopyranosyl)-1-propene. To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-α-D-glucopyranosyl)-1-propene (252 mg, 0.68 mmol, 1 equiv) in anhyd. MeOH (4.5 mL, 0.15M) at rt under N_2 was added NaOMe (15 mg, 0.27 mmol, 40 mol %) in anhyd. MeOH (1.1 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). To a stirred suspension of the resulting tetrol in pyridine (5.6 mL, 0.12M) at rt under N_2 was added PivCl (0.83 mL, 0.82 g, 6.77 mmol, 10 equiv) and DMAP (41 mg, 0.34 mmol, 0.5 equiv) then heated to 100 °C for 24 h. After cooling to rt, the reaction mixture was diluted with CH_2Cl_2, washed with sat. aq. $CuSO_4$ soln. (2x), H_2O (2x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (95:5) as the eluent to give perpivalated α-*C*-allyl glucopyranoside (307 mg, 84%) as a white solid.

$\mathbf{R}_f$ = 0.66 (hexanes/EtOAc 4:1).

m.p. 99-101 °C.

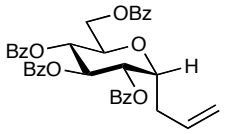
$[\alpha]_D^{23}$ 61.6 (c 1.34, CH_2Cl_2).

IR (film, NaCl) 3081, 2974, 2938, 2909, 2876, 1740, 1642, 1528, 1479, 1462, 1397, 1368, 1332, 1283, 1230, 1205, 1148, 1095, 1033, 988, 939, 915, 894, 825, 805, 788, 764, 711 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (dddd, 1H, ^3J = 6.2, 7.3, 10.2, and 17.1 Hz, CH_2CH=CH_2), 5.41 (t, 1H, ^3J = 9.5 Hz, H3′), 5.15 (ddd, 1H, ^2J = 1.7 Hz, $J_{H1trans,H3}$ = 3.1 Hz, ^3J = 17.1 Hz, CH_2CH=CH_{trans}), 5.09 (ddd, 1H, ^2J = 1.6 Hz, $J_{H1cis,H3}$ = 2.7 Hz, ^3J = 10.1 Hz, CH_2CH=CH_{cis}), 5.08 (dd, 1H, ^3J = 6.1, 9.9 Hz, H2′), 5.02 (dd, 1H, ^3J = 9.3, 9.9 Hz, H4′), 4.27 (ddd, 1H, ^3J = 3.9, 6.1, and 11.8 Hz, H1′), 4.08 (dd, 1H, ^3J = 1.9 Hz, ^2J = 12.2 Hz, H6′a), 4.01 (dd, 1H, ^3J = 5.6 Hz, ^2J = 12.2 Hz, H6′b), 3.83 (ddd, 1H, ^3J = 1.9, 5.6, and 10.0 Hz, H5′), 2.61 (ddd, 1H, ^3J = 7.4, 11.8 Hz, ^2J = 15.5 Hz, $CH_{(3a)}HCH$=CH_2), 2.24 (dddd, 1H, $J_{H1,H3b}$ = 1.9 Hz, ^3J = 4.0, 7.9 Hz, ^2J = 15.6 Hz, $CH_{(3b)}CH$=CH_2), 1.19 (s, 9H, ^{t}Bu), 1.15 (s, 9H, ^{t}Bu), 1.14 (s, 9H, ^{t}Bu), 1.11 (s, 9H, ^{t}Bu).

^{13}C NMR (75 MHz, $CDCl_3$) δ 178.3, 177.3, 177.2, 176.8, 133.3, 118.0, 72.5, 70.8, 70.2, 69.0, 68.7, 62.7, 39.0, 38.9, 30.0, 27.4, 27.3, 27.2, 26.7.

HRMS (+FAB, *m/z*): calcd for $C_{29}H_{49}O_9$ (MH^+), 541.3376; found, 541.3379.



3-(2′, 3′, 4′, 6′-Tetra-*O*-benzoyl-α-D-glucopyranosyl)-1-propene.[5] To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-α-D-glucopyranosyl)-1-propene (257 mg, 0.69 mmol, 1 equiv) in anhyd. MeOH (4.6 mL, 0.15M) at rt under N_2 was added NaOMe (15 mg, 0.28 mmol, 40 mol %) in anhyd. MeOH (1.1 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). To a stirred suspension of the resulting tetrol in pyridine (5.8 mL, 0.12M) at rt under N_2 was added BzCl (1.3 mL, 1.55 g, 11.06 mmol, 16 equiv) and DMAP (42 mg, 0.35 mmol, 0.5 equiv). After stirring at rt for 15 h, the reaction mixture was diluted with CH_2Cl_2, washed with sat. aq. $CuSO_4$ soln. (2x), H_2O (2x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (9:1) as the eluent to give perbenzoylated α-*C*-allyl glucopyranoside (382 mg, 89%) as a white solid.

$\mathbf{R}_f$ = 0.35 (hexanes/EtOAc 4:1).

m.p. 121-122 °C.

$[\alpha]_D^{23}$ 35.5 (c 1.14, CH_2Cl_2).

IR (film, NaCl) 3068, 3036, 3007, 2954, 2917, 2848, 1724, 1691, 1642, 1601, 1585, 1491, 1450, 1417, 1377, 1315, 1270, 1176, 1095, 1070, 1025, 976, 919, 854, 805, 711, 686 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91-8.15 (m, 9H, PhH), 7.30-7.56 (m, 11H, PhH), 6.01 (t, 1H, ^3J = 8.5 Hz, H3′), 5.81 (dddd, 1H, ^3J = 6.2, 7.3, 10.2, and 17.1 Hz, CH_2CH=CH_2), 5.57 (t, 1H, ^3J = 8.4 Hz, H4′), 5.53 (dd, 1H, ^3J = 5.4, 8.8 Hz, H2′), 5.19 (dd, 1H, ^2J = 1.4 Hz, ^3J = 17.1 Hz, CH_2CH=CH_{trans}), 5.03 (dd, 1H, ^2J = 1.1 Hz, ^3J = 10.2 Hz, CH_2CH=CH_{cis}), 4.52-4.64 (m, 3H, H1′, H6′a, and H6′b), 4.37 (ddd, 1H, ^3J = 3.5, 6.3, and 8.5 Hz, H5′), 3.34-3.41 (m, 2H), 2.76-2.88 (m, 1H, $CH_{(3a)}HCH$=CH_2), 2.46-2.55 (m, 1H, $CH_{(3b)}CH$=CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 165.9, 165.5, 133.9, 133.7, 133.6, 133.5, 133.3, 133.1, 130.4, 130.1, 130.0, 129.2, 129.1, 128.7, 128.6, 128.5, 118.2, 71.9, 71.1, 70.4, 70.0, 69.6, 63.2, 31.4.

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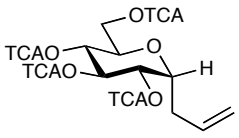
[5] Martin, M. G. G.; Horton, D. *Carbohydr. Res.* **1989**, *191*, 223-229.

HRMS (+FAB, *m/z*): calcd for $C_{37}H_{33}O_9$ (MH^+), 621.2124; found, 621.2128.



3-(2′, 3′, 4′, 6′-Tetra-*O*-trichloroacetyl-α-D-glucopyranosyl)-1-propene. To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-α-D-glucopyranosyl)-1-propene (236 mg, 0.63 mmol, 1 equiv) in anhyd. MeOH (4.2 mL, 0.15M) at rt under N_2 was added NaOMe (14 mg, 0.25 mmol, 40 mol %) in anhyd. MeOH (1.0 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). To a stirred suspension of the resulting tetrol in pyridine (6.3 mL, 0.1M) at rt under N_2 was added trichloroacetyl chloride (0.71 mL, 1.15 g, 6.33 mmol, 10 equiv) and DMAP (39 mg, 0.32 mmol, 0.5 equiv). After stirring at rt for 16 h, the reaction mixture was diluted with CH_2Cl_2, washed with sat. aq. $CuSO_4$ soln. (2x), H_2O (2x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (95:5) as the eluent to give TCA protected α-*C*-allyl glucopyranoside (399 mg, 80%) as a white solid.

R_f = 0.43 (hexanes/EtOAc 9:1).

m.p. 150-151 °C.

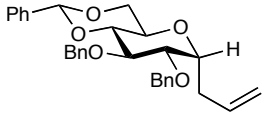
$[\alpha]_D^{23}$ 45.7 (c 1.17, CH_2Cl_2).

IR (film, NaCl) 3530, 3081, 3015, 2987, 2970, 2946, 2934, 2852, 1781 br, 1642, 1503, 1442, 1417, 1368, 1344, 1332, 1291, 1266, 1238 br, 1164, 1152, 1099, 1082, 1046, 1025, 993, 960, 943, 923, 854, 841, 825, 776, 747, 682, 592 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (dddd, 1H, ^3J = 5.9, 7.3, 9.9, and 17.2 Hz, CH_2CH=CH_2), 5.77 (t, 1H, ^3J = 9.6 Hz, H3′), 5.40 (dd, 1H, ^3J = 6.2, 9.8 Hz, H2′), 5.36 (t, 1H, ^3J = 9.6 Hz, H4′), 5.17-5.30 (m, 2H, CH_2CH=CH_2), 4.53 (ddd, 1H, ^3J = 4.2, 6.2, and 11.8 Hz, H1′), 4.51 (dd, 1H, ^3J = 1.9 Hz, ^2J = 12.2 Hz, H6′a), 4.41 (dd, 1H, ^3J = 5.1 Hz, ^2J = 12.2 Hz, H6′b), 4.18 (ddd, 1H, ^3J = 1.9, 5.0, and 10.0 Hz, H5′), 2.72 (ddd, 1H, ^3J = 7.4, 11.7 Hz, ^2J = 15.6 Hz, $CH_{(3a)}HCH$=CH_2), 2.49 (m, 1H, $CH_{(3b)}CH$=CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 160.9, 160.7, 160.6, 131.4, 119.5, 89.3, 88.9, 88.8 (2C), 74.1, 74.0, 72.3, 72.1, 68.1, 66.1, 30.0.

HRMS (+FAB, *m/z*): calcd for $C_{17}H_{13}Cl_{12}O_9$ (MH^+), 780.6821; found, 780.6826.



3-(2′, 3′-Di-*O*-benzyl-4′, 6′-*O*-benzylidene-α-D-glucopyranosyl)-1-propene.[6] To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-α-D-glucopyranosyl)-1-propene (255 mg, 0.69 mmol, 1 equiv) in anhyd. MeOH (4.6 mL, 0.15M) at rt under N_2 was added NaOMe (15 mg, 0.28 mmol, 40 mol %) in anhyd. MeOH (1.1 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). To a stirred suspension of the resulting tetrol in MeCN (20 mL, 0.07M) at rt under N_2 was added benzylidene dimethylacetal (0.17 mL, 167 mg, 1.10 mmol, 1.6 equiv) and *p*TsOH•H_2O (13 mg, 0.07 mmol, 10 mol %). After stirring at rt for 16 h, the reaction mixture was neutralized with Et_3N then concentrated under reduced pressure. To a suspension of the 4′, 6′-*O*-benzylidene protected α-*C*-allyl glucopyranoside in DMF (4.6 mL, 0.15M) at 0 °C under N_2 was added NaH (60% in oil) (219 mg, 5.46 mmol, 8 equiv) in portions. After stirring for 15 min, BnBr (0.65 mL, 0.93 g, 5.46 mmol, 8 equiv) was added dropwise over 30 min followed by TBAI (cat.). After warming to rt and stirring for 16 h, the reaction mixture was poured into ice-water and extracted with CH_2Cl_2 (3x). The combined organic

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[6] Xiaoliu, L.; Hiro, O.; Hideyo, T.; Shiro, I. *Synlett* **2001**, 1885-1888.

extracts were washed with sat. aq. $NaHCO_3$ soln. (2x), brine (2x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (95:5) as the eluent to give 2′,3′-di-*O*-benzylated α-*C*-allyl glucopyranoside (238 mg, 74%) as a white solid.

R_f = 0.25 (hexanes/EtOAc 9:1); 0.53 (hexanes/EtOAc 4:1).

m.p. 86-87 °C.

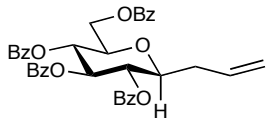
$[\alpha]_D^{23}$ 12.6 (c 1.21, CH_2Cl_2).

IR (film, NaCl) 3081, 3064, 3032, 3011, 2983, 2925, 2901, 2868, 1642, 1499, 1471, 1454, 1393, 1377, 1360, 1344, 1328, 1279, 1262, 1213, 1164, 1156, 1095, 1066, 1037, 1029, 997, 976, 919, 756, 711, 694, 678, 649 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.54 (m, 2H, PhH), 7.29-7.44 (m, 13H, PhH), 5.80 (ddt, 1H, ^3J = 6.9, 10.2, and 17.1 Hz, CH_2CH=CH_2), 5.59 (s, 1H, acetal H), 5.09-5.20 (m, 2H, CH_2CH=CH_2), 4.90 (ABq, 2H, ^2J = 11.5, 34.7 Hz, benzylic CH_2), 4.73 (ABq, 2H, ^2J = 11.7, 42.0 Hz, benzylic CH_2), 4.23-4.32 (m, 1H), 4.11 (ddd, 1H, ^3J = 5.8, 7.4, and 7.8 Hz, H1′), 3.86-3.95 (m, 1H), 3.78 (dd, 1H, ^3J = 5.7, 8.5 Hz), 3.65-3.73 (m, 3H), 2.56 (br t, 2H, J = 7.1 Hz, CH_2CH=CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 138.4, 137.6, 134.5, 129.1, 128.7, 128.5 (2C), 128.2, 128.0 (2C), 127.8, 126.2, 117.5, 101.4, 83.0, 79.7, 79.0, 75.1 (2C), 73.8, 69.7, 63.6, 30.9.

HRMS (+FAB, *m/z*): calcd for $C_{30}H_{33}O_5$ (MH^+), 473.2328; found, 437.2326.



3-(2′, 3′, 4′, 6′-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-1-propene.[5] To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-1-propene (231 mg, 0.62 mmol, 1 equiv) in anhyd. MeOH (4.1 mL, 0.15M) at rt under N_2 was added NaOMe (13 mg, 0.25 mmol, 40 mol %) in anhyd. MeOH (1.0 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). To a stirred suspension of the tetrol in pyridine (5.2 mL, 0.12M) at rt under N_2 was added BzCl (1.2 mL, 1.39 g, 9.91 mmol, 16 equiv) and DMAP (38 mg, 0.31 mmol, 0.5 equiv). After stirring at rt for 15 h, the reaction mixture was diluted with CH_2Cl_2, washed with sat. aq. $CuSO_4$ soln. (2x), H_2O (2x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (9:1) as the eluent to give perbenzoylated β-*C*-allyl glucopyranoside (348 mg, 90%) as a white foam.

R_f = 0.32 (hexanes/EtOAc 4:1).

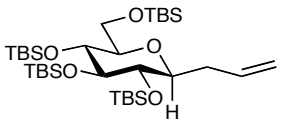
$[\alpha]_D^{23}$ 64.4 (c 1.14, CH_2Cl_2).

IR (film, NaCl) 3068, 3032, 3007, 2954, 2921, 2856, 1728, 1642, 1601, 1585, 1491, 1450, 1368, 1315, 1266, 1176, 1095, 1070, 1025, 972, 919, 854, 800, 711, 686 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-8.04 (m, 2H, PhH), 7.89-7.95 (m, 4H, PhH), 7.79-7.82 (m, 2H, PhH), 7.47-7.57 (m, 3H, PhH), 7.32-7.43 (m, 7H, PhH), 7.24-7.29 (m, 2H, PhH), 5.88 (t, 1H, ^3J = 9.6 Hz, H3′), 5.87 (ddt, 1H, ^3J = 6.8, 10.3, and 17.1 Hz, CH_2CH=CH_2), 5.63 (t, 1H, ^3J = 9.8 Hz, H4′), 5.44 (t, 1H, ^3J = 9.6 Hz, H2′), 5.08 (ddd, 1H, ^2J = 1.4 Hz, $J_{H1trans,H3}$ = 3.1 Hz, ^3J = 17.2 Hz, CH_2CH=CH_{trans}), 5.03 (ddd, 1H, ^2J = 1.2 Hz, $J_{H1cis,H3}$ = 2.9 Hz, ^3J = 10.3 Hz, CH_2CH=CH_{cis}), 4.60 (dd, 1H, ^3J = 3.1 Hz, ^2J = 12.1 Hz, H6′a), 4.45 (dd, 1H, ^3J = 5.5 Hz, ^2J = 12.1 Hz, H6′b), 4.09 (ddd, 1H, ^3J = 3.1, 5.5, and 9.9 Hz, H5′), 3.84 (ddd, 1H, ^3J = 3.9, 7.4, and 9.7 Hz, H1′), 2.36-2.48 (m, 2H, CH_2CH=CH_2).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 166.0, 165.3 (2C), 133.3 (2C), 133.1, 133.0, 132.9, 129.8 (2C), 129.7 (2C), 128.5, 128.4 (2C), 128.3, 128.2, 117.9, 77.8, 76.0, 74.5, 72.2, 70.0, 63.4, 35.8.

HRMS (+FAB, *m/z*): calcd for $C_{37}H_{33}O_9$ (MH^+), 621.2124; found, 621.2128.



3-(2′, 3′, 4′, 6′-Tetra-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-1-propene. To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-1-propene (163 mg, 0.44 mmol, 1 equiv) in anhyd. MeOH (2.9 mL, 0.15M) at rt under N_2 was added NaOMe (9 mg, 0.17 mmol, 40 mol %) in anhyd. MeOH (0.7 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). To a stirred suspension of the resulting tetrol in CH_2Cl_2 (6.3 mL, 0.07M) at 0 °C under N_2 was added 2,6-lutidine (0.51 mL, 0.47 g, 4.37 mmol, 10 equiv) and TBSOTf (0.80 mL, 0.92 g, 3.50 mmol, 8 equiv) then warmed to rt. After stirring at rt for 8 h, the reaction mixture was diluted with CH_2Cl_2, washed with sat. aq. $CuSO_4$ soln. (2x), H_2O (2x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (95:5) as the eluent to give TBS protected β-*C*-allyl glucopyranoside (268 mg, 93%) as a clear, colorless viscous oil.

R_f = 0.53 (hexanes/EtOAc 9:1).

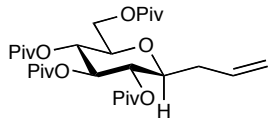
$[\alpha]_D^{23}$ -7.6 (c 1.05, CH_2Cl_2).

IR (film, NaCl) 3077, 2954, 2929, 2897, 2856, 2803, 1642, 1471, 1462, 1442, 1434, 1405, 1389, 1360, 1344, 1287, 1258, 1217, 1189, 1111, 1091 br, 1005, 956, 939, 915, 882, 862, 837, 813, 776, 670 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (ddt, 1H, ^3J = 6.7, 10.3, and 17.2 Hz, CH_2CH=CH_2), 5.08 (ddd, 1H, ^2J = 1.5 Hz, $J_{H1trans,H3}$ = 3.4 Hz, ^3J = 17.2 Hz, CH_2CH=CH_{trans}), 5.04 (m, 1H, CH_2CH=CH_{cis}), 3.89 (ddd, 1H, ^3J = 1.2, 2.4, and 3.6 Hz), 3.76 (t, 1H, ^3J = 1.9 Hz), 3.69-3.71 (m, 2H), 3.62-3.66 (m, 2H), 3.55 (dt, 1H, ^3J = 1.4, 5.9 Hz), 2.42 (dddt, 1H, $J_{H1,H3a}$ = 1.3 Hz, ^3J = 4.3, 7.0 Hz, ^2J = 14.6 Hz, $CH_{(3a)}HCH$=CH_2), 2.24 (dddt, 1H, $J_{H1,H3b}$ = 1.3 Hz, ^3J = 6.6, 8.0 Hz, ^2J = 14.6 Hz, $CH_{(3b)}CH$=CH_2), 0.90 (s, 9H, ^{t}Bu), 0.89 (s, 9H, ^{t}Bu), 0.88 (s, 18H, 2 ^{t}Bu), 0.10 (s, 6H, 2 SiMe), 0.08 (s, 9H, 3 SiMe), 0.06 (s, 3H, SiMe), 0.05 (s, 6H, 2 SiMe), 0.05 (2s, 6H, 2 SiMe).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.0, 116.4, 81.0, 78.3 (2C), 75.9, 71.2, 64.4, 38.5, 26.2, 26.1 (2C), 18.6, 18.2 (3C), -3.4, -3.8, -3.9, -4.1, -4.5 (2C), -4.8, -5.0.

HRMS (+FAB, *m/z*): calcd for $C_{33}H_{73}O_5Si_4$ (MH^+), 661.4535; found, 661.4537.



3-(2′, 3′, 4′, 6′-Tetra-*O*-pivaloyl-β-D-glucopyranosyl)-1-propene. To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-1-propene (234 mg, 0.63 mmol, 1 equiv) in anhyd. MeOH (4.2 mL, 0.15M) at rt under N_2 was added NaOMe (14 mg, 0.25 mmol, 40 mol %) in anhyd. MeOH (1.0 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). To a stirred suspension of the resulting tetrol in pyridine (5.2 mL, 0.12M) at rt under N_2 was added PivCl (0.77 mL, 0.76 g, 6.28 mmol, 10 equiv) and DMAP (38 mg, 0.31 mmol, 0.5 equiv) then heated to 100 °C for 24 h. After cooling to rt, the reaction mixture was diluted with CH_2Cl_2, washed with sat. aq. $CuSO_4$ soln. (2x), H_2O (2x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (9:1) as the eluent to give perpivalated β-*C*-allyl glucopyranoside (296 mg, 87%) as a white solid.

R_f = 0.67 (hexanes/EtOAc 4:1).

m.p. 81-82 °C.

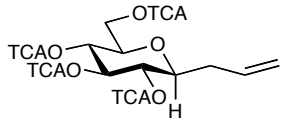
$[\alpha]_D^{23}$ 7.3 (c 1.27, CH_2Cl_2).

IR (film, NaCl) 3081, 2974, 2938, 2909, 2876, 1744, 1642, 1524, 1479, 1462, 1434, 1397, 1368, 1328, 1283, 1230, 1144 br, 1107, 1033, 997, 980, 939, 919, 890, 862, 837, 805, 764 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddt, 1H, ^3J = 6.8, 10.3, and 17.1 Hz, CH_2CH=CH_2), 5.27 (t, 1H, ^3J = 9.3 Hz, H3′), 5.01-5.08 (m, 2H, CH_2CH=CH_2), 5.06 (t, 1H, ^3J = 9.8 Hz, H2′), 4.93 (t, 1H, ^3J = 9.6 Hz, H4′), 4.18 (dd, 1H, ^3J = 1.9 Hz, ^2J = 12.2 Hz, H6′a), 3.98 (dd, 1H, ^3J = 5.9 Hz, ^2J = 12.2 Hz, H6′b), 3.64 (ddd, 1H, ^3J = 1.9, 5.8, and 10.1 Hz, H5′), 3.49 (ddd, 1H, ^3J = 3.2, 7.7, and 9.8 Hz, H1′), 2.21-2.26 (m, 1H, $CH_{(3a)}HCH$=CH_2), 2.13-2.20 (m, 1H, $CHH_{(3b)}CH$=CH_2), 1.20 (s, 9H, ^{t}Bu), 1.15 (s, 9H, ^{t}Bu), 1.14 (s, 9H, ^{t}Bu), 1.10 (s, 9H, ^{t}Bu).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.3, 177.5, 176.8, 176.7, 133.3, 118.1, 77.8, 76.2, 73.9, 71.5, 68.6, 62.5, 39.0 (2C), 38.9, 35.7, 27.4, 27.3 (2C).

HRMS (+FAB, *m/z*): calcd for (MH^+), $C_{29}H_{49}O_9$ (MH^+), 541.3376; found, 541.3379.



3-(2′, 3′, 4′, 6′-Tetra-*O*-trichloroacetyl-β-D-glucopyranosyl)-1-propene. To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-1-propene (164 mg, 0.44 mmol, 1 equiv) in anhyd. MeOH (2.9 mL, 0.15M) at rt under N_2 was added NaOMe (9.5 mg, 0.18 mmol, 40 mol %) in anhyd. MeOH (0.7 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). To a stirred suspension of the resulting tetrol in pyridine (4.4 mL, 0.1M) at rt under N_2 was added trichloroacetyl chloride (0.49 mL, 0.80 g, 4.42 mmol, 10 equiv) and DMAP (27 mg, 0.22 mmol, 0.5 equiv). After stirring at rt for 16 h, the reaction mixture was diluted with CH_2Cl_2, washed with sat. aq. $CuSO_4$ soln. (2x), H_2O (2x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (95:5) as the eluent to give TCA protected β-*C*-allyl glucopyranoside (291 mg, 84%) as a white solid.

R_f = 0.36 (hexanes/EtOAc 9:1).

m.p. 165-167 °C.

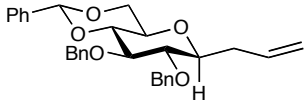
$[\alpha]_D^{23}$ 14.9 (c 1.19, CH_2Cl_2).

IR (film, NaCl) 3085, 2970, 2921, 2876, 2852, 1773, 1732, 1642, 1438, 1377, 1332, 1291, 1283, 1234, 1221, 1123, 1111, 1082, 1033, 993, 956, 919, 854, 845, 825, 772, 747, 682 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddt, 1H, ^3J = 6.9, 10.2, and 17.1 Hz, CH_2CH=CH_2), 5.67 (t, 1H, ^3J = 9.5 Hz, H3′), 5.39 (t, 1H, ^3J = 9.7 Hz, H2′), 5.22 (t, 1H, ^3J = 9.6 Hz, H4′), 5.17 (dd, 1H, ^2J = 1.0 Hz, ^3J = 10.2 Hz, CH_2CH=CHH_{cis}), 5.12 (ddd, 1H, ^2J = 1.5 Hz, $J_{H1trans,H3}$ = 2.9 Hz, ^3J = 17.1 Hz, CH_2CH=CHH_{trans}), 4.63 (dd, 1H, ^3J = 1.9 Hz, ^2J = 12.2 Hz, H6′a), 4.42 (dd, 1H, ^3J = 5.0 Hz, ^2J = 12.2 Hz, H6′b), 4.03 (ddd, 1H, ^3J = 2.0, 5.0, and 10.0 Hz, H5′), 3.83 (ddd, 1H, ^3J = 3.5, 6.9, and 9.8 Hz, H1′), 2.48 (m, 1H, $CH_{(3a)}HCH$=CH_2), 2.33 (m, 1H, $CHH_{(3b)}CH$=CH_2).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 161.1, 160.5, 131.1, 120.1, 89.4, 89.1, 88.9, 88.8, 77.4, 77.1, 75.1, 74.5, 71.9, 65.7, 35.3.

HRMS (+FAB, *m/z*): calcd for $C_{17}H_{13}Cl_{12}O_9$ (MH^+), 780.6821; found, 780.6812.



3-(2′, 3′-Di-*O*-benzyl-4′, 6′-*O*-benzylidene-β-D-glucopyranosyl)-1-propene.[6] To a stirred solution of 3-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-1-propene (291 mg, 0.78 mmol, 1 equiv) in anhyd. MeOH (5.2 mL, 0.15M) at rt under N_2 was added NaOMe (17 mg, 0.32 mmol, 40 mol %) in anhyd. MeOH (1.3 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the

crude product azeotroped with toluene (2x). To a stirred suspension of the resulting tetrol in MeCN (11 mL, 0.07M) at rt under N_2 was added benzylidene dimethylacetal (0.19 mL, 191 mg, 1.25 mmol, 1.6 equiv) and *p*TsOH•H_2O (15 mg, 0.08 mmol, 10 mol %). After stirring at rt for 16 h, the reaction mixture was neutralized with Et_3N then the solids were filtered and washed with hexanes. To a stirred suspension of the 4′, 6′-*O*-benzylidene protected β-*C*-allyl glucopyranoside in DMF (5.2 mL, 0.15M) at 0 °C under N_2 was added NaH (60% in oil, 250 mg, 6.26 mmol, 8 equiv) in portions. After stirring for 15 min, BnBr (0.74 mL, 1.07 g, 6.26 mmol, 8 equiv) was added dropwise over 30 min followed by TBAI (cat.). After warming to rt and stirring for 16 h, the reaction mixture was poured into ice-water and extracted with CH_2Cl_2 (3x). The combined organic extracts were washed with sat. aq. $NaHCO_3$ soln. (2x), brine (2x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (9:1) as the eluent to give 2′, 3′-di-*O*-benzylated β-*C*-allyl glucopyranoside (270 mg, 73%) as a white solid.

R_f = 0.58 (hexanes/EtOAc 4:1).

m.p. 87-88 °C.

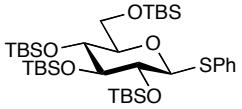
$[\alpha]_D^{23}$ -22.3 (c 1.00, CH_2Cl_2).

IR (film, NaCl) 3064, 3032, 2983, 2913, 2893, 2880, 1748, 1642, 1499, 1471, 1454, 1401, 1385, 1373, 1347, 1335, 1306, 1274, 1266, 1237, 1212, 1163, 1135, 1102, 1086, 1074, 1029, 996, 975, 910, 755, 743, 693, 653 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.52 (m, 2H, PhH), 7.27-7.41 (m, 13H, PhH), 5.87 (dddd, 1H, ^3J = 6.2, 7.6, 10.4, and 17.0 Hz, $CH_2C\boldsymbol{H}{=}CH_2$), 5.58 (s, 1H, acetal H), 5.07-5.12 (m, 2H, $CH_2CH{=}C\boldsymbol{H_2}$), 4.90 (ABq, 2H, ^2J = 11.2, 105.9 Hz, benzylic CH_2), 4.81 (ABq, 2H, ^2J = 10.8, 160.1 Hz, benzylic CH_2), 4.35 (dd, 1H, ^3J = 5.0 Hz, ^2J = 10.4 Hz, H6′a), 3.85 (dd, 1H, ^3J = 8.6, 9.1 Hz, H3′), 3.72 (t, 1H, J = 10.3 Hz, H6′b), 3.67 (t, 1H, ^3J = 9.3 Hz, H2′), 3.49 (ddd, 1H, ^3J = 3.3, 7.2, and 9.5 Hz, H1′), 3.42 (ddd, 1H, ^3J = 5.0, 9.6, and 9.9 Hz, H5′), 3.38 (dd, 1H, ^3J = 8.5, 9.5 Hz, H4′), 2.60 (dtt, 1H, $J_{H1,H3a}$ = 1.6 Hz, ^3J = 4.7 Hz, ^2J = 14.8 Hz, $C\boldsymbol{H_{(3a)}}HCH{=}CH_2$), 2.30 (m, 1H, $CH\boldsymbol{H_{(3b)}}CH{=}CH_2$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.4, 137.7, 134.5, 129.1, 128.7, 128.6 (2C), 128.5, 128.3, 128.2, 128.0, 127.9, 126.2, 117.6, 101.3, 83.6, 82.8, 81.1, 79.5, 75.6, 75.3, 70.4, 69.2, 36.3.

HRMS (+FAB, *m/z*): calcd for $C_{30}H_{33}O_5$ (MH^+), 473.2328; found, 437.2326.



***S*-Phenyl 2, 3, 4, 6-tetra-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside.** To a stirred solution of *S*-phenyl 2, 3, 4, 6-tetra-*O*-acetyl-β-D-glucopyranoside (**3**, R=Ac) (0.67 g, 1.52 mmol, 1 equiv) in anhyd. MeOH (10.0 mL, 0.15M) at rt under N_2 was added NaOMe (30 mg, 0.61 mmol, 40 mol %) in anhyd. MeOH (2.0 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). The resulting tetrol was suspended in CH_2Cl_2 (8.0 mL, 0.2M) at rt under N_2 to which 2,6-lutidine (1.4 mL, 1.30 g, 12.17 mmol, 8 equiv) and then TBSOTf (2.1 mL, 2.41 g, 9.13 mmol, 6 equiv) were added. After stirring at rt for 6 h, the reaction mixture was diluted with CH_2Cl_2, washed with sat. aq. $CuSO_4$ soln. (2x), H_2O (2x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (98:2) as the eluent to give the TBS protected glucopyranoside (1.04 g, 93%) as a clear, colorless viscous oil.

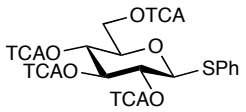
R_f = 0.78 (hexanes/EtOAc 9:1).

$[\alpha]_D^{23}$ -18.7 (c 1.83, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.49 (m, 2H, PhH), 7.16-7.29 (m, 3H, PhH), 5.02 (d, 1H, ^3J = 7.7 Hz, H1), 3.97 (m, 1H), 3.77-3.87 (m, 5H), 0.89, 0.90, 0.91 (3s, 36H, 4 ^{t}Bu), 0.05, 0.06, 0.08, 0.09, 0.11 (5s, 24H, 8 SiMe).

^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 130.1, 128.9, 126.4, 86.3, 83.5, 78.2, 76.0, 70.2, 64.4, 26.2 (2C), 26.1, 18.6, 18.3, 18.2, 18.1, -3.8, -3.9, -4.2 (2C), -4.4, -4.5, -5.0.

HRMS (+FAB, *m/z*): calcd for $C_{36}H_{71}O_5SSi_4$ ($[M-1]^+$), 727.4099; found, 727.4096.



***S*-Phenyl 2, 3, 4, 6-tetra-*O*-trichloroacetyl-β-D-glucopyranoside.** To a stirred solution of *S*-phenyl 2, 3, 4, 6-tetra-*O*-acetyl-β-D-glucopyranoside (**3**, R=Ac) (1.08 g, 2.45 mmol, 1 equiv) in anhyd. MeOH (16.0 mL, 0.15M) at rt under N_2 was added NaOMe (50 mg, 0.98 mmol, 40 mol %) in anhyd. MeOH (4.0 mL, 0.25M). The reaction mixture was stirred at rt for 4 h then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). The resulting tetrol was dissolved in pyridine (20 mL, 0.12M) at rt under N_2 to which DMAP (0.15 g, 1.23 mmol, 0.5 equiv) and then trichloroacetyl chloride (2.7 mL, 4.46 g, 24.53 mmol, 10 equiv) were introduced dropwise. After stirring at rt for 14 h, the reaction mixture was quenched with MeOH then concentrated under reduced pressure. The residue was taken up in CH_2Cl_2, washed with 1M HCl soln. (1x), sat. aq. $NaHCO_3$ soln. (3x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (7:3) as the eluent to give the TCA protected glucopyranoside (1.85 g, 88%) as a white solid.

R_f = 0.79 (hexanes/EtOAc 7:3).

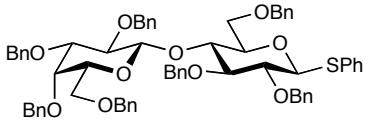
m.p. 180-181 °C.

$[\alpha]_D^{23}$ -8.2 (c 1.05, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.55 (m, 2H, PhH), 7.32-7.43 (m, 3H, PhH), 5.70 (t, 1H, ^3J = 9.5 Hz, H2), 5.36 (t, 1H, ^3J = 9.8 Hz, H3), 5.19 (t, 1H, ^3J = 9.8 Hz, H4), 4.91 (d, 1H, ^3J = 10.0 Hz, H1), 4.68 (dd, 1H, ^3J = 1.5 Hz, ^2J = 12.3 Hz, H6a), 4.47 (dd, 1H, ^3J = 5.0 Hz, ^2J = 12.3 Hz, H6b), 4.12 (ddd, 1H, ^3J = 1.5, 4.8, and 10.0 Hz, H5).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7, 160.9, 160.4, 160.1, 134.4, 129.8, 128.7, 129.6, 92.2, 89.3, 89.1, 88.7, 85.7, 76.6, 75.2, 72.8, 71.2, 65.6.

HRMS (+FAB, *m/z*): calcd for $C_{20}H_{12}Cl_{12}O_9S$ (M^+), 847.6464; found, 847.6461.



***S*-Phenyl 2, 2′, 3, 3′, 4′, 6, 6′-hepta-*O*-benzyl-β-D-lactopyranoside.** To a stirred solution of *S*-phenyl 2, 2′, 3, 3′, 4, 6, 6′-hepta-*O*-acetyl-β-D-lactopyranoside[7] (1.59 g, 2.19 mmol, 1 equiv) in anhyd. MeOH (15 mL, 0.15M) at rt under N_2 was added NaOMe (80 mg, 1.53 mmol, 70 mol %) in anhyd. MeOH (3.0 mL, 0.5M). The reaction mixture was stirred at rt overnight then neutralized with Amberlite™ IR-120 resin, filtered, washed with MeOH, concentrated under reduced pressure and the crude product azeotroped with toluene (2x). A solution of the heptol in dry DMF (5.5 mL, 0.4M) was added slowly dropwise to a suspension of NaH (60% in oil) (0.88 g, 21.88 mmol, 10 equiv) in dry DMF (2.5 mL, 0.9M) at 0 °C under N_2 and stirred for 10 min. To the resulting mixture was added dropwise BnBr (3.1 mL, 4.49 g, 26.25 mmol, 12 equiv) and TBAI (cat.) then stirred at 0 °C for 1 h. After warming to rt and stirring overnight, the reaction mixture was poured into ice-water and extracted with EtOAc (3x). The combined organic extracts were washed with H_2O (3x), brine (2x), dried over Na_2SO_4, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (9:1) as the eluent to give the benzylated lactopyranoside (1.37 g, 59%) as a white solid.

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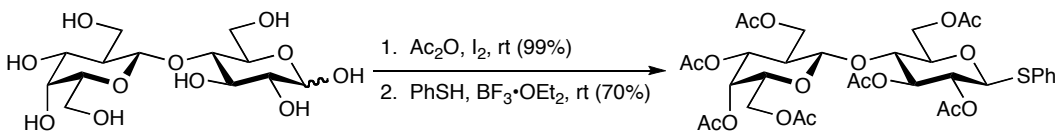
[7] Prepared by a route analogous to that used for S-phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside:



$\mathbf{R}_f$ = 0.23 (hexanes/EtOAc 9:1); 0.54 (hexanes/EtOAc 3:1).

m.p. 114-116 °C.

$[\alpha]_D^{23}$ -5.4 (c 1.31, CH_2Cl_2).

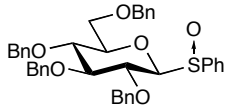
IR (film, NaCl) 3089, 3060, 3027, 3007, 2917, 2864, 1605, 1585, 1495, 1479, 1454, 1438, 1401, 1364, 1332, 1307, 1274, 1209, 1091 br, 1025, 1001, 911, 841, 817, 735, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.61 (m, 2H, PhH), 7.10-7.44 (m, 38H, PhH), 4.91 (ABq, 2H, ^2J = 10.5, 123.3 Hz, benzylic CH_2), 4.79-4.86 (m, 4H, benzylic CH_2), 4.79 (ABq, 2H, ^2J = 11.4, 127.7 Hz, benzylic CH_2), 4.73 (ABq, 2H, ^2J = 11.7, 13.7 Hz, benzylic CH_2), 4.66 (d, 1H, ^3J = 9.8 Hz, H1), 4.49 (ABq, 2H, ^2J = 11.9, 35.4 Hz, benzylic CH_2), 4.48 (d, 1H, ^3J = 7.7 Hz, H1′), 4.31 (ABq, 2H, ^2J = 11.8, 29.0 Hz, benzylic CH_2), 3.95-4.02 (m, 2H), 3.77-3.88 (m, 3H), 3.64 (t, 1H, ^3J = 8.8 Hz), 3.55 (t, 1H, ^3J = 6.8 Hz), 3.34-3.51 (m, 5H).

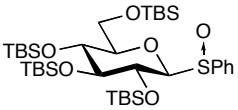
^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 139.1, 138.9, 138.7, 138.5, 138.2, 133.9, 132.2, 129.0, 128.6, 128.4 (2C), 128.2, 128.1, 128.0, 127.9, 127.7, 127.6 (2C), 127.4, 103.0, 87.5, 85.2, 82.7, 80.3, 80.2, 79.6, 77.4, 76.7, 75.8, 75.7, 75.5, 74.9, 73.8, 73.6, 73.2, 72.8, 68.6, 68.2.

HRMS (+FAB, *m/z*): calcd for $C_{67}H_{67}O_{10}S$ ($[M-1]^+$), 1063.4454; found, 1063.4466.

General procedure for preparation of glycosyl sulfoxides: To a stirred solution of the *S*-phenyl glycoside (1 equiv) and $NaHCO_3$ (3.5 equiv) in CH_2Cl_2 (0.16M) at -78 °C under N_2 was slowly added dropwise a solution of *m*CPBA (1.2 equiv) in CH_2Cl_2 (0.15M). After stirring at -78 °C for 1 h and then at -20 °C overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with sat. aq. $Na_2S_2O_3$ soln. (1x), sat. aq. $NaHCO_3$ soln. (1x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel to give the desired sulfoxide.



Phenylsulfenyl 2, 3, 4, 6-tetra-*O*-benzyl-β-D-glucopyranoside (5, R=Bn).[8]



Phenylsulfenyl 2, 3, 4, 6-tetra-*O-tert*-butyldimethylsilyl-β-D-glucopyranoside (R=TBS). To a stirred solution of *S*-phenyl 2, 3, 4, 6-tetra-*O-tert*-butyldimethylsilyl-β-D-glucopyranoside (0.95 g, 1.30 mmol, 1 equiv) and $NaHCO_3$ (0.38 g, 4.56 mmol, 3.5 equiv) in CH_2Cl_2 (8 mL, 0.16M) at -78 °C under N_2 was slowly added dropwise a solution of *m*CPBA (0.31 g, 1.82 mmol, 1.4 equiv) in CH_2Cl_2 (12 mL, 0.15M). After being stirred at -78 °C for 1 h and then at -20 °C overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with sat. aq. $Na_2S_2O_3$ soln. (1x), sat. aq. $NaHCO_3$ soln. (1x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue which was purified by column chromatography on silica gel using hexanes/EtOAc (9:1) as the eluent to give the *R* and *S* sulfoxides (0.96 g, 99%) as a clear, colorless viscous oil. R_f = 0.38 and 0.51 (hexanes/EtOAc 9:1).

Higher R_f diastereomer:

$[\alpha]_D^{23}$ -49.9 (c 1.10, MeOH).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.76 (m, 2H, PhH), 7.45-7.49 (m, 3H, PhH), 4.50 (d, 1H, ^3J = 3.1 Hz, H1), 4.31 (m, 1H), 3.92-4.02 (m, 2H), 3.61-3.73 (m, 3H), 0.87, 0.89, 0.95 (3s, 36H, 4 ^{t}Bu), -0.02, 0.02, 0.08, 0.12, 0.15, 0.16, 0.17, 0.24 (8s, 24H, 8 SiMe).

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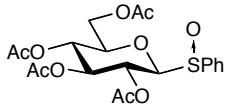
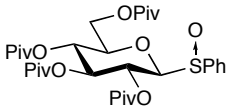
8 Karkarla, R.; Dulina, R.G.; Hatzenbuhler, N.T.; Hui, Y.W.; Sofia, M.J. *J. Org. Chem.* **1996**, *61*, 8347-8349.

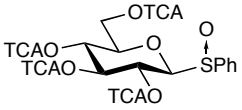
^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 131.0, 128.8, 125.6, 97.7, 78.5, 76.5, 71.0, 68.8, 62.4, 26.1, 18.4, 18.2 (2C), 18.1, -3.6 (2C), -4.4, -4.5, -4.7, -5.2 (2C).



Phenylsulfenyl 2, 3, 4, 6-tetra-*O*-acetyl-β-D-glucopyranoside (5, R=Ac).[8]



Phenylsulfenyl 2, 3, 4, 6-tetra-*O*-pivoyl-β-D-glucopyranoside(5, R=Piv).[8]



Phenylsulfenyl 2, 3, 4, 6-tetra-*O*-trichloroacetyl-β-D-glucopyranoside (5, R=TCA). To a stirred solution of *S*-phenyl 2, 3, 4, 6-tetra-*O*-trichloroacetyl-β-D-glucopyranoside (1.12 g, 1.31 mmol, 1 equiv) and $NaHCO_3$ (0.38 g, 4.57 mmol, 3.5 equiv) in CH_2Cl_2 (8 mL, 0.16M) at -78 °C under N_2 was slowly added dropwise a solution of *m*CPBA (0.32 g, 1.83 mmol, 1.4 equiv) in CH_2Cl_2 (12 mL, 0.15M). After being stirred at -78 °C for 1 h and then at -20 °C overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with sat. aq. $Na_2S_2O_3$ soln. (1x), sat. aq. $NaHCO_3$ soln. (1x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (85:15) as the eluent to give *R* and *S* sulfoxides (0.55 g, 49%) as a white solid.

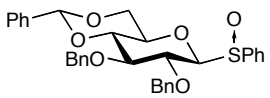
R_f = 0.28 (hexanes/EtOAc 85:15).

m.p. 160 (dec.) °C.

$[\alpha]_D^{23}$ 3.3 (c 1.06, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) *Major diastereomer*: δ 7.69-7.76 (m, 2H, PhH), 7.54-7.61 (m, 3H, PhH), 5.75 (t, 1H, ^3J = 9.4 Hz, H2), 5.48 (t, 1H, ^3J = 9.7 Hz, H3), 5.30 (t, 1H, ^3J = 9.8 Hz, H4), 4.69 (dd, 1H, ^3J = 1.8 Hz, ^2J = 12.7 Hz, H6a), 4.69 (d, 1H, ^3J = 9.8 Hz, H1), 4.34 (dd, 1H, ^3J = 4.0 Hz, ^2J = 12.7 Hz, H6b), 4.10 (ddd, 1H, ^3J = 1.7, 4.0, and 10.0 Hz, H5). *Minor diastereomer*: δ 7.69-7.76 (m, 2H, PhH), 7.60-7.66 (m, 3H, PhH), 5.80 (t, 1H, ^3J = 9.3 Hz, H2), 5.72 (t, 1H, ^3J = 9.3 Hz, H3), 5.34 (t, 1H, ^3J = 9.8 Hz, H4), 4.55 (d, 1H, ^3J = 9.4 Hz, H1), 4.52 (dd, 1H, ^3J = 1.7 Hz, ^2J = 12.5 Hz, H6a), 4.35 (dd, 1H, ^3J = 5.5 Hz, ^2J = 12.5 Hz, H6b), 4.03 (ddd, 1H, ^3J = 1.7, 5.5, and 10.0 Hz, H5).

^{13}C NMR (75 MHz, $CDCl_3$) *Major diastereomer*: δ 161.4, 160.8, 160.2 (2C), 138.0, 133.0, 129.7, 126.1, 91.5, 89.1, 88.9, 88.8, 88.6, 76.4, 75.8, 71.5, 70.4, 64.6. *Minor diastereomer*: δ 161.5, 161.0, 160.3, 159.8, 137.4, 132.6, 129.7, 125.7, 91.5, 89.1, 88.9, 88.8, 88.6, 76.4, 76.1, 70.8, 70.5, 65.1.



Phenylsulfenyl 3-(2′, 3′-Di-*O*-benzyl-4′, 6′-*O*-benzylidene-β-D-glucopyranoside.[9]

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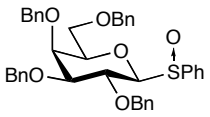
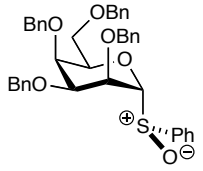
[9] Crich, D.; Cai, W. *J. Org. Chem.* **1999**, *64*, 4926-4930.



Phenylsulfenyl 2, 3, 4, 6-tetra-*O*-benzyl-β-D-galactopyranoside. To a stirred solution of *S*-phenyl 2, 3, 4, 6-tetra-*O*-benzyl-β-D-galactopyranoside (1.23 g, 1.95 mmol, 1 equiv) and $NaHCO_3$ (0.57 g, 6.82 mmol, 3.5 equiv) in CH_2Cl_2 (12 mL, 0.16M) at -78 °C under N_2 was slowly added dropwise a solution of *m*CPBA (0.40 g, 2.34 mmol, 1.2 equiv) in CH_2Cl_2 (16 mL, 0.15M). After being stirred at -78 °C for 1 h and then at -20 °C overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with sat. aq. $Na_2S_2O_3$ soln. (1x), sat. aq. $NaHCO_3$ soln. (1x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (4:1) as the eluent to give *R* and *S* sulfoxides (1.06 g, 86%) as a white solid. R_f = 0.09 and 0.18 (hexanes/EtOAc 4:1). The analytical data matches values reported in literature.[10]

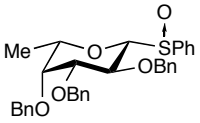


(*R*)-Phenylsulfenyl 2, 3, 4, 6-tetra-*O*-benzyl-α-D-mannopyranoside. To a stirred solution of *S*-phenyl 2, 3, 4, 6-tetra-*O*-benzyl-α-D-mannopyranoside (1.62 g, 2.57 mmol, 1 equiv) and $NaHCO_3$ (0.75 g, 8.98 mmol, 3.5 equiv) in CH_2Cl_2 (16 mL, 0.16M) at -78 °C under N_2 was slowly added dropwise a solution of *m*CPBA (0.53 g, 3.08 mmol, 1.2 equiv) in CH_2Cl_2 (21 mL, 0.15M). After being stirred at -78 °C for 1 h and then at -20 °C overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with sat. aq. $Na_2S_2O_3$ soln. (1x), sat. aq. $NaHCO_3$ soln. (1x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (85:15) as the eluent to give *R* sulfoxide (1.28 g, 77%) as a white solid.

$\mathbf{R}_f$ = 0.26 (hexanes/EtOAc 4:1).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 138.3, 138.2 (2C), 137.7, 131.5, 129.3, 128.6 (2C), 128.5, 128.2 (2C), 128.1, 127.9, 127.8, 124.6, 96.1, 79.7, 77.9, 75.4, 74.2, 73.6, 72.7, 72.3, 71.8, 69.6.

The analytical data matches values reported in literature.[11]



Phenylsulfenyl 2, 3, 4-tri-*O*-benzyl-β-L-fucopyranoside. To a stirred solution of *S*-phenyl 2, 3, 4-tri-*O*-benzyl-β-L-fucopyranoside[12] (g, mmol, 1 equiv) and $NaHCO_3$ (g, mmol, 3.5 equiv) in CH_2Cl_2 (mL, 0.16M) at -78 °C under N_2 was slowly added dropwise a solution of *m*CPBA (0. g, 1. mmol, 1.2 equiv) in CH_2Cl_2 (mL, 0.15M). After being stirred at -78 °C for 1 h and then at -20 °C overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with sat. aq. $Na_2S_2O_3$ soln. (1x), sat. aq. $NaHCO_3$ soln. (1x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (7:3) as the eluent to give *R* and *S* sulfoxides (g, 90%) as a white solid.

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[10] (a) Best, W. M.; Ferro, V.; Harle, J.; Stick, R. V.; Tilbrook, D. M. G. *Aust. J. Chem.* **1997**, *50*, 463-472. (b) Ayadi, E.; Czernecki, S.; Xie, J. *J. Chem. Soc., Chem. Commun.* **1996**, 347-348.

[11] (a) Basha, A.; Lipton, M.; Weinreb, S. M. *Tetrahedron Lett.* **1977**, *18*, 4171-4174. (b) Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, *22*, 3815-3818. (c) Shimizu, T.; Osako, K.; Nakata, T.-i. *Tetrahedron Lett.* **1997**, *38*, 2685-2688. (d) Miyashita, M.; Toshimitsu, Y.; Shiratani, T.; Irie, H. *Tetrahedron: Asymmetry* **1993**, *4*, 1573-1570.

[12] Komba, S.; Ishida, H.; Kiso, M.; Hasagawa, A. *Bioorg. Med. Chem.* **1996**, *4*, 1833-1847.

Higher R_f diastereomer: Isolated in a 30% yield.

R_f = 0.34 (hexanes/EtOAc 7:3).

$[\alpha]_D^{23}$ -73.0 (c 1.00, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.69 (m, 2H, PhH), 7.27-7.51 (m, 18H, PhH), 5.02 (ABq, 2H, ^2J = 10.3, 14.4 Hz, benzylic CH_2), 4.85 (ABq, 2H, ^2J = 11.9, 75.0 Hz, benzylic CH_2), 4.77 (t, 2H, ^2J = 12.2 Hz, benzylic CH_2), 4.47 (t, 1H, ^3J = 9.6 Hz, H2), 3.90 (d, 1H, ^3J = 9.6 Hz, H1), 3.69 (dd, 1H, ^3J = 2.7, 9.5 Hz, H3), 3.61 (br d, 1H, ^3J = 2.0 Hz, H4), 3.35 (br q, 1H, ^3J = 6.5 Hz, H5), 1.05 (d, 3H, ^3J = 6.3 Hz, Me).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 138.6, 138.2, 138.1, 130.8, 129.0, 128.7 (2C), 128.6, 128.5, 128.3, 128.1, 127.9, 127.7, 125.6, 94.2, 84.7, 76.1, 76.0, 75.7, 74.6, 73.9, 72.8, 16.8.

Lower R_f diastereomer:

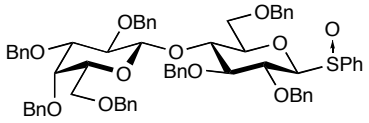
R_f = 0.19 (hexanes/EtOAc 7:3).

$[\alpha]_D^{23}$ -63.2 (c 1.12, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.64 (m, 2H, PhH), 7.24-7.46 (m, 16H, PhH), 7.12-7.15 (m, 2H, PhH), 4.86 (ABq, 2H, ^2J = 10.8, 17.0 Hz, benzylic CH_2), 4.71 (ABq, 2H, ^2J = 11.8, 105.8 Hz, benzylic CH_2), 4.68 (ABq, 2H, ^2J = 11.8, 17.4 Hz, benzylic CH_2), 4.46 (d, 1H, ^3J = 9.3 Hz, H1), 3.99 (t, 1H, ^3J = 9.1 Hz, H2), 3.68 (dd, 1H, ^3J = 2.6, 9.0 Hz, H3), 3.57-3.63 (m, 2H, H4 and H5), 1.20 (d, 3H, ^3J = 6.3 Hz, Me).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 138.7, 138.2, 138.1, 131.2, 129.0, 128.7 (2C), 128.5, 128.3, 128.1 (2C), 127.8, 127.5, 126.4, 95.6, 84.7, 76.0, 75.5, 74.7, 74.4, 74.0, 72.7, 17.0.

The physical and spectral data matches values reported in literature.[13]



Phenylsulfenyl 2, 2′, 3, 3′, 4′, 6, 6′-hepta-*O*-benzyl-β-D-lactopyranoside. To a stirred solution of *S*-phenyl 2, 2′, 3, 3′, 4′, 6, 6′-hepta-*O*-benzyl-β-D-lactopyranoside (1.23 g, 1.15 mmol, 1 equiv) and $NaHCO_3$ (0.34 g, 4.03 mmol, 3.5 equiv) in CH_2Cl_2 (7.0 mL, 0.16M) at -78 °C under N_2 was slowly added dropwise a solution of *m*CPBA (0.24 g, 1.38 mmol, 1.2 equiv) in CH_2Cl_2 (9.0 mL, 0.15M). After being stirred at -78 °C for 1 h and then at -20 °C overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with sat. aq. $Na_2S_2O_3$ soln. (1x), sat. aq. $NaHCO_3$ soln. (1x), brine (1x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (3:1) as the eluent to give an inseparable mixture of *R* and *S* sulfoxides (1.03 g, 83%) as a white amorphous solid.

R_f = 0.22 and 0.29 (hexanes/EtOAc 3:1).

$[\alpha]_D^{23}$ -19.5 (c 1.57, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.67 (m, PhH), 7.11-7.44 (m, PhH), 4.89-5.20 (m), 4.61-4.83 (m), 4.43-4.57 (m), 4.06-4.37 (m), 3.64-4.01 (m), 3.25-3.56 (m).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 139.2, 139.1, 138.8, 138.6, 138.5, 138.2, 138.0 (2C), 131.4, 131.1, 128.9 (2C), 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.4, 126.2, 125.5, 103.2, 103.0, 95.4, 93.6, 85.0, 84.5, 82.7 (2C), 80.9, 80.1, 79.6, 77.4, 76.6, 76.2, 76.1, 76.0, 75.8, 75.6, 75.4, 75.3, 74.9 (2C), 74.1, 73.7 (2C), 73.6, 73.4, 73.3, 73.2 (2C), 72.8 (2C), 68.2, 68.0.

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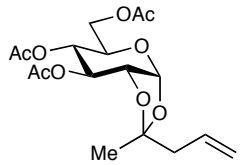
[13] (a) Kahne, D.; Yan, L. *J. Am. Chem. Soc.* **1996**, *118*, 9239-9248. (b) Gildersleeve, J.; Pascal, R. A. J.; Kahne, D. *J. Am. Chem. Soc.* **1998**, *120*, 5961-5969.

LRMS (+FAB, *m/z*): calcd for $C_{67}H_{69}O_{11}S$ (MH^+), 1080.4; found, 1080.0.

General procedure for preparation of α-*C*-allyl glycosides (Method A): To a stirred solution of the glycosyl sulfoxide (1 equiv) in CH_2Cl_2 (0.03M) at rt under argon was added DTBMP (1.2 equiv) and allyl-$SiMe_3$ (2.5 equiv). The solution was cooled to -78 °C and Tf_2O (1.1 equiv) was added slowly dropwise. After stirring at -78 °C for 30 min then warming to rt, the reaction mixture was quenched with sat. aq. $NaHCO_3$ soln. and extracted with CH_2Cl_2 (3x). The combined organic extracts were washed with brine (2x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel to afford the *C*-allyl glycoside.

General procedure for preparation of β-*C*-allyl glycosides (Method B): To a stirred solution of the glycosyl sulfoxide (1 equiv) and DTBMP (1.2 equiv) in CH_2Cl_2 (0.03M) at -78 °C under argon was added Tf_2O (1.1 equiv) slowly dropwise. The solution was stirred for 10 min, allyl-$SnBu_3$ (2.5 equiv) was added dropwise, and then stirred an additional 30 min at -78 °C. After warming to rt, the reaction mixture was quenched with sat. aq. $NaHCO_3$ soln. and extracted with CH_2Cl_2 (3x). The combined organic extracts were washed with brine (2x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel to afford the *C*-allyl glycoside.

Inverse addition procedure for preparation of α-*C*-allyl glycosides (Method C): To a stirred solution of the nucleophile (allyl-M, 2.5 equiv), DTBMP (1.2 equiv), and Tf_2O (1.1 equiv) in CH_2Cl_2 (0.14M) at -78 °C under argon was slowly added dropwise a solution of the glycosyl sulfoxide (1 equiv) in CH_2Cl_2 (0.05M) over 1 h. After complete addition, the reaction mixture was stirred at -78 °C for 10 min. then warmed to rt. The reaction mixture was quenched with sat. aq. $NaHCO_3$ soln. and extracted with CH_2Cl_2 (3x). The combined organic extracts were washed with brine (2x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel to afford the *C*-allyl glycoside.



3, 4, 6-Tri-*O*-acetyl-1, 2-*O*-[1′-(*exo*-allyl)ethylidene]-α-D-glucopyranose. To a stirred solution of phenylsulfenyl 2, 3, 4, 6-tetra-*O*-acetyl-β-D-glucopyranoside (**3**, R=Ac, 227 mg, 0.50 mmol, 1 equiv) in CH_2Cl_2 (17 mL, 0.03M) at rt under argon was added DTBMP (122 mg, 0.60 mmol, 1.2 equiv) and allyl-$SiMe_3$ (0.20 mL, 142 mg, 1.24 mmol, 2.5 equiv). The solution was cooled to -78 °C and Tf_2O (0.09 mL, 154 mg, 0.55 mmol, 1.1 equiv) was added dropwise. After stirring for 30 min and warming to rt, the reaction mixture was quenched with sat. aq. $NaHCO_3$ soln. and extracted with CH_2Cl_2 (3x). The combined organic extracts were washed with brine (2x), dried over $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by column chromatography on silica gel using hexanes/EtOAc (4:1) as the eluent to give *exo*-allyl acetal (142 mg, 77%) as a white solid.

R_f = 0.16 (hexanes/EtOAc 4:1); 0.46 (hexanes/EtOAc 3:2).

mp 82-83 °C.

$[\alpha]_D^{23}$ 20.3 (c 1.28, CH_2Cl_2).

IR (film, NaCl) 3081, 2987, 2962, 2942, 1748, 1646, 1434, 1368, 1230, 1144, 1082, 1042, 1017, 919, 870, 804 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (dddd, 1H, ^3J = 7.3, 9.5, 12.4, and 14.7 Hz, CH_2CH=CH_2), 5.63 (d, 1H, ^3J = 4.9 Hz, H1), 5.20 (t, 1H, ^3J = 3.3 Hz, H3), 5.16 (m, 1H, CH_2CH=C***H***H), 5.09-5.13 (m, 1H, CH_2CH=CH***H***), 4.89 (ddd, 1H, J = 0.4 Hz, ^3J = 3.1, 9.5 Hz, H4), 4.14-4.26 (m, 3H, H2, H6a, and H6b), 4.10 (ddd, 1H, ^3J = 2.9, 5.3, and 9.5 Hz, H5), 2.35 (d, 2H, ^3J = 7.2 Hz, C***H***$_2$CH=CH_2), 2.11 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.55 (s, 3H, Me).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 169.9, 169.5, 132.5, 119.4, 111.1, 97.0, 73.7, 70.8, 68.4, 67.1, 63.3, 43.8, 24.4, 21.0.

HRMS (+FAB, *m/z*): calcd for $C_{17}H_{25}O_9$ (MH^+), 373.1498; found, 373.1501.

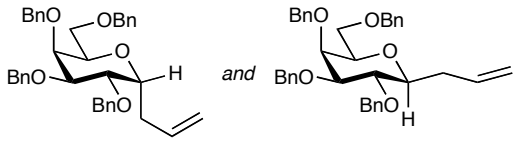


Table 2, Entries 1 and 2.[3b,14]

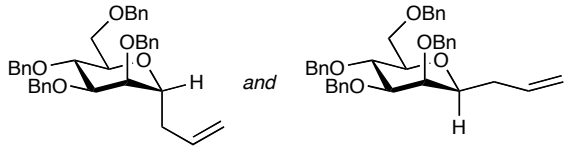


Table 2, Entries 3 and 4.[3b,15]

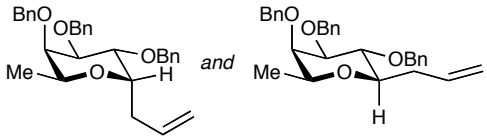


Table 2, Entries 5 and 6.[16]

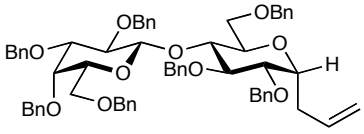


Table 2, Entries 7 and 8.[17]

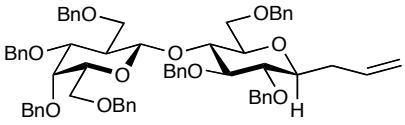


Table 2, Entries 7 and 8.

R_f = 0.64 (hexanes/EtOAc 3:1); 0.43 (hexanes/EtOAc 85:15).

m.p. 99-100 °C.

$[\alpha]_D^{23}$ 13.6 (c 1.05, CH_2Cl_2).

IR (film, NaCl) 3089, 3064, 3027, 3007, 2913, 2864, 1642, 1605, 1585, 1495, 1454, 1397, 1360, 1307, 1209, 1095, 1074, 1025, 1001, 915, 821, 735, 698 cm^{-1}.

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15 Bertozzi, C; Bednarski, M. *Carbohydr. Res.* **1992**, *223*, 243-253.

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^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.36 (m, 35H, PhH), 5.92 (ddt, 1H, ^{3}J = 6.9, 10.2, and 17.2 Hz, $CH_2C\boldsymbol{H}{=}CH_2$), 5.05-5.13 (m, 2H, $CH_2CH{=}C\boldsymbol{H_2}$), 4.93 (ABq, 2H, ^{2}J = 10.5, 246.3 Hz, benzylic CH_2), 4.81 (s, 2H, benzylic CH_2), 4.79 (ABq, 2H, ^{2}J = 10.8, 176.1 Hz, benzylic CH_2), 4.78 (ABq, 2H, ^{2}J = 11.5, 214.6 Hz, benzylic CH_2), 4.72 (s, 2H, benzylic CH_2), 4.50 (ABq, 2H, ^{2}J = 12.2, 76.7 Hz, benzylic CH_2), 4.47 (d, 1H, ^{3}J = 7.7 Hz, H1′), 4.31 (ABq, 2H, ^{2}J = 11.8, 54.5 Hz, benzylic CH_2), 3.97 (t, 1H, ^{3}J = 9.6 Hz), 3.92 (d, 1H, ^{3}J = 2.8 Hz), 3.82 (dd, 1H, ^{3}J = 4.0, 11.1 Hz), 3.78 (dd, 1H, ^{3}J = 7.7, 9.7 Hz), 3.70 (dd, 1H, ^{3}J = 1.5, 11.1 Hz), 3.62 (t, 1H, ^{3}J = 8.6 Hz), 3.52 (t, 1H, ^{3}J = 10.5 Hz), 3.43 (dd, 1H, ^{3}J = 2.9, 9.7 Hz), 3.28-3.40 (m, 5H), 2.56-2.63 (m, 1H, $C\boldsymbol{H}HCH{=}CH_2$), 2.30 (p, 1H, J = 7.1 Hz, $CH\boldsymbol{H}CH{=}CH_2$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 139.3, 139.0, 138.8 (2C), 138.7, 138.4, 135.1, 128.6 (2C), 128.5, 128.4, 128.3, 128.2, 128.1 (2C), 128.0, 127.9, 127.7 (2C), 127.6 (3C), 127.5, 127.3, 117.1, 102.9, 85.7, 82.7, 81.2, 80.3, 79.6, 79.0, 77.2, 75.5 (2C), 75.3, 74.9, 74.0, 73.6, 73.3, 72.9, 68.6, 68.3, 36.3.

HRMS (+FAB, *m/z*): calcd for $C_{64}H_{67}O_{10}$ ($[M\text{-}1]^{+}$), 995.4734; found, 995.4744.