Highly Efficient Cationic Palladium Catalyzed Acetylation of Alcohols and Carbohydrate-Derived Polyols

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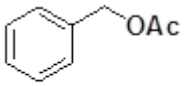
S1. Methods and Reagents

All reactions were performed in an oven-dried and argon flushed round bottom flask. Analytical thin-layer chromatography (TLC) was routinely used to monitor the reaction progress, and was performed using a pre-coated glass plates with 230-400 mesh silica gel. The dichloromethane used to prepare the catalyst was distilled from calcium hydride under an argon atmosphere at 760 torr. The cationic palladium (II) catalyst was prepared according to the literature procedure [S1]. All other chemicals were obtained from commercial vendors and used without further purification.

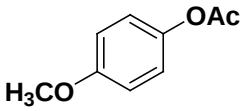
S2. Instrumentation

Identification of the products was carried out using IR, ^{1}H NMR and ^{13}C NMR. All proton (^{1}H) NMR spectra were recorded on a Varian 500 Mz, 600 MHz and 700 MHz spectrometers. All carbon-13 (^{13}C) NMR spectra were recorded on a Varian 125 MHz, 150 MHz and 175 MHz using $CDCl_3$ as a reference solvent. Chemical shifts (δ) are expressed in parts per million (ppm).



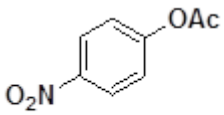
3

Spectral Data: ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.43 – 7.24 (m, 5H), 5.09 (d, *J* = 1.4 Hz, 2H), 2.08 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 170.8, 135.9, 128.5, 128.2, 77.3, 77.1, 76.9, 66.2, 21.0. **IR (film, cm^{-1})** 3067, 3035, 2955, 1736, 1456, 1380, 1362, 1222, 1024.



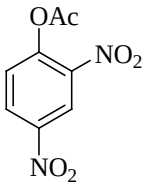
4

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 6.99 (d, *J* = 12.0 Hz, 2H), 6.87 (d, *J* = 6.0 Hz, 2H), 3.77 (s, 3H), 2.26 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 169.8, 157.4, 144.2, 122.3, 114.4, 77.3, 77.1, 76.8, 55.5, 21.0. **IR (film, cm^{-1})** 2917, 2838, 1760, 1505, 1369, 1249, 1215, 1190.



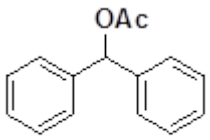
5

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.22 (d, *J* = 7.7 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 2.16 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 170.5, 147.7, 143.2, 128.3, 123.7, 77.2, 77.0, 76.8, 64.7, 20.8. **IR (film, cm^{-1})** 2934, 1737, 1517, 1344, 1220, 1043, 859, 854.



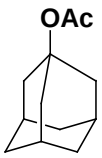
6

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.51 (ddd, *J* = 8.9, 2.6, 1.9 Hz, 1H), 7.47 (dd, *J* = 8.9, 1.6 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 167.6, 148.7, 129.0, 126.7, 121.7, 77.2, 77.0, 76.8, 20.7. **IR (film, cm^{-1})** 3113, 1780, 1610, 1535, 1344, 1167, 1069, 1009.



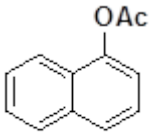
7

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.36 – 7.30 (m, 8H), 7.30 – 7.24 (m, 2H), 6.88 (s, 1H), 2.15 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 170.0, 140.2, 128.4, 127.9, 127.1, 77.2, 77.0, 76.9, 76.8, 21.3. **IR (film, cm^{-1})** 2939, 1737, 1495, 1454, 1370, 1226, 1185, 1081, 1020, 972.



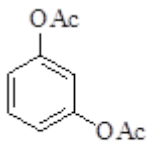
8

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 2.16 – 2.11 (m, 3H), 2.10 – 2.06 (m, 6H), 1.94 (s, 3H), 1.68 – 1.59 (m, 6H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 170.3, 80.3, 77.2, 77.0, 76.8, 41.3, 36.2, 30.8, 22.7. **IR (film, cm^{-1})** 2911, 2853, 1732, 1457, 1367, 1354, 1243, 1060, 1017.



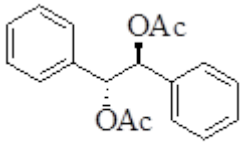
9

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.88 – 7.81 (m, 2H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.44 (t, *J* = 6.0 Hz, 1H), 7.23 (d, *J* = 6.0 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 169.5, 146.6, 134.7, 128.1, 126.8, 126.5, 126.04, 125.4, 121.2, 118.1, 77.3, 77.1, 76.9, 21.0.
IR (film, cm^{-1}) 1757, 1599, 1368, 1390, 1192, 1077, 1041, 1013.



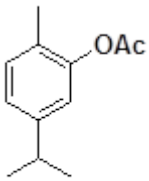
10

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.35 (t, *J* = 8.2 Hz, 1H), 6.98 (dd, *J* = 12.0, 6.0 Hz, 2H), 6.91 (t, *J* = 2.2 Hz, 1H), 2.26 (s, 6H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 168.9, 151.1, 129.67, 118.9, 115.4, 77.2, 77.1, 76.9, 21.0. **IR (film, cm^{-1})** 1764, 1599, 1485, 1370, 1187, 1120, 1013, 963, 914.



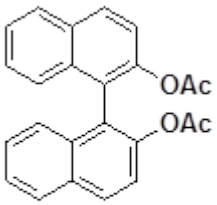
11

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.31 – 7.26 (m, 3H), 7.23 – 7.17 (m, 2H), 6.10 (s, 1H), 2.01 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 169.6, 136.0, 128.3, 128.0, 127.6, 77.3, 77.0, 76.8, 76.4, 20.9. **IR (film, cm^{-1})** 3038, 1732, 1605, 1497, 1458, 1427, 1372, 1239, 1216, 1043, 1028.



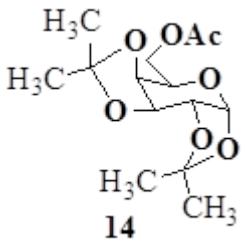
12

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.19 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.80 (s, 1H), 3.01 – 2.92 (m, 1H), 2.31 (s, 6H), 1.19 (d, *J* = 1.4 Hz, 3H), 1.18 (d, *J* = 1.4 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 169.7, 147.9, 136.9, 136.5, 127.1, 126.4, 122.7, 77.2, 77.0, 76.8, 27.1, 23.0, 20.9, 20.8. **IR (film, cm^{-1})** 2964, 2928, 1760, 1507, 1458, 1369, 1203, 1146, 1088, 1058, 1016.



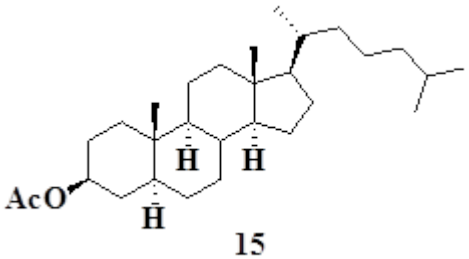
13

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.49–7.42 (m, 4H), 7.29 (ddd, *J* = 8.1, 7.5, 4.1 Hz, 2H), 7.20 (d, *J* = 6.0 Hz, 2H), 1.87 (s, 6H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 169.4, 146.8, 133.3, 131.5, 129.5, 128.0, 126.7, 126.2, 125.7, 123.4, 121.9, 77.3, 77.1, 76.9, 20.6. **IR (film, cm^{-1})** 3061, 1759, 1594, 1509, 1431, 1366, 1183, 1075, 1011, 968



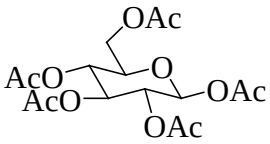
14

^{1}H NMR (600 MHz, CDCl3) δ (ppm) 5.54 (d, J = 4.9 Hz, 1H), 4.64 – 4.60 (m, 1H), 4.35 – 4.31 (m, 1H), 4.28 (ddd, J = 11.6, 4.6, 1.4 Hz, 1H), 4.24 (dd, J = 7.9, 1.7 Hz, 1H), 4.18 (ddd, J = 11.6, 7.8, 1.5 Hz, 1H), 4.05 – 4.00 (m, 1H), 2.09 (s, 3H), 1.52 (s, 3H), 1.45 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H). **^{13}C NMR (150 MHz, CDCl3)** δ (ppm) 170.9, 109.6, 108.9, 96.3, 77.3, 77.1, 76.8, 71.08, 70.7, 70.5, 65.9, 63.5, 53.4, 26.0, 26.0, 25.0, 24.5, 20.9. **IR (film, cm-1)** 2989, 1740, 1371, 1236, 1211, 1167, 1116, 1068, 1005.



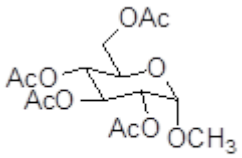
15

^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm) 4.72 – 4.63 (m, 1H), 2.01 (s, 3H), 1.99 – 1.93 (m, 1H), 1.85 – 1.77 (m, 2H), 1.75 – 1.69 (m, 1H), 1.68 – 1.62 (m, 1H), 1.61 – 1.45 (m, 5H), 1.40 – 1.30 (m, 5H), 1.29 – 1.19 (m, 4H), 1.18 – 1.06 (m, 6H), 1.05 – 0.94 (m, 5H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.88 – 0.83 (m, 6H), 0.82 (s, 3H), 0.68 – 0.60 (m, 4H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 170.6, 77.2, 77.0, 76.8, 73.7, 56.4, 56.3, 54.2, 49.0, 48.1, 44.6, 42.6, 39.9, 39.5, 36.7, 36.1, 35.8, 35.4, 35.4, 34.0, 32.0, 28.6, 28.2, 28.0, 27.5, 24.2, 23.8, 22.8, 22.5, 21.40, 21.2, 18.6, 12.2, 12.0. **IR (film, cm^{-1})** 2934, 2868, 2852, 1728, 1469, 1368, 1262, 1028, 908.



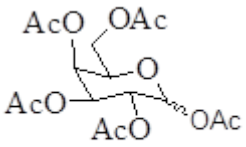
16

^{1}H NMR (600 MHz, CDCl$_3$) δ(ppm) 6.33 (d, *J* = 3.7 Hz, 1H), 5.51 – 5.43 (m, 1H), 5.17 – 5.12 (m, 1H), 5.10 (ddd, *J* = 10.3, 3.7, 1.0 Hz, 1H), 4.27 (dd, *J* = 12.3, 4.0 Hz, 1H), 4.15 – 4.07 (m, 2H), 2.18 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ (ppm) 170.5, 170.1, 169.6, 169.3, 168.7, 89.0, 77.2, 76.8, 69.8, 69.1, 67.8, 61.4, 20.8, 20.6, 20.6, 20.5, 20.4. **IR (film, cm^{-1})** 1744, 1433, 1368, 1207, 1150, 1036, 1012, 925.



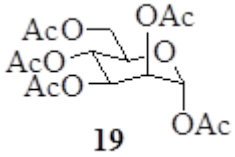
17

^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm) 5.48 (t, *J* = 9.8 Hz, 1H), 5.07 (t, *J* = 9.8 Hz, 1H), 4.96 (d, *J* = 3.7 Hz, 1H), 4.90 (ddd, *J* = 6.7, 4.2, 3.5 Hz, 1H), 4.27 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.11 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.99 (ddd, *J* = 10.3, 4.6, 2.3 Hz, 1H), 3.42 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ (ppm) 170.5, 170.0, 169.9, 169.5, 96.7, 77.3, 77.0, 76.8, 70.7, 70.0, 68.5, 67.1, 61.8, 55.4, 20.6, 20.6, 20.5. **IR (film, cm^{-1})** 2939, 1742, 1367, 1214, 1170, 1131, 1029, 930.



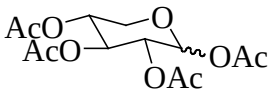
18

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.35 (d, J = 2.2 Hz, 1H), 5.48 (s, 1H), 5.37 – 5.26 (m, 2H), 4.32 (t, J = 6.7 Hz, 1H), 4.13 – 4.02 (m, 2H), 2.14 (s, 3H), 2.13 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ (ppm) 170.2, 170.1, 170.0, 169.8, 168.8, 89.7, 77.3, 77.1, 76.8, 68.7, 67.4, 67.3, 66.4, 61.2, 20.8, 20.6, 20.5, 20.4. **IR (film, cm^{-1})** 2947, 1742, 1370, 1208, 1113, 1069, 1046, 1010, 931.



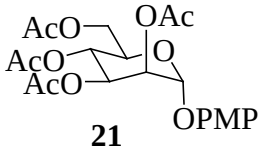
19

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 6.09 (s, 1H), 5.38 – 5.32 (m, 2H), 5.29 – 5.25 (m, 1H), 4.29 (ddd, *J* = 6.5, 5.8, 2.6 Hz, 1H), 4.18 – 4.04 (m, 2H), 2.18 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 170.5, 169.9, 169.6, 169.4, 168.0, 90.5, 77.3, 77.1, 76.9, 73.2, 70.5, 68.7, 68.3, 65.5, 62.0, 20.8, 20.7, 20.6, 20.6, 20.5. **IR (film, cm^{-1})** 2928, 1742, 1433, 1369, 1208, 1147, 1086, 1050, 1025, 972, 912.



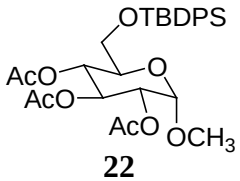
20

^{1}H NMR (700 MHz, $CDCl_3$) δ (ppm) 6.22 (d, *J* = 3.6 Hz, 1H), 5.68 (d, *J* = 6.9 Hz, 0.2H), 5.43 (t, *J* = 9.8 Hz, 1H), 5.17 (t, *J* = 8.3 Hz, 0.2H), 5.02 – 4.96 (m, 2H), 4.94 (m, 0.2H), 4.11 (dd, *J* = 12.0, 5.0 Hz, 0.2H), 3.90 (dd, *J* = 11.2, 5.9 Hz, 1H), 3.67 (t, *J* = 11.0 Hz, 1H), 3.49 (dd, *J* = 12.1, 8.4 Hz, 0.2H), 2.14 (s, 3H), 2.07 (s, 0.6H), 2.02 (s, 0.6H), 2.01 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H). **^{13}C NMR (175 MHz, $CDCl_3$)** δ (ppm) 170.1, 169.8, 169.7, 169.7, 169.65, 169.2, 169.0, 168.9, 92.0, 89.2, 77.2, 77.0, 76.8, 70.9, 69.4, 69.3, 68.6, 68.3, 62.8, 60.6, 20.8, 20.8, 20.7, 20.6, 20.5, 20.4. **IR (film, cm^{-1})** 2939, 1745, 1368, 1208, 1042, 1012, 935, 733.



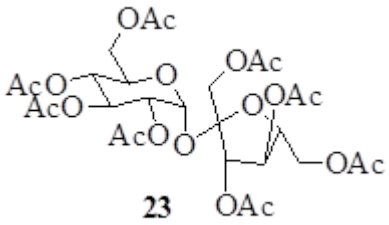
21

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, *J* = 9.1 Hz, 2H), 6.83 (d, *J* = 9.1 Hz, 2H), 5.55 (dd, *J* = 10.0, 3.5 Hz, 1H), 5.47 – 5.39 (m, 2H), 5.36 (t, *J* = 10.1 Hz, 1H), 4.28 (dd, *J* = 12.2, 5.4 Hz, 1H), 4.14 (ddd, *J* = 10.1, 5.4, 2.3 Hz, 1H), 4.09 (dd, *J* = 12.2, 2.3 Hz, 1H), 3.77 (s, 3H), 2.19 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ(ppm) 170.5, 169.9, 169.9, 169.7, 155.4, 149.6, 117.7, 114.6, 96.6, 77.3, 77.0, 76.8, 69.4, 69.0, 68.9, 66.0, 62.2, 55.6, 20.8, 20.6, 20.6.
IR (film, cm^{-1}) 2958, 1743, 1507, 1442, 1368, 1206, 1126, 1034, 981, 830.



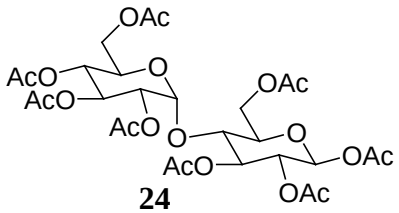
22

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.61 (m, 4H), 7.46 – 7.35 (m, 6H), 5.46 (t, *J* = 9.8 Hz, 1H), 5.07 (t, *J* = 9.8 Hz, 1H), 4.97 (d, *J* = 3.6 Hz, 1H), 4.89 (ddd, *J* = 10.3, 3.7, 0.7 Hz, 1H), 3.86 (dd, *J* = 9.8, 3.8 Hz, 1H), 3.76 – 3.65 (m, 2H), 3.40 (s, 3H), 2.08 (s, 3H), 2.00 (s, 3H), 1.88 (s, 3H), 1.05 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 170.1, 169.4, 135.6, 133.1, 129.7, 127.6, 96.4, 77.2, 77.0, 76.8, 71.0, 70.5, 69.9, 68.9, 62.6, 55.1, 26.7, 20.7, 20.7, 20.5, 19.2. **IR (film, cm^{-1})** 2932, 1749, 1428, 1368, 1220, 1167, 1113, 1039.



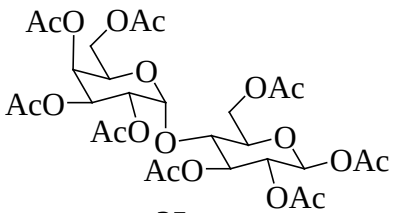
23

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 5.69 (d, *J* = 3.7 Hz, 1H), 5.48 – 5.42 (m, 2H), 5.37 (t, *J* = 5.9 Hz, 1H), 5.08 (t, *J* = 9.8 Hz, 1H), 4.87 (dd, *J* = 10.4, 3.7 Hz, 1H), 4.35 (dd, *J* = 12.0, 4.3 Hz, 1H), 4.32 – 4.24 (m, 3H), 4.23 – 4.19 (m, 1H), 4.17 (s, 2H), 4.16 – 4.09 (m, 2H), 2.18 (s, 3H), 2.12 (s, 6H), 2.11 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 170.7, 170.4, 170.1, 170.0, 169.9, 169.8, 169.6, 169.5, 103.9, 89.8, 79.0, 77.3, 77.0, 76.8, 75.6, 74.9, 70.2, 69.5, 68.4, 68.1, 63.6, 62.8, 61.7, 20.7, 20.7, 20.6, 20.6, 20.6, 20.5, 20.5. **IR (film, cm^{-1})** 2963, 1742, 1435, 1370, 1217, 1037, 902.



24

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 6.17 (d, *J* = 3.7 Hz, 1H), 5.45 (dd, *J* = 10.1, 8.9 Hz, 1H), 5.37 (d, *J* = 4.0 Hz, 1H), 5.35 – 5.30 (m, 1H), 5.04 – 4.97 (m, 1H), 4.90 (dd, *J* = 10.2, 3.7 Hz, 1H), 4.81 (dd, *J* = 10.6, 4.0 Hz, 1H), 4.39 (dd, *J* = 12.4, 2.5 Hz, 1H), 4.21 – 4.13 (m, 2H), 4.07 – 4.03 (m, 1H), 3.98 (ddd, *J* = 9.3, 7.5, 5.8 Hz, 2H), 3.90 – 3.86 (m, 1H), 2.16 (s, 3H), 2.08 (3, *J* = 2.9 Hz, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H), 1.93 (d, *J* = 3.5 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) 170.5, 170.4, 170.4, 169.9, 169.9, 169.8, 169.3, 168.9, 95.7, 88.7, 77.3, 77.1, 76.9, 72.2, 72.2, 70.0, 69.9, 69.6, 69.2, 68.5, 67.8, 62.3, 61.3, 20.9, 20.9, 20.7, 20.6, 20.6, 20.5, 20.5, 20.4. **IR (film, cm^{-1})** 2961, 1744, 1432, 1368, 1209, 1141, 1030, 913.



25

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.25 (d, *J* = 3.7 Hz, 1H), 5.47 (dd, *J* = 10.0, 9.5 Hz, 1H), 5.36 (dd, *J* = 3.5, 0.8 Hz, 1H), 5.12 (dd, *J* = 10.4, 7.9 Hz, 1H), 5.12 (dd, *J* = 10.4, 7.9 Hz, 1H), 5.01 (dd, *J* = 10.3, 3.7 Hz, 1H), 4.97 (dd, *J* = 10.4, 3.5 Hz, 1H), 4.50 (d, *J* = 7.9 Hz, 1H), 4.45 (dd, *J* = 12.2, 2.0 Hz, 1H), 4.19 – 4.07 (m, 3H), 4.01 (ddd, *J* = 10.1, 4.2, 2.0 Hz, 1H), 3.91 (t, *J* = 6.8 Hz, 1H), 3.83 (t, *J* = 12.0 Hz, 1H), 2.18 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 2.07 (s, 6H), 2.06 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 170.3, 170.2, 170.1, 169.9, 169.85, 169.5, 169.1, 168.9, 126.3, 101.09, 88.9, 77.3, 77.1, 76.9, 75.70, 70.9, 70.6, 69.5, 69.3, 69.0, 66.5, 61.4, 60.7, 20.9, 20.8, 20.7, 20.6, 20.5, 20.4. **IR (film, cm^{-1})** 2962, 1743, 1432, 1368, 1210, 1047, 1014, 911, 729.

Reference

S1. Mensah, E.A.; Azzarelli, J. M.; Nguyen, H.M. Palladium-controlled β-selective glycosylation in the absence of the C(2)-ester participatory group. *J. Org. Chem*. **2009**, *74*, 1650–1657.