Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

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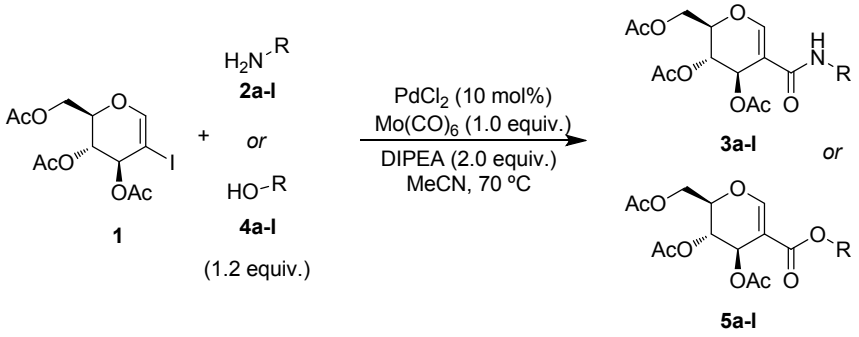
Contents:

1. General methods

The compounds were all identified by usual analytical methods: ^{1}H NMR, ^{13}C NMR, IR, and HR-MS (ESI). ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$, in a Bruker DPX-300 instrument. ^{1}H chemical shifts were reported in ppm referenced relative to TMS internal standard (0.00 ppm) or the residual chloroform peak (7.26 ppm). Abbreviations to denote the multiplicity of a particular signal are: m (multiplet), s (singlet), d (doublet), t (triplet) and dd (double of doublets). ^{13}C chemical shift were reported in ppm relative to the $CDCl_3$ triplet (77.16 ppm). IR spectra were measured on an Agilent Technologies Cary 630 and were reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Shimadzu LCMS-TOF, using ESI with 50% solution of acetonitrile/H_2O and 0.1% formic acid as ionization method. Thin layer chromatography (TLC) was performed using silica gel UV_{254}. 0.20 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine or acidic vanillin solution. The solvents were purified by distillation or used without any purification in the case of HPLC-grade material. All other compounds were used as received. A balloon of CO was used in the reactions involving this gas.

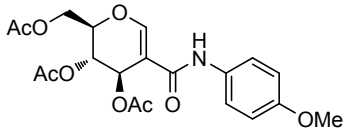
2. General procedure for the carbonylation reaction



To a vial equipped with a magnetic stirrer bar and sealed with a rubber septum connected to a deflated balloon with a needle were added the tri-*O*-acetylated iodoglucal (0.5 mmol), acetonitrile (4.0 mL), $PdCl_2$ (10 mol %), $Mo(CO)_6$ (0.5 mmol, 1 equiv.), the amine or alcohol derivatives (0.6 mmol, 1.2 equiv.) and DIPEA (1.0 mmol). The reaction mixture was vigorously stirred at 70 ºC for 5 to 12 h. In the case of amidoglycals, the product was then washed with HCl 1 M in order to remove any excess of the amine starting material present. For the glycal esters, the resulting mixture was washed with water and extracted with ethyl acetate. The organic layers were then combined and

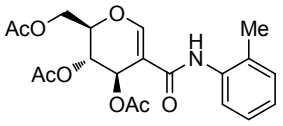
evaporated. The crude products were purified by flash chromatography using mixtures of hexane and ethyl acetate as eluent.

3. Characterization data



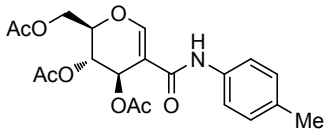
3a

The product **3a** was obtained as a yellow oil (206 mg, 0.49 mmol, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (s, 1H), 7.67 (s, 1H), 7.37 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 5.68 (s, 1H), 5.10 (t, *J* = 2.9 Hz, 1H), 4.53 – 4.45 (m, 1H), 4.41 – 4.10 (m, 2H), 3.65 (s, 3H), 2.05 – 1.93 (m, 9H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.2, 170.3, 169.4, 162.7, 156.2, 154.4, 131.3, 121.7, 113.9, 106.1, 74.3, 66.0, 62.3, 61.2, 55.3, 20.8, 20.6, 20.5. IR (υ, cm^{-1}) = 3225, 2896, 2862, 2743, 1682, 1601, 1549, 1460, 1138, 1177, 989, 802; HRMS (ESI-TOF) calcd [$C_{20}H_{23}NO_9Na^+$] 444.1271, found 444.1268.



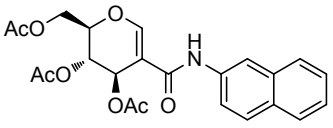
3b

The product **3b** was obtained as a yellow oil (162 mg, 0.40 mmol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (s, 1H), 7.69 (d, *J* = 7.0 Hz, 2H), 7.32 (d, *J* = 6.7 Hz, 2H), 5.78 – 5.70 (m, 1H), 5.15 (t, *J* = 2.9 Hz, 1H), 4.53 (m, 1H), 4.38 (m, 1H), 4.22 (dd, *J* = 12.0, 4.5 Hz, 1H), 2.23 (s, 3H), 2.09 – 2.01 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.3, 169.4, 163.1, 155.1, 137.7, 134.7, 130.3, 128.9, 125.0, 124.3, 105.7, 74.4, 66.2, 62.6, 61.1, 20.8, 20.7, 20.6, 17.9. IR (υ, cm^{-1}) = 3252, 2977, 2918, 1687, 1460, 1326, 1184, 1153, 1017, 994. HRMS (ESI-TOF) calcd [$C_{20}H_{23}NO_8Na^+$] 428.1321, found 428.1317.



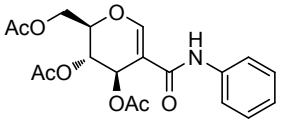
3c

The product **3c** was obtained as a yellow oil (182 mg, 0.45 mmol, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.43 (s, 1H), 7.82 (s, 1H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.77 (s, 1H), 5.19 (s, 1H), 4.60 (s, 1H), 4.47 – 4.25 (m, 2H), 2.30 (s, 3H), 2.16 – 2.07 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.4, 170.3, 169.4, 162.6, 155.0, 135.6, 133.7, 129.3, 120.0, 105.9, 74.3, 66.1, 62.3, 61.2, 20.9, 20.8, 20.7, 20.6. IR (υ, cm^{-1}) = 3260, 1682, 1601, 1547, 1462, 1324, 1143, 1179, 1013, 989, 707. HRMS (ESI-TOF) calcd [$C_{20}H_{23}NO_8Na^+$] 428.1321, found 421.1323.



3d

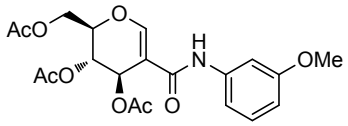
The product **3d** was obtained as a yellow oil (165 mg, 0.37 mmol, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.63 (s, 1H), 8.18 (s, 1H), 7.78 (s, 1H), 7.72 – 7.52 (m, 3H), 7.35 – 7.18 (m, 3H), 5.71 (d, *J* = 3.0 Hz, 1H), 5.10 (d, *J* = 3.5 Hz, 1H), 4.56 – 4.44 (m, 1H), 4.41 – 4.26 (m, 1H), 4.17 (dd, *J* = 12.0, 4.8 Hz, 1H), 1.99 (q, *J* = 6.5, 6.0 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.7, 170.4, 169.5, 163.1, 155.5, 135.7, 133.9, 130.6, 128.6, 127.7, 127.5, 126.4, 124.9, 120.1, 116.9, 106.0, 74.5, 66.2, 62.3, 61.3, 21.0, 20.8, 20.7. IR (υ, cm^{-1}) = 3200, 1670, 1575, 1460,1324, 1175, 1151, 1117, 991, 853, 724. HRMS (ESI-TOF) calcd [$C_{23}H_{23}NO_8Na^+$] 464.1316, found 464.1318.



3e

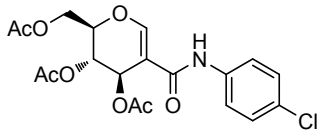
The product **3e** was obtained as a yellow oil (160 mg, 0.41 mmol, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45 (s, 1H), 7.74 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 8.8, 6.9 Hz, 2H), 7.04 – 6.91 (m, 1H), 5.69 (dd, *J* = 3.2, 1.5 Hz, 1H), 5.11 (t, *J* = 2.8 Hz, 1H), 4.51 (m, 1H), 4.44 – 4.14 (m, 2H), 2.13 – 1.89 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.4, 170.3, 169.4, 162.8, 155.2, 138.1, 128.8, 124.1, 120.0, 105.9, 74.4, 66.1, 62.2, 61.2, 20.9, 20.7, 20.6. IR (υ, cm^{-1}) = 3220, 2872, 1682, 1601, 1486, 1397, 1324, 1177,

1143, 989, 735, 709. HRMS (ESI-TOF) calcd [$C_{19}H_{21}NO_8Na^+$] 414.1159, found 414.1158.



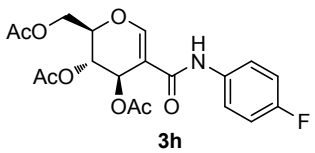
3f

The product **3f** was obtained as a yellow oil (185 mg, 0.43 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 7.72 (s, 1H), 7.27 (s, 1H), 7.15 – 6.90 (m, 2H), 6.54 (dd, *J* = 8.2, 2.4 Hz, 1H), 5.68 (s, 1H), 5.11 (s, 1H), 4.49 (s, 1H), 4.39 – 4.08 (m, 2H), 3.68 (s, 3H), 2.14 – 1.91 (m, 9H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.3, 170.3, 169.4, 162.8, 160.0, 154.9, 139.4, 129.5, 112.1, 110.0, 106.0, 105.6, 74.4, 66.0, 62.2, 61.2, 55.1, 20.8, 20.6, 20.5. IR (υ, cm^{-1}) = 3220, 2862, 1682, 1611, 1601, 1547, 1493, 1324, 1179, 989, 883, 707. HRMS (ESI-TOF) calcd [$C_{20}H_{23}NO_9Na^+$] 444.1271, found 444.1273.



3g

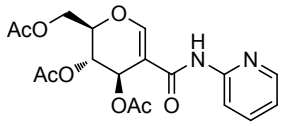
The product **3g** was obtained as a yellow oil (165 mg, 0.39 mmol, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (s, 1H), 7.78 (d, *J* = 1.5 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 5.66 (s, 1H), 5.11 (s, 1H), 4.54 (s, 1H), 4.42 – 4.19 (m, 2H), 2.08 – 2.01 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.7, 170.3, 169.4, 162.7, 155.7, 136.8, 128.9, 128,8, 121.1, 105.5, 74.5, 66.0, 62.1, 61.2, 20.9, 20.7, 20.6. IR (υ, cm^{-1}) = 3222, 2872, 1685, 1611, 1544, 1443, 1145, 1162, 991, 981, 883, 707. HRMS (ESI-TOF) calcd [$C_{19}H_{20}ClNO_8Na^+$] 448.0775, found 448.0770.



3h

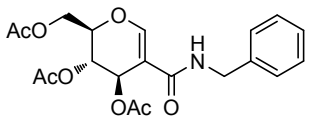
The product **3g** was obtained as a yellow oil (155 mg, 0.38 mmol, 76%).^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (s, 1H), 7.75 (s, 1H), 7.46 (dd, *J* = 8.9, 5.0 Hz, 2H), 6.99 – 6.80 (m, 2H), 5.67 (dd, *J* = 3.0, 1.5 Hz, 1H), 5.11 (t, *J* = 2.7 Hz, 1H), 4.52 (m, 1H), 4.35 (dd, *J* = 12.0, 8.0 Hz, 1H), 4.21 (dd, *J* = 12.0, 4.6 Hz, 1H), 2.13 – 1.97 (m, 9H).^{13}C NMR (75 MHz, $CDCl_3$): δ = δ 171.6, 170.3, 169.4, 162.8, 159.22 (d, *J* = 243.2 Hz), 155.3,

134.2, 121.74 (d, J = 7.7 Hz), 115.44 (d, J = 22.4 Hz), 105,6, 74.47, 66.04, 62.21, 61.23, 20.91, 20.70, 20.61. IR (υ, cm^{-1}) = 3200, 2978, 1685, 1601, 1562, 1493, 1458, 1324, 1168, 1145, 989, 806. HRMS (ESI-TOF) calcd [$C_{19}H_{20}FNO_8Na^+$] 448.1069, found 448.1068.



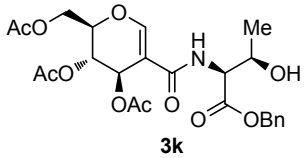
3i

The product **3i** was obtained as a yellow oil (114 mg, 0.29 mmol, 59%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.87 (s, 1H), 7.36 – 7.14 (m, 2H), 6.90 – 6.79 (m, 1H), 6.41 (d, J = 3.0 Hz, 1H), 5.74 (d, J = 2.9 Hz, 1H), 5.22 – 5.11 (m, 1H), 4.56 (dd, J = 8.0, 4.1 Hz, 1H), 4.49 – 4.37 (m, 1H), 4.16 (dd, J = 12.1, 4.6 Hz, 1H), 2.07 – 1.96 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3, 169.5, 169.3, 164.7, 157.3, 133.7, 128.1, 125.6, 115.9, 111.4, 102.7, 74.8, 66.0, 62.5, 60.9, 20.8, 20.7, 20.6. IR (υ, cm^{-1}) = 3287, 2994, 1680, 1577, 1432, 1326, 1173, 1153, 1099, 991, 704.HRMS (ESI-TOF) calcd [$C_{18}H_{20}N_2O_8Na^+$] 415.1112, found 428.1121.



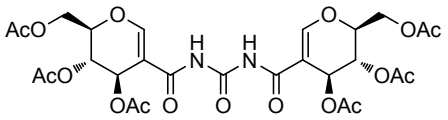
3j

The product **3j** was obtained as a yellow oil (176 mg, 0.43 mmol, 87%).^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (s, 1H), 7.24 – 7.11 (m, 5H), 6.69 (t, J = 5.7 Hz, 1H), 5.57 (d, J = 3.6 Hz, 1H), 5.06 (t, J = 3.2 Hz, 1H), 4.49 – 4.38 (m, 2H), 4.25 (dd, J = 9.0, 3.3 Hz, 2H), 4.14 (dd, J = 12.0, 4.5 Hz, 1H), 2.08 – 1.87 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.7, 170.2, 169.3, 164.5, 153.7, 138.3, 128.5, 127.6, 127.3, 105.8, 74.1, 66.2, 62.5, 61.0, 43.4, 20.6, 206, 20.5. IR (υ, cm^{-1}) = 3115, 2931, 2883, 1680, 1601, 1486, 1324, 1145, 1177, 1108, 989, 950, 678. HRMS (ESI-TOF) calcd [$C_{20}H_{23}NO_8Na^+$] 428.1316, found 428.1311.



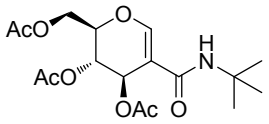
3k

The product **3k** was obtained as a yellow oil (172 mg, 0.34 mmol, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (s, 1H), 7.27 (s, 5H), 6.73 (d, *J* = 8.5 Hz, 1H), 5.67 (s, 1H), 5.12 (s, 2H), 4.60 (dd, *J* = 8.5, 2.7 Hz, 1H), 4.47 (d, *J* = 4.8 Hz, 1H), 4.39 – 4.13 (m, 2H), 2.66 (s, 1H), 2.02 (d, *J* = 2.1 Hz, 9H), 1.09 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.7, 170.6, 170.3, 169.3, 165.2, 154.3, 135.3, 128.5, 128.3, 128.2, 128.0, 105.6, 74.3, 67.2, 66.2, 62.7, 61.0, 57.7, 20.8, 20.7, 20.6, 20.0. IR (υ, $cm^{-1)}$ = 3319, 2875, 1680, 1601, 1475, 1326, 1177, 1119, 1015, 989, 883, 709, 678. HRMS (ESI-TOF) calcd [$C_{24}H_{29}NO_{11}Na^{+}$] 530.1633, found 530.1628.



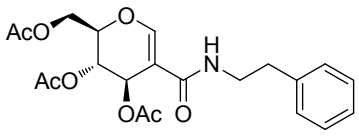
3l

The product **3l** was obtained as a yellow oil (269 mg, 0.41 mmol, 82%). (2,4 equiv. of amine was used). The product was purified by silica flash chromatography and eluted with ethyl acetate/hexane 9:1. ^{1}H NMR (300 MHz, $CDCl_3$): 9.70 (s, 1H), 7.79 (s, 1H), 5.69 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.15 (t, *J* = 2.2 Hz, 1H), 4.58 – 4.49 (m, 1H), 4.43 – 4.32 (m, 1H), 4.17 – 4.08 (m, 1H), 2.03 (d, *J* = 4.8 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3, 169.7, 169.3, 166.1, 155.8, 155.4, 106.1, 74.6, 65.6, 61.7, 61.0, 20.7, 20.6, 20.5. IR (υ, cm^{-1}) = 3215, 3115,1873, 1682, 1654, 1579, 1454, 1324, 1177, 1153, 1011, 991, 737. HRMS (ESI-TOF) calcd [$C_{27}H_{32}N_2O_{17}Na^{+}$] 679.1593, found 428.1591.



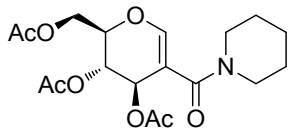
3m

The Product **3m** was obtained as a colorless oil (78 mg, 0.21 mmol, 42%). ^{1}H NMR (300 MHz, $CHCl_3$): δ = 7.61 (s, 1H), 6.04 (s, 1H), 5.61 (d, *J* = 3.2 Hz, 1H), 5.11 (t, *J* = 3.2 Hz, 1H), 4.59 – 4.44 (m, 1H), 4.38 (t, *J* = 5.9 Hz, 1H), 4.24 (dd, *J* = 12.0, 4.5 Hz, 1H), 2.10 (s, 9H), 1.36 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.3, 169.4, 163.74, 153.4, 106.5, 74.0, 66.4, 62.7, 61.1, 51.4, 28.7, 20.8, 20.7, 20.6. IR (υ, cm^{-1})= 3274, 2872, 1685, 1601, 1559, 1484, 1158, 1182, 1017, 991. HRMS (ESI-TOF) calcd [$C_{17}H_{25}NO_8Na^{+}$] 394.1472 found 394.1423.



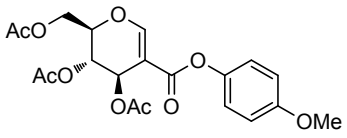
3n

The Product **3n** was obtained as a colorless oil (157 mg, 0.37 mmol, 75%). ^{1}H NMR (300 MHz, $CHCl_3$): δ = 7.64 (s, 1H), 7.38 – 7.06 (m, 5H), 6.31 (t, *J* = 5.4 Hz, 1H), 5.54 (dd, *J* = 3.1, 1.6 Hz, 1H), 5.10 (t, *J* = 3.0 Hz, 1H), 4.52 (dt, *J* = 6.8, 3.6 Hz, 1H), 4.38 (dd, *J* = 11.9, 7.8 Hz, 1H), 4.21 (dd, *J* = 12.0, 4.7 Hz, 1H), 3.71 – 3.33 (m, 2H), 2.88 – 2.69 (m, 2H), 2.15 – 1.90 (m, 9H).^{13}C NMR (75 MHz, $CDCl_3$): δ =170.7, 170.3, 169.3, 164.7, 153.9, 138.8, 128.6, 128.5, 126.4, 105.4, 74.1, 66.1, 62.3, 61.1, 40.7, 35.3, 20.7, 20.7, 20.6. IR (υ, cm^{-1}) = 3270, 2872, 1680, 1602, 1554, 1485, 1159, 1180, 1015, 992. HRMS (ESI-TOF) calcd [$C_{21}H_{25}NO_8Na^+$] 442.1472 found 442.1389



3o

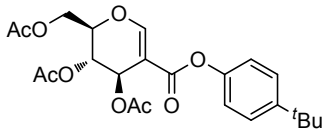
The Product **3o** was obtained as a colorless oil (172 mg, 0.45 mmol, 90%). ^{1}H NMR (300 MHz, $CHCl_3$): δ = 6.63 (s, 1H), 5.71 (d, *J* = 4.9 Hz, 1H), 5.20 (t, *J* = 5.6 Hz, 1H), 4.44 (dd, *J* = 12.1, 6.3 Hz, 1H), 4.33 (dd, *J* = 6.6, 3.4 Hz, 1H), 4.11 (dd, *J* = 12.1, 3.2 Hz, 1H), 3.63 – 3.32 (m, 4H), 2.19 – 1.81 (m, 9H), 1.71 – 1.45 (m, 6H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3, 169.5, 169.5, 165.8, 146.4, 107.9, 74.2, 66.6, 66.4, 60.9, 46.0, 26.09, 24.5, 20.7, 20.7, 20.6. IR (υ, cm^{-1}) = 2842, 2764, 1682, 1566, 1387, 1324, 1177, 1141, 989, 881, 707. HRMS (ESI-TOF) calcd [$C_{18}H_{25}NO_8Na^+$] 406.1472 found 406.1410.



5a

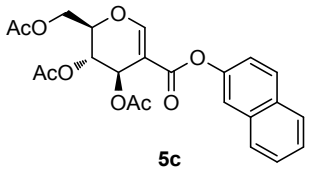
The product **5a** was obtained as a collorless oil (205 mg, 0.48 mmol, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.02 – 6.70 (m, 4H), 5.75 – 5.66 (m, 1H), 5.14 (d, *J* = 1.7 Hz, 1H), 4.54 (m, 1H), 4.47 – 4.36 (m, 1H), 4.14 (m, 1H), 3.69 (s, 3H), 2.09 – 1.91 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 169.2, 169.1, 164.0, 157.4, 157.2, 143.8, 122.2, 114.3, 103.5, 74.9, 65.9, 62.3, 60.8, 55.5, 20.6, 20.6, 20.5. IR (υ, cm^{-1}) =

2916, 2747, 1682, 1579, 1179, 1149, 991,728. HRMS (ESI-TOF) calcd [$C_{20}H_{22}O_{10}Na^+$] 445.1105, found 445.1101.



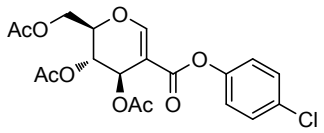
5b

The product **5b** was obtained as a yellow oil (199 mg, 0.44 mmol, 89%). ^{1}H NMR (300 MHz, $CHCl_3$): δ = 7.89 (s, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 5.75 (dd, *J* = 3.1, 1.6 Hz, 1H), 4.69 – 4.56 (m, 1H), 4.48 (dd, *J* = 12.0, 7.8 Hz, 1H), 4.21 (dd, *J* = 12.0, 4.3 Hz, 1H), 2.05 (d, *J* = 14.7 Hz, 9H), 1.30 (m, 9H). ^{13}C NMR (75 MHz, $CHCl_3$): δ = 186.4, 170.2, 169.2, 169.1, 163.8, 157.5, 148.6, 148.0, 126.2, 120.8, 103.6, 74.9, 65.9, 62.3, 60.8, 34.4, 20.7, 20.6, 20.6. IR (υ, cm^{-1}) = 2866, 1672, 1579, 1460, 1324, 1151, 1132, 992, 843, 706. HRMS (ESI-TOF) calcd [$C_{23}H_{28}O_9Na^+$] 471.1626, found. 471.1622.



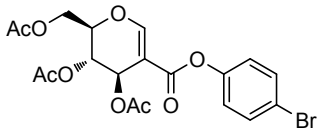
5c

The product **5c** was obtained as a colorless oil (183 mg, 0.41 mmol, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (s, 1H), 7.76 – 7.60 (m, 3H), 7.50 (s, 1H), 7.34 (t, *J* = 1.7 Hz, 1H), 7.22 – 7.11 (m, 2H), 5.73 (dd, *J* = 3.1, 1.5 Hz, 1H), 5.16 (dd, *J* = 3.7, 2.6 Hz, 1H), 4.60 – 4.48 (m, 1H), 4.42 (d, *J* = 4.2 Hz, 1H), 4.13 (dd, *J* = 12.1, 4.3 Hz, 1H), 1.97 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 169.3, 169.2, 163.8, 157.8, 148.1, 133.7, 131.4, 129.3, 127.7, 127.6, 126.5, 125.7, 121.0, 118.5, 103.6, 75.0, 65.9, 62.3, 60.8, 20.7, 20.6, 20.6. IR (υ, cm^{-1}) = 1670, 1575, 1460,1324, 1175, 1151, 1117, 991, 853, 724. HRMS (ESI-TOF) calcd [$C_{23}H_{22}O_9Na^+$] 465.1162, found 465.1150.



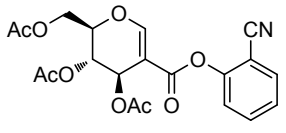
5d

The product **5d** was obtained as a colorless oil (160 mg, 0.37 mmol, 75%).^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 5.68 (dd, *J* = 3.1, 1.6 Hz, 1H), 5.15 (t, *J* = 3.1 Hz, 1H), 4.60 – 4.51 (m, 1H), 4.46 – 4.38 (m, 1H), 4.14 (m, 1H), 2.01 m, 9H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5, 167.5, 167.4, 161.7, 156.2, 147.1, 129.3, 127.6, 121.1, 101.5, 73.3, 64.1, 60.4, 59.0, 18.9, 18.9, 18.8. IR (υ, cm^{-1}) = 2872, 1685, 1611,1544, 1443, 1145, 1162, 991, 981, 883, 707. HRMS (ESI-TOF) calcd [$C_{19}H_{19}ClO_9Na^+$] 449.0615, found 449.0610.



5e

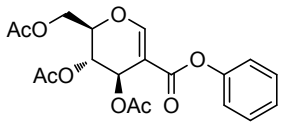
The product **5e** was obtained as a colorless oil (173 mg, 0.37 mmol, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 7.39 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.70 – 5.63 (m, 1H), 5.15 (t, *J* = 2.9 Hz, 1H), 4.57 (s, 1H), 4.48 – 4.37 (m, 1H), 4.19 – 4.09 (m, 1H), 1.99 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5, 167.5, 167.4, 161.6, 156.3, 147.8, 130.6, 121.7, 117.0, 101.5, 73.4, 64.1, 60.4, 59.1, 19.0, 18.9, 18.8. IR (υ, cm^{-1}) = 1672, 1575, 1436, 1324, 1177, 1127, 1145, 992, 978, 842, 732. HRMS (ESI-TOF) calcd [$C_{20}H_{19}NO_9H^+$] 471.0212, found 471.0219.



3f

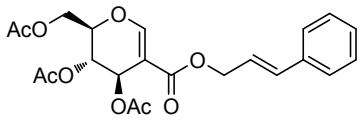
The product **5f** was obtained as a colorless oil (116 mg, 0.28 mmol, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (s, 1H), 7.61 – 7.47 (m, 2H), 7.34 – 7.21 (m, 2H), 5.72 (dd, *J* = 3.1, 1.6 Hz, 1H), 5.18 (t, *J* = 3.1 Hz, 1H), 4.61 (m, 1H), 4.49 – 4.34 (m, 1H), 4.26 – 4.15 (m, 1H), 2.02 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5, 169.7, 169.3, 162.7, 159.1, 151.9, 134.0, 133.2, 126.3, 123.3, 120.2, 106.7, 102.5, 75.3, 65.6, 62.0, 60.8, 20.7,

20.7, 20.6. IR (υ, cm^{-1}) = 2160, 1680, 1574, 1553, 1406, 1326, 1141, 1158, 989, 734. HRMS (ESI-TOF) calcd [$C_{20}H_{19}NO_9Na^+$] 440.0958, found 440.0981.



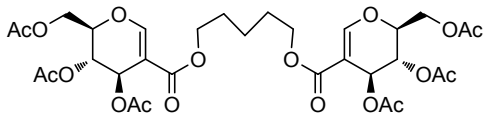
5g

The product **5g** was obtained as a colorless oil. (162 mg, 0.41 mmol, 83%). ^1H (300 MHz, $CHCl_3$): δ = 7.84 (s, 1H), 7.32 – 7.25 (m, 2H), 7.09 – 6.97 (m, 2H), 5.71 (s, 1H), 5.15 (t, *J* = 3.1 Hz, 1H), 4.55 (m, 1H), 4.43 (td, *J* = 9.2, 7.8, 2.5 Hz, 1H), 4.15 (m, 1H), 2.19 – 1.87 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 169.3, 169.1, 163.7, 157.6, 150.4, 129.3, 125.7, 121.5, 103.5, 75.0, 65.8, 62.2, 60.8, 20.7, 20.6, 20.5. IR (υ, cm^{-1}) = 1670, 1577, 1441, 1324, 1177, 1145, 1127, 991, 883. HRMS (ESI-TOF) calcd [$C_{19}H_{20}O_9Na^+$] 415.1005, found. 415.1010.



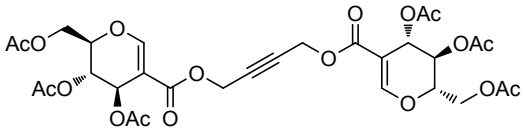
5h

The Product **5h** was obtained as a yellow oil (147 mg, 0.34 mmol, 68%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.67 (s, 1H), 7.40 – 7.05 (m, 5H), 6.63 – 6.47 (m, 1H), 6.20 (m, 1H), 5.63 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.10 (t, *J* = 3.1 Hz, 1H), 4.85 – 4.61 (m, 2H), 4.54 – 4.44 (m, 1H), 4.37 (d, *J* = 19.8 Hz, 1H), 4.20 – 4.02 (m, 1H), 2.08 – 1.84 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 169.4, 169.2, 165.0, 156.5, 136.1, 134.1, 128.6, 128.0, 126.5, 123.0, 103.9, 74.6, 66.0, 64.9, 62.3, 60.8, 20.7, 20.7, 20.6. IR (υ, cm^{-1}) = 2924, 1685, 1654, 1579 C=C, 1324, 1177, 1151, 1015, 991, 724, 674. HRMS (ESI-TOF) calcd [$C_{22}H_{24}O_9Na^+$] 455.1318, found 455.1315.



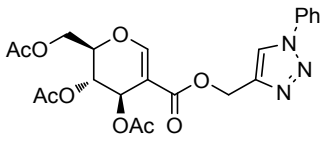
5i

The Product **5i** was obtained as a colorless oil (257 mg, 0.37 mmol, 73%). (2,4 equiv. of amine was used) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (s, 1H), 7.63 (s, 1H), 5.65 – 5.50 (m, 2H), 5.11 (m, 2H), 4.65 – 4.45 (m, 2H), 4.38 (m, 2H), 4.19 – 3.99 (m, 4H), 3.55 (t, *J* = 6.4 Hz, 2H), 2.12 – 1.89 (m, 18H), 1.69 – 1.43 (m, 4H), 1.32 (dd, *J* = 7.4, 3.8 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 170.1, 169.3, 169.2, 169.1, 169.0, 165.3, 160.5, 159.5, 156.2, 103.8, 103.5, 75.4, 74.5, 65.9, 65.3, 64.4, 62.3, 62.2, 61.7, 60.8, 60.6, 32.4, 28.5, 25.6, 25.3, 20.6, 20.6, 20.6, 20.5, 20.5, 20.5. IR. 2840, 1682, 1648, 1572, 1326, 1177, 1151, 978, 853, 745, 715. HRMS (ESI-TOF) m/z = (M^+ + Na^+). HRMS (ESI-TOF) calcd [$C_{32}H_{42}O_{18}Na^+$] 737.2269, found 737.2265.



5j

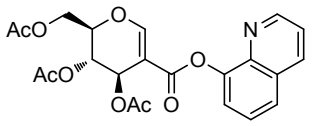
The product **5j** was obtained as a colorless oil (136 mg, 0.20 mmol, 40%).(2,4 equiv. of amine was used) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (s, 2H), 5.66 – 5.56 (s, 2H), 5.10 (s, 1H), 4.80 – 4.60 (m, 4H), 4.50 (m, 2H), 4.38 (m, 2H), 4.10 (m, 2H), 2.01 (m, 18H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 170.2, 169.4, 169.3, 169.2, 169.2, 164.5, 164.4, 157.1, 157.1, 103.4, 103.3, 85.2, 80.7, 79.4, 74.8, 65.9, 65.8, 62.2, 62.1, 60.7, 52.2, 51.9, 50.8, 20.7, 20.7, 20.6, 20.6, 20.6, 20.6. IR. 2868, 1682, 1663, 1577, 1324, 1177, 1153, 1015, 989, 933, 737. HRMS (ESI-TOF) calcd [$C_{30}H_{34}O_{18}$ Na^+] 705.1643, found 705.1631.



5k

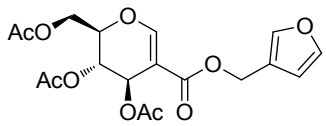
The Product **5k** was obtained as a colorless oil. (193 mg, 0.41 mmol, 82%) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (s, 1H), 7.67 (d, *J* = 7.1 Hz, 2H), 7.56 – 7.26 (m, 4H), 5.64 (s, 2H), 5.43 – 5.20 (m, 1H), 5.18 – 5.04 (m, 1H), 4.60 – 4.44 (m, 1H), 4.43 – 4.02 (m, 1H), 4,25-4,07 (m, 1H), 2.10 – 1.91 (m, 9H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.8,

170.2, 169.4, 169.1, 165.0, 157.0, 137.7, 128.9, 122.1, 121.7, 120.5, 103.5, 74.8, 65.9, 62.1, 61.2, 60.8, 20.7, 20.6, 20.6. IR (υ, $cm^{-1)}$ = 2870, 1916, 1877, 1682, 1663, 1579, 1324, 1177, 1153, 1011, 991, 881, 707. HRMS (ESI-TOF) calcd [$C_{22}H_{23}N_3O_9Na^+$] 496.0809, found 496.0805.



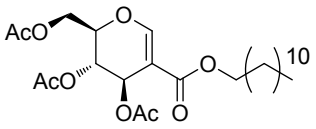
5l

The Product **5l** was obtained as a yellow oil. (195 mg, 0.44 mmol, 88%). ^{1}H NMR (300 MHz, $CHCl_3$): δ = 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.14 – 7.94 (m, 2H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.41 (d, *J* = 9.3 Hz, 2H), 7.31 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.83 (dd, *J* = 3.3, 1.5 Hz, 1H), 5.20 (t, *J* = 3.4 Hz, 1H), 4.58 (d, *J* = 5.0 Hz, 1H), 4.50 – 4.39 (m, 1H), 4.22 (dd, *J* = 12.1, 4.3 Hz, 1H), 2.13 – 1.94 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3, 169.4, 169.3, 163.9, 158.0, 150.3, 146.9, 141.1, 136.1, 129.5, 126.1, 125.8, 121.7, 121.6, 103.6, 75.0, 66.1, 62.6, 60.9, 20.7, 20.7, 20.6. IR (υ, cm^{-1}) = 2900, 1680, 1579, 1452, 1177, 1153, 1128, 991, 730, 761, 707. HRMS (ESI-TOF) calcd [$C_{22}H_{21}NO_9H^+$] 443.1216, found 443.1213.



5m

The Product **5m** was obtained as a colorless oil (146 mg, 0.37 mmol, 74%). ^{1}H NMR (300 MHz, $CHCl_3$): δ = 7.72 (s, 1H), 7.42 (s, 1H), 6.39 (dd, *J* = 12.7, 3.0 Hz, 2H), 5.67 (s, 1H), 5.28 – 5.12 (m, 2H), 5.04 (d, *J* = 13.0 Hz, 1H), 4.61 – 4.51 (m, 1H), 4.42 (dd, *J* = 12.0, 7.6 Hz, 1H), 4.16 (dd, *J* = 12.0, 4.4 Hz, 1H), 2.15 – 1.93 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ =^{13}C NMR (75 MHz, $CDCl_3$) δ 170.23, 169.33, 169.19, 164.81, 156.73, 149.38, 143.22, 110.63, 110.56, 103.74, 74.70, 66.04, 62.32, 60.80, 57.92, 20.71, 20.58, 20.56. IR (υ, cm^{-1}) =2870, 1685, 1654, 1579, 1579, 1324, 1177, 1151, 985, 726. HRMS (ESI-TOF) calcd [$C_{18}H_{20}O_{10}Na^+$] 419.0954 found 419.0876.

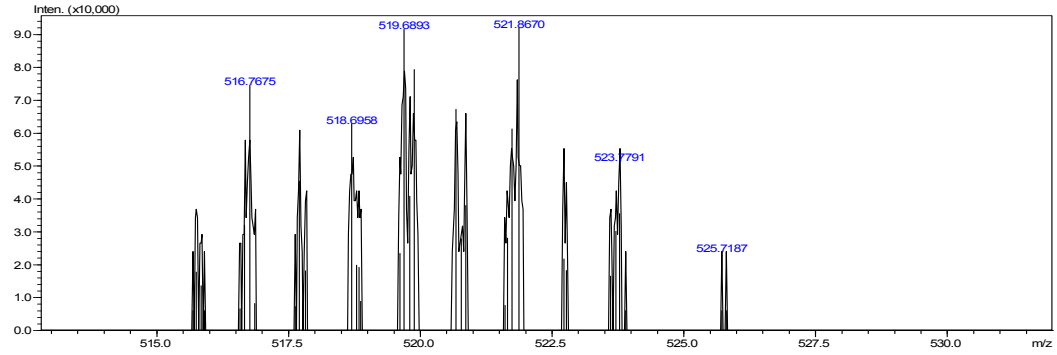


5n

The Product **5n** was obtained as a colorless oil (103 mg, 0.24 mmol, 48%). ^{1}H NMR (300 MHz, $CHCl_3$): δ = 7.70 (s, 1H), 5.67 (s, 1H), 5.16 (s, 1H), 4.77 – 4.49 (m, 1H), 4.51 – 4.36 (m, 1H), 4.35 – 4.03 (m, 2H), 2.25 – 2.02 (m, 9H), 1.65 (m, 2H), 1.28 (m, 19H), 1.00 – 0.73 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.25, 169.30, 169.21, 165.34, 156.13, 104.04, 74.58, 66.07, 64.65, 62.35, 60.88, 31.88, 29.60, 29.59, 29.56, 29.50, 29.30, 29.24, 28.64, 25.91, 22.64, 20.74, 20.70, 20.61, 14.06. IR (υ, cm^{-1}) = 2829, 2760, 1689, 1657, 1583, 1326, 1179, 1153, 1017, 992. HRMS (ESI-TOF) calcd [$C_{25}H_{40}O_9Na^+$] 507.2565, found 507.2551.

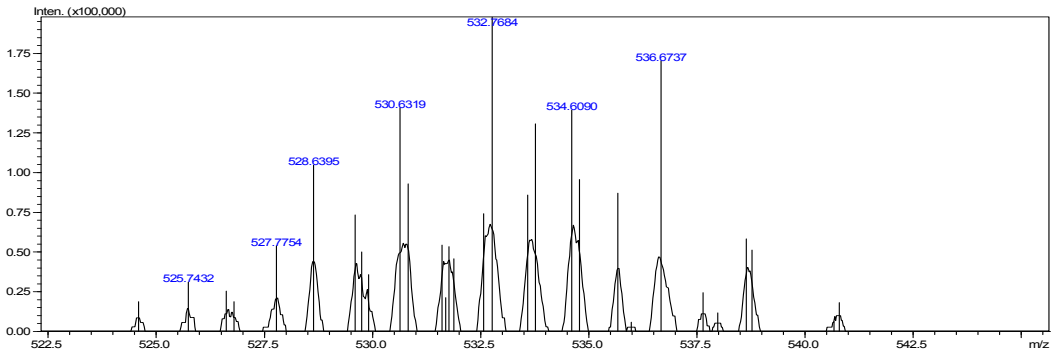
4. HRMS studies

ESI Intermediate I, CH_3CN + 0, 1% TFA



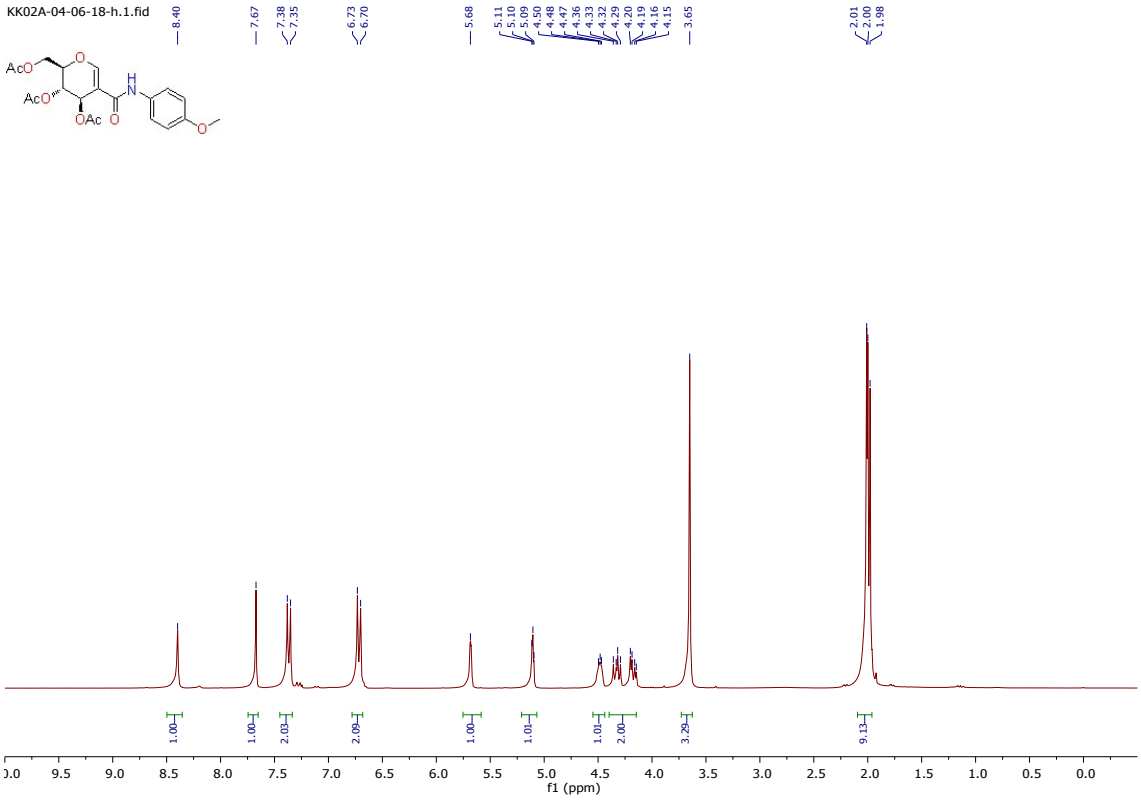
Calcd. for $C_{13}H_{18}IO_9Pd$ $(M + H_2O)^+$: 521.8997; Found: 521.8670.

ESI Intermediate II, CH_3CN + 0, 1% TFA

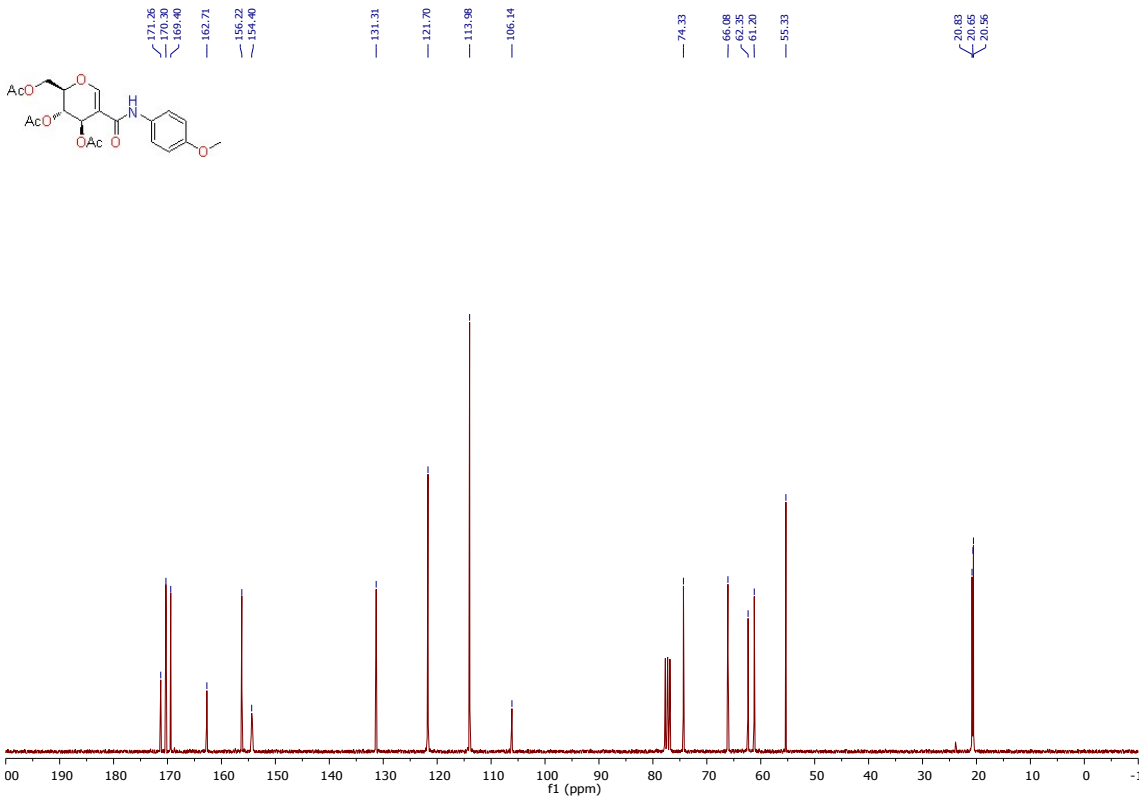


Calcd. for $C_{13}H_{16}IO_8Pd$ $(M + H)^+$: 532.8919; Found: 532.7684.

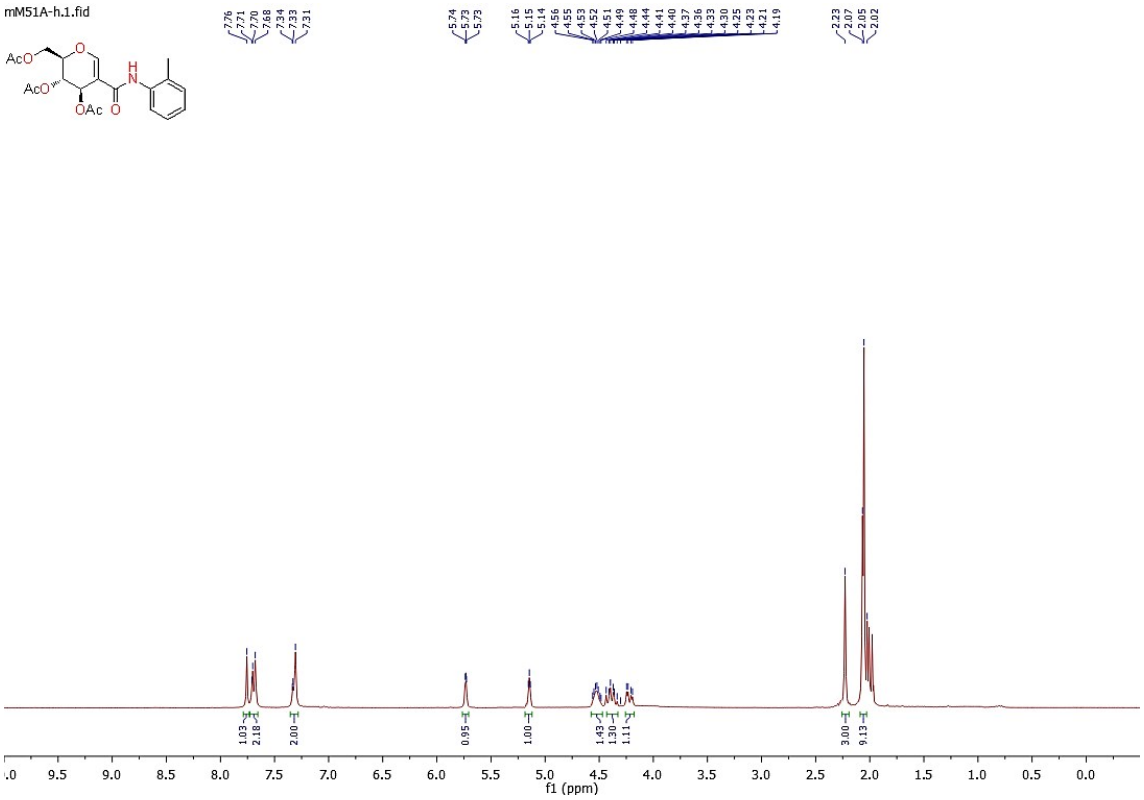
5. ^{1}H and ^{13}C spectra



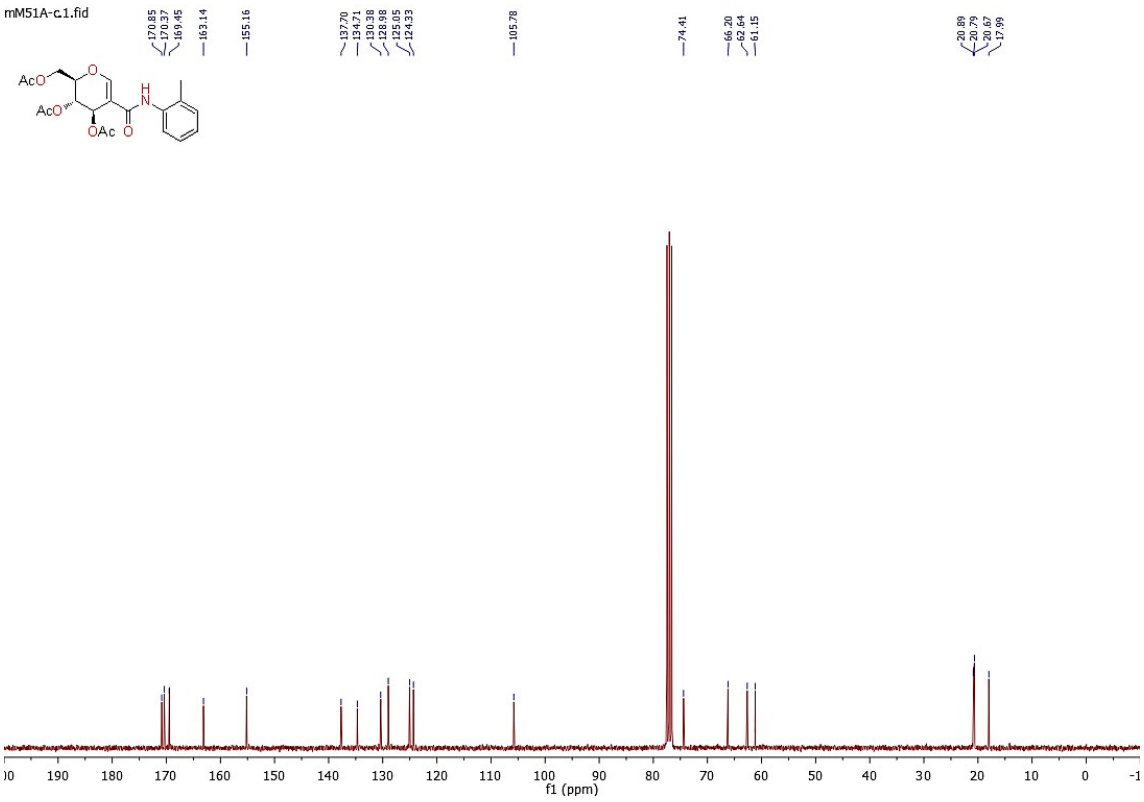
^{1}H NMR (300 MHz, $CDCl_3$) **3a**.



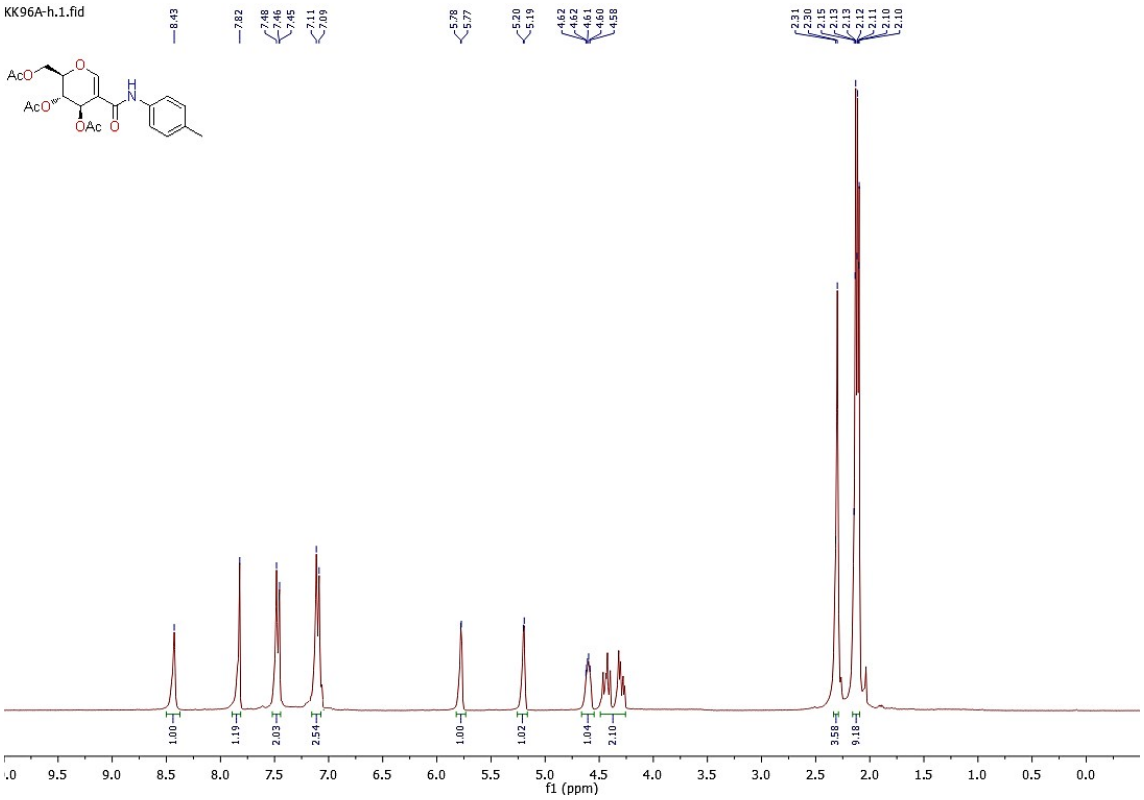
^{13}C NMR (75 MHz, $CDCl_3$) **3a**.



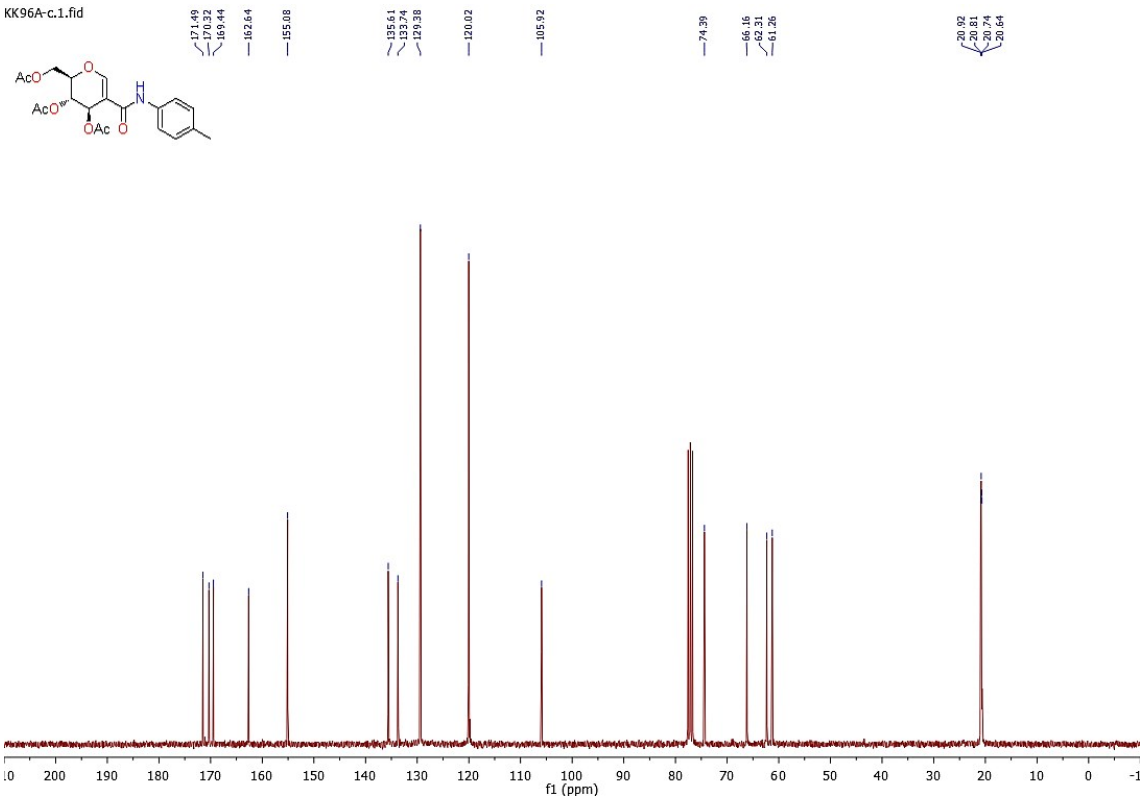
^{1}H NMR (300 MHz, $CDCl_3$) **3b**.



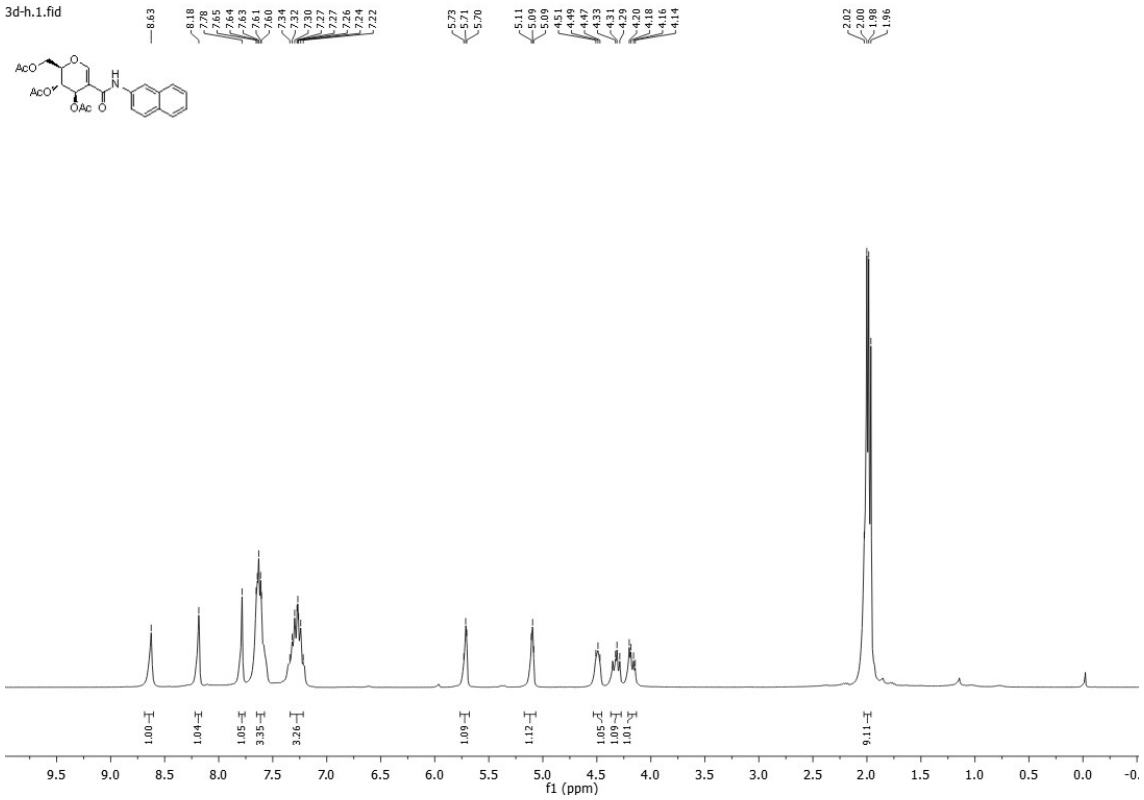
^{13}C NMR (75 MHz, $CDCl_3$) **3b**.



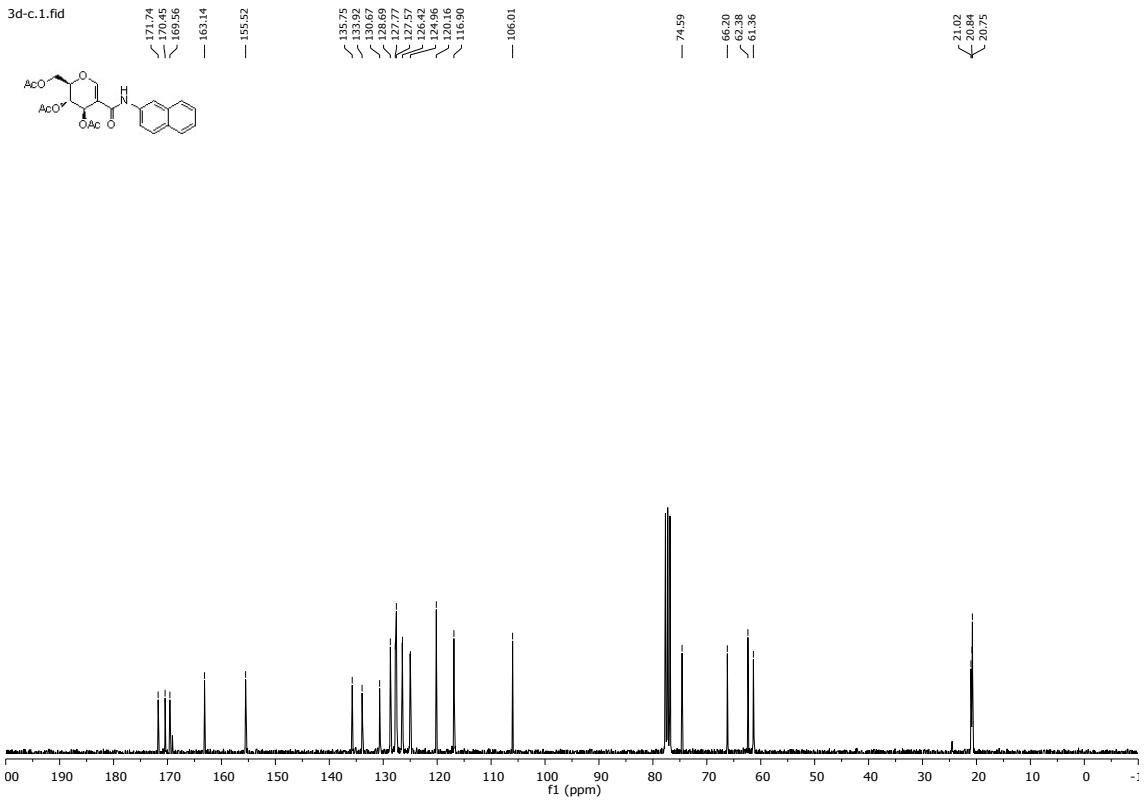
^{1}H NMR (300 MHz, $CDCl_3$) **3c**.



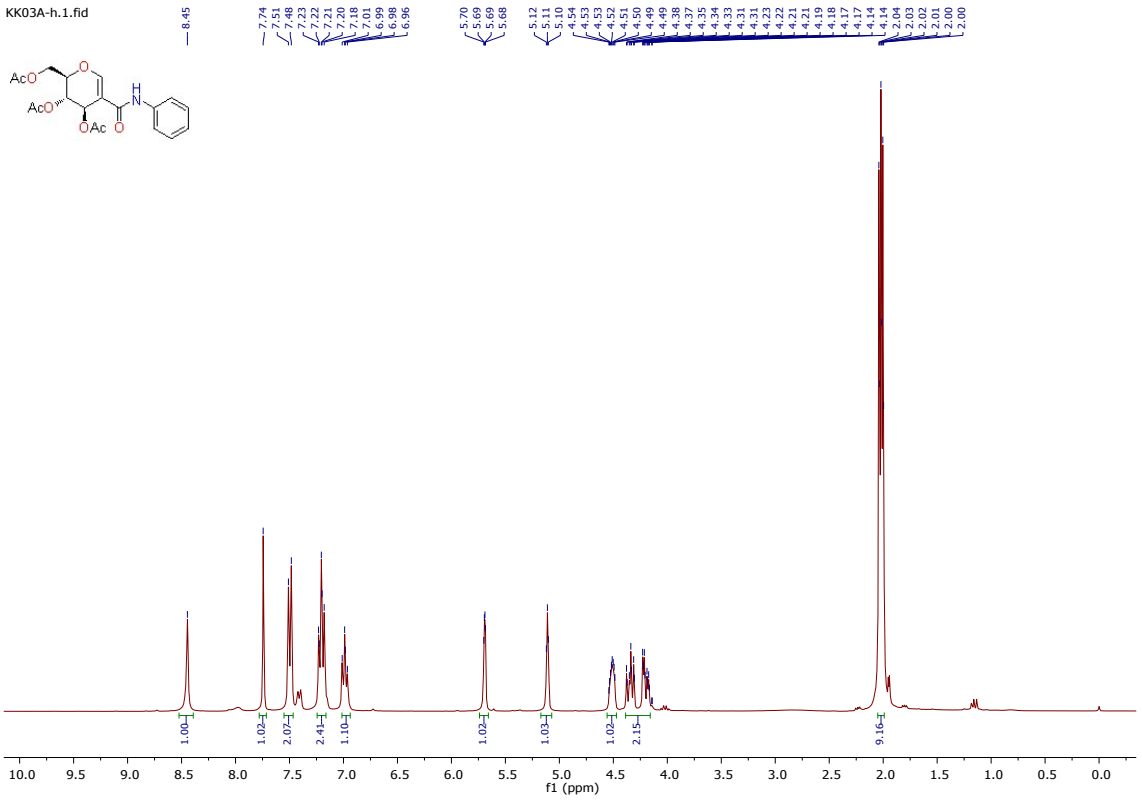
^{13}C NMR (75 MHz, $CDCl_3$) **3c**.



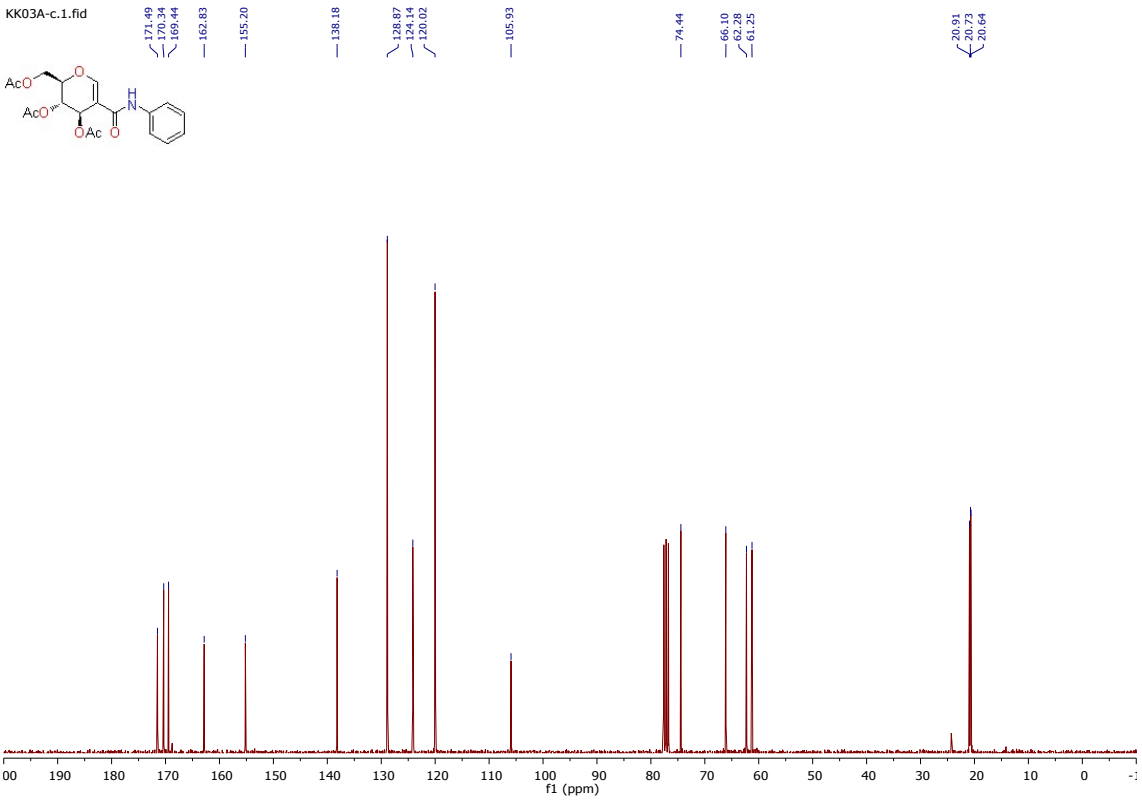
^{1}H NMR (300 MHz, $CDCl_3$) **3d**.



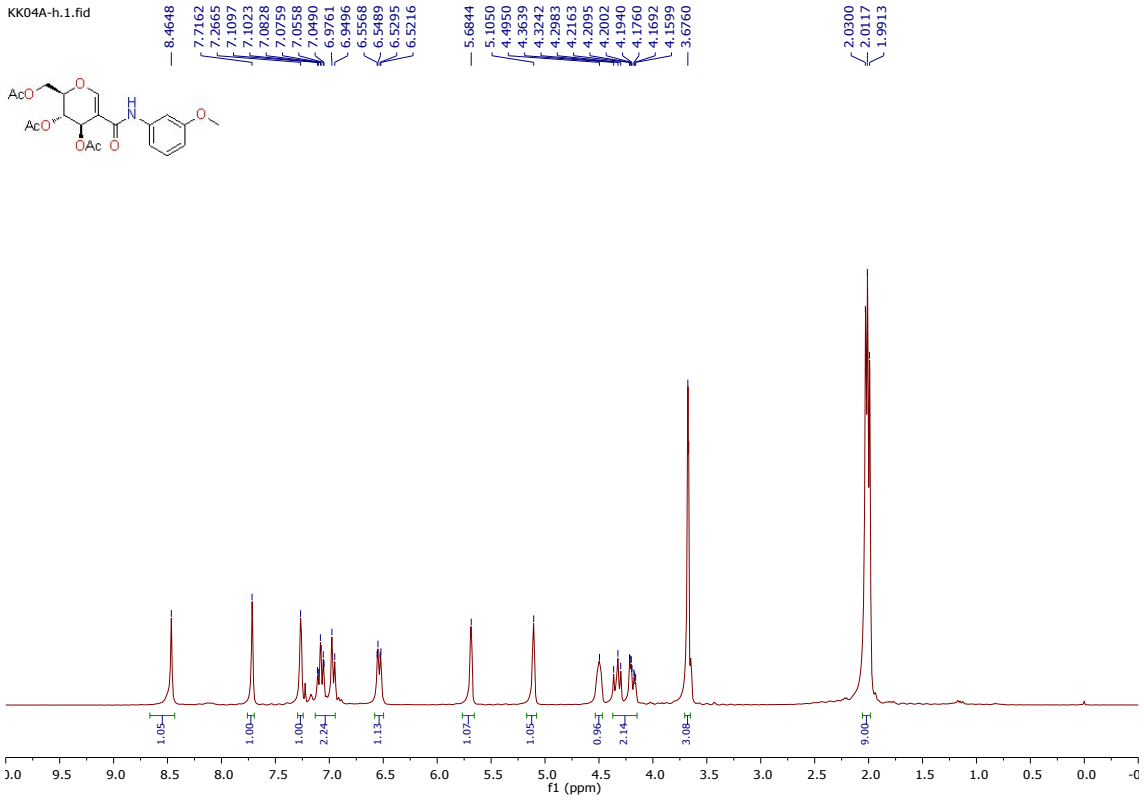
^{13}C NMR (75 MHz, $CDCl_3$) **3d**.



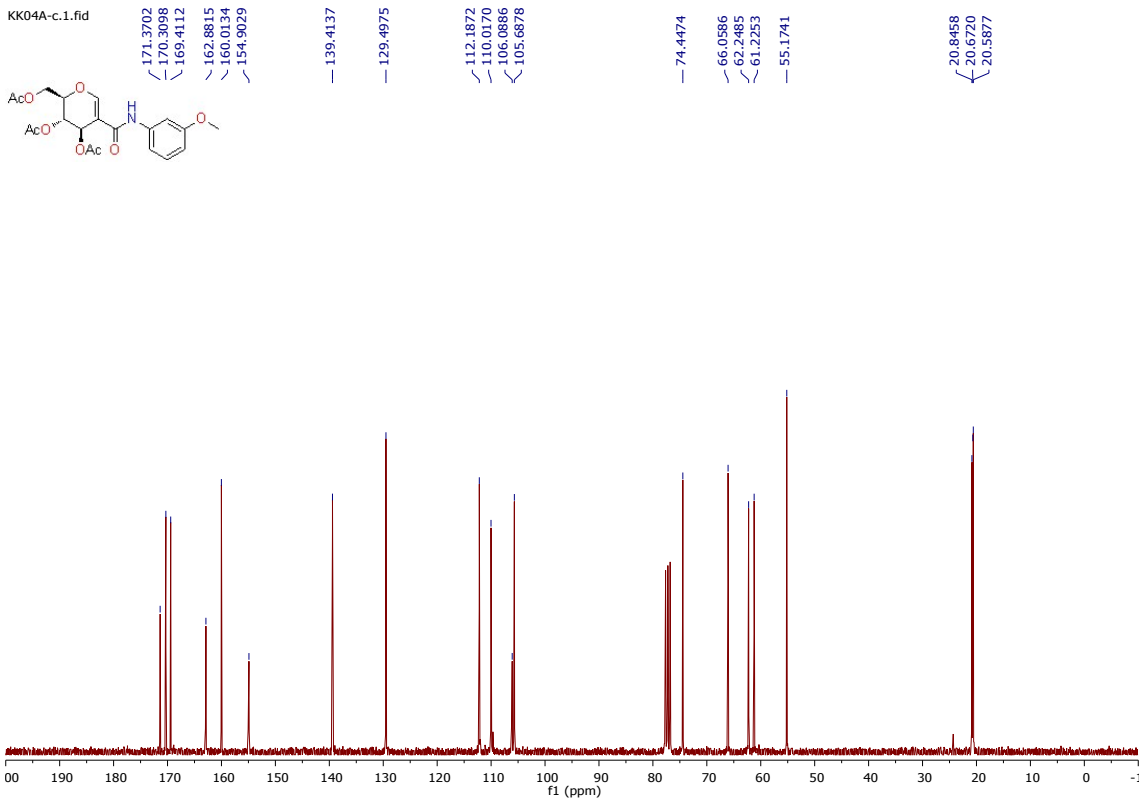
^{1}H NMR (300 MHz, $CDCl_3$) **3e**.



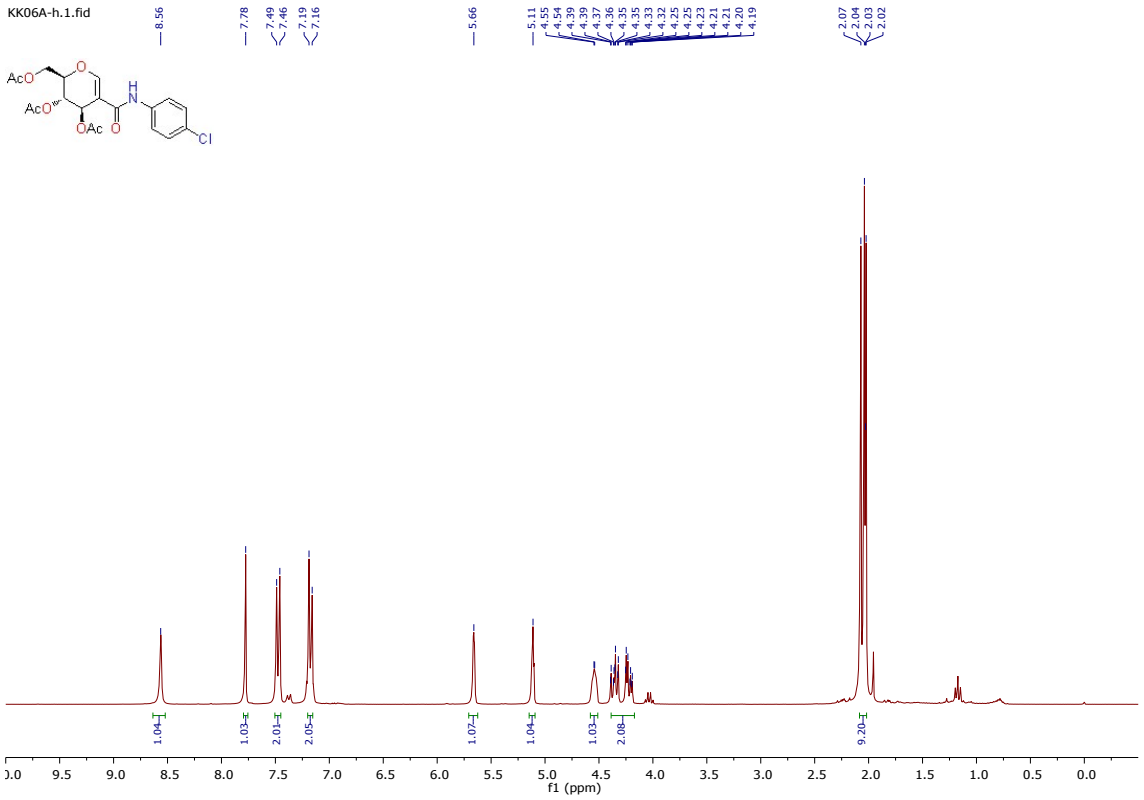
^{13}C NMR (75 MHz, $CDCl_3$) **3e**.



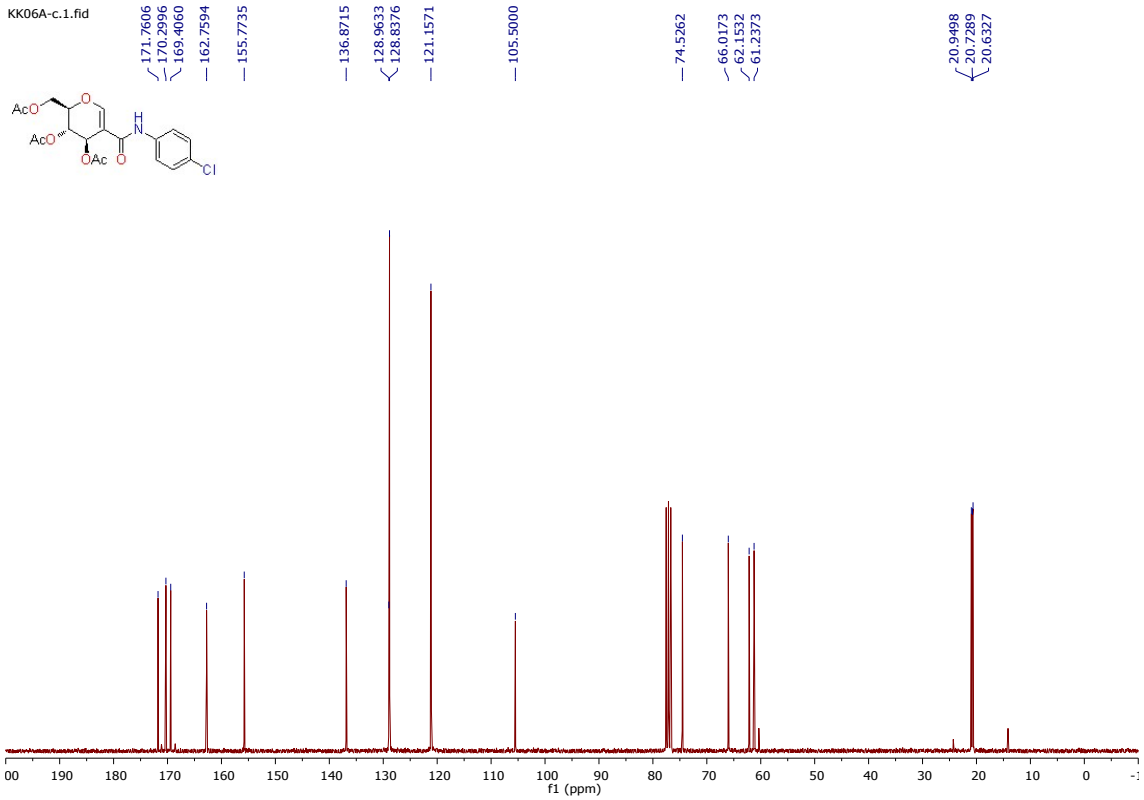
^{1}H NMR (300 MHz, $CDCl_3$) **3f**.



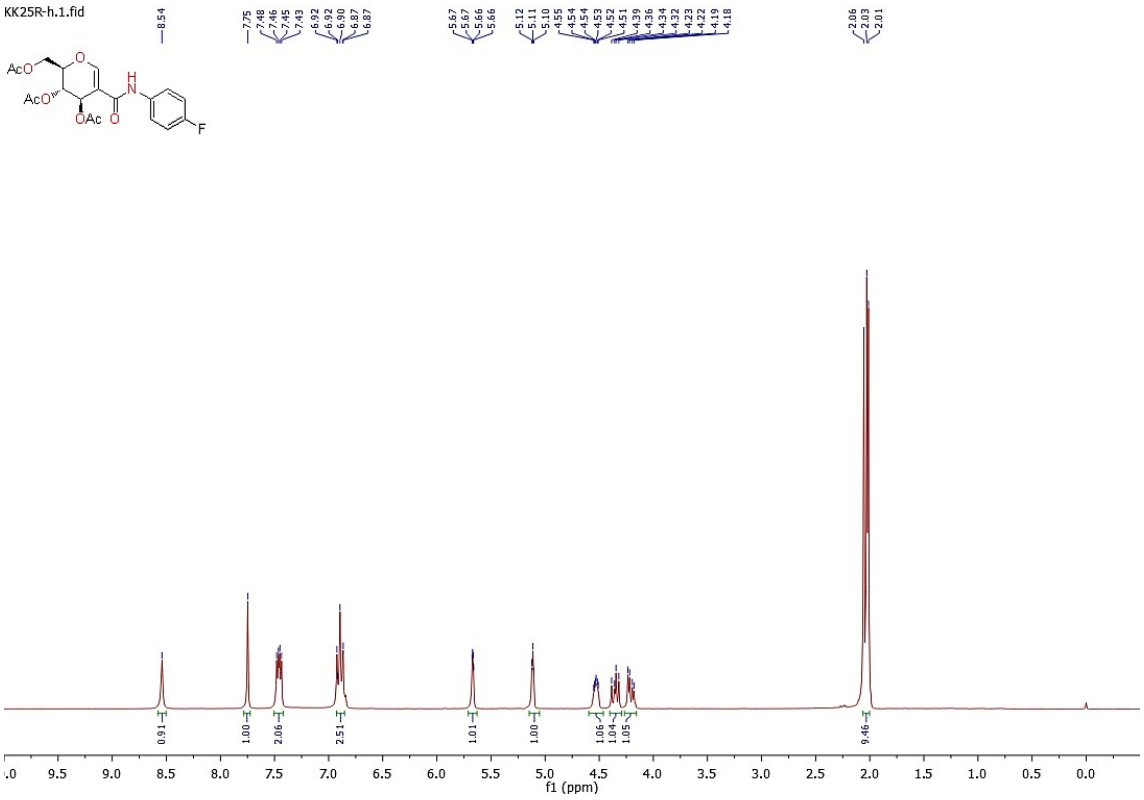
^{13}C NMR (75 MHz, $CDCl_3$) **3f**.



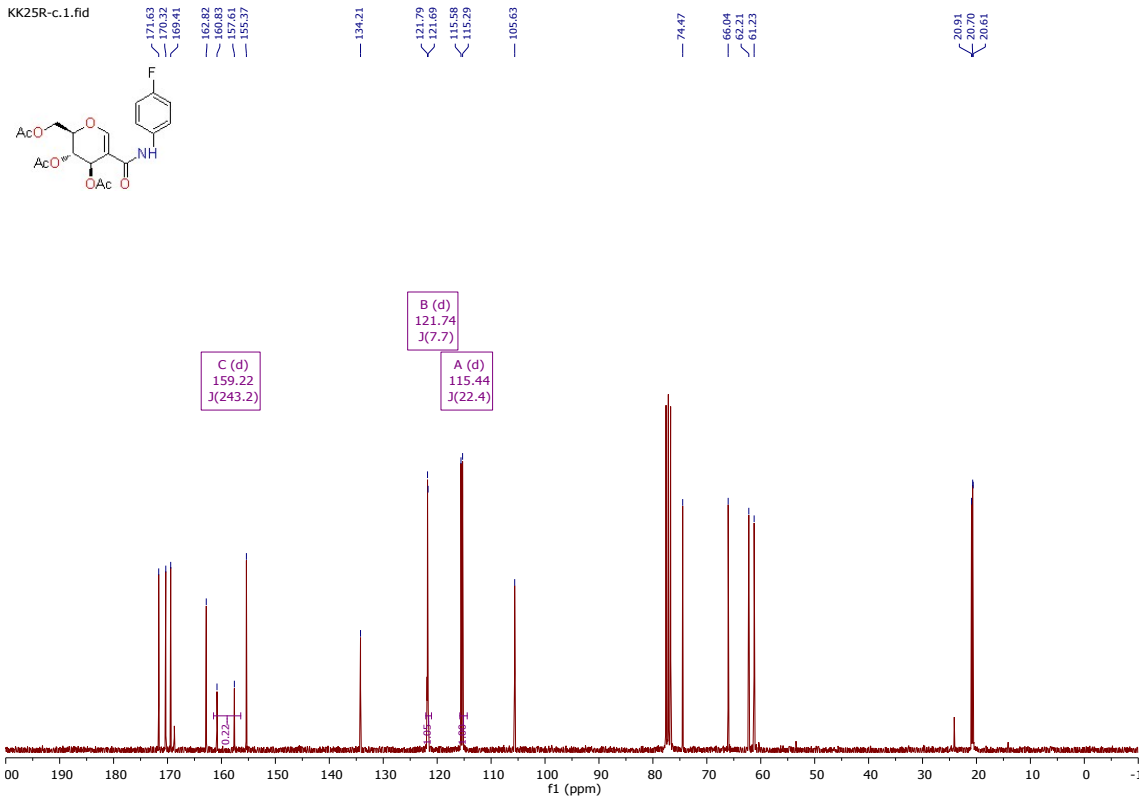
^{1}H NMR (300 MHz, $CDCl_3$) **3g**.



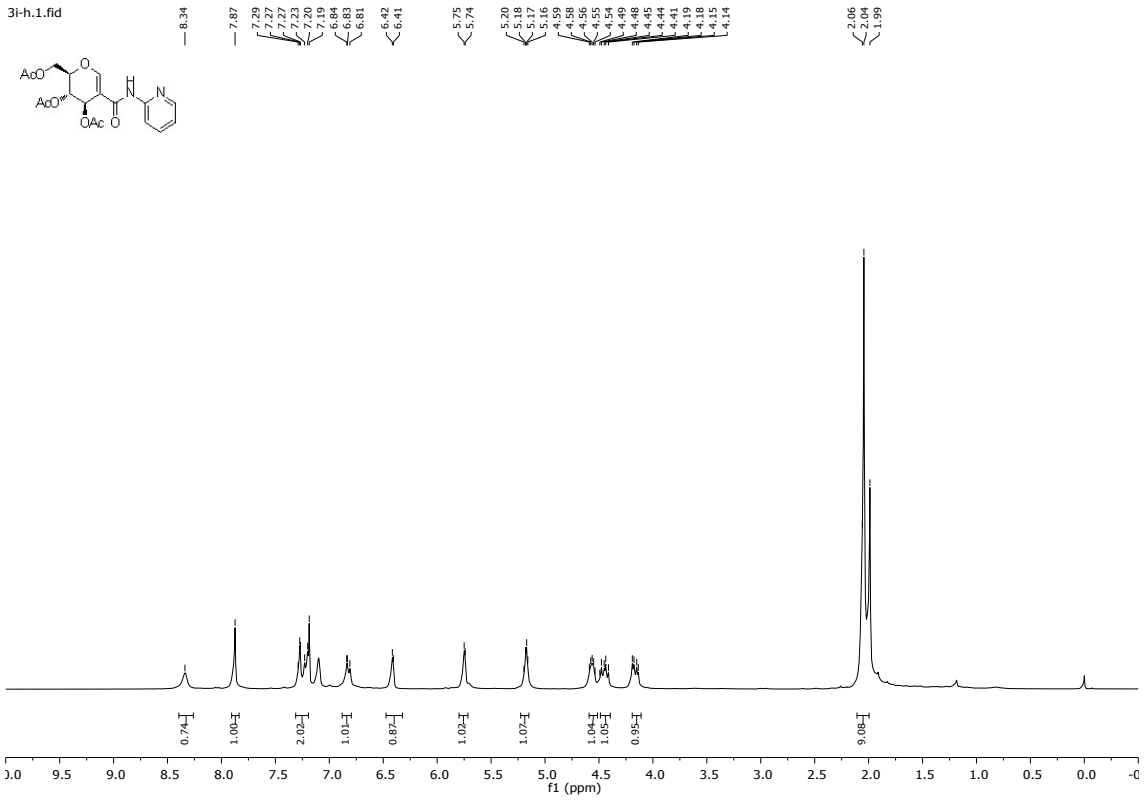
^{13}C NMR (75 MHz, $CDCl_3$) **3g**.



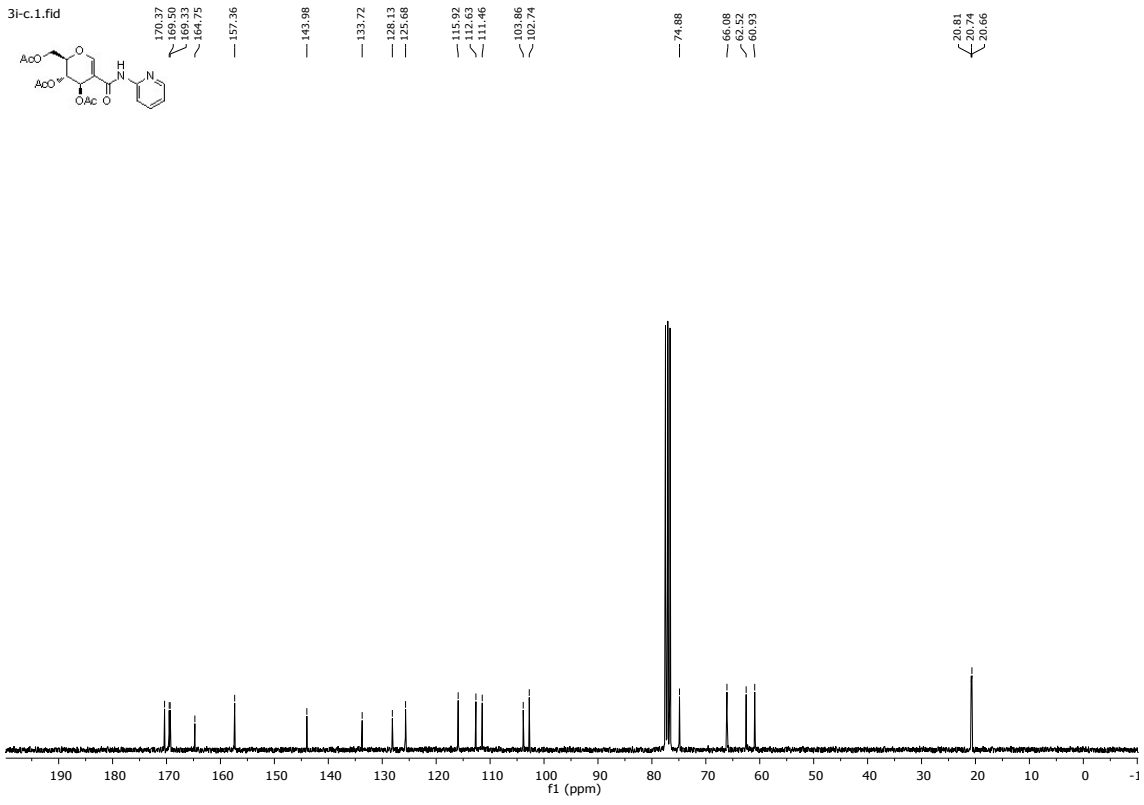
^{1}H NMR (300 MHz, $CDCl_3$) **3h**.



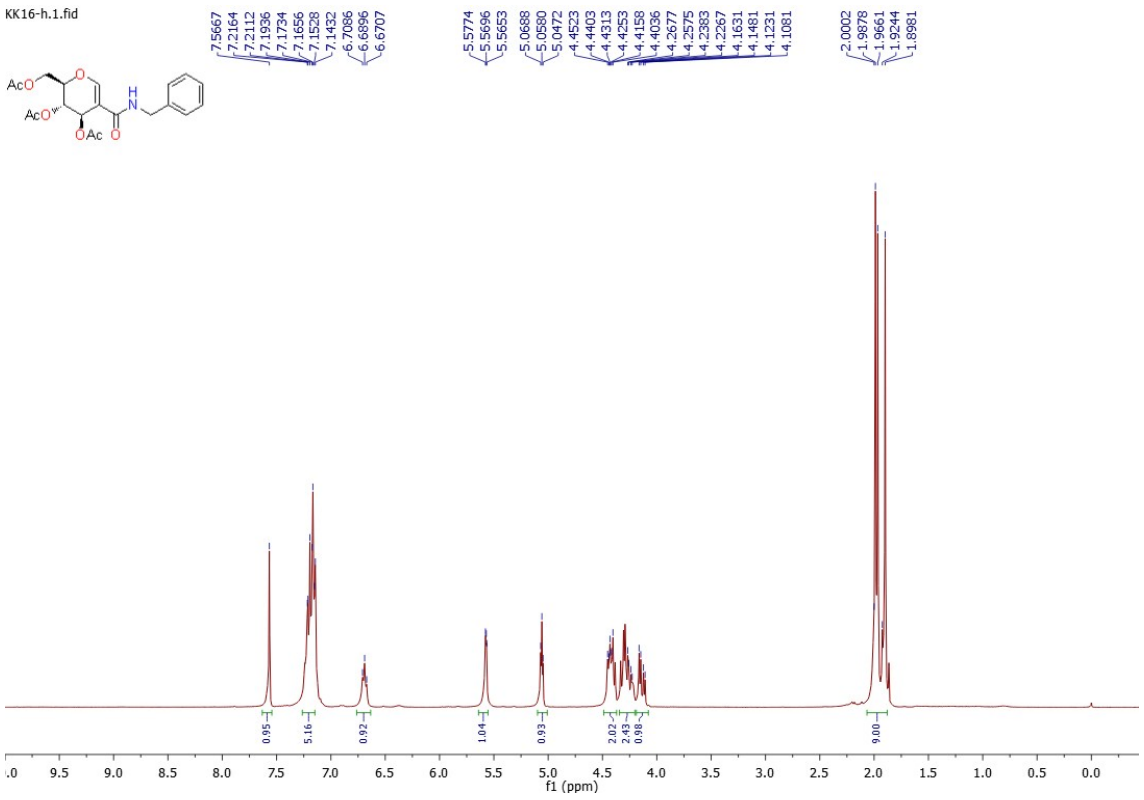
^{13}C NMR (75 MHz, $CDCl_3$) **3h**.



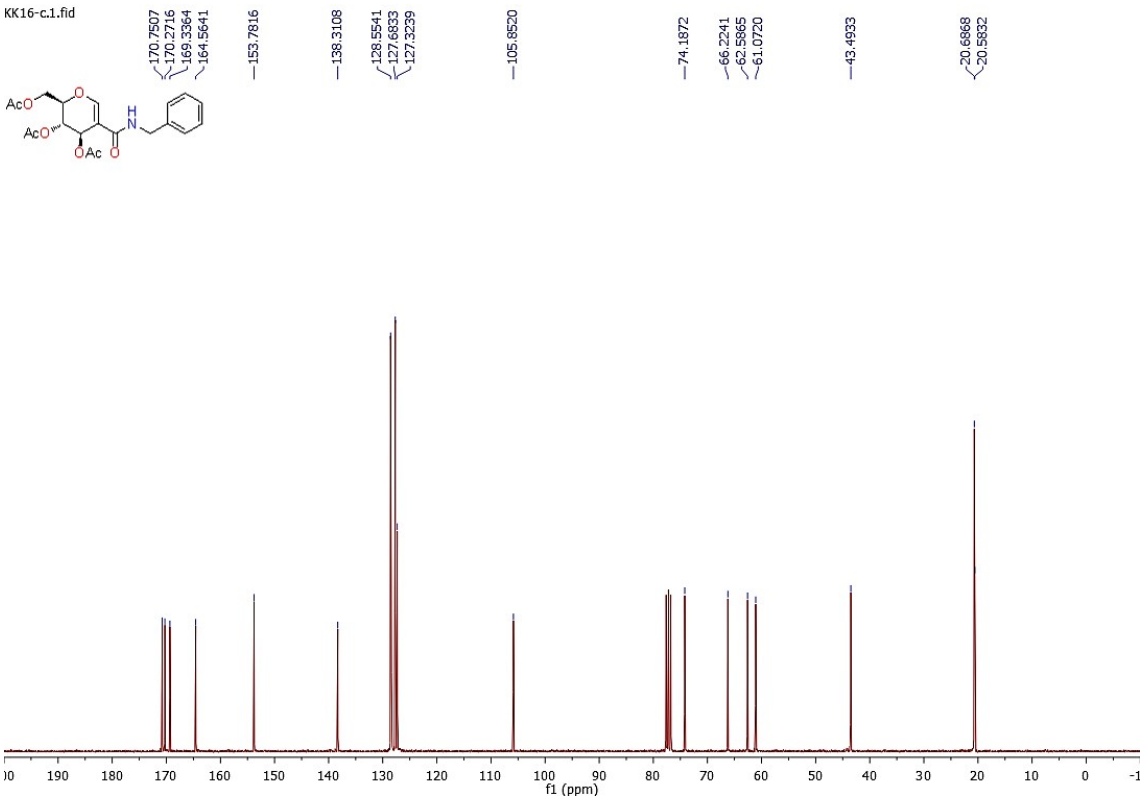
^{1}H NMR (300 MHz, $CDCl_3$) **3i**.



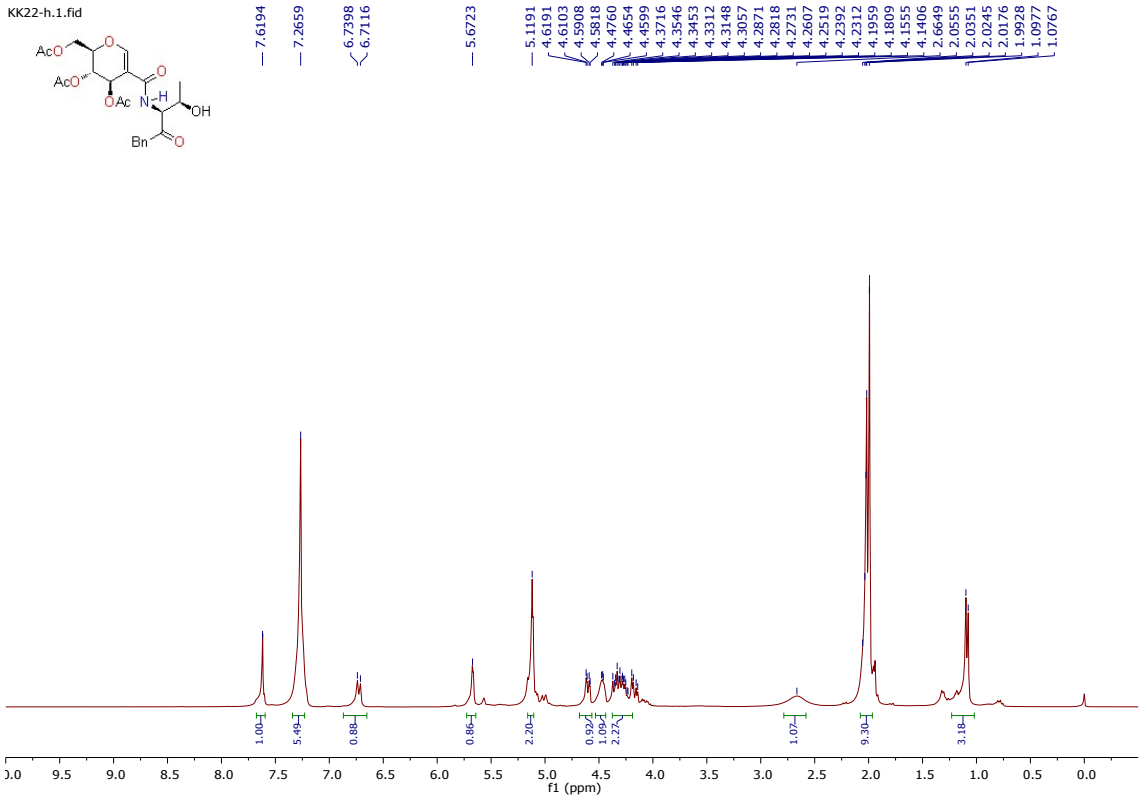
^{13}C NMR (75 MHz, $CDCl_3$) **3i**.



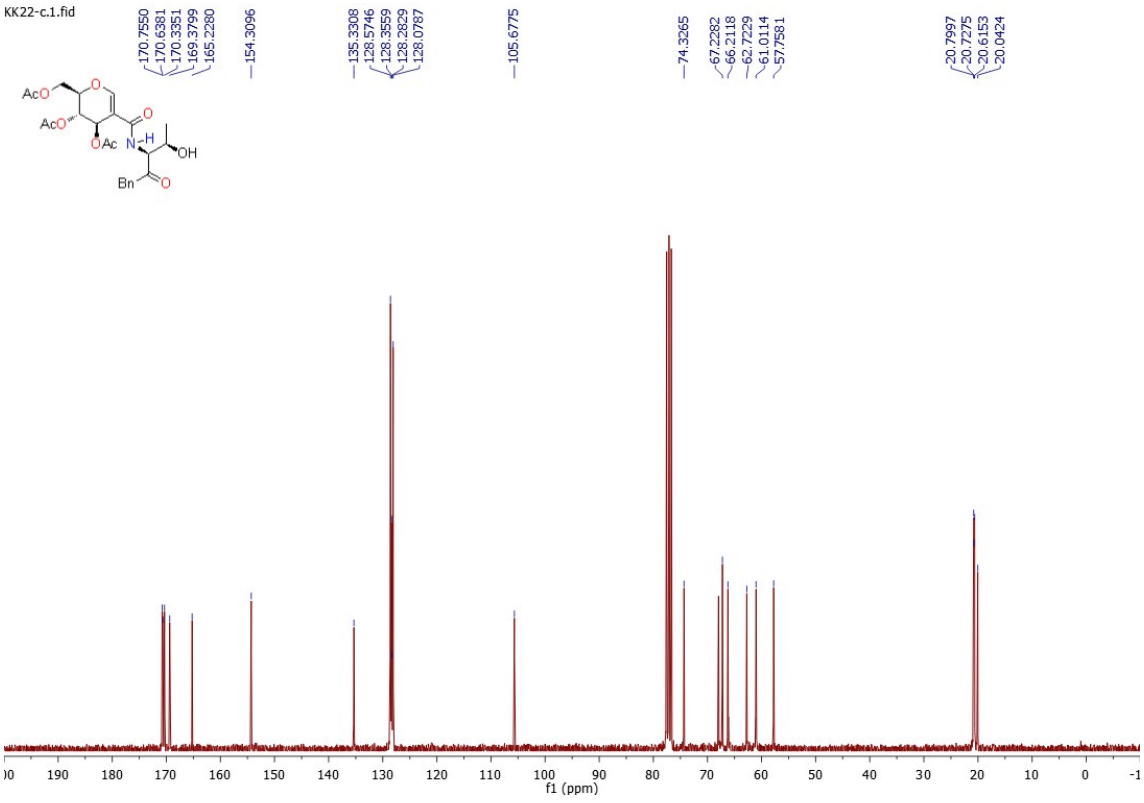
^{1}H NMR (300 MHz, $CDCl_3$) **3j**.



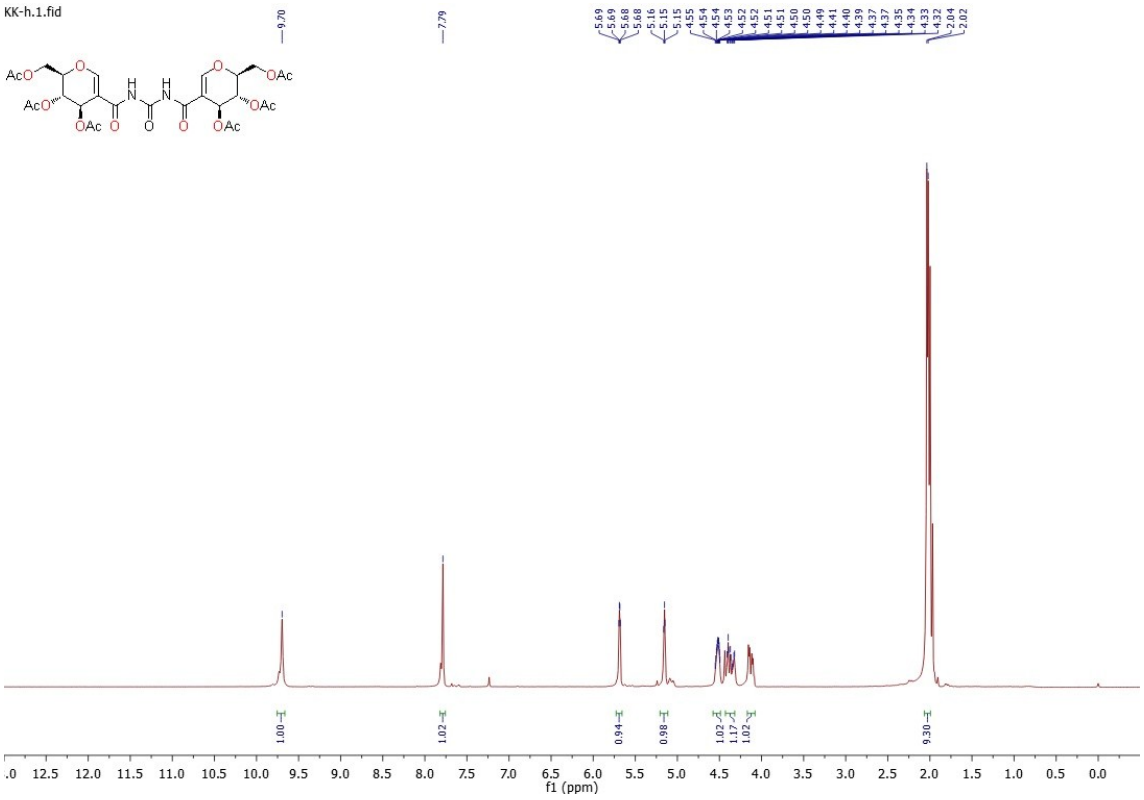
^{13}C NMR (75 MHz, $CDCl_3$) **3j**.



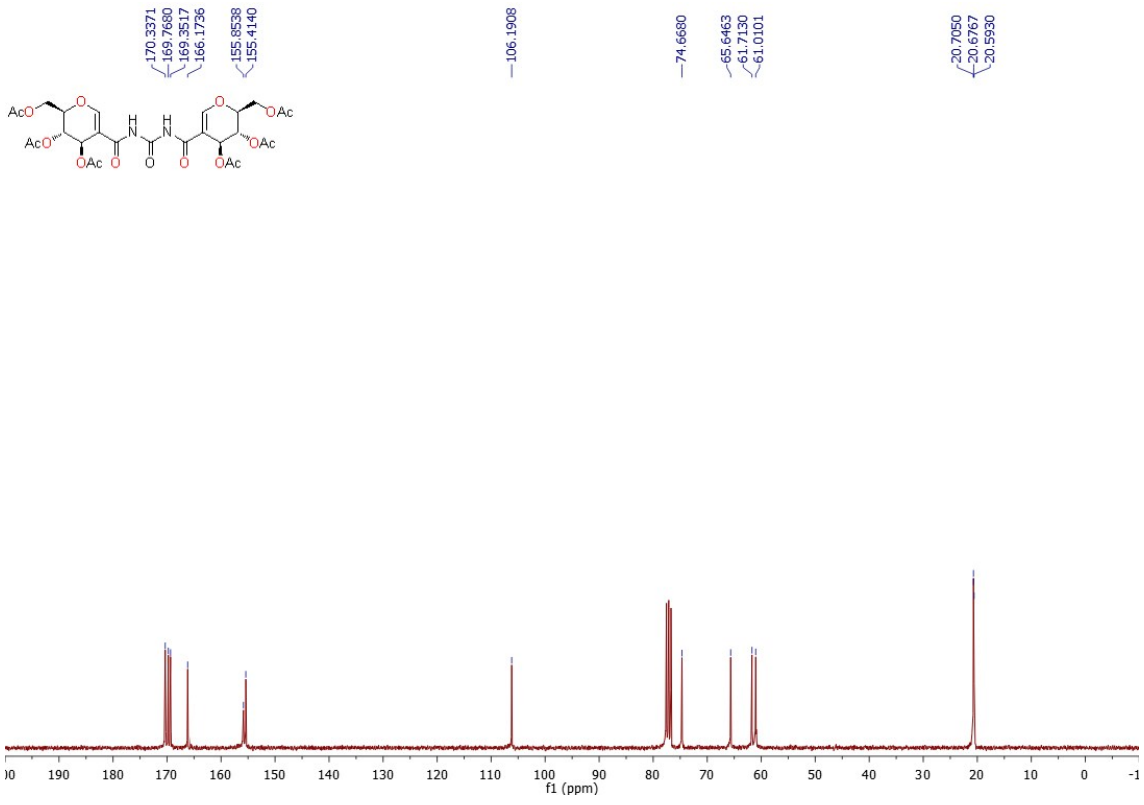
^{1}H NMR (300 MHz, $CDCl_3$) **3k**.



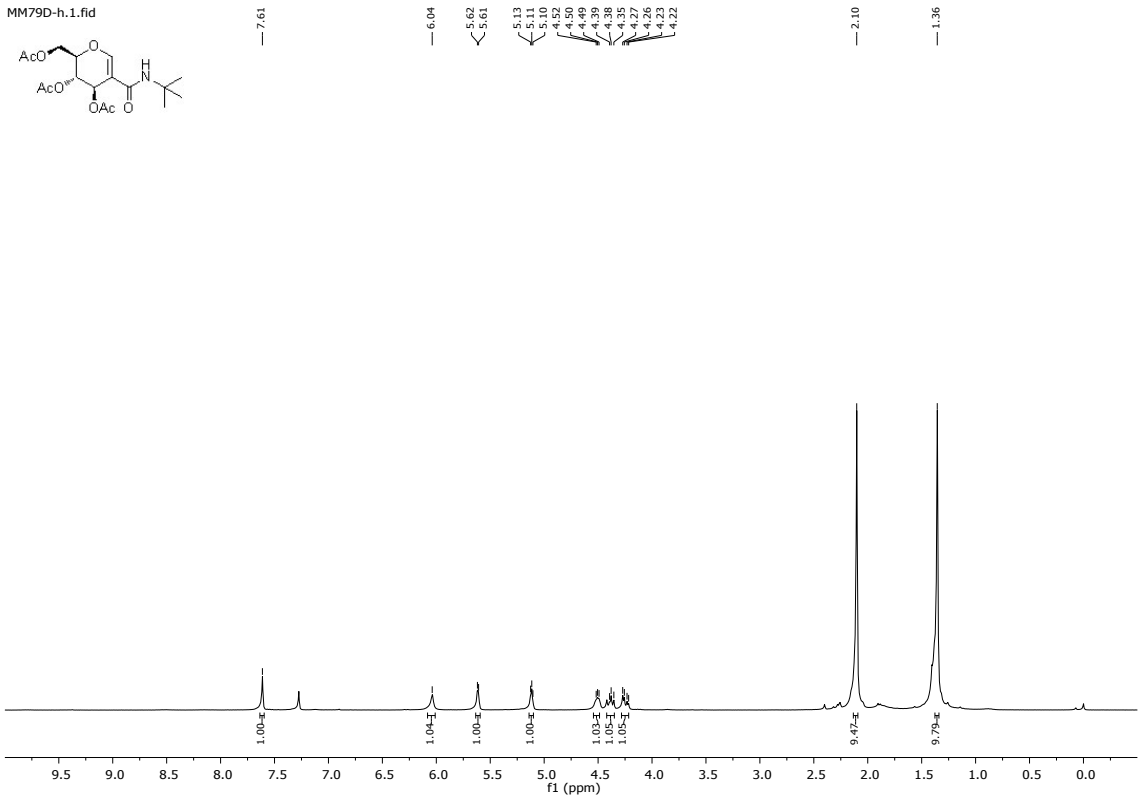
^{13}C NMR (75 MHz, $CDCl_3$) **3k**.



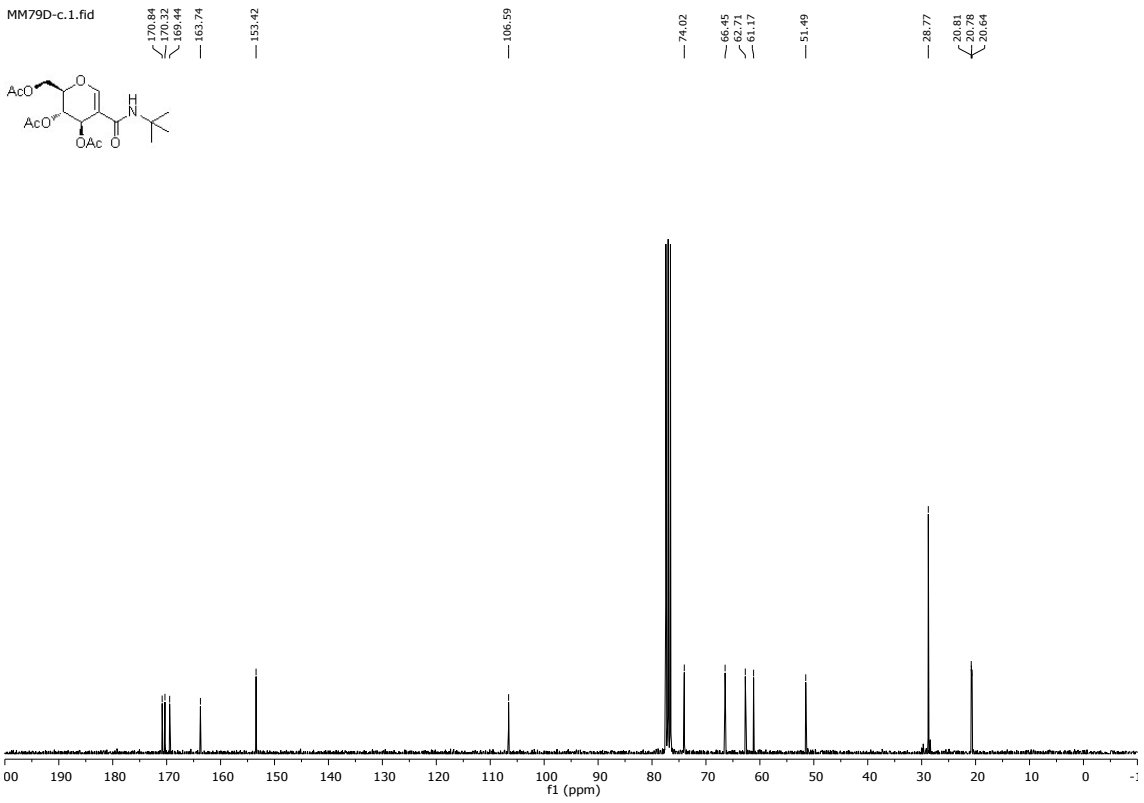
^{1}H NMR (300 MHz, $CDCl_3$) **3l**.



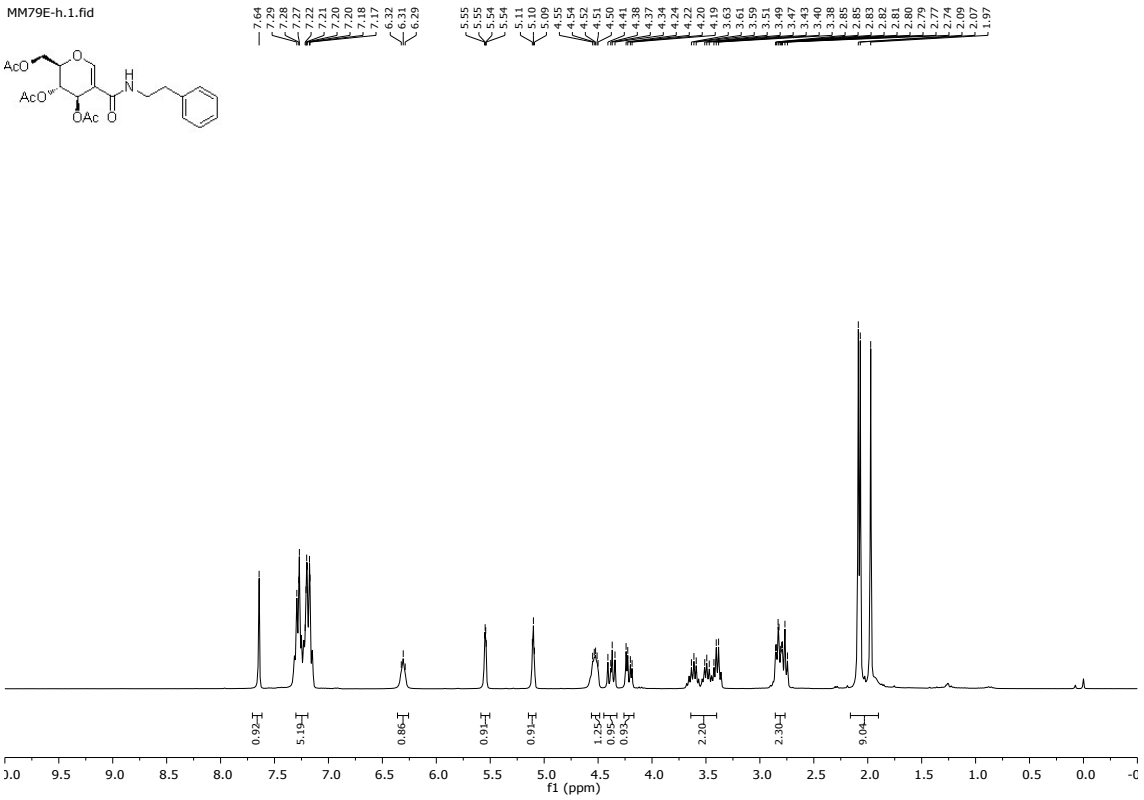
^{13}C NMR (75 MHz, $CDCl_3$) **3l**.



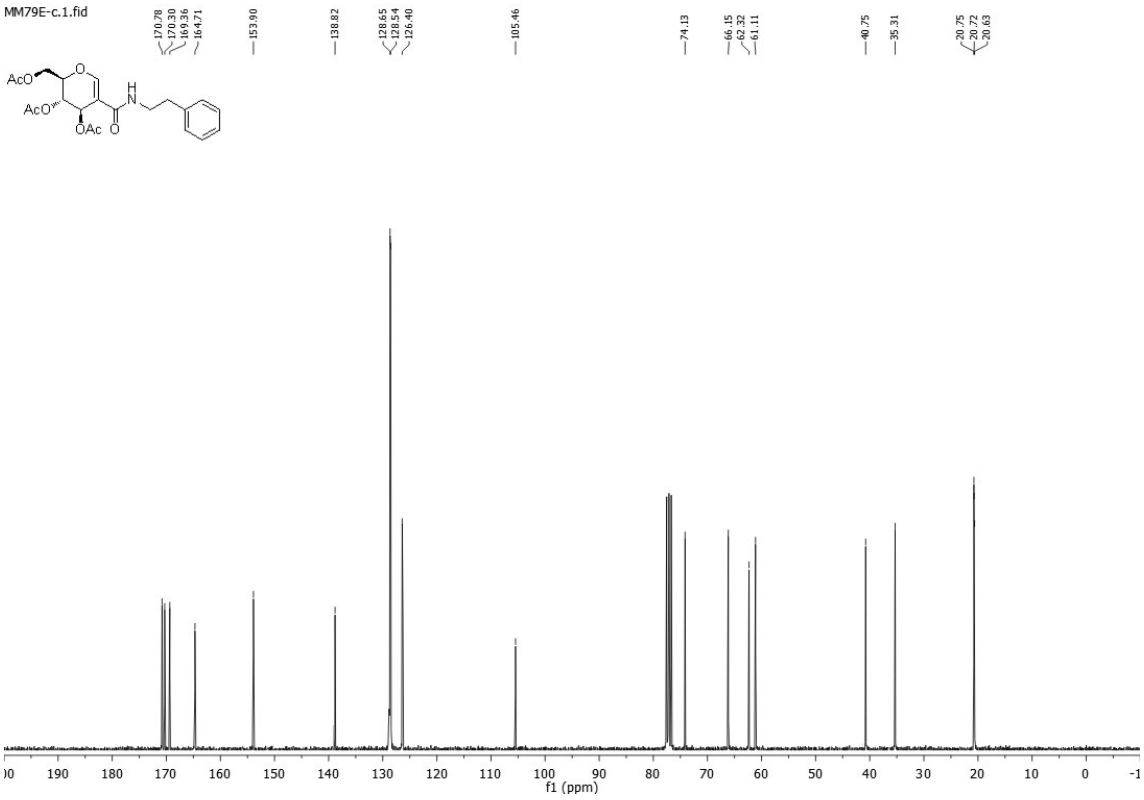
^{1}H NMR (300 MHz, $CDCl_3$) **3m**.



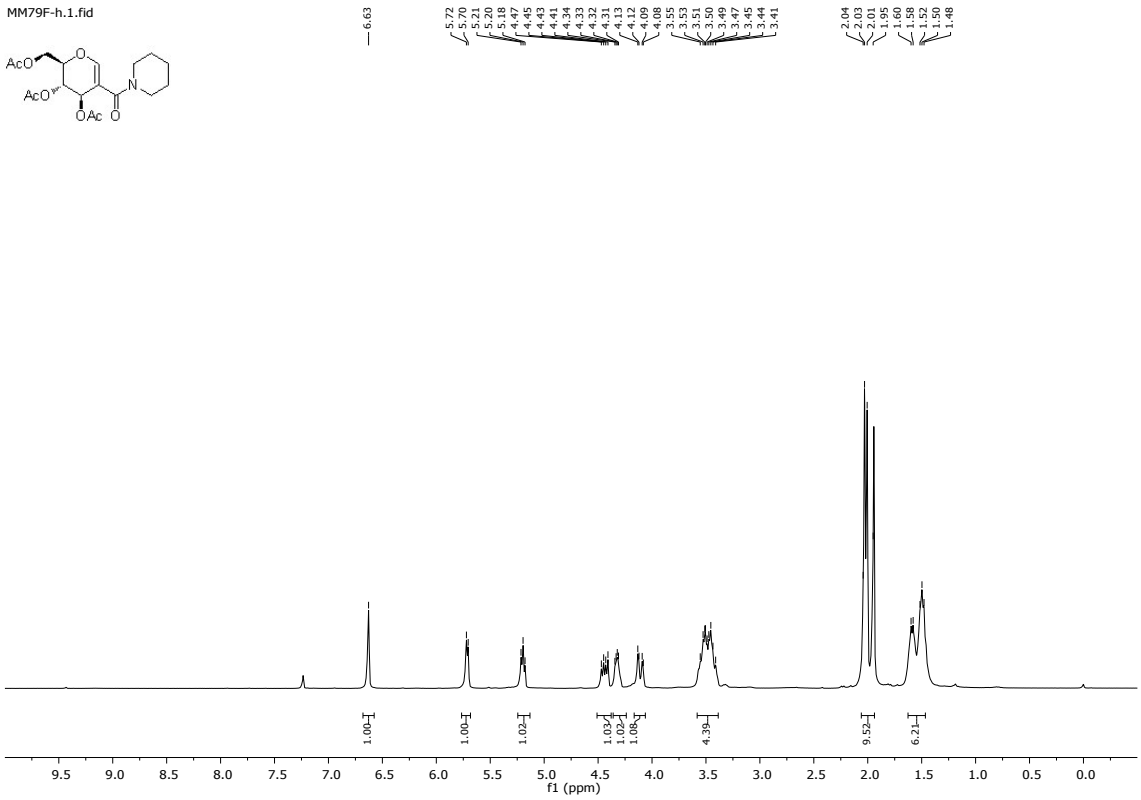
^{13}C NMR (75 MHz, $CDCl_3$) **3m**.



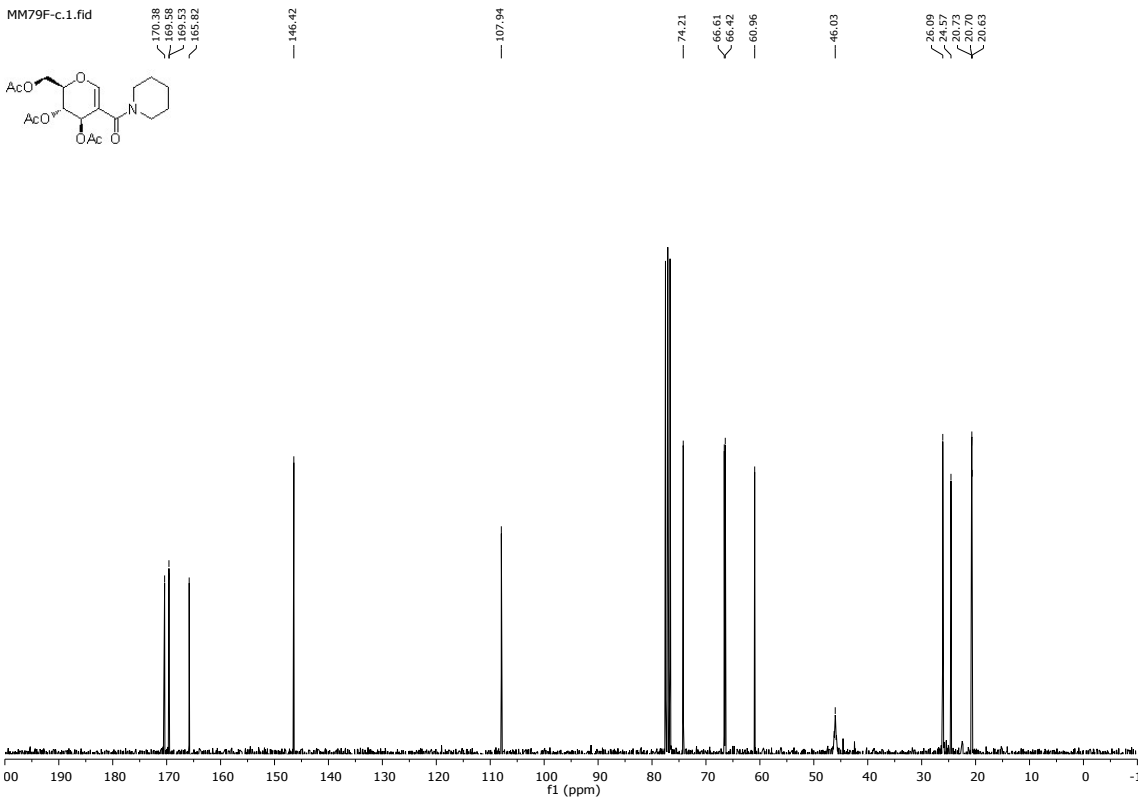
^{1}H NMR (300 MHz, $CDCl_3$) **3n**.



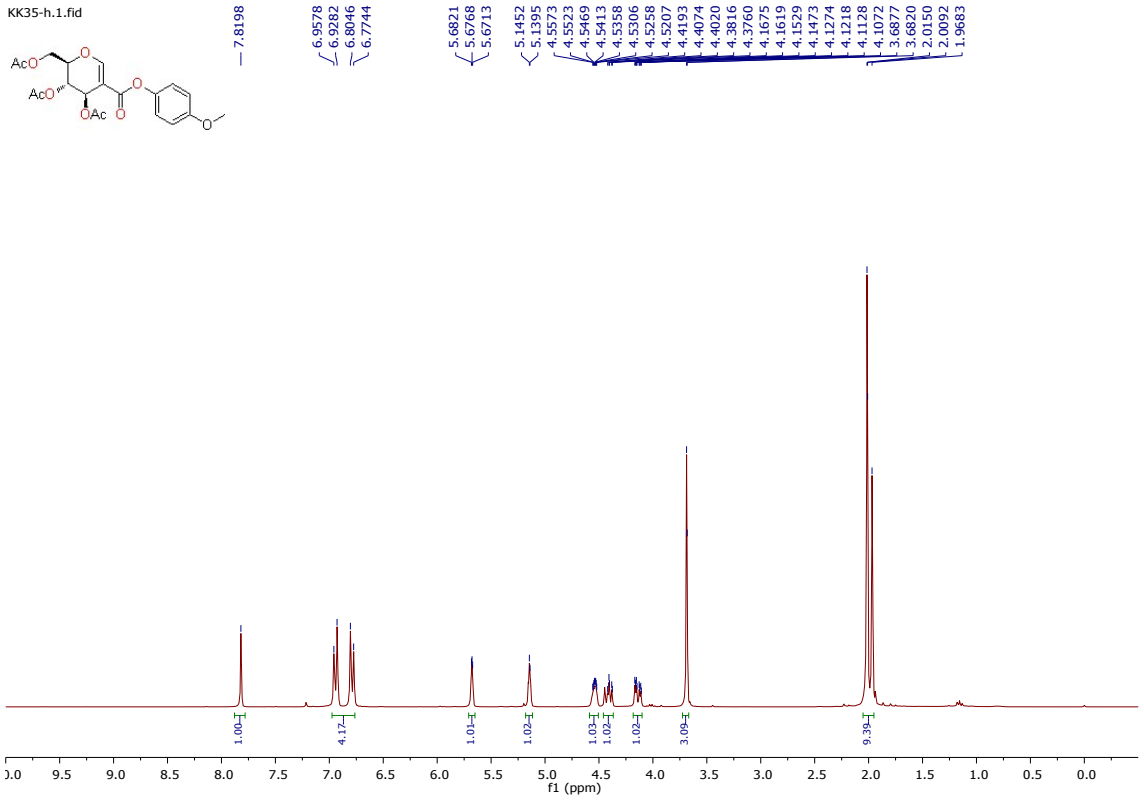
^{13}C NMR (75 MHz, $CDCl_3$) **3n**.



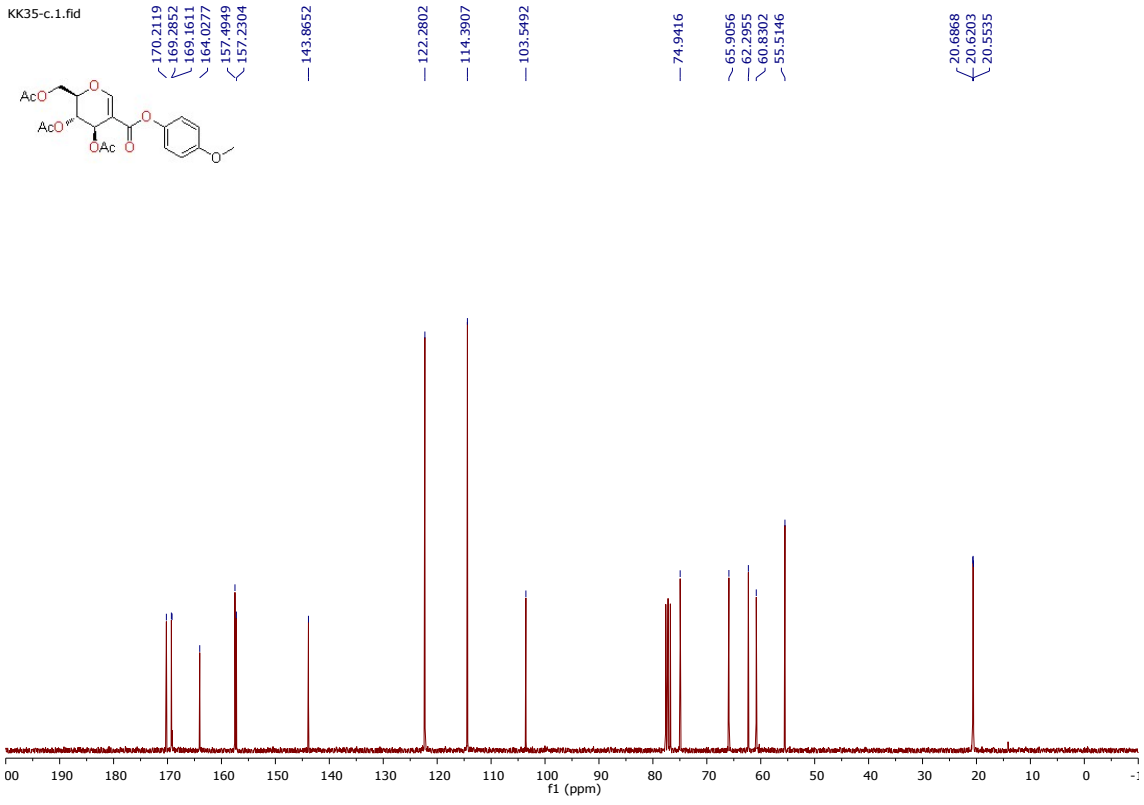
^{1}H NMR (300 MHz, $CDCl_3$) **3o**.



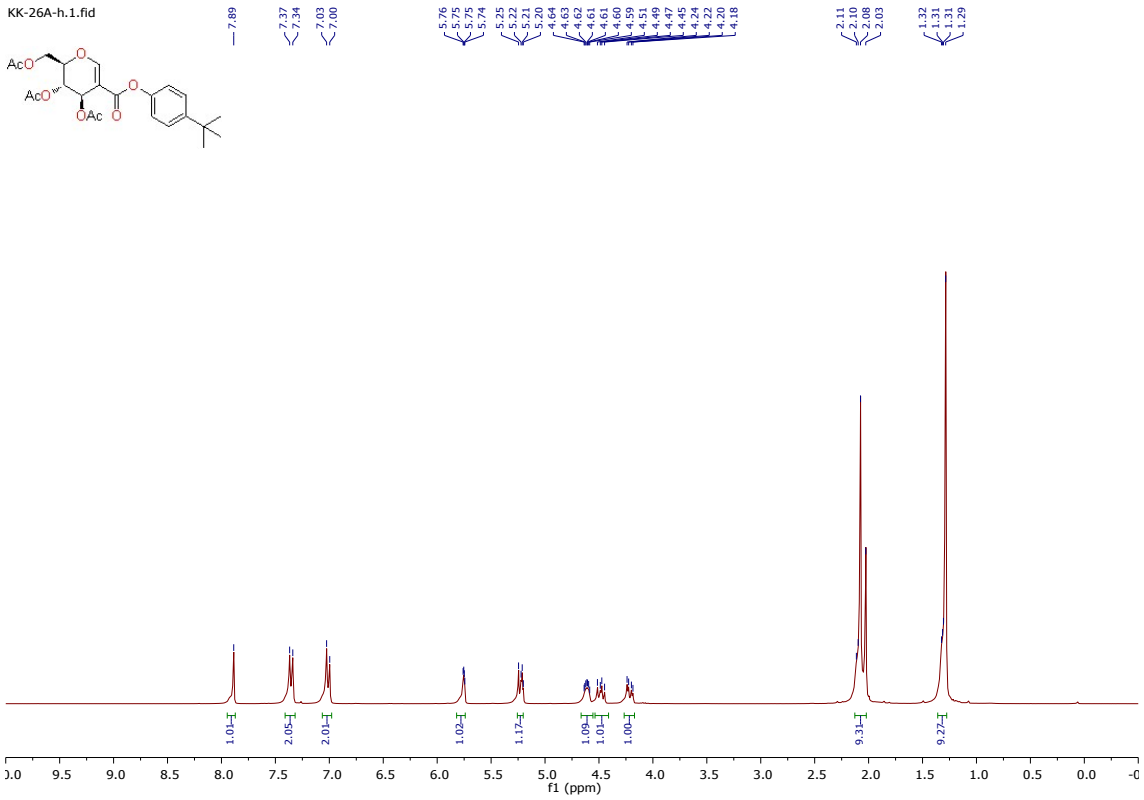
^{13}C NMR (75 MHz, $CDCl_3$) **3o**.



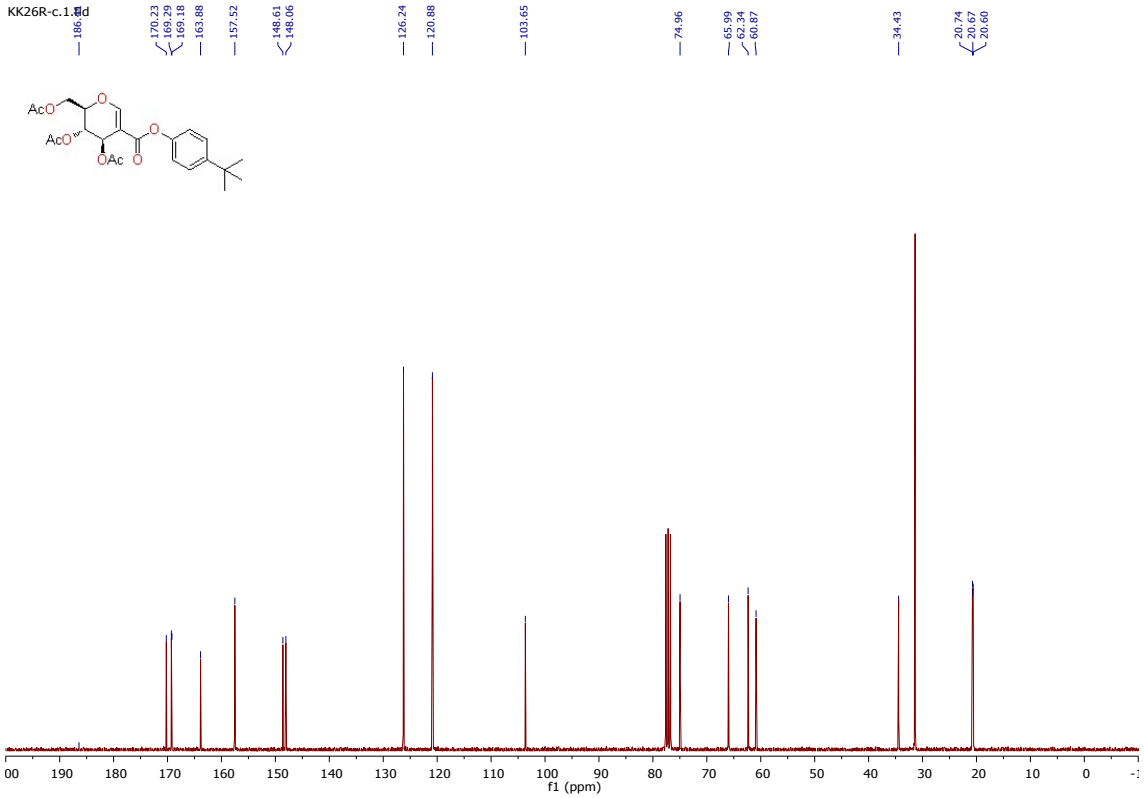
^{1}H NMR (300 MHz, $CDCl_3$) **5a**.



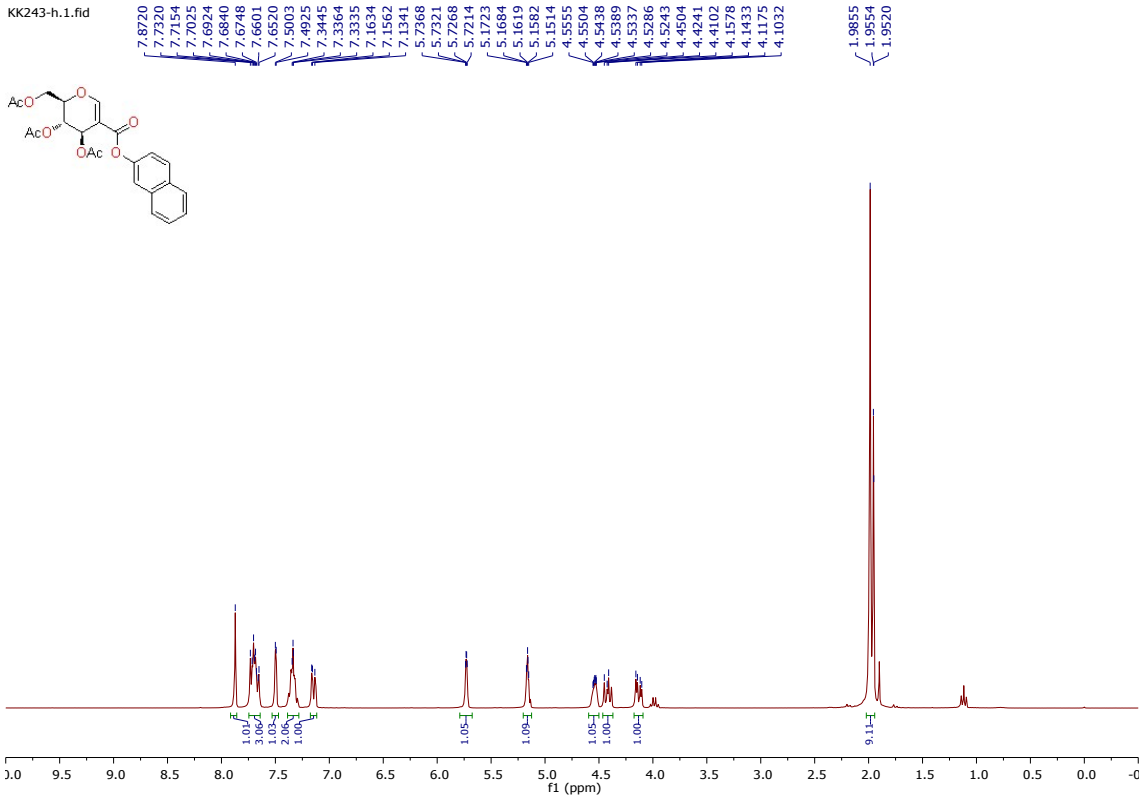
^{13}C NMR (75 MHz, $CDCl_3$) **5a**.



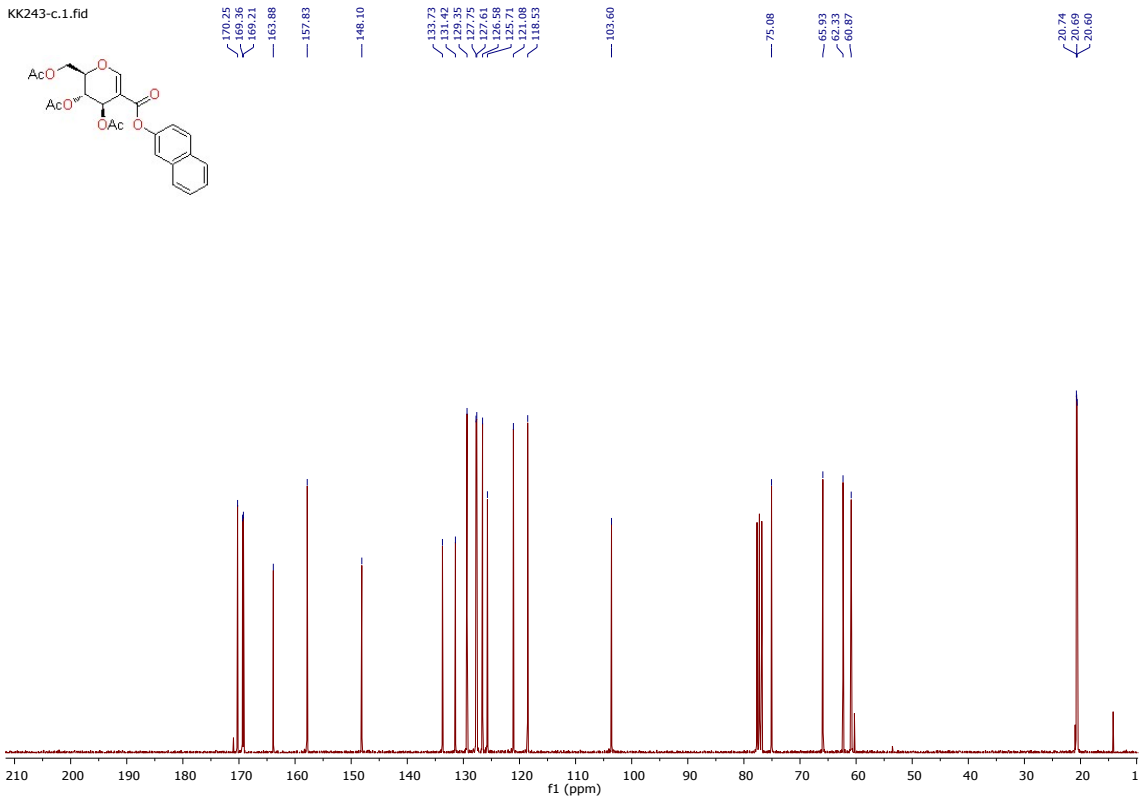
^{1}H NMR (300 MHz, $CDCl_3$) **5b**.



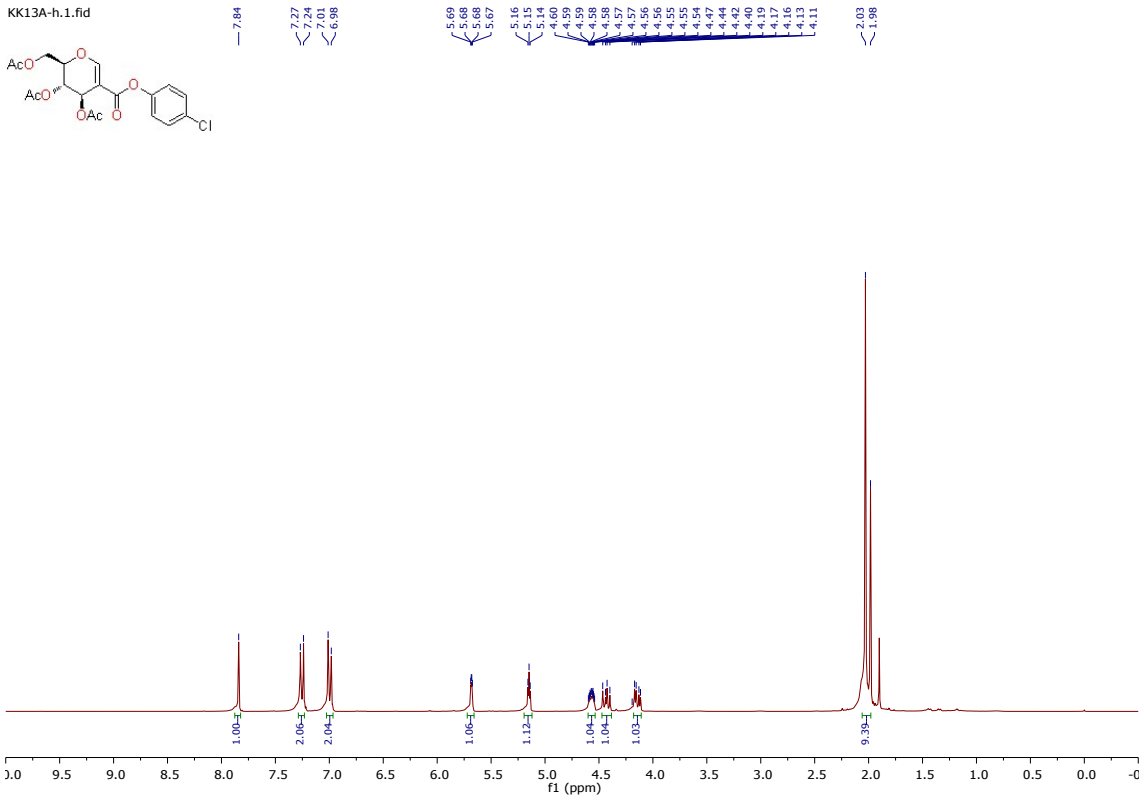
^{13}C NMR (75 MHz, $CDCl_3$) **5b**.



^{1}H NMR (300 MHz, $CDCl_3$) **5c**.

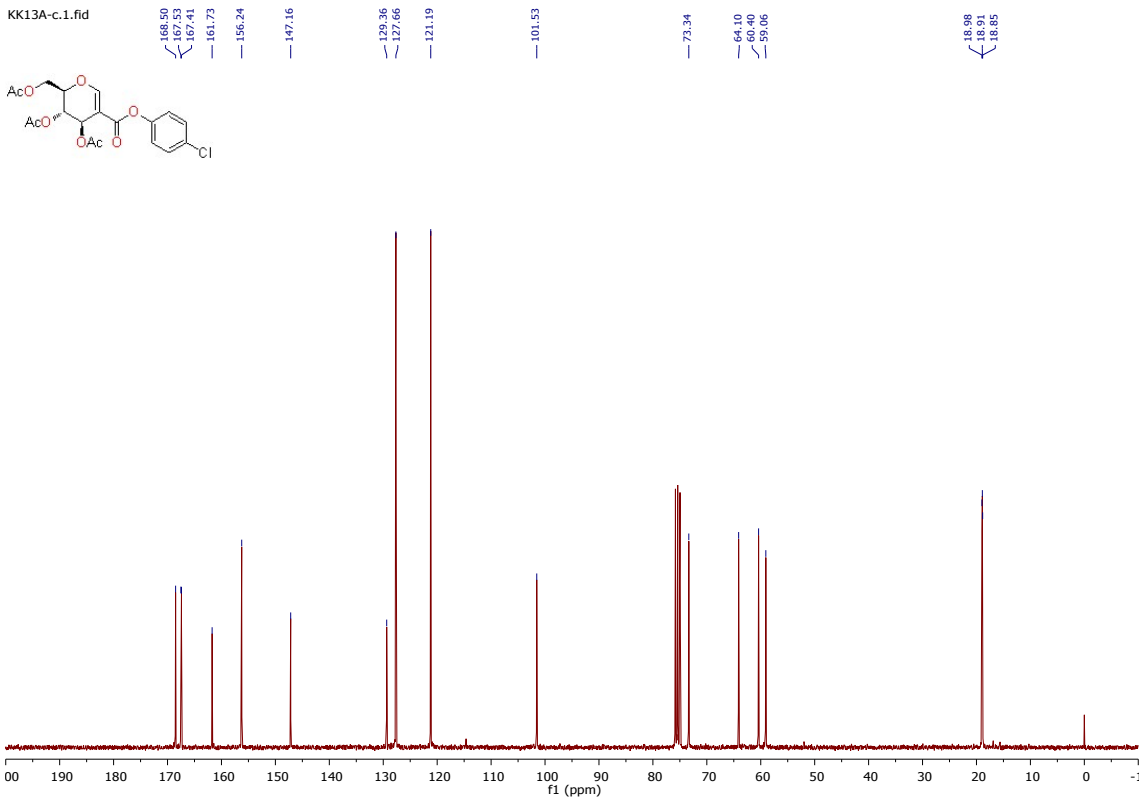


^{13}C NMR (75 MHz, $CDCl_3$) **5c**.

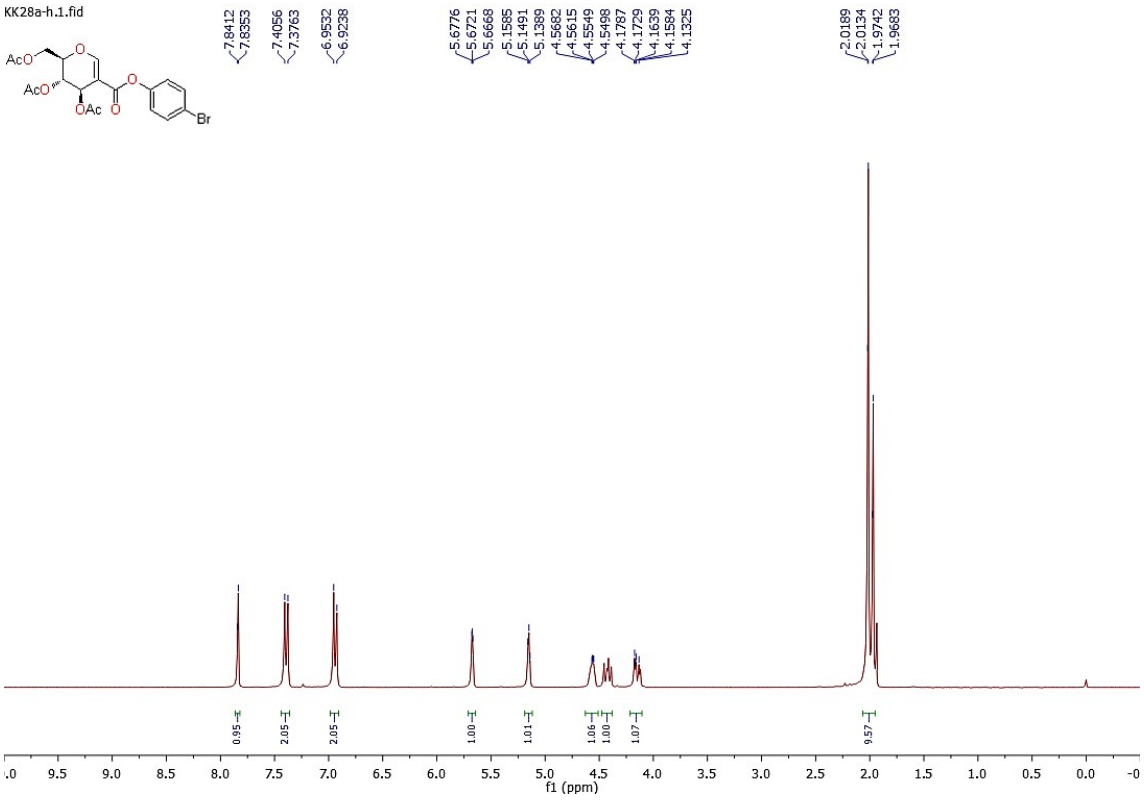


^{1}H NMR (300 MHz, Chloroform-*d*) δ

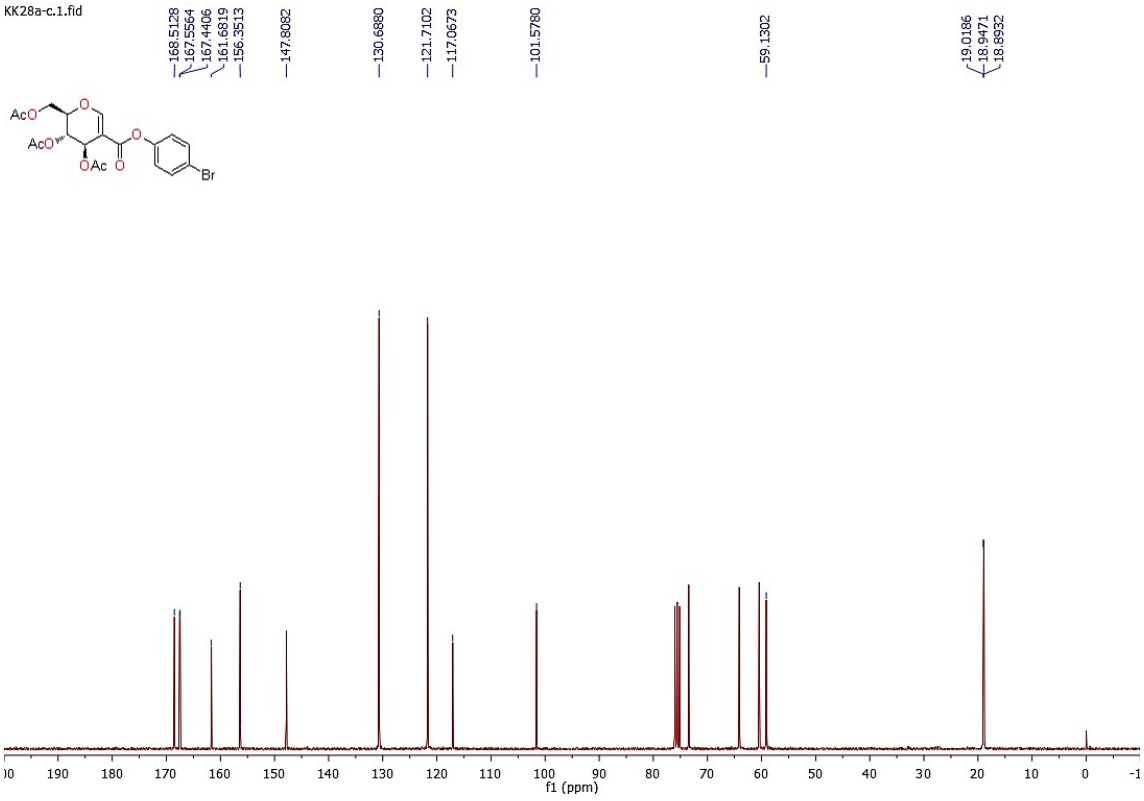
^{1}H NMR (300 MHz, $CDCl_3$) **5d**.



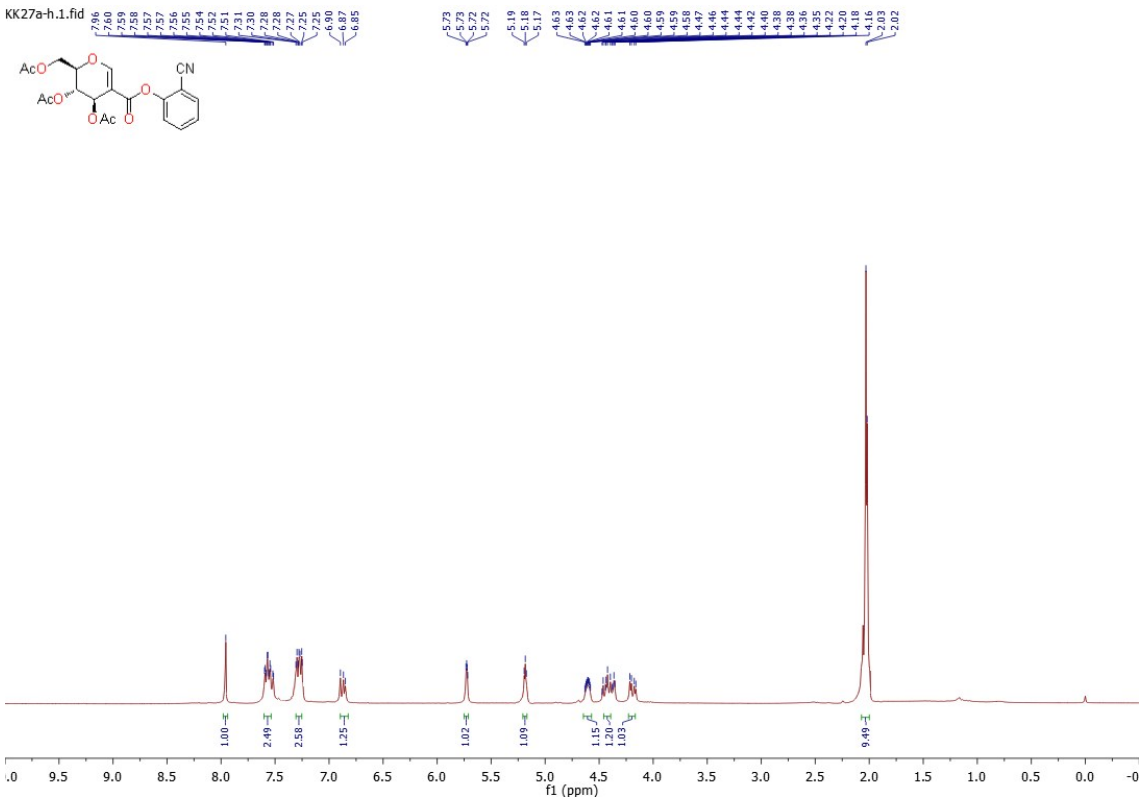
^{13}C NMR (75 MHz, $CDCl_3$) **5d**.



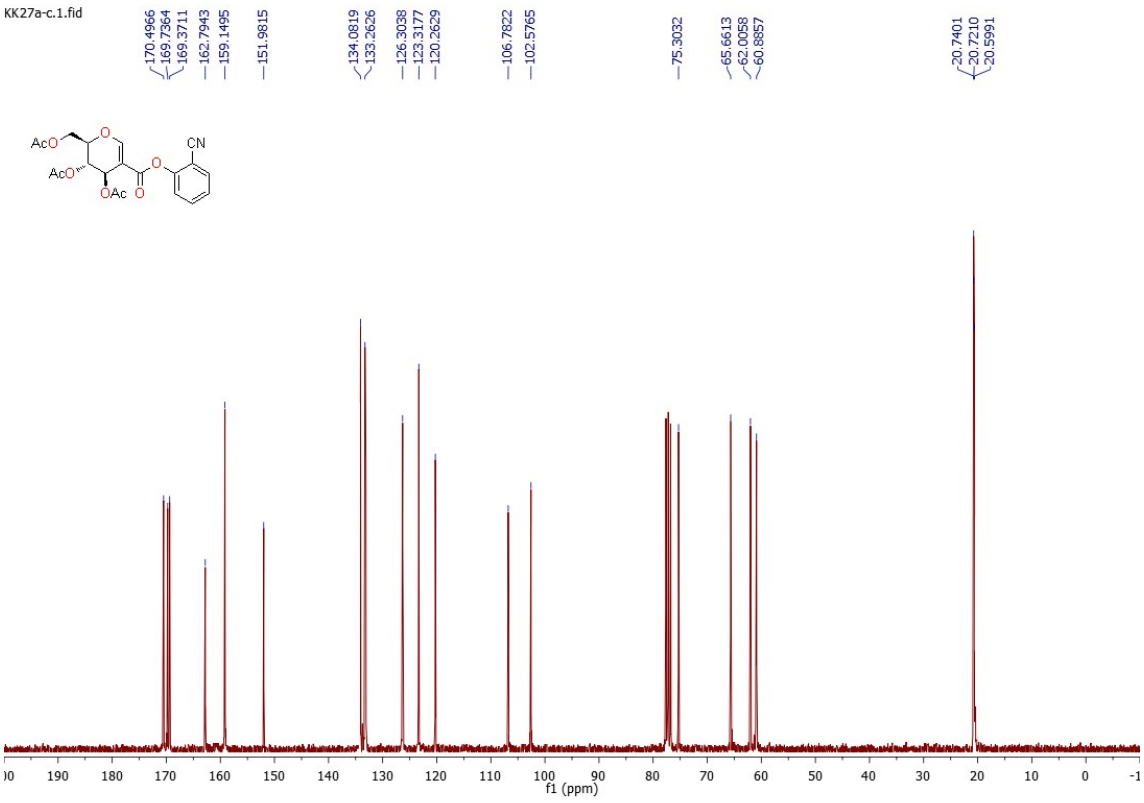
^{1}H NMR (300 MHz, $CDCl_3$) **5e**.



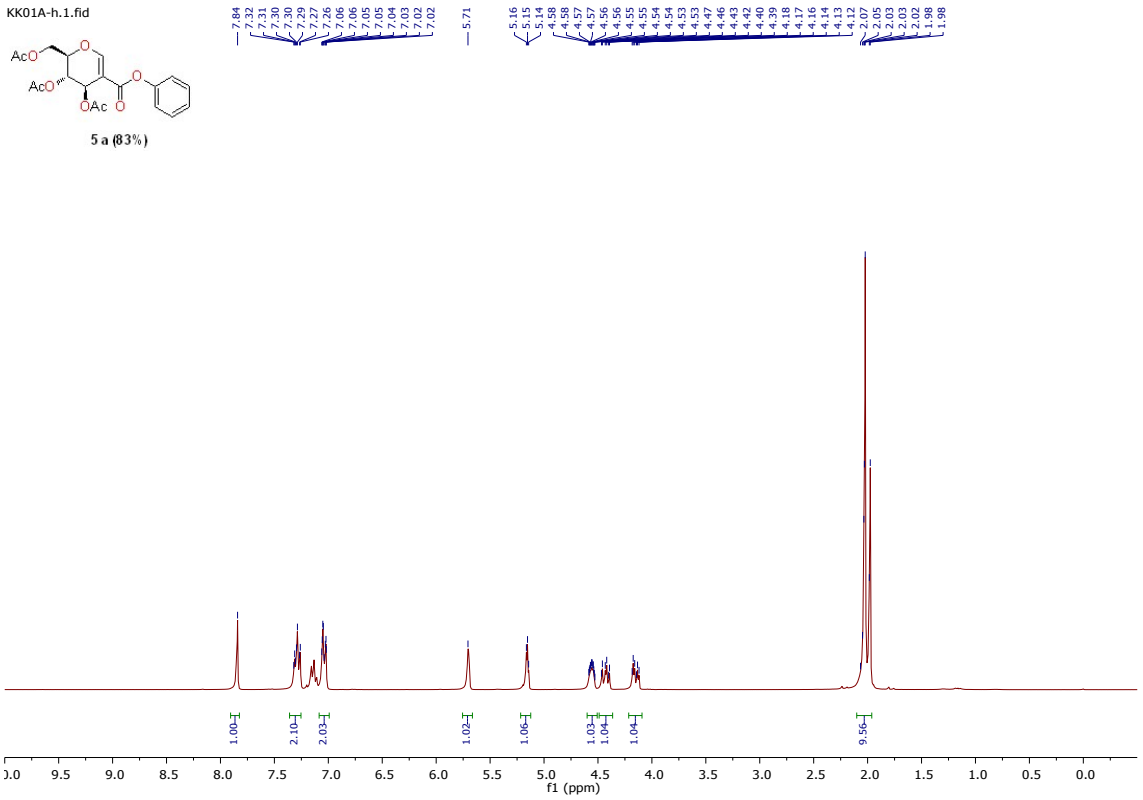
^{13}C NMR (75 MHz, $CDCl_3$) **5e**.



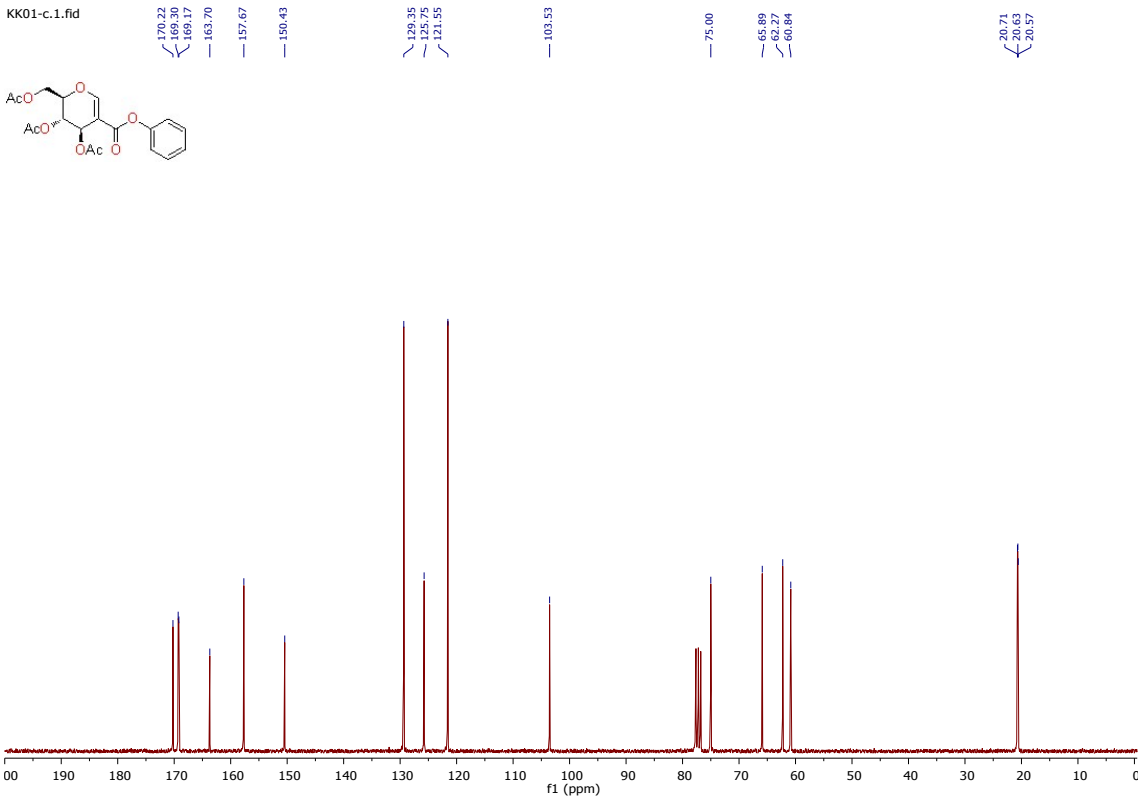
^{1}H NMR (300 MHz, $CDCl_3$) **5f**.



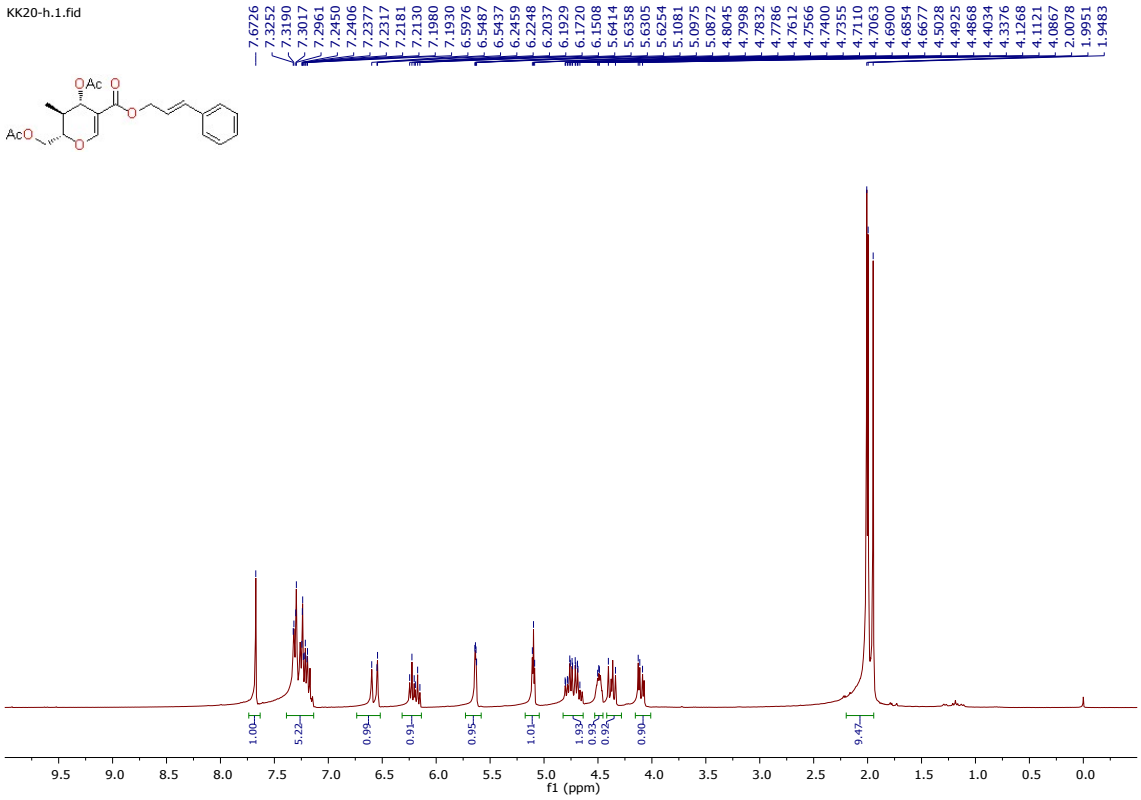
^{13}C NMR (75 MHz, $CDCl_3$) **5f**.



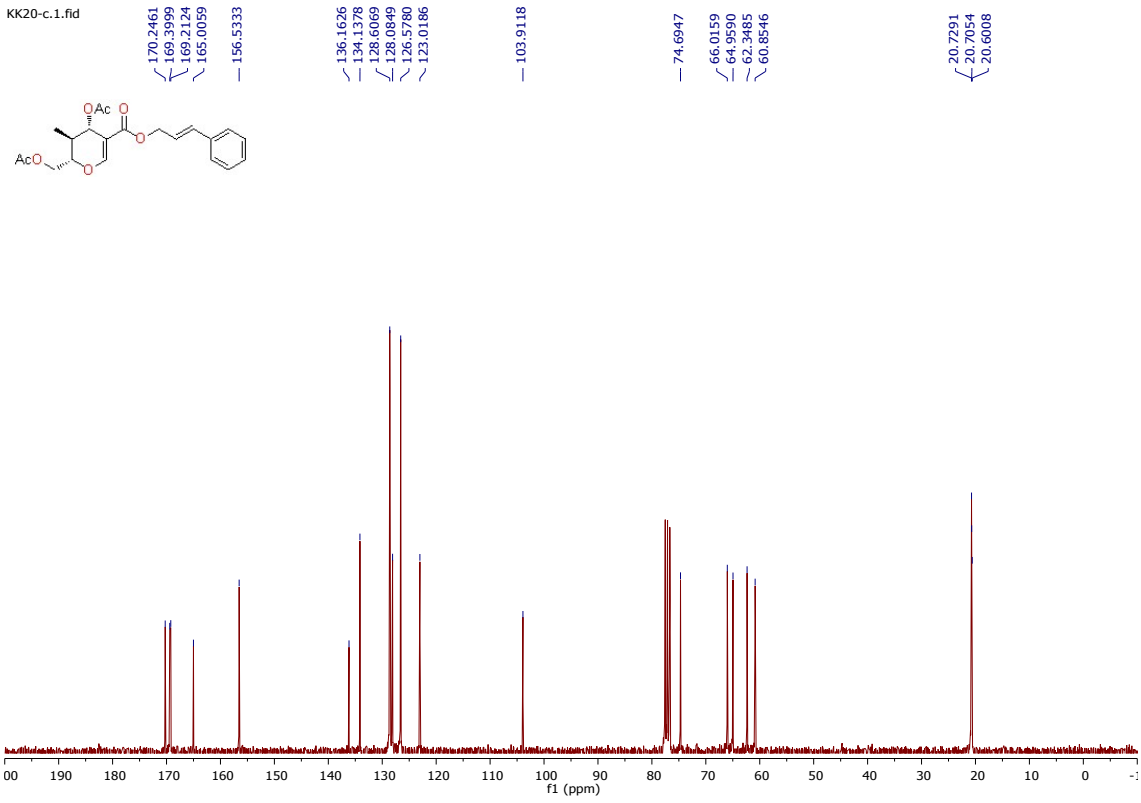
^{1}H NMR (300 MHz, $CDCl_3$) **5g**.



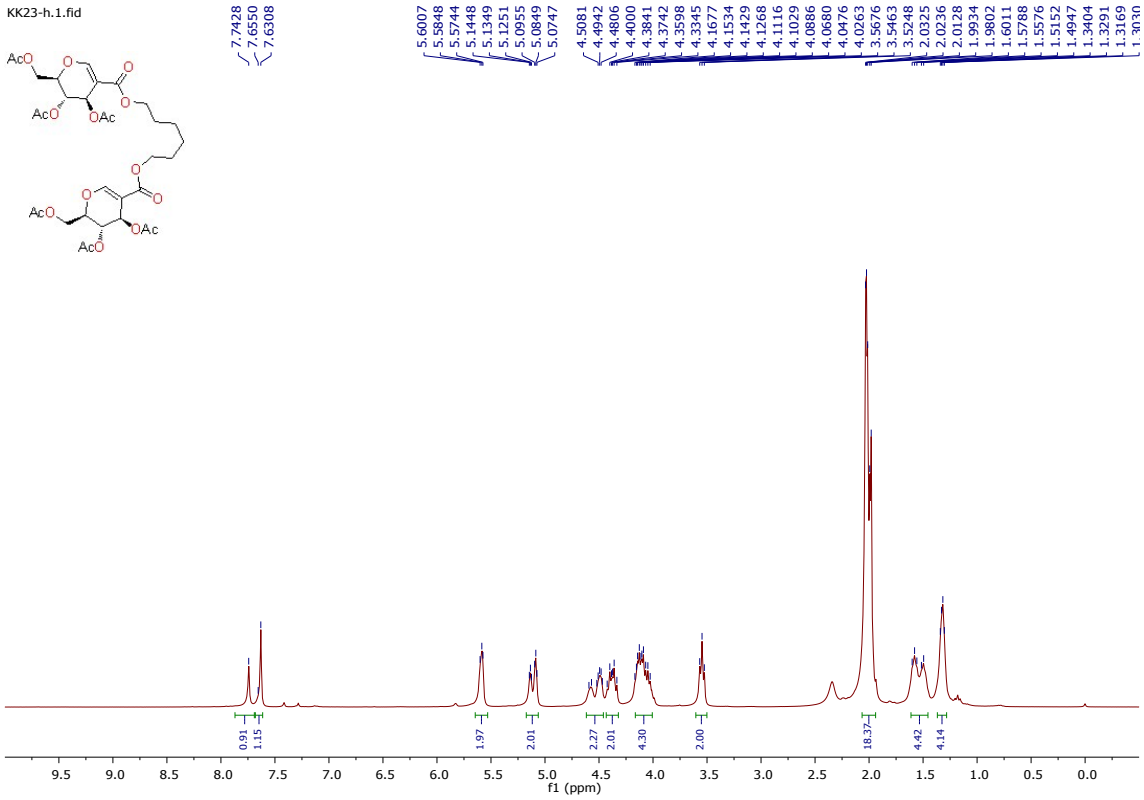
^{13}C NMR (75 MHz, $CDCl_3$) **5g**.



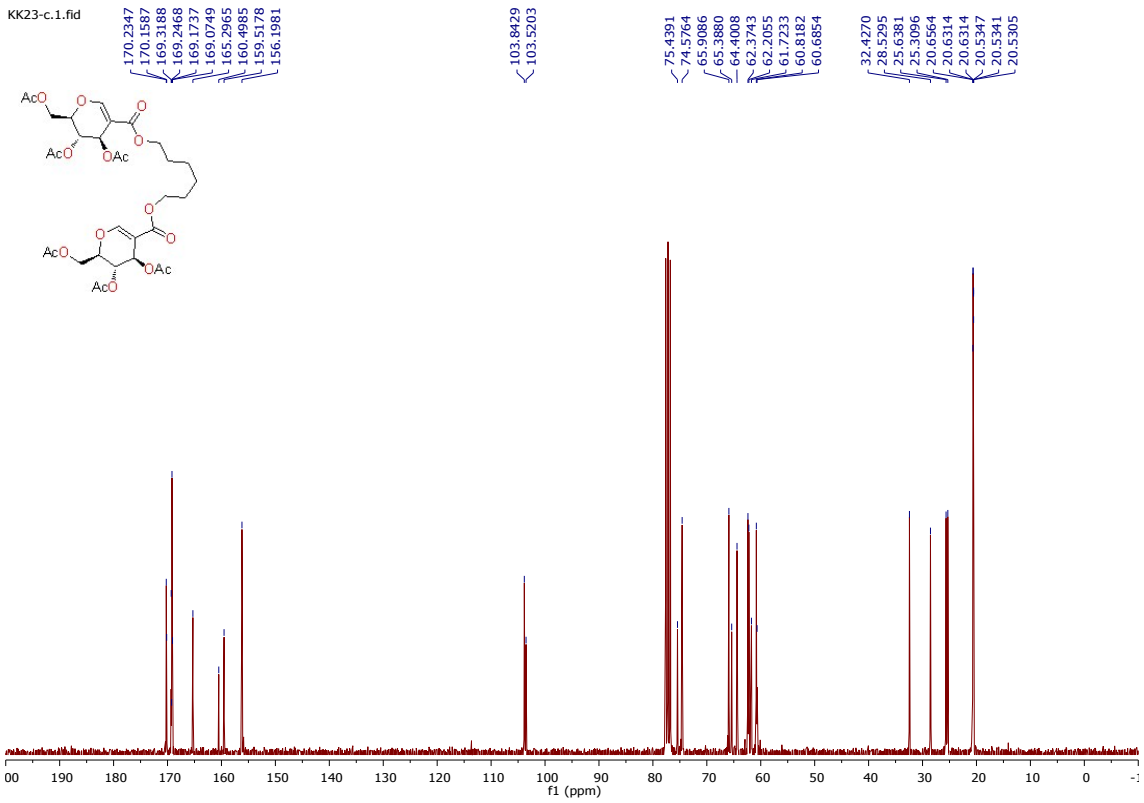
^{1}H NMR (300 MHz, $CDCl_3$) **5h**.



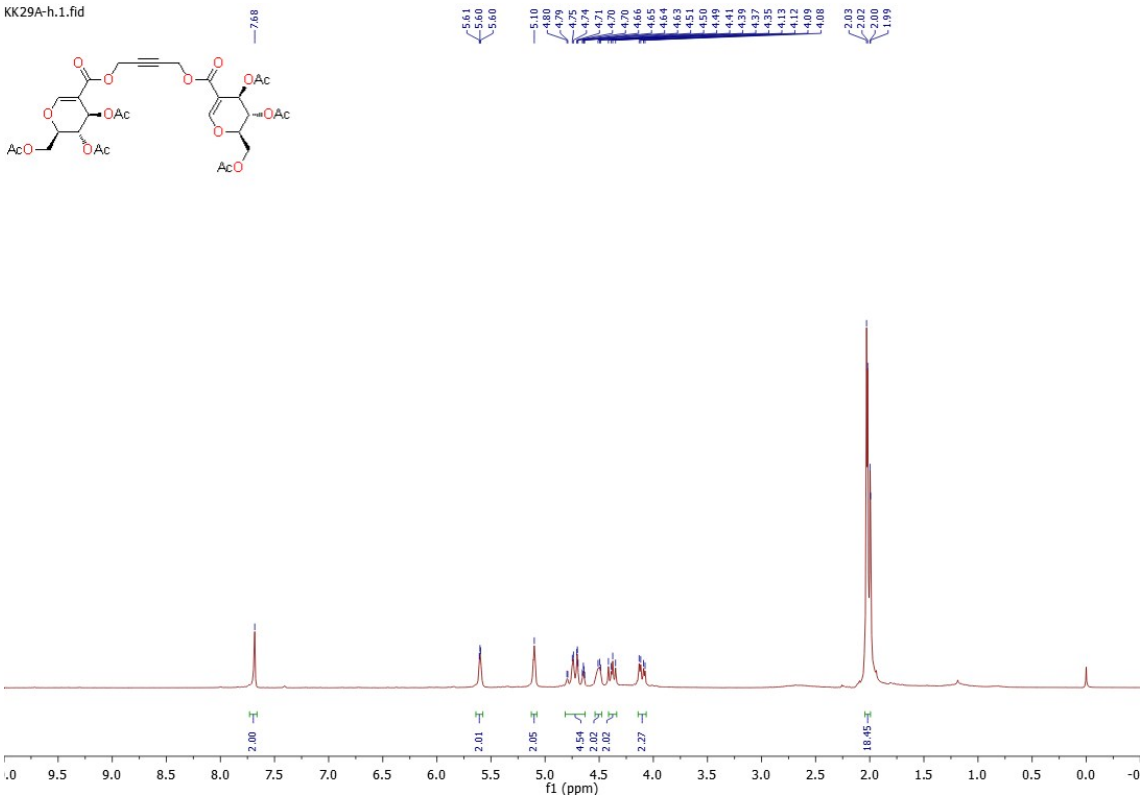
^{13}C NMR (75 MHz, $CDCl_3$) **5h**.



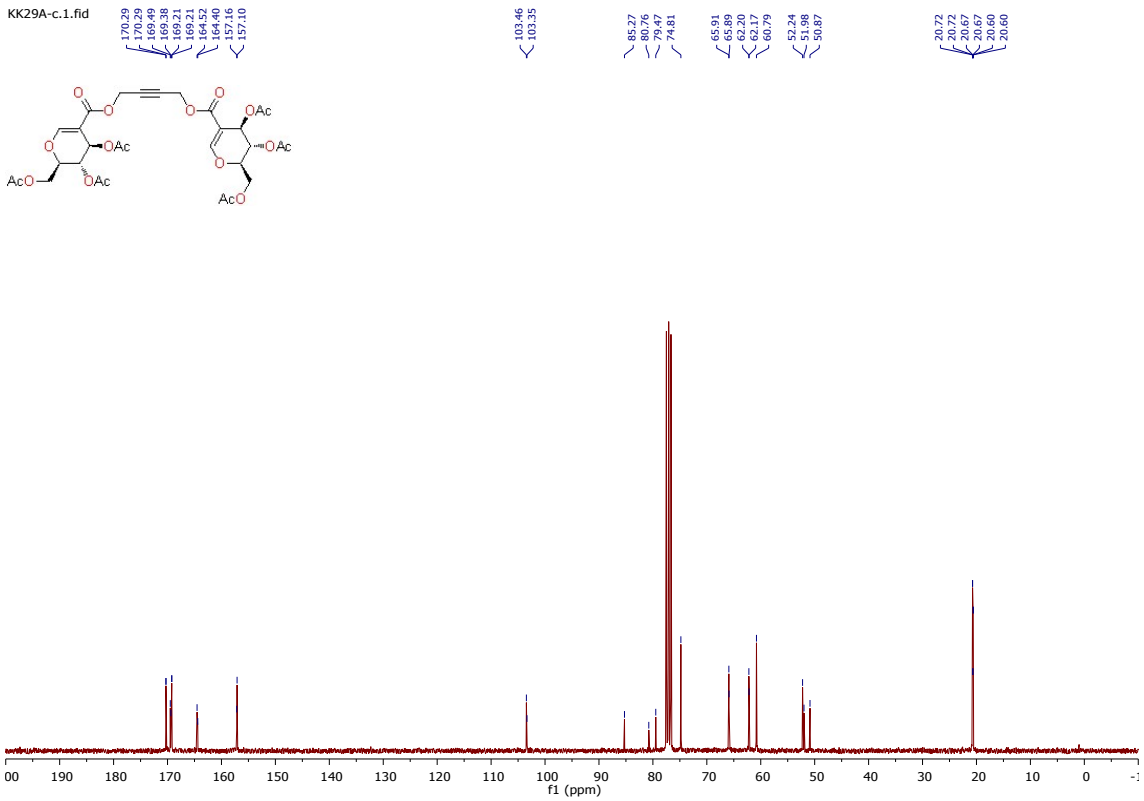
^{1}H NMR (300 MHz, $CDCl_3$) **5i**.



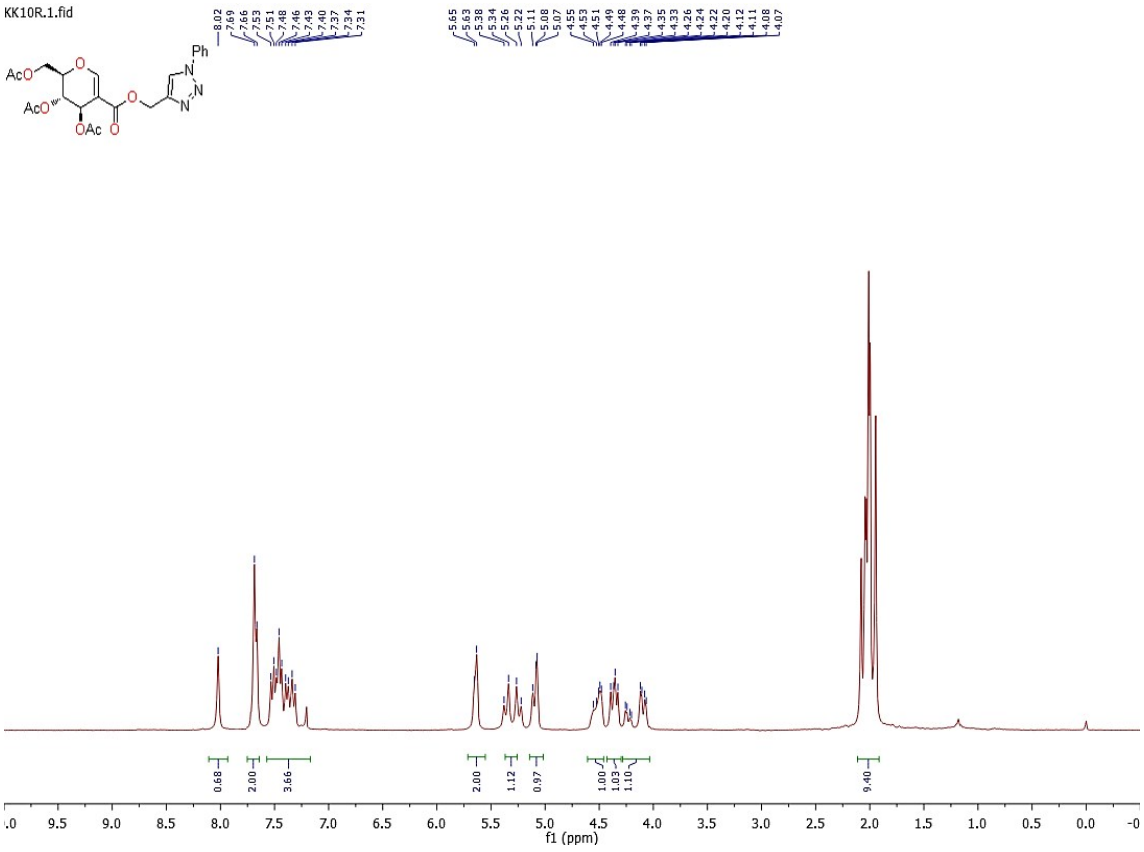
^{13}C NMR (75 MHz, $CDCl_3$) **5i**.



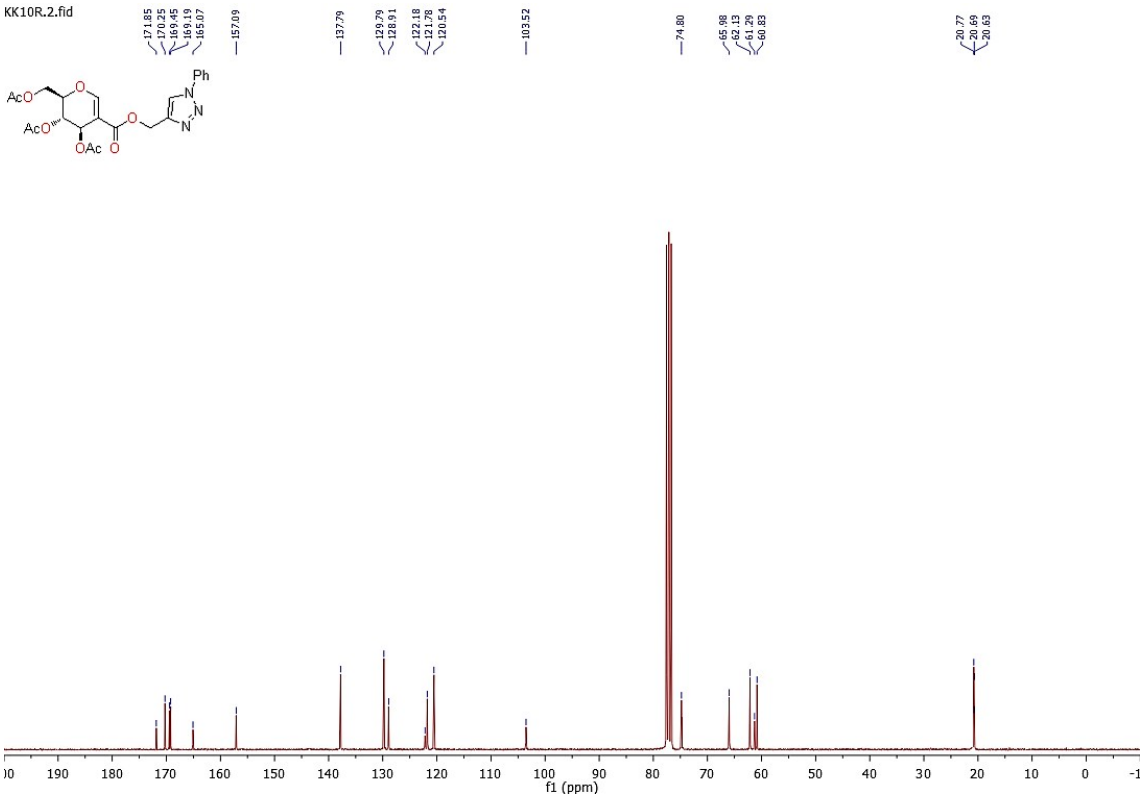
^{1}H NMR (300 MHz, $CDCl_3$) **5j**.



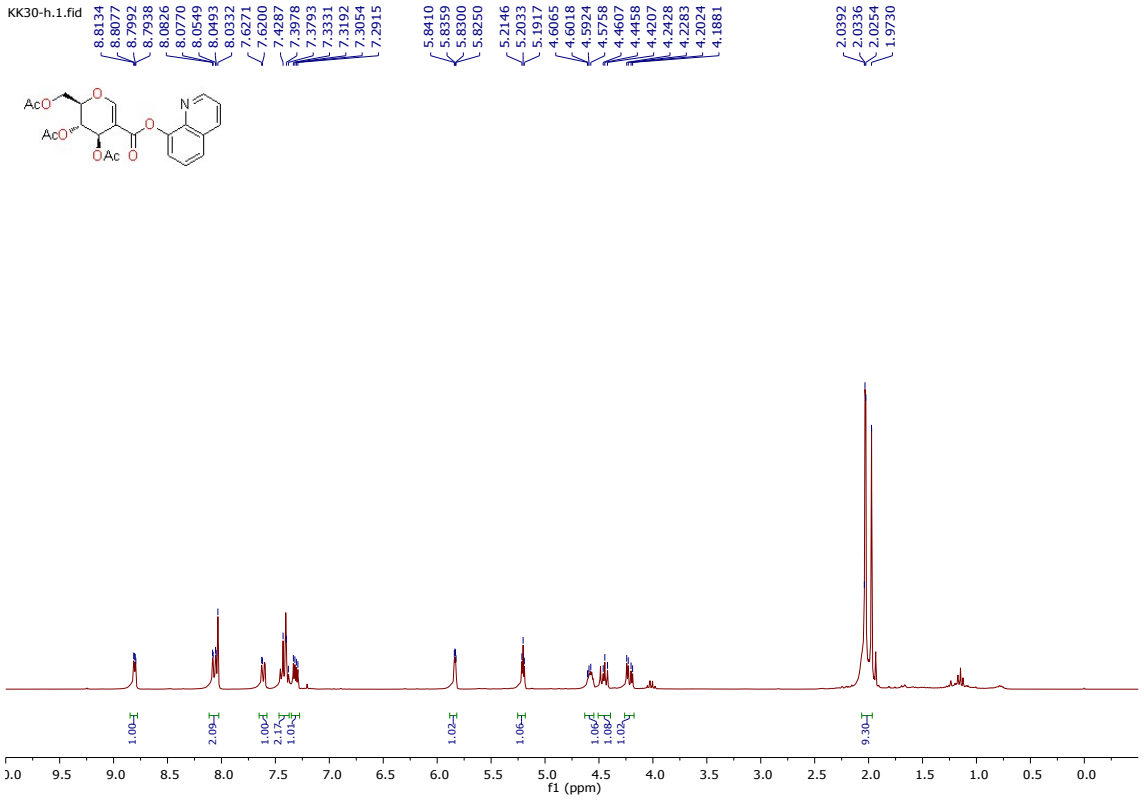
^{13}C NMR (75 MHz, $CDCl_3$) **5j**.



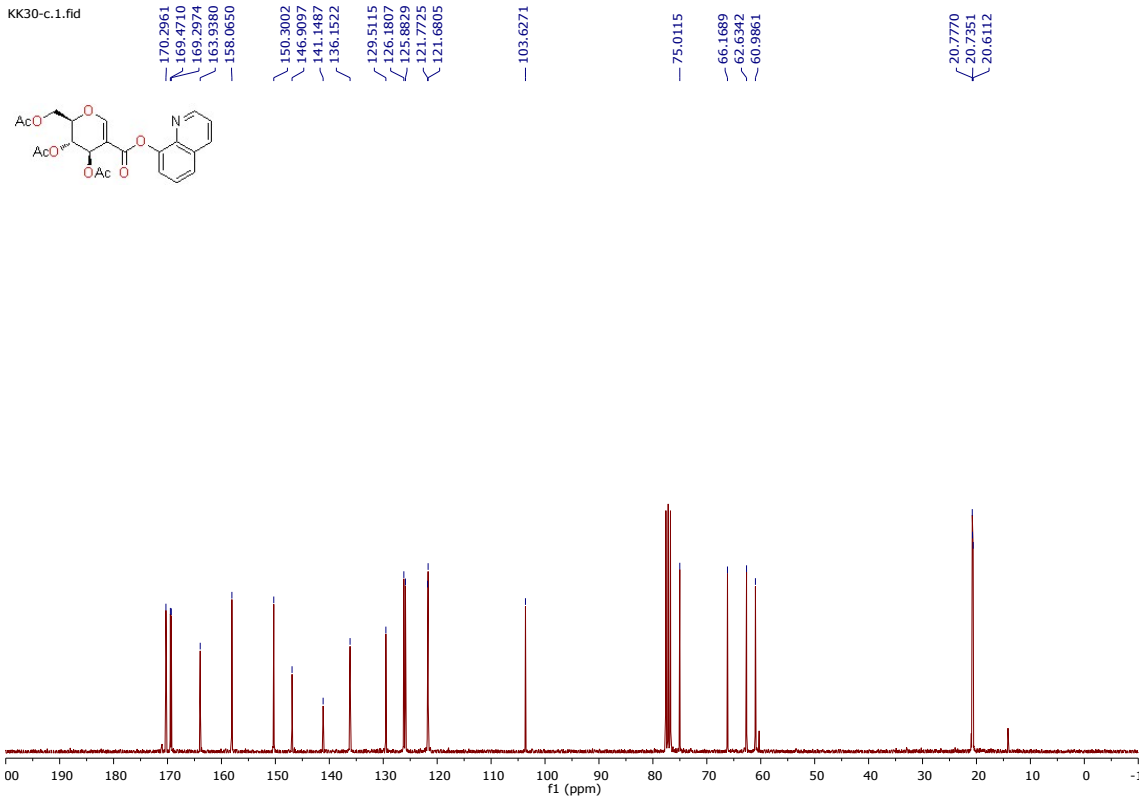
^{1}H NMR (300 MHz, $CDCl_3$) **5k**.



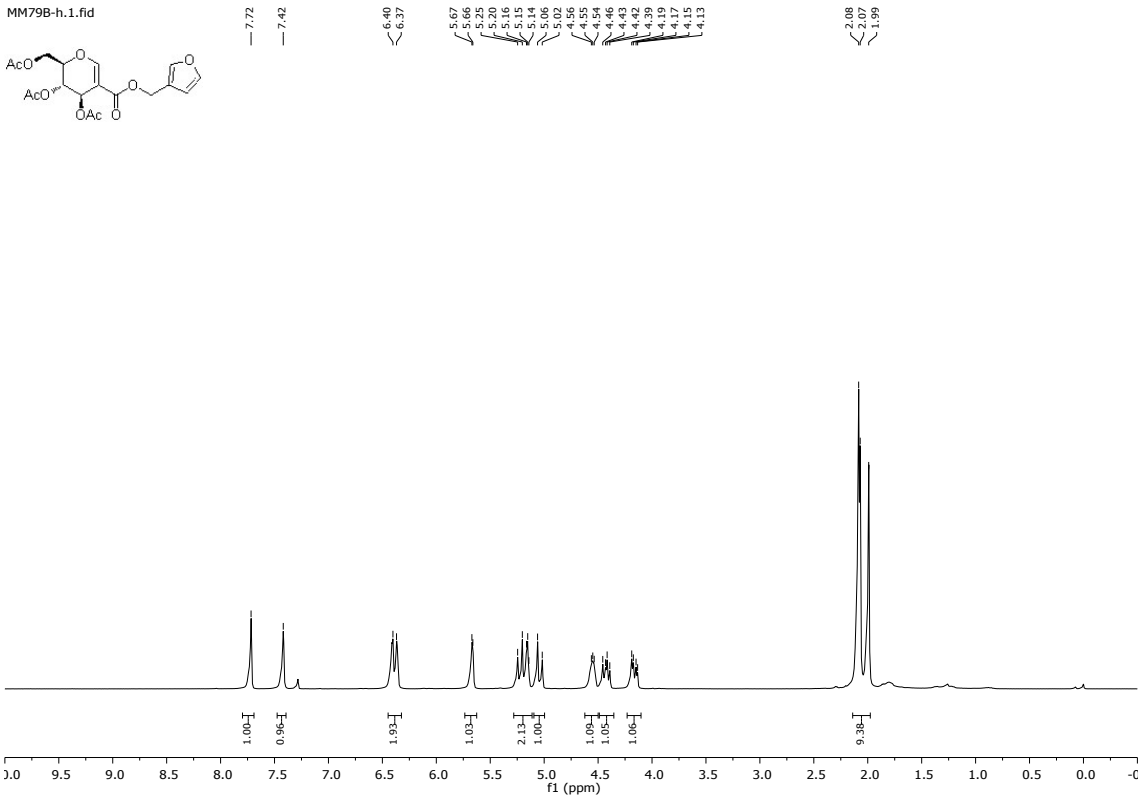
^{13}C NMR (75 MHz, $CDCl_3$) **5k**.



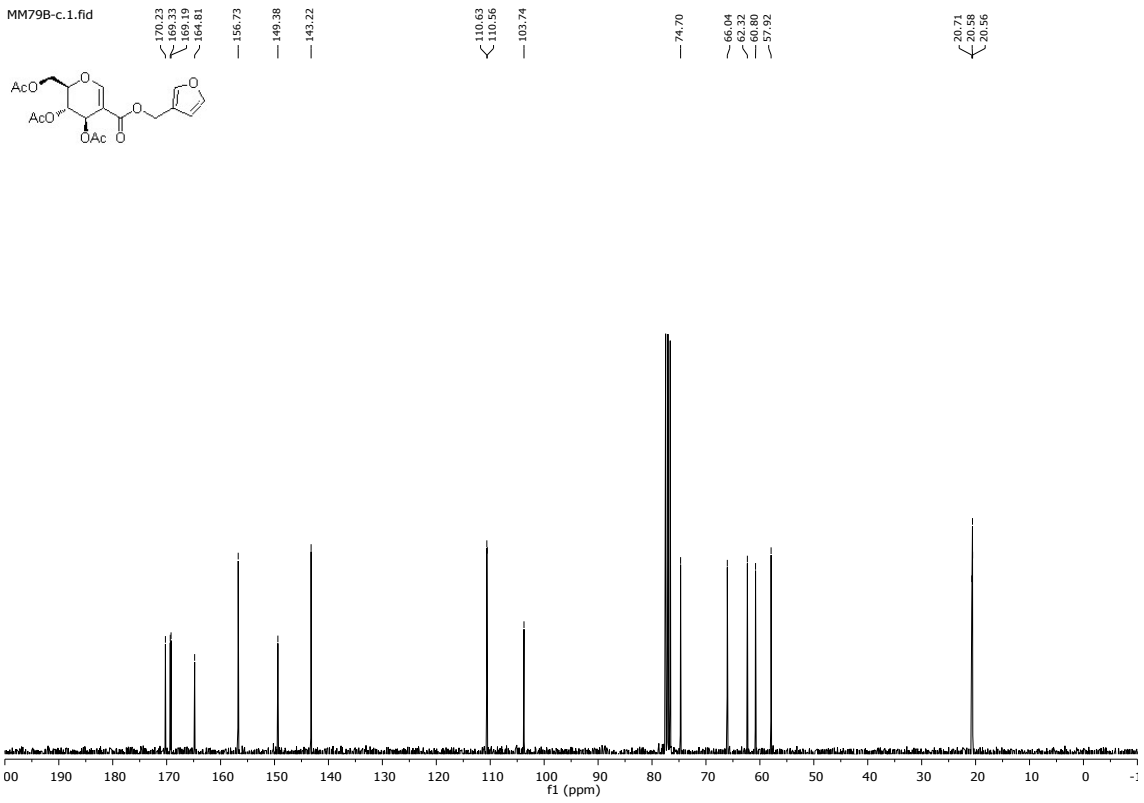
^{1}H NMR (300 MHz, $CDCl_3$) **5l**.



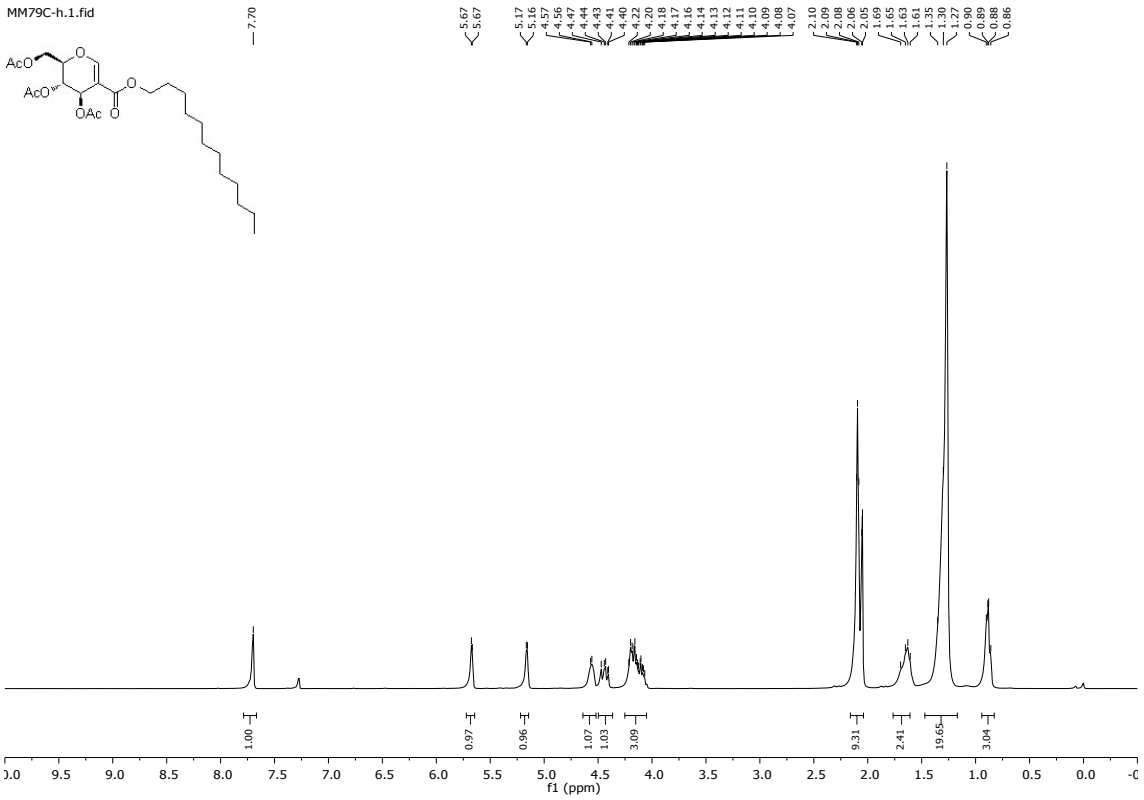
^{13}C NMR (75 MHz, $CDCl_3$) **5l**.



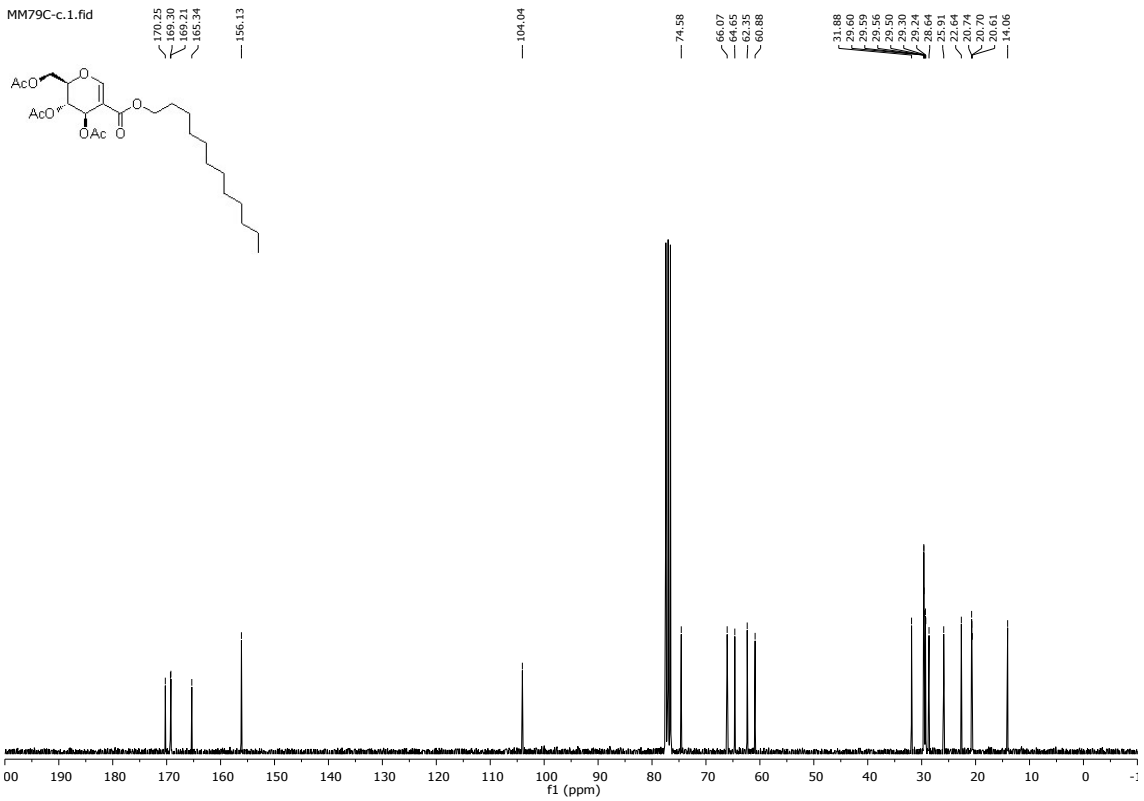
^{1}H NMR (300 MHz, $CDCl_3$) **5m**.



^{13}C NMR (75 MHz, $CDCl_3$) **5m**.



^{1}H NMR (300 MHz, $CDCl_3$) **5n**.



^{13}C NMR (75 MHz, $CDCl_3$) **5n**.