Supporting Information

Synthesis of D-Glyco-alkynone Derivatives via Carbonylative Sonogashira Reaction

Mariana P. Darbem[a], C. Henrique A. Esteves[a], Isadora M. de Oliveira[b], Joel S. Reis[a], Daniel C. Pimenta[c], Hélio A. Stefani[a]*

[a] Faculdade de Ciências Farmacêuticas, Universidade de São Paulo, São Paulo, SP – Brasil.
[b] Instituto de Química, Universidade de São Paulo, São Paulo, SP – Brasil.
[c] Instituto Butantã, São Paulo, SP - Brasil
Correspondent Author: +55 11 3091-3654, hstefani@usp.br

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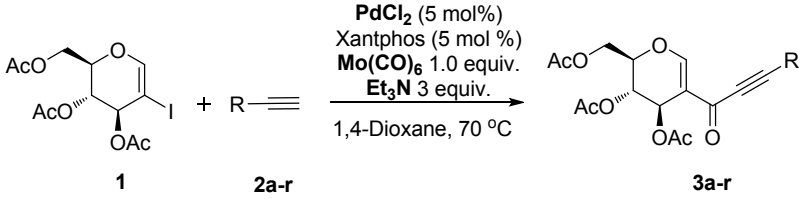
1. General methods

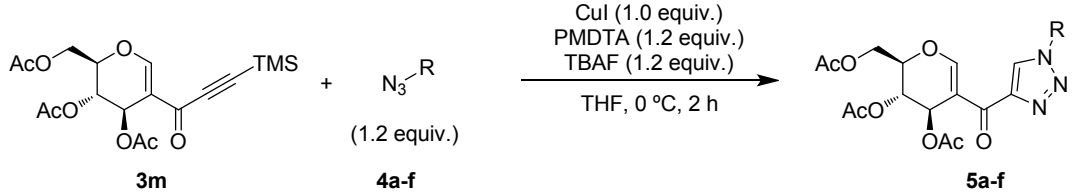
The compounds were all identified by usual analytical methods: ^{1}H NMR, ^{13}C NMR, IR, and HR-MS (ESI). ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$, in a Bruker DPX-300 instrument. ^{1}H chemical shifts were reported in ppm referenced relative to TMS internal standard (0.00 ppm) or the 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 (doublet 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.

2. General procedure A: carbonylative Sonogashira coupling



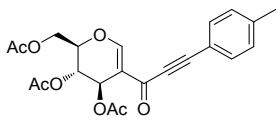
To a vial equipped with a magnetic stirrer bar and sealed with a rubber septum connected to a deflated balloon with a needle were added the tri-*O*-acetylated iodoglucal (0.2 mmol), 1,4-Dioxane(3.0 mL), $PdCl_2$ (5 mol %), Xantphos (5 mol%), $Mo(CO)_6$ (0.2 mmol, 1 equiv.), the alkyne (0.3 mmol, 1.5 equiv.) and Et_3N (0.6 mmol, 3 equiv.). The reaction mixture was vigorously stirred at 70 ºC for 2 to 4h. 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 hexanes and ethyl acetate as eluent (7:3).

3. General procedure B: synthesis of glyco-triazoles

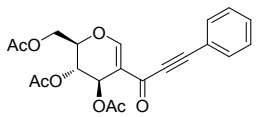


To a vial (20 mL) equipped with a magnetic stirrer bar under a nitrogen atmosphere containing CuI (0.25 mmol, 1 equiv.), THF (4 mL), an organic azide (0.3 mmol, 1.2 equiv.) and **3m** (0.25 mmol, 1 equiv.) was added PMDETA (0.3 mmol, 1.2 equiv.) and the reaction mixture was stirred at 0 ºC for 2 h. After this period, the reaction mixture was diluted with ethyl acetate and washed with aqueous NaCl. The organic phase was collected, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. Purification was performed using flash chromatography (ethyl acetate/ hexanes, 4:6).

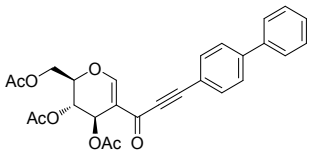
4. Characterization data



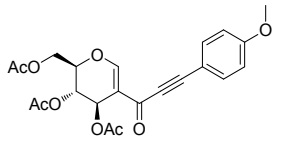
3a was synthesized according to General Procedure A and product **3a** was obtained as a yellow oil (83 mg, 0.20 mmol, 99%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.00 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.73 (dd, *J* = 3.1, 1.6 Hz, 1H), 5.15 (t, *J* = 3.0 Hz, 1H), 4.70 – 4.51 (m, 1H), 4.40 (dd, *J* = 12.1, 7.8 Hz, 1H), 4.14 (dd, *J* = 12.1, 4.4 Hz, 1H), 2.31 (s, 3H), 2.15 – 1.89 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.5, 170.2, 169.4, 169.1, 160.7, 141.3, 132.8, 129.4, 116.7, 114.9, 91.4, 84.8, 75.6, 65.6, 61.2, 60.9, 21.6, 20.7, 20.6, 20.6. **IR** (ν, cm^{-1}) = 2877, 2112, 1685, 1564, 1177, 1328, 1197, 1154, 1143, 991. **HRMS** (ESI-TOF) calc. [$C_{22}H_{22}O_8Na^+$] 437.1212, found 437.1212.



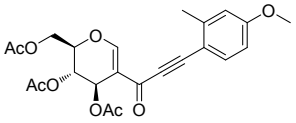
3b was synthesized according to General Procedure A and product **3b** was obtained as a yellow oil (72 mg, 0.18 mmol, 92%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 7.65 – 7.55 (m, 2H), 7.49 – 7.34 (m, 3H), 5.82 (d, *J* = 1.8 Hz, 1H), 5.23 (t, *J* = 3.0 Hz, 1H), 4.74 – 4.60 (m, 1H), 4.48 (dd, *J* = 12.1, 7.8 Hz, 1H), 4.21 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.18 – 2.01 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.4, 170.2, 169.4, 169.1, 160.9, 132.8, 130.6, 128.6, 119.8, 114.9, 90.8, 84.9, 75.6, 65.6, 61.2, 60.9, 20.7, 20.6, 20.6. **IR** (ν, cm^{-1}) = 2959, 2864, 2127, 1682, 1566, 1324, 1266, 1175, 1151, 992. **HRMS** (ESI-TOF) calc. [$C_{21}H_{20}O_8Na^+$] 423.1056, found 423.1051.



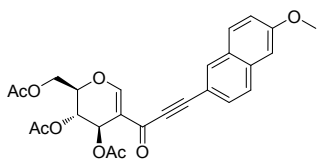
3c was synthesized according to General Procedure A and product **3c** was obtained as a yellow oil (84 mg, 0.18 mmol, 88%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.10 (s, 1H), 7.74 – 7.53 (m, 6H), 7.49 – 7.36 (m, 3H), 5.93 – 5.79 (m, 1H), 5.24 (t, *J* = 3.1 Hz, 1H), 4.75 – 4.64 (m, 1H), 4.49 (dd, *J* = 12.0, 7.8 Hz, 1H), 4.22 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.19 – 1.98 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.4, 170.2, 169.4, 169.1, 160.8, 143.5, 139.7, 133.3, 128.9, 128.1, 127.3, 127.1, 118.5, 114.9, 90.9, 85.7, 75.7, 65.6, 61.2, 60.9, 20.7, 20.6, 20.6. **IR** (ν, cm^{-1}) = 2959, 2931, 2123, 1685, 1566, 1438, 1324, 1264, 1175, 1151, 991. **HRMS** (ESI-TOF) calc. [$C_{27}H_{24}O_8Na^+$] 499.1363, found 499.1361.



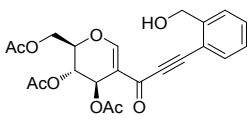
3d was synthesized according to General Procedure A and product **3d** was obtained as a yellow oil (78 mg, 0.18 mmol, 90%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.06 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.87 – 5.78 (m, 1H), 5.23 (t, *J* = 3.0 Hz, 1H), 4.72 – 4.62 (m, 1H), 4.47 (dd, *J* = 12.1, 7.9 Hz, 1H), 4.21 (dd, *J* = 12.2, 4.5 Hz, 1H), 3.84 (s, 3H), 2.19 – 1.99 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.5, 170.2, 169.4, 169.1, 161.6, 160.3, 134.8, 114.7, 114.4, 111.6, 91.9, 84.8, 75.5, 65.7, 61.3, 60.9, 55.4, 20.7, 20.6, 20.6. **IR** (ν, cm^{-1}) = 2866, 2747, 2119, 1685, 1549, 1460, 1175, 1151, 1134, 991. **HRMS** (ESI-TOF) calc. [$C_{22}H_{22}O_9Na^+$] 453.1156, found 453.1159.



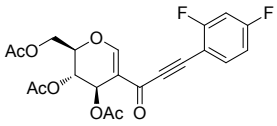
3e was synthesized according to General Procedure A and product **3e** was obtained as a yellow oil (88 mg, 0.19 mmol, 99%).**^{1}H NM**R (300 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 6.61 – 6.47 (m, 2H), 5.67 – 5.59 (m, 1H), 5.05 (t, *J* = 3.4 Hz, 1H), 4.54 – 4.41 (m, 1H), 4.33 – 4.23 (m, 1H), 4.12 – 3.95 (m, 1H), 3.62 (s, 3H), 2.29 (s, 3H), 1.96 – 1.80 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.5, 170.2, 169.4, 169.1, 161.5, 160.4, 144.1, 135.2, 115.4, 115.0, 111.8, 111.6, 90.8, 88.4, 75.6, 65.6, 61.2, 60.9, 55.3, 21.0, 20.7, 20.6, 20.5. **IR** (ν, cm^{-1}) = 2821, 2756, 2112, 1685, 1566, 1549, 1324, 1259, 1179, 1151, 992. **HRMS** (ESI-TOF) calc. [$C_{23}H_{24}O_9Na^+$] 467.1313, found 453.1311.



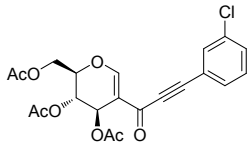
3f was synthesized according to General Procedure A and product **3f** was obtained as a yellow oil (91 mg, 0.19 mmol, 95%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.05 (s, 1H), 7.98 (s, 1H), 7.64 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.11 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.04 (d, *J* = 2.6 Hz, 1H), 5.85 – 5.70 (m, 1H), 5.28 – 5.06 (m, 1H), 4.64 – 4.56 (m, 1H), 4.52 – 4.35 (m, 1H), 4.24 – 4.11 (m, 1H), 3.85 (s, 3H), 2.19 – 1.96 (m, 9H).**^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.5, 170.2, 169.4, 169.2, 160.7, 159.3, 135.4, 133.9, 129.7, 128.9, 128.1, 127.2, 119.9, 114.9, 114.4, 105.9, 92.1, 85.0, 75.6, 65.7, 61.3, 61.0, 55.4, 20.7, 20.6, 20.6. **IR** (ν, cm^{-1}) = 2913, 2866, 2117, 1680, 1560, 1436, 1324, 1177, 1151, 991. **HRMS** (ESI-TOF) calc. [$C_{26}H_{24}O_9Na^+$] 503.1313, found 503.1312.



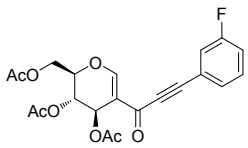
3g was synthesized according to General Procedure A and product **3g** was obtained as a yellow oil (73 mg, 0.17 mmol, 85%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 9.21 (s, 1H), 7.70 (s, 1H), 7.55 – 7.33 (m, 4H), 5.93 (s, 1H), 5.37 (s, 2H), 5.23 (t, *J* = 3.4 Hz, 1H), 4.60 – 4.52 (m, 1H), 4.47 (dd, *J* = 11.6, 7.7 Hz, 1H), 4.20 (dd, *J* = 11.8, 4.1 Hz, 1H), 2.12 – 2.03 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 171.5, 170.3, 169.6, 169.3, 154.2, 144.0, 131.9, 130.9, 128.3, 128.0, 120.4, 114.5, 96.0, 90.3, 74.3, 73.9, 66.2, 62.5, 61.0, 20.7, 20.7, 20.6. **IR** (ν, cm^{-1}) = 2861, 2080, 1680, 1574, 1527, 1324, 1177, 1145, 981, 732. **HRMS** (ESI-TOF) calc. [$C_{22}H_{22}O_9Na^+$] 453.1156, found 453.1156.



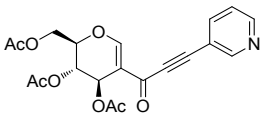
3h was synthesized according to General Procedure A and product **3h** was obtained as a yellow oil (67 mg, 0.15 mmol, 77%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.93 (s, 1H), 7.45 – 7.30 (m, 1H), 6.80 – 6.68 (m, 2H), 5.63 – 5.56 (m, 1H), 5.05 (t, *J* = 2.8 Hz, 1H), 4.54 – 4.45 (m, 1H), 4.34 – 4.21 (m, 1H), 4.13 – 3.94 (m, 1H), 2.01 – 1.79 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 173.9, 170.2, 169.3, 169.1, 164.4, 164.3 (dd, *J* = 253.5 Hz, *J* = 7,5 Hz), 161.6, 135.7, 135.6, 115.0, 112.3, 112.2 (dd *J* = 22.2 Hz, 3,3 Hz), 105.2 (dd, *J* = 3.7 Hz), 104,7 (t, *J* = 24.7 Hz) 89.4, 75.7, 65.5, 61.0, 60.9, 20.7, 20.6. **IR** (ν, cm^{-1}) = 2976, 2136, 1685, 1560, 1456, 1326, 1175, 1151, 992, 937, 711. **HRMS** (ESI-TOF) calc. [$C_{21}H_{18}F_2O_8Na^+$] 436.0862, found 436.0869.



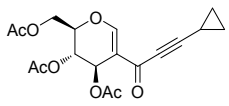
3i was synthesized according to General Procedure A and product **3i** was obtained as a yellow oil (74 mg, 0.17 mmol, 85%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.57 (s, 1H), 7.51 – 7.39 (m, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 5.85 – 5.75 (m, 1H), 5.23 (t, *J* = 3.0 Hz, 1H), 4.70- 4.68 (m, 1H), 4.56 – 4.42 (m, 1H), 4.23 (d, *J* = 4.5 Hz, 1H), 2.22 – 1.92 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.1, 170.2, 169.3, 169.1, 161.2, 134.5, 132.4, 130.9, 130.8, 129.9, 121.5, 114.9, 88.7, 85.5, 75.8, 65.5, 61.0, 60.9, 20.7, 20.6, 20.6. **IR** (ν, cm^{-1}) = 2975, 2130, 1682, 1562, 1426, 1365, 1266, 1173, 1151, 991. **HRMS** (ESI-TOF) calc. [$C_{21}H_{19}ClO_8Na^+$] 457.0661, found 457.0660.



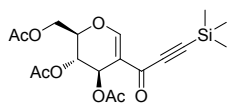
3j was synthesized according to General Procedure A and product **3j** was obtained as a yellow oil (56 mg, 0.13 mmol, 67%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.07 (s, 1H), 7.43 – 7.37 (m, 2H), 7.32 – 7.23 (m, 1H), 7.24 – 7.07 (m, 1H), 5.88 – 5.78 (m, 1H), 5.23 (t, *J* = 3.0 Hz, 1H), 4.82 – 4.64 (m, 1H), 4.49 (dd, *J* = 12.1, 7.9 Hz, 1H), 4.21 (dd, *J* = 12.2, 4.5 Hz, 1H), 2.18 – 2.01 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.1, 170.2, 169.3, 169.12, 162.53 (d, *J* = 246.7 Hz), 161.1, 130.4 (d, *J* = 8.5 Hz), 128.7 (d, *J* = 3.2 Hz), 121.6 (d, *J* = 9.3 Hz), 119.4 (d, *J* = 23.3 Hz), 118.1 (d, *J* = 21.2 Hz), 114.9, 88.9 (d, *J* = 3.4 Hz), 85.2, 75.8, 65.5, 61.0, 60.9, 20.7, 20.6, 20.5. **IR** (ν, cm^{-1}) = 2970, 2132, 1685, 1564, 1326, 1268, 1177, 1151, 1113, 985, 849. **HRMS** (ESI-TOF) calc. [$C_{21}H_{19}FO_8Na^+$] 441.0956, found 441.0956.



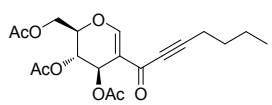
3k was synthesized according to General Procedure A and product **3k** was obtained as a yellow oil (52 mg, 0.13 mmol, 65%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.74 (s, 1H), 8.60 (d, *J* = 4.0 Hz, 1H), 8.01 (s, 1H), 7.87 – 7.73 (m, 1H), 7.28 (dd, *J* = 7.9, 5.0 Hz, 1H), 5.74 (s, 1H), 5.16 (s, 1H), 4.68 – 4.58 (m, 1H), 4.42 (dd, *J* = 12.2, 7.9 Hz, 1H), 4.13 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.09 – 1.90 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 173.9, 170.2, 169.3, 169.1, 161.3, 153.0, 150.6, 139.6, 123.2, 117.2, 114.9, 87.5, 86.8, 75.8, 65.5, 61.0, 60.8, 20.7, 20.6, 20.6. **IR** (ν, cm^{-1}) = 2859, 2119, 1680, 1566, 1326, 1181, 992. **HRMS** (ESI-TOF) calc. [$C_{20}H_{19}NO_8Na^+$] 424.1003, found 444.1002.



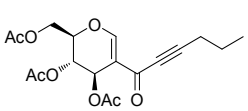
3l was synthesized according to General Procedure A and product **3l** was obtained as a yellow oil (53 mg, 0.14 mmol, 72%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.90 (s, 1H), 5.72 (s, 1H), 5.18 (s, 1H), 4.64 – 4.54 (m, 1H), 4.44 (dd, *J* = 12.1, 7.8 Hz, 1H), 4.19 (d, *J* = 4.5 Hz, 1H), 2.19 – 1.91 (m, 9H), 1.45 – 1.42 (m, 1H), 1.07 – 0.86 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.8, 174.8, 170.5, 169.7, 169.5, 160.8, 115.1, 98.5, 75.8, 66.0, 61.5, 61.3, 21.0, 21.0, 20.9, 9.8, 9.8. **IR** (ν, cm^{-1}) = 2915, 2138, 1682, 1566, 1365, 1175, 1149, 991, 864. **HRMS** (ESI-TOF) calc. [$C_{18}H_{20}O_8Na^+$] 387.1050, found 387.1051.



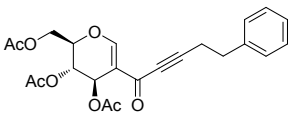
3m was synthesized according to General Procedure A and product **3m** was obtained as a yellow oil (64 mg, 0.16 mmol, 80%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 5.60 – 5.48 (m, 1H), 5.02 (t, *J* = 3.1 Hz, 1H), 4.51 – 4.39 (m, 1H), 4.26 (dd, *J* = 12.2, 7.9 Hz, 1H), 4.01 (dd, *J* = 12.2, 4.5 Hz, 1H), 1.99 – 1.81 (m, 9H), 0.08 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.8, 170.9, 170.03, 169.8, 162.1, 115.6, 99.7, 98.6, 76.4, 66.3, 61.7, 61.7, 21.4, 21.3, 21.3, 0.0. **IR** (ν, cm^{-1}) = 2864, 2028, 1914, 1685, 1566, 1324, 1261, 1175, 1151, 987, 817. **HRMS** (ESI-TOF) calc. [$C_{18}H_{24}O_8SiNa^+$] 419.1133, found 419.1135.



3n was synthesized according to General Procedure A and product **3n** was obtained as a yellow oil (53 mg, 0.14 mmol, 70%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.95 (s, 1H), 5.73 (dd, *J* = 3.1, 1.7 Hz, 1H), 5.19 (t, *J* = 3.1 Hz, 1H), 4.69 – 4.58 (m, 1H), 4.45 (dd, *J* = 12.1, 7.8 Hz, 1H), 4.17 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.39 (t, *J* = 7.0 Hz, 2H), 2.18 – 1.96 (m, 9H), 1.69 – 1.36 (m, 4H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.7, 170.2, 169.3, 169.1, 160.7, 114.9, 94.1, 77.0, 75.5, 65.6, 61.1, 60.9, 29.7, 22.0, 20.7, 20.6, 20.6, 18.6, 13.4. **IR** (ν, cm^{-1}) = 2838, 2862, 2147, 1685, 1566, 1365, 1324, 1175, 1149, 991, 864. **HRMS** (ESI-TOF) calc. [$C_{19}H_{24}O_8Na^+$] 403.1363, found 403.1361.

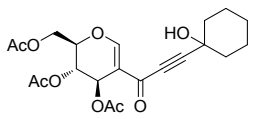


3o was synthesized according to General Procedure A and product **3o** was obtained as a yellow oil (45 mg, 0.12 mmol, 62%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.76 (s, 1H), 5.53 (dd, *J* = 3.1, 1.7 Hz, 1H), 4.99 (t, *J* = 3.1 Hz, 1H), 4.49 – 4.37 (m, 1H), 4.25 (dd, *J* = 12.1, 7.8 Hz, 1H), 3.97 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.17 (t, *J* = 7.1 Hz, 2H), 1.94 – 1.81 (m, 9H), 1.44 (h, *J* = 7.2 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.7, 170.2, 169.3, 169.1, 160.7, 114.9, 93.9, 77.8, 75.5, 65.6, 61.1, 60.9, 21.2, 20.8, 20.7, 20.6, 20.6, 13.5. **IR** (ν, cm^{-1}) = 2916, 2879, 1680, 1560, 1141989, 836, 724. **HRMS** (ESI-TOF) calc. [$C_{18}H_{22}O_8Na^+$] 389.1207, found 403.1361.

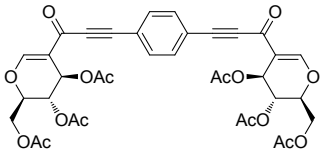


3p was synthesized according to General Procedure A and product **3p** was obtained as a yellow oil (67 mg, 0.15 mmol, 78%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.61 (s, 1H), 7.32 –

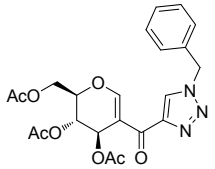
7.11 (m, 5H), 5.65 – 5.52 (m, 1H), 5.16 – 5.04 (m, 1H), 4.57 – 4.49 (m, 1H), 4.36 (dd, *J* = 11.8, 7.8 Hz, 1H), 4.07 (dd, *J* = 12.0, 4.5 Hz, 1H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.63 (t, 2H), 2.05 – 1.94 (m, 9H).**^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.5, 170.2, 169.3, 169.1, 161.1, 139.5, 128.5, 128.3, 126.7, 114.9, 92.7, 78.3, 75.4, 65.6, 60.9, 60.8, 33.8, 21.0, 20.7, 20.6, 20.6. **IR** (ν, cm^{-1}) = 2926, 2840, 2149, 1685, 1566, 1324, 1261, 1175, 1151, 1017, 991, 678. **HRMS** (ESI-TOF) calc. [$C_{23}H_{24}O_8Na^+$] 451.1363, found 451.1361.



3q was synthesized according to General Procedure A and product **3q** was obtained as a yellow oil (73 mg, 0.17 mmol, 86%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 5.68 (d, *J* = 2.3 Hz, 1H), 5.12 (t, *J* = 3.0 Hz, 1H), 4.62 – 4.52 (m, 1H), 4.37 (dd, *J* = 12.2, 7.8 Hz, 1H), 4.12 (dd, *J* = 12.1, 4.4 Hz, 1H), 2.68 (s, 1H), 2.09 – 1.98 (m, 9H), 1.93 – 1.84 (m, 2H), 1.72 – 1.43 (m, 8H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.3, 170.2, 169.5, 169.1, 161.0, 114.7, 95.5, 79.9, 75.6, 65.5, 61.1, 60.9, 39.1, 39.1, 24.9, 22.9, 20.7, 20.6, 20.6. **IR** (ν, cm^{-1}) = 3363, 2840, 2766, 2136, 1691, 1568, 1326, 1182, 1156, 996. **HRMS** (ESI-TOF) calc. [$C_{21}H_{26}O_9Na^+$] 445.1469, found 445.1467.

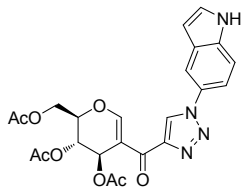


3r was synthesized according to General Procedure A and product **3r** was obtained as a yellow oil (101 mg, 0.14 mmol, 70%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.07 (s, 2H), 7.61 (d, *J* = 2.6 Hz, 4H), 5.95 – 5.73 (m, 2H), 5.29 – 5.10 (m, 2H), 4.77 – 4.58 (m, 2H), 4.58 – 4.46 (m, 2H), 4.23 (dd, *J* = 9.7, 5.6 Hz, 2H), 2.25 – 1.97 (m, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.0, 170.2, 169.3, 169.1, 161.2, 132.8, 122.0, 114.9, 89.0, 87.0, 75.8, 65.5, 61.0, 60.8, 20.7, 20.6, 20.6. **IR** (ν, cm^{-1}) = 2870, 2129, 1685, 1564, 1324, 1264, 1177, 1151, 989. **HRMS** (ESI-TOF) calc. [$C_{36}H_{34}O_{16}Na^+$] 745.1739, found 745.1735.

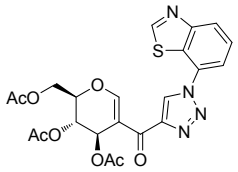


5a was synthesized according to General Procedure B and product **5a** was obtained as a yellow oil (61 mg, 0.13 mmol, 67%).^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.15 (s, 1H), 8.02 (s, 1H), 7.46 – 7.34 (m, 5H), 5.96 – 5.85 (m, 1H), 5.55 (d, *J* = 1.4 Hz, 1H), 5.30 (s, 2H), 4.64 (d, *J* = 5.3 Hz, 1H), 4.54 – 4.44 (m, 1H), 4.23 (dd, *J* = 12.2, 4.7 Hz, 1H), 2.19 – 2.05 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.3, 169.3, 168.4, 168.2, 161.0, 132.6, 128.3, 128.1,

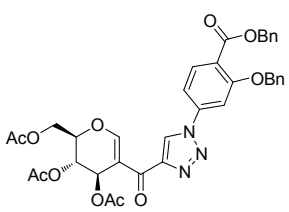
127.3, 126.5, 126.5, 111.5, 73.6, 64.9, 60.5, 60.1, 53.4, 19.7, 19.6, 19.6. IR (ν, cm^{-1}) = 3261, 2866, 2836, 1680, 1560, 1475, 1324, 1179, 1149, 989, 706. HRMS (ESI-TOF) calc. [$C_{22}H_{23}N_3O_8Na^+$] 480.1377, found 480.1375.



5b was synthesized according to General Procedure B and product **5b** was obtained as a yellow oil (69 mg, 0.14 mmol, 72%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 9.15 (s, 1H), 8.67 (s, 1H), 8.45 (s, 1H), 7.87 (s, 1H), 7.55 – 7.42 (m, 2H), 7.30 (d, *J* = 2.8 Hz, 1H), 6.68 – 6.52 (m, 1H), 5.97 – 5.84 (m, 1H), 5.23 (t, *J* = 2.9 Hz, 1H), 4.65 – 4.56 (m, 1H), 4.46 (m, 1H), 4.21 (m, 1H), 2.06 – 1.97 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 181.5, 170.3, 169.5, 169.3, 162.0, 148.1, 135.90, 128.1, 126.7, 126.2, 126.2, 115.5, 113.5, 112.6, 112.1, 103.5, 74.7, 66.0, 61.6, 61.2, 20.8, 20.7, 20.6. **IR** (ν, cm^{-1}) = 2834, 2862, 2779, 1682, 1560, 1475, 1460, 1324, 1162, 1011, 989, 700. **HRMS** (ESI-TOF) calc. [$C_{23}H_{22}N_4O_8Na^+$] 505.1330, found 505.1329.

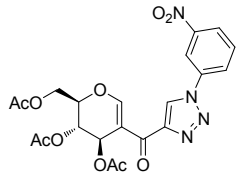


5c was synthesized according to General Procedure B and product **5c** was obtained as a yellow oil (70 mg, 0.14 mmol, 70%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 9.13 (s, 1H), 9.07 (s, 1H), 8.58 (s, 1H), 8.37 (t, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 5.93 – 5.89 (m, 1H), 5.24 – 5.22 (m, 1H), 4.64 – 4.57 (m, 1H), 4.47 (dd, *J* = 12.0, 7.8 Hz, 1H), 4.20 (dd, *J* = 12.0, 4.5 Hz, 1H), 2.08 – 1.94 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 181.1, 170.3, 169.4, 169.2, 162.2, 162.1, 156.2, 148.6, 135.2, 126.0, 124.9, 120.0, 119.3, 115.1, 112.7, 74.8, 65.9, 61.5, 61.1, 20.8, 20.7, 20.6. **IR** (ν, cm^{-1}) = 2985, 2864, 2037, 1687, 1562, 1186, 1154, 994, 838, 855. **HRMS** (ESI-TOF) calc. [$C_{22}H_{20}N_4O_8SNa^+$] 523.0894, found 523.0890.

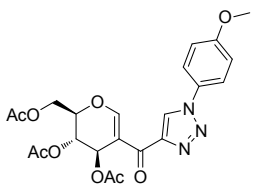


5d was synthesized according to General Procedure B and product **5d** was obtained as a yellow oil (89 mg, 0.13 mmol, 65%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 9.09 (s, 1H), 8.48 (s, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.49 (s, 1H), 7.40 – 7.21 (m, 11H), 6.28 (d, *J* = 3.5 Hz, 1H), 5.98 – 5.85 (m, 1H), 5.29 (s, 2H), 5.18 (s, 2H), 4.68 – 4.54 (m, 1H), 4.50 – 4.41 (m, 1H), 4.18 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.10 – 1.92 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 201.9, 180.2, 170.4, 169.8, 169.1, 164.9, 163.5, 159.3,

139.6, 135.6, 135.5, 133.7, 128.7, 128.5, 128.2, 128.2, 128.2, 127.2, 125.6, 121.5, 113.7, 112.7, 111.6, 105.9, 71.8, 71.1, 67.1, 65.3, 61.1, 60.5, 20.8, 20.6, 20.5. **IR** (ν, cm^{-1}) = 2967, 2931, 1687, 1559, 1195, 1169, 1046, 998. **HRMS** (ESI-TOF) calc. [$C_{36}H_{33}N_3O_{11}Na^+$] 706.2007, found 706.2004.

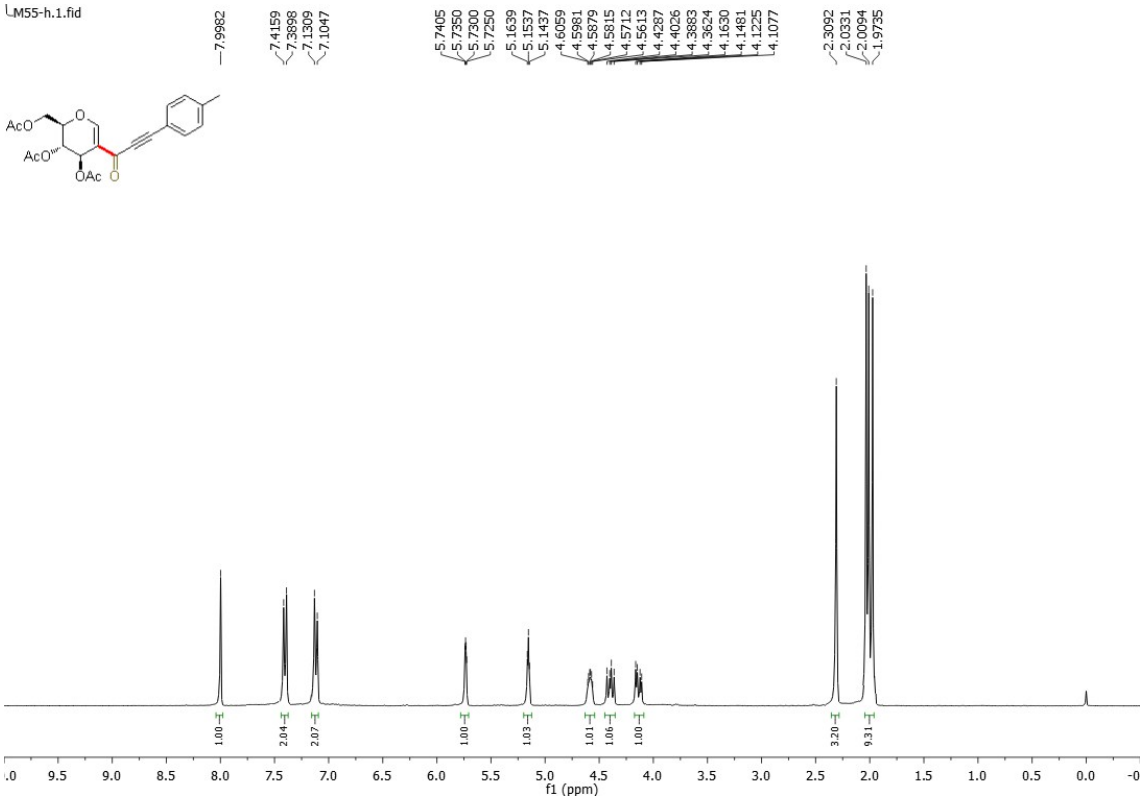


5e was synthesized according to General Procedure B and product **5e** was obtained as a yellow oil (57 mg, 0.12 mmol, 58%).**^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.07 (s, 1H), 8.69 – 8.59 (m, 2H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.74 (t, *J* = 8.1 Hz, 1H), 6.28 (d, *J* = 3.5 Hz, 1H), 5.92 – 5.83 (m, 1H), 4.66 – 4.57 (m, 1H), 4.52 – 4.41 (m, 1H), 4.19 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.09 – 1.98 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 180.1, 170.4, 169.8, 169.1, 163.6, 137.0, 131.2, 126.0, 125.7, 123.9, 115.8, 115.8, 113.7, 112.7, 74.9, 71.8, 61.5, 61.1, 20.7, 20.7, 20.6. **IR** (ν, cm^{-1}) = 2868, 1687, 1562, 1486, 1309, 1188, 1171, 994, 717. **HRMS** (ESI-TOF) calc. [$C_{21}H_{20}N_4O_{10}Na^+$] 511.1072, found 511.1071.

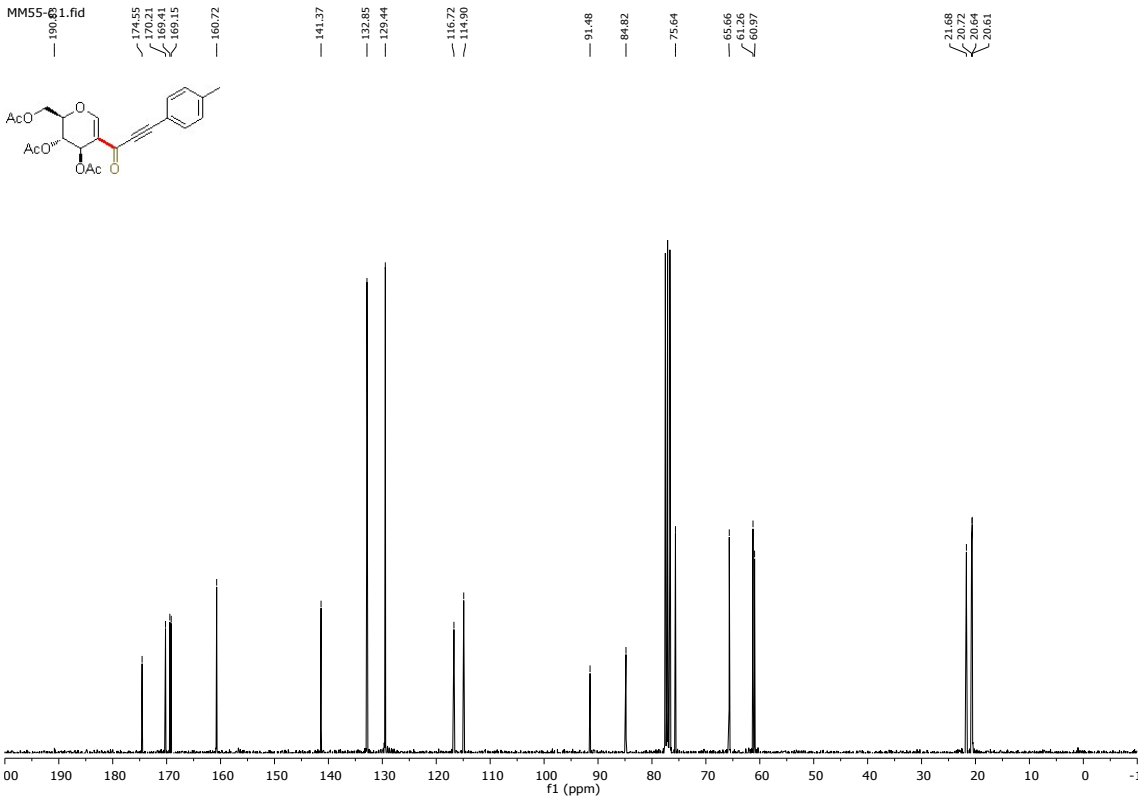


5f was synthesized according to General Procedure B and product **5f** was obtained as a yellow oil (81 mg, 0.17 mmol, 86%).**^{1}H NMR** (300 MHz, $CDCl_3$): δ = 9.11 (s, 1H), 8.41 (s, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 5.89 (t, 2H), 5.21 (t, *J* = 3.1 Hz, 1H), 4.64 – 4.55 (m, 1H), 4.44 (dd, *J* = 12.1, 7.7 Hz, 1H), 4.19 (dd, *J* = 12.0, 4.8 Hz, 3H), 2.08 – 1.94 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 181.3, 170.3, 169.4, 169.2, 162.0, 160.3, 129.6, 127.8, 125.7, 122.3, 115.0, 112.6, 74.7, 65.9, 61.6, 61.1, 55.6, 20.7, 20.7, 20.6. **IR** (ν, cm^{-1}) = 2902, 2875, 1687, 1564, 1471, 1326, 1262, 1184, 1153, 998, 838. **HRMS** (ESI-TOF) calc. [$C_{22}H_{23}N_3O_9Na^+$] 496.1327, found 496.1329.

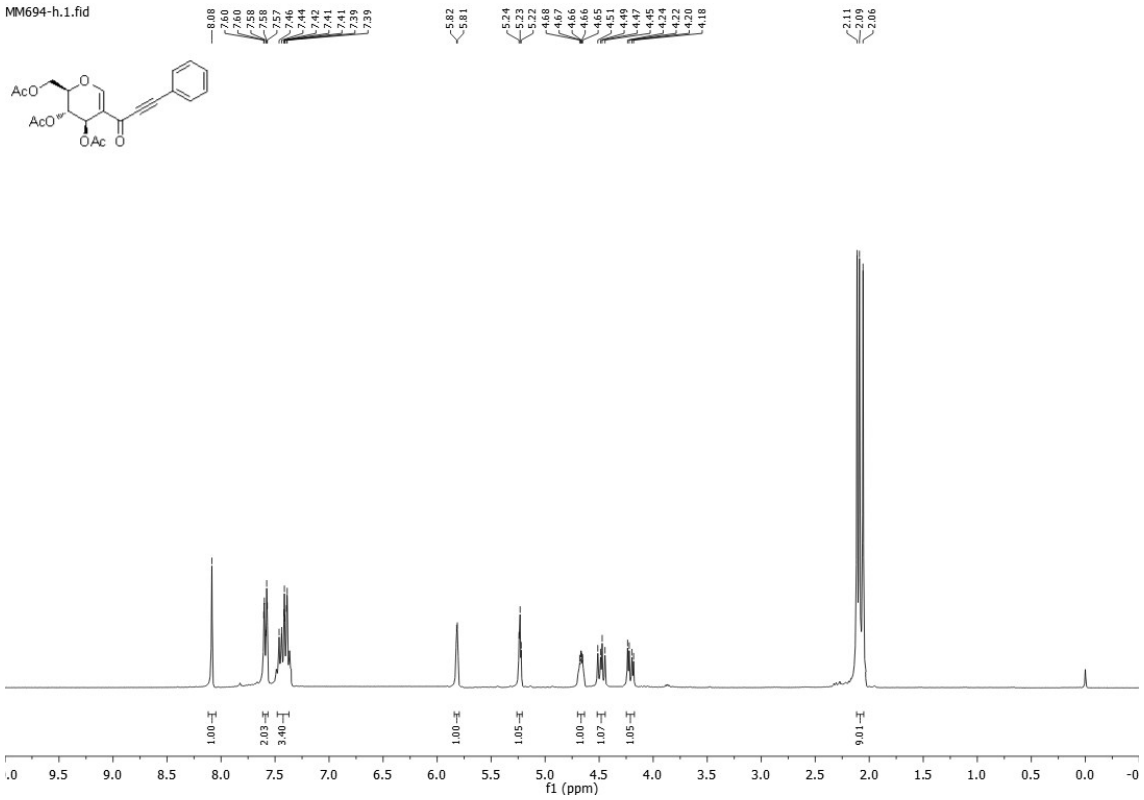
5. ^{1}H and ^{13}C spectra



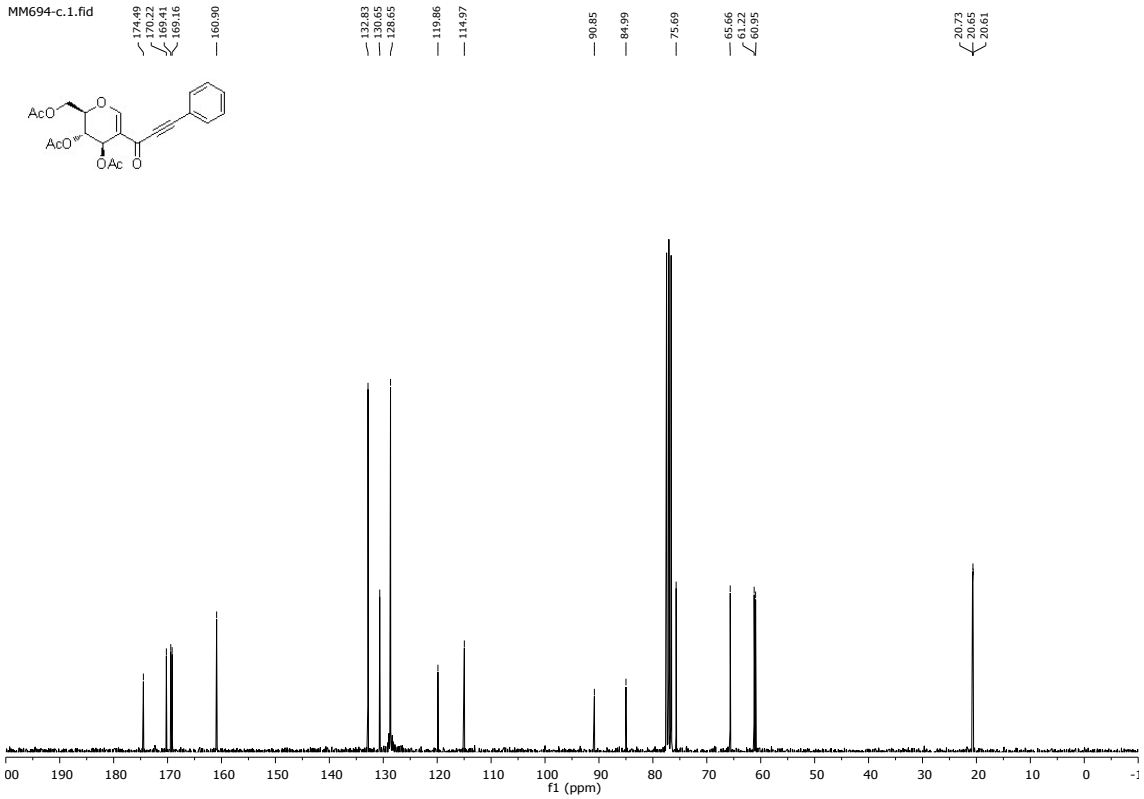
^{1}H NMR (300 MHz, $CDCl_3$) **3a**.



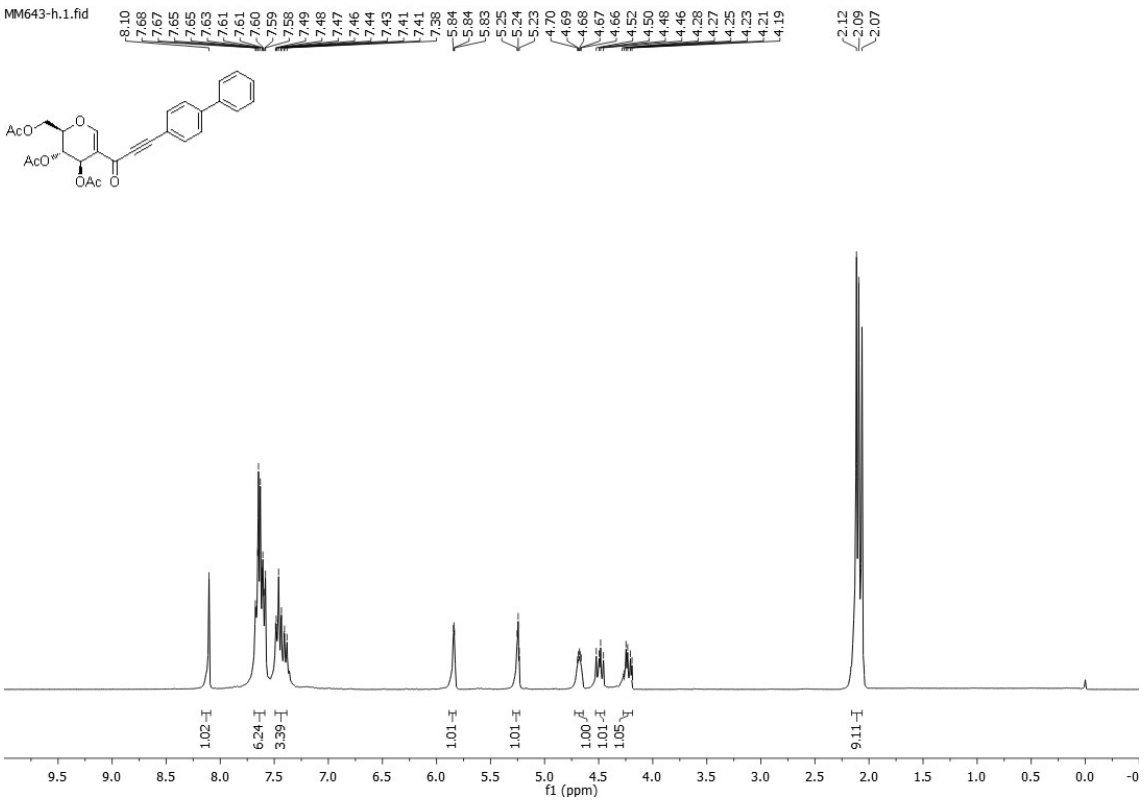
^{13}C NMR (75 MHz, $CDCl_3$) **3a**.



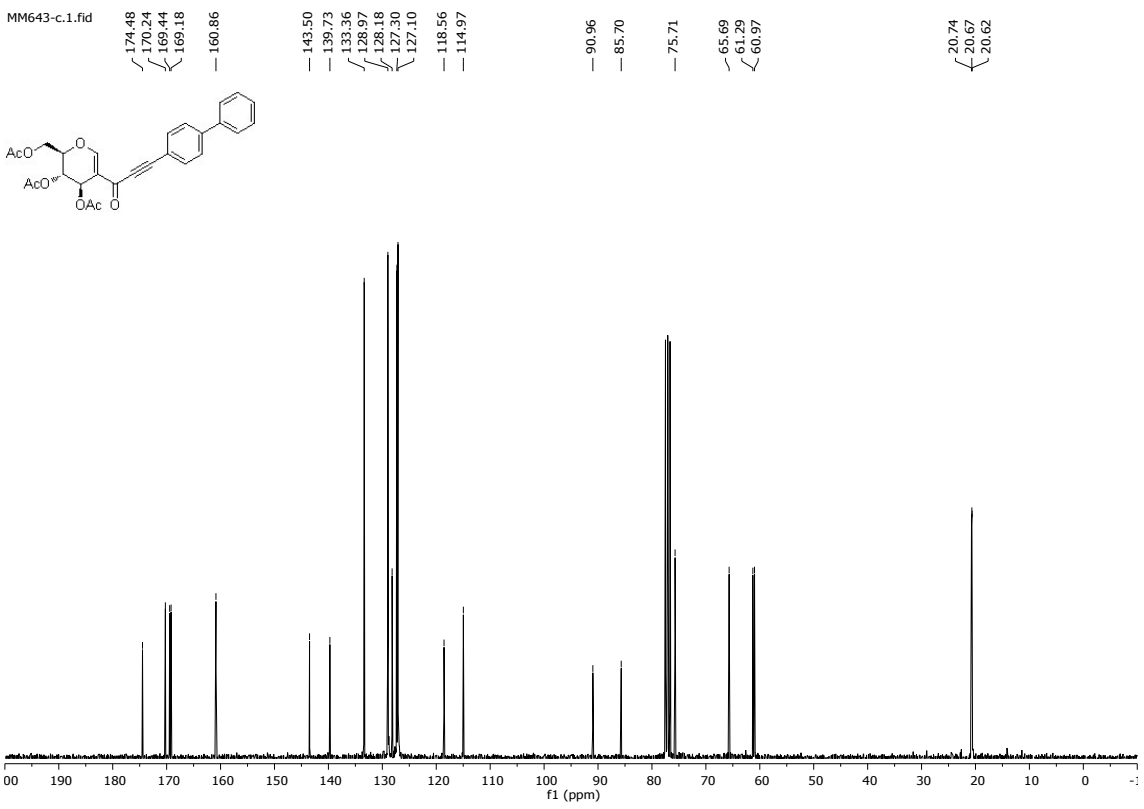
^{1}H NMR (300 MHz, $CDCl_3$) **3b**.



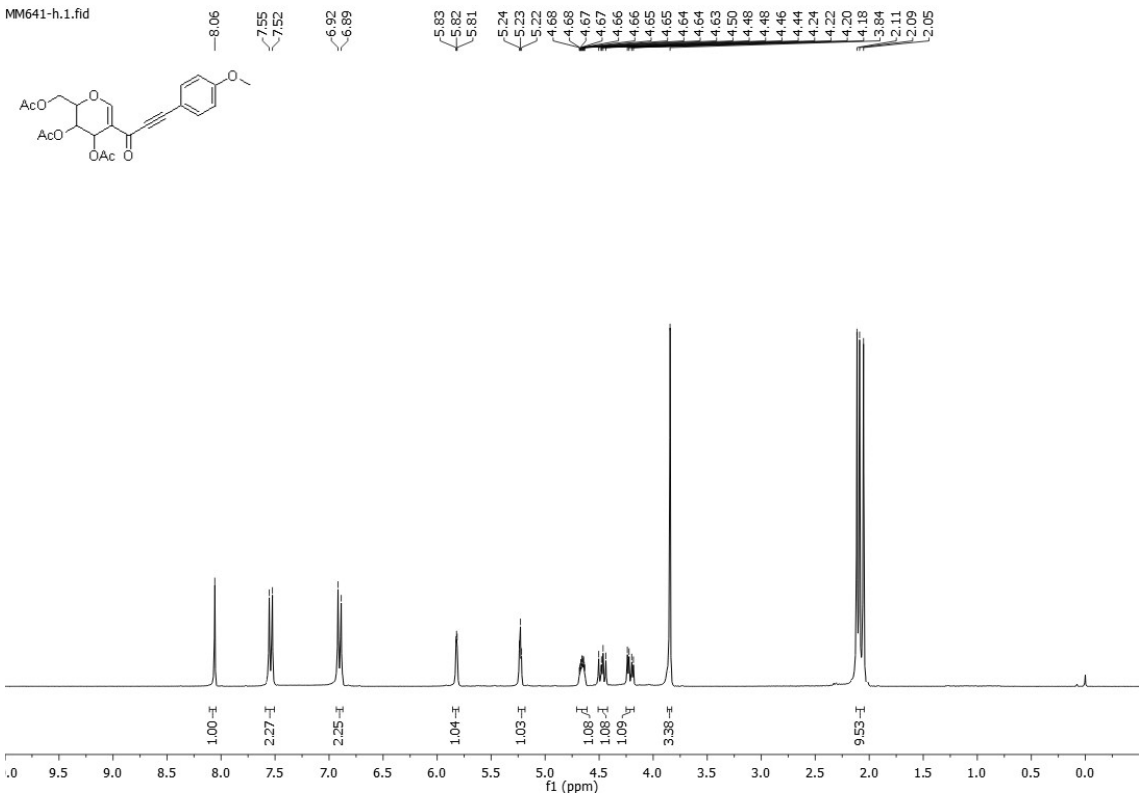
^{13}C NMR (75 MHz, $CDCl_3$) **3b**.



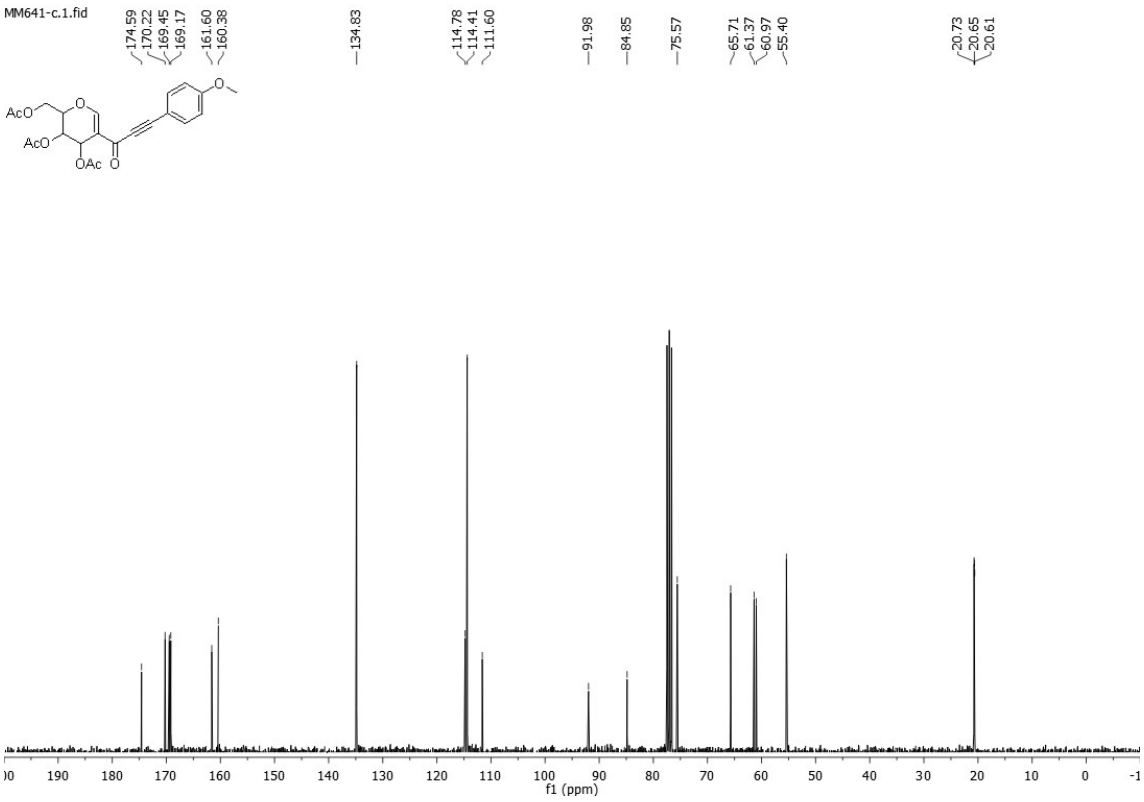
^{1}H NMR (300 MHz, $CDCl_3$) **3c**.



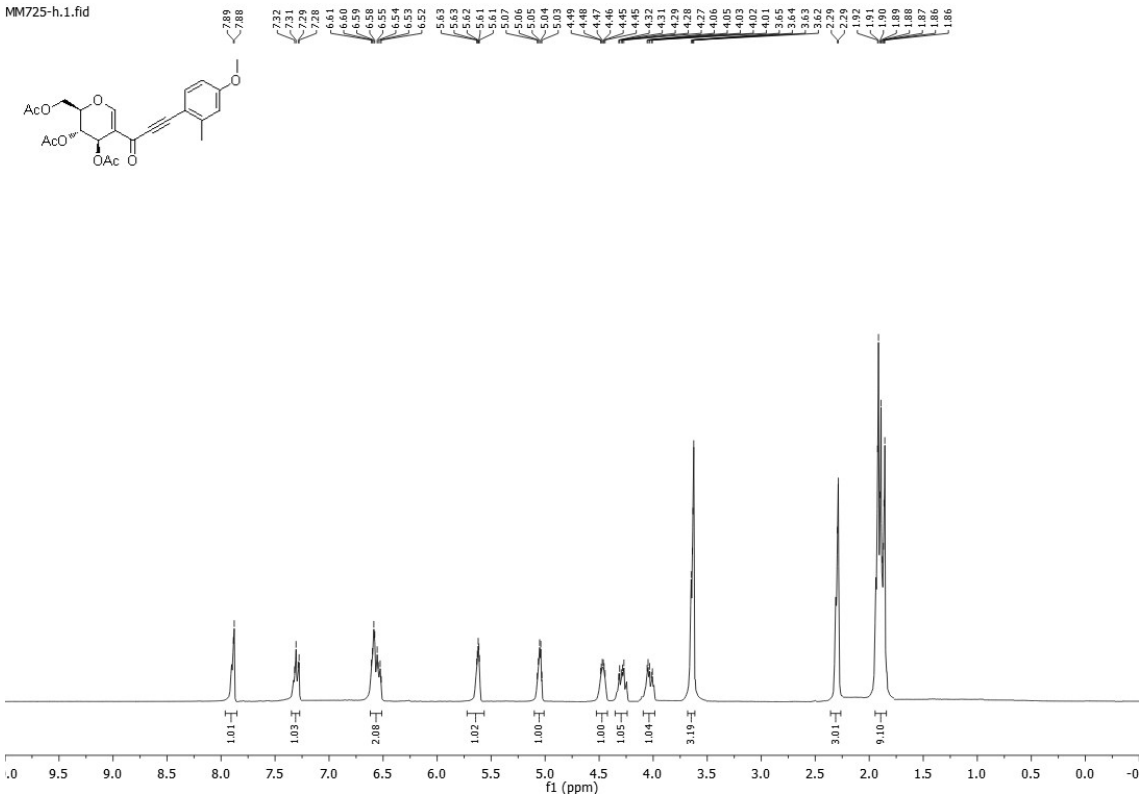
^{13}C NMR (75 MHz, $CDCl_3$) **3c**.



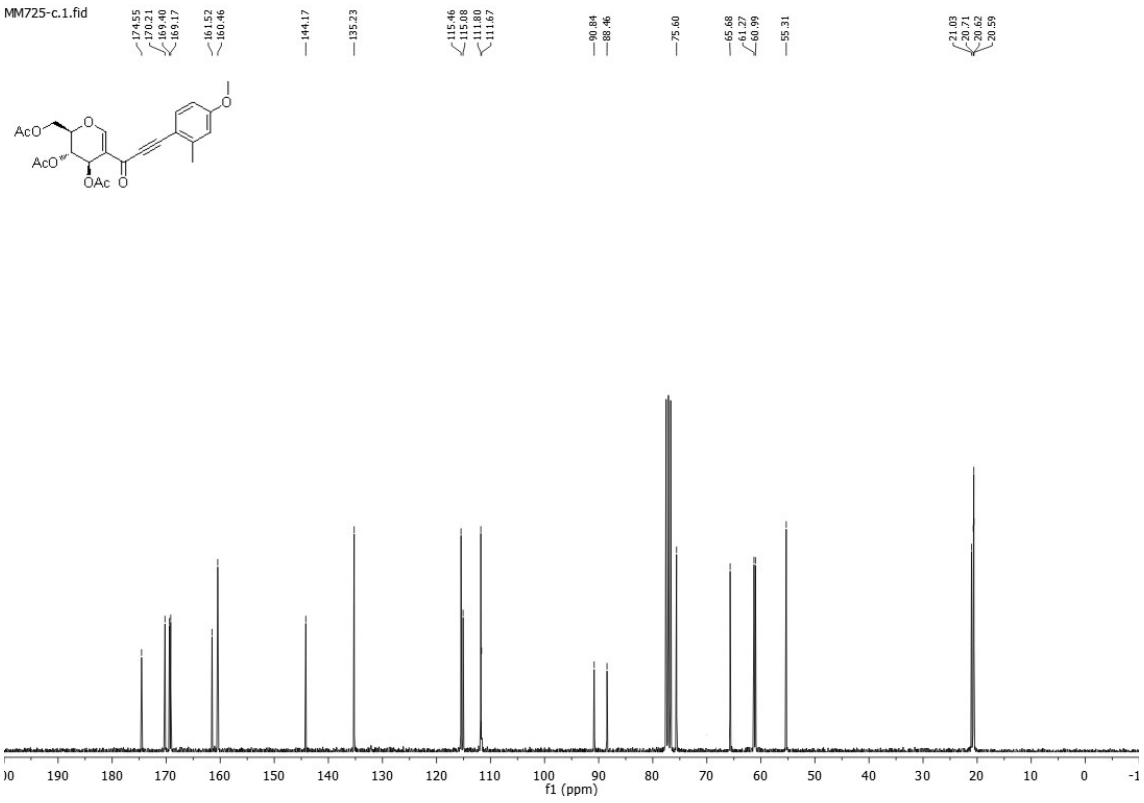
^{1}H NMR (300 MHz, $CDCl_3$) **3d**.



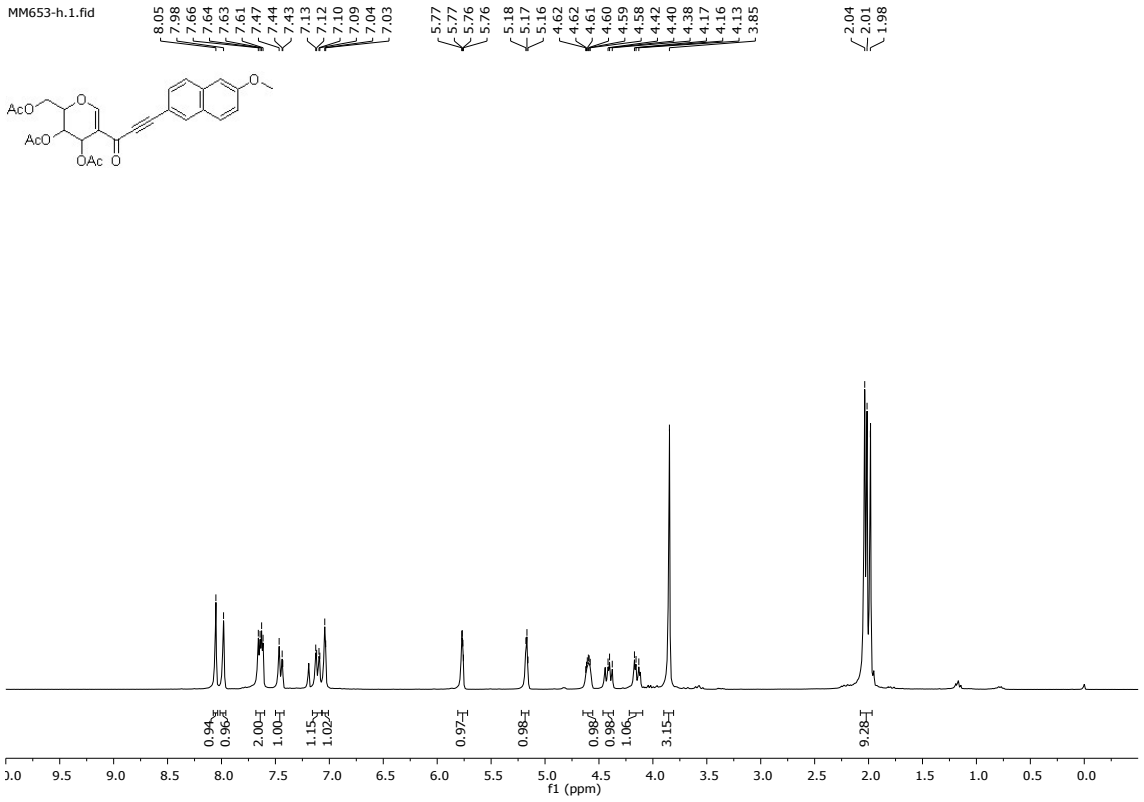
^{13}C NMR (75 MHz, $CDCl_3$) **3d**.



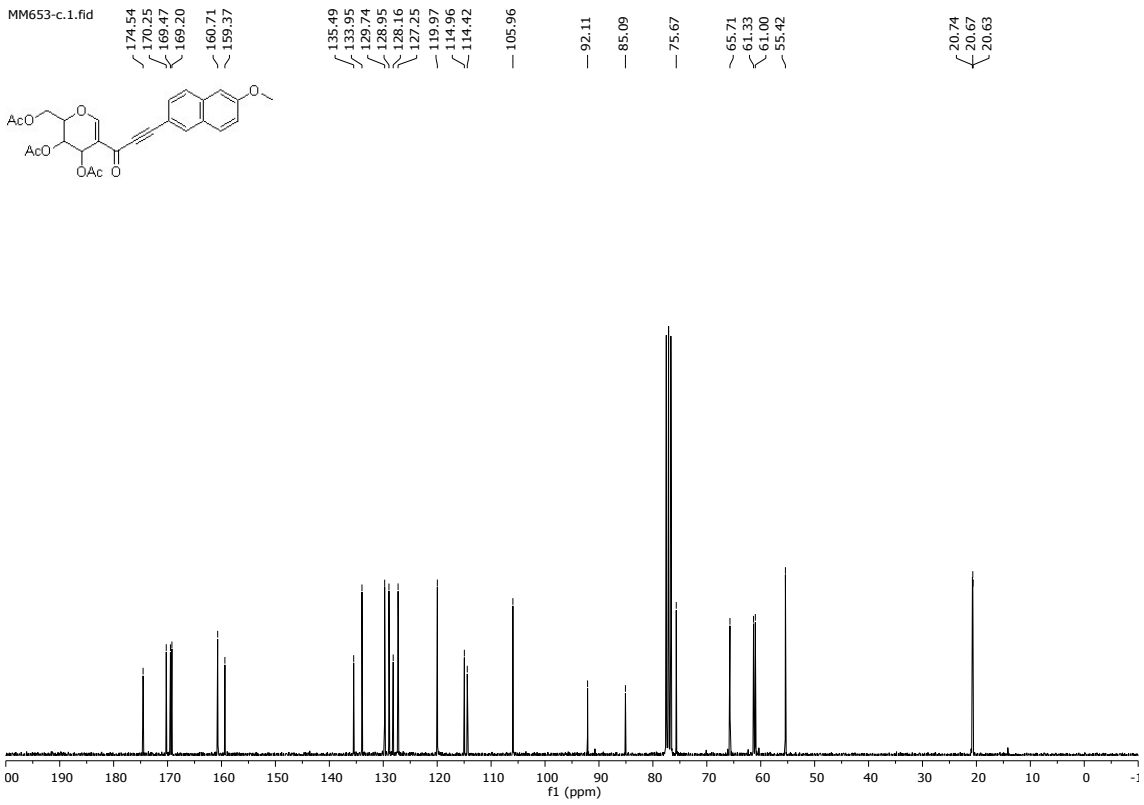
^{1}H NMR (300 MHz, $CDCl_3$) **3e**.



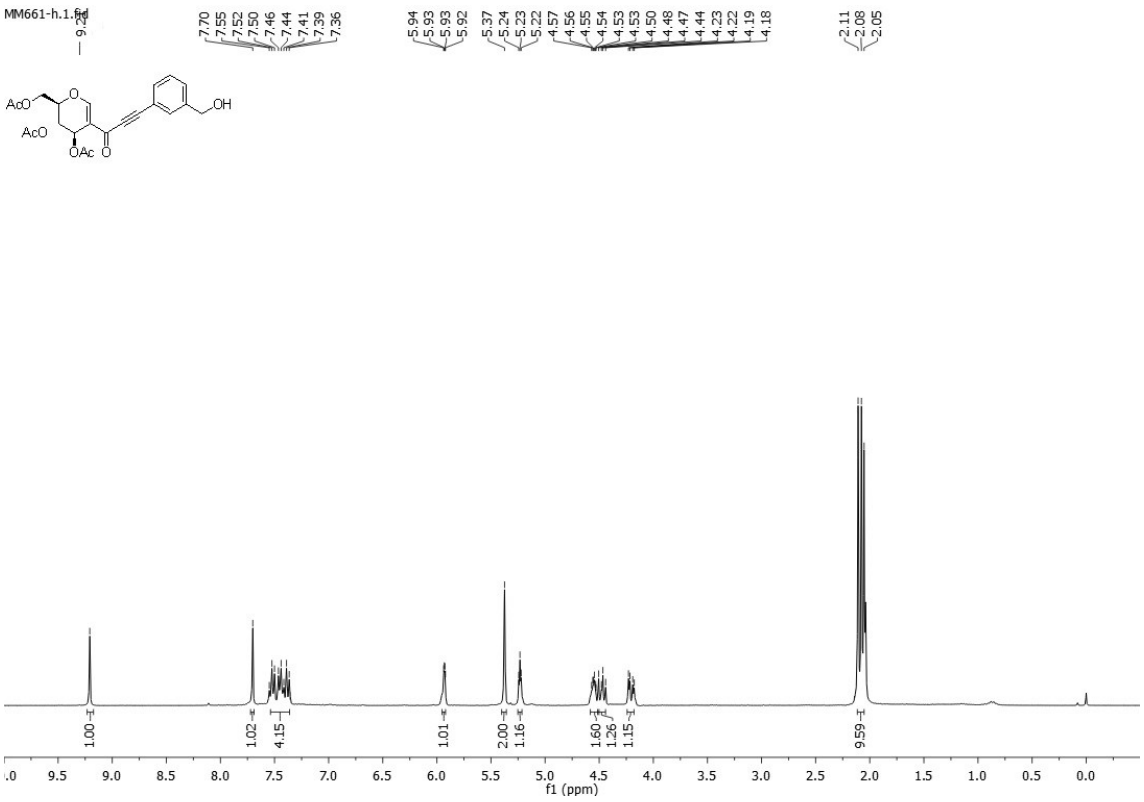
^{13}C NMR (75 MHz, $CDCl_3$) **3e**.



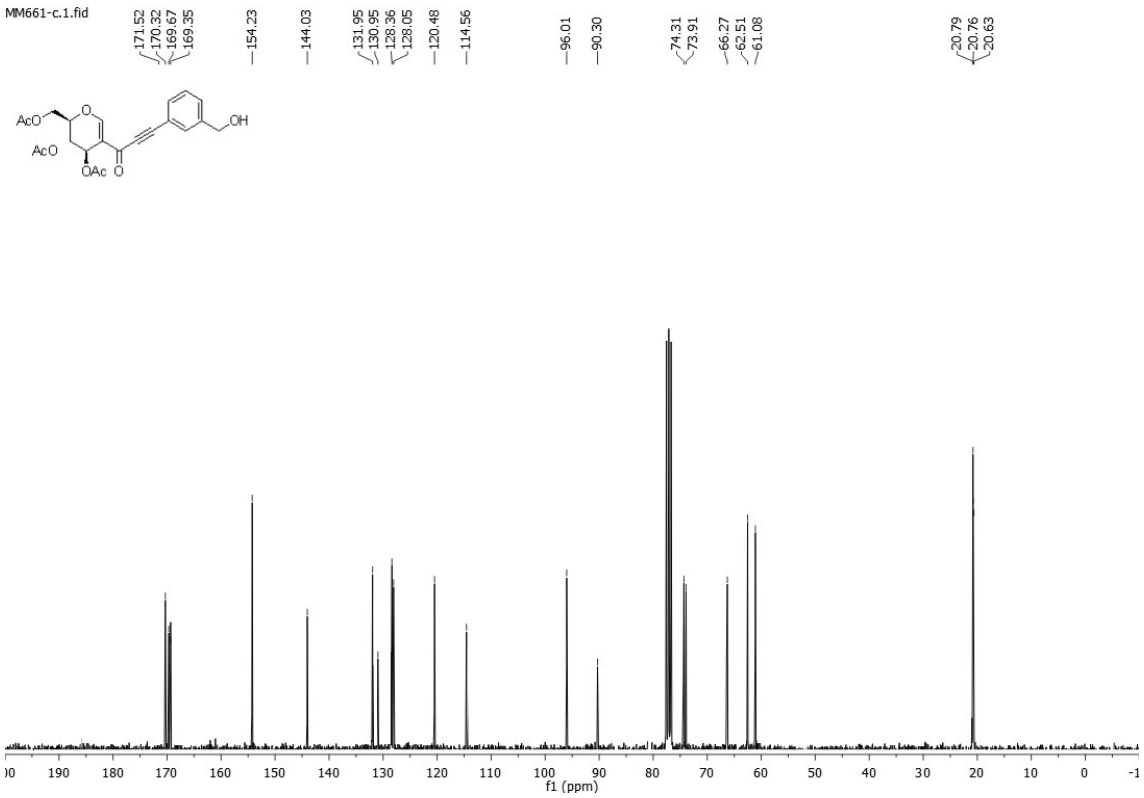
^{1}H NMR (300 MHz, $CDCl_3$) **3f**.



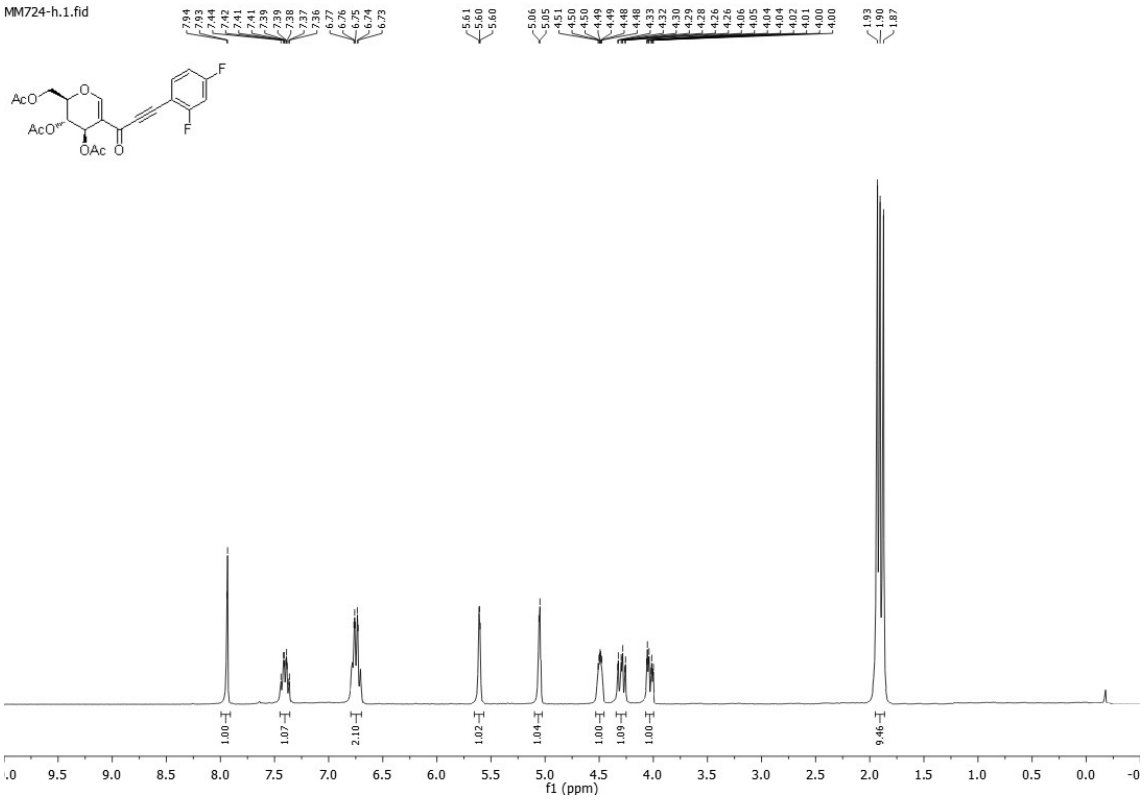
^{13}C NMR (75 MHz, $CDCl_3$) **3f**.



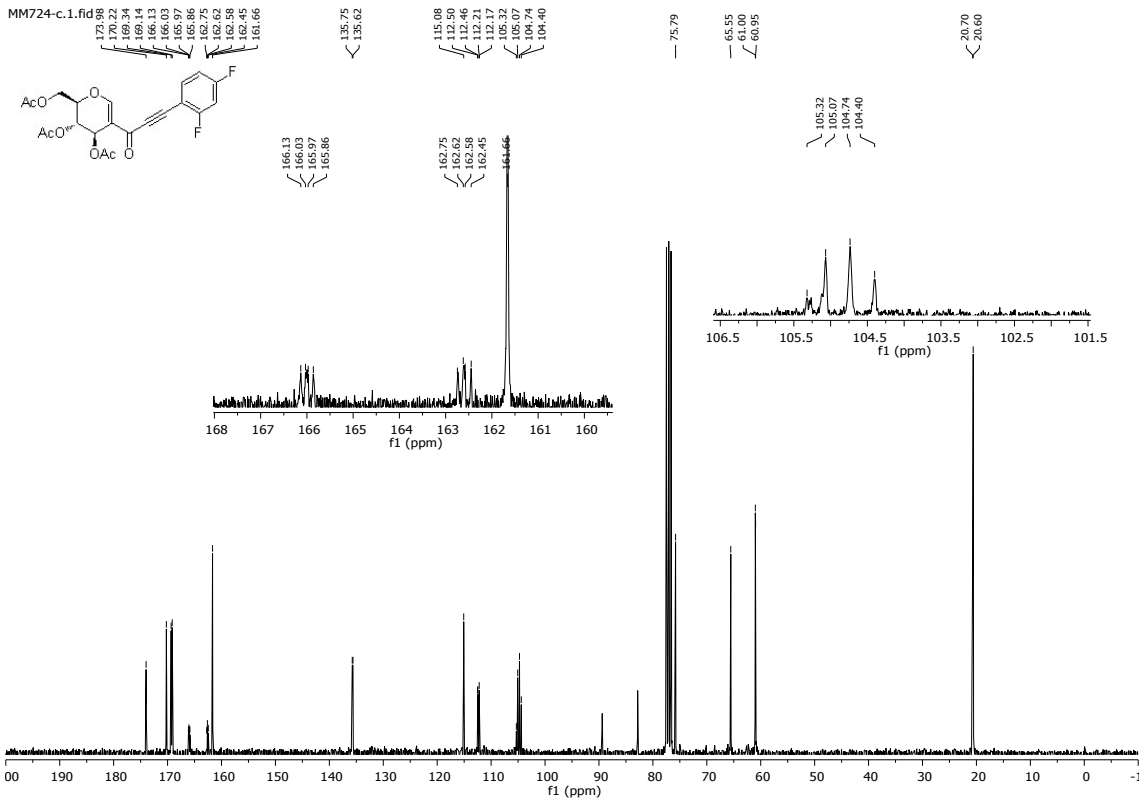
^{1}H NMR (300 MHz, $CDCl_3$) **3g**.



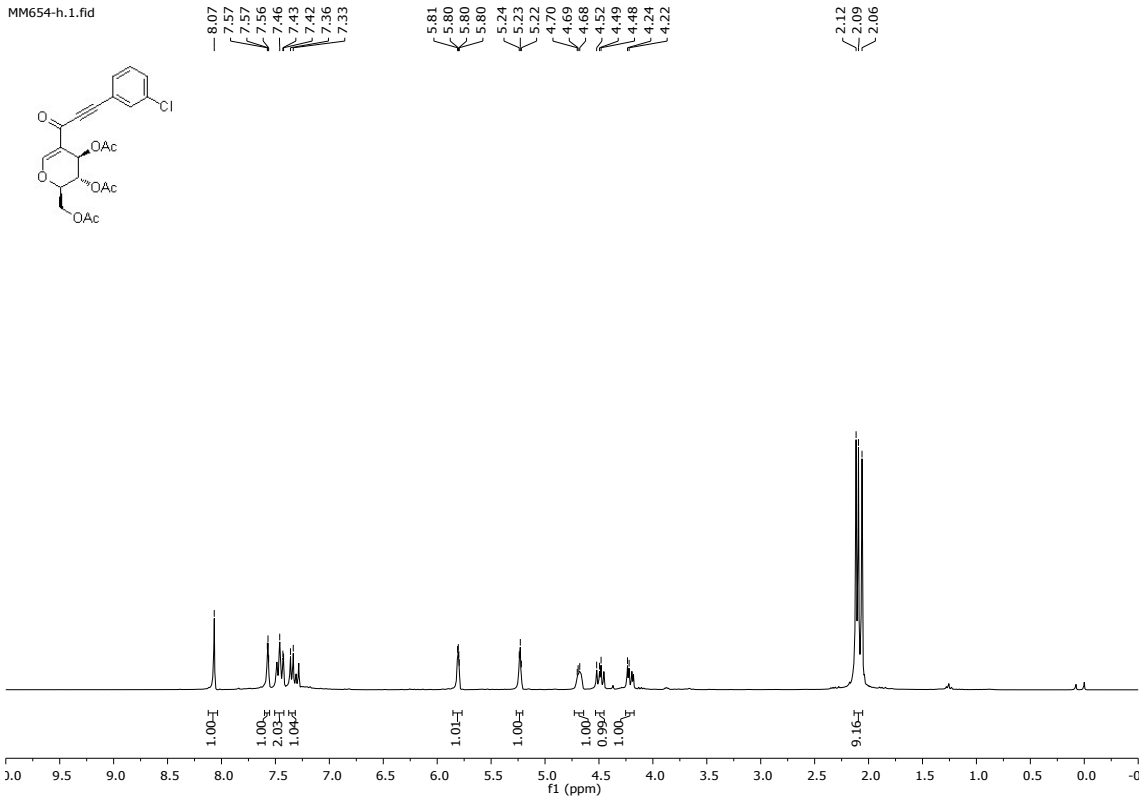
^{13}C NMR (75 MHz, $CDCl_3$) **3g**.



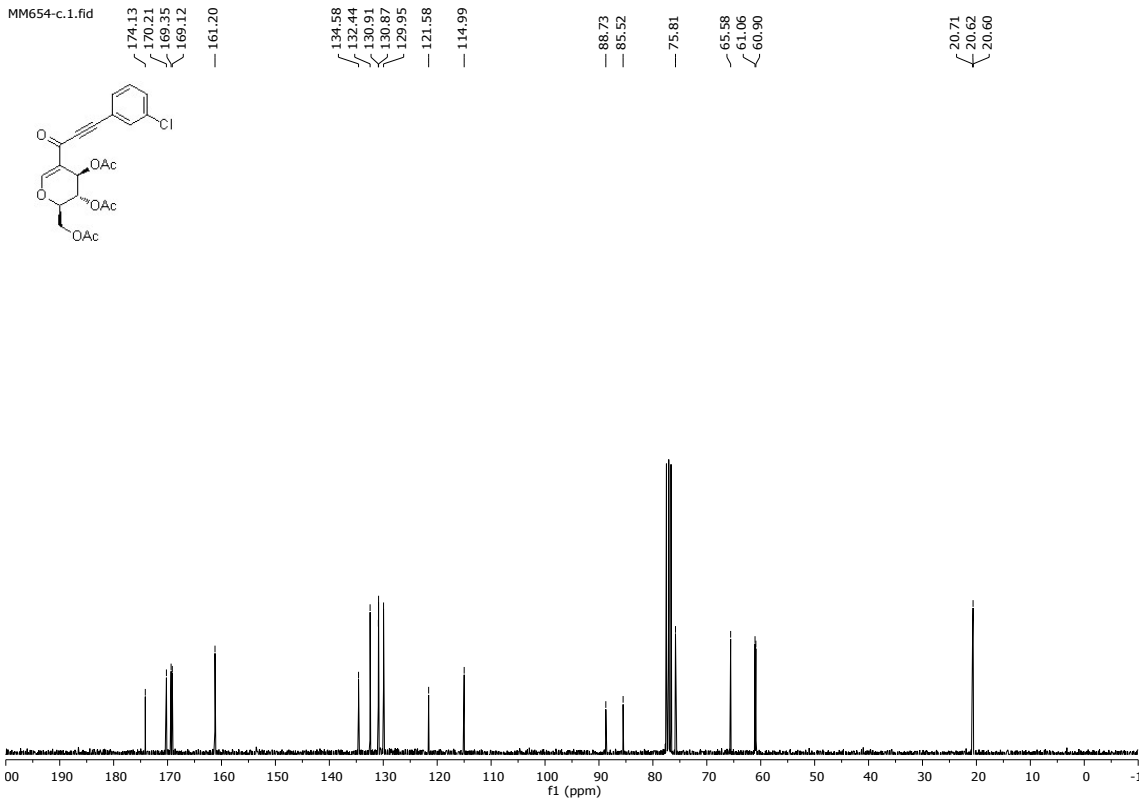
^{1}H NMR (300 MHz, $CDCl_3$) **3h**.



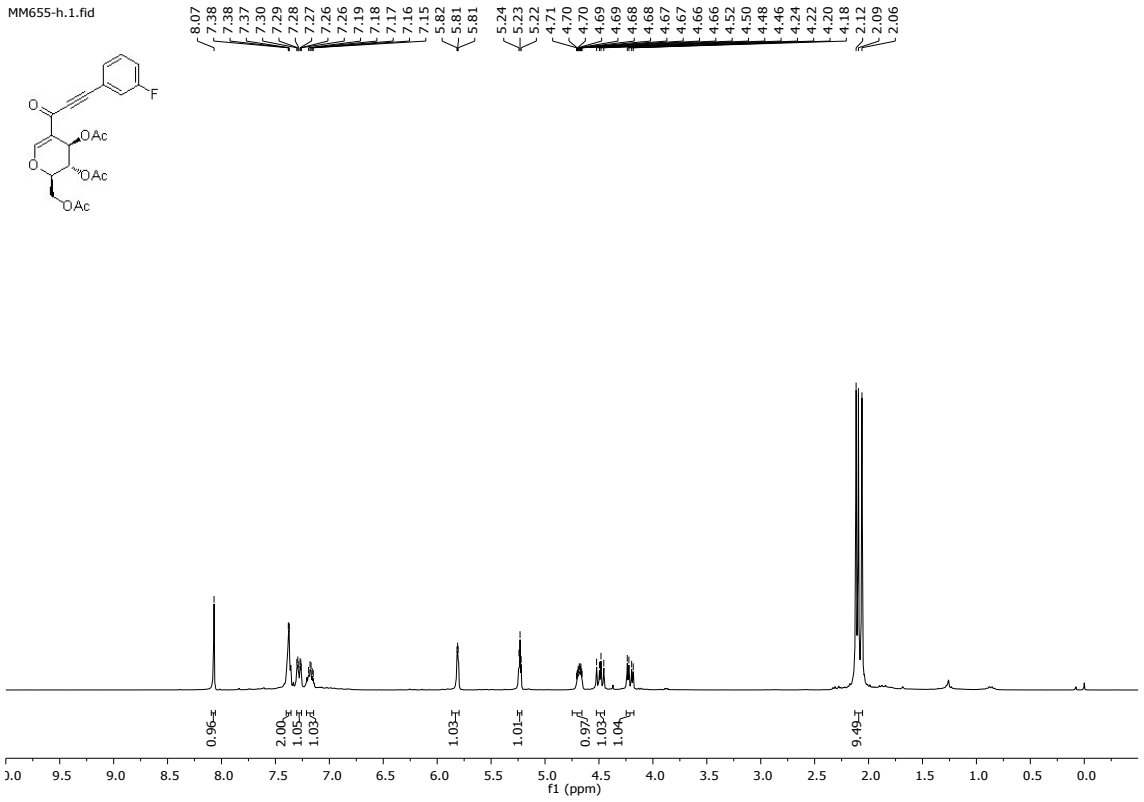
^{13}C NMR (75 MHz, $CDCl_3$) **3h**.



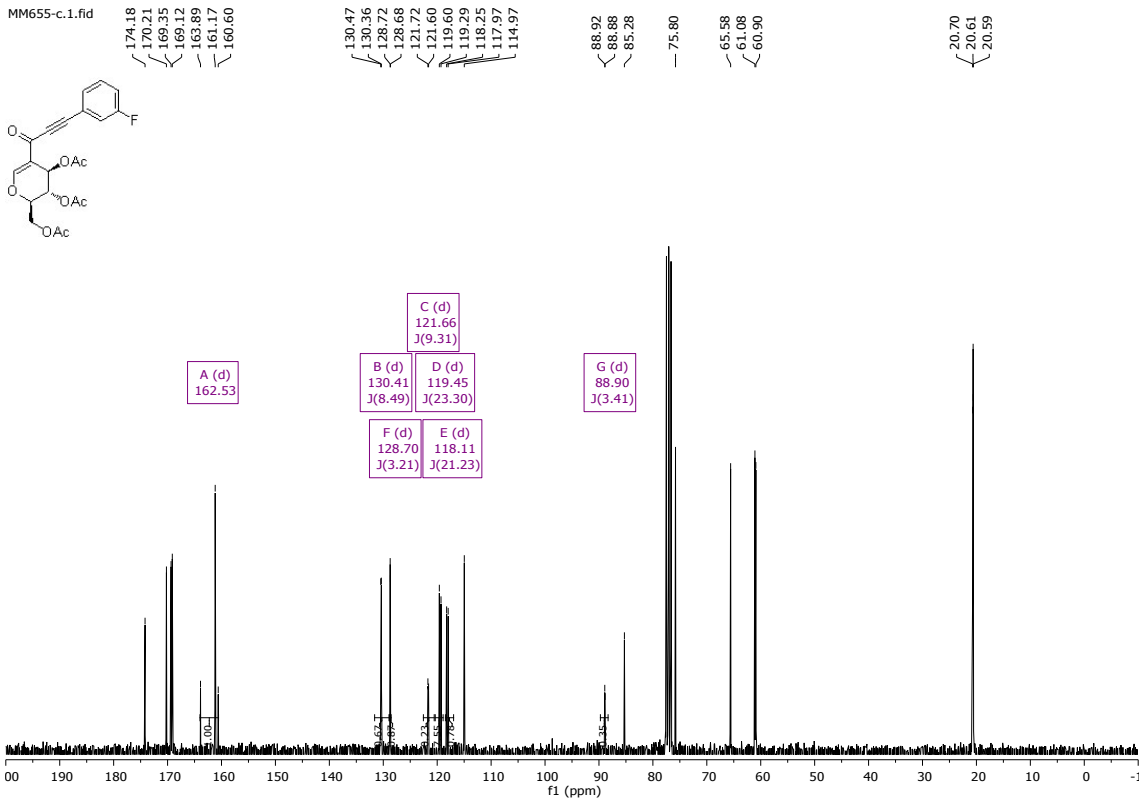
^{1}H NMR (300 MHz, $CDCl_3$) **3i**.



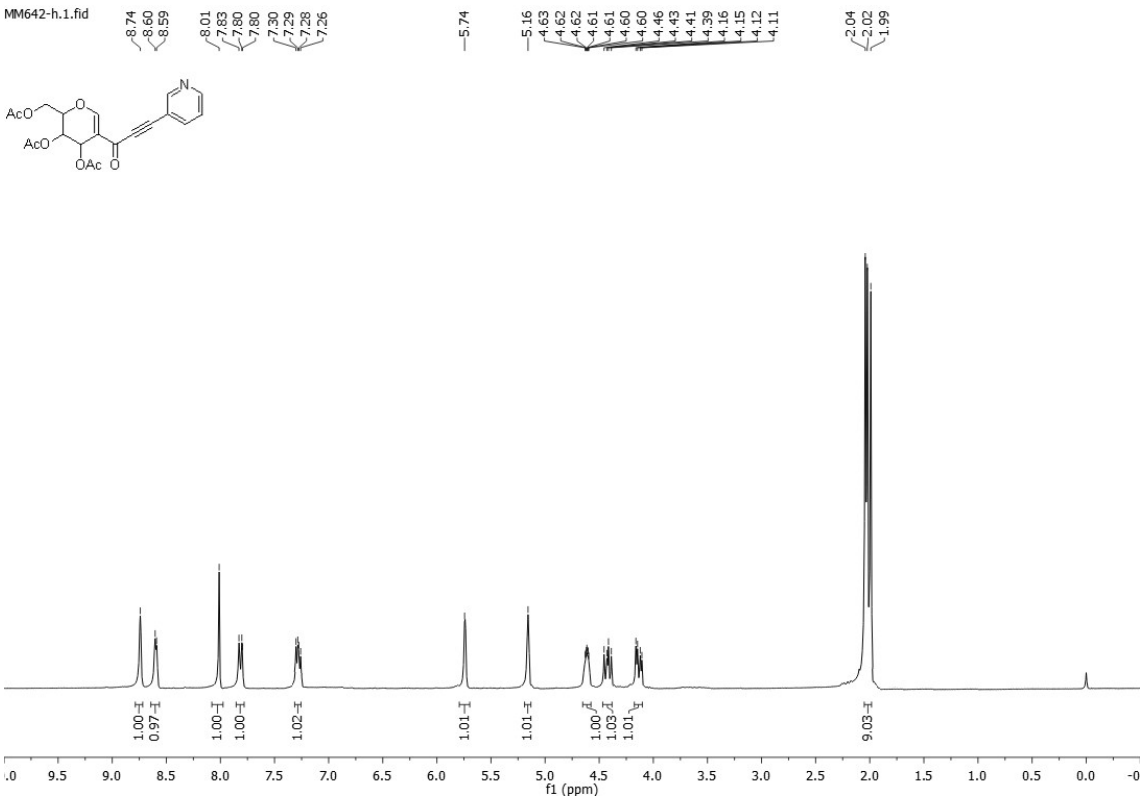
^{13}C NMR (75 MHz, $CDCl_3$) **3i**.



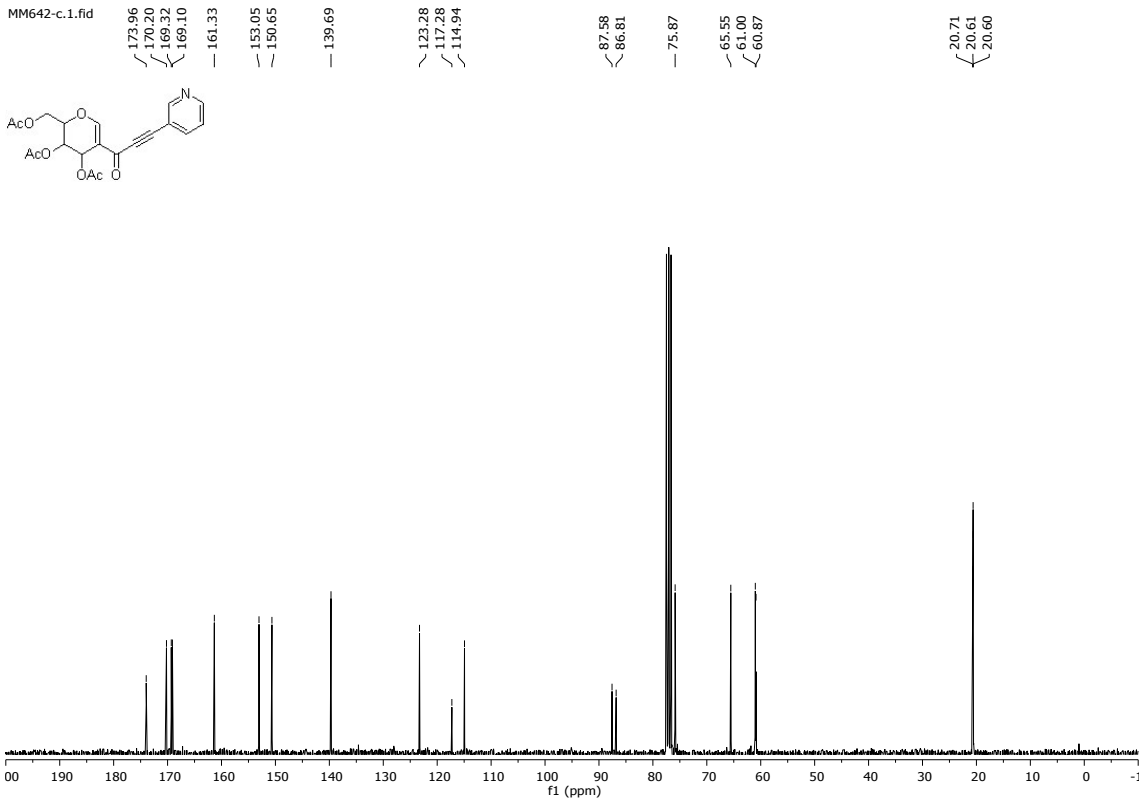
^{1}H NMR (300 MHz, $CDCl_3$) **3j**.



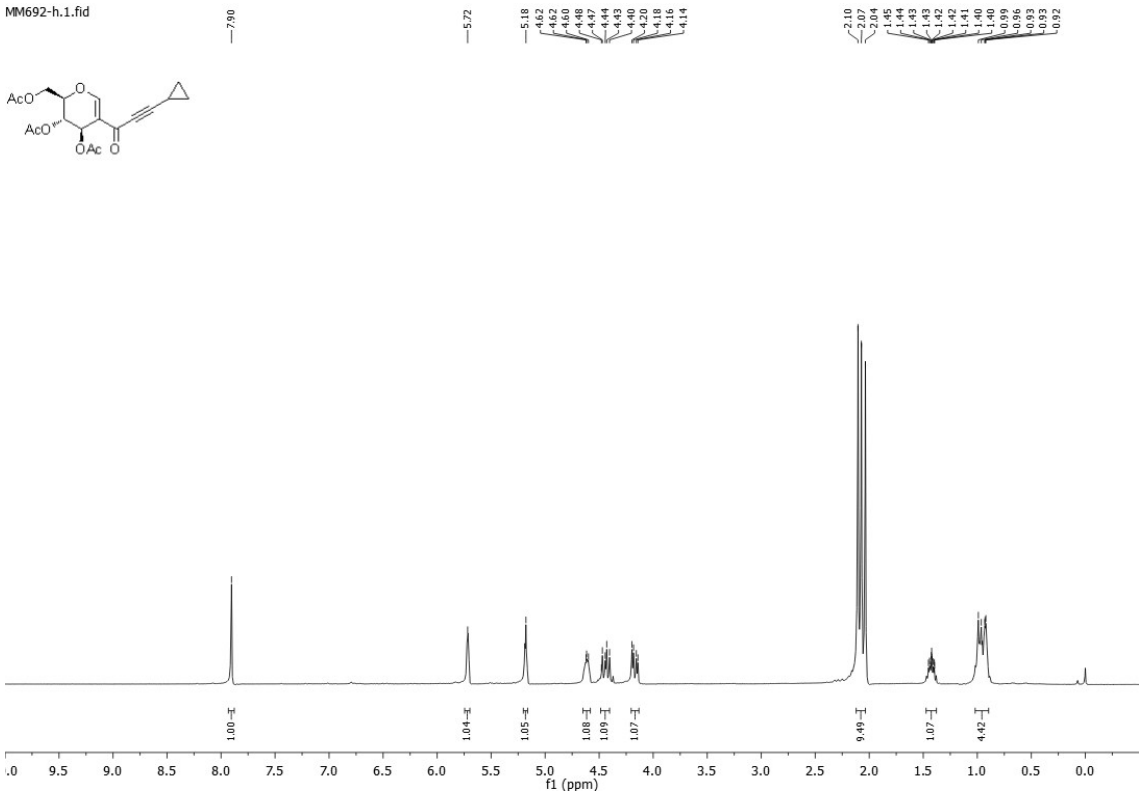
^{13}C NMR (75 MHz, $CDCl_3$) **3j**.



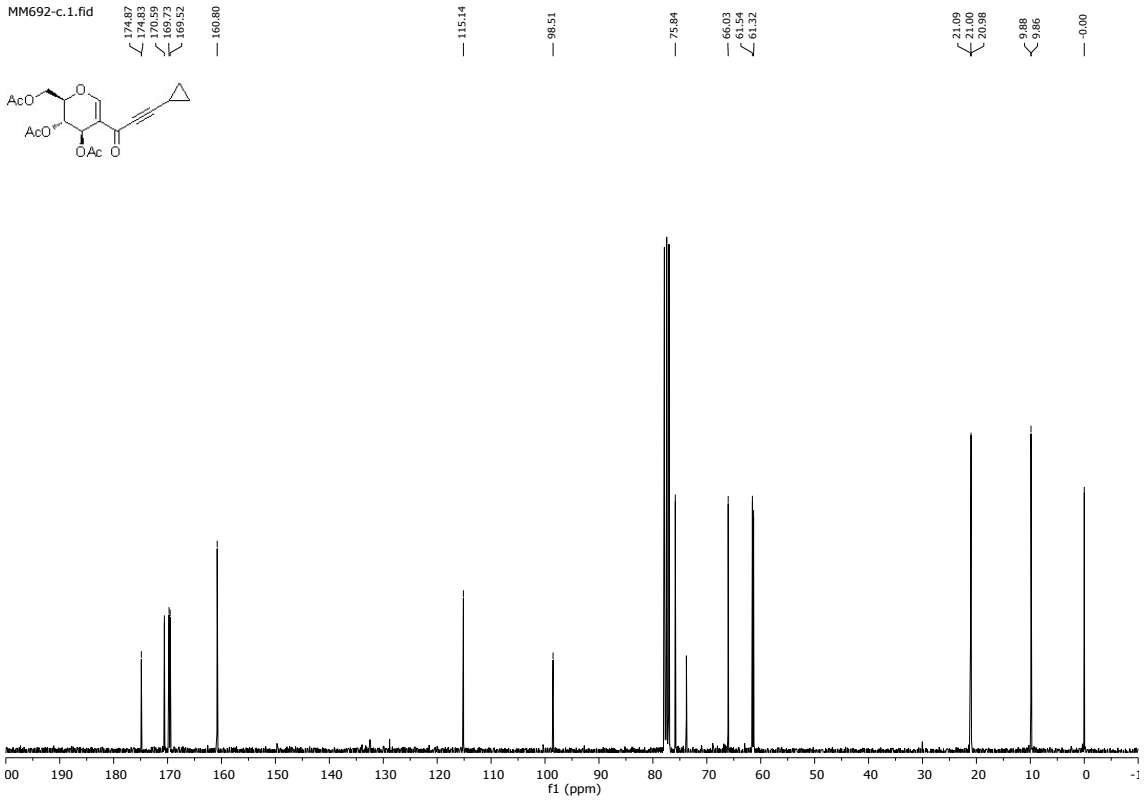
^{1}H NMR (300 MHz, $CDCl_3$) **3k**.



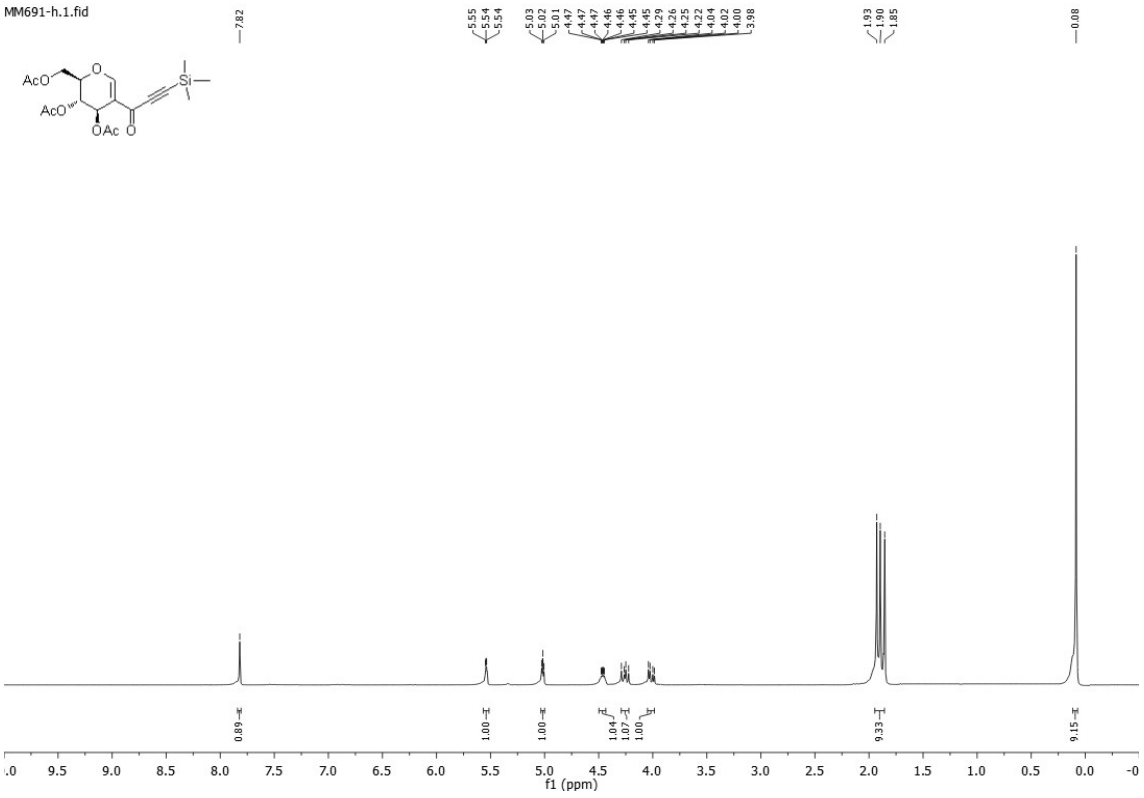
^{13}C NMR (75 MHz, $CDCl_3$) **3k**.



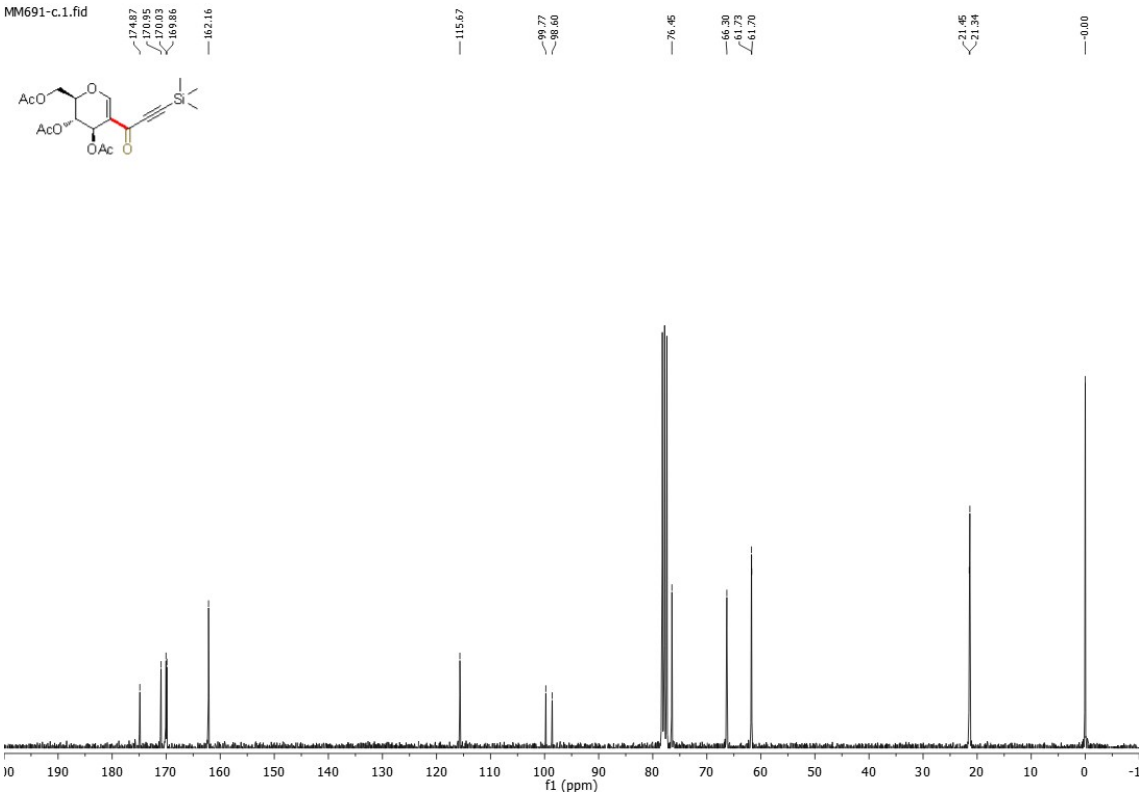
^{1}H NMR (300 MHz, $CDCl_3$) **3l**.



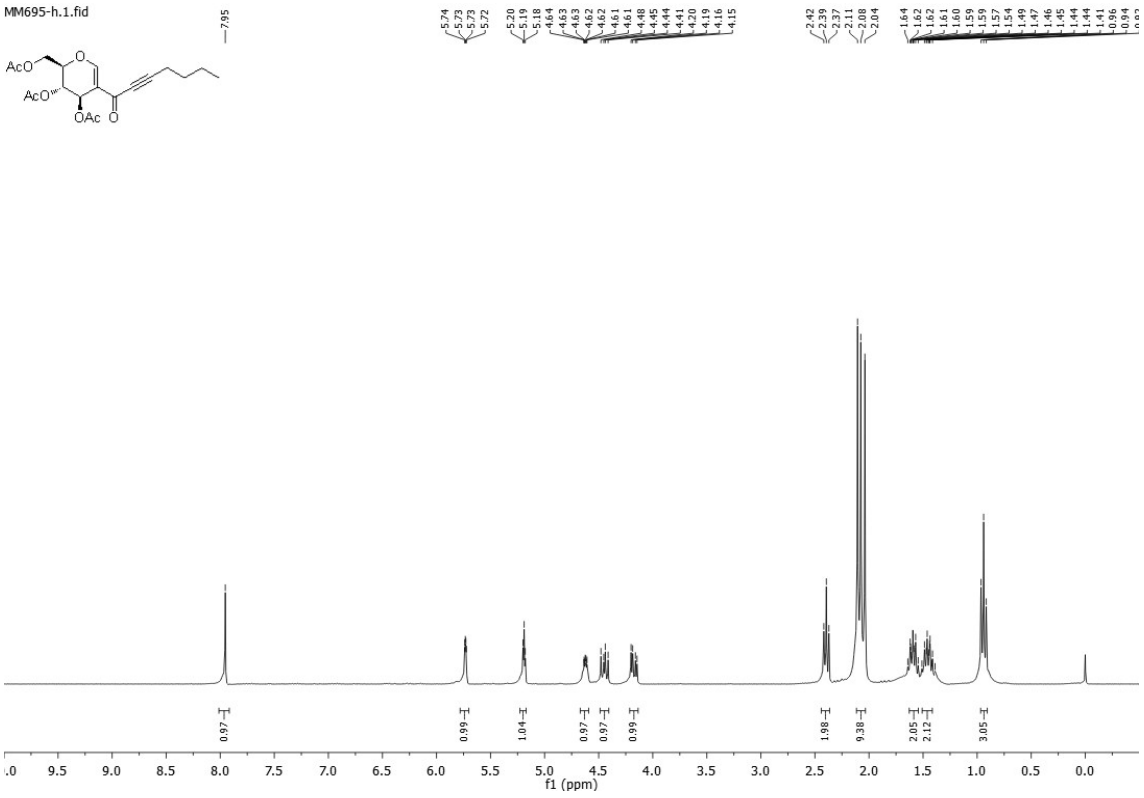
^{13}C NMR (75 MHz, $CDCl_3$) **3l**.



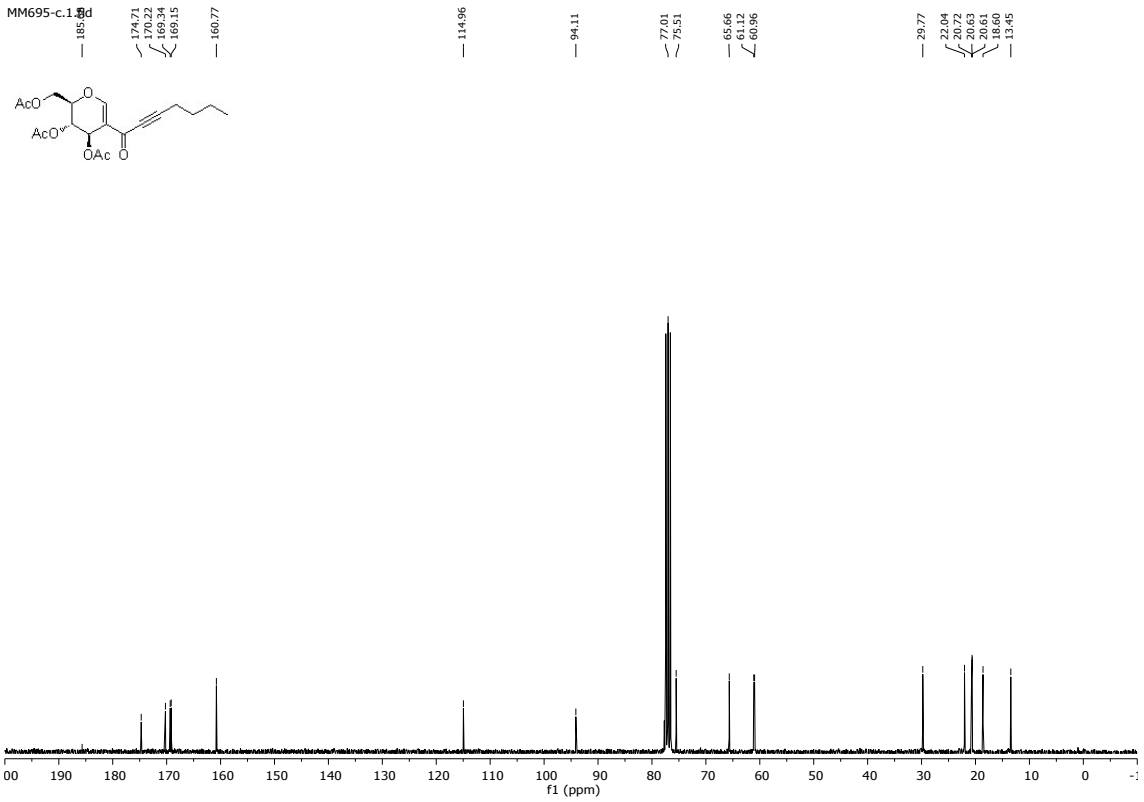
^{1}H NMR (300 MHz, $CDCl_3$) **3m**.



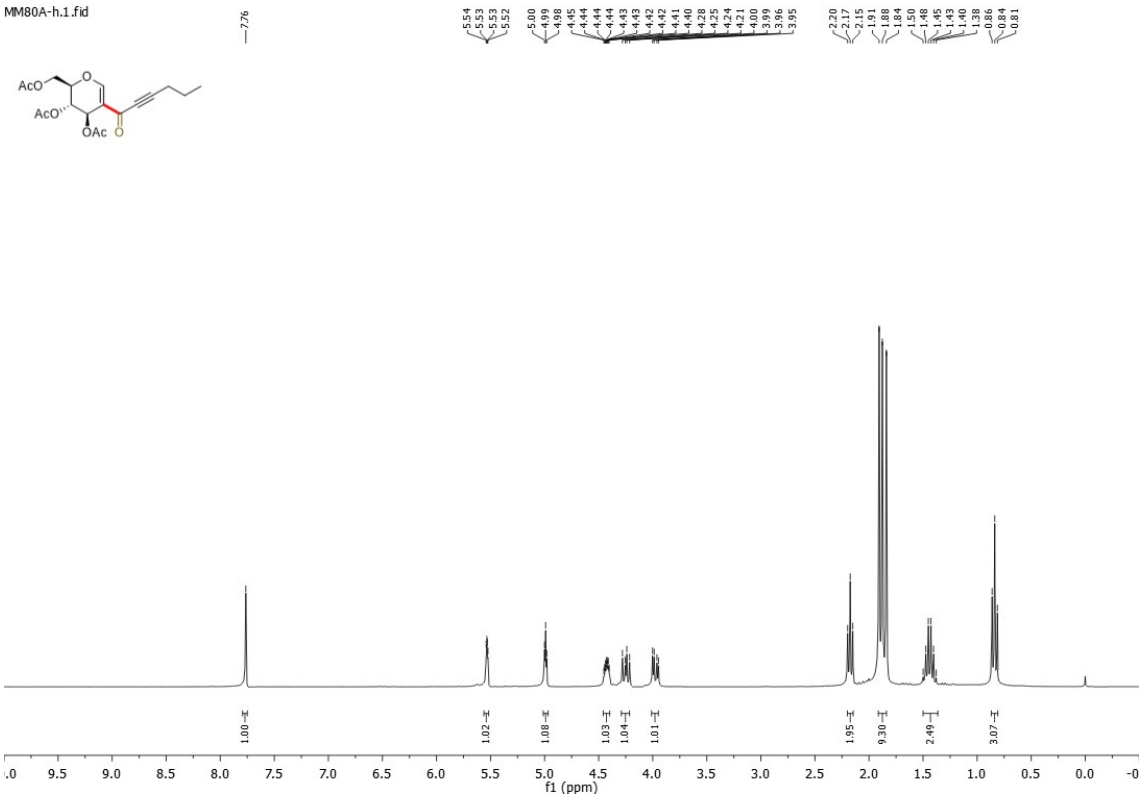
^{13}C NMR (75 MHz, $CDCl_3$) **3m**.



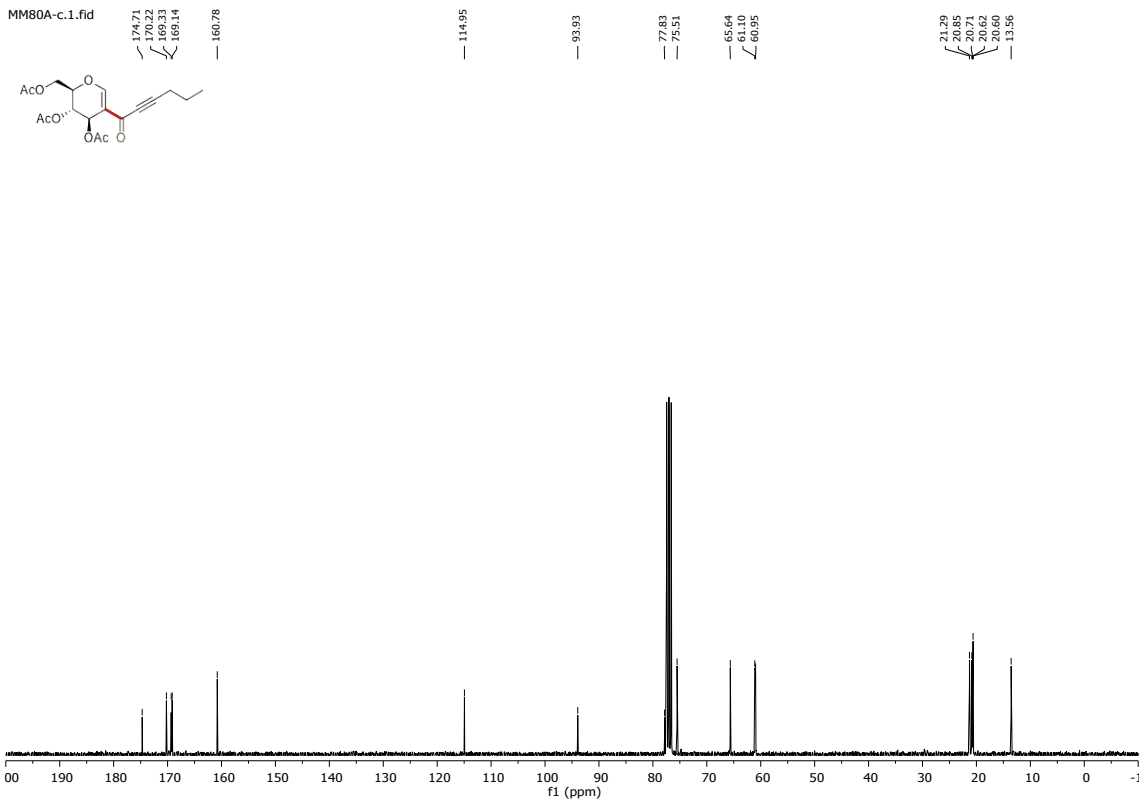
^{1}H NMR (300 MHz, $CDCl_3$) **3n**.



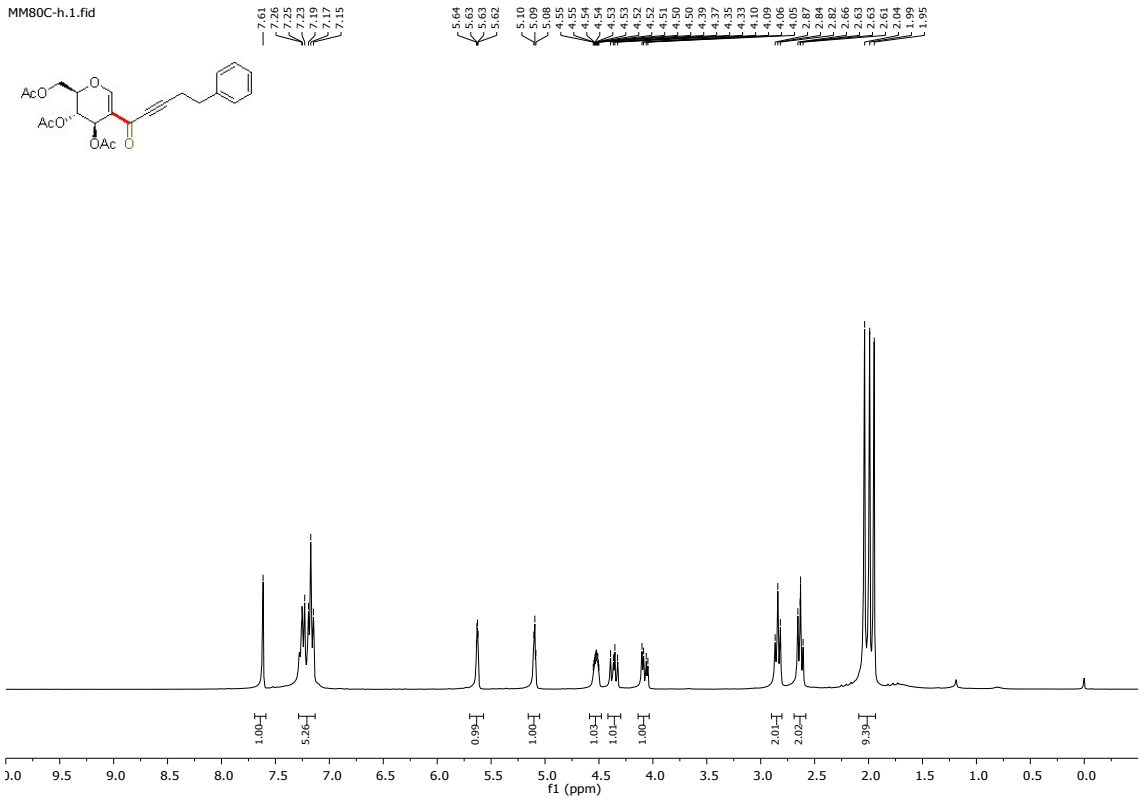
^{13}C NMR (75 MHz, $CDCl_3$) **3n**.



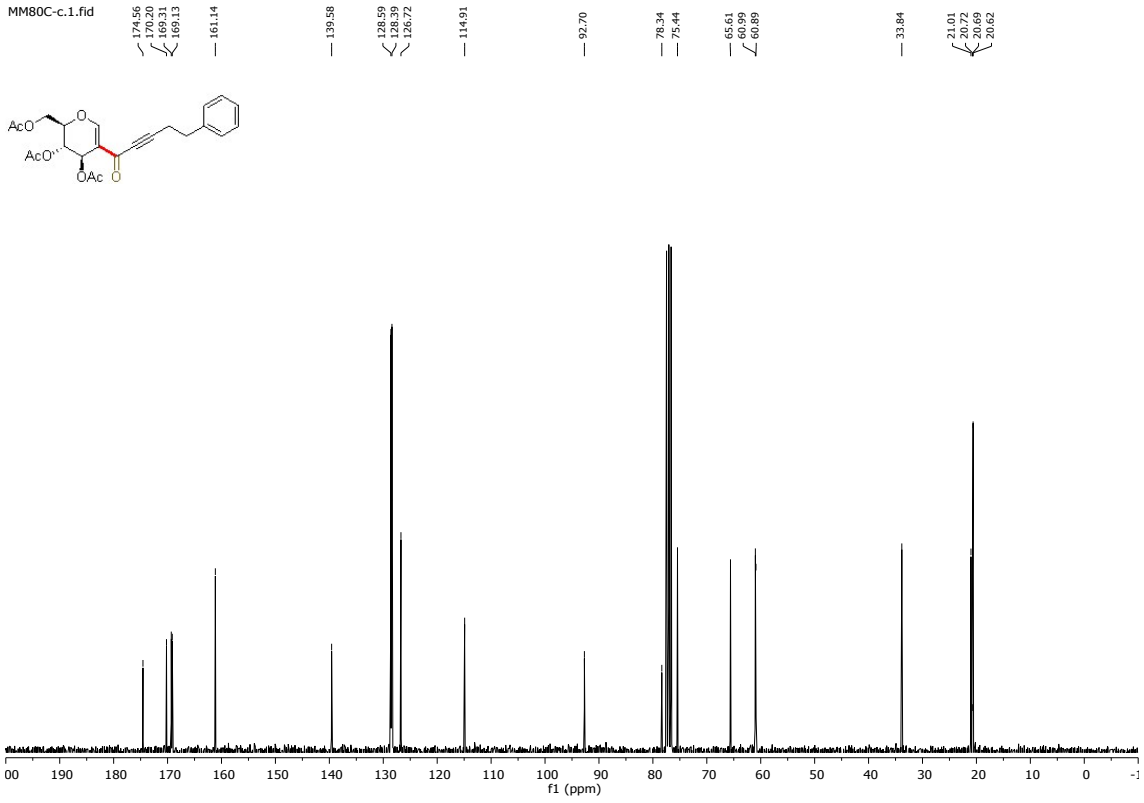
^{1}H NMR (300 MHz, $CDCl_3$) **3o**.



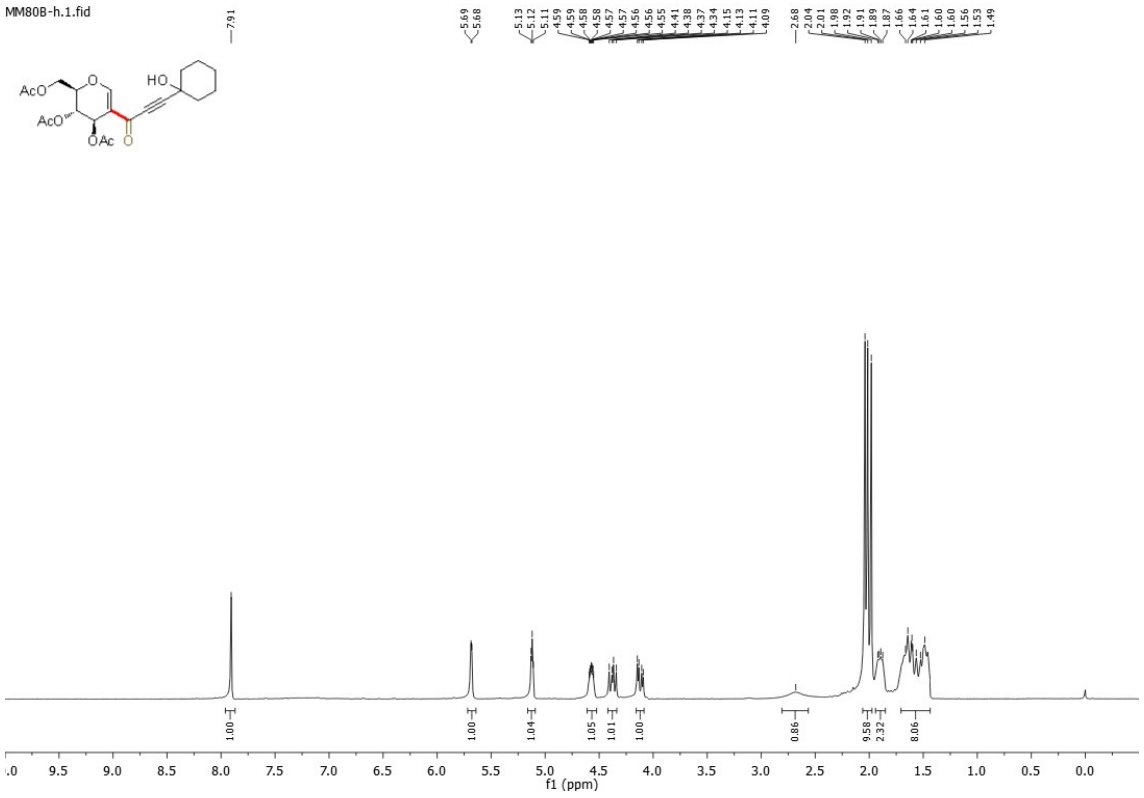
^{13}C NMR (75 MHz, $CDCl_3$) **3o**.



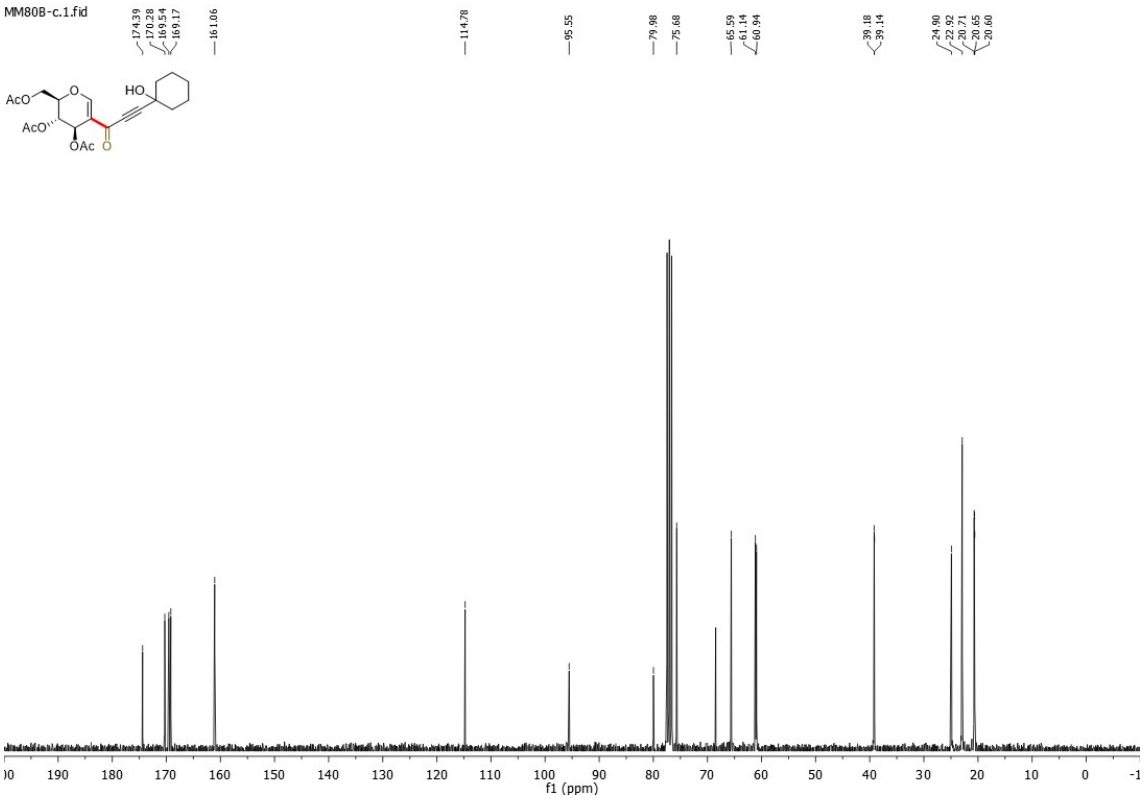
^{1}H NMR (300 MHz, $CDCl_3$) **3p**.



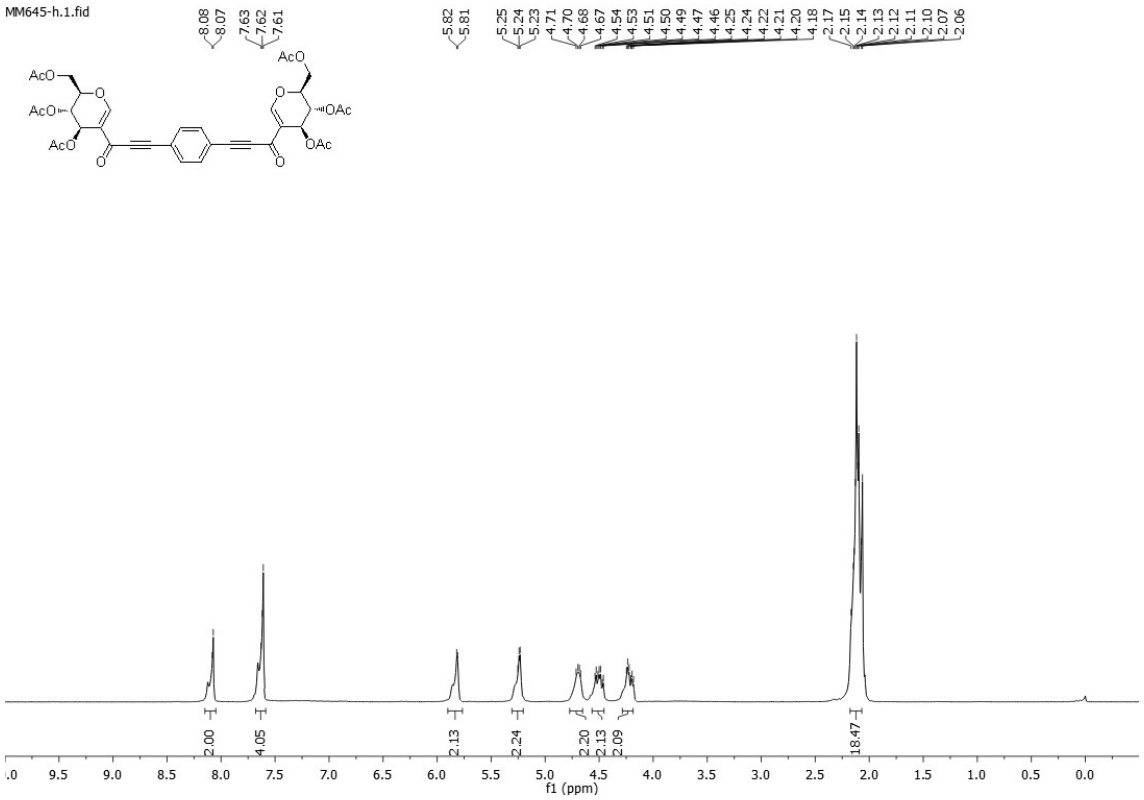
^{13}C NMR (75 MHz, $CDCl_3$) **3p**.



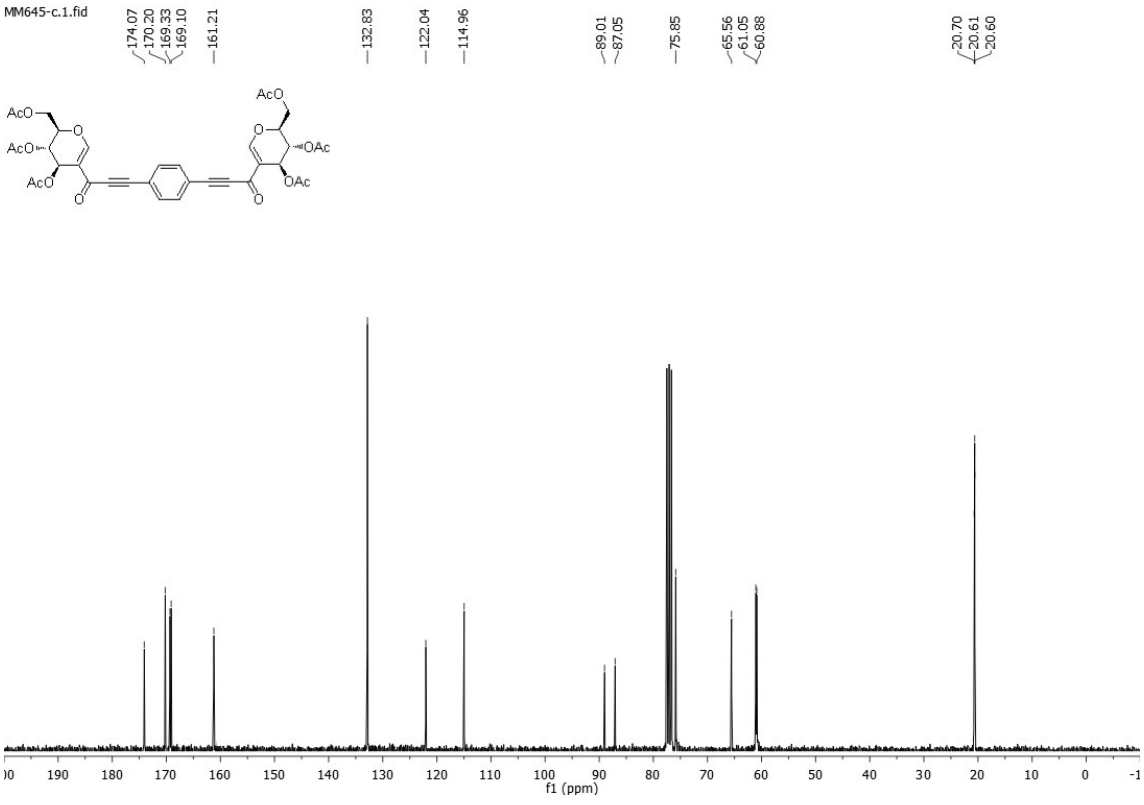
^{1}H NMR (300 MHz, $CDCl_3$) **3q**.



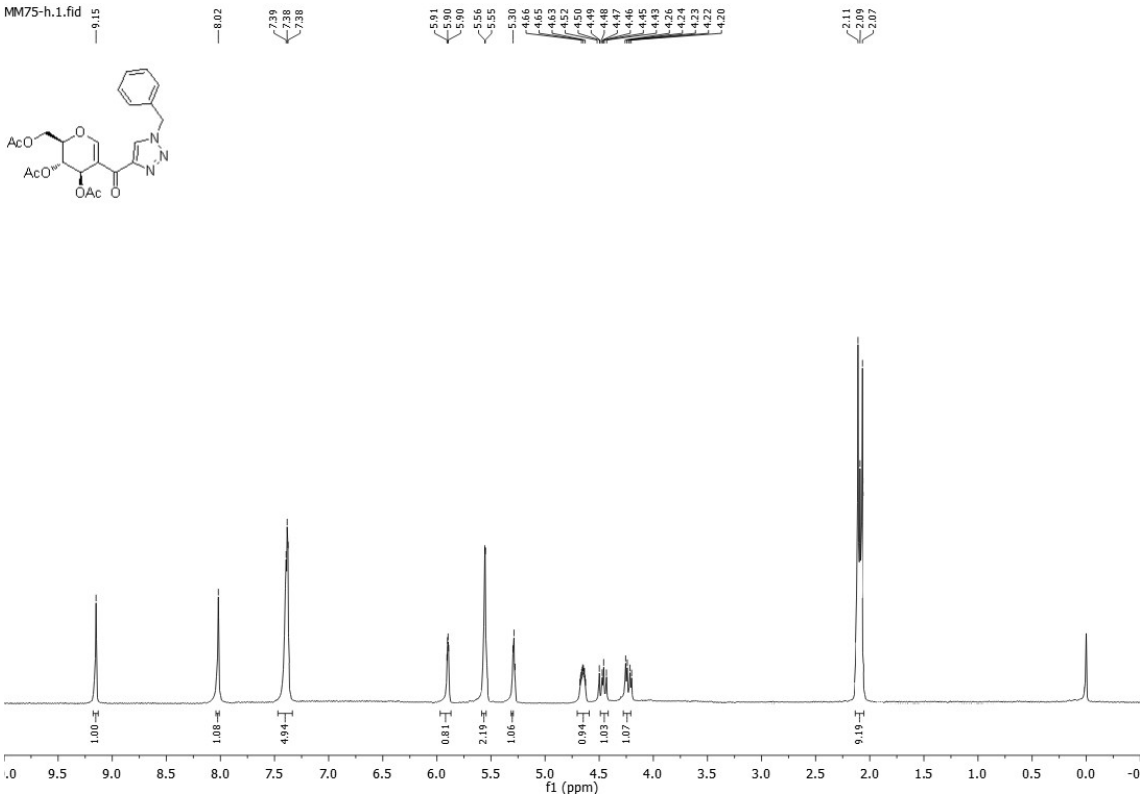
^{13}C NMR (75 MHz, $CDCl_3$) **3q**.



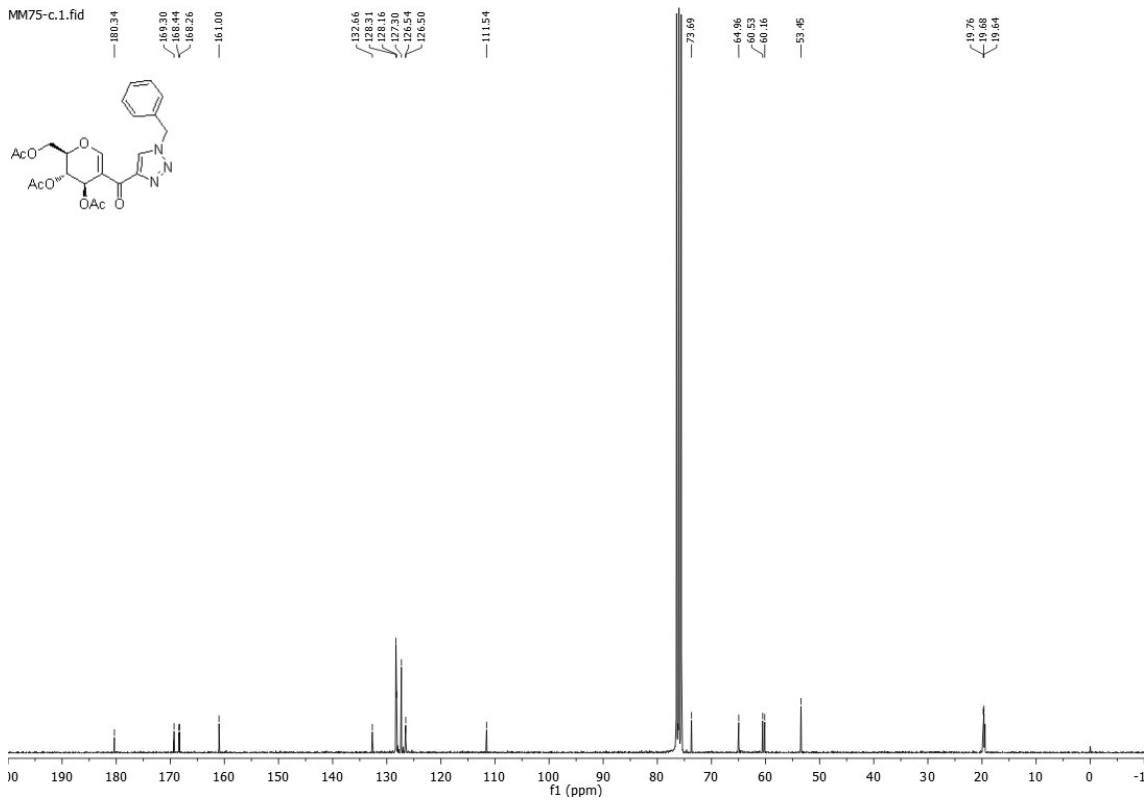
^{1}H NMR (300 MHz, $CDCl_3$) **3r**.



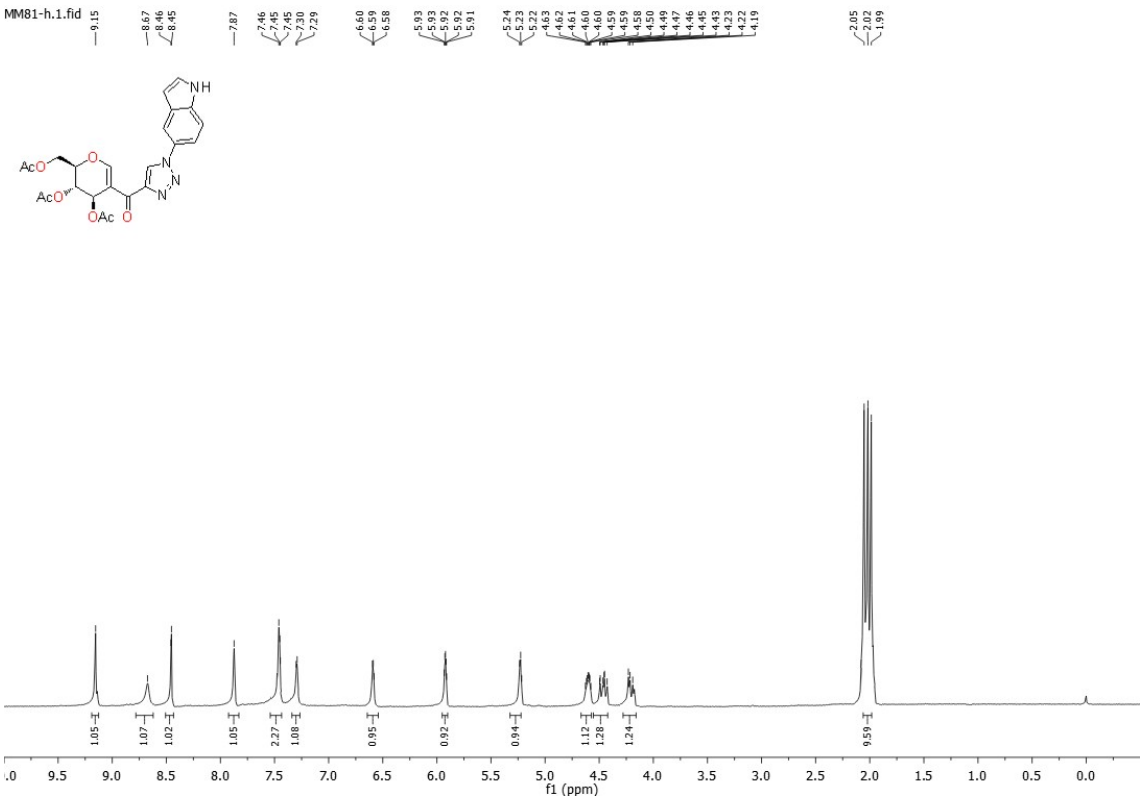
^{13}C NMR (75 MHz, $CDCl_3$) **3r**.



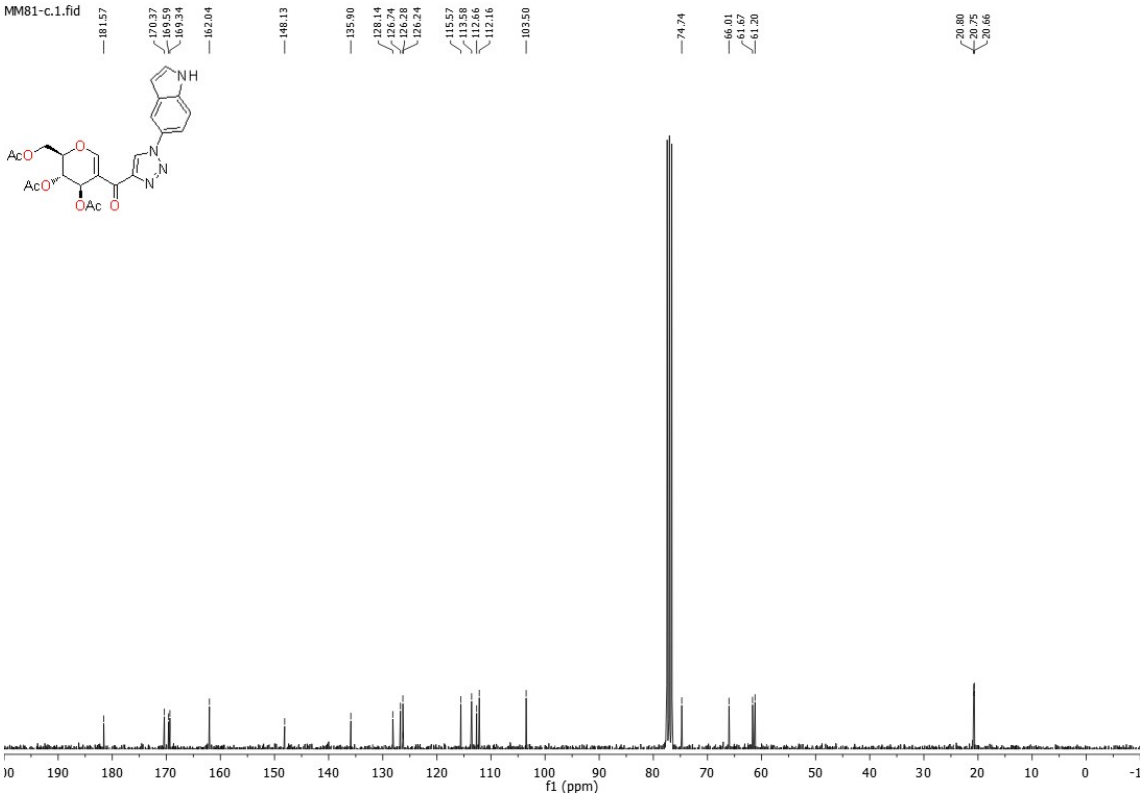
^{1}H NMR (300 MHz, $CDCl_3$) **5a**.



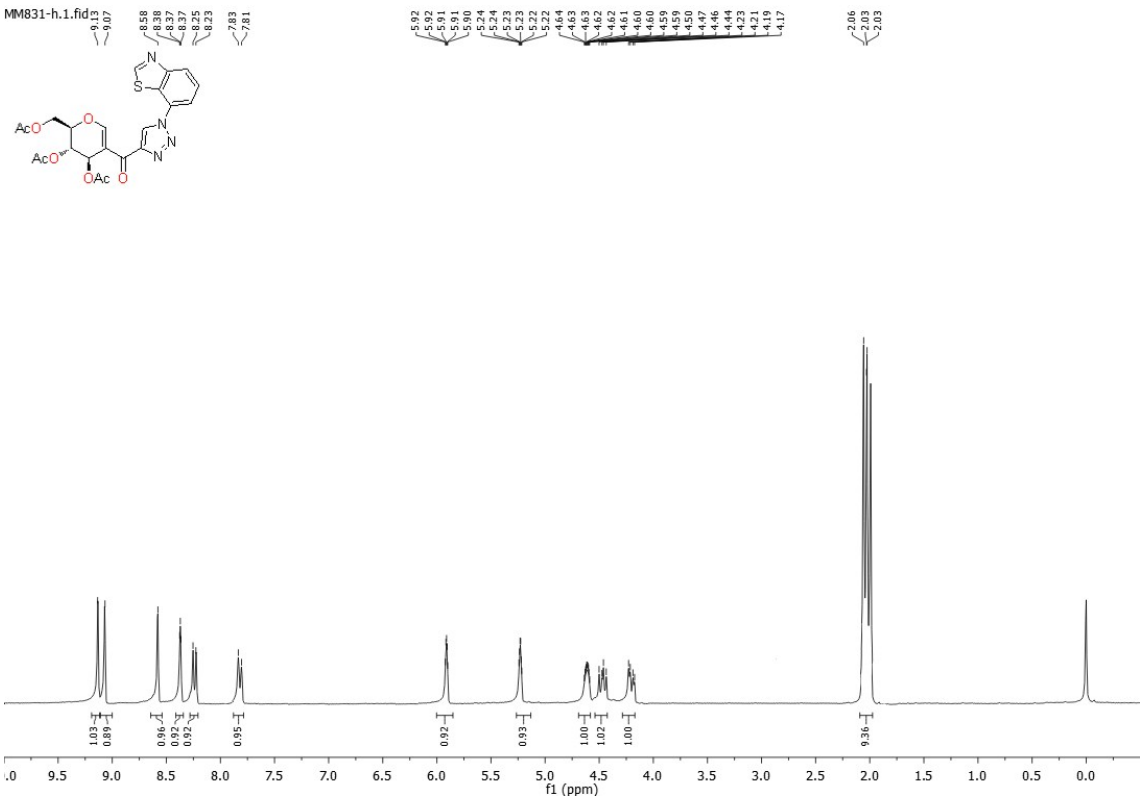
^{13}C NMR (75 MHz, $CDCl_3$) **5a**.



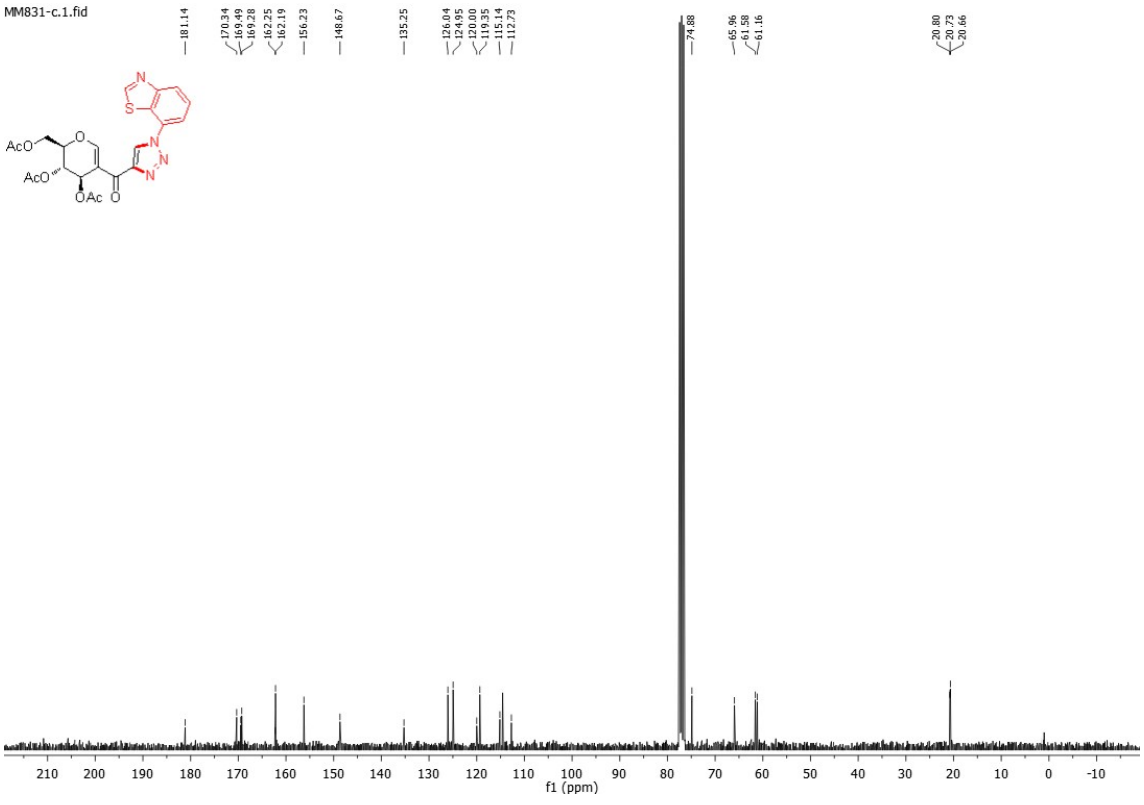
^{1}H NMR (300 MHz, $CDCl_3$) **5b**.



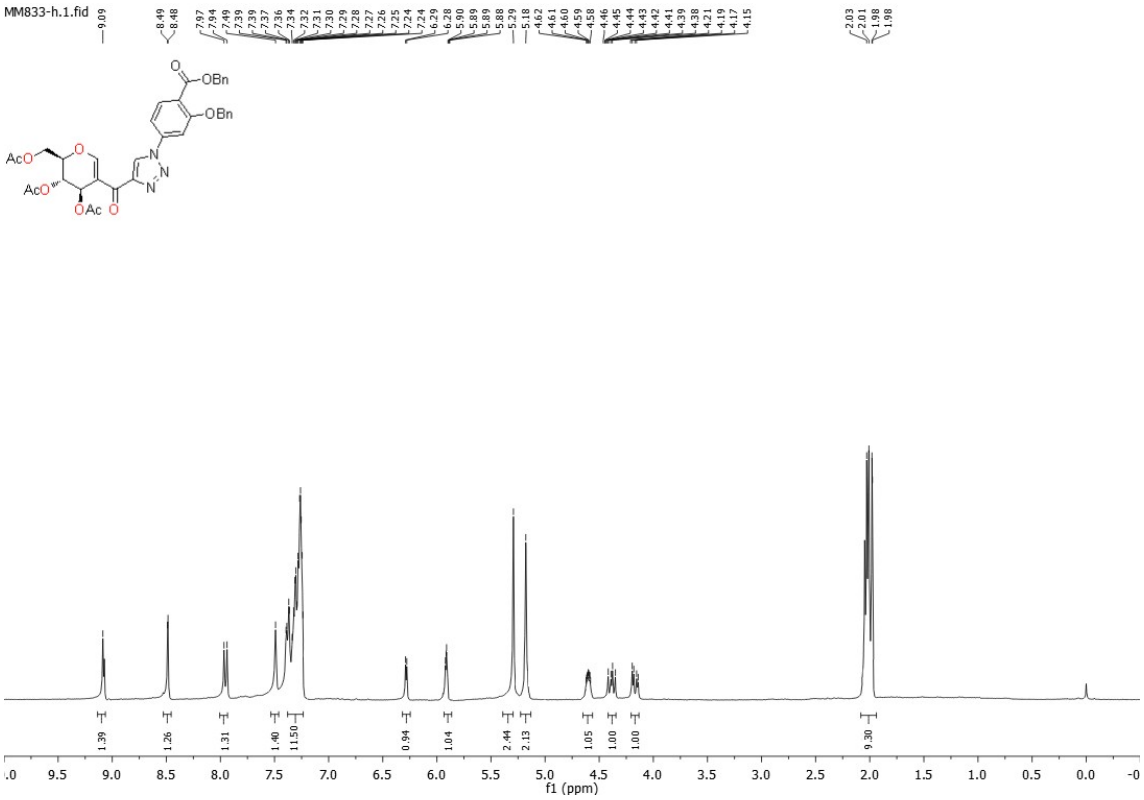
^{13}C NMR (75 MHz, $CDCl_3$) **5b**.



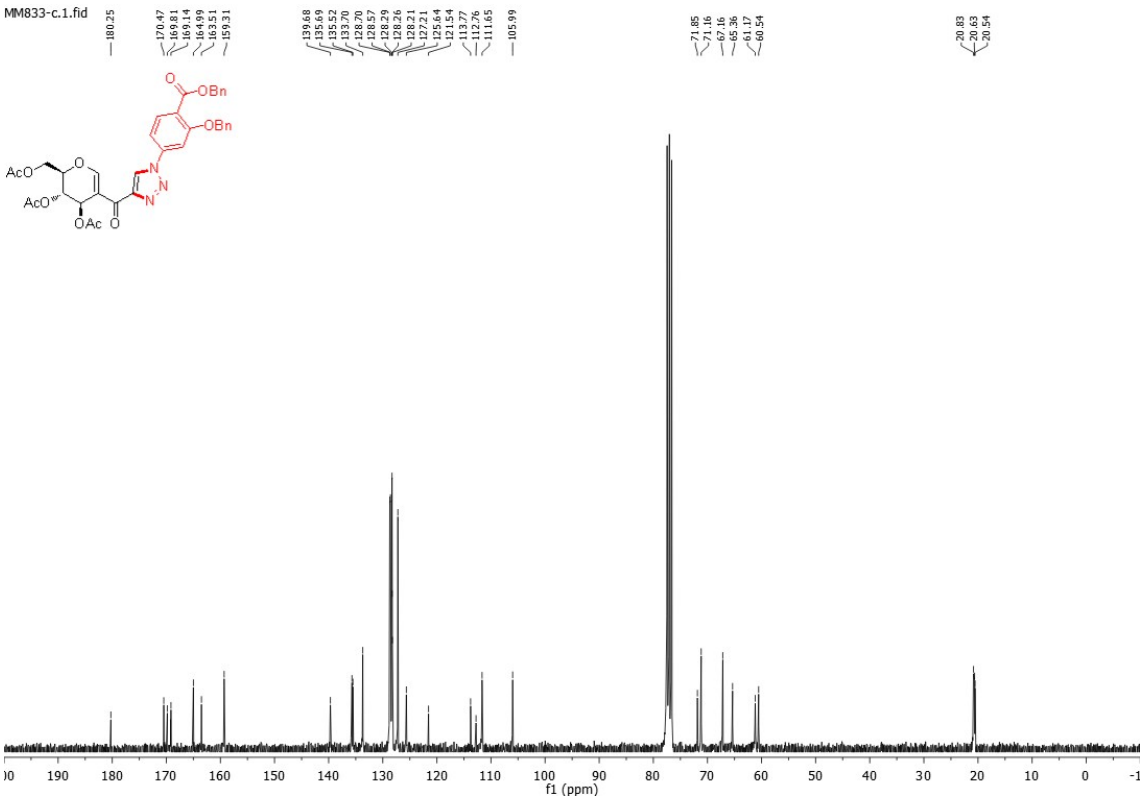
^{1}H NMR (300 MHz, $CDCl_3$) **5c**.



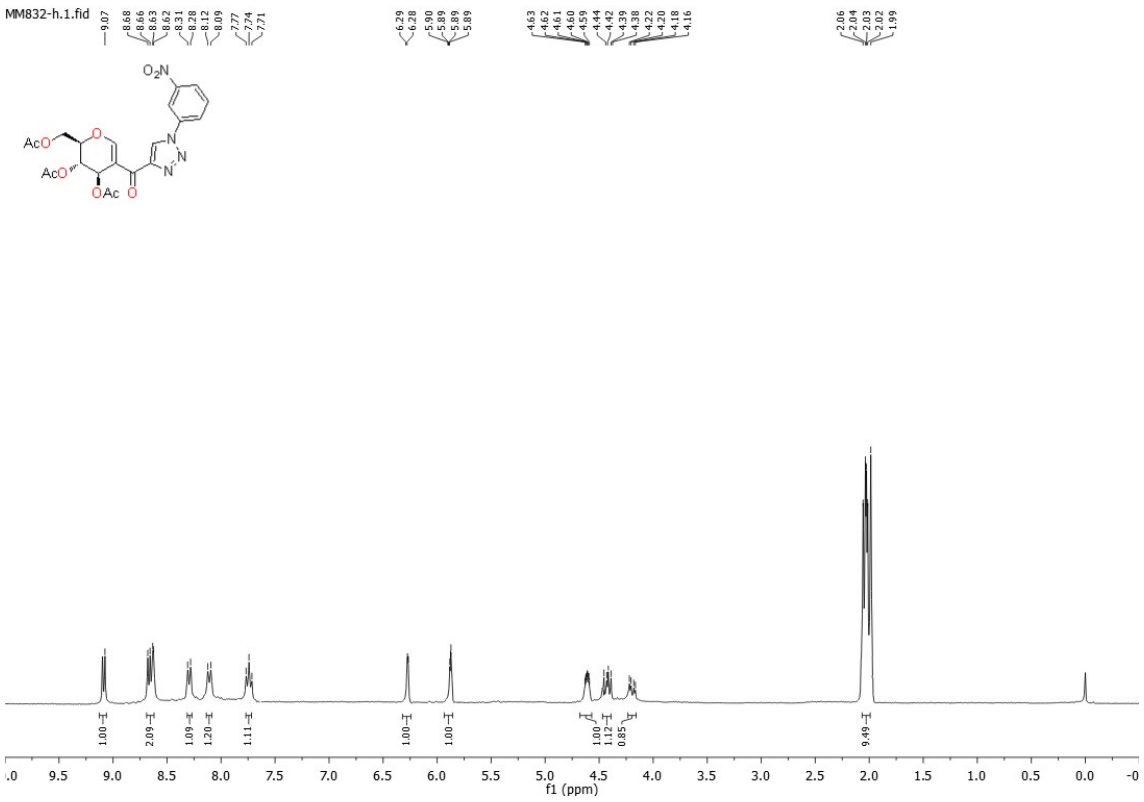
^{13}C NMR (75 MHz, $CDCl_3$) **5c**.



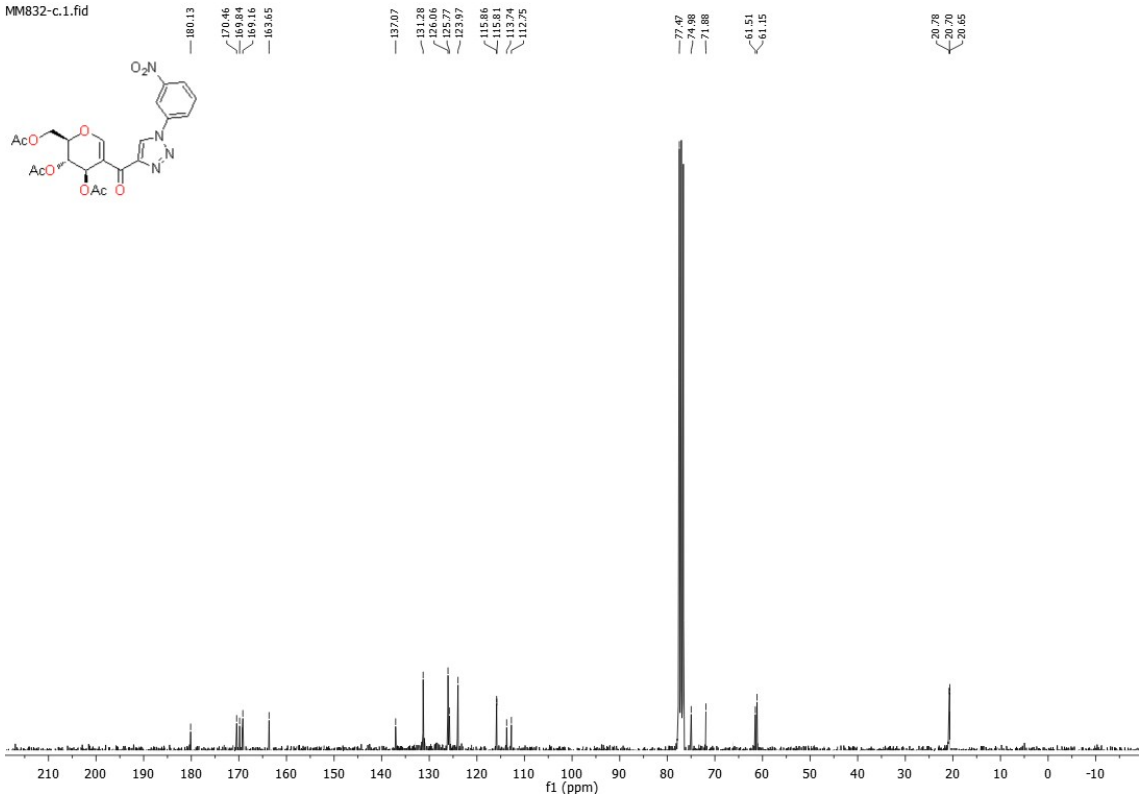
^{1}H NMR (300 MHz, $CDCl_3$) **5d**.



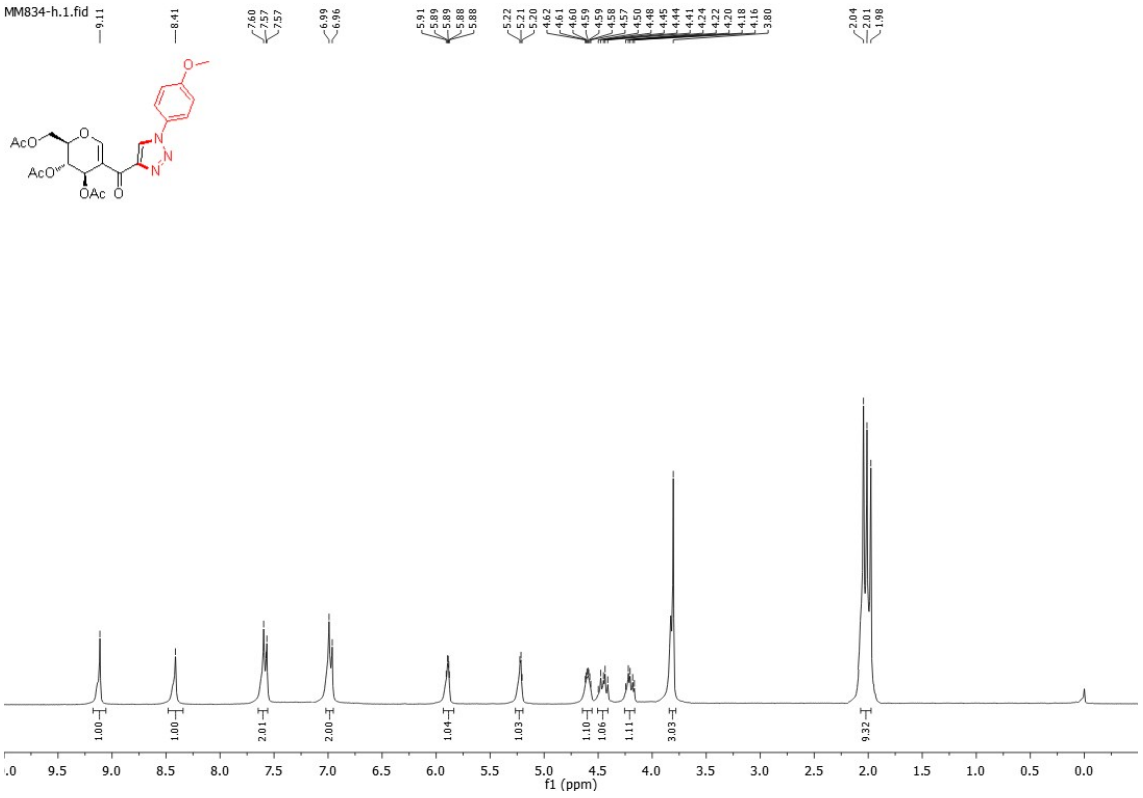
^{13}C NMR (75 MHz, $CDCl_3$) **5d**.



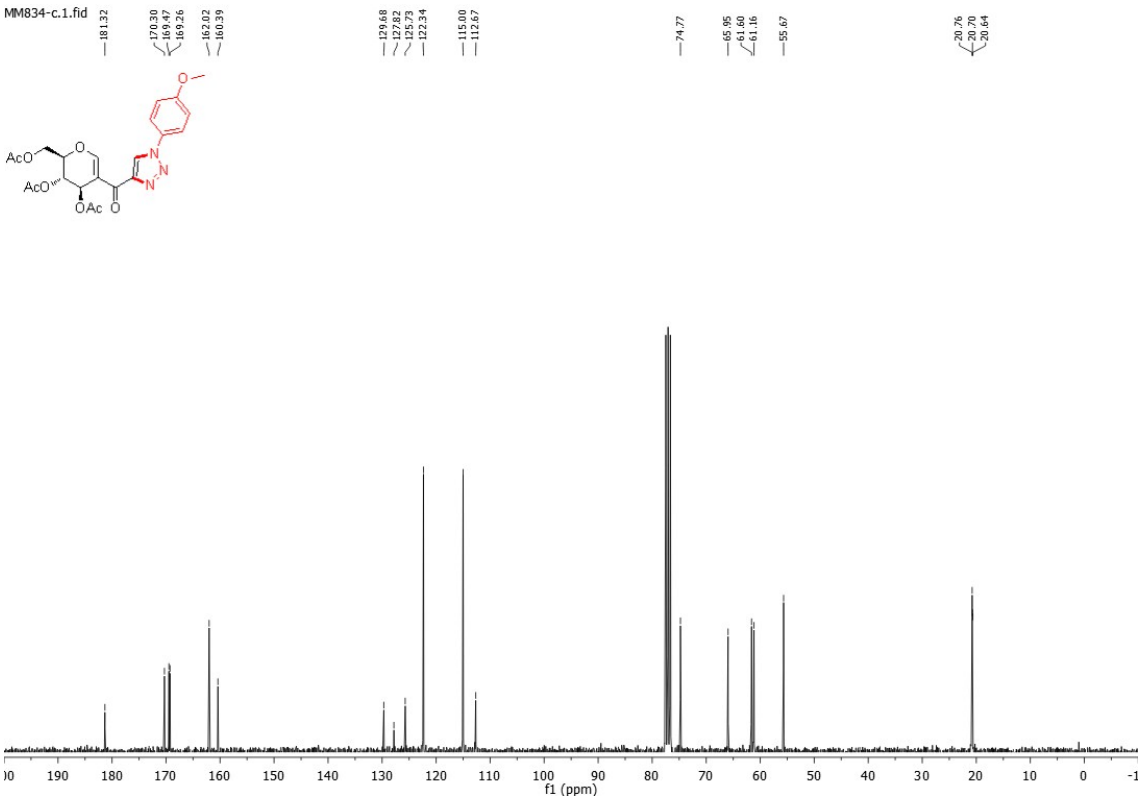
^{1}H NMR (300 MHz, $CDCl_3$) **5e**.



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



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



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